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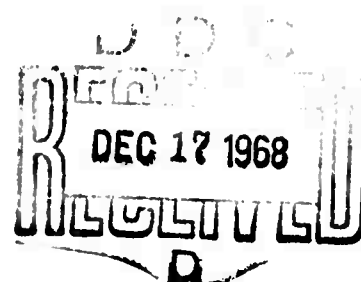
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The Intersystem Crossing to and the Phosphorescence from
the Individual Sublevels of the Lowest Triplet State in Pyrazine at 1.6°K

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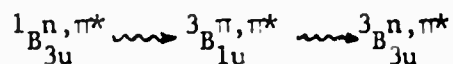
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ABSTRACT

The observed exponential phosphorescence decay of pyrazine in cyclohexane or benzene matrix at 77°K, with lifetime of 18 millisecc, is found to change into a complex decay below 10°K. At 1.6°K, the decay is resolved into three first-order decays of lifetimes 6, 130 and 400 millisecc. These lifetimes are sensitive to changes in temperature and magnetic field strength (Hall, Armstrong, Moomaw and El-Sayed, J. Chem. Phys., 48, 1395 (1968)). Two mechanisms are proposed to explain the observed results, but both propose that at 1.6°K, the spin-lattice relaxation process between the sublevels of the triplet state is slow compared to the 6-millisecc radiative lifetime of the τ_y spin sublevel. In the first mechanism, the 130- and 400-millisecc lifetimes measure the τ_x or $\tau_z \rightsquigarrow \tau_y$ spin-lattice relaxation (S.L.R.) times, but the long- and medium-lived emissions originate from the τ_y sublevel. In the second mechanism, the 130- and 400-millisecc lifetimes correspond to radiative lifetimes of the transitions to the ground state from the τ_z and τ_x sublevels respectively. The recent time-resolved polarization measurements of pyrazine phosphorescence in durene (Moomaw, Tinti and El-Sayed, J. Chem. Phys., in press) indicate that the second mechanism should be at least partially responsible for the observed results.

The steady state intensity of the emission from the different sublevels of the $^3B_{3u}^{n,\pi^*}$ state is determined from the decay curves. For molecules with high phosphorescence yield, when the spin-lattice relaxation process is much slower than the radiative lifetimes, it can be shown that the ratio of the steady state intensity of the emission from the individual sublevels is equal to the ratio of the rate constants for the intersystem crossing processes to these sublevels. It is then concluded that the intersystem crossing process



is ~30 times faster than other processes which require either vibronic interaction or strong enough crystal field to destroy the internal D_{2h} pyrazine symmetry.

The different radiative spin-orbit mechanisms which might give the different sublevels of the $^3B_{3u}^{n,\pi^*}$ state their radiative properties are discussed and the relative values of the spin-orbit interaction energies involved are determined from the observed decay constants.

Alfred P. Sloan and John Simon Guggenheim Fellow.
Contribution No. 2285 from UCLA.

I. Introduction

In the field of triplet state spectroscopy, two of the most active research areas are those involved in determining: 1) the exact mechanism(s) by which the absorbed singlet-singlet excitation is transferred to the lowest triplet state and 2) the exact mechanism(s) by which the lowest triplet state loses its energy by the emission of radiation (phosphorescence).

Studies in the first field consist of examining the fluorescence:phosphorescence intensity ratio as a function of the order of, and energy separation between, the low energy triplet states and the lowest singlet state. Nitrogen heterocyclics present an interesting series of compounds for such studies.

Using the Born-Oppenheimer approximation, the one-electron spin-orbit operators, and the first-order perturbation theory, the following simple selection rules are concluded:¹ $S_{n,\pi^*} \rightarrow T_{\pi,\pi^*}$; $S_{n,\pi^*} \rightarrow T_{n,\pi^*}$; and $S_{\pi,\pi^*} \rightarrow T_{\pi,\pi^*}$.

The luminescence properties of a great number of heterocyclic compounds are found to be explained using these simple selection rules. Exceptions can also be found. However, this qualitative technique is subjected to complications resulting from photochemical changes and radiationless transitions from the lowest singlet state to the ground state. Recently, the decay results of quinoxaline (1,4 diazanaphthalene) phosphorescence in durene and its dependence on magnetic field have been found to be at least qualitatively explained² by an intersystem crossing process which follows the above selection rules. Instead of using flash techniques,² we have used steady state experiments which have enabled us to extract more constants characterizing the decay and the intersystem crossing processes in pyrazine (1,4 diazabenzene) in host lattices.

Studies concerning the phosphorescence mechanisms are done by determining the emission polarization of the molecule of interest dissolved in a suitable

host at low temperatures.³ All the polarization measurements have been done so far at temperatures for which the spin-lattice relaxation between the three sublevels is faster than the radiative lifetime. Under these conditions, the observed emission is a superposition of the emission from the different sublevels of the triplet state. If the zero field splitting in the emitting triplet state is large enough to be resolved on a high-resolution spectrograph, one can measure the polarization of the individual emission lines from each sublevel of the triplet state. So far, this method has not yet been employed (perhaps due to the large line width as compared to the zero field splitting). However, one might be able to observe individual sublevel emissions by resolving them in time rather than in energy. This is possible at very low temperatures and in cases for which the spin-lattice relaxation process between the different spin sublevels is slower than the radiative lifetimes from these states. When this is possible, the phosphorescence mechanisms from the individual sublevels of the lowest triplet state can be revealed. The preliminary results obtained for the pyrazine emission are here summarized, discussed and compared with theoretical predictions.

