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Comment on "Scanning-probe Raman spectroscopy with single-molecule sensitivity"

Katrin F. Domke* and Bruno Pettinger
Department of Physical Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany

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We reinterpret the scanning-probe Raman spectra shown in the paper of Neacsu *et al.* [Phys. Rev. B **73**, 193406 (2006)] and compare it to a variety of single-molecule surface-enhanced Raman studies. The observed blinking behavior and spectral features must be attributed to carbon contaminations rather than to malachite green single molecules, because, under the given experimental conditions, the extremely high-field enhancement of 5×10^9 will inevitably lead to a quick (photo)decomposition of the adsorbate.

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In a recent paper,[1] Neacsu *et al.* present an atomic force microscopy (AFM) tip-enhanced Raman (TER) study on malachite green (MG) at gold films. They analyze near-field (tip ~5 nm above sample surface) and far-field (tip several 100 nm above sample surface) spectra of a Au surface covered with MG at low adsorbate concentration in correlation with a density-functional theory (DFT) calculation as well as of the clean Au surface. In a time series of 100 AFM-TER spectra (1 s integration time per spectrum) for a submonolayer MG surface coverage, spectral diffusion is observed and interpreted as characteristic single-molecule (SM) behavior due to "random surface diffusion of MG in and out of the near-field-confined surface area under the tip, facilitated by the thin most likely liquid water layer on the gold surface." A Raman enhancement of up to 5×10^9 is derived from comparison of tip-enhanced versus far-field response of the same surface monolayer.

Figures 2(b) and 2(c) in Ref. 1 show a near-field (tip approached) and a far-field (no tip) spectrum of MG on Au, respectively. The far-field spectrum exhibits the typical Raman features of MG which can be assigned according to Lueck *et al.*[2] and a DFT calculation performed by the authors [Fig. 2(c) in Ref. 1], but the near-field spectrum does not resemble neither the far-field nor the DFT spectrum.

The authors state that "The pronounced spectral difference between the tip-enhanced and far-field Raman response resembles the observation frequently made in SERS" (surface-enhanced Raman spectroscopy) and claim that "This characteristic difference is the result of the strong optical field localization, and related to different selection rules for the tip-scattered Raman response, akin to SERS".

Different selection rules cannot be held responsible for the so remarkable differences between near-field and far-field spectra presented by Neacsu *et al.* Note in this context that SER as well as TER spectra usually strongly resemble the far-field spectra of the investigated species in the band positions, in a way that the unambiguous identification of the molecule is always possible. In fact, a comparison of the Raman bands found in literature for MG in water (far field, Ref. 2) and MG on silver colloids (near field, Ref. 3) does not reveal any band displacements larger than ±3 cm^{-1}, and also the relative band intensities are similar.

Variations in band intensities may occur according to surface selection rules (changes in the polarizability perpendicular to the surface, i.e., those parallel to the incident field are preferentially enhanced). However, large shifts (>5 cm^{-1}) in band positions (or the appearance of bands that do not belong to vibrational modes of the adsorbate) are not at all a common difference between near-field and far-field spectra of adsorbates[4] and are, in particular, not expected for physisorbed species such as MG.

We will show that the differences between Figs. 2(b) and 2(c) in Ref. 1 must be attributed solely to decomposition of the investigated species during the experiment and contamination of the sample.

The authors of Ref. 1 also present a time series of TER spectra of a submonolayer MG [Fig. 3(a) in Ref. 1] and claim that it shows spectral diffusion characteristic for MG single molecules. According to Neacsu *et al.*, "spectral diffusion and intensity fluctuations" in this time series "can be interpreted by a random surface diffusion of MG in and out of the near-field confined surface area under the tip." According to the authors, the temporal evolution of the 1480–1630 cm^{-1} spectral region exhibits a Gaussian intensity distribution for an ensemble changing to discrete fluctuations for a small sample amount, as shown in Fig. 3(b) in Ref. 1, supporting the interpretation that they observe single molecules.

However, according to Le Ru *et al.*,[5] Poisson-like probability oscillations observed for samples of ~100 events have their origin in the very peculiar characteristics of long-tail distributions and cannot hold as a proof for single-molecule detection.

