cw Laser Ionization of C_{60} and C_{70}

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"Delayed" photoionization of the all-carbon cage fullerene molecules C_{60} and C_{70} is observed using a weakly focused cw argon ion laser (flux $I < 10^5$ W/cm^2). At these fluxes photoexcitation occurs incoherently and so slowly that intersystem crossing must be occurring simultaneously. A "thermionic emission" model adequately describes the delayed ionization.

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The ionization of certain clusters in a higher power *pulsed* laser field has been shown to occur as a result of the absorption of many photons, leading to the ejection of electrons which are "delayed" (on a time scale longer than 10^{-6} sec) relative to the exciting laser pulse [1–7]. Thermionic emission has been invoked to explain the phenomenon [4–7], and theoretical aspects of this suggestion have been developed by Klots [8]. We have previously employed multiphoton ionization photoelectron spectroscopy (MPI-PES) to show that both direct and delayed ionization occur for the icosahedral C_{60} molecule in a pulsed laser field (flux densities of 10^7–10^9 W/cm^2) for the wavelength range from 250 to 750 nm [6]. The absence of delayed ionization at 193 nm was attributed to direct photoionization of the lowest triplet state of C_{60} produced by fast singlet-triplet intersystem crossing (ISC). Zhang and Stuke (ZS) have demonstrated this more clearly by reporting a sharp transition from "delayed" to direct ionization at 212.5 nm [9], implying a triplet/ground-state separation of 1.79 eV. At the wavelengths of 308 and 248 nm, where delayed ionization does occur, ZS found that the C_{60}^+ ion signal varies as the laser flux rose to a power slightly greater than 4. This observation prompted ZS to propose a delayed ionization mechanism involving the intramolecular interaction of many (> 4) triplet states in one C_{60} molecule. Their model relies upon stored electronic energy (Frenkel excitons) as opposed to stored vibrational energy in the "thermionic emission" description.

If it is assumed that delayed ionization results from thermionic emission, the photoionization of C_{60} will strongly depend upon the laser fluence (J/cm^2) but only weakly on the laser flux density (J/sec cm^2). This consideration motivated us to photoionize C_{60} in a novel manner. We describe in this Letter the ionization of C_{60} and C_{70} by a cw Ar ion laser with only moderate flux. It represents the first observation, to our knowledge, of ionization of a large molecule by a cw laser. We expect it to be general, whenever thermionic emission can compete with dissociation.

A cw Ar ion laser, operating at either all-line (with a combined power of ≤ 3 W) or single-line (power ≤ 1 W) output, was employed. For all-line output, the laser produced nine narrow lines in the region from 454 to 529 nm, with the two most intense lines at 488.0 and 514.5 nm representing almost 70% of the all-line power. Using different focal length lenses ($f = 12.5$ or 35 cm), the maximum laser power density I could be varied from 10^3 to 10^5 W/cm^2 for all-line output, much lower power density than those used in conventional MPI experiments. Measurements of C_{60} ionization were performed in a thermal effusive beam of commercially pure sample with a linear time-of-flight mass spectrometer (TOFMS) operating under the Wiley-McLaren space focusing conditions, in a vacuum chamber with a background pressure of 10^{-7} Torr. The C_{60} beam could be aligned orthogonally or collinearly to the laser beam in the ion extraction region of the TOFMS in order to change the laser-fullerene interaction time. As expected, much higher count rates were observed in the collinear geometry. A 5 μsec width pulsed extraction field of ~ 250 V/cm was applied to extract any ionic species into the acceleration region at a high repetition rate (5 kHz). After flight in the 15 cm drift tube, ions were detected by a microchannel plate detector. The TOFMS has a mass resolution ($m/\Delta m$) of greater than 100. The single-ion pulses were counted by a PC computer-based pulse counting and TOF data acquisition system. All intensities reported herein are summations of ion counts for a given mass.

Sample mass spectra obtained using a collinear beam setup with the all-line laser output are given in Figs. 1(a)–1(c). At the highest laser power density [1.1×10^4 W/cm^2, in Fig. 1(a)] a dominant C_{60}^+ signal is seen together with a C_{70}^+ peak from an impurity in the sample. There are no small fragment ions (C^+ to C_{12}^+) in the low-mass range (not shown). The intensity of the C_{70}^+ peak is comparable with or even larger than C_{60}^+ at low laser fluxes [see Figs. 1(b) and 1(c)], although it shows a greater tendency to saturate at high flux levels. This enhancement of C_{70}^+ over C_{60}^+ was most pronounced at higher oven temperatures (> 450 °C), consistent with the relative heats of sublimation [10] of the neutrals. It is interesting to note that the C_{70} impurity is present at a level much less than 1% (vendor stated purity was $> 99.9\%$ C_{60}) in the sample, as determined by laser desorption Fourier transform mass spectrometer analysis. A typical power dependence (ion counts as a function of laser flux in a double logarithmic plot) is shown in Fig.

