Phosphorescent State of *p*-Fluorobenzaldehyde

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Phosphorescence spectra of *p*-fluorobenzaldehyde have been observed in (i) the vapor phase at room temperature and in (ii) methylcyclohexane and (iii) methyl benzoate matrices at 4.2 K. From the vibrational analysis and deuteration effect it is established that the phosphorescent state is $n\pi^*$ in cases i and ii while it is $\pi\pi^*$ in case iii. A close similarity between the vapor phase emission spectra of *p*-fluorobenzaldehyde and benzaldehyde leads us to the conclusion that the substitution of the fluorine atom for the para hydrogen atom of benzaldehyde has little effect to the both triplet states. Several experimental data for low frequency vibrations in the excited $^3n\pi^*$ state will be given by analyzing hot sequence bands of the vapor phosphorescence spectrum.

Benzaldehyde may be considered as the prototype aromatic aldehyde. Its electronic spectra, especially the phosphoresence spectra from the low lying $^3n\pi^*$ and $^3\pi\pi^*$ levels, have so far been investigated to a great extent.[1-3] The results show that an inversion of the triplet levels can occur such that the $^3n\pi^*$ and $^3\pi\pi^*$ states interchange simply by a change of environments employed. A variety of substituted benzaldehydes were also investigated spectroscopically by several groups, and the following issues came into questions:[4-15] (1) Which is the lowest triplet state, $^3n\pi^*$ or $^3\pi\pi^*$?; (2) how much is the energy separation between them ?; (3) what are main coupling perturbations thereof ?; and so on. Up to the present it seems that almost all the groups have attained to a general understanding even if there remain several points to be settled more quantitatively.

Recent spectroscopic works on benzaldehyde itself give impetus to explore the breakdown of Born–Oppenheimer approximation in more detail than previously. Detailed studies on untangling the tangled $T_{1,2} \leftarrow S_0$ spectra of benzaldehyde have made clear the physical meaning of the energy separation between the $^3n\pi^*$ and $^3\pi\pi^*$ levels and the detailed coupling scheme between their vibronic levels.[16,17] The extention of these quantitative analyses to other simple derivatives will be useful for the generalization of the method.

Fluorobenzaldehydes, simple mono-substituted benzaldehyde derivatives, are thus interesting. In addition, another spectroscopical interest arises from the fact that what are attached to the benzene ring are a strongly electron withdrawing and mesomeric aldehyde group and a strongly electron withdrawing and inductive fluorine atom. Despite its importance, only a few papers describe $n\pi^*$ emission[18-20] and absorption[21] spectra of fluorobenzaldehydes. No $\pi\pi^*$ phosphorescence has been reported as yet.

Several reasons such as mentioned above motivate us to review the phosphorescence spectra of fluorobenzaldehydes. The purpose of this paper is thus to observe the phosphorescence spectra of *p*-fluorobenzaldehyde (hereafter abbreviated as FB; the simplest of such fluorobenzaldehydes in the vibrational nomenclature), and its aldehyde deuterated derivative (FB-$1d_1$) and to compare them with the phosphorescence spectra of benzaldehyde (B) and its aldehyde deuterated derivative (B-$1d_1$).

Experimental

The guest molecule, FB (a GR grade reagent from Tokyo Kasei Co.), was purified by trap-to-trap distillation under vacuum. The aldehyde deuterated derivative (FB-$1d_1$) was obtained after reduction of *p*-fluorobenzoyl chloride (Tokyo Kasei GR reagent) with brandnew lithium tri-*t*-butoxodeuteridoaluminate(III) (i.e., $Li[Al(t\text{-}BuO)_3D]$)[22] in diethylene glycol dimethyl ether. The isotopic purity was found to exceed 95%, at least, from ^1H NMR measurements. For the emission measurements, two host reagents were employed: one was methylcyclohexane (MCH, Dotite nonfluorescent grade reagent) and the other methyl benzoate (MB, Tokyo Kasei GR grade). The former was used as received while the latter was purified by repeated distillation under vacuum. Sample concentrations were about 10^{-3} M[#] unless mentioned otherwise. The samples were degassed by freeze-pump-thaw cycles and sealed off in homemade pyrex cells with 200—300 μm thickness. Except for the employed spectrometer (we used a Nalumi 3/4 m spectrometer), the detailed methods and procedure were similar to those described elsewhere.[1]

