# Temperature Dependence of the Homogeneous Broadening of Resonant Raman Peaks Measured by Single-Molecule Surface-Enhanced Raman Spectroscopy

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ABSTRACT: The temperature dependence of the homogeneous and inhomogeneous broadenings of the 590 cm^{-1} Raman peak of the dye Nile Blue (excited at 633 nm) was measured by means of single-molecule surface-enhanced Raman spectroscopy (SM-SERS). In the investigated temperature range (298−77 K), frequency variations among single molecules are the dominant contribution to the inhomogeneous broadening, with a negligible temperature dependence. By contrast, the homogeneous broadening of SM spectra shows a sharp decrease at low temperatures, down to ∼0.9 cm^{-1}, a remarkably low figure. The temperature dependence of the homogeneous broadening follows the predictions of the vibrational energy exchange model (VEE), with exchange modes at ∼160 cm^{-1}, close to the Debye frequency of Ag, suggesting anharmonic coupling of the molecule with the substrate. SM-SERS provides a unique tool for observing a yet inaccessible fundamental aspect of vibrational spectroscopy of molecules, that is, anharmonic interactions of a single adsorbed molecule on a surface.

SECTION: Kinetics, Spectroscopy
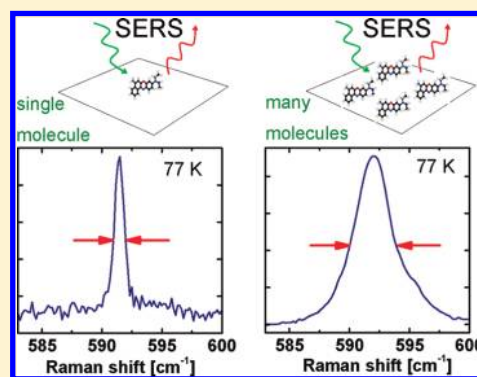
A basic concept in spectroscopy (Raman in particular) is that of homogeneous/inhomogeneous broadening of peaks.[1] While the former has its origin in intramolecular anharmonic interactions and is a fundamental property of a vibration of an isolated molecule, the latter is representative of a population of molecules and their inevitable variabilities at different places in the sample. Hence, inhomogeneous broadenings are due to either intermolecular interactions or slightly varying interactions on a substrate. Instrumental broadenings, produced by the finite resolution of spectrometers, are an added ingredient to the actual measured width of a Raman peak, but they are not (as such) fundamental, that is, they can be controlled by the chosen spectral resolution. Surface interactions can introduce small perturbations in the electronic structure of adsorbed molecules. A small ∼1% perturbation of the molecular equilibrium state is expected to result in a vibrational frequency shift of the same magnitude and therefore on the order of ∼5 cm^{-1} for a typical low-frequency Raman mode at ∼500 cm^{-1}. The inhomogeneous broadening can be, therefore, a substantial contribution to the actual measured peak width (asuming the instrumental resolution to be <1 cm^{-1}, which is easily achieved). Being able to measure the intrinsic homogeneous broadening of a Raman mode is interesting for several fundamental reasons. The homogeneous broadening is ultimately related to the anharmonic interactions that are at the heart of both the population (T_1) and dephasing (T_2') relaxation times (typically measured with ultrafast optical techniques[2]). Anharmonic interactions also play a fundamental role in the relaxation pathways of vibrations toward equilibrium, that is, on

how the energy is distributed over time once a vibration has been excited[3] (also called intramolecular vibrational relaxation, IVR). Intrinsic anharmonic interactions tend to dominate the relaxation pathways of vibrations for many molecules,[4] but interactions with the susbtrate can provide additional pathways that dominate the relaxation in other cases.

