

Unusual Photoluminescence Behavior of C₇₀

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Well-resolved photoluminescence (PL) spectra of C₇₀ and ¹³C₇₀ in a glassy methylcyclohexane matrix have been obtained over the range 10 000–16 000 cm⁻¹ at temperatures between 4 and 77 K. The PL spectrum consists of a short-lived, red fluorescence system extending from 14 000 to 15 500 cm⁻¹ and a longer-lived, IR phosphorescence system extending from 10 000 to 12 500 cm⁻¹. The PL spectrum is unusual in several aspects: the line widths are nearly 10-fold narrower than those of catacondensed hydrocarbons under similar conditions, and the temperature dependence suggests the presence of multiple emitting states (of the same spin multiplicity) or several emitting species in the highly dilute glassy matrix. To better understand the photophysical behavior of C₇₀, we have attempted to correlate vibrational frequencies in the IR and Raman spectra of C₇₀ and ¹³C₇₀ with the vibronic intervals observed in the PL spectra. The study of ¹³C₇₀ enabled a more detailed analysis of the vibronic structure of the fluorescence and phosphorescence spectra.

Introduction

In the past few years there has been intense interest in the photophysical properties of the fullerenes. C₆₀ and C₇₀ have received the most attention due to the availability of high-purity samples. As a result, these two fullerenes have been examined with a wide variety of spectroscopic techniques including NMR, IR, Raman, and electronic spectroscopy.

The electronic absorption spectrum of C₇₀ in solution has been recorded in detail in a variety of solvents.^{1–4} The red photoluminescence (PL) of C₇₀, although less thoroughly examined, has also been obtained in several solvents at room temperature.^{3–5} Several groups have examined the infrared PL of C₇₀ at ~77 K in glassy matrices and have reported fairly well-resolved spectra.^{2,6–8} The vibronic intervals of the PL spectra can be measured with sufficient accuracy to attempt a vibronic analysis that would lead to an identification of the orbital symmetry of the emitting states and a better understanding of the photodynamics of this extraordinary molecule. However, in the absence of a clear and convincing assignment of the Raman and IR vibrational spectra of C₇₀, it has not been previously possible to carry out a detailed vibronic analysis of the PL spectra. Such an analysis is further complicated by the variability of the PL spectra with temperature and solvent.

The PL spectra of C₇₀ in glassy matrices exhibit an unusual temperature dependence. Several of the most prominent features of the 77 K spectrum are completely absent from the 4 K spectrum. The C₇₀ spectrum also shows unexpected matrix effects. Features of the vibronic spectrum show significant relative intensity changes in different glassy hydrocarbon matrices. Collectively, the solvent and temperature sensitivity of the PL spectrum raises the possibility of multiple-state emission or emission from several different species in the glassy matrix.

As a result of the variable nature of the PL spectrum only a partial vibrational analysis has been published,⁸ and other aspects of the photophysical behavior of C₇₀ remain unexplained. We

have carried out a study of the temperature dependence of the PL spectrum of C₇₀ and ¹³C₇₀ between 4 and 100 K to improve the analysis of the vibronic structure and to better characterize the behavior of the emitting states. These studies have enabled us to make a more detailed analysis of the vibrational structure.

Experimental Section

Sample Preparation. The C₇₀ used for these studies was 98 wt % purity and was obtained from the MER Corp. ¹³C₇₀ was prepared from isotopically pure carbon-13 rods using the method described by Huffman and Kratschmer.^{9,10} To prepare the rods, ¹³C powder (99% ¹³C, Aldrich) was placed in a 0.125-in.-i.d. quartz tube between two tantalum rods. The assembly was evacuated to <2 Torr. A constant pressure of 2000 lb/in.² was applied to the tantalum rods while 10-A current pulses of 2–3-s duration were passed through the sample to drive out air and water. The carbon rods were then formed by increasing the applied current in steps while maintaining the powder under compression. A sequence of 10-, 50-, and 100-A currents, each applied for 10 s, resulted in the formation of high-quality rods. The rods were 10–15 mm long and similar in density to commercial graphite rods. The ¹³C rods were vaporized in the arc reactor, and pure ¹³C₇₀ was isolated from the resulting carbon soot by chromatography, as described previously.⁸