II. Theoretical Considerations Concerning the Intersystem Crossing Process in Pyrazine

A. Direct Spin-Orbit Perturbation

Pyrazine molecule belongs to the D_{2h} point group. Its lowest singlet state is of the ${}^1B_{3u}^{n,\pi^*}$ type (the x and z axes correspond to the out-of-plane and the N...N axes, respectively, in the pyrazine molecule). The three spin functions, τ_x , τ_y and τ_z , belong[†] to the b_{3g} , b_{2g} and b_{1g} irreducible representation respectively, whereas the singlet state spin function is of an a_g symmetry. For an allowed intersystem crossing process between two states,

[†] It is shown² that these three functions describe the two spins in the yz, xz and xy planes, respectively, for molecules possessing C_{2v} as their point group or as a subgroup of their point group.

selection rules require that the electronic integral of the radiationless transition probability between the two states not vanish. Independent of which theory, Robinson's and Frosch's or Gouterman's, the electronic integral involves the mixing of the singlet and triplet states with the spin-orbit type of interaction. In both theories, the Born-Oppenheimer approximation is assumed. If the perturbation results from the direct spin-orbit interaction ($H_{s.o.}$), the electronic integral can be shown to have the following form:

$$\langle {}^1\Psi_{n,\pi^*} | H_{s.o.} | {}^3\Psi_x \rangle \dots \dots \dots (1)$$

There are at least two triplet states, ${}^3B_{1u}(\pi,\pi^*)$ and ${}^3B_{3u}(n,\pi^*)$, below the lowest singlet state, with the latter state being lowest in energy. The ${}^3B_{2g}(n,\pi^*)$ might be above the lowest triplet state. The corresponding spin-orbit functions of these triplet states are given in Table 1.

The spin-orbit function of the lowest singlet state is $B_{3u} \times a_g = B_{3u}$. Since $H_{s.o.}$ is an interaction energy, it should be totally symmetric (even though the individual orbital part or the spin part of the operator is non-totally symmetric in the electron space and spin domain respectively). Thus the only nonradiative transitions involved in the intersystem crossing process from the ${}^1B_{3u}^{n,\pi^*}$ state are those crossing to a triplet state of total spin-orbit function of symmetry B_{3u} . Only the ${}^3B_{1u}^{\pi,\pi^*}$ state having a spin function τ_y satisfies this selection rule. This is in agreement with previous theoretical predictions¹ that $S_{n,\pi^*} \rightarrow T_{\pi,\pi^*}$ is allowed but $S_{n,\pi^*} \rightarrow T_{n,\pi^*}$ is forbidden.

It is clear that, as a result of the selection rules imposed on the intersystem crossing process in pyrazine, the triplet state is initially formed from the lowest singlet state with its unpaired electrons in the xz molecular plane. It is thus obvious that as a result of excitation in the singlet manifold and because of the selection rules of the intersystem crossing process, the triplet state is first formed in a spin-polarized state. At temperatures for which the spin-lattice relaxation time is slower than

10^{-11} sec (the time for the internal conversion process in the triplet manifold), the molecule loses vibration and electronic energy, but not spin direction, until it finally reaches the lowest triplet state. Since the lowest triplet state is of ${}^3B_{3u}^{n,\pi^*}$ spatial symmetry and the spin of the molecule is polarized in the xz plane ($\Gamma_{T_y} = b_{2g}$), the triplet total function is of B_{1u} symmetry. At temperatures for which the spin-lattice relaxation is slower than the emission lifetime from the B_{1u} sublevel, the emission characteristics of the molecule are completely determined by the radiative properties of this sublevel.

B. Spin-Vibronic and Second-Order Perturbations

One might wonder whether or not spin-vibronic or second-order (spin-orbit-vibronic) perturbations could introduce new intersystem crossing routes which could result in forming the lowest triplet state with its spin polarized in the other two planes (the xy and yz planes). The spin-vibronic perturbation is written in the following form:

$$H_{s.v.} = \sum_a \left(\frac{\partial H_{s.o.}}{\partial Q_a} \right)_0 Q_a \dots \dots \dots (2)$$

where the Q_a 's are the normal coordinates of the different normal modes of the pyrazine molecule. Since $H_{s.v.}$ is totally symmetric, $\Gamma \left(\frac{\partial H_{s.o.}}{\partial Q_a} \right)_0$ would have

the same symmetry property in the electron-spin-space domain as does Q_a in the nuclear domain. The spin vibronic integral can then be written as:

$$\begin{aligned} \langle {}^1\Psi {}^1\theta {}^1\chi | H_{s.v.} | {}^3\Psi {}^3\theta {}^3\chi \rangle = \\ \sum_a \langle {}^1\Psi {}^1\chi | \left(\frac{\partial H_{s.o.}}{\partial Q_a} \right)_0 | {}^3\Psi {}^3\chi \rangle \langle {}^1\theta | Q_a | {}^3\theta \rangle \dots \dots \dots (3) \end{aligned}$$

where Ψ , θ and χ are the electronic, vibration and spin functions respectively. Since ${}^1\theta$ is of a_g symmetry at low temperatures (the zero point function of the lowest singlet state), the perturbation in electronic space $\left(\frac{\partial H_{s.o.}}{\partial Q_a} \right)_0$ must have the same symmetry as Q_a . The latter should have the same symmetry as ${}^3\theta$, the perturbing vibration in the triplet state, i.e.,

$$\frac{\Gamma_{\partial H_{s.o.}}}{\partial Q_a} = \Gamma_{3_\theta}. \text{ From equation (3), and the last conclusion, } \Gamma_{1_{\psi_X}} \times \Gamma_{3_{\psi_X}} = \Gamma_{3_\theta}.$$

