

$\text{cm}^{-1} \text{kbar}^{-1}$ observed for the E_{2g} in-plane Raman active mode of graphite and the $0.42 \text{ cm}^{-1} \text{kbar}^{-1}$ for the ring breathing mode of benzene which is predominantly due to C-C stretching. The normal coordinate analysis of Stanton and Newton [7] showed that the three highest frequency vibrations in C_{60} would have much larger C-C stretching content than that of the low-frequency vibration and their pressure dependences would be expected to be close to those of bands of similar origin in benzene and graphite.

Since the C_{60} spectrum reverted mainly to its original form after removal of the pressure, we do not have evidence for polymerization as occurs in benzene [10], or other reactions, but this may be possible at higher pressure and temperature and is being explored.

In summary the pressure dependences of C_{60} infrared active vibrations have been obtained and shows that there are two classes of vibrations in agreement with the normal coordinate calculations and that the assignment proposed in those calculations is correct.

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Extraction of giant fullerene molecules, and their subsequent solvation in low boiling point solvents

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Carbon soot produced by the graphite arc-synthesis method was solvated to varying extents in four different solvents, after previous removal of some fullerenes, particularly C_{60} and C_{70} , by toluene extraction. The solvents and weight percentages of soot solvated (in parentheses) are: xylenes (3.5), 1,3,5-trimethylbenzene (7.4), 1,2,4-trichlorobenzene (31.1), and 1-methylnaphthalene (22.5). If one accounts for the C_{2n} fullerene molecules, primarily C_{60} and C_{70} , extracted from virgin soot by toluene, roughly 37% of the virgin carbon soot can be solvated by the use of 1,2,4-trichlorobenzene. A rough value for the enthalpy of solvation difference is determined for C_{70} and C_{60} , by van 't Hoff analysis, to be $\Delta\Delta H = 5 \text{ kcal/mol}$. This method is suggested as a valuable indicator for the difference of enthalpies of binding of C_{2n} molecules to the soot matrix. After filtration and removal of the solvents used in the extractions, the residues can be redissolved in low-boiling-point solvents such as methylene chloride and toluene, two solvents which dissolved essentially none of the (previously) toluene-extracted starting material. This underscores the importance of the soot matrix in inhibiting solvation of C_{2n} fullerene molecules, and suggests that chromatographic separation of large fullerene molecules can be done with low-boiling-point solvents, and may therefore be feasible.

1. Introduction

Carbon soot, produced by the arc-synthesis method, invented by Krätschmer et al. [1], and extended in utility by Haufler et al. [2], is known to contain fullerene molecules of formula C_{2n} , with n as large as 300 [3]. The experimental techniques used to determine that very large-mass C_{2n} molecules exist have in common mass spectrometric detection^{#1}. The structures of such giant fullerenes are not yet known, although possible structures have been suggested [6]. There is now no doubt that C_{60} has the truncated icosahedral structure of buckminsterfullerene [1,7-11].

There have been recent reports of solvation of larger fullerenes with high-boiling-point solvents [12,13]. For example, Parker et al. [13] report that up to 44% of the soot produced is extractable. Our

^{#1} Ref. [3] - laser ablation, FT-ICR technique; ref. [4] - ion sputtering with TOF-MS technique; ref. [5] - laser desorption of raw soot, LMMS technique.

work addresses new aspects of solvation of giant fullerenes.

Several important questions arise: how much of the virgin soot is fullerenes? Toluene extraction of the initial soot removes only about 5-10% by weight, which consists mainly of C_{60} and C_{70} , with only traces of slightly heavier fullerenes. The nature of the binding of the C_{2n} molecules in the soot matrix is also of interest. For example, can we assign a number to the difference in enthalpies of binding of C_{60} and other C_{2n} molecules, such as C_{70} , by using different reflux temperatures? Also, is solvation an activated process, that is, is temperature the controlling factor? Perhaps most importantly, can a scheme be developed that will allow separation and isolation of each unique C_{2n} fullerene, in useful quantities? These issues are addressed herein.

