

## Double Core Hole Creation and Subsequent Auger Decay in $\text{NH}_3$ and $\text{CH}_4$ Molecules

J. H. D. Eland,<sup>1,2</sup> M. Tashiro,<sup>3</sup> P. Linusson,<sup>4</sup> M. Ehara,<sup>3</sup> K. Ueda,<sup>5</sup> and R. Feifel<sup>2</sup>

<sup>1</sup>*Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom*

<sup>2</sup>*Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden*

<sup>3</sup>*Institute for Molecular Science, Okazaki 444-8585, Japan*

<sup>4</sup>*Department of Physics, Stockholm University, AlbaNova University Centre, SE-106 91 Stockholm, Sweden*

<sup>5</sup>*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

(Received 14 July 2010; published 19 November 2010)

Energies of the hollow molecules  $\text{CH}_4^{2+}$  and  $\text{NH}_3^{2+}$  with double vacancies in the  $1s$  shells have been measured using an efficient coincidence technique combined with synchrotron radiation. The energies of these states have been determined accurately by high level electronic structure calculations and can be well understood on the basis of a simple theoretical model. Their major decay pathway, successive Auger emissions, leads first to a new form of triply charged ion with a core hole and two valence vacancies; experimental evidence for such a state is presented with its theoretical interpretation. Preedge 2-hole-1-particle ( $2h-1p$ ) states at energies below the double core-hole states are located in the same experiments and their decay pathways are also identified.

DOI: 10.1103/PhysRevLett.105.213005

PACS numbers: 33.80.Eh, 33.70.Ca, 34.50.Gb

Double core-hole (DCH) states of atoms and molecules, with two vacancies in inner shells, have long been objects of interest. DCH atoms have been studied both theoretically and experimentally [1–10]. For molecules, however, only theoretical studies [11–18] have been available hitherto. More than two decades ago, Cederbaum *et al.* [11] predicted that the energies of DCH states where the  $1s$  vacancies are situated on different atomic sites (two-site DCH) will exhibit more sensitive chemical shifts than the corresponding single core-hole (SCH) states, while those where the  $1s$  vacancies are situated on the same atomic site (one-site DCH) exhibit much larger orbital relaxation effects than the corresponding SCH states. These predictions were reinforced by recent works of Tashiro *et al.* [17,18]. Experimentally, both atomic and molecular DCH states can be formed by high energy impact of photons, electrons, or ions, but because of the line broadening consequent upon nuclear motion, molecular DCH states are difficult to detect either as “hypersatellite” Auger lines or in x-ray absorption.

The main experimental impediment to their study by single photon double ionization is that the cross sections are very small, of the order of  $10^{-4}$  of the single core-hole cross sections for one-site DCH and  $10^{-7}$  for two-site DCH. It has recently been pointed out that both DCH states should be efficiently formed and readily accessible to study by two-photon transitions using intense soft x-ray pulses from free-electron lasers (FELs) [16], and experimental evidence for this has most recently been reported [19,20]. Their formation and subsequent decay by multiple electron emission will be of considerable relevance to development of the hoped-for technique of structure determination by single-molecule x-ray diffraction using the same x-ray pulses [20].

In this Letter we show that the difficulty of the small cross sections for the single photon double ionization can be overcome, at least for one-site DCH states, by a very efficient multicoincidence technique combined with synchrotron radiation from a storage ring. We report the energies of the “hollow molecule”  $1s^{-2}$  states in  $\text{CH}_4$  and  $\text{NH}_3$  and also, thanks to the versatility of the coincidence technique, the energies of associated “preedge resonances” and of the major decay products from all the DCH states. We show that the energies of the DCH states are accurately reproduced by high level (CASSCF) molecular structure calculations, and can also be well understood by a simple physical model. The major decay pathway from the DCH states is found to be successive Auger emissions, leading first to a newly observed form of triply ionized state with one core-hole and two valence (CVV) vacancies, then finally to quadruply charged products. The main decay path of the DCH  $2h-1p$  “resonance” is similar spectator Auger emission leading to a  $3h-1p$  doubly charged excited state.

