

# Photo-Induced Dynamics and Reactions at Solid Surfaces

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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 Coherent Phonon Dynamics at Well-Defined Surfaces<sup>1)</sup>

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 the excitation mechanism of coherent surface phonons at K-covered Cu(111) surfaces in comparison with Na adsorbates.

At the coverages from 0.22 to 0.35 monolayer (ML), TRSHG traces show the oscillatory component with a frequency of  $3.05 \pm 0.05$  THz. The amplitude of this component decreases as coverage increases higher than  $\sim 0.35$  ML, whereas another oscillating component with a frequency of  $1.26 \pm 0.03$  THz grows. Both components are ascribed to K–Cu stretching motion. The spectral changes with coverage suggest that the overlayer structure varies with lateral compression.

The fast transient peak in TRSHG traces at around zero delay changes its sign from negative to positive when coverage exceeds  $\sim 0.22$  ML. Since the quantum-well state (QWS) is partly filled at around this coverage, electrons in the QWS are principally responsible for the transition of the electronic response. Furthermore, the excitation photon energy dependence of TRSHG traces indicates that the excitation of substrate d-band electrons, giving rise to rapid charge fluctuations in the QWS, generates the coherent K–Cu stretching vibration. Consequently, the QWS plays a major role in the electronic and nuclear dynamics induced by pump pulses at  $h\nu = 2.2$  eV.

## 2. Ultrafast Vibrational Energy Transfer in Thin Layers on Pt(111) Surfaces<sup>2)</sup>

Ultrafast dynamics of vibrational energy transfer in overlayers of D<sub>2</sub>O and CO on Pt(111) have been investigated by

femtosecond time-resolved (TR) IR-visible sum-frequency-generation (SFG) spectroscopy under ultrahigh-vacuum conditions. About 10 layers of D<sub>2</sub>O ice were epitaxially grown on c(4×2)-CO/Pt(111). The surface was excited by subpicosecond laser pulses, and subsequent energy transfer through low-frequency modes of adsorbates was monitored in terms of peak shifts and broadenings of C–O and O–D stretching bands in SFG spectra as a function of the pump–probe delay. Because D<sub>2</sub>O ice forms islands, there are two types of CO: one interacting with D<sub>2</sub>O and the other free from D<sub>2</sub>O. Simulations of the TR-SFG spectra by using a phenomenological model for the energy-transfer dynamics indicate that the coupling rate of perturbed CO is larger than that of free CO by a factor of 1.7; this is probably because CO 2π\* states shift toward the Fermi level due to interaction with D<sub>2</sub>O. Two isolated bands at 2668 and 2713 cm<sup>-1</sup> were assignable to the OD stretching bands of D<sub>2</sub>O directly interacting with CO at the D<sub>2</sub>O/CO interface and D<sub>2</sub>O at the vacuum/ice interface, respectively. Analysis of the temporal spectral changes of free D<sub>2</sub>O by using a diffusive thermal transport model indicates that heat transfer through low-frequency phonons of the ice layers occurs within 3 ps; this is substantially faster than the pulsed laser-induced melting of thin ice films reported previously.

### 3. Spectroscopy of Molecules at Interfaces in Organic Field Effect Transistors by a Sum Frequency Generation Microscope

Organic field effect transistors (OFETs) have gained substantial attentions recently. In order to understand the efficiency of the device and the mechanism of charge transport, it is important to know carriers at the interface between a gate

electrode and an organic semiconductor thin film. Since the interface is buried in the device, there are a few methods to investigate what is really happening at the interface. Sum frequency generation (SFG) is one of promising methods to realize it, since this is sensitive to the molecules at interfaces. SFG is a nonlinear optical process and, in particular, when visible and infrared beams are used, SFG is a powerful means for vibrational spectroscopy. We have developed a SFG microscope and applied it to the interface between pentacene and silicon oxide at the gate electrode. SFG signals generated at the interface are spatially resolved by the SFG microscope.

We observed clear SFG microscopic images of source and drain electrodes and the channel regions between them of the OFET devices. Upon application of a gate voltage of –50 V while keeping the voltage between the drain and source electrodes zero, the SFG signal intensity homogeneously increased only in the channel region about ten times and clear peak structures emerged in the SFG spectra. The observed peak structures are attributed to poly vinylphenol (PVP) used as a gate insulating layer of this device; they are enhanced by the local electric field induced by carriers injected into the semiconductor/dielectric interface. Thus, the spatial distributions of carriers in the channel region at the interface were sensitively mapped by use of the vibrational resonance of PVP in the SFG images.

#### Reference

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- 2) M. Nagao, K. Watanabe and Y. Matsumoto, *J. Phys. Chem. C* **113**, 11712–11719 (2009).

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