2. Experimental

All extractions were done under an atmosphere of

dry nitrogen, and in the absence of ambient light, as a precautionary measure. Toluene, xylenes, 1,3,5-trimethylbenzene (TMB), and 1-methylnaphthalene were dried over CaCl_2 , and distilled prior to use. Reagent grade 1,2,4-trichlorobenzene (TCB), and spectrophotometric grade methylene chloride were used as received from the supplier, without further purification. Soot samples, depleted of C_{60} and C_{70} by prior toluene extraction, were obtained from Research Materials, Inc., or from Bell Labs, Murray Hill, NJ. A sample of virgin soot (i.e. soot not previously extracted with toluene) was obtained from Texas Fullerenes Inc., and was used as received.

A typical extraction procedure was as follows: 1 g of $\text{C}_{60}/\text{C}_{70}$ -depleted soot was placed in a two-necked, round-bottomed flask. The flask was purged with dry nitrogen and 200–300 ml of the selected solvent was added. The mixture was stirred magnetically while under reflux for a period of 24 h. The resulting mixture was filtered hot, through paper, and the filtrates (ranging in color from light pink to black) were kept from exposure to air and light as much as possible.

In the case where TMB was used as the extraction solvent, an extraction was also done using virgin soot in place of the $\text{C}_{60}/\text{C}_{70}$ -depleted soot: a flask was purged with nitrogen and charged with 185 ml of distilled mesitylene and 0.9103 g of virgin soot. The contents of the flask was maintained at the reflux temperature for 24 h, at which time the mixture was filtered while hot, a dark brown filtrate. The concentration of dissolved carbon in this filtrate was found to be 0.720 mg/ml.

For the purpose of measuring the extent of solvation of the soot in each of the extractions, the solvent was removed from a sample of each filtrate, in vacuo. The results and conditions are summarized in table 1. Interestingly, it was found that once the sol-

Table 1
Summary of yields in high temperature extractions

Solvent and reflux temperature	Solvent volume per 1.0 g soot (ml)	Concentration of extract (mg/ml)	% of "depleted" soot in solution
xylenes (139°C)	300	0.12	3.6
mesitylene (162°C)	300	0.25	7.4
1,2,4-TCB (214°C)	200	1.56	31.1
methylnaphthalene (240°C)	215	1.05	22.5

vent had been removed from a filtered sample from any of the extractions, most of the residue could be redissolved in low-boiling solvents such as methylene chloride and toluene. In the case of the mesitylene extracted residue, $\approx 90\%$ of the solid could be redissolved in methylene chloride and $\approx 90\%$ could be redissolved in toluene.

The materials obtained by solvation were characterized by static secondary ion mass spectrometry (SSIMS) using a system designed by Eldridge [14]. Targets were prepared for analysis by evaporation of about 50 microdroplets from a 50 μl pipette spread over about a square centimeter of a silicon wafer. Data were acquired with a total ion dose of about 10^{11} Ar ions/ cm^2 , i.e. far below the generally accepted damage dose of 10^{13} . Under such conditions the structural information is retained in the observed mass spectra.

The materials were also characterized by laser microprobe/Fourier transform mass spectrometry (LMMS) [15]. Samples of varying thicknesses were prepared by evaporating solution on glass slides, and mass spectra were obtained by laser desorption/ionization with a 266 nm laser pulse. Some differences were observed from the SSIMS spectra due to differences in the ionization efficiency and mass spectrometer performance. For example, LMMS provides less reliable quantitative information on relative intensities of C_{60} to C_{70} than SSIMS, but a higher mass distribution can be measured due to the higher mass range of FTMS.

3. Results and discussion

As shown in table 1, we observed that significant amounts of carbon were soluble in the high-boiling

organic solvents, even after prior extraction of the raw soot with toluene. In the most extreme case, we saw that more than 31% of the mass of the $\text{C}_{60}/\text{C}_{70}$ -depleted soot was soluble in TCB. Assuming a previous loss of $\approx 10\%$ due to the extraction of C_{60} and C_{70} with toluene, would predict a total soluble carbon content of at least 37% in the virgin soot. Owing to the insolubility of graphite under the extraction conditions of table 1, it is reasonable to assume that the entire amount of extractable material is due to fullerene cage molecules. This assumption is strongly supported by mass spectra data, *vide infra*.

