

$$d\sigma^2 = dx^2 + dy^2 + dz^2 - dt^2. \quad (2)$$

For $a=b=c=0$, the line element (1) takes the form

$$ds^2 = (dx^2 - dt^2) + e^{2x}(dy^2 + dz^2), \quad (3)$$

which is not considered as the background metric because (i) it is not a flat space-time as its curvature tensor components R_{1212} , R_{1313} and R_{2323} are non-zero, and (ii) it is not a space of constant curvature as the relation

$$R_{hijk} = k(g_{ik}g_{hj} - g_{ij}g_{hk}), \quad (4)$$

where k is constant is not valid.]

The matter content with a source-free electromagnetic field is given by the energy momentum tensor

$$T_i^j = (\varepsilon + p)v_i v^j + p g_i^j + E_i^j \quad (5)$$

where

$$E_i^j = F_{ir} F^{jr} - \frac{1}{4} F_{ab} F^{ab} g_i^j. \quad (6)$$

Here p is the isotropic pressure, ε the matter density, E_i^j the electromagnetic energy tensor, F_{ij} the electromagnetic field tensor, and v^i the four velocities of the fluid which are so chosen that $v^1 = v^2 = v^3 = 0$ and $v^4 = e^{-a}$.

The non-vanishing components of F_{ij} are F_{12} , F_{13} , F_{24} and F_{34} such that

$$F_{12} = \pm F_{24} \quad (7)$$

$$\text{and } F_{13} = \pm F_{34}. \quad (8)$$

For details one may refer to Roy and Singh².

The field equations of bimetric relativity

$$K_i^j = N_i^j - \frac{1}{2} N g_i^j = -8\pi k T_i^j \quad (9)$$

where

$$N_i^j = \frac{1}{2} \gamma^{\alpha\beta} (g^{hj} g_{hi|\alpha})_{|\beta} \quad (10)$$

$$N = N_\alpha^\alpha, k = (g/\gamma)^{1/2} \quad (11)$$

and the bar (|) stands for γ -differentiation.

$$8\pi k(p + \rho) = \frac{1}{2}(\bar{b} + \bar{c}) \quad (12)$$

$$8\pi k p = \bar{a} - \frac{1}{2}(\bar{b} - \bar{c}) \quad (13)$$

$$8\pi k p = \bar{a} + \frac{1}{2}(\bar{b} - \bar{c}) \quad (14)$$

$$8\pi k(\varepsilon + \rho) = -\frac{1}{2}(\bar{b} + \bar{c}) \quad (15)$$

$$8\pi k \rho = 0 \quad (16)$$

$$\text{where } \dot{a} = \frac{da}{dt}, \quad \ddot{a} = \frac{d^2 a}{dt^2}, \text{ etc.}$$

and

$$\rho = \frac{e^{2c} F_{24}^2 + e^{2b} F_{34}^2}{e^{2a+2b+2c+2x}} \quad (17)$$

Equations (7), (8), (16) and (17) imply that F_{12} , F_{13} , F_{24} and F_{34} are zero and consequently there is no contribution to the Bianchi type-V model from F_{ij} in bimetric theory of gravitation.

1. Rosen, N., *Found. Phys.*, 1980, 10, 673.

2. Roy, S. R. and Singh, J. P., *Aust. J. Phys.*, 1985, 38, 763.

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Preparation and characterization of buckminsterfullerene and measurement of its heat of sublimation

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The recent discovery of an easy method for the production of all-carbon molecules C_{60} and C_{70} (called fullerenes) in macroquantities has led to a number of interesting investigations on the properties of these molecules and their derivatives. We have prepared these molecules and characterized them in our laboratory. The fullerenes were extracted from the graphite soot generated in an arc between two graphite electrodes by Soxhlet extraction. They were characterized by UV, visible and IR spectroscopy, high-performance liquid chromatography, X-ray diffraction and mass spectrometry. Column chromatography was used to separate C_{60} and C_{70} . Here we describe the procedures employed, and report data on heat of sublimation of C_{60} and C_{70} measured by high-temperature mass spectrometry.

THE preparation and isolation of macroscopic quantities of the all-carbon molecule C_{60} (buckminsterfullerene) by Kratschmer *et al.*¹ has opened up an exciting area of research. Though the actual practical applications of the fullerenes have not been identified yet, their chemistry promises to be a fascinating subject with many interesting possibilities.

Though polymeric carbon species were observed in the mass spectra of graphite from the fifties², the study of clusters existing in graphite soot received special attention only towards the eighties, when astronomers

noticed certain features in the absorption and emission spectra of interstellar matter that were difficult to explain. In particular, an intense absorption band at 217 nm was seen which was attributed to small particles of graphite. In experiments aimed at understanding the mechanisms by which long-chain carbon molecules could be formed in interstellar space, Kroto *et al.*³ demonstrated the formation of a remarkably stable carbon cluster containing 60 carbon atoms. They suggested that the stability of the C₆₀ species might be caused by a highly resonance-stabilized rigid structure of a truncated icosahedron, akin to a football.

