

LASER DEPOSITION, VIBRATIONAL SPECTROSCOPY, NMR SPECTROSCOPY AND STM IMAGING OF C₆₀ AND C₇₀

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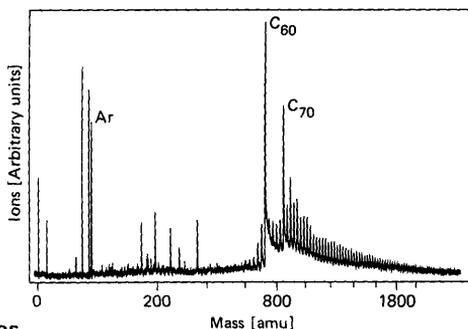
ABSTRACT

We recently demonstrated that C₆₀ and C₇₀, as well as other fullerenes, can be deposited and accumulated on surfaces using laser ablation of graphite in an inert gas atmosphere. After learning of the work of Krätschmer et al. indicating the presence of C₆₀ in carbon soot, we showed that samples consisting almost exclusively of C₆₀ and C₇₀ can be sublimed from such soot. Vibrational Raman spectra of C₆₀ and C₇₀ were obtained from these samples. The C₆₀ spectrum is consistent with the calculated spectrum of Buckminsterfullerene, and the strongest three lines can be assigned on the basis of frequency and polarization. The NMR spectrum of dissolved C₆₀ was then obtained, and found to consist of a single resonance, establishing the icosahedral symmetry of this molecule. STM images of the C₆₀ molecules on a Au(111) crystal face show that these clusters form hexagonal arrays with an intercluster spacing of 11.0 Å and are mobile at ambient temperature. Distinctly taller species evident in the arrays are believed to be C₇₀ clusters. Vibrational Raman and infrared spectra have also been obtained for separated C₆₀ and C₇₀.

Five years have passed since Kroto, Heath, O'Brien, Curl and Smalley, inspired by the work of R. Buckminster Fuller, realized that there was a most elegant solution to the problem of explaining the extraordinary inertness and stability observed for 60 atom pure-carbon clusters¹. The solution proposed was the beautifully symmetric arrangement familiar as the soccerball pattern - a truncated icosahedron consisting of 12 pentagons and 20 hexagons. As Kroto would write: "This structure necessitated the throwing of all caution to the wind ... and it was proposed immediately; after all, it was surely too perfect a solution to be wrong."² The experimental evidence required to substantiate this intuitive leap proved difficult to obtain, however. While many ingenious experiments indirectly supported the picture that not only C₆₀ but *all* of the observed carbon clusters with an even number of atoms ($n \geq 24$) can exist in the form of 2-d closed nets of 12 pentagons and ($n/2 - 10$) hexagons³, doubts persisted, and some investigators suggested alternative structures for these clusters^{4, 5}. Over the last few months the gap between intuition and experiment has been closing rapidly. With the discovery that macroscopic samples of fullerenes can be produced and accumulated⁶⁻⁸, it has become possible to rapidly obtain a wealth of new information about them^{6, 7, 9-13}. In this paper we describe the course of our work on carbon cluster deposition, vibrational spectroscopy, NMR spectroscopy, and scanning tunnelling microscopy during this period of time.

Early this year, we began an effort to develop a new approach to studying carbon clusters by trying to deposit them on surfaces using laser ablation of graphite under a static inert gas atmosphere⁸. A highly sensitive surface analytical mass spectrometer¹⁴ was used to analyze the deposited material. The observed mass spectrum, shown in Figure 1, showed a broad range of fullerenes, with C₆₀ and C₇₀ particularly prominent.

Figure 1 Time-of-flight mass-spectrum of laser deposited carbon clusters, taken using the laser desorption jet-cooling detection apparatus. The horizontal axis is linear in time-of-flight and the corresponding (nonlinear) mass scale is indicated.



An isotope scrambling experiment was carried out which demonstrated conclusively that the clusters were present as stable species in the deposit, ruling out the possibility that they were produced only in the desorption plume in the mass spectrometer¹⁴. Encouraged, we began working to accumulate and refine the clusters. At about this time we became aware of the work of Krätschmer, Fostiropoulos, and Huffman, who reported UV-Vis and IR spectra taken of carbon dust deposits produced by resistively heating graphite under 100 Torr of He⁶. They had found four sharp, strong infrared absorption lines with characteristics which led them to believe that their sample contained significant quantities of Buckminsterfullerene (~1%), and that they had observed its infrared spectrum. Using our surface mass spectrometer, we were subsequently able to directly verify that carbon deposits made as described by Krätschmer et al., indeed contain a significant fraction of C₆₀¹⁵. This result strongly supported the conclusion that the sharp lines seen in the carbon dust IR spectrum were due to this species. Adopting the method of Krätschmer et al. for producing carbon dust, we found that fractional sublimation from the raw dust could be used to produce solid films consisting almost entirely of mixtures of C₆₀ and C₇₀. Compositions of the deposited films were determined using the surface analytical mass spectrometer, and vibrational Raman spectra of both C₆₀ and C₇₀ were obtained⁹, as shown in Figure 2.

