

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

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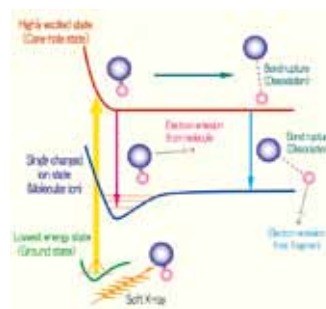
The detailed comprehension of the electronic structure of molecules is an important step toward understanding the chemical and physical properties of matter, and also provides a link between atomic and solid-state physics. Information on photoexcitation, photoionization, and photodissociation processes derived from molecular spectroscopy is of fundamental importance, and also useful in various scientific disciplines, including astrophysics, planetary sciences, radiation chemistry, and biology.

Synchrotron radiation combined with a suitable monochromator is a powerful research tool for systematic investigations of outer- and inner-shell excitation and ionization processes in molecules, because the spectral range matches the binding energies of the valence and core electrons of the elements which form molecules of physical and chemical interest, namely low-Z molecules. In order to promote inner-shell electrons of low-Z molecules efficiently, it is indispensable to utilize monochromatized synchrotron radiation in the soft X-ray region.

Inner-shell excited states of low-Z molecules relax mainly through Auger decay, leading to the formation of highly excited singly or multiply charged molecular ions with outer-shell holes. These molecular ions are in general quite unstable, and immediately break apart into fragment ions and neutrals.

The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

The major aim for investigating molecular inner-shell excitation is to determine what happens to molecules following the excitation and ionization of an inner-shell electron by using various spectroscopic techniques to define the initial photoexcitation process itself, and to characterize and correlate the electrons, ions, neutrals, and metastables that are produced as a result.



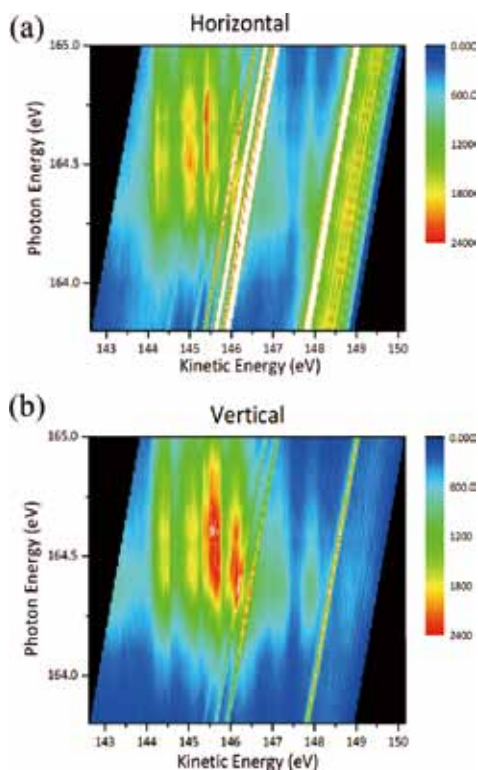
**Figure 1.** Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

#### Selected Publications

- E. Shigemasa and N. Kosugi, "Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications," in *Advances in Chemical Physics*, Eds., S.A. Rice and A. Dinner, Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, "Ultrafast Dynamics in C 1s Core-Excited CF<sub>4</sub> Revealed by Two-Dimensional Resonant Auger Spectroscopy," *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).

## 1. Decay Processes Following Sulfur 2p Photoexcitation in OCS Studied by High-Resolution Two-Dimensional Electron Spectroscopy

In the current study, angle-resolved two dimensional (2D) electron spectroscopy,<sup>1)</sup> where resonant Auger-electron spectra are recorded as a function of the photon energy, has been applied to the de-excitation processes in the S 2p excitation region of OCS, with previously unprecedented resolution.



**Figure 2.** 2D maps of resonant Auger electron spectra after the  $S\ 2p_{3/2} \rightarrow \pi^*$  excitation of OCS, measured at horizontal (a) and vertical (b) directions relative to the electric vector of the incident radiation.

