Fragmentation and Ionization Dynamics of C_{60} in Elliptically Polarized Femtosecond Laser Fields

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Ionization and fragmentation of C_{60} fullerenes is studied in elliptically polarized, intense fs laser fields at 797 nm [$I = (0.5\text{–}4.3) \times 10^{14}$ W cm^{-2}] and contrasted with Xe^+, utilizing time-of-flight mass spectrometry. Very pronounced changes of parent and fragment ion yield as a function of ellipticity are observed. At lower intensities reduction of the ion yield for circular polarization establishes a coherent two-photon process connected with the key role of the LUMO + 1(t_{1g}) "doorway state" and multielectron dynamics. Comparison with the behavior at 399 nm corroborates this finding. At high intensities enhanced fragmentation is observed which is tentatively attributed to returning loops of electron trajectories by the combined action of the C_{60}^+ field and the circular laser field.

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The interaction of intense, ultrashort laser pulses with large, finite molecular systems attracts considerable attention (see, e.g., Ref. [1]). Because of its highly symmetric structure and its large number of electronic and nuclear degrees of freedom C_{60} fullerene is a particularly interesting model case for studying the complex mechanisms of energy deposition and migration in such systems. A variety of experimental studies and model calculations have been devoted in the past to a detailed understanding of ionization and fragmentation dynamics in C_{60} (see Ref. [2] and references given there), and very recent theoretical work underlines the continuing interest [3–7]. Interesting phenomena have been discovered such as a massive change of the ionization patterns when the pulse duration is varied from few fs to the ps range [8,9], above threshold ionization (ATI) for short pulses [8], thermionic emission [10,11], population of Rydberg states [12,13], excitation of giant breathing motion [14] as well as characteristic changes of ionization yields and relaxation times [15,16].

Many photons are typically absorbed when a femtosecond (fs) laser pulse interacts with C_{60} as a prerequisite for the observed substantial yield of multiply charged fullerene like fragment ions $C_{60-2m}{}^{q+}$. They are formed from ensembles of very hot $C_{60}{}^{q+}$ on a ns and μs time scale by sequential evaporation of several C_2 units. To allow, e.g., the appearance of $C_{50}{}^{3+}$ about 120 eV of energy is needed, equivalent to ~80 Ti:sapphire photons. The role of intermediate states in the initial process of energy deposition in large molecules has been addressed in various contexts (see, e.g., [17]). For C_{60}, several pieces of experimental evidence as well as theoretical model simulations indicate that the t_{1g} state plays a crucial role as "doorway state" [18] in the excitation mechanism, followed by coupling to electronic and vibrational degrees of freedom. The t_{1g} orbital can be excited through the first dipole allowed HOMO(h_u) → LUMO + 1(t_{1g}) transition by blue photons ($\lambda \simeq 400$ nm) as well as by two infrared photons ($\lambda \simeq 800$ nm). The selective relevance of an intermediate state is also corroborated by experiments with C_{60} in intense fs pulses at much longer wavelengths $\lambda \geq 1500$ nm where no such resonances can be accessed. Consequently, mostly intact $C_{60}{}^{q+}$ ions with charge states up to $q = 12$ were observed and only very few $C_{60-2m}{}^{q+}$ fragments [19,20]. However, these fragments were found to be significantly more abundant when using linearly rather than circularly polarized light, which was seen as evidence for electron recollision to play an important role in vibrational excitation of the $C_{60}{}^{q+}$ ions—at these long wavelengths (quasistatic regime). The Keldysh parameter [21] $\gamma = \sqrt{W_I/2U_p}$ used there was 0.2, implying a ponderomotive potential $U_p = 95$ eV $\propto I\lambda^2$ (I being the laser intensity and $W_I = 7.6$ eV the ionization potential of C_{60}). Hence, energies of the rescattered electrons of up to $3.17U_p = 300$ eV or even more [20] are encountered in this process that can safely be described by a single active electron (SAE) [4].

