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# Excitation of $C_{60}^+$ by electrons in a Fourier transform ion cyclotron resonance ion trap: an experimental determination of the radiative cooling rate through its competition with $C_2$ evaporation

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**Abstract**

$C_{60}^+$ ions are produced in an ion trap by crossing a collimated effusive beam of $C_{60}$ and an electron beam of energy lower than the $C_{58}^+$ fragment appearance energy. Being trapped, the $C_{60}^+$ ions can be further excited by another electron impact, inducing the well-known $C_2$ evaporation. By varying the electron pulse length while counterbalancing it with the intensity in order to maintain a constant total number of electrons in a pulse, the mean time between two successive electron impacts can be modified. The influence of this time on the amount of fragmentation is direct experimental evidence of the competition between radiative cooling and dissociation, invoked to explain the abnormally high internal energies needed to observe fragmentation even at long times. For ions with internal energies in the range 15.4–22.4 eV, a mean radiative rate constant of $3.3 \times 10^2\ s^{-1}$ has been determined. (Int J Mass Spectrom 189 (1999) 93–102) © 1999 Elsevier Science B.V.

*Keywords:* Fullerene ions; Fourier transform ion cyclotron resonance (FTICR); Radiative cooling; Electron impact induced fragmentation

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## 1. Introduction

Ionization and dissociation of the $C_{60}$ fullerene molecule has been the subject of a large number of experimental and theoretical investigations [1–9]. One of the most striking features is the very large energy shift observed for the dissociative ionization:

$$C_{60} + e^- \rightarrow C_{58}^+ + C_2 + 2e^- \tag{1}$$

The appearance energy of $C_{60}^+$ (7.6 eV) is well established and the binding energy of ($C_{58}^+$–$C_2$) has been recently calculated at 10.2 eV [10]. However, the first ionic fragmentation threshold following electron impact under single collision conditions is observed at an electron energy close to 45 eV [6,11].

As a consequence of this large energy shift, the energetics of the first fragmentation step:

$$C_{60}^+ \rightarrow C_{58}^+ + C_2 \tag{2}$$

is still controversial (see for example Fig. 1 in [12]).

The fragmentation activation energies are determined by fitting experimental and calculated quantities like kinetic energy release distributions (KERD), breakdown curves (BDC), appearance energies (AE), or time resolved metastable fraction (MF). To calculate these quantities one has to introduce a theoretical

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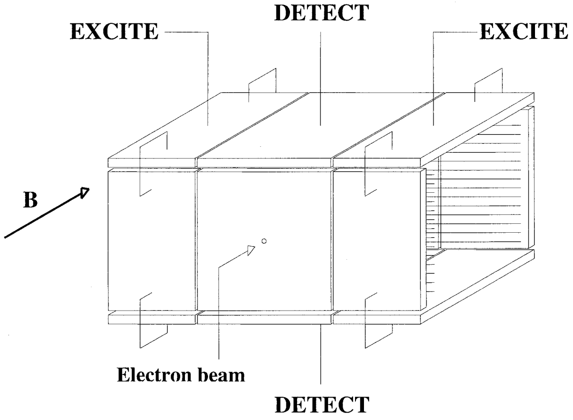

Fig. 1. View of the open-ended trap cell.

model of the unimolecular fragmentation; the fragmentation energies derived from fitting the experimental and theoretical curves depend, of course, on the model.

As an example, by comparing measured and calculated breakdown curves Foltin et al. [2] found 7.4 eV using the finite heat bath (FHB) model of Klots [13] and 7.2 or 6.8 eV with the Rice–Ramsperger–Kassel–Marcus (RRKM) theory depending on whether the transition state $C_{60}^{+*}$ is supposed to be loose or tight. Calculation of $C_{58}^{+}$–$C_2$ binding energy by fitting experimental BDC with BDC calculated with the RRKM theory [5] gave $\Delta E(C_{58}^{+}–C_2) = 7.06$ eV. The calculated binding energy was shown to increase as the transition state becomes looser. A very loose transition state leading to a binding energy of 9.2 eV was considered unrealistic and the upper limit for the binding energy was set at 7.6 eV.

The basic assumption of all these treatments was that the ions are losing their energy by sequential evaporation of $C_2$ fragments and that radiative cooling is negligible in the time range of conventional mass spectrometry experiments (a few microseconds). The importance of radiative cooling has been pointed out by Hansen and Campbell [14]. Using a time of flight (TOF) mass spectrometer, they showed that the metastable fragmentation probabilities for flight times up to 20 $\mu$s are smaller than predicted by the evaporative ensemble theory. This has been interpreted as an indication of the existence of a competitive radiative cooling.

Laskin and Lifshitz [7] extended this type of study up to 100 $\mu$s using a combination of quadrupole ion trap and TOF mass spectrometer. They showed that the experimental time-resolved metastable decay of $C_{58}^{+}$ can be modeled only by taking into account the radiative cooling. Their model included radiative rate constants derived from the radiative energy loss rates calculated by Chupka and Klots for neutral $C_{60}$ [15] and dissociation rates calculated via RRKM/QET (quasi-equilibrium theory). The best fit between experimental and calculated metastable decay probability of $C_{58}^{+}$ was obtained with dissociative activation parameters $\Delta E(C_{60}^{+}) = 8.3$ eV and $\Delta E(C_{58}^{+}) = 8.1$ eV.

