Evidence of Single-Photon Two-Site Core Double Ionization of C_2H_2 Molecules

P. Lablanquie,[1,2] T. P. Grozdanov,[3] M. Žitnik,[4] S. Carniato,[1,2] P. Selles,[1,2] L. Andric,[1,2] J. Palaudoux,[1,2] F. Penent,[1,2]
H. Iwayama,[5] E. Shigemasa,[5] Y. Hikosaka,[6] K. Soejima,[6] M. Nakano,[7] I. H. Suzuki,[7] and K. Ito[7]
[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]*Institute of Physics, University of Belgrade, Pregrevica118, 11080 Belgrade, Serbia*
[4]*Jožef Stefan Institute, P. O. Box 3000, SI-1001 Ljubljana, Slovenia*
[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*
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We observe the formation in a single-photon transition of two core holes, each at a different carbon atom of the C_2H_2 molecule. At a photon energy of 770.5 eV, the probability of this 2-site core double ionization amounts to $1.6 \pm 0.4\%$ of the 1-site core double ionization. A simple theoretical model based on the knockout mechanism gives reasonable agreement with experiment. Spectroscopy and Auger decays of the associated double core hole states are also investigated.

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Double ionization (DI) of multibody systems following the absorption of a single photon offers a particularly interesting way to study the effects of electron-electron interaction. In the last decade much progress has been achieved both in the experimental and theoretical description of the double ionization process for He [1] and H_2 [2]. More recently, new aspects of the problem have been revealed in heavier atomic systems involving double K-shell ionization [3,4], and in weakly bound systems such as van der Waals clusters [5] and He_2 dimers [6]. One other important and interesting aspect of electron correlation would be to study single-photon double ionization involving K-shell electrons belonging to two different atoms in a molecule. However, this process is expected to be of extremely low cross section and has not, to our knowledge, been investigated in ordinary molecules, apart from the exotic He_2 system [6].

In this Letter we present the first observations of the single-photon 2-site core DI in a molecule, namely C_2H_2. At 770.5 eV photon energy its probability is measured to be as low as $2.2 \pm 0.6 \times 10^{-5}$ with respect to the single K-shell ionization, and $1.6 \pm 0.4 \times 10^{-2}$ with respect to the double ionization of two K-shell electrons from the same atomic site (1-site core DI process). The additional interest of our work lies in the possibility to explore the detailed spectroscopy of double core hole (DCH) states. Its importance had been pointed out already 25 years ago by Cederbaum *et al* who predicted that the creation of a double core hole, each at a different atomic site, shows more sensitive chemical shifts than conventional inner-shell spectroscopy [7]. Theoretical interest in DCHs revived [8,9] with the arrival of x-ray free electron lasers (XFELs) and with the possibility to create DCHs in a 2-photon process. One-site DCH formation has been observed recently both using XFELs [10] and synchrotron radiation [11,12], but the more informative 2-site DCH signal had escaped detection up to now. In XFEL experiments this signal is masked by strong contribution from ionization of ionic fragments and could be isolated only very recently [13]. The present experiment uses an alternative, single photoionization path to create DCHs and, in addition, it makes it possible to follow their decay thanks to the sensitivity of the coincidence techniques.

Experiments were performed at the undulator beam line BL-16A of the Photon Factory synchrotron, operated in single-bunch top-up mode. We used a magnetic bottle time-of-flight analyzer. Its characteristics and the acquisition procedure have been described in detail previously [14], so that only important points for this study are recalled here. Detection efficiency was calibrated with $3d$ photoelectron-Auger electron coincidences in Kr and found to decrease slowly with electron kinetic energy E from $75 \pm 5\%$ ($E = 0$ eV) to $43 \pm 5\%$ ($E = 800$ eV). The 15 ns detector dead time prevents detection of electrons with close energies; in practice, after detection of a 250 eV electron, the following electron must be of less than 220 eV to be detected. In order to observe the weak 2-site core DI process, a 12 hours long multielectron coincidence data set was accumulated at photon energy 770.5 ± 0.5 eV and 0.3 eV bandwidth. To minimize false coincidences the count rate was limited to 20 kHz, corresponding to an average of one ionization per every 80 light bunches.

