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Electron attachment to negative fullerene ions: a Fourier transform mass spectrometric study

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Abstract

Fullerene dianions were prepared by low-energy electron attachment to negatively charged fullerene ions C_{76}^- and C_{86}^- stored in a commercial Penning trap spectrometer under UHV conditions. Up to 85% of trapped monoanions can be converted to dianions upon long-term irradiation with electrons having kinetic energies averaging 6 eV corresponding to an attachment cross-section on the order of 100 Å^2 for C_{76}^-. The lifetime of the resulting C_{76}^{2-} was determined to be $>10^4$ s—limited by collisions with residual gas molecules. A model for statistical electron emission based on Klots' theory is used to provide an upper limit for the dianion temperature.

Keywords: FT-ICR mass spectrometry; Fullerene dianions; Multianions; Electron attachment; Coulomb barrier

1. Introduction

The transport of charge through individual molecules deposited onto a nanostructured electrode assembly is presently of great interest in the nascent area of molecular electronics [1]. Both the energetics and charging/discharging dynamics of the corresponding isolated species (e.g., in high negative charge states) are of obvious relevance.

There has been a recent flurry of activity in the areas of experimental characterization and theoretical description [2] of gas-phase multiply charged anions. This has been triggered both by the development of suitable gas-phase ion sources and by the realization that for many multianions well-known from the condensed phase, it is not clear a priori how to account for their stability as isolated entities. In particular, fullerenes have attracted considerable interest as model systems mainly due to their exceptional stability towards fragmentation and their relative theoretical tractability. So far, a number of experimental techniques have been applied to generate doubly charged fullerene anions in the gas-phase. First observations of C_{60}^{2-} were made upon laser desorption from a fullerene target [3,4] and later C_{84}^{2-} and C_{90}^{2-} were observed by use of electrospray sources [5]. In a different approach, Compton et al. have studied electron attachment to C_{84} within the ion source of a hybrid magnetic sector/quadrupole mass spectrometer to yield the corresponding mono- and dianion [6]. In this experiment, the dianions were found to be significantly vibrationally excited (ca. 15 eV) upon the two subsequent electron attachment steps required. Such excitation leads to electron autodetachment within the experimental time scale of about 60 μs. In the latter study, the attachment cross-section for the second electron was found to be greater than 1 Å^2—albeit for a broad and not easily quantifiable electron energy distribution reflecting mediation of the electron beam by nitrogen buffer gas. In an earlier FT-MS study fluorinated fullerenes $C_{60}F_x$ (x = 44, 46, 48)—again laser desorbed from a target—were also subjected to a beam of low-energy electrons. The resulting negative ion mass spectra were indicative of a dissociative second electron attachment step as the dominant channel [7]. In yet another type of experiment doubly charged (fluorinated) fullerene anions have been observed by means of charge exchange collisions (in the keV energy regime) with atomic and molecular targets [8,9].

Recently, experiments in a FT-ICR cell were performed to investigate the effect of the potential well depth on

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the efficiency of electron attachment to C_{70}^-. In this study, electrons from a heated filament were used and also moderated using a pulse of nitrogen buffer gas [10]. A trapping potential threshold of about 6 eV for dianion formation was observed. This was rationalized in terms of two contributing factors: the height of the Coulomb barrier which has to be overcome for electron attachment to occur, as well as radiative cooling of the electron cyclotron motion which leads to a reduction in trapped electron kinetic energy with increasing trapping times.

We have recently made the electrospray production of high fullerene dianions (C_{2n}^{2-}, $124 \geq 2n \geq 70$ (except for $2n = 72$)) more efficient by adding the electron donor tetrakis-dimethylaminoethylene (TDAE) to fullerene solutions prior to spraying [11]. C_{60}^{2-} was not observable under these conditions, presumably due to a metastable lifetime significantly shorter than the FT-ICR study time scale of about 0.1 s. Trapped C_{70}^{2-} was detected and found to be metastable with a half-life of about 80 s towards electron autodetachment. All larger fullerene dianions were found to be stable at room temperature and UHV within the upper bound of the experimental time scale ($t_{1/2} > 10^4$ s, i.e., decay rates comparable to collision frequencies) consistent with rough estimates of their (positive) second electron affinities. While this production method provides stable dianion signals suitable for analytical applications, signal intensity (particularly for the lighter fullerenes) is barely sufficient for ongoing depletion spectroscopic probes. Consequently, we have pursued alternate trap-based production schemes for fullerene dianions.