For shorter wavelengths U_p is typically much smaller and the ionization process is more complex due to competition between multiphoton ionization, tunnelling, excitation of intermediate electronic states and nonadiabatic multielectron dynamics (NMED). The present study addresses the role of ellipticity of the interacting light in the energy deposition mechanisms via the doorway state. Key questions are whether here too, recollision effects can be identified, and/or whether a particular signature of the doorway state can be found. Femtosecond pulses of ≃797 and 399 nm are used for ionization and fragmentation of C_{60}.

While the influence of polarization on high-order harmonic generation (HHG) and ATI is well understood [22,23], only few systematic experimental studies about ellipticity in strong field ionization have been concerned with "recollision" and nonsequential double ionization (NSDI) of atoms [22,24,25]. Typically, a reduction of ion and HHG yield is attributed to the recolliding electron being driven away from its origin by circularly as opposed

to linearly polarized light. If multiphoton absorption dominates, special angular momentum selection rules may also be significant. As to molecules, aside from C_{60}, mainly some special cases have been investigated, such as D_2 [26] and anthracene [27], where the angle between laser field and induced dipole moment may change in each of several multiphoton steps so that circular polarization can even enhance specific fragmentation channels. From a theoretical perspective, the generalization of advanced concepts "to an elliptically polarized field is extremely demanding if not impossible" [28]. Hence, the present investigation of such phenomena for a highly symmetric molecule may provide a fruitful testing ground for future theoretical efforts.

A description of our experimental setup is found in Ref. [13]. Briefly, a commercial multipass Ti:Sapphire laser provides 27 fs (FWHM) pulses at 797 nm with 1 kHz repetition rate and pulse energies up to 800 μJ. They are focused by a $f = 50$ cm concave mirror inside the vacuum chamber onto an effusive molecular beam created by evaporation of C_{60} powder at 775 K. The laser beam, molecular beam, and ion extraction field are perpendicular to each other. The ions are detected by multichannel plates after passing a reflecting time-of-flight mass spectrometer. A small amount of Xe gas is continuously added for adjustment and calibration. After signal amplification the mass spectra are accumulated with an ADC card (Acqiris). The laser intensity is computer controlled by an attenuator (Altechna) consisting of a $\lambda/2$ plate between two polarizers. Second harmonic radiation at 399 nm can be generated by a 100 μm beta barium borate (BBO) crystal. The ellipticity of laser pulses is changed from linear to circular by rotating a zero-order $\lambda/4$ plate through an angle $0 \leq \vartheta \leq 45°$. Typically, mass spectra are accumulated over 5000 laser shots for each intensity and ellipticity, which are repetitively modulated many times to average over fluctuations.

We find it convenient to plot the results as a function of ellipticity angle β which defines [29] the general polarization vector $\vec{e} = e^{-i\delta}(\cos\beta)\vec{e}_{+1} - e^{i\delta}(\sin\beta)\vec{e}_{-1}$ ($\vec{e}_{\pm 1}$ refer to left and right circular polarization and δ to the alignment of the polarization ellipse). It is directly derived from ϑ with respect to linear polarization by $\beta = \pi/4 - \vartheta$ and relates to the often used ellipticity as $\epsilon = \cot(\beta + \pi/4)$. With a pulse averaged intensity I_0 and $\omega = 2\pi c/\lambda$ the instantaneous intensity is given by

$$I(t, \beta) = I_0[1 - \sin(2\beta)(1 - 2\sin^2(\omega t + \varphi))]. \quad (1)$$

As a supposedly still simple test case we have first measured the Xe^+ ion yield as function of β for a series of different intensities. This is shown in the 3D plot Fig. 1, where the signal is normalized at each intensity to the ion yield for linear polarization ($\beta = 45°$). A dramatic drop of the signal is observed when the polarization changes from linear to circular ($\beta = 0°$), most significantly so for the

