Photoionization and Fragmentation Dynamics of C_{60}

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(Received 28 March 1994)

Photoionization of C_{60} by 15 ns laser pulses at 193 and 308 nm and by ca. 100 fs pulses at 310 and 620 nm has been studied with reflectron time-of-flight mass spectrometry. The initial fragmentation process is seen to be the ejection of C_n, $n > 2$, as opposed to successive C_2 evaporation. The fragment ions produced in this initial fragmentation step have sufficient internal energy to cool, by the emission of a C_2 molecule in the field-free region of the mass spectrometer. Pump-probe experiments with 90 fs laser pulses at 620 nm give additional insights into the ionization mechanism.

PACS numbers: 36.90.+f, 33.80.Eh, 33.90.+h

One of the great puzzles in fullerene research is the fragmentation mechanism that leads to the well known bimodal fragment-ion mass spectra. This distribution was first observed in the photofragmentation experiments of the Smalley group in 1987 [1]. In this pioneering paper photofragmentation of mass-selected carbon-cluster ions produced by laser desorption of graphite was studied at various laser wavelengths and fluences. The bimodal fragmentation pattern of C_{60}^+ showed the large fragment ions separated by C_2 ending abruptly at C_{32}^+. The small fragment distribution appeared predominantly between C_7^+ and C_{25}^+ with mass peaks separated by C^+. The authors discussed the sequential loss of C_2 but concluded that the level of excitation that would be needed to obtain the very high order fragmentations observed were prohibitively large and instead suggested an "unzipping" mechanism, in which neutral carbon chains could be produced. These experiments were carried out with laser pulse widths on the order of nanoseconds so that one could not be sure whether the fragments observed were produced directly from the parent fullerene or were arising from fragments after a second absorption process in the later part of the laser pulse. In the meantime, similar fragmentation patterns have also been observed in experiments in which pure buckminsterfullerene samples have been excited by collisions, either with atoms or molecules [2–4], with electrons [5], or at surfaces [6]. In the collision experiments the appearance of the large fragments (from C_{58}^+ down to C_{50}^+ or further) can often be plausibly explained by a successive statistical "evaporation" of C_2 molecules from the highly vibrationally excited C_{60}^+ [3,4,7,8]; however, it is not possible to explain the presence of the smaller fragments using such a model.

In this Letter we report femtosecond photoionization and fragmentation experiments of C_{60} in the gas phase and compare them with novel nanosecond laser studies, combining both excitation schemes with a reflectron time-of-flight (RETOF) mass spectrometer. This allows us also to obtain information on the relative importance of fast vs metastable fragmentation processes and thus gives information on the content of internal energy of the fragments. These results help to shed new light on the ionization and fragmentation dynamics and on the time scale for electronic to vibrational coupling within free fullerenes.

A molecular beam of C_{60} is produced by evaporating pure (>99.5%) C_{60} powder in an oven at a temperature of 420 °C. The beam passes between two wire meshes where it is ionized (and fragmented) by the laser pulse. The ions are immediately extracted by a pulsed electric field and detected by channel plates after passing through the RETOF. The potentials on the reflectron are adjusted so that fragment ions produced directly in the extraction region (i.e., up to 2 μs after the laser pulse) can be distinguished from so-called metastable fragment ions which are formed in the field-free flight region of the mass spectrometer in a time window of 5 to 75 μs, after the laser interaction. For the experiments with nanosecond laser pulses, standard ArF (193 nm) and XeCl (308 nm) excimer lasers were used (pulse width approximately 15 ns) focused to spot sizes of ca. 1 mm^2. For the femtosecond experiments we used the output from a colliding-pulse mode-locked (CPM) laser centered around 620 nm, with a pulse width of 90 fs (FWHM), or its second harmonic at 310 nm (pulse width 120 fs). The femtosecond pulses were focused to a spot size of $\leq$ 0.2 mm diameter. A standard delay-line geometry was used for single-color pump-probe experiments.