Figure 1 shows the evidence concerning DCH states in a C_2H_2 molecule. First, Fig. 1(a) presents the signal of populated 1-site DCH states. This is retrieved following the procedure we used in our previous work [11], by constructing the histogram of the sum of the energies of the two associated photoelectrons, when detected in coincidence

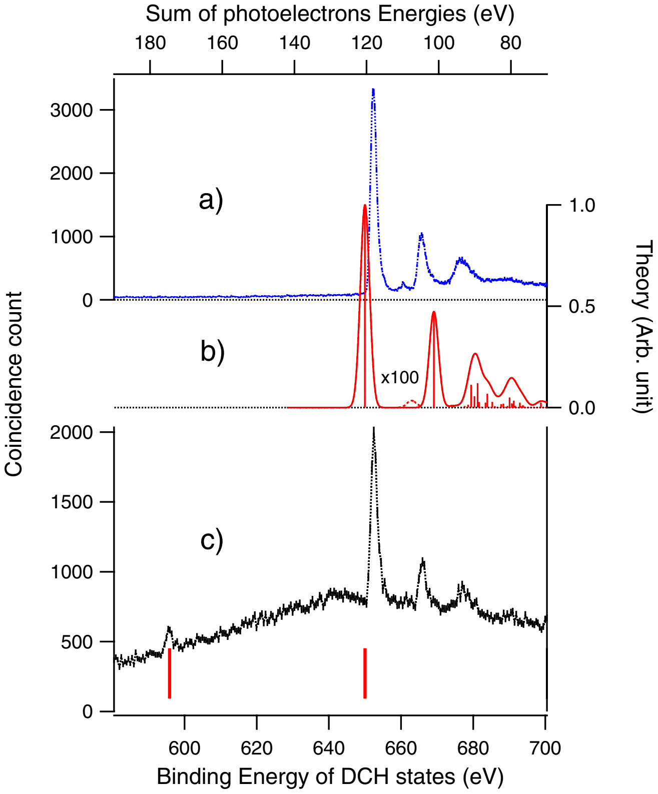

FIG. 1 (color online). (a) Histogram of the sum of the energies of the 2 photoelectrons associated with core DI, when detected in coincidence with the two released Auger electrons of 200–270 and 270–320 eV. (b) Our predictions for the 1-site DCH spectrum (bars convoluted with a 3 eV FWHM Gaussian to mimic experimental resolution). A ×100 magnifying factor is used to visualize the position of the lowest energy satellite state (dotted line). (c) Same as in (a) but coincidence is with only one Auger electron of 230–250 eV. Electrons of less than 10 eV in (a) and (c) and of more than 60 eV in (c) have been discarded to reduce background. Vertical bars at the bottom correspond to our theoretical calculations for the position of the DCH main lines. A photon energy of $h\nu = 770.5$ eV was used.

with the two Auger electrons released upon their decay. The resultant spectrum shows the main line at 652.5 ± 0.5 eV (650.0 eV in our calculation) and a large probability for the formation of satellite states; it is very similar to what we obtained for the isoelectronic N_2 molecule [11]. As the two Auger electrons emitted on decay of a 2-site DCH are of similar energies and in the 220–250 eV range (as we will demonstrate later), our experiment cannot distinguish one from another. The 2-site DCH signal is therefore not present in the 4-electron coincidence spectra of Fig. 1(a), but is revealed at 595.6 ± 0.5 eV in Fig. 1(c) when considering 3-electron coincidence events. This peak is predicted at a very close binding energy of 595.86 eV in our density-functional theory calculation performed with the B3LYP exchange-correlation functional of the GAMESS(US) package [15]. Energy splitting between the 1-site and 2-site DCHs was underestimated by earlier calculations [7], but is well reproduced both here and in the recent calculations by Tashiro *et al.* [9].

The theoretical profiles for the 1-site DCH satellite states in Fig. 1(b) were estimated in the sudden approximation [16]. They are proportional to the overlaps between the N-2 electronic wave functions of the ground and core-ionized states. Our calculations in Fig. 1(b) match very well our experimental observation. They show that the first satellite band of the observed 665.5 eV binding energy originates from a $\pi_u \rightarrow \pi_g$ excitation while the second band at 677 eV contains multiple unresolved components. Experiment detects a weak satellite line at 660.5 eV. A $\pi_u \rightarrow \pi_g$ satellite state is predicted in this region, but is found to be of weak intensity in our calculations. As they rely on the sudden approximation, a different mechanism for its formation, such as conjugate shakeup, is suggested.

