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Molecular fusion within fullerene clusters induced by femtosecond laser excitation

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Abstract. Molecular fusion is induced in clusters of fullerene molecules on excitation with fs laser pulses. The dependence of the mass distributions of the fused products on the initial cluster distribution are studied and results for $(C_{60})_N$ and $(C_{70})_N$ clusters are compared. The fused products decay by emitting C_2 molecules and the fragmentation spectrum is used to determine the initial excitation energy of the fused species. The threshold excitation energy needed to induce fusion is consistent with the energetic thresholds for molecular fusion of fullerenes determined previously in single collision experiments.

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1 Introduction

Over the years since their discovery in 1985, fullerenes have become favourite model systems for studying the dynamical and statistical behaviour of highly excited molecules [1–5]. Due to their relative simplicity and ease of handling, it has been possible to study many interesting aspects of the dynamical behaviour of large molecules with many degrees of freedom and to develop and refine theoretical models that can describe the fullerene properties and can also be developed for and applied to other complex systems such as atomic clusters or large biomolecules. One of the interesting properties of fullerenes that has been studied over the years, using a range of different experimental techniques, is the ability to undergo molecular fusion. When highly excited fullerenes collide it is possible that they fuse together to form a larger fullerene molecule. This fusion product then stabilises by e.g. emitting C_2 molecules. Evidence for such behaviour was initially found in laser desorption experiments on fullerene films where, for high laser fluence, fullerene mass peaks higher than the fullerenes deposited on the substrate were detected by mass spectrometry [6–8]. More controlled experiments involving fullerene ion collisions with fullerene films [9] and gas phase fullerene ion — neutral fullerene collisions carried out under single collision conditions [10–12] provided further information on the mechanisms involved in the formation of the larger fullerenes. It was shown that there is a narrow collision energy window where the products of the fusion reaction can be detected with a high energetic barrier for the fusion process, lying at approximately 85 eV for $C_{60}^+ + C_{60}$ collisions and increasing with the number of atoms involved [1,10,12]. We have recently shown [13] that a similar process can take place inside van der Waals bound clusters of C_{60} that have been excited with a fs laser. The reaction is not observed using ns laser excitation [14]. For ns pulses, the absorption of individual photons takes place over a much longer timescale than for fs pulses and each photon energy will be converted to vibrational excitation before the following photon is absorbed. In other words, it is not possible to absorb sufficient energy to induce the rearrangement of the individual fullerene monomers into larger fullerene species before the cluster dissociates. It has also not been possible to observe the molecular fusion channel in collision experiments between highly charged ions and fullerene clusters [15] where charge transfer and monomer evaporation are the observed channels.

In our earlier report [13] we interpreted the fragmentation spectrum of the fused species by assuming that the same energetic barrier to fusion exists as for the single collision experiments. The maximum fragment ion mass coming from a fused dimer could then be estimated making reasonable assumptions for the fragmentation rate and considering the experimental time windows [13]. This estimate was found to be in very good agreement with the experimental results. In this paper, we extend our earlier measurements and compare the C_{60} cluster results with C_{70} clusters. We also study the fragment distributions from the fused products as a function of the initial cluster distribution.

