Fragmentation of C_{60}: Experimental detection of C, C_2, C_3, and C_4 by xuv postionization

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(Received 16 January 1995)

We report experimental evidence for the loss of neutral C_2 from photoexcited C_{60} and C_{70}. These species are detected by postionization with xuv radiation. Interestingly, C, C_3, and C_4 also are products in the nascent distribution. An upper limit to the translational energy release into C atoms has been obtained using a resonant autoionization transition. The detection of these products gives insight into the fragmentation mechanism of fullerenes and may also have an impact on the field of fullerene formation.

PACS number(s): 36.40.+d, 82.30.Lp, 33.80.Eh

There has been much experimental [1–12] and theoretical work [13–18] on the dissociation of C_{60} since its discovery in 1985 [19]. Most of the studies have focused on the detection of only even-numbered carbon clusters (C_n, n even) appearing in the mass spectra of fragmented C_{60} [1,14,16]. The original idea that these even numbers occur because of C_2 loss by C_{60} has been taken as truth until recently [9,12,20]. Another possibility is that C_{60} may initially fragment via loss of a C atom to a metastable C_{59}, followed by loss of another C atom to yield C_{58}. We have used (2+1) multiphoton ionization to detect C atoms from C_{60} photodissociation previously, but were unable to determine if the C atoms resulted from the initial prompt dissociation of C_{60} (i.e., in the fullerene stage, $n > 32$) or from smaller fragments after total disintegration of the cage [20].

We have also detected large neutral fragments (C_{58}–C_{32}) from photodissociation of C_{60} using 118-nm (10.5 eV) radiation for single-photon ionization of the photoproducts [21]. In these measurements, the neutral fragment distribution matched the ionized fragment distribution. Unfortunately, the high ionization potentials for the small C_n species [22] precluded their detection with this vacuum ultraviolet light (for fragments smaller than about C_6). We have recently installed an extreme-ultraviolet (xuv) light source on our mass spectrometer to photoionize all species with ionization potentials $< \sim 14$ eV, including all C fragments. In this paper, we report the first observation of C, C_2, C_3, and C_4 in the nascent distribution of dissociated fullerenes and show that C_2 loss is not the only small-fragment channel.

The time-of-flight mass spectrometer (TOFMS) has been described in detail previously [20]. We utilize laser desorption for the generation of C_{60} or C_{70} vapor [7], followed by either 266 nm [from the same Nd:YAG (yttrium aluminum garnet) laser that generates the xuv light] or 308-nm (XeCl excimer) laser light for dissociation. The dissociation products are then probed by an xuv laser. The xuv generating system consists of two Nd:YAG-pumped dye-laser systems, a frequency mixing cell, and a capillary waveguide for transport of the xuv beam [23] (see Fig. 1). One of the dye lasers is tuned to 557 nm and mixed with 354.7 nm from the frequency-tripled Nd:YAG to generate 216.67 nm [using a *B*-barium borate (BBO) crystal]. This uv beam is then combined on a dichroic mirror with the output of the second dye laser and focused with a 20-cm fused silica lens into the four-wave-mixing medium (Kr in a pulsed free jet or an effusive cell) [24]. The xuv light is then transported into the source region of the TOFMS with an ~1-mm-diam capillary waveguide. The waveguide is utilized both for transmission of the xuv light and as an efficient differential pumping aperture. The delay between photodissociation and xuv postionization for the experiments reported here is ~50–300 nsec. A delay line of ~15 m (~50-nsec fixed delay) is utilized for the 266-nm dissociation experiments. A separate excimer laser with adjustable delay is used for the 308-nm dissociation experiments (set at ~270 nsec for the results reported here).

Shown in Fig. 2 is a mass spectrum of C_{60} photodissociation by 266-nm radiation, followed by single-photon-resonant excitation of the $^3S_1 \leftarrow {}^3P_1$ autoionization C-atom resonance at $\sim 105\,780$ cm^{-1} (94.54 nm, 13.11 eV) [25]. This spectrum is typical for photoionization of C_{60} by 266-nm photons, displaying the even-numbered fullerenes (C_{34}–C_{60}) and the long "tail" [7,26] to the high m/z side of C_{60} [for a TOFMS, the m/z scale is proportional to (time)^2]. These large fullerene fragments are caused by the 266-nm photodissociation and photoionization of C_{60} and are present without the xuv laser. The peak labeled "prompt $C_{60}{}^+$" is caused by the desorption laser (337-nm N_2 laser) only. (As explained in the past, laser desorption produces mainly neutral molecules, but some direct ions are formed and detected). The desorption laser causes no fragmentation of the neutral C_{60} molecules as evidenced by the lack of photoproducts when the 266-nm dissociation laser is blocked. The inset to the figure shows the region around C, C_2, C_3. These species are from xuv photoionization of the fragments that originate in the first few nanoseconds after photodissociating C_{60}. Clearly evident is the detection of C atoms before the onset of extreme dissociation (i.e., no fragments smaller than $\sim C_{36}$ are observed in the mass spectrum). This implies that C atoms do result from the prompt dis-

