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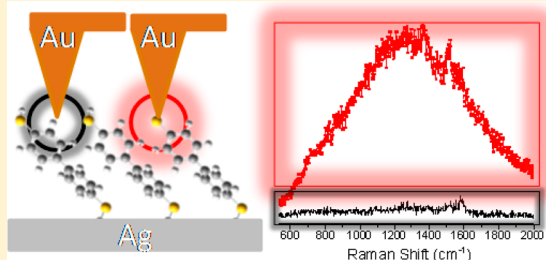
Raman Scattering at Plasmonic Junctions Shorted by Conductive Molecular Bridges

Patrick Z. El-Khoury,[†] Dehong Hu,[†] V. Ara Apkarian,^{*,‡} and Wayne P. Hess^{*,†}

[†]Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, United States

[‡]Chemistry Department, University of California, Irvine, California 92617, United States

ABSTRACT: Intensity spikes in Raman scattering, accompanied by switching between line spectra and band spectra, can be assigned to shorting the junction plasmon through molecular conductive bridges. This is demonstrated through Raman trajectories recorded at a plasmonic junction formed by a gold AFM tip in contact with a silver surface coated either with biphenyl-4,4'-dithiol or biphenyl-4-thiol. The fluctuations are absent in the monothiol. In effect, the making and breaking of chemical bonds is tracked.



KEYWORDS: Tip-enhanced, surface-enhanced, plasmons, fluctuations, quantum limit

Tapping light waves as a result of their resonant interaction with free electrons in the conduction band of metals is the concept behind several emerging nanophotonic technologies. In chemical and biological sensing, it is evident that ultimate detection limits can be reached by taking advantage of plasmonic nanostructures. This is bolstered by demonstrations of single molecule sensitivity attained in surface enhanced Raman spectroscopy (SERS) at hot spots of plasmonic nanojunctions.^{1–3} A variant of SERS is tip-enhanced Raman scattering (TERS),^{4–7} a technique that combines scanning probe (e.g., atomic force or scanning tunneling) microscopy and Raman microspectroscopy. The strong localization of optical fields at the apexes of metallic tips^{8,9} afford single molecule sensitivity,^{10,11} but now with spatial resolution of order 10 nm, significantly finer than the diffraction limit of light. Here, we report on TERS measurements in which the plasmonic nanojunction is formed by the gold tip of an AFM and a thin film of silver.

Spectroscopy at plasmonic nanojunctions is subject to rich physics. Beyond nonlinearities in scattering imposed by the strong local fields and their gradients, the interaction of molecules with the collective electron oscillations that generate the local fields becomes an important consideration. As a useful platform to interrogate such effects, we have carried out a series of studies on the prototypical plasmonic dumbbell antenna,^{12–14} engineered by chemically linking two silver nanospheres using byphenyldithiol (BPDT) as the linker.¹⁵ The elimination of orientational averaging in single molecule measurements carried out on single dumbbells restores the full tensor nature of SERS, allowing detailed analysis of spectral fluctuations in terms of local motions of molecule and field.¹⁴ Raman trajectories recorded during the fusion of the spheres identified the signature of charge transfer plasmons, which have been recently characterized through theory^{16,17} and experiments.¹⁸ The conductivity limit of plasmons is reached when

junction gaps are reduced to a few Angstroms, whereby plasmons tunnel across the gap. Dramatic enhancement in scattering intensities, spectral shift, and broadening occurs when molecules short the junction. The more compelling evidence for this process was provided by the Stark shift and spectral broadening of CO molecules caught in the junction of fusing nanospheres,¹⁴ and the observed staircase in its scattering intensity was modeled as quantized conductivity through atomic contacts.¹⁹ The measurements we report here give further support to the model. We further establish that junction plasmons can tunnel through conductive molecules that bridge the gap through chemical bonds. As such, the dramatic change in scattering associated with the shorting of the plasmon serves as a method for monitoring the making and breaking of bonds with what appears to have single bond sensitivity. The measurements are carried out on mono- and dithiolated biphenyl molecules adsorbed on a thin silver substrate (15 nm). We record their TERS using an AFM equipped with a gold tip (<50 nm cone radius).

