Recent results on multiple-ionization and fragmentation of negatively-charged fullerene ions by electron impact

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Employing the dynamic crossed-beams technique, absolute cross section for the electron-impact multiply-ionization and fragmentation of mass-selected negatively-charged fullerene ions $C_m^- \to C_{m-n}^{q+}$ ($m = 60, 70, 84$; $q = 1, 2, 3$; $n = 0, 2, 4$) have been measured. The electron energy shans from the respective threshold up to 1 keV. A scaling law has been observed for the magnitude of the cross sections that is a function of the fullerene size m and the charge state q of the product ion. The data indicate that different mechanisms account for the detachment of the extra electron from the negatively-charged fullerene and the formation of a positively-charged ion, respectively. Moreover, the multiple-ionization of a fullerene anion is found to be a sequential process. A novel ionization mechanism is proposed which can be expected to be valid for all negatively-charged molecular or cluster ions which are able to shield the attached electron from the incident electron.

Suppport by Deutsche Forschungsgemeinschaft (DFG) is gratefully acknosledged. P.S. thanks the Austrian Academy of Sciences for his APART-fellowship.

In the last decade the formation of positively-charged ions out of neutral fullerenes has been studied extensively [1]. Whereas the threshold energy for different ionization processes has been determined repeatedly [2–5], only a few references contain information about the absolute magnitude of these cross section [6–9]. Parallel to the experimental work several papers have been published on the calculation of the ionization energies [10–13] and the ionization cross sections of fullerens [14–15].

Völpel et al. have measured cross sections for the electron-impact ionization of positively-charged fullerene ions [16]. Since the cross section for the attachment of free electrons to a neutral molecule [17] is large, intense beams of negatively-charged fullerene ions can also be produced easily. Additionally, electron attachment to fullerenes does not lead to the production of negatively-charged fragments.

The properties of C_{84} were investigated less extensively in comparison to C_{60} and C_{70} due to the relatively small amount of larger fullerenes present in the soot. Moreover, the separation with chemical methods is complicated and thus, pure C_{84} soot is very expensive. Mass-separation is a possible solution in order to separate fullerenes of different sizes. For positively-charged ions there exists the problem that fragmentation processes of larger fullerenes may contribute to the ion signal of smaller carbon clusters. The presently used technique allows the separation of these different fullerenes free of fragmentation processes.

1. Experimental

The measurements were performed employing the electron-ion crossed-beams set-up describedin detail by Tinschert et al. [18]. A commercially available mixture of fullerenes mainly containing C_{60} and C_{70}, but also trace amounts of larger fullerenes, was used. The sample of fullerene soot (with a purity greater than 96%) was heated up to a temperature of about 800 K with an expecially developed oven. The neutral vapor was introduced into a 10 HGz Electron Cyclotron Resonance (ECR) ion source [19]. The ion source was operated at a low microwave power. High ion yields of negatively-charged fullerenes and stable conditions of the ECR plasma were maintained after argon at a pressure of about 10^{-4} Pa was introduced into the ion source. The electron-impact ionization of Ar leads to slow electrons which may attach to the fullerenes. The ion beam extracted was collimated to 2×2 mm after mass and energy analysis and crossed with an intense electron beam providing currents up to 450 mA [20]. The energy of the electrons can be varied between 10 and 1000 eV. In order to avoid unwanted effects on the ionizing electrons caused by the strong stray field of the analyzing magnet, the acceleration voltage was reduced from nominally 10 to 4 kV for the cross section measurements of C_{84}^- into singly-charged positive ions. After the electron-ion interaction the product ions were separated from the incident ion beam by a 90°-magnet and detected by a single-particle detector located about 1 m behind the interaction region. The current of the parent ion beam was measured simultaneously in a Faraday cup.

The absolute cross sections were measured using the dynamic cressed-beams technique [21] where the electron beam is moved up and down through the ion beam with simultaneous registration of both actual beam currents and the signal of the observed fragment ions. The total experimental uncertainties are typically ±10% at the maximum of the cross sections resulting from the quadrature sum of the non-statistical errors of about 8.9% and the statistical error at 95% confidence level.