The vapor emission were obtained photographically on Kodak T-Max P-3200 films or photoelectrically on an HTV R375 photomultiplier tube using a Nalumi 3/4 m Czerny–Turner grating spectrometer. Other experimental conditions for the vapor experiments were almost the same as described previously.[23]

Results and Discussion

Phosphorescence Spectra in MCH Matrices. The phosphorescence is very bright and its lifetime is ≈2 ms at 4.2 K. The strong band at 25390±3 cm^{-1} is taken as the 0-0 band of the phosphorescence transition (see the band designated as *o* in Fig. 1a). The emission spectrum is typical. It agrees well with the spectra obtained in other hydrocarbons such as pentane and hexane. The vibrational analysis is given, using available Raman and infrared data, in terms of Mulliken mode numbering.[18,24] A progres-

[#] 1 M=1 mol dm^{-3}.

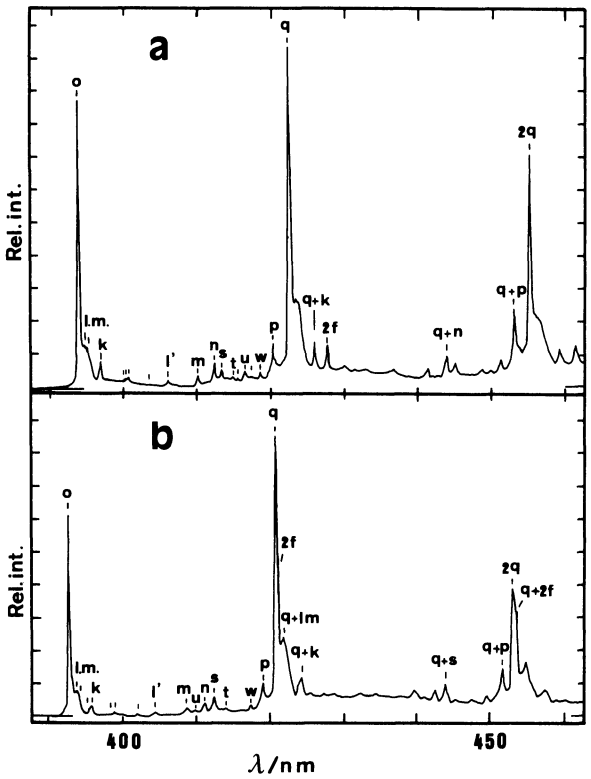

Fig. 1. Phosphorescence spectra of (a) FB and (b) FB-$1d_1$ in MCH at 4.2 K. See the text and Table 1 for band designations.

sion in ν_6 [i.e., ν (C=O)] vibration dominates the spectrum (see bands q and $2q$). Band q is located at 1715 cm^{-1} from the origin band. Except for these strong bands, seven weak bands [i.e., $\nu_{25}(k)$, $\nu_{18}(m)$, $\nu_{16}(n)$, $\nu_{15}(s)$, $\nu_{11}(u)$, $\nu_8(w)$, and $\nu_7(p)$] come out distinctly between bands o and q. The band spacings from the origin band are 201, 1014, 1146, 1203, 1385, 1567, and 1608 cm^{-1}, respectively. All these vibrations belong to totally symmetric in-plane (a') species. On going from the energy position of band q to longer wavelengths, almost all of the prominent bands are ascribed to combinational bands between each fundamental and ν (C=O) vibration. The exception is a sharp band which is located at 2008 cm^{-1} (see band 2f in Fig. 1a). The band is assigned as the overtone band of aldehyde H-wagging out-of-plane (a'') vibration. Its intensity amounts to 7% of the origin band intensity, being a manifestation that the phosphorescence transition is due to $^3A''(n\pi^*) \rightarrow {}^1A'$.[25] Another support for the transition assignment is also obtained from the determination of an origin band shift upon substitution of the D atom for the aldehyde H atom of B: The phosphorescence origin band of FB shifts by 51 cm^{-1} toward shorter wavelengths on its deuterium substitution (see Figs. 1a and b). The shift is of the same magnitude and direction as observed in B and B-$1d_1$.[1,3,23] The large blue shift guarantees a massive

