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Delayed ionisation of C_{76}

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Abstract

A delayed ionisation experiment has been carried out on laser excited C_{76} molecules. Ions and electrons are detected in coincidence to distinguish the ionisation of C_{76} from that of C_{74} molecules created by the dominant process, emission of C_2. From the power-law dependence of the $C_{76}{}^+$ yield on time we deduce the dissociation energy, $E_d = 8.2 \pm 0.3$ eV. The relative yield of $C_{74}{}^+$ is consistent with very similar Arrhenius parameters for C_{76} and C_{74}, both for ionisation and for C_2 emission. With the assumption of a frequency factor for dissociation, $A_d = 10^{19}\ \mathrm{s}^{-1}$, the power of photon emission from neutral C_{76} is also determined from the experiment. It is consistent with predictions based on oscillator strengths derived from inelastic electron scattering.

PACS: 36.40.-c Atomic and molecular clusters; 36.40.Cg Electronic and magnetic properties of clusters; 36.40.Qv Stability and fragmentation of clusters

Keywords: Arrhenius parameter; Fullerene; Monte-Carlo simulation; Mass spectrum; Photon emission

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The dissociation energy, E_d, for C_2 emission from fullerene molecules has been the subject of many experimental and theoretical studies [1–9]. This process dominates the decay of very hot fullerenes, and for an internal energy of order 40 eV the lifetime for statistical decay is of order microseconds. The rate constant may be written in Arrhenius form [10,11] and, in principle, the two Arrhenius parameters, the dissociation energy E_d and the frequency factor A_d, may be determined from an Arrhenius plot. However, it is very difficult to prepare fullerene molecules with well defined internal energies of order 40 eV, and when E_d is estimated from the magnitude of the decay rate, there is a large uncertainty due to the unknown magnitude of A_d [2]. Additional uncertainty derives from the competition by photon emission, i.e., from radiative cooling of the hot molecules.

An independent check of the magnitude of the dissociation energies can be obtained from accurate measurements of the heats of formation of C_{60}, C_{70} and C_2 [7]. The sum of the dissociation energies of the five molecules from C_{62} to C_{70} is estimated to be 40.93 ± 0.54 eV, corresponding to an average dissociation energy of 8.2 eV. For this to be consistent with measurements of decay rates, the A-factor should be very large, and today there is general consensus that the value is of order $A_d \sim 2 \times 10^{19}\ \mathrm{s}^{-1}$ [2]. However, both the dissociation energy and the A-factor should be larger than these average values for the very stable, 'magic' fullerenes C_{60} and C_{70}. From detailed balance, A_d is found to be proportional to the ratio between the level densities of the daughter and mother molecules [11,12], and the level density is normally lower for molecules with high stability. Hence, A_d is expected to be larger for C_{60} and C_{70} than for the other fullerenes and lower for C_{62} and C_{72}.

To study these questions we have previously measured delayed ionisation of both C_{60} and C_{70} and applied an analysis first suggested by Hansen and Echt [3]. For hot neutral fullerenes with microsecond lifetimes, the decay is dominated by C_2 emission and ionisation is a weak channel. For an ensemble with a broad distribution in excitation energy, the ionisation

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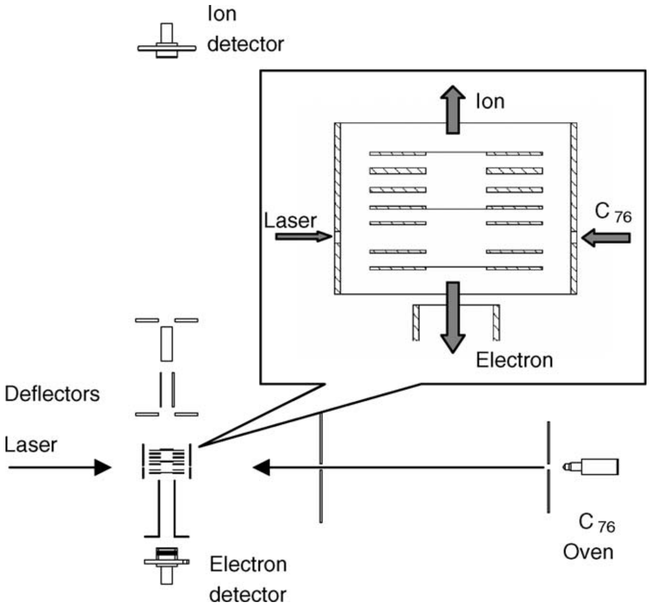

Fig. 1. Schematics of the experimental setup.

yield as a function of time should then follow a power law with a power close to minus the ratio of the ionisation and dissociation energies, provided that no other channel is significant [3,13]. Since the ionisation energies have been measured or can be estimated rather accurately [14], this gives a method for determining the dissociation energies without an assumption about the value of A_d.