Photoluminescence Measurements. Spectrophotometric grade methylcyclohexane (MCH) was used to prepare 10⁻⁵ M solutions of C₇₀ and ¹³C₇₀. Here and throughout, the notation C₇₀ refers to the fullerene with the naturally occurring carbon isotopic distribution. The solutions were degassed in quartz tubes by several freeze–evacuate–thaw cycles and sealed under vacuum. Photoluminescence spectra of the glassy solutions were recorded at temperatures from 4 to 77 K by cooling the samples in a Janis 10DT cryostat with a flow of cold N₂ or He gas or by direct immersion in the cryogen liquid.

PL spectra could be excited with either the filtered output of a high-pressure 1-kW xenon arc lamp or the 488-nm line of an argon ion laser. All PL spectra shown in this paper were obtained by employing broad-band excitation into the weak, long-

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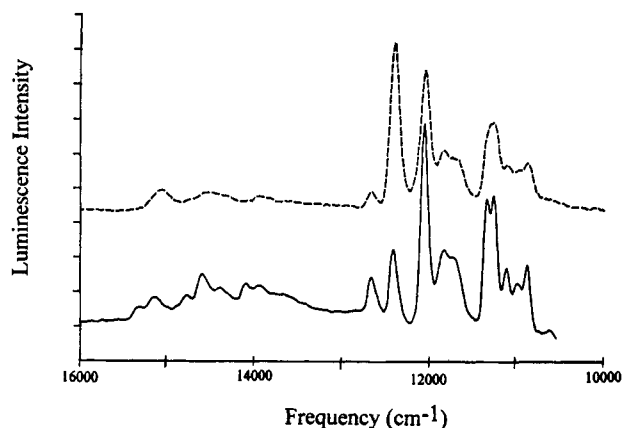


Figure 1. PL spectra in toluene (dashed) and MCH (solid) glasses.

wavelength absorption band of C₇₀ using a CuSO₄ solution that transmits between 29 400 and 18 300 cm⁻¹. The luminescence was passed through a Corning 2-63 glass filter to remove scattered excitation wavelengths and then dispersed with a 1-m scanning monochromator. The red fluorescence was detected with a cooled Hamamatsu R375 photomultiplier tube, and the IR phosphorescence was detected with a cooled, red-sensitivity-enhanced, Hamamatsu R1767 photomultiplier tube. To reduce noise in the weak PL spectra, the signal was modulated with a mechanical chopper, demodulated with a lock-in amplifier, and digitally recorded using a Keithley Model 575 interface.

To improve the accuracy of the wavelength measurements, the spectrum was calibrated with an atomic emission source. The atomic emission of rubidium has several lines in the IR that fall close to the lines of the C₇₀ PL spectrum. The wavelengths of the IR luminescence peaks were determined by measuring their positions relative to atomic rubidium lines that were recorded simultaneously with the sample luminescence using a beam splitter. The error in the wavelengths for peak positions is estimated to be approximately ± 5 cm⁻¹ and is determined chiefly by the line width of C₇₀ features.

Lifetime Measurements. Lifetimes were recorded using a 10-J xenon flash lamp with a 2- μ s duration to excite photoluminescence. The transient luminescence was monitored at selected wavelengths using the optical system described above. Because the PL excited in this manner was weak, it was necessary to average several hundred decay events with a transient averager in order to obtain improvement in the signal/noise ratio.

