Photoluminescence of molecular C_{70} at 1.5 K. On the nature of the lowest excited states

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Abstract

We report Shpol'skii-type luminescence spectra of C_{70} in n-pentane at 1.5 K with vibronic linewidths of 3 cm^{-1}. The vibronic structure of both fluorescence and phosphorescence has been unravelled. The fluorescence intensity largely shows up in vibronic bands corresponding to transitions to ground-state infrared-active vibrational modes and it is concluded that the first excited singlet state of C_{70} in alkanes is of A'_2 character.

1. Introduction

The investigation of the lowest electronically excited states of fullerenes like C_{60} and C_{70} is both interesting and difficult because of the large density of close-lying and mostly degenerate states. For C_{70} the electronic structure of the lowest excited states of singlet and triplet multiplicity is an open question. In quantum-chemical calculations on C_{70} of D_{5h} symmetry by Hückel and Hartree–Fock methods the LUMO (lowest unoccupied molecular orbital) and LUMO + 1 orbitals were found too close in energy to infer which one is lowest [1,2]. The orbital character of the lowest excited state is predicted to be either A'_2 or E'_1 corresponding to, respectively, an electric-dipole forbidden and a (weakly) allowed transition to the ground state. From INDO/CI calculations Feng et al. [3] concluded to an S_1 of A'_2 symmetry. Fulara et al. [4] suggested that the vibra-

tional structure of the $S_1 \leftarrow S_0$ absorption of C_{70} in a neon matrix is indicative of an S_1 of E'_1 symmetry, while Leach [5] proposed an alternative assignment of this structure corresponding to an S_1 of A'_2 symmetry.

The long-wavelength absorption derives from a number of overlapping transitions which suggests that the study of the luminescence may well provide an easier access to the nature of the lowest excited states. Indeed, for the icosahedral C_{60} molecule we have recently reported well-resolved fluorescence spectra both from solution and from single crystals at 1.2 K [6]. Analysis of the vibronic intensity distribution led us to conclude that the first excited singlet state of molecular C_{60} has a mixed T_{1g}, G_g, and T_{2g} character. Among a number of low-temperature luminescence studies on C_{70} [7–14], those in a frozen methylcyclohexane solution [10–13] and in a crystalline toluene matrix [14] have led to well-resolved

fluorescence and phosphorescence spectra. The fluorescence in methylcyclohexane extends from about 15600 down to 12650 cm^{-1} where it gets overshadowed by the more intense phosphorescence whose vibronic structure could be followed down to about 10600 cm^{-1}. The positions of both the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ electronic origins were determined and the intensity of these 0–0 transitions relative to that of the vibronic bands was reported to depend strongly on the solvent [13]. In this study the vibronic structure was largely assigned to e'_2 modes and S_1 and T_1 were identified as of E'_1 symmetry.

Both theoretical and experimental limitations as yet preclude definite conclusions regarding the nature of the lower excited states. On the one hand, calculations of the expected vibronic intensity patterns of the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions including the activity of Herzberg–Teller and Jahn–Teller active modes are missing. On the other hand, a measurement of the fully resolved vibronic structure of the luminescence is necessary. In this Letter we describe luminescence spectra in three n-alkanes at liquid-helium temperatures and show that under fast cooling of a solution of C_{70} in n-pentane luminescence spectra are obtained with vibronic lines of about 3 cm^{-1} width. Besides the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ origins, these Shpol'skii-type spectra reveal 12 vibronic bands in the fluorescence and 19 in the phosphorescence with a relative intensity larger than 2% of the most intense band. We show that the occurrence of many vibronic bands in the fluorescence corresponding to transitions to ground-state vibrational levels involving infrared-active modes refers to the activity of Herzberg–Teller active modes in inducing fluorescence. Analysis of this vibronic coupling leads us to conclude that S_1 of C_{70} in alkanes is of A'_2 character.

