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A femtosecond laser study of the endohedral fullerenes Li@C_{60} and La@C_{82}

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Abstract. The endohedral fullerenes La@C_{82} and Li@C_{60} have been studied in the gas phase with femtosecond laser excitation. The two molecules show qualitatively the same behaviour with respect to ion yield vs. pulse energy, but markedly different fragmentation patterns, with La@C_{82} fragmenting via the shrink-wrap mechanism and Li@C_{60} predominantly losing the metal atom in the first fragmentation step. The ion yields and electron energy distributions of La@C_{82} agree well with a recently developed model for fs laser ionisation of C_{60}.

PACS. 61.48.+c Fullerenes and fullerene-related materials – 36.40.Qv Stability and fragmentation of clusters – 31.15.Bs Statistical model calculations (including Thomas-Fermi and Thomas-Fermi-Dirac models)

1 Introduction

Endohedral fullerenes are among the most fascinating fullerene-based derivates with a wide range of atom and molecule containing fullerenes having been produced and studied [1,2]. Even although many different endohedral fullerenes have been available in macroscopic amounts for at least a decade, little is known about their behavior when excited to high internal energies in the gas phase. The processes that occur (ionisation, fragmentation) are normally studied in mass spectrometry experiments. A large number of experiments of this type have been performed on C_{60}, and, as more information about the processes of this molecule at high internal energies becomes available, it is increasingly interesting to test hypotheses and theories by studying other similar systems. Many endohedral fullerenes, such as the well-studied metal containing C_{82} based species, are suited for this purpose as they are as stable as C_{60} under the conditions and time scales of the mass spectrometry experiments. We have for example recently shown that it is possible to model the delayed ionisation of laser desorbed excited La@C_{82}, applying unimolecular decay theories previously applied to excited C_{60} [3]. Similarly the fragmentation of highly excited La@C_{82} on microsecond timescales resembles that of C_{60} which experiences loss of the fullerene structure above approximately 80 eV [4].

In comparison with the nanosecond lasers primarily used for these earlier studies, femtosecond lasers are capable of creating multiply charged cluster ions on time scales comparable to and lower than the coupling time between the excited electronic subsystem and the vibrational degrees of freedom. They are thus useful for studies of very fast interactions, such as energy redistributions, in excited fullerenes and have previously been used for investigations of C_{60} [5–8].

In this letter we present results from a femtosecond laser investigation of the molecules La@C_{82} and Li@C_{60} and analyse the results using theories recently developed for C_{60} [9].

2 Experimental

The endohedral fullerenes were prepared with two different methods. The Li@C_{60} material was produced using low energy Li^+ ion bombardment of thin fullerene films under high vacuum conditions [10]. The resulting thin films contained 10% endohedral Li@C_{60}. The arc-discharge production method was used for the preparation of La@C_{82} [1]. Both fullerene species were purified to above 95% purity using High-Pressure-Liquid-Chromatography (HPLC).

The vacuum apparatus used for the ionisation and fragmentation experiments has been described previously [7,8]. Briefly, the main excitation source is a

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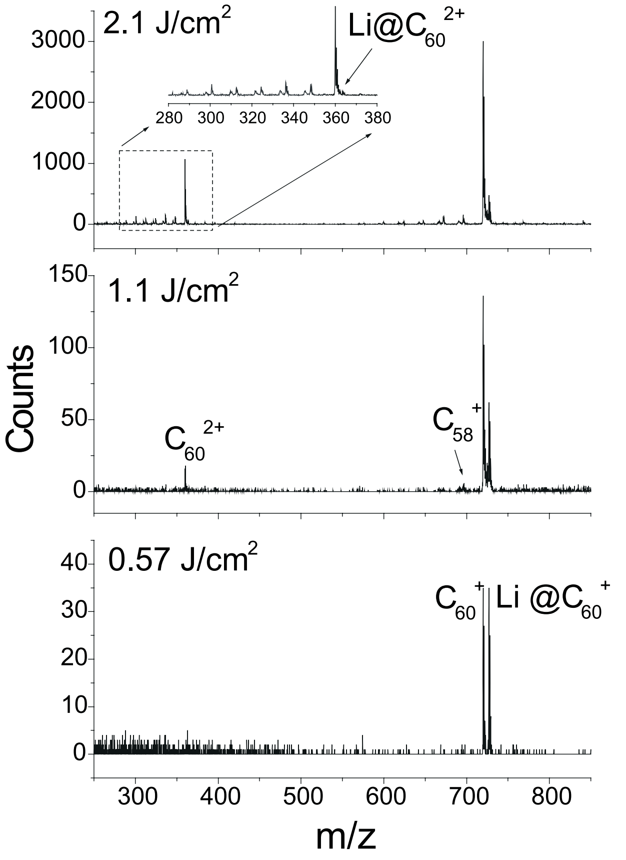

