Vibrational pumping and heating under SERS conditions: fact or myth?

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We address in this paper the long debated issue of the possibility of vibrational pumping under Surface Enhanced Raman Scattering (SERS) conditions, both theoretically and experimentally. We revisit with simple theoretical models the mechanisms of vibrational pumping and its relation to heating. This presentation provides a clear classification of the various regimes of heating/pumping, from simple global laser heating to selective pumping of a single vibrational mode. We also propose the possibility of extreme pumping driven by stimulated phonon emission, and we introduce and apply a new experimental technique to study these effects in SERS. Our method relies on correlations between Raman peak parameters, and cross-correlation for two Raman peaks. We find strong evidence for local and dynamical heating, but no convincing evidence for selective pumping under our specific experimental SERS conditions.

1. Introduction

Surface Enhanced Raman Spectroscopy (SERS)[1,2] has recently been the subject of renewed interest, motivated in part by the observation of SERS from single molecules.[3,4]

The possibility of direct pumping of vibrations in molecules using SERS was first proposed in 1996.[5] In this early paper, vibrational pumping was inferred from experimental measurements of a quadratic power dependence of the anti-Stokes signal and from an anomalous anti-Stokes/Stokes ratio. The validity of this interpretation has been questioned by several groups and alternative explanations have been provided.[6–8] In particular, most experimental results such as anomalous anti-Stokes/Stokes ratios, could be explained by heating effects[7,9] and/or the influence of underlying plasmon resonances.[6–8,10] Despite these studies, the debate about 'heating *vs.* pumping' is still ongoing. We believe that the main issue is that 'heating' or 'pumping' can correspond to different physical realities, depending on the context, and they could even mean the same in some situations. For example, it is important to distinguish between global and local heating. In the first case, the whole system is in thermal equilibrium at a higher temperature than what it should be without laser excitation. In the second, the heating is localized to places where the laser is more absorbed; these places remaining out of thermal equilibrium with the rest of the system. Local heating can occur for example in the metallic SERS substrate (such as colloids), or even in the molecule. For the latter case, the molecule is at a higher temperature than its environment as a result of laser excitation, and the distinction between heating and pumping becomes blurred and a matter of vocabulary.

In this study, we aim to clarify some of the issues related to this debate. To do so, we first analyze the possible different regimes of vibrational pumping, which depend on how the pumping rate compares to other characteristic time scales of the system: vibrational relaxation, intramolecular vibrational relaxation or redistribution (IVR), and thermalization with the environment (solvent and metal). Different regimes are identified: selective pumping of a single vibrational mode (molecule not in internal thermal equilibrium), global pumping of all the modes (molecule not in

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equilibrium with its environment as a whole), or local or global heating of the molecule through thermalization with its environment. SERS experiments were carried out in colloidal solutions to try to find evidence for these regimes. To avoid the known problems associated with anomalous anti-Stokes/Stokes ratios, we studied instead the correlations in peak parameters on the Stokes side, during fluctuations of the SERS signal. The peaks show significant shifts, which are shown to be associated with a high internal temperature of the molecules. These shifts are also shown to be strongly correlated to the SERS intensity. This shows that the vibrational temperature of the molecule is directly correlated to the SERS intensity, and indicates that the molecules are *dynamically heated/pumped*. This can be the result of direct vibrational pumping and IVR, or through thermalization with the metal colloids. Cross-correlation measurements for two Raman peaks do not show any evidence of selective pumping of a single vibrational mode.

2. General considerations

In any Stokes Raman process a quantum of vibration is created in the molecule. If the Raman cross section and/or the laser power are large enough, it is then conceivable that phonons are pumped in the molecule at a faster rate than their relaxation rate. This reasoning was the basis for the original proposal of vibrational pumping under SERS conditions.[5] Although the experimental evidence presented in Ref. 5 has been questioned and re-interpreted since,[6–8] there is still no clear-cut argument against the existence of vibrational pumping.

2.1. Model case: a single harmonic mode

In a molecule at a temperature T, it is well known that the anti-Stokes (AS) signal I_A is related to the Stokes (ST) signal by a Boltzmann factor (we ignore here the correction due to the ω^4 dependence of the Raman cross-sections). More precisely, for a vibrational mode of a given energy $\hbar\omega$, the AS to ST ratio R is given by $R = \exp(-\hbar\omega/(kT))$, where k is the Boltzmann constant. For the subsequent discussion it is worth reminding at this stage the origin of this factor, which is sometimes subject to confusion. It is not a result of the vibration quanta following the Boltzmann statistics (which is wrong), nor is it an approximation to the Bose–Einstein occupation factor $n_v = (\exp(\hbar\omega/(kT)) - 1)^{-1}$, which gives the average population of the vibrational mode. It is in fact a result of the dependence of anti-Stokes I_A and Stokes I_S intensities on phonon occupations:

$$I_S = C(1 + n_v) \text{ and } I_A = Cn_v. \tag{1}$$

The constant C is the same for AS and ST because both processes have in general the same cross section. This is, however, no longer true for Resonance Raman Scattering (RRS), or in SERS conditions, because of the wavelength dependence of the SERS enhancements. The two expressions in (1) come from standard Raman scattering theory;[11] they can be understood simply by analogy with photon absorption and emission. The anti-Stokes process corresponds to the *absorption* of a phonon and is proportional to the phonon population. The Stokes process corresponds to the *creation* of a phonon. By analogy with photons, this can occur either by *spontaneous* (factor 1) or *stimulated* (factor n_v) creation. This simple aspect of stimulated phonon emission has often been overlooked when one works with the final result for the anti-Stokes/Stokes ratio, but it is one of our aims here to show that it can have some interesting implications. This is of course always present and accounts for the boson-character of vibrations in molecules: without the n_v factor in I_S, the AS/ST ratio would be a Bose–Einstein factor, and not a Boltzmann factor. In a situation of non-negligible vibrational pumping, it is also important to take this aspect into account, as we shall show later. For strong vibrational pumping, we could have $n_v \gg 1$, and stimulated emission of phonon dominates the Stokes signal.

