

# A photoluminescence study of C<sub>60</sub> and C<sub>70</sub>

S.P. Sibley, S.M. Argentine and A.H. Francis

*Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109, USA*

Received 24 September 1991

The luminescence spectra of C<sub>60</sub> and C<sub>70</sub> have been recorded in glassy toluene solution at 77 K and as neat solids at 5 K. The C<sub>70</sub> spectrum consists of two band systems each with resolved vibronic structure. The red system of C<sub>70</sub> begins at 15012 cm<sup>-1</sup>, exhibits a lifetime of < 20 μs and is assigned as S<sub>1</sub> → S<sub>0</sub> fluorescence. The infrared emission system begins at 12614 cm<sup>-1</sup>, decays with a 30 ms lifetime and is assigned as T<sub>1</sub> → S<sub>0</sub> phosphorescence. A weak luminescence maximum at 13579 cm<sup>-1</sup> is assigned tentatively as the S<sub>1</sub> → S<sub>0</sub> fluorescence of C<sub>60</sub>.

## 1. Introduction

Since their discovery by Smalley and co-workers [1,2], there has been considerable interest in the spectroscopic characterization of fullerenes, in particular the C<sub>60</sub> (buckminsterfullerene) and C<sub>70</sub> forms that may be produced in reasonable yields using a method described by Krätschmer et al. [3]. The first electronic absorption spectrum of solid fullerenes (a C<sub>60</sub>/C<sub>70</sub> mixture) was reported by Krätschmer et al. [4]. Both Ajie et al. [5] and Hare et al. [6] have studied the electronic absorption spectra of pure C<sub>60</sub> and C<sub>70</sub> in *n*-hexane in the 200–800 nm region and report similar results. Slight differences in the reported peak positions occur principally in the weak long-wavelength region, reflecting the difficulty of a precise determination of the actual onset of absorption.

Arbogast et al. [7] determined a number of important photophysical properties of C<sub>60</sub> in hexane and benzene solutions. Neither fluorescence nor phosphorescence could be detected from C<sub>60</sub> at room temperature. However, the triplet state was detected in high yield by triplet–triplet absorption measurements, and photoquenching studies placed the triplet state energy between 11541 and 14688 cm<sup>-1</sup>.

The luminescence of C<sub>70</sub> in toluene glass at 77 K was reported by Wasielewski et al. [8], and the luminescence spectra of C<sub>60</sub> films by Reber et al. [9]. A number of authors have measured other photoex-

cited state properties of C<sub>60</sub> and C<sub>70</sub> including transient absorption [10] and triplet state energies by calorimetric [11] methods.

We have examined the photoluminescence of C<sub>60</sub> and C<sub>70</sub> in toluene glasses at 77 K and obtained spectra from both materials. These results and their preliminary analysis are the subject of this Letter.

## 2. Experimental

### 2.1. Sample preparation

C<sub>60</sub> and C<sub>70</sub> samples were prepared by a slight modification of the method described by Krätschmer et al. [3]. Two graphite rods were arranged in a vertical, co-linear fashion so that gravity held the upper rod in contact with the lower by a constant 0.2 kgf. The assembly was placed inside a bell jar containing 150 Torr of helium gas and a discharge was ignited between the graphite rods at the point of contact. The discharge was sustained for about 1 min at a current of about 125 amp during which approximately 0.3 g of graphite was converted to a soot-like material deposited on the surfaces of a pyrex envelope surrounding the graphite rods. C<sub>60</sub> and C<sub>70</sub> were isolated and purified by methods described in the literature [5,6,12]. The "soot" was collected, extracted with toluene and the C<sub>60</sub> and C<sub>70</sub> components separated by column chromatography on

alumina using mixtures of hexane and toluene as eluents. A purple ( $C_{60}$ ) and orange-red ( $C_{70}$ ) solution were obtained. Solid  $C_{60}$  and  $C_{70}$  samples were obtained by evaporation of the chromatographic solvents. The solid was redissolved in toluene for spectroscopic studies.

The purity of the samples was ascertained from HPLC chromatograms (with hexane as eluent) and from UV absorption spectra. The HPLC chromatograms showed only single peaks corresponding to the pure materials. The UV spectra were recorded in hexane solution and compared with those reported for the pure materials. No evidence of the strong ( $\epsilon \approx 10^5$ )  $C_{60}$  absorption peaks could be detected in the  $C_{70}$  sample. The purity of the isolated  $C_{60}$  and  $C_{70}$  materials was estimated to be  $> 99$  mol%.