The technique adopted by Kroto *et al.* involved vaporization of carbon species from the surface of graphite by laser ablation, and detection of the species formed by time-of-flight mass spectrometry after supersonic expansion and photoionization. Using this technique, they also demonstrated⁴ the possibility of formation of stable carbon clusters incorporating metal atoms such as La, Ca, Ba and Sr.

It was however, Kratschmer *et al.*¹ who provided the crucial breakthrough in 1990. They described a simple technique for preparation and isolation of the fullerenes in macroquantities, and also reported a number of properties of the fullerenes. The properties (such as IR spectrum, NMR spectrum and UV-vis absorption spectrum) turned out to be amazingly close to the properties predicted on the basis of theoretical calculations.

The discovery of Kratschmer *et al.* was quickly followed by the work of Haufler *et al.*⁵, who reported an efficient method for production of fullerenes. They also reported a method for the production of C₆₀H₃₆, and the formation of 'buckide' ions in cyclic voltammetry. Ajie *et al.*⁶ reported chromatographic methods for the separation of pure C₆₀ and C₇₀ and also their optical absorption spectra.

In the short period of one year following the reports on preparation and purification of fullerenes, a number of derivatives have been prepared (e.g. ref. 7); superconductivity has been reported in alkali-metal compounds of C₆₀ (refs. 8–10); the possibility of substitution of carbon atoms by boron has been demonstrated¹¹; the compressibility of C₆₀ has been measured¹²; and it has been shown that fullerenes can be formed in benzene flames¹³. (The first report from India on this subject^{13a} appeared after this paper was submitted.)

We have undertaken studies on various aspects of the chemistry of fullerenes. In this paper we describe preparation and characterization, and data on heat of sublimation of C₆₀ and C₇₀ measured by high-temperature mass spectrometry.

In our preparation procedure (see legend to Figure 1), similar to the 'contact arc' procedure⁵, each arcing run, consisting of several 5-min operations, produced soot of

