Recollision during the High Laser Intensity Ionization of C_{60}

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Through C_{60}, we address the role of electron recollision in the nonresonant, femtosecond laser ionization of large, highly polarizable molecules. We show how the electron trajectories are influenced by the laser field, the laser induced dipole field, and the Coulomb field of the ion core. Working at long wavelengths we observe recollision in C_{60} through the ellipticity dependence of the fragmentation it produces. The ionizing electron emerges from C_{60}^{z+} ($z = 3, 4$) with a lateral velocity of $\sim$12 Å/fs, approximately half its Fermi velocity. Despite the large lateral velocity and competing forces on the electron, recollision remains relatively probable for this scale of molecule.

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A strong laser field ionizing an atom or molecule accelerates the released electron first away from the ion and then drives it back to the parent ion where it can recollide with significant energy [1]. This *recollision* is a central process in intense field physics. In atoms, it has led to an efficient source of x-ray and extreme ultraviolet radiation and to attosecond optical pulses [2]. In diatomic molecules, it has allowed attosecond time resolved dynamics [3]. We show that recollision occurs in large multielectron molecules. Understanding recollision in such systems is important for three reasons. First, the ionized electron retains information about the molecule from which it has just departed. Recollision gives us access to this information, providing a probe to interrogate the molecule in the presence of a strong field. An example is the signature of quantum interference in the ionization of benzene found in the recollision dynamics [4]. Second, chemical outcomes can be controlled by learning to manipulate the recollision. Third, recollision in large molecules has important potential applications. The electron can diffract from its parent ion core, determining the structure of the molecule [5] or it might produce high harmonics more efficiently [6].

We identify recollision in $C_{60}^{z+}(z = 3 - 4)$ through the fragmentation that it produces. By treating C_{60} as a conducting sphere we show how the polarizability of the molecule can influence the trajectory of the ionized electron. Recollision can still occur because the laser-induced dipole force on the electron that initially kicks the electron away is countered by Coulomb attraction of the ion core. We show that the electron that emerges from $C_{60}^{z+}(z = 3 - 4)$ has approximately twice the lateral momentum that it would have for an atom or for a small molecule [4,7,8]. The lateral velocity that we measure is approximately half the electron's Fermi velocity.

C_{60} is an ideal molecule to study recollision in multielectron systems because of its: (i) very high polarizability $\sim$80 Å^3 [9]; (ii) large electron impact ionization and fragmentation cross sections [10]; (iii) spherical symmetry and electronic structure that allows it to be modeled as a conducting sphere, thereby reducing the theoretical complexity; (iv) the conducting sphere model accurately describes ionization and the electronic response of the ion-core to the field, providing a firm foundation for calculation [11].

We use long wavelength light (1.2–2.2μm range) to work in a regime where ionization is quasistatic [12]. In benzene, at these wavelengths and at modest intensities, all fragmentation is due to recollision [4]. The effect of using infrared radiation in C_{60} is shown in Fig. 1 where our results at 1500 nm are compared to 800 nm [13]. Ionization at long wavelengths is simplified, fragmentation is more controlled, and highly charged C_{60} cations up to C_{60}^{12+} are generated [11]. In addition, at longer wavelengths recollision is more sensitive to laser polarization and maximum electron recollision energies (3.2 U_p) of

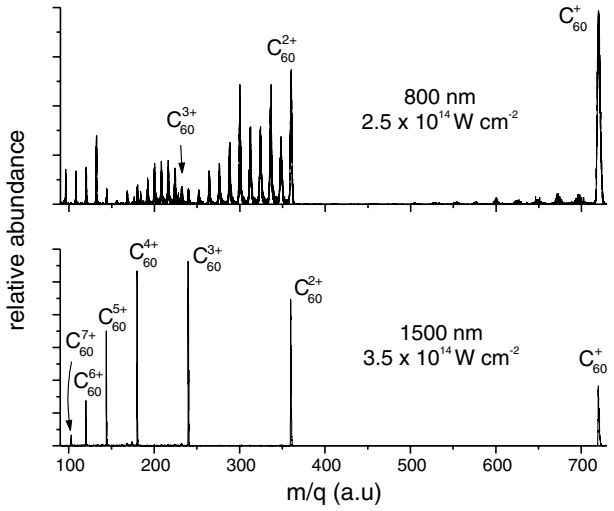

FIG. 1. Comparison of mass spectra obtained from the intense field laser ionization of C_{60} at 800 (40 fs) and 1500 nm (70 fs). The spectrum at 800 nm is similar to that reported previously [13].

the order of 50–150 eV can be obtained at modest intensities where low charge states can be studied ($U_p = E^2/4\omega^2$ is the ponderomotive energy in atomic units). Ionization and fragmentation cross sections are maximum in this range.

