Review article

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Coherent Raman scattering with plasmonic antennas

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Abstract: Coherent Raman scattering (CRS) techniques are recognized for their ability to induce and detect vibrational coherences in molecular samples. The generation of coherent light fields in CRS produces much stronger signals than what is common in incoherent Raman spectroscopy, while also enabling direct views of evolving molecular vibrations. Despite the attractive attributes of CRS spectroscopy, the technique's sensitivity is insufficient for performing measurements on single molecules, thus precluding the ability to coherently drive, manipulate and observe individual vibrational quantum oscillators with light. The single-molecule sensitivity that has been achieved in surface-enhanced Raman scattering (SERS) with the aid of plasmonic antennas suggests that a similar approach may be used to push CRS techniques to the single-molecule detection limit. Compared with SERS, however, experimental successes in surface-enhanced coherent Raman scattering (SE-CRS) are few, and a theoretical understanding of surface-enhancement in CRS is still incomplete. In this review, we discuss some of the principles and challenges in SE-CRS and summarize the latest advances in the quest of performing routine CRS experiments on single molecules.

Keywords: coherent Raman scattering; plasmonic antennas; single molecule spectroscopy; vibrational coherence.

1 Introduction

1.1 Surface-enhanced vibrational spectroscopy

Molecular vibrational modes contain a wealth of information about a molecule's structure, conformation and immediate environment. With energies in the mid-infrared (MIR) range, the most direct approach to probe molecular vibrations with light is through dipole-allowed transitions in the MIR. Although the effective cross sections of such transitions are weaker than electronic transitions by about a factor of 10^3 , the use of MIR photons is one of the most efficient mechanisms of optically driving ground state molecular vibrations. In comparison, the off-resonant Raman transition requires a two-photon interaction with the material to drive its Raman-active vibrational modes. Relative to excitation in the MIR, the Raman cross sections of comparable molecular vibrations are lower by almost ten orders of magnitude. Hence, from a molecular point of view, it requires a lot more effort to drive the molecule's vibrational modes through a Raman process compared with the direct resonant driving mechanism provided by the dipole-allowed MIR transitions.

Yet, from an experimental point of view, spectroscopy based on the Raman effect is often much more practical than IR spectroscopy. Raman spectroscopy uses visible or near-infrared (NIR) optics, laser light sources and detectors, all of which are readily available. In addition, Raman scattered signals are shifted from the excitation frequencies, enabling detection in a new frequency window free of spurious contributions of the light source. Although these advantages have helped Raman spectroscopy grow into a popular analytical technique, the fundamentally weak light-matter interaction limits its detection sensitivity. For typical experimental settings, molecular concentrations below a few mM within the probing volume are out of reach for conventional Raman spectrometers. As a consequence, Raman spectroscopy was deemed irrelevant for measuring molecules at very low concentrations and detecting single molecules was simply out of question.

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In this context, it is not surprising that the technique of surface-enhanced Raman spectroscopy (SERS) has triggered a revolution in the field of vibrational spectroscopy since its inception in the 1970s [1–4]. By adsorbing molecules onto nanostructured metals, enormous enhancements of the Raman signal have been observed, an effect that has been attributed to the presence of surface plasmon resonances (SPRs) of the metal. The metal nanostructures act as antennas, coupling propagating electromagnetic radiation to focused near-fields, enhancing the optical response of molecules adsorbed to the metal surface, while also efficiently outcoupling near-field polarizations to far-field radiation [5–7]. Using plasmonic antennas as amplifiers of the molecular response, Raman spectroscopy could now be carried out on samples with much lower concentrations, turning Raman spectroscopy into one of the most sensitive vibrational spectroscopy methods available. The subsequent optimization of the plasmonic antennas, in terms of the enhancement capabilities of plasmonic nano-cavities or hotspots, has led to Raman-based trace molecule detection and even single-molecule vibrational spectroscopy [8–11].

1.2 Coherent Raman scattering

The demonstration that single-molecule Raman sensitivity can be reached with the help of plasmonic nano-cavities has also opened up possibilities for developing surface-enhanced spectroscopy based on CRS. CRS makes it possible to directly probe the phase coherence of vibrational oscillators. In regular Raman spectroscopy and SERS alike, the vibrational modes of the molecules in the probing volume are not synchronized, which implies that different points in the sample produce signal fields with phases that are random relative to one another. The Raman scattered signal is, therefore, incoherent. In contrast, in CRS *two* light fields couple the molecule's ground state with its vibrationally excited state and do so with a phase that is fully determined by the phase of the incident fields. The nonlinear polarization induced in the molecule thus oscillates with a well-defined phase at its onset, and, within the coherence time of the vibrational mode, the radiation that follows maintains a definite phase relation with the driving fields. If the sample consists of numerous molecules, then the CRS radiation from different Raman scatterers in the probing volume exhibits phase coherence, resulting in a signal that displays both spatial and temporal coherence [12].

The coherent properties of CRS give the technique two major advantages over spontaneous Raman scattering:

(1) constructive interference between the signal fields from individual Raman scatterers gives rise to strong and directional signals, and (2) it is possible to time-resolve the response of vibrational modes, thus enabling a direct look at the evolution of mutual coherences between different modes and between molecules in the ensemble. The coherent enhancement of the signal due to constructive interference can be significant, especially in concentrated samples, giving rise to CRS signals that may exceed the corresponding incoherent Raman signal by a factor of 10^6 or more. The coherent amplification of the molecular Raman response speeds up signal acquisition by many orders of magnitude. This property of CRS has been leveraged efficiently in CRS microscopy, which enables the generation of point-scanned images at much higher acquisition rates than what can be achieved with incoherent Raman microscopy [13–15]. In combination with surface enhancement, the coherent amplification effect obtained from an ensemble of target molecules would enhance the magnitude of the signal relative to SERS, thus promising even faster detection rates. This capability would render SE-CRS an attractive approach for increasing the signal acquisition speed and efficiency of Raman-based chemical sensors [16].

Since the inception of the field of CRS in the early 1960s [17–20], its ability to provide a time-domain picture of vibrational coherences has received a great deal of attention. The quest for observing molecular mode vibrations in real time has been an important driver for the CRS field. Whereas early work focused on time-resolving the molecular vibrations of crystalline structures and gases with picosecond pulses [21], advances in ultrafast light sources have made it possible to capture the evolution of molecular vibrations on the femtosecond timescale [22, 23]. With excitation pulses that prepare various Raman-active modes coherently, the time-dependent interference between modes manifests itself as quantum beats, offering a direct time-consecutive view of multiple vibrational coherences in the ensemble. Femtosecond CRS proved a powerful time-domain analogue of the frequency domain information of molecular vibrations in the electronic ground state, as revealed by spontaneous Raman scattering.

Nonetheless, the new information uncovered by time-resolved third-order CRS spectroscopy of molecules in their electronic ground state is rather limited, as identical information can be obtained by a Fourier transformation of the linear Raman spectrum. Additional information can be obtained if higher-order CRS experiments are conducted. In principle, fifth- and seventh-order Raman measurements have the capability to examine correlations

in the time evolution of different vibrational modes or to single out the dynamic dephasing of the ensemble coherence in the presence of static inhomogeneity [24, 25]. Unfortunately, such higher-order Raman experiments have proven extremely challenging [26], and ultrafast MIR techniques have been much more successful in retrieving correlative motions between modes that remain otherwise hidden in linear vibrational spectra [27, 28]. Hence, the promise of CRS to offer new insights by delivering a time-domain picture of ground state vibrational motions has not yet come to full fruition. The notable exception is the application of CRS to study the ultrafast dynamics on excited state potentials. In this case, a time-resolved view of the molecule's vibrations can reveal the time-ordered conformational changes that cannot be reconstructed from the linear Raman spectrum alone [29, 30].

The success of single-molecule SERS experiments has opened up new perspectives for femtosecond CRS spectroscopy as well. By focusing on a single molecule, a time-resolved CRS experiment would record the evolution of the molecule's vibrational modes in the absence of ensemble dephasing. The CRS measurements in the single-molecule limit are sensitive to the evolution of individual quantum oscillators [31]. For instance, such experiments could reveal the phase evolution of single vibrational oscillators and uncover time-ordered vibrational trajectories that cannot be retrieved from the Raman spectrum. In addition, correlations between two neighboring vibrational modes could be examined directly, as well as quantum correlations within the oscillator's immediate environment. A single vibrational oscillator could also serve as a single photon source, producing photons with a well-defined phase relative to the excitation fields and a spectral width of only a few cm^{-1} under ambient conditions. Thus, bringing femtosecond CRS experiments into the realm of single-molecule spectroscopy would re-emphasize some of the unique capabilities of the coherent Raman approach that have remained untapped in ensemble measurements.

1.3 Surface enhancement of the coherent Raman response

The use of surface enhancement to improve coherent Raman techniques is not a new idea. Early stimulated Raman scattering (SRS) experiments in the late 1970s already pointed out that the CRS signals of molecules adsorbed onto silver films can be extraordinarily strong, suggesting the possible involvement of surface plasmons [32, 33]. By exciting surface plasmon polariton (SPP) modes at a silver/liquid benzene interface, it was shown

decisively in 1979 that Raman-active vibrations can be driven coherently by the evanescent fields associated with surface plasmons and subsequently detected by a detector in the far-field [34]. Despite the theoretical studies on surface enhanced CRS (SE-CRS) [35] and the further characterization of enhanced four-wave mixing (FWM) signals at plasmonic metal structures in the 1980s [36], progress in SE-CRS has been sporadic. In 1994, Liang et al. reported the first frequency domain SE-CARS measurements on benzene enabled by the localized surface plasmon resonances (SPRs) of colloidal silver [37]. Although the signal was enhanced by a factor of $\sim 10^2$ relative to the CARS signal in the absence of colloidal silver, the overall enhancement of the signal was far below theoretical predictions. Further studies in the early 2000s confirmed the feasibility of SE-CRS [38, 39], even claiming single-molecule sensitivity [40], but the enhancements were found to be smaller than anticipated and experiments proved difficult to reproduce. It has become clear that the successes in SERS spectroscopy cannot be carbon copied into the domain of CRS without a careful consideration of the rather different excitation conditions used in CRS. More recent work has focused on understanding the nature of the SE-CRS signal [41–44] and optimizing the nano-plasmonic antennas specifically for SE-CRS experiments [45–48].

With a renewed interest in surface-enhancement in the nonlinear coherent regime, SE-CRS is establishing itself as a field of research that has grown independent from the SERS technologies that seeded it. Recent advances have provided glimpses of single-molecule SE-CRS [49–51], reinforcing the prospects of experimentally observing and manipulating individual quantum oscillators at ambient conditions. Turning single-molecule SE-CRS into a robust tool requires detailed knowledge of the rich physics at play in the plasmonic nano-cavities, including the understanding of temporal coherence between the molecule and its surroundings, heating of the metal's free electrons, lattice heating and thermally induced photodamage of the molecule under pulsed illumination, as well as the third-order response of the plasmonic antennas in the absence of the molecule. In this review, we highlight several concepts and issues that are pertinent to the SE-CRS experiments from the perspective of single molecules and summarize several recent studies that have paved a path toward single-molecule SE-CRS. We limit our discussion to the surface enhancement of nonlinear Raman processes that are classified as coherent, third-order optical techniques. Other interesting surface-enhanced Raman techniques that exhibit a nonlinear dependence on the intensity of the incident radiation but do not produce a coherent signal, such as surface-enhanced hyper-Raman

spectroscopy (SEHRS) and related techniques [52–54], are considered beyond the scope of the current overview.

2 Enhancement by surface plasmons

The surface plasmon plays a central role in enhancing the signals measured in the SE-CRS experiments. The description and interpretation of the surface plasmon have immediate implications for the interpretation of the enhanced CRS signals. For this reason, we briefly discuss some aspects of surface plasmons supported by the nanostructured noble metals.

2.1 Collective motion and damping

Plasmonic antennas are metal nanostructures that, upon optical illumination, show substantial modulation of the surface charge density. The simplest picture of the surface plasmon considers the optical response of the metal nanostructure to be dictated by the metal's free electrons, which move against the lattice of positive charges (ions). In the bulk metal, the free electron is driven by the external forces provided by the applied optical field. At the surface, however, the displacement of mobile negative charges relative to static positive ions gives rise to polarization charges, which in turn, set up a restoring force. This produces an oscillator system of the particle's conduction electrons, with a resonance frequency ω_0 that is related to the volume plasma frequency, the surrounding dielectric medium and the particle's geometry [55]. The charge density oscillations at the particle's surface that are associated with this resonance are recognized as the surface plasmon. The surface plasmon oscillator system of nanostructured noble metals typically has a significant dipolar component in the *collective* electron motion, which means that it can be driven efficiently with optical radiation. Therefore, the linear optical response of plasmonic antennas is dominated by the presence of the surface plasmon.