Figures 1(a)–1(d) show mass spectra obtained from nanosecond 308 nm laser pulses with increasing laser intensity. The fragments "grow in" in the laser energy range between 0.3 and 3 mJ with the threshold energy gradually increasing as the fragment ion mass decreases. Beyond a laser energy of 1 mJ all fragments which can have a fullerene structure, i.e., down to C_{32}^+, are present in the mass spectra. One remarkable fact is that after the fragment ions become clearly distinguishable from the noise in the mass spectra their intensity relative to the other fragments does not change significantly over a very large range of laser energies. In other words, the maximum of the fragment distribution for fragments C_n^+ with $n \geq 32$ does not shift significantly to smaller

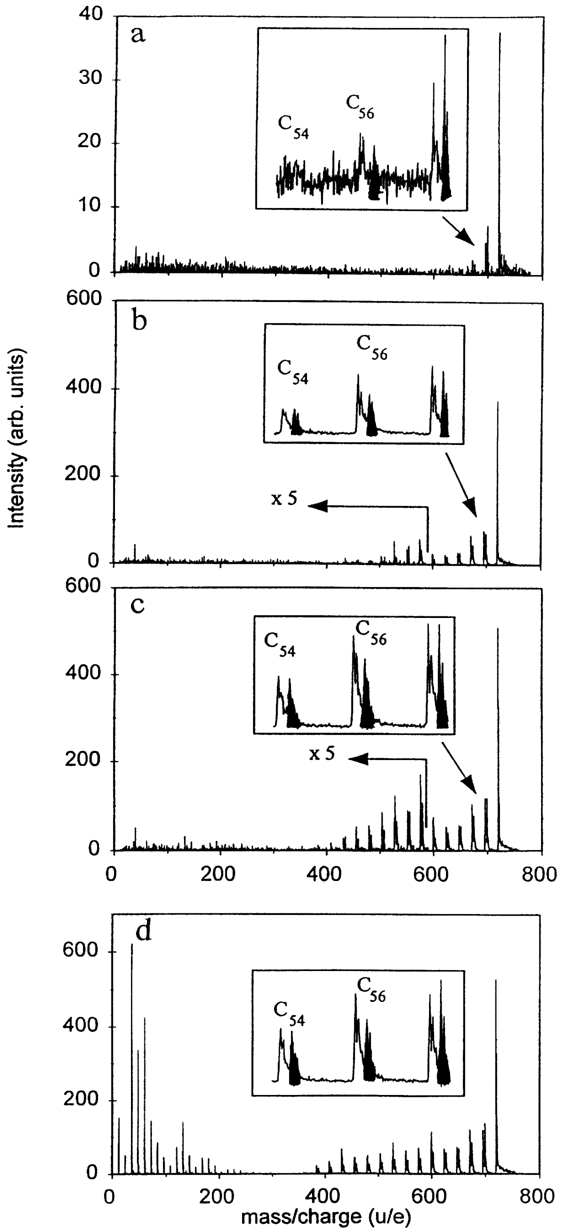

FIG. 1. Mass spectra obtained from ionization and fragmentation of C_{60} with 308 nm excimer laser pulses (pulse duration ca. 15 ns). (a) 0.4 mJ, (b) 0.93 mJ, (c) 1.3 mJ, and (d) 3.6 mJ. The laser spot size was ca. 1 mm^2. Dark peaks arise from metastable decay.

masses with increasing laser intensity. As the laser energy is increased further (3.6 mJ), small fragment ions with $n \leq 23$ begin to dominate the spectra. Astonishingly, even for such very high energies the large fragment distribution does not change very much but decreases in absolute intensity as the laser energy is increased and the small fragments become increasingly important. We have observed a similar dependence of relative fullerene ion fragment intensities on laser energy for excitation with 193 nm excimer laser pulses, although the details of the mass distribution were slightly different. Similar photofragmentation mass spectra have been published for excitation with 212.8 nm photons [9]. Unfortunately the authors did not show the small mass range of the spectra nor did they go to high enough laser intensities to show the effect reported here. Our results are in contrast to the spectra reported by O'Brien *et al.* [1] at 353 nm with laser fluences comparable to those used to obtain the spectra in Fig. 1, however, for photofragmentation of C_{60}^+ produced by laser ablation of graphite. Their results showed a clear shift to smaller fullerene fragment masses with increasing fluence. There are probably two main factors contributing to the difference in the results: First, the C_{60} in the experiments of O'Brien *et al.* produced by laser ablation of graphite may have contained different isomers, whereas we evaporated C_{60} powder. Second, O'Brien *et al.* fragmented positively charged ions, whereas we ionized and fragmented the C_{60} with the same laser pulse so that the electron could carry away a substantial amount of the excitation energy.