In order to understand vibrational pumping, one needs to write rate equations to describe the dynamics of phonon populations. Previous models[5,6] have been limited to two-state systems and to average populations, where stimulated emission cannot be accounted for properly. Indeed, a vibrational mode with zero, one, or two phonons will behave very differently and it is therefore unlikely that the average population provides a good representation of the physical system. For example, an average population of 0.5 could mean that half of the molecules have 0 phonon and half have 1, or that 1/4 have two phonons and 3/4 have 0. This would lead to different dynamics. It is therefore more realistic, when possible, to enumerate all possible configurations of our molecules (microstates) and study the evolution of the number of molecules in each microstate. Considering only one vibration, we denote N_i the number of molecules with i quanta of vibration. It is known that vibrations can be thermally excited and relax. Let us denote γ_{exc} and γ_{rel} these rates. The rate equations for such a system in the absence of laser excitation could be written (equations are only shown for N_0, N_1, and N_2) as:

$$\frac{\mathrm{d}N_0}{\mathrm{d}t} = -\gamma_{\mathrm{exc}}N_0 + \gamma_{\mathrm{rel}}N_1, \tag{2}$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -\gamma_{\mathrm{rel}}N_1 + \gamma_{\mathrm{exc}}N_0 - 2\gamma_{\mathrm{exc}}N_1 + 2\gamma_{\mathrm{rel}}N_2, \tag{3}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -2\gamma_{\mathrm{rel}}N_2 + 2\gamma_{\mathrm{exc}}N_1 - 3\gamma_{\mathrm{exc}}N_2 + 3\gamma_{\mathrm{rel}}N_3. \tag{4}$$

The factor 2 and 3 in front of the γ's can be justified because of degeneracies. Leaving a factor of 1 everywhere does not affect the results at this stage. Solving the stationary state for these rate equations gives:

$$\frac{N_{i+1}}{N_i} = \frac{\gamma_{\mathrm{exc}}}{\gamma_{\mathrm{rel}}} = \alpha. \tag{5}$$

If N is the total number of molecules, we then have

$$N_i = N(1 - \alpha)\alpha^i, \tag{6}$$

and the average number of phonons is, therefore

$$n_v = \frac{1}{N}\sum_{i=1}^{\infty} iN_i = \frac{\alpha}{1-\alpha}. \tag{7}$$

Equating n_v to the Bose–Einstein factor for bosons, this gives us a relation between thermal excitation and relaxation of phonons:

$$\alpha = \frac{\gamma_{\mathrm{exc}}}{\gamma_{\mathrm{rel}}} = e^{-\frac{\hbar\omega}{kT}}. \tag{8}$$

The considerations above give us an alternative way of describing the temperature effect. There is a constant excitation and relaxation of phonons within any given molecule which creates the Bose–Einstein distribution, and the AS/ST ratio is as expected $R = \alpha$. γ_{rel} and γ_{exc} characterize the interactions of the vibrational mode with its environment. We can at this stage distinguish two contributions, which will be important for the rest of the discussion:

- Interaction with other vibrational modes: it is well known that vibrational energy can relax to other vibrational modes through Intramolecular Vibrational Relaxation or Redistribution (IVR).[12] This mechanism ensures that all vibrational modes are in thermal equilibrium with each other and that the molecule can therefore be described by a single temperature T_{mol}.
- Interaction with the environment of the molecule: this is mainly interactions with the solvent molecules, and for SERS with the metallic substrate.[13] These interactions lead to a constant exchange of energy between the molecule and the environment and ensures that the molecule is in thermal equilibrium with its environment.

It is straightforward to generalize this model to the case where Raman processes are excited in the molecule, and in particular to SERS. For this, we denote n_L the number of photons per unit time and unit area, which scales simply with the laser power. σ_{S} and σ_{A} are the cross sections for the Stokes and anti-Stokes scattering (we will allow them to be different, since it could be the case in SERS conditions). In this model, these cross sections already contain any enhancement factors (chemical or electromagnetic). With these notations, $\sigma_{\mathrm{S}}n_L\mathrm{d}t$ ($\sigma_{\mathrm{A}}n_L\mathrm{d}t$) is simply the probability that a molecule in the ground state (first excited state) undergoes Stokes (anti-Stokes) Raman scattering within dt. For a molecule which has already one quanta of vibration, this probability will be twice this value (one for spontaneous emission, one for stimulated emission). The rate equations can be modified accordingly by adding such terms.

Because of phonon stimulation the effective Stokes Raman cross section increases for molecules which are already excited. However, it is important to note that the effective anti-Stokes cross section also increases in a similar manner since it is proportional to the number of phonons already present. This is similar to the symmetry between absorption and stimulated emission of photons. In a laser, the threshold is reached by blocking absorption and enhancing emission. This is achieved by population inversion, and this is only possible because fermions are involved in the process and Pauli blocking can occur. Without inversion, absorption and emission would always balance each other. In Raman, population inversion has no effect, because only bosons are involved and no Pauli blocking occurs to create an imbalance between emission and absorption of phonons. We see easily in the rate equations that the only way to create an imbalance between emission and absorption is if Stokes and anti-Stokes cross sections are different. This is not normally the case, but it could happen under SERS conditions. This condition is a prerequisite to observe a 'threshold effect' associated to phonon stimulation.

