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Detection of electron tunneling across plasmonic nanoparticle-film junctions using nitrile vibrations

Hao Wang, Kun Yao, John A. Parkhill*, and Zachary D. Schultz*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, 46556, USA

Abstract

The significant electric field enhancements that occur in plasmonic nanogap junctions are instrumental in boosting the performance of spectroscopy, optoelectronics and catalysis. Electron tunneling, associated with quantum effects in small junctions, is reported to limit the electric field enhancement. However, observing and quantitatively determining how tunneling alters the electric fields within small gaps is challenging due to the nanoscale dimensions and heterogeneity present experimentally. Here we report the use of a nitrile probe placed in the nanoparticle-film gap junctions to demonstrate that the change in the nitrile stretching band associated with the vibrational Stark effect can be directly correlated with the local electric field environment modulated by gap size variations. The Stark shift arises correlates with plasmon resonance shifts associated with electron tunneling across the gap junction. Time dependent changes in the nitrile band with extended illumination further support a build up of charge associated with optical rectification in the coupled plasmon system. Computational models agree with our experimental observations that the frequency shifts arise from a vibrational Stark effect. Large local electric fields associated with the smallest gap junctions give rise to significant Stark shifts. These results indicate that nitrile Stark probes can measure the local field strengths in plasmonic junctions and monitor the subtle changes in the local electric fields resulting from electron tunneling.

Introduction

The Recent advances in nanotechnology and nanophotonics allow for more exquisite control of electric fields on subwavelength dimensions.¹⁻⁴ Through localized surface plasmons, nanostructured plasmonic devices provide an ideal platform to confine electric fields in sub-diffraction limited volumes, while simultaneously achieving several orders of magnitude of field enhancement, thus enabling opportunities in numerous applications such as: heterogeneous photocatalysis^{5, 6}, single molecule detection^{7, 8}, and nonlinear optics^{9, 10}. Conventionally, solutions of Maxwell's equations predict the enhancement and distribution of local electric fields around the nanostructures well; however, experiments and quantum calculations of nanoparticles with narrow gaps indicate a "quantum regime" exists where Maxwell's equations break down.¹¹⁻¹⁶

* Schultz.41@nd.edu; john.parkhill@nd.edu. .

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Evidence for the quantum regime derives from experiments, such as those reported by Savage et al. where changes in the plasmon resonance are observed to deviate from classical descriptions as two nanoparticle scanning probe microscope tips are brought into contact.¹¹ Classically as nanoparticles come into close proximity, the formation of coupled plasmon resonances gives rise to a red shift in the resonance frequency. However, at sub-nanometer distances, the sudden onset of a blue-shifted resonance has been observed and attributed to quantum effects. Calculations suggest that at these extremely small particle separations, effects such as electron tunneling, can have pronounced effects on the local electric fields in the gaps.¹⁷ However, calculations are somewhat limited by the cost of full quantum treatment of realistically sized nanoparticles.^{14, 18, 19}

Quantitatively determining the electric fields around real nanostructures is challenging. Experimentally, this typically involves transmission electron microscopy (TEM) and indirect approaches such as electron energy loss spectroscopy (EELS)^{20, 21} or surface-enhanced Raman scattering (SERS)²². Based on experimentally determined geometries, electric fields can be calculated and compared with the EELS results, although caution must be taken when correlating the EELS mode maps with the plane-wave induced electric fields. The physical dimensions (sub 1 nm gaps) associated with the onset of the quantum regime also occur near the resolution limit of electron microscopy.^{12, 23, 24} SERS measurements are further complicated by challenges with determining the number of molecules experiencing the intense local electric fields and the molecular orientation that contribute to the SERS intensity.^{25, 26} Tip enhanced Raman scattering (TERS) provides some additional control relative to SERS;^{27, 28} however, recent results suggest effects not adequately explained by classical field enhancements.^{7, 29}

The vibrational Stark effect (VSE) provides another route to monitor electric fields associated with nanostructures. Acting as a molecular voltmeter³⁰⁻³², the vibrational frequency shifts can be utilized as a direct indicator of the local electric fields. The VSE occurs when the local electric field perturbs the electronic environment of a chemical bond and results in a change in its vibrational energy, which can be directly measured with infrared or Raman spectroscopy.³³ Due to these advantages, the VSE has been used to quantify local electric fields in a diverse range of chemical environments including organic solvents^{34, 35}, ionic liquids^{36, 37}, catalysts^{31, 38}, proteins^{39, 40} and biomembranes⁴¹.

