

# Ultrafast Dynamics of Photo-induced Surface Reactions

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Chemical reactions occur usually in the electronic ground state, whereby reaction barriers are overcome by thermal activation. Exceptions from this rule are photo-induced or electron stimulated processes, where the activation is mediated by electronic excitation to an excited state which initiates a nuclear motion along the reaction pathway. Examples are photo-chemical processes and chemical reactions induced by electron attachment or charge transfer. A key concept of chemical reaction dynamics relies on the Born-Oppenheimer (BO) approximation whereby electrons are assumed to follow the nuclear motion instantaneously and thus the reaction evolves electronically adiabatically on a BO potential energy surface. Thereby, non-adiabatic coupling effects between the nuclear motion and the electronic degrees of freedom are neglected. However, electronic non-adiabatic processes can occur at metal surfaces where a continuum of electron-hole pair excitations in the metal may lead to a coupling between electronic and nuclear degrees of freedom and a breakdown of the BO approximation. This is relevant for laser-induced surface femtochemistry at molecule-metal interfaces. The dynamics of such processes occur on ultrafast (typically femto- to picosecond) timescales. In this talk, I will briefly review the mechanisms of surface femtochemistry using the example of oxidation and desorption of CO on Ru(001). Recent experiments performed with time-resolved resonant inelastic x-ray scattering (trRIXS) at the X-ray free electron laser LCLS provide direct insight into the changes of the electronic structure and chemical bonding after fs laser excitation, leading to a pronounced bond weakening and CO desorption or oxidation. Thereby, motions of CO and O on a Ru(0001) surface are excited allowing the reactants to collide and react leading to the appearance of new electronic states in the O K-edge spectrum. These studies provide new insights into details of the free energy landscape and into dynamics of transient species in the transition state region.

# Quantum electron-ion dynamics at interface from TDDFT

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Real-time time-dependent density functional theory (TDDFT) has been implemented using local atomic basis, which enables large scale simulations on electron-ion dynamics at more realistic complex interface systems. The electron-ion evolution is driven by a Hamiltonian that builds upon excited state electron density. This allows us to demonstrate the working principles of hybrid solar cells especially that involving charge separation and collection dynamics purely based on quantum mechanics. The method also yields precise prediction of the timescale for ultrafast electron injection from chromophores to semiconductors, in response to various interface structural details (molecular size, anchor group, binding mode, defects) and environment (excitation level, solvents). Consequently we could build a “virtual solar cell” producing macroscopic current-voltage relationships with only input being molecular composition. The methods are also used for investigating ultrafast electron transfer in dichalcogenides heterostructures and plasmonic molecular splitting, where interesting insights on atomistic mechanism have been obtained.

# **Ultrafast energy transfer from THz pulses to bulk water and to clusters: towards a new activation strategy for time-resolved reaction dynamics?**

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Pump-probe studies of chemical reactions are almost exclusively limited to photochemistry applications, in which typically a short UV-Vis laser pulse initiates the photoreaction of interest by electronic excitation. In contrast, chemical reactions in the ground electronic state start by random thermal fluctuations of the environment, which randomly supplies the necessary "kicks" in order to climb the energy barrier between reactants and products through the transition state.

In this contribution I discuss how the interaction of a strong sub-ps THz pulse with bulk water and with water clusters can result in a T-jump of several hundred Kelvin within about one picosecond [1], and how the transferred energy flows from the environment to solute molecules via collisional energy transfer with the hot solvent [2]. Finally, the possible applicability of ultrafast T-jumps as a way to trigger thermal chemical processes and to study their dynamics is analyzed.

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# **Weak bond is not weak: The crucial role of van der Waals forces in hybrid inorganic-organic systems**

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The understanding of electronic properties of complex organic/metal interfaces requires a reliable method for the prediction of their structure and stability. Recently, we developed a method based on density-functional theory (DFT) with vdW interactions (DFT+vdWsurf) to accurately model adsorbates on surfaces. Our DFT+vdWsurf calculations lead to a few peculiar findings: (1) The vdW energy can contribute more to the binding of covalently bonded systems than it does in physisorbed interfaces; (2) the binding energies of similar molecules can be identical, despite significantly different adsorption heights; (3) the physically bound (precursor) state for aromatics on Pt(111) can be prominently stabilized and long-lived, making it potentially useful in molecular switches. We also present a detailed theoretical study of silicene monolayer containing three types of defects: vacancy clusters, extended line defects (ELDs), and di-adatoms. We demonstrated that the introduction of single and double silicon adatoms significantly enhances the stability of the system, and provides an effective approach on tuning the magnetic moment and band gap of silicene.

# Chemical processes at nanostructured surfaces: a theoretical perspective

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Many technologically relevant processes happen on nanostructured and defective surfaces. In the present contribution, we study chemical processes taking place in two selected systems. First, the charge segregation in an organic dye adsorbed on a titanium oxide nano-crystallite is investigated by means of time-dependent configuration interaction. Upon excitation by light, we observe how the dye transfers an electron to the environment via the nano-crystallite within a few femtoseconds. Using time-resolved electronic fluxes and flux density maps, we provide an insightful microscopic description of the charge injection process. Second, we investigate the catalytic oxidation of CO on gold clusters deposited on MgO surfaces using point charge embedding within a density functional theory framework. The stability of the co-adsorbed species is such that the catalytic cycle is either broken or the reaction remains thermally unaccessible, explaining the observed absence of catalytic activity. We study by means of reduced dimension quantum dynamics possibilities for restoring the catalytic cycle using simple infrared laser sources.