The experiment was carried out in a Wiley-McLaren time-of-flight mass spectrometer (TOFMS). Differential pumping allows the source chamber to be operated at up to 10^{-5} Torr, while maintaining the flight chamber under high vacuum. We evaporate C_{60} powder (purity 99.5%, MER Corporation) in a 550 °C oven to produce an effusive beam of C_{60}. The neutral C_{60} beam is partly collimated by passing through a 1 mm diameter pinhole located 2 cm above the oven. The oven was located below the ion optics of the spectrometer midway between the electrodes.

We use a 50 fs, 750 μJ, 800 nm, pulse to pump an optical parametric amplifier (OPA). The OPA produces orthogonally polarized signal and idler beams in the wavelength range of 1200 to 2200 nm. Either the signal or idler is selected using a broadband cube polarizer. The pulse energy is $\sim$75 μJ. We measure the pulse duration to be 70 fs at 1500 nm. We focus with an $f/25$ lens to obtain intensities up to $\sim 3 \times 10^{14}$ W/cm^2. Under these conditions (beam waist of 17 μm and confocal parameter of 605 μm) the 0.5 mm slit at the entrance to the drift region of the TOFMS collects only ions produced in the focal volume [14]. Microchannel plates operating in conjunction with a multichannel scaler detect the ions. We obtain ion yields by integrating the appropriate peaks.

Our procedure to identify recollision is to measure the dependence of double ionization or fragment ion yields on the laser polarization [1,7,8]. An electron born into elliptically polarized light experiences a lateral displacement, $\Delta y \approx 5\varepsilon E/\omega^2$ where $\varepsilon = E_y/E_x$ is the ellipticity, due to the transverse field component. For relatively small ellipticities the electron is offset sufficiently to miss the parent ion. We use a Berek variable wave plate in $\lambda/4$ configuration to change the ellipticity of the laser polarization. We analyze the ellipticity of the laser polarization using a broad bandwidth polarizer and a photodiode. The ellipticity is less than 0.02 for linear polarization. Intensity calibration is obtained by measuring the saturation intensity of Xe^+ and comparing it with known values [14].

The probability of recollision resulting in multiple ionization or fragmentation depends on the energy of the electron on its return and on electron impact ionization or fragmentation cross sections. In He atoms, where electron recollision was observed at 800 nm [15], the cross section for $He^+ + e \rightarrow He^{2+}$ is 0.094 Å^2 at impact energies of $\sim$100 eV [16]. In contrast, the cross sections for $C_{60}{}^+ + e \rightarrow C_{60}{}^{2+}$, $C_{60}{}^{2+} + e \rightarrow C_{60}{}^{3+}$, and $C_{60}{}^+ + e \rightarrow C_{58}{}^+$ are 21, 25, and 3 Å^2, respectively. Therefore nonsequential ionization and fragmentation due to recollision might be expected to be highly probable in C_{60}. Figure 1 indicates that, at the least, fragmentation is not overwhelming. Does this imply that recollision is switched off in highly polarizable molecules due to the initial kick the laser induced dipole gives to the electron?

We answer this question by treating the motion of the ionizing electron classically. In atoms double ionization is quantitatively described [4,16] by a 3-step semiclassical model [1]. (i) Under the influence of the field, the electron tunnels from the atom. (ii) A swarm of classical electron trajectories are launched with initial conditions determined by the quantum mechanics of tunneling. The electron moves in the combined laser and ion field. (iii) recollision excites or ionizes the ion according to established cross sections. This approach explains many features of recollision in simpler systems [1].

There are critical differences between atoms and large molecules in the motion of the electron in the continuum. We concentrate on these differences. We include the finite size and polarizability of C_{60} by treating it as a conducting sphere (CS) of effective radius $a = (a' + \delta a)$ where $a'(= 3.54$ Å) is the C_{60} radius and δa ($= 1.13$ Å) is the spillout [17–19]. In the presence of a conducting sphere of charge z in an external electric field of magnitude E the electron moves on the potential $\Phi(\mathbf{r})$ given by

$$\Phi(\mathbf{r}) = -E\left(r - \frac{a^3}{r^2}\right)\cos\theta - \frac{q}{4\pi\epsilon}\left[\frac{a}{2(r^2 - a^2)} + \frac{z - \frac{a}{2r}}{r}\right], \tag{1}$$

where $\mathbf{r}$ is the position vector of the electron referenced to the center of the sphere [20]. θ is the angle between $\mathbf{r}$ and $\mathbf{E}$, the electric field, with $\cos\theta$ given by $\mathbf{E}\cdot\mathbf{r}/Er$. Note that a^3 is directly related to the polarizability, α of the sphere.