Illuminating nano-junctions at the gap plasmon resonance frequency will induce a current, an effect explained by optical rectification.⁴²⁻⁴⁴ In optical rectification, optical excitation results in a DC bias associated with the movement of the electrons in the sample. The bias is dependent upon illumination. Using the formalism of optical rectification and VSE, the local electric fields in plasmonic nanostructures have been measured in the range of 1~100 MV/cm with CO^{30, 45} and CN^{27, 46} Stark probes. Recently, Natelson et al. reported an intricate interplay of Stark physics and bias-induced charging both modifying the vibrational energies of a molecule.⁴⁷ Two distinct frequency shift behaviours were identified for molecules with different permanent dipoles through a biastuned SERS approach. Importantly, their work revealed that for molecules with a permanent dipole residing in a nanostructured plasmonic junction, the VSE could significantly alter the observed vibrational frequencies.

In the present work, we report how nitrile frequencies change with the local electric fields modulated by the gap size between a nanoparticle and a thin Au film, the so-called nanoparticle-on-mirror (NPoM) geometry. We use a nitrile Stark probe because its vibrational energy lies in the spectrally preferable “silent-region” and is largely decoupled from the rest of the molecule. The nitrile vibrations show anomalous shifts in gap junctions of 1 nm or smaller. For larger gap sizes, the vibrational frequency does not change. Our results indicate that both the particle-film gap distance and inter-particle coupling play a key role in enhancing the local electric fields in these small junctions and contributing to the large Stark shifts observed experimentally. Theoretical calculations of the nitrile vibrations with applied electric fields also agree with the experimental observations. Additionally, in both the plasmon resonance shift and the time-dependence of the nitrile vibrations, we observe changes suggestive of an electron tunneling process that can modify the local field environment in the sub-nanometer gaps.

Results and discussion

NPoM gap size modulation with self-assembled monolayers

To investigate the change in nitrile frequencies associated with the local electric fields, we constructed NPoM systems consisting of gold nanoparticles functionalized with different length ligands deposited onto a self-assembled monolayer of 4-mercaptobenzenenitrile (MBN) on a gold film. The use of varying length alkylthiolate ligands has been reported previously to modify gap distances.^{10, 48} Figure 1a illustrates the NPoM system. PM-IRRAS measurements of the MBN film show a single nitriled peak at 2229 cm^{-1} with a width of 14 cm^{-1} (ESI, Fig. S1a), indicating a single nitrile geometry and a well ordered monolayer on a ultra-flat Au surface (ESI, Fig. S1b). The AuNPs were encapsulated with a particular alkylthiolate monolayer and the thickness of this alkyl-thiolate monolayer then modulates the gap size between the NPoM junctions. The thickness of the SAM on the AuNPs is estimated using Chem3D molecular modeling to be 0.5 nm, 1.0 nm and 1.6 nm for TGA, MHA and MUA, respectively. Assuming a thickness of $\sim 0.5\text{ nm}$ for the MBN SAM on the gold film, close to that of the benzenedithiol as measured by TEM,⁴⁹ we derive estimated gap distances of 1.0 nm, 1.5 nm, 2.1 nm for AuNP@TGA, AuNP@MHA and AuNP@MUA NPoMs, respectively (ESI, Fig. S2). The NPoM features a sub-monolayer of AuNP assemblies with varying degrees of clustering: single nanoparticles, dimers and multi-mers are all evident by scanning electron microscopy (SEM) (Fig. 1b). Real color dark field images (Fig. 1c) of these NPoMs typically demonstrate a characteristic red “doughnut” point spread function as a result of strong plasmonic coupling between the polarizable dipole in the AuNP and that of its mirror image in the gold film.⁵⁰ This distinctive doughnut pattern is associated with single AuNPs interacting with the gold film,⁵¹ directly differentiating single isolated AuNPs from aggregated ones for our Raman and plasmon resonance measurements discussed later. The red color of the resonant scattering of single AuNPs, which typically scatter around 520–580 nm or ‘green’ in uniform dielectrics such as water and air, suggests strong coupling of plasmon resonances at the gap due to the tight spacing between the AuNP and the gold film. The formation of such gap plasmon resonance is essential for producing strong local electric fields and sufficient SERS enhancements.