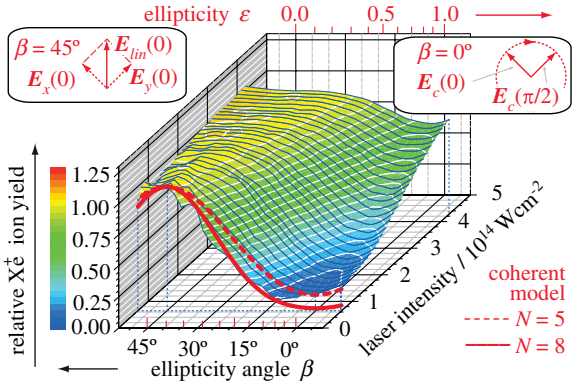

FIG. 1 (color). Xe ion yield as a function of ellipticity angle β obtained with 27 fs laser pulses at 797 nm. The polarization changes from linear ($\beta = 45°$) to circular ($\beta = 0°$). The ion yield is normalized at each intensity [(0.65–4.3) $\times$ 10^{14} W cm^{-2}] to its value for linear polarization. Full and dashed lines at $I = 0.65 \times 10^{14}$ W cm^{-2} correspond to coherent excitation in an eight- and five-photon process, respectively.

lower intensities. The overall dependence of the Xe^+ ion yield on laser pulse intensity (linearly polarized) is well known from the literature [30]: at the lower end of the present intensity range the signal roughly follows a power law $\propto I^5$ while at the upper end saturation is reached, characterized by a $\propto I^{3/2}$ dependence. To understand the presently observed ellipticity dependence we note that the *maximum* field amplitude for linear polarization is $\sqrt{2}$ times the *constant* circularly polarized field for any given average intensity, as schematically indicated in the two insets in Fig. 1 Consequently, the instantaneous intensity (1) oscillates. And while for a one photon process its average is still I_0 in both cases, for a process depending on the Nth power of I the relevant average is

$$\langle I^N(t, \beta)\rangle = \frac{\omega}{2\pi}\int_0^{2\pi/\omega}[I(t, \beta)]^N dt,$$

$$\text{specifically } \langle I^5(t, \beta)\rangle = I_0^5\frac{1}{64}[269 - 220\cos(4\beta) + 15\cos(8\beta)]. \quad (2)$$

This function for $N = 5$ (normalized) is shown in Fig. 1 as a dashed line, which roughly reflects the observed trend at $I = 0.65 \times 10^{14}$ W cm^{-2}. An even better fit is found if we assume a coherent eight-photon process, as shown by the full line $\propto \langle I^8(t, \beta)\rangle$. Interestingly, ionization of Xe requires indeed at least $\simeq 8\hbar\omega$ ($\lambda = 797$ nm). We have no conclusive explanation for this finding. We note, however, that the slope I^5 intensity dependence is usually attributed to "dynamic trapping" in high lying states, i.e., energy levels are shifted into multiphoton resonance by the dynamic Stark effect—which is obviously not reflected in the β dependence.

We now turn to our main subject. The measured ion yield for $C_{60}{}^{3+}$ is shown as an example in Fig. 1 (upper

panel). C_{60}^{+}, C_{60}^{2+}, and C_{60}^{4+} (not shown) behave very similarly. In all cases, a small but very clear reduction of the signal for circularly polarized light is seen at low intensities (0.9×10^{14} W cm^{-2}). Here the ponderomotive potential is only $\simeq 5$ eV and we do not expect recolliding electrons to play a significant role. However, a nearly perfect match of the observed (low intensity) β dependence is found with an average intensity distribution $\langle I^2(t, \beta)\rangle$ for a *coherent two-photon* process as indicated by the full red line [31]. This remarkable result manifests the importance of the t_{1g} doorway state which can be populated by such a coherent two-photon excitation. At higher intensities the β dependence decreases and the ion yields become almost independent of ellipticity. We attribute this to saturation of the ionization process.

