Direct Observation of Transition from Delayed Ionization to Direct Ionization for Free C_{60} and C_{70}: Thermionic Emission?

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Transition from direct ionization to delayed ionization for free C_{60} and C_{70} is observed below the ionization potential (IP = 7.5 eV). It depends on the excitation wavelength as well as the pulse energy. The appearance threshold for direct ionization is found at ~5.8 eV. These can hardly be explained by thermionic emission; therefore, we propose that triplet states at ~1.7 eV (=7.5 − 5.8 eV) should play an important role in the multiphoton ionization of free C_{60} and C_{70} and the *intramolecular* interaction of many triplet states gives rise to delayed ionization. To confirm our proposition, we have carried out further experiments using two laser ionization.

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Delayed ionization is ionization that occurs after the excitation pulse is over. It has been found in atoms [1], molecules [2], molecular adducts [3], and clusters [4]. Although different mechanisms were proposed for delayed ionization in different systems, interaction with *long-lived electronic excitation* was generally involved [1–4]. Since 1990, however, thermionic emission has replaced long-lived electronic excitation as the mechanism for clusters [5,6]. For free C_{60} and C_{70}, decay tails due to delayed ionization were observed in multiphoton ionization and vanished in single-photon direct ionization [7,8]. It looked similar for different wavelengths in the 248–532 nm (5–2.3 eV) range [8] but depended on pulse energies (fluences) [9], where the measured slope $n > 4$ could not be understood by simple multiphoton ionization; thermionic emission was therefore considered the mechanism again. Recently, we found delayed ionization to be absent in multiphoton ionization of free C_{60} and C_{70} using high intensity subpicosecond laser excitation at 248 nm [10]. As the mechanism for this, direct ionization through *coherent* two-photon absorption under very high intensity excitation may not directly question the general validity of thermionic emission. Based on Klots's model [11], nearly ten 4–5 eV photons are supposed to be absorbed by one free C_{60} or C_{70} molecule in order to arrive at a temperature of 3000–4000 K leading to thermionic emission [8,9]. However, it was reported [12] that C_{60} starts to decompose at 1300 K. Here, we report direct observation of a transition from delayed ionization to direct ionization in the multiphoton absorption, where the appearance threshold for direct ionization of C_{60} is found at 5.8 eV rather than at ionization potential IP = 7.5 eV. Based on our new results, we may ask, "Does delayed ionization for free C_{60} and C_{70} really result from thermionic emission of electrons following multiphoton absorption?"

Free C_{60} and C_{70} were generated by heating an oven (~500 °C) containing pure C_{60}/C_{70} powder [13] under a 5×10^{-8} mbar vacuum. The oven was mounted ~1 cm below an ionization area that was located between two ion optics electrodes of our linear time-of-flight mass spectrometer. The extraction voltage was held constant. The apparatus and measurements have been fully described previously [14]. Standard excimer lasers as well as excimer laser pumped dye lasers were used for excitation (~16 ns) in the wavelength range from 193 to 770 nm.

Under 193–770 nm excitation (~16 ns) of free C_{60} and C_{70}, the transition from direct to delayed ionization has been observed in the wavelength range 210–220 nm, depending on the pulse energy. Figure 1(a) shows three typical ionization cases (only C_{60}^+ shown): For 193 nm, *only* direct ionization is detected even though *no* decay tail due to delayed ionization can be found when strong fragmentation is observed [15]; for 248 nm, delayed ionization is always found even for *fragmentation-free* ionization; and for 215 nm, the decay tail is observed at high pulse energies but *vanishes* when the energy is decreased. A difference in the slope n for the energy dependence of the ion signal in the log-log plot was found between the two kinds of ionization: $n = 2$ at 193 nm for direct ionization, whereas $n > 4$ at 248 and 308 nm for delayed ionization. The appearance threshold for direct ionization can therefore be detected so long as the energy is kept low enough to avoid delayed ionization. Figure 1(b) gives the result for C_{60}^+, where the direct ionization threshold is found at *213.5 nm (5.8 eV)*. For delayed ionization, the appearance threshold is dependent on the pulse energy (fluence). The decay appears similarly nonexponential for all wavelengths in the 248–770 nm range and depends on the pulse energy, i.e., the higher the pulse energy (fluence), the faster the decay [9]. Selective delayed ionization of C_{70} (enrichment factor $\beta = 8$) from the C_{60}/C_{70} (80% C_{60}:20% C_{70}) vapor has been observed in the 430–550 nm range (not shown in figures).

