

IX-L Photochemistry on Well-Defined Surfaces

Upon the irradiation of light in the wavelength range from visible to ultraviolet, a number of adsorbed molecules on metal surfaces reveal variety of photochemical processes, including photo-stimulated desorption, rearrangement of adsorbed states, photodissociation, and photo-initiated reactions with coadsorbates. A central and fundamental question in the surface photochemistry is to clarify how adsorbate-substrate systems are excited by photon irradiation. In addition, since photo-initiated reactions can be induced without any thermal activation of reactants, they may provide good opportunities for studying a new class of surface reactions that may not be induced thermally. We have studied photochemistry of various adsorption systems on well-defined metal and semiconductor surfaces mainly by temperature-programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), x-ray photoelectron spectroscopy (XPS), work function measurements, and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation. In this year, the photochemistry of cyclic alkane on Pt(111) and Cu(111) surfaces was studied mainly by TPD, XPS, and IRAS.

IX-L-1 Photochemistry of Cyclohexane on Cu(111)

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The photochemistry of cyclohexane on Cu(111) and its excitation mechanism have been studied by temperature-programmed desorption, ultraviolet and X-ray photoelectron spectroscopy. Cyclohexane weakly adsorbed on Cu(111) has been known to show a broadened and redshifted CH stretching band, *i.e.*, CH vibrational mode softening. Although no dehydrogenation takes place thermally on this surface and by the irradiation

of photons at 5.0 eV, adsorbed cyclohexane is dissociated to cyclohexyl and hydrogen by the irradiation of photons at 6.4 eV. This is a marked contrast to cyclohexane in the gas phase where the onset of absorption is located at 7 eV. When the surface irradiated by 6.4-eV photons is further annealed, cyclohexyl is dehydrogenated to form cyclohexene that desorbs at 230 K. The systematic measurements of photochemical cross sections at 6.4 eV with linearly polarized light as a function of incident angle indicate that the electronic transition from the highest occupied band of cyclohexane to a partially occupied hybridized band near the Fermi level is responsible for the photochemistry. The hybridized band is formed by the interactions between the electronic states of cyclohexane and the metal substrate. The role of the hybridized band in the photochemistry and the CH vibrational mode softening is discussed.

IX-M Ultrafast Dynamics at Well-Defined Surfaces

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 demonstrate 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. This year, in particular, we have demonstrated that coherent phonon modes can be selectively excited by tailored pulse trains.

IX-M-1 Femtosecond Wavepacket Dynamics of Cs Adsorbates on Pt(111): Coverage and Temperature Dependences

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Femtosecond time-resolved second harmonic generation has been used to observe vibrational wavepacket

dynamics at a Cs-covered Pt(111) surface. The creation and dephasing of vibrational coherence are monitored *via* the intensity modulations in the second harmonic of probe pulses as a function of pump-probe delay. The TRSHG trace obtained from the clean surface shows an instantaneous sharp rise right after the excitation. This is followed by a fast decaying component ($t < 1$ ps) and a slowly decaying one persistent to the longest delay ($t = 6$ ps) of the measurements. When the surface is covered with Cs, SH signals are enhanced by about 70 times and strongly modulated waveforms are superimposed on the TRSHG traces. The oscillatory signals are found in

TRSHG signals upon the excitations at 580 and 800 nm, which are the manifestation of nuclear wavepacket dynamics on the surface. The Cs-coverage dependence studied in detail indicates that the wavepacket dynamics of Cs–Pt stretching modes and Pt surface phonon modes are responsible for the TRSHG signals. The cos-like initial phase of the oscillatory signals and the coverage dependence of the initial amplitude suggest that the vibrational coherence is associated with the resonant excitation between Cs-derived states in the quantum well of the Cs overlayer. The rate of Cs–Pt vibrational dephasing increases with the surface temperature. This behavior cannot be accounted for by the increasing contribution from hot bands of low frequency modes. Instead, pure dephasing caused by anharmonic coupling between Cs–Pt stretching and parallel modes in the Cs overlayer is likely the dominant mechanism for the vibrational dephasing.

