The vibrational Raman spectra
of purified solid films of C_{60} and C_{70}

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A technique to produce samples consisting primarily of C_{60} and C_{70} by fractional sublimation of carbon soot was found and used to produce solid films of these molecules. Film compositions were determined using a surface analytical mass spectrometric technique. Vibrational Raman spectra of the purified films were measured and vibrational lines of both C_{60} and C_{70} are identified. A C_{60} line at 273 cm^{-1} is observed, in agreement with theoretical predictions for the lowest frequency H_g "squashing" mode of Buckminsterfullerene. The two strongest C_{60} lines, found at 1469 and 497 cm^{-1}, can consistently be assigned to the two totally symmetric A_g modes on the basis of their frequencies and measured depolarization ratios.

1. Introduction

The notion of a 60-atom, pure carbon molecule with the structure of a soccerball – a spherical shell made up of 20 hexagons and 12 pentagons arranged as a truncated icosahedron – was conceived of by several authors as a purely theoretical possibility as early as 1970 (for this history, see ref. [1]). It was independently hit upon by Kroto et al. [2] in their effort to understand the extraordinary abundance and inertness of C_{60}, observed in pioneering carbon cluster beam experiments carried out at Exxon [3] and Rice [2]. Buckminsterfullerene, as the molecule was dubbed, captured the imaginations of theorists and experimentalists alike, leading to intense efforts to understand the properties of such a molecule. While theorists have produced numerous studies of the electronic, vibrational, and rotational properties of Buckminsterfullerene [4–9] [#1], experimentalists have had a more difficult time trying to measure these properties during the brief span of time between the creation of these clusters in a laser-produced carbon plasma and the end of their flight through a molecular beam machine. Until recently the only spectroscopic feature attributed to C_{60} was a single line at

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[#1] Ref. [5] contains an extensive set of references to theoretical work up to about 1989.

386 nm measured by Heath et al. [10].

This situation is now changing rapidly. In a recent Letter, Krätschmer, Fostiropoulos and Huffman reported UV–VIS and IR spectra taken of carbon dust deposits produced by resistively heating graphite under 100 Torr of He [11]. At that pressure (but not at 10 Torr) four sharp lines appeared on top of broad absorption features. The number, frequencies, intensities and isotope shifts of these lines led the authors to believe that their sample contained significant quantities of Buckminsterfullerene ($\approx 1\%$), and that they had observed its infrared spectrum.

At about the same time, we developed an alternative method for depositing carbon clusters on surfaces using laser ablation of graphite under a static inert gas atmosphere [12]. We used a surface analytical mass spectrometric technique to analyze the deposited material. In our apparatus, a laser desorption jet-cooling mass spectrometer, species present on a surface are brought into the gas phase by laser desorption and are entrained in a supersonic Ar expansion. This cools and transports the sample material into a high vacuum region where it is laser ionized between the acceleration plates of a time-of-flight mass spectrometer. The apparatus has been fully described in a recent publication [13]. Under the conditions we use, this technique samples carbon clusters *already present on the surface* and does not

produce them in the desorption process. This has been demonstrated by carrying out an isotope scrambling experiment [12].

Using this surface analytical technique, we were also able to verify that soot deposits made as described by Krätschmer, Fostiropoulos and Huffman [11] indeed contain a significant fraction of C_{60} [14]. This result strongly supports their conclusion that the sharp lines seen in their carbon dust IR spectrum are indeed due to this species.

In this paper we report the production of purified solid films of C_{60} and C_{70} by fractional sublimation of carbon soot. Film compositions were determined using the mass spectrometric technique described above. Vibrational Raman spectra of these films were obtained and vibrational lines of both C_{60} and C_{70} are identified. A C_{60} line at 273 cm^{-1} is observed, in agreement with theoretical predictions for the lowest frequency H_g "squashing" mode of Buckminsterfullerene. The two strongest C_{60} lines, found at 1469 and 497 cm^{-1}, can consistently be assigned to the two totally symmetric A_g modes on the basis of their frequencies and measured depolarization ratios.

2. Sample preparation

Carbon dust produced by resistively heating 99.99% pure graphite bars under 100 Torr of He quenching gas, as described by Krätschmer et al. [11], was collected on a glass disc. The deposited material was scraped from the disc (in air), yielding a black powder. Approximately 20 mg of this crude material was loaded into a small stainless steel cell equipped with a 2 mm inner diameter nozzle, and this was placed in a vacuum chamber pumped to $\approx 10^{-5}$ Torr. In a preliminary run, the cell was heated to 460°C to bake out higher vapor pressure contaminants. Two more runs which we label by a and b were made, with the same soot sample in the cell. In these runs the cell was held at 500° and 600°C, respectively, for several minutes, with cooled suprasil slides placed ≈ 3 mm from the nozzle. In each case a 3 mm wide strip of tungsten foil was fixed to the slide, with its edge ≈ 1 mm off center. The films produced varied in color from light brown at the edges to dark brown in the center. Visible interference fringes near the periphery of the deposit indicated that the layer

of material was at least several microns thick.

