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# Unambiguous observation of F atom core-hole localization in CF<sub>4</sub> through body-frame photoelectron angular distributions

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A dramatic symmetry breaking in K-shell photoionization of the CF<sub>4</sub> molecule in which a core-hole vacancy is created in one of four equivalent fluorine atoms is displayed in the molecular frame angular distribution of the photoelectrons. Observing the photoejected electron in coincidence with an F<sup>+</sup> atomic ion after Auger decay is shown to select the dissociation path where the core hole was localized almost exclusively on that atom. A combination of measurements and *ab initio* calculations of the photoelectron angular distribution in the frame of the recoiling CF<sub>3</sub><sup>+</sup> and F<sup>+</sup> atoms elucidates the underlying physics that derives from Ne-like valence structure of the F (1s<sup>-1</sup>) core-excited atom.

Electronic states of isolated molecules reflect the symmetry of the molecule. Symmetric ionic states arising from the removal of an electron from a core orbital in symmetry-equivalent atoms have energies that can lie entirely or partly within their Auger decay widths and are effectively degenerate. The <sup>2</sup>A<sub>1</sub> and <sup>2</sup>T<sub>2</sub> states of CF<sub>4</sub><sup>+</sup> with a fluorine K-shell vacancy in this study are examples of such states, and there are numerous other examples previously investigated by Auger spectroscopy [1–4]. For more than four decades, experimental and theoretical studies have been directed toward understanding how combinations of such states break molecular symmetry and the role they play in molecular dynamics and spectroscopy. In the case of a homonuclear diatomic molecule, the detection of the photoelectron in coincidence with the electron subsequently ejected by Auger decay has been shown in both theory and experiment to allow the experimental selection of the linear combination of effectively degenerate <sup>2</sup>Σ<sub>g</sub> and <sup>2</sup>Σ<sub>u</sub> states of N<sub>2</sub><sup>+</sup>, for example, that localizes the 1s vacancy on either atom [1].

In polyatomic molecules with symmetry equivalent atoms the dynamics of core hole localization produces rich structure in near-edge X-ray absorption spectra, because the presence of asymmetric vibrational modes leads to vibronic coupling between molecular electronic states constructed from equivalent core holes and the localization of a K-shell hole on a single atom on the time scale of molecular vibration [2]. Consequently, the vibrational structure in the C (1s<sup>-1</sup>) → π\* band in both acetylene [3] and ethylene [4] are well described by a theoretical treatment of vibronic coupling in both the core and valence orbital spaces with broken-symmetry orbitals.

The signature of core-hole localization can in principle also be observed in dynamical processes such as core-level photoionization, when viewed in the body-frame. Evidence of this effect has been seen, using momentum imaging techniques, in molecular frame photoelectron angular distributions (MFPAD) from K-shell ionization. Although the origin of hole localization in polyatomics with symmetry equivalent atoms has been well understood for many years, its unambiguous observation in dynamical processes is far from straightforward.

With targets such as CO<sub>2</sub> [5–7] and acetylene [8], symmetry breaking results appear as relatively small asymmetries in angular distributions that are expected to be symmetric. The observed asymmetries are on the order of a few percent. In this letter we report far more dramatic and definitive evidence of core hole localization that appears in the recoil frame photoelectron angular distribution (RFPAD) in fluorine K-shell photoionization of CF<sub>4</sub>. In fact, we will show that the MFPADs in this case can exhibit effects of either a localized or delocalized hole, depending on the details of the observation. While the observed effects are tied to the details of the Auger decay following F K-shell photoionization, we will show that the magnitude of these effects is essentially chemical in origin and related to the extreme electronegativity of atomic fluorine.

The observed process occurs in steps: X-ray photoionization within a few eV of the fluorine K-edge is followed by Auger decay and dissociation of the resulting molecular ion: CF<sub>4</sub> + hν → CF<sub>4</sub><sup>+</sup>(1s<sub>F</sub><sup>-1</sup>) + e<sup>-</sup> → CF<sub>3</sub><sup>+</sup> + F<sup>+</sup> + 2e<sup>-</sup>. The RFPAD measured by detecting the photoelectron in coincidence with the F<sup>+</sup> atom is not expected to be sym-

