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Recent Studies on Triplet-Singlet Transitions in Aromatic Molecules

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ABSTRACT

The paper is divided into four parts. The first part discusses the selection rules of the intersystem crossing process in systems having both n,π^* and π,π^* types of states. Using the Born-Oppenheimer approximation, first-order selection rules predict that the nonradiative singlet $\rightsquigarrow$ triplet transitions between states of different types (e.g., $S_{n,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$ or $S_{\pi,\pi^*} \rightsquigarrow T_{n,\pi^*}$) should be two orders of magnitude more probable than those involving singlet and triplet states of the same electronic type (e.g., $S_{\pi,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$ and $S_{n,\pi^*} \rightsquigarrow T_{n,\pi^*}$). This type of selection rule is shown to result in high degree of spin polarization in the triplet states formed in these systems as well as in other systems in which one of the possible routes involved in the intersystem crossing process is favored over all the others (except when the molecule under examination belongs to the Ci or the cubic point groups). The detection of the polarized state by observing the phosphorescence emission requires that the radiative lifetime of the latter from at least one of the three sublevels of the lowest triplet state be shorter than the characteristic time for the spin-lattice relaxation processes between the three sublevels of the triplet state. This is demonstrated to be the case for pyrazine in its n,π^* triplet state at low temperatures (1.6°-10°K) and discussed in Section III. The different mechanisms proposed for the spin-lattice relaxation process are briefly discussed. The observed spin-lattice relaxation times for pyrazine at 1.6° are found to be comparable to those observed for a number of ionic paramagnetic impurities in inorganic systems at the same temperature.

In the third part of the paper (Section IV), a summary of the theory of the triplet-singlet radiative transitions is given. A comparison of phosphorescence properties of the different systems is made and the observed differences are explained in the framework of the present theory. The phosphorescence of aromatic hydrocarbon is known to be the most forbidden electronic dipole transition known for polyatomic molecules. The reason for this is discussed, and the consequence of this fact is shown to be a great sensitivity of the triplet $\rightsquigarrow$ singlet radiative transition of these molecules to weak perturbations such as those produced by solvent effects and halogen substitution. Proposed explanations are given for the observed changes in the polarization of this transition resulting from these different weak perturbations.

In the last part of this paper (Section V), the important experiments needed in this field are recommended.

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I. Introduction

Ever since Jablonski[1] put forward his extremely useful energy level diagram, known after him, which he successfully used to explain the different emission characteristics of molecules, spectroscopists and molecular physicists have been trying to understand in detail the important factors that determine those characteristics, and in particular, the rates and mechanisms of the different radiative and nonradiative processes involved. In this paper I would like to summarize an active part of our research efforts in this direction and to show how they integrate with the present understanding of these different processes. The order of the presentation follows the order of the different events that take place following the excitation of an aromatic molecule to its excited singlet state. Our interest will be focused more on the triplet-singlet transitions.

It might be useful to describe qualitatively the different processes that follow the absorption of light by an aromatic molecule. For this purpose, a Jablonski type diagram is required and is given in Figure 1. In this figure, radiative processes are indicated by solid arrows and given the numbers I for absorption, IV for fluorescence (i.e., multiplicity allowed emission) and VI for phosphorescence (multiplicity forbidden emission). The numbers II, V and VIII represent internal conversion processes (multiplicity allowed unimolecular nonradiative processes) and III and VII represent the intersystem crossing processes (multiplicity forbidden unimolecular nonradiative processes). Bimolecular processes can also take place for excited molecules in S_1 or T_1. At large concentrations and rate constants, photochemical processes might even take place for excited molecules in higher singlet and triplet states (e.g., photochemical reaction with solvents). This interesting branch of chemistry occupies the research time of a number of physical organic chemists and will not be discussed in this paper.

It might prove valuable to give the range of the observed values for these different rate constants in two different types of systems, those having π,π^* states as their low-lying energy states, e.g., aromatic hydrocarbons and their haloderivatives, and those with their lower states of the n,π^* and π,π^* type, e.g., nitrogen heterocyclics and aromatic ketones. These values are summarized in Table 1. It is the observed large variation of these rate constants in different systems that has stimulated a great amount of interest and research by many scientists in this active field.

In Section II, the singlet $\rightsquigarrow$ triplet nonradiative transitions will be discussed (process III in Fig. 1). In this section, a summary of the important conclusions of the present theory of nonradiative processes is given. In Section III, the properties of molecules excited in their lowest triplet state will be discussed, with particular emphasis on pyrazine in its n,π^* triplet state. In this section a summary of the important mechanisms involved in the spin-lattice relaxation processes is given, and the manner in which the latter modulate the observed phosphorescence decay is explained. In Section IV, the theory of the phosphorescence process in polyatomic molecules is summarized. The observed behavior of the phosphorescence characteristics of different aromatic systems and their derivatives is explained in the framework of the present theory. In the last section, Section V, recommendations are made concerning the important areas of research that need to be investigated in order to make our understanding of these processes more sound.

II. Nonradiative Singlet $\rightsquigarrow$ Triplet Transitions

It is now believed that in reasonably large molecules, e.g., benzene, naphthalene, etc., nonradiative transitions can take place because of the perturbation caused by interactions within the molecule undergoing the nonradiative transition. The solvent is believed to act as a sink for the energy given off by the solute molecule at a rate determined by the latter.

In the framework of the Born-Oppenheimer approximation, the perturbation theory gives the following expression[2] for the probability of a nonradiative transition between states I and II:

$$W_{I,II(sec^{-1})} = \frac{8\pi^2\tau}{h^2} \Pi_{i,j}[<\theta_{Ii}|\theta_{IIj}>]^2[<\Phi_I|H'|\Phi_{II}>]^2 \quad \ldots\ldots\ldots \text{(1)}$$

where θ_{Ii} and θ_{IIj} are the vibrational wavefunctions i and j of the electronic states I and II, respectively; Φ_I and Φ_{II} are the electronic wavefunctions of states I and II, respectively; τ is the relaxation time of the vibronic levels; H' is the perturbing Hamiltonian. For transitions between states of similar multiplicity, H' is the electron-electron repulsion, the vibronic-electronic or the rotational-electronic interaction term. For nonradiative transitions between states of different multiplicity, H' must contain the spin-orbit interaction between the intercombining states with or without the other terms involved in spin-allowed transitions.

In the following section, the nonradiative processes in molecules containing low-energy n,π* and π,π* states, e.g., nitrogen heterocyclics and aromatic carbonyl compounds, will be discussed. Selection rules will be derived assuming the validity of the Born-Oppenheimer approximation. The consequences of the breakdown of such an approximation will be briefly discussed.

Selection Rules for the Intersystem Crossing Process

It has been shown that in the framework of the Born-Oppenheimer approximation, the electronic integrals for the nonradiative transitions $S_{\pi_i, \pi_j^*} \rightsquigarrow T_{\pi_k, \pi_j^*}$ $S_{n_i, \pi_j^*} \rightsquigarrow T_{n_i, \pi_k^*}$ and $S_{\pi_i, \pi_j^*} \leftrightsquigarrow T_{\pi_i, \pi_k^*}$ have vanishing[3] one- and two-center spin-orbit terms. On the other hand, the electronic integrals for the nonradiative transitions $S_{n_i, \pi_j^*} \rightsquigarrow T_{\pi_k, \pi_j^*}$ and $S_{\pi_i, \pi_j^*} \rightsquigarrow T_{n_k, \pi_j^*}$ have one-center spin-orbit interaction terms, the largest one being on the nitrogen atom. The vibrational overlap integrals for the latter transitions are an order of magnitude larger[3] than those for the nonradiative transitions $S_{n,\pi^*} \rightsquigarrow T_{n,\pi^*}$ or $S_{\pi,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$. These considerations give rise to the following radiationless selection rules:

$S_{n,\pi^*} \leftrightsquigarrow T_{\pi,\pi^*}$; $S_{\pi,\pi^*} \leftrightsquigarrow T_{n,\pi^*}$; $S_{n,\pi^*} \not\leftrightsquigarrow T_{n,\pi^*}$ and $S_{\pi,\pi^*} \not\leftrightsquigarrow T_{\pi,\pi^*}$.

Transitions connected by $\leftrightsquigarrow$ are predicted[3] to be faster than those interconnected by $\leftrightsquigarrow$ by a factor of $\sim 10^2$.

