Electron vacancy-level dependent hybrid photoionization of the \( F^{-}@C_{60}^{+} \) molecule: a novel effect

Esam Ali\(^1\), Taylor O'Brien\(^1\), Andrew Dennis\(^1\), Mohamed El-Amine Madjet\(^1,2\), Steven T Manson\(^3\) and Himadri S Chakraborty\(^1,\ast\)

\(^1\) Department of Natural Sciences, D.L. Hubbard Center for Innovation, Northwest Missouri State University, Maryville, Missouri 64468, United States of America
\(^2\) Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany
\(^3\) Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303, United States of America

E-mail: eaagx2@mst.edu and himadri@nwmissouri.edu

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Abstract

Our previous studies (Shields et al 2020 J. Phys. B: At. Mol. Opt. Phys. 53 125101; Shields et al 2020 Euro. Phys. J. D 74 191) have predicted that the atom-fullerene hybrid photoionization properties for \( X = \text{Cl}, \text{Br} \) and I endohedrally confined in \( C_{60} \) are different before and after an electron transfers from \( C_{60} \) to the halogen. It was further found as a rule that the ionization dynamics is insensitive to the \( C_{60} \) level the electron originates from to produce \( X^{-}@C_{60}^{+} \). In the current study, we report an exception to this rule in \( F^{-}@C_{60} \). It is found that when the electron vacancy is situated in the \( C_{60} \) level that participates in the hybridization in \( F^{-}@C_{60}^{+} \), the mixing becomes dramatically large leading to strong modifications in the photoionization of the hybrid levels. This novel effect is fundamentally based on a level-crossing phenomenon driven by the electron transfer in \( F^{-}@C_{60} \). But when the vacancy is at any other pure level of \( C_{60} \), the level-invariance is retained showing weak hybridization. Even though this case of \( F^{-}@C_{60} \) is an exception in the halogen@\( C_{60} \) series, the phenomenon can be more general and can occur with compounds of other atoms caged in a variety of fullerences. Possible experimental studies are suggested to benchmark the present results.

Keywords: photoionizations, hybridization, endofullerenes, level-crossing, DFT, electron-transfer

(Some figures may appear in colour only in the online journal)

1. Introduction

Progress in synthesis and isolation techniques [1] of endohe- dral fullerenes, an atom taken hostage in a fullerene cavity, or endofullerenes for short, present opportunities for their experimental and motivations for their theoretical studies. One attraction for such studies arises from the interesting symmetry and great stability of these systems of natural molecular traps. The other is the fact that a vast range of existing and potential technologies, encompassing photovoltaics [2], superconductivity [3], quantum computations [4, 5], molecular device [6] and bio-medics [7], uses materials that have endofullerenes at their core. Such technologies and their further developments may find underpinnings of success from the information obtained via fundamental spectroscopic studies of these molecules.

In order to study the ionizing response of vapor-phase endofullerenes to UV electromagnetic radiations, a series of
measurements [8–10] was conducted using merged beam techniques at the Berkeley Advanced Light Source. With the increase of sample production rates, there are future possibilities of performing photoelectron spectroscopic experiments [11] on these systems. A swath of theoretical studies at various levels of approximation on the photoionization of endofullerenes with closed shell atoms also exists [12, 13]. In particular, hybridization of high-lying orbitals of the central atom with C₆₀ and explorations of the photoionization properties of these hybrid levels have regularly been predicted [14–18]. Hybrid levels are unique, for they expose interference features from the atom-fullerene coherent ionization which are absent in the isolated systems.

Endofullerenes of open-shell atoms, on the other hand, may also have interesting applied relevance [19]. At a rather exotic level, N@C₆₀ exhibited uniquely long spin relaxation times driven by the confinement [20], P@C₆₀ displayed an enhancement in hyperfine coupling of the phosphorous’ unpaired electrons with its nucleus [21], and muonium@C₆₀ indicated a diminution of the hyperfine interaction between the positively-charged muon and the unpaired electrons [22].

