IX-N 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, near edge x-ray absorption fine structure (NEXAFS) and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation. In this year, the photochemistry of alkane on Pt(111) and Cu(111) surfaces was studied mainly by TPD, XPS, and IRAS.

IX-O 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.

IX-O-1 Direct Time-Domain Observation of Ultrafast Dephasing in Adsorbate-Substrate Vibration under the Influence of a Hot Electron Bath: Cs Adatoms on Pt(111)

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Femtosecond time-resolved second harmonic generation has been used to observe vibrational wave-packet 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-P 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 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA).

IX-P-1 Ultrafast Excited State Dynamics in 3,4,9,10-Perylene Tetracarboxylic Dianhydride (PTCDA) Thin Films

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Ultrafast decay dynamics of the excited state in the thin films of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) have been directly observed by using fs time-resolved two-photon photoelectron spectroscopy. The lifetimes were measured up to the excess energy of 2 eV above the S_1 state. The highly excited state presumably S_2 decays with $\tau = 70$ fs and S_1 with $\tau = 360 \pm 12$ fs. The lifetime in the S_1 manifold decreases with increase of excess energy, which manifests itself in a time-dependent energy shift of the photoelectron peak originated from the S_1 state.

IX-Q 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-Q-1 Dynamic Formation of Reaction Sites at Nano-Structured One-Dimensional Surface Compounds

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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×1) (n = 2 ~ 7) depending on the fractional O coverage due to repulsive inter-chain interactions. Scanning tunneling microscopy is utilized to investigate the structural changes of AgO chains on clean and carbidic-carbon containing Ag(110) surfaces under UV photoirradiation and CO exposure. Although AgO chains are arranged with the (2×1) structure on both of the surfaces, AgO chains are bundled to make the (2×1) bands on the C-containing surface, whereas they make much larger domains on the entire surface of clean Ag(110). The photo-induced elimination of O in AgO chains occurs only on the C-containing surface. Kinetics of oxygen elimination by CO exposure are very different between the two surfaces. Oxygen coverage decreases steadily on the C-containing surface with CO exposure, whereas the reaction is accelerated in the lower O coverage range where AgO chains with (n×1) ($n \geq 4$) configurations show significant structural fluctuation. Comparison between the two surfaces and simulations based on the Ising model indicate that the acceleration of the reaction originates from the dynamical formation of active O adatoms by fluctuation of AgO chains.

IX-R Adsorbate Structure and Surface Chemistry on Well-Defined Surfaces

Surface reactions have been playing an important role in production of many useful compounds and also fabrication of electronic devices. In particular, investigations on the structures of adsorbates and their reactivity are the first step for understanding more complicated catalytic reactions. We investigate surface reactions and kinetics by means of various techniques including temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), work function measurements, Auger electron spectroscopy (AES), infrared reflection absorption spectroscopy (IRAS) and scanning tunneling microscopy (STM).

IX-R-1 Reactivity of Molecular Oxygen: Conversion of Methanol to Formate at Low Temperatures on Pt(111)

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The oxidation of methanol by molecular oxygen on a Pt(111) surface has been investigated by infrared reflection absorption spectroscopy and X-ray photoelectron spectroscopy. Formate is produced when the surface coadsorbed with molecular oxygen and methanol is annealed to 70 K; the temperature is far much lower than the dissociation temperature of molecular oxygen on a clean Pt(111) surface. The attractive interaction between the coadsorbates is postulated to lower a dissociation barrier of molecular oxygen. When a methanol-precovered Pt(111) surface is exposed to O_2, the sticking probability of O_2 decreases with increase of surface temperature and the major product of methanol oxidation is changed from formate to CO.