Results

Photoluminescence of C₇₀. The phosphorescence spectra of C₇₀ in glassy toluene and MCH matrices at 77 K are shown in Figure 1, and the band positions are reported in Table 1. The spectrum consists of a weak, short-lived fluorescence system from 15 606 to 13 979 cm⁻¹ and a stronger, longer-lived phosphorescence system from 12 659 to 10 603 cm⁻¹. The relatively small separation between the singlet and triplet states (2947 cm⁻¹) is due to the weak electron-electron repulsion expected in large molecules and suggests delocalization of the HOMO and LUMO orbitals over the molecular dimension of C₇₀.¹¹

The solvent matrix clearly alters the relative intensity of vibronic features in both the red fluorescence and IR phosphorescence systems. The dramatic changes in the relative intensity of the first two vibronic bands of the IR PL spectrum are most evident. Although a slight line broadening occurs in toluene glass, the vibronic features of the PL spectrum of C₇₀ exhibit unusually narrow line widths relative to those of condensed ring aromatic hydrocarbons recorded using similar conditions. The dramatic decrease in line width is revealed in Figure 2 by comparing the PL of corannulene (C₂₀H₁₀) and C₇₀, both recorded in MCH at 77 K with the same energy dispersion. The corannulene spectrum

TABLE 1: PL Bands of C₇₀ in MCH (¹³C₇₀ Bands Are in Parentheses)

freq (cm ⁻¹)	difference (cm ⁻¹)	analysis ^a	description ^c
10 603	1801	0-569-1165	w
		0-358-1447	
10 717	1687	0-569-1062	w
		0-358-1313	
10 859 (10 958)	1545 (1469)	0-358-1165	s, m
		0-1523	
10 969 (11 069)	1435 (1390)	0-358-1062	s, m
		0-1447	
11 096 (11 188)	1308 (1266)	0-1313	s, m
11 248 (11 333)	1165 (1121)	0-1165	s, m
11 324 (11 414)	1080 (1041)	0-1062	s, m
11 480 (11 581)	924 (873)	0-358-569	s, w
11 709 (11 796)	695 (659)	0-2*358	sh, m
11 827 (11 912)	577 (542)	0-569	m
12 056 (12 115)	348 (339)	0-358 ^b	s, st
12 404 (12 454)	0 (0)	0-0	T ₁ -S ₀ , sh, m
12 659			temp dep
13 123			
13 756			
13 976	1231	0-1227	s, m
14 138	1069	0-1062	m
14 334	873	0-358-569	sh
14 430	777	0-766	s, m
14 543	664	0-674	sh
		0-228-409	
14 642	565	0-569	s, st
14 805	402	0-409	s, m
14 852	355	0-358	sh
14 973	234	0-228	sh
15 336			temp dep
15 606			onset, temp dep

^a C₇₀ Raman frequencies from ref 34. ^b Exception to (a). This peak is from ref 36. ^c w = weak, m = medium, s = sharp, st = strong, sh = shoulder.

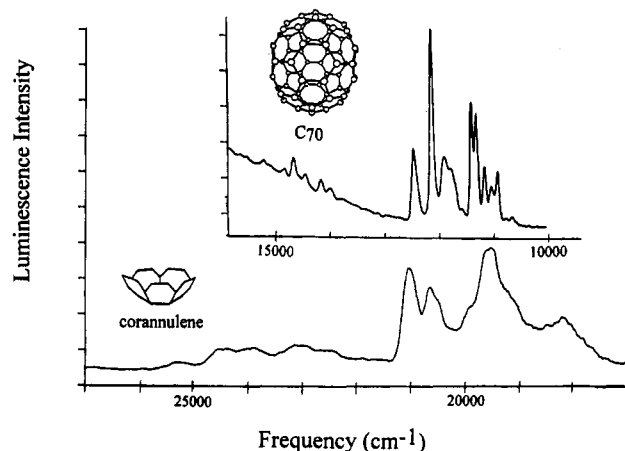


Figure 2. Corannulene and C₇₀ spectra in MCH glass.

is typical of large aromatic hydrocarbons in rigid glasses and is of particular interest because the corannulene carbon skeleton forms the dish-shaped end caps of C₇₀. A representative line width in the C₇₀ spectrum is ~ 80 cm⁻¹ (fwhm = full width at half-maximum), while a typical line width in the corannulene spectrum is ~ 400 cm⁻¹.