The insets in Fig. 1 clearly show a double peak structure for the fullerene fragments C_n^+, the peaks marked in dark arising from ions produced by metastable loss of C_2 from C_{n+2}^+ occurring in the field-free region of the mass spectrometer. The ions contributing to the left-hand peaks are produced in the extraction region. The structure superimposed on the peaks is due to the isotope distribution of pure carbon (1% ^{13}C). There are some very surprising aspects to these results: We only observe one metastable C_2 loss for each fullerene fragment ion. Even at the highest laser energies used in our experiments we could see no evidence for successive C_2 evaporations or metastable C_4 or C_6 fragmentations in our experimental time window of 5 to 75 μs, although these processes should easily be resolved by our mass spectrometer. The relative intensity of the metastable fragment to the direct fragment is a direct measure of the fragment's internal energy as it enters the field-free region of the mass spectrometer. In contrast to intuition, it stays constant as the laser energy is increased for all fullerene fragments (with the one exception of C_{58}^+, which has a larger metastable peak at very low laser energies). From these intensity ratios and the knowledge of the time the ions spend in each part of the mass spectrometer it is possible to determine the rate constants for each metastable fragmentation [10]. An estimate of the internal energy of the fragments needed to produce such decay rates can be obtained from the Rice-Ramsberger-Kassel-Marcus (RRKM) theory by considering the statistical evaporation of C_2 from excited fullerene ions [7]. We use RRKM theory to relate our measured decay rates to the internal energy of the fragments, making use of the known experimentally determined dissociation energies for the fullerene fragments [7]. This procedure will be discussed in more detail in a forthcoming publication

[11]. The internal energies which we obtain decrease only very slightly with decreasing size of the fragment which undergoes metastable fragmentation. For example, the processes $C_{60}^{\#+} \rightarrow C_{58}^{+} + C_2$, $C_{58}^{\#+} \rightarrow C_{56}^{+} + C_2$, and $C_{56}^{\#+} \rightarrow C_{54}^{+} + C_2$ require internal energies of ca. 49, 48, and 46 eV, respectively, to produce our measured intensity ratio. (The symbol # means that the molecule is internally excited.) This is very different from what would be expected if the fragmentation of the laser excited C_{60} occurred by a successive statistical evaporation of C_2. In this case, the internal energies of the smaller fragments would be much less than what we observe, since each C_2 evaporation would lead to a loss of the activation energy of approximately 7 eV [7]. These results combined with the fact that the relative intensities of the fullerene fragment ions do not change significantly over a large laser energy range provide conclusive evidence against a successive statistical evaporation of C_2 after laser excitation of buckminsterfullerene.

Additional evidence comes from experiments with 100 fs laser pulses at 310 nm. Three mass spectra, obtained with increasing laser energy, are shown in Fig. 2. The laser fluences were chosen so that approximately the same C_{60}^{+}/(total ion intensity) ratio was observed as in the spectra shown in Fig. 1 for excitation with ns pulses. The most striking difference between the spectra in Figs. 1 and 2 is the relatively large intensity of C_{60}^{++} and doubly charged fragments in the femtosecond experiments. The most striking, and unexpected, similarity is that the ratio of metastable to direct fragment peaks for C_n^{+} and C_n^{++} is the same as in the nanosecond case, although one would expect the excitation mechanism to be different with fs pulses. Experiments which show the lack of delayed ionization after excitation of C_{60} with 1 ps 248 nm laser pulses support a different excitation mechanism for ultrashort laser pulses [12]. It should also be noted that the minimum fullerene ion fragment size observed at a given laser energy is the same for the singly charged fragments as for the doubly charged fragments. These results would tend to confirm the unzipping mechanism suggested by O'Brien *et al.* [1] and further developed in a model proposed by DeMuro *et al.* [13] in which they considered the most energetically favorable way of removing carbon chains from the fullerene. We thus suggest that at low laser energies [Figs. 1(a)–1(c) and Fig. 2] the excited fullerene predominantly fragments a chain of carbon atoms—the size of the chain increasing with increasing internal energy of C_{60}. The power-law dependence of the fragment intensities as a function of laser energy for the femtosecond laser pulses tells us that fragmentation and ionization for the larger fragments need at least 6 photons (the ionization step itself requires 2 photons). This fragmentation could occur "directly" or be a statistical process similar to the C_2 evaporation discussed above. However, the fact that we do not observe metastable fragmentation of species larger than C_2 between 5 and 75 μs argues against a statistical mechanism. The fullerene fragments produced by this fast process have considerable internal energy (over 40 eV if the RRKM estimates are to be believed—i.e., 10 photons of 310 nm or 20 photons of 620 nm in addition to the ionization and primary fragmentation energy) and are then able to evaporate one C_2 molecule during their flight path through our mass spectrometer. At higher laser energies [Fig. 1(d)] the highly excited C_{60} does not produce fragments with much higher internal energies, as is evidenced by the lack of successive C_2 evaporation which would be observed in our experiment [11], but can undergo a fast multiple fragmentation into three or, at the highest laser energies investigated, many more fragments, none of which are large enough to rearrange into a fullerene structure. The fragment with the smallest ionization potential is likely to carry the positive charge and thus be the one which we detect in our experiment, leading to the structure observed, e.g., in the lower mass range of the spectrum in Fig. 1(d). The ionization potentials of the small