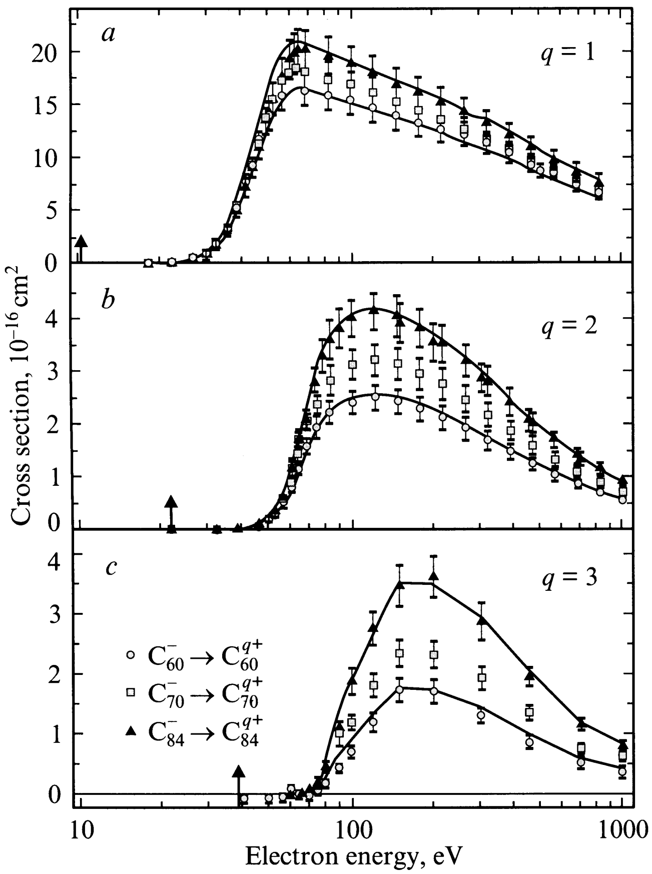

Figure 1. Absolute cross sections for electron-impact double (a), triple (b) and quadruple (c) ionization of C_{60}^- (circles), C_{70}^- (squares) and C_{84}^- (triangles) ions, respectively. Solid lines are calculated cross sections using a new scaling law. For more details, see text. The error bars represent the total experimental uncertainties including the statistical error at 95% confidence level. The expected thresholds of the ionization processes are shown as arrows.

2. Results

The measured absolute cross sections for double, triple and quadruple ionization of C_{60}^-, C_{70}^- and C_{84}^- are shown in Fig. 1. The error bars indicate the total experimental uncertainties. The expected thresholds of the ionization processes are shown as arrow. In case of the quadruple ionization of C_{60}^-, the product ion C_{60}^{3+} overlaps with the fragment ion C_{20}^+. This contribution was subtracted from the cross-section data by extrapolation of the C_{20}^+ production cross section.

The shape of the cross sections as a function of electron energy for a given ionization process is the same for the three different fullerene sizes. The measurement of three different fullerenes C_m (m = 60, 70 and 84) shows an increase of the cross sections with m. This effect becomes larger for higher charge states of the product cations. This begavior can be described by a scaling law which allows to predict an electron-impact ionization cross section $\sigma(m, q)$ of a negatively-charged fullerene ion C_m^- as a function of the fullerene size m and the charge state q of the product ion C_m^{q+} [22]. To calculate the cross section $\sigma(m, q)$, the knowledge of either the ratio of the geometrical cross sections of C_m and C_n as well as the electron-impact ionization cross section $\sigma(n, q)$ is necessary. Since the cross section data $\sigma(60, 3)$ are corrected for the contribution of C_{20}^+ ions, the scaling law is applied to the measured basis of the C_{70}^- ($n = 70$) cross sections. The results for $m = 60$ and 84 are shown as lines in Fig. 1 and agree well with the respective measurements.

The appearance energies of the measured cross sections are about 10 eV higher than expected for a direct ionization process. In order to create a positively-charged ion from a precursor anion, one would expect that the kinetic energy of the electron has to be enlarged by the electron affinity compared to a neutral precursor fullerene.

In addition to the pure ionization, the cross sections for double and triple ionization including the evaporation of either a C_2 or two C_2 molecules are measured for all three fullerene sizes. Fig. 2 shows, as an example, the cross

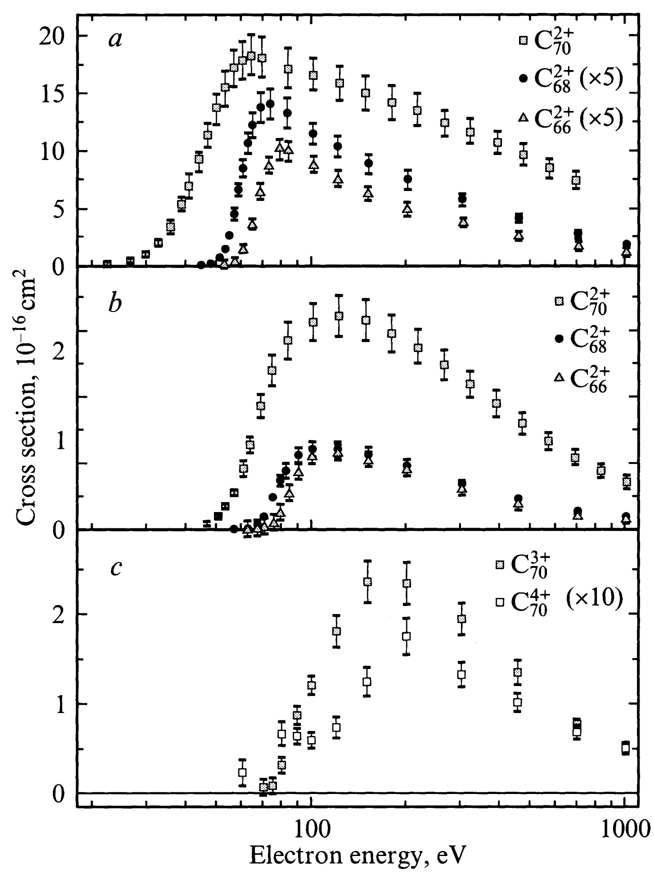

Figure 2. Absolute cross section for the electron-impact double (a), triple (b), quadruple, and quintuple (c) ionization of C_{70}^- ions into various product ions. The squares represent the cross section data for pure ionization. The circles and triangles correspond to the fragment ions C_{68}^{q+} and C_{66}^{q+}, respectively ($q = 1$ and 2). The error bars represent the total experimental uncertainties including the statistical error at 95% confidence level.

