Single Photon K^{-2} and $K^{-1}K^{-1}$ Double Core Ionization in C_2H_{2n} ($n = 1$–3), CO, and N_2 as a Potential New Tool for Chemical Analysis

M. Nakano,[1,2] F. Penent,[3,4,*] M. Tashiro,[5] T. P. Grozdanov,[6] M. Žitnik,[7] S. Carniato,[3,4] P. Selles,[3,4]
L. Andric,[3,4] P. Lablanquie,[3,4] J. Palaudoux,[3,4] E. Shigemasa,[5] H. Iwayama,[5] Y. Hikosaka,[8]
K. Soejima,[8] I. H. Suzuki,[1] N. Kouchi,[2] and K. Ito[1]

[1]*Photon Factory, Institute of Materials Structure Science, Oho, Tsukuba 305-0801, Japan*
[2]*Department of Chemistry, Tokyo Institute of Technology, O-okayama, Tokyo 152-8551, Japan*
[3]*UPMC, Université Paris 06, LCPMR, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[4]*CNRS, LCPMR (UMR 7614), 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[5]*Institute for Molecular Science, Okazaki 444-8585, Japan*
[6]*Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*
[7]*Jožef Stefan Institute, P.O. Box 3000, SI-1001 Ljubljana, Slovenia*
[8]*Department of Environmental Science, Niigata University, Niigata 950-2181, Japan*
(Received 14 November 2012; published 18 April 2013)

We have observed single photon double K-shell photoionization in the C_2H_{2n} ($n = 1$–3) hydrocarbon sequence and in N_2 and CO, using synchrotron radiation and electron coincidence spectroscopy. Our previous observations of the K^{-2} process in these molecules are extended by the observations of a single photon double photoionization with one core hole created at each of the two neighboring atoms in the molecule ($K^{-1}K^{-1}$ process). In the C_2H_{2n} sequence, the spectroscopy of $K^{-1}K^{-1}$ states is much more sensitive to the bond length than conventional electron spectroscopy for chemical analysis spectroscopy based on single K-shell ionization. The cross section variation for single photon $K^{-1}K^{-1}$ double core ionization in the C_2H_{2n} sequence and in the isoelectronic C_2H_2, N_2 and CO molecules validates a knock-out mechanism in which a primary ionized $1s$ photoelectron ejects another $1s$ electron of the neighbor atom. The specific Auger decay from such states is clearly observed in the CO case.

Electron spectroscopy for chemical analysis (ESCA) [1] is a very powerful analytical method relying on the chemical shift that reflects the environment of a given atom in a molecule. For hydrocarbon molecules this shift is generally very small but, it was predicted [2] that double K-shell ($K^{-1}K^{-1}$) ionization in C_2H_{2n} ($n = 1$–3) series could reveal a much stronger effect. More than two decades later, the perspective of new experiments using x-ray free electron laser (XFEL) stimulated theoreticians to develop new models and methods [3,4] to study double-core-hole (DCH) states and resuscitated earlier studies [2,5]. The very high photon flux delivered by XFEL opens the possibility of x-ray two-photon photoelectron spectroscopy (XTPPS) [3,4] due to possible multiphoton inner-shell ionization in a time scale (~ 5 fs) shorter than Auger lifetime [6]. Recently, DCH states, resulting from double K-shell ionization in the same or in different atoms in a molecule, were indeed observed experimentally with XFEL [6,7] but also with synchrotron light sources [8–10]. The proof of principle of XTPPS [3,4] on two different atoms in a molecule was demonstrated on CO [7] and further extended to other molecules [11]. However, present self-amplified spontaneous emission operation mode of XFELs results in low photon resolution [11] and technical improvements are needed before XTPPS could be considered as a routine technique similar to

''conventional'' ESCA [1,12]. We present here the results obtained with the alternative spectroscopic method for the study of DCH states that is based on single photon double K-shell ionization and electron coincidence spectroscopy [9,10]. We have obtained high resolution spectroscopy of DCH states for C_2H_{2n}, ($n = 1$–3), N_2, and CO molecules that compares very well with present theories [13] and validates the original proposal [2]. The knock-out (KO) mechanism [10] for single photon creation of $K^{-1}K^{-1}$ DCH states is validated and confirms the dependence of the probability of the process on the bond lengths in the sequence C_2H_{2n}, ($n = 1$–3). The full Auger decay of $K^{-1}K^{-1}$ DCH states is extracted in the CO case.