From the number of coincidence events and taking into account detection efficiencies, we estimate the experimental probability ${P_X}^{\mathrm{exp}}$ of 1-site ($X = 1\mathrm{si}$) and 2-site ($X = 2\mathrm{si}$) core DI, with respect to the dominant K-shell single ionization. We deduce ${P_{1\mathrm{si}}}^{\mathrm{exp}} = (13.6 \pm 3) \times 10^{-4}$ and ${P_{2\mathrm{si}}}^{\mathrm{exp}} = (2.2 \pm 0.6) \times 10^{-5}$, so that the experimental ratio of the 2-site to 1-site core DI is $R^{\mathrm{exp}} = 1.6 \pm 0.4\%$. It turns out that these values are in reasonable agreement with relatively simple theoretical arguments. Similar to several previous treatments of DI in atoms [4,17], the probabilities are calculated by incoherent summation of two contributions coming from the shakeoff (SO) and knockout (KO) mechanisms: $P_X = P_X^{\mathrm{SO}} + P_X^{\mathrm{KO}}$.

The probability ${P_{1\mathrm{si}}}^{\mathrm{SO}}(\varepsilon)$ of the SO mechanism as a function of the photon excess energy ε over the C_2H_2 carbon K-shell double ionization threshold is estimated by the Thomas formula [18] (see also [19] and Eq. 7 of [20]) with the following three parameters: the binding energy of the $1s$ electron of the $C^+(1s^{-1})$ ion (358.47 eV), the K-shell radius ($r_{1s} \approx 0.14$ Å), and the asymptotic probability ${P_{1\mathrm{si}}}^{\mathrm{SO}}(\infty) = 0.0019$. The latter is related to the rapid removal of an atomic electron due to photoabsorption and calculated from the overlap of the atomic (C) and ionic $C^+(1s^{-1})$ $1s$ orbitals [21]. It follows that ${P_{1\mathrm{si}}}^{\mathrm{SO}} \approx 5 \times 10^{-4}$ at experimental excess energy, still much smaller probability than its asymptotic value.

The KO mechanism is dominant at lower photon energies: it is assumed that the first (primary) K-shell electron absorbs a photon in the vicinity of a nucleus and afterwards collides with either the second K-shell electron on the same site (the KO-1site process [17]) or with one of the two K-shell electrons on the other site (the KO-2site process [6]), the net result being that both colliding electrons end up in the continuum. Following [4,17], the KO-1site contribution is estimated by ${P_{1\mathrm{si}}}^{\mathrm{KO}}(\varepsilon) = a{\sigma_{1s}}^{+}(\varepsilon)$ where ${\sigma_{1s}}^{+}$ is the cross section for electron impact K-shell ionization of the $C^+(1s^{-1})$ ion, calculated here by using the binary encounter Bethe (BEB) model (Eq. 6 with $N = 1$ of

[22]). The proportionality factor $a = 3.8 \times 10^{20}$ m^{-2} is determined by requiring that the maximum value $P_{1\mathrm{si}}{}^{\mathrm{max}}$ obeys the empirical $1/Z^{1.6}$ scaling with the atomic number Z [4,20]. At an experimental photon energy 770.5 eV, this leads to $P_{1\mathrm{si}}{}^{\mathrm{KO}} = 1.9 \times 10^{-3}$, giving finally $P_{1\mathrm{si}} = 2.4 \times 10^{-3}$. The discrepancy with respect to the experimental value $P_{1\mathrm{si}}{}^{\mathrm{exp}}$ may be attributed to an overestimation of $P_{1\mathrm{si}}{}^{\mathrm{max}}$ in [4,20] that likely includes an unresolved contribution of M satellites.