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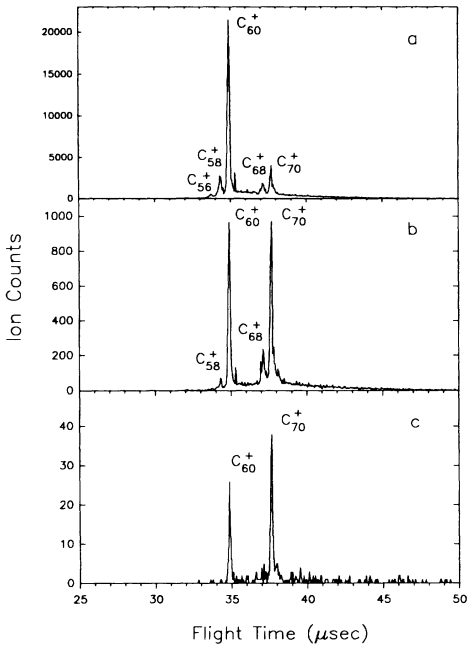

FIG. 1. Mass spectra from the ionization of cw Ar ion laser with different power of the all-line output: (a) 1.1×10^4 W/cm^2, (b) 5.2×10^3 W/cm^2, and (c) 2.0×10^3 W/cm^2. The thermal beam was operated at $T \sim 500\,^\circ$C. Besides C_{60}^+ and C_{70}^+, the peaks corresponding to fragment ions C_{56}^+, C_{58}^+, and C_{68}^+ are also obvious in (a). For all of these spectra, the collinear beam geometry is used and the accumulation time is the same (15 min).

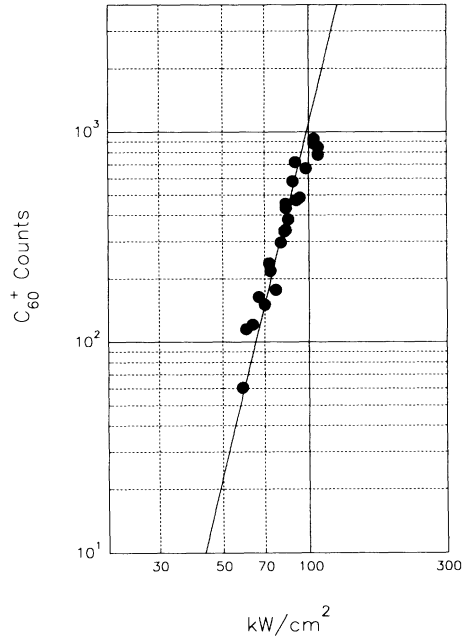

FIG. 2. Laser power dependence of the C_{60}^+ ion counts in the orthogonal beam setup at an operating beam temperature of $\sim 400\,^\circ$C. The laser is all-line output, and the calculated slope (the solid line) is 5.6 ± 1.0.

2 for C_{60}^+ ions with an orthogonal beam setup and an all-line output laser. The data shown in Fig. 2 reflect a C_{60}^+ ion yield of about one ion per second at 8.3×10^4 W/cm^2. In the collinear configuration it was possible to obtain data using a single 488.0 or 514.5 nm line [at an even lower laser power density of $(1\text{–}4) \times 10^3$ W/cm^2]. Roughly the same slopes are obtained for the power dependencies at both laser lines.

The photoionization of C_{60} in the present work cannot be attributed to coherent MPI. The data shown in Fig. 1(a) correspond to a count rate of 100/sec. Using the focal properties of the lens (35 cm), the beam divergence of the laser (1 mm rad), and the approximate C_{60} molecule beam density (3.6×10^{10}/cm^3), we calculate that a generalized three-photon ionization cross section of approximately 2×10^{-73} cm^6 sec^2 is needed if MPI is occurring. This cross section is many orders of magnitude larger than would be expected for a molecule. Nonresonant three-photon ionization cross sections for atoms vary from a maximum of approximately 10^{-77} cm^6 sec^2 for cesium to 10^{-82} cm^6 sec^2 for xenon [11]. Cross sections for molecules are expected to be smaller. Furthermore, the probability of the photoionization by stepwise multiple-photon absorption is very small because photoexcited C_{60} rapidly relaxes by an IC or ISC process, as shown in fluorescence measurements [12].