This study has been extended recently [9] to a set of ions from $C_{58}^{+}$ to $C_{52}^{+}$ using a more elaborate kinetic scheme and the same method as before to calculate the dissociative and radiative rate constants. The best fit between experimental and calculated time resolved MF's for all four ions, and also for the peak positions of the breakdown curves, was obtained for $\Delta E(C_{60}^{+}) = 9.5$ eV. This gives for the neutral: $\Delta E(C_{60}) = 10.04$ eV—in excellent agreement with recent ab initio calculations.

Another interesting result is that the dissociation rate becomes larger than the cooling rate at an energy close to the appearance energy of fragmentation (see Fig. 3 in [9]).

These results clearly indicate that radiative decay plays an important role and that using the radiative rate calculated for neutral $C_{60}$ for the ions is an acceptable approximation. To our knowledge no calculation for the $C_{60}^{+}$ ions has been published to date, but in the energy domain where $C_{60}^{+}$ can dissociate, electronic emission is predicted to largely dominate over vibrational cooling and, because $C_{60}^{+}$ absorbs at longer wavelengths than $C_{60}$, its emission rate is expected to be larger [15].

Emission of radiation from ions is very difficult to observe, especially when the lifetimes are longer than $10^{-6}$ s (emission rate smaller than $10^{6}$ s$^{-1}$); therefore, an indirect method to determine the cooling rate of $C_{60}^{+}$ has to be worked out.

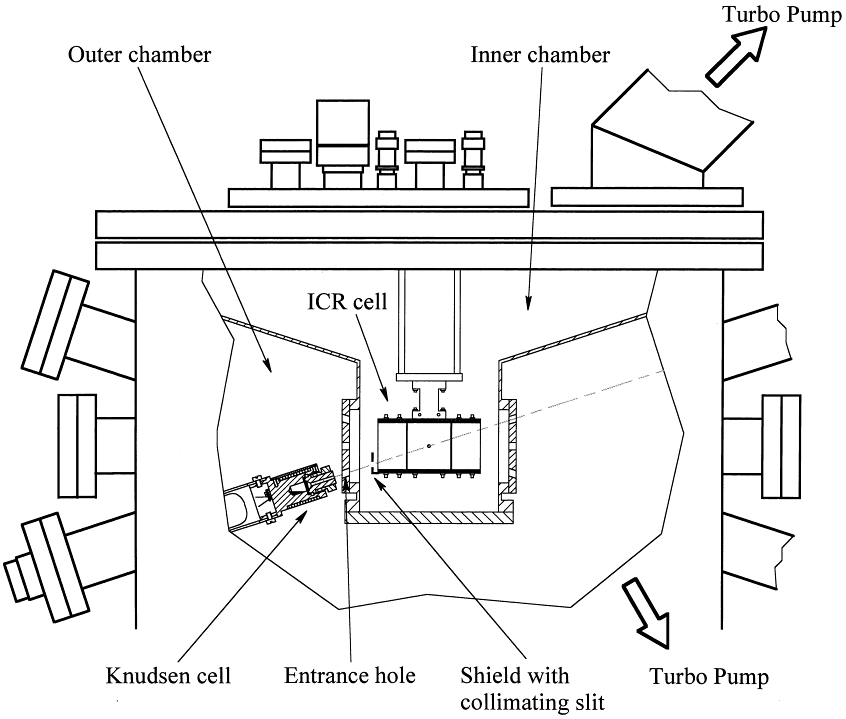

Fig. 2. General view of the experiment.

The monitor ion technique has been successfully used to follow slow decays of excited levels in small (diatomic and triatomic) ions [16,17]. For large ions, mainly aromatic hydrocarbons, the infrared radiative cooling has been investigated by different groups (see, for example, the 1992 review paper by Dunbar [18]). Most of the experimental techniques were based on the dissociation of an ion by sequential absorption of two photons:

$$A^+ \xrightarrow{h\nu_1} A^{+*} \xrightarrow{h\nu_2} A^{+**} \rightarrow \text{fragment} \tag{3}$$

The first photon excites $A^+$ below its dissociation limit. The absorption of the second photon by $A^{+*}$ is in competition with its radiative relaxation and the internal energy of $A^{+**}$, i.e. its capability to dissociate, depends on this competition.

The extent of photodissociation can be calculated via the kinetics of this competition and compared to the experimental fragmentation in order to deduce the radiative relaxation rate of $A^{+*}$.

More recently Boissel et al. [19] used the multiphoton fragmentation of anthracene ions as a tool to determine their radiative cooling rate. Comparison of the experimental results with a numerical simulation allowed the determination of the absorption lines

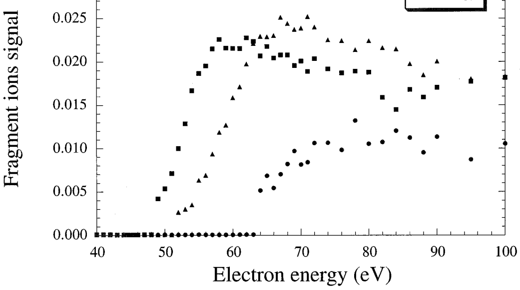

Fig. 3. Appearance potential curves for $C_{58}^+$, $C_{56}^+$, $C_{54}^+$ fragment ions obtained at low electron beam intensity.

oscillator strength and showed that the contribution of electronic emission is dominant in the energy range where the dissociation rate becomes comparable to the cooling rate.

