Delayed Ionization of C_{60} and C_{70}

E. E. B. Campbell, G. Ulmer, and I. V. Hertel

Freiburger Materialforschungszentrum (FMF) der Albert-Ludwigs-Universität, Stefan-Meier-Strasse 31a,
W-7800 Freiburg, Germany

Delayed ionization with average lifetimes on the order of several μsec has been observed for two-photon 308-nm excimer laser ionization of C_{60} and C_{70}.

Buckminsterfullerene, C_{60}, as well as its companions such as C_{70}, is a truly remarkable molecule, or atomic cluster, depending on the viewpoint. After its discovery and first speculations about its structure [1], a flood of publications (see, e.g., a recent review article by Smalley [2]) has emerged on carbon clusters and fullerenes, culminating in the isolation of pure C_{60} and C_{70} by Krätschmer et al. [3]. Since then, intense work has identified the atomic structure of these fascinating species, confirming early speculations on the "football" structure by NMR, x-ray diffraction, etc. [3,4]. Presently, in addition to exploring the many applications of C_{60} in materials research [5], surface physics [6,7], and chemistry [8,9], the quest for understanding the electronic structure has started. For example, optical spectra in the liquid phase have been reported [4] as well as mass spectroscopic observations after laser surface desorption [10–12] which provide, in principle, the ground for studying optical excitation and multiphoton ionization of the isolated species C_{60} and C_{70}. Surprising features, such as the discovery of a long-lived triplet state [12], seem to be the very nature of C_{60}. In the present Letter we report another astonishing observation: the delayed ionization after two-photon excitation with an average lifetime of several μsec, a phenomenon which to our knowledge has so far not been reported for any molecule or cluster.

The apparatus has already been described in detail for experiments involving laser ablation of polymers [13]. For the present investigations the polymer sample was replaced with a sample of fullerite (consisting predominantly of C_{60} and C_{70} [3]) obtained from Krätschmer and collaborators. The fullerite is dissolved in toluene and deposited on an aluminum substrate. The solvent is allowed to evaporate, leaving a deposit of the carbon material. A 248-nm excimer laser at a fluence of 10 mJ cm^{-2} is used to desorb the C_{60} and C_{70} from the surface under high-vacuum conditions (10^{-7} Torr) where the target is mounted on a rapidly rotating disk in order to avoid subsequent multiple shots onto the same spot, thus stabilizing the average ion signal. The desorbed material is allowed to drift until the gas pulse reaches a volume between two metal meshes separated by 1 cm with the first mesh 2.5 cm away from the substrate. A schematic diagram of the geometrical arrangement and the potentials applied in the extraction region is shown in Fig. 1. After a delay of 55 μsec a 308-nm ($\cong 4$ eV) excimer laser pulse is fired, fo-

cused at a point between the two wire meshes. Ions produced by the second laser (crossfired at about 3 mm away from the first mesh) may then be extracted by a first electric field which can be pulsed between the positions indicated in Fig. 1. Ions then enter into a second field and are finally detected in a Reflectron time-of-flight mass spectrometer (not shown in Fig. 1). The delay between the two lasers is kept constant at 55 μsec. The delay between the second, ionizing laser pulse and the pulsed extraction field can be varied. Prior to extraction an electric field of 312 V cm^{-1} is present between the substrate and the first wire mesh to repel positive ions that are produced directly by the desorbing laser; in the extraction zone a field is applied to remove ions produced between the laser pulse and the switching on of the extraction field (C_{60}^{+} ions are swept out in less than 1 μsec). Measurements of the fluence dependence of the ion production with no delay between the ionizing laser pulse and the pulsed extraction field give a quadratic dependence on the fluence, thus showing that the observed prompt ionization is a two-photon process, consistent with the recently measured IP range for C_{60} of 7.5–7.7 eV [14].

