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## The Fluorescence and Phosphorescence Spectra of Pyrazine in Benzene at 4.2°K

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The fluorescence and phosphorescence spectra of pyrazine-*h*<sub>4</sub> and pyrazine-*d*<sub>4</sub> in benzene at 4.2° K are presented and analyzed. The Frank-Condon patterns of *a*<sub>1g</sub> modes in the fluorescence spectrum are quite similar to those in the phosphorescence spectrum for both pyrazine-*h*<sub>4</sub> and pyrazine-*d*<sub>4</sub>.

The *ν*<sub>5</sub> (*b*<sub>2g</sub>) and *ν*<sub>10a</sub> (*b*<sub>1g</sub>) out-of-plane bending modes appear with quite different intensities in the fluorescence and phosphorescence spectra. The 0 → 1 transitions in these modes only appear in the fluorescence spectra while the 0 → 2 transitions are more intense in the phosphorescence spectra. These results are interpreted in terms of a vibronic interaction between <sup>1,3</sup>B<sub>3u</sub> (*nπ\**) and the <sup>1,3</sup>B<sub>2u</sub> (*ππ\**) and <sup>1,3</sup>B<sub>1u</sub> (*ππ\**) states.

No spectroscopic evidence is found for a forbidden <sup>1</sup>*nπ\** state below <sup>1</sup>B<sub>3u</sub> (*nπ\**).

### INTRODUCTION

The luminescent properties of azines have been the source of considerable scientific investigation. Low-temperature emission spectra of azines in mixed crystals can yield sharp spectra which are easily analyzed in terms of the ground-state vibrational assignments provided by infrared and Raman spectroscopists. These spectra may reveal much about excited-state geometries and interactions between excited states. The present study is a composite of work performed concurrently at the University of Pennsylvania (by C. M.) and the University of Chicago (by E. Z.) on the mixed crystal emission spectra of pyrazine in benzene.

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The lowest singlet excited state of pyrazine has been assigned as  $^1B_{3u}(n\pi^*)$  by Innes *et al.* (1) on the basis of the type-C rotational structure found for the 0-0 band in the vapor absorption spectrum. The molecule has been found to fluoresce with a low quantum yield both in solution (2) and in the vapor (3). It shows strong phosphorescence in the vapor phase (3) and in rigid glass solvents at 77°K (4). The phosphorescent state has been assigned as  $^3B_{3u}(n\pi^*)$  (4, 5). Since the lowest singlet and triplet excited state have similar energies and are derived from the same configuration, they should to a first approximation be similar electronically. A major difference in these states is their nearness to  $\pi\pi^*$  states of the same multiplicity. Because the singlet-triplet splitting is much larger for  $\pi\pi^*$  states than for  $n\pi^*$  states, the  $^3B_{3u}(n\pi^*)$  state is expected to be much closer to the  $^3B_{2u}(\pi\pi^*)$  and  $^3B_{1u}(\pi\pi^*)$  than  $^1B_{3u}(n\pi^*)$  is to  $^1B_{2u}(\pi\pi^*)$  and  $^1B_{1u}(\pi\pi^*)$ . A theoretical treatment of the effect of nearby states on some aspects of the pyrazine- $h_4$  emission spectra has been presented previously (6). In this article we present and analyze the complete emission spectra of pyrazine- $h_4$  and pyrazine- $d_4$  in benzene at 4.2°K.

#### EXPERIMENTAL

Pyrazine (Aldrich Chemical Co.) and pyrazine- $d_4$  (Merck Sharp and Dohme of Canada) were purified by repeated zone melting or by vacuum sublimation. The samples were placed in a quartz cell and immersed in liquid helium in a quartz double dewar. Samples were excited either with a General Electric A H-6 mercury lamp or with 450-W Xenon lamp filtered with a  $\text{NiSO}_4$  solution and a Corning 754 filter.

