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Single-Photon Multiple-Detachment in Fullerene Negative Ions: Absolute Ionization Cross Sections and the Role of the Extra Electron

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We have obtained experimental photo double- and triple-detachment cross sections for the fullerene negative ion using Advanced Light Source photons of $17-90$ eV. The cross sections are 2 and 2.5 times larger than those for C_{60} and appear to be compressed and shifted in photon energy as compared to C_{60}. Our analysis reveals that the additional electron in C_{60}^- leads primarily produces screening which is responsible for the modification of the spectrum. Both screening effects, the shift and the compression, can be quantitatively accounted for by a linear transformation of the energy axis. Applying the transformation allows us to map the neutral and negative ion cross sections onto each other pointing out the close relationship of correlated few-electron dynamics in neutral and negatively charged extended systems. In contrast, dynamics of neutral and negatively charged atoms or small molecules are typically not closely related.

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Many clusters and large molecules exhibit novel properties that, if understood and exploited, have the potential to revolutionize technology and fundamental knowledge [1, 2]. These large systems readily form negative ions which often play a central role in the behavior of the condensed state. Electron impact experiments on C_{60}^- have shown that different mechanisms account for the detachment of the extra electron from the negatively charged fullerene than in neutral and positive charged systems, which has led to the proposal of a novel mechanism in electron-impact ionization of molecular and cluster anions [3]. Despite this, while negative ion photodetachment [4] has been the subject of intense research (e.g., see [5–7]), photodetachment studies of negative ion clusters and large molecules remain limited, mainly due to experimental challenges.

Interest in negative ions stems in part from the fact that photodetachment spectra of negative ions are very different, both qualitatively and quantitatively, from photoionization spectra of neutral and positively charged systems. This sometimes dramatic difference in behavior arises from the different binding potential in negative ions. In contrast to the Coulomb potential (proportional to r^{-1}, with r being the distance from the nucleus) that binds the electrons in neutral and positive atoms, atomic negative ions are bound in an induced-dipole potential (proportional to r^{-4}) which results in dramatic differences in the electronic structure and photodetachment dynamics [7–15]. On the other hand, in systems where the charge is distributed within a large, extended volume, the addition of a single electron cannot be expected to affect the spectrum significantly. This is true even for collective plasmon resonances in clusters and large molecules such as fullerenes: The photo single ionization spectrum of C_{60} and C_{60}^- hardly differ except near threshold [16]. Hence, the question arises naturally, how double and triple electron removal yields for the neutral and the negative fullerene ion are related to each other: Are they as different as in the case for small systems?

In the following we will present our measured single photon multiple-detachment yields of C_{60}^- and contrast them with the photo multiple-ionization yields of C_{60}[17]. As we will show, they are indeed quite different, yet they can be systematically related to each other even quantitatively by interpreting the attached electron in the negative ion as a "spectator" which does not actively participate in the correlated electron dynamics. It has primarily a twofold screening effect on the multiple-detachment dynamics: (i) the spectra of C_{60}^- appear compressed and (ii) the thresholds for two- and three-electron removal are shifted as compared to the thresholds in C_{60} spectra. The combined effect can be expressed as a linear transformation of the energy variable.

Absolute double- and triple-detachment cross sections for C_{60}^- ions leading to C_{60}^+ and C_{60}^{2+} were measured in the photon energy range $h\nu = 17-90$ eV using the ion-photon-beam end station on undulator beamline 10.0.1 at the Advanced Light Source [9]. A 6 keV C_{60}^- ion beam was produced by evaporating 99.5% pure C_{60} powder into a 10-GHz electron cyclotron resonance ion source [18], mass selected (1% resolution), and merged with a counter-propagating synchrotron radiation beam ($25-90$ meV bandwidth). Although the ECR source was run at minimal RF power, the plasma temperature in the source

