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Letter

First prediction of inter-Coulombic decay of C$_{60}$ inner vacancies through the continuum of confined atoms

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Abstract

Considering the photoionization of Ar@C$_{60}$ and Kr@C$_{60}$ endofullerenes, the decay of C$_{60}$ innershell excitations through the outershell continuum of the confined atom via the inter-Coulombic decay (ICD) pathway is detailed. Excitations to atom-C$_{60}$ hybrid states, when these states exist, can induce coherence between ICD and electron-transfer mediated decay (ETMD). This should be the dominant above-threshold decay process for a variety of confined systems, and the strength of these resonances is such that they should be amenable for study by photoelectron spectroscopy.

Keywords: ICD, photoionization, ETMD, endofullerene, hybridization

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

The resonant energy transfer from a donor to a near-neighbor acceptor molecule is a ubiquitous phenomenon in matter [1]. In complex materials, comprising a variety of light absorbing components called chromophores with clean absorption and fluorescence bands, the photoexcitation at the donor site is commonly followed by a migration of the energy to a closely separated acceptor chromophore which can subsequently relax to emit a fluorescent photon. The Coulomb interaction between donor-acceptor active electrons is the conduit of such non-local energy transfer. This fluorescence resonant energy transfer (FRET) spectroscopy has a vast range of applications in biological, nanoscale [2], and nano-bio hybrid [3] systems. For relatively smaller aggregations of matter, such as clusters and dimers with limited electronic and vibrational degrees of freedom, the excited state of an inner electron at the donor site can often be embedded in the ionization continuum of the acceptor, resulting in a non-radiative release of an acceptor electron as the excitation energy relocates. In other words, an outer electron of the donor fills the inner vacancy and the released energy transfers to the acceptor to ionize it. This phenomenon, known as inter-Coulombic decay (ICD), was predicted [4] and was first observed for Ne clusters [5] some years ago. Novel experiments on the ICD process focusing on fundamental science are abundant [6–10]. Furthermore, ICD driven slow electrons may potentially find applications in controlled radiation damage in medical sciences [11, 12] as well as, potentially, in nanoscale antenna technology [13]. On the other hand, another process can take place, that is, the donor vacancy can be occupied by an acceptor electron. This may happen if the original excitation entails the transit of an electron from one center (donor) to the excited state of
another center (acceptor). In this case the decay with the creation of an outer shell vacancy on either center is called resonant electron-transfer mediated decay (ETMD) [14, 15].

From a fundamental spectroscopic viewpoint, probing resonant ICD (RICD) processes [16–18] in relatively simpler gas-phase materials is of great interest [16, 17, 19, 20]. One class of such systems undergoing significant current theoretical and experimental scrutiny is atomic endofullerene complexes, in which an atom is encapsulated in a fullerene molecule. These are unique heterogeneous and nested dimers of weak atom-fullerene bonding exhibiting very different electronic properties from the atom to the fullerene. From the experimental side, the synthesis techniques for these materials are fast-developing [21] with the huge advantage of their room-temperature stability. Moreover, these materials promise a plethora of applied contexts [21]. The earliest prediction of the shortening of the decay time of a Ne excited state through the ICD pathway when Ne is confined in C_{60} was made in 2006 [22]. Later, such broadening of atomic Auger lines due to non-local Coulomb-mediated decay in endofullerenes were also suggested by others [23, 24].

The first detailed calculations of RICD resonances corresponding to Ar inner 3s excitations in the photoionization of the levels of the encapsulating C_{60}, the atom-to-fullerene forward RICD, was recently performed by us [25]. In addition, a dominant and novel effect was found in the coherence between the Auger and ICD transition amplitudes to produce resonance structures in the photoionization of atom-fullerene hybridized states [25, 26]. These resonant hybrid Auger-ICD (RHA-ICD) features, with their various shapes and widths, bear signatures of this coherence. However, to the best of our knowledge, no RICD of a C_{60} inner vacancy producing a purely atomic outer vacancy in the engaged atom, the fullerene-to-atom backward RICD, has been predicted until now. Only, as a reverse analogy, but for a non-resonant spectral effect from atom to fullerene, even when the participating charge densities are pure non-hybrid, was seen earlier [27].

