# Ultrafast Raman Scattering in Plasmonic Nanocavities



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This dissertation is submitted for the degree of Doctor of Philosophy

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### Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and acknowledgements. The use of the first-person plural is strictly a matter of style. This dissertation contains fewer than 60,000 words including abstract, tables, footnotes and appendices, but excluding table of contents, diagrams, figure captions, bibliography and acknowledgements.

Lukas Andreas Jakob September 2023

### Abstract

#### Ultrafast Raman Scattering in Plasmonic Nanocavities by Lukas A. Jakob

When bound to metals, molecular vibrations play a key role in sensing, catalysis, molecular electronics and beyond, but investigating their coherence and dynamics is difficult as pulsed experiments prove very challenging. In this thesis, I study vibrations of 1-1000 molecules in a plasmonic nanocavity when driven by picosecond pulsed lasers out of the linear regime. This unravels new non-linear effects such as room-temperature vibrational pumping, giant optomechanical spring shifts, collective molecular vibrations, accelerated decay of vibrational coherence, and the generation of correlated photon pairs.

In plasmonic nanocavities, optical fields are enhanced 100-fold and focused to a nanometrethin gap. Vibrations of molecules placed in the cavity interact strongly with the optical resonances, forming a coupled optomechanical system. Using pulsed laser illumination, I find that surface-enhanced Raman scattering can significantly increase the phonon population above the thermal equilibrium. This vibrational pumping leads to non-linear anti-Stokes scattering observable at room temperature. Further, the optomechanical coupling induces a red-shift of the vibrational energy by >100 cm<sup>-1</sup> and broadening of the Raman line at high peak laser powers (optomechanical spring shift). These non-linear effects are strongly enhanced by the excitation of collective molecular phonon modes. Further experiments show that Stokes-induced anti-Stokes scattering exhibits strong cross-frequency photon bunching. These correlated Stokes – anti-Stokes photon pairs show non-classical behaviour and could be used for applications in quantum computing and communication.

To study the dynamics of molecular vibrations, I use time-resolved incoherent and coherent anti-Stokes Raman scattering. Developing a new single-photon lock-in detection technique, it is possible to simultaneously record the decay of the vibrational population and vibrational dephasing for each nanocavity. The vibrational dephasing is found to strongly accelerate depending on the exciting laser intensity. Understanding these modified vibrational dynamics on plasmonically-active substrates is crucial for improving surface-enhanced catalysis of chemical reactions and heat transfer in molecular electronics.

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## Chapter 1

## Preamble

Molecules are the building blocks of our world. From nitrogen and oxygen molecules in the air to DNA, proteins and other organic molecules that make up all forms of life – molecules are ubiquitous. These molecules are always in motion, even in solid state materials: At room temperature, vibrations are excited in molecules by the thermal energy from their surroundings. Therefore, molecular vibrations are vital factors influencing the properties of materials and can be harnessed for a plethora of applications. For example, vibrations are the carriers of thermal energy and thus define thermal transport through materials and interfaces [1]. Further, the vibrational motion of molecules is the starting point of chemical reactions [2]. By exciting a particular vibration, energy can be deposited in a molecule initiating bond-selective chemistry [3]. With the emergence of molecular electronics, the interaction of molecular vibrational states with electronic states is of increasing interest to understand electronic transport through molecules [4]. Since vibrational modes are characteristic for each molecule's structure, vibrational spectroscopy is an indispensable tool for countless applications in analytical chemistry and biomedical sensing.



**Figure 1.1.** The wavelength of light (here 633 nm) is orders of magnitude larger than a single, vibrating molecule ( $\sim$ 1 nm, to scale). Using plasmonic nanoantennas, the interaction of light with the molecule can be increased by enhancing the electric near-field in the location of the molecule.

For most applications, molecular vibrations are studied using optical spectroscopy. Molecules can interact with light by the absorption of infrared light or via an inelastic scattering process, so-called *Raman scattering*. In Raman scattering, a photon is scattered to lower or higher energy under the excitation or annihilation of a molecular vibration, respectively. However, the wavelength of visible light (400 to 700 nm) is orders of magnitude larger than the size of a small organic molecule (~1 nm, see Fig. 1.1), thus making it experimentally challenging to access vibrational properties of individual molecules due to the optical diffraction limit [5]. Additionally, the Raman process is extremely inefficient with typical scattering cross-sections (the effective area of a beam of light scattered by an individual molecule) on the order of  $\sim 10^{-11} - 10^{-15}$  nm<sup>2</sup> [6].

Therefore, it is necessary to concentrate the light beyond the optical diffraction limit which is possible with the help of *plasmonics* [7]. Since noble metal nanoparticles can focus the light propagating in the far-field down to the near-field around the particle, they are often referred to as plasmonic nanoantennas [8]. Confining the light to a tiny hot spot with high optical field enhancement boosts interactions of molecules with the light (see Fig. 1.1). In *Surface-Enhanced Raman Scattering* (SERS) the field-enhancement at the surface of plasmonic nanostructures is exploited to drastically increase the Raman signal obtained from molecules by enhancement factors reaching  $10^8$  or even higher [6, 9]. Using SERS, it is possible to investigate the vibrations of individual molecules [10, 11].



**Figure 1.2.** (a) Organic molecules are placed in a plasmonic nanocavity which focuses the light down below the diffraction limit. (b) The plasmonic nanocavity enhances the interaction of molecular vibrations with the optical near-field.

Particularly high field enhancements are generated by plasmonic structures with nanometrethin gaps [12]. Since these nanostructures exhibit well-defined optical resonances and strongly enhance the light in the gap, they can be called *plasmonic nanocavities*. These cavities combine tiny mode volumes (<100 nm<sup>3</sup>) with strong field enhancement, boosting light-matter interactions [13] and enabling the observation of SERS from individual molecules [14]. In this thesis, organic molecules will be placed in plasmonic nanocavities to probe vibrational signatures of a few hundred molecules, and even down to individual molecules, via SERS (see Fig. 1.2).

The main objective of this work is to reveal new physical effects arising from the interaction of molecular vibrations with the tightly-confined optical fields in the plasmonic nanocavity. To achieve this aim, SERS experiments are carried out with *ultrafast laser pulses*. Compared to continuous-wave (CW) lasers, a pulsed laser applies light of very high intensity for a short amount of time thus probing the molecules in the nanocavity under extreme optical fields. In this regime, non-linear effects from the coupling of optical and mechanical modes become apparent. Additionally, the use of laser pulses enables time-resolved vibrational spectroscopy to probe the dynamics of vibrational excitation and relaxation. However, pulsed SERS experiments here suffer from very low signal count rates and damage incurred by the molecules and plasmonic nanostructures. This thesis will address these experimental challenges and explore the physics of molecular vibrations in plasmonic nanocavities.

#### **Thesis Outline**

In **Chapter 2**, fundamental physical principles are introduced that will be important throughout this thesis. First, the interaction of metals with light is elaborated to understand the concept of plasmonics. Then, two theories of Raman scattering are presented and compared: the classical approach describing Raman scattering through the polarisability of molecules, and the quantum-mechanical theory of molecular optomechanics. Finally, the chapter concludes by summarising the principles of time-resolved vibrational spectroscopy, including a brief introduction to coherent Raman scattering. Additionally, previous experimental work on ultrafast Raman scattering is reviewed.

**Chapter 3** provides an overview of experimental techniques employed in this work. This includes the fabrication of plasmonic nanocavities with defined, nm-thin gaps as well as spectroscopy techniques to characterise these nanostructures. Most importantly, the laser system and spectroscopy setup for ultrafast Raman experiments on individual nanostructures will be introduced.

In **Chapter 4**, the theory of molecular optomechanics is expanded to better describe the plasmonic nanocavities investigated here. This opens up the understanding of two new phenomena in SERS originating from the non-linear interaction of plasmonic (optical) modes with molecular vibrations (mechanical modes). Firstly, in a nanocavity with multiple plasmonic modes molecular vibrations experience a shift of the vibrational frequency (optical spring shift). Secondly, vibrations of many molecules in the cavity couple via the plasmonic modes forming collective vibrational modes. Experimental evidence is presented for both effects and compared to theoretical predictions.

In **Chapter 5**, a new single-photon detection setup is established to improve experiments suffering from very low optical signal count rates. By recording the arrival time of photons at the detector with picosecond accuracy using a field-programmable gate array (FPGA) chip, lock-in detection can be achieved in a photon counting experiment. Some applications are discussed, including coherent anti-Stokes Raman spectroscopy and photon correlation experiments which are relevant for the following chapters.

**Chapter 6** investigates the dynamics of molecular vibrations and how they are modified by the plasmonic nanocavity. Combining coherent and incoherent time-resolved Raman scattering techniques, both the vibrational population lifetime and the vibrational dephasing time can be measured. Here, the plasmonic confinement leads to accelerated dephasing depending on the pump laser intensity, an effect which is not observed outside a plasmonic cavity.

In **Chapter 7**, correlated photon pairs arising from molecular Raman scattering are studied. Since Stokes and anti-Stokes scattering are connected processes, scattered photons can be entangled in time and polarisation. Here, plasmonic nanocavities allow to demonstrate this effect in SERS with low driving laser powers compared to bulk Raman experiments.

Finally, **Chapter 8** summarises the results obtained in the previous chapters and draws overarching conclusions. Additionally, the results are judged in the context of possible applications and key areas for potential future work are identified.

## Chapter 2

## **Fundamentals**

In this chapter, fundamental principles are introduced essential for the understanding of the rest of the thesis, with the main focus on the interaction of light with matter on the nanoscale. First, Section 2.1 summarises how noble metal nanoparticles respond to incident optical fields, a topic called *plasmonics*. In this context, the *nanoparticle-on-mirror* (NPoM) geometry is introduced which serves as foundation for all experiments carried out in this work. In Section 2.2, molecular vibrations and inelastic scattering of light, so-called *Raman scattering*, are discussed. Combining plasmonics and Raman scattering, the field of *surface-enhanced Raman scattering* (SERS) is introduced. As an alternative model to the classical description of SERS, the theory of *molecular optomechanics* is summarised in Section 2.3. Finally, Section 2.4 gives an introduction to time-resolved spectroscopy and reviews the literature on ultrafast SERS experiments.

### 2.1 Plasmonics

This section introduces how metals interact with light. While light is reflected from bulk metals, the optical properties of the material change drastically when the size of the metal is constrained in one or more dimensions. The interesting optical behaviour of noble metal nanoparticles has already been known since ancient times and was employed to stain glass. The most famous example for this historical application is the Lycurgus cup, shown in Figure 2.1 [15]. When viewed from the outside, the Roman cup from the 4<sup>th</sup> century AD looks green. However, illuminated from the inside the cup looks red due to the extinction of the green light. Modern examinations have concluded that the staining of the cup is caused by a mixture of gold and silver colloids scattering predominantly green light [15]. While metal nanoparticles have been manufactured and utilised for millennia, our understanding of their optical properties has evolved. The pioneering work by Michael Faraday in the 1850s has shaped the modern interpretation of the optical properties of colloidal gold [16], and Gustav Mie published a theory in 1908 for the scattering and absorption of small spherical particles [17]. In recent decades, fabrication and analytical techniques have rapidly improved and highly sophisticated metal nanostructures are designed to modify light on the nanoscale [18].



**Figure 2.1.** Pictures of the Lycurgus Cup illuminated (a) from the outside and (b) from the inside. The Roman cup, originating in the  $4^{th}$  century AD, is made of glass stained with colloidal gold and silver. Photograph by The British Museum, reproduced under license CC BY-NC-SA 4.0.

The optical properties of metal nanoparticles are captured by the field of plasmonics [19]. Due to the high density and mobility of electrons in the metal's conduction band, metal nanoparticles can be easily polarised by an applied electric field. Similarly, the optical fields of visible light can induce a collective oscillation of the electrons in the metal. Such collective oscillations of the electron density are called *plasmons*. The movement of charges in the metal induces electromagnetic near-fields strongly localised to the surface of the particle, which can exceed the intensity of the incident light. Since this excitation has contributions from both electronic oscillations (plasmons) and the electromagnetic field (polaritons), they are commonly called *localised surface plasmon polaritons* (LSPPs). When two plasmonic particles are brought into close proximity, their charge oscillations interact with each other forming coupled plasmonic modes. In the gap between the particles, the near-field can be enhanced by many orders of magnitude focused in an exceptionally small volume. In this work, such nanometre-thin gaps exhibiting strong electromagnetic field enhancement will be called plasmonic nanocavities.

Section 2.1.1 summarises basic principles of the field of plasmonics to give an intuition about phenomena described above. In Section 2.1.2, an experimental realisation of a plasmonic nanocavity will be introduced: the nanoparticle-on-mirror (NPoM) geometry. This type of nanostructure combines high field enhancement and small mode volumes, providing an excellent substrate for surface-enhanced Raman scattering (see Section 2.2). Finally, we will explore an avenue towards single-molecule sensing in plasmonic nanocavities in Section 2.1.2.

#### 2.1.1 From the Free Electron Gas to Plasmonics

#### The Drude model

To understand the optical properties of metal nanoparticles, we start by considering the response of a bulk metal to an electric field oscillating at optical frequencies. A theory for the behaviour of electrons in the metal under an external electric field has been suggested by Paul Drude in 1900 [20]. Despite the simplicity of this model (details of the lattice potential and electron-electron interactions are neglected), it predicts the dielectric properties of gold well across a wide range of frequency and provides a basis for understanding plasmonics [19].

The electrons in the free electron gas ('plasma') of the metal are accelerated by the external electric field **E** and their motion is damped by collisions at rate  $\gamma$ . This give the equation of motion for an electron in the metal's conduction band

$$m_e^* \frac{d^2 \mathbf{x}}{dt^2} + m_e^* \gamma \frac{d \mathbf{x}}{dt} = -e \mathbf{E}$$
(2.1)

describing the displacement **x** for the electron with effective mass  $m_e^*$  and charge *e*. The effective mass here takes into account details of the band structure of an electron moving through the metal lattice. If the motion is driven by a harmonically oscillating field  $\mathbf{E}(t) = \mathbf{E}_0 \exp(-i\omega t)$  with frequency  $\omega$ , we can find a solution for Eq. 2.1:

$$\mathbf{x}(t) = \frac{e}{m_e^* \left(\omega^2 + i\gamma\omega\right)} \mathbf{E}(t)$$
(2.2)

This shows that the motion of electrons follows the applied electric field, causing a polarisation  $\mathbf{P} = -ne\mathbf{x}$  in the metal with electron density *n*. Explicitly, the polarisation takes the form

$$\mathbf{P} = \frac{ne^2}{m_e^* \left(\omega^2 + i\gamma\omega\right)} \mathbf{E}.$$
(2.3)

Finally, the response of a material to an applied electric field can be described by its frequencydependent permittivity  $\varepsilon(\omega)$ . The displacement field is defined as  $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \varepsilon \mathbf{E}$ , linking the polarisation to the materials permittivity. From this relation, we obtain the metal's dielectric function

$$\varepsilon_m(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega},\tag{2.4}$$

where the plasma frequency  $\omega_p^2 = ne^2/\varepsilon_0 m_e^*$  gives a characteristic frequency for the response of the material to light. Here, the parameter  $\varepsilon_{\infty}$  accounts for a residual polarisation at very high frequencies ( $\omega > \omega_p$ ) due to contributions from bound electrons. This description of the frequency-dependent metallic response to an oscillating electric field is called the *Drude model*.

Comparing the Drude model to experimental data for the dielectric function of gold shows that the model describes response of the metal to incident light very well for photon energies below 2 eV (wavelengths above 620 nm). At higher photon energies, electrons can be excited from the Fermi level to the *d*-band. This interband transition leads to absorption of light in the material and hence contributes strongly to the imaginary part of the dielectric function. For gold, the threshold energy for interband transitions is 2.38 eV [21]. In this thesis, all experiments will be conducted with light of wavelength  $\lambda > 633$  nm ( $\hbar \omega < 1.96$  eV) and thus the Drude model is a good approximation for the optical response of the metal.



**Figure 2.2.** (a) Real part and (b) imaginary part of the dielectric function of gold. Experimental data from Johnson and Christy, 1972 [22] (black data points). The Drude model (red line) fits the data well for photon energies below the gold interband transition. Drude fit parameters:  $\varepsilon_{\infty} = 9.5$ ,  $\hbar \omega_p = 9$  eV,  $\hbar \gamma = 0.01$  eV [23].

#### Surface plasmon polaritons

At the interface of a metal to a dielectric material (for example air), a plasmonic mode can exist bound to the surface of the metal. Since these travelling excitations are a combination of collective oscillations of charges (plasmons) and electromagnetic waves (polaritons), they have been termed *surface plasmon polaritons* (SPPs) (see Fig. 2.3a). First predicted by R. Ritchie in 1957 [24], SPPs are confined electromagnetic waves decaying exponentially away from the interface. Due to this evanescent character, SPPs are not able to propagate away from the surface meaning they are non-radiative [25]. Depending on losses in the metal and their wavelength, SPPs can travel along the interface for 10–100  $\mu$ m [25].

Using Maxwell's equations with suitable boundary conditions, it is possible to deduce the dispersion relation of an SPP which describes the wave-vector  $k_x$  in travelling direction x (along the surface) as a function of frequency  $\omega$  as [26]

$$k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d \varepsilon_m(\omega)}{\varepsilon_d + \varepsilon_m(\omega)}}$$
(2.5)

with the permittivity of the dielectric material  $\varepsilon_d$  (positive real-valued) and the metal  $\varepsilon_m(\omega)$  (complex-valued and frequency-dependent), and the speed of light *c*. The wave vector in the *z*-direction (perpendicular to the surface) is imaginary and the wave hence decays rapidly with distance from the interface (evanescent character). The dispersion of an SPP assuming a Drude metal is shown in Figure 2.3c (red) compared to light travelling freely through air ( $k_0 = \omega/c$ , black). Since the two curves do not intersect, energy and momentum matching of a photon in free-space and an SPP is not possible. Therefore, the excitation of SPPs directly from free-space is momentum-forbidden. Instead, momentum-matching techniques such as Kretschmann prism or grating coupling have to be employed to excite SPPs [27]. For prism coupling (see Fig. 2.3b), a glass prism is coated with a thin film of metal and the incidence angle of light into the prism is tuned. At a particular angle, the momentum-matching condition is satisfied and the SPP excited, leading to a drop in reflectivity of the light. This angle is highly sensitive to the refractive index at the metal-dielectric interface and is therefore commonly applied as a detector for molecules binding to the gold surface [28].



**Figure 2.3.** Surface plasmon polaritons (SPPs). (a) On the interface of a metal to a dielectric material, charge oscillations couple to electromagnetic waves can travel along the surface. (b) SPPs can be excited by prism coupling to match the momentum of the SPP to the light in free-space. (c) Disperion relation of an SPP (red) at the interface of a Drude metal to air, compared to light travelling through air (black) and glass (grey). Due to the momentum mismatch of free space wave-vector  $k_0$  with  $k_{SPP}$ , SPPs can only be excited by prism coupling. The LSPP (blue) only exists at its resonance frequency, but can be excited directly with light.

#### Localised surface plasmon polaritons

An alternative to overcome the momentum mismatch is to confine the SPP to a metal nanoparticle. Due to the curved metal surface, an effective restoring force arises for the electron plasma localising the SPPs. These non-propagating excitations are called *localised* surface plasmon polaritons (LSPPs) and correspond to a collective charge oscillation within the entire nanostructure (see Fig. 2.4a). In contrast to SPPs, LSPPs only exist at a single resonance frequency (the localised surface plasmon resonance, LSPR) but can be excited directly with light from the far-field (see Fig. 2.3c) [29]. The LSPR, which strongly depends on the size and shape of a metal nanoparticles as well as the used metal and dielectric surroundings [30, 31], amplifies the optical fields in the near-field surrounding the plasmonic material (see Fig. 2.4b) [32]. For single gold nanoparticles, this field enhancement is typically on the order of  $|E/E_0| \sim 10$  [33]. The light is hence focused to volumes below the optical diffraction limit, enabling many novel applications such as nanoscale sensing and non-linear optics [34, 35]. As will be discussed in Section 2.2, the near-field enhancement of plasmonic nanoparticles also leads to a drastic increase of the Raman scattering signal from molecules bound to the particle, here with  $|E/E_0|^4 \sim 10^4$  as both the laser excitation and Raman emission are enhanced [36].

Assuming a spherical particle with radius *r* much smaller than the wavelength of light  $\lambda$ , the plasmonic resonance condition can be derived. Since  $r \ll \lambda$ , the metal nanoparticle is polarised by a nearly constant electric field (quasi-static approximation, see Fig. 2.4a). The polarisation induced in the particle by the electric field **E** is thus given by

$$\mathbf{P} = \varepsilon_0 \varepsilon_d \alpha(\omega) \mathbf{E} \,. \tag{2.6}$$

Since the induced polarisation follows the oscillations of the electric field at the optical frequency, the polarisability  $\alpha(\omega)$  characterises the frequency-dependent response of the nanoparticle. For spherical particles, the polarisability can be expressed as [19, 37]

$$\alpha(\omega) = 4\pi r^3 \frac{\varepsilon_m(\omega) - \varepsilon_d}{\varepsilon_m(\omega) + 2\varepsilon_d}.$$
(2.7)



**Figure 2.4.** Localised surface plasmon polaritons (LSPPs) in metal nanoparticles. (a) Gold nanoparticle polarised by the electric field of a light wave. The particle is smaller than the wavelength of the incident light and experiences a near-constant electric field. (b) Electric near-field enhancement of spherical gold nanoparticle with diameter 20 nm in air ( $\lambda = 522$  nm). Simulation with Boundary Element Method (BEM) [38]. Adapted with permission from [33]. (c) Experimentally measured absorbance spectrum of gold nanoparticles with diameter 20 nm (solid line), compared with Mie theory (dotted line). Adapted with permission from [39].

Importantly, the polarisability is given by the complex, frequency-dependent dielectric function of the metal  $\varepsilon_m(\omega)$ , which was discussed above. The polarisability here reaches a maximum if the denominator  $|\varepsilon_m(\omega) + 2\varepsilon_d|$  is at its minimum. For metals with small imaginary contribution to the dielectric function, the Fröhlich condition for the LSPR of spherical nanoparticles follows [19]:

$$\operatorname{Re}\left(\varepsilon_{m}(\omega)\right) = -2\varepsilon_{d}.$$
(2.8)

For noble metal nanoparticles, this resonance often lies in the visible range of the electromagnetic spectrum and colloidal gold nanoparticles thus exhibit a resonance in extinction spectra (see Fig. 2.4c). While the quasi-static approximation predicts the occurrence of a plasmonic resonance in nanoparticles due to the metal dielectric properties, the model does not reproduce the dependence of the LSPR on particle size or shape. Additionally, the quasi-static approximation is not valid as the nanoparticle size approaches the wavelength of light, leading to the observation of quadrupolar modes [40]. More rigorous calculations with Mie theory [17] can be employed to account for these effects [39].

#### **Coupled plasmonic systems**

The plasmonic near-field decays exponentially away from the metal nanoparticle. However, when two plasmonic structures are placed in close proximity to each other (distance smaller than their diameter), their electromagnetic fields interact and new plasmonic modes can emerge [41]. In these coupled plasmonic modes, the collective charge oscillations of the two particles are coupled through the electromagnetic fields. Coupled plasmonic systems are of great importance to this work and will be explored here in the example of a nanoparticle dimer, which has been studied extensively in the literature [42–47].

For small particles, the plasmonic coupling in a dimer can be approximated by dipole-dipole interactions. With inter-particle separations on the order of a few nm, the dipolar coupling is strong and the plasmonic modes hybridise. In analogy to the formation of molecular orbitals in the hydrogen atom, the coupled plasmonic modes can be understood as bonding (lower in energy than original modes) and anti-bonding (higher in energy than original modes) hybridised modes [43]. Figure 2.5 schematically shows the energy diagram of new hybridised plasmonic modes. Unlike for the single nanoparticle, the optical properties of the dimer now



**Figure 2.5.** Energy of coupled plasmonic modes in a nanoparticle dimer. (a) Dimer excited with light polarised across the gap, exciting longitudinal modes. (b) Dimer excited with light polarised perpendicular to the gap, exciting transverse modes. Only modes with net dipole moment can radiate to the far-field (bright modes).

depend on the polarisation of the incident light. For polarisation along the dimer, longitudinal coupled modes can be excited which concentrate the field in the dimer gap (see Fig. 2.5a). With excitation polarisation perpendicular to the dimer, transverse modes are excited without field confinement in the gap (see Fig. 2.5b). However, only if the plasmonic mode has a net dipole moment can it radiate to the far-field. These modes are called bright plasmonic modes (particle dipoles oscillate in phase), in contrast to dark modes which cannot scatter with light from the far-field since dipoles of the individual particles cancel out (particle dipoles oscillate out of phase). This model neglects any modes with higher order hybridisation.

The most interesting coupled plasmonic mode is the bright longitudinal mode since it confines the optical field in the gap between the two particles and appears red-shifted to the individual particle plasmon. For very closely spaced dimers (~1 nm), the electric field can be enhanced by factors  $|E/E_0| \sim 10^2 - 10^3$  (see Fig. 2.6a,b) [48, 49]. In this geometry, the optical field is strongly concentrated to a small volume between the two particles, called the *plasmonic hot spot*. The field enhancement in the hot spot depends on the inter-particle separation, strongly increasing as particles are moved closer together. However for separations < 1 nm, the field enhancement reduces again due to the nonlocality of the metal's dielectric response [50] and quantum tunneling between the nanoparticles [51–53]. Therefore, gaps of ~1 nm are desirable for applications providing maximum field enhancement and confining the field to a hot spot volume < 100 nm<sup>3</sup>.



**Figure 2.6.** Coupled plasmonic mode of a silver nanoparticle dimer (radius 60 nm). (**a,b**) Electric near-field enhancement of the coupled dimer mode calculated with the finite element method (FEM) [54] for inter-particle gap of (a) 1 nm ( $\lambda$  = 700 nm) and (b) 30 nm ( $\lambda$  = 570 nm) at the wavelength of maximum field enhancement. (**c**) Far-field extinction cross section of the dimer. The coupled mode resonance strongly depends on the gap between the particles. Adapted with permission from [49].

In addition to the near-field enhancement, the resonance wavelength of the coupled plasmonic mode also strongly depends on inter-particle distance [49], shape of the particles [48] and refractive index of the material in the gap. With decreasing distance between the particles, the hybridisation of modes increases and the coupled (longitudinal) mode thus shifts to lower energies. Figure 2.6c shows that tuning of the resonance wavelength over several hundred nm can be achieved by varying the particle separation. Additional modes at lower wavelength are observed in the scattering spectrum due to higher order coupled modes which cannot be captured with the simple model of dipolar coupling. Such higher order modes will be discussed in more detail in Section 2.1.2.

While nanoparticle dimers with nm-thin gap have enormous potential for applications such as single-molecule spectroscopy, the experimental realisation remains challenging. Using top-down fabrication with electron beam lithography, nanoparticle dimers can be produced (for example bow tie antennas [55, 56]). However, the fabrication of nm-thin gaps is usually limited to > 5 nm by the resolution of lithography techniques [57, 58] and thus nanostructures with extreme field confinement are not accessible. Instead using bottom-up and self-assembly techniques, inter-particle gaps can be designed with atomic precision employing molecular spacers [59, 60]. The yield of dimer formation in self-assembly processes is however low and many monomers remain (or aggregates with higher particle number are formed), making isolation of well-defined dimers difficult. Here, a different geometry will thus be used: the nanoparticle-on-mirror structure.

### 2.1.2 NanoParticle-On-Mirror (NPoM)

In this work, all Raman scattering experiments are carried out with nanoparticle-on-mirror (NPoM) samples [61]. In the NPoM geometry, gold nanoparticles (AuNP) are deposited on a gold mirror with a thin spacer layer in-between, defining a nm-thin gap. Here, the plasmonic charge oscillations of the AuNP now couple to image charges in the mirror forming coupled plasmonic modes similar to the dimer discussed above (see Fig. 2.7a). While this structure confines the light to a small volume (< 100 nm<sup>3</sup> [13]) with high field enhancement ( $\sim 10^2$  [12]) comparable to the dimer, the fabrication of NPoM samples is much simpler and more reproducible than dimers since every particle deposited on the mirror forms a nanocavity and any material forming a thin layer on gold can be used as spacer. Hence, samples with millions of (nearly) identical plasmonic nanocavities can easily be produced, with a layer of molecules under study placed in the hot spot. The fabrication of NPoM samples is explained in detail in Section 3.1.

Due to the high field enhancement, reproducibility and variety of spacer layers, the NPoM structure is ideal for optical investigations of nanoscale systems. Studies with a plethora of different spacer materials have been carried out in the literature, for example using self-assembled monolayers (SAM) of organic molecules [62], larger molecular assemblies (such as organic dye molecules inside larger host molecules [13] or embedded in DNA origami [63, 64]), thin films of polymers [65–67], metal oxides [68], quantum dots [69, 70], or exfoliated 2D materials (such as graphene [71], transition metal dichalcogenides [72–74] or hexagonal boron nitride [75]). This has enabled many interesting applications, such as the study of chemical reactions down to single molecules [76, 77] and monitoring of defects in memristive devices [78]. Additionally, the extreme field confinement boosts light-matter interactions and allows for the observation of single-molecule strong coupling [13] and quantum electrodynamics in the nanocavity [79].

Since AuNPs used here (typically 80 nm diameter) are large enough to support higher order plasmonic modes, the simple picture of coupled dipoles from the previous section does not suffice to explain the scattering spectrum of the NPoM. Additionally, commercially synthesised AuNPs are not perfect spheres but instead have facets corresponding to the gold crystal lattice planes. Hence, in a realistic NPoM nanostructure the AuNP is in contact with the spacer layer with a flat facet of  $\sim 10$  nm in size (see Fig. 2.7a). This leads to the observation of higher order cavity modes characterised by the electric near-field within the nanocavity (see Fig. 2.7c) [81]. Figure 2.7b shows a simulated scattering spectrum of the NPoM with contributions of different cavity modes indicated [80]. Modes are labelled with



**Figure 2.7.** NanoParticle-on-Mirror (NPoM) scattering and plasmonic modes. (a) The gold nanoparticle couples to image charges in the gold, similar to a dimer. Important nanoscale parameters are the particle size *d*, the spacer thickness *t* and refractive index *n*, and the facet width *w*. (b) Simulated scattering spectrum of an NPoM (d = 80 nm, t = 1.5 nm, n = 1.5, w = 24 nm). Contributions from different cavity modes are plotted in colours. (c) Electric field in *z*-direction (across the gap) for the most prominent NPoM cavity modes. (b,c) adapted from [80].

the number of radial nodes n and azimuthal nodes l as (nl). The fundamental (10) mode is equivalent to the bright longitudinal coupled mode discussed for the dimer and has the highest field enhancement in the centre of the facet. In contrast, the (11) mode enhances the optical fields most at two sides of the facet (fields with opposing signs) and only contributes weakly to the scattering spectrum due to its lower radiative efficiency. Many higher order modes overlap around 550 nm, giving rise to a broader resonance in the scattering spectrum (often called the plasmonic pseudo-mode (PPM)). It should be noted that symmetric (even) modes (i.e. (10), (20), ...) have a net dipole moment perpendicular to the gold mirror and hence emit light at high angles, while anti-symmetric (odd) modes (i.e. (11), ...) have an in-plane dipole and scatter light normal to the mirror [81]. This gives rise to the characteristic appearance of NPoMs as rings in dark-field microscopy explained in Section 3.2.

As expected, the plasmonic resonances of the NPoM structure are influenced by the spacer layer thickness and refractive index [65]. However, in this work molecular self-assembled monolayers are used which are highly consistent across the entire sample and cannot be tuned in thickness for a particular molecule of interest. Thus, the dependence of the plasmonic modes on the AuNP size and shape is more relevant here [82]. The (10) mode resonance wavelength strongly depends on the size of the AuNP, red-shifting for increasing particle size while higher order modes (PPM) are only little affected by the size of the particle (see Fig. 2.8a) [82]. Additionally, the plasmonic modes vary for NPoMs with differently shaped

contact facets [80]. Experimentally, this dependence of the plasmonic resonances on the particle is particularly challenging since commercially available AuNPs contain a wide range of sizes and shapes (see Fig. 2.8b). This leads to variations in the electric field enhancement and thus modifies the signal obtained in SERS experiments. To compare hundreds of different NPoMs in an experiment, it is therefore necessary to compensate for the in- and out-coupling efficiency of the nanocavity, which will be established in Chapter 4. Attempts to control the AuNP synthesis for a defined particle geometry (ultraspherical and dodecahedral AuNPs are available) have allowed to reduce the variation between NPoMs on a sample [83]. Instead of spherical AuNPs, nanocubes are often used to increase sample stability with the well-defined facet [84, 85] (in the literature, silver nanocube-on-mirror structures are commonly referred to as nanopatch antennas [86–88]). The different particle and facet shape modifies the scattering spectrum and plasmonic cavity modes compared to spherical AuNPs [89].

For experiments carried out in this thesis, the NPoM geometry provides an excellent tool to investigate the interaction of molecular vibrations with plasmonic nanocavities. Using a self-assembled monolayer as spacer, the molecules can be placed directly in the plasmonic hot spot and it is easily possible to obtain data from thousands of nanocavities. The extreme field enhancement enables to investigate the molecules with surface-enhanced Raman scattering (SERS) and the small volume of the hot spot restricts the number of molecules probed (1-1000 molecules).



**Figure 2.8.** Dependence of NPoM resonances on particle size and shape. (a) Resonance wavelengths of cavity modes for samples with different particle sizes. (b) Electron microscopy images of commercially available gold nanoparticles (nominal diameter: 80 nm). Particle size and shape varies strongly within the same sample. Facets can have different shapes depending on the gold crystal lattice planes (colours). Scale bars 70 nm. Adapted from [82].
#### **NPoM variations**

To tailor the plasmonic modes to specific experimental requirements, the NPoM nanostructure is modified slightly for some experiments presented in this thesis. The main aim is to boost the SERS signal measured from the sample by either tuning plasmonic resonances for maximum field enhancement at the emission wavelength or improve the out-coupling efficiency of light from the cavity to the far-field.

In a simple modification, the entire NPoM sample can be covered with a thin film of polymer with high refractive index (see Fig. 2.9a). The dielectric layer on top of the NPoM modifies the resonance wavelength of plasmonic modes [90]. Both (10) and (20) modes red-shift with increasing polymer thickness (see Fig. 2.9b). If the polymer fully covers the AuNP, the radiative efficiency of all modes increases improving the in- and out-coupling of light into the nanocavity [90]. Notably, the previously (almost) dark (11) and (21) modes become radiative with the additional coating and add significantly to the NPoM scattering spectrum. Since these modes scatter light normal to the surface, they improve the excitation and collection of light with objectives of limited numerical aperture. These effects significantly increase the SERS signal measured from NPoMs covered with a dielectric layer [90]. In this thesis, polymer-coated NPoM samples will be used to boost the out-coupling of anti-Stokes signals between 600 and 700 nm in Chapters 4 and 6.



**Figure 2.9.** Modifying NPoM resonances with a polymer coating. (a) NPoM nanostructure covered with a thin layer of polymer with high refractive index. (b,c) Simulated scattering spectrum of polymer-coated NPoM samples with illumination (b) parallel and (c) normal to the surface. Plasmonic modes red-shift and radiative efficiencies are enhanced by the dielectric coating. Polymer refractive index: 1.45. (b,c) adapted from [90].

A more complex modification of the NPoM structure is the fabrication of so-called 'superefficient plasmonic nanoarchitectures for Raman kinetics' (SPARK) [91]. These composite nanostructures are designed to increase SERS signals to enable the acquisition of Raman spectra with extremely short exposure times (kinetic Raman). A glass nanolens is grown around the AuNPs before deposition to direct the light emitted at high angles towards the objective, increasing the in- and out-coupling into the cavity (see Fig. 2.10) [91]. In addition to the lensing effect, the large SiO<sub>2</sub> structure attached to the AuNP also changes how the AuNPs deposit on the sample. Instead of landing on a nanoparticle facet, the AuNP contacts the SAM with an edge or a tip in most cases. This strongly increases the field-enhancement and reduces the size of the hot spot. Hence, only  $\sim 10$  molecules are investigated with this nanostructure and SERS count rates  $10-10^3$  times higher than from NPoMs can be obtained [91]. However, in many SPARKs (especially with very large nanolenses, > 500 nm) the AuNP often does not come into contact with the SAM, limiting the yield of particles on the sample with observable SERS signal. In Chapter 4, SPARK constructs are used to investigate Raman signals of single molecules with ms time resolution, while Chapter 7 makes use of the improved out-coupling efficiency of SPARKs.



**Figure 2.10.** Superefficient plasmonic nanoarchitectures for Raman kinetics (SPARK). (a) Schematic of a SPARK nanostructure with the gold particle embedded in a glass nanolens. The light emitted to high angles is directed to lower angles. (b) Scanning electron microscopy image of SPARKs on a gold mirror. Inset: transmission electron microscopy image of a single SPARK. (c) Simulated out-coupling of light from a dipole in the SPARK nanocavity. Adapted with permission from [91].

#### **Picocavities**

In SERS experiments, fast fluctuations of the SERS signal in time are often observed, in particular when individual nanostructures are studied [92–94]. Since the SERS signal strongly depends on the electric field enhancement ( $\propto E^4$ , see Section 2.2.3), the signal fluctuations have been attributed to atomic changes in the plasmonic structure varying the field confinement in the hot spot. For the NPoM geometry, Benz et al. concluded that an individual gold atom is moved from the gold surface to the inside of the cavity, increasing the field enhancement in the direct vicinity of the gold adatom (see Fig. 2.11a) [14]. Since the optical field is now confined to volumes < 1 nm<sup>3</sup> (see Fig. 2.11c,d) [14], these events have been termed *picocavities* [95]. In SERS spectra, a picocavity is characterised by the occurrence of new, intense Raman lines spectrally fluctuating in time (see Fig. 2.11b). Therefore, picocavities probe the Raman signal of a single molecule [14, 96].

The generation of picocavities is driven by the application of optical fields to the NPoM nanocavity [97]. Since a few microwatts of focused (continuous-wave) laser power are sufficient to promote picocavity formation, they often appear as spectral fluctuations in SERS experiments. Due to the confinement of the electric field to volumes comparable to the size a molecule, the gradient field across a single molecule is not negligible anymore and leads to the emergence of new Raman lines (gradient Raman scattering) [98]. Since the fields (and gradients) experienced by the molecule now depend on the exact position of the gold adatom relative to the molecule, each picocavity event is characterised by a unique set of SERS lines shifting as the adatom moves around [98].

Further, the small mode volume of the picocavity enhances the interaction of molecular vibrations with the cavity mode, thus showing signatures of optomechanical coupling of a single molecule to the optical modes [14]. Molecular optomechanics will be discussed in more detail in Section 2.3, and effects arising from the enhanced optomechanical coupling in picocavities will be investigated in Chapter 4.



**Figure 2.11.** Plasmonic picocavities inside NPoM. (**a**) A picocavity is generated when a gold adatom moves into the cavity. (**b**) Kinetic SERS spectra of biphenyl-4-thiol (BPT), including a picocavity event. During the picocavity (blue bracket), new SERS lines appear spectrally fluctuating in time. (**c**,**d**) Simulation of the field enhancement in the NPoM with a picocavity. The field is strongly enhanced around the gold adatom. Adapted with permission from (a,b) [96] and (c,d) [14].

## 2.2 Raman Scattering

First discovered in 1928 by Raman and Krishnan [99] (and simultaneously by Landsherg and Mandelstam [100]), Raman scattering of light is an inelastic process occurring when photons are scattered by molecules or other forms of matter. The frequency of the scattered light experiences a spectral shift characteristic for the vibrational structure of the molecule. In particular, the photon energy of the scattered light is reduced or increased by the energy of a molecular vibration via Stokes or anti-Stokes scattering, respectively. This is depicted in Figure 2.12, where energy diagrams of Raman scattering are compared to the elastic scattering process (Rayleigh scattering). In Stokes scattering, vibrations are induced in the molecule and the molecular phonon population increases, whereas anti-Stokes scattering reduces the molecular vibrations and effectively cools down the molecule. Since Raman scattering depends on the exact vibrational structure of the analyte molecules, each molecule has a characteristic spectrum enabling a plethora of spectroscopic studies [101].



**Figure 2.12.** Energy diagrams for elastic (Rayleigh) and inelastic (Stokes, anti-Stokes) scattering of light by a molecule. Solid lines represent real vibrational states, dashed lines are virtual energy levels.  $E_0$ : ground state energy,  $\hbar\omega_l$ : laser photon energy,  $\hbar\omega_v$ : molecular vibrational energy.

In this work, molecular vibrations are the basis for Raman scattering. Hence, Section 2.2.1 briefly introduces how molecules vibrate and give an intuition of the energy scales involved. Building on this, Section 2.2.2 describes the well-established model of Raman scattering based on classical electrodynamics. While Raman scattering is generally a very weak process, plasmonic substrates provide high field-enhancement to boost signals obtained from the Raman process. This surface-enhanced Raman scattering (SERS) is introduced in Section 2.2.3. In contrast, Section 2.3 proposes a theory for SERS based on the framework of cavity optomechanics, so-called molecular optomechanics.

## 2.2.1 Molecular Vibrations

While the vibrational modes of di- or triatomic molecules are easy to understand, organic molecules made up of tens of molecules can exhibit a large number of different vibrations. A molecule with N atoms possesses 3N - 6 independent vibrational modes (3N - 5 for linear molecules) [102]. However, not all of these vibrations have signatures in vibrational spectroscopy. As will be seen in Section 2.2.2 below, a vibration is only Raman-active if the polarisability of the molecule changes due to the movement of atoms in the vibrational mode. Generally, molecules with a high polarisability (e.g. due to delocalised electrons) exhibit strong Raman scattering. In contrast, molecular vibrational modes are IR-active (i.e. can absorb infrared light) if the dipole moment of the molecule changes during the vibration. Infrared spectroscopy will not be covered in this thesis.

For a diatomic molecule, the frequency of the (only) vibrational mode can be calculated with the model of a simple harmonic oscillator as

$$\omega_m = \sqrt{\frac{k}{m^*}} \tag{2.9}$$

with the force constant k and the reduced mass  $1/m^* = 1/m_1 + 1/m_2$  given by the masses of the two atoms. In the picture of molecular vibrations, the force constant corresponds to the bond strength of the covalent bond of the molecule. As a quantum-mechanical system, the energy of the vibrational harmonic oscillator (see Fig. 2.13) is quantised with discrete energy levels

$$E_{\mathbf{v}} = \hbar \omega_m \left( \mathbf{v} + \frac{1}{2} \right) \tag{2.10}$$

with quantum number v of integer value. Vibrational spectroscopy probes transitions with  $\Delta v = 1$  facilitated by the absorption or inelastic scattering of a photon (for IR and Raman spectroscopy, respectively). The energy difference  $\Delta E = E_{v+1} - E_v$  is in the following called vibrational energy and measured with vibrational spectroscopy. Often, molecules deviate from a perfectly harmonic vibrational potential and are better described by a Morse potential (red in Fig. 2.13). This anharmonicity modifies the vibrational energy levels and leads to a lower energy difference at higher quantum numbers. Effects from vibrational anharmonicity are usually only relevant when vibrations are strongly excited by high laser intensities.



**Figure 2.13.** Molecular vibrational potentials. In first approximation, the energy of the molecule vibrating along the normal mode coordinate Q follows a harmonic potential (black) with energy levels quantised according to Eq. 2.10 (quantum number v. In reality, anharmonicity modifies the energy levels of the vibration and a Morse potential (red) is a better model for the vibrational energy.

The frequency of molecular vibrations is typically in the range of 5 to 100 THz, corresponding to a vibrational energy of approximately 20 to 400 meV. In vibrational spectroscopy, the vibrational energy is commonly measured as wavenumber  $\tilde{v} = \omega/2\pi c$  in units of cm<sup>-1</sup>. These different units are compared in Figure 2.14, along with the wavelength of a photon corresponding to this energy. Exciting a molecular vibration by the absorption of a photon requires mid-infrared light with wavelength 3 to 60 µm.

