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SPECTROMETRIC CHARACTERIZATION OF PURIFIED C60 AND C70

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ABSTRACT

C_{60} and C_{70} were synthesized and purified according to published procedures. Both nanosecond and picosecond laser desorption from coated substrates gave copious positive and negative ions. Mass spectra (TOF and FTMS) with excellent signal to noise, showing only the C_{60} and C_{70} mass peaks, have been observed. Well-resolved isotopic structure was seen in the FTMS spectra in agreement with the natural abundance of carbon. Laser desorption and multiphoton ionization/photodissociation of the neutral species, as well as electronic absorption, FTIR, and fluorescence spectra, have been obtained.

INTRODUCTION

Clusters of carbon have been studied extensively over the past decade. The discovery that the high-mass, even clusters of carbon are stable was made by Rohlfing et al. in 1984.[1] Kroto et al.[2] suggested that the very stable C_{60}, produced by laser vaporization of graphite, has the icosahedral "soccerball" structure and gave it the name of 'Buckminsterfullerene.' Since that time, there have been numerous publications on the cluster species observed in jet expansions. Recently, a simple method of synthesis [3,4] for bulk quantities of C_{60} and higher fullerenes has been described. Separation of C_{60} from condensed graphite 'smoke' [5,6] has stimulated a renewed interest in the physicochemical properties of this unusual material.

In this paper, we describe some recent experiments involving the production, separation, and various methods of characterization of C_{60} and C_{70}. These methods include laser desorption mass spectroscopy [both Fourier transform mass spectrometry (FTMS) and time of flight (TOF)], photodissociation of laser-desorbed neutrals, and fluorescence spectroscopy of solutions of C_{60}. Other measurements performed in our laboratory, such as UV-visible absorption spectroscopy and FTIR of thin films of C_{60}, will not be discussed here. In general, the results confirm those obtained by others [3-5,7,8].

EXPERIMENTAL

The synthesis and separation of milligram amounts of C_{60} and C_{70} were carried out according to published accounts.[3,4,6,9] Graphite rods were resistively heated in ~100-200 Torr of He in a reaction vessel that consisted of a surplus water-cooled Ti sublimation pump. The deposit formed on the stainless steel shim stock surrounding the graphite rods was removed by scraping with a razor blade. Later, the apparatus was modified with the addition of a translatable graphite rod and the use of a contact arc.[8,10] C_{60} and the higher fullerenes were extracted with hot toluene, giving deep red solutions that were centrifuged and placed on a chromatographic column of neutral alumina. Hexane was utilized as the column eluent. The first fraction to come off the column was C_{60}, as evidenced by UV absorption and mass spectroscopy (see below). The C_{70} fraction eluted somewhat later.

The laser desorption/time-of-flight apparatus has been discussed in detail before,[11] necessitating only a brief discussion here. The mass spectrometer is established by a sample surface, an acceleration field, and a field-free region with an ion detector at the end of the flight path (see Fig. 1). The TOF mass spectrometer can be operated in two regimes. First, for measuring the mass spectrum of laser desorbed ions, the sample is held at 8 kV and the grids are held at ground. Second, for the postionization/photodissociation experiments, a two-step acceleration is used with the sample at 8 kV, the first grid at 7.6 kV, and the second grid at ground. In practice, the extraction potentials in the ion source can be adjusted to optimize resolution for the ions formed by photoionization of desorbed neutral molecules. The overall flight path length is 120 cm with acceleration distances of 4 mm for each of the two acceleration regions. The ions thus accelerated are detected using a dual-channelplate detector with a modest postacceleration potential. Data are recorded in a transient recorder with a maximum time resolution of 5 ns. Further processing of the data is accomplished in a PC-based software system. The typical operating vacuum is ~ 2 x 10^{-9} Torr. The resolving power ($m/\Delta m$) of the apparatus is approximately 400 (FWHM) using a 5 ns laser pulse, while a < 100 psec, 266 nm laser pulse yields a resolution exceeding 1500 with the same apparatus.