Ensemble SERS behavior in distance controlled NPoMs

We first assessed the ensemble SERS behavior over a large area ($\sim 70 \times 70 \mu\text{m}^2$) on three different NPoMs, disregarding the number of nanoparticles within the detection volume and their aggregation states. As revealed from Figure 2a-c, the nitrile SERS signal (2223 cm^{-1}) drops significantly as the gap distance increases from 1 nm (AuNP@TGA NPoM) to 1.5 nm (AuNP@MHA NPoM): the population of high intensity pixels is much larger for 1 nm gap (Fig. 2a), whereas it only decreases slightly when the gap extends from 1.5 nm to 2.1 nm (Fig. 2b-c). Figure 2d-f present 2D plots of SERS spectra corresponding to the maps shown on the left. Prominent SERS band at 2223 cm^{-1} , corresponding to nitrile stretch, is observed across all NPoMs. Statistical peak analysis of this band shows that the distribution of peak intensity (Fig. 2g-i) and width (Fig. 2j-l) is notably different and correlates well with the change in gap distance: smaller gaps ($\sim 1 \text{ nm}$) correspond to high intensity (mean ~ 1000 counts) and broader width (fwhm $\sim 29 \text{ cm}^{-1}$), while larger gaps low intensity and narrower width (mean ~ 500 counts and fwhm $\sim 17 \text{ cm}^{-1}$ for $\sim 1.5 \text{ nm}$ gap; mean ~ 400 counts and fwhm $\sim 17 \text{ cm}^{-1}$ for $\sim 2.1 \text{ nm}$ gap). The signal from the MBN monolayer is only detected in the NPoM geometry. The slight shift in the CN stretch frequency, relative to the IR, can be explained by interactions with adsorbed nanoparticle. This observed distance dependence of the signal intensity has been previously established in SERS with similar NPoM systems^{51, 52} and other nanostructures⁵³. In the wider gaps, the width of the CN stretch is similar to that observed in the IR; however, in the smallest nano-junctions, a significant spectral broadening of the CN vibrational band has been observed, a signature previously associated with stark shifts and molecular tunneling.^{30, 54, 55} In addition, a red-shifted band ($\sim 2125 \text{ cm}^{-1}$) was observed in AuNP@TGA NPoM (Fig. 2d), whereas the signal was negligible or completely absent in the case of the other two NPoMs (Fig. 2e-f). This distinctive lower energy peak is nearly 100 cm^{-1} removed from the nitrile peak at 2223 cm^{-1} and disappears with increasing gap distance.

Charging induced peak shift

To explain the broadening of the nitrile stretch (2223 cm^{-1}) and the emergence of the lower energy peak ($\sim 2125 \text{ cm}^{-1}$) in small NPoM gaps, we consider two different manifestations of peak shifts: one is the small and gradual shifts induced by VSE, which relates to the observed peak broadening; the other is the large and sudden shifts caused by molecular charging, leading to a separate peak with a well-separated energy. We first briefly discuss the origin of the lower energy peak ($\sim 2125 \text{ cm}^{-1}$) and note that such shifted nitrile peaks have been reported before and assigned to nitriles interacting with the SERS active electrode at negative potentials.^{56, 57} Previous theoretical calculations further show that simply adding an extra charge can give rise to a large vibrational peak shift.⁵⁸ In our experiment, no bias was applied, however, the charging of nitriles is possible by electron tunneling between the AuNP surface and the MBN assembled gold film, especially for short gaps such as AuNP@TGA NPoMs. With the junction irradiated, plasmon-assisted electron tunneling becomes a probable event. Similar to classic tunnelling, the distance between the nanoparticle and the film is important. This tunneling can further modify the optical absorption properties⁵⁹ and enhance the conductance of these small molecular junctions⁶⁰. We consider this tunneling as a charge transfer process from using a simple Au4 / MBN / Au3 model system (Fig. 3a). The molecular orbital distribution and the decrease of charge

transfer energy calculated for reduced gap distances (ESI, Fig. S3) are consistent with our observation that the lower energy peak is only prominent in small gap junctions. We then performed constrained density functional theory (CDFT)⁶¹ calculations where one electron is constrained to the MBN molecule to partially fill the anti-bonding orbitals of the nitrile and obtained a red shift of $\sim 80\text{ cm}^{-1}$ (Fig. 3b), in reasonable agreement with the experimentally observed $\sim 100\text{ cm}^{-1}$ peak shift. Similar frequency shifts have also been observed for charge-localized mixed-valence compounds.⁶² Our calculated value of the shift also agrees with that obtained by Ratner et al. for charged species in molecular junctions.⁵⁸ The low intensity of this charging-induced peak compared to the 2223 cm^{-1} peak and its sporadic distribution across the mapped region (ESI, Fig. S4) suggest that only a small number of nitriles in the gap junction undergo such a molecular charging event.

