Low energy electron impact on C_{76} and C_{84}: excitation, metastable anion formation, and lifetime

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Abstract

Low energy (0–15 eV) electron impact on gas phase fullerenes C_{76} and C_{84} has been investigated in an e^- beam experiment (electron energy resolution 0.050 eV). Electron energy loss spectroscopy results are presented for C_{76} at intermediate and low incident energy and are compared with the UV–visible absorption spectrum. The lowest triplet state $^3B_3$ has not been detected; however, two bands at 1.70 and 2.58 eV, clearly of triplet character are observed. The band at 1.70 eV is assigned to $^3B_1$ and $^3B_2$ states. Ion yields of C_{76}^- and C_{84}^- versus e^- energy are presented in the range 0–10 eV. The capture threshold is shown to appear at zero energy (within 0.030 eV), indicating the occurrence of an s-wave capture. The nature of other features due to resonances appearing on the spectrum is discussed. Lifetimes τ of C_{76}^- and C_{84}^- are observed to be strongly dependent of the electron energy. They are reported in the range 10–15 eV. For the capture of a 14 eV electron we have measured $\tau(C_{76}^-) = 100$ μs and $\tau(C_{84}^-) = 180$ μs. Comparison between the lifetimes of C_{60}^-, C_{70}^-, C_{76}^-, and C_{84}^- shows that τ behaves exponentially with the number of carbon atoms involved in the fullerene anion. (Int J Mass Spectrom 205 (2001) 17–25) © 2001 Elsevier Science B.V.

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1. Introduction

It is a particular pleasure to give a contribution to the special issue devoted to Alex Stamatovic. Indeed, one of us (R.A.) started to work in the field of electron–molecule scattering and negative ions production processes, after a short stay of two months in summer 1972, working at Yale in the George Schulz's group, on the very original trochoidal electron monochromator device that Alex had built with George

Schulz just a few years earlier [1]. Coming back to Orsay, he has adapted a similar trochoidal electron gun device on a magnetic mass spectrometer, and he always found it an exceptional tool, able to give an excellent balance between electron beam intensity and energy resolution. As the present works deals also with low energy electrons, we should emphasize how convenient was the trochoidal gun, almost free from intensity variations with energy, and very easy to work with at very low energy compared to the electrostatic analysers, which are far more difficult to handle correctly when the energy is decreased below 1 eV. As long as no angular information is needed, the trochoidal electron monochromator is certainly one of

the best device to obtain rather intense currents with good electron energy resolution.

In the field of low energy electron collisions with molecules, fullerenes C_{60} and C_{70} have been shown to behave differently from other polyatomic molecules. Indeed, the major process in the energy range 0–10 eV, i.e. the formation of very short lived negative ions states (resonances), decaying into resonant vibrational excitation of the neutral, or to dissociation via the dissociative attachment process, is not observed for fullerenes in the gas phase. Instead, very long lived metastable anions are detected, living ten orders of magnitude longer than usual resonances, produced with a huge cross section, in a surprisingly wide energy range from 0 to about 12 eV [2–6].

On the other hand, electron energy loss (EEL) spectroscopy at incident energy above 50 eV have revealed, in the isolated molecule, the existence of collective excitations ("plasmons") besides the usual one electron transitions [7–9]. Most of these results were obtained for the highly symmetric species $C_{60}(I_h)$ and $C_{70}(D_{5h})$, only a very few concern higher fullerenes. The present work extends low energy electron collision experiment to fullerenes of lower symmetry C_{76} (D_2) and C_{84} (D_2 and/or D_{2d}), to study both the incidence of size and symmetry on the properties observed for C_{60} and C_{70}.

2. Experimental

The data have been recorded using an electron spectrometer equipped with double hemispherical energy analysers in tandem, both in the electron gun and in the electron energy analysis. Optics and magnetic shielding have been carefully designed to allow a good behaviour of the electron gun down to zero energy, preserving an electron energy resolution of about 0.050 eV (FWHM). Mass analysis of the ions has been performed using a time of flight system based on a Mac Laren-Wiley geometry, the ions being collected onto microchannel plates. To avoid strong perturbations while collecting the negative ions, the incident electron beam is pulsed. The fullerene gas molecules are produced by heating solid samples

(Technocarbo, France) in a double stage tantalum oven, using a needle on top to have a better definition of the collision zone. After one or two days of outgassing at 500 K to remove the solvent, temperatures of 900–950 K were needed to get enough density of molecules to run the experiments.