Inspired by the pioneering reports of Schweikhard et al. on electron attachment of trapped monoanions as mediated by a buffer gas we have specifically investigated electron attachment to trapped fullerene anions C_{76}^- and C_{86}^- *under rigorously ultra-high vacuum (UHV) conditions*. This was attempted in order to preclude subsequent collisional decay or Penning type ionization processes. Here we demonstrate that it is indeed possible to generate fullerene dianions by charging monoanions within a commercial Penning trap using a simple heated filament type electron impact source. Furthermore, we have studied the stability of the dianions so obtained by using an MS^2 experimental sequence—in order to obtain an upper limit for resulting vibrational excitation.

2. Experimental

Studies were carried out using a Fourier transform ion cyclotron resonance mass spectrometer FT-ICR-MS (Apex II, Bruker Daltonics) equipped with a cylindrical Infinity® cell as described previously [12]. Negative ions of fullerenes were generated in an external electrospray source upon spraying solutions of fullerene samples—produced and enriched in the higher fullerenes C_{76} and C_{86} in our laboratory—and TDAE in *ortho*-dichlorobenzene (*o*-DCB). The latter substance acts as an electron donor in solution to yield mainly singly and doubly charged fullerene anions [11]. After spraying, ions were pretrapped in a hexapole trap for typically 0.5 s at about 10^{-3} mbar at ambient temperature before being accelerated to about 2.5 keV and transferred into the ICR cell. The vibrational excitation of ions entering the ICR cell was estimated to be near room temperature. So as to allow ions to enter the trap the potential of the front trapping plate was pulsed open for a given delay. This time window allows a coarse preselection of ions of a certain mass/charge range due to their different time-of-flight between hexapole ion guide and ICR cell. After being trapped all unwanted ions can be ejected from the cell by applying a dipolar excitation at the appropriate ICR frequencies (correlated sweep). Applied trapping voltages were varied in the range of 1–6 V. Ions of interest were then allowed to interact with slow electrons for a variable time period.

These low-energy electrons were generated by means of a heated rhenium filament located at the rear side (on axis and about 18 cm downstream from the center) of the ICR cell—facing the ion beam. The filament was floated at a variable potential relative to the trapping voltage. In order to carry out time dependence studies it was possible to pulse this potential (after filling the cell with monoanions). Best results in terms of attachment efficiency were obtained for filament potentials about 1 V above the trapping voltage of the cell. We estimate the electron kinetic energy in the interaction region of the trap to be 6 ± 5 eV. The conservatively estimated error is mostly due to the energy distribution of the incident electron beam from the filament.

The total electron flux in the cell was determined by measuring the current on the second trapping electrode (held at ground potential) using a picoampmeter and estimated to be on the order of $10^{10}\ s^{-1}\ mm^{-2}$. Primary electrons directly from the filament were used for the experiments described; no buffer gas was admitted to moderate the primary electrons or to produce any secondary electrons. Therefore, typical pressures in the region of the ion trap were maintained in the 10^{-10} mbar region. To improve the dianion yield it was found advantageous to apply a quadrupolar rf pulse prior to the e-gun admission pulse. Those quadrupolar fields are used in Penning trap techniques to interconvert magnetron and cyclotron type of ion motion while leaving the total kinetic energy of the ions unaltered [13]. Here, the quadrupolar rf field apparently increases the spatial overlap between incident electrons and negative ions in the trap.

In order to study the stability of the dianions formed upon electron attachment, we also performed MS–MS experiments by first isolating the dianion of interest in the trap using a second correlated sweep and then acquiring mass spectra after a variable delay time. Mass spectra were taken using conventional FT-ICR techniques (for a recent review see [14]) with typical time scales for free induction decay (FID) transients of 50 ms.

