PRL **116,** 073001 (2016) PHYSICAL REVIEW LETTERS week ending 19 FEBRUARY 2016

Ultrafast Molecular Three-Electron Auger Decay

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(Received 29 May 2015; revised manuscript received 13 November 2015; published 19 February 2016)

Three-electron Auger decay is an exotic and elusive process, in which two outer-shell electrons simultaneously refill an inner-shell double vacancy with emission of a single Auger electron. Such transitions are forbidden by the many-electron selection rules, normally making their decay lifetimes orders of magnitude longer than the few-femtosecond lifetimes of normal (two-electron) Auger decay. Here we present theoretical predictions and direct experimental evidence for a few-femtosecond three-electron Auger decay of a double inner-valence-hole state in CH_3F. Our analysis shows that in contrast to double core holes, double inner-valence vacancies in molecules can decay exclusively by this ultrafast three-electron Auger process, and we predict that this phenomenon occurs widely.

DOI: 10.1103/PhysRevLett.116.073001

Auger decay [1] is a universal phenomenon in all forms of matter. When an inner-shell vacancy is created in an atom, its refilling by a valence electron can be accompanied by emission of one or more electrons. The most common processes are two-electron transitions, the simplest being the celebrated Auger effect [2,3], where a single vacancy is refilled and a single electron is emitted. Less frequently, electron correlation leads to higher-order effects involving three- and even four-electron transitions, such as the single-step contributions to double [4] and triple [5] Auger effects where two or three electrons are ejected, collective decay of double core holes [6,7], and collective interatomic decay [8–10]. These many-electron transitions are forbidden to low order and represent minor decay channels, with rates much lower than those of normal (two-electron) Auger decay, generally characterized by lifetimes in the range 1–10 fs. In special cases where a three-electron mechanism is the only energetically possible nonradiative pathway (e.g., Ref. [8]), the higher-order process is still much slower than two-electron transitions in related systems where they are energetically allowed.

In this Letter we present experimental and theoretical evidence for a hitherto unknown ultrafast three-electron Auger decay in molecules following double inner-valence ionization. In inner-valence ionization, vacancies are created in orbitals based on the innermost atomic orbitals of the valence shell, e.g., in $2s$-based orbitals where bonding is mainly by $2p$ combinations. If two such inner-valence holes are filled simultaneously, enough energy is provided for one other electron to be ejected. This collective process is the only possible nonradiative decay channel for doubly inner-valence ionized states of a variety of species, and we find that it proceeds on the few-femtosecond time scale reminiscent of normal Auger transitions. We trace this unexpected ultrafast character of the molecular three-electron transition to partial breakdown of the simple single-configuration picture [11] both in the initial (doubly inner-valence-ionized) and in the final (triply ionized) states of the decay process.

A three-electron transition consisting of collective refilling of two holes and emission of a single Auger electron was first proposed for double $n = 2$ vacancies in Ar [12], but demonstrated only later by Afrosimov *et al.* [6] who found that its rate is 3 to 4 orders of magnitude smaller than that of the normal two-electron Auger transition. Subsequently, Lee *et al.* [7] suggested a similar mechanism for decay of the final state of a spectator resonant Auger transition in Kr (main configuration $3d^{10}4s^04p^65p$) to different levels of the lowest $(3d^{10}4s^24p^4)$ configuration of Kr^{2+}, a mechanism whose existence has recently been unambiguously confirmed [13]. Three-electron processes similar to the one studied by Afrosimov *et al.* [6] have also been observed in collisions of multiply charged ions with surfaces [14] and foils [15] following electron capture to the outer shells. The rate of these decays relative to normal Auger transitions has been estimated to be 10^{-4}–10^{-6} [16]. Thus, none of these known collective atomic processes can match the normal (two-electron) Auger transition in magnitude of the rate, remaining so far rare and weak channels. In clusters, the collective interatomic Coulombic decay (CICD) can be the only nonradiative decay channel [8–10], but the corresponding CICD lifetimes are still an order of magnitude longer than the typical ICD ones (cf. Refs. [8,17]). We are not aware of any previous experimental collective Auger studies in molecules.

