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The transition from direct to delayed ionisation of C_{60}

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Abstract. The timescale for the coupling of electronic and vibrational excitation in isolated fullerenes is determined by recording positive ion time-of-flight mass spectra on excitation with ultrashort laser pulses at 790 nm of the same fluence but different pulse durations. The coupling leads to the onset of a delayed ionisation "tail" on the parent fullerene ion peak. This occurs for a pulse duration of 500-1000 fs, depending on laser fluence.

PACS. 36.40.-c Atomic and molecular clusters

1 Introduction

Fullerenes have shown many interesting properties and have become fruitful model systems for studying the behaviour of complex molecules and clusters [1]. One of their most interesting properties is their tendency for undergoing delayed (μs) ionisation after excitation with ns laser pulses where the photon energy lies below the ionisation potential [2–6]. This is generally considered to be a statistical process akin to thermionic emission although some evidence has accumulated recently to indicate that a purely thermionic emission interpretation is perhaps not always justified [1]. We have recently shown, using a combination of ion time-of-flight mass spectrometry and photoelectron spectroscopy that the ionisation mechanism of C_{60}, using near IR laser pulses (790 nm), is dependent on the timescale for excitation (*i.e.* on the laser pulse duration) [7]. For very short laser pulses (25 fs) a direct sequential multiphoton (or, at high intensities, tunnel) ionisation occurs on the timescale of the excitation [7,8]. As the pulse duration is increased beyond 100 fs, keeping the intensity constant, a statistical, thermal electron emission occurs from the electronic manifold of states. This statistical ionisation occurs promptly *i.e.* no delay is observable in the experiments indicating that the ionisation process must occur on the sub-50 ns timescale. For these short laser pulses the ion mass spectra are characterised by a strong contribution of multiply charged ions [9,8]. If the pulse duration is increased to a few ps the multiply charged species disappear and a "tail" is observed on the C_{60}^+ ion peak extending to longer times [7]. This "tail" is a characteristic feature of delayed ionisation as is normally observed on ns laser excitation [3,4]. In this paper we further investigate the transition from a prompt ionisation to a delayed (μs) ionisation using 790 nm laser pulses of variable pulse duration but keeping the fluence (*i.e.* the energy per pulse) and the laser bandwidth constant by using a chirped pulse. The transition to delayed ionisation is seen to occur for times on the order of 500-750 fs and is related to the electron-phonon coupling timescale in the fullerene molecule.

2 Experimental setup

A schematic diagram of the apparatus used in the experiments is shown in Fig. 1. It consists of three differentially pumped vacuum chambers. The central chamber contains an effusive fullerene source. On opposite sides of this source chamber there are a reflectron time-of-flight mass spectrometer for determining mass spectra of positively charged ions and a double μ-metal shielded electron time-of-flight spectrometer for determining photoelectron spectra. The fullerene oven is situated below the centre of the extraction field for the ion mass spectrometer. The photoelectron spectra were generally obtained without an extraction field. A focused laser beam crossed the uncollimated effusive C_{60} beam perpendicular to the beam and spectrometer axes. The energy scale of the photoelectron spectrometer was calibrated by comparing the fullerene spectra to photoelectron spectra from Xe. The laser intensity was calibrated by determining the dependence of the Xe^{q+} ion signals on intensity [9].

For the present experiments, a Ti:sapphire laser (Quantronix) producing 170 fs pulses at 790 nm and a bandwidth of 10 meV was used for the experiments reported here, unless otherwise stated. Longer pulses were produced by de-tuning the compressor of the laser amplifier thus keeping the bandwidth and near-Gaussian pulse

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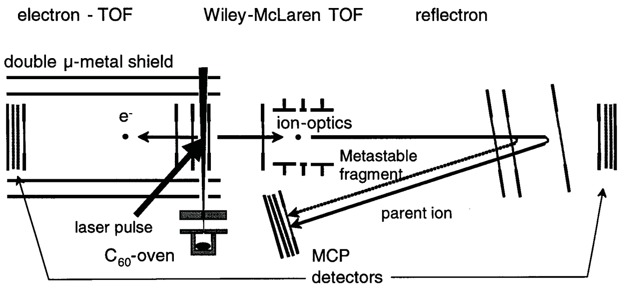

Fig. 1. Schematic diagram of apparatus.

shape constant as the pulse duration was changed. The pulse energy was adjusted by using a set of thin neutral density filters.