When driven by coherent radiation, the surface charge density oscillations consist of the coherent and collective motion of electrons near the surface. The effective spill-out distance of the surface electrons from the ion lattice is of the order of 1 Å, thus forming a charge density *volume* near the surface [56], as depicted in Figure 1A. As the electrons oscillate in unison near ω_0 , following the driving field, they set up an electric field with which they then interact. Although the surface plasmon is seen as a

Figure 1: The driving and damping of a surface plasmon resonance (SPR).

(A) An incident light field $E(t)$ couples to the metal's free electrons, providing an external source acting on the plasma. At the metal's surface, the resulting charge density oscillations give rise to strong, evanescent electromagnetic fields (E_z), extending both inside the metal and into the adjacent dielectric. (B) The damping of the surface plasmon through radiation. (C) Electron-hole pair generation following Landau damping of the surface plasmon.

collective effect, it is helpful to cast the damping of this motion in terms of the response of individual electrons within the coherent oscillation. As electrons dephase from the collective motion, destructive interference reduces the amplitude of the surface plasmon. This implies that energy is exchanged between the surface plasmon and its immediate surrounding. An important channel of energy exchange is the formation of electron-hole pairs in the metal at energies $\hbar\omega_0$. The exchange of such energy quanta from the collective motion into individual electron-hole pairs is recognized as a form of Landau damping [55]. This dephasing model has its origin in the distribution of electron velocities of the plasma and provides a collision-less mechanism for damping. As Landau damping applies to the free electrons of the bulk, the spatial location of the energy exchange is not necessarily limited exclusively to the metal's surface. Another channel through which $\hbar\omega_0$ quanta are released from the surface plasmon is through radiation, i.e. radiative damping. The combined Landau and radiative damping channels, shown schematically in Figure 1B and C, are thought to account for the rapid dephasing of the charge density oscillations near the surface, on the order of 1–100 fs, resulting in spectrally broad resonances.

2.2 Surface enhancement

Plasmonic antennas make use of SPRs to focus electromagnetic energy to the spatially confined regions of the nanostructure [7]. Energy originally contained in the

incident radiation is captured through the dipolar SPR of the antenna, which concentrates the electromagnetic energy into the particle's near-fields. The electric fields associated with the charge density oscillations are spatially confined to the surface and can be much stronger than the field strength of the incident radiation due to this spatial confinement. The strong near-fields make such nanostructures very attractive as optical antennas, as the optical response of molecules placed in these enhanced fields is correspondingly enhanced as well. Plasmonic antennas that can focus electromagnetic energy efficiently to nanometer-sized volumes, such as plasmonic junctions and cavities, and can produce local fields with very high enhancement factors, making it possible to improve the efficiency of otherwise weak light-matter interactions by orders of magnitude.

Various mechanisms are thought to contribute to the overall enhancement of the molecule's response. The enhancement is commonly sub-divided into a pure electromagnetic enhancement mechanism and in an enhancement mechanism that is due to the changes in the molecule's geometric and electronic structure as it interacts with the metal surface. The latter mechanism is often referred to as the chemical mechanism. SERS experiments have provided strong evidence that the chemical mechanism is likely to play a minor role in most experiments and that the bulk of the observed enhancement can be understood as electromagnetic enhancement [57, 58]. Although SERS experiments can be taken as a good starting point for interpreting the SE-CRS experiments, higher-order light-matter interactions can amplify the contribution of the chemical mechanism in the overall enhancement of the molecule's response [59].

In the simplest form of the electromagnetic enhancement model for SERS, the molecule is driven by the strong near-fields of the SPR. If the total electric field at driving frequency ω_1 experienced by the molecule is written as $E(\omega_1) = f(\omega_1)E_0(\omega_1)$, where $E_0(\omega)$ is the amplitude of the incident field and $f(\omega)$ is the effective field enhancement factor, then the polarization $p(\omega)$ of the molecule at the Stokes-shifted frequency ω_2 due to Raman scattering can be written as

$$p(\omega_2) = \alpha^R(\omega_1 - \omega_2)E(\omega_1) = \alpha^R(\omega_1 - \omega_2)f(\omega_1)E_0(\omega_1), \quad (1)$$

where $\alpha^R(\omega)$ is the Raman contribution to the molecule's electronic polarizability. As the polarization of the molecule radiates, it does so through the dipolar mode of the plasmonic antenna, which couples to the radiative field with an enhanced efficiency $f(\omega_2)$. The SERS intensity can then be formulated as

$$I_{\text{SERS}}(\omega_2) \propto |f(\omega_2)p(\omega_2)|^2 = |\alpha^R(\omega_1 - \omega_2)|^2 |f(\omega_2)|^2 |f(\omega_1)|^2 |E_0(\omega_1)|^2. \quad (2)$$

This simple description predicts an overall enhancement of the Raman response of $\sim f^4$. More thorough electromagnetic models, which are based on the local fields resulting from the mutual influence of the molecule's and the plasmonic particle's polarizabilities, also predict an overall enhancement of f^4 [60–64]. This view of electromagnetic enhancement, namely, an electric field enhancement of the excitation and a subsequent field enhancement associated with the dipole radiation, has been very useful for predicting the SERS enhancement of antenna designs and for quantitatively assessing SERS data.

Another aspect of the electromagnetic model considers the spatial properties of the local near-fields. The spatial confinements of local fields in the junctions can reach the nanometer scale, which approaches the size of the molecule. In some junctions, the atomic details on the metal surface can dictate the spatial extent of the interaction between the field and the molecule on the sub-nanometer scale [65–68]. Clearly, in these situations, the amplitude and phase of the field are no longer uniform on the length scale of the molecule, resulting in a molecular response that can deviate significantly from the case of plane wave illumination. One consequence of field confinement on the molecular scale is that the molecule can respond efficiently to field gradients, thus allowing a multipolar response of the molecule and the involvement of vibrational modes that are Raman-inactive in the absence of field gradients [69–71].

An implication of the prominence of the electromagnetic model is that virtually all optical effects at the plasmonic nano-antennas are understood in terms of the enhanced fields near the surface. In this picture, the response of the molecule is enhanced by the strong local fields extending from the metal's surface into the adjacent dielectric. In the same view, the field that extends into the metal is also enhanced, thus amplifying the optical response of the metal's bulk electrons that fall within its range. Optical radiation from the metal at frequencies shifted from ω_0 , such as radiation resulting in harmonic generation or FWM processes, is then attributed to the nonlinear susceptibility of the bulk metal. However, this view excludes radiative processes that can be assigned *directly* to the coherent motion of the electrons that constitute the surface plasmon itself. As the surface charge density is subject to a restoring force, direct dipolar transitions of conduction electrons are allowed, thus forming

an additional mechanism for radiation resulting from momentum-matched, nonlinear optical transitions.

and heat dissipation kinetics may differ from the situation in SERS [72].

3 Surface-enhancement in the nonlinear regime

In this Section, we discuss some of the noted differences between linear SERS and nonlinear SE-CRS measurements. First, we highlight the issue of heating of surface plasmon-active systems under ultrafast illumination. Second, we address the experimental complications related to background radiation of plasmonic antennas used in SE-CRS experiments. Finally, we zoom into the process of Raman saturation, which may affect SE-CRS measurements in a much more significant way than the typical SERS experiments.

3.1 Heating of plasmonic antennas

The illumination of plasmonic systems inevitably results in energy exchange between light and the antenna, especially near plasmonic resonances. Whereas photothermal heating is often an undesired side-effect in SERS measurements, heating under ultrafast laser illumination can be a severe problem that may directly affect the success of the experiment. Early SE-CRS experiments on plasmon-active antenna systems indicated that the photothermal effects might be more significant when ultrafast pulsed radiation is used compared to the cw illumination conditions used in SERS. Morphological changes to plasmonic antennas seen after illumination with NIR femtosecond laser pulses suggest that heating

3.1.1 Heating kinetics of the metal near plasmonic junctions

When surface plasmons are driven by a coherent pulse of light at frequency ω_0 , a charge density near the surface oscillates is driven coherently at ω_0 . The dephasing of this coherent motion causes an energy exchange from the electromagnetic wave to the material. As discussed above, this plasmon damping is thought to occur through Landau damping [73, 74], which transfers the quanta of $\hbar\omega_0$ from the coherent plasma oscillation to the metal by exciting electron-hole pairs near the Fermi level E_F , as shown in Figure 2A. This process occurs on the 1–100 fs timescale and produces hot electrons with maximum energies of $E_e = E_F + \hbar\omega_0$ and their associated holes at energies $E_h = E_F - \hbar\omega_0$. The subsequent inelastic electron-electron interactions redistribute the energy among the electron population, reaching a thermalized Fermi-Dirac distribution on the 100 fs–1 ps timescale, as shown in Figure 2B. Energy is then transferred from the electrons to the lattice through electron-phonon interactions on the 1 ps–100 ps (Figure 2C), resulting in the heating of the metal and the subsequent energy exchange with the surrounding.

The temperature of the antenna on the ultrafast timescales is dynamic and thus different from the steady state conditions that are relevant for SERS. In addition, because the temperature evolves on the ultrafast timescale, the effective temperatures for picosecond and femtosecond CRS experiments may differ. In this context, the temperature of the free electrons must be distinguished from the temperature of the lattice and the molecule. Although the

Figure 2: The heating and cooling of the electron gas.

(A) The electron (blue) and hole (red) populations near the Fermi level after Landau damping of the coherent surface plasmon oscillations. (B) The redistribution of energy due to the electron-electron scattering, forming a thermalized Fermi-Dirac distribution of the joint electron-hole states on the 0.1–1 ps timescale. (C) Electron-phonon scattering transfers to the lattice. This leads to cooling of the electron temperature on the 1–100 ps timescale.

timescale of electron heating is reasonably well understood, the spatial distribution of hot electrons is less clear. The Landau damping model does not limit the generation of electron-hole pairs exclusively to the surface, implying that heating of the plasma may occur in the metal away from the interface. It is not trivial to determine the temperature of the affected electron distribution near the hotspot quantitatively. One of the most direct measures is the broad emission of the metal itself after excitation. This broad continuum, often considered parasitic in SERS measurements, has been attributed to electronic Raman scattering (see Section 3.3.1). On the picosecond timescale, this Raman process probes the Fermi-Dirac distribution of the joint density of the electron-hole states, which can be approximated by a Boltzmann distribution for larger spectral shifts [75, 76]. An analysis of the anti-Stokes Raman emission after picosecond excitation yields accurate estimates of the electron temperature in the vicinity of the hotspot. The experimental results show that, on this timescale, the electronic temperatures near plasmonic junctions can reach thousands of Kelvin. An example is shown in Figure 3, where a gold dumbbell-shaped antenna is excited by a NIR picosecond pulse and the electron temperature is determined from the incoherent anti-Stokes emission.

Figure 3: The temperature of the electron gas measured in the vicinity of a gold plasmonic junction through electronic Raman scattering (ERS).

The anti-Stokes Raman signal is shaped by the temperature dependent electron-hole population near the Fermi level. The curve (i) is obtained under cw illumination at 634 nm using an average power of $30 \mu\text{W}/\text{cm}^2$. The extracted temperature is 385 K. Curves (ii)–(iv) are obtained under 6 ps pulsed illumination at 785 nm, using an average power of $100 \mu\text{W}/\text{cm}^2$. The extracted temperatures on the ps timescale are several thousands of Kelvin. Adapted from Ref. [42].

3.1.2 Heating of the molecule on the ultrafast timescales

While the electron gas near the plasmonic junction becomes hot on the picosecond timescale after ultrafast excitation, the question remains as to how this environment affects the temperature of a molecule placed in the hotspot. Full thermal equilibration between the metal and molecule is thought to be mediated through lattice phonons and is expected to occur on longer timescales (>1 ps) [77–79]. In the context of coherent Raman scattering with pulsed illumination, a perhaps more interesting question is the possible energy exchange between the hot junction and the molecule on the fs–ps timescales, producing rapid increases in the molecular temperature on the timescale relevant to probing the coherent Raman response. The most direct way of assessing the molecule's temperature is through the ratio of the anti-Stokes to Stokes (AS-to-S) Raman response of its Raman-active modes. To avoid ensemble averaging, AS-to-S measurements are best performed on the single-molecule level. Such single-molecule SERS experiments have been carried out, but are not without difficulties [80]. Although the purpose of this form of optical thermometry is to probe the temperature of the molecule as a consequence of energy exchange with its immediate surrounding, several additional mechanisms may contribute to the population of the molecule's vibrational states ($\nu=1$ and higher). First, the strong optical fields in the junction may lead to vibrational up-pumping through an optical Raman transition, effectively populating $\nu=1$ and subsequent vibrational states. The population of the vibrationally excited states increases the likelihood of anti-Stokes Raman transitions which, in turn, raise the AS-to-S ratio. This mechanism has been invoked to explain the anomalous (non-thermal) AS-to-S ratios seen in SERS measurements [81–85]. The optical up-pumping mechanism operates independently from tentative energy exchange with the metal and thus complicates the measurement of molecular temperature in the absence of direct optical excitation.