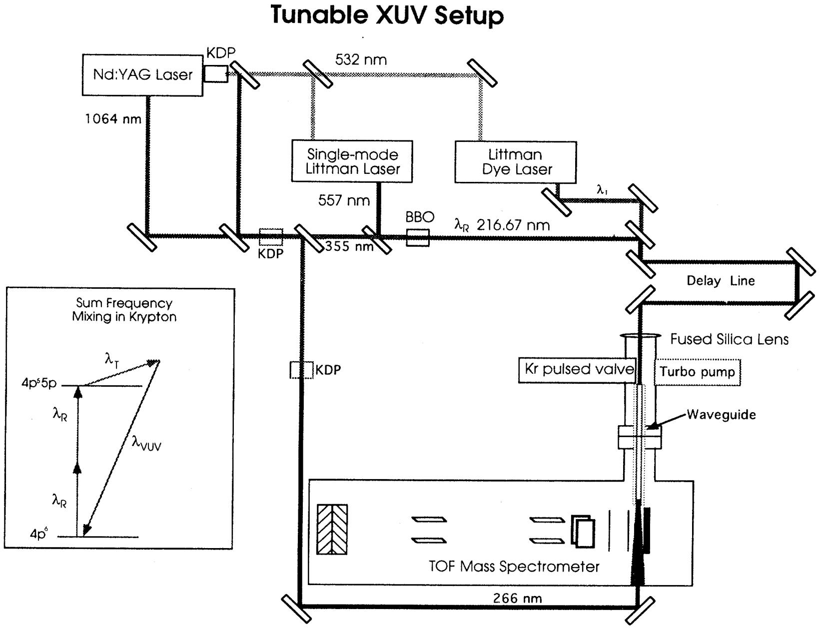

FIG. 1. Tunable xuv setup to detect the products from photodissociation of fullerenes. The lower left part of the figure displays the four-wave-mixing process involved in generation of the tunable xuv light.

sociation of C_{60}. However, there may be other small fragments, as observed in graphite itself ($C:C_2:C_3 = 1.0:1.9:3.1$ at 4000 K [27]). In fact, C_2 and C_3 are indeed present in the spectrum, although at somewhat reduced intensities compared with the C-atom (resonant) peak.

Shown in Fig. 3 is a wavelength scan through the C-atom autoionization resonance, with a recording of the signal from direct ionization of acetone backfilled into the chamber at $\sim 5\times 10^{-8}$ Torr ($\sim 5\times 10^{-10}$-Torr base pressure). This ionization signal from acetone is a direct measure of the xuv photon fluence; the dispersion-shaped curve is caused by the transition from positive to negative dispersion in the four-wave-mixing gas [24]. The C-atom resonance appears to be ~ 2.5 cm^{-1} wide, given by the Doppler width of the transition and partially by the xuv linewidth of ~ 1.3 cm^{-1}. [The xuv linewidth was measured by 1+1 ionization of Kr through the $4p$-$7s\,^2P_{3/2}(J=1)$ transition that also fixed the measured line position of the C-atom resonance.] This width places an upper limit to the velocity of C atoms from dissociation of C_{60} at $\sim(1\ \mathrm{cm}^{-1}/105\,800\ \mathrm{cm}^{-1})\times 3\times 10^{10}$ cm/sec $=2.8\times 10^{5}$ cm/sec corresponding to ~ 0.5 eV energy release in the dissociation (or an effective C-atom temperature of ~ 4000 K). We can only place an upper limit to this because of the unknown inherent autoionization width of the resonance.

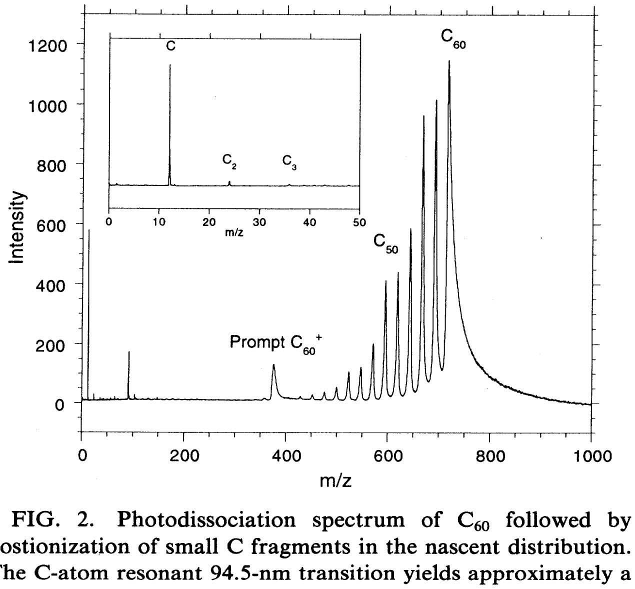

FIG. 2. Photodissociation spectrum of C_{60} followed by postionization of small C fragments in the nascent distribution. The C-atom resonant 94.5-nm transition yields approximately a hundredfold increase in C-atom detection sensitivity.