Spectra were taken with a 3.4 m Ebert mount Jarell-Ash spectrograph at the University of Chicago and with a Baird-Atomic 3-m concave grating spectrograph with an Eagle mount at the University of Pennsylvania. The spectra showed a major spectrum and several similar minor spectra which are due to pyrazine in energetically different sites in the benzene lattice. In what follows we have analyzed only the spectrum of the major site.

#### DESCRIPTION OF THE SPECTRA

The complete emission spectrum of pyrazine- $h_4$  in benzene at 4.2°K is shown in Fig. 1. Vibrational analyses for the pyrazine- $h_4$  and pyrazine- $d_4$  spectra are listed in Tables I-IV. Most vibrational assignments were made on the basis of ground-state infrared and Raman data (7, 8). Many of the modes we see in emission are also present in the hot band absorption spectrum of the pyrazine vapor (1, 2). A schematic representation of the important symmetry modes of pyrazine is shown in Fig. 2. We find that the fluorescence and phosphorescence spectra are remarkably similar in both pyrazine- $h_4$  and pyrazine- $d_4$ .<sup>3</sup> The totally

<sup>3</sup> The notation is that of Ref. (12), *a* and *b* refer to the nodes of the  $\pi$  orbital being through atoms and through bonds, respectively.

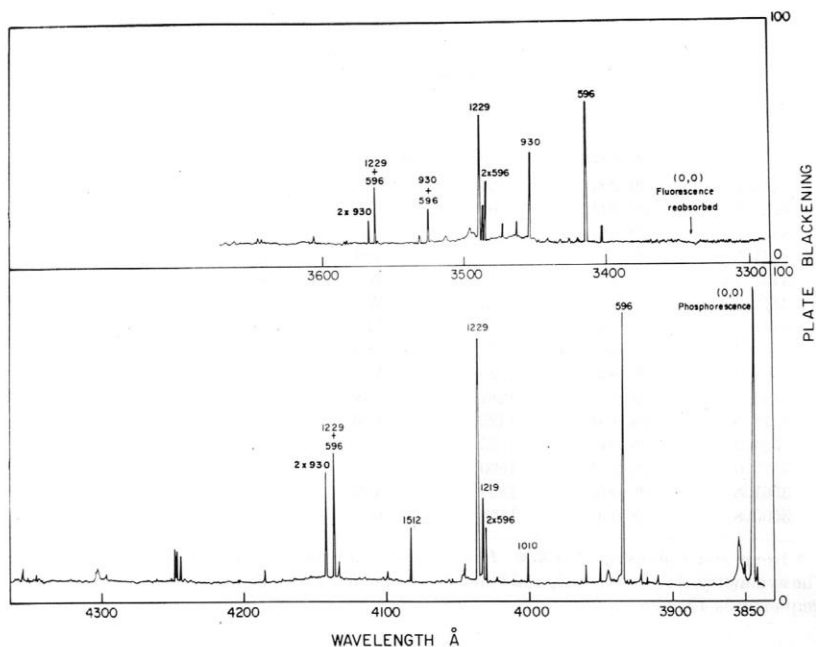


FIG. 1. The fluorescence and phosphorescence spectrum of pyrazine in benzene at 4.2°K.

symmetric modes  $\nu_{6a}$  (596  $\text{cm}^{-1}$ ) and  $\nu_{9a}$  (1229  $\text{cm}^{-1}$ ) dominate the pyrazine- $h_4$  spectra. In pyrazine- $d_4$   $\nu_1$  (881  $\text{cm}^{-1}$ ),  $\nu_{9a}$  (998  $\text{cm}^{-1}$ ) and a Fermi doublet (578  $\text{cm}^{-1}$  and 591  $\text{cm}^{-1}$ ) involving  $\nu_{6a}$  and  $\nu_4$  ( $b_{1g}$ ) are the most prominent bands. These and other weaker  $a_g$  modes appear with similar intensities in the fluorescence and phosphorescence spectra. This is exactly what has been found in the emission spectra of pyrimidine (10) in benzene at 4.2°K and indicates that the molecule has a similar equilibrium geometry in its singlet and triplet states.

