Raman scattering from 1,3-propanedithiol at a hot spot: Theory meets experiment

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ABSTRACT

Using tools of density functional theory, we compute the Raman spectra of 1,3-propanedithiol (PDT) isolated in the gas phase, solvated in methanol, tethered either to the face or vertex of a tetrahedral Ag_{20} cluster, and bridging two Ag_{20} clusters. The derived molecular polarizability derivative tensors are used to simulate molecular orientation-dependent Raman scattering, achieved by rotating the polarizability tensors relative to vector components of the incident/scattered radiation fields. Our framework is weighed against SERS experiments which probe the optical response at a hotspot formed by an Ag surface coated with PDT and a single 60-nm Ag nanosphere.

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1. Introduction

To gauge the contribution of chemical enhancement to the total enhancement in surface-enhanced Raman scattering (SERS), practitioners mainly rely on tools of computational chemistry/photochemistry [1]. The typical sizes of SERS reporters and model silver clusters used in such computations as well as the current implementations of Raman calculations in popular modern *ab initio* packages defaults the user to tools of density functional theory (DFT). For an ensemble-averaged measurement performed using the right-angle scattering geometry, with the polarization axis of the incident radiation perpendicular to the scattering plane, and with the scattered light collected without an analyzer, the experimental quantities of relevance are the Raman scattering activities (S_n) and the absolute differential Raman scattering cross-sections $\frac{d\sigma_n}{d\Omega}$. Within the aforementioned experimental constraints and as a result of orientational averaging (over all Euler angles), the Raman scattering activity is given by [2]:

$$S_n = g_n \left[45\bar{\alpha}_n'^2 + 7\beta_n'^2 \right] \tag{1}$$

where g_n is the degeneracy of the nth vibrational mode; $\bar{\alpha}_n'^2$ and $\beta_n'^2$ are the spherical part and anisotropy, respectively. The differential Raman scattering cross sections are defined in terms of the scattering intensities according to [3]:

$$\frac{d\sigma_n}{d\Omega} = \frac{(2\pi)^4}{45} \frac{h\omega_s^4}{8\pi^2 c\omega_n} \left(1 - e^{-\frac{hc\omega_n}{k_B T}} \right)^{-1} S_n \tag{2}$$

in which ω_s and ω_n are the scattering frequency and frequency of the nth vibrational normal mode. In the past few years, several methods which demonstrate single molecule sensitivity in SERS measurements have been documented [4–6]. In this regard, constructs featuring 'hot spots' formed by plasmonic nano-particles are increasingly popular, due to the enhanced electromagnetic fields at metal nano-gaps which can be harnessed to raise the scattered radiation from a single molecule to detectable levels [7]. In particular, metallic (e.g. silver) nano-sphere dimers – where local field enhancements $\left(\frac{E}{E_0} \right)^4$ exceeding 10^7 are attainable at a 1–2 nm wide gap – are particularly attractive [8,9]. In this regard, the common practice of using orientationally averaged scattering intensities is no longer justifiable in simulating SERS spectra at hot spots. In a recent report which probed SERS trajectories of a single biphenyl-4,4′-dithiol (BPDT) molecule linking two silver nano-spheres [10], it was suggested that the full tensor nature of Raman scattering needs to be analyzed in order to account for the observables in single molecule SERS. As such, the intensity of a vibrational mode is dictated by the orientation of a single molecule relative to the vector components of the local field defined by the metal nano-spheres as [10]:

$$S_n^2 = \sum_n \left| E_s^L \alpha_n'(\Omega) E_i^L \right|^2 \tag{3}$$

where $E_{i,s}^L$ are the enhanced local fields along the incident and scattered directions, α_n' is the molecular polarizability derivative tensor for the nth vibrational state, and $\Omega = \{\alpha, \beta, \gamma\}$ are the Euler angles which determine molecular orientation relative to the local electric fields. In principle, if molecular ensembles assume a preferred orientation on a metal substrate, a similar treatment is necessary to faithfully account for SERS observables.

In this concept study, we simulate single molecule non-resonant SERS spectra, using 1,3-propanedithiol (PDT) as a model system. The large polarizability associated with π-conjugated

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electrons in typical SERS active molecules (such as BPDT [9–11]) results in α'_{xx} components which largely predominate over α'_{yy}, α'_{zz}, and $\alpha'_{ij}(i \neq j)$. In this case study, elements of the spherical part of the α' tensor derived for PDT are comparable in magnitude for the observable vibrational states. As such, PDT is a fine gauge of the incident and scattered fields, as small rotations of this molecule induce a significant change in the simulated single molecule Raman spectra. We illustrate the concept through simulations ultimately aimed at deducing the vector components of a local electric field from single molecule SERS spectra – given the molecular polarizability derivative tensors – or *vice versa*. In addition, we perform SERS measurements which probe a PDT ensemble at a nano-junction formed by a 60-nm Ag nanosphere and a flat silver surface. We find that the agreement between our experiment and theory – even in our experiments which are geared towards probing the response of molecular ensembles – can be significantly improved by accounting for the tensor nature of Raman scattering within the outlined framework.