The two lasers utilized in this work are a XeCl excimer laser for the desorption step and a frequency-doubled Coumarin 540A dye laser pumped by a second XeCl excimer laser for the ionization/photodissociation step. The respective wavelengths of desorption and ionization are 308 nm and ~ 270 nm. The lasers are independently triggered, allowing their relative timing to be adjusted. They are operated at a 1 to 50-Hz repetition rate with laser pulse widths of approximately 20 ns. An iris is used to pick out the central portion of the beam, and a series of neutral density filters is used to regulate the beam intensity. The desorption laser is obliquely incident on the sample, and its energy is typically less than 0.5 mJ/pulse with a spot size of approximately 0.2 mm by 2 mm. The ionization/photodissociation laser energy is typically ~ 1 mJ/pulse with a beam diameter of approximately 2 mm. Focusing is accomplished with 300 mm spherical lenses for both the desorption and ionization lasers. The postionization/photodissociation laser beam is typically placed from 0.5 to 3 mm in front of the sample surface.

The laser desorption/Fourier transform mass spectrometer was constructed in-house and includes a superconducting solenoid (~ 7 Tesla), a heatable and coolable sample introduction stage, a LiF laser port, a 2"x 2"x 3" ICR cell for storing and detecting the laser desorbed ions, an Ionspec data collection system, and a 1500 l/sec cryopump. The base pressure is ~ 10^{-9} Torr. An electron beam that passes through the cell helps in optimization of the FTMS parameters and allows for electron ionization of laser desorbed neutrals. Additionally, this apparatus includes an FTIR spectrometer to monitor the surface of the sample before and subsequent to laser desorption. For the experiments described here, the C_{60} and C_{70} species were laser desorbed/ionized into the FTMS cell with a 20 ns, 308 nm XeCl excimer laser beam.

Laser Desorption/Time-of-Flight Mass Spectrometer
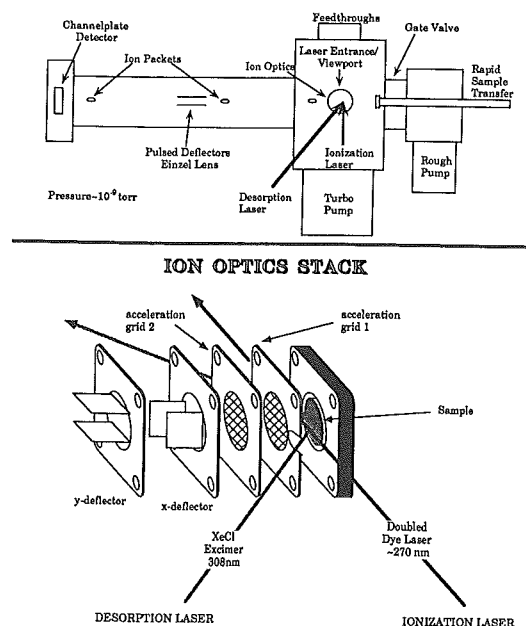

ION OPTICS STACK

Figure 1
Schematic diagram of the LDTOF mass spectrometer, showing the overall apparatus (top) and a close-in view of the ion optics (bottom).

Solutions of C_{60} or C_{70} were placed onto a copper substrate and after solvent evaporation, inserted into the vacuum chamber prior to laser desorption.

RESULTS AND DISCUSSION

Shown in Fig. 2 is a composite of laser desorption TOF negative ion mass spectra of different fractions obtained in the separation of C_{60} from C_{70}. The lower panel (a) is a mass spectrum of the evaporated toluene raw extract showing a number of high mass peaks, with C_{60} as the most abundant ion. The lower masses are C_2, C_3, C_4, etc.. The higher masses consist of C_{60}, C_{70}, C_{78}, C_{84}, and some still higher mass fullerenes. Panel (b) is a negative ion mass spectrum of the first fraction to come off the chromatographic column with C_{60} as the only species detected. A mass spectrum of a sample from the second fraction is shown in panel (c). It is comprised of a mixture of C_{60} and C_{70}. The third fraction off the column [panel (d)] consists solely of C_{70}.