Computations of nonlinear optical response were done on endofullerene dimers where F@C₆₀ is used as one monomer [23]. A recent calculation [24] revealed a whole electron transfer from C₆₀ to the molecular F₂, despite C₆₀’s high electron affinity, forming F₂@C₆₀⁺. Very recently, we performed theoretical photoionization studies of isolated halogen endofullerenes Cl@C₆₀ [25], Br@C₆₀ and I@C₆₀ [26]. A halogen atom with an outer-shell electron vacancy (hole) can be reactive and can readily capture an electron from C₆₀ to acquire a stable configuration. However, this transfer will need energy, since the electron affinity level energies of halogens are higher than the binding energy of C₆₀ HOMO level. Of course, there will be extra binding due to the electrostatic attraction between F⁻ and C₆₀⁺. However, some such stable configurations with the electron coming from deeper C₆₀ levels may actually be metastable due to the need for larger transition energies. In any case, the realistic ground state of the compound may be a mixture of configurations, before and after the electron transfer. Therefore, knowledge of photoionization properties of all molecular states can be useful to reveal the actual configuration of the molecule by photoelectron spectroscopic experiments. Furthermore, multiple metastable states are known to form in other processes, such as, in slow electron collisions leading to the formation of negative ions of fullerene molecules [27]. Therefore, a knowledge repository of endofullerenes with various stable and metastable electronic structures accessed by photoionizing the atom-fullerene hybrid levels can have cross-topical relevance as well.

2. Novel effects of level-crossings

There may arise a new phenomenon originating from the near-degeneracy due to energy-crossing between an atomic and a fullerene level driven by the electron transfer. Fundamental effects generated by level-crossing are abound. A simple example is the transition metals in the periodic table: up to Ca, the 3d level is an excited state being above 4s. But by Sc, 3d moves into the ground state by crossing 4s and the ground state photoionization cross section of Sc changes dramatically from Ca. Another example is the near-threshold dramatic photoionization behavior of Si⁺⁺ in the Ne isoelectronic sequence [28]. This happens as the inner 2s → 3p excited (autoionizing) state crosses the 2pₓ² 3pᵧ/2 ionization threshold along the sequence such that the resulting resonance just straddles the ionization limit at Si⁺⁺. A maximum entanglement between nuclear and electron spins is predicted for atoms at avoided crossings demonstrating a relation between the level crossings and Berry phases at the level of the Breit-Rabi Hamiltonian [29]. Recently, the effect of chirped laser-pulse control in the interference between different pathways to study the momentum-dependent wave-packet using molecular level-crossing spectroscopy is studied [30]. Experimentally, a very efficient transfer through molecular bound states is shown by magnetically tuned mixing of two neighboring molecular levels [31]; this activated forbidden radio-transitions. Hence, exploring effects of atom-fullerene level-crossing on absorption properties as a function of spectral charge distribution can unfurl new horizon of studies in endofullerene materials. In other words, new phenomena can arise from level-crossings; in particular, from the near-degeneracy due to a level-crossing between an atomic and a fullerene level driven by the electron transfer.

It was found in our previous studies [25, 26] that the photoionization properties of the configurations of Cl⁻ @C₆₀⁺, Br⁻ @C₆₀⁺ and I⁻ @C₆₀⁺ were not sensitive to the particular C₆₀ level where the hole is located. This is because, as shown in figure 1, the valence np levels of the isolated X = Cl, Br, and I are energetically above the 2p level of empty C₆₀ (in the jellium model) that participates in the hybridization. When an electron in X@C₆₀ is captured by the central atom, the resulting screening effect shifts the atomic np level even higher. So the separation of interacting levels gets so large that it becomes irrelevant whether the electron that moved was a pure C₆₀ electron or a hybrid electron of X@C₆₀. Thus, the modification of the hybridization after the transfer becomes effectively insensitive to the vacancy level of X⁻@C₆₀⁺.

The situation, however, is very different if the free atomic level locates, on the other hand, below 2pC₆₀ as is the case for the smallest halogen F (see figure 1). In forming F⁻ @C₆₀⁺, the screening from the electron transfer will cause 2p to rise and move toward 2pC₆₀ from below it (figure 1, bottom left panel). This will create the condition of a reduced level separation, instead of the increase as happens for other halogens. The effect may sensitize the hybridization mechanism. For example, the transfer of a hybrid versus a pure C₆₀ electron could make a difference. These transfers are illustrated in figure 1, which also displays the resulting hybrid energy-levels and radial wavefunctions, respectively, in the middle and the right bottom panels. As we demonstrate in this paper, the hybridization indeed becomes dramatically higher when the vacancy is generated in the hybrid-active level of F@C₆₀ (bottom middle panel). To illustrate the effect of the vacancy at a pure (hybrid-passive) level which greatly minimizes the hybridization, HOMO C₆₀ is considered (bottom
right panel), since the result is found practically identical for any pure C_{60} vacancy. Strong implications of this phenomenon on the hybrid level photoionization of F@C_{60}^+, a hitherto unknown effect, will be presented by comparing cross sections calculated with the hole in different C_{60}^+ levels.