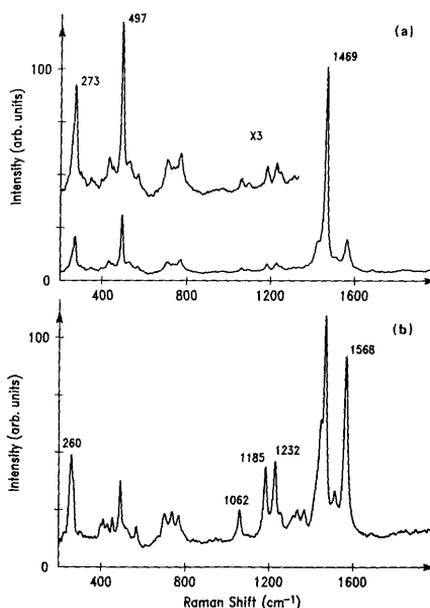
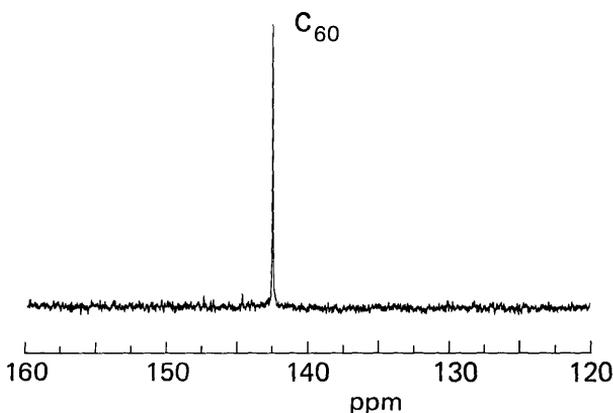


Figure 2 Unpolarized Raman spectra of purified films of C₆₀ and C₇₀ on suprasil substrates with a and b corresponding to films with C₆₀/C₇₀ ion ratios of 12:1 and 2:1 respectively. The labelled lines in spectra a and b are assigned to C₆₀ and C₇₀, respectively. In both spectra the intensity of the line at 1469 cm⁻¹ is normalized to 100.

The three strongest C_{60} lines can be assigned based on their frequencies and depolarization ratios. The lowest frequency line at 273 cm^{-1} agrees very well with theoretical predictions¹⁶⁻²¹ for the Buckminsterfullerene (Bf) H_g squashing mode ($273 \pm 10\text{ cm}^{-1}$). The strong lines at 497 and 1469 cm^{-1} are highly polarized, suggesting that they are due to totally symmetric vibrational modes. Bf has only two such modes, the breathing mode and a "pentagonal pinch" mode, with the hexagons and pentagons expanding and contracting out of phase. The calculated frequencies for these modes are in reasonable agreement with those of the two strongly polarized lines.

A crucial prediction of the icosahedrally symmetric Buckminsterfullerene model for C_{60} is that every atom is chemically equivalent. This prediction can be directly tested using NMR spectroscopy. By dissolving our (at that time) minute samples of refined C_{60}/C_{70} in various solvents, we were able to obtain the NMR spectrum of C_{60} ¹⁰ shown in Figure 3. The C_{60} NMR spectrum consists of a single sharp resonance.

Figure 3 Aromatic region of the ^{13}C NMR spectrum of $\sim 200\text{ }\mu\text{g}$ of C_{60} in CCl_4 , without ^1H decoupling, obtained with a Bruker AM-500 NMR spectrometer operating at 125.7 MHz at 25°C , with 13,000 scans over a 14 kHz bandwidth digitized into a 64 kword dataset; chemical shift referenced to CCl_4 at 96.1 ppm . The resonance at 142.5 ppm is assigned to C_{60} .

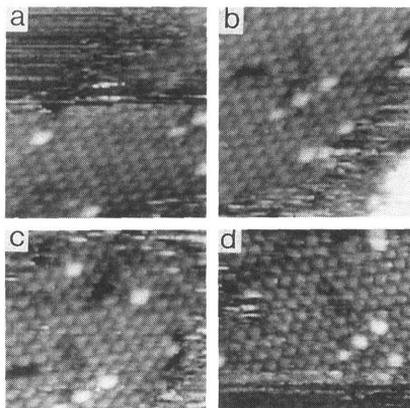


This result, which was also obtained by the Sussex group of Kroto¹¹, confirms the chemical equivalence of all 60 carbon atoms in the cluster and establishes its icosahedral symmetry. The Sussex group was also able to obtain the five line spectrum of C_{70} . Subsequent NMR work carried out at IBM has produced some very interesting results on both solutions and solid-state samples of fullerenes²².

