From Above Threshold Ionization to Statistical Electron Emission: The Laser Pulse-Duration Dependence of C_{60} Photoelectron Spectra

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The photoelectron spectra of C_{60} ionized using a 790 nm laser with pulse durations varying from 25 fs to 5 ps have been determined. For 25 fs pulses, in the absence of fragmentation, the ionization mechanism is direct multiphoton ionization with clear observation of above threshold ionization. As the pulse duration is increased, this becomes dominated by a statistical ionization due to equilibration among the electronic degrees of freedom. For pulse durations on the order of a ps coupling to the vibrational degrees of freedom occurs and the well-known phenomenon of delayed (μs) ionization is observed.

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Fullerenes are extremely interesting model systems for studying the dynamics of ionization and energy coupling in relatively complex systems with a large number of degrees of freedom [1,2]. Their behavior under irradiation with ns lasers has been studied extensively in recent years. The characteristic features such as delayed ionization [3], a high excitation energy threshold for fragmentation [4,5], and a bimodal fragment distribution at high excitation energies [6,7] can all be reasonably well explained in terms of highly statistical behavior with an efficient coupling of electronic excitation to vibronic degrees of freedom. The ionization and fragmentation of fullerenes with ultrashort pulsed lasers (<ps) have also been studied by a number of groups in recent years [7–14]. It is particularly interesting to probe the dynamical behavior as the laser pulse duration is reduced below the time scale of electron-phonon coupling, expected to be on the order of a few hundred femtoseconds. All of the studies with ultrashort pulse lasers have involved the detection of positively charged ions. Much of the emphasis has been on the high intensity range leading to a high degree of multiple ionization accompanied by Coulomb explosion and the production of ions with extremely high (keV-MeV) kinetic energies. Two studies covering the low intensity threshold region for ionization with laser pulse duration on the order of 100 fs and less have produced results indicating very different ionization mechanisms. Hunsche *et al.* [10] presented evidence that the plasmon resonance plays an important role in the ionization and fragmentation of C_{60}. In contrast, recent results from our laboratory provide evidence that the ionization is dominated by direct multiphoton ionization with no indication of the excitation of the plasmon [15].

The conclusions concerning the ionization mechanisms drawn by Hunsche *et al.* [10] and Tchaplyguine *et al.* [15] are based on measuring the power law of the total ion yield as a function of the incident laser intensity. However, it is well known that such measurements are difficult and may lead to inconclusive results. The energy spectra of the photoelectrons resulting from the interaction with the laser pulse is known from many studies with atoms to carry more information than the ions [16,17]. Many features of atomic ionization in strong laser fields that had remained hidden in total ion yield measurements were uncovered by electron spectroscopy [18]. In this Letter we report for the first time systematic studies of the dependence of the photoelectron spectra from the interaction of ultrashort 790 nm laser pulses with C_{60} on the laser pulse duration and intensity. We show that there are three different ionization mechanisms depending on the pulse duration τ: for $\tau < 100$ fs ionization is due predominantly to multiphoton ionization, for $100 < \tau <$ ps we have evidence for statistical ionization after equilibration among the electronic degrees of freedom, and, finally, for $\tau >$ ps we have the well-known phenomenon of delayed ionization after coupling between the electronic and vibrational degrees of freedom.

The experimental setup 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 reflection time-of-flight mass spectrometer for determining mass spectra of positively charged ions and a μ-metal shielded electron time-of-flight spectrometer for determining the photoelectron spectra. The neutral C_{60} effusive beam was produced by evaporating commercial gold grade C_{60} powder (Hoechst) in an oven at a temperature of 450–500 °C. Prior to the measurements the sample was heated to ca. 200 °C overnight to evaporate any residual solvent molecules. The oven was located beneath the center of the extraction field that served for both the ion and the electron spectrometers. A focused

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laser beam crossed the uncollimated effusive C_{60} beam perpendicular to the beam and spectrometer axes. The electron spectra shown here were all obtained without using an extraction voltage. The energy scale was calibrated by comparing with photoelectron spectra from Xe.

A Ti:sapphire laser system producing a pulse train of 25 ± 5 fs light pulses was used. Longer pulses in the range up to a few hundred fs were produced by dispersive stretching. Picosecond pulses were produced by bypassing the compressor. The near Gaussian laser beam was focused on the fullerene target with a 50 cm lens. The intensity was calibrated by determining the focal spot size and by carrying out calibration measurements with Xe [15]. The pulse energy was adjusted using a set of thin neutral density filters.