Using this equality, the symmetry type of perturbing vibrations in the triplet manifold (Γ_{3_θ}) that might be responsible for the different intersystem crossing processes between the B_{3u}^{n,π^*} state and the three triplet states below it is concluded and given in Table 2. The spin polarization that results from the spin-vibronic interaction with the different vibrations in different triplet states is also given in the same table. Since the molecular vibrations in pyrazine are distributed over all the symmetry species in the D_{2h} point group, it is concluded that group theory does not impose restrictions on the route to be followed by the pyrazine molecule undergoing an intersystem crossing process under spin-vibronic-type perturbation. But how important is the spin-vibronic interaction as compared to the direct spin-orbit interaction? In order to answer this question, let us use Albrecht's⁶ approximate equation:

$$\langle \psi_T | \left(\frac{\partial H_{s.o.}}{\partial Q_a} \right)_0 Q_a | \psi_S \rangle = \int \langle \psi_T | H_{s.o.} | \psi_S \rangle \dots \dots \dots (4)$$

where $\int$ is a constant $\approx \frac{\text{a typical nuclear displacement}}{\text{molecular dimension}} \ll 10^{-1}$. It thus follows that:

$$|\langle \psi_T | \left(\frac{\partial H_{s.o.}}{\partial Q_a} \right)_0 Q_a | \psi_S \rangle| \leq 10^{-1} |\langle \psi_T | H_{s.o.} | \psi_S \rangle|. \dots \dots (5)$$

This equation is found to explain the fact that more than 99% of the total intensity of the pyrazine emission is explained by direct spin-orbit orbit perturbation. It is thus concluded that, according to group theory, spin-vibronic perturbation can give rise to spin polarization in any direction, but the perturbation is probably weaker than the direct spin-orbit perturbation in the framework of the Born-Oppenheimer approximation.

Let us turn our attention to the second-order spin-orbit-vibronic perturbation, but neglect the second-order spin-vibronic-vibronic perturbation. In this type of perturbation, vibronic coupling mixes states in the triplet

manifold. This is then followed by spin-orbit interaction with the $^1B_{3u}^{n,\pi*}$ state. The latter state interacts only with states of $^3B_{1u}$ and $^3B_{2u}$ symmetry via spin-orbit perturbation. The interaction with the first state results in a spin polarization in the xz plane and that with the latter state gives rise to spin polarization in the xy plane. The $^3B_{1u}$, $^3B_{2g}$ and $^3B_{3u}$ states that are located below the lowest singlet state can vibronically couple to the $^3B_{2u}$ state by vibration of b_{3g} , a_u and b_{1g} symmetry respectively. This is the only vibronic coupling that can give rise to spin polarization different from that produced by the direct spin-orbit interaction.

In conclusion, if the crystal field is very weak and pyrazine is assumed to have D_{2h} symmetry, group theory predicts that the intersystem crossing process gives rise to spin polarization only in the xz plane if direct spin-orbit perturbation is important, in the xz and xy planes if second-order spin-orbit-vibronic perturbation is important, and in all three planes if spin-vibronic perturbation is important. If spin-lattice relaxation is very slow, spin polarization can be obtained under steady state excitation in the latter case if the three different spin-vibronic routes have different transition probabilities or if the rate of deactivation of the three sublevels is different. It should be mentioned that the above selection rules can be relaxed if the crystal field is strong and the site symmetry strongly changes the internal D_{2h} symmetry of the molecule.

III. Intramultiplet Nonradiative Processes in the Lowest Triplet State.

Spin-Lattice Relaxation

As a result of the intersystem crossing process in pyrazine, the phosphorescence can originate from a spin-polarized state under the following conditions:

1. The spin-lattice relaxation time is slower than both the triplet-triplet internal conversion process and the phosphorescence process.

2. The perturbation(s) responsible for the intersystem crossing process ($S_1 \rightsquigarrow T_1$ and $T_1 \rightsquigarrow S_0$) are such that they result in different population for the three different multiplets of the triplet manifold.

It was concluded in the previous section that a) first-order (direct) spin-orbit perturbation can populate only one sublevel (τ_y), b) the second-order spin-orbit-vibronic perturbation can populate both τ_y and τ_z , and c) the spin-vibronic perturbation can populate the three sublevels. The relative probability of populating the different sublevels by the last two perturbations is unknown theoretically. However, it is expected that the direct spin-orbit perturbation is the most probable. Therefore if condition 1 is satisfied, it is expected that the phosphorescence is emitted from a spin-polarized state. For this reason, we will summarize below the factors that determine spin-lattice relaxation time.