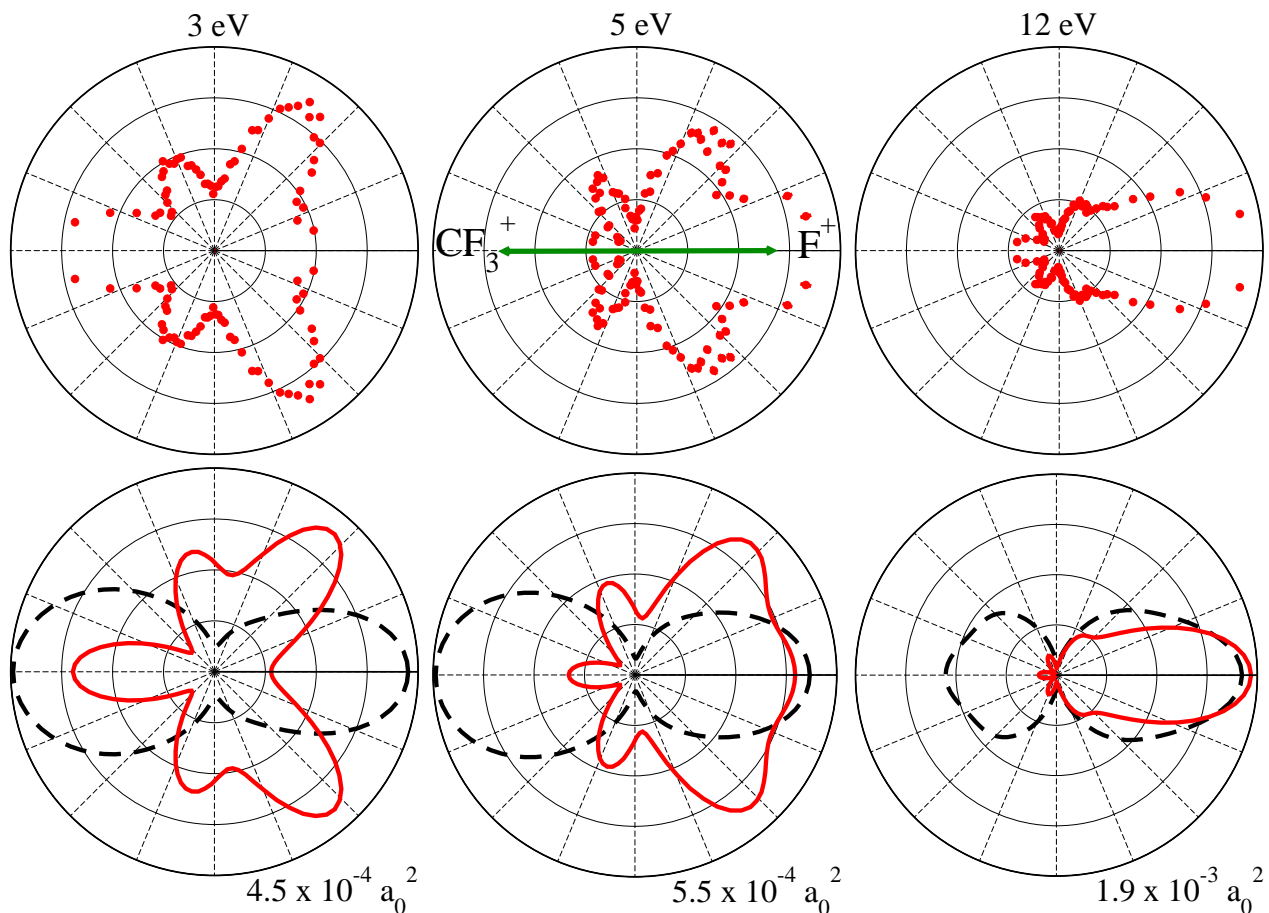


FIG. 1. (Color online) Experimental (relative) and theoretical (absolute) RFPADs for polarization parallel to C-F recoil axis. The experimental RFPADs use data for KER > 5.5 eV. Left to right: ejected electron energies 3 eV, 5 eV and 12 eV. Upper panels experiment. Lower panels theory: dashed lines are for delocalized and solid red lines localized fluorine 1s hole, with delocalized results for 3 and 5 eV multiplied by 1/4 and for 12 eV multiplied by 1/5. Labels indicate theoretical RFPAD cross section at the outer ring of the polar coordinates.

metric, but the comparison between the experimentally observed RFPAD and *ab initio* calculations with the hole localized on the fluorine atom, while the molecule still has tetrahedral symmetry, show that the fluorine atom that dissociates as  $F^+$  after Auger decay must have been the one with the 1s vacancy. Calculations of the photoelectron angular dependence arising from the creation of a delocalized vacancy in the symmetric molecular orbitals involving fluorine 1s orbitals bear no resemblance to the observed RFPADs, while the localized hole results reproduce them faithfully, providing definitive evidence that the fluorine ion detected was the one initially having the core vacancy.