## 2.2. Spectroscopic measurements

Photoluminescence (PL) spectra were recorded of solid, polycrystalline samples and glassy solutions at both 5 and 77 K. Samples were cooled in a Janis 10DT cryostat by a flow of cold  $N_2$  or He gas or by direct immersion in liquid cryogen.

Luminescence was excited with the filtered output of a high-pressure 450 W xenon arc lamp. The luminescence intensity was optimized with broad-band excitation into the weak, long wavelength absorption band using a  $CuSO_4$  solution that transmits between 29400–18300  $cm^{-1}$ . The luminescence was passed through a Corning 2-63 glass filter to remove scattered excitation wavelengths, then dispersed with a 1 m scanning monochromator and detected with a cooled, red-sensitivity enhanced, Hamamatsu R1767 photomultiplier tube. The spectra were digitally recorded through a Keithley model 575 interface and corrected by computer for the response of the photometric system.

The wavelengths of luminescence peaks were determined by measuring their positions relative to atomic iron and neon emission lines that were superimposed directly upon the sample luminescence spectra. The error in peak position is estimated to be approximately  $\pm 5$   $cm^{-1}$ .

## 2.3. Lifetime measurements

The PL lifetimes were recorded using a 10 J xenon flash lamp with a 10  $\mu s$  duration to excite emission. The transient luminescence was monitored at selected wavelengths using the optical system described above. The output of the photomultiplier was processed by a transient averager to record the luminescence decay.

## 3. Results and discussion

### 3.1. $C_{70}$ luminescence

Fig. 1 illustrates the photoluminescence spectrum obtained from  $\approx 10^{-4}$  M glassy toluene solution of  $C_{70}$  at 77 K. The spectrum has been corrected for the response of the photomultiplier. The spectrometer bandpass (indicated in fig. 1) was substantially less than the linewidths of the narrowest lines recorded. The positions of the luminescence peaks are collected in table 1.

The PL spectrum can be divided into two parts: a weak, red system between 15000–14000  $cm^{-1}$  composed chiefly of three or four weak, broad peaks, and an infrared system between 12500–10000  $cm^{-1}$  composed of a larger number of relatively intense, sharp bands. The red system begins with a weak peak at 15012  $cm^{-1}$ ; the first peak of the infrared system is observed at 12614  $cm^{-1}$ . The approximately 2600  $cm^{-1}$  separation between the red and infrared systems is too large to represent a vibronic interval and is more typical of the separation between the first excited singlet and triplet states of larger molecules. The emission lifetime of the red system was determined to be  $< 20$   $\mu s$ , whereas the infrared emission decayed with a lifetime of  $30 \pm 3$  ms. Therefore, the two systems must represent either emission from two different chemical species, or from two electronic states of the same chemical species.

The first emission peak of the red system (15012  $cm^{-1}$  in toluene glass at 77 K) is nearly coincident with the first absorption band reported by Hare et al. [6] (15038  $cm^{-1}$  in benzene at 300 K). However, detailed comparison is made ambiguous by matrix differences that can cause slight shifts of the absorption and emission origins. For example, Aije et al.

