BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1205—1212 (1971)

The Emission Spectra of Pyrazine and Deuterated Pyrazines in the Vapor and in Rigid Matrices at 90°K

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(Received August 31, 1970)

Emission spectra of pyrazine and its deuterated derivatives have been observed in the vapor and the vibronic structure has been analyzed in detail. The vibronic structures of the phosphorescence spectra of these compounds have been explained all in terms of totally symmetrical vibrations, while the first main bands of the fluorescence spectra were anomalous as well as their progression bands in respect to the band position and intensity distribution. For comparison, the fluorescence spectra have also been studied in rigid matrices at 90°K.

The fluorescence and phosphorescence spectra of pyrazine-d_0 and -d_4 in the vapor were first observed by Logan and Ross.[1] The 0—0 bands of the phosphorescence spectra of these compounds coincided with those of the lowest T←S absorption spectra, and the shorter-wavelength region emissions were identified with the fluorescence spectra. The observation of the fluorescence spectrum of pyrazine gave a great sensation together with a similar report on 1,2- and 1,3- diazines[2] since it had been generally accepted that the fluorescence should be, if any, too weak to be observed for such a compound with a $^1(n,\pi^*)$ level as the lowest excited singlet state. The fluorescence spectrum has also been studies in rigid solution,[1] in fluid solutions,[3] and in the crystal at 77°K.[4] However, no vibrational analyses of those spectra have yet been made in detail. On the other hand, photoisomerization efficiency from pyrazine to pyrimidine has been discussed in the vapor[5] and in solutions.[6]

The fluorescence and phosphorescence spectra of pyrazine and deuterated pyrazines have been studied here in the vapor. For comparison the fluorescence spectra of pyrazines were also observed in rigid solutions at 90°K. The vibronic structures will be discussed. It is interesting that the phosphorescence spectra from photochemically produced pyrimidines have been observed when the pyrazines in solutions have been excited with the 2537 Å line of the Hg-lamp in agreement with the result by Lahmani *et al.*[6] in which the photochemical products were detected by gas chromatography.

Experimental

A quartz cell for study of emissions in the vapor is essentially the same as that reported by Base and Sponer.[7] A super high pressure Hg-lamp was used as a light source. Two filter systems were employed. One was a combination consisting of a path of 5 cm saturated *aq.* solution of $NiSO_4$ with a little amount of $CoSO_4$ added and that of 1 cm *aq.* solution of mono sodium phthalate of sufficient concentration to cut off the exciting light shorter in wavelength than 3000 Å for observation of the emissions in the vapor and the other consisted of the former of the above filter combination and a path of 1 cm D_3P[8] *aq.* solution for the emissions in solutions. The former combination is suitable for taking out mainly 3130 Å of the Hg-lamp and so is the latter for 2537 Å. The vapor pressure was estimated from the temperature near the outside of the bottom of a side tube where a sample was placed,

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[1] L. M. Logan and I. G. Ross, *J. Chem. Phys.*, **43**, 2903 (1965).

[2] B. J. Cohen, H. Baba, and L. Goodman, *J. Chem. Phys.*, **43**, 2902 (1965).

[3] H. Baba, L. Goodman, and P. C. Valenti, *J. Amer. Chem. Soc.*, **88**, 5410 (1966).

[4] P. Loustauneau and G. Nouchi, *Compt. Rend.*, **261**, 4693 (1965).

[5] F. Lahmani and N, Ivanoff. *Tetrahedron Lett.*, **40**, 3913 (1967).

[6] F. Lahmani, N. Ivanoff, and M. Magat, *Compt. Rend.*, **263**, 1005 (1966).

[7] A. M. Bass and H. Sponer, *J. Opt. Soc. Amer.*, **40**, 389 (1950).

[8] L. C. Braga and M. D. Lumb, *J. Sci. Instrum.*, **43**, 341 (1966).

according to the equations cited in Ref. 1. The temperature of the sample vapor was assumed equal to the inside temperature of the main oven in which the main part of the fluorescence cell was mounted. With an increase in temperature of the vapor the phosphorescence decreased considerably in intensity while the fluorescence remained unchanged in intensity. Pyrazine obtained from Tokyo Kasei Co., Ltd. was first converted into its salt form with sulfuric acid, recrystallized from alcohol, delivered from the salt form, and sublimed several times in vacuum. Pyrazine-d_4 and -2,3-d_2 were synthesized in the same way as that previously given,[9,10] and sublimed several times in vacuum. Spectra were photographed with a Shimadzu quartz spectrograph type QM-60. Slitwidths employed were 50 μ and 100 μ for measurement of the emissions in the vapor and solutions, respectively. The spectral position was determined within an accuracy of 3 cm^{-1} for the phosphorescence in the vapor, and 5 cm^{-1} and 20 cm^{-1} for the fluorescence in the vapor and in solution, respectively.

Results and Discussion

The Phosphorescence Spectra in the Vapor State. The phosphorescence spectra of pyrazine-d_0, -2, 3-d_2 and -d_4 were observed in the vapor. The microphotometer tracings and the spectral data are given in Figs. 1—3 and Tables 1—3, respectively. As has been pointed out by Logan and Ross,[1] the origin bands of the phosphorescence spectra of pyrazine-d_0 and -d_4 coincided exactly within experimental errors with those of the previously reported T←S absorption spectra.[11] The 0—0 band of pyrazine-2,3-d_2 was located at 26895cm^{-1} and the promotion energy in substitution of an H with a D was found to be 37 cm^{-1} in the vapor, very close to a value of 35 cm^{-1} in the crystal.[9] The overall spectral pattern is rather simple in all three cases as can be seen in Figs. 1—3. Active vibrations observed in the phosphorescence