Our experimental setup, shown in Fig. 1, allows the detection in coincidence of the ions and the electrons, and this enables us to get more detailed information on the decay. For both C_{60} and C_{70}, we have determined the A-factor as well as the dissociation energy. The dissociation energies, $E_d = 10.6 \pm 0.3$ eV and $E_d = 9.7 \pm 0.3$ eV, were indeed found to be larger than for 'normal' fullerenes [15,16]. Furthermore, in agreement with the argument above, A_d was found to be about two orders of magnitude larger for C_{60} than for the daughter molecule C_{58} and, similarly, A_d for C_{70} is about one order of magnitude larger than for C_{68}. The radiative cooling was also determined for both of these magic fullerenes. The results are consistent with a dielectric model based on oscillator strengths from inelastic electron scattering [17]. The frequency-dependent oscillator strength introduced in the model is proportional to frequency at low frequencies and scales approximately with the number of carbon atoms in the fullerene molecule. Relative to the resulting predictions, the radiation power was found to be reduced by factors of 2.6 and 1.4, respectively, for C_{60} and for C_{70}, and this can be accounted for by introduction of a smooth lower frequency cut-off in the model, corresponding to effective gaps of 2.7 and 1.6 eV [16].

We supplement here with a measurement of delayed ionisation for a 'normal' fullerene, C_{76}. From both theory [8] and experiments [5], it is predicted that the dissociation parameters for this molecule should be very similar to those for the neighbouring fullerenes, and confirmation of this by measurements of delayed ionisation gives further support for the method of analysis and underpins the results obtained earlier for the magic fullerenes. Furthermore, the competition from photon emission can be determined for a fullerene with a rather small energy gap. Measurements of inelastic electron scattering in solid C_{76} yield an oscillator strength for photon absorption and emission which is well reproduced by the simple dielectric model with a gap of order 1 eV, only [17].

The C_{76} powder used in the experiment was derived from soot produced by a direct-current (40 A) arc discharge of carbon rods under a 500 Torr He atmosphere. Fullerenes were extracted from the raw soot by refluxing with 1,2,4-trichlorobenzene for 8 h. The isolation of C_{76} was accomplished by high-performance liquid chromatography with a COSMOSIL Buckyprep column (20 × 250 mm, Nacalai Tesque; 12 mL/min flow rate; toluene eluent). The purity of the isolated C_{76} was confirmed by laser-desorption time-of-flight mass spectrometry. No other fullerenes were detected in the sample.

The experimental setup shown in Fig. 1 has been described elsewhere [15]. Briefly, an effusive beam of C_{76} molecules was aligned anti parallel to a collimated laser beam (third harmonic from a pulsed Nd:YAG laser). Electrons and ions were extracted by an electrostatic field perpendicular to the direction of the two beams and were detected in coincidence. The time difference between the electrons and ions determines the ion mass. Most of the decays are very fast and the electron signal is coincident with the laser pulse. The distribution in Fig. 2 of ion detection times relative to the laser pulse can therefore be interpreted as a time-of-flight mass spectrum of the ions, except for the tails of delayed ionisation. The tails from neighbouring peaks have a small overlap but the delayed ionisation from a single molecule can be extracted by gating on the ion–electron time difference. The comparison of the results to simulations is discussed briefly below and in more detail in [15].

Fig. 3 presents the yields of delayed ionisation for both C_{76} and its fragment C_{74} after emission of C_2. The results are compared with calculations based on a statistical model describing the evolution of the internal energy distribution [15,18]. The

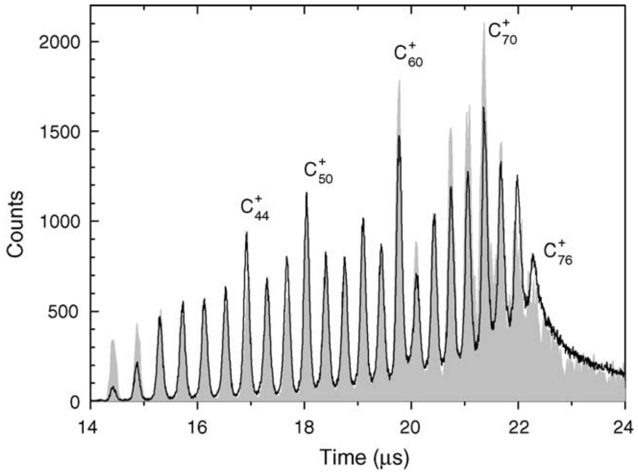

Fig. 2. Time-of-flight mass spectrum of the ionic fragments. The time is relative to the laser pulse. The shaded area shows the yield from the Monte-Carlo simulation described in the text, with a distribution in excitation energy proportional to E^{-2}.