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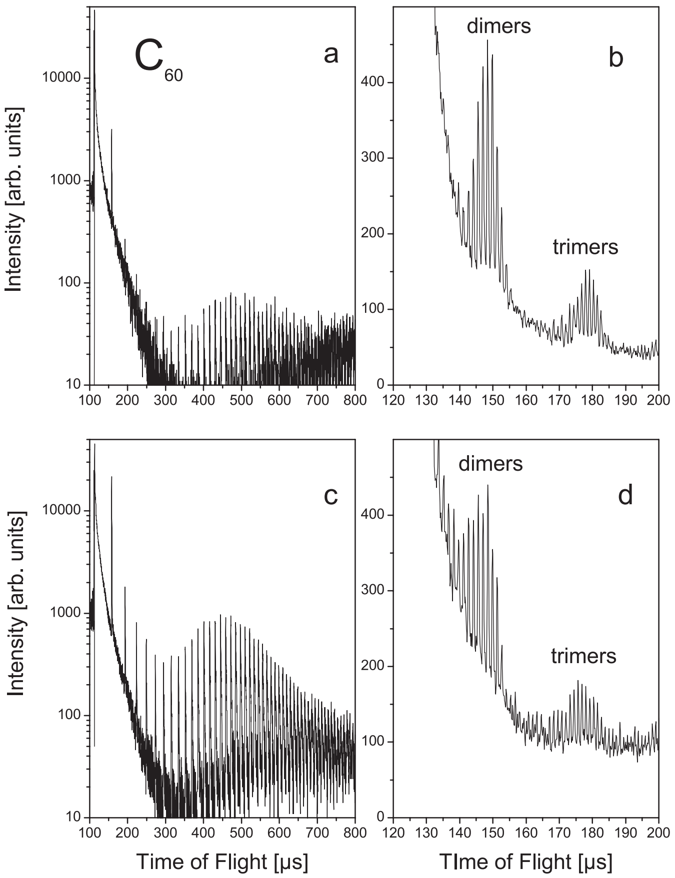

Fig. 1. Time of flight mass spectra obtained from ionising $(C_{60})_N$ clusters. (a) ns F_2 excimer laser single-photon ionisation of neutral clusters, He pressure 35 mbar. Note the logarithmic scale. (b) 800 nm, 200 fs laser ionisation of the same cluster distribution as in (a). (c) F_2 laser single-photon ionisation of neutral clusters. He pressure 14 mbar. (d) 800 nm, 200 fs laser ionisation of the same cluster distribution as in (c).

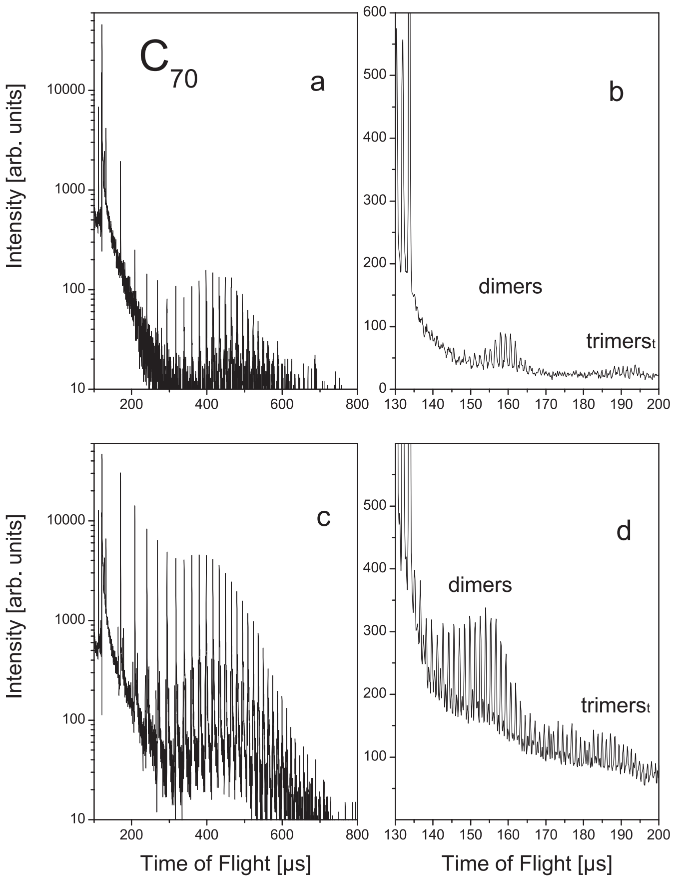

Fig. 2. Time of flight mass spectra obtained from ionising $(C_{70})_N$ clusters. (a) ns F_2 excimer laser single-photon ionisation of neutral clusters, He pressure 30 mbar. Note the logarithmic scale (b) 800 nm, 200 fs laser ionisation of the same cluster distribution as in (a). (c) F_2 laser single-photon ionisation of neutral clusters. He pressure 18 mbar. (d) 800 nm, 200 fs laser ionisation of the same cluster distribution as in (c).