The mechanisms involved in the spin-lattice relaxation process of a paramagnetic impurity in an ionic solid have been carefully examined both experimentally and theoretically.⁷ Waller⁸ proposed a mechanism in 1932 in which the modulation of the magnetic dipolar interaction by the phonon field of lattice vibrations causes spin-lattice relaxation. This mechanism does not explain the observed temperature and magnetic field effects on the relaxation process. Heitler and Teller⁹ pointed out that the modulation of the electric field by the lattice vibrations could modulate the orbital motion of the electron, which is coupled to the spin motion via spin-orbit coupling. The modulation of the orbital motion is then felt by the spin system and as a result undergoes spin relaxation. The theory for this mechanism was later developed quantitatively.¹⁰ A number of processes are now known to be responsible for the spin-lattice relaxation and they differ in their temperature

dependence. The direct process prevails at low temperatures and involves the exchange of the spin quantum with one phonon. This process is found to have a spin relaxation time T_1 which is inversely proportional to the absolute temperature (T). The Raman process in which the spin system absorbs a quantum of one frequency and scatters that of another is important at higher temperatures. This process is found to give a relaxation time T_1 , which is proportional to T^{-7} (or T^{-9}). In some systems in which the crystal field splitting Δ is smaller than the maximum phonon energy, a third mechanism is found which accounts for their relaxation process. This mechanism involves the simultaneous absorption of a phonon of energy δ' , and the emission of another of energy $\delta' + \delta$ along with spin flip from one spin level to a lower one having a separation of δ . This process¹¹ has a relaxation time $T_1 \alpha_e^{-\Delta/kT}$.

Spin-lattice relaxation processes of a spin impurity in molecular crystals have not as yet been carefully investigated. The presence of spin system in the ground state of molecular crystals (free radicals) is not too common. The triplet state, however, can offer a method of introducing unpaired spins in molecular crystals. It would be interesting to determine T_1 in molecular crystals, compare it with that observed in ionic crystals, and examine the importance of the above mechanisms in the process of spin-lattice relaxation in molecular crystals. In all the above mechanisms, the relaxation time is found to be inversely proportional to the square of both the orbital-lattice interaction (H_{OL}) and the spin-orbit interaction (H_{SO}). In addition to H_{OL} and H_{SO} , quantities like the velocity of sound, phonon density and occupation number enter into the expression for the spin-lattice relaxation time.

IV. Summary and Discussion of the Decay Results

It is well-known³ that the pyrazine phosphorescence in rigid glasses has a lifetime of ~ 20 millisecc at 77°K. The fact that the quantum yield is

0.5 indicates that the observed lifetime is very close to the radiative one. The calculated lifetime, using the S. O. coupling between the ${}^3B_{3u} \rightsquigarrow {}^1A_g$ transition and both the ${}^3B_{3u} \rightsquigarrow {}^3B_{2g}$ and ${}^1B_{1u} \rightarrow {}^1A_g$ transitions, is found¹² to be in good agreement with the observed one.

In cyclohexane or benzene matrix, the pyrazine phosphorescence is found to be exponential with only one lifetime of 18 millisecc at 77°K. At 1.6°K, a nonexponential decay is observed which can be resolved¹³ into three exponential decays of lifetimes: 6, 130 and 400 millisecc. These lifetimes remain constant in the temperature range 1.6-3°K. At 4.2°K, the three lifetimes resolved are: 6, 60 and 320 millisecc. Between 4.2-10°K, the decay is rather nonexponential and complex and above 10°K, the decay becomes exponential with only one lifetime, 18 millisecc (the same as that observed at 77°K). The decay characteristics change by the application of a magnetic field at 1.6°K (see Figure 1) and 4.2°K but not at 77°K.

The fact that the long- and medium-lived components disappear above 10°K eliminates the possibility that the emission is due to impurities. The great change in the decay curve between 1.6°K and 10°K is not accompanied by any change in the relative intensity of the emission of the different sites. This eliminates the possibility that the three decays belong to emission from three different sites. In addition, the same decay constants are obtained in two different hosts, cyclohexane and benzene, in which the distribution and the energy of the different sites are different. The fact that the three different decays are observed for the 0,0 as well as for other vibronic bands might eliminate the possibility that the emission results from states of different electronic origin (e.g., ${}^3B_{3u}$ as well as ${}^3B_{2g}$ or ${}^3B_{1u}$). It is thus very probable that we are observing emission from molecules in different sublevels of the triplet state. In support of this is the great sensitivity of the three decay constants to the magnetic field strength. In the following

section, we will propose mechanisms that might successfully explain the observed results.

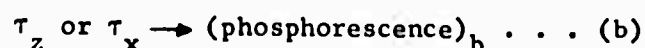
Following the absorption process (see Figure 2), the excited pyrazine molecules are deactivated to the zero point level of the lowest ${}^1B_{3u}^{n,\pi^*}$ state in $\sim 10^{-11}$ sec. This is followed by the intersystem crossing processes discussed in Section II. The ${}^1B_{3u}^{n,\pi^*} \rightsquigarrow {}^3B_{1u}^{\pi,\pi^*}$ (which corresponds to a transition between states of total functions of B_{3u} symmetry) is the most probable intersystem crossing process in pyrazine because of its strong first-order spin-orbit interaction. Let us thus follow the fate of those molecules that follow the latter route.

