

Unambiguous observation of F-atom core-hole localization in CF₄ through body-frame photoelectron angular distributions

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A dramatic symmetry breaking in *K*-shell photoionization of the CF₄ 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⁺ 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 CF₃⁺ and F⁺ atoms elucidates the underlying physics that derives from the Ne-like valence structure of the F(1s⁻¹) core-excited atom.

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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 ²A₁ and ²T₂ states of CF₄⁺ 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 ²Σ_g and ²Σ_u states of N₂⁺, 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 a 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 structures in the C(1s⁻¹) → π* bands 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 (MFPADs) 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 CO₂ [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 Rapid Communication 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 CF₄. 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: CF₄ + *hν* → CF₄⁺(1s_F⁻¹) + e⁻ → CF₃⁺ + F⁺ + 2e⁻. The RFPAD measured by detecting the photoelectron in coincidence with the F⁺ atom is not expected to be symmetric, 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, shows 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 ~ 3 , ~ 5 , and ~ 12 eV above the fluorine K -edge vertical ionization energy in CF_4 of 695.37 ± 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 analyzer 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 a full solid angle, static magnetic fields of 8.2 and 4.2 G 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 CF_3^+ and F^+ ion on a shot-by-shot basis and for known orientations 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 CF_4 [15].

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

$$\frac{d^2\sigma^{\Gamma_0}}{d\Omega_{\hat{\epsilon}}d\Omega_{\hat{c}}} = \frac{8\pi\omega}{3c} |\hat{\epsilon} \cdot \langle \Psi_{\Gamma_0, \mathbf{k}_{r_0}}^- | \hat{\mu} | \Psi_0 \rangle|^2, \quad (1)$$

where $\hat{\mu}$ is the dipole operator, ω is the photon energy, and c is the speed of light. Equation (1) defines the cross section for polarization $\hat{\epsilon}$ and ejected electron momentum \mathbf{k}_{r_0} , leaving the ion in state Γ_0 . The complex Kohn scattering calculation produces the final-state wave function $\Psi_{\Gamma_0, \mathbf{k}_{r_0}}^-$ in this expression. Here, this wave function is the result 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 Γ_0 .

In the ground-state electronic configuration of 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 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 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 Γ_0 corresponding to localized $1s$ vacancy. To construct RFPADs, these cross sections in all cases were averaged numerically for rotation of the 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 CF_3^+ and F^+ ions. The calculations reproduce the experimental RFPADs in almost every detail, but only in the case of complete localization of the $F(1s^{-1})$ 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