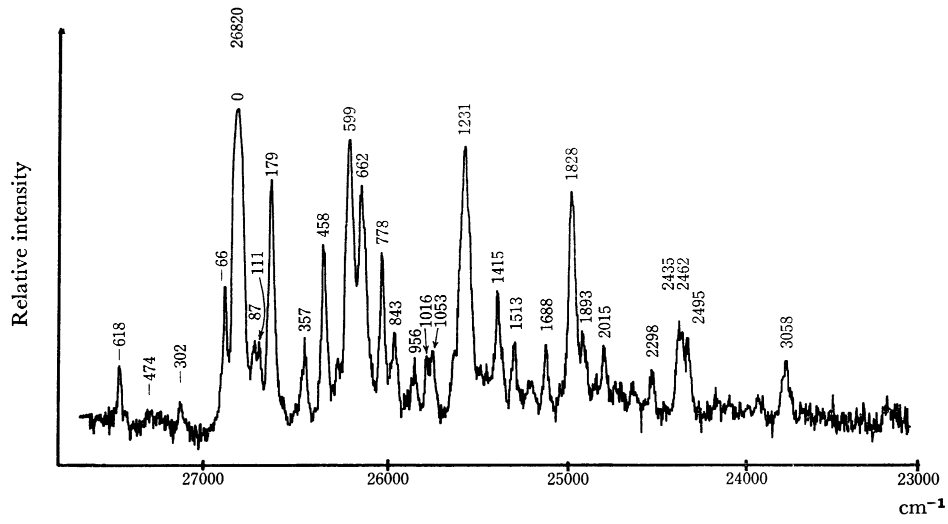

Fig. 1. Phosphorescence spectrum of pyrazine-d_0 in the vapor.

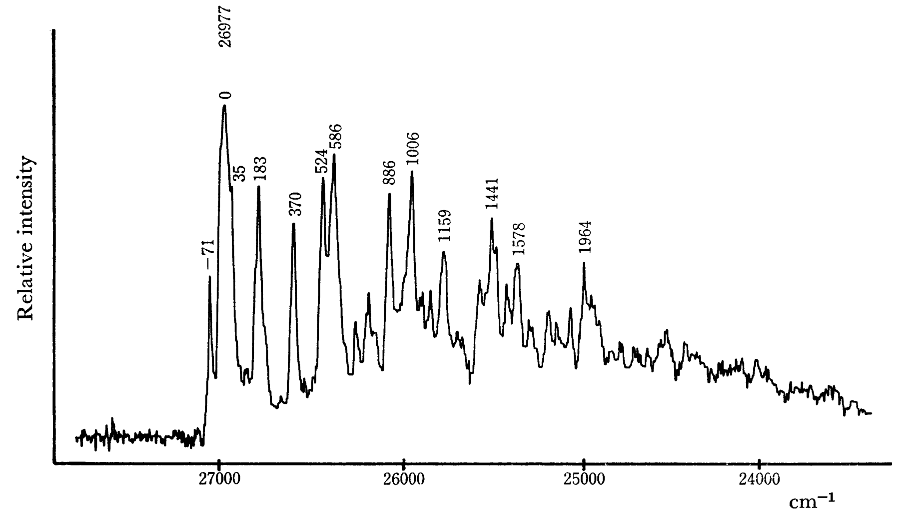

Fig. 2. Phosphorescence spectrum of pyrazine-d_4 in the vapor.

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[9] M. Koyanagi, T. Shigeoka, and Y. Kanda, "Molecular Luminescence," E. C. Lim, ed., Benjamin, Inc., New York, (1969), p. 765.

[10] S. Califano, G. Adembri, and G. Sbrana, *J. Mol. Spectrosc.*, **20**, 385 (1964).

[11] K. K. Innes, J. P. Burne, and I. G. Ross, *ibid.*, **22**, 125 (1967), (Review).

Table 1. Vibrational analysis of the phosphorescence spectrum of pyrazine-d_0 in the vapor

ν (cm^{1-})	Rel.[a] Int.	$\Delta\nu$ (cm^{-1})	Assignment[b]
27438	m	−618	$0+\nu_{6a}'$
27294	mw	−474	$0+\nu_{16b}'\times 2$
27237	w	−417	
27122	m	−302	
26886	m	− 66	$=(5)$
26841	w	− 21	$0+\nu_{6a}'-\nu_{6a}$
26820	ss	0	$=0$: 0—0 band
26733	m	87	$=(6)$: $0+\nu_{9a}'-\nu_{9a}$
26709	m	111	
26641	s	179	$=(1)$: $0+\nu_{16b}'-\nu_{16b}$
26483	m	337	sh.
26463	m	357	$0+(\nu_{16b}'-\nu_{16b})\times 2$
26362	s	458	$=(2)$: $\nu_5'-\nu_5$
26292	w	528	$(5)-\nu_{6a}$
26221	s	599	$0-\nu_{6a}$
26158	s	662	$=(3)$: $0-\nu_{16a}\times 2$
26135	m	685	$(6)-\nu_{6a}$
26042	s	778	$(1)-\nu_{6a}$
25977	s	843	$(3)+(\nu_{16b}'-\nu_{16b})$
25881	w	939	sh.
25864	m	956	$0+(\nu_{16b}'-\nu_{16b})\times 2-\nu_{6a}$
25804	m	1016	$0-\nu_1$
25767	m	1053	$(2)-\nu_{6a}$
25657	m	1163	$(5)-\nu_{9a}$
25589	s	1231	$0-\nu_{9a}$
25566	w	1254	$(3)-\nu_{6a}$
25504	w	1316	$(6)-\nu_{9a}$
25475	w	1345	
25405	ms	1415	$(1)-\nu_{9a}$ or $0-\nu_4\times 2$
25307	m	1513	$0-\nu_{10a}\times 2$
25228	w	1592	$25405+(\nu_{16b}'-\nu_{16b})$
25207	w	1613	$0-\nu_{6a}-\nu_1$
25132	m	1688	$(2)-\nu_{9a}$
25049	w	1771	
24992	s	1828	$0-\nu_{6a}-\nu_{9a}$
24978	w	1842	$0-\nu_5\times 2$
24927	m	1893	$(3)-\nu_{9a}$
25854	w	1966	
24805	m	2015	$25405-\nu_{6a}$
24739	w	2081	$25405-\nu_{16a}\times 2$
24628	m	2192	$25405+(\nu_{16b}'-\nu_{16b})-\nu_{6a}$
24572	w	2248	$0-\nu_1-\nu_{9a}$
24522	m	2298	
24385	ms	2435	$25405-\nu_1$
24358	ms	2462	$0-\nu_{9a}\times 2$
24325	ms	2495	$(3)-\nu_{6a}-\nu_{9a}$
24212	mw	2608	$25405+(\nu_{16b}'-\nu_{16b})-\nu_1$
24175	mw	2645	$25405-\nu_{9a}$
24145	mw	2675	$((3)+(1))-\nu_{6a}-\nu_{9a}$
24082	mw	2738	$0-\nu_{10a}\times 2-\nu_{9a}$
23996	w	2824	$25405+(\nu_{16b}'-\nu_{16b})-\nu_{9a}$
23972	w	2848	$0-\nu_{6a}-\nu_1-\nu_{9a}$
23762	ms	3058	$0-\nu_{6a}-\nu_{9a}\times 2$
23748	w	3072	$0-\nu_5\times 2-\nu_{9a}$
23622	mw	3198	
23574	mw	3246	$25405-\nu_{6a}-\nu_{9a}$
23477	mw	3343	
23294	mw	3526	