3. Results and discussion

Fullerene C_{76} is built with 12 pentagons and 28 hexagons. According to the isolated pentagon stability rule [10] C_{76} can be predicted to be of D_2 or T_d symmetry [11]. However, due to its open shell structure, the T_d isomer is less stable [12]. The D_2 symmetry has been proved by nuclear magnetic resonance (NMR) studies showing 19 different sites for the carbon atoms [13]. It is also interesting to mention that C_{76} (D_2) is a chiral molecule. The two enantiomers have been separated [14,15].

The C_{84} molecule contains 32 hexagons to add to the usual 12 pentagons. The isolated pentagon rule leads to 24 possible geometries. Other stability rules have been proposed by Okada et al. [16] reducing the number of "most preferred isomers" to 7. In fact 2 of these 7 isomers are actually extracted, isolated and identified by NMR studies to be of D_{2d} and D_2 symmetry [17]. The D_2 isomer could possibly be more stable than the D_{2d} structure as it is twice more abundant in the soot [18].

3.1. Electronic excitation by EEL spectroscopy in C_{76}

Symmetry species in the D_2 group are A, B_1, B_2, and B_3. Selection rules for dipolar allowed transitions from the ground state ^1A state forbid only the transitions to the ^1A states, all transitions to the $^1B_{1,2,3}$ being allowed.

Quantum chemical calculations have been carried out by Orlandi et al. [12,19], at various degrees of computational complexity (QCFF in [12], and CNDO/S and INDO/S in [19]), to obtain the energy location of the electronic states up to 4 eV, as well as

the oscillator strengths of dipolar transitions from the ground state.

The various UV–visible absorption experiments [13,20–22] are all in good agreement, showing absorption starting very weakly around 900 nm, and increasing smoothly to about 240 nm. The most recent results of Bensasson et al. [22] show that the principal peaks occur at 1.73; 2.16; 3.05; and 3.76 eV, a very weak absorption being observed on the low energy side between 1.26 and 1.37 eV. Several other shoulders are also observed. By reference to Orlandi et al. [19] the very low absorption bands are attributed to $^1B_3$, $^1B_1$, and $^1B_2$ states, the lowest singlet state at 1.37 eV being $^1B_3$. The calculations give this state at 1.72 eV, i.e. 0.35 eV above the experimental value. However the methods used for the calculations have already yielded to systematic errors of that amount in previous calculations on C_{60} [23].

Several electron energy loss spectra recorded at different residual energies and at a small scattering angle are displayed on Fig. 1. Intermediate incident electron energy ($E_i \gg E_{exc}$) strongly favours the dipolar transitions to the singlet states, and our spectrum at $E_r = 76$ eV resembles the absorption spectrum (Fig. 2). About 5 peaks and/or shoulders appear around 1.74; 3.05; 3.8; 4.54; and 5.57 eV. The low energy peaks show a good agreement with the absorption spectrum of Ettl et al. [20], whereas a shift of about 0.4 eV is observed for the peak at 5.57 eV in the EEL spectrum compared to 5.12 eV in the absorption experiment. This discrepancy is attributed to the contribution in the EEL experiment of a collective excitation ("π plasmon") besides the one electron transition at 5.12 eV. Indeed, similar observations have been made in C_{60} and C_{70} [7,8,9,24]. At electron energy of several kiloelectron volts, the plasmon is dominant and a value of 6.1 eV has been reported in thin C_{76} films [25]. Plasmon excitations around 5.5–6 eV in several fullerenes are shown for comparison (Fig. 3).