This qualitative argument can be developed more quantitatively by solving the stationary state of the rate equations under laser excitation. We now have

$$\frac{N_{i+1}}{N_i} = \alpha\beta, \tag{9}$$

where

$$\beta = \frac{1 + \alpha^{-1}\phi_S}{1 + \kappa\phi_S}, \tag{10}$$

with

$$\phi_\mathrm{S} = \sigma_\mathrm{S} n_L {\gamma_\mathrm{rel}}^{-1} \tag{11}$$

and

$$\kappa = \sigma_\mathrm{A}/\sigma_\mathrm{S}. \tag{12}$$

If N is the total number of molecules, we then have:

$$N_i = N(1 - \alpha\beta)\,(\alpha\beta)^i. \tag{13}$$

The average number of phonons is now

$$n_v = \frac{1}{N}\sum_{i=1}^{\infty} iN_i = \frac{\alpha\beta}{1 - \alpha\beta}. \tag{14}$$

The calculations can be carried on to express I_S, I_A, and R. In particular, we obtain $R = \alpha\beta\kappa$. The solution is therefore the same as without the laser, only changing α for $\alpha\beta$. Moreover, at low laser power, *i.e.* when $\phi_\mathrm{S} \ll (\alpha,\kappa^{-1})$, $\beta \approx 1$, and we come back to the previous solution, which means that pumping is negligible. In this limit $\phi_\mathrm{S} \ll 1$, this model is in fact equivalent to previous models,[5,6] although the interpretation can be different.

The most interesting aspects of these rate equations is that they become unstable for $\alpha\beta \geq 1$. This defines a threshold for a phonon stimulation 'explosion'. This condition can be expressed as:

$$\phi_\mathrm{S}(1 - \kappa) \geq 1 - \alpha \tag{15}$$

It is interesting to see that this can only happen if $\sigma_\mathrm{S} > \sigma_\mathrm{A}$ and n_L is large enough. This is equivalent to the population inversion condition in a laser. Such a condition could in principle be met under SERS conditions. The underlying plasmon resonances can lead to the required imbalance between σ_S and σ_A, leading to a small κ. In general, $\alpha \ll 1$, so for typical values of $n_L \approx 10^{24}$

photons cm^2 s^{-1} and $\gamma_{\text{rel}}{}^{-1} \approx 10$ ps, we would need $\sigma_{\text{S}} \geq 10^{-13}$ cm^{-2} under SERS conditions. This figure is towards the highest limit of estimates found in the literature for single molecule SERS, but it is not impossible that the threshold condition could be met for some events under SERS or SERRS conditions.

If the condition is met, it means that the average phonon population will diverge to infinity. It is possible to model some transient trajectory using Monte Carlo techniques, and one finds that the phonon population tends to fluctuate and quickly build up within 10–1000 $\gamma_{\text{rel}}{}^{-1}$. In practice, there are obviously physical limitations to this divergence. First, the molecule would break up when the number of phonons reaches a given threshold (at most, when the vibrational energy compares to the ionization energy). Such photo-dissociation induced by strong vibrational pumping has been observed for small molecules in other contexts.[14–16] Photo-bleaching is a well-known effect in the context of SERS, but it may have other origins and there are no evidence so far that it could be a result of strong vibrational pumping. Most probably, the main effect preventing a catastrophic ‘explosion’ by phonon stimulation is the anharmonicities of the vibrational modes. The picture presented so far of phonons being perfect bosons is obviously an approximation. It gives a good description of phonon populations in the limit of weak pumping, $\phi_{\text{S}} \ll 1$ and the results are then equivalent to previous models[5,6] although the interpretation is different. It also led to some interesting new possibilities such as bond breaking by stimulated phonon emission. However, we will now try to adapt this model to more realistic cases.

2.2. Effects of anharmonicities

Corrections to the picture of perfect bosons are needed to account for the anharmonicity of the potential. These anharmonicities introduce terms of order 3 or more in the Hamiltonian describing the vibrations. These terms produce a number of effects:

- There are small corrections in the energies of states $n \geq 2$, which are in general slightly red-shifted compared to their normal value relative to the ground state of $n\hbar\omega$.
- The lifetimes of vibrations in $n \geq 2$ are decreased compared to $n = 1$ due to increasing coupling to the other vibrational modes, which leads to IVR.
- For large n, the harmonic oscillator description becomes irrelevant. In particular, there is an energy threshold above which the vibrational excitation will break the molecule.

It is possible to take into account phenomenologically some of these effects by introducing relaxation rates γ^n_{rel} and excitation rates γ^n_{exc} which increase with n. To keep the model simple, we also assume that $\gamma^n_{\text{rel}}/\gamma^n_{\text{exc}} = \alpha$ for all n. This ensures that the thermal equilibrium is not affected and that without illumination the vibrations follow the Bose–Einstein statistics. The rate equations from the previous section can then be modified accordingly and this leads for the stationary state to:

$$\frac{N_{i+1}}{N_i} = \frac{\gamma^{i+1}_{\text{exc}} + \sigma_{St} n_L}{\gamma^{i+1}_{\text{rel}} + \sigma_{As} n_L} = \alpha\beta_{i+1}, \tag{16}$$

where

$$\beta_i = \frac{1 + \alpha^{-1} a_i^{-1} \phi_S}{1 + \kappa a_i^{-1} \phi_S}, \tag{17}$$