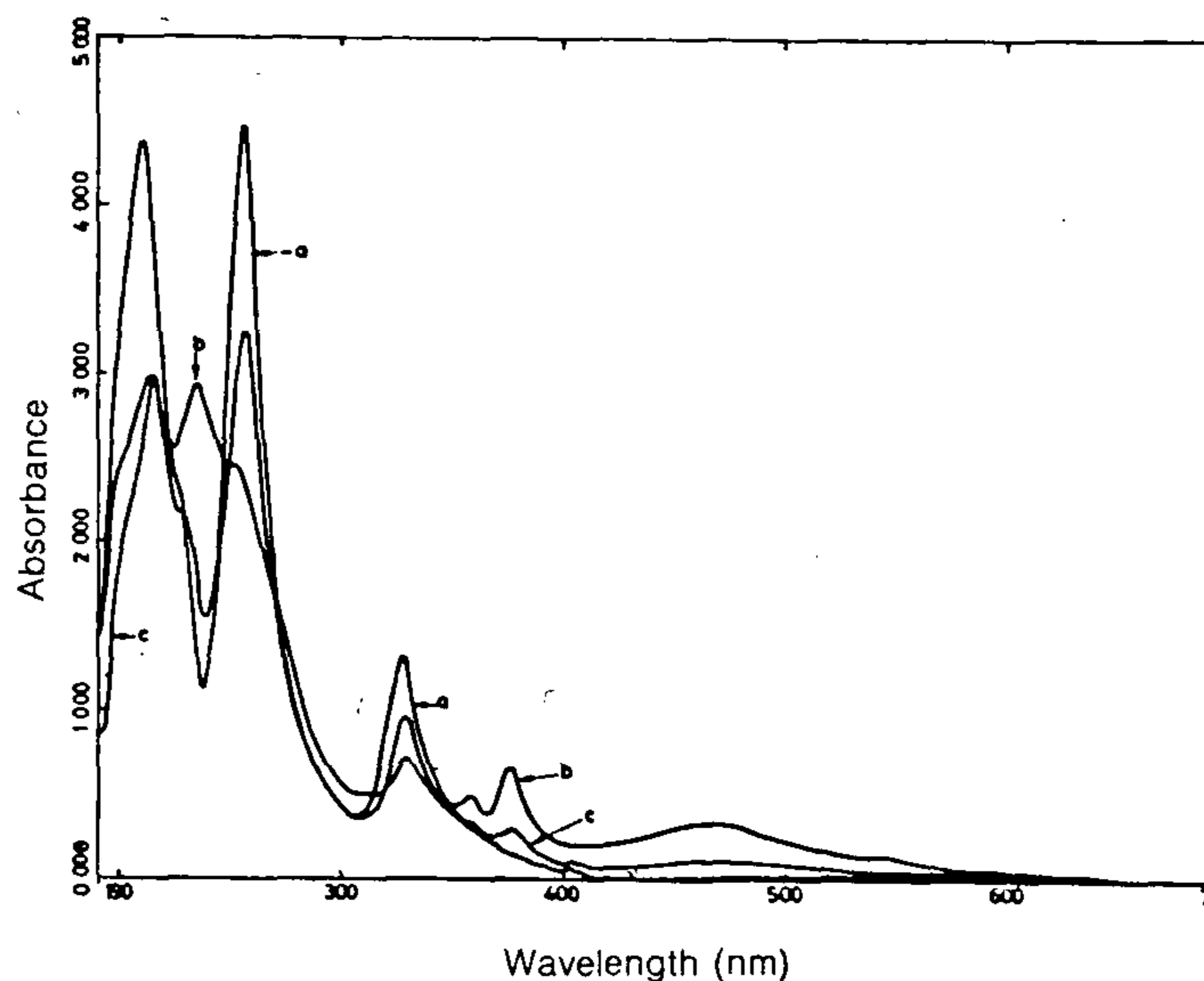


Figure 1. Absorption spectra in *n*-hexane of (a) C₆₀, (b) C₇₀, (c) mixture as obtained from soot extraction.

Methods: The procedure used for preparation of C₆₀ was similar to the 'contact arc' procedure⁵. An existing arc melting set-up was used for this purpose without any significant modification. The set-up consisted of a cylindrical glass chamber held between two brass flanges, one incorporating a water-cooled copper hearth, and the other a movable brass rod with a standard drill chuck to hold the electrode. A 6-mm-dia graphite rod of spectroscopic purity held by the chuck formed the anode, and a graphite disc placed on the copper hearth formed the cathode. An arc-welding generator was used to supply DC electric power. A current of 100–150 amp was employed during the arcing step. The apparatus was initially evacuated to 10⁻³ torr (~0.13 Pa) by employing a rotary vacuum pump, and then filled with helium. The evacuation-refill cycle was repeated a number of times, and the chamber pressure was finally set at approx. 200 torr (~2.7 × 10⁴ Pa) of helium. In most experiments, no attempt was made to maintain the pressure during arcing. In some experiments, however, a jet of helium was directed towards the arc, to drive the C₆₀ formed away from the arc. These experiments were conducted in dynamic vacuum, and a helium pressure of 100 torr was maintained. The graphite soot that was collected on the hearth as well as the walls of the glass chamber was gathered and subjected to Soxhlet extraction using toluene or carbon tetrachloride as the solvent. The extract was evaporated using a rotary evaporator and the residue used for studies. UV-visible spectra were obtained on a Shimadzu UV 2100 spectrophotometer. Spectroscopic-grade solvents were employed.

the order of 10 grams, and the quantity of fullerenes extracted from this soot amounted to approx. 200 mg (yield approx. 2%). The reason for the low yield is suspected to be poor control of arc length. The yields with static atmosphere were lower than runs in which flowing helium gas was used, which lends credence to the view that the C₆₀ formed undergoes some degradation even during preparation on account of its exposure to intense UV radiation¹⁴.

