

Dissociation Energy for C₂ Loss from Fullerene Cations in a Storage Ring

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We have stored positively charged fullerene ions C_n^+ (n even, from 48 to 70 and 76), C_{60}^{2+} and C_{70}^{2+} in an electrostatic storage ring and have measured the rate of emission of neutral fragments as a function of time. In the time range of the measurements, 50 μ s to a few milliseconds, the rate decreases strongly due to radiative cooling of the molecules. Using the cooling rate predicted from a dielectric model, we have extracted the dissociation energies for C₂ loss from the measurements. As expected, the energies are largest for the “magic” fullerenes, C₅₀, C₆₀, and C₇₀, and the value of 9.8 ± 0.1 eV for C₂ loss from C_{60}^+ is in reasonable agreement with theory and with other recent experiments.

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It is generally accepted that the dominant decay process for a highly excited C₆₀ molecule is loss of a neutral C₂ molecule. Since the discovery of C₆₀, intense research has been carried out to determine the dissociation energy for this process, but a strong disagreement between theoretical and experimental values has persisted. Theory predicts a dissociation energy E_d between 10 and 11 eV [1], while experiments have mostly resulted in a value below 8 eV. The difficulties in determining the dissociation energy experimentally have mainly been due to the influence of radiative cooling and to the unknown magnitude of the preexponential factor A in the Arrhenius decay law [2],

$$k(T) = A \exp(-E_d/k_B T). \quad (1)$$

The importance of radiative cooling for fullerene decay was first established by Hansen and Campbell [3] through a statistical analysis of fragmentation of fullerene cations on a time scale of 10–100 μ s. Recently, Laskin *et al.* [4] measured time resolved metastable fractions for C₂ evaporation with a trap/reflectron apparatus. They included radiative cooling in the analysis, and from a combination with previously obtained experimental breakdown curves [5] they derived the dissociation energies for C_n^+ ($n = 48$ to 60). A very large value of the preexponential factor was used, $A = 2 \times 10^{19} \text{ s}^{-1}$, and for C_{60}^+ they obtained the value $E_d = 9.5$ eV. Since the ionization energy is larger for C₆₀ than for C₅₈ by about 0.5 eV [6,7], their result corresponds to a dissociation energy of 10.0 eV for C₂ emission from C₆₀.

This new interpretation of experiments was prompted by an independent determination of the dissociation energy for C₆₀ by Hansen and Echt [8]. From measurements of electron emission from laser excited neutral molecules, they derived a value of E_d that is independent of assumptions about the magnitude of the preexponential factor. Although rather uncertain, the result, $E_d = 11.4 \pm 1.9$ eV, was clearly much larger than contemporary values from fragmentation experiments.

An independent check of the absolute magnitude of the C₂ dissociation energies can be obtained from a comparison with the gas phase heats of formation of C₆₀, C₇₀,

and C₂, which are all known quite accurately. The total energy required for the transformation $C_{70} \rightarrow C_{60} + 5C_2$ has been calculated to be 40.5 eV [9]. However, application of this result requires a measurement of relative dissociation energies.

The experimental information on the dependence on n of the dissociation energy for C₂ emission from fullerene cations, C_n^+ , has been discussed by Lifshitz in a recent review [2]. The conclusion was that the available data confirm the idea originally proposed by Klots [10] that C_{60}^+ sits on the leading edge of a magic shell, i.e., that there is a step at $n = 60$ in the dissociation energy as a function of n rather than a single, very high value at $n = 60$. This conclusion is apparently in conflict with the relative dissociation energies derived by Barran *et al.* from a statistical analysis of fragmentation of very hot fullerenes created by laser ablation of graphite [11]. This experiment had the advantage that the time scale was so short that radiative cooling should be unimportant. However, the authors considered it possible that a saturation effect for C₆₀ in their experiment could be responsible for the discrepancy.

Thus the situation regarding the C₂ binding in fullerenes is still unclear. We have used a new method to determine dissociation energies for fullerene cations based on observations of the decay of excited molecules in a storage ring. The decay is quenched by radiative cooling and, applying theoretical values of the radiation intensity as a function of the internal ion temperature, we can use this as a thermometer to determine the temperature of the decaying molecules. The dissociation energy can then be derived from the Arrhenius expression in Eq. (1).

The theoretical predictions of the radiation intensity are based on a dielectric model [12], which is in fair agreement with the results of detailed experimental studies of radiative cooling of fullerene anions C_n^- , with even n from 36 to 96 [13,14]. The model is expected to be even more accurate for fullerene cations at the very high temperatures where fragmentation occurs [12]. The predicted intensity of thermal radiation is 3.3×10^4 eV/s for C_{60}^+ at 3000 K, and it should be proportional to n , the number of atoms, and to the sixth power of the temperature.