The intersystem crossing process is then followed by the internal conversion process ${}^3B_{1u}^{\pi,\pi^*}(\tau_y) \longleftrightarrow {}^3B_{3u}^{n,\pi^*}(\tau_y)$, which takes place in $\sim 10^{-11}$ sec. At 1.6°K, this time is short compared to the spin-lattice time, T_1 . Thus the molecules are found in the ${}^3B_{3u}^{n,\pi^*}$ state with the spinning electrons in the xz plane. Whether the emission will result only from the τ_y sublevel of the triplet state or from the others depends mainly on the magnitude of the spin-lattice relaxation time (T_1) between the different spin levels as compared to the radiative lifetime of the transition from the τ_y sublevel to the ground state. In pyrazine, the triplet sublevel τ_y of the ${}^3B_{3u}^{n,\pi^*}$ state strongly couples to the ${}^1B_{1u}^{\pi,\pi^*}$ by first-order spin-orbit perturbation to give rise to the observed N...N-polarized[†] phosphorescence. Thus the sublevel which is populated as a result of the most probable intersystem crossing process is the one that has the strongest radiative transition probability. The observed radiative lifetime of the ${}^3B_{3u}^{n,\pi^*}(\tau_y) \rightarrow {}^1A_g$ is thus 6 millisec (not 18 millisec as has been previously assumed).

There are at least two possible mechanisms that might explain the medium- and long-lived emission. In both mechanisms, we will assume that either vibronic

[†] The mixing between the ground state and τ_y function of the ${}^3B_{2g}^{n,\pi^*}$ state gives rise to N...N polarized emission¹² due to the radiative transition ${}^3B_{3u}^{n,\pi^*}(\tau_y) \longleftrightarrow {}^3B_{2g}^{n,\pi^*}$.

and second-order spin-orbit-vibronic or crystal field perturbations succeed in populating the other two sublevels of the lowest triplet state (τ_x and τ_z). The observed medium- or long-lived emission can result from one (or both) of the following mechanisms:



Mechanism (a) is effective when spin-lattice relaxation (S.L.R.) time is shorter than the radiative lifetime from sublevels τ_x or τ_z . Mechanism (b) is operative if the spin-lattice relaxation process is slower than the radiative process from the three sublevels. If mechanism (a) is the correct one, then the lifetimes of 130 and 400 millisec observed at 1.6°K represent spin-lattice relaxation times from τ_x or τ_z to τ_y .

It is obvious that the polarization of phosphorescence (a) and that of (b) should be different. The polarization of phosphorescence (a) should be similar to that for the short-lived emission (along the N...N axis), whereas that of phosphorescence (b) should be differently polarized. The polarization of the decay curve has recently been measured,¹⁶ and the results show that at least the medium- and short-lived emissions appear to have slightly different polarizations. This indicates that at least part of the medium-lived emission originates according to mechanism (b).

V. Comparison of Theory and Experiments

A. The Radiative Process

Goodman and Krishna calculated¹² for the radiative lifetime of the ${}^3B_{3u} \rightarrow {}^1A_g$ transition a value of one millisec. They used the ${}^1B_{1u} \leftrightarrow {}^1A_g$ and the ${}^3B_{2g} \leftrightarrow {}^3B_{3u}$ to perturb the ${}^3B_{3u}$ and 1A_g states respectively. In both cases one can show that the τ_y sublevel of the triplet state is involved.

They compared their calculated result with the lifetime observed at 77°K instead of the radiative lifetime of the τ_y sublevel. The relation between the observed value of the lifetime and those observed for the individual components is given below.

At temperatures for which the S.L.R. is very fast compared to the radiative lifetimes, the observed rate constant for the emission is given² by:

$$k = \sum_i^3 n_i k_i$$

where n_i and k_i are the fraction population and the radiative rate constant of sublevel i of the lowest triplet state. At this temperature $n_i = 1/3$ and the above formula is written as: $k = 1/3 (k_{\tau_x} + k_{\tau_y} + k_{\tau_z})$. For pyrazine, one can neglect k_{τ_x} and k_{τ_z} as compared to k_{τ_y} . This leads to a value of $k = 1/3 \times 1/6 = 1/18 \text{ millisecc}^{-1}$, corresponding to a lifetime of 18 millisecc, in excellent agreement with the observed value at 77°K. It is interesting to point out that only if $k_{\tau_x} = k_{\tau_y} = k_{\tau_z}$ would the observed lifetime equal that observed from any of the individual lifetimes at very low temperatures.

Let us discuss the radiative mechanism of the medium-lived emission. If one assumes that the short-lived emission is polarized along the N...N axis (z axis), then the medium-lived emission might be polarized along the y or the x-molecular axes. Work is now in progress to determine the exact polarization direction. Theoretically, in addition to the z-polarized emission, only y-polarized emission is predicted to originate as a result of direct spin-orbit interaction in the D_{2h} point group. Since most of the emission is a result of direct spin-orbit perturbation, x-polarized emission should not be emitted if the molecule has a D_{2h} site symmetry. The medium-lived emission might thus be y-polarized and thus originate from perturbing the emitting triplet state $B_{3u}^{n,\pi*} (\tau_z)$ with the $B_{2u}^{\pi,\pi*} \longleftrightarrow {}^1A_g$. Certainly, the latter transition is electric dipole-allowed. Its inferior perturbation

(as compared to that giving rise to the short-lived emission) is blamed on the fact that the spin-orbit interaction involved has no one-center terms on the nitrogen, as shown below:

$$\begin{aligned} \langle {}^3B_{3u}^{n,\pi*}(\tau_z) | H_{s.o.} | {}^1B_{2u}^{\pi,\pi*} \rangle &= \langle (n,\pi_4) | H_{s.o.} | \pi_3, \pi_4 \rangle \\ &= \langle n | H_{s.o.} | \pi_3 \rangle \dots \dots \dots (6) \end{aligned}$$