The above results might account for a number of qualitative observations. The intersystem crossing rate constant in benzophenone, and in many other aromatic carbonyls (e.g., benzaldehyde and acetophenone) whose lowest singlet is an n,π^* state below which there is a triplet π,π^* state, is extremely fast ($\sim 10^{10}$ sec^{-1}). These compounds show strong phosphorescence in rigid media but no fluorescence. On the other hand, aliphatic carbonyls show both fluorescence and phosphorescence (as well as giving rise to photodecomposition) upon excitation. The fluorescence rate constant in the latter compound is $\sim 10^{+5}$ sec^{-1}. Since fluorescence has been observed in a number of these aliphatic carbonyls, the intersystem crossing rate constant in these compounds is $< 10^{+7}$ sec^{-1}. The major difference between aliphatic and aromatic carbonyls is that the former compounds have no triplet π,π^* level in between the lowest singlet and triplet n,π^* levels. Aromatic carbonyls have a triplet level of π,π^* type located in between the lowest singlet and the lowest triplet levels, which are of the n,π^* type. This fact might facilitate the intersystem crossing process in aromatic carbonyls.

Similar conclusions could be reached upon examining the following qualitative results. Benzene shows both fluorescence and phosphorescence, and the rate constant of the intersystem crossing process is believed to be $\sim 10^{+6}$ sec^{-1}. Pyrazine, on the other hand, whose lowest singlet and triplet levels are of the n,π^* type, shows very strong phosphorescence and extremely feeble fluorescence with observed lifetime 10^{-9} sec. The radiative lifetime of pyrazine fluorescence is $\sim 10^{-6}$ sec, and one is tempted to believe that the observed 10^{-9} sec for the lifetime of pyrazine fluorescence is determined by an intersystem crossing rate constant of $\sim 10^{+9}$ $\sec^{-1}$, which is 10^3 times faster than that observed for benzene in which no n,π* levels exist between the π,π* states. It must be mentioned that the above conclusions are based on observations which are qualitative and insufficient in number. Accurate values of quantum yields are perhaps the most desperately needed quantities at present. Our understanding of nonradiative processes suffers greatly from the lack of these quantities. Observed lifetimes are now being measured, but unless they are coupled with quantum yield data, it will be rather difficult to determine the path of the nonradiative transitions.

Should quantum yield be made available for many of these molecules, a reexamination of the above selection rules will be helpful. Since the above selection rules are derived using the Born-Oppenheimer approximation, an examination of the extent of the applicability of this approximation would then be carried out. The failure of the Born-Oppenheimer approximation would have the effect of relaxing the above selection rules. If both the n,π* and π,π* states are strongly intermixed via out-of-plane normal modes, then a nonradiative transition from the lowest level of one state proceeds to an isoenergetic vibronic level which is an admixture of the two states (n,π* and π,π*), irrespective of the order of the levels. Should this be the case, then one expects the rate of radiationless processes in molecules containing n,π* and π,π* to be faster (but not very sensitive to the order of the levels) than the rates in molecules containing only one type or the other. Thus, the intersystem crossing process should be faster in aromatic ketones and nitrogen heterocyclics than in unsaturated aliphatic ketones and aromatic hydrocarbons.

It should also be mentioned that strong mixing between the n,π* and π,π* states of the same multiplicity can take place by crystal field type mixing of the solvent. This is especially effective in cases where n,π* and π,π* states of the same multiplicity are energetically close to one another. In this case, the situation will be similar to the one that arises when the Born-Oppenheimer approximation is not valid.

Selection Rules and Spin Polarization

The triplet state of an aromatic molecule is made up of three sublevels corresponding to the $M_z = 0, \pm 1$ states. For molecules having a plane of symmetry in addition and perpendicular to the molecular symmetry plane, i.e., for molecules with C_{2v} point group (e.g., quinoxaline) or having C_{2v} point group as a subgroup of their point group (e.g., pyrazine), the three triplet sublevels correspond[4] to those states having their spin lined up or polarized in three perpendicular planes; two are the symmetry planes and the third one is perpendicular to the other two. In this case, the three spin functions belong to the three different irreducible representations to which the three perpendicular axes of molecular rotation belong (Γ_{R_x}, Γ_{R_y} and Γ_{R_z}).

The electronic integral in expression 1 for the direct intersystem crossing process can be rewritten in the following form:

$$\langle \Phi_I | H' | \Phi_{II} \rangle = \langle \chi_I \Psi_I | \xi \vec{L} \cdot \vec{S} | \chi_{II} \Psi_{II} \rangle$$

$$= \xi [\langle \Psi_I | \vec{L} | \Psi_{II} \rangle \cdot \langle \chi_I | \vec{S} | \chi_{II} \rangle] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where χ and Ψ represent the spin and space wavefunctions respectively, $\xi \vec{L} \cdot \vec{S}$ is the spin orbit Hamiltonian, and I and II represent S_1 and T_x respectively, with T_x as the triplet level to which the intersystem crossing process has the largest nonradiative transition probability. Because of the dot product of $\vec{L}$ and $\vec{S}$ one can write:

$$\vec{L} \cdot \vec{S} = L_x S_x + L_y S_y + L_z S_z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

L_x and S_x belong to the Γ_{R_x}, L_y and S_y belong to Γ_{R_y}, and L_z and S_z belong to Γ_{R_z} in the point group to which the molecule belongs.

Equation (2) imposes the symmetry selection rules for the intersystem crossing process. The integral $<\Psi_I|\vec{L}|\Psi_{II}>$ will be nonvanishing if $\Gamma_{\Psi_I} \times \Gamma_{\Psi_{II}}$ contains or is the same as that for Γ_{L_x} $(\equiv\Gamma_{R_x})$, Γ_{L_y} $(\equiv\Gamma_{R_y})$, or $\Gamma_{L_z}$$(\equiv\Gamma_{R_z})$. Let us say that for a certain transition, $\Gamma_{\Psi_I} \times \Gamma_{\Psi_{II}} = \Gamma_{L_x}$. This imposes selection rules on the spin integral $<\chi_I|\vec{S}|\chi_{II}>$. For the latter not to vanish, $\Gamma_{\chi_I} \times \Gamma_{\chi_{II}}$ must contain Γ_{S_x} $(\equiv\Gamma_{R_x})$. It is thus obvious that the intersystem crossing process in this case would populate one of the three triplet sublevels discussed above in which the spin magnetic moment is polarized in the x-direction in the molecular framework. In most molecules, the triplet level involved in the intersystem crossing process is not usually the lowest triplet state. Thus, following the intersystem crossing process (and spin polarization), two situations might arise:

1. Spin polarization might be destroyed before the molecule undergoes an internal conversion to the lowest triplet state.

2. The molecule might undergo an internal conversion process keeping the same spin direction. In this case all the molecules in the triplet state would have their spin lined up in the same direction with reference to the molecular framework (in our example discussed above, the spin moment would be in the x-direction).

Situation (1) above would be found for systems at temperatures for which the spin-lattice relaxation process is faster than 10^{+11} sec^{-1} (the rate constant for the internal conversion process between the triplet levels). This should be the limiting behavior at high temperatures. At very low temperatures, the rate of the spin-lattice relaxation might be decreased below 10^{+11} sec^{-1}, thus leading to situation (2) above.

It should also be pointed out that 100% spin polarization resulting in situation (2) above can only be obtained if the intersystem crossing process involves either one route or more than one route which forms triplet states all having the same spin direction. If the intersystem crossing process involves routes that populate triplet states having the three orthogonal spin directions with equal probability, then it is obvious that spin polarization cannot be achieved at any temperature. Of course, this latter situation is unlikely for aromatic systems whose phosphorescence emission (the mechanism of which is based on spin-orbit selection rules similar to those involved in the intersystem crossing process) has been found to be polarized.[5]

For molecules in which the intersystem crossing process for one route is much larger than for all the others (as a result of spin-orbit interaction), group theory predicts that, except for molecules that belong to the C_i or the cubic point groups, the intersystem crossing process should give rise to a triplet state with its spin being polarized in one or, at the most, in two directions. For molecules having C_{2v} symmetry or belonging to a group having C_{2v} as its subgroup (e.g., D_{2h} point group), the triplet state resulting in this case would have its spin polarized in only one direction. These conclusions are based on direct spin-orbit selection rules and on the fact that in all the point groups mentioned, the rotation around the three different molecular axes never belongs to the same irreducible representation of these point groups (except for the C_i and the cubic point groups). In all but the C_{2v}, D_2 and D_{2h}, the rotation about two of the axes belongs to one of the irreducible representations whereas the rotation about the third axis belongs to a different representation. Thus, spin polarization can be along one or two directions. For molecules that belong to the C_{2v}, D_2 and D_{2h} point groups, each of the different axes of rotation belongs to a different irreducible representation. Thus if only one route is considered (e.g., $S_1 \rightsquigarrow T_3$), the spins in the resulting triplet state (T_3) will have one unique direction in this case.

