# Properties of hollow molecules containing a double core hole, probed by single-photon double ionization

P. Lablanquie[1], F. Penent[1], J. Palaudoux[1], L. Andric[1], P. Selles[1], S. Carniato[1], K. Bučar[2], M. Žitnik[2], M. Huttula[3], J. H. D. Eland[4], E. Shigemasa[5], K. Soejima[6], Y. Hikosaka[6], I. H. Suzuki[7], M. Nakano[7], and K. Ito[7]

*[1] LCP-MR, CNRS & Université P. et M. Curie, 11 rue P. et M. Curie, 75231 Paris Cedex 05, France*
*[2] Jožef Stefan Institute, P. O. Box 3000, SI-1001 Ljubljana*
*[3] Department of Physical Sciences, University of Oulu, Box 3000, 90014, Oulu, Finland*
*[4] Department of Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, United Kingdom*
*[5] UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan*
*[6] Department of Environmental Science, Niigata University, Niigata 950-2181, Japan*
*[7] Photon Factory, Institute of Materials Structure Science, Oho, Tsukuba 305-0801, Japan*

Although hollow atoms were known and observed for a long time, it is only very recently that experimental observation of hollow molecules ($N_2$) was possible thanks to sequential inner-shell ionization using x-ray free electron laser [1]. We have demonstrated [2] that such double core hole states can also be studied in detail by single photon double core ionization using synchrotron radiation, even if the associated double photoionization cross section is extremely weak.

The experiments were performed on BL-16A beamline at Photon Factory (Japan) and on TEMPO beamline at SOLEIL (France) using a magnetic bottle time-of-flight spectrometer.

We studied $N_2$, $O_2$, CO and $CO_2$ molecules. The formation and decay process is the following:

$$h\nu + M \rightarrow M^{2+}(K^{-2}) + 2\,e^-_{\text{Photoelectron}} \quad (1a)$$
$$\rightarrow M^{3+}(K^{-1}v^{-2}) + e^-_{\text{Auger Hypersatellite}} \quad (1b)$$
$$\rightarrow M^{4+}(v^{-4}) + e^-_{\text{Auger Satellite}}, \quad (1c)$$

where v designates a valence shell, and the emitted Auger electrons are called 'hypersatellite' or simply satellite, depending on whether the K-shell is filled in the presence of a second K hole or of valence holes. The hypersatellite Auger electron line has higher energy than the main Auger line associated with single K-shell ionization, and is characteristic of double K-shell ionization. By detecting in coincidence all four electrons released in the process (1), we have been able to characterized double core-hole states with two K-shell vacancies on the same atom and their satellites. We deduced in this way the binding energy of $N_2^{2+}$ ($K^{-2}$) states (and their satellites), their respective Auger decay paths and their relative intensity with respect to $N_2^{+}$ ($K^{-1}$) states. Single photon double ionization in the K-shell ($K^{-2}$) represents a small fraction ($10^{-4}$ to $10^{-3}$) of single K-shell ionization for $N_2$, $O_2$, CO and $CO_2$ molecules. In $N_2$, we could set an upper limit of 1.2% for the 2-site double K-shell ionization ($K^{-1}K^{-1}$) on neighbor atoms compared to 1-site ($K^{-2}$).

These results raise important questions for the theoretical description of the formation, spectroscopy and decay mechanism of the highly excited species involved. We will also present at the conference our most recent results on 1-photon double K-shell ionization.

[1]. L. Young *et al.*, Nature (London) **466**, 56 (2010).
[2]. P. Lablanquie *et al.*, Phys. Rev. Lett. **106**, 063003 (2011).