Generally extractions with carbon tetrachloride were found to be very slow, the refluxing period often extending to 20 h or more. With toluene, however, the extraction was generally complete in about 8 h. Ether washing of the residue obtained from rotary evaporation was useful in removing sticky (hydrocarbon?)

material and in making the product a free-flowing powder.

The X-ray diffraction (XRD) pattern of the ether-washed material clearly indicated the prominent peaks of C_{60} , but also indicated the presence of some graphite in the sample, presumably resulting from the physical carry-over of fines during the Soxhlet-extraction step.

For isolation of pure C_{60} and C_{70} , the chromatographic technique described was found to give satisfactory separation as evidenced from the UV-vis spectra of the sample. Though pure C_{60} and C_{70} could be obtained by this technique, the use of hexane solution for loading of the sample restricted the quantity that could be conveniently processed at a time.

UV-visible absorption spectrum. The absorption spectra of the C_{60} and C_{70} fractions collected in the column chromatography run, evaporated, and redissolved in *n*-hexane (Figure 1) agree very well with the spectral data reported by Ajie *et al.*⁶ The C_{60} solution has a magenta colour, while the C_{70} solution is reddish in colour.

IR spectrum. The IR spectra were recorded first by evaporating the extract directly onto KBr discs. In these measurements, the use of CCl_4 for extracting the fullerenes proved to be advantageous because of the fairly simple spectrum of CCl_4 and hence minimum background interference. One sample of the fullerene was also prepared by vacuum sublimation onto zinc selenide disc. The spectrum of this sample (Figure 2) shows the four major peaks of C_{60} at 526.6, 576.2, 1182.4 and 1428.8 cm^{-1} . This spectrum was recorded at a resolution of 1 cm^{-1} . The positions as well as the widths of the peaks agree within $\pm 1 cm^{-1}$ with the values reported by Haufler *et al.*⁵

Mass-spectrometric characterization. The mass spectra recorded show four peaks at mass numbers 720, 840, 360 and 420. The peaks at mass numbers 720 and 840 were attributed to C_{60}^+ and C_{70}^+ ions respectively. The doubly charged ions of these species, C_{60}^{2+} and C_{70}^{2+} , were observed at mass numbers 360 and 420 respectively. Peaks corresponding to other clusters (e.g. C_{84}) as well as other isotopic peaks of C_{60} and C_{70} were not measured.