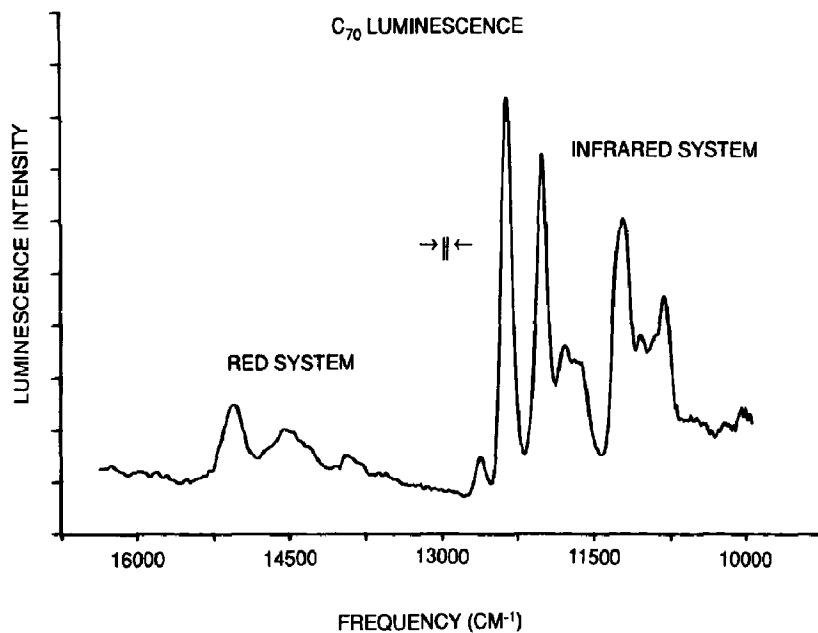


Fig. 1. Photoluminescence spectrum of  $C_{70}$  in glassy toluene solution at 77 K. The spectrum has been corrected for phototube response.

Table 1  
Photoluminescence and absorption bands observed in the spectra of  $C_{70}$

Photoluminescence				Absorption in hexane at 25°C (from ref. [6])		
frequency <sup>a)</sup> ( $cm^{-1}$ )	difference ( $cm^{-1}$ )	analysis <sup>b)</sup>	description	frequency <sup>a)</sup> ( $cm^{-1}$ )	difference ( $cm^{-1}$ )	description
10830	1784		med.	14925	0	onset
10929	1685		shoulder	15038	466	weak
11064	1550	0-1568	weak	15504	1091	weak
11224	1390	0-260-2×571	med.	16129	1629	weak
11252	1362		med.	16667		weak
11669	945		shoulder, med.	18182		weak
11796	818	0-260-571	med.	21368		med., broad
12014	600	0-571	sharp, strong	26455		med.
12360	254	0-260	sharp, strong	27778		med.
12614	0	0-0	$T_1 \rightarrow S_0$ , sharp, weak	30211		med.
13777	1235			42373		strong
13863	1149		weak	46729		strong
14284	728		shoulder			
14503	509		weak			
14681	331		shoulder			
15012	0	0-0	$S_1 \rightarrow S_0$ , weak			
15244			onset			

<sup>a)</sup> The infrared system frequencies of sharp, med. and strong bands are estimated to be accurate to  $\pm 5 \text{ cm}^{-1}$ ; red system frequencies are estimated to be accurate to  $\pm 10 \text{ cm}^{-1}$ .

<sup>b)</sup>  $C_{70}$  Raman frequencies from ref. [13].

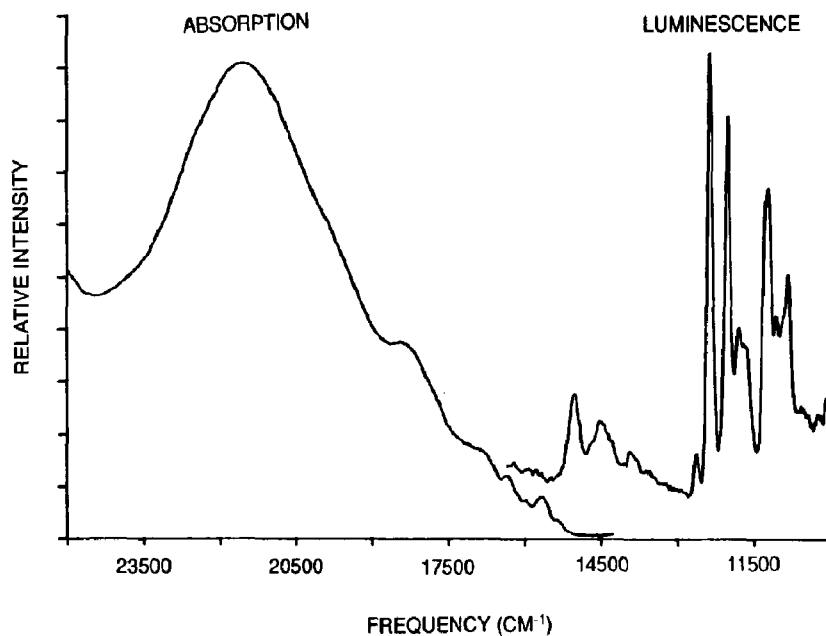


Fig. 2. Comparison of the absorption (in hexane at room temperature) and the photoluminescence (toluene glass at 77 K) spectra of C<sub>70</sub>.

