PHYSICAL REVIEW A **71**, 055201 (2005)

Molecular fusion of $(C_{60})_N$ clusters in the gas phase after femtosecond laser irradiation

M. Hedén, K. Hansen, and E. E. B. Campbell*
Dept. of Physics, Göteborg University, SE-41296, Göteborg, Sweden

(Received 29 December 2004; published 26 May 2005)

We report observation of molecular fusion of $(C_{60})_N^+$ clusters to form large fullerene molecules after excitation by 800-nm femtosecond laser pulses. The fused species decay by undergoing C_2 fragmentation. Such fragmentation behavior for excited clusters of fullerene molecules can be understood in terms of the energetics of molecular fusion as determined previously from fullerene-fullerene collision experiments. Within a certain excitation energy window, there is sufficient time for a substantial atomic rearrangement to take place within the clusters before they dissociate. Below this energy window there is not sufficient internal energy for molecular fusion to occur while above the energy window multiple ionization followed by breakup of the clusters dominates.

DOI: 10.1103/PhysRevA.71.055201 PACS number(s): 36.40.−c, 78.66.Tr, 82.30.Nr

Fullerenes have been the subject of extensive research since their discovery in 1985 and have, e.g., become favorite model systems for studying the dynamical and statistical behavior of highly excited molecules [1–3]. Studies involving both collisional and laser excitation have uncovered a wealth of interesting phenomena that have helped our understanding of the behavior of molecules with many degrees of freedom and have contributed to the development of models and ideas that are now being applied to more complex molecular systems. Recently, gas phase studies have been concerned with probing the mechanisms and time scales for ionization and energy transfer within the fullerene molecules [4–6]. In this paper we extend such studies to the interaction of clusters of fullerene molecules [7,8] with intense femtosecond laser radiation. In contrast to collision experiments with highly charged ions where the fullerene clusters are seen to evaporate monomer fullerene units [9], femtosecond laser excitation can induce an extreme, ultrafast rearrangement of the atoms to form a more stable large fullerene molecule before the parent cluster is completely dissociated. This, perhaps intuitively unexpected, observation can be rationalized in terms of our knowledge of the behavior of highly excited fullerenes and could have consequences for controlled laser-induced modification of carbon-based nanomaterials.

The clusters of fullerene molecules are produced in a gas aggregation source, in which the fullerenes are sublimed from an oven at approximately 500 °C and cooled via collisions with He gas in contact with a liquid-nitrogen reservoir (77 K) [10]. The temperature measured at the exit nozzle, expected to be the highest temperature in the gas aggregation source, was 106 K. The neutral fullerene cluster beam that expands sonically through this nozzle is expected to be slightly colder. The cluster beam passes two differential pump stages before entering the ionization chamber of a time-of-flight mass spectrometer. The clusters are ionized by a femtosecond laser (200 fs, 800 nm), focused to produce a laser fluence at the interaction region in the range of a few J/cm^2. After ionization, the product ions were accelerated to 4 keV and entered a reflectron optimized for time resolution. The ions were detected with a dual channel plate detector biased to 2.5 keV.

Figure 1 shows a comparison between the ions produced from the beam emerging from the aggregation source and that from a normal "hot" effusive C_{60} source where no clusters are present. The spectra were obtained with exactly the same laser and mass spectrometer settings on the same day. The laser fluence is estimated to be in the range 5–10 J/cm^2. The absolute intensities of the two spectra are not directly comparable but the relative distributions are. The spectra are dominated by singly charged fragments from fullerenes, showing the typical bimodal mass distribution. Both spectra also contain doubly charged C_{60}^{2+} and fullerenelike doubly