A possible complication in the detection of the nascent products from photodissociated C_{60} concerns the time constant for dissociation. As we have described in detail

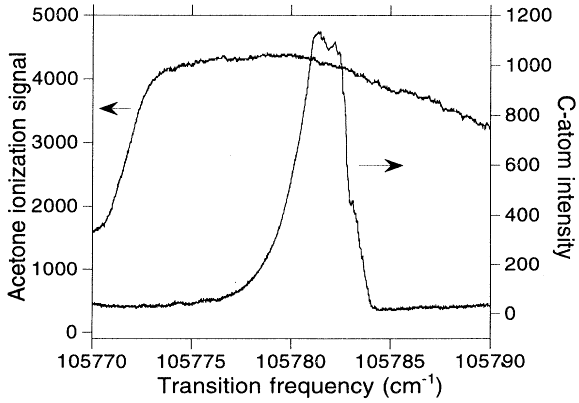

FIG. 3. The $^3S_1 \leftarrow {}^3P_1$ autoionization resonance in C atoms from photodissociation of C_{60}. Also shown is the ionization signal from acetone (proportional to xuv radiation).

in the past [7], C_{60} absorbs many uv photons before dissociating or ionizing. In fact, we have experimental evidence that C_{60} may accumulate up to 55 eV of internal energy before fragmentation occurs. This is caused by fast internal conversion of electronic to vibrational energy in this large molecule with many degrees of freedom ($3n-6=174$ vibrational degrees of freedom) and large activation energy for dissociation. The rate of dissociation for C_{60} at 55-eV internal energy has been calculated by Rice-Ramsberger-Kassel-Marcus theory [7] to be $\sim 10^8$ sec^{-1} (10 nsec $1/e$ time), while it is $\sim 5\times 10^5$ sec^{-1} (2 μsec $1/e$ time) at 40-eV internal energy. However, we have used absolute rate theory [28] to calculate that C_{60} with 55-eV internal energy will dissociate down to at least C_{32} on our experimental time scale. It will only dissociate to $\sim C_{54}$ with 40-eV internal energy initially deposited in the C_{60} species. We have also calculated that ~ 0.5 eV is liberated in the initial dissociation (in good agreement with the observed upper limit to the kinetic energy release mentioned above), and because of kinematic constraints, almost all of this energy goes into the smallest fragment in the dissociating step. Assuming the fragment is C, the velocity of the C will be $\sim 2\times 10^5$ cm/sec. This species will travel ~ 2 mm in 1 μsec, almost out of the detection region. Therefore, there is a small intermediate regime where the internal energy is high enough to dissociate the C_{60} in a reasonable time (before the fragment leaves the detection region), but not too high to dissociate the C_{60} species into its very small fragments ($n<30$) and thus preclude a measurement of the nascent distribution of fullerene fragments. This effect is much less pronounced in C_{70} (should obtain ~ 5 more C_2's than from C_{60} if it is the only loss channel) and since C_{60} and C_{70} behave very similarly in photodissociation, we can use dissociation of C_{70} to further characterize the fragment distribution.

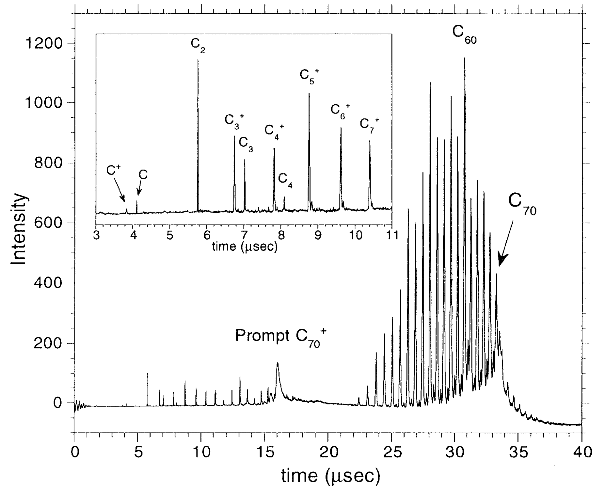

FIG. 4. Nonresonant postionization of fragments from photodissociation of C_{70}. The desorption laser precedes the 308-nm dissociation laser by ~ 17 μsec, and the 90.67-nm xuv laser is delayed relative to the dissociation laser by 270 nsec. The peak labeled prompt C_{70}^+ is caused by the desorption laser alone. The inset displays the small fragment distribution.