The detection of the state of polarization depends on the resolving time of the measurement used in comparison with the spin-lattice relaxation time in the triplet state. A few observations have recently been reported which indicate the presence of spin polarization in the lowest triplet state of some aromatic molecules at low temperatures.[6] In the following section, it will be shown that the decay characteristics of n,π* phosphorescence of pyrazine can be explained if the triplet state is formed with spins being greatly polarized at 1.6°K. Pyrazine (D_{2h} point group) has a lowest triplet state of n,π* type and the selection rules mentioned in the first part of this section predict that the route $S_{n,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$ should be most favorable. Thus, according to the group theoretical spin polarization predictions given above, the resulting triplet state should have its spin in only one direction, as observed and discussed in Section III.

III. Intramultiplet Nonradiative Processes in the Lowest Triplet State.

Spin-Lattice Relaxation

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] In 1932, Waller[8] proposed a mechanism in which the modulation of the magnetic dipolar interaction by the phonon field of lattice vibrations causes spin-lattice relaxation. This mechanism is found not to explain the observed temperature and magnetic field effects on the relaxation process. Heitler and Teller[9] indicated that the modulation of the electric field by lattice vibrations could modulate the orbital motion of the electron. Since the latter is coupled to the spin motion via spin-orbit coupling, the modulation of the orbital motion is then felt by the spin system which, as a result, undergoes spin relaxation. Van Vleck[10] and others[7] have subsequently developed the theory for this mechanism. 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}). A third mechanism is found to account for the relaxation process in systems with crystal field splitting Δ smaller than the maximum phonon energy. This mechanism involves the simultaneous absorption of a phonon of energy δ_1 and the emission of another of energy $\delta_1 + \delta$, along with spin flip from one spin level to a lower one having a separation of δ. Such a process is found[11] to have 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}). Since the binding in ionic crystals is stronger than in molecular crystals, H_{OL} for the valence electrons is expected to be stronger in the former than in the latter. Furthermore, the impurities generally used in ionic crystals have atomic numbers, and thus H_{SO}, greater than those for the atoms in organic molecules. Therefore, due to the difference in the size of H_{OL} and H_{SO}, it is expected that, for the same mechanism and the same temperature, inorganic systems would have shorter spin-lattice relaxation times than molecular impurities in molecular crystals. In addition to H_{OL} and H_{SO}, quantities like the velocity of sound, phonon density and occupation number enter in the expression for the spin-lattice relaxation time.

It is well known[5] that the pyrazine phosphorescence in rigid glasses has a lifetime of ~20 millisec 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 coupling scheme $^3B_{3u} \overset{\text{s.o.}}{\leftrightsquigarrow} {}^1B_{1u}$, is found[12] 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 millisec at 77°K. At 1.6°K, a nonexponential decay is observed which can be resolved[12] into three exponential decays of lifetimes: 6, 130 and 400 millisec. At 4.2°K, three lifetimes can be resolved: 6, 60 and 320 millisec. 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 millisec (the same as that observed at 77°K). The decay characteristics change by the application of a magnetic field at 1.6 (see Fig. 2) and 4.2°K but not at 77°K.

The above results are explained[13] using the scheme shown in Fig. 3[*] for energy degradation. Following the absorption process, the excited pyrazine molecules are deactivated to the zero point level of the lowest $^1B_{3u}^{n,\pi^*}$ state in ~10^{-11} sec. This is followed by the intersystem crossing process $B_{3u}^{n,\pi^*} \rightsquigarrow B_{3u}^{\pi,\pi^*}$ (where the symmetry species here represents that for the total (space x spin) wavefunction). This corresponds to a radiationless transition between states having a spatial symmetry of B_{3u}^{n,π^*} and B_{1u}^{π,π^*} and spin function of symmetry A_g (singlet) and B_{2g} (τ_y, triplet), respectively. This is the most probable intersystem crossing process in pyrazine,[14] because of its strong first-order spin-orbit interaction as well as its relatively large vibration overlap integral compared to the other alternative processes $^1B_{3u}^{n,\pi^*} \leftrightsquigarrow {}^3B_{3u}^{n,\pi^*}$ (or $^3B_{2g}^{n,\pi^*}$), as was pointed out in Section II.

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[*] The N...N axis is taken to be the z-axis (B_{1u}), the other in-plane axis is taken as the y-axis (B_{2u}), and the axis normal to the molecular plane is the x-axis (B_{3u}).

In the $^3B_{1u}^{\pi,\pi^*}$ state, the two electrons have the spin function τ_y of symmetry B_{2g}, i.e., the spin moment is in the y direction in the molecular framework (see Fig. 3). The transition $^3B_{1u}^{\pi,\pi^*}(\tau_y) \leftrightsquigarrow {}^3B_{3u}^{n,\pi^*}(\tau_y)$ is an internal conversion process and takes place in ~10^{-11} sec, which is a short time compared to the spin-lattice time, T_1, at this temperature. Thus the molecule is found in the $^3B_{3u}^{n,\pi^*}$ state with the spin lined up in the y-direction, i.e., the excitation by absorption has resulted in a spin polarization in y-direction in the molecular framework. 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) relative to the radiative lifetime from the τ_y sublevel to the ground state. In pyrazine, the triplet sublevel τ_y of the $^3B_{3u}^{n,\pi^*}$ strongly couples to the $^1B_{1u}^{\pi,\pi^*}$ by first-order spin-orbit perturbation to give rise to the observed N...N-polarized phosphorescence.[15,16] Thus the sublevel which is populated as a result of the intersystem crossing selection rules is the one that has the strongest radiative transition probability. The observed radiative lifetime of the $B_{3u}^{n,\pi^*}(\tau_y) \rightarrow {}^1A_g$ is thus 6 millisec (not 18 millisec as has been previously assumed).

The other routes to the τ_x and τ_z sublevels have small, but nonvanishing, transition probability. Molecules that reach these sublevels might return to the ground state by going to the τ_y sublevel by a spin-lattice relaxation process which is then followed by phosphorescence from the τ_y sublevel. If this is the case, the medium and long lifetimes observed at 1.6°K might then be a measure of the spin-lattice relaxation times for the $\tau_x \leftrightsquigarrow \tau_y$ and $\tau_z \leftrightsquigarrow \tau_y$ processes.* This would indicate that the spin-lattice relaxation

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* It is interesting to point out that if the proposed explanation is correct, then the radiative and nonradiative lifetimes for the τ_x, $\tau_z \rightarrow S_0$ in pyrazine must be longer than 120 and 320 millisec at 1.6°K.

times in organic system are 0.1-0.3 sec at 1.6°K, which is comparable to those found for a number of ionic systems[6] at this temperature. The difference in phonon occupational numbers between organic and inorganic systems, being larger for the former on account of its small lattice vibration spacing, might offset the difference in H_{OL} and H_{SO} between the two systems.

As the temperature increases, the spin-lattice relaxation time decreases and a competition between radiation from τ_y and relaxation between the three sublevels takes place. Above 10°K, the relaxation rate exceeds that of the radiation from τ_y. The population of the molecules in sublevel τ_y is now in thermal equilibrium with those in the other sublevels. The observed lifetime, k, is given by:

$$k = \sum_{i}^{3} k_i n_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where k_i is the radiative rate constant from sublevel τ_i ($i = x,y,z$) and n_i is its fraction population. At thermal equilibrium and at relatively high temperature, $n_i = 1/3$. If the radiative rate constants from the τ_x and τ_z sublevels are neglected in comparison with that from the sublevel τ_y, the observed lifetime above 10°K should be $= 1/3 \times 1/6 = 1/18$ millisec^{-1}, as observed.

The change of the medium lifetime with temperature indicates that the spin-lattice relaxation proces of which this lifetime might be a measure is of the direct type. The other process does not behave according to any of the mechanisms discussed in the first part of this section.

IV. The Triplet → Singlet Radiative Process

The phosphorescence emission of organic molecules in rigid media was first observed[17] in 1895. In 1942, the emission was shown[18] to be electric dipole radiation and in 1944 it was identified[19,20] as radiative intercombination between the lowest triplet state and the ground singlet state.