The photoexcitation behavior of fullerenes described here is reminiscent of the ir laser multiphoton dissociation previously observed for polyatomic molecules (e.g., SF_6) [13]. Multiphoton dissociation through the "quasicontinuum" has been exhaustively studied for many years. In the case of fullerenes, the electronic excited state created by single-photon absorption can be regarded as a discrete level embedded in a quasicontinuum, consisting of vibrational levels of the lower electronic states. The coupling between the discrete levels and the quasicontinuum (i.e., IC and ISC) is very strong because of the large density of states. Thus, multiple-photon absorption might eventually produce a superheated C_{60}^{**} at high enough energy to boil off an electron.

We now examine whether the thermionic emission model is compatible with the observed laser power dependence. A set of rate equations can be introduced to describe the incoherent photoexcitation process [14]. Because of the rapid ISC and the low fluxes used here, a constant photoabsorption cross section can be assumed [15]. Furthermore, since cw lasers are free of intensity fluctuations, we may also assume a Poisson distribution for the probability of having absorbed n photons,

$$P(\bar{n}, n) = \frac{\bar{n}^n}{n!} \exp(-\bar{n}), \tag{1}$$

where $\bar{n}$ is the average number of photons absorbed per molecule, estimated simply by $\bar{n} = \sigma I \tau$, where σ is the photoabsorption cross section, I is the number photons/cm^2 sec, and τ is the molecule-photon exposure

time. This exposure time is given by the C_{60} transit time through the laser beam. The predicted number of ions, produced from thermionic emission of C_{60}^{**}, can then be estimated from a summation of weighted probabilities from Eq. (1),

$$S(\bar{n}) = \sum_{n=0}^{\infty} P(\bar{n}, n)\{1 - \exp[-k(E)\tau_0]\}, \qquad (2)$$

where $k(E)$ is the rate constant for thermionic emission from the superheated C_{60}^{**} with an internal energy $E = nh\nu + E_{\text{th}}$ (E_{th} is the contribution from thermal heating and is equal to 3.3 eV at $T = 400\,^{\circ}\text{C}$) and τ_0 is the observation time for the electron emission, typically of the order of 10^{-4} sec.

This model is most easily tested using the orthogonal beam setup and a long (35 cm) focal length lens. Under these conditions, the interaction volume can be readily estimated. At the low power densities used in these cw laser experiments, a value of $\sigma \sim (1.3 \pm 0.7) \times 10^{-17}$ cm^2 may be adapted from the absorption spectra of the triplet and singlet states [15]. For photon fluxes in the range covered by the data of Fig. 2 a value $\bar{n} \approx 4$ is obtained. Using previously published rate constants $k(E)$ [8(b)], a slope of 5.6 ± 1 for the log-log change of count rate with laser flux is then calculated. This slope is much less than the total number of photons actually needed to induce observable thermionic emission, yet is compatible with the data. An alternative mechanism [9] invoking a small number of triplet excitons, while not excluded, is thus not needed.

Using measurements of the oven temperature (400 °C), the known vapor pressure [10], and an assumption of effusive flow from the oven, we can obtain an estimate of the C_{60} beam density in the laser focal volume. Our laser did not afford the threefold higher intensity needed to begin to see saturation of the C_{60}^+ signal. Nevertheless, the thermionic model can be used to extrapolate back to, say, I equal to 8×10^4 W/cm^2. Under these conditions the calculated count rate is 10/sec while the measured rate was $\sim$ 1/sec. This represents adequate agreement, given the finite collection efficiency of the TOFMS and electron multiplier and our neglect of dissociation. The dissociative process had at one time [8(b)] been predicted to be much faster than thermionic emission. More recent estimates of the bond strength [16] leave the role of dissociation less certain.

The mass spectrum given in Fig. 1 deserves further comment: (1) The C_{70}^+ signal is over-represented ($\sim 10^3$) relative to C_{60}^+ in the spectrum, as has also been noted previously [6,17]. We find that this effect disappears at high flux. These observations support the above model if one notes the sensitivity of $\bar{n}$ upon σ, and that the value of σ for C_{70} is at least 1 order of magnitude greater than that for C_{60} in this wavelength region [18]. It is also consistent with our observation that the wavelength dependence of the total ion yield from C_{60} ionization by a tunable pulsed laser at constant laser power follows the photoabsorption spectrum of neutral C_{60}. (2) Unlike the spectra obtained from high power pulsed laser ionization, only a small signal due to the fragment ions (C_{58}^+, C_{56}^+) is produced using the collinear setup with the longer interaction time. When using the orthogonal beam setup, these fragment ions are completely absent. This is probably because of the vanishingly small intensity fluctuations in a cw laser, such that excursions in the energy absorption are confined to those intrinsic to Poisson statistics. (3) The close agreement between the predicted and measured number of C_{60}^+ counts suggests that electron emission competes favorably with dissociation of the parent molecule. (4) The well-defined C_{60} peak is accompanied by a tail extending to longer flight time. The origin of this tail is ionization occurring during the ion draw-out pulse. The ratio of the intensity of the signal in the tail to that in the main C_{60}^+ peak is approximately the ratio of the on time to off time of the ion draw-out pulse ($\sim 1/40$).