with $a_i = \gamma^i_{\text{rel}}/\gamma^{i-1}_{\text{rel}}$ and $a_1 = 1$. For $i > 1$, $a_i > 1$ and it represents the increase in relaxation rates from level $i - 1$ to level i because of anharmonicities. In this framework, the effect of anharmonicities is to effectively decrease the incident laser power by a factor of a_i for processes between level $n = i - 1$ and $n = i$. If a_i increases monotonically with i, we now see that $\alpha\beta_i$ will always be smaller than 1 for sufficiently large i and there is no longer the possibility of a threshold of stimulation as observed before. However, depending on the exact variation of a_i and the incident laser power, a significant phonon pumping can still occur, and may be enough to break the molecule. Because of the lack of experimental values for γ^i_{rel}, it is very difficult to make quantitative predictions. We will not develop further this model here but only emphasize one important aspect: when the conditions are such that there is a significant phonon pumping in one mode, a large proportion of the energy pumped in this mode is actually relaxed to other modes through IVR. This is what prevents the ‘explosion’ condition to occur and is reflected in the increasing values of γ^i_{rel} because of anharmonicities. This means that when one mode is strongly pumped, all the other vibrational modes could also be pumped indirectly through IVR (or equivalently thermalization of the molecule). The relative values of the IVR and pumping rates will determine whether the vibrational modes of the molecule are in thermal equilibrium or not. If pumping is strong enough, then one mode could be significantly pumped and be at an effective temperature higher than the other modes. Such an internal non-equilibrium of a molecule can be directly observed in another context in time-resolved Raman spectroscopy under pulsed excitation.[12] If IVR rates dominates, then, despite the strong pumping of only one or two modes, energy is redistributed through IVR and the vibrational modes remains in thermal equilibrium with each other as if all the vibrational modes were pumped together. These two different scenarios have not been distinguished in the literature before to the very best of our knowledge.

2.3. The various regimes of pumping and heating

The simple models and considerations presented so far now enable us to identify several regimes of pumping/heating for molecules in SERS conditions. To describe a possible non-thermal equilibrium, we will assign a temperature to each part of our system. In SERS, the metallic substrate (or colloid) plays an important role, and its temperature is denoted T_{met}. The environment, in general water or air, is assigned a temperature T_{env}. The average phonon populations in each vibrational mode of a molecule can define an effective mode temperature T_i^{eff} for each mode i. When the vibrational modes are in thermal equilibrium with each other, then all T_i^{eff} are equal and define the molecule temperature T_{mol}.

We will now identify possible regimes of increasing thermal non-equilibrium. We will see that for some of these regimes, whether we call them ‘heating’ or ‘pumping’ is really a question of vocabulary, and that the descriptions in terms of thermal equilibria are more accurate.

(1) For an unperturbed system, say with sufficiently small laser power, the whole system is in thermal equilibrium at room temperature $T_{\mathrm{room}} = T_{\mathrm{env}} = T_{\mathrm{met}} = T_{\mathrm{mol}}$.

(2) As the laser power is increased, more energy is dissipated into the system and it can increase locally the temperature. The most common situation, and the one most probably referred to as ‘heating’, is when this results in a higher temperature for the whole system, which still remains in thermal equilibrium: $T_{\mathrm{env}} = T_{\mathrm{met}} = T_{\mathrm{mol}} > T_{\mathrm{room}}$. There is a ‘global heating’.

(3) However, when the sources of heat (where light is absorbed) are localized, this could result in non-equilibrium inside our system. This is particularly relevant to SERS, where most absorption is likely to occur in the metal. Depending on the relative values of absorption rate, thermal conductivity and heat capacity, we can have a situation where $T_{\mathrm{met}} > T_{\mathrm{env}}$. This is very different to the previous case, in particular for colloidal solutions. In regime 2, the system is at a *constant* stationary temperature $T_{\mathrm{env}} = T_{\mathrm{met}}$ determined by the laser power. In regime 3, T_{env} is also stationary but T_{met} can be strongly colloid-dependent. Size and shape will affect light absorption, obviously because of different volume, but also because of different plasmon resonance conditions. Because colloids are constantly moving by Brownian motion, the local temperature T_{met} of the observed colloid(s) then becomes time-dependent. Because the adsorbed molecule interacts much more with the metal than with the solvent or air, we have in this case $T_{\mathrm{mol}} = T_{\mathrm{met}} > T_{\mathrm{env}} \geq T_{\mathrm{room}}$. There is a ‘local heating’ and, for colloidal solutions, ‘dynamical heating’.

(4) Now, if we assume that the SERS cross section are such that vibrational pumping can occur in the molecule, this represents another localized heat source in the system. Pumping means that the molecule is now out of thermal equilibrium with its environment, both solvent and metal. When IVR rates dominate over pumping rates, the molecule can still be assigned a temperature $T_{\mathrm{mol}} > T_{\mathrm{met}} \geq T_{\mathrm{env}} \geq T_{\mathrm{room}}$. Because the SERS enhancement is mediated by the plasmon resonances, T_{mol} would then be time-dependent as in the previous case. This situation could be obtained either by pumping of all vibrational modes or by the combination of pumping of one single mode (with a high cross section) and fast IVR. This situation corresponds to ‘local and dynamical heating/pumping’ of the molecule.

(5) Finally, we have seen that the pumping rate of one mode (say $i = 1$) could be higher than IVR rates. This mode would then be out of equilibrium with the rest of the molecule (other vibrational modes): $T_1^{\mathrm{eff}} > T_{\mathrm{mol}} \geq T_{\mathrm{met}} \geq T_{\mathrm{env}} \geq T_{\mathrm{room}}$. We then have ‘selective pumping’ of a single vibrational mode.

We have therefore identified 5 regimes from 'no heating' (1), through 'global heating' (2), to 'pumping' (5). The other regimes may be described as 'local heating in the metal' (3), and 'molecule heating through pumping' (4).

We will now try to determine the relevant regime for a particular experimental case of SERS in colloidal solutions.

