Competition between Fission and Intra-Cluster Fusion in Highly Excited Fullerene Clusters

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Abstract. The occurrence of intra-cluster fusion of fullerene molecules inside van der Waals bound fullerene clusters can be observed following femtosecond laser excitation. We show that the fusion reaction competes with the fission of multiply charged clusters. Energetic barriers to the reaction of at least 85 eV have to be overcome, similar to the energetic barriers to molecular fusion observed in fullerene ion–neutral fullerene collision experiments.

INTRODUCTION

Since fullerenes were discovered in 1985, they have proved to be very interesting model systems for studying the dynamics of particles with many degrees of freedom. Due to the ease of handling the molecules and the possibility of easily obtaining molecular beams of fullerenes, they have provided an attractive and convenient stepping-stone from the world of atomic and simple molecular collisions to large (bio)molecules.[1] There are many interesting aspects of the behavior of excited fullerenes. One of the unusual reactions that has been studied is the molecular fusion of two fullerenes that can be seen to occur in single collisions between fullerene ions and neutral fullerenes at center-of-mass collision energies of around 100–200 eV.[2,3] The energetic barrier for this reaction is very high (ca. 85 eV for the fusion of C_{60}^+ and C_{60} to form a highly excited C_{120}^+), and there are some interesting aspects of the dynamics, not all of which are completely understood.[4]

Clusters of atoms or molecules have been proposed as interesting systems for studying the behavior of matter under extreme conditions of temperature and pressure.[5] By colliding clusters with a substrate, it should be possible to observe exotic reaction products due to the extreme conditions that occur within the cluster on the short (fs) timescale before it dissociates.[6] Extreme plasma conditions have been produced in the interaction of atomic clusters with intense ultrashort laser pulses, providing intense X-ray pulses[7] or even nuclear fusion reactions.[8] Much less has been studied in the laser excitation regime prior to plasma ignition, where high temperature and pressure conditions within the cluster on the femtosecond to picosecond timescale after excitation could be conducive to the occurrence of exotic chemical reactions, and more akin to the conditions that can occur on cluster–surface impact. In this report we explore what can happen when clusters of fullerenes are exposed to intermediate intensity femtosecond laser pulses (ca. 10^{12}–10^{13} W/cm^2). We show that the occurrence of intra-cluster fusion of fullerenes within these clusters competes with a cluster fission mechanism. By analyzing the fragment ion distribution of the fused species, it can be determined that the same energetic threshold for the fusion reaction needs to be overcome for the intra-cluster fusion as for the single-collision reaction.

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EXPERIMENTAL

Clusters of fullerene molecules are produced in a gas aggregation source, in which fullerenes (purified C_{60} or C_{70}) are sublimed from an oven at approximately 500 ºC and cooled via collisions with He gas in contact with a liquid-nitrogen reservoir (77 K). The temperature measured at the exit nozzle, and expected to be the highest temperature in the gas aggregation source, is 106 K. 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 either a nanosecond F_2 excimer laser (photon energy 7.9 eV) or by a Ti:sapphire femtosecond laser (photon energy 1.55 eV, 200 fs pulse duration), focused to produce a laser fluence at the interaction region in the range of a few J/cm^2. After ionization, the product ions are accelerated to 4 keV and enter a reflectron before being detected with a dual channel plate detector biased to 2.5 kV. The F_2 laser photons are sufficiently energetic to ensure single-photon ionization of the clusters and thus give a good indication of the initial neutral cluster distribution in the beam without significant fragmentation. It should, however, be noted that the detection efficiency of the clusters decreases strongly with increasing cluster size,[9] so that the measured mass spectra produce a skewed distribution exaggerating the contribution of the smallest clusters. The neutral cluster size distribution can be changed by changing the pressure of He gas in the aggregation source.

