In another study[34] the dienol **73**, which was produced by the action of methyllithium on the dienone **72**,[35] has been treated with formic acid to give what is almost certainly the bicyclic alcohol **74**. We envisage extending this reaction to the cyclization of the tetraenol **75** which, we hope, will give a significant amount of the

tetracyclic diene **76**.[35a] The latter substance, on ozonolysis, would be expected to yield the triketo aldehyde **77** which, by analogy to previous work,[36] should undergo a double intramolecular aldol condensation to give 16-dehydroprogesterone (**78**).

(34) W. S. Johnson and L. A. Dolak, work in progress.
(35) F. B. LaForge, N. Green, and W. A. Gersdorff, *J. Am. Chem. Soc.*, **70**, 3707 (1948).
(35a) NOTE ADDED IN PROOF. M. U. S. Sultanbawa and M. F. Semmelhack have prepared the tetraenol **75** and shown that it gives, on treatment with formic acid, a significant amount of a single crystalline tetracyclic hydrocarbon which we suspect is the substance **76**.
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The Triplet State: Its Radiative and Nonradiative Properties

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The triplet–singlet radiative transition in aromatic hydrocarbons is the most forbidden electronic transition known for polyatomic molecules. It is thus found that the spin–orbit interaction mechanisms that give the lowest triplet state its radiative properties are sensitive to weak perturbations, *e.g.*, solvent effects, halogen substitution, and lattice vibrations. Explanations are proposed for the observed sensitivity of the mechanisms of these transitions to the different perturbations. In mixed, as well as in pure, aromatic crystals and in some of their derivatives, polarization results indicate that lattice vibrations do not modify the $\pi^* \rightarrow \pi$ phosphorescence mechanisms. On the other hand, a strong coupling between the electronic motion and the lattice motion has been observed in the $\pi^* \rightarrow n$ phosphorescence of the pyrazine crystal in which the intermolecular $C—H \cdots N$ hydrogen bonding constitutes a major part of the lattice energy. The rate of the nonradiative process involving change in multiplicity (intersystem crossing) in compounds having n,π^* and π,π^* states is predicted to be approximately two to three orders of magnitude faster than in compounds having only one of these types of transitions. The importance of the order and the type of the energy levels depends on the validity of the Born–Oppenheimer approximation. The emission decay of pyrazine at very low temperatures (4.2°K) indicates that: (1) intersystem crossing favors the population of one of the triplet sublevels over the others (spin polarization) and (2) spin lattice relaxation between the triplet sublevels is slower than the phosphorescence process.

I. Introduction

The phosphorescence emission of organic molecules in rigid media was first observed[3] in 1895. In 1942, the emission was shown[4] to be electric dipole radiation and in 1944 it was identified[5,6] as radiative intercombination between the lowest triplet state and the ground singlet state. The paramagnetic character of the emitting triplet state was first demonstrated[7] in 1945.

Singlet–triplet transitions are spin forbidden, hence phosphorescence emission requires spin–orbit interac-

tion. In molecules, spin–orbit interactions may have different forms and thus a number of mechanisms can be written down to account for the radiative properties of the T $\rightarrow$ 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 (0.10–100 cm⁻¹ or 0.3–300 cal/mol), the emission mechanism is not unique and is sensitive to rather weak perturbations, *e.g.*, solute–solvent interactions, halogen substitution, and lattice vibrations in certain crystals. These studies are described in more detail in section II.

Until 1961, there was no expression for the intramolecular nonradiative transition probability between

(1) Alfred P. Sloan and Simon Guggenheim Fellow.
(2) Contribution No. 2118.
(3) E. Wiedemann and G. C. Schmidt, *Ann. Physik*, **56**, 201 (1895).
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(7) G. N. Lewis and M. Calvin, *J. Am. Chem. Soc.*, **67**, 1232 (1945).

(8) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

different states. It was concluded[8] from experimental data that the rate constant of radiationless transitions between excited states of the same multiplicity (internal conversion) is approximately 10^{12} sec^{-1} while that between excited states of different multiplicity (intersystem crossing) is approximately 10^6 sec^{-1}. The study of the dependence of the observed lifetime on deuterium substitution leads eventually to the development of the theory of nonradiative transitions[9] we presently have for polyatomic molecules.

The rate of the intersystem crossing process between two states of different electronic origin (e.g., n,π^* and π,π^*) is found[10] to be 1000 times faster than that between two states of the same electronic origin (e.g., $\pi,\pi^* \rightsquigarrow \pi,\pi^*$ or n,$\pi^* \rightsquigarrow$ n,π^*). If the nuclear and electronic motions are interdependent, the above selection rules break down and give rise to new selection rules: If in a molecule containing both n,π^* and π,π^* states [(e.g., carbonyls, nitrogen heterocyclics) the two states are strongly intermixed, the rate of the nonradiative transitions should be about two orders of magnitude faster than in compounds with only one type of state or the other. These and other aspects of nonradiative transitions are covered in section III.

