

## Probing the Raman Scattering Tensors of Individual Molecules

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Received: October 9, 2005; In Final Form: December 5, 2005

Single-molecule experiments provide new views into the mechanisms behind surface-enhanced Raman scattering. It was shown previously that spectra of individual rhodamine 6G molecules adsorbed on silver nanocrystal aggregates present stronger fluctuations in two low-frequency bending modes, at 614 and 773  $\text{cm}^{-1}$ . Here we use polarization spectroscopy to show that these bands are enhanced by a resonant process whose transition dipole is rotated by  $15 \pm 10^\circ$  with respect to the molecular transition dipole. We also show that the polarization function remains stable over the whole time scale of a measurement, indicating that molecular reorientation with respect to the surface is unlikely. Together these findings provide further support to the involvement of a charge-transfer resonance in the enhancement of the low-frequency bands and allow us to suggest a model for the orientation of rhodamine 6G molecules at Raman hot spots.

Three decades after the discovery of surface-enhanced Raman scattering (SERS),<sup>1–3</sup> the mechanism of this phenomenon continues to be the subject of intense scrutiny. Local electromagnetic field enhancement is almost universally implicated as the main factor that enables SERS.<sup>4,5</sup> A clear involvement of charge transfer (CT) resonances has also been described.<sup>6,7</sup> Recent interest has been aroused by the observation of Raman signals from individual molecules.<sup>8,9</sup> It was observed that single-molecule SERS (smSERS) occurs only at a small number of “hot spots” on nanocrystal aggregates or rough surfaces of silver or gold. Calculations showed that at the junction between colloidal particles the enhancement can reach the high values required for single-molecule detection, establishing the major role of electromagnetic enhancement in smSERS.<sup>10–13</sup> Some experimental work supported this observation.<sup>14–16</sup> Yet, several experiments pointed to the concurrent importance of CT phenomena,<sup>13,17</sup> including a recent interesting report showing single-molecule Raman spectra in the absence of surface enhancement.<sup>18</sup>

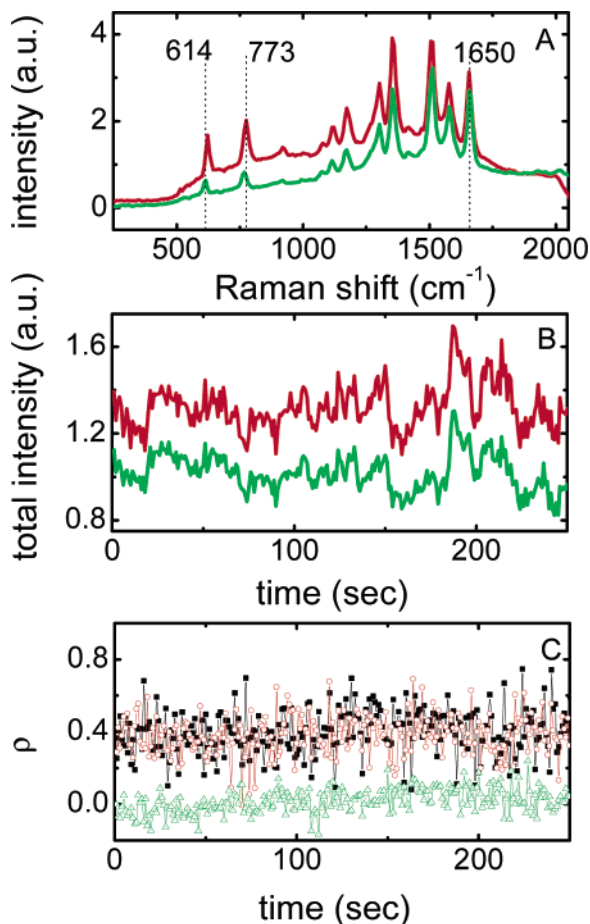
smSERS of rhodamine 6G (R6G) was used in our lab to shed new light on the CT mechanism.<sup>17,19</sup> Dramatic temporal variations in both the overall intensity and the intensities of particular Stokes bands were found. In particular, the fluctuations of two low-frequency bending modes were shown to be much more pronounced than those of the rest of the spectrum (these two bands, at 614 and 773  $\text{cm}^{-1}$ , were assigned to in-plane bending vibrations in a very recent DFT calculation<sup>20</sup>). Further, the fluctuation rate was sensitive to the laser power, as well as to the concentration of chloride ions in solution,<sup>17</sup> and its viscosity.<sup>19</sup> These findings led us to suggest a significant chemical contribution to the enhancement of the two low-frequency bands. We proposed that the fluctuations arise from lateral motion of the molecules and sampling of sites with different local work function, effectively moving the molecules in and out of resonance with the charge transfer transition. The above findings cannot be considered as direct evidence for CT