Since π_3 has a node plane perpendicular to the molecular plane and passing through the nitrogen atoms, integral (6) has no one-center terms on the nitrogen. The only one-center terms that can result from integral (6) are those on the carbon atoms arising because of the delocalization of the lone pair of electrons on the C-C and C-H bonds. It might be interesting to estimate the ratio of the spin-orbit interaction resulting from this mechanism as compared to that resulting from the radiative perturbation of the τ_y sublevel. The latter is perturbed by the ${}^1B_{1u}^{\pi,\pi*}$ state, which gives rise to the following integral:

$$\begin{aligned} \langle {}^3B_{3u}^{n,\pi*}(\tau_y) | H_{s.o.} | {}^1B_{1u}^{\pi,\pi*} \rangle &= \langle (n,\pi_4) | H_{s.o.} | \pi_2, \pi_4 \rangle \\ &= \langle n | H_{s.o.} | \pi_2 \rangle \dots \dots \dots (6) \end{aligned}$$

Since π_2 has no nodes through the nitrogen atoms, one-center terms on the nitrogen as well as the carbon atoms (because of the delocalization of the lone pairs) are nonvanishing.

If one makes the following assumptions: a) the observed 6-millisec and 120-millisec lifetimes for the short- and medium-lived emission correspond to radiative lifetimes, and b) the intensity and energy of the ${}^1B_{1u} \longleftrightarrow {}^1A_g$ and ${}^1B_{2u} \longleftrightarrow A_g$ transitions are comparable, then

$$\left| \frac{\langle {}^3B_{3u}^{n,\pi*} | H_{s.o.} | {}^1B_{1u}^{\pi,\pi} \rangle}{\langle {}^3B_{3u}^{n,\pi} | H_{s.o.} | {}^1B_{2u}^{\pi,\pi} \rangle} \right|^2 \geq \frac{1/6}{1/120} \geq \frac{120}{6} \geq 20$$

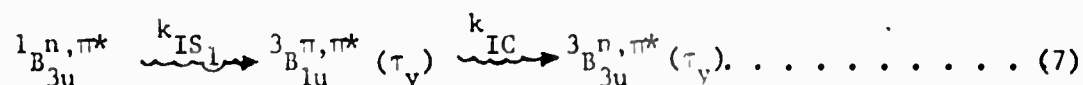
- i.e., the spin-orbit interaction having one-center terms on the nitrogen and

carbon is ≥ 4.5 times larger than that with only one-center terms on carbon. This fact might support the recent calculations¹⁷ showing large delocalization of the lone pairs in pyrazine.

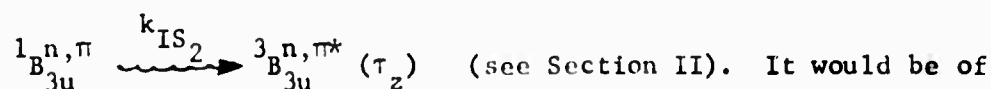
B. Nonradiative Intersystem Crossing Processes

The decay measurements are performed in the following manner. The steady state illumination of pyrazine is cut off in 1 millisecc with a shutter which simultaneously triggers the scope. The reproducibility of the decay curve is excellent. Decay curves are followed up to 2 sec, i.e., over 300 short lifetimes, seventeen medium lifetimes and five long lifetimes. From log I vs. time plots, the different decay components can be resolved successfully at 1.6°K. By extrapolating log I vs. time to $t = 0$, the initial steady state intensity I_s^0 , I_m^0 and I_l^0 of the emission from molecules in the τ_y , τ_z and τ_x sublevels is determined.

Let us consider the short- (s) and medium- (m) lived emission. The short-lived emission originates from the τ_y sublevel. The population of this sublevel is accomplished by an intersystem crossing process for which the direct spin-orbit interaction is responsible. This process is represented by:



The medium-lived emission is probably from the τ_z sublevel; but more important, a vibronic-type interaction (in the form of spin-vibronic or second-order spin-orbit-vibronic) or strong crystal field that relaxes the D_{2h} selection rules is involved in the intersystem crossing process



theoretical interest to calculate the ratio $\frac{k_{IS1}}{k_{IS2}}$. It can be shown that in the steady state approximation at 1.6°K:

$$k_{IS1} \left[^1_{B_{3u}} \right] = k_{IC} \left[^3_{B_{1u}} \right] = k_{\tau_y} \left[\tau_y \right] = CI_S$$

where [], k_τ and C represent concentration sign, radiative rate constant and a constant, respectively. This equation assumes that:

a) the intersystem crossing takes place only from the lowest singlet level ($^1B_{3u}$), b) the only deactivating mechanism for molecules in the τ_y sublevel is via radiation to the ground state. The latter assumption is based on the fact that the quantum yield is reasonably high and at 1.6-3°K, the spin-lattice relaxation is slow, as shown by the insensitivity of the decay constants to temperature in this region. Using similar assumptions, one can write for the intersystem crossing process populating τ_z the following equations, depending on the mechanism involved:

$$k_{IS_2}[^1B_{3u}] = k_{IC}[\tau_z] = k_{\tau_z}[\tau_z] = CI_m^0 \dots \dots \dots (9a)$$

$$k_{IS_2}[^1B_{3u}] = k_{\tau_z}[\tau_z] = CI_m^0 \dots \dots \dots (9b)$$

From equations 8 and 9:

$$\frac{k_{IS_1}}{k_{IS_2}} = \frac{I_s^0}{I_m^0} \approx 30^\dagger ; \quad \text{i.e., } k_{IS_1} = 30 \times k_{IS_2} .$$

Thus the transition probability for the intersystem crossing process is ~30 times greater if the process is a result of the direct first-order spin-orbit perturbation than when it involves spin-vibronic, second-order spin-orbit-vibronic, or crystal field perturbations.

