Observation of Single Molecule Plasmon-Driven Electron Transfer in Isotopically Edited 4,4'-Bipyridine Gold Nanosphere Oligomers

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ABSTRACT: We clarify mechanistic questions regarding plasmon-driven chemistry and nanoscale photocatalysis within optically confined near-field plasmonic systems. Using surface-enhanced Raman scattering (SERS), we directly monitor the photoinduced reaction dynamics of 4,4'-bipyridine molecules, localized in plasmonic hot spots within individual gold nanosphere oligomers. Our experiment generates surface electrons from the gold nanoparticle using an intense off-molecular resonance continuous wave pump field, and detects radical anion products via SERS. This is done by adopting a dual-wavelength spectroscopic approach. Empirical evidence of plasmon-driven electron transfer is provided for the first time by direct detection of the 4,4'-bipyridine radical anion species localized in the plasmonic hot spots of individual gold nanosphere oligomers, corroborated by open-shell density functional theory calculations. An isotopologue approach using both protonated and deuterated 4,4'-bipyridine molecules demonstrates the single molecule response of plasmon-driven electron transfer occurring in single nanosphere oligomer systems with a 3% yield, a phenomenon unobserved in ensemble measurements under analogous experimental conditions. This mechanism has broad applicability to using nanoscale chemical reactors for surface redox reactions on the subnanometer scale.

INTRODUCTION

Energy harvesting and dissipation at plasmonic surfaces has generated substantial interest within the research community.\(^1\)–\(^9\) Specifically, recent studies show substantially enhanced yields of various photochemical reactions within the sub-nanoscale gaps, or “hot spots”, occurring in between closely spaced or coalesced noble metal nanoparticles.\(^2\)–\(^16\) To achieve such substantially enhanced photochemical yields, the frequency of incident light is tuned into the nanoparticle localized surface plasmon resonance (LSPR).\(^16\)–\(^19\) The phenomenon of LSPR features intense light focusing within the hot spots and is also an effective source of highly energetic electrons, resulting in the opening of new reaction mechanisms or dramatically enhancing existing pathways.\(^17\)

Recent examples of dynamic interaction between localized surface plasmon resonances and highly energetic electrons include water splitting,\(^2\)–\(^5\) dissociation of molecular hydrogen,\(^24\)–\(^29\) heterogeneous catalysis,\(^26\)–\(^28\) photopolymerization,\(^29\) isomerization,\(^30\) and selective bond breaking.\(^3\) The findings are of substantial interest for basic energy science research\(^31\)–\(^35\) and for designing the next generation of photovoltaics,\(^26\)–\(^38\) nanocatalysts,\(^21\)–\(^42\) and molecular-scale devices.\(^5\)–\(^7\),\(^33\)–\(^48\) Previous research has highlighted metal–semiconductor heterojunction (i.e., Au-CdSe, Au-MO₂) 2D interfacial pathways as being sources of highly efficient electron transfer, ultimately leading to low cost solar energy devices.\(^36\),\(^37\) Progress has also been made in the realization of single molecule break junctions toward molecule-based nanoscale electronics, both experimentally,\(^49\)–\(^52\) and theoretically.\(^51\),\(^52\) Limited knowledge of the precise mechanisms underlying LSPR-mediated chemistry in nanogaps restricts widespread technological applications. Specifically, recent studies find conflicting results on the origins of plasmon-assisted spectral fluctuations in nanoscale junctions.\(^53\)–\(^58\) Experimental atomic force microscopy (AFM) approaches suggest the dominance of electron tunneling and modified charge transfer plasmon (CTP) modes in nanogaps within the crossover regime (\(d < 0.3 \text{ nm}\)).\(^55\) The local plasmon charge distribution within the nanogap is modified by the creation of a quantum conductance channel that also exhibits optical rectifying behavior.\(^55\) Other studies suggest a renormalization of plasmon-polariton energy within the nanogap, giving rise to both dipolar and multipolar behavior due to presence of highly localized electromagnetic fields within the junction.\(^54\),\(^55\) Coupling of atomic-scale transport to CTPs and hybridized plasmons within the nanogap have also been considered.\(^56\)–\(^58\)