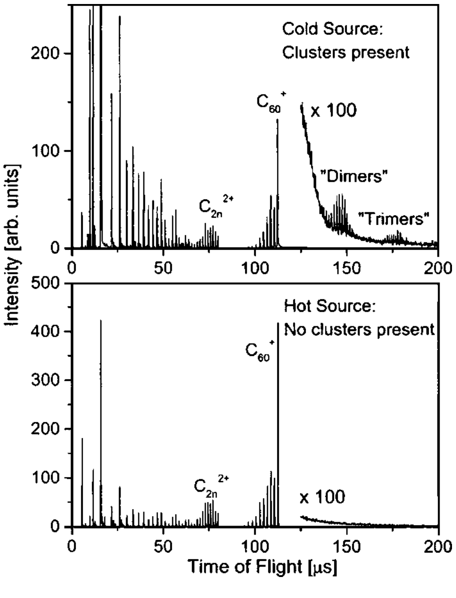

FIG. 1. Time-of-flight mass spectra obtained from femtosecond (800 nm, 200 fs) excitation/ionization of (upper) a molecular beam, cooled to below 100 K, containing clusters of fullerene molecules, (lower) a standard fullerene effusive source heated to a temperature of 520 °C. Note that there is a significant contribution of pump oil in the upper spectrum for arrival times below 50 μs; however, the intensity of the small fragments from the fullerenes is still significantly higher than in the lower spectrum.

---

*Author to whom correspondence should be addressed. Email address: eleanor.campbell@fy.chalmers.se

1050-2947/2005/71(5)/055201(4)/$23.00

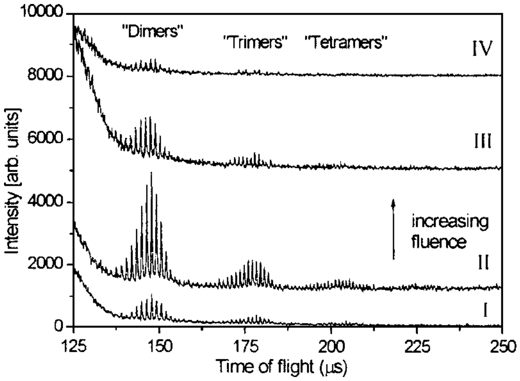

FIG. 2. Laser fluence dependence of the high mass ions corresponding to fragments from coalesced fullerenes from van der Waals bound clusters. The fragment ion distributions corresponding to each parent cluster ion mass do not change significantly with changing laser fluence.

charged fragments at a flight time of around 75 μs, as is expected for fullerene ionization under the laser conditions used in this study. There are some differences in the spectra. The upper spectrum, obtained in the presence of clusters of fullerene molecules, shows a much higher proportion of small, singly charged carbon fragments compared to the spectrum from C_{60} monomers. There is an unresolved tail on the $C_{60}{}^{+}$ mass peak extending to longer flight times, and clearly resolved mass peaks can be seen superimposed on this. These heavy ions appear in well-separated groups where the mass peaks within each group are separated by 24 units (C_2). The highest mass observed in each case is slightly lower than the corresponding $(C_{60})_N$ cluster mass. The unresolved tail has no connection to the well-known delayed ionization behavior of C_{60}. This is only observed for laser pulse durations longer than the time scale for electron-phonon coupling and is therefore not significant for excitation with 200-fs laser pulses [4]. This is confirmed in the mass spectrum from the hot cluster source [Fig. 1(b)]. Instead, the $C_{60}{}^{+}$ tail is due to the fragmentation of cluster ions to produce $C_{60}{}^{+}$ ions while the parent cluster species are still in the extraction region of the mass spectrometer.

Figure 2 shows a series of mass spectra, concentrating on the region beyond $C_{60}{}^{+}$, that have been obtained for different values of the laser fluence. Spectrum III is identical with the spectrum in Fig. 1. It is interesting to note that the distribution of masses associated with each cluster "parent" does not change significantly as the laser fluence is increased. There is a very slight shift in the distribution towards smaller masses as the fluence increases but the range of masses stays basically the same. A more detailed look at the mass distribution for each cluster size is given in Fig. 3. The data were obtained for a laser fluence close to but slightly lower than that used for spectrum II in Fig. 2. This is the condition where we have obtained the maximum intensity of the cluster signals.