Cooling the C₇₀/MCH glassy solution to 4 K produces only a slight decrease in line width but causes significant changes in the relative intensity of the vibronic features (see Figure 3). The changes are most apparent in the first band (band A) of the IR system. As the temperature is decreased below 77 K, the intensity of band A decreases continuously and the intensity of all the other bands in the spectrum increases. The relative intensity of the partially resolved bands at 11 324 and 11 248 cm⁻¹ is also affected by cooling.

Similar changes with temperature are seen in the red system (Figure 4). As the temperature decreases only slightly below 77

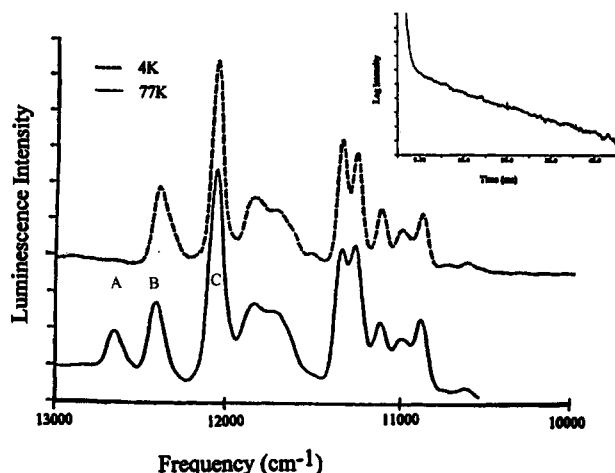


Figure 3. Comparison of C_{70} phosphorescence spectra in MCH glass taken at 77 and 4 K. Inset: phosphorescence lifetime at 77 K.

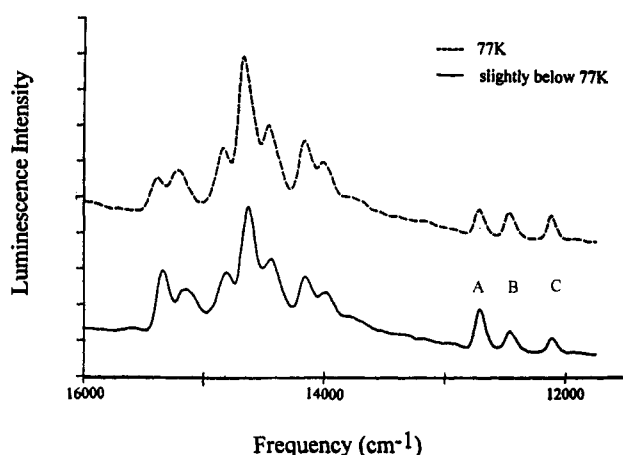


Figure 4. Comparison of the C_{70} fluorescence spectra in MCH taken at 77 K and slightly below.

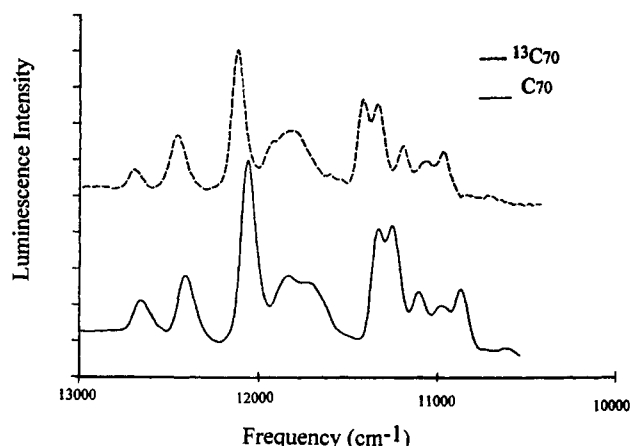


Figure 5. PL spectra of C_{70} and $^{13}C_{70}$ compared.

K, the very weak feature at $15\,606\text{ cm}^{-1}$ and the band at $15\,366\text{ cm}^{-1}$ both decrease in intensity relative to the other bands in the system.

Photoluminescence of $^{13}C_{70}$. The PL spectrum of $^{13}C_{70}$ is shown in Figure 5. All of the peaks in the spectrum are shifted to higher energy with respect to the C_{70} peaks, as expected. The positions of the bands are given in Table 1.