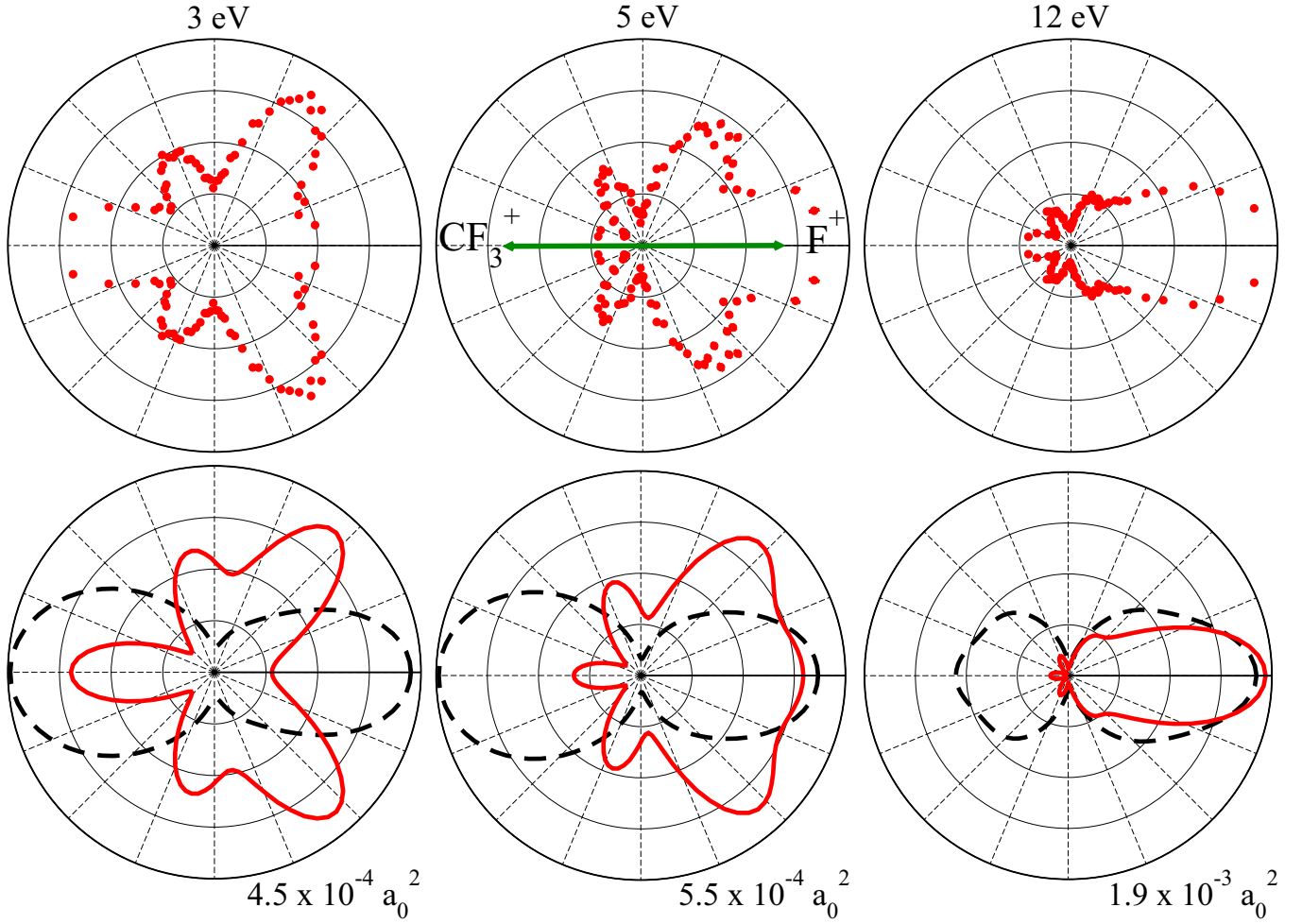


FIG. 1. Experimental (relative) and theoretical (absolute) RFPADs for polarization parallel to the C-F recoil axis. The experimental RFPADs use data for KER > 5.5 eV. Left to right: Ejected electron energies 3, 5, and 12 eV. Upper panels: Experiment. Lower panels: Theory. Dashed lines are for delocalized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

which each appears with the probability amplitude that contributes to the body-frame photoionization cross section in Eq. (1),

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

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 Ψ_{final} in Eq. (2). In this experiment the subsequent Auger decay leads to a breakup of the resulting dication, from which a single fluorine ion, say, 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, $\langle \Psi_{1sF_{\gamma}^+, \mathbf{k}_p}^- | \hat{\mu} | \Psi_0 \rangle$, to produce a core hole on F_{γ} with the amplitude that the hole on each resulting F_{γ}^+ decays to ultimately produce the decay product $CF_3^+ + F_a^+$, while producing an Auger electron of momentum \mathbf{k}_A which in our experiment is not

detected,

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

We denote the amplitude for the hole on F_b , for example, to produce the detected 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.

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

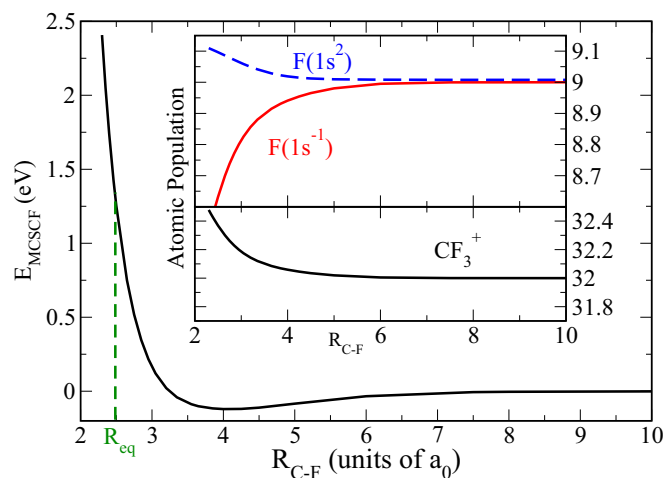


FIG. 2. Potential curve for CF_4^+ dissociation from SCF calculation with $1s$ vacancy enforced on dissociating fluorine. Inset: Mulliken populations showing that the dissociating fluorine atom has a population of nine electrons and is therefore neutral while the CF_3^+ fragment has 32 electrons.

