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Letter

New evidence in favor of a high (10 eV) C_2 binding energy in C_{60}

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Abstract

Time resolved metastable fractions (MFs) for C_2 evaporations from C_n^+ ions ($n = 52,54,56,58$) were measured on an ion trap/reflectron and modeled using both microcanonical dissociative and radiative decay rate constants. The concomitant fitting procedure required the use of highly loose transition states with activation entropies, $\Delta S^{\#} = 14$–19 eu. Using the same modeling procedure also allows one to reproduce the major features of previously published breakdown curves for these ions. The present modeling leads also to high C_2 binding energies with a value for C_{60}^+ of $\Delta E = 9.5$ eV. Using a simple thermochemical cycle leads to a value in slight excess of 10 eV for the binding energy of neutral C_{60}, in excellent agreement with recent ab initio calculations. (Int J Mass Spectrom 177 (1998) L9–L13) © 1998 Elsevier Science B.V.

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The major decay reaction of moderately excited C_{60}^{+*} proceeds via sequential unimolecular loss ("evaporation") of C_2 units [1]. Nevertheless, and in spite of intense research, the energetics for the first step,

$$C_{60}^+ \rightarrow C_{58}^+ + C_2 \tag{1}$$

is still controversial [2]. There is a particularly strong disagreement between experimental values that place this energy around 7–8 eV and theoretical ab initio results, which support a fragmentation energy around 10–11 eV. The appearance energy of C_{58}^+ from C_{60} demonstrates a large intrinsic kinetic shift, which prevails at long times after excitation, due to competition of radiative decay of C_{60}^+ with dissociation [3]. As a result, the binding energy cannot be easily deduced from appearance energy measurements. An alternative approach that we have taken is to determine the kinetic energy release distribution (KERD) for reaction (1) and applying finite heat bath theory (FHBT) [4] to deduce the binding energy from the KERD [5,6]. Another experimental approach we have taken has been the comparison of measured and calculated breakdown curves [7,8]. These different

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approaches gave an internally consistent binding energy $\Delta E = 7.1–7.2$ eV. However, in the analysis of all of these studies (KERDs and breakdown curves), a transition state of about equal tightness was assumed for reaction (1). This was achieved through the use of the Gspann parameter $\gamma = \ln A - \ln k_{mp}$, where A is the pre-exponential factor in the Arrhenius equation for reaction (1) and k_{mp} is the most probable rate constant sampled in the experiment. A value $\gamma = 23.5 \pm 1.5$ has been considered to be the "best value" [9] for clusters of different composition and different sizes and was employed in the modeling of the KERDs [5,6]. It is in agreement with $A = 1.6 \times 10^{15}$ s^{-1} and $k_{mp} = 1 \times 10^5$ s^{-1}. A somewhat higher value, $\gamma = 25.6$, has been obtained for C_{60}^+ by Wörgötter et al. [8] from modeling of experimental appearance energies of fullerenes. It has been realized by the present authors [8] that a very loose transition state, given the notation TS-3, with $\gamma = 34.2$, would lead to a very high $\Delta E = 9.2$ eV value, but we considered this value of γ to be outside the range typical of evaporations from cluster ions occurring in the time window of our experiments. Hansen and Campbell [10] analyzed metastable fractions (MFs) of fullerenes and found a very high Gspann parameter ($\gamma = 31$). Applying this value in the analysis of the KERDs led to $\Delta E(C_{60}^+) = 9.7$ eV [6]. The Gspann parameter is related through the Arrhenius A factor to the activation entropy of reaction (1) and there are obvious energy–entropy tradeoffs.

