Investigating the fragmentation of \( \text{C}_60 \) induced by nanosecond laser

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Abstract. The \( \text{C}_60 \) fragmentation induced by nanosecond (ns) laser was studied using a time-of-flight mass spectrometer. The average kinetic energies of fullerene ions \( \text{C}_{60-2n}^+ \) (1 \( \leq \) \( n \) \( \leq \) 14) was extracted from the measured full width at half maximum of ion beam profiles. The measured data show approximately linear increase with the mass decreasing and little variation in the present range of laser fluences. To describe the primary formation of fullerene ions, a sequential decay chain including one ionization step and one or several \( \text{C}_2 \) emission is assumed and a second photo-absorption process in later part of the laser pulse is considered. The experimental results can be explained reasonably by the description of photoion formation.

1. Introduction

Photo-fragmentation of \( \text{C}_60 \) has been studied after the discovery of fullerenes by ns laser excitation. Mass spectra of fragment ions \( \text{C}_n^+ \) (n \( \leq \) 58) reveal a bimodal distribution with a minimum around \( n = 30 \)\(^ {[1]} \). Above \( n = 30 \), only even-numbered fragment ions are observed. By contrast, both odd- and even-numbered fragment ions are found in the mass spectrum below \( n = 30 \). Kinetic energy release (KER) of fragment ions deserves a specific study as it brings additional information on the process of fragmentation. Most work on KER has focused on single dissociation of fullerene ion\(^ {[2-4]} \). Until most recent experiment\(^ {[5]} \), the average kinetic energies of the global decay chain from \( \text{C}_{60}^+ \) to \( \text{C}_{44}^+ \) have been determined using velocity map ion-imaging technique, and the primary formation mechanism of fullerene ion is assumed to be a sequential decay chain including one ionization step and one or several \( \text{C}_2 \) emission. However, up to now, no work has been devoted to measuring and calculating the relation between the average kinetic energies of the global decay chain and laser fluences.

In the present paper, we measured the time-of-flight spectrum of fragment ions resulting from the photoexcitation of \( \text{C}_{60} \). The relation between average kinetic energies for the fullerene ions \( \text{C}_{60-2n}^+ \) (1 \( \leq \) n \( \leq \) 14) and laser fluences was determined (Section 2). A new theoretical description of fullerene ion formation was presented, and experimental result is in agreement with the theoretical description (Section 3). A general summary is given in section 4.

2. Experiment and results

The experimental set-up combines a vacuum chamber and a time of flight mass spectrometer (TOFMS). The \( \text{C}_{60} \) powder (purity \( > \) 99.5\%) is sublimed in a resistively heated oven at 400°C. Optical excitation is achieved using the second harmonic of a Nd:YAG laser. The produced ions are immediately extracted by a static electric field and detected by a MCP detector. The ion signal is
recorded with a digital oscilloscope. Fig. 1 displays the TOF spectrum of the fullerene ions produced in the different laser fluences.

\[ \overline{E} = \frac{\left( W_{FWHM}^{\text{total}} \times qE_s \right)^2 / m - 5.538(tg\alpha)^2 k_B T}{8} \]  

(1)

where \( W_{FWHM}^{\text{total}} \) is the broadening induced by total initial kinetic energy of ions, \( T \) is the temperature of the \( C_{60} \) vapour, \( \alpha \) is the half angle of divergence of the \( C_{60} \) beam, and \( E_s \) is the electric field of ionization region. The constants \( k_B, m \) and \( q \) are respectively the Boltzmann constant, the mass and the charge of ion.

The \( W_{FWHM}^{\text{total}} \) can be derived from experimental mass peak. The measured peaks shapes of fullerene ions \( C_{60-2n}^+ \) (3 ≤ n ≤ 14) are almost symmetrical as shown in Fig.1. It implies that almost all these fullerene ions are produced promptly. However the peaks shapes of fullerene ions \( C_{60-2n}^+ \) (n=1, 2) have obvious asymmetry due to delayed ionization. In order to obtain the broadening, the approach adopted by us is based on the assumption that the sharp mass peak part induced by promptly produced ions has a Gaussian shape \([7]\). The width of Gaussian fit is regarded approximately as the broadening induced by total initial kinetic energy of promptly produced ions.

The average kinetic energies for fullerene ions \( C_{60-2n}^+ \) (1 ≤ n ≤ 14) are shown in Fig. 2. To compare with other work, Climen’s data \([5]\) (open symbol) are also plotted. The two works give similar results. Formation of fullerene ions from \( C_{60} \) results from a sequential decay chain. Thus, it is not surprising that their average kinetic energies show approximately linear increase with the mass decrease. It can also be seen that the data show, within the experimental error, little variation with the laser fluences in the present range. This point will be discussed in Section 3.