The paramagnetic properties of the emitting triplet state were first demonstrated[21] in 1945.

Singlet-triplet transitions are spin-forbidden; hence the appearance of the emission requires spin-orbit interaction. In molecules, spin-orbit interactions may have different forms, and thus a number of mechanisms can be written to account for the radiative properties of the $T \rightsquigarrow S$ transition. A large portion of our research efforts during the past few years has been spent on the problem of elucidating these mechanisms and explaining the observed polarization characteristics of the phosphorescence radiation. It is found that, due to the small spin-orbit interactions in organic molecules (0.1-10 cm^{-1} or 0.2-20 cal/mol), the emission mechanism is not unique and is sensitive to rather weak perturbations, e.g., solute-solvent interactions and halogen substitution.

The total molecular Hamiltonian, including spin-orbit interaction, is given[22] by:

$$H = H_0^0 + H^0_{s.o.} + \sum_a \left(\frac{\partial H^0_{s.o.}}{\partial Q_a}\right)_{Q_a=0} Q_a + \sum_a \left(\frac{\partial H^0}{\partial Q_a}\right)_{Q_a=0} Q_a$$

$$= H_I + H_{II} + H_{III} + H_{IV}$$

where H_I is the part of the Hamiltonian containing the kinetic energy as well as all the electrostatic interaction terms, and H_{III} is the spin-vibronic interaction, whereas H_{IV} and H_{II} constitute the second-order vibronic spin-orbit terms, and $H_{s.o.}$ is the spin-orbit interaction term that represents the interaction between the orbital motion of an electron with its own spin magnetic moment or with the spin magnetic moment of another electron; the latter interaction is generally smaller than the former, especially in atoms beyond the first row in the periodic table.

As a result of spin-orbit interaction, a singlet state is contaminated by a triplet character and vice versa. The first-order mixing coefficient is proportional to the spin-orbit interaction energy and inversely proportional to the energy separation of the intercombining singlet and triplet states. The transition moment of the T → S transition can then be written as:

$$\vec{M}_{T_1 \rightarrow S_0} = \sum_i \lambda_{i1}\vec{M}_{io} + \sum_j \lambda_{jo}\vec{M}_{j1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where λ_{i1} is the mixing coefficient between the singlet state i and the lowest triplet state T_1 and λ_{jo} is the mixing coefficient between triplet state j and the ground state. $\vec{M}_{io}$ is the electric dipole moment of the transition between the singlet state i and the ground state and $\vec{M}_{j1}$ is the moment of the transition between triplet state j and the lowest triplet state T_1. The polarization of the phosphorescence emission (i.e., the direction of $M_{T_1} \rightarrow S_0$) thus reflects the polarization of $\vec{M}_{io}$ and/or $\vec{M}_{j1}$. If one measures the polarization of the 0,0 band, the mechanisms in which λ_{i1} or λ_{jo} involves direct spin-orbit coupling (H_{II}) can be identified. On the other hand, the measurements of the polarization of the vibronic bands whose intensity is not accounted for by the Franck-Condon principle should give information about mechanisms involving spin-vibronic (H_{III}) and second-order spin-orbit-vibronic (H_{II} + H_{IV}) interactions.

In the following sections, results obtained in our laboratory are summarized. Possible explanations for the observed results are discussed using the above mechanisms.

Radiative Strength of Triplet → Singlet Transitions

Table 2 gives a comparison between the oscillator strengths and the radiative lifetimes of spin-allowed ($S_1 \rightarrow S_0$) and spin-forbidden ($T_1 \rightarrow S_0$) transitions of different electronic origins. The ratio of the oscillator strength for the most orbitally-allowed and the most orbitally-forbidden transitions is equal to 10^3 and 10^5 for S-S and S-T, respectively. The values of the oscillator strength of T → S transitions cover a wider range than those for S → S transitions. This reflects mainly the sensitivity of the spin-orbit interaction to the intermolecular and intramolecular perturbations and the different oscillator strengths of the mixing transitions (see equation 6). The most forbidden molecular electronic transition known is the triplet-singlet transition in aromatic hydrocarbons. The high degree of forbiddenness is due to the fact that in planar molecules,[23] the strong spin-allowed π,π^* radiative transitions have very small direct spin-orbit interaction with the triplet-singlet transition (small mixing coefficients λ_{i1} and λ_{jo}). Only the relatively radiatively weak (σ,π) transitions (small M_{io} and M_{j1}) have relatively strong direct spin-orbit interaction with the $T_1 \rightarrow S_0$ transition. Spin-orbit mixing between singlet and triplet π,π^* states occurs through spin-vibronic interaction or second-order spin-orbit-vibronic interaction, neither of which gives strong radiative properties to the $T_{\pi,\pi^*} \rightarrow S_0$ transition in comparison with the direct spin-orbit coupling with σ,π or other out-of-plane polarized transitions.

In haloaromatics in which the halogen is coplanar with the aromatic ring, the mixing between singlet and triplet π,π^* states involving the π-system of the halogen atom is shown[24] to be vanishingly small as in the parent hydrocarbon; therefore, the only important direct spin-orbit interaction occurs between σ,π and the S-T transition leading to the first-order spectrum (Subspectrum I in reference 25). However, the importance of the second-order spin-orbit-vibronic interaction relative to the direct spin-orbit interaction is increased in haloaromatics.[25] The spectrum resulting from the former interaction (leading to Subspectrum II in reference 25) has intensity comparable to that resulting from the latter type of interaction (leading to Subspectrum I). This explains the observed out-of-plane carbon-halogen vibration in the phosphorescence of haloaromatics (Subspectrum II). Since the second-order interaction couples π,π^* transitions to the S-T transition, Subspectrum II is in-plane polarized.

The intramolecular heavy-atom effect on triplet-singlet n,π^* transitions is not as pronounced[26] as it is on π,π^* transitions. Substituting bromine atom for an α-hydrogen atom attached to a carbonyl group increases the molar extinction coefficient of the triplet-singlet n,π^* absorption by a factor of ten at the most. Similar substitution for a hydrogen atom attached to the naphthalene ring, on the other hand, increases the molar extinction coefficient of the π,π^* transition by a factor of $\sim 10^3$. The difference in the heavy-atom effect in the two cases is due to the fact that n,π^* T-S transitions are strongly coupled to the radiatively strong π,π^* transition by direct spin-orbit interaction, and thus are not sensitive to heavy-atom perturbations. The observed intramolecular heavy-atom effect on the T-S transitions of aromatic hydrocarbons is thus a result[25] of the inherent high degree of forbiddenness of this transition due to the <u>weak radiative spin-orbit perturbation</u> in these molecules. As a result of this high degree of forbiddenness, strong solvent effects have been observed on the mechanism of these transitions, as discussed in the following sections.

Mechanism of Phosphorescence and Polarization Results

1. Aromatic Hydrocarbons: Table 3 summarizes the relative probability distribution[27] of the total phosphorescence emission along the three orthogonal molecular axes, L (long axis), M (short axis) and N (normal to the molecular plane) of d_8-naphthalene, quinoxaline and d_{10}-phenanthrene in different solvents. It is clear that the direction of the emitting oscillator is not fixed in the molecular framework and that its direction is highly sensitive to the host in which the molecule is dissolved. Two mechanisms have been proposed to explain these results. In the first mechanism,[28] it is proposed that the triplet-singlet transition is mixed with σ,π transitions via direct spin-orbit (s.o.) coupling (H_{II}) with a coefficient δ. The σ,π transition of the guest molecule (g) under consideration is proposed to be strongly mixed with the nearby solvent transitions by electrostatic interaction (e.s.) with a coefficient k. This mechanism can be summarized as follows:

solvent transitions $\xleftrightarrow{e.s.}$ $(\sigma,\pi)_g$ $\xleftrightarrow{s.o.}$ $(T_{\pi,\pi^*} \leftrightarrow S_o)_g \rightarrow$ guest phosphorescence

According to this mechanism, the transition moment of the phosphorescence of the guest can then be written as:

$$\vec{M}_{T\rightarrow S_0} = \delta\vec{M}_{(\sigma,\pi)}g + \delta k\vec{M}_{(solvent)} \quad \dots\dots\dots\dots\dots \quad (7)$$

Since $M_{(\sigma,\pi)}g$ is probably an order of magnitude smaller than $\vec{M}_{(solvent)}$, then if $k = 0.2$, the part of phosphorescence intensity borrowed from the solvent transitions would be four times as intense as that borrowed from σ,π transitions of the emitting molecule itself. This indicates that mixing the guest σ,π^* states with as little as 4% of host states leads to phosphorescence which is predominantly borrowed from solvent transitions. This mechanism explains the fact that the phosphorescence polarization depends greatly on the solvent used. It might also account for the small change in the observed lifetime of $C_{10}D_8$ (which is believed to be wholly radiative) as the solvent changes. The fact that all solvents used have strong transitions nearby those of the σ,π transitions of the guest makes $[kM_{solvent}]^2$ have similar values for the solutes used in different solvents.