3. Theoretical model in brief

The details of the theoretical schemes are described in reference [15] and more recently in reference [25]. Choosing the photon polarization along the z-axis, the photoionization dipole transition cross section in a linear response approximation of time-dependent density-functional theory (DFT) is given by,

$$
\sigma_{nl-\ell_\ell'} = |\langle \psi_{\ell_\ell'} | z + \delta V | \phi_{nl} \rangle|^2.
$$

(1)

Here \( \mathbf{k} \) is the momentum of the continuum electron, \( z \) is the one-body dipole operator, \( \phi_{nl} \) is the single electron bound wavefunction of the target level, and \( \psi_{\ell_\ell'} \) is the respective outgoing dipole-allowed continuum wavefunction, with \( \ell' = l \pm 1 \). \( \delta V \) represents the complex induced potential that accounts for electron correlations within the linear response of the electrons to the photon field. The computation of \( \delta V \) involves determining photon energy dependent induced change in the electron density to be obtained by varying the ground state potential with respect to the ground state electron density as described in reference [32].

We model the bound and continuum states, and the ground state potential, using the independent particle DFT approximation that utilizes the Leeuwen–Baerends (LB) exchange-correlation functional [33]. This functional involves the gradient of the electron density in the scheme described earlier [34]. We chose the spherical frame with F or F\(^-\) situated at the center of C_{60}. The polarization interaction of F\(^-\) may induce some offset in its position from the center. However, a DFT simulation with Born–Oppenheimer molecular dynamics found F\(^-\) oscillation within neutral C_{60} to be rather small [35] and a relatively weak effect on the photoionization process from such small offset was predicted [36]. Earlier studies also showed small effects of the cage polarization except very close to the ionization threshold [37].

A core of 60 C\(^{4+}\) ions for C_{60} is constructed by smearing the total positive charge over a spherical jellium shell with known molecular radius \( R = 6.70 \) a.u. (3.54 Å) [11] and thickness \( \Delta \). The Kohn–Sham equations for the system of 240 C_{60} electrons (four valence 2s^22p\(^2\) electrons from each carbon atom), plus all electrons of the central atom/ion, are then solved self-consistently. The values of \( \Delta \) and a pseudo potential used are determined both by requiring charge neutrality and obtaining the experimental value [38] of the first ionization threshold of C_{60}, \( \Delta = 2.46 \) a.u. (1.30 Å) thus obtained closely agree with the value extracted from measurements [11, 39]. Within this framework, we also selectively omit either F (F\(^-\)) or C_{60} (C_{60}^+) to obtain the corresponding empty C_{60} (C_{60}^+) and free F (F\(^-\)) results. Parametric optimization of LB functional followed the scheme utilized in the previous work [26] to reproduce the values of the ionization potential and the electron affinity of F from the NIST database within 20%.

4. Results and discussion

4.1. Ground state hybridization versus vacancy levels

In an endofullerene system, an eigenstate of the free atom can only couple with an eigenstate of the empty C_{60} of the same angular momentum symmetry (due to the orthogonality of spherical wavefunctions) to produce a pair of hybrid eigenstates of the composite system. For F@C_{60} this occurs between valence 2pF and 2pC_{60} states to produce symmetric and antisymmetric hybrid states of F@C_{60} as,

$$
| F \pm C_{60} \rangle = \eta_\alpha | \phi_{2pF} \rangle \pm \eta_\beta | \phi_{2pC_{60}} \rangle
$$