Peak broadening and Stark shift sensitivity

In addition to the charge-induced peak shift, we observe prominent peak broadening for the nitrile stretch at $\sim 2223\text{ cm}^{-1}$ as the gap distance decreases, while the benzene ring modes from 1000 to 1600 cm^{-1} show little difference in fwhm (Fig. 4a-b). This mode selectivity (nitrile vs. ring modes) of the broadening effect can be explained by VSE and the significantly larger Stark tuning rate for the nitrile vibration³³. Figure 4c shows the DFT simulated Raman spectra of the MBN / Au₃ cluster under homogeneous DC electric fields in the range of $\pm 50\text{ MV/cm}$, matching commonly measured field strength associated with plasmonic nanostructures^{30, 46}. The calculated shift ($\sim 40\text{ cm}^{-1}$) at maximum field strength agrees well with those observed in experiments for nitrile stretch ($\sim 30\text{ cm}^{-1}$, ESI, Fig. S5), while other vibrational modes are relatively insensitive to the field change. In contrast to prior nitrile frequency measurements in nanostructured substrates^{27, 32}, the broadening observed here in the presence of the alkanethiolate spacers appears to be more symmetric (ESI, Fig. S5a). This symmetric broadening is likely associated with the ensemble averaging effect. Nonetheless, asymmetrical peak shifts are sometimes present for small gaps such as TGA@AuNP NPoMs (ESI, Fig. S5b). In other studies^{30, 32, 42}, optical rectification caused by electron tunneling has been invoked to explain the asymmetrically-broadened peaks. To explore this effect more systematically, we investigated single isolated NPoMs and the associated nitrile peak shifts.

SERS of single isolated NPoM assemblies

In the ensemble measurement, the contributions of multiple nanoparticles and inter-particle coupling complicate our interpretation of the spectral changes in the nitrile stretch. To avoid these complications and focus on the effect of gap distance, we examined nitrile vibrations associated with individual isolated AuNP NPoMs. These isolated AuNPs were identified by their characteristic red “doughnut” pattern in the dark field microscopy, as opposed to bright white scattering in the case of AuNP aggregates (ESI, Fig. S6). Figure 5a presents SERS spectra from 3 different single AuNP@TGA NPoMs: several intense peaks at ~ 1069 , 1170 , 1578 cm^{-1} and a strong band at $\sim 2223\text{ cm}^{-1}$ were observed and assigned to various benzene ring modes and the nitrile stretch, respectively (ESI, Fig. S7). Figure 5b demonstrates that a single Gaussian peak cannot accurately capture the asymmetric lineshape and peak shifts of the nitrile vibrational bands. Deconvolution of the nitrile bands shows an isotropic nitrile vibration at 2222 cm^{-1} and its blue and/or red-shifted components (Fig. 5c).

The nitrile frequency shifts observed in Figure 5c can be interpreted within the framework of the VSE. In our previous work,³² changes in the nitrile stretching frequency were correlated with different electric field environments. Depending on the local field strength and its orientation with respect to the nitrile, the transition can either gain (blue-shift) or lose energy (red-shift) due to VSE. Assuming Stark tuning rate (μ_{CN}) to be $0.61 \text{ cm}^{-1}/(\text{MV}/\text{cm})$ for aromatic nitrile group⁶³ and a linear Stark shift relation $\nu = -\mu_{CN} \cdot E$, we can calculate the strength of local electric fields: $-41.0 \text{ MV}/\text{cm}$ and $+41.0 \text{ MV}/\text{cm}$ from the blue ($\nu = +25 \text{ cm}^{-1}$) and red ($\nu = -25 \text{ cm}^{-1}$) shifted nitrile frequencies, respectively. The observed shifts are larger than those induced by solvent effects ($<15 \text{ cm}^{-1}$ red shift)³⁴ and ion-pairing environments ($<16 \text{ cm}^{-1}$ red shift)³⁷, indicating larger local fields within these NPoM gaps. Compared with the ensemble measurement, the nitrile peaks in single isolated NPoMs are more asymmetric (Fig. 5c). The onset of this-asymmetry in the smallest gaps suggests that electron tunneling may explain these altered local electric fields.

For single AuNP@MHA NPoMs and AuNP@MUA NPoMs (Fig. 6a-b), the vibrational bands in the ring stretch region were identical to those in AuNP@TGA NPoMs. However, in the nitrile region, instead of the broad and asymmetric bands observed in the AuNP@TGA NPoMs, narrow and symmetric nitrile peaks were identified for both AuNP@MHA and AuNP@MUA single NPoMs. These nitrile bands in Figure 6 can be well fit with a single Gaussian function centered at $\sim 2223 \text{ cm}^{-1}$. The peak width and symmetry from these single NPoMs also agree with those in the ensemble measurements (Fig. 2k-l).

The absence of the peak shifts or broadening in the larger-gap NPoMs confirms that the observed frequency shift in our experiments arises from an electric field effect (vibrational Stark effect), not a chemical effect (e.g. hydrogen bonding)⁶⁴. Hydrogen bonding can be ruled out because the nitriles interact in similar fashions with the carboxylate terminating groups in all three NPoMs. Hence, the narrow bandwidth and the missing of peak shifts are associated with the weaker local electric fields in the larger gaps.