# Quantum simulation of hydrogen and lithium phase diagrams

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Experiments and computer simulations have shown that the melting temperature of solid hydrogen drops with pressure above about 65 GPa [1,2], suggesting that a liquid state might exist at low temperatures. It has also been suggested that this low temperature liquid state might be non-molecular and metallic, although evidence for such behaviour is lacking [3,4]. Here, we report results for hydrogen at high pressures using ab initio path-integral molecular dynamics methods, which include a description of the quantum motion of the protons at finite temperatures [5,6]. We have determined the melting temperature as a function of pressure by direct simulation of the coexistence of the solid and liquid phases [7,8], and have found an atomic solid phase from 500 to 800 GPa which melts at  $< 200$  K. Beyond this and up to pressures of 1,200 GPa a metallic atomic liquid is stable at temperatures as low as 50 K. The quantum motion of the protons is critical to the low melting temperature in this system as ab initio simulations with classical nuclei lead to a considerably higher melting temperature of  $\sim 300$  K across the entire pressure range considered. Some of our recent studies on the phase diagram of lithium will also be discussed in the end [9].

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# **Electrochemical interfaces studied by sum-frequency vibrational spectroscopy**

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Electrochemical (EC) reactions are crucial in many applications, yet most EC analytical tools lack the sensitivity to access molecular-level information of reactants and products. By combining sumfrequency vibrational spectroscopy (SFVS) and surface plasmon resonance (SPR) at EC interfaces, we demonstrated the feasibility of measuring in situ and real-time vibrational spectra during EC reactions at noble metal electrodes. Application of the technique to EC reactions at a gold surface helped understand how the surface in a basic solution was oxidized and reduced during a cyclic voltammetry cycle. Study of desorption of a thiol self-assembled monolayer from gold through EC reactions in a basic solution showed that contrary to intuition, the desorbed thiols by reductive reaction remained as an ordered layer near the gold interface, but did diffuse away if they are desorbed oxidatively from gold. Recently, we also probed the interfacial water structures under the electric static field applied by an electrode using SFVS, and found the field response of OH bands of different origins.

# **Unraveling interfacial vibrionic and intermolecular interactions via doubly-resonant sum frequency spectroscopy**

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Obtaining molecular structure for aggregated states of photosensitizers at semiconductor interfaces has been challenging. We have demonstrated that Doubly-Resonance Sum Frequency Generation (DR-SFG) spectroscopy can be used as a surface and species-selective probe in order to characterize sensitized nanocrystalline interfaces and gain molecular-level information about changes in orientation and intermolecular couplings for different surface aggregation states of chalcogenorhodamine dyes. The selenium-containing class of dyes used in this study have shown to be promising candidates for dye sensitized solar cells and solar hydrogen production due to their broad absorption spectra, high photoelectrochemical conversion efficiencies, and prolonged stability. The increased efficiency has been attributed to formation of H type of aggregates at the titania interface. However, a detailed molecular-level picture of this process has not been developed. In this work, we study different anchoring groups and dye conformations on a mesoporous TiO<sub>2</sub> film and compare the DR-SFG results for different by vibrational excitations selectively coupled to the aggregated and non-aggregated species via an upconverting excitation. Our results show gradual appearance and disappearance of vibrational peaks as the upconverting excitation is tuned towards the blue region of the absorption band which is consistent with the H-type aggregation region. Therefore, we demonstrate that DR-SFG can be used to selectively probe the structure of monolayer sub-groups by means of vibrionic coupling of interfacial species. We expand the DR-SFG studies to various fullerene films and single-walled carbon nanotubes where we examine the vibrionic coupling and interfacial structure in a similar approach.

# Probe Adsorption Structures of Methanol on TiO<sub>2</sub>(110) Under Both UHV and High Pressure Conditions

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Although the photochemistry of methanol on TiO<sub>2</sub>(110) has been widely investigated as a prototypical model of the photocatalytic reaction of organic molecules, the most fundamental question of the adsorption state of methanol on TiO<sub>2</sub>(110) is still unclear. We have investigated the structure of methanol adsorbed on TiO<sub>2</sub>(110) using sum frequency generation vibrational spectroscopy (SFG-VS) under both ultrahigh vacuum and high pressure conditions. The results indicate that both molecularly adsorbed methanol and dissociatively adsorbed methanol (methoxy) adsorb on five-coordinated Ti sites to form the first layer in comparable fractions, which resolves a long-standing debate regarding the adsorption state of methanol on TiO<sub>2</sub>(110). However, the dissociated molecules in the first layer gradually decrease as the coverage increases from one to two layers, and vanish when multilayer coverage is reached. We also have found only molecular adsorptive methanol on this surface under the high pressure condition due to the entropic effect. Therefore, the adsorption structure of methanol on TiO<sub>2</sub>(110) shows a high dependence on the coverage and pressure, which not only provides a detailed insight into the adsorption structure of methanol on TiO<sub>2</sub>(110), but also shed light on the photochemistry on this surface at the molecular level.

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# Electric charge and molecular adsorption at oil/water interfaces

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The adsorption of molecules, including surfactants at the oil/water interfaces in emulsions has been investigated by many experimental techniques. However, the obtaining of the parameters such as the adsorption free energy, molecular density and structure at the interfaces is not an easy task. We show that Second Harmonic Generation could be used to help understand this issue. Recently we have demonstrated that the interfacial potential and molecular adsorption at the hexadecane/water interface could be evaluated with second harmonic generation.<sup>1-2</sup> With the modification of this oil/water interface by molecules with different charges, we found that the increasing of the negative potential at the interface enhanced the SHG radiation from the interface, proving a better orientational ordering of water molecules at the interface.

Using second harmonic generation, we also studied the adsorption of a positively charged dye molecule, Malachite Green, at the surface of oil droplet in hexadecane/water emulsion. The influence of surfactants with different charges were also detected. It was found that charge-charge interaction and competition adsorption are dominant factors that determine the molecular interactions at the interface.