Lifetime Measurements. The IR PL spectrum exhibits a biexponential decay at 77 K (see Figure 3) that may be decomposed into a long-lived component with $\tau = 100 \pm 15\text{ ms}$ and a short-lived component with $\tau < 2\text{ ms}$. By examining the dependence of the PL spectrum on the modulation frequency of

the excitation source, it was possible to demonstrate that the highest-energy band has only the short-lived component, while the remaining vibronic features exhibit both short- and long-lived components.

Discussion

The unusual behavior of the IR photoluminescence is largely reproduced in the red fluorescence system where the first few members of the vibronic spectrum also exhibit matrix and temperature sensitivity. We have focused our analysis on the IR phosphorescence system. The variations in the vibronic structure of the IR spectrum with temperature and solvent indicate that the spectrum is composed of at least two superimposed spectra. There are several possible sources of the superimposed spectra, including multiple emitting states, multiple emitting species in solution, or multiple matrix environments. In the following discussion we examine the evidence for each of these possibilities.

Multiple Emitting Species. Recent investigations of the optical absorption spectra and the classical light scattering behavior of room temperature C_{60} and C_{70} solutions have suggested that these species associate in solution to form weakly bound clusters.^{2,6,12} For example, Sun and Bunker¹²⁻¹⁴ have shown that the absorption spectrum of C_{70} in a toluene/acetonitrile mixture changes abruptly as the volume fraction of acetonitrile increases above about 0.6. The results suggest the association of the solute C_{70} into clusters as the fraction of acetonitrile, a poor solvent for C_{70} , increases. Ying, Marecek, and Chu¹⁵ have carried out classical light scattering measurements on benzene solutions of C_{60} at room temperature and have concluded that aggregation occurs slowly in solutions at concentrations of about 10^{-3} M . The mean radius of gyration at optical frequencies suggests the formation of weakly bound clusters of about 16.5 nm in diameter. In addition, Martin et al.¹⁶ have reported recently that the clusters of C_{60} were found in the solid state where the highest aggregation number observed was 55.

Since the solubility of C_{70} in MCH is quite poor, it is possible that C_{70} clusters form in solution upon standing or as the temperature is lowered to the glass transition temperature ($T_G = 126\text{ K}$). Although association may occur in MCH, we do not believe that this is the origin of the observed spectral changes. The relative intensity of the temperature-dependent features appears to be insensitive to concentration, solvent, rate of cooling, or other details of the sample preparation that would be expected to affect the relative concentrations of associated species. For example, the temperature-dependent changes in the vibronic structure of the C_{70} IR system are similar in both toluene and MCH glass.

Moreover, cluster formation is expected to produce a diffuse spectrum and a shift of absorption to longer wavelength as observed by Sun and Bunker.¹² Similar effects should be observed in the luminescence of clusters but are not observed in our spectra. For these reasons, we have tentatively discarded the formation of clusters as the origin of the anomalous behavior of the PL spectrum.

Multiple-State Emission. Multiple-state emission (MSE) from large molecules is an uncommon phenomenon since, according to Kasha's rules, fluorescence typically occurs only from the lowest vibrational state of the lowest excited state of a given multiplicity.¹⁷ The MSE of azulene and many of its derivatives is a well-known example of this phenomenon.^{18,19} Here, the MSE is believed to be due to slow relaxation from the second singlet state as a consequence of its large energy separation from the lowest excited singlet. As a result, radiative relaxation from the second singlet state competes successfully with nonradiative relaxation to the lowest excited singlet state, and two fluorescence systems with distinct lifetimes and greatly different energies are observed.

Multiple-state fluorescence has also been observed in a number of compounds that have close-lying thermally equilibrated singlet

states. The compounds shown to exhibit this behavior contain at least two distinct but weakly coupled chromophores, as in homopolar diaryl molecules such as 1,1'-binaphthyl²⁰ and others.^{21,22} Multiple-state phosphorescence from the phenyl alkyl ketones^{23,24} is phenomenologically similar to the multiple-state fluorescence of the biaryls. A short-lived intense emission dominates in rigid solution, with a long-lived and lower-energy emission increasing its contribution as the viscosity decreases.