The temperature (T) dependence of the homogeneous width of a Raman mode provides information on the anharmonic coupling of that particular mode with the rest of the vibrations and/or the substrate[5] and becomes potentially explainable by density functional theory (DFT) calculations of anharmonic couplings. Accordingly, the most important bottleneck to access the simpler picture of the spectroscopy of molecules with homogeneous contributions is to develop the experimental tools to obtain the data. From the point of view of conventional Raman spectroscopy, the intrinsic homogeneous broadening is very seldom accessible for molecules in liquids or on surfaces. The reason is that (even if all instrumental contributions are eliminated) we cannot turn "off" the interactions with other molecules (or the substrate) at will. Furthermore, any real measurable signal will always imply the monitoring of (at least) ∼10^4−10^6 molecules. The only way to disentangle the contributions to the inhomogeneous broadening in this situation is to either measure individual molecules or to perform time-resolved coherent

experiments (with a natural increase in complexity). Hence, a rare but important exception to the rule is provided by the field of single-molecule surface-enhaced Raman spectroscopy (SM-SERS).[6−13] After a slow progression since the original reports,[14,15] SM-SERS is now an established technique that can address issues beyond the mere demonstration of single-molecule sensitivity.[13,16−23] SM-SERS allows for the detection of the intrinsic homogeneous broadening of a Raman peak of a molecule on a surface. In refs 10 and 18, a systematic study of the origin of the inhomogeneous broadening in SM-SERS spectra (and the origin of frequency variations) was carried out. Moreover, an important application of SM-SERS to disentangle the inhomogeneous contributions to the Raman excitation spectrum has also been demonstrated in ref 24. Here, we make use of this approach to measure the temperature dependence of the homogeneous broadening of a Raman mode of single molecules adsorbed on Ag surfaces.

To this end, SM-SERS experiments have been carried out for the dye Nile Blue (NB) excited resonantly at 633 nm, focusing, in particular, on the ~590 cm^{-1} Raman mode. The conditions under which SM-SERS can be observed in this system have been previously studied in detail.[18,23,25] Briefly, the samples consisted of Si wafers covered by a thin layer of poly-L-lysine (1%-by weight in H_2O) on which Ag colloids + dye solution were drop-casted and siphoned off after ~15 min (leaving a sparse collection of clusters on the surface).[18] For different spatial maps, we used both citrate-reduced Lee & Meisel[26] and borohydrate reduced Ag colloids;[27] comparable results were obtained with both. Solutions were prepared as follows: 0.475 mL of Ag colloids and 0.475 mL of 20 mM KCl solution were mixed and left to rest for 40 min. KCl promotes the formation of small aggregates necessary to observe large SM-SERS signals.[28] The final solution was then prepared by adding 50 μL of 100 nM NB, achieving a final dye concentration of 5 nM. Raman spectra were acquired using a Jobin-Yvon Labram spectrometer with a ×100 long working distance objective (NA = 0.6) with excitation at 633 nm (2.5 mW on the sample) and a high-resolution 2400 L/mm grating. The latter allows one to distinguish small frequency variations as well as individual contributions from more than one molecule to the line width.[18] The temperature was varied from 77 K to room temperature with a Linkam-Scientific THMS600 stage for optical microscopy, which keeps the sample under a N_2 atmosphere. SM-SERS spectra were obtained from several spatial maps of 30 × 30 scans with varying steps (1−5 μm) and 1 s integration time per point; 3600 spectra were acquired at each T. Each spectrum was fitted with a pseudo-Voigt line shape. A large number of low-intensity events (below noise level) were then discarded as they corresponded to locations with no signals. This large amount of "waste" is unavoidable to ensure the single-molecule nature of the remaining observable spectra. In fact, given the experimental conditions described above, we know from previous studies[18,23,25] that a largest fraction of these are indeed SM events.