IX-M-2 Mode Selective Excitation of Coherent Surface Phonons on Alkali-Covered Metal Surfaces

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We demonstrate the mode selective excitation of coherent phonons at Pt(111) surfaces covered with submonolayer cesium atoms. A burst of 150-fs laser

pulses with the repetition rate of 2.0 ~ 2.9 THz was synthesized by using a spatial-light modulator, and used for the coherent surface phonon excitation. The coherent nuclear motion was monitored by time-resolved second harmonic generation. By tuning the repetition rate, we succeeded in controlling the relative amplitude of the vibrational coherence of the Cs–Pt stretching mode (2.3 ~ 2.4 THz) to that of the Pt surface Rayleigh phonon mode (2.6 or 2.9 THz, depending on the Cs coverage).

IX-M-3 Excitation Mechanism of Coherent Surface Phonons on Alkali-Metal Covered Surfaces

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We 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-wave-length 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 when the photon energy is resonant to the transitions from the ground state to image states. Thus, these measurements clearly indicate that the resonant excitation of electronic state of the adsorbate is essential for creation of the coherent surface phonons.

IX-N Multiphoton Photoelectron Spectroscopy of Electronic States of Nano-Structured Materials on Surfaces

Electronic structure and excited state dynamics of nano-structured materials on surfaces are very important for exploring their properties, thermal reactivity and nonthermal processes including photochemistry and photo-induced charge transfer. For this purpose, we performed multiphoton photoelectron spectroscopy with the fs time resolution. In this year we applied this method to thin films of tris-(8-hydroxyquinoline) aluminum (Alq₃).

IX-N-1 The Electronic Structure and Femtosecond Electron Transfer Dynamics at Noble Metal/tris-(8-hydroxyquinoline) Aluminum Interfaces

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The electronic structures of tris-(8-hydroxyquinoline) aluminum (Alq₃) on Cu(111) and Au(111) surfaces are studied by using ultraviolet photoelectron spectroscopy and two-photon photoelectron (2PPE) spectroscopy.

The work function decreases with increase of the coverage due to surface dipole of 5.1 D along the surface normal. The ionization potential from the highest occupied state 6.38 eV does not depend on the metal substrates used in this study. The anion states of Alq₃ adsorbed is created by photoinduced electron transfer from the metal substrates and are located at 2.85 and 3.71 eV above the Fermi level on Cu(111) and Au(111) surfaces, respectively. The full width at half maximum of the anion states is 0.2 eV on both the surfaces. Time-resolved 2PPE measurements show that the anion state created by electron transfer from the metal decays with the lifetime of 31±2 fs on Cu(111) and about three times shorter on Au(111). The angle-resolved 2PPE and the coverage dependence of the lifetime of the anion state

indicate that the electron transferred from the metal surface is localized at a molecule in the first layer. Thus, the ultrafast electron back transfer from the anion state

of Alq_3 in the first layer dominates over the electron hopping to the second layer.

IX-O Chemistry of One-Dimensional Nano-Surface Compounds Studied by Scanning Tunneling Microscopy

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, one-dimensional (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.

IX-O-1 In-Situ Observation of CO Oxidation on $\text{Ag}(110)(2 \times 1)\text{-O}$ by Scanning Tunneling Microscopy: Structural Fluctuation and Catalytic Activity

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It is well known that the adsorption of O on $\text{Ag}(110)$ 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 inter-chain interactions. On the added-row reconstructed $\text{Ag}(110)(n \times 1)\text{-O}$ surfaces where one-dimensional -Ag-O-Ag-O- chains arrange periodically, the clean-off reaction of O adatoms by CO was investigated using variable temperature scanning tunneling microscopy (VT-STM). Based on the in situ STM observations of the surface structure variation in the course of the reaction at various temperatures, we found that the reaction kinetics are significantly affected by the structural transition of AgO chains from a solid straight line configuration to dynamically fluctuating configurations. Below 230 K where the chains are straight, the reaction takes place only at the end of the chains, so that the reaction progresses in the zero-order kinetics with the reaction front propagating along the chain. The temperature dependence of the reaction rates yields the activation barrier of 41 kJ/mol and the pre-exponential factor of $1.7 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$. At room temperature, the reaction rate is drastically accelerated when almost half of the O adatoms are eliminated and the chains start fluctuating. The dynamic formation of active sites equivalent to the end of chains upon the chain fluctuation results in the nonlinear increase of the reaction rate.