Core-level Anionic Photofragmentation of Gaseous CCl_4 and Solid-state Analogues

K.-T. Lu (盧桂子)[1], J.-M. Chen (陳錦明)[1], J.-M. Lee (李振民)[1,2], T.-L. Chou (周大磊)[1], S.-A. Chen (陳興安)[1], S.-C. Haw (何樹智)[1], and T.-H. Chen (陳天豪)[1]

[1]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[2]Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan

The spectral properties of CCl_4 are imperative for its technical importance in the reactive ion etching of microelectronics. CCl_4 and halomethanes adsorbed on single-crystalline surfaces are model systems for studies of surface photochemistry. In this work, we investigated the dissociation dynamics of anionic and excited neutral fragments of gaseous CCl_4 following excitation of Cl 2*p* electrons to various resonances on combining measurements of anionic photodissociation, x-ray absorption, and uv or visible dispersed fluorescence.

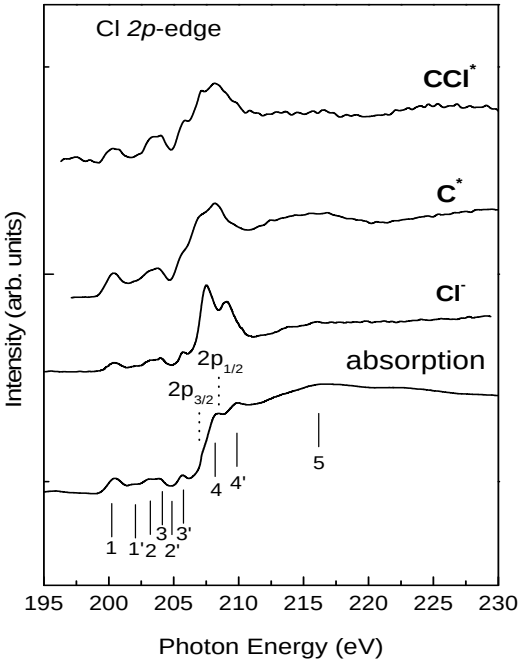

Fig. 1: Yields of Cl^- anion fragment and excited neutral fragments (C^* and CCl^*) from gaseous CCl_4 following Cl 2*p* core-level excitation, with the Cl *L*-edge x-ray absorption spectrum.

Discernible in Fig. 1, the relative intensities of Cl^- yield spectrum and fluorescence excitation spectra of excited neutral fragments (C^* and CCl^*) differ notably from those of Cl L_{23}-edge absorption spectrum of gaseous CCl_4. Excitations of the Cl 2*p* electrons to Rydberg orbitals and doubly excited states (absorptions labeled 3' and 4) near the Cl *2p* ionization threshold of gaseous CCl_4 enhance both the excited neutral atomic fragments C^* and excited neutral diatomic fragments CCl^*, relative to the ratio of intensity of the corresponding transition to the core-to-valence excitation (absorption labeled 1) in the Cl L_{23}-edge X-ray absorption spectrum. In particular, excitations of Cl *2p* electrons to higher Rydberg orbitals near the Cl $2p_{3/2}$ threshold (at ~207 eV) or doubly excited states (at ~208.2 eV) of gaseous CCl_4 remarkably enhance the production of excited neutral fragments. The Cl^- anion is significantly reinforced in the vicinity of the Cl $2p_{1/2,3/2}$ ionization threshold of gaseous CCl_4. The maximum anion enhancement about 207.5 eV is just above the threshold, 206.9 eV, for Cl $2p_{3/2}$ ionization of gaseous CCl_4. The Cl^- anion might thus be enhanced by the same dissociation channels that produced the excited neutral fragments.

Shake-up modified resonant Auger decay and PCI-mediated shake-down near the ionization threshold accordingly produce highly excited ionic Rydberg states, efficiently producing excited neutral fragments, because the wave function of a diffuse Rydberg electron has less overlap with the molecular-ion core; consequently the 2h1e or mhme states dissociate to produce the excited-state fragments before the excited Rydberg electron can relax. Recapture of a PCI-mediated photoelectron increases the probability of capture by the departing Cl atom during dissociation, and then enhances the Cl^- yield near the Cl *2p* ionization threshold of gaseous CCl_4. The detection of excited neutral particles and anion fragments is demonstrated to be a sensitive probe for investigating shake-modified resonant Auger decay, doubly excited states embedded in core-shell ionization continua, and PCI dynamics.

The Cl $2p \rightarrow 7a_1^*$ excitation for CCl_4/Si(100) enhances the Cl^- desorption yield at a submonolayer level, whereas the Cl^- anion is significantly enhanced near the Cl $2p_{1/2,3/2}$ ionization threshold of gaseous CCl_4. The transitions of core electrons to high Rydberg states near Cl 2*p* ionization thresholds and doubly excited states of gaseous CCl_4 greatly enhance excited neutral fragments (C^* and CCl^*), originating from shake-modified resonant Auger decay or/and post-collision interaction. The notably enhanced Cl^- anion near the Cl $2p_{1/2,3/2}$ ionization threshold of gaseous CCl_4 is affected by PCI-mediated photoelectron recapture. The resonant enhancement of the Cl^- yield at the $7a_1^*$ resonance in the Cl 2*p* edge at a submonolayer level occurs through a formation of high-lying molecular-ion states for CCl_4 adsorbed on a Si surface, mediated by polarization induced by the substrate. Our experimental results provide important insight concerning the roles and relative importance of dissociative electron attachment and high-lying molecular-ion states on dissociation dynamics of negative ion for adsorbates on surfaces. These complementary results provide insight into the anionic and excited neutral fragmentations of gaseous molecules and solid-state analogues via core-level excitation.