a) Estimated intensity: ss > s > ms > m > mw > w. b) Bands (1)···(6), see also Fig. 4.

Table 2. Vibrational analysis of the phosphorescence spectrum of pyrazine-d_4 in the vapor

ν (cm^{-1})	Rel. Int.	$\Delta\nu$ (cm^{-1})	Assignment[a]
27546	mw	−569	$0+\nu_{6a}'$
27401	w	−424	$0+\nu_{16b}'\times 2$
27193	w	−216	
27101	w	−124	
27048	m	− 71	$=(5)$
26996	w	− 19	sh.
26977	ss	0	$=0$: 0—0 band
26938	m	39	pyrazine-d_3 0—0
26857	mw	120	
26794	s	183	$=(1)$: $0+(\nu_{16b}'-\nu_{16b})$
26607	s	370	$=(2)$: $0+(\nu_5'-\nu_5)$
26453	s	524	$=(3)$: $0-\nu_{16a}\times 2$
26391	s	586	$0-\nu_{6a}$
26281	m	696	
26219	w	758	
26207	m	770	$(1)-\nu_{6a}$
26162	m	815	$(5)-\nu_1$
26091	s	886	$0-\nu_1$
26019	m	956	$(2)-\nu_{6a}$
25971	s	1006	$0-\nu_{9a}$
25912	m	1065	$(1)-\nu_1$
25871	m	1106	$(3)-\nu_{6a}$
25818	ms	1159	$0-\nu_{10a}\times 2$
25802	m	1175	$0-\nu_{6a}\times 2$
25783	mw	1194	$(1)-\nu_{9a}$
25724	mw	1253	$(2)-\nu_1$
25690	mw	1287	
25602	m	1375	$(2)-\nu_{9a}$
25570	mw	1407	$(3)-\nu_1$
25536	ms	1441	$0-\nu_5\times 2$
25507	ms	1470	$0-\nu_{6a}-\nu_1$
25447	m	1530	$(3)-\nu_{9a}$
25399	m	1578	
25386	m	1591	$0-\nu_{6a}-\nu_{9a}$
25323	mw	1654	$(1)-\nu_{6a}-\nu_1$
25306	mw	1671	
25213	m	1764	$0-\nu_1\times 2$
25169	mw	1808	
25092	m	1885	$0-\nu_1-\nu_{9a}$
25013	ms	1964	$(2)-\nu_1-\nu_{9a}$ or $(3)-\nu_5\times 2$
24972	mw	2005	$0-\nu_{9a}\times 2$
24951	mw	2026	$0-\nu_{6a}-\nu_5\times 2$
24929	mw	2048	$0-\nu_{6a}\times 2-\nu_1$
24870	w	2107	$(3)-\nu_{6a}-\nu_{9a}$
24854	w	2123	
24798	mw	2179	$0-\nu_{6a}\times 2-\nu_{9a}$
24776	w	2201	

a) Bands (1)···(6), see also Fig. 4.

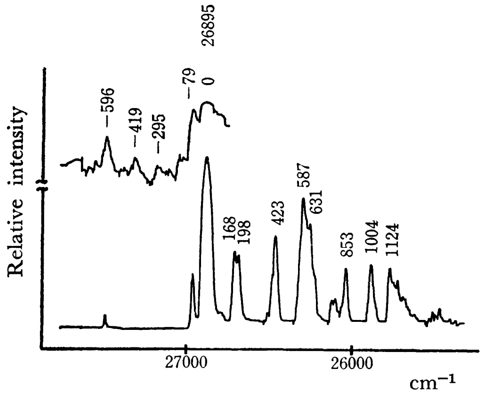

Fig. 3. Phosphorescence spectrum of pyrazine-2,4-d_2 in the vapor.