According to Eq. 2.9, lighter atoms lead to a higher vibrational frequency. Hence, vibrations involving a single H atom, for example the O–H stretch of water or the C–H stretch of benzene, have a vibrational energy >3000 cm<sup>-1</sup> [102]. When heavier atoms are involved, the vibrational frequency depends mostly on the strength of the molecular bond. Therefore, covalent triple bonds (for example nitrile ( $-C\equiv N$ ) groups) have vibrational energies >2000 cm<sup>-1</sup> and are often employed as vibrational markers in vibrational bioimaging [103]. Other chemical groups with double bonds, for instance carbonyl (-C=O) groups, also have prominent vibrational features between 1600 and 2000 cm<sup>-1</sup>. Covalent C–C single bonds in organic molecules typically have stretch vibrations with energy ranging from 800 to  $1500 \text{ cm}^{-1}$ . However for larger molecules with 10s of atoms, a vibrational mode often includes the movement of many atoms and bonds in the molecule. In this case, an estimation of the frequency from the harmonic oscillator model is more difficult. Such vibrations including many atoms often have vibrational energies <1000 cm<sup>-1</sup> due to large effective masses involved. Since these vibrations strongly depend on the exact structure of the entire

molecule, the vibrational spectrum in this region is characteristic for each molecular species and is hence often called the 'molecular fingerprint' (shaded red in Fig. 2.14. An important tool to understand the vibrational spectrum of complex molecules and assign vibrational modes to spectral lines are density functional theory (DFT) calculations.

An important comparison for the energy scale of molecular vibrations is the thermal energy at room temperature. Under ambient conditions,  $k_BT \sim 25 \text{ meV} \sim 200 \text{ cm}^{-1}$  (green dashed in Fig. 2.14), much lower than most vibrational energies. This means that molecular vibrations are only weakly excited at room temperature and most molecules are in the vibrational ground state in the experiments considered here.



**Figure 2.14.** Energy scale of molecular vibrations. The energy of different vibrational modes is compared in different units for vibrational energy. Stretch vibrations of H atoms (here shown for benzene and water) have highest vibrational energies, while the energy of other modes depends on the strength of the bond vibrating (here shown: triple bond - nitrile group, double bond - nitro group in p-nitrophenol, single bond - carbon backbone modes of biphenyl-dithiol). Below 800 cm<sup>-1</sup>, vibrational modes usually involve the movement of many atoms in the molecule. Hence, this region is called the 'molecular fingerprint'. The thermal energy at room temperature (RT) is ~200 cm<sup>-1</sup> (green dashed).

## 2.2.2 Classical Model of Raman Scattering

Over the last decades, a theoretical model for Raman scattering has been developed and successfully applied to understand many Raman experiments [36]. This model is based on the classical electrodynamic description of a dipole induced in the molecule by an external electric field oscillating with the laser frequency  $\omega_l$ . Figure 2.15 schematically shows a diatomic molecule that is being polarised by the external optical field while vibrating.



**Figure 2.15.** A diatomic molecule is polarised by an incoming light wave. *E*: electric field,  $\alpha$ : polarisability of the molecule,  $Q_v$ : displacement along molecular coordinate in vibrational normal mode *v*.

The motion of the molecule in the vibrational normal mode v along the molecular coordinate  $Q_v$  with frequency  $\omega_v$  can be simply described by

$$Q_{\nu}(t) = Q_{\nu}^{0} \cos(\omega_{\nu} t + \phi) \tag{2.11}$$

with the vibrational amplitude  $Q_v^0$  and an arbitrary phase  $\phi$ . In the vibrational ground state, the amplitude is given by the quantum-mechanical zero-point amplitude  $Q_v^0 = \sqrt{\hbar/2\omega_v}$ . The incoming optical field oscillates with amplitude  $\mathbf{E}_0$  at laser frequency  $\omega_l$  as

$$\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega_l t) \tag{2.12}$$

and induces a polarisation p in the molecule. Hereby, the linear optical polarisability tensor  $\hat{\alpha}$  of the molecule links the induced Raman polarisation with the electrical field by

$$\mathbf{p}(t) = (L_m)^{1/4} \hat{\boldsymbol{\alpha}}(Q_v) \mathbf{E}(t)$$
(2.13)

where the electromagnetic local field correction  $(L_m)^{1/4} = (\varepsilon + 2)/3$  ( $\varepsilon$ : permittivity of the medium) is accounting for the difference between the applied electric field and the local field inducing the molecular dipole. Moreover, the polarisability depends on the one-dimensional normal coordinate  $Q_v$  of the vibrational motion in the molecule. In approximation, the molecular polarisability can be expanded around the equilibrium configuration  $Q_v = 0$  with

$$\hat{\alpha}(Q_{\nu}) = \hat{\alpha}(Q_{\nu} = 0) + \left(\frac{\partial \hat{\alpha}}{\partial Q_{\nu}}\right)_{Q_{\nu} = 0} Q_{\nu} + \dots$$
(2.14)

Putting Eqs. 2.11 to 2.14 together, one finds that the polarisation possesses three terms oscillating at different frequencies:

$$\mathbf{p}(t) = \hat{\boldsymbol{\alpha}}(0)\mathbf{E}_0\cos(\omega_l t) + \frac{Q_v^0}{2}\hat{R}_v\mathbf{E}_0\cos((\omega_l + \omega_v)t) + \frac{Q_v^0}{2}\hat{R}_v\mathbf{E}_0\cos((\omega_l - \omega_v t))$$
(2.15)

The first term with  $\hat{\alpha}(0)$  describes the elastic excitation of the molecule, the so-called Rayleigh scattering with a frequency equal to the laser frequency  $\omega_l$ . The remaining term in Eq. 2.14 leads to oscillations of the Raman dipole with frequencies  $\omega_{aS} = \omega_l + \omega_v$  and  $\omega_S = \omega_l - \omega_v$ , resulting in Stokes and anti-Stokes scattering, respectively. Therefore, the first derivative of the polarisability is called the Raman tensor  $\hat{R}_v = (\partial \alpha_L / \partial Q_v)_{Q_v=0}$ . The change in polarisability due to the molecular vibration hence causes scattering of light shifted by the vibrational frequency  $\omega_v$  from the laser.

#### Raman cross-section and vibrational population

In optical spectroscopy, the cross-section  $\sigma$  of an object (for example a molecule) quantifies the probability that it interacts with light. The cross-section is defined as the effective area in which every photon of an incoming beam of light interacts with the object via a specific process. For many optical processes, the cross-section is much smaller than the actual size of the object (the geometrical cross-section) since the probability of interaction is low. Hence, the cross-section is a suitable measure to compare the efficiency of different optical processes [36]. Raman scattering is an inherently weak process. The Raman scattering cross-section of an individual molecule is typically on the order of  $\sim 10^{-11} - 10^{-15}$  nm<sup>2</sup> [6]. In comparison, photoluminescence is a much more efficient process with cross-sections of dye molecules on the order of  $\sim 10^{-3}$  nm<sup>2</sup> [104]. Following the classical description of Raman scattering above, one finds that the Stokes  $\sigma_S$  and anti-Stokes  $\sigma_{aS}$  cross-sections of the Raman process are defined as [36]:

$$\sigma_{S} = \frac{8\pi}{3} \left( \frac{Q_{\nu}^{0} R_{\nu}}{4\pi\varepsilon_{0}c^{2}} \right)^{2} \omega_{S}^{4} L_{m} \left( 1 + n_{\nu} \right)$$
(2.16)

$$\sigma_{aS} = \frac{8\pi}{3} \left( \frac{Q_{\nu}^0 R_{\nu}}{4\pi\epsilon_0 c^2} \right)^2 \omega_{aS}^4 L_m n_{\nu} \tag{2.17}$$

Most importantly, the Stokes and anti-Stokes cross-sections are a function of the molecular vibrational population  $n_v$ . While the anti-Stokes process is directly proportional to  $n_v$ , Stokes scattering is proportional to  $(1 + n_v)$ . Since the populations remain small in typical experimental configurations ( $n_v \ll 1$ ), Stokes scattering is often approximated to be independent of the phonon occupation.

In the case of weak incident laser power, the vibrational population is dominated by thermally excited vibrations given by a Bose-Einstein distribution as  $n_v \approx n_v^{th} = [\exp(\hbar\omega_v/k_BT) - 1]^{-1}$  at temperature *T*. Hence, in this regime the ratio of anti-Stokes to Stokes Raman scattering is given by

$$\frac{S_{aS}}{S_S} = \frac{\sigma_{aS}}{\sigma_S} = \left(\frac{\omega_{aS}}{\omega_s}\right)^4 \left(\frac{n_v}{1+n_v}\right) \approx \left(\frac{\omega_{aS}}{\omega_s}\right)^4 e^{-\frac{\hbar\omega_v}{k_B T}}$$
(2.18)

and only depends on the temperature of the environment T. Consequently, this quantity has been employed as a molecular probe sensitive to the temperature of the sample [105]. The phonon population will be very helpful comparing the classical description of Raman scattering to the quantum-mechanical approach which is introduced in Section 2.3.

#### Vibrational pumping

Since every Stokes scattering event creates a phonon and every anti-Stokes event destroys one, the vibrational population will be affected by the incident radiation due to the different rates of Stokes and anti-Stokes scattering. This effect can be included phenomenologically in the classical model of Raman scattering by dividing the total phonon population  $n_v$  into a thermal contribution  $n_v^{th}$ , and a vibrationally pumped population  $n_v^{vp}$  induced by the Stokes transitions [106]. Since usually  $n_v \ll 1$ , the cooling of the vibration due to anti-Stokes scattering can be neglected as Stokes scattering dominates (see Eqs. 2.16 and 2.17). The rate of phonon creation by Stokes scattering is  $\sigma_S I_l/\hbar\omega_S$  (with laser intensity  $I_l$  and energy of a Stokes photon  $\hbar\omega_S$ ), and the molecular vibrations decay with a rate  $\gamma_v$ . Since in some cases not every Stokes scattered photon is emitted to the far-field, the radiative yield  $\eta(\omega_S)$ accounts for non-radiative processes not included in  $\sigma_S$  also inducing vibrations [107, 108]. Therefore, the phonon population including vibrational pumping by Stokes scattering is

$$n_{\nu} = n_{\nu}^{th} + n_{\nu}^{\nu p} = n_{\nu}^{th} + \frac{1}{\gamma_{\nu} \eta(\omega_{S})} \frac{\sigma_{S} I_{l}}{\hbar \omega_{S}}.$$
(2.19)

Under normal Raman scattering conditions and at room temperature, very high laser intensities are required to induce a population compared to the thermal population. However, plasmonic field-enhancement can drastically increase the Raman scattering rates as will be described in the following Section 2.2.3. In this case, surface-enhanced Stokes scattering can strongly pump the population of a Raman active vibration, a mechanism termed 'vibrational pumping' [109]. The first evidence for vibrational pumping was based on the quadratic laser power dependence of the anti-Stokes signal from electronically-resonant rhodamine 6G adsorbed onto metal colloids [110]. Since the phonon population scales linearly with the laser intensity under vibrational pumping conditions (Eq. 2.19) and  $\sigma_{aS} \propto n_v$  (Eq. 2.17, the anti-Stokes signal  $S_{aS} \propto \sigma_{aS} I_l$  scales with  $S_{aS} \propto I_l^2$ .

The mechanism of vibrational pumping was debated heavily in the literature, with other mechanisms including laser-induced heating [111], pumping of vibrations through the decay of electronic excitations [112], and plasmon resonance effects explaining anomalous anti-Stokes/Stokes ratios [113, 114]. Temperature-dependent experiments however provided further evidence for the existence of vibrational pumping [105, 115], and the mechanism is now widely accepted in the SERS community. Additionally, the study of vibrational pumping has helped to estimate SERS cross-sections [108, 116] and plasmonic field enhancement factors [117].

## 2.2.3 Surface-Enhanced Raman Scattering (SERS)

Raman scattering is a very inefficient process with molecular scattering cross-sections of only  $\sim 10^{-11} - 10^{-15}$  nm<sup>2</sup>. Therefore, it is experimentally difficult to measure a Raman spectrum of only a few or even a single molecule. However, using the electric near-field enhancement of a plasmonic surface the Raman signal can be enhanced by many orders of magnitude. This effect was first discovered in 1974 by Fleischmann et al. who observed increased Raman scattering of molecules adsorbed to an electrochemically roughened silver electrode [118]. In 1977, this phenomenon was independently identified by Jeanmaire and Van Duyne [119] and by Albrecht and Creighton [120] as enhancement originating from the surface of the electrode. Soon after its discovery, the effect was linked to plasmonic field enhancement at the rough silver surface [121, 122] and later named surface-enhanced Raman scattering (SERS). Today, SERS is a research field with thousands of articles published each year and applications ranging from biomedical sensing to catalysis of chemical reactions [6, 9].

In the simplest model (only considering electromagnetic Raman enhancement), the increased near-field at a plasmonic surface enhances both the incoming light (at laser frequency  $\omega_l$ ) exciting the molecule as well as the emission of the molecule (at frequency of the SERS emission  $\omega_{SERS}$ . The increase of the Raman signal is thus proportional to the fourth power of the local near-field enhancement. Hence, the enhancement factor is defined by the ratio of SERS signal  $I_{SERS}$  to the normal Raman signal  $I_{NRS}$  (both normalized to the number of contributing molecules  $N_{surf}$  and  $N_{vol}$ , respectively) and can be written as [36]:

$$EF_{SERS} = \frac{I_{SERS}/N_{surf}}{I_{NRS}/N_{vol}} = \left|\frac{E(\omega_l)}{E_0}\right|^2 \left|\frac{E(\omega_{SERS})}{E_0}\right|^2$$
(2.20)

Under typical conditions supported by plasmonic nanoantennas, SERS enhancement factors as high as  $10^8 - 10^{12}$  can be reached [50, 123]. These extreme enhancements have finally led to the observation of Raman signals from single molecules [10, 11]. For the first observations of SERS from single molecules, electronically-resonant dye molecules were used providing further enhancement which is then called surface-enhanced *resonant* Raman scattering (SERRS).

To take the field enhancement by a nearby metal surface into account, the enhancement factor of the electric field  $EF(\omega)$  is added to Eqs. 2.16 and 2.17. In the classical model of Raman scattering, plasmonic enhancements influence the signal in two different ways [106,

123]: Firstly, by a higher excitation rate due to the enhancement of the incident laser with  $EF(\omega_l)$ , and secondly, by an accelerated emission of the Stokes and anti-Stokes photon with  $EF(\omega_S)$  and  $EF(\omega_{aS})$ , respectively (see Eq. 2.20). Thus the equations for the scattering cross-sections are modified to

$$\sigma_{S} = \frac{8\pi}{3} \left( \frac{Q_{\nu}^{0} R_{\nu}}{4\pi\varepsilon_{0}c^{2}} \right)^{2} \omega_{S}^{4} L_{m} (1+n_{\nu}) EF(\omega_{l})^{2} EF(\omega_{S})^{2}$$
(2.21)

$$\sigma_{aS} = \frac{8\pi}{3} \left( \frac{Q_v^0 R_v}{4\pi\varepsilon_0 c^2} \right)^2 \omega_{aS}^4 L_m n_v EF(\omega_l)^2 EF(\omega_{aS})^2$$
(2.22)

In addition to the electromagnetic enhancement considered here, the presence of the metal surface also modifies the electronic structure of adsorbed molecules transferring electrons to or from the molecule under the formation of a metal-molecule bond [124, 125]. Due to the change in electron density, the molecular polarisability and hence the obtained Raman spectrum are modified. In the SERS community, this effect is known as chemical enhancement.

Since the SERS signal strongly depends on the near-field on the plasmonic surface, it is important to understand the physical principles of plasmonics. Therefore, a brief introduction into the field of plasmonics is given in Section 2.1. While noble metal particles provide near-field enhancements on the order of  $EF \sim 10$ , even higher enhancements can be achieved in nm-thin gaps between to plasmonic particles with  $EF \sim 100$ . In this work, the NanoParticle-on-Mirror (NPoM) nanostructure is used for SERS experiments since it reproducibly provides plasmonic hot spots with high field enhancement confined to a monolayer of organic molecules [62]. Using this plasmonic geometry, SERS signals can be measured with single molecule sensitivity [14].

We note that the classical model of SERS here neglects any back-action of the molecular vibration on the plasmonic modes. While this model successfully describes SERS in most experimental configurations, the vibrational population can be substantially increased by surface-enhanced Stokes scattering in samples with particularly high field confinement such as the NPoM ('vibrational pumping', see Section 2.2.2). In these situations, the interaction of vibrations with the optical modes can be included in a quantum-mechanical model of SERS in the framework of molecular optomechanics, introduced in Section 2.3.

## 2.3 Molecular Optomechanics

In the previous section, the enhancement of Raman scattering by plasmonic substrates was discussed. For most applications [9], reproducible SERS enhancement is desirable and thus local hot spots with high field enhancement are avoided [126]. Additionally, sharp resonances in the near-field enhancement spectrum make it difficult to compare SERS intensities of different vibrational lines and can be prevented by illuminating a large area on inhomogeneous substrates [127]. In this work however, SERS experiments are carried out on individual plasmonic nanocavities. As discussed in Section 2.1.2, the nanoparticle-on-mirror (NPoM) nanostructures provide defined plasmonic resonances with small mode volumes. Therefore, the NPoM can also be characterised as a nanoscale optical cavity [12]. In the following, we explore how placing the vibrating molecules in a cavity enhances the SERS signal but also modifies the molecular vibrations. Here, the classical model of Raman scattering discussed in Section 2.2.2 may no longer hold and we thus introduce the quantum-mechanical model of molecular optomechanics [128–130], which applies the concept of cavity optomechanics [131] to SERS.

## 2.3.1 Plasmonic cavities and SERS

Coupled plasmonic systems, such as the NPoM, can be described as a nanoscale optical cavity. An optical cavity can enhance light-matter interactions by retaining the light and thus extending the timescale of the interaction. In general, the optical properties of the cavity are characterised by its quality factor Q and mode volume  $V_m$ . The Q factor is a measure for losses in the cavity and describes how long a photon can be trapped in the cavity. For a cavity with a resonance frequency  $\omega_c$  and spectral width  $\kappa_c$ , the Q factor can be calculated as

$$Q = \frac{\omega_c}{\kappa_c} = 2\pi \frac{\text{energy stored}}{\text{energy dissipated per cycle}}.$$
 (2.23)

Alternatively, the Q factor can be interpreted as the ratio of (optical) energy stored in the cavity compared to the loss of energy per cycle around the cavity. A high-Q optical cavity, such as photonic crystals fabricated from silicon [132], can reach quality factors of  $10^5$  or even higher. The concept of the quality factor can also be applied to mechanical oscillators, here provided by molecular vibrations, and is sometimes considered in the field of cavity optomechanics [131, 133].

The mode volume  $V_m$  of an optical cavity measures the volume in which the optical field is confined and hence describes the spatial localisation of the field by the cavity. For normal optical cavities, the volume of a cavity is limited by the diffraction limit to a minimum of  $V_\lambda \approx (\lambda/n)^3$  (at wavelength  $\lambda$  and cavity refractive index *n*), however a typical Fabry-Pérot cavity has volumes of several  $\mu m^3$ . Since this volume is large compared to the size of a molecule ( $\sim nm^3$ ), the overlap of the optical mode with the molecule is poor. To compensate for the large mode volume, very high *Q* factors are needed to boost light-matter interactions.

In contrast to typical optical cavities, this consideration changes for plasmonic cavities. Due to absorption losses in the metal, the quality factor of NPoM nanocavities is on the order of  $Q \sim 10$  [13]. While photons only remain in the cavity for a short time, the plasmonic near-field enhancement confines the electric field to volumes below the diffraction limit. In NPoM, the mode volume is estimated to be < 100 nm<sup>3</sup> (estimation from the optomechanical coupling) [13, 134]. Therefore, the enhancement of light-matter interactions in plasmonic nanocavities is dominated by small mode volumes rather than high Q factors.

In the context of surface-enhanced Raman scattering, the plasmonic cavity leads to a strong wavelength-dependence of the optical field enhancement. Hence, Stokes and anti-Stokes scattering can experience different enhancement depending on the detuning of the laser wavelength from the cavity resonance. If the enhancement on the anti-Stokes side of the laser is much stronger than on the Stokes side, the vibrational population can even be decreased leading to cooling of the molecule. In this case, the relation of the anti-Stokes/Stokes ratio to temperature derived in the classical model of Raman scattering (Eq. 2.18) is no longer valid. Additionally, Raman scattered photons are emitted to the cavity mode and can interact with the same vibrating molecule again. This leads to coherent coupling of molecular vibrations with the optical cavity mode [135], not included in the classical Raman model. To overcome the limitations of the classical Raman model, Roelli et al. and Schmidt et al. simultaneously developed a new model for SERS based on cavity optomechanics [128, 129].

The field of cavity optomechanics studies the interaction of electromagnetic radiation in a cavity with a mechanical system coupled to the cavity. The most intuitive optomechanical system is composed of a Fabry-Pérot cavity with one mirror mounted on a spring (see Fig. 2.16a). The light circulating between the mirrors exerts radiation pressure on the mirrors, applying a force to the mirror on the spring. When the mirror is set in motion, the resonance of the cavity is modified changing the intensity of light in the cavity and hence the force on the mirror. Therefore, the optical mode in the cavity and the mechanical motion of the mirror interact with each other and form a coupled optomechanical system [131, 136].

In *molecular* optomechanics, the optical mode is provided by a plasmonic nanocavity while vibrating molecules present mechanical modes. Here, the light in the cavity interacts via Raman scattering with the molecular vibrations. The back-action of the vibrations on the cavity is governed by the change of the induced dipole moment during the vibration which modifies the cavity resonance frequency [129]. The behaviour of the optomechanical system depends on the detuning  $\Delta = \omega_c - \omega_l$  of the laser to the cavity resonance. If the laser is blue-detuned to the cavity mode ( $\Delta < 0$ ), Stokes scattering experiences stronger enhancement by the cavity mode than anti-Stokes scattering (Fig. 2.16c). This leads to the creation of more phonons by the Stokes process than are annihilated by anti-Stokes scattering, and the molecular vibration is effectively heated up. Contrarily, a red-detuned laser ( $\Delta > 0$ ) favours anti-Stokes over Stokes scattering, hence 'cooling' the vibration by reducing the population below the thermal equilibrium (Fig. 2.16b).

The optomechanical interaction can therefore either amplify or reduce the population of the mechanical mode depending on the laser detuning [131, 133]. This behaviour is not captured by the classical model of Raman scattering and Eqs. 2.18 and 2.19 may thus not be correct for SERS from plasmonic nanocavities since they do not account for the back-action of the molecular vibration on the cavity. However, for most other SERS experiments the optomechanical coupling is weak and the classical Raman model still gives a good approximation. In the following, a model for SERS in the context of cavity optomechanics is introduced.



**Figure 2.16.** (a) Optomechanical system composed of Fabry-Pérot cavity with one mirror on a spring. The optical cavity with resonance frequency  $\omega_c$  is coupled to the mechanical mode at  $\omega_v$ . (b) Stokes and anti-Stokes scattering with a laser red-detuned to the cavity resonance ( $\omega_l < \omega_c$ ). The mechanical mode (here harmonic potential) is depopulated by enhanced anti-Stokes scattering . (c) Scattering with a blue-detuned laser ( $\omega_l > \omega_c$ ). Enhanced Stokes scattering populates the mechanical mode.

## 2.3.2 Quantum-mechanical model of SERS

In order to develop a quantum-mechanical model of SERS, both the molecular vibrations and the electromagnetic field are now quantised as bosonic excitations. As a starting point, the interaction Hamiltonian for the energy of a molecular dipole in the electric field is described by [106, 129, 130]

$$\hat{H}_{int} = -\frac{1}{2}\hat{\mathbf{p}}(t)\cdot\hat{\mathbf{E}}(\mathbf{r}_m,t)$$
(2.24)

Here,  $\hat{\mathbf{p}}(t)$  is the time-dependent operator for the quantised molecular polarisation and  $\hat{\mathbf{E}}(\mathbf{r}_m, t)$  is the electric field operator depending on the position of the molecule  $\mathbf{r}_m$  and time. For a localized plasmonic resonance with Lorentzian-like spectral response centred around  $\omega_c$ , the electric field is given by [137, 138]

$$\hat{\mathbf{E}}(\mathbf{r},t) = \mathbf{u}_E \sqrt{\frac{\hbar\omega_c}{2\varepsilon_0 \varepsilon V_m}} \left[ \hat{a}(t)u(\mathbf{r}) + \hat{a}^{\dagger}(t)u^*(\mathbf{r}) \right]$$
(2.25)

with the effective volume  $V_m$  and the permittivity of the surrounding medium  $\varepsilon_0 \varepsilon$ .  $\hat{a}$  and  $\hat{a}^{\dagger}$  are the bosonic annihilation and creation operators for the plasmonic excitations, respectively. The polarisation of the field is indicated by the unit vector  $\mathbf{u}_E$  and  $u(\mathbf{r})$  gives the spatial variation within the cavity, normalized to the point of maximum field strength.

Similar to the classical Raman model (Eq. 2.13), the molecular polarisation  $\hat{\mathbf{p}}(t)$  is induced by the electric field  $\hat{\mathbf{E}}(\mathbf{r}_m, t)$  according to

$$\hat{p}(t) = (L_m)^{1/4} \alpha(Q_v) \hat{E}(\mathbf{r}_m, t)$$
(2.26)

and the molecular polarisability  $\alpha$  is approximated for the vibrational motion along normal mode coordinate  $Q_v$  as in Eq. 2.14. Since the vibrational potential can be approximated with a harmonic potential [139], the vibrational energy is quantised with the phonon creation and annihilation operators  $\hat{b}$  and  $\hat{b}^{\dagger}$ , respectively:

$$Q_{\nu} = Q_{\nu}^{0} \left( \hat{b} + \hat{b}^{\dagger} \right) \tag{2.27}$$

with zero-point amplitude of the vibration  $Q_v^0 = \sqrt{\hbar/2\omega_v}$  as in the classical Raman model.

Putting the above equations together, we obtain the interaction Hamiltonian for the optomechanical system

$$\hat{H}_{int} = -(L_m)^{1/4} Q_V^0 R_V \frac{\hbar \omega_c}{4\epsilon_0 \epsilon V_m} \left(\hat{b} + \hat{b}^\dagger\right) \left[\hat{a}(t)u(\mathbf{r}_m) + \hat{a}^\dagger(t)u^*(\mathbf{r}_m)\right]^2 (\mathbf{u}_E \cdot \mathbf{u}_V)^2 \qquad (2.28)$$

Expanding the square brackets in Eq. 2.28, terms proportional to  $\hat{a}^2$  and  $(\hat{a}^{\dagger})^2$  are neglected since they will not contribute to the interaction [106]. With the bosonic commutation rule  $\hat{a}^{\dagger}\hat{a} + \hat{a}\hat{a}^{\dagger} = 2\hat{a}^{\dagger}\hat{a} + 1$ , the remaining two terms can be rewritten, again omitting the last term without contribution from the optical cavity. Moreover, placing the molecule in the position of highest field intensity ( $|u(\mathbf{r}_m)|^2 = 1$ ) and assuming the direction of the vibrational mode is parallel to the electric field ( $\mathbf{u}_E \cdot \mathbf{u}_V = 1$ ) further simplifies the equation [106]:

$$\hat{H}_{int} \approx -(L_m)^{1/4} Q_{\nu}^0 R_{\nu} \frac{\hbar \omega_c}{2\varepsilon_0 \varepsilon V_m} \hat{a}^{\dagger} \hat{a} \left( \hat{b} + \hat{b}^{\dagger} \right)$$
(2.29)

Adding expressions for the energy of the electromagnetic cavity mode ( $\hbar\omega_c$ ) and for the molecular vibration ( $\hbar\omega_v$ ) as well as coherent excitation with the laser at frequency  $\omega_l$  and pumping rate  $\Omega$  (relation to the laser intensity:  $\Omega^2 \propto I_l$ ), the full Hamiltonian for the molecular optomechanical system reads:

$$\hat{H} = \hbar \omega_c \hat{a}^{\dagger} \hat{a} + \hbar \omega_v \hat{b}^{\dagger} \hat{b} - \hbar g_0 \hat{a}^{\dagger} \hat{a} \left( \hat{b}^{\dagger} + \hat{b} \right) + i\hbar \Omega \left( \hat{a}^{\dagger} e^{-i\omega_l t} - e^{i\omega_l t} \right)$$
(2.30)

Here,  $g_0$  is the single-photon optomechanical coupling rate characteristic for the strength of the interaction of optical and mechanical mode:

$$g_0 = (L_m)^{1/4} \frac{Q_\nu^0 R_\nu \omega_c}{2\varepsilon_e \varepsilon V_m} \,. \tag{2.31}$$

The term proportional to  $\hbar g_0$  in Eq. 2.30 introduces the interaction of the molecular vibrations and electromagnetic cavity modes to the model. Remarkably, this term coincides exactly with the interaction term found for a traditional optomechanical system [131].

Since the the optomechanical interaction is usually weak ( $g_0 \ll \kappa_c$ ), the cavity population driven by the laser will remain close to its coherent state ( $\alpha$ ) with only small deviations ( $\delta a$ ) from the optomechanical coupling [106]. The operator  $\hat{a}$  can hence be rewritten for small fluctuations around the coherent state as  $\alpha + \delta \hat{a}$ , where  $|\alpha|^2$  corresponds to the average number of plasmons in the cavity. Similarly, the phonon operator  $\hat{b}$  is modified for small fluctuations around a coherent population as  $\beta + \delta \hat{b}$  [106]. Using these new operators, the Hamiltonian for the optomechanical system in Eq. 2.30 can be linearised and an analytical solution is obtained [129]. In the following, we discuss the consequences of the optomechanical coupling for the vibrational population and signal in SERS.

#### Vibrational population in molecular optomechanics

In the quantum-mechanical model, the vibrational population is given by  $n_V = \langle \hat{b}^{\dagger} \hat{b} \rangle$ . Including intrinsic vibrational losses  $\gamma_V$  and the thermal population  $n_V^{th}$ , a rate equation for the phonon population can be obtained from the optomechanical model [106, 130]:

$$\frac{\partial n_{\nu}}{\partial t} = -n_{\nu}(\gamma_{\nu} + \Gamma_{-}) + (n_{\nu} + 1)\Gamma_{+} + n_{\nu}^{th}\gamma_{\nu}$$
(2.32)

Here,  $\Gamma_+$  and  $\Gamma_-$  are the optomechanical pumping and damping rates and modify the phonon population. The optomechanical interaction creates vibrations with rate  $(n_v + 1)\Gamma_+$  and destroys them with  $n_v\Gamma_-$ , corresponding to Stokes and anti-Stokes scattering, respectively. The optomechanical rates are given by

$$\Gamma_{\pm} = \frac{g_0^2 |\alpha|^2 \kappa_c}{\left(\Delta \pm \omega_v\right)^2 + \left(\kappa_c/2\right)^2} \tag{2.33}$$

with the plasmonic decay rate  $\kappa_c$ , coherent plasmon amplitude  $\alpha$  (with  $|\alpha|^2 \propto I_l$ ) and plasmonlaser detuning  $\Delta = \omega_c - \omega_l$ . As depicted in Figure 2.17a,  $\Gamma_+$  and  $\Gamma_-$  depend strongly on the laser detuning: for a laser blue-detuned from the cavity resonance ( $\Delta < 0$ ), the cavity benefits the Stokes transitions ( $\Gamma_+ > \Gamma_-$ ) and phonons are pumped into the molecule amplifying the phonon population. In the red-detuned laser regime ( $\Delta > 0$ ), phonons are removed from the molecule since ( $\Gamma_+ < \Gamma_-$ ), cooling the vibration. The total optomechanial damping rate  $\Gamma_{opt} = \Gamma_- - \Gamma_+$  can therefore be either positive or negative, damping or pumping the vibration, respectively.



**Figure 2.17.** Optomechanical pumping of the vibrational population. (a) Optomechanical rates  $\Gamma_{opt}$  (grey),  $\Gamma_+$  (green) and  $\Gamma_-$  (blue) *vs* detuning of the laser from the cavity ( $\Delta = \omega_c - \omega_l$ ). (b) Vibrational population *vs* detuning for moderate (pumped population comparable to thermal population, brown) and high (optomechanical pumping comparable to vibrational losses, red) laser intensity. (a,b) assume a single-mode plasmonic cavity with  $\kappa_c = \omega_v$ . Adapted from [130].

From the rate equation in Eq. 2.32, the steady-state phonon population can be calculated:

$$n_{\nu} = \frac{\gamma_{\nu} n_{\nu}^{th} + \Gamma_{+}}{\gamma_{\nu} + \Gamma_{opt}}$$
(2.34)

The vibrational population here is pumped by the optomechanical interaction with  $\Gamma_+$ . This is equivalent to the vibrational pumping by the Stokes process discussed in the classical Raman model (Sec. 2.2.2). For moderate laser intensities, where the pumped population is comparable to the thermal population  $(\gamma_{\nu} n_{\nu}^{th} \approx \Gamma_{+})$ , the phonon population depends on the laser detuning similar to the optomechanical pumping rate  $\Gamma_+$  (Fig. 2.17b, brown). Only with a blue-detuned laser ( $\Delta < 0$ ), an amplification of the population can be achieved. In the red-detuned case, the population is damped and hence dominated by the thermal population. However, the optomechanical rates also depend on the laser intensity  $I_l$  with  $\Gamma_+$ ,  $\Gamma_- \propto I_l$ . At very high intensity, the total optomechanical damping rate can become comparable to the vibrational losses ( $|\Gamma_{opt}| \approx \gamma_v$ ). In this case, the detuning and hence the sign of  $\Gamma_{opt}$  becomes particularly important. Since the vibrational losses  $\gamma_v$  are modified by the optomechanical coupling to  $\gamma_v + \Gamma_{opt}$ , the optomechanical interaction can be understood as either broadening  $(\Gamma_{opt} > 0)$  or narrowing  $(\Gamma_{opt} < 0)$  of the vibrational lines in Raman scattering. Additionally, for very strong, blue-detuned optomechanical pumping ( $\gamma_v + \Gamma_{opt} \approx 0$ ) the vibrational losses are overcome and the population diverges (Fig. 2.17b, red). This regime is called parametric instability, and is an effect that cannot be captured by the classical Raman model.

#### Non-linearities in the SERS signal

The easiest way to access the signatures of optomechanical coupling experimentally is through the dependence of SERS signals on laser intensity. The spectral signal from the cavity can be calculated by [106]

$$S(\boldsymbol{\omega}) = \boldsymbol{\omega}^4 \int_{-\infty}^{\infty} \mathrm{d}t \, e^{i\boldsymbol{\omega}t} \left\langle \hat{a}^{\dagger}(t)\hat{a}(0) \right\rangle.$$
(2.35)

The SERS signal integrated over the width of the emission peaks are then given by [106, 140]

$$S(\omega_{aS}) \propto \omega_{aS}^4 \Gamma_- n_V , \quad S(\omega_S) \propto \omega_S^4 \Gamma_+ (n_V + 1)$$
 (2.36)

for anti-Stokes and Stokes scattering, respectively. Notably, these intensities exhibit the same dependence on the phonon population as the scattering cross-sections in Eqs. 2.16 and 2.17 as derived in the classical model. Here, the SERS intensities are however modified by the optomechanical rates  $\Gamma_+$  and  $\Gamma_-$ . This directly includes the field enhancement at the Stokes and anti-Stokes frequencies into the SERS signal.



**Figure 2.18.** Dependence of the anti-Stokes signal on laser intensity in the molecular optomechanical model. At low intensity, the signal is proportional to laser intensity (thermal regime), while quadratic scaling is observed at intermediate intensity (vibrational pumping regime). At high laser intensity, the signal either saturates (red-detuned laser) or diverges (blue-detuned laser), an effect called parametric instability. Adapted from [130].

To analyse the dependence of the SERS signal on the laser intensity, we combine Eq. 2.36 with the phonon population and intensity-dependent optomechanical rates from Eqs. 2.33 and 2.34, respectively. While the Stokes signal scales linearly with intensity in most cases (except at parametric instability), three different regimes can be identified for the anti-Stokes signal (see Fig. 2.18):

- Thermal regime: For weak laser illumination, the optomechanical rates are weak and the phonon population is dominated by the thermal pumping  $n_v = n_v^{th}$ . Stokes and anti-Stokes scale proportional to illumination intensity as the phonon population is independent of intensity ( $S_{aS} \propto I_l$ ). This is the case for most SERS experiments with continuous-wave excitation, and the classical model of Raman scattering is sufficient to describe this regime.
- Vibrational pumping regime: With increasing intensity, the population induced by the Stokes process with Γ<sub>+</sub> dominates over the thermal population. In this regime (Γ<sub>+</sub> ≤ n<sub>v</sub><sup>th</sup> γ<sub>v</sub> and |Γ<sub>opt</sub>| ≪ γ<sub>v</sub>), the phonon population n<sub>v</sub> ∝ Γ<sub>+</sub> ∝ I<sub>l</sub> increases linearly with laser intensity, leading to quadratic scaling of the anti-Stokes signal (S<sub>aS</sub> ∝ I<sub>l</sub><sup>2</sup>). This behaviour can also be included in the classical model by modifying the population with an extra term depending on laser intensity (see Eq. 2.19).
- Strong illumination: The behaviour of the anti-Stokes signal at very high laser intensity (|Γ<sub>opt</sub>| ≈ γ<sub>V</sub>) depends on the laser-cavity detuning. For a blue-detuned laser (Γ<sub>opt</sub> < 0), the effective vibrational losses vanish leading to narrowing of the SERS line and divergence of the population and both anti-Stokes and Stokes signal. This regime called parametric instability is however difficult to probe experimentally as the extreme pumping of vibrations usually leads to the breakdown of molecules. For a red-detuned laser (Γ<sub>opt</sub> > 0), vibrational losses γ<sub>V</sub> + Γ<sub>opt</sub> are increased. This results in broadening of the vibrational line and eventually the saturation of the phonon population. Here, the anti-Stokes signal returns to linear scaling with the laser intensity.

The quadratic scaling of the anti-Stokes signal with illumination power has been observed for single molecules in picocavities [14]. Here, it was possible to access the vibrational pumping regime due to the extreme field enhancement in the plasmonic hot spot. In SERS experiments with pulsed lasers, a super-linearity in the Stokes signal was observe at very high (peak) illumination intensities [141, 142]. This is attributed to the onset of the parametric instability regime. However, at slightly higher powers the signal saturates and even irrevocably decreases as molecules are damaged by the intense light.

### Limitations of the model

To derive the quantum-mechanical model of SERS, several approximations were made. This limits the applicability of the theory to complex system encountered in the experiment. For example, the plasmon resonance is approximated by a single Lorentzian-shaped mode. However, plasmonic nanocavities typically possess multiple modes (see Section 2.1.2) which can be either radiating to the far-field (bright modes) or not (dark modes). Even though the dark modes cannot be observed in scattering spectroscopy, they produce an optical near-field and can hence interact with the molecular vibrations. A more general approach to incorporate the full plasmonic response into the optomechanical model is a continuum-field description [143, 144].

Furthermore, the optomechanical model so far only considers a single molecule in the plasmonic cavity. However in a typical experimental setup, tens to hundreds of molecules are located in the plasmonic hot spot. This can give rise to collective effects where vibrations of multiple molecules are coupled via the plasmonic mode. This inter-molecular coupling effectively increases the optomechanical interaction with the plasmon and can be included in the optomechanical model by placing many vibrational dipoles in the cavity and summing over all interactions [145].

In Chapter 4, the optomechanical model presented here will be expanded with the continuumfield description to account for the complex plasmonic response. Additionally, collective molecular vibrational modes will be included in the model. Using this advanced model of molecular optomechanics, we will explore new effects found in experiments, such as the optomechanical spring shift (giving an intensity-dependent shift of vibrational lines, neglected in the model introduced above) and the modification of vibrational pumping by collective vibrations.

# 2.4 Ultrafast Vibrational Spectroscopy

Ultrafast spectroscopy has the potential to study molecular dynamics on femto- or picosecond timescales. Many different techniques have been developed to combine the molecular sensitivity provided by SERS with the time resolution of ultrafast spectroscopy [146, 147]. Pushing the limits of these methods, it is possible to observe time-resolved vibrational signatures from single molecules [148, 149]. After discussing the basics of ultrafast spectroscopy, this section introduces the timescales of several molecular processes to highlight the challenges in time-resolved vibrational spectroscopy. Then, several experimental techniques that utilise pulsed lasers to investigate the physics of molecular vibrations are summarised, with focus on SERS techniques. This includes both spontaneous SERS experiments conducted with pulsed lasers instead of the usual continuous-wave lasers (Section 2.4.2) as well as coherent Raman scattering experiments under surface-enhanced conditions (Section 2.4.2).

To investigate the ultrafast optical response of any material, the use of laser pulses is indispensable. Time-resolved optical experiments follow the pump-probe principle: A first laser pulse (pump pulse) creates an excitation in the material and a second laser pulse (probe pulse) with a defined time delay probes the response of the perturbed material. Laser pulses can easily be delayed by changing the path length of the laser beam with a mechanical delay stage (a change in path length of 0.3 mm corresponds to 1 ps delay). This allows very precise tuning of the pulse delay in comparison to the delay of electronic signals, where jitter usually limits the timing precision to several picoseconds.

Fundamentally, the temporal and spectral resolution of optical experiments with pulsed lasers is limited by the time-bandwidth product. Since the temporal shape of the laser pulse is related to its spectrum via Fourier transformation, a laser pulse of given duration  $\Delta t$  (full-width at half-maximum, FWHM) has a minimum spectral width  $\Delta v$  (FWHM) given by

$$\Delta t \,\Delta v \ge K. \tag{2.37}$$

Here, *K* depends on the temporal shape of the pulse. In this thesis, all pulses are spectrally filtered and hence of Gaussian shape, giving K = 0.441. For Raman spectroscopy, spectrally narrow laser pulses are required to resolve individual vibrational modes. Therefore, pulses are spectrally filtered to a bandwidth  $\Delta v = 1.5$  nm, limiting the the temporal resolution to 500 fs (at 700 nm laser wavelength). This compromise between spectral and temporal resolution has to be made for every time-resolved Raman experiment.

The use of laser pulses for spectroscopy also allows to probe non-linear optical effects. Enabled by the high peak powers of pulsed lasers, such processes require excitation by multiple photons at once. In vibrational spectroscopy, several non-linear optical processes are relevant for applications (see Fig. 2.19). For example, vibrational sum-frequency generation (SFG) combines the absorption of one infrared photon exciting the vibration and subsequent anti-Stokes Raman scattering. On the other hand, hyper Raman scattering (HRS) describes Raman scattering of the frequency-doubled laser (although this process is typically extremely weak). Most relevant for this thesis however are coherent Raman scattering processes, such as coherent anti-Stokes Raman scattering (CARS). Here the Raman process is stimulated by two laser photons with energy difference tuned to the vibrational energy. This allows time-resolved Raman experiments and is described in more detail in Section 2.4.2.



**Figure 2.19.** Energy diagrams for several linear (top row) and non-linear (bottom row) vibrational spectroscopy techniques. Straight arrows indicate excitation by laser photons, wavy arrows emission of a photon. The length of the arrow is representative for the photon energy. Solid lines represent real vibrational states while dashed lines signal virtual energy levels.

## 2.4.1 Timescales of Molecular Processes

To apply time-resolved spectroscopy techniques for the investigation of molecular vibrations, it is useful to consider the timescale of different molecular processes that can be probed by optical spectroscopy. In this thesis, we employ laser pulses of 500 fs duration to investigate the behaviour of molecular vibrations. This pulse duration sets the temporal resolution of any time-resolved experiment that can be conducted. The application of faster pulses is limited here by the time-bandwidth product and the requirement to spectrally resolve Raman scattering of different vibrational modes, as discussed above. As Figure 2.20 shows, this pulse duration sets which molecular processes can be observed here.

