Eur. Phys. J. D **34**, 191–194 (2005)
DOI: 10.1140/epjd/e2005-00142-5

THE EUROPEAN PHYSICAL JOURNAL D

Delayed ionisation of C_{70}

B. Concina[1], S. Tomita[1,2], J.U. Andersen[1,a], and P. Hvelplund[1]

[1] Department of Physics and Astronomy, University of Aarhus, 8000 Aarhus C, Denmark
[2] Present Address: Institute of Applied Physics, University of Tsukuba, Ibaraki 305-0006, Japan

Received 6 September 2004

Abstract. A delayed ionisation experiment has been carried out on laser excited C_{70} molecules. Ions and electrons are detected in coincidence to distinguish the ionisation of C_{70} from that of C_{68} molecules created by the dominant process, emission of C_2. From the time dependence of the C_{70}^+ yield and the ratio to the C_{68}^+ yield, we can deduce both the dissociation energy, $E_d = 9.7 \pm 0.3$ eV, and the pre–exponential factor, $A_d = 1.7 \times 10^{20}$ s^{-1}, in the Arrhenius decay law for C_2 emission. The power of photon emission from neutral C_{70} is also determined.

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

The dissociation energy for C_2 emission from fullerene molecules has been the subject of many experimental and theoretical studies for more than a decade [1–8]. The difficulty in determining E_d experimentally has been mainly due to radiative cooling and to the unknown magnitude of the pre–exponential factor A_d in the Arrhenius expression for the rate constant [9]:

$$k_d(T) = A_d \exp\left(-\frac{E_d}{k_B T_e}\right). \quad (1)$$

The emission temperature T_e equals the microcanonical temperature T in the initial state with a finite–heath–bath correction, $T_e \cong T - E_d/2C$, where C is the heat capacity. Initially, the pre–exponential factor was assumed to be of order 1.6×10^{15} s^{-1} [10], and analysis of fragmentation experiments with this value lead to a dissociation energy below 8 eV for C_{60}, in strong disagreement with theoretical values above 10 eV [2]. A turning point was an experiment on delayed ionisation of laser excited C_{60} which gave convincing evidence for a much higher value, $E_d = 11.9 \pm 1.9$ eV [3]. A larger pre–factor, $A_d = 2 \times 10^{19}$ s^{-1}, was then derived from a combined analysis of breakdown curves and metastable fractions [4]. This finding was in agreement with the Gspann parameter deduced from a series of metastable fractions measured in a time–of–flight spectrometer [5]. Additional evidence was provided by measurements in a storage ring of the influence of radiative cooling on C_2 emission [6]. The sum of dissociation energies from C_{62}^+ to C_{70}^+, deduced by an analysis with $A_d^+ = 2 \times 10^{19}$ s^{-1} for all five molecules, was shown to be consistent with the accurately measured heats of formation for C_{60}, C_{70} and C_2.

There is consensus today that this is the order of magnitude of A_d. However, the value should not be the same for all the fullerenes. From detailed balance, A_d is found to be proportional to the ratio between the level densities of the daughter and mother molecules [9,11], and the level density is normally lower for molecules with high stability. Hence, A_d is expected to be larger for the magic molecules C_{60} and C_{70} than for the other fullerenes and lower for C_{62} and C_{72}.

In the analysis of the first measurement of delayed ionisation of laser excited C_{60} [3] it was shown that the yield as a function of the time should follow a power law with exponent equal to minus the ratio of the ionisation and dissociation energies, provided that ionisation is a weak channel compared with C_2 emission and that no other channel is significant. The measurements could be fitted with such a law in the time range $0.1-10$ μs, and the dissociation energy was deduced from the measured exponent and the known ionisation energy. Our experimental setup allows detection in coincidence of ions and electrons, and this enables us to get more detailed information on the decay. In a previous experiment [12], we were able to determine both the dissociation energy E_d for C_{60} and the ratio of the A_d factors for C_{60} and C_{58}. In agreement with the argument above, A_d was found to be about two orders of magnitude larger for C_{60}. In addition, the power of photon emission from hot C_{60} molecules was determined, and it was verified that radiative cooling does not influence the decay significantly for times shorter than 30 μs. Here we present similar results for the other magic molecule, C_{70}.