While saturation for C_{60}^{q+} is also observed in the absolute ion yield [15] at intensities $I \simeq (1\text{–}2) \times 10^{14}$ W cm^{-2}, the clear signature of a two-photon process leaves us with a puzzle: at these wavelengths, pulse durations, and intensities the ion yield is $\propto I^N$ with, e.g., $N = 5$ for C_{60}^{+} and $N = 11$ for C_{60}^{3+}. Why is there (in contrast to the Xe^{+} case) no such dependence observed as a function of ellipticity? We consider this strong evidence for genuine multielectron processes dominating the ionization and energy deposition in C_{60} as tentatively invoked in our earlier work: once the doorway state is reached, many electrons can absorb energy through transitions in a quasicontinuum of states, which in fact explains the high number of photons absorbed. For a process which requires an energy equivalent of at least five photons (such as C_{60}^{+} formation), the intensity dependence will nevertheless be $\propto I^5$ since five photons must be absorbed during the laser pulse by a single C_{60}. These processes are, however, no longer coherent since several electrons are involved independently, hence, they do not depend on the phase φ, which, according to (1), is the basis for the ellipticity dependence.

As a crucial test we have also measured the ellipticity dependence of the C_{60}^{q+} signals at $\lambda = 399$ nm for intensities $I \sim (0.2\text{–}3.9) \times 10^{13}$ W cm^{-2}. One example of the corresponding 3D plots is shown in Fig. 2(bottom). They all are absolutely flat to within $\simeq 1\%$—while the ion yields at this wavelength were found to be $\propto I^3$ and $\propto I^4$ for C_{60}^{+} and C_{60}^{2+}, respectively [9]. This strongly confirms the key role of the doorway state, being excited by absorption of a single 399 nm photon so that its population depends only on I_0 and not on β.

Even more surprising are the fullerene like fragments C_{60-2m}^{q+} for which Fig. 3 shows the singly and triply charged ion yield summed over all fragments $m \geq 1$. For the lower intensities we recognize again the coherent two-photon signature $\langle I^2(t, \beta)\rangle$ (at least for C_{60-2m}^{3+} while C_{60-2m}^{+} fragments are very weak and the noisy signal does not allow a clear conclusion). However, at higher intensities a significant enhancement of the fragment signal is observed with circularly polarized light. At first sight,

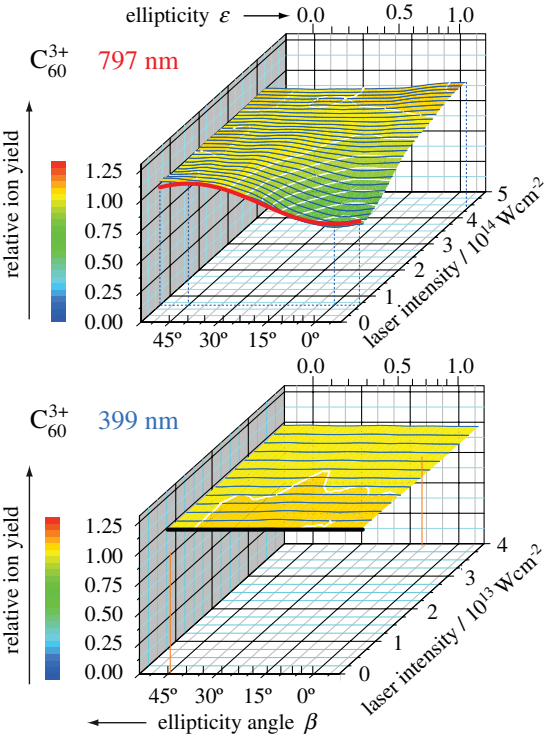

FIG. 2 (color). Normalized ion yield as a function of ellipticity angle for C_{60}^{3+} at 797 nm (top) and 399 nm (bottom). The red line at the lowest intensity represents coherent two-photon transitions, the black line single photon excitation. Otherwise as Fig. 1.

this appears to be against all common wisdom: typically the signals decrease with circularly polarized light. One potential explanation could be complicated multiphoton processes with absorption and induced emission steps leading to constructive interference.