Turning now to the 2-site DI process, the SO contribution has been neglected, $P_{2\mathrm{si}}{}^{\mathrm{SO}} \approx 0$, as it follows from the estimates based on the Thomas model and the fact that the initial-state correlations [19] are considerably smaller for the K-shell electrons belonging to different C sites. The probability for the 2-site KO process is written as the product of two factors: $P_{2\mathrm{si}}{}^{\mathrm{KO}} = P_\Omega P_{1s}{}^{M}$. The first factor is purely geometrical $P_\Omega \approx r_{1s}^2/4R_{\mathrm{CC}}^2 = 3.4 \times 10^{-3}$ and gives the probability that the primary electron is ejected from one C site into the solid angle, defined by the spherical interaction region of radius r_{1s}, centered at the other C site at distance $R_{\mathrm{CC}} = 1.203$. The second factor $P_{1s}{}^{M} \approx \sigma_{1s}{}^{M}/\pi r_{1s}^2$ is the probability for the K-shell ionization at the opposite C site in the molecule C_2H_2 by the primary electron impact. The ionization cross section $\sigma_{1s}{}^{M} = c\sigma_{1s}$ is assumed to be proportional to the atomic ionization cross section σ_{1s}. The constant c is roughly estimated by the ratio of "survival probabilities" of the projectile when traversing the valence shells of the oriented molecule and randomly oriented atom. Assuming that the main loss mechanism of the primary electron is the ionization of valence electrons, we find $c = (1 - P_{2s}/2 - 3P_{2p}/2)/(1 - P_{2s} - P_{2p})$, where $P_{2s} = \sigma_{2s}/\pi r_{2s}^2$ and $P_{2p} = \sigma_{2p}/\pi r_{2p}{}^2$ are probabilities for ionization of $2s$ and $2p$, atomic electrons. The two prefactors in the numerator take into account that the two electrons of the σ bond in C_2H_2 occupy two hybridized sp orbitals. Using $r_{2s} \approx r_{2p} \approx 0.65$ Å and employing the BEB model (Eq. 1 with $N = 2$ of [23]) to calculate the σ_{2s} and σ_{2p} at electron impact energy 478.97 eV (equal to the photon excess energy above the first K-shell ionization threshold at 291.53 eV), we find $c \approx 0.69$. The atomic ionization cross section σ_{1s} is calculated at the same electron impact energy (Eq. 1 with $N = 2$ in [22]), so that finally $P_{2\mathrm{si}} \approx P_{2\mathrm{si}}{}^{\mathrm{KO}} \approx 7.7 \times 10^{-5}$. Although of the same order of magnitude, this value is 3.5 times higher than the experimental value. The estimated ratio $R = P_{2\mathrm{si}}/P_{1\mathrm{si}} \approx 3.2\%$ is twice the observed value $R^{\mathrm{exp}} = 1.6\%$. As the de Broglie wavelength of the primary electron (0.8 Å) is in fact comparable to R_{CC}, a full quantum treatment of the scattering problem with reliable estimates of satellite intensities may be required to further improve the agreement with the experimental data.

We examine now the Auger decay of the 1-site and 2-site DCHs. The spectra of the two Auger electrons emitted upon decay of the different DCH states are compared in Fig. 2 with the Auger spectrum associated with the decay of the single $1s$ core hole [Fig. 2(d)]. Decay of the 1-site DCH main line [Fig. 2(b)] and of the main satellite line at 665.5 eV [Fig. 2(c)] present similar characteristics as what we observed for the isoelectronic N_2 case [11]: the first hypersatellite Auger electron is found in the 270–340 eV kinetic energy range (solid line) and is faster than K-VV Auger electrons [Fig. 2(d)]. The second satellite Auger electron released in the last step of the decay is found in the 200–270 eV range (dotted lines). The predominance of the spectator decay for the DCH satellite state is evidenced by the similarity of the Auger spectra in Figs. 2(b) and 2(c). A shoulder at 314 eV in Fig. 2(c) indicates nevertheless presence of the participator decay. As for the 2-site DCH decay, Fig. 2(a) demonstrates that the two Auger electrons are emitted with similar energies and in the 220–250 eV

