Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 228 (2003) 913–920

www.elsevier.com/locate/ijms

Oxygen reactivity of La@C_{82} investigated with laser desorption mass spectrometry

A. Lassesson[a], A. Gromov[a], M. Jönsson[a], A. Taninaka[b], H. Shinohara[b], E.E.B. Campbell[a,*]

[a] Department of Experimental Physics, Göteborg University/Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[b] Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan

Received 25 November 2002; accepted 15 April 2003

Dedicated to Prof. H. Schwartz on the occasion of his 60th birthday.

Abstract

Laser desorption mass spectrometry is used to study thin films of purified La@C_{82}. The films are changed on exposure to atmosphere due to oxidation reactions with molecular oxygen. The endohedral fullerene oxides fragment more readily on laser desorption leading to the formation of small lanthanum carbide species and LaO. The half life of the oxidation reaction is found to be on the order of a few days.

Keywords: Oxygen reactivity; La@C_{82}; Laser desorption mass spectrometry

---

1. Introduction

Among the different kinds of molecules created using fullerenes as a main component, the endohedral metallofullerenes have attracted much attention. By putting an atom inside a fullerene, several different properties of the fullerene can be altered. We have recently reported on the fragmentation and delayed ionization of La@C_{82} that was found to be significantly different from that of C_{60} [1]. Furthermore, empty fullerenes are not particularly sensitive to influences from air, but placing metal atoms inside fullerenes changes the electronic properties and hence the sensitivity of the host molecule. Mass spectrometry has previously been used to investigate the interaction of oxygen with fullerene soot containing empty fullerenes, La@C_{60}, La@C_{70}, and higher metallofullerenes such as La@C_{82} [2]. The metallofullerene ion signal decreased after the soot material was exposed to air and similar effects were seen during thermal desorption of the mixture in the presence of several Torrs of oxygen.

Little has, however, been done to study the reactivity of pure solid La@C_{82}. As smaller La containing fullerenes are difficult to purify from the soot prepared with the arc-discharge method [3], the La@C_{82} fullerenes are the most likely to be used in different applications. In particular, thin films of fullerenes show potential as building blocks for nanoelectronics. It is, therefore, important to understand what influence oxygen from air will have on their properties.

---

[*] Corresponding author. Tel.: +46-31-772-3272; fax: +46-31-772-3496.
E-mail address: eleanor.campbell@fy.chalmers.se (E.E.B. Campbell).

1387-3806/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00235-5

We have used laser desorption time-of-flight mass spectrometry (LD-TOF-MS) to investigate thin films of La@C_{82} deposited on different substrates.

2. Experimental

La@C_{82} dissolved in CS_2 was inserted into quartz ampules with a length of 20 mm and a width of 5 mm. The ampules were inserted into a vacuum chamber that could be evacuated to a pressure of 10^{-7} mbar. The ampules were heated to a temperature of 550–650 °C to evaporate the material onto substrates of glass or aluminum. No degassing was performed. The substrate was positioned 2 cm from the quartz ampule. The rate of deposition was estimated from profilometer measurements and evaporation time to be 0.1–0.2 Å/s. The films used in the following studies were 50–100 nm thick.

After deposition, the samples were transferred in argon to a linear time-of-flight mass spectrometer that could be evacuated to 10^{-7} mbar. The samples were positioned on a sample holder that could be pulsed with a voltage of 2.1 kV. At a distance of 5 cm from the sample holder, a grid was held at ground creating an electric field. After the grid, a field free region of 0.8 m length was followed by a MSP detector. A 337 nm N_2-laser with a pulse length of 10 ns was used for the laser desorption of the fullerene material from the sample surface. The laser was focussed onto the sample with a lens. To control the laser fluence on the substrate surface, the lens was moved in the beam direction thus changing the laser spot size and hence the fluence on the sample. To expose the samples to air, they were removed from the mass spectrometer vacuum chamber and kept in the laboratory.