---

[a] e-mail: `jua@phys.au.dk`

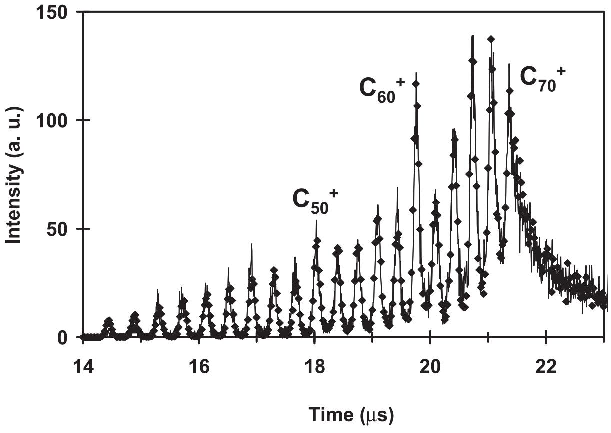

Fig. 1. Time–of–flight mass spectrum of the ionic fragments. The time is relative to the laser pulse. The diamonds indicate the results of the Monte Carlo simulation described in the text, with a distribution in excitation energy proportional to $E^{-2.5}$.

The experimental setup has been described elsewhere [12]. Briefly, an effusive beam of C_{70} molecules is aligned antiparallel to a collimated laser beam (third harmonic radiation from a pulsed Nd:YAG laser). Electrons and ions are extracted by an electrostatic field perpendicular to the direction of the two beams and are detected in coincidence. The time difference between the electrons and the 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 Figure 1 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 with a gate on the ion–electron time difference. Figure 2 presents the yield of delayed ionisation for both C_{70} and its fragment C_{68} after emission of C_2. The comparison of the results to calculations is discussed briefly below and in more detail in reference [12].

The calculation of the yield of delayed ionisation is based on a statistical model describing the evolution of the internal energy distribution [13]. The 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 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 the Arrhenius–type formula given in equation (1). In our analysis, the dissociation energy for C_2 emission from C_{70} is deduced from the slope of the C_{70}^+ 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_{70} (7.4 eV [14]) and only to second order on the pre–exponential factors for C_2 emission and ionisation. The value of A_d for C_{70} is determined from the ratio of the yields of C_{70}^+ and C_{68}^+ and this requires an assumption about the decay parameters for C_{68}. The decay parameters used in the analysis are discussed below.

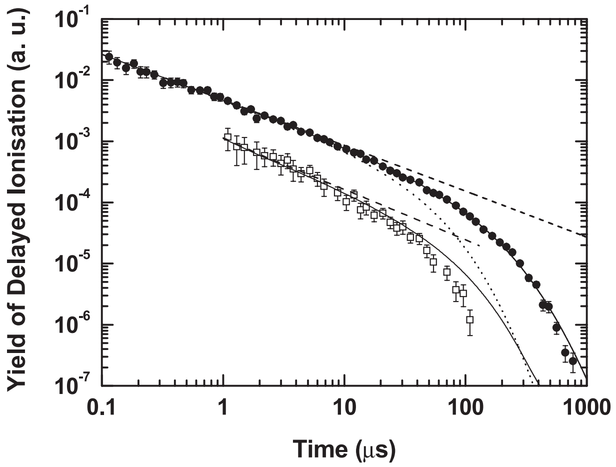

Fig. 2. Yields of delayed ionisation of C_{70} (full circles) and C_{68} (open squares). The curves result from the calculations described in the text, without radiative cooling (dashed lines), with the radiation power spectrum calculated from a dielectric model [15] (dotted line for C_{70} and full line for C_{68}) and with this radiation spectrum modified by a low–energy cut off, corresponding to a HOMO–LUMO gap (full line for C_{70}).

