Properties of Hollow Molecules Probed by Single-Photon Double Ionization

P. Lablanquie,[1,2] F. Penent,[1,2] J. Palaudoux,[1,2] L. Andric,[1,2,3] P. Selles,[1,2] S. Carniato,[1,2] K. Bučar,[4] M. Žitnik,[4] M. Huttula,[5] J. H. D. Eland,[6] E. Shigemasa,[7] K. Soejima,[8] Y. Hikosaka,[8] I. H. Suzuki,[9] M. Nakano,[9] and K. Ito[9]

[1]*UPMC, Université Paris 06, LCPMR, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[2]*CNRS, LCPMR (UMR 7614), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[3]*Université Paris-Est, 5 boulevard Descartes, 77454 Marne-la-Vallée Cedex 2, France*
[4]*Jožef Stefan Institute, P.O. Box 3000, SI-1001 Ljubljana, Slovenia*
[5]*Department of Physics, P.O. Box 3000, 90014 University of Oulu, Finland*
[6]*Department of Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, United Kingdom*
[7]*UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan*
[8]*Department of Environmental Science, Niigata University, Niigata 950-2181, Japan*
[9]*Photon Factory, Institute of Materials Structure Science, Oho, Tsukuba 305-0801, Japan*

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The formation of hollow molecules (with a completely empty K shell in one constituent atom) through single-photon core double ionization has been demonstrated using a sensitive magnetic bottle experimental technique combined with synchrotron radiation. Detailed properties are presented such as the spectroscopy, formation, and decay dynamics of the N_2^{2+} K^{-2} main and satellite states and the strong chemical shifts of double K holes on an oxygen atom in CO, CO_2, and O_2 molecules.

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Hollow atoms are transient species with a completely empty K shell. They were first observed [1] and investigated [2] in nuclear reactions where a K-shell electron is captured by the nucleus and a second one is ejected. Multicharged ions [3] and electron [4] collisions have also been used to study them, but substantial progress occurred when the more selective photons, first from x-ray tubes [5] and then from synchrotrons [6,7], could be used to probe them.

Hollow species raise important questions on their formation, structure, and decay. The probability for their formation by core double photoionization (DPI), for instance, is considered as a fine test of electron correlations [5–7]. Hollow atoms decay by successive filling of the two K holes leading to the emission of two x-ray photons or Auger electrons. Coincidences between the two cascade x rays were detected by Briand *et al.* [2] who also established that the first emitted x ray, the so-called $K_\alpha{}^{\mathrm{H}}$ hypersatellite associated to the $K^{-2} \rightarrow K^{-1}L^{-1} + h\nu$ transition, is a clear signature of a hollow atom. Since then, most experiments relied on observation of these $K_\alpha{}^{\mathrm{H}}$ lines [3–7]. Reports of hypersatellite Auger electrons are much more scarce and limited to neon [8].

If we except the atypical helium [9], lithium [10], and beryllium [11] atoms where hollow states were observed in photoabsorption experiments, the situation is that only heavy hollow atoms have been created by photoionization so far. No result exists on the most common light ($Z =$ 5–9) atoms nor on molecules. Some particular spectroscopic properties of hollow molecules were, however, already noticed 24 years ago [12], as they were found to show more sensitive chemical shifts than conventional inner-shell spectra. Recently, hollow molecules regained interest because it was predicted [13,14], and demonstrated [15], that they can be formed in two-photon core double ionization with x-ray free electron lasers (XFELs).

In this Letter we present the first observation of hollow molecules, as formed through single-photon core DPI. The weak signal was separated from the dominant core single ionization thanks to a very sensitive magnetic bottle-type experiment based at synchrotron sources, by coincidence detection of the four released electrons (two photoelectrons and two Auger electrons). This experimental method not only succeeds in providing core DPI probabilities, but also reveals detailed properties of hollow molecules, such as their spectroscopic information, chemical shifts, dynamics of formation, and decay.