Fig. 1. Mass spectra produced by excitation of Li@C_{60} with a 180 fs laser at 800 nm.

regeneratively amplified Ti:Sapphire laser system providing a 180 femtosecond pulse, centered at 800 nm.

Quartz crucibles, filled with approximately 0.1 mg of endohedral fullerene material, were inserted into a resistively heated oven, which could be heated to 500–550 °C to generate a sufficiently dense vapour target. The molecular beam propagated perpendicular to both the laser and the TOF axes.

Ions created by the laser could be measured with a Reflectron TOF mass spectrometer while electrons were measured using a linear TOF spectrometer. The time-of-flight of the electrons is then converted into kinetic energy.

3 Results and discussion

Three mass spectra from Li@C_{60} vapour at varying laser fluences are shown in Figure 1. At low fluence (see bottom figure) only the two ions C_{60}^+ and Li@C_{60}^+ can be seen. As the laser fluence increases so do the ion signals and at a fluence of around 1.1 J/cm^2 both doubly ionised species and fragments created by C_2-loss from C_{60}^+ appear in the mass spectra. The doubly ionised C_{60}^{2+} species usually appears at similar laser fluences as the singly charged fragments C_{2n}^+ in similar experiments on C_{60} [7]. The Li@C_{60}^{2+} ions are detected at similar laser fluences as the C_{60}^{2+} even although no fragments from C_2-loss, e.g. Li@C_{58}^+, can be distinguished with the resolution of our mass spectrometer. Fragmentation with C_2-loss without loss of the guest atom (shrink-wrapping) is usually considered to be strong evidence for an endohedral position of the guest atom. The endohedral fullerene N@C_{60} has however been shown to fragment predominantly via loss of the nitrogen atom [11] and the absence of Li@C_{60-2n}^+, $n = 1, 2...$, in our mass spectra may have the same reason. In contrast, shrink-wrapping of Li@C_{60} has been detected in ns-laser experiments using an ArF-laser with a photon energy of 6.4 eV [12]. The ionisation potential of Li@C_{60} has been calculated to be around 6 eV, reduced from the 7.6 eV of C_{60}, due to doping of the cage by the Li valence electron [13]. The ionisation efficiency of Li@C_{60} is hence expected to be higher than that of C_{60}. The low Li@C_{60}^+ signal relative to C_{60}^+ in our mass spectra is, considering the high purity of the material inserted into the oven, thus rather unexpected. This could be due to thermal destruction combined with polymerisation of the endohedral fullerene material in the oven. A recent IR and Raman study [2] of purified Li@C_{60} material suggests that it exists as a combination of dimer and trimer structures. These are structures that may be precursors to polymers. Destruction or polymerisation in the oven is supported by the observation that the Li@C_{60}^+ ion signal decreased relative to the C_{60}^+ signal over time with an approximate half-life of 40 minutes at a temperature of 500 °C. An additional process resulting in low Li@C_{60}^+ ion intensity is, as already mentioned, fragmentation of the gaseous molecules by loss of the internal atom. The energy needed for insertion of a Li^+ ion into C_{60} is not more than 5–6 eV [14] and emission of the Li will therefore compete strongly with the emission of C_2, which can be expected to require a significantly higher activation energy [12]. This is supported by the observation that Li@C_{60}^{2+} are significantly lower in intensity compared to C_{60}^{2+} than Li@C_{60}^+ is to C_{60}^+ suggesting a stronger branching to the Li-loss channel rather than double ionisation. One can expect a higher loss of Li from the doubly charged species due to the higher excitation energy. We note that a higher average energy is required to ionise the molecule twice if the ionisation mechanism is the one described in [9]. Unfortunately a strong background of singly and doubly charged hydrocarbon ions is present at lower masses and makes the identification of any Li^+ ion difficult. The origin of the hydrocarbon ions is most probably the solvents, e.g. dichlorobenzene, used in the preparation of the samples and they were present at all laser fluences used.