A series of photoelectron spectra is shown in Fig. 1 as a function of laser pulse duration. The laser intensities were similar for (a)–(d), lying within the range $(8 \pm 2) \times 10^{13}$ W/cm^2. This is close to the observable threshold for double ionization and fragmentation using fs pulses [15]. Figure 1(e) was obtained with an intensity of ca. 5×10^{12} W/cm^2. Corresponding mass spectra are shown in Fig. 2. For pulse durations up to and including 110 fs practically only C_{60} ions are observed. There is a signal due to doubly charged species. The relative intensity of the multiply charged ions with respect to the singly charged ions is considerably exaggerated in the figure due to the differences in detection efficiencies. The ionization also clearly occurs promptly with no asymmetric broadening of the ion peak due to delayed ionization, as can be clearly seen from the insets in Figs. 2(a)–2(c). This is in agreement with earlier measurements that showed no evidence for delayed ionization from fullerenes using laser pulses shorter than 500 fs [7–9]. The situation changes for pulses of 500 fs and 5 ps duration. Considerable fragmentation is observed and for 5 ps there is also a clearly observable broadening of the parent ion signal to higher mass (longer times) due to delayed ionization within the extraction field on a time scale of a few microseconds. In addition, no multiply charged species are observed with 5 ps pulses.

There is a very distinct and reproducible structure in the photoelectron spectra for pulse durations of 25 and 70 fs [Figs. 1(a) and 1(b)]. This becomes much less distinct at 110 fs, and a broad structureless background signal begins to dominate.

The oscillatory structure seen for short pulses can be attributed to the above threshold ionization (ATI). This is a well known phenomenon for atoms and has been extensively studied, particularly in rare gases, for a number of years [17–20]. It is convincing proof of the multiphoton character of the ionization under these conditions and strongly supports the conclusions drawn by us earlier concerning the direct multiphoton ionization mechanism of

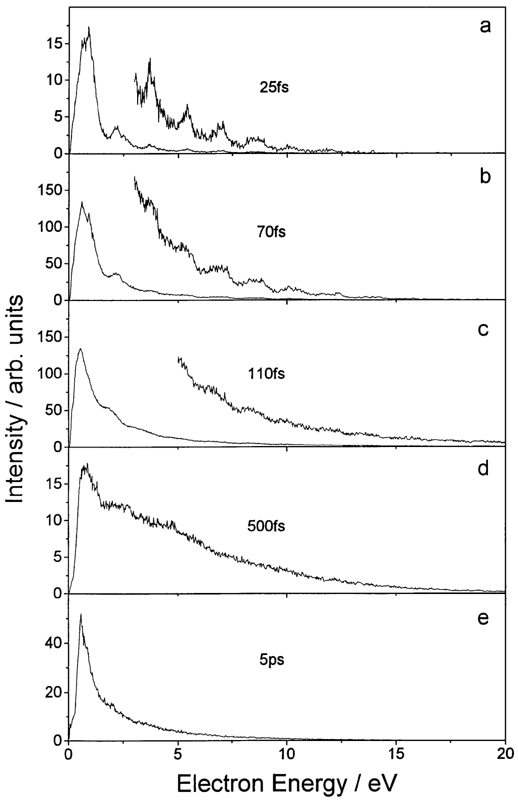

FIG. 1. PES from C_{60} as a function of laser pulse duration (a)–(d) $(8 \pm 2) \times 10^{13}$ W/cm^2, and (e) 5×10^{12} W/cm^2.

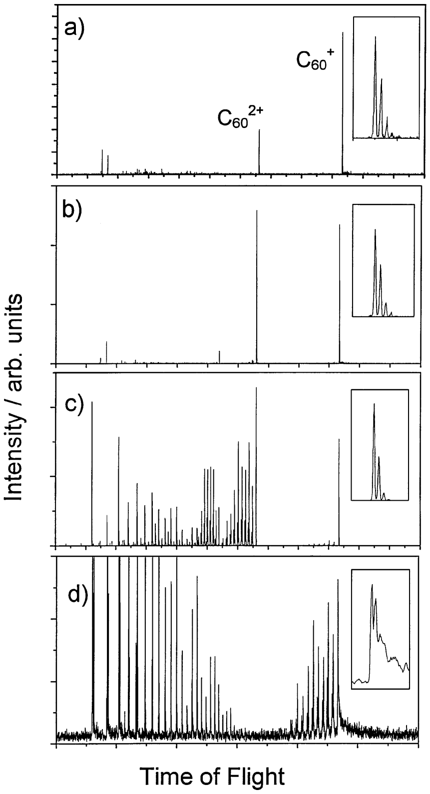

FIG. 2. Positive ion mass spectra as a function of laser pulse duration. Intensities and pulse durations are the same as in Figs. 1(a), 1(c), 1(d), and 1(e), respectively.