The key to extracting the very faint DCH signal from the strong background of more probable events is detection and analysis of at least three of the four electrons ejected in the overall process. A multiple coincidence technique is thus essential, together with a source of the monochromatic soft x-ray radiation. The major interfering background comes from emission of secondary electrons when primary high energy photoelectrons or Auger electrons hit solid surfaces. To clarify spectra of processes weaker than the main DCH formation we have modeled the secondary electrons as smooth distributions based on the observed low energy electron spectra, and have subtracted the resulting background in the form of two-dimensional

coincidence maps, from the raw coincidence data. This procedure, which cannot generate false peaks but only remove false peaks from the spectra, will be described in detail elsewhere [21].

Experiments were done on beam line U49/2-PGM-2 [22] at the storage ring BESSY-II in Berlin, using a magnetic bottle time-of-flight (TOF) analyzer [23,24] for multiparticle coincidence detection. All ( $> 90\%$ ) electrons from the intersection of the soft x-ray beam with an effusive jet of target gas were directed to a  $\sim 2$  m distant microchannel plate detector by the inhomogeneous field of a conical permanent magnet and a homogeneous solenoidal guiding field. The measured detection efficiency in these experiments was 53% and the numerical energy resolution,  $E/\Delta E$ , for single electrons was about 50. Calibration of the conversion from electron TOF to energy was done using the known energies of Auger electrons from Xe, refined for each individual target gas, by the accurately known  $K$ -shell single ionization energies. Spectra of the DCH states in  $\text{CH}_4$  and  $\text{NH}_3$  are shown in Fig. 1 from experimental runs of about 2h duration, and the state energies are listed in Table I. Similar spectra were acquired at other photon energies ( $h\nu = 1000$  eV for  $\text{NH}_3$ ,  $h\nu = 720$  eV, and  $h\nu = 680$  eV for  $\text{CH}_4$ ) to confirm the observed features; they all show peaks at the same positions within the experimental uncertainty, though with statistics that are not as good. The spectra were extracted as electron pair energy sums from triple coincidences, where the sum of all three electron energies was constrained to lie within a range of  $\pm 50$  eV from the expected position of the CVV triply ionized state in DCH decay. Attempts to extract similar spectra from either coincident

pairs or from 4-electron coincidences were less successful, as the expected signals were lost in intense background noise. For  $\text{CH}_4$ , at  $h\nu = 750$  eV (99 eV above the DCH, 458 eV above the SCH) the DCH cross section is found from the coincidence counting rates and known detection efficiency to be  $1/4000$  of the SCH cross section. For  $\text{NH}_3$  at  $h\nu = 950$  eV (58 eV above DCH, 544 eV above SCH) the ratio is  $1/6000$ .

In a second stage of analysis, knowing the energy of the DCH state we can extract from the same triple coincidence data, a spectrum which should reveal both the CVV intermediate state and the second Auger electron. The spectrum so obtained for  $\text{NH}_3$  is shown as Fig. 2, showing the main CVV triply ionized state at 475 eV and the quadruply ionized state around 133 eV; the caption gives more details. Because the CVV state spectrum is broader on the energy scale than the single DCH states, the statistics are not as good, and in the case of  $\text{CH}_4$  they are not sufficient yet to yield a useful spectrum. However, from the  $\text{CH}_4$  data we can report that the main CVV intensity is in the ionization energy range of 350 to 370 eV.

Similarly, a spectrum of singly charged ions showing DCH  $2h-1p$  preedge resonances could be extracted from the triple or double coincidence data for  $\text{NH}_3$ , and is shown in Fig. 3(a). A broad peak representing the expected  $2h-1p$  preedge group of resonance states is found at 880 eV ionization energy, 12 eV below the DCH edge. This is about 4 times the comparable gap in single core-hole formation (3.3 eV), as expected from the  $Z^2$  dependence of binding energy. The peak is detected in coincidence with electrons emitted in decay from the preedge states to form a group of doubly charged states at around 456 eV. These are  $3h-1p$  states created by spectator Auger emission, where a normal valence electron, not the excited electron falls into the core hole. They have one core hole, two valence holes, and an excited electron in a higher orbital. A weaker peak at 432 eV in Fig. 3(b) represents normal core-valence (CV) double ionization of  $\text{NH}_3$ , and possibly a contribution from participant Auger decay from the  $2h-1p$  resonance. The total intensity of normal CV double ionization at this photon energy is much higher than indicated in the figure, however, because the figure includes only those states formed in coincidence with one electron at the energy of the resonance. The observed CV intensity in Fig. 3(b) is no more than expected on the basis of the accepted fraction of the full electron energy range, so we conclude that the resonance decay is predominantly by the spectator process.