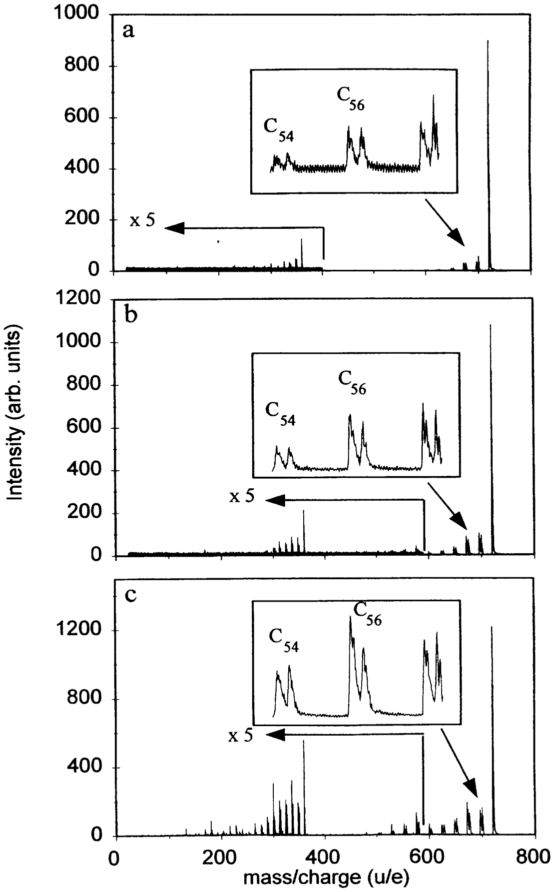

FIG. 2. Mass spectra obtained from ionization and fragmentation of C_{60} with 310 nm CPM laser pulses (pulse duration 120 fs). (a) 7.3 μJ, (b) 10.5 μJ, and (c) 15 μJ. The laser spot size was $\leq 0.1 \times 0.2$ mm.

carbon species are all higher than those of the fullerenes with the possible exception of the "magic number" fragments with $n = 11$, 15, 19, and 23 [14,15].

Insight into the ionization-fragmentation mechanism is obtained from 90 fs one-color pump-probe experiments at 620 nm. The fragmentation spectra for excitation with 620 nm do not differ significantly from those obtained with the second harmonic (Fig. 2). The intensity of the C_{60}^{+} ion signal from a pump-probe delay scan is shown in Fig. 3. Four 620 nm photons are required to ionize C_{60}; however, we find that the signal depends on the third power of the laser energy. There is an orbitally forbidden $^1T_{1g}$-^1A_g transition at 620 nm which can be Herzberg-Teller induced and for which the upper electronic state will be subject to Jahn-Teller dynamic distortions [16]. It would thus appear that we are saturating this transition with 1 photon at very low laser energies and require 3 additional photons to ionize from this state. The latter process occurs on an ultrashort time scale below 90 fs, possibly being a genuine 3 photon process. This hypothesis is borne out by the pump-probe delay curve, which at zero delay is approximately a factor of 10 higher than the average intensity at long delay times. This enhancement is the theoretical average for coherent superposition of the 2 photons of the same wavelength at zero delay, if 3 photons are absorbed on a time scale shorter than the laser pulse width. The oscillatory structure on the pump-probe curve has a period of around 110 fs and is most likely due to vibrational excitation of the intermediate $^1T_{1g}$ state. The averaged observed oscillatory period corresponds to a vibrational frequency of $311 \pm 24\ \mathrm{cm}^{-1}$ which is in reasonably good agreement with the frequency of the $h_g(8)$ mode in the ground electronic state ($273\ \mathrm{cm}^{-1}$) and thus confirms the excitation of a Jahn-Teller active h_g mode in the forbidden $^1T_{1g}$-^1A_g transition for which some evidence was found in solution spectra [16].