The vibrational movement of atoms in the molecule occurs with 10–100 THz frequencies, as discussed in Section 2.2.1. In the time domain, this corresponds to timescales of 10–100 fs. Directly probing the molecular vibrational motion thus requires fast pulses with duration  $\sim$ 10 fs or shorter. While the bandwidth of such pulses makes it impossible to directly record Raman spectra, two photons from the pulse can excite the vibration via stimulated Raman scattering, and the perturbation of a second fast laser pulse is monitored with time delay between the pulses. This process is called impulsive stimulated Raman scattering (ISRS) and records the nuclear motion of the molecule in time [150]. Fourier transformation of this signal yields the Raman spectrum of the molecule. Since pulses fast enough for ISRS are not available in this work (they require different laser systems and dispersion compensation), the timescale of molecular vibrational motion is not accessible here. The relaxation of molecular vibrations is typically much slower and occurs on the scale of several picoseconds [151]. However, the vibrational dynamics can be strongly accelerated when molecules are bound to a surface [152].

Electronic excited states in molecules can exhibit much longer lifetimes than vibrational excitations. For typical dye molecules, fluorescence lifetimes of several nanoseconds are measured [153, 154]. This timescale is accessible for electronic measurements and time-correlated single-photon counting (TCSPC) is usually employed to analyse fluorescence lifetimes. Here, the time delay between the excitation pulse and the emitted photon is recorded with timing electronics (this will be introduced in more detail in Chapter 5). Some molecules can occasionally transition from the excited singlet electronic state to a triplet state (inter-system crossing) where relaxation to the ground state via emission of a photon is forbidden. Consequently, the molecule can remain in the excited state for µs to ms before a photon is emitted (then called phosphorescence) [155].



**Figure 2.20.** Timescales of molecular processes. The period of molecular vibrational motion is 10 to 100 fs, and vibrations typically decay on femto- to picosecond timescales. Electronic excited states exhibit longer lifetimes, with typical fluorescence decays on nanosecond timescales. If the molecule transitions to a non-emitting state ('dark states', e.g. triplet, radical or trapped states), the resulting phosphorescence can last for micro- to milliseconds. Adapted from [154].

In this work, molecules are embedded in plasmonic nanocavities which can drastically alter the dynamics of all molecular processes. Firstly, the chemical binding of molecules changes the dynamics of vibrational relaxation. The chemical bond provides a dissipation pathway of vibrational energy to the metal via so-called electron friction (a damping force atomic nuclei experience as they move near metallic electrons) [152, 156], accelerating vibrational relaxation. Secondly, the rate of radiative processes is enhanced by the high density of photonic states provided by the optical cavity, the so-called purcell enhancement [157]. In the NPoM cavity, Purcell factors  $F_P > 10^6$  have been estimated [13, 158] leading to accelerated spontaneous emission rates of dye molecules in the cavity below the time resolution (~ 100 ps) of a typical TCSPC experiment [79, 159].

## 2.4.2 Ultrafast Surface-Enhanced Raman Scattering

#### Spontaneous SERS with pulsed lasers

Although the widely used single-colour, continuous-wave (CW) SERS is a very powerful technique able to identify molecules by their vibrational spectrum, it is possible to gain further information about molecule-plasmon and molecule-molecule interactions by using ultrafast laser sources. These often offer a wide tunability of the laser wavelength and thus enable experiments with variable detuning of the excitation frequency with respect to the plasmon resonance [160]. However, spectroscopy with ultrafast laser sources is fundamentally limited by the time-bandwidth product. Therefore, a compromise has to be made between temporal and spectral resolution in every experiment.

The key advantage of SERS experiments with pulsed excitation lasers is that higher optical fields are accessible compared to CW light sources. With peak laser powers of a pulsed laser orders of magnitude higher than their average power, it is possible to probe molecules with intense fields while average powers stay below the damage threshold. In the context of molecular optomechanics, the dependence of the SERS signal on the illumination intensity has been extensively discussed in Section 2.3 from a theoretical standpoint. Pulsed SERS experiments have demonstrated optical pumping of the vibrational population investigating anomalous Stokes/anti-Stokes ratios [161]. Therefore, pulsed Stokes pumping and time-resolved anti-Stokes probing enables to measure the vibrational relaxation of adsorbed molecules [162, 163]. Further, SERS with pulsed lasers has been applied to demonstrate other optomechanical effects such as the onset of parametric instability indicated by super-linear scaling of Stokes signals [141, 142]. However, such experiments are always complicated by laser pulses inflicting damage to nanostructures and molecules [164].

Besides optical pumping of vibrations and electronic excitations, the high illumination intensities reached with pulsed lasers can be utilized to promote two-photon excitation processes. In the context of Raman spectroscopy, hyper-Raman scattering (HRS) is the most relevant technique exploiting two-photon excitation (see Fig. 2.19). Here, two photons of frequency  $\omega_l$  scatter inelastically with a molecule under emission of a photon with frequency  $2\omega_l - \omega_v$  corresponding to Stokes scattering (or  $2\omega_l + \omega_v$  corresponding to anti-Stokes scattering). HRS is an intrinsically weak process with scattering cross-sections in the order of  $10^{-46}$  nm<sup>2</sup>, comparable to the product of two linear Raman scattering events [165]. Therefore, the use of pulsed lasers is essential for HRS experiments. Furthermore, surface-enhancement can increase the signal by many orders of magnitude enabling the detection of

single molecules with HRS [166]. One advantage of HRS is that it can access vibrational states that are forbidden for one-photon scattering [167]. Furthermore, HRS has been applied on biological samples [165] where the higher penetration depth of infrared radiation enables new fields of application compared to linear Raman scattering [168]. However, due to the extremely low efficiency of the HRS process, other non-linear processes - in particular coherent Raman scattering discussed below - are more relevant for applications.

#### **Coherent SERS**

An important technique for time-resolved vibrational spectroscopy is coherent anti-Stokes Raman scattering (CARS). CARS is a non-linear Raman scattering process of third order, involving three incident laser photons [169]: A pump pulse (with frequency  $\omega_p$ ) and a Stokes pulse ( $\omega_S$ ) induce a coherent polarisation in the sample, which is then probed by anti-Stokes scattering of a probe pulse ( $\omega_x$ ) at a defined time later (see Figure 2.19). When the frequency difference of pump and Stokes photons matches the frequency of a Raman active mode ( $\omega_p - \omega_S = \omega_v$ ), the vibration is coherently driven by the electric fields. The measured CARS signal has the frequency  $\omega_{CARS} = \omega_p - \omega_S + \omega_x$ . By delaying the probe pulse in comparison to the other two pulses and recording the intensity of the CARS signal, it is possible to track the induced sample polarisation as a function of time. Time-resolved CARS has been used to study vibrational dynamics of many different molecules in the bulk [170–174], as well as to investigate nanomaterials [175–177]. Moreover, CARS has been applied in biological applications for label-free imaging of cells offering high resolution and chemical information [178–180].

However to investigate a small number of or even single molecules, the CARS signal needs to be increased significantly. As for linear Raman scattering, the electric field enhancement provided by plasmonic nanoparticles can be exploited. Since the CARS signal depends on the intensity of all three laser beams, the enhancement factor in Eq. 2.20 is now modified to:

$$EF_{CARS} = \left|\frac{E(\omega_p)}{E_0}\right|^2 \left|\frac{E(\omega_S)}{E_0}\right|^2 \left|\frac{E(\omega_x)}{E_0}\right|^2 \left|\frac{E(\omega_{CARS})}{E_0}\right|^2$$
(2.38)

Hence, the enhancement of CARS signals by a nearby plasmonic surface is even higher than for regular SERS. The first surface-enhanced CARS (SE-CARS) experiments were performed by Chen et al. in 1979 who obtained a CARS spectrum of benzene adsorbed to a silver surface [181]. Many studies on a range of plasmonic substrates demonstrated that SE-CARS has the potential to detect (bio)molecules with higher sensitivity than SERS with enhancement factors depending on the plasmon resonance [182–187]. Further, tip-enhanced CARS has been employed for vibrational nanoimaging [188, 189].

Due to electronic non-linearties, SE-CARS experiments often suffer from a four-wave mixing (FWM) signal obscuring the CARS signal at the same emission wavelength. In plasmonic materials, the FWM signal can be generated by either (non-resonant) electronic CARS or electronic two-photon absorption. In most cases, the FWM signal is distinguished from SE-CARS by its (typically very fast) temporal response or spectral investigations separating resonant CARS and non-resonant FWM.

Recent experimental progress in the field of SE-CARS made it possible to observe timeresolved dynamics of molecular vibrations [190]. Voronine et al. demonstrated time-resolved SE-CARS in 2012 observing vibrational dephasing of pyridine-water complexes near gold nanoparticles [191]. A strong non-resonant background is observed at time zero while molecular signatures are visible at longer time delays. Furthermore, pulse shaping is used to optimise the trade-off between spectral and temporal resolution and suppress the non-resonant background [191].



**Figure 2.21.** Two plasmonic structures achieving putative single-molecule sensitivity in SE-CARS. (a) Diluted molecules on a gold nano-quadrumer. Adapted with permission from [148]. (b) Gold nanoparticle dimer with molecules in the gap, encapsulated in a silica shell. Adapted with permission from [149].

In 2014, two research groups achieved SE-CARS with single molecule sensitivity [148, 149]. The plasmonic substrates used for these experiments are depicted in Figure 2.21. Zhang et al. exploited the Fano resonance of lithographically prepared gold quadrumers optimised to match the wavelengths of the lasers, achieving enhancement factors up to 10<sup>11</sup> [148]. SE-CARS spectra were recorded using a broadband Stokes beam generated with a photonic crystal fibre and single-molecule sensitivity was demonstrated by bi-analyte detection of p-mercaptoanilin and adenine [148].

Using a gold nanoparticle dimer with molecules in the gap, Yampolsky et al. investigated the time-resolved SE-CARS response of individual molecules [149]. Investigating bispyridylethylene which has two Raman lines with a separation of 35 cm<sup>-1</sup>, they observed a quantum beating of the two vibrational modes (see Fig. 2.22a). The observation of a single molecule was here confirmed by a long-lived (~10 ps), coherent beating signal obeying phase noise with statistics characteristic for a single emitter. However, in more recent experiments by the same research group, no time-resolved molecular signal could be measured even though the same nanostructures were investigated [164]. Here, only a quickly-decaying signal at t = 0 was observed attributed to non-resonant four wave mixing in the metal (see Fig. 2.22b). Instead, damage to the nanostructures was reported during the experiment. The origin of these seemingly contradicting results remains unclear and only few studies on SE-CARS have been published since [192, 193].



**Figure 2.22.** Two measurements of time-resolved SE-CARS on the nanostructure in Fig. 2.21b. (a) A coherent beating signal was observed attributed to a single, vibrating molecule (orange, grey). Adapted with permission from [149]. (b) Only the short-lived non-resonant FWM signal of the metal can be observed (black). Instead, damage to the nanostructure leads to the decay of the count rate during the experiment (grey). Adapted with permission from [164].

The experimental advances in SE-CARS demonstrate the great potential of this technique to study molecular vibrations and their dynamics. However, combining surface-enhancement with time-resolved measurements is still challenging due to interfering background signals, the stability of plasmonic nanostructures under pulsed laser illumination and the generally accelerated molecular dynamics near metal surfaces. Especially recent contradicting results on time-resolved SE-CARS [149, 164] emphasise that more experimental work is required to reliably probe vibrational dynamics using SE-CARS. Chapter 6 of this thesis will focus on time-resolved Raman experiments using the nanoparticle-on-mirror structure.

# Chapter 3

# **Experimental Methods**

This chapter summarises the experimental methods and techniques used to carry out the research presented in this thesis. In this work, nanoscale self-assembly allows the simultaneous fabrication of billions of nanostructures. Section 3.1 documents the fabrication procedure for nanoparticle-on-mirror (NPoM) cavities using self-assembled monolayers (SAMs) of molecules forming a precisely defined, nm-thin gap. The fabrication of samples in this thesis is simple and avoids the use of expensive equipment. Using automated optical spectroscopy, hundreds of nanoparticles can be investigated and meaningful statistics are generated providing insights about physical effects on the nanoscale. Dark-field spectroscopy, introduced in Section 3.2, is an important tool to visualise the plasmonic nanocavities and characterise their plasmonic resonances. The experimental work in this thesis however focuses on Raman scattering using laser pulses. Section 3.3 introduces the pulsed laser system, microscope and detection setup used for these experiments.

# 3.1 Sample Fabrication

## 3.1.1 NanoParticle-on-Mirror

All experiments in this thesis are carried out on self-assembled plasmonic nanocavities related to the NanoParticle-on-Mirror (NPoM) geometry described in section 2.1.2. The general process of producing NPoM samples is described below, with modifications of this process for particular experiments specified in detail in the corresponding chapters.

The sample fabrication begins with the production of an atomically-flat gold mirror by template-stripping (see Fig. 3.1) [194]. A gold film is prepared by thermal evaporation of 100 nm of gold on a silicon wafer. Then, glass substrates are glued on the gold film with UV glue Norland 81 (Thorlabs NOA81) and UV-cured. A fresh sample is stripped off the silicon wafer for each use. The exposed gold surface inherits its flatness from the silicon wafer and is free from contaminants directly after template-stripping.



**Figure 3.1.** Fabrication of template-stripped gold substrates. Gold is evaporated on a silicon wafer. Glass substrates are glued to the gold film. The samples can be stored and stripped off the wafer for a clean, atomically-flat gold surface.

Self-assembled monolayers (SAMs) of 1,1'-biphenyl-4-thiol (BPT) are fabricated by soaking a template-stripped gold substrate in 1 mM BPT (97%, Sigma-Aldrich) solution in 200-proof anhydrous ethanol overnight. After SAM formation, the sample is cleaned with ethanol and blown dry with nitrogen. Nanoparticle-on-mirror samples are prepared by depositing 50  $\mu$ L of 80 nm gold nanoparticles (AuNPs, BBI Solutions) on BPT SAMs on template-stripped gold, which are then rinsed off with deionised water after 30 s and blown dry with nitrogen. The density of NPoM structures on the sample can be tuned by varying the deposition time. All steps in the NPoM fabrication process are summarised in Figure 3.2.


**Figure 3.2.** Nanoparticle-on-mirror (NPoM) fabrication. On the template-stripped gold substrate a organic SAM is assembled. Then, gold nanoparticles are deposited on top of the SAM. Optionally, the NPoM sample can be coated with a thin film of polymer.

Polymer-coated NPoM samples are prepared by spin coating a 100 nm layer of poly(methyl methacrylate) (PMMA, 950k molecular weight, 2wt% in anisole) with a first cycle at 500 rpm for 10 s and a second cycle at 2000 rpm for 45 s. Samples were then left to bake on a hotplate at 50°C for 5 min to remove residual anisole solvent. The polymer coating changes the plasmonic modes of the NPoM and improves in- and out-coupling of light to the nanocavity (see dark-field spectra in Fig. 3.7) [90].

For the generation of 'superefficient plasmonic nanoarchitectures for Raman kinetics' (SPARK) samples, composite gold-silica particles are deposited on the sample instead of AuNPs. The SPARK constructs are produced by organosilica synthesis using AuNPs as seeds for nucleation and growth [91]. The silica lens surrounding the AuNP changes the optical properties of the nanostructure and allows for better in- and out-coupling of light into the nanogap. Additionally, AuNPs often land on an edge instead of a flat facet, as the case for NPoM structures. This increases the field enhancement and reduces the size of the plasmonic hot spot. The three types of samples used in this work, NPoM, NPoM with polymer coating, and SPARKs, are sketched in Figure 3.3.



**Figure 3.3.** Variations of NPoM samples. (a) Standard NPoM sample. (b) NPoM sample coated with a thin film of polymer for improved in- and out-coupling. (c) SPARK sample with silica lens on top of the gold particle. The silica lens increases coupling to the far-field and leads to stronger field enhancement.

#### 3.1.2 Biphenyl-4-thiol

For most investigations in this work, we focus on a simple organic molecule: 1,1'-biphenyl-4-thiol (BPT). BPT has proven to be a suitable model molecule for many surface-enhanced Raman scattering studies due to the combination of multiple advantageous properties.



Figure 3.4. Chemical structure of 1,1'-biphenyl-4-thiol (BPT).

The thiol(-SH) group has a very strong affinity to the gold surface. The formation of a covalent gold-sulphur bond binds the molecules strongly to the metal [195], replacing other contaminants on the surface. This leads to the formation of a robust self-assembled monolayer (SAM) of molecules on gold [196]. Organic SAMs are highly ordered layers of molecules with well-defined thickness and can be easily fabricated via a self-assembly process. Inter-molecular interaction between aromatic systems, so-called  $\pi$ - $\pi$  stacking [197], aid this process of self-organisation for aromatic molecules like BPT and lead to SAMs with crystalline order. Further, the high electron density of the aromatic rings means the molecules can be easily polarised by light. This increased polarisability leads to a high Raman cross section compared to non-aromatic molecules (such as alkanethiols).

SAMs of BPT have been studied extensively in the literature. Scanning tunneling microscopy (STM) on BPT SAMs shows the formation of hexagonal molecular superstructures [198], proving that BPT forms highly ordered molecular layers. Additionally, X-ray spectroscopy revealed that BPT molecules are bound to the surface with a tilt angle of 15° [199] and hence form a layer of 1.3 nm thickness [200]. Therefore, BPT is a well-characterised model system ideal for our fundamental SERS investigations.

In Figure 3.5, the Raman spectrum of molecular BPT powder (97%, Sigma-Aldrich) is compared to the SERS spectrum of a SAM of BPT in the NPoM gap (high-resolution Raman spectra acquired with Renishaw inVia Reflex commercial Raman microscope). The vibrational spectrum of BPT is strongly modified upon binding to gold. Due to the covalent bond to a Au atom with high mass, the vibrational energy of some modes is changed and Raman lines are shifted in NPoMs. Moreover, the increased asymmetry in the molecule breaks the degeneracy of the two ring stretching modes ( $\sim$ 1586 cm<sup>-1</sup>) leading to a double line in NPoMs. Additionally, the peak ratios of different vibrational modes changes. In particular, the Raman activity of the sulphur-ring stretch (1080 cm<sup>-1</sup>) is increased compared to the other vibrations since the bond to the metal increases the electron density and hence polarisability in this area of the molecule. This effect is often called chemical enhancement in SERS. Finally, the molecular environment seems to be more inhomogeneous in NPoMs than in (crystalline) BPT powder since Raman lines are broader.

The molecular movement of atoms in different vibrational modes is schematically indicated in Figure 3.5c. Raman active vibrational modes are identified from DFT simulations. At low vibrational energies, the vibrational motion is delocalised across the entire molecule. Observable modes are a bending of the benzene rings against each other (292 cm<sup>-1</sup>), a twisting of the rings (405 cm<sup>-1</sup>), and a stretching vibration across the entire molecule (481 cm<sup>-1</sup>). Higher energy vibrations are more localised in specific areas of the molecule. At 1080 cm<sup>-1</sup>, the sulphur-benzene ring stretch vibration is characteristic for aromatic thiols bound to gold. The coupled ring stretch vibration at 1280 cm<sup>-1</sup> is common for molecules with two (or more) benzene rings bound to each other. Finally, the vibrational mode with highest Raman activity is the benzene ring stretch vibration. In NPoM, this mode is split in two modes with separation ~13 cm<sup>-1</sup> as the two rings experience slightly different environments due to binding to the gold surface. However, in pulsed SERS experiments this separation cannot be resolved and the mode will thus be labelled 1586 cm<sup>-1</sup> in the following chapters. Most experiments in this thesis focus on the 1586 cm<sup>-1</sup> due to its high Raman activity and low thermal vibrational population compared to other lower-energy modes.



**Figure 3.5.** Vibrational modes of 1,1'-biphenyl-4-thiol (BPT). (**a**) Raman spectrum of BPT powder. (**b**) SERS spectrum of a BPT SAM in the NPoM nanocavity. Vibrational modes are modified upon binding to gold. (**c**) Schematic illustration of vibrational modes for BPT bound to gold. Low wavenumber modes involve movement of the entire molecule, while only parts of the molecule move for higher energy vibrations.

## **3.2 Dark-field Spectroscopy**

Dark-field spectroscopy is an important tool to characterise the plasmonic resonances of metal nanostructures. In dark-field contrast, only light scattered by the sample is collected. Since reflected light is rejected, non-scattering samples appear dark. On a well-fabricated NPoM sample (flat gold surface, no other impurities), only the NPoM nanostructures scatter the light and are hence visible on the dark background despite their small scattering cross-section. Therefore, dark-field microscopy is an excellent technique to visualise the plasmonic nanocavities on the sample. Since the focus of this work is mainly on vibrational spectroscopy instead of plasmonic modes, dark-field microscopy and spectroscopy are only used here to locate the nanoparticles, verify their desired plasmonic properties and confirm that the nanostructures were not damaged during the experiment. At the end of this section, exemplary dark-field spectra of NPoM structures will be presented which are representative for all samples used in this thesis.

Dark-field contrast is here implemented experimentally by illuminating the sample at high angles and collecting only light scattered to lower angles. Figure 3.6 schematically shows the dark-field spectroscopy setup used in this work. The dark-field contrast is achieved with an Olympus MPlanFLN 100x/0.90 dark-field objective. In addition to the objective lens, this objective includes a system of mirrors to focus a ring of light entering the objective onto the sample at high angles. The ring of white light is prepared by the illuminator arm of an Olympus BX51 microscope equipped with a dark-field cube which blocks the central part of the beam and reflects only a ring to the objective with a ring mirror. While the microscope is otherwise custom-built to increase stability (as detailed below), the commercial illuminator arm is included to provide a ring of collimated white light matching the requirements of the objective. Light scattered by the sample is then collected by the lens system of the same objective at angles lower than the illumination. Here, the objective with highest available numerical aperture (NA = 0.9) was chosen since NPoM structures predominantly scatter light (and emit SERS) at high angles. The scattered light is divided with a 50:50 beam splitter for both imaging and spectroscopy. The dark-field image is recorded with a Lumenera Infinity 2 camera. For spectroscopy, the scattered light is coupled into a 50 µm core multi-mode fibre (Thorlabs AFS50/125Y) and detected with an OceanOptics QE65000 spectrometer cooled to -20°C. Dark-field spectra are background-subtracted and referenced to the spectrum of a diffuse scatterer. Here, the gold mirror of the NPoM samples was used as background spectrum and white paper as reference spectrum.



**Figure 3.6.** Schematic setup for dark-field microscopy and spectroscopy. The sample is illuminated with light from high angles (orange) and only light scattered to lower angles is collected (yellow). The ring of light for illumination is prepared by an illuminator arm from a commercial microscope. A dark-field objective, consisting of an outer mirror system a central objective lens, illuminates the sample and collects scattered light. The signal is recorded by a camera for imaging and a fibre-coupled spectrometer (split with 50:50 beam splitter).

Figure 3.7a show a typical dark-field image of an NPoM sample. NPoM structures appear as red circles on a dark background. Since the plasmonic (10) mode (see Section 2.1.2) is reminiscent of a dipole standing vertically on the sample (optical fields in *z*-direction dominate), it emits radially polarised light which interferes destructively in the centre of the spot on the camera, leading to circles in the scattering image. The deposition time of nanoparticles on the sample (see Section 3.1.1) is optimised to give good coverage of well-separated NPoMs on the sample. Using the dark-field image, individual NPoM structures can by located and centred in the focus of the laser for SERS experiments.

By centring a NPoM in the collection spot of the fibre connected to the spectrometer (corresponding to focusing into the fibre core), the dark-field scattering spectrum of individual nanostructures can be recorded. Using the scattering spectrum, plasmonic modes can be identified which depend strongly on the exact nanoscale properties of the structure. For NPoM samples with a BPT SAM in the gap and 80 nm particle diameter, the main (10) coupled mode scatters light at around 800 nm wavelength (Fig. 3.7b). Since this resonance shifts strongly for different molecules or particle sizes, spectral dark-field measurements are suitable to confirm successful sample fabrication and exclude scattering impurities (which may look like NPoMs in the image) from SERS experiments. Additional, higher-order plasmonic modes are located between 500 and 600 nm.

Coating the NPoM sample with a thin layer of polymer changes the plasmonic properties of the nanocavity [90]. The dielectric film on top of the structure allows for odd cavity modes (e.g. (11) and (21), with azimuthal nodes) to become radiative. Since these modes possess an in-plane dipole, they scatter light mostly perpendicular to the surface. Hence, the polymer-coated NPoMs appear as bright dots (instead of circles) in the dark-field image. This is also reflected in the dark-field spectrum (see Fig. 3.7c). NPoMs covered with a polymer film exhibit strong scattering between 600 and 700 nm, corresponding to higher order modes. The fundamental (10) resonance is red-shifted to the NIR outside the experimentally accessible range [90]. In general, the polymer coating enhances the NPoM scattering and particles appear brighter in dark-field contrast.



**Figure 3.7.** (a) Exemplary dark-field image of an NPoM sample. Since the fundamental plasmonic modes scatters light at high angles, NPoMs appear as rings in imaging. (b) Scattering spectrum of a representative NPoM nanostructure. The (10) coupled mode scatters light at 800 nm, while higher-order modes scatter light around 600 nm. The position of plasmonic resonances is sensitive to the nanoscale properties of the structure. (c) Scattering spectrum of a representative polymer-coated NPoM. The coating enhances scattering (also of previously non-radiative modes) and red-shifts the position of resonances.

### 3.3 Ultrafast Raman Spectroscopy

To conduct SERS experiments on individual nanostructures, a microscope combining darkfield imaging and laser spectroscopy is required. Moreover, the use of pulsed lasers necessary for time-resolved studies poses additional challenges for the setup. Finally, experiments carried out in this work require an elaborate setup of detectors for single-photon spectroscopy. This section summarises how pulsed laser excitation and SERS spectroscopy are incorporated in the dark-field setup described above.

#### **3.3.1** Pulsed Laser System

For ultrafast Raman experiments, a pulsed laser system is required. A SpectraPhysics MaiTai Ti:Sapphire pump laser provides pulses of 100 fs duration at 80 MHz repetition rate. The pump laser is tunable in wavelength from 700 to 1100 nm and provides up to 2.9 W power (at 820 nm). Such high laser powers are necessary for non-linear optics converting the NIR wavelengths of the pump laser to the visible. Here, the pump laser drives an optical parametric oscillator (OPO, SpectraPhysics Inspire) generating a signal beam with wavelength tunable from 530 to 730 nm. Furthermore, a small fraction of the laser beam is reflected towards a fast photodiode by a beam sampler to monitor the repetition rate.

For operation with the OPO, the pump laser is set to 820 nm. The working principle of the OPO is schematically drawn in Figure 3.8. The OPO makes use of two non-linear optical processes to create light in the visible: second harmonic generation (SHG) and parametric down conversion [201, 202]. First, the pump laser beam is frequency-doubled with SHG. Two photons of the pump laser at frequency  $\omega_{pump}$  are combined to emit one photon with doubled frequency

$$\omega_{SHG} = 2\omega_{pump} \,. \tag{3.1}$$

The SHG beam is created by focusing the pump laser beam through a crystal with high second-order non-linear susceptibility ( $\chi^{(2)} > 0$ ). In addition to energy conservation (Eq. 3.1), the momentum of photons has to be conserved (phase-matching). This is achieved by rotating the SHG crystal until maximum SHG power is obtained. Optimisation of the SHG power is automated in the OPO, tuning both crystal angle and distance of the focusing lens.

The SHG photons at 410 nm are subsequently focused through another non-linear crystal for parametric down conversion. Here, one high energy photon is split in two photons of lower energy given energy conservation

$$\omega_{signal} + \omega_{idler} = \omega_{SHG} \,. \tag{3.2}$$

The two output beams are called signal and idler, with  $\omega_{signal} > \omega_{idler}$ . To fix the frequencies of this process and increase its efficiency, it is seeded with light at  $\omega_{signal}$ . In an OPO, this is achieved by integrating the non-linear crystal in a cavity for the signal beam. If the cavity length matches the time between laser pulses (given by the repetition rate), the non-linear process leads to gain in the signal and idler beams (and corresponding loss in the SHG beam). The phase-matching condition is tuned by the crystal angle and sets the wavelength of signal and idler. Again, the OPO automatically tunes and constantly optimises the signal power and wavelength with feedback from an integrated spectrometer. The signal wavelength is tunable from 550 to 750 nm (100 fs, 80 MHz) and reaches up to 300 mW power (at 550 nm).

Besides the signal and idler beams, the OPO also offers an output for the unconverted pump laser beam (transmitted through the SHG crystal). Additionally, the SHG signal can be out-coupled with a flip mirror, however stopping the emission of signal and idler beams. In the ultrafast SERS experiments here, only the signal and pump laser beams are required and sent to the microscope.



**Figure 3.8.** Schematic setup of pump laser and optical parametric oscillator (OPO). First, the second harmonic of the pump beam is generated. Then, the SHG beam is converted in a non-linear parametric process to the signal and idler beams, with wavelengths set by phase-matching via the OPO crystal angle. The signal beam is coupled to a cavity to provide gain for the non-linear process.

#### 3.3.2 Single-Particle SERS Spectroscopy

#### Microscopy

The laser pulses from the OPO are then coupled into the dark-field microscope described in Section 3.2 for SERS spectroscopy on individual NPoMs (see Fig. 3.9. In this setup, laser pulses are focused on the sample with the Olympus MPlanFLN 100x/0.90 dark-field objective. The SERS signal is collected in reflection with the same objective. Here, the objective with highest available NA was chosen as in- and out-coupling of light into NPoM nanocavities is most efficient at high angles. To separate the SERS signal from the incoming laser pulses, a 90:10 (reflection:transmission) beam splitter is used. While this leads to the loss of 90% of laser power, it also preserves 90% of the signal. Since the pulsed laser system provides very high laser powers (enough to easily damage the nanostructures), this loss is acceptable. The spare laser power reflected by the beam splitter is sent on a power meter to monitor the laser power on the sample.

Since some experiments carried out in this thesis require very long integration times (up to several hours for non-linear, single-photon counting experiments), the stability of the microscope is critical. To reduce vibrations and slow drift of the sample (as is common in commercially available dark-field microscopes), a custom-build, heavy-duty microscope frame combines the Olympus BX51 illuminator arm, dark-field objective and sample stage in an inverted microscope. The XY sample stage (Thorlabs MLS203) and a piezoelectric Z stage (Piezoconcept FOC100) for focusing which holds the objective are installed on a metal base plate mounted on four metal posts. This configuration enables measurements on a single nanostructure over several hours without realignment.

#### **Beam delivery**

Up to three different laser beams (depending on the experiment) are prepared and sent into the microscope, as detailed in Figure 3.9. One beam line aligns the spare pump laser beam from the OPO into the microscope, while the OPO signal beam is split in two beam lines with a 50:50 beam splitter. All three laser beams can be filtered by independently tunable bandpass filters (PhotonETC LLTF contrast) with a spectral bandwidth of 1.5 nm giving pulses with 0.5 ps duration. The bandpass filters provide a compromise between spectral and temporal resolution. With the bandwidth of 1.5 nm, individual molecular vibrational modes can be



**Figure 3.9.** Combining dark-field microscopy and pulsed laser spectroscopy. Up to three laser beams are prepared from the OPO (Fig. 3.8) and individually filtered by bandpass filters ( $\lambda_{1,2,3}$ ), modulated with electro-optical modulators (EOM), temporally aligned with mechanical delay lines and expanded. After beams are combined with beam splitters (50:50), the laser power is adjusted with a neutral density filter wheel. The laser beams are coupled into the microscope with a 90:10 beam splitter (reflecting 90% of on a power meter for calibration). The signal collected by the objective is separated from the laser by the 90:10 beam splitter and sent to the detection setup (Fig. 3.10).

resolved while 0.5 ps pulses are still fast enough to probe vibrational relaxation dynamics. The spectral tunability of individual beams is required to excite molecular vibrations with coherent Raman scattering. Here, the energy difference between photons of two laser beams is matched to the vibrational energy to coherently drive the vibration. This will be employed for time-resolved coherent anti-Stokes Raman spectroscopy (CARS) in Chapter 6.

Further, two of the three beams can be modulated with electro-optical modulators (EOM) for lock-in detection. The visible beam from the OPO is modulated with a Thorlabs EO-AM-NR-C4 EOM while the pump laser beam (NIR) is modulated with a Conoptics 360-80 EOM. Both EOMs are driven with square waves at 50 kHz by two function generators which can be phase-locked. The modulation of laser beams will be particularly important for the development of single-photon lock-in detection in Chapter 5.

The temporal alignment of laser pulses is ensured with motorized delay stages which can vary the time delay between pulses for time-resolved experiments (Chapter 6). Moreover, all laser beams are expanded to completely cover the entrance pupil of the objective and make use of the full numerical aperture. This is critical for SERS experiments on NPoMs as only light at high angles is in-coupled into the nanocavity. For beams with Gaussian beam profile, it can thus be beneficial to overfill the objective aperture to provide a more homogeneous intensity profile across all angles. The polarisation of all beams is controlled with half wave plates and polarisers, and the three beams can be individually controlled by Thorlabs SH1 laser shutters for flexible experimental design. Finally, the three beams are combined by two 50:50 beam splitters.

An important aspect for many experiments in this thesis is their dependence on the excitation laser power. This is especially relevant in the context of molecular optomechanics in Chapter 4. The laser power on sample is controlled by a neutral density filter wheel (Thorlabs NDC-50C-2) on an automated rotational stage. This filter wheel provides continuous tuning of power with optical density ranging from 0.04 to 2. Additional (non-automated) filter wheels are placed in the individual beams for relative adjustment of power. The power on sample for each position of the filter wheel is calibrated with a power meter measuring the laser reflected by the 90:10 beam splitter in the microscope (given a correction factor calibrating to the power on sample).

In case high spectral resolution is required (or as reference for pulsed experiments), it is also possible to couple continuous-wave lasers into the objective by removing a mirror from the pulsed laser beam line. Both a 633 nm helium-neon laser (JDS Uniphase 1107P) and a 785 nm diode laser (Thorlabs FPV785S) with appropriate clean-up filters are available.

All instruments described above are controlled with a custom Python library (nplab [203]). To enable the generation of large data sets including hundreds of nanostructures, an automated particle tracking algorithm is implemented. The algorithm centres individual nanostructures in the laser focus before carrying out each experimental routine. This allows for dark-field and SERS measurements to be conducted on the same nanoparticle in quick succession.

#### Signal detection

The microscope utilised in this work features several different detection setups for the variety of experiments carried out, as sketched in Figure 3.10. Here, a more general overview of the different arrangements for detection is provided while the remaining chapters of this thesis detail the exact setup used for each experiment. Different arrangements for detection can be adjusted by removing or adding mirrors on magnetic bases. The camera and spectrometer for dark-field microscopy, which is described in detail in Section 3.2, are coupled in to the beam path with a mirror on a linear translation stage (Thorlabs ELL20) with position feedback for reproducible alignment. The stage allows for automated switching between dark-field and SERS detection during the experiment while preventing the loss of signal when using beam splitters.

In typical SERS experiments, the laser is filtered out with notch filters (Iridian 785-20 NNF for 785 nm lasers, two notch filters are required for full extinction of the laser pulses). To accommodate for the tunable laser wavelength of the pulsed laser system, variable edgepass filters (Fianium Superchrome) are employed to remove laser beams of uncommon wavelengths. This is particularly important for CARS experiments, where the tunable short and long pass filters are used in combination as a band pass filter for the CARS signal of the molecular vibration under study.

SERS and CARS spectra are recorded with an Andor iDus DU416A EMCCD (electronmultiplying charge-coupled device) camera mounted on an Andor Shamrock monochromator (SR-303i-B). All spectra recorded in this work are resolved with a grating with 600 lines/mm, providing enough dispersion to cover the full Stokes and anti-Stokes spectrum. Alternatively, filtered signals can be detected with a single-photon avalanche diode (SPAD) from Micro Photon Devices (SPD-100-CTD) for enhanced sensitivity and time-resolved photon counting. The single-photon detector is used in combination with a field-programmable gate array (FPGA) board (Digilent Arty Z7) programmed to record the arrival time of photons on the detector. The development of this single-photon lock-in detection is detailed in Chapter 5 and applied for time-resolved CARS experiments (Chapter 6) and SERS photon correlation spectroscopy (Section 7).



**Figure 3.10.** Photon detection setups. The signal (purple) collected in the microscope is sent to the detectors by a 90:10 beam splitter. Scattered light for dark-field spectroscopy is detected with a spectrometer and a camera for imaging. After spectral filtering, SERS and CARS spectra are recorded with a spectrometer and EMCCD camera, or alternatively with a single-photon avalanche diode (SPAD). For correlation spectroscopy, Stokes (red) and anti-Stokes (blue) signals are separated with a dichroic mirror and detected by separate SPADs after band pass filtering with angle-tunable filters.

For Stokes-anti-Stokes correlation spectroscopy experiments carried out in Chapter 7, Stokes and anti-Stokes signals are separated by a dichroic mirror (Semrock FF01-776). To reduce distortions of the polarisation<sup>1</sup>, the dichroic mirror is here use at near-normal incidence. To measure correlated photon pairs, it is essential to collect only light scattered by the same vibrational mode on both detectors. Hence, narrow band pass filtering is implemented with two sets of angle tunable edge pass filters (a combination of a long and short pass filter for each detector) with sharp cut-off transition (Stokes: Semrock TSP01-887 and TLP01-887, anti-Stokes: Semrock TSP01-790 and TLP01-790). The filters are mounted on rotational stages (Thorlabs ELL18) for automated variation of band pass wavelengths. For the precise alignment of tunable filters, transmitted white light is coupled back to the Raman spectrometer and compared to SERS spectra taken on the same spectrometer. For polarisation-resolved correlation experiments, polarisers are mounted in the Stokes and anti-Stokes beam paths (before the band pass filters to avoid polarisation scrambling<sup>1</sup>). A half wave plate is mounted on a rotational stage (Thorlabs ELL14) in the anti-Stokes detection path to switch the detected polarisation direction relative to the Stokes detector. The entire detection setup is connected with black lens tubes to minimise ambient light on the detectors.

<sup>&</sup>lt;sup>1</sup>The reflection/ transmission on interfaces can lead to a phase shift between s- and p-polarised light, depending on the incident angle and refractive indices (particularly strong for thin-film filters/dichroics).

#### **3.3.3** Spectral Correction

The detection efficiency of optical detectors, as well as the transmission through filters and other optical components varies over the visible/NIR spectrum. Especially in the NIR, the efficiency of the EMCCD spectrometer camera declines towards higher wavelengths. In order to compare Raman peaks at different emission wavelengths (especially Stokes and anti-Stokes peaks), the spectral efficiency of the setup has to be calibrated.

First, the (relative) spectral efficiency of an OceanOptics QD6500 fibre-coupled spectrometer is calibrated with a halogen lamp of known spectrum. Then, the spectrum of the white light from the microscope illuminator arm on the sample is measured by focusing the light into the fibre of the calibrated spectrometer with the dark-field objective (see Fig. 3.11a). In every experimental configuration (filter settings), the spectrum of the white light scattered from a diffuse scatterer (here: white paper) is measured with the Raman spectrometer (see Fig. 3.11b). By comparing this spectrum to the actual spectrum of the white light in the sample plain, the spectral efficiency of the setup can be corrected (see Fig. 3.11c).

Every NPoM SERS spectrum presented in this thesis is first background-subtracted to account for laser leak through the filters (background: SERS spectrum on gold mirror) and then corrected with the spectral efficiency of the setup.



Figure 3.11. Spectral efficiency correction. (a) Spectrum of the white light source of the microscope illuminator arm on the sample, measured with a calibrated spectrometer. (b) White light scattered by a diffuse scatterer, recorded with the Raman spectrometer. (c) Spectral efficiency of the detection setup used to correct SERS spectra.

## **Chapter 4**

# Non-linear Phonon Interactions from Molecular Optomechanics

The contents of Sections 4.2 - 4.4 were previously published in *Nature Communications* in 2023 [204], and a second manuscript of Section 4.5 is currently in preparation.

#### Author contributions:

Yuan Zhang, Ruben Esteban, Adrian Juan Delgado, Tomas Neuman and Javier Aizpurua developed the optomechanical model and conducted all simulations presented in this chapter. Elena Pavlenko, William M. Deacon and Bart de Nijs collected experimental data in Section 4.4. The author of this thesis collected experimental data in Section 4.5 and analysed all data in the context of molecular optomechanics, establishing the connection between experiment and theory. Samples were prepared by Bart de Nijs, Marlous Kamp, Niclas S. Müller, Shu Hu and Rakesh Arul.

## 4.1 Introduction

Molecular vibrations are of increasing importance in many fields such as molecular electronics [205–207], electronic transport in photovoltaic devices [208–211], and bond-selective chemistry [212, 213]. Exciting the vibrations of molecules with optical techniques allows for directly influencing the rate and selectivity of chemical reactions [213–216]. Vibrations also underpin label-free molecular sensing [217], harnessed with metal-induced plasmonic enhancements to overcome small Raman cross sections. Surface-Enhanced Raman Spectroscopy (SERS) is well-established for studying molecular vibrations [9, 218], exciting the molecular ground state to the first vibrational level simultaneously with emission of a Stokesshifted longer-wavelength photon. To enhance SERS signals, plasmonic nanostructures are designed to maximize the nanocavity optical field confinement in intense localized hot-spots in which molecules are immersed [139]. The measured SERS signal is hence increased by up to 10 orders of magnitude enabling single-molecule detection [10, 218, 219].

Recently it was shown that SERS can be described in the context of cavity optomechanics, as so-called 'molecular optomechanics' [128–130]. In cavity optomechanics, a mechanical vibration interacts with an optical cavity mode via optomechanical coupling giving rise to new effects such as dynamical back-action, vibrational amplification, or cooling [131] (Fig. 4.1a). In contrast to other optomechanical systems, the mechanical modes in SERS are provided by molecular vibrations exhibiting vibrational energies  $\hbar \omega_V \gg k_B T$  at room temperature, and thus do not require cryogenic cooling to bring the system into the mechanical ground state. When a layer of molecules is placed in a plasmonic nanocavity (Fig. 4.1b), the molecular vibrations and the optical nanocavity are highly coupled via surface-enhanced Stokes and anti-Stokes Raman scattering. As a result, Stokes scattering excites the vibrational mode while anti-Stokes scattering depopulates it.

Despite the large resonance linewidths ( $\kappa_c$ ) of nanoparticle-on-mirror (NPoM) nanocavities, the ~200 nm<sup>3</sup> effective mode volumes V yield single-plasmon optomechanical couplings g exceeding 3 meV, approaching room temperature thermal energies [14, 106, 141]. So far, optomechanical models for plasmonic cavities used descriptions based on cavity-QED, extended to account for plasmonic losses, and were often restricted to a single resonant photonic mode [106]. The Stokes scattering spectrum,  $S_S(\omega_V) \propto g^2(1+n_V)I_l$  at Raman shift  $\omega_V$  did not vary in shape with pump laser intensity  $I_l$  for the vibrational population  $n_V$ .



**Figure 4.1.** Molecular optomechanics in plasmonic nanocavities. (a) Schematic of a macroscopic optomechanical system of a cavity with one mirror attached to a spring. The optical cavity resonance at  $\omega_c$  and the mechanical mode with  $\omega_v$  are coupled through the optomechanical interaction. (b) Nanoparticle-on-mirror (NPoM) plasmonic cavity confining light to a monolayer of biphenyl-4-thiol (BPT) molecules supporting vibrations with frequency  $\omega_v$ .

Experimental demonstrations of molecular optomechanical effects to date include singlemolecule vibrational pumping at low temperature [220] and non-linear vibrational instabilities under pulsed laser illumination [141, 142]. Further, molecular optomechanical systems have been utilised for the detection of mid-infrared photons by frequency up-conversion to visible light [221–223].