The mass spectra in Figs. 2 and 3 are quite different from those obtained in collision experiments between highly charged ions and neutral clusters of fullerene molecules [9]. In this case, as for the situation where the clusters of fullerenes are excited with ns laser pulses [10], the only observed fragmentation channel is the evaporation of monomer C_{60} molecules. This can be understood if one considers the mechanisms and time scales involved in the different experiments. In the collision experiments, electrons are extracted from the clusters in large impact parameter collisions where very little energy is transferred to internal degrees of freedom of the clusters. The mass spectrum consists of singly and doubly charged clusters of fullerenes with the smallest detected doubly charged cluster for $N=5$. In ns laser experiments, where the photon energy is less than the ionization potential of the cluster, there is sufficient time between the absorption of consecutive photons for the electronic excitation energy to be transferred to vibrational degrees of freedom. The binding energy of the van der Waals bound clusters of fullerenes is relatively low and one can easily absorb sufficient energy to evaporate monomer units before sufficient energy is absorbed to cause thermal ionization of the clusters. In the present experiments, a large amount of energy is absorbed by the electrons on a very short time scale (200 fs). From earlier experiments with C_{60} we know that for an excitation time scale on the order of 200 fs the predominant ionization mechanism of the molecule is the thermal emission of electrons from the equilibrated hot electron bath [4,5]. This occurs before a significant amount of energy is transferred to vibrational degrees of freedom. For excitation energies in the range of a few tens of eV (typical for leading to subsequent C_2 fragmentation on a microsecond time scale) the rate constant for electron emission has been estimated to be on the order of $10^{15}\ s^{-1}$ [5]. We can assume that a similar ionization mechanism is dominating in the present cluster experiments. If so, the internal excitation energy needed to induce fs thermal electron emission from the hot electron bath will be more than sufficient to cause dissociation of the cluster when subsequently transferred to nuclear degrees of freedom after the ionization has occurred. We also know from the collision experiments [9] that small multiply charged cluster ions are unstable so that any multiply charged clusters in our experiment are expected to dissociate into singly charged species and monomers and will not be detected. We are therefore only sensitive to any surviving (on a microsecond time scale) small singly charged clusters (our detection efficiency discriminates against large masses). The mass spectra in Figs. 1–3 clearly show that C_2 emission has occurred from singly charged van der Waals bound clusters of fullerenes. This implies that a fast rearrangement of the atoms in the cluster to form a more stable fullerenelike coalesced or fused structure has to happen before the monomer units of the cluster ion can evaporate. Fullerene coalescence or molecular fusion has been observed previously, e.g., when a high density of excited fullerenes is present during laser vaporization from a substrate [11] or in single collision experiments between fullerenes [12]. From the latter we know that a high energetic barrier to fullerene fusion exists. For the fusion of two C_{60} molecules to form a C_{120} the threshold energy is approximately 80–85 eV [1,13]. Therefore in order to detect such a fused species in the present experiments, the parent singly charged fullerene dimer must have at least this amount of internal excitation energy. In addition to the threshold energy, there will also be the energy released in the molecular fusion process. This can be up to 20 eV for the