At the mass spectrometer settings used, the flight times of the metastable ions created in the first field free region are shorter than for the prompt fragments, see Figure 1. The metastable ions seem to be solely from fragmentation of C_{60}^+ with no discernible contribution from endohedral fragments.

The mass spectra shown in Figure 2, from La@C_{82} vapour, show a strong presence of La-containing fullerenes with no or little empty fullerene ions present. At low laser fluences the only ions detected are the La@C_{82}^+ with small traces of La@$C_{82}O^+$. The latter is from reactions

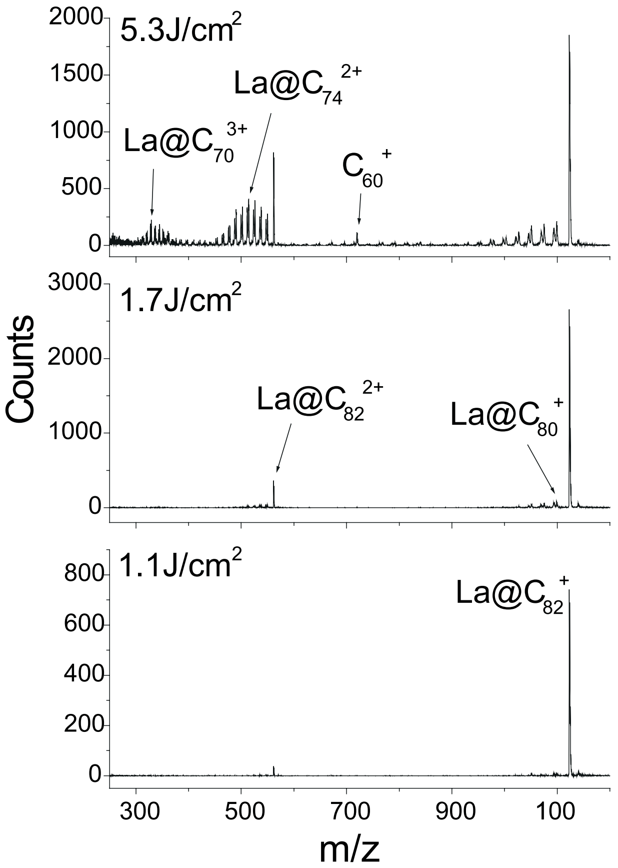

Fig. 2. Mass spectra produced by excitation of La@C_{82} with a 180 fs laser at 800 nm. The metastable fragment ions appear, as for C_{60} in Figure 1, on lower nominal masses than the ions fragmented in the acceleration region.

with molecular oxygen during transport of the sample in air into the vacuum chamber as earlier observed on thin films of La@C_{82} [15]. When the laser fluence increases above 1.1 J/cm^2 we see doubly ionised La@C_{82}^{2+} as well as singly charged fragments La@C_{82-2n}^{+} from C_2-loss and appearing at even higher laser intensities are triply ionised La-fullerenes. As is normally the case for C_{60} in similar experiments (compare to Fig. 1) the fragment distributions show a higher intensity for the multiply charged than for the singly charged species. Generally we also observe higher intensities of La-fullerene fragments compared to the parent ion than for C_{60} as parent molecule. For the triply charged endohedral fullerenes there is very little La@C_{82}^{3+} compared with triply charged La@C_{82-2n}^{3+} fragments. The fragment distribution for the singly charged species is qualitatively similar to that observed from fragmentation of C_{60} after ns excitation. This has been understood quantitatively as a consequence of the distribution of absorbed energy in the molecular ensemble [16]. If we apply this logic here, the increase in the degree of fragmentation with charge state is evidence for an increased amount of excitation energy. This is also the expected trend if the ionisation proceeds via the mechanism suggested in [9], as already mentioned for the Li@C_{60} case above. Note that the laser pulse duration is 180 fs, similar to that of [9]. While the fragment distribution for the singly charged ions is rather flat without any "magic numbers", the doubly charged fragments are highest in intensity around La@C_{74}^{2+} while the most abundant triply charged fragment is the La@C_{70}^{3+}. We note that the latter is isoelectronic to neutral C_{70}.

