

## 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 $X_3Si(CH_2)_nSi(CH_3)_3$ ( $X = F$ or $Cl$ , $n = 0-2$ ) Condensed on a Si(111) Surface

NAGAOKA, Shin-ichi; MASE, Kazuhiko<sup>1</sup>; NAGASONO, Mitsuru<sup>2</sup>; TANAKA, Shin-ichiro<sup>3</sup>; URISU, Tsuneo; OHSHTA, Joji<sup>4</sup>; NAGASHIMA, Umpei<sup>5</sup>

(<sup>1</sup>KEK-PF; <sup>2</sup>MAX-lab; <sup>3</sup>Nagoya Univ.; <sup>4</sup>Hiroshima Univ.; <sup>5</sup>Natl. Inst. Adv. Interdisciplinary)

[*Chem. Phys.* **249**, 15 (1999)]

We used photoelectron spectroscopy and the energy-selected-photoelectron photoion coincidence (ESPEPICO) method to study site-specific phenomena in the Si:2p photoionization of  $X_3Si(CH_2)_nSi(CH_3)_3$  ( $X = F$  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 electron-yield spectra and the photoelectron spectra of  $F_3Si(CH_2)_nSi(CH_3)_3$  ( $n = 1, 2$ ), although they were not clearly revealed in those of  $Cl_3SiSi(CH_3)_3$ . We conclude that these site-specific phenomena are easily observed in molecules in which the two Si sites are located far apart and in which electron migration between the two Si-containing groups does not occur. This was supported by our ab initio calculation. Site-specific fragmentation was revealed in the ESPEPICO spectrum of  $F_3SiCH_2CH_2Si(CH_3)_3$ , although it was negligible for  $Cl_3SiSi(CH_3)_3$  and was less remarkable in  $F_3SiCH_2Si(CH_3)_3$  than in  $F_3SiCH_2CH_2Si(CH_3)_3$ . Site-specific fragmentation also occurred when the two Si sites were located far apart.

### VI-M-2 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

NAGAOKA, Shin-ichi; TANAKA, Shin-ichiro<sup>1</sup>; MASE, Kazuhiko<sup>2</sup>

(<sup>1</sup>Nagoya Univ.; <sup>2</sup>KEK-PF)

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 ( $CF_3CH_3$ , 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 ( $CF_3CH_2OSi\{substrate\}$ ). 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

MASE, Kazuhiko<sup>1</sup>; TANAKA, Shin-ichiro<sup>2</sup>; NAGAOKA, Shin-ichi; URISU, Tsuneo

(<sup>1</sup>KEK-PF; <sup>2</sup>Nagoya Univ.)

[*Surf. Sci.* **451**, 143 (2000)]

The recent investigations of ion desorption induced by core-electron transitions using electron-ion coincidence (EICO) spectroscopy are described. In a study of  $CF_3CH(OH)CH_3$  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  $-CF_3$  site, while  $H^+$  desorption is predominantly induced by C 1s photoionization at the  $-CH_3$  site. A study of condensed  $H_2O$  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  $H_2O$  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 PEPICO and photoelectron spectra showed that the surface core-level shift of condensed H<sub>2</sub>O is 0.7 eV. This study shows that PEPICO 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 TiO<sub>2</sub>(110) Surface

**TANAKA, Shin-ichiro<sup>1</sup>; MASE, Kazuhiko<sup>2</sup>; NAGASONO, Mitsuru<sup>3</sup>; NAGAOKA, Shin-ichi; KAMADA, Masao**  
(<sup>1</sup>Nagoya Univ.; <sup>2</sup>KEK-PF; <sup>3</sup>MAX-lab)

[*Surf. Sci.* **451**, 182 (2000)]

Photo-stimulated desorption from the TiO<sub>2</sub>(110) surface was investigated by using electron-ion coincidence spectroscopy and synchrotron radiation. The desorption of O<sup>+</sup> 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<sup>+</sup> 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<sup>+</sup> 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

**MASE, Kazuhiko<sup>1</sup>; NAGAOKA, Shin-ichi**  
(<sup>1</sup>KEK-PF)

An electron-ion coincidence spectrometer for vapor-phase dynamics study is being built now. 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-M-6 High-Resolution Angle-Resolved Ion-Yield Measurements of H<sub>2</sub>O and D<sub>2</sub>O in the Region of O 1s to Rydberg Transitions

**OKADA, Kazumasa<sup>1</sup>; UEDA, Kiyoshi<sup>2</sup>; TOKUSHIMA, Takashi<sup>1</sup>; SENBA, Yasunori<sup>1</sup>; YOSHIDA, Hiroaki<sup>1</sup>; SHIMIZU, Yuuichiro<sup>2</sup>; SIMON, Mare<sup>3</sup>; CHIBA, Hisashi<sup>2</sup>; OKUMURA, Hiroki<sup>4</sup>; TAMENORI, Yuusuke<sup>5</sup>; OHASHI, Haruhiko<sup>5</sup>; SAITO, Norio<sup>6</sup>; NAGAOKA, Shin-ichi; SUZUKI, Isao H.<sup>6</sup>; ISHIGURO, Eiji<sup>7</sup>; KOYANO,**

**Inosuke<sup>4</sup>; IBUKI, Toshio<sup>8</sup>; HIRAYA, Atsunari<sup>1</sup>**  
(<sup>1</sup>Hiroshima Univ.; <sup>2</sup>Tohoku Univ.; <sup>3</sup>LURE; <sup>4</sup>Himeji Inst. Tech.; <sup>5</sup>JASRI; <sup>6</sup>Electrotech. Lab.; <sup>7</sup>Univ. Ryukyus; <sup>8</sup>Kyoto Univ. Edu.)