We found that once we had removed the solvent from the extracts containing high molecular weight fullerenes, the residues were very soluble in more volatile solvents. The fact that 90% of the mesitylene-extracted residue readily dissolved in methylene chloride was surprising considering the low yield of soluble carbon observed when virgin soot is extracted with methylene chloride [16]^{#2}. Toluene was also effective in solvating the residues of higher fullerenes.

Fig. 1a shows the SSIMS spectrum of the C_{60} fraction chromatographically separated from higher fullerenes using the toluene extractable portion of the virgin soot. Note the intense appearance of the C_{60} at $m/z=720$ and the substructure on the low-mass side of this peak resulting from successive loss of $(\text{C}_2)_n$ with n ranging from 1 to 6.

The $(\text{C}_2)_n$ loss has also been observed using the LMMS, jet cooling laser mass spectrometry technique [17], and electron impact ionization [18]. Therefore, the lower mass peaks are probably due to fragmentation, and may not be present in the extract. The absence of the C_{70} peak at $m/z=840$ attests to the success of the chromatographic separation of C_{60} and C_{70} .

Fig. 1b is the SSIMS spectrum obtained from the toluene extract which served as the starting solution for the chromatographic separation. The $\text{C}_{70}/\text{C}_{60}$ ratio was found to be in good agreement with the number ratio found by chromatography indicating nearly identical ionization probabilities for these fullerenes. This has also been observed by Ajie et al. [18]. For

^{#2} A 24 h reflux with methylene chloride yielded 3.3 wt% soluble carbon.

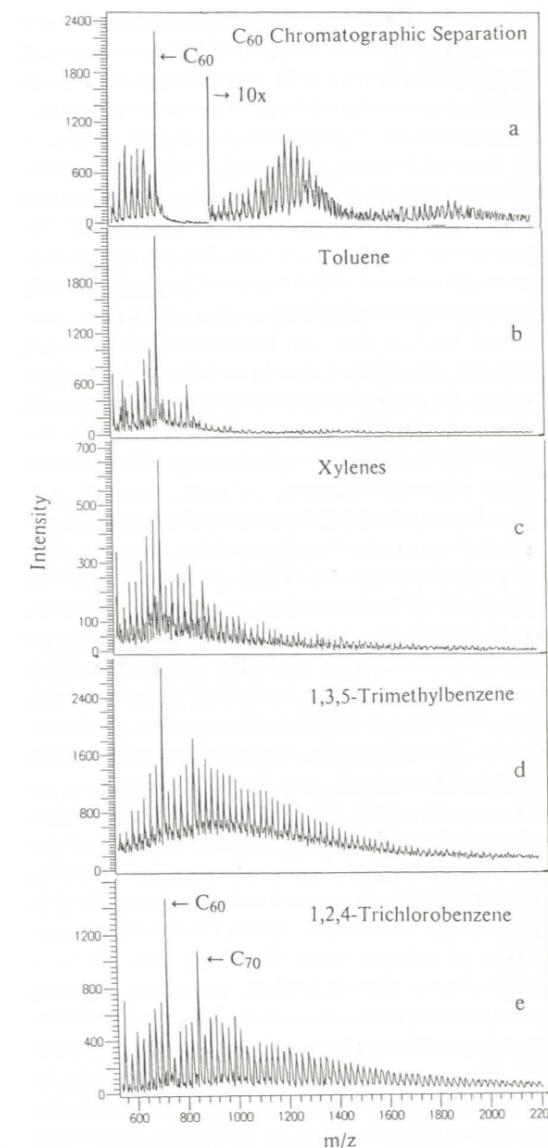


Fig. 1. SSIMS spectra of solvated carbon soot, as further described in the text.

$m/z > 840$, there is only a weak indication of the presence of higher fullerenes.