Table 3. Vibrational analysis of the phosphorescence spectrum of pyrazine-2,3-d_2 in the vapor

ν (cm^{-1})	Rel. Int.	$\Delta\nu$ (cm^{-1})	Assignment[a]
27491	m	−596	$0+\nu_{6a}'$
27314	w	−419	$0+\nu_{16b}'\times 2$
27190	w	−295	$0+\nu_{16a}'\times 2$
26974	m	− 79	=(5)
26895	ss	0	=0: 0—0 band
26803	w	92	=(6)
26782	w	113	
26727	ms	168	=(4): $0+(\nu_{16a}'-\nu_{16a})$
26697	ms	198	=(1): $0+(\nu_{16b}'-\nu_{16b})$
26472	s	423	=(2): $0+(\nu_5'-\nu_5)$
26386	w	509	$(5)-\nu_{6a}$
26344	w	551	
26308	s	587	$0-\nu_{6a}$
26264	ms	631	=(3): $0-\nu_{16a}\times 2$
26235	m	660	sh.
26140	m	755	$(4)-\nu_{6a}$
26116	m	779	$(1)-\nu_{6a}$
26042	ms	853	=(7): $0-\nu_{15}$
25891	s	1004	$0-\nu_1$
25771	s	1124	$0-\nu_{9a}$

a) Bands (1)⋯(7), see also Fig. 4.

spectra are the modes of ν_{6a}, ν_{9a}, and ν_1 and their combinations.[12] However, there are many bands that lie with considerable intensity between 27100 and 25900 cm^{-1} and it is impossible to analyze them in terms of the normal mode frequencies in the ground state only. They are schematically reproduced in Fig. 4, and referred hereafter to the band (1), (2),⋯(7). The assignments are wholly based on the band positions since no other information is available. For instance a study of temperature dependence of the vapor spectra proved of no help, since it was practically impossible to compare the band intensities under different temperatures. With an increase in temperature, the continuous emission from the vapor overlapping on the phosphorescence spectrum increased in intensity, while the phosphorescence spectrum decreased in intensity. This made a precise measurement of the band intensity impossible.

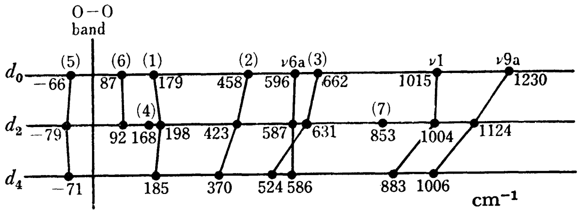

Fig. 4. Schematic representation of first main bands of the phosphorescence spectra of pyrazines in the vapor.

The band (1) may be ascribed to the 1–1 transition of the ν_{16b}, since hot bands −474 (d_0), −419 (d_2), and −424 cm^{-1} (d_4) could be assigned to the overtones of this vibrational mode in the excited state, and fundamental frequencies of this mode are 416, 409, and 399 cm^{-1} in the ground state, respectively. This situation is analogous to the first S←S (π^*–n) absorption spectrum of pyrazine-d_0.[13] Similarly, the band (2) may arise from the 1–1 transition due to the mode ν_5 if we take 461, 442, and 351 cm^{-1} as ν_5 frequencies in the triplet state which are smaller in frequency by about 50% than those in the ground state, but still greater as compared with the value in the lowest singlet (n,π^*) state.[14] Here, the ν_5 mode frequency of pyrazine-2,3-d_2 in the ground state has been taken to be 865 cm^{-1}. Whether this is valid will be discussed later in connection with the band (7). On the basis of the numerical relationships found in the pyrazine-2,3-d_2 spectrum, the band (3) was assigned to an overtone frequency of a non-totally symmetrical mode in the ground state. These are; 631↔316×2 (ground state), −295↔−148 ×2 (excited state), 168 (band (4))↔316−148 (1-1 transition). Thus the frequencies 331 (d_0), 316 (d_2), and 262 cm^{-1} (d_4) were obtained as fundamentals of a non-totally symmetrical mode in the ground state of the respective compounds in the parentheses, which could be assigned to the ν_{16a} vibrational mode. The experimental value of the frequency has not yet been established but a value of 340 cm^{-1} (d_0) has tentatively been given, which has been taken from the Raman data in the liquid phase[15] and has been supported by the normal mode calculation based on the valency force constants transferred from benzene.[16] The band (5) has its counterpart in the T←S absorption spectrum, but has not been assigned.[17] The band (6) is the 1–1 transition of the ν_{9a} according to a list of designation in Ref. 11. The band (7) has a frequency difference of 853 cm^{-1} from the 0–0 band and this is too large to be interpreted as 1–1 transition. This band is also too strong in intensity to be accounted for as 2–2 transition, *e.g.*, overtone of the 423 cm^{-1} band. From its magnitude

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[12] The mode numbers employed here are the same as those used in, J. D. Simmons, K. K. Innes, and G. M. Begun, *J. Mol. Spectrosc.*, **14**, 190 (1964).

[13] M. Ito, R. Shimada, T. Kuraishi, and W. Mizushima, *J. Chem. Phys.*, **26**, 1508 (1957).

[14] K. K. Innes, J. D. Simmons, and S. G. Tilford, *J. Mol. Spectrosc.*, **11**, 257 (1963).

[15] R. C. Lord, A. L. Marston, and F. A. Miller, *Spectrochim. Acta*, **9**, 113 (1957).

[16] D. B. Scully, *ibid.*, **17**, 233 (1961).

[17] K. K. Innes and L. E. Giddings, Jr., *Discuss. Faraday Soc.*, **35**, 192 (1963).

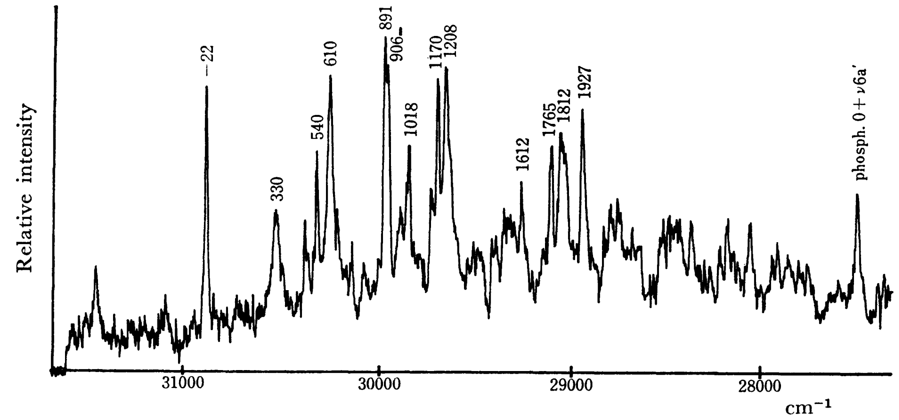

Fig. 5. Fluorescence spectrum of pyrazine-d_0 in the vapor.