To validate and extend these experimental observations we have carried out high level molecular structure calculations at the equilibrium neutral geometries of  $\text{CH}_4$  and  $\text{NH}_3$  using the state-averaged complete-active-space SCF (SA-CASSCF) method [26] with the correlation-consistent polarized valence triple-zeta ( $cc-pVTZ$ ) basis set of Dunning [27]. Depending on whether singly or doubly ionized states were considered, the configurations in the CASSCF method were restricted to those having one or two holes in the  $K$ -shell orbitals, respectively. The active

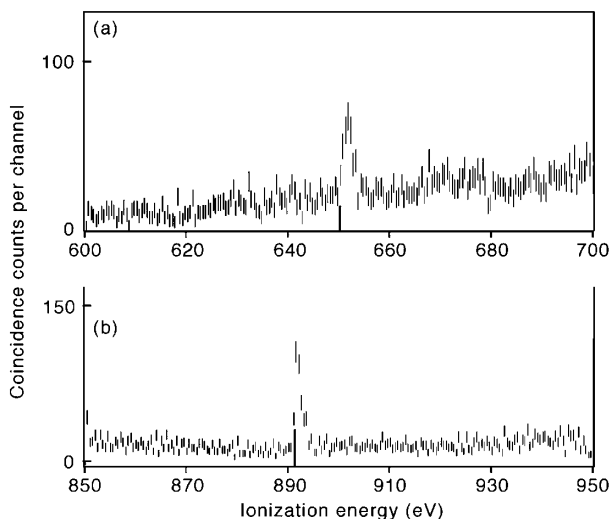


FIG. 1. Double core-hole spectra (a) for  $\text{CH}_4$  at  $h\nu = 750$  eV and (b) for  $\text{NH}_3$  at  $h\nu = 950$  eV. The spectra have been extracted from triple coincidence data (see text). The experimental peak widths (ca. 1.5 eV for  $\text{NH}_3$  and 2.5 eV for  $\text{CH}_4$ ) are mainly due to the estimated instrumental resolution (1.2 and 2 eV) at the electron energies involved. Theoretical DIP values are shown as bars for direct comparison.

TABLE I. Experimental ( $E$ ) and calculated ( $T$ ) DIP and IP values for the  $1s^{-2}$  and  $1s^{-1}$  states of  $\text{CH}_4$  and  $\text{NH}_3$ , respectively (the experimental IPs are taken from Refs. [24,25]). The energy difference  $\Delta E$  [cf. Eq. (1)], half of the excess energy  $\text{ERC}/2$  [cf. Eq. (5)], and the strict relaxation energy  $R$  (see text) are also given. All energies are in eV.

	DIP		IP		$\Delta E$		ERC/2		$R$
	$E$	$T$	$E$	$T$	$E$	$T$	$E$	$T$	$T$
$\text{CH}_4$	$651.5 \pm 0.5$	650.2	290.7	290.8	70.1	68.6	12.6	13.4	12.9
$\text{NH}_3$	$892 \pm 0.5$	891.0	405.6	405.7	80.8	79.6	15.7	16.3	16.2

space included the full valence orbitals consisting of all possible bonds derived from  $2s$  and  $2p$  orbitals. Calculations were carried out using the MOLPRO 2008 quantum chemistry package [28]. The results are compared with the experimental data in Table I. The table also contains ionization potentials (IP) for single core-hole creation, both experimental (cf. Refs. [24,25]) and calculated by CASSCF. The agreement between the experimental and theoretical values is good, as shown in Fig. 1 where the theoretical double ionization potentials (DIP) are shown as bars below the experimental spectra.