Several portions of the depleted soot were extracted with xylene, TMB, TCB, and 1-methylnaphthalene with the boiling point of the solvent increas-

ing in that order. The spectra with xylene, TMB, and TCB are shown in fig. 1c–1e. With the exception of 1-methylnaphthalene, with increasing solvent temperature we not only observe an increase in the C_{70}/C_{60} ratio, but also higher fullerenes at least up to C_{180} and beyond become extractable with the highest-boiling-point solvent used in this study. The results are summarized in table 2. The C_{70}/C_{60} intensity ratio increases by a factor of four. We are also listing, as a rough measure of solvation of larger fullerenes, the summation of all fullerenes from C_{72} to C_{180} normalized to C_{60} . For the higher-boiling-point solvents, the values listed should be taken as lower limits since the mass-dependent detector response will decrease in the high mass range. For example, the FTMS results, see below, indicate a much higher percentage of giant fullerenes.

Fig. 2 shows the LMMS spectra of the material extracted from soot using the various solvents. The spectra show systematic evidence that as the boiling point of the solvent increases, again with the exception of 1-methylnaphthalene, higher mass fullerenes are extracted from the soot. For these mass spectrometer conditions, the individual fullerenes with $m/z > 2500$ are not resolved, although they are clearly present. The ratios of the integrated intensities of the higher fullerenes to C_{60} are shown in table 3.

One might expect that solvation of C_{2n} fullerene molecules from the carbon soot is a function of the reflux temperature T . Again, if we exclude 1-methylnaphthalene, such appears to be the case. Fig. 3 is a plot of $\log x$ versus $1/T$, where x is the weight percentage of original mass dissolved. The fit to a straight line is almost perfect, indicating that solvation from the soot is an activated process. It is clear that solvent effects play a role for 1-methylnaphthalene. We speculate that it differs significantly in its interaction with the fullerenes in comparison to the substituted benzenes used in this study, but clearly

Table 2
SSIMS-TOF integrated intensity ratios

Solvent	b.p. (°C)	C_{70}/C_{60}	$\sum_{72}^{180} C_n/C_{60}$
toluene	110	0.21	0.30
xylene	139	0.40	2.45
1,3,5-trimethylbenzene	162	0.64	9.71
1,2,4-trichlorobenzene	214	0.85	12.60

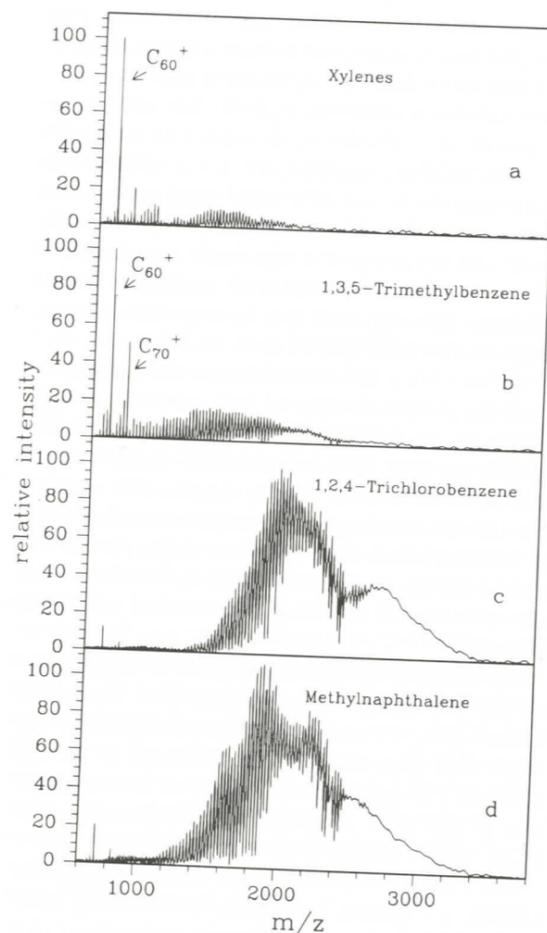


Fig. 2. LMMS spectra of solvated carbon soot, as further described in the text.