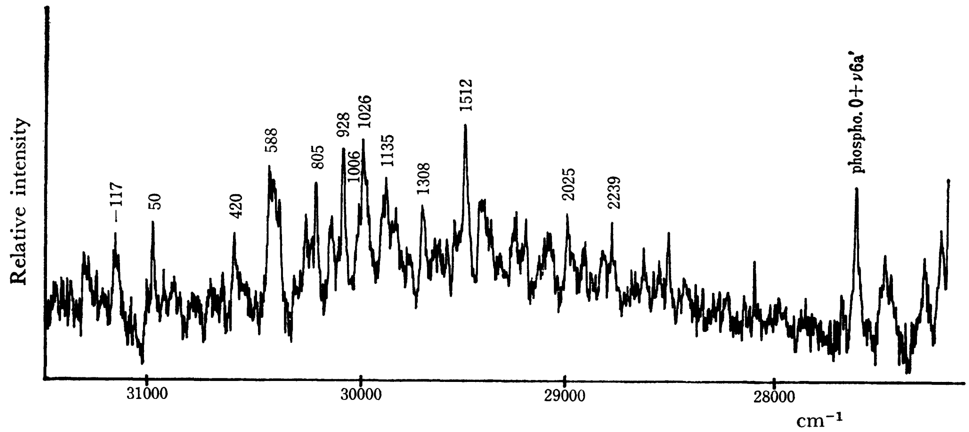

Fig. 6. Fluorescence spectrum of pyrazine-d_4 in the vapor.

Table 4. Vibrational analysis of the fluorescence spectrum of pyrazine-d_0 in the vapor

ν (cm^{-1})	Rel. Int.	$\Delta\nu$[a] (cm^{-1})	Band relation[b]
31315	w	−440	$=(1)$: (ν_{6a})
31292	w	−417	
31207	w	−332	
31130	w	−255	
31099	w	−224	
30897	s	− 22	$=(2)$: (ν_1)
30829	w	46	
30811	w	64	
30746	w	129	
30726	w	149	$=(3)$: $(\nu_{6a}\times 2)$
30687	mw	188	$=(4)$: (ν_{9a})
30633	w	242	
30570	mw	305	
30545	m	330	$=(1')$: [c]
30400	m	475	$(1)-\nu_5$
30335	ms	540	$=(2')$: $(\nu_5'-\nu_5)$
30265	s	610	$=(3')$: (ν_{6a})
30191	m	684	
30152	m	723	
30090	mw	785	$(1)-\nu_{9a}$
29984	s	891	$(2)-\nu_5$
29969	ms	906	
29857	ms	1018	$=(4')$: (ν_1)
29804	m	1071	$(3)-\nu_5$
29740	m	1135	$(2')-\nu_{6a}$
29705	s	1170	$(2)-\nu_{6a}\times 2$
29667	s	1208	$(2)-\nu_{9a}$ or $(3')-\nu_{6a}$
29605	w	1270	
29427	m	1448	$(2')-\nu_5$
29312?	mw	1563	$(1')-\nu_{9a}$
29263	ms	1612	$(4')-\nu_{6a}$
29110	ms	1765	$(2')-\nu_{9a}$ or $(2)-\nu_{6a}\times 3$
29063	ms	1812	$(2)-\nu_5\times 2$
28948	ms	1927	$(4')-\nu_5$
28830	mw	2045	$(2')-\nu_{6a}-\nu_5$
28797	m	2078	$(2)-\nu_{6a}\times 2-\nu_5$
28757	m	2118	$(2)-\nu_5-\nu_{9a}$
28669	w	2206	$(4')-\nu_{6a}\times 2$
28630	mw	2245	$(4')-\nu_{9a}$
28502	m	2373	$(2')-\nu_5\times 2$
28479	m	2396	$(2)-\nu_{6a}\times 2-\nu_{9a}$
28356	m	2519	$(4')-\nu_{6a}-\nu_5$
28196	m	2679	$(2')-\nu_5-\nu_{9a}$ or $(2)-\nu_{6a}\times 3-\nu_5$
28156	m	2719	$(2)-\nu_{6a}-\nu_5-\nu_{9a}$
28027	m	2848	$(4')-\nu_5\times 2$ or $(4')-\nu_{6a}-_{9a}$
27872	m	3003	$(2)-\nu_{6a}\times 3-\nu_{9a}$

a) $\Delta\nu=\nu_{abs}^{0-0}-\nu$ $(\nu_{abs}^{0-0}=30875$ cm$^{-1})$.

b) Bands (1′)···(4′) could be assigned as are shown in parentheses, but agreement between the observed vibrational frequencies and the data in Ref. 12 in the case for pyrazine-d_0 are rather worse than that of pyrazine-d_4 emission (see also Table 5). Bands (1)···(4) are assigned as are shown in parentheses on the assumption that a false origin lies at 31913 cm^{-1}.

c) The frequency difference is in agreement with that of a hot band observed in Ref. 13 in the ultraviolet absorption spectrum in the vapor, but its assignment remains unknown.