3 Results and discussion

The spectacular difference observed in the mass spectra when changing the laser pulse duration is illustrated in Fig. 2. These mass spectra were obtained for similar laser pulse energies (fluences) of about 20 J/cm^2. A different Ti:sapphire laser system, with a laser bandwidth of 85 meV was used to obtain the spectrum in Fig. 2(a). The strong contribution of multiply-charged species is very clearly seen in the 25 fs spectrum. In contrast, only singly-charged ions are observed with 5 ps pulses. As has been discussed previously, the fragment ions in both cases are highly vibrationally excited and undergo metastable fragmentation on the μs timescale of the ion passage through the reflectron [8,9]. Fig. 2(b) also shows the typical delayed ionisation tail on the C_{60}^+ mass peak which is not present in the 25 fs mass spectrum.

The onset of the delayed ionisation signal is more clearly seen in Fig. 3. Here the raw time-of-flight signal has been plotted in a log-log plot. All the spectra were obtained for the same laser fluence (5.5 J/cm^2). The delayed tail starts to appear between 500 fs and 750 fs at this fluence. There is a signal beyond the parent ion peak for a pulse duration of 500 fs however the isotope resolved peaks of the C_{60}^+ are still very sharp and we believe that the small but significant broad peak to larger times is an artefact. It scales with the intensity of the prompt ion signal and remains unchanged for all pulse durations below 500 fs measured in this series of experiments (down to 175 fs). A small but significant tail can be seen for a pulse duration of 750 fs and this grows in intensity as the pulse duration is further increased. The delayed ionisation tail measured for excitation with ns lasers has been shown to follow a power law [10] which should give a linear behaviour on a log-log plot. The full line drawn through the tails in Fig. 3 has a slope of -0.7, in good agreement with the power law behaviour for electron emission on excitation with ns laser pulses as shown by Hansen and Echt [10]. The slope does not change with pulse duration and is related to the ratio of ionisation potential to the activation energy for C_2 loss from neutral C_{60}. An onset of delayed ionisation for pulse durations greater then 500 fs is in good agreement with early work using UV laser pulses that showed no observable delay for excitation with 500 fs pulses [11]. It is interesting to note that the ratio of metastable fragments to prompt fragments and the relative fragment intensities (*e.g.* C_{58}^+:C_{56}^+) do not change throughout the measurement series. This indicates that the relative intensities of the prompt singly-charged fragments and their temperature do not depend on the timescale for excitation but only on the total amount of energy available in the pulse (the fluence).