The composition of the samples on the tungsten strips was determined using the surface mass spectrometer. A KrF laser (60 μJ in a 0.25 mm spot) was used for desorption, and ionization was accomplished with an ArF laser (200 μJ in a 1.5 mm spot). The mass spectra of the films from runs a and b are displayed in fig. 1. Spectrum a shows that sample a consists almost entirely of C_{60}. The observed C_{60}^+/C_{70}^+ peak ratio is 12. Small peaks of C_{58}^+, C_{56}^+ and C_{54}^+ also appear. Spectrum b is similar, except that the C_{60}^+/C_{70}^+ peak ratio is reduced to 2.1. Therefore sample b, produced at the higher cell temperature, has six times more C_{70} relative to C_{60} than sample a. The mysterious long tails to the high mass sides of both the C_{60} and C_{70} peaks are not yet understood, but they may be reaction products with air. The variation of the "tail signals" with ArF laser fluence suggests that these species are one-photon ionized and
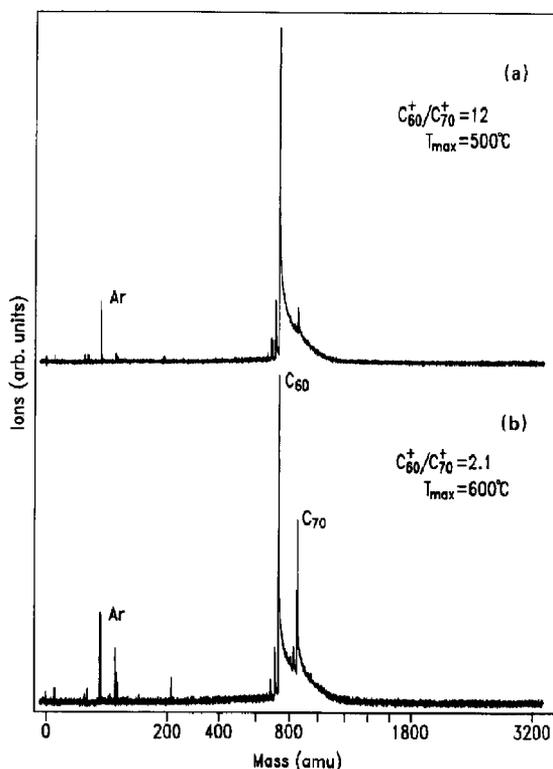

Fig. 1. Time-of-flight mass-spectra of purified films of C_{60} and C_{70} on tungsten foil, taken using the laser-desorption jet-cooling mass spectrometer. The horizontal axis is linear in time-of-flight and the corresponding (nonlinear) mass scale is indicated. The maximum sublimation cell temperatures, T_{max} are indicated.

are therefore detected with high sensitivity. It is possible that these species are responsible for the observed color of the samples, since C_{60} and C_{70} are not expected to have absorptions in the visible spectral region [15,16].

3. Raman spectra

Raman spectra of the samples on the suprasil slides were taken in air at room temperature with a micro-Raman spectrometer. The Ar ion laser beam (140 μW at 514 nm) was focused to a 13 μm diameter spot on the sample film. A back-scattering geometry was used, and the instrumental resolution was ≈ 9 cm^{-1}. Unpolarized spectra obtained from samples a and b are shown in figs. 2a and 2b, respectively. In

Table 1
Observed Raman line positions (± 2 cm^{-1}), intensities relative to the 1469 cm^{-1} C_{60} lines ($\equiv 100$), depolarization ratios ($\rho \equiv I_\perp / I_\parallel$), and assignments. I_a and I_b refer to intensities in spectra a and b in fig. 2

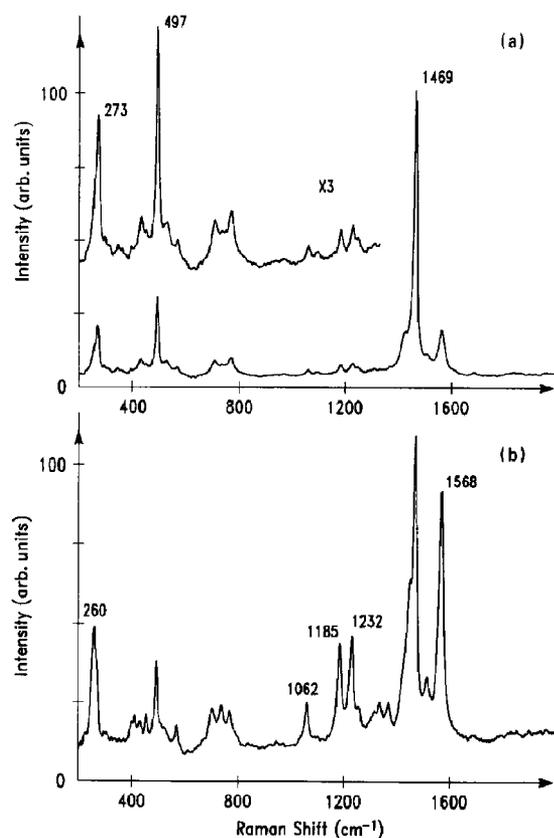| ν (cm^{-1})	I_a	I_b	$\rho(\pm 0.02)$	Assignments
260	7	34		C_{70}
273	17	17		C_{60}, H_g
413		9		
435	5	6		
457		9		
497	27	27	0.16	C_{60}, A_g
571	2	9		
705		13		
711	4			
739		13		
773	6	13		
1062	2	14	0.23	C_{70}
1185	4	34	0.19	C_{70}
1232	4	36	0.19	C_{70}
1336		11		
1370		11		
1430	13			
1448		32		
1469	100	100	0.11	C_{60}, A_g
1513	3	15		
1568	15	88	0.24	C_{70}