According to the Arrhenius expression in Eq. (1), the decay temperature T is proportional to the dissociation energy E_d for observation on a fixed time scale. Hence the cooling rate for decaying molecules should be very sensitive to the magnitude of E_d .

The decay curves of fullerene cations were measured as follows: The ions were produced in a plasma ion source, where a mixture of C_{60} and C_{70} was heated to about 600 K in a nitrogen buffer gas. The molecules were ionized and heated by electron bombardment inside the source, and beams of fullerene cations, C_n^+ with even n , were extracted. For the most abundant molecules, $n = 60$ and 70 , sufficient intensity was also obtained for the doubly charged cations. After acceleration by a 22 kV potential, mass selected ions were injected into the electrostatic storage ring ELISA [15]. As illustrated in Fig. 1, the ring consists of two ~ 2.5 m long straight sections connected by electrostatic deflection plates. The pressure was a few times 10^{-11} mbar and the lifetime of stored fullerene beams was about 10 s.

Neutral particles were detected by a microchannel plate detector located at the end of one of the straight sections. At short times, this signal is dominated by decay products (C_2) from unimolecular fragmentation of very hot molecules. To establish a well-defined initial condition, the stored ions were exposed to a pulse of first or second harmonic radiation from a Nd:YAG laser, and the decay rate was recorded as a function of the time after this irradiation. We estimate that there is an uncertainty of less than ± 0.5 m in the average position of the excited ions, owing to the uncertainty of the overlap of the ion and laser beams.

It is essential for the interpretation that the heating is sufficient to saturate the decay rate. For the second harmonic radiation (2.33 eV), the energy in the pulse was about 0.2 J in an area of about 1 cm^2 . This was sufficient for most cases. As a check, we varied the delay of the laser pulse and thereby the radiative cooling of the molecules before the laser excitation. In most cases, the signal was independent of the delay but not for C_{60}^+ , which cools very rapidly (by about 500 K in the first revolution). In this case, we hit the ions with the laser pulse during their first revolution and used the first harmonic radiation with a pulse energy of 0.45 J. We believe that the signal was then close to saturation. The dissociation energy is particularly low for C_{62}^+ ,

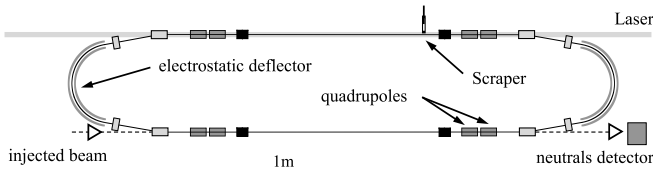


FIG. 1. Schematics of electrostatic storage ring (ELISA). A mass selected beam was injected from the lower left side, and neutral particles were detected by a microchannel plate located at the lower right side. A Nd:YAG laser pulse was injected from the upper left to heat molecules in the upper straight section.

and for this ion we had to reduce the power by a factor of 2 to avoid too much depletion in the first half revolution in ELISA after the excitation.

In Fig. 2 is shown a typical time spectrum measured for C_{58}^+ . The length of the bunch stored in ELISA was approximately $75 \mu\text{s}$, and the revolution time in the ring about $100 \mu\text{s}$. The peak width before laser irradiation corresponds to the length of the bunched beam. After irradiation, the decay rate of the molecules heated by the laser is increased by about 2 orders of magnitude and the width of the peaks corresponds roughly to the length of a straight section, i.e., about $30 \mu\text{s}$.

The analysis has been carried out as described in Ref. [14]. The statistical treatment is similar to that described in Ref. [13] but the quantization of photon energy is taken into account. In the expression for the decay rate in Eq. (1), the preexponential factor A was assumed to be independent of temperature and cluster size, and given by $A = 2 \times 10^{19} \text{ s}^{-1}$ as suggested by Laskin *et al.* [4]. For times t of the order of $1 \mu\text{s}$ the Gspann parameter $G = \ln(At)$ is then about 30, in agreement with the finding in Ref. [11].

