Velocity distributions and photodissociation of neutral C_{60} and C_{70} clusters

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Purified samples of C_{60} and C_{70} are synthesized according to recently published procedures. Desorption with 308 nm laser light from solid C_{60} and C_{70} samples is used as a neutral cluster source to study the ionization and concurrent fragmentation in the gas phase by interaction with intense laser radiation. According to a well-known classification scheme, the ionization/fragmentation behavior of C_{60} and C_{70} clusters is clearly identified as of class A type. Also, the laser desorption process itself has been investigated by measuring the velocity distributions of laser desorbed neutral C_{60} and C_{70} clusters. Good agreement of the experimental data with a Maxwell-Boltzmann distribution is found. We conclude that at the applied laser fluences, C_{60} and C_{70} clusters are desorbed by evaporation induced by the incident radiation, providing no fragmentation in the desorption process.

I. INTRODUCTION

Carbon clusters have been studied extensively over the past decade. Since the discovery of large carbon clusters consisting of an even number of atoms,[1] termed "fullerenes,"[2] research on these substances has increased. In particular, the finding that some of these clusters are chemically very stable molecules[3] has triggered further interest due to their potential for yet unknown new materials, and because of their unique molecular properties. The special stability of some of these clusters appears to be related to a cage structure.[4] The 60 carbon atom cluster with the geometry of a truncated icosahedron,[5] called Buckminsterfullerene,[2] is the most prominent representative of the fullerenes, along with other stable closed shell clusters (e.g., C_{70} and C_{84}). Until recently, these clusters had been formed by laser vaporization of graphite, either within a high pressure nozzle,[1-3,6-9] or by direct expansion into the vacuum.[10] The development of a straightforward method for the synthesis of macroscopic quantities of C_{60} and C_{70} (Refs. 11 and 12) makes it possible to carry out well-defined experiments with purified C_{60} and C_{70} samples, and has stimulated a renewed interest in the physical and chemical properties of these fascinating materials.

Due to the increasing interest in these carbon clusters, it is desirable to have a better understanding of the photoionization and the associated photofragmentation process; both occur when laser ionization is used for the detection of neutral clusters. Up to now, detailed photofragmentation data have been available only for the smaller cluster sizes[13] or for positive cluster ions mass selected from a cluster ion beam generated by laser ablation of graphite samples.[8,9] In mass spectra from the latter experiments, it was found that large even-numbered fragment ions are by far the dominant species for $n>30$. Fragmentation of these cluster ions occurs primarily by loss of neutral C_2, or to a lesser extent by loss of C_4;[8] smaller cluster ions ($n<30$) fragment mainly by loss of the thermodynamically more stable molecule C_3, and to some extent by loss of C, C_5, C_{10}, and C_{14}.[7,13] This sudden change in fragmentation behavior of the clusters around $n=30$ was attributed to a change from a three-dimensional cage structure to a two-dimensional structure, or to one-dimensional chains.[8] Although closed shell structures are possible down to clusters of 20 atoms, only clusters containing more than 30 atoms are found to be stable, as reported in a recent theoretical work.[4] In this paper, we report data on the ionization and fragmentation of pure neutral C_{60} and C_{70} clusters arising from interaction with intense laser radiation. These neutral clusters are generated by laser desorption from the pure solid coated onto a substrate. Furthermore, we present the first data of velocity distributions of laser-desorbed carbon clusters.

II. EXPERIMENT

The experiments are performed in a laser-desorption time-of-flight (TOF) mass spectrometer developed at Argonne, which has been discussed in detail previously.[14] Therefore, only a brief discussion is given here. 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 apparatus can be operated in two modes: either measuring the mass spectrum of positive or negative ions emitted directly in the desorption process from the sample, or measuring the mass spectrum of desorbed neutrals by postionization with intense laser light. Potentials in the ion optics stack are optimized for best mass resolution in each mode. The mass resolution of the apparatus ($m/\Delta m$) is 400 under these experimental conditions. The typical operating vacuum is $\approx 2\times 10^{-9}$ Torr. In our experiment, neutral and ionized C_{60} or C_{70} clusters are desorbed from an appropriately coated substrate by a pulsed desorption laser. Subsequently, the desorbed neutral clusters are ionized by a second pulsed ionization laser. For a regular mass spectrum, the desorbed particles are ionized in close proximity to the sample surface (0.3 mm). To measure velocity distributions, the desorbed neutrals are allowed to travel approximately 2 mm before being ionized in the acceleration field.

