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## Ionization and Fragmentation of $C_{60}$ via Multiphoton-Multiplasmon Excitation

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We study the intensity dependence of ionization and fragmentation of buckminsterfullerene ( $C_{60}$ ) in strong laser fields. Our data provide strong evidence that at intensities  $\leq 10^{14}$  W/cm<sup>2</sup> these processes occur predominantly via multiphoton excitation of the 20 eV plasmon resonance of  $C_{60}$ . At least two plasmons have to be created to initiate fragmentation or multiple ionization. [S0031-9007(96)01124-6]

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During the last ten years, a huge amount of work has been done in order to understand the physics of fullerenes, in particular, of the highly symmetric buckminsterfullerene  $C_{60}$ . Apart from the intrinsic fascination of this soccer ball-like molecule, which may also be regarded as a carbon cluster, its well-characterized structural and electronic properties facilitate obtaining fundamental insight into the physics of clusters, which form a bridge between free particles and condensed matter. From this point of view, the stability of  $C_{60}$  with respect to ionization and fragmentation is of particular interest.

Some rather puzzling facts have been discovered in studies addressing these aspects of fullerenes by, e.g., photoexcitation, electron-impact, and ion-impact excitation, including the existence of both direct and delayed ionization [1–5] and fragmentation [6,7] processes. Several experiments indicate that fragmentation of  $C_{60}$ , which generally occurs via the loss of one or more  $C_2$  segments, happens only after excitation above a certain threshold energy. Quite surprisingly, this threshold appears to be much higher than the activation energy for “evaporation” of individual  $C_2$  [6,8–11]. Most of these findings have been successfully ascribed to the very large number of internal degrees of freedom of the  $C_{60}$  molecule that leads to a fast diffusion of the excitation energy followed by statistical, i.e., inefficient, redistribution into ionizing or fragmenting modes.

In this Letter, we present experimental evidence that the ionization and fragmentation of  $C_{60}$  are not only strongly influenced by the efficiency of the internal energy transfer following the excitation, but also by the initial excitation step. Our experimental data on high-intensity femtosecond laser excitation indicate that the interaction of  $C_{60}$  with a sufficiently strong electromagnetic field is completely dominated by the “giant” plasmon resonance of its delocalized valence electrons [9,12,13]. Thus, an efficient energy transfer to the cluster is possible only in discrete steps corresponding to the creation of single plasmons with an energy of  $\approx 20$  eV. Our results further indicate that the excitation of at least two plasmons is required to initiate fragmentation or multiple ionization,

in agreement with data on direct single-photon excitation of this resonance, where neither fragmentation nor multiple ionization was observed [9]. This conclusion provides a rather natural interpretation of the previously observed threshold energies for fragmentation. In spite of the apparently indirect ionization and fragmentation mechanism via plasmon excitation, we do not find evidence for significant delayed or sequential fragmentation or ionization, as often observed in experiments with ns laser pulses [4,5]. These results suggest a strong coupling of the plasmon to ionizing or fragmenting modes.

Our experiments are standard time-of-flight (TOF) measurements of the ionic fragments produced in the interaction of free  $C_{60}$  molecules with high-intensity femtosecond laser pulses. A molecular beam of  $C_{60}$  is produced in a vacuum chamber (background pressure  $5 \times 10^{-8}$  mbar) by an effusive source consisting of a Ta tube that is filled with purified  $C_{60}$  powder (99.8%, Hoechst AG) and resistively heated to  $\approx 600$ – $700$  K, as monitored with a platinum thermoresistance. The orifice of the oven has a diameter of 0.7 mm, and a well-collimated beam—as monitored by the  $C_{60}$  deposition on a glass plate—is defined by a 1 mm diameter aperture at a distance of 1 cm. The beam passes between the plates of the TOF setup, where it interacts with laser pulses that are focused by a 50 cm lens outside the vacuum chamber. The ions produced in the laser focus are accelerated by an electric field of typically 0.5 kV/cm, pass the upper plate through a 3 mm diameter aperture into the 30 cm field-free drift region, and are detected by a secondary-electron multiplier. TOF spectra are registered with a digital oscilloscope and transferred to a personal computer. High-power laser pulses are obtained from a 10 Hz chirped-pulse amplified Ti:sapphire system that delivers 100 fs laser pulses with up to 200 mJ pulse energy at a wavelength of 790 nm. Experiments were done with both the fundamental laser frequency and frequency-doubled pulses obtained by second-harmonic generation in a 1.5 mm KDP crystal and subsequent frequency separation. For the experiments presented here, we used only a small fraction of the available laser energy in a central

part of the beam to improve the homogeneity of the illumination. The intensity dependence of selected ion yields is obtained by integrating over the corresponding peak in the TOF spectra and “binning” these data according to the energy of single laser shots, as measured by a calibrated photodiode. We estimate the focal intensities from calibration measurements with noble gases; however, within this work we do not attempt to establish absolute values of the laser intensity better than an order of magnitude. All data shown in the following were obtained below the apparent ionization threshold of Xe, i.e., in an intensity range  $\approx 10^{13} - 10^{14}$  W/cm<sup>2</sup>.

