Analysis of the Low Temperature Fluorescence and Phosphorescence Spectra of p-Difluorobenzene

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The low temperature fluorescence spectra (4.2 K) of solid solutions of p-difluorobenzene-h_4 (pDFB-h_4) and $-d_4$ have been recorded and analyzed. The absence of fluorescence from vibrationally excited states at 4.2 K eliminates the sequence and "hot band" structure which complicate the analysis of the vapor fluorescence spectrum. On the basis of a comparison of our vibrational analysis with those published for the vapor phase fluorescence, several incorrect assignments in the latter have been identified. The high resolution and lack of spectral congestion obtained in the low temperature matrix isolated fluorescence spectra also allowed additional vibrational assignments to be made. These results are of added importance because of the extensive use which has been made of pDFB for radiationless relaxation studies in the vapor phase. The phosphorescence spectrum of crystalline pDFB-h_4 was observed with sufficient intensity to locate the electronic origin to make several vibrational assignments. Additionally, the zero-field splitting of the first triplet excited state was measured by optically detected magnetic resonance techniques.

INTRODUCTION

para-Difluorobenzene has been the subject of frequent spectroscopic investigation over the last 30 years because of its stability, large fluorescence quantum yield, and manageable number of degrees of freedom. Previous studies have concentrated on the electronic absorption and fluorescence spectrum of pDFB in the vapor phase. The most recent published analysis of the vapor phase electronic spectrum is that by Cooper (*3*), but there is also an unpublished reanalysis by Zimmerman and Dunn (*4*). Recently, pDFB has been employed in a number of studies of intermolecular and intramolecular vibrational energy redistribution in the vapor phase (*12–19*). In these investigations, the dependence of the fluorescence quantum yield and the non-radiative lifetime upon the vibrational quantum state of the emitting level has been obtained. These results have substantially been compared with theoretical calculations based on different models for nonradiative relaxation in polyatomic molecules (*12–15, 17, 18*). The theory predicts a dependence of the nonradiative relaxation rate on the "excess vibrational energy" in the excited electronic state in qualitative agreement with the experimental results. Comparison of theory and experiment requires a detailed vibrational analysis of the absorption and fluorescence spectra and researchers have generally referred to those previously published by Cooper (vide infra).

The low temperature (4.2 K) emission spectrum of pDFB is simpler than that of the vapor phase. This is principally due to the absence of sequence and hot band structure. While the loss of sequence and hot band structure removes significant useful information from the spectrum regarding the changes in the electronic potential

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surface between the ground and excited electronic state, the simplification of the spectrum makes the assignment of the gross vibronic features observed far easier. Because of the low temperature employed, we may be completely certain that all features observed in the spectrum correspond to ground state fundamentals, their overtones, or combination bands. The narrow-line spectrum obtained from a correctly chosen low temperature matrix is largely free of phonon side-band structure.

Our study of the low temperature fluorescence spectra of $pDFB\text{-}h_4$/hexane solid solutions reveals several misassignments of the vapor phase fluorescence and resolves some conflicting assignments. Additionally, due to the simplicity of the low temperature fluorescence spectrum, it has been possible to make several additional assignments of vibrational features. When the vibrational assignments are corrected, the agreement between experiment and theory for quantum yield and nonradiative lifetime is improved.

Use of the low temperature matrix technique does present some disadvantages for comparison with vapor phase spectra. In particular, the reduction in site symmetry may effect the selection rules for electric dipole radiation, resulting in the appearance of vibronic features not observed in the vapor phase. Although this does occur, the matrix induced features are extremely weak and are readily identified.

