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Extreme Near-Field Enhancement for Gaseous Plasma Generation and Fundamental Plasma Chemistry

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14. ABSTRACT
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1. Abstract

In this project, plasmon-driven surface reactions and other gas phase reactions involving ions have been investigated experimentally and theoretically. The experimental effort has been focused on mechanistic understanding of plasmon-driven photochemistry. Before the publication of our results from this project, the mechanism of plasmon-driven reactions has been discussed mainly in terms of hot electron transfer. Our results obtained in this project indicate that photochemistry on plasmonic nanoparticles can be induced by hot electron transfer from the nanoparticle to an unoccupied orbital of the adsorbate and/or by plasmon-pumped electron transitions from occupied molecular orbitals to unoccupied molecular orbitals of the adsorbate. The branching photochemical reaction of para-aminothiophenol on plasmonic gold surfaces depending on the presence of cetyltrimethylammonium bromide surface ligands that influence the hot electron concentration is used to highlight reactions driven by hot carriers. The importance of plasmon-pumped electronic excitation of adsorbates in initiating surface photochemistry is demonstrated based on the N-demethylation of methylene blue (MB) on gold nanostructures depending on excitation wavelengths. At excitation wavelength that overlaps with the resonances of MB and the gold nanoparticles, conversion of MB to thionine is observed in the presence of oxygen in the atmosphere and water in the surface-molecule complex. Considering that MB is a well-known photosensitizer, this observation suggests that the photochemical N-demethylation reaction involves singlet oxygen molecules that can be generated via energy transfer from MB triplet excited state to O_2 triplet ground state. Theoretical work has been mostly focused on a deeper understanding of ion-molecule reactions and other processes involving ions. Several levels of theory have been carried out. For large systems, the reaction kinetics has been treated with statistical models on *ab* initio determined reaction paths. For small systems, quantum mechanical dynamical investigations were performed on global potential energy surfaces. These theoretical studies shed valuable light on the experimental observations.

2. Experimental investigation of plasmon-driven surface reactions

Driving photochemical processes such as generation of reactive chemical species, molecular transformation, dissociation and ionization at low incident photon flux is desirable for many important applications including conversion of solar energy into fuel, plasma generation, chemical sensing and decontamination of chemical wastes as well as various defense applications. Plasmonic metal nanoparticles (with size scale less than 100 nm) that are resonant to the incident light can enable photochemistry at photon flux comparable to that of solar radiation. Excitation of localized surface plasmon resonances (collective oscillation of conduction electrons) in the metal nanoparticles can create large electromagnetic field enhancement around the surface of the nanoparticles. The enhanced and localized surface field increases the interaction of molecules adsorbed on the metal nanoparticles with electromagnetic radiation, resulting in simultaneous enhancements of surface photochemistry and spectroscopic signals in particular Raman scattering to the extent signals from single molecule can be detected. In this project, the experimental group led by Habteyes has effectively used the dual effect of localized surface plasmon resonances to investigate the mechanism of plasmon-driven photochemistry.[1-3] By choosing appropriate model molecular systems, we have shown the important roles of both hot electron transfer and plasmon-pumped electron transitions from the highest occupied molecular orbitals to the lowest unoccupied molecular orbitals to initiate photochemical reactions on plasmonic surface. The results from these activities have recently been summarized in a Feature Article of the *Journal of Physical Chemistry*.[4] Here, the important findings are briefly summarized highlighting the relevance of hot electron transfer and plasmon-pumped adsorbate excitation in plasmon-driven reaction mechanisms based on the photochemistry of para-aminothiophenol (PATP)[1] and methylene blue (MB).[2, 3]