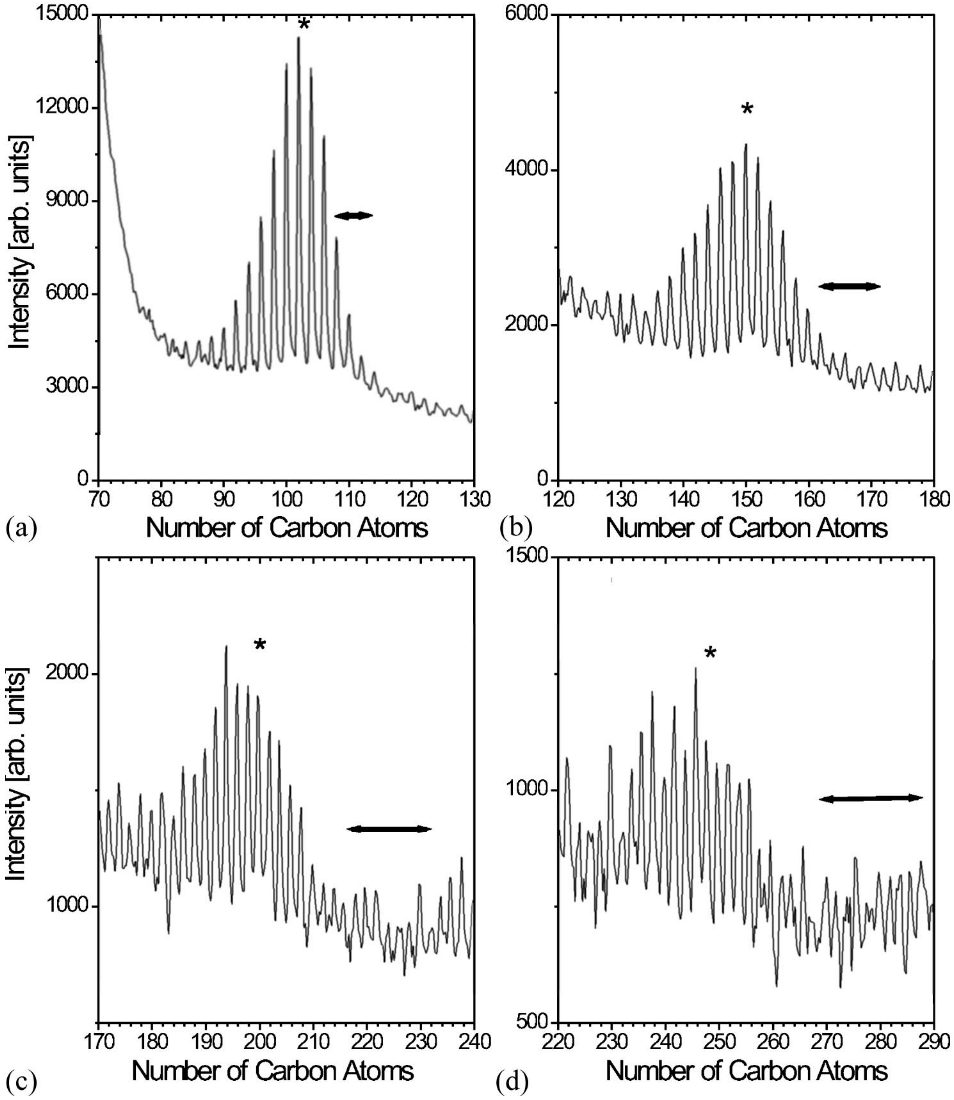

FIG. 3. Expanded regions of the mass spectrum around the fragment groups coming from the (a) dimer, (b) trimer, (c) tetramer, and (d) pentamer cluster parent. The spectrum was obtained for a laser fluence close to that used to obtain spectrum II in Fig. 2. The horizontal arrows indicate the maximum fragment ion size that can be expected in the mass spectrum considering the energetics of the fullerene fusion mechanism. The asterisk marks the expected maximum in the fragment ion distributions assuming that the internal energies of the higher clusters scale with the number of fullerenes (see text for details).

