

## Auger Electron Emission from Inner-shell Satellite States in Molecules

We have studied Auger decays of the inner-shell satellite states in molecules with a very efficient coincidence method. The multi-electron coincidences allow us to reveal the overall features of Auger transitions from individual satellite states. The decay features of the satellite states can be interpreted as spectator and participator behavior of the excited electrons.

When an inner-shell electron in an atom or molecule is removed, the core-hole state decays via the Auger transition. The kinetic energy of the Auger electron is element-specific, and for this reason Auger electron spectroscopy is widely used as a powerful analytical tool in many different fields of research. However, the detailed interpretation of Auger spectra is difficult, even for atoms and small molecules. This is because inner-shell ionization is concomitant with the excitation and ionization of valence electrons, and all of these core-hole states contribute to the conventional Auger electron spectra. In theory, it is possible to filter out structures due to individual satellite states by using the photoelectron-Auger electron coincidence method, which allows one to correlate initial core-hole states with the relevant Auger decays. In practice however, the acceptance solid angle of a conventional electron spectrometer is too low to allow the recording of such a coincidence spectrum with suf-

ficient statistics. Instead of using conventional electron spectrometers, we have applied a magnetic bottle electron spectrometer [1, 2] to photoelectron-Auger electron coincidence spectroscopy. We describe here how we can reveal the Auger decays from the individual inner-shell satellite states in  $N_2$  molecules [3].

The experiment was performed at the undulator beamline, BL-2C, and the multi-electron coincidences were recorded at a photon energy of 510.2 eV. Figure 1(a) displays a two-dimensional map showing coincidences between  $1s$  photoelectrons and Auger electrons. The conventional photoelectron and Auger electron spectra are plotted in Figs. 1(b) and 1(c), respectively. The photoelectron spectrum is plotted on a binding energy scale relative to the  $1s^1$  state (409.94 eV). Inner-shell satellite structures ( $S_1$ - $S_4$ ) as well as the  $1s$  mainline are clearly observed.

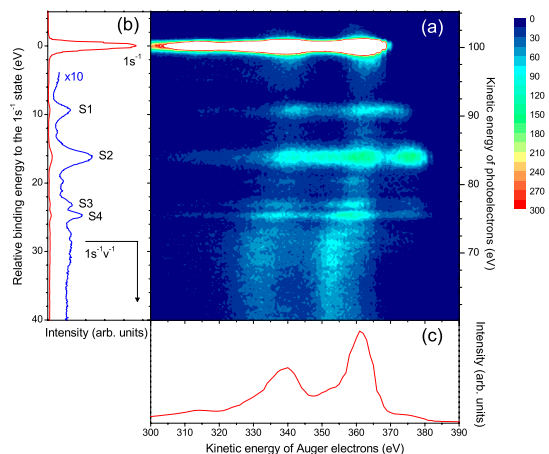


Figure 1  
(a) Two-dimensional map of electron-electron coincidences, represented as a function of the kinetic energies of the photoelectrons and Auger electrons. (b) Conventional N  $1s$  photoelectron spectrum. (c) Conventional Auger spectrum.

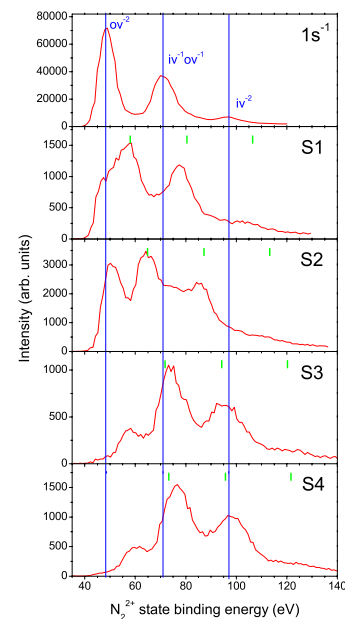


Figure 2  
Coincidence Auger electron spectra for decays from the  $1s^{-1}$  and satellite states. The peak positions of the  $2h$  structures resulting from the Auger decays of the  $1s^{-1}$  state are indicated by vertical lines. The vertical bars indicate the  $3h1e$  final state energies expected from the initial excitation energies.