In section IV, an outline showing the direction in which research in these two fields ought to be pursued is put forward.

II. Radiative Properties

Introduction. The phosphorescence emission[11] is now firmly believed to be due to a triplet → singlet electronic transition. If the spin and orbital motions of the electron are independent of one another, this transition does not give rise to electric dipole radiation, because of spin selection rules. However, in actuality, the spin and orbital motions of the electrons are not independent, even in atoms with very small nuclear charge. The orbital motion of the electron induces a magnetic field which interacts with its spin magnetic moment. This spin–orbit interaction results in a change of the direction of the spin-angular momentum of one electron, thereby changing a singlet state into a triplet state and vice versa. The strength of this interaction depends greatly on the nuclear charge. In molecules, the following additional mechanisms could be introduced as a result of nuclear motion: (a) The spin–orbit interaction can be modulated by the molecular vibration. This is known as the spin vibronic interaction and might directly change a triplet state into a singlet state and vice versa (i.e., first-order interaction). (b) The molecule is first deformed by a nontotally symmetric vibration. In the deformed molecular configuration, new spin–orbit interactions might result which are vanishing in the original nondeformed geometry. This type of interaction is second order in nature.

(9) G. W. Robinson, J. Mol. Spectry., 6, 58 (1961); G. W. Robinson and R. Frosch, J. Chem. Phys., 37, 1962 (1962); ibid., 38, 1187 (1963).
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(11) For a recent review: S. K. Lower and M. A. El-Sayed, Chem. Rev., 66, 199 (1966).

Table I
Relative Oscillator Strengths and Radiative Lifetimes of Molecular Electronic Transitions in Aromatic Compounds

Spin-allowed transitions	Oscillator strength	Rad. lifetime, sec
π,π^*	0.001–1	10^{-7}–10^{-9}
σ,π^* or π,σ^*	$<10^{-2}$	$>10^{-6}$
n,π^*	$\sim10^{-2}$	$\sim10^{-6}$
Spin-forbidden transitions		
n,π^* (σ,π^* or π,σ^*)	10^{-7}–10^{-5}	10^{-2}–10^{-4}
π,π^* in haloaromatics	10^{-9}–10^{-6}	1–10^{-3}
π,π^* in unsatd hydrocarbons	10^{-11}	~100

Thus, the total Hamiltonian including spin–orbit interaction is given by[12]

$$\mathcal{H} = \mathcal{H}^0{}_0 + \mathcal{H}^0{}_{s.o.} + {}_a\sum\left(\frac{\partial\mathcal{H}_{s.o.}}{\partial Q_a}\right)_{Q_a=0} Q_a + {}_a\sum\left(\frac{\partial\mathcal{H}^0{}_0}{\partial Q_a}\right)_{Q_a=0} Q_a$$
$$= \mathcal{H}_I + \mathcal{H}_{II} + \mathcal{H}_{III} + \mathcal{H}_{IV} \qquad (1)$$

where $\mathcal{H}_I$ is the part of the Hamiltonian containing the kinetic energy as well as all the electrostatic interaction terms, $\mathcal{H}_{III}$ is the spin vibronic interaction, whereas $\mathcal{H}_{IV}$ and $\mathcal{H}_{II}$ constitute the second-order vibronic spin–orbit terms, and $\mathcal{H}_{s.o.}$ 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 first 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 mixing coefficient λ 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

$$\vec{M}_{T_1 \rightarrow S_0} = {}_i\sum\lambda_{i1}\vec{M}_{i0} + {}_j\sum\lambda_{j0}\vec{M}_{j1} \qquad (2)$$

where λ_{i1} is the mixing coefficient between the singlet state i and the lowest triplet state T_1 and λ_{j0} is the mixing coefficient between triplet state j and the ground state. $\vec{M}_{i0}$ 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., $\vec{M}_{T_1 \rightarrow S_0}$) thus reflects the polarization of $\vec{M}_{i0}$ and/or $\vec{M}_{j1}$. If one measures the polarization of the 0,0 band, one can identify the mechanisms in which λ_{i1} or λ_{j0} involves direct spin–orbit coupling ($\mathcal{H}_{II}$). On the other hand, the measurements of the polarization of the vibronic bands whose intensity is not accounted for by the Franck–Condon principle can yield information about mechanisms involving spin vibronic ($\mathcal{H}_{III}$) and second-order spin–orbit vibronic ($\mathcal{H}_{II} + \mathcal{H}_{IV}$) interactions.

(12) A. Albrecht, J. Chem. Phys., 38, 354 (1963).