EXPERIMENTAL DETAILS

$pDFB\text{-}h_4$ was obtained from Aldrich Chemical Company (>99% purity) and was used without further purification. $pDFB\text{-}d_4$ was prepared by deuterium exchange in D_2SO_4 and purified by repeated distillation. Mass spectral analysis of the DFB-d_4 sample showed that it contained 97 at.% deuterium and 94% $pDFB\text{-}d_4$. Solutions of 10^{-4} molar pDFB in cyclohexane were prepared using Aldrich Gold Label cyclohexane. Solvent blanks yielded no detectable fluorescence. The sample solutions were contained in 4-mm-o.d. cylindrical quartz tubes which were cooled at a rate of 1–2 K/min to 77 K and at a more rapid rate to the final temperature of 5 K in a Janis 10DT liquid helium cryostat. More rapid cooling to 77 K resulted in multiple site emission spectra due to inclusions of a high temperature metastable cubic phase in the low temperature monoclinic cyclohexane lattice (20, 21).

Emission was excited by the 2650-Å line emission of a 1-kW high pressure Xe–Hg lamp isolated with a Heath EU-700 grating monochromator. Emission was observed at 90° to the direction of excitation and dispersed in the second order of a 1-m Jarrell–Ash scanning monochromator. In this mode the effective band-pass of the monochromator is 1 cm^{-1}. The strong fluorescence signal was detected with a cooled EMI 6256-RF photomultiplier tube in combination with an SSR 1105 photon counter. The fluorescence spectra were calibrated with an iron/neon hollow-cathode discharge lamp to an estimated accuracy of ±1 cm^{-1}. The weak phosphorescence spectra were recorded in a similar manner. However, lower signal levels resulted in greater uncertainty in band positions (±5 cm^{-1}). The apparatus and techniques used for optically detected magnetic resonance (ODMR) measurements has been described in detail previously (22).

DISCUSSION

The molecular symmetry of $pDFB$ is D_{2h} (z parallel to the $F\text{-}F$ axis, y in plane) in both the ground and first singlet excited states. The first spin-allowed electronic

excitation is $^1B_{2u} \leftrightarrow {}^1A_g$, which is derived from the forbidden $^1B_{2u} \leftrightarrow {}^1A_{1g}$ (D_{6h}) transition of benzene which, in turn, derives its intensity from the electronically allowed $^1E_{1u} \leftrightarrow {}^1A_{1g}$ state. Since the ground state symmetry is preserved in the $^1B_{2u}$ state, only the six totally symmetric normal modes are formally active in the $^1B_{2u} \rightarrow {}^1A_g$ fluorescence spectrum.