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# Atomic Layer Deposition—Sequential Self-limiting Surface Reactions for Advanced Catalyst “bottom-up” Synthesis

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Atomic layer deposition (ALD), is a variation on chemical vapor deposition wherein metals, oxides, and other materials are deposited on surfaces via a sequence (usually binary) of self-limiting surface reactions between gaseous precursor molecules and a substrate on the atomic level. ALD can deposit uniform and conformal coatings on various substrates regardless of whether the substrate is flat or possesses high aspect ratio features, high surface area, or high porosity, because of the unique feature of self-limiting surface reactions in each deposition cycle. As a consequence, surface engineering and functionalization of a high surface area substrate to achieve “bottom-up” designing advanced catalysts becomes possible by ALD on the atomic level. In this presentation, I will first focus on the surface chemistry of oxide ALD on transition metals and bimetallic ALD. Next, atomic-level “bottom up” design of advanced supported metal catalysts will be discussed.

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# **Vibrational energy pooling in multilayer CO on NaCl(100) studied with nanosecond time resolution using a superconducting nanowire single photon detector**

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Laser induced infrared fluorescence from multilayer CO (ca.1600 layers) on NaCl(100) is studied in both time and frequency domain using a superconducting nanowire single photon detector (SNSPD). Upon overtone ( $v=0\rightarrow 2$ ) excitation with a 6 ns laser pulse, infrared CO emission originates from states  $v=1$  up to  $v=29$  were detected. The time profile of dispersed emission signals were characterized by a fast rise followed by a multi-exponential decay on a millisecond timescale. With increasing quantum number the rise time increases from 0.2  $\mu\text{s}$  for  $v=10$  to 50  $\mu\text{s}$  for  $v=26$ . The vibrational energy pooling dynamics in solid CO was time resolved for the first time.

# Probing Solid-Liquid Interface Using APXPS

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Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5 keV- 5 keV). By using X-ray up to 5 KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study the electrolyte/ electrode interface of many important electrochemical devices.

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# **Nanoparticle-Biomolecule Interactions in Aqueous Solutions Probed by Sum Frequency Generation Vibrational Spectroscopy**

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The interactions between nanoparticles and biomolecules play important roles in the toxicity and biomedical functions of nanomaterials. However, there is still a lack of the molecular-level understandings of how biomolecules chemically attach to the nanoparticle surfaces in aqueous solutions as well as how nanoparticles affect the biological molecular systems. In this presentation, we will demonstrate a couple of recent progresses in the in situ characterization of nanoparticle-bimolecular interactions using the sum frequency generation vibrational spectroscopy, a surface-selective nonlinear optical probe. The first example illustrates the binding configurations of small carboxylate group on the ceria nanoparticle and how the oxidation states of the ceria surface affect the binding conformations, revealing the detailed interplays between the biological ligands and the functional nanoparticles which are designed for the biomedical applications. In the second part of this presentation, the molecular orientations and interfacial assembly structures of the phospholipid Langmuir monolayer influenced by the hematite nanoparticles will be discussed, implying the molecular mechanism of how the nanoparticles affect the model system of the lung surfactants and transport through the biological membranes. These results clearly show that the sum frequency generation vibrational spectroscopy is fully capable of exploring the surface chemistry between nanoparticles and biomolecules.

# Molecular Structures and Dynamics of Proteins at the Interface

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Determination of the structure and intermolecular interaction holds the key for understanding or controlling the functionalities of biological systems. Sum frequency generation vibrational spectroscopy (SFG-VS) has been demonstrated to be a powerful technique to obtain the interfacial structures and interactions at the molecular level. By probing backbone amide I vibration of the membrane proteins, we have successfully characterized the structures and orientation of peptides and proteins in different chemical environments. Using alamethicin as a model, we observed a model ion channel gating action in cell membranes in real time in situ. Yet amide I band alone is not always sufficient to describe the detailed behaviors of complex proteins at surface and interface. On the basis of our previous study, we developed a method for unambiguously differentiating the interfacial protein secondary structures by combining surface-sensitive amide I and amide III spectral signals. Such a combination offers a powerful tool to directly distinguish random-coil (disordered or loop) and  $\alpha$ -helical structures in proteins. From a systematic study of several antimicrobial peptides, it is found that the spectral profiles of the random-coil and  $\alpha$ -helical structures are well separated in the amide III spectra, appearing below and above  $1260\text{ cm}^{-1}$ , respectively. For the peptides with a straight backbone chain, the strength ratio for the peaks of the random-coil and  $\alpha$ -helical structures shows a distinct linear relationship with the fraction of the disordered structure deduced from independent NMR experiments reported in literatures. The established experimental protocols in our lab are ready to be employed in determining the interfacial structures and interaction of complex biomolecules in situ and real time without extraneous labels.

## Probing interfacial water structure on $\alpha\text{-Al}_2\text{O}_3(0001)$

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Alumina surface are ubiquitous in technologically relevant applications and a useful model system for more complicated, environmentally abundant, alumino-sicate phases. The properties of these surfaces – e.g. their conductivity, reactivity, and structure – are strongly influenced by the presence of even small amount of water. Experimentally characterizing water/ $\alpha\text{-Al}_2\text{O}_3$  interaction is challenging because the problem is inherently multi-scale: while the thermodynamics and kinetics of interaction with  $\alpha\text{-Al}_2\text{O}_3$  are important, the macroscopic properties of liquid water/ $\alpha\text{-Al}_2\text{O}_3$  interfaces cannot be recovered by adding single molecule effects. To overcome this problem experimental tools that characterize interfacial water, and  $\alpha\text{-Al}_2\text{O}_3$  surface, structure and dynamics over  $>10^{10}$  mbar in water pressure are required. We address this problem for the most stable  $\alpha$ -Alumina surface, the  $\alpha\text{-Al}_2\text{O}_3(0001)$ , using all optical, interface specific vibrational spectroscopy, called vibrational sum frequency (VSF) spectroscopy. Here we characterizing water structure at the  $\alpha$ -Alumina/ liquid water interface by probing the vibrational relaxation dynamics of surface hydroxyls with interfacial specificity (in an IR pump/ VSF probe scheme). This work demonstrates that interfacial water at the  $\alpha$ -Alumina/ liquid water interface is hydrophobic: it interacts very weakly with bulk liquid.