Figure 1 depicts typical TOF spectra, which exhibit the well-known distribution of large even-numbered fragments [1] that reflects the stability of the cage-like carbon clusters ( $C_{2n}$ ,  $n = 16, \dots, 30$ ) and—at high intensities, where “catastrophic disintegration” [14] of the  $C_{60}$  occurs—the bimodal pattern of small fragments. The larger abundance of odd-numbered small fragments corresponds to the instability of odd-numbered fullerenes, which—if formed by multifragmentation of the parent  $C_{60}$ —are expected to disintegrate further by emission of a small odd-numbered fragment. The overall fragment size distribution is very similar to that observed in high-energy collisions with heavy ions, which has been qualitatively explained by considering individual bond-breaking probabilities [14]. Alternatively, it can be explained by complete fragmentation of (highly charged)  $C_{60}$  into dimers and trimers and partial reformation of larger clusters [15].

We note that the spectra show no sign of delayed ionization on a  $\mu$ s time scale [2]. Although the resolution of our TOF spectrometer is not sufficient to distinguish delayed emission of a single  $C_2$ , as observed in Ref. [7],

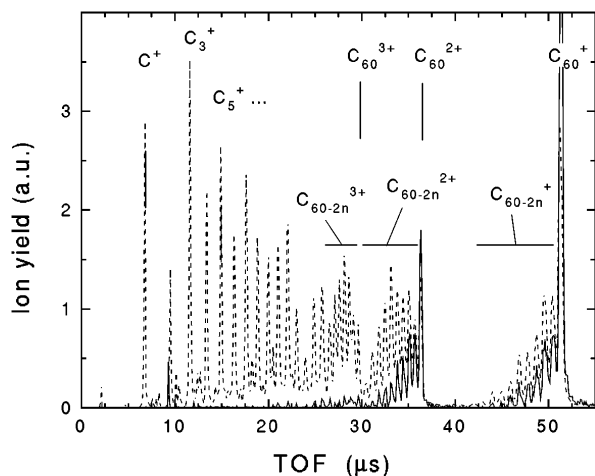


FIG. 1. Typical TOF spectra after ionization and fragmentation of  $C_{60}^+$  with near-infrared femtosecond laser pulses. All data shown in this Letter were obtained below the apparent ionization threshold of Xe, i.e., in an estimated intensity range  $\approx 10^{13} - 10^{14}$  W/cm<sup>2</sup>. Solid line: medium intensity in this range; dashed line: maximum intensity

we also conclude that the observed fragmentation does not proceed via consecutive emission of several  $C_2$  segments. This process would lead to a shift between measured and expected peak positions or at least an asymmetric broadening, which is not observed for any of the detected ions.

The spectra clearly show multiply charged fragments  $C_{60-2m}^{q+}$  (with  $q = 2, 3$  and  $m = 0, 1, \dots$  as indicated in Fig. 1) that form replicas of the singly charged fullerene series at moderate laser intensity. However, while the size distribution of the singly charged fullerenes hardly changes upon increasing the intensity [7], there is a shift toward smaller fragments for  $q = 2$  and  $q = 3$ . Also, the ratio of fragments to unfragmented  $C_{60}$  gets much larger for the multiply ionized species and the measured number of highly charged fragments becomes comparable to that of the singly ionized clusters at high excitation intensity.

Figures 2 and 3 present the main results of the present Letter, namely, the measured intensity dependence of the ion yield for some of the observed ion species. In Fig. 2 we show the ion yield of  $C_{60}^+$ ,  $C_{60}^{2+}$ , singly charged large fragments, and triply charged fragments after excitation of  $C_{60}$  with the near-infrared laser pulses. Since the size distribution of the  $C_{60-2m}^+$  ions does not change significantly with the laser intensity and these fragments appear to result from “direct” (as opposed to sequential)