HPLC characterization. Initially a 60% isopropanol-40% toluene mixture was used as the mobile phase. With a mobile-phase flow rate of 1 $ml\ min^{-1}$, good separation of C_{60} and C_{70} was obtained (retention time 4.90 min and 5.77 min respectively). Decreasing the toluene concentration in the mobile phase to 25% further improved the separation. (Retention time for C_{60} and C_{70} 8.7 min and 12.12 min respectively.) The peak ratio of C_{60} to C_{70} was found to vary from sample to sample, but was approximately in the range

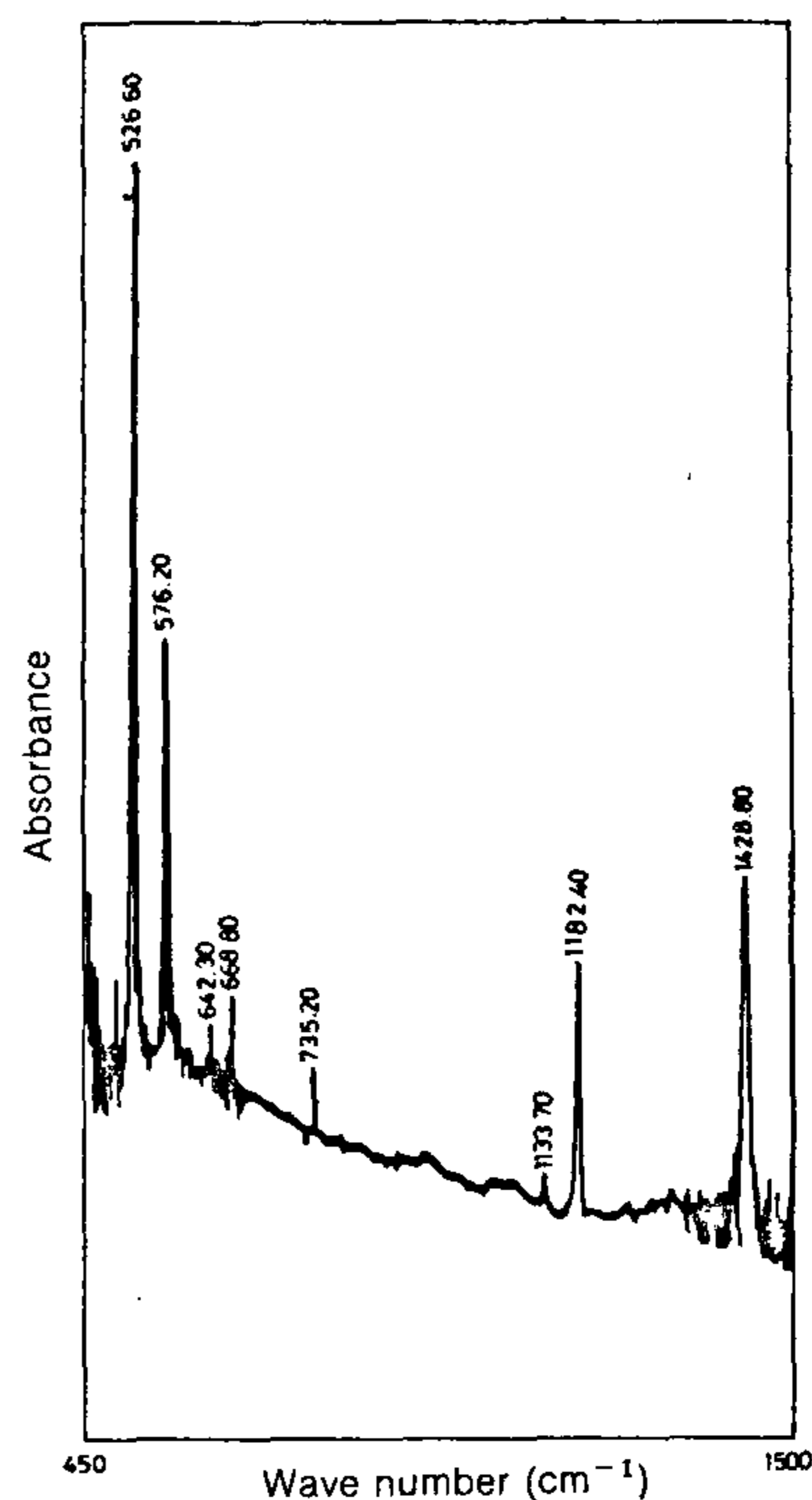


Figure 2. IR spectrum of fullerene. The spectrum was recorded on a Digilab FTS 15/90 FTIR spectrometer.

of 80:20. Further decrease in toluene concentration was however not useful, since the retention time increased considerably, with the attendant broadening of the peaks. Figure 3 shows typical chromatograms. The superior separation obtained in this work can perhaps be attributed to the use of a reversed-phase column, as against the silica column used conventionally⁶.

