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Delayed electron emission from photoexcited C_{60}

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When using laser ionization time-of-flight (TOF) instruments for mass spectroscopic investigations of fullerenes, it was found that C_{60} and C_{70} mass peaks exhibit long tails on the order of microseconds towards longer flight times, which could not be explained at that time.[1-3] In a recent publication, we attributed these tails to delayed ionization of C_{60} and C_{70} molecules.[4] In this paper, we shall distinguish between direct ionization and delayed ionization. Direct ionization means that optical excitation directly excites a single electron above the ionization potential so that electron detachment occurs without observable delay on the time scale of these experiments. The process of delayed ionization involves the coupling of the vibronic energy in the cluster so that a single electron reaches an unbound level. There are only a few reports in the literature of delayed emission of electrons from clusters after laser excitation. For metal clusters, such as Nb, W, and Ta,[5,6] it was concluded that thermionic emission is the physical process responsible for the delayed emission of electrons. It still remains to be shown whether the delayed ionization we[4] and others[7,8] have seen for fullerenes is indeed thermionic emission rather than long-lived electronic excitation. Since previous studies[5-8] used a laser desorption cluster source, which produces a size distribution of clusters, fragmentation of metastable higher mass cluster ions may complicate the interpretation of these results. Furthermore, laser desorption lacks the desired signal stabilities necessary for this kind of investigation. To overcome these limitations, we used an effusive source that provided a pure and stable C_{60} cluster beam. Interactions of C_{60} with photons at various harmonics of a Q-switched Nd: YAG laser (118, 212.8, 266, 355, and 532 nm, corresponding to 10.5, 5.83, 4.66, 3.50, and 2.33 eV, respectively) are reported. A broad fluence range from the detection limit of the photoions to several orders or magnitude higher is investigated. Additionally, the electrons arising from delayed ionization are detected directly, thus eliminating the possibility of observing the fragmentation of metastable cluster ions.[9]

The experiments are performed in a laser-desorption/laser-ionization TOF mass spectrometer. The spectrometer can be operated in two modes, either measuring the mass spectrum of directly emitted positive or negative ions or measuring the mass spectrum of desorbed neutral particles after postionization by a second laser. The instrument has been described in detail previously, thus we only give a brief description here.[3] The TOF mass spectrometer consists of an ion optics stack for acceleration, deflection plates, a field-free region, and a dual channel plate assembly for detection of ions. The instrument has a mass resolution ($m/\Delta m$) of up to 1500. The typical operating vacuum is $\approx 2\times 10^{-9}$ Torr. For the current set of experiments we added a C_{60} effusive source above the ionization region of the ion source of the spectrometer. The effusive source, filled with pure C_{60} (99.9%), is held at 529°C for the entire set of experiments, and produces a very stable cluster beam. Mass spectroscopic data are recorded on a transient recorder with a maximum time resolution of 5 ns. Further processing of data is accomplished with a PC-based software system.

The synthesis and separation of gram amounts of C_{60} and C_{70} is carried out according to previously published accounts.[10-12] A plasma is ignited between carbon electrodes in an evacuated vacuum chamber, which is backfilled with 200 Torr of helium. The resulting carbon soot with a high concentration of fullerenes[12] is collected, and fullerenes are extracted from the raw soot with toluene and subjected to column chromatography for further purification. The effusive source is loaded by repeatedly filling and evaporating with a solution of C_{60} in toluene.

Figure 1 shows a comparison of photoionization of C_{60} with 266 and 212.8 nm laser radiation. For 266 nm photons we observe extensive fragmentation and delayed ionization in the mass spectrum. Analysis shows that delayed ionization has almost the same fluence dependence as fragmentation. A detailed report of these results will be presented in a forthcoming publication. We observe similar fluence dependences for 266, 355, and 532 nm ionization but shifted to higher fluence for longer wavelengths. Additional evidence for the observation of delayed ionization is the detection of the arrival time of the photoelectrons, also depicted in Fig. 1. In our apparatus, all photoelectrons produced are detected in the same way as photoions, by switching the polarity of the acceleration voltages (no electron energy dispersion). We find *identical* tails for photoions and electrons. If we switch to ionization with 212.8 nm laser wavelength, much less delayed ionization and fragmentation is observed compared to ionization with longer wavelengths. At very low laser fluences, delayed ionization and fragmentation vanish. Additionally, the electron spectrum does not exhibit any tail of the signal peak at these low fluences. However, this is merely an observation of limited detection sensitivity rather than a threshold for these processes. Fragmentation-free ionization without any delays is observed only for 118 nm at all accessible laser fluences (see inset of Fig. 1).