Following laser-tip alignment, 1000 spectra were sequentially acquired with an integration time of 0.1s per spectrum. Spectral fluctuations, which are seen at early time, subside after ~40 s of data acquisition. The time averaged stationary spectrum obtained by summing over spectra recorded between $t = 40$ and 100 s is shown in Figure 1. The agreement between the measured and computed spectrum, modeled as a BPDT molecule chemisorbed on a Ag₂₀ pyramid, is remarkable. Notably, the splitting observed in the C–S stretching vibration at ~1100 cm⁻¹ as a result of the different environments about the two sulfur atoms of BPDT (S–H versus S–Ag) is well-captured by the theoretical model. Although the agreement

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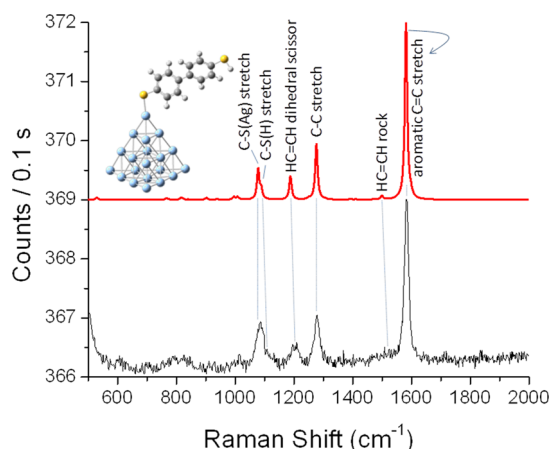


Figure 1. (Upper plot) The B3LYP/Def2-TZVP Raman spectrum based on the Ag₂₀-BPDT model (structure shown in the inset). (Lower plot) SERS spectrum of DBDT obtained by averaging over the spectra measured between 40 and 100s. See Figure 2 for more details.

may be fortuitous, if taken at face value, it would suggest that the stationary spectra belong to molecules chemisorbed on nanoasperities sustained on a corrugated surface, where the S–Ag bond is strongest. The AFM resolution is too coarse to corroborate this suggestion. However, we note that the typical surface roughness measured on freshly evaporated silver films indicates a root-mean-square height distribution of 3 nm.

The spectral fluctuations are summarized in Figure 2. The evolution of the intensity of the most prominent line, the C=C stretch at 1580 cm⁻¹, is tracked in Figure 2a. At early time, the

intensity shows spikes: events that last 0.1–0.2 s, during which the scattering response is suddenly enhanced. The intensity spikes subside and the underlying continuous background reaches a plateau at $t \sim 40$ s. The spectrum under the spike is dominated by a structureless band centered on the molecular response (Figure 2b). The spectra between spikes, although weak, contain the molecular lines over a flat background. This is clarified by the sum over all spectra collected in the first 40 s (Figure 2c). In contrast with the strictly line spectra observed after the fluctuations subside (Figure 2d), the time-averaged spectrum during $0 < t < 40$ s shows mixed character. It contains both the line spectrum of the molecule and its broadened background, reminiscent of spectra recorded during the fusion sequence of an Ag nanodumbbell linked via a single BPDT molecule. Following the assignment made there,¹⁴ here too, we associate the enhanced band spectrum to scattering driven by the conducting plasmons of the junction. The improved sensitivity in the current measurement allows us to integrate for much shorter time intervals. Even so, the spiking events appear under-sampled, typically lasting 0.1–0.2 s, with off-on transitions that are shorter than the integration time of 0.1 s.

That the spikes are the result of BPDT molecules bridging the junction by making and breaking S-metal bonds is most convincingly established by repeating the measurements using the monothiol: BPT. In this case, only single-ended bonding is possible to the substrate. The time evolution of the TERS spectra of BPT is shown in Figure 3a. Once again we see a decay in scattering intensity as a function of time. However, the decay is uneventful, and we only observe line spectra. Averaging over 900 sequentially recorded spectra yields the background-