dimer [14]. We cannot expect an intact fused dimer molecule with an internal energy of 85–105 eV to survive the 4-μs time window of the extraction stage of the mass spectrometer. Instead it will fragment by emitting C_2 molecules, as we observe in the mass spectra. One would perhaps intuitively expect that such a high internal energy will lead to a very rapid evaporation of the monomer species before extensive atomic rearrangement can take place. However, rough estimates indicate that even for such high internal energies it would take a time scale on the order of ps for the fullerene molecules to leave the cluster. Molecular-dynamic simulations [15] indicate that the necessary atomic rearrangement to induce molecular fusion can occur on a time scale of a few hundred fs. The threshold energy for fusion plus the energy released in the fusion reaction can give us an upper bound for the size of fragments that can be detected. The C_2 dissociation energy for large fullerene cations seems to saturate at a value of around 8.5 eV [16,17] with the value of the pre-exponential term in the Arrhenius fragmentation expression estimated to be 2×10^{19} s^{-1} [18]. If we assume that the last step in the fragmentation chain takes the longest time and is related to the time window of our extraction stage, then we can estimate the expected fragment size for a given internal energy. For the fused dimer this gives us $N=108-114$ for an internal energy range of 85–105 eV. This range is shown by the horizontal arrow in Fig. 3(a) and is in excellent agreement with the experimental observations. We can extend this argument to the larger clusters by simply scaling the threshold energy for fusion by the size of the cluster $(85N/2\ \text{eV})$ and considering the potentially larger release of energy when the fused molecule is formed. The results are shown by the horizontal arrows in Figs. 3(b)–3(d) and again are in good agreement with the observations.

Similarly, we can estimate the internal energy of the dimer ion that leads to the maximum of the fragment distribution. For the spectrum in Fig. 3 this amounts to 136.5 eV. The absorbed photon energy was therefore approximately $136.5+7.6-10=134.1$ eV. For this estimate we have assumed that half of the additional binding energy (assuming the most stable dimer configuration) was released during the reaction and have accounted for the energy needed to remove an electron from one C_{60}. This amounts to roughly 67 eV absorbed per C_{60} monomer and is in surprisingly good agreement with estimates based on average C_{60} absorption cross sections extracted from photoemission experiments [5]. Assuming that the absorption cross section per monomer does not significantly change as the cluster size is increased, we can estimate the most probable internal energy of the larger clusters and therefore the maxima of the fragment distributions. This is indicated by the asterisks in Fig. 3.

All that remains is to explain the cutoff in the fragment distribution on the low mass side. As can be seen in Fig. 2, this does not change significantly as the laser fluence is increased. We believe that this is due to the competition with multiple ionization of the clusters as the amount of absorbed energy is increased, leading to increased decay into excited monomers. The lower mass limit is therefore expected to be determined by the probability for double ionization of the parent species. More detailed experiments and modeling are underway to test this hypothesis.

The experimental fragment ion distributions for each precursor cluster of fullerene molecules can be rather well fitted by Poisson distributions. We summarize our findings in Fig. 4 by plotting the mean number of C_2 units lost (squares) and from our model considerations discussed above, assuming that the photoabsorption cross section scales linearly with the number of fullerene monomers in the precursor cluster (circles, also indicated by the asterisks in Fig. 3). The agreement is very good, with a linear dependence on precursor size in each case, although the model considerations predict a slightly smaller slope. The shaded area is given by ±2 standard deviations, obtained from the experimental fragment ion distributions. The lower dashed line gives our predictions of the lowest observable number of lost C_2 units (or highest observable fragment ion mass) considering the energetic barrier to molecular fusion, and assuming, as above, that half of the additional binding energy was released during the reaction. This corresponds to the center of the horizontal arrows in Fig. 3. Below this line, the precursor cluster does not have sufficient internal energy to induce molecular fusion on the hundred-femtosecond time scale and the cluster dissociates before fusion can take place. This correlates rather well with the high fragment size cutoff in the experimental distributions and provides strong support for our model. The low fragment size cutoff is more difficult to model quantitatively but can be qualitatively understood in terms of the competition with multiple ionization of the precursor cluster. Further extensive modeling and experiment are needed to clarify the details of this competition and studies are underway.