Figure 2 shows mass spectra produced for three different delays and an ionizing laser energy of 1 mJ corresponding to a fluence of about 20 mJ cm^{-2}. For zero delay [Fig. 2(a)] we see the C_{60}^{+} and C_{70}^{+} peaks accompanied by a number of peaks due to fragment ions as well
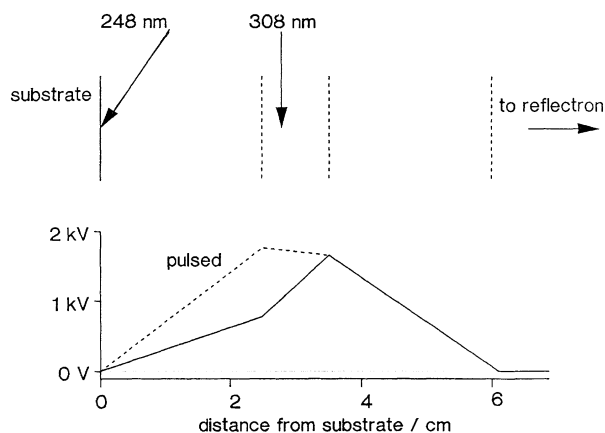

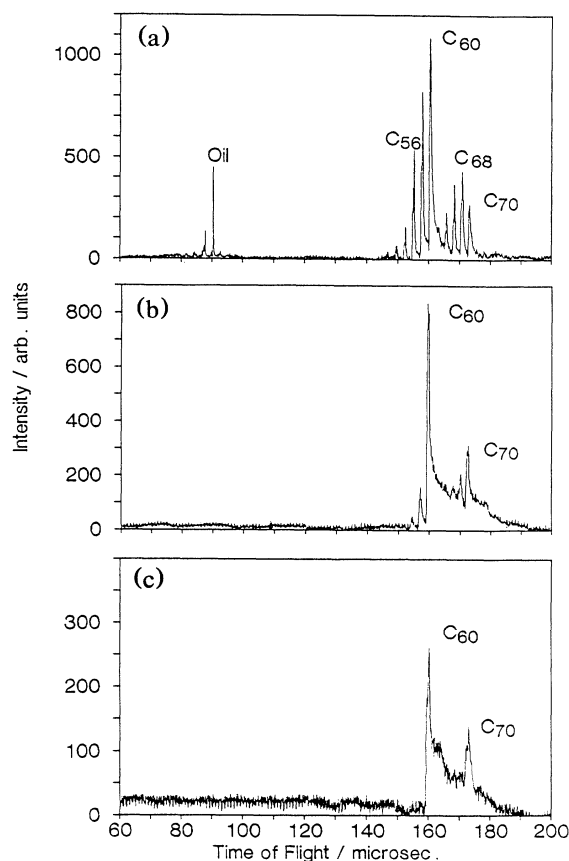FIG. 1. Schematic diagram of the ionization and ion extraction region of the apparatus.

FIG. 2. Mass spectra produced from ionization with a 20-mJcm^{-2}, 308-nm excimer laser with a delay between laser and pulsed extraction field of (a) 0, (b) 2, and (c) 8 μsec.

FIG. 3. Part of a mass spectrum obtained with a delay of 9 μsec. The full line is a Gaussian fit to the mass peak.