MSE often exhibits this substantial dependence on solvent viscosity. At high viscosities and in solid solution, only higher-energy emission is observed; at low viscosity MSE is observed. This behavior has generally been attributed to a solvent-mediated molecular deformation in the excited state to produce a double minimum in the potential with one minimum directly above the ground-state minimum and the other somewhat displaced. Evidently, MSE can arise from the separate conformations when they are sufficiently stabilized by a viscous solvent medium. These mechanisms do not appear to apply to the fullerenes in which the chromophore subunits are strongly coupled and there is little possibility of solvent-modified deformation of the relatively rigid molecular geometry.

However, the orbital degeneracy of many low-energy states and the exceptionally high density of excited states may lead to MSE from the C₆₀ and C₇₀ fullerenes. In the case of C₆₀, for which more computations have been completed, there are 15 symmetry-forbidden transitions^{25,26} predicted in the range 21 280–17 540 cm⁻¹. The second excited singlet has been computed²⁷ to be only 240 cm⁻¹ above the first excited singlet state. Therefore, we must consider the possibility that MSE of C₇₀ arises from transitions involving nearby excited states.

The spin-orbital degeneracy of the T₁ state leads to the possibility that the MSE may arise from different magnetic substates of the triplet. This situation is commonly observed in the triplet luminescence of many aromatic hydrocarbons.²⁸ Molecular orbital calculations^{29,30} for D_{5h} C₇₀ have identified a HOMO of a''₂ symmetry and a LUMO of e''₁ symmetry. Thus, the ground-state configuration is of overall symmetry A'₁, and the first excited-state configuration (a''₂)(e''₁)¹ has symmetry E'₁. Spin-dipolar interaction and spin-orbit coupling may remove the 6-fold degeneracy of the ³E'₁ state, giving rise to states of spin-orbital symmetries A''₁, A''₂, E'₁, and E''₂.

Electric dipole emission to the vibrationless ground state may be observed from the E'₁ and A''₂ states but is forbidden from the other spin-orbital states. However, vibronic transitions terminating on ground-state non-totally-symmetric modes may be observed from the other spin-orbital states. In order for MSE to occur from either higher electronic states or higher spin-orbit states, the higher states must satisfy at least one of the following conditions: (1) they must be in thermal equilibrium with the longer-lived lowest emitting state or (2) they must relax slowly to lower states relative to their luminescence lifetime.

If MSE from thermally equilibrated states is the cause of the superimposed PL spectra, then the emission intensity from one state must decrease as the emission intensity from the other state increases. We can see that this is clearly the case. MSE from spin-orbital states is a very plausible explanation for the unusual phosphorescence behavior of C₇₀. However, the fact that the fluorescence system is exhibiting the same temperature-dependent behavior weakens this possibility and leads us to believe that MSE arises instead from higher electronic states.

Multiple Emitting Matrix Sites. The apparent superposition of PL spectra may arise from the existence in the matrix of multiple distinct solvent environments as occurs, for example, in a Shpol'skii matrix. It is believed that the MCH matrix is completely vitreous. The PL spectra of many aromatic hydrocarbons in MCH glasses exhibit only inhomogeneously broadened, Gaussian line shapes. If multiple, distinct solvent environments are responsible for the

spectral behavior observed, they would probably arise through unusual fullerene-solvent interactions (e.g., weak complex formation).

Vibronic Analysis. A satisfactory vibronic analysis of the PL spectrum can be achieved in terms of the Raman-active fundamentals of C₇₀ and *single* electronic origins for the red fluorescence and IR phosphorescence systems. We have assumed that all temperature-independent peaks arise from emission from the C₇₀ monomer.