[*Chem. Phys. Lett.* **326**, 314 (2000)]

Angle-resolved energetic-ion yield spectra have been observed in the O 1s excitation region of H<sub>2</sub>O and D<sub>2</sub>O 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<sup>-1</sup>2π<sub>u</sub> Excited States of CO<sub>2</sub> Probed by the Triple-Differential Measurement of Fragment Ions

**SAITO, Norio<sup>1</sup>; UEDA, Kiyoshi<sup>2</sup>; SIMON, Mare<sup>3</sup>; OKADA, Kazumasa<sup>4</sup>; SHIMIZU, Yuuichiro<sup>2</sup>; CHIBA, Hisashi<sup>2</sup>; SENBA, Yasunori<sup>4</sup>; OKUMURA, Hiroki<sup>5</sup>; OHASHI, Haruhiko<sup>6</sup>; TAMENORI, Yuusuke<sup>6</sup>; NAGAOKA, Shin-ichi; HIRAYA, Atsunari<sup>4</sup>; YOSHIDA, Hiroaki<sup>4</sup>; ISHIGURO, Eiji<sup>7</sup>; IBUKI, Toshio<sup>8</sup>; SUZUKI, Isao H.<sup>1</sup>; KOYANO, Inosuke<sup>5</sup>**  
(<sup>1</sup>Electrotech. Lab.; <sup>2</sup>Tohoku Univ.; <sup>3</sup>LURE; <sup>4</sup>Hiroshima Univ.; <sup>5</sup>Himeji Inst. Tech.; <sup>6</sup>JASRI; <sup>7</sup>Univ. Ryukyus; <sup>8</sup>Kyoto Univ. Edu.)

[*Phys. Rev. A* in press]

Measurement of mass-, energy-, and angle-resolved fragment ions revealed that the β value for C<sup>+</sup> with kinetic energy ≥ 3 eV is ~ 0.9 in the region of the O 1s → 2π<sub>u</sub> excitation and that β value for O<sup>+</sup> with kinetic energy ≥ 4 eV varies from -0.23 to -0.57 across the O 1s → 2π<sub>u</sub> resonance. These findings postulate that the CO<sub>2</sub> molecule excited to the lower branch of the vibronically split O 1s<sup>-1</sup>2π<sub>u</sub> 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

**NAGAOKA, Shin-ichi; IBUKI, Toshio<sup>1</sup>; SAITO, Norio<sup>2</sup>; SHIMIZU, Yuuichiro<sup>3</sup>; SENBA, Yasunori<sup>4</sup>; KAMIMORI, Katsuya<sup>4</sup>; TAMENORI, Yuusuke<sup>3</sup>; OHASHI, Haruhiko<sup>3</sup>; SUZUKI, Isao H.<sup>2</sup>**  
(<sup>1</sup>Kyoto Univ. Edu.; <sup>2</sup>Electrotech. Lab.; <sup>3</sup>JASRI; <sup>4</sup>Hiroshima Univ.)

[*J. Phys. B* in press]

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**

UEDA, Kiyoshi; YOSHIDA, Hiroaki<sup>2</sup>; SENBA, Yasunori<sup>2</sup>; OKADA, Kazumasa<sup>2</sup>; SHIMIZU, Yuuichiro<sup>3</sup>; CHIBA, Hisashi<sup>1</sup>; OHASHI, Haruhiko<sup>3</sup>; TAMENORI, Yuusuke<sup>3</sup>; OKUMURA, Hiroki<sup>4</sup>; SAITO, Norio<sup>5</sup>; NAGAOKA, Shin-ichi; HIRAYA, Atsunari<sup>2</sup>; ISHIGURO, Eiji<sup>6</sup>; IBUKI, Toshio<sup>7</sup>; SUZUKI, Isao H.<sup>5</sup>; KOYANO, Inosuke<sup>4</sup>

(<sup>1</sup>Tohoku Univ.; <sup>2</sup>Hiroshima Univ.; <sup>3</sup>JASRI; <sup>4</sup>Himeji Inst. Tech.; <sup>5</sup>Electrotech. Lab.; <sup>6</sup>Univ. Ryukyus; <sup>7</sup>Kyoto Univ. Edu.)

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 CO<sub>2</sub> 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**

OHASHI, Haruhiko<sup>1</sup>; ISHIGURO, Eiji<sup>2</sup>; TAMENORI, Yuusuke<sup>1</sup>; OKUMURA, Hiroki<sup>3</sup>; HIRAYA, Atsunari<sup>4</sup>; YOSHIDA, Hiroaki<sup>4</sup>; SENBA, Yasunori<sup>4</sup>; OKADA, Kazumasa<sup>4</sup>; SAITO, Norio<sup>5</sup>; SUZUKI, Isao H.<sup>5</sup>; UEDA, Kiyoshi<sup>6</sup>; IBUKI, Toshio<sup>7</sup>; NAGAOKA, Shin-ichi; KOYANO, Inosuke<sup>3</sup>

(<sup>1</sup>JASRI; <sup>2</sup>Univ. Ryukyus; <sup>3</sup>Himeji Inst. Tech.; <sup>4</sup>Hiroshima Univ.; <sup>5</sup>Electrotech. Lab.; <sup>6</sup>Tohoku Univ.; <sup>7</sup>Kyoto Univ. Edu.)

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<sup>4</sup> was confirmed.