2.1 Ligand-mediated hot-electron induced branching reaction

The plasmon driven photochemistry of PATP is believed to be initiated by hot electron transfer to O_2. Before our studies, oxidative azo coupling reaction that leads to formation of p,p′-dimercaptoazobenzene (DMAB) was reported based on surface enhanced Raman scattering (SERS) spectra observed for PATP adsorbed on roughened silver surface and citrate coated gold nanoparticles. However, the effect of surface bound ligands that are inherent to colloidal nanoparticles was not investigated systematically. In this project, the surface ligand effect has been investigated by comparing the photochemistry of PATP adsorbed in three different interfaces as displayed in the schematics in Figures 1a-c.[1] In Figure 1a, the PATP molecules are self-assembled on gold film, and gold nanorods (AuNRs) with citrate surface ligand are placed on top. The vibrational bands observed in the SERS spectrum (Figure 1d) for this sample are consistent with previous results obtained on roughened silver surfaces and on citrate coated silver and gold nanoparticles. The vibrational bands at 1143, 1392 and 1437 cm^{-1} are characteristic of DMAB product formed via an oxidative coupling reaction of self-assembled PATP molecules, while the peaks at 1080 cm^{-1} and 1580 cm^{-1} can be due to both PATP and DMAB.

When the surface ligand is changed to cetyl trimethyl ammonium bromide (CTAB) for nominally the same size of AuNRs (40 nm diameter and 80 nm length), a new prominent peak is observed at 1328 cm^{-1} in addition to the vibrational signatures of DMAB as shown in Figure 1e. The peak at 1328 cm^{-1} is assigned to N-O vibration, and it indicates the oxidation of PATP to para-nitrothiophenol (PNTP). In contrast, when the PATP molecules are directly adsorbed on the AuNRs by replacing the CTAB surface ligands, the N-O vibrational band has completely disappeared as shown in Figure 1f. CTAB bound to gold nanoparticles has characteristic Raman scattering peak at ~180 cm^{-1} due to Au-Br stretching vibration frequency, and we have used this band to confirm the correlation between CTAB content and PNTP product signal. After the electron is transferred to the adsorbed species, the halide anions can react with the positive charge on the metal surface. As a result, the lifetime of the hot electron can be prolonged as the rate of electron return to the surface is slowed down. The increased hot electron concentration can activate larger number of oxygen molecules. Electron transfer to molecular oxygen can produce O_2^- superoxide that is strongly adsorbed to the surface of the nanoparticles. A reaction of the superoxide with the NH_2 group of PATP can produce nitrosobenzene. DMAB can be formed when the nitrosobenzene reacts with left over PATP reactants. However, at high concentration of hot electrons, the PATP initial reactant can quickly be depleted and another channel that involves oxidation of the nitrosobenzene to PNTP can be important, resulting in a branching photochemical reactions.