Fig. 2. Unpolarized Raman spectra of purified films of C_{60} and C_{70} on suprasil substrates with a and b corresponding to mass spectra a and b shown in fig. 1. The labelled lines in spectra a and b are assigned to C_{60} and C_{70}, respectively. In both spectra the intensity of the line at 1469 cm^{-1} is normalized to 100.

spectrum a four strong lines and numerous weaker ones are apparent. In spectrum b, obtained from the sample with the higher C_{70}/C_{60} ratio, additional bands appear and some of the features already recognizable in spectrum a increase markedly in intensity. The positions and intensities of the observed lines in these spectra are summarized in table 1. In both spectra the intensity of the line at 1469 cm^{-1} is normalized to 100. In going from spectrum a to b, some lines keep the same relative intensity, whereas others grow by roughly a factor 6. The three strongest lines in spectrum a, at 1469, 497 and 273 cm^{-1}, belong to the first group, and are therefore assigned to C_{60}. The lines indicated in spectrum b at 1568, 1232, 1185, 1062 and 260 cm^{-1} belong to the second group and are assigned to C_{70}. Note that the lowest C_{60} and C_{70} lines overlap. Additional weaker lines at 1513 and 571 cm^{-1} are also likely to be due to C_{70} vibrations. Between 700 and 800 cm^{-1} there is a feature which seems to include overlapping lines of both C_{60} and C_{70}. These lines cannot be deconvolved from these spectra. No lines were observed in the ranges 90–200 and 2000–2500 cm^{-1}.

For the strongest non-overlapped lines in spectrum b we measured the depolarization ratio $\rho \equiv I_\perp / I_\parallel$, where $I_\perp$ and $I_\parallel$ are the intensities of the Raman scattered light polarized perpendicular and parallel to the incident laser polarization. As seen from table 1 the two strongest C_{60} lines are highly polarized, strongly suggesting that they are associated with totally symmetric vibrational modes. We are assuming the C_{60} molecules are randomly oriented. In fact they may even be undergoing rotational motion in the solid films at 300 K.

At this point it is instructive to compare the observed Raman frequencies of C_{60} to the predicted frequencies of the 10 Raman-active modes obtained assuming the truncated icosahedral structure [5-8]. The lowest frequency vibration of this structure is the Raman active H_g "squashing" mode, an almost entirely radial distortion of the spherical structure into an ellipsoid. For this mode the various calculations are in striking agreement with each other, predicting a value of 273 ± 10 cm^{-1} [5-8]. Furthermore, this frequency is well below the next Raman active mode, which all calculations place above 400 cm^{-1}. In this picture, therefore, the observed C_{60} line at 273 cm^{-1} is due to the lowest frequency H_g mode. The polarization data suggest that the C_{60} lines observed at 1469 and 497 cm^{-1} may well be due to totally symmetric modes. In this case they would necessarily be the two A_g modes, corresponding to the double-bond stretching "pentagonal pinch" mode and the "breathing" mode [6]. The frequencies calculated for these modes are in the range 1627-1830 and 510-660 cm^{-1}, respectively. Considering that the calculated frequencies are likely to be too high [7], as also suggested by a comparison of calculated IR frequencies of Buckminsterfullerene to the experimental IR data [11], the observed Raman lines at 1469 and 497 cm^{-1} can consistently be assigned to the A_g modes.

For C_{70}, only one set of vibrational frequencies has been calculated, assuming a structure with D_{5h} symmetry [5]. Comparison of our data with this more complicated predicted spectrum has not yet been attempted.

4. Conclusions

We have shown that C_{60} and C_{70} can be purified by fractional sublimation of carbon soot. In this way purified films of a known composition were produced and Raman spectra of these films were taken. Vibrational frequencies of both C_{60} and C_{70} are found from these spectra. A strong low frequency mode of C_{60} is found at 273 cm^{-1}. The two strongest C_{60} Raman lines at 1469 and 497 cm^{-1} have very low depolarization ratios, and are likely to be due to totally symmetric modes. These data, together with the recently published IR spectrum of C_{60} [11], can be consistently interpreted in terms of the vibrational spectrum calculated for the truncated icosahedral structure of Buckminsterfullerene. With techniques to produce macroscopic amounts of purified C_{60} now available, many measurements to confirm this structure will undoubtedly soon be made. But it looks already as if the notion of a 60-atom, pure carbon molecule with the structure of a soccerball is realized in nature.

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