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In an effort to clarify these open questions concerning the origin of spectral fluctuations in nanoscale plasmonic systems, the current work focuses on studying transient molecular behavior. Specifically, we demonstrate the first direct spectroscopic evidence of plasmon-driven electron transfer to the 4,4′-bipyridine (BPY) molecule localized in the plasmonic hot spot of the gold nanoparticle oligomer. Our measurements first photoexcite (pump) electron transfer from the nanoparticle hot spot, then record (probe) the ensuing reaction dynamics using surface-enhanced Raman spectroscopy (SERS). The detection methodology benefits from the fact that the Raman signal within hot spots is strongly amplified (up to 8 orders of magnitude), thus constituting a sensitive nanoscopic optical probe of the charge transfer reaction. Interestingly, despite a submonolayer covering the entire surface of the nanoparticles, an isotopologue proof suggests that the photoinduced electron transfer reaction and subsequent radical anion formation are essentially single-molecule events. Moreover, this reaction has a sharp turn-on threshold with respect to incident pump optical field intensity. Our interpretation of experimental results is supported by density functional theory (DFT) calculations and time-resolved resonance Raman (TR3) literature data. These findings advance the fields of plasmon-driven chemistry and nanoscale photocatalysis by shedding light on the near-field optical and electronic response within plasmonic nanogaps.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Nanosphere oligomers (also referred to as nanotags, nanoparticle assemblies, nanoantennae, nanodumbbells, etc.) consisted of aggregated 90 nm diameter gold spherical cores functionalized with submonolayer coverage of a 50:50 mixture of protonated (h$_8$) and deuterated (d$_8$) 4,4′-bipyridine molecules (BPY-h$_8$ and BPY-d$_8$). The dual functionalized (BPY-h$_8$ + BPY-d$_8$) nanoparticle oligomer sample allows for an isotopologue approach to studying plasmon-driven chemical events present in SERS spectra. The use of isotopologues is a well-established and rigorous method that has been utilized in frequency domain proofs of single molecule detection in SERS.17,60,61

The choice of BPY was made due to its well-known optical, chemical, and electronic properties. In polymer and crystal engineering, BPY is an ideal bridging ligand for propagating structural motifs, resulting in the creation of thousands of coordination complexes ranging from one- to three-dimensional topologies by anion exchange.62–66 Moreover, BPY’s rod-like rigidity and strength along with its ability to mediate intramolecular electron transfer are responsible for the molecule’s widespread use in creating new materials.67–72 In addition to these useful electrochemical properties, BPY has figured prominently in both resonance and surface-enhanced Raman scattering studies. BPY reduction has been extensively documented in both the SERS3–5 and resonance Raman literature.73–76 In particular, the radical anion resonance Raman spectrum is known for both protonated and deuterated BPY species.74

A protective silica shell encapsulates the molecule-core system (STA Technologies Inc., Albuquerque, NM) as depicted in **Figure 1.** The subnanometer intercore separation (<1 nm) provides a SERS signal enhancement of up to 10$^6$ for wavelengths near 785 nm.16 The initial stock solution was diluted to 1:300 parts in methanol, vortexed, and drop-cast onto carbon thin film 300 nm mesh copper TEM grids (Ted Pella, Inc., Redding, CA). Excess drop-casted liquid was siphoned off using sterile lab fiber tissue (Kimtech®, Kimberly-Clark Professional). The dilution procedure resulted in evenly coated grids where each mesh contained an average of less than one SERS active nanosphere oligomer.

Microscope glass coverslips (VWR International, No.1, 25 mm diameter) underwent piranha treatment (3:1 H$_2$SO$_4$:30%H$_2$O$_2$) followed by thorough rinsing with Milli-Q water (18.2 MΩ·cm).

**Figure 1.** Single particle pump–probe scheme for generation and detection of radical anion species due to plasmon-driven electron transfer in 4,4′-BPY-h$_8$/d$_8$ gold nanoparticle oligomers.

Coverslips were then immersed in a base treatment, (5:1:1 H$_2$O:NH$_4$OH:30%H$_2$O$_2$), sonicated for 60 min, and again thoroughly rinsed with Milli-Q water. Sample grids were positioned on top of N$_2$ dried coverslips and mounted inside a sample stage above the microscope objective.