In the present article we propose a similar method using two electron dissociative ionization of $C_{60}$ at electron energies where the single electron process does not occur.

## 2. Experimental

The present work has been performed with a Fourier transform ion cyclotron resonance (FTICR) spectrometer built "in house," using an IonSpec console for detection. The basis of this new machine is an open-ended trap cell (see Fig. 1), designed to allow easy access for molecular and laser beams (pulsed or not), while being accommodated in a classical electromagnet. Only the details pertinent to the present work are given here.

In a conventional electromagnet, access to the cell has to be perpendicular to the magnetic field. In order to obtain direct access to the center of the cell the two excitation plates are suppressed and each of them is replaced by a set of four electrodes electrically connected together. The resulting two lateral sections act as the end plates of a normal cubic cell, and have been used in this work to apply the ion excitation signal, thus avoiding time sharing of the same pair of electrodes for excitation and detection, as reported in [20]. Because of the relatively low value of the magnetic field (0.85 Tesla), trajectory calculations for $C_{60}^{+}$ ions performed using SIMION [21], showed the necessity of a large enough cell (35 × 35 mm cross section) and the need to screen the trapping plates with grounded wires, following Wang and Marshall [22].

The cell is enclosed in a vacuum chamber pumped by a 180 $\mathrm{ls}^{-1}$ turbomolecular pump. This chamber is located inside a larger chamber, pumped by a 450 $\mathrm{ls}^{-1}$ turbomolecular pump. Six channels of 6 mm diameter and length allow differential pumping while ensuring entrance and exit of either molecular or laser beams. These beams are crossing the electron beam in the center of the cell.

For the present work, the outer chamber is equipped with a Knudsen cell, as shown in Fig. 2. The oven containing the $C_{60}$ powder is heated resistively in order to obtain a suitable density of neutral $C_{60}$ crossing the electron beam. Its temperature, measured with a platinum resistor, is maintained around 663 K. The effusive beam coming out of the exit channel of the Knudsen cell is collimated twice, first by the entrance hole in the cell chamber, then by a slit parallel to the magnetic field (and to the electron beam), to prevent soot deposition on the cell electrodes.

Because of the relatively low temperature of the cell chamber wall, most of the $C_{60}$ neutrals condense outside this enclosure around the entrance hole, and inside around the opposite exit hole after crossing the cell. Observation of the deposits around the two holes and the possibility to work for days without cleaning the cell strongly suggest that rebound of molecules on these surfaces is negligible and that consequently the background pressure remains low in the cell, outside the neutral beam. This low background pressure is confirmed by the fact that the coherent motion of the ions during FTICR detection is not perturbed by the continuous neutral beam.

The density of molecules in the effusive beam can be evaluated from the vapor pressure in the Knudsen cell and the geometry of the experimental setup. The vapor pressure in the Knudsen cell (in the temperature range 723–1096 K) is given by Matsumoto et al. [23]

$$\log(P_{\mathrm{atm}}) = 4.91 - \frac{8209.7}{T} \tag{4}$$

Extrapolation to $T = 663$ K gives $P = 3.37 \times 10^{-10}$ atm.

The flux of molecules coming out of the cell, obtained following Pauly [24], is $I = 6.4 \times 10^{12}$ molecules steradian$^{-1}$ s$^{-1}$. Finally, the density of molecules at the center of the cell, located 7 cm away from the oven exit hole, is $[C_{60}] = 9.6 \times 10^{6}$ mol cm$^{-3}$.

With this density of neutrals in the cell the collision frequency of an ion with $C_{60}$ can be evaluated using the Langevin rate constant $k_L$. For a polarisability $\alpha = 80$ A$^3$ [25], $k_L = 1.1 \times 10^9$ cm$^3$ s$^{-1}$ and the collision frequency $\nu_c = k_L \cdot [\mathrm{M}] = 0.0106$ s$^{-1}$ corresponds to a mean time between collisions $\tau_c = 94$ s. Therefore, ion molecule collisions during an experimental sequence (maximum 100 ms) can be neglected.

Ions are formed in the central part of the cell at the crossing of the electron beam and the neutral beam of $C_{60}$. Whereas the neutral molecules exit from the cell, the ions remain trapped in pressure conditions where collisional relaxation can be neglected. Depending on the neutral precursor velocity the ions can either stay inside the electron beam or only cross it every 55 $\mu$s (period of the cyclotron motion in the 0.85 Tesla magnetic field). Commercial $C_{60}$ with a purity of 99.9% from ThermUSA (New York, NY), stored under vacuum, has been used without further purification.

## 3. Appearance energies of fragment ions

Although our apparatus is not particularly suitable for appearance energies measurements (because of the limited dynamic range inherent to the FTICR technique), it is clear from Fig. 3 that when the electron beam intensity is low enough to ensure single electron collision conditions, threshold for fragmentation of $C_{60}^+$ in our machine is compatible with recently published values (43.7 eV by electron impact [11], 45 eV in a photoionization study [26]). This is in agreement with the conclusion of Lifshitz et al. [6] that the long delays achievable in an FTICR trap do not significantly decrease the energy shift of the appearance energies, showing that there is a very large intrinsic kinetic shift.