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By changing the delay between the desorption and the ionization laser, a TOF spectrum of a particular species is obtained, which is subsequently converted to a velocity distribution. 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. Velocity distributions are recorded on a chart recorder using a gated integrator set on the flight time of the desired species.

A XeCl excimer laser is used for desorption. A frequency-doubled Coumarin 540 A dye laser pumped by a second excimer laser is used for ionization. Both lasers are operated at 1 to 50 Hz repetition rate with laser pulse widths of approximately 20 ns. The relative timing of these lasers is controlled with a digital delay unit. The wavelengths are 308 and 270 nm for desorption and ionization, respectively. The fluence of the desorption laser is held constant at approximately 10–100 mJ/cm^2 for all experiments. The fluence of the ionization laser is varied by inserting neutral density filters in the beam path.

The synthesis and separation of milligram amounts of C_{60} and C_{70} is carried out according to previously published accounts.[11,12,15,16] A contact arc between two translatable graphite rods is used to generate carbon vapor in a reaction vessel filled with 100 to 200 Torr He. The deposit formed on the water-cooled stainless steel chamber surrounding the graphite rods is removed by scraping. C_{60} and higher fullerenes are extracted with hot toluene, giving deep red solutions that are centrifuged and placed on a chromatographic column of neutral alumina. Hexane is utilized as a column eluent. Solutions of C_{60} or C_{70} are placed onto a polished stainless steel substrate and are inserted into the vacuum chamber after solvent evaporation.

The four panels in Fig. 1 show consecutive steps in the separation sequence of C_{60} and C_{70} from the raw deposit. These are laser desorption negative ion mass spectra. Panel (a) shows a mass spectrum of the evaporated toluene raw extract exhibiting a number of high mass peaks, with the clusters C_{60}, C_{70}, C_{78}, and C_{84} being most abundant. Some low number carbon clusters are also present in the raw extract. In the first fraction coming off the chromatographic column [panel (b)] only C_{60} is detected. The second fraction [panel (c)] is a mixture of C_{60} and C_{70} and finally, the third fraction [panel (d)] consists almost entirely of C_{70}. Samples of C_{60} and C_{70} made from fractions one and three, respectively, are used in the experiments described later in this paper. The assignment of the mass peaks has been confirmed by high resolution mass spectroscopic investigations of these samples using a Fourier transform mass spectrometer.[17]