The 2D map shows horizontal structures at the  $1s$  main line and the satellite states, which correspond to the Auger decays of these states. In order to investigate the decay mechanisms of the individual satellite states, we have extracted the coincidence Auger spectra from the 2D map. In Fig. 2, the coincidence spectra associated with the satellite states are plotted on the  $N_2^{2+}$  binding energy scale, together with the coincidence spectrum associated with the  $1s^{-1}$  state. The  $1s$  Auger spectrum

shows three band structures corresponding to the two-hole ( $2h$ ) final states. The same  $2h$  final states can be produced in the Auger decays of the satellite states when the excited electrons participate in the decay. In addition to the  $2h$  final states, the Auger spectra exhibit band structures at higher energies than the  $2h$  states. These structures originate from spectator Auger decay: the three-hole one-electron ( $3h1e$ ) final states may be populated when the excited electrons behave as spectators, and these states should lie at higher binding energies than the  $2h$  states.

We have shown that this very efficient spectrometer is indispensable for photoelectron-Auger electron coincidence observations, and demonstrated its usefulness for investigating the Auger structures from inner-shell satellite states which have unfavorable cross sections for formation. The magnetic bottle electron spectrometer possesses powerful capabilities in multi-electron coincidence observation for atomic and molecular inner-shell photoionization processes, which manifests itself as some outstanding research accomplishments [1, 2]. Thanks to the multi-electron coincidence technique, our understanding has been extended up to Auger decays forming triply [3] and quadruply [4] charged states in atoms and molecules.

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### BEAMLINE

2C

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## Evidence of Core-hole Localization in the C 1s Photoionization of C<sub>2</sub>H<sub>2</sub> and Interference between the Photoelectron Waves from Two Carbon Atoms

For core-level photoionization of highly symmetric molecules, the question arises as to whether a core hole should be considered as being localized to one specific atom. To answer this question, we have investigated the C 1s photoionization processes for C<sub>2</sub>H<sub>2</sub> molecules. Carbon 1s photoelectron angular distributions (PADs) relative to the fragmentation axis (fragmentation occurs following the photoionization) have been measured using a multi-coincidence technique. The PAD for non-symmetric fragmentation provides evidence of a localized core-hole and preferential bond breaking. Moreover, the PAD for symmetric fragmentation is interpreted as showing interference between the de Broglie waves of the photoelectrons from the two carbon atoms.

For core-level photoionization, we intuitively think that a core hole is localized on the ionized atom (a localized core-hole picture). On the other hand, the description of the pure eigenstates requires a symmetry-adapted picture. Currently, it is accepted that the two descriptions are identical for core-hole states, since the overlap between the core orbitals is negligible, and the lifetime of the hole state is so short that the pure eigenstate is not realized. Thus it is necessary to take into account the mixed eigenstates to obtain a comprehensive description. To elucidate the core-level photoionization dynamics for highly symmetric molecules, we have investigated the C 1s photoionization processes for C<sub>2</sub>H<sub>2</sub> molecules.

The experiment was performed at the soft x-ray undulator BL-2C. Photoelectrons and photoions from C<sub>2</sub>H<sub>2</sub> were detected using a multi-coincidence, velocity-map imaging spectrometer [1]. Figure 1 shows the C 1s PADs relative to the fragmentation axis for the two channels of CH<sup>+</sup>-CH<sup>+</sup> (**sym**) and H<sup>+</sup>-C<sub>2</sub>H<sup>+</sup> (**asym**), which were measured with linearly polarized light at 311.2 eV, producing C 1s photoelectrons having a kinetic energy of 20 eV. Primary focus should be on the inversion (*i.e.*, the left-right mirror) symmetry of the PADs, because a discussion of this symmetry provides the key for recognizing core-hole localization.