TABLE 5. VIBRATIONAL ANALYSIS OF THE FLUORESCENCE SPECTRUM OF PYRAZINE-d_4 IN THE VAPOR

ν (cm^{-1})	Rel. Int.	$\varDelta\ \nu$[a] (cm^{-1})	Band relation[b]
31281	m	−251	
31157	ms	−117	=(1*)
31130	m	−100	
31005	m	25	
30980	ms	50	=(1): (ν_{9a})
30885	m	150	=(2*)
30788	w	242	
30772	w	258	
30719	m	311	
30664	m	366	
30610	ms	420	=(1′): ($\nu_5'-\nu_5$)
30593	w	437	
30570	m	460	(1*)$-\nu_{6a}$
30514	m	516	
30442	s	588	=(2′): (ν_{6a})
30434	w	596	
30396	s	634	(1)$-\nu_{6a}$
30382	w	648	
30319	ms	711	
30295	w	735	(2*)$-\nu_{6a}$
30275	ms	755	(1*)$-\nu_1$
30225	s	805	=(2): ($\nu_1\times 2$)
30154	ms	876	(1*)$-\nu_{9a}$
30144	m	886	=(3′): (ν_1)
30102	s	928	(1)$-\nu_1$
30041	w	989	
30024	m	1006	=(4′): (ν_{9a}) or (1′)$-\nu_{6a}$
30004	s	1026	(2*)$-\nu_1$
29990	m	1040	(1*)$-\nu_{6a}\times 2$
29980	w	1050	(1)$-\nu_{9a}$
29959	m	1071	
29945	w	1085	
29919	m	1111	
29898	ms	1135	
29860	w	1170	(2′)$-\nu_{6a}$
29852	ms	1178	
29808	w	1222	(1)$-\nu_{6a}\times 2$
29785	m	1245	
29745	w	1285	
29722	ms	1308	
29660	m	1370	(1′)$-\nu_1$
29646	m	1384	(2)$-\nu_{6a}$
29602	m	1428	(1′)$-\nu_{9a}$
29566	m	1464	(1*)$-\nu_{6a}-\nu_{9a}$
29552	w	1478	
29539	w	1491	
29518	s	1512	(1)$-\nu_{6a}-\nu_1$
29441	ms	1589	(2′)$-\nu_{9a}$
29385	m	1645	
29344	m	1686	(2)$-\nu_1$
29278	m	1752	(2′)$-\nu_{6a}\times 2$
29268	m	1762	(1*)$-\nu_1-\nu_{9a}$
29219	m	1811	(2)$-\nu_{9a}$
29140	m	1890	(3′)$-\nu_{9a}$
29122	m	1908	
29095	m	1935	(1)$-\nu_1-\nu_{9a}$
29065	w	1965	(2)$-\nu_{6a}\times 2$
29020	w	2010	(4′)$-\nu_{9a}$
29005	m	2025	
28930	mw	2100	(1)$-\nu_{6a}\times 2-\nu_1$
28892	w	2138	
28853	mw	2177	(4′)$-\nu_{6a}\times 2$
28837	w	2193	
28791	m	2239	

a) $\varDelta\ \nu=\nu_{\text{abs}}^{0-0}-\nu$ ($\nu_{\text{abs}}^{0-0}=31030\ cm^{-1}$).

b) Bands (1′)⋯(4′) could be assigned as are shown in parentheses, and those are possible in contrast to the pyrazine-d_0 spectrum since the numerical agreement is fair and the vibrational modes are the same as those observed in the fluorescence in solution. Bands (1) and (2) are assigned as are shown in parentheses on the assumption that a false origin lies at 31988 cm^{-1}.

in frequency two assignments may be possible; ν_5(a_2 in C_{2v}) and ν_{15}(a_1 in C_{2v}). In order to clarify this point, the hot bands of the lowest S←S absorption spectrum of pyrazine-2,3-d_2 in the vapor was investigated and two bands were found at 854 and 865 cm^{-1} from the 0—0 band located at 30952 cm^{-1}, the latter being much stronger in intensity. The fact that ν_5 appears strongly in the absorption spectra of pyrazine-d_0 and -d_4 in the vapor[14] suggests that 865 cm^{-1} may be of the mode ν_5 and 853 cm^{-1} the mode ν_{15}, in good agreement with Ref. 18.[19] Therefore, it has been concluded that all the progressions observed in the phosphorescence spectra of pyrazines in the vapor with sufficient intensity are of totally symmetrical, *i.e.*, a_g (or a_1) mode, overtone vibration, or arise from *v*–*v* transitions.

The Fluorescence Spectra in the Vapor State. The fluorescence spectra of pyrazine-d_0 and -d_4 have been studied in the vapor. The microphotometer tracings and the spectral data are given in Figs. 5 and 6 and Tables 4 and 5, respectively, although no unambiguous interpretation of these spectra has yet completely been made. It seems strange to say that the emission spectrum of pyrazine between 31500 and 28000 cm^{-1} is not explainable. But this is not a result conflicting with Ref. 1, in which the identification of the fluorescence spectra was based on the rough coincidence in the Franck-Condon contour between the emissions and the hot bands of the lowest S←S absorption spectra in the vapor. The details will be discussed in the following: At first, let us consider a difference between the tracing curves given by Logan and Ross and those of the present work (Figs. 5 and 6). The most remarkable one lies on a band denoted as $-22\ cm^{-1}$ in pyrazine-d_0 spectrum in Fig 5 ($-22\ cm^{-1}$ means its distance from the origin band of the first S←S (π^*-n) absorption spectrum). This is one of the strongest bands in our fluorescence spectrum but missing from that by Logan

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[18] E. F. Zalewski, Ph. D. Thesis, University of Chicago, 1968.