for F@C_{60}, and the same for F^+ @C_{60}^+ with F and C_{60} replaced by F\(^-\) and C_{60}\(^+\). Here \( \eta_\alpha = \sqrt{\alpha} \) and \( \eta_\beta = \sqrt{1 - \alpha} \), where \( \alpha \) is the mixing parameter that renders the hybrid states orthonormal. We use the hydrogenic Coulomb notation of labeling for F and F\(^-\), such that the corresponding 2p wavefunctions are radially nodeless. The standard harmonic oscillator notation is used for C_{60} and C_{60}\(^+\) where their 2p wavefunctions have one radial node. The radial component of these hybrid wavefunctions are, respectively, shown in figures 2(a) and (b). In general, the hybridization is favored when the energy separation between the reacting levels decreases and their wavefunction overlap increases; these energies and wavefunctions are also shown in figure 2. While the free 2p F level is just below empty 2pC_{60}, their wavefunction overlap is small owing to the small size of F leading to a weak hybridization in F@C_{60}. As seen, the deeper symmetric hybrid F + C_{60} [figure 2(a)] still retains significant F character, while the weaker-bound antisymmetric hybrid F − C_{60} [figure 2(b)] continues to remain largely C_{60}-like. On the other hand, the hybrid states of F\(^-\) @C_{60}^{4+} [11] with the vacancy at the HOMO
C_{60} level (which does not participate in hybridization), also plotted in figure 2, present the opposite picture: the significantly weaker bound antisymmetric hybrid [figure 2(b)] now becomes F-type, while the symmetric hybrid [figure 2(a)] is of C_{60} type. We find practically the same degree of mixing when the vacancy is at any other hybrid-passive C_{60} level, like HOMO, that remains pure in the compound. Note the following in going from F@C_{60} to F−@C_{60}^{+1}\(-\) in figure 2: (i) the binding energy of the F−-dominant hybrid level is significantly lower than that of the F-dominant hybrid level which is because of the stronger screening of the F nucleus due to the extra electron that was transferred to the atomic zone. However, (ii) the cage-dominant hybrids remain energetically close primarily due to the fact that the relocation of a single electron hardly affects the screening of the cage states owing to the large electron population of C_{60}. In effect, therefore, the F-dominated level swings past the almost stagnant cage-dominated level as the molecular configuration switches from F@C_{60} to F−@C_{60}^{+1}\(-\). However, if we choose the configuration F−@C_{60}^{+2p}, that is the vacancy in the hybrid-active 2p\(\text{C}_{60}\) level, the hybridization becomes very strong with the hybrid level energies being very close, as figure 2 further displays. For a quantitative estimate of this effect, we fit equation (2) to the hybrid wavefunctions of F−@C_{60}^{+2p}, to obtain \(\eta_{F} = 0.541\) and \(\eta_{C} = 0.841\); the fitted curves are included in figure 2. The bottom three panels of figure 1 together summarize the essence of the total phenomenon.

To understand the underlying physics that leads to the enhancement of the hybridization in F−@C_{60}^{+} when the vacancy is in 2p\(\text{C}_{60}\) versus in HOMO C_{60}, we use a qualitative picture. Although the calculation is done by placing a F− ion in a C_{60}^{+} cage directly, it is convenient to consider a two-step model. First consider the ground state of F@C_{60}. Then we use the levels of F@C_{60}, including its hybrid levels, as the basis to analyze the hybridization after an electron moves from C_{60} to F. This electron transfer is considered selectively from two levels: (i) from HOMO of F@C_{60} which is also HOMO of C_{60} and a pure C_{60} level and (ii) from F−− C_{60} which is a hybrid level of F@C_{60} but of dominantly cage-type and energetically shallower than the other hybrid F + C_{60} which is dominantly F-type (figure 2). In the first case it is a ‘whole’ electron that transfers to the F-zone and causes a ‘complete’ screening of the atomic nucleus. This causes the F-dominant hybrid of F@C_{60} to energetically shift upward, cross the practically unmoved cage-dominant hybrid and move far above to result in yet another weak hybridization in F−@C_{60}^{+1}\(-\), albeit a symmetry reversal as noted above and seen in figure 2. This effect will be quite general as long as the transferring electron originates from any of the pure C_{60} states of F@C_{60}, even though the total energy of resulting configurations will be different in each case. However, when the electron comes from the hybrid F − C_{60}, level, effectively a ‘partial’ electron transfers, inducing a rather ‘incomplete’ screening effect. Consequently, the F-dominant level will still up-shift, but under a weaker screening will not be able to separate far enough from the C_{60}-dominated hybrid level. This, along with the fact that the overlap between F − C_{60} and F + C_{60} wavefunctions is large due to their non-vanishing amplitudes on both F and C_{60} regions, will favor their increased mixing in the resulting configuration of F−@C_{60}^{+2p}. Thus, the electron-transfer induced near-degeneracy as a ‘novel tipping-point’ accentuates the atom fullerene hybrid emission as shown in the following.