Figure 1 displays the fluorescence spectra of pDFB-h_4 and -d_4 in cyclohexane matrix at 4.2 K. The vibrational assignments are annotated directly above the most prominent bands in the spectrum. The complete vibrational analyses of pDFB-h_4 and -d_4 fluorescence are given in Tables I and II, respectively. The frequencies of the ground state normal modes used in the vibrational analyses are those found by Zimmerman and Dunn ((10), hereinafter referred to as ZD), which are reproduced here in columns 1 and 2 of Table III. This list includes "hot band" frequencies obtained in the analysis
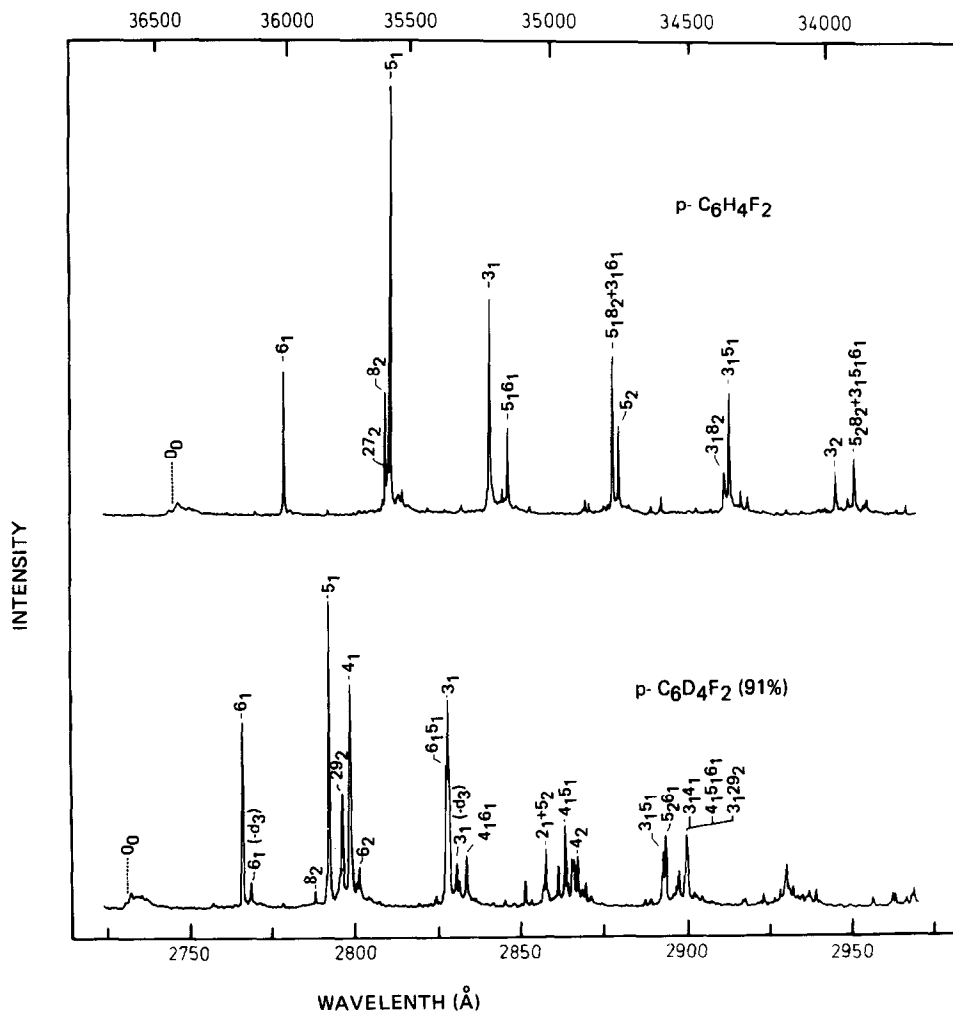

FIG. 1. Fluorescence of pDFB-h_4 and -d_4 in cyclohexane matrix at 5 K.

TABLE I

p-C$_6$H$_4$F$_2$ Fluorescence Frequencies and Assignments

ν (± 1 cm^{-1})	Relative Intensity (0–50)	cm^{-1} from Origin	Assignment
36480	--	0.0	origin
36147	0.5	333	30_2
36026	16.0	454	6_1
35842	0.6	638	26_1
35648	1.7	832	28_1
35638	13.7	842	8_2
35628	5.4	852	27_2
35620	46.9	860	5_1
35590	2.1	890	(phonon S.B. of 5_1)
35571	2.8	909	6_2
35344	1.1	1136	4_1
35227	23.7	1253	3_1
35184	2.9	1296	$6_1 8_2$
35165	9.6	1315	$6_1 5_1$
35065	0.8	1415	16_2
34886	1.4	1594	9_2
34870	1.1	1610	2_1
34815	0.9	1665	28_2
34805	0.9	1675	8_4
34779	17.6	1701	$3_1 6_1 + 5_1 8_2$
34752	9.8	1728	5_2
34719	0.6	1761	$6_2 5_1$
34658	2.8	1822	15_2
34496	0.6	1984	$<4_1 5_1$
34386	4.5	2094	$3_1 8_2$
34369	13.3	2111	$3_1 5_1$
34327	2.5	2153	$6_1 5_1 8_2 + 3_1 6_2$
34302	1.9	2178	$5_2 6_1$ (21_2)
34147	0.6	2333	--
34091	0.2	2389	--
33980	4.4	2500	3_2
33941	1.7	2539	$3_1 6_1 8_2$
33918	5.9	2562	$3_1 5_1 6_1$
33891	0.7	2589	20_2
33878	1.4	2602	5_3

of the electronic spectrum by ZD (*4*). Table III also contains the vibrational analyses published by Gates (*8*) in columns 3 and 4, respectively.