This chapter summarises theoretical and experimental efforts to expand the model of molecular optomechanics beyond a single plasmonic mode coupled to a single molecule. To fully describe the NPoM optomechanical system, it is necessary to account for the complexity of the plasmonic multi-mode cavity [143, 144] as well as inter-molecular vibrational coupling of hundreds of molecules tightly packed in the nanocavity [145, 204, 224]. Section 4.2 elaborates on these advances in optomechanical modelling providing a framework to compare experimental results to<sup>1</sup>. We show that a full multi-modal treatment of the nanocavity is necessary to explain optomechanical effects only seen when driving molecules at higher powers. In Section 4.4, we report experimental indications of a vibrational frequency shift associated with the optical spring effect, a novel effect in the context of molecular nanotechnology. Further, we investigate how optomechanical vibrational pumping can excite molecular vibrations in plasmonic nanocavities at room temperature under pulsed laser illumination in Section 4.5. Using this effect, we experimentally demonstrate that molecules in the nanocavity form collective vibrational modes enhancing the optomechanical interaction.

<sup>&</sup>lt;sup>1</sup>Here, only a summary of the theoretical modelling is provided. For full technical detail see Refs. [144], [145] and Supplementary Information to Ref. [204].

## 4.2 Molecular Optomechanics for NPoM

#### 4.2.1 Continuum-field Description of Plasmonic Nanocavities

We start by theoretically considering a realistic plasmonic nanocavity which optimises molecular optomechanical coupling<sup>2</sup>. Here, we use the nanoparticle-on-mirror (NPoM) geometry, where a self-assembled monolayer (SAM) of active molecules is formed on a flat Au substrate before deposition of gold nanoparticles (AuNPs) on top (Fig. 4.2a) [12]. This places a few hundred molecules in the ~10 nm-wide optical hot spot, highly-confined within the nanogap (thickness  $d \sim 1.3$  nm) between the flat bottom facet of the AuNP and the Au surface underneath (Fig. 4.2b). In our simulations, the NPoM nanocavity is formed by a truncated Au sphere of diameter 90 nm (slight deviation from experimental size to match the resonance wavelength) and a bottom facet of 16 nm radius separated from a gold substrate by a dielectric layer of 1.3 nm thickness and dielectric constant  $\varepsilon_g = 2.1$ . The dielectric function  $\varepsilon_{Au}$  of gold is taken from Johnson-Christy [22], and the full system is placed in air. This NPoM structure provides optical field enhancement factors  $EF \sim 300$  leading to SERS enhancements  $\propto EF^4 \sim 10^{10}$  or more [12, 139].



**Figure 4.2.** Optomechanical interaction in NPoM. (a) Schematic of 80 nm NPoM containing 1.3 nm-thick SAM of BPT molecules, showing benzene ring stretch at 1586 cm<sup>-1</sup>. (b) The nanogap supports localized plasmon modes (red). BPT molecular Raman dipoles (s,s') interact via their image charges (pink arrow) and through plasmon modes (blue arrow).

<sup>&</sup>lt;sup>2</sup>The optomechanical model was developed by Yuan Zhang, Ruben Esteban and Javier Aizpurua.

The electromagnetic response of the NPoM nanocavity can be simulated<sup>3</sup> with the Boundary Element Method (BEM) [225, 226] as implemented in the Metal Nanoparticle BEM toolkit [38, 227]. The NPoM nanostructure is illuminated by a plane-wave with an incident angle of 55° with respect to the normal of the substrate, and the scattered photons are collected along the reflected direction. The computed NPoM far-field scattering spectrum shows two peaks around 830 nm and 670 nm (Fig. 4.3a black line), which match those measured in the experiments (see Fig. 3.7b), and two peaks at the same wavelengths in the near-field spectrum (Fig. 4.3a red line). We identify these peaks as the (10) and (20) plasmon modes according to the nomenclature in Ref. [228] whose near-field distributions in the nanocavity show anti-nodes in the radial direction, as shown in Figure 4.3b,c (offset from cavity centre due to illumination conditions). Recent work demonstrated that the out-coupling efficiency of the (20) mode strongly depends the shape of the NP facet [80], and triangular facets (as most prevalent in NPs used here [14]) lead to even weaker out-coupling of the (20) mode compared to circular facets. However, the (20) mode still provides high near-field enhancement and is thus important in the optomechanical modelling below. Additionally, a weak peak in the scattering spectrum is observed at 520 nm which is identified as the plasmonic pseudo-mode (PPM) formed by many overlapping higher-order plasmonic modes. While the PPM does not contribute much to the scattering cross section or field enhancement of the NPoM, it will play a crucial role in the optomechanical behaviour of the system.



**Figure 4.3.** Simulated electromagnetic response of the NPoM nanocavity. (a) Far-field scattering spectrum (black) and near-field enhancement  $|E_z/E_0|$  at the centre of the nanocavity (blue). The peaks in the spectra are identified as the (10) plasmonic mode at 830 nm and the (20) plasmonic mode at 670 nm. (b,c) Electric field enhancement mapping in the x-y plane through the nanocavity centre for the wavelengths (b)  $\lambda_{(10)}$  and (c)  $\lambda_{(20)}$ . Particle diameter: 90 nm, facet diameter: 16 nm, gap: 1.3 nm.

<sup>&</sup>lt;sup>3</sup>All simulations presented here were carried out by Yuan Zhang.

Previous optomechanical models typically considered a dominant single cavity mode. Here, we expand this model to include the full plasmonic response of the NPoM nanocavity in a continuum-field description [143, 144]. In molecular optomechanics, this is more crucial than for classical optomechanics since plasmonic nanocavities can have complex mode structures with several spectral resonances (see Fig. 4.3a) and the electric field enhancement varies on the nanometre scale (see Fig. 4.3b,c). The spectral and spatial electromagnetic response of the plasmonic nanocavity is included by the dyadic Green's function  $\vec{G}$ . In electromagnetic theory, the dyadic Green's function links a radiating electric dipole  $\mu$  at position  $\mathbf{r}'$  with the electric field  $\mathbf{E}$  at position  $\mathbf{r}$  generated by the dipole. With the permeability of the medium  $\mu_0\mu$ , this is can be written as [229]

$$\mathbf{E}(\mathbf{r},\boldsymbol{\omega}) = \boldsymbol{\omega}^2 \boldsymbol{\mu}_0 \boldsymbol{\mu} \boldsymbol{G}(\mathbf{r},\mathbf{r}') \boldsymbol{\mu}.$$
(4.1)

Using the dyadic Green's function, it is possible to understand how the plasmonic cavity modifies the response of a molecular vibrational dipole as well as how these dipoles interact with each other (see Fig. 4.2b). The influence of the plasmonic environment on the molecule *s* at position  $\mathbf{r}_s$  is described by the self-interaction Green's function  $\overset{\leftrightarrow}{G}(\mathbf{r}_s, \mathbf{r}_s, \omega)$ . This covers the full spectral response of the nanocavity and thus includes all plasmonic modes. Further, different vibrating molecules (*s* and *s'*, at positions  $\mathbf{r}_s$  and  $\mathbf{r}_{s'}$ ) interact with each other due to their vibrational dipoles via the Green's function  $\overset{\leftrightarrow}{G}(\mathbf{r}_s, \mathbf{r}_{s'}, \omega)$ . Hence, the plasmon mediates and enhances this inter-molecular vibrational coupling. Importantly, the Green's function is generally complex-valued. In the context of our optomechanical model, the imaginary part of  $\overset{\leftrightarrow}{G}$  is linked to the optomechanical pumping and damping rates  $\Gamma^{\pm}$  while the real part of  $\overset{\leftrightarrow}{G}$ leads to a vibrational frequency shift, as discussed in detail in Section 4.2.2.

We obtain the dyadic Green's function of the NPoM nanocavity from electromagnetic simulations. Since vibrational dipoles are arranged vertically in the gap, we focus on the component  $G_{zz}$  for the interaction of two dipoles in *z*-direction. The self-interaction Green's function at the centre of the NPoM gap shows the relevant landscape of plasmonic modes (solid lines in Fig. 4.4a). We compare the full plasmonic response of the NPoM with a single-mode plasmonic cavity at the position of the (20) mode (dashed lines in 4.4a). While the (20) mode alone could be modelled as a single-mode cavity, the contribution of other modes, especially the PPM, becomes clear. Importantly, Re(G) for the full NPoM cavity is 10-fold higher compared to the single-mode cavity due to a large positive offset from the PPM. This highlights the importance of fully incorporating all plasmonic modes (including the PPM, which is often not visible in scattering spectra) to correctly address the optomechanics.



**Figure 4.4.** Simulated Green's function of the NPoM nanocavity. (a) Complex self-interaction Green's function ( $\operatorname{Re}(G)$  red,  $\operatorname{Im}(G)$  blue) for a vertical dipole in the gap centre. Plasmonic modes in scattering spectrum are indicated are indicated as vertical dashed lines. Dashed curves show *G* when a single optical mode is considered in the model. (b) Two-point Green's function between spatially separated locations in the gap (separation  $\rho$ ), at  $\lambda_{(20)} = 670$  nm as obtained numerically (solid line) and with an analytic model based on image dipoles (dashed lines).

The spatial distribution of plasmonic modes impacts differently the real and imaginary parts of *G* (Fig. 4.4b). We explore the spatial dependence by fixing one molecule at the centre of the cavity ( $\mathbf{r}_{s'} = 0$ ) and calculate the Green's function for a second molecule at  $\mathbf{r}$  for different separation  $\rho = |\mathbf{r}_{s'} - \mathbf{r}_{s}|$  between the molecules. While  $\text{Im}(G(\rho))$  (blue solid line in Fig. 4.4b) extends across the whole facet and follows the near-field of the (20) mode at  $\lambda_{(20)} =$ 670 nm (blue dashed in Fig. 4.4b),  $\text{Re}(G(\rho))$  is seen to be extremely short-ranged due to the self-interaction of highly localized dipole image charges in the gap (red solid line in Fig. 4.4). This short-range interaction is important for the optical spring shift of many molecules, is nearly spectrally independent (dominated by the PPM, see Fig. 4.4a), and can be analytically derived from the coupling of image dipoles in the gap (red dashed in Fig. 4.4b) [204].

#### 4.2.2 Optical Spring Effect and Collective Phonon Modes

To incorporate multiple vibrating molecules and the full plasmonic response into the optomechanical model, two modifications have to be made to the original molecular optomechanics model presented in Section 2.3. Firstly, instead of a single Lorentzian cavity resonance (Eq. 2.25), the electromagnetic response of the plasmonic nanocavity is included in the Hamiltonian via the Green's function introduced above. This requires a different approach to solving the Hamiltonian (see Supplementary Information in [144]), and we only summarise the consequences for the optomechanical interaction here. Secondly, collective vibrational effects are included by placing many vibrational dipoles and summing over all interactions between the molecules and the cavity [145]. For  $N_m$  molecules indicated with index *s*, the interaction Hamiltonian now reads

$$\hat{H}_{int} = -\hat{a}^{\dagger}\hat{a}\sum_{s}^{N_{m}}\hbar g_{s}\left(\hat{b}_{s}+\hat{b}_{s}^{\dagger}\right)$$

$$(4.2)$$

with the modified optomechanical coupling rate  $g_s = f_s g_0$ , where  $f_s \leq 1$  accounts for the location and orientation of each molecule *s*. Similar to the single molecule model, the phonon population of one molecule *s* is given by the expectation value of the phonon creation and annihilation operators as  $n_s = \langle \hat{b}_s^{\dagger} \hat{b}_s \rangle$ . Including many molecules however leads to correlations between molecules which correspond to coherent collective phonon modes. These correlations are defined by  $c_{ss'} = \langle \hat{b}_s^{\dagger} \hat{b}_{s'} \rangle$  (with  $s \neq s'$ ). Interestingly, Raman scattering rates now depend on both the vibrational population of single molecules as well as the molecule-molecule correlations [145]. Furthermore, within a general scheme of optomechanical dynamics, increasing the optical pumping predicts spectral changes of the scattering due to vibrational shifts induced by optomechanical interactions with the plasmonic modes [131]. Such shifts were neglected in the original model for molecular optomechanics, but collective vibrational coupling enhances this effect called an *optical spring shift* [145].

The effects above, an optical spring shift and collective phonon modes, can be obtained in the continuum-field model from the dynamics of the vibrational amplitude  $\beta_s = \langle \hat{b}_s \rangle$  of the *v*th vibrational mode of the *s*th molecule:

$$\frac{\partial \beta_s}{\partial t} = -i \left[ \left( \omega_v - \frac{1}{2} \operatorname{Re}(v_{ss}) \right) - i \frac{1}{2} \left( \gamma_v + \operatorname{Im}(v_{ss}) \right) \right] + i \sum_{s' \neq s} \frac{1}{2} v_{s's} \beta_{s's}$$
(4.3)

Here, the vibrational frequency  $\omega_v$  and decay rate  $\gamma_v$  are both modified by the term  $v_{s's}$  which is defined as

$$v_{s's} = \left(\Omega_{s's}^{+} + \Omega_{ss'}^{-}\right) - i\left(\Gamma_{s's}^{+} - \Gamma_{ss'}^{-}\right)$$
(4.4)

The real part  $\operatorname{Re}(v_{ss}) = \Omega_{ss}^+ + \Omega_{ss}^-$  describes the effective reduction of the vibrational frequency due to the optomechanical coupling of an individual molecule (s = s') with the cavity, while the imaginary part  $\operatorname{Im}(v_{ss}) = \Gamma_{ss}^- - \Gamma_{ss}^+$  includes the change of the vibrational decay rate and is analog to the total optomechanical damping rate  $\Gamma_{opt}$  in Section 2.3. The terms with  $v_{s's}$  incorporate coupling between different molecules mediated by the cavity mode. In the continuum-field description, the optomechanical parameters  $\Omega^{\pm}$  and  $\Gamma^{\pm}$  are defined via the dyadic Green's function  $\widetilde{G}(\mathbf{r}_s, \mathbf{r}_{s'}; \omega_l \mp \omega_v)$  according to

$$\Omega_{ss'}^{\pm} = \frac{1}{2\hbar\varepsilon_0} \left(\frac{\omega_l \mp \omega_v}{c}\right)^2 \left[\mathbf{p}_s(\omega_l)\right]^* \cdot \operatorname{Re}\overset{\leftrightarrow}{G}(\mathbf{r}_s, \mathbf{r}_{s'}; \omega_l \mp \omega_v) \cdot \mathbf{p}_{s'}(\omega_l), \quad (4.5)$$

$$\Gamma_{ss'}^{\pm} = \frac{1}{4\hbar\varepsilon_0} \left(\frac{\omega_l \mp \omega_v}{c}\right)^2 \left[\mathbf{p}_s(\omega_l)\right]^* \cdot \operatorname{Im} \overset{\leftrightarrow}{G}(\mathbf{r}_s, \mathbf{r}_{s'}; \omega_l \mp \omega_v) \cdot \mathbf{p}_{s'}(\omega_l), \quad (4.6)$$

where  $\hbar$ ,  $\varepsilon_0$ , *c* are the reduced Planck constant, vacuum permittivity and speed of light. Here,  $\mathbf{p}_s(\omega_l) = \overset{\leftrightarrow}{\alpha}_v \mathbf{E}(\mathbf{r}_s, \omega_l)$  is the Raman dipole of the *s*th molecule induced by the local electric field  $\mathbf{E}(\mathbf{r}_s, \omega_l)$  excited by a laser of frequency  $\omega_l$  and acting on the molecule at position  $\mathbf{r}_s$ with Raman polarisability of the *v*th vibrational mode  $\overset{\leftrightarrow}{\alpha}_v$ . As observed in Eqs. 4.5 and 4.6, the Green's function of the plasmonic system at the Stokes ( $\omega_l - \omega_v$ ) and anti-Stokes ( $\omega_l + \omega_v$ ) frequencies is the key magnitude that governs the optomechanical interaction.

The term  $v_{ss}$  (with s = s') is explicitly separated in Eq. 4.3, and describes the self-interaction of the Raman-induced dipoles for a single molecule, where the imaginary part  $\text{Im}(v_{ss})$  leads to an increase of the decay rate (broadening the Raman lines by  $\text{Im}(v_{ss}) \propto \text{Im}(\vec{G})$ ), as reported in previous work [106, 143]. On the other hand,  $\text{Re}(v_{ss})$  leads to a reduction of the vibrational frequency of the mode (spectral shift of Raman lines,  $\Delta \omega_v \propto \text{Re}(\vec{G})$ ), corresponding to the optical spring effect in cavity optomechanics [131]. In the case of many molecules, the terms  $v_{s's}$  with  $s \neq s'$  couple the different molecules, and the resulting collective response modifies the optomechanical effects, as explained below.

We examine first the vibrational shift experienced by a single molecule at the centre of the cavity. The spectral dependence of the optomechanical frequency shift,  $\Omega_{ss}^{\pm}$ , for the Stokes

(+) and anti-Stokes (-) frequencies is shown in Fig. 4.5a. Compared to the single-mode optomechanical model (dashed lines), the values of  $\Omega_{ss}^{\pm}$  are about ten-fold larger when considering the full plasmonic response (solid lines) because of the larger value of the real part of the Green's function (Fig. 4.4a). Additionally, in the single-mode model  $\Omega_{ss}^{\pm}$  both approach a maximum around the single plasmon cavity resonance (set to  $\lambda_{(20)}$  here) but with opposite sign. This results in a small total frequency shift from the optomechanical optical spring effect

$$\Delta_{os}^{1} = \frac{1}{2} \left( \Omega_{ss}^{+} + \Omega_{ss}^{-} \right) \tag{4.7}$$

due to cancellation of frequency shifts from combining both Stokes and anti-Stokes contributions. In contrast, in the full plasmonic model  $\Omega_{ss}^{\pm}$  both approach a maximum around plasmon modes but have the same sign, which results in a much larger total frequency shift than in the single cavity mode description. We therefore predict a substantial optical spring effect in our NPoM configuration.



**Figure 4.5.** Optical spring effect in NPoM. (a) Optical spring shift *vs* laser wavelength for  $\omega_v = 1586 \text{ cm}^{-1}$  for a single molecule in the NPoM gap, showing contributions of  $\Omega_{ss}^+$  (blue) and  $\Omega_{ss}^-$  (red) to the total vibrational shift,  $\Delta_{os}^1$ .  $\Omega_{ss}^+$  and  $\Omega_{ss}^-$  scale linearly with laser intensity (shown here for  $10^7 \,\mu\text{W}\,\mu\text{m}^{-2}$ ). Dashed curves show single-mode plasmonic cavity results. (b) Dependence of spring shift  $\Delta_{os}^N$  on the number of molecules  $N_m$  arranged in the gap at  $5 \times 10^7 \,\mu\text{W}\,\mu\text{m}^{-2}$ . (c) Simulated Stokes spectrum in the full multi-molecule model for the  $\omega_v = 1586 \text{ cm}^{-1}$  mode with 633 nm laser at  $10^5 \,\mu\text{W}\,\mu\text{m}^{-2}$  (blue, multiplied by  $\times 50$ ) and at  $5 \times 10^7 \,\mu\text{W}\,\mu\text{m}^{-2}$  (red). At the larger intensity the broad peak is down-shifted by  $\Delta_{os}^N \sim 170 \text{ cm}^{-1}$  from  $\omega_v$  due to the dominant bright Raman collective phonon mode. Top inset: square array of 100 molecules centred in the facet (dashed, radius 16 nm). Bottom inset: each molecule's contribution to the fundamental bright collective phonon mode.

This significant optical spring effect in NPoM nanocavities is further enhanced by collective coupling of many molecules in the gap. The term  $v_{ss'}$  with  $s \neq s'$  in Eq. 2.19 describes the interaction between the Raman-induced dipoles, which leads to formation of collective phonon modes by superposing vibrations in individual molecules. In the mid-infrared, such collective molecular phonons (often called 'vibrational excitons') are mediated by the permanent molecular dipole [208, 230, 231], while here the interactions are dynamically induced by laser driven Raman dipoles. This collective response results in the emergence of Raman-bright collective phonons across all  $N_m$  molecules (which fit inside the NPoM facet), together with other dark collective modes. The optical spring shift induced by the fundamental bright collective mode scales linearly with  $N_m$  (Fig. 4.5b). This dependency is obtained by calculating the optomechanical parameters for an increasing number of molecules in the cavity all with vibrational frequency  $\omega_V = 1586 \text{ cm}^{-1}$ . The shift for 100 molecules forming a dense square patch at the centre of the NPoM gap (inset Fig. 4.5c) is 32 times larger than when only the molecule in the corner is present (corresponding to  $N_m = 1$  in Fig. 4.5b) and 12 times larger than for a molecule in the gap centre.

Raman spectra can be obtained by applying the quantum regression theorem to the patch of 100 molecules in the centre of the NPoM gap. The spectra (Fig. 4.5c) show a single narrow peak for weak illumination (blue line) at the vibrational energy  $\omega_v$  of the individual molecules, corresponding to the standard Raman line. In contrast, the collective SERS spectrum under strong pumping (red line) comprises a broad and strongly down-shifted line (by  $\Delta_{os}^N$ , arrow) associated with the fundamental collective bright mode (vertical dotted line), superposed on contributions from the remaining  $N_m - 1$  weaker near-unshifted modes. Thus, the model predicts a redistribution of the scattered Raman signal from a frequency near  $\omega_v$ , towards the softened frequency of the broad bright molecular phonon mode. The individual molecular contributions to the broad bright phonon mode are displayed in the inset of Figure 4.5c with a clear symmetric maximum at the central position of the gap.

In Section 4.4, we explore experimental evidence for this optical spring effect predicted in the NPoM nanocavity. Section 4.5 then focuses on investigating how collective molecular phonon modes enhance the optomechanical interaction by studying vibrational pumping.

## 4.3 Experimental Setup

#### 4.3.1 Power-Dependent Pulsed SERS

In the custom-built inverted darkfield microscope, NPoM nanocavities are located automatically by particle tracking algorithms and centred moving the sample stage. On each NPoM nanocavity, Raman and dark-field spectra are acquired in quick succession (Fig. 4.6). Dark-field spectra (see Fig. 4.6a) are compared before and after laser illumination to ensure that no damage to the nanostructure was incurred. For pulsed Raman spectroscopy, laser pulses with 2 nm bandwidth and 0.5 ps duration are prepared by the setup detailed in Section 3.3, with wavelength tunable through the visible and near-infrared spectrum. Laser pulses are focused on the sample by a high-NA dark-field objective, which also collects the light scattered by the sample. The SERS signal is filtered by a tunable long pass filter (or notch filters at 785 nm wavelength when anti-Stokes is also recorded). The SERS spectrum is recorded with a Raman spectrometer.

For power-dependent SERS experiments, the average laser power is varied over two orders of magnitude with a variable neutral density filter. To achieve comparable signal-to-noise at all laser powers and avoid damage by laser pulses at high powers, integration times are scaled inversely with laser power to keep constant fluence. In general, the shortest possible exposure times are chosen to prevent damage. Therefore, the exact integration times vary between experiments as SERS signal enhancement depends on the excitation wavelength. For experiments recording anti-Stokes signals, much longer integration times are required. Specific exposure times are specified in the text (see Sections 4.4 and 4.5). In each experiment, we record thousands of SERS spectra by examining hundreds of individual NPoMs for long periods of time.

The SERS signals of individual Raman lines are extracted by peak fitting. First, spectra are normalised for the spectral efficiency of the detection setup as described in Section 3.3.3. Then, a high-order polynomial regression is performed to fit the spectral background without peaks. Finally, the background-subtracted spectra are fit with multiple Gaussian peaks for each Raman line (line shapes are dominated here by the laser bandwidth and hence Gaussian). Such a peak-fitting analysis is not possible for experiments investigating the optical spring shift, since Raman lines broaden significantly. Here, the integrated SERS signal of the Raman lines is obtained by calculating the area underneath the spectra in a 40 cm<sup>-1</sup> wide window centred on the peak. The SERS background area (which increases as a result of

the spring shift) is obtained by integrating a 150 cm<sup>-1</sup> wide window between the Raman lines (1350 cm<sup>-1</sup> to 1500 cm<sup>-1</sup>) (see Fig. 4.6c). To compare the acquired signal intensities with theoretical calculations, the average laser power is converted to the peak intensity of the pulsed laser. For our laser pulses of 0.5 ps duration and 80 MHz repetition rate, an average power of 1  $\mu$ W corresponds to a peak power of 2.5x10<sup>4</sup>  $\mu$ W and a peak intensity of 3.2x10<sup>4</sup>  $\mu$ W  $\mu$ m<sup>-2</sup> in a diffraction limited focal spot.



**Figure 4.6.** Pulsed Raman scattering from plasmonic nanocavities. (**a**) Dark-field spectrum of a typical 80 nm nanoparticle-on-mirror (NPoM) containing BPT molecular SAM. The pump laser (red dashed) is spectrally tunable, shaded region shows range of SERS emission, and individual plasmon modes (yellow dashed) are labelled. (**b**) Pulsed SERS experiment combined with white-light dark-field scattering on individual NPoMs. Spectrally-tuned 0.5 ps pump pulses excite individual NPoM (with white light off), and laser is filtered from the collected SERS emission. (**c**) Pulsed Stokes SERS spectrum of BPT for three vibrational modes indicated. Blue shading shows 1586 cm<sup>-1</sup> peak area, grey shading shows background region.

#### 4.3.2 Correction for NPoM In-Coupling

In this experiment, power-dependent SERS spectra from thousands of NPoMs are recorded. The data shows that SERS signal intensities vary strongly between individual nanocavities by up to one order of magnitude at the same laser power. Due to variations in nanoparticle size and contact facet shape (limitations from nanoparticle synthesis) [82], light is coupled from the far-field to the cavity with different efficiency [80]. We account for these variations through re-normalising the laser intensities  $I_l$  with the in-coupling efficiency of each NPoM (*i*) by calculating the in-coupled laser intensities  $I_i^{in} = \eta_i I_l$ . Each in-coupling efficiency  $\eta_i$  can be estimated using the SERS signal  $S_i$  at the lowest laser intensity using  $\eta_i = S_i/\text{mean}(S_i)$ assuming linear scaling of the signal with power  $(S_i \propto I_l)$ . When quadratic scaling of the signal with laser power is expected ( $S_i \propto I_i^2$ , for anti-Stokes signal in case of vibrational pumping), the in-coupling efficiency is given by  $\eta_i = \sqrt{S_i/mean(S_i)}$ . Since each vibrational line leads to scattering at a different wavelength and field enhancement depending on the NPoM plasmonic resonances, the in-coupling efficiency is calculated separately for each vibrational mode and for Stokes and anti-Stokes signals. This correction accounts for the in-coupling efficiency so at the same low input power, each NPoM gives the same normalized SERS emission. The effectiveness of this correction is demonstrated in Figure 4.7. Without correction of in-coupling efficiency, particles show SERS signal varying by up to one order of magnitude. Only by correcting the in-coupled laser intensity, it is possible to compare many different nanostructures and obtain the common trend. However, the key experimental trends are also seen for individual NPoMs.



**Figure 4.7.** NPoM in-coupling correction. (a) Integrated SERS from ~60 NPoMs ( $\omega_v = 1586 \text{ cm}^{-1}$ ) *vs* actual laser intensity on sample (colours), excited by a pulsed 658 nm laser. Red arrows indicate correction of in-coupling efficiency by re-normalising laser intensity for each particle with signal at lowest intensity. (b) Integrated SERS *vs* in-coupling corrected laser intensity. All particles now coincide to form a linear trend before saturation at high laser intensity. Data as shown in Fig. 4.8e.

## 4.4 Optomechanical Spring Shift

In this section, the optomechanical spring shift in NPoM predicted by simulations is investigated experimentally. Since the spring shift remains too small to detect for usual SERS experiments with NPoM, either very high laser intensities or additional field enhancement is necessary to reach this optomechanical regime. Here, we follow two approaches to demonstrate the optical spring shift in experiments: Firstly, we use pulsed lasers to reach laser intensities high enough to cause an optical spring shift modifying the SERS spectra (Section 4.4.1). Secondly, we demonstrate that a weak but detectable spring shift can also be obtained under continuous-wave (CW) laser excitation for picocavities with improved field enhancements (Section 4.4.2). The results from both experimental approaches are compared and discussed in Section 4.4.3.

#### 4.4.1 Optical Spring Shift in Pulsed SERS

Most SERS experiments use CW excitation, where the spring shifts remain small. In order to probe these optical spring shifts in a nanocavity, high instantaneous powers are demanded, which are first here supplied through pulsed laser excitation in combination with NPoM constructs that localize light fields to a very small volume. The use of laser pulses however smears out the power-dependent SERS spectrum predicted by our model (see Fig. 4.5c), although the effects appear consistent with what is observed as a repeatable intensity-induced saturation of the sharp vibrational peak.

To explore the theoretical predictions, we use 0.5 ps laser pulses and concentrate on a strong SERS peak together with the region where the shifted mode is expected to appear<sup>4</sup>. For each of hundreds of NPoMs, the plasmonic dark-field scattering spectra and power-dependent SERS response  $S(\omega_V, I_l)$  are characterised (see Section 4.3.1). The plasmonic gap size, nanoparticle diameter, facet size, and gap contents control the spectral position of the main coupled plasmon  $\lambda_{(10)} \sim 800$  nm and the higher-order mode  $\lambda_{(20)} \sim 650$  nm. For the SAM of biphenyl-4-thiol (BPT) used here, we concentrate on the strong  $\omega_V = 1586$  cm<sup>-1</sup> ring breathing mode. Power series are recorded when blue-detuned from  $\lambda_{(20)}$  (laser  $\lambda_l = 633$  nm), near-resonance ( $\lambda_l = 658$  nm), and red-detuned ( $\lambda_l = 700$  nm).

<sup>&</sup>lt;sup>4</sup>All experimental data in this section was much earlier collected by Elena Pavlenko and William M. Deacon. The author of this thesis performed the analysis of experimental data and comparison with the optomechanical theory.

On samples with extreme plasmonic confinement, pulsed laser excitation easily causes permanent damage from the high peak fields through irreversible chemistry or gold surface melting [141, 147, 164, 232]. Hence, we develop here a strategy that employs the shortest possible illumination times and measures many plasmonic nanocavities through fully automated experiments (see Section 4.3.1). To reduce structural damage [141], the exposure time is scaled to keep the measurement fluence constant (10  $\mu$ J) while the average laser power ramps from 100 nW to 60  $\mu$ W (100 s exposure at 100 nW). To compare each NPoM with slightly different size and shape (limited by the precision of nanoscale fabrication) which varies their excitation and collection efficiencies, we normalize laser power experienced by each NPoM with its in-coupling efficiency. This in-coupling correction is described in more detail in Section 4.3.2. Enabled by this experimental correction, we explicitly present here the entire data set on hundreds of NPoMs to show the reproducibility of the effect across many nanostructures and avoid bias incurred when selecting individual particles. However, all observations can be confirmed by data on individual cavities.

Despite the intensity averaging from using laser pulses (which smears out the spectral shifts and makes direct identification of the  $\Delta_{os}^N$  shift challenging), the evolution of the average SERS spectra for increasing  $I_{in}$  shows clear non-linear changes (Fig. 4.8a-c, normalized by in-coupled power). A repeatable weakening of the original sharp vibrational peak is seen in the power-dependent SERS, while the region at lower wavenumber grows super-linearly, indicating the energy redistribution into collective modes as predicted by the optomechanical theory (Fig. 4.5c).

To quantitatively analyse this SERS saturation, we extract the integrated SERS areas  $S_i$  from the emission around the peak at  $\omega_v = 1586 \text{ cm}^{-1}$  (Fig. 4.8b, blue shaded). This is compared to the integrated emission from a region at lower wavenumbers (Fig. 4.8b, grey shaded), which contains contributions from the red-shifted molecular vibrations as well as from the SERS background. This ever-present background mainly arises from electronic Raman scattering (ERS) inside the Au [12]. At low powers ERS dominates this background, while for intense pulsed illumination it also contains the (smeared-out) shifted modes from the broad collective phonon.

The integrated Raman peak emission  $S_i$  shows a clear saturation with laser intensity, consistently for different vibrational peaks, NPoMs, pump wavelengths, and power series (Fig. 4.8d-f). To better show this, we also plot the SERS signal  $S_i$  normalized to  $I_{in}^i$  (Fig. 4.8g-i). The non-linearity in pulsed SERS is clearly visible, with up to ten-fold suppression of linear scaling of the sharp vibrational peak area at the highest pulsed powers.



**Figure 4.8.** Saturation of pulsed Raman scattering from many NPoMs. (**a-c**) Averaged powernormalized SERS spectra for increasing in-coupled average powers at different pump wavelengths  $\lambda_l$ . (**d-f**) Integrated SERS emission from  $\omega_v = 1586 \text{ cm}^{-1} \text{ mode}$  (colors show laser power) and integrated background + shifted SERS (grey, x6). Open points are averages of individual measurements in each power range. Insets show relative position of pump wavelength and plasmon resonances. (**g-i**) Integrated SERS normalized by in-coupled peak intensity and integration time, error bars indicate their standard deviation. The critical laser intensity for saturation is marked as  $I_c$ ).

Examining the high power spectra shows that as the vibrational peaks saturate, SERS emission in the shifted mode region at lower wavenumbers correspondingly increases (see Fig. 4.9a, also evident in Fig. 4.8e,h). This indeed points towards a redistribution of vibrational frequencies of many hundreds of  $cm^{-1}$  (as predicted in Fig. 4.5c), consistent with unprecedentedly large optical spring shifts of the vibrational frequencies in the optical nanocavity. Similar behavior is seen for pump wavelengths of 785 nm (see Section 4.5).

Another possible origin for these observations could be through the anharmonicity of the vibrational potentials. Transiently exciting molecules in solution [213, 233, 234] can give slightly red-shifted Raman peaks [161, 235–237] arising from vibrational anharmonicity. However in our case, based on the reported biphenyl peak shifts with temperature [213, 238, 239], shifts of only  $\Delta \omega_V < 30 \text{ cm}^{-1}$  would result [204], much smaller than observed here. The observed optical spring effect is also very different from dc bias-induced vibrational Stark shifts where sharp lines shift by  $\leq 10 \text{ cm}^{-1}$  [240].

The correspondence between the spectral shifts predicted in theory and the experimentally identified saturation is analyzed in Fig. 4.9. The continuum-field optomechanical model indicates that above a critical pump power, a bright collective vibrational mode rapidly broadens and red-shifts linearly with power (Fig. 4.9b), producing a redistribution of vibrational frequencies that appears as a saturation of the originally-sharp SERS line and a super-linear increase in the background region (Fig. 4.9c). We note that the saturation obtained with this model agrees well with the experiment (Fig. 4.9c,d), although the ERS and smearing masks the direct identification of shifts in Fig. 4.9a. In both theory and experiment, the total Raman yield integrated over all wavenumbers remains linear with power, but is redistributed by the optomechanical interaction. To match the experimental and theoretical saturation it is only necessary to consider a slight scaling of the pump intensity. This scaling is not surprising since the calculations do not include all molecules in the gap due to the high computational cost. Moreover, the exact spectral distribution of the collective Raman peaks and their relative weights will be influenced by the plasmon-mediated interaction of induced Raman dipoles, as well as the specific configuration and orientation of molecules within the cavity.



**Figure 4.9.** Non-linear vibrational coupling model *vs* experiment. (a) Experimental power-normalized SERS spectra at low (blue) and high (red) powers. Constant ERS background is estimated by dashed lines. (b) Corresponding theoretical results showing the SERS spectra vs CW illumination power, for 100 molecules arranged around the cavity centre. (c,d) Extracted SERS integrated in the region around the 1586 cm<sup>-1</sup> peak (blue line/circles) and in the background region between 1350 – 1500 cm<sup>-1</sup> (grey line/circles) for theory and experiment (SERS normalized by power in d). Experimental data are averages of many particles with error bars indicating standard deviation of individual measurements. In c,d, scaling of in-coupled power from theory by 0.24 is used to match with experiment. The transfer in intensity from the 1586 cm<sup>-1</sup> peak to lower wavenumbers arises from the redistribution of emission to the red-shifted bright Raman collective mode.

From Eqs. 4.5 and 4.7 in combination with analytical approximations for the plasmonic Green's function, it is possible to derive a simplified analytical equation [204] that predicts the critical illumination power needed to shift the Raman line outside its  $\gamma_v = 20 \text{ cm}^{-1}$  low-power linewidth:

$$I_{c}\left[10^{6}\,\mu\mathrm{W}\,\mu\mathrm{m}^{-2}\right] \simeq a \,\frac{(2\pi c)^{3}m_{u}\varepsilon_{g}d^{3}}{\eta_{1}'N_{m}EF^{2}R_{v}^{2}} \,e^{(1.1\rho/d)^{2}}\left[\mathrm{Re}\left(\frac{\varepsilon_{Au}-\varepsilon_{g}}{\varepsilon_{Au}+\varepsilon_{g}}\right)\right]^{-1}\omega_{v}\left[\mathrm{cm}^{-1}\right]\gamma_{v}\left[\mathrm{cm}^{-1}\right]$$

$$(4.8)$$

with proportionality constant  $a = 1.2 \times 10^6$  (from unit conversions), gap permittivity  $\varepsilon_g = 2.1$ , gap size d and intermolecular spacing  $\rho$  in nm, permittivity of Au at 658 nm  $\varepsilon_{Au} = -13.5$  [22], and  $R_v \sim 960$  (in units of  $\varepsilon_0 Å^2 / \sqrt{amu}$ , where  $R_v^2$  is the Raman activity of the 1586 cm<sup>-1</sup> line, and *amu*  $m_u = 1.7 \times 10^{-21}$  kg). The effective coupling to the collective Raman bright mode is accounted for by the factor  $\eta_1(\rho) \approx \eta'_1 \exp\{-(1.1\rho/d)^2\}$ , here obtained as  $\eta_1 \sim 0.12$  (at  $\rho = 0.6$  nm) from the discussion in Fig. 4.5b. We note this simplification provides a useful intuition and compares well with the full model used for Fig. 4.9, while omitting the dependence on plasmonic resonances. With the field enhancement factor  $EF(\lambda_l) \sim 300$  of NPoM at the laser wavelength, for the 1586 cm<sup>-1</sup> mode, Eq. 4.8 gives  $I_c \sim 3 \times 10^6 \,\mu\text{W }\mu\text{m}^{-2}$  at 670 nm for  $N_m \sim 100$  molecules, in good agreement with the experiments. This formula shows why nanocavities are essential to bring the optical powers into a viable domain that does not damage the sample, since  $I_c$  scales cubically with gap size and inversely with the power enhancement  $EF^2$  (overall factors in excess of  $10^6$  compared to free space). Eq. 4.8 also clearly shows close-packed molecules in SAMs ( $\rho < d$ ) are needed to observe such collective effects (though molecular ordering is not required).

The fractional reduction in bond strength from the optical spring shift in the nanocavity is then

$$\frac{\Delta\omega_{\nu}}{\omega_{\nu}} = b \,\eta_1 N_m \left(\frac{EF \,R_{\nu}}{\omega_{\nu}}\right)^2 I_l \,, \tag{4.9}$$

where for  $\omega_v$  in cm<sup>-1</sup> and  $I_l$  in 10<sup>6</sup> µW µm<sup>-2</sup>,  $b = 2.23 \times 10^{-8}$ . Hence, the relative lineshift can become even larger for low frequency lines, implying irradiation even more strongly weakens rotations, librational and shearing deformations of molecules and macromolecules.
## 4.4.2 Single-Molecule Optical Spring Shift in Picocavities

Whilst pulsed excitation of nanocavities red-shifts and smears out SERS spectra (see Fig. 4.9a), direct visualization of the optical spring shifts is desirable. This requires CW illumination, but to reach observable spring shifts requires extra field enhancement. To show this we use NPs with integrated nanolenses to enhance coupling efficiencies (called 'Superefficient plasmonic nanoarchitectures for Raman kinetics' (SPARK) [91], Fig. 4.10a). These nanocontructs can support picocavities inside them [241] which are formed when single gold adatoms are pulled from the facet into the gap and additionally confine light below the 1 nm scale [14, 96] (Fig. 4.10b). Picocavities, as compared to nanocavities (which lack the atomic protrusion), give particularly strong optomechanical coupling and focus the optical fields down to the scale of an individual molecule [14, 96]. <sup>5</sup>

As previous work on picocavities has shown, SERS lines in picocavities fluctuate in position on multi-second timescales due to the single-molecule nature of the signal [14, 96, 98]. Hence, the meaningful extraction of the optical spring shift is experimentally challenging. Here, we greatly increase the speed at which power sweeps are performed, by 10<sup>4</sup> compared to previous investigations [14], to avoid slower spectral wandering.

SPARK constructs are produced by organosilica synthesis using AuNPs as seeds for nucleation and growth [91] and deposited similar to NPoMs. Such SPARK samples provide sufficient signal to allow the acquisition of SERS spectra with sub-ms integration times. To repetitively probe the power dependence of SERS spectra, a 633 nm continuous-wave laser is modulated with an acousto-optic modulator driven by a sawtooth voltage at 50 Hz supplied by a function generator (Fig. 4.10c). The power modulation is calibrated by measuring the minimum (60  $\mu$ W) and maximum power (300  $\mu$ W) with a power meter and characterising the shape of the modulated SERS background. Spectra are acquired with an Andor Newton 970BVF using the Fast Kinetic readout mode. An automated darkfield microscope is used to scan hundreds of nanoparticles and collect successive kinetic spectral scans for several minutes on each particle. The spectra are then screened for the generation of picocavities (characterised by the emergence of new, intense Raman lines) and the optical spring shift is analysed by fitting Lorentzian peaks to each individual vibrational line.

<sup>&</sup>lt;sup>5</sup>All experimental data in this section was collected by Bart de Nijs and SPARK constructs were synthesised by Marlous Kamp. The author of this thesis performed the analysis of experimental data and comparison with the optomechanical theory.



**Figure 4.10.** Optical spring shift in picocavities. (a) Schematic of nanolens on NPoM (SPARK construct). (b) A picocavity enhances the field at a single BPT molecule. (c) Sawtooth power modulation of 633 nm CW laser power from 60 to 300  $\mu$ W at 50 Hz. (d,e) Fast spectral scans (0.5 ms integration time) of Stokes emission from the SPARK nanocavity (d), and after formation of a picocavity (e). (f-h) Extracted fits to the 1586 cm<sup>-1</sup> line in the nanocavity (grey) and the 1501 cm<sup>-1</sup> picocavity line (red). The optical spring effect in the picocavity leads to a repeatable shift in position (g) and broadening (h) of the vibrational line. (i,j) Spectra of vibrational lines averaged over 4 periods of laser modulation. Nanocavity line (i) shows constant width and position while picocavity line (j) shifts and broadens (colour gives laser power). (k) Optical spring shift  $\Delta_{os}^1$  dependence on laser intensity for several vibrational lines in nano- and picocavities.

The spectral scans repetitively probe the power dependence of the SERS in the nanocavity and picocavity within 20 ms, faster than any spectral drift (Fig. 4.10d,e, respectively). Fitting the vibrational lines gives the peak area, position, and linewidth vs laser power (Fig. 4.10f-h). For the picocavity lines, increasing illumination leads to a reversible red-shift in the vibrational energy as well as strong broadening by a factor of 2, while vibrations in the nanocavity remain unchanged. This behaviour can be clearly seen in power-dependent spectra averaged over four laser modulation cycles for the nano- and picocavity (Fig. 4.10i,j respectively). Extracting the position of different vibrational lines shows that all vibrational modes in the picocavity experience a different shift rate (Fig. 4.10k), but are always reversible. The strongest shifts of 5 cm<sup>-1</sup> are observed for the 1501 cm<sup>-1</sup> and 1586 cm<sup>-1</sup> lines in the picocavity (Fig. 4.10k). This observation of a reversible peak shift with laser power in picocavities is found to be widely reproducible across many particles and picocavity events. Figure 4.11 shows data from further six picocavity events clearly demonstrating the repeatability of the experiment. A detectable spring shift was found in over two thirds of stable picocavity events recorded from >150 SPARKs, with undetectable shifts only for particles with weaker light in-coupling. A combined statistical analysis of all picocavities (as conducted above for nanocavities) is however not possible, since each picocavity is characterized by a different set of vibrational lines [96].