Second, driven and hot junction electrons can scatter inelastically on the molecule, leaving the molecule in a vibrationally excited state [86, 87]. If the energy exchange takes place with the coherently driven electrons that constitute the plasmon resonance, i.e. inelastic scattering of electrons in the spill-out region on the molecule, then the excited vibrational population is not a direct measure of electron gas temperature near the junction. Rather, the damping of the surface plasmon occurs directly by scattering on the molecule. This electron-vibrational (e-v) pumping channel, a non-optical mechanism, has been suggested as a possible explanation for anomalous

AS-to-S ratios, which is indicative of vibrational population inversion, as seen in some picosecond SERS experiments [76]. These measurements paint a picture, in which the temperature of the metal's electron gas and the molecule are uncorrelated and effectively decoupled on the picosecond timescale, the timescale relevant to the evolution of molecular vibrations.

Recent ultrafast surface-enhanced Raman spectroscopy experiments [88] underline that, although the electron temperature can be very high on the ultrafast timescales (thousands of Kelvin), the molecular temperature, as probed through the AS-to-S ratio of selected modes, appears only moderately influenced by plasmon-molecule energy exchange [89]. Figure 4 shows the time dependent temperature of 4-nitrobenzenethiol molecules adsorbed to gold nanoparticle aggregates following excitation with a ~ 250 fs pulse centered at 1035 nm. As can be seen, the temperature reported through different vibrational modes increases on the picosecond timescale after excitation, followed by a temperature decrease within ~ 10 ps. The timescale of the heating process suggests that thermalized hot electrons near the junction are responsible for warming the molecule. However, the effective temperature

increase is less than 100 K, when pumped at peak powers of the order of 10^7 W/cm². Under these conditions, the ultrafast energy increase carried by the vibrational modes appears to dissipate into the surrounding on the ~ 10 ps timescale, which also happens to coincide with the lifetime of the vibrational mode itself. The ultrafast temperature increase is in addition to a steady state temperature of the molecule, as determined by the thermalized lattice under laser illumination, which amounts to less than 100 K under the relevant experimental conditions. These experiments indicate that the molecular temperature is largely determined by the thermally equilibrated state of the metal antenna system and that the effective molecular temperature on the timescale of vibrational lifetimes is surprisingly moderate despite the hot electron gas temperature near the junction. The latter notion suggests that the molecular temperature would be greatly influenced by the heat capacity of the medium surrounding the plasmonic particles. Indeed, steady state molecular temperatures have been found to be a lot higher, by several hundreds of Kelvin when excited at peak powers between 10^7 and 10^8 W/cm², when the plasmonic antennas are encapsulated by a host of low heat capacity such as silica [90]. Given that these experiments were performed on ensembles in aqueous suspensions, even more steady state heating can be expected in the case of experiments on deposited single nanoplasmonic antennas in the absence a liquid medium.

Figure 4: The temperature of 4-nitrobenzenethiol adhered to a plasmonic antenna determined using AS-to-S ratios obtained with ultrafast Raman spectroscopy.

The energy flows from the hot electrons into different modes of the molecule within 1–5 ps, followed by cooling of the molecule on the 10 ps timescale. These experiments show that hot electrons in the vicinity of the plasmon junction are likely not the main source of molecular change or photodamage. Adapted with permission from Ref. [89].

3.1.3 Molecular photodamage in plasmonic antennas

Although the ultrafast temperature increase of the molecule appears moderate when the plasmon antenna system is illuminated with pulsed radiation of peak intensities up to 10^8 W/cm², we may expect additional effects to play a role in controlling the fate of the molecule. Assuming a field enhancement factor of $f=100$ at the antenna's hotspot, the peak intensities experienced by a molecule placed in the junction are approaching 10^{12} W/cm² for incident pulses of peak power 10^8 W/cm². At these peak intensities, close to the strong field limit of 10^{12} – 10^{13} W/cm² [91], we may expect direct ionization within the molecule due to the bending of atomic potentials and subsequent electron tunneling. Such strong field effects occur instantaneously under the application of the field and are thus independent of the temperature of the metal's electron gas. The SERS measurements of dipyrindyl ethylene in individual gold dumbbell-shaped antennas reveal that when the system is irradiated with 100 fs NIR pulses, clear photo-induced chemical changes are seen as pump intensities approach 10^9 W/cm², corresponding to 10^{13} W/cm² in

the junction [42]. Arching and ionization effects have also been observed in the cw SERS measurements, at intensities of 10^{11} – 10^{12} W/cm² in the junction [92], further corroborating that molecular charging might be a more significant mechanism of molecular change than the rise in temperature on the ultrafast timescales. This discussion underlines that photodamage effects to the molecule can be expected if intensities reach $\sim 10^{12}$ W/cm² in the hotspot, which translates to incident energies of $\sim 10^8$ W/cm² for a typical gold antenna with $f \sim 100$. Note that such limits are easily achieved under pulsed illumination. For instance, for a 100 fs laser pulse at 80 MHz, an average intensity of a few mW focused by a high numerical aperture lens ($NA > 1$) is already sufficient to reach this molecular photodamage limit in an antenna with $f \sim 100$.

3.2 Raman saturation

Even below photodamaging irradiation intensities, the high fields to which molecules in hotspots are exposed in the SE-CRS experiments can induce effects that affect the ability to efficiently and reliably probe molecular Raman transitions. For instance, increasing the Raman transition rate through surface enhancement implies that the Raman saturation limit may be reached at even moderate incident intensities. In diatomic gases characterized by narrow linewidths and thus very long dephasing times, the saturation of CARS signals are commonly observed at peak intensities of $\sim 10^8$ W/cm² [93–95]. In the solid phase and under ambient conditions, linewidths are wider and vibrational energy is dissipated much faster (~ 1 – 100 ps), implying that, in a typical CRS experiment, the vibrational ground state is reached in between pulses. Nonetheless, the onset of saturation effects in CARS has been observed when pumping the 1332.5 cm^{−1} mode in diamond microcrystals at peak intensities as low as 10^9 W/cm² [96]. In SRS experiments, using the same mode in diamond, almost complete saturation of the $\nu=0 \rightarrow \nu=1$ transition has been observed for peak intensities of $\sim 10^{11}$ W/cm² [97]. Even more significantly, using pulses with approximately the same peak intensities, SRS saturation was achieved for the 802 cm^{−1} ring mode of cyclohexane [97]. These experiments show that saturation in SE-CRS may occur well before the damage threshold at illumination intensities that are very typical for CRS microscopy measurements.

Given that saturation can set in at peak intensities lower than the onset of photodamage in SE-CRS experiments, tuning the incident intensities beyond the saturation limit will no longer grow the SRS signal, while

the likelihood of photodamage continues to increase for higher pulse intensities. The window in which the signal yield of SE-CRS experiments displays a good signal-to-noise ratio may be narrow, as it is capped not only by the onset of photodamage, but also by the stunted growth of the CRS signal near the saturation limit.

3.3 Radiation from the metal

The main purpose of the plasmonic antenna is to boost the Raman response of the adsorbed molecules. Yet, the plasmonic antenna system also radiates signal contributions that are independent of the molecule, thus providing an unwanted background. When ultrafast incident radiation is used, the number of mechanisms that produce background radiation is significantly increased relative to the situation in regular SERS experiments. Thus, the background radiation is best sub-divided into incoherent and coherent signal contributions of the metal antenna.

3.3.1 Incoherent radiation

Incoherent contributions include electronic Raman scattering and fluorescence from the metal. The electronic Raman response, briefly discussed above, is manifest in cw and pulsed experiments alike. It produces a broadband profile that stretches from blue-shifted anti-Stokes contributions to an extended continuum on the Stokes side of the excitation energy [98]. Although alternative interpretations have been given [99], most models attribute the radiation to a Raman process between partially filled states near the Fermi level as a result of the Fermi-Dirac distribution of electrons and holes [100–104] (see Figure 5A and B). A fit based on the joint electron-hole (e-h) density of states largely reproduces the main features of the broad spectral profile [75, 103]. In gold, such intraband electron-hole pair excitations are thought to take place near the Fermi level in the *sp*-band. Due to the dispersion of the band, there is a momentum mismatch between the initial and final states involved in the intraband Raman transition, indicating that the transition is optically forbidden. This would imply that the necessary momentum Δq would need to be supplied indirectly by phonon modes, a low probability process; thus, one may expect very little Raman from the metal. However, it has been suggested that the necessary momentum is provided by the nanoscale spatial confinement of the fields at the gold nanostructure, which then expands the photon-momenta of the excitation and emission fields [105]. The presence

Figure 5: The incoherent radiation from the metal at frequencies shifted from the incident frequency, shown here for gold near the L symmetry point in the Brillouin zone.

(A) Electronic Raman scattering (ERS) in the conduction band, producing a Stokes-shifted continuum. The necessary momentum Δq can be supplied either by phonon modes from the lattice or by expansion of photon momenta due to nanofocusing. The inset shows the population of states near the Fermi level, illustrating that the resulting continuum is sensitive to the thermal occupation of e-h states. (B) Anti-Stokes ERS. (C) Two-photon excited interband excitation of *d*-electrons to the *sp*-conduction band, followed by relaxation of electrons and holes and radiative recombination near the Fermi level. The expanded photon momenta can broaden the emission.

of Raman-allowed transitions in metallic plasmon-active antenna is particularly relevant for SE-SRS experiments, as these provide a mechanism for a strong electronic

background from the substrate at the Stokes-shifted frequencies that is independent of the Raman response of the molecule.

The fluorescence from plasmonic metals also constitutes a background contribution in SE-CRS experiments. Fluorescence in gold, often referred to as photoluminescence, is attributed to an interband excitation of the *d*-electrons to the *sp*-band, followed by radiative electron-hole recombination after relaxation [106], as schematically shown in Figure 5B. The likelihood of radiative e-h recombination is increased around the symmetry points in the Brillouin zone wherein the density of states in the conduction band is high. This condition is met near the Fermi level at the L and X symmetry points, which produce emissions with maxima near 520 and 690 nm, respectively, upon the recombination of momentum-matched electrons and holes [107]. The otherwise weak fluorescence is enhanced upon nanofocusing in structured gold antennas. In addition, the nano-confinement relaxes the photon-momenta, allows higher order multipolar transitions and opens up the possibility of permitted intraband transitions, factors that contribute to a spectral broadening of the emission, especially towards longer wavelengths [105]. In the case of excitation with NIR ultrafast pulses of nanostructured gold, the dominant mechanism of e-h generation is two-photon excitation. The observed visible emission is broad, stretching from 480 nm to well beyond 700 nm, with only a weak coloration related to the wavelength-dependent plasmon resonances [72, 105, 108–110]. This radiation may complicate the SE-CRS measurements, as it contributes an ubiquitous background, both at the energies that are Stokes-shifted and anti-Stokes-shifted relative to the NIR excitation energy.

3.3.2 Coherent radiation

Aside from the incoherent radiation from the metal substrate, ultrafast illumination of plasmonic antennas is accompanied by coherent signal contributions that can also be assigned to the metal. The nonlinear optical response of nano-structured gold has been investigated since the 1970s. Enhanced second-harmonic generation (SHG) at metallic interfaces was first reported in 1974 [111], followed by SHG studies of roughened gold films and colloids [112, 113]. The common interpretation of surface-enhanced SHG assumes that the nonlinear surface polarization is enhanced by the presence of enhanced electric fields near the metal/host interface. The requirement for non-centrosymmetry would then be fulfilled at the interface, where the signal

is generated within only a few lattice constants from the surface.

The involvement of surface polaritons in FWM was first discussed theoretically in 1976 [114] and experimentally demonstrated on GaP solids in the same year [115]. FWM on nanostructured gold and silver date back to the early 1980s [36], demonstrating that third-order optical frequency mixing in plasmon-active metal substrates can be very efficient. The enhanced FWM signals from plasmonic antennas can be particularly strong [116], and the coherent radiation has been used extensively as an optical probe in near-field microscopy [117, 118] and far-field optical imaging [119–122]. The FWM radiation is generally attributed to the $\chi^{(3)}$ of the *bulk* metal. The FWM signal is strong because the strong surface field generated by the surface plasmon penetrates the metal sufficiently to drive $\chi^{(3)}$ processes in the bulk metal.