Doubly core-ionized molecular states have recently gained attention as relevant to x-ray free electron laser experiments [18], where the high radiation intensity leads to sequential double core ionization. As in the atomic cases, these double core holes can decay collectively, but the corresponding rates are orders of magnitude slower than normal Auger transitions [19,20]. Double inner-valence holes are more promising for studying the collective decay since in small species they are not energetic enough to decay by a two-electron Auger mechanism and the three-electron process can be the only available nonradiative decay channel. But such states, derived, e.g., from double $2s$ ionization of an O, N, or F atom in a molecule, often present an assignment problem because of the so-called molecular orbital (MO) picture breakdown [11]. Inspired by Koopmans's theorem [21] for single ionization, we often think of a doubly ionized state as formed by removal of electrons from two spin orbitals. Even for single ionization this simple assignment is not possible in the inner valence region for large enough species because of the very efficient mixing of the main one-hole ($1h$) and two-hole–one-particle ($2h$-$1p$) configurations [11] (cf. Ref. [22]). In doubly ionized species, the corresponding configuration interaction is no less important and doubly inner-valence-ionized states can often not be assigned to any single two-hole configuration. We thus restrict our attention to small molecular species bearing relatively deep (e.g., F $2s^{-2}$) double inner-valence vacancies. Table I gives a few such double vacancies with the corresponding energies, triple ionization thresholds, and calculated collective (three-electron) decay widths.

To guide experiments, *ab initio* energy calculations have been carried out using the extended second-order algebraic diagrammatic construction [ADC$(2)x$] [26] method for doubly [23] and triply ionized states [24]. The decay widths were calculated using the Fano-ADC method for doubly ionized states [25]. Briefly, this $\mathcal{L}^2$ method rests on evaluation of the generalized Fano expression [27] for the decay width Γ through the matrix element of the full many-electron Hamiltonian ($\hat{H}$) between the boundlike (Φ) and the continuumlike ($\chi_{\alpha,\varepsilon_\alpha}$) components of the wave function at the energy of the decaying state (E_r):

$$\Gamma = 2\pi \sum_{\alpha=1}^{N_c} |\langle \Phi | \hat{H} - E_r | \chi_{\alpha,\varepsilon_\alpha} \rangle|^2. \qquad (1)$$

Here the summation is over N_c decay channels and ε_α is the electron kinetic energy for channel α. The many-electron wave functions Φ and $\chi_{\alpha,\varepsilon_\alpha}$ are obtained using the ADC$(2)x$ scheme for double ionization [23]. At the heart of the Fano-ADC procedure is the configuration selection scheme that sorts out the many-electron ADC basis states into those contributing to the expansion of the initial (boundlike) state and to the final (continuumlike) state. In all the calculations we employed the energy-based configuration selection scheme [28]. As part of the Fano-ADC procedure, Stieltjes imaging [29] was applied to the discretized spectrum of the final states of the decay obtained using extended Gaussian bases. Further details are given in the Supplemental Material [30].

The common striking feature of the calculated three-electron Auger processes presented in Table I is the anomalously high decay width, comparable to those of normal two-electron Auger transitions and larger than the three-electron decay widths of double core holes. The predicted decay lifetimes are similar in magnitude to vibrational periods of the chemical bonds involved, so a full description would need to account for nuclear motion.

One reason for the large decay widths is the relatively low energy of secondary electrons emitted in the collective Auger transitions with both initial vacancies in the inner valence shell. This, however, cannot fully account for the ultrafast character of the three-electron transitions. The second reason for the fast three-electron dynamics is the very efficient configuration interaction both in the initial and final states of the decay [see Eq. (1)]. In the frozen-orbital single-configuration picture the process is forbidden, i.e., the main $2h$ configuration of the initial state is not coupled directly to the final state that has got three holes and an ionized electron. However, our calculations

TABLE I. Collective Auger decay in a series of species: initial states, initial state energies, triple ionization thresholds, collective decay widths, lifetimes, and total $2h$ pole strengths of the initial states (weights of the main $2h$ configurations in brackets). The last column gives secondary electron energies in terms of the main peaks or most intense bands (total spread in brackets where applicable). The energies and decay widths Γ are computed for the equilibrium geometries by the ADC$(2)x$ [23,24] and Fano-ADC$(2)x$ [25] methods, respectively.