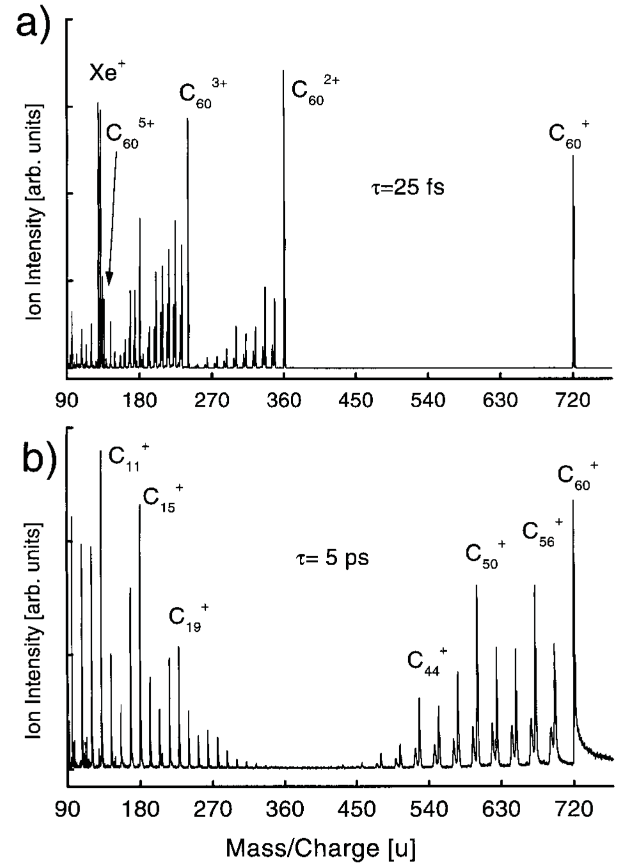

Fig. 2. Mass spectra obtained for approximately the same laser fluence (20 J/cm^2) but different pulse durations: (a) 25 fs (b) 5 ps. Laser wavelength of 790 nm.

A summary of the data obtained for two different fluences (5.5 and 4.6 J/cm^2) is shown in Fig. 4. In this figure we have plotted the relative intensity of the delayed tail to the prompt ion intensity for both fluences. The onset of delayed ionisation, as determined by a linear fit to the data in the threshold region (insert in Fig. 4), occurs for a pulse duration of 550 ± 150 fs and 750 ± 300 fs for 5.5 and 4.6 J/cm^2, respectively. Although the error bars are rather large, it is clear that the onset of the observable signal is fluence dependent, as one would expect. A certain amount of internal vibrational excitation is needed before delayed ionisation can be observed on the experimental timescale. The amount of electronic excitation transferred to

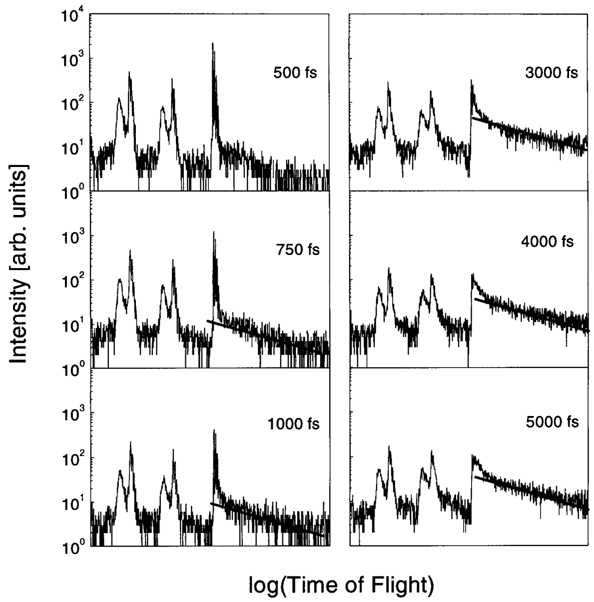

Fig. 3. Log-log plot of time-of-flight mass spectra obtained for the same laser fluence (5.5 J/cm^2) but different pulse durations: Laser wavelength of 790 nm. The full lines drawn through the tail region give a power law dependence with an exponent of −0.7. See text for details.

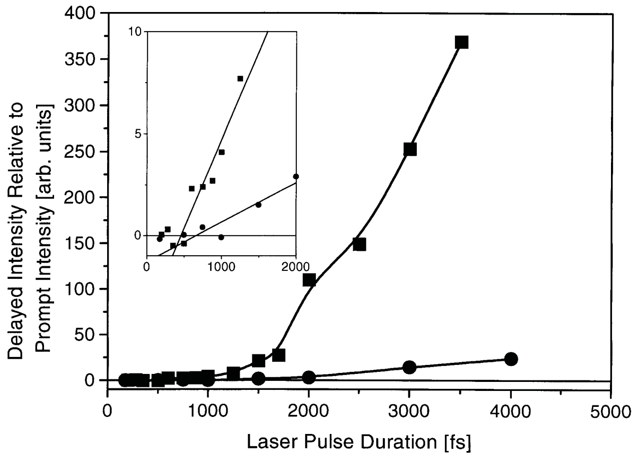

Fig. 4. Relative intensity of delayed ionisation tail to the prompt parent ion signal as a function of pulse duration for two different laser fluences. Squares: 5.5 J cm^{-2}, circles: 4.6 J cm^{-2}. The lines in the main diagram are to aid the eye. The lines in the insert are least squares fits used to determine the onset of delayed ionisation.

vibrational excitation depends on the electronic-vibrational (electron-phonon) coupling timescale (and thus on the laser pulse duration) and on the total amount of excitation available for conversion to vibrational excitation (laser fluence dependent).