Table II
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

		—E.P.A.—	—————————————Solvent—————————————					
		P_L	—Biphenyl—			—Durene—		
Molecule	P_N	$+ P_M$	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

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 I gives a comparison between the oscillator strengths and radiative lifetimes of spin-allowed ($S_1 \longleftrightarrow S_0$) and spin-forbidden ($T_1 \longleftrightarrow S_0$) 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 10^6 for S–S and S–T, respectively. The oscillator strength of T → S transitions covers a wider range; this reflects mainly a sensitivity of the spin–orbit interaction to intermolecular and intramolecular perturbations and the different oscillator strengths of the mixing transitions (see eq 2). 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[13] 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_{j0}). Only the relatively weak (σ,π) transitions (small M_{i0} and M_{j1}) have relatively strong direct spin–orbit interaction with T → S 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 $T_{\pi,\pi} \longleftrightarrow S_0$ 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[14] 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 subspectrum I.[15] However, the relative importance of the second-order spin–orbit vibronic interaction to the direct spin–orbit interaction is increased in haloaromatics. The spectrum resulting from the former interaction (subspectrum II in ref 15) has comparable intensity to that resulting from the latter type interaction (subspectrum I). This explains the

observed out-of-plane 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[13] as on π,π^* transitions. Substituting a bromine atom for an α-hydrogen atom attached to a carbonyl group increases the molar extinction coefficient of the n,π^* transition 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 10^3–10^4. 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. Thus, the T–S n,π^* transition is inherently strong and thus is not sensitive to heavy-atom perturbations. The observed intramolecular heavy-atom effect on the T–S transitions of aromatic hydrocarbons is thus a result[16] of the inherent high degree of forbiddenness of this transition due to the weak radiative spin–orbit perturbation 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 II summarizes the relative probability distribution[17] 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 naphthalene-d_8, quinoxaline, and phenanthrene-d_{10} 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,[18] it is proposed that the triplet–singlet transition is mixed with σ,π transitions *via* direct spin–orbit (s.o.) coupling ($\mathfrak{K}_{II}$) 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 $\xrightarrow{\text{e.s.}} (\sigma,\pi)_g \xrightarrow{\text{s.o.}} (T_{\pi,\pi^*} \longleftrightarrow S_0)_g \to$ guest phosphorescence
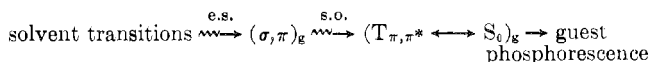
According to this mechanism, the transition moment of the phosphorescence of the guest can then be written as

$$\vec{M}_{T \to S_0} = \delta \vec{M}_{\sigma,\pi}g + \delta k \vec{M}_{\text{solvent}} \qquad (3)$$

$\vec{M}_{\sigma,\pi}g$ is probably an order of magnitude smaller than $\vec{M}_{\text{solvent}}$, so, if $k = 0.2$, the part of phosphorescence in-

(13) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952).
(14) M. A. El-Sayed, *ibid.*, **43**, 2864 (1965).
(15) T. Pavlopoulos and M. A. El-Sayed, *ibid.*, **41**, 1082 (1964).

(16) M. A. El-Sayed, *ibid.*, **41**, 2462 (1964).
(17) N. K. Chaudhuri and M. A. El-Sayed, *ibid.*, **43**, 1423 (1965); *ibid.*, **44**, 3728 (1966).
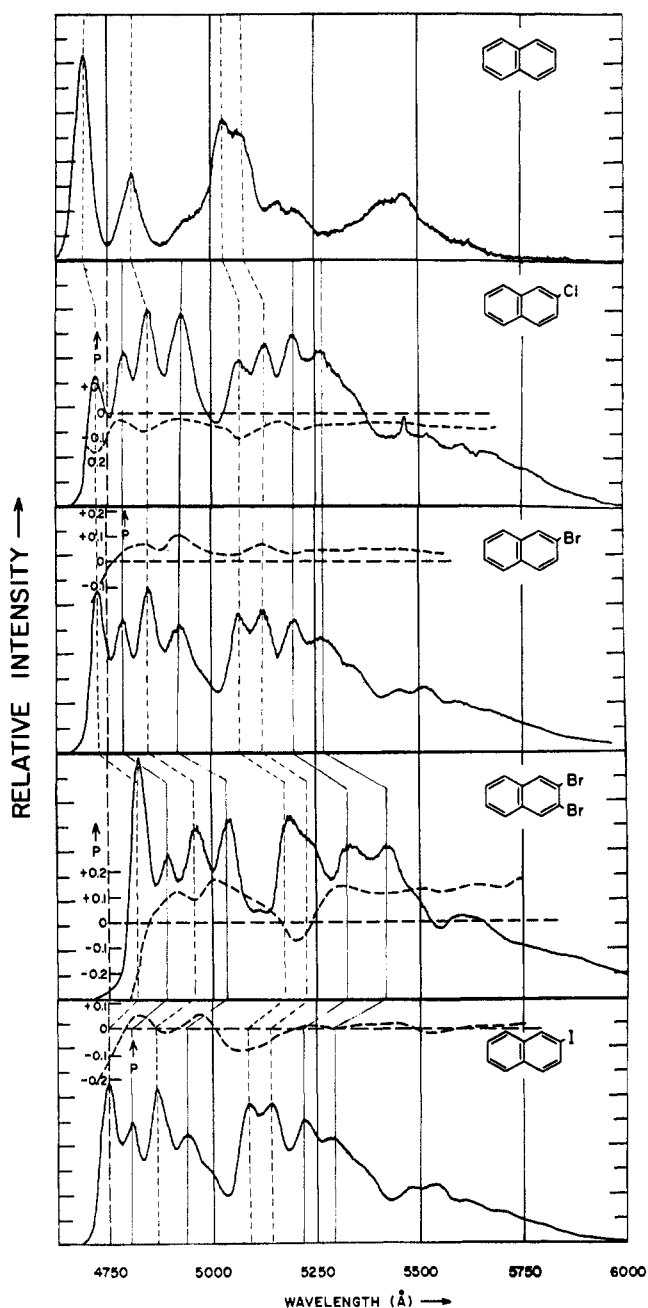(18) M. A. El-Sayed, *ibid.*, in press.