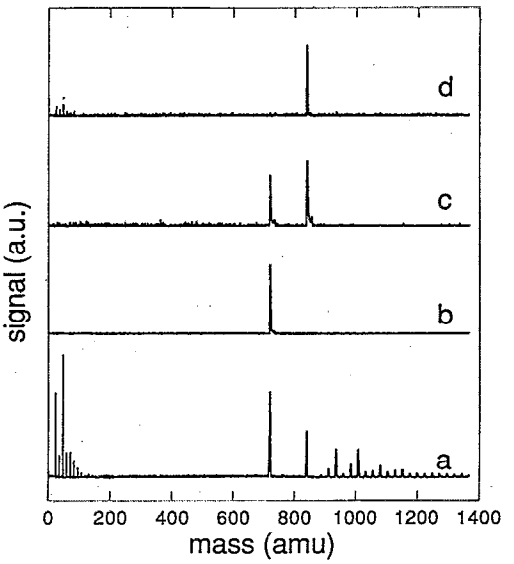
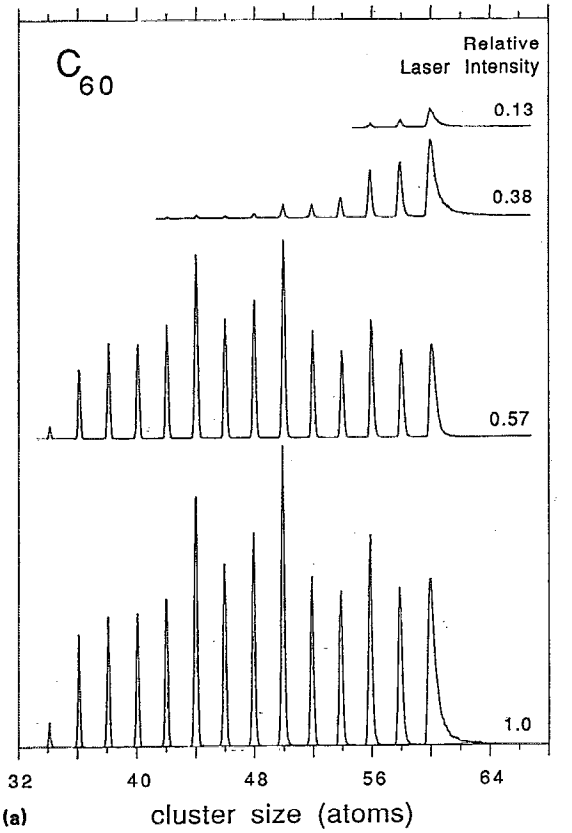


FIG. 1. Laser desorption TOF negative ion mass spectra of raw toluene extract (a), first fraction off the chromatographic column (b), second fraction (c), and third fraction (d). In the raw extract the most abundant mass peaks are C_{60}, C_{70}, C_{78}, and C_{84}, besides the low mass carbon clusters. C_{60} dominates in the first fraction, and C_{70} in the third; the second is a mixture of both.

III. RESULTS AND DISCUSSION

The first set of measurements focuses on laser-ionization/laser-dissociation of C_{60} and C_{70} clusters. It should be noted that fragmentation is not caused by the desorption laser, as can be seen in Fig. 1. This is confirmed by a recent investigation, where alternating layers of isotopically pure ^{12}C or ^{13}C clusters have been deposited onto a substrate, and subsequent analysis with laser desorption mass spectrometry reproduced these layers without any change.[10] Fragmentation can only be observed for as long as it takes place in the acceleration region. Once the ion reaches the field free drift region further fragmentation will not show up in the mass spectrum. Figure 2 shows photofragmentation of C_{60} and C_{70} for various laser intensities. For clusters consisting of at least 32 atoms, only clusters of even numbers of atoms are observed for both species. Below C_{32} fragmentation occurs by loss of neutral C_3 clusters,[7] and odd clusters also appear in the fragmentation spectra. As most of these low mass species are neutral and difficult to account for, the low mass range is omitted from Fig. 2 and from further discussions in this paper. Not surprisingly, fragmentation increases drastically with increasing laser intensity. It takes place only by loss of an even number of atoms, yielding the final distribution of even clusters, down to C_{32}, and no odd cluster sizes are found in the range between C_{70} and C_{32}. Some propensity is observed for enhanced abundance of clusters with "magic" numbers, presumably due to the more stable structures of these species. Thus, fragmentation of C_{60} gives prominent yields of C_{50} and C_{44}, while fragmentation of C_{70} gives enhanced yields of C_{60} and C_{50}. In the spectra for C_{70}, mass peaks originating from fragmentation of C_{78} are seen, since this sample was not entirely pure (Fig. 1). Previous investigations on fragmentation of large carbon clusters have been restricted to positive cluster ions produced in jet expansions of laser evaporated graphite. Similar fragmentation patterns were observed in some of these studies[8] whereas much less fragmentation of the parent cluster is reported by another group.[9]

By looking carefully at the peak shapes in the mass spectra, we notice an asymmetric broadening towards