The recent analysis [11] of the rate of delayed (thermionic) ionization of photoexcited C_{60} molecules that occurs in competition with C_2 evaporation from neutral C_{60} gave a very high experimental value for the binding energy of C_2 in neutral C_{60}, $\Delta E(C_{60}) = 11.9 \pm 1.9$ eV. The treatment did not require knowledge of the Arrhenius prefactor A and was therefore independent of assumptions concerning the activation entropy. Using a simple thermochemical cycle connecting the ionic and neutral binding energies [1a], $\Delta E(C_{60}^+) = \Delta E(C_{60})–0.5_4$ eV, leads to $\Delta E(C_{60}^+) = 11.4 \pm 1.9$ eV. Furthermore, the recent most accurate density functional theory (DFT) calculations [12] place the ionic binding energy at $\Delta E(C_{60}^+) = 10.2$ eV and the neutral one at $\Delta E(C_{60}) = 10.8$ eV, which is within experimental error in agreement with the result of Hansen and Echt [11]. In a recent discussion [13,14] of the thermionic emission paper [11] it was claimed [14] that the large discrepancies among the various experimental determinations of the C_2 dissociation energy [2] mainly arise from the use of different frequency factors (i.e. pre-exponential A factors) in the expressions being used for the rate constants to analyze the data.

The important question arises, from the discussion given above, whether the value for the dissociation energy for C_{60}^+ can be determined from modeling of mass spectrometric data that do require assumptions concerning the degree of tightness of the transition state. The present Letter will demonstrate that under certain circumstances (complete data sets) it is indeed possible. However, measurements of decay properties, such as KERDs or breakdown graphs, at a single reaction time cannot provide a unique answer. We have determined recently [15] time-resolved metastable fractions (MFs) for the C_2 elimination from C_{58}^+. These results were successfully modeled by dissociative and radiative microcanonical $k(E)$ dependencies. In these calculations we assumed for the description of the dissociative decay of C_{60}^+ and C_{58}^+ the prefactor to be the same and to have a value of $A = 5 \times 10^{15}$ s^{-1}, which corresponds to a rather tight transition state with an activation entropy of $\Delta S^{\#} = -0.2$ e.u. We have extended this study to include time-resolved MFs of C_{52}^+, C_{54}^+, C_{56}^+, and C_{58}^+. These ions satisfy the evaporative ensemble requirement, i.e. they are formed as a result of C_2 evaporation from the corresponding precursor ions. The width of the corresponding ensemble is directly related to the C_2 binding energy. In contrast, C_{60}^+ is formed by direct ionization from the fullerene sample without undergoing a prior evaporation. As a result, the energy distribution of C_{60}^+ ions is very wide due to the large kinetic shift. Consequently, the MF for C_{60}^+ is very low and its modeling requires the knowledge of the energy deposition function upon ionization, which is unknown. Because C_{58}^+ is formed from C_{60}^+ in the ion source, the ion source distribution of C_{58}^+ used in our modeling, as described in [15], depends on the C_2 binding energy assumed for C_{60}^+. Therefore, although we do not model the MF of C_{60}^{+}, the kinetic parameters for the C_{60}^{+} fragmentation are obtained from modeling of the metastable fraction of C_{58}^{+}. We have therefore concentrated on the modeling of MFs for C_{52}^{+}–C_{58}^{+}. Time-resolved MFs of these ions were modeled in an internally consistent fashion, which led to much larger prefactors, and thus larger binding energies will be presented in this Letter.

The experimental apparatus and the methods employed have been described by us in detail previously [15,16]. The instrument consists of a reflectron time-of-flight (TOF) mass spectrometer with a quadrupole ion trap as an ion source. The fullerene sample is evaporated from a Knudsen cell at a temperature of 400–500°C and ionized by the fourth harmonic of a Nd:YAG laser (266 nm; photon energy 4.66 eV) which passes directly through the trap. Ions produced by multiphoton ionization (MPI) are stored in the quadrupole ion trap by applying an rf potential to the ring electrode of the trap. After a variable delay time, the trapping potential is shut off and subsequently an extraction pulse is applied to the exit endcap. The ions are analyzed in a reflectron type TOF mass spectrometer.

The various operating modes of the reflectron have been reviewed in [17]. In order to record TOF spectra of the parent and metastable ions, the reflectron operated in the "hard reflection" mode. The "daughter only" spectrum was detected by scaling the voltage of the first grid by the M_d/M_p ratio (M_d and M_p are the masses of the fragment and parent ion, respectively) and setting the last grid to a negative potential, ensuring that all the parent ions escape to the wall. The spectra were averaged over 1000–8000 laser shots in order to get a sufficient signal-to-noise ratio. The peaks were numerically integrated and MFs were obtained by dividing the area of the metastable peak by the sum of the parent and metastable peak areas.