Table 1. Wavenumbers and Assignments of the Main Bands in the Phosphorescence Spectra of FB and FB-$1d_1$ in MCH

FB			FB-$1d_1$			Assign.[a]
ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Rel. int.	ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Rel. int.	
25390	0	100	25441	0	100	0-0; *o*
25330	≈60 br[b]	12	25386	≈55 br	13	l.m.
25310	≈80 br	10	25361	≈80 br	7	l.m.
			25254	187	3	0-0';[c]
25189	201	7	25242	199	7	0-ν_{25}; *k*
24997	393	0.5	25050	393	0.5	0-ν_{24}
24991	399	0.5				0-2×ν_{25}
24969	421	1	25022	419	1	0-ν_{23}
24778	612	1	24832	609	1	0-ν_{22}
24617	773	2	24677	764	2	0-ν_{20}; *l'*
24376	1014	3	24430	1011	3	0-ν_{18}; *m*
24244	1146	8	24296	1145	6	0-ν_{16}; *n*
24187	1203	4	24223	1218	8	0-ν_{15}; *s*
24098	1292	1.5	24151	1290	1	0-ν_{13}; *t*
24078	1312	0.5				0-ν_{12}
24005	1385	2.5	24381	1060	2	0-ν_{11}; *u*
23989	1401	0.5	24027	1414	0.5	0-ν_{15}—ν_{25}
23876	1514	1				0-ν_{10}
23823	1567	4	23891	1550	3	0-ν_8; *w*
23782	1608	14	23839	1602	14	0-ν_7; *p*
			23551	1890	6	0'-ν_6
23675	1715	115	23733	1708[d]	138	0-ν_6; *q*
23476	1914	8	23536	1905	11	0-ν_6—ν_{25}
23382	2008	7	23715	1726[d]	25	0-2×ν_{26}; *2f*
21976	3414	102	22062	3379[d]	55	0-2×ν_6; *2q*
			22040	3401[d]	45	0-ν_6—2×ν_{26}; *q*+*2f*

a) Italicized alphabets indicate band designations for Fig. 1. b) The symbol br means broad. c) Different site's emission. Their intensities are dependent upon the cooling rate and procedure in samplings. d) Bands in Fermi-resonance.

involvement of the carbonyl group in the transition as in the case of B.[8,16,17] Frequencies and assignments of main phosphorescence bands thereof are summarized in Table 1. Several characteristic local modes are picked up and compared in Table 2 with the corresponding vibrational frequencies of B which have been observed in same matrix.[1,23]

Phosphorescence Spectra in MB Matrices. The phosphoresence of FB in MB is as strong as that in MCH, but its lifetime is about 20 times longer. The phosphorescence spectrum in MB is shown in Fig. 2a.

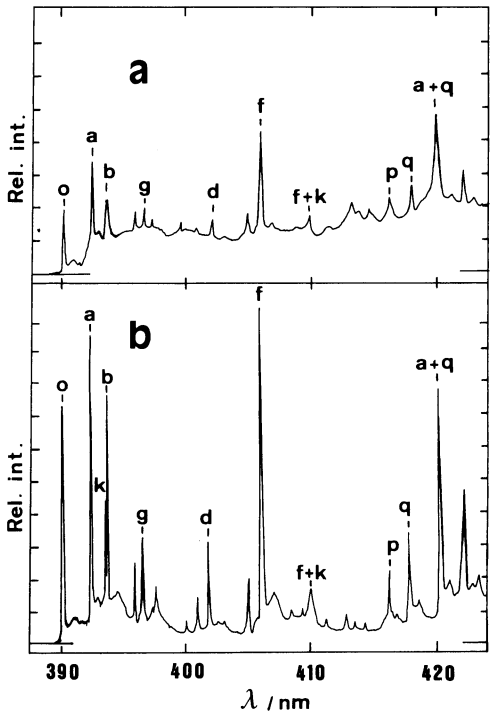

Fig. 2. Phosphorescence spectra of (a) FB in MB and (b) B in acetophenone at 4.2 K. See Table 2 for band designations.