In this communication, considering the photoionization of the valence ns subshell of the atoms X, Ar and Kr, in X@C_{60}, we predict autoionizing resonances from the RICD of C_{60} inner excitations. Owing to the hybridization of some of the excited states of the compound, the RICD amplitude is also found to admix coherently with the ETMD process. The results, along with our previous findings [25, 26], complete the full ICD landscape in a photon-driven endofullene molecule, highlighting these materials, in gas or condensed phase, as possible candidates for experiments.

Kohn–Sham density functional theory is used to describe the ground state electronic structure of the compounds [28]. The C_{60} molecule is modeled by smudging sixty C^{4+} ions over a classical spherical jellium shell, fixed in space, with an experimentally known C_{60} mean radius 3.5 Å and thickness Δ. The nucleus of the confined atom is placed at the center of the sphere. The Kohn–Sham equations for the system of a total of 240 + N electrons (N= 18 for Ar, N = 36 for Kr and 240 delocalized electrons from C_{60}) are then solved to obtain the electronic ground state properties in the local density approximation (LDA). The gradient-corrected Leeuwens and Baerends exchange-correlation (XC) functional [LB94] [29] is used for the accurate asymptotic behavior of the ground state radial potential

\[ V_{\text{LDA}}(\mathbf{r}) = V_{\text{jel}}(\mathbf{r}) - \frac{Z_{\text{atom}}}{r} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[\rho(\mathbf{r})], \]

(1)

which is solved self-consistently in a mean-field framework. The requirement of charge neutrality produced Δ = 1.3 Å, in agreement with the value inferred from experiment [30].

The time-dependent local density approximation (TDLDA) is employed to simulate the dynamical response of C_{60} to incident photons [31]. The dipole operator, \( z \), corresponding to light that is linearly polarized in \( z \)-direction, induces a frequency-dependent complex change in the electron density arising from dynamical electron correlations. This can be written, using the independent particle (IP) susceptibility \( \chi_0 \), as

\[ \delta \rho(\mathbf{r}; \omega) = \int \chi_0(\mathbf{r}, \mathbf{r}'; \omega) (z' + \delta V(\mathbf{r}'; \omega)) d\mathbf{r}', \]

(2)

in which

\[ \delta V(\mathbf{r}; \omega) = \int \frac{\delta \rho(\mathbf{r}'; \omega)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \left[ \frac{\partial V_{\text{xc}}}{\partial \rho} \right]_{\rho = \rho_0} \delta \rho(\mathbf{r}; \omega), \]

(3)

where the first and second terms on the right-hand side are, respectively, the induced changes of the Coulomb and the
Figure 2. Photoionization cross sections of $4s$ subshell for free and confined Kr (a) and $3s$ subshell of free and confined Ar (b). The total cross section of empty $C_{60}$ $3s$ is also presented. Various $C_{60}$ ionization thresholds of respective complexes are shown. For either system, note the red-shift of the position of the Cooper minimum due to the confinement.

exchange-correlation potentials. Obviously, $\delta V$ includes the dynamical field produced by important electron correlations within the linear response regime. In this method, the photoionization cross section corresponding to a bound-to-continuum dipole transition $n\ell \rightarrow k\ell'$ is given by

$$
\sigma_{n\ell \rightarrow k\ell'} \sim |\langle k\ell' | z + \delta V | n\ell \rangle|^2,
$$

where the TDLDA matrix element $M = D + \langle \delta V \rangle$, with $D$ being the independent-particle LDA matrix element. Obviously, $\langle \delta V \rangle$ in equation (4) is the contribution of many-body correlations within TDLDA [31].