It is true that the relatively weak hybridization in F@C_{60} does not, as such, suggest too strong a reduction of screening to support a small enough up-shift of the F-dominant level so that the effect justifies the strong enhancement of hybridization as seen in F−@C_{60}^{+2p}. But we argue that this is a limitation of the two-step model we use here to visualize the basic effect qualitatively, but not to quantify it. The real mechanism is a one-step adiabatic process where a F− anion is so rapidly formed that it does not allow the states of F@C_{60} to relax enough. In effect, in the real system, the mixing and

![Figure 2](image-url)
the transfer happen simultaneously between the same levels that hybridize. This feature is also borne out in our observation that equation (2), that includes wavefunctions of neutral F and C\textsubscript{60}, provides a somewhat better fit (figure 2) to F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1/2}p} hybrids than using wavefunctions of ionic systems in equation (2). As pointed out, in the F atom, unlike other halogens, the valence 2p level has a higher binding energy than 2p C\textsubscript{60}, and that is the key here. This is so that with smaller screening in F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1/2}p} the participant levels can still stay within a narrow energy proximity to strongly hybridize, while for F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1}} higher partial charge on F in the compound by using the density-derived electrostatic and chemical scheme\[41\] to find the charge of the F atom to be a fractional −0.43. The method was based on calculating the ground state partial charge distribution of F@C\textsubscript{60} using the PBE exchange-correlation functional. The result likely corroborates our assertion in the Introduction that the real ground state may be a mixture of configurations, before and after the electron transfer. The HOMO electron showing a tendency to move to the F site already at the ground state also favors the likelihood to undergo a complete transfer upon excitation.

We note that previous structure calculations indeed predicted partial electron transfer from C\textsubscript{60} to F in F@C\textsubscript{60} with net charge on F to be −0.29 [40]. This study asserted no possibility of reverse transfer from F to C\textsubscript{60} and indicated ionization signals from hybridized 2F\textsubscript{p} orbitals. Separately, we have also computed the partial charge on F in the compound by using the density-derived electrostatic and chemical scheme [41] to find the charge of the F atom to be a fractional −0.43. The method was based on calculating the ground state partial charge distribution of F@C\textsubscript{60} using the PBE exchange-correlation functional. The result likely corroborates our assertion in the Introduction that the real ground state may be a mixture of configurations, before and after the electron transfer. The HOMO electron showing a tendency to move to the F site already at the ground state also favors the likelihood to undergo a complete transfer upon excitation.

4.2. Hybrid photoionization versus vacancy levels

Cross sections calculated in linear response time-dependent DFT for three systems F@C\textsubscript{60}, F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1}H}, and F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1/2}p} are presented in figure 3 with panel (a) and (b), respectively, for emissions from the symmetric and the antisymmetric F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1/2}p}\textsuperscript{H} hybrid levels of F@C\textsubscript{60}\textsuperscript{+\textsubscript{1/2}p}. Cross sections of 2pF (F\textsuperscript{−}) and 2pC\textsubscript{60} are also presented.

Figure 3. Photoionization cross sections of the symmetric (a) and antisymmetric (b) hybrid levels of F@C\textsubscript{60}, F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1}H}, and F\textsuperscript{−} @ C\textsubscript{60}\textsuperscript{+\textsubscript{1/2}p}\textsuperscript{H}. Cross sections of 2pF (F\textsuperscript{−}) and 2pC\textsubscript{60} are also presented.

