

VI-Q 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-Q-1 Site-Specific Fragmentation Following C:1s Core-Level Photoionization of 1,1,1-Trifluoroethane Condensed on a Au Surface and of a 2,2,2-Trifluoroethanol Monolayer Chemisorbed on a Si(100) Surface

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We used photoelectron spectroscopy, the energy-selected-photoelectron photoion coincidence (ESPEPICO) method, the Auger-electron photoion coincidence (AEPICO) method and the ab initio method to study site-specific phenomena in the C:1s photoionization of 1,1,1-trifluoroethane (CF₃CH₃, TFEt) condensed on a Au surface. Site-specific excitation and occurrence of different chemical shifts at two carbon 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 (CF₃CH₂OSi{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-Q-2 Si:2p Site-Specific Excitation and Fragmentation of Bridged Trihalosilyltrimethylsilyl Molecules: Role of the Bridge and Final-State Effect

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To elucidate site-specific phenomena, we

experimentally and computationally studied the spectroscopy and dynamics caused by Si:2p core-level photoexcitation of bridged trihalosilyl-trimethylsilyl molecules. We used the photoionization efficiency curve and the photoelectron photoion coincidence method to study the site-specific phenomena in the Si:2p photoexcitation of F₃SiCH₂CH₂CH₂Si(CH₃)₃, F₃SiCH=CHSi(CH₃)₃ and Cl₃SiC≡CSi(CH₃)₃ in the vapor phase. The site-specific excitation was revealed in the photoionization efficiency curves of all the molecules. The site-specific fragmentation is likely to be more evident when the distance between the two Si sites is large. For the site-specific fragmentation to occur, there should not be a triple bond between the atomic site of interest and any other near atomic-site around which bond dissociation is undesirable. Not only initial-state effect but also final-state effect is likely to contribute to the occurrence of the different chemical shifts between the two Si sites of the bridged trihalosilyl-trimethylsilyl molecules.

VI-Q-3 Site-Specific Fragmentation Caused by Core-Level Photoionization: Effect of Chemisorption

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We used the energy-selected-photoelectron photoion coincidence (ESPEPICO) method to clarify site-specific fragmentation caused by C:1s photoionization of 1,1,1-trifluoro-2-propanol-*d*₁ (CF₃CD(OH)CH₃, TFIP-*d*₁) on a Si(100) surface. The formation of the monolayer was verified by the layer-resolved shifts in the photoelectron and Auger spectra. By using high-resolution electron energy loss spectroscopy, it was shown that TFIP-*d*₁ is dissociatively chemisorbed like (CF₃)(CH₃)CDO-Si(100). Occurrence of different chemical shifts at the three carbon sites was observed by photoelectron spectroscopy. Site-specific fragmentation was clearly revealed in the ESPEPICO spectra of the monolayer at room temperature. From the results of the site-specific fragmentation, it is considered that TFIP-*d*₁ in the monolayer at room temperature has an O-Si bond oriented in the trans position with respect to the C-CF₃ bond. The fragmentation processes were discussed on the basis of the results of the ESPEPICO method and

the Auger-electron photoion coincidence method.

VI-Q-4 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 has been built. The equipment consists of an electron gun, a cylindrical mirror analyzer (CMA) and a reflectron-type time-of-flight ion 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-Q-5 Electron-Ion Coincidence Spectroscopy as a New Tool for Surface Analysis—an Application to the Ice Surface

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Electron-ion coincidence (EICO) spectroscopy [K. Mase, M. Nagasono, S. Tanaka, M. Kamada, T. Urisu and Y. Murata, *Rev. Sci. Instrum.* **68**, 1703 (1997)] has recently been developed to investigate the process of ion desorption induced by the core level excitation. In the present study, we apply EICO spectroscopy to determine the O1s level of condensed H₂O (ice) at 100 K. The kinetic energy of O1s photoelectrons which gives the highest coincidence yield of H⁺ desorption is shifted by about -0.7 eV compared to the O1s peak observed in the conventional core-level photoelectron spectroscopy. It is ascribed to a core-level shift in the O1s level from which hydrogen ions desorb. The results indicate the advantages and the possibilities of the EICO spectroscopy for surface analysis.