3. Results and discussion

Fig. 1a shows a typical negative ion mass spectrum taken upon spraying a solution containing C_{76} and TDAE. Specifically, it was acquired directly after trapping of the ions transferred from the electrospray source. The assignment of the main peaks is given in the figure. Apart from the primary signal of C_{76}^- at $m/z = 912$ there is some C_{76}^{2-} dianion formed in the electrospray source as described previously [11] and ion signal due to a reaction product between C_{76} and TDAE, namely $C_{76}N(CH_3)_2^-$. We also observe a small peak due to a remainder of C_{60} in the fullerene sample as well as a peak (marked by an asterisk) that we can clearly assign to the third harmonic of the major signal C_{76}^-—a well-known instrumental artifact in ICR mass spectrometry. Fig. 1b demonstrates the capability of ejecting unwanted ions from the ICR cell as described in Section 2. Note in particular that residual second harmonic signal is negligible.

The same ion trapping/selection sequence was applied prior to intersecting the singly charged anions with low-energy electrons. Fig. 2 shows a sequence of mass spectra taken at three different electron irradiation times (10, 60 and 120 s). Very clearly we observe the peak at $m/z = 456$ to grow in with time at a constant electron current. The inset in the bottom graph displays a magnified portion of this peak resolving the isotopomer structure due to the natural content of ^{13}C in the sample. Note the

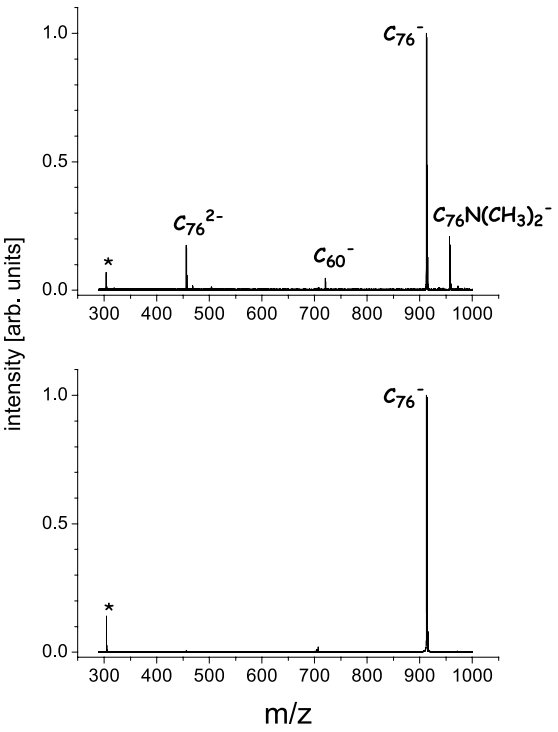

Fig. 1. Negative ion electrospray FT-ICR mass spectra acquired upon spraying a fullerene solution in *o*-dichlorobenzene enriched in C_{76} and TDAE. Shown are measurements of as trapped anions (a) and of the isolated singly charged anion C_{76}^- prior to electron attachment (b).