Experiments were performed at the BL-16A undulator beam line of the Photon Factory (PF), Japan, and at the TEMPO undulator beam line of SOLEIL, France. The second one allowed study of O 1s core DPI. In both cases the storage ring was operated in single bunch and in top up modes. We used two similar electron time-of-flight spectrometers of the magnetic bottle type [16]. Their principle was described previously [17,18]; briefly, all electrons ($> 95\%$) from the ionization volume are collected by an inhomogeneous magnetic configuration and guided along a 2 m solenoid to a detector. Multicoincidences are recorded between electrons ejected in the same light pulse by multihit time-to-digital converters which record the arrival time of each electron with respect to the light bunch. The system achieves an energy resolution $\Delta E/E$ of 1.6% and a high detection efficiency which decreases slowly with electron kinetic energy as was estimated from Kr 3d photoelectron–Auger-electron coincidences.

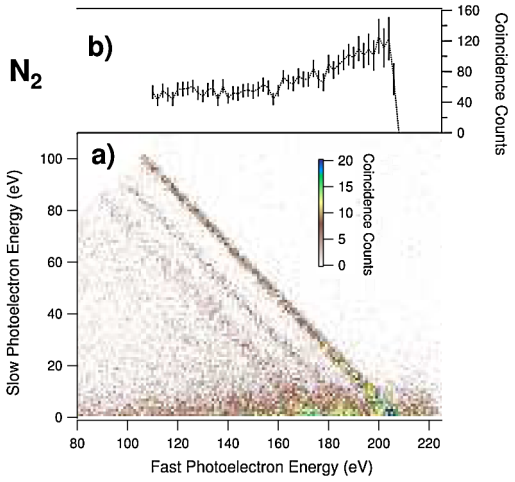

FIG. 1 (color online). (a) Energy correlation between the two photoelectrons in N_2. The signal is filtered by coincidence detection of the two associated Auger electrons of 375–450 and 300–375 eV. Energy sharing in (b) is deduced from the intensity along the diagonal line projected on the x axis after subtraction of false coincidences, mostly attributed to slow secondary electrons (< 10 eV) emitted from surfaces. We used photons of 1110 eV with a resolution of 1 eV. Accumulation time was 12 h.

Hollow N_2^{2+} states created by single-photon core DPI decay by emitting 2 Auger electrons along the sequence:

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

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

$$\rightarrow N_2^{4+}(v^{-4}) + e^-_{\text{Auger satellite}}, \quad (1c)$$

where v designates a valence shell.

In order to extract hollow molecule formation, we isolate reactions (1) by detecting in coincidence the four released electrons. Figure 1(a) displays the correlation between the kinetic energies E_1 and E_2 of the two photoelectrons. As expected for reaction (1a), one observes a strong diagonal line at constant $E_1 + E_2$ which demonstrates the formation of a hollow N_2^{2+} K^{-2} state.

Let us consider now the spectroscopy of these new species. The histogram of the sum of photoelectron energies in Fig. 2(a) leads to a measure of the N_2^{2+} K^{-2} binding energy as the photon energy is precisely known. A set of similar measurements as in Fig. 2(a) gave a binding energy BE $= 902.55 \pm 0.5$ eV, in reasonable agreement with recent predictions [14] and our calculations (Table I). Figure 2(a) also reveals weaker lines associated with the faint diagonal lines of Fig. 1(a), which correspond to K^{-2} satellite states where the double core hole ionization is accompanied by a simultaneous excitation of a valence electron. The peak at BE $= 918.9$ eV in Fig. 2(a) can be assigned to a N_2^{2+} $K^{-2}\pi_u^{-1}\pi_g$ configuration by analogy with the well-documented K^{-1} satellite states [19]. It is quite intense, of the order of 25% of the main K^{-2} line, which is more than twice the value (10%)