While it will be very interesting to utilize powerful structural probes such as x-ray and electron diffraction to study these species, and some steps in this direction have already been taken⁷, these techniques require fairly large amounts of pure material with a high degree of long range order. On the other hand, Scanning Tunneling Microscopy (STM)²³ can provide the capability to image molecules^{24, 25} even with a mixture of species on the surface and despite long range disorder. In addition, STM studies can provide information about the size, local ordering, and mobility of species on surfaces. We have used an UHV STM to obtain images of C_{60} on a Au(111) crystal at a room temperature²⁶. Figure 4 shows a sequence of images

showing numerous similar dots which we are confident are images of individual Buckminsterfullerenes.

Figure 4 Sequence of four STM images taken several minutes apart showing ordered arrangements of C_{60} clusters on a Au(111) surface. The brighter dots are believed to be due to C_{70} clusters. Bilinear interpolation has been used in rendering the raw data. The fast scan width (horizontal axis) is about 150 Å and the slow scan width is about the same, but varies due to piezoelectric creep following translation of the tip to a new area.



The clusters tend to order in hexagonal arrays. From this and similar images, the cluster spacing has been determined to be 11.0 ± 0.5 Å using the Au(111) atomic spacing as a calibration²⁷. This is in reasonable agreement with the sum of the 7.1 Å diameter calculated for Buckminsterfullerene^{28, 29} and the 3.35 Å graphite layer separation. The orientation of the straight rows of clusters is close to the orientation of the Au atomic rows. Looking more closely, one notices that a subset of the ordered dots is distinctly brighter, corresponding to a greater apparent height. The peak-to-vacancy corrugation is about 4 Å for the C_{60} peaks, while the taller features appear to be about 2 Å higher. The corrugation in close packed regions is about 1.5 Å. The same ordered arrays and two heights of peaks are observed at other bias voltages of either polarity. The taller features appear quite stable, even at the island edges. The most likely explanation for these brighter dots is that they are C_{70} clusters. The elongation of the C_{70} molecule, together with the reduction in the gap between occupied and unoccupied electronic states for C_{70} relative to C_{60} , as observed experimentally³⁰, could easily account for the apparent height increase of the C_{70} clusters in the STM images. The packing of the clusters into ordered arrays seems to be essential for their observation on this surface. When they are not in such arrays the clusters are apparently highly mobile, which gives rise to image noise in areas outside the close packed islands. The motion could be either thermal or STM induced³¹, or both. Motion of clusters within the arrays can be seen by comparing frames *b* and *d*, for example, where vacancies above the line of three bright dots fill in, and the bright dot below and to the right moves toward the line.

We have not yet observed internal structure for individual Fullerenes. NMR spectroscopy of solid state samples indicates that these molecules rotate rapidly at ambient temperature^{22, 32}, and it is possible that this motion blurs the atomic detail. This difficulty might be overcome by reducing the temperature or by using a more reactive substrate where strong, localized metal-C bonding could hinder such rotations²⁵.

More recently, the use of arc methods for carbon cluster production, as pioneered by Krätschmer and Huffman^{33, 34} and recently adapted specifically for fullerene production by Hauffler et al.¹³, has allowed large (gram) quantities of C_{60} and C_{70} to be produced. Chemical separation has been demonstrated¹², and experiments can now be carried out on pure samples of these molecules. We chromatographically separated C_{60} and C_{70} on a neutral alumina column, with elution by hexane/benzene mixtures, and vacuum sublimed the pure species to give thin film samples on suprasil or KBr windows. Vibrational Raman and transmission infrared studies have been carried out on these samples. The Raman spectra obtained for purified C_{60} and C_{70} are shown in Figures 5 and 6 respectively.

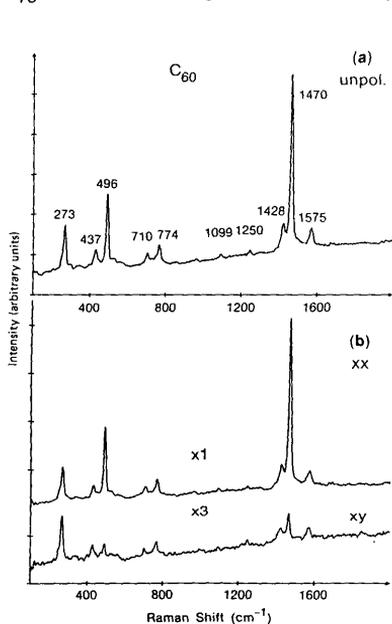


Figure 5 Raman spectra of a film of purified C_{60} on a suprasil substrate. a) unpolarized, and b) polarized.