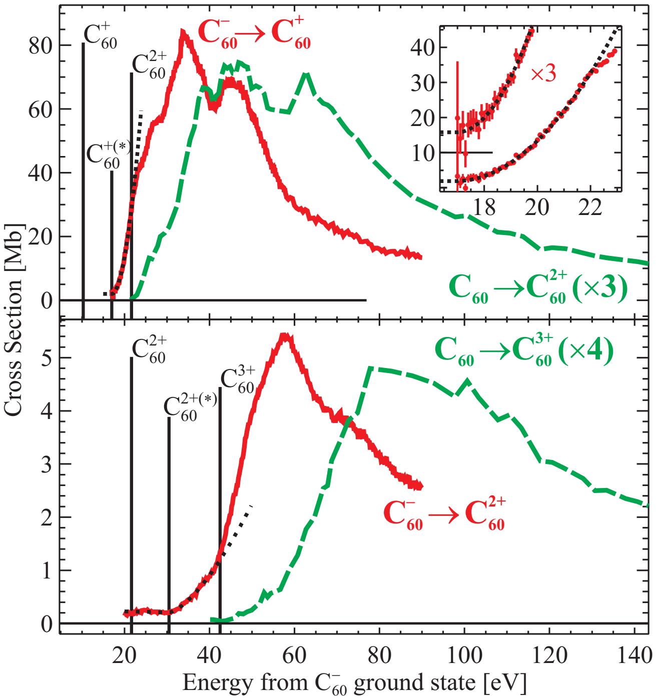

FIG. 1: (Color online) Measured absolute photoion yields from the removal of 2 (top) or 3 (bottom) electrons. Solid curves are present C_{60}^{-} photodetachment results. For comparison, photoionization results for C_{60} [17] are also plotted (broken curves, relative to the C_{60}^{-} ground state), magnified by a factor of 3 (C_{60}^{2+}) and 4 (C_{60}^{3+}) for presentation purposes. Vertical lines indicate positions of relevant state energies [17, 25, 26]. Dotted curves are threshold region best-fit results. Near-threshold data (dots, 1 SD statistical errors bars) are shown in the inset, and also magnified by a factor of 3 with a 10 Mb shift, for clarity.

can excite molecules by a few eV. While electronic excitations above the C_{60}^{-} binding energy (2.666 eV) can autodetach, the electronic energy can also be converted to vibrational excitations. Thus the ions could retain some internal vibrational energy even after the ∼100μs flight time from the source to the interaction region [19]. Regardless, one would expect this potential residual internal energy to be comparable to those found in studies on the neutral system (e.g., [17]), and therefore the comparisons and conclusions presented here are appropriate. The yields of charge- and mass-state selected photoions were measured as a function of the photon energy. Neutral particles cannot be detected in the apparatus. All plots herein have been scaled to measured absolute cross sections for C_{60}^{+} production, as with previous experiments [12, 13, 20]. The C_{60}^{2+} cross sections were scaled from these absolute measurements using measured cross section ratios as done in previous experiments [10, 12]. We estimate an uncertainty of 22% on the absolute scale [all uncertainties quoted at 1 standard deviation (SD) confidence].

TABLE I: Appearance thresholds for removal of n electrons from the h_u shell of the negative ion (I_n^-) and the neutral (I_n). Figures in parentheses give uncertainties in the last digit.

n	I_n^- [eV]	I_n [eV]	ΔI_n(exp) [eV]	ΔI_n(theo) [eV]
2	17.0(7)	19.00(3)[a]	2.0(7)	1.97
3	30.5(7)	35.8(3)[b]	5.3(8)	4.97

[a] ref. [26], [b] ref. [27].

Figure 1 shows the photo double-detachment and photo triple-detachment cross sections observed for C_{60}^{q+} production from C_{60}^{-} along with previous C_{60} photoionization results [17]. Since in [17] cross sections relative to C_{60}^{+} were measured, we have multiplied those results by the observed C_{60}^{+} relative cross section, scaled to the estimated absolute cross section at $h\nu = 40.8$ eV [21]. Threshold energies were estimated by fitting a power law to the near-threshold data: $A(h\nu - t)^p + \sigma_{bg}$, where A is the amplitude, t the threshold energy, p the power law exponent, and σ_{bg} the background cross section. To establish the fit range to use, sequences of fits were made including several ranges of data varying the maximum energy included. For C_{60}^{+} we obtained $t = 17.0(7)$ eV (error estimates include the possibility of non-linear σ_{bg}). Although very consistent results were returned for ranges including data up to 22.2 eV, the lack of data below 17 eV (the beamline limit) reduces the confidence we can have in the fit results. As previously noted in [10, 11, 22], threshold law fits with a zero-slope onset are notoriously sensitive to variations in the σ_{bg}.