3. Results

Examining a thin film of La@C_{82} with positive LD-MS-TOF reveals mass spectra such as depicted in Fig. 1a. The film was kept in air (normal laboratory conditions) for 1 week. The laser fluence used was 18 mJ/cm^2. The higher mass range around the main La@C_{82}^+ peak shows a C_2-loss fragmentation pattern typical for fullerenes. When a fullerene is highly excited to internal energies of several tens of eV via laser desorption or other processes it has a high probability of shrinking by loss of C_2 molecules from the cage. If the internal atom in a metallofullerene is strongly bonded in the cage, the fullerene will simply “shrink wrap” around the atom. In Fig. 1a, the La@C_{82} can be seen to shrink into smaller metallofullerenes down to La@C_{68}^+, which is the smallest metallofullerene resolved in the mass spectrum. When looking closer at the peaks around La@C_{82} in Fig. 1b, one can see that there are several other ions detected apart from the C_2-loss fragments. Not only are La@$C_{82}O^+$ ions detected, but also ions from La@$C_{76}O^+$, La@$C_{80}O^+$, and empty fullerenes such as C_{82}^+. The tail to the high-mass side of the parent ion peak is due to delayed ionization [1,4]. To investigate the effect of oxygen on the material, thin films were made and investigated with both positive and negative LD-TOF-MS. The samples were exposed to normal laboratory air conditions at room temperature and the effect of air exposure on the mass spectra was investigated.

A comparison of three mass spectra taken with a laser fluence of 15 mJ/cm^2 on a film exposed to air for different lengths of time is shown in Fig. 2. After less than 5 min of air exposure, only shrink wrapping and delayed ionization of the parent molecule are seen. After only 140 min in air, LaO^+ starts to appear in the mass spectra (Fig. 2, middle). The film exposed to air for a total of 210 min shows high peaks of the small ions LaO^+ and LaC_n^+, $n = 0, 2, 4$. In comparison, small molecules LaC_n, $n = 0, 1, \ldots, 15$, were found by Suzuki et al. [5] from laser vaporization of La-containing carbon rods. A mixture of carbon and La can thus give rise to small mixed products in similar experiments to ours. We note, however, that in the laser vaporization experiments a much broader range of fragments were detected than in our experiments and that ions of LaC_n^+, where n is an odd number, were detected. We do not detect the odd carbon fragments or the higher fragments with more than six carbon atoms. Our mass spectra bear, however, a stronger