When the residual energy is decreased, transitions to singlet states are less favoured in the EEL spectrum and the contribution of triplet states can appear. As observed in Fig. 1 the spectrum is progressively modified from $E_r = 76$ to $E_r = 6$ eV. At $E_r = 6$ eV
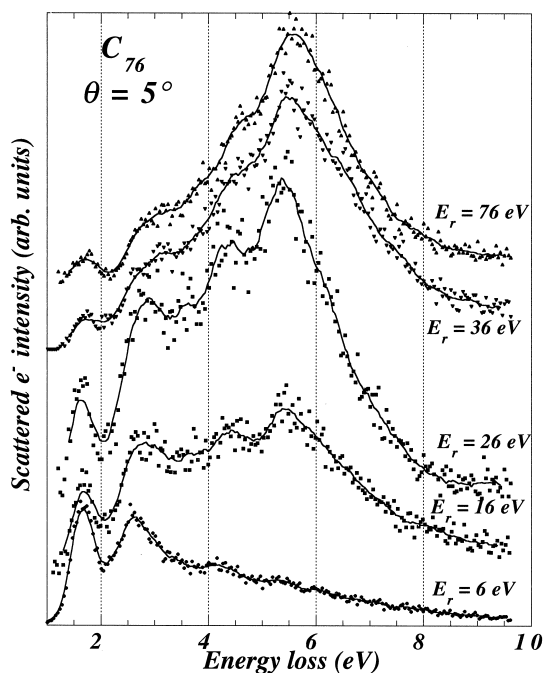

Fig. 1. Energy loss spectra recorded at a scattering angle θ of 5°, for residual energies ranging from $E_r = 76$ eV to $E_r = 6$ eV. At 76 eV the dipole allowed transitions are favoured, whereas at 6 eV transitions to triplet states can be observed.

two peaks are observed at 1.70 and 2.58 eV with shoulders at 4.17 and 5.38 eV. Besides a small energy shift of the peaks, the 5.57 eV peak has almost completely disappeared whereas the 1.70 and 2.58 eV
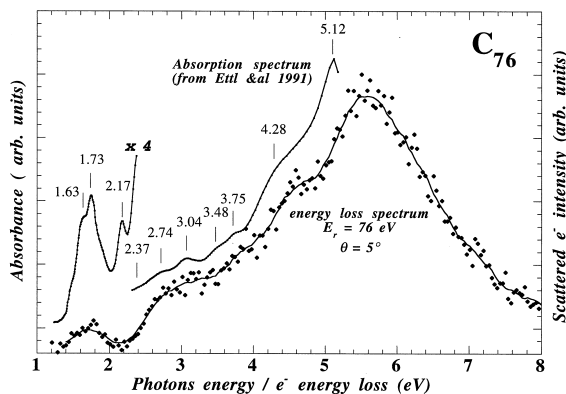

Fig. 2. Comparison between UV–visible absorption spectrum [20] and EEL spectrum at $E_r = 76$ eV and $\theta = 4°$. The transition at 5.57 eV in the EEL spectrum is likely due to a collective excitation (π plasmon) besides the one electron transition at 5.12 eV.
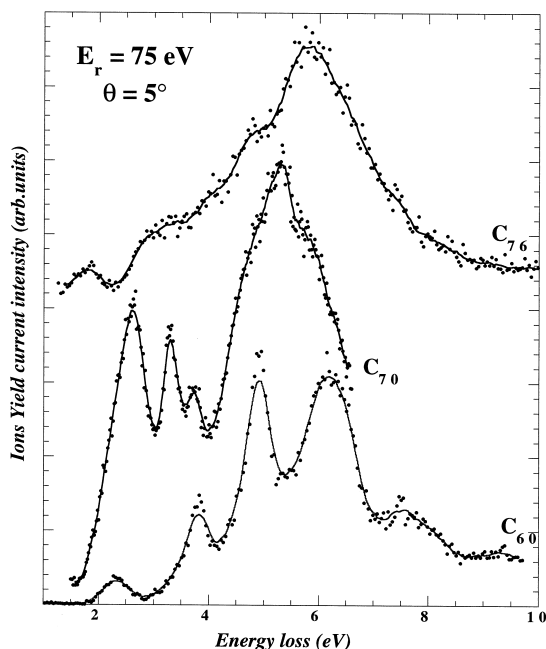
Fig. 3. Comparison between EEL spectra of C_{60}, C_{70}, and C_{76} at $E_r = 75$ eV and $\theta = 5°$. π plasmons occur, respectively, at 6.1, 5.3, and 5.57 eV.