The 2D measurements were performed on the soft x-ray beam line BL6U at UVSOR. The undulator radiation was monochromatized by a variable included angle, varied line-spacing plane grating monochromator. For 2D electron spectroscopy, the monochromator bandwidth was set to  $\Delta E_{ph} \sim 20$  meV at  $h\nu = 165$  eV. The kinetic energy of the emitted electrons was measured by a hemispherical electron energy analyzer (MBS-A1) placed at a right angle with respect to the incident photon beam direction. The direction of the electric vector was set to be either parallel (horizontal) or perpendicular (vertical) to the axis of the electrostatic lens of the analyzer. The energy resolution of the analyzer was set to  $\Delta E_k \sim 15$  meV.

Figure 2 shows 2D maps of resonant Auger electron spectra following the  $S\ 2p_{3/2} \rightarrow \pi^*$  resonant excitation of OCS measured in the horizontal (a) and vertical (b) directions. The diagonal lines can be attributed to valence photoelectron lines, and clearly show vibrational side bands indicating that the net

energy resolution is much better than 50 meV.

Clear island-like structures elongated in the vertical direction can be seen in both Figure 2(a) and Figure 2(b) in the kinetic energy region from 144 to 148 eV. In sharp contrast to the valence photoelectron lines, these structures do not show strong anisotropic angular distributions. To our knowledge, no detailed assignments have previously been given to them. In order to understand the origins of the structures, sophisticated theoretical calculations are highly desired.

## 2. Lifetime Broadening of Atomic Lines Produced upon Ultrafast Dissociation of HCl and HBr<sup>2)</sup>

The excitation of a core electron to the lowest unoccupied antibonding orbital in a molecule reduces the molecular bond strength and in general populates a dissociative state. When the timescales of the nuclear motion and of the core-hole relaxation are similar, this leads to a peculiar situation which has been named ‘ultrafast dissociation.’ Here, the excited state starts to dissociate, and electronic decay can occur at any point during the dissociation, up to the point where dissociation can be considered as completed. The first evidence for such a process was reported in 1986 by Morin and Nenner.<sup>3)</sup>

In the present study we revisit ultrafast dissociation following  $Cl\ 2p_{3/2}$  excitation in HCl and  $Br\ 3d_{5/2}$  excitation in HBr. The improved experimental resolution allows us to observe in detail the line-widths of both the atomic and molecular peaks. The atomic peaks are observed to be broader than the molecular vibrational peaks which are due to direct photoionization. We suggest that this broadening is due to the lifetime of the neutral, core-excited  $Cl^*$  or  $Br^*$  atomic fragment and can be retrieved from our experimental data.

The experiments were carried out at BL6U. The kinetic energies of electrons emitted perpendicular to the photon beam direction were measured by the MBS-A1. The energy resolution was set to  $\sim 12$  meV or  $\sim 6$  meV. The degree of linear polarization of the incident light was calibrated by measurements with rare gases and found to amount to 90–100%. The direction of the electric vector was set to be either parallel or perpendicular to the axis of the electrostatic lens of the analyzer.

After careful analysis of the experimental data, the Lorentzian broadenings of the atomic peaks in HCl and HBr were found to be  $96 \pm 5$  meV and  $91 \pm 5$  meV, respectively. We suggest that these values correspond in good approximation to the lifetimes of the  $2p_{3/2}$  hole in the  $Cl^*$  atom and the  $3d_{5/2}$  hole in the  $Br^*$  atom.

## References

- 1) M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).
- 2) P. Lablanquie, H. Iwayama, F. Penent, K. Soejima and E. Shigemasa, *J. Electron Spectrosc. Relat. Phenom.* **195**, 96–100 (2014).
- 3) P. Morin and I. Nenner, *Phys. Rev. Lett.* **56**, 1913–1916 (1986).