Formation of C_{60}^{2-} Dianions in Collisions between C_{60}^{-} and Na Atoms

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We have observed the formation of C_{60}^{2-} and C_{70}^{2-} in collisions between C_{60}^{-}/C_{70}^{-} and Na atoms. Cross sections for the electron transfer to the monoanion are determined to be 36 ± 9 and 57 ± 14 Å^2 for C_{60}^{-} and C_{70}^{-}, respectively. A simple model investigation suggests that the electron is transferred from a Na atom to a low-lying electronic state of the fullerene to form a dianion. The method leads to pico-ampere energetic beams of C_{60} dianions that can be used for spectroscopy and lifetime studies.

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The formation and energetics of gas-phase multiply charged anions is a subject that has attracted much attention over the past decade [1–3]. One of the most interesting properties of a dianion is the existence of a Coulomb barrier due to the combination of two interactions, the attractive short-range interaction between an excess electron and the charged molecular "core" and the long-range Coulomb repulsion. The Coulomb barrier can even trap an excess electron that has a negative electron binding energy [4].

The cluster dianions are interesting because they make it possible to study the evolution of the electron binding energy and the barrier height as a function of cluster size. Especially, dianions of metal clusters and fullerenes have been studied intensively using recently developed techniques. The existence of C_{60}^{2-} produced in laser desorption of fullerenes was reported by Hettich *et al.* [5] and Limbach *et al.* [6]. The lifetime of C_{60}^{2-} was considered to be at least 1 ms even though many calculations predict slightly negative binding energies for the second electron [7–10].

As an alternative method to produce fullerene dianions, fullerenes dissolved in organic solvents were electrosprayed together with an organic electron donor. Thus, Khairallah and Peel [11] observed C_{84}^{2-} and C_{90}^{2-} by electrospray mass spectrometry. Recently, Hampe *et al.* [12] improved the technique and generated C_n^{2-} ions ($n =$ 70–124). In addition, free electron attachment to fullerene anions has also been performed. Electron attachment to C_{84}^{-} [13] was reported earlier and, recently, electron attachment to both C_{76}^{-} [14] and C_{70}^{-} [15] was performed in a Penning ion trap. Despite intensive efforts, the C_{60}^{2-} has not yet been observed by electrospray or by free electron attachment to the monoanion.

Dianion formation of fluorinated fullerenes through charge transfer reactions with several different gas targets has been demonstrated by Boltalina *et al.* [16,17]. Tuinman and Compton [18] measured the threshold behavior for dianion formation in the reaction $C_{60}F_{36}^{-} + CH_4 \rightarrow C_{60}F_{36}^{2-} + CH_4^{+}$ and found a high threshold energy compared to the energetic requirement. Although the technique was also applied to formation of fullerene dianions, no dianions were observed with CH_4 as target gas [18]. In the present Letter, we used Na as target gas and observed dianions of both C_{60}^{2-} and C_{70}^{2-}, produced through charge transfer from Na atoms. This method is similar to the charge transfer processes taking place between neutral particles, such as alkali atoms/alkali clusters and halogen molecules, where the effect is known as "harpooning" [19,20]. This technique was recently applied also to the formation of a dianion of adenosine 5'-monophosphate (a building block of RNA) [21] and to initiate the Coulomb explosion of molecular dianions [22]. The purpose of this Letter is to shed light on our understanding of the mechanism for dianion formation through charge transfer from an atomic target.