**Visible–NIR Nanoparticle Extinction Characterization.** The extinction spectrum for BPY nanoparticle oligomers was obtained in solution using a spectrophotometer in double beam mode (Cary 5000, Agilent Technologies). The nanoparticles were scanned over a wavelength range of 400–1000 nm. Extinction spectroscopy yields insight into the monomer (i.e., single core) and multicores resonances present in the aggregated nanoparticle oligomer samples. The isotopologue BPY nanoparticle oligomers have optical and structural properties similar to molecule-functionalized nanoparticle oligomers used in previous SERS experiments.16

**Pump–Probe Measurements.** During measurements, samples were imaged using dark-field optical microscopy (Nikon condenser, NA = 0.80–0.95) and irradiated with two spatially overlapped, collinear beams in an epi-illumination microscope setup (Nikon Ti–U) using a 40× objective (NA = 0.60). A 10–90 beam splitter (ThorLabs, Newton, NJ) was used to couple the pump and probe beams prior to entering the microscope. Individual particles were indexed using a CCD camera (UNIQ vision, Inc., Santa Clara, CA) attached to an auxiliary microscope port. The two-color experimental setup allows for simultaneous illumination with a 785 nm CW laser (Renishaw Inc.) and 532 nm CW laser (Spectra-Physics, Santa Clara, CA). LabVIEW software used in conjunction with WinSpec (Princeton Instruments, Trenton, NJ) was used to automate pump and acquisition times by interfacing between a USB optical shutter (Picard Industries, New York) and the logic output of a PIXIS 400BR CCD Camera (Princeton Instruments, New Jersey) set to a 2 MHz digitization rate for fast spectral acquisition.

Ensemble pump–probe measurements were conducted in solution phase and at high concentrations of nanoparticle oligomers immobilized on a glass substrate. Single particle measurements were then performed under identical experimental conditions and pump–probe fluences. For all particles studied, a 532 nm pump power density of 12 µW/µm$^2$ and a 785 nm probe power density of 0.32 µW/µm$^2$ was used. Many pump power densities were tested ranging from 1.244–12.44 µW/µm$^2$ and ultimately 12.44 µW/µm$^2$ was selected as the optimal power at which spectral fluctuations could be induced with minimal decay in neutral molecule intensity (see Figure S1). A systematic pump power dependence study was performed on the same single nanoparticle oligomer and showed a sudden “turn on” fluorescence at which new spectral modes or events were observed. A minimum pump power density of 9.95 µW/µm$^2$ was determined sufficient to induce new spectral modes for the acquisition parameters used.

Prior to pump–probe measurements, each nanoparticle oligomer was irradiated with a single color 785 nm probe field (300 s). The probe fluence was sufficiently low to prevent any appreciable change in the spectra, and consequently all new vibrational spectral features are due to the intense pump field. A total of 25 nanoparticle oligomers were studied, all of which had a stable neutral molecule signal (BPY-h$_8$).
nσ, respectively, with acquisition parameters were calculated according to the following equation:

\[
\frac{\partial \sigma}{\partial \Omega} = \frac{\sigma^3}{\epsilon_0^2} \left( \omega - \alpha_p \right)^4 \frac{\hbar}{8\pi \alpha_p^2 S_c} \left( \frac{1}{45(1 - \exp(-\hbar c \omega / k_B T))} \right)
\]

where \(S_c\) represents the Raman activity for the \(p\)th vibrational mode \((\omega_p)\) and the remainder of the expression contains the fourth order dependence of scattering on frequency and the thermal Boltzmann distribution. An excitation of 12738.85 cm\(^{-1}\) was used, corresponding to 785 nm excitation and temperature was assumed to be 298 K. All theoretical spectra were broadened to Lorentzian lineshapes with full-width half-maximum widths of 20 cm\(^{-1}\).