Finally, we note a rather remarkable observation which initially prompted the cw laser ionization experiments described above. Two experiments suggested the incoherent excitation nature of the thermionic emission from fullerenes. In one experiment, C_{60} ionization was observed with 10 ns and 30 ps pulsed Nd:YAG lasers [19]. Under the same total fluence per pulse, it was found that C_{60} ionization is about the same for the two laser pulse durations even though the picosecond laser peak power density (W/cm^2) is at least 2 orders of magnitude higher than that for the nanosecond laser, suggestive of incoherent excitation. Those differences in the fragmentation patterns which do exist occur at low masses, and can be attributed to differing levels of fluctuation. This important point is also shown through a comparison of ionization of C_{60} using laser and amplified stimulated emission (ASE) light. In this second experiment, a dye laser consisting of a laser oscillator and two traveling wave amplifiers, pumped by the second harmonic radiation of a Nd:YAG laser (see Ref. [6]), was employed to produce pulsed laser as well as ASE light [20]. With high-gain dyes such as Rhodamine or LDS, when the oscillator optical cavity was misadjusted, powerful ASE was obtained from the amplifiers under a high pump power. The ASE was well collimated and consisted of broad spectral band incoherent light of $\sim$ 10 ns duration. Figure 3 presents mass spectra of C_{60} excited by a laser (upper trace) and ASE (lower trace) light pulses with the same light power density (1.8×10^8 W/cm^2) and the orthogonal beam geometry. Ion intensities and distributions in the region C_{60}^+–C_{32}^+ are identical for the same flux, regardless of whether the dye laser was operative (oscillator tuned) or not. The only difference is for the lower mass fragment ions (C^+ to C_{10}^+) where coherence is known to be important [6].

In summary, we have shown that incoherent sequential photoexcitation at low flux is consistent with a model of delayed ionization of C_{60}. The observed dependence

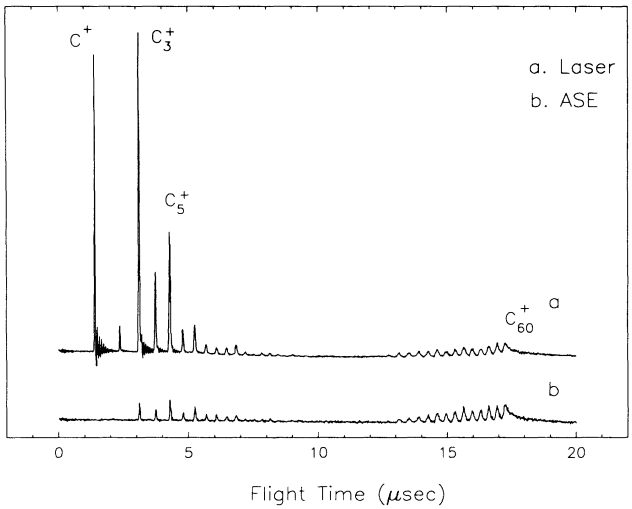

FIG. 3. Comparison of the mass spectra observed using laser (565 nm) or ASE (in the same wavelength region) pulses from a Nd:YAG-pumped dye laser. The light flux density is 1.8×10^8 W/cm^2 for both cases.

on flux of the ionization signal for the low-power cw laser is similar to that observed for high-power pulsed lasers. Using a Poisson distribution for the C_{60} population in the photoexcited energy states, the thermionic emission model is found to be compatible with the observed ionization rate and the laser power dependence of the ionization. Furthermore, the model calculation reported here also accounts for the power dependence observed in the pulsed laser experiments [5,6]. The present results, along with previous measurements and calculations of the photoelectron energy distribution [6], thus strongly support the thermionic emission model. The study also represents the first observation of ionization of a large molecule by a cw laser and suggests its general use for mass spectroscopy of those polyatomic molecules where ionization is not overwhelmed by dissociation of the parent molecule. cw laser ionization has the additional feature of minimizing dissociation following or during ionization, because of the greater control it offers over fluctuations in the number of absorbed photons.

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