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Even-odd effects in the ionization cross sections of $[C_{60}]_2$ and $[C_{60}C_{70}]$ dimers

H. Zettergren, H. T. Schmidt, P. Reinhed, and H. Cederquist
Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden

J. Jensen
Angstrom Laboratory, Uppsala University, Box 534, SE-75121 Uppsala, Sweden

P. Hvelplund
Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

S. Tomita
Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-0006, Japan

B. Manil, J. Rangama, and B. A. Huber
Centre Interdisciplaire de Recherches Ions Lasers (CIRIL), Boulevard Henry Becquerel, Boîte Postale 5133,
F-14070 Caen Cedex 05, France

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We report strong even-odd effects in multiple ionization yields of van der Waals dimers in slow $Xe^{30+}+[C_{60}]_2([C_{60}C_{70}])\rightarrow\cdots+[C_{60}]_2{}^{r+}([C_{60}C_{70}]^{r+})$ electron-transfer collisions as functions of $r\leq 7$. This behavior may be due to even-odd variations in the sequences of dimer ionization energies as calculated with an electrostatic model including an electrical fullerene-fullerene contact at the $19a_0$ center-center separation in $[C_{60}]_2{}^{+}$. Prompt dissociations predominantly yield *intact* fullerenes $[C_{60}]_2{}^{r+}\rightarrow C_{60}{}^{r_1+}+C_{60}{}^{r_2+}$ in the same ($r_1=r_2$, even r) or nearby ($r_1=r_2\pm 1$, odd $r>1$) charge states.

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Many previous studies of fullerenes concern interactions between neutral *isolated fullerenes (monomers)* and simple projectiles such as fast or slow atomic ions, photons, or electrons (see, e.g., [1]). There have also been studies of fullerene-fullerene [2–4] and fullerene-surface collisions [5,6] and of interactions with van der Waals clusters of fullerenes [7–13]. Such investigations reveal details of electron-transfer, energy deposition, and fragmentation processes in complex molecular systems. Apart from the fundamental interest, this may also be important in relation to the strongly emerging new field of molecular radiation damage (see, e.g., [14]) where fullerene materials may serve as highly symmetric model systems. Further, fullerenes are used in nanoelectronic developments and studies of their stabilities, charge-transport, and contacting properties are thus important. The dimers are the simplest fullerene aggregates and may as such (and in their multiply charged forms) reveal inherent properties of, in particular, fullerene-fullerene contacts valid also for more complex fullerene materials and devices. Previous studies of fullerene dimers have, however, in contrast to those for fullerene monomers [15–22], been limited to the neutral and the singly charged systems.

Here, we present the first results on *multiple ionization* of fullerene *dimers* and report on: (i) Relative ionization cross sections for $Xe^{30+}+[C_{60}]_2([C_{60}C_{70}])\rightarrow Xe^{(30-s)+}+[C_{60}]_2{}^{r+}([C_{60}C_{70}]^{r+})+(r-s)e^-$ electron-transfer collisions ($v=0.4$ a.u. and $r\leq 7$) showing the same surprising *even-odd variations* as functions of r for $[C_{60}]_2{}^{r+}$ and $[C_{60}C_{70}]^{r+}$. (ii) Branching ratios and kinetic energy releases for the dominant fragmentation processes, which leave the fullerene molecules intact with the same ($r_1=r_2$, even r) or nearby ($r_1=r_2\pm 1$, odd $r>1$) charge states ($[C_{60}]_2{}^{r+}([C_{60}C_{70}]^{r+})\rightarrow C_{60}{}^{r_1+}+C_{60}{}^{r_2+}(C_{70}{}^{r_2+})$). As the geometry of the collision system often is such that one of the fullerenes is closer to the projectile trajectory the latter results indicate an efficient electrical contact between the fullerenes already at the van der Waals distance. An electrostatic model for dimer ionization will be presented and used to discuss these findings.

The experiment was performed at Centre Interdisciplinaire de Recherche Ions Lasers in Caen, France. We used an ECR (electron cyclotron resonance) ion source, a fullerene cluster aggregation source, and a 1 m long time-of-flight spectrometer (Fig. 1). The fullerene sublimation oven in the cluster aggregation source was normally operated at 565 °C, and after leaving the oven the hot fullerene monomers (internal energies roughly 5 eV) were cooled through collisions with He at 80 K and 1 mbar [11]. This was necessary as the binding energy for the neutral $[C_{60}]_2$ van der Waals dimer only is around 0.3 eV [10]. Note that $C_{60}+C_{60}$ collisions at 80 K are much to slow [23] to overcome the 1.6 eV barrier [24] for forming dimers in a $[2+2]$ cycloaddition [24–27] or to break the fullerene cage. Thus our dimer target is of the van der Waals type.