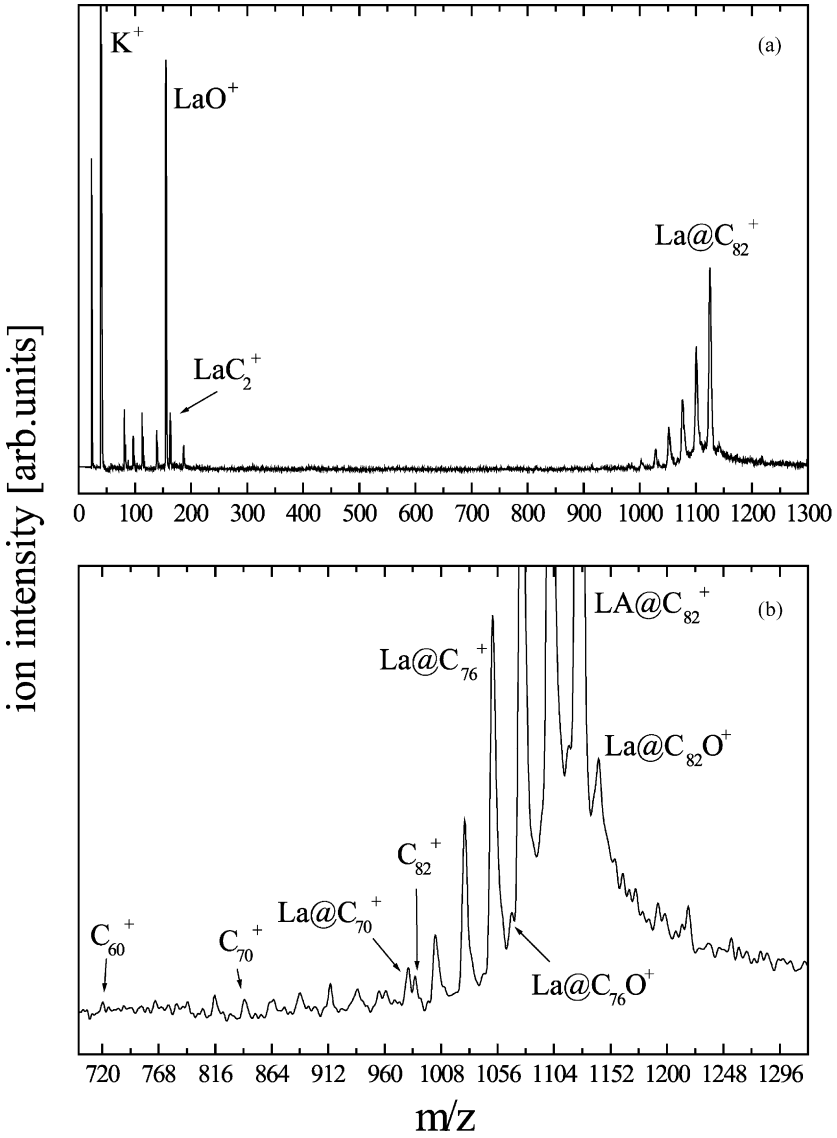

Fig. 1. (a) Mass spectrum taken with LD-TOF-MS in positive ion mode on a thin film of La@C_{82} kept in air for 1 week prior to investigation. (b) Close-up of the higher masses in (a) showing the delayed ionization of the parent ion and oxygen attachment to the metallofullerenes as well as the empty fullerenes.

resemblance to studies of collisions between La@C_{82}^+ and H_2 [6]. In the collision experiment, the LaC_n^+ ions were produced by fragmentation of the cage with loss of the La atom and C_2-units. The La atom in La@C_{82} is known to be positioned off-center (see [7] and references therein) in the cage, and if the closest C_2 or C_4 atoms are removed from the La@C_{82}, a stable LaC_{2n}^+ ion might form. The production of LaC_n^+ was related to central collisions between the encapsulated metal atom and H_2 leading to a direct expulsion of the metal atom with or without a small number of carbon atoms from the cage. This

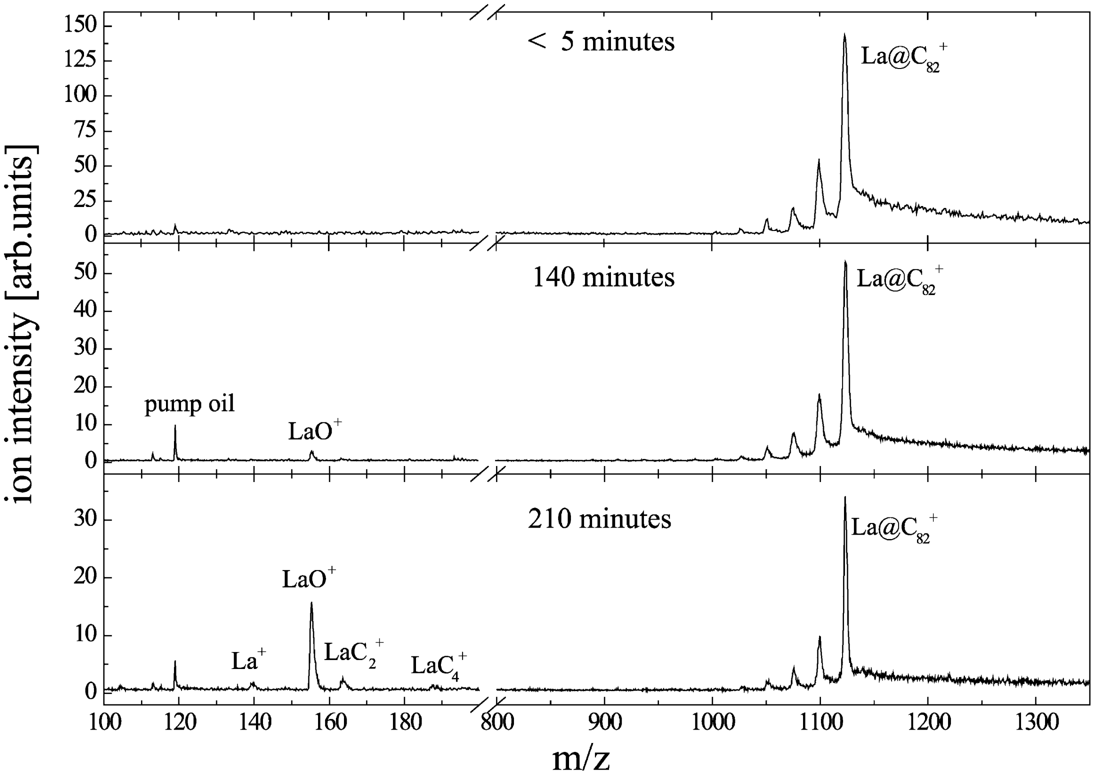

Fig. 2. Positive ion mass spectrum taken after different exposure times on a thin film of La@C_{82}.