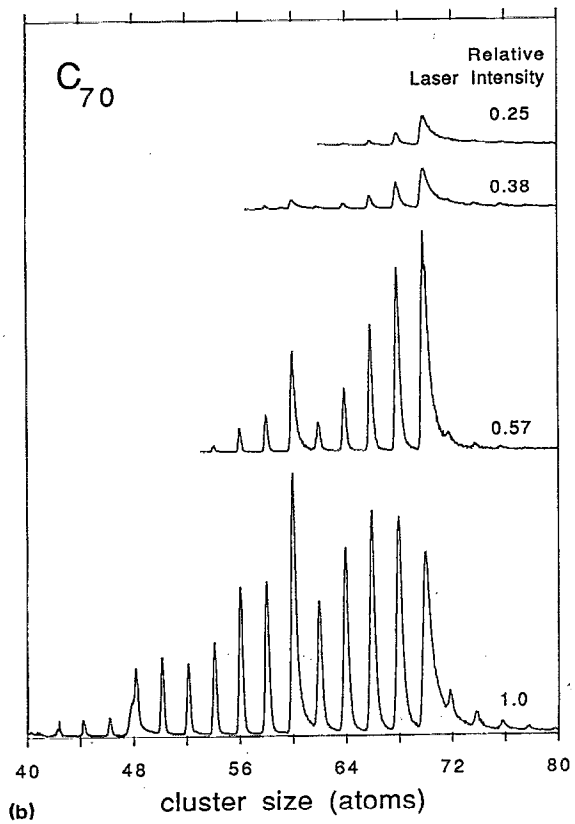
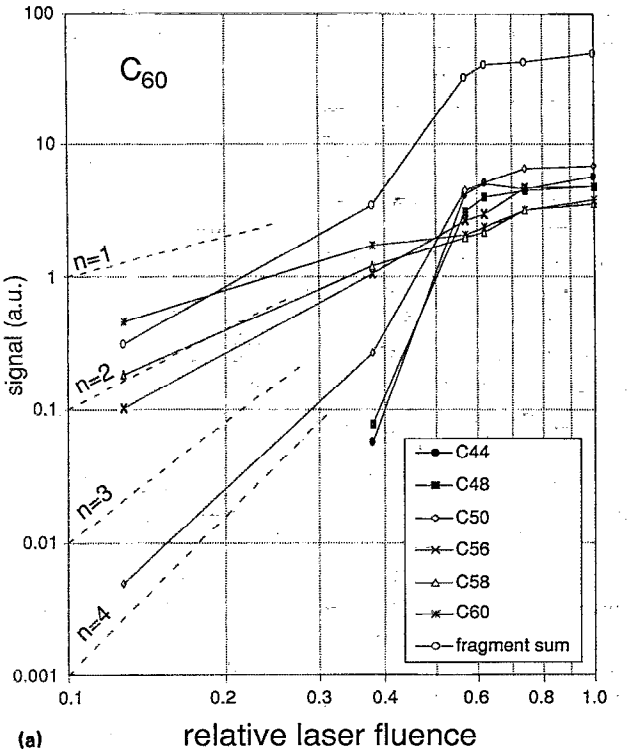


FIG. 2. Mass spectra of postionization and fragmentation of neutral C_{60} (top panel) and C_{70} (bottom panel) laser desorbed from a copper substrate. Relative laser fluence of 1.0 corresponds to 40 mJ/cm^2 and 110 mJ/cm^2 for C_{60} and C_{70}, respectively.

longer flight times. In the case of the fragment peaks, this can be caused by delayed fragmentation of a metastable ion in the acceleration region. However, this does not apply to the parent peaks. We attribute the tails seen for C_{60} and C_{70} parent cluster signals to delayed ionization following photoexcitation of these species. The time constant for delayed ionization is several microseconds in both cases, which is remarkably long. Delayed photoionization has been observed recently for NbC clusters, and has been attributed to a slow process involving nonadiabatic coupling of electronic and vibrational states.[18] A more elaborate report of the delayed ionization will be given in the upcoming publication. This process may also explain the "tail signals" found in a previous TOF experiment for postionization of fullerenes with 193 nm laser light.[10,19]

