Photo-Induced Dynamics and Reactions at Solid Surfaces

Laser Research Center for Molecular Science Division of Ultrahigh Resolution Optical Measurement



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Solid surfaces provide an interesting environment where two completely different electronic systems meet to each other: localized electronic system, *i.e.*, atoms and molecules and delocalized one, *i.e.*, solid bulk surfaces. Charge transfer at surfaces is fundamental to adsorbate-metal interactions and reactions. Moreover, dynamic processes including chemical reactions on surfaces, particularly metal surfaces, are associated with continuous nonadiabatic transitions. This research program aims for understanding electron and nuclear dynamics at surfaces. Photo-induced processes including photochemistry at surfaces are the major focus in this program. Photons are used for not only exciting electronic states of adsorbate and substrate, but also for probing those states with various types of nonlinear optical spectroscopy.

1. Ultrafast Dynamics at Well-Defined Surfaces $^{1-3)}$

To understand the mechanism of surface photochemistry, it is vital to know how photoinduced electronic excitation induces adsorbate nuclear motions that ultimately lead to chemical reactions. We have demonstrated the real-time observations of surface phonons and adsorbate-substrate vibrational modes by fs time-resolved second harmonics generation (TRSHG). If an excitation light pulse has a duration sufficiently shorter than a period of a vibrational mode or a phonon mode, it can excite the mode with a high degree of temporal and spatial coherence. This coherent nuclear motion modulates the second-order susceptibility $\chi^{(2)}$. Thus, by monitoring the intensity modulation of the second harmonics (SH) generation of a probe pulse, we can observe the evolution of the coherent nuclear motion subsequent to the electronic excitation at the surfaces. We have focused on K on Pt(111), and Na and K on Cu(111) adsorption systems.

We have investigated coherently excited surface phonons at K-covered Pt(111) surfaces by using femtosecond timeresolved second harmonic generation spectroscopy. The frequency of the K–Pt stretching phonon mode depends on the superstructure of K: 5.0-5.3 and 4.5-4.8 THz for (2×2) and $(\sqrt{3}\times\sqrt{3})R30^{\circ}$ superstructures, respectively. In addition to the stretching mode, a couple of Pt surface phonon modes are simultaneously observed when the $(\sqrt{3}\times\sqrt{3})R30^{\circ}$ superstructure is formed. The dephasing time of the K–Pt stretching mode becomes shorter and its frequency redshifts as the absorbed fluence of a pump pulse increases. This is in stark contrast to the Pt surface phonon modes whose frequencies are independent of fluence. The fluence dependence of the K–Pt stretching mode is interpreted to be due to anharmonic coupling between the K–Pt stretching and lateral modes.

We have also observed time-resolved second harmonic signals from the Cu(111) surface with a full monolayer of Na in ultra-high vacuum and investigated the excitation-wavelength dependence of the wave packet dynamics of the coherently excited Na-Cu stretching mode. Changing the photon energy of the pump pulse (25 fs) from 2.0 to 2.5 eV, the oscillation amplitude derived from the Na-Cu stretching motion is enhanced. The careful measurements of photonenergy dependence indicates that the excitation efficiency mimics the absorbance of bulk Cu. Holes created in the dbands by the optical transitions could be filled by electrons in the adsorbate-induced occupied state of the metallic quantum well by an Auger-type transition. Hence, holes can be created in the adsorbate-induced occupied state. Moreover, since this Auger decay can occur significantly faster than the oscillation period of the Na-Cu stretching mode, the substrate excitation may be a possible excitation mechanism for the coherent oscillation.

2. Spectroscopy and Chemistry of Metal Nanoclusters on Surfaces⁴⁾

The structure and reactivity of metal nanoclusters are important issues because of their relevance to heterogeneous catalysis. In particular, Au nanoclusters on titanium oxide surfaces has attracted a lot of interest since the discovery of its catalytic activity on CO oxidation. We apply various surface science techniques to clarify correlations between structures and reactivity of metal nanoclusters deposited on surfaces. We use alkanethiolate-coated gold nanoclusters as a primary target in collaboration with Tsukuda (IMS) and Al-Shamery (U. Oldenburg) groups.