is in contrast to the statistical nature of the successive C_2 emission producing the larger fullerene-like fragments. In our case, there is no possibility for a direct impulsive expulsion of the metal atom and there must, therefore, be a stronger tendency for cage-opening in the fullerene exposed to air. An earlier laser desorption study on La@C_{82} found small fragments of La oxides and LaC_n, $n = 0, 2, 4$ at fluences higher than 30 mJ/cm^2 [8]. The material used for that study probably contained small amounts of oxygen impurities. Laser excitation of gas phase La@C_{82} is able to produce small LaC_n fragments but at high laser intensities where the fullerene cage structure is lost [9]. This is analogous to the breakup of highly excited C_{60} into chains and rings leading to a bimodal fragment distribution [10,11].

As the oxides La@$C_{82}$$O^+$ and LaO^+ were detected in the mass spectra of films stored in air, oxygen containing molecules are obviously reacting with the endohedral fullerene resulting in deterioration of the sample. A film was exposed to air for several days and, during this time, was investigated with mass spectrometry. The ratio $R = \mathrm{LaO}^+/\mathrm{La@C}_{82}{}^+$ has been plotted in Fig. 3 for a time-span of 30 days. All data points were averaged over three to four mass spectra taken at different places on the film with a laser fluence of 15 mJ/cm^2. It is a fair assumption that the La in the measured LaO^+ originates from fragmentation of the metallofullerenes. If the time-dependent destruction of La@C_{82} follows an exponential decay with a rate constant k, the increase of the ratio R can be fitted with a function $R = \sigma(\exp(kt) - 1)$, where σ is a factor correcting for differences in ionization and detection efficiencies for the different molecules. The fit in Fig. 3 gives the values $k = (1.3 \pm 0.5) \times 10^{-6}\,\mathrm{s}^{-1}$ (corresponding to a half-life of ca. 9 days)

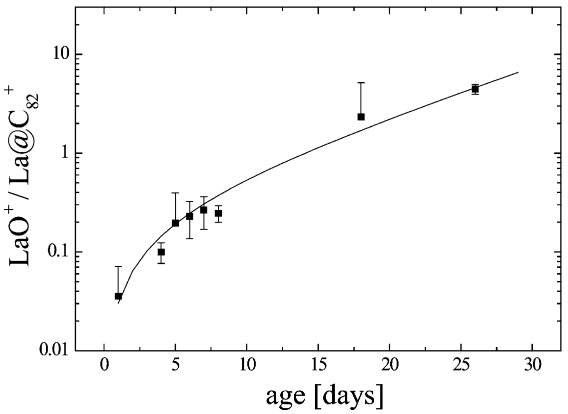

Fig. 3. The ratio $R = LaO^+/La@C_{82}^+$ plotted against the exposure time for a thin $La@C_{82}$ film. A fit to the data points using $R = \sigma(\exp(kt) - 1)$ gave a reaction rate for the parent molecule decay, $k = (1.3 \pm 0.5) \times 10^{-6}\,s^{-1}$ with $\sigma = 0.25 \pm 0.1$.

and $\sigma = 0.25 \pm 0.10$. A similar fit to the ratio with $LaC_n^+/La@C_{82}^+$, $n = 0, 2, 4$, gave a value of $k = (1.55 \pm 0.1) \times 10^{-6}\,s^{-1}$, within the margin of error of the rate for $LaO^+/La@C_{82}^+$. The factor σ was, in this case, found to be smaller (0.08 ± 0.05).