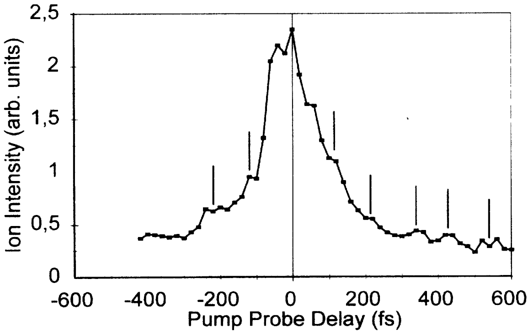

FIG. 3. Single-color pump-probe delay scan at 620 nm. Pump pulse 30 μJ, probe pulse 20 μJ.

In conclusion, we have shown that C_{60} predominantly fragments via ring or chain ejection after photoexcitation. First fs pump-probe photoionization experiments on C_{60} in the gas phase indicate that this could be a very powerful method to obtain information on the dynamics occurring in such a complicated molecular system.

[1] S.C. O'Brien, J.R. Heath, R.F. Curl, and R.E. Smalley, J. Chem. Phys. **88**, 220 (1988).

[2] For example, R.J. Doyle and M.M. Ross, J. Phys. Chem. **95**, 4954 (1991); K.A. Caldwell, D.E. Giblin, and M.L. Gross, J. Am. Chem. Soc. **114**, 3743 (1992); E.E.B. Campbell, A. Hielscher, R. Ehlich, V. Schyja, and I.V. Hertel, in *Nuclear Physics Concepts in the Study of Atomic Cluster Physics*, edited by R. Schmidt, H.O. Lutz, and R. Dreizler, Lecture Notes in Physics (Springer-Verlag, Berlin, 1992), Vol. 404, p. 185.

[3] E.E.B. Campbell, R. Ehlich, M. Westerburg, and I.V. Hertel, in *The Pysics of Electronic and Atomic Collisions*, edited by T. Andersen, B. Fastrup, F. Folkmann, H. Knudsen, and N. Andersen, AIP Conference Proceedings No. 295 (AIP, New York, 1993), p. 697.

[4] P. Hvelplund, L.H. Andersen, H.K. Haugen, J. Lindhard, D.C. Lorents, R. Malhotra, and R. Ruoff, Phys. Rev. Lett. **69**, 1915 (1992).

[5] R. Völpel, G. Hofmann, M. Steidl, M. Stenke, M. Schlapp, R. Trassl, and E. Salzborn, Phys. Rev. Lett. **71**, 3439 (1993).

[6] Th. Lill, H.-G. Busmann, B. Reif, and I.V. Hertel, Appl. Phys. A **55**, 461 (1992).

[7] M. Foltin, M. Lezius, P. Scheier, and T.D. Märk, J. Chem. Phys. **98**, 9624 (1993).

[8] J.F. Christian, Z. Wan, and S.L. Anderson, J. Chem. Phys. **99**, 3468 (1993).

[9] P. Wurz and K.R. Lykke, J. Phys. Chem. **96**, 10129 (1992).

[10] E.E.B. Campbell, G. Ulmer, H.-G. Busmann, and I.V. Hertel, Chem. Phys. Lett. **175**, 505 (1990).

[11] H. Hohmann, R. Ehlich, S. Furrer, O. Kittelmann, J. Ringling, and E.E.B. Campbell, Z. Phys. D (to be published).

[12] Y. Zhang, M. Späth, W. Krätschmer, and M. Stuke, Z. Phys. D **23**, 195 (1992).

[13] R.L. DeMuro, D.A. Jelski, and T.F. George, J. Phys. Chem. **96**, 10603 (1992).

[14] S.B.H. Bach and J.R. Eyler, J. Chem. Phys. **92**, 358 (1990).

[15] J.A. Zimmerman, J.R. Eyler, S.B.H. Bach, and S.W. McElvany, J. Chem. Phys. **94**, 3556 (1991).

[16] S. Leach, M. Vervloet, A. Despres, E. Breheret, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor, and D.R. Walton, Chem. Phys. **160**, 451 (1992).