resonance. In fact, such direct evidence is available only for a handful of molecules,<sup>21</sup> R6G not included. In the current paper we report polarization spectroscopy measurements of the Raman scattering tensors of individual R6G molecules. Our results provide further support for the involvement of CT resonance in the enhancement of the low-frequency bands, as well as a model for the orientation of R6G molecules at hot spots.

The experimental setup used for this work was a modification of the system used before in our single-molecule Raman experiments,<sup>22</sup> and allowed simultaneous registration of two polarized Raman spectra,  $I_{\parallel}(\vec{\nu})$  and  $I_{\perp}(\vec{\nu})$ , on a back-illuminated CCD camera (Princeton). A 532 nm laser (Coherent), with intensity of  $\sim 10 \mu\text{W}$ , was used for excitation. Raman-scattered light was separated from background scattering using a HQ545 emission filter (Chroma) and sent into a spectrograph (SpectraPro-150, Acton) equipped with a 600 grooves/mm diffraction grating (providing a 10  $\text{cm}^{-1}$  resolution). Concurrent rotation of the laser polarization direction (using a  $\lambda/2$  waveplate) and a beam-displacing polarizer (BD40, Thorlabs) in front of the camera enabled changing the angular relation between the laboratory reference frame and the molecular reference frame. Sample preparation closely followed previously described procedures.<sup>22</sup> R6G/colloid complexes were adsorbed on a glass surface, hot spots were identified, and several hundred spectra were typically collected from each, with an exposure time of 1 s per spectrum. From the spectra, we computed the wave-number-dependent polarization function,  $\rho(\vec{\nu}) = [I_{\parallel}(\vec{\nu}) - I_{\perp}(\vec{\nu})]/[I_{\parallel}(\vec{\nu}) + I_{\perp}(\vec{\nu})]$ .

A previous measurement of polarized spectra from a limited number of molecules did not detect band-specific changes.<sup>13</sup> We measured angle-dependent Raman spectra from more than 60 single molecules. 80% of the molecules showed a constant polarization function across the spectrum. However, 20% (which we will call “the minority molecules”) presented clear differences between the scattering polarization of the fluctuating, low-frequency bands and that of the rest of the spectrum. A particular example of such spectra is shown in Figure 1A. The overall

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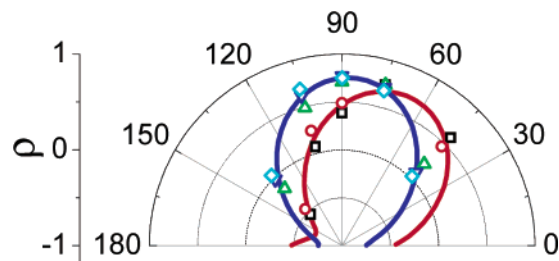


**Figure 1.** (A) Polarized Raman spectra of an individual R6G molecule. Red ( $\parallel$ ) and green ( $\perp$ ). (B) Total intensity fluctuations, obtained by integration of time-dependent series of spectra similar to (A). (C) Time dependence of the polarization function for three R6G bands. Green:  $1650\text{ cm}^{-1}$ , black:  $614\text{ cm}^{-1}$ , red:  $773\text{ cm}^{-1}$ .

intensity fluctuations of this molecule in the two polarization channels as a function of time are shown in Figure 1B. Note that despite strong temporal variations of the two SERS intensities, they remain highly correlated, as noted by Bosnick et al.<sup>16</sup> This indicates that the mechanism of the intensity fluctuations does not involve either molecular reorientational dynamics or large changes in the geometry of the silver clusters.<sup>23</sup> A detailed examination of the polarization function exposes band-specific trends (Figure 1C). In particular, the polarization function of the  $614$  and  $773\text{ cm}^{-1}$  bands (calculated for each band after subtraction of the broad background) is  $0.4$ , while that of the other bands, (represented here by the  $1650\text{ cm}^{-1}$  band) is  $\sim 0$ . The difference between these values is stable over the whole 250-second-long trajectory.