RESULTS AND DISCUSSION

Experimental Mass Distributions

Figure 1 shows a series of $(C_{60})_N$ cluster mass spectra obtained for different He gas pressures in the cluster source. The spectra were obtained by single-photon ionization of the neutral clusters using the F_2 excimer laser. The spectra are smooth, without any prominent "magic numbers" indicating that the cluster ions are relatively cold and do not undergo major fragmentation after ionization.[10] However, the small tail to the high-mass side of the monomer ion peak does indicate the presence of some photo- or collisional fragmentation of cluster ions down to the monomer species. The peak of the monomer ion intensity remains approximately constant as the He pressure is increased from 8 mbar to 30 mbar, but the cluster distribution is seen to change significantly over this range of source stagnation pressures. The maximum detected cluster signal is found at a He pressure of 18 mbar. As the pressure is increased beyond this, the detected cluster signal decreases but the mass distribution moves to much higher masses and thus the detection efficiency decreases.[9] The inset in the lowest spectrum in Fig. 1 shows that there is a large unresolved signal corresponding to very heavy cluster ions for the highest He pressure investigated (30 mbar).

Figure 2 shows the corresponding mass spectra when the clusters are ionized with the femtosecond laser. No

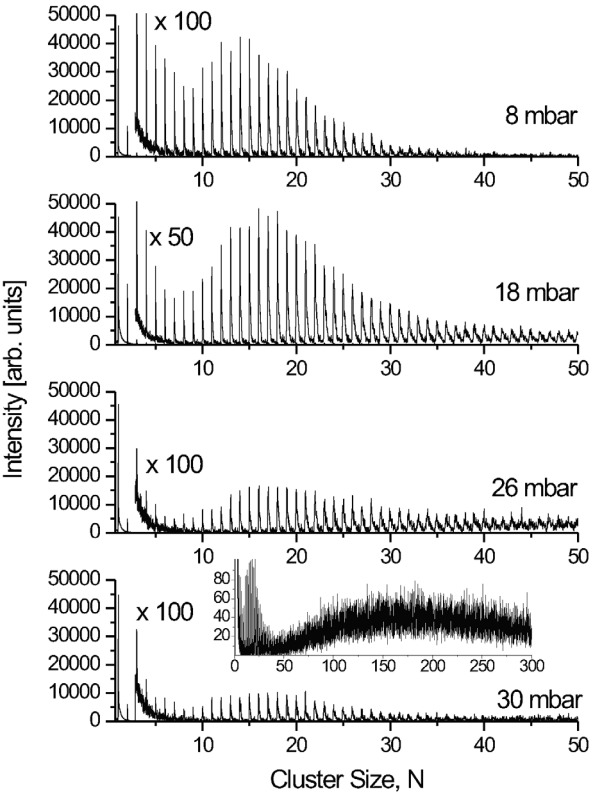

Fig. 1. Mass spectra obtained from single photon F_2 excimer laser photoionization of $(C_{60})_N$ clusters produced in a gas aggregation source for different He cooling gas pressures (measured at the gas inlet).

intact cluster ions can be detected. As reported previously,[11,12] we see groups of mass peaks shifted downwards in mass from the corresponding cluster parent mass. The separation between the mass peaks corresponds to C_2, strongly indicating that they arise from evaporative decay of a larger fullerene-like molecule. The emission of C_2 is a very characteristic signature of fullerene fragmentation; other carbon-containing molecules are much more likely to fragment by emitting large ring-like fragments, C_3 or carbon atoms.[13,14] Similar spectra are obtained from $(C_{70})_N$ clusters,[12] but in this case the observed mass distributions are shifted to higher masses. This is illustrated in Fig. 4, measured with a source He pressure of 30 mbar.