peaks dominate the spectrum. The band peaking at 1.70 eV is attributed to triplet states, likely $^3B_2$ and $^3B_1$ states, corresponding to the $^1B_1$ and $^1B_2$ observed at 1.6 and 1.73 eV in the UV absorption spectrum. Our observation is in full agreement with Bensasson et al. [22] indicating that the triplet would lie very close to the related singlet state (about 0.1 eV, in contrast with C_{60} where a shift of 0.4 eV was observed [26]).

The lowest triplet state, $^3B_3$, is expected to be at about 1 eV or below [22]. We have not been able to find an evidence of this state as our measurements at lower residual energy and at larger observation angles showed a too poor signal to noise ratio to give a reliable information. Other experiments at low E_r and larger θ are necessary to detect this triplet state.

The band observed at 2.58 eV in the EEL spectrum could possibly be associated with the 7 $^3B_3$ state as the corresponding singlet has been located around 3 eV [19]. Excited states studies of the C_{84} molecule could not be performed due to the weakness of the

neutral C_{84} density in the effusive beam even up to 950 K. However due to the very large cross section for electron capture the C_{84}^- ions have been observed.

3.2. Metastable C_{76}^- and C_{84}^-

The early work of Lezius et al. [2] has shown that the C_{60} molecule is able to capture low energy electrons in a wide energy range (0–12 eV), with a huge cross section of the order of 10^{-14} cm^2, leading to metastable anions having very long lifetimes ($\tau > 1$ ms), even after the capture of an electron of several electron volts.

The question of whether or not C_{60} was able to capture 0 eV electrons (*s*-wave capture) was extensively debated for several years (see [6] for a detailed discussion and references therein). We have shown in an electron beam experiment that the s wave capture occurred despite symmetry arguments. Indeed, due to the T_{1u} symmetry of the ground negative ion state, a *p*-wave behaviour at threshold is expected and observed by some groups but not by others. In short, the discrepancy with other e^- beam experiments concerning the threshold energy was likely to be due to calibration problems. The disagreement with flowing afterglow (FALP) data [4] seemed more serious. However a temperature argument, not considered in [6] should be taken into account.

To understand both the agreement between our data and the Rydberg electron transfer (RET) data, and the discrepancy with FALP experiment, it should be emphasized that all these data are not taken in the same gas temperature conditions.

Both RET and e^- beam data are obtained at low pressure ($<10^{-6}$ Torr) in condition of unique collision. Therefore, the temperature of the C_{60} gas is certainly very close to the temperature of the oven, about 750 K. On the opposite, in the FALP set up, the C_{60} powder is vaporized in the carrier gas at a pressure of several torrs. This can give rise to multiple collisions relaxing somehow the hot C_{60} molecules, leading them to a rovibrational temperature substantially lower than in RET or e^- beam experiments.