The experimental arrangement is shown in Fig. 1 and described in detail in Ref. [16]. Fullerene anions were produced in an electrospray ion source. The spray solution consisted of 50 μl of a solution of C_{60} or C_{70} (1 mM) 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 C_{60} as an acceptor. The solution was sprayed through a needle at -4 kV with a flow rate of 4 μl/min. The electrospray ion source was located on a high voltage platform. After acceleration to 50 keV the fullerene anions

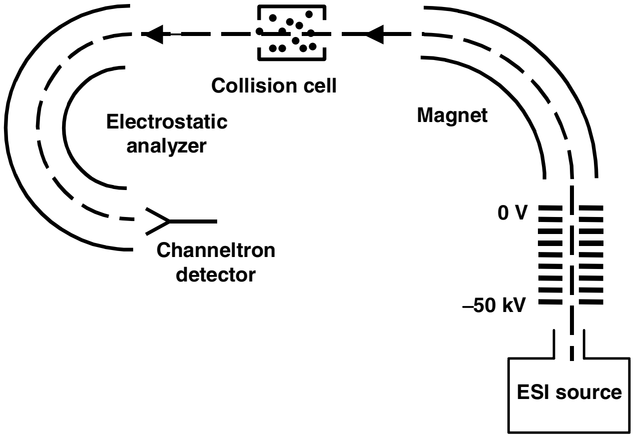

FIG. 1. Illustration of experimental setup.

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 temperatures around 200 °C. The absolute target thickness was obtained from the measured oven temperature by use of the known vapor pressure versus temperature curves [23]. 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. Absolute cross sections were determined by measuring the ratio of the intensities of the product and precursor ions as a function of target thicknesses, the so-called initial growth method.

In Fig. 2, mass spectra of negative ions obtained after collisions with Na at 210 °C are shown. Peaks corresponding to dianions are clearly observed for both C_{60}^- and C_{70}^-. Dianion formation is the dominant reaction channel against the very weak signals of C_{59}^- and C_{58}^- which are also observed in collision with rare gases [24]. The lifetime of the dianions is longer than the flight time from the collision cell to the detector, which is about 10 μs. The cross sections for dianion formation are determined to be 36 ± 9 and 57 ± 14 Å^2 for C_{60}^{2-} and C_{70}^{2-}, respectively. 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%. We have also measured the cross section at different energies (50, 75, 100 keV), but no strong variation with energies was found. With Xe as a target atom instead of Na, we could not find any clear signal of dianions, though dianion formation had been observed in $C_{60}F_n^- + \mathrm{Xe}(18 < n < 48)$ reactions [16,17]. Hence, the cross section for C_{60}^- and C_{70}^{2-} formation in a Xe target is much lower than 1 Å^2. The cross sections observed here with Na are very large compared to cross sections observed for $C_{60}F_{35}^-$ with "conventional" target gases (< 1 Å^2) [17].

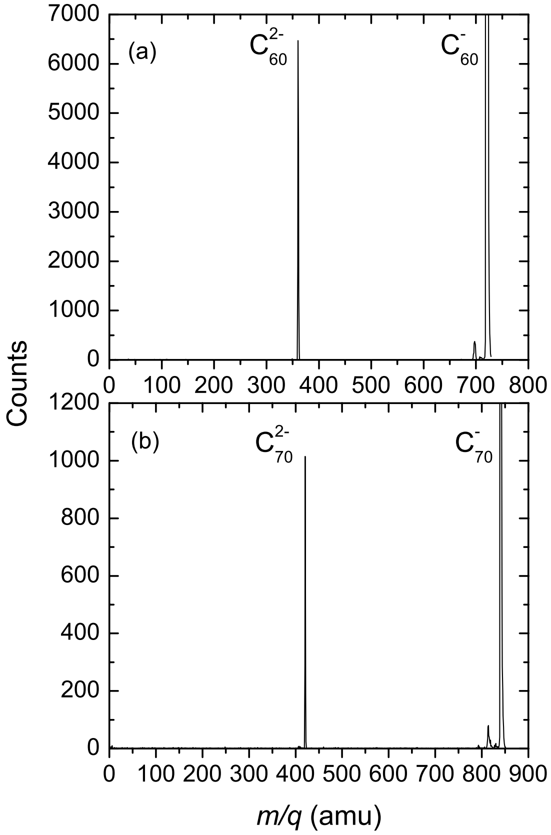

FIG. 2. Mass spectra of negative ions obtained after collisions with Na atoms, (a) $C_{60}^- + \mathrm{Na}$, (b) $C_{70}^- + \mathrm{Na}$.

