

Formation of higher-order fullerene dianions in collisions with Na atoms

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Abstract. We have measured electron capture cross sections in collisions between higher order fullerene anions C_n^- ($n = 76, 78, 82, 84, 86, 90$ and 96) and Na atoms. The ions were produced in an electrospray ion source (ESI) and accelerated to an energy of 50 keV. The measured cross section for dianion formation is three times larger for C_{96} than that for C_{60} . The latter cross section was earlier found to be 36 \AA^2 . The dramatic increase of the cross section with fullerene size is explained by means of the curve crossing model for electron transfer.

PACS. 36.40.Wa Charged clusters – 34.70.+e Charge transfer

1 Introduction

Gas phase multiply charged molecular anions have been studied intensely during the last decade [1,2] and it is found that the ability to bind more than one electron depends strongly on the molecular size [3]. Fullerenes are ideal for studying this dependence since the size can be varied without large shape variations. Apart from the first electron the extra electrons that are added to the neutral molecule can be confined by a Coulomb barrier and that holds even for unbound electrons [2]. The Coulomb barrier is created in a combination of a short range attractive polarization force and a long range repulsive Coulomb force.

The smallest fullerene dianion observed so far is C_{60}^{2-} , which is predicted to have slightly negative binding energy for the second electron [4–6]. C_{60}^{2-} was first observed as a result of laser desorption of a mixture of C_{60} and C_{70} deposited on a metal plate [7,8]. Despite intensive efforts, C_{60} dianions have not been observed by electrospray or by free electron attachment to monoanions. However, both methods have been used successfully for production of heavier fullerenes [9–13]. We have earlier reported on formation of dianions of C_{60} and C_{70} in collisions between energetic monoanions and Na atoms [14].

Collisions with alkali metal atoms are successfully used to produce not only fullerene dianions but also trianions of fluorofullerenes [15]. The method is even employed to produce metastable dianions of DNA, RNA [16], and also to study electron capture induced dissociation of peptide

ions [17]. Therefore the mechanism for the charge transfer process involving large molecules like fullerenes is interesting, and, for that purpose, fullerene dianions are ideal because of their differing sizes.

In the present study we extend these measurements of fullerenes to include heavier ones. The second electron affinity and the height of the repulsive Coulomb barrier are important parameters when discussing formation and stability of fullerene dianions [14,18]. Both quantities are found to increase with cluster size resulting in a strong increase in measured cross sections for dianion formation in collisions between 50-keV monoanions and Na atoms. The cross sectional dependence on cluster size is modeled within the curve crossing model and good agreement is observed. Similar model calculations by Ehrler et al. [19] even predicted that the onset for stable fullerene trianions can be expected to be at $n = 96$. In spite of strong efforts to observe trianions with the present experimental method, we failed to observe trianions of C_{96} . It should be added that earlier we have observed formation of fluorofullerene trianions using the same experimental procedure [15].

2 Experiments

The experimental arrangement is shown in Figure 1 and described in detail in reference [20]. Fullerene anions were produced in an electrospray ion source. The spray solution consisted of $50 \mu\text{l}$ of a solution of a higher-order fullerene mixture (MER Fullerene Products, Tucson AZ) ($\sim 1 \text{ mM}$)

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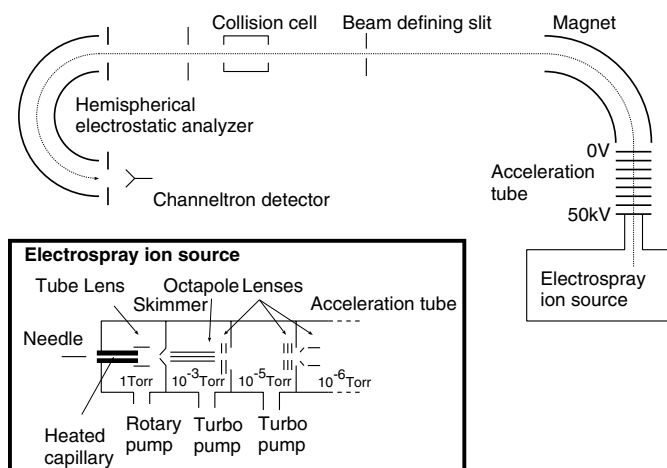