2. Experimental

Highly purified C_{70} ($\geqslant$ 99.9%) was dissolved in sodium-dried n-heptane, n-hexane and n-pentane. The solutions were degassed and sealed in suprasil tubes with a diameter of 4 mm. Two methods of cooling were applied. Quick cooling consisted of plunging the sample directly into liquid helium. Slow cooling was achieved by immersing the sample tubes into

liquid nitrogen under a controlled rate of the order of centimeters per hour. The samples were then transferred into a liquid-helium filled cryostat.

For excitation either the 514 nm line of an Ar^+ laser, from which all other lines were suppressed using a band filter, or an Ar^+ pumped dye laser was used. Laser fluence was always kept low, with a maximum of 3 mW/mm^2. The emission of the sample was focussed onto the entrance slit of a 1 m monochromator and detected using an optical multichannel analyser (EG&G OMA-vision-CCD). Each CCD read-out in the region of interest covered about 200 cm^{-1} with an effective resolution of about 0.5 cm^{-1}. We calibrated all of these read-outs using a neon calibration lamp and merged them with specially designed software, which included a correction for the wavelength dependence of the quantum efficiency of the CCD.

3. Results and discussion

In Fig. 1 luminescence spectra at 1.5 K, upon excitation at 514 nm, are shown of frozen solutions of 5×10^{-6} M C_{70} in n-heptane, n-hexane, and n-pentane. The top spectrum concerns n-heptane (Fig. 1a). The fluorescence origin occurs at 15242 cm^{-1}, the phosphorescence origin at 12455 cm^{-1} and all bands have full-width at half-maximum somewhat less than 100 cm^{-1}. The spectrum is comparable to well-resolved spectra in similar solvents reported in the literature, e.g., those in methylcyclohexane [10–13]. For n-hexane, Fig. 1b, the spectrum looks quite different. While some relatively narrow features may still be recognized, these are superimposed upon a broad spectrum with a first band at 14740 cm^{-1}. In contrast to the spectrum from the n-heptane solution, that from the n-hexane solution depends on the rate of cooling and the position in the sample tube. A slow cooling results in a large contribution of the broad spectrum for irradiation of the centre of the tube, as in Fig. 1b. A similarly unstructured spectrum has been observed upon slow cooling of a solution in n-pentane, the first band being slightly narrower and shifted to 14830 cm^{-1}. As shown in Fig. 1c, for n-pentane sufficiently slow cooling may even lead to the virtual absence of the narrow-band spectrum. We attribute
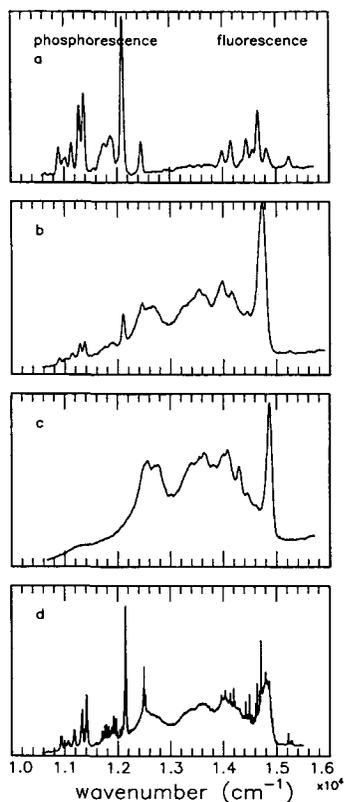
Fig. 1. The emission at 1.5 K of a 5×10^{-6} M solution of C_{70} in (a) n-heptane (slowly cooled), (b) n-hexane (slowly cooled), (c) n-pentane (slowly cooled), and (d) n-pentane (quickly cooled). Excitation at 514 nm.

the broad luminescence spectra (e.g., that in Fig. 1c) to clusters of C_{70} molecules because of their occurrence upon slow cooling and the low solubility of C_{70} in n-alkanes.