The reason that this experiment can unambiguously detect the localization of the core hole is due to the effect of the Ne-like valence electronic structure of the  $F(1s)^{-1}$  core-excited atom on the dynamics of dissociation of the cation,  $CF_4^+(1s_F^{-1})$ . The nature of the dissociation dynamics was suggested by related experiments in 2003 that probed this dissociation in  $CF_4$  via the doppler

effect [9] and explored nuclear dynamics effects in  $CF_4$  Auger spectra [10], but the present experiment is only interpretable by complete core hole localization.

In the present study, the RFPAD for ionization of  $CF_4$  at the fluorine K-edge was measured using the COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS) method [11–13] in a coincidence measurement of the momentum of the photoelectron with respect to that of the  $F^+$  and  $CF_3^+$  ions produced by dissociation of  $CF_4^+$  after Auger decay. In this way the electron's momentum distribution is determined relative to both the  $CF_3^+ - F^+$  recoil axis (bond dissociation axis) and the polarization axis of the ionizing X-ray. The experiments were performed at X-ray energies  $\sim 3$ ,  $\sim 5$  and  $\sim 12$  eV above the fluorine K-edge vertical ionization energy in  $CF_4$  of  $695.37 \pm 0.1$  eV [14].

The experiments were performed at beamline 4.0.2 and 11.0.2.1 at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL). In both investigations the ion arm of the COLTRIMS ana-

lyzer consisted of a single acceleration region with slightly different lengths of 4.0 and 3.65 cm respectively. The electron arm employed a McLaren time-focusing scheme consisting of an accelerating region of 7.2 cm and a drift region of 13.8 cm in both measurements. The recoiling ions and electrons experience the same electric field of approximately 7 V/cm at beamline 4.0.2 and 12 V/cm at beamline 11.0.2.1. In order to detect the electrons of interest with full solid angle a static magnetic field of 8.2 and 4.2 Gauss parallel to the momentum spectrometer time-of-flight axis were employed in both investigations. In each experiment the photoelectron was recorded in coincidence with a  $\text{CF}_3^+$  and  $\text{F}^+$  ion on a shot-by-shot basis and for known orientation of the linear polarized light. Other details of the experimental setup were the same as those in an earlier COLTRIMS study of carbon K-shell ionization in  $\text{CF}_4$  [15].

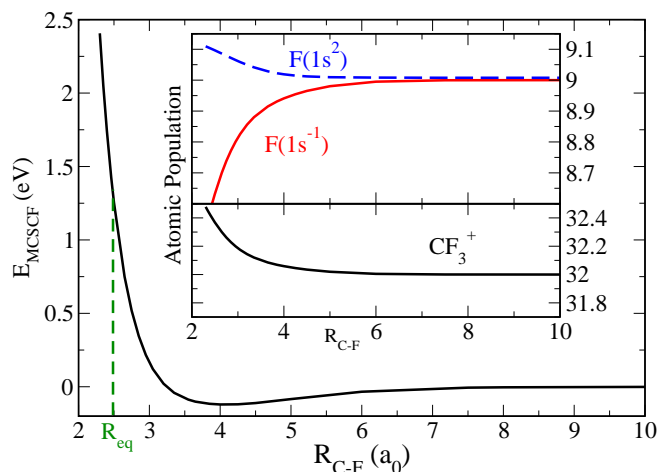


FIG. 2. (Color online) Potential curve for  $\text{CF}_4^+$  dissociation from SCF calculation with  $1s$  vacancy enforced on dissociating fluorine. Inset: Mulliken populations showing that dissociating fluorine atom has a population of 9 electrons and is therefore neutral while the  $\text{CF}_3^+$  fragment has 32 electrons.

Theoretical calculations of the RFPADs corresponding to those measured in the COLTRIMS experiment were performed with the complex Kohn variational method for electron scattering with modifications to treat electron-ion scattering [16]. The application of this *ab initio* scattering method to molecular photoionization has been described at length previously [6, 15, 17–19]. The MFPAD is the body frame cross section given by the expression

$$\frac{d^2\sigma_{\Gamma_0}}{d\Omega_{\hat{k}}d\Omega_{\hat{\epsilon}}} = \frac{8\pi\omega}{3c} \left| \hat{\epsilon} \cdot \langle \Psi_{\Gamma_0, \mathbf{k}_{\Gamma_0}}^- | \hat{\mu} | \Psi_0 \rangle \right|^2 \quad (1)$$

where  $\hat{\mu}$  is the dipole operator,  $\omega$  is the photon energy and  $c$  is the speed of light. Eq. 1 defines the cross section for polarization  $\hat{\epsilon}$  and ejected electron momentum  $\mathbf{k}_{\Gamma_0}$  leaving the ion in state  $\Gamma_0$ . The complex Kohn scattering calculation produces the final state wave function  $\Psi_{\Gamma_0, \mathbf{k}_{\Gamma_0}}^-$  in this expression. Here this wave function is the result