4.2.1. Low energy spectra. Comparing all the hybrid level results with the 2p cross sections of free F and F\textsuperscript{−}, which practically overlap with each other, and with 2p of empty C\textsubscript{60} indicates plasmon driven enhancements and structures at lower photon energies [14, 17, 18, 43]. In the framework of interchannel coupling (IC) due to Fano [44], the correlation-modified matrix element of the photoionization of X ± C\textsubscript{60} can be written perturbatively as

\[
\mathcal{M}_\pm(E) = D_\pm(E) + \sum_{\ell l} \int dE' \frac{\langle \psi_{nl}(E') | \frac{1}{\epsilon_{nl}} | \psi_\pm(E) \rangle}{E - E'} \times D_{\ell l}(E')
\]

in which the single electron (uncorrelated) matrix element, that is the matrix element without \(\delta V\) in equation (1), is

\[
D_\pm(E) = \langle ks(dl) | z | \psi_\pm \rangle
\]

and |\psi_{nl}\rangle in the IC integral is the (continuum) wavefunction of the \(nl \rightarrow kl\) channel. Taking the hybridization into account,
the channel wavefunctions in equation (6) become
\[ |\psi_\pm\rangle = \eta_\pm |\psi_{2pC_60}\rangle \pm \eta\mp |\psi_{2pC_60}\rangle. \] (5)

Substituting equation (5) into equation (6), and noting that the overlap between a pure \( X \) (antisymmetric) bound state and a pure \( C_60^- (C_60^+) \) bound state is negligible, since they occupy different regions of space, we separate the atomic and fullerene contributions to the integral to get the full (correlated) matrix element for \( X \pm C_60 \) and \( X^- \pm C_60^+ \) levels as,
\[ \mathcal{M}_{\pm}(E) = \eta_\pm \mathcal{M}_{2p\psi_{2pX}}(E) \pm \eta\mp \mathcal{M}_{2p\psi_{2pC_60}}(E), \] (6)
where the first and second terms, respectively, on the right-hand side describes IC effects of atomic and fullerene channels. Note that \( \mathcal{M}_{2p\psi_{2pX}} \) and \( \mathcal{M}_{2p\psi_{2pC_60}} \) are the IC matrix elements constructed via coupling respectively among pure atomic and fullerene channels.

Dominant fullerene characters of \( F^- + C_60^{+}(1) \) and \( F^- - C_60 \) wavefunctions (figure 2) ensure dominant fullerene IC effects in equation (6). This explains why the corresponding cross sections at lower energies almost follow the empty \( 2pC_60 \) result in figure 3. For \( F^- - C_60^{+}(1) \) and \( F^- + C_60 \) cross sections, on the other hand, while their dominant atomic character brings them close to the free \( 2pF^- \) results at higher energies, their enhancements at lower energies are notable. This enhancement is due to an IC driven mechanism discussed previously [43] that siphons off giant-size strengths from the fullerene plasmonic emission even though the fullerene admixture of these hybrid wavefunctions is quite small. However, note a rather dramatic difference between the symmetric \( F^- + C_60^{+}(2p) \) and \( F^- + C_60^{+}(1) \) results in figure 3(a) over, in fact, the entire energy range shown. This owes to the increased hybridization process in the \( F^- + C_60^{+}(2p) \) discussed as above in the main finding of this study. The process subsequently yields comparable atomic and fullerene IC effects in equation (6) including a comparable contribution of their coherence. On the other hand, there is not-so-dramatic differences between antisymmetric \( F^- - C_60^{+}(2p) \) and \( F^- - C_60^{+}(1) \) results in figure 3(b). In sum, if we find a most interesting and unexpected phenomenology; the symmetric case, figure 3(a), is very strongly dependent upon the location of the \( C_60 \) vacancy, but the antisymmetric case is not. This must mean that there are cancellations in the matrix elements in the antisymmetric case that are not present for the symmetric case.

4.2.2. Higher energy spectra. As the plasmonic effect weakens with increasing energy, oscillatory modulations at varied degrees of prominence show up in the cross sections. These oscillations are a consequence of a well-known interference mechanism [45] due to the cavity structure of \( C_60 \) which was modeled earlier in detail in reference [46]. At such high energies the IC in equation (6) is no longer important, but the hybridization remains, so that equation (6) simplify to
\[ D_{\pm}(E) = \eta_\pm D_{2p\psi_{2pX}}(E) \pm \eta\mp D_{2p\psi_{2pC_60}}(E). \] (7)