This observation is in agreement with the conclusion that both emissions are occurring from states of the same spatial term, namely,  $B_{3u}(n\pi^*)$ . Evidently the small exchange splitting in  $n\pi^*$  terms results in singlet and triplet states which are almost identical electronically. As found in pyrimidine (10) the denteration shifts are similar for the fluorescence and phosphorescence 0-0 bands. For pyrazine we find shifts of 156  $\text{cm}^{-1}$  and 150  $\text{cm}^{-1}$ , respectively.

There are several prominent bands which appear with different relative intensities in the fluorescence and phosphorescence spectra. An intense band at 930  $\text{cm}^{-1}$  (728  $\text{cm}^{-1}$  in pyrazine- $d_4$ ) appears in the fluorescence spectrum and is extremely weak in the phosphorescence spectrum. Two quanta of this mode appears

TABLE I  
VIBRATIONAL ANALYSIS OF THE FLUORESCENCE SPECTRUM OF PYRAZINE- $L_4$   
IN BENZENE AT 4.2°K

$\lambda$ (Å)	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$	Rel. int.	Analysis	Error
3344.4	29 892	0	reabsorbed		
3412.5	29 296	596	VS	$\nu_{6a}$	
3423.4	29 202	690	VW	$\nu_4$	
3430.7	29 140	752	VW	$\nu_5$	
3451.8	28 962	930	MS	$\nu_{10a}$	
3461.4	28 881	1011	W	$\nu_1$	
3471.3	28 799	1093	W		
3483.3	28 700	1192	M	$2 \times \nu_{6a}$	0
3485.2	28 685	1207	MW	$\nu_{11} + \nu_{16b}^a$	
3487.8	28 663	1229	MS	$\nu_{9a}$	
3494.1	28 611	1281	VW	$\nu_{6a} + \nu_4$	+5
3511.5	28 470	1422	MW		
3524.2	28 367	1525	W	$\nu_{6a} + \nu_{10a}$	1
3529.6	28 332	1560	W		
3561.8	28 068	1824	MW	$\nu_{6a} + \nu_{9a}$	1
3565.8	28 036	1856	W	$2 \times \nu_{10a}$	+4

<sup>a</sup> Hong and Robinson (*J. Chem. Phys.*, to be published) assign this band as  $2 \times \nu_{6b}$ . The symmetry of  $\nu_{11} + \nu_{16b}$  is  $A_g$  and from the assignments of Califano *et al.* (8) the combined frequency is 1203 cm<sup>-1</sup>.

TABLE II  
VIBRATIONAL ANALYSIS OF THE FLUORESCENCE SPECTRUM OF PYRAZINE- $d_4$   
IN BENZENE AT 4.2°K

$\lambda$ (Å)	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$	Rel. int.	Analysis	Error
3327.0	30 048	0	reabsorbed	0, 0	
3392.3	29 470	578	S	$\nu_{6a}$ } <sup>a</sup>	
3393.8	29 457	591	MS	$\nu_4$ }	
3409.7	29 320	728	MS	$\nu_{10a}$	
3427.8	29 165	883	S	$\nu_1$	
3441.3	29 050	998	S	$\nu_{9a}$	
3461.4	28 882	1166	MW	$\nu_{6a} + \nu_4$	+3
3478.6	28 739	1309	W	$\nu_{6a} + \nu_{10a}$	-3
3496.1	28 595	1453	W	$2 \times \nu_{10a}$	+3
3496.8	28 589	1459	MW	$\nu_{6a} + \nu_1$ } <sup>a</sup>	0
3498.4	28 576	1472	MW	$\nu_4 + \nu_1$ }	0
3511.1	28 473	1575	MW	$\nu_{6a} + \nu_{9a}$ } <sup>a</sup>	+1
3512.8	28 459	1589	W	$\nu_4 + \nu_{9a}$ }	0
3515.2	28 440	1609	W	$\nu_1 + \nu_{10a}$ } <sup>a</sup>	0
3529.5	28 324	1724	MW	$\nu_{9a} + \nu_{10a}$ }	+2
3534.3	28 286	1762	MW	$2 \times \nu_1$	0
3548.9	28 170	1878	M	$\nu_1 + \nu_{9a}$	+1
3563.8	28 052	1996	VW	$2 \times \nu_{9a}$	0