We further investigated the effect of inter-particle coupling on the vibrational frequency shifts with aggregated nanoparticles on the gold film. Inter-particle coupling is known to significantly alter the local electric fields through rehybridizing the plasmon modes and redistributing the local charge densities within the particle-particle and particle-film gaps^{65, 66}. We should note here that, in our NPoM construct, the nitriles reside only in the particle-film gaps and therefore should only report the local electric fields within those gaps. Regardless of gap sizes, we observe significant frequency shifts and asymmetry in the nitrile vibration, indicative of local electric fields of higher magnitude in these gaps (ESI, Fig. S8). This result is compelling evidence that inter-particle coupling can enhance the electric fields in the particle-film gap^{67, 68}. It also reinforces the point that the observed Stark shifts are highly dependent on the local field enhancement around the nanostructures.

Given that the Stark shift is electric field dependent, we further reduced the gap distance and increased the local electric fields using citrate-AuNPs (c-AuNPs) to form NPoM. Citrate capping layer on AuNP has an estimated thickness of $\sim 0.4 \text{ nm}$ as measured from the Au surface to the CH_2 carbon atom by Chem3D, assuming a flat conformation on the gold surface.⁶⁹ This allow us to achieve NPoM gaps smaller than 1 nm , a distance where strong

local electric fields are expected but also approaching the regime where quantum tunneling occurs.¹⁵ Figure 7a shows SERS spectra obtained from single isolated c-AuNP NPoMs. The nitrile vibrational bands, similar to those observed in AuNP@TGA NPoMs, can be resolved into multiple components that correspond to the isotropic ($\nu_0 \sim 2220 \text{ cm}^{-1}$), blue ($\nu_{R1} \sim 2232 \text{ cm}^{-1}$, $\nu_{R2} \sim 2258 \text{ cm}^{-1}$) and red ($\nu_{L1} \sim 2208 \text{ cm}^{-1}$, $\nu_{L2} \sim 2181 \text{ cm}^{-1}$) shifted peaks of the nitrile vibrations (Fig. 7b). Further towards the red, a transition ($\nu_{L3} \sim 2129 \text{ cm}^{-1}$) previously assigned to charged nitrile species is present in these c-AuNP NPoMs, indicative of intense local fields and electron transfer. The shifted frequencies ν_{R1} (ν_{L1}) and ν_{R2} (ν_{L2}) correspond to local electric fields of -19.7 MV/cm ($+21.3 \text{ MV/cm}$) and -62.3 MV/cm ($+63.9 \text{ MV/cm}$), even larger than the values obtained from AuNP@TGA NPoMs ($\pm 41.0 \text{ MV/cm}$). We can further derive local electric fields as large as $+70 \sim 100 \text{ MV/cm}$, based on the red-shifted peak ν_{L2} ranging from 2177 to 2157 cm^{-1} observed in clustered NPoMs (ESI, Fig. S9). The magnitude of these intense local electric fields approaches a value reported by Apkarian et al. using CO as a Stark probe chemisorbed on a fusing silver nano-dumbbell junction (100 MV/cm)³⁰. We note that the local electric fields of this magnitude are in the range of the field ionization threshold (E_{th} typically $1 \sim 10 \text{ GV/m}$)^{70, 71} where photo-damage can be expected when local electric field $E_{Loc} \geq E_{th}$. For those clustered NPoMs where E_{Loc} extends beyond 70 MV/cm , we indeed observe an increase of bands likely associated with photoproducts (ESI, Fig. S9). It should be further noted that the asymmetric lineshape varies from particle to particle for single NPoMs (Fig. 5c & Fig. 7b). While the origin of this variation is not fully understood, this is likely caused by the differences in atomistic details of the gap morphology, such as particle vertices, facets, and steps that also affect the local field environment.⁷² The asymmetry observed also seems to qualitatively agree with the simulated lineshape when nitriles are subject to intense local electric fields (ESI, Fig. S10).

These results from the single and clustered NPoMs suggest that the peak broadening and asymmetry can only happen in those small gaps where large local electric fields exist. For single NPoMs, the observed anomalous peak-shifts in nitrile vibrations seems to correlate with the critical distance that electron tunneling is believed to occur ($\sim 1 \text{ nm}$).^{15, 59, 73, 74}

Gap plasmon resonances

To further correlate the observed vibrational Stark shifts to quantum tunneling in these small gap junctions, we measured localized surface plasmon resonances of single NPoMs by hyper-spectral dark-field scattering microscopy. This approach allows simultaneous acquisition of a spatial-spectral 3-D plasmon resonance map from every single NPoM assembly in the field of view. Representative plasmon resonance spectra from different NPoMs are presented in Figure 8a. The distribution of the plasmon resonances from each type of NPoM is plotted in a histogram (Fig. 8b-e). Each histogram is obtained from scattering profiles of over 50 single NPoMs. The center of the plasmon resonances (λ_{Res}) first redshift, as expected, from 640 nm to 647 nm , and to 671 nm , as the gap decreases from $\sim 2.1 \text{ nm}$ to $\sim 1.5 \text{ nm}$, and to $\sim 1.0 \text{ nm}$, respectively, due to stronger coupling in smaller gaps. However, when the gap size shortens further to $\sim 0.9 \text{ nm}$, instead of shifting further red, a blue shift to 656 nm is observed. A broadening of the plasmon resonance is also evident at gap size 1.0 nm . The distribution of the λ_{Res} results from system heterogeneities, e.g. variation in nanoparticle size (ESI, Fig. S11), incomplete or disordered SAM on the AuNP