The interference model is based on the following mechanism. The matrix element \( D_{\pm} \) can generally be separated into two components, one arising from the atomic region and other from the \( C_60 \) shell region, and can be written down, respectively, as follows [46]
\[ D_X \sim D_{\text{atom}}(k) + A^{\text{eff}}(k) \left[ e^{-ikD_a} e^{-iV_a X \pm} - e^{-ikD_i} \right] \] (8a)
\[ D_C \sim A^{\text{shell}}(k) e^{-ikR_0} [a_i e^{-ikR_i} - a_o e^{-ikR_o}], \] (8b)
where the photoelectron momentum \( k = \sqrt{2(E - e\pm)} \) in atomic units, \( a_i \) and \( a_o \) are the values of \( \phi_{\text{C}_60^-} \) at the inner and outer radii \( R_i \) and \( R_o \) of \( C_60 \), and \( V_0 \) is the average depth of the shell potential. In equation (8a) \( D_{\text{atom}} \) represents the direct ionization amplitude from the atomic region. The second term in this equation embodies the reflection of this outgoing photoelectron wave from both inner and outer surfaces of the shell. Quantitatively, this induces oscillations as a function of the photoelectron momentum with amplitude \( A^{\text{shell}} \) and frequencies related to \( D_i \) and \( D_o \), the inner and outer diameters of the shell. The direct and the reflected parts coherently interfere in the cross section.

Since \( A^{\text{eff}} \) is proportional to \( D_{\text{atom}} \), the larger the atomic component of a hybrid wavefunction, the stronger is the reflection and the higher is the chances that the oscillations occur about the free atom (ion) result. This is exactly what is seen for the high energy cross section of the \( F \)-dominant levels of \( F@C_60 \) and \( F^- @C_60^{+}(1) \) that follow the \( 2pF \) result in figure 3. On the other hand, equation (8b), resulting from the overlap integral in the shell region, produces two localized emissions in the vicinities of the shell edges, where the available ionizing forces maximize due to rapid variations of the shell potential there. Such a diffraction-type effect translates into another oscillation in frequencies related to \( R_i \) and \( R_o \). This part will also add to the coherent interference in the cross section and will dominate if a hybrid level has a stronger \( C_60 \) character, like for the \( C_60 \)-dominant levels of \( F@C_60 \) and \( F^- @C_60^{+}(1) \) in figure 3. Indeed, the oscillation structures in the cross section of these hybrid levels intensify at higher energies while the average value fall lower than free \( 2pF \) as exhibited in figure 3.

As already noted above, for the \( F^- @C_60^{+}(2p) \) hybrids, due to their almost comparable share of atom-\( C_60 \) character, the differences in the corresponding cross section shapes arise from the interference among strong direct atomic, reflective and relatively comparable diffusive emissions. As pointed out above, the particularly strong differences between the high-energy results of symmetric \( F^- + C_60^{+}(2p) \) and \( F^- + C_60^{+}(1) \) and relatively weaker differences between antisymmetric \( F^- - C_60^{+}(2p) \) and \( F^- - C_60^{+}(1) \) are noted in figure 3. These differences further identify the importance of hybrid versus pure vacancies in \( F^- @C_60^{+} \) in the spectroscopic details of higher energy emission structure and properties.

4.3. Experimental possibilities

Figure 4 presents the results of the subtraction of total \( C_60 \) cross section from the total cross sections of the compound in two configurations \( F^- - C_60^{+}(2p) \) and \( F^- - C_60^{+}(1) \). The deviation of the results from the total cross section of free \( F^- \) ion (shown) captures the net effect of the atom-fullerene
coherence following the electron transfer. As is evident, constructive interferences from this coherence is seen near the C₆₀ giant plasmon resonance energies. Surprisingly, however, this effect at the higher energy (weaker) plasmon resonance around 40 eV is found rather destructive; probing this can also be interesting given experimental abilities to observe this resonance [47]. Thus, such coherence effects can be directly probed by total photoionization cross section measurements by, for instance, the techniques utilized earlier based on detection and analysis of photoions [8–10]. In fact, such measurements can be extended for other halogen endofullerenes as well. Since the results in figure 4 also accounts for the differences between vacancy positions, the comparison with measurements may further shed light on the possible configuration of the molecule in its ground state. Figure 3 indicates that going up to 60 eV the calculated cross sections can drop as much as by three orders of magnitude which may pose challenges in measurements. However, the experimental signal will likely also include contributions from the atomic carbon ionization to augment the data with increasing energies [11]. Therefore, the cross section differences in figure 4 become particularly useful, since carbon contributions may largely cancel out to capture the effects of hybridization.