Figure 2 shows how the polarization functions of the low-frequency bands and three high-frequency bands in the spectrum of a different molecule change as the polarization of the incident light is rotated. The difference in behavior of the  $614$  and  $773\text{ cm}^{-1}$  bands on one hand and the  $1363$ ,  $1509$ , and  $1650\text{ cm}^{-1}$  bands on the other hand is evident. A cosine function can be used to fit each of the two groups, and these fits are shown as solid lines in the figure.

To understand these results one first needs to appreciate the effect of the symmetry of nanocrystal aggregates on the local electromagnetic field. In the simplest form of an aggregate, i.e., a dimer, the local field is always mostly in the direction of the vector connecting the centers of the two nanocrystals. Therefore, when the external field is rotated, the local field changes its



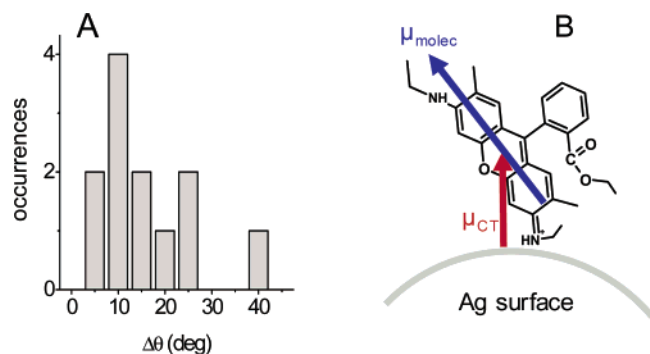
**Figure 2.** Polar plot of the polarization as a function of the laser angle of rotation for three bands in the spectrum of an individual R6G molecule. Green triangles:  $1363\text{ cm}^{-1}$ , blue triangles:  $1509\text{ cm}^{-1}$ , cyan diamonds:  $1650\text{ cm}^{-1}$ , black squares:  $614\text{ cm}^{-1}$ , red circles:  $773\text{ cm}^{-1}$ . The solid lines are cosine fits. Error bars are smaller than symbol sizes.

magnitude but not its direction.<sup>24</sup> The Raman-scattered field is also enhanced only along the same direction. It can be readily shown that in this case the polarization function is of the form  $\rho = \cos[2(\gamma - \gamma_0)]$ , where  $\gamma$  is the rotation angle of the external field, and  $\gamma_0$  is direction of the symmetry axis of the dimer with respect to the laboratory frame. Thus the polarization function does not contain any information about the molecule and cannot show any band-specific pattern.

The situation is different for aggregates containing three or more nanocrystals, since in this case the coupling to the electromagnetic field can be isotropic or near-isotropic. Indeed, there is experimental evidence for a nearly isotropic response to the external field.<sup>24</sup> Also, Xu recently presented calculations showing that in higher-order aggregates the local field at particular sites can be essentially constant<sup>25</sup> (the polarization dependence of the local field was not reported, though). A simple example is also given by Bosnick et al.<sup>16</sup> At the center of a symmetric arrangement of four identical particles the local field is isotropic (one of course ignores in this artificial example the question of whether a molecule can reside at the center and what the intensity of the local field will be there). The direction of the local field will thus follow the direction of the external field as it rotates, and bands with different Raman tensors will show different functional dependence of their polarization factor on the rotation of the field. Therefore, the behavior of the minority molecules (Figure 2) suggests that they do not reside on colloidal dimers but on aggregates that can provide sites with near-isotropic response to the external electromagnetic field. TEM analysis shows that as many as 60% of the aggregates in our sample contain more than two particles (data not shown); some of these might present near-isotropic sites.

In the case of an isotropic local field, the measured polarization function depends only on the *molecular* symmetry, i.e., on the symmetry of the Raman scattering tensor. Since R6G adsorbed on silver has a low symmetry, all the Raman bands discussed in this work are totally symmetric. Raman scattering is mostly enhanced via Franck–Condon overlap integrals (A-term) and Herzberg–Teller vibronic coupling (B-term).<sup>26</sup> It was suggested by Hildebrandt and Stockburger<sup>27</sup> that the two low-frequency bend modes gain their SERS intensity via a B-term. This assumption was based on the fact that a rich family of overtones and combinational bands was observed for high-frequency modes, while only fundamentals were found for the low-frequency modes. However, A-term enhancement can also show no overtones if the dimensionless shift ( $\Delta$ ) of the excited state is small.<sup>26</sup>

Assuming first that all bands are resonance-enhanced by an A-term mechanism, their scattering tensors have only a single element ( $\alpha_{xx}$ ), dictated by the transition dipole of the enhancing electronic transition.<sup>26</sup> On isotropic sites, the polarization



