

## III-G 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 which 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), x-ray photoelectron spectroscopy (XPS), work function measurements, near edge x-ray absorption fine structure (NEXAFS) and angular-resolved time-of-flight (TOF) spectroscopy of photodesorbed species associated with pulsed laser irradiation. We have shown that methane weakly adsorbed on Pt(111) and Pd(111) is dissociated or desorbed by irradiation of 6.4-eV photons, which is far below the excitation energy for the first optically allowed transition of methane in the gas phase. This work has been extended to Cu(111), where photo-induced C-C coupling takes place. In addition, more thorough investigations have been done on the photodesorption of rare gas atoms from clean and modified Si(100) surfaces.

### III-G-1 Photo-stimulated Desorption of Rare Gas Atoms Induced by UV-NIR Photons at a Semiconductor Surface

[*Surf. Sci.* in press]

WATANABE, Kazuya; MATSUMOTO, Yoshiyasu

[*Surf. Sci. Lett.* submitted]

Desorption induced by electronic transitions (DIET) of rare gases provides a good opportunity for understanding fundamental questions in electron- and photon-induced surface processes because no internal nuclear motions are involved compared with other DIET of polyatomic adsorbates. The DIET of rare gas atoms has been observed in the past by using electrons or photons whose energy exceeds 7 eV, since it requires high energy to ionize or excite valence- and core-electrons of rare gas atoms. However, we show that heavy rare gas atoms (Kr and Xe) are desorbed from clean and modified Si(100) surfaces by irradiating photons with energy as low as 1.16 eV.

Rare gas atoms are adsorbed on the surfaces at 50 K. UV and visible photons are irradiated onto the surfaces. Post-irradiation TPD is observed as a function of irradiated photon numbers. The area of TPD peaks decreases with increase of the number of photons, indicating the coverage of Xe is reduced by the photon irradiation. On the clean Si(100) surface, the kinetic energy distributions of the rare gas atoms are well represented by the Maxwell-Boltzmann distribution, but the obtained temperature is quite higher than that expected by surface heating with employed laser fluence. Furthermore, they do not depend on the excitation photon energy from 1.16 eV to 6.43 eV nor on the laser fluence. Thus, these features cannot be explained by conventional laser-induced thermal desorption. The most plausible mechanism for the desorption is that hot surface phonons created by recombination of photo-generated electron-hole pairs at a semiconductor surface directly couple to the desorption channel before they decay into bulk phonons.

### III-G-2 Photochemistry of Methane on Cu(111)

WATANABE, Kazuo; MATSUMOTO, Yoshiyasu

Conversion of methane into useful chemical reagents has been extensively studied for several decades owing to the increasing industrial and environmental importance. However, methane is the most stable hydrocarbon and the previous efforts to break the methane C-H bond *thermally* have not necessary been successful regarding the efficiency and costs even with sophisticated catalysts.

In this work photochemistry of methane physisorbed on Cu(111) at 35 K have been investigated by temperature-programmed desorption (TPD). Methane is photodissociated into hydrogen, methylene, and methyl by 6.4-eV photon irradiation as in the case of Pt(111) and Pd(111). However, there are unique features on Cu(111). Post-irradiation TPD showed new desorption peaks of ethylene at 115 K and 380 K, in addition to the 430 K peak reported before. They are attributed to molecular desorption of ethylene formed by methane photodissociation at 35 K, associative recombination of two methylene groups, and concerted reactions of four methyl groups, respectively. The photoreaction cross section is estimated  $2.0 \times 10^{-20} \text{ cm}^2$ . Thus, photochemical C-C coupling in the photochemistry of methane is observed for the first time.

### III-G-3 Coadsorption Effect of Cs on Photochemistry of Methane on Pt(111)

ANAZAWA, Toshihisa; WATANABE, Kazuo; MATSUMOTO, Yoshiyasu

We have reported that methane on Pt(111) is dissociated by irradiating uv photons.<sup>1)</sup> The excitation is understood as a transition from the ground state localized at methane to the excited state of the methane-substrate atoms complex where the excited Rydberg-like state of methane significantly mixed with the substrate empty states. Another way to understand the excitation mechanism is in the following. When the complete charge transfer to the substrate is assumed in the excited state of methane, the image force stabilizes the excited state by 1.9 eV. The ionization potential of physisorbed methane should then be reduced by 1.9 eV + the work function of the metal. Taking a work

function of 5.6 eV and the gas phase ionization potential of 12.6 eV, the excitation energy for the complete charge transferred state is calculated to be 5.1 eV, which is accessible with a 6.4-eV photon. When Cs is adsorbed, the work function is significantly reduced. By using this feature, we measured how the photochemical cross section is affected by the coadsorption of Cs to examine further the excitation mechanism. The

measurements show that the cross section is significantly reduced by the Cs coadsorption, in agreement with the expectation of the complete charge transfer model.

#### Reference

1) Y. Matsumoto, Y. A. Gruzdkov, K. Watanabe and K. Sawabe, *J. Chem. Phys.* **105**, 4775 (1996).

## III-H Multiphoton Photoelectron Spectroscopy of Electronic States at Metal Surfaces

A central and fundamental question in surface photochemistry is to clarify how adsorbate-substrate systems are excited with photon irradiation. Thus, direct information on the excited states at surfaces is needed. One of the best methods, and most relevant to surface photochemical measurements, is multiphoton photoelectron spectroscopy. We have extended this method by using two-color (visible and VUV) beams for pump-and-probe experiments. In this year, the method is applied to surface states of clean and Xe-covered Pt(111) surfaces.

### III-H-1 Visible and VUV Two-Photon Photoelectron Spectroscopy of the Surface State of a Clean Pt(111) Surface

**KINOSHITA, Ikuo<sup>1</sup>; WATANABE, Kazuya; INO, Daisuke<sup>2</sup>; MATSUMOTO, Yoshiyasu**  
(<sup>1</sup>Yokohama City Univ.; <sup>2</sup>GUAS)

The sp-derived surface state of a clean Pt(111) surface has been experimentally confirmed by visible two-photon photoelectron spectroscopy.<sup>1)</sup> We have extended this measurement by using visible and VUV photons. This method allows us to detect empty states near the Fermi level. The VUV photons are generated by tripling the frequency-doubled Ti:sapphire output in a Xe cell. Photoelectrons are detected and analyzed by a time-of-flight electron energy analyzer. The surface state is located at 0.2 eV below the Fermi level when detected along the surface normal. Since this state has a free-electron like parabolic dispersion curve, the state is expected to be unoccupied at large parallel momenta. In fact, we found that the photoelectron peak originating in the empty surface state appears at large detection angles from the surface normal. This gives a more complete picture of the dispersion curve of the surface state.

#### Reference

1) I. Kinoshita, T. Anazawa and Y. Matsumoto, *Chem. Phys. Lett.* **229**, 445 (1996).