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Ultrafast dynamics and fragmentation of C_{60} in intense laser pulses

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ABSTRACT

The radiation-induced fragmentation of the C_{60} fullerene was investigated by the tight-binding electron–ion dynamics simulations. In intense laser field, the breathing vibrational mode is much more strongly excited than the pentagonal-pinch mode. The fragmentation effect was found more remarkable at long wavelength $\lambda \geqslant 800$ nm rather than the resonant wavelengths due to the internal laser-induced dipole force, and the production ratio of C and C_2 rapidly grows with increasing wavelength. By such fragmentation law, C atoms, C_2 dimers or large C_n fragments could be selectively obtained by changing the laser wavelength. And the fragmentation of C_{60} by two laser pulses like the multi-step atomic photoionization was investigated.

1. Introduction

Interactions of intense ultrashort laser pulses with molecules and the competition between ionization and fragmentation have attracted considerable attentions [1–3]. Because of the highly symmetric structure, C_{60} fullerene is regarded as a particular model for studying the mechanisms of molecular energy deposition and migration in intense laser field. Various experimental and theoretical studies have been carried out to explore the dynamics of C_{60} in intense laser pulses [4–8], and a great deal of phenomena about the interactions between C_{60} and intense laser pulses have been discovered. For example, a massive change in ionization patterns [9,10], above-threshold ionization (ATI) [9], population of Rydberg states [11,12], excitation of giant breathing motion [13], thermionic emission [14,15] and high-order harmonic generation (HHG) [16–18].

Several studies have focused on the specific ions and fragments of C_{60} generated in intense laser. The first systematic study was done by O'Brien et al. using nanosecond laser pulses. By the fragment detection of time-of-flight spectrometers [19], the primary channel of photodissociation was found to be the loss of neutral C_2 or C_3 units [20]. Then, the dynamic evolution of C_{60} was observed under different laser wavelengths. By wavelengths below 1000 nm, C_{60} cluster mainly gains photon energy by excited electrons out of occupied states [21]. And the dipole force plays a role in the situation of longer wavelengths [22]. For short wavelengths, the role of intermediate states in the initial process of energy deposition in large molecules has been addressed [23]. Several experimental and theoretical studies indicated that the LUMO + 1 state, which can be excited through the first dipole-allowed HOMO → LUMO + 1 transition and followed by coupling to electronic and vibrational degrees of freedom, plays a crucial role as doorway state in the excitation mechanism [1]. Recently, ionization and fragmentation of C_{60} fullerenes via the excitation of LUMO + 1 state was studied in elliptically polarized intense femtosecond laser field [24,25] to weaken ATI and HHG by reduced electronic recollision. And molecular dynamics (MD) simulations [26,27] were employed to generalize the rules of laser-induced fragmentation of C_{60} fullerenes. However, for studying such ultrafast electronic excitation progress, MD simulation is not an appropriate theoretical approach because the motion of C_{60} is beyond the Born–Oppenheimer approximation.

In this work, the interactions between C_{60} fullerenes and intense laser pulses were investigated by tight-binding electron–ion dynamics (TBED) [28–31] in a wavelength range of 300–1500 nm. The breathing mode was found much more strongly excited rather than the pentagonal-pinch mode in intense radiation field. At short loser wavelength the open-cage distortion is induced by the radial stretch of the breathing mode, while the internal laser-induced dipole force plays an important role in producing C atoms or C_2 dimers at a wavelength longer than 800 nm. The production ratio of C and C_2 rapidly grows with increasing laser wavelength and the fragmentation law could be used to obtain C atoms, C_2 dimers or large C_n fragments. In order to enhance the fragmentation efficiency, the excitation of continuous electronic transitions by two laser pulses was investigated.