*p*DFB-*h$_4$* Fluorescence

The analysis of the *p*DFB-*h$_4$* fluorescence spectrum is at variance with the analyses of the vapor phase fluorescence in several important respects. Previous analyses of the vapor fluorescence have involved a ground state fundamental of ~250 cm^{-1} in

TABLE II

p-$C_6D_4F_2$ Fluorescence Frequencies and Assignments

$\nu(cm^{-1}\pm2)$	Relative Intensity (0-50)	cm^{-1} from origin	Assignment
36622	2	0.0	origin
36300	0.7	322	30_2
36171	26	451	6_1
36135	3	487	6_1(pDFB-d_3)
36010	0.7	612	26_1 or 9_1
35879	2	743	$8_2(28_1)$
35838	5	784	15_1
35831	43	791	5_1
35793	5	829	--
35785	15	837	29_2
35760	31	862	4_1
35735	3	887	--
35725	5	897	6_2
35431	1	1191	16_2
35386	20	1236	6_15_1
35381	30	1241	3_1
35378	18	1244	$9_2,26_2$
35344	6	1278	3_1(pDFB-d_3)
35332	4	1290	6_129_2
35302	6	1320	4_16_1
35300	7	1322	--
35192	1	1430	28_2
35113	3	1509	5_117_2
35090	1	1532	24_1
35042	2.5	1580	15_2
35035	8	1587	$2_1 + 5_2$
34986	5	1636	5_129_2
34958	11	1664	4_15_1
34950	2	1672	29_4
34933	7	1688	3_16_1
34927	6.5	1695	--
34924	6	1698	4_129_2
34911	8	1711	4_2
34893	2	1729	--
34881	3	1741	--
34857	2	1765	--
34660	1	1962	--
34642	1	1980	--
34600	8	2022	3_15_1
34592	11	2030	5_26_1
34552	3	2070	--
34546	5	2076	$5_16_129_2 + 3_129_2$
34523	4	2099	3_14_1
34517	10	2105	$4_15_16_1$
34491	1	2131	6_129_4
34488	1	2134	--
34480	1	2142	--
34463	1	2159	$4_16_129_2$

TABLE III

Ground State Vibrational Fundamental Frequencies of p-$C_6H_4F_2$ and p-$C_6D_4F_2$

	ν_i	$C_6H_4F_2$ (10)	$C_6D_4F_2$ (10)	$C_6H_4F_2$ (8)	$C_6D_4F_2$ (8)
a_g	1	3083.	2309.	3084	2313
	2	1615.	1595	1617	1595
	3	1257.3	1249.7	1245	1229
	4	1140.	866.9	1142	847
	5	858.6	793.0	858	780
	6	449.8	446.3	451	453
$\overline{a_u}$	7	945	780	943	--
	8	420	367	405	--
$\overline{b_{1g}}$	9	800	614	800	614
b_{1u}	10	3073	2276.	3065	2277
	11	1514.	1440.	1511	1435
	12	1228.	1129.	1225	1130
	13	1014.	858.	1012	859
	14	740.	685.	737	685
$\overline{b_{2g}}$	15	928	780	928	780
	16	692	600	692	600
	17	374.	358.	375	366
b_{2u}	18	3073.	2307.	3074	2310
	19	1633.	1328	1437	1328
	20	1306.	1286.	1285	1287
	21	1085.	802	1085	802
	22	348.	343.5	350	348
b_{3g}	23	3085	2304.	3084	2304
	24	1617	1523	1617	1523
	25	1285	1008	1285	1008
	26	635.	614.	635	614
	27	434	406	430	406
$\overline{b_{3u}}$	28	835.	731.	833	732
	29	505.	424.	509	422
	30	157.5	155.5	170	163

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Frequencies quoted correct to 1 decimal place are from vapour phase
infrared, Raman, fluorescence and electronic absorption studies.  Where
the accuracy is only ± 1 cm⁻¹, i.e., there is no precise measurement
from the electronic spectrum, and the measurement is from the
vapour phase, the number is followed by a period (e.g. 424.).

Out-of-plane vibrations are indicated by a bar over the vibration
class.
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many of the band assignments (3, 9). Initial concern about this assignment was raised by the absence of a Raman band at this frequency.