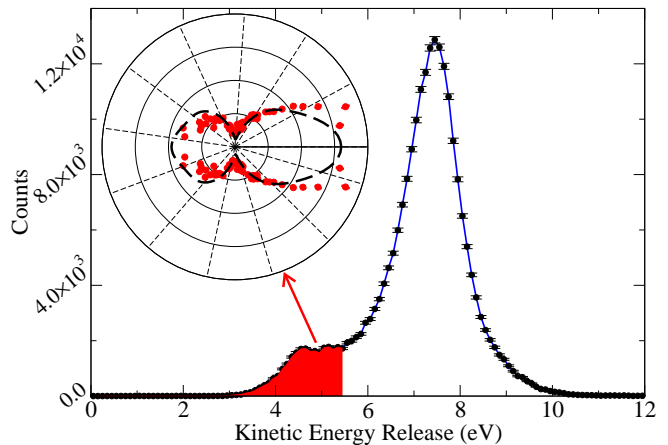


FIG. 3. (Color online) Kinetic energy release (KER) for ejected electron energy of 12 eV. Inset: RFPAD for polarization parallel to C-F recoil axis (horizontal) measured using only data for  $\text{KER} < 5.5$  eV compared with calculations for delocalized fluorine  $1s$  hole (from Fig. 1 bottom right).

of a close-coupling description of electron-ion scattering, and in the absence of experimental conditions that select one of the four degenerate channels the total cross section is the sum over all degenerate  $\Gamma_0$ .

In the ground state electronic configuration of  $\text{CF}_4$  with  $T_d$  symmetry, the four fluorine  $1s$  orbitals give rise to four molecular orbitals, one with  $a_1$  and three with  $t_2$  symmetry. To calculate MFPADs that correspond to the ionization of a hole delocalized on the four fluorines, four target ion states, corresponding to a vacancies in the  $a_1$  and  $t_2$  orbitals constructed from the F atom  $1s$  orbitals, were coupled in a four-channel calculation. The four, effectively degenerate target states were described by single configuration wave functions constructed from Hartree-Fock orbitals of  $\text{CF}_4$ . The close-coupling treatment guarantees that the correct  $T_d$  symmetry of the electron-ion scattering wave function is reflected in the MFPAD. The cross sections for the four channels were summed to produce the results we present here for delocalized holes.

To describe ionization that produces a core hole on a single fluorine we constructed the target states from Hartree-Fock orbitals obtained in a calculation that stretched one C-F bond slightly from equilibrium to lower the symmetry, resulting in one molecular orbital that consists exclusively of the  $1s$  orbital on that fluorine and three others, effectively degenerate with it but with  $C_{3v}$  symmetry, to which the other three F-atom  $1s$  orbitals contribute. Single configurations with vacancies in those four orbitals defined the four coupled channels for this calculation, and we report the ionization cross section in Eq.(1) with only the channel  $\Gamma_0$  corresponding to localized  $1s$  vacancy. To construct RFPADs, these cross sections in all cases were averaged numerically for rotation of the  $\text{CF}_3$  entity around the axis of the dissociating C-F

bond, requiring separate calculations for each orientation if the polarization and recoil axes were not identical.

In Fig. 1 we compare the experimentally determined RFPADs with those from the Kohn variational calculations at several electron kinetic energies for the case that the polarization vector lies along the recoil axis connecting the center of mass of the recoiling  $\text{CF}_3^+$  and  $\text{F}^+$  ions. The calculations reproduce the experimental RFPADs in almost every detail, but only in the case of complete localization of the  $\text{F}(1s^{-1})$  hole on the fluorine on the axis of dissociation. The delocalized calculations in Fig. 1 produce somewhat asymmetric figures (as would be expected for a molecule whose symmetry does not include a center of inversion or a reflection perpendicular to the recoil axis) that show the photoelectron being ejected primarily along the polarization vector, but with none of the detail and gross asymmetry of the experimental and localized-hole RFPADs.