We now compare the observed shift for CW excitation of picocavities in SPARKs to the shifts in our pulsed experiments in NPoMs (Figs. 4.8, 4.9). Eq. 4.9 shows that the spring shift depends on the local field and the number of molecules (including correction factor  $\eta_1$ ). Using the experimentally observed ratio of SERS from SPARK nanocavities and standard NPoMs, we estimate the field in the latter is 7-fold smaller [91]. Additionally, near-field focusing around the atomic tip of picocavities enhances the local field further by  $\sim$ 3 times (which is consistent with observed experimental enhancements of SERS from picocavities of  $3^4 \approx 100$ ). Collective vibrations lead to a 12-times larger spring shift for 100 molecules than a single molecule (see Fig. 4.5b). The CW laser has a much lower power than the pulsed peak laser power, with  $I_l(CW)/I_l(pulsed) = 3x10^{-4}$ . Assuming that the Raman crosssection of molecules in the picocavity does not change (full calculation not yet possible), the pulsed nanocavity containing several molecules should give  $\sim 100$  times larger shift than a single molecule in a CW-pumped SPARK picocavity. Experimentally, we observe a shift >250 cm<sup>-1</sup> with laser pulses compared to  $\sim$ 5 cm<sup>-1</sup> in SPARK picocavities, giving a factor of  $\sim$ 50 consistent with the above approximation. For comparison, in SPARK nanocavities (Fig. 4.10i) the spring shift is below the instrument resolution due to the  $\sim$ 3 times lower optical fields. Importantly, we note that the analytical model in Eq. 4.9 uses a simplified description of the plasmonic modes of the metal-dielectric nanostructure. Since the plasmonic modes of SPARKS are not yet known in detail (since darkfield scattering is obscured by reflections from the silica nanolens), the above approximation can only confirm that the order of magnitude of the spectral shift observed is consistent with the optomechanical spring shift expected. Further, modifications of the Raman tensor induced by the picocavity might give different field enhancements and effective number of molecules involved in the picocavity-induced optical spring. However, the consistency of our estimates reinforces the optomechanical origin of the experimental results, while these picocavity observations directly evidence the repeatable spring shift from optomechanical coupling.



**Figure 4.11.** Additional data from more picocavities supporting observation of optomechanical spring shift. (**a-f**) Fast spectral time scans (left panels) while sweeping laser power on six NPoMs with picocavities, with position and width of SERS line (red arrows) extracted via Lorentzian fits (two right panels). Same experimental conditions as in Figure 4.10. This data underlines the reproducibility of the optical spring effect for different nanostructures and picocavity events.

### 4.4.3 Discussion

The effect of the optomechanical interaction of the molecules, apparently observed here in plasmonic nanocavities, is to effectively decrease the bond strengths during a pulse. This effect is analogous to the Lamb shift in excitonic emitter-cavity coupling. It provides a new way to manipulate bonds which should be contrasted both with coherent control (based on electronic wavepacket excitation of light-absorbing molecules [154]), and with vacuum Rabi splitting (based on infrared light-matter coupling without any light present [135]). In the latter, strong coupling at mid-infrared frequencies causes energy to cycle between vibrational dipoles and photons, completely different from the optomechanical effect here where optical radiation pressure weakens the bonds themselves.

Our results indicate that in nanocavities, vibrational shifts much larger than the linewidths  $(\gg 20 \text{ cm}^{-1})$  can be attained, comparable with the largest vibrational strong-coupling Rabi splitting [242]. The estimated  $\Delta \omega_v$  implies fractional bond energy reductions of >10% (exceeding thermal energies), corresponding to light-controlled weakening of the bond spring constants by  $\sqrt{\Delta \omega_v / \omega_v} \sim 25\%$ . Stronger pumping seems to reach light-induced dissolution of the collective bond, leading to irreversible bond breaking. Such effects are impossible to observe for molecules in solution [213, 233, 234] which are too far apart ( $\gg d$ ) to coherently couple, and without the nearby metal surface they show negligible shifts.

We conclude by summarizing our results in the context of optomechanics. The large value of  $\operatorname{Re}{G}$  associated with the short-ranged interaction dramatically enhances the optical spring effect in plasmonic gaps. Indeed, calculating the optical spring effect for single molecules in our NPoM gap as a function of laser wavelength (Fig. 4.5a) shows the light-induced spectral shift of the Raman line of a molecule,  $\Delta_{os}^1 \propto \operatorname{Re}{G}$ , can be more than hundred-fold enhanced over that obtained in traditional dielectric cavities. This is a consequence of (i) fully including image charges from the transient Raman dipoles through the Green's function (tenfold enhancement), and (ii)  $\operatorname{Re}{G}$  being positive at both Stokes and anti-Stokes frequencies, so that the two contributions  $\Omega_{ss}^+$ ,  $\Omega_{ss}^-$  add up instead of largely cancelling, as occurring in single-mode optical resonances (another tenfold enhancement, Fig. 4.5a).

The continuum-field optomechanical model for multi-mode plasmonic cavities reveals that ultrasmall mode-volume plasmonic nanocavities yield SERS emission from pumped molecular collective vibrations red-shifted by 10-100-fold more than in single-mode systems, leading to a redistribution of energy and a saturation of emission from the original sharp vibrational lines. This physical picture is commensurate with experimental observations of SERS saturation under pulsed illumination, and reversible SERS lineshifts under CW illumination of picocavities. Independently, the two experiments cannot unambiguously confirm the existence of the proposed optical spring shift, however both are in good agreement with the optomechanical model developed in Section 4.2. This also gives implications beyond simply limiting the maximum Raman yield from molecules (to <10<sup>12</sup> cts/s). [12] In the plasmonic cavities, light transiently softens the bonds of molecules near metal interfaces, which may find use in optical catalysis of reactions and photodecomposition for recycling, as well as controlling molecular photodetectors and other molecular nanoscale optoelectronic devices. We also note that permanent damage to molecules occurs when bond softening starts, suggesting its mechanism may be related. Such plasmon-induced bond softening opens up fruitful possibilities to explore correlations of vibrations at room temperature, since  $\hbar\Delta\omega_v > k_BT$ . We emphasize that the results here operate not just for molecular layers, but also for 2D layered crystals such as transition metal dichalcogenides or graphene, and will lead to their drastically different optomechanical device operation when paired with plasmonic nanocavities [142].

## 4.5 Vibrational Pumping and Collective Vibrations

Another consequence of the optomechanical coupling of molecular vibrations to the NPoM nanocavity is the pumping of the vibrational population by Stokes scattering. This vibrational pumping is predicted by optomechanical simulations and will be investigated experimentally in Section 4.5.1 using pulsed SERS. Compared to experiments showing the optical spring shift in Section 4.4.1, both Stokes and anti-Stokes spectra are recorded here to estimate vibrational populations of molecules. Additionally, we show the importance of collective vibrational modes by experimentally varying the spacing and number of molecules in the nanocavity (Section 4.5.2). This is achieved by preparing mixed monolayers of different molecular species with distinct vibrational spectra and probing the strength of vibrational pumping. All experimental results can be reproduced well with optomechanical simulations.

For experiments in this section, we cover the NPoM structures with a thin film of poly(methyl methacrylate) (PMMA) [90]. This coating with a high refractive index polymer (n = 1.49) enhances in-coupling of light into the nanocavity and tunes the plasmonic resonance closer to the wavelength of anti-Stokes emission ( $\sim$ 700 nm) [90], allowing us to probe the anti-Stokes signal more reliably which is essential for estimating vibrational populations. The additional PMMA layer is also introduced in optomechanical simulations with 100 nm thickness. All other parameters are unchanged from simulations described in Section 2.3.

The simulated scattering cross section for the polymer-coated NPoM<sup>6</sup> (Fig. 4.12a, black) shows radiative plasmonic modes at 660 nm and 890 nm and fits the experimentally-observed dark-field spectrum well (see Fig. 3.7c). The radiative plasmonic modes are also reflected by the simulated near-field enhancement  $|E_z|/E_0$  (Fig. 4.12a, red), with  $E_0$  the amplitude of the incident electric field and  $E_z$  the amplitude of the z-component of the total electric field at 6 nm (radial distance) from the centre of the cavity. In this position, maximum field enhancement is observed (at 700 nm), offset from the cavity centre due to illumination conditions (see Fig. 4.3b,c). For optomechanical simulations, a patch of 217 molecules (here arranged in circles, see Fig. 4.22a) is placed around this position of maximum field enhancement. The plasmonic modes are again included in the optomechanical model via the Green's function  $\vec{G}$ . In contrast to the field enhancement, the self-interaction Green's function also of the non-radiative plasmonic modes. We observe that the self-interaction

<sup>&</sup>lt;sup>6</sup>All simulations in this section carried out by Adrian Juan Delgado.

Green's function exhibits a strong pseudo-mode at  $\lambda_{PPM} \approx 520$  nm similar to the uncoated NPoM, showing that the PMMA coating does not alter significantly the non-radiative modes of the plasmonic cavity.

For vibrational pumping, the optomechanical damping and pumping rates  $\Gamma_-$  and  $\Gamma_+$  (see Eq. 4.6), respectively, are of particular interest since the population in the vibrational mode is modified with the total optomechanical damping rate  $\Gamma_{opt} = \Gamma_- - \Gamma_+$  due to the plasmonic nanocavity [106, 145]. The rates  $\Gamma_-$  and  $\Gamma_+$  for the vibrational mode  $\omega_v = 1586 \text{ cm}^{-1}$  of a molecule situated at the centre of the molecular patch show two peaks at the wavelengths of the radiative plasmonic modes.  $\Gamma_{opt}$  is positive over almost all of the spectral range (indicating  $\Gamma_- > \Gamma_+$ ) and has a maximum at 650 nm (Fig. 4.12c). In the context of single-mode cavity optomechanics, this would correspond to the case of excitation red-detuned to the cavity for any accessible laser wavelength. Due to the spectral efficiency of detectors and availability of suitable notch filters, we thus only employ excitation with 785 nm lasers here. At other excitation wavelengths, similar effects are expected with magnitude according to the scaling of optomechanical rates.



**Figure 4.12.** Optomechanical simulations of polymer-coated NPoM. (a) Simulated scattering crosssection of the NPoM nanocavity (black) and field enhancement in the centre of the molecular patch (red). (b) Simulated Green's function (red: real part, blue: imaginary part) of the NPoM in the centre of the molecular patch, used for optomechanical simulations. (c) Optomechanical pumping ( $\Gamma_+$ ) and damping ( $\Gamma_-$ ) rates vs excitation laser wavelength for a vibrational mode at  $\omega_v = 1586$  cm<sup>-1</sup> (laser intensity 10<sup>7</sup> µW µm<sup>-2</sup>). Particle diameter: 90 nm, facet diameter: 16 nm, gap: 1.3 nm, polymer thickness: 100 nm.

### 4.5.1 Vibrational pumping in pulsed SERS

To investigate the molecular optomechanics of the plasmonic-molecular system, we perform laser-power dependent SERS spectroscopy with picosecond laser pulses (see Section 4.3.1, here at wavelength 785 nm). Average laser powers  $\tilde{P}_l$  are varied from 500 nW to 20  $\mu$ W with integration times scaling inversely with power (200 s integration at 1  $\mu$ W) to achieve comparable signal-to-noise at low powers and limit damage at high powers. Using notch filters, both Stokes and anti-Stokes scattered light from the nanocavity can be recorded and experiments are carried out on hundreds of NPoMs using automated particle tracking algorithms. To compare the results of the experiments to optomechanical simulations, average laser powers are converted to peak laser intensities.

We obtain power-dependent SERS spectra from averaging over 70 individual nanostructures and normalise by integration time and laser power (Fig. 4.13). In this normalisation, constant SERS spectra indicate a linear scaling proportional to the laser power. The anti-Stokes spectra instead exhibit a strongly super-linear scaling, with both SERS peaks and background increasing with laser power (Fig. 4.13a). The super-linear increase of anti-Stokes SERS lines (with higher energy vibrations showing a stronger effect than lower energy vibrations) indicates a rise in the vibrational population and will be analysed in more detail below. On the other hand, the increased SERS background is representative of electronic excitations. Such broadband signals from electronic Raman scattering (ERS) are studied in more detail below (see Fig. 4.19). While the low wavenumber background indicates the temperature of a thermalised population of electrons [243], non-thermalised ('hot') electrons lead to an almost constant background signal reaching up to high wavenumbers [244].

In contrast to the anti-Stokes signal, Stokes spectra scale linearly with laser power for most of the powers investigated here (Fig. 4.13b). Only at highest laser powers does the area of SERS lines reduce, while the background red-detuned from the SERS lines increases. This effect was previously identified as the optomechanical spring shift redistributing the vibrational energy, red-shifting and broadening the SERS emission. This leads to weakening of the main SERS peak and a non-linear increase of the background red-shifted to the vibrational mode [204]. Here, we also observe the occurrence of a shoulder in anti-Stokes spectra to the lower energy side of the 1586 cm<sup>-1</sup> mode increasingly visible at higher laser powers (Fig. 4.13a). This observation provides further evidence that the optical spring effect in this molecular optomechanical system can lead to vibrational energy shifts >100 cm<sup>-1</sup>, and is consistent with previous experiments (see Section 4.4).



**Figure 4.13.** Power-dependent pulsed SERS spectra. (a) Anti-Stokes and (b) Stokes SERS spectra of BPT in NPoM nanocavities, excited with a pulsed laser (785 nm, 80 MHz, 0.5 ps) of average power  $\tilde{P}_l$  ranging from 0.5 to 20  $\mu$ W (colours). Spectra are sorted by in-coupled laser power, averaged over 70 NPoMs, and normalised by integration time and excitation power. Vibrational modes investigated in Fig. 4.14 are labelled in (b).

From individual SERS spectra of each NPoM, SERS intensities of multiple vibrational modes are extracted by fitting a Gaussian peaks after background subtraction. Comparing the results of different NPoMs is however difficult since the light is coupled from the far field to the nanocavity with varying efficiency due to variations in nanoparticle size and contact facet shape [80, 82]. We again account for these variations by re-normalising the laser intensities  $I_l$  with the in-coupling efficiency of each NPoM as described in Section 4.3.2. Since each vibrational line leads to scattering at a different wavelength and field enhancement depending on the NPoM plasmonic resonances, the in-coupling efficiency is calculated separately for each vibrational mode and for Stokes and anti-Stokes signals.

To investigate the power-dependent behaviour of modes with different vibrational energies, we focus on more evident vibrations at  $\omega_v = 292 \text{ cm}^{-1}$ , 1080 cm<sup>-1</sup> and 1586 cm<sup>-1</sup> (Fig. 4.14). While the lowest energy mode exhibits a high thermal population  $n_v^{th}$  at room temperature, the vibrationally pumped population  $n_v^{vp}$  will dominate for the highest energy vibration which is not thermally excited. For the 292 cm<sup>-1</sup> vibration, both Stokes and anti-Stokes signals scale linearly with laser intensity  $I_l$  (Fig. 4.14a). The 1586 cm<sup>-1</sup> vibration on the other hand shows quadratic scaling of the anti-Stokes signal with  $I_l$  while the Stokes signal is proportional to  $I_l$  (Fig. 4.14c). This is clear evidence for vibrational pumping of the phonon population by the surface-enhanced Stokes scattering rate. We note that at high laser intensities the experimentally-observed signal saturates which has above been explained with the optomechanical spring effect red-shifting and broadening the vibrational line (Section 4.4.1). Interestingly, the transition from the thermally-dominated to the vibrational pumping

regime can be observed for the 1080 cm<sup>-1</sup> vibration (Fig. 4.14b). This is evidenced by a transition of linear to quadratic scaling of the anti-Stokes signal. The laser intensity threshold for reaching the regime of vibrational pumping can be extracted by fitting the signal with the sum of linear and quadratic scaling. Here, we observe a threshold intensity  $I_l^{th} \approx 10^5 \,\mu\text{W}\,\mu\text{m}^{-2}$  at which  $n_v^{th} = n_v^{vp}$ . In Section 4.5.2, we will investigate the influence of collective vibrations on vibrational pumping by analysing changes in this threshold intensity with inter-molecular distance. For the other two investigated vibrational modes, the threshold intensity is either above (292 cm<sup>-1</sup>) or below (1586 cm<sup>-1</sup>) the accessible laser intensity range in this experiment.



**Figure 4.14.** SERS signal *vs* laser intensity. (**a-c**) Extracted Stokes and anti-Stokes signal *vs* incoupled peak laser intensity for (a)  $292 \text{ cm}^{-1}$ , (b)  $1080 \text{ cm}^{-1}$  and (c)  $1586 \text{ cm}^{-1}$  vibrational modes. Linear dependence of anti-Stokes signal on laser intensity in the thermal regime changes to quadratic dependence in the vibrational pumping regime. (**d-f**) Anti-Stokes to Stokes ratio for the (d)  $292 \text{ cm}^{-1}$ , (e)  $1080 \text{ cm}^{-1}$  and (f)  $1586 \text{ cm}^{-1}$  vibrational modes. (**g-i**), Phonon population of the (g)  $292 \text{ cm}^{-1}$ , (h)  $1080 \text{ cm}^{-1}$  and (i)  $1586 \text{ cm}^{-1}$  modes, including the thermal population at 293 K (dotted line). Filled points are data from 70 individual NPoMs, open circles are averages. Solid lines are simulations with the optomechanical model, dotted lines show the indicated scaling law.

The optomechanical model predicts the experimental scaling of the SERS signal with laser intensity well (solid lines in Fig. 4.14a-c). The SERS signal from optomechanical simulations was scaled with a free fitting parameter to match the experimental units and account for collection efficiencies of the setup. Additionally, to reproduce the intensity threshold for vibrational pumping of the 1080 cm<sup>-1</sup> mode, laser intensities from the simulation needed to be scaled with a factor 0.4. This implies that in the simulation, vibrational pumping is underestimated and laser intensities three-fold lower than predicted are required in the experiment. This discrepancy is likely due to an underestimation of the in-coupling efficiency of light from the far-field, the Raman activity of this mode, or the collective coupling between molecules. For the 292 cm<sup>-1</sup> and 1586 cm<sup>-1</sup> vibrations, no scaling of the powers was necessary as no threshold is observed.

In Raman scattering experiments, the anti-Stokes/Stokes signal ratio  $S_{aS}/S_S$  is commonly used as a measure for the vibrational population or local temperature [245, 246]. In Fig. 4.14d-f, we show  $S_{aS}/S_S$  for the three vibrational modes. Again, the regime with thermally dominated population (constant  $S_{aS}/S_S$ ) can be clearly distinguished from the vibrational pumping regime ( $S_{aS}/S_S \propto I_l$ ). Remarkably, the optomechanical model reproduces the experimentally measured ratio for 1080 cm<sup>-1</sup> and 1586 cm<sup>-1</sup> very well and only small scaling factors for the ratios obtained from the simulation of 1.2 and 0.9 are necessary, respectively. Again, the intensities of simulations for the 1080 cm<sup>-1</sup> mode were scaled by 0.4 to match the threshold intensity. This shows that our simulations capture the ratio of field enhancements at the Stokes and anti-Stokes wavelengths well for the NPoM structures. At high laser intensities, the optomechanical simulation predicts deviations from linear scaling which are difficult to verify in this experiment as molecular damage occurs at these intensities (likely linked to strong vibrational pumping).

The phonon population  $n_v$  of any vibrational mode v can be estimated from the  $S_{aS}/S_S$  ratio via (derived from Eq. 2.36 in the single-mode optomechanics model)

$$n_{\nu} = \frac{\omega_{S}^{4}\Gamma_{+}}{\omega_{a}S^{4}\Gamma^{-}} \left(\frac{S_{S}}{S_{aS}} - \frac{\omega_{S}^{4}\Gamma_{+}}{\omega_{a}S^{4}\Gamma^{-}}\right)^{-1}.$$
(4.10)

Experimentally, the optomechanical rates  $\Gamma_{-}$  and  $\Gamma_{+}$  cannot be measured directly and are hence neglected in most publications which use the  $S_{aS}/S_S$  ratio to measure the sample temperature. However, in plasmonic systems with pronounced optical resonances (such as NPoMs)  $\Gamma_{-}$  and  $\Gamma_{+}$  will differ significantly due to different field enhancement at anti-Stokes and Stokes emission wavelengths. This leads to difficulties calibrating the absolute temperature obtained from SERS measurements [247, 248]. Here, populations seem to be slightly underestimated for all three vibrational modes (Fig. 4.14g-i) as shown by comparing the low-intensity population with the expected thermal phonon population  $n_v^{th} = [\exp(\hbar\omega_v/k_bT) - 1]^{-1}$  (dotted lines in Fig. 4.14g-i).

At higher laser powers (above the vibrational pumping threshold), the optomechanical model predicts the increase of the population well for the 1080 and 1586 cm<sup>-1</sup> modes (solid lines in Fig. 4.14g-i). The linearly increasing phonon population clearly shows the occurrence of vibrational pumping in SERS, here demonstrated at room temperature using pulsed laser excitation. For the 292 cm<sup>-1</sup> vibration, a constant population is expected from simulations, however a slight increase is observed in the experiment. This might be an indication of other laser-induced heating processes as opposed to vibrational pumping. To investigate the mechanism of the vibrational pumping observed here in more detail, we extract the phonon populations of six vibrational modes and develop an analytical model to fit the phonon population.

#### Analytical model of vibrational pumping

We develop a simple analytical model from the classical model of Raman scattering (Section 2.2.2) for the phonon population to separate the thermal contribution  $n_v^{th}$  from the population induced by vibrational pumping  $n_v^{vp}$ , and understand the mechanism of the population increase. The thermal population is given by a Bose-Einstein distribution at temperature T as  $n_v^{th}(T) = [\exp(\hbar\omega_v/k_bT) - 1]^{-1}$ . In a phenomenological model of the optomechanical system [106], each Stokes scattering event excites a vibration with the Stokes scattering rate  $\Gamma_S = \sigma_S I_l / \hbar \omega_S$ , and the phonon population decays again with the vibrational decay rate  $\gamma_v$ . However, not every Stokes scattered photon is emitted to the far-field. The radiative yield of the Stokes emission  $\eta(\omega_S)$  takes into account that these non-radiative processes can also induce vibrations. The total phonon population is thus described by

$$n_{\nu} = n_{\nu}^{th} + n_{\nu}^{\nu p} = n_{\nu}^{th} + \frac{1}{\gamma_{\nu}} \frac{\Gamma_S}{\eta(\omega_S)} = n_{\nu}^{th} + \frac{\sigma_S I_l}{\gamma_{\nu} \eta(\omega_S) \hbar \omega_S}.$$
(4.11)

Here, the surface-enhanced Stokes scattering cross-section  $\sigma_S$  determines the amount of vibrational pumping and is given by

$$\sigma_{S} = \frac{8\pi}{3} \left( \frac{Q_{\nu}^{0} R_{\nu}}{4\pi\varepsilon_{0}c^{2}} \right)^{2} \omega_{S}^{4} L_{m} (1+n_{\nu}) EF(\omega_{l})^{2} EF(\omega_{S})^{2}$$
(4.12)

with zero-point amplitude of the vibration  $Q_v^0 = \sqrt{\hbar/2\omega_v}$ , Raman activity  $R_v^2$ , vacuum permittivity  $\varepsilon_0$ , speed of light *c*, electromagnetic local field correction  $L_m = (\varepsilon_g + 2)/3$  (here with gap permittivity  $\varepsilon_g = 2.1$ ) [36] and the electromagnetic field enhancement factor *EF* at the laser and Stokes emission frequencies  $\omega_l$  and  $\omega_s$ , respectively. From equation 4.11, we find the vibrational pumping rate

$$\Gamma_{\nu p} = \frac{n_{\nu}^{\nu p}}{I_l} = \frac{\sigma_S}{\gamma_{\nu} \eta(\omega_S) \hbar \omega_S}$$
(4.13)

which can be extracted for each vibrational mode v by fitting the dependence of the population on laser intensity. We define the threshold laser intensity  $I_l^{th}$  for vibrational pumping as the intensity at which the thermal and induced population are equal  $(n_v^{th} = n_v^{vp})$ . From a fit of the analytical model to the data, the vibrational pumping threshold can be easily extracted as

$$I_l^{th} = \frac{n_v^{th}}{\Gamma_{vp}} \tag{4.14}$$

This provides an experimentally more reliable measure for the vibrational pumping since the absolute calibration of the phonon population does not influence the result. We note that this simple model does not capture any non-linear optomechanical effects such as collective molecular vibrations, the optical spring effect, or parametric instability at high laser power. Additionally, the plasmonic modes are only included as field enhancement factors.

In the following, we analyse the vibrational population of six vibrational modes with this model. We extract the population of each mode and plot the average intensity dependence of 70 NPoMs in Figure 4.15a. To calibrate the populations and account for different field enhancement of Stokes and anti-Stokes, we introduce a correction factor to the  $S_{aS}/S_S$  ratio that matches the constant population at lowest laser intensity to the expected thermal population at 293 K.



**Figure 4.15.** Analytical model of vibrational pumping. (a) Vibrational populations extracted from the  $S_{aS}/S_S$  ratio for six vibrational modes. Open circles indicate averages of 70 NPoMs, with error bars showing standard errors. Populations are corrected to match thermal population at room temperature for low laser intensities. Dotted lines are thermal population at 293 K, solid lines fit with analytical model  $n_V = n_V^{th} + \Gamma_{vp}I_l$ . (b) Comparison of vibrational pumping rates  $\Gamma_{vp}$  from the analytical model (black circles) and from calculations with Raman cross-sections from DFT (blue diamonds). (c) Laser intensity threshold for vibrational pumping extracted from the analytical model (black circles) and calculated with parameters described in the text (blue diamonds).

The analytical model  $n_v = n_v^{th} + \Gamma_{vp}I_l$  fits the phonon populations of high wavenumber modes very well (see Fig. 4.15a). Optomechanical modelling predicts these modes to show vibrational pumping at the investigated excitation intensities. However, the fit of lower wavenumber modes is of lower quality (in particular 481 cm<sup>-1</sup> mode). Due to the high thermal population and generally lower Raman cross section of these modes (see spectra in Fig. 4.13), vibrational pumping is not expected from our optomechanical simulations (see also Fig. 4.14d,g). This is further highlighted by analysing the vibrational pumping rate  $\Gamma_{vp}$  extracted from the fit (black dots in Fig. 4.15b).  $\Gamma_{vp}$  can be calculated from equations 4.12 and 4.13 with field enhancement factors from the optomechanical model above (see Fig. 4.12a), Raman activities from DFT simulations [144], and phonon decay rate  $1/\gamma_v =$ 0.6 ps which will be measured with time-resolved incoherent anti-Stokes Raman scattering in Chapter 6 [249]. The radiative yield is used as a free parameter to match the pumping rate of the 1080 cm<sup>-1</sup> mode, giving  $\eta(\omega_S) = 2.5\%$  (the low radiative yield of NPoM is further elaborated in Chapter 7). While the calculation matches the experiment well for the three high energy vibrations, the lower energy vibrations seem to experience much stronger excitation than expected from vibrational pumping via their Raman cross-sections (see blue diamonds in Fig. 4.15b). Similarly, the threshold intensities observed in the experiment for low frequency modes is much lower than expected from the theory while high frequency vibrations fit the model well (see Fig. 4.15c). Therefore, we suggest that there must be another mechanism of laser heating in the experiment which dominates for lower energy vibrations. For example, this could be due to local heating of the sample by absorption of the laser or inter-vibrational redistribution of energy from high frequency modes (which are populated by vibrational pumping) to lower frequency modes.

As an alternative model, we attempt fitting the phonon population with simple laser heating [248]. Here, the phonon population is entirely thermalised  $(n_v = n_v^{th})$  with an intensitydependent temperature increase  $T = 293K + \Gamma_T I_l$ , with the rate of laser-induced heating  $\Gamma_T$ . For low wavenumber modes, this laser-heating model fits the data equally well as the vibrational pumping model with  $\Gamma_T \approx 0.04 \text{ mK}/(\mu\text{W} \mu\text{m}^{-2})$  (see Fig. 4.16a). The populations of high wavenumber modes however cannot be reproduced by the heating model, especially when the heating rate is kept constant for all modes (which would be required for a fully thermalised system, see Fig. 4.16b). This shows that there may be a small contribution to the population increase by weak laser heating, however molecular vibrations with energy >1000 cm<sup>-1</sup> are clearly dominated by vibrational pumping in this system. Hence, this investigation demonstrates that vibrational pumping by SERS can be observed at room temperature in NPoM nanocavities, however there can be other heating mechanisms adding to the population increase which are more important for lower energy modes.



**Figure 4.16.** Analytical model of laser-induced heating. (**a**,**b**) Vibrational populations extracted from the  $S_{aS}/S_S$  ratio for six vibrational modes, averaged over 70 NPoMs (corrected for thermal population at low intensity). Dotted lines are thermal population at 293 K, solid lines fit with laser-heating model  $n_V = n_V^{th}(T)$  with  $T = 293K + \Gamma_T I_l$ . In (a), the rate of laser-induced heating  $\Gamma_T$  is varied, while it is kept constant at  $\Gamma_T = 0.04 \text{ mK}/(\mu \text{W }\mu\text{m}^{-2})$  in (b). The model fits the populations of low energy modes as well as the analytical model for vibrational pumping (Fig. 4.15). However, high energy modes cannot be reproduced with the laser-induced heating model.

### **Comparison with continuous-wave SERS**

Using a continuous-wave (CW) laser at 785 nm wavelength, we investigate whether vibrational pumping is also observable without a pulsed laser. Analogous to the experiments described for pulsed lasers, power-dependent SERS experiments are carried out with the CW laser. Sweeping the average CW laser power from 5  $\mu$ W to 200  $\mu$ W, SERS spectra averaged over many NPoMs scale linearly with laser power (see Fig. 4.17), in contrast to strongly non-linear scaling of the pulsed SERS spectra in Figure 4.13.

Extracting the SERS signal of the same vibrational modes as in Figure 4.14, both Stokes and anti-Stokes signals for all modes exhibit linear scaling (see Fig. 4.18a-c). Hence, the  $S_{aS}/S_S$  ratio and phonon population  $n_v$  are constant over the entire range of in-coupled laser intensities probed in the experiment ( $10^1$  to  $10^3 \mu W \mu m^{-2}$ ). Similar to pulsed experiments, the vibrational population at room temperature is underestimated due to different field enhancement of Stokes and anti-Stokes emission (giving  $T \sim 270$  K here). Only the 1586 cm<sup>-1</sup> mode shows a slight super-linear increase at highest laser intensities indicating the onset of vibrational pumping between  $10^3$  and  $10^4 \mu W \mu m^{-2}$  for NPoM cavities with particularly large enhancement, consistent with pulsed experiments. For the 1080 cm<sup>-1</sup> vibration, we obtain a vibrational pumping threshold of  $10^5 \mu W \mu m^{-2}$  under pulsed illumination (see Fig. 4.14e). Exciting the NPoM with a CW laser of such high intensity would strongly damage the nanostructure and molecules. Therefore, the high peak intensities of the pulsed laser are required for this investigation of molecular optomechanics in NPoM at room temperature.



**Figure 4.17.** Power-dependent CW SERS spectra. (a) anti-Stokes and (b) Stokes SERS spectra of BPT in NPoM nanocavities, excited with a CW laser (785 nm) with average power ranging  $\tilde{P}_l$  from 5 to 200  $\mu$ W (colours). Spectra were sorted by in-coupled laser power, averaged over 80 NPoMs, and normalised by integration time and excitation power.



**Figure 4.18.** SERS signal vs CW laser intensity. (**a-c**) Extracted Stokes and anti-Stokes signal vs in-coupled laser intensity for (a)  $292 \text{ cm}^{-1}$ , (b)  $1080 \text{ cm}^{-1}$  and (c)  $1586 \text{ cm}^{-1}$  vibrational modes. (**d-f**) Anti-Stokes to Stokes ratio for the (d)  $292 \text{ cm}^{-1}$ , (e)  $1080 \text{ cm}^{-1}$  and (f)  $1586 \text{ cm}^{-1}$  vibrational modes. (**g-i**) Phonon population of the (g)  $292 \text{ cm}^{-1}$ , (h)  $1080 \text{ cm}^{-1}$  and (i)  $1586 \text{ cm}^{-1}$  modes, including the thermal population at 293 K (dotted line). Filled points are data from 80 individual NPoMs, open circles are averages. Dotted lines show the indicated scaling law.

#### The electronic Raman scattering background

Surface-enhanced Raman scattering experiments often show a strong background due to electronic Raman scattering (ERS) of electrons in the metal. In the pulsed SERS experiments presented above, this ERS background depends on the intensity of the excitation laser and exhibits strongly non-linear scaling, especially in the anti-Stokes spectrum. Here we analyse this background signal in more detail to understand excitations of the conduction band electrons in the metal, which follow different physics than the molecular vibrations investigated so far.

Figure 4.19 shows the power-dependent SERS spectra presented before (Fig. 4.13a) across a wider range of Raman shifts. This highlights that the spectra contain two components to the ERS background: (i) a contribution nearly constant across the entire spectrum and scaling super-linearly with laser power, and (ii) a contribution at low energies decaying rapidly to higher energies. We attribute these two contributions to different populations of electrons, (i) the thermalised distribution of electrons in equilibrium with the metal lattice [243] and (ii) a population of 'hot' carriers induced by the laser pulses [244]. Since thermalisation of hot electrons occurs on timescales <100 fs via electron-electron scattering [250], the use of pulsed lasers drastically enhances the importance of the latter population for the spectral background.

Recent experimental work (unpublished) has shown that the ERS intensity of the thermalised electrons can be described with a Bose-Einstein distribution, since the light inelastically scatters from (bosonic) waves of the electron gas [251]. In contrast, the population of hot electrons follows a Fermi-Dirac distribution as the laser photons excite individual electrons to higher energies. The Bose-Einstein and Fermi-Dirac distributions are defined as:

$$n_{BE}(\tilde{\mathbf{v}}, T) = [\exp(hc\tilde{\mathbf{v}}/k_B T) - 1]^{-1}$$
  

$$n_{FD}(\tilde{\mathbf{v}}, T) = [\exp(hc\tilde{\mathbf{v}}/k_B T) + 1]^{-1}$$
(4.15)

The total anti-Stokes ERS signal  $S_{ERS}$  at Raman shift  $\tilde{v}$  can hence be modelled with

$$S_{ERS}(\tilde{\mathbf{v}}) \propto a_{el} n_{BE}(-\tilde{\mathbf{v}}, T_{el}) + a_{hot} n_{FD}(-\tilde{\mathbf{v}}, T_{hot}), \qquad (4.16)$$

where  $a_{el}$  and  $a_{hot}$  are the spectral amplitudes of thermalised and hot electrons, respectively, and account for the relative contribution of the two electronic populations. While the

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thermalised electron population is in equilibrium at  $T_{el}$ , the hot electron distribution should exhibit a much higher temperature  $T_{hot}$ . We fix  $T_{hot}$  corresponding to the energy of photons of the laser at  $\hbar \omega_l = k_B T_l$ , as it is impossible to extract the temperature of this flat background from the spectral range encompassed. With a 785 nm laser ( $\hbar \omega_l = 1.6 \text{ eV}$ ), this corresponds to temperatures  $T_l \approx 18,000 \text{ K}$  giving a nearly flat background across the range of energies observable in the spectra ( $\sim 3000 \text{ cm}^{-1}$ ). We note that representing this energy as an extreme temperature is misleading since the distribution is not thermalised and instead merely represents the pumping energy.



**Figure 4.19.** The electronic Raman scattering (ERS) background. (a) Average anti-Stokes spectra of 70 NPoMs recorded with a pulsed laser (785 nm, 80 MHz, 0.5 ps) at different powers  $\tilde{P}_l$  (colours). The ERS background is approximated with the model in Eq. 4.16 (black dashed). (b) Power-dependent anti-Stokes spectra (colours) and ERS fit (black dashed) at low Raman shifts. (c) Spectral amplitude of the hot electron population from fitting spectra of individual particles. After overcoming the experimental noise, the signal scales quadratically with laser intensity. (d) Spectral amplitude of the thermalised ERS contribution from the fit, scaling sub-linearly. (e) Electronic temperature extracted from the thermalised ERS fit. A laser induced heating model with  $T_{el} = T_0 + \Gamma_T I_l$  fits the data well. Filled points are data from 70 individual NPoMs, open circles are averages.

In Figure 4.19a,b the model for the ERS in Eq. 4.16 is fit to the anti-Stokes background with free parameters  $a_{el}$ ,  $a_{hot}$  and  $T_{el}$ . At high Raman shifts, the flat signal from hot electrons dominates (see Fig. 4.19a) while the contribution from thermalised carriers fits the background feature at low shifts well (see Fig. 4.19b).

Fitting power-dependent spectra of 70 individual NPoM structures, the fit parameters give insight about the excitation of electronic states under pulsed laser illumination. As shown in Figure 4.19c, the population of hot electrons increases quadratically with in-coupled laser intensity (after overcoming the experimental detection limit). This observation is analogous to the quadratic scaling of the anti-Stokes signal in the vibrational pumping regime: a first photon excites the electron to higher energy before a second photon is anti-Stokes scattered by the hot carrier (before relaxation can occur). We would term this thus an electron-pumping regime. In contrast, the thermalised ERS background shows sub-linear scaling (see Fig. 4.19d). This might be due to a reduction of the population of thermalised electrons as they are excited by the laser pulses. It also might be due to the time it takes to equilibrate the heated thermalised electrons, which can exceed the pulse duration so it is probed before heating has fully saturated.

Finally, we analyse the temperature extracted from the thermalised ERS background, which should be representative of the (local) sample temperature during the laser pulse. We observe that the temperature rises linearly with laser intensity fitting a simple model of laser-induced heating  $T_{el} = T_0 + \Gamma_T I_l$ . From this data, we estimate the heating rate  $\Gamma_T \approx 0.5 \text{ mK}/(\mu\text{W} \mu\text{m}^{-2})$ . We note room temperature is slightly underestimated by this fit, due to slight corrections from the out-coupled spectrum modified by the plasmon resonance. The laser-induced heating rate from the ERS background is an order of magnitude higher than the heating rate obtained for low energy vibrations above (0.04 mK/( $\mu$ W  $\mu$ m<sup>-2</sup>)). This suggests that the plasmon-molecule system does not reach the full thermal equilibrium within the duration of the laser pulses. Instead, thermalisation between electronic and molecular sub-systems seems to occur on timescales > 0.5 ps. Time-resolved SERS studies could give further insight on the dynamics of this energy exchange.

### 4.5.2 Collective Vibrational Modes

In this section, we investigate how collective vibrations influence vibrational pumping in the NPoM system. Previous experiments have established that it is possible to increase the spacing of molecules in the SAM by mixing them with another species of molecules with a distinctly different vibrational spectrum (Fig. 4.20a) [224, 252]. With this approach, it was demonstrated that IR active vibrations form a collective state by IR transition dipole-dipole coupling which leads to a frequency shift of the vibration in the Raman and IR spectra [224, 252]. Here instead, we study the optomechanical coupling of induced Raman dipoles through the Green's function of the plasmonic nanocavity. In comparison to the vibrational IR transition dipoles oscillating at mid-IR frequencies  $\omega_v$ , the induced Raman dipoles oscillate at visible/near-IR frequencies  $\omega_s$ .



**Figure 4.20.** Characterisation of mixed SAMs. (a) Mixed monolayers of BPT and QTH allow experimental changes of BPT inter-molecular spacing *d* to tune collective coupling. (b) Average CW Raman spectra from  $\sim 100$  NPoMs for SAMs with different ratio of BPT to QTH (in solution). The areas of the indicated SERS peaks of BPT and QTH (grey shaded) are analysed in c,d. (c) Box plots of BPT SERS signal on each sample, normalised to median of 100% BPT sample. The actual dilution of BPT on the sample can be estimated from reduction in BPT SERS signal. (d) Histograms of ratios of QTH SERS signal to sum of QTH and BPT signal from  $\sim 100$  NPoMs for each sample with different mixing fraction in solution. Narrow histograms indicate good mixing of BPT and QTH.

To tune the spacing of BPT molecules, mixed molecular layers with 2-quinolinethiol (QTH) are prepared with different concentrations (Fig. 4.20a). QTH was chosen since its SERS spectrum (grey in Fig. 4.20b) does not overlap with the vibrational modes under investigation in BPT (red in Fig. 4.20b), in particular the 1080  $\text{cm}^{-1}$  mode. Additionally, the aromatic structure of QTH ensures good mixing with BPT in the SAM without the formation of domains [224]. Solutions with molar mixing fractions 100:0, 50:50, 10:90 and 0:100 of BPT:QTH are prepared and used for NPoM sample fabrication as before. We note that Au mirror substrates are coated with a monolayer of Pd atoms before SAM formation to suppress the occurrence of picocavities where individual Au adatoms are pulled by optical forces out of the facet. To characterise the actual molecular fractions of the mixed SAMs, we record continuous-wave SERS spectra of >100 NPoMs for each sample. The average spectra of all particles are shown in Figure 5b. From the intensity of BPT 1080  $cm^{-1}$  SERS, we determine the BPT fraction of the SAMs to be 76% and  $54\% \pm 4\%$  for the 50:50 and 90:10 mixing in solution, respectively (see Fig. 4.20c). This shows that BPT has a higher binding affinity to the substrate than QTH and higher dilutions would be needed to form a sparser layer of BPT. Further, we confirm homogeneous mixing of the two molecules in the SAM by measuring the ratio of the QTH 1320 cm<sup>-1</sup> to BPT 1080 cm<sup>-1</sup> peaks (see Fig. 4.20d). While the QTH signal is much weaker than BPT, the histogram of all NPoMs is narrow and shows clear differences in the ratios for different mixing fractions during sample preparation. This confirms that both molecules mix well and do not form domains on the length scale  $\sim 10$  nm probed by NPoM cavities (i.e. the molecular environment under each NPoM is similar). Hence, we conclude that BPT and QTH form homogeneous mixed SAMs and this method is suitable to investigate collective effects in molecular optomechanics.

To investigate how vibrational pumping is changed by the increased inter-molecular separation, power dependent SERS measurements are carried out as described above. The intensity-dependent phonon population for the 1080 cm<sup>-1</sup> mode is extracted for ~100 individual NPoMs on each sample, corrected for in-coupling efficiency, and averaged. The threshold for vibrational pumping is pushed to higher laser intensity when BPT is diluted and hence the inter-molecular spacing increases (Fig. 4.21a). The same effect is observed in optomechanical simulations when a fixed number of molecules (217) is spaced out over a larger area similar to the dilution in experiment (see Fig. 4.21b). To quantify the vibrational pumping rate, the analytical model from equation 4.11 is used to fit the experimental data and simulations. In Fig. 4.21c, a 3-fold reduction of the vibrational pumping rate  $\Gamma_{vp}$  at the highest dilution compared to the pure BPT SAM is observed. Accordingly, the intensity threshold for vibrational pumping  $I_l^{th}$  increases when molecules are spaced further apart (see Fig. 4.21d). The optomechanical model shows a similar trend but does not reproduce the magnitude of the effect fully. This discrepancy may be due to miscalibrations in measuring the actual concentration of BPT in the monolayers, or possible additional disorder of the molecules in the mixed SAM. This change in pumping rate however provides clear experimental evidence for the importance of collective vibrations in SERS from NPoM nanocavities.



**Figure 4.21.** Collective vibrational effects. (a) Experimentally measured and (b) simulated vibrational population with laser intensity, with different molecular dilutions of BPT for the 1080 cm<sup>-1</sup> vibrational mode (corrected to match thermal population at room temperature, dotted line). Higher concentration of BPT increases vibrational pumping rates, indicating stronger collective effects. (c) Vibrational pumping rate for the 1080 cm<sup>-1</sup> mode of SAMs with different BPT dilution from experiment (black dots) and optomechanical simulation (blue diamonds). (d) Intensity threshold for vibrational pumping for the 1080 cm<sup>-1</sup> mode for different BPT dilutions.

