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# Thermal stability of Li@C$_{60}$

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**Abstract.** The thermal stability of purified endohedral Li@C$_{60}$ has been studied. There are two endohedral compounds produced from Li$^+$ irradiated C$_{60}$ that have slightly different stabilities. The endohedral species decay at elevated temperatures on a time scale of a few hours when in solution and exposed to light and air. The dry, purified material has a higher thermal stability and can be sublimed in vacuum to produce thin films of pure endohedral fullerenes.

**PACS.** 81.05.Tp Fullerenes and related materials; diamond, graphite

## 1 Introduction

Low-energy lithium ion irradiation of fullerene monolayers has been shown to be an efficient method of producing endohedral fullerenes (known in IUPAC notation as incarfullerenes) [1,2]. One of the advantages of this technique is that it can be used to produce macroscopic amounts of purified endohedral metal@C$_{60}$. It appears to be difficult to extract metal-containing C$_{60}$ using the standard arc-discharge method even although these species can be detected in the mass spectra of the unpurified soot [3]. The possibility of a very low-yield production of M@C$_{60}$ (M = Y, Ba, La, Ce, Pr, Nd, Gd, Ca, Sr) has been reported recently [4], but there has not been sufficient amounts of material produced for the study of the properties of these species in any detail. There is also some doubt that the isomer of the carbon cage has the same symmetry as the empty, icosahedral C$_{60}$ [5]. Our method overcomes this problem by inserting the metal ions directly into the stable fullerene rather than building the carbon cage around the metal.

We have shown that it is possible to dissolve our films in CS$_2$ to obtain solutions containing only the initial fullerene and its endohedral counterpart(s). The endohedral material can then be purified using standard HPLC techniques [6]. Once the endohedral material has been extracted from the films with CS$_2$, it can then be dissolved in a range of different solvents such as toluene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and pyridine.

The solubility is considerably less than that of C$_{60}$. It is possible to isolate two distinct endohedral fractions [6]. The UV-Vis-NIR spectroscopy of these fractions show that they are chemically distinct species [6,7]. The evidence that we have accumulated points strongly towards one of these fractions being a dimer, (Li@C$_{60}$)$_2$.

The stability of endohedral fullerenes is obviously an important point if they are to be useful materials. In this context, they are useful either from the materials science point of view as, e.g., building blocks for new nanotechnologies or as nonlinear optical materials [8], or from the fundamental point of view as model systems for investigating the dynamical properties of captured atoms and complex molecular systems. The stability of Li@C$_{60}$ is the subject of the present paper. There have been few studies of the stability of other purified endohedral fullerenes. Shimshi *et al.* studied the thermal decomposition of Ne@C$_{60}$ [9], and Ishibashi *et al.* studied the decomposition of La@C$_{82}$ in solution under UV irradiation [10]. Fullerenes and some fullerene derivatives have been shown to undergo a range of degradation reactions when stored in air [11].

## 2 Production and purification

The method we use for producing Li@C$_{60}$ has been described before [2,7]. Fullerenes are deposited from a small quartz oven, heated to 500 °C, onto a rotating metal cylinder. For practical reasons, we normally cover the cylinder with aluminum cooking foil to ease the extraction of the endohedral material. The rotation speed of the cylinder is chosen to be such that one monolayer of fullerenes is deposited on each rotation. The cylinder is irradiated at right angles to the fullerene beam by a beam of Li$^+$ ions. The

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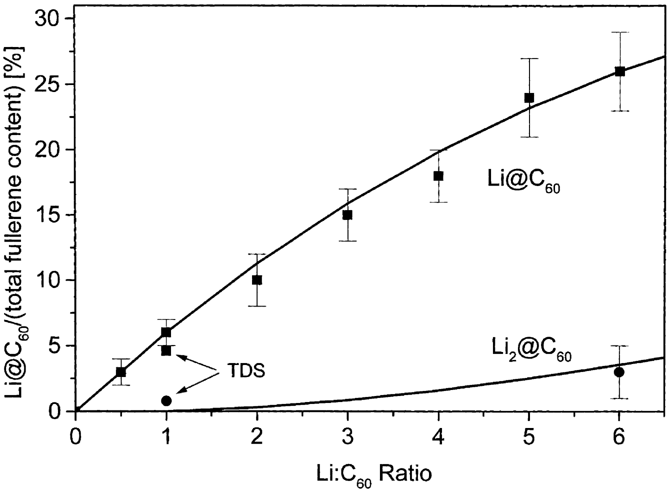

**Fig. 1.** Dependence of endohedral production on the ratio of Li ions to $C_{60}$. The intensity was determined by laser desorption mass spectrometry and is a lower limit. The full line is calculated with the assumption that every collision between Li and $C_{60}$ leads to capture with a 6% probability. TDS indicates that these values were determined by thermal desorption spectroscopy.