Heats of sublimation. The measurements were made by Knudsen-cell mass spectrometry. The intensities of C_{60}^+ and C_{70}^+ ions were measured as a function of temperature between 640 and 787 K. Three different lots of samples were used for experiments and a total of seven runs were conducted. To start with each sample was heated and kept at the lowest temperature of the range for about 2 h to achieve a stable ion-intensity value. Then the temperature was increased in steps of 20 K and allowed to stabilize for 20 min before measurement of ion intensities.

Table 1 gives the relative ion intensities of C_{60}^+ to C_{70}^+ along with the calculated partial-pressure ratios. The partial pressure (p) is related to the ion intensity (I^+) by the expression $p = k' I^+ T / \sigma s h$, where T is the temperature, k' the instrumental sensitivity factor, σ the ionization cross-section, s the yield of the secondary electron multiplier, and h the isotopic abundance. The value of s for C_{60} and C_{70} was taken to be the inverse

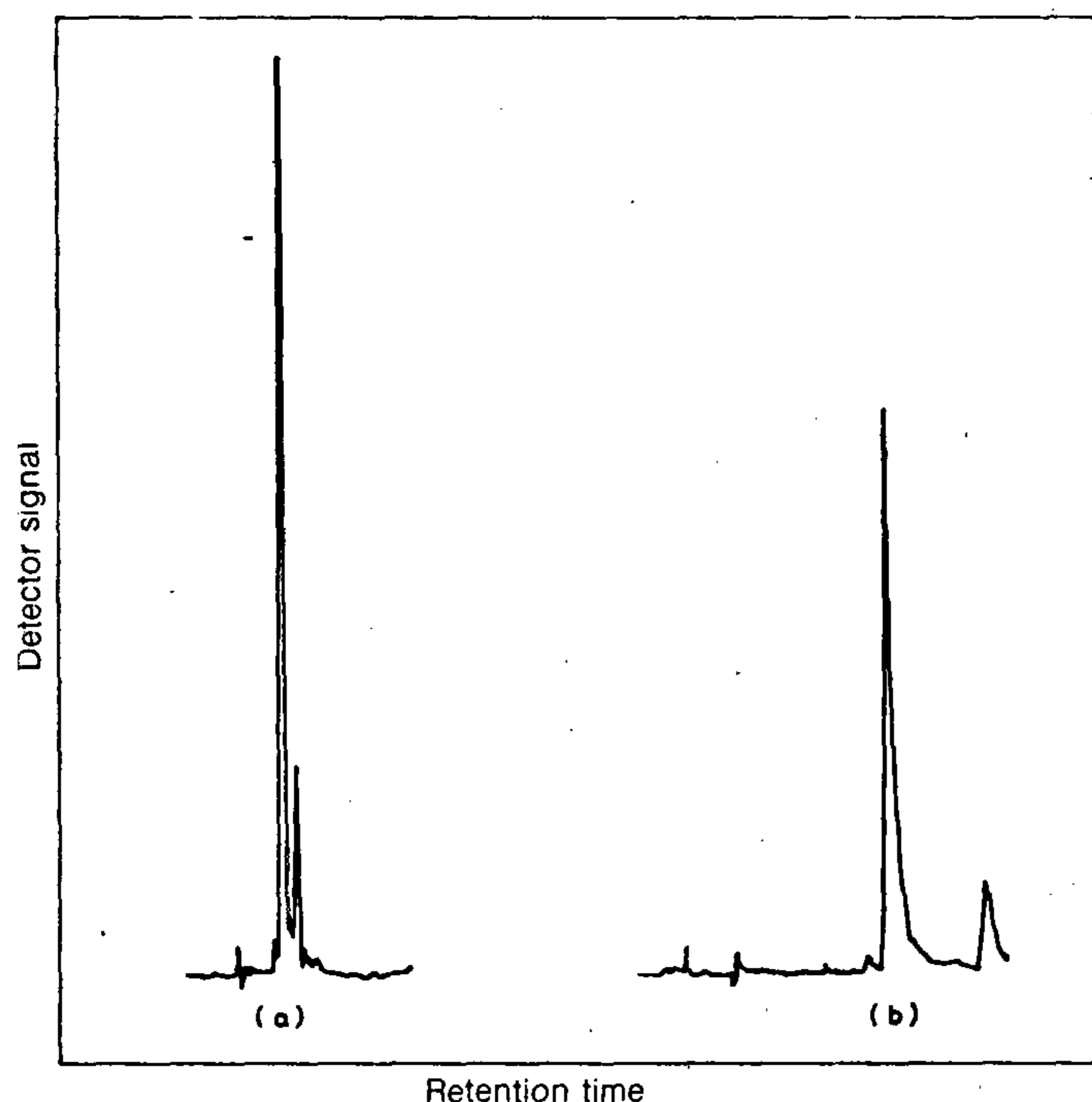


Figure 3. HPLC separation of C_{60} and C_{70} . The HPLC system used consisted of a solvent delivery system (Micromeritics 750), a loop-filled injector (Rheodyne 7125) with a 100- μ l loop, and a variable-wavelength photometric detector (Micromeritics 787) with a 12- μ l flow cell. The output of the detector was recorded and the data processed by a Chromatopack C-R6A (Shimadzu) integrator-printer-plotter. The column employed was a reverse-phase column (ODS-C18, 25 cm long, 4.6 mm i.d., 5 μ m particle size). The UV detector was set at 329 nm. For column chromatography, a neutral alumina column was employed. Sample was loaded in the form of hexane solution, and C_{60} was eluted with a hexane-5% toluene mixture. C_{70} could be eluted by increasing the toluene concentration to 25%. Elution of fullerenes was followed by measuring the UV-vis absorption spectrum of the eluate fractions.

Table 1. Relative ion intensities C_{60}^+/C_{70}^+ and ratio of partial pressures C_{60}/C_{70}

Sample no.	Run no.	$T=660$ K		$T=760$ K	
		C_{60}^+/C_{70}^+	C_{60}/C_{70}	C_{60}^+/C_{70}^+	C_{60}/C_{70}
1	1	5.40	5.20	4.70	4.50
	2	5.70	5.50	4.90	4.70
2	1	6.50	6.30	5.70	5.50
	2	7.20	6.90	5.30	5.10
3	1	11.70	11.30	8.30	8.00
	2	11.10	10.70	7.20	7.00
	3	13.90	13.40	7.50	7.20

Methods: A Knudsen-cell mass spectrometer (VG Micromass 30 BK) was used. The sample was taken in an alumina cell (height 10.0 mm, i.d. 7.5 mm, o.d. 10.0 mm, orifice dia 0.5 mm) and this was placed inside a tantalum cup. This was heated by electron bombardment. The vapour effusing out of the cell was ionized by electron impact and mass-analysed by a 90°-sector magnetic analyser. The ions were detected and their intensities measured by means of a secondary electron multiplier. 38-eV electrons were used to ionize the molecular beam from the Knudsen cell.

square root of the masses. The value of σ was assumed to be proportional to the number of carbon atoms. Using this relation the ion-intensity ratios were converted to the partial-pressure ratios. Figure 4 shows