3. Experimental results

3.1. Determination of mode temperature

In order to determine which regime we are in, it is necessary to devise techniques which measure the various local temperatures in our system. In SERS experiments, the most readily accessible signals are obviously the SERS signals from the molecules. The easiest way to determine temperature from a Raman signal is to measure the anti-Stokes to Stokes ratio. This has been widely used before in SERS, but it presents a severe flaw in SERS conditions: the SERS cross section of AS and ST processes can be very different and sometimes fluctuating in SERS conditions, and this leads to anomalous ratios and erroneous temperatures. The main reason for this difference is the SERS enhancement mechanisms, mediated by plasmon resonances, which can be strongly wavelength dependent. In most cases, these plasmon resonances cannot be characterized with sufficient accuracy to correct for AS/ST ratio anomalies and infer the temperature. Moreover, in colloidal systems, the shape, size, and orientation of the colloid(s) in the scattering volume are constantly changing with time, affecting constantly the SERS enhancement factors.

For these reasons, we present here an alternative way of determining the mode temperature in a molecule. This is based on the fact that the main properties of a Raman peak, frequency and line-width, are temperature dependent. In general, as temperature increases, the peaks tend to red-shift and broaden slightly. These effects are due to the anharmonicities of the potential and are small and peak-dependent. However, they can easily be observed using a high resolution grating, such as 1800 lines cm^{-1} or larger in a single spectrometer. To test this technique, we carried out temperature-dependence experiments on Rhodamine 6G (RH6G) adsorbed on a silicon substrate. The substrate temperature was varied from 295 to 380 K using a heating stage, and Raman scans were collected exciting with a 633 nm, at low excitation density to avoid photodecomposition. We monitored the main Raman peaks at 612, 1362, 1511, and 1650 cm^{-1}, and for each of them determined the frequency and line-width by fitting a Voigt profile. The temperature dependence of the frequency and line-width is shown in Fig. 1 for the 1511 (a) and 1650 (b) cm^{-1} modes. It is clear that both peaks red-shift as the temperature is increased, with shifts as large as 4 cm^{-1} measured for the 1511 cm^{-1} mode. There is a concomitant broadening of the peaks, by as much as 50%.

As the temperature is increased, more and more excited vibrational states are populated. For these high energy modes, the population in the excited states remain negligible and it is unlikely that they could affect so dramatically the peak shape. However, for lower energy modes, significant population of the excited states can occur. We believe that the measured shifts and broadening for the 1511 and 1650 cm^{-1} modes are a result of the coupling to the lower energy modes, which are strongly affected by temperature; *i.e.* they are the result of inter-mode coupling. Because the molecule is in thermal equilibrium, the shifts and broadening observed in all peaks should be strongly correlated and directly related to the molecule temperature. In Fig. 1(c) is shown a plot of the frequency of the 1511 cm^{-1} mode against that of the 1650 cm^{-1} mode for the various temperatures considered here. The correlation is clear, and we also see that the shifts for the 1511 cm^{-1} mode are approximately twice as large as for the 1650 cm^{-1} mode. This means that the 1511 cm^{-1} mode must be more coupled (through anharmonicities) to other low energy modes than the 1650 cm^{-1} mode. This assertion is consistent with the larger line-width of the 1511 cm^{-1} mode at room temperature (20 meV compared to 12 meV). The 1362 cm^{-1} mode (with a line-width of 12 meV at room temperature) exhibits a behavior similar, qualitatively and quantitatively, to the 1650 cm^{-1} mode (not shown). The 612 cm^{-1} mode, on the other hand, with a line-width of only 5 meV at 300 K exhibits a smaller red-shift of less than 1 cm^{-1} at 360 K. Finally, in all these experiments, the signal was lost at a temperature around 370 K, which is probably due to a heat-induced desorption or chemical reaction related to water in the environment.

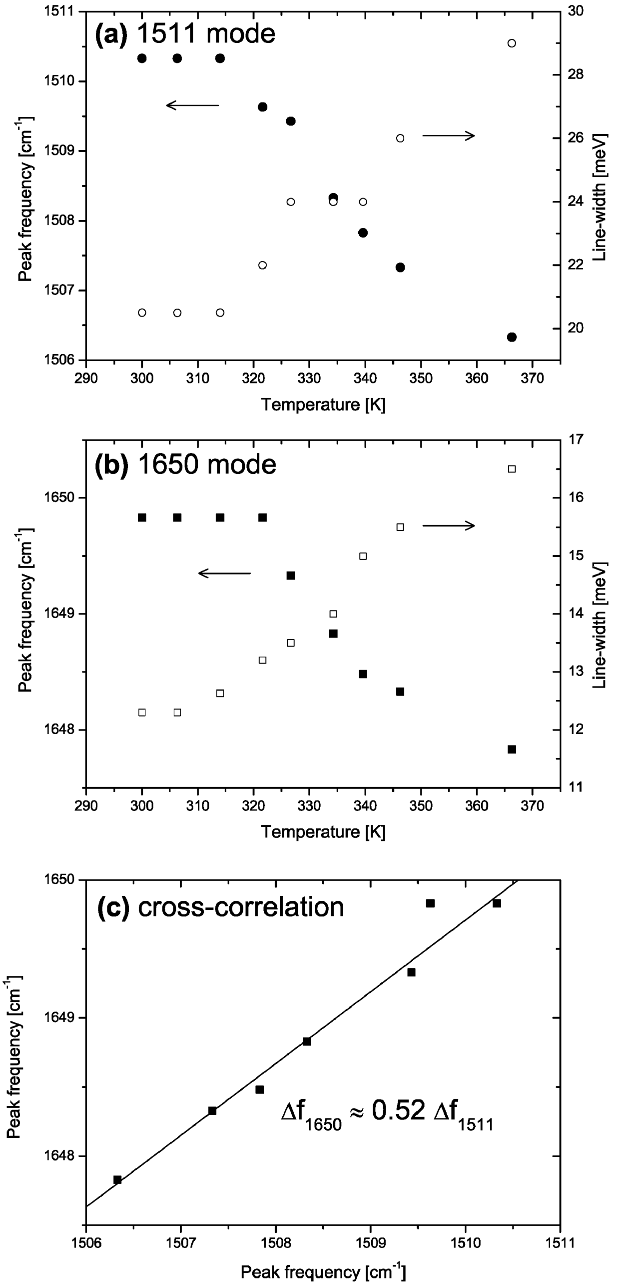

Fig. 1 Temperature dependence of the Raman spectra of Rhodamine 6G dried on silicon. (a) Peak frequency (solid symbols) and line-width (open symbols) of the 1511 cm^{-1} mode as a function of temperature. (b) Same as (a) for the 1650 cm^{-1} mode. (c) Correlation between peak frequencies of these two modes.