The metastable fragmentation probability is higher for La@C_{82}^{+} fragments than for C_{60}^{+} fragments. The metastable fragment probability is even higher for the doubly charged La species. These two observations can be understood in the framework of the evaporative ensemble model and radiative cooling [17]. In the absence of radiative cooling the amount of metastable fragmentation increases with the heat capacity of the species. Radiative cooling will suppress the fragmentation, and for the smaller fullerene fragments it is known that the suppression is quite strong, on the order of a factor 3–4 for experimental conditions similar to those used here. In this light, the difference between the smaller, empty fullerenes and the larger, endohedral, species is rather small. This indicates that the radiative cooling is similar in these two cases. This suggestion is indeed confirmed in dedicated experiments [18] to be published.

At lower masses (not shown) small lanthanum-carbide ions La^{+}, LaC_2^{+} and LaC_4^{+} can be discerned from a background of hydrocarbons. These La-carbide ions were also seen in the earlier experiments in our groups using a 337 nm ns-laser to excite a vapour of La@C_{82} [4] and are due to loss of fullerene structure at high internal energies.

To explore the possibility that the data can be explained by a transient hot electron mechanism, as previously described in [9], the electron distributions and the ion yields have been simulated with the same formalism. The idea is, briefly, that the laser heats the electronic system of the molecule leading to the emission of one or more charges in a boil-off process before the energy is coupled to the vibrational degrees of freedom. The emission rate constant in the model is given by detailed balance and numerical evaluations require the ionisation energies and the electronic level densities of neutral and charged species as input. Ideally the electron-phonon vibrational coupling time can be fitted from the data but we here assume the value of 240 fs, derived from the data on C_{60} [9]. For the ionisation energies we use $\Phi = 6.2$ eV + $(z-1) \times 3.5$ eV (z is the final charge) [19]. The electronic level density was calculated with the LDA single particle levels of C_{60}, in the manner described in [9]. The levels were scaled linearly to give the same Fermi energy as for C_{60}, and the small correction introduced in [9] was not used here. The addition of the 91 extra electrons for the neutral La@C_{82} relative to C_{60} prevents the large gap present in the spectrum of the latter from having an undue influence on the calculation. The energy dependent electron absorption cross-section, which is needed to calculate the emission rate constant, was chosen to be identical to the C_{60} value. The numerical details of the results will depend on these choices, but the general picture is insensitive to the precise values of the parameters.

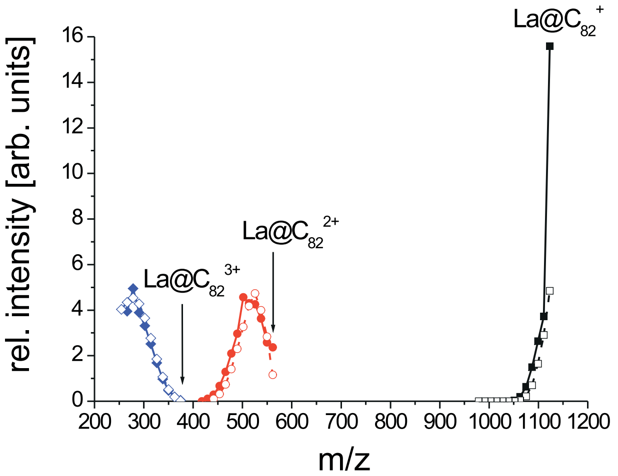

Fig. 3. The abundance of singly, doubly and triply ionised fragments taken from a mass spectrum produced with a laser fluence of 5.3 J/cm^2. The experimental data (full symbols and lines) are compared to the simulation (open symbols) for the different charge states.