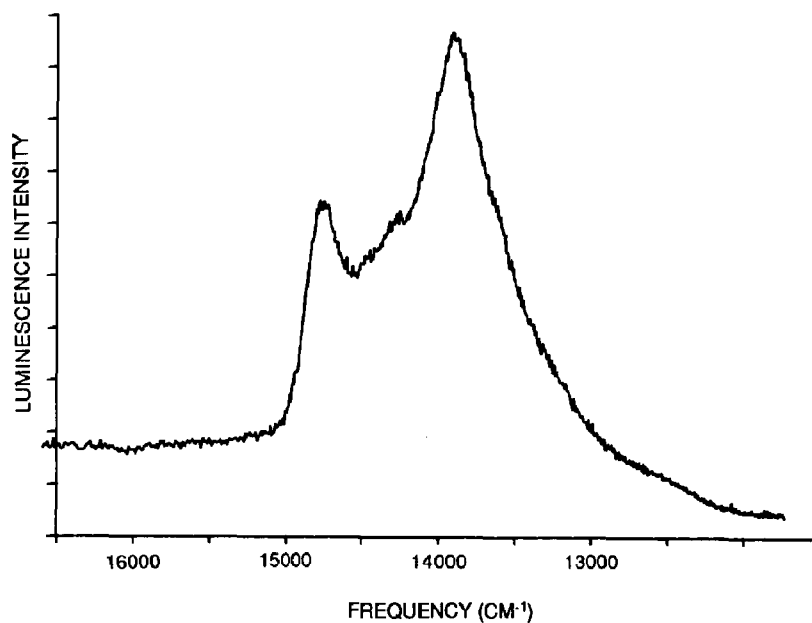


Fig. 3. Photoluminescence spectrum of solid, polycrystalline C<sub>70</sub> at 5 K.

[5] report the first absorption peak in hexane at 15699 cm<sup>-1</sup>, or 687 cm<sup>-1</sup> to higher energy of our first emission peak in toluene glass (see comparison

in fig. 2). Coincidence of the absorption and emission origins seems probable, based on our comparison of the spectra, but cannot be regarded as estab-

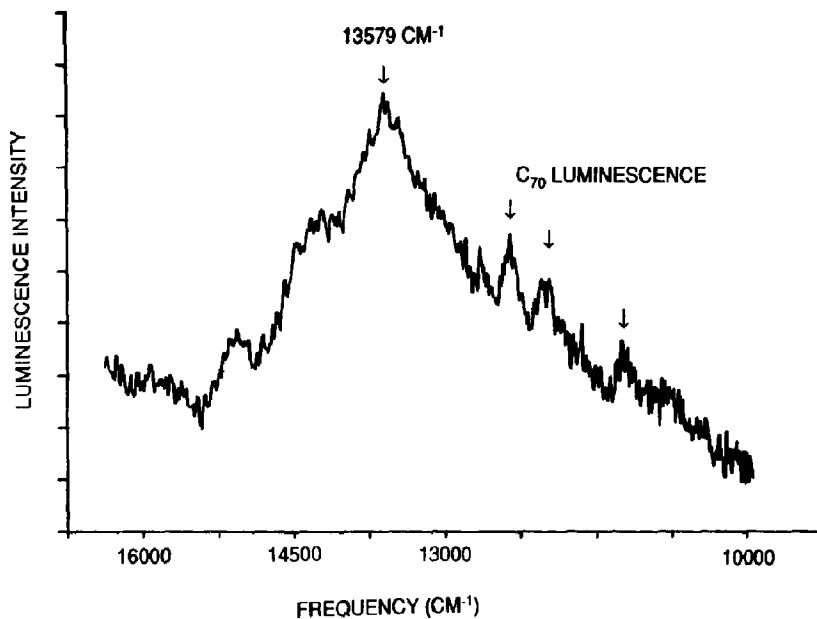


Fig. 4. Photoluminescence of C<sub>60</sub> in 10<sup>-4</sup> M glassy toluene solution at 77 K.