A few comments need to be made concerning the rate of the S.L.R. process and the nonradiative transitions between the lowest triplet state and the ground state. If the polarization results are interpreted correctly, then a lower limit for the S.L.R. time and the lifetime of the nonradiative processes between the lowest triplet state and the ground state can be set at 130-400 millisecc at 1.6°K.

[†] Experimentally determined: L. Hall and M. A. El-Sayed, J. Chem. Phys., in press.

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Table 1. The spin-orbit functions of the different triplet states that are located below the lowest singlet state ($^1B_{3u}^{n,\pi^*}$) in pyrazine.

triplet state	spin function	spin orbit functions*
$^3B_{1u}^{(\pi,\pi^*)}$	τ_x	B_{2u}
	τ_y	<u>B_{3u}</u>
	τ_z	A_u
$^3B_{2g}^{(n,\pi^*)}$	τ_x	B_{1g}
	τ_y	A_g
	τ_z	B_{3g}
$^3B_{3u}^{(n,\pi^*)}$	τ_x	A_u
	τ_y	B_{1u}
	τ_z	B_{2u}

* The underlined state has nonvanishing electronic integral in the radiationless transition probability expression for the intersystem crossing process from the $B_{3u}^{(n,\pi^*)}$ singlet level.

Table 2. The types of vibrations involved in the spin vibronic perturbations that might be involved in the intersystem crossing process in pyrazine.

triplet state	spin function	vibration of the triplet state
${}^3B_{1u}^{\pi,\pi^*}$	τ_x	b_{1g}
	τ_y	a_g
	τ_z	b_{3g}
${}^3B_{2g}^{n,\pi^*}$	τ_x	b_{2u}
	τ_y	b_{3u}
	τ_z	a_u
${}^3B_{3u}^{n,\pi^*}$	τ_x	b_{3g}
	τ_y	b_{2g}
	τ_z	b_{1g}

FIGURE CAPTIONS

Figure 1. The effect of 4.8 k Gauss magnetic field on the decay of pyrazine phosphorescence in benzene matrix at 1.6°K. The horizontal axis represents time (5 msec/div.) and the vertical axis is a linear relative intensity scale. The decay curve at bottom is recorded in the absence of the magnetic field, whereas that on top is that in the presence of the field. The apparent increase in lifetime on the application of the field is actually a result of an increase in the lifetime of the short-lived component and a decrease in the lifetimes of the other two long-lived components of the decay.

Figure 2. Spin polarization and phosphorescence resulting from the most probable intersystem crossing route and following the direct absorption in pyrazine at temperatures for which the spin-lattice relaxation is slower than the phosphorescence as well as the internal conversion processes. The different spin sublevels of the ${}^3B_{1u}^{\pi,\pi^*}$ and ${}^3B_{3u}^{\pi,\pi^*}$ triplet states are drawn arbitrarily in the order of increasing energy, $\tau_x(B_{3g})$, $\tau_y(B_{2g})$ and $\tau_z(B_{1g})$.