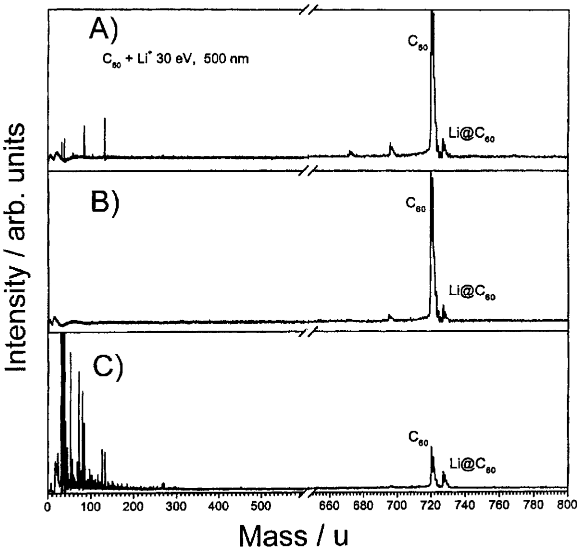

**Fig. 2.** Laser desorption mass spectra. (a) unpurified film on aluminium foil; (b) soluble $CS_2$ extract; (c) insoluble material.

optimum ion beam energy for production of endohedral Li@$C_{60}$ has been found to be 30 eV [2]. It is important that this energy be well defined. A high-energy tail will cause destruction of the fullerenes in the film. The ratio of $Li^+$ ions deposited per fullerene is also critical for the efficient purification of the endohedral material. The absolute amount of endohedral fullerenes produced in the film increases as the ratio of metal ions to fullerenes increases. This is illustrated in Fig. 1 for $Li^+$ irradiation at the optimum energy of 30 eV. The data was obtained from laser desorption mass spectra (LDMS) of the unpurified films. LDMS cannot give the absolute yield of endohedral fullerenes in the film, since the probability for ionization and fragmentation is likely to be different from that of $C_{60}$. Comparison with the amounts of material separated by HPLC methods shows that LDMS, under the conditions used to obtain the data shown in Fig. 1, underestimates the proportion of endohedral fullerenes compared to empty fullerenes in the films by approximately 50%. This depends on the time window of the mass spectrometer and is due predominantly to fragmentation at the high temperatures reached during desorption [12]. However, the relative behavior, which is what is important in Fig. 1, is not affected by this, because the same laser desorption conditions are used for all the films investigated. The full lines drawn through the points are calculated, with the assumption that there is a constant 6% probability that a collision will lead to the formation of an endohedral fullerene (the fragmentation that occurs in the mass spectrometer means that this is a lower limit). The fact that this probability remains constant as the amount of Li increases is strongly supportive of a direct capture mechanism involving penetration of the intact carbon cage by the $Li^+$ ion to form an endohedral species. In other words, the capture probability (or the probability of making the species with mass 727 u) depends only on the frequency of collisions between $Li^+$ and $C_{60}$ and is not affected by the amount of exohedral Li in the films. The capture of two Li ions to produce $Li_2$@$C_{60}$ can also be modeled in this way. The ratio measured in thermal desorption spectroscopy experiments [13] using the unpurified films is also given in Fig. 1. This is in good agreement with the laser desorption mass spectrometry; however, there are also fragmentation problems related to the energetic (70 eV) electron impact ionization (see also the discussion below). The significance of metastable fragmentation during mass spectrometric detection is the subject of ongoing studies.

Although it is possible to produce much more endohedral Li@$C_{60}$ as the ratio of ions to fullerenes during deposition is increased, it becomes increasingly difficult to dissolve the films. Over 90% of the film material can be dissolved in $CS_2$ for films produced with an ion to fullerene ratio of 1:1. This decreases to approximately 25% for films produced with a ratio of 6:1. We therefore use the low ratio of 1:1 for producing films for extraction purposes.

A laser desorption mass spectrum from such a film in the unpurified state is shown in Fig. 2a. One can see mainly the empty and filled fullerene mass peaks and some impurities with masses below 200 u. The small peaks at 696 u and 672 u are due to $C_2$ fragmentation from the fullerene cage during laser desorption. The soluble $CS_2$ extract (Fig. 2b) shows only the two fullerene species; all the impurities have been left in the filter (Fig. 2c). There is also a larger proportion of endohedral fullerenes compared to empty fullerenes left in the filter, indicating the lower solubility of the endohedral fullerene.