The groups of mass peaks lying to the high mass side of the monomer ion in the femtosecond laser mass spectra have been interpreted previously as being due to molecular fusion of the fullerene molecules in the clusters to form larger fullerenes.[11,12] It is possible to clearly observe up to four groups of mass peaks, corresponding to fragments from a fused dimer, trimer, tetramer, and pentamer.[11] The fragment ion mass groups are characteristically narrow, and the mass distributions do not change

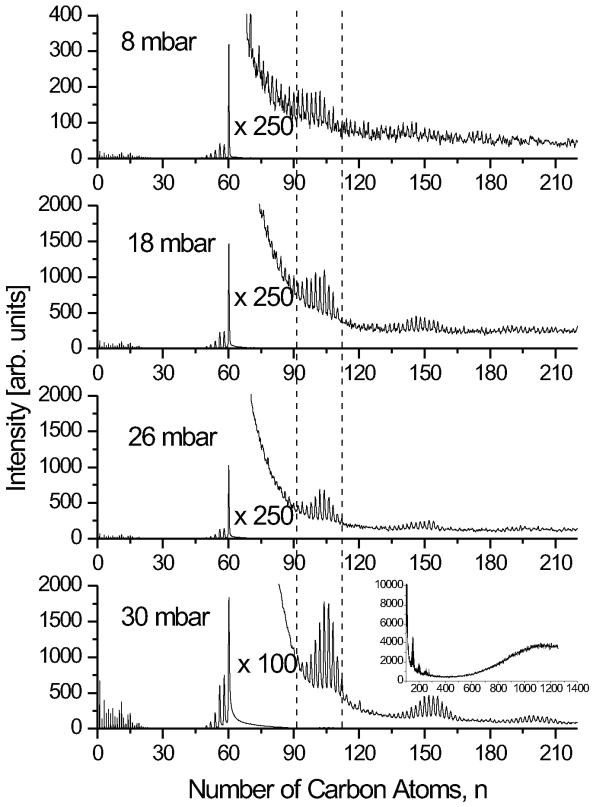

Fig. 2. Mass spectra obtained from 800 nm, 200 fs laser ionization of $(C_{60})_N$ beams produced under the same source conditions as used for the spectra in Fig. 1.

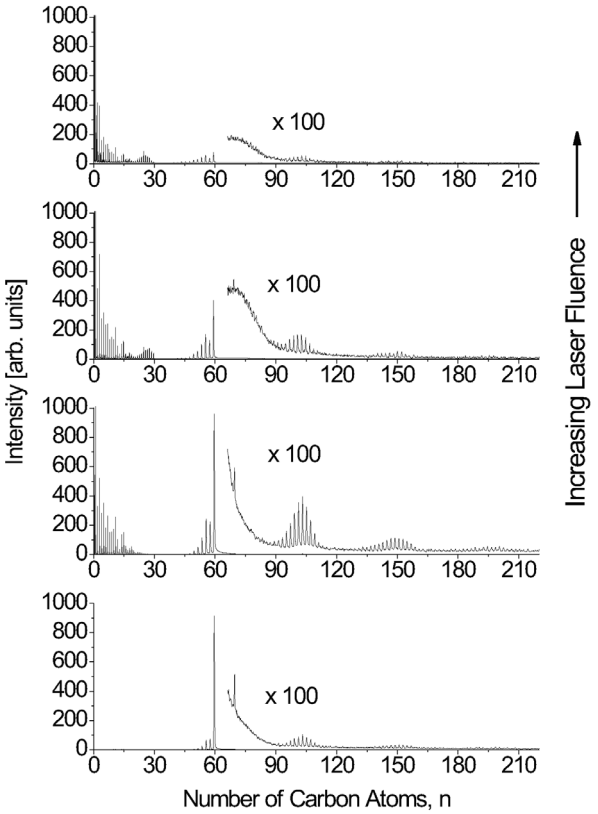

Fig. 3. Mass spectra obtained from 800 nm, 200 fs laser ionization of $(C_{60})_N$ clusters produced under identical cluster source conditions but for different laser intensities.

significantly with source pressure (Fig. 2) or ionizing laser fluence (Fig. 3). In particular, the high mass cut-off is remarkably constant. The distribution does, however, seem to broaden slightly towards smaller masses for low He pressures (i.e., small initial cluster distribution). This effect is more noticeable for C_{70}.[12] From considering the spectra in Figs. 1 and 2 it is obvious that there is not a strict one-to-one correspondence between the intensity of, e.g., the neutral dimer cluster and the intensity of the fused dimer fragmentation peaks. As the He pressure (and hence the average neutral cluster size) increases, there is a contribution to both the monomer ion peak intensity and the intensities of the fused fragment ion peaks in the femtosecond laser mass spectra coming from larger clusters.

