Properties of Hollow Molecules Probed by Single Photon Core Double Ionization

We observed for the first time the formation of hollow molecules (with a completely empty *K* shell in one constituent atom) through single photon core double ionization. The key of the success to detect this weak process was the use of a sensitive magnetic bottle experimental technique combined with synchrotron radiation. We obtained information on the core double ionization mechanism and detailed properties of hollow molecules such as the spectroscopy and decay dynamics of the N_2^{2+} K^{-2} main and satellite states.

Single core holes are widely known and used for material identification, since the development of ESCA (Electron Spectroscopy for Chemical Analysis) by Siegbahn *et al.* [1] and the advent of Auger electron spectroscopy. Much less is known on double core holes. We are interested here more specifically in atoms or molecules with one completely empty *K* shell, which are called hollow atoms or molecules. In fact hollow atoms have been quite studied [2] since their first observation in nuclear reactions in 1953 [3], thanks to their peculiar radiative decay with the release of a characteristics K_α^H "hypersatellite" X-ray, more energetic than the usual K_α line associated to the decay of a single core hole. No experimental result on hollow molecules existed before we began these experiments. However the interest of hollow molecules was established 25 years ago by Cederbaum *et al.* [4], who demonstrated that they show more sensitive chemical shifts than conventional inner-shell spectra.

We present here our first results on hollow molecules, created by single photon core double ionization [5]. Experiments were carried out at the undulator BL-16A in single bunch top-up mode and used the magnetic bottle analyzer [6] we developed. For the N_2 molecule the formation and the cascade decay process of the hollow molecule is:

$$h\nu + N_2 \rightarrow N_2^{2+}(K^{-2}) + 2\,e^-_{\text{Photoelectron}} \quad (1)$$

$$\rightarrow N_2^{3+}(K^{-1}v^{-2}) + e^-_{\text{Auger Hypersatellite}} \quad (2)$$

$$\rightarrow N_2^{4+}(v^{-4}) + e^-_{\text{Auger Satellite}} \quad (3)$$

where *v* designs 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 another *K* hole or of valence holes.

The key of the success to filter out the weak signal from the dominant single ionization path was to detect all the 4 emitted electrons in coincidence. From the number of observed events we estimate the probability of double to single *K*-shell ionization to be as low as $8.4 \pm 1 \times 10^{-4}$ at a photon energy of 1100 eV. The possibility exists that the two 1*s* electrons ejected in the core double photoionization (DPI) path (1) originate from the 2 different N atoms of the molecule (2-site core DPI). We did not detect such a process but our experiment permits to set here an upper limit of 1.2% to the 2-site versus 1-site core DPI.

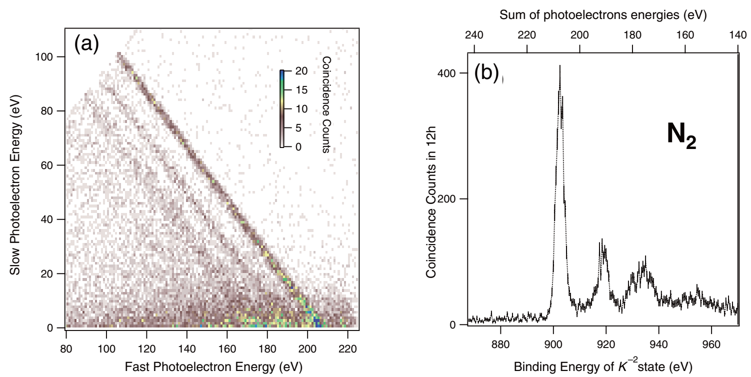

Figure 1
a) Energy correlation map for the two photoelectrons emitted upon creation of the N_2 hollow molecule. b) Histogram of the sum of the energies of the two photoelectrons, deduced from a) by integration along the diagonal lines. A 1100eV photon energy was used.

These 4-electrons coincidences can be displayed in a variety of ways. Figure 1(a) shows the energy correlation between the two photoelectrons (when detected in coincidence with the two successive Auger electrons). One observes a strong diagonal line associated to the formation of the hollow N_2^{2+} (K^{-2}) state. Weak lines are associated to the formation of satellite states (see Fig. 1(b)) in which a valence electron is simultaneously promoted to a vacant orbital. These satellite lines are quite intense, much more than the corresponding satellite in single core hole formation. This reflects nicely the stronger perturbation imparted to the valence shell when 2 core electrons are removed rather than one.

Figure 2 examines the decay of the hollow molecule by successive Auger decay (reactions 2 and 3). It compares the Auger spectrum of a single *K*-shell hole (red) with the Auger spectrum of a double *K* hole (black) and with that of a double *K* hole satellite (green). We resolve two components in the 375-450 eV range associated with the emission of the first Hypersatellite Auger (2), and only broad bands in the 300-375 eV range where contribution of the second satellite Auger electron of reaction (3) is expected. Decay of the K^{-2} satellite line produces mainly a hypersatellite Auger line of the same kinetic energy (416 eV) as for the decay of the main K^{-2} line. We infer a dominant spectator decay where the excited electron does not take part in the first step (2) of the double core hole decay.

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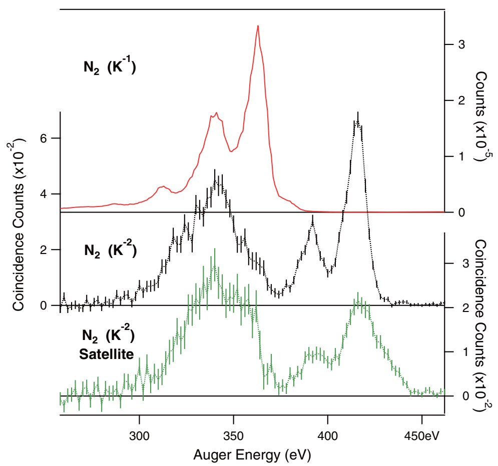

Figure 2
Comparison of the Auger spectra emitted upon decay of a single *K*-shell core hole (red) a double core hole (black) and a double core hole satellite (green).