

Electronic Structure and Decay Dynamics in Atoms and Molecules Following Core Hole Creation

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The dynamics of the inner-shell photoexcitation, photoionization, and subsequent decay processes is much more complex, in comparison to outer-shell photo-processes. For instance, the inner-shell photoionization is concomitant with the excitation and ionization of valence electrons, which reveal themselves as shake-up and shake-off satellite structures in the corresponding photoelectron spectrum. The one-photon multi-electron processes, which are entirely due to the electron correlation in the system, are known to happen not only in the primary inner-shell hole creation processes, but also in their relaxation processes. Our research project is focused on elucidating the electronic structures and decay dynamics in core-excited atoms and molecules, by utilizing various spectroscopic techniques together with monochromatized synchrotron radiation in the soft x-ray region.

1. Dissociation Dynamics in Polyatomic Molecules Following Core Hole Creation

Auger decay is the main relaxation process following core ionization in molecules composed of light atoms. In the decay process, a valence electron fills the core-hole while another valence electron is ejected. Doubly charged molecular ions with two holes in the valence shell, thus formed, often break up into ion fragments, due to the Coulomb repulsion between the nuclear charges. The coincidence detection between the energy-selected Auger electrons and fragment ions is one of the most powerful methods to gain a close insight into the dissociation mechanism of the Auger final states. To realize efficient coincidences among these charged particles, we have developed an Auger electron-ion coincidence spectrometer which consists of a double toroidal electron analyzer and a three-dimensional ion momentum spectrometer.

The Auger electron emission from the S $2p^{-1}$ core-hole

states of OCS and subsequent dissociation processes of the doubly charged states have been investigated. The measurement has provided direct correlation between the doubly charged ion states and the dissociation pathways. The lowest-lying $(3\pi)^{-2}$ states located at about 32 eV binding energy produce the metastable OCS^{2+} and their lifetimes are expected to be much longer than 3.5 μs . The $(9\sigma)^{-1}(3\pi)^{-1}$, $(8\sigma)^{-1}(3\pi)^{-1}$ and $(2\pi)^{-1}(3\pi)^{-1}$ states around 36 eV are associated with both the formation of metastable OCS^{2+} and the dissociation into $\text{CO}^+ + \text{S}^+$. The three-body dissociation into $\text{O} + \text{C}^+ + \text{S}^+$ originates only from the high-lying states above 42 eV, whose main configurations are $(9\sigma)^{-2}$ and $(8\sigma)^{-1}(9\sigma)^{-1}$.

In order to investigate the influence of the localized core-hole creation to the formation of the valence two-hole states, and to elucidate their characters, the Auger decays following the C 1s and O 1s ionization in OCS have also been studied by using the same experimental setup. It was found that the lowest-lying $(3\pi)^{-2}$ states related to the production of the metastable OCS^{2+} are formed mainly via the Auger decay from the S $2p^{-1}$ core-hole states, which is explained by the localized nature of the 3π molecular orbital at the S atom.

2. One-Photon Multi-Electron Emission Processes Studied by Multi-Electron Coincidence Spectroscopy

When an inner-shell electron in atoms and molecules is removed, the core-hole state decays via the Auger electron transition. The kinetic energy of the Auger electron is element specific and therefore Auger electron spectroscopy is widely used as a powerful analytical tool in many different fields of research or even application. However, the detailed interpretation of the measured Auger spectra is difficult, even for atoms and small molecules. This is because inner-shell

ionization of atoms and molecules is concomitant with the excitation and ionization of valence electrons, and all these core-hole states contribute to the conventional Auger electron spectra. Recently, we have successfully applied a magnetic bottle electron spectrometer to multi-electron coincidence spectroscopy for different systems.^{1–4} We describe here the results for the photoelectron-Auger-electron coincidence study in N₂ molecules, where the Auger decays from the individual inner-shell satellite states have been revealed.¹⁾

Figure 1(a) displays a two-dimensional (2D) map showing coincidences between 1s photoelectrons and Auger electrons. The conventional photoelectron and Auger electron spectra are plotted in Figures 1(b) and 1(c), respectively. Here the photoelectron spectrum is plotted in a binding energy scale relative to the 1s⁻¹ state (409.94 eV). Inner-shell satellite structures (S₁–S₄) as well as the 1s mainline are clearly observed in the photoelectron spectrum. The 2D map shows horizontal structures at the 1s main line and the satellite states, which correspond to the Auger decays of these states. The decay mechanisms of the individual satellite states have been examined by extracting the coincidence Auger spectra from the 2D map. The decay features of the satellite states can be interpreted as spectator and participator behavior of the excited electrons.