We can draw several conclusions from this simple experiment.

- Raman peak shift and broadening can be used as an alternative to AS/ST ratios to measure the molecule temperature. Even in cases where an absolute temperature cannot be derived from the shifts (this requires a preliminary calibration), relative temperature changes can still be inferred from different red-shifts.

- The shifts and broadenings are a result of anharmonicities and in particular of coupling to lower energy modes.
- If the molecule is in thermal equilibrium, there is a very strong correlation between the frequency shifts and broadenings of different modes. These properties are in principle determined only by temperature and inter-mode coupling.

3.2. Local temperature for SERS in colloidal solutions

We will now apply the results of the preceding section to study colloidal solutions in SERS conditions. Silver colloids were prepared according to standard methods.[17] The colloids have an average radius of $a = 30$ nm, as measured by dynamic light scattering in solution and electron microscopy of dry colloids. They exhibit an absorption spectrum peaking at 454 nm. Spheres of $a = 30$ nm should have a resonance around 430 nm, and the observed small red-shift is attributed to small variations in the shape of the particles. The colloid concentration is estimated to be around 10^{11} colloids cm^{-3}. The samples were prepared by mixing 0.5 mL of colloidal solution with 0.5 mL of KCl (concentration 20 mM). After several hours, the dye (RH6G) was added to a concentration of 0.2 μM, which corresponds to a few thousand dye molecules per colloids. The KCl concentration was chosen such that no colloid aggregation occurs and the samples are therefore stable for several weeks at room temperature. However, the addition of KCl is important to screen the repulsive forces between colloids, making the occurrence of colloid interactions (closely spaced pairs) more likely either by dynamical collisions or by creation of stable dimers. This is enough to observe a large increase in the SERS signal, which strongly profits from coupled plasmon resonances. SERS measurements were carried out on a confocal Raman spectrometer, using a ×100 immersion objective and exciting with a 633 nm HeNe laser. Raman spectra are recorded in a multi-channel configuration using a cooled CCD detector.

Under these conditions, there is on average just under one colloid/cluster in the scattering volume at a time. The diffusion coefficient of the colloids is around $D = 8$ μm^2 s^{-1}, and the diffusion time across the scattering volume is in the range $\tau = 0.2{-}0.5$ s. We therefore use an integration time of 0.1 s. This ensures that each event corresponds to the signal coming from only one, or may be two colloids/clusters. We then record the SERS spectra as a function of time. Low intensities correspond to cases where the probed colloid/cluster was not highly SERS active, or where no colloid was present, except may be at the periphery of the scattering volume. Large intensities correspond to a colloid/cluster which was strongly SERS active, *i.e.* with a plasmon resonance close to the laser wavelength. Given the relatively high dye concentration, it is likely that the signal comes from many dyes on the surface of the SERS-active colloid, but we cannot exclude the presence of a strong hot-spot on this particular colloid/cluster resulting in a strong signal from a single dye.

In order to measure the dye temperature for each event, we measure the frequency shifts of the Stokes peak of a given mode. However, when monitoring only one mode, it is difficult to interpret the result because it is not possible in this case to say whether this mode is selectively pumped (regime 5) or if the molecule is simply at a higher temperature (regime 3 or 4). For this, we believe it is necessary to monitor two Raman peaks at the same time and to study the correlations between the parameters of these two peaks. To combine a high resolution and the ability to observe simultaneously two peaks, the peaks need to be relatively close to each other. Such correlations studies are possible for example with Rhodamine 6G, between the 1511 and 1650 cm^{-1} modes, and between the 1511 and 1362 cm^{-1} modes, respectively.

We carried out correlation measurements for these two pairs of modes, by analyzing 1000 successive Raman spectra. The peak properties and intensities are extracted for each spectrum using Voigt fits and the results can then be summarized in correlation plots for relevant parameters. Such plots are shown in Fig. 2 for the 1511/1650 cm^{-1} mode correlations. As seen in Fig. 2(a–d), there is a clear correlation for both peaks between red-shift, broadening, and intensity. Moreover, Fig. 2(e) shows an even stronger correlation between frequency shifts of 1511 and 1650 cm^{-1} modes. In the light of the results of the previous section, this indicates that:

- the probed molecules are in thermal equilibrium at a temperature T_{mol},
- T_{mol} vary widely between each event,
- T_{mol} is strongly correlated to the SERS intensity.