Vasil'ev et al. [5] have demonstrated that the number of C_{60} molecules excited in the four first t_{1u}
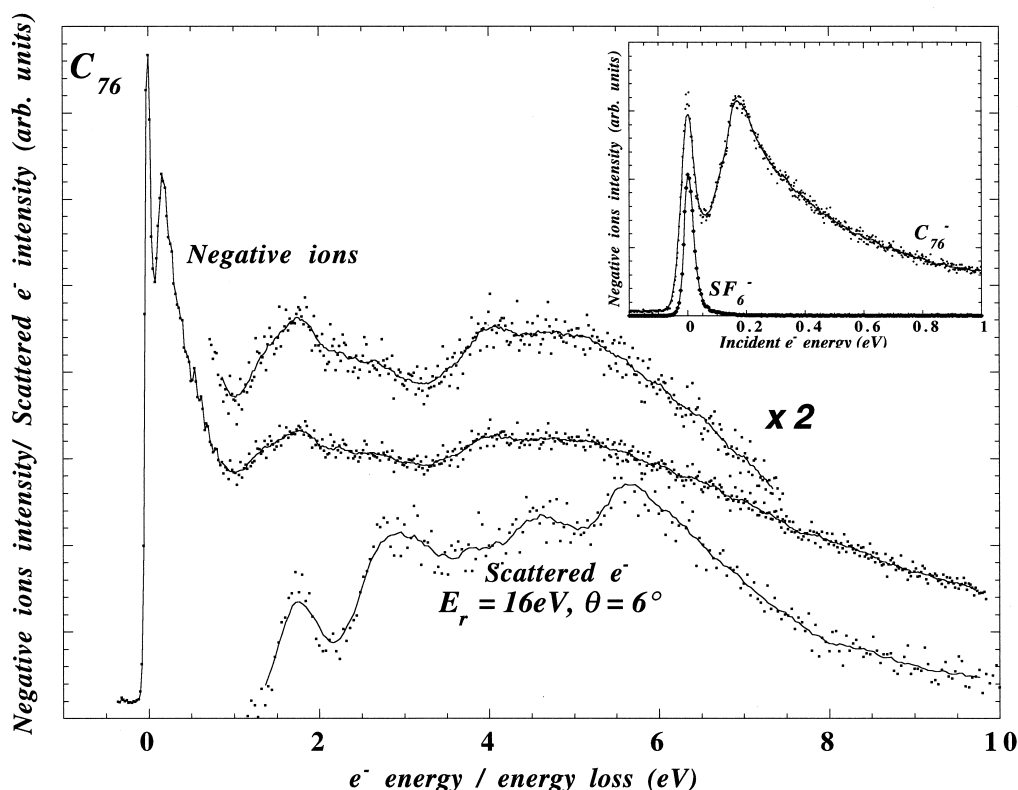
Fig. 4. Ion yield of C_{76}^- vs. incident electron energy and EEL spectrum of C_{76} at $E_r = 16$ eV and $\theta = 6°$ showing the electronic excited states. Detail of the ion yield close to zero presents also a comparison with SF_6^-.

vibrational states (for which a s wave capture is possible), increases very quickly with T, being 6 times stronger at 700 K compared to 300 K. In the FALP experiment the contribution of these t_{1u} states is likely to be smaller leading thus to very low electron capture rates.

Le Garrec et al. [27] in their CRESU ("Cinetique de Reaction en Ecoulement Supersonique Uniforme") experiment where both the electron and the gas temperatures are controlled, have shown in CF_3Br that the capture rate varies dramatically with the gas temperature, decreasing by 2 orders of magnitude between 300 and 100 K. They attributed this effect to the contribution of vibrationally excited CF_3Br molecules.

If such an effect is present in C_{60}, the capture at zero energy via the s wave process by hot C_{60} through the vibrational t_{1u} states can then be considerably

stronger than the attachment at lower temperature. To give an unambiguous experimental answer to the question of the s wave capture on C_{60}, capture rate coefficients data should performed at very low temperature, in conditions where the rovibrational temperature of the C_{60} gas is controlled. Comparison with C_{70}, where some s wave capture has been observed in the FALP experiments would certainly be interesting.

Our results concerning the metastable C_{76}^- and C_{84}^- ion yield versus electron energy are displayed on Figs. 4 and 5. The energy scale has been carefully calibrated using both SF_6^- at zero and the inelastically scattered electrons on N_2, using the peaks in the resonant vibrational excitation cross section of the $v = 1$ levels which have been established within 0.01 eV [28].