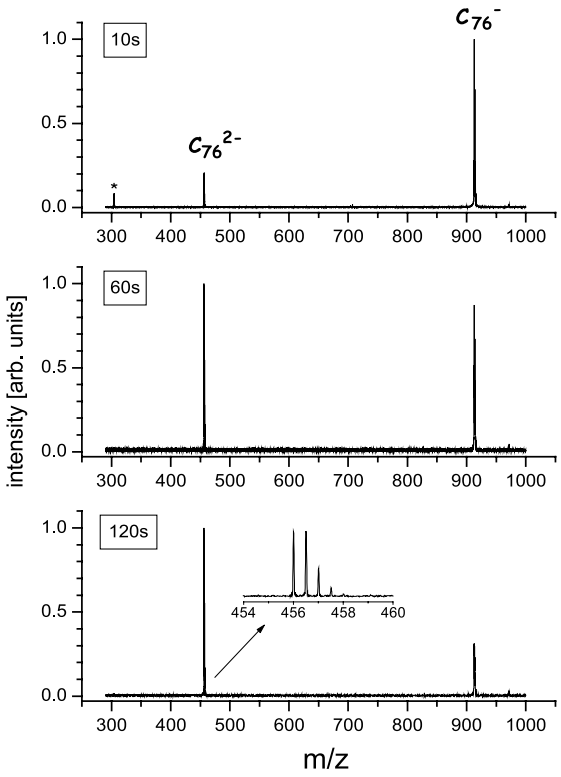

Fig. 2. "Snap shot" mass spectra taken after isolation of C_{76}^- and subsequent irradiation at with low-energy electrons for various reaction times (see text for details).

half-integer spacing between individual peaks as proof for a doubly charged anion: C_{76}^{2-}.

In order to quantify the time dependence and efficiency of the electron attachment process (described by Eq. (1)) we take the integrals under the respective ion peaks (in the frequency domain) and correct for the fact that the measured ICR signal of an ion is proportional to its charge state. The ion abundance ratios $R = A(C_{76}^{1-})/[A(C_{76}^{1-}) + A(C_{76}^{2-})]$ are plotted logarithmically in Fig. 3 as a function of electron irradiation time. Note that this data representation is chosen to account for the approximately 10–20% overall ion loss encountered over trapping times of 20 s (due mainly to field inhomogeneities and/or high charge densities upon electron irradiation). The data points shown in Fig. 3 for C_{76} are taken from three different days of experiments to indicate the reproducibility of the observed effect:

$$C_{76}^- + e^- \rightarrow C_{76}^{2-} \quad (1)$$

For both fullerenes, the data very nicely follow a straight line in this semilogarithmic graph indicative of a pseudo-first-order kinetics. This does not come as a surprise since a rough assessment of the electron versus ion densities in the trap under our experimental conditions indicates that ions see an excess number of electrons. The slope of the fitted line is therefore a measure of the attachment cross-section σ. This can be evaluated from $-\ln R = \sigma\phi$ where ϕ refers to the electron flux. Given our experimental parameters we

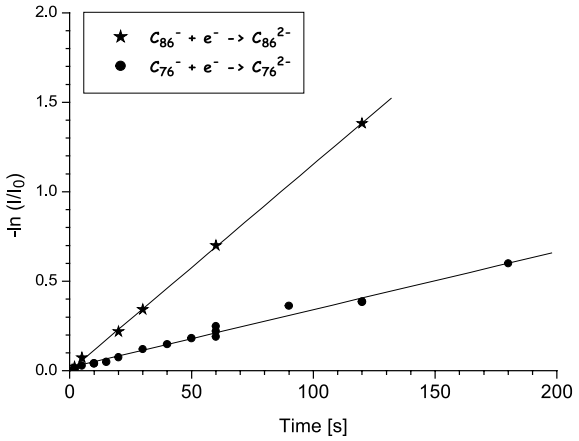

Fig. 3. Logarithmic plot of relative monoanion to total ion abundances ($-\ln(I/I_o) = -\ln\{A(C_{76}^{1-})/[A(C_{76}^{1-}) + A(C_{76}^{2-})]\}$) as a function of time for the two fullerenes C_{76} and C_{86}. The fitted straight lines indicate pseudo-first-order kinetics. Their slope is a measure of relative electron attachment cross-sections.

obtain as a coarse estimate for the cross-section of electron attachment to C_{76}^- on the order of 100 Å^2.

Note that it was possible to take the charging reaction almost to completion, i.e., to obtain abundance ratios $A(C_{76}^{2-})/[A(C_{76}^{1-}) + A(C_{76}^{2-})]$ of 0.85 for electron irradiation times of up to 5 min. Fig. 3 also displays a data set for electron attachment to the bigger fullerene congener C_{86}^-, taken under virtually identical trapping and electron beam conditions. Here the relative electron attachment cross-section is bigger by a factor of 3. Beyond a slight increase in geometric cross-section, this is very likely attributable to variations in the energy dependence of effective electron attachment efficiencies (also taking into account the rates of potential metastable decay processes). These will be the subject of future work.