The matrix fluorescence spectrum does not show a band near 0–250 cm^{-1}, thus eliminating any possibility of a ground state vibrational assignment. It is clear that this band is associated with an excited state fundamental and that bands involving this mode in the vapor phase fluorescence spectrum are part of the "hot band" spectrum. The band 0–250-cm^{-1} is properly assigned as 8_1^1, the first member of the prominent $\nu_8(a_\nu)$ sequence (4). It should be noted that the prominent band 0–250 cm^{-1} and several related bands in the "hot band" spectrum have been treated as ground state fundamentals in studies of the nonradiative lifetime of pDFB-h_4 single excited vibronic levels in the vapor phase. This error in assignment results in an error

in the "excess vibrational energy" assigned to the level. When the assignment is corrected, the experimental value of the nonradiative lifetime is in far better agreement with theory (12).

Difficulty was encountered in locating the strongly reabsorbed electronic origin of the $^1B_{2u} \rightarrow {}^1A_g$ transition in both the pDFB-h_4 and -d_4 spectra. By adjusting the sample orientation to minimize the possibility of reabsorption, it was possible to observe the pDFB-h_4 origin directly. The position of the pDFB-d_4 origin was determined from the vibrational analysis.

The most interesting and controversial area of the spectrum is the region 800–900 cm^{-1} below the electronic origin. The major features include a strong band at 842 cm^{-1}, a moderately intense band at 852 cm^{-1}, and the strongest band in the spectrum at 860 cm^{-1}. All the bands in this region have been reported as polarized in the Raman spectrum of pDFB-h_4 and are undoubtedly in Fermi resonance. The 842- and 860-cm^{-1} bands were assigned as totally symmetric fundamentals by Ferguson et al. (2). Later, Stojiljkovic and Whiffen (5), in a study of a series of p-dihalogen benzenes, decided that a "more plausible assignment" for the 842-cm^{-1} band (854 cm^{-1} in their study) is $2\nu_{27}(b_{3g})$ in resonance with the $\nu_5(a_g)$858-cm^{-1} fundamental. Gates et al. (8) asserted that this assignment is supported by the Teller–Redlich product rule analysis of the pDFB-h_4 and -d_4 data. ZD (10), however, reassigned the 842-cm^{-1} band to $2\nu_8(a_u)$ which yields product rule agreement and is also consistent with the analysis of the prominent vapor phase sequences involving ν_8. It is noted that ν_8 is observed as a prominent vibronic origin in the two-photon $^1B_{2u} \leftarrow {}^1A_{1g}$ transition investigated by Robey and Schlag (11). The low temperature fluorescence spectrum clearly shows three bands in this region, which can, at once, accommodate the ZD $2\nu_8$ and Whiffen $2\nu_{27}$ assignments, both deriving intensity from Fermi resonance with the ν_5 fundamental.

It should be noted that combinations of the 842-cm^{-1} band are necessary to complete the assignment of the spectrum. In this respect, the second harmonic behaves much as an a_g fundamental. In the pDFB-d_4 spectrum, a band of equal relative intensity at 837 cm^{-1}, assigned as the second harmonic of the non-totally symmetric $2\nu_{29}(b_{3u})$, plays a similar role in forming combination bands. The importance of $2\nu_8$ and $2\nu_{29}$ in the spectra of pDFB-h_4 and -d_4 must be attributed to Fermi resonance interactions with nearby totally symmetric modes.