The experimental setup and procedure are those used in previous experiments [9,10] and only a short description is given here, with more details being given in Ref. [14]. The experiments were performed on BL-16 undulator beam line at the Photon Factory (PF) operated in single bunch with top up. The photon flux in the interaction region is about 10^{10} ph/s with a resolution of $\Delta h\nu \approx 150$ meV at $h\nu = 750$ eV.

The 2.5 m long magnetic bottle time of flight electron spectrometer [14] provides a good energy resolution, $\Delta E/E = 1.6\%$, and allows the detection of electrons with very high efficiency ($\eta = 70 \pm 5\%$ below 200 eV, $\eta = 50 \pm 5\%$ around 500 eV) [10]. Four-electron

coincidence events, that are the signature of DCH states formation and decay are hence detected with a typical 15%–20% efficiency. Time of flight to energy conversion is determined using Ar(2p) photoelectrons at different kinetic energies $KE = h\nu\text{-IP(Ar}2p)$ after calibration of photon energy on the well-known atomic and molecular (Ar, O_2, Ne) inner-shell resonances.

Data accumulation was performed with electron count rates around 20 kHz ($\ll$ 1.6 MHz single bunch frequency) keeping random coincidences negligible. The prominent process is single K-shell ionization followed by single Auger decay. K^{-2} and $K^{-1}K^{-1}$ double ionization processes correspond to typical 10^{-3} and 10^{-5} fractions of this process [9,10]. Accumulation times of about 12 h allow the extraction of 3 and 4 electron coincidence events with sufficient statistical accuracy.

In Fig. 1(a), we present the results obtained for C_2H_{2n} ($n = 1$–3) molecules by filtering out four-electron coincidence events [9,10], two photoelectrons and two Auger electrons: hypersatellite Auger electron in the energy range [270–320 eV] and second Auger electron [200–270 eV]. The three molecules were studied successively at fixed and stable photon energy of 770 eV to obtain very accurate relative energy shifts in the C_2H_{2n} series. We plot the number of coincidence events as a function of the binding energy (BE) of the DCH states: $BE = h\nu\text{-}(E_{Ph1} + E_{Ph2})$ where $E_{Ph1} + E_{Ph2}$ is the sum of the two photoelectrons energies. We observe clearly K^{-2} states and also satellite

FIG. 1. Spectroscopy of K^{-2} double core hole states and satellites. (a) C_2H_{2n} ($n = 1$–3) at $h\nu = 770$ eV. (b) CO at $h\nu = 953.6$ eV. (c) N_2 at $h\nu = 1005$ eV.

peaks ($K^{-2}V^{-1}V'$) where a valence electron from orbital V is excited simultaneously to a vacant orbital V' [9,10]. The relative chemical shifts for C_2H_{2n} ($n = 1$–3) K^{-2} states, reported in Table I, are stronger than for the K^{-1} case [15], but with moderate energy resolution (~ 2 eV here), this would not allow a clear differentiation between C_2H_4 and C_2H_6. Nevertheless, the satellite structures are very distinctive of the different species and much more intense than in single ionization [9] and will be discussed in a forthcoming paper. Interestingly, between isoelectronic C_2H_2, CO [Fig. 1(b)], and N_2 [Fig. 1(c)] molecules, those satellite structures look rather similar.

The most important results, directly related to Cederbaum et al.'s original proposal [2], are shown in Fig. 2(a) where the signal associated with $K^{-1}K^{-1}$ two-site double ionization in C_2H_{2n} ($n = 1$–3) molecules clearly emerges from the statistical noise. The two Auger electrons emitted during the filling of each vacancy on different atoms have too close energies to allow detecting both of them, due to the dead time of the detection system (15 ns). Hence, as described in Ref. [10] in the case of C_2H_2, these results were obtained by filtering out three-electron events and selecting only one Auger electron, between the two emitted, in coincidence with two photoelectrons. Absolute energies and relative shifts with respect to C_2H_2 are reported in Table I. The very good agreement between experiment and recent theory [13] and also with present density-functional theory (DFT) calculations based on the model described in Refs. [9,10] shows that relaxation and correlation effects [16] are properly taken into account in both theoretical models.