The fragment distribution was compared with the model predictions. Assuming that the amount of fragmentation reflects the internal energy transferred to the molecules, the molecules are expected to fragment to lower sizes for higher charge states. For a quantitative comparison, the number of lost C$_2$ units was assumed to be given by the relation $\Delta N_{\mathrm{C}_2} = [(nh\nu - 65\ \mathrm{eV} - \sum \Phi(z))/8\ \mathrm{eV}]$, this quantity is set to 0 if it is less than 1. The square brackets indicate the integer part. The term involving the photon energy is the absorbed energy, the 65 eV is the appearance energy, which is estimated as the value for C$_{60}$ scaled by the number of atoms, 83/60. The ionisation potential, $\Phi(z)$, takes the values above, and 8 eV represents the average activation energy for C$_2$ loss. These numbers can be discussed and the results do not represent fits, but mainly serve as an illustration of the difference between the charge states. For the purpose of this calculation, an equal weight was given to the absorption of different numbers of photons. This simplification eliminates the need to introduce the cross section as an extra parameter. For each photon number, the yield of singly, doubly and triply charged fragments was calculated from the simulation and binned according to the fragment size assignment, ΔN_{C_2}, above. The result is shown in Figure 3. The agreement between experiment and simulation is generally good, and one notes that the increase in degree of fragmentation with charge state is reproduced. In the simulations the abundance of singly charged species peak around 40 absorbed photons, the doubly charged at 70 photons, and the triply charged at 100. This corresponds to a downward shift in the fragment distribution of $30 \times 1.55\ \mathrm{eV}/8\ \mathrm{eV} = 5-6$ C$_2$ losses for each additional charge. The experimental shift is slightly less but of the same order. Note that the model abundances are averaged over all numbers of absorbed photons that lead to a certain fullerene size. The only adjustable parameter in this plot is an overall factor for the simulated intensities. The main difference between experiments and simulation is the somewhat suppressed signal for the unfragmented species in the simulations, in particular for the singly charged species.

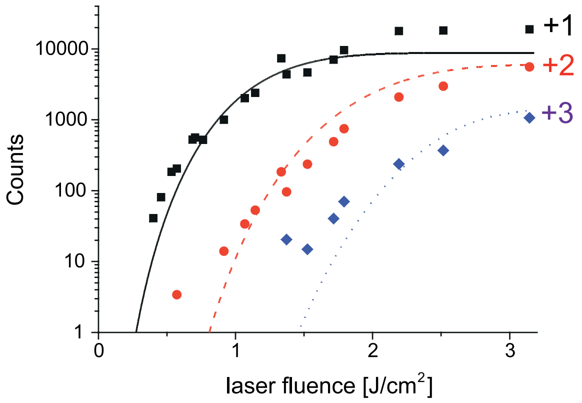

Fig. 4. The laser fluence dependence of the Σ_nLa@C$^{z+}_{82-2n}$, $z = 1-3$, ion yields. An average photo-absorption cross-section of 0.04 Å^2 gave the best fit between model and experiment.

The fluence dependence of the La@C$^{z+}_{2n}$, z = 1, 2, 3, ion signals is plotted in Figure 4. As seen in earlier studies [9], the intensity decreases with increasing charge number. Also shown are the simulated ion yields, assuming a photon absorption cross-section of 0.04 Å^2. The agreement between experiment and simulation is reasonably good, considering the fact that only the photon absorption cross-section and an arbitrary ordinate scale has been optimised. As in [9] we see a powerlaw behaviour for the low fluence ion yields for all charge states (not shown on the figure), in spite of the fact that the processes are manifestly not simulated as multiphoton absorption. Specifically, the low fluence fits yielded powers of 6.65, 14.1, 23.3 and 34.4 for z = 1, 2, 3 and 4, respectively.