To understand these results we start by noting that to produce a photoelectron with momentum  $\mathbf{k}_p$ , the quantum description of the initial photoionization event must make a superposition of the four degenerate core hole states, in which each appears with the probability amplitude that contributes to the body frame photoionization cross section in Eq.(1)

$$\Psi_{\text{final}} \propto \sum_{\gamma=1}^4 |\Psi_{1sF_\gamma}^-, \mathbf{k}_p\rangle \langle \Psi_{1sF_\gamma}^- | \hat{\mu} | \Psi_0 \rangle. \quad (2)$$

We are free to label those channels as localized core holes, since transforming those degenerate states to states formed from delocalized symmetry orbitals is merely a unitary transformation of basis that does not change  $\Psi_{\text{final}}$  in Eq.(2). In this experiment the subsequent Auger decay leads to breakup of the resulting dication, from which a single fluorine atom, say  $\text{F}_a^+$  is detected in coincidence with the photoelectron with momentum  $\mathbf{k}_p$ . The cross section for that event is given by the product of the photoionization amplitude,  $\langle \Psi_{1sF_a}^-, \mathbf{k}_p | \hat{\mu} | \Psi_0 \rangle$ , to produce a core-hole on  $\text{F}_a$  with the amplitude that the hole on each resulting  $\text{F}_\gamma^+$  decays to ultimately produce the decay product  $\text{CF}_3^+ + \text{F}_a^+$ , while producing an Auger electron of momentum  $\mathbf{k}_A$  which in our experiment is not detected

$$\begin{aligned} \sigma(F_a^+, \mathbf{k}_p) \propto & \int \left| \langle \Psi_{F_a^+ + CF_3^+, \mathbf{k}_A} | V | \psi_{1sF_a^+} \rangle \langle \Psi_{1sF_a^+}^- | \hat{\mu} | \Psi_0 \rangle \right. \\ & + \langle \Psi_{F_a^+ + CF_3^+, \mathbf{k}_A} | V | \psi_{1sF_b^+} \rangle \langle \Psi_{1sF_b^+}^- | \hat{\mu} | \Psi_0 \rangle \\ & + \langle \Psi_{F_a^+ + CF_3^+, \mathbf{k}_A} | V | \psi_{1sF_c^+} \rangle \langle \Psi_{1sF_c^+}^- | \hat{\mu} | \Psi_0 \rangle \\ & \left. + \langle \Psi_{F_a^+ + CF_3^+, \mathbf{k}_A} | V | \psi_{1sF_d^+} \rangle \langle \Psi_{1sF_d^+}^- | \hat{\mu} | \Psi_0 \rangle \right|^2 d\mathbf{k}_A. \end{aligned} \quad (3)$$

We denote the amplitude for the hole on  $\text{F}_b$ , for example, to produce the detected  $\text{F}_a^+$  ion via Auger decay by  $\langle \Psi_{F_a^+ + CF_3^+, \mathbf{k}_A} | V | \psi_{1sF_b^+} \rangle$ . The measurements in Fig. 1 evidently project onto only the first term in

Eq.(3), i.e. the pathway corresponding to the amplitude  $\langle \Psi_{F_a^+ + CF_3^+, \mathbf{k}_A} | V | \psi_{1sF_a^+} \rangle$ , while the other pathways to the same products are negligible for those conditions.