**Figure 3.** (A) Histogram of angular difference between the principal directions of the Raman tensors of the 614 and 773  $\text{cm}^{-1}$  bands and the 1650  $\text{cm}^{-1}$  band, as determined by fitting plots of angle-dependent polarization functions similar to Figure 2. The histogram contains only data for the 12 molecules that showed a difference angle significantly larger than zero. The average is  $15 \pm 10^\circ$ . (B) Proposed average orientation of an R6G molecule that matches the observed, with the two involved transition dipoles shown. The molecule is attached to the surface with one of its amino groups.<sup>27</sup> The scheme does not show additional surfaces, which must be nearby in order to make the local field near-isotropic. The CT reaction will be dominated by the nearest surface to the molecule.

function for the  $i$ th band will therefore depend on the polarization of the incident light according to  $\rho_i = \cos[2(\gamma - \theta_i)]$ , where  $\theta_i$  is the angle between the principal axis of the Raman tensor of the band and the laboratory frame. Indeed, the experimental polarization functions match well the cosine dependence on laser polarization. Obviously, the excitation at 532 nm, which is at the peak of  $S_0-S_1$  absorption band of R6G, should lead to molecular resonance enhancement. However, why should the low-frequency bands have a rotated scattering tensor with respect to the other bands? This implies that a second mechanism is involved in the enhancement of these bands, likely to be a CT resonance, as inferred previously based on the fluctuations and their behavior.<sup>17,19</sup>

If instead we assume that vibronic coupling is involved in the enhancement of the low-frequency bands, then there are two possibilities. (a) If this vibronic coupling involves two electronic states of the molecule, then by symmetry both must be in-plane and parallel excitations, and so the polarization function will still transform as  $\rho = \cos[2(\gamma - \theta)]$ , but with the same  $\theta$  as that of the high-frequency bands. This is not consistent with what is found experimentally. (b) Another option is that the vibronic coupling involves an electronic excitation of the molecule AND a surface-molecule CT band. In this situation the polarization dependence is complicated, probably not giving rise to a  $\rho_i = \cos[2(\gamma - \theta_i)]$  dependence, but it might be close to that. We cannot rule out such a scenario, although an initial attempt to fit such a tensor to our results did not lead to a satisfactory fit for all molecules.

To conclude, both if A-term scattering or B-term scattering enhances the low-frequency bands, it appears that a charge-transfer excitation is involved, but the A-term mechanism seems to better describe our data. The cosine fits of the data allow us then to extract  $\Delta\theta$ , which is the angular difference between the principal axes of the tensors of the low-frequency bands and the rest of the bands in the spectrum. A histogram of all  $\Delta\theta > 0$  is shown in Figure 3A. Interestingly, the data show that in each molecule  $\Delta\theta$  does not significantly change with time, in contrast with the strong fluctuations observed in the intensity of the low-frequency bands. An involvement of molecular reorientation in the dynamics is thus unlikely. We previously attributed the spectral fluctuations to lateral motion accompanied

by sampling of different local work function values, which leads to modulation of the CT resonance.<sup>17,19</sup> However, spectral modulation could in principle also arise from jumps between several molecular orientations on the surface. The lack of reorientational dynamics evidenced in the current work proves that this is not the case. Further, the current result puts constraints on the types of motions that might occur. Lateral jumps within a small hot spot might maintain the surface–molecule angular relations.

Interpreting  $\Delta\theta$  as the angular shift between the molecular and CT transition dipoles (strictly speaking, this interpretation is correct for the A-term scattering case), we can offer a model of the orientation of R6G molecules at SERS hot spots (Figure 3B). Assuming that the CT transition dipole points from the surface to the center of the xanthane ring system of R6G, while the molecular transition dipole is in the xanthane plane, it is deduced that R6G molecules sit on the surface with a slight tilt of size  $\Delta\theta$ .

In summary, we discover that the enhancement of the fluctuating bands in the Raman spectra of individual R6G molecules is likely to involve a resonant process whose transition dipole is rotated with respect to the molecular transition dipole. We also find that the polarization functions remain stable over the whole time scale of a measurement, ruling out a role for molecular reorientation and the surface selection rule in the fluctuations previously seen. Together these results provide further support to the involvement of CT resonance in the enhancement of the low-frequency bands and allow us to suggest a model for the orientation of the molecules on the surface.

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