Ionisation of fullerenes and fullerene clusters using ultrashort laser pulses

Eleanor E. B. Campbell,*[a] Klavs Hansen,[a] Martin Hedén,[a] Mikael Kjellberg[a] and Alexander V. Bulgakov[b]

Received 4th September 2006, Accepted 18th October 2006
First published as an Advance Article on the web 3rd November 2006
DOI: 10.1039/b612749e

We give a brief review of the literature concerning the ultra-short pulse ionisation of fullerenes in the gas phase. Emphasis is placed on the excitation time dependence of different ionisation regimes as manifested by photoelectron spectroscopy. The ionisation rates are modelled for the intermediate situation where the excitation energy is equilibrated between electronic degrees of freedom but not yet coupled to vibrational degrees of freedom. The model is shown to describe many aspects of the experiments. New results are presented on the intra-cluster molecular fusion of fullerene molecules when van der Waals bound clusters of fullerenes are exposed to ultra-short laser pulses. Pump–probe measurements give a decay time constant for the intra-cluster fusion reaction of 520 ± 55 fs. A comparison with monomer ionisation results suggests that the time window for the fusion reaction is influenced by the coupling of the electronic excitation energy to vibrational degrees of freedom of the molecules in the cluster.

Introduction

Fullerenes have been used since their first discovery as model systems for studying the behaviour of highly excited molecules or clusters with a large number of degrees of freedom. Gas phase studies allow the properties of the individual molecules to be probed in detail without the complications arising from interactions with liquid or solid surroundings. For the past 15 years, the ionisation and fragmentation behaviour of highly excited fullerenes in the gas phase have been the subject of much attention.[1–5] In this context "highly excited" typically refers to the situation where the molecules have more internal excitation energy than the energy required to remove an electron. A number of interesting and, initially, surprising phenomena were observed in such experiments such as the observation of delayed ionisation occuring up to many microseconds after excitation with ns laser pulses,[6] the observation of a very large kinetic shift in the metastable fragmentation of fullerene ions[7] and the occurrence of black-body-like radiation from laser desorbed fullerenes.[8] It is now fairly well established that all of these phenomena can be understood by considering statistical decay mechanisms of the molecules, assuming that the excitation energy is equilibrated among all degrees of freedom,[5] although a few uncertainties concerning the details remain.[9] Fullerenes are especially interesting and almost unique in this context since it is possible to observe the three main decay channels (electron emission, fragmentation and radiation) on the microsecond timescales that are easily accessed by mass spectrometers.[2] The reason for this is that the ionisation potential (7.59 eV for C_{60})[10] is much less than the energy required for fragmentation (10.8 ± 0.3 eV for C_2 emission from neutral C_{60}).[11] Statistical behaviour is observed for excitation of fullerenes with ns laser pulses as well as in many collision experiments.[12]

Our interest in recent years has been to explore how the statistical behaviour develops with time. On what timescale can we consider the excitation energy to be statistically distributed among the degrees of freedom of the molecule? In the following we will briefly review the results using ultra-short laser pulse excitation and statistical modeling that provide information on such processes. In addition, we will describe results concerning the excitation of clusters of fullerenes. We show that if sufficient energy is absorbed by fullerene clusters on a sub-picosecond timescale then it is possible to observe intra-cluster molecular fusion where the individual fullerene molecules in the weakly-bound cluster fuse together to produce large fullerenes. Intense ultra-short pulse laser excitation of clusters could prove to be a useful tool to study chemical reactions under extreme excitation conditions.

Experimental

All of the results presented here have been obtained with the kind of equipment schematically illustrated in Fig. 1. Fullerene beams are produced by evaporating "gold grade" C_{60} powder in an oven at a temperature of typically 500 °C. Beams containing clusters of fullerenes are produced in a cluster aggregation source, cooled by liquid nitrogen and using helium as a carrier gas.[13] The monomer and cluster fullerenes that emerge from this source have a vibrational temperature of 100 K or slightly less. Both fullerene sources are oriented at right angles to the flight axes of a reflectron ion time-of-flight mass spectrometer and a μ-metal

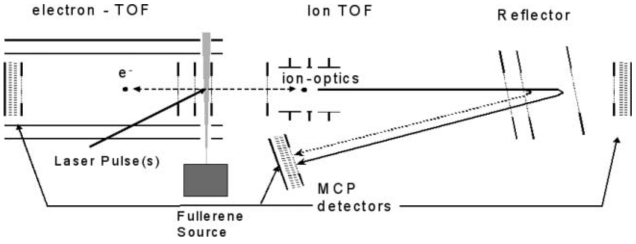

Fig. 1 Schematic diagram of a typical experimental setup to study the ionisation and fragmentation of fullerenes with ultra-short laser pulses.

---

[a] Department of Physics, Göteborg University, SE-41296, Göteborg, Sweden. E-mail: eleanor.campbell@physics.gu.se; Fax: +46 31 772 3496; Tel: +46 31 772 3272
[b] Institute of Thermophysics, SB-RAS, 1Acad Lavrentyev Ave., 630090, Novosibirsk, Russia

shielded electron time-of-flight spectrometer. The beam from the gas aggregation source passes through two differential pump stages before entering the region between the two spectrometers. The clusters are ionised by either a ns F_2 excimer laser or a kHz Ti:sapphire regenerative amplifier system. The laser beams are oriented at 90° to the plane defined by the spectrometer axes and the molecular beam. The laser intensity was calibrated by determining the saturation intensity for the photoionisation of Xe from a measurement of the laser intensity dependence of the Xe^+ ion signal.[14] Positive ions are extracted with a static electric field into the reflectron. Photoelectrons are detected without an extraction field. Photoelectrons from Xe were used to calibrate the energy scale of the electron spectrometer. A disadvantage with the linear time-of-flight electron spectrometer used throughout this work is that it is insensitive to low energy electrons (< 0.5 eV) and this needs to be considered when interpreting the electron kinetic energy distributions. It is not possible to detect positive ions and electrons simultaneously (or in coincidence) with the present set-up. However, it is possible to switch quickly between the detection modes or the fullerene sources without breaking the vacuum which allows a direct comparison under practically identical conditions.