A mixed beam of monomers, dimers, and larger clusters of fullerenes exit the He-collision region through the 80 K nozzle, traverses a region for differential pumping, and crosses the 600 keV Xe^{30+} beam. The directly measured $C_{60}{}^{r+}$ and $C_{70}{}^{r+}$ monomer ions (at low oven temperature for negligible cluster formation), yielded a C_{70} vapor content of $4.7\pm 0.2\%$ and a $[C_{60}]_2/[C_{60}C_{70}]$ target mixing ratio of 10.1 ± 0.5 using the ionization energies [28] and the over-the-barrier scaling [29].

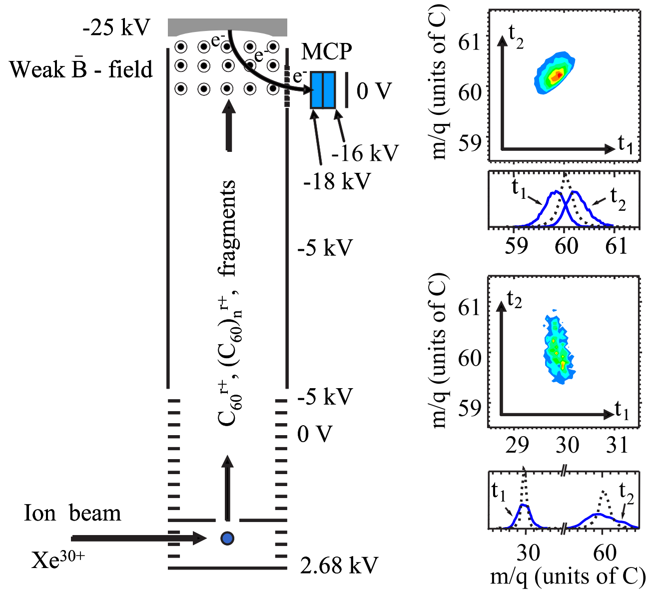

FIG. 1. (Color online) Left: A schematic of the setup. Right: Time-correlations between the first (t_1) and the second (t_2) hits on the detector (cf. text).

The Xe^{30+} beam was pulsed at 2 kHz with 10 μs long pulses. The ionized dimers and their fragments were extracted 1 μs after the passage of the ion beam pulse. The time-of-flight spectrometer was operated in the time-focusing mode and after the field free drift region the ions hit a conversion plate at -25 kV [11]. This gave high secondary electron emission yields for intact and dissociated $[C_{60}]_2^{r+}$ and $[C_{60}C_{70}]^{r+}$. The secondary electrons were guided by a weak magnetic field to a microchannel plate detector (MCP) ensuring the very high detection efficiencies necessary for fragment-ion correlation analysis. The time measurement was started by the extraction pulse and (multi-) stopped by the MCP.

In Fig. 1, we also show the two-stop correlation data (events with exactly two charged fragments) for $[C_{60}]_2^{2+} \to C_{60}^{+}+C_{60}^{+}$ (upper right) and $[C_{60}]_2^{3+} \to C_{60}^{2+}+C_{60}^{+}$ (lower right). The full t_1 and t_2 curves in Fig. 1 are the projected distributions in flight times for the first (t_1) and second (t_2) hits on the MCP. The dashed curves are flight-time distributions for singly and doubly ionized C_{60} *monomers* from the *one-stop* spectrum (events with only one ion), which we use as experimental response functions (electron transfer from C_{60} to slow Xe^{30+}-ions only yield very small monomer recoil energies [29]).