Figure 1. The phosphorescence spectra (solid curves) and polarization (broken curves) of naphthalene and its β-halo derivatives 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.

tensity 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 the 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 with energies comparable to 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[17] 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 change of hybridization is caused either by the crystal field of the methyl groups of the durene host or by forcing the guest molecule to be slightly nonplanar. As a result of mixing P_x and P_y into 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 π and σ 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 (Figure 1).[15] The degree of polarization is shown as a function of wavelength in Figure 1 with broken lines while the actual spectrum is shown with solid lines. Subspectra I of the different halo derivatives 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 or 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
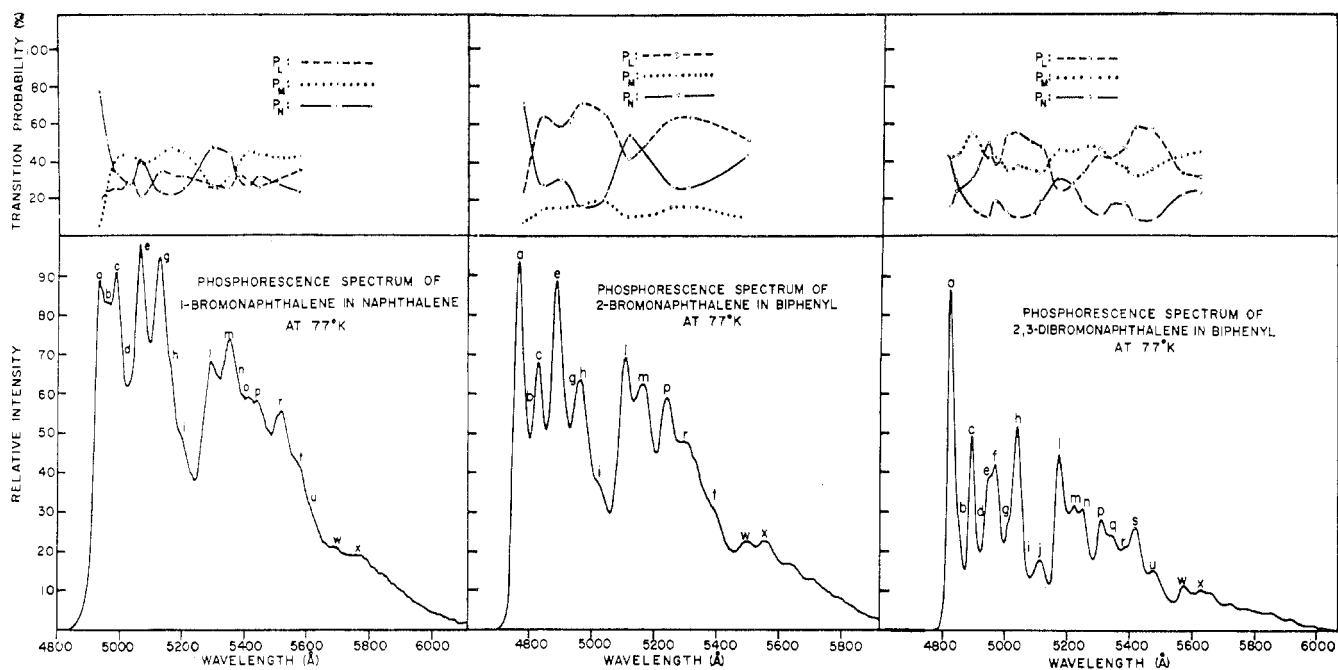
Figure 2. The spectra and polarization of some bromonaphthalenes in host crystals showing the sensitivity of the emission mechanism to the position and number of the halogen atoms as well as to the ratio of the sizes of the guest molecule to the host hole. The smaller the ratio, the broader the spectrum.

were determined[19] 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 III.

