Fullerene Science and Technology

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PREPARATION, SEPARATION AND CHARACTERISATION OF FULLERENE – C_{60} AND C_{70}

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ABSTRACT: This paper reports a simple apparatus for the synthesis of fullerenes and an efficient method for the separation of C_{60} and C_{70} in large amounts. The positive and negative ion mass spectra of C_{60} and C_{70} were measured using electron ionization and in-beam methods. Vibrational Raman spectra showed that the C_{60} molecule adsorbed on the substrate surface may be distorted and its symmetry may be reduced under the action of the substrate surface.

INTRODUCTION

Since the late 1990 a lot of research work has been reported on the fullerenes C_{60}/C_{70} around the world. In P.R. China there are also many scientists involved in fullerene studies and rich results have been obtained. In the present paper some of the C_{60}/C_{70} research work conducted in our laboratory shall be briefly reported.

1. Preparation and separation of fullerenes C_{60} and C_{70}.

Since the method for the macroscopic preparation of C_{60} was discovered by Krätschmer and Huffman et al. [1,2], a variety of apparata for fullerene synthesis has appeared in the literature, but those are relatively complex and expensive. Our apparatus (Fig. 1) is so simple that most laboratories can set it up easily and generate their own samples.
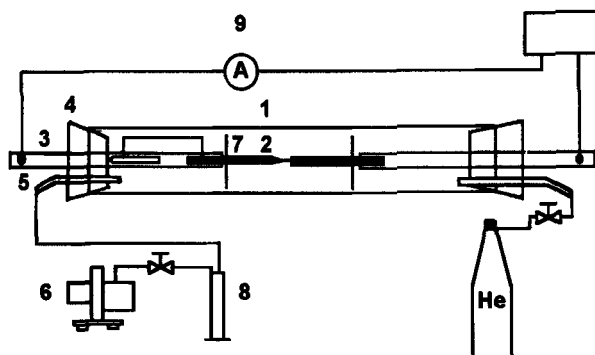
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Fig. 1 Diagram of the graphite arc evaporator

The reactor is a quartz glass cylinder with 8 cm i.d. and 30 cm length (1) with two graphite electrodes (2) fixed in it by two copper rods (3), two rubber stoppers (4) at the end of the cylinder were used as electrode holders. In addition, a thin copper tube (5) on each stopper was used as an He inlet or evacuation port which was then connected to a mechanical rotary pump (6). The circular copper plates (7) around the copper rods in the cylinder prevent the thermal radiation from damaging the stoppers during the vaporization of graphite. The whole cylinder with the stoppers and copper electrodes was submerged in flowing water to quickly remove the generated heat during the operation of the reactor. The helium pressure in the cylinder was 110 Torr (8) at an evacuation rate; 1-2 l/min. The electric arc was created by driving a 150-200 A current (9) between the two electrodes at a voltage of 25-35 V. Black soot was collected on the cylinder surfaces. The C_{60}/C_{70} mixture was extracted from the soot with benzene or toluene. After a slow evaporation of the solution, a brown or black solid material was left behind. The yield of the material was about 9% of the soot. It was analyzed by mass spectroscopy (VG ZAB 3F) using the 70eVEI source at source/probe temperature of 340°C. The results showed that this material contained mainly C_{60} and a small amount of C_{70}.

The use of graphite as a stationary phase in liquid chromatography has recently been demonstrated by Vassallo et al. [3,4]. It is a simple and effective method for the separation of C_{60} and C_{70} in larger amounts. About 400-450 g
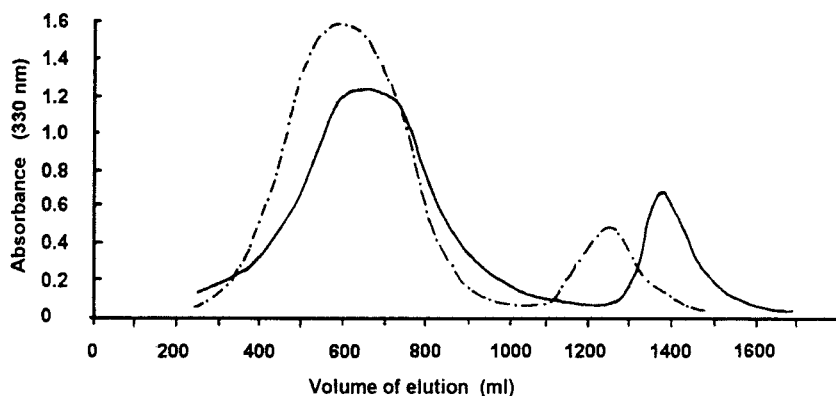
Fig. 2 Elution curves. Volume of eluate (ml). Absorbance at 330 nm

spectroscopically pure graphite powder (100-200 mesh) was packed into a 65 x 3 cm column. 100 mg of fullerene mixture C_{60}/C_{70} dissolved in about 30 ml toluene was added to the top of the column. The column was eluted with hexane-toluene (8:2) or hexane-toluene (9:1) mixture at a flow rate of 0.7-1 ml/min, with the C_{60} fraction eluted first. The mixture of fullerenes C_{60}/C_{70} was eluted with toluene (Fig.2).