For excitation under IP = 7.5 eV (IP = 7.54 ± 0.04 eV for C_{60} and IP = 7.3 ± 0.2 eV for C_{70}) [16], ionization of free C_{60} and C_{70} should be a *multiphoton* process. Thermionic emission of electrons following multiphoton absorption has been considered as the mechanism for delayed ionization [7,8]. However, the following facts can hardly be explained with thermionic emission: (i) The

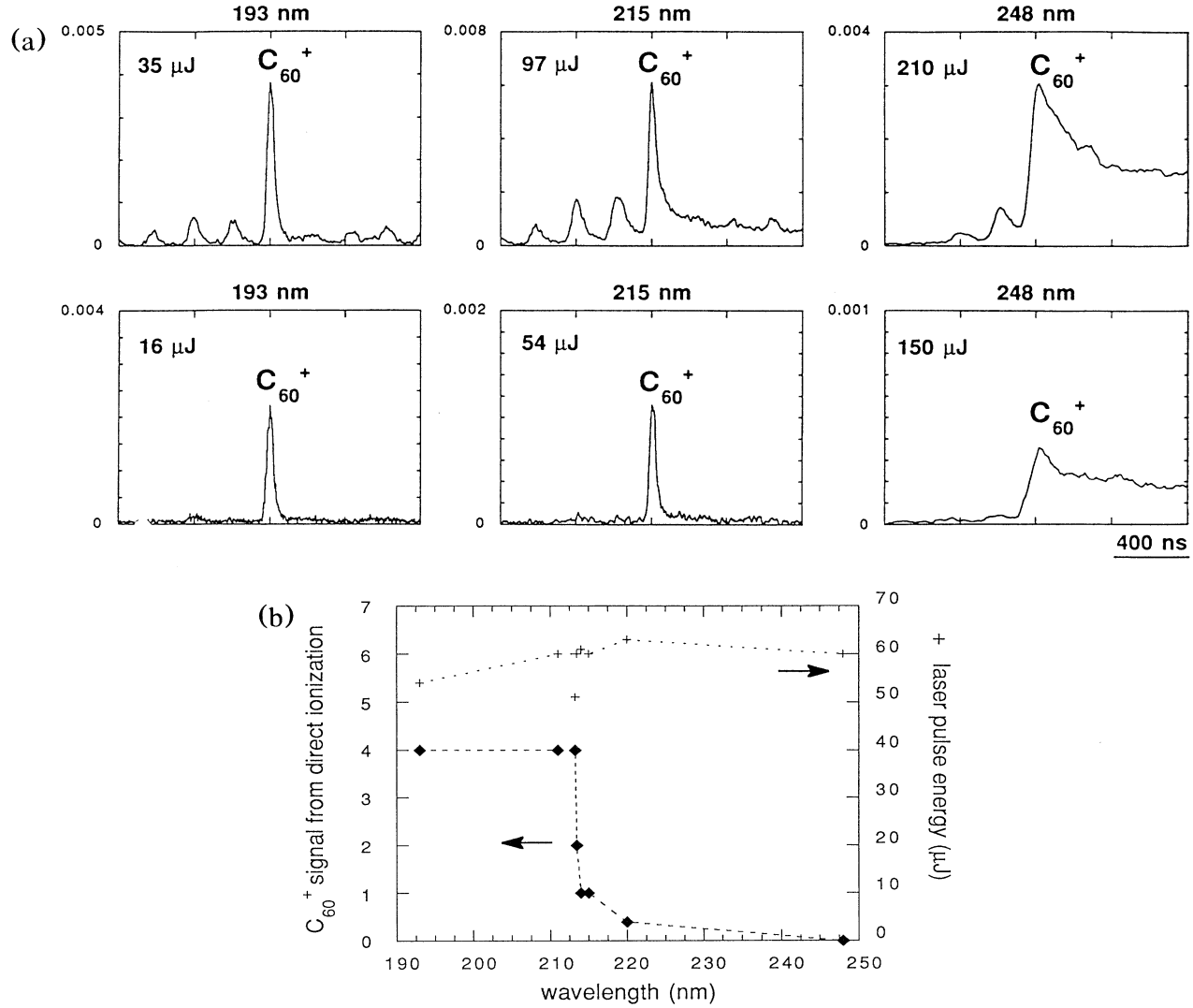

FIG. 1. (a) Three typical cases for multiphoton ionization of free C_{60}^+: For 193 nm, *only* direct ionization is detected, even *no* decay tail due to delayed ionization can be found when strong fragmentation is observed at 35 μJ; for 215 nm, the decay tail is observed at 97 μJ but vanishes at 54 μJ; for 248 nm, delayed ionization is always found, even for *fragmentation-free* ionization. The fragments are known to be C_{60-2m} ($m=1,2,\ldots$). (b) The wavelength dependence of the C_{60}^+ signal from *direct* ionization results in the appearance threshold at 213.5 nm (5.8 eV). Here, the laser pulse energy is kept at 56 ± 5 μJ, being too low to generate delayed ionization [see (a) for 215 nm].