High Mass Cutoff

The high mass cutoff of the fragment peak distributions can be well explained by considering the energetics of the molecular fusion process. Fusion of fullerenes has been observed previously in experiments in which highly excited fullerenes are desorbed from fullerene films using intense ns laser pulses,[15] or in experiments in which fullerene ions were collided with a fullerene

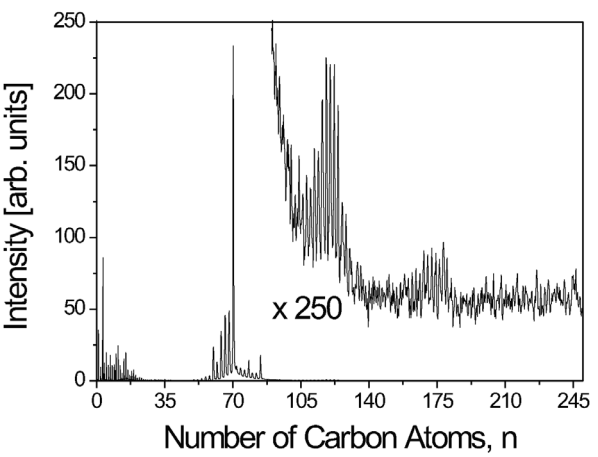

Fig. 4. Mass spectra obtained from 800 nm, 200 fs laser ionization of $(C_{70})_N$ clusters

film at an energy of 275 eV.[16] In more recent years it has also been possible to fuse chains of fullerenes that have been inserted inside single-walled nanotubes in order to form double-walled nanotubes by heating at elevated temperatures (1200 ºC for a few hours).[17] The most detailed studies of fullerene fusion, and the ones

most relevant for the present discussion, were a series of studies of the collision energy dependence of molecular fusion in single-collision experiments between singly-charged fullerene ions and neutral fullerenes.[1–4] It was found that there is a narrow collision energy window in which the fullerenes can form a metastable compound fullerene-like species that stabilizes by undergoing C_2 emission. The threshold energy for the formation of the fused product was determined for $C_{60}^+ + C_{60}$, $C_{60}^+ + C_{70}$, $C_{70}^+ + C_{60}$, and $C_{70}^+ + C_{70}$ collisions and found to scale with the number of carbon atoms in the collision, from 85 ± 5 eV for $C_{60}^+ + C_{60}$ to 100 ± 10 eV for $C_{70}^+ + C_{70}$.[1] Note that these values are the experimentally determined thresholds obtained from fitting the data to a simple steric model plus an estimated additional 25 eV initial vibrational excitation energy of the projectile ion and the neutral target. Other model considerations give similar values.[4] If we assume that the energetic threshold for the femtosecond laser-induced intra-cluster fusion, observed in the present studies, is the same as that observed in the collision experiments, then it is possible to estimate the upper limit for the fragment mass distributions corresponding to the different cluster precursors. This was reported previously[11,12] and the agreement was very satisfactory. For example, the molecular fusion of a singly-charged $(C_{60})_2^+$ dimer cluster should occur if the cluster has a total energy of at least 85 ± 5 eV. The relaxation energy that can be expected when a fullerene-like C_{120}^+ ion is formed from the two fullerenes lies in the range of 0–20 eV.[18] Therefore the minimum internal energy after fusion takes place will be in the range of 80–110 eV. Since the experimental time window for extracting the ions into the mass spectrometer is known, we can estimate how much fragmentation of the highly excited C_{120}^+ will take place before the fragment mass spectrum is determined. To do this we assume fragmentation takes place via sequential C_2 emission that can be described using an Arrhenius form for the fragmentation rate constant, with a frequency factor of 2×10^{19} s^{-1} [19] and a dissociation energy of 8.5 eV for the large fullerene ions.[20] The value of the frequency factor may seem unreasonably large, but it is a value that, together with the high dissociation energy, is consistent with the vast majority of experimental results.[21] Such an estimate leads to a maximum detectable fragment ion in the range of C_{108}^+ to C_{118}^+, consistent with the experimental observations (high mass cutoff at C_{114}^+, Fig. 2). Although the uncertainties in the threshold energy and the estimate of the relaxation energy are large, the comparison between the results for the dimer fragment ions from C_{60} and C_{70},[12] as well as the trend observed in the comparison of the dimer, trimer, tetramer, and pentamer fragment distributions for C_{60},[11] provide convincing support for the interpretation of the high mass cutoff in terms of a minimum excitation energy needed to overcome the energetic barrier to the fusion reaction. The likelihood of detection of fusion fragments decreases with increasing cluster size since the energetic barrier for complete cluster fusion rapidly becomes prohibitively high. However, the presence of much larger neutral clusters in the original beam can contribute to the intensity of the dimer (or trimer, etc.) fusion fragments (as seen in Fig. 2) by being precursors of singly charged dimer fragments that can subsequently undergo molecular fusion.