However, even in the classical trajectory picture one might imagine loops of recolliding electrons in a circularly polarized electric field—if the electrons ejected have initial kinetic energy [28]. This aspect can be amplified by the structure of C_{60}: in contrast to atoms the photoionized (or tunnelling) electrons emerge from a sphere with radius $\gtrsim a \simeq 8.12$ a.u., the C_{60} shell radius [32]. They may be ejected with relatively high initial kinetic energy. If, e.g., the C_{60} plasmon resonance supports the photoabsorption process in the continuum [15] one expects initial kinetic energies of 10 to 30 eV. Assuming the electrons to be ejected radially this will lead most trajectories in a linearly polarized field to miss the C_{60} on return. In contrast, one may find a number of trajectories in a circularly polarized field which return, even several times, as exemplified in Fig. 4. We have used here a model potential for the C_{60}^{+} ion similar to that previously used [15], with polarization screening [19] adopted in such a way that the field is zero inside. Inspection of several such trajectories shows that electrons may return with kinetic energies up to 60 eV. This may lead to significant heating of C_{60}^{q+}, especially so if

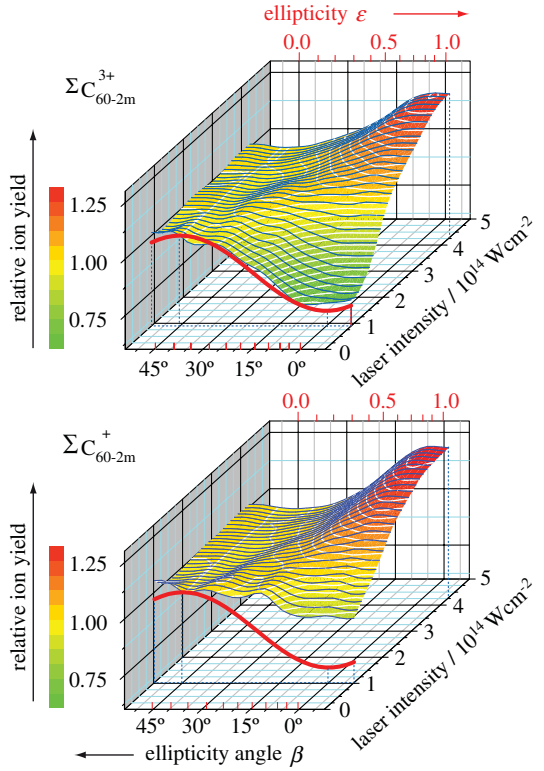

FIG. 3 (color). Normalized ion yield (enlarged scale) as a function of β for $C_{60-2m}{}^{+}$ and $C_{60-2m}{}^{3+}$ at 797 nm, otherwise as Fig. 2.

several electrons ejected from higher charge states return. We do not claim this to be a conclusive explanation of enhanced fragmentation, but one which may be worthwhile to follow in more depth.

In summary, we have observed a significant influence of ellipticity on ionization and fragmentation processes in C_{60} fullerene in intense fs laser pulses. The decrease of ion yields at lower intensities gives strong evidence for the crucial role of the t_{1g} state as a doorway state for energy deposition, followed by efficient multielectron dynamics. In contrast, at higher intensities a remarkable increase of fullerenelike fragments is observed in circularly polarized light. This might be caused by closed loops of recolliding electrons in circularly polarized light due to the particular structure of C_{60}.

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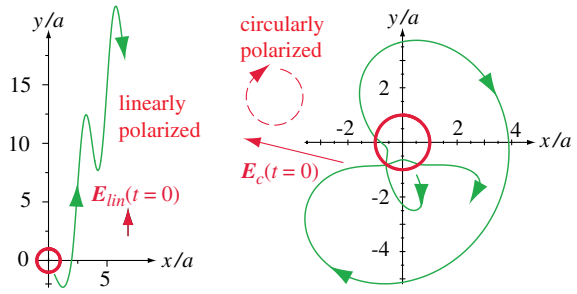

FIG. 4 (color online). Examples of classical electron trajectories in the combined field of $C_{60}{}^{+}$ and linearly or circularly polarized light ($I = 4.3 \times 10^{14}$ W cm^{-2}, 797 nm, initial kinetic energy 15 eV). At time $t = 0$ the field points into the directions indicated. Trajectories are calculated for $0 \le t \le 2\pi/\omega$. The red circle indicates the C_{60} shell radius a (note the different x, y scales).

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