The second mechanism is proposed[27] to account for the fact that while most of the phosphorescence emission is polarized perpendicular to the molecular plane in rigid glasses and in biphenyl host, most of the emission is found to be in-plane polarized in durene host crystal. It is proposed that the hybridization around one of the carbon atoms of the emitting guest molecule in durene is not pure sp^2. The π-system (made of P_z atomic orbitals when unperturbed) would then possess a small amount of the P_x and P_y carbon atomic orbitals. This can be accomplished either by the crystal field of the methyl groups of the durene host or by forcing one of the H-atoms of the guest molecule to assume slightly nonplanar configuration. As a result of mixing P_x and P_y with the π-system, the direct spin-orbit coupling between the strong radiative π,π^* transitions and the triplet-singlet transition becomes nonvanishing. Since strong π,π* spin-allowed radiative transitions are in-plane polarized, the phosphorescence in durene becomes in-plane polarized. According to this mechanism, the emitting molecules in biphenyl host or in glasses have their σ- and π-systems orthogonal to one another. The triplet-singlet transitions of the guest molecules are intramolecularly mixed with the σ,π or other out-of-plane spin-allowed transitions. This leads to the observed out-of-plane polarization of the phosphorescence emission in these solvents.

2. Haloaromatics: The phosphorescence spectrum of haloaromatics shows, in addition to the out-of-plane part of the emission observed in the parent hydrocarbons (Subspectrum I), an in-plane polarized emission with its origin separated from the 0,0 band by the frequency of an out-of-plane molecular vibration. These conclusions were made from the polarization results obtained by the method of photoselection in rigid medium[25] (Fig. 4). The degree of polarization is shown as a function of wavelength in Fig. 4 with broken lines while the actual spectrum is shown with solid lines. Subspectra I of the different haloderivatives are correlated with the parent hydrocarbon spectrum (vertical broken lines). The new subspectra induced by vibrations are connected with solid vertical lines. Subspectrum I results from direct spin-orbit coupling between σ,π transitions and the S-T transition. On the other hand, Subspectrum II results from vibronic spin-orbit interaction between π,π* transitions and the S-T transition. The relative importance of Subspectrum I and II depends on the position and number of the halogen atoms. In order to determine the relative importance of the short- and long-axis-polarized emission of Subspectrum II, it was found essential to determine the polarization of the phosphorescence emission of these molecules in host lattices of known crystal structures. The polarization ratios b/a, b/c' and a_0/c_0 of the phosphorescence emission of 2-chloro-, 2-bromo-, 2-iodo- and 2,3-dibromonaphthalene in biphenyl host crystal are determined[29] at 77°K.

The relative transition probability of the emitting oscillators along the long axis (P_L), short axis (P_M) and normal to the halonaphthalene molecular plane (P_N) has been determined for each vibronic band in the spectrum. This is accomplished by a three-dimensional analysis, using the observed polarization ratios from any two host crystal faces and the normalization condition: $P_L + P_M + P_N = 100$, applied to any vibronic emission band. The relative importance of the different spin-allowed transitions in rendering the triplet-singlet spin-forbidden transition allowed is concluded from the three-dimensional analysis. These results are summarized in Table 4.

In all the compounds studied, the out-of-plane electric dipole-allowed transitions contribute 20-40% of the intensity of the phosphorescence of the halonaphthalenes by direct spin-orbit perturbation (Subspectrum I). The in-plane electric dipole-allowed transitions contribute 60-80% of the intensity via spin-orbit-vibronic perturbation (Subspectrum II). The relative amounts of the long- and short-axis-polarized emissions are very sensitive to the position of the halogen atom in the naphthalene ring, as shown in Fig. 5. The long-axis-polarized emission constitutes 55%, 23% and 42% of the total emission of the 2-halo-, 1-bromo- and 2,3-dibromonaphthalene, respectively. The short-axis-polarized emission constitutes 10-20%, 40% and 41% of the total emission of the 2-halo-, 1-bromo- and 2,3-dibromonaphthalenes, respectively. These observed variations in the long and short axis in-plane-polarized emission are readily explained by the valence bond method if the perturbing transitions involve the (intramolecular) charge transfer states formed from the ionic structures resulting from transferring electrons from the halogen atoms to the ring or to other halogens if present.

The relative amount of the out-of-plane emission is found to be largest for the 2,3 derivative (~37%) in rigid glasses but lowest (~17%) for the same compound in biphenyl host. The decrease in the relative amount of the out-of-plane emission in biphenyl host is a result of host-guest interaction. The fact that the different bands involving the lattice vibrations of the host are found to have polarization similar to that of the phononless band indicates that the host-guest interaction is static in nature. Two mechanisms are proposed. In the first mechanism, the intramolecular spin-orbit perturbation is slightly changed either by forcing the halogen to be slightly nonplanar with the aromatic ring due to the packing forces of the host lattice or by mixing of the P_π and P_σ of the halogen by the crystal field of the host. The second mechanism involves mixing between the host and guest electronic states as proposed for the case of the parent hydrocarbon in the previous section.

V. Future Studies

The radiative properties of the triplet state are far more quantitatively understood now than 23 years ago when it was first shown that the phosphorescence was a result of a triplet-singlet transition. Since then a large amount of research has been carried out on the triplet state which has not only answered a great number of questions but also raised others. The main questions which are presently awaiting answers are:

1. What is the natural radiative lifetime of the phosphorescence of aromatic hydrocarbons?
2. What is the exact perturbation effect of the solvent?
3. What is the relative importance of the different terms of the spin-orbit Hamiltonian in giving the triplet-singlet transition its radiative power in different molecules?

To answer the first two questions, research directed at accurate determination of the T-S absorption cross-section in the gas phase as well as in different media is required. Accurate quantum yield data in different media are also needed. The third question requires the collaboration of the vibration, electronic and magnetic resonance spectroscopists. An accurate assignment should be made for the different vibrations that appear in the high-resolution phosphorescence spectra of different molecules. From the type of vibration and the polarization of the vibronic band involving it, the exact mechanism responsible for its appearance can be deduced. The elucidation of the magnetic sublevel giving rise to the emission, using optical-esr double resonance as well as Zeeman experiments, will also be valuable.

The intramolecular nonradiative processes in condensed medium are less understood than the radiative ones. The role played by the solvent in assisting the molecule to cross potential energy surfaces has not yet been examined. The extent of the validity of the Born-Oppenheimer approximation is not known. The dependence of the rate of radiationless processes on the ordering and the type of energy levels is not thoroughly examined. The reason for this is undoubtedly the unknown, yet badly needed, accurate values of quantum yields of the radiative and nonradiative processes for different molecules in different media. When these values become available, our understanding of nonradiative processes will be more accurate and correct. The exact mechanism involved in the recently observed spin-lattice relaxation process between the triplet sublevels needs to be investigated, both theoretically and experimentally.

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Table 1. Approximate values for the rate constants ($k\ \mathrm{sec}^{-1}$) of the different radiative and nonradiative processes in simple aromatic systems in rigid media at 77°K.

System	$k_{II}=k_V$	k_{III}	k_{IV}	k_{VI}	k_{VII}	k_{VIII}
Aromatic Hydrocarbons	10^{11}	10^5-10^8	10^5-10^9	10^{-2}	-*	10^7
Halo-aromatic	10^{11}	10^6-10^{10}	10^5-10^9	10^{-1}-10^3	-	10^7
Heterocyclics**	10^{11}	10^9-10^{10}	10^5-10^9	10^{-1}-10^3	10^2	10^9

*This value varies from one sec^{-1} for benzene to zero for perdeuterobenzene to 10^{+2} sec^{-1} for anthracene to much larger values for large condensed aromatics.

**The rate constants k_{IV} and k_{VI} are $\sim 10^{+5}$ and $\sim 10^{+2}$ if the lowest singlet and triplet states are of the n,π^* type, but $\sim 10^8$ and ~ 10 if the lowest singlet and triplet are of the π,π^* type respectively.