The experimental branching ratios of the cross sections for $K^{-1}K^{-1}$ and K^{-2} double ionization to K^{-1} single ionization are given in Table I. These ratios are deduced experimentally from the number of recorded events taking into account the experimentally determined electron detection efficiencies [10]. It is possible to estimate these branching ratios by employing simple (semi)classical models based on an incoherent summation of the contributions of the shake-off (SO) and the KO ionization mechanisms (see Ref. [10] and references therein). In SO, the rapid photon absorption causes a sudden change of the potential seen by the second electron and therefore a non-zero probability of transition into the continuum. In KO the first electron absorbs a photon in the vicinity of a nucleus and afterwards collides either with the second K-shell electron on the same site or with one of the two K-shell electrons on the other site, the net result being that both colliding electrons end up in the continuum. In the case of a K^{-2} process the contribution of SO is estimated by using Thomas model [17] and KO contribution is proportional to the K-shell electron impact ionization cross section of the hollow atomic site [18]. Here, for an easier comparison between experimental and theoretical trends, a constant of proportionality for C-sites was fixed by
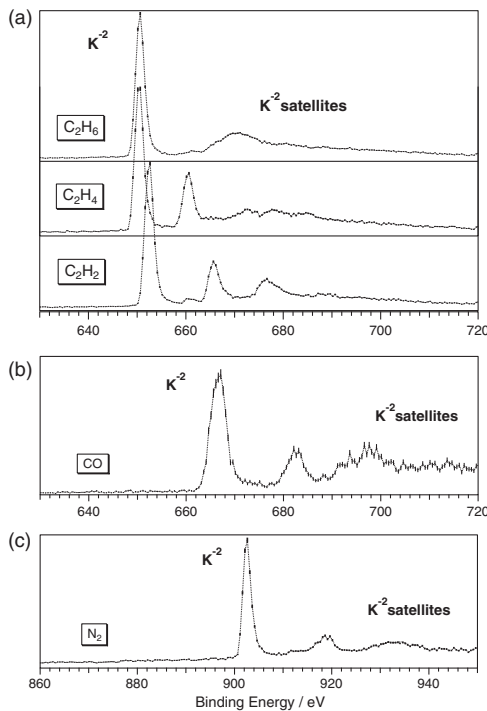
TABLE I. Binding energies and branching ratios for the K^{-2} and $K^{-1}K^{-1}$ double core hole states. Comparison between experiments and theories. Branching ratios are measured at photon energies of, respectively, 770, 953.6 and 1005 eV for the C_2H_{2n}, CO, and N_2 molecules. For CO, K^{-2} corresponds to the C1s core double ionization, as the O1s core double ionization channel at 1178 eV (Ref. [9]) is not open.

	K^{-2} binding energies (eV)				$K^{-1}K^{-1}$ binding energies (eV)				Branching ratios			
	This expt.	Calc. [13] CASSCF	This calc. DFT	Expt. [11]	This expt.	Calc. [13] CASSCF	This calc. DFT	Expt. [11]	K^{-2}/K^{-1} expt. ±20%	K^{-2}/K^{-1} theor.	$K^{-1}K^{-1}/K^{-1}$ expt. ±20%	$K^{-1}K^{-1}/K^{-1}$ theor.
C_2H_2	**652.5** ± 0.5	650.228	650.02		**596.0** ± 0.5	594.590	595.86		1.02 (−3)	1.02(−3)	2.0(−5)	2.00(−5)
C_2H_4	**650.4** ± 0.5	648.556	647.97		**593.3** ± 0.5	591.514	592.60		0.87 (−3)	1.02(−3)	1.34 (−5)	1.69(−5)
$\Delta E_{C_2H_4/C_2H_2}$	**−2.1** ± 0.2	−1.672	−2.05		**−2.7** ± 0.2		−3.26					
C_2H_6	**650.6** ± 0.5	648.827	648.11		**590.2** ± 0.5	589.007	589.47		1.15 (−3)	1.02(−3)	1.26 (−5)	1.32(−5)
$\Delta E_{C_2H_6/C_2H_2}$	**−1.9** ± 0.2	−1.401	−1.91		**−5.8** ± 0.2		−6.39					
N_2	**902.5** ± 1	901.155	900.41	903.3 ± 1.1	**835.9** ± 1	835.784	837.04	836.2 ± 1.6	0.66 (−3)	0.46(−3)	0.83 (−5)	0.96(−5)
CO	**666.7** ± 1	664.418	665.08	667.9 ± 3.6	**855.4** ± 1	854.743	855.0	855.3 ± 1.2	0.31 (−3)[a]	0.55(−3)[a]	1.9 (−5)[a]	1.08(−5)[a]