The first strong band at 25617±5 cm^{-1} is taken as the origin band. The spectral band pattern extremely contrasts well with that in MCH (see Fig. 1a). For the latter the substantial intensity comes from the origin band and long ν (C=O) progression bands while for the former it does from several out-of-plane bands and their combination bands with one quantum of ν (C=O) vibration. Vibrational assignments for such false origin bands in the MB host case are possible on the basis of band spacing, deuteration shift, and Franck–Condon analysis. Most all the prominent bands are thus attributed to out-of-plane vibrational modes (see bands *a*—*f* given in Fig. 2a). For comparison, the spectrum of B in acetophenone is shown in Fig. 2b. A surprisingly nice correspondence in the frequency location and intensity distribution for such main bands (e.g., bands *a*, *b*, *f*, and *g*) is found between the two aldehydes. Band designations given in Fig. 2 are the same as described previously (cf. Ref. 23 for a change to the Mulliken numbering from the Wilson one which was employed in earlier papers for banzaldehyde[1,3]). Vibrational frequencies of several representative bands are summarized in Table 2 together with band designations given in Fig. 2. Two most intense bands are due to τ (CHO) and aldehyde H-wag modes just as in the case of B in acetophenone. The validity of such vibrational assignments is also confirmed most clearly by analyzing the phosphorescence spectrum of FB-$1d_1$. Within the experimental errors, the origin band of FB-$1d_1$ appears at almost the same wavenumber position as that of FB. Almost no deuteration shift and poor ν(C=O) progression assure the assignment that the phosphorescent state is $^3\pi\pi^*$. A long lifetime of ≈40 ms also supports that this is the case. Although its $\pi\pi^*$ type phosphorescence is obtained in other matrices such as acetophenone and *p*-dihalobenzenes, MB is the best host for the $\pi\pi^*$ phosphorescence spectra of FB to our knowledge.

Vapor Phosphorescence Spectra. Vapor phase FB

Table 2. Frequencies of Several Main Vibrations of FB and B in the Ground State

Vib. mode[b]	FB			B[a]			
	Vapor	MCH	MB	Vapor	MCH	MB	AC
In-plane							
δ (CHO): *k*	199	201	227	217	217	222	233
ν (ϕ-CHO); *s*	1203	1203		1204	1204	1207	
δ (H); *u*	1384	1385		1389	1385	1393	1412
ν_{8a}; *p*	1608	1608	1600	1611	1603	1598	1600
ν (C=O); *q*	1728	1715	1695	1728	1714	1700	1698
Out-of-plane							
τ (CHO); *a*	(93)[d]		137	111	128	138	141
ω (CHO); *b*	(208)[d]		235	224		240	245
ν_{16a}; *g*			408	417[c]		409[c]	405
H-wag; *f*	1003	1004	1008	1004	1004	1007	1008

a) Taken from Refs. 3 and 23. Because comparing modes of the two different molecules, we employed Wilson numbering in this table. b) Italicized alphabets denote the band designations for Figs. 1—3. c) Taken from Ref. 23. d) Taken from Ref. 18.

phosphorescence spectrum in the 390—430 nm region is shown in Fig. 3. With a moderate resolution such as employed in the present experiment, most all bands look somewhat diffuser than bands in the vapor phase phosphorescence spectrum of B.[23] This may be attributed to the difference between the two band contours. The band at 25486 cm^{-1} is tentatively taken as the origin band and designated as *o*. This is in agreement with the Haque-Thakur (H-T) assignment.[18] Eleven prominent bands are $0_0^0(o)$, $25_1^0(k)$, $18_1^0(m)$, $16_1^0(n)$, $15_1^0(s)$, $11_1^0(u)$, $8_1^0(w)$, $7_1^0(p)$, $6_1^0(q)$, $6_1^0 25_1^0(q+k)$, and $26_2^0(2f)$; and are located at 0, −199, −1013, −1148, −1203, −1386, −1570, −1608, −1728, −1927 and −2005 cm^{-1} from the origin band, respectively. Here and hereafter a minus sign means that the relevant band is located at longer wavelength side from the origin band and a plus at a shorter wavelength side. Most intense bands are the origin band itself and