In order to explain the other experimental observations, such as the sharp cutoff on the low mass side, the independence of the fragment ion distribution on gas pressure or laser fluence, and the relatively small intensity of the fusion fragment mass peaks compared to the monomer ion peak, we consider a simple model that takes into account the competition between the fusion reaction and multiple ionization of the clusters. We will assume that multiply-charged clusters immediately fragment before fusion can take place (i.e., sub-ps). We will also consider the contributions of clusters up to N = 5 for the production of a singly-charged dimer fragment and suppose that fusion takes place if the internal energy of the dimer ion exceeds the energetic threshold for fusion. We do not consider that the main effect leading to the fusion reaction is recoil within the clusters due to a Coulomb explosion of singly-charged monomer species (we do not observe any doubly-charged monomers under the laser excitation conditions reported in this paper), since the kinetic energy released in such a process is only on the order of an eV.[22]

Competition Between Multiple Ionization and Intra-Cluster Molecular Fusion

It is known from collision experiments with highly charged ions that doubly-charged fullerene clusters $(C_{60})_N^{2+}$ are unstable for $N < 5$.[23] We do not observe any clear signal from doubly- or more highly-charged species within the range where we detect the singly-charged fragments from fusion products. We therefore assume that any multiply-charged small clusters will be unstable and will rapidly dissociate into singly-charged species before the fusion reaction can take place. The ionization of fullerene monomers has been studied in detail experimentally for conditions similar to those used in the present study. For visible or near IR excitation with ps or ns laser pulses the dominant ionization mechanism is seen to be thermionic electron emission from vibrationally hot molecules.[24] This is in contrast to excitation with near-IR (800 nm) photons with 200 fs duration laser pulses, as used in the present study, where the dominant ionization mechanism for fullerene molecules has been

shown to be thermal ionization from the hot electronic subsystem, before coupling of the electronic energy to vibrational modes takes place.[25] The ionization behavior with respect to electron energy distributions, total ion yields, ratio of charge states, etc., is well understood in terms of a simple model.[26] The model involves transient heating of the valence electrons, which, due to the small electronic heat capacity, are heated to very high temperatures and emit electrons quasi-thermally on very short timescales (fs) before the energy is coupled to the vibrational modes and the excitation energy is fully dissipated. We assume that the ionization of the fullerene clusters is most likely to proceed with the same mechanism as the ionization of the monomer.