The energy differences

$$\Delta E(S_i^{-2}) = \text{DIP}(S_i^{-2}) - 2 \times \text{IP}(S_i^{-1}), \quad (1)$$

obtained experimentally and theoretically are also given in the table. Here,  $S_i$  denotes the  $i$ th atomic site of the molecular species ionized. A large part of  $\Delta E$  stems from the hole-hole repulsive energy and thus can be expected to be proportional to the atomic number  $Z$ . Indeed,  $\Delta E$  is larger for the  $N$   $1s$  DCH state than the  $C$   $1s$  DCH state.

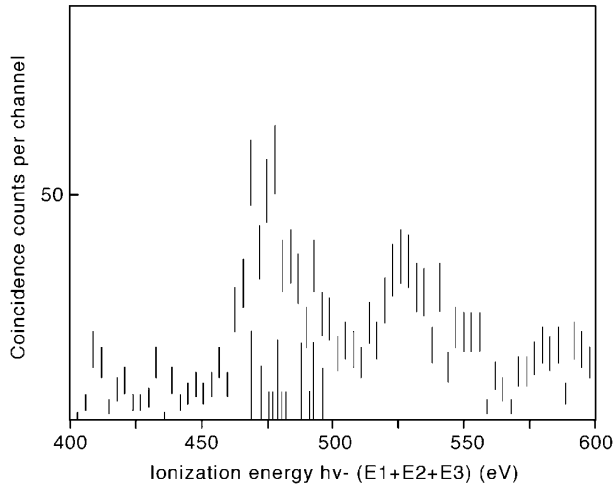


FIG. 2. Triple coincidence spectrum selected within the range of the peak in Fig. 1(b) for DCH formation in  $\text{NH}_3$  at  $h\nu = 950$  eV. The main feature around 475 eV ionization energy represents the CVV triply ionized state reached by the first step of Auger decay from the hollow ammonia molecule. Part of the peak around 525 eV is an artifact caused by secondary electrons, but part, particularly around 550 eV, is attributed to the second Auger electron which terminates in quadruply charged final products at an ionization energy around 133 eV. Calculated CVV states (see text) are shown as bars.

A more rigorous discussion about the DIPs can be formulated following the recipe given by Refs. [11,17]. The SCH IP of a molecule can be approximated as

$$\text{IP}(S_i^{-1}) = -\epsilon_{S_i} - \text{RC}(S_i^{-1}), \quad (2)$$

where  $\epsilon_{S_i}$  is the orbital energy of the neutral molecule and  $\text{RC}(S_i^{-1})$  is the generalized relaxation energy that includes both orbital relaxation energy and correlation energy. Analogously, a DCH DIP of the molecule at the same atomic site can be approximated as

$$\text{DIP}(S_i^{-2}) = -2\epsilon_{S_i} - \text{RC}(S_i^{-2}) + V_{S_i S_i S_i S_i}. \quad (3)$$

Here  $V_{S_i S_i S_i S_i}$  is the one-site two-hole electron repulsion integral which is available from *ab initio* calculations.

Furthermore, the DCH relaxation energy  $\text{RC}(S_i^{-2})$  can be decomposed into

$$\text{RC}(S_i^{-2}) = 2 \times \text{RC}(S_i^{-1}) + \text{ERC}(S_i^{-2}), \quad (4)$$