2. Methods

2.1. Computational

The geometry of the isolated PDT molecule was optimized using the B3LYP [12,13] functional in conjunction with the Def2-TZVP [14] basis set. Frequencies and static (0 frequency) Raman scattering activities were computed at the same level of theory, and vertical transition energies were calculated from the optimized minimum using time-dependent DFT (TD B3LYP/Def2-TZVP). The frequency-dependent molecular polarizability derivatives of the isolated molecule were computed using an incident wavelength of 532 nm [15–17], ∼300 nm red-shifted from the lowest lying excited electronic singlet state in the system. Single molecule SERS spectra are simulated according to Eq. (3), by rotating the frequency-dependent molecular polarizability tensors with respect to defined E_s^L and E_i^L fields, *vide infra*. To simulate the spectroscopic properties of PDT in solution, the molecule was optimized in methanol using the ONIOM QM:MM scheme [18]. PDT was computed at the QM level (DFT/Def2-TZVP) and the surrounding solvent molecules were simulated at the MM level (UFF). A pre-equilibrated cubic methanol box of 10 Å centered at the solute was generated. The UFF force field parameters were used for PDT, its restrained electrostatic potential (RESP) point charges generated at the HF/6-31G* level. Frequency calculations and static Raman scattering activities were again computed at the same level of theory used for geometry optimization.

To mimic the polarizability changes induced by tethering the molecule to silver clusters, DFT calculations were performed on PDT tethered either to one or two tetrahedral Ag_{20} clusters [19], see Figure 1. For the singly-substituted model, two binding motifs were tested: PDT either bound to the vertex (PDT-Ag_{20}V) or to the face (PDT-Ag_{20}F) of the tetrahedron. For these calculations, unconstrained geometry optimizations and frequency calculations were employed, and TD DFT calculations were performed from the fully relaxed minima. We also tested different charge/multiplicity combinations for the PDT-Ag_{20}V and PDT-Ag_{20}F systems. Homolytic bond breaking of one of the SH bonds followed by attaching the resulting HS–CH$_2$–CH$_2$–CH$_2$–S· radical to Ag_{20} results in an overall charge/multiplicity of 0/2 in the resulting system on one hand. On the other hand, heterolytic bond breaking results in an overall charge/multiplicity of −1/1. Technically speaking, this defaults the method of choice to either unrestricted or restricted DFT for the neutral doublet and charged singlet, respectively. For the purpose of this study, we found that the overall computed Raman spectra for the different combinations of charge and multiplicity

are very similar, and we opted to present the restricted B3LYP results for consistency. For the PDT-Ag_{20}V model, the polarizability derivatives were computed at an incident wavelength of 2000 nm, more than 1000 nm detuned from the lowest excited state predicted with TD DFT, *vide infra*. These calculations were performed using the methodologies implemented in GAUSSIAN 09 [20]. The computed UV–Vis and Raman spectra are represented as sums of GAUSSIANS and LORENTZIANS broadened by 0.1 eV and 8 cm^{-1}, respectively.

3. Experimental

3.1. Sample preparation

The sample consists of a 10 nm thick silver film evaporated onto a glass substrate by arc-discharge physical laser vapor deposition. The sputtering target was purchased from Ted Pella Inc. (99.99% purity), and the film thickness was monitored in situ using a quartz crystal microbalance. A 1 mM solution of PDT in ethanol was spin-casted onto the substrate, and the solvent was vacuum-evaporated. This was followed by spin-casting a 0.01 mg/mL colloidal suspension of ∼60 nm citrate capped silver nanoparticles (nano-Composix, Inc.), which yielded a sparse distribution of Ag nanospheres on the surface.

3.2. Combined AFM and SERS measurements

Combined AFM/Raman measurements were conducted under ambient laboratory conditions using an AFM (Nanoscope IIIa, Veeco Metrology) mounted on an inverted optical microscope (Axiovert 200, Zeiss). The incident 514 nm continuous wave monochromatic light (Innova 300, Coherent) is attenuated using a variable neutral density filter wheel (0.1–1 mW/μm^2), reflected off a dichroic beamsplitter, and focused using an oil-immersion objective (1.3 NA, 100×) onto the silver nano-particle sample surface. The AFM probe (50 nm Au tip, MicroMasch) was aligned with the laser by maximizing the intensity of the backscattered molecular response, which is collected through the same objective, transmitted though the beamsplitter, and filtered using a long pass filter. The resulting light is detected using a liquid nitrogen cooled charge coupled device coupled (CCD) to a spectrometer (Holespec f/1.8i, Kaiser Optical System). The current effective instrument resolution in the micro-Raman experiments is on the order of 8 cm^{-1}.

4. Results and discussion

The different systems considered in this study are illustrated in Figure 1. Those include the isolated PDT molecule, PDT solvated in methanol, PDT tethered to the vertex/face of the tetrahedral Ag_{20} model silver cluster, as well as PDT linking two Ag_{20} clusters. Figure 2 shows simulated TD B3LYP/Def2-TZVP UV–Vis and static B3LYP/Def2-TZVP Raman spectra of the isolated and solvated molecule. Besides a few negligible differences, the computed spectral properties of the two systems are nearly identical. The changes in electron density ($\Delta\rho$) associated with the major transitions at wavelengths greater than 180 nm are plotted in the inset of the left panel of Figure 2. The two transitions centered at ∼204 and 188 nm are mostly associated with changes in the electron density of the nonbonding orbitals on sulfur. The computed Raman spectra are thus dominated by two degenerate modes at 2678 cm^{-1} assigned to the symmetric and asymmetric S–H stretching vibrations.

The changes in molecular polarizability induced by chemically tethering PDT to a single Ag_{20} cluster can be immediately discerned by inspecting both the computed static Raman and UV–