2 Experimental setup

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 [14]. The cluster beam passes two differential pumping stages before entering the ionisation chamber of a time-of-flight mass spectrometer. The clusters are ionised by either a ns F_2 excimer laser (photon energy 7.9 eV) or 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 ionisation, 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.

3 Results and discussion

Figures 1 and 2 show typical mass spectra for $(C_{60})_N$ and $(C_{70})_N$ clusters before and after fs laser excitation. Figures 1a, 1c and 2a, 2c are single photon ionisation mass spectra obtained using the F_2 laser. Note the logarithmic scale on these plots. These mass spectra are expected to provide reliable relative comparisons of the initial cluster distributions although one needs to bear in mind that the detection efficiency decreases as the mass of the clusters increases. One does not expect significant fragmentation on single photon ionisation although the small tail on the monomer ion peaks is perhaps indicative of some photo- or collisional-fragmentation from clusters. The different cluster distributions have been produced by varying the pressure of the He gas inside the cluster aggregation source. Figures 1b, 1d and 2b, 2d show the region to the high mass side of the monomer ion when the fs laser is used for ionisation. As we have shown previously for $(C_{60})_N$ [13], we observe groups of ions where the peak mass separation within each group corresponds to C_2. Such a peak separation is strongly indicative of fragmentation from a highly excited fullerene ion. We therefore consider that each group of peaks is the product of fragmentation from a

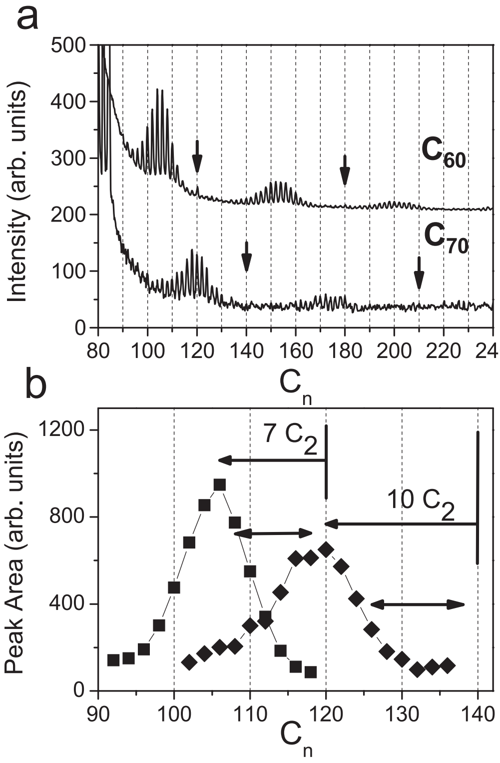

Fig. 3. (a) Mass distributions of fusion products from small $(C_{60})_N$ and $(C_{70})_N$ clusters (corresponding to Figs. 1b and 2b). The arrows mark the positions of non-fragmented fusion products from the dimer and trimer clusters. The spectrum from C_{60} has been shifted upwards for clarity. (b) Integrated mass peaks of the dimer fragment ion distribution. The double-headed arrows indicate the expected upper cut-off of the fragment distributions assuming that the same energy barrier to molecular fusion has to be overcome as for gas phase collisions.

highly excited fusion product from the fullerene molecules present within the initial cluster. As one would expect, the peaks observed in the $(C_{70})_N$ spectra are shifted to longer arrival times than those in the $(C_{60})_N$ spectra. This can be seen most clearly in Figure 3a where we have plotted the spectra from Figures 1b and 2b on the same plot. In this case the arrival time has been converted to the number of carbon atoms C_n. The vertical arrows mark the positions where unfragmented dimer or trimer cluster ions would appear. In Figure 3b the integrated peak areas are plotted for both sets of dimer fragment ions. In order to obtain the integrated peak intensities, a smooth background function was fitted to the spectra in Figure 3a and subtracted from the intensity before the peaks were integrated.