In contrast, as shown in Fig. 4, fragmentation can be observed in our ion trap at energies well below 45 eV if the density of electrons in the beam is increased. Both spectra in Fig. 4 have been obtained at 30 eV with the same number of ionizing electrons in a pulse. When these electrons are spread along a 30 ms pulse no fragmentation is observed [Fig. 4(a)], but concentrating them in a 2 ms pulse leads to a small fragmentation [Fig. 4(b)].

Because the energy of one electron is lower than the appearance energy for fragmentation, a multielectron process has to be assumed. It has already been shown that multielectron collision reactions can, at high enough electron beam current, lead to fragmentation for electron energies well below the true appearance energy of these fragments [27]. In the present experiment at least two electrons of 30 eV are needed. Fragmentation occurs when the number of electrons per time unit, i.e. the density of electrons in the beam, is large enough so that an excited $C_{60}^+$ ion formed by a first electron still has enough internal energy when interacting with a second electron to be fragmented. When, on the contrary, the electron beam intensity is low, the “primary” excited ions have enough time to radiatively lose their internal energy before encountering a second electron.

This is direct experimental evidence of the competition between radiative cooling and fragmentation invoked to explain the anomalous fragmentation energy thresholds observed for these ions [6] and it can also be the basis of an experimental determination of the radiative cooling rate.

## 4. Radiative cooling measurements

The number of electrons involved in the dissociative ionization of a $C_{60}$ molecule can be determined simply by varying the electron beam intensity $I_e$ at a constant pulse length. Because the $C_{60}^+$ ions fragment sequentially into $C_{58}^+$, $C_{56}^+$, . . . [3] the dependence on $I_e$ of the ratio of the total number of fragment ions over the total number of ions ($R = \Sigma[F^+]/\Sigma[I^+]$) gives the number of electrons involved in the dissociation of $C_{60}^+$. As shown in Fig. 5, $R$ is proportional to the electron beam intensity, indicating that one electron is needed to dissociate $C_{60}^+$ into $C_{58}^+$.

Therefore, the dissociative ionization of $C_{60}$ is a two electron process and the dissociation of $C_{60}^+$ induced by the second electron can be used to probe the internal energy of the $C_{60}^+$ produced by the first electron.