A more interesting observation follows upon fast cooling of the n-pentane solution (Fig. 1d). The broad spectrum is still there and in addition a spectrum consisting of narrow bands shows up both in the fluorescence and in the phosphorescence region. A closer look reveals that these bands consist of repetitive multiplet structures. Such a structure is illustrated for the strongest feature in the phosphorescence around 12150 cm^{-1} in Fig. 2a. At least eight lines spread over 90 cm^{-1} are recognized and the individual lines have widths of about 4 cm^{-1}. All bands in the phosphorescence show the same multiplet structure, i.e. line splitting and intensity distribu-

tion, except for the electronic origin. For the 0–0 transition (Fig. 2b) a similar splitting is present but the intensity ratio of the various lines is different from that for the vibronic multiplets. For the fluorescence the observations are qualitatively alike. Multiplets spread over 120 cm^{-1} are seen for all bands with a characteristic intensity distribution for all vibronic bands (Fig. 2c) and a different one for the origin (Fig. 2d).

The observations represented in Figs. 1d and 2 are reminiscent of the Shpol'skii effect [15], previously reported for C_{70} in a crystalline toluene matrix [14]. Upon cooling the n-pentane solution, rapid enough to avoid clustering of all C_{70} molecules, probably a glassy matrix is formed with crystalline regions. Within these microcrystals C_{70} molecules apparently occupy well-defined sites with a weak electron–phonon coupling and, correspondingly, the luminescence spectrum consists of narrow lines. The exceptional position of n-pentane compared to the longer n-alkanes may be related to the approximate match between the van der Waals dimensions of solvent and solute molecule. The length of n-pentane amounts to 7.4 Å and the width of C_{70} to 7.0 Å, while
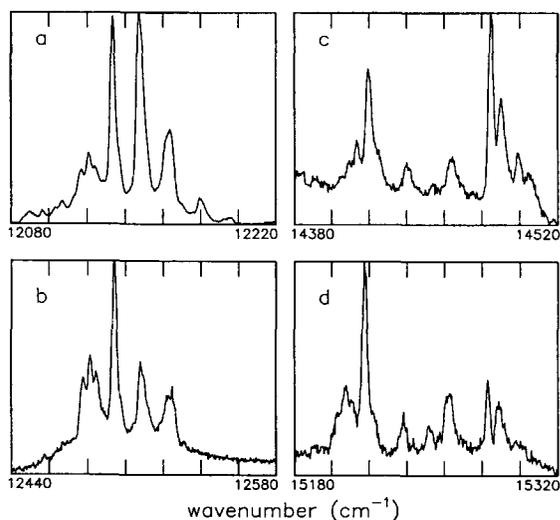

Fig. 2. Multiplets observed in the emission at 1.5 K of C_{70} in n-pentane upon cooling quickly and exciting at 514 nm. (a) A typical multiplet of a vibronic band in the phosphorescence, (b) the phosphorescence onset, (c) a typical multiplet of a vibronic band in the fluorescence, and (d) the fluorescence onset.

comparison of the molecular volumes suggests that one C_{70} molecule might replace two n-pentane molecules.

The C_{70} molecules are incorporated in a limited number of ways. These distinct sites make up for the multiplet structure of each band (see Fig. 2) owing to a slight variation in the solute–solvent interaction from site to site. The multiplets in the fluorescence cover a wider frequency range than those in the phosphorescence and there is no straight one-to-one relation between the lines in the fluorescence and phosphorescence multiplets. As the intensity distribution within the multiplets is the same for all vibronic bands in the phosphorescence, we conclude that this distribution reflects the number of C_{70} molecules in the various sites. The same reasoning holds true for the fluorescence and the resulting multiplet structure

is different from that for the phosphorescence because the coupling of singlet-excited C_{70} to the solvent matrix need not be the same as that of triplet-excited C_{70}. The distinct intensity patterns of vibronic and origin multiplets indicate that the mechanism by which the vibronic bands and the 0–0 transition get their intensity is different. This probably means that we have to do with intrinsically symmetry (D_{5h})-forbidden transitions (vide infra). In that case the intensity of the 0–0 transition depends on the (site-dependent) interaction with the environment of lower symmetry while the vibronic bands may acquire intensity through intramolecular (site-independent) vibronic coupling.