# Who by fire: combustion synthesis of nanomaterials and complex surfaces – mechanism, diagnostics and applications

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The current state-of-the-art in the field of gas-surface scattering dynamics calls for expanding its unique experimental approaches to the investigation of fundamental molecular interactions at complex surfaces. Despite the demonstrated importance of simple crystalline surfaces, molecular interactions with which presently dominate the field of surface dynamics, it is widely understood that more sophisticated systems are needed to make progress on realistic problems in surface chemistry.

Gas-phase high-temperature synthesis (e.g. combustion, plasma or chemical vapor deposition (CVD)) is an important tool for production of a plethora of metal/metal oxide materials, which play important role in heterogeneous catalysis. With respect to purity and surface composition, particles and films generated via gas-phase synthesis are preferred compared to materials from wet synthesis with surface active additives. The combination of high temperature gas phase synthesis with mass selective molecular beam sampling merges the advantages of flame-assisted synthesis for bulk nanopowders such as process stability, wide size-tuning range (particle sizes from a few to  $\sim 500$  nm are commonly accessible) and wide material library availability with those of mass-selective cluster beam deposition in terms of direct integration of nanoparticles on support substrates, monodispersity, substrate coverage control, spatial resolution and spatial distribution manipulation, thus providing an excellent opportunity to obtain samples for systematic studies of molecular interaction with catalytic surfaces.

One aspect of our work focuses on the input gained from well-controlled experiments providing a necessary prerequisite for production of functional materials with tailored functionalities. High-temperature particle-laden environment imposes considerable challenges on in-situ and in-line diagnostics and methods addressing both solid and gas phase products and intermediates are required. In our recent study we have applied combination of molecular beam sampling and laser-based techniques to study iron oxide nanoparticle formation in flame (doped with  $\text{Fe}(\text{CO})_5$ ) synthesis reactor. These experiments deliver data able to make contact with outputs of detailed kinetic modeling. I will highlight our recent results, indicating that in contrast to the commonly accepted mechanism, postulating the decomposition of the precursor followed by oxidation of the nascent Fe atoms and late formation of iron oxide nanoparticles, the actual synthesis mechanism is considerably more rich and complex.

Another aspect of our work concerns NO molecule interaction with CVD-prepared  $\text{VO}_2$  films. Vanadia-based catalysts are being used for selective catalytic reduction of  $\text{NO}_x$  emissions, the partial oxidation of o-xylene to phthalic anhydride, dehydrogenation of propane and the oxidative destruction of volatile organic compounds. It provides a unique testing ground for molecular interactions at surfaces as it can morph itself from insulator to metal in only a few degrees temperature range (known as Mott transition). The dependence of the metallic properties of  $\text{VO}_2$  films on their temperature should clearly bear on their propensity to interact with molecular vibrational coordinate and hence, possibly influence the chemistry of heterogeneous catalysis. Our preliminary molecular beam scattering experiments aiming towards understanding the underlying dynamics, will be presented.

# **Engineering and characterizing hybridized nanostructures**

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Two dimensional layered transition metal dichalcogenides (LTMDs) have become a much sought after material in recent years with promising applications for catalytic, electronic and optics. Combining with the advanced features of LTMDs, unique three-dimensional (3D) nanoarchitecture of graphene aerogel motivates it as one of promising building blocks for creating new nanoarchitectures. Here, we will introduce a facile bottom-up route to realize various hybridized structures for specific applications. The advanced characterized tools, including atomic microscope and synchrotron radiation-based X-ray absorption fine structures, will be employed on the obtained hybrids to provide useful insight for understanding the relationship between the specific structure and the properties, along with the density functional theory calculations.

## HCl Dissociation on Au(111)

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Quantum dynamics calculations looking at the dissociation of HCl on Au(111) surface have been reported [1]. These calculations show that the dissociation reaction is activated by both translational and vibrational energy of the incident HCl molecules with nearly equal efficiency. We have undertaken an experimental study of this reaction and report some of our important results here. Clean Au(111) surface under UHV conditions was dosed with a pulsed, seeded molecular beam of HCl with incidence translation energies up to 2.5 eV, prepared using a heated nozzle. Auger electron spectroscopy measurements carried out subsequent to the dosing show the presence of Cl atoms on the surface resulting from the dissociation of the incident HCl molecules. We observe that the initial sticking probability ( $S_0$ ) increases from  $10^{-4}$  to  $10^{-1}$  as the nozzle is heated from 300 to 870 K. In order to disentangle the effect of vibrational vs translational promotion of the dissociation, additional experiments varying the normal component of the incident kinetic energy at constant nozzle temperature were performed. Our results suggest that the energy in the vibrational degree of freedom is much more effective in overcoming the dissociation barrier. I will be discussing these results in the context of previously extensively studied systems  $H_2$ ,  $D_2/Cu(111)$  and  $N_2/Ru(0001)$ . Further, I will provide some possible explanations for the large vibrational activation observed in this particular case and also for the large discrepancy between the theory and experiment.

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# Unveiling Microscopic Structures of Charged Water Interfaces

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Sum frequency spectroscopy (SFS) has been developed into a versatile analytical tool for surface studies because it is highly surface-specific dictated by symmetry under electric dipole approximation. However, there still exist challenges for the current SF spectroscopy, which desiderates further development of the technique.