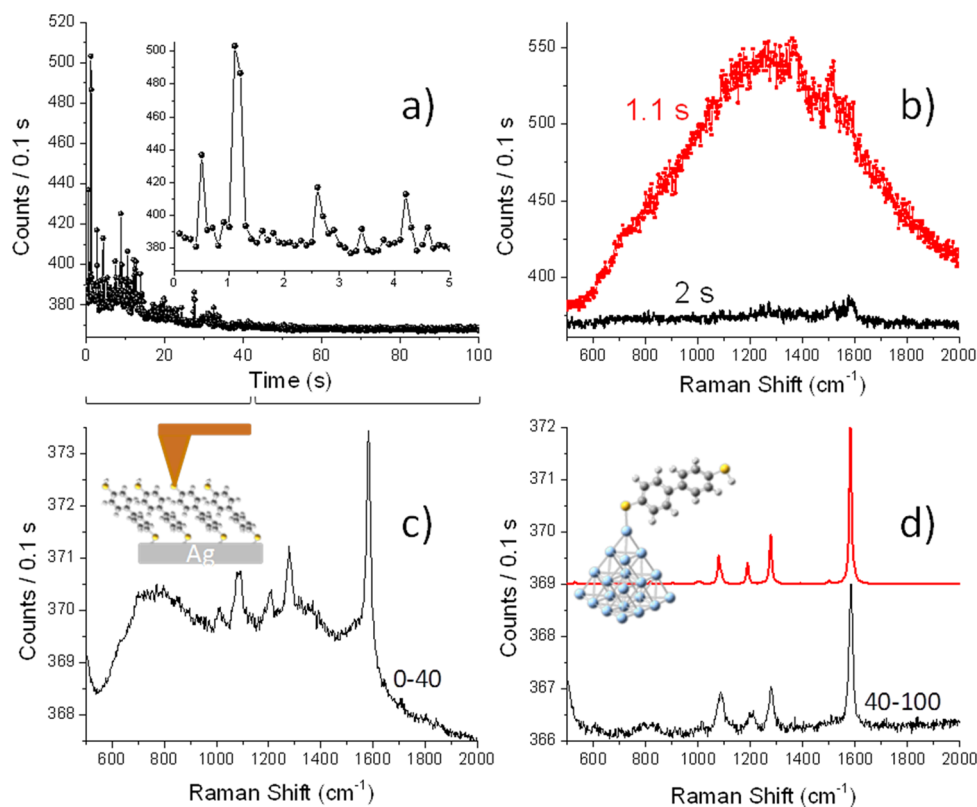


Figure 2. (a) Time evolution of the Raman scattering signal recorded from the BPDT-functionalized substrate monitored at 1580 cm⁻¹. (b) Raman spectra collected at 1.1 and 2s. (c) Raman spectrum obtained by averaging over the first 400 spectra (0–40s). (d) Raman spectrum obtained by averaging over the spectra recorded between 40 and 100 s.

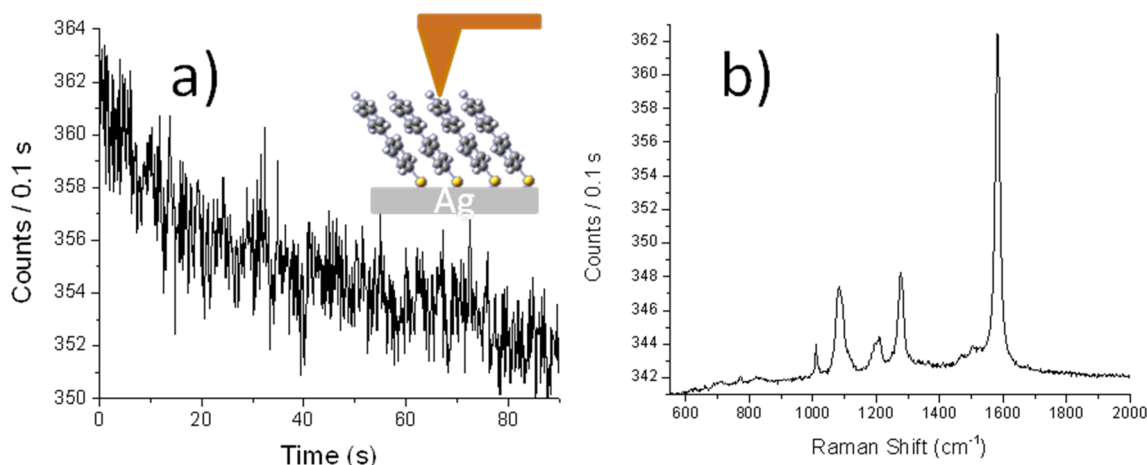


Figure 3. (a) Time evolution of the Raman scattering signal recorded from the BPT-functionalized substrate monitored at 1580 cm^{-1} . (b) Raman spectrum obtained by averaging over the spectra recorded 0 and 90 s.

free molecular Raman response shown in Figure 3b. Attempts to further test this premise by measuring SERS spectra of an insulating molecule, *n*-propyl dithiol (PDT), were unsuccessful. The scattering intensities of alkane dithiols is too weak to detect, as is well-known by the fact that such capping agents are not observable in the SERS spectra of colloidal nanospheres and nanodumbbells.¹² Recognizing that PDT can serve as an insulating layer that does not interfere with the SERS spectra, we have repeated the BPDT measurements with a gold cantilever coated with multilayers of PDT. With the insulated tip, the SERS fluctuations are absent, we only observe the background-free line spectra of BPDT.