Excitation time dependence of C_{60} ionisation mechanism

The ionisation and fragmentation of fullerenes with ns laser pulses have been extensively investigated.[1–3,5] There are two very characteristic features. Both of these features can be seen in the mass spectrum obtained with shorter, 4.5 ps, laser pulses Fig. 2(a). The first is a tail on the monomer ion peak that extends to longer flight times. This has been shown to be due to delayed ionisation of the fullerenes. There have been many discussions in the literature concerning whether this delayed ionisation can be regarded as purely statistical thermionic emission or not.[1,3] It now seems that at least for excitation with ns laser pulses where there is sufficient time between the absorption of individual photons for the energy to be equilibrated within the molecule, this is a good description. The experimental data interpretation has often been complicated by a lack of knowledge of the internal energy distribution of the fullerene ensemble or by insufficient information concerning the extent and influence of competing decay mechanisms.[5] However, it now appears that models assuming a statistical distribution of the excitation energy and statistical decay are best able to explain the experimental observations. The second characteristic feature that is apparent in Fig. 2(a) is the bimodal, singly-charged fragment ion distribution. This can also be reproduced using relatively simple statistical models.[15] The fragments on the high mass side of the distribution come predominantly from sequential C_2 emission from the excited parent ion whereas the small mass fragments (carbon rings and chains) come from the catastrophic break-up of the fullerene cage if this is sufficiently highly excited.[15,16] In ns laser experiments with visible and UV laser pulses, the internal energy distribution of the fullerene ensemble is typically very broad due to the large average number of photons that are absorbed and the Gaussian spatial distribution of the laser beam,[16] leading to the very broad fragment distribution observed for relatively high fluence excitation. The small peaks that can be seen just to the low mass side of the fullerene fragment peaks are due to metastable emission of C_2 from the ions produced in the extraction region that decay while traversing the first field-free region of the time-of-flight mass spectrometer. This occurs some microseconds after excitation and can be used as a means of monitoring the internal energy of the fragment ions and how this is influenced by competing decay channels such as photon emission.[17–19]

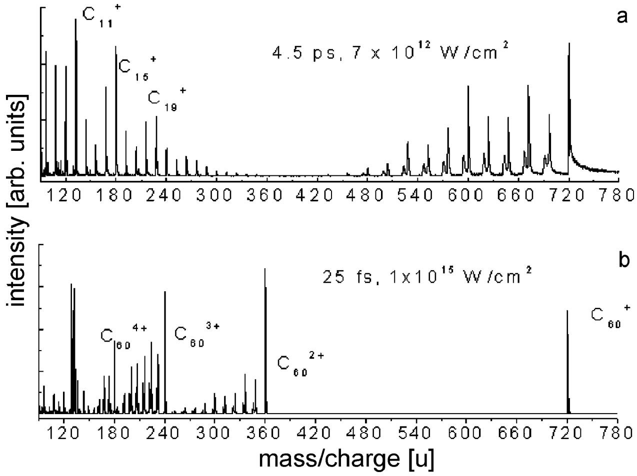

Fig. 2 Ion mass spectra obtained from exciting C_{60} with 4.5 ps (a, top) and 25 fs (b, bottom) long 800 nm laser pulses. The energy width of the laser pulses was identical and the spectra were obtained for approximately equal laser fluences (*ca.* 25–30 J cm^{-2}).

The spectrum shown in Fig. 2(a) was taken using 4.5 ps, 800 nm laser pulses at a laser fluence of approximately 20 J cm^{-2}. For this pulse duration the ionisation and fragmentation is already predominantly occuring from a vibrationally highly excited molecule that undergoes thermionic electron emission. Only singly-ionised species are observed. The mass spectrum indicates that the width of the internal energy distribution of the excited fullerenes is very large with those in the centre of the laser beam focus having vibrational energies well in excess of 100 eV.[16] As the pulse duration is decreased, the mass spectrum changes dramatically. For a pulse duration of 25 fs (Fig. 2(b)), but approximately the same laser fluence, one sees much less fragmentation but there is a strong contribution of multiply charged species. Note also that the delayed ionisation tail on the parent ion peak is no longer present. For these experiments, the shortest available pulse duration was 25 fs. Longer pulses up to a few hundred fs could be produced by dispersive stretching while ps pulses were produced from the same laser by bypassing the compressor.[20] In this way the energy width of the ultra-short pulses was kept constant throughout the experiments. A simple explanation of the pulse duration dependence is that for the shortest pulses there is no time during the 25 fs laser pulse for the electronic excitation energy to be coupled to vibrational degrees of freedom. Electrons are emitted, carrying away most of the excess energy, leaving behind a relatively cold molecule. The degree of fragmentation for the very high intensity excitation used for the example in Fig. 2(b), increases with the charge state of the parent molecule. This can also be rationalised within the context of statistical fragmentation models.[21] Since increasing amounts of energy are needed to remove electrons from increasing charge states, the more highly charged parent molecules will, on average have a higher excess energy after the final ionisation step thus leading to increased fragmentation. The fragmentation will take place on a longer timescale, after the excess energy has been transferred to vibrational degrees of freedom.

