



Two-state analysis of single-molecule Raman spectra of crystal violet

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Abstract

Surface-enhanced Raman spectra of individual crystal violet molecules adsorbed on silver colloids were measured and analyzed. It was found that, because of the small number of hot spots on the surface of the colloids, the single-molecule limit is attained already at a molecule to colloid ratio of 10^3 . Series of time-dependent spectra measured from individual molecules showed significant spectral jumps, involving essentially only the low-frequency part of the spectrum. Each spectrum could therefore be analyzed as belonging to one of two groups, depending on the ratio between its two parts. Spectral trajectories were converted into simplified two-state (high/low) trajectories. Probability distributions of the dwell times in the two states were constructed from the trajectories, and statistical analysis showed that the dynamic process underlying the spectral jumps is likely to be Markovian. We suggest that the jumps originate in fluctuations of molecule-surface charge transfer interactions, although our studies did not provide evidence for lateral motion of the molecules, as found previously with rhodamine 6G.

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1. Introduction

Single-molecule surface-enhanced Raman scattering (smSERS), first measured in 1997 with rhodamine 6G (R6G) molecules [1,2], has since been observed with several different molecules [3–8], including proteins [9–11] and DNA [12]. Single molecules seem to exhibit a particularly large scattering cross-section on silver colloids and other rough silver surfaces. For example, a cross-section of up to 10^{-13} cm² was measured for individual R6G molecules on silver colloids [13]. What are the microscopic mechanisms behind such a phenomenal enhancement factor?

The main contribution to SERS comes from the enhancement of electromagnetic (EM) fields close to the surface through interaction with surface plasmon

excitations (for reviews see [14–16]). The local EM field depends on the microscopic shape of the metallic surface, such as the presence of sharp edges. Calculations by several authors [17–24] suggest that the EM field generated inside junctions between nanoparticles forming small aggregates may lead to a giant enhancement of Raman scattering, up to a factor of 10^{11} . Some experimental work supports this observation [9,25,26].

A second (and smaller) contribution to the enhancement of Raman scattering is a specific interaction of the adsorbed molecule with the metal surface [15,27], which leads to charge transfer from the molecule into the empty levels on the metal surface or from occupied surface levels to the molecule. This electron transfer can in fact be viewed as an electronic excitation of the coupled molecule-surface system, and should therefore lead to the appearance of a new band in the electronic spectrum of the molecule. Charge transfer (CT) bands have been demonstrated in optical [28] and electron energy loss spectra [29] of adsorbed molecules, and their

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relevance to SERS was discussed by Persson [30] and others. The contribution of CT transitions to SERS enhancement can be seen as a resonance Raman process [31], and since the energy of a CT band depends on surface potential, the Raman enhancement can be modified by tuning this potential. This has been verified in many systems, the classical examples being those of pyridine and pyrazine [32,33]. The CT enhancement mechanism is restricted, by its nature, to molecules adsorbed directly on the metal, as opposed to the EM effect which extends a certain distance beyond the surface. It was recently suggested that in some cases the CT mechanism can be strong enough to allow single-molecule observation in the absence of an EM contribution [34].

We previously reported strong fluctuations in specific bands of the Raman spectra of individual R6G molecules adsorbed on colloidal silver particles, and these were the basis for our assertion that the CT mechanism is operative in the case of these molecules [13,35]. The fluctuations appeared in two low-frequency bending bands, at 614 and 774 cm^{-1} , and were uncorrelated with the much weaker fluctuations of other bands in the spectrum. The lack of correlation between various parts of the spectrum suggested that it is unlikely to attribute the fluctuations to orientational motion of the molecules. We therefore proposed that the two fluctuating bands are resonance-enhanced by coupling to a CT transition that the rest of the bands are not coupled to.

In this paper, we analyze fluctuations in the smSERS spectra of crystal violet (CV) molecules. Single-molecule Raman spectra of CV were presented by Kneipp et al. [36] and by Krug et al. [5]. Here, we examine SERS signals from CV molecules adsorbed on silver colloids. We show rigorously that the single-molecule limit is reached at molecular concentrations where many more than one molecule reside on each colloid, pointing again to the importance of the very rare “hot spots” in providing enough enhancement for single-molecule observation. We then focus on time-dependent changes in the spectra and show that these can be analyzed in terms of jumps between two states, whose probability distributions are presented. Analysis of the distributions suggests that the underlying dynamic process is Markovian in nature.