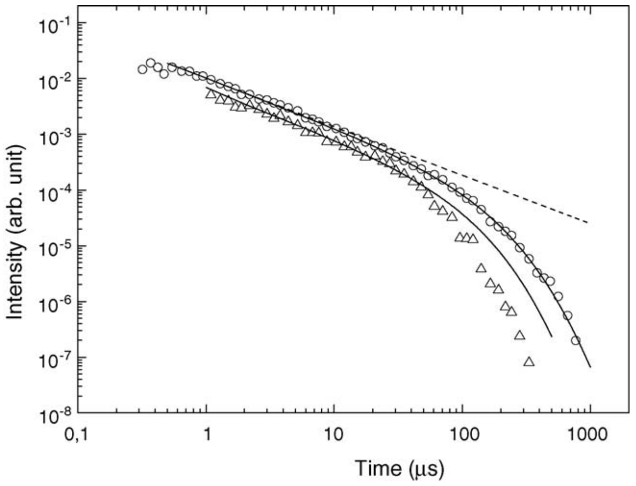

Fig. 3. Yields of delayed ionisation of C_{76} (circles) and C_{74} (triangles). The curves result from the calculations described in the text with a radiation spectrum derived from a dielectric model [17]. For C_{76}, the radiation spectrum is modified by a low-energy cut-off corresponding to a HOMO-LUMO gap of 0.91 eV. The dashed curve is calculated without photon emission.

distribution changes partly due to depletion by ionisation and C_2 emission, partly due to cooling by photon emission, which dominates at long times, corresponding to low excitation energies, but it is insignificant at short times. At times less than about 10 μs, the magnitude and the time evolution of the yield of ionisation are then the result of a competition between ionisation and C_2 emission. The rate constants are modelled with an Arrhenius-type formula [10,11],

$$k_{\mathrm{d}}(T) = A_{\mathrm{d}} \cdot \exp\left(-\frac{E_{\mathrm{d}}}{k_{\mathrm{B}} T_{\mathrm{e}}}\right) \tag{1}$$

Here, the emission temperature T_e equals the microcanonical temperature T in the initial state with a finite-heat-bath correction, $T_e \cong T - E_d/2C$, where C is the heat capacity which may be obtained from the calculated spectrum of vibrational frequencies. In our analysis, the dissociation energy for C_2 emission from C_{76} is deduced from the slope of the C_{76}^+ yield which determines the ratio between the ionisation and dissociation energies. Hence, the extracted value of E_d depends mainly on the ionisation energy for C_{76} (7.1 eV [14]) and only to second order on the pre-exponential factors for dissociation and ionisation. The value of A_d for C_{76} relative to that for C_{74} is determined from the ratio of the yields of C_{76}^+ and C_{74}^+ for fixed values of the other parameters. The decay parameters used in the analysis are given in Table 1.

At long times the cooling by photon emission gives a cut-off of the power-law dependence (Fig. 3). It has been modelled with the power spectrum obtained from a dielectric model [17], which has been used successfully to describe the cooling of both fullerene anions [18] and cations [6]. The photon spectrum has been modified by a lower cut-off corresponding to a HOMO-LUMO gap for C_{76}, and the magnitude of the gap is determined from a fit to the measurements. No fitting has been attempted for C_{74}^+ because the yield of this ion is reduced at long times ($t > 30$ μs) by a geometrical effect, caused by the recoil of C_{74} in dissociation of C_{76} [15].

In the calculation of the ionisation yield, the slope of the initial distribution in internal energy is needed. The laser beam is narrower than the molecular beam and hence the energy distribution just after photo-absorption results from a spatial average over regions with laser intensities varying from zero to the maximum value. Over a limited range, the distribution should follow a power law E^{-x}, where x depends on the laser profile [19]. We have performed a Monte-Carlo simulation of the chain of ionisation and C_2-emission events during and after absorption of the laser pulse. The results are compared to the time-of-flight mass spectrum of the ions (Fig. 2) and the best agreement is reached for $x = 2.0$. In the previous study of delayed ionisation of C_{60} and C_{70} [16], the power was set equal to 2.5. The laser system had been realigned and the beam had been refocused before the present experiment, and we now find the best agreement with the

Table 1

Parameters used for the Monte-Carlo simulation of the chain of ionisations and C_2 emissions induced by laser