<sup>a</sup> Fermi doublets.

TABLE III  
 PHOSPHORESCENCE SPECTRUM OF PYRAZINE- $h_4$  IN BENZENE AT 4.2°K

$\lambda$ (Å)	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$	Rel. int.	Analysis	Error
3845.9	25 994	0	VS	origin	
3936.2	25 398	596	VS	$\nu_{6a}$	
3951.1	25 302	692	W	$\nu_4$	
3961.0	25 239	755	W	$\nu_5$	
4001.3	24 985	1009	V		
4001.6	24 983	1011	W	$\nu_1$	
4023.0	24 850	1144	VW		
4030.6	24 803	1191	M	$2 \times \nu_{6a}$	-1
4033.2	24 787	1207	S	$\nu_{11} + \nu_{16b}$	
4036.6	24 766	1228	VS	$\nu_{9a}$	
4056.8	24 643	1351	VVW	$\nu_{6a} + \nu_5$	0
4083.1	24 484	1510	M	$2 \times \nu_5$	0
4099.5	24 386	1608	VW	$\nu_1 + \nu_{6a}$	-1
4136.2	24 170	1824	S	$\nu_{9a} + \nu_{6a}$	0
4141.8	24 137	1857	S	$2 \times \nu_{10a}$	
4172.3	23 961	2033	VVW		
4174.8	23 889	2105	VW	$2 \times \nu_5 + \nu_{6a}$	+1
4246.5	23 542	2452	VW	$2 \times \nu_{10a} + \nu_{6a}$	+1
4247.6	23 536	2458	VW	$2 \times \nu_{9a}$	-2

<sup>a</sup> See footnote in Table I.

with more intensity in the phosphorescence spectrum than in the fluorescence spectrum. Innes *et al.* see these frequencies in the hot band absorption of the pyrazine- $h_4$  and pyrazine- $d_4$  vapors (11). They find that the 1-0 band shows a type-A rotational structure and assign the active mode as  $\nu_5(b_{2g})$ . This assignment, however, could be in error due to the similarity of the two in-plane moments of pyrazine. Califano *et al.* (8) assign the mode to  $\nu_{10a}(b_{1g})$ . We will discuss the assignment of the 930 cm<sup>-1</sup> mode later in the paper. In the phosphorescence spectra we find intense bands at 1510 cm<sup>-1</sup> ( $2 \times 755$ ) for pyrazine- $h_4$  and at  $2 \times 646$  cm<sup>-1</sup> in pyrazine- $d_4$  which are absent in the fluorescence spectra. One quanta of these frequencies is absent in fluorescence and extremely weak in phosphorescence. These modes are assigned as  $\nu_{10a}(b_{1g})$  by Innes (7) and as  $\nu_5(b_{2g})$  by Califano (8).

