VI-M Dynamics and Relaxation of Atoms and Molecules Following Core-Level Excitation

Monochromatized X-ray from synchrotron radiation excites a core electron of an atom or molecule, and the core hole thereby created is usually filled by an outer-orbital electron through an Auger process. In molecules, the core electrons are localized near the atom of origin, in contrast to valence electrons, which are often delocalized over the entire molecule. Although core electrons do not participate in chemical bonding, the energy of an atomic core-level in the molecule depends on the chemical environment of the atom. Site-specific excitation and fragmentation are thus of considerable interest. To elucidate the dynamics and relaxation of atoms and molecules following core-level excitation, we have used photoelectron spectroscopy and the energy-selected-photoemission photoion coincidence method.

VI-M-1 Site-Specific Phenomena in Si:2p Core-Level Photoionization of X3Si(CH2)nSi(CH3)3 (X = F or Cl, n = 0–2) Condensed on a Si(111) Surface

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We used photoelectron spectroscopy and the energy-selected-photoelectron photoion coincidence (ESPEPICO) method to study site-specific phenomena in the Si:2p photoionization of X3Si(CH2)nSi(CH3)3 (X = F or Cl, n = 0–2) condensed on a Si(111) surface. The site-specific excitation and the occurrence of different chemical shifts at two Si sites were revealed in the total site-specific excitation and the occurrence of different chemical shifts at two Si sites were evident in the total electron-yield spectrum and the photoelectron spectrum, and site-specific fragmentation was evident in the ESPEPICO spectrum. The fragmentation processes inferred from the ESPEPICO and AEPICO results were very different from those occurring in the vapor phase. We also studied the effect of the surface on the site-specific phenomena observed in a 2,2,2-trifluoroethanol (TFEtOH) monolayer chemisorbed on a Si(100) surface (CF2CH2OSi(substrate)). The molecular structure of TFEtOH is the same as that of TFEt except that it has a hydroxyl group substituted for one of the hydrogen atoms. Although site-specific phenomena were also observed in TFEtOH, the fragmentation process was very different from that of TFEt because of the chemisorption structure of TFEtOH on Si(100).

VI-M-3 Ion Desorption Induced by Core-Electron Transitions Studied with Electron–Ion Coincidence Spectroscopy

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The recent investigations of ion desorption induced by core-electron transitions using electron–ion coincidence (EICO) spectroscopy are described. In a study of CF3(CH(OH)CH3) chemisorbed on a Si(100) surface using photoelectron photoion coincidence (PEPICO) spectroscopy, site-specific ion desorption is directly verified, that is, F+ desorption is predominant for C 1s photoionization at the –CF3 site, while H+ desorption is predominantly induced by C 1s photoionization at the –CH3 site. A study of condensed H2O using Auger electron photoion coincidence (AEPICO) spectroscopy showed that H+ desorption is stimulated by O KVV Auger processes leaving two-hole states. The H+ desorption probability is found to depend on the bonding character of the orbitals where holes are created and on the effective hole–hole Coulomb repulsion. AEPICO investigations of H+ desorption induced by resonant core-electron excitations of condensed H2O clearly showed that one-electron–one-core hole or one-electron–two-valence hole states are responsible for the H+ desorption mechanism. These
investigations demonstrate that EICO spectroscopy combined with synchrotron radiation is a novel and powerful tool for the study of ion desorption induced by core-electron excitations. Furthermore, a comparison of PEPCO and photoelectron spectra showed that the surface core-level shift of condensed H2O is 0.7 eV. This study shows that PEPCO spectroscopy is also promising as a method to investigate the electronic structure of the specific sites responsible for ion desorption.

VI-M-4 Electron–Ion Coincidence Study for the TiO2(110) Surface

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Photo-stimulated desorption from the TiO2(110) surface was investigated by using electron–ion coincidence spectroscopy and synchrotron radiation. The desorption of O+ ions was observed to be coincident with the emission of photoelectrons from the O1s, Ti2s, Ti2p, Ti3s and Ti3p levels, and their satellite peaks due to the shake-up excitation. However, no ion desorption was observed in coincidence with the O2s or valence photoelectrons. The O+ peak intensities in the coincidence spectra are analyzed, and the result is unexpected from a simple expansion of the Knotek-Feibelman model. The shake-up excitation of O1s levels yields O+ desorption more efficiently than does the O1s single-electron excitation.

VI-M-5 Development of Electron-Ion Coincidence Spectroscopy for Study of Vapor-Phase Dynamics

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An electron-ion coincidence spectrometer for vapor-phase dynamics study is being built now. The equipment consists of an electron gun, a cylindrical-mirror electron-energy analyzer (CMA) and a reflectron-type time-of-flight mass analyzer. Sample gas is excited with the electron beam and the CMA analyzes energy of emitted or scattered electrons. Mass spectra of produced ions are measured with a multichannel scalar taking the energy-analyzed electron signal as the starting trigger.

VI-M-6 High-Resolution Angle-Resolved Ion-Yield Measurements of H2O and D2O in the Region of O 1s to Rydberg Transitions

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Angle-resolved energetic-ion yield spectra have been observed in the O 1s excitation region of H2O and D2O with the incident photon-energy resolution better than 14000. Vibrational structures appear in most of the Rydberg members and are ascribed to the bending vibrations. The assignments of the electronic states are established on the basis of the angular distribution data for the energetic ions.

VI-M-7 Molecular Deformation in the O 1s→2πu Excited States of CO2 Probed by the Triple-Differential Measurement of Fragment Ions

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Measurement of mass-, energy-, and angle-resolved fragment ions revealed that the β value for C+ with kinetic energy ≥ 3 eV is ~ 0.9 in the region of the O 1s → 2πu excitation and that β value for O+ with kinetic energy ≥ 4 eV varies from ~0.23 to ~0.57 across the O 1s → 2πu resonance. These findings postulate that the CO2 molecule excited to the lower branch of the vibronically split O 1s→2πu excited states deforms into a bent geometry while the molecule excited to the higher branch remains in a linear geometry.

VI-M-8 Resonant Auger Spectrum Following Kr:2p → 5s Photoexcitation

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Resonant Auger electron spectra following Kr:2p → 5s photoexcitation have been measured for the first time using monochromatized undulator radiation and a cylindrical-mirror electron-energy analyzer. It is found that the kinetic energy of the resonant Auger electron is higher than that of the corresponding normal Auger electron. The angular distribution of the resonant Auger
electrons is nearly isotropic relative to the polarization direction of the incident light.

**VI-M-9 Angle-Resolved Electron and Ion Spectroscopy Apparatus on the Soft X-Ray Photochemistry Beamline BL27SU at SPring-8**

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We have designed and constructed the apparatus for the angular distribution measurements of photoejected electrons and ions from free molecules, as a part of the endstation of a c-branch of the beamline 27SU, a soft X-ray photochemistry beamline at SPring-8. The experimental procedures are described in combination with the use of a capability to switch the horizontal and vertical directions of the linear polarization of the light produced by the figure-8 undulator. As typical examples of the experimental results, we present angle-resolved energetic ion yield spectra of the O 1s excitation region of CO2 and the angle-resolved resonant Auger emission of Ne following the 1s → 3p excitation.

**VI-M-10 Monochromator for a Soft X-Ray Photochemistry Beamline BL27SU of SPring-8**

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A high-resolution monochromator using varied line space plane gratings (VLSG) and spherical focusing mirrors was installed in one of three branches of BL27SU. The performance of the monochromator was evaluated from the photoabsorption spectrum of nitrogen molecule. The resolving power over 10^4 was confirmed.