The exact origin of the $\chi^{(3)}$ of the nano-structured metal is still a topic of discussion. In gold, the nonlinear susceptibility has been ascribed to both intraband and interband contributions, as well as to changes in the electron distribution related to nonequilibrium electron heating (hot electrons) [123–125]. The contributions from intraband (s–s) transitions in gold would relate to nonlinear translational motions of free-electrons. However, as the free electrons in the bulk metal experience no restoring force, no nonlinear motions are to be expected in the electric-dipole approximation. Yet, a nonlinear response may grow to prominence when the motion of electrons becomes constricted due to mean free-path restrictions or to quantum-size effects, effectively altering the $\chi^{(3)}$ -values of the metal [123, 126]. The intraband $\chi^{(3)}$ contribution has been difficult to verify, as several studies observed that an intrinsic size-dependent contribution to the third-order susceptibility is minimal [127, 128]. Recently, an alternative mechanism of the free-electron response in gold has been suggested to contribute to the FWM signals, namely, intraband transitions associated with longitudinal nonlinear currents that, on the nanoscale, are allowed to out-couple to transverse propagating waves [129]

Interband contributions in gold, which are dipole-allowed, are thought to result from the transition of *d*-electrons to the *sp* conduction band, which resonantly enhance $\chi^{(3)}$ [127]. The interband transitions add to the imaginary part of $\chi^{(3)}$. Finally, the hot-electron contribution also originates from *d*–*sp* interband transitions, where excess energy is redistributed in the conduction band. The heating of conduction band electrons alters the corresponding Fermi-Dirac distribution of electrons and holes [78, 130]. These temporary changes in the distribution function essentially change the dielectric function of the metal, which, in turn,

effectively increases the $\chi^{(3)}$ of the metal. This mechanism, often referred to as Fermi-smearing, has been suggested as a major contributor to the third-order nonlinear response of nano-structured gold [124, 127, 128].

The $\chi^{(3)}$ response of the metal can be phase-coherent with the $\chi^{(3)}$ -derived CRS signal of the molecule. Under such conditions, the metal and molecular response will interfere, which may significantly affect the latter. In the frequency domain, the interference of the electronic signal from the metal and the vibrational signal from the molecule can produce distorted lineshapes, a feature we will further discuss in Section 4.2.2. Aside from possible interferences, the metallic $\chi^{(3)}$ response can also add a significant background, which may overwhelm the molecular signal of interest.

4 Surface enhancement of stimulated and parametric CRS

4.1 SRS and CARS

4.1.1 Classical vibrational motions

In this Section, we briefly review some of the basic aspects of CRS in the absence of a plasmonic antenna. Given that plasmonic cavities can approach or exceed the volume occupied by a molecule, we will consider the process of CRS from a single-molecule perspective. Rather than considering the sample as a medium with given dielectric properties, we consider a single molecule as a polarizable point object. In this picture, the points are driven by the fields, resulting in a nonlinear polarization in the object. The object subsequently radiates as a dipole, producing radiation that is captured by a detector in the far-field. At this stage, the fields and the vibrational motion in the molecule are considered classically. The use of quantized vibrations and fields is briefly discussed in Section 4.1.2.

We assume that the molecule is placed at position $\mathbf{r}$ and that it is illuminated by two time-harmonic fields E_1 and E_2 , the pump and the Stokes field, respectively. The incident fields are assumed to be linearly polarized, propagating plane waves with their component along the polarization direction written as

$$E_j(\mathbf{r}, t) = E(\omega_j) e^{i(k_j \mathbf{r} - \omega_j t)} + \text{c.c.}, \quad (3)$$

where E_j is the amplitude and k_j is the wavenumber of the propagating field. Here, $j = \{1, 2\}$ to indicate pump or

Stokes, respectively. The pump frequency is ω_1 , the Stokes frequency is ω_2 and we assume that $\omega_1 > \omega_2$. The pump and Stokes field couple to the electronic polarizability $\alpha(\omega)$ of the molecule in a nonlinear fashion, setting up electron motions at frequencies $\Omega = \omega_1 - \omega_2$. The charge density oscillations at this difference frequency act as an oscillating force that is felt by vibrational mode Q . Modeling the molecular vibration Q as a classical harmonic oscillator with reduced mass m , resonance frequency ω_v , and damping constant Γ , the amplitude of vibrational motion at frequency Ω can be computed by using the equation [131]

$$Q(\Omega) = \frac{1}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_0 \frac{E(\omega_1)E^*(\omega_2)}{\omega_v^2 - \Omega^2 - 2i\Omega\Gamma} = \beta(\Omega)E(\omega_1)E^*(\omega_2). \quad (4)$$

The amplitude of the vibrational motion depends on the amplitude of the driving fields $E(\omega_1)$ and $E(\omega_2)$ and on the frequency-dependent responsiveness of the molecule, as captured here by $\beta(\Omega)$. When Ω approaches the vibrational resonance ω_v , the amplitude of the vibrational mode grows in prominence, effectively altering the polarizability of the molecule as it interacts with a third field E_j . After interacting with E_j , the nonlinear polarization of the molecule, $\mathbf{p}(\mathbf{r}, t) = \mathbf{p}(\mathbf{r}, \omega_k)e^{-i\omega_k t} + \text{c.c.}$, exhibits different frequency components ω_k . Here we consider only two mixing frequencies where the last interaction has the pump frequency ($E_j = E_1$), resulting in a polarization oscillating at the anti-Stokes frequency $\omega_{as} = \omega_1 + \Omega$ (as measured in CARS) and at the Stokes frequency $\omega_s = \omega_1 - \Omega$ (as measured in SRG). Within this classical model, the corresponding amplitudes of the nonlinear polarization at these frequencies are given by

$$\begin{aligned} \mathbf{p}(\mathbf{r}, \omega_{as}) &= \left\{ \left(\frac{\partial \alpha}{\partial Q} \right)_0 \beta(\Omega) \right\} E^2(\omega_1)E^*(\omega_2) \\ &= \gamma_v(\omega_{as})E^2(\omega_1)E^*(\omega_2), \end{aligned} \quad (5)$$

$$\begin{aligned} \mathbf{p}(\mathbf{r}, \omega_s) &= \left\{ \left(\frac{\partial \alpha}{\partial Q} \right)_0 \beta(\Omega) \right\}^* |E(\omega_1)|^2 E(\omega_2) \\ &= \gamma_v^*(\omega_s) |E(\omega_1)|^2 E(\omega_2), \end{aligned} \quad (6)$$

where $\gamma_v(\omega_{as})$ and $\gamma_v(\omega_s)$ are the frequency-dependent third-order hyperpolarizabilities of the molecule for the CARS and SRG light-matter interactions, respectively. Alternatively, when the last interaction is with the Stokes field, nonlinear polarization components at frequencies $\omega_{cs} = \omega_2 - \Omega$ (as measured in coherent Stokes Raman scattering) and $\omega_p = \omega_2 + \Omega$ (as measured in stimulated Raman loss), adding up to a total of four coherent Raman signals, as depicted in Figure 6.

Figure 6: Dual-color coherent Raman scattering (CRS).

(A) Two fields with frequencies ω_1 and ω_2 are incident on a molecule, inducing a vibrational coherence at $\Omega = \omega_1 - \omega_2$ and producing four different signal fields. (B) CRS gives rise to signal fields at frequencies $\omega_{cs} = \omega_2 - \Omega$, $\omega_s = \omega_2$, $\omega_p = \omega_1$ and $\omega_{as} = \omega_1 + \Omega$.

The nonlinear polarization is prepared by the incident fields and initially assumes an oscillation that is coherent relative to the driving fields. However, the phase of the oscillation might change due to interactions with the mode's environment. In addition, the magnitude of the oscillation is affected by the lifetime of the vibrational mode, which is determined by the probability of dissipating vibrational energy to the surroundings. If the excitation pulses are short compared the timescales of the relevant damping mechanisms, then the coherence of the vibrational motion relative to its original driving motion is diminishing probabilistically on the timescale determined by Γ .

In addition, the electron motion itself, without the involvement of a vibrational mode, can exhibit nonlinearities and thus develop the oscillating components at mixing frequencies. This purely electronic component produces an additional source for the molecule's response at ω_{as} and ω_s (as well at ω_{cs} and ω_p). The third-order hyperpolarizability can thus be sub-divided into a vibrational and a purely electronic component, i.e. $\gamma(\omega) = \gamma_e(\omega) + \gamma_v(\omega)$, and the nonlinear polarization $\mathbf{p}(\omega)$ depends on γ rather than on γ_v alone.

The goal of CRS experiments is to measure the induced nonlinear polarization related to the γ_v of the molecule, either in the time domain or in the frequency domain. The information about the vibrational (and electronic) motion in the molecule can be detected optically by relying on the radiative properties of the nonlinear polarization. The time-varying polarization of the molecule results in a signal field, which is radiative in the

far-field. The dominant dipolar contribution to this propagating field with wavenumber k at a point $\mathbf{R}$ in the far-field is given by

$$E_d(\mathbf{R}, \mathbf{r}, \omega) = \frac{e^{ik|\mathbf{R}-\mathbf{r}|}}{4\pi|\mathbf{R}-\mathbf{r}|^3} [(\mathbf{R}-\mathbf{r}) \times \mathbf{p}(\mathbf{r}, \omega)] \times (\mathbf{R}-\mathbf{r}). \quad (7)$$

The signal field is thus a spherical wave that is intercepted by the detector in the far field, see the illustration in Figure 7A. The intensity of the single-molecule CARS signal registered by the detector at point $\mathbf{R}$ within the detection surface dS is then found as

$$I_{as} \propto \int |E_d(\mathbf{R}, \omega_{as})|^2 dS \propto |E(\omega_1)|^4 |E(\omega_2)|^2 |\gamma(\omega_{as})|^2. \quad (8)$$

The CARS signal is the squared modulus of the dipole radiation field. In the coherent Raman literature, this detection mode is commonly referred to as homodyne detection [15]. In this scheme, the anti-Stokes frequency is shifted to the blue relative to the incident fields ω_1 and ω_2 , without a spectral overlap between the incident fields and

the radiated signal field. The CARS signal is thus detected in a new frequency channel, which can be spectrally isolated and is consequently free from background radiation originating from the incident fields. We see that the CARS signal from the molecule scales to the fourth power with the pump field amplitude $E(\omega_1)$ and to the second power with the Stokes field amplitude $E(\omega_2)$. The CARS signal also depends on the absolute square of the third-order hyperpolarizability. Note that since $\gamma(\omega_{as})$ has electronic and vibrational components, the absolute square $|\gamma(\omega_{as})|^2$ will give rise to cross terms between the purely electronic and vibrational signal contributions of the molecule.

Whereas the CARS signal is detected in a new frequency channel, the latter is not the case for the SRG signal at the Stokes frequency, which is radiated against a background formed by the incident field at ω_2 (Figure 7B). As the signal field of the radiating dipole displays a phase coherence relative to the ω_2 field, the signal at $\omega_s = \omega_2$ is the coherent sum of the two fields, as shown below.

$$I_s \propto \int |E_d(\mathbf{R}, \omega_2) + E_2(\mathbf{R}, \omega_2)|^2 dS = \int |E_d(\mathbf{R}, \omega_2)|^2 dS + \int |E_2(\mathbf{R}, \omega_2)|^2 dS + I_{het}. \quad (9)$$

Figure 7: Far-field detection of the radiating nonlinear polarization. (A) CARS. A nonlinear polarization in molecule at $\mathbf{r}$ is prepared by incoming fields $E(\omega_1)$ and $E(\omega_2)$, producing dipole radiation at $\omega_{as} = 2\omega_1 - \omega_2$. The resulting field $E_d(\omega_{as})$ is detected on a far-field detector in a homodyne fashion. (B) SRG. The nonlinear polarization radiates at $\omega_s = \omega_2$, giving rise to the interference between $E_d(\omega_s)$ and $E(\omega_2)$ in the far-field. The SRG signal is proportional to the mixing term.

The first term on the right-hand side is the homodyne contribution of the molecular signal, while the second term is simply the intensity of the incident field E_2 at the detector after passing through the sample. The third term is the interference between the two fields, which is proportional to $\text{Re}\{E_d(\mathbf{R})E_2^*(\mathbf{R})\}$ and is usually referred to as the (self-)heterodyne contribution. Compared with the CARS signal, the signal at the Stokes frequency contains more terms. First, the homodyne detected signal from the radiating dipole scales as $|E(\omega_1)|^4 |E(\omega_2)|^2 |\gamma(\omega_2)|^2$ and has signal properties that are very similar to the homodyne detected CARS signal [132]. The magnitude of this signal is similar to the magnitude of the homodyne detected CARS signal, and its contribution is much smaller than the second and third terms in Equation (9). Consequently, this contribution usually plays no role in actual SRS experiments. The second term contributes a strong background $|E_2|^2$ against which the heterodyne contribution is measured. It is the heterodyne contribution I_{het} that is the signal of interest in SRG.