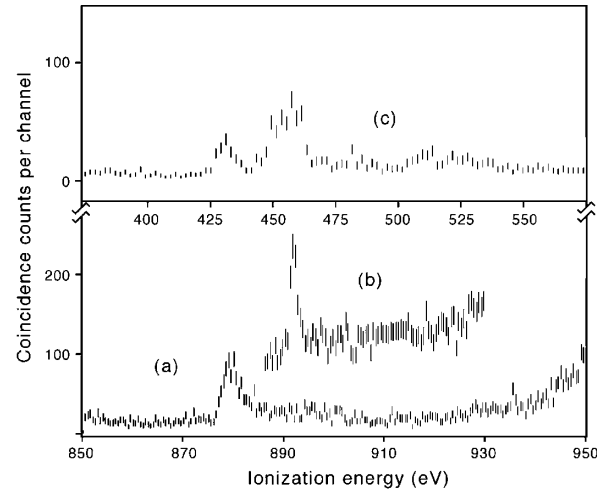


FIG. 3. Spectra for  $\text{NH}_3$  ionization at  $h\nu = 950$  eV. (a) Preedge  $2h-1p$  singly ionized states from twofold coincidences after background subtraction compared with a simply filtered DCH spectrum (b) from the data of Fig. 1(b). (c) Spectrum of doubly charged products in coincidence with the  $2h-1p$  peak at 880 eV shown in (a). The peak at 432 eV represents direct core-valence ionization which occurs for all energies of the electrons, while the peak at 456 eV appears only in coincidence with  $70 \pm 5$  eV electrons from formation of the  $2h-1p$  “resonance.”

where  $\text{ERC}(S_i^{-2})$  is the excess generalized relaxation energy. From Eqs. (1)–(3) we find

$$\Delta E(S_i^{-2}) = V_{S_i S_i S_i S_i} - \text{ERC}(S_i^{-2}). \quad (5)$$

In Table I we present correspondingly the values  $\text{ERC}(S_i^{-2})/2$ . According to second-order perturbation theory,  $\text{ERC}(S_i^{-2})$  should be approximately twice the SCH relaxation energy  $R(S_i^{-1})$  [11]. The difference between the  $\Delta\text{SCF}$  calculation for IP and the binding energy  $-\epsilon_{S_i}$  obtained by the HF calculation gives the strict relaxation energy  $R(S_i^{-1})$  for which this relation holds. We thus compare the values of  $\text{ERC}(S_i^{-2})/2$  extracted from the experiments and CASSCF calculations with *ab initio* values of  $R(S_i^{-1})$  thus obtained. A reasonable agreement confirms the validity of the present treatment.

The  $1s^{-2}$  DCH states themselves are single valued apart from vibrational structure, which from comparison with the SCH spectra can be expected to be resolvable for  $\text{CH}_4$  but are less likely to be resolved for  $\text{NH}_3$ . By contrast, the CVV, the fourfold valence (VVVV) ionized, and the preedge spectra will contain manifolds of electronic states. Because the overlap of the valence ( $2p$ -based) orbitals with  $1s$  is weak, we expect the CVV spectra to resemble the pure double valence (VV) ionization spectra [29] quite closely, with little spin splitting from the core. In  $\text{NH}_3$ , the low energy VV spectrum contains three main bands covering a range of about 10 eV from the ionizations  $3a_1^{-2}$ ,  $1e^{-1}3a_1^{-1}$ , and  $1e^{-2}$  relative to the ground state configuration  $1s^2 2s^2 1e^4 3a_1^2$ . The measured and calculated Auger spectra [30] contain bands from higher configurations extending up to 35 eV above the lowest state. The CVV complex seen in Fig. 2 at around 475 eV is about 20 eV wide, compared with an estimated experimental resolution of 9 eV, so the DCH decay may populate states from all the configurations. To calculate the energies of the CVV states, the same SA-CASSCF method was used, with frozen HF orbitals of the neutral molecules for  $1s$ . The calculated energies of the CVV states associated with the configurations  $1s^{-1}3a_1^{-2}$ ,  $1s^{-1}1e^{-1}3a_1^{-1}$ ,  $1s^{-1}1e^{-2}$ ,  $1s^{-1}2s^{-1}3a_1^{-1}$ , and  $1s^{-1}2s^{-1}1e^{-1}$  are shown as bars in Fig. 2. From these calculations we can say that the states associated with the first three configurations cover the range from 470 to 497 eV, a 27 eV range, in close agreement with the model of a displaced VV spectrum. For the final quadruply ionized products our theoretical calculations of the states of an imaginary intact  $\text{NH}_3^{4+}$  molecule also agree well with experimental results. For  $\text{CH}_4$  the CVV triply ionized states are calculated to lie in a range from 352 to 373 eV, in line with experiment, while the VVVV states are predicted in the range 119–145 eV [31].