The FTMS laser desorption spectrum of C_{60} is shown in Fig. 3. This is a positive ion spectrum whose resolving power of ~ 8000 is limited by the transient length. The isotopic abundances of the $^{12}C_{60}^+$, $^{12}C_{59}^{13}C^+$, etc. species are within ~ 2-3% of the theoretical values, assuming an isotopic abundance for $^{13}C/^{12}C$ of ~ 1.108/98.892.

The laser desorption TOF apparatus has also been utilized for the study of the photodissociation (PD) of neutral C_{60} and C_{70}. Neutral molecules are

Figure 3 LDFTMS of the raw toluene extract. This positive ion spectrum of C_{60} and C_{70} shows the isotopic abundances within 2-3% of their theoretical values.
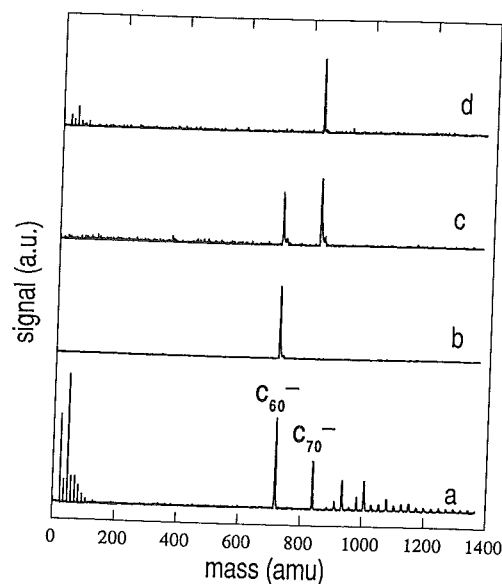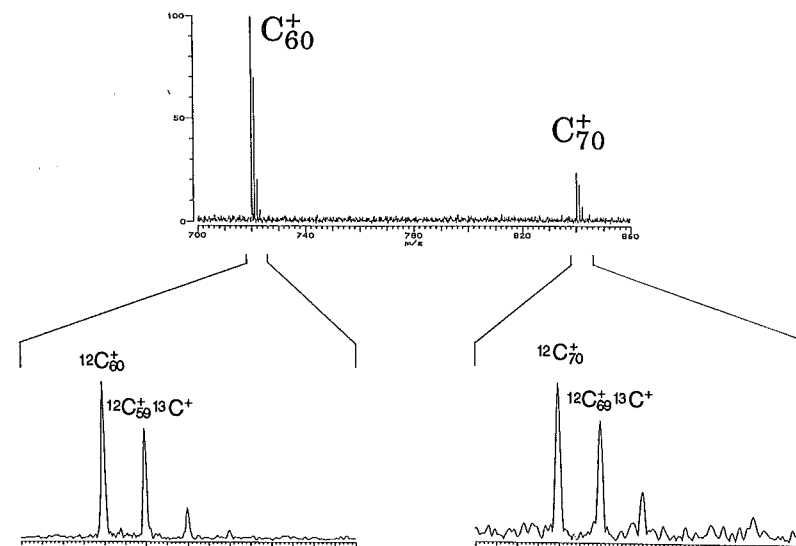

Figure 2 LDTOF negative ion mass spectra of raw toluene extract (a), first fraction off the chromatographic columnm (b), second fraction (c), and third fraction (d). C_{60} predominates in the first fraction, C_{70} in the third fraction, with a mixture in the middle fraction.

laser desorbed from pure C_{60} and C_{70}, and these molecules are photodissociated and ionized by a second laser as already described. Typical PD spectra of C_{70} are shown in Fig. 4. The top spectrum is for very low laser fluence (≤ 1 mJ/cm^2), resulting in minimal fragmentation. The bottom panel is for much higher laser fluence (≥ 10 mJ/cm^2) and shows extensive fragmentation. An intermediate regime is shown in the middle panel. We have demonstrated that fragmentation occurs only during the ionization step and is not a result of the desorption step. Figure 5 presents a montage of PD spectra for C_{60} at a variety of laser intensities with extensive fragmentation being evident at the higher laser fluences.