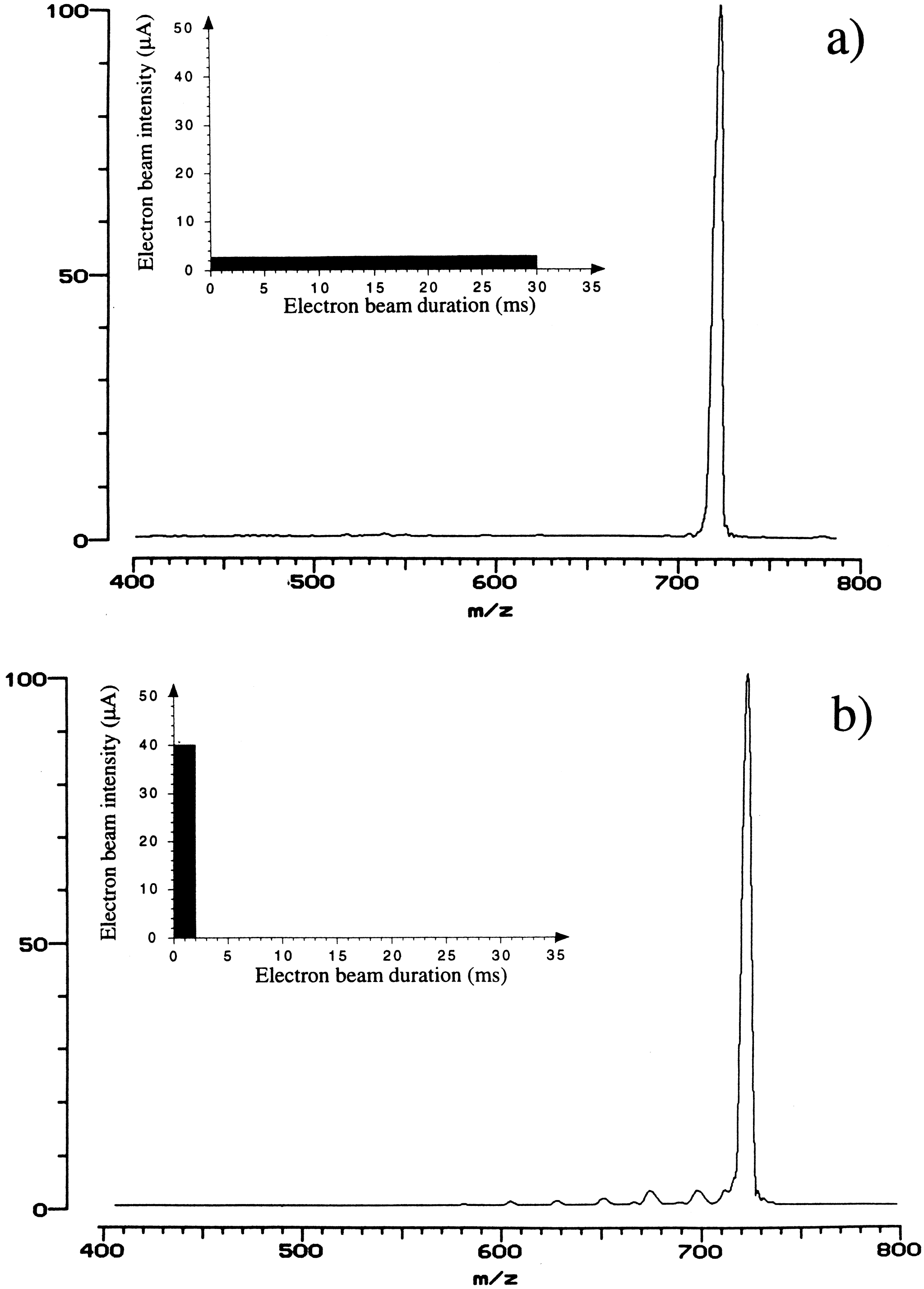

Fig. 4. Spectra obtained with the same number of 29 eV electrons (the areas corresponding to the product of the beam intensity by duration are the same). $C_{60}^{+}$ fragmentation is occurring when the electron beam pulse is very short (b) and does not when the electron beam pulse is lengthened (a). The small peak appearing between $C_{60}^{+}$ and $C_{58}^{+}$ is due to a combination of the cyclotron and magnetron motion.

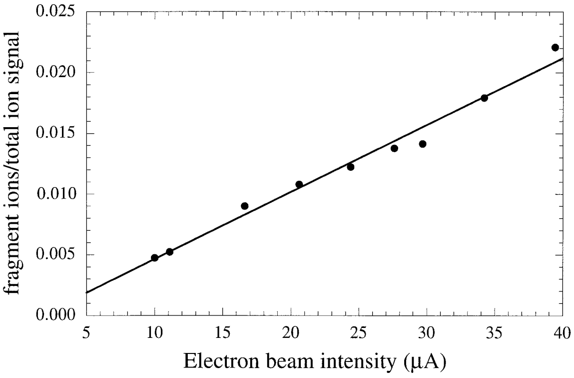

Fig. 5. Variation of the fragmentation ratio as a function of electron beam intensity.

Data presented in Fig. 6 have been obtained in the same way as the two spectra of Fig. 4. The number of electrons in a pulse is kept constant so that $Q_e = I_e t_e$ is constant; therefore the electron current ($I_e$) has to be decreased when the electron pulse duration ($t_e$) is increased. When the electron density in the beam decreases the mean time between ionization and further excitation of the ion by a second electron increases, and as a consequence the mean relaxation time experienced by the primary excited $C_{60}^+$ ions increases.

As expected, the relative amount of fragmentation decreases when the electron density decreases and from the curve presented in Fig. 6, it is possible to gain insight on the radiative cooling rate by fitting the experimental data with a kinetic model.

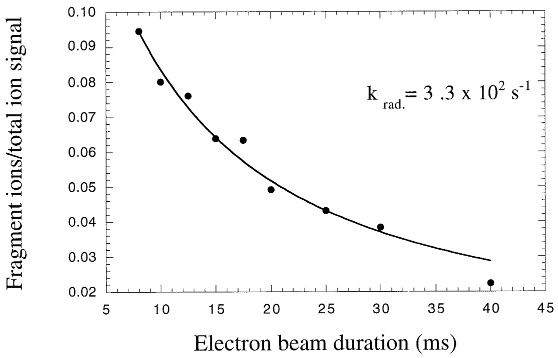

Fig. 6. Fragmentation ratio as a function of the electron beam pulse duration. The electron beam intensity is varied simultaneously in order to keep the number of electrons constant. Fitting the analytical function resulting from the kinetic model to the experimental data gives $k_{\text{rad}} = 3 \times 10^2\ \text{s}^{-1}$.

The question arises of whether the observed decay is entirely due to radiative cooling of the ions or partly due to their progressive diffusion out of reach of the well-collimated electron beam.

Among the three phenomena that can cause expansion of the ion cloud in an ICR cell, collisions with neutrals can be ruled out because the mean time between collisions is of the order of 90 s, and increase of the magnetron motion amplitude because of the detection circuit impedance [28] occurs on a time scale much longer than the maximum electron beam pulse length (40 ms). Finally, self repulsion of the ions due to space charge could have been a problem but the presence of a continuous electron beam during the production and excitation of the ions counter balances the space charge of positive ions, preventing their diffusion. Therefore, the contribution of diffusion to the observed decay must be negligible.

## 5. Kinetic model

The following kinetic model has been used to describe the time evolution of the fragmentation ratio as a function of the electron pulse length, in experiments where the electron beam duration and intensity are varied simultaneously so as to keep constant the number of electrons in the pulse.

The radiative cooling rate depends of course on the initial and final energy of the ions, but we make the simplifying assumption of a single radiative rate over the whole energy domain of the ions. This is naturally not true if the internal energy domain is large and the radiative lifetime obtained from the experimental data will be an average over the internal energy domain considered.