Because of the large cross section, around 30% of the C_{60}^- ions can be converted to C_{60}^{2-}, while the beam current of the C_{60}^- precursor can be in the order of 1 pA. It implies that charge exchange in Na is an attractive production method for intense beams of C_{60}^{2-}. This enables spectroscopy and lifetime experiments on C_{60}^{2-}.

To describe the electron transfer process, we approximate fullerenes by a conducting sphere of radius a. The radii $a = 4.24$ and 4.67 Å were derived from the polarizabilities of neutral fullerenes, 76.5 [25] and 102 Å^3 [26] for C_{60} and C_{70}, respectively. The process is described as that of an electron moving between a negatively charged conducting sphere and a singly charged ion located at a distance R from the center of the sphere. By applying the over-the-barrier model for a conducting sphere and an atomic ion [27], the potential felt by an electron at a distance r from the center of the conducting sphere can then be written as

$$V(r) = e^2\left[\frac{1}{r} - \frac{a}{Rr} - \frac{1}{R-r} + \frac{a}{Rr - a^2} - \frac{1}{2}\frac{a^3}{r^2(r^2 - a^2)}\right]. \tag{1}$$

When the maximum of the potential is lower than the Stark shifted ionization potential of the target atom, the active electron can be transferred to the corresponding state of C_{60}. This shifted ionization potential can be written as [27]

$$I^* = I + e^2\left[-\frac{1}{R} + \frac{a}{2R^2} - \frac{a}{2(R^2 - a^2)}\right]. \tag{2}$$

From Eqs. (1) and (2), the critical distance R_c, where the barrier becomes lower than the ionization potential, is calculated to be 8.2 and 8.7 Å for electron transfer from a Na atom ($I = 5.14$ eV [23]) to C_{60} and C_{70}, respectively. For Xe ($I = 12.1$ eV [23]), we obtained $R_c = 6.2$ Å for C_{60}. If there is a corresponding resonance state into which the electron can be transferred on the projectile, the electron can be transferred. The resulting binding energy of the electron after the electron transfer can be obtained from a resonance condition

$$I^* = E_b^*, \tag{3}$$

where the binding energy E_b^* is also Stark shifted [27],

$$E_b^* = E_b + e^2/R. \tag{4}$$

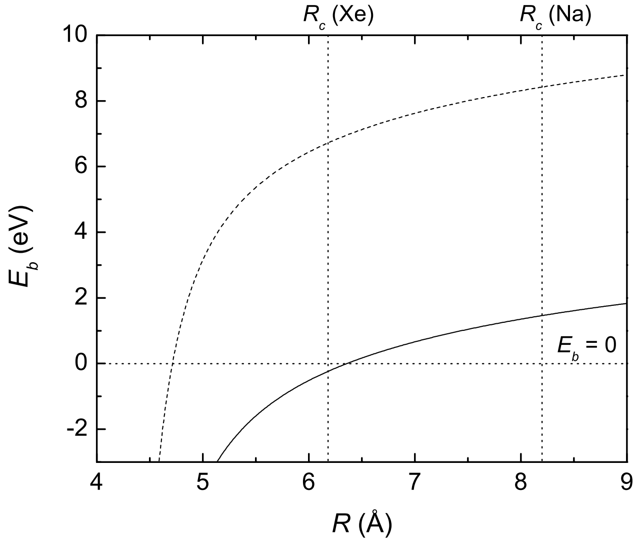

FIG. 3. The resonance binding energy for C_{60}^{2-} after electron transfer at a distance of R, for Na (solid line) and Xe (dashed line). Dotted lines indicate the positions of critical distances. The horizontal dotted line indicates the second electron binding energy of C_{60}.