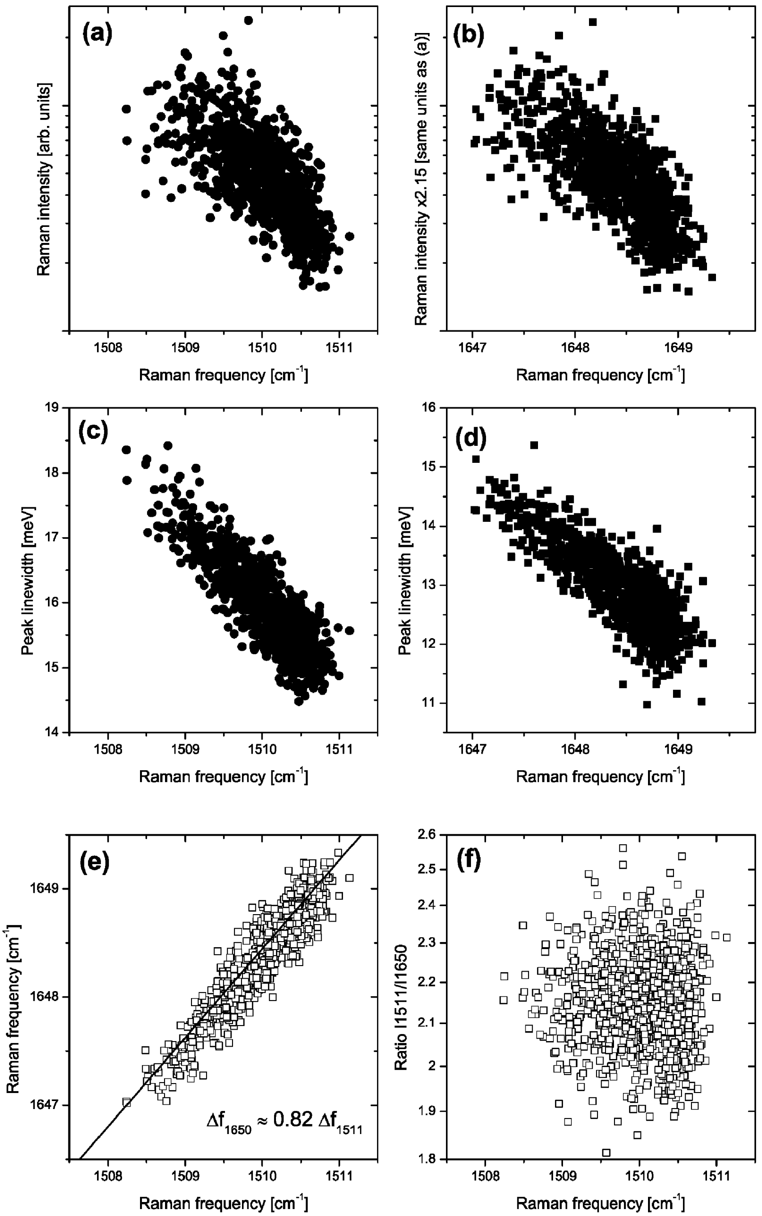

Fig. 2 Cross-correlation plots of the properties of the 1511 and 1650 cm^{-1} peaks. (a) SERS intensity *vs.* peak frequency for 1511 cm^{-1} mode. (b) Same as (a) for 1650 cm^{-1} mode. A scale factor of 2.15 was applied to the intensity so that the average intensity is the same as in (a), the intensity axis scale and units are the same in (a) and (b). (c) Line-width *vs.* peak frequency for 1511 cm^{-1} mode. (d) Same as (c) for 1650 cm^{-1} mode. (e) Correlation between 1511 and 1650 cm^{-1} peak frequencies. (f) Correlation between the ratio of intensities of 1511 over 1650 cm^{-1}, and the 1511 cm^{-1} peak frequency. For all plots, events on the left-hand side correspond to 'hot ' events.

Moreover, it is well known that the relative intensities of the Raman peaks can fluctuate in SERS conditions. It is interesting to see if these fluctuations are correlated with T_{mol} (or equivalently the SERS intensity). The ratio of the intensities of the 1511 and 1650 cm^{-1} modes is plotted in Fig. 2(f)

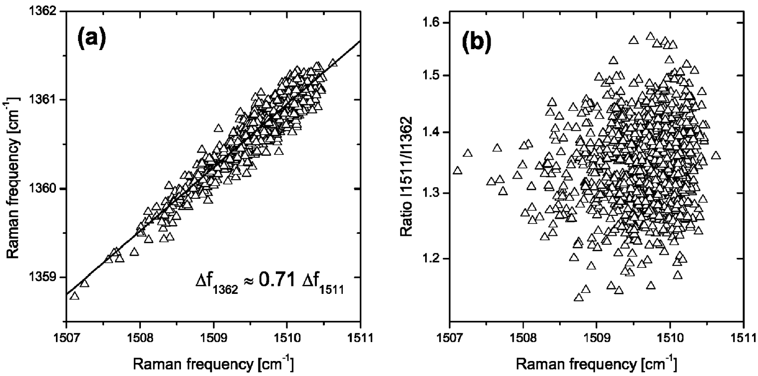

Fig. 3 Cross-correlation plots of the properties of the 1511 and 1362 cm^{-1} peaks. (a) Correlation between peak frequencies. (b) Ratio of peak intensities against peak frequency. No correlation is observed in this plot showing that high intensity (or 'hot') events do not favor one peak with respect to the other.

against the 1511 cm^{-1} peak frequency (on a log plot to retain the symmetry between 1511 and 1650 cm^{-1} modes). Note that the 1511 cm^{-1} peak frequency on the x-axis is an indirect measure of T_{mol}. The intensity ratio remains in the range 2.2 ± 0.4, which is a consequence of the correlation between intensities of the two modes. The variations in this range are attributed to the underlying plasmon resonances, which are different for each individual events, and can increase or decrease slightly the SERS cross-section of one peak with respect to the other. The average ratio of 2.2 reflects the intrinsic ratio of cross-sections of these two peaks for RH6G adsorbed on silver convoluted with the average effect of the plasmon resonances. From Fig. 2(f), we see that the fluctuations of this ratio are not correlated to the 1511 cm^{-1} peak frequency (and therefore to T_{mol}). This indicates that there are as many hot events with a high ratio than hot events with a low ratio for these modes. The same conclusion holds for cold events. This is another argument against selective pumping of one of these two peaks. If it were the case, stronger events would correspond to stronger pumping and one of the peaks should become even more prominent as the event intensity increases. This would result in a correlation between peak ratio and T_{mol}. Similar results are obtained for the correlations of the 1511 and 1362 cm^{-1} modes, as shown in Fig. 3.