When shifting the laser excitation towards the absorption onset, site selection has been observed with a concomitant simplification of the lumines-

Table 1
Band positions and intensities in the luminescence spectrum of a 5×10^{-6} M solution of C_{70} in n-pentane at 1.5 K upon excitation at 656 nm (15235 cm^{-1}). The positions (σ) and relative positions with respect to the electronic origin ($\Delta\sigma$) are listed in wavenumbers. The accuracy is about 1 cm^{-1}, slightly worse for the band at 14921.1 cm^{-1}. The intensity is given relative to that of the strongest vibronic band. The onset and the first vibronic band of the fluorescence were too close to the laser frequency and could not be seen during site selection; the positions of these bands have been inferred from the fluorescence spectrum upon excitation at 514 nm. IR or R in columns 4 and 8 indicate that that particular frequency corresponds to an infrared- or Raman-active mode, respectively (from Refs. [17,21–26])

Fluorescence				Phosphorescence			
σ (cm^{-1})	$\Delta\sigma$ (cm^{-1})	Rel. int. (%)		σ (cm^{-1})	$\Delta\sigma$ (cm^{-1})	Rel. int. (%)	
15217.6		36.0		12494.8		14.3	
				12221.2	273.6	2.0	
14921.1	296.5	9.5					
				12134.1	360.7	100.0	R
				12102.9	391.9	6.7	
14797.5	420.1	28.0		12076.0	418.8	3.8	
14757.0	460.6	4.0	IR/R	12035.4	459.4	5.7	IR/R
				11982.0	512.8	2.0	
				11957.8	537.0	14.3	IR
14636.7	580.9	100.0	IR	11915.3	579.5	18.1	IR
				11872.5	622.3	4.8	
14540.4	677.2	24.0	IR	11818.8	676.0	8.6	IR
14505.9	711.7	10.0		11784.7	710.1	7.6	
				11748.0	746.8	10.0	
14420.0	797.6	56.0	IR	11697.2	797.6	7.4	IR
14128.4	1089.2	32.0		11405.4	1089.4	38.6	
				11317.5	1177.3	27.6	
13965.0	1252.6	15.2	IR				
13894.8	1322.8	2.0		11171.8	1323.0	12.9	
13789.1	1428.5	3.2	IR				
				11062.1	1432.7	2.7	IR
13735.4	1482.2	4.0					
				11002.5	1492.3	2.5	
				10930.1	1564.7	10.5	R

1.08   1.10   1.12   1.14   1.16
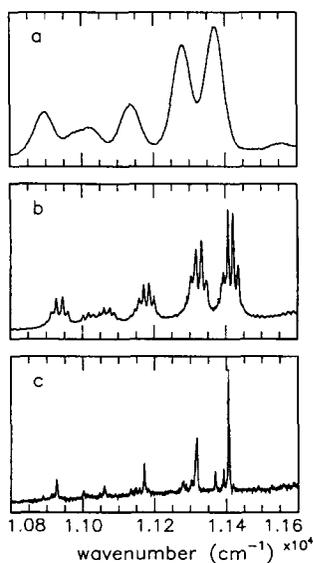wavenumber (cm^{-1}) $^{\times 10^4}$

Fig. 3. Resolution enhancement and simplification of a part of the phosphorescence spectrum of C_{70}. Spectrum of (a) a solution in n-heptane upon excitation at 514 nm with linewidths of 90 cm^{-1}, (b) a quickly cooled solution in n-pentane upon excitation of 514 nm, and (c) a quickly cooled solution in n-pentane upon excitation at 656 nm with linewidths of 3 cm^{-1}.