For the ps pulses, Fig. 2(a), there is time between photon absorptions for the energy to be coupled to vibrations before sufficient energy can be accumulated in the electrons to lead to "direct" ionisation, thus removing energy from the electrons and suppressing the multiple ionisation channels.

Experiments with high intensity IR pulses (1800 nm) have shown mass spectra with charge states up to C_{60}^{12+} and almost no fragmentation.[22] However, under these experimental conditions the dominant ionisation mechanism is likely to be a rapid "over the barrier" model and in a different regime than the 800 nm results discussed above.[22] The IR experiments are thus more comparable to collision experiments with highly charged ions[23] where the electrons are very rapidly extracted from the fullerene by the strong Coulomb field and very little energy is coupled to internal modes thus inhibiting fragmentation. When observed carefully, a small amount of fragmentation is seen to be present from the more highly charged ion species in the IR laser experiments.[24] This has been interpreted as being due to a re-collision effect where the emitted electron can return in the laser field and collide with the molecule it has just left. Although such a process may contribute to the molecular excitation at high laser intensities also for the lower wavelengths of main interest here, it is unlikely to be a dominant effect. Multiple electron excitation and internal electron–electron interactions are considered to be the main mechanisms for the high internal energies produced, as discussed below.

Photoelectron spectra, shown in Fig. 3, provide more insight into the mechanisms.[20] In this case, the photoelectron spectra have been recorded for much lower laser fluences (*ca.* 1–4 J cm^{-2}). Under these excitation conditions there is practically no fragmentation observed for the two lowest pulse durations so that we can be sure that the electrons are coming from the parent molecules and not from any neutral fragments. The ps mass spectrum is very similar to that shown in Fig. 2 with strong bimodal fragmentation and a significant delayed tail on the parent ion peak.[25]

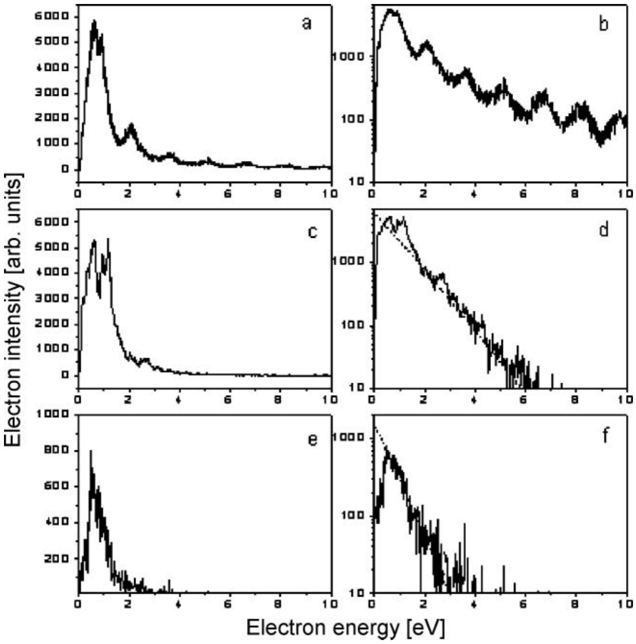

Fig. 3 Photoelectron spectra measured with a time-of-flight electron spectrometer for excitation with 800 nm laser pulses of different pulse duration: (a,b) 25 fs, *ca.* 1 J cm^{-2}; (c,d) 250 fs, *ca.* 3 J cm^{-2}; (e,f) 5 ps, *ca.* 3 J cm^{-2}.

The photoelectron spectrum obtained with 25 fs pulses shows a series of broad peaks separated by the photon energy, Fig. 3(a,b). This is due to above threshold ionisation, well known from ionisation of atoms in strong laser fields. Calculations using time-dependent density functional theory[26] have confirmed a picture of direct multiphoton ionisation for such short 800 nm laser pulses and also shown above threshold ionisation structure in the photoelectron spectra for laser intensities below *ca.* 2×10^{13} W cm^{-2}.[27] This is approximately an order of magnitude lower in intensity than the maximum intensity for which residual above threshold ionisation structure can be seen in the experiments, *ca.* 10^{14} W cm^{-2}.[28] Experimentally, the decrease in the above threshold ionisation peaks is correlated with an increase in a broad background photoelectron signal and the onset of fragmentation.[28] The calculations give some more insight into what may be happening.[4] The peaks can be understood in terms of the multiphoton excitation of a single electron from the highest occupied molecular orbital. The "smearing out" and disappearance of the peaks is due firstly to an Autler-Townes splitting caused by intermediate resonances and secondly to the increasing importance of multiple electron excitation as the laser intensity increases. This leads to a time-dependent effective potential where the energy levels are not well defined and thus to the disappearance of the maxima at well defined electron kinetic energies.