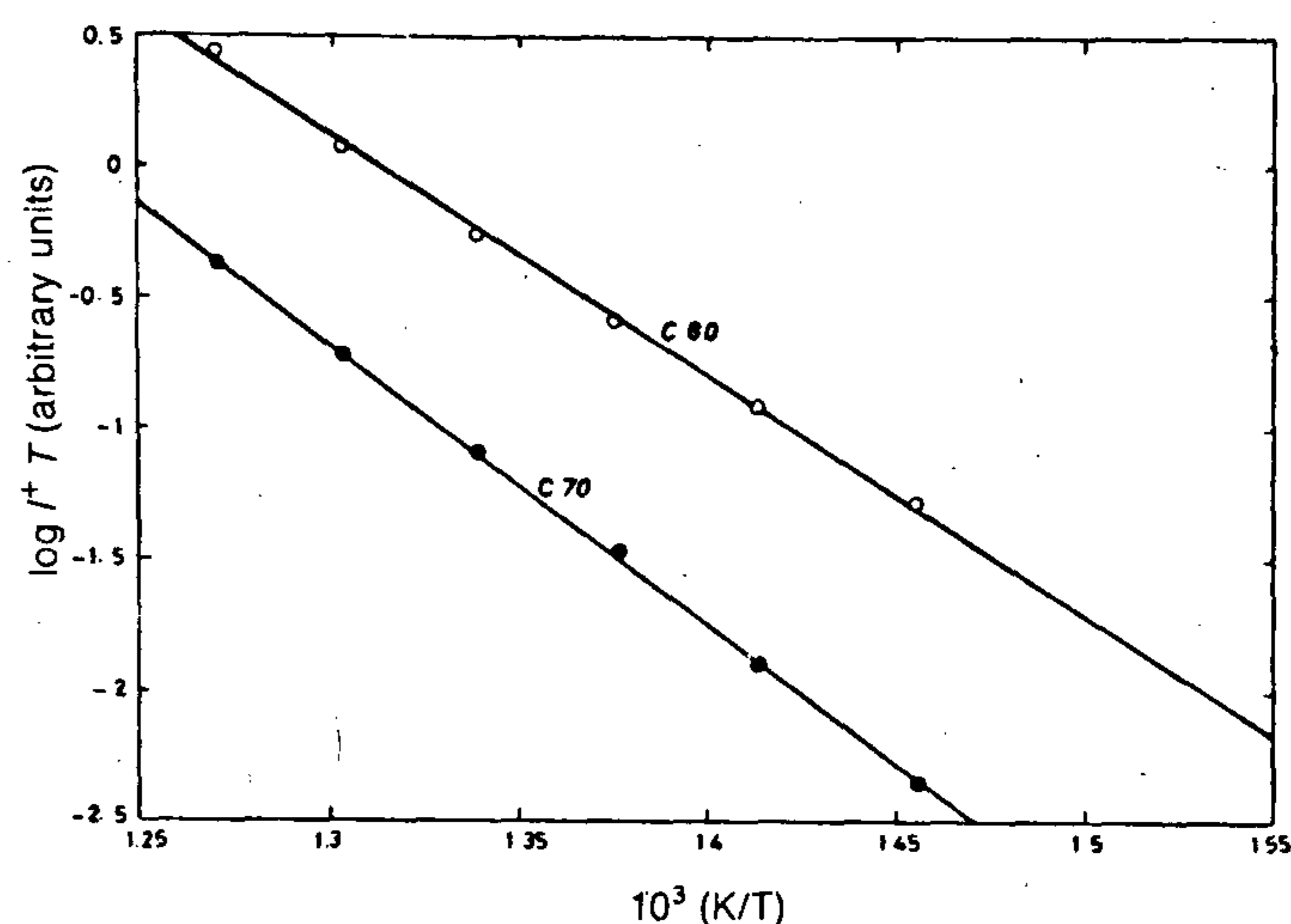


Figure 4. Temperature dependence of ion intensity for C_{60} and C_{70} .

the plots of $\log(I^+T)$ vs $1/T$ for C_{60}^+ and C_{70}^+ ions. Enthalpy of sublimation of C_{60} and C_{70} was obtained by second-law method¹⁵ (Table 2). The errors quoted are the statistical variations.

While discussing the data, it is necessary to mention that the ion intensity was found to be stable and more reproducible during the measurements with sample 3, whereas the signals from samples 1 and 2 were found to decay with time. Samples 1 and 2 were obtained by directly evaporating the CCl_4 extract in the Knudsen cell. Sample 3 was obtained by sublimation of the fullerenes, and annealing of the sublimed material in vacuum at 500 K for about 15 h. Thus preconditioning of sample appears to be an important factor in obtaining stable ion intensity. Such an observation has also been made by Pan *et al.*¹⁶ It is also possible that sample 3 had a different ratio of C_{60} to C_{70} because of the sublimation step. A close look at our enthalpy values reveals that those of C_{60} are lower by about 10 kJ for sample 3 compared to samples 1 and 2. For C_{70} there was no such trend observed and the values are more uniform for all the samples. The reason for this must be found in either the greater purity of the sublimed sample, or its lower C_{70} content. We are

Table 2. Enthalpy of sublimation of C_{60} and C_{70}

Sample no.	Run no.	Temp. range (K)	ΔH^0 (kJ mol ⁻¹)	
			C_{60}	C_{70}
1	1	658-758	186 \pm 1	192 \pm 3
	2		182 \pm 3	188 \pm 1
2	1	640-740	193 \pm 7	198 \pm 6
	2		190 \pm 2	203 \pm 2
3	1	667-787	175 \pm 2	190 \pm 4
	2		176 \pm 2	194 \pm 1
	3		177 \pm 2	203 \pm 1
		Mean*:	176 \pm 2 ^a	196 \pm 7 ^b

*Based on sample 3 only; ^a $T=727$ K, ^b $T=737$ K.

planning further experiments with pure C₆₀ and C₇₀ to resolve this issue.

The mean values quoted in Table 2 are calculated on the basis of the values for sample 3 alone. Pan *et al.*¹⁶ obtained a mean value of 168 ± 5 kJ mol⁻¹ (at 707 K) for C₆₀ and 180 ± 9 kJ mol⁻¹ (739 K) for C₇₀. Within error limits our values are consistent with those obtained by them. Guo *et al.*¹⁷ made theoretical calculations and reported a cohesive energy of 171 kJ mol⁻¹ for C₆₀ and 194 kJ mol⁻¹ for C₇₀, which agree very well with our values. Our experimental data are based on measurement of the abundant singly charged species, C₆₀⁺ and C₇₀⁺, which were beyond the mass range of the quadrupole mass analyser employed by Pan *et al.*¹⁷, and therefore can be considered more reliable.