appearance threshold for *direct* ionization was found at 5.8 eV rather than 7.5 eV. Actually, the threshold behavior has already been observed but was regarded as an observation of limited detection sensitivity [8]. Here, under low pulse energies, our observation of delayed ionization for fragmentation-free ionization at 248 nm [Fig. 1(a)] confirms that the disappearance of the decay tail at 215 nm is not due to the limited detection sensitivity. The higher order energy dependence ($n > 4$) for delayed ionization can easily account for the disappearance at 215 nm with decreasing energy. (ii) Much less delayed ionization is induced at 210–220 nm compared to that at 235–270 nm. The contrary result would be expected for thermionic emission since the absorption coefficients of C_{60} and C_{70} between 210–220 nm [$\log_{10}\varepsilon(210\text{ nm}) = 5.24$ for C_{60} and $\log_{10}\varepsilon(220\text{ nm}) = 5.05$ for C_{70}] [17] are as large as those between 235–270 nm [$\log_{10}\varepsilon(270\text{ nm}) = 5.17$ for C_{60} and $\log_{10}\varepsilon(236\text{ nm}) = 5.06$ for C_{70}] [17] and since photon energy for shorter wavelengths is converted into more thermal energy. (iii) The yield for delayed ionization shows an excitation wavelength dependence, which can hardly be explained by the model of Klots [11].

In order to explain our above observations, we propose

the following mechanism: (i) Triplet states with ~1.7 eV energy are efficiently generated when the excitation wavelength is longer than 220 nm; (ii) for 16 ns excitation, a single-photon absorption results in such a triplet state and thus multiphoton absorption during a laser pulse leads to a generation of *a number of* triplet states in *one* C_{60} or C_{70} fullerene molecule; and (iii) *intramolecular* interaction involving these triplet states leads to ionization of free C_{60} or C_{70}. The first process is consistent with many previous studies [17,18] showing that the triplet states, which have ~1.7 eV energy with a lifetime of more than 40 μs, are generated with a very high quantum yield about 1 ns after visible and UV excitation. The second is based on the fact that the coherent two-photon absorption occurs only under high intensity subpicosecond laser excitation leading to no delayed ionization [10]. In the third process, while more than four 1.7 eV triplet states are needed to overcome IP=7.5 eV, in agreement with the measured slope $n > 4$ for delayed ionization, photon (singlet)-triplet interaction can easily account for the appearance threshold found at 5.8 eV =7.5−1.7 eV as well as the measured slope $n=2$ for direct ionization. Since there is no or nearly no luminescence from excited C_{60} and C_{70} [17], annihilation of these triplet states should efficiently result in delayed ionization [19] rather than delayed luminescence [20]. The higher the pulse energy (fluence), the higher the triplet state density per fullerene ball, which may result in increasing triplet interaction and lead to the observed faster decay.

From the molecular point of view, our above mechanism may cause surprise that there are *many* excited electrons in a single C_{60} or C_{70} molecule. Actually, however, the fullerene molecule may be considered as a finite-size system consisting of many identical units and so the exciton concept may usefully be applied [21,22]. The consideration of a model that can predict the rates of delayed ionization using exciton dynamics was under way [23]. In order to confirm that delayed ionization is indeed due to electronic excitation rather than thermal emission, we have carried out the following experiments using two laser ionization.

(1) For the 215 nm excitation at 54 μJ, delayed ionization vanishes since the triplet states are too few to lead to it [see Fig. 1 for 215 nm and Fig. 2 (bottom panel)]. If we prepare some triplet states using KrF laser preexcitation, delayed ionization is introduced, as shown in Fig. 2 (top panel).

(2) For the 248 or 308 nm excitation, with decreased pulse energy, the triplet states are too few to give rise to delayed ionization and the excitation is far below the threshold for direct ionization; thus no signal can be detected by either KrF laser or XeCl laser alone (see Fig. 3, top and bottom traces). Again, delayed ionization can be obtained under KrF laser preexcitation (Fig. 3, middle