Odd quanta changes in  $b_{1g}$  and  $b_{2g}$  modes may appear in the emission spectrum via a Hertzberg-Teller vibronic coupling mechanism. For a vibronic band to show up in an emission spectrum it must have intensity comparable with the allowed part of the spectrum. Out-of-plane bending modes are known to effectively mix  $n\pi^*$  and  $\pi\pi^*$  states of the same multiplicity. In pyrazine the three lowest observed states are  ${}^1B_{3u}(n\pi^*)$  at 30 900 cm<sup>-1</sup>,  ${}^1B_{2u}(\pi\pi^*)$  at 37 800 and  ${}^1B_{1u}(\pi\pi^*)$  at 50 800 cm<sup>-1</sup> (12). These have oscillator strengths of 0.01, 0.10 and 0.15, respectively. Since the singlet-singlet  $\pi \rightarrow \pi^*$  transitions in pyrazine are so much more intense

TABLE IV  
 PHOSPHORESCENCE SPECTRUM OF PYRAZINE- $d_4$  IN BENZENE AT 4.2°K

$\lambda$ (Å)	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$	Rel. int.	Analysis	Error
3823.9	26 144	0	VS	origin	
3910.2	25 567	577	VS	$\nu_{6a}$ <sup>a</sup>	
3912.1	25 554	590	VS	$\nu_4$	
3920.7	25 498	646	VW	$\nu_5$	
3944.6	25 344	800	VVW		
3950.3	25 307	837	VVW		
3957.2	25 263	881	VS	$\nu_1$	
3975.6	25 146	998	VS	$\nu_{9a}$	
4002.4	24 978	1166	M	$2 \times \nu_{6a}$	-12 <sup>b</sup>
4005.4	24 959	1185	VVW		
4022.7	24 852	1292	W	$2 \times \nu_5$	0
4048.9	24 691	1453	S	$2 \times \nu_{10a}$	
4049.9	24 685	1459	M	$\nu_1 + \nu_{6a}$ <sup>a</sup>	-1
4051.8	24 673	1471	W	$\nu_1 + \nu_4$	0
4053.7	24 662	1482	VVW		
4056.9	24 642	1502	VVW		
4069.2	24 568	1576	M	$\nu_{9a} + \nu_{6a}$ <sup>a</sup>	-1
4071.3	24 555	1589	W	$\nu_{9a} + \nu_4$	-1
4085.5	24 470	1674	VW		
4100.4	24 381	1763	W	$2 \times \nu_1$	-1
4120.0	24 265	1879	M	$\nu_{9a} + \nu_1$	0
4139.6	24 150	1994	VW	$2 \times \nu_{9a}$	+2
4147.5	24 104	2040	VW	$\nu_1 + 2\nu_{6a}$ <sup>a</sup>	-4
4148.5	24 098	2046	VVW	$\nu_1 + \nu_{6a} + \nu_4$	
4198.7	23 810	2334	VVW	$2 \times \nu_1 + \nu_{6a}$	-2
4219.1	23 695	2449	VVW	$\nu_2$	+5

<sup>a</sup> Fermi doublets.<sup>b</sup> Does not take into account the shift in the fundamental due to Fermi resonance.

than the  $n \rightarrow \pi^*$  transitions, one expects odd quanta of out-of-plane bending modes to be prominent in the fluorescence spectra of pyrazine. In the triplet manifold it is expected and found that the  $n \rightarrow \pi^*$  transitions will be at least an order of magnitude more intense than the  $\pi \rightarrow \pi^*$  transitions (13). This is because spin orbit coupling effectively mixes triplet  $n\pi^*$  and  $\pi\pi^*$  states with singlet  $\pi\pi^*$  and  $n\pi^*$  states, respectively. We therefore do not expect odd quanta of out-of-plane bending modes which borrow intensity from the triplet  $\pi\pi^*$  states to be prominent in the phosphorescence spectra of pyrazine.