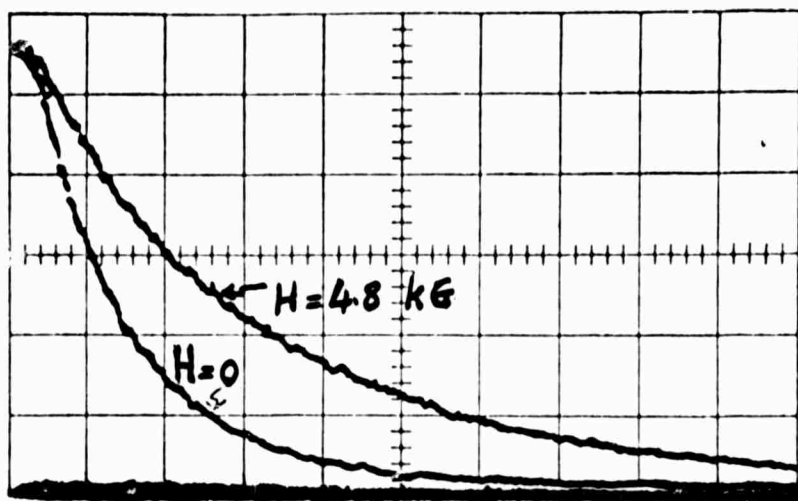


Figure 1

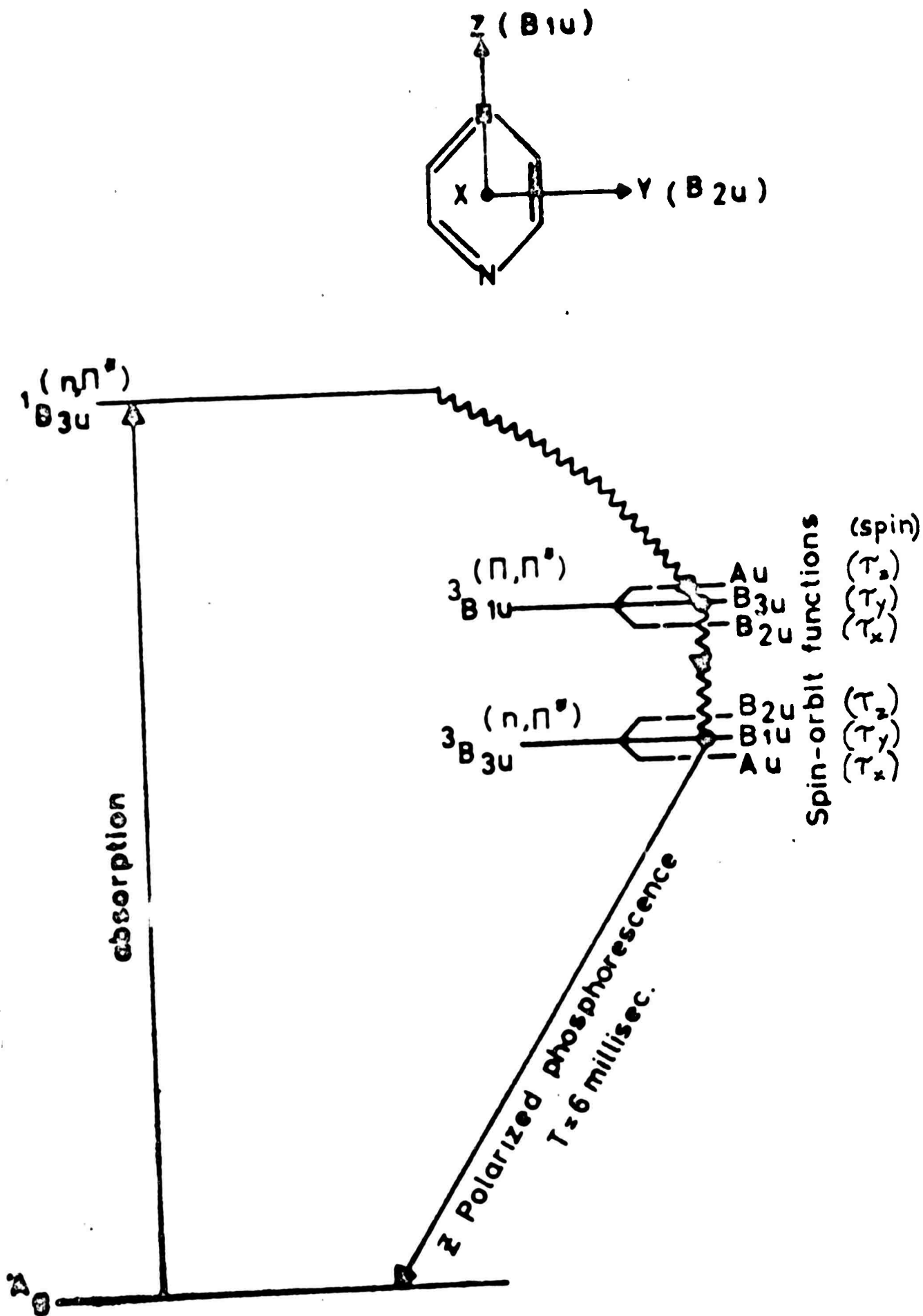


Figure 2

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13. ABSTRACT
The observed exponential phosphorescence decay of pyrazine in cyclohexane or benzene matrix at 77°K, with lifetime of 18 millisecc, is found to change into a complex decay below 10°K. At 1.6°K, the decay is resolved into three first-order decays of lifetimes 6, 130 and 400 millisecc. These lifetimes are sensitive to changes in temperature and magnetic field strength (Hall, Armstrong, Moomaw and El-Sayed, J. Chem. Phys., <u>48</u>, 1395 (1968)). Two mechanisms are proposed to explain the observed results, but both propose that at 1.6°K, the spin-lattice relaxation process between the sublevels of the triplet state is slow compared to the 6-millisecc radiative lifetime of the τ_y spin sublevel. In the first mechanism, the 130- and 400-millisecc lifetimes measure the τ_x or τ_z or τ_y spin-lattice relaxation (S.L.R.) times, but the long- and medium-lived emissions originate from the τ_y sublevel. In the second mechanism, the 130- and 400-millisecc lifetimes correspond to radiative lifetimes of the transitions to the ground state from the τ_z and τ_x sublevels respectively. The recent time-resolved polarization measurements of pyrazine phosphorescence in durene (Moomaw, Tinti and El-Sayed, J. Chem. Phys., in press) indicate that the second mechanism should be at least partially responsible for the observed results.
(Continued on next page)

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
triplet state spin-lattice relaxation phosphorescence pyrazine intersystem crossing						
<u>ABSTRACT, continued</u> The steady state intensity of the emission from the different sublevels of the $^3B_{3u}^{n,\pi*}$ state is determined from the decay curves. For molecules with high phosphorescence yield, when the spin-lattice relaxation process is much slower than the radiative lifetimes, it can be shown that the ratio of the steady state intensity of the emission from the individual sublevels is equal to the ratio of the rate constants for the intersystem crossing processes to these sublevels. It is then concluded that the intersystem crossing process $^1B_{3u}^{n,\pi*} \rightsquigarrow ^3B_{1u}^{n,\pi*} \rightsquigarrow ^3B_{3u}^{n,\pi*}$ is ~30 times faster than other processes which require either vibronic interaction or strong enough crystal field to destroy the internal D_{2h} pyrazine symmetry. The different radiative spin-orbit mechanisms which might give the different sublevels of the $^3B_{3u}^{n,\pi*}$ state their radiative properties are discussed and the relative values of the spin-orbit interaction energies involved are determined from the observed decay constants.						