One challenge is to probe the first few monolayers at charged interface, e.g. charged water interface. Generally, water molecules within a distance of a few monolayers away from the charged surface, forming an interface-specific bonding network (labeled as “the bonded interface layer”), governs the properties and functionality of the interface. Unfortunately, the bonded interface layer is usually buried under thick diffuse layer set by screening ions. Despite extensive studies over the years, still little is known about its microscopic structure. We develop a new SFS scheme that allows us for the first time to obtain the vibrational spectrum, and hence the microscopic structural information, of the bonded interface layer of charged water interfaces. This novel spectroscopic technique provides unique opportunities to validate molecular theories of charged water interfaces and to search for better understanding of electrochemistry and biological aqueous interfaces at a deeper molecular level.

# **Ultrafast energy transfer in interfacial water molecules underneath a surfactant layer**

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The structure and energy dynamics of water in contact with the negatively charged industrial surfactant sodium dodecyl sulphate (SDS) is explored using ultrafast time resolved 2-dimensional sum frequency generation spectroscopy (2D-SFG). This surface-specific technique is used to observe the time-dependent frequency fluctuations of the O-H stretch vibration, which sheds light on the energy transfer and relaxation of the water molecules below the surfactant. Two coupled types of O-H vibrations are observed, which is in marked contrast to the pure air-water interface where only one type of water has been observed. This 2D-SFG technique has given remarkable insight into how the interfacial hydrogen bonding network is influenced by the presence of a surfactant monolayer.

# **Structure Evolution of Metal Nanoparticles in Water Environment**

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Metal nanoparticles have drawn extensive attentions in materials science due to their widespread applications in electronics, engineering and catalysis. A very fundamental question is their structure evolution and surface segregation. Many recent observations have shown that reactive gases or supports may have strong effects on the morphology change and surface segregation. However, the effect of water—the most common solvent and environment—has not received enough attention. Here, we will give two examples to show water adsorption could induce the morphology change and strong surface segregation tendencies for the metal nanoparticles. This finding not only prompts us to re-examine the potential effects of water on metal nanoparticles, but would be also very helpful as a guide for the further theoretical and experimental studies in this field.

# The mechanism of the water evaporation

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Evaporation is the process by which water changes from a liquid to a gas or vapor, and is a key step in the earth's water cycle. At the molecular level, evaporation requires breaking at least one very strong intermolecular bond between two water molecules at the interface. Despite the importance of this process, the molecular mechanism by which an evaporating water molecule gains sufficient energy to escape from the surface, has remained elusive. Here, we show, using molecular dynamics simulations at the water-air interface with polarizable classical force field models, that the high kinetic energy of the evaporated water molecule is enabled by a well-timed making and breaking of hydrogen bonds involving at least three water molecules at the interface, the recoil of which allows one of the molecules to escape. The evaporation of water is thus enabled by concerted, ultrafast hydrogen-bond dynamics of interfacial water, and follows one specific molecular pathway.

# Structure and dynamics of hydrogen bonding and proton transfer at aqueous solution interface

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Understanding the structure, structural dynamics and energy flow dynamics of hydrogen bond and proton transfer process is very important for many field of science including the catalysis, the corrosion, and the atmospheric chemistry. We use time-resolved (two-dimensional) sum-frequency generation spectroscopy [1, 2] to elucidate the structure and energy flow dynamics of water in contact with the semi-soluble ionic solid  $\text{CaF}_2$  and air/water interface at  $\text{pH}=2$ .

Our approach provided the direct observation of structural heterogeneity of interfacial water through the spectral heterogeneity of the O-D/O-H stretch vibration of interfacial water  $\text{D}_2\text{O}/\text{H}_2\text{O}$  and made it possible to study the dynamics of hydrogen bonds and proton transfer reactions in the time-domain at a time scale between a few femtoseconds and approximate 10 picoseconds. We presented results of the ultrafast dynamics at the air/water and solid/liquid interfaces at varying pH. The spectral heterogeneity decays on a sub-picosecond timescale, indicating both energy transfer between interfacial water molecules and ultrafast interfacial structural reorganization. Furthermore no evident effect of protons found on interfacial water dynamics (even at negative pH) at the water-air interfaces and was the water/ $\text{CaF}_2$  interface.

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# Ultrafast low-energy electron diffraction

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Time-resolved high-energy electron diffraction experiments have unraveled ultrafast structural and electronic processes in bulk media [1]. Ultrafast diffraction with low-energy electrons would be ideal to investigate the structural dynamics of quasi-two-dimensional systems such as ultrathin films and surfaces. However, the realization of such experiments remains demanding, due to the challenges in creating suitable electron pulses [2].

Here, we discuss the development of ultrafast low-energy electron diffraction (ULEED) with first applications in transmission and reflection geometries [3]. Low-energy electron pulses of few-picoseconds duration are generated with a laser-driven tungsten needle emitter and are employed in a laser-pump/electron probe scheme.

In a first application, we study the structural dynamics of an ordered polymer adsorbate on free-standing graphene by ULEED in transmission [3]. We give a detailed account of the characteristic time scales of the superstructure dynamics, including the energy transfer from the graphene to the adsorbate layer, the loss of crystalline order in the polymer, and the formation of amorphous components at extended spatial frequencies.

Furthermore, we extend ULEED to a backscattering geometry by developing a miniaturized laser-driven photoelectron source. At low electron energies around 100 eV, we can resolve the nearly commensurate charge density wave (CDW) [4] at a 1T-TaS<sub>2</sub> surface, demonstrating the capability of ULEED to access complex electronic and structural dynamics at surfaces. As a first example, we present results on the optically driven transition of the nearly commensurate CDW to an incommensurate phase, with subsequent excitation-dependent relaxation processes on nanosecond time scales.