The heterodyne signal relies on the interference between E_d and the E_2 background field, implying that it depends on the relative phase between these two fields. The phase difference is dictated both by the spectral properties of the molecule as well as by geometrical phase effects. The geometrical phase is dependent on the spatial properties of the incident field and the placing of the molecule within it. In the current scenario, where the E_d

from the single molecule is a spherical wave and E_2 is a plane wave, the geometrical phase shift ϕ at the far-field position $\mathbf{R}$ of the detector is zero, and the heterodyne term is proportional to $|E(\omega_1)|^2 |E(\omega_2)|^2 \text{Re}\{\gamma(\omega_2)\}$ [133]. Given that this configuration probes the real part of $\gamma(\omega)$, the measurement would produce dispersive lineshapes. If the incident radiation is focused with a high numerical objective to a tightly focused spot and the molecule is placed in the focal plane, then the heterodyne term is proportional to $|E(\omega_1)|^2 |E(\omega_2)|^2 \text{Im}\{\gamma(\omega_2)\}$ [15, 133]. The latter is a familiar result, as it corresponds to a gain signal as probed in SRG experiments. In this case, the signal is proportional to $\text{Im}\{\gamma(\omega)\}$, which gives rise to dissipative (absorptive) lineshapes. Hence, this discussion underlines that the details of the experimental layout are important in determining how much of the real and imaginary parts of the complex third-order hyperpolarizability is probed in the measurement.

The heterodyne detected signal at ω_2 scales with the square of both $E(\omega_1)$ and $E(\omega_2)$, thus exhibiting a different dependence on the incident intensities than the CARS signal. This signal is classified as stimulated, which in this classical picture, implies that the dipole field interferes with the background field, resulting in an enhanced contribution through this interference. In the case of a gain signal, the wave interference is constructive and the total amplitude of the field in the frequency channel ω_2 has been enhanced. The gain of energy in the ω_2 channel, along with the accompanying loss in the ω_1 channel, has led to an overall loss in the energy carried by the fields. This energy loss is equivalent to the energy absorbed into a vibrational mode of the molecule. Hence, the presence of both pump (E_1) and Stokes (E_2) fields has stimulated the absorption of energy by the molecule through a Raman process. Although this classical wave interference picture is helpful, it is difficult to quantify the energy exchange between light and matter, especially in the case of a single molecule. This is more naturally done in a quantized picture, to which we will turn next.

4.1.2 Quantized vibrational states and fields

Time-resolved CRS experiments are commonly described in a semi-classical picture, where the vibrational states of the molecule are treated quantum mechanically and the fields are described classically [17, 134]. This approach is very useful for describing the response of ensembles of molecules. In such experiments, light-matter interactions produce intensity changes in the light fields, which are registered by a photodetector. From the intensity changes

in the fields, changes in the molecules can subsequently be inferred. However, in the limit of single molecules, the fact that the fields and the molecule can exchange energy only in fixed quanta becomes important. In the case of the SRS process, for instance, a single pump photon is lost and a single Stokes photon is gained during the interaction. Thus, describing the field in a quantized manner is a more direct approach. A quantum-field description also produces a clearer understanding of the nature of stimulated versus non-stimulated CRS signals.

The number of photons in a given field mode j is given by the expectation value of the photon occupation number operator $\hat{N}_j = \hat{a}_j^\dagger \hat{a}_j$, where $\hat{a}_j^\dagger$ and $\hat{a}_j$ are the photon creation and annihilation operators, respectively. From a field perspective, the signal detected in mode j is then defined by the change in $\langle \hat{N}_j \rangle$. On the one hand, if the detection mode is initially empty, i.e. $\langle \hat{N}_j \rangle = 0$, and the light-matter interaction raises the occupation number by 1, then the process is said to be spontaneous in the detection mode. This is the case for spontaneous Raman scattering, which adds one photon to the initially empty Stokes detection mode. The CARS signal is another example of a process that is spontaneous in the detection mode. Although spontaneous, the photon created in the anti-Stokes detection mode still retains a phase relationship with the driving fields, which implies that the overall CARS process is coherent. On the other hand, if the detection mode is occupied by one of the incident fields, then $\langle \hat{N}_j \rangle \gg 1$. In the SRG process, the occupation of the ω_2 detection mode is raised by 1, i.e. $\langle \hat{N}_2 \rangle + 1$. This interaction is classified as stimulated, because the detection mode was already occupied, providing a coherent field to stimulate the process.

As the field is quantized, the vibrational transitions in the molecule are directly linked to the change in the number of photons. If we define the transition rate between $\nu=0$ and $\nu=1$ as W , then the ratio between the molecular transition rate in the stimulated process versus the spontaneous process is given by

$$\frac{W_{\text{stim}}}{W_{\text{spont}}} = \langle \hat{N}_2 \rangle + 1. \quad (10)$$

The stimulated process thus enhances the molecular transition rate by a factor that is proportional to the photon occupation number of the detection mode. From this perspective, the enhancement in the transition rate achieved in the SE-SRS compared with that obtained in the SERS is thus related to the number of photon quanta that are contained in the plasmonic junction. Given that the changes in the fields and molecule are coupled, the overall loss/gain of the energy contained in the combined

optical fields must be related to the gain/loss of energy in the molecule. Assuming no thermal occupation of the molecule's vibrational states $\nu > 0$, changes in the total energy of the field modes then correspond to the dissipative CRS contributions of the molecules [135, 136]. In the case of two input fields ω_1 and ω_2 , the combined energy S contained in the incident field mode can be written as $S_{\text{in}} = S_1 + S_2$. The stimulated Raman process gives rise to changes in the energy contained in the combined field modes, so that the energy of the combined detection modes S_{det} is different from the incident energy. In SRS we find that $S_{\text{in}} > S_{\text{det}}$, which makes the process sensitive to probing the dissipative molecular response. The lowest order dissipative Raman response is a two-photon process that transfers the energy difference $\hbar(\omega_1 - \omega_2)$ from the fields to the molecule. The stimulated Raman scattering process is indeed recognized as a two-photon process, as illustrated by the Jablonski diagram in Figure 8A. In comparison, the dissipative CRS signals are classically understood as wave interference phenomena that take place at the detector, we see that energy exchange between light and a single molecule follows more naturally from a quantum description.

The CARS and CSRS processes do not change the energy of the combined field modes, which means that they do not probe dissipative Raman pathways in the molecule. Instead, the molecule mediates an energy exchange between the different field modes without affecting the sum of the energies of the participating field modes. This property classifies CARS and CSRS as parametric processes. The lowest order parametric response that

involves only Raman transitions is a four-photon process, as captured by the Jablonski diagram in Figure 8B.

4.2 SRS and CARS in the presence of a plasmonic antenna

4.2.1 SE-CARS

The goal of the plasmonic antenna is to enhance the optical signal that reports on the Raman transition in the molecule. Although a detailed theory of surface-enhancement in CRS has not yet been developed, most of the SE-CRS experiments have been interpreted in a manner similar to SERS experiments. In this view, the primary mechanism for the signal enhancement is governed by the electromagnetic mechanism. Early work by Kerker et al. in the 1980s considered the radiative properties of a molecular dipole in close proximity to a spherical polarizable particle [62]. When a pump field $E(\omega_1)$ is incident on a molecule placed at $\mathbf{r}$, the actual field E_{loc} experienced by the molecule is modified due to the presence of the particle, and is written as

$$E_{\text{loc}}(\mathbf{r}, \omega_1) = E(\mathbf{r}, \omega_1) + E_p(\mathbf{r}, \omega_1), \quad (11)$$

where $E_p(\mathbf{r}, \omega_1)$ is the field elastically scattered by the antenna. The same consideration applies to the externally applied Stokes field $E(\omega_2)$. The molecule is driven by these local fields $E_{\text{loc}}(\omega_1)$ and $E_{\text{loc}}(\omega_2)$, which set up a polarization in the molecule. Note that the driving phase of the local fields can be different from the phases of the incident fields, as they are dressed by the spectral resonance of the antenna. We may write the amplitude of the molecular nonlinear polarization at the ω_{as} and ω_s frequencies as in Equations (5) and (6) above. The field radiated from the nonlinear polarization of the molecule observed at a far-field point $\mathbf{R}$ can then be written as

$$E(\mathbf{R}, \mathbf{r}, \omega) = E_d(\mathbf{R}, \mathbf{r}, \omega) + E_{\text{sc}}(\mathbf{R}, \mathbf{r}, \omega), \quad (12)$$

where $E_{\text{sc}}(\mathbf{R}, \mathbf{r}, \omega)$ is the dipole scattered field from the particle positioned at $\mathbf{r}$ to the observation point $\mathbf{R}$. For a particle with plasmonic resonances, E_{sc} is much larger than the molecular dipole field and the molecule effectively radiates through the particle's dipolar mode. This analysis was applied for CARS as early as 1984 by Chew et al., who pointed out that the overall enhancement of the CARS signal by the plasmonic antenna can be orders of magnitude higher than what was observed in SERS [35]. If we simplify Equation (11) to $E(\mathbf{r}, \omega_1) \approx [1 + F(\mathbf{r}, \omega_1)]E(\mathbf{r}, \omega_1)$

Figure 8: Jablonski diagrams of the SRS and CARS processes. (A) SRS. (B) CARS. The upward pointing arrow indicates the annihilation of a photon, while the downward arrow denotes the creation of a photon. SRS is a two-photon process, in which ω_1 is absorbed and ω_2 is emitted. The SRL detects the loss in the ω_1 detection mode and the SRG detects the gain in the ω_2 detection mode. The CARS is a four-photon process, in which two ω_1 photons are absorbed, one ω_2 photon is emitted and one ω_{as} photon is emitted. The CARS can detect the changes in the ω_{as} detection mode.

and Equation (12) to $E(\mathbf{R}, \mathbf{r}, \omega) \approx [1 + F(\mathbf{r}, \omega)]E_d(\mathbf{R}, \mathbf{r}, \omega)$, then the CARS signal field can be written as shown below.

$$E(\mathbf{R}, \mathbf{r}, \omega) \propto [1 + F(\mathbf{r}, \omega_{as})]\gamma(\omega_{as}) \cdot [1 + F(\mathbf{r}, \omega_1)]^2 E^2(\mathbf{r}, \omega_1) [1 + F(\mathbf{r}, \omega_2)]^* E^*(\mathbf{r}, \omega_2) \quad (13)$$

As the fields scattered by the particle are much stronger than the incident fields or the fields scattered by the molecule alone, we can further write $[1 + F(\mathbf{r}, \omega)] \approx f(\omega)$. A schematic illustration of the CARS excitation and radiation of a point dipole in the presence of a plasmonic antenna is shown in Figure 9. The CARS intensity detected at the far-field photo-detector is then proportional to

$$I_{as} \propto |f(\omega_1)E(\omega_1)|^4 |f(\omega_2)E(\omega_2)|^2 |f(\omega_{as})\gamma(\omega_{as})|^2. \quad (14)$$

From this simple analysis, we can see that the surface-enhanced CARS signal shows a $|f(\omega_1)|^4 |f(\omega_2)|^2 |f(\omega_{as})|^2$ enhancement or, effectively, a $\sim |f|^8$ enhancement. This dependence of the CARS signal on the electromagnetic field enhancement has been pointed out in several studies [31, 35, 42, 64]. This enhancement derives from the notion that each field involved in the CARS process correspondingly benefits from the local field enhancement or radiative enhancement provided by the plasmonic antenna. With four field interactions, the overall field enhancement is thus proportional to f^6 and the overall intensity enhancement is proportional to f^8 . Note that the overall enhancement is expected even in the case of a single molecule, as the squaring of f^6 is an intrinsic property of the homodyne detection scheme, which is independent of the number of scatterers. Another way of interpreting the enhancement of the CARS signal is the notion that CARS is a four-photon process and that the creation/annihilation rate of each photon mode is accelerated by a factor $\sim f^2$. This produces an enhanced Raman transition rate

in the molecule, which is independent of the number of molecules. We will briefly revisit this issue in Section 4.3.