For the following experiments, both endohedral fractions (A, the "dimer", and B, the "monomer") were isolated and purified using the method described in [6]. The purity of the final samples was $\geqslant 95\%$.

## 3 Thermal stability

### 3.1 Unpurified films

We studied the thermal stability of the original, unpurified film material by scraping the film off the substrate used for the deposition and dividing it among a number of small ovens. Laser desorption mass spectrometry was used to investigate the material in each oven before heating to determine the relative concentration of endohedral species. Each oven was then heated to a given temperature for 90 min under vacuum. After this, the material was again tested by laser desorption mass spectrometry so that the relative concentration of endohedrals could be determined. The thermal decay rate at a given temperature was estimated from the difference in intensity of the endohedral mass peak relative to the C$_{60}$ intensity before and after heating to that temperature, and an exponential behavior was assumed. An Arrhenius plot of the data yielded an extremely low activation energy for the decay of Li@C$_{60}$ ($0.6 \pm 0.3$ eV) but also an exceptionally low pre-exponential factor ($3\,\mathrm{s}^{-1}$) [12]. The results are more reminiscent of an equilibrium reaction than unimolecular decay and indicate the presence of impurities that react with the fullerene cage and thus aid the destruction of the endohedral molecules. There are many species such as oxygen, water, and carbonates present in the unpurified film material that could contribute to such a process. Similar, but not quite as drastic, effects have been observed for Na endohedral C$_{60}$ species. It has recently been postulated that microscopic trace amounts of radicals are responsible for the low activation energies measured for endohedral rare gas compounds [9]. Although we observe a very low activation energy, the extremely low pre-exponential factor indicates that the endohedral fullerenes in the unpurified films are predicted to be stable at room temperature for many years. This agrees with our observations that the relative amount of endohedral fullerenes in the films (stored at room temperature in air), as determined by laser desorption mass spectrometry, does not change on a time scale of over a year. However, the amount of extractable material does decrease with time; we believe this is due to polymerization reactions.

### 3.2 Purified material

We have not yet been able to carry out detailed investigations of the thermal dissociation of the purified endohedral fullerenes in the solid state. However, we have observed no change in the mass spectra of the two separated, purified endohedral materials when heating them for 60 h at 200 °C in vacuum. The same behavior is observed for the film extract, partially purified material dissolved from the original films that consists of C$_{60}$ and Li@C$_{60}$. This implies a rate constant for thermal decay that is at least an order of magnitude lower than that of the unpurified material. It is also possible to sublime the purified or partially purified material in a vacuum at 550 °C. In this way, we can produce thin films of purified endohedral fullerenes on a wide range of substrates. The mass spectra of the sublimed films do not show any degradation as compared to the original material.

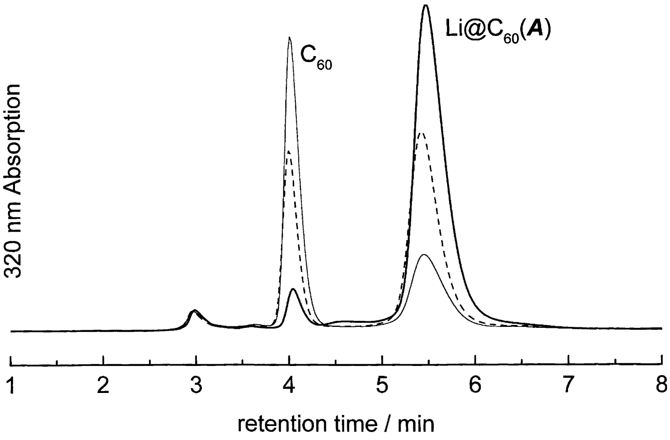

**Fig. 3.** HPLC chromatogram of endohedral fraction A in o-dichlorobenzene. Full, thick line: before heating; dashed line: after heating for 60 min at 120 °C; full, thin line: after heating for 60 min at 150 °C.

The thermal stability of free endohedral fullerenes in the gas phase has been studied by investigation of the metastable fragmentation of the molecules after pulsed laser desorption [12]. Preliminary results are consistent with an activation energy of 5 eV, which is in agreement with the experimentally determined threshold energy for penetration of the Li$^+$ through the carbon cage [2, 14]. More detailed experiments are in progress.