The multiple active electron picture becomes even more important as the pulse duration is increased, keeping the laser fluence constant. As can be seen in Fig. 3(b,d) the above threshold ionisation structure has almost disappeared for excitation with 250 fs pulses, where the intensity is approximately an order of magnitude smaller than in Fig. 3(a,c). Two features are worthy of note in these plots. One can clearly see structure in the kinetic energy range 1–1.6 eV. This can also be seen in the 25 fs data but is much less pronounced due to the above threshold ionisation peaks. The structure has been identified as being due to the single-photon ionisation of Rydberg states populated during the same laser pulse.[29] The mechanism for populating these states is still unclear and we will not discuss them further in this article. The second feature is the underlying thermal electron kinetic energy distribution that is more apparent in the log-lin plot shown in Fig. 3(d). A fit to the data yields an electron temperature on the order of 20000 K. For these longer laser pulses it is less likely that a single electron will absorb 5 or more photons coherently as is needed to produce the above threshold ionisation peaks in the photoelectron spectrum. Instead one has time during the laser pulse for multiply excited electrons to interact, leading effectively to an equilibration of the electronic energy followed by a thermal ionisation.[30] This thermal ionisation happens promptly (fs timescale), before the electronic excitation couples to vibrational modes. When the pulse duration is further increased to 5 ps, the electron kinetic energy distribution is still thermal but the temperature is much lower. This, combined with the lack of multiply ionised species and the presence of a delayed ionisation tail shows that excitation energy has coupled to the vibrational modes before ionisation takes place. In other words, it is not possible to accumulate sufficient energy in the electronic system to induce thermal ionisation from the hot electrons before coupling to the vibrations takes place. Once energy is equilibrated among the vibrations, the singly-charged fragmentation channel will dominate over a thermionic double ionisation mechanism. The situation is illustrated by the calculated rate constants shown in Fig. 4. Ionisation from the hot electronic system before vibrational coupling takes place, was modelled by Hansen *et al.*[30] The same model has also been used successfully to describe fs laser ionisation of sodium clusters.[31,32] For the same total excitation energy, the rates for ionisation before vibrational coupling are orders of magnitude higher than those for thermionic electron emission due to the large number of vibrational degrees of freedom. The rate constant for fragmentation (C_2 emission) from C_{60}^+ was calculated using a simple Arrhenius expression with a dissociation energy of 10.3 eV[11] and a frequency factor of 2.3×10^{21} s^{-1}.[33] This may seem an unreasonably large value for the frequency factor but it is a value that, together with the high dissociation energy, is consistent with the vast majority of experimental results. The situation has recently been reviewed in some detail.[5] The main reason for the exceptionally high value is the rotational–vibrational–electronic partition function of C_2 which at 4000 K has a value close to 10^4.

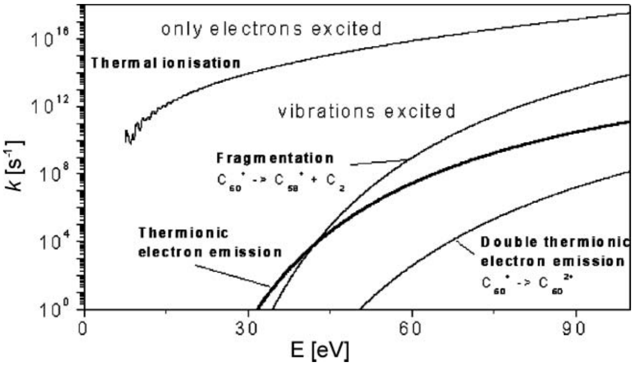

Fig. 4 Calculated rate constants as a function of excitation energy for statistical ionisation comparing the rates for single and double ionisation in the situation where the energy is confined to the electronic sub-system with the thermionic emission case where energy is equilibrated among electronic and vibrational degrees of freedom. The energy dependence of the rate constant for statistical fragmentation of C_{60}^+ *via* emission of C_2 is shown for comparison.

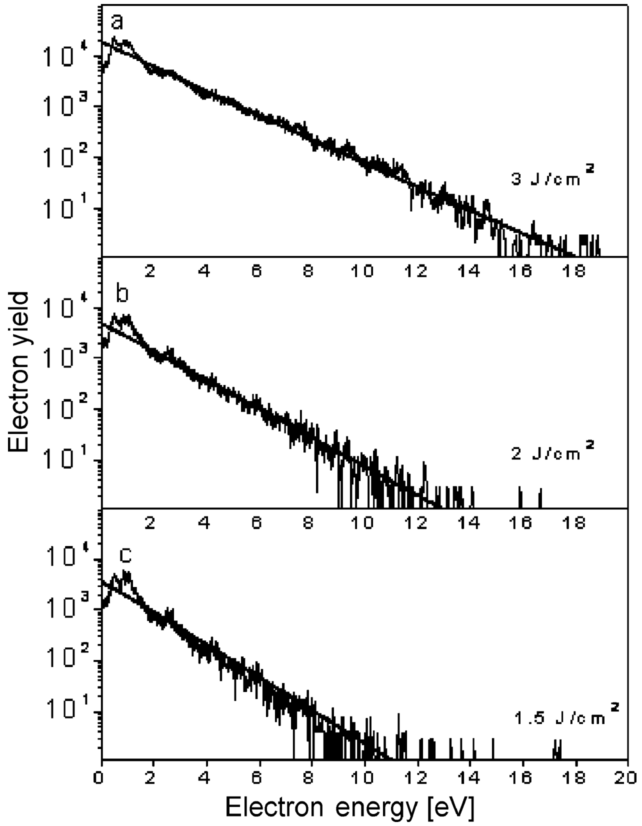

Fig. 5 Photoelectron spectra measured for a laser pulse duration of 180 fs. The experimental data are compared to calculations according to the thermal ionisation model described in the text: (a) 3 J cm^{-2}, $\bar{n}_0 = 75$; (b) 2 J cm^{-2}, $\bar{n}_0 = 50$; (c) 1.5 J cm^{-2}, $\bar{n}_0 = 37$.