The dependence of the parent and fragment mass peaks on the laser fluence is shown in more detail in Fig. 3 for C_{60} and C_{70}. For clarity, only the signals for the parent, selected fragments and the sum of all fragments consisting of more than 30 carbon atoms are shown. For both samples, the signal of the parent rises with fluence. However, fragmentation of the parent rises faster than ionization. This is seen not only from the evolution of the fragment peaks in the mass spectra (Fig. 2), but also from the sum of fragments in Fig. 3, which rises more steeply with laser fluence than the C_{60}^+ peak. For the C_{60} sample, we observe a saturation of the parent and the fragment ion signals, with most of the fragment ions having almost equal or even larger signal sizes than the parent ion. For the C_{70} sample, we observe a drop of the signal for the parent, and most of the fragment ions at the highest investigated fluence. At the highest investigated laser intensity, fragmentation dominates, as evidenced in Fig. 3. The drop of the sum of fragments, observed for the highest investigated laser fluence in the C_{70} spectrum, results from an enhanced abundance of low-mass clusters, which are not accounted for in the sum of fragments. The fragmentation behavior shows that C_{60} is more stable than C_{70}, since C_{70} fragments to a greater extent at lower laser fluences, in agreement with structural considerations.

From the fluence dependences we can derive the order of the processes leading to ionization and fragmentation. For C_{60} and C_{70}, ionization appears to be a first order process. However, single-photon ionization is surprising, because the ionization potential of these clusters is considerably higher than the 4.61 eV provided by the ionizing laser photon. For both clusters the ionization potential is 7.61 eV.[20,21] Presumably the desorbed clusters have received enough internal energy (vibrational, electronic, rotational) by the desorption process to account for the difference. Evidence for high internal energies had already been inferred in an experiment where carbon clusters were generated by laser evaporation in a pulsed nozzle, and had not been allowed to cool sufficiently before ionization.[6] In that experiment, cooling of clusters was reduced significantly by shortening the extender tube of the pulsed cluster source. Under those conditions, single-photon ionization was achieved with 5 eV photons. In our case, the desorbed clusters are emitted directly into the vacuum, so little cool-



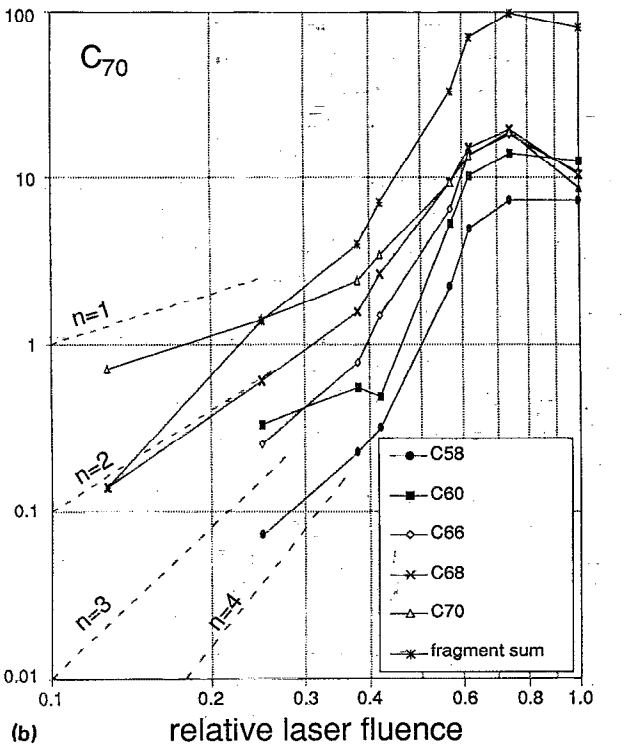


FIG. 3. Dependence of the ionization and the fragmentation on the laser intensity for C_{60} (top panel) and C_{70} (bottom panel). Relative laser fluence of 1.0 corresponds to 40 mJ/cm^2 and 110 mJ/cm^2 for C_{60} and C_{70}, respectively. Sum of fragments extends from C_{34} to C_{58} for C_{60} and from C_{42} to C_{68} for C_{70}.