Given that C_{76}^{2-} and C_{86}^{2-} generated directly by electrospray at internal excitation levels near room temperature were known to be stable under UHV, it was of interest to probe whether these same dianions formed by electron attachment might undergo measurable metastable relaxation. We therefore studied the stability of the C_{76}^{2-} formed upon electron attachment in a MS–MS sequence as already described. After turning the e-gun off all but the C_{76}^{2-} ions were ejected from the trap and stored for another variable time period. Only very slow electron autodetachment according to Eq. (2) was observed. The corresponding rate constant of 10^{-4} s^{-1} is on the order of the average collision rate with background gas molecules and therefore represents an upper bound:

$$C_{76}^{2-} \rightarrow C_{76}^- + e^- \quad (2)$$

Note also, that this rate constant is an average value for those ions which survived the first 50 ms—corresponding to the time required for excitation/detection in an FT-ICR experiment.

In order to understand the efficiency of the attachment process and the unexpected stability of the dianion given the comparatively high electron kinetic energies used (at least nominally) it is informative at this point to look at the interaction potential of an electron with a negative ion. Treating the electron as a point charge and the fullerene anion as a charged and polarizable sphere the potential energy [15] is given as

$$E = e^2\left(\frac{1}{R} - \frac{\alpha}{2R^4}\right) \quad (3)$$

where R denotes the distance between the center of the fullerene anion and the second electron, α is the polarizability of the fullerene and e is the elemental charge. A simple expression for R_{max}, the distance at which the Coulomb barrier reaches a maximum, and E_{max} the amplitude of the Coulomb barrier is then easily obtained to $R_{max} = (2\alpha)^{1/3}$ and $E_{max} = 3e^2/(4R_{max})$. The latter expression can also be written as $E_{max} = 10.8/(2\alpha)^{1/3}$ eV Å, when the polarizability α is given in Å^3. For the polarizability of the fullerenes we extrapolate from the experimentally determined value for C_{60} of 76.5 Å^3 [16] by approximating the fullerene cage as a conducting shell where the polarizability scales with $n^{3/2}$ with n being the number of carbon atoms [17].

Usage of the polarizability value for the neutral rather than charged fullerene seems to be justified since recent LDA-DFT calculations suggest only small differences between polarizability of neutral and anionic fullerene C_{84} [6].

Fig. 4 displays the potential energy curves given by Eq. (3) for different fullerene sizes. Fig. 4 shows that the barrier height is a smooth function of fullerene size as is the distance R_{max}. Equating this distance with a hard sphere electron capture radius and neglecting centrifugal barrier effects, i.e., assuming that electrons with an energy $E > E_{max}$ undergo attachment with a cross-section of πR_{max}^2 one obtains cross-sections on the order of 100 Å^2 in

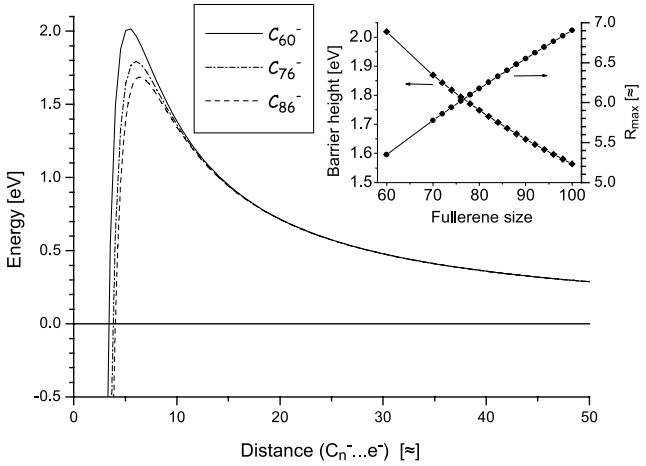

Fig. 4. Classical estimates of Coulomb barriers (see Eq. (3) in the text) for various fullerenes. The inset highlights the maximum of the respective barriers as well as the radius of the potential maximum as a function of fullerene size.