[19] However, ν_5 mode has been observed with moderately strong intensity in the phosphorescence spectra of pyrazine-d_0, -d_2, and -d_4 at the isotopically mixed crystal experiments. M. Koyanagi, T. Shigeoka, and Y. Kanda, This Bulletin, to be submitted.

and Ross. The observation was repeatedly made at various temperatures and pressures with and without foreign gas (air). A careful comparison of the curve by Logan and Ross with our various tracing curves showed that the $-22\ \mathrm{cm}^{-1}$ band was possibly reabsorbed by the origin band and the hot bands lying close to it in the curve by Logan and Ross since the curve in a region between -500 to $+1000\ \mathrm{cm}^{-1}$ coincided well with one of the tracing curves with a strong continuous background of the exciting light source and an intense absorption or reabsorption appearing on it.

No bands that correspond to the hot bands in the absorption were observed in the fluorescence spectrum of gaseous pyrazine-d_0, but several bands in that of gaseous pyrazine-d_4. These phenomena shoud not be attributed to reabsorption or difference in absorbance due to low population of "hot molecules" in the ground state. On the other hand, there are many bands that can be analyzed in terms of four normal mode frequencies of pyrazines, such as the modes of ν_1, ν_5, ν_{6a}, and ν_{9a}, if several origins are tentatively assumed as given in Tables 4 and 5. One of the most probable interpretations of the fluorescence spectra in the vapor may be based on the so-called resonance spectra. An attempt along this line shows that several strong bands become explainable with pseudo-origins. Another may be to assume many abnormally populated emitting levels higher than the zero vibrational level in the excited state. This is probable but too speculative.

Fluorescence in Solution at Low Temperature. The fluorescence spectra of pyrazine-d_0 and -d_4 in methyl cyclohexane and pyrazine-d_0 in benzene have been measured at 90°K. The fluorescence spectrum of pyrazine in methyl cyclohexane consists of somewhat broad bands but becomes rich in structure in benzene solution. The 0—0 band diminishes its intensity with an increase of the concentration. N_{6a} and ν_5 are active vibrations in pyrazine-d_0 in methyl cyclohexane, but whether its $600\ \mathrm{cm}^{-1}$ long progressions are overtones of ν_{6a} or combinations of ν_{6a} and ν_{9a} was not certain bacause of its broad linewidth. In a benzene solution they are clearly of the latter type. The spectrum in a benzene solution was rather complicated because there are several sub-systems besides its main progressions.

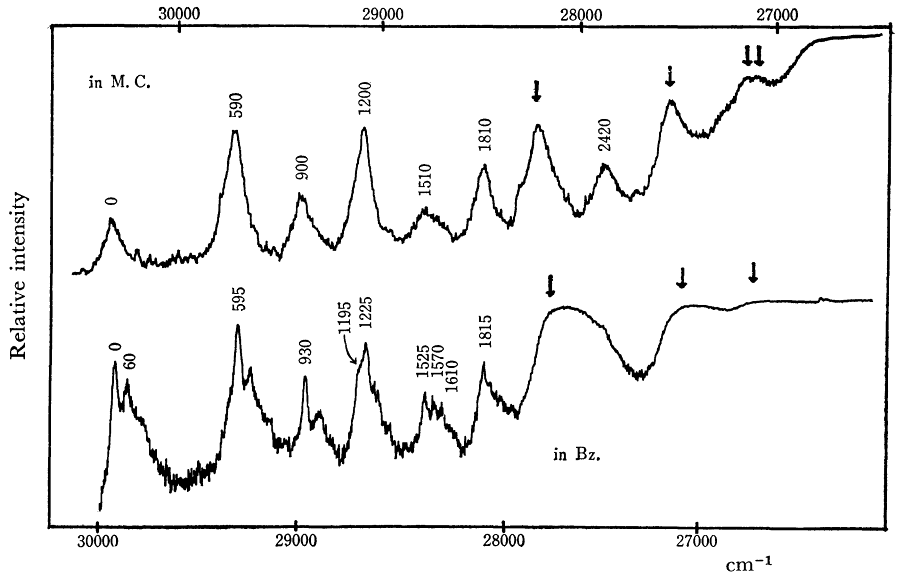

Fig. 7. Fluorescence spectra of pyrazine-d_0 in solutions at 90°K. Downward arrows denote the phosphorescence from pyrimidine-d_0.

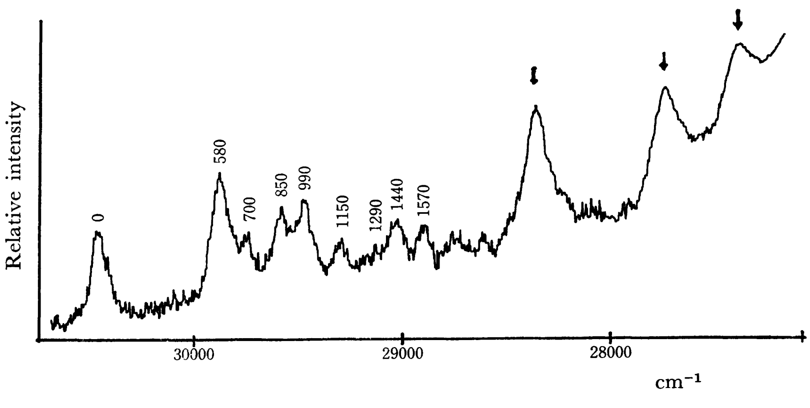

Fig. 8. Fluorescence spectrum of pyrazine-d_4 in methyl cyclohexane at 90°K. Downward arrows denote the phosphorescence from pyrimidine-d_4.