Fullerene size	E_d (eV)	A_d (s^{-1})	E_d^+ (eV)	A_d^+ (s^{-1})	E_i (eV)	A_i (s^{-1}) at $T = 4000$ K
76	**8.20**	$\mathbf{1.00 \times 10^{19}}$	8.20	1.00×10^{19}	7.1	5×10^{14}
74	8.15	1.00×10^{19}	8.15	1.00×10^{19}	7.1	
72	7.50	2.35×10^{18}	7.80	4.71×10^{18}	7.1	
70	$\mathbf{\underline{9}.70}$	$\mathbf{1.70 \times 10^{20}}$	9.40	8.50×10^{19}	7.4	1×10^{15}
68	$\underline{8}.60$	2.00×10^{19}	8.60	2.00×10^{19}	7.1	5×10^{14}
66	$\underline{8}.40$		8.40			
64	$\underline{8}.00$		8.00			
62	$\underline{6}.20$	1.75×10^{17}	6.70	3.48×10^{17}		
60	**10.60**	$\mathbf{2.30 \times 10^{21}}$	10.10	1.15×10^{21}	7.6	1×10^{15}
58	8.40	2.00×10^{19}	8.40	2.00×10^{19}	7.1	5×10^{14}
56	8.60		8.60			
54	8.40		8.40			
52	8.40		8.40			
50	8.80		8.80			
<50	8.30		8.30			

This table shows the Arrhenius parameters for C_2 emission from both neutrals (E_d and A_d) and ions (E_d^+ and A_d^+) and for ionisation (E_i and A_i). Parameters in bold result from measurements of delayed ionisation. The sum of the underlined dissociation energies is in agreement with the heats of formation of C_{70}, C_{60} and C_2 [7].

power 2.0. The measurement covers a wide range of the initial excitation energy and therefore it is not surprising that the fit is not perfect. Because we use this fit to estimate the slope of the energy distribution at fairly low energies (30–40 eV) where the end product can be C_{76}^+, the power has been chosen to fit the variation of the yield in the range C_{60}^+–C_{70}^+.

The Arrhenius parameters used in the Monte-Carlo simulation are given in Table 1. A relation between the dissociation energies for C_2 emission from ions and neutrals and the ionisation energies is provided by the requirement that the final energy should be the same when a sequence of ionisation and dissociation is inverted. We use the same parameters as in the analysis of the earlier experiments [16] for fullerenes C_{2n} with $2n \leq 70$. The parameters for C_{74} and C_{76} are constrained by the measurement of delayed ionisation in Fig. 3, as discussed below. The ionisation energies have been taken from [14]. For 72 the higher stability and lower level density of C_{70} has been taken into account [15]. The frequency factors for dissociation of C_{76} and C_{74} had to be decreased by a factor of two relative to the 'normal' value to get reasonable agreement with the data. As seen in the figure, the yields of C_{74}^+ and C_{76}^+ in the simulations are still a little lower than in the experiment while the simulated yields are a little higher than the measured yields in the range C_{60}^+–C_{70}^+.

From the comparison between experiment and modelling, we obtain the dissociation energy for C_{76}, $E_d = 8.2 \pm 0.3$ eV. The relative yield of C_{76}^+ and C_{74}^+ is consistent with identical pre-factors, chosen as $10^{19}\,s^{-1}$, and a dissociation energy for C_{74} which is lower by 0.05 eV. The radiative cooling of C_{76}, reflected in the cut-off of the power-law dependence of the ion yield in Fig. 3, is consistent with the dielectric model with an energy gap of 0.91 eV. Such a small gap gives a reduction of the radiation intensity of only about 10% at 4000 K [17].

The error on the dissociation energy E_d for C_{76} given above reflects mainly an uncertainty of about 0.1 eV of the ionisation energy of C_{76} and an uncertainty of about 0.5 of the exponent x in the power law for the energy distribution. It is an important feature of the experiment that E_d depends very weakly on other parameters in the analysis. In contrast, the frequency factor A_d is sensitive to many of the parameters; we have previously estimated the error to be of order a factor of four [15]. In addition, the experiment only determines the ratio of the A_d values for C_{76} and C_{74}.

The dashed curve in Fig. 3 shows the power-law time dependence of the C_{76}^+ yield which is obtained without cooling by photon emission. The log–log slope is −0.872, very close to the simple prediction, $-E_i/E_d = -0.866$, and distinctly different from the slope of about −0.7 observed for delayed ionisation of C_{60} [15]. The radiative cooling which must be included to fit the data corresponds to the prediction by the dielectric model with a much smaller HOMO-LUMO gap than for C_{60} and C_{70}, as expected. Thus the results of the present experiment confirm the observation of delayed ionisation as an accurate method for determination of dissociation energies of fullerenes and of the cooling of hot fullerenes by photon emission.

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