**RESULTS**

**Ensemble Measurements.** Extinction characterization reveals the presence of two plasmon resonances as shown in Figure 2. The transverse resonance occurs in the visible region at \(~588\) nm, which contains contributions from primarily single core nanoparticles (monomers). A second broader resonance, attributed to the longitudinal resonance, occurs in the near-infrared spectral region and corresponds to contributions from multicomponent resonances such as dimers, trimers, etc. The BPY-d\(_8\)/d\(_8\) extinction profile is very similar to the trans-1,2-bis(4-pyridyl)ethylene (BPE) nanosphere oligomers sample used in our previous work. The similarity of optical, structural, electronic, and chemical behavior between the BPY-d\(_8\)/d\(_8\) and BPE nanosphere oligomers serves as a convenient point of comparison. The sample is photoexcited using high intensity 532 nm irradiation resonant with the transverse plasmon mode, while probing with 785 nm light that produces a maximal enhancement factor, thus providing the necessary signal enhancement for observing plasmon-driven chemical events. The ensemble SERS spectra are shown in Figure 3, where contributions from the BPY-d\(_8\) and BPY-d\(_8\) isotopologues are clearly identified in the mixed (BPY-d\(_8\) + BPY-d\(_8\)) aggregated nanosphere oligomer sample (Figure 3). The mode assignments for the neutral protonated and deuterated species can be found in literature.

**Figure 2.** Visible–NIR extinction spectrum of BPY-d\(_8\)/d\(_8\) gold nanosphere oligomers in solution phase. Monomer resonance is observed at 588 nm, while the multicomponent resonance is the broad feature in the near-infrared.

**Figure 3.** Ensemble SERS of 90 nm gold nanosphere oligomers functionalized with BPY-d\(_8\) and BPY-d\(_8\) molecules. SERS spectrum of pure BPY-d\(_8\) (blue), pure BPY-d\(_8\) (red), and 50:50 mixture of BPY-d\(_8\)/d\(_8\) (black) molecules are shown above.
value which is consistent with expected ensemble behavior (see Figure S4). Anionic modes were observed only in the single particle case, as illustrated in the following analysis.

**Single Particle Measurements.** Figure 4 presents data collected from two nanosphere oligomers, each of which displays predominantly either BPY-\(h_8\) anionic behavior (1666, 1511, 1354, and 1105 cm\(^{-1}\)) or BPY-\(d_8\) anionic behavior (1584, 1458, and 839 cm\(^{-1}\)). In Figure 4A, a 2D waterfall plot depicts the presence of strong neutral contributions from BPY-\(h_8\) and BPY-\(d_8\) in early time frames for one nanosphere oligomer. Beginning at 148 s of 532 nm optical pumping, the BPY-\(h_8\) radical anion is observed and persists for many frames (hundreds of seconds). During this period, the neutral BPY-\(h_8\) + BPY-\(d_8\) signal is stable and at a consistent intensity. Following the disappearance of BPY-\(h_8\) anionic modes, the neutral signal begins to decay with a prominent drop-off in intensity occurring around 600 s pump time. Figure 4D depicts similar behavior for both neutral species and the BPY-\(d_8\) radical anion which appears at 209 s of pump time. BPY-\(d_8\) anionic modes persist for several frames at a time, blinking on and off throughout the course of over 50 acquisition frames before disappearing entirely.

Representative \(h_8\) anion and \(d_8\) anion events are shown in the bottom panels of Figure 4, namely in C and D. The top spectra in bottom panels show contribution from neutral species only (\(h_8 + d_8\)), which is the most frequently occurring spectrum in all data collected for each nanosphere oligomer. However, in a small but significant number of frames, we observe the sudden appearance of well-defined modes for the radical anion. Representative anion events for both BPY-\(h_8\) (Figure 4C, middle spectrum) and BPY-\(d_8\) (Figure 4D, middle spectrum) are shown with neutral features (top black spectrum) subtracted. Modes corresponding to anion peaks are labeled, while unlabeled modes are due to either imperfect subtraction of the neutral features or due to other unassigned species present. For the \(h_8\) anion, we see sharp modes at 1666, 1511, 1354, and 1105 cm\(^{-1}\), which persist for many frames. In particular, the vibrational modes appearing at 1609, 1511, and 1354 cm\(^{-1}\) are consistent with resonance Raman spectra of the \(h_8\) anion probed at 532 nm.\(^{77}\) There is also good agreement between two-color anion spectra and DFT calculations for the protonated anionic species. For the \(d_8\) anion, sharp modes appear at 1458 and 839 cm\(^{-1}\) that persist for many frames and are in good agreement with DFT calculations. These modes along with the presence of the 1584 cm\(^{-1}\) mode are also consistent with resonance Raman time-dependent spectra of the \(d_8\) anion detected at 532 nm.