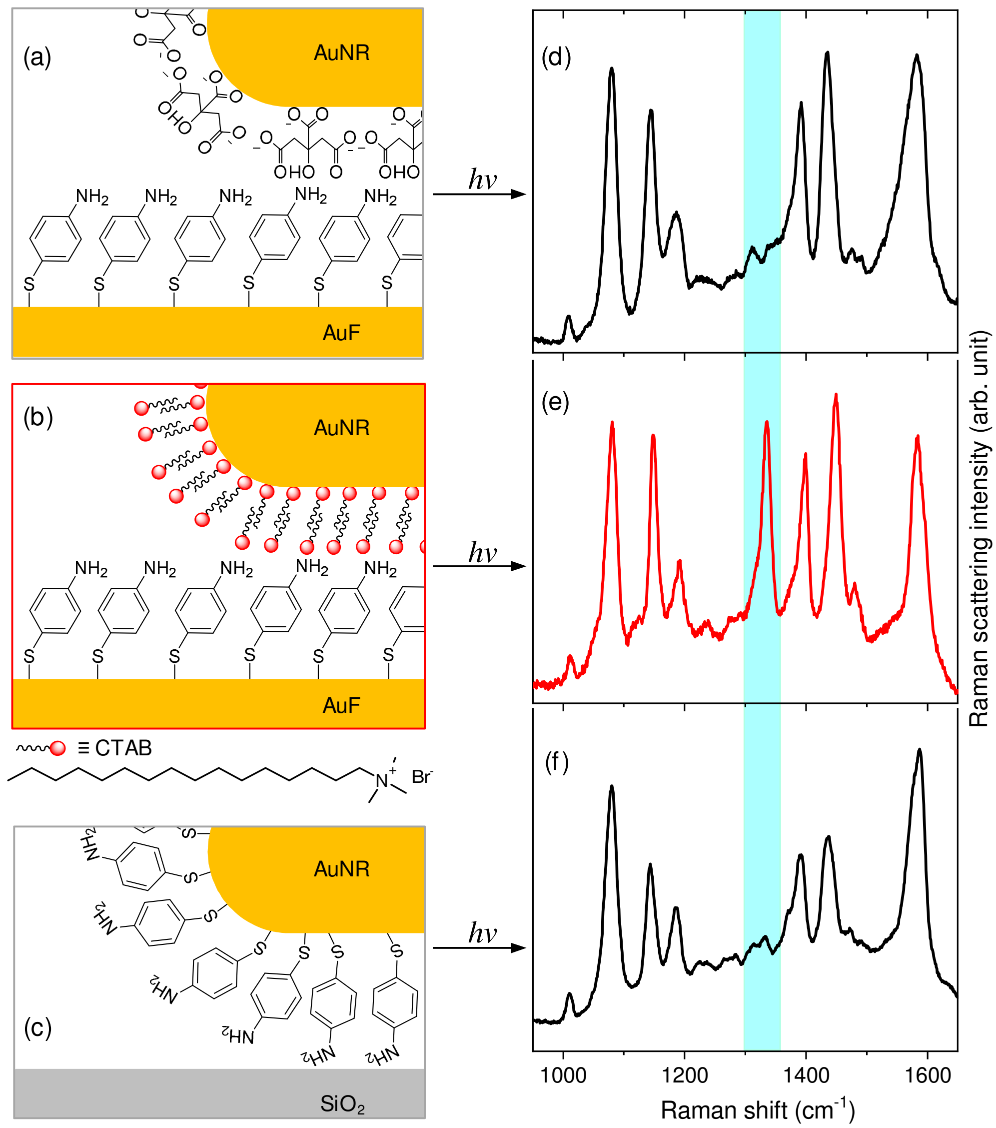

Figure 1 Effect of surface ligand. (a, d) When the PATP molecules are self-assembled on gold film and AuNRs with citrate surface ligand placed on top (a), vibrational frequencies characteristic of DMAB are observed (d). (b, e) When AuNRs with CTAB surface ligand are used (b), strong vibration peak (due to N-O stretch) is observed at 1328 cm^{-1} (e). (c, f) The N-O peak is absent when the PATP molecules are self-assembled on the AuNRs replacing CTAB.

2.2 Plasmon-pumped adsorbate excitation and photochemistry

When particle plasmon resonances spectrally overlap with the electronic transition energy of molecules adsorbed on the nanoparticles, the adsorbate experiences enhanced rate of electron transition from its highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) due to the high mode density of the plasmon surface field. This plasmon-pumped electronic excitation of adsorbates can initiate important photochemistry at photon flux comparable to that of the solar radiation but interpretations of experimental results has mainly been based on hot electron transfer mechanism. In this project, we have demonstrated that plasmon-pumped adsorbate excitation can lead to selective photochemical transformation as it has been highlighted using plasmon-enhanced N-demethylation of methylene blue (PEND-MB) on plasmonic gold nanoparticles as model reactions.[2, 3]

The temporal evolution of the MB SERS spectra obtained under continuous illumination at 633 nm excitation wavelength in ambient atmosphere is shown in Figure 2. The prominent changes can be observed comparing the spectra recorded at 0.5 s and 200 s exposure times as shown in Figure 2a. The intensity map (Figure 2b) that represents 400 spectra acquired sequentially shows the appearance of new vibrational bands as a function of exposure time. The new peak that appears at 479 cm^{-1} is assigned to the skeletal deformation mode of thionine product, while the peak at 804 cm^{-1} is assigned to the NH_2 rocking vibration that requires complete N-demethylation at least at one of the N-terminals. Therefore, we conclude that plasmon driven reaction has resulted in the conversion of methylene blue to thionine.

The mechanism of the PEND-MB reaction has been investigated by performing the experiments at different reaction conditions as listed below.

(i) Excitation wavelength dependent: PEND-MB reaction has been observed at 633 nm excitation wavelength but not at 532 nm and 808 nm.[2] Since the 633 nm wavelength overlaps with the MB absorption band, this observation indicates the requirement of adsorbate excitation for the reaction to take place.