Table 2. Relative oscillator strengths and radiative lifetimes of molecular electronic transitions in aromatic compounds.

	Oscillator Strength	Rad. Lifetime
Spin-Allowed Transitions		
π,π^*	0.02 - 1	10^{-7} - 10^{-9} sec
σ,π^* or π,σ^*	$\sim 10^{-2}$	$\sim 10^{-6}$ sec
n,π^*	$\sim 10^{-2}$	$\sim 10^{-6}$ sec
Spin-Forbidden Transitions		
n,π^* (σ,π^* or π,σ^*)	10^{-7} - 10^{-6}	10^{-4} - 10^{-2} sec
π,π^* in halo-aromatics	10^{-8} - 10^{-6}	1.0 - 10^{-3} sec
π,π^* in unsat. hydrocarbons	10^{-11}	100 sec

Table 3. The percentage distribution of the total π,π^* phosphorescence emission transition probability (P) among the three molecular axes (L, M, N) of some aromatics in different hosts.

	Solvent							
	E.P.A.		Biphenyl			Durene		
Guest	P_N	$P_L + P_M$	P_N	P_L	P_M	P_N	P_L	P_M
Naphthalene-d_8	~70	~30	≥75	~5	~20	≤17	≥70	≤13
Quinoxaline	~70	~30	~75	~5	~20	~10	>75	>15
Phenanthrene-d_{10}	~80	~20	~75	~14	~11	≤38	≥50	≤12

Table 4. The distribution* of the total phosphorescence emission of the halonaphthalenes in host lattice along the long axis (P_L), short axis (P_M) and normal to the molecular plane (P_N).

GUEST	HOST	P_L	P_M	P_N
2-chloronaphthalene	Biphenyl	$54^{(58)}$	$21^{(15)}$	$25^{(27)}$
2-bromonaphthalene	Biphenyl	50	11	39
2-iodonaphthalene	Biphenyl	53	10	37
2,3-dibromonaphthalene	Biphenyl	$39^{(42)}$	$44^{(23)}$	$17^{(35)}$
1-bromonaphthalene	Naphthalene	21	36	43

* The values given in parentheses are those obtained in rigid glasses using the method of photoselection.[25]

FIGURE CAPTIONS

Figure 1. Jablonski-type diagram showing the different electronic molecular processes that follow the excitation of an aromatic molecule to its excited singlet states.

Figure 2. The effect of 4.8 k-Gauss magnetic field on the decay of pyrazine phosphorescence in benzene matrix at 1.6°K. 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 lifetime of the other two long-lived components of the decay.

Figure 3. Spin polarization and phosphorescence 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 ${}^3B_{3u}^{n,\pi*}$ are drawn arbitrarily in the order of increasing energy: $\tau_x(B_{3g})$, $\tau_y(B_{2g})$ and $\tau_z(B_{1g})$.

Figure 4. The phosphorescence spectra (solid curves) and polarization (broken curves) of naphthalene and its β-haloderivatives in rigid glass at 77°K. The spectra show that new spectra (Subspectra II) appear (connected with broken vertical lines) which have opposite (in-plane) polarization to that of naphthalene (out-of-plane polarized). An out-of-plane vibration seems to be responsible for the appearance of the new subspectra.

Figure 5. The spectra (bottom) and polarization (top) of some bromonaphthalenes in host crystals, showing the sensitivity of the emission mechanism to the position and number of the halogen atoms.

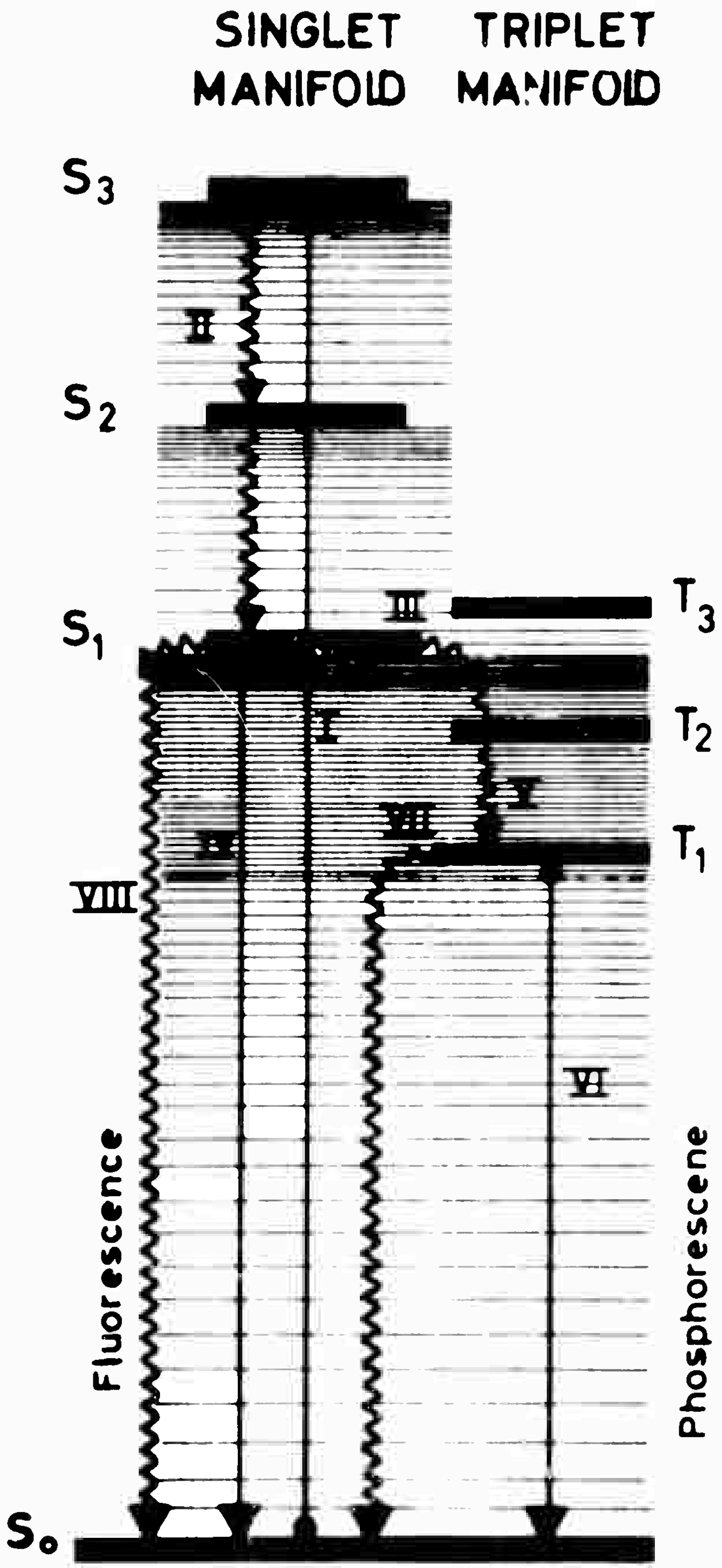

SINGLET MANIFOLD
TRIPLET MANIFOLD
S_3
II
S_2
III
T_3
S_1
I
T_2
V
VII
T_1
VIII
VI
Fluorescence
Phosphorescene
S_o