cence spectrum. Only one line of each multiplet in the fluorescence remains and by tuning the laser through the onset region we step from one line (i.e. site) to the other. A similar behaviour is observed for the phosphorescence but the selection appears less complete. For excitation at 656 nm (15235 cm^{-1}) all multiplets, both in fluorescence and in phosphorescence, reduce to a more or less single line. This is illustrated in Fig. 3 for some of the vibronic bands of the phosphorescence. Instead of a multiplet for each vibronic band upon excitation at 514 nm (Fig. 3b), one dominant feature with a width of 3 cm^{-1} is left for each vibronic band upon excitation at 656 nm accompanied by some smaller contributions from

other sites (Fig. 3c). Comparison with the corresponding part of the phosphorescence spectrum in n-heptane (Fig. 3a) reveals the gain in resolution achieved by site selection in the n-pentane Shpol'skii matrix. After elimination of the n-pentane Raman lines from the fluorescence region we are left with a luminescence spectrum from which the positions of the origin and the vibronic bands of fluorescence and phosphorescence have been obtained with a relative accuracy of about 1 cm^{-1}. Frequencies of 12 vibronic bands in the fluorescence and 19 in the phosphorescence with a relative intensity larger than 2% of the most intense band are summarised in Table 1. For the fluorescence the vibronic band 581 cm^{-1} from the $S_1 \rightarrow S_0$ origin is most intense, for the phosphorescence one band stands out at 361 cm^{-1} from the $T_1 \rightarrow S_0$ origin. The frequency shifts of the vibronic bands with respect to the electronic origins refer to vibrational quanta in the electronic ground state. The fluorescence and phosphorescence spectrum have at least eight vibrational frequencies below about 1500 cm^{-1} in common.

Convolution of the lines observed by site selection in n-pentane with a Gaussian envelope of 90 cm^{-1} width results in a vibronic intensity distribution similar to that observed in, e.g., n-heptane or methylcyclohexane. We infer from this that the description of the electronic structure of C_{70} in n-pentane to be given below may well apply for alkanes in general.

In order to find out about the electronic nature of S_1 and T_1, we consider which vibronic bands may occur in the luminescence spectrum for certain assignments. According to quantum-chemical calculations, the lowest excited singlet state S_1 of C_{70} is expected to transform as either A'_2 or E'_1 [1,2]. If $S_1 \equiv E'_1$, the $S_1 \rightarrow S_0$ transition is electric-dipole allowed and a'_1 vibrations may show up. This transi-

Table 2
Survey of symmetries of Herzberg–Teller active vibrational modes. The labels IR and R indicate which modes are infrared- and Raman-active, respectively

Electronic transition	Symmetry of Herzberg–Teller active vibrational modes
$^1A'_2 \rightarrow \, ^1A'_1$	a''_1, e'_1(IR)
$^1E'_1 \rightarrow \, ^1A'_1$	a'_1(R), a'_2, e''_1(R), e'_2(R)
$^3A'_2 \rightarrow \, ^1A'_1$	a''_1, a''_2(IR), e'_1(IR), e''_2
$^3E'_1 \rightarrow \, ^1A'_1$	a'_1(R), a'_2, e''_1(R), e'_2(R), e''_2

tion may well be weak and gain intensity through Herzberg–Teller coupling. The symmetry of the vibronic modes that could be involved is given in Table 2. If, on the other hand, $S_1 \equiv A'_2$, the $S_1 \rightarrow S_0$ transition is electric-dipole forbidden and vibronic bands may acquire intensity through Herzberg–Teller coupling (see Table 2). In particular, intensity may be borrowed from allowed $E'_1 \rightarrow A'_1$ transitions via coupling modes of e'_1 symmetry. The Herzberg–Teller active modes for the transition from $^3A'_2$ or $^3E'_1$ to the totally symmetric ground state are listed in Table 2 as well. For a molecule of D_{5h} symmetry, IR-active modes belong to a''_2 or e'_1 irreducible representations and Raman-active modes to a'_1, e''_1 or e'_2 irreducible representations. Consideration of Table 2 reveals that, as long as the Herzberg–Teller vibronic coupling scheme is appropriate, IR-active modes are expected in the luminescence only if the lowest excited state (singlet or triplet) has A'_2 orbital symmetry, and Raman-active modes only for E'_1 orbital symmetry. Besides, Jahn–Teller active modes (e'_1 or e'_2) may be present in the luminescence spectrum.