We further investigate the properties of the collective modes in our simulation. By varying the size of the patch within the cavity from  $N_m = 1$  to 217 molecules (Fig. 4.22a), we track the influence of collective coupling on the vibrational pumping threshold of the  $1080 \,\mathrm{cm}^{-1}$  mode. Increasing the number of molecules  $N_m$  and thereby enhancing the collective optomechanical coupling, the vibrational pumping rate is enhanced and the threshold intensity hence decreases  $\propto 1/\sqrt{N_m}$  (see Fig. 4.22b). Even with 217 molecules (the maximum number under current computational capabilities), the simulated intensity threshold is still higher than observed in the experiment (dotted line in Fig. 4.22b). If this  $1/\sqrt{N_m}$  scaling is robust, almost  $N_m$ = 1500 molecules would be needed in the simulation to match the threshold observed in experiments (which is indeed comparable to the number fitting underneath the NPoM facet,  $\sim$ 2100). The scaling factor used to co-align experiment and simulations could therefore simply be the consequence of our model not utilising the required number of molecules. Other potential sources of error include the calculation of Raman activities from DFT and the in-coupling efficiency of the plasmonic nanostructure. The strong dependence of the threshold intensity on the number of molecules in the simulation however emphasises the importance of including collective vibrational coupling in the optomechanical modelling.



**Figure 4.22.** Collective mode and number of molecules. (a) Simulated molecular patches in the NPoM facet. The number of molecules is tuned by adding circles of molecules. The patches are offset from the cavity centre by 6 nm to match the maximum field enhancement (shifted due to illumination conditions in the simulation). (b) Intensity threshold for vibrational pumping of the 1080 cm<sup>-1</sup> mode (blue diamonds) vs. number of molecules in the gap. The experimentally observed threshold for a 100% BPT sample is indicated (black dotted line).

### 4.5.3 Discussion

Both experiments and simulations show that collective vibrational modes emerge in highly ordered molecular layers in plasmonic nanocavities. These thus correspond to phonons in solid state layers. To understand the SERS signal and other optomechanical properties of the system, it is necessary to account for inter-molecular vibrational coupling and the formation of collective vibrational modes delocalised across hundreds of molecules [145]. At very high laser intensities, such collective modes can experience a frequency shift by the optical spring effect as discussed in Section 4.4. Additionally, the occurrence of collective molecular vibrations implies synchronised oscillation of many molecules in this tightly-confined system.

We have investigated the laser power dependence of Stokes and anti-Stokes scattering of molecules in NPoM cavities. Analysing data from >100 individual nanostructures, we have shown that super-linear scaling of the anti-Stokes signal indicates vibrational pumping by the pulsed laser illumination under ambient conditions. To simulate the experimental results, we have developed a model based on molecular optomechanics accounting for the full multi-mode plasmonic response in a continuum field model. Additionally, to fully capture the magnitude of the optomechanical effects it is necessary to include collective molecular vibrational modes by calculating the response of up to 217 coupled vibrational dipoles in the cavity. Moreover, we have experimentally demonstrated that inter-molecular vibrational coupling significantly affects the magnitude of optomechanical effects by tuning the spacing of molecules using mixed SAMs. Understanding and manipulating the molecular optomechanics in plasmon-driven chemistry, phonon lasing through optomechanical instabilities and beyond.

## 4.6 Summary

This chapter explored the optomechanical interaction of vibrating molecules with the optical modes of the plasmonic nanoparticle-on-mirror nanocavity. To model SERS signals obtained from the complex NPoM system, the theory of molecular optomechanics was expanded to include the full plasmonic response as well as hundreds of molecules in the cavity. While the continuum-field approach allowed to include all optical cavity modes via the Green's function, inter-molecular coupling was added to the optomechanical Hamiltonian by summing over all molecular contributions. This advanced optomechanical model predicts several non-linear signatures in the SERS signal: (i) The optical spring shift effectively reduces the vibrational energy under incident light, thus softening molecular bonds and shifting SERS lines by >100 cm<sup>-1</sup>. (ii) Enhanced Stokes scattering in the nanocavity strongly drives the molecular vibrations increasing their population above the thermal occupations (vibrational pumping). (iii) Due to the plasmonic enhancement of inter-molecular coupling, collective vibrational modes are excited with all molecules in the cavity oscillating coherently. Since the vibrational amplitude is now delocalised across a layer of hundreds of molecules, the vibrational modes can be referred to as *molecular phonons*. Instead of one photon scattering with one molecule, as is usually assumed in classic Raman scattering, photons here scatter with the collective vibrational mode, directly populating a coherent vibration of all molecules. Coherence in molecular vibrations and SERS is further discussed in Chapter 6.

The experimental demonstration of the optomechanical effects here relied on the dependence of SERS signals on laser intensity. Using ultrafast laser pulses, it was possible to investigate the regime of non-linear phonon-plasmon interactions in the NPoM nanocavity. While the optical spring shift leads to a saturation of Stokes signals, vibrational pumping causes quadratic scaling of the anti-Stokes signal. Both effects are enhanced by collective vibrational coupling and hence occur at lower laser intensity than expected for a single molecule. To experimentally investigate the influence of collective vibrations, mixed SAMs were prepared to tune the effective spacing of molecules in the cavity. The larger separation of molecules increased the threshold intensity for vibrational, showing the importance of collective vibrations to understand SERS from NPoM structures. Beyond the effects studied in this chapter, optomechanical coupling also leads to second-order correlations between Stokes and anti-Stokes scattered photons [129, 253]. In Chapter 7, Stokes – anti-Stokes bunching will be investigated as a direct consequence of optomechanical vibrational pumping. In these experiments, quantum-mechanical signatures of the SERS process become apparent and can be harnessed to obtain pairs of entangled photons.

# Chapter 5

# **Single-Photon Lock-In Detection**

The contents presented in this chapter were previously published in Optica in 2021 [254].

### Author contributions:

The development of the FPGA platform for single-photon timestamping was carried out by Oliver Hicks of Cambridge Consultants Ltd. Optical implementation, testing and data acquisition and analysis was performed by the author of this thesis. Data for example applications was collected by Junyang Huang (Section 5.6.3) and Rohit Chikkaraddy (Section 5.6.2).

## 5.1 Introduction

Extracting signals at low single-photon count rates from large backgrounds is a challenge in many optical experiments and technologies. Here we demonstrate a single-photon lock-in detection scheme based on continuous photon timestamping to improve the signal-to-noise ratio (SNR) by more than two orders of magnitude. By time-resolving the signal modulation induced by periodic perturbations, 98% of dark counts are filtered out through digital photon gating and the <1 cts/s contributions from several different non-linear processes are identified. In particular, the setup is designed for coherent anti-Stokes Raman scattering (CARS) measurements on plasmonic nanocavities which will be demonstrated as proof-of-concept experiment among other applications. This detection scheme can be applied to all single-photon counting experiments with any number of simultaneous modulation frequencies, greatly increasing the SNR through photon gating and resolving physical processes with nanosecond time resolution while keeping photon dosage small.

Transient or time-resolved optical experiments often require elaborate experimental setups designed to measure very low signal intensities over ultrashort time scales, and hence they often suffer from poor SNR [201]. Typically, the linear response dominates over any perturbation, giving small induced changes in the signal. Increasing the strength of a repetitive perturbation (for instance the optical pulse intensity) to enhance the non-linear signal is often problematic since this can damage the samples, preventing stroboscopic measurement. For probing single nanostructures or individual quantum systems, the strong perturbation needed to obtain clear signals unfortunately often induces irrevocable structural changes such as bond cleavage [141], atomic displacements [164], reshaping [255] or ablation [256].

A technique commonly applied to extract such weak signals from a noisy background is lock-in detection. By introducing a modulation to the sample, the amplitude and phase of the emerging signal can be determined using phase-sensitive heterodyne detection while noise at other frequencies is rejected [257]. For instance, in all-optical experiments such as four-wave-mixing in semiconductor optical amplifiers [258] or stimulated emission from single nanocrystals [259], the pump pulse train is amplitude-modulated at high frequency  $f_{mod}$ . In scanning near-field optical microscopy, this modulation is provided by the vibration of a tip above the sample [260]. Optical lock-in detection is also used for stimulated-emission-depletion microscopy to enhance contrast in fluorescence microscopy [261], and in many other scenarios.

### 5.1.1 The Lock-In Amplifier

The lock-in amplifier is an essential piece of equipment for many experiments in electronics, optics and other applied sciences. As a phase-sensitive detector, it can be used to determine the phase of a modulated signal to a reference signal, or recover a signal with poor signal-to-noise ratio [257].

For the detection of a noisy signal with a lock-in amplifier, a reference with a single frequency, high amplitude and low noise is required. The detection signal is first multiplied with the reference signal and then integrated over a defined time interval (usually ms to s). The resulting output is a constant (DC) signal, as illustrated by Figure 5.1. The working principle of a lock-in amplifier is based on the orthogonality of the trigonometric functions: When two sine waves of different frequencies  $f_1$  and  $f_2$  are multiplied, the integral over times much longer than the period of the two waves is zero. Similarly, the product of two waves with the same frequency but 90° phase shift will result in a zero output. Only when both waves are of equal frequency ( $f_1 = f_2$ ) and in-phase, the lock-in amplifier returns a DC output signal. Most lock-in amplifiers have two detectors and carry out the same calculations also with a 90° phase shift to the reference. This allows to measure both the in-phase and out-of-phase component of the signal and ensures that the maximum possible amplitude is detected. Using lock-in detection hence allows to measure the amplitude and phase of an oscillating signal.



**Figure 5.1.** Working principle of a lock-in amplifier. The noisy detection signal is multiplied with a reference signal. The resulting signal is integrated over a predefined time interval, providing a constant (DC) output signal.

The lock-in amplifier improves the SNR of a noisy signal by filtering it in the frequency domain. The integration acts as bandpass filter at the frequency of the reference signal with a width set by the time constant of the integration. Longer integration times thus improve the SNR (by narrowing the detection bandwidth) but reduce the response time of the measurement. While traditional lock-in amplifiers are implemented with analog frequency mixers and filters, modern digital lock-in amplifiers are implemented with fast digital signal processing, for example on field programmable gate array (FPGA) boards. This enables operation at high frequencies (>100 MHz) and allows simultaneous analysis with multiple reference signals of different frequencies.

## 5.1.2 Single-photon Counting Experiments

In experiments with extremely low light levels, single-photon counters are required if amplified photodiodes do not provide sufficient gain to detect the signal. Single-photon avalanche diodes (SPADs) are photodiodes operated under high reverse bias above the breakdown voltage. When a photon hits the detector, the voltage breaks down causing an avalanche current across the photodiode junction. After some recovery time ('dead time', typically 10s of ns), the bias voltage is restored and the SPAD is ready to detect another photon. In this so-called Geiger counting mode, the SPAD outputs a voltage pulse for every incident photon.

For single-photon counting experiments, the dominant source of noise is photon shot noise. The statistics of shot noise is described by the Poisson distribution. Since the standard deviation of this distribution is given by  $\sqrt{N}$  (with the average number of detected photons N), the SNR of a single-photon experiment depends only on the number of photons counted as  $SNR = N/\sqrt{N} = \sqrt{N}$ . Hence, increasing the number of photons counted by a longer integration time improves the SNR.

Improving the SNR by applying a modulation to the signal and using lock-in detection, however, proves more difficult for single-photon experiments. Unlike photodiodes under low reverse bias, SPADs do not produce a continuous voltage signal but instead voltage pulses. Hence, they are not suited for the use with traditional lock-in amplifiers which require a continuous voltage waveform to be supplied (as described in Section 5.1.1). In this chapter, we introduce and implement a new concept for single-photon lock-in detection based on photon timestamping.

# 5.2 Concept

The detection challenge is to identify ~1 cts/s (counts per second) under a large background >100 cts/s. Several versions of phase-sensitive detection have been implemented for single-photon counting detectors [262–267]. However, these rely on binning photon counts in successive time intervals to recreate a continuous signal for traditional lock-in analysis instead of analysing each photon individually (see Fig. 5.2a). Here, we present a new approach to single-photon lock-in detection utilising continuous picosecond timestamping of each individual photon to resolve the temporal evolution of an optical signal undergoing modulation. By recording the arrival time of each photon at the detector alongside timestamps from synchronised reference clocks (see Fig. 5.2c), the time dynamics of the signal is extracted. For each photon, the phase ( $\tau_i$ ) and frequency ( $f_i$ ) of each reference clock at the photon arrival time ( $t_0$ ) is accurately determined from the timestamp data of the previous N clock counts. In the post-experimental data analysis, experimental noise and background signals can be removed through temporal gating, implementing lock-in amplification individually for every photon and each reference clock suitable for increasing the SNR of single-photon counting experiments by many orders of magnitude (here by a factor >100).

The signal-processing technology to convert the arrival time of an electronic pulse to a digital timestamp is well established and widely used in high-energy physics [268, 269]. Field programmable gate array (FPGA) boards are capable of performing logical operations with digital electronic signals in real time with bandwidths exceeding 100 MHz. Time-to-digital converters (TDCs) implemented with FPGAs can now achieve timing precision <10 ps [270] while it is possible to parallelise devices using 264 channels or more on one board [271].

Combining picosecond timestamping with pulsed optics holds enormous potential to improve existing and enable new applications. Although the proposed design can increase the SNR in all single-photon experiments, it is particularly advantageous in the areas of quantum correlation, time-of-flight spectroscopy, and scanning near-field microscopy. A particular new capability provided by continuous photon timestamping is the ability to compare photon signals to multiple reference clocks at once. Here, this allows single-photon lock-in synchronisation simultaneously to: (i) the optical pulse repetition rate, (ii) the laser power modulation, and (iii) extra triggers (here pulse delay scan). This retrieves the maximum possible information content of each detected photon. In comparison, start-stop photon detection schemes for time-correlated single-photon counting (TCSPC) synchronise only to one reference signal (typically optical pulses), greatly limiting their use (see Fig. 5.2b) [272].



**Figure 5.2.** Single-photon lock-in techniques. (a) Previous single-photon lock-ins: photons are counted in time bins to recover an analogue signal for analysis with a standard lock-in algorithm. (b) Time-correlated single-photon counting: the time interval  $\Delta t$  between a reference pulse and the photon detection is recorded to resolve the time decay of an optical signal. (c) Timestamping single-photon lock-in: Continuous timestamping of photon arrivals ( $t_0$ ) and multiple reference signals with frequency  $f_i$  allows identification of the phase  $\tau_i$  of every individual photon in each reference signal.

Here, coherent anti-Stokes Raman spectroscopy (CARS) is used as an example of a typical non-linear experiment that benefits from our scheme with low single-photon count rates [149, 188]. While a more in-depth introduction to coherent Raman scattering can be found in Chapter 6, we here briefly describe the CARS measurements. In CARS, molecular vibrations with frequency  $\omega_v$  are excited by coherently pumping with two laser pulses (pump  $\omega_p$ and Stokes  $\omega_S$ , Fig. 5.3a,b), tuned so their frequency difference matches the vibration,  $\omega_p - \omega_s = \omega_v$ . Subsequently, anti-Stokes scattering to  $\omega_x + \omega_v$  of a time-delayed probe pulse at  $\omega_x$  is used to measure the molecular vibrational dynamics. To access a domain capable of observing CARS from single molecules [148, 149], nanoscale optical confinement is needed which is accessed here using plasmonic nanocavities [12]. These are based on a nanoparticle-on-mirror (NPoM) geometry in which an ordered molecular monolayer (here biphenyl-4-thiol, BPT) is sandwiched in a nm-thin gap between Au facets [62]. A background of non-resonant four-wave mixing dominates the detected signal at  $\omega_x + \omega_y$  [164, 273] while additional noise is introduced by electronic dark counts and stray light. Our detection scheme here isolates <1 cts/s rates of this non-linear CARS signal using picosecond photon timestamping through a low-cost FPGA board.



**Figure 5.3.** (a) Schematic experimental setup of single-photon coherent anti-Stokes Raman spectroscopy (CARS). Three pulsed lasers with repetition period  $T_{rep}$  are focused on a nanoparticle-onmirror (NPoM) nanocavity sample, with Stokes and probe beams modulated with period  $T_{mod}$ . The emerging signal detected by a single-photon detector (SPAD) contains photons from the non-linear CARS process, which need to be isolated from other contributions. (b) Excitation scheme of CARS, with pump and Stokes exciting a molecular vibration, probed by anti-Stokes scattering of the probe beam with time delay  $\Delta t$ . (c) Schematic modulation of the SPAD signal. Only when all three beams are turned on can the non-linear 3-pulse CARS signal be observed (green).

# 5.3 Implementation

The basis for detecting a non-linear optical signal above other contributions is to identify and subtract the linear components and separate the multitude of other non-linear signals. Here, this is achieved by modulating two laser beams exciting the sample (Fig. 5.3a). For CARS experiments, each of the three laser beams contributes to the total recorded count rate (Fig. 5.3c). Pump and probe pulses generate broadband contributions across the detected spectral window through electronic anti-Stokes Raman scattering. With pump and Stokes beams exciting the sample, a 2-pulse CARS process is also possible but cannot be time-resolved since the pump then both excites and probes. Only all three pulses together excite emission of the desired 3-pulse CARS signal, enabling investigation of the ultrafast vibrational dynamics. In systems with high signal and stability, these contributions can be separated by sequential acquisition of spectra without fast laser modulation. However with a fixed photon budget on samples such as nanoscopic structures and single molecules, a new approach is required to increase signal-to-noise and avoid damage.

### 5.3.1 Optical Setup

A widefield microscope guides the laser pulses onto the nanocavity sample (Fig. 5.4), which are generated at 820 nm (Stokes), 726 nm (pump) and 722 nm (probe) from an  $f_{rep} = 80$  MHz pumped optical parametric oscillator (see Chapter 3). The three laser beams are spectrally tuned so that pump and Stokes pulses can resonantly drive the molecular vibration while the Stokes pulse is off-resonant to vibrations excited by the probe pulse. With ultrafast pulses of 0.5 ps duration, the spectral resolution of the exemplar experiment here is 50 cm<sup>-1</sup>. Stokes and probe beams are each modulated with electro-optic modulators (EOM) driven by function generators (HP 33120A) producing square wave output at variable frequency  $f_{mod}$ . The two function generators are phase locked and operate with a fixed phase difference of 90°. For CARS experiments, probe beam pulses are delayed by  $\Delta t$  with respect to the other two laser beams using a delay stage running in a continuous loop around  $\Delta t = 0$  ( $f_{delay}$ = 1 Hz). The Stokes pulses are temporally aligned to the pump pulses (by optimising the 2-pulse CARS signal), after which this zero relative delay is fixed. All three beams are spatially overlapped and co-focused on the sample.


**Figure 5.4.** Experimental setup for CARS experiments with photon timetagging. Three laser beams are produced by an 80 MHz pulsed pump laser and optical parametric oscillator (OPO). Two of these beams are 50 kHz modulated by electro-optic modulators (EOM) driven with square waves. The probe beam delay is continuously varied by moving a mirror, giving trigger synchronization pulses at the beginning of each loop. All beams are spatially overlapped and focused onto the sample in a microscope. A single-photon avalanche diode (SPAD) detects the spectrally filtered signal photons. A reference signal for the pulsed laser is provided by a fast photodiode (PD). The electronic signals (*V-t* diagrams) are passed to a central FPGA board, where the signal and clock timestamps are recorded digitally.

In the detection path, the laser light is blocked using spectral filters and a single-photon avalanche diode (SPAD, Micro Photon Devices PDM SPD-100-CTD) detects the signal photons. Each arriving photon leads to an electronic pulse with timing accuracy of 35 ps. Typical count rates in our experiment range from 1 to 1000 cts/s obscured by at least 100 cts/s of dark counts and stray light. In addition to the photon counts, three reference signals are recorded. A fast photodiode monitors the pulse repetition rate of the Ti:Sapphire pump laser (photodiode integrated into laser head) producing a digitally-conditioned  $f_{rep} = 80$  MHz pulse train. Together with a synchronised TTL (transistor-transistor logic) square-wave at  $f_{mod}$  and TTL trigger pulses at the beginning of each delay stage loop ( $f_{delay}$ ), all electronic signals are passed to the FPGA board.

### 5.3.2 FPGA Design

All electronic signals (one signal channel and three reference channels) are connected to an FPGA board. The board continuously converts the arrival times of all electronic signals to digital timestamps that are streamed to a computer and saved. This time-to-digital conversion is achieved by combining a fine time-to-digital converter (TDC) and a 32-bit coarse counter (Fig. 5.5a). The fine TDC consists of a tapped delay line that provides 30 ps accuracy with a range of 5 ns. The coarse counter simply counts increments of the 200 MHz internal FPGA clock and hence covers the nanosecond to second regime.



**Figure 5.5.** Time-to-digital conversion with an FPGA. (a) Timestamps with ps precision are recorded by combining a fine time-to-digital converter (TDC) and a coarse counter. Data is streamed to the computer via gigabit Ethernet (GBE) when triggered by a signal photon. (b) In the fine TDC, an electronic signal is carried along a tapped delay line connected to a tap register. When the signal is stopped by the FPGA clock, the register entry is recorded.

In a tapped delay line (as commonly applied in time-to-digital conversion [269]), each element is connected to a register that records the state of the carried signal and hence the current position of the signal within the carry line (Fig. 5.5b). To determine the photon arrival time, an incoming electronic signal launches a pattern that travels along the delay line until it receives a stop signal which causes the position of the signal to be read from the register. Since the stop signal is provided by the FPGA clock, the arrival time of the signal is the time the signal spent propagating along the delay line before the latest clock. The propagation distance is converted to time in post-experimental data processing.

Since the laser pulse reference clock is at 80 MHz, recording every pulse arrival time would require a data transfer rate >25 GB/s. Therefore, a trigger system was implemented to only record reference timestamps when a signal photon is detected: every time a photon arrives at the SPAD, a defined (and tunable) number of most recent timestamps from all reference clocks are sent to the host PC by the readout controller alongside the photon timestamp. This allows the user to control the number of reference timestamps recorded for each signal event, and thus optimise signal-to-noise by maximising the accuracy of the laser reference given the maximum data transfer rate at each SPAD count rate. As we show below, even a stable repetitive laser system experiences variations of <0.1% in cavity length, which if not tracked greatly reduce the timing precision. Here, ten timestamps per reference clock sufficed to reach the optimum time resolution and thus minimise the required data size.

The TDC was implemented on a Digilent Arty Z7 development board specifically programmed for this application<sup>1</sup>. Here, we demonstrate the function of this system with three reference clocks and one signal channel. However, the FPGA board supports up to eight input signals which can be assigned to record either reference or signal channels, allowing for more complex experimental setups.

To test the performance of the TDC on the FPGA board, timing precision measurements are carried out. A random train of voltage pulses is generated by (attenuated) room light on a SPAD. By passing the pulses through a radio-frequency power splitter, the sequence of pulses is duplicated and sent to two channels on the FPGA board with cables of different length to induce a constant delay between pulses (see Fig. 5.6a). The arrival time of all pulses is recorded by the TDC and the time difference between corresponding pulses on the two channels is analysed.

<sup>&</sup>lt;sup>1</sup>The code for the FPGA was developed by Oliver Hicks, Cambridge Consultants Ltd.

Plotting a histogram of all time differences between the two channels allows to analyse the timing precision of the TDC. Due to timing jitter, the histogram is broadened as shown in Fig. 5.6b. The standard deviation of 27 ps gives a benchmark of the FPGA's timing precision. This precision is comparable to the timing jitter of the SPADs used in the experiment (35 ps), which have been chosen giving the best available timing accuracy. While TDCs with higher timing accuracy (<10 ps) have been realised, this requires continuous calibration of individual delay line elements or the combination of multiple delay lines per channel [269, 270].



Figure 5.6. Measurement of the timing precision for the implemented time-to-digital converter (TDC).
(a) Schematic setup of the experiment. A series of random electronic pulses was split between two channels of the TDC via cables of different length. Arrival times of all pulses at the TDC are recorded.
(b) Histogram of time differences between counts on the two channels. The width of the histogram (standard deviation 27 ps) indicates the timing precision of the TDC.

### 5.3.3 Data Analysis

The data files recorded by the TDC contain a list of timestamps. For each photon detected by the SPAD, the arrival time at the detector is recorded along with a number of reference timestamps for each clock signal. In the following, 10 clock timestamps were recorded per photon timestamp as more timestamps did not improve the timing accuracy. To extract meaningful information from this list of arrival times, a data analysis protocol is required which is detailed below.

The TDC saves timestamps as a combination of the number on the coarse counter and the position on the delay line when the photon was detected. This raw timestamp is converted to an actual time by subtracting the time propagated through the delay line (obtained from the stopping position and total length of the line) from the coarse counter time (given by the internal FPGA clock period). The times are subtracted in this implementation, since the photon detection starts the delay line and the FPGA clock stops it.

Due to the limited size of the coarse counter variable (32-bit), it resets every 21.5 s (at 200 MHz FPGA clock here). Hence, timestamps have to be corrected if integration times are longer than this reset time to avoid artefacts in the analysis. The chronological record of timestamps allows to detect the reset of the coarse counter simply by comparing each timestamp to the previous one. If the more recent timestamp has a lower coarse counter value, the reset time is added to the timestamp.



**Figure 5.7.** Data analysis of multiclock timestamp data. For every reference clock *i*, *N* clock timestamps (referenced to photon arrival at  $t_0$ ) are fit to extract frequency  $f_i$  and phase  $\tau_i$  relative to the photon timestamp.

Then, photon timestamps can be compared to reference timestamps. This analysis is carried out separately for each reference clock *i*. First, the time differences of clock timestamps to the photon arrival are calculated. Second, a linear fit is performed to these time differences (see Fig. 5.7). From the slope of this fit, the frequency of the clock  $f_i$  can be obtained. More interestingly, the offset of the fit gives the phase  $\tau_i$  (in units of time) with which the photon was detected compared to the reference signal. This phase can be independently measured for each photon compared to each reference clock.

By plotting histograms of the arrival phases  $\tau_i$  of photons, this analysis allows to recreate the modulation of the signal during the clock period. Since all photons are projected into one period of the modulation, signals with much less than one photon per period emitted can be recorded by this technique and the SNR can be greatly increased. As the frequency and phase of the reference clock sets which signal modulation is recreated, this effect is similar to traditional lock-in amplification and we thus implement single-photon lock-in detection. With the arrival phase of each photon compared to multiple reference signals known, further analysis is now possible such as removing dark counts or isolating non-linear signals by time gating. This is detailed in the following sections.

## 5.4 Testing

With the setup described above, experiments are carried out to evaluate the capabilities of the photon timestamping approach. As an initial calibration experiment, two reference clock signals are chosen: the laser repetition rate  $f_{rep}$  and the modulation of the laser at  $f_{mod}$ . In general, any periodic reference signal can be chosen as a clock enabling a plethora of different applications. Here, a single laser beam modulated at  $f_{mod} = 1$  kHz (average laser power on sample 2  $\mu$ W) is focused on the NPoM sample and spontaneous Stokes SERS from the nanocavity is recorded by the SPAD (see Fig. 5.8 for the spectrum detected here).

From the periodic clock timestamps, the frequency  $f_i$  of the clock at the time of arrival of each photon at the detector is determined. For each of the detected photons, the measured clock frequency slightly varies as seen in the histograms of Fig. 5.9a,b. Over this 100 s data set, the measured average pulse repetition rate of the laser was  $f_{rep} = 79.64$  MHz with a standard deviation of 25 kHz. This corresponds to (apparent) fluctuations of 4 ps in the laser period, likely limited by the timing accuracy of the FPGA (here better than the 27 ps measured before due to the lock-in analysis). For the EOM modulation of the laser, a frequency of 1.00001 kHz is found  $\pm 0.78$  mHz as expected for this source, giving fluctuations of  $\sim 1$  ns in the modulation period. These measurements vary little between successive data sets, demonstrating the accuracy of our global clock.



**Figure 5.8.** Pulsed SERS spectrum of biphenyl-4-thiol (BPT) in the nanoparticle-on-mirror (NPoM) cavity. Laser wavelength 722 nm, average power 1  $\mu$ W. The dotted line indicates the long pass filter cut off. This signal was detected by the single photon detector in the calibration measurements of the lock-in setup (Figs. 5.9 and 5.10).



**Figure 5.9.** Analysis of timestamp data from spontaneous Raman scattering. (**a,b**) Histograms of the clock frequency f for (a) the laser pulses and (b) the EOM modulation, over 100 s. (c) Reconstruction of the laser pulse shape discriminating signal (green) and dark counts (grey). Inset: 0.2 ns time window  $\Delta \tau$  including 60% of signal counts (dashed). Bin size 25 ps. (**d**) Reconstruction of the laser modulation cycle, recording Raman scattering from a nanocavity with single laser pump turned off and on (laser power 2  $\mu$ W). Bin size 2  $\mu$ s.

We then calculate the time in the clock cycle  $\tau_i$  when each signal photon was detected. Extracting this value for all photons detected during a measurement, we reconstruct the signal modulation through the clock cycle of length set by the inverse of the clock frequency. First, we apply this temporal reconstruction to the periodically pulsed laser. Using the laser repetition rate to wrap the signal within the  $T_{rep} = 12.5$  ns long clock period places most counts near a specific time which depends on a system electronic delay from optical paths, cables and latency (Fig. 5.9c). All photons emerging from the sample due to excitation by the periodic laser pulses are detected within a  $\Delta \tau \sim 200$  ps wide window, because Raman scattering is an instantaneous process. Even though the photons are emitted within the 0.5 ps optical pulse width, this peak is broadened by the detection electronics. In contrast, electronic dark counts and stray light are uncorrelated with the excitation pulses and hence give a constant background signal spread over the whole period. Exploiting this property of dark counts, we can distinguish the background counts from SERS photons and remove them from the data. This results in a >98% reduction in dark counts and thus an increase of  $T_{rep}/\Delta\tau > 60$  in SNR (Fig. 5.9c inset). The approach to remove dark counts in the time domain is similar to previous reports of time-gated single-photon counting which has been demonstrated both with actively quenched detectors [274–276] and digitally by TCSPC [277].

The same concept of temporal reconstruction is applied to determine which lasers are exciting the sample when each signal photon was generated. This is crucial for separating linear and non-linear components of the signal. To demonstrate this functionality in our calibration experiment, the single pump laser is switched on and off at frequency 1 kHz and 50% duty cycle. Consequently, two temporal regions with constant count rates are observed during the laser modulation cycle, with the laser-off background being simply identified (Fig. 5.9d).

When the power of the laser is reduced by near hundred-fold (50 nW on sample), the modulation depth of the signal is greatly reduced since the dark count rate is now larger than the Raman signal (Fig. 5.10a). Dark counts outside the 200 ps window centred on the laser pulse in Fig. 5.9c are now removed, reducing the count rate outside the laser window close to zero (Fig. 5.10b) with only the residual 2% unfiltered dark counts remaining. This dark count rejection increases the modulation visibility by 400%, but in measurements with even lower laser power or more stray light/dark counts, this enhancement can exceed 4000%. Analysing the distribution of the noise in the modulation reveals two Poisson distributions for the laser on and off states (Fig. 5.10c). These arise from the single-photon counting statistics in the experiment and show that the SNR is now only limited by photon shot noise, which can thus be improved by increasing the integration time to collect more photons.

To quantify the improvements made by eliminating dark counts, the window (outside which counts are removed) is centred on the pulse and increased in width (see Fig. 5.9c inset). For each width, the percentage of dark counts that are removed is calculated as well as the photon events preserved (Fig. 5.11a). A window width of  $\Delta \tau = 200$  ps retains ~60% of real photon events and only 1.6% of all dark counts. To remove a higher percentage of dark counts, the window width has to be reduced thus decreasing the signal counts. The ratio of signal counts to dark counts (Fig. 5.11b) shows that by filtering out dark counts, this ratio can be increased by almost two orders of magnitude from 1.3 in the unfiltered data to >100. Since a compromise between best SNR and maximum retained signal counts is demanded, we choose a window width of 200 ps which retains signal counts most efficiently (before green curve in Fig. 5.11a saturates). This filtering increases the signal-to-noise 60-fold.



**Figure 5.10.** Demonstration of dark count removal. (a) Reconstruction of laser-modulated spontaneous Raman scattering from a nanocavity at low average laser power (50 nW) over 100 s, with Raman signal smaller than the dark count rate. (b) Reconstruction of modulated signal after dark count removal. Bin size for (a,b) 2  $\mu$ s. (c) Distribution of noise in (b), with fitted Poisson distributions (lines) indicating the single-photon statistics of the experiment.

Currently, limitations of the timing precision in this setup are observed in the distorted pulse shape. Even though the laser pulses are < 1 ps, the reconstructed pulse shape (Fig. 5.9c) has a width of  $\sim$ 200 ps. The SPAD has a nominal jitter of only 35 ps and the FPGA board has a timing precision of 30 ps (see Fig. 5.6), but further inaccuracies are introduced by the fast photodiode (internal in Spectra Physics Mai Tai pump laser) and amplification of the MHz clock signal by two amplifiers (Mini-Circuits ZFL-1000LN). Additionally, the detector electronic response adds a shoulder to the peak, thus decreasing the percentage of preserved signal counts after filtering out dark counts. Improvements in the detection electronics can thus further increase the fraction of dark counts removed by this technique. For instance, without FPGA noise and reaching the SPAD resolution of 35 ps would give another  $\sim$ 10-fold improvement.



**Figure 5.11.** Characterisation of dark count removal with varying filter window width  $\Delta \tau$  (see Fig. 5.9c inset). (a) Percentage of signal counts preserved and dark counts removed for increasing window widths. (b) Ratio of signal counts to dark counts, compared to unfiltered data (horizontal grey line at 1.3). Vertical dashed lines at  $\Delta \tau = 200$  ps indicate the window width chosen for experiments.

## 5.5 Comparison of Photon Detectors

To highlight the potential of the developed detection setup, Fig. 5.12 compares different photodetectors. Depending on the photon count rates, different detectors must be selected. For single-photon experiments, SPADs are suitable while traditional photodiodes (PD) are needed for spectroscopies delivering higher light intensities (>nW). In between, avalanche photodiodes (APD) and photomultiplier tubes (PMT) provide detection of photocurrents with high gain.

The crucial experiment signal-to-noise ratio strongly depends on signal detection and amplification. A SPAD delivers one voltage pulse for every detected photon and thus the only source of noise is photon shot noise and dark events. For photodiodes, where an electrical current induced by light is produced, additional noise sources include the electronic shot noise due to the diode dark current and thermal detector noise as well as noise from amplifiers necessary to record the small output currents.



**Figure 5.12.** Comparison of different photon detection techniques. Single-photon avalanche diodes (SPAD), avalanche photo diodes (APD), and photomultiplier tubes (PMT) can detect single-photon count rates whereas photodiodes (PD) operate at higher light intensities. The signal-to-noise ratio of the detectors can either be improved by lock-in amplifiers in the high signal regime, or with the photon timestamping setup (SPAD + timetag) presented here for single-photon detection, which can be extended to higher count rates using a combination of several SPADs (multiSPAD + timetag).

Table 5.1 lists relevant specifications of available photodetectors. When counting individual photons, the minimum required photon count rate for detection of a signal with a SPAD is dictated by the detector dark count rate. To simplify, we assume that the minimum photon count rate needs to equal the detector dark count rate to achieve a signal-to-noise ratio (SNR) of 1. Available detectors have dark count rates of 5 - 1000 cts/s. The maximum count rate of a single-photon detector is limited by its dead time after a photon was detected. Typical dead times are 20 - 100 ns, leading to saturation count rate should be limited to at least five times lower rates. In single-photon experiments, the SNR is limited by photon shot noise and scales with the square root of the number of detected photons. Note that other properties of the detector such as detection efficiency or timing jitter are not considered here.

The minimum detectable power of an APD can be calculated from its noise equivalent power (NEP, in units of  $W/\sqrt{Hz}$ ) and bandwidth (BW), listed in Table 5.1 for several available devices. Compared to normal PDs, APDs provide higher gain and thus can detect lower light intensities. The maximum detectable power is limited by saturation of the detector. Note that the dynamic range is strongly influenced by the required bandwidth, so direct comparison of detectors depends on the desired application. For APDs, sources of noise are detector dark current and multiplication noise from the electron avalanche. Traditional PDs (without high reverse bias voltage for avalanche detection applied) are available with a plethora of dynamic ranges, spanning from low light to high intensity applications. The SNR of PDs is limited by the diode dark current and thermal detector noise, as well as noise from amplifiers needed to detect the output.

For PDs and APDs, a typical way to improve this signal-to-noise is to modulate the excitation light source (or sample perturbation) at a fixed frequency and use a lock-in amplifier to record the amplitude of the modulated detected photocurrent. For the use of a PD with a lock-in detector, the improvement in signal-to-noise strongly depends on the exact experimental setup. To exemplify the possible improvement in SNR by a lock-in amplifier, we consider an optical detector of bandwidth 100 MHz with noise equally distributed across all frequencies (white noise). Applying a frequency filter of 1 Hz width with the lock-in amplifier (with integration time constant 1 s), the improvement in SNR is  $\sqrt{100 \text{ MHz}}/\sqrt{1 \text{ Hz}} = 10^4$ . Higher improvements are possible with narrower frequency filters thus requiring longer integration time.

**Table 5.1.** List of available SPADs and APDs from different manufacturers with their dynamic range (minimum and maximum detectable count rate/power). Best available models were chosen if several specifications available. For the selection of APDs, the required bandwidth is crucial and limits the available dynamic range. At 600 nm, 1 pW power equals  $\sim$ 3 Mcts/s. (DC: dark count rate, DT: dead time, NEP: noise equivalent power, BW: bandwidth)

Туре	Company	Model	DC	DT	NEP	BW	Min	Max
			(cps)	(ns)	(fW/Hz)	(MHz)		
SPAD	MPD	PDM series	5	77	-	-	5 cps	3 Mcps
SPAD	Excelitas	AQRH	25	22	-	-	25 cps	9 Mcps
SPAD	Hamamatsu	C11202	7	30	-	-	7 cps	7 Mcps
SPAD	Thorlabs	SPCM20A	25	35	-	-	25 cps	6 Mcps
APD	Hamamatsu	C12703-01	-	-	20	0.1	6 pW	60 nW
APD	Hamamatsu	C10508-01	-	-	20	10	63 pW	10 mW
APD	Hamamatsu	C12702-03	-	-	600	100	3 nW	10 mW
APD	Thorlabs	APD440A	-	-	3.5	0.1	1 pW	15 nW
APD	Thorlabs	APD410A	-	-	40	10	0.1 nW	1.5 μW

Analogously, our FPGA system can enhance the signal-to-noise ratio in single-photon experiments by more than two orders of magnitudes. By resolving the modulation of the signal, it is possible to filter out unwanted background photons and those from other contributions. As demonstrated above, it is possible to remove up to 98% of dark counts from the data acquired by a SPAD. Therefore, the minimum detectable photon count rate can be lowered by up to two orders of magnitude compared to detection without lock-in. Below (Section 5.6) we will show that it is possible to detect a 3-pulse CARS signal at 1 cts/s within a background of 300 cts/s hence increasing SNR by >10<sup>2</sup>. This improvement in SNR is remarkable for a single-photon experiment, but can increase even further for applications with high backgrounds such as stray light.

If the timing precision is improved by optimising detector and amplification jitter as well as the time-to-digital conversion precision, we estimate that the improvement in SNR (scaling with  $T_{rep}/\Delta \tau$ ) could reach up to 10<sup>4</sup> (limited by pulse duration). In experiments with signal count rates >1 Mcts/s, the signal could be split over multiple SPADs connected to different channels of the FPGA to avoid saturation of the detector and benefit from a higher SNR. In combination with a spectrometer grating, a SPAD array could even resolve the spectral dependence of the signal.

## 5.6 Applications

### 5.6.1 Coherent anti-Stokes Raman Spectroscopy

The main application this detection technique was developed for is coherent anti-Stokes Raman scattering (CARS). Hence, this application captures the full potential of the setup and makes use of the ability to lock-in to multiple different reference signals. Here, the technical performance of the detection setup for this application is evaluated while Chapter 6 focuses on the physical insights from the experiments.

In order to demonstrate the ability of the setup to detect a small non-linear signal upon a large background, CARS experiments are carried out. The detected CARS spectra are shown in Fig. 5.13. Since two beams are now modulated, each at  $f_{mod} = 50$  kHz but with one phase-shifted by 90° (with the third beam at constant intensity), the signal modulation shows four distinct windows of different height (Fig. 5.14a) as expected from the experimental design (Fig. 5.3c). Dark counts in the CARS experiments throughout the entire modulation period were removed as detailed above. The measured count rate is highest when all three beams illuminate the sample and lowest when only the pump beam is on. Analysing the different windows allows the contributions from each individual laser combination to be determined (yellow, orange and red in Fig. 5.14a). Subtracting these values from the count rate when all lasers illuminate the sample allows the non-linear 3-pulse CARS count rate to be extracted (green in Fig. 5.14a).

With this method to extract the non-linear signal, time-resolved CARS measurements can now be performed by delaying the probe pulse compared to pump and Stokes pulses. This is achieved by mechanically scanning a delay line for the probe pulse. Conventionally slow scans are performed, integrating until sufficient signal-to-noise is achieved at each time point. However, this produces strong artefacts in the delay scan due to transient changes in the emission spectrum (caused by picocavities [14, 278]) and damage to the nanostructure. Hence, the delay stage is continuously scanned back and forth at  $f_{delay} = 1$  Hz and a third reference trigger is introduced into the FPGA from the scanning delay line. This allows each photon detected to also be tagged with the time-delay at which it was measured, thus building up the entire time-delay curve simultaneously, without any artefacts.



**Figure 5.13.** CARS spectrum from a NPoM nanocavity with all three lasers on the sample (4  $\mu$ W average power per beam). Colours indicate the contributions from the 3-pulse (green) and 2-pulse CARS process (red) as well as a broad background of electronic Raman scattering from pump (orange) and probe (yellow) pulses. Dotted lines show the long and short pass filter cut off. This signal was detected by the SPAD for lock-in CARS experiments (Fig. 5.14).

Time-resolved tracks for all contributions identified by the laser modulation are compared in Fig. 5.14b. The 2-pulse CARS signal induced by pump and Stokes beams (red) stays constant as well as the electronic Raman scattering from the pump (orange). While electronic Raman scattering from the probe also leads to a constant signal, vibrational pumping by pump and probe photons adds a time-dependent signal to the yellow contribution in Fig. 5.14a. This signal decays equally to both positive and negative delays as pump and probe both excite the sample identically. On the other hand, the 3-pulse CARS count rate decreases for both positive and negative delay, but is not symmetric around 0 ps (Fig. 5.14c). When the probe pulse arrives before the molecules are excited, the signal vanishes quickly with a rise time corresponding to the pulse length of 0.5 ps (orange dashed, Fig. 5.14c). For probe pulses arriving after pump and Stokes, the signal decreases exponentially. From an exponential fit, the lifetime of the 1586 cm<sup>-1</sup> vibration of BPT is estimated as  $1.6\pm0.4$  ps. This signal is emitted from only a few hundred molecules in the nanocavity gap, billions of times fewer than for solution measurements. Previous attempts to measure this without single-photon detection required average laser powers >4  $\mu$ W per beam, at least ten-fold more than in this photon-counting lock-in mode, and which is enough to perturb and destroy the nanocavity structures. With safe powers of  $I = 0.2 \mu W$  per beam employed here, the CARS signal is 1000-times smaller (since it scales as  $I^3$ ), below the limits of integrating detectors. As the signal strongly varies from nanoparticle to nanoparticle, further experiments and theory are required for full analysis, and are presented in Chapter 6.



**Figure 5.14.** Time-resolved CARS experiments. (a) CARS signal during 50 kHz laser modulation period (dark counts removed). Contributions from the different lasers are marked in orange (pump), red (Stokes) and yellow (probe), with the non-linear signal CARS signal in green. Bin size 40 ns. (b) Extracted contributions from (a) locked-in to the delay stage sweep as the probe (Pr) pulses are delayed with respect to pump (Pu) and Stokes pulses. (c) Time-resolved CARS signal with exponential decay fit to extract a vibrational lifetime of 1.6 ps of the BPT molecules in the nanocavity. For negative delays, the signal follows a Gaussian matching the 500 fs pulse width. Average laser power on sample per beam is  $0.2 \mu$ W.