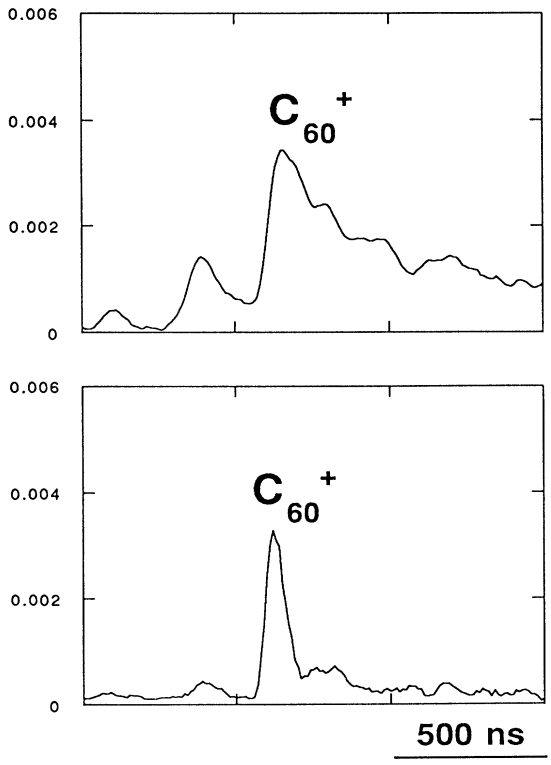

FIG. 2. Top panel: 248 nm laser + 215 nm laser (4.3 μs); bottom panel: 215 nm laser alone. The enhanced *delayed* ionization for 215 nm laser under KrF laser preexcitation can be seen (top panel), whereas not enough triplet states are generated to give rise to delayed ionization under the 215 nm laser alone (bottom panel).

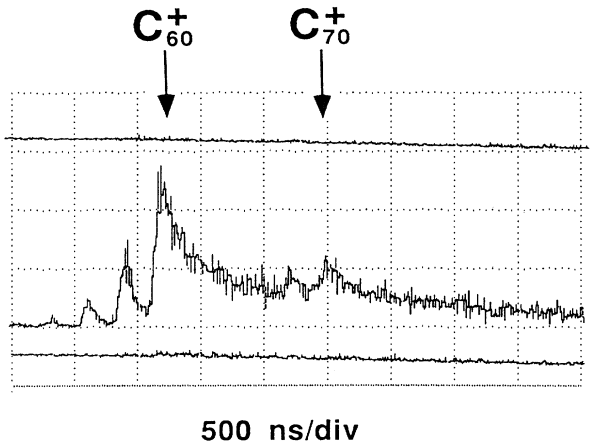

FIG. 3. Top trace: 248 nm laser alone; middle trace: 248 nm laser + 308 nm laser (0.1 μs); bottom trace: 308 nm laser alone. The KrF laser preexcitation enhanced delayed ionization can be seen in the middle trace, whereas no ion signal is induced by either KrF or XeCl laser alone. This effect can still be observed by changing the order of the two lasers and by increasing the time interval as much as 20 μs, but it can hardly be found using 193 nm ArF laser as the first laser.

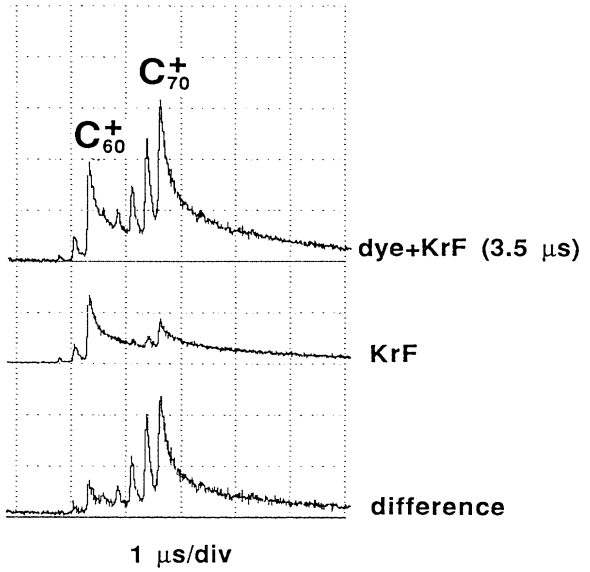

FIG. 4. Top trace: 540 nm laser + 248 nm laser (3.5 μs); middle trace: 248 nm laser alone; bottom trace: a difference between top trace and middle trace. As seen in the bottom trace, the 540 nm preexcitation enhanced delayed ionization for the 248 nm laser favors C_{70}^+, indicating selective excitation of C_{70}.

trace), indicating that the triplet states are indeed stored in the excited C_{60} and C_{70} molecules. Further, changing the order of the two lasers and extending the time interval between the lasers as much as 20 μs, the preexcitation enhanced delayed ionization can still be observed since the same triplet states are generated by KrF and XeCl lasers. However, this effect can barely be observed using ArF laser for the preexcitation, which is consistent with the above observation that no delayed ionization is found at 193 nm [see Fig. 1(a)].

(3) Under preexcitation in the 430–550 nm range, the enhanced delayed ionization for the KrF laser favors C_{70}^+ (Fig. 4, bottom trace), resulting from selective excitation of C_{70}. This is consistent with the fact that the selective delayed ionization of C_{70} from the C_{60}/C_{70} vapor is observed in this wavelength range.

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