The high count rates in Fig. 2, just after injection and just after laser heating, correspond to C_2 emission from hot fullerenes. The rapid decrease of the rate can be due to either depletion by the decay or quenching of the process by radiative cooling of the molecules. Owing to the rapid variation of the exponential in Eq. (1), the decay by C_2 emission is much faster than the radiation processes at very high temperatures, whereas radiative cooling dominates at low temperatures. As shown in Refs. [13,14], a characteristic decay time τ_c separates the regimes with depletion and quenching by cooling. It is given by

$$1/\tau_c = -(E_d/k_B T)(d/dt \ln T), \quad (2)$$

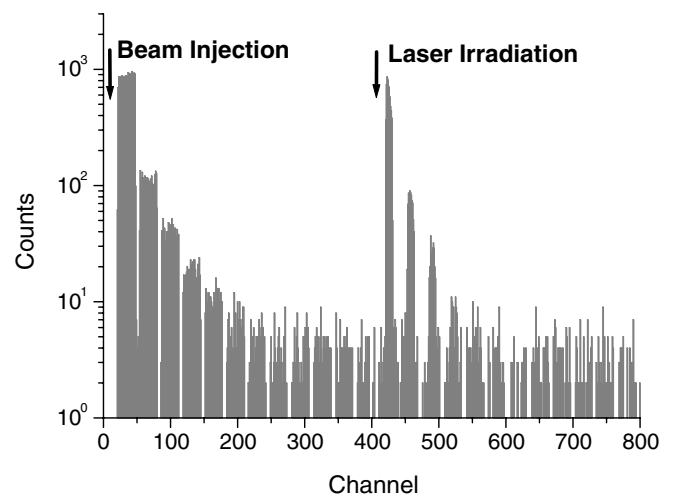


FIG. 2. Typical spectrum of the neutrals yield after injection of a pulse of C_{58}^+ ions into ELISA. The laser was fired after 12 revolutions of the stored ions in the ring. The time resolution of the spectrum is $3 \mu\text{s}/\text{channel}$.

evaluated at the upper cutoff T_c of the distribution in temperature of the molecules at the time τ_c ,

$$T_c = E_d / [k_B \ln(A\tau_c)]. \quad (3)$$

As shown in Ref. [12] (see Fig. 7 and the related text), this temperature is close to $T_c = 3000$ K and the characteristic time is about $\tau_c = 50 \mu\text{s}$ with the value of A given above and with a dissociation energy of $E_d \sim 8$ eV. The storage ring measurements are therefore expected to be mainly in the time and temperature regime dominated by radiative cooling.

Because of the cooling, the decay rate decreases nearly exponentially with a lifetime which according to Eqs. (1) and (2) is near τ_c for $t \geq \tau_c$. Approximating the large logarithm $\ln(A\tau_c)$ by a constant, we find from Eqs. (2) and (3) that a variation with temperature of the cooling as $(d/dt)T \propto T^6$ leads to the scaling $\tau_c \propto E_d^{-5}$.

Figure 3 shows comparisons of the simulations with typical decay curves for C_{60}^+ and C_{58}^+ , obtained by integration of the counts from each revolution of the stored ions in the ring after the heating by a laser pulse. The low, nearly constant count rate at long times is due to collisions with rest gas molecules. The rapid decrease at short times due to quenched unimolecular fragmentation is reproduced by a simulation with an optimum choice of the dissociation energy.

The dissociation energies obtained in this way for a range of fullerene cations C_n^+ are shown in Fig. 4. According to the scaling discussed above, an error of 25% in the calculated radiation intensity will result in an error of about 5% in the derived dissociation energy. As expected, the values of E_d are highest for the magic numbers 50, 60, and 70. When it is taken into account that the ionization energy of C_{60} is 0.54 eV higher than that of C_{58} [2,6], the value $E_d(C_{60}^+) = 9.8 \pm 0.1$ eV is in good agreement with the theoretical predictions of

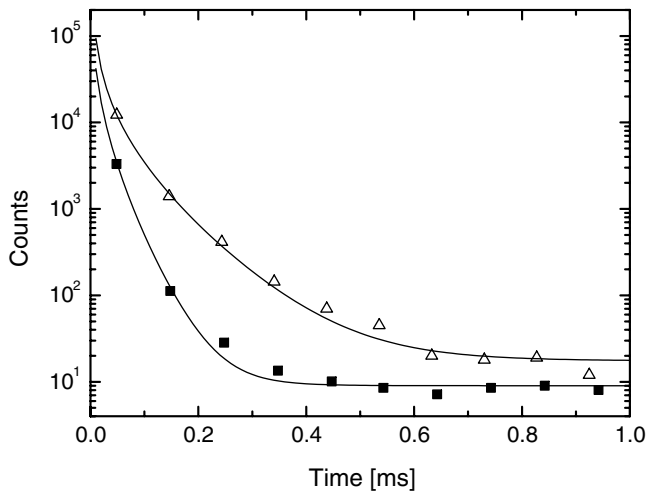


FIG. 3. Typical decay curve for C_{58}^+ (triangles) and C_{60}^+ (squares). The lines represent the simulation result with the optimum values of the dissociation energy.

$E_d(C_{60}) = 10$ to 11 eV. The relative magnitudes of the dissociation energies for the different fullerenes are in poor agreement with the results reported in Ref. [4] but in reasonable agreement with Ref. [11].