The rate of formation of $C_{60}^+$ ions following the impact of the first electron is

$$\frac{d}{dt}[C_{60}^+] = \sigma_{\text{ion}} I_e [C_{60}] \tag{5}$$

where $\sigma_{\text{ion}}$ is the ionization cross section and $I_e$ is the electron beam intensity.

The number of neutral $C_{60}$ molecules in the ionization volume can be considered constant because they are renewed by the effusive beam flux much faster than they disappear by ionization. The total number of $C_{60}^+$ ions produced during the electron beam pulse, which is equal to the total number of ions appearing on the mass spectrum, is

$$\sum \lfloor I^+ \rfloor = \lfloor C_{60}^+ \rfloor = \sigma_{\text{ion}} I_e t_e [C_{60}] \tag{6}$$

where $t_e$ is the electron beam duration.

The number of $C_{60}^+$ ions that can be dissociated by a second electron—denoted hereafter as $C_{60}^{+*}$—follows the differential equation:

$$\frac{d}{dt}[C_{60}^{+*}] = \alpha \sigma_{\text{ion}} I_e [C_{60}] - (k_{\text{rad}} + \sigma_{\text{frag}} I_e)[C_{60}^{+*}] \tag{7}$$

where $\alpha$ is the fraction of $C_{60}^+$ initially produced in the internal energy domain where they can be dissociated by a second electron, $\sigma_{\text{frag}}$ is the fragmentation cross section of $C_{60}^{+*}$ by a second electron, and $k_{\text{rad}}$ is their radiative rate constant down to energies too low to allow dissociation by a second electron.

If the depletion of $C_{60}^{+*}$ ions by the two electron dissociation process is small compared to the depletion by radiative cooling, then $\sigma_{\text{frag}} I_e \ll k_{\text{rad}}$. This should be a reasonable approximation because the fraction of $C_{60}^+$ ions that are dissociated in the two-electron process is very small. Then, Eq. (7) simplifies to

$$\frac{d}{dt}[C_{60}^{+*}] = \alpha \sigma_{\text{ion}} I_e [C_{60}] - k_{\text{rad}} [C_{60}^{+*}] \tag{8}$$

Integrating this equation gives the total number of $C_{60}^{+*}$ ions as a function of time $t$ (with $0 \leq t \leq t_e$)

$$[C_{60}^{+*}] = \frac{\alpha \sigma_{\text{ion}} I_e [C_{60}]}{k_{\text{rad}}} [1 - \exp(-k_{\text{rad}} t)] \tag{9}$$

The production rate of fragment ions by the second electron is

$$\frac{d}{dt}\left(\sum [F^+]\right) = \frac{\alpha \sigma_{\text{ion}} \sigma_{\text{frag}} I_e^2 [C_{60}]}{k_{\text{rad}}} \cdot [1 - \exp(-k_{\text{rad}} t)] \tag{10}$$

and integration of this equation gives the number of fragment ions:

$$\sum [F^+] = \frac{\alpha \sigma_{\text{ion}} \sigma_{\text{frag}} I_e^2 [C_{60}]}{k_{\text{rad}}} \cdot \left[ t_e + \frac{\exp(-k_{\text{rad}} t_e) - 1}{k_{\text{rad}}} \right] \tag{11}$$

Finally, the fragmentation ratio is

$$R = \frac{\sum [F^+]}{\sum [I^+]} = \frac{\alpha I_e \sigma_{\text{frag}}}{k_{\text{rad}} t_e} \times \left[ t_e + \frac{\exp(-k_{\text{rad}} t_e) - 1}{k_{\text{rad}}} \right] \tag{12}$$

The fact that at constant pulse length $t_e$, $R$ is found to be proportional to $I_e$ (see Fig. 5) is an experimental confirmation of the validity of the simplifying approximation: $\sigma_{\text{frag}} I_e \ll k_{\text{rad}}$.

In experiments where the total number of electrons $Q_e = I_e t_e$ is kept constant, the fragmentation ratio can be expressed as a function of $t_e$:

$$R(t_e) = \alpha Q_e \sigma_{\text{frag}} \left[ \frac{1}{k_{\text{rad}} t_e} + \frac{\exp(-k_{\text{rad}} t_e) - 1}{k_{\text{rad}}^2 t_e^2} \right] \tag{13}$$

The fitting of this simple analytical function to the experimental fragmentation ratio allows one to determine the normalization factor $A = \alpha Q_e \sigma_{\text{frag}}$ and the radiative rate constant $k_{\text{rad}}$.

## 6. Results and discussion

Experimental results have been obtained for electron beam energies of 22, 26, 30, and 35 eV. At lower energies, where more than two electrons are needed, the signal to noise ratio was very low. Fitting the analytical function described above to the experimental curve gives a radiative rate constant of the $C_{60}^{+*}$ averaged over the internal energy domain probed by the experiment. Fig. 6 shows the experimental points and the fitting curve obtained for 30 eV electrons and $Q_e = 10^{-7}$ C.