surfaces, or surface defects on the gold mirror. Nonetheless, the shifting behavior (Fig. 8f) and the broadening of the gap plasmon resonance as the gap shortens follow a trend associated with quantum tunneling events.⁷⁵⁻⁷⁷ Previous scattering and EELS experiments have reported such effects in the gaps ~ 0.5 nm^{11, 13, 78, 79}. In our case, the onset of the quantum-coupling regime (~ 1 nm) is closer to the values reported for silver nanocubes⁴⁶ (1.2 nm), AgNP dimers⁷⁴ (1 nm) and AuNP dimers⁷⁵ (1 nm) assembled through alkyl-dithiol linkers.

The correspondence between the onset of a blue shift in the plasmon resonance and the emergence of peak asymmetry in nitrile vibrations in the small gaps indicates that the nitriles can act as a sensor for tunneling effects in gap junctions. In addition, the electron tunneling within these short gaps suggests an explanation for the asymmetry observed in the nitrile vibration. It is worth noting that nanoscale heterogeneity can also influence these charge transfer processes and modulate the local field environment.

Time dependent evolution of local electric fields in small gaps

The nitrile frequency shift changes with extended illumination in the short-gap NPoMs. This time dependent evolution was not seen for the larger-gap NPoMs. Figure 9 shows a time-series of SERS spectra in the nitrile region obtained from an isolated single c-AuNP NPoM and AuNP@MHA NPoM with gap sizes of ~ 0.9 nm and ~ 1.5 nm, respectively. The aromatic ring stretches show no significant change (ESI, Fig. S12); while the nitrile modes show intriguing behaviors. Over the course of 30 seconds, two prominent nitrile vibrational bands were identified for the small-gap NPoM (~ 0.9 nm): a red-shifting component and a stable isotropic nitrile band at ~ 2224 cm⁻¹ (Fig. 9a). Fitting these changes with Gaussian functions (ESI, Fig. S13a), we obtained a shift of -12 cm⁻¹ (from 2209 cm⁻¹ to 2197 cm⁻¹) and a corresponding change in local electric field of $+19.7$ MV/cm. Assuming a simplified capacitance model for such NPoM system, where $C=3*(4\pi R)$,⁸⁰ we can estimate the net difference of electrons transferred during the spectral evolution of ~ 150 electrons (ESI, Fig. S13). On the other hand, for larger gaps of 1.5 nm (Fig. 9b) and 2.1 nm (ESI, Fig. S14), the nitrile vibration was observed to remain unchanged at ~ 2223 cm⁻¹ and time-dependent variation was negligible. In the case of the 1.0 nm gap size (AuNP@TGA NPoM), the peak shift behavior is less pronounced than in the 0.9 nm gap due to the lower intensity of the red-shifted components (ESI, Fig. S13b).

This time-dependent behavior of the nitrile vibrational shift in different gap sizes correlated well with the VSE data and plasmon resonance shifts. The optical rectification process associated with the VSE agrees with the onset of electron tunnelling effects. These processes modify the local electric fields and contribute to the asymmetry of the observed Stark shifts. In a recent paper, calculations suggest that the dipole in the adsorbates dictates the direction of electron transfer across the gap junction.⁴³ The time dependent Stark shifts to lower frequency are consistent with the CN dipole controlling the direction of electron tunneling. The time dependent changes appear to result from capacitive charging across the smallest nanogaps.

Conclusions

Gap-dependent changes in electron tunneling modulate the local electric fields plasmonic junctions and give rise to Stark shifts from nitrile probes. These changes are observed without external dc bias tuning, and arise from plasmon excitation. The local electric fields determined by the Stark effect showed a strong correlation with the gap sizes in NPoM systems. Inter-particle coupling was observed to increase the local electric fields in the gap junctions in comparison to single NPoMs. Measurements of plasmon resonances and time-dependent SERS agree that quantum tunneling is involved in the observed frequency shifts. Taken together, these results demonstrate that nitrile Stark probes provide an experimental indicator of the local fields between highly coupled nanoparticle systems and can be used to monitor subtle changes in local fields. In the future, inclusion of VSE probes into plasmonic devices may potentially allow real-time reporting of changes in local electric fields due to precise control of temperature, dielectrics, and chemical reactions.