Figure 1a−e shows a representative collection of SM-SERS spectra at different T's, where the frequency variations can be easily appreciated, together with the change in the intrinsic broadening of the peaks. Average spectra are also shown in Figure 1f. Clearly, the frequency variations are the dominant contribution to the inhomogeneous broadening (i.e., that of the average). A more detailed statistical analysis based on pseudo-Voigt fits was done to further reveal the T dependence of both homogeneous broadening and frequency shifts. To this end, we used the full widths at half-maximum (fwhm) Γ obtained from the fits to discriminate
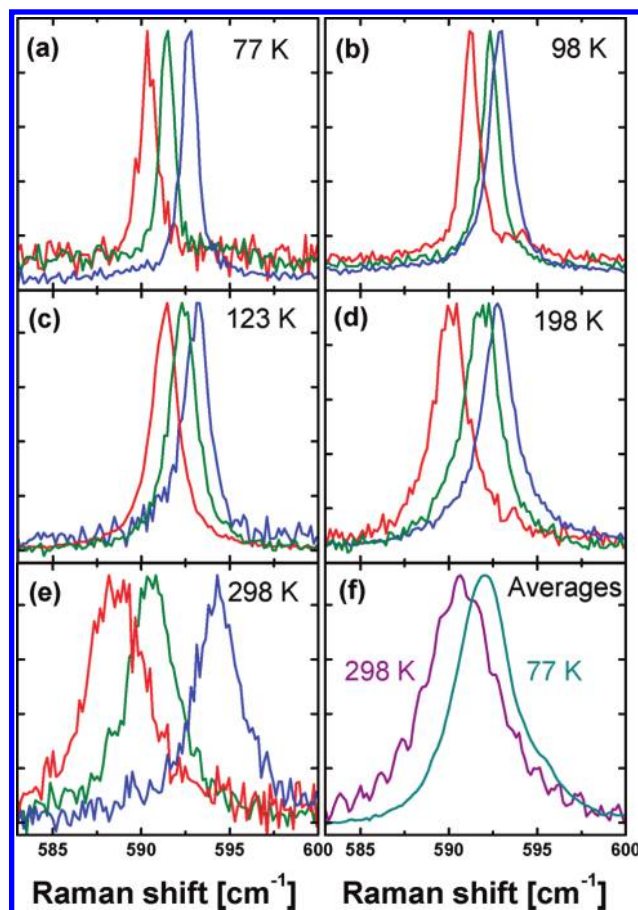

Figure 1. (a−e) Representative SM-SERS signals at different T's (for the 590 cm^{-1} mode of NB, 633 nm laser excitation, 2.5 mW, and 1 s integration time; all spectra are normalized in intensity). We use different colors for different spectra (SM-SERS events) at each temperature for ease of visualization only. The change in (homogeneous) broadening of the peaks with T is readily seen by eye. The frequency variations from one SM event to another are, however, sufficiently large to wash out most of the information on the homogeneous broadening in the average spectra (for an ensemble of molecules), as shown in (f) for the two extreme temperatures. The small red shift in peak frequency for increasing T's is visible in both the average spectra and the average position of SM spectra.

SM events. This analysis is summarized in Figure 2. As can be appreciated, there is a clear "threshold" for the narrowest events, which increases steadily as a function of T. Moreover, these narrowest spectra (examples of which are shown in Figure 1a−e) are all pure Lorentzian, within the uncertainties of the fits. This minimum broadening, $\Gamma_{SM}(T)$ is therefore assigned to the single-molecule (homogeneous) broadening of the Raman mode on the surface at a given T. By contrast, spectra whose fit resulted in a much larger fwhm than the threshold for a given T often exhibit (after direct inspection) a double or multipeak line shape. These can therefore be attributed to multimolecule events.[18] The remaining spectra, exhibiting a single peak of larger fwhm than the threshold, are also probably two-molecule events with closely spaced Raman frequencies, but we cannot exclude the possibility that some of these are SM spectra with a slightly larger homogeneous broadening than the others.