Fig. 1. Schematic drawings of the experimental setup.

in toluene, mixed with 50 μl of a solution of tetrathiafulvalene (TTF) (1 mM) in dichloromethane and diluted with dichloromethane to 1 ml. TTF acts as an electron donor with fullerenes as an acceptor. A typical composition of the mixture is around 20% C_{76} , 20% C_{78} , 40% C_{84} with small amounts of other higher-order fullerenes. The solution was sprayed through a needle at 4 kV with a flow rate of 4 $\mu\text{l}/\text{min}$. The electro spray ion source was located on a high voltage platform. After acceleration to 50 keV the fullerene anions were selected by a sector magnet and directed at a low pressure gas cell. The collision cell was a resistively heated cylinder with a 4-cm central part defined by 1- and 2-mm entrance and exit apertures. The temperature was monitored by a thermocouple attached to the oven. Solid sodium was placed in the midsection of the tube and heated to a temperature of around 200 $^{\circ}\text{C}$. Product ions were analyzed by a hemispherical electrostatic analyzer 1 m downstream from the cell and ions were detected with a channeltron in the pulse counting mode.

3 Results

In Figure 2, the mass spectrum of negative ions obtained after collisions of C_{84}^- with Na is shown. Peaks corresponding to dianions are clearly observed. Dianion formation is the dominant reaction channel against the very weak signals of C and C_2 loss which are also observed in collisions with rare gases [21]. The yield of the dianion increases with larger fullerenes. No trianions are observed for $n \leq 96$. Since the experimental method was used to observe metastable trianions of other molecules, the lifetime of the trianions C_{96}^{3-} is probably much shorter than the flight time from the collision cell to the detector, which is about 10 μs .

The ratio of the intensity of the dianion Y_{2-} to that of the monoanion Y_{1-} is given by

$$Y_{2-}/Y_{1-} \sim \sigma \rho x \quad (1)$$

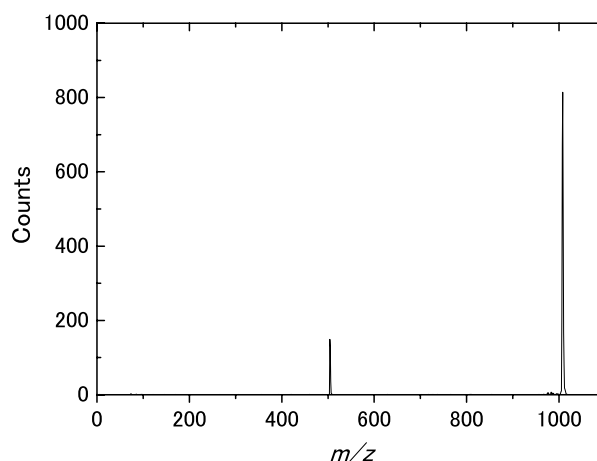


Fig. 2. Typical mass spectrum of doubly charged fullerenes formed in collisions between C_{84}^- and Na.

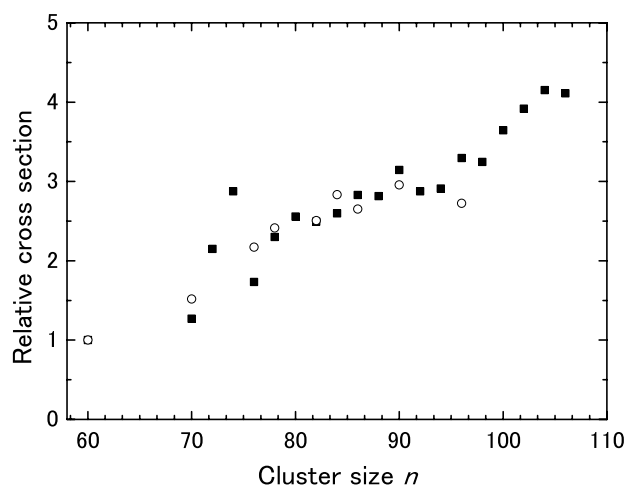


Fig. 3. Relative cross sections for formation of fullerene dianions. Open circles show experimental values and filled squares show the calculated values using equation (5).