The Li@C$^{z+}_{60}$, z = 1, 2, ion yield (not shown) was not simulated using the model. It shows a quite different behaviour if compared to that of C$_{60}$ and La@C$_{82}$, with a relative increase of ion signal with laser fluence much smaller than that of the other two fullerenes. This is again understood as due to the loss of the endohedral atom. With increasing average excitation energy we expect a stronger fragmentation of the Li@C$_{60}$ into empty fullerenes. A modeling of the ion yield would therefore not only have to consider the ionisation, but also the fragmentation into empty fullerenes and would have to include much more assumption about activation energies and branching ratios than is the case for La@C$_{82}$ where we expect almost all molecules to survive as endohedral fullerenes.

The photoelectron spectrum of La@C$_{82}$ [20], measured at a laser fluence where there is almost only singly ionised La@C$^{+}_{82}$ detected, is illustrated in Figure 5 and shows a similar thermal distribution as measured for C$_{60}$ [9]. The electron energy spectra were also calculated in the simulation. As for C$_{60}$, they show an almost perfect Boltzmann distribution. Apart from the lowest energy electrons this agrees with the experimental spectrum shown in Figure 5. If only energies above 2 eV are used, the reciprocal slope

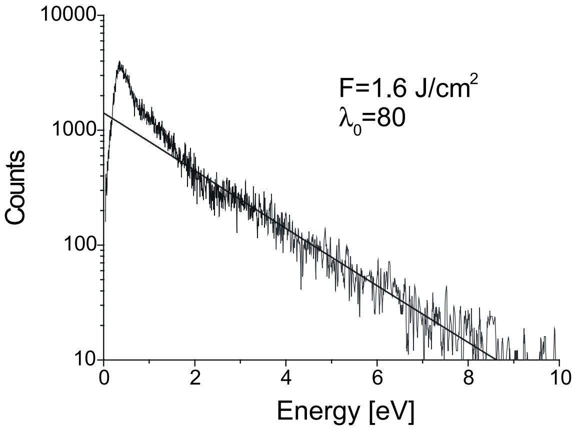

Fig. 5. A photoelectron spectrum of La@C_{82} taken at a laser fluence of 1.6 J/cm^2 and compared to a model calculation with an average of 80 absorbed photons in the center of the laser focus. The comparison model-experiment gave an average photoabsorption cross-section of 0.06 Å^2.

corresponds to an electron emission temperature of 1.8 eV (21 000 K). Also this number is similar to the pseudo temperatures fitted for C_{60}. Due to the somewhat higher heat capacity, this high temperature is only achieved after absorption of about 80 photons, which is at the end of the simulated range. A comparison of this number with the experimental laser fluence gives a second value of the photon absorption cross section of 0.06 Å^2. The agreement between the two independent values is quite satisfactory, considering the number of quantitative assumptions made. This cross-section should be compared with the value for C_{60}, which was determined in [9] to an average value of 0.04 Å^2.

In the photoelectron spectra from C_{60} one observes a series of well-defined peaks that can be attributed to excited Rydberg states of the molecule [20]. We do not observe discrete peaks in the photoelectron spectra from La@C_{82}, however, some of the signal contributing to the structure below 1.55 eV may be due to unresolved molecular Rydberg states. More experiments are needed to resolve this issue.

4 Conclusions

In conclusion, we have measured the ion yield of the endohedral fullerenes Li@C_{60} and La@C_{82} upon exposure to 180 fs laser pulses with photon energy 1.55 eV. For the La@C_{82} data, a simple model, previously applied to C_{60}, is able to account semi-quantitatively for the differences in the fragmentation pattern with charge state, the yield of singly, doubly and triply charged species, and the electron energy spectrum. The only fit parameter used was the photo-absorption cross-section which was found to be on the order of 0.05 Å^2.

From the Li@C_{60} ion yields we see a much lower increase of signal than for both La@C_{82} and C_{60}. This can be explained in terms of competing fragmentation channels, such as loss of the Li ion or atom, already at low laser intensities, which will result in a lower rate of increase of the ion signal.

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