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# Localized Excitation of $\text{Ti}^{3+}$ Ions in the Photoabsorption and Photocatalytic Activity of Reduced $\text{TiO}_2$

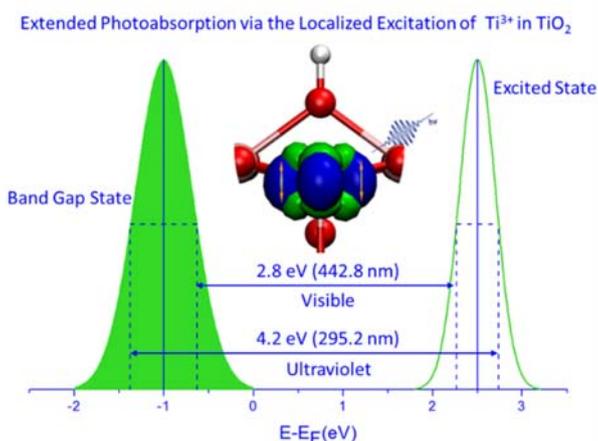
Chuanyao Zhou,<sup>1,\*</sup> Zhiqiang Wang,<sup>1</sup> Bo Wen,<sup>2</sup> Qunqing Hao,<sup>1</sup> Li-Min Liu,<sup>2</sup> Anabella Selloni,<sup>3</sup> Xueming Yang<sup>1</sup>

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In reduced  $\text{TiO}_2$ , electronic transitions originating from the  $\text{Ti}^{3+}$ -induced states in the band gap are known to contribute to the photoabsorption, being in fact responsible for the material's blue color and visible light photocatalysis, but the excited states accessed by these transitions have not been characterized in detail. In this work we investigate the excited state electronic structure of the prototypical rutile  $\text{TiO}_2(110)$  surface using two-photon photoemission spectroscopy (2PPE) and density functional theory (DFT) calculations. Using 2PPE, an excited resonant state derived from  $\text{Ti}^{3+}$  species is identified at  $2.5 \pm 0.2$  eV above the Fermi level (EF) on both the reduced and hydroxylated surfaces. DFT calculations reveal that this excited state is closely related to the gap state at  $\sim 1.0$  eV below EF, as they both result from the Jahn-Teller induced splitting of the  $3d-t_{2g}$  orbitals of  $\text{Ti}^{3+}$  ions in reduced  $\text{TiO}_2$ . Localized excitation of  $\text{Ti}^{3+}$  ions via  $3d \rightarrow 3d$  transitions from the gap state to this empty resonant state increases significantly the  $\text{TiO}_2$  photo-absorption and extends the absorbance to the visible region, consistent with the observed enhancement of the visible light induced photocatalytic activity of  $\text{TiO}_2$  through  $\text{Ti}^{3+}$  self-doping. Our work reveals the physical origin of the  $\text{Ti}^{3+}$  related photoabsorption and visible light photocatalytic activity in prototypical  $\text{TiO}_2$ , and also paves the way for the investigation of the electronic structure and photoabsorption of other metal oxides.



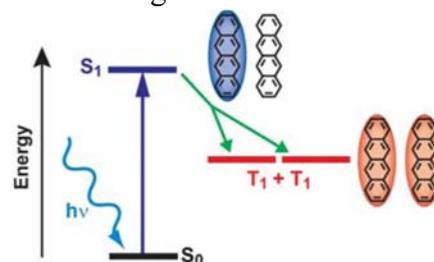
# Using Singlet Exciton Fission to Harvest Solar Energy

Aaron K. Le, Jon Bender, Ravindra Pandey, Aaron P. Moon, & Sean T. Roberts

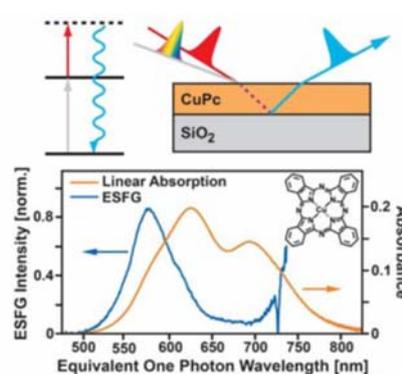
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One of the primary loss mechanisms that impacts the performance of silicon photovoltaic cells is the thermalization of high energy charge carrier produced by photons with energy in excess of silicon's bandgap. An appealing strategy for negating these losses is to coat silicon with a material that can absorb high energy photons and use their energy to excite multiple electron hole pairs that can be passed to the silicon layer. Materials that undergo singlet exciton fission (SF) can fill this role. SF is a process that occurs in select organic materials that possess low lying triplet exciton states. In such materials, photogenerated singlet excitons that have energy in excess of two triplets can divide their energy to excite a pair of spin-correlated triplet excitons, generating two excited electrons from a single photon absorption event (Figure 1). However, using SF to boost photovoltaic efficiency requires organic materials that both efficiently undergo SF and are capable of passing triplet excitons to silicon. Here, we report the results of ultrafast transient absorption measurements performed on a series of perylene diimide (PDI) compounds. PDI monomers possess the correct energetic alignment of singlet and triplet energies to achieve SF (ES1 ~ 2.3 - 2.4 eV; ET1 ~ 1.1 - 1.2 eV), however excitonic interactions between neighboring molecules in the solid state can strongly modify both the energetic driving force for SF and the electronic couplings between neighboring molecules that guide SF. By adding different functional groups to the imide position of the PDI core, we can systematically alter the packing structure that PDI molecules adopt in polycrystalline thin films and tune the level of excitonic interaction between neighboring molecules. We find that subtle shifts in PDI intermolecular structure, particularly along the long axis of the PDI core, have a substantial impact on SF rates and yield. We also report the results of electronic sum frequency generation (ESFG) measurements carried out on thin films of small molecule organic

semiconductors. While PDI triplet excitons possess an energy comparable to silicon's bandgap and should thus be capable of transferring to silicon via resonant energy transfer, band bending of either the PDI or silicon density of states near their interface can strongly impact this process. As an even order technique, ESFG can be used to probe the PDI density of states at the silicon interface. However, this requires isolating the portion of the emitted ESFG signal that originates from the buried interface as ESFG can be generated from both this interface and the air-exposed PDI surface. To accomplish this goal, we have built a transfer matrix-based interference model that is capable of accounting for ESFG emitted each interface within a sample and used this to describe ESFG spectra of a thin-film system consisting of copper phthalocyanine (CuPc) deposited on SiO<sub>2</sub> (Figure 2). We are now working to extend these measurements to the PDI:silicon interface.