The mode assignments for the BPY-\(h_8\) and BPY-\(d_8\) anion radicals can be found in Table S1 that consist primarily of CH interplanar bending and pyridine ring stretching modes. The calculated Raman cross section for the BPY anion is 10x larger than the neutral BPY cross section. Consequently, the anion signal dominates over the neutral BPY signal at the single molecule level. The theoretical spectra for both neutral and
radical anion BPY-$h_g/d_g$ species are shown in Figure S5, where the CAM-B3LYP was chosen for comparison against experimental spectra because of its agreement with TR² literature and its long-range corrected behavior (Figure 4).

Spectral variance of the identified anion modes was assessed with peak analysis using automated software packages in Matlab to identify the degree of vibrational mode localization. Intensity and location of peaks were extracted from a nonlinear optimization algorithm with quadratic interpolation using the peakfinder.m function in Matlab. A threshold value equivalent to $(\max(x) - \min(x))/4$ in counts was specified. Integrated peak area and peak widths were obtained by automating the peakfit.m function in Matlab with unconstrained Gaussian fits and linear baselineing after background subtraction. Spectra were smoothed using a Savitsky–Golay filter before plotting. All neutral and anionic modes identified are unique, stable, and spectrally well-defined. Figure S6 shows representative frequency histograms for the $h_g$ neutral molecule (1609 and 1025 cm⁻¹), $d_g$ neutral molecule (1584 and 1195 cm⁻¹), $h_g$ anion molecule (1511 and 1354 cm⁻¹), and $d_g$ anion molecule (1458 and 839 cm⁻¹). Additional histograms can be found in Figure S7 of the Supporting Information.

The two most intense modes each from the $h_g$ neutral molecule (1609 and 1025 cm⁻¹) and the $d_g$ neutral molecule (1584 and 1195 cm⁻¹) have well-defined modes with frequency ranges of 8 cm⁻¹ or less. The full-width-half-max (fwhm) of these modes is ≤3.35 cm⁻¹. In comparison to the neutral molecules, the frequency range for the $h_g$ anion modes is broader than the neutral species, spanning ≤15 cm⁻¹ for the four most intense pure anion modes (1666, 1511, 1354, and 1105 cm⁻¹). Likewise, the fwhm of $h_g$ anion modes are also broader with fwhm of ≤6 cm⁻¹. Both 1511 and 1611 cm⁻¹ modes exhibit minimal spectral wandering. When fitted to a normal distribution, these modes have fwhm values of 4.35 and 5.49 cm⁻¹ respectively. Anionic modes located at 1105, 1354, and 1666 show greater spectral wandering with normal distribution fwhm values of 11.65, 8.08, and 15.36 cm⁻¹. Similarly, for the most intense pure $d_g$ anion modes (1458 and 839 cm⁻¹), the frequency spans a slightly smaller range of ≤10 cm⁻¹ with a fwhm of ≤6 cm⁻¹.

The observed frequency variance can be explained by a variety of molecule–surface effects. Immobilization of the anion on the surface of gold nanoparticles could contribute to observed frequency shifts resulting from distortion of vibrational modes. Atomic scale surface deformation or welding caused by the high intensity pump field could also lead to variance in spectral location due to changing orientation and local environment of molecules near the surface.²² As the surface within the hot spot junction evolves and undergoes dynamic change under intense irradiation, charge carrier injection rates improve with increasing surface contact area according to Fowler theory.³³ Differences in polarizability and molecular absorption sites can also account for variation in spectral locations of anion modes.

**Discussion**

In our experiment, after an electron transfers to the lowest unoccupied molecular orbital (LUMO) of an absorbed BPY molecule an anionic species is created. After a time delay, the probe beam then creates a Raman scattered photon. Similarly, the pump field can also promote an electron from the molecule to the gold surface, resulting in the generation and detection of a cationic species. Cation signatures were identified in one particle through corroborration with theoretical calculations (see Figure S8). Neutral molecules that did not undergo an electron transfer process are probed using SERS as well. The following discussion addresses the decay lifetime of the radical anion, the degree to which the observed anion modes exhibit time-dependent correlation, as well as a qualitative estimation, using isotopologues, of the number of molecules participating in this plasmon-driven electron transfer reaction.