Time resolved metastable decay probabilities (MFs) for C_2 evaporations from C_n^{+} (n = 52,54,56,58) are plotted as a function of $\ln(t_2/t_1)$ in Fig. 1, where t_1 is the entrance time into, and t_2 is the exit time from, the TOF field free region. Included are our own experimental results covering a wide time range by virtue of ion trapping (open circles), the results of Hansen and Campbell obtained for a more limited time range [10,18] (crosses), and the model calculations (solid lines). Agreement between the two sets of experimental results is quite good, as is the agreement with the calculated results. The model that we have applied previously to the results for C_{58}^{+} [15] took into account radiative cooling, in competition with dissociative decay of the fullerene ions. Dissociative microcanonical rate constants were calculated by RRKM theory, whereas radiative decay in the visible was modeled following Chupka and Klots [19]. The radiative cooling leads to (i) suppression of the contribution of dissociative decay and (ii) the nonlinearity observed for the plots of the metastable decay probabilities (Fig. 1), which without radiative decay are expected to be nearly linear with a zero intercept.

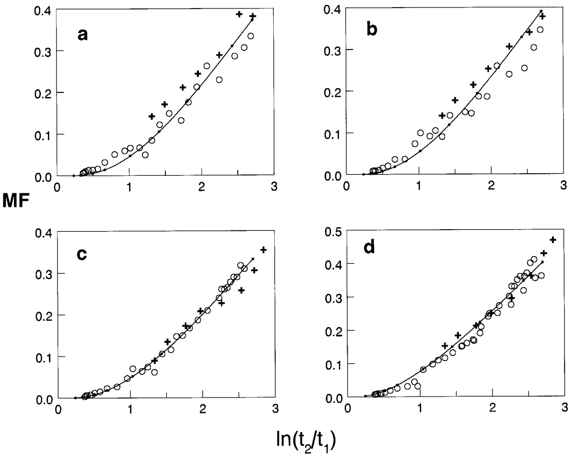

Fig. 1. Metastable decay probabilities as a function of $\ln(t_2/t_1)$. Open circle: present experimental results; cross: experimental results from [10,18]; solid line: calculated (see text); a-C_{52}^{+}; b-C_{54}^{+}; c-C_{56}^{+}; d-C_{58}^{+}.

The modeling of the present extended data set requires setting up a collection of kinetic equations. Originally [15], these were solved analytically. Only single photon emission was allowed, in competition with dissociation. In the present modeling, details of which will be published elsewhere [20], a much more elaborate and accurate kinetic scheme was set up and integration of the kinetic equations was done numerically. It was specifically found that emission of several photons is very important during the time the "evaporative ensemble" is formed in the ion source. A relatively narrow internal energy distribution then enters the field free region and dissociates there, so that emission of more than one photon is unlikely. As a result, eq. (2) of [15] remains valid.

A major point that we would like to make is that one cannot get a unique set of activation parameters—activation energy (ΔE) and activation entropy ($\Delta S^{\#}$)—by analyzing only the MFs, even when time resolved data are modeled. It has already been demonstrated [8] that modeling the BDCs on their own can lead to different sets of $\Delta S^{\#}$ and ΔE. In the present study we have made it a point to reproduce not only the set of time resolved MFs, but also the set of breakdown curves published previously [8]. It turned out that MF modeling was very sensitive to the inclusion of the radiative decay contribution, whereas the BDCs were not as sensitive to radiative decay. The original preferred set of $\Delta S^{\#} = -0.8$ eu. and $\Delta E = 7.06$ eV chosen to fit the BDCs [8] could not fit the MFs. A much looser transition state, for reaction (1) and its analogues for the lower fullerene ions, had to be modeled with $\Delta S^{\#}$ in the range of 14–19 e.u.. Best agreement with both the MF data as well as the BDC data was obtained with $\Delta S^{\#} = 18.8$ eu.. This corresponds to a preexponential A factor of $A = 2.1 \times 10^{19}\ s^{-1}$ and if $k_{mp} = 1 \times 10^{5}\ s^{-1}$, then the corresponding Gspann parameter is $\gamma = 33$.