The eluates were analyzed by mass spectroscopy. The results showed that a few fractions are pure fullerene-C_{60} (without the m/z 840 ions in their mass spectra). The average C_{60}:C_{70} ratio is 100.00:0.27, and that of the C_{60} to C_{70} in the toluene fractions 100.00 : 3.11. After the slow evaporation of the solvents under reduced pressure and in the dark, 45 mg of C_{60} fullerene was recovered. The separation with the hexane-toluene (8:2) mixture was quicker than with the hexane-toluene (9:1) mixture. The purity of the fullerene-C_{60} fraction separated by both elution methods is better than 99%. As in a single separation step one can obtain nearly 50% pure fullerene-C_{60}, this separation technique can be used as a method to obtain pure C_{60} in larger amounts. In order to separate quickly and obtain a high C_{70} fullerene concentration after the elution of C_{60} fullerene the graphite was extruded from the column and extracted with toluene in a Soxhlet-extractor. The concentrated extract is added to the crude fullerenes and separated again.

Table 1
The relationship between positive ion intensity and electron energy
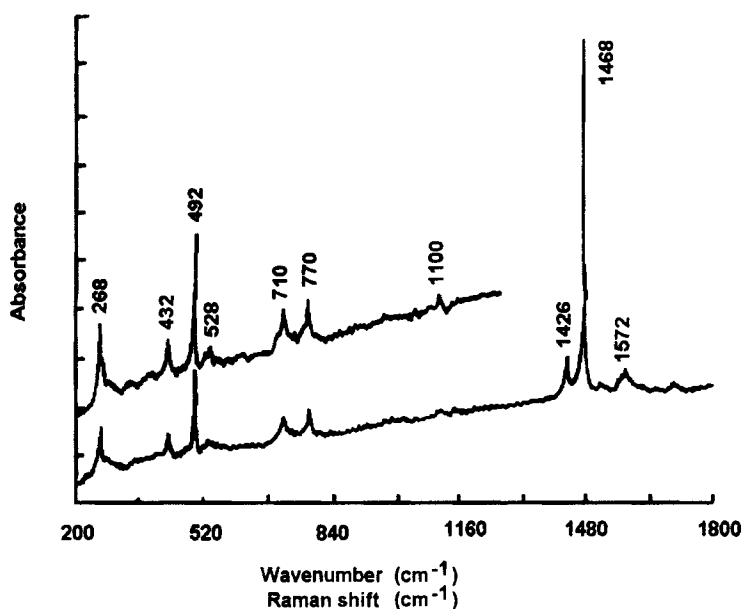
Electron energy (eV)	Relative intensity			
	C_{60}^+	C_{60}^{2+}	C_{70}^+	C_{70}^{2+}
70	100	60.73	100	27.23
60	100	41.73	100	21.61
50	100	22.49	100	12.96
40	100	12.55	100	1.99
30	100	8.64	100	0
20	100	4.81	100	0
10	100	0	0	0

Table 2
The relationship between negative ion intensity and electron energy

Electron energy (eV)	Intensity of ions (v)	
	C_{60}^-	C_{70}^-
2.5	0.45	0.60
5.0	0.25	1.25
7.5	0.23	1.50
10.0	0.18	1.50
12.5	0.10	1.80
15.0	0.04	1.05
17.5	0	0.60
20.0	0	0.15
22.5	0	0

2. Electron ionization mass spectrometry of C_{60} and C_{70}.

Positive and negative ion mass spectra of C_{60} and C_{70} were measured using electron ionization and in-beam methods. Source temperature was 250°C. In the positive ion spectra, the C_{60}^+ (m/z 720) and C_{70}^+ (m/z 840) peaks are the dominant features, the doubly charged ions C_{60}^{2+} (m/z 360) and C_{70}^{2+} (m/z 420) are the second and third largest peaks, resp.,while the triply charged ions C_{60}^{3+} (m/z 240) and C_{70}^{3+} (m/z 280) are also clearly visible. In addition the relative intensity of the doubly charged ions is strongly affected by electron energy, the relationship between the intensity and electron energy is shown in Table 1. Negative ion mass spectra of the C_{60}/C_{70} mixture were very simple, there were only C_{60}^-, C_{70}^- and their isotopic ions present, no fragment ions or multi-charged ones. As indicated in Table 2. the C_{60}^- and C_{70}^- ions were formed under considerable lower electron energy.