Fig. 1

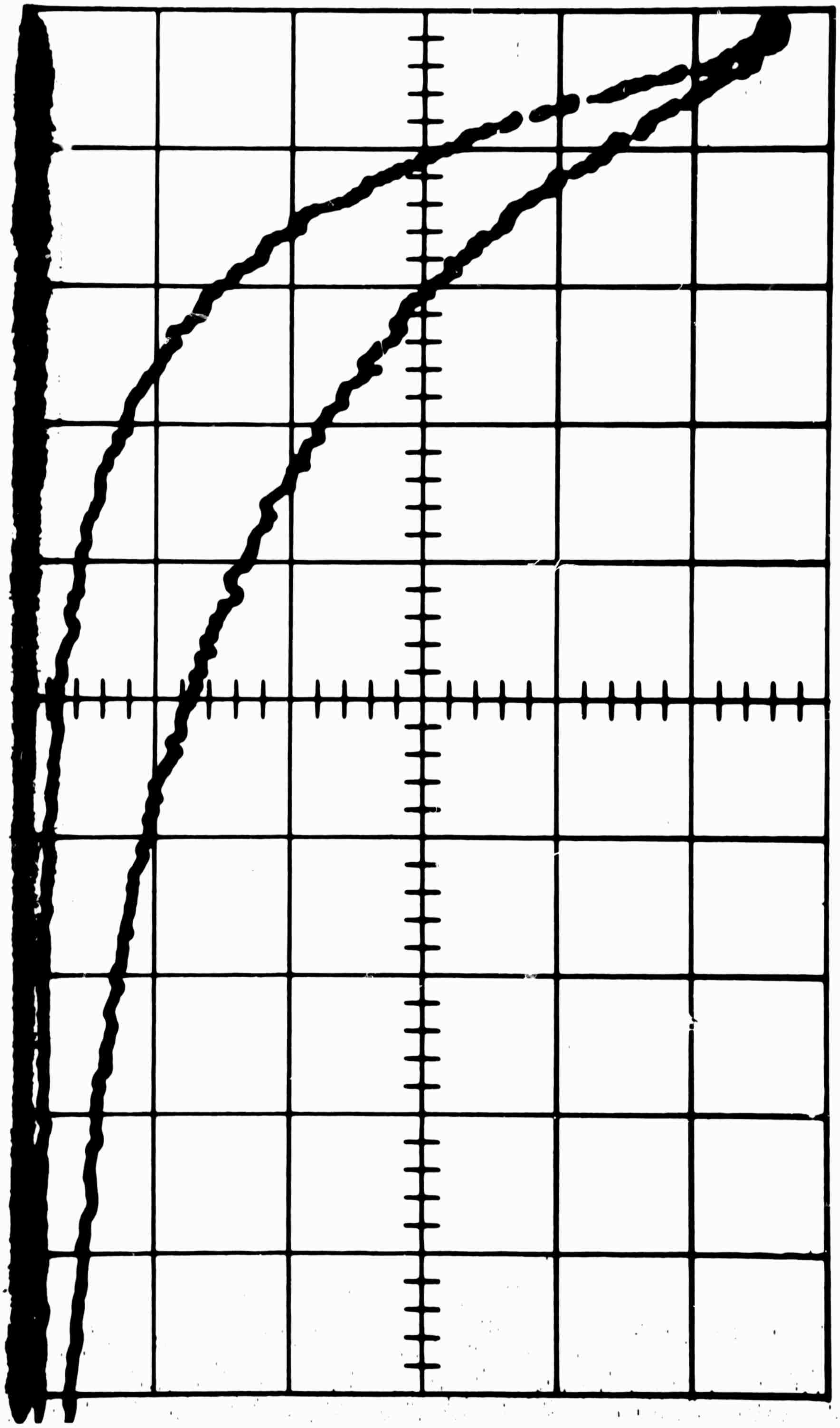


Fig. 7

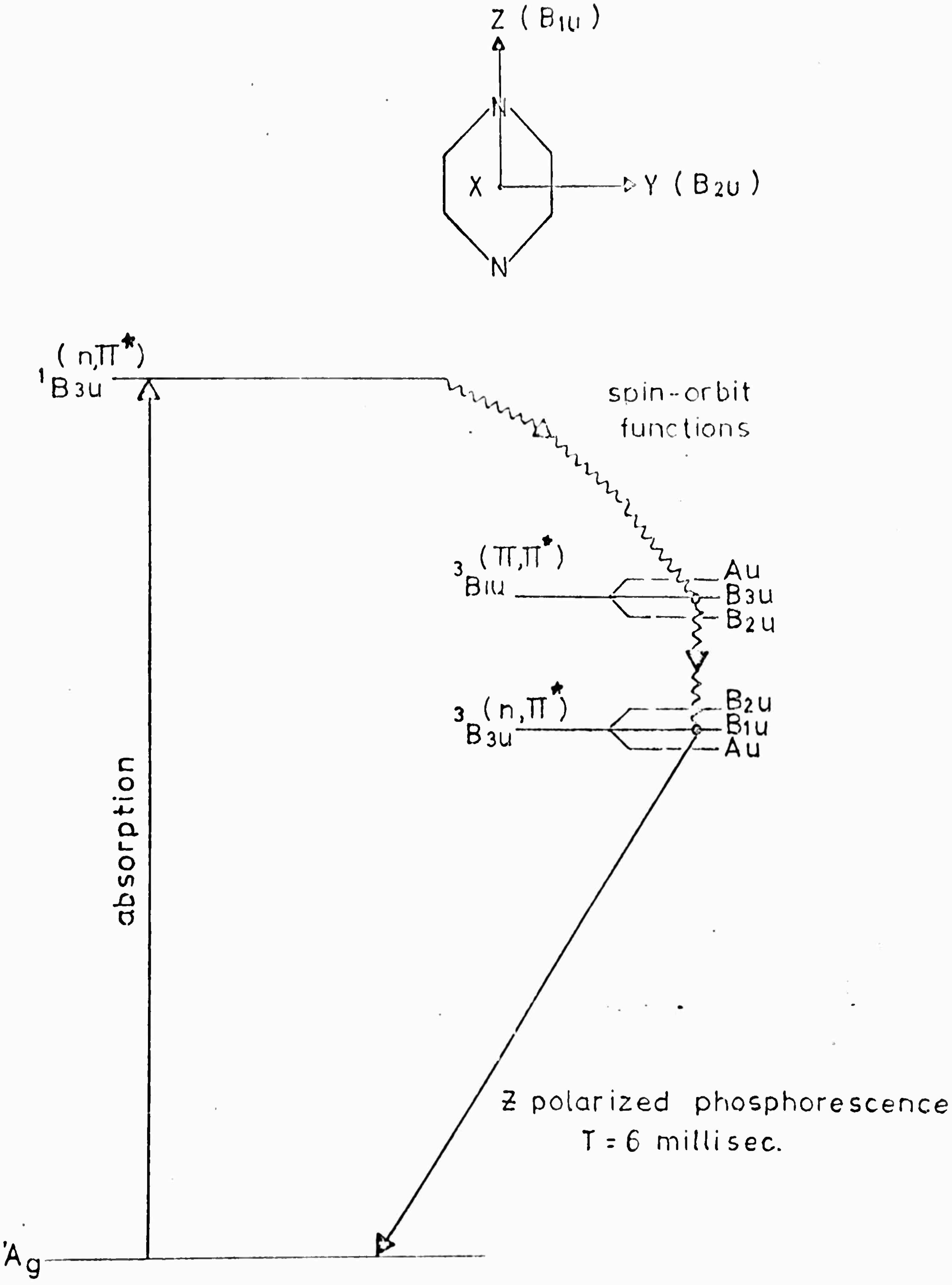

Z (B1u)
N
X
Y (B2u)
N
(n,π*)
1B3u
spin-orbit
functions
3B1u (π,π*)
Au
B3u
B2u
3B3u (n,π*)
B2u
B1u
Au
absorption
Z polarized phosphorescence
T = 6 millisec.
1Ag