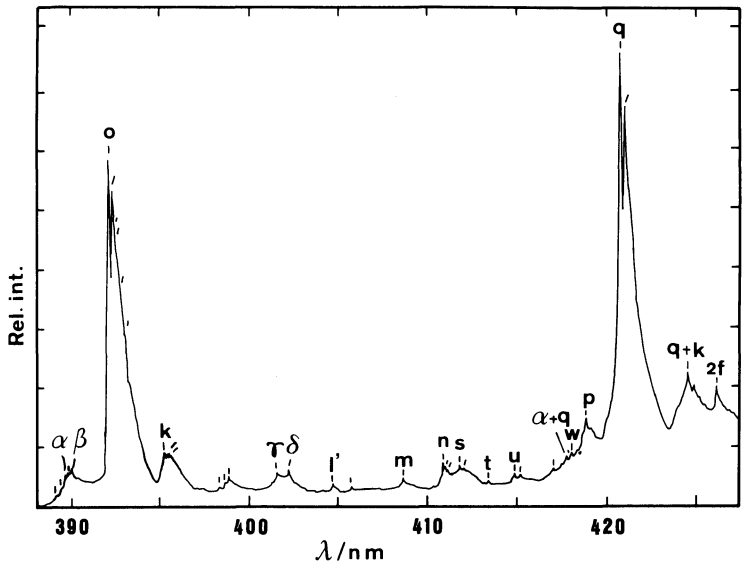

Fig. 3. Phosphorescene spectrum of FB in the vapor phase. See the text for Greek-lettered bands.

Table 3. Vibrational Assignment of Bands in the FB Vapor Phosphorescence

$\Delta\nu$[a]	Int.[b]	Assignment	Remarks[c]	$\Delta\nu$[a]	Int.[b]	Assignment	Remarks[c]
211	vvw			776(1′)	vw	20_1^0	
186	vw			840	vw	?	
174	w	25_0^1	25_0^1=174; α	857	vvw	19_1^0	
157	mw	$25_0^1 36_1^1$		1013	w	18_1^0	*m*
150	mw		β	1148	m	16_1^0	*n*
9	mw			1161	mw	$16_1^0 36_1^1$	
5	m	Envelop		1177	w	$16_1^0 25_1^1$	
0[d]	vvs	0_0^0	*o*	1203	m	15_1^0	*s*
≈3	vs	Envelop		1217	mw	$15_1^0 36_1^1$	
14	vs	36_1^1		1295	vvw	14_1^0	*t*
25.6	s	25_1^1		1384	mw	11_1^0	*u*
30.8	s	36_2^2?		1401	mw	$11_1^0 36_1^1$	
≈40	mw	36_3^3?		1514	w	9_1^0	
50	m	25_2^2		1555	mw	$6_1^0 25_0^1$	(Calcd=1554); $\alpha+q$
199	ms	25_1^0	25_1^0=199; *k*	1570	mw	$6_1^0 25_0^1 36_1^1$	(Calcd=1571)
214	m	$25_1^0 36_1^1$		1577	m	8_1^0	*w*
230	m	25_2^1	(Calcd=227)	1608	ms	7_1^0	*p*
401	vvw	25_2^0	(Calcd=398)	1728	vvs	6_1^0	*q*
420	vw	23_1^0		1744	vs	$6_1^0 36_1^1$	(Calcd=1743)
588	w	26_1^1	26_0^1=415; γ	1927	ms	$6_1^0 25_1^0$	(Calcd=1927); $q+k$
620	mw	$34_0^1 26_1^0$	34_0^1=383; δ	2005	ms	26_2^0	26_1^0=1003; 2*f*

a) Values in this column denote band separation (in cm^{-1} units) from the origin band. Italicized bands lie at higher wavenumbers than the origin band. b) Relative intensity. Its ordering is: vvs>vs>s>ms>m>mw>w>vw>vvw. c) Calculated from the first fundamental combination frequencies. Band designations are for Fig. 3. d) Determined to be 25486 cm^{-1}.