Experimental section

Film-nanoparticle assembly preparation

Carboxylic acid terminated alkane-thiols (80uL, 1 mM) were self-assembled onto the gold nanoparticles (80nm; Nanocomposix, San Diego; 5 mL, 16 pM) by a ligand exchange reaction (ligand/NP molar ratio $\sim 1 \times 10^6$). The molecular linkers: thioglycolic acid (TGA), mercapto-hexanoic acid (MHA) and mercapto-undecanoic acid (MUA) were purchased from Sigma Aldrich and used as received. The SAM modified nanoparticles were rinsed with ultrapure water (18 M Ω cm, Barnstead) 3 times to remove residual carboxylic acid terminated alkanethiols in the solution. These nanoparticles were stable at pH ~ 7 after modification and used within a week. Dynamic light scattering (DLS) measurements were used to check the stability of the SAM modified nanoparticles. 1×1 cm² template stripped ultra-thin gold chips (Platypus Technologies, Madison, WI, USA) were then immersed overnight in 5mM 4-mercaptopbenzenenitrile (MBN, synthesized by the Notre Dame Chemical Synthesis Core and verified to be of $>98\%$ purity by NMR) in ethanol, after which the gold surfaces were immediately rinsed 3 times with copious amount of ethanol. The functionalized nanoparticles were then deposited onto the MBN modified gold film by drop coating ~ 10 uL of the colloid solution, dried at room temperature and stored in vacuum before use.

Raman measurement

Large-area SERS mapping of the nanoparticles on the gold film was conducted on a Renishaw system (InVia, $\lambda=633$ nm HeNe laser). Laser power was set at 0.75mW to minimize possible photodamage of the sample. An area of $\sim 65 \times 65$ μm^2 and 1 s acquisition per pixel were used to map the ensemble SERS signal. A Leica (20x, NA=0.4) objective was used for the illumination and collection in this measurement. For SERS investigation of isolated AuNP assemblies on MBN covered gold films, a home-built Raman microscope equipped with a dark-field objective (100x, NA=0.9, LMPlanFI BD Olympus) was used for dark-field visualization, excitation and collection of SERS signals. Here again a HeNe laser ($\lambda=633$ nm, Melles Griot), with a power of 0.25mW at the sample level, was used. Raman

acquisition time was 1s. Investigation on the effect of extended illumination on SERS was carried out using 1s acquisition consecutively for 30s.

Dark-field scattering measurement

The scattering profiles of the nanoparticles were obtained using a similar setup as previously reported⁸¹. Briefly, single particle scattering images were recorded on a dark field microscope (Olympus, BX51) using a 100x objective (NA=0.9, LMPlanFI BD Olympus) and a liquid crystal tunable filter (LCTF, Varispect CRI) placed before a CMOS CCD camera. The LCTF was scanned with 4 nm increments in the range of 500 to 720 nm (2s/frame), generating images of the scattering intensity at each individual wavelength interval that can be reconstructed to produce scattering spectra for all the spatially resolved nanoparticles in the field of view. A white reflectance standard (SRS) was used to correct for the lamp background in all the scattering profiles of the single nanoparticles.

Data analysis

Matlab R2015b was used in all spectral presentations. An open-source peak-fitting algorithm was used to fit a single Gaussian peak to evaluate the change in peak intensity, peak width, peak position, etc. All SERS figures presented in this article are raw spectra if no specific notification is added. Commercially available software ENVI 5.1 (Exelis Visual Information Solutions) was used to preprocess the hyperspectral data-cubes to extract scattering profiles of individual AuNPs on the gold mirror.

DFT calculation

All the DFT calculations were performed with Q-Chem 4.2 package⁸². Long-range corrected exchange-correlation functional ω B97X is applied.⁸³ 6-31g** basis is used for H, C, N and S. LANL2DZ with ECP is used for Au. A cluster of three gold atoms is used to simulate the gold film and a cluster of four gold atoms is used to simulate the gold nanoparticle. Constrained density functional theory (CDFT) is used to simulate the vibrational response when a charge is transferred to the MBN-Au₃ cluster from the gold nanoparticle. To predict the change of nitrile frequencies changes under various electric field strengths, we placed positive and negative point charges on two parallel planes separated by 100 Å to simulate a plate capacitor, between which the electric fields are constant. Subsequently, Raman spectra were calculated for different field intensities.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Different length alkane thiols are used to form NPoM systems with controlled spacing between the gold nanoparticle (AuNP) and the gold film. (a) The spacing molecules are thioglycolic acid (TGA), mercapto-hexanoic acid (MHA) and mercapto-undecanoic acid (MUA), which differ by approximately $5 \text{ \AA}$, respectively. TGA, MHA or MUA form self-assembled monolayers on the surface of the 80nm AuNPs. 4-mercaptobenzenenitrile (MBN) monolayer was prepared on the gold film. (b) The SEM image shows that AuNPs absorbed on the MBN modified gold film exist as monomers, dimer and some larger aggregates. (c) True color dark field image of AuNPs absorbed on the MBN covered gold film show characteristic red "doughnut" scattering patterns from single AuNPs.