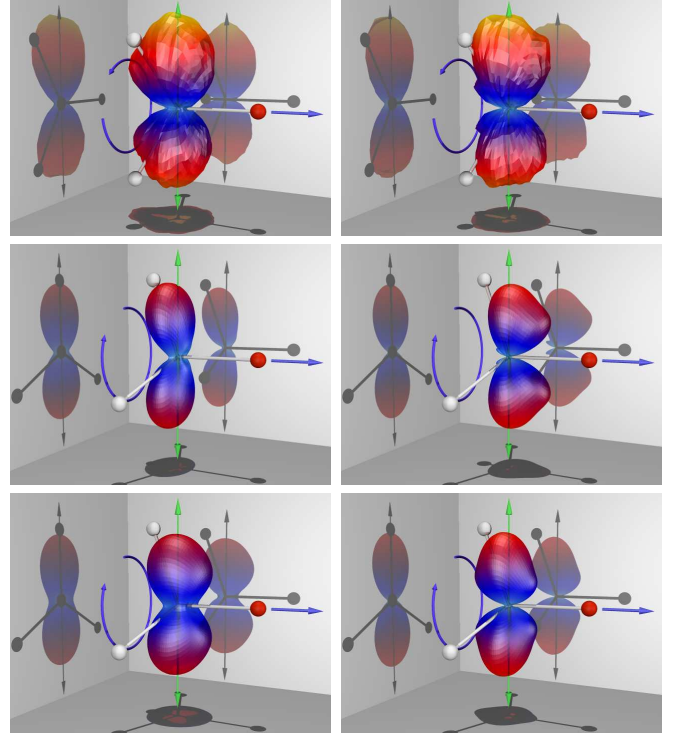


FIG. 4. (Color online) RFPADs for polarization perpendicular to C-F recoil axis and KER > 5.5 eV. Left 3 eV and right 12 eV ejected electron energy. Rows top to bottom: Experiment, theory for localized F core vacancy, theory for delocalized F vacancy.

The calculations in Fig. 2 suggest why this may be the case, at least for a significant subset of the many possible events following the initial photoionization in Eq.(2). It has been pointed out in earlier theoretical calculations [20, 21], using the “equivalent core” representation of a  $\text{F}^+(1s)^{-1}$  core-hole atom as a  $\text{Ne}^+$  atom, that the a  $\text{F}^+(1s)^{-1}$  core-hole atom is so electronegative that in this molecule the dissociation of  $\text{CF}_4^+$  with a localized core hole in one fluorine can proceed via dissociation of a neutral  $\text{F}^*$  atom with a core vacancy but filled valence shell that removes a valence electron from the  $\text{CF}_3$  fragment. However, the measured Auger-electron energies in the  $\text{CF}_4$  [10] show no direct evidence for an isolated  $\text{F}^*$  atomic decay which occur  $\approx 10$  eV higher [22, 23] in energy. Thus the  $\text{F}^*$  atomic decay must occur when the  $\text{F}^*$  is still near the  $\text{CF}_3^+$  fragment, consistent with the previously calculated Auger lifetime of 3.8 fs for the  $\text{F}^*$  atom [24]. The calculations in Fig. 2 show that in a self-consistent-field (SCF) description, an F atom with a localized core hole becomes neutral during dissociation on a strongly repulsive potential surface. Recently Arion *et al.* [10] measured the Auger spectra of  $\text{CF}_4$ , and they



have interpreted this spectrum using a model that involves Auger decay with a slightly elongated C–F\* bond. Ueda *et al.* [9] observed a feature similar to that reported by Arion *et al.* [10], Doppler split for dissociation along the polarization axis. Evidently Auger decay early on the curve in Fig. 2 initiates the mechanism which in our experiment allows a coincidence measurement to detect the distinctive angular dependence of a photoelectron being ejected from the core of a single F atom in this molecule.

This is not the only mechanism for Auger decay and breakup of the  $\text{CF}_4^+$  ion into  $\text{CF}_3^+$  and  $\text{F}^+$  of course, and in Fig. 3 we show the kinetic energy release (KER) of the  $\text{F}^+$  which shows a large peak at 7.5 eV and a shoulder below 5.5 eV. The data in Fig. 1 are from coincidence measurements for  $\text{KER} > 5.5$  eV, but in Fig. 3 we show the RFPAD for 12 eV electrons measured in coincidence with  $\text{F}^+$  with  $\text{KER} < 5.5$  eV. Strikingly, it matches the angular distribution from the calculations for a delocalized  $\text{F}(1s^{-1})$  vacancy, and so those photoelectrons apparently come from the other pathways in Eq.(3) that produce the detected  $\text{F}^+$  ion when the core vacancy was created elsewhere. Similar comparisons at photoelectron energies of 3 eV and 5 eV of the RFPADS for the low KER shoulder of the distribution also do not show the signature multiple lobes of the RFPADs at high KER in Fig. 1, and they too more closely resemble the dipole-like RFPADs in that figure calculated with delocalized  $\text{F}(1s^{-1})$  vacancy.

As pointed out previously [10] Auger decay can occur while the molecule has barely moved from geometries within the range of zero point motion. Those decays can also involve ejection of electrons from the other F atoms, as discussed by Arion *et al.* [10], producing dissociation along other axes and excited products. There are many such processes that would produce an  $\text{F}^+$  ion when the hole was initially created on any of the other F atoms, and they would correspond to an RFPAD reflecting the sum of ionization from all equivalent F cores.