[a]For CO, K^{-1} includes C1s^{-1} (28%) and O1s^{-1} (72%).

adjusting the theoretical estimate of the branching ratio for C_2H_2 [10] to the experimental value at $h\nu = 770$ eV. The corresponding constant for N-sites was obtained according to the $1/Z^{1/6}$ scaling of the maximum values of the atomic branching ratios [19]. In the case of a $K^{-1}K^{-1}$ process it is assumed that the KO contribution determines the branching ratio and is given as a product of two factors [10]. The first is a geometric factor, proportional to $1/R^2$, where R is the bond length and the second factor is proportional to the K-shell ionization cross section of the second site by the primary electron. An overall multiplicative constant is again fixed by fitting the theoretical estimate of the branching ratio for C_2H_2 at $h\nu = 770$ eV to the experimental result. The same constant was used for all cases in Table I. All ionization cross sections were calculated using binary-encounter Bethe approximation [20].

In the case of a C_2H_{2n} sequence, as indicated in Table I, the model predicts the same K^{-2}/K^{-1} ratios, which, considering the error bars ($\sim 20\%$), agrees with the experiment. On the other hand, the systematic decrease of the experimental $K^{-1}K^{-1}/K^{-1}$ ratios along the C_2H_{2n} sequence is in agreement with the model's prediction that this ratio scales as $1/R^2$ with the C-C bond length (C ≡ C: 1.2 Å, C = C: 1.34 Å, C-C: 1.54 Å). This is a strong indication that the KO mechanism is predominantly responsible for the double site ionization process.

The results for N_2 and CO are presented in Figs. 1(b), 1(c), 2(b), and 2(c) and reported in Table I. We can observe, now, both K^{-2} and $K^{-1}K^{-1}$ states in N_2 while in our previous study [9], neither statistics nor resolution were good enough to reveal $K^{-1}K^{-1}$ states. For N_2, the theoretical estimates of branching ratios for both K^{-2} and $K^{-1}K^{-1}$ are in reasonable agreement with experiment (Table I).

In the case of CO, we chose a 953.6 eV photon energy to avoid any overlap between the energies of $O(K^{-1})$ and $C(K^{-1})$ photoelectrons and respective Auger electrons, and so that four electrons can be detected in coincidence with sufficient energy resolution for the $K^{-1}K^{-1}$ process.

Previously [9], we measured $[CO(K^{-2})]^{2+}$ level at 1178 ± 0.8 eV (two holes on the oxygen atom). At $h\nu = 953.6$ eV this channel is closed but both $[C(K^{-2})O]^{2+}$ [Fig. 1(b)] and $[C(K^{-1})O(K^{-1})]^{2+}$ [Fig. 2(b)] channels are open. The peak at 855.4 eV in Fig. 2(b), is unambiguously attributed to $[C(K^{-1})O(K^{-1})]^{2+}$ state formation. In the fourfold electron coincidences, random coincidences are negligible; hence the background is assigned to a double shake-off process populating $CO^{3+}(K^{-1}V^{-2})$ states that decay by Auger electron emission.
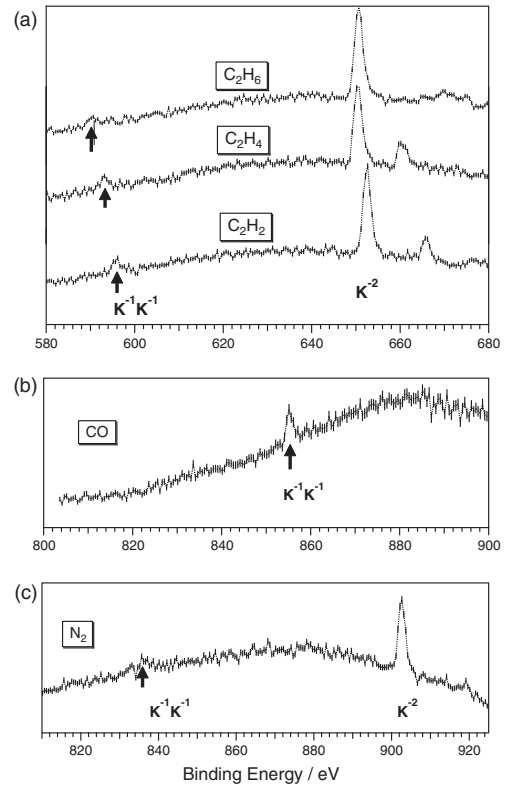