Fig. 3

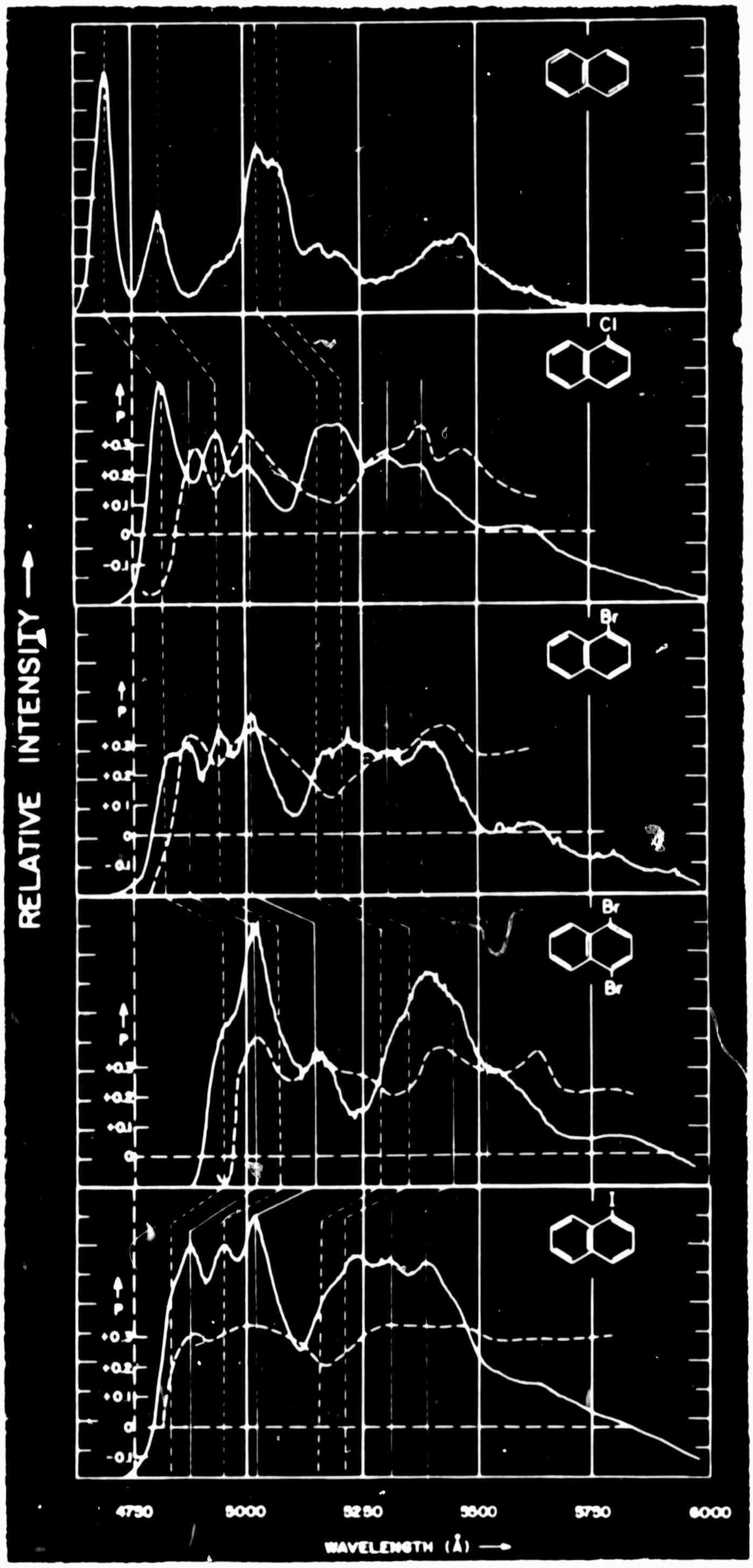
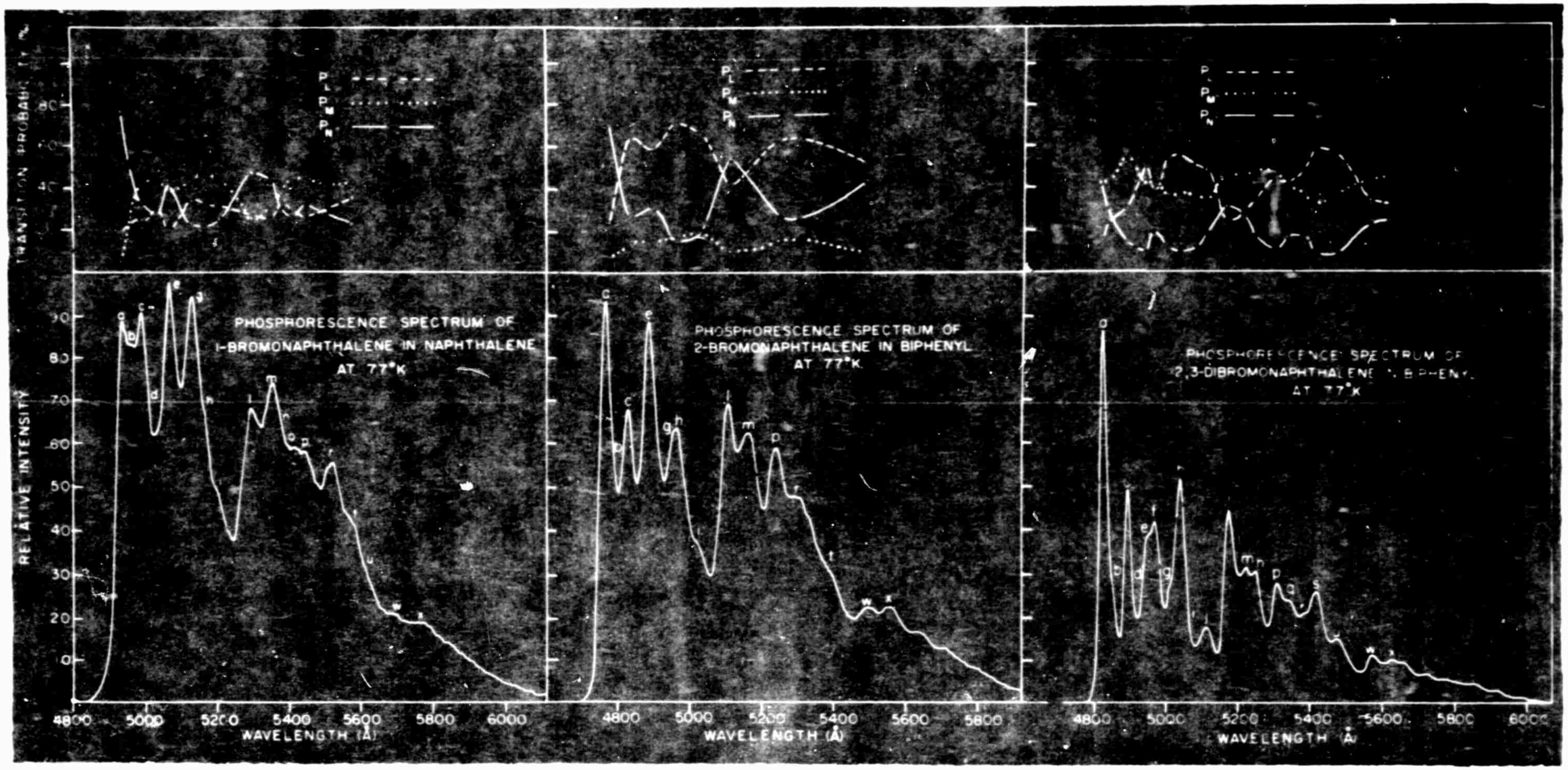

RELATIVE INTENSITY →
Cl
Br
Br
Br
I
P →
+0.3
+0.2
+0.1
0
-0.1
4750
5000
5250
5500
5750
6000
WAVELENGTH (Å) →

Fig. 4



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ABSTRACT

The paper is divided into four parts. The first part discusses the selection rules of the intersystem crossing process in systems having both n,π* and π,π* types of states. Using the Born-Oppenheimer approximation, first-order selection rules predict that the nonradiative singlet → triplet transitions between states of different types (e.g. [illegible] $S_{\pi,\pi^*} \rightarrow T_{n,\pi^*}$) should be two orders of magnitude more probable than those involving singlet and triplet states of the same electronic type (e.g., $S_{\pi,\pi^*} \rightarrow T_{\pi,\pi^*}$ and $S_{n,\pi^*} \rightarrow T_{n,\pi^*}$). This type of selection rule is shown to result in high degree of spin polarization in the triplet states formed in these systems as well as in other systems in which one of the possible routes involved in the intersystem crossing process is favored over all the others (except when the molecule under examination belongs to the Ci or the cubic point groups). The detection of the polarized state by observing the phosphorescence emission requires that the radiative lifetime of the latter from at least one of the three sublevels of the lowest triplet state be shorter than the characteristic time for the spin-lattice relaxation processes between the three sublevels of the triplet state. This is demonstrated to be the case for pyrazine in its n,π* triplet state at low temperatures (1.6°-10°K) and discussed in Section III. The different mechanisms proposed for the spin-lattice relaxation process are briefly discussed. The observed spin-lattice relaxation times for pyrazine at 1.6° are found to be comparable to those observed for a number of ionic paramagnetic impurities in inorganic systems at the same temperature.

(continued on next p.)

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
review triplet state phosphorescence intersystem crossing polarization heavy atom effects						

ABSTRACT, continued

In the third part of the paper (Section IV), a summary of the theory of the triplet-singlet radiative transitions is given. A comparison of phosphorescence properties of the different systems is made and the observed differences are explained in the framework of the present theory. The phosphorescence of aromatic hydrocarbon is known to be the most forbidden electronic dipole transition known for polyatomic molecules. The reason for this is discussed, and the consequence of this fact is shown to be a great sensitivity of the triplet $\rightsquigarrow$ singlet radiative transition of these molecules to weak perturbations such as those produced by solvent effects and halogen substitution. Proposed explanations are given for the observed changes in the polarization of this transition resulting from these different weak perturbations.

In the last part of this paper (Section V), the important experiments needed in this field are recommended.

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