VI-V Site-Specific Fragmentation Following Core-Level Photoexcitation

Monochromatized synchrotron radiation can excite core electrons of an atom in a specific chemical environment selectively, discriminating the core electrons from those of like atoms having different chemical environments. This site-specific excitation often results in site-specific fragmentation, which is of importance in understanding localization phenomena in chemical reactions and which is potentially useful for synthesizing materials through selective bond breaking. Synchrotron radiation can indeed play the part of an optical knife for molecules. When bond dissociation around an atomic site is required in the synthesis, one can use the optical knife that has the photon energy corresponding to the specific excitation of that site. To elucidate the site-specific fragmentation, we have used photoemission spectroscopy and the energy-selected-photoemission photoion coincidence method to study site-specific phenomena in the C:1s and Si:2p photoexcitation of organic and organosilicon molecules condensed on a Si surface and in the vapor phase.

VI-V-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[1]; NAGASONO, Mitsuru[2]; TANAKA, Shin-ichiro[3]; URISU, Tsuneo; OHSHITA, Joji[4]; NAGASHIMA, Umpei[5]
([1]KEK-PF; [2]MAX-lab; [3]Nagoya Univ.; [4]Hiroshima Univ.; [5]Natl. Inst. Adv. Interdisciplinary)

[*Chem. Phys.* in press]

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-V-2 Ion Desortpion Induced by Core-Electron Transitions Studied with Electron-Ion Coincidence Spectroscopy

MASE, Kazuhiko[1]; TANAKA, Shin-ichiro[2]; NAGAOKA, Shin-ichi; URISU, Tsuneo
([1]KEK-PF; [2]Nagoya Univ.)

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. This study demonstrates that PEPICO spectroscopy combined with synchrotron radiation is a novel and powerful tool for the study of ion desorption induced by core-electron excitations and that it is also a prospective method to investigate the electronic structure of the specific sites responsible for ion desorption.

VI-V-3 Development of Electron-Ion Coincidence Spectroscopy for Study of Surface and Vapor-Phase Dynamics

MASE, Kazuhiko[1]; NAGAOKA, Shin-ichi
([1]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 time-of-flight ion mass analyzer (TOF-MS). Sample gas is excited with the electron beam and the CMA analyzes energy of emitted or scattered electrons. TOF spectra of desorbed ions are measured with a multichannel scalar taking the energy-analyzed electron signal as the starting trigger.