We determine relative multiple ionization cross sections $[\sigma_{\mathrm{expt}}(r)]$ for $[C_{60}]_2^{r+}$ ($[C_{60}C_{70}]^{r+}$) by adding, for each r in the range $2 \leq r \leq 7$ ($2 \leq r \leq 6$), the two-stop events for the $[C_{60}]_2^{r+}([C_{60}C_{70}]^{r+}) \to C_{60}^{r_1+}+C_{60}^{r_2+}(C_{70}^{r_2+})$ dissociation channels. This is possible since the fragmentation of individual fullerene cages are found to be negligible and since we have strong indications that $[C_{60}]_2^{r+}$ and $[C_{60}C_{70}]^{r+}$ are unstable except for $r=1$ (see below). In the $[C_{60}]_2^{r+}$ cases with $r=2$, 4, and 6 (where the ions arrive close in time at the detector), we need to correct for dead-time effects. In order to make a dead-time correction, we use SIMION [30] to calculate distributions of ion arrival-time differences (t_2-t_1) for a range of assumed values of kinetic energy releases E_{KER}. In these simulations, we use the actual spectrometer geometry, a finite source region, and assume isotropic fragmentation. Each (t_2-t_1) distribution, one for each assumed E_{KER}, is then convoluted with the experimental response function. The best fit to the right part of the (t_2-t_1) distribution gives a minimum in $\chi^2(E_{\mathrm{KER}})$ and yields the dead-time correction essentially as the difference between the simulated/convoluted and the measured (t_2-t_1) distributions (shaded area in Fig. 2). The left part of the (t_2-t_1) distribution is reproduced by assuming a Gaussian dead-time distribution of 45±12 ns. For $[C_{60}]_2^{r+} \to C_{60}^{r_1+}+C_{60}^{r_2+}$ and $r_1 \neq r_2$ (Fig. 2; right), and for $[C_{60}C_{70}]^{r+}$, the product ions are well-separated in time *for all values of r* and no dead-time corrections are necessary.

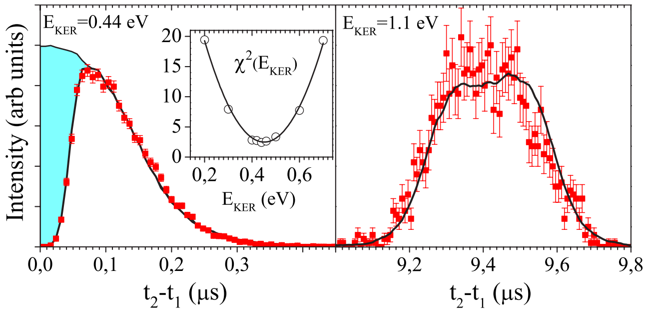

FIG. 2. (Color online) Measured (squares) and simulated (full curves) (t_2-t_1) distributions for $[C_{60}]_2^{2+} \to C_{60}^{+}+C_{60}^{+}$ (left) and $[C_{60}]_2^{3+} \to C_{60}^{2+}+C_{60}^{+}$ (right) dissociation processes. The simulated curves are for $E_{\mathrm{KER}}=0.44$ eV with a detection dead time of 45±12 ns (left) and for $E_{\mathrm{KER}}=1.1$ eV with no dead time (right) and yield minima in χ^2 (cf. inset/text).

Even-odd oscillations [in relation to smoothly decreasing values of $\sigma_{\mathrm{expt}}(r)$] are clearly seen for $[C_{60}]_2$ *and* $[C_{60}C_{70}]$ in Fig. 3 (top panel). The two data sets fall on top of each other (relying on the $[C_{60}]_2/[C_{60}C_{70}]$ mixing ratio 10.1±0.5), which strongly supports our dead-time correction procedure. The data in Fig. 3 include the minor contributions from charge asymmetric dissociation (cf. Table I). The experimental E_{KER} values in Table I are substantially lower than those from the electrostatic model in [18,31], which may be due to dissociation-induced internal excitations of the separating ions (cf. [32]).

We calculate simple $[C_{60}]_2^{r+}$ fullerene-fullerene potentials as superpositions of the Girifalco potential [33] for the neutral dimer and the electrostatic interaction in the charged system modeled as two conducting spheres with radii $a=8.37a_0$ [18,31]. In this way, we get model binding energies for $[C_{60}]_2$ and $[C_{60}]_2^{+}$, of 0.277 and 0.362 eV (fullerene-fullerene distance $\sim 19a_0$), which agrees with the experimental results [10] of 0.275±0.08 and 0.372±0.08 eV. We do indeed observe a $[C_{60}]_2^{+}$ peak but no $[C_{60}]_2^{r+}$ peaks (or $[C_{60}C_{70}]^{r+}$ peaks) with $r>2$ ($r>1$) in the one-stop time-of-flight spectrum. This is consistent with our model calculations (superimposing the potentials in [31] and [33]) which also show that dimers in higher charge states are inherently unstable [18]. In addition, $[C_{60}]_2^{2+}$ should dissociate