X	X^{2+} state	$E(X^{2+})$ (eV)	$E(X^{3+})$ (eV)	Γ (meV)	τ (fs)	$2h$ pole strength, %	ε_α (eV)
CH_3F	F $2s^{-2}$	95.5	69.1	217	3.0	63.8 (61.3)	3–11 (0–23)
F_2	F $2s^{-2}$	101.6	87.6	50	13	60.4 (54.3)	1, 6–8
OH^-	O $2s^{-2}$	57.4	46.7	575	1.1	69.5 (63.9)	6, 8, 11
ClF	F $2s^{-2}$	96.8	69.1	90	7.3	66.8 (63.7)	4, 8, 14–19 (3–19)
F^-	F $2s^{-2}$	69.6	60.6	425	1.5	78.9 (75.3)	7

show (see Table 1) that the doubly inner-valence-ionized state is only about 60%–70% $2h$, the remaining 30%–40% being shake-up type configurations, some of which directly couple to the collective decay final states. And vice versa, the final states with three holes in the outer valence are efficiently mixed with the states of the same type with a hole in the inner valence, again leading to direct coupling of the correlated initial and final states.

In the specific case of CH_3F, analysis of individual contributions to the decay width shows that the configuration mixing in both the initial and final states is indeed important, which is in agreement with the previous findings of Ivanov *et al.* [36] for the three-electron Auger decay in atoms. However, it is not possible to identify any particular shake-up configuration as dominant, which is characteristic for the breakdown of the MO picture. All valence vacancies are present comparably in the configurations contributing to the initial state wave function as well as in the triply ionized final states that are significantly populated by the collective decay.

To search for three-electron Auger decay experimentally we combined energy-selected synchrotron light from BESSY II with a magnetic bottle time-of-flight electron spectrometer [37,38]. The spectrometer can detect three or more electrons from each ionization event with about 50% overall efficiency and a numerical resolution of about 2%. We use it to investigate the predicted ultrafast decay of the F $2s$ double inner valence vacancy state in CH_3F that has been located in both the carbon and fluorine Auger spectra [39] near 98 eV ionization energy. By examining the electron spectra at 150 eV for coincident electron pairs and triples, we first verified that this double vacancy state is also formed directly by one-photon two-electron ionization. It is seen clearly at 150 eV photon energy in both twofold and threefold electron coincidences as a weak band with a width of about 5 eV at half height [see Figs. 1(c) and 1(d)], in agreement with the form of the band in the F $1s$ Auger spectrum [39]. The cross section for this direct formation is small and other processes produce a strong background. The fact that this state is observed at all as an intermediate in formation of electron triples demonstrates, however, that it decays, at least partly, by triple ionization.

Examination of the coincident Auger spectra produced by single core hole formation on the carbon and fluorine atoms is somewhat impeded in our experiments by the low resolution of the time-of-flight apparatus at the high electron energies involved. To detect coincidences, full multiplex capability over the whole energy range must be maintained, so no retardation can be used, and therefore the resolution is about 5 eV for the ~200 eV electrons from C $1s^{-1}$ and 15 eV for the ~600 eV electrons from F $1s^{-1}$. Nevertheless, the F $2s^{-2}$ band at 98 eV is seen in the spectra of electrons coincident with the C $1s$ and F $1s$ photolines with greater intensity in the fluorine than in the carbon case [cf. Figs. 1(a) and 1(b)].

By choosing events where one electron of three signals the initial $1s$ hole formation and a second electron is chosen to select the 98 eV F $2s^{-2}$ state, we extracted triple-coincidence spectra produced through intermediate formation of the target $2s$ double vacancies. In the left panel of Fig. 2, the levels involved are sketched for both initial C $1s$ and F $1s$ ionization; the orbitals in the valence shell include F $2p$, C $2p$, and H $1s$ contributions, but, for simplicity, the levels are denoted as (highest occupied molecular orbital) $HOMO^{-x}$ ($x = 2, 3, 4$).