**Figure 1:** SF materials can prepare two electrons from a single photon by generating triplet pairs.



**Figure 2:** Comparison of ESFG and absorption spectra of a 40 nm CuPc film (structure inset).

# Ultrafast electron dynamics at interfaces

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Charge transfer processes across hybrid interfaces, such as formed by the connection of molecules to semiconductors, play an increasingly important role in a variety of emerging technologies. Detailed understanding of interfacial charge transfer in these systems, however, remains a major challenge for experiments and theory. In my talk I will present a new approach to monitor photo-induced electron transfer from a molecule to a semiconductor material with sub-picosecond temporal resolution and from the perspective of well-defined atomic sites [1]. Combining femtosecond time-resolved X-ray photoelectron spectroscopy with constrained density functional theory, we are able to identify the nature of an intermediate electronic state that precedes free charge carrier generation in a film of dye-sensitized ZnO nanocrystals after photoexcitation of the dye with visible light. The findings demonstrate a new capability to monitor charge transfer in complex hybrid materials. This presentation will further include our latest results of electron dynamics at interfaces.

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# **Atomically Precise Nitrogen-doped and Sulfur-doped Graphene Nanoribbons on Au(111)**

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Graphene nanoribbons (GNRs) have a bandgap which can be tuned by controlled doping. Using the on-surface synthesis technique, atomically precise nitrogen-doped and sulfur-doped graphene nanoribbons have been fabricated on Au(111) surfaces. Scanning tunneling microscopy/spectroscopy and density functional theory calculation results indicate that the cyclodehydrogenation of the precursors generates several distinct types of building blocks for GNRs synthesis and these building blocks have different energy gaps. The GNRs constructed by these different building blocks was confirmed to be type-I heterojunctions.

# Experimental results of hydrogen recombination on metal surface

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In this work, we investigated the recombinative desorption of hydrogen from metal (Cu, Ag, or Au) surfaces using a hydrogen permeation technique. We used the principle of detailed balance to extract quantitative information about dissociative adsorption dynamics from the time-of-flight (TOF) distributions of molecules desorbed from the surface. We detected highly translationally excited hydrogen molecules of different internal states. The translational excitation goes down as the vibrational excitation increases. We will investigate the dependence of the reaction probability on rotational, vibrational and translational energy of hydrogen molecules. The angular distributions of products would be another intriguing issue to study. We can also study hydrogen recombination on stepped surfaces. This will be an ideal benchmark data-set for testing modern theories of surface chemistry. Specifically, we wish to know if electronically adiabatic theory can succeed to describe these dynamical measurements. This system was chosen because of recent chemi-current measurements attributed to the recombinative desorption of hydrogen on Au.[1, 2] The investigations will help us to understand to what extent the Born-Oppenheimer approximation can break down in a simple chemical reaction at a metal surface.

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# Theoretical Investigation of Chemical Reaction on Metal/h-BN Monolayer

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The surface chemical reactivity of low-dimensional materials is one key to realize many nanotechnology, such as electronics, sensor, and catalyst in the nanoscale. On the basis of first-principles calculations, we investigate the chemical reactivity on metal/h-BN monolayer. The h-BN monolayer is chemical inert. We will show that when single Au atom is supported by h-BN monolayer, an enhanced CO oxidation can be obtained with new tri-molecular reaction mechanism. Alternatively, Moreover, by depositing h-BN monolayer on metal substrate, the h-BN monolayer has an enhanced chemical reactivity toward O<sub>2</sub> activation. Increasing the number of layers of h-BN sheets will decrease the chemical reactivity of the top h-BN layer. The enhanced chemical activity of h-BN monolayer can be explained by the charge transfer between h-BN monolayer and metal substrate. In addition, metal cluster, instead of metal substrate, has similar effect. This study present a novel design of metal/h-BN hybrid structures with enhanced surface chemical reactivity.

# **Graphene Growth on Metal Surfaces: From Mechanism Understanding to Protocol Design**

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Graphene is an important material with unique properties and many potential applications. A promising way to produce wafer-size graphene is chemical vapor deposition (CVD) on metal surfaces. To improve sample quality, it is important to understand the atomic details during graphene CVD growth. In this talk, we focus on theoretical studies of growth mechanisms. A universal lattice mismatch induced nonlinear growth mechanism is revealed by first principles calculations and kMC simulations. A significant carbon adsorption/diffusion induced surface relaxation is predicted characterized by the formation of bridging-metal (BM) structures. On Cu(111) surface, dimer is found to be the growth supply species, which leads to the experimentally observed diffusion-limited growth behavior. Carbon atom is found to be able to penetrate a graphene overlayer on Cu surface via an exchange mechanism. Using such a process, a protocol to grow high-quality bilayer graphene is proposed.

# How quantum is the hydrogen bond?

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Quantum behaviors of protons in terms of tunneling and zero-point motion have significant effects on hydrogen-bonding interaction even at room and at higher temperature. Despite enormous theoretical efforts on pursuing proper treatment of the nuclear motion at a quantum - mechanical level, accurate and quantitative description of the quantum component of hydrogen bond has proven experimentally challenging for decades. The main difficulty lies in that the quantum states of hydrogen nuclei are extremely sensitive to the coupling with local environments, leading to significant broadening and averaging effects when using conventional spectroscopic or diffraction techniques. Using a low-temperature scanning tunneling microscope (STM), we are able to resolve in real space the internal structure, that is, the O-H directionality, of individual water molecules adsorbed on a solid surface [1,2]. The key steps are decoupling electronically the water from the metal substrate by inserting an insulating NaCl layer and gating the molecular density of states of water around the Fermi level via tip-water coupling. These techniques allow us not only to directly visualize the many-body quantum tunneling of protons within the H-bonded network [3], but also to quantify the impact of quantum fluctuation on the strength of hydrogen bonds by tip-enhanced enhanced inelastic electron tunneling spectroscopy (TE-IETS) [4]. Our work opens up the possibility of exploring the quantum nature of hydrogen bonds at single-bond limit.