**Decay Rate of Anion Events and Charge Stabilization.**

Pyridine derivatives are known to form stable radical anions. Specifically, the stable BPY anion radical has been studied both in resonance Raman⁷⁵–⁷⁸ and absorption experiments.⁸⁴ The decay process for the radical anion was examined in our single nanoparticle experiments where an anion event was defined as the appearance of either $h_g$ anion modes (1666, 1511, 1354, and 1105 cm⁻¹) or $d_g$ anion modes (1584, 1458, and 839 cm⁻¹) or contribution from both. Lifetimes of the radical anion were determined by cataloguing the time period between “on” and “off” anion spectra. Figure 5 shows the distribution of lifetimes for each observable anion event, defined from the time at which anion modes first appear (“on”) through when anion modes disappear (“off”). The distribution of lifetimes can be fit to an exponential decay and a τ = 46.1 ± 4.55 s, which is consistent with a single rate process. In our experiment, the 532 nm field generates surface electrons that become self-trapped at the surface.⁸⁵,⁸⁶ Surface accumulation of electrons on gold nanoparticles has been recently experimentally observed under continuous visible irradiation ($λ ≅ 532$ nm, $P = 0.9 \times 10^{-2}$ μW/µm²).⁸⁷ At this power density, a significant population of electrons (ca. 8500 electrons) can be generated at the nanoparticle surface due to a decrease in activation barrier, resulting in a surface potential as high as 240 mV. Recent experiments involving photodriven hole transfer have also established a photocurrent surface accumulation on the second time scale in gold-silica nanoparticles.⁸⁸ In our experiments, the 532 nm pump field is three orders-of-magnitude greater in power density, leading to a plausible accumulation of enough surface electrons to be successfully scavenged by a neutral BPY molecule within the hot spot.

![R² = 0.98](image)

**Figure 5.** Distribution of radical anion lifetimes defined as period of time between “on” and “off” spectra containing anion events. Functional form fit corresponds to an $e^{-x/τ}$ decay rate.
In the solid state, polarization variances within the local environment contribute to stabilization of charged species. Nearby a metal, charged states are further stabilized through the image potential.\(^{89}\) Image potentials arise from Coulomb attraction between an ion at a distance \(z\) from a metal and its image mirrored at \(-z\) inside the metal, with binding energy, \(V(z) = -e^2/4ez\), where \(e\) is the local dielectric.\(^{85,86}\) The image potential supplies the differential solvation energy between the neutral and ion. Assuming \(e = 1\), the molecule must be within a distance of \(\leq 2.7\) Å from the surface, for the sum of the image potential and electron affinity to be greater than the energy of the pump photons (2.3 eV) required for the photostability of the radical anion. The electron affinity for the anion is also greater than that of the neutral molecule, making the anion a more energetically favorable state when compared to the neutral molecule when in the presence of an electron (see Figure S9).

**Correlation Coefficient of Anion Modes and Semi-quantitative Agreement with Theory.** Time-dependent correlation between identified anion modes was established using eigenvector decomposition of the time series SERS data. The calculated DFT anion modes are used as a reference signal, and the theoretical eigenvector is defined as

\[
q_i = \{\omega_i, \gamma_i, \beta_i\}
\]

where \(i\) is the eigenvector index, \(\omega_i\) is the theoretical mode frequency, \(\gamma_i\) is the peak width, \(\beta_i\) is the peak intensity, and \(c\) is a function defined as a third order polynomial that accounts for the baseline shift between experiment and theory. After accounting for uniform spectral shifts between theory and experiment, the experimental mode frequencies are defined by the expression \(\nu_i = \omega_i\). The four most intense \(h_8\) anion modes \(\nu = (1666, 1511, 1354, \text{ and } 1105 \text{ cm}^{-1})\) and three most intense \(d_8\) anion modes \(\nu = (1584, 1458, \text{ and } 839 \text{ cm}^{-1})\) were analyzed using this method. The eigenvector index for \(h_8\) anion modes corresponds to \(i = (1, 2, 3, 4)\) and for \(d_8\) anion modes to \(i = (1, 2, 3)\). The time-dependent correlation coefficient, \(a_i(t)\), is defined as the matrix multiplication between the theoretical eigenvector and the experimental time series matrix, normalized by the length of both eigenvectors. The fitted parameters of experimental peak frequency location (\(\nu_i\)), peak width (\(\gamma_i\)), and peak intensity (\(\beta_i\)) are given by \(j = (\nu, \gamma, \beta)\) where the experimental time dependent signal is given by \(\psi(t)\):

\[
a_i(t) = \frac{\langle q_i(t) \cdot \psi(t) \rangle}{|q_i| \cdot |\psi_i|}
\]

\[
a_j(t) = \frac{\langle \gamma_j(t) \cdot \psi(t) \rangle}{|q_j| \cdot |\psi_i|}
\]

\[
a_p(t) = \frac{\langle \beta_p(t) \cdot \psi(t) \rangle}{|q_p| \cdot |\psi_p|}
\]