It is well known that in X@$C_{60}$ the atomic valence $np$ electrons strongly hybridize with the energetically shallower $p$ electrons of the host $C_{60}$ [25, 26, 32]. The subvalent $ns$ levels of X, however, maintain their purity, as seen in figure 1(a) which shows predominantly atom-like Ar $3s@$ radial wavefunction from the ground LDA spectrum of Ar@$C_{60}$. Single-electron excitations from a number of $C_{60}$ inner levels $n\ell'$ (whose ionization thresholds are indicated in figure 2) occur at energies higher than the Ar $3s@$ and Kr $4s@$ thresholds, 30.1 eV and 26.5 eV respectively. Of these $C_{60}$ levels, $@3d$ and $@1s$ wavefunctions are presented in figure 1(a). (Although these levels are the quantum states of the whole compound, we use $n\ell@$ and $n\ell'$ respectively to ascertain their atom- or $C_{60}$-dominant character.) Using the well-known approach by Fano [33] to describe the dynamical correlation through the interchannel coupling, the RICD amplitudes of these $C_{60}$ photo-vacancies via $X$ $ns@$ ionization can be expressed by $M^{d-c}$ that denotes the coupling of $C_{60}$ discrete (d) excitation channels $@n\ell' \rightarrow \eta\lambda$ with the $ns@ \rightarrow kp$ continuum (c) channel of X. This correlation from discrete-continuum interchannel coupling, that accounts for the resonances, is included in $\langle \delta V \rangle$ in equation (4). Following [25],

$M^{d-c}$ can be written as:

$$
M_{n\ell@ \rightarrow kp}^{d-c}(E) = \sum_{\eta\lambda} \sum_{n\ell'} \langle \psi_{n\ell' \rightarrow \eta\lambda} | \frac{1}{|r_1 - r_2|} | \psi_{n\ell@ \rightarrow kp}(E) \rangle D_{n\ell' \rightarrow \eta\lambda},
$$

where $E_{n\ell' \rightarrow \eta\lambda} = D_{n\ell' \rightarrow \eta\lambda}$ are, respectively, excitation energies and LDA matrix elements of channels $@n\ell' \rightarrow \eta\lambda$ and $E$ is the photon energy corresponding to the $ns@ \rightarrow kp$ transition. In equation (5) the $\psi$ are independent-particle (LDA) wavefunctions that represent the final states (channels) for transitions to excited $\eta\lambda$ or continuum $kp$ states. Obviously, the Coulomb matrix element in the numerator of equation (5) acts as the ‘corridor’ for energy transfer from the $C_{60}$ de-excitation across to the atomic ionization process, producing ICD resonances in the $@ns$ cross sections.

These $C_{60}$-to-X ICD resonances are displayed in figure 2 both for $4s$ (figure 2(a)) and $3s$ (figure 2(b)) photoionization of, respectively, confined Kr and Ar. As seen, the spectra are rather dramatically structured. Note that the corresponding results for free atoms are flat, since the current energy range does not include any regular autoionizing (Auger) decay of atomic innershell vacancies. The resonances in figures 2 are strong, of varied shapes, and should be easily accessible via photoelectron spectroscopy. Furthermore, the narrow width of these resonances, which is very different than characteristic atomic Auger resonances that are generally broad, is directly related to the $C_{60}$ excitations. Indeed, like generic cluster wavefunctions, $C_{60}$ wavefunctions are typically delocalized, spreading out over a large volume, in contrast to atomic localized electrons (see, figure 1). Since the autoionization rate involves the matrix element of $1/r_{12}$ (equation (5)), spread-out (delocalized) wavefunctions translate to a decrease in the value of the matrix element, as compared to atomic compact (localized) wavefunctions.

Figure 2 exhibits three particularly notable features: (i) the above-threshold vacancy decay is completely dominated by ICD. (ii) For both Kr $4s@$ and Ar $3s@$, the characteristic Cooper minima are moved lower in energy to 35 eV and 36 eV from their well-known positions of 41 eV and 42 eV [34], respectively, for free atoms. This shift is a consequence of the atom-$C_{60}$ dynamical coupling, particularly the coupling of $X$ $ns@ \rightarrow kp$ ionization with a host of $C_{60}$ continuum channels. Note that this coupling was not included in equation (5), which only captures the resonances, but is certainly present in the full dipole matrix element $M$ (see equation (4)). (iii) A comparison with the empty $C_{60}$ cross section in figure 2(b) reveals a few extra resonances in both the Kr $4s@$ and the Ar $@3s$ results. These are present owing to the additional excited states in the excited spectrum of the whole compound, since it now also includes the excited states of the caged atom. In fact, many of these excited states of the compound must be hybrids between the atomic and $C_{60}$ pure states—a fact addressed below suggests that some of these resonances are the result of the coherent mixing of ICD and ETMD amplitudes.
As an example, consider a hybridized dipole-allowed excited state \(4p^+\) from \(C_{60}^0 \oplus 3d\) (figure 1(a)) in \(Ar@C_{60}\). The radial wavefunction of \(4p^+\), shown in figure 1(b), results from a symmetric hybridization of free \(Ar\) and empty \(C_{60}^0 4p\) excited states as