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# Controlled metalation of pyrphyrin molecules on Au(111): Preparation of a water reduction catalyst on a solid substrate

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Within the search for new materials and methods for renewable energy resources, photocatalytic water splitting is a very promising field of study. In this framework, a tetradentate, bipyridine-based macrocycle was investigated which was already described in 1984 but only superficially examined [1]. It shares some similarities to porphyrins but with pyridyl subunits instead of pyrrol, hence the given trivial name: pyrphyrin. A high stability of the pyrphyrin and corresponding complexes is indicated due to its conjugation, planarity and cyclic nature. Furthermore, metal complexes based on pyrphyrin show promise as water reduction catalysts [2].

In this study, we examined the preparation of a pyrphyrin metal complex on a single crystalline surface in ultrahigh vacuum. In a first step, pyrphyrin coverages of approximately one monolayer and less, as determined by XPS measurements, were obtained by sublimation of the molecules on a Au(111) surface at room-temperature. By means of Low-Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM), two distinct phases depending on the surface coverage were identified and structurally characterized. In a second step, deposition of Co metal at the level of 5% of a monolayer and subsequent annealing led to the formation of 90% of Co-ligated pyrphyrin molecules.

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# Shell-isolated plasmonic nanoparticle-enhanced Raman spectroscopy

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Surface-enhanced Raman spectroscopy (SERS) is a powerful technique that yields fingerprint vibrational information with ultra-high sensitivity. However, only roughened Ag, Au and Cu surfaces can generate strong SERS effect. The lack of materials and morphology generality has severely limited the breadth of SERS practical applications on surface science, electrochemistry and catalysis.

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS)[1] was therefore invented to break the long-standing limitation of SERS. In SHINERS, Au@SiO<sub>2</sub> core-shell nanoparticles were rationally designed. The gold core acts as plasmonic antenna and encapsulated by an ultra-thin, uniform and pinhole-free silica shell, can provide high electromagnetic field to enhance the Raman signals of probed molecules. The inert silica shell acts as tunneling barrier prevents the core from interacting with the environment.

SHINERS has already been applied to a number of challenging systems,[2] such as hydrogen and CO on Pt(hkl) and Rh(hkl), which can't be realized by traditional SERS. Combining with electrochemical methods, we have in-situ monitored the surface electro-oxidation at Au(hkl) electrodes.[3] These pioneering studies demonstrate convincingly the ability of SHINERS in exploring correlations between structure and reactivity as well as in monitoring intermediates at the interfaces. SHINERS was also explored from semiconductor surface for industry, to living bacteria for life science, and to pesticide residue detection for food safety.[1]

The concept of shell-isolated nanoparticle-enhancement is being applied to other spectroscopies such as infrared absorption, sum frequency generation and fluorescence. [4, 5]

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## **Effect of ions on ice nucleation and its application for anti-icing application**

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Heterogeneous nucleation of ice on ionic surfaces is ubiquitous in a wide range of atmospheric aerosols and biological interfaces. Despite its great importance in cirrus cloud formation and cryopreservation of cells, plenty of open questions remain, in particular the ion-specific effect on ice nucleation. Here we report the heterogeneous nucleation of ice on polyelectrolyte brush (PB) surfaces can be tuned by simply exchanging counterions of PB, and the temperature window can be tuned as large as 10 °C; more importantly, the efficiency of ions in tuning ice nucleation follows the Hofmeister series. Our simulation results show that small amount of counterions at the PB/water interfaces could regulate the structure and dynamics of interfacial water, which is regarded as the key for tuning the ice nucleation. In this talk, application of PBs on anti-icing coatings will also be demonstrated.

# **A theoretical study of photo-induced electron kinetics in composite functional materials**

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In any optoelectronic applications utilizing photo-excitations of functional materials, one has to efficiently harvest photo-excited electronic states in the materials towards high quantum efficiency. Using first-principle based theoretical tools, we have performed theoretical investigations on the photo-induced electron kinetics behavior in composite structures, including: 1) Develop a quantum mechanics/molecular mechanics simulation protocol for nonlinear spectroscopy of interesting composite-structures under the environmental fluctuations; 2) Develop a rate equation model based on density matrix to capture electronic movements and transitions in the photo-excited material and thereby reflect the inter- and intra-system interactions. Theoretical simulations together with experimental non-linear spectroscopy characterizations, reveal information for photon-electron interactions, electron-hole recombination, and charge migrations, most of which are of key importance for the design of composite photocatalytic systems.

# Surface Scattering with Controlled Molecular Beams

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Multi-quantum relaxation of highly vibrationally excited nitric oxide (NO) on noble metals has become one of the best studied examples of the Born-Oppenheimer approximation's failure to describe molecule-surface interactions and is believed to be promoted by an electron transfer from the surface to the molecule. We combine a molecular beam surface scattering apparatus with optical excitation methods and strong electric fields to perform surface scattering experiments with NO molecules of well-defined quantum states. Using spectroscopic methods we analyze energy transfer processes during surface collisions concerning vibration, rotation and orientation on different surfaces. We observe a significant steric influence on the vibrational energy transfer to the surface. In addition, we measure that the vibrational relaxation probability and the average vibrational energy loss are much higher when scattering NO from different metal surfaces. These results show that the electron transfer from the surface to the molecule crucially depends on the molecular orientation and the metal's work function.