Two non-totally symmetric modes, $\nu_{26}(b_{3g})$ and $\nu_{28}(b_{3u})$ are active as vibronic origins in both the pDFB-h_4 and -d_4 spectra. Although unexpected, it is difficult to justify another assignment of these bands. It is likely that they are induced by the lower than D_{2h} site symmetry of the matrix.

pDFB-d_4 Fluorescence

The presence of small amounts of pDFB-d_3 complicates the vibronic analysis of the pDFB-d_4 fluorescence spectrum. The bands at 487 and 1278 cm^{-1}, each 36 cm^{-1} lower in energy than intense ν_6 and ν_3 fundamentals, are due to pDFB-d_3 impurity. Both ν_6 and ν_3 are nearly unaffected by deuterium substitution. The origin shift from -d_4 to -h_4 is 142 cm^{-1}, or 35.5 cm^{-1} per deuterium. This places the pDFB-d_3 origin at approximately 36 586 cm^{-1} and ν_6 and ν_3 at 487 and 1277 cm^{-1} with respect to

the $-d_4$ origin, in excellent agreement with the observed band positions. The other $-d_3$ bands which may be present are more difficult to identify because their frequencies are significantly affected by isotopic substitution.

The vibrational analysis of the region 0–800 cm^{-1} of the $-d_4$ spectrum presents more complications than that of $-h_4$. Previous studies of the vibrational spectrum of pDFB-d_4 have been carried out by ZD (Table III and Ref. (10)) and Gates (Table III and Ref. (8)). As expected, there is considerable similarity between the low temperature fluorescence and the vapor phase Raman spectra, as both are dominated by a_g fundamentals. The Raman doublet at 862/867 cm^{-1} is also observed as a doublet band in the low temperature fluorescence spectrum. However, the Raman singlet at 792 cm^{-1} is observed as a doublet 791/793 cm^{-1} in the fluorescence spectrum. The Raman doublet at 841 cm^{-1} is present in the fluorescence spectrum. First observed by ZD (10), it was attributed by asymmetric rotor splitting; however, its persistence in the matrix isolated fluorescence spectrum requires an alternative assignment. Gates observed two polarized Raman bands at 828/867 cm^{-1} and used the average frequency for the value of the a_g fundamental ν_5. ZD assigned the 862/867 cm^{-1} doublet to the $\nu_5(a_g)$ and the single band at 841 cm^{-1} as $2\nu_{29}$, an assignment also considered by Gates (8).

There is a very well-resolved doublet in the fluorescence spectrum at 1236/1241 cm^{-1} which corresponds to a feature in the pDFB-d_4 vapor phase Raman spectrum recorded by ZD (10). The $\nu_5 + \nu_6$ combination band should be located here and is probably in Fermi resonance with ν_3. Finally, the 30_2 assignment in both pDFB-h_4 and pDFB-d_4 is questionable. However, there is no obvious alternative. The fundamental is known to an accuracy of better than 0.5 cm^{-1} implying a large anharmonicity for the overtone which differs for each isomer.

pDFB-h_4 Phosphorescence

Phosphorescence ($^3B_{1u} \rightarrow {}^1A_g$) from pDFB-h_4 in cyclohexane matrix at 4.2 K could not be detected; however, it was possible to record a weak phosphorescence spectrum using the pure crystalline material. Phosphorescence from pDFB, in either the vapor or condensed phase, has not been previously reported. The spectrum , shown in Fig. 2, was recorded in detail sufficient to permit assignment of only the most intense features and location of the electronic origin. As in the phosphorescence spectra of p-dichlorobenzene (pDCB) and p-dibromobenzene (pDBB), the most prominent feature of the pDFB phosphorescence spectrum is the $b_{2g}(\nu_{17})$ 375-cm^{-1} progression. The two remaining b_{2g} fundamentals, (ν_{15}) 928 cm^{-1} and (ν_{16}) 692 cm^{-1}, are also observed in the phosphorescence spectrum (Table IV).