The negative ion is formed by the addition of an electron in the t_{1u} orbital (1.6 eV above the fully filled 5-fold degenerate h_u orbital in the neutral [23]), with a binding energy of 2.666(1) eV [24]. Therefore, the threshold is clearly inconsistent with the C_{60}^{+} ground state $E(C_{60}^{+}) = 10.31(2)$ eV [25] ($E(x)$ denotes the energy of state x relative to the C_{60}^{-} ground state), which would correspond to detachment of the t_{1u} electron and an h_u electron. In fact, we can identify the small $\sigma_{bg} \approx 1.6$ Mb (see Fig. 1 inset) as this weak 2-electron photodetachment process. The onset of the dominating signal at 17 eV is instead from the much more likely process (a factor of 10 from a statistical standpoint alone) of simultaneously removing 2 of the 10 h_u electrons to an excited $C_{60}^{+(*)}$ state, analogous to the C_{60} photo double-ionization threshold at $h\nu = 19.00(3)$ eV [26]. For triple detachment, i.e., for fits to the C_{60}^{2+} product, we obtain $t = 30.5(7)$ eV, well above [8.8(7) eV] the C_{60}^{2+} ground state, but 5.3(8) eV below the 3-electron threshold of C_{60} at $h\nu = 35.8(3)$ eV [27]. We similarly conclude that detachment of 3 h_u electrons is responsible.

The differences in the appearance thresholds t° and t^- between C_{60} and C_{60}^{-} for multiple ionization by a single photon reveal the geometry in the process. Consider double ionization of C_{60} as a cluster of individual atoms:

The photo electron produces an atomic ion with positive charge $q_{\rm first} = +1$. From atoms one knows that multiple ionization proceeds by initial photo absorption and subsequent "knock outs" of other bound electrons by the photo electron [28, 29]. However, in C_{60} it is, a priori, not clear where on the cage the second electron will be ionized by the primary photo electron. Most likely, this will happen on the equator which contains the largest number of atoms. At the position of the second (or in general last atom ionized) the impacting and the ionized electron escape very slowly since we investigate photo processes near threshold. This leads to an initial net charge of $q_{\rm last} = -1$ at the last atom ionized. Hence, the geometrically induced potential between the first and the last atomic site ionized is $q_{\rm first}q_{\rm last}\sqrt{2}/R = -\sqrt{2}/R$. This attractive energy is *not* generated in C_{60}^- since there the spectator electron screens the first ion, producing a net charge $q_{\rm first} = 0$. Therefore, it is by $\Delta I_2 = \sqrt{2}/R$ easier to double ionize C_{60}^- than C_{60}, where $R = 9.75$ au is the valence radius [30] of C_{60}.

In contrast to double ionization the photo electron has kicked out an electron from another atom before ionization of the last (third) atom in triple ionization. While, the intermediate ionization does not contribute to the potential since this ion together with its very slow (threshold) electron remain initially neutral, the additional impact ionization step adds the strong propensity of favored forward scattering. The largest angle of more than 170° in a triangle of three ion sites is formed by adjacent sites on the cage. Moreover, the arrangement is the most abundant triatomic configuration on the cage. Then, the first and last ionization site have a distance of almost $2r_{\rm cc}$, where $r_{\rm cc} = 2.73$ a.u. is the average carbon bond length [31]. This leads to a difference $\Delta I_3 = 1/(2r_{\rm cc})$ in the ionization potential of the neutral and negatively charged fullerene. The geometrically induced differences in the appearance threshold agree within error bars with the experimental observations (see Table I). Taking these considerations regarding threshold energies with a grain of salt, one may speculate along the same lines about preferred geometries for ΔI_n with $n > 3$ which would be valuable with corresponding experiments in the future.