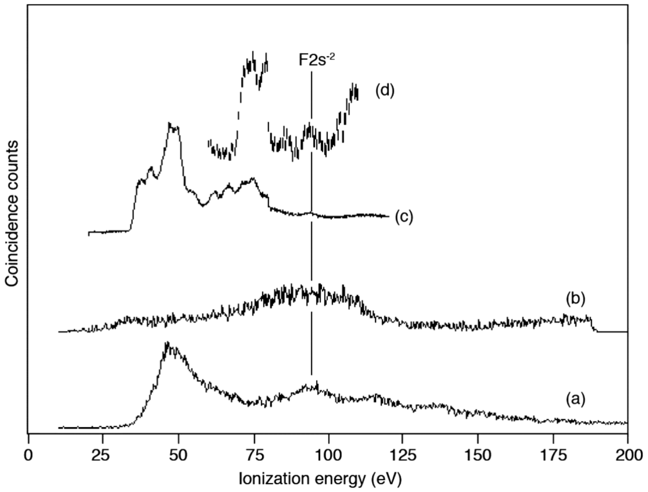

FIG. 1. Spectra showing the summed energy of electron pairs from CH_3F, (a) in coincidence with C $1s^{-1}$ ionization at the photon energy $h\nu = 360$ eV, (b) in coincidence with F $1s^{-1}$ ionization at $h\nu = 770$ eV, (c) pairs alone at $h\nu = 150$ eV and (d) pairs as components of electron triples at 150 eV. The intensity scales of the different spectra have been adjusted for presentation and are not related, as the data come from different experiments. The strong onset in spectrum (d) probably represents the molecular triple ionization energy (i.e., photon energy minus kinetic energy sum of electron triples) at about 70 eV, in agreement with the calculated value in Table I.

The coincidence spectra are shown for comparison with calculations in Fig. 3. In evaluation of these spectra it should be remembered that some contamination of the selected $2s^{-2}$ states is possible because of the limited resolution, particularly in formation via F $1s^{-1}$. Nonetheless, the fact that they extend on the low ionization energy side no lower than 70 eV and peak near 90 eV suggests that the process populating the triply ionized states from the intermediate F $2s^{-2}$ state is very rapid, as illustrated in the right panel of Fig. 2. If it did not occur on a roughly fs time scale, Coulomb explosion of the molecular ion would precede it and the spectra would show the production of separated fragments of lower energy.

The collective decay electron spectra in CH_3F were simulated using a semiclassical approach, namely, considering the electronic decay process quantum mechanically, while approximating the nuclear motion classically. Only the essential C–F bond length degree of freedom R was taken into account. The cuts of the relevant potential energy surfaces along the C–F bond are shown for the C $1s$ case in the right panel of Fig. 2 (and for both the C $1s$ and F $1s$

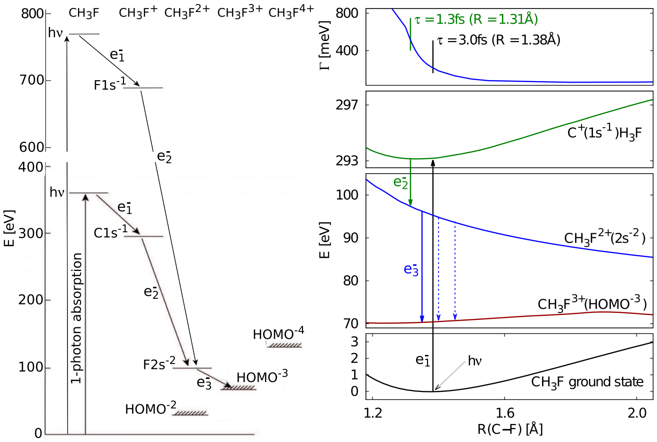

FIG. 2. Left panel: Energy levels of ionized CH_3F involved in the three-electron transition after initial creation of a single vacancy in the C 1*s* and F 1*s* orbital, respectively. The detection of the three electrons in coincidence proves the existence of the final step where two electrons fill the double hole in F 2*s* while a third is ejected. Right panel: Potential energy curves (PECs) along the C–F bond for the states relevant for the C 1*s* Auger decay route. The black arrow corresponds to vertical excitation from the ground to the core-ionized state at the equilibrium distance. The green arrow shows at which geometry the doubly inner-valence ionized state is populated assuming classical dynamics on the C $1s^{-1}$ PEC and a C 1*s* Auger lifetime $\tau_C = 8.7$ fs. Uppermost panel shows the decay width of the $CH_3F^{2+}(2s^{-2})$ state with the collective Auger decay lifetime τ indicated for the significant geometries.

case in Fig. 1 of the Supplemental Material [30]). The electron spectra σ were obtained as averages over the fixed-geometry spectra $\sigma(R)$, weighted by the adiabatically changing decaying state population

$$\sigma = \int_0^\infty \sigma(R(t)) e^{-\int_0^t \Gamma(R(t'))dt'}, \tag{2}$$

where $t = 0$ corresponds to the instantaneous population of the decaying double inner-valence hole by normal Auger decay. Both C 1*s* and F 1*s* Auger decay routes were considered and are shown in the upper and lower panels of Fig. 3. Good agreement with the experiment is obtained, especially in the former case. We attribute the high-energy shoulder in the spectra corresponding to the F 1*s* route to opening of the spectator-hole normal Auger decay channels that are closed in our ADC(2)*x* calculations by a margin that is comparable to the accuracy of the method. Another cause of the high-energy shoulder could be a population of shake-up states upon F 1*s* Auger decay. This possibility we consider less likely, because according to our estimates, it would require anomalously high population of a specific series of selected satellites.