We have observed that some incorrect tunings of the e^- gun could lead to discrepancy of 0.100 eV or
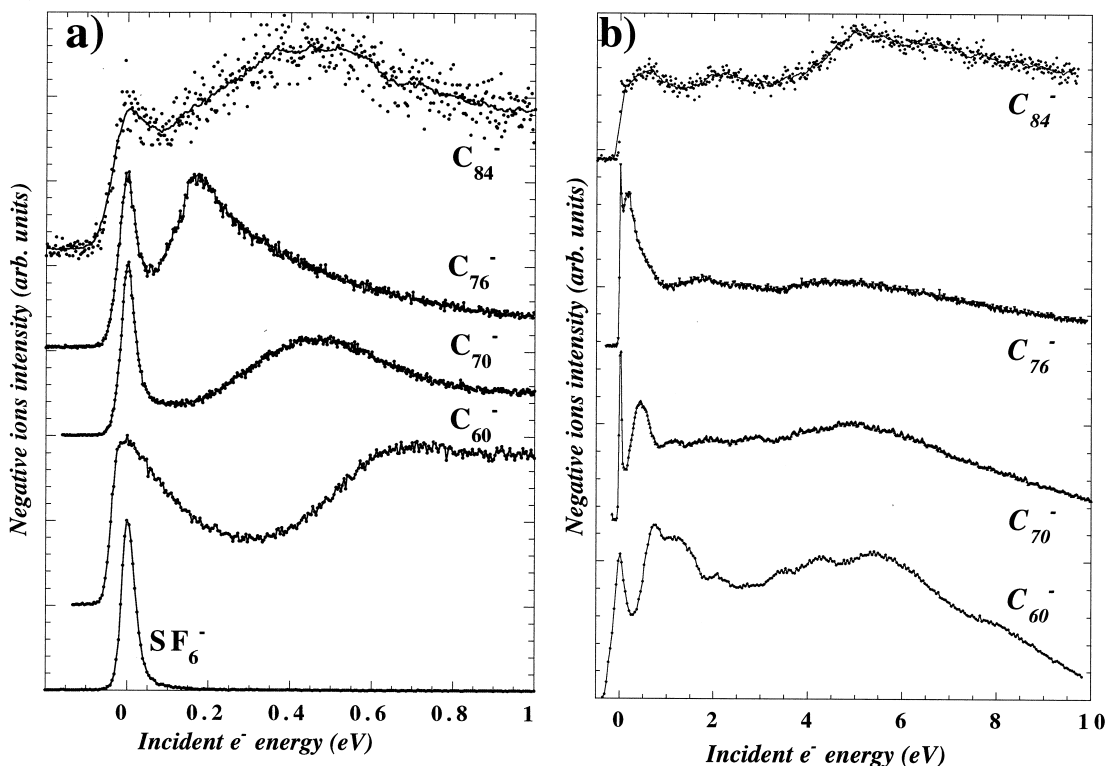
Fig. 5. (a) Details of the region below 1 eV. The sharp peak observed at zero for C_{70}^- and C_{76}^-, if it exists for C_{84}^- could have be missed as more intense currents (and poorer energy resolution) have been used to compensate for the weak density of the C_{84} molecules. (b) Ion yields vs. incident electron energy are presented from 0 to 10 eV for C_{84}^-, C_{76}^- and for C_{60}^- and C_{70}^- for comparison.

more between the two calibrations. In these cases the SF_6^- peak is troncated on the low energy side, and it appears strongly asymmetrical, showing that the very zero region is missed.

On Fig. 4 a strong thin peak appears clearly at 0 eV (within 0.030 eV), confirming the occurrence of the s-wave capture process in C_{76} in our experimental conditions. Another well defined band is located at 0.2 eV followed by four other structures more or less defined at 1.7; 2.6; 4 and 5.3 eV. An energy loss spectrum is also presented on Fig. 4 for comparison of the structures in the negative ion spectrum with the lcoation of the excited electronic states. The peak at 0 eV is interpreted as a nuclear Fesbach resonance, associated to the motion of the nuclei whereas the band at 0.2 eV, well below the first excited states is understood as the lowest shape resonance associated with the ground state.

The four structures in the negative ion spectrum are somewhat related to the four bands of the excited state spectrum. Note that neither the intensity nor the energy location of the structures in the two spectra are supposed to be identical. However, the existence of four bands in the negative ion spectrum, shifted by about 0.1–0.4 eV below the four bands observed in the excited states spectrum, favours the assignment of the bands in C_{76}^- spectrum to Feshbach resonances. These resonances, associated with excited states, would have electron affinities ranging from 0.1 to 0.4 eV, a value very common for Feshbach resonances.