ing of the clusters is expected under these conditions, thus conserving the high internal energy originating from the desorption process. Radiative cooling of the cluster can be expected to be negligible.[22,23] Besides observing a true first order process, there are at least two reasons why a higher order process could appear as a first order process. First, if the laser fluence is either close to saturation of the C_{60}^+ signal or is saturating an intermediate excitation step, a higher order process would appear with decreased slope as a consequence. The latter could be possible, because the wavelength of the ionization laser is approximately at the edge of strong absorption bands of C_{60} and C_{70} found in liquid solutions.[15] Unfortunately, detection efficiency prevents access to very low laser fluences, thus limiting the investigated range at the low fluence side. Therefore, the slope has to be extracted only from few low fluence measurements, resulting in some uncertainties. Second, the measured fluence dependence for ionization is convoluted with that for fragmentation of the parent cluster or parent cluster ion. If the fragmentation channels are added to the parent signal, the rise in signal is larger than first order.

One can also deduce the order of the generation process for the fragment peaks seen in the mass spectra. The nature of the laser desorption technique introduces signal fluctuations, which cannot be completely overcome by signal averaging. Minor structures in the measurements are attributed to these signal fluctuations and the discussion of the fluence dependence has to be restricted to more general observations. We find that the number of photons necessary to give a certain fragment ion ranges from two to four, for cluster sizes from C_{58} until C_{46}, with a trend to higher orders for higher fragmentation. The same can be said for the C_{70} sample. For production of the C_{70} fragment ions C_{68} to C_{56}, two to four photons are needed. In summary, only a few photons are necessary for creating the observed fragment distribution. For high fragmentation, this implies that fragmentation is not always a stepwise process, removing C_2 by C_2 from the cluster for every absorbed photon, but that a single photon can in some cases remove larger entities, too. The same conclusion was found for photofragmentation of positive carbon cluster ions, where the authors propose mechanisms for loss of C_2 to C_8 fragments.[8] But their finding that at least three 6.41 eV photons are needed for fragmentation of C_{60}^+ is in contrast to the much more facile fragmentation of neutrals we find. Nothing can be said about smaller cluster sizes in this respect, due to negligible signals for low laser intensities.

In another set of measurements, we determined the velocity distributions for C_{60} and C_{70} clusters laser desorbed from a stainless steel substrate by allowing the desorbed neutral molecules to travel a short distance before being ionized and accelerated into the mass spectrometer. Several velocity distribution measurements for both samples were taken to insure reproducibility. These velocity distributions are fitted with a Maxwell-Boltzmann distribution, giving reasonably good agreement with the measured data. Figure 4 shows a velocity distribution for each sample together with a best fit with a Maxwell-Boltzmann distribution. Theoretical calculations are done to gauge the

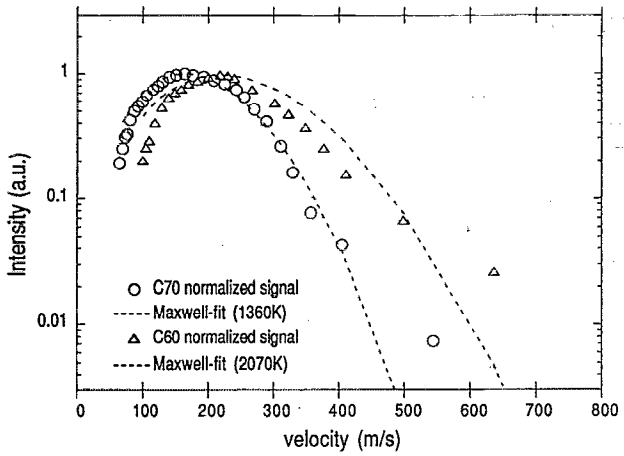


FIG. 4. Velocity distributions for laser desorbed neutral C_{60} and C_{70}. Dashed curves give best fits of Maxwell-Boltzmann distributions with the measured data.

effect of angular and lateral distributions of the desorbed species on the measured velocity distribution for our particular setup. We found that these have only a small effect compared to other uncertainties encountered in the measurement, although there is a systematic underestimation of the temperature of about 50 K. Taking this into account, we obtain average values for the temperatures of 2300 $\pm$200 K and 1500$\pm$100 K for the C_{60} and the C_{70} sample, respectively.