2. Experimental

2.1. Silver colloids preparation

Silver nanocrystals were prepared by the Lee-Meisel citrate-reduction method [37]. Forty-five milligrams of AgNO_3 (Merck) were dissolved in 250 mL of ultrapure deionized water (Mili QRG purification system, Millipore), and heated to 100 °C; 5 mL of a 1% solution of sodium citrate (BDH), was added dropwise to the boiling solution under vigorous stirring. The solution was

kept boiling for 90 min. Transmission electron microscopy and ESEM showed average particle size of 50 nm. In some cases aggregates and small clusters were found. It was found that a 15 min treatment in a sonication bath reduced their number.

2.2. Samples for SERS

Samples in a wide range of crystal violet (CV) concentrations (3×10^{-6} – 3×10^{-10} M) were prepared. An aliquot of the silver colloid solution was sonicated for 15 min in order to reduce unnecessary aggregation, before adding the dye to the required final concentration, as well as 10 mM NaCl. The prepared solution was incubated overnight. For the low CV concentrations no evidence for an increasing number of aggregates of particles resulting from this process could be observed, as opposed to the higher concentrations. Polylysine (Sigma–Aldrich) was adsorbed on microscope cover slides for 35 min before a thorough rinsing. The incubated samples were sonicated for 15 min (to reduce aggregation) and allowed to adsorb on the polylysine-coated slides for 1 h, then rinsed with deionized water in order to get rid of access colloids which did not adsorb. Experiments were conducted either on dried samples or on samples covered with deionized water or glycerol solutions.

2.3. Raman measurements

A home-built Raman spectrometer constructed around an inverted microscope (Olympus) and a 0.15 m spectrograph (Acton) was used for these studies. The sample was illuminated by the 632.8 nm beam of He–Ne laser (Coherent). An area of $\sim 7 \mu\text{m}$ diameter was epi-illuminated by focusing the laser beam at the back focal plane of a 100 \times , N.A. 1.3 objective (Fluar, Zeiss). Raman-scattered light was collected by the same objective and passed through a dichroic mirror (z633rdc, Chroma) and a 633 nm notch filter (to filter out light at the excitation wavelength) before being focused on the entrance slit of the spectrograph. The resolution of our spectrometer was found to be 20 cm^{-1} , enough to resolve most of the bands in the SERS spectrum of CV. The spectra were registered by a back-illuminated, thermoelectrically cooled CCD camera (Princeton Instruments). Raman spectra were collected continuously, with an integration time of 1 s, until the signal was irreversibly lost.

3. Results and discussion

3.1. Attaining the single-molecule limit

An inherent problem in smSERS is the lack of a method to prove unequivocally that the single-molecule

limit has been reached. This is quite different from the situation with fluorescence, where either the photophysics (anti-bunching) or the photochemistry (photobleaching) of a dye can provide direct evidence that one molecule is involved in signal generation. Since the excited-state lifetime in a Raman process is extremely short, it is not possible to obtain an anti-bunching signal. The short lifetime is also the reason for the lack of single-step bleaching, another useful indicator for single molecules. In the past, the single-molecule limit was inferred in Raman studies from the dilution of the molecules studied, as well as from the observation of signal fluctuations, e.g., blinking. To quantitatively assess this issue, we looked at the intensity of the Raman signal obtained from surface-adsorbed silver colloids prepared with a range of concentrations of CV molecules, from 10^{-6} to 10^{-10} M (corresponding to a ratio of molecules to colloids ranging from 10^5 to 10). Hot spots emitting Raman signals were identified and Raman spectra were collected from them. The spectra were integrated to obtain an average intensity, which was then averaged over 20 hot spots. This average intensity as a function of CV concentration is shown in Fig. 1. It can be seen that the intensity decreases significantly going from 10^{-6} to 10^{-7} M CV, then a small decrease occurs when going from 10^{-7} to 10^{-8} M CV, with the intensity reaching a plateau at lower concentrations. From these series of experiments we conclude that at 10^{-8} M the single-molecule limit is attained. We found that even at 10^{-6} M 90% of the CV molecules were adsorbed on the colloids, ruling out differences in adsorption as a possible explanation for the result of Fig. 1. Note also that the mean value of the total intensity at 10^{-6} M is larger than the value at 10^{-10} M by a factor of ~ 25 , although the difference in the concentration is four orders of magnitude. This probably indicates that only a small part of the colloids shows enough enhancement to permit single molecule detection. This observation is similar to what was