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. The long axis polarized emission constitutes 55, 21, 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, 36, and 44% 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 in-

volve 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 ($\sim$35%) in rigid glasses but lowest ($\sim$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 by forcing the halogen to be slightly nonplanar with the aromatic ring due to the packing forces of the host lattice. The second mecha-

Table III

The Distribution[a] 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	Naphtha-lene	21	36	43

[a] The values given in parentheses are those obtained in rigid glasses using the method of photoselection.[15]

(19) N. K. Chaudhuri and M. A. El-Sayed, J. Chem. Phys., in press.

nism involves mixing between the host and guest electronic states.

(3) *Effect of Lattice Vibrations.* The low radiative probability of the triplet–singlet transition raises the question: Can lattice vibrations cause enough change in the spin–orbit interaction to induce phosphorescence? Two different systems have been examined: mixed crystals and pure crystals. Mixed crystals of $C_{10}D_8$, $C_{14}D_{10}$, quinoxaline, 2-bromonaphthalene, and 2,3-dibromonaphthalene have been examined in biphenyl and/or durene host lattices at 4.2°K. Both the spectra and the polarization of the different vibronic bands have been determined.[20] The general conclusions reached are: (a) The polarization of the emission appearing with or without coupling to the lattice modes is found to be the same. (b) If the guest is incorporated in a host lattice with a hole having a comparable or slightly larger size than the size of the guest molecule, the vibronic bands are found to be relatively broad and strongly coupled to the lattice vibrations of the host (Figure 2). (c) If the size of the host hole is relatively smaller than that of the guest molecule, the vibronic bands appear sharp with little or no coupling to the lattice vibrations (Figure 2).

Result a indicates that in the systems studied, the appearance of lattice vibrations has no perturbational effects on the spin–orbit interaction for molecules in a mixed crystal. The appearance of these lattice vibrations merely indicates that the excited guest molecule would like to have a disposition in the lattice that is different from that in the ground state. Results b and c seem to support this explanation. If the guest molecule librates in a time shorter than the radiative lifetime (result b above), emission takes place from a relaxed orientation of the guest excited molecule which is different from its orientation in the ground state. Since one might obtain a distribution of the relaxed configuration, the different vibronic bands could be broad. The appearance of the lattice vibrations in this case merely satisfies the Franck–Condon principle as a result of the difference in the disposition of the guest molecule in the excited and ground states. In case c, the guest molecule is probably prevented from rotating in the excited state and thus the guest molecule has the same molecular disposition in the lattice in both the excited and the ground states. In this case, the lattice vibrations are not expected to appear (Franck–Condon principle).

For pure crystal phosphorescence, we studied emission from quinoxaline, 2,3-dibromonaphthalene,[20] and pyrazine[21] at 4.2°K. The phosphorescence emission of the first two molecules is a result of a $\pi^* \rightarrow \pi$ transition whereas that of pyrazine results from a $\pi^* \rightarrow n$ transition. The following conclusions can be drawn from the observed spectra of these molecules: (a) At least in pyrazine, the origin of the emission spectrum is found to

be lower in energy than the origin of the S–T absorption by 102 cm^{-1}. (b) The phosphorescence spectra of quinoxaline and 2,3-dibromonaphthalene from pure crystals seem to be very similar to that from mixed crystals (see Figure 3). (c) The phosphorescence spectrum of pyrazine crystals gives evidence of a strong coupling between the electronic and the lattice motions as well as between the molecular vibration and lattice vibration motions.