To make a more quantitative comparison of the small fragments, we have employed a nonresonant postionization source. Shown in Fig. 4 is a spectrum of photodissociation of C_{70} with 308-nm dissociation and with the postionization laser delayed by ~ 270 nsec and tuned away from the C-atom resonance (90.67 nm, 13.67 eV). In addition, we used a higher efficiency effusive source and a different tunable laser for sum-frequency generation for production of nonresonant xuv radiation [24] (approximately a tenfold increase in the number of photons per pulse). The relative cross section for ionization of $C:C_2:C_3:C_4$ is unknown, but a study of xuv ionization of laser-desorbed graphite showed that the cross sections are within a factor of 3 of each other (the absolute cross section for C-atom ionization has been calculated [29] to be $\sim 10^{-17}$ cm^2). One could assign relative cross sections from the laser-desorbed graphite data, but the exact temperature of the laser-heated graphite is unknown and the different desorption velocities need to be taken into account. However, since we do not need to actually quantify the relative abundance of any of the fragments in this paper, we shall assume that the relative detection efficiencies are comparable (order-of-magnitude) for all four entities (C, C_2, C_3, and C_4). The intensity of each of these species is displayed in the inset to Fig. 4. The ionized fragments from the dissociation laser are labeled as positive ions, while the neutral fragments are labeled as neutrals. These positive ions are either from multiphoton ionization of small fragments by the 308-nm laser pulse or are ionized fragments from the dissociation process itself. The detection sensitivity for these ionized species is much higher than the neutral species that are ionized by the xuv light in our mass spectrometer, so the peaks labeled as positive ions are in relatively low abundance. The C_3 peak is only $\sim \frac{1}{3}$ of the intensity of C_2. If C_2 were the only fragment down to C_{32}, the C_2 peak should be >20 times larger than any other fragment. This is obviously not the case here, and we must try to understand the origin of these other fragments.

Geusic *et al.* [30] and Radi *et al.* [31,32] have shown that C_3 loss is the predominant dissociation pathway for a majority of the small ($n<30$) carbon clusters, although C and C_2 do originate from a small fraction of these clusters. However, $C_{54}-C_{60}$ were given as the only possible candidates for losing C_4. Thus, our detection of C_4 in the C_{60} photodissociation channel proves that C_4 is indeed present in the initial distribution. The lack of observation of C_5 implies that $C_{15}-C_{28}$ may not be present in the initial fragmentation from C_{60}. That is, since C_5 is a major channel for these small carbon clusters, and since we can photoionize it (IP of approximately 12.2 eV), we should observe it as a major species in the postionization spectra if it were present.

A recent paper addresses the shape and entropy of C_{60} as a function of temperature [18]. The various stages of fullerene evolution as the cage is heated have been given the descriptive names "solid" (1000 K), "floppy" (3000 K), "pretzel" (4200 K), "linked chains" (5000 K), "fragments" (5400 K), and "chain gas" (10 200 K) stages. A possible source for the C_2 and C_4 molecules in the fragment distribution is the floppy or pretzel stage, whereas the C and C_3 species may originate from the linked chains and fragment stages. However, these different stages have no clear-cut divisions, and there must be interconversions between each on a short time scale.

In conclusion, we have shown that C_{60} does indeed fragment by loss of C_2 as the lowest-energy channel (during the so-called floppy or pretzel stage). However, C, C_3, and C_4 may also be ejected during the fullerene-size stage (i.e., before the $n < 32$ occurs). This "linked-chains" stage may allow the ejection of fragments other than C_2 and the subsequent annealing of the chain back into a fullerene before further destruction. These findings may have some impact on the discrepancy [15,33] between the theoretical numbers for C_{60} dissociation energetics ($\sim 10-12$ eV for C_2 loss) [15,34] and the experimental numbers ($\sim 5-7$ eV) [2,3,7,8,33]. Basically, the theoretical results are for loss of C_2 from a closed, fullerenelike structure, whereas experiments probe loss of C-containing species ($C-C_4$) from the different, more-open structures discussed above. These structures depend on the amount of internal energy and have different dissociation energies. In fact, in a typical dissociation experiment, C_{60} is initially excited to very high energies and loses energy by dissociating rapidly (picosecond to nanosecond time scale) by loss of these small carbon species. After enough energy has been lost, the molecule will assume a fullerene-type structure and may then dissociate by loss of C_2 on a nanosecond to microsecond time scale. An interesting future experimental may be to probe the time scales for these different processes by varying the time delays and excitation energies of the C_{60} molecules.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract No. W-31-109-ENG-38.

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