\[
|4p^+\rangle = \sqrt{\alpha} |Ar4p\rangle + \sqrt{1 - \alpha} |C_{60}^04p\rangle .
\]  

(6)

Based on equation (6), the hybridizations in \(\psi\) and \(D\) for this transition are then

\[
|\psi@3d\rightarrow4p^+\rangle = \sqrt{\alpha} |\psi@3d\rightarrow Ar4p\rangle + \sqrt{1 - \alpha} |\psi@3d\rightarrow C_{60}^04p\rangle ,
\]  

(7)

\[
D@3d\rightarrow4p^+ = \sqrt{\alpha} D@3d\rightarrow Ar4p + \sqrt{1 - \alpha} D@3d\rightarrow C_{60}^04p .
\]  

(8)

Using equations (7) and (8) in equation (5) for the transition \(@3d\rightarrow 4p^+\), and assuming that the overlap between \(Ar\) \(4p\) and \(C_{60}^0\) \(4p\) states is negligibly small, we can break up \(M^{d-\varepsilon}\) as

\[
\begin{align*}
M^{d-\varepsilon} & = \epsilon - \frac{1}{|r_1 - r_2|} \psi_{3s\rightarrow 4p}(E) \\
& + (1 - \alpha) \left[ E - E_{@3d\rightarrow 4p^+} \right] \times D_{@3d\rightarrow C_{60}^04p} .
\end{align*}
\]  

(9)

The processes that equation (9) embodies are schematically shown in figure 1. The first term denotes the release of energy from a transfer de-excitation (blue arrow) of the atomic part of the \(4p^+\) hybridized electron state to \(C_{60}^0 \oplus 3d\) inner hole, and the subsequent migration (purple curved arrow) of that energy to \(Ar\) knocking out a \(3s\) electron (red arrow). This process is essentially an ETMD. The second term is the direct de-excitation (black arrow) of the \(C_{60}\) part of \(4p^+\) to \(@3d\) followed by the regular ICD. Obviously, ETMD and ICD coherently mix to produce the ensuing resonance structure in the cross section (equation (4)). Thus, some resonances in figure 2 occur from decay rates underpinning this coherence; a detailed characterization of the structures based on Fano-fitting is forthcoming.

To summarize, the first theoretical prediction for RICDs of fullerene innershell photoexcitations producing outershell vacancies in the caged atom is described. In fact, this generally appears to be the dominant, if not the only, single-excitation above-threshold decay mechanism through the atom’s non-hybrid outer levels for any endofullerene molecule. The hybridized character of some of the excited states of the compound points to a coherence of ICD with the ETMD process. The resulting resonances are found aplenty and are quite amenable to being probed experimentally. Although the present calculation only includes participant RICDs, where the precursor hole is filled by the excited electron itself, it is of great interest to access the influence of spectator processes; these could significantly affect the situation and certainly need study. Furthermore, with contemporary focus [35] on photoemission phase and time delay studies by interferometric metrology [36], we hope that the current results will stimulate similar temporal spectroscopy with ICD resonances.

Finally, based upon our explanation of the details of multicenter decay, the resonant ICD predicted here is expected to be a strong process in general for any atom or molecule encaged in any fullerene, in any position, central or not. The ICD-ETMD coherence, that involves hybridization in the final excited state, should also be abundant—all it would require is that both the fullerene and the trapped atom or molecule have dipole-allowed excited states of the same (angular momentum) symmetry so they can hybridize.

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