Table 3
LMMS integrated intensity ratios

	C_{70}^+/C_{60}^+	total ^{a)} C_n^+/C_{60}^+
xylene	0.26	17
1,3,5-trimethylbenzene	0.57	33
1,2,4-trichlorobenzene	0.28	1620
α,α,α -trichlorotoluene	0.35	430
methylnaphthalene	0.45	1164

^{a)} $m/z > 864$.

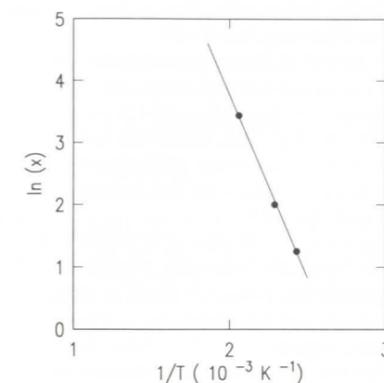


Fig. 3. Van 't Hoff plot of $\ln x$ versus $1/T$, x =weight percent extract.

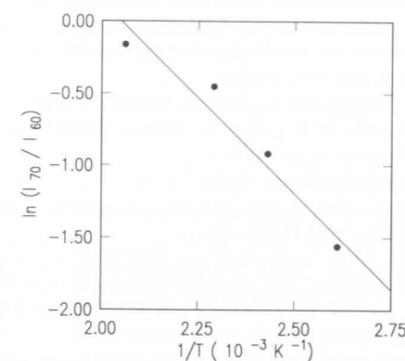


Fig. 4. Van 't Hoff plot of $\ln(C_{70}/C_{60})$ versus $1/T$.

a detailed understanding of solvation will only come with further work.

Fig. 4 is a van 't Hoff plot that allows calculation of a rough value for the enthalpy difference between C_{60} and C_{70} . We assume that the ratio of SSIMS intensities at 840 and 720 amu, table 2, represents the ratio of concentration of C_{70} to C_{60} . This is a reasonable assumption, given the similar ionization potentials and cross sections of C_{60} and C_{70} . Clearly the data do not fall on a perfect straight line, and there is a roll-off at high T . If we assume the slope of the best fit line is $\Delta\Delta H/R$ the value determined is $\Delta\Delta H=5$ kcal/mol. This value is an indicator of the difference of binding energies to the soot matrix. It is also close to the 3 kcal difference in C_{60} and C_{70} sublimation enthalpies determined at 700 K for a C_{60} , C_{70} mixture [19].

It is of particular interest that the filtrate from the higher-boiling-point solvents can be dissolved in methylene chloride and toluene. Each of these solvents were incapable of unlocking any fullerenes from the (previously) toluene extracted soot. The fullerene molecules are apparently bound in the soot, and must first be unlocked from the soot with more vigorous methods. As discussed, we have used the reflux temperature as the experimental parameter to achieve this.

It is important to note that in these multicomponent mixtures solvation is a coupled process: solvation kinetics of a crystal of $(C_{540})_n$ and of a crystal of $(C_{60})_{20n}$ will likely be dramatically different than solvation of an amorphous $(C_{540})_n(C_{60})_{20n}$ solid, where on average each C_{540} is surrounded by twenty C_{60} s. This is because in the latter case, when the solvent plucks C_{60} off, the C_{540} can be solvated, whereas the binding energy of $(C_{540})_2$ is much larger than that of $C_{540}-C_{60}$. Therefore, it is reasonable to expect that the higher fullerenes will be harder to dissolve, and therefore require a higher temperature than the lower weight fullerenes. This also suggests the possibility that very large fullerenes may not be soluble in a thermodynamic sense relative to their pure crystalline state, and may be only metastable in solution, in either the low or high boiling solvents. In addition, once the fullerenes are solvated at high temperature, they may retain solvent molecules in a coordination sphere as they dry, thus allowing them to be redissolved more easily.