From Eqs. (2)–(4), the binding energy of the electron transferred at a distance of R can be written as

$$E_b = I + e^2\left[-\frac{2}{R} + \frac{a}{2R^2} - \frac{a}{2(R^2 - a^2)}\right]. \qquad (5)$$

In Fig. 3, the binding energy of the transferred electron is shown as a function of R for the electron transfer from Na and Xe. It is seen that the binding energy decreases when R becomes small. If electron transfer occurred at the critical distance R_c, the binding energy would be about 1.5 and 6.2 eV for Na and Xe, respectively. Since the second electron affinity of C_{60} is estimated to be around 0 eV [7–10], there is no corresponding binding state at the critical distance R_c and the active electron cannot be transferred to C_{60}^-. To satisfy the resonance condition, the atomic ion has to approach closer until it reaches the resonance distance R_r. R_r estimated from Eq. (5) with $E_b = 0$ eV is 6.4 and 4.7 Å for Na and Xe, respectively. The resonance distance for Xe is only slightly longer than the C_{60} radius. Therefore, almost no dianions will be formed in a collision with a Xe target. However, the resonance distance for Na is large compared to the size of C_{60} and smaller than the critical distance for the over-the-barrier condition. Thus the active electron can be transferred into the ground state of C_{60}^{2-} with no or only little excitation.

This model is probably too simple to explain the cross sections quantitatively. For example, it was suggested that the barrier height derived from the conducting sphere model is overestimated by a factor of 2 [28] and also the probability of electron transfer (such as described in the Landau-Zener formalism) is unknown. The precise size of the geometrical fragmentation (πR_0^2) is difficult to estimate and consequently also the calculated capture cross section $\pi(R_r^2 - R_0^2)$ could be rather uncertain. However the R_0 calculated from the experimental capture cross section of 36 Å^2 is 5.4 Å which is in reasonable agreement with calculated fragmentation cross sections based on the Thomas-Fermi potential [29].

The calculation for C_{70}^{2-} gives similar results. The binding energy for C_{70}^{2-} was calculated to be 1.31 eV based on MOPAC AM1 calculations [11]. Considering the fact that the calculation tends to give too large a value and that the second electron affinity of C_{84} was recently measured to be 0.41 ± 0.07 eV [28], we think that the value for C_{70}^{2-} should be somewhat lower. One of the experimental studies shows that the C_{70}^{2-} is metastable and has a lifetime of 80 s. The authors estimate the binding energy to be −0.3 eV [12]. Based on our model, the resonance condition would be fulfilled with distances 7.0 and 6.2 Å for binding energies of +0.5 and −0.5 eV, respectively. These distances are large compared to the size of C_{70} and smaller than the over-the-barrier distance (8.7 Å).

An interesting observation which should be noted from this model is not only the fact that the low ionization energy of Na results in an easy transfer of the active electron to the anion but also that the binding energy of the dianion shifts during the collision and hence at some intermolecular distance fulfills the resonance condition so that the active electron can be captured to the ground state of the dianion. For free electron capture in contrast the electron has to overcome or tunnel through the Coulomb barrier and hence is captured in a high electronic state. The electronic energy in this case is converted to vibrational energy and heats the molecule [13].

To summarize, we have observed the formation of C_{60}^{2-} and C_{70}^{2-} in collisions between C_{60}^-/C_{70}^- ions and Na atoms. We measured the electron transfer cross sections to be 36 ± 9 Å^2 and 57 ± 14 Å^2 for C_{60}^- and C_{70}^-, respectively. A simple analysis based on the over-the-barrier model shows the importance of a resonance condition where the Stark shift plays an important role in the case where the final charge states of projectile and target ions have opposite signs. The Stark shift also results in the interesting fact that the active electron from an atom can be captured into the ground state while free electron capture occurs to a high electronic state. The survival probability of dianions generated by charge transfer processes may thus be much larger than that of dianions generated by free electron attachment.

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