Ultrafast dynamics and fragmentation of C\textsubscript{60} in intense laser pulses

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\begin{abstract}

The radiation-induced fragmentation of the C\textsubscript{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 $\lambda \geq 800 \text{ nm}$ rather than the resonant wavelengths due to the internal laser-induced dipole force, and the production ratio of C and C\textsubscript{2} rapidly grows with increasing wavelength. By such fragmentation law, C atoms, C\textsubscript{2} dimers or large C\textsubscript{n} fragments could be selectively obtained by changing the laser wavelength. And the fragmentation of C\textsubscript{60} by two laser pulses like the multi-step atomic photoionization was investigated.

\end{abstract}

\begin{keywords}
C\textsubscript{60} fullerenes
Laser fragmentation
\end{keywords}

\section{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\textsubscript{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\textsubscript{60} in intense laser pulses [4–8], and a great deal of phenomena about the interactions between C\textsubscript{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\textsubscript{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\textsubscript{2} or C\textsubscript{3} units [20]. Then, the dynamic evolution of C\textsubscript{60} was observed under different laser wavelengths. By wavelengths below 1000 nm, C\textsubscript{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 $\rightarrow$ 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\textsubscript{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\textsubscript{60} fullerenes. However, for studying such ultrafast electronic excitation progress, MD simulation is not an appropriate theoretical approach because the motion of C\textsubscript{60} is beyond the Born–Oppenheimer approximation.

In this work, the interactions between C\textsubscript{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 laser 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\textsubscript{2} dimers at a wavelength longer than 800 nm. The production ratio of C and C\textsubscript{2} rapidly grows with increasing laser wavelength and the fragmentation law could be used to obtain C atoms, C\textsubscript{2} dimers or large C\textsubscript{n} fragments. In order to enhance the fragmentation efficiency, the excitation of continuous electronic transitions by two laser pulses was investigated.

\section{TBED simulations}

To investigate the interactions between C\textsubscript{60} and intense laser, TBED is introduced in our simulations. The electronic states in C\textsubscript{60}
are described by the linear combination $|\psi_j\rangle = \sum c_i |\psi_i\rangle$ of covalent s and p orbitals $|\psi_i\rangle$ of C atoms, i.e. the column vector

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

and the molecular Hamiltonian $\hat{H}_0$ is presented in the matrix form $H_{ij}$, which can be derived by the non-self-consistent approach of a density-functional-based theory [32–34]. The laser field is treated classically by vector potential $\vec{A}$ in the Coulomb gauge and the total Hamiltonian reads

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

For laser pulse with wavelength much longer than the size of C60, the field $\vec{A}$ is treated as uniform and the Hamiltonian matrix should be

$$
H_{ij} = H_{0ij} + \frac{ihe}{mc} \cdot \vec{r}_j - \frac{e^2 \vec{A}^2}{2mc^2} S_{ij},
$$

where the overlap matrix element $S_{ij} = \int \psi_i \psi_j^* \, d^3r$ and $\vec{r}_j$ is the position of atom carrying $\psi_j$. 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]

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

where $H$ and $S$ are 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

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

By a time step $\Delta t$, a unitary evolution of Schrödinger equation for $\psi_j$ is carried out by Cayley algorithm [33]

$$
\psi_i(t + \Delta t) = (1 + iS^{-1} H \Delta t/2h)^{-1} \cdot (1 - iS^{-1} H \Delta t/2h) \psi_i(t),
$$

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

Before investigating the dynamics of C60 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 C60 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

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

with the duration $T = 50$ fs. With the peak intensity $I_0 = 0.2 A_0^2/4\pi$ and the wavelength $\lambda$ in a range of $(1 \times 10^{13}) - (2 \times 10^{14})$ W/cm² 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 C60 are 1.39 Å, 1.43 Å and 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 C60 locate at 638, 646 and 380 nm with relative strength 2.4:1.0:1, corresponding to the HOMO $→$ LUMO, HOMO $→$ LUMO + 1 and HOMO $→$ LUMO + 2 transitions, respectively, while the HOMO $→$ 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/cm² (much lower than the intensity for fragmentation) were performed at every wavelength $\lambda$, and the average energy of C60 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 $I_0 = (1 \times 10^{12})$–
(5 × 10^{12}) \text{ 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 \(I_0 = 1 \times 10^{12} \text{ W/cm}^2\), while the latter is still dominant at \(I_0 = 5 \times 10^{12} \text{ W/cm}^2\) [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 \(I_0 > 3 \times 10^{13} \text{ W/cm}^2\). 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 completion of the laser pulse. If enough energy is gained from the radiation field, 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 \(\lambda\), and C_{60} clusters can be hardly generated at long \(\lambda\). For example, for \(I_0 = 8 \times 10^{13} \text{ W/cm}^2\), the production of C_{2} dimers is much higher than C atoms or C_{60} clusters at \(\lambda = 640 \text{ nm}\) (the upper panel of Fig. 2(d)), while at \(\lambda = 1064 \text{ nm}\) the ratio of C and C_{2} becomes 1:13 (the middle panel of Fig. 2(d)). At \(\lambda = 1500 \text{ nm}\), the fragmentation produces much more C atoms than C_{2} dimers without any C_{60} 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 more energy than that at the resonant \(\lambda\). 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 \(\lambda\), and C_{60} clusters can be hardly generated at long \(\lambda\). For example, for \(I_0 = 8 \times 10^{13} \text{ W/cm}^2\), the production of C_{2} dimers is much higher than C atoms or C_{60} clusters at \(\lambda = 640 \text{ nm}\) (the upper panel of Fig. 2(d)), while at \(\lambda = 1064 \text{ nm}\) the ratio of C and C_{2} becomes 1:13 (the middle panel of Fig. 2(d)). At \(\lambda = 1500 \text{ nm}\), the fragmentation produces much more C atoms than C_{2} dimers without any C_{60} clusters (the lower panel of Fig. 2(d)).

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 \(\lambda_1 = 640 \text{ nm}\) and then break the C_{60} by the laser-induced dipole force via \(\lambda_2 \geq 800 \text{ nm}\), like the multi-step photoionization for atoms. The simulation system was setup by simultaneously irradiating the two laser pulses \(\lambda_1\) and \(\lambda_2\) with \(T = 50 \text{ fs}\) and zero phase difference on the C_{60}. In the range of \(\lambda_2 = 800–1500 \text{ nm}\), simulations were performed several times for every wavelength, however, no any enhancement was found. For example, by the irradiation of the first
with HOMO-LUMO+1 transitions. For long-wavelength laser pulses, the fragmentation effect is more remarkable at long wavelength $\lambda > 800 \text{ nm}$ 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 multistep 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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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 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO + 1 and HOMO $\rightarrow$ LUMO + 2 transitions. For intense laser pulses, the fragmentation effect is more remarkable at long wavelength $\lambda > 800 \text{ nm}$ 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 multistep 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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