III-J 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, 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), Pd(111) and Cu(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. We have found that rare gas atoms are also photodesorbed from clean and modified Si(100) surfaces. These are all physisorbed systems where electronic states of adsorbate and substrate are well separated in the ground state. In contrast, we have extended the project to photochemistry of strongly chemisorbed, or compound systems on metal surfaces: AgO chains on an Ag(110) surface.

III-J-1 Excitation Mechanisms and Photochemistry of Adsorbates with Spherical Symmetry

WATANABE, Kazuo; MATSUMOTO, Yoshiyasu

[*Faraday Discuss.* **117**, 207 (2000)]

By comparing the photo-stimulated desorption of Xe from an oxidized Si(100) surface with the photochemistry of methane on metal surfaces, we try to deduce a common concept in the excited state and the excitation mechanism responsible for the photo-induced processes. Xe atoms are desorbed from the oxidized Si(100) surface by the irradiation of photons in the range of 1.16–6.43 eV. The two velocity components with average kinetic energy of 0.85 eV and 0.25 eV are observed in the time-of-fight distributions. The fast component appears only if the photon energy exceeds ~3 eV, but the slow component does in the entire photon energy range. By analogy with the photochemistry of methane on the metal surfaces, the excitation mechanism responsible for the fast component is postulated to be a transition from the 5p state of Xe to the excited state originating in strong hybridization between the 6s-state of Xe and the dangling bond at a surface silicon atom bonded with oxygen inserted in the dimer bond. In this scheme an excited electron is transferred from the adsorbate to the substrate, which is the reverse direction compared with the substrate-mediated excitation frequently assumed in surface photochemistry.

III-J-2 Photo-induced Oxygen Elimination Reaction at an Ag(110)-p(2×1)-O Surface

OTA, Michiharu[1]; WATANABE, Kazuya; MATSUMOTO, Yoshiyasu
([1]*GUAS)*

When an Ag(110) surface is extensively exposed to oxygen gas, well-ordered AgO chains are formed on the surface. It has been reported that oxygen atoms in the chains are eliminated by UV photon irradiation. However, the excitation mechanism for the photoreaction is completely unknown. Furthermore, there is no information on how oxygen is eliminated and where it goes. We try to uncover these questions by using LEED, XPS, TOF and TPD measurements. After confirming a characteristic LEED pattern of the Ag(110)- p(2×1)-O surface, the surface is irradiated by UV light. The depletion of the oxygen coverage is measured by post-irradiation XPS as a function of the irradiated photon numbers. The most important finding in the photoreaction is that the cross-sections for the photochemical oxygen elimination reaction strongly depend on the coverage of carbon atoms remained at the surface; the cross-section increases with the coverage of carbon atoms. Interestingly, carefully designed experiments show that carbon atoms believed to be at subsurface are more effective than carbon adatoms on the surface. Photodesorbed species are detected by a quadruple mass spectrometer. No oxygen atoms/molecules are detected, but only CO_2 molecules are detected. Therefore, subsurface carbon plays an important role in the reaction. We tentatively assign the subsurface carbon is carbidic and the carbon adatoms is graphitic. Further characterization of the carbon atoms are underway.

Reference

1) Y. Matsumoto, Y. Okawa, K. Suzuki, K. Mukai and K. Tanaka, *J. Am. Chem. Soc.* **118**, 9676 (1996).