Thermal electron emission from hot electrons

The statistical model describing thermal electron emission from the hot electronic sub-system of vibrationally cold C_{60} is described in detail by Hansen *et al.*[30] and was used in that publication to calculate the fluence dependence of photoelectron spectra and the total ion yields for excitation with 180 fs pulses. This pulse duration is long enough to ensure that the above threshold ionisation contribution is negligible but short enough to rule out the influence of thermionic electron emission from vibrationally excited fullerenes.[25] A comparison of the model calculations with photoelectron spectra obtained for different laser fluences is shown in Fig. 5. The calculated probability for electron emission as a function of total absorbed photon energy, E_{tot}, is integrated over time. The cooling of the electronic sub-system due to coupling to vibrational degrees of freedom is accounted for by introducing a time constant τ, $E(t) = E_{\mathrm{tot}} \exp(-t/\tau)$. The value used for the time constant (240 fs) was determined independently by fitting Penning ionisation yields.[34] The calculations also account for the distribution of absorbed photons in the experiment. For a given laser fluence, a Poisson distribution is assumed with the mean number of absorbed photons $\bar{n}$ given by the product of the fluence and the photoabsorption cross section divided by the photon energy. Since the photoabsorption cross section is not known for the conditions holding in the experiments, a comparison with the experimental results can be used to determine the relationship between the mean number of absorbed photons and the fluence.[30] Finally the absorbed photon distributions are averaged over the Gaussian profile of the laser beam. The agreement with the experimental data is very good. For the comparisons shown in Fig. 5, the average number of photons absorbed in the centre of the laser beam is $\bar{n}_0 = 37$, 50 and 75 for 1.5, 2 and 3 J cm^{-2} respectively. The estimated excitation energies are also consistent with the lack of fragmentation observed in low fluence (1–2 J cm^{-2}) experiments with pulse durations below 300 fs. After thermal emission of one or two electrons there is not sufficient internal energy in the ensemble of molecular ions to induce significant fragmentation once the energy has been distributed among the vibrational degrees of freedom.

The electron kinetic energy spectra have been used to obtain a rough estimate of the energy dissipation time constant.[30] For short pulses, the apparent electron temperature that is obtained from the photoelectron spectra shows a linear dependence on the laser fluence which is very well fitted by the thermal ionisation model (Fig. 5). As the pulse duration is increased beyond *ca.* 350 fs, the gradient of this dependence decreases, indicating the cooling of the electron temperature *via* coupling to vibrations during the laser pulse. This data are plotted in Fig. 8 and will be discussed further in the next section.

A comparison between the model and the experimental results has also been made for the positive ion yields. Fig. 6 shows a log–log plot of the calculated ion yields as a function of the average number of absorbed photons in the beam focus, $\bar{n}_0$. The calculations are compared with experimental results for 35 fs pulses.[14] The experimental measurements have been used to justify a direct multiphoton ionisation picture since the fitted gradients are consistent with the number of photons needed for single and double ionisation.[4,14,25] Interestingly, and somewhat puzzling in view of our discussions above, the experimentally determined log–log slopes did not change significantly as the pulse duration was increased from 35 fs to 120 fs. Surprisingly, our calculations based on a statistical ionisation mechanism fit the experimental data very well! Not only that, if a linear fit is made to the low fluence ($\bar{n}_0 <$ 10) range of the calculated curves, *the slopes that are obtained are exactly equal to the energy needed for the ionisation step in units of the photon energy.*[30,35]

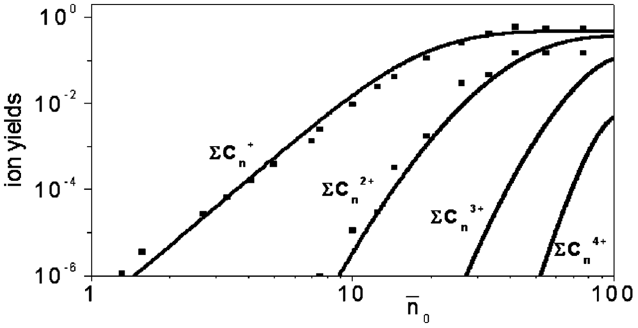

Fig. 6 Theoretical total ion yields, calculated with the statistical, thermal ionisation model discussed in the text, *versus* average number of absorbed photons in the laser focus for charge states +1 to +4. The results are compared with experimental data from Tchaplyguine *et al.*[14]

This is a surprising result and it has major consequences for the interpretation of log–log data. Contrary to established practice, the observation of a power dependence in fluence measurements is obviously not sufficient to allow one to conclude that a process occurs *via* direct multiphoton absorption. Although we have only demonstrated this behaviour so far for fullerenes, we believe that it is a more general result.

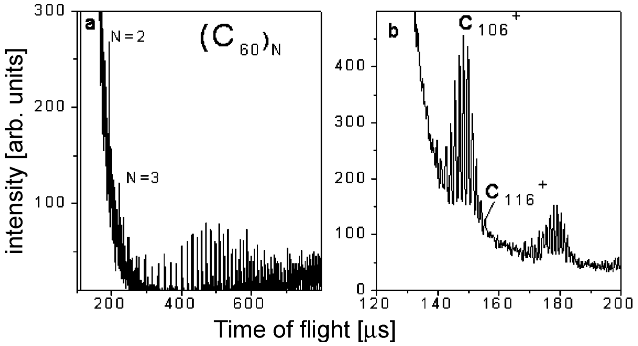

Fig. 7 (a) Time-of-flight mass spectrum obtained by single-photon ionisation of $(C_{60})_N$ clusters (using a F_2 excimer laser) from a gas aggregation source. (b) Small section of ion time-of-flight mass spectrum from an identical cluster distribution ionised with 200 fs laser pulses providing evidence for intra-cluster molecular fusion.