To illustrate the problem in the analysis of the time series, let us assume that the spectra shown in Fig. 3 in Ref. 1 are due to a single MG molecule, and the intensity and spectral fluctuations arise from the diffusion of this single MG in and out of the strongest field-enhancement region of the tip-metal gap. If the authors' assumption that the near-field spectrum for MG located at the strongest enhancement site is different from the far-field spectrum was correct, then a molecule, drifting many times through a region of strongly varying enhancements, should show characteristically different spectra: For MG at sites of moderate enhancement, one would expect a spectrum that resembles much the well-known far-field spectrum. At locations of strongest enhancement, one would expect a spectrum that also has a characteristic but modified appearance due to different selection rules as proposed by the authors. The line markers added by us to Fig. 3 in Ref. 1 (Fig. 1 in this Comment) show where the far-field bands of MG are to be expected. However, the weak intensity spectra do not show any correlation with the far-field

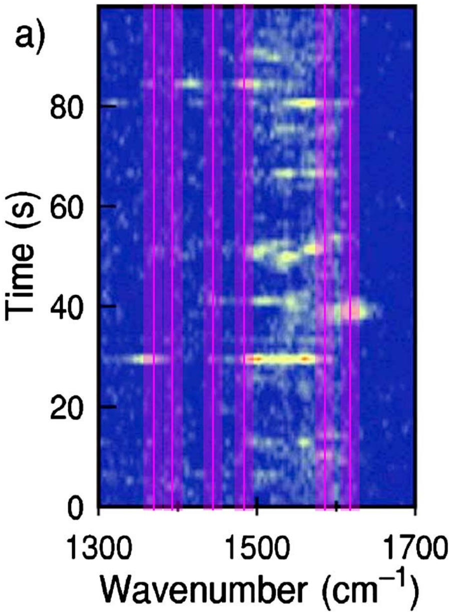

FIG. 1. (Color online) Figure 3(a) taken from Ref. 1, modified with markers for six characteristic and intense MG bands according to Refs. 1 and 2. A bandwidth of 25 cm^{-1} is indicated with broad, semitransparent bars. Comparison reveals no correlation between the expected and the recorded Raman bands.

spectrum of MG, nor do the high intensity spectra show a new spectral characteristic that would be typical for the giant enhancement situation. On the contrary, both low and high intensity spectra show a random variation of the spectral characteristics and intensities.

Obviously, the observed spectral features in Fig. 3(a) in Ref. 1 do not at any time resemble a typical fingerprint far-field spectrum of MG that would allow identification of the adsorbate, nor do the spectra show similarities with each other. In general, SM SERS literature reports spectra that are clearly characteristic for the investigated molecule and thus allow identification of the adsorbed species, also at any time during serial acquisition.[6–13]

Surface diffusion may indeed account for intensity fluctuations in SERS, where a rough surface provides a variety of different adsorption sites or hot spots for the molecule.[6,12] Changes in the band positions which have been observed in SM SERS studies include a narrowing or splitting of bands[11] and slight shifts of ±2–5 cm^{-1} of band positions (which by far exceeds the resolution of the instrument of 25 cm^{-1} employed by Neacsu *et al.*).[6,12] It is important to notice that these band shifts occur simultaneously for several modes, i.e., the whole spectrum shifts slightly.[11,12]

Adding SM spectra (i.e., averaging over a time series) must lead to a spectrum which is similar to an "ensemble" spectrum, a spatial average over many molecules, for example, an adsorbate monolayer.[14] Clearly, SM SER or TER scattering cannot lead to spectra that have nothing in common with a characteristic ensemble spectrum of the molecule. The substantially different Raman spectra presented in Fig. 3(a) in Ref. 1 point to different species, probably evolving from ongoing (photo)decomposition of MG and possible diffusion of carbonaceous species on the surface.