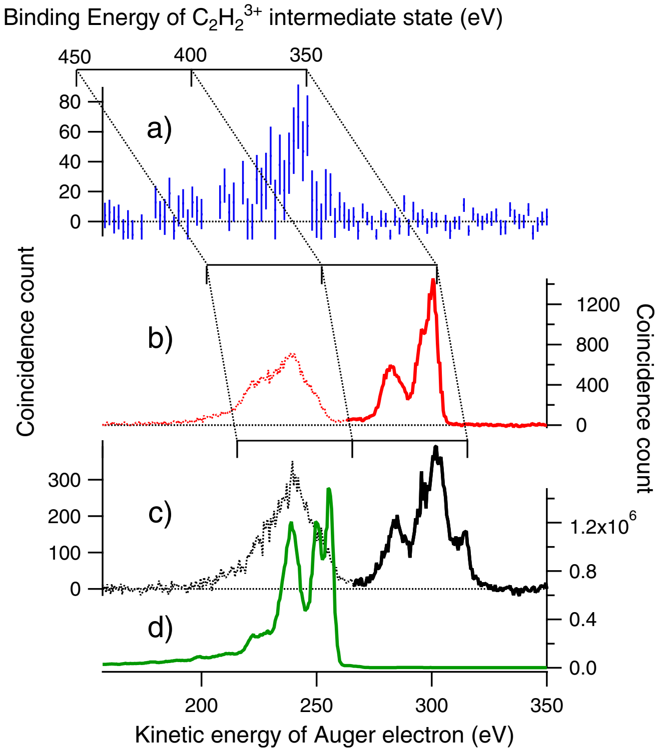

FIG. 2 (color online). Auger spectra associated with the decay of: (a) a 2-site DCH, (b) a 1-site DCH, (c) a 1-site DCH satellite and (d) a single K-shell core hole, (d) was obtained from coincidences with a $1s$ photoelectron. (a) to (c) was obtained from coincidences with a pair of photoelectrons whose energy sum defines the corresponding DCH states. Four-electron coincidence events were used for (b) and (c) and 3-electron ones for (a). Background was estimated from adjacent zones of energy sums and subtracted. In (b) and (c) the solid line displays the first emitted hypersatellite Auger electron, while the dotted line corresponds to the second emitted, satellite Auger electron; the top scale applies only for the first hypersatellite Auger electron (solid line).

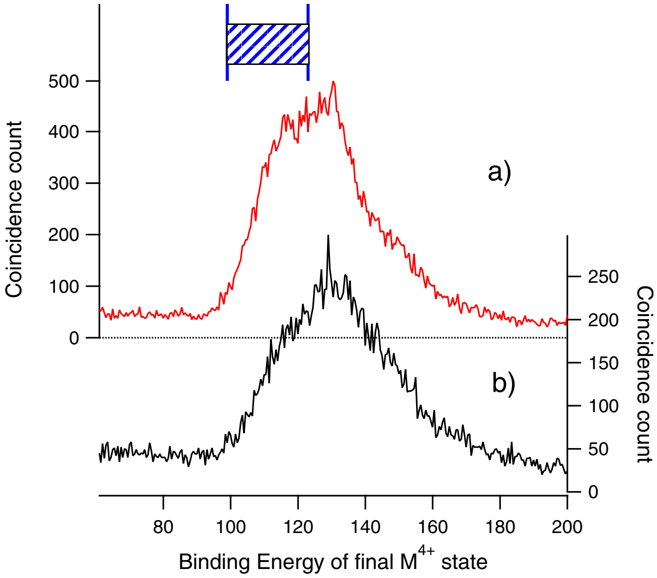

FIG. 3 (color online). Binding energy of the $C_2H_2{}^{4+}$ final states populated by the complete Auger decay of 1-site (a) and 1-site satellite (b) DCHs. They are deduced from 4-electron coincidence events and the histogram of $h\nu$ (sum of 4 electron energies). Events with electrons of less than 10 eV were discarded to reduce background.

range. The binding energies of the $C_2H_2{}^{3+}$ intermediate states created in the first step of the Auger cascade are indicated in Fig. 2. They are equal to $h\nu - (E_{\mathrm{Ph1}} + E_{\mathrm{Ph2}} + E_{\mathrm{Auger1}})$ where E_{Phi} and E_{Auger1} are the kinetic energies of the ith photoelectron and the 1st Auger, respectively. Figures 2(a) and 2(b) suggest that similar $C_2H_2{}^{3+}$ intermediate states are reached in the decay of 2-site and 1-site DCHs, whereas more excited intermediate states result from the decay of 1-site satellite DCHs [Fig. 2(c)].