Investigations of the thermal stability of the two separated endohedral fractions were carried out in o-dichlorobenzene solution. The two solutions were analyzed by HPLC, and then equal amounts were put into a series of ampules under air. The individual ampules were put in a preheated bath at a given temperature for 60 min. After heating, the solutions were again analyzed by HPLC. Figure 3 shows the HPLC analysis of endohedral fraction A (the "dimer" fraction) before and after the solutions were heated to 120 °C and 150 °C. The peak at a retention time of 3 min which has the same intensity in all three samples is due to the solvent. One can clearly see a decrease of the endohedral fraction and a corresponding increase of the C$_{60}$ fraction after heating. After one hour at 150 °C, approximately 70% of the dissolved fullerenes are C$_{60}$, compared with about 4% before heating. The total integrated peak area decreases as the temperature increases. One cannot explain this effect by invoking different extinction coefficients (the absorption coefficient for both species is very similar at 320 nm [16]), but it can be inferred that part of the initially dissolved material (about 40%) has dropped out of solution after the heating at 150 °C for one hour (about 30% for heating at 120 °C for the same time).

The decay of the second endohedral fraction, B (the "monomer") is more complicated. This decays into two different species with retention times corresponding to those

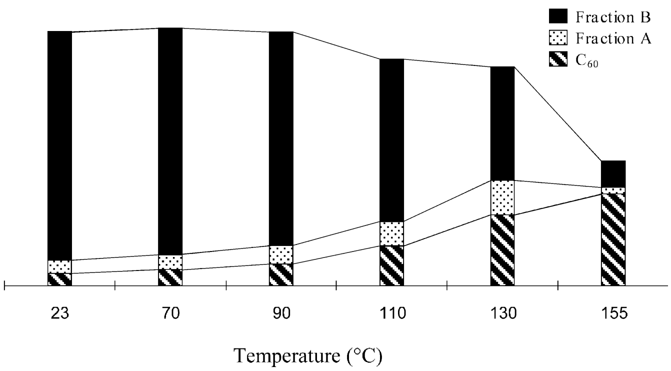

**Fig. 4.** Thermal decay of endohedral fraction B. The bars show the integrated HPLC peak intensities after fraction B is heated in o-dichlorobenzene for 60 min at the given temperatures.

of $C_{60}$ and the endohedral fraction A. This is illustrated in Fig. 4, where the integrated peak areas for the three different species detected are plotted as a function of temperature.

Arrhenius plots of the data are shown in Fig. 5. We do not want to imply that the decay is a simple unimolecular process. This is certainly not the case. However, the plots are consistent with Arrhenius-type behavior and enable us to get a good indication of the long-term stability of the solutions. We are interested in quantifying the loss of the purified endohedral fractions from their respective solutions. A number of different reaction possibilities could contribute to this loss process (see discussion below). The combination of possible processes leads to an overall behavior that can be fitted by a single Arrhenius-like decay. The fits to the data give activation energies of $1.1 \pm 0.2$ eV and $0.8 \pm 0.1$ eV for fractions A and B, respectively. The corresponding pre-exponential factors are $10^9$–$10^{11}\,\mathrm{s}^{-1}$ and $10^5$–$10^7\,\mathrm{s}^{-1}$. Although the error bars are large, it is safe to say that the stability of both solutions at room temperature is sufficient for carrying out many experiments and is at least on the order of days. However, the purified endohedral fractions should not be stored in solution but rather in the much more stable solid state. On longer storage, the solid endohedral fractions become partially insoluble, because of polymerization reactions.