C_{60} for sub-100 fs pulses [15]. The spectra can be satisfactorily fitted by a series of Lorentz curves. This is illustrated in Fig. 3(a) for the same spectrum shown in Fig. 1(a). The peaks are separated by the photon energy of 1.57 eV. The multiphoton ATI character of the ionization with 25 fs pulses under conditions where no fragmentation occurs [Fig. 3(a)] has been confirmed by determining the angular dependence of the photoelectrons. The ATI electrons become more sharply peaked in the direction of the laser polarization as their kinetic energy increases, as expected in the classical limit [18].

The photoelectron spectra start to change significantly on expanding the pulse duration but keeping the intensity constant (Figs. 1 and 3). The clear ATI structure, still visible for $\tau = 70$ fs, becomes less well defined. There is also an underlying broad signal extending to beyond 10 eV. This is even more apparent for 110 fs where the ATI structure has become much less distinct [Figs. 1 and 3(b)]. In Figs. 3(b) and 3(c) the photoelectron spectra are fitted to a combination of ATI peaks [using the same parameters with the exception of the absolute intensity as in the fit to the 25 fs data in Fig. 3(a)] and a thermal electron distribution. The thermal distribution used for the fit is that given previously for thermal electron emission from a cluster of finite size [21,22]. Note that since we are using a time-of-flight electron spectrometer without an extraction field we are discriminating against the very low energy electrons (<1 eV). If we have a purely multiphoton ionization mechanism, then the intensity of the laser pulse is the most suitable parameter for comparison. However, if we have a statistical thermal mechanism, then we would expect the fluence of the laser pulse (i.e., the total available energy) to be the more appropriate parameter. In order to be sure that the change in the photoelectron spectra (PES) on increasing the pulse duration from 25 to 110 fs is due to a change in the ionization mechanism we show a PES measured for 110 fs pulse duration and an intensity of 3×10^{13} W/cm^2 well below the fragmentation onset. This looks similar to the spectrum in Fig. 3(b) but the thermal distribution has a lower temperature as would be expected for the lower laser fluence. As the pulse intensity is reduced further, the residual ATI peaks recover their apparent dominance due to the decreasing thermal component although their overall intensity is much less than for the shorter laser pulses. No ATI structure is left for a pulse duration of 500 fs where the PES can be fitted by a purely thermal distribution even at very low intensities or fluences where no fragment ions can be observed [Fig. 3(e)].

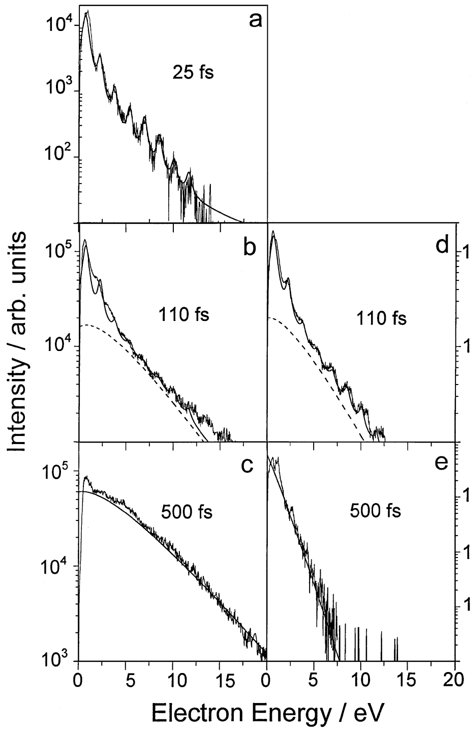

FIG. 3. PES fitted to a combination of ATI peaks and a thermal distribution. For details, see text. (a)–(c) Same spectra as in Fig. 1: (a) No thermal distribution. (b) $T = 32\,000$ K. (c) $T = 39\,000$ K. (d) $I = 3 \times 10^{13}$ W/cm^2, $T = 25\,000$ K. (e) $I = 8 \times 10^{12}$ W/cm^2, $T = 10\,000$ K.