The cooling by photon emission gives a cut–off of the power–law dependence at long times (Fig. 2). It has been modelled with the power spectrum obtained from a dielectric model [15], which has been used successfully to describe the cooling of both fullerene anions [13] and cations [6]. The photon spectrum has been modified by a lower cut–off corresponding to a HOMO–LUMO gap for C_{70} and the magnitude of the gap is determined from a fit to the measurements. No fitting has been attempted for C_{68}^+ because the yield of this ion is reduced at long times ($t > 30$ μs) by a geometrical effect, caused by the recoil in C_2 emission from C_{70} [12].

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 energy range, the distribution should follow a power law E^{-x} where x depends on the laser profile [16]. 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 $x = 2.5$. In the previous study of delayed ionisation of C_{60} [12], the power was set equal to 2 but an equally good fit was obtained with $x = 2.5$. The simulation of the decay chain from C_{70} leads to a more reliable power value because of the larger number of fullerenes for which the decay parameters are known. The experimental conditions were nearly identical in the

Table 1. Parameters used for the Monte-Carlo simulation of the chain of ionisation and C_2 emission induced by laser (energies in eV and the values of A_i at 4000 K). The 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_{60}, C_{70} and C_2 [8].

Size	E_d	A_d (s^{-1})	E_d^+	A_d^+ (s^{-1})	E_i	A_i (s^{-1})
70	$\underline{\mathbf{9.7}}$	$\mathbf{1.7 \times 10^{20}}$	9.4	8.5×10^{19}	7.4	1×10^{15}
68	$\underline{8.6}$	2×10^{19}	8.6	2×10^{19}	7.1	5×10^{14}
66	$\underline{8.4}$		8.4			
64	$\underline{8.0}$		8.0			
62	$\underline{6.2}$	2×10^{17}	6.7	4×10^{17}		
60	**10.6**	$\mathbf{2.3 \times 10^{21}}$	10.1	1.2×10^{21}	7.6	1×10^{15}
58	8.4	2×10^{19}	8.4	2×10^{19}	7.1	5×10^{14}
56	8.6		8.6			
54	8.4		8.4			
52	8.4		8.4			
50	8.8		8.8			
<50	8.3		8.3			

two measurements, and we have reanalysed the C_{60} data with $x = 2.5$.

The Arrhenius parameters used in the Monte–Carlo simulation are given in Table 1. The dissociation energies for C_2 emission from non–magic fullerenes are close to the values derived from observation of the cut off of the decay rate by radiative cooling [6]. We use the same pre–exponential factor for C_2 emission as in the analysis of this experiment, $A_d = A_d^+ = 2 \times 10^{19}$ s^{-1}, except for C_{60}, C_{70} and C_{62} for which an exceptional level density for either the mother or the daughter molecule is taken into account. It may be argued that A_d should be smaller than A_d^+ because the polarisation interaction between C_2 and a fullerene ion should increase the cross section for attachment. As in [12], this has not been taken into account.

The ionisation energy is taken from measurements for C_{60} (7.6 eV) [17] and C_{70} (7.4 eV) [14] and the estimate $E_i = 7.1$ eV has been used for the non–magic fullerenes [12]. The pre–exponential factor, A_i, for ionisation is estimated from the cross–section for electron attachment by detailed–balance considerations [18]. A_i is proportional to T and the value at $T = 4000$ K is chosen to be 5×10^{14} s^{-1} for the normal fullerenes and twice as large for the magic molecules C_{60} and C_{70}, accounting roughly for the lower level density of the neutral molecules when there is a large HOMO–LUMO gap [12]. 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. The sum of the dissociation energies of the five molecules from C_{62} to C_{70} (underlined in Tab. 1) equals 40.9 eV and this agrees with the estimate (40.93 ± 0.54 eV) based on the heats of formation of C_{60}, C_{70} and C_2 [8].

