

Study for ultra-fast-dissociation of molecular core-excited states by ultra-high-resolution Auger electron spectroscopy

M. Kitajima^a (6368), H. Shindo^a (7751), A. De Fanis^b (6276), M. Machida^c (5913), M. Nagoshi^c(7082), K. Ueda^b (3219), and H. Tanaka^a (5673)

^aSophia Univeristy, ^bTohoku University, ^cHimeji Institute of Technology

If the dissociation of highly symmetric molecules such as CF₄ and SiF₄ is anisotropic and faster than the Auger decay, one can observe the energy-split of the Auger emission line from the atomic fragment due to Doppler effects, as a direct probe of symmetry breaking caused by the nuclear motion in the core-excited state. In case of the CF₄ molecule, molecular dissociation following the F 1s excitation is anisotropic and the Doppler energy split of the Auger emission from the F atomic fragment is observed in the resonant Auger spectra, as shown in Fig. 1. This is a direct proof that asymmetric ultrafast dissociation takes place within the time scale of a few femtoseconds, corresponding to the lifetime of the F 1s excited states.

Considering the similarity between CF₄ and SiF₄, the Doppler energy split of the Auger emission from the F atomic fragment is likely to be observed also in the resonant Auger spectra of SiF₄. Thus we have investigated the resonant Auger spectra of SiF₄ near the F 1s ionization threshold.

Spectra were recorded with an electron spectrometer (Gammadata-Scienta SES2002) equipped with a gas cell. The data recorded at several photon energies, at 0° (solid curve) and 90° (broken curve) directions relative to the polarization vector, are presented in Fig. 2, together with the total ion yield spectrum. Although the SiF₄ molecule exhibits anisotropic dissociation following the F 1s excitation as in the case of CF₄, no Auger emission from the F fragment is observed in the resonant Auger spectra. The absence of the Auger emission from the F atomic fragment indicates that the ultra-fast-dissociation does not take place in the F 1s-excited states of SiF₄.

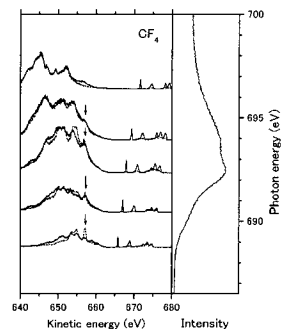


Fig.1 Resonant Auger spectra of CF₄ near the F 1s ionization threshold. A feature marked by arrows corresponds to an F atomic Auger line that appears as a result of ultra-fast-dissociation of the core-excited state.

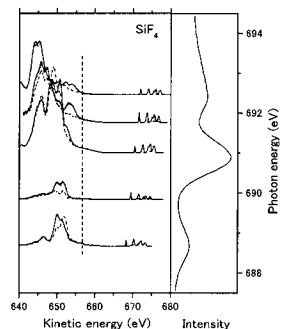


Fig.2 Resonant Auger spectra of SiF₄ near the F 1s ionization threshold. Vertical broken line corresponds to the expected kinetic energy for an F atomic Auger line that appears.

Photoelectron diffraction of free molecules: PF₃ and SiF₄ illuminated from within

Alberto De Fanis (6279)^{*,*}, Masatake Machida (5913)^b, Mitsuru Nagoshi (7082)^b, Masaki Oura (356)^c, Alexandra Knapp (8363)^d, Juergen Nickles (8362)^d, Yoko Muramatsu (4833)^a, Inosuke Koyano (1307)^b, Norio Saito (3191)^c, Kiyoshi Ueda (6279)^a

^{*}Tohoku University, ^bHimeji Institute of Technology, ^cRIKEN, ^dFrankfurt University, ^eNational Institute of Advanced Industrial Science and Technology

We aimed to measure inner shell photoelectron angular distribution in the molecular frame (PAD) in polyatomic molecules at ~50 eV of kinetic energy. Experimentally, PAD can be obtained by measuring the momentum vector of the photoelectron and of all the fragmenting ions in coincidence, so that the complete kinematic of the photoemission process can be reconstructed during off-line analysis. We employed a time-of-flight spectrometer in which electrons and ions are detected at opposite sides by two 2-dimensional position- and time-sensitive detector. By using the time structure of the storage ring, from the measurements of position and time of arrival, the components of the 3-dimensional momentum vector of each particle can be reconstructed. The kinetic energy of the photoelectrons is chosen so that the de Broglie wavelength of the photoelectron is comparable to the internuclear distance, resulting in a sufficiently structured diffraction pattern, but that can still be angularly resolved by the experiment.

The original plan was to perform the experiment with BF₃ and SiF₄. However, these reactive species can be handle only with following difficult safety procedure and it was eventually decided to run the experiment on CO₂.

Figure 1 shows the O 1s (upper) and C 1s (lower) PAD from fixed-in-space CO₂ measured at hv=586 and 341 eV, which correspond to approximately 45 eV above the ionization threshold. The X-axis is the angle between the CO⁺-O⁺ axis and the direction of

the emitted photoelectron. Photoelectrons are mainly ejected parallel to the molecular axis, with this effect more pronounced for the C 1s measurements.

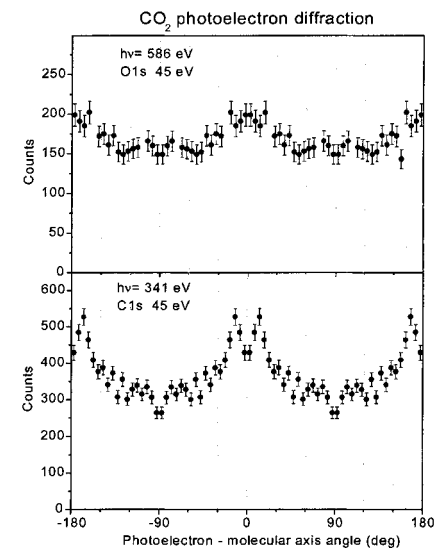


Figure1. O 1s and C 1s photoelectron angular distribution of CO₂ in the molecular frame, measured 45 eV above the ionization thresholds.