ν_6 progression bands. Except an about +100 cm^{-1} origin band shift, the phosphorescence spectral features are in good agreement with those in MCH at 4.2 K. Main vibrational modes appearing in the spectra are common and their frequencies are close to each other (see Figs. 1a and 3 and Tables 1 and 3). In this sense, the H-T assignment for the vapor phosphorescence spectrum is rationalized to a great extent as long as it concerns in-plane ground state modes. However, there are several discrepancies between H-T's assignment and ours, especially for several sequence bands and several fundamentals in the excited state.

From comparison between the vapor spectrum at room temperature and the rigid spectrum at 4.2 K, we find that several additional bands appear in each other. For the rigid spectrum they are clearly phonon side bands. For the vapor spectrum, on the other hand, they are (i) several prominent peaks (especially peaks designated as α and β in Fig. 3) lying at +100—+200 cm^{-1} from the origin band; (ii) intense 0_0^0 band group in the 0—−100 cm^{-1} region; (iii) the band at −588 cm^{-1} (γ); and (iv) the band at −620 cm^{-1} (δ).

Bands γ and δ are the two strongest in the 250—900 cm^{-1} region. H-T have proposed $24_1^0 25_1^0$ and $23_1^0 25_1^0$ assignments for these, respectively.[18] The fact that no corresponding bands were observed for the phosphorescence spectrum in MCH at 4.2 K (see Fig. 1a), however, inclines us to other assignments. From viewpoints of the band spacing and intensity distribution, the bands at −587 and −620 cm^{-1} in the B vapor phosphorescence seem to correpond to the −588 and −620 cm^{-1} bands in the FB spectrum, respectively. The −587 cm^{-1} phosphorescence band of B has been established to be 26_1^1 (where ν_{26} of B means aldehyde H-wag)[17,23,26] while the −620 cm^{-1} band of B has been suggested to be a cross sequence band $34_0^1 26_1^0$. By analogy we assign band γ in the FB spectrum as 26_1^1 and band δ as $33_0^1 26_1^0$.[27] Two prominent bands at −541 and −470 cm^{-1} observed for the vapor phase phosphorescence spectrum of FB-$1d_1$ suggest that the relevant modes may involve aldehyde motion because of their large red shifts in the spectrum of FB-$1d_1$. Our assignments for bands γ and δ do not contradict this deuteration effect.

All bands belonging to group (i) are, without doubt, attributed to so-called hot bands. In the B phosphorescence case, the most intense band in this region was 25_0^1 which was observed at +190 cm^{-1}.[23] This assignment has been supported by the observation of only one prominent band at 0+190 cm^{-1} in the 0—400 cm^{-1} region of the T←S phsophorescence excitation spectrum of B in MCH at 4.2 K.[17] In the present FB phosporescence case, however, three prominent bands were observed at +174(α), +157 and +150 cm^{-1} (β). H-T assigned band β as 25_0^1 from its intensity, deducing 25_1^1=—50 cm^{-1} (obsd −49.6 cm^{-1}).[18] We found that there is some pro and con evidence for the assignment +150 cm^{-1} (β)=25_0^1. The intensity of band β inclines us to support it, but a weak intensity of the resultant 25_1^1 band around −50 cm^{-1} to disapprove it. Almost no discriminative evidence between them was obtained by observing the vapor phase phosphorescence spectrum of FB-$1d_1$. An alternative assignment is $25_0^1 \approx$+174 cm^{-1} and 25_1^1—−25 cm^{-1}. An about 12.5% decrease in frequency of the vibration upon excitation from the ground state to the $^3n\pi^*$ state in FB is very close to an about 12.4% decrease in B.[3] In order to descriminate between the alternative assignments, we observed the T←S phosphorescence excitation spectrum of FB in MCH at 4.2 K (Fig. 4). Only a prominent band was observed at 0+177 cm^{-1} in the 0—400 cm^{-1}. This band may safely be assigned to 25_0^1. This δ (ϕ-CHO) vibrational frequency has been known to be stable, almost independent of environments employed.[3] We therefore take the 25_0^1=+174

