

A Molecular Knife - Control of Chemical Reactions using Core Ionization -

When we cut a corner from a sheet of paper, we usually use a pair of scissors (Fig. 1). When the piece of paper is small, a knife is necessary. However, when the target becomes smaller and smaller towards the size of a molecule, a molecular assembly, or a nanoscale device, we have not yet found an appropriate cutting tool. As a candidate for such a molecular knife, we may consider localized photoexcitation. In contrast to valence electrons delocalized over the entire molecule, core electrons can be localized near the nucleus of one particular atom. Accordingly, controlled bond breaking following photoexcitation or photoemission of localized core electrons can be considered a molecular knife.

To select an atom not only of one specific element, e.g., carbon but also in a specific chemical environment inside the molecule, the corresponding core-electron binding energy differences, that is, chemical shifts in ESCA, can be used. This quantity has been used to study site-specific fragmentation [1], where bonds around the site of core-ionized atoms are dissociated selectively.

In this work, we employed an energy-selected-photoelectron photoion/photoion-photoion coincidence (PEPICO/PEPIPICO) method [2] to study site-specific fragmentation caused by Si:2*p* core-level photoionization of F₃SiCH₂CH₂Si(CH₃)₃ (FSMSE) in the vapor phase. The coincidence apparatus was installed at the c branch of **BL7SU** [3]. FSMSE was chosen for this study because the chemical environment of a Si atom bonded to three F atoms (as denoted here Si[F]) is very different from that of Si bonded to three methyl groups (Si[Me]). Therefore, the two peaks in the photoelectron spectrum (PES) of FSMSE vapor assigned to Si[Me]:2*p* and Si[F]:2*p* photoelectron emission [4] are clearly separated in Fig. 2(a). The PEPICO spectra measured in coincidence with the Si[Me]:2*p* and Si[F]:2*p* photoelectrons are shown in Figs. 2(b) and 2(c), where site-specific fragmentation is clearly evident. For example, the site selectivity for the production of F₃SiCH₂CH₂⁺ and F⁺ is almost 100%. The bond dissociations mostly occur at the Si site where the photoionization has taken place. Site-specific

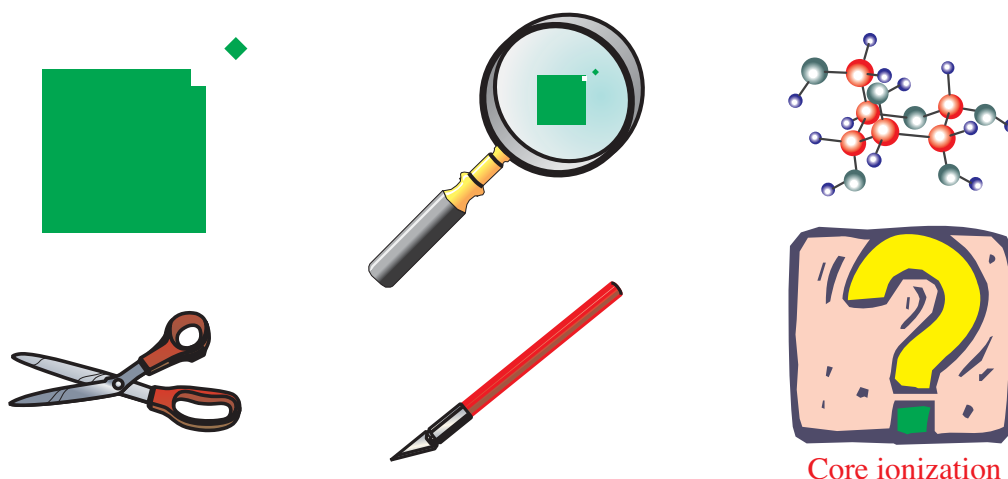


Fig. 1. Molecular knife.