TABLE 6. VIBRATIONAL ANALYSIS OF THE FLUORESCENCE SPECTRA OF PYRAZINE-d_0 IN SOLUTION AT 90°K

in M.C.			in benzene			Assignment
ν (cm^{-1})	Rel.[a)] Int.	$\Delta\nu$[b)] (cm^{-1})	ν (cm^{-1})	Rel.[a)] Int.	$\Delta\nu$[b)] (cm^{-1})	
30310	3	0	29895	7	0	=0: 0-0 band
			29835	6	60	$0-(60)$
29720	8	590	29300	9	595	$0-\nu_{6a}$
			29245	7	650	$0-\nu_{6a}-(55)$
			29150	sh	745	$0-\nu_{10a}$
29410	4	900	28965	7	930	$0-\nu_5$
			28900	6	995	$0-\nu_5-(65)$
29100	7	1200	28700	sh	1195	$0-\nu_{6a}\times 2$
			28670	8	1225	$0-\nu_{9a}$
			28615	6	1280	$0-\nu_{9a}-(55)$
28800	2	1510	28370	6	1525	$0-\nu_{6a}-\nu_5$
			28325	6	1570	$0-\nu_{8a}$
			28285	6	1610	$0-\nu_{11}\times 2$
28500	5	1810	—	—	—	$0-\nu_{6a}\times 2$
			28080	7	1815	$0-\nu_{6a}-\nu_{9a}$
			28045	6	1850	$0-\nu_{6a}\times 2$
28220	(s)	(0)	27750	(s)	(0)	pyrimidine-d_0 phospho. 0—0
27890	3	2420	—	—	—	$0-\nu_{6a}\times 4, 0-\nu_{9a}\times 2$
27540	(s)	(680)	27100	(s)	(650)	pyri.-d_0 phospho.
27150	(s)	(1070)	—	—	—	pyri.-d_0 phospho.
27100	(s)	(1120)	—	—	—	pyri.-d_0 phospho.

a) sh: shoulder, s: strong.
b) ( ): phosphorescence bands of pyrimidine-d_0.

TABLE 7. VIBRATIONAL ANALYSIS OF THE FLUORESCENCE SPECTRUM OF PYRAZINE-d_4 IN METHYL CYCLOHEXANE AT 90°K

ν (cm^{-1})	Rel.[a)] Int.	$\Delta\nu$[b)] (cm^{-1})	Assignment
30460	4	0	=0: 0—0 band
29880	6	580	$0-\nu_{6a}$
29760	2	700	$0-\nu_5$
29610	4	850	$0-\nu_1$
29470	4	990	$0-\nu_{9a}$
29310	2	1150	$0-\nu_{6a}\times 2$
29170	1	1290	$0-\nu_{6a}-\nu_5$
29020	3	1440	$0-\nu_{6a}-\nu_1$
28890	3	1570	$0-\nu_{6a}-\nu_{9a}$
28730	0	1730	$0-\nu_{6a}\times 3$
28590	0	1870	$0-\nu_{6a}\times 2-\nu_5$
28330	(s)	(0)	pyrimidine-d_4 phospho. 0—0
27680	(s)	(650)	pyri.-d_4 phospho.
27280	(s)	(1050)	pyri.-d_4 phospho.

a) s: strong.
b) ( ): phosphorescence bands of pyrimidine-d_4.

A separation of about 60 cm^{-1} associated with this spectrum may be due to a lattice vibration.[20)] In pyrazine-d_4, ν_{6a}, ν_5, ν_{9a}, and ν_1 are active. This last mode was not found in pyrazine-d_0. The observation of the $0-\nu_5$ band in the fluorescence spectra at low temperature in both -d_0 and -d_4 favors the interpretation given by Innes *et al.* that all strong vibronic bands of the 3200 Å absorption system of pyrazine must be assigned to a single electronic transition of mixed character in polarization.[14)] An alternative assignment had been given to this band by Ito *et al.* as belonging to an electronically forbidden transition into an another $^1(n, \pi^*)$ state.[13)] However, in the case of ordering of energy levels, the fluorescence will occur solely from the lower one at low temperature, especially if the higher transition is of forbidden character and the lower one is of allowed one. Thus it has been concluded that the fluorescence spectrum in solution is explainable by one electronic transition and is a normal one.

The phosphorescence spectra from photochemically produced pyrimidines were also observed, whose 0—0 bands were located at 28220 (d_0) and 28330 cm^{-1} (d_4) and separated by about 1500 cm^{-1} to the shorter wavelengths from that of the pyrazine phosphorescence. This additional emission did not appear when the 3130 Å system of the Hg-lamp was used as an exciting light in agreement with the results by Lahmani *et al.*[5)] The mechanism of the photoisomerization of pyrazine has been discussed by several investigators,[6,5,21)] and a diazavenzvalene has been proposed as a reaction intermediate. A thermally promoted rearrangement has also been reported.[21)] It may be of another interest to examine whether the reversed photoreaction, *i.e.*, pyrimidine into pyrazine, may occur or not.

From the analyses of the vibronic structure of the emission spectra of pyrazine and its deuterated compounds in the vapor, it has been found that the phosphorescence spectrum is straightforward but the fluorescence spectrum is anomalous, and several fundamentals of the vibrations including ν_{16a} mode have been found. They are summarized in Table 8. It has also been found that the fluorescence spectrum of pyrazine in solution at liquid air temperature is of single electronic transition and the photochemical reaction of pyrazine occurs even at such temperature.

TABLE 8. FUNDAMENTAL FREQUENCIES OF PYRAZINES OBSERVED IN THE PHOSPHORESCENCE SPECTRA IN THE VAPOR

vib. mode	elec.[a)] state	fundamental frequencies (cm^{-1})		
		-d^0	-2,3-d^2	-d^4
ν_{16b}	T	237	210	214
ν_{16a}	G	331	316	262
	T		148	
ν_5	T	461	442	351
	G		(865)	
ν_{15}	G		853	

a) T: triplet, G: ground state.

The authors wish to thank Dr. R. Shimada for his helpful advice on instruments for the vapor spectra measurement, and Dr. T. Edamura for his information to us about his unpublished results on the absorption and fluorescence spectra of crystalline pyrazine.

[20)] A similar interpretation has been given by T. Shigeoka, Master Thesis, Kyushu Univ., 1967.

[21)] W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, **27**, 3115 (1968).