(ii) Atmospheric condition: PEND-MB reaction takes place in oxygen atmosphere but not in inert nitrogen gas, indicating the involvement of oxygen.[3] This observation together with (i) above indicates the role of singlet oxygen considering that MB is a well-known photosensitizer.

(iii) Hydration effect: PEND-MB reaction is nearly absent when MB is adsorbed to the surface from non-aqueous medium, indicating that water is involved in the reaction. [3]

(iv) Surface-molecule proximity: PEND-MB appears to be favored when molecular spacing is introduced.[3] This supports a reaction mechanism induced by plasmon-pumped adsorbate excitation.

(v) Excitation on non-plasmonic surface: Excitation of MB adsorbed on bulk gold film or other non-plasmonic surfaces does not lead to N-demethylation.[2] This observation indicates either threshold excitation field intensity needed to speed up the rate of adsorbate excitation or the involvement of hot electron transfer. Considering that singlet oxygen can interact with the surface strongly, we speculate that the singlet oxygen generation and hot electron transfer take place in concert.

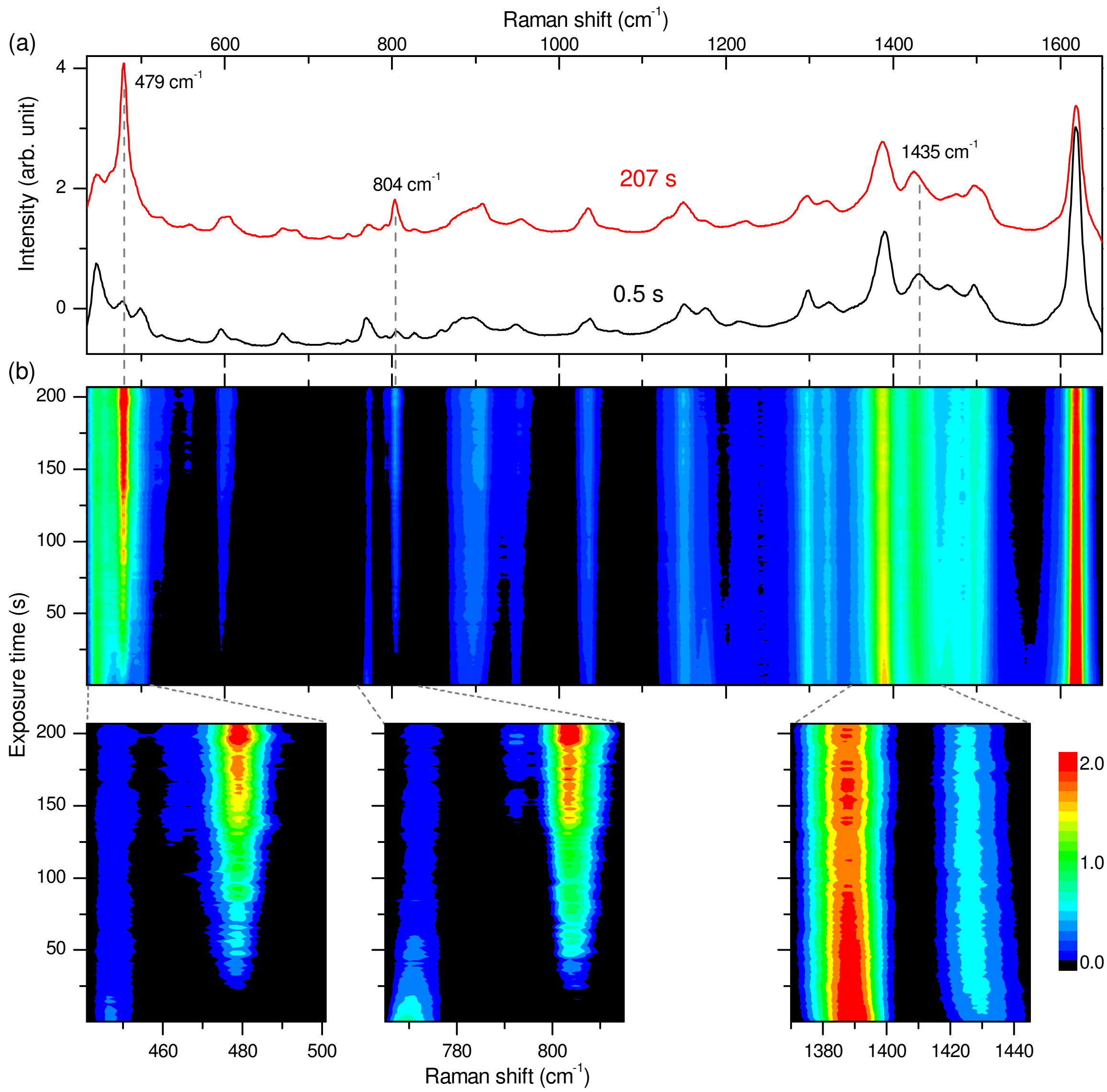

Figure 2. Temporal evolution of SERS spectra of MB adsorbed on resonant plasmonic gold nanorods demonstrating PEND-MB. (a) Representative SERS spectra recorded in ambient atmosphere at the beginning (black line) and after 200 seconds of illumination using 633 nm excitation wavelength. (b) Intensity map representing 400 spectra acquired sequentially during illumination for about 207 seconds. The zoom-in intensity maps at the bottom show the important spectral changes with time. Each spectrum is recorded with 0.5 s acquisition time at 0.4 mW incident power focused with 0.7 NA objective.

2.3 Other experiments

In addition to investigating the photochemistry of adsorbed molecules, plasmon coupling have been investigated to understand the interaction when the separation between two surfaces determined by the inherent surface ligands on metal nanoparticles.[5] Our results on the coupling of gold nanorods to gold film indicate that surface ligands (cetyl trimethyl ammonium bromide) on the gold nanorods do not provide complete electrical isolation, resulting in charge transfer plasmon coupling. This fundamental understanding of plasmon coupling is important to propose a mechanism of plasmon-driven chemistry of molecules sandwiched between the plasmonic surfaces. We have also investigated the coupling of plasmonic nanoparticles with semiconductors based on distance dependent exciton-plasmon interaction.