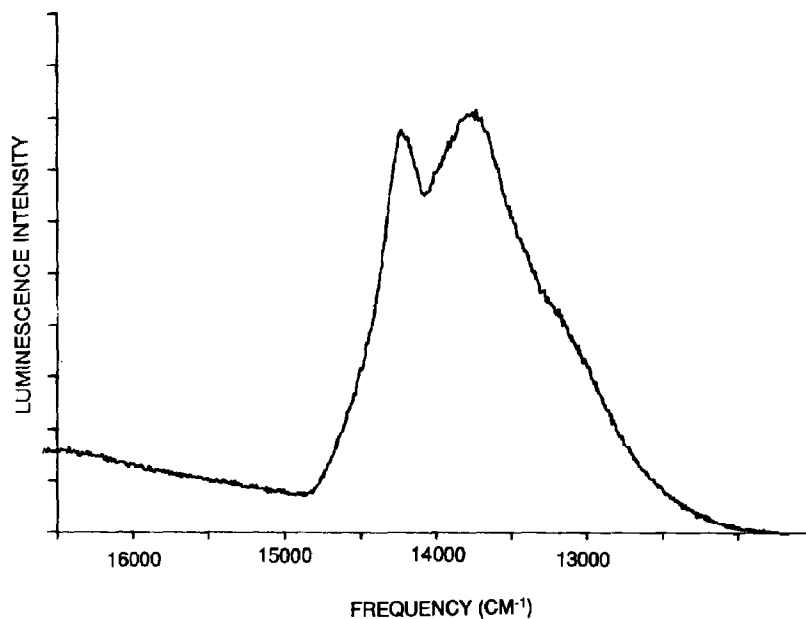


Fig. 5. Photoluminescence spectrum of solid, polycrystalline C<sub>60</sub> at 5 K.

lished by our measurements.

Collectively, these observations suggest that the red system luminescence corresponds to C<sub>70</sub> S<sub>1</sub>→S<sub>0</sub> fluorescence. The apparent coincidence of the absorp-

tion and fluorescence origins implies that the transition is electric dipole allowed. Its relatively low molar extinction may indicate that the transition is "overlap forbidden" due to poor spatial overlap of

the HOMO and LUMO orbitals.

The luminescence spectrum of solid microcrystalline  $C_{70}$  obtained at  $\approx 5$  K is shown in fig. 3. The spectrum consists of a short wavelength peak ( $14815\text{ cm}^{-1}$ ) followed by a broad region of luminescence exhibiting several inflections. The first solid  $C_{70}$  luminescence peak is red shifted by about  $197\text{ cm}^{-1}$  relative to the corresponding toluene glass luminescence. The solid luminescence most likely corresponds to the  $S_1 \rightarrow S_0$  red system luminescence of  $C_{70}$  in toluene glass.

The vibrational envelope of the infrared system agrees well with a broad emission spectrum of  $C_{70}$  in toluene glass at 77 K reported by Wasielewski et al. [8]. These authors were able to demonstrate that the infrared luminescence is associated with a strong photocxcited triplet EPR signal. Moreover, both the luminescence and the paramagnetic signal decayed with the same 51 ms lifetime. We obtained a  $30 \pm 3$  ms lifetime in degassed toluene glassy solutions at 77 K. These results contrast markedly with a lifetime of 0.41 ms determined for  $C_{70}$  cooled in a supersonic jet and measured by R2PI [14]. From these observations, we assign the infrared band system to  $T_1 \rightarrow S_0$  luminescence. The relatively small separation of  $S_1$  and  $T_1$  implied by these assignments ( $\Delta E_{ST} \approx 2600\text{ cm}^{-1}$ ) is about a third the value typically found in aromatic condensed ring hydrocarbons. The small separation is consistent with a considerably reduced value of the electron correlation expected if the HOMO and LUMO orbitals are delocalized over the large dimensions of  $C_{70}$ .

The positions of the infrared system bands are reported in table 1. The weak, sharp band at  $12614\text{ cm}^{-1}$  has a markedly shorter lifetime than the other bands in the infrared and may originate from a different spin sublevel of  $T_1$ .

The Raman spectrum of  $C_{70}$  solid has been reported by Bethune et al. [13] and several of the Raman frequencies reported may be observed as combination bands in the infrared system. It was not possible to observe directly the very weak  $T_1 \leftarrow S_0$  absorption, since the concentration of  $C_{70}$  required exceeded its solubility in the toluene glass at 77 K. If the  $T_1 \rightarrow S_0$  transition is symmetry allowed, then the  $12614\text{ cm}^{-1}$  band may correspond to the electronic origin and the remaining features to Raman modes built upon the weak electronic origin. A tentative

partial analysis is based on this assumption. If the transition is symmetry forbidden, then the  $12614$ ,  $12360$  and  $12014\text{ cm}^{-1}$  bands probably correspond to vibronic origins and cannot be further analyzed without more detailed information concerning the infrared active modes of  $C_{70}$ .