For an electronic transition to be allowed, integrals of the transition moment integral must all be nonzero: $\langle \Phi_e^* | \mu | \Phi_g \rangle$. In D_{5h} symmetry, the x and y components of the transition dipole moment operator transform as e'₁ and the z component as a''₂. The pure electronic transition from the lowest triplet state to the ground state is then allowed since $\langle E'_1 | e'_1 | A'_1 \rangle$ contains the totally symmetric representation (a₁). $\langle \Phi_e^* | \mu | \Phi_g \rangle$ must be nonzero for an allowed vibronic transition. Since Φ_g^* is a₁ for emission at low temperature, μ must correspond to a Raman mode or combinations for vibronically allowed transitions.

Based on the symmetry of the C₇₀ molecule as D_{5h}, there are 53 allowed Raman modes: 12 a₁', 22 e₂', and 19 e₁'. The calculated normal mode Raman assignments and frequencies reported in the literature vary considerably.^{27,31–33} However, the experimental frequencies reported by several authors are in good agreement.^{34–36} The vibronic intervals of the phosphorescence system can be assigned as totally symmetric a₁' Raman modes or combinations of these modes using the frequencies reported in the literature^{27,32} if an electronic origin at 12 404 cm⁻¹ is assumed. All of these fundamental Raman modes have been observed in room-temperature Raman studies, with the exception of the 0–1 transition at 349 cm⁻¹. This Raman mode was observed in a SERS investigation³⁶ of C₇₀ and in a Raman study of C₇₀ at low temperature (T = 23 K).³⁷ It appears that this mode is a weakly allowed Raman transition at room temperature, but it is a strongly allowed electronic transition at low temperature. It is also of interest that the interval between the first two peaks of the corannulene phosphorescence is of nearly the same frequency (386 cm⁻¹). This mode may, therefore, correspond to a distortion that is largely localized in the "dish"-shaped end caps of the C₇₀ structure. The peak at 12 659 cm⁻¹ is tentatively determined to arise from the multiple state emission from a nearby second electronic state.

The positions of the phosphorescence bands of ¹³C₇₀ can be predicted from the positions of the C₇₀ phosphorescence bands since the vibrational intervals are proportional: $\Delta\nu^{(13)} = \sqrt{12/13} \Delta\nu^{(12)}$. Our experimental band positions of ¹³C₇₀ are in very good agreement with the predicted values; they differ by no more than 2.5%. This isotopic study helps us establish that the bands are not due to impurity. While not completely convincing, the ¹³C₇₀ analysis suggests that the peak marked B in Figure 3 is the electronic origin.

The modes of the fluorescence system can be treated in much the same manner as the modes of the phosphorescence system. We observe the highest-energy band of the fluorescence system at 77 K in MCH glass at 15 366 cm⁻¹, in reasonable agreement with Wang⁶ (15 361 cm⁻¹) and Palewska² (15 400 cm⁻¹). A very weak feature at higher energy (15 606 cm⁻¹) appears at temperatures slightly above liquid nitrogen temperature. This feature may correspond to a band reported by Catalan et al.⁴ at 15 576 cm⁻¹ in the fluorescence spectrum of C₇₀ in cyclohexane at 77 K. The band increases with temperature and is a much stronger feature in the room temperature solution fluorescence spectrum. The peaks at 15 606 and 15 366 cm⁻¹ are tentatively assigned as MSE. The peak at 15 207 cm⁻¹ is regarded as the allowed electronic origin, and the remaining features correspond to Raman modes and combinations of these modes built upon this origin.

Origin of the Anomalous Narrow PL Line Width. It is not

possible to determine the origin of the unusually narrow line widths observed in the luminescence spectra of C_{70} in hydrocarbon glasses. However, we have had excellent success in predicting the temperature dependence of the line width, peak intensities, and the displacement of the first absorption and luminescence maxima in the spectrum of C_{60}^- ions in solution and glassy matrices using the classical Condon approximation.³⁸ The success of this approach suggests that the relatively rigid fullerene carbon skeleton can be treated as a rigid body that couples weakly to low-frequency lattice modes described by a single configuration coordinate.

Conclusion

The PL spectrum of C_{70} in glassy matrices consists of at least two superimposed spectra. The spectra are best analyzed in terms of multistate emission from a single photoexcited molecular species. The multistate emission may involve the magnetic substates of the lowest photoexcited triplet state.

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