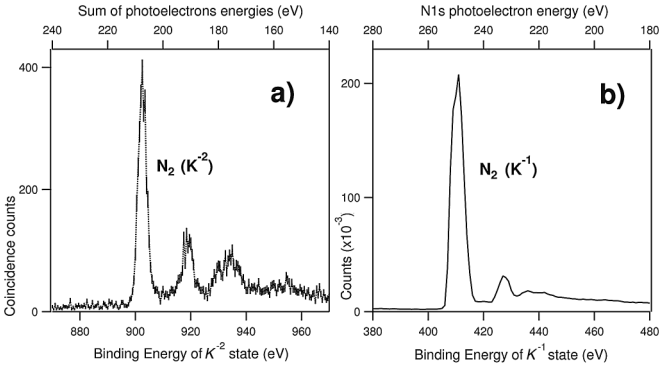

FIG. 2. (a) Histogram of the sum of the energies of the 2 photoelectrons. The same data set as in Fig. 1 has been used, filtering by detection of the two associated Auger electrons. Electrons of less than 10 eV have been discarded to reduce background. The binding energy scale has been checked in SOLEIL experiments by a simultaneous measurement of the Au $4f$ photoelectron peaks in the surface experiment chamber on the second branch of the beam line. (b) Single photoelectron spectrum with associated satellite lines measured at $h\nu = 659$ eV.

for the corresponding satellite in single core hole formation, N_2^+ $K^{-1}\pi_u^{-1}\pi_g$, when observed at a comparable excess energy [Fig. 2(b)]. This reflects nicely the stronger perturbation imparted to the valence shell when two core electrons are removed rather than one, and confirms recent predictions [13].

Chemical shifts associated with hollow molecules are now addressed by comparing O K^{-2} states in O_2, CO, and CO_2 in Fig. 3. All spectra suggest the presence of satellite lines, though the limited statistics prevents their detailed study. Binding energies of the main lines are reported in Table I. We observe here a stronger chemical shift than for O K^{-1} states (3.3 eV compared to 1.94 eV [14] for CO with respect to CO_2). We calculated the hollow states' binding energies with the GAMESS(US) package [20] at second-order Møller-Plesset MP2 level of theory with large cc-pVQZ basis set for both the initial neutral ground state and the final double core K^{-2} ionized state. The addition of static atomic differential relativistic terms deduced from [21] to frozen core ΔMP2 values gives K^{-2} ionization energies in excellent agreement with experiments (with an average deviation energy within the experimental error bars) and in reasonable agreement with recent estimates [14].

TABLE I. Binding energies of K^{-2} hollow states relative to the respective neutral ground states.

	Experiment	Calculations (eV) This work	Ref. [14]
N_2	902.55 ± 0.5	902.91	901.704
O_2	1179.2 ± 0.8	1180.17	
CO	1178.0 ± 0.8	1178.39	1175.376
CO_2	1174.7 ± 0.8	1174.09	1172.821

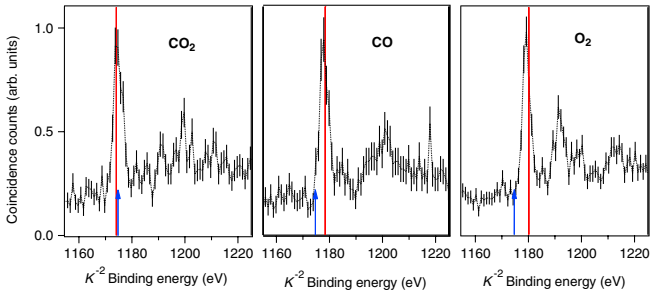

FIG. 3 (color online). Histogram of the sum of the energies of the two photoelectrons ejected from oxygen K shell in different molecules. The blue arrows indicate the experimental CO_2 K^{-2} level. The observed strong chemical shift is reproduced by calculations (vertical red lines). Experiments were performed at 1300 eV photon energy.