Figure 2 compares the ionization for various laser wavelengths. Laser fluences are selected to show mass spectra with similar abundances of fragment ions. Here we show only the C_{60} mass peak with its delayed ionization. Details on the fragmentation of neutral C_{60} and C_{70}

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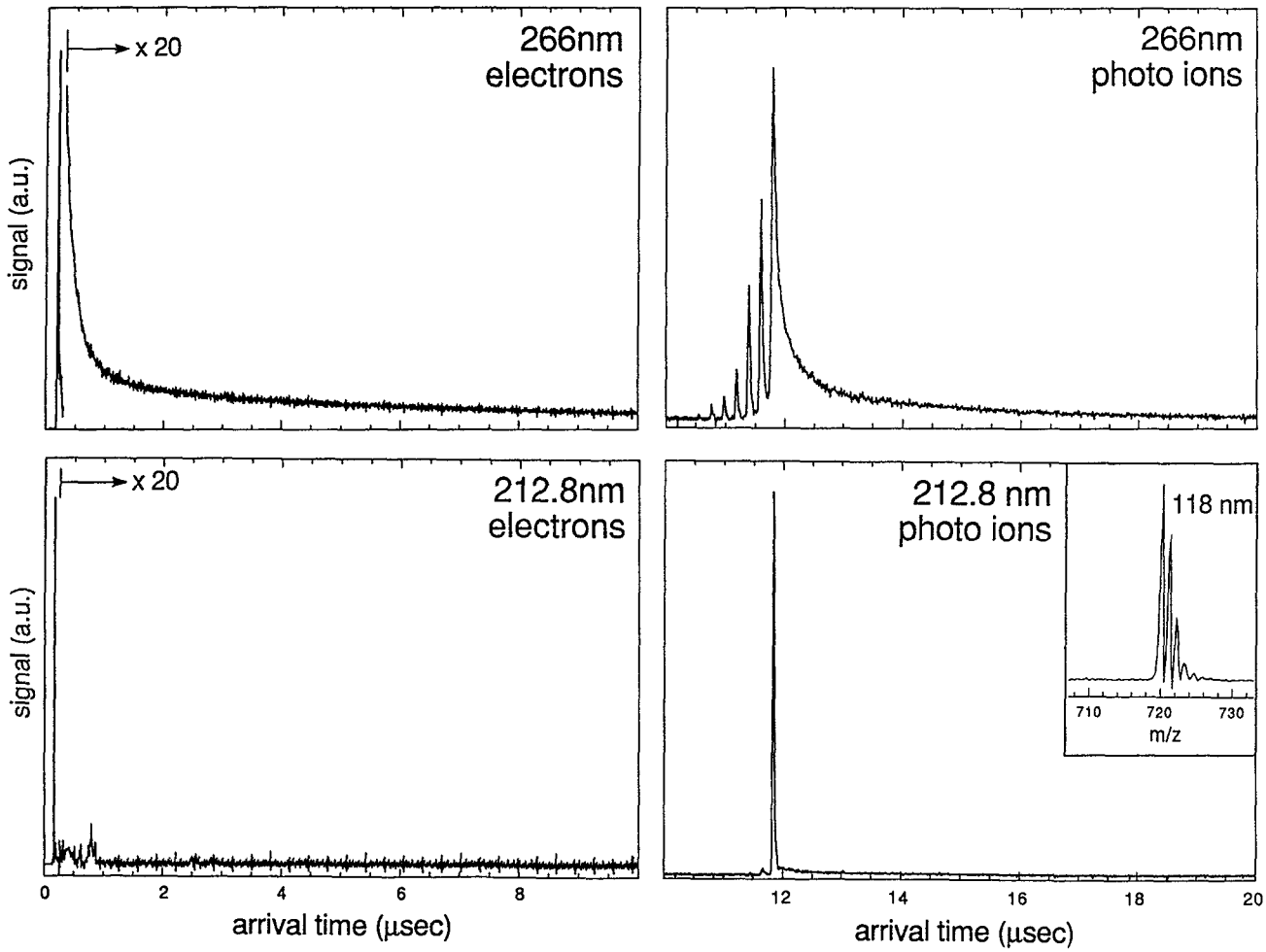

FIG. 1. Time of arrival of photoelectrons and photoions for ionization of C_{60} with 212.8 and 266 nm laser light. The signal tails are identical for electrons and photoions. For 266 nm (top right) the C_{60} parent ion and the even numbered fragment ions C_{58}, C_{56},..., C_{48} are identified. For 212.8 nm (bottom right) the C_{60} parent ion and very little amounts of C_{58} fragment ions are seen. Inset shows isotope distribution of C_{60} mass peak ($^{12}C_{60}$, $^{12}C_{59}{}^{13}C$, $^{12}C_{58}{}^{13}C_2$,...) by ionization with 118 nm light. Mass 720 and 721 are separated by 25 ns.

clusters[4] and positive C_{60}^+ and C_{70}^+ ion clusters[13] have been published earlier, and the current findings are in full agreement with the earlier results. There are at least two exponential decay processes leading to delayed ionization with decay constants of 2.4 ± 0.2 μs and 10 ± 0.5 μs. For laser wavelengths in the range from 212.8 to 532 nm we observe approximately the same decay constants. No change in the decay constants is found for increasing laser fluences, apart from an additional time constant of 0.8 ± 0.3 μs which appears at high fluences. Even for laser desorption of neutral C_{60} from solid samples (Fig. 2, panel d), we find the same decay constants although the clusters leave the surface with a temperature of ≈ 2000 K, as determined by velocity distribution measurements.[4] These findings are in good agreement with reported delay times using an excimer laser at 308 nm wavelength for ionization.[8] Similar time constants for delayed electron emission have been reported for photodetachment of cold C_{60}^- clusters.[14] It is of interest to note that, in our work on UV-laser desorption of C_{60}^- clusters from C_{60} films, we also encounter delayed electron emission of these clusters on this time scale.