Absorbance

268 432 492 528 710 770 1100 1426 1468 1572

200   520   840   1160   1480   1800

Wavenumber (cm^{-1})
Raman shift (cm^{-1})

Fig. 3 The Raman Spectrum of C_{60}

3. Vibrational Raman spectra

The C_{60} fullerene molecule has icosahedral structure and is assigned to the I_h point group. It has 174 normal modes of which 4 are infrared active and 10 are Raman active. The symmetry species of the IR and Raman modes are $4T_{1u}$, and $2A_g + 8H_g$ resp. [5-8]. The IR and Raman spectra obtained in our experiments are identical to those in Ref. [5]. The infrared spectrum of C_{60} deposited on a KBr plate has four strong bands at 1426, 1181, 576 and 525 cm^{-1}. The Raman spectra of the C_{60} fullerene film coated on a silver surface shows ten bands (Fig. 3, Table 4).

In further studies of the Raman spectra of the fullerene films coated on Ni, Si, Cu, Ag, KBr and quartz plate surfaces were observed. The depolarization ratios ($\rho = I/I_1$) of the 1466 cm^{-1} band (belonging to the totally symmetric A_g species) are shown in Table 3. The different depolarization ratio values suggested that the interaction between the C_{60} molecule and the surface of each substrate is different in each case. The interaction is increasing in the order:

Table 3
The depolarization ratio (ρ) of C_{60} coated on different substrates

Substrate	I	I_1	$\rho(I/I_1)$
KBr	34	209	0.16
Cu	47	278	0.17
Ni	39	184	0.21
Quarz	99	365	0.27
Si	60	195	0.31
Ag	225	325	0.69

Fig. 4 The SER spectrum of C_{60} adsorbed on an Ag film

KBr, Cu, Ni, quartz, Si and Ag. This result showed that the spherical C_{60} fullerene molecule of high I_h symmetry is easy to distort and its symmetry is reduced under the action of the substrate surface. The surface enhanced Raman (SER) spectrum of the fullerene C_{60} adsorbed on a silver surface film has also demonstrated the distortion of the spherical C_{60} molecule under the action of the silver film surface. Garrell [9] observed that in the SER spectrum of pure C_{60}

Table 4
SER and Raman bands (cm^{-1}) of C_{60}

SER C_{60} on Au[10]	[b]SER C_{60} on Ag	Raman [b]C_{60}	C_{70}[5]
175w			
256sh			261m
270s	268w	272m	
340m	338m		
398w			400w
419m	428m	432w	411w
			450w
488s	490s	492s	
			501w
510w-m	524m		
551w	554w		
575w			573w
700m,br	706m-s	710w	706m
730m			739m
766m	770m	770m	770w
	826w		
962w,br	966w		
	1062m		
1088w	1086w	1100w	
1186w	1204w		1186s
1235w	1244w	1250w	1231s
1307vw			1298w
			1317w
			1336w
1393w	1354w		1370m
1422w-m	1424m-s	1428w-m	1424m
			1448s
1452vs	1466vs	1466vs	1471m
			1517m
1559s	1564m-s		1562vs
	1596m	1570w	
	1676w		

Abbreviations: w=weak, m=medium, s=strong, vs=very strong, ms=medium strong, br=broad, sh=shoulder

[b] Raman data obtained from our experiments

adsorbed on a gold electrode with no applied potential 22 bands can be identified. In addition to bands similar to those in the bulk C_{60} Raman spectrum there is a band that may correspond to a metal-C_{60} molecule vibration and other new bands agree closely to bands in the C_{70} Raman spectrum. Garrell proposed that the symmetry of C_{60} is decreased in the interfacial environment and this causes the new modes to become Raman-active. Moskovits [10] has also observed similar effects. In our SER spectrum of C_{60} adsorbed on silver film 18 bands could be identified (Fig. 4). A comparison with the bands in the Raman spectrum of bulk C_{60} and C_{70}, and the SER spectrum of C_{60} on Au electrode is listed in Table 4. It may be seen from Table 4. that most of the bands in the SER spectrum of C_{60} on a silver film are similar to those on the gold electrode, but that there are fewer bands on the silver film than on the gold electrode. This observation may be explained by considering the different deformability of the electron clouds on the silver and gold atoms. The deformability the Au electron cloud is greater than that of the Ag atom, so the induced polarization is greater on gold. Therefore the C_{60} molecules adsorbed on an Au surface could undergo a greater distortion and a more extensive symmetry reduction.

Our observation of the depolarization ratio of the symmetric vibration band and of the SER spectrum of C_{60} provided more support to the conclusion that the C_{60} molecules adsorbed on a substrate surface undergo distortion and symmetry reduction. On the other hand this effect may also be used for the investigation of the interaction between the adsorbate and the surface of the adsorbent.

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