2. TBED simulations

To investigate the interactions between C_{60} and intense laser, TBED is introduced in our simulations. The electronic states in C_{60}

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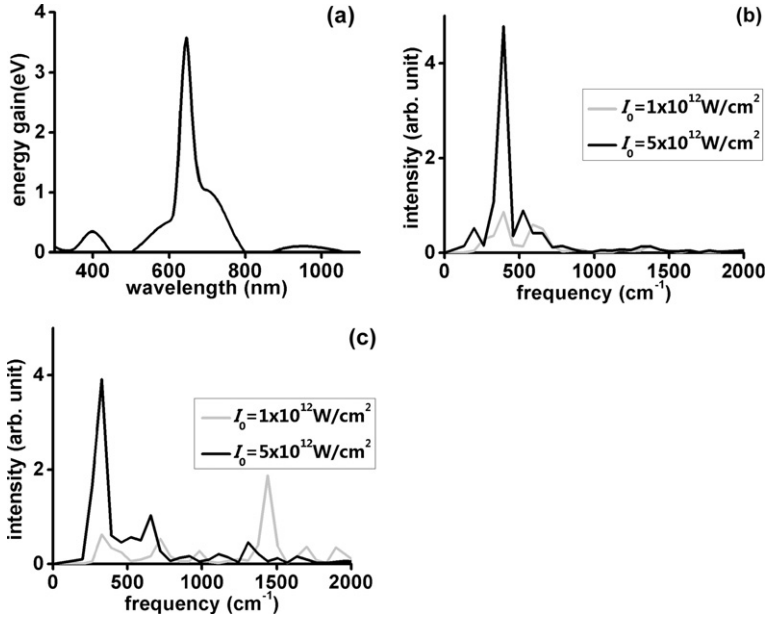

Fig. 1. The energy of C_{60} gained from the radiation field by $I_0 = 1 \times 10^{10}$ W/cm^2 (a), and the vibrational spectrum of C_{60} after being subjected to $I_0 = (1 \times 10^{12})$–(5×10^{12}) W/cm^2 laser pulses at wavelengths of 640 (b) and 1500 nm (c).

are described by the linear combination $|\psi_j\rangle = \sum_i c_{ji}|\varphi_i\rangle$ of covalent s and p orbitals $|\varphi_i\rangle$ of C atoms, i.e. the column vector form

$$\psi_j = \begin{pmatrix} c_{j1} \\ c_{j2} \\ \vdots \\ c_{jN} \end{pmatrix}, \tag{1}$$

and the molecular Hamiltonian $\hat{H}_0$ is presented in the matrix form H_{0ij}, which can be derived by the non-self-consistent approach of a density-functional-based theory [32,33]. The laser field is treated classically by vector potential $\vec{A}$ in the Coulomb gauge and the total Hamiltonian reads

$$\hat{H} = \hat{H}_0 - \frac{i\hbar e\vec{A}\cdot\nabla}{mc} + \frac{e^2\vec{A}^2}{2mc^2}. \tag{2}$$

For laser pulse with wavelength much longer than the size of C_{60}, the field $\vec{A}$ is treated as uniform and the Hamiltonian matrix should be

$$H_{ij} = H_{0ij} + \frac{i\hbar e}{mc}\vec{A}\cdot\frac{\partial S_{ij}}{\partial\vec{r}_j} + \frac{e^2\vec{A}^2}{2mc^2}S_{ij}, \tag{3}$$

where the overlap matrix element $S_{ij} = \int \varphi_i\varphi_j\, d^3\vec{r}$ and $\vec{r}_j$ the position of atom carrying φ_j. For uniform field $\vec{A}$, this calculation method is rigorous rather than by the approximate Peierls substitution [28–31]. The total energy is expressed as the sum of electronic energies and a short-range repulsive pair potential [32–34]

$$E_{tot} = \sum_i \left(\psi_i^+ H\psi_i\right)/\left(\psi_i^+ S\psi_i\right) + U_{rep}, \tag{4}$$

where H and S the matrix of H_{ij} and S_{ij}, respectively. Here, H_{ij}, S_{ij} and U_{rep} were calculated by Sankey and Niklewski's technique [34]. The Hellmann–Feynman force on the k-th atom reads

$$M_k\ddot{\vec{r}}_k = -\sum_i \psi_i^+\left(\frac{\partial H}{\partial\vec{r}_k} - \frac{\partial S}{\partial\vec{r}_k}S^{-1}H\right)\psi_i/\left(\psi_i^+ S\psi_i\right) - \frac{\partial U_{rep}}{\partial\vec{r}_k}. \tag{5}$$

By a time step Δt, a unitary evolution of Schrödinger equation for ψ_j is carried out by Cayley algorithm [33]

$$\psi_i(t+\Delta t) = \left(1 + iS^{-1}H\Delta t/2\hbar\right)^{-1} \cdot \left(1 - iS^{-1}H\Delta t/2\hbar\right)\psi_i(t), \tag{6}$$

and Eq. (5) is solved by the velocity Verlet algorithm.