Fig. 2 represents the calculated and the experimental BDCs. The model is observed to reproduce the peak positions of the breakdown curves of the various ions. No effort was presently made to reproduce the lowering of the relative abundances of the experimental curves with decreasing size of the fullerene ion. This effect is known to be due to a declining energy deposition function [8].

Fig. 3 represents a comparison of the dissociative and radiative rate constants used in the modeling for C_{58}^{+}. The crossing point of the two curves is at ≈42 eV internal energy, which is somewhat lower than what we have found when we modeled the MFs on their own before [15] and at a rate constant $10^{4} \leq k(E) \leq 10^{5}\ s^{-1}$. The energy at the crossing point is in agreement with the large intrinsic shift observed in time resolved appearance energy measurements [3].

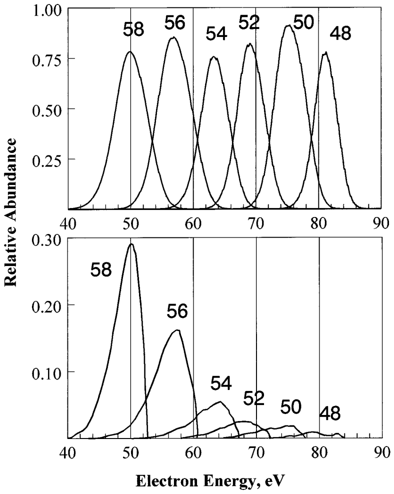

Fig. 2. Calculated (top, see text) and experimental (bottom, [8]) breakdown curves for C_{58}^{+}, C_{56}^{+}, . . . , C_{48}^{+} fragment ions of C_{60}.

The rate constant at the crossing point demonstrates that radiative decay cannot be neglected even on short time scales of several μs.

The theory derived by Klots and successfully employed for cluster evaporations [4,9, and references therein] works very well for systems that have no parallel reactions to dissociative decay. Because radiative decay is of major importance in the fullerenes, the definition of γ must be modified and a different modeling scheme [20] has to be employed. What has been found here, in agreement with Campbell, Hansen, and Echt [10,11,14] is a very loose transition state for the C_2 evaporation. This agrees with a mechanism [21] according to which an intermediate is

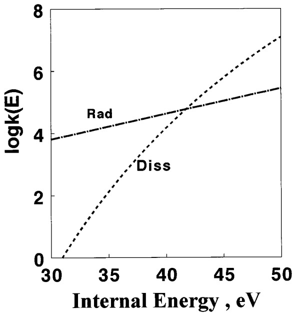

Fig. 3. Rate-energy curves for radiative cooling (solid line); dissociation of C_{58}^{+} (dashed line).

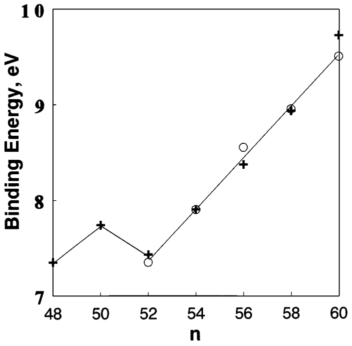

Fig. 4. C_2 binding energies in ionic fullerenes C_n^+ as a function of size n. Open circles present results; crosses: results from [8] for TS-3 normalized to the present results at $n = 54$.

formed with a seven-membered ring C_{58} isomer bound to a C_2 stick, which can become loosely bound and freely rotating in the transition state.

The modeling of time resolved MFs and of the breakdown curves for the same set of ions led to a unique determination of the binding energies shown in Fig. 4. The open circles are the present results, whereas the crosses are taken from [8] and normalized to the present data at $n = 54$. The value for C_{60}^+ derived is $\Delta E(C_{60}^+) = 9.5$ eV, which gives for neutral C_{60}: $\Delta E(C_{60}) = 10.04$ eV, in excellent agreement with recent ab initio calculations [12].

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