Since pyrazine is the only known molecular crystal in which strong coupling between molecular and lattice motions is demonstrated, we will discuss it in more detail. Figure 4 compares[21] the crystal spectrum (bottom) with the molecular spectrum in cyclohexane matrix (top). For each vibronic band, several lines appear due to the different sites of pyrazine in the cyclohexane matrix. The vibration analysis of the crystal
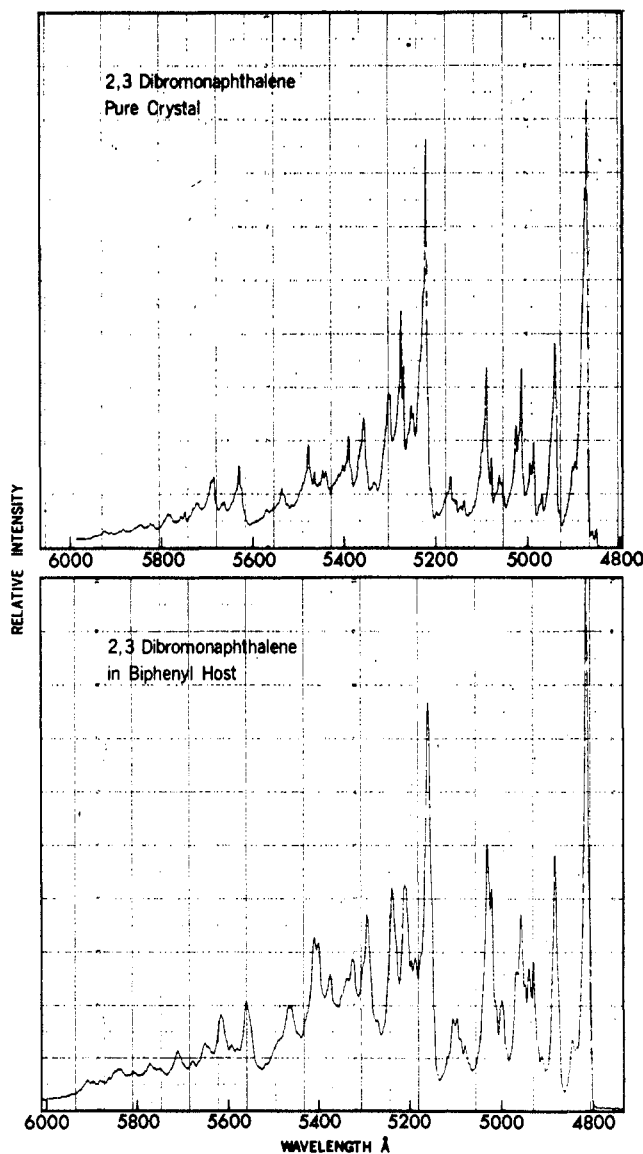

Figure 3. A comparison of the phosphorescence of 2,3-dibromonaphthalene in biphenyl with that obtained from the pure crystal at 4.2°K. The strong resemblance of the two spectra indicates that host lattice vibrations do not have great perturbational effects on the phosphorescence mechanisms in these systems.

(20) N. K. Chaudhuri and M. A. El-Sayed, in preparation.
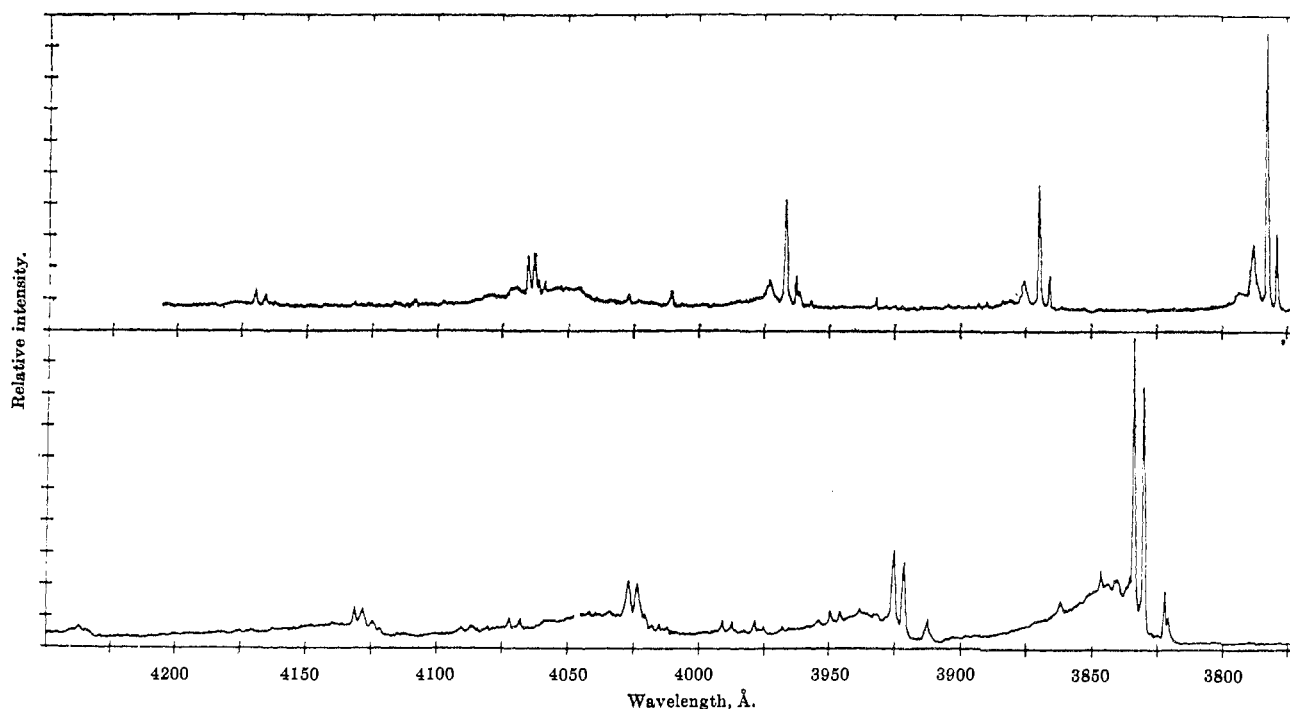(21) W. Moomaw and M. A. El-Sayed, *J. Chem. Phys.*, **47**, 2193 (1967).