Figure 6 shows the time-dependent correlation coefficient as a function of optical pump time for both the (A) \(h_8\) anion (1666, 1511, 1354, and 1105 cm\(^{-1}\)) and (B) \(d_8\) anion (1584, 1458, and 839 cm\(^{-1}\)) modes, where a zero value of the correlation coefficient corresponds to no correlation between modes and a value of one corresponds to strong correlation between anion modes. Properties of vibrational modes such as the peak location (or frequency), peak width, and peak intensity were considered. A clear jump in the correlation coefficient is observed at 150 s of pumping time (Figure 6A), coinciding with the simultaneous appearance of new spectral lines at frequency locations corresponding to the \(h_8\) anion (see also Figure 4) and a general decrease in neutral molecule signal. This behavior persists for 130 s of pumping with 532 nm, after which there are no new spectral lines other than the neutral BPY-\(h_8\) and BPY-\(d_8\) species. Likewise, in a different particle, a jump in the correlation coefficient occurs at 210 s of pumping time for the spectral regions corresponding to the 1458 and 839 cm\(^{-1}\) modes (Figure 6B). The appearance of \(d_8\) anion modes coincides with the simultaneous decrease in neutral reporter molecule signal, suggestive of a small number of molecules actively undergoing transitions from neutral to anionic states within the nanoparticle hot spot.

Overall, we observe a downward trend of SERS intensity in time, indicating a loss of neutral molecule signal. This could correspond to diffusion of molecules away from enhancing regions if a large number of molecules contribute to the SERS signal. However, there are many oscillations and spikes in the time-dependent peak area data, suggesting that contributions from individual molecules are substantial (see Figures S10 and S11). The switching-like behavior suggests that one, or a few molecules, are undergoing many changes back and forth between anionic and neutral states throughout the course of an acquisition, while diffusing into and out of the hot spot.
Although there are many neutral molecules contributing to the overall SERS signal, only a few molecules at a time are contributing to the anionic signal due to their location in highly enhancing regions in the nanosphere oligomers.

The time-dependent intensity distribution of pure anionic modes was also examined for both protonated and deuterated species. Figure S12a depicts the distribution of intensities for the four most intense \( h_8 \) anion modes. In our ensemble-averaged studies, intensity fluctuations of no greater than 1.4× the smallest value were observed (Figure S4). An intensity distribution of greater than 2× is known to be a signature of single molecule behavior.\(^{60}\) Here we see an intensity fluctuation as great as nearly 3× the minimum value, suggestive of few molecule events. Figure S12b also shows a broad range of intensities for the \( d_8 \) anion further suggesting that electron transfer initiated state changes are actively occurring within only a small collection of molecules (see Figure S4 for comparison with ensemble behavior).

An explanation for the sudden appearance of spectral lines after considerable pumping time suggests accumulated thermal factors in the creation of the anionic species. The disappearance of spectral fluctuations and loss of neutral molecule signal could also be due to thermally driven diffusion of molecules away from the hot spot. Bleaching of the molecule and deformation of the nanoparticle surface on the second time scale may also contribute.\(^{60}\) Recent atomic-force microscope tip-enhanced Raman (AFM-TERS) experiments have proposed a correlation between peak width and internal temperature of single molecule dynamics, with a 10 cm\(^{-1}\) range corresponding to a temperature difference of as much as 300 K.\(^{91}\) Longer-lived thermalized carriers are known to dominate spectral signatures at wavelengths close to gold nanoparticle interband resonance (530 nm).\(^{92}\) Peak widths for both the \( h_8 \) and \( d_8 \) neutral species become more dynamic after the appearance of the \( d_8 \) anion and exhibit a wider wavenumber range over time (Figure 6). The width of the \( h_8 \) anion mode varies considerably (10 cm\(^{-1}\)) over the course of optical pumping. This is mirrored by a similar distribution in peak width of the \( h_8 \) neutral molecule. The neutral \( d_8 \) molecule does not fluctuate in peak width. This suggests the appearance of the anion is accompanied by the creation of highly localized hot-spots effecting the \( h_8 \) neutral and anion but not the \( d_8 \) site on the same nanocluster, or location of more \( h_8 \) neutral molecules in hot spot regions where electron hopping is stabilized and detectable by SERS.