as a series of peaks with a flight time of around 90 μsec due to ionization of vacuum pump oil. These ions are all produced immediately on absorption of the two 308-nm photons. When we have a delay of 2 μsec between the ionizing laser and the extraction field [Fig. 2(b)] we see that the oil peaks have disappeared completely as we would expect. The amount of fragment ions present in the spectrum has decreased substantially but the C_{60}^{+} and C_{70}^{+} peaks have similar intensities to those shown in Fig. 2(a). These peaks are all due to ions formed between about 1 and 2 μsec after the ionizing laser pulse; ions formed in the time interval between 0 and about 1 μsec are swept out of the extraction region due to the electric field present before the pulsed extraction field is switched on. At 8-μsec delay the fragment peaks have also disappeared but there are still strong signals from C_{60}^{+} and C_{70}^{+}. The large "tails" to the high mass sides of the C_{60}^{+} and C_{70}^{+} peaks which are most apparent in Figs. 2(b) and 2(c) are due to ions which are produced after the delay but while the extraction pulse is still on; they therefore arrive at the detector later than ions accelerated immediately on switching on the electric field.
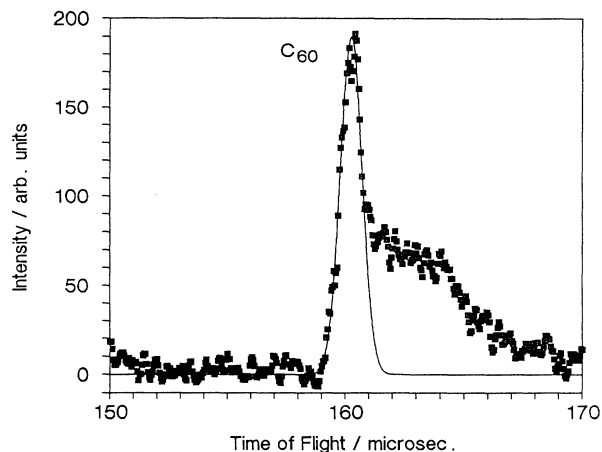
A blown up picture of the C_{60}^{+} mass peak is shown in Fig. 3 for a delay of 9 μsec. To understand its shape qualitatively, one has to consider that we use spatial focusing (two-stage extraction field) and energy focusing (by the Reflectron). Thus, when the extraction field is switched on all ions in this field are focused into a sharp mass peak (including those ions created in the previous 1 μsec). The length of the tail is determined by the time that neutral molecules travel with their original thermal velocity (about 500 m/sec) before leaving the extraction-field region. For instance, the break in the tail in Fig. 3 (delay 9 μsec), occurring at about 4 μsec after the "peak," corresponds to a total distance traveled of [(9+4) μsec](500 m/sec)$\sim$7 mm which is just the distance between the ionizing laser beam and the end of the first extraction field. The further decrease of the tail arises in the second extraction field. In order to obtain an accurate indication of the ionization rate of the C_{60}/C_{70} we have to extract the "peak" from the tail. The method is illustrated in Fig. 3. A Gaussian curve is fitted to the mass peak measured for a short delay where the tail has a significantly lower intensity than the peak. The width of this fitted Gaussian curve is then kept constant and the intensity adjusted for each delay as shown in Fig. 3.

Figure 4 shows a log-linear plot of the integrated peak intensity versus delay between ionizing laser pulse and pulsed extraction field for an ionizing laser fluence of 20 mJcm^{-2}. There are two exponential-decay processes leading to ionization processes of both the C_{60} and C_{70}. The average lifetimes for the two species are identical within experimental error and are exceptionally long for an ionization process, 2.5 ± 0.5 and 15 ± 3 μsec. The biexponential supports the assumption of a unimolecular type of process with well-defined energy deposition into the molecule (two- and one-photon absorption, respectively). This explanation obtains additional support from the following observation. When the fluence of the ioniz-
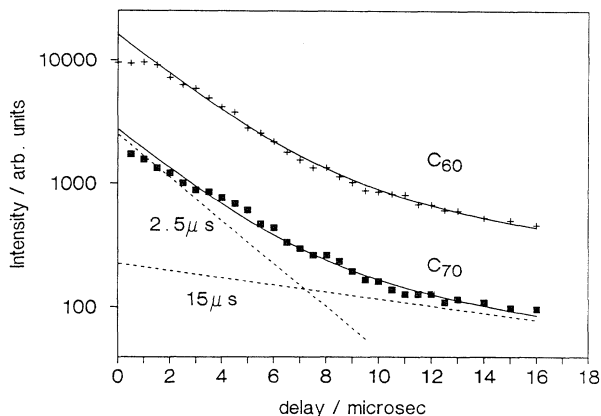
FIG. 4. Integrated peak intensity vs delay between ionizing laser (20 mJcm^{-2}, 308 nm) and pulsed extraction field. The full lines are fits to two exponential decays with different lifetimes. The dashed lines show these two exponential decays for the C_{70} ionization.

ing laser is increased to 100 mJcm^{-2} an additional exponential decay with an average lifetime of about 1 μsec is also seen due to the absorption of an additional photon.

This fascinating and unexpected phenomenon could be speculatively attributed to thermionic electron emission [15] or—in molecular language—coupling of rovibronic and electronic states in the molecule. Investigations of the laser fluence and wavelength dependence as well as for a broader range of fullerenes are under way and will be discussed in detail in a forthcoming publication.

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