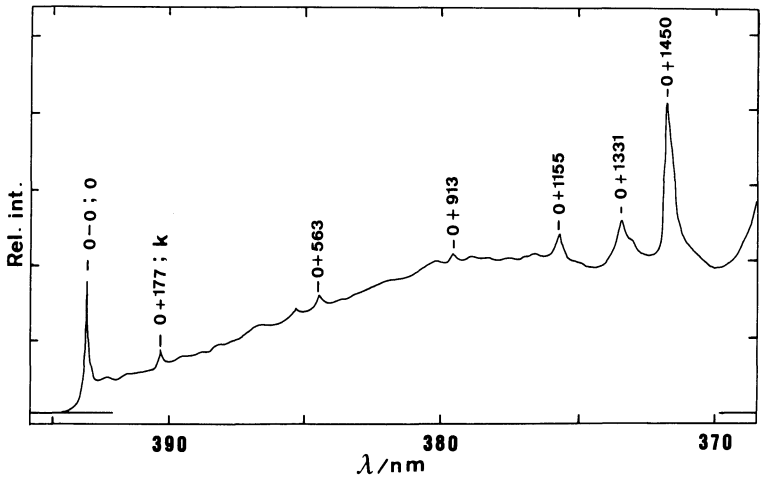

Fig. 4. $T_{1,2}$←S_0 phosphorescence excitation spectrum of FB in MCH at 4.2 K. Concn: 3×10^{-3} M.

cm^{-1} (α) for the vapor spectrum.

The phosphorescence origin band regions for FB and FB-$1d_1$ are shown in Fig. 5. In FB there are several sequence systems such as bands at −14, −25, −31, −40, and −50 cm^{-1} from the origin band. The first two and the last two were assigned by H-T to 36_1^1, 36_2^2, 35_1^1, and 25_1^1, respectively. The Boltzmann factors were calculated at 300 K by taking $36^1 \approx 75$, $25^1 \approx 175$, $35^1 \approx 200$, $34^1 \approx 300$, $33^1 \approx 380$, and $26^1 \approx 415$ cm^{-1}: 0: 36^1: 36^2: 25^1: 35^1: 36^3: 34^1: 25^2: 33^1: 26^1=100: 70: 50: 50: 40: 35: 25: 20: 17: 14. The intensity ordering observed for the origin band region is $I(0)>I(-3\ cm^{-1})>I(-14)>I(-25)\geqq I(-31)>I(-50)>I(-40)$. Possible assignments for two very intense bands at −3 cm^{-1} and −14 cm^{-1} are the origin band head and 36_1^1, respectively, in agreement with the H-T assignment.[18] Although the intensity of the first sequence bands X_1^1 do not always reflect population differences, the four strongest sequence bands in the vapor phosphorescence spectrum of B are 36_1^1, 25_1^1, 36_2^2, and 35_1^1 in its intensity order. The calculated population order seems to be in qualitative agreement with that of first several strong sequence bands observed. By analogy two bands at −25 and −31 cm^{-1} were thus tentatively assigned to 25_1^1 and 36_2^2, respectively.