Note that the discussion so far only considers the CARS signal from the molecule, and that a coherent background at ω_{as} originating from the metal's $\chi^{(3)}$ response has not been considered. We may include the contribution of the metal by writing the total field at the detector as

$$E_{\text{tot}}(\mathbf{R}, \mathbf{r}, \omega_{as}) = E_{\text{metal}}(\mathbf{R}, \mathbf{r}, \omega_{as}) + E_{\text{mol}}(\mathbf{R}, \mathbf{r}, \omega_{as})e^{i\Delta\phi(\omega_{as})}, \quad (15)$$

where E_{metal} is the field at ω_{as} radiated by the metal that is independent of the presence of the molecule. The molecular contribution E_{mol} also radiates by means of the metal, but depends on the polarization of the molecule near the antenna. For simplicity, the location of both molecule and antenna in Equation (15) is set to $\mathbf{r}$. Given that the detected signal at ω_{as} is proportional to $|E_{\text{tot}}|^2$, the molecular contribution to the signal may interfere with a strong contribution from the antenna. The spectral features that result from this interference depend on the phase difference $\Delta\phi$ between E_{metal} and E_{mol} . Note that the metal's response originates from both the real and imaginary components of $\chi^{(3)}$, which may dress $\Delta\phi$ with a spectral dependence originating from both the metal and molecule. It can be expected that the actual phase difference depends strongly on experimental conditions, including the frequency and temporal width of the incident laser pulses. On the one hand, most femtosecond SE-CARS experiments reveal spectra that are accompanied by a strong electronic FWM background from the antenna and exhibit distorted lineshapes [50, 99]. On the other hand, a picosecond study retrieved SE-CARS spectra that displayed surprisingly low background contributions from the metal and relatively undistorted lineshapes [42]. A comprehensive theory that considers the relation between the molecular and metal contributions in SE-CARS measurements in detail is currently lacking.

Experimentally, the contribution from E_{metal} can be suppressed in time-resolved SE-CARS, based on the notion that the dephasing time of the metal response is on the 10–100 fs timescale, whereas the vibrational response evolves on the picosecond timescale. Indeed, clean, background-free molecular SE-CARS spectra have been obtained with fs pulses when probing the vibrational coherence after 1 ps, well beyond the dephasing time of the metal [137].

4.2.2 SE-SRS

Given that the SRS process is a two-photon process, we may expect that both the excitation rate and the emission

Figure 9: The CARS excitation and radiation of a point dipole in the presence of a plasmonic antenna.

(A) The incident fields $E(\omega_1)$ and $E(\omega_2)$ couple to the antenna, setting up local fields that are enhanced by a factor $f(\omega_1)$ and $f(\omega_2)$, respectively. The point dipole is driven by the local fields, setting up a nonlinear polarization. (B) The nonlinear polarization at frequency ω_{as} radiates through the antenna, producing dipolar radiation that is enhanced by a factor $f(\omega_{as})$.

rate are enhanced with a factor $|f|^2$, for an overall enhancement of $|f(\omega_1)|^2 |f(\omega_2)|^2$. In this simple model, the enhancement of the molecule's stimulated Raman response due to the presence of the plasmonic antenna is similar to the enhancement of spontaneous Raman scattering in SERS. Relative to SERS, however, the overall Raman transition rate of the molecule is enjoying an additional enhancement because of the mode occupation at ω_2 , which raises the transition rate by a factor proportional to $|E_2|^2$. Hence, although the relative enhancement due to the surface plasmon is identical to SERS, we may expect a much stronger signal. This additional enhancement can be expected to scale with the ω_2 photon occupation number contained in the mode volume defined by the nanoscale local field.

In a more refined model, McAnally et al. used classical fields and Maxwell's wave equation to solve for the SRG signal from a collection of molecular oscillators equipped with plasmonic antennas [44]. Their analysis considers that the molecular nonlinear polarization (ω_2), which itself is enhanced by a factor $|f(\omega_1)|^2 f(\omega_2)$ due to enhancement of the driving fields, receives a radiative enhancement of $f(\omega_2)$ from the plasmonic antenna. This results in a total enhancement of $|f(\omega_1)|^2 f^2(\omega_2)$. Given the complexity of the field enhancement factors, this result is somewhat different from the simple analysis above, as $|f(\omega_2)|^2$ and $f^2(\omega_2)$ have different phases. Hence, in the model by McAnally et al., the emitted field $E(\omega_2)$ by the antenna picks up another phase shift $\Delta\phi_{\text{rad}}$ relative to the phase of the nonlinear polarization. The intensity at ω_2 measured at the far-field detector is then $|E(\omega_2)e^{i\Delta\phi_{\text{rad}}} + E_2(\omega_2)|^2$, which is different from the SRG result of an ensemble of molecular oscillators in the absence of plasmonic antennas. The extra phase factor alters the interference between the $E(\omega_2)$ signal field and the background field, thus producing a signal that may contain portions of both $\text{Im}\{\gamma(\omega_2)\}$ and $\text{Re}\{\gamma(\omega_2)\}$. This mechanism has been suggested as a possible explanation for the dispersive lineshapes seen in SE-SRS measurements [44].

In addition to an enhanced signal field $E(\omega_2)$ originating from the nonlinear polarization of the molecule, we may also expect that the plasmonic antenna itself contributes a coherent nonlinear optical field at ω_2 . Indeed, various experiments have pointed out that the plasmonic antenna system produces a strong coherent, nonlinear optical field $E_{\text{metal}}(\omega_2)$ that appears independent of the molecule [51, 76]. This nonlinear optical signal results from the FWM contributions that derive from the antenna's $\chi^{(3)}$ response. The magnitude of the $E_{\text{metal}}(\omega_2)$ field is enhanced by plasmonic resonances and thus scales as $\sim f^3$. The presence of this additional field complicates the

analysis of the SE-SRS considerably. First, in addition to the far-field interference terms between $E(\omega_2)$ and the background field, which scale as $\sim f^6$, there will be mixing terms between $E(\omega_2)$ and $E_{\text{metal}}(\omega_2)$ as well [43, 138]. These latter contributions scale as $\sim f^8$ and thus produce a signal with an overall enhancement factor that is rather different from the intuitive $\sim f^6$ SRS enhancement. An analysis by Mandal et al. revealed that these additional interference contributions may, in some cases, dominate the overall SRS signal [43]. Second, the spectral profile of the SRS signal strongly depends on the relative phases between the interfering fields, which implies that knowledge of the phase properties of each of the three fields is needed for a spectral analysis of the signal. A study of the nonlinear optical field from the plasmonic antenna under conditions typical for femtosecond SRS experiments suggests that the phase of the $E_{\text{metal}}(\omega_2)$ is such that strongly dispersive lineshapes can be anticipated [43].

Although current models for the spectral dependence of the SE-SRS signal offer possible explanations for the observation of dispersive lineshapes, recent studies make it clear that none of the existing theories so far can fully account for the experimental observations. Buchanan et al. found that the SE-SRS spectral profiles varied dramatically as the excitation frequencies of ω_1 and ω_2 were systematically changed relative to the spectral resonance of the antenna's surface plasmon [139]. This dependence deviates from the predictions of current theories, underlining that a full understanding of the SE-SRS signal is still incomplete.

4.3 Ensembles versus singles

Our discussion so far has focused mainly on the SE-CRS signal in the context of a single molecule equipped with a plasmonic antenna. Many SE-CRS experiments, however, have been carried out on ensembles of plasmonic antennas with adhered molecules. The ensemble signal can vary markedly from the single-molecule SE-CRS signal. Here, we discuss several ensemble relevant effects, including the issue of coherent amplification, spectral dispersion in the plasmonic resonances of a collection of antennas and extinction effects as the number density of plasmonic particles is increased.

In Section 4.2.1, the SE-CARS field from a single molecule was shown to scale as $f(\omega_{\text{as}})\gamma(\omega_{\text{as}})f^2(\omega_1)f^*(\omega_2)$, and the detected intensity as $\sim f^8 |\gamma(\omega_{\text{as}})|^2$. This signal is coherent in the sense that it maintains a phase relation with the incident fields that prepared the nonlinear polarization of the molecule. In the case of two or more molecules, the

total signal detected at far-field point $\mathbf{R}$ is the coherent sum of the fields from each of the antenna-bound molecules, as shown below [140]

$$I(\mathbf{R}, \omega_{as}) \propto |E(\mathbf{R}, \omega_{as})|^2 = \left| \int E(\mathbf{R}, \mathbf{r}, \omega_{as}) d\mathbf{r} \right|^2. \quad (16)$$

For two molecules, both equipped with a plasmonic antenna but placed at different positions $\mathbf{r}$ and $\mathbf{r}'$, respectively, we may write the total field at the detector position as $E(\mathbf{R}, \omega_{as}) = E(\mathbf{R}, \mathbf{r}, \omega_{as}) + E(\mathbf{R}, \mathbf{r}', \omega_{as})$. The detected signal $|E(\mathbf{R}, \omega_{as})|^2$, contains contributions from the two homodyne contributions of the individual molecules, each enhanced by $\sim f^8$, as well as a mixing term. If the fields emanating from the two antenna/molecule systems are in phase at $\mathbf{R}$, then the mixing term contributes $2|E(\mathbf{R}, \mathbf{r})||E(\mathbf{R}, \mathbf{r}')|$ to the total CARS signal. This mixing term also scales as $\sim f^8$. Hence, the presence of the inter-particle interference enhances the overall signal beyond a simple addition of single particle contributions. The extra contribution to the signal due to in-phase contributions among the two molecules also implies that the rate with which each molecule mediates energy exchange among the participating photon modes is effectively enhanced. In other words, inter-particle coherence increases the molecular CARS response. For an ensemble of N molecules that radiate in unison, the magnitude of the coherent enhancement scales as $N(N-1)$. The amplification of the CARS signal due to *ensemble coherence* is one of its most celebrated features, as it produces very strong signals in the limit of very large N .

In conventional CRS experiments, the coherence in the polarization among different molecules is prepared by the excitation fields. This coherence is sustained as the molecular dipoles radiate with identical phases immediately after preparation, and phase differences among dipole radiators mostly develop as the ensemble evolves as a function of time. However, in the SE-CRS experiments, the molecules are driven by the near-field phases that are modified by the plasmon resonance of their antennas. In addition, given that radiation occurs through the antenna dipole, the radiation phase is also modified by the spectral properties of the antenna's surface plasmon. Heterogeneity in an ensemble of plasmonic antennas inevitably leads to variations in the amplitude and phase with which the antennas radiate at the CRS signal frequency. Hence, even though the ensemble is prepared in a phase coherent manner by the driving fields, the radiation phase among different antennas can vary dramatically. This heterogeneity in the phase can reduce the signal relative to a fully coherent ensemble of dipole radiators, thus counteracting the signal gain

expected from the ensemble coherence. In addition, phase variations within the ensemble can produce position-dependent lineshape variations as the signal field interferes with the background. Hua et al. observed CARS lineshapes that changed from additive to dispersive and to subtractive relative to the FWM background as the focal spot was moved within a layer of randomly aggregated gold nanoparticles [41], as shown in Figure 10. In a follow-up study, the CARS spectra were observed to have neighboring vibrational resonances that appeared with opposite phases [141]. Using a simple model that assumed an ensemble of antenna systems with a distribution of spectral resonances and a FWM background field with uniform phase, they retrieved lineshapes that mimicked the experimental observations. Even more variation can be anticipated if spectral heterogeneity within the FWM background field is considered.

This discussion underlines that spectral heterogeneity in the antenna ensemble can reduce the overall CRS signal and average out the spectral features originating from different hot spots in the sample. This phenomenon has been suggested as a possible explanation for the lower-than-expected signal enhancement in most *ensemble* SE-CRS experiments [41].

Figure 10: SE-CARS spectra obtained near the 968 and 1064 cm^{-1} modes of pyridazine near a layer of aggregated colloidal gold particles.

As the probing spot was moved over the sample, differences in the lineshapes of the two modes were observed, varying from positive peaks (A), to dispersive lineshapes (B), to dips (C) relative to an electronic FWM background. Adapted with permission from Ref. [41].

In addition to the phase variation within the ensemble, the SE-CRS signal is also affected by linear absorption and scattering effects as the number of nanoparticles in the probing spot is increased. Both the re-absorption and scattering of the signal field give rise to loss mechanisms that, in turn, reduce the signal registered by the far-field photo-detector. These loss mechanisms counteract the signal gain otherwise expected, and give rise to an optimum effective signal gain that can be derived from the ensemble. Balancing the effects of enhancement and extinction, theory indicates that SE-SRS experiments benefit from a higher concentration of particles relative to the SERS measurements [138]. The experiments corroborate this finding, as the optimum gain in the SE-SRS experiments is reported in higher concentrations than those in the SERS experiments [142].

5 Experimental advances in SE-CRS

5.1 CRS with surface plasmon polaritons

Surface plasmon polaritons (SPPs) are surface charge density oscillations at the planar interfaces formed between a (noble) metal and a dielectric medium. The SPP charge density oscillations exhibit a spatial phase supporting an electromagnetic surface wave that propagates in the direction parallel to the surface, but which is evanescent in the direction perpendicular to the surface. The propagation and polarization characteristics of the surface-bound SPP waves are well understood in the literature [143, 144]. The ability of SPPs to transfer electromagnetic energy along the surfaces has been recognized as a promising waveguiding mechanism in nanoscale devices [145], and their sensitivity to the properties of the dielectric medium has been used extensively in SPR sensing applications [146].