The low KER peak in Fig. 3 can be resolved into at least two contributions with different KER values. The contribution to that peak at  $\sim 5$  eV is at just the KER for fragmentation of  $\text{CF}_4^{2+}$  into  $\text{CF}_3^+$  and  $\text{F}^+$  in their ground states formed by direct double photoionization [25]. However, the threshold for double ionization is 38 eV [25] which is somewhat lower than the lowest state populated by the Auger decay of  $\text{CF}_4^+$  ( $1s^{-1}$ ) which occurs at 44 eV [14]. The higher KER peak at 7.5 eV [26] is thus probably coming from a higher lying state which is directly dissociating, e.g. a dication state with an electron removed from one of the bonding C-F  $\sigma$  orbitals, for which earlier calculations indicate there are many candidates in this energy range [27].

The RFPADs in Fig. 1 and 3 are cylindrically symmetric because the polarization and recoil axes are the same. In Fig. 4 we show the results of experiments and theory at 3 and 12 eV for the case of the polarization perpendicular to the recoil axis, for which the RFPADs are not cylindrically symmetric even though they repre-

sent averages around the dissociating C–F bond. Here the photoelectron primarily exhibits the angular effect of being ejected by the incident radiation along the polarization axis, as is frequently seen in MFPADs [15, 19], and the effects of localization on the RFPAD are much less pronounced. Indeed, the calculated RFPADs for localized and delocalized F core vacancies in this case are too close in shape to be distinguished by experiment.

In summary, through the combination of experiment and theory we have seen that under particular experimental conditions the observation in coincidence of  $\text{F}^+$  ions and photoelectrons ionized near the fluorine K-edge in  $\text{CF}_4$  unambiguously exhibit a dramatic signature of core hole localization in the body-frame angular dependence of the ejected electron. The pronounced difference we see in the RFPADs for F K-shell photoionization in  $\text{CF}_4$  using localized or delocalized orbitals is fundamentally a chemical effect. Even if Auger decay occurs while the molecule has moved only a few tenths of an Angstrom from its initial geometry, the  $1s$  vacancy that is initially created can localize on one of the F atoms. That atom can achieve a closed-shell (neon-like) valence configuration by withdrawing an electron from the  $\text{CF}_3$  fragment, which then produces a steeply repulsive interaction between  $\text{CF}_3^+$  and  $\text{F}^*$ .

In other polyatomics with symmetry-equivalent atoms, like  $\text{HCCH}$  [28] and  $\text{CO}_2$  [7] there is a much smaller propensity for an initially stretched bond with a localized core hole to dissociate directly. For example, there is no great propensity for  $\text{H}^+ + \text{C}(1s^{-1})\text{CH}^+$  dissociation over  $\text{H}^+ + \text{CC}(1s^{-1})\text{H}^+$  dissociation, so when the RFPADs for both channels are summed, the asymmetry in the photoelectron angular distribution measured in coincidence is small. The dynamics of Auger decay and subsequent dissociation of the  $\text{CF}_4$  dication would seem to provide unique conditions that allow this observation. However, those conditions may be duplicated in other molecules containing symmetry equivalent F atoms, because the Ne-like valence electronic structure of the  $\text{F}(1s^{-1})$  core-excited atom is the origin of the conditions that allow a measurement to project onto a single member of the quantum superposition of states created in photoionization.