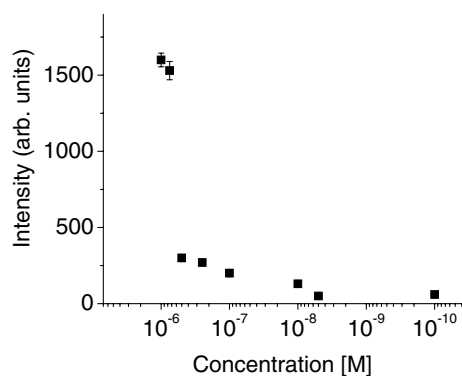


Fig. 1. Average intensity of SERS signal from silver colloids with CV molecules adsorbed on them, prepared from solutions of decreasing concentration of the dye. The SERS signal is seen to drop strongly between 10^{-6} and 10^{-7} M, indicating that the single-molecule limit is attained close to the latter concentration.

reported by other workers in the field [38–40]. Since SERS spectra obtained at a dye concentration down to 10^{-8} M were nicely reproducible, and we already showed that this concentration is in the single molecule limit of detection, the following experiments were done at this CV concentration. The strong intensity and spectral fluctuations reported below lend further credence to the identification of the spectra as coming from single molecules.

3.2. Intensity fluctuations

As already noted by other workers [1,3,5], and also in our previous work with R6G molecules [13], the total SERS intensity of molecules studied on the single molecule level shows fluctuations, although the stability varies from one molecule to another. Fig. 2 presents the time dependence of the total intensity of Raman scattering for 20 CV molecules illuminated with a laser intensity of 40 W/cm^2 . Each row represents one molecule, whose scattering intensity was obtained by integration of the Raman spectra; each intensity trajectory is normalized to its highest value. Note that the overall collection time is not equal for different molecules; data collection was usually stopped when the signal became smaller than a certain value or when it was lost totally. As can be noticed, there is variety of behaviors. Some molecules show several strong intensity jumps, while others show more gradual reduction of intensity. Some of the molecules are seen to lose most of their scattering intensity in a single, sharp step. In general, the loss of the Raman signal is reminiscent of a similar loss discussed in both electrochemical [41] and ultra high vacuum SERS systems [42,43], where it was attributed to diffusion of silver adatoms. The strong intensity fluctuations, and particularly the abrupt signal loss, are indicative of single molecule behavior. The latter is probably not due to a photobleaching reaction, as the low fluorescence quantum yield of CV on silver implies

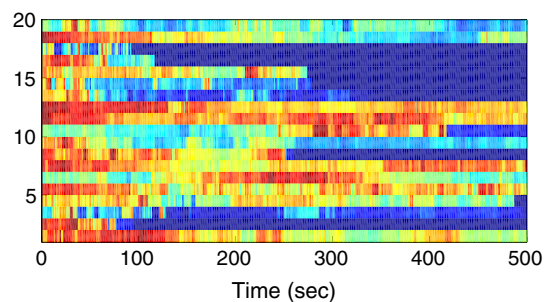


Fig. 2. Total intensity trajectories for 20 CV molecules illuminated with a laser power of 40 W/cm^2 . Each row shows the intensity trajectory of a single molecule, obtained by integration of time-dependent Raman spectra, and normalized to the highest value. Total data collection time was not equal for all molecules.

very short excited-state dwell time and therefore very low overall probability for excited-state chemistry.

3.3. Spectral jumps

While in R6G spectral fluctuations were continuous in nature [13], observation of the spectra of CV molecules showed that they can be collected into two groups, depending on the ratio between two parts of the spectrum. Typical spectra of the two groups are shown in Fig. 3. The difference between these two spectra lies in the intensity of the low-frequency part of the spectrum relative to the high-frequency part. Notable is the fact that the intensity change is seen both in the sharp bands and in the diffuse background. Thus, fluctuations in the intensity of specific bands in the vibrational spectrum are accompanied by similar fluctuations in the intensity of the background signal. We therefore infer that a common process is responsible for these two wavenumber-specific responses. A diffuse background has been one of the hallmarks of the SERS phenomenon for many years [3,13,44–46]. Otto suggested [15] that the background is a by-product of a non-radiative CT process between the surface and the molecule, which has a very short dephasing time, leading to a broad and diffuse spectrum.