Coupling propagating radiation to the SPPs leads to the confinement of electromagnetic energy in the direction perpendicular to the surface, and, therefore, to an enhancement of the surface field relative to the incident field. As this confinement is along one dimension, the resulting enhancement is moderate compared with the surface plasmon modes that enjoy confinement in more dimensions. For visible/NIR light, the field enhancement factor f is ~ 5 – 7 . However, compared with the antenna systems designed to support nm³-sized localized plasmon modes, the planar surfaces suitable for the SPP excitation are much easier to fabricate and reproduce. Given that the analytical solutions for SPP fields on smooth gold or silver

surfaces are readily available, the properties of the surface fields are known quantitatively, and such information can greatly simplify the interpretation of surface-enhanced Raman measurements.

The possibility of performing nonlinear optical measurements with SPP waves was examined first in the 1970s, when theoretical studies predicted strong SHG signals generated by surface-bound waves on silver [111]. These insights were corroborated by experiments [147], and related studies generalized the notion that optical mixing at interfaces can be performed with surface polaritons, including surface phonon polaritons and surface plasmon excitons, thereby setting the stage for the first SE-CRS experiments [114, 115].

In the SE-CARS experiment performed by Chen et al. in 1979, the pump and Stokes excitation fields were coupled to a planar interface formed between silver and liquid benzene, setting up the propagating SPP fields of frequencies ω_1 and ω_2 along the interface [34]. In this scenario, the nonlinear polarization of benzene is driven by the surface fields and not by the freely propagating radiation. The nonlinear polarization subsequently couples to the SPP mode at ω_{as} in the phase-matched direction parallel to the surface, and couples out in the form of leakage radiation at an angle at which the ω_{as} surface field is momentum matched with its freely propagating counterpart. The experiments revealed a clear dependence of the $\omega_1 - \omega_2$ detuning near the 992 cm⁻¹ vibrational mode of benzene, convincingly demonstrating that vibrationally-sensitive CRS signals can be generated by surface plasmon waves.

Despite the simplicity and early success of the SPP approach to SE-CRS, in search of higher enhancement factors in the years following the seminal paper by Chen et al., research activities shifted in the direction of the SE-CRS experiments with colloidal substrates and suspensions. A renewed interest in optical mixing with SPP waves emerged in the 2000s, this time with an emphasis on the nonlinear susceptibility of the metal itself for generating surface waves and the ensuing outcoupled radiation at new frequencies. In the case of FWM, the outcoupling of the SPP wave at $2\omega_1 - \omega_2$, which is generated by the corresponding SPP modes at ω_1 and ω_2 , was studied in detail for gold films [148]. Making use of the SPP phase-matching conditions in the direction parallel to the surface, it was further shown that $2\omega_1 - \omega_2$ SPPs can be produced with the proper combination of freely propagating incident fields, which are not individually coupled to SPP modes themselves [149]. Using films equipped with gratings, the surface bound FWM waves generated by the metal's $\chi^{(3)}$ can subsequently be coupled out, giving rise

to coherent radiation with a well-defined propagation direction and polarization state [150]. Although field confinement is moderate, the FWM involves four fields and the resulting signal field thus enjoys a f^4 enhancement (f^8 enhancement in intensity), suggesting that gold or silver surfaces could be used as efficient nonlinear media for the generation of new frequencies. Theoretical studies confirm this notion, underlining that the FWM signals can be generated with very high efficiency through the involvement of SPPs [151].

This new focus on nonlinear optics enabled by SPP waves also re-animated research aimed at producing nonlinear optical signals from materials placed in the vicinity of the SPP-supporting metal film. Contrary to the groundbreaking work in the 1970s, which focused on bulk liquids and solids, the emphasis was now placed on generating the SPP-induced nonlinear optical signals from small objects with (sub-) μm dimensions. By performing the SPP-enabled experiments in an optical microscope, the individual objects can be singled out, offering an opportunity to increase the particle detection sensitivity by reducing the probing volume. This led to FWM in a single Si nanosphere placed on a gold surface, driven by the counterpropagating SPP waves, as shown in Figure 11 [152, 153]. Subsequent studies demonstrated that SPP pump and Stokes waves can induce vibrationally sensitive CARS signals from the CH_2 symmetric stretching mode of (sub-) μm lipid clusters, which are placed on a gold surface [154]. Using a Kretschmann excitation geometry for the pump and Stokes beams in an optical microscope, the molecular CARS signal was shown

to couple out at the expected Kretschmann angle for the anti-Stokes radiation, allowing the efficient detection of the SPP-enhanced CARS response [155]. A comparison between CARS signals excited by freely propagating light and the corresponding SE-CARS signals of identical objects further revealed that the SE-CARS was generated with a much higher efficiency, amounting to an enhancement of $\sim 10^6$ relative to the CARS signal without the gold surface. Assuming $f \sim 7$ for the SPPs at the relevant wavelengths used in the experiment, the predicted f^8 enhancement for the SE-CARS signal would give rise to a total enhancement of $(7)^8 = 6 \times 10^6$, in close agreement with the experiment.

As the field profiles, field enhancement, phase matching and outcoupling characteristics of the SPP waves are fully understood, the SSP-mediated CRS experiments offer a useful approach for examining some of the basic properties of surface-enhanced CRS. The fact that experiments seem to quantitatively confirm the predicted f^8 enhancement is encouraging. Although the observed surface enhancement is currently insufficient for enabling single-molecule measurements, opportunities exist to implement additional enhancement mechanisms, such as an electronic resonance of the target molecule.

5.2 CRS at atomically sharp tips

The important advances made in SPP-based CRS notwithstanding, the quest for higher sensitivities has naturally led to significant efforts in improving the signal enhancing properties of plasmonic antennas. By confining the surface plasmon waves to the nanometer scale, much higher signal enhancement can be achieved. The use of atomically sharp metal tips is a popular approach to confine electromagnetic fields, enabling the formation of nano-plasmonic junctions with exquisite precision. The ability to laterally move the tip on and off a molecular target, apart from the ability to axially retract the tip from the sample, provides excellent conditions for performing controlled SE-CRS experiments.

Sharp metal tips represent an antenna system that supports localized surface plasmon modes at its apex and propagating surface plasmon on its shaft. The localized surface plasmon can be directly excited with focused light in an optical microscope, resulting in enhanced fields with spatial dimensions on the order of the tip radius ($r \approx 10\text{--}30\text{ nm}$) [156, 157]. The localized mode at the apex can also be driven efficiently by coupling propagating radiation to the SPP modes on the shaft, which subsequently propagate and nano-focus electromagnetic energy at the tip apex [158]. By placing the tip in close

Figure 11: Frequency mixing in a nanoscopic Si particle with surface waves.

Two light fields at ω_1 and ω_2 are coupled to counterpropagating SPP modes at a gold/air interface. The surface fields set up a nonlinear polarization in the Si nanoparticle, subsequently generating the SPP fields at $2\omega_1 - \omega_2$. Outcoupling of the SPP field produces FWM radiation seen at the CCD detector in the far-field, giving rise to an image with a bright spot at the location of the particle. Adapted with permission from Ref. [152].

proximity to the sample, further field confinement can be achieved. Moreover, in case the sample is a material that supports surface plasmons, nano-cavities can be formed with very high field enhancement factors.

The local fields at the tip's apex are known to enhance the Raman response of molecules in the near-field and efficiently couple the near-field Raman polarization to the far-field photodetector. This is the operating principle of tip-enhanced Raman spectroscopy (TERS) and imaging [159, 160]. Similarly, the nonlinear optical response of the nanoscale targets can be enhanced by the tip's proximity, as shown, for instance, in the case of tip-enhanced two-photon excited fluorescence [161]. Using a silver coated tip, Ichimura et al. demonstrated that the same configuration can be used to enhance the CARS signal from aggregated DNA bundles deposited on glass coverslips [39, 162]. For this purpose, the pump and Stokes field were focused by a high numerical aperture lens and the tip was placed in the region of the focal volume with the highest polarization component parallel to the tip-axis. This geometry ensures the efficient driving of the surface plasmon mode in the longitudinal direction. When the $\omega_1 - \omega_2$ frequency difference was tuned to the 1337 cm^{-1} mode of the DNA, the signal displayed a significant increase compared with the off-resonant excitation condition, indicating that the tip antenna efficiently induces and radiates with the nonlinear Raman polarization of the deposited molecules. Using radially polarized excitation fields and illumination with a high numerical aperture lens, the longitudinally polarized surface plasmon mode at the apex can be driven more efficiently, resulting in a 6-fold improved coupling of the incident fields to the tip antenna. This approach has been used to generate tip-enhanced CARS images based on the 2845 cm^{-1} CH_2 mode vibration of polystyrene beads [163]. Even though these studies did not examine the actual enhancement in quantitative detail, the experiments performed thus far provide strong evidence that the surface-enhancement of the CARS signal can be achieved with metal tips. Further studies are likely to focus on the contribution of the FWM background from the tip, the role of linear and non-linear heating effects and the achievable sensitivity in tip-enhanced CARS.

The number of tip-enhanced CARS studies remains limited, a direct indication of the conceptual and experimental challenges associated with such experiments. Even fewer studies have attempted to detect the stimulated gains or losses of the incident fields due to the presence of molecules in the tip-sample junction. In a recent work, Wickramasinghe et al. observed the tip-enhanced Raman signal from the 1142 cm^{-1} mode of azobenzene on a gold surface, with and without an additional stimulating

light field [164]. When a stimulating light field was coupled to the gold tip and tuned to $\omega_2 = \omega_1 - \omega_p$, a significant increase in the number of scattered photons in the ω_2 channel was observed. A modulation technique revealed that the enhanced scattering originated from the tip-sample junction. A subsequent analysis indicated a signal enhancement relative to the TERS signal of 10^9 . This experiment suggests that the enhancement due to ω_2 mode occupation can be substantial. Despite these encouraging results, the tip-enhanced SRS has been difficult to implement, as no additional studies in this direction have been reported so far.

The tip-enhanced CRS examples discussed above relied on the antenna to couple near-field information to a far-field photo-detector. Alternative non-optical detection schemes employ different mechanisms of probing the molecule's induced polarization. One example is force detection, where the electromagnetic force between the induced dipoles in the tip and molecule is measured directly in the near-field. Rajapaksa et al. monitored the photo-induced force exerted on a gold-coated tip as the tip-sample junction is illuminated by both cw pump and Stokes beams [165]. They observed that the photo-induced force increased correspondingly as $\omega_1 - \omega_2$ was tuned over the 1625 cm^{-1} vibrational resonance of the chromophore Coomassie Blue. The Raman sensitive force signals were obtained from very small clusters and the suggestion was made that single-molecule sensitivity may have been reached. Comparable results were acquired on molecules without a nearby electronic resonance, suggesting that the nonlinear Raman polarization driven by $\omega_1 - \omega_2$ is sufficient to induce a detectable attractive force on the tip without further electronic resonance enhancement [166]. As the photo-induced force technique directly probes the induced polarization in the molecule, it would be possible to observe the real-time evolution of coherently prepared vibrational modes, including their quantum beats, in a time-resolved version of the force-detected CRS experiment. Preliminary measurements suggest that the Raman-sensitive forces are also detectable when the junction is irradiated with fs pump and Stokes beams [167], keeping the door open for the possibility of time-resolving CRS experiments through force detection.

Another impressive example of a CRS experiment with non-optical detection uses the electron tunneling current in a scanning-tunneling microscopy (STM) junction as an indirect read out mechanism for probing vibrational coherences [168]. In experiments conducted by Li et al., a junction formed between an etched silver tip and a copper surface is illuminated by a pair of short fs pulses (see Figure 12A). The junction contains a single pyrrolidine

Figure 12: Non-optical detection of vibrational coherence in a single molecule using electron tunneling as a probe in a scanning tunneling microscopy (STM) junction.