The double-headed arrows in Figure 3b indicate what the maximum detectable fragment peak should be under our experimental conditions if we assume that the threshold energy for fusion of the two monomer fullerenes is the same as was determined experimentally in collision experiments [1,10,12]. The length of the double-headed arrows indicates the effect of the uncertainty in the value of the collisional fusion threshold energy (85 ± 5 eV and 100 ± 10 eV for C_{60} and C_{70} respectively, including the initial vibrational excitation in the projectile ion) and the possible relaxation energy (ca. 0–20 eV) that can be expected [1]). The minimum internal energy after fusion is thus 80–110 eV for C_{120}^+, leading to a maximum detectable fragment ion in the range of C_{118}^+–C_{108}^+. For this estimate we have used the same parameters for the unimolecular fragmentation rate as were used in our previous work [13]. An Arrhenius form was assumed with a pre-exponential factor of 2×10^{19} s^{-1} [16] and a dissociation energy of 8.5 eV for the large fullerene ions [17,18]. The estimated upper limit of the fragment ion distribution is consistent with the experimental data. Although the uncertainties in the threshold energy and the estimate of the relaxation energy are quite large, the comparison between the results for the dimer fragment ions from C_{60} and C_{70} as well as our earlier comparison of the dimer, trimer, tetramer and pentamer fragment distributions for C_{60} [13] provide convincing evidence for our interpretation of the data in terms of intracluster molecular fusion.

The fragment ion distributions are surprisingly sharp and symmetrical. In order to reach C_{106}^+ (the maximum of the dimer fragment distribution) from C_{120}^+ in our experimental timescale, the C_{120}^+ fusion product ion must have had an internal vibrational energy of approximately 125 eV. This is estimated assuming sequential C_2 emission and using the fragmentation rate constant discussed above. We believe that the sharp drop in fragment ion intensity on the low mass side of the distributions could be due to competition between the intra-cluster fusion reaction in the singly-ionised small cluster and the rapid (i.e. before electronic energy couples to vibrations) thermal ionisation of the singly charged dimer to produce a doubly charged dimer. Such fast thermal emission from the excited electronic subsystem, before the excitation energy has time to couple to vibrational modes, has been observed and successfully modelled for fullerene monomers [19,20]. We can estimate the rate for double ionisation assuming a thermal emission from the hot electronic subsystem, using a simple Fermi gas model for calculating the electronic level densities [21] and taking the ionisation potential of $(C_{60})_2^+$ to be 8.5 eV [22]. An electronic excitation energy of 125 eV in the $(C_{60})_2^+$ would imply a double ionisation rate constant for the dimer molecule on the order of 6×10^{13} s^{-1}, corresponding to a time scale of ca. 20 fs. It therefore appears plausible that, for such high excitation energies, rapid multiple ionisation can take place before the internal fusion reaction can occur. Since doubly-charged small clusters are unstable [15] they will undergo immediate Coulomb repulsion and the cluster will rapidly dissociate. It is the competition between the two reactions (intracluster fusion and double ionisation) that determines the shape of the fusion fragment ion distribution. In a recent study it was found that the internal conversion rate of single-photon excited C_{60}^- anions was significantly faster than that of neutral C_{60} due to the influence of Jahn-Teller distortion [23]. In the situation discussed here, the competing decay branches: multiple ionisation versus