3. Theoretical description and discussion

To explain the measured average kinetic energies, certain assumption regarding the formation mechanism of fragment ions is necessary. Our results for fullerene ions sustain the idea of formation from \( C_{60} \) result from a competition between sequential \( C_2 \) emission and delayed ionization. From fig.2 of ref. [5], one can see that \( C_{60} \) precursor with temperature about 5000K can decay to \( C_{54}^+ \). However the \( C_{60} \) lifetime until \( C_2 \) evaporation has been found on the time scale of picoseconds at this temperature \([8]\). That means \( C_{60} \) precursor already evaporates one or several \( C_2 \) to fullerene ions at certain time during laser pulse. Fullerene ions \( C_{60-2n}^+ \) will keep evaporating \( C_2 \) after a second photo-absorption from later part of the laser pulse.
The formation chain of fullerene ion from photo-excited C\textsubscript{60} is shown in Fig. 3. There are many pathways to form fullerene ion C\textsubscript{60-2n}\textsuperscript{+}. To simplify discussion, we consider here only one pathway corresponding to the ionization of C\textsubscript{60}. The common characteristic of ns photo-excited C\textsubscript{60} is that the electronic system is excited on a long time scale compared to the electron-phonon coupling time (ca. 250fs) \cite{9, 10}. Therefore, a general statistical model based on detailed balance is used to describe relaxation processes \cite{11, 12}. The average kinetic energy of C\textsubscript{60-2n}\textsuperscript{+} (n \leq 14) in the considered formation pathway is given by

\[ \overline{E}_{\text{60-2n}} = \sum_{m=1}^{n} \frac{3}{2} \frac{60 - 2n}{60 - 2m} \frac{2}{60 - 2(m-1)} k_B T_m \]  

(2)

where \( T_m \) is the microcanonical temperature of intermediate ion C\textsubscript{60-2m}\textsuperscript{+} (1 \leq m \leq n). The internal energy of C\textsubscript{60-2m}\textsuperscript{+} is calculated from each step photo-absorption energy, the relevant dissociation and ionization energy. Assuming same photo-absorption cross section between C\textsubscript{60} molecule and C\textsubscript{60} ion, the internal energy of C\textsubscript{60-2m}\textsuperscript{+} can be written as

\[ E_{\text{C60-2m}} = \sum_{i=0}^{m-1} (\sigma_i F_i - D_i) - IP \]  

(3)

and

\[ F_i = \begin{cases} F & t_{i+1} - t_i > w \\ \frac{F}{w} (t_{i+1} - t_i) & t_{i+1} - t_i \leq w \end{cases} \]  

(4)

where \( F \) and \( w \) are respectively the laser fluence and the laser pulse duration, \( \sigma \) is the photo-absorption cross section of C\textsubscript{60-2i}\textsuperscript{+}, \( D_i \) and \( IP \) are respectively the dissociation energy of C\textsubscript{60-2i}\textsuperscript{+} and the ionization potential of C\textsubscript{60}, \( t_0 \) is the time point of laser pulse arrival, \( t_i \) is the time point of formation of C\textsubscript{60-2i}\textsuperscript{+}. In Eq. (4), \( t_{i+1} - t_i \) is regarded as the C\textsubscript{60-2i}\textsuperscript{+} lifetime until C\textsubscript{2} evaporation. Eq. (3) and (4) show that the internal energy of C\textsubscript{60-2m}\textsuperscript{+} is a function of \( F \) and \( t_{i+1} - t_i \). To obtain the qualitative relation between the energy of C\textsubscript{60-2m}\textsuperscript{+} and laser fluence \( F \), we discuss here only single dissociation C\textsubscript{60}\textsuperscript{+} \( \rightarrow \) C\textsubscript{58}\textsuperscript{+} + C\textsubscript{2}. The internal energy of daughter ion C\textsubscript{58}\textsuperscript{+} corresponding to \( m=1 \) in Eq. (3) can be written by

\[ E_{\text{C58}} = \begin{cases} \sigma_0 F_0 - D_0 - IP & t_0 > w \\ \sigma_0 \frac{F}{w} t_0 - D_0 - IP & t_0 \leq w \end{cases} \]  

(5)

where \( t_0 \) is the lifetime of C\textsubscript{60} precursor until C\textsubscript{2} evaporation. The photo-absorption cross section of C\textsubscript{60} precursor for 532nm can be extrapolated from ref. \cite{13, 14}. The caloric curve of C\textsubscript{60} precursor in the range of T >1500K is derived from ref. \cite{15}, and the lifetime of C\textsubscript{60} precursor as a function of temperature is derived from ref. \cite{8}. Thus, the relation between internal energy of C\textsubscript{58}\textsuperscript{+} and laser fluence is obtained in Fig. 4.

One remarkable fact is that the energy value does not change significantly after the laser fluence exceeds 0.2J/cm\textsuperscript{2}. In other words, the kinetic energy release during C\textsubscript{2} evaporation from C\textsubscript{60}\textsuperscript{+} does not change significantly with increasing laser fluence after \( t_0 \) is less than laser pulse duration. Internal energy of other intermediate ion C\textsubscript{60-2m}\textsuperscript{+} as a function of laser energy has the same trend because all...
fullerene ions have similar properties. Therefore, combining Eq. (2), the experimental result about the kinetic energies for fullerene ions $C_{60-2n}^+$ ($1 \leq n \leq 14$) regardless of laser fluence can be explained.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{The internal energy of daughter ion $C_{58}^+$ by nanosecond laser excitation as a function of laser fluences.}
\end{figure}

4. Summary
By carrying out detailed studies of the average kinetic energies for fullerene ions $C_{60-2n}^+$ ($1 \leq n \leq 14$) produced from $C_{60}$ excited by nanosecond laser pulses, we have been able to provide convincing evidence that fullerene ion is formed by a sequential decay chain. Considering a second absorption process in later part of the laser pulse, the puzzle about the average kinetic energies of fullerene ions, which show little variation regardless of laser fluences, is solved reasonably.

Acknowledgments
This work is supported by West Light doctoral foundation of The Chinese Academy of Sciences and the National Natural Science Foundation (Grant No.10605034, 10434100, 10504037).

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