There are two distinct models to describe laser desorption by UV photons. These are (i) desorption due to excitation of an antibonding state of the parent or a fragment (bondbreaking), and (ii) thermal desorption due to localized heating by the laser beam.[24,25] It is known that velocity distributions of laser desorbed particles broaden with laser fluence for low laser fluences.[24–26] If the laser fluence exceeds a certain value, a change to an even broader distribution has been observed,[26] where the Maxwell-Boltzmann equation no longer fits the experimental data, indicating a change to a different desorption process. As a general trend, for low fluences thermal desorption is favored, whereas for high fluences bondbreaking is expected.[24] We kept the fluence of the desorption laser constant a little above the threshold for direct ion production. However, at this fluence, abundant neutral particle desorption already occurs, and negligible interference from secondary ions in the mass spectra is observed. A possible explanation for the difference of the temperatures found in the Maxwell-Boltzmann distributions for C_{60} and C_{70} is a different vapor pressure for the two species. The species with the lower vapor pressure, C_{70}, loses more energy by breaking the surface bond and therefore ends up with less kinetic energy.[27] Different vapor pressures for C_{60} and C_{70} have been found in a recent experiment.[28] Also, the difference of the temperatures found in the Maxwell-Boltzmann distributions for C_{60} and C_{70} can be caused by a difference in absorption of the ablation laser photons at this wavelength,[15] or by a difference in the thresholds for ion production for the two samples.

In summary, we conclude that in our experiment, laser desorption of C_{60} and C_{70} clusters is a thermal process, because the measured velocity distributions are well represented by a fit with the Maxwell-Boltzmann equation. Also, the temperatures found are comparable to temperatures reported for laser desorption of polymers[25] or laser desorption of C_2 from graphite.[29] Furthermore, we do not observe fragmentation by the desorption process, which would be expected if the bondbreaking mechanism is operative.

IV. CONCLUSIONS

The use of purified samples in our experiments enabled us to obtain data on the ionization and fragmentation of neutral C_{60} and C_{70} clusters in the gas phase due to interaction with intense laser light. According to a well known classification scheme,[30] the ionization/fragmentation behavior of C_{60} and C_{70} clusters is clearly identified as of class A type. The main features of this type of ionization/fragmentation behavior are (i) the first step is ionization before fragmentation occurs; (ii) molecular ions are produced for low laser power, then fragmentation increases for higher laser powers until total atomization of the molecule takes place; and (iii) the low-power order of the process is $\approx$IP/$h\nu$. Additional support for this assignment stems from the similarity of our data on neutrals with the fragmentation spectra of positive ions.[8] We attribute the difference of the fragmentation spectra between our results and those given in the previously published works of others[9] to the different laser wavelength used for fragmentation, which further implies that we assume a wavelength dependence of the fragmentation in contrast to conclusions derived in Ref. 8. Differences between the fluence dependencies that we have presented, and those previously obtained by other groups are attributed to our use of pure samples, as opposed to laser-evaporation cluster sources. Furthermore, these pure samples allowed us to determine the velocity distribution of these laser desorbed molecules without interference from decaying higher mass clusters. The velocity distributions, which are well described by the Maxwell-Boltzmann equation, and the absence of fragmentation in the desorption process show that the desorption laser leads to thermal desorption of the clusters from the substrate. Assuming thermal equilibrium between translational, vibrational, and rotational temperatures, which has been found for laser fluences close to threshold,[28] a cluster consisting of 60 atoms at the measured translational temperature would have sufficient internal energy to make single photon ionization possible. Furthermore, this gives a lower boundary for the thermal stability of C_{60} and C_{70} clusters.

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