In order to calculate ionization yields for the clusters assuming this mechanism, some information concerning the properties of the fullerene clusters is needed. One is the level densities, i.e., the number of states in a small energy interval around E. The other is the ionization energies, which play the role of the activation energies in the ionization process. There is no information currently available in the literature concerning the ionization energies of the fullerene clusters, so we will make the rather rough, simplifying assumption that the charge state of a cluster arises from the ionization of independent monomers in the cluster. This will lead to an overestimation of the yield of multiply-charged clusters (since the true double and higher ionization potential of the clusters is likely to be higher than the first ionization energy of the monomer species).

The calculation proceeds as follows: First, we sum over all distributions of the numbers of photons absorbed by the clusters, from zero to 100 photons per monomer molecule. Each of these distributions gives a yield of total charge, determined by the ionization probability of each molecule when a given number of photons is absorbed. The charge yield is calculated according to the procedure described in detail by Hansen et al.[26] After ionization, the ionization yield for a given cluster is stored as a function of total charge and total energy. The total energy is the total absorbed energy minus the ionization energies of the charge states produced. This gives different energies for, e.g., the situation where two singly-charged monomers are formed in the cluster versus the situation where one monomer unit is doubly ionized. The first gives a total energy of $nh\nu - 2IE_1$ and the second $nh\nu - IE_1 - IE_2$, where n is the number of photons absorbed, $IE_1 = 7.6$ eV, and $IE_2 = 11.4$ eV.

After the ionization we assume that all charge is equally distributed in the cluster, justified by the high mobility of the electrons within the clusters.[23] The charge of the cluster is then reduced to unity by loss of singly-charged monomers, which each also carry away

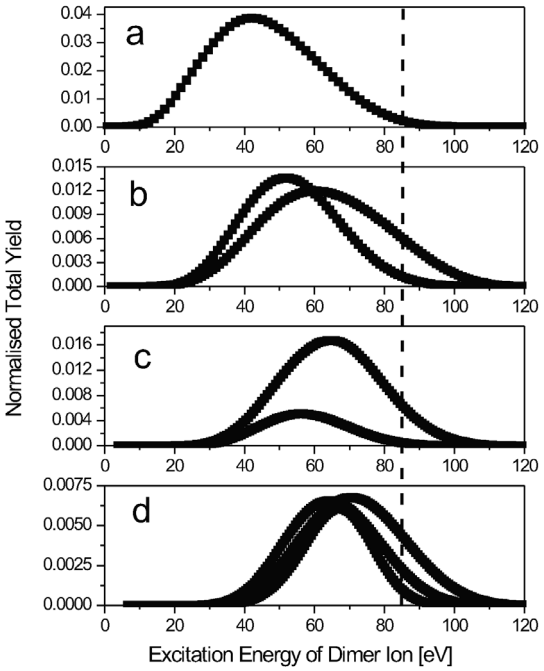

Fig. 5. Internal excitation energy dependence of the yield of singly-charged dimer ions for different neutral cluster precursors $(C_{60})_N$. (a) N = 2. (b) N = 3. (c) N = 4. (d) N = 5. The results have been normalized to the same total yield for each precursor cluster species. Details of the calculation are given in the text.

1/N of the total excitation energy left in the cluster after ionization. This is all assumed to happen rapidly, i.e., before fusion takes place. This process leaves us with a singly-charged cluster with some internal excitation energy E_0. There will be a distribution of excitation energies for cluster ions of a given size. This is illustrated in Fig. 5 for the singly-charged dimer ions produced from neutral clusters with N = 2, 3, 4, and 5. In this plot, the total dimer ion yield has been normalized for each neutral cluster precursor. Note that for N = 3–5 there is more than one route to produce a singly-charged dimer, as discussed above. If the excitation energy is less than the fusion barrier of 85 eV, no fusion will occur and the cluster will just fragment at some later stage into a neutral and a singly-charged C_{60}. These may or may not then later fragment or undergo delayed (thermionic) ionization, depending on the internal energy captured by the molecule during the decay of the cluster. Those dimer ions that have an internal energy higher than the fusion barrier will undergo fusion to form an excited C_{120}^+. To calculate the degree of fragmentation of this product, we use the relation