FIG. 2. Spectroscopy of $K^{-1}K^{-1}$ double core hole states. (a) C_2H_{2n} ($n = 1$–3) at $h\nu = 770$ eV. (b) CO at $h\nu = 953.6$ eV. (c) N_2 at $h\nu = 1005$ eV.

According to the knock-out model [10], two mechanisms can create $[C(K^{-1})O(K^{-1})]^{2+}$ states: first ionization in O1s then knock-out on C1s electron and conversely. At 953.6 eV, the relative probability for initial K-shell ionization on the O atom is 72% and 28% on the C atom. The estimated branching ratios for $[C(K^{-1})O(K^{-1})]^{2+}$ and $[C(K^{-2})O]^{2+}$ formations with respect to $[C(K^{-1})O]^{+}$ + $[CO(K^{-1})]^{+}$, are respectively, about a factor of 2 lower and 1.7 times higher than the experimental values shown in Table I. These and previous discrepancies can be attributed to simplifying assumptions of the model, in particular, to the (semi)classical approximation in which interferences of various amplitudes leading to the same final configurations are neglected. Full quantum mechanical treatment of inelastic electron scattering, where both the site selected electron source and the site selected electron target are within the same molecule, remains a challenging task for the future.

The Auger decay spectrum of $[C(K^{-1})O(K^{-1})]^{2+}$ states can be extracted from four-electrons coincidence events, by selecting two photoelectrons in the energy window E_{Ph1} + E_{Ph2} = [85–100 eV] and by subtracting an average contribution from adjacent windows. The Auger spectrum is given in Fig. 3(c) and is directly compared with single Auger decay [Fig. 3(a)] and double Auger from $[C(K^{-2})O]^{2+}$ [Fig. 3(b)]. The calculation of the Auger spectra from DCH states is detailed in Ref. [21]. It is based on the Wentzel's formula combined with the multiconfigurational wave functions of the initial, intermediate, and final electronic states. If we assume nonconcerted successive Auger decay on the two sites, two pathways are possible with first Auger decay on O and second on C, or the opposite.

The calculation predicts close ratio for these two pathways due to similar lifetimes of $O(K^{-1})$ and $C(K^{-1})$ holes. The theoretical Auger spectra for the two decay pathways are plotted in Fig. 3. The total Auger spectrum is the sum of the two channels. A good agreement with experiment is found. A further step in the calculation would be to include the effect of Coulomb explosion during the successive Auger decay processes.

In conclusion, we have demonstrated that single photon double ionization coupled to coincidence technique has the potential to become a new sensitive spectroscopic tool of chemical interest. We have clearly observed $K^{-1}K^{-1}$ double K-shell ionization of different molecules by single photon absorption using synchrotron radiation and coincidence electron spectroscopy. The experiment validates the early predictions for the C_2H_{2n} sequence [2] and compares well with recently published theoretical calculations [13] of K^{-2} and $K^{-1}K^{-1}$ energies and with our present DFT calculations. With a typical resolution of ~2–4 eV for K^{-2} and $K^{-1}K^{-1}$ states, the relative chemical shift in the C_2H_{2n} sequence is obtained here with ~200–400 meV precision (1/10 of peak width) at fixed photon energy. The energy difference between K^{-2} and $K^{-1}K^{-1}$ states is obtained with similar accuracy. These results provide a stringent test
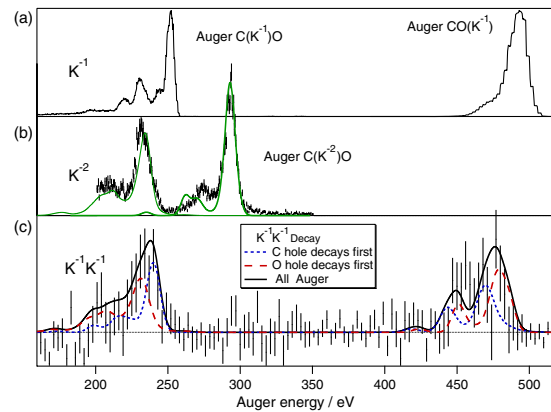