[6] Our study on self-assembled colloidal CdSeTe/ZnS core-shell quantum dots has revealed that alloy quantum dots can be transformed to binary and more stable ternary alloys when the quantum dots are exposed to air due to lattice strain and atomic interdiffusion.[7]

3. Theory

The theory group led by Guo has collaborations with several experimental groups on plasma chemistry and ion-molecule reactions in general. Specifically, we have provided theoretical support to the experimental investigations by the Viggiano group at the Air Force Research Lab in the following projects:

i. Auto-ionization of CF_3^-. By computing full-dimensional potential energy surfaces for both the anionic and neutral species, we have examined the ionization process in this system.[8] The calculated ionization barrier is consistent with experimental data and previous models.

ii. The X^- + YZ (X, Y, Z = F, Cl, Br, and I) reactions. Quantum chemical calculations have been performed to help interpreting the surprising kinetic data for these reactions.[9]

iii. The Fe^+ + CH_3X (X=Cl, Br and I) reactions. Density functional theory calculations have been used to help assisting statistical modeling of the kinetics of this reaction.[10]

iv. The F^- + HCl reaction. A highly accurate potential energy surface is developed for this reaction.[11] It is found that the shorter range attraction is responsible for the deviation of the new experimental data from the conventional capture model. Further, the product state distribution is found to deviate from the statistical limit.

v. The MnO_2^+ + H_2/D_2 reactions. The reaction paths have been explored with various density functional theory methods for this reaction.[12] Unlike the FeO_2^+ + H_2 reaction, no spin inversion was found in the rate limiting step of the reaction, but might be important for product formation. This is consistent with the experimental observations.

vi. The Au_2^+ activation of methane. In contrast to an earlier claim that methane can be activated by Au_2^+, new experimental evidence found this process does not occur, consistent with our theoretical results.[13] The earlier experiment might have been contaminated by electronically excited ions.