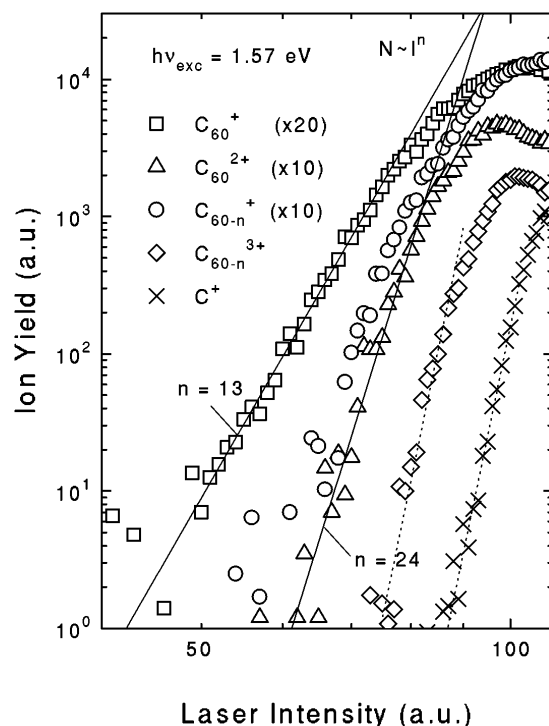


FIG. 2. Intensity dependence of single and double ionization of  $C_{60}$  and fragmentation into  $C_{60-2n}^+$ ,  $n = 1, \dots, \approx 9$ . For better visibility, some of the data have been shifted, as indicated in the legend. Solid lines are fits to the  $C_{60}^+$  and  $C_{60}^{2+}$  data according to a power law. The photon energy of the exciting laser pulses is 1.56 eV.

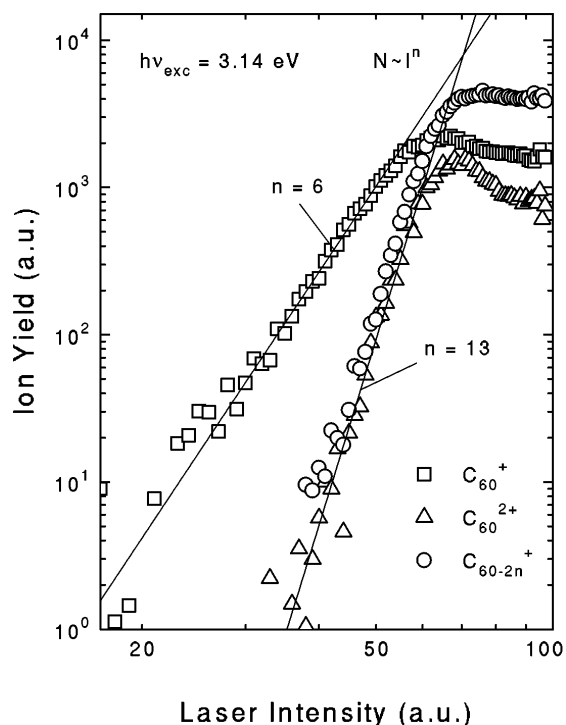


FIG. 3. Same as Fig. 2, but excitation with frequency-doubled laser pulses, i.e., photon energy of 3.1 eV.

fragmentation processes, we show the total integrated yield of all these fragments. This also applies for the threefold ionized ions, where the signal-to-noise ratio and the mass resolution were not sufficient to allow one to distinguish reliably between individual fragment sizes. We note that the data points corresponding to the threefold ionized particles should be regarded with some caution, since we cannot completely exclude a certain overlap with intermediate-size fragments  $C_n^+$ ,  $n \geq 16$ ). For illustration, we also show the yield of single carbon ions which mark the onset of a qualitative change in the fragmentation behavior: a complete destruction of the fullerene structure by creation of a hot carbon plasma associated with strong x-ray emission, as observed in Ref. [16]. This effect clearly also leads to a saturation and even decrease of the yield of large fullerene fragments in our experiment. Below saturation, however, the ionization and fragmentation data can be well described by a power law indicative of a multiphoton process. This is illustrated by the straight lines in the log-log plot that show fits of the experimental data. While the slope of the  $C_{60}^+$  data corresponds to a 13-photon excitation, the  $C_{60}^{2+}$  yield has a slope of approximately 24, both with an estimated error of  $\pm 1$ . The singly ionized fragments appear at comparable intensities as doubly ionized  $C_{60}$  and their number increases with the same power of intensity (for clarity, we do not show a fit of these data in Fig. 2), while the yield of threefold ionized fragments increases with an even larger slope [17].