The photoelectron spectra confirm the picture obtained from the ion mass spectra. For pulse durations on the order of a few 100 fs the electron energy distribution corresponds predominantly to thermal electrons with very high temperatures (on the order of 10000 K). When the cross-over to delayed, thermionic electron emission occurs, after energy has been transferred and distributed among the vibrational degrees of freedom, the temperature of the thermal electrons drops dramatically [7]. This is illustrated in Fig. 5 where we show the photoelectron spectra and the corresponding positive ion mass spectra for two different pulse durations. The laser fluence was approximately the same in both cases and less than the experiments discussed above (*ca.* 3 J/cm^2). For 500 fs excitation the electrons are rather hot (≈10000 K) and for this fluence value practically no fragmentation is observed in the mass spectrum. For the 5 ps pulse the electrons are still hot, but significantly less so than before and extensive fragmentation of the core is seen. The fitted electron temperature (*ca.* 5000 K) is also in fairly good agreement with the vibrational temperature that would be needed to produce such a fragmentation pattern, indicating that the system is in thermal equilibrium.

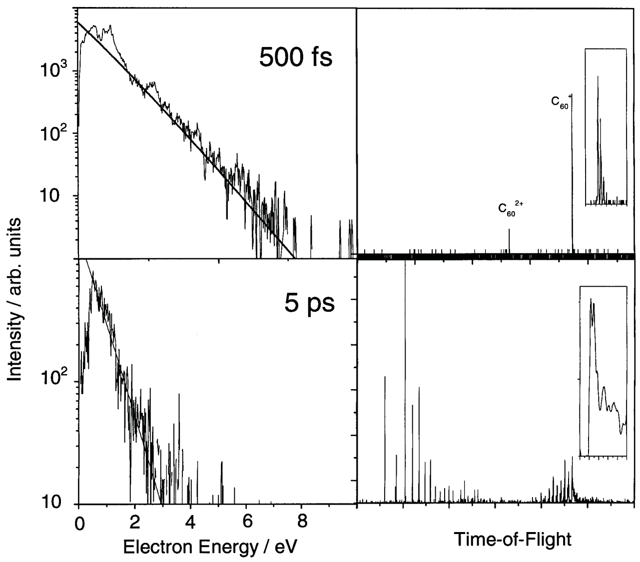

Fig. 5. Photoelectron spectra (left) and mass spectra (right) measured for two different pulse durations. The abrupt change on going from 500 fs to 5 ps is due to the coupling of electronic to vibrational excitation within the duration of the laser pulse. For 500 fs the energy is still confined to the electronic degrees of freedom during the time available for excitation. For 5 ps pulses a substantial amount of the energy has been transferred to vibrational degrees of freedom leading to a significant decrease in the electron temperature and an increase in the ion fragmentation.

In summary, we have shown that the onset of delayed, "thermionic" electron emission from C_{60} occurs on a timescale of 500-1000 fs, depending on the fluence of the ultrashort laser pulses. The relative intensity of the delayed ionisation signal increases strongly with increasing pulse duration and fluence. The power law behaviour of the signal does not change with pulse duration (within the experimental error bars). Only a very small amount of delayed ionisation is observed from neutral fragments with practically none being observable in these experiments from fragments smaller than C_{58}. Keeping the laser fluence constant but changing the timescale for excitation does not influence the intensities of the singly charged fragment ions with respect to the prompt parent ions nor does it influence the amount of metastable fragmentation from these excited fragment ions or from C_{60}^{+}, indicating that the vibrational temperature of the ions, on the microsecond timescale of the mass spectra, is dependent only on the total energy available in the laser pulse and not on the timescale for excitation.

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