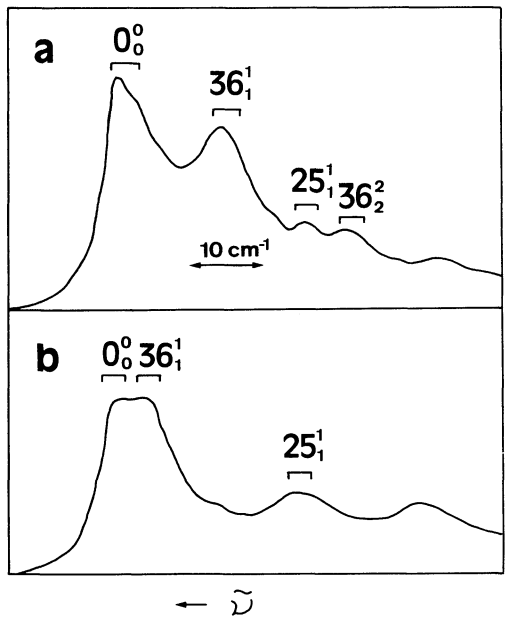

Fig. 5. Spectral profiles of the 0_0^0 band group in the vapor phosphorescence spectra of (a) FB and (b) FB-$1d_1$.

The band structures for the origin band region of the vapor phosphorescence spectra of FB and FB-$1d_1$ (Figs. 5a and b, respectively) are different from each other. Apart from several minor bands, however, the main band structure in the latter is understandable only if the −14 cm^{-1} band of FB is taken to shift toward the higher wavenumber side by 10—12 cm^{-1} upon the deuterium substitution. This band overlapping between 0_0^0 and 36_1^1 brings forth apparent band broadening for the vapor phosphorescence spectrum of FB-$1d_1$.

Conclusions and Remarks

Both $\pi\pi^*$ and $n\pi^*$ phosphorescence spectra of FB have many resemblances to those of B, respectively. They are, for example, 0-0 band proximity, close deuteration effect [cf. Table 4 for these points], vibronic pattern's similarity, and so on. By summing these up, we can conclude that the substitution of the fluorine atom for the para hydrogen atom of B has little effect to the related electronic states. There remain, however, several important points to be made clear. Two of them may be interesting. One concerns the difference between the CHO-torsional potential surfaces of each molecule in the T_1 ($n\pi^*$) and S_0 states and the difference between such potentials of the two molecules in each electronic state. The 36_i^i (i=1,2,··) sequence bands for vapor phase B extend to the shorter wavelengths from the 0_0^0 band while those for vapor phase FB do to the opposite direction. A detailed analysis of these sequence bands with much higher resolution at moderate temperatures will be fruitful and be preferable to jet-cooled experiments for the studies of those aromatic aldehydes because the main part of the CHO-torsional potentials is dominated as a term V_2 and the activity of 36_i^{i+1} or 36_{i+1}^i is expected to

Table 4. Comparison of Frequency Shifts in the Phosphorescence Origin Bands of FB, B, and Their Deuterated Derivatives[a]

	FB	B	Δ_{F-H}[b]	FB-$1d_1$	B-$1d_1$	Δ_{F-D}[c]
Vapor	25486	25179	307	25529	25222	307
Δ_D[d]				43	43	
MCH	25390	25068	322	25441	25119	322
Δ_D[d]				51	51	
MB	25617	25532	85	25615	25524	91
Δ_D[d]				−2	−8	
AC	25733	25613	120	—	25613	—
Δ_D[d]				—	0	

a) In cm^{-1} units. b) $\Delta_{F-H}=E^{0,0}(FB)-E^{0,0}(B)$ and $\Delta_{F-D}=E^{0,0}(FB\text{-}1d_1)-E^{0,0}(B\text{-}1d_1)$. c) The data for B and B-$1d_1$ are taken from Ref. 3. d) The origin band shift upon substitution of the aldehyde H-atom for the D-atom: $\Delta_D=E^{0,0}$(FB-$1d_1$ or B-$1d_1$)−$E^{0,0}$(FB or B).

be very small. The other concerns vibronic analysis of the T←S phosphorescence excitation spectrum of FB in MCH at 4.2 K (see Fig. 4). The vibronic band pattern in the ν (C=O) band region is extremely different from that of the $^1n\pi^*\leftarrow S_0$ spectrum, suggesting that the T←S spectrum should considerably be tangled in this region. The precise data on out-of-plane vibrational frequencies in the excited state will be required for performing similar untangling calculation as demonstrated previously for the B/MCH system.[17]

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