In Fig. 4, negative ion mass spectra are depicted for a freshly prepared film (top), a film kept in air for 140 min and stored in the mass spectrometer under a vacuum of 10^{-7} mbar for 4 days (middle) and a film kept in air for a total of 100 days. The laser fluence was $15\,mJ/cm^2$ which for positive ion mass spectra is high enough to create a significant fragmentation pattern (see Fig. 2). Fresh films of $La@C_{82}$ investigated in negative ion mode show, however, no or only very small amounts of fragments. This is similar to mass spectrometry in the negative mode on fullerenes such as C_{60}. The electron affinities of C_{60}

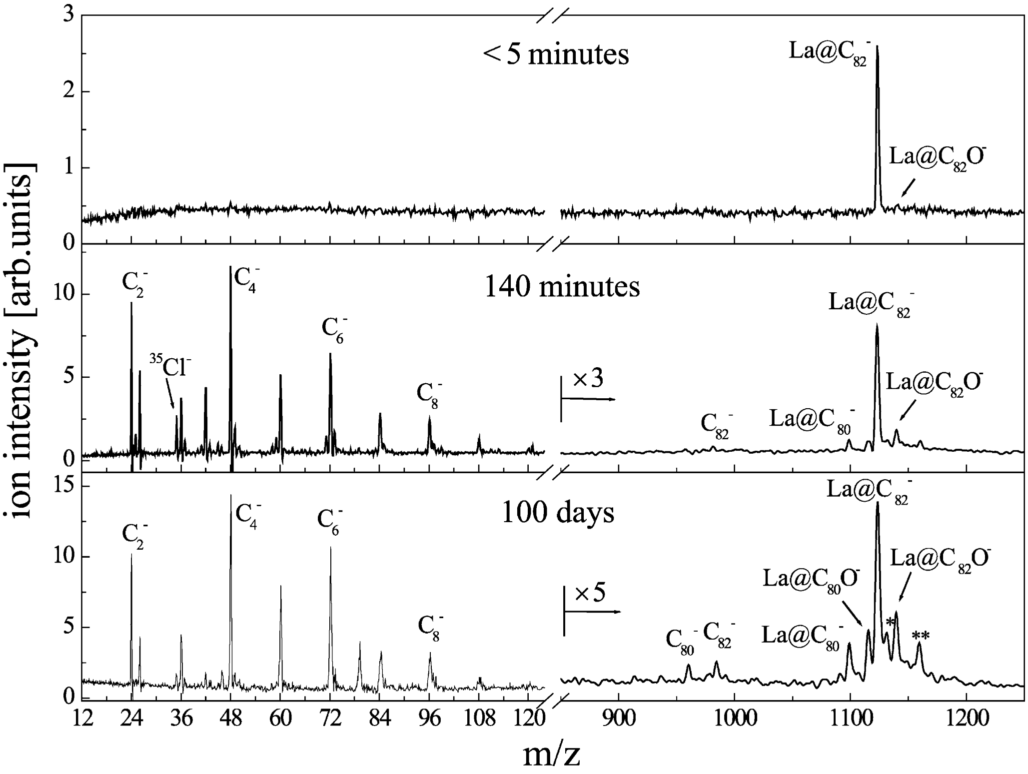

Fig. 4. Negative ion mass spectra taken after different exposure times on a thin film of $La@C_{82}$. The lower masses (left) show small carbon clusters while the higher masses reveal metallofullerene oxides and empty fullerenes.

(2.67 eV [12]) and La@C_{82} (3.35 eV [13]) are low and the dominating fragmentation channel in the negatively charged excited fullerene is the loss of the extra electron. Therefore, it is rather surprising to find a La@C_{80}^- ion in the middle and bottom mass spectra. As it is not seen in the fresh film mass spectrum and increases with size for storage in air it is obviously formed as a consequence of reactions with the ambient atmosphere. The La@C_{80} also appears as the oxide ions La@$C_{80}O^-$ and La@$C_{80}O_2^-$ (marked with a single asterisk in Fig. 4, right bottom). Even though the La@$C_{82}O^-$ and La@$C_{82}O_2^-$ can be detected, they are not as high in intensity compared to La@C_{82}^- as the La@C_{80} oxides are to La@C_{80}^-. In addition to the oxide peaks, there is an ion (marked with a double asterisk) detected in the air-exposed mass spectra with a mass that of La@C_{82} plus approximately 36 mass units. The origin of this peak is not clear, but it could be a chlorine atom attached to the metallofullerene cage. Ions of chlorine are detected in the negative ion mass spectra on exposed films and are probably from salt impurities, possibly due to the maritime climate in Göteborg. Similarly, sodium and potassium ions are detected in positive mass spectra.

A few empty fullerenes are detected at lower masses. The C_{82}^- is the highest fullerene with C_{80}^- as the next highest with smaller fullerenes barely detected. At even lower masses (left column of figures) small carbon clusters are detected. There might be tiny amounts of C_4^- and C_6^- in the fresh film spectrum, but much less than in the exposed film spectra.