1. Kratschmer, W., Lamb, L. D., Fostiropoulos, K. and Huffman, D. R., *Nature*, 1990, **347**, 354.
2. Chupka, W. H. and Inghram, M. G., *J. Phys. Chem.*, 1955, **59**, 100.
3. Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. and Smalley, R. E., *Nature*, 1985, **318**, 162.
4. Heath, J. R., O'Brien, S. C., Zhang, Q., Liu, Y., Curl, R. F., Kroto, H. W., Tittel, F. K. and Smalley, R. E., *J. Am. Chem. Soc.*, 1985, **107**, 7779.
5. Hauffler, R. E., Conceicao, J., Chibante, L. P. F., Chai, Y., Byrne, N. E., Flanagan, S., Haley, M. M., O'Brien, S. C., Pan, C., Xiao, Z., Billups, W. E., Ciufolini, M. A., Hauge, R. H., Margrave, J. L., Wilson, L. J., Curl, R. F. and Smalley, R. E., *J. Phys. Chem.*, 1990, **94**, 8634.
6. Ajie, H., Alvarez, M. M., Anz, S. J., Beck, R. D., Diederich, F., Fostiropoulos, K., Huffman, D. R., Kratschmer, W., Yves Rubin, Schriver, K. E., Sensharma, D. and Whetten, R. L., *J. Phys. Chem.*, 1990, **94**, 8630.
7. Fagan, P. J., Calabrese, J. C. and Malone, B., *Science*, 1991, **252**, 1160.
8. Hebard, A. F., Rosseinsky, M. J., Haddon, R. C., Murphy, D. W., Glarum, S. H., Palstra, T. T. M., Ramirez, A. P. and Kortan, A. R., *Nature*, 1991, **350**, 600.
9. Wang, H. H., Kini, A. M., Savall, B. M., Carlson, K. D., Williams, J. M., Lykke, K. R., Wurz, P., Parker, D. H., Pellin, M. J., Gruen, D. M., Welp, U., Kwok, W., Fleshler, S. and Crabtree, G. W., *Inorg. Chem.*, 1991, **30**, 2838.
10. Holczner, K., Klein, O., Huang, S., Kaner, R. B., Fu, K., Whetten, R. L. and Diederich, F., *Science*, 1991, **252**, 1154.
11. Guo, T., Jin, C. and Smalley, R. E., *J. Phys. Chem.*, 1991, **95**, 4948.
12. Fischer, J. E., Heiney, P. A., Mcghee, A. R., Romanow, W. J., Denenstein, A. M., McCauley, Jr. J. P. and Smith, A. B., III, *Science*, 1991, **252**, 1288.
13. Baum, R., *Chem. Eng. News*, 1991, **69**, 6.
14. Pradeep, T., D'Souza, F., Subbanna, G. N., Krishnan, V. and Rao, C. N. R., *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1991, **103**, 685.
15. Taylor, R., Parsons, J. P., Avent, A. G., Rannard, S. P., Dennis, T. J., Hare, J. P., Kroto, H. W. and Walton, D. R. M., *Nature*, 1991, **351**, 277.
16. Cater, E. D., in *Physicochemical Measurements in Metals Research* (ed. Rapp, R. A.), vol. IV, Part I of *Techniques of Metals Research*, (series editor, Bunshaw, R. F.), Wiley, New York, 1970.
17. Pan, C., Sampson, M. P., Chai, Y., Hauge, R. H. and Margrave, L., *J. Phys. Chem.*, 1991, **95**, 2944.
18. Guo, Y., Karasawa, N. and Goddard, W. A., III *Nature*, 1991, **351**, 464.

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Partitioning of assimilated CO₂ in *Pisum sativum* plants inoculated with Hup⁺ or Hup⁻ *Rhizobium leguminosarum*

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The partitioning of assimilated ¹⁴CO₂ in different plant parts was studied in pea (*Pisum sativum*) plants inoculated with Hup⁺ strain Vp 1 or its plasmid-cured Hup⁻ derivative Vm 1. At the early stage of plant growth, nearly 50% of the total ¹⁴CO₂ assimilated by plants was observed in nodules, whereas at the pod filling stage, it decreased to less than 10%. The relative translocation of ¹⁴CO₂ towards roots and nodules of Hup⁺ strain Vp 1 was lower compared to the Hup⁻ strain Vm 1.

IN nodulated legume crops, the oxidation of hydrogen by uptake hydrogenase of bacteroids is coupled to energy release, protection of nitrogenase from oxygen damage and conservation of host photosynthates¹. Based on theoretical considerations, complete hydrogen oxidation has been reported to yield 16% reduction in the energy expenditure in nodules². Conservation of photosynthates has been shown indirectly by significantly higher accumulation of dry matter in plants inoculated with Hup⁺ rhizobial strains³⁻⁵. However, the effect of Hup⁺ strains on symbiotic performance with pea and cowpea miscellany groups has been reported to be nonsignificant^{6,7}. Such results have been attributed to the use of Hup⁺ and Hup⁻ field isolates, which may have some other differences also⁸. Under oxygen limitations also, there is no Hup⁺ superiority over Hup⁻ at least in soybean⁹. Utilization of photosynthates in different plant processes has been studied by the partitioning of assimilated ¹⁴CO₂ in many crops¹⁰⁻¹². The import of assimilates has been reported to be linked with the demand for respiratory substrate in the nodules¹³. From the studies on Hup⁺ strain of *Rhizobium leguminosarum* and its plasmid-cured Hup⁻ mutant, we reported superior symbiotic performance of the Hup⁺ strain¹⁴. The bacteroids of Hup⁺ strain were also found to contain hydrogen-dependent increased level of reductant and ATP¹⁵. Results reported here concern