Before investigating the dynamics of C_{60} in intense laser field, the geometry is optimized by a damped trajectory method [35] with the electronic occupations given by the Fermi–Dirac distribution at 0 K. By a time step of $\Delta t = 0.01$ fs, the C_{60} is set in an equilibrium of 300 K for 1000 fs by Riley's thermal bath [36], and then subjected to a Gaussian laser pulse

$$\vec{A} = \vec{A}_0 \sin(\omega t)\exp\left(-16\left(\frac{t}{T} - \frac{1}{2}\right)^2\right) \tag{7}$$

with the duration $T = 50$ fs. With the peak intensity $I_0 = \omega^2 A_0^2/4\pi$ and the wavelength λ in a range of (1×10^{13})–(2×10^{14}) W/cm^2 and 300–1500 nm, respectively, simulations were performed 10 times for every intensity and wavelength to obtain average results.

3. Results and discussion

The calculated bond lengths and the HOMO–LUMO gap in C_{60} are 1.39 Å, 1.43 Åand 1.43 eV, which were found close to the density-functional calculation (1.41 Å, 1.46 Å and 1.67 eV) via the Perdew–Burke–Ernzerhof functional [37]. By the electronic level and oscillator strength calculations, the main peaks in the absorption spectra of C_{60} locate at 638, 646 and 380 nm with relative strength 2.4:1.0:1, corresponding to the HOMO $-1 \rightarrow$ LUMO, HOMO $\rightarrow$ LUMO $+1$ and HOMO $\rightarrow$ LUMO $+2$ transitions, respectively, while the HOMO $\rightarrow$ LUMO transition was found to be dipole-forbidden. To test the calculation program, simulations for the peak intensity $I_0 = 1 \times 10^{10}$ W/cm^2 (much lower than the intensity for fragmentation) were performed at every wavelength λ, and the average energy of C_{60} gained from the radiation field [Fig. 1(a)] shows a strong peak at 640 nm and a weak peak at 400 nm, which is in good agreement with the absorption spectra calculation. Then, the excitation of optically-active vibrational modes was investigated by the simulations for $I_0 = (1 \times 10^{12})$–