Figure 4. The phosphorescence spectra of pyrazine in cyclohexane matrix (top) and of the pure crystal (bottom). The vibration analysis identifies the latter as resulting from pyrazine emission. The predominance of the emission resulting from the coupling of the b_{3g} lattice vibrations strongly indicates the strong coupling of the lattice vibration with electronic motion. This is the first case known where lattice vibrations seem to induce phosphorescence emission.

spectrum corresponds in every respect with that of pyrazine in cyclohexane, thus leaving no doubt that the emission of the crystal is a result of the pyrazine $T_1 \rightarrow S_0$ transition. It is clear in the crystal spectrum that the strongest peaks in any vibronic band are those whose appearance is attributed to a coupling with the b_{3g} lattice modes of frequencies 57 and 82 cm^{-1}. The unusual intensity distribution of these bands might indicate that these lattice vibrations play a specific role in the spin–orbit perturbation of the n,π^* transition. As in the perturbation by intramolecular vibration, lattice vibration might affect the T–S transition by two mechanisms: The first involves the spin-phononic term $_a\sum(\partial \mathfrak{IC}_{s.o.}/\partial Q_a)_{Q_a=0}Q_a$ (where Q_a is a normal coordinate of a lattice mode) and the second involves $\mathfrak{IC}_{s.o.} + _a\sum(\partial \mathfrak{IC}/\partial Q_a)_{Q_a=0}Q_a$. It is not yet known whether or not these two types of perturbations are actually effective in pyrazine or in any other molecular crystal, but investigations along these lines are now in progress.

III. Nonradiative Properties

Introduction. It is now believed that in reasonably large molecules, e.g., benzene, naphthalene, etc., nonradiative transitions take place because of 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[9] for the probability of a nonradiative transition between states I and II

$$W_{I,II}(\text{sec}^{-1}) = \frac{8\pi^2 \tau}{h^2} II_{ij}\langle\theta_{Ii}|\theta_{IIj}\rangle^2\langle\Phi_I|\mathfrak{IC}'|\Phi_{II}\rangle^2 \quad (4)$$

where θ_{Ii} and θ_{IIj} are the vibrational wave functions i and j of the electronic states I and II, respectively; Φ_I and Φ_{II} are the electronic wave functions of states I and II, respectively; τ is the relaxation time of the vibronic levels; $\mathfrak{IC}'$ is the perturbing Hamiltonian. For transitions between states of similar multiplicity, $\mathfrak{IC}'$ could be the electron–electron repulsion term and/or the vibronic interaction terms. For nonradiative transitions between states of different multiplicity, $\mathfrak{IC}'$ should contain the spin–orbit interaction between the intercombining states.

The Born–Oppenheimer approximation is probably not valid when the transitions between the closely spaced excited states are considered. An expression for $W_{I,II}$ has recently been derived[22] in which the Born–Oppenheimer approximation is not made. In the following section, the radiationless processes in molecules containing low-energy n,π^* and π,π^* states, e.g., nitrogen heterocyclics and 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 then be briefly discussed.

Selection Rules for the Intersystem Crossing Process. It has been shown[23] that in the framework of the Born–Oppenheimer approximation, the electronic integrals for the nonradiative transitions $S_{\pi_i,\pi_j}* \rightsquigarrow T_{\pi_k,\pi_j}*$,

(22) S. H. Lin, J. Chem. Phys., 44, 3759 (1966).
(23) M. A. El-Sayed, ibid., 38, 3032 (1963).

$S_{n_i,\pi_j}* \rightsquigarrow T_{n_i,\pi_k}*$, and $S_{\pi_i,\pi_j}* \rightsquigarrow T_{\pi_j,\pi_k}*$ have vanishing 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 is on the nitrogen atom. The vibrational overlap integrals for these transitions are an order of magnitude larger than that 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
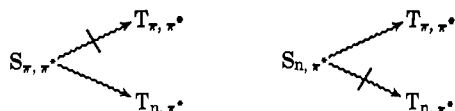
Transitions connected by $\rightsquigarrow$ should be faster than those interconnected by $\rightarrow\!\!|\!\!\rightarrow$ by a factor of $\sim 10^3$.

The above results might account for a number of qualitative observations. The intersystem crossing rate constant in benzophenone and 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 is $\sim 10^5$ sec^{-1} in aliphatic carbonyls. Since fluorescence has been observed in a number of these aliphatic carbonyls, the intersystem crossing rate constant in these compounds might be $\sim 10^7$ sec^{-1}. The major difference between aliphatic and aromatic carbonyls is that the former compounds have no triplet π,π^* level between the lowest singlet and triplet n,π^* levels. Aromatic carbonyls possess a triplet level of π,π^* type located between the lowest singlet and the lowest triplet levels which are of the n,π^* type. This might facilitate the intersystem crossing process in aromatic carbonyls.