4. Discussion

Fragmentation patterns with oxidized fullerenes $C_{60}O_n$ have previously been measured in mass spectrometry experiments. Fragmentation into C_{58}^- and $C_{58}O^-$ was seen in gas phase collisions between laser ablated hot fullerenes and oxygen clusters [14]. The oxygen clusters reacted with the fullerenes creating fullerene oxides and small carbon clusters C_n^-. It was suggested that the C_n^- clusters formed through disintegration of $C_{60}O$ into CO and the relatively unstable C_{59}. Fullerene oxides and odd numbered carbon clusters such as C_{59} were also reported from laser desorption mass spectrometry experiments on samples of $C_{60}O_n$, $n = 1, 2, 3$, [15] and C_{60} treated with *m*-chloroperoxybensoic acid [16]. Photofragmentation studies of metal–fullerene clusters have been shown to lead to detection of fullerene like species $C_{59}M^+$ (M = Fe, Rh, Ir) [17] where a carbon atom in the fullerene cage is substituted with a metal atom. Even though small C_n^- clusters appear after oxygen exposure in our spectra (see Fig. 3, left column), odd numbered clusters such as La@C_{81}^- can not be detected, possibly due to low stability. The pathway to La@$C_{80}O_n^-$, $n = 0, 1, 2$, through oxygen catalyzed loss of units of C_2, CO, or C_2O from La@$C_{82}O_2$ seems supported by similarity to the earlier studies on C_{60}. The difference is that the fullerene oxides in those reports were prepared quite differently from the La@C_{82} oxides, we have investigated. Thin films of C_{60} are normally stable in air and do not oxidize as quickly as the metallofullerene films. However, it is well known that oxygen diffuses into fullerene solids with a half-life on the order of days [18]. This leads to a dramatic decrease in conductivity and increase in the permittivity of the films due to charge transfer reactions between the fullerenes and the oxygen molecules [18]. La@C_{82} has a significantly higher electron affinity than C_{60} and the interaction with the diffusing oxygen molecules is expected to be larger, possibly leading to oxidation of the endohedral fullerenes, as the present results indicate. The appearance of LaO^+ and LaC_n^+, $n = 0, 2, 4$, can be explained as a side-effect of the loss of CO, etc. from the metallofullerenes via cage-opening. The low reaction rate found from the measurements of the ratio LaO^+/La@C_{82}^+ could then be due to the slow diffusion of O_2 into the thin film and/or oxidation into La@$C_{82}O$ or La@$C_{82}O_2$, depending on which of these is the slowest, rate-determining step.

The empty C_{80} and C_{82} were not detected on fresh films of La@C_{82} neither in the positive nor the negative detection mode. They are, therefore, most probably formed from the destruction via cage-opening of the metallofullerene oxide during laser desorption. It is worth noting the appearance of the C_{82} fullerene in both positive and negative ion mass spectra. In arc-discharge production of fullerenes C_{82} is less abundant than, for example, C_{84}. The most stable isomer of La@C_{82} produced in arc-discharge has C_{2v} symmetry [19] while the most stable empty fullerene C_{82} has C_2 symmetry [20]. It is unreasonable to expect that the C_2 isomer forms from the destruction of La@C_{82} into C_{82}. Thus, the fullerene we detect probably has C_{2v} symmetry. The difference in stability is not expected to be significant at our excitation energies and a fairly large amount of $C_{82}{}^{\pm}$ is detected in the mass spectra.

The fullerenes $C_{80}{}^{-}$, $C_{78}{}^{-}, \ldots$ could be due to sequential C_2 loss from C_{82}, but considering the dominating electron loss at high excitation energies it is more likely that these ions are formed from the fragmentation of La@C_n or La@C_nO, $n = 82, 80, \ldots$, with loss of LaO or La-carbides. This seems to support the idea that the loss of La from La@C_{82} occurs in the laser desorption process as any C_{82} in the thin film would not be expected to stay negatively charged and lose C_2-units at the same time in the laser desorption.