There are three different processes that compete following the absorption of photons: direct ionization, delayed ionization, and fragmentation. For low laser fluences of 212.8 nm light, direct ionization is the dominant process but as laser fluence increases, delayed ionization and fragmentation become more important until they dominate. The fragmentation takes place by loss of even numbers of carbon atoms yielding the fragment ions C_{58}, C_{56}, ... down to C_{32} if the laser fluence is sufficiently high.[4] Summing up all these fragments ion peaks, we find fragmentation the most important process for high laser fluences, followed by delayed ionization and direct ionization. For 266 nm and longer wavelengths, direct ionization never dominates; there is always considerable delayed ionization and fragmentation present.

We believe delayed ionization is due to thermionic emission for several reasons. (1) Direct ionization is expected to be inefficient since at least two photons for 212.8 or 266 nm wavelength are needed to overcome the ionization potential of C_{60} at 7.61 eV.[15] Hence considerable heating of the cluster is expected following multiphoton ab-

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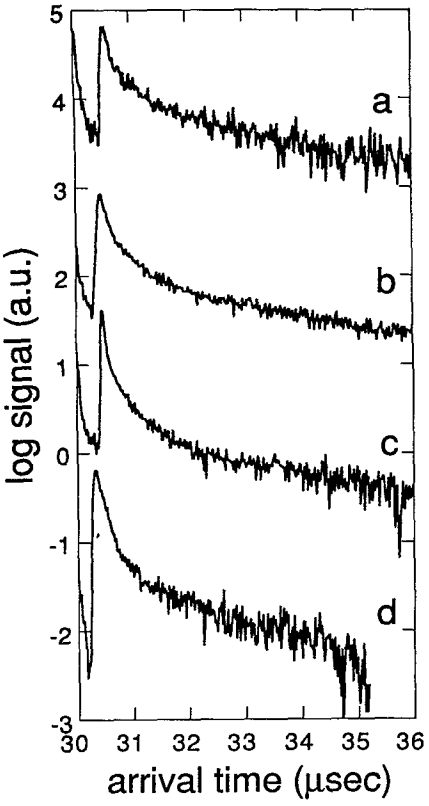

FIG. 2. Comparison of delayed ionization of C_{60} from the effusive source at 529 °C (panels a, b, and c) and from laser desorption from solid C_{60} with 308 nm (panel d) at various ionization laser wavelengths: (a) 212.8 nm at 21 mJ/cm^2; (b) 266 nm at 53 mJ/cm^2; (c) 532 nm at 1.75 J/cm^2; (d) 270 nm at 29 mJ/cm^2. Laser fluences have been selected that yield the same abundance of fragment ions.

sorption. The only wavelength investigated by us that allowed single photon ionization was 118 nm radiation, and neither fragmentation nor delayed ionization is observed over the whole investigated fluence range. In the absence of delayed ionization, we are able to resolve the isotope pattern of C_{60} ($m/\Delta m \approx 1500$) with the peak width limited by the laser duration (5 ns) and the resolution of the digitizer (5 ns), which is depicted in the inset of Fig. 1. (2) Using pure C_{60} from an effusive source eliminates the possibility of decay of metastable higher mass ions, which certainly is a complication when working with samples containing a mixture of fullerenes.[7,8] Furthermore, we detect the delayed electrons in the same way as the photoions, which was not used in earlier work.[4,7,8] The comparison of our previous laser desorption/postionization data with the current gas-phase ionization data shows (see Fig. 2) that the initial temperature does not play an important role and that the observed processes are initiated solely by the ionization laser. (3) Observing the same time constants for different wavelengths (212.8–532 nm), over the whole fluence range and at different initial temperatures (800 and 2000 K) of the neutral cluster, is rather unexpected. This strongly suggests that energy is not stored in a specific state of the molecule. We believe this is caused by the interplay of heating and cooling of these clusters. Heating is due to photon absorption while cooling is due to thermionic emission and atom evaporation (fragmentation). A simple estimate, utilizing thermionic emission[16] to model the delayed ionization, predicts an upper limit for the effective temperature reached by C_{60} of about 4000 K. The two cooling channels compete with each other since fragmentation reduces the number of available parent clusters. Since both processes are of an exponential nature, an upper limit to the effective temperature of C_{60} as exhibited by the thermionic emission is conceivable.

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