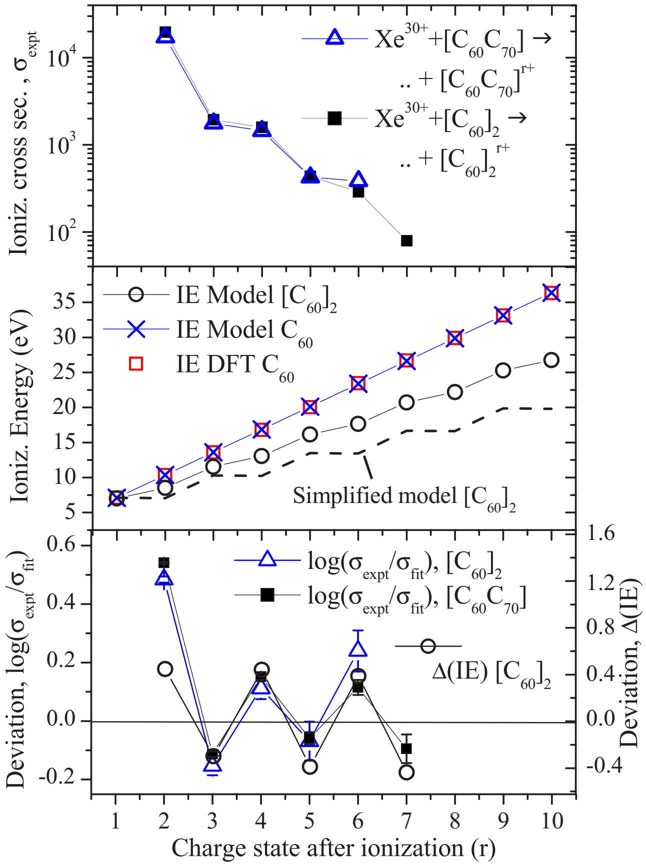

FIG. 3. (Color online) Top: Ionization cross sections for fullerene dimers in arbitrary units. Middle: Ionization energies (IE) for monomers and dimers [modeled as two conducting spheres *with* (○) and *without* (dashed curve) mutual electrostatic interactions]. Below: Deviations from linear r dependencies for dimer ionization cross sections (left scale) and ionization energies (right scale).

promptly (overlaps with C_{60}^{+} in the one-stop spectrum) as we calculate a shallow potential minimum of only 0.05 eV [18,31,33].

The dimer equilibrium distance ($19a_0$) lies inside the critical distance for electron transfer between two conducting spheres with charge state $r \geq 1$ (modeling $[C_{60}]_2^{r+}$), which we calculate (using the method described in [31]) to be slightly larger than $20a_0$. This readily explains the instabilities of $[C_{60}]_2^{r+}$ and its *preferred symmetric or close to symmetric charge break up* when $r > 1$ (Table I), high charge mobilities in larger van der Waals clusters [11], and previously reported subfemtosecond, nonfragmenting, charge redistribution in $C_{60}^{q+}+C_{60}$ collisions [4]. We thus consider the following collision scenario: The Xe^{30+} projectile sequentially removes electrons from the dimer system, which in most cases is oriented such that the projectile is closer to one of the fullerenes. However, as shown above, the charge may move between the two fullerenes in an over-the-barrier fashion [18,31] and on time scales shorter than the time between the sequential electron transfers. We will consider these aspects in the following model for dimer ionization.

The ionization energies (IE) for C_{60}^{r+} *monomers* have been calculated earlier using density functional theory [34]. These results are consistent with experiments [28,35], and may be reproduced by the classical expression [36] for a conducting sphere $\mathrm{IE}(r) = W - 1/2a + r/a = 7.106 + 3.252 \times (r-1)$ eV ($W = 5.48$ eV is the work function, r is the charge *after* ionization, and $a = 8.37a_0$). For the model dimer system, we then get $\mathrm{IE}(r) = W + r/2a + \Delta U_{\mathrm{int}}(r)$ for odd r and $\mathrm{IE}(r) = W - 1/2a + r/2a + \Delta U_{\mathrm{int}}(r)$ for even r (Fig. 3). Here, $\Delta U_{\mathrm{int}}(r) = U_{\mathrm{int}}(r) - U_{\mathrm{int}}(r-1)$ are the differences in sphere-sphere interaction energies for r and $r-1$ and are calculated from [31].

