Multiplet Structure in the Absorption, Fluorescence, and Phosphorescence of Mixed Molecular Crystals

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Solid solutions of one aromatic hydrocarbon in another have frequently been used to examine the details of the electronic states of the substitutional impurities (guests).[1,2] In the course of a detailed optical study of phenanthrene and decadeuterophenanthrene (guests) in biphenyl and decadeuterobiphenyl (host lattices) at 4·2° K we have observed that the absorption ($^1A_1 \rightarrow {}^1A_1$), fluorescence ($^1A_1 \leftarrow {}^1A_1$), and phosphorescence ($^1A_1 \leftarrow {}^3B_1$) bands of the guest are actually multiplets of two or more closely spaced bands. These materials are mutually soluble over all concentration ranges. Every vibronic band in the 4·2° K spectra consists of a prominent doublet; the other

[1] D. S. McClure, *J. Chem. Phys.*, 1954, **22**, 1668.
[2] D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals," Solid State Physics, Vol. 8, ed. F. Seitz and D. Turnbull, Academic Press, New York, 1959.

components of the multiplets are weaker by a factor of about one hundred. A few of the doublet components are given in the Table.

The possibility that the observed multiplet structure is due to an impurity was dismissed because the associated multiplet splittings for the different host–guest pairs are identical within

rotate slightly to minimize internuclear repulsions. Any large rotations would be inconsistent with the well-polarized absorption spectra we have observed on the bc^1 face. Our measurements on this face confirm that the (o, o) transition is allowed and polarized along the short molecular axis (M).[5] The components of the doublet arise from two
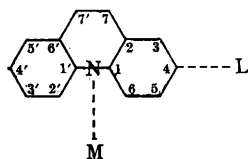
Band positions of multiplet components[a]

	Phenanthrene[b] in	Decadeuterophenanthrene	Decadeuterophenanthrene
	in biphenyl[c]	in biphenyl	in decadeuterobiphenyl[c]
Absorption..		28,634s, 28,620m; (0, 0)	
Fluorescence	28,143s, 28,123m; (0—405)[d]	28,240s, 28,222m; (0—394)[e]	28,238s, 28,223m; (0—394)
	21,375m, 21,365s; (0, 0)	21,466m, 21,456s; (0, 0)	21,462m, 21,454s; (0, 0)
Phosphorescence ..	20,969m, 20,957s; (0—405)		21,070m, 21,063s; (0—394)

[a] Experimental procedure and analyses will be described in a later publication.
[b] Anthracene free; zone-refined 30 passes.
[c] Zone-refined 30 passes.
[d] Raman[1]. R. Manzoni-Ansidei, *Ricerca Sci.*, 1936, **7**, 314.
[e] Deuterium analogue of 405 cm.[-1].

experimental error. The strong doubling in each vibronic band is not the result of coupling with any of the six normal optical and accoustical rotational lattice modes of the host since the multiplet splittings are about $\frac{1}{3}$ to $\frac{2}{3}$ of the lowest librational frequency of the biphenyl unit cell (known to be 30 cm.$^{-1}$).[3] In fact we also observe, and have analyzed, the librational frequencies in our spectra.

Our interpretations of the mixed crystal spectra are based on the biphenyl X-ray data of Trotter.[4] If it is assumed that the phenanthrene molecules are oriented in the lattice parallel to the biphenyl molecules, and that the centres of the C_1–C_1' bonds of phenanthrene and biphenyl lie at the same lattice site, calculations show that two of the distances between hydrogens on the phenanthrene and the nearest biphenyl are less than twice the Van der Waals radius of hydrogen. Because the phenanthrene molecule has no centre of inversion there is no symmetry restriction on its location in the lattice. The phenanthrene may translate and

states that appear to correspond to two inequivalently located guest molecules. The multiplet splittings and the intensity distribution within the multiplets are independent of guest concentration over the range from 10^{-2} to 10^{-5} mole/mole. The polarization ratios (I_b/I_a), from absorption measurement on the ab-face at 4·2° K, are 2·25 and 1·50 for the higher and lower component of the absorption origin doublet, respectively, which shows that the inequivalent guests are rotated with respect to one another in the ground state. Small rotations about the N axis increase internuclear repulsions so we disregard these. Rotations about the polarization axis (M) would cause no absorption polarization ratio difference between the two multiplet components on ab as observed. The measurements are consistent with two inequivalent species angularly related by a rotation about the phenanthrene L axis. This result confirms the conclusion of Brandon, Gerkin, and Hutchison that the molecular planes of phenanthrene (guest) in its phosphorescent state and

[3] K. Krebs, S. Sandroni, and G. Zerbi, *J. Chem. Phys.*, 1964, **40**, 3502.
[4] J. Trotter, *Acta Cryst.*, 1961, **14**, 1135.
[5] D. S. McClure, *J. Chem. Phys.*, 1956, **25**, 481.

biphenyl (host) are not parallel.[6] In addition, we suggest that these mixed crystals contain inequivalently oriented guest molecules.

The intensity ratios of the two strong components of each band in fluorescence and absorption are $1\cdot5 : 1$ (peak to peak) in favour of the higher-energy component. In the phosphorescence spectra the intensity ratio is $2\cdot1 : 1$ in favour of the lower-energy component. The average splitting in absorption and fluorescence is 17 ± 2 cm.$^{-1}$; and in phosphorescence 9 ± 1 cm.$^{-1}$.

Using antisymmetrized products of guest and host wavefunctions the interaction of the singlet guests and the singlet exciton states of the host reduces to the difference between two-centre coulomb and exchange integrals between host and guest orbitals. The interaction of the lowest triplet state of the guest and the nearby (1500 cm.$^{-1}$) triplet exciton band[7] of the host involves only exchange terms that are considerably smaller[8] than the singlet coulomb interactions. The displacement of a guest can lead to a decreased energy of its singlet state and to an increased energy of its triplet state if the overlap of excited host and guest orbitals is different for the two orientations.

The multiplet splittings in these crystals are about the same magnitude as those observed in the emission spectra of frozen solutions of aromatic molecules in paraffin hydrocarbons.[9] We suggest, by analogy, that the so-called quasi-linear spectra observed in the Shpol'skii effect are to some extent caused by inequivalently located solute molecules, substitutionally dissolved in a paraffin crystal. As yet we are unable to exclude the possibility that the hydrogen–hydrogen repulsions in the mixed crystals are partially relieved by a rotation of the phenyl rings of the neighbouring biphenyl molecule. That situation would be analogous to the existence of frozen-in rotational isomers of paraffin molecules[10] giving rise to inequivalent solute molecules in the Shpol'skii effect.

(Received, February 11th, 1965.)

[6] R. W. Brandon, R. E. Gerkin, and C. A. Hutchinson, jun., *J. Chem. Phys.*, 1964, **41**, 3717.
[7] R. E. Merrifield, *J. Chem. Phys.*, 1955, **23**, 401.
[8] W. R. Heller and A. Marcus, *Phys. Rev.*, 1951, **84**, 809.
[9] 'E. V. Shpol'skii, *Soviet Phys. Uspekhi*, 1960, **3**, 372.
[10] 'E. V. Shpol'skii, A. A. Il'ina, and L. A. Klimova, *Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, 935.