The activity of the b_{2g} fundamentals in the phosphorescence spectrum is not unexpected. They are associated with phosphorescence from the τ_y spin sublevel of the $^3B_{1u}$ state of overall (spin × orbit) symmetry B_{3u}. These transitions are, therefore, allowed by a vibronic mechanism of the Herzberg–Teller type and are polarized parallel to the allowed $^1B_{1u} \leftrightarrow {}^1A_g$ transition. The totally symmetric fundamentals which appear in the phosphorescence spectrum of pDFB are associated with either the τ_y or τ_x spin sublevel spectra and are expected to have a polarization perpendicular to that of the b_{2g} vibronic origins.
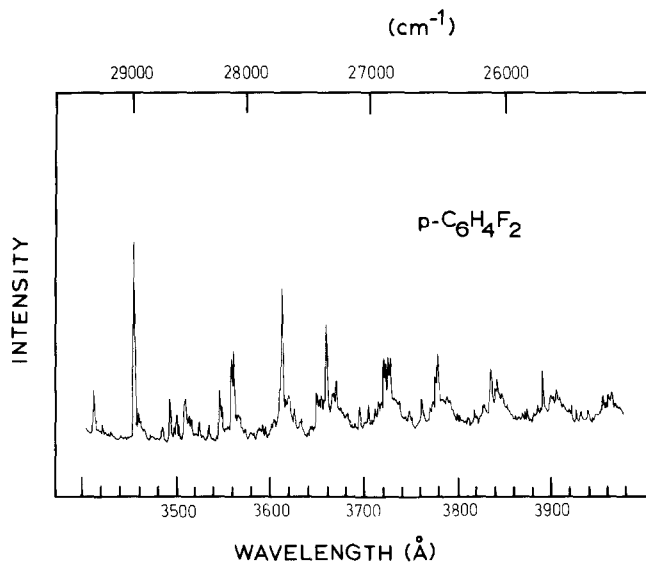
FIG. 2. Phosphorescence spectrum of crystalline pDFB-h_4 at 5 K.

Although the phosphorescence spectrum was extremely weak, it was possible to measure the zero-field splitting of the $^3B_{1u}$ state using the optically detected magnetic resonance technique. The resonance frequencies obtained from the microwave spectrum of pDFB monitoring the entire pDFB phosphorescence spectrum are 2704.9 and 3517.8 MHz which correspond to the $D + E$ ($\tau_x \leftrightarrow \tau_y$) and $D - E$ ($\tau_x \leftrightarrow \tau_z$) zero-field transitions, respectively. The $2E$ ($\tau_z \leftrightarrow \tau_y$) transition is expected to be weak

TABLE IV

p-$C_6H_4F_2$ Phosphorescence Frequencies and Assignments

ν (± 10 cm^{-1})	cm^{-1} from origin	Assignment
29283	0	origin
28912	371	17_1
28595	688	16_1
28540	743	17_2
28342	941	15_1
28135	1148	17_3
28054	1229	3_1
27665	1618	$17_1 3_1$
27648	1635	2_1
27350	1933	$16_1 3_1$
27288	1995	$17_1 2_1$
26810	2473	$2_1 5_1$
26793	2490	3_2

TABLE V

$^3B_{1u}$ Electronic Origin and Zero-Field Splitting Parameters for p-Dihalogenated Benzenes

Origin	Compound	D(GHz)	E (GHz)	Reference
29283	p-Difluorobenzene	+3.111	-0.406	
27410[+]	p-Dichlorobenzene	+4.3235	-0.6845	(23)
27318[+]	p-Dibromobenzene	+8.055	-1.800	(23)

[+] p-xylene lattice

(23, 24) and could not be observed. The values of the fine structure parameters D and E computed from the observed zero-field splittings are reported in Table V, where they are compared with the previously reported values of these parameters for other members of the p-dihalogen benzene family. The magnitude of E is directly related to the deviation from axial symmetry about the x axis (normal to the molecular plane); D is directly related to spin–dipolar interactions along the D axis. However, it is likely that the value of D is affected by spin–orbit coupling, making the detailed comparison between different members of the family less meaningful.

CONCLUSION

The low temperature, narrow-line fluorescence spectra of $pDFB$-h_4 and -d_4 in cyclohexane matrices have been recorded and vibrationally analyzed. The simplicity of these spectra, relative to vapor phase fluorescence, has permitted elimination of ambiguities and correction of misassignments of the vapor phase fluorescence spectrum.

The weak phosphorescence of $pDFB$-h_4 has been observed and partially vibrationally analyzed. The triplet state fine structure parameters measured for $pDFB$ complete the set of measurements for the p-dihalogen benzenes.

ACKNOWLEDGMENTS

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