4. Conclusions

We have demonstrated that roughly 40% of the soot produced in the Krätschmer–Huffman method is soluble, and that the filtrate is soluble in low-boiling-point solvents such as methylene chloride and toluene. SSIMS and LMMS spectra of the solvated material show only C_{2n} mass peaks. It is clear from the data collected on 1-methylnaphthalene that solvent type, and not just temperature, influences solvation. However, for the substituted benzenes employed, both mass spectrometric techniques clearly show the solvation of more giant fullerenes as reflux temperature increases. These results have several significant implications, among them: there is a much larger

quantity of fullerenes, including C_{60} , than one would find from toluene extraction alone; larger fullerene molecules are accessible in useful amounts with the judicious use of higher-boiling-point solvents; because the fullerene residues of the extractions using high-boiling solvents are almost completely soluble in low-boiling-point solvents, chromatographic separation of useful amounts of "giant" fullerenes may be achievable. We are proceeding with chromatographic work and attempts to isolate chemically meaningful quantities of these larger fullerenes.

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Isolation and identification of fullerene family: C_{76} , C_{78} , C_{82} , C_{84} , C_{90} and C_{96}

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A preparative high-performance liquid chromatography was examined for the isolation of higher fullerenes from CS_2 extracts of the carbon soot produced by arc heating of graphite in inert atmosphere. At least eight all-carbon compounds C_{60} , C_{70} , C_{76} , C_{78} , C_{82} , C_{84} , C_{90} and C_{96} were confirmed as a "stable fullerene". C_{82} and C_{96} are new members of fullerene family which have not been reported so far. The presence of stable C_{82} seems to be closely related with the recent success of macroscopic quantities of production of LaC_{82} reported by Smalley's group.

1. Introduction

Krätschmer et al. [1] were the first to report the isolation of macroscopic quantities of the soccer ball-like molecule C_{60} in 1990. This new hollow-cage molecule is obtained from the benzene-soluble fraction of a soot-like material produced through resistive heating of graphite in inert atmosphere. In addition to C_{60} , the soluble extract contains C_{70} as well. On the other hand, very recently, Diederich et al. [2] have demonstrated the presence of higher all-carbon molecules, in addition to C_{60} and C_{70} . The higher fullerenes such as C_{76} , C_{84} , C_{90} and C_{94} were separated by a gravity chromatography of the toluene extract of the carbon soot materials produced by resistive heating of graphite. Results on measurements of UV/VIS optical absorption as well as ^{13}C NMR have been briefly reported for these all-carbon molecules designated as a new fullerene family.

On the other hand, an efficient isolation method for these higher fullerenes has been proposed by the present authors, in which a preparative HPLC (high-performance liquid chromatography) was used with benzene [3]. As a result, the fullerenes, C_{78} , C_{76} and C_{84} have successfully been isolated by this method.

In the present work, we further improved the previous method, and succeeded in the isolation of the higher fullerenes up to C_{96} with quantities of the or-

der of milligrams. Main difference between the previous and the present methods is the eluted solvent. In the present work, we used CS_2 as an eluent. By this method, we were safely and efficiently able to isolate the higher fullerenes such as C_{76} , C_{78} , C_{82} , C_{84} , C_{90} and C_{96} , among which the fullerenes of C_{82} and C_{96} are new members of the fullerene family. The UV and visible absorption measurements were also carried out on these isolated "pure" fullerenes and compared with each other in the present work.

2. Isolation of higher fullerenes by HPLC

The soot-like materials were prepared by an arc heating of graphite (99.997%) under ≈ 200 Torr He, condition which is essentially the same as those reported so far [4,5]. Soluble materials (mostly composed of fullerenes) were separated by the Soxhlet extraction, using CS_2 . A preparative HPLC (model LC-908 with JAIGEL 2H, 2H, Japan Analytical Industry Co.) was used to isolate the fullerenes after rinsing the CS_2 soluble extracts with diethyl ether. In the present experiments, for the first time, CS_2 was examined as an eluent of HPLC. It should be noteworthy that the solubility of the fullerenes in CS_2 is, roughly speaking, about 8 times larger than that in benzene. This fact was a critical point that we were