Having identified SM events, it is possible to study their frequency spread at a fixed T by plotting a histogram of their
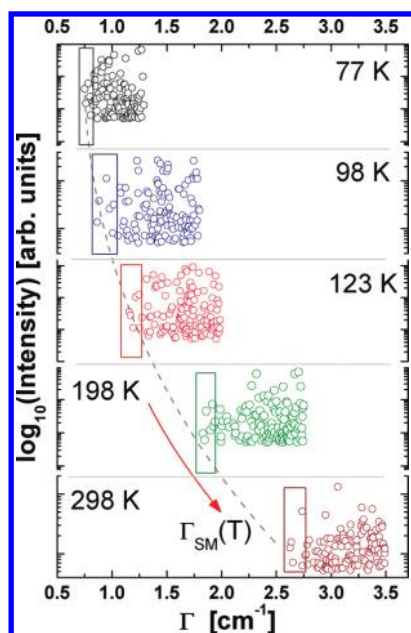
Figure 2. The fwhm (Γ) of different SM-SERS events for the 590 cm^{-1} mode of NB as a function of T. The vertical axis is logarithmic, and therefore, the different events represent signals with widely varying intensities. Lowest-intensity events (below noise level) are removed. At all T's, a clear minimum "threshold" broadening is observed (boxes). Events at this threshold broadening all have a pure Lorentzian line shape and correspond to the minimum possible width that a SM can have at a specific T. The variation of this threshold $\Gamma_{SM}(T)$ provides a measurement of the dependence of the homogeneous broadening as a function of T (schematically shown by dashed line).
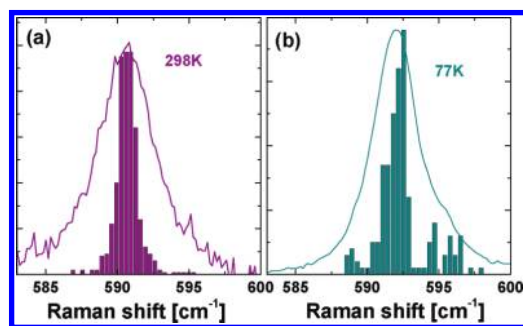

Figure 3. Histograms of the Raman peak positions for SM-SERS events at 298 (a) and 77 K (b). Superimposed is also the actual average spectrum for these T's. The frequency variations of SM events dominates the line width of the average, which masks the true homogeneous broadening and its temperature dependence. Rare events at 595 cm^{-1} are tentatively attributed to natural isotopic substitutions or contamination by a similar (but not identical to NB) molecular species (e.g., a byproduct of the dye synthesis reaction).

frequency positions, as shown in Figure 3 (for the two extreme temperatures). From these, we conclude that the magnitude of the frequency shifts from one molecule to another has little (if any) T dependence, and this narrows down their possible origin as surface interactions. This is in stark contrast with the decrease of Γ_{SM} from ~2.7 to as little as ~0.9 cm^{-1} at 77 K (Figure 2). The small variation of the average broadening is well accounted for by a dominant constant contribution from frequency variations, convoluted with a smaller T-dependent homogeneous line width.
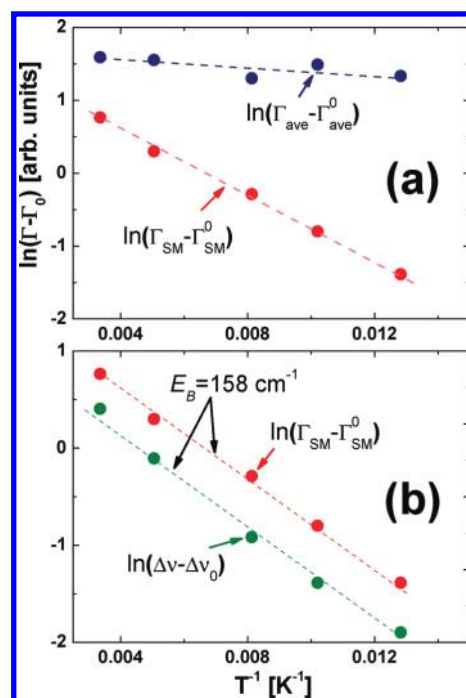

Figure 4. (a) Arrhenius plots for the T dependence of the homogeneous broadening $\Gamma_{SM}(T)$ (red circles) as opposed to the line width of the average signal $\Gamma_{ave}(T)$ (blue circles). The T dependence of the average signal is "weaker" because it is dominated by the inhomogeneous broadening. (b) The T dependence of the average Raman shift $\Delta\nu(T)$ (green circles) and that of the homogeneous broadening $\Gamma_{SM}(T)$ (red circles) can be fitted using the VEE model (dashed lines). From these, the energy of the exchange mode E_B (eqs 1 and 2) is found to be ~158 cm^{-1}, indicating a dominant anharmonic coupling to the substrate (Ag) phonons (the Debye frequency of Ag is ~160 cm^{-1}). See the text for further details.