To study recollision, we follow the electron motion in this time and position dependent potential. The derivative of the four terms in Eq. (1) can be identified with four competing forces on the electron due to the laser field, the laser induced dipole potential, the image potential, and the Coulomb potential. We calculate trajectories numerically as the electron responds to the potential gradient with $\mathbf{E}$, the time dependent field, given by $\mathbf{E} = E_0[\mathbf{i}\cos(\omega t + \phi) + \varepsilon\mathbf{j}\sin(\omega t + \phi)]$ where ϕ is the phase of birth of the electron.

Trajectories are run until a recollision, numerically defined as approach closer to the core than the starting position, occurs. If the electron does not recollide in 3 cycles it is assumed to have escaped. The electron is assumed to start at rest at the top of the barrier. Recollision energies (U_{ret}) are calculated from the electron velocity immediately prior to the impact. They depend on when the electron is released during the laser cycle, i.e., phase of birth. Recollision is characterized by the phase of birth (ϑ_{max}) that gives the highest energy return (U_{max}).

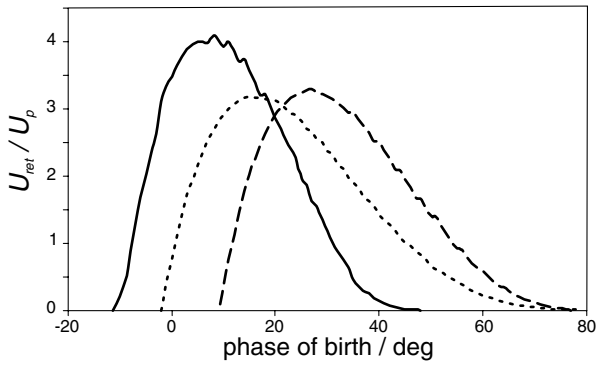

FIG. 2. Dependence of the ratio of the return energy, U_{ret}, to the ponderomotive energy, U_p, on the phase of birth of the electron ($I = 8 \times 10^{13}$ W cm^{-2}, $z = 4$) for linearly polarized light ($\varepsilon = 0$), ignoring the dipole and charge (dotted line), including the dipole (dashed line) and including the dipole and the Coulomb interaction with a charged conducting sphere (solid line).

When both Coulomb and dipole terms are ignored in Eq. (1), the result (dotted line in Fig. 2) is that obtained for recollision in atoms, i.e., $\vartheta_{\max} = 17°$ and $U_{\max} = 3.2U_p$. When the field dependent dipole is included in calculation (dashed line Fig. 2) recollision still occurs but the electrons have to be born later in the optical cycle for them to return with significant energy. Since the probability of ionization depends on the phase (peaks strongly at $\vartheta = n\pi$), the probability of electrons returning with significant energy drops markedly as $\vartheta_{\max}$ moves towards 90°. The effect of the dipole is twofold. It reduces the likelihood of recollision by providing a kick to the electron early in its trajectory and also raises the potential barrier making it harder to ionize. Including the Coulomb attraction, for charge state $z = 4$, brings $\vartheta_{\max}$ back to the atomic value or even slightly less (solid line in Fig. 2). Under these circumstances the electron energy can be greater than $3.2U_p$.

These classical calculations indicate that recollision should be at least as likely for C_{60} as for an atom despite the competing forces on the electron. From the C_{60}^{z+} appearance intensities, we predict recollision energies of 13, 20, 34, and 47 eV for $z = 1$ to 4, respectively. With the known energy dependent cross sections for $C_{60}^{z+} \rightarrow C_{58}^{z+}$ [21] one might expect fragmentation to occur for $z \geq 2$.

Although fragmentation is not very evident in Fig. 1 at 1500 nm, there is more than is first apparent. This is because the yield is spread over many fragments and because the fragments pick up translational energy during dissociation and their mass peaks are broadened. For instance, at an intensity of $\sim 2 \times 10^{14}$ W cm^{-2} 10% of the ion yield is in fragments. Figure 3(a) compares the sum of the triply charged fragment yields, C_{60-2m}^{3+} ($m = 1 - 3$), with the yields of C_{60}^{3+} and C_{60}^{4+} as a function of intensity. We did not observe any singly and