Other theoretical studies in this area of research include

i. The OH^+ + H_2 and H_2O^+ + H_2 reactions. These reactions are believed to be involved in interstellar formation of water. We have carried out theoretical calculations to understand the recently observed isotope effects in the H_2O^+ + HD reaction.[14] In collaboration with the Kreckel group at Heidelberg, we investigated the low-temperature kinetics of the OH^+ + H_2 and H_2O^+ + H_2 reactions.[15] Our calculations using the ring-polymer molecular dynamics method on our ab initio potential energy surfaces yielded excellent agreement with experiment.

ii. The S_N2 reaction between F^- and CH_3I. In collaboration with the Wester group at Innsbruck, we recently published a paper on the spectator nature of the C-H stretching modes in the S_N2 reaction between F^- and CH_3I.[16] Our sudden vector projection model is shown to provide insights into the reaction dynamics of this prototypical ion-molecule reaction. This reaction was also studied in a theoretical collaboration with the Hase group at Texas Tech,[17] which clarified the origin of the double inversion mechanism as a result of frustrated proton transfer.

iii. The Be^+ + H_2O reaction. In collaboration with the groups of Hudson and Campbell at University of California Los Angeles,, we provided a theoretical interpretation of the experimental results on the Be^+ + H_2O reaction at low temperatures.[18] The rates for this reaction and its kinetic isotope effect are obtained by using a quasi-classical method on a global potential energy surface.[19]

Significant efforts have also been devoted to understanding of dynamics of photodetachment of polyatomic negative ions. Two reviews on our quantum dynamics of polyatomic atomic molecules are published.[20, 21]

i. CCH_2^-: In collaboration with the Neumark group at University of California at Berkeley, full-dimensional quantum dynamical investigations of photodetachment of the vinylidide anion have been performed on newly developed potential energy surfaces to elucidate the dynamics of the vinylidene-acetylene isomerization. The quantum dynamical results on these potential energy surfaces helped to assign the spectral features in the photoelectron spectrum of the anion, including some rather irregular features, which were attributed to Herzberg-Teller coupling with an excited state.[22] In addition, the auto-detachment of the vibrationally excited anion was investigated, and the results are in good agreement with experiment.[23]

ii. CH_3OHF^-. The photodetachment of this anion provides valuable information on the F + $CH_3OH \rightarrow HF + CH_3O$ reaction. We performed reduced dimensional quantum dynamical calculations on full-dimensional potential energy surfaces, which reproduced the experimental photoelectron spectrum of Neumark, shedding valuable light on the transition-state dynamics and the associated Feshbach resonances.[24]

iv. FH_2O^- and ClH_2O^-. In collaboration with the Continetti group at University of California San Diego, we investigated the photodetachment of vibrationally excited FH_2O^-,[25] which showed the strong impact of vibration on reaction dynamics. We have also investigated the photodetachment of ClH_2O^-, and found many Feshbach resonances in its photoelectron spectrum.[26]

Theoretical investigations on the adsorption of methylene blue on coinage metal surfaces were carried out in support of the experimental effort by Habteyes.[27] We have further collaborated with Yu Zhang, Sergei Tretiak and George Schatz to explore a more detailed description of plasmon-facilitated photocatalysis.[28]

Finally, we have devoted some efforts to method development. For example, we have explored a new ways to construct global potential energy surfaces using a machine learning method based on Gaussian regression,[29] which might be useful in certain circumstances

References

(1) Kafle, B.; Poveda, M.; Habteyes, T. G., Surface Ligand-Mediated Plasmon-Driven Photochemical Reactions. *J. Phys. Chem. Lett.* **2017,** *8*, 890-894.

(2) Tesema, T. E.; Kafle, B.; Tadesse, M. G.; Habteyes, T. G., Plasmon-Enhanced Resonant Excitation and Demethylation of Methylene Blue. *J. Phys. Chem. C* **2017,** *121*, 7421-7428.

(3) Tesema, T. E.; Annesley, C.; Habteyes, T. G., Plasmon-Enhanced Autocatalytic N-Demethylation. *J. Phys. Chem. C* **2018,** *122*, 19831-19841.

(4) Tesema, T. E.; Kafle, B.; Habteyes, T. G., Plasmon-Driven Reaction Mechanisms: Hot Electron Transfer Versus Plasmon-Pumped Adsorbate Excitation. *J. Phys. Chem. C* **2019,** *123*, 8469-8483.