These results seem to exclude the possibility of selective pumping in these modes (regime 5) under the present SERS conditions. However, they do show evidence for significant heating/pumping. T_{mol} for the highest events can be estimated to be around 360 K, much larger than room temperature. More importantly, T_{mol} fluctuates between each event, on a time scale smaller than a second. This excludes the possibility of global heating of the environment by the laser (regime 2), which would give a constant (higher) temperature. The two remaining possibilities, regimes 3 or 4, are, however, very difficult to distinguish. They both correspond to local and dynamical heating. In the first case, hot events are a result of strong light absorption in the colloid, resulting in colloid heating, and therefore a high T_{mol}. The strong absorption would be due to a resonance between the plasmon and the laser, which is also necessary for high SERS enhancements, hence the correlation between SERS intensity and T_{mol}. Regime 4 could equally explain the results. When the SERS intensity is high, there could be a significant pumping of vibrations, either pumping in all modes, or in only a few modes followed by fast IVR. This would also result in a correlation between SERS intensity and T_{mol}. The answer to this would require an independent way of monitoring the colloid temperature. Another approach could be to theoretically study the plasmon resonances, and determine whether high SERS enhancements are necessarily associated with large absorption in the metal. Despite this remaining open question, our results show unambiguously the presence of strong *local* heating in SERS.

Finally, two more remarks about these results:

- It is interesting to note that the maximum molecule temperature inferred from these plots is around 360 K, close to the temperature where the signal disappeared under normal conditions. In similar experiments at higher laser power (3 times larger), we observed the same limit. Therefore, there seems to be a threshold for the local temperature, above which the molecules do not survive, or desorb from the surface.

- The correlation between the red-shifts of the peaks in Figs. 2(e) and 3(a) is slightly different to that observed in non-SERS conditions in Fig. 1(c). The relative red-shifts of the 1650 and 1362 cm^{-1} modes with respect to that of the 1511 cm^{-1} mode are larger than expected. We attribute this change to different inter-mode coupling strengths when RH6G is adsorbed on silver as opposed to silicon. This could be the result of a different adsorption mechanism or adsorption energy.

3.3. Consequences on AS/ST ratios

Anomalous AS/ST ratios in SERS conditions are common and have been explained as a result of one or both of the following effects:

- The relative cross sections of AS and ST processes can be different and possibly fluctuating because of the wavelength dependence of the plasmon resonances.
- Heating of the molecule or vibrational pumping can increase the population of the vibrational states and therefore the measured AS/ST ratio.

Because we used an alternative technique to assess the importance of the second effect, we can now estimate its contribution to the AS/ST ratio anomalies.

To do so, we concentrate on the correlation measurements of the 1511/1650 cm^{-1} modes. We then determine the temperature of each of the 1000 events. This is achieved in the following way: we assume that the red-shift for the 1511 cm^{-1} mode is a linear function of the temperature, and that the minimum and maximum temperatures are, respectively, 295, and 360 K. The same procedure is applied to the red-shift of the 1650 cm^{-1} mode, which leads to a second estimate of the temperature. We then take the average of the two estimates as the event temperature. Because of the strong correlation shown in Fig. 2(e), both estimates are similar, but this procedure enables us to reduce experimental errors. For each event, we also know the SERS intensity of the Stokes process. Using the event temperature, and the Boltzmann factor, we can deduce the intensity of the corresponding anti-Stokes process, under the assumption that the cross sections are identical. We then sum the AS intensities of the 1000 events and the corresponding ST intensities and derive a predicted AS/ST ratio. This is the ratio which should be measured if the SERS cross sections were the same for ST and AS. For the 1511 (1650) cm^{-1} mode we obtain a ratio of 2.0 (2.1) times higher than its theoretical value in the absence of local heating ($T_{\mathrm{mol}} = 295$ K). This corresponds to an effective or average temperature of 325 K. Much larger AS/ST anomalies, with factors of 50 to 100, have been reported. In particular, for the present SERS conditions, we have measured anomalies by a factor of 10 to 50 for these two modes.[10] This is a clear demonstration that heating/pumping alone cannot explain these anomalies and that the SERS-induced imbalance between the AS and ST cross-section is the dominant contribution in most cases. This asymmetry in cross sections from the Stokes to the anti-Stokes side due to the underlying plasmon resonances is the subject of intense interest in SERS.

4. Conclusion

The purpose of this paper was twofold. The first goal was to clarify the issue of 'heating/pumping' in SERS by providing simple models leading to a classification of the possible various regimes. By concentrating on the thermal equilibria between the different sub-systems, we were able to provide a more detailed description of the problem, with 5 distinct regimes rather than the usual vague opposition between 'heating' and 'pumping'. This framework also led to the discussion of other interesting aspects, such as stimulated emission of vibrations, of which there is no experimental evidence at the moment. Secondly, we have presented and applied an alternative technique for the study of these problems. This relies on the study of the correlations between parameters of the Stokes Raman peaks. This method avoids the problems associated with anomalous AS/ST ratios and further clarifies the use of peak correlations to address issues of pumping/heating in SERS. By studying the correlations between two Raman peaks, it is also possible to test for the occurrence of selective vibrational pumping in one mode. We found no evidence for this under our experimental conditions. However, we showed clear evidence for a significant local and dynamical heating for SERS in colloidal solutions.

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