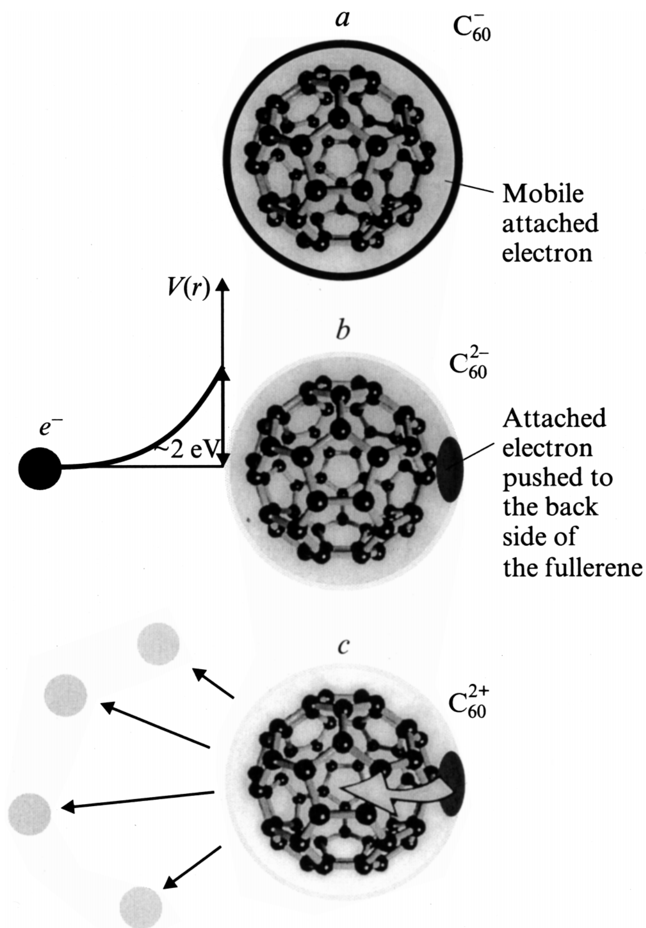

Figure 3. Proposed model for the collision between an electron and a negatively-charged fullerene ion on the example of a C_{60}^{-} ion (a). The approaching electron pushes the attached electron to the back and, after passing a barrier, ejects electrons (b). The attached electron resombines with the fullerene ion which leads to an excitation of almost 8 eV (c).

section curves measured for the product ions of the C_{70} primary ion. From a comparison of all electron-impact cross section data for the negatively-charged fullerene ions with cross section for the respective neutral fullerene [5,7,23,24] further conclusions can be drawn: (i) only a small shift between the threshold energies of the fragment ions for neutral and negatively-charged precursor ions is observed: (ii) the relative amount of fragment ions is in the case of negatively-charged presursor ions about 3.5 times larger than for neutral fullerenes: (iii) ion-efficiency curves for neutral fullerene can be matched perfectly with the cross section data of the same product ion. In contrast, the removal of the same number of electrons from a negatively-charged or a neutral fullerene does not lead to similar cross section curves.

The following simple model (Fig. 3) describes a mechanism which agrees well with all experimental findings [25].

(1) During the approach of the projectile electron the attached electron is pushed to the back side of the fullerene by Coulomb repulsion. Thereby the attached electron is shielded by the fullerene itself and does not interact with the incoming electron strong enough to be detached. The approach of the projectile electron against the repulsive force of the fullerene anion needs about 2 eV (the Coulomb energy of two charges at a distance of 7 Å) which is taken from the kinetic energy of the projectile. An intermediate highly excited dianion is formed. The electron affinities of some fullerene dianions have been determined to be very small [10,26].

(2) The incident electron collides with the fullerene and ejects several electrons from the fully occupied π-orbital of the fullerene with the lowest energy. The kinetic energy of the ejected electrons is cupplied by the approaching projectile taking into account the potential barrier formed by the Coulomb repulsion, the interaction with the image charge the electron forms at close distances [27], and the attractive force between the emitted electrons and the charged fullerene ion.

(3) The attached electon drops into the vacancies of the HOMO. The energy difference is transferred into vibrational degrees of freedom.

The described mechanism for the electron-impact ionization of negatively-charged fullerene ions can be expected to apply also for other large molecular and cluster anions. The only necessity is that the attached electron has to be mobile enough in order to avoid a direct collision with the projectile electron.

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