(5) Kafle, B.; Gieri, P.; Kookhaee, H.; Tesema, T. E.; Haq, S.; Manjavacas, A.; Habteyes, T. G., Robust Charge Transfer Plasmons in Metallic Particle–Film Systems. *ACS Photon.* **2018,** *5*, 4022-4029.

(6) Haq, S.; Addamane, S.; Kafle, B.; Huang, D.; Balakrishnan, G.; Habteyes, T. G., Active Mediation of Plasmon Enhanced Localized Exciton Generation, Carrier Diffusion and Enhanced Photon Emission. *Sci Rep* **2017,** *7*, 864.

(7) Kafle, B.; Tesema, T. E.; Kazemi, A.; Habteyes, T. G., Stripping and Transforming Alloyed Semiconductor Quantum Dots Via Atomic Interdiffusion. *J. Phys. Chem. C* **2016,** *120*, 12850-12859.

(8) Han, H.; Alday, B.; Shuman, N. S.; Wiens, J. P.; Troe, J.; Viggiano, A. A.; Guo, H., Calculations of the Active Mode and Energetic Barrier to Electron Attachment to CF_3 and Comparison

with Kinetic Modeling of Experimental Results. *Phys. Chem. Chem. Phys.* **2016,** *18*, 31064-31071.

(9) Shuman, N. S.; Martinez, O.; Ard, S. G.; Wiens, J. P.; Keyes, N. R.; Guo, H.; Viggiano, A. A., Surprising Behaviors in the Temperature Dependent Kinetics of Diatomic Interhalogens with Anions and Cations. *J. Chem. Phys.* **2017,** *146*, 214307.

(10) Ard, S. G.; Shuman, N. S.; Martinez, O.; Keyes, N. R.; Viggiano, A. A.; Guo, H.; Troe, J., Temperature and Pressure Dependences of the Reactions of Fe^+ with Methyl Halides CH_3x (X = Cl, Br, I): Experiments and Kinetic Modeling Results. *J. Phys. Chem. A* **2017,** *121*, 4058-4068.

(11) Xie, C.; Liu, X.; Sweeny, B. C.; Miller, T. M.; Ard, S. G.; Shuman, N. S.; Viggiano, A. A.; Guo, H., Probing the Rate-Determining Region of the Potential Energy Surface for a Prototypical Ion–Molecule Reaction. *Phil. Trans. Royal Soc. A* **2018,** *376*, 20170146.

(12) Sweeny, B. C.; Pan, H.; Ard, S. G.; Shuman, N. S.; Viggiano, A. A.; Keyes, N.; Xie, C.; Guo, H.; Ushakov, V. G.; Troe, J., Mechanistic Details of the MnO^+ + H_2/D_2 Reaction through Temperature-Dependent Kinetics and Statistical Modeling. *Int. J. Mass Spectrom.* **2019,** *435*, 26-33.

(13) Shuman, N. S.; Ard, S. G.; Sweeny, B. C.; Pan, H.; Viggiano, A. A.; Keyes, N. R.; Guo, H.; Owen, C. J.; Armentrout, P. B., Au^{2+} Cannot Catalyze Conversion of Methane to Ethene at Low Temperature: An Exploration of the Relevant Chemistry Using Selected-Ion Flow Tube, Guided Ion Beam Mass Spectrometry, and Theory. *Catal. Sci. Tech.* **2019,** *in press*.

(14) Song, H.; Li, A.; Yang, M.; Guo, H., Competition between the H- and D-Atom Transfer Channels in the H_2O^+ + Hd Reaction: Reduced-Dimensional Quantum and Quasi-Classical Studies. *Phys. Chem. Chem. Phys.* **2017,** *19*, 17396-17403.

(15) Kumar, S. S.; Grussie, F.; Suleimanov, Y. V.; Guo, H.; Kreckel, H., Low Temperature Rates for Key Steps of Interstellar Gas-Phase Water Formation. *Sci. Adv.* **2018,** *4*, eaar3417.

(16) Stei, M.; Carrascosa, E.; Dörfler, A.; Meyer, J.; Olasz, B.; Czakó, G.; Li, A.; Guo, H.; Wester, R., Stretching Vibration Is a Spectator in Nucleophilic Substitution. *Sci. Adv.* **2018,** *4*, eaas9544.