At first sight it might not appear as particularly surprising that double ionization of a large molecule requires about twice as many photons as single ionization. However, the amount of energy that corresponds to these numbers—20 and 38 eV ( $\pm 1.57$  eV)—is much larger than the ionization potentials of  $E_1 = 7.6$  eV and  $E_2 = 11.4$  eV which have been determined both experimentally and theoretically [9,11,15]. Therefore, the data clearly rule out direct photoionization, i.e., excitation of single electrons close above the ionization potential. Given the fact that the overall dielectric response of  $C_{60}$  is completely dominated by the plasmon resonance centered at 20 eV [9,12,13], our data strongly suggest that this collective motion of the  $\pi$  electrons can also be excited by multiphoton processes and that even multiple excitation of the plasmon resonance is possible at sufficiently high laser intensity. This is further supported by our experimental data taken with frequency-doubled excitation pulses (see Fig. 3). Again, the intensity dependence of single and double ionization of  $C_{60}$  can be well fitted by a power law, but with half the slope as in the experiment with 1.57 eV photon energy, i.e., indicating the same “activation” energy. Also, we find again the same slope and threshold for fragmentation and double ionization.

Therefore, our results indicate that multiphoton excitation of the plasmon resonance of  $C_{60}$  forms the dominant excitation mechanism in the intensity range covered by our experiments. The strong coupling of the valence electrons in the fullerene molecule obviously inhibits efficient single-electron excitation above the ionization potential. As the laser frequency is much smaller than the resonance frequency of the  $\pi$ -electron plasma one might intuitively expect barrier-suppression or tunnel ionization to be the dominant ionization mechanism in a strong laser field. However, the binding potential for the  $\pi$  electrons in  $C_{60}$  will more resemble a spherical well than a Coulomb potential and, more important, the high electron density leads to very efficient screening of the laser field inside the  $C_{60}$ . Assuming for simplicity a homogeneous distribution of the  $\pi$  electrons over the  $C_{60}$  cluster and an electron temperature of 700 K, the observed plasma frequency corresponds to a Debye length of  $\lambda_D = 3.4 \times 10^{-10}$  cm [18], which is the length scale over which the field of an isolated charge is effectively screened. Since the average electron “extension,”  $n_e^{-1/3}$ , is 2 orders of magnitude larger, even very strong laser fields will hardly be “seen” by the electrons. As a consequence of screening, the interior of the  $C_{60}$  stays field-free, and the height of the potential barrier for the electrons inside the molecule remains unchanged by the laser field. Therefore, barrier suppression, which accounts for the main features of optical field ionization of isolated atoms [19], will not occur in  $C_{60}$ . On the other hand, assuming a homogeneous charge distribution within the  $C_{60}$ , the energy gained by the  $C_{60}$  in a quasistatic electric field is simply the field energy density times the volume of the molecule. For a laser

intensity of  $5 \times 10^{13}$  W/cm<sup>2</sup> this gives a value of 6 eV. This number indicates that, at the intensities reached in our experiments, excitation of the plasmon resonance may still be considered to be in a perturbative regime, justifying our interpretation of the experimental data in terms of a multiphoton process.

As we exclusively observe singly ionized C<sub>60</sub> in the low-intensity range of our experiments, our results confirm the observation in Ref. [9] that excitation of a single plasmon is not sufficient for multiple ionization or fragmentation of the parent fullerene. This is quite remarkable, since numerically the plasmon energy is larger than the energy required for double ionization or ionization plus ejection of a C<sub>2</sub> molecule. As a qualitative interpretation, we believe that this result indicates a strong coupling of the plasmon to single-electron continuum states, which may lead to fast ejection of one electron with nonzero kinetic energy. On the other hand, from the data presented here, we also conclude that (only) after excitation of two or more plasmons fragmentation becomes possible and forms an alternative relaxation channel for the excited fullerene. Competition between coupling to the C<sub>60</sub> lattice, as required for efficient fragmentation, and electron emission may probably explain why multiple ionization of C<sub>60</sub> is generally not observed in experiments using ns laser pulses. In addition, at laser intensities that are not sufficient to drive the multiphoton-plasmon excitation reported here, ionization can still proceed via sequential excitation of specific molecular states [4,5] or continuous heating of the molecule. However, these processes are not expected to lead to efficient multiple ionization because of saturation effects and the strong electron-lattice coupling, respectively.

In conclusion, we have observed multiphoton excitation of the plasmon resonance in C<sub>60</sub> and find that double excitation of this resonance is required to fragment or multiply ionize the molecule. We believe that this result might also provide a clue to understand the apparent fragmentation and double ionization threshold energies found in earlier studies on synchrotron radiation [8,9], electron-impact [6,11] and ion-impact excitation [10] of fullerenes.

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