Another method to explore the situation experimentally is to use one laser pulse to excite F@C₆₀ by inducing an electron transfer and another pulse to ionize the hybrid levels to probe excited state cross sections. Such two-color two-step photoionization measurement techniques have been used earlier [48–50]. Based on this technique, an electron can be selectively promoted from a chosen C₆₀ level, namely C₆₀ HOMO or a hybrid level, to form metastable configurations. The comparison between spectra for photoelectrons driven by the subsequent second laser allows access to ionization properties as a function of the vacancy level.

Synthesis of halogen endofullerenes in vapor-phase has not been reported yet. But this may be possible by, for instance, halogen ion implantation techniques as adopted for other systems [51]. Perhaps because of the noncovalent interactions of these molecules with the environment their photoionization response will remain largely intact in some stable salt form, or in solutions or as thin films.

5. Conclusions

We previously studied [25, 26] the photoionization of various halogen-atomic (Cl, Br and I) endofullerene molecules with a C₆₀ electron relocated to the halogen atom likely forming metastable configurations. Those studies predicted that the effect of atom-C₆₀ hybridization on both ground state and photoemission properties is practically insensitive to the location of the vacancy level in C₆₀. In the current investigation we find a strong exception to this rule for such a metastable system F@C₆₀⁺ made of the remaining halogen atom F. This exception reveals a novel effect based on the relative positions of the levels that hybridize in the compound. It is found that since, unlike to other halogens, the participating F level is more bound than the partner C₆₀ level, the increased screening due to the transfer of the electron results in a level crossing mechanism. Due to this mechanism, the degree of hybridization is significantly altered based on the vacancy creation in the hybrid-active versus a pure C₆₀ level. Consequently the hybrid photoemission properties become a very sensitive function of the vacancy position. The calculations are performed in a linear-response time-dependent density functional scheme, as was also employed in previous studies. We have discussed ideas for experiments to verify the predictions. Even though the effect is unique for F@C₆₀⁺ for the halogen series, the precondition of such level-crossing effect can easily be satisfied for some of the other atoms, or small molecules, or metal cluster trapped in C₆₀ or even, in general, for different choices of the fullerenes itself, given that the atom-fullerene hybridization is a ubiquitous phenomenon in a host of these materials. In other words, we expect that this is a very general phenomenon and studies extended to the host of fullerene derivatives can uncover new spectroscopic effects possibly charting a new sub-field.

In our calculations, the C₆₀ ion core is smeared in a jelium spherical shell that freezes lattice vibrations. Effectively, this mimics results at absolute zero sample temperature. However, it was shown earlier [32] that finite oven temperature effects, such as, the electron–phonon coupling [52] and fluctuation of the shape around the shape at absolute zero [53], approximately needed an extra width less than 1 eV to compare with measurements for C₆₀. This width is smaller than an energy resolution of about 5 eV required to measure broad structures in figures 3 and 4. Thus, while the thermal vibration will likely wash out the autoionizing spikes, it would not qualitatively alter the key results of this study. Furthermore, possible temperature driven oscillations [54] of the confined atom may broaden and lower some narrow structures in the signal, but most of the features in the current results...
being broad enough will survive. As an example, the measurement of the confinement induced structures in Xe@C_{60} was possible in the laboratory at a temperature well above absolute zero [9, 10]. Of course, the colder the sample temperature, the closer to the predictions the measurements can come. Besides encouraging experiments, the other aim of the study is to motivate simulations including fullerene lattice vibration and phonon coupling effects. However, this will be rather challenging. Because, while the molecular structure can readily be improved by employing sophisticated methods to include lattice vibrations, the photoionization will require calculations of continuum wavefunctions including electron correlation in the electron–phonon coupled frame.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Esam Ali  https://orcid.org/0000-0002-4836-8520
Mohamed El-Amine Madjet  https://orcid.org/0000-0002-8910-2278
Steven T Manson  https://orcid.org/0000-0002-7072-4122
Himadri S Chakraborty  https://orcid.org/0000-0001-5758-6418

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