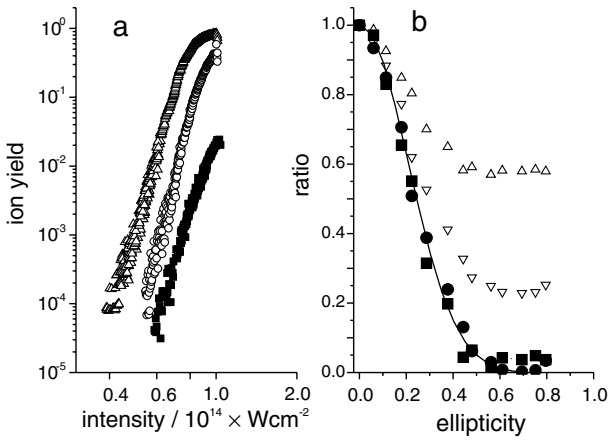

FIG. 3. Recollision in the intense field ionization of C_{60}: (a) intensity dependence of the sum of the yields of C_{60-2m}^{4+}, $m = 1, 2, 3$ fragments (■) compared to the precursors C_{60}^{3+} (△) and C_{60}^{4+} (○); (b) ellipticity dependence of the ratios $C_{60-2m}^{3+}/C_{60}^{4+}$ [raw data (▽), background corrected (●)] and $C_{60-2m}^{4+}/C_{60}^{5+}$ [raw data (△), background corrected (■)] at an intensity of 8×10^{13} W cm^{-2}.

doubly charged fragment ions. Both ion-neutral dissociation and asymmetric fission, dominated by sequential C_2 loss from C_{60}^{3+} and C_2^{+} loss from C_{60}^{4+} can contribute to the yield of C_{60-2m}^{z+} according to electron impact studies [22].

We identify fragmentation due to recollision from the ellipticity dependence of the ratio, R_z, $= C_{60-2m}^{z+}/C_{60}^{(z+1)+}$, for $z = 3, 4$ [Fig. 3(b)]. Recollision is switched off in circularly polarized light because the field imparts lateral momentum to the electron. We show the fragment yield referenced to the next highest parent charge state as required if the asymmetric fission channel dominates. We find superimposable behavior (not shown in the figure) if we reference to the same charge state assuming the neutral channel dominates. We observe a background fragmentation that is not dependent on laser polarization and is higher for C_{60-2m}^{4+} production. When background is subtracted both R_3 and R_4 show identical polarization dependence that is characteristic of recollision.

From the width of the ellipticity dependence curve in Fig. 3(b) we can measure the spread of the electron wave packet following C_{60} ionization. This lateral velocity is a characteristic signature of the quantum mechanical nature of the ionization process. As the ellipticity increases, the electron wave packet is pushed further from the ion in the direction of the minor component of the laser field. As a result the recollision probability decreases with increasing transverse separation Δy between the ion and the electron on its return. The observed ellipticity dependence of the fragments has a Gaussian form similar to that predicted by atomic tunneling theory [16]. The $1/e$ width of $\varepsilon = 0.29$ corresponds to Δy of ~ 40 Å and a transverse velocity of the electron of ~ 12 Å/fs, approximately twice greater than in an atom of the same ionization

potential. In this regard the strong field ionization of C_5H_6 and H_2 is atomiclike [4,5] but C_{60} is not. The transverse velocity is close to half the Fermi velocity, 20 Å/fs, calculated treating C_{60} as a conducting sphere with the 60 π electrons completely delocalized.

Normally recollision also manifests itself in nonsequential multiple ionization. This is the prime symptom in atom ionization and has been observed in molecules as large as benzene [4]. Our ellipticity studies showed no discernible evidence for nonsequential ionization in C_{60}. We credit this to the dominance of sequential ionization. In C_{60} the relatively small increase in ionization potential with charge is countered largely by the increase in the charge (the barrier suppression $\propto \phi_{IP}^4/z^2$) so that the sequential channel opens up rapidly and typically we find ${C_{60}}^{z+}/{C_{60}}^{z+1} \sim 10$. In atoms the equivalent ratio is $\sim$1000.

In conclusion, we have shown that recollision occurs in C_{60} although the electron emerges from the molecule with large transverse velocity. These studies will have an impact on the future experiments where electron recollision is used to probe nuclear wave packet motion or to diffract from the molecular framework revealing molecular structure [5].

Recollision occurs as long as the laser-induced dipole and Coulomb forces can be balanced. However, this may not always be possible, especially for lower charge states. Under those circumstances, working at much longer wavelengths ($\gtrsim 3\mu$m) can minimize the effects of polarizability on recollision. The large initial velocity acquired by the electron due to the dipole force is offset by the longer time it spends in the laser field. Therefore the electron returns with significant energy when born at a phase similar to atoms.

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