Cross sections for hollow molecule formation by single-photon core DPI are of high interest as a measure of correlation between the two ejected K-shell electrons. As all ionization events are recorded in our experiment and energy-dependent electron detection efficiencies are measured, the ratio of double to single core photoionization, R_{DS}, can be extracted directly from our data. The values, reported in Table II, are of similar magnitude to what is observed for heavy atom core DPI [7] and provide stringent tests for calculations. Study of the R_{DS} excess photon energy dependence is under way and expected to bring fuel to the debate on electron correlation at the origin of core DPI and its current modeling in terms of shakeoff versus knockout mechanisms [7]. In this respect, the energy sharing between the two $1s$ N photoelectrons is of interest. It is given here at an excess energy of $E_{xc} = 208$ eV by the intensity along the diagonal line in Fig. 1(a), and is reported in Fig. 1(b) after subtraction of the false coincidences background. Only the upper half of the distribution is represented here by projection on the x axis, as the remaining low energy part obtained by projection of the same data on the y axis is symmetric with respect to $E_{xc}/2$. One deduces from Fig. 1(b) a relatively flat U-shaped energy sharing between the 2 photoelectrons, characteristic of the DPI process. If we take into account the scaling effect due to the N effective charge Z_N^* (Slater's rules), the energy distribution in N_2 [Fig. 1(b)] at an excess energy of $E_{xc} = 208$ eV should be comparable to the one obtained in He at E_{xc} $(Z_{He}/Z_N^*)^2 \sim 13$ eV. Both are quite flat [22], suggesting an important knockout contribution at this photon energy. It should be noted, however, that indirect processes which are absent in He DPI must be present here and add intensity for unequal energy sharing; they are linked to the existence of intense K^{-2} satellites [see Fig. 2(a)] and the probable indirect core DPI paths mediated through excited N_2^+ Rydberg states built with such a core.

The possibility exists that the two K electrons ejected in a core DPI path (1a) originate from the two different N atoms of the molecule (2-site core DPI). However, one expects a very weak contribution, as single-photon DPI relies on electron correlation and the Coulomb interaction is orders of magnitude weaker between two K electrons from different N atoms than between the two K electrons from the same N atom. Our experiment, however, allows us to set an upper limit for the cross section of this process. Binding energy of the 2-site core hole N_2^{2+} $K^{-1}K^{-1}$ is predicted at 839.9 eV [14]. It should not be revealed in our four electron coincidence data of Fig. 1, as the two satellite Auger electrons released upon its decay are expected to have similar kinetic energies and will not be differentiated by our setup, because of the 10 ns detector dead time. The 2-site N_2^{2+} $K^{-1}K^{-1}$ states should, however, appear in three electron coincidences (two photoelectrons plus one Auger). The corresponding spectra, similar to the one in Fig. 2(a) but with higher background due to the less stringent coincidence criterion, did not reveal any signal, but allow us to set here an upper limit of 1.2% on 2-site versus 1-site core DPI.

TABLE II. Branching ratio R_{DS} for the double to single core photoionization cross sections.

	Excess energy above K^{-2} threshold	R_{DS}
N_2	208 eV	$8.4 \pm 1 \times 10^{-4}$
O_2	121 eV	$3.6 \pm 0.6 \times 10^{-4}$
CO	123 eV	$2.7 \pm 0.5 \times 10^{-4}$
CO_2	126 eV	$3.5 \pm 0.6 \times 10^{-4}$

We turn now to the decay dynamics of K^{-2} main and associated satellite states by successive Auger decay [reactions (1b) and (1c)]. Note that, based on the supposed shorter lifetime of K^{-2} than $K^{-1}v^{-2}$ states [23], we use a two step description that might be questioned. Figure 4(a) compares the Auger spectrum of a single K hole (top in red) with the Auger spectrum of a double K hole (middle in black) and that of a double K hole satellite (bottom in green). We resolve two components in the 375–450 eV range associated with the emission of the first hypersatellite Auger (1b), and only broad bands in the 300–375 eV range where contribution of the second satellite Auger electron of reaction (1c) is expected. Coincidences between these two groups in Fig. 4(b) effectively confirm this description. From these measurements one can deduce the spectroscopic information on the N_2^{3+} levels involved in the cascade (1b) and (1c) and of the final N_2^{4+} states. The binding energy of the latter is simply deduced from the histogram of the sum of the energies of all four electrons emitted in the process [Fig. 4(c)]. We observe that the decay of the K^{-2} hole leads to formation of possibly two N_2^{4+} resolved states with 149 and 165 eV binding energies. The spectrum of hypersatellite Auger originating from the K^{-2} main line [middle of Fig. 4(a)] reveals two $N_2^{3+}K^{-1}v^{-2}$ intermediate states with binding energies of 487.5 and 510.9 eV (Auger energies of 415 and 391.6 eV, respectively); these energies suggest that