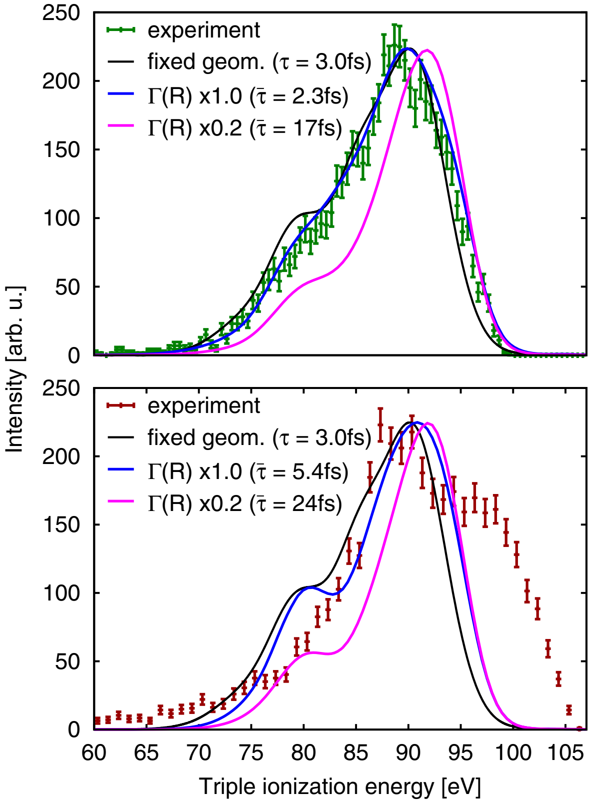

FIG. 3. Experimental triple ionization spectra acquired from the C 1*s* (upper panel) and F 1*s* (lower panel) initiated cascade (green and red error bars, respectively). The black curves show the theoretical spectra calculated at fixed equilibrium geometry. The blue spectra were obtained with the inclusion of nuclear motion in the $CH_3F^{2+}(2s^{-2})$ state, assuming this state is populated by the Auger decay at $R_{(\text{C-F})} = 1.315$ Å (C 1*s* case) and at $R_{(\text{C–F})} = 1.4$ Å (F 1*s* case), respectively, as detailed in the Supplemental Material [30]. The magenta spectra were calculated in the same way but with the *ab initio* decay width scaled down by a factor of 5. $\bar{\tau}$ is the fixed-geometry decay lifetime averaged over the classical C–F bond dynamics analogously to Eq. (2). In all theoretical spectra, only the decay channels accessible exclusively by the three-electron Auger decay were taken into account.

The spectra are sensitive to the decay rates since slower decay samples a wider range of C–F bond length compared to the faster one and the energies of the secondary electrons depend on molecular geometry, as sketched for the carbon case in the right panel of Fig. 2. We verify this effect by artificially scaling down the collective decay width which evidently produces much poorer agreement with the experimental spectrum in the C 1*s* case, and a somewhat poorer agreement in the main peak region in the F 1*s* case. This is experimental support for the ultrafast nature of collective decay in CH_3F.

In conclusion, we have identified, both theoretically and experimentally, a first ultrafast three-electron decay process occurring upon double inner-valence-hole formation in molecules. The latter seem to behave differently from double core holes, and the collective decay of the "inner-valence hollow molecules" studied here is orders of magnitude faster than the collective decay of the hollow molecules formed by double core ionization [18]. Our theoretical analysis shows this feature to be a combined effect of the low energy of the emitted Auger electrons and efficient configuration interaction in the initial and final states of the three-electron decay, making it a partly allowed radiationless transition.

This work has been financially supported by the Swedish Research Council (V. R.) and the Knut and Alice Wallenberg Foundation, Sweden. We thank the Helmholtz Zentrum Berlin for the allocation of synchrotron radiation beam time. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under Grant Agreement No. 312284. P. K. acknowledges financial support by the Czech Science foundation (Project GAČR P208/12/0521). V. A. acknowledges the financial support of the Engineering and Physical Sciences Research Council (EPSRC, United Kingdom) through the Career Acceleration Fellowship (Grant No. EP/H003657/1) and the Programme Grant on Attosecond Dynamics (Grant No. EP/I032517/1).

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