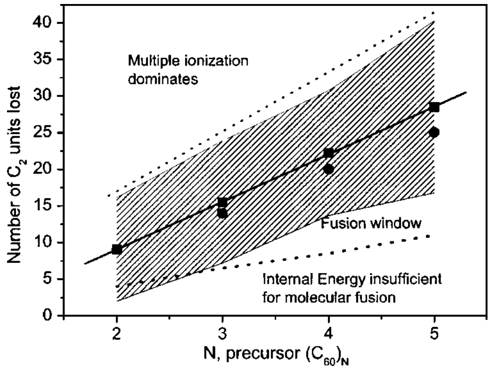

FIG. 4. Number of C_2 units lost as a function of precursor fullerene cluster size. Squares and full line: mean number of lost C_2 units obtained from fitting the experimental data with Poisson distributions. The shaded area indicates ±2 standard deviations obtained from the experimental data. Circles: Calculated maxima in the fragment distributions assuming that the photoabsorption cross sections scale linearly with the number of fullerene monomers in the precursor, normalized for $N=2$. Lower dashed line: Minimum expected number of C_2 units lost considering the molecular fusion mechanism. Upper dashed line indicates the transition to where multiple ionization dominates, leading to the disappearance of the singly charged, large fragment ions in the mass spectrum.

Financial support from Swedish National Research Council (VR) and the K. & A. Wallenberg Foundation (fs laser system) is gratefully acknowledged.

---

[1] E. E. B. Campbell, *Fullerene Collision Reactions* (Kluwer Academic, Dordrecht, 2003).
[2] E. E. B. Campbell and R. D. Levine, Annu. Rev. Phys. Chem. **51**, 65 (2000).
[3] J. U. Andersen, E. Bonderup, and K. Hansen, J. Phys. B **35**, R1 (2002).
[4] E. E. B. Campbell, K. Hansen, K. Hoffmann, G. Korn, M. Tchaplyguine, M. Wittmann, and I. V. Hertel, Phys. Rev. Lett. **84**, 2128 (2000).
[5] K. Hansen, K. Hoffmann, and E. E. B. Campbell, J. Chem. Phys. **119**, 2513 (2003).
[6] V. R. Bhardwaj, P. B. Corkum, and D. M. Rayner, Phys. Rev. Lett. **93**, 043001 (2004).
[7] T. P. Martin, U. Näher, H. Schaber, and U. Zimmermann, Phys. Rev. Lett. **70**, 3079 (1993).
[8] K. Hansen, H. Hohmann, R. Mueller, and E. E. B. Campbell, J. Chem. Phys. **105**, 6088 (1996).
[9] B. Manil *et al.*, Phys. Rev. Lett. **91**, 215504 (1993).
[10] K. Hansen, R. Mueller, H. Hohmann, and E. E. B. Campbell, Z. Phys. D: At., Mol. Clusters **40**, 361 (1997).
[11] C. Yeretzian, K. Hansen, F. D. Diederich, and R. L. Whetten, Nature (London) **359**, 44 (1992).
[12] F. Rohmund, E. E. B. Campbell, O. Knospe, G. Seifert, and R. Schmidt, Phys. Rev. Lett. **76**, 3289 (1996).
[13] E. E. B. Campbell, A. Glotov, A. Lassesson, and R. D. Levine, C. R. Phys. **3**, 341 (2002).
[14] G. Seifert, R. Gutierrez, and R. Schmidt, Phys. Lett. A **211**, 357 (1996).
[15] F. Rohmund, A. V. Glotov, K. Hansen, and E. E. B. Campbell, J. Phys. B **29**, 5143 (1996).
[16] S. Tomita, J. U. Andersen, C. Gottrup, P. Hvelplund, and U. V. Pedersen, Phys. Rev. Lett. **87**, 073401 (2001).
[17] P. E. Barran, S. Firth, A. J. Stace, H. W. Kroto, K. Hansen, and E. E. B. Campbell, Int. J. Mass Spectrom. Ion Processes **167/168**, 127 (1997).
[18] J. Laskin, B. Hadas, T. D. Märk, and C. Lifshitz, Int. J. Mass Spectrom. Ion Processes **177**, L9 (1998).