In agreement with this conclusion we find significant intensity for the 930 cm<sup>-1</sup> band (728 cm<sup>-1</sup> in pyrazine- $d_4$ ) only in fluorescence. As mentioned above this band can be due to either the  $\nu_{10a}(b_{1g})$  or the  $\nu_5(b_{2g})$  out-of-plane bending modes depending on whose vibrational assignments are chosen (8, 11). These modes will mix  ${}^1B_{3u}(n\pi^*)$  with  ${}^1B_{2u}(\pi\pi^*)$  and  ${}^1B_{1u}(\pi\pi^*)$ , respectively. From first-order per-

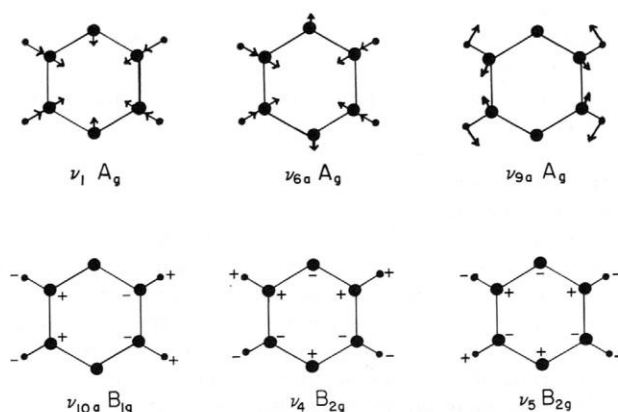


FIG. 2. The important symmetry modes in the pyrazine emission spectra.

turbation theory the vibronic coupling matrix element  $V_{n\pi^*-\pi\pi^*(p)}$  between  ${}^1B_{3u}(n\pi^*)$  and a given  ${}^1\pi\pi^*$  state via the appropriate mode  $p$  is given by the following formula:

$$V_{n\pi^*-\pi\pi^*(p)}^2 = \frac{E_{\pi\pi^*} \cdot f_{n\pi\pi^*}^p}{E_{n\pi^*} \cdot f_{\pi\pi^*}} (E_{\pi\pi^*} - E_{n\pi^*})^2,$$

where  $E_{\pi\pi^*}$  and  $E_{n\pi\pi^*}$  are the transition energies,  $f_{n\pi\pi^*}^p$  is the oscillator strength in the  $\pi^* \leftarrow n$  transition of the vibronically induced intensity and  $f_{\pi\pi^*}$  is the total oscillator strength of the appropriate  $\pi^* \leftarrow \pi$  transition. Substituting the experimental quantities for the two possible choices of the vibronic assignment we obtain a value of  $700 \text{ cm}^{-1}$  for the  $\nu_{10a}$  choice and  $3300 \text{ cm}^{-1}$  for the  $\nu_5$  choice. The value of  $700 \text{ cm}^{-1}$  for  $V_{n\pi^*-\pi\pi^*}$  is comparable with the value of vibronic coupling matrix elements found in other azines (13). A value of  $3300 \text{ cm}^{-1}$ , on the other hand, is about three times larger than that found in any azine. Since  $\nu_5$  mixes  ${}^1B_{3u}(n\pi^*)$  with  ${}^1B_{1u}(\pi\pi^*)$ , such a large matrix element would not be expected. This is because  ${}^1B_{3u}(n\pi^*)$  is largely made up of  $n\pi^*_{bb}$  and  ${}^1B_{1u}(\pi\pi^*)$  is largely  $\pi_a\pi_{ab}^*$  (1). To a first approximation the vibronic coupling operator is a one-electron operator so the matrix element between these two states should be small since they do not have a common  $\pi^*$  orbital. Also the ratio of the frequencies of the  $\nu_{10a}$  mode for pyrazine- $d_4$  and pyrazine- $h_4$  is 0.783 compared to a calculated product rule ratio of 0.784. We will present one further piece of evidence for the assignment of the  $930 \text{ cm}^{-1}$  mode as  $\nu_{10a}(b_{1g})$  after discussing the out-of-plane modes which appear in phosphorescence.