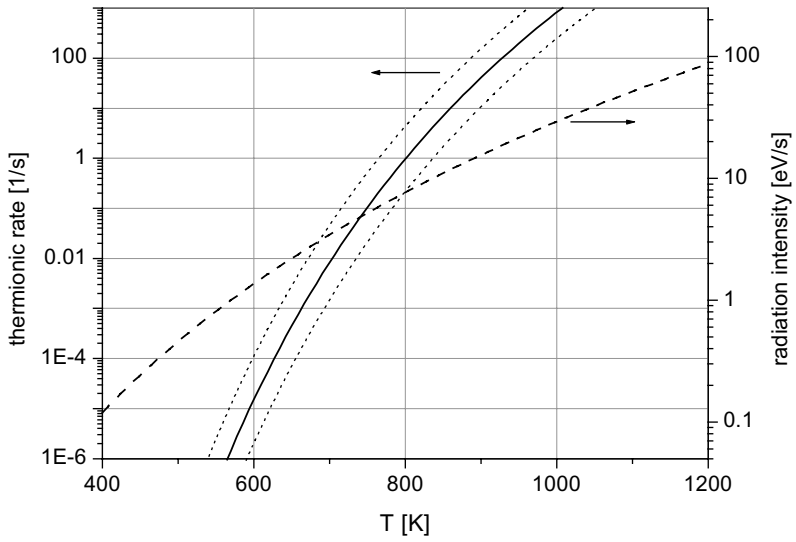

Fig. 5. Thermionic rates for electron emission (solid line) from hot C_{76}^{2-} based on Eq. (4) using a barrier of $E_0 = 2.1$ eV. Dotted lines (for 2.0 and 2.2 eV barrier height) indicate that predicted rates are quite insensitive to the electron detachment barrier. The observed lower limit to the liftetime of C_{76}^{2-} ($k < 10^{-4}\,s^{-1}$) corresponds to a temperature of 615 ± 30 K. Photon radiation intensity (dashed) for hot C_{76}^{2-} based on data from [23] is given for comparison.

(likely fortuitous) agreement with our experimental finding. Note that the recent lower limit for the electron attachment cross-sections of C_{84}^{-} is consistent with our results [6].

The stability of C_{76}^{2-} can be used to estimate an upper limit for the temperature of the dianion. Describing electron emission from a fullerene dianion as a statistical process, the rate constant $k(T)$ can be expressed as [18]:

$$k(T) = \left(\frac{2k_B T}{h}\right)\left(\frac{2m_e R_{max}^2 k_B T}{\hbar^2}\right)\left(\frac{g_f}{g_i}\right)\exp\left(\frac{-E_b}{k_B T}\right) \quad (4)$$

where k_B denotes the Boltzmann constant, E_b is the energy barrier for electron emission which equals $E_{max} + EA_2$ and m_e is the electron mass. The ratio of the electronic degeneracies g_f/g_i of final and initial states (here singly and doubly charged ions) is expected to be 2 since C_{76} (D_2 isomer) has a non-degenerate LUMO [19]. Eq. (4) has been derived assuming that the vibrational partition functions are equal for final and initial state (singly versus doubly charged anion, respectively). Experimental data on second electron affinities (EA_2) of fullerenes are scarce with the noteworthy exception of a recent photoelectron spectroscopic study of C_{84}^{2-} yielding $EA_{2,adiab} = 0.41 \pm 0.05$ eV [20] in good agreement with recent DFT calculations predicting 0.44 eV [6]. For the smaller C_{76} we therefore extrapolate a value of 0.3 eV which gives a total barrier for electron emission of 2.1 eV. Fig. 5 shows a plot of the resulting electron emission rate constants $k(T)$ for C_{76}^{2-} as function of temperature. Our experimental finding of $10^{-4}\,s^{-1}$ sets an upper limit for the temperature of the dianion of $T = 615 \pm 30$ K.

This temperature can in turn be used to work back to the maximum internal energy which can be stored in the fullerene dianion in order for it to be stable on the experimental time scale.