where σ is the cross section for the electron capture, ρx is the target thickness. The measurements were carried out for all fullerene sizes with the same target temperature. Thus the ratio is proportional to the dianion formation cross section [14]. The relative cross sections for C_n^- were obtained measuring the ratio between the two intensities and are shown in Figure 3. The cross section increases with size as expected. The main contributions to the experimental error are instability of the ion beam and fluctuations of the oven temperature. We estimate the systematic error to be about 25%.

4 Model calculations and discussion

The important parameters for the estimate of the cross sections are radius and second electron affinity of the fullerenes. The fullerenes are often approximated with a conducting sphere with radius R . The radius R of 4.24 \AA for C_{60} can be obtained from its polarizability

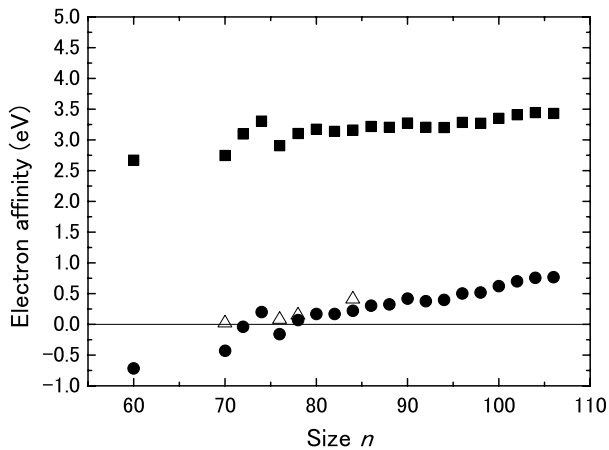


Fig. 4. First electron affinities from reference [24] (filled squares), calculated second electron affinities (filled circles) using equation (3) and experimentally obtained second electron affinities from references [19,25,26] (open triangles).

of 76.5 \AA^3 [22]. The radius agrees well with the sum of the radius of the ionic cage (3.51 \AA) and half the thickness of the electron cloud (1.5 \AA) [23]. Therefore the radius for other fullerenes can be found as

$$R_n = 3.51\sqrt{n/60} + 0.75 \text{ \AA}. \quad (2)$$

The estimated radius of 4.90 \AA for C_{84} as an example corresponds to a polarizability of 118 \AA^3 which agrees with average values calculated using density functional theory [11]. To calculate the curve crossing distance, we need to know the second electron affinities of the fullerenes which are unknown so far. The second electron affinity however can be estimated by assuming that the second electron affinity differs only by the difference in electrostatic energy. The charge distributions for the fullerene dianions are unknown. Therefore we assume that the excess charge would be delocalized. Using the assumptions, the second electron affinity can be approximated as

$$EA(2) = EA(1) - e^2/R_n. \quad (3)$$

In Figure 4, the second electron affinities estimated from experimentally determined first electron affinities [24] are shown together with experimentally determined values [19,25,26]. Although this procedure tends to underestimate the second electron affinity, it shows reasonable agreement with the experimental values. The difference could be the result of the greater electronic radii due to the Coulomb repulsion.

The charge transfer cross sections are estimated using the over-the-barrier model and the curve crossing model [14]. The application of the model for the reactions including large molecules like fullerenes are very crude because the cross sections are given by the difference between two large numbers. Therefore a small error in the estimate of electron affinities and radius would result in large differences in the estimation of the cross section. Even with the crudeness, the model is still useful to discuss qualitative

Table 1. The calculated radius of C_n by using equation (2), and second electron affinity $EA(2)$ using equation (3). Critical distances for over-the-barrier R_c and curve crossing point R_r are calculated using the radii and second electron affinities.