Because of the small oscillator strengths of singlet-triplet  $\pi^* \leftarrow \pi$  transitions relative to  $\pi^* \leftarrow n$ , odd quanta of the  $b_{1g}$  and  $b_{2g}$  modes should not and do not



appear in the pyrazine phosphorescence spectra. The appearance of such bands involves intensity stealing and there is just too little intensity available to be stolen. On the other hand even quanta of such modes should and do appear in the pyrazine- $h_4$  phosphorescence spectrum (6). Their appearance results from a vibronic interaction between the  $n\pi^*$  and  $\pi\pi^*$  states which causes the potential energy surface to distort along the appropriate normal coordinates. In first order this interaction will reduce the force constant of the normal mode in the lower state and raise it in the higher state. The result is a redistribution of the Frank-Condon intensity into even quanta of these out-of-plane modes. The distortion will depend on the vibronic coupling matrix element and on the energy difference between the states. The vibronic coupling matrix element between  $B_{3u}(n\pi^*)$  and  $B_{1u}(\pi\pi^*)$  or  $B_{2u}(\pi\pi^*)$  should be similar in the singlet and triplet manifolds. The energy gaps, on the other hand, will be much smaller in the triplet manifold. As a result the distortion of the potential energy surfaces of the  $b_{1g}$  and  $b_{2g}$  normal coordinates should be more severe in the  ${}^3B_{3u}(n\pi^*)$  state than in the  ${}^1B_{3u}(n\pi^*)$  state. That such distortions can cause even quanta of the modes to appear in the emission spectra is demonstrated by the fact that we find the  $1857\text{ cm}^{-1}$  ( $2 \times 930$ ) and  $1510\text{ cm}^{-1}$  ( $2 \times 755$ ) bands in the pyrazine- $h_4$  phosphorescence spectrum. As we mentioned before the  $1857\text{-cm}^{-1}$  band is considerably more intense in the phosphorescence spectrum than in the fluorescence spectrum and the  $1510\text{-cm}^{-1}$  band only appears in the phosphorescence spectrum. In pyrazine- $d_4$  the  $1452\text{-cm}^{-1}$  ( $2 \times 726\text{ cm}^{-1}$ ) band is more intense in the phosphorescence spectrum and one at  $1292\text{ cm}^{-1}$  ( $2 \times 646\text{ cm}^{-1}$ ) only appears in phosphorescence. The lack of appearance of  $2 \times 755\text{ cm}^{-1}$  ( $2 \times 646\text{ cm}^{-1}$  in pyrazine- $d_4$ ) in fluorescence leads us to lean toward the  $\nu_5$  assignment for these modes and therefore for the  $\nu_{10a}$  assignment of the  $930\text{-cm}^{-1}$  mode ( $728\text{ cm}^{-1}$  in pyrazine- $d_4$ ). If the reverse assignment were correct one would expect  $2 \times 755\text{ cm}^{-1}$  to be more intense than  $2 \times 930$  in the fluorescence spectrum. The lack of appearance of  $2 \times 755\text{ cm}^{-1}$  in fluorescence is therefore interpreted as due to a large energy gap between  ${}^1B_{3u}(n\pi^*)$  and  ${}^1B_{1u}(\pi\pi^*)$ .

#### THE FORBIDDEN ${}^1n\pi^*$ STATE?

We have examined the singlet-singlet absorption spectrum of the pyrazine crystal at  $4.2^\circ\text{K}$  in an effort to find a forbidden  $\pi^* \leftarrow n$  singlet-singlet transition below the allowed origin. The origin of the  ${}^1B_{3u}(n\pi^*) \leftarrow {}^1A_g$  transition occurs at  $30\,057\text{ cm}^{-1}$ . With crystals as large as several millimeters long no sharp absorptions were found below this origin band that did not split in a magnetic field. If the  ${}^1B_{2g}(n\pi^*) \leftarrow {}^1A_g$  origin were below the allowed singlet origin it would surely have enough magnetic dipole intensity to show up under these conditions. Accordingly we conclude that  ${}^1A_{2g}(n\pi^*)$  is not below  ${}^1B_{3u}(n\pi^*)$ .

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