The internal energy is essentially given as the internal energy of the singly charged fullerene plus the kinetic energy of the attached electron, if we neglect radiative dissipation of energy. Based on the microcanonical definition of temperature:

$$\frac{1}{k_B T} = \frac{d\ln \rho(E)}{dE} \quad (5)$$

one uses the vibrational density of states $\rho(E)$ to convert internal energies into a temperature.

The density of states was deduced from the vibrational frequencies of C_{76} [21] applying the Haarhoff approximation [22]. The frequencies for all 222 vibrational modes originate from DFT calculations employing a BLYP functional and were scaled by a factor of 1.01 (for the IR active modes) to match the experimental FT-IR spectrum.

This allows us to plot a thermionic emission rate for C_{76}^{2-} as a function of internal energy as shown in Fig. 6 using the same parameters as for Eq. (4) (Fig. 5).

The observed lower limit to the liftetime of the dianions implies a maximum internal energy of about 4 eV. Subtracting the internal energy of singly charged C_{76} at room temperature of about 0.77 eV, the kinetic energy of the electrons that were attached to generate such dianions must lie in the range between 2.1 eV (the barrier height) and about 3.2 eV. Electrons with significantly higher energy would lead to a heating of the fullerene and much faster (thermal) autodetachment rates than observed in the experiment.

Finally, one might ask whether the assumption of negligible radiative cooling is justified. In other words: is it conceivable that a dianion heated by more than 3.2 eV radiates fast enough to compete with thermionic electron detachment? In order to answer this question we estimate the radiation intensity of a hot fullerene ion based on the recent experimental

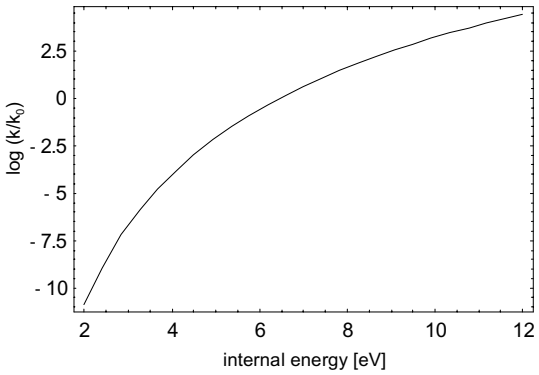

Fig. 6. Thermionic rates (see Fig. 5) mapped onto an energy scale. The plot allows determination of the maximum electron beam energy such that the singly charged C_{76}^- can attach without rapid autodetachment (see text).

results of Andersen et al. [23]. They found cooling rates for hot fullerene anions consistent with total radiation intensities that scale with T^6. Applying their findings to C_{76}^-, a radiation intensity as plotted in Fig. 5 is obtained. We note that these cooling rates can be considered an upper limit since they were obtained at temperatures around 1500 K where IR absorption was neglected and radiation from electronic relaxation come into play.

From Fig. 5 we note, that a C_{76}^{2-} created by attaching a 10 eV electron and thereby heated to about 1000 K will autodetach within 1 ms, but will radiate away only about 30 meV on this time scale. Only for temperatures near the limit inferred here does radiative cooling become competitive with thermal autodetachment. Generally speaking, a hot fullerene dianion will autodetach its second excess electron before it can substantially dissipate energy by photon emission.

4. Conclusion

Direct electron attachment of low-energy electrons to fullerene anions C_{76}^- and C_{86}^- trapped in a commercial FT-ICR mass spectrometer has been achieved under UHV/room temperature conditions. Dianions may be generated without collisional moderation of the electrons and/or cooling of the ions. For irradiation times of greater than 5 min, >85% of trapped monoanions can be converted to dianions. For C_{76}^{2-} generated in this fashion, the lifetime with respect to autodetachment was found to be greater than 10^4 s. Classical estimates for the Coulomb barrier to be surmounted by the attached electron indicate that the "electronically stable" fullerene dianions studied have average (microcanonical) temperatures of less than 615 ± 30 K, when probed following electron attachment (neglecting IR radiative relaxation or vibration mediated tunneling emission). Expressed in terms of internal energies our analysis shows that electrons with kinetic energies of about 2–3 eV are most likely to attach to the singly charged anions to form dianions which are stable on the experimental time scale.

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