### 3.2. $C_{60}$ luminescence

Luminescence has not been previously observed from  $C_{60}$  in glassy solution at 77 K. However, the luminescence of solid  $C_{60}$  films has been reported [9]. Fig. 4 illustrates the very weak PL spectrum obtained from a  $\approx 10^{-4}$  M solution of  $C_{60}$  in toluene glass at 77 K. The spectrum has not been corrected for photomultiplier response. The purity of the  $C_{60}$  sample was  $> 99$  mol%, yet several of the bands (indicated) clearly arise from  $C_{70}$  impurity. Although the quantum efficiency for  $C_{70}$  luminescence is very low, it is evidently much greater than for  $C_{60}$  luminescence and we have found it difficult to reduce  $C_{70}$  contamination to levels sufficient to permit observation of only  $C_{60}$  luminescence.

The  $C_{60}$  PL spectrum exhibits a maximum at  $13579\text{ cm}^{-1}$  and spans  $\approx 2500\text{ cm}^{-1}$ . The onset of luminescence appears to be at approximately the same frequency as for  $C_{70}$ , but cannot be located accurately. The lifetime of the red  $C_{60}$  emission is  $< 20\text{ }\mu\text{s}$  and it appears most likely that the luminescence is  $S_1 \rightarrow S_0$  fluorescence.

The PL spectrum of a  $C_{60}$  polycrystalline sample (shown in fig. 5) is considerably more intense and qualitatively similar to the corresponding  $C_{70}$  PL spectrum. The crystal luminescence is observed in the same energy range as the luminescence from  $C_{60}$  in glassy toluene at 77 K. The spectra are distinctly different, however, and we do not believe that the solution luminescence is due to polycrystalline material that crystallized from solution upon cooling.

### Acknowledgement

The authors acknowledge support from the National Science Foundation (DMR 8818371) and the Donors of the Petroleum Research Fund, administered by the American Chemical Society. The authors thank Jeffrey Schkeryantz for his help in the

purification and purity analysis of the fullerene materials.

## References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, *Nature* 318 (1985) 162.
- [2] R.E. Smalley, in: *Atomic and molecular clusters*, ed. E.R. Bernstein (Elsevier, Amsterdam, 1990).
- [3] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* 347 (1990) 354.
- [4] W. Krätschmer, K. Fostiropoulos and D.R. Huffman, *Chem. Phys. Letters* 170 (1990) 167.
- [5] H. Ajie, M.M. Alvarez, S.J. Anz, R.D. Beck, F. Diederich, K. Fostiropoulos, D.R. Huffman, W. Krätschmer, Y. Rubin, K.E. Schriver, D. Sensharma and R.L. Whetten, *J. Phys. Chem.* 94 (1990) 8630.
- [6] J.P. Hare, H.W. Kroto and R. Taylor, *Chem. Phys. Letters* 177 (1991) 394.
- [7] J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz and R.L. Whetten, *J. Phys. Chem.* 95 (1991) 11.
- [8] M.R. Wasielewski, M.P. O'Neil, K.R. Lykke, M.J. Pellin and D.M. Gruen, *J. Am. Chem. Soc.* 113 (1991) 2774.
- [9] C. Reber, L. Yee, J. McKiernan, J.I. Zink, R.S. Williams, W.M. Tong, D.A.A. Ohlberg, R.L. Whetten and F. Diederich, *J. Phys. Chem.* 95 (1991) 2127.
- [10] Y. Kajii, T. Nakagawa, S. Suzuki, Y. Achiba, K. Obi and K. Shibuya, *Chem. Phys. Letters* 181 (1991) 100.
- [11] R.R. Hung and J.J. Grabowski, *J. Phys. Chem.* 95 (1991) 6073.
- [12] R. Taylor, J.P. Hare, A.K. Abdul-Sada and H.W. Kroto, *J. Chem. Soc. Chem. Commun.* (1990) 1423.
- [13] D.S. Bethune, G. Meijer, W.C. Tang and H.J. Rosen, *Chem. Phys. Letters*, in press.
- [14] R.E. Haufler, L.-S. Wang, L.P.F. Chibante, C. Jin, J. Conceicao, Y. Chai and R.E. Smalley, *Chem. Phys. Letters* 179 (1991) 449.