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- [1] M. S. Schöffler, J. Titze, N. Petridis, T. Jahnke, K. Cole, L. P. H. Schmidt, A. Czasch, D. Akoury, O. Jagutzki, J. B. Williams, N. A. Cherepkov, S. K. Semenov, C. W. McCurdy, T. N. Rescigno, C. L. Cocke, T. Osipov, S. Lee, M. H. Prior, A. Belkacem, A. L. Landers, H. Schmidt-Böcking, T. Weber, and R. Dörner, *Science* **320**, 920 (2008).
- [2] W. Domcke and L. Cederbaum, *Chem. Phys.* **25**, 189 (1977).
- [3] B. Kempgens, B. Itchkawitz, J. Feldhaus, A. Bradshaw, H. Köppel, M. Döschner, F. Gadea, and L. Cederbaum, *Chem. Phys. Lett.* **277**, 436 (1997).
- [4] F. X. Gadea, H. Köppel, J. Schirmer, L. S. Cederbaum, K. J. Randall, A. M. Bradshaw, Y. Ma, F. Sette, and C. T. Chen, *Phys. Rev. Lett.* **66**, 883 (1991).
- [5] X.-J. Liu, H. Fukuzawa, T. Teranishi, A. De Fanis, M. Takahashi, H. Yoshida, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, K. Wang, B. Zimmermann, V. McKoy, I. Koyano, N. Saito, and K. Ueda, *Phys. Rev. Lett.* **101**, 083001 (2008).
- [6] S. Miyabe, C. W. McCurdy, A. E. Orel, and T. N. Rescigno, *Phys. Rev. A* **79**, 053401 (2009).
- [7] R. R. Lucchese, H. Fukuzawa, X.-J. Liu, T. Teranishi, N. Saito, and K. Ueda, *J. Phys. B* **45**, 194014 (2012).
- [8] J. Adachi, K. Hosaka, T. Teramoto, M. Yamazaki, N. Watanabe, M. Takahashi, and A. Yagishita, *J. Phys. B* **40**, F285 (2007).
- [9] K. Ueda, M. Kitajima, A. De Fanis, T. Furuta, H. Shindo, H. Tanaka, K. Okada, R. Feifel, S. L. Sorensen, H. Yoshida, and Y. Senba, *Phys. Rev. Lett.* **90**, 233006 (2003).
- [10] T. Arion, O. Takahashi, R. Püttner, V. Ulrich, S. Barth, T. Lischke, A. M. Bradshaw, M. Füstel, and U. Hergenhahn, *J. Phys. B* **47**, 124033 (2014).
- [11] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking, *Physics Reports* **330**, 95 (2000).
- [12] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [13] T. Jahnke, Th. Weber, T. Osipov, A. L. Landers, O. Jagutzki, L. P. H. Schmidt, C. L. Cock, M. H. Prior, H. Schmidt-Böcking, and R. Dörner, *J. Elec. Spect. and Rel. Phen.* **141**, 229 (2004).
- [14] W. Griffiths, S. Svensson, A. N. de Brito, N. Correia, C. Reid, M. Langford, F. Harris, C. Liegener, and H. Ågren, *Chem. Phys.* **173**, 109 (1993).
- [15] A. Menssen, C. S. Trevisan, M. S. Schöffler, T. Jahnke, I. Bocharova, F. Sturm, N. Gehrken, B. Gaire, H. Gassert, S. Zeller, J. Voigtsberger, A. Kuhlins, F. Trinter, A. Gatton, J. Sartor, D. Reedy, C. Nook, B. Berry, M. Zohrabi, A. Kalinin, I. Ben-Itzhak, A. Belkacem, R. Dörner, T. Weber, A. L. Landers, T. N. Rescigno, C. W. McCurdy, and J. B. Williams, *J. Phys. B* **49**, 055203 (2016).
- [16] A. E. Orel, T. N. Rescigno, and B. H. Lengsfeld III, *Phys. Rev. A* **42**, 5292 (1990).
- [17] T. N. Rescigno, B. H. Lengsfeld, and A. E. Orel, *J. Chem. Phys.* **99**, 5097 (1993).
- [18] T. N. Rescigno, N. Douguet, and A. E. Orel, *J. Phys. B* **45**, 194001 (2012).
- [19] C. S. Trevisan, C. W. McCurdy, and T. N. Rescigno, *J. Phys. B* **45**, 194002 (2012).
- [20] O. Goscinski, J. Müller, E. Poulain, and H. Siegbahn, *Chem. Phys. Lett.* **55**, 407 (1978).
- [21] J. Müller, E. Poulain, O. Goscinski, and L. Karlsson, *J. Chem. Phys.* **72**, 2587 (1980).
- [22] S. Svensson, L. Karlsson, N. Mrtensson, P. Baltzer, and B. Wannberg, *Journal of Electron Spectroscopy and Related Phenomena* **50**, C1 (1990).
- [23] O. P. Sairanen, H. Aksela, S. Aksela, and M. Hotokka, *Chem. Phys. Lett.* **215**, 353 (1993).
- [24] B. Schimmelpfennig, B. Nestmann, and S. Peyerimhoff, *J. Elec. Spect. and Rel. Phen.* **74**, 173 (1995).
- [25] K. Codling, L. J. Frasinski, P. A. Hatherly, M. Stankiewicz, and F. P. Larkins, *J. Phys. B* **24**, 951 (1991).
- [26] M. K. Thomas, B. O. Fisher, P. A. Hatherly, K. Codling, M. Stankiewicz, and M. Roper, *J. Phys. B* **32**, 2611 (1999).
- [27] F. O. Gottfried, L. S. Cederbaum, and F. Tarantelli, *J. Chem. Phys.* **104**, 9754 (1996).
- [28] J. ichi Adachi, K. Hosaka, T. Teramoto, M. Yamazaki, N. Watanabe, M. Takahashi, and A. Yagishita, *J. Phys. B* **40**, F285 (2007).