The derivation of dissociation energies from our observations depends on the validity of the model prediction for the thermal radiation. The argument for high accuracy of the model is that the radiation intensity at high temperatures is mainly governed by the surface plasmon resonances, which are very similar in the different fullerenes [12], and depends only weakly on the detailed structure of the absorption strength at low photon energies (see Fig. 9 of Ref. [12]). A test of this argument is obtained from a comparison between singly and doubly charged cations of C_{60} and C_{70} . Breaking of the closed-shell electronic structure of these magic molecules has a strong influence on their absorption spectrum at low photon energies, as revealed by the strong absorption of the first harmonic radiation from the Nd:YAG laser. An additional ionization is expected to increase further the absorption strength at low energies. However, the dissociation energies derived from our measurement on the dications are close to those for the singly charged molecules. Matt *et al.* [16] also found no significant dependence of C_2 emission on the charge state of fullerenes.

An independent check of the absolute magnitudes of the C_2 dissociation energies is obtained from a comparison with heats of formation. The sum of dissociation energies from C_{62}^+ to C_{70}^+ is 40.4 ± 0.8 eV in the present experiment. Since the difference in ionization energy between C_{60} and C_{70} is very small, this value may be compared to the total energy required for the transformation $C_{70} \rightarrow C_{60} + 5C_2$. Hennrich *et al.* [9] calculated the

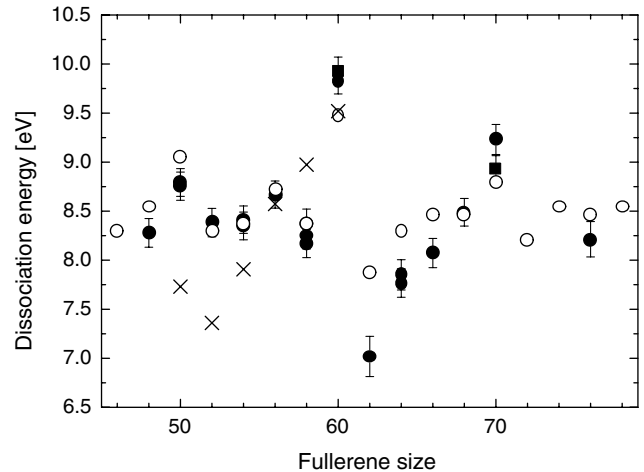


FIG. 4. Dissociation energies of fullerene cations. The values obtained in the present work are indicated by filled circles for singly charged ions and filled squares for doubly charged ions. The error bars do not include the uncertainty of the radiation intensity. Results from Refs. [4] (crosses) and [11] (open circles) are shown for comparison. The latter values have been normalized to our data at $n = 54$.

change in enthalpy for this reaction from the gas phase heats of formation of C_{60} , C_{70} , and C_2 , which are all known quite accurately. The result of 40.5 eV is in excellent agreement with our value.

Although we find E_d to be quite low just above $n = 60$, our results hardly support the concept of a “magic shell” at $n = 60$ [2,10]. The high stability is confined to the highly symmetric buckminsterfullerene C_{60} and, to a lesser extent, to other magic molecules, C_{50} and C_{70} . This is consistent with the calculations in Ref. [17], which predict similar magnitudes of the dissociation energies but somewhat larger wiggles in the E_d curve at the magic numbers. On the other hand, the amplitude of the wiggle at $n = 60$ is seen in Fig. 4 to be lower for the data from Ref. [11] than for our results. Perhaps this discrepancy can be explained by the possible saturation effect mentioned in Ref. [11].

In conclusion, we have measured time resolved decay curves for fullerene cations stored in an electrostatic ring. The time scale of the measurement, from 50 μ s to a few milliseconds, corresponds to a regime where C_2 emission is quenched by radiative cooling. The experimental results are well reproduced by simulations based on an Arrhenius formula with preexponential factor $A = 2 \times 10^{19} \text{ s}^{-1}$ and a cooling rate predicted from a dielectric model of fullerene molecules. From a comparison of the experimental results with simulations, we have obtained the dissociation energies for C_2 loss from fullerene cations C_n^+ , with even n values from 48 to 70 and 76.

The analysis relies on model predictions of the intensity of thermal radiation, and hence the accuracy of our results depends on the accuracy of these predictions. The model parameters were selected to account for the main features of the measured absorption of radiation by fullerenes [12]. The predicted heat radiation agrees within a factor of 2 with cooling rates of fullerene anions, and the predictions should be much more accurate for fullerene ions at the higher temperatures corresponding to C_2 dissociation. Nevertheless, this dependence on model predictions constitutes the most important source of uncertainty in the experiment.

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