Above 6 eV, the decrease in the ion yield is likely to be due both to a less efficient capture, and to a faster autodetachment of the metastable C_{76}^-. Fig. 5 shows the variation of the ion yield versus electron energy for C_{84}^- compared with other fullerenes. The threshold occurs also at zero but not with a sharp peak

behaviour. Several other bands are observed at 0.6; 2.2 and 5 eV. The absence of an excited state spectrum does not allow further attribution of these bands. However, by analogy with the other fullerenes, the bands at 2.2 and 5 eV are believed to be Feshbach resonances. Note that due to the very weak density of neutral C_{84} even at 950 K, we had to use more intense electron currents, to the prejudice of energy resolution. In these conditions we could have missed a sharp peak at zero if it exists.

3.3. Lifetimes of C_{76}^- and C_{84}^-

Very long lived metastable C_{76}^- and C_{84}^- anions have been observed at incident energies even higher than for C_{60}^- and C_{70}^- [6]. Variation of the extraction and acceleration voltages in our TOF mass analysis system allowed variation of the flight time of the negative ions in the range 30–220 μs. This time window appeared convenient to measure lifetimes τ up to about 700 μs. Extension of the time window to longer flight times needed too low extraction voltages leading to non reliable results.

Due to different trajectories and to possible variation of detection efficiency, discrimination effects were observed between the "low" and the "fast" ions. Correction of these effects has been done using several thermodynamically stable negative ions produced by dissociative attachment (O^-/N_2O, SO^-/SO_2, SF_5^-/SF_6, . . .). Like for C_{60}^- we have observed that C_{76}^- and C_{84}^- produced after capture of a 1 eV electron had the same behaviour as the calibrating gases. Considering the lifetime τ of these fullerenes anions produced at 1 eV to be about 2 orders of magnitude longer than τ at incident energy above 10 eV, the discrimination correction has been achieved using these anions at 1 eV for calibration. Measurements of τ are reported in the range 10–14 eV for C_{76}^-, and 11 to 15 eV for C_{84}^-. At lower capture energy τ was too long ($>$700 μs) to be measured. The corrected anion signal was found to vary exponentially with the flight time in the range of our measurements: I^- $(t, E) = I_0(E) \exp[-t/\tau(E)]$. τ is deduced from the semilog plot $I^-(t, E)$ represented on Fig. 6(a). The different values of the extrapolation at zero flight

time obtained at different energies reflect different capture efficiencies.

Similarly, in the reduced energy range were τ could be measured in our device, τ appeared to vary exponentially with the incident electron energy [Fig. 6(b)]. Extrapolation to zero energy (which clearly might not be meaningful), lead to lifetimes of the order of 10 ms like for C_{60}^- and C_{70}^-.

Comparison of the measured lifetimes of a series of fullerene anions produced at the same capture energy of 10 eV shows that τ varies approximately exponentially with the number of carbon atoms involved in the fullerene [Fig. 6(c)]. Extrapolation of the curve predicts that C_{120}^- in the gas phase would present a lifetime of about 20 ms, still after the capture of an electron of 10 eV.

4. Conclusion

Electron energy loss spectra at different residual energies have been reported in C_{76}. The EEL spectrum at intermediate energy is very similar to the absorption spectrum. However, the small shift of the band at 5.57 eV suggests the contribution of a collective excitation (π plasmon) besides the one electron transition observed at 5.12 eV in the absorption spectrum. At low residual energy, two bands of triplet character are observed at 1.70 and 2.58 eV. The band at 1.70 eV attributed to $^3B_1$ lies very close from the transition to the corresponding singlet state in agreement with [22]. Further work is needed with better signal to noise ratio at lower residual energy and at larger observation angle to observe the lowest triplet state expected around 1 eV.