As shown in Fig. 7, the maximum internal energy

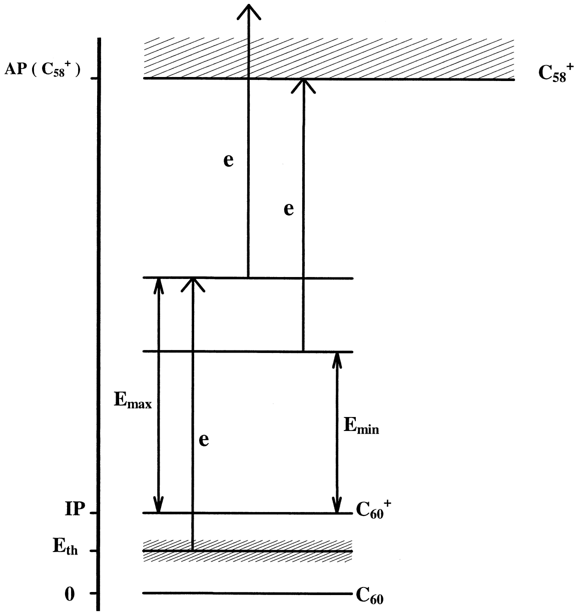

Fig. 7. Energetic scheme of the two electron dissociation process.

of $C_{60}^{+*}$ is the sum of the thermal energy of the $C_{60}$ neutrals $E_{th}(C_{60})$, plus the electron kinetic energy $E_{el}$, minus the ionization energy $IE(C_{60})$:

$$E_{max} = E_{th}(C_{60}) + E_{el} - IE(C_{60}) \tag{14}$$

The minimum internal energy required to allow dissociation by a second electron is the fragmentation threshold energy minus the electron kinetic energy. In single electron dissociative ionization conditions (low $I_e$) formation of $C_{58}^+$ fragment ions is observed at electron kinetic energies above $AE(C_{58}^+) = 45$ eV. The corresponding $C_{60}^+$ internal energy is $AE(C_{58}^+) + E_{th}(C_{60}) - IE(C_{60})$ and only $C_{60}^{+*}$ ions having an internal energy higher than

$$E_{min} = AE(C_{58}^+) + E_{th}(C_{60}) - IE(C_{60}) - E_{el} \tag{15}$$

can be dissociated by the second electron.

The thermal energy distribution of $C_{60}$ at 663 K, calculated using the Whitten and Rabinovich formula for the density of state [29] and the vibrational frequencies of Stanton and Newton [30], scaled by a factor of 0.88 [31] is peaked at its mean value $E_{th}(C_{60}) = 4.0$ eV as shown in Fig. 8.

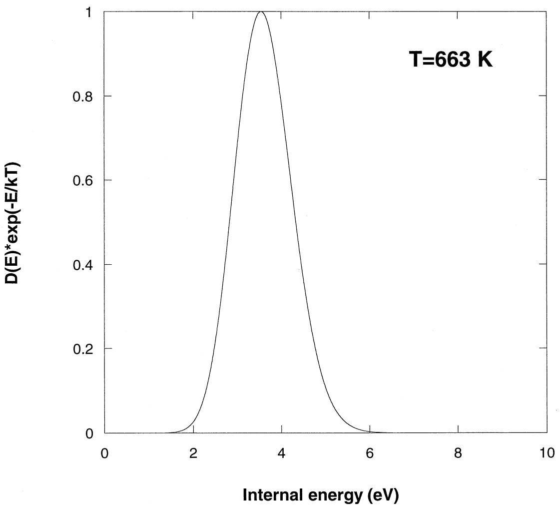

Fig. 8. Thermal energy distribution of $C_{60}$ at 663 K.

Therefore, the internal energy domain probed with 26 eV electrons extends from $E_{min} = 15.4$ to $E_{max} = 22.4$ eV ($\Delta E = 7$ eV). When the electron energy is increased, the width of the internal energy domain increases ($\Delta E = 15$ eV for 30 eV electrons), but the median value stays around 19 eV.

To get a better definition of the $C_{60}^+$ internal energy one should decrease the electron energy, but below 26 eV the signal to noise ratio becomes too low.

The total number of electrons in a pulse ($Q_e = I_e t_e$) cannot be varied very much either; the maximum is limited by the trapping capacity of the cell and the minimum by the detection sensitivity. Experiments have been performed at different values of $Q_e$ and the radiative rates obtained are the same within the experimental uncertainties for $Q_e$ values differing by a factor of 2.

Thus, in the internal energy domain (19 ± 3.5) eV the mean radiative rate (obtained with 26 eV electrons) is $k_{rad} = (3.3 \pm 1) \times 10^2\ s^{-1}$. When the electron energy is increased the radiative rate is averaged over a broader internal energy distribution but no significant variation of $k_{rad}$ is observed.

This result can be compared to the radiative rates modeled recently by Laskin et al. At an internal energy of 30 eV the value extracted from Fig. 3 in [9] is $6 \times 10^3\ s^{-1}$. In the energy range of our experiments the radiative rate is expected to be significantly lower, in agreement with our experimental result.

Calculations of the cooling rate of $C_{60}^{+*}$ as a function of its internal energy, similar to those performed for anthracene [19], are in progress.