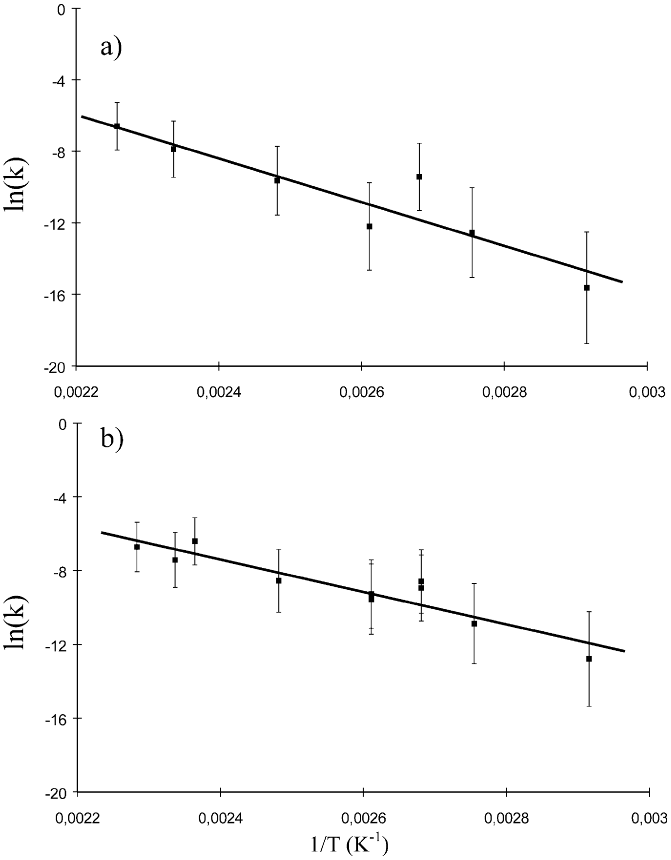

**Fig. 5.** Arrhenius plots of the decay of endohedral Li@$C_{60}$. (a) fraction A, $E_{\mathrm{act}} = 1.1 \pm 0.2$ eV, $A = (1.2 \pm 0.4) \times 10^9\,\mathrm{s}^{-1}$; (b) fraction B, $E_{\mathrm{act}} = 0.8 \pm 0.1$ eV, $A = (9 \pm 2) \times 10^5\,\mathrm{s}^{-1}$.

### 3.3 Discussion

Spectroscopic and other evidence that we have collected is consistent with the idea that fraction A is a dimer and fraction B a monomer (and not vice versa) [7,16]. It may seem strange that the "dimer" (fraction A) decays to $C_{60}$, whereas the "monomer" (fraction B) decays to the dimer and to $C_{60}$. However, it should be pointed out that a monomer Li@$C_{60}$ is a radical and would be expected to show a strong tendency towards dimerization. Calculations estimate that dimer formation is exothermic by about 20 kcal/mol [15]. The dimer is likely to be formed in the first stage by a weak single bond between the two carbon cages that may then stabilize by forming a double bond, in analogy with the $C_{60}$ dimer. In a similar way, further bonds may be formed with other monomers, leading to oligomerization and a reduction in solubility. Increased temperature and thus increased mobility will favor this reaction in solutions of both fractions A and B. The activation energy for the decay of the $C_{60}$ dimer in solution was determined, using the same method as described above, to be $1.2 \pm 0.2$ eV [16], in good agreement with the value found for the endohedral fraction A. This value is somewhat lower than the calculated binding energy of the $C_{60}$ dimer, 1.6 eV [17]. We thus infer from our data (Fig. 4) that there is an almost equal probability for the monomer fraction to decay either to produce $C_{60}$ or to produce the endohedral dimer. Further oligomerization occurs at higher temperatures/longer times to produce the insoluble product. It cannot be ruled out at this stage that the insoluble product also contains a contribution from the destruction of the fullerene cage. Pure $C_{60}$ is known to decay to an insoluble brown decomposition product when stored in solution under air for a period of a few days [11]. A similar decay of the fullerene content of fullerene-containing soot occurs on storage in the dark in the presence of air. Although the mechanism of this decay is not understood, it has been suggested that radical centers in the soot accelerate the process [11]. The action of radical enhancers has also been invoked to explain the low activation energy for decay of rare gas endohedral fullerenes in solution [9]. The value obtained for the activation energy depends critically on the purity of the sample [9]. A fast decomposition of La@$C_{82}$ kept in solution under air and in the presence of light has also been reported [10]. We believe that the presence of radical species in our solutions also contributes to the loss of the endohedral atom from the fullerene cage in both the "monomer" and "dimer" fractions. The significantly higher stability of the dry, sublimed, and purified material supports this statement. More work is needed, however, to determine the details of the decomposition mechanisms occurring in solution.

## 4 Conclusion

Endohedral Li@$C_{60}$ can be produced in macroscopic amounts by low-energy $Li^+$ irradiation of thin $C_{60}$ films. One can isolate the endohedral species from the rest of the film material by dissolving it in $CS_2$, followed by HPLC. The purified material in the solid state can be sublimed to produce thin films of pure endohedral Li@$C_{60}$ on a range of substrates. Solutions of the two endohedral fractions isolated by HPLC have lower thermal stabilities as compared to the solid material. The monomer fraction decays with approximately equal probability, either by forming a dimer or by losing the endohedral atom from the cage to form $C_{60}$. The dimer fraction first decays to produce $C_{60}$, indicating that the dimer bond breaks before the "escape" of the endohedral atom occurs. At higher temperatures or longer times, both fractions decay to an insoluble product.

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