A large database on C_{60} photodissociation has been generated in the last few years,[7,12-15] but a much more limited data set exists for PD of neutral C_{60} and C_{70} molecules. C_{60}^+ photofragmentation is known to be dominated by loss of fragments containing an even number of carbon atoms, mainly C_2.[7] The same conclusion can now be drawn for PD of neutral C_{60} and C_{70}, as evidenced in Figs. 4 and 5. It must be recognized, however, that the sequence for fragmentation/ionization is by no means clear at this time. Whether the C_{60} species first photodissociates and then ionizes, or whether ionization precedes photodissociation, is still an open but interesting question.
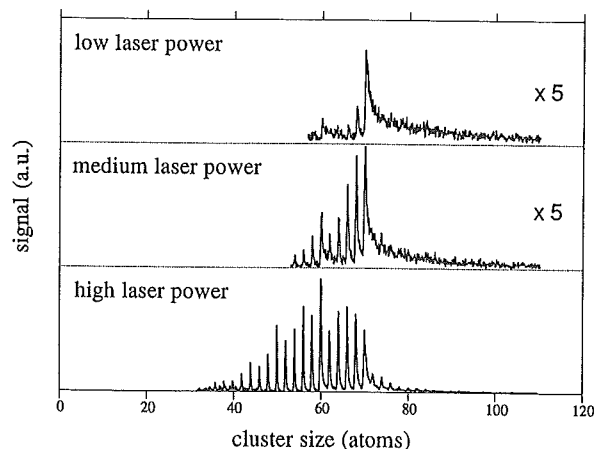
Figure 4 LDTOF photodissociation spectra of C_{70}, illustrating the effect of increasing laser intensity for ionization.
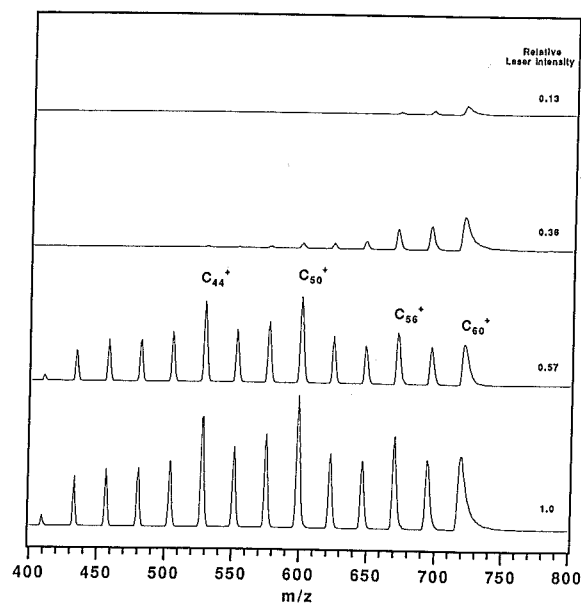

Figure 5 LDTOF photodissociation spectra of C_{60}.