We can only present a tentative description of the vibronic structure of fluorescence and phosphorescence because knowledge of the vibrations of C_{70} is still limited. Various calculations of the 122 normal modes have led to different results [16–20] and a clear-cut assignment of the vibrational frequencies in infrared and Raman spectra to particular symmetry species is missing. Of the other vibrations even the frequencies are not known accurately enough to be of help in the interpretation of the luminescence spectra. In our description we only make use of experimental data [17,21–26]. On the basis of reported infrared and Raman spectra we have identified a number of vibrational quanta in fluorescence and phosphorescence as corresponding to infrared- or Raman-active modes. This is indicated in Table 1. A band at 459 ± 1 cm^{-1} shows up with considerable intensity both in infrared and Raman spectra. Other vibrational modes in the luminescence, in particular those of 420, 513, 747, 1089, 1177, 1323, and 1492 cm^{-1}, have been observed as weak bands both in infrared and in Raman spectra. One should note that there is, as far as we know, no infrared data available below 400 cm^{-1}.

As seen in Table 1, the most intense vibronic band of the fluorescence at 581 cm^{-1} from the

origin concerns an IR-active mode and the same holds for at least five of the other vibronic bands. As outlined above, this suggests that the first excited singlet state is of A'_2 character. The fluorescence origin is relatively strong in view of the A'_2 assignment of S_1. We presume that the electronic origin gets its intensity through matrix-induced static perturbations lowering the symmetry and mixing the close-lying A'_2 and E'_1 states. This would account for the strong dependence of the origin intensity on solvent as noticed earlier [13], and for the different intensity distribution among the multiplet lines of origin and vibronic bands. Preliminary emission experiments as a function of temperature reveal the occurrence of an additional fluorescence spectrum at higher temperatures in which the origin is the most prominent band. This is consistent with observations by Argentine and coworkers [12,13] and suggests to us that the $S_2 \rightarrow S_0$ transition is electric-dipole allowed, which points to an E'_1 character of S_2.

The many vibronic bands corresponding to IR-active modes in the phosphorescence (see Table 1) point to an A'_2 orbital character of the lowest triplet state as well (see Table 2). However, the most intense vibronic band at 361 cm^{-1} from the origin seems to concern a Raman-active mode and the same applies to the 1565 cm^{-1} band which indicates E'_1 orbital character of T_1. This suggests a mixed character of the lowest triplet state and the present picture might well turn out to be too naive. A further description of the luminescence spectra and of the lowest electronic states of C_{70} requires a theoretical analysis of the expected vibronic intensity distribution in fluorescence and phosphorescence.

4. Conclusion

The luminescence spectrum of a low-concentrated solution of C_{70} in n-pentane after quickly cooling to liquid-helium temperatures shows a superior resolution. Site selection, observed for excitation at the absorption onset, results in linewidths of 3 cm^{-1} and largely simplifies both the fluorescence and the phosphorescence spectrum. The vibronic intensity distribution of the fluorescence points to an A'_2 character of the lowest excited singlet state. The presence of intensity at the origin reveals that S_1 has

E'_1 character as well, which most probably results from the mixing of $S_1(A'_2)$ with the close-lying S_2 (E'_1) in an environment of symmetry lower than D_{5h}.

Acknowledgement

Note added in proof

While this paper was refereed we became aware of a paper by Negri and Orlandi (J. Phys. B., submitted) which describes the vibronic structure of the phosphorescence of C_{70} from a theoretical point of view. According to their calculations the most intense feature in our phosphorescence spectrum at 361 cm^{-1} from the origin probably concerns an infrared-active (e'_1) mode as well. We thank professor Orlandi for sending us a presprint of their paper.

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