pointed out in earlier theoretical calculations [20,21], using the “equivalent core” representation of a $\text{F}^+(1s)^{-1}$ core-hole atom as a Ne^+ atom, that the $\text{F}^+(1s)^{-1}$ core-hole atom is so electronegative that in this molecule the dissociation of CF_4^+ with a localized core hole in one fluorine can proceed via dissociation of a neutral F^* atom with a core vacancy but a filled valence shell that removes a valence electron from the CF_3 fragment. However, the measured Auger-electron energies in the CF_4^+ ion [10] show no direct evidence for an isolated F^* atomic decay which occurs ≈ 10 eV higher [22,23] in energy. Thus the F^* atomic decay must occur when the F^* is still near the CF_3^+ fragment, consistent with the previously calculated Auger lifetime of 3.8 fs for the 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 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], a 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 CF_4^+ ion into CF_3^+ and F^+ , of course, and in Fig. 3 we show the kinetic energy release (KER) of the 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 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 F^+

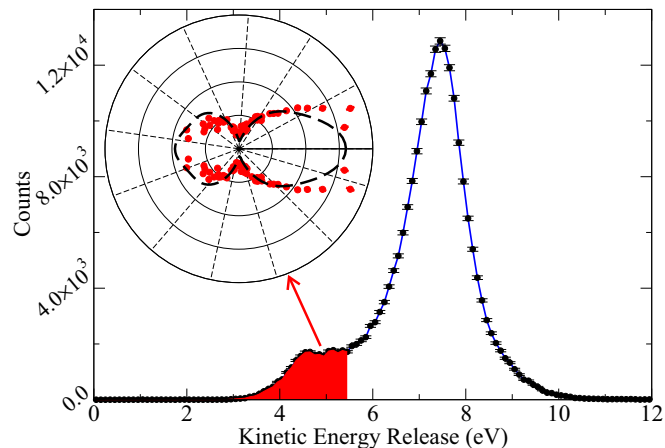


FIG. 3. Kinetic energy release (KER) for ejected electron energy of 12 eV. Inset: RFPAD for polarization parallel to the C-F recoil axis (horizontal) measured using only data for $\text{KER} < 5.5$ eV compared with calculations for the delocalized fluorine $1s$ hole (from Fig. 1, bottom right).

ion when the core vacancy was created elsewhere. Similar comparisons at photoelectron energies of 3 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 dipolelike 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 the 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 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 ~ 5 eV is coincidentally at the KER for fragmentation of CF_4^{2+} into CF_3^+ and 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 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 σ orbitals, for which earlier calculations indicate there are many candidates in this energy range [27].

The RFPADs in Figs. 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 represent 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],

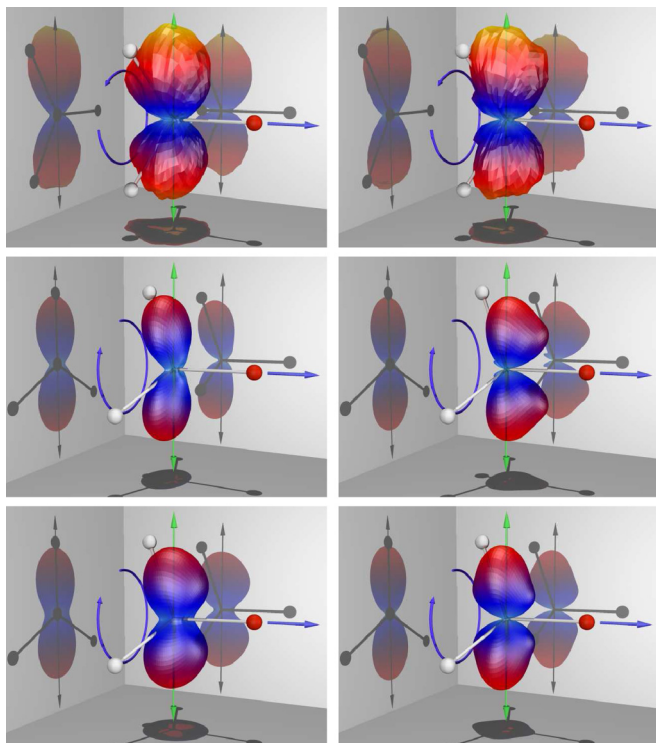


FIG. 4. RFPADs for polarization perpendicular to the C-F recoil axis and $\text{KER} > 5.5$ eV. Left, 3 eV, and right, 12 eV, ejected electron energy. Rows top to bottom: Experiment, theory for localized F core vacancy, and theory for delocalized F vacancy.

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 a combination of experiment and theory, we have seen that under particular experimental conditions the observation in coincidence of F^+ ions and photoelectrons ionized near the fluorine K edge in 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 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 (neonlike) valence configuration by withdrawing an electron from the CF_3 fragment, which then produces a steeply repulsive interaction between CF_3^+ and F^* .

In other polyatomics with symmetry-equivalent atoms, such as HCCH [8] and 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 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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