The contrast between TERS trajectories of the monothiol and dithiol of biphenyl is the principle experimental result of the present report. Neither spiking in SERS intensities nor switching between line and band spectra occurs for the monothiol, which cannot chemisorb to the tip and surface simultaneously, eliminating the possibility of shorting the junction through chemical contacts. The measurements with a PDT-coated insulated tip confirm this conclusion. Several important conclusions seem inescapable. Clearly, conductive molecular bridges effectively shunt the junction plasmon. In the process, Raman scattering cross sections are dramatically enhanced, and the Raman spectra are significantly perturbed. At least two effects can be identified for the enhancement mechanism: the sliding of the charge transfer plasmon into resonance and direct scattering of the current carrying plasmons on the molecule. According to the prior analysis of quantized conductivity channels,¹⁹ the spike height may be associated with the number of bonds made during a given event. In effect, the modulation of the conductivity of the junction plasmon broadcasts the making and breaking of bonds. Here, the pulse height distribution of the spikes does not show obvious quantization. Besides the limited statistics in this open system, the bridging events appear faster than the sampling time of 0.1 s. In this limit, the pulse heights would be determined by the time duration of events, the distribution of which would be expected to be continuous. We note that both scattering intensity and its fluctuations subside with time. We would expect mobile molecules to migrate away from the junction, driven by the locally generated photocurrent and the thermal gradient established by the tightly focused laser field. Nevertheless, once the fluctuations subside, stationary, background free line spectra of the DBDT is observed for extended

periods. The plasmonic field of a cone of $\sim 50\text{ nm}$ is much larger than the 1 nm length of the molecules under study. Only molecules at the closest approach between tip and substrate can be expected to bridge the gap and modulate the conductivity of the junction; the majority of the interrogated molecules should be simply subject to the standard field enhancement effect. While there is not yet a quantitative treatment of the band spectra that we can associate with the current carrying molecule, the red shift and broadening of the molecular bands can be rationalized as extreme Stark effects in which the molecule oscillates between its neutral and anionic configuration.

Methods. The samples were prepared using 1 mM solutions of biphenyl-4,4'-dithiol (BPDT, Santa Cruz Biotech., Inc.) or biphenyl-4-thiol (BPT, Sigma-Aldrich) in ethanol (Gold Shield, 200 proof), spin-casted onto $\sim 15\text{ nm}$ Ag films evaporated on 0.1 mm thick microscope slides by arc-discharge physical laser vapor deposition (target: Ted Pella Inc., 99.99% purity). TERS measurements were conducted under ambient laboratory conditions using an atomic force microscope (Nanoscope IIIa, Veeco Metrology) operating in contact mode, mounted on an inverted optical microscope (Axiovert 200, Zeiss). We employ commercial Au tips (MicroMasch) with sub-50 nm radius of curvature at the apex. The incident 514 nm continuous wave laser (Innova 300, Coherent) is attenuated to $\sim 100\text{ }\mu\text{W}/\mu\text{m}^2$ using a variable neutral density filter wheel, reflected off a dichroic beamsplitter and focused onto the sample using an oil-immersion objective (1.3 NA, 100 \times). The AFM probe was aligned with the laser using noncontact 1D TERS imaging that resolves a spot size of $\sim 260\text{ nm}$ at the sample. No feedback mechanism was used to stabilize the AFM tip, which is allowed to drift on the time scale of our measurement. The scattered signal is collected through the same objective, transmitted through a beamsplitter, and filtered through a long pass filter. The resulting light is detected by a liquid nitrogen cooled charge coupled device coupled to a spectrometer (Holespec f/1.8i, Kaiser Optical System). The effective instrument resolution is $\sim 8\text{ cm}^{-1}$.

Calculations were performed using the methodologies implemented in Gaussian 09.²⁰ Full B3LYP/def2-TZVP geometry optimization was performed to locate the global minimum of BPDT bound to a finite tetrahedral silver cluster consisting of 20 Ag atoms. The computed frequencies at the optimized structure were scaled by a single factor of 0.976.

AUTHOR INFORMATION

Corresponding Author

*E-mail: (V.A.A.) aapkaria@uci.edu; (W.P.H.) wayne.hess@pnnl.gov.

Notes

The authors declare no competing financial interest.

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