The energy shifts of the appearance thresholds reveal the geometry of multiple ionization as we have seen. In addition, the C_{60}^- photoion spectra are compressed in photon energy compared to those of neutral C_{60}. This phenomenon contains information about the orbital energies as will be explained below and can be interpreted as another screening effect by the extra electron. Since the dipole matrix element is larger for more strongly bound electrons viewed in a picture of occupied orbitals, multiple ionization/detachment will preferentially start by the photon absorption of the most strongly bound electron that can be ionized. On its way out the photo electron then knocks out one or more electrons by subsequent collisions as discussed above. The energy scale of such a collision is given by the instantaneous total binding energy shared by the remaining more loosely bound electrons which are to be knocked out. The process is akin to what is found in photo double-ionization of He, where the photo double ionization probability corresponds to that of electron impact ionization of He^+ if the energy is scaled by the ratio of the effective binding energies [29]. Here, the excess electron of C_{60}^- reduces the binding energy of the electron to be detached to an effective one which sets the energy scale of the detachment yield.

We define dimensionless energy variables $x^a = \varepsilon^a/\alpha^a$, where $a =$ '$-$' stands for C_{60}^- and $a =$ '$\circ$' for C_{60}. With $\varepsilon^a = h\nu - t^a$ we measure energy from the respective threshold t^a. Together with the scaling α^a this constitutes the linear transformation of the original energy $h\nu$.

The energy scales are set by the effective binding energy α^a of the electrons to be knocked out by the photoelectron as described above. If these arguments hold, the excess energy in C_{60}^- photodetachment is mapped onto that in C_{60} photoionization with the transformation $\varepsilon^\circ = \beta\varepsilon^-$, where $\beta = \alpha^\circ/\alpha^-$. The negative ion cross section can be expressed in terms of the energy scale ε° of the neutral as

$$\sigma_\beta^-(\varepsilon^\circ) = \sigma^-(\beta\varepsilon^-)/\beta\,, \tag{1}$$

with the normalization $\int \sigma_\beta^-(\varepsilon^\circ)\,d\varepsilon^\circ = \int \sigma^-(h\nu)\,d(h\nu)$ to maintain the oscillator strength in the scaled coordinates. For two electron removal in neutral C_{60}, $\alpha^\circ = 7.61$ eV, since the more strongly bound photoelectron knocks off the valence electron. For two electron removal in C_{60}^-, there is the additional valence electron. The total binding energy of both electrons is then $2.666 + 7.61 = 10.28$ eV and the knocked-off electron has an effective binding energy of $\alpha^- = 10.28/2 = 5.14$ eV. Thus, we can estimate $\beta_2 \approx 1.48$. Similarly, for three electron removal, the effective binding energies of the two knocked-off electrons are $\alpha^\circ = 19.0$ eV and $\alpha^- = \frac{2}{3}(19.00 + 2.666)$ eV, giving $\beta_3 \approx 1.32$.

Figure 2 shows the results of least-squares fits of σ_β^- to the corresponding C_{60} cross sections, $\sigma_\beta^- = R\sigma^\circ$, with β and the overall cross section amplitude ratio R (shown as a magnification factor in the figure) as the only fit parameters. Including data up to $h\nu = 55$ eV for photo double-detachment yields best-fit $\beta^{\rm fit} = 1.50$, essentially coincident with the expected value. The amplitude ratio returned is $R_2^{\rm fit} = 2.00$, i.e., the cross section for C_{60}^- photo double-detachment is considerably larger than that for C_{60} photo double-ionization. From a similar fit for photo triple-detachment including all the data (lower panel of Fig. 2) we obtain $\beta_3^{\rm fit} = 1.57$ and $R_3^{\rm fit} = 2.47$, rendering the removal of three electrons by one photon in C_{60}^- about 2.5 times more likely than in C_{60}. Finally, the ratio $R_3/R_2 = 1.24$ carries a reduced uncertainty (we estimate $\approx 10\%$), as it does not depend on the absolute scale. It indicates an increase in ease of n-electron removal in the negative ion with increasing n as compared