Similar conclusions could be reached upon examining the presently available qualitative results. Benzene shows both fluorescence and phosphorescence and the rate of intersystem crossing 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 $\sim 10^{-9}$ sec. The radiative lifetime of pyrazine is $\sim 10^{-6}$ sec and one is tempted to believe that the 10^{-9} sec observed lifetime of pyrazine 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 its π,π^* states. It must be mentioned that the above conclusions are based on qualitative and an insufficient number of observations. Accurate values of quantum yields are perhaps the most desperately needed quantities at present. Our understanding of nonradiative processes greatly suffers from the lack of these quantities. Observed lifetimes are now being measured, but unless they are coupled with

quantum yield data it is rather difficult to determine the path of the nonradiative transitions.

Should quantum yields become available for many of these molecules, a reexamination of the above selection rules will be advisable. Since the above selection rules are derived using the Born–Oppenheimer approximation, an examination of the extent of the applicability of the approximation would then be possible. 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 would expect 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 in molecules containing only one type or the other. Thus, the intersystem crossing process should be faster in ketones and nitrogen heterocyclics than in unsaturated aliphatic and aromatic hydrocarbons.

Spin Lattice Relaxation between the Triplet Sublevels. The fact that the phosphorescence emission is strongly polarized indicates that spin–orbit interaction leading to the emission is specific and is stronger for transitions from one of the three sublevels of T_1 than from the others.[24] One might also expect, in the intersystem crossing process, the rates of the transitions from S_1 to the three sublevels of the triplet state to be unequal.[25] Let us examine the case of pyrazine. It is most likely that the intersystem crossing process involves $S_{n,\pi}* \rightsquigarrow T^x_{\pi,\pi}*$, where x indicates one of the sublevels of $T_{\pi,\pi}$ in which the spins are polarized in a certain direction in the molecular framework and with which the spin–orbit interaction with $S_{n,\pi}*$ is strong. This process is then followed by the rapid (10^{-12} sec) process $T^x_{\pi,\pi} \rightsquigarrow T^x_{n,\pi}$. In this process the spin polarization has not changed, yet the electronic state has changed its spatial electronic characteristics. Spin depolarization can take place by spin relaxation, a process which is much slower than 10^{-12} sec, the time required for the internal conversion process $T_{\pi,\pi}* \rightsquigarrow T_{n,\pi}*$. The emitting triplet ($T_{n,\pi}$) is thus populated initially in a manner that is mainly determined by the path followed in the intersystem crossing process. The observed characteristics of the phosphorescence decay is determined by the following conditions: (1) If spin lattice relaxation between the different sublevels of $T_{n,\pi}*$ is slower than the radiative lifetime, a decay is observed which can be resolved into two (or perhaps three) exponential components with different decay constants. (2) If the rate of spin relaxation is comparable to the phosphorescence radiative lifetime of the different emissions, a complicated, nonexponential

(24) If this is not the case, the emission from three sublevels would be equally probable along the three molecular axes; i.e., the emission would be depolarized.
(25) M. S. DeGroot, I. A. Hesselmann, and J. H. van der Waals, Mol. Phys., 12, 259 (1967).

decay is observed.   (3) As the rate of the spin relaxation exceeds that of the radiative lifetime, the emission decay becomes exponential.   This behavior has recently been demonstrated[26] for pyrazine emission obtained in cyclohexane, in dioxane, and in benzene matrix at low temperature.   At 4.2°, three decay constants are obtained, one being ten and fifty times larger than the others. A complicated decay is obtained between 4 and 11°K, but above 11°K an exponential decay is observed with a constant equal to that known for pyrazine.   In previous observations made on lifetimes, the temperature (77°K) and medium used are such that the rate of spin relaxation is faster than the radiative lifetime.   In such cases an exponential decay is observed with a rate constant k which is given by $K = \Sigma_i {}^3k_i N_i$, where k_i is the rate constant of the transition from one of the sublevels of T_1 to the ground state ($T_1{}^i \rightarrow S_0$) and N_i is the fraction of the total molecules in T_1 that occupy $T_1{}^i$.

IV. 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 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 perturbation effect of the solvent?   (3) What is the relative importance of the different terms of the spin–orbit Hamiltonian in providing the triplet–singlet transition with its radiative power in different molecules?

To answer the first two questions, research directed at accurate determination of the T–S absorption cross sec-

(26) L. Hall and M. A. El-Sayed, *J. Chem. Phys.*, in press.

tion 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 collaboration between 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 media 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 thorougly examined.   The reason for this is undoubtedly the unknown, yet badly needed, accurate values of quantum yields of the radiative and nonradiative processes of 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.