Figure 2.

The SERS maps of the 2223 cm^{-1} nitrile peak area are shown for three different NPoM systems: (a) AuNP@TGA, (b) AuNP@MHA, and (c) AuNP@MUA absorbed onto the MBN modified gold films (area $\sim 70 \times 70\text{ }\mu\text{m}^2$). Each row consists of data from a specific NPoM system. (d,e,f) The SERS spectra corresponding to each map are shown in 2-D plots. Each map consists of 1296 spectra. These spectra are all baseline-subtracted and their color scales are normalized for comparison. The averaged SERS spectra for each corresponding 2-D plot are shown right above itself. (g, h, i) Peak intensity distribution of the nitrile vibration at 2223 cm^{-1} determined from a fit to a single Gaussian function is plotted for corresponding NPOMs. (j, k, l) Peak width distribution of the nitrile vibration according to a single Gaussian peak fit for corresponding NPOMs.

Figure 3.

(a) HOMO and LUMO of the Au₄ / MBN / Au₃ cluster model system. HOMO populates the Au₄ close to the nitrogen and the C-N bonding orbital. LUMO populates the Au₃ attached to the sulfur atom, the C-N anti-bonding orbital and the benzene ring. (b) Calculated nitrile vibrational band with one electron constrained to the MBN / Au₃ cluster compared to that of the neutral cluster (no constraint) using CDFT. The Raman intensity is normalized to unity.

Figure 4.

Ensemble averaged SERS spectra for different NPoMs in the benzene ring mode region (a) and the nitrile stretch region (b). These spectra are offset for clarity. DFT simulated Raman spectral evolution (c) under different DC electric field strengths. The inset in (c) shows an enlarged view of the nitrile stretch region where the nitrile vibrational mode shows more responsiveness to the change in electric field strength than the ring modes. The color scale is used to indicate the sign and strength of the electric fields applied.

Figure 5.

SERS spectra from AuNP@TGA NPoMs and peak analysis are shown. (a) SERS spectra obtained from 3 single isolated AuNP@TGA NPoMs. (b) Analysis of the nitrile band with a single Gaussian is inadequate to explain the observed lineshape. (c) Inclusion of high (ν_R) and low (ν_L) energy vibrational peaks provides a better fit to the observed lineshape. The red, green and blue curves correspond to three different isolated NPoMs in (a). Black lines are the Gaussian fit components contributing to the colored line, the fit result. ν is the fitted peak position; Δ is the fitted fwhm; ν_0 is the isotropic nitrile stretch; ν_L and ν_R are the red-shifted and blue-shifted nitrile stretch, respectively. Dotted lines are provided as guides.

Figure 6.

SERS spectra from single isolated (a) AuNP@MHA, (b) AuNP@MUA NPoMs and the corresponding nitrile peak analysis (c and d) are shown. In these spectra, the nitrile peak is fit with a single Gaussian lineshape. The red, green and blue correspond to the similarly colored spectra to the left. ν is the fitted peak position; Δ is the fitted fwhm.

Figure 7.

SERS from single isolated c-AuNP NPoMs and peak analysis. (a) SERS spectra from two separate single c-AuNP NPoMs. (b) Peak fitting using multiple-peak Gaussian functions for corresponding SERS spectra shown in (a). (Black curves are the decomposed Gaussian fits and the colored lines are the total of the contributing fits. ν_0 is the isotropic nitrile stretch; ν_L and ν_R are the red-shifted and blue-shifted nitrile stretch, respectively. Dotted lines are provided as guides.

Figure 8.

Spectroscopic response from single-particle dark field scattering of different NPoM assemblies. (a) The dark-field scattering spectra from different single NPoMs with gaps established by the ligands on the NPs. (b-e) Histograms show the distribution of the plasmon resonance frequency for each NPoM system and a Gaussian fit of the spread. (f) The centers of the Gaussian fit are plotted against the estimated gap distance. The error bars in (f) are the fwhms of the gaussian fits.

Figure 9.

Representative time series of SERS response from a single isolated NPoM assembly with 0.9 nm (a) and 1.5 nm (b) gap size, respectively. The acquisition time is 1 second per spectrum and a total of 30 spectra were acquired consecutively. The SERS spectra were all normalized for comparison. The dashed lines are used as guides: a red dash arrow points to a red shift of the nitrile frequency and black dash arrow no obvious shift.