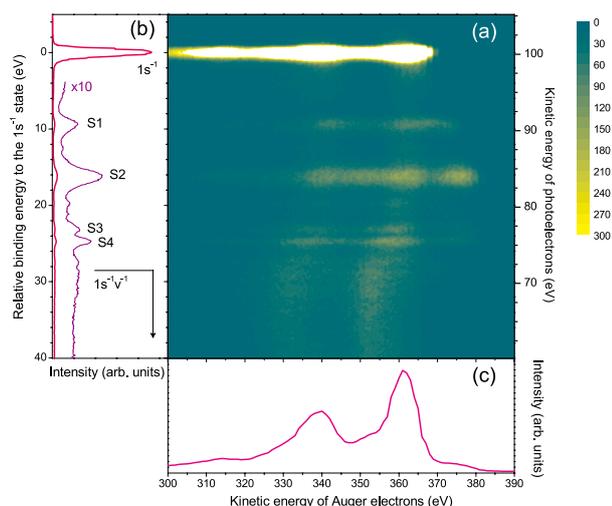


Figure 1. (a) Two-dimensional map of electron-electron coincidences, represented as a function of kinetic energies of photoelectrons and Auger electrons. (b) Conventional N 1s photoelectron spectrum. (c) Conventional Auger electron spectrum.

3. X-Ray Absorption Spectroscopy Measured in Resonant Auger Scattering Mode

The element specific information obtained by x-ray absorption spectroscopy (XAS) has a long history of application in various fields of research. A well-known bottleneck for XAS is the rather poor spectral resolution caused by the lifetime broadening of the core-excited states. Thanks to the rapid technological development related to synchrotron radiation,

the possibilities of super-high resolution beyond the inherent lifetime widths have attracted considerable interest. The simple idea behind XAS with super-high resolution is to measure x-ray absorption in resonant x-ray Raman scattering (RXRS) or resonant Auger scattering (RAS) modes. Thus, an immediate advantage can be taken from the fact that the spectral resolution of RXRS and RAS is independent of the lifetime broadening of the core-excited states. The width of the XAS resonance in resonant scattering mode is then determined by the spectral function width of the incident x-ray radiation. Sharpening of the x-ray absorption resonances was indeed experimentally evidenced by scanning over the incident photon energy of these scattering processes within fixed narrow scattered-energy windows.

Recently it has been demonstrated that the super-narrow x-ray absorption profiles obtained in the RAS mode for the CO molecules give wrong resonance positions, owing to the lifetime vibrational interference between coherently populated core-excited levels.⁵⁾ Figure 2 denotes the 2D map of the resonant Auger scattering yields, as a function of photon energy and electron kinetic energy, measured around the O1s → 2π resonance. The slight deviations of the positions of the hilltops from the vibrational progression of the core excited state can be seen in Figure 2.

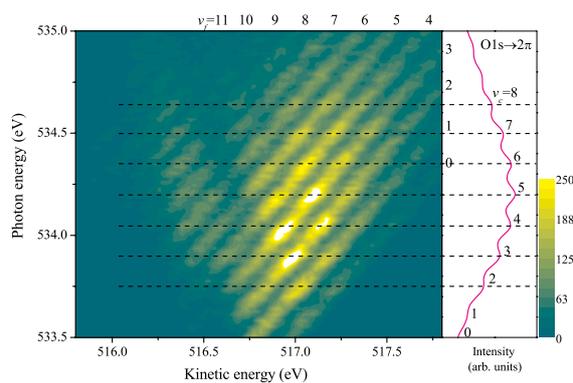


Figure 2. Two-dimensional map of the resonant Auger scattering yields from CO as a function of photon energy and electron kinetic energy, measured around the O1s → 2π resonance.

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