Ionisation and fragmentation of fullerene clusters

A gas aggregation source can be used to produce clusters of fullerenes.[36] Monomer fullerene units in the clusters are bound together by relatively weak van der Waals forces. The cluster distribution can be measured by singly-photon ionising the neutral clusters using a VUV laser pulse *e.g.* a F_2 laser with a photon energy of 7.9 eV. If the photon energy is reduced below the ionisation potential of the clusters the energy is efficiently coupled to vibrational modes and the clusters fragment in the neutral channel before ionisation takes place. An example of a typical $(C_{60})_N$ cluster distribution in our experiments is shown in Fig. 7(a). The distribution extends to very large masses but it is important to realise that the detection efficiency decreases strongly as a function of mass and thus the mass spectra significantly underestimate the presence of very large clusters. We have shown previously that when clusters of fullerenes are irradiated with fs laser pulses it is possible to observe the results of intra-cluster molecular fusion where the highly excited fullerenes can fuse together to form larger fullerenes.[37] An example of this can be seen in Fig. 7(b). When ionisation occurs with intense 800 nm fs pulses it is not possible to observe the presence of intact fullerene clusters, as is the case when singly ionising with VUV pulses. This observation is also in contrast to the situation where such fullerene clusters are ionised by collisions with highly charged ions.[38] Similar to the situation discussed above for multiple ionisation of monomers, the electrons are rapidly removed from the clusters by above barrier ionisation in collisions with highly charged ions and there is very little coupling of energy to internal modes. For ionisation with 800 nm, 200 fs pulses, we observe groups of mass peaks with a separation between peaks corresponding to C_2. Each group of peaks can be associated with a parent cluster. For example, in Fig. 7 we show the peaks corresponding to the dimer and trimer clusters. The peaks can therefore be identified as fragment ions from the associated clusters. Since the fragment ion peaks are separated by C_2 one can infer that the molecules in the cluster have undergone a fast rearrangement to form a fused, larger fullerene. The upper limit of each fragment distribution can be used to estimate the internal energy within the original fused cluster.[37] It was found that this upper limit does not change as a function of laser fluence.[37] Analysis of the spectra reveals that one requires a minimum cluster excitation energy in order to induce the intra-cluster molecular fusion reaction. This energy is, within experimental error, identical to the energetic barrier for the fusion reaction that was determined earlier in fullerene ion–fullerene single collision experiments.[12,39] For the $(C_{60})_2^+$ fusion reaction to form C_{120}^+, the energetic barrier is 85 ± 5 eV.[12,39] On the timescale of our experiment, a fused C_{120}^+ with this amount of internal energy will fragment down to C_{116}^+ *via* sequential emission of two C_2 molecules. Higher initial internal energies will lead to the production of smaller fragment ions. At present we believe the small mass cut-off of the distributions may be due to competition between the fusion reaction channel and the rapid multiple ionisation of the clusters. If the clusters are rapidly multiply charged they will undergo Coulomb fission and there will be no time for the molecular fusion reaction to take place. The competition between these two reaction channels will depend on initial excitation energy.

Collision experiments have shown that doubly charged clusters are unstable up to $N = 5$.[38] It is worthy of note that we do not observe any multiply charged cluster fragment peaks but we do observe a strong fragmentation to C_{60}^+ from large clusters.

To obtain more information on the possible mechanisms leading to the intra-cluster fusion reaction, we have carried out pump–probe experiments using 200 fs, 800 nm pulses. The laser beam was split into two equal intensity beams where the intensity was adjusted so that it was just below the threshold for observing the fusion reaction with one of the beams (a few J cm^{-2}). The dimer fragment ion peak intensities were then integrated and the integrated intensity plotted as a function of the pump–probe delay. The results are shown in Fig. 8. One sees an exponential decay of the fused product signal with a time constant of 520 ± 55 fs but with a significant offset. The measured time constant is approximately the same timescale as has been determined for the coupling of electronic to vibrational excitation in the fullerene monomers.[30] As an illustration of this, we show on the same plot the extracted gradients of the temperature *versus* fluence plots obtained from the monomer photoelectron spectra as a function of pulse duration (stars). As discussed above, these data give an indication of the timescale for the cooling of the electronic degrees of freedom due to coupling to the vibrational modes of the molecules. It is apparent that the intra-cluster fusion reaction is more probable if sufficient energy to overcome the fusion barrier is available in the electronic sub-system on the sub-ps timescale, *i.e.* before vibrational modes of the cluster are excited, leading to rapid (ps) dissociation of the neutral or singly-charged cluster. The fusion reaction itself is also expected to occur on the ps timescale so that there is a delicate balance between fusion and cluster break-up. The constant (on the ps timescale) offset in the pump–probe signal is presumably due to the presence of excited dimers after the first pulse that can survive on this timescale and absorb sufficient energy from the second pulse to bring them over the fusion threshold. The possible role of larger clusters and their fragments in this process is still the subject of ongoing investigations.

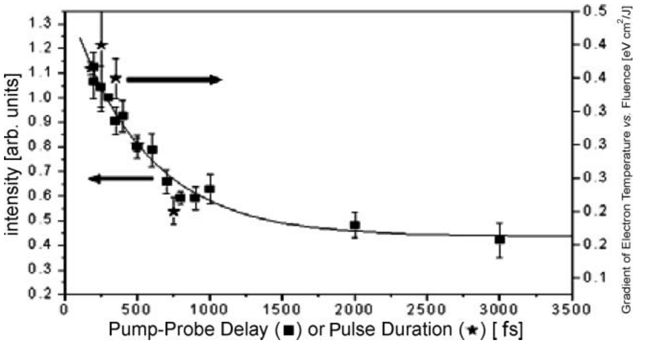

Fig. 8 Integrated dimer fragment ion intensity from the intra-cluster molecular fusion of fullerene clusters (squares, left hand *y*-axis) as a function of pump–probe delay for a single colour (800 nm) pump–probe experiment with equal intensities in both laser beams. The intensity of either the pump or the probe pulse alone is not sufficient to produce a detectable fused product. The decay is fitted to an exponential decay with a time constant of 520 ± 55 fs. For comparison, data from Hansen *et al.*[30] are shown (right hand *y*-axis) that indicate how the electronic temperature in a monomer fullerene decreases as a function of the timescale for excitation, showing the influence of coupling to vibrational degrees of freedom.