From the comparison between experiment and modelling, we obtain the following Arrhenius parameters for the C_2 emission from C_{70}: $E_d = 9.7 \pm 0.3$ eV and $A_d = 1.7 \times 10^{20}$ s^{-1}. For C_{60}, the reanalysis leads to: $E_d = 10.6 \pm 0.3$ eV and $A_d = 2.3 \times 10^{21}$ s^{-1}. The pre–exponential factor is in both cases larger than the one generally assumed for fullerenes (2×10^{19} s^{-1}), by one order of magnitude for C_{70} and by two orders of magnitude for C_{60}. The power of photon emission at $T = 4000$ K is 1.5×10^5 eV/s for C_{70} and 6.9×10^4 eV/s for C_{60}. These values correspond to reduction by factors 1.4 and 2.6, respectively, relative to the radiation power predicted by the dielectric model without a gap [15]. These reductions are reproduced with a smooth lower cut off in the radiation spectrum at 1.6 eV for C_{70} and at 2.7 eV for C_{60}.

The error on the dissociation energy E_d for C_{70} given above reflects mainly an uncertainty of about 0.1 eV of the ionisation energy of C_{70} and an uncertainty of about 0.5 of the exponent n 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 pre–factor A_d is sensitive to many of the parameters; we have previously estimated the error to be on the order of a factor of four [12]. In addition, the experiment only determines the ratio of the A_d values for C_{70} and C_{68}, and the value for C_{70} given above is based on $A_d = 2 \times 10^{19}$ s^{-1} for C_{68}.

This work was supported by the Danish National Research Foundation through the research centre ACAP (Aarhus Center for Atomic Physics) and by an EU Research Training Network, contract HPRN-CT-2000-0002.

References

1. C. Lifshitz, Int. J. Mass Spectrom. **198**, 1 (2000)
2. S. Matt, O. Echt, P. Scheier, T.D. Märk, Chem. Phys. Lett. **348**, 194 (2001)
3. K. Hansen, O. Echt, Phys. Rev. Lett. **78**, 2337 (1997)
4. J. Laskin, B. Hadas, T.D. Märk, C. Lifshitz, Int. J. Mass Spectrom. **177**, L9 (1998)
5. P.E. Barran, S. Firth, A.J. Stace, H.W. Kroto, K. Hansen, E.E.B. Campbell, Int. J. Mass Spectrom. Ion Process **167/168**, 127 (1997)
6. S. Tomita, J.U. Andersen, C. Gottrup, P. Hvelplund, U.V. Pedersen, Phys. Rev. Lett. **87**, 073401 (2001)

7. S. Diáz–Tendero, M. Alcami, F. Martin, J. Chem. Phys. **119**, 5545 (2003)
8. K. Gluch, S. Matt–Leubner, O. Echt, B. Concina, P. Scheier, T.D. Märk, J. Chem. Phys. **121**, 2137 (2004)
9. J.U. Andersen, E. Bonderup, K. Hansen, J. Chem. Phys. **114**, 6518 (2001)
10. C.E. Klots, Z. Phys. D **20**, 105 (1991)
11. K. Hansen, Philos. Mag. B **79**, 1413 (1999)
12. S. Tomita, J.U. Andersen, K. Hansen, P. Hvelplund, Chem. Phys. Lett. **382**, 120 (2003)
13. J.U. Andersen, C. Gottrup, K. Hansen, P. Hvelplund, M.O. Larsson, Eur. Phys. J. D **17**, 189 (2001)
14. O.V. Boltalina, I.N. Ioffe, L.N. Sidorov, G. Seifert, K. Vietze, J. Am. Chem. Soc. **122**, 9745 (2000)
15. J.U. Andersen, E. Bonderup, Eur. Phys. J. D **11**, 413 (2000)
16. K. Mehlig, K. Hansen, M. Hedén, A. Lassesson, A.V. Bulgakov, E.E.B. Campbell, J. Chem. Phys. **120**, 4281 (2004)
17. J. de Vries, H. Steger, B. Kamke, C. Menzel, B. Weisser, W. Kamke, I.V. Hertel, Chem. Phys. Lett. **188**, 159 (1992)
18. J.U. Andersen, E. Bonderup, K. Hansen, J. Phys. B **35**, R1 (2002)