Figure 6 shows the fluorescence spectra of C_{60} and C_{70} in hexane at ambient temperatures using 250 nm excitation. The concentrations of C_{60} and C_{70} are each about 10^{-7} M. Fluorescence spectra were obtained in 1 cm cuvettes using a Perkin-Elmer MPF-2A fluorimeter interfaced to an IBM PC. The emission was measured 90° to the excitation beam. Based on a naphthalene standard, the fluorescence quantum yield of C_{60} is about 0.01, while that of C_{70} is about 0.0025. No emission was observed at wavelengths > 460 nm under the conditions of our measurement. The fluorescence excitation spectrum of C_{60} shows that excitation of the 260 nm band in C_{60} results in the observed emission at 283 nm, while that of C_{70} shows that the 280 nm shoulder in C_{70} results in the emission observed at 325 nm. Since the fluorescence quantum yields of C_{60} and C_{70} are low, we cannot completely preclude the possibility that the observed emission is due to very low levels of highly fluorescent impurities. Nevertheless, if we assign these emission features to the $S_0 \leftarrow S_1$ transition in C_{60} and C_{70}, the S_1 energy of C_{60} in hexane is 4.39 eV while that of C_{70} is 3.82 eV.
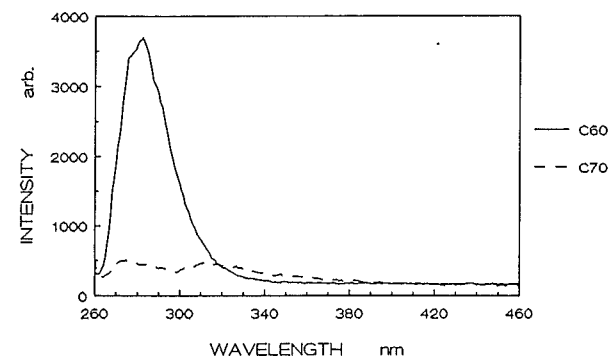
Figure 6 Fluorescence spectra of C_{60} and C70 in hexane, with excitation at 250 nm.

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POSSIBLE ISOMERS AND ELECTRONIC STRUCTURE OF $C_{60}H_{36}$

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ABSTRACT

Newly developed empirical hydrocarbon potentials and self-consistent first-principles local density functional methods are used to investigate possible isomers and the electronic structure of $C_{60}H_{36}$. Within the high symmetry T_h structure conjectured by the groups at Rice University there are two inequivalent sets of hydrogen atoms containing twelve and twenty-four atoms respectively. Binding each set either inside or outside of the C_{60} cage leads to four isomers of $C_{60}H_{36}$ with inequivalent strain energies. Although we find that placing twelve hydrogens inside the cage can lead to a metastable structure, our calculated total energies suggest that the isomer with all the hydrogens on the outside of the cage is the energetically most stable.

Recently C_{60} has been isolated in macroscopic quantities in several laboratories[1-6]. Carbon-13 NMR of pure C_{60} disolved in hexane shows that this molecule has only one symmetry-inequivalent atom[2-5] and therefore can only have the proposed icosahedral (I_h) structure.[7] Quite recently Haufler et al.[6] have hydrogenated C_{60} using Birch reduction to yield $C_{60}H_{36}$. $C_{60}H_{36}$ is perhaps only the first in a series of new molecules and cluster materials that will be synthesized starting from C_{60}. We have chosen to study the geometry and electronic structure of this new molecule using empirical potentials[8] and local density functional (LDF) calculations[9].

A conformation of $C_{60}H_{36}$ with the twelve remaining double bonds as far apart as possible on the surface yields one of five equivalent T_h structures for the molecule. In all five structures, the double bonds, four at a time, are bisected by three mutually orthogonal planes passing through the center of the molecule, and each double bond is now associated with a different pentagon of the original buckminsterfullerene (Bf). The remaining 36 saturated carbon sites are divided by the group into a set of 12 and a set of 24 CH groups. The smaller, symmetry-equivalent set of 12 CH groups lie in the planes that bisect the 12 double bonds and are second nearest neighbors to double-bond carbon atoms. Each carbon atom of the larger, symmetry-equivalent set of 24 CH groups is a nearest neighbor to carbon atoms involved in two different double bonds. Therefore, this second set of carbons cannot exchange their hydrogen atoms with the double-bond carbon atoms to form another of the original five equivalent T_h structures considered here.

If this $C_{60}H_{36}$ structure is made from a molecular modeling kit using flexible tubes of roughly equal length to form nearest neighbor bonds, then the bonds connecting saturated carbon atoms bend inward while the bonds connecting saturated and unsaturated carbon atoms are quite planar. Because the inward curvature of this model for these saturated C-C bonds is as great as the outward curvature of a similarly constructed Bf molecule, we were led to consider not only the structure depicted in Figure 1 with all the hydrogens attached to the exterior surface of the C_{60} cage but also whether some of the hydrogen atoms might prefer to be bonded to the interior surface of this cage. Interior bonding, even