We found that all individual spectra of CV could be categorized as belonging to either one of the two groups. Further, transitions between the two types of spectra were always abrupt, occurring either in the time between two frames or within a frame. The spectra shown in Fig. 3 span such a jump event; the green spectrum is the one preceding the jump, while the red spectrum follows it. This allowed us to ‘digitize’ the spectra in the following manner. The ratio between two parts of the spectrum, with a division line at 1100 cm^{-1} (see Fig. 3), was calculated for each frame. The numerical derivative of the trajectory of ratio values was then calculated, and an increase of the absolute value of the derivative above a pre-defined threshold identified a

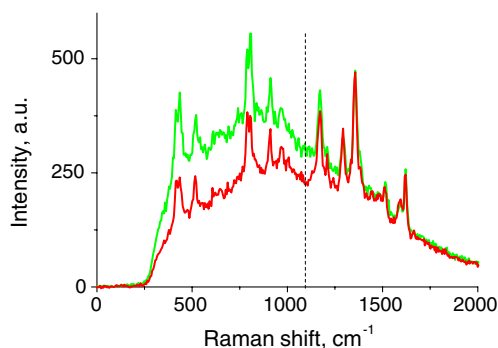


Fig. 3. The two types of Raman spectra seen in single-molecule trajectories of CV. The two specific spectra shown here span a spectral jump, with the green spectrum preceding the jump and red spectrum following it. The dashed vertical line at 1100 cm^{-1} marks the division between two parts of the spectrum, the ratio of which was used in order to digitize the trajectories.

spectral jump. A ‘‘high’’ value of the ratio was assigned the number 1, and a ‘‘low’’ value was assigned the number 0. A trajectory of the ratio values for a single molecule is shown in Fig. 4(a), and the digitized trajectory generated from it is shown in Fig. 4(b). We carefully tested this algorithm to make sure that it does not introduce artifactual transitions.

Probability distributions of dwell times in the ‘‘high’’ state ($P(t_{\text{high}})$) and ‘‘low’’ state ($P(t_{\text{low}})$) were constructed from the trajectories, and are shown in Figs. 5(a) and (b), respectively. Clearly, both distributions present long-time tails, particularly evident in the distribution of t_{high} . These long-time tails imply that simple exponential kinetics cannot describe the dynamics of the system. The mean t_{high} calculated from the distribution of Fig. 5(a) is 51 s, compared to a decay time of 15 s obtained from a single-exponential fit. The mean t_{low} calculated from the distribution of Fig. 5(b) is 23 s, which is also significantly longer than the time obtained from the fit, 12 s.

The non-exponential decay found in both distributions suggests that the two-state model used to analyze the data is in fact a simplification of the real physics. Non-exponential dynamics in single-molecule trajectories are sometimes interpreted in terms of non-Markovian models, indicating temporal correlations in the trajectories [47–49]. In order to test whether the dynamics in our smSERS trajectories deviate from Markovian behavior, we compared the convolution of the distributions $P(t_{\text{high}})$ and $P(t_{\text{low}})$ to the distribution of sums of adjacent dwell times, $P(t = t_{\text{high}} + t_{\text{low}})$ [50]. These two functions are identical for a Markovian process. We found that this is indeed the case within the noise level of our data, as shown in Fig. 5(c). We also analyzed

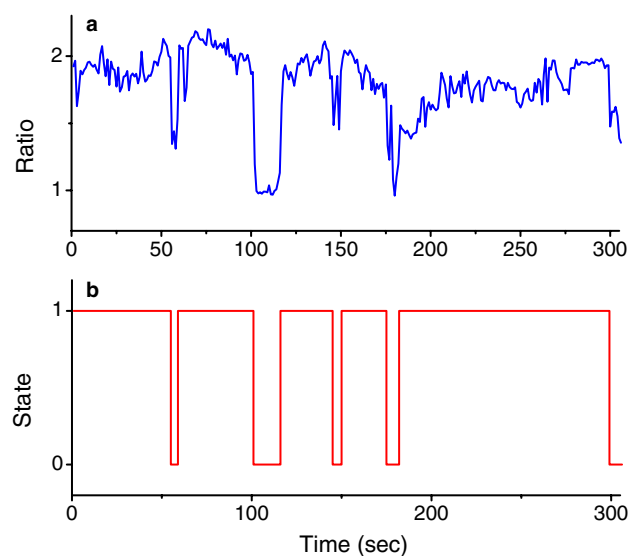


Fig. 4. Analysis of a two-state like trajectory, generated by taking the ratio between two parts of each spectrum. (a) Trajectory of the ratio values. (b) Digitized trajectory constructed from the trajectory in a.