$$E_0 + \Delta E_{Fusion} - \Delta C_2 \times 8.5\ eV = E(\Delta C_2) \qquad (1)$$

where E_0 is the initial energy before fragmentation, ΔE_{Fusion} is the energy released in the fusion process, 8.5 eV is an estimate of the C_2 dissociation energy of the fusion products, and ΔC_2 is the number of C_2 units lost. $E(\Delta C_2)$ is the energy content after fragmentation. A calculation, including the finite heat bath correction,[27] gives

$$E(\Delta C_2) = \frac{8.5eV}{\ln(At)}(3\times 120 - 7 - 6\Delta C_2) - (E_Z - 8.5\text{eV}/2) \quad (2)$$

where A = 2 × 10^{19} s^{-1} and t = 1 μs (time before mass separation). The term E_Z is the zero-point energy of the vibrations in the molecule, for which we use the value 9.9 eV, which is the value for C_{120} scaled from the C_{60} vibrational frequencies with the number of degrees of freedom. The term 8.5eV/2 is the finite heat bath correction. Isolating ΔC_2 gives

$$\Delta C_2 = \frac{E_0 + \Delta E_{Fusion} + E_Z - 8.5eV(3\times 120 - 7)/G - 8.5eV/2}{8.5eV(1 - 6/G)} \quad (3)$$

where $G = \ln(At) = \ln(2 \times 10^{13})$.

This is plotted in Fig. 6 for the dimer ion internal energy distributions shown in Fig. 5. The intensity has been normalized to the same total intensity from each original neutral cluster precursor (N = 2–5). Results are shown for two different assumptions for the energy released on fusion, ΔE_{Fusion} = 10 eV and ΔE_{Fusion} = 20 eV, the maximum expected value.[18]

The results in Figs. 5 and 6 help explain the main observations concerning the fusion fragment signal. The excitation energy distributions of dimer ions shown in Fig. 5 show that only a very small fraction of these ions will be able to undergo fusion. Most of the ions have energies below the fusion barrier and will decay by separating into monomer molecules. The monomers may later decay via delayed ionization or fragmentation. Any dimer ions produced have a finite internal energy of at least ca. 10 eV. Even for such a large system as $(C_{60})_2^+$ this is not a negligible energy and it will very efficiently promote the fragmentation of the dimer ion (the dissociation energy is approximately 0.4 eV[28]), causing this species to disappear before they are accelerated and mass selected. This explains the absence of any intact cluster ions in the mass spectra, Figs. 2 and 3. Excited monomer ions from the breakup of clusters contribute to the increased monomer and small fragment ion intensity in Fig. 2 as the gas pressure and hence the average cluster size increases.

Dimer ions produced via the rapid fragmentation of large clusters can make a significant contribution to the fusion fragment signal. The excitation energy distribution of these dimer ions leads to relatively more ions