This reinforces the idea that only SM measurements can directly access the homogeneously broadened spectra. Figure 4 summarizes the measured T dependence of the homogeneous Γ_{SM} and inhomogeneous Γ_{ave} broadening, together with the average Raman frequency $\Delta\nu$. We first note that the small line widths observed here place a lower bound on the dephasing T_2' and population relaxation time T_1 of this vibration (from the fundamental relation $\Gamma = 1/(2\pi c T_1) + 1/(\pi c T_2')$,[2] where Γ is in cm^{-1}). For example, at 298 K, $\Gamma_{SM} \approx 2.7$ cm^{-1} implies $T_2' \geq 4$ ps and $T_1 \geq 2$ ps, while at 77 K, $\Gamma_{SM} \approx 0.9$ cm^{-1} implies $T_2' \geq 12$ ps and $T_1 \geq 6$ ps. Moreover, the observed dependence of Γ_{SM} and $\Delta\nu$ is suggestive of the vibrational energy exchange (VEE) model,[29] which we used to fit the data, namely, (expressing both in wavenumbers)

$$\Gamma_{SM} = \Gamma_0 + \frac{(\delta\omega\tau)^2}{1 + (\delta\omega\tau)^2}\frac{1}{\pi c\tau}\exp(-E_B/kT) \qquad (1)$$

$$\Delta\nu = \Delta\nu_0 + \frac{\delta\omega\tau}{1 + (\delta\omega\tau)^2}\frac{1}{2\pi c\tau}\exp(-E_B/kT) \qquad (2)$$

where $\delta\omega$ represents the coupling strength between the Raman and the exchange modes, τ is the correlation time of the exchange mode, and E_B is its energy. As shown in Figure 4, a satisfactory fit to both quantities is obtained using the parameters $\Gamma_0 = 0.65$ cm^{-1}, $\Delta\nu_0 = 592.1$ cm^{-1}, $\tau = 0.77$ ps, $\delta\omega\tau = 0.67$, and $E_B = 158$ cm^{-1}. Uncertainties in these parameters are mainly associated with the

determination of the limit of Γ_{SM} at low temperatures from Figure 2. Nevertheless, it is interesting to note that E_B closely matches the Debye frequency of Ag. This suggests a natural interpretation; the dominant contribution to the T dependence of the homogeneous broadening is through anharmonic coupling to the phonons of the Ag substrate, which most likely consists of dephasing rather than population relaxation (because the Debye frequency is *not* an obvious multiple of the Raman one, and a direct population decay is less likely). The dephasing time associated with this process can be estimated from $\Gamma_{SM} - \Gamma_0$ to be ~5.2 ps at room T.

In conclusion, SM-SERS opens yet unaccessible experimental information to study anharmonic couplings and intramolecular vibrational relaxation beyond time-resolved techniques. The results illustrate the power of SM-SERS to provide textbook-like examples of the simplicity of SM spectroscopy, as opposed to measuring ensembles. This is evidenced here in the T dependence of the homogeneous line width and follows recent examples of SM-SERS such as the discrimination of the homogeneous resonant excitation spectrum[24] or the detection of natural isotopic substitutions.[30] We are not aware of any previous reports where the T-dependent spectroscopic properties of single molecules has been studied, and in that sense, the results here open a new unexplored landscape to unveil subtle interactions of molecules on surfaces. We can envision many possibilities from here by taking advantage of experimental techniques like SM-SERS that access the homogeneous spectral properties and circumvent the standard ensemble average that is associated with less sensitive techniques.

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