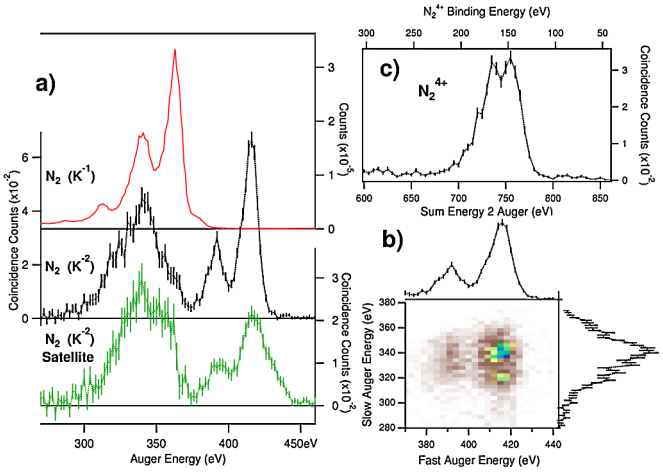

FIG. 4 (color online). (a) Auger spectrum associated with decay of double K^{-2} core hole (middle, black) compared to the Auger decay of a single K^{-1} core hole (top, red) and of double K^{-2} core hole satellite (bottom, green). The same data set as in Fig. 1 has been used, but only three electron coincidences are considered here. As for the decay of the K^{-2} main line, energy correlation between the first Auger electron of 375–430 eV and the second one of 300–375 eV is displayed in (b). We deduce the spectroscopy of N_2^{4+} final state in (c).

at least one valence electron involved in the excited level at 510.9 eV has a N 2*s* character. Note that the decay of an atomic hollow N^* $(2s, 2p)^2$ $3l^5$ atom has been shown to produce a 408 eV hypersatellite Auger electron [24], a value close to the 415 eV we obtain here in the N_2 molecule. Decay of the K^{-2} satellite line of presumed N_2^{2+} $K^{-2}\pi_u^{-1}\pi_g$ configuration produces mainly a hypersatellite Auger line of roughly the same kinetic energy (416 eV) as for the decay of the main K^{-2} line. This implies an excited N_2^{3+} intermediate state of 502.9 eV binding energy. We infer a spectator decay where the π_g excited electron does not take part in the double core hole decay, and a $K^{-1}v^{-2}\pi_u^{-1}1\pi_g$ configuration for the N_2^{3+} intermediate. The participator decay to the lower N_2^{3+} $K^{-1}v^{-2}$ states contributes to the shoulder at high energy in Fig. 4(a) bottom curve.

Three Letters [25–27] on hollow molecules have been published after our Letter was submitted. The first two demonstrated two-photon core double ionization using a XFEL source; however, the information gained on N_2 hollow molecules is far less detailed than in our coincidence experiments. As an example, while we confirm fully that their observed 413 eV peak is a signature of the formation of a hollow molecule, our results demonstrate that their 442 eV peak cannot be assigned to a K^{-2} shakeup state [26] because these states preferentially decay in a spectator process with emission of slower electrons. Hollow CH_4 and NH_3 molecules have also been studied with synchrotron radiation [27], although the lower statistics of the data and the restriction to three electron coincidences prevented detection of K^{-2} satellite states.

In conclusion, we have been able to observe hollow molecules formed by single-photon double ionization and report details of their spectroscopy and the dynamics of their formation and decay. These properties are important inputs for atomic and molecular physics: a knockout mechanism is inferred for the single-photon core DPI process, K^{-2} chemical shifts are larger and possibly more informative than K^{-1} ones [13]. Knowledge of the properties and decay dynamics of hollow states is also of primary importance in the new XFEL field because these species can be readily formed in multiphoton ionization processes with XFELs and serve as a diagnostic of the laser characteristics [15].

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