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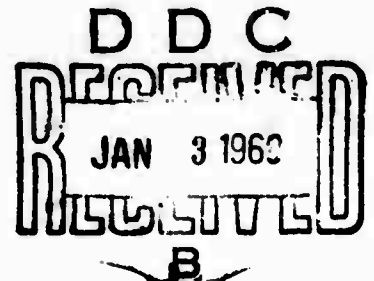
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Determination of the Rate Constants
of the Intersystem Crossing Processes to the
Individual Multiplets of the Lowest Triplet State

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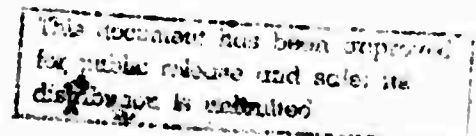


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DETERMINATION OF THE RATE CONSTANTS
OF THE INTERSYSTEM CROSSING PROCESSES TO THE
INDIVIDUAL MULTIPLETS OF THE LOWEST TRIPLET STATE

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The decay of the phosphorescence emission from the three individual sublevels of the lowest triplet state has recently been reported⁽¹⁾ for the first time for pyrazine at 1.6°K. This is observed when the spin-lattice relaxation processes between the three sublevels are slower than the radiative processes from the individual sublevels.^{(1),(2)} Furthermore, the three observed emission lifetimes should be different so that they may be resolved in time. There are a good number of molecules for which these conditions are satisfied.⁽³⁾ It thus appears that one can study the radiative and nonradiative properties of the individual sublevels of the lowest triplet state of phosphorescent molecules.

A number of properties are now being examined in our laboratories. We report here on a new method that can be used to determine the rate constants of the intersystem crossing processes leading to the population of the three different sublevels of the lowest triplet states of phosphorescent molecules. A knowledge of these constants (or their ratios) is vital in determining the relative importance of the different routes of the intersystem crossing processes in molecules.

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The System:

1. A molecule excited to a singlet state loses its energy by internal conversion processes and finally reaches the lowest singlet state, S_1 .
2. Intersystem crossing process proceeds from S_1 to the different triplet sublevels τ_1 , τ_2 and τ_3 of the lowest triplet state, either directly or indirectly via other triplet states located between S_1 and the lowest triplet state. The pumping rates of the τ_1 , τ_2 and τ_3 sublevels from S_1 have the rate constants k_1 , k_2 and k_3 , respectively. Each one of these rate constants may or may not be a composite of other rate constants, depending on the exact mechanism involved in the $S_1 \rightarrow \tau_i$ radiationless transitions.
3. The system is at temperatures for which the S.L.R. processes between τ_1 , τ_2 and τ_3 are much slower than the radiative and nonradiative processes from the three sublevels to the ground state.

Simple Relationships:

The application of the steady state approximation to the formation and disappearance of any of the multiplets, e.g., τ_1 , of the above system gives the following relation:

$$K_{(IS)i}[S_1] = K_i[\tau_i] \quad (1)$$

where $K_{(IS)i}$ is the rate constant for the intersystem crossing process from S_1 to the τ_i sublevel, $K_i (=K_{(rad)i} + K_{(nonradiative)i})$ is the observed rate constant of the decay of sublevel i , and $[S_1]$, $[\tau_i]$ represent the steady state concentrations of the lowest singlet state and sublevel (i) of the lowest triplet state, respectively. The observed steady state intensity, I_i , of the emission from sublevel τ_i is given by:

$$I_i = K_{(rad)i}[\tau_i] = K_i[\tau_i]\varphi_i = K_{(IS)i}[S_1]\varphi_i \quad (2)$$

where $\varphi_1 = \frac{K_{(rad)1}}{K_1}$ is the phosphorescence quantum yield of sublevel 1.

Applying equation (2) to the emission from any two of the sublevels, e.g.,

τ_1 and τ_2 , one obtains:

$$\frac{I_1}{I_2} = \frac{K_{(IS)1}}{K_{(IS)2}} \times \frac{\varphi_1}{\varphi_2} \quad (3)$$

If one determines φ_1 , φ_2 and φ_3 at these temperatures, two independent equations can be obtained relating $\frac{I_1}{I_2}$ and $\frac{I_1}{I_3}$ to ratios involving $K_{(IS)1}$. If the total K_{IS} ($= K_{(IS)1} + K_{(IS)2} + K_{(IS)3}$) is determined in the usual manner, one can solve for $K_{(IS)1}$, $K_{(IS)2}$ and $K_{(IS)3}$ individually.

Applications to Pyrazine-d₄:

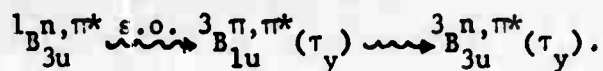
Since φ_1 , φ_2 and φ_3 are not yet known for any molecule, we selected a molecule with very high phosphorescent quantum yield, pyrazine-d₄. The change of the phosphorescence lifetime upon deuteration is found to be absent for the short-lived emission and only small for the medium- and long-lived emissions. These results strongly suggest that the observed lifetime is near the radiative one for a molecule having as high a triplet-state energy as pyrazine.⁽⁵⁾

These facts justify making the assumption that $\varphi_1 = \varphi_2 = \varphi_3 = 1$. The initial intensity of the three decay components is determined from the decay curve. From polarization and theoretical considerations⁽⁶⁾ the short-, medium-, and long-lived emissions are assigned to radiation from the τ_y , τ_z and τ_x sublevels of the $^3B_{3u}$ state, respectively.[†] Using equation (3), one determines the ratios $\frac{K_{IS}(\tau_z)}{K_{IS}(\tau_y)}$ and $\frac{K_{IS}(\tau_x)}{K_{IS}(\tau_y)}$ to be 2% and 4%, respectively. This means

that the most probable intersystem crossing route in pyrazine is the one(s) that populates the τ_y sublevel of the $^3B_{3u}^{n,\pi^*}$ state. Such a conclusion is in agreement with predictions made previously⁽⁷⁾ which proposed that the most

[†] The N...N and the out-of-plane axes are designated as the z and x axes, respectively.

probable intersystem crossing process in pyrazine is:



The ${}^1B_{3u}^{n,\pi^*} \xrightarrow{s.o.} {}^3B_{1u}^{\pi,\pi^*}$ is the only route allowed by spin-orbit selection rules. The other two levels, τ_z and τ_x , are thus populated by processes involving spin orbit-vibronic or spin-vibronic type interaction. From the determined ratio, it is clear that these processes are 25-50 times less probable than the first-order-allowed processes in pyrazine.

The application of this method to other systems is now in progress, and a complete account of the work will be published later.

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