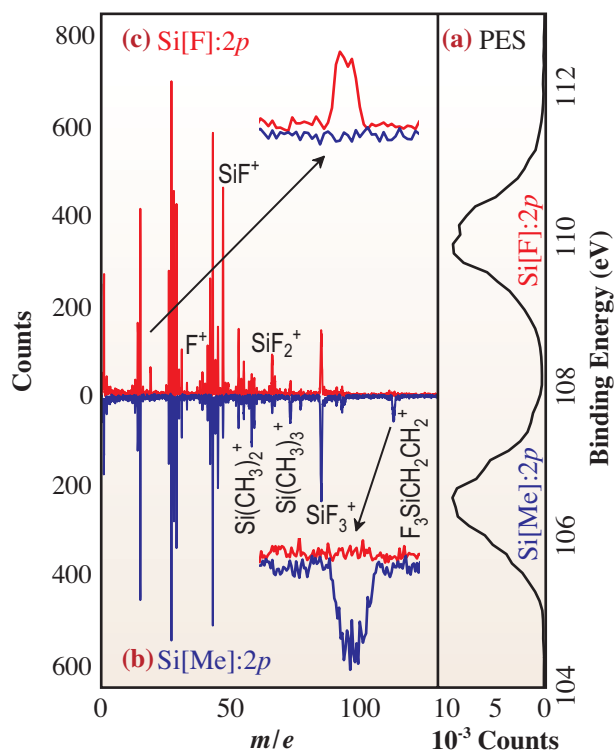


Fig. 2. (a) Si:2p PES of FSMSE vapor. (b) and (c) PEPICO spectra measured in coincidence with the Si[Me]:2p and Si[F]:2p photoelectrons. The insets show the regions of F⁺ and F₃SiCH₂CH₂⁺ with enlarged scales.

fragmentation is also revealed in ion-pair formation. Figure 3 shows the PEPICO counts of F₃SiCH₂CH₂⁺-Si(CH₃)₃⁺ and SiF⁺-SiCH₃⁺ versus the photoelectron binding energy, together with the PES of FSMSE. The site selectivity for the production of these ion pairs was also almost 100%.

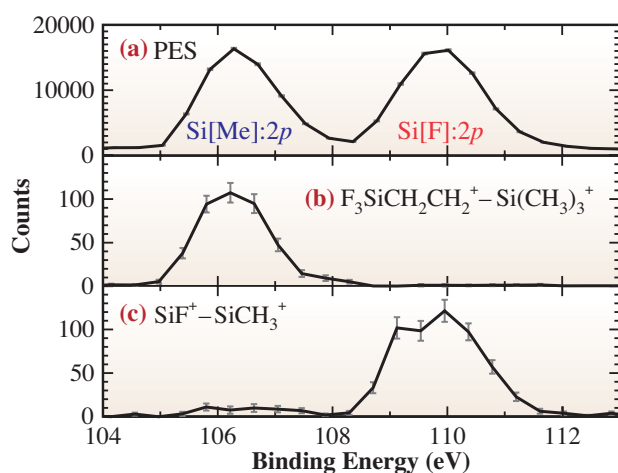


Fig. 3. (a) Si:2p PES of FSMSE vapor. (b) and (c) Plots of the PEPICO counts of F₃SiCH₂CH₂⁺-Si(CH₃)₃⁺ and SiF⁺-SiCH₃⁺ versus the photoelectron binding energy.

Site-specific fragmentation thus offers an approach to control chemical reactions by selecting the sites at which holes are created. The elucidation of the details of the fragment production mechanism brings the goal of a molecular knife one step closer to realization.

S. Nagaoka^{a,*}, G. Prümper^b and K. Ueda^b

^a Graduate School of Science and Engineering, Ehime University

^b Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

*E-mail: nagaoka@ehimegw.dpc.ehime-u.ac.jp

References

- [1] S. Nagaoka *et al.*: J. Chem. Phys. **129** (2008) 204309 and references cited therein.
- [2] G. Prümper *et al.*: J. Electron Spectrosc. Relat. Phenom. **144-147** (2005) 227.
- [3] H. Ohashi *et al.*: Nucl. Instrum. Methods A **467-468** (2001) 529.
- [4] S. Nagaoka, G. Prümper, H. Fukuzawa, M. Hino, M. Takemoto, Y. Tamenori, J. Harries, I. H. Suzuki, O. Takahashi, K. Okada, K. Tabayashi, X.-J. Liu, T. Lischke and K. Ueda: Phys. Rev. A **75** (2007) 020502(R).