FIG. 3 (color online). Auger spectra associated to the decay of single and double core holes in CO. (a) Single Auger decay from O and C. (b) Auger decay from $[C(K^{-2})O]^{2+}$ main state. (c) Auger decay from $[C(K^{-1})O(K^{-1})]^{2+}$; the calculations consider the successive Auger decay on C and O dashed (red) curve: first Auger decay on O; dotted (blue) curve: first Auger decay on C; solid (black) curve: sum of the calculated contributions of the two pathways.

for different theories and unique information on interatomic relaxation energy [13,16,22].

Single photon double K-shell ionization (K^{-2} and $K^{-1}K^{-1}$) relies on electron correlations often described by shake-off and knock-out approximations. A simple model reproduces the main trends of the measured experimental cross section ratio for the different molecules. The specific property of single photon double K-shell ionization is that the creation of double core hole states, mediated by the primary photoelectron, occurs on a much shorter time scale (as) than Auger decay (~ fs). The electron coincidence method allows extraction of clear Auger spectra. These experiments give a complementary approach to XFEL based experiments where coincidence measurements are not possible yet.

*Corresponding author.
francis.penent@upmc.fr

[1] K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1971).
[2] L. S. Cederbaum, F. Tarantelli, A. Sgamellotti, and J. Schirmer, J. Chem. Phys. **85**, 6513 (1986).
[3] S. Santra, N. V. Kryzhevoi, and L. S. Cederbaum, Phys. Rev. Lett. **103**, 013002 (2009).
[4] M. Tashiro, M. Ehara, and K. Ueda, Chem. Phys. Lett. **496**, 217 (2010).

[5] H. Ågren and H. J. A. Jensen, Chem. Phys. **172,** 45 (1993).

[6] L. Fang *et al.*, Phys. Rev. Lett. **105,** 083005 (2010).

[7] N. Berrah *et al.*, Proc. Natl. Acad. Sci. U.S.A. **108,** 16912 (2011).

[8] J. H. D. Eland, M. Tashiro, P. Linusson, M. Ehara, K. Ueda, and R. Feifel, Phys. Rev. Lett. **105,** 213005 (2010); M. Mucke, P. Linusson, L. Hedin, K. Ueda, M. Tashiro, M. Ehara, O. Takashi, J. H. D. Eland, and R. Feifel (private communication).

[9] P. Lablanquie *et al.*, Phys. Rev. Lett. **106,** 063003 (2011).

[10] P. Lablanquie *et al.*, Phys. Rev. Lett. **107,** 193004 (2011).

[11] P. Salén *et al.*, Phys. Rev. Lett. **108,** 153003 (2012).

[12] L. J. Sæthre, K. J. Børve, and T. D. Thomas, J. Electron Spectrosc. Relat. Phenom. **183,** 2 (2011).

[13] M. Tashiro, M. Ehara, H. Fukuzawa, K. Ueda, C. Buth, N. V. Kryzhevoi, and L. S. Cederbaum, J. Chem. Phys. **132,** 184302 (2010).

[14] K. Ito, F. Penent, Y. Hikosaka, E. Shigemasa, I. H. Suzuki, J. H. D. Eland, and P. Lablanquie, Rev. Sci. Instrum. **80,** 123101 (2009).

[15] V. Myrseth, J. D. Bozek, E. Kukk, L. J. Sæthre, and T. D. Thomas, J. Electron Spectrosc. Relat. Phenom. **122,** 57 (2002).

[16] T. D. Thomas, J. Phys. Chem. A **116,** 3856 (2012).

[17] T. D. Thomas, Phys. Rev. Lett. **52,** 417 (1984).

[18] T. Schneider and J. M. Rost, Phys. Rev. A **67,** 062704 (2003).

[19] J. Hoszowska *et al.*, Phys. Rev. Lett. **102,** 073006 (2009).

[20] J. P. Santos, F. Parente, and Y.-K. Kim, J. Phys. B **36,** 4211 (2003).

[21] M. Tashiro, K. Ueda, and M. J. Ehara, J. Chem. Phys. **135,** 154307 (2011).

[22] K. Ueda and O. Takahashi, J. Electron Spectrosc. Relat. Phenom. **185,** 301 (2012).