### 5.6.2 Time-Correlated Single-Photon Counting

While the timestamping setup developed in this chapter was primarily designed for single-photon lock-in detection, it can also be used for traditional time-correlated single-photon counting (TCSPC). In TCSPC, time differences between the arrival of photons at the detector and a reference signal are recorded. As our setup records the full arrival timestamps of both photons and reference signals, the time differences can easily be calculated from the data. A typical application of TCSPC is the measurement of the fluorescence lifetime of dye molecules or semiconducting materials. Here, the time difference between fluorescence photon arrival and the excitation laser pulse is recorded. This technique is utilised for example to improve the contrast in fluorescence imaging [279, 280] or characterise the dynamics of charge carriers in novel materials and devices [281–283].

Here, we demonstrate an application of TCSPC for SERS experiments. As Raman scattering is an instantaneous process, photons are only emitted during laser pulses. Therefore, there is no physical lifetime that could be extracted from the data. Hence, we now introduce perturbations to the SERS signal using mid-infrared (MIR) laser pulses and probe the response time of the sample to heating by the MIR light  $[284]^2$ . MIR pulses, provided by a Block LaserTune IR quantum cascade laser at  $f_{rep} = 320$  kHz with 100 ns duration, are focused on NPoM nanocavities using a reflective objective (Thorlabs LMM40X-P01). Visible light from a 633 nm CW laser for SERS is co-focused with the infrared light from the opposing direction (Fig. 5.15a). To allow optical access to the nanocavity through the glass substrate and gold mirror, only a thin gold film (10 nm) is deposited on the sample thus making so-called nanoparticle-on-foil (NPoF) constructs [285].

Recording SERS spectra from the NPoF nanostructures with and without perturbation by MIR pulses, a suppression of the Stokes signal by 20% is observed (Fig. 5.15b,c). Tuning the MIR wavelength, the SERS suppression follows the absorption spectrum of the SiO<sub>2</sub> substrate [284]. Hence, the effect is attributed to heating of the sample by MIR light. However, the physical mechanism leading to a decrease of the SERS signal cannot be determined from spectral data alone. Possible explanations include a change in the optical deflection by a build up of heat in the substrate, a thermal expansion of the substrate, or the evaporation of water around the nanocavity.

<sup>&</sup>lt;sup>2</sup>The experiments for MIR-perturbed SERS experiments were performed by Rohit Chikkaraddy.



**Figure 5.15.** MIR-perturbed SERS. (a) Nanoparticle-on-foil (NPoF) constructs are illuminated by both MIR and visible light. (b) SERS spectra of BPT from an NPoF nanocavity with (brown) and without (orange) MIR pumping. (c) Difference spectrum of SERS spectrum with and without MIR pumping. Stokes scattering is suppressed by MIR illumination. Adapted from [284].

To determined which effect leads to suppression of SERS by MIR light, the timescale of the SERS perturbation is analysed with TCSPC. The arrival times of SERS photons on a SPAD are recorded with the FPGA board along with a reference signal from the MIR laser, which sends a voltage pulse for every pulse emitted (Fig. 5.16a). By calculating the time difference from the last MIR pulse to the photon detection, the time-resolved SERS signal can be recovered. The SERS intensity first decreases sharply during the 100 ns MIR pulse (Fig. 5.16b). When the pulse is over, the signal recovers with a rise time of  $\sim$ 700 ns. The observable time window is here limited by the repetition rate of the MIR laser. Since the repetition rate can be tuned, the window of observation can be optimised to match the process under investigation to achieve good SNR.

Interestingly, the timescale observed here for the recovery of the signal ( $\sim$ 700 ns) is much faster than expected for any process relying on thermal diffusion to dissipate the heat in the substrate ( $\sim$ 100 µs) [284]. Therefore, the suppression of SERS cannot be caused by a change in optical deflection or expansion of the substrate. Instead, evaporation of water in the crevice around the nanocavity and fast condensation would be consistent with the observed timescales [284].

For this complex nanoscale system, the investigation of MIR-perturbed SERS with TCSPC allowed an insight in the timescales of the system. The developed FPGA system proved versatile and TCSPC was implemented simply using the internal reference signal from a pulsed laser. This setup can easily be transferred to any optical experiment using laser pulses to investigate the dynamics of photon emission.



**Figure 5.16.** TCSPC measurements for time-resolved MIR-perturbed SERS. (a) Experimental setup for TCSPC using the photon timestamping setup. SERS photons from NPoFs are detected with a SPAD. The FPGA board records photon arrival times and compares them with the MIR laser pulse reference signal. (b) Time-resolved perturbation of the SERS intensity (red) by the MIR pulses. The SERS signal drops during the MIR pulse (100 ns duration indicated by brown area) and then increases again slowly with rise time ~700 ns (black line: exponential fit). Adapted from [284].

### 5.6.3 Photon Correlation Spectroscopy

So far, photon counting experiments were carried out with only one single-photon detector. However, the FPGA system can also be configured to record the signal of two or more SPADs (independent of whether more references are recorded for lock-in analysis). This allows to correlate the photon arrival times on several detectors and carry out photon correlation spectroscopy. A typical photon correlation experiment uses a Hanbury Brown–Twiss (HBT) interferometer which splits signal intensity between two detectors by a 50:50 beam splitter [286]. With this setup, the statistical character of a light source can be quantified by measuring the intensity autocorrelation function  $g^{(2)}(\tau)$  (this will be introduced in more detail in Chapter 7). In short, for a source of light  $g^{(2)}(\tau)$  describes the probability to emit a photon at time  $t = \tau$  given another photon was emitted at t = 0 (normalised to  $g^{(2)}(\infty) = 1$ ) [229].

In the context of nanotechnology, it is often interesting to study a single dye molecule or lightemitting quantum dot (QD). As these are isolated quantum systems, they can emit a photon by energy relaxation and thus need to be re-excited before a second photon can be emitted. The light emitted by such a single-photon emitter is hence antibunched characterised by the autocorrelation function  $g^{(2)}(0) < 1$  (i.e. the emitter is less likely to emit two photons at the same time than with some delay between them). Therefore, photon correlation spectroscopy is a useful tool to verify that an individual emitter is being investigated.



**Figure 5.17.** Photon statistics of different QD samples. (a) Comparison of individual well-separated QDs with a film of QDs. antibunching is only observed for a single QD. (b) Light emitted from a single quantum dot on quartz glass or on gold. The gold quenches and accelerates the emission of photons from the QD, making it impossible to measure antibunching with this setup.

Here, we demonstrate the capability of the developed detection setup for photon correlation spectroscopy by investigating light emitted from CdSe quantum dots<sup>3</sup>. The QDs (CdSe/CdS core shell with 12 nm diameter) are first deposited on a quartz glass substrate, either by spin coating to space out individual emitters on the sample or by drying of a drop of solution to cover the entire sample with a film of QDs. The QDs are excited by a 488 nm CW laser and emitted light is filtered with a bandpass filter (centre wavelength 640 nm, width 10 nm). In an HBT interferometer setup, the light is detected by two SPADs connected to the FPGA board and time differences between the photon arrivals are recorded. The autocorrelation function  $g^{(2)}(\tau)$  can be obtained by normalising the histogram of arrival time differences.

If a single QD is investigated, a dip at  $\tau = 0$  is measured characteristic for antibunched light from a single-photon emitter (Fig. 5.17a). Here,  $g^{(2)}(0) \approx 0.2$  is obtained confirming that the collected light originated from a single QD. Instead exciting a film of QDs (with many emitters hence in the focal spot), no antibunching is observed. Further, to integrate QDs with plasmonic systems deposition on a gold substrate is studied. The contact with the metal however quenches the emission of the QDs and low count rates are observed [287]. Additionally, the emission of photons is strongly accelerated by Purcell enhancement [157] and hence the antibunching feature in the autocorrelation function cannot be resolved (Fig. 5.17b).

These experiments show the potential of the FPGA setup for photon correlation spectroscopy, particularly interesting for quantum optics experiments. While experiments on individual emitters incorporated with plasmonics remain challenging due to the fast emission below system resolution, the setup will be employed to measure the emission statistics in pulsed SERS from plasmonic nanocavities in Chapter 7. In these experiments, cross-frequency photon bunching will be observed due to the optomechanical connection of the Stokes and anti-Stokes processes.

<sup>&</sup>lt;sup>3</sup>Correlation spectroscopy on quantum dots was performed by Junyang Huang.

## 5.7 Summary

In this chapter, we have demonstrated the working principle of our single-photon lock-in detection setup using laser pulses, laser modulation and a delay stage sweep as reference clocks. However, any periodic signal can act as a reference, making our setup attractive for a wide range of experimental research fields. In particular, the additional time resolution of the signal during a reference period can enable a plethora of new applications. For example, the light emission from an optoelectronic device induced by an alternating voltage can be tracked in time to characterize the response time of the device. In scanning near-field optical microscopy, an oscillating tip above the sample can provide a reference frequency, both drastically increasing the signal-to-noise and recording the signal as a function of tip-sample distance. Moreover with a dispersive fibre, photons can be delayed depending on their colour enabling optical time-of-flight spectroscopy [288] with the 80 MHz lock-in frequency. Finally, the switching of photoactive molecules can be resolved in time with modulated lasers. We suggest this is of particular interest for single-molecule fluorescence spectroscopy and microscopy.

In conclusion, we developed a method to separate different contributions to a signal by resolving the variation of the detected single-photons over the period of a reference signal. The technique relies on continuously recording the arrival time of each photon at a single-photon detector with an FPGA board and comparing it to reference clock timestamps. With this setup, we reconstructed the periodic modulation of a excitation laser allowing 98% of stray light and dark counts to be filtered out. The capability of this method was demonstrated in a CARS experiment, where single-photon per second count rates of a non-linear signal were detected. Additionally, the potential to carry out photon correlation spectroscopy and time-correlated single-photon counting with the same setup was explored. Due to the high flexibility for different reference clock signals from Hz to MHz frequencies this concept can be applied universally to all single-photon experiments, drastically increasing their signal-to-noise.

In the following chapters, the detection setup established here will be employed for photon counting experiments. Chapter 6 benefits from the lock-in detection for coherent anti-Stokes scattering and explores the dynamics of molecular vibrations in NPoM. Since full photon timestamping implemented here also enables photon correlation experiments, Chapter 7 investigates photon entanglement in SERS by measuring Stokes – anti-Stokes cross-frequency correlations.

## **Chapter 6**

# Time-Resolved Raman Spectroscopy and Vibrational Dynamics

The contents of this chapter are currently under submission at *Physical Review X* and were previously published as preprint in 2022 [249].

#### Author contributions:

The experimental setup was developed by William M. Deacon and the author of this thesis. Samples were prepared by Rakesh Arul, Bart de Nijs and Niclas S. Müller. All experimental data presented in this chapter was recorded by the author of this thesis.

## 6.1 Introduction

The intense optical fields elicited by plasmonic nanostructures allow routine access to spectra of single/few-molecules under ambient conditions [12, 289, 290]. This starts to open prospects for understanding dynamics and chemistry of individual molecules in real time. Using high-speed imaging, it is possible to track the dynamics of few molecules on the microsecond scale [93] using surface-enhanced Raman spectroscopy (SERS). However, pushing the time resolution down to the scale of molecular vibrations (picoseconds) with ultrafast time-resolved spectroscopies has proven extremely difficult [147, 164]. Early measurements of molecular phonon dynamics through surface-enhanced coherent anti-Stokes Raman spectroscopy (SE-CARS) on single nanostructures suggested great promise [149, 186, 188], however since then little progress has been made [164, 192]. Molecular dynamics studied recently in ultrafast pump-probe spectroscopy of spontaneous SERS instead averages over many molecules [162, 163].

Single- and few-molecule SE-CARS and SERS measurements are possible only due to the high field intensities and Raman enhancements achieved when exciting plasmonic cavities with ultrafast pulses [148]. However, an unwanted consequence of these extreme peak fields is a rapid increase in nanoscale damage compared to continuous wave measurements [141, 164, 291, 292], which modifies both the metallic and molecular components of the system. This is particularly a problem for electronically-resonant molecules which enhance signals, but are damaged much more easily. As a result, time-resolved SE-CARS (trCARS) measurements which demand the structure be stable throughout, become impractical. Although the damage thresholds are known, the mechanisms behind this damage remain unresolved [232], being most likely due to non-equilibrium heating and optical forces acting directly on the surface gold atoms [97, 141].

The second problem with SE-CARS is the large overlapping four-wave mixing (FWM) signal due to electronic FWM [293–295]. Claims that the fast timescale of FWM enables separation of this from SE-CARS [296] assume that the molecular vibrational lifetime is much longer than the electronic lifetimes which, as we demonstrate below, is not the case for molecules under strong confinement.



**Figure 6.1.** Time-resolved Raman scattering. (**a,b**) Excitation scheme of (a) coherent anti-Stokes Raman scattering (trCARS) and (b) incoherent anti-Stokes Raman scattering (trIARS). Spontaneous/incoherent (wavy arrows) vs stimulated/coherent (straight arrows) processes.

To circumvent these problems, we develop a three-colour trCARS scheme to measure the dephasing lifetimes of exemplar biphenyl-4-thiol (BPT) molecules in tightly-confined plasmonic cavities. Surprisingly, the electronic FWM contribution is now found to be small (<10%) despite the penetration of light into the metal, enabling extraction of SE-CARS signatures from ~100 molecules. Further, we combine trCARS measurements with timeresolved incoherent anti-Stokes Raman scattering (trIARS) which probes an incoherent phonon population with spontaneous anti-Stokes scattering, and has previously been used to study carbon nanomaterials [297–300]. Using a newly developed single-photon timestamping technique (see Chapter 5) [254], we can simultaneously measure *coherent* trCARS (Fig. 6.1a) and *spontaneous* trIARS (Fig. 6.1b) on individual nanostructures at sub-µW powers to independently probe the coherence ( $T_2$ ) and population lifetimes ( $T_1$ ), respectively [171]. This ultrasensitive three-color CARS scheme thus allows us to independently determine the population decay and dephasing in few-molecule plasmonically-enhanced systems, giving insight into phonon dynamics of molecules tightly coupled to metallic interfaces.

## 6.2 Experimental Setup

NanoParticle-on-Mirror (NPoM) plasmonic nanocavities confine light to the nanometrescale gap between a metallic nanoparticle and the underlying metal substrate [61, 68]. This platform for few-molecule vibrational spectroscopy traps optical fields to zeptolitre volumes, filled only by the molecules under study [13].

We utilise NPoM structures built from 80 nm gold nanoparticles separated from a gold substrate by a self-assembled monolayer (SAM) of biphenyl-4-thiol (BPT) (see methods in Chapter 3). To improve the out-coupling of the CARS signal and increase sample stability, the NPoM structures are covered with a thin film of PMMA which enhances the NPoM scattering resonance in the signal range around 650 nm (see Fig. 3.7) [90]. Due to molecular binding to the gold surface atoms, the molecular SERS spectra are modified compared to their powder Raman spectrum (see Fig. 6.2). Notably, the coupled ring mode at 1586 cm<sup>-1</sup> (see inset in Fig. 6.2a) splits into two modes with separation 13 cm<sup>-1</sup> and is broadened in the NPoM structure compared to the powder spectrum. However, this effect is only observable with narrow-linewidth continuous-wave lasers since picosecond-pulsed lasers have a larger spectral bandwidth, thus broadening the Raman peak linewidth.



**Figure 6.2.** Raman scattering of biphenyl-4-thiol (BPT). (a) Continuous-wave Raman spectrum of BPT powder (black) compared with SERS from BPT in the NPoM cavity (red). Inset: BPT molecule with arrows indicating the coupled ring vibrational mode (1586 cm<sup>-1</sup>). (b) Detailed view of coupled ring vibration in BPT. Binding to the gold surface splits and broadens the vibrational line.

Nanoparticles are automatically located and characterised using a custom-built reflective dark-field microscope, prior to each trCARS measurement (Fig. 6.3a). In our implementation, three temporally and spectrally independent input beams are required in the pulse train: the pump (set as t = 0,  $\lambda_p$ ), the Stokes ( $t = \tau_S$ ,  $\lambda_S$ ), and the probe pulses ( $t = \tau_x$ ,  $\lambda_x$ ) (Fig. 6.3b). The spectral shift between the pump and the Stokes pulse is chosen to populate the vibrational mode under study with frequency  $\omega_v$  (here  $\omega_p - \omega_S = \omega_v = 1586 \text{ cm}^{-1}$ ). To achieve this, a tunable pulse from an optical parametric oscillator (OPO) provides  $\lambda_p$  and  $\lambda_x$  while the 820 nm pump laser provides  $\lambda_S$  (see Chapter 3). Bandpass filtering sets all pulses to 0.5 ps pulse width (1.5 nm spectral width) to balance spectral and temporal resolution and reduce damage. The spectrum of  $\lambda_{p,x}$  is selected from the 10 nm-wide OPO pulse by independently-tuned bandpass filters. Pulse energies are kept low enough to avoid damage to the NPoM constructs (average powers <4  $\mu$ W  $\mu$ m<sup>-2</sup>, pulse energies <50 fJ  $\mu$ m<sup>-2</sup>). After filtering out the laser pulses from the emitted light, signals are detected by either a spectrometer or by a single-photon detector for single-photon lock-in detection with improved signal-to-noise ratio (which is described in detail in Chapter 5 and reference [254]).



**Figure 6.3.** Experimental setup. (a) An automated darkfield microscope combines three laser beams with variable time delay for SE-CARS. The signal is spectrally filtered and detected with a spectrometer (monochromator + CCD) or with a single-photon avalanche diode (SPAD). (b) Temporal-spectral alignment for pump (yellow), Stokes (red), and probe pulses (green), giving emission (blue) from two-pulse CARS (2pCARS) and three-pulse time-resolved CARS (trCARS). Top left shows BPT SERS spectrum from pump pulses, bottom left BPT SE-CARS spectrum from all three pulses.

The three-pulse scheme for SE-CARS allows different non-linear contributions to be distinguished. Three distinct non-linear processes can occur: two-pulse CARS ( $\omega_{2pCARS}$ ), three-pulse trCARS ( $\omega_{trCARS}$ ) and FWM ( $\omega_{FWM}$ ) (Fig. 6.4b), with frequencies

$$\omega_{2pCARS} = \omega_p - \omega_S + \omega_p = \omega_p + \omega_v$$
  

$$\omega_{trCARS} = \omega_p - \omega_S + \omega_x = \omega_x + \omega_v$$
  

$$\omega_{FWM} = \omega_1 + \omega_2 - \omega_3$$
  
(6.1)

when assuming that the CARS process is on-resonance, hence  $\omega_p - \omega_S = \omega_v$ . Any of the photons involved in CARS can also interact via non-resonant FWM such that  $\omega_{1,2,3}$ can be equal to  $\omega_{p,S,x}$ . With degenerate pump and probe pulses used to perform trCARS  $(\omega_p = \omega_x)$ , spectral separation of the 2-pulse and trCARS signals is inherently impossible as  $\omega_{2pCARS} = \omega_{trCARS}$ . This adds a varying background in trCARS signals. Note that phase matching is not relevant for these experiments on single sub-wavelength-sized NPoMs due to the tight focusing of light.

To spectrally separate 2-pulse and trCARS, the probe wavelength  $\lambda_x$  must be significantly detuned from the pump wavelength  $\lambda_p$ . While often achieved by frequency-doubling of the pump or Stokes, this unfortunately directly pumps Au interband transitions, considerably increasing nanoscale damage. Other approaches using non-linearly generated or electronically synchronised non-degenerate pulses reduce timing resolution (>1 ps), exceeding the phonon lifetime. The approach here retains spectral and temporal resolution by spectrally filtering the 10 nm-wide OPO output to create two 1.5 nm pulses for the pump and probe beams. A similar approach has recently been employed for biological imaging using stimulated Raman scattering [301].

### 6.3 Results

### 6.3.1 Coherent anti-Stokes Raman Scattering

The three-colour CARS scheme allows the BPT-filled NPoM to be driven at  $\lambda_p = 726$  nm,  $\lambda_S = 820$  nm and  $\lambda_x = 722$  nm, generating non-linear emission spectra (see Fig. 6.4a, with  $\tau_S = \tau_x = 0$  ps, average laser intensity 4 µW µm<sup>-2</sup>). Two strong peaks are observed at  $\omega_{2pCARS} = 652$  nm and  $\omega_{trCARS} = 649$  nm (slightly chirped). However, the third peak at  $\omega_{FWM}$ = 646 nm from FWM ( $\omega_{FWM} = 2\omega_x - \omega_S$ ) is very weak. This FWM contribution is thus ten times smaller than the on-resonant CARS signals and may originate from off-resonant molecular CARS, electronic Raman scattering, or 2-photon gold luminescence. Further, the SE-CARS emission is only observed when the resonance condition  $\omega_p - \omega_S = \omega_v$  is satisfied, confirming that the vibrationally-resonant, molecular CARS dominates over other FWM processes.

These non-linear experiments on BPT NPoMs demonstrate that the signal observed is dominated by molecular CARS. This is surprising in the context of many previous measurements that show FWM from metallic plasmonic components is very large [164, 191, 273, 302]. The disparity arises from the different field distributions of different plasmonic architectures. The optical fields in NPoMs are tightly confined to the gap (of width *d* and permittivity  $\varepsilon_g$ ) where the molecules reside, while field leakage into the metal (of permittivity  $\varepsilon_m$ ) decays spatially within  $\delta = d/2\varepsilon_g \operatorname{Re}\{1/\varepsilon_m\} \sim 1 \operatorname{nm}$  [12]. Although both are enhanced by the plasmonic gap, the ratio of integrated SE-CARS to FWM is approximated by the ratio of  $|E|^8$  in the gap and in the metal. Thus for NPoM structures, the ratio is given by  $2|\varepsilon_m\lambda_c/\varepsilon_g|^7 \sim 10^6$ , much larger than in other plasmonic substrates (for spherical Au nanoparticles this ratio is of order unity). This also explains observations of weaker FWM in closely-spaced dimers [148]. Small-gap plasmonic structures hence generate large SE-CARS signals ( $\sim 10^7 \operatorname{counts/nJ}^3$ here) and weak FWM in comparison to other plasmonic structures with  $10 - 10^8$ -fold weaker SE-CARS [188, 189, 191].



**Figure 6.4.** SE-CARS spectro-temporal scan. (a) SE-CARS signal from BPT NPoM at 0 ps probe delay showing clear peaks at  $\omega_{2pCARS}$  and  $\omega_{trCARS}$ , but minimal peak at  $\omega_{FWM}$ . (b) Excitation schemes for 2pCARS, trCARS and FWM. (c) Time-resolved SE-CARS spectra. (d) Integrated trCARS signal normalised by 2pCARS. Black line: Gaussian with 650 fs FWHM, red dashed line: expected vibrational decay from CW SERS. Laser intensity 4  $\mu$ W  $\mu$ m<sup>-2</sup> per beam.

The clear evidence that trCARS signals originate from molecular vibrations allows us to explore their phonon dynamics. Scanning the time delay of the probe pulse  $\tau_x$  allows a spectro-temporal map to be built (Fig. 6.4c). Since the 2pCARS (at 652 nm) is independent of the probe pulse, no change is expected in its intensity. However, sporadic fluctuations are observed in time-scans, most likely due to nanoscale modifications leading to changes in molecular coupling efficiency [14, 96, 278]. This simultaneous 2pCARS allows the trCARS signal (at 649 nm) to be suitably normalised to reveal the true time-resolved intensity independent of transient signal fluctuations (Fig. 6.4d). The extracted trCARS signal fits a Gaussian with FWHM of 650 fs corresponding to the convoluted excitation of pump and probe pulses of 500 fs. The molecular dephasing time  $T_2$  here is thus below the instrument response.

The expected molecular trCARS signal can also be calculated via Fourier-transform analysis of CW Raman spectra [149]. The SERS line investigated with CARS is multiplied with a window function corresponding to the spectral width of the resonant excitation by laser pulses (18 cm<sup>-1</sup>) (Fig. 6.5a). Fourier transformation of the windowed spectrum converts the spectral response to the temporal response yielding the expected trCARS time track from BPT in either the NPoM nanocavity or in the molecular powder (Fig. 6.5b). For BPT powder, this analysis suggests a dephasing time ~2 ps, while the broadened vibrational lines in SERS imply faster dephasing with  $T_2/2 \sim 0.6$  ps. Additionally, a weak beat of the trCARS signal from NPoM is predicted at 2 ps delay due to the split SERS line with separation 13 cm<sup>-1</sup>. Therefore, Fourier-analysis of the CW SERS spectrum suggests that it should be possible to measure the dephasing response with the trCARS setup shown here.

The discrepancy between dephasing times obtained from SE-CARS and CW SERS implies that the two measurements are probing the vibrational dephasing under different conditions. Critically, the peak powers of the pulsed lasers employed in SE-CARS are orders of magnitudes higher than the CW average power, thereby driving the entire system (both vibrational states in molecules and metal as well as electronic and plasmonic states) out of the thermal equilibrium [141]. To explore the effect of pulsed laser power on the vibrational dephasing, trCARS experiments are carried out with strongly reduced laser power in Section 6.3.3. As a third-order non-linear process, trCARS signals decrease drastically with laser power and single-photon detection is thus required.



**Figure 6.5.** Fourier transformation of CW Raman spectra. (a) BPT ring stretch vibration  $(1586 \text{ cm}^{-1})$  in powder Raman (black) and NPoM SERS (red) with window function (grey dashed) corresponding to pulsed excitation. Spectra recorded with a 785 nm CW laser. (b) Fourier transform of 1586 cm<sup>-1</sup> mode in BPT powder Raman (black) and NPoM SERS (red) spectra. The calculated time tracks simulate the expected trCARS response of the system. Fourier transform of window function represents the instrument response (grey dashed).

### 6.3.2 Incoherent anti-Stokes Raman Scattering

To explore the origin of accelerated dephasing times  $T_2$  measured in trCARS, we investigate the phonon population lifetime  $T_1$  with trIARS under similar laser intensities. Here, the Stokes laser beam at  $\omega_S$  is blocked and molecular vibrations are populated by spontaneous (incoherent) Stokes scattering of the pump or probe laser at  $\omega_{p,x}$ . In SERS, this process is known as vibrational pumping [109] which has been explored in detail in Chapter 4. trIARS experiments are carried out with only two laser beams on the sample, with photon energy difference not matching the energy of any vibration (here  $\lambda_p = 787$  nm and  $\lambda_x =$ 779 nm). These laser pulses are prepared by sending the pump laser (now at 780 nm) through a short single mode fiber (for spectral broadening of 50 nm), and subsequent filtering by two independently-tunable bandpass filters. Both lasers are attenuated to 1  $\mu$ W  $\mu$ m<sup>-2</sup> average intensity on the sample. Full SERS spectra are acquired by removing the laser with 785 nm notch filters.

In the recorded spectra, two sets of SERS peaks are visible, originating from scattering of the pump or probe pulses (labelled with differently coloured arrows in Fig. 6.6a,b). Scanning the time delay of the probe pulses leaves the Stokes spectrum unchanged (Fig. 6.6e). The anti-Stokes spectrum on the other hand shows increased signal when both pulses overlap in time, with an increase in SERS peaks from molecular vibrations as well as an increase of the broadband ERS background originating from hot electrons pumped by the laser pulses. Here, we focus our analysis on the peak area of the vibrational mode excited with trCARS in Fig. 6.4 at  $1586 \text{ cm}^{-1}$ .

From the ratio of Stokes ( $S_S$ ) to anti-Stokes ( $S_{aS}$ ) scattering, the phonon population  $n_V$  of the corresponding vibrational mode can be estimated using

$$n_{\mathcal{V}} = \frac{\omega_S^4}{\omega_{aS}^4} \left(\frac{S_S}{S_{aS}} - \frac{\omega_S^4}{\omega_{aS}^4}\right)^{-1} \tag{6.2}$$

with the frequency of Stokes and anti-Stokes photons  $\omega_S$  and  $\omega_{aS}$ , respectively. In Fig. 6.6f, the phonon population with changing probe delay is calculated for both the pump-probe (green) and probe-pump (yellow) process for the 1586 cm<sup>-1</sup> vibration. Both time tracks show an exponential decay but to opposing temporal ordering since both the pump and probe pulses excite the vibration with equal laser intensity. Exponential fits of these two measurements result in similar vibrational population lifetimes of  $T_1 = 600 \pm 300$  fs.

In contrast to trCARS experiments where a coherent polarisation is induced in the sample by resonant laser pulses, the trIARS process excites an incoherent phonon population  $n_v$ . The coherence of the two processes is discussed in more detail in Section 6.4.2. Hence, trIARS measures the energy relaxation of the vibrational population  $T_1$ , which is here observed to be longer than the dephasing time  $T_2$  measured by trCARS. This result demonstrates that trCARS and trIARS indeed probe different molecular properties and the accelerated coherence decay in trCARS is dominated by increased dephasing (instead of a higher phonon population decay rate).



**Figure 6.6.** trIARS spectro-temporal scan. (a) Anti-Stokes and (b) Stokes spectra of BPT NPoM at 0 ps probe delay with two sets of SERS peaks from scattering of the pump ( $\lambda_p = 787$  nm, yellow arrows) and probe ( $\lambda_x = 779$  nm, green arrows). (c) Excitation scheme for trIARS. (d) Time-resolved anti-Stokes and (e) Stokes trIARS spectra. (f) Phonon population of the 1586 cm<sup>-1</sup> vibrational mode extracted from the Stokes/anti-Stokes ratio. Both the pump-probe (green) and probe-pump (yellow) process can excite the vibration. An exponential decay fit (lines) of both time tracks yields  $T_1 \approx 600$  fs. Laser intensity 1 µW µm<sup>-2</sup> per beam.

### 6.3.3 Single-Photon Experiments

To investigate why pulsed laser illumination in trCARS leads to accelerated dephasing compared to CW measurements, we reduce the pulsed laser intensity  $I_l$  by 20-fold to 200 nW  $\mu$ m<sup>-2</sup> per beam (for pump, Stokes and probe lasers). Since trCARS signals scale  $\propto I_l^3$ , recorded count rates are now almost four orders of magnitude lower and cannot be detected with a spectrometer/EMCCD. Instead, we use single photon avalanche detectors in combination with single-photon lock-in detection. Different non-linear contributions to the signal count rate are distinguished by modulating Stokes and probe beams at 50 kHz (Fig. 6.8a) as described in detail in Chapter 5. Using this lock-in detection, we can simultaneously record time delay scans of the 2pCARS, trCARS and trIARS signals (which were not accessible with spectral analysis) on each individual NPoM. To acquire sufficient photon counts at these low excitation powers, time tracks are integrated for 60 minutes. We emphasise that this is the lowest laser intensity used for CARS experiments so far reported [192], which prevents damage to the nanostructures and molecules. The stability of the sample throughout the measurement is demonstrated by stable count rates on the single photon detector (see Fig. 6.7).



**Figure 6.7.** Sample stability under pulsed laser illumination. Signal count rate on the single-photon detector during the trCARS measurement shown in Fig. 6.8. Short spikes in count rate are due to transient events such as picocavity formation, but no damage to nanostructure or molecules is observed at 200 nW  $\mu$ m<sup>-2</sup> per beam during the integration time of 1 h. Dark count rate is <100 cts/s.


**Figure 6.8.** Single-photon trCARS and trIARS experiments on an individual NPoM. (a) Laser modulation scheme to identify different contributions to the signal with single-photon lock-in detection (50 kHz) [254]. (b) 2pCARS signal remains unchanged during probe delay scan. (c) trIARS signal decays on both sides of probe delay scan with population lifetime  $T_1$ . (d) trCARS shows one-sided decay with probe delay giving coherence lifetime  $T_2/2$ . Blue solid lines: exponential decay fit. Grey dashed lines: instrument response from a pure FWM sample (without molecular layer). Laser intensity 200 nW  $\mu$ m<sup>-2</sup> per beam. Error bars represent standard deviation of photon shot noise in each case.

As expected, the 2pCARS signal is not modulated by sweeping the probe delay, showing the overall stability of the setup (Fig. 6.8b). In contrast, both trIARS and trCARS signals vary with time delay of the probe pulses. Since both pump and probe pulses can excite the vibration in trIARS and single-photon detection does not allow for spectral separation of the two components (as in Section 6.3.2), the trIARS signal decays exponentially in both temporal directions (Fig. 6.8c). To fit the trIARS signal, three components have to be accounted for: The pump-probe and probe-pump process each lead to an exponential decay convoluted with the system response (Gaussian of FWHM 650 fs, see Fig. 6.4d). Since laser intensities can vary slightly, the intensity of these two signals is adjusted individually. Additionally, the fast ERS response (which cannot be separated spectrally here but was visible in Fig. 6.6d) gives a quickly decaying contribution which is included in the fit with a Gaussian corresponding to the system response at t = 0. Since the two-sided decay makes fitting the population lifetime difficult, we here fix the value to  $T_1 = 0.6$  ps as obtained in Section 6.3.2. Figure 6.8c hence shows that the low-power trIARS measurement is consistent with the vibrational relaxation time measured in Section 6.3.2. Therefore, we conclude that the rate of vibrational population relaxation is independent of pump power.

The trCARS signal at low laser power here shows a decay slightly longer than the instrument response (grey dashed in Fig. 6.8) at positive probe pulse delay (probe pulses arriving after pump and Stokes, Fig. 6.8d). For trCARS, two processes contribute to the signal. The molecular vibrational response can again be fitted by an exponential decay convoluted with the system response (only towards one side compared to trIARS). In addition, the non-resonant FWM leads to a background that is accounted for by a Gaussian at t = 0. By fitting the trCARS data with this model, the vibrational dephasing time can be extracted as  $T_2/2 = 0.6$  ps =  $T_1$  (the restriction  $T_2 \le 2T_1$  was set, see discussion in Section 6.4.1). However, the trCARS signal suffers from poor SNR due to photon shot noise of the single-photon experiment. Here, a compromise is necessary between the photon count rate and the lowest possible laser power. Despite the high noise, the low-power experiment here contrasts with the data acquired at high power in Section 6.3.1 where only the system response could be measured.

To increase confidence in these results, we carry out the experiment on many NPoM nanostructures. The trIARS and trCARS signal from each NPoM is normalised to the maximum of the fit to the time track and shown in Figure 6.9. For trIARS measurements, the individual nanostructures consistently show a time-resolved response significantly longer than the system response. In contrast, trCARS time tracks are noisy and the molecular response cannot clearly be distinguished from the system response. However, when individual trCARS measurements are examined,  $\sim$ 30% of NPoMs show the molecular vibrational decay (as in Fig. 6.8d) while other particles follow the system response. Hence, the trCARS signal of most NPoMs seems to be dominated by the fast response of FWM and other backgrounds. In particular, a quickly-decaying, broadband background from electronic Raman scattering cannot be distinguished from the trCARS signal in single-photon experiments (spectral investigation of the signal is not possible in this setup).



**Figure 6.9.** Single-photon (a) trIARS and (b) trCARS experiments on 77 NPoMs. Individual measurements are small grey circles, average response is indicated by coloured circles. The system response is indicated as dashed black line.

We therefore select NPoMs clearly showing the molecular response in trCARS to compare the vibrational dynamics to previous experiments. The average trIARS time track of 22 NPoMs fits a molecular relaxation with  $T_1 = 0.6$  ps well as observed before (Fig. 6.10a). In trCARS, the molecular dephasing seems consistent across all particles showing the molecular response, with the system response outside the standard deviation of individual measurements (Fig. 6.10b). Fitting the vibrational dephasing again yields  $T_2/2 = 0.6$  ps =  $T_1$ . Therefore, we conclude that dephasing occurs on the similar characteristic timescales in all NPoMs when the molecular signal can be distinguished from other backgrounds.

In comparison to high-power experiments in Sections 6.3.1 and 6.3.2, single-photon measurements at lowest possible laser powers thus show that vibrational dephasing is modified in NPoM by processes depending on excitation intensity. While the vibrational relaxation is independent of laser power, vibrational dephasing is accelerated at high powers suggesting power-dependent dephasing processes in NPoM. Potential physical processes leading to this effect are discussed in the following section.



**Figure 6.10.** Single-photon (a) trIARS and (b) trCARS experiments from selected 22 NPoMs showing molecular response. The average response is indicated by coloured circles while the grey shaded area indicates the standard deviation of individual measurements. Coloured lines are fit of the vibrational decay. The system response is indicated as dashed black line.

## 6.4 Discussion

#### 6.4.1 Acceleration of Vibrational Dephasing in NPoM

We now compare the results obtained from different experimental settings in previous sections. For trIARS experiments, both high and low power measurements agree measuring  $T_1 = 0.6$  ps. Therefore, the vibrational relaxation of BPT in the plasmonic nanocavity seems unaffected by decay processes depending on laser power. In contrast, different results were obtained for the dephasing time from different experiments. While trCARS at low laser power measured  $T_2/2 = 0.6$  ps, high power trCARS was unable to probe the vibrational decay and instead just recorded the system response. Consistent with low-power experiments, the linewidth of CW SERS spectra also suggests dephasing times of  $T_2/2 = 0.6$  ps. Moreover, vibrational population relaxation and dephasing are not completely independent measurements. In the Markovian approximation (no inhomogeneous broadening), the vibrational dephasing time  $T_2$  is linked to the population lifetime  $T_1$  via the pure dephasing time  $T_2^*$  through [171]

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*} \,. \tag{6.3}$$

Hence, both vibrational relaxation and pure dephasing processes contribute to the dephasing time  $T_2$  experimentally measured with trCARS. In general, any vibrational coherence induced in the sample cannot last longer than the lifetime of the vibrational population, thus limiting  $T_2 \leq 2T_1$ . In low power measurements carried out here (both CW SERS and single-photon trCARS), we observe  $T_2 = 2T_1$  indicating that pure dephasing processes are slow compared to the vibrational relaxation. However, increasing the laser power accelerates dephasing while vibrational relaxation remains constant. Therefore, pure dephasing processes depending on excitation power must be present for molecules in the NPoM nanocavity.

We now discuss physical processes that could lead to accelerated dephasing under high excitation intensity. As highlighted in Chapter 4, illuminating the NPoM structures with laser pulses strongly drives the system out of thermal equilibrium. While molecular vibrations are populated by vibrational pumping [109], electronic excitations ('hot electrons') are directly induced by the laser pulses followed by fast thermalisation of electronic states [250]. Therefore, trCARS probes the dephasing of molecular vibrations in a system in a non-equilibrium state, with effective temperatures (representing vibrational/electronic populations) transiently increased far above room temperature.

Excitation-induced dephasing (EID) is well known for excitonic systems, such as semiconductors [303] or carbon nanotubes [304]. In EID, electronic excited-state interactions, such as excitonic screening, accelerate dephasing depending on the concentration of excited carriers which typically scales linearly with pump laser power [304]. Electronic excitations can however also induce dephasing of vibrational states via electron-phonon interactions. In graphene, hot carriers induced by ultrafast laser pulses can increase vibrational dephasing by electron-phonon scattering, leading to a laser power dependent broadening of Raman lines [305]. Since molecular vibrations and metal are separated in our experiments in NPoM, a corresponding model might involve excitation of hot electrons in the metal which then interact with vibrations of molecules bound to the metal. For Cs atoms adsorbed to a Pt surface, a fast vibrational dephasing process depending on laser intensity was observed attributed to scattering of hot electrons at the adsorbate [306]. A similar mechanism could explain power-dependent dephasing in our experiments, however further theory is required.

In addition to electron-phonon scattering, phonon-phonon interactions could also be a source of vibrational dephasing. A previously-postulated explanation for increasing vibrational dephasing is the vibrational energy exchange (VEE) model [235–237]. Here, the vibrational mode under investigation couples to another vibrational exchange mode, resetting the vibrational phase via scattering to the coupled mode and back. This interaction importantly depends on the population in the exchange mode, thus increasing here as (all) vibrational modes are transiently populated by laser pulses. Previously, the VEE model has only been employed to explain the temperature-dependent Raman linewidth at cryogenic temperatures and coupling to lower energy vibrations was found [235, 237]. Here, the system is transiently excited by laser pulses, opening up the possibility of VEE with higher energy vibrations.

Another possible explanation for increased dephasing under strong driving is vibrational anharmonicity which slightly shifts vibrational frequencies leading to phase drift. However, there is no evidence for such frequency shifts in SERS spectra at laser powers employed here (see Chapter 4). Other mechanisms that lead to an accelerated phonon decay, such as electron friction from the bond to the metal surface have been discussed in the literature but would not depend on the excitation intensity [174]. This observation that vibrational dephasing of molecules is increased under strong excitation is relevant for understanding many complex molecular phenomena, in particular on substrates providing high plasmonic surface-enhancement. These include metal contact effects in molecular electronics, catalysis of chemical reactions at metal surfaces, heat transfer from molecules at metals for organic thermoelectrics, and other situations where the coupling of vibrational modes to electronic and energy transport is relevant.

#### 6.4.2 Coherence in SERS Vibrational Pumping

Most time-resolved Raman experiments to study molecular vibrational dynamics use the coherent Raman techniques CARS or stimulated Raman scattering (SRS). As coherent techniques, these methods probe the decay of vibrational coherence in the material, thus measuring the dephasing lifetime  $T_2$ . In the first experiments to instead investigate the decay of the vibrational population  $T_1$ , vibrations were excited coherently by SRS and spontaneous anti-Stokes scattering was separated from CARS by a detection angle outside the phase matching condition [170, 307]. Since the experiments in this paper are carried out in subwavelength-sized hot spots, trCARS and trIARS here cannot be distinguished by the angle of detection. A different approach to measure  $T_1$  is to generate an incoherent phonon population by excitation and subsequent incoherent decay of electron-hole pairs [308, 309], as well established for trIARS studies of carbon nanomaterials [297-300]. In these experiments (often conducted under focused laser excitation conditions), it is not necessary to separate coherent and incoherent contributions through the detection angle since the laser pulse energy differences are not tuned resonantly to the molecular vibrations and the SRS process is hence not possible. In the experiment presented in this chapter, we similarly excite an incoherent phonon population for trIARS but avoid direct electronic excitation. Instead, the strong surface-enhanced optical fields in plasmonic nanocavities enable direct vibrational pumping of the molecules by increasing spontaneous Stokes scattering rates (while keeping laser photon energies far below the band gap of any electronic excited states).



**Figure 6.11.** Comparison of spontaneous non-linear processes. **a** Excitation scheme of spontaneous parametric down-conversion involving three photons. **b** Excitation scheme of spontaneous Stokes scattering involving two photons (straight arrows) and one phonon (curved arrow). The phase of the phonon  $\varphi_v$  is random if the Stokes photon is generated spontaneously.

To understand whether the phonon population produced in vibrational pumping by spontaneous Stokes scattering is coherent, we compare this process to spontaneous parametric down-conversion of a pump photon (Fig. 6.11). In this non-linear process, one photon of the pump laser at  $\omega_p$  is converted into two photons of lower energy (signal at  $\omega_{sig}$  and idler at  $\omega_{id}$ ) under conservation of energy and momentum. The phase of the outgoing photons is connected to the phase of the pump photon via  $\varphi_p = \varphi_{sig} + \varphi_{id}$  [202]. Similarly, in spontaneous Stokes scattering the phase of the Stokes photon  $\varphi_S$  and the phase of the generated vibration  $\varphi_v$  obey  $\varphi_p = \varphi_S + \varphi_v$ . Hence, the molecular vibrations are generated with random phase by vibrational pumping if the process is not stimulated by laser pulses at the Stokes frequency (which fixes  $\varphi_S$  with respect to  $\varphi_p$ ). In our experiment, the plasmonic nanocavities are a very lossy optical cavity (Q-factor ~10 [13]), light in the cavity decays fully between laser pulses, and Stokes signal emission rates (1 kHz) are much lower than the laser repetition rate (80 MHz) and scale linearly with laser intensity (see Chapter 4). Therefore, the system is far below the SRS threshold and phonons will be generated with random phase. The resulting phonon population  $n_v$  is thus incoherent, and its decay probes the phonon lifetime  $T_1$ .