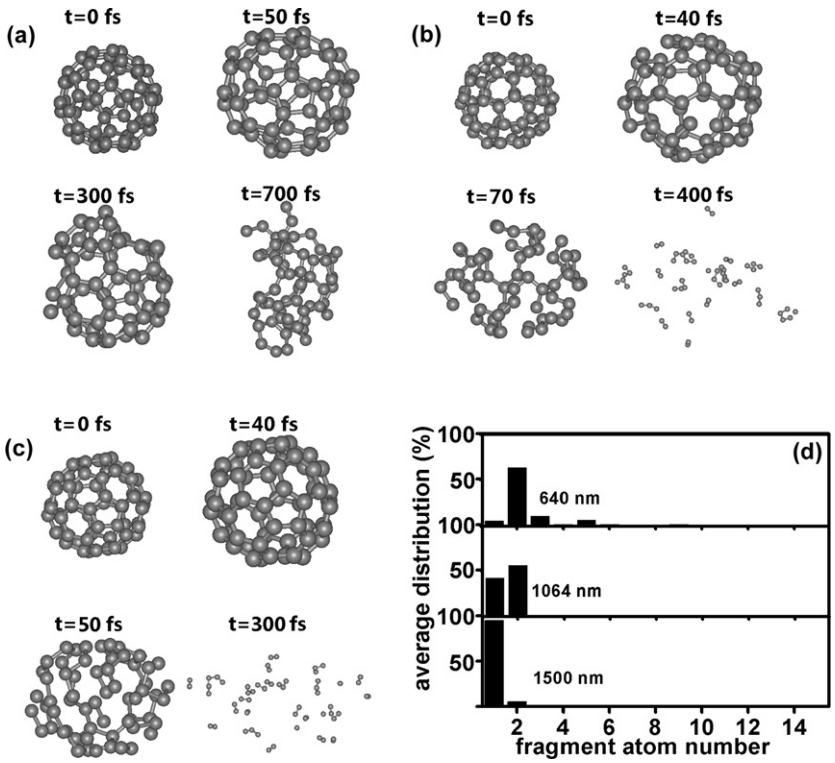

Fig. 2. Fragmentation progresses of C_{60} by a laser pulse of $\lambda = 450$ nm, $I_0 = 1 \times 10^{14}$ W/cm^2 (a), $\lambda = 640$ nm, $I_0 = 8 \times 10^{13}$ W/cm^2 (b) and $\lambda = 1064$ nm, $I_0 = 5 \times 10^{13}$ W/cm^2 (c). For $I_0 = 8 \times 10^{13}$ W/cm^2, the fragment size distribution at $\lambda = 640$, 1064 and 1500 nm is shown in (d).

(5×10^{12}) W/cm^2, in which the C_{60} still remains intact. The vibrational spectrum was obtained by the Fourier transform of the velocity autocorrelation function over an interval of 1 ps following the completion of the laser pulse. For laser wavelength below 800 nm, the most noticeable feature is the excitation of the breathing mode at 390 cm^{-1}, especially for the absorption peak 640 nm [Fig. 1(b)]. For longer wavelength, the excitation of the pentagonal-pinch mode at 1440 cm^{-1} is more remarkable than the breathing mode at low laser intensity $I_0 = 1 \times 10^{12}$ W/cm^2, while the latter is still dominant at $I_0 = 5 \times 10^{12}$ W/cm^2 [Fig. 1(c)]. The decrease in relative amplitude of the pentagonal-pinch mode with increasing laser fluence agrees with the measurements of Fleisher et al. [38] and the time-dependent density-functional-theory calculations of Torralva et al. [39].

The open-cage distortion [Fig. 2(a)] or fragmentation [Fig. 2(b) and (c)] takes place when the C_{60} is subjected to laser pulses of $I_0 > 3 \times 10^{13}$ W/cm^2. The breathing mode is remarkably excited in the radiation field, leading the rapid inflation of C_{60} with increasing molecular temperature to 2000–3500 K following the laser pulse. If enough energy is gained from the radiation field, the C_{60} breaks into small fragments during the violent radial stretch. In the range of $\lambda = 300$–500 nm, only open-cage distortion occurs even when I_0 is up to 1×10^{14} W/cm^2 [Fig. 2(a)]. For λ near the absorption peak 640 nm, more energy is gained and the fragmentation takes place when $I_0 \geqslant 8 \times 10^{13}$ W/cm^2 [Fig. 2(b)], mainly producing C_2 dimers along with a few C atoms or small C_n clusters. For longer wavelength $\lambda \geqslant 800$ nm, which is far away from the absorption peak, the fragmentation can even happen in lower I_0 with fewer C_n clusters [Fig. 2(c)]. At $\lambda = 800$–1064 nm, the fragmentation threshold for I_0 decreases from 4×10^{13} W/cm^2 to 2×10^{13} W/cm^2. In intense infrared radiation, the energy of C_{60} gained at the resonant $\lambda = 400$ or 640 nm is not remarkable due to the rapid change of electronic levels in the inflation progress. At long wavelength, the C_{60} is strongly pulled by the laser-induced dipole force [40] along the electric field of linearly polarized laser and obtains more energy than that at the resonant λ. For laser pulses with lower intensity in which the C_{60} keeps intact, the molecular vibration along the dipole force has been found in the quantum wavepacket simulations [5]. For higher laser intensity the C_{60} breaks under the effect of the dipole force. Under the same laser intensity I_0, more and more C atoms rather than C_2 dimers are produced with increasing λ, and C_n cluster can be hardly generated at long λ. For example, for $I_0 = 8 \times 10^{13}$ W/cm^2 the production of C_2 dimers is much higher than C atoms or C_n clusters at $\lambda = 640$ nm (the upper panel of Fig. 2(d)), while at $\lambda = 1064$ nm the ratio of C and C_2 becomes 1:1.3 (the middle panel of Fig. 2(d)). At $\lambda = 1500$ nm, the fragmentation produces much more C atoms than C_2 dimers without any C_n clusters (the lower panel of Fig. 2(d)). In the electric field direction of laser, the concentration of fragments is slightly higher than other directions due to the strong laser-induced dipole force. In general, the motion of C_{60} in intense laser field has an obvious relation with the wavelength. The open-cage distortion takes place in the case of short wavelength, and the fragmentation into C_2 dimers or C atoms takes place in long wavelength. The above result is slightly different with the simulation which deals the effect of laser as a sudden heating and obtains a continuous distribution of C_n fragments [26,27]. Such difference was also mentioned in Ref. [39]. Actually, the TBED simulation gives a more real physical picture than the simulation method of injecting energy into the C_{60} molecule.

