Dissociation Dynamics of Ionic and Neutral Fragments of Gaseous SiCl4 following Si 2p Core-level Excitation

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The electronic relaxation processes and subsequent profound fragmentation processes of polyatomic molecules following core-level excitation have been a subject of extensive research over decades because of scientific importance and technological applications. Comprehensive understanding of bond-selective x-ray generated molecular photolysis is important gateways for the development of evolving technology in the fabrication of microelectronic devices into the nanometer range. With synchrotron radiation of tunable energy, one can prepare the molecule in a well defined core-excited state and investigate the associated electronic relaxation channels and fragmentation pathways.

In Fig. 1, the fragmented ion yields of Cl+, Si+, SiCl+, SiCl2+, and SiCl3+ for gaseous SiCl4 following Si 2p core-level excitation to various resonances are reproduced along with the Si L-edge x-ray absorption spectrum for comparison. The doublet structures labeled 1 and 1' were ascribed to transitions from the Si(2P3/2,1/2) initial states to the 8a1* state. The next doublet structures labeled 2 and 2' were assigned to excitations to the 9t2* state. The absorption features between 105 and 106.5 eV have mainly valence character. In contrast, the high-energy peaks between 108 and 110 eV possess strong Rydberg character.1 As shown in Fig. 1, the photon-energy dependence of various fragmented ion yields, Cl+, SiCl+, SiCl2+, and SiCl3+, of gaseous SiCl4 resembles the Si L23-edge photoabsorption spectrum. In contrast, a comparison between the Si+ yield spectrum and the Si L23-edge absorption spectrum in Fig. 1 shows that the Si 2p → Rydberg excitation at ~ 110 eV produces enhancement of the Si+ yield, as compared to the Si 2p → 8a1* and Si 2p → 9t2+ excitations.

The main features of the dispersed fluorescence spectrum of gaseous SiCl4 taken with the excitation photon of 230 eV are due to transitions from Si* atoms, SiCl4+ C → X, SiCl4+ C → A, and Si+*.2 Fig. 2 shows the yields of the excited fluorescing species following Si 2p core-level excitation. For comparison, the Si L-edge x-ray absorption spectrum of gaseous SiCl4 is also plotted in Fig. 2. As noted from Fig. 2, the excitation spectra of all light-emitting species show the same gross features as the Si L-edge absorption spectrum. However, there are dramatic differences in the relative intensities of peaks due to excitation to valence levels and that due to excitation to Rydberg orbitals. As noted, the Si 2p core-to-Rydberg excitation leads to a significant production of excited atomic (Si*, Si+*) fragments, particularly for excited neutral atomic fragments Si*. Accordingly, the Si 2p → Rydberg excitation produces enhancement of the Si+ yield, as compared to the Si 2p → 8a1* and Si → 9t2* excitations as shown in Fig. 1. In contrast, the Si 2p core-to-valence excitation generates an enhancement of excited molecular-ion SiCl4+. The experimental results provide deeper insights into the state-selective dissociation dynamics for excited neutral fragments of molecules via core-level excitation.

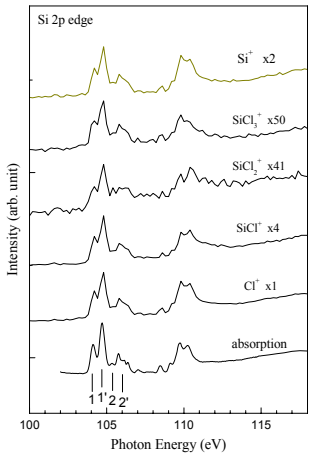

Figure 1. Fragmented ion yields of Cl+, Si+, SiCl+, SiCl2+, and SiCl3+ of gaseous SiCl4 as a function of photon energy in the vicinity of Si 2p edge.

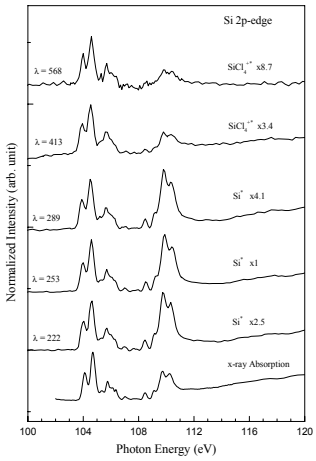

Figure 2. Photon-energy dependence of various excited fluorescing species at the Si 2p edge along with the Si L-edge x-ray absorption spectrum of gaseous SiCl4.

Reference:
1.J. M. Chen, R. Klauser, S. C. Yang, and C. R. Wen, Chem. Phys. Lett. 246, 285 (1995).
2. K. T. Lu, J. M. Chen, J. M. Lee, S. C. Ho, and H. W. Chang, Radiat. Phys. Chem. (2006) (in press).