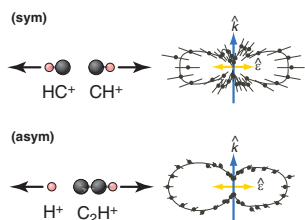


Figure 1  
Polar plots of C 1s photoelectron angular distributions for C<sub>2</sub>H<sub>2</sub> molecules relative to the dissociation molecular axis for two different two-body molecular fragmentation channels; symmetric (**sym**) and asymmetric (**asym**). The polar plots are in the geometry of the dissociation axis relative to the electric vector of the incident light for parallel geometry, which corresponds to parallel transitions ( $\Delta\lambda = 0$ ).

The PAD for the **sym** channel shows an asymmetric shape. This result is considered to be evidence of both the temporally localized core-hole and selective bond breaking (see Fig. 2). The photoelectrons are subjected to the molecular potential with the localized core-hole, and move away immediately from the molecular region. The core-hole lifetime (7.3 fs) is shorter than the core-hole hopping time ( $\sim 40$  fs). Thus, Auger decay occurs before the core-hole moves to the neighboring atom. If bond breaking depends on the core-hole position, this should result in an asymmetric shape of the PAD. The present results mean that there is a preference for bond breaking. We note that the observed appearance of the asymmetric shape is not trivial. That is, if there is no preference for bond breaking, the PAD should be symmetric.

Next, we focus on the differences between the PADs for the **sym** and **asym** channels. The shape of the PAD for the **sym** channel can be explained by the interference between two *p* partial waves (*i.e.*, the de Broglie wave of the photoelectrons in this case), with a model

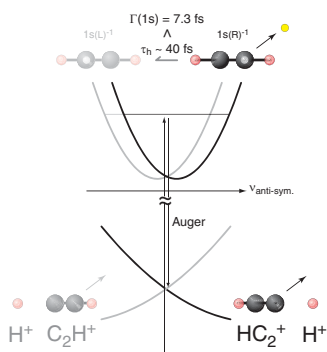


Figure 2  
Preferential bond breaking following Auger decay. There are two possible ways that bond breaking can occur relative to the initial core-hole position. The present results can be explained by the existence of a preference for one of these channels.

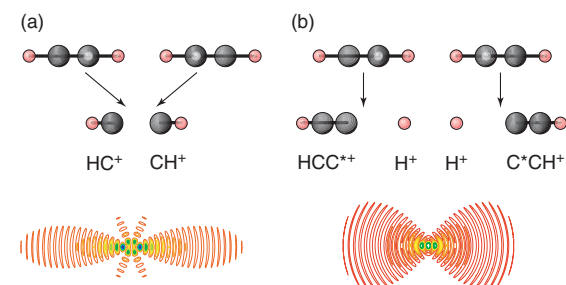


Figure 3  
Calculated contour maps for photoelectron probability density for a) the coherent sum, and b) the incoherent sum of the two *p* partial waves from the two different sources in the free field. Shown above the contour maps are schematic representations for the photoionization and decay processes with and without interference.

of a local (to one carbon atom) 1s  $\rightarrow$  *kp* transition. This model gives the contour map shown in Fig. 3(a) for the photoelectron probability density which results from the coherent sum of the free-particle *p* waves from two sources. This map reproduces the nodal structure observed in the experimental results. On the other hand, the PAD for the **asym** channel can be explained by an absence of interference. This situation gives the contour map of photoelectron probability density shown in Fig. 3(b). The map reproduces the nodal structure observed in the PAD, except for the asymmetry. The asymmetric shape comes from the effect of the asymmetric molecular potential, which is excluded in the present model. The difference between the PADs for the **sym** and **asym** channels seems analogous to the opening and shutting of a slit in Young's double slit experiment.

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### BEAMLINE

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