The binding energies of the final $C_2H_2{}^{4+}$ states populated by the complete decay of the DCHs can be retrieved by considering the complete energy balance of the 4 released electrons. This can be done exactly only for the 1-site DCHs, where we observe that satellite decay [Fig. 3(b)] leads to energetically higher excited final states than the main line [Fig. 3(a)]. On the other hand, 2-site DCH states decay to lower lying $C_2H_2{}^{4+}$ states. Here only the energy region is proposed (the blue hatched zone) as only the energy range of the two released Auger electrons is measured, and not their energy correlation. This reasoning also demonstrates that our observations are compatible with a sequential decay of the two 1s core holes of the 2-site DCHs. Further research is needed to evidence a possible concerted decay.

In conclusion, single-photon 2-site core DI is found to be $2.2 \pm 0.6 \times 10^{-5}$ times less intense than single core ionization for 770 eV photons. A KO mechanism with inclusion of the bond electrons' scattering effect confirms this order of magnitude but predicts a somewhat higher value. The same method, used for different excess energies and different systems (and especially comparison between C_2H_2, C_2H_4 and C_2H_6) is expected to provide valuable information on the DI processes at play.

Our results also bring important information on the spectroscopy, chemical shifts, and decay paths of the 1-site and 2-site DCHs. These properties can in principle be obtained more readily by XFEL experiments where DCHs can be abundantly created in a 2-photon ionization mechanism, if the time scale of the interaction is short enough compared to the lifetimes of inner-shell holes. The "soft" single-photon path that we use creates an electron probe inside the molecule, and creates very few DCHs; it offers, however, a powerful alternative to the 2-photon route used in XFEL experiments, thanks to the sensitivity of the coincidence techniques. This also suggests that implementation of such techniques in XFEL experiments would be very profitable. Finally our results are very important in understanding the mechanism of the basic first step processes occurring when imaging proteins with XFELs [24,25].

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[1] L. Avaldi and A. Huetz, J. Phys. B **38**, S861 (2005).
[2] T. J. Reddish *et al.*, Phys. Rev. Lett. **100**, 193001 (2008) and references therein.
[3] S. Huotari *et al.*, Phys. Rev. Lett. **101**, 043001 (2008).
[4] J. Hoszowska *et al.*, Phys. Rev. Lett. **102**, 073006 (2009); Phys. Rev. A **82**, 063408 (2010).
[5] L. S. Cederbaum, J. Zobeley, and F. Tarantelli, Phys. Rev. Lett. **79**, 4778 (1997); N. Sisourat *et al.*, Nature Phys. **6**, 508 (2010).
[6] T. Havermeier *et al.*, Phys. Rev. Lett. **104**, 153401 (2010).
[7] L. S. Cederbaum *et al.*, J. Chem. Phys. **85**, 6513 (1986).
[8] R. Santra, N. V. Kryzhevoi, and L. S. Cederbaum, Phys. Rev. Lett. **103**, 013002 (2009).
[9] M. Tashiro *et al.*, J. Chem. Phys. **132**, 184302 (2010).
[10] L. Fang *et al.*, Phys. Rev. Lett. **105**, 083005 (2010).
[11] P. Lablanquie *et al.*, Phys. Rev. Lett. **106**, 063003 (2011).
[12] J. Eland *et al.*, Phys. Rev. Lett. **105**, 213005 (2010).
[13] N Berrah *et al.*, Proc. Natl. Acad. Sci. U.S.A. **108**, 16912 (2011).
[14] K. Ito *et al.*, Rev. Sci. Instrum. **80**, 123101 (2009) and references therein
[15] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).
[16] S Carniato *et al.*, (to be published).

[17] T. Schneider and J. M. Rost, Phys. Rev. A **67**, 062704 (2003).
[18] T. D. Thomas, Phys. Rev. Lett. **52**, 417 (1984).
[19] T. Pattard *et al.*, J. Phys. B **36**, L189 (2003).
[20] E. P. Kanter *et al.*, Phys. Rev. A **73**, 022708 (2006).
[21] R. C. Forrey *et al.*, Phys. Rev. A **51**, 2112 (1995).
[22] J. P. Santos *et al.*, J. Phys. B **36**, 4211 (2003).
[23] Y. K. Kim and J. P. Desclaux, Phys. Rev. A **66**, 012708 (2002).
[24] H. N. Chapman *et al.*, Nature (London) **470**, 73 (2011).
[25] M. M. Seibert *et al.*, Nature (London) **470**, 78 (2011).