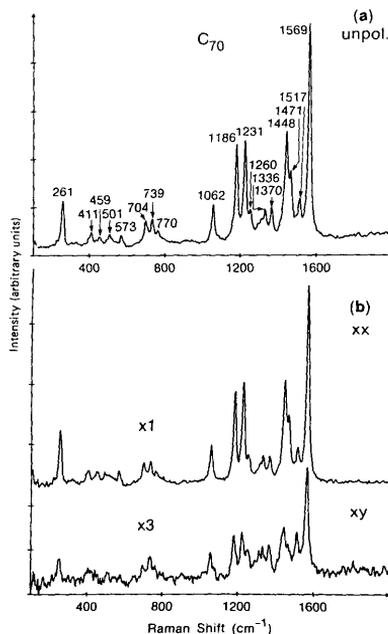
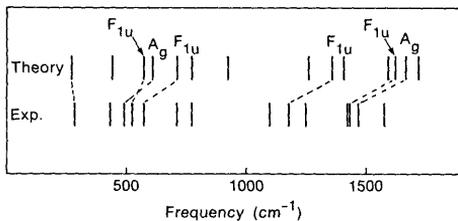


Figure 6 Raman spectra of a film of purified C_{70} on a suprasil substrate. a) unpolarized, and b) polarized.

The C_{60} spectrum shows eight clear lines at 273, 437, 496, 710, 774, 1428, 1470 and 1575 cm^{-1} . Two weaker lines at 1099 and 1250 cm^{-1} are tentatively assigned to C_{60} as well. The high degree of polarization of the lines at 496 and 1470 cm^{-1} and the depolarization of the line at 273 cm^{-1} are apparent from the polarized spectra shown in Figure 5b. The numerous Raman lines observed for purified C_{70} are labelled in Fig. 6a, while 6b shows the polarized spectra for this molecule. FTIR spectra obtained in transmission for

purified C_{60} and C_{70} films on KBr windows are shown in Figs. 7a and 7b. The data were taken in vacuum, and were referenced against spectra obtained using windows that had undergone identical preparation steps, but with the fullerene sample omitted. For C_{60} , the frequencies of the four strong lines (labelled in Fig. 7a) are in agreement with those reported earlier for this molecule by Krätschmer et al.^{6, 7} The infrared lines attributed to C_{70} are labelled in Fig. 7b. Infrared data for the separated species have also been obtained by Cox et al.³⁵ For C_{60} the observed vibrational frequencies (from both Raman and infrared spectroscopy) can be compared to the spectrum calculated for Buckminsterfullerene. Such a comparison is shown in Fig. 8, where the theoretical values are those of Stanton and Newton¹⁹. The dashed lines indicate the assignments of the IR active modes, the totally symmetric A_g modes, and the lowest frequency mode (H_g squashing mode) at 273 cm^{-1} . The spectra are in striking qualitative agreement. For the low frequency modes the calculated frequencies are close to correct, while for the higher frequency modes the systematic overestimate of the frequencies is about what is expected from the calculational method employed¹⁹.



These new results have narrowed the gap between inspiration and experimental fact to the point where we can be quite certain that the immensely appealing notion of pure carbon molecular soccerballs is realized in nature. The effort to further understand their properties, as well as those of the other stable fullerenes, and their derivatives will surely be an interesting and fruitful occupation for some time to come.

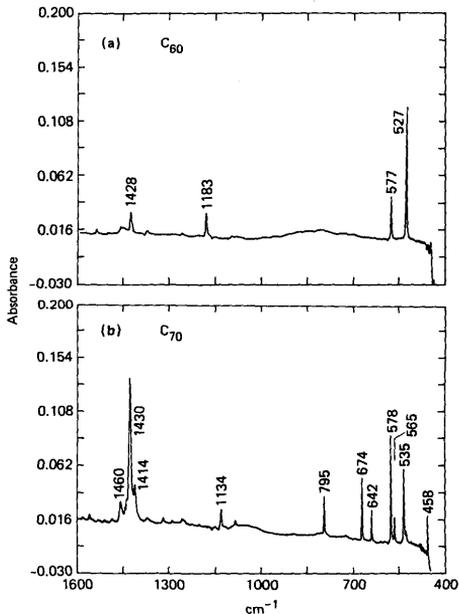


Figure 7 Absorbance FTIR spectra of films of purified a) C_{60} , and b) C_{70} on KBr substrates. Absorbance values are for samples with undetermined thicknesses.

Figure 8 Frequencies of the Raman active A_g and (unlabeled) H_g and IR active F_{1u} modes calculated for Bf in Ref. 19 (upper) with the observed Raman and infrared frequencies for C_{60} (lower). Dashed lines indicate assignments for the IR lines, the highly polarized Raman lines at 496 and 1470 cm^{-1} , and the depolarized Raman line at 273 cm^{-1} .

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