The ion yields of C_{76}^- and C_{84}^- versus electron energy present a threshold at zero energy, indicating an s-wave capture like for C_{60} and C_{70}. The lowest shape resonance is observed at 0.2 eV for C_{76}. Several other structures in these spectra are attributed to Fesbach resonances.

The lifetimes τ of C_{76}^- and C_{84}^- appear to be longer than those of C_{60}^- and C_{70}^-. Comparison of τ for these four fullerenes indicates an exponential behaviour
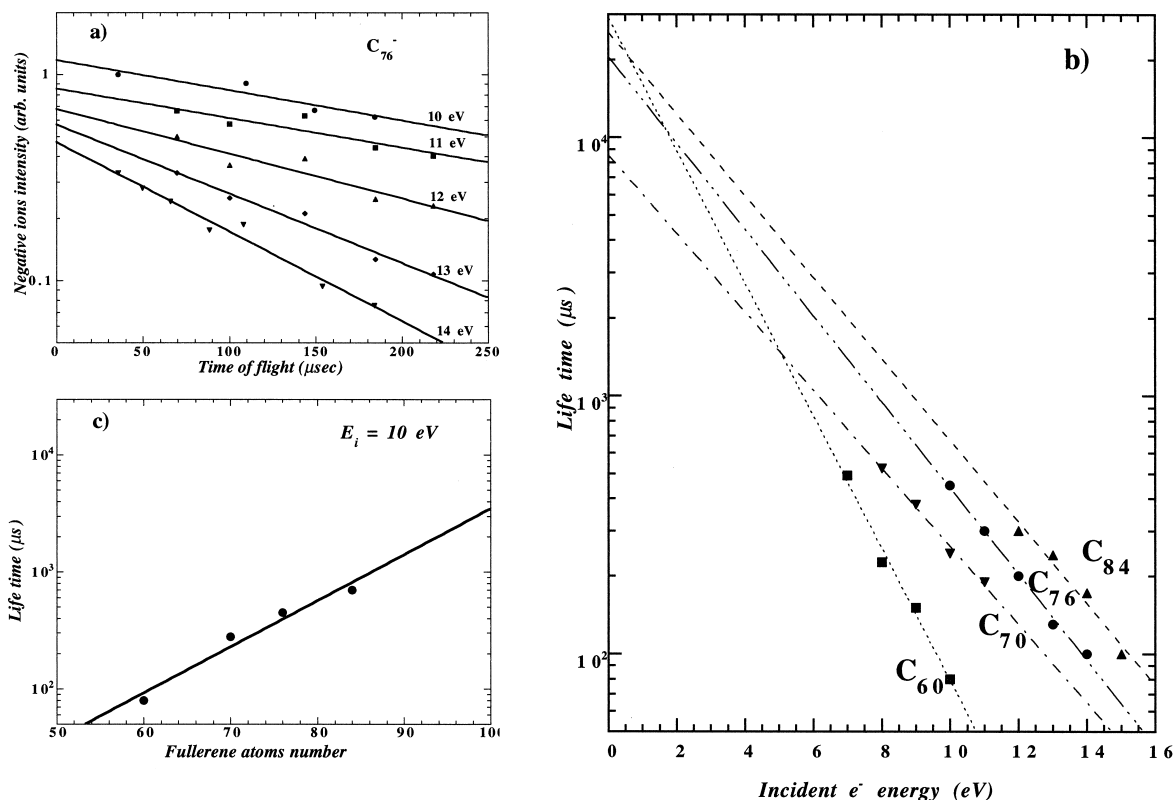
Fig. 6. (a) Semilog plot of C_{76}^- ion yield vs. flight time after electron capture at energies ranging from 10 to 14 eV. Lifetimes $\tau(E_i)$ are extracted from the slope of these graphs. (b) Semilog plot of the lifetimes $\tau(E_i)$ for C_{76}^- and C_{84}^-, C_{60}^- and C_{70}^- are also shown for comparison. (c) Semilog plot of the lifetimes $\tau(E_i)$ of C_{60}^-, C_{70}^-, C_{76}^-, and C_{84}^- after the capture of a 10 eV electron.

with respect to the number of carbon atoms of the fullerenes concerned.

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