VI-Q-6 Photo-Stimulated Ion Desorption from TiO₂(110) Surface

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Photo-stimulated desorption of O⁺ from TiO₂(110) surface is investigated by using the electron-photoion coincidence spectroscopy. It is found that O⁺ desorbs as a result of the multi-electron excitation/decay of the O1s electron, which can be explained within the expansion of the well-known Knotek-Feibelman mechanism. On the other hand, the Knotek-Feibelman mechanism does not seem to work for the O⁺ desorption following the Ti-core excitation. We propose a new model in which the O⁺ desorption is induced by the excitation of a Ti-

core level; the charge transfer from O2p to Ti3d induced by the Ti3p-core hole potential is responsible for the creation of O⁺ ions and its desorption. A discussion on the new model is made for ion desorption from other materials.

VI-Q-7 Ion Desorption Induced by Core-Level Excitation on H₂O/Si(100) Surface

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Ion desorption from H₂O/Si(100) induced by the O1s-excitation is investigated by the use of the photoelectron, the photon-stimulated desorption and the electron-ion coincidence spectroscopy. It is shown that ion desorption induced by the soft-X-ray is mainly caused by shake-up/off excitation accompanied with the core-excitation and with the Auger decay that results in the multi-holes final state. The core-excitation to the anti-bonding orbital or normal Auger decay that creates the two-holes final state is less important.

VI-Q-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-Q-9 Molecular Deformation in the O 1s⁻¹2π_u 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 $O\ 1s \rightarrow 2\pi_u$ excitation and that β value for O^+ with kinetic energy ≥ 4 eV varies from -0.23 to -0.57 across the $O\ 1s \rightarrow 2\pi_u$ resonance. These findings postulate that the CO_2 molecule excited to the lower branch of the vibronically split $O\ 1s^{-1}2\pi_u$ excited states deforms into a bent geometry while the molecule excited to the higher branch remains in a linear geometry.

VI-Q-10 Monochromator for a Soft X-ray Photochemistry Beamline BL27SU of SPring-8

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A high-resolution monochromator with varied line space plane gratings (VLSPG) and spherical focusing mirrors was installed in one of three branches of BL27SU in SPring-8. The performance of the monochromator was roughly evaluated from the photo ion yield of nitrogen molecule. Furthermore, the kinetic energy of the photoelectron from Xe $5p_{3/2}$ orbital was also measured at the same photon energy with the N_2 to avoid the influence of natural width. The resolving power over 10^4 has been confirmed at the N K-edge.

VI-Q-11 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 BL27SU, 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 a typical example of the experimental results, we present angle-resolved energetic ion yield spectra in the $O\ 1s$ excitation region of CO_2 .

VI-Q-12 Resonant Auger Spectra of Kr Near the L_3 Threshold

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Auger electron spectra were studied by scanning the photon energy near the L_3 threshold of krypton. Two resonant transitions were observed in the photon energy region 1673–1678 eV for the first time. They were identified to be the resonant $3d^{-2}5s$ and $3d^{-2}4d$ states originating from the $2p_{3/2}^{-1}5s$ and $2p_{3/2}^{-1}4d$ excitations, respectively.

VI-Q-13 Auger Electron Spectra of Kr2p Holes Using Monochromatic Soft X-Rays

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Normal Auger electron spectra from Kr2p hole states, $L_{23}M_{45}M_{45}$ and $L_{23}M_{23}M_{45}$, have been measured using monochromatized synchrotron radiation and a high resolution electron spectrometer. Measured spectra were reproduced with a fitting calculation, where Voigt functions including an instrumental resolution and natural lifetime widths of related core hole states were used. At most final states estimated energies for spectral peaks agree with those by electron and ion beam techniques. Relative intensities for some peaks are appreciably different from the previous results.