In summary, we have demonstrated that an efficient multiple coincidence technique makes it possible to acquire spectra of single-site DCH states in molecules formed by single photon ionization, without the need for intense soft x rays from a FEL. The  $1s^{-2}$  DCH states of  $\text{CH}_4$  and  $\text{NH}_3$  have been located. The coincidence technique allows the related preedge resonances and the decay pathways of all the

core-hole and core-excited states to be extracted from a single set of experimental data. The energies of the DCH states themselves and of the states involved in their decay can be accurately calculated and physically understood; similar calculations may guide future experiments.

This work has been financially supported by the Swedish Research Council (VR), the Göran Gustafsson Foundation (UU/KTH), and the Knut and Alice Wallenberg Foundation, Sweden. This work was also supported by the European Community–Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”—Contract No. R II 3-CT-2004-506008). M. E. acknowledges the support from JST-CREST and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science, as well as from the Next Generation Supercomputing Project. K. U. acknowledges the support for the X-ray Free Electron Laser Utilization Research Project of Ministry of Education, Culture, Sports, Science and Technology of Japan.

- 
- [1] C. P. Bhalla, *Phys. Rev. A* **12**, 122 (1975).
  - [2] R. P. Madden *et al.*, *Phys. Rev. Lett.* **10**, 516 (1963).
  - [3] H. Ågren *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **14**, 27 (1978).
  - [4] R. D. Deslattes *et al.*, *Phys. Rev. A* **27**, 923 (1983).
  - [5] W. Wölfi *et al.*, *Phys. Rev. Lett.* **35**, 656 (1975).
  - [6] M. Deutsch and M. Hart, *Phys. Rev. A* **29**, 2946 (1984).
  - [7] S. T. Salem and A. Kumar, *J. Phys. B* **19**, 73 (1986).
  - [8] T. Kaneyasu *et al.*, *Phys. Rev. A* **76**, 012717 (2007).
  - [9] J. Hozzowska *et al.*, *Phys. Rev. Lett.* **102**, 073006 (2009).
  - [10] S. H. Southworth *et al.*, *Phys. Rev. A* **67**, 062712 (2003).
  - [11] L. S. Cederbaum *et al.*, *J. Chem. Phys.* **85**, 6513 (1986).
  - [12] H. Ågren *et al.*, *Chem. Phys.* **172**, 45 (1993).
  - [13] L. S. Cederbaum, *Phys. Rev. A* **35**, 622 (1987).
  - [14] L. S. Cederbaum *et al.*, *J. Chem. Phys.* **86**, 2168 (1987).
  - [15] E. M.-L. Ohrendorf *et al.*, *Chem. Phys. Lett.* **183**, 1 (1991).
  - [16] R. Santra, N. V. Kryzhevoi, and L. S. Cederbaum, *Phys. Rev. Lett.* **103**, 013002 (2009).
  - [17] M. Tashiro *et al.*, *J. Chem. Phys.* **132**, 184302 (2010).
  - [18] M. Tashiro, M. Ehara, and K. Ueda, *Chem. Phys. Lett.* **496**, 217 (2010).
  - [19] M. Hoener *et al.*, *Phys. Rev. Lett.* **104**, 253002 (2010).
  - [20] L. Young *et al.*, *Nature (London)* **466**, 56 (2010).
  - [21] J. H. D. Eland *et al.* (to be published).
  - [22] D. R. Batchelor *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. A* **467–468**, 470 (2001).
  - [23] J. H. D. Eland *et al.*, *Phys. Rev. Lett.* **90**, 053003 (2003).
  - [24] J. H. D. Eland *et al.*, *Chem. Phys. Lett.* **485**, 21 (2010).
  - [25] J. W. D. Connolly *et al.*, *J. Chem. Phys.* **58**, 4265 (1973).
  - [26] H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985).
  - [27] T. H. Dunning Jr., *J. Chem. Phys.* **90**, 1007 (1989).
  - [28] H.-J. Werner *et al.*, MOLPRO, version 2008.
  - [29] J. H. D. Eland, *Chem. Phys.* **323**, 391 (2006).
  - [30] F. Tarantelli *et al.*, *Chem. Phys. Lett.* **117**, 577 (1985).
  - [31] M. Tashiro *et al.* (to be published).