Deposition and fabrication of films of Au nanoclusters protected by alkanethiolate ligands are attempted on a TiO₂ (110) surface and the structures of films are observed by a scanning tunneling microscope (STM). Effects of oxygen- and hydrogen-plasma etching in addition to UV irradiation on the structure and chemical composition of the films are also investigated by using STM and X-ray photoelectron spectroscopy. Alkanethiolate Au nanoclusters are produced using a modified Brust synthesis method and their LB films are dipcoated on TiO₂(110). Alkanethiolate Au nanoclusters are weakly bound to the substrate and can be manipulated with an STM tip. Net-like structures of alkanethiolate Au nanoclusters are formed by a strong blast of air. Oxygen plasma etching removes alkanethiolate ligands and simultaneously oxidizes Au clusters. At room temperature, prolonged oxygen plasma etching causes agglomeration of Au nanoclusters. UV irradiation removes ligands partly, which makes Au nanoclusters less mobile. The net-like structure of alkanethiolate Au clusters produced by a blast of air is retained after oxygen- and hydrogen-plasma etching.

3. Observation of Spatial Patterning by a Sum Frequency Generation Microscope

For understanding of heterogeneous reactions on solid surfaces, it is crucial to obtain how reactions evolve in time and spatial domains. For this purpose, a new microscope for observation of spatial patterning of reactants and products at surfaces is needed. It is highly desirable that the microscope is capable to identify chemical species.

Sum frequency generation (SFG) is a nonlinear optical process. In particular, when visible and infrared beams are used, SFG is a powerful means for vibrational spectroscopy.



Figure 1. Setup of the sum frequency generation microscope.

Thus, we are developing a SFG microscope. So far, the first prototype of a microscope (Figure 1) has been built and micropatterns of self-assembled monolayer have been observed. The spatial resolution of the current microscope is about 5 μ m.

4. Chemistry of One-Dimensional Nano-Surface Compounds

The fluctuating configurations of low-dimensional structures can be thermodynamically favorable at finite temperatures, because the energy gain overcomes the energy cost that accompanies local structural fluctuation. In particular, onedimensional (1D) systems have a propensity to be sensitive to these fluctuations as described by one of the maxims of condensed matter physics, *i.e.*, one chain does not make a crystal. Thus, the dynamical formation of active species and sites by these fluctuations is a key factor in establishing a microscopic model for chemical reactions at surfaces and nano-structured compounds. It is well known that the adsorption of O on Ag(110) results in the formation of quasi-1D structures, AgO chains, accompanied by the mass transfer of substrate atoms.

AgO chains arrange periodically to form $(n \times 1)$ $(n = 2 \sim 7)$ depending on the fractional O coverage due to repulsive interchain interactions. On the added-row reconstructed Ag(110) (n×1)-O surfaces, one-dimensional -Ag-O-Ag-O- chains arrange periodically. Scanning tunneling microscopy was used for studying spatiotemporal evolution of the disproportionation reaction of H₂O with O adatoms on oxidized Ag(110) surfaces where quasi-one dimensional AgO chains form ordered structures. Initially the reaction takes place slowly on Ag(110)-(5×1)O at the end of AgO chain, whereas the reaction accelerates explosively upon the appearance of a chemical wave that propagates along the direction perpendicular to the chain. The surface morphology of the region swept over by the chemical wave completely changes from (5×1)-O to that with many rectangular islands, indicating the formation of H₂O (OH)₂. The induction time and explosive acceleration with the propagating chemical wave imply that the reaction is autocatalytic. Water clusters hydrating OH produced likely play a central role in serving as a reservoir of H₂O to feed to the reaction and enhancing the reactivity of H₂O with O adatoms in AgO chains.

References

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