**Qualitative Estimation of Number of Molecules Involved in Anion Events.** Plasmon-driven electron transfer yields were quantified using statistical analyses across all particles showing either \( h_8 \) or \( d_8 \) anionic behavior. The isotopologue analyses reveals interesting information regarding the nature of plasmon-driven electron transfer within the hot spot. Figure 7 shows representative spectra containing pure \( h_8 \) anion events, pure \( d_8 \) anion events, and mixed anion events. The 1511 and 1354 cm\(^{-1}\) modes are the most intense identifiers for the \( h_8 \) anion while the 1458 cm\(^{-1}\) mode signifies the \( d_8 \) anion. In this way, an isotopologue approach is used to quantify pure \( h_8 \) or \( d_8 \) anion events, as well as mixed anion events. Figure 8A–8C presents data across three different nanosphere oligomers. Events are classified as pure \( h_8 \) events when they contain at least two pure \( h_8 \) anion modes and no contributions from the \( d_8 \) anion. If a \( h_8 \) event contained at least one mode from the \( d_8 \) anion, the event was counted as a mixed event. An identical process was applied to assigning pure \( d_8 \) events. The total number of acquired frames, \( N_i \), is denoted in the upper right corner for each particle where all frames contain spectra from both neutral BPY-\( h_8 \) and BPY-\( d_8 \). The histogram shows the number of events of the total frames \((N)\) that had anionic behavior. The nanosphere oligomers shown in Figure 8A and 8C both show a preference for \( h_8 \) anionic behavior, while the particle shown in Figure 8B favors \( d_8 \) anion behavior, even though both neutral species are always present. No events for \( d_8 \) were observed in two nanosphere oligomers (Figure 8A and 8C).

The composite histogram across three nanosphere oligomers in Figure 8D displays a bimodal distribution suggesting plasmon-driven electron transfer is a subensemble process where a few molecules are actively undergoing electron transfer within the hot spot. Interplay between the aforementioned molecular and electronic properties has profound impact on
accessibility of various redox pathways and their respective kinetic rates, which consequently influences the occurrence and detection of these events. The 3% yield reported in this work refers to the likelihood that an electron, once produced, will jump to a nearby molecule and form a radical anion. The value was determined by dividing the number of frames in which at least three anion modes of the same isotopologue were detected ($h_8$ anion or $d_8$ anion or both = 66 spectra) by the total number of spectra acquired (total = 2200 spectra). Our estimated yield considers the probability that an electron can form a negative anion, and is to be distinguished from other definitions of quantum yield such as that referring to the likelihood of producing electrons at the nanoparticle surface.

## CONCLUSION

We have demonstrated the first direct detection of the radical anion species created through plasmon-driven electron transfer. The new spectral modes corresponding to the radical anion are sharp and well-defined, while also exhibiting strong time-dependent correlation. The single molecule response of plasmon-driven electron transfer occurring at the subnanometer scale is shown in the BPY molecule using an isotopologue approach with a yield of 3% across all experimental data collected. Strong evidence for plasmon-driven electron transfer is demonstrated by agreement between experimental data containing the vibrational signatures of both the $h_8$ and $d_8$ anions, known from DFT calculations and existing literature.77 Utilization of this new phenomenon will have profound impact on nanoscale photocatalysis and conductive molecular junctions. The understanding of alternate reaction pathways through plasmon-driven chemistry can be applied to basic energy research and nanoscale devices.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08868.

- Pump power dependence, TEM images, Digital timing diagram, DFT calculations, Ensemble intensity variance, Energy diagrams and potential energy surfaces, Anion mode assignments, frequency variance histograms, Integrated peak areas for neutral and anion radical, Intensity variance for BPY-$h_8/d_8$ anion modes, Radical cation signature (PDF)

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### Notes

The authors declare no competing financial interest.

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