An explanation for the electron energy distributions seen for $\tau = 110$ and 500 fs is a rapid ($25 < t < 110$ fs) statistical redistribution of the excitation energy among the electronic degrees of freedom. Statistical electron emission can then occur from this excited subsystem. Such a model has recently been proposed to explain results of Penning ionization of fullerenes in thermal energy collisions with metastable rare gas atoms [21]. The Penning ionization results were interpreted by considering that the ionization probability was limited by the time scale for electron-phonon coupling (assumed to be 1.4 ps). We interpret our broad thermal electron energy distributions that gradually dominate over multiphoton ionization on increasing the pulse duration from 70 to 500 fs as being due to statistical emission from the electronic subsystem. As can be seen from Fig. 2, there is no evidence for delayed ionization on the order of microseconds in the mass spectra, indicating that the ionization time scale is on the order of nanoseconds or less. The temperatures obtained from the fits are extremely high, on the order of 10 000 K [Fig. 3(e)] to approximately 40 000 K [Fig. 3(c)]. Using the caloric curve given by Weber *et al.* [21] we can obtain a rough estimate of the excitation energy of between ca. 20 and 400 eV. After ionization has occurred, this excitation energy can be transferred to vibrational degrees of freedom on a longer time scale, leading to subsequent fragmentation as seen in Fig. 2(c). The excitation energy corresponding to the temperature obtained for the data in Fig. 3(e), 20 eV (10 000 K), is too low to lead to a longer time scale statistical fragmentation of the ions, on our experimental time scale, explaining their absence in the corresponding mass spectrum (not shown).

Evidence for statistical energy distribution between the electronic and vibrational degrees of freedom is seen at a pulse duration of 5 ps. Under these conditions there

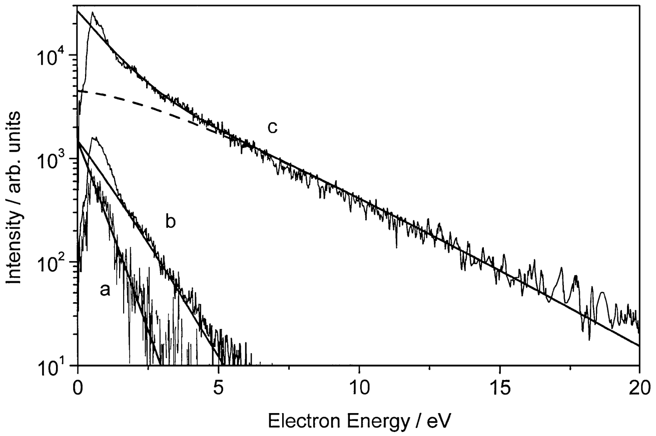

FIG. 4. PES from 5 ps laser pulses. (a) 1.2×10^{12} W/cm^2, $T = 6000$ K. (b) 2.5×10^{12} W/cm^2, $T = 10\,000$ K. (c) 5×10^{12} W/cm^2, $T = 30\,000$ K (dashed line). Full line is the sum of 2 distributions ($T = 30\,000$ K and $T = 10\,000$ K).

is clearly delayed ionization occurring as illustrated by the mass spectrum [Fig. 2(c)]. The electron distribution is also of a predominantly thermal nature as shown in Fig. 4. The time scale for electron-phonon coupling in C_{60} thus lies in the range 500 fs–5 ps. The temperatures of the thermal electrons for the data in Fig. 4 range from 6000 K (6 J/cm^2) to 30 000 K (24 J/cm$^2 \equiv 5 \times 10^{12}$ W/cm^2) corresponding to total excitation energies, assuming statistical distribution among the vibrational degrees of freedom, of ca. 85–400 eV. This is the range that one would expect from considering the form of the mass spectra. A bimodal singly charged fragment distribution is observed at all three laser fluences with the distribution shifting towards smaller masses as the fluence increases. The highest fluence data can clearly be better fitted by a combination of all three temperatures, indicating a broad temperature range. We conclude that the ionization of C_{60} for laser pulse durations less than an upper limit of 70 fs is due to a direct multiphoton mechanism in the intensity range below the onset of fragmentation. For pulse durations on the order of 70 fs and longer there is a statistical redistribution of the electronic excitation among the electronic degrees of freedom leading to a statistical (but still prompt on the time scale of mass spectra) electron emission and the loss of ATI structure. This is the dominant ionization mechanism for pulses of 110 fs–1 ps duration. The high electronic excitation possible for high laser fluences can couple to vibrational degrees of freedom on a longer (ps) time scale after ionization leading to considerable fragmentation. For 5 ps pulses there is time for statistical distribution also among vibrational degrees of freedom during the laser pulse. This leads to the observation of delayed ionization (thermonic emission for a completely statistical process) on the μs time scale accompanied by considerable fragmentation of the excited fullerenes.

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