It is not possible to estimate the exact amount of empty fullerenes compared to metallofullerenes as the ionization potential and electron affinities are different. The amount of $C_{82}{}^{-}$ and $C_{82}{}^{+}$ ions in the mass spectra is a lower limit as the C_{82} and other empty fullerenes such as the C_{60} are thought to ionize with a lower probability than the La@C_{82} at the high energies generated in the laser desorption process [1]. The amount of destruction of La@C_{82} into empty C_{82} is nevertheless considerable. The small negative carbon clusters which are detected on exposed films might be formed in the laser desorption process due to destruction of the unstable empty fullerenes or odd numbered clusters such as La@C_{81} produced via loss of CO and similar small molecules as is the case for C_{60}O.

5. Conclusions

We have shown changes in the laser desorption mass spectra of thin films of purified La@C_{82} when exposed to atmospheric conditions for the period of a few days. The fullerenes react with atmospheric oxygen to produce oxides which then show a greater tendency to fragment during laser desorption mass spectrometry than the pristine material. The observed behavior from films exposed to atmosphere for a few hours or days is similar to that of C_{60}O. The endohedral fullerenes show an enhanced tendency to oxidize under ambient conditions and care should be taken with their handling and storage.

Acknowledgements

Financial support from the EU funded FET-IST project NICE (Nanointegrated circuits from endohedral fullerenes) is gratefully acknowledged.

References

[1] A. Lassesson, K. Mehlig, A. Gromov, A. Taninaka, H. Shinohara, E.E.B. Campbell, J. Chem. Phys. 117 (2002) 9811.
[2] J.H. Callahan, S.W. McElvany, M.M. Ross, Int. J. Mass Spectrom. Ion Processes 138 (1994) 221.
[3] Y. Chai, T. Guo, C.M. Jin, R. Haufler, L.P.F. Chibante, J. Fure, L. Wang, M. Alford, R.E. Smalley, J. Phys. Chem. 95 (1991) 7564.
[4] E.E.B. Campbell, G. Ulmer, I.V. Hertel, Phys. Rev. Lett. 67 (1991) 1986.
[5] S. Suzuki, H. Torisu, H. Kubota, T. Wakabayashi, H. Shiromaru, Y. Achiba, Int. J. Mass Spectrom. Ion Processes 138 (1994) 297.
[6] D.C. Lorents, D.H. Yu, C. Brink, N. Jensen, P. Hvelplund, Chem. Phys. Lett. 236 (1995) 141.
[7] H. Shinohara, Rep. Prog. Phys. 63 (2000) 843.
[8] S. Suzuki, Y. Kojima, H. Shiromaru, Y. Achiba, T. Wakabayashi, R. Tellgmann, E.E.B. Campbell, I.V. Hertel, Z. Phys. D 40 (1997) 410.
[9] A. Lassesson, A. Gromov, K. Mehlig, A. Taninaka, H. Shinahara, E.E.B. Campbell, J. Chem. Phys., in press.
[10] E.E.B. Campbell, T. Raz, R.D. Levine, Chem. Phys. Lett. 253 (1996) 261.
[11] H. Hohmann, R. Ehlich, S. Furrer, O. Kittelmann, J. Ringling, E.E.B. Campbell, Z. Phys. D 33 (1995) 143.
[12] C. Brink, L.H. Andersen, P. Hvelplund, D. Mathur, J.D. Voldstad, Chem. Phys. Lett. 233 (1995) 52.
[13] R.S. Ruoff, K.M. Kadish, P. Boulas, E.C.M. Chen, J. Phys. Chem. 99 (1995) 8843.
[14] W. Lu, R. Huang, S. Yang, Chem. Phys. Lett. 241 (1995) 373.
[15] R.D. Beck, C.S. Stoermer, C. Schulz, R. Michel, P. Weis, G. Bräuchle, M.M. Kappes, J. Phys. Chem. 101 (1994) 3243.

[16] M.P. Barrow, N.J. Tower, R. Taylor, T. Drewello, Chem. Phys. Lett. 293 (1998) 302.

[17] W. Branz, I.M.L. Billas, N. Malinowski, F. Tast, M. Heinebrodt, T.P. Martin, J. Chem. Phys. 109 (1998) 3425.

[18] B. Pevzner, A.F. Hebard, M.S. Dresselhaus, Phys. Rev. B 55 (1997) 16439.

[19] T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, R. Nagahata, X. Gao, F.v. Camaelbecke, K.M. Kadish, J. Am. Chem. Soc. 122 (2000) 9316.

[20] Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, M. Kainosho, Mater. Res. Soc. Symp. Proc. 359 (1995) 3.