(17) Ma, Y.-T.; Ma, X.; Li, A.; Guo, H.; Yang, L.; Zhang, J.; Hase, W. L., Potential Energy Surface Stationary Points and Dynamics of the F^- + CH_3I Double Inversion Mechanism. *Phys. Chem. Chem. Phys.* **2017,** *19*, 20127-20136.

(18) Yang, T.; Li, A.; Chen, G. K.; Xie, C.; Suits, A. G.; Campbell, W. C.; Guo, H.; Hudson, E. R., Optical Control of Reactions between Water and Laser-Cooled Be^+ Ions. *J. Phys. Chem. Lett.* **2018,** *9*, 3555-3560.

(19) Chen, G. K.; Xie, C.; Yang, T.; Li, A.; Suits, A. G.; Hudson, E. R.; Campbell, W. C.; Guo, H., Isotope-Selective Chemistry in the $Be^+(^2S_{1/2})$ + HOD → $BeOD^+/BeOH^+$ + H/D Reaction. *Phys. Chem. Chem. Phys.* **2019,** *in press, DOI 10.1039/C8CP06690F*.

(20) Continetti, R. E.; Guo, H., Dynamics of Transient Species in Polyatomic Photodetachment. *Chem. Soc. Rev.* **2017,** *46*, 7650-7667.

(21) Ma, J.; Guo, H., Quantum Dynamics in Photodetachment of Polyatomic Anions. *Adv. Chem. Phys.* **2018,** *163*, 45-76.

(22) DeVine, J. A.; Weichman, M. L.; Laws, B.; Chang, J.; Babin, M. C.; Balerdi, G.; Xie, C.; Malbon, C. L.; Lineberger, W. C.; Yarkony, D. R.; Field, R. W.; Gibson, S. T.; Ma, J.; Guo, H.; Neumark, D. M., Encoding of Vinylidene Isomerization in Its Anion Photoelectron Spectrum. *Science* **2017,** *358*, 336-339.

(23) DeVine, J. A.; Weichman, M. L.; Xie, C.; Babin, M. C.; Johnson, M. A.; Ma, J.; Guo, H.; Neumark, D. M., Autodetachment from Vibrationally Excited Vinylidene Anions. *J. Phys. Chem. Lett.* **2018,** *9*, 1058-1063.

(24) Weichman, M. L.; DeVine, J. A.; Babin, M. C.; Li, J.; Guo, L.; Ma, J.; Guo, H.; Neumark, D. M., Feshbach Resonances in the Exit Channel of the F + CH_3OH → HF + CH_3O Reaction Observed Using Transition-State Spectroscopy. *Nat. Chem.* **2017,** *9*, 950-955.

(25) Ray, A. W.; Ma, J.; Otto, R.; Li, J.; Guo, H.; Continetti, R. E., Effects of Vibrational Excitation on the F + H_2O → HF + OH Reaction: Dissociative Photodetachment of Overtone-Excited $[F-H-OH]^-$. *Chem. Sci.* **2017,** *8*, 7821-7833.

(26) Zhao, H.; Xie, D.; Guo, H., Quantum Dynamics of ClH_2O^- Photodetachment: Isotope Effect and Impact of Anion Vibrational Excitation. *J. Chem. Phys.* **2018,** *148*, 064305.

(27) Zhou, L.; Johnson, R.; Habteyes, T.; Guo, H., Adsorption of Methylene Blue and Its N-Demethylated Derivatives on the (111) Face of Coinage Metals: The Importance of Dispersion Interactions. *J. Chem. Phys.* **2017,** *146*, 164701.

(28) Zhang, Y.; Nelson, T.; Tretiak, S.; Guo, H.; Schatz, G. C., Plasmonic Hot-Carrier-Mediated Tunable Photochemical Reactions. *ACS Nano* **2018,** *12*, 8415-8422.

(29) Kolb, B.; Marshall, P.; Zhao, B.; Jiang, B.; Guo, H., Representing Global Reactive Potential Energy Surfaces Using Gaussian Processes. *J. Phys. Chem. A* **2017,** *121*, 2552-2557.