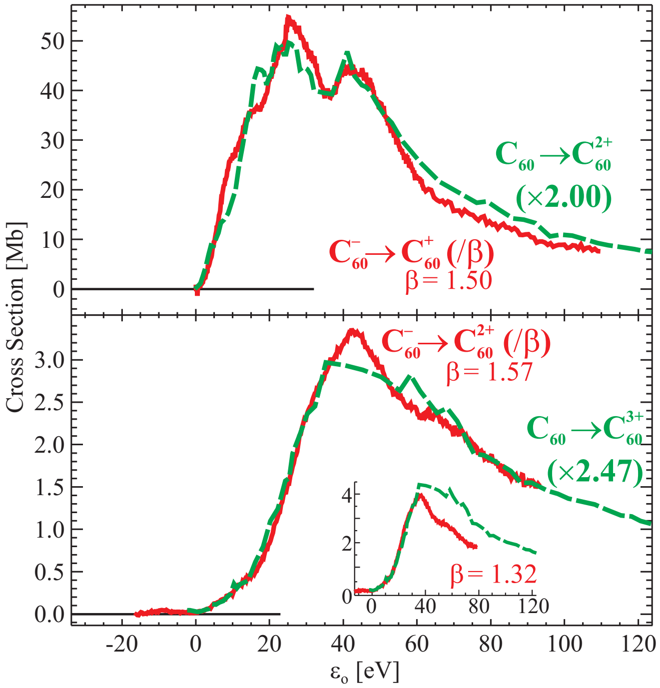

FIG. 2: (Color online) Scaled C_{60}^- photodetachment cross section $\sigma_\beta^-(\varepsilon^\circ)$ (see Eq. 1) (solid curve) compared to C_{60} photoionization from [17] (broken curve) for the removal of 2 (top) or 3 (bottom) electrons. (ε° is the excess energy for photo double-ionization or triple- photoionization of C_{60}.)

to neutral C_{60}, yet another effect of the screening through the additional electron in the negative ion.

The correspondence between the scaled spectra of Fig. 2 is striking. Indeed, we can immediately correlate all the major features for photo double-detachment with photo double-ionization, albeit with slightly varying amplitudes. In addition, for photo triple-detachment, if we instead fix β to the theoretical value (1.32) and set $R_3 = 3.66$ so as to match the leading edges, we obtain the curve in the inset. Features common to both spectra then suggest themselves more readily, adding support to our interpretation. (Note that the identity of these features remain elusive, see discussion in [32].) It should be noted that without the concept of the spectator electron and its twofold effect on the energy variable this similarity is almost impossible to infer from the C_{60} spectra shown in [17] as Fig. 13.

In summary, we have shown that the cross section for multiple electron removal by a photon from the fullerene negative ion can be mapped onto the corresponding cross section for the neutral C_{60} by quantitatively assessing the two-fold effect of the screening by the extra electron which leads to a shift and a compression of the energy variable. In addition, the screening increases the oscillator strength for the negative ion spectra compared to the neutral.

The energy scaling for multi-electron ionization observed here is not specific to C_{60} and C_{60}^- because it is an atomic property [29] relying on *"local"* few-electron correlation. Therefore, investigations in extended systems, such as other fullerenes or metal clusters, should reveal a similar energy scaling.

We may conclude that in contrast to few-electron atoms or molecules, the photo electron spectra of the neutral and its negative ion in extended systems are quite closely related: For removal of a single electron the spectra are almost identical except near threshold. This is certainly expected owing to the small difference in the oscillator strength between n and n+1 electrons participating in the photo absorption. More surprising is the connection between neutral and negative ion spectra for removal of more than one electron as we have worked out and illustrated here: Essentially, the strongly correlated electron dynamics required for multiple electron removal is quite similar. The difference in the dynamics is largely due to the screening in the negative ion by the additional electron whose effect is fully described by a linear transformation of the energy variable. This has allowed us to map the neutral and negative ion spectra onto each other illustrating their close relationship.

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