Conclusions

Fullerenes have been shown to be fascinating model systems for exploring ionisation and fragmentation phenomena after excitation with ultra-short laser pulses. It is possible to detect various stages on the way to the full equilibration of energy within these large molecular systems. The occurrence of a thermal ionisation from the highly excited electronic sub-system before coupling to vibrational modes takes place is particularly worthy of mention. Statistical modelling of the ionisation process shows that the ion intensities exhibit power dependencies with powers identical to the exact energy required for ionisation (in units of the photon energy). One should therefore be very careful in interpreting log–log plots of ion intensity *versus* laser intensity in terms of coherent multiphoton excitation. The origin for this surprising behaviour has been found to be related to averaging over Poisson photon absorption statistics.[35]

Clusters of fullerenes have also shown interesting behaviour when excited with fs laser pulses. If sufficient energy is introduced to the cluster before there is time for the energy to be coupled to vibrational degrees of freedom, one can observe intra-cluster molecular fusion to form large fullerenes (C_{120}^+), (C_{180}^+) *etc.* that fragment by emitting C_2 molecules on the ps–μs timescale of the mass spectrometer. The detected fragment ion distributions allow conclusions to be made regarding the initial excitation energy needed to induce the reaction. This is found to be compatible with energetic fusion thresholds found earlier in fullerene ion–neutral fullerene single collision experiments.

Acknowledgements

The authors acknowledge financial support from Vetenskapsrådet, K. & A. Wallenberg Foundation (fs laser system), INTAS (project 03-51-5208) and RFBR ((project 05-03-32409).

References

1 E. E. B. Campbell and R. D. Levine, Delayed Ionisation and Fragmentation en route to Thermionic Emission: Statistics and Dynamics, *Annu. Rev. Phys. Chem.*, 2000, **51**, 65–98.
2 C. Lifshitz, Some recent aspects of unimolecular gas phase ion chemistry, *Chem. Soc. Rev.*, 2001, **30**, 186–192.
3 J. U. Andersen, E. Bonderup and K. Hansen, Thermionic Emission from Clusters, *J. Phys. B*, 2002, **35**, R1–R30.
4 I. V. Hertel, T. Laarmann and C. P. Schulz, Ultrafast Excitation, Ionization and Fragmentation of C_{60}, *Adv. At. Mol. Opt. Phys*, 2005, **50**, 219–286.
5 K. Hansen, E. E. B. Campbell and O. Echt, The frequency factor in statistical fullerene decay, *Int. J. Mass Spectrom.*, 2006, **252**, 79–95.
6 E. E. B. Campbell, G. Ulmer and I. V. Hertel, Delayed Ionization of C_{60} and C_{70}, *Phys. Rev. Lett.*, 1991, **67**, 1986–1988.
7 M. Foltin, M. Lezius, P. Scheier and T. D. Märk, On the unimolecular fragmentation of C_{60}^+ fullerene ions: the comparison of measured and calculated breakdown patterns, *J. Chem. Phys.*, 1993, **98**, 9624–9634.
8 R. Mitzner and E. E. B. Campbell, Optical emission studies of laser desorbed C_{60}, *J. Chem. Phys.*, 1995, **103**, 2445–2453.
9 G. Von Helden, I. Holleman, A. J. A. van Roij, G. M. H. Knippels, A. P. G. van der Meer and G. Meijer, Shedding New Light on Thermionic Electron Emission of Fullerenes, *Phys. Rev. Lett.*, 1998, **81**, 1825–1828.
10 H. Steger, J. Holzapfel, A. Hielscher, W. Kamke and I. V. Hertel, Single-photon ionization of higher fullerenes C_{76}, C_{78}, and C_{84}. Determination of ionization potentials, *Chem. Phys. Lett.*, 1995, **234**, 455–459.