n	$R_c(\text{\AA})$	$R_r(\text{\AA})$	n	$R_c(\text{\AA})$	$R_r(\text{\AA})$
60	8.20	5.89	88	9.08	7.04
70	8.53	6.23	90	9.14	7.16
72	8.59	6.51	92	9.18	7.14
74	8.67	6.74	94	9.24	7.19
76	8.73	6.50	96	9.30	7.32
78	8.78	6.69	98	9.35	7.35
80	8.84	6.80	100	9.40	7.48
82	8.90	6.83	102	9.45	7.58
84	8.96	6.90	104	9.51	7.67
86	9.02	7.00	106	9.55	7.70

behaviour. With the radii and electron affinities discussed above, the critical distances R_c , where the barrier for the transferring electron becomes lower than the ionization potential, is calculated as described in reference [14] and listed in Table 1. The values should be compared with the curve crossing points R_r which can be obtained by solving the following equation

$$EA(2) = I + e^2 \left[-\frac{2}{R_r} + \frac{R_n}{2R_r} - \frac{R_n}{2(R_r^2 - R_n^2)} \right] \quad (4)$$

where I is ionization potential of a sodium atom. The obtained values are listed in Table 1. Since all the critical distances for the over-the-barrier model are larger than the curve crossing distances, the formation cross section should be mainly determined by the latter value. The cross section is thus,

$$\sigma = \pi (R_r^2 - R_f^2) \quad (5)$$

where R_f is the radius within which collisional fragmentation takes place. R_f should be about 1 \AA larger than R_n considering energy transfer to the carbon atom from the Na target atom [27]. For the dianions, the energy required to remove an extra electron is much lower than fragmentation, therefore R_f should be larger for the present case. When we assume $R_f = R_n + 1.35 \text{ \AA}$, we obtained a good agreement in relative cross sections (Fig. 3), even though the absolute value for C_{60} is a factor of 3 different from what we obtained earlier. We think that the qualitative behaviour of the cross section is mainly determined by the second electron affinities, the quantitative disagreement is most probably due to the simple model where the cross section is defined as a difference between two large numbers.

With the model described above, the lifetime of the trianion can also be estimated. With the conducting sphere model, the third electron affinity is given by

$$EA(3) = EA(1) - 2e^2/R_n. \quad (6)$$

The Coulomb-barrier for the third electron is then given by

$$U_e(r) = \frac{2e^2}{r} - \frac{e^2 R_n^3}{2r^2 (r^2 - R_n^2)} + \frac{e^2 a_0}{r^2}, \quad (7)$$

where $a_0 = 0.53 \text{ \AA}$ is the Bohr radius. An electron with positive energy E can tunnel through the barrier with a rate given in the WKB approximation by

$$k = \nu \exp(-W) \quad (8)$$

$$W = \frac{2}{\hbar} \int_{r_1}^{r_2} \sqrt{2m(U_e(r) - E)} dr \quad (9)$$

where the limits of the integral are the classical turning points and m is the electron mass. A rough estimate of the attempt frequency ν can be obtained from the uncertainty principle [15,18]. According to this estimate, the lifetime of C_{96}^{3-} is found to be on the order of picoseconds, which is too short to be observed in the present setup.

5 Conclusions

We have measured electron capture cross sections in collisions between higher order fullerene anions C_n^- ($n = 76, 78, 82, 84, 86, 90$ and 96) and Na atoms. The measured cross section for dianion formation is three times larger for C_{96} than that for C_{60} . The large increase of the cross section with fullerene size is successfully explained by means of the curve crossing model for electron transfer using simple scaling rules to estimate the size and the second electron affinity of fullerenes. Even though the absolute value of the capture cross section is a factor of 3 larger than our previously reported value for C_{60} , we believe that the model explains the qualitative behaviour of the cross section as a function of fullerene size based on estimates of second electron affinities. Therefore the scaling of the sizes and electron affinities of fullerenes are reliable, so that we can use the scaling rule to estimate third electron affinities. The lifetime of C_{96}^{3-} is calculated with this scaling rule using the WKB approximation. This estimate gives a lifetime on the order of picoseconds, which is much too short to be observed. Since the qualitative results are explained very well by scaling and the curve crossing model, this charge transfer mechanism would most probably work not only for fullerenes but also for other large molecules like DNA and peptide ions.

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