(A) A pyrrolidine molecule is irradiated in the junction by two fs pulses, separated by a time delay τ . (B) Two conformers of pyrrolidine on the copper surface. The “up” position promotes a high tunneling current, while the “down” position gives rise to a low tunneling current. The flip-flop rate is indicated by R_{flop} . (C) The flopping rate as a function of time delay τ . The coherent oscillations of the 230 cm^{-1} mode of pyrrolidine are evident in the measured R_{flop} . No such oscillations are seen with cw excitation or when the light is blocked. Modified with permission from Ref. [168].

molecule, which is adhered to the copper surface and is subjected to the strong local optical fields. The spectral width of the first pulse is sufficient to impulsively excite the Raman active 230 cm^{-1} bending mode of the adhered pyrrolidine molecule. The evolving vibrational coherence is then probed by the second pulse, which translates the coherence into energy transfer (Raman absorption) into the molecule. The efficiency of the Raman absorption depends on the time delay between the preparation and probing pulses, alternately leaving the molecule in the ground state or in the excited state with a periodicity of $1/\omega_v = 145\text{ fs}$. After extracting energy from the light fields, the molecule exhibits an excess of energy (230 cm^{-1}). This additional energy may facilitate motions along the molecule’s various coordinates, including motion along the coordinate of a flip-flop mode. The flip-flop changes the molecule’s conformation between lying flat on the surface or standing up. The more energy flows into the molecule through nonlinear Raman absorption, the faster the transition rate between the molecule’s conformers. We may thus expect that the flopping rate R_{flop} peaks every 145 fs

as the delay time between the pulse is increased. Hence, R_{flop} indirectly reports on the vibrational coherence of the 230 cm^{-1} bending mode. The STM junction can measure R_{flop} directly, as the up and down position of pyrrolidine on the surface results in a significant change in the junction’s electron tunneling efficiency. The time-dependent R_{flop} , shown in Figure 12C, reveals the evolution of the vibrational coherence.

The beauty of probing vibrational dynamics through tunneling electrons is that it eliminates interpretation problems related to phase interferences between optical fields at a far-field photo-detector. As discussed in Section 4 for the optical detection of the SE-CRS response, the presence of background fields and field interference produces spectra with distorted lineshapes which are difficult to decipher without full knowledge of the mutual phase shifts between the different field contributions. Direct probing in the near-field avoids the far-field interferences and thus yields a clearer picture of the molecular response. As the example above illustrates, non-optical detection can be exceptionally sensitive,

allowing a clean recording of vibrational dynamics on a single molecule.

5.3 CRS at the plasmonic nanoparticles

Given the success of SERS studies based on colloidal silver and gold antennas, it is perhaps not surprising that numerous SE-CRS studies have been undertaken using similar antenna systems. The focus of most of these studies has been to examine experimentally whether the CRS in combination with surface-enhancement yields the expected signal increase relative to SERS. The dominant observation in the SE-CRS experiments with colloidal metal antennas is that, although the CRS signal appears enhanced, the overall enhancement of the signal is lower than expected. For instance, Liang et al. performed frequency domain CARS measurements on the 992 cm^{-1}

mode of liquid benzene with nanosecond pulses, with and without the presence of colloidal silver particles [37]. The maximum signal enhancement was found to be less than 10^2 . Related frequency domain CARS experiments on pyridine, this time with fs pulses, showed similar results, reporting an overall enhancement factor of 10 for the molecular response [169]. A study by Koo et al. reported single-molecule sensitivity in the SE-CARS measurements on deoxyadenosine monophosphate in a silver colloidal suspension [40]. However, as the SE-CARS signal was not examined both on and off the molecular resonance in this work, the observed signal cannot be distinguished from the non-resonant electronic background. Hence, these results remain ambiguous.

Ichimura et al. improved on these studies by performing SE-CARS measurements in an optical microscope, enabling experiments on single antennas and antenna clusters formed from 60 nm gold particles [38]. Their picosecond

Figure 13: The gold quadrumer antenna with optimized properties for the SE-CARS.

(A) The experimental (top) and calculated (bottom) scattering spectra of the quadrumer antenna determined before (black) and after (red) molecule adsorption. Green dashed line: the pump beam (800 nm); red zone: the Stokes scattering region (848–952 nm); blue zone: the anti-Stokes scattering region (756–690 nm). (B) The charge densities on the top surface of the quadrumer excited at 800 nm pump (top) and 900 nm Stokes (bottom), corresponding to the subradiant and superradiant modes, respectively. (C) The field enhancement intensity distribution at the anti-Stokes (left), pump (middle) and Stokes (right) frequencies at mid-height of the quadrumer. Adapted with permission from Ref. [50].

CRS measurements show a strong electronic background from the individual particles and clusters, as well as an enhanced response near the 1330 cm^{-1} mode of adsorbed adenine molecules. Although the overall signal from the antenna/molecule system was enhanced by a factor $\sim 10^3$, the vibrational component of the signal appeared with a rather low signal-to-background ratio. In recent frequency domain SE-CARS experiments using periodic gold pyramidal structures on graphene as plasmonic antennas, the SE-CARS signal from the adhered molecular targets was found to be up to 10^2 higher compared to the corresponding SERS signal [170]. In another study, Steuwe et al. used structured gold surfaces and fs pump and Stokes pulses to enhance the CARS signal from thiolbenzene [171]. The SE-CARS signal of the 1070 cm^{-1} ring stretching mode was found to be enhanced by $\sim 10^5$ relative to the sample

without the structured gold surface. This enhancement factor is significantly higher than what has been reported in earlier work. However, even when assuming a very moderate enhancement factor of $f \sim 10$, the observed enhancement remains well below the $|f|^8 \approx 10^8$ enhancement that one would expect for these measurements. These observations illustrate the difficulty in experimentally determining enhancement factors for SE-CRS and in finding conditions for which the enhancement is maximized.

Whereas SE-CRS experiments on colloidal antenna structures have shown, at the very least, that enhancement of the coherent Raman response can be achieved, other studies have focused specifically on reaching the single-molecule limit by employing optimized nano-antennas. Zhang et al. designed a quadrumer structure formed from gold nanodisks, shown in Figure 13, which

Figure 14: SE-CARS measurements of dipyrindyl ethylene (BPE) on individual gold dumbbell antennas.

(A) The picosecond SE-CARS of C=C stretching modes (dots). Black and red traces represent the consecutive spectral scans. The grey spectrum is the SERS signal measured on the same antenna. (B) Transmission electron microscopy (TEM) image of the gold antenna with silica coating. (C) Femtosecond time-resolved CARS from an ensemble of BPE molecules. The oscillations originate from the quantum beat of the two coherently prepared modes. (D) Time-resolved SE-CARS trace from an individual antenna equipped with BPE. The experiment (red) shows sustained quantum beats well beyond the dephasing time of the ensemble. Blue is a simulation based on the stick spectrum shown in the inset of (C). Adapted with permission from Ref. [49].

minimizes losses at the pump frequency and displays superradiant properties at the anti-Stokes frequency [50]. Given that broadband fs pulses were used, the SE-CARS spectra appeared broadened, but the spectral contrast was sufficient to discriminate between the spectra of different molecular targets. The antenna itself produces a significant FWM background, most of which could be suppressed by polarization sensitive detection. Using a bi-analyte approach, a statistical analysis revealed that the antenna structure enabled single-molecule detection through the SE-CARS. This measurement shows convincingly that the surface-enhanced nonlinear polarization of a single molecule can be translated into detectable far-field radiation when properly designed plasmonic antennas are used.

Another example of a SE-CARS experiment in the single-molecule limit used dumbbell-shaped gold antennas with adhered bipyridyl ethylene (BPE) molecules and encapsulated in a 90 nm-thick silica coating. When the pump and Stokes driving fields were coupled to the

red side of the dipolar surface plasmon mode and the anti-Stokes frequency is tuned close to the maximum of the dipolar antenna response, the signatures of the 1600 and 1640 cm^{-1} C=C stretching modes of the molecule could be clearly resolved in the frequency domain picosecond SE-CARS experiments [42]. The SE-CARS spectra were reproducible for many individual dumbbell antennas, fostering confidence that the observations are general and not limited to individual cases. Although no definite proof for single molecules was provided, the plasmonic junctions in the dumbbell have dimensions of $\sim 1 \text{ nm}^3$ and can support only a handful of molecules. Whereas molecular SE-CARS spectra could be obtained with limited FWM background from the antenna, simultaneously recorded SE-SRS spectra produced no clear signatures [76]. Instead, a strong electronic background from the antenna was observed in the SRL channel, showing that when surface-enhancement is involved, SRS measurements are not necessarily favored over CARS.

Figure 15: Broadband SE-SRS spectra of bipyridyl ethylene pumped at different wavelengths relative to the spectral resonance of a gold dumbbell antenna.

The top panels show a schematic of the extinction spectrum of the plasmon antenna relative to the incident fields and the bottom panels show the experimental results. (A) Pump at 750 nm. (B) Pump at 800 nm. (C) Pump at 840 nm. The SRL is shown in blue and SRG is shown in red. Note that the spectra are highly dispersive and that the lineshape is a function of the excitation and probing wavelengths. Reproduced with permission from Ref. [139].

The same dumbbell antenna systems were used in a time-resolved SE-CARS experiment. In this experiment, BPE's 1600 cm^{-1} and 1640 cm^{-1} modes were coherently excited and their mutual quantum beat was observed as a function of time delay between the pump/Stokes and probe pulses [49]. Whereas the time-resolved SE-CARS signal of some antennas showed a trend similar to the time-resolved CARS signal measured in bulk BPE, other antennas showed sustained quantum beats well beyond the ensemble dephasing time. An example is shown in Figure 14, where the phase coherent evolution of the prepared vibrational modes can be observed up to 10 ps, even though the ensemble coherence has disappeared beyond 5 ps. The sustained quantum beat is a manifestation of single-molecule behavior. In the case of a single molecule, ensemble dephasing is absent and coherences can be observed on a time scale defined solely by the vibrational lifetime. Such measurements offer opportunities for more advanced quantum correlation measurements, using individual vibrational oscillators as probes.

On the one hand, the combined SE-CARS studies, thus far, have shown that the concept of surface enhancement can be translated to the domain of CRS if experimental conditions are chosen carefully. SE-SRS experiments, on the other hand, require their own optimization of experimental conditions. As briefly discussed above, picosecond SE-SRS on dumbbell antenna systems revealed a strong electronic background from the antenna and limited molecular contrast. Using the same antennas but employing a femtosecond probe, however, Frontiera et al. showed decisively that a molecular response is present on top of an electronic background in frequency domain SE-SRS measurements [172]. The much better molecular contrast seen in femtosecond versus picosecond excitation in SE-SRS is perhaps surprising and can possibly indicate that the coherence between the antenna and molecule at ω_1 or ω_2 cannot be sustained for the full duration of the picosecond pulse [76]. The SE-SRS lineshapes obtained with femtosecond probe pulses were found to be strongly dispersive and to depend on the frequencies of the incident fields relative to the SPR [139], as shown by the example in Figure 15. As discussed in Section 4.2.2, the intrinsic presence of background fields makes the analysis of SE-SRS spectra more complicated compared with the SE-CARS measurements. Nonetheless, the observation of strong molecular signals in the SE-SRS experiments with dedicated antenna systems is encouraging. Very recently, Zong et al. performed frequency domain SE-SRS experiments on adenine molecules deposited on a layer of colloidal gold particles [51]. Using a special denoising algorithm, it proved possible to discriminate adenine

from its isotopically labeled analogue in bi-analyte experiments, thus successfully demonstrating single-molecule sensitivity.

6 Conclusion

In this overview, we have discussed various aspects of CRS with surface enhancement. The exciting developments in SERS technology have certainly been a strong motivation for using the principle of signal enhancement with plasmonic antennas for the CRS techniques. The early successes in SERS were quickly followed by proof-of-principle demonstrations of SE-CRS in the 1970s. However, a direct translation of experimental protocols that work well for SERS have not resulted in immediate successes in SE-CRS. In general, the experimentally determined enhancement factors in SE-CRS have been lower than what can be expected based on simple theoretical models.

Clearly, the decidedly different excitation conditions in SE-CRS compared with SERS require specific optimization of experimental parameters. The potential heating of the molecule in the plasmonic hotspot under pulsed irradiation is a serious problem. In addition, the plasmonic antenna itself produces background contributions under conditions typical for SE-CRS measurements, beyond what is commonly seen in SERS experiments. In this regard, the development of antennas designed to focus the pump and Stokes field to a common cavity, and that have strong radiative properties at the CRS signal frequency, is an important step in making SE-CRS a more practical technology. Another hurdle is the rather incomplete theoretical description of the joint response of the molecule and antenna in the SE-CRS experiments. A better description of the signal fields generated in SE-CRS would significantly help in the further improvement of experimental designs.

Despite the steeper challenges faced in SE-CRS compared with SERS, developments during the last 10 years or so have led to several breakthroughs. The experimental demonstrations of single-molecule detection in both SE-CRS and SE-SRS have not only opened up the possibility of improved sensing through SE-CRS, but also raised the possibility of performing controlled experiments on single vibrational oscillators. The ability to drive, manipulate and observe a single quantum oscillator with light at ambient conditions is significant, as it could set in motion a new wave of quantum science.

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