TABLE I. Experimental branching ratios (BR) and kinetic energy releases (E_{KER}) for $[C_{60}]_2^{r+}$ dimers.

Dimer	Dissociation	BR (%)	E_{KER} (eV)
$[C_{60}]_2^{2+}$	$C_{60}^{+}+C_{60}^{+}$	100	0.44±0.02
$[C_{60}]_2^{3+}$	$C_{60}^{2+}+C_{60}^{+}$	100	1.1±0.1
$[C_{60}]_2^{4+}$	$C_{60}^{2+}+C_{60}^{2+}$	~95	2.2±0.2
	$C_{60}^{3+}+C_{60}^{+}$	~5	
$[C_{60}]_2^{5+}$	$C_{60}^{3+}+C_{60}^{2+}$	~94	1.7±0.3
	$C_{60}^{4+}+C_{60}^{+}$	~6	
$[C_{60}]_2^{6+}$	$C_{60}^{3+}+C_{60}^{3+}$	~96	5.6±0.7
	$C_{60}^{4+}+C_{60}^{2+}$	~4	
$[C_{60}]_2^{7+}$	$C_{60}^{4+}+C_{60}^{3+}$	~90	7.9±1.6
	$C_{60}^{5+}+C_{60}^{2+}$	~10	

Hypothetical dimer ionization energies, obtained by ignoring the $\Delta U_{\mathrm{int}}(r)$ contributions are shown as a dashed curve in Fig. 3. This would lead to a situation in which the transfer of a second electron to the projectile would be possible at the same distance as the transfer of the first electron. Thus for this hypothetical sequence ("Simplified Model $[C_{60}]_2$" in Fig. 3), there would be no finite range of impact parameters for the transfer of just one electron. The same argument could be made for all odd charge states and the corresponding ionization cross sections would be zero, while those for dimers in even charge states would be large. With the full model dimer ionization energies ("IE Model $[C_{60}]_2$"), however, there are finite ranges of impact parameters leading to odd final charge states even though nearby ranges giving even charge states are wider. We believe that this geometrical argument may be the main reason for the characteristic even-odd variations in the dimer ionization cross sections.

In the lower panel of Fig. 3, we plot *deviations* $[\log(\sigma_{\mathrm{expt}}/\sigma_{\mathrm{fit}})]$ from a linear fit, σ_{fit}, to $\sigma_{\mathrm{expt}}(r)$, for $[C_{60}]_2^{r+}$ and $[C_{60}C_{70}]^{r+}$. We also show deviations, $\Delta(\mathrm{IE}) = (\mathrm{IE})_{\mathrm{fit}} - (\mathrm{IE})_{\mathrm{model}}$, between a linear fit, $(\mathrm{IE})_{\mathrm{fit}}$, to the $[C_{60}]_2$ model ionization energies ("IE Model $[C_{60}]_2$") and the $(\mathrm{IE})_{\mathrm{model}}$ values themselves. There are clearly correlations between lower ionization energies [i.e., positive $\Delta(\mathrm{IE})$] and larger cross sections for dimers in even charge states. In spite of decades of studies, such oscillations have never been observed for fullerene monomers (see, e.g., [17,37]) or for any other atomic or molecular target [38].

The surprising even-odd effect in the present experimental relative ionization cross sections for $[C_{60}]_2^{r+}$ *and* $[C_{60}C_{70}]^{r+}$ dimers correlates strongly with even-odd variations in the present model dimer ionization energies. These energies are also found to be significantly lower than the ones for monomers, which readily explain why there is substantially less fullerene-cage fragmentation for multiple-electron transfer from dimers than from monomers. Further, the even-odd variations in the model and the experiment may suggest that one unit of charge (for dimers in odd charge states) mostly is found at one of the fullerenes over some non-negligible time (a model assumption of instantly and completely delocalized charges would remove the even-odd variations). Still, this time cannot be very long as we have learned that electron transfer between the fullerenes occurs on subfemtosecond time scales.

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