11 S. Tomita, J. U. Andersen, K. Hansen and P. Hvelplund, Stability of Buckminsterfullerene, C_{60}, *Chem. Phys. Lett.*, 2003, **382**, 120–125.
12 E. E. B. Campbell, *Fullerene Collision Reactions*, Kluwer Academic Publishers, Dordrecht, 2003.
13 K. Hansen, R. Mueller, H. Hohmann and E. E. B. Campbell, Stability of clusters of fullerenes, *Z. Phys. D: At., Mol. Clusters*, 1997, **40**, 361–364.
14 M. Tchaplyguine, K. Hoffmann, O. Duhr, H. Hohmann, G. Korn, H. Rottke, M. Wittmann, I. V. Hertel and E. E. B. Campbell, Ionization and fragmentation of C_{60} with sub-50 fs laser pulses, *J. Chem. Phys.*, 2000, **112**, 2781–2789.
15 E. E. B. Campbell, T. Raz and R. D. Levine, Internal energy dependence of the fragmentation pattern of C_{60}, *Chem. Phys. Lett.*, 1996, **253**, 261–267.
16 K. Mehlig, K. Hansen, M. Hedén, A. Lassesson, A. V. Bulgakov and E. E. B. Campbell, Energy distributions in multiple photon absorption experiments, *J. Chem. Phys.*, 2004, **120**, 4281–4288.
17 K. Hansen and E. E. B. Campbell, Radiative cooling of fullerenes, *J. Chem. Phys.*, 1996, **104**, 5012–5018.
18 J. Laskin, B. Hadas, T. D. Märk and C. Lifshitz, New evidence in favour of a high (10 eV) C_2 binding energy in C_{60}, *Int. J. Mass Spectrom.*, 1998, **177**, L9–L13.
19 M. Hedén, K. Hansen, F. Jönsson, E. Rönnow, A. Gromov, E. E. B. Campbell, A. Taninaka and H. Shinohara, Thermal radiation from C_N^+ and La@C_n^+, *J. Chem. Phys.*, 2005, **123**, 044310.
20 E. E. B. Campbell, K. Hansen, K. Hoffmann, G. Korn, M. Tchaplyguine, M. Wittmann and I. V. Hertel, From Above Threshold Ionization to Statistical Electron Emission: The Laser Pulse Duration Dependence of C_{60} Photoelectron Spectra, *Phys. Rev. Lett.*, 2000, **84**, 2128–2131.
21 A. Lassesson, K. Hansen, M. Jönsson, A. Gromov, E. E. B. Campbell, M. Boyle, D. Pop, C. P. Schulz, I. V. Hertel, A. Taninaka and H. Shinohara, A femtosecond laser study of the endohedral fullerenes Li@C_{60} and La@C_{82}, *Eur. Phys. J. D*, 2005, **34**, 205–209.
22 V. R. Bhardwaj, P. B. Corkum and D. M. Rayner, Internal Laser-Induced Dipole Force at Work in C_{60} Molecule, *Phys. Rev. Lett.*, 2003, **91**, 203004.
23 H. Cederquist, A. Fardi, K. Haghighat, A. Langereis, H. T. Schmidt, S. H. Schwartz, J. C. Levin, I. A. Sellin, H. Lebius, B. Huber, M. O. Larsson and P. Hvelplund, Electronic response of C_{60} in slow collisions with highly charged ions, *Phys. Rev. A*, 2000, **61**, 022712.
24 V. R. Bhardwaj, P. B. Corkum and D. M. Rayner, Recollision During the High Laser Intensity Ionization of C_{60}, *Phys. Rev. Lett.*, 2004, **93**, 043001. vfill="yes"/
25 E. E. B. Campbell, K. Hoffmann and I. V. Hertel, The transition from direct to delayed ionization of C_{60}, *Eur. Phys. J. D*, 2001, **16**, 345–348.
26 D. Bauer, F. Ceccherini, A. Macchi and F. Cornolti, C_{60} in intense femtosecond laser pulses: nonlinear dipole response and ionization, *Phys. Rev. A*, 2001, **64**, 063203.
27 D. Bauer, *Intense laser field-induced multiphoton processes in single- and many-electron systems*, *Habilitation Thesis*, Fachbereich Physik, Technische Universität Darmstadt, Germany, 2002.
28 E. E. B. Campbell, K. Hoffmann, H. Rottke and I. V. Hertel, Sequential ionisation of C_{60} with femtosecond laser pulses, *J. Chem. Phys.*, 2001, **114**, 1716–1719.
29 M. Boyle, K. Hoffmann, C. P. Schulz, I. V. Hertel, R. D. Levine and E. E. B. Campbell, Excitation of Rydberg Series in C_{60}, *Phys. Rev. Lett.*, 2001, **87**, 273401.
30 K. Hansen, K. Hoffmann and E. E. B. Campbell, Thermal electron emission from the hot electronic sub-system of vibrationally cold C_{60}, *J. Chem. Phys.*, 2003, **119**, 2513–2522.
31 R. Schlipper, R. Kusche, B. Von Issendorff and H. Haberland, Thermal emission of electrons from highly excited sodium clusters, *Appl. Phys. A*, 2001, **72**, 255–259.
32 M. Maier, M. Schatzel, G. Wrigge, M. A. Hoffmann, P. Didier and B. Von Issendorff, Bulk-like electron–phonon coupling in small free sodium clusters, *Int. J. Mass Spectrom.*, 2006, **252**, 157–165.
33 B. Concina, S. Tomita, J. U. Andersen and P. Hvelplund, Delayed ionisation of C_{70}, *Eur. Phys. J. D*, 2005, **34**, 191–194.
34 J. M. Weber, K. Hansen, M.-W. Ruf and H. Hotop, Penning ionization of C_{60} and C_{70}, *Chem. Phys.*, 1998, **239**, 271–286.
35 K. Hansen, E. E. B. Campbell and I. V. Hertel, Laser power dependence in femtosecond ionization of fullerenes, *J. Phys.; Conf. Series*, 2005, **4**, 282–285.
36 T. P. Martin, U. Näher, H. Schaber and U. Zimmermann, Clusters of Fullerene Molecules, *Phys. Rev. Lett.*, 1993, **70**, 3079–3082.
37 M. Hedén, K. Hansen and E. E. B. Campbell, Molecular fusion of $(C_{60})_N$ clusters in the gas phase under femtosecond laser irradiation, *Phys. Rev. A*, 2005, **71**, 055201.
38 B. Manil, L. Maunory, B. A. Huber, J. Jensen, H. T. Schmidt, H. Zettergren, H. Cederquist, S. Tomita and P. Hvelplund, Highly Charged Clusters of Fullerenes: Charge Mobility and Appearance Sizes, *Phys. Rev. Lett.*, 2003, **91**, 215504.
39 E. E. B. Campbell, A. Glotov, A. Lassesson and R. D. Levine, Cluster–cluster fusion, *C. R. Phys.*, 2002, **3**, 341–352.