## 7. Conclusion

An overall radiative rate constant of $C_{60}^{+*}$ excited ions has been determined using two electron dissociative ionization of $C_{60}$ in a pulsed ICR ion trap. Varying the electron beam intensity $I_e$ and the pulse length $t_e$ so as to keep constant the product $Q_e = I_e t_e$, resulted in a variation of the experimental fragmentation ratio $R = \Sigma[F^+]/\Sigma[I^+]$. This ratio has been modeled using a simplified kinetic scheme of the competition between radiative cooling and electron impact dissociation of $C_{60}^{+*}$. Because the internal energy distribution is not known, the radiative cooling rate is supposed to be the same for all the $C_{60}^{+*}$. Therefore, fitting of the experimental curves to our model provides an overall radiative rate constant integrated over a rather large internal energy domain: (19 ± 3.5) eV. Our experimental value $[(3.3 \pm 1) \times 10^2\ \mathrm{s}^{-1}]$ is compatible with the more recent calculation of Laskin et al. [9]: $6 \times 10^3\ \mathrm{s}^{-1}$ at an internal energy of 30 eV.

Experiments are planed to get a better definition of the $C_{60}^{+*}$ internal energy and try to determine the internal energy dependence of the radiative rate.

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## References

[1] P.P. Radi, M.T. Hsu, J. Brodbelt-Lustig, M. Rincon, M.T. Bowers, J. Chem. Phys. 92 (1990) 4817.

[2] M. Foltin, M. Lezius, P. Scheier, T.D. Mark, J. Chem. Phys. 98 (1993) 9624.

[3] C. Lifshitz, Mass Spectrom. Rev. 12 (1993) 261.

[4] E. Kolodney, B. Tsipinyuk, A. Budrevich, J. Chem. Phys. 102 (1995) 9263.

[5] R. Wörgötter, B. Dünser, P. Scheier, T.D. Märk, M. Föltin, C.E. Klots, J. Laskin, C. Lifshitz, J. Chem. Phys. 104 (1996) 1225.

[6] J. Laskin, J.M. Behm, K.R. Lykke, C. Lifshitz, Chem. Phys. Lett. 252 (1996) 277.

[7] J. Laskin, C. Lifshitz, Chem. Phys. Lett. 277 (1997) 564.

[8] J. Laskin, C. Weickhardt, C. Lifshitz, Int. J. Mass Spectrom. Ion Processes 161 (1997) L7.

[9] J. Laskin, B. Hadas, T.D. Märk, C. Lifshitz, Int. J. Mass Spectrom. Ion Processes 177 (1998) L9.

[10] A.D. Boese, G.E. Scuseria, Chem. Phys. Lett. 294 (1998) 233.

[11] R. Wörgötter, B. Dünser, P. Scheier, T.D. Märk, J. Chem. Phys. 101 (1994) 8674.

[12] S. Matt, O. Echt, R. Wörgötter, P. Scheier, C.E. Klots, T.D. Märk, Int. J. Mass Spectrom. Ion Processes 167/168 (1997) 753.

[13] C.E. Klots, Z. Phys. D 21 (1991) 335.

[14] K. Hansen, E.E.B. Campbell, J. Chem. Phys. 104 (1996) 5012.

[15] W.A. Chupka, C.E. Klots, Int. J. Mass Spectrom. Ion Processes 167/168 (1997) 595.

[16] G. Mauclaire, J. Lemaire, M. Heninger, S. Fenistein, D.C. Parent, R. Marx, Int. J. Mass Spectrom. Ion Processes 149/150 (1995) 487.

[17] J. Lemaire, F. Mouchère, M. Heninger, S. Fenistein, R. Marx, G. Mauclaire, Int. J. Mass Spectrom. Ion Processes 172 (1998) 129.

[18] R.C. Dunbar, Mass Spectrom. Rev. 11 (1992) 309.

[19] P. Boissel, P. de Parseval, P. Marty, G. Lefèvre, J. Chem. Phys. 106 (1997) 4973.

[20] G. Mauclaire, J. Lemaire, M. Heninger, Rapid Commun. Mass Spectrom. 1 (1996) 591.

[21] D.A. Dahl, SIMION 3D version 6.0, in Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, GA, May 1995, p. 717.

[22] M. Wang, A.G. Marshall, Anal. Chem. 61 (1989) 1288.

[23] K. Matsumoto, E. Schönherr, M. Wojnowski, Journal Cryst. Growth 135 (1994) 154.

[24] H. Pauly, in Atomic and Molecular Beam Methods, G. Scoles (Ed.), Oxford University Press, Oxford, 1988, p. 83.

[25] F. Willaime, L.M. Falicov, J. Chem. Phys. 98 (1993) 6369.

[26] A. Schmalz, H. Hess, C. Lenski, H. Kanzow, A. Ding, J. Laskin, Y. Ling, C. Lifshitz, S. Matt, H. Drexel, T.D. Märk, in Proceedings of the Symposium on Atomic and Surface Physics and Related Topics, Going/Kitzbühel, Austria, 1998, p. 4–56.

[27] S. Matt, D. Muig, A. Ding, C. Lifshitz, P. Scheier, T.D. Märk, J. Phys. Chem. 100 (1996) 8692.

[28] S.C. Beu, J.D.A. Laude, Int. J. Mass Spectrom. Ion Processes 108 (1991) 255.

[29] G.Z. Whitten, B.S. Rabinovitch, J. Chem. Phys. 38 (1963) 2466.

[30] R.E. Stanton, M.D. Newton, J. Phys. Chem. 92 (1988) 2141.

[31] R.K. Yoo, B. Ruscic, J. Berkowitz, J. Chem. Phys. 96 (1992) 911.