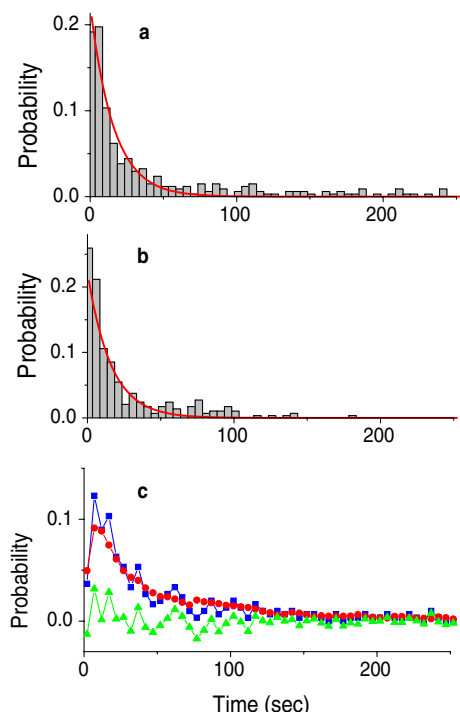


Fig. 5. (a) Probability distribution of high t_{high} . (b) Probability distribution of t_{low} . The two distributions were constructed from ~ 80 trajectories containing about 300 “high” dwell times and 300 “low” dwell times. The red lines are fits to exponential functions, emphasizing the long-time deviations from simple exponential decays. (c) Comparison of the distribution $P(t = t_{\text{high}} + t_{\text{low}})$ (in blue squares) to the convolution of the distributions in a and b (in red circles). The difference between the two, in green triangles, is essentially zero, especially at long times, indicating a Markovian behavior. (For interpretation of the references to color in this figure legend, the reader is referred to the web of this article.)

$P(t = t_{\text{high}} + t_{\text{high}})$ and $P(t = t_{\text{low}} + t_{\text{low}})$ in the same manner. $P(t = t_{\text{high}} + t_{\text{high}})$ does show somewhat larger deviations at the very early times from the corresponding convolution. However, considering that this distribution is inherently more noisy than $P(t = t_{\text{high}} + t_{\text{low}})$, we refrain from drawing any conclusions out of these deviations. This is, therefore, a curious case where non-exponential dynamics might not necessarily arise from temporal correlations. As shown by Flomenbom et al. [50], a multiplicity of kinetic schemes can lead to such a behavior, but the lack of correlations prohibits differentiating between them.

In our previous studies of the smSERS of R6G, we showed that the fluctuation rate depended linearly on the power of the illuminating laser [13]. We also found that the fluctuation rate was dependent on the viscosity of the solution covering the surface-attached silver colloids [35]. These findings were interpreted as evidence for the involvement of surface motion in the dynamics seen in R6G spectra. We tested whether the same behavior is also seen in smSERS spectra of CV molecules. Interestingly, it was found that *the jumps in CV spectra*

were neither dependent on laser power nor on solution viscosity.

What is the origin of spectral jumps we see in CV spectra? One possibility is infrequent orientational jumps of CV molecules on the metallic surface. It was shown by Schneider et al. [51] and by Jiang et al. [52] that CV molecules lie flat on a silver surface, interacting with it through the central carbon atom. Such an orientation should enhance out-of-plane vibrations over in-plane vibrations, due to the surface selection rule [53]. If a molecule reorients so that the molecular plane is not parallel to the surface any more, in-plane vibrations will be enhanced and out-of-plane vibrations reduced. This is not what happens in the case of CV molecules. Rather, it is only the low-frequency part of the spectrum, comprising mostly out-of-plane vibrations, that changes its intensity, while the high-frequency part does not change significantly. Thus, it is likely that reorientational dynamics are not at the origin of the spectral jumps.

A second possible mechanism for spectral jumps involves CT dynamics. In R6G spectra, CT-enhanced SERS couples mainly to two low frequency out-of-plane vibrations [13], as already noted in the introduction. It is possible that a similar phenomenon operates in the case of CV. Jiang et al. [52] indeed showed that the central carbon breathing mode at 208 cm^{-1} is enhanced by CT (we are not able to measure this low-frequency band in our single-molecule apparatus). However, to explain spectral dynamics in R6G we invoked molecular motion on the surface, and the dependence of the dynamics on laser power and solution viscosity were taken as supporting evidence for this mechanism. Since the jumps in CV spectra do not depend on these two variables, there seems to be no evidence so far for lateral motion that might modulate molecule–surface CT interactions. Therefore, even if CT excitations are responsible for some of the enhancement in CV SERS spectra, it is not clear why these spectra fluctuate. The identification of the mechanism behind the two-state like spectral jumps in CV spectra awaits further experimentation or modeling.

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