A particularly good example of a time-dependent spectral trajectory of SM SERS is shown in Fig. 3 of a paper by Weiss and Haran.[12] The intensity fluctuations and small band displacements that occur over a measuring time of 650 s (note the weak laser power of 10 W/cm^2) do not result in a loss of the characteristic spectral fingerprint of the adsorbate. To point out the large difference between the time series of Weiss and Haran and Neacsu *et al.*, we reproduced Fig. 3(a) of Neacsu *et al.* and marked the band positions of the six most intense MG bands in the spectral region between 1350 and 1650 cm^{-1} (see Fig. 1). A bandwidth of 25 cm^{-1} (the resolution of the instrument employed in Ref. 1) is indicated by semitransparent bars. Evidently, the spectral features in Fig. 1 do not sufficiently match the MG bands (red lines). Thus, in contrast to the spectra of Weiss and Haran, identification of MG is not possible in the time series presented by Neacsu *et al.*

In order to explain the observed features and substantial spectral fluctuations in Fig. 3(a) of Ref. 1, we refer to SER studies on carbon chain segments by Kudelski and Pettinger[15] and on single carbon domains on individual Ag nanoparticles by Moyer *et al.*[16] We claim that the broad bands between 1530 and 1590 cm^{-1} and between 1295 and 1342 cm^{-1} are due to carbon contamination and that the MG near-field spectra presented in Ref. 1, in fact, show carbonaceous species resulting from the (photo)decomposition of MG.

Dye molecules are known to decompose very quickly when exposed to intense electromagnetic fields (in particular, if exposed to the extremely enhanced fields that are created underneath an illuminated tip).[17–19] A study on the bleaching behavior on malachite green isothiocyanate (MGITC), a "sister dye" of MG, revealed a bleaching time constant τ of 0.7 s for MGITC/Au(111) in the presence of the tip for a similar incident intensity of ~5 mW and a 10^3-fold intensity increase near the tip.[20,21]

For MG, which lacks only the SCN group in comparison to MGITC, photodecomposition will occur at a similar or even higher rate, because in the experiment reported in Ref. 1, the estimated 5×10^9 TER enhancement is accompanied by a 7×10^4-fold enhanced intensity underneath the tip. In this context, note that for the experimental conditions used by Neacsu *et al.*, the local intensity underneath the tip reaches about 4×10^9 W/cm^2, clearly sufficient for rapid bleaching of the dye.[22] In other words, in the reported case of MG, the bleaching rate is 70 times faster than in the reported case of MGITC, and the dye will be decomposed before the first spectrum is recorded. To monitor unbleached MG over some time would have required an about 1000-fold lower incident intensity than used in the experiments of Neacsu *et al.*

Both carbon SER studies illustrate the temporal progression of the spectral features. Broad bands are found at 1590 and 1380 cm^{-1} for carbon on Ag (Ref. 10) and at 1580 and 1340 cm^{-1} for carbon at Au,[15] respectively, denoted in the literature as *D* and *G* bands. The spectra show large fluctuations over time, similar to the ones observed by Neacsu *et al.* (Fig. 3 in Ref. 1), and are assigned to "thermally activated diffusion of the carbon domain through a local hot spot"[16] and "substantial variations of the local carbon chain configurations as well as of the local carbon-metal bonds."[15]

In the case of Neacsu *et al.*, the carbon contaminations most likely stem from (photo)decomposition products of the adsorbate. Upon the given experimental conditions, considering the huge field enhancement of 5×10^9, bleaching of the dye molecules is inevitable. Therefore, all conclusions of the authors of Ref. 1, based on the assumption that spectra in Figs. 2(b) and 3(a) in Ref. 1 are near-field spectra of MG, are invalid.

In summary, regarding the extremely high-field enhancement that can be reached by excitation of surface plasmons in the tip-substrate cavity, single-molecule detection is feasible for TER studies.[23] However, experimental conditions and contamination-free samples are two important aspects that must not be overlooked in data analysis, especially when decreasing the number of investigated species and thus leaving a large part of the sample uncovered. Reinterpretation of the data presented in Ref. 1 leads to the conclusion that the near-field spectra stem from carbonaceous species (photodecomposition products of MG and/or contamination) rather than from single MG molecules.

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*Electronic address: domke@fhi-berlin.mpg.de

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