In order to try to find a more efficient way, C_{60} fragmentation by two laser pulses was preliminarily investigated. The basic idea is to pump electrons to excited states via a resonant $\lambda_1 = 640$ nm and then break the C_{60} by the laser-induced dipole force via $\lambda_2 \geqslant 800$ nm, like the multi-step photoionization for atoms. The simulation system was setup by simultaneously irradiating the two laser pulses λ_1 and λ_2 with $T = 50$ fs and zero phase difference on the C_{60}. In the range of $\lambda_2 = 800$–1500 nm, simulations were performed several times for every wavelength, however, no any enhancement was found. For example, by the irradiation of the first

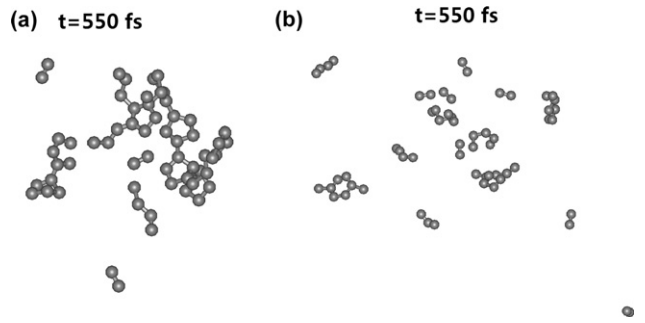

Fig. 3. Fragmentation of C_{60} by two laser pulses of $\lambda_1 = 640$ nm, $I_0 = 1.5 \times 10^{13}$ W/cm^2 and $\lambda_2 = 1064$ nm, $I_0 = 1.5 \times 10^{13}$ W/cm^2 (a) and by a laser pulse of $\lambda = 1064$ nm, $I_0 = 3 \times 10^{13}$ W/cm^2 (b).

laser pulse $\lambda_1 = 640$ nm, $I_{0,1} = 1.5 \times 10^{13}$ W/cm^2 and the second one $\lambda_2 = 1064$ nm, $I_{0,2} = 1.5 \times 10^{13}$ W/cm^2, the C_{60} breaks into large C_n fragments with a few C_2 dimers [Fig. 3(a)], while more C_2 and small fragments are produced by one laser pulse with $\lambda = 1064$ nm, $I_0 = I_{0,1} + I_{0,2} = 3 \times 10^{13}$ W/cm^2, whose intensity is the sum of the above two pulses. This may be because the C_{60} is away from the resonance with λ_1 in the inflation progress due to the strong excitation of the breathing motion, and so, λ_1 does not work for the pumping. Further study could focus on the phase difference, pulse duration and time order of the two lasers.

4. Summary

In this work, TBED simulations were performed to study the fragmentation of C_{60} in intense laser. The breathing mode was found much more strongly excited than the pentagonal-pinch mode in intense radiation field. Below the laser intensity for fragmentation, strong energy absorption at the wavelengths coupled with HOMO $-$ 1 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO + 1 and HOMO $\rightarrow$ LUMO + 2 transitions. For intense laser pulses, the fragmentation effect is more remarkable at long wavelength $\lambda \geqslant 800$ nm rather than the resonant wavelengths. For long wavelength, the internal laser-induced dipole force plays an important role in producing C and C_2 fragments, and the production ratio of C and C_2 rapidly grows with increasing laser wavelength. Such fragmentation law could be used to obtain C atoms, C_2 dimers or large C_n fragments by changing the laser wavelength. By simultaneously irradiating the two laser with a same pulse duration and zero phase difference, the enhancement of fragmentation efficiency by the multi-step excitation was not found since the C_{60} is away from the resonance with the laser pulse due to its strong motion in intense laser field.

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