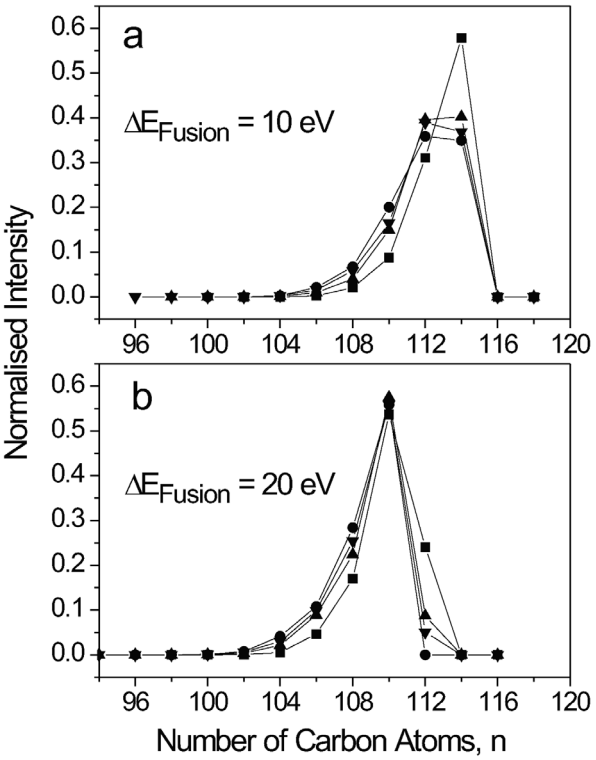

Fig. 6. Calculated dimer fragment ion distributions, expected for the experimental conditions, for the internal energy distributions plotted in Fig. 5. Squares: from N = 2, circles: N = 3, Up-triangles: N = 4, Down-triangles: N = 5. (a) Calculated assuming a relaxation energy of 10 eV on fusion. (b) Calculated assuming a relaxation energy of 20 eV on fusion.

with an internal energy greater than the fusion threshold as the neutral precursor cluster size increases. This explains the increase in the fusion fragment ion signal as the gas pressure and hence the average cluster size in the original cluster beam increases. The decrease in the normalized yield as a function of dimer excitation energy, plotted in Fig. 5, is due to the competition with further ionization. This decrease in the singly-charged dimer ion yield, in turn, leads to the low mass cutoff in the fusion fragment distributions, plotted in Fig. 6. In Fig. 6, the relatively narrow fusion fragment distribution and the independence of the distribution on the size of the initial neutral precursor cluster is clearly demonstrated. The high mass cutoff observed in the experiments is very well reproduced. The fragment ion distribution is narrower than observed experimentally, but this can be attributed to the oversimplified ionization model. The ionization energy used in the calculations overestimates the first ionization energy for the clusters but underestimates the higher ionization energies. This implies that the energy cutoff in the singly-charged dimer intensity due to further ionization will happen at lower excitation

energies in the model, compared to the experimental situation, and the calculated dimer fragment ion distribution will thus appear narrower than the experimentally determined distribution.

CONCLUSIONS

We have shown that the presence of groups of ion peaks lying beyond the mass of the monomer ion in mass spectra obtained from intense fs laser pulse excitation of fullerene clusters is due to intra-cluster molecular fusion. The groups of ion peaks are characteristically narrow with well-defined cutoff masses at both the high- and low-mass end of each distribution.

The high-mass cutoff can be explained in terms of the minimum excitation energy needed to induce molecular fusion of the fullerenes in the cluster. This minimum energy is then equilibrated among the vibrational degrees of freedom of the fused molecule and, together with the relaxation energy due to the fusion reaction, will lead to fragmentation of the fused species before mass selection takes place in the mass spectrometer. A simple Arrhenius model for the fragmentation, using established parameters for fullerene C_2 emission, gives excellent agreement with the experimentally determined high mass cutoff if the energetic threshold for fusion is assumed to be the same as determined previously in single collision fullerene ion–neutral fullerene experiments.

The low mass cutoff is explained in terms of competition with multiple ionization leading to fission of the clusters. A simple statistical ionization model, developed previously for describing the rapid but thermal ionization of monomer fullerene molecules from the hot electronic sub-system, before energy is coupled to the vibrational degrees of freedom, was developed for treating the ionization of the fullerene clusters. We showed that the multiple ionization of the fullerene clusters does compete with fusion of the small singly-charged species and can indeed explain the very narrow fragment ion distributions that are observed in the experiments. The model also explains the relatively low intensity of the fusion ion signal and the constancy of the fusion fragment ion distributions as the original neutral cluster distribution or the laser fluence is changed.

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