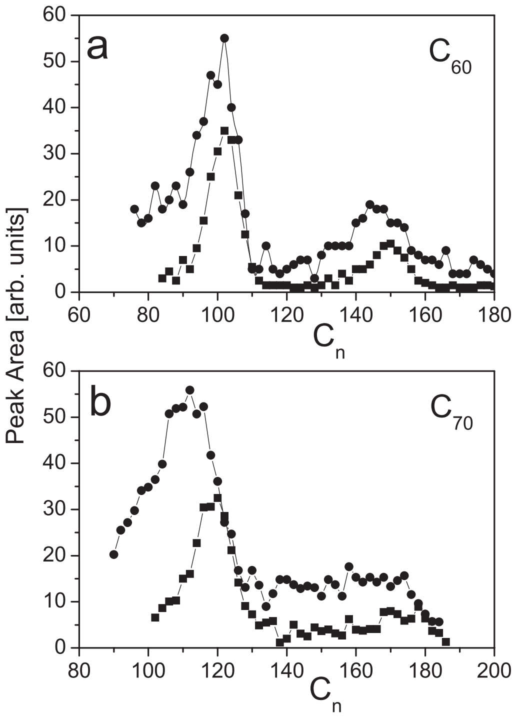

Fig. 4. Comparison of the integrated fragment ion peak areas from neutral cluster beams with small (squares, Figs. 1b and 2b) and large (circles, Figs. 1d and 2d) fullerene clusters. (a) $(C_{60})_N$ precursors. Note that the peak areas taken from spectrum 1b have been reduced by a factor of 2 for clarity. (b) $(C_{70})_N$ precursors.

intracluster fusion and cluster break-up are expected to be strongly dependent on the charge state. Cluster break-up would appear to dominate over intra-cluster fusion for multiply charged small clusters. This may be related to a faster internal conversion rate for more highly charged clusters.

It was noted earlier [13] that the width of the fusion fragment ion distributions did not change significantly as the laser fluence was increased. As can be seen in Figures 1 and 2, the distribution does seem to change as the initial cluster distribution changes. The C_{60} data shown in Figures 3 and 1b are very similar to the data published earlier for C_{60}. The parent cluster spectrum (Fig. 1a) shows a significant dimer mass peak but much smaller intensities for larger clusters. However there are many very large clusters that appear to have very low intensities due, mainly, to the poor detection efficiency, and these may be affecting the results, as discussed below. For C_{70} (Fig. 2), there do not seem to be so many very large clusters in the neutral beam and the fusion ion intensity is relatively low compared to the C_{60} case. When there are many small and intermediate sized clusters (Figs. 1c and 2c) the fusion fragment mass distribution seems broadened towards lower masses. This is most apparent for the C_{70} case and can be clearly seen in Figure 4 where the integrated peak intensities are compared. It appears that the upper limit of the fragment mass distribution for a given cluster parent does not change and is still determined by the energetic threshold for fusion. The broader fragment ion distribution that is observed when there are more small and intermediate sized parent clusters present could be due to charged dimer fragments coming from larger parent clusters. The parent clusters can fragment when some energy is coupled to vibrational modes (thus reducing the electronic temperature). This is more likely to occur the larger the cluster becomes since the fusion barrier (for fusing the entire cluster) increases with cluster size. A singly charged dimer fragment can then undergo fusion (or could be at least partially fused when leaving the parent cluster) but since energy has already been removed from the electronic subsystem there is no longer competition with double ionisation and smaller fragment ions can be detected.

For the C_{60} example in Figure 1b the relatively high dimer fragment ion intensities are indicating that there is some contribution from the very large clusters present in the parent cluster beam. In this case, we tentatively suggest that the increased signal comes from the rapid Coulomb explosion caused when large clusters become strongly multiply charged (the larger the cluster, the higher the absorption cross section). In this case singly charged dimer ions can be very rapidly formed in the break-up before the electronic energy has a chance to couple to vibrations. These ions will therefore lead to a dimer fragment ion distribution that is identical to the distribution caused by neutral parent dimer species. These explanations are still speculative and more experimental results and modelling is needed to be sure about the mechanisms involved.

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