In Chapter 4, it was demonstrated that a monolayer of molecules inside the NPoM nanocavity can exhibit collective vibrations of hundreds of molecules [145, 204, 224]. This implies coherence between vibrations of different molecules even under spontaneous Raman scattering conditions. However, this does not contradict the above discussion since the pump photons scatter directly with the bright collective phonon mode in this optomechanical system and populate this new collective mode directly. In the optomechanical description, this can be shown by a transformation of the equations to a set of collective phonon operators which leads to identical results as treating all molecules individually [145]. While components of the vibration in individual molecules are coherent to each other, different phonons in the collective mode are still generated with random phase by spontaneous Stokes scattering and hence give an incoherent (collective) phonon population from which incoherent anti-Stokes scattering is observed in our trIARS experiment. Dephasing of individual molecules with respect to each other can now lead to an apparent population decay in the collective mode while preserving its phase relative to the laser excitation.

### 6.5 Summary

In summary, this chapter demonstrates that it is possible to investigate the molecular vibrational dynamics in plasmonic nanocavities with time-resolved coherent and incoherent Raman scattering. In the NPoM geometry, the molecular CARS signal dominates over FWM as well as other electronic Raman contributions since the field is tightly focused to the gap where molecules are located, enabling experiments probing vibrational dynamics. Combining both coherent and incoherent Raman techniques, we show here a simultaneous measurement of vibrational relaxation  $T_1$  and dephasing  $T_2$  selected by the excitation process. While the vibrational population decay is independent of excitation intensity, an acceleration of vibrational dephasing is observed in experiments using laser intensities of a few  $\mu W \mu m^{-2}$ . Only with laser intensities lowered 20-times and using single-photon lock-in detection, the vibrational dephasing can be measured and is now limited by population relaxation. Thus, pure dephasing processes for molecules in plasmonic nanocavities are very sensitive to the driving laser intensity, indicating the importance of optical near-field enhancement and metal-molecule interactions for vibrational dynamics in these nanoscale systems.

In the future, vibrational dynamics in plasmonic systems could be further investigated using mid-infrared (MIR) excitation in combination with a visible probe laser. In vibrational sumfrequency generation (vSFG) spectroscopy, a MIR pump pulse directly excites the molecular vibrations via absorption of an MIR photon and a visible probe pulse measures the vibrational dephasing  $(T_2)$  through anti-Stokes scattering. Instead of the coherent vSFG signal, dye molecules probed with a visible laser below the electronic resonance can also emit MIR vibrationally-assisted luminescence (MIRVAL). Here, the vibrational population induced by MIR pulses provides the energy missing to excite the molecules electronically with the below-resonance visible photons [310]. Since MIRVAL is an incoherent process, it probes the vibrational relaxation  $(T_1)$  and opens another pathway to probe both dephasing and population decay simultaneously - here enabled by the detection of different signals instead of different excitation schemes (as is the case for trCARS and trIARS). However, since the NPoM cavity only provides field enhancement for visible light, modifications to the nanostructures are necessary to combine visible and infrared resonances [223]. Additionally, co-focusing of infrared and visible light in the same microscope is challenging and usually requires two-sided illumination with different objectives (see Section 5.6.2) [284]. In comparison to trCARS and trIARS, time-resolved vSFG and MIRVAL could avoid some of the fast laser-induced dephasing processes encountered here as MIR illumination avoids generation of hot carriers and other excitations in the metal.

# Chapter 7

# **Stokes – anti-Stokes Photon Correlations**

#### Author contributions:

The experimental setup was developed and all experimental data recorded by the author of this thesis. Samples were prepared by Bart de Nijs, Marlous Kamp and Chenyang Guo. Simulations were developed and carried out by Yanji Yang, Asha Devi, Daniel Wigger and Ortwin Hess.

## 7.1 Introduction

#### 7.1.1 Raman Scattering as Correlated Photon Source

Sources of quantum-mechanically entangled photons are essential for quantum telecommunication [311–313] and processing [314–316]. For example, polarisation-entangled photon pairs can be generated in non-linear optical crystals via parametric down conversion [317] or in semiconductor quantum dots through a biexciton-exciton cascade [318, 319]. Amongst a plethora of other applications, entangled photon pairs can be used as quantum repeaters [320] or for two-photon quantum imaging [321, 322].

Another process to create entangled photon pairs is Raman scattering, where Stokes and anti-Stokes photons can exhibit non-classical correlations through the generation and annihilation of the same phonon [323–325]. When a laser photon inelastically scatters under the excitation of a phonon in a material (Fig. 7.1a), the generated Stokes photon and the phonon can be described by an entangled light-matter state [325]. Since the phonon exists in the material for an extended amount of time (limited by phonon relaxation times), the quantum information is retained and can be read out via anti-Stokes scattering some time later, destroying the phonon and transferring the entanglement to the anti-Stokes photon (Fig. 7.1b) [326]. Due to this ability to store entanglement information, this process was suggested to implement quantum repeaters for long-distance quantum communication networks (the so-called DLCZ scheme) [327]. This type of phononic quantum memory was demonstrated for phonons in diamond with a lifetime ( $T_1$ ) of several picoseconds [326, 328–331] and is particularly attractive as the high energy of optical phonons in diamond (1332 cm<sup>-1</sup>, [332]) suppresses thermal excitation at room temperature.



Figure 7.1. (a) Stokes Raman scattering creates a phonon in the material. (b) The quantum information stored in the phonon can be read out via anti-Stokes scattering.

In Raman scattering experiments on diamond, Stokes and anti-Stokes photons exhibit strong bunching statistics [333], meaning that anti-Stokes photons are most likely accompanied by a correlated Stokes photon (with a small contribution from spontaneous Raman scattering). Since the observed bunching is higher than allowed for a classical light source, Stokes – anti-Stokes photon correlations are of quantum-mechanical origin [331, 334] and have been employed for quantum communication schemes [335]. Besides diamond, correlated Stokes – anti-Stokes photon pairs have also been measured in water [334] and liquid carbon disulfide [336]. However, the vibrational population relaxation limits the storage of quantum information to a few picoseconds.

Stokes – anti-Stokes photon correlations are also observed in optomechanical systems [337, 338]. Similar to Raman scattering of molecular vibrations, quantum memory via photonphonon entanglement has been implemented using optomechanical systems [339]. Here, the mechanical resonance is provided by breathing modes of a photonic crystal nanobeam, which also supports an optical cavity resonance. Since the frequency of this mechanical oscillation (few GHz) is far below the frequency of molecular vibrations (few tens of THz), cryogenic cooling is necessary to bring the system into the vibrational ground state. The optomechanical system however outperforms molecular systems significantly for applications in quantum memory with phonon lifetimes up to seconds if the mechanical resonator is isolated suitably [340]. Additionally, the optomechanical devices can be integrated on-chip in photonic circuits enabling implementation in quantum technologies.

In this chapter, we measure Stokes – anti-Stokes (SaS) photon pairs from molecules in plasmonic nanocavities, which have been predicted by the theory of molecular optomechanics [129, 253]. To date, SaS photon correlations from surface-enhanced Raman scattering (SERS) have not been reported in the literature. In comparison to bulk Raman experiments, the increased photon count rates from SERS promise entangled photon sources with high brightness. Additionally, the ability to probe individual molecules using plasmonic nanocavities removes heterogeneous broadening as a source of uncorrelated photons. However, the nanoscale stability of this few-molecule system makes correlation spectroscopy challenging as signals are often integrated over several hours.

#### 7.1.2 Photon Bunching and Antibunching

To understand Stokes – anti-Stokes photon correlations investigated in this chapter, we first discuss photon correlation spectroscopy in general. Every source of light exhibits characteristic photon emission statistics. For example, an individual dye molecule or quantum dot can only emit one photon at a time and needs to be re-excited before it can radiate another photon. Therefore, photons sent out by a single-photon emitter are spaced out in time and the probability to detect two photons at the same time is very low, a characteristic called *antibunching* (Fig. 7.2). In contrast, photon *bunching* is observed if a light source always emits multiple photons at the same time (or in close succession). For example, this is observed for light emitted from a thermal source as random fluctuations in the field amplitude lead to bunches in the emitted intensity [229]. In coherent light emitted from a laser, photons are not correlated to each other and the photon stream is thus random.

Photon correlations of a light source can be characterised by the probability to detect a photon at time  $t + \tau$  given another photon is detected at a defined time t. This is quantified by the second-order intensity autocorrelation function  $g^{(2)}(\tau)$  which is defined as

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$
(7.1)

where  $\langle \rangle$  denotes time averages [229]. The intensity autocorrelation function is normalised to the average intensity  $\langle I(t) \rangle$ . Since correlations between two photons emitted very long times apart vanish,  $g^{(2)}(\tau \to \infty)$  is normalised to 1 at long time delays.



**Figure 7.2.** Photon stream emitted from different light sources. Top (green): antibunched light from single photon emitter. Middle (blue): coherent light, for example from a laser. Bottom (red): bunched light, for example from a thermal light source.



**Figure 7.3.** Intensity autocorrelation function  $g^{(2)}(\tau)$  for (a) antibunched and (b) bunched light.  $g^{(2)}(\tau)$  quantifies the probability to detect a photon a time  $t = \tau$  when another photon was detected at t = 0, normalised to 1 at  $\tau \to \infty$ .

For antibunched light, the probability to collect two photons at the same time is low. Hence, the autocorrelation function shows a dip at  $\tau = 0$  ( $g^{(2)}(0) < 1$ ) characteristic for single-photon emitters (Fig. 7.3a). Here, the value of  $g^{(2)}(0)$  indicates the purity of the single-photon source and the temporal width is influenced by the fluorescence lifetime of the emitter and the re-excitation rate. Contrarily, bunched light exhibits a peak with  $g^{(2)}(0) > 1$  as photons are more likely to be emitted at the same time (Fig. 7.3b).

In this chapter, we investigate the correlations of Stokes and anti-Stokes scattered photons. Therefore, we will measure the intensity cross-correlation function at the Stokes (*S*) and anti-Stokes (*aS*) frequencies. Similar to Eq. 7.1, the cross-correlation of the Stokes and anti-Stokes intensities  $I_S$  and  $I_{aS}$ , respectively, is defined by [333]

$$g_{S,aS}^{(2)}(\tau) = \frac{\langle I_{aS}(t)I_{S}(t+\tau)\rangle}{\langle I_{aS}(t)\rangle\langle I_{S}(t)\rangle},$$
(7.2)

representing the probability  $P(S, aS, \tau)$  to detect a Stokes photon and an anti-Stokes photon with time delay  $\tau$  between them. Normalising by the independent probabilities to detect Stokes (P(S)) and anti-Stokes (P(aS)) photons, the cross-correlation function can also be rewritten using photon detection probabilities as [333]

$$g_{S,aS}^{(2)}(\tau) = \frac{P(S,aS,\tau)}{P(S)P(aS)} = \frac{P(S|aS,\tau)}{P(S)},$$
(7.3)

where the conditional probability  $P(S|aS, \tau)$  is added in the second step (using  $P(A|B) = P(A \cap B)/P(B)$ ). For the SaS process, P(S|aS,0) is the probability to detect a Stokes photon under the condition that an anti-Stokes photon is detected at the same time. Accordingly,  $g_{S,aS}^{(2)}(0)$  is a measure for the Stokes – anti-Stokes bunching and will be measured experimentally in this chapter. Since  $g_{S,aS}^{(2)}(0)$  in Eq. 7.3 scales with 1/P(S) and spontaneous Stokes scattering depends on the laser intensity as  $P(S) \propto I_l$ , a dependence of SaS bunching  $\propto 1/I_l$  is expected and experiments are thus conducted at lowest possible excitation intensities.

Since phonons in the molecular system decay quickly, SERS from a pulsed laser is utilised for correlation experiments, probing the intensity cross-correlation function at discrete time delays spaced by 12.5 ns. Here, we thus compare the probabilities of detecting Stokes and anti-Stokes photons in the same laser pulse or from subsequent pulses. While the Stokes – anti-Stokes process always leads to the emission of both photons from the same pulse (the phonon lifetime is much shorter than 12.5 ns), accidental coincidences from spontaneous SERS generate photon pairs both in the same as well as in subsequent pulses (see Fig. 7.4). In addition to spontaneous SERS, uncorrelated coincidences can also be caused when only one of the two correlated photons is detected. The rate of accidental coincidences is limiting the observable bunching  $g_{S,aS}^{(2)}(0)$  and increases with the spontaneous SERS count rate, hence justifying the scaling  $\propto 1/I_l$  as suggested by Eq. 7.3.



**Figure 7.4.** Stokes – anti-Stokes (SaS) processes. (a) Correlated SaS photon pair detected in one laser pulse. (b,c) Uncorrelated photons detected in the same pulse from (b) spontaneous Raman and (c) missed detection of a correlated photon. (d,e) Uncorrelated photons detected in subsequent pulses from (d) spontaneous Raman and (e) missed detection of a correlated photon. Red arrow: Stokes photon, Blue arrow: anti-Stokes photon, black arrow: phonon, black circle: photon detection.

#### 7.1.3 Experimental Setup

To measure the intensity autocorrelation function, photon correlation spectroscopy is carried out. In a typical experiment, a Hanbury Brown–Twiss (HBT) interferometer [286] is used where the signal intensity is split between two detectors by a 50:50 beam splitter. The arrival times of photons at each single-photon detector are correlated by a coincidence counter that records time differences between the detection events.

The experiments conducted here differ from usual autocorrelation measurements as crosscorrelations of light at two different frequencies is investigated (Fig. 7.5a). Surface-enhanced Stokes and anti-Stokes signals are separated by a dichroic mirror and independently detected by two single-photon avalanche diodes (SPADs). As Stokes – anti-Stokes correlations are mediated by the excitation of a molecular vibration, it is crucial to compare photon counts originating from the same vibrational mode on both detectors. Therefore, narrow filtering of SERS lines is required, achieved here using angle tunable bandpass filters. Photon counts are correlated through picosecond photon timestamping using the FPGA board developed in Chapter 5. The read-out of timestamps is triggered by anti-Stokes signals (as many uncorrelated Stokes photons are emitted by spontaneous Raman scattering) which are delayed electronically (via a longer cable) to allow probing correlations with Stokes photons arriving before the anti-Stokes photon. While full timestamps are initially recorded, only the time difference of counts on the two detectors is needed to measure the intensity cross-correlation. However, the full timestamp information can be used for time-gating to post-select light from picocavity events or assign photon events to the state of a polariser in front of the detector.

The SERS signal is obtained from BPT molecules in plasmonic nanocavities excited by laser pulses at 785 nm (0.5 ps at 80 MHz). For improved collection efficiency, 'superefficient plasmonic nanoarchitectures for Raman kinetics' (SPARKs) are employed, confining the excitation laser tightly to only ~10 molecules (Fig. 7.5b,c). In photon correlation experiments, the quantum efficiency of the plasmonic nanoantenna is crucial as for every anti-Stokes photon the corresponding Stokes photon needs to be detected. To avoid accidental coincidences, laser intensities are reduced to  $0.5 \,\mu\text{W} \,\mu\text{m}^{-2}$ , in turn requiring integration times of at least one hour.



**Figure 7.5.** (a) Experimental setup to measure Stokes – anti-Stokes cross-correlations. The SERS signal is split with a dichroic mirror in Stokes and anti-Stokes on separate single-photon counters (SPADs). Angle-tunable bandpass filters are used to select light from individual vibrational modes. (a) The SPARK nanostructure focuses the light tightly to the molecular SAM. (b) Vibrations in BPT molecules interact with laser pulses via SERS, producing correlated Stokes and anti-Stokes photons.

### 7.2 Results

#### 7.2.1 Spectrally-Resolved SERS Photon Correlations

In the pulsed SERS spectrum of BPT in SPARKs, the vibrational modes are clearly visible on both the Stokes and anti-Stokes side of the 785 nm laser. By adjusting the angles of long and short pass filters in front of the SPADs, the filter transmission is matched to the  $1586 \text{ cm}^{-1}$ vibration of BPT with spectral width of 2 nm (corresponding to the laser bandwidth, see Fig. 7.6a). With this setup, it is possible to cross-correlate only photons scattered by the same vibrational mode. As was observed in Chapter 4, the optomechanical system is in the regime of vibrational pumping at pulsed laser powers employed here. In Figure 7.6b, this is indicated by quadratic scaling of the anti-Stokes signal with laser intensity (when corrected for NPoM in-coupling efficiency, see Section 4.3.2). Hence, anti-Stokes photons from the correlated SaS process dominate over spontaneous anti-Stokes scattering from the thermal phonon population. If Stokes and anti-Stokes photons can be detected with sufficiently high efficiency, it should thus be possible to observe SaS correlated photon pairs in this system.

When photon correlation spectroscopy is carried out with a pulsed laser, the intensity crosscorrelation function  $g_{SaS}^{(2)}(\tau)$  is probed at discrete time delays  $\tau$  corresponding to the laser pulses. Accordingly, peaks spaced by 12.5 ns are observed in the SaS coincidence histograms measured here from SERS of the 1586 cm<sup>-1</sup> vibration in BPT (Figs. 7.6c,d). For a correlated SaS photon pair, both photons are detected in the same laser pulse at  $\tau = 0$  time delay. However, spontaneous Stokes scattering (or detector dark counts) leads to accidental coincidences which can occur either in the same laser pulse or in any consecutive pulse. Therefore, the degree of SaS bunching  $g_{SaS}^{(2)}(0)$  can be calculated by dividing the number of photons from the coincidence pulse with the average number of photons in pulses with  $\tau \neq 0$  (indicated as dotted line in Figs. 7.6c,d).

In Figure 7.6, two examples for coincidence histograms measured from SPARKs are shown. For the first particle (7.6c), 131 coincidence counts were measured over the integration time of 1 h. However, also 65 accidental coincidences per pulse were collected. Therefore, the probability of detecting Stokes and anti-Stokes photons in the same pulses is about twice as high as detecting them in subsequent pulses, characterised by  $g_{SaS}^{(2)}(0) = 2.0 \pm 0.1$ . This particle had a comparatively high anti-Stokes count rate of ~300 cts/s on average. In comparison, a particle with much lower anti-Stokes count rate is shown in 7.6d (~ 5 cts/s, dark count rates subtracted). Here, only 10 coincidence counts were detected, with accidental

coincidences difficult to quantify but now dominated by dark counts (no regular laser pulses observed in coincidence histogram). While the second particle showed SaS photon pairs at much lower rate, the purity of correlated photons was higher with  $g_{SaS}^{(2)}(0) = 38 \pm 3$ . The error in  $g_{SaS}^{(2)}(0)$  is calculated from the variation of photon counts in all pulses with  $\tau \neq 0$ .

When SaS bunching is measured for 30 SPARK nanostructures, a wide range of values is measured for  $g_{SaS}^{(2)}(0)$ . From the anti-Stokes count rate of each particle, the in-coupled laser intensity can be calculated according to Section 4.3.2. When  $g_{SaS}^{(2)}(0)$  is plotted against incoupled laser intensity, scaling with  $\propto 1/I_l + 1$  is observed as would be expected from Eq. 7.3. Particles with higher anti-Stokes count rate (and thus higher in-coupled intensity) also emit stronger spontaneous SERS signals leading to accidental coincidences hence suppressing the observation SaS correlations.



**Figure 7.6.** Stokes – anti-Stokes correlations in SERS from SPARKs. (a) Pulsed SERS spectrum of BPT (black, 785 nm laser,  $0.5 \,\mu W \,\mu m^{-2}$ ), with normalised transmission through bandpass filters in front of Stokes (red) and anti-Stokes (blue) single-photon detectors. (b) Intensity-dependence of Stokes (red) and anti-Stokes (blue) SERS signals of 30 SPARKs, corrected for each particles in-coupling efficiency. (c,d) SaS coincidence histograms for two particles with overall (c) high or (d) low count rate. (e) SaS bunching *vs* in-coupled laser intensity for each of 30 SPARKs, calculated from the count rate during the correlation experiment.

A similar effect can be observed when comparing SaS correlations from nano- and picocavities. During the correlation experiments, the count rate on the anti-Stokes detector fluctuates strongly (Fig. 7.7a). Throughout the entire integration time, spikes in the count rate lasting for several seconds can be observed corresponding to the emergence of picocavities – adatoms moving from gold surface into the cavity, increasing field confinement to a single molecule. Using the full timestamping capabilities of the FPGA board, photon counts can be assigned to picocavities in post-processing when the count rate peaks at >50% above the average count rate (see Fig. 7.7a inset). In the signal originating from the SPARK nanocavity,  $g_{SaS}^{(2)}(0) = 10$  is observed for this particle showing a low rate of accidental coincidences (Fig. 7.7b). However for picocavities in the same particle, the rate of accidental coincidences is increased and  $g_{SaS}^{(2)}(0)$  thus reduces to ~ 3. While picocavities are a promising approach to obtain correlated photon pairs from a single molecule, the spontaneous SERS process is also enhanced limiting the ability to detect pure SaS coincidences.



Figure 7.7. Stokes – anti-Stokes correlations in nano- and picocavities. (a) Anti-Stokes count rate over the duration of a correlation experiment, Showing spikes caused by picocavities. Inset: Count rate in a 100 s window, indicating the threshold when counts are attributed to a picocavity (red shaded).
(b) SaS coincidence histogram from the SPARK nanocavity (without picocavity active). (c) SaS coincidence histogram during an active picocavity (all picocavity events accumulated).

We then investigate cross-correlations between different vibrational modes and the electronic Raman scattering (ERS) background. For this experiment, five filter positions are defined equally for the Stokes and anti-Stokes bandpass filters (see Fig. 7.8a). Three of them select SERS lines ( $v_1 = 1586 \text{ cm}^{-1}$ ,  $v_2 = 1280 \text{ cm}^{-1}$ ,  $v_3 = 1080 \text{ cm}^{-1}$ ) while the other two lie between Raman active vibrations and thus probe only the ERS signal (880 cm<sup>-1</sup>, 1420 cm<sup>-1</sup>). Correlation experiments are carried out for all 25 possible combinations of filters to map

out the frequency-resolved SaS correlations. Since this experiment requires illuminating the nanostructure for 25 hours, the laser intensity is decreased to 0.2  $\mu$ W  $\mu$ m<sup>-2</sup> to reduce slow damage to particle and molecules. For measurements without photon bunching, (accidental) coincidences are extremely rare at such low count rates and thus  $g_{SaS}^{(2)}(0) = 1$  is assumed if less than 3 correlated photon pairs were recorded during the integration time.

As the frequency-resolved correlation map in Figure 7.8b shows, SaS bunching is predominantly observed when the same frequency is selected for Stokes and anti-Stokes photons. Along this diagonal, strong bunching with  $g_{SaS}^{(2)}(0) > 10$  is observed as excitation powers were reduced compared to previous experiments, decreasing accidental coincidences. Interestingly, both the ERS background and all vibrations exhibit SaS bunching. Quantitatively analysing the bunching obtained from different vibrations is here difficult due to low coincidence rates. The result, that vibrational modes are not required for SaS correlations is in agreement with theoretical calculations for a general optomechanical system [253]. Similar results were previously obtained for Raman scattering on diamond and was attributed to a 'virtual' SaS process without a vibrational resonance [341, 342] (also called 'leapfrog' process [253] from coherent wave mixing). Further, slight bunching of 1586 cm<sup>-1</sup> Stokes and 1080 cm<sup>-1</sup> anti-Stokes photons is observed ( $g_{SaS}^{(2)}(0) = 1.7 \pm 0.9$ ). This suggests intramolecular vibrational energy redistribution (IVR), which is a common relaxation pathway for molecular vibrations [343, 344], from the 1586 to the 1080  $\text{cm}^{-1}$  mode. While further investigations are here necessary due to the very low coincidence counts in this measurement, this result highlights that SaS correlation spectroscopy is a useful tool to study the dynamics of molecular vibrations.



**Figure 7.8.** Frequency-resolved Stokes – anti-Stokes correlations. (a) Filter settings for five different spectral windows, three on vibrational modes ( $v_1 = 1586 \text{ cm}^{-1}$ ,  $v_2 = 1280 \text{ cm}^{-1}$ ,  $v_3 = 1080 \text{ cm}^{-1}$ ) and two on the ERS background. BPT Stokes spectrum in the background (black). (b) Cross-correlations of different frequencies on Stokes and anti-Stokes detectors. Only when the same frequency is selected, SaS bunching can be observed.

#### 7.2.2 Polarisation-resolved SERS Photon Correlations

For applications based on photon entanglement, it is important to investigate whether SaS photon pairs are entangled beyond their time-correlations. Often, polarisation entanglement is chosen to prove non-locality and establish protocols for quantum telecommunication [325]. Previously, polarisation-dependent SaS bunching has been demonstrated for Raman scattering of water [334] and quantum communication protocols were used to entangle phonons in diamond [325, 335]. In SERS however, polarisation entanglement is more challenging as the Raman scattered photons undergo emission from the near- to the far-field via the plasmonic structure's antenna modes. Therefore, SaS polarisation entanglement in SERS strongly depends on the emission characteristics of the employed nanostructures.

Similar to frequency-resolved correlation experiments in the previous section, Stokes and anti-Stokes photons are selected from a single vibrational mode using bandpass filters (1586 cm<sup>-1</sup>, as in Fig. 7.6a). Additionally, polarisers are now added in front of the photodetectors with a half wave plate added for the anti-Stokes detector to select either horizontally or vertically polarised photons (Fig. 7.9a). For SPARK samples, the emission profile is strongly depending on the shape of the silica nanolens and thus more complex than the NPoM emission (especially as darkfield spectroscopy is obscured by reflections on the large nanolens). We here investigate two different SPARKs with distinct polarisation-resolved emission characteristics. In Figure 7.9, the first particle shows an almost unpolarised anti-Stokes emission count rate (Fig. 7.9b), while the second particle emits highly polarised anti-Stokes light (Fig. 7.9c). Further studies are necessary to understand the microscopic origin of this polarisation dependence. In comparison, the (10) plasmonic mode of the NPoM structure emits radially polarised light which would be observed as unpolarised emission here similar to the first particle [345]. However, the polarisation emitted by NPoM structures is highly sensitive to the nanoscale shape of the particle [346] and precise control of the morphology is thus desirable for applications using SERS polarisation-entanglement.

We measure the SaS bunching with polarisers in front of the two detectors with parallel orientation or crossed. For the first particle with unpolarised anti-Stokes emission, photon bunching comparable to previous experiments without polarisers is observed when Stokes and anti-Stokes photon with the same polarisation are detected (Fig. 7.9d). In contrast, SaS bunching is suppressed when the polarisers are crossed (Fig. 7.9e), indicating that the polarisation of the anti-Stokes photon is set by the polarisation of the correlated Stokes photon. Since this is a condition for polarisation entanglement, it presents a promising step towards using SERS as source of entangled photon pairs [334]. However, when the same

experiment is carried out on a SPARK nanostructure that shows highly polarised anti-Stokes emission, SaS bunching is observed for both parallel and crossed polarisers (Fig. 7.9f,g). This result suggests that the plasmonic nanoantenna here converts the polarisation of Stokes and anti-Stokes fields in the near-field to a different polarisation in the far-field defined by the emitting antenna mode. Thus, these experiments highlight that careful engineering of the emission characteristics of the plasmonic nanostructure is required to reproducibly create polarisation-entangled SaS photon pairs. A promising approach could be NPoM structures using ultra-spherical nanoparticles from well-controlled colloidal synthesis [83].



**Figure 7.9.** Polarisation-resolved Stokes – anti-Stokes correlations. (a) Experimental setup to measure SaS correlations with additional polarisers. (b,c) Polarisation-dependent anti-Stokes emission rate of two SPARK nanostructures. (d,e) SaS coincidence histograms for the first SPARK particle with Stokes and anti-Stokes polarisers oriented (d) in parallel and (e) crossed. (f,g) SaS coincidence histograms for the second SPARK particle with polarisers (f) parallel and (g) crossed.

## 7.3 Experimental Limitations

While SaS photon correlations from SERS were successfully measured in this chapter, the obtained bunching with  $g_{SaS}^{(2)}(0) \sim 10$  is much weaker than achieved in previous experiments from bulk Raman (up to  $g_{SaS}^{(2)}(0) \sim 500$  in water for a vibration of similar energy [334]). In this section, we discuss current limitations of the SERS approach in probing the SaS process experimentally.

To detect a correlated SaS photon pair both the Stokes and anti-Stokes photon have to be detected. Therefore the emission efficiency of the sample and detection efficiency of the optical setup are crucial to measure photon bunching. While efforts were made to optimise the setup, we estimate the detection efficiency for anti-Stokes and Stokes detection at 50% and 30%, respectively (with the SPAD efficiency dominating losses and causing the difference between anti-Stokes and Stokes wavelengths). Improved photodetectors (and using a shorter laser wavelength more suitable for silicon-based detectors) could boost the SaS bunching measured in these experiments. However, the experimental losses are likely dominated by the emission efficiency of the plasmonic nanostructures, as simulations in Figure 7.10 demonstrate<sup>1</sup>.



**Figure 7.10.** Photon emission efficiency of SPARKs. (a) Schematic of the simulated SPARK nanostructures with a dipole in the nanogap emitting light. The power in a box around the gap is compared with transmission through a collection cone corresponding to an objective with NA = 0.9. (b) Quantum efficiency of photon emission at the anti-Stokes ( $\lambda$  = 700 nm, blue) and Stokes ( $\lambda$  = 900 nm, red) wavelengths. The diameter of the SPARK silica lens is varied, and the NPoM without nanolens is shown in comparison (open diamonds).

<sup>&</sup>lt;sup>1</sup>Simulations were developed and carried out by Yanji Yang, Asha Devi, Daniel Wigger and Ortwin Hess.

To estimate the quantum efficiency of the plasmonic constructs used here, we carry out finite-difference time-domain (FDTD) simulations (see [91]). The generation of Stokes and anti-Stokes photons in the gap between nanoparticle and mirror is simulated by placing an emitting dipole in the cavity and selecting the corresponding wavelengths. The power radiated by the dipole into the gap is calculated by analysing the power inside a box around the nanocavity (see Fig. 7.10a). This power is then compared to the power emitted to the far-field through a spherical sector with half-angle of 64.14° which corresponds to the collection with the 0.9 NA objective used here. For NPoM nanostructures, we find that the emission efficiency of anti-Stokes and Stokes photons is only 9% and 1.6%, respectively<sup>2</sup>. The addition of a nanolens in SPARK constructs enhances the quantum efficiency slightly with 17% and 4% at anti-Stokes and Stokes wavelengths, respectively. As >50% of the light in the far-field is emitted towards the collection cone, the quantum efficiency of the nanostructure is limited by the conversion from the near- to the far-field. Potential loss mechanisms include the emission of surface plasmon polaritons (SPPs) travelling along the gold mirror away from the particle, or absorption in the plasmonic metal.

The quadratic intensity scaling of the anti-Stokes count rate observed for pulsed SERS suggests that vibrational pumping dominates over thermal excitations in this experiment. Therefore, each anti-Stokes photon should originate from a previous Stokes scattering event. However, only 1.2% of Stokes photons are detected with this setup (0.5% for NPoM, combined optical setup and plasmonics efficiency), drastically limiting the bunching that can be obtained here. Additionally, only 8.5% of anti-Stokes photons are collected (4.5% for NPoM), reducing the count rate on the detector (correlation measurements here are triggered by anti-Stokes photon counts). These calculations suggests that coincidence count rates 1000-times higher could theoretically be possible although the increased efficiencies would in turn also lead to more accidental coincidences limiting the achievable  $g_{SaS}^{(2)}(0)$ .

We verify the simulations by comparing SaS bunching from SPARKs with NPoM nanostructures in Figure 7.11. For NPoMs, the calculations suggest emission efficiencies approximately two-times lower than for SPARKs. From an uncoated NPoM sample, no bunching can be observed ( $g_{SaS}^{(2)}(0) \sim 1$ ). Only when NPoMs are covered with a high-index polymer (poly(pentabromophenyl methacrylate), n = 1.78) which slightly improves the emission efficiency [90], weak photon bunching bunching is obtained with  $g_{SaS}^{(2)}(0) \leq 2$  (i.e. within

<sup>&</sup>lt;sup>2</sup>Notably, this emission efficiency of the Stokes process is in agreement with the radiative efficiency extracted from vibrational pumping in Chapter 4. To account for high vibrational pumping rates observed in pulsed SERS, the radiative yield of Stokes scattering in (polymer-coated) NPoM was estimated at 2.5% to match the model to the data. The polymer coating for NPoMs may explain deviations from simulations here.

classical limits, Fig. 7.11a). Therefore, the improved quantum efficiency of SPARK samples is crucial to measure non-classical SaS photon pairs while still leaving a lot of room for improvement. This demonstrates the importance of optimising the plasmonic substrate for these experiments. In previous SERS experiments, the main focus was on improving SERS signal count rates and thus the optical field enhancement was optimised (high spontaneous SERS count rates actually limit SaS bunching through accidental coincidences). For SaS correlation experiments however, the quantum efficiency of far-field emission is more important and therefore a new approach to designing plasmonic nanostructures for SERS is encouraged in order to enable quantum applications.



**Figure 7.11.** Stokes – anti-Stokes correlation in NPoMs and SPARKs. (a) SaS bunching measured from NPoM nanostructures covered with high-index polymer. Bunching with  $g_{SaS}^{(2)}(0) \le 2$  is observed. (b) SaS bunching measured from SPARK structures, demonstrating non-classical SaS correlations with  $g_{SaS}^{(2)}(0) > 2$  for many particles.

Despite current (experimental) limitations, surface-enhanced Raman scattering is a promising approach to access correlated Stokes – anti-Stokes photon pairs for quantum applications. Compared to bulk Raman experiments where pulsed laser powers of several mW are needed [333], we here demonstrated SaS bunching with < 1  $\mu$ W. In principle, the peak powers of lasers used in our experiment could also be generated by continuous-wave lasers, allowing CW-generated pairs of entangled photons. However as with bulk Raman, the signal is contaminated by spontaneous SERS photons which currently make it impossible to detect SaS bunching with CW lasers. In general, the development of an entangled photon source using SERS will always be limited by a trade off between brightness and purity due to the large background of spontaneous Raman photons.

### 7.4 Summary

In this chapter, we clearly demonstrate that it is possible to detect correlated Stokes – anti-Stokes photon pairs from surface-enhanced Raman scattering of molecules in a plasmonic nanocavity, as predicted by the theory of molecular optomechanics. Experimentally, this requires pulsed laser illumination, narrow bandpass filtering, and plasmonic nanostructures with high emission efficiency. We observe SaS photon bunching with  $g_{SaS}^{(2)}(0) > 10$  for some ideal SPARK nanostructures at very low laser powers (< 1 µW) compared to bulk Raman experiments. However, the achievable  $g_{SaS}^{(2)}(0)$  is limited by accidental coincidences due to spontaneous Raman scattering. Frequency-resolved correlation spectroscopy shows that both SERS from vibrations and ERS can exhibit bunching if the same frequency is selected for both Stokes and anti-Stokes photons. Additionally, correlations in the polarisation of the emitted SaS photon pairs are possible however require plasmonic nanostructures with polarisation-preserving emission characteristics. These results suggest that SERS could in the future be used as a source of entangled photon pairs, but further work is required to optimise nanostructures and experimental settings.

The insights obtained in this chapter clearly lay out the route to enable quantum applications based on entangled photon pairs from SERS. Most importantly, the quantum efficiency for the emission of photons from the plasmonic near-field needs to be improved. Likely avenues include the suppression of surface plasmon polaritons (SPPs) and the use of plasmonic materials with lower losses. Here, the addition of a silica nanolens already provided some improvements to the NPoM nanostructure, however the potential for further development is high. The ideal plasmonic architecture should also preserve the polarisation of fields during emission from the near- to the far-field to allow for polarisation entanglement. Following these guidelines, it could be possible to generate quantum-entanglement in vibrations of individual molecules while emitting pairs of entangled photons with surface-enhanced rate compared to bulk Raman scattering but without the need of cryogenic cooling as for traditional optomechanical systems.

## Chapter 8

## **Conclusions and Outlook**

In summary, this thesis explored the interaction of molecular vibrations with optical resonances in plasmonic nanocavities. Surface-enhanced Raman scattering (SERS) experiments were carried out with ultrafast pulsed lasers to uncover non-linear effects of the plasmonmolecule system. For these experiments, the nanoparticle-on-mirror (NPoM) structure proved to be a suitable model system for the optomechanical interaction between optical cavity modes and molecular vibrations, with a simple fabrication and high reproducibility. Using the NPoM geometry, the optical fields were focused to nanoscale volumes filled with a well-ordered monolayer of organic molecules, probing the vibrations of several hundreds of molecular. In this regime of extreme field enhancement and molecular confinement, the molecular vibrations are modified by the optical properties of the surrounding plasmonic nanostructure and new physics emerge in the experiments presented in this thesis. Below, both the new physical insights as well as novel experimental techniques developed to conduct the research here are summarised along with a perspective on future directions for research and applications.

#### Novel physical effects

The experiments carried out in this thesis improved our understanding of the interaction of molecular vibrations with light confined in plasmonic nanocavities. New physical effects were discovered with unique experimental signatures and requiring the development of novel theoretical models. In particular, progress was made in three key areas:

- (i) SERS experiments with pulsed lasers allowed us to investigate the optomechanical interaction of molecular vibrations with the optical fields in the nanocavities, sparking advances in the theory of molecular optomechanics. To describe experimentally-observed non-linear SERS effects, the full plasmonic response of the nanocavity had to be included in the model and hundreds of vibrating molecules were simulated in the gap. With the improved theory, an optical spring shift from the optomechanical interaction was found, shifting and broadening vibrational lines by >100 cm<sup>-1</sup>. Additionally, collective vibrational modes of hundreds of molecules vibrating together strongly enhance optomechanical effects such as vibrational pumping. Experimentally, this effect was demonstrated by tuning the spacing of vibrating molecules in mixed molecular monolayers. Previously, Raman scattering only assumed the interaction of a single photon with a single vibrating molecule. Instead, in plasmonic nanocavities we found that a photon is scattered directly by collective vibrational modes involving coherent movement of hundreds of molecules.
- (ii) With time-resolved SERS experiments, the dynamics of molecular vibrations under confinement in plasmonic nanocavities were investigated. In these conditions, an acceleration of vibrational dephasing with laser intensity was observed and extremely low laser powers were required to probe the coherent signal in time. In contrast, the incoherent relaxation of the vibrational population was not affected by laser intensities. A laser power-dependent pure dephasing process such as excitation-induced dephasing (EID) or vibrational energy exchange (VEE) is consistent with this observation.
- (iii) Using pulsed SERS from NPoM nanocavities, we demonstrated the generation of correlated Stokes – anti-Stokes (SaS) photon pairs for the first time in a SERS setting. To observe SaS bunching, a plasmonic nanostructure with high emission efficiency is crucial to detect both correlated photons. Here, we measured frequency-resolved cross-correlations between photons originating from scattering with the same molecular vibration. This common quantum-mechanical origin promises quantum entanglement of the generated photon pair, which was observed as correlated polarisation of the two photons in polarisation-preserving plasmonic structures.

#### **Experimental advancements**

The physical insights gained in this thesis were enabled by the improvement of existing or development of novel experimental techniques. Particular advances were made in the following fields:

- (i) An experimental protocol for pulsed SERS was established, focused on probing the power-dependence of SERS from plasmonic nanostructures. Important considerations here are the trade-off of spectral and temporal resolution, and the limited pulsed laser power tolerated by molecules and nanostructures before damage occurs. The impact of laser-induced damage was reduced by scaling exposure times inversely with laser powers. Moreover, experimentally SERS signals from NPoM nanostructures vary by up to one order of magnitude due to different particle sizes and facet shapes. This was accounted for by correcting the laser power experienced by the molecules with each NPoMs in-coupling efficiency. Hence, the power-dependence of hundreds of NPoMs could be compared to uncover non-linear effects in SERS.
- (ii) To improve the signal-to-noise ratio (SNR) of single-photon experiments, a novel photon detection setup was developed implementing the lock-in effect for individual photons. Comparing the arrival time of the photon at the detector with timestamps of several periodic reference signals, the modulation of the signal in time during the reference period could be recovered. Using this lock-in scheme, 98% of dark counts could be removed improving SNR by two orders of magnitude. Furthermore, this setup relying on picosecond photon timestamping was applied for many different experiments such as time-correlated single-photon counting (TCSPC) and photon correlation spectroscopy.
- (iii) For time-resolved SERS experiments, coherent and incoherent excitation was implemented to compare the vibrational population relaxation with  $T_1$  and dephasing with  $T_2$  simultaneously. Exploiting the excitation of molecular vibrations through spontaneous Stokes scattering, it is possible to excite an incoherent phonon population while coherent Raman scattering induces a coherent polarisation affected by dephasing.
- (iv) The investigation of SaS photon correlations required the development of a modified Hanbury Brown–Twiss intensity interferometer. To probe correlations between photons from the same vibration, narrow bandpass filtering was established aligned precisely to the SERS spectrum. Moreover, all optical components were optimised for the best possible detection efficiency and arranging optics at near-normal incidence avoided altering the polarisation of photons.

#### Future work and applications

The results of this thesis should inspire further research and applications exploiting the modified molecular vibrations in plasmonic nanocavities. In the field of molecular optomechanics, many open questions remain regarding collective molecular vibrations. For instance, effects of molecular disorder, the interplay of different collective modes, and the importance of vibrational coherence have not been addressed so far. As demonstrated here using ultrafast laser pulses, the optical spring shift reduces the vibrational energy, effectively softening molecular bonds. In combination with vibrational pumping, the excitation of vibrations with SERS leads to the breaking of molecular bonds inducing chemical reactions and photodecomposition. These processes are currently not well understood and often limit available laser powers in SERS experiments. However, with improved control of the optomechanical modification of molecular vibrations, novel applications are possible such as bond-selective plasmonic chemistry, collective parametric instabilities, and phonon lasing.

While we showed that plasmonic cavities can modify the dynamics of molecular vibrations, the physics behind this effect could not be conclusively explored and thus further experiments and theoretical modelling are required. In particular, questions on vibrational coherence under spontaneous Raman excitation are an interesting field of research that could help clarify some of the observed effects. To prevent the accelerated dephasing in CARS experiments, molecular vibrations could instead be excited through infrared absorption. Probing vibrational sum frequency generation (vSFG), the coherent vibrational dephasing can be measured. In contrast, mid-IR vibrationally assisted luminescence (MIRVAL) probes the incoherent relaxation of the vibration. Combining these two techniques in plasmonic nanocavities could allow to investigate the dynamics of IR active molecular vibrations.

Furthermore, we have demonstrated the potential of SERS as a source of entangled photon pairs for applications in quantum communication and processing. To further advance research in this field, improvements to the emission efficiency of the plasmonic substrate are paramount. Potential avenues include avoiding the generation of non-radiative surface plasmon polaritons, and choosing plasmonic materials with lower losses. Additionally, the polarisation characteristics of the plasmonic structure should be tuned to preserve polarisation entanglement of the photon pair. With optimised plasmonic samples, SERS could allow to generate entangled photon pairs from a low-power, continuous-wave light source. Since molecular vibrational energies are high compared to thermal energies at room temperature, this application has great potential for integration in cheap, on-chip optical devices exploiting quantum entanglement without the requirement for cryogenic cooling. Finally, the single-photon detection scheme based on photon timestamping could enable a plethora of novel optical technologies. For example, in dispersive optical fibres the light from a pulsed source experiences a time delay depending on its spectral composition. Exploiting the timestamping technique, the colour of each photon could be determined by its arrival time on the detector. In the context of photon correlation spectroscopy, this optical time-of-flight spectroscopy could remove the requirement for physical bandpass filters as photons from a specific spectral band can be selected in post-processing. Further, the ability to separate dark counts and stray light from any signal can be universally applied to improve existing optical applications such as light detection and ranging (LIDAR).

In conclusion, the research carried out in this thesis should spark further developments in the field of vibrational spectroscopy and beyond. Both the experimental techniques developed for this work as well as the novel physical effects explored will be of importance to researchers in different communities, and could in the future be translated to applications.

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