EXCITED-STATE PHENOMENA ASSOCIATED WITH SOLVATION SITE HETEROGENEITY

By

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To My Family . . . .

ABSTRACT

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Organic molecules that undergo a large change in dipole moment upon excitation may exhibit large shifts in absorption or emission spectra. Interesting excited-state phenomena involving solvent-solute interactions and solvent-cage relaxation may occur when such polar molecules are excited in a polar matrix. These phenomena include: temperature-dependent inhomogeneous spectral broadening, solvent-assisted electronic energy transfer, time-dependent spectral shift, lack of fluorescence depolarization, and excitation-wavelength dependent red shift of fluorescence and phosphorescence in rigid media (Red-Edge Effect). These phenomena can be explained in terms of the statistical interaction between the polar solute molecules and their immediate polar environment. Thus, even in a homogeneous condensed phase the polar solute molecules are

expected to occupy a variety of solvation sites at any given time giving rise to different absorption energies corresponding to the same electronic transitions. Such variation in solute-solvent local interactions introduces a significant source of broadening of both the absorption and emission spectra.

We have examined the role of microenvironmental heterogeneity in electronic spectra by studying the effects of medium polarity, rigidity, temperature, concentration and excitation-wavelength dependence of the spectra of pyridine merocyanine dye, 2-amino-7-nitrofluorene (ANF), 4,4'-aminonitrodiphenyl (AND) and methyl- and tertbutyl-esters of 9-anthroic acid (9MA and 9TBA respectively). Pyridine merocyanine dye represents a class of organic molecules that undergo a decrease in dipole moment upon electronic excitation while ANF and AND represent a class of organic molecules that undergo a substantial increase in dipole moments upon electronic excitation. 9MA and 9TBA represent a class of organic molecules that are flexible and undergo geometrical changes upon electronic excitations.

The absence of excitation wavelength dependence of the fluorescence at room temperature in fluid polar media is explained in terms of orientational and translational relaxations of various "solute-solvent conformations" that occur prior to fluorescence. The fluctuations in the interaction of solutes with different solvation sites are dynamic in fluid

media. Once the solution is made rigid (glass, polymer matrix, etc.) the dynamic character is lost. One may think of a viscosity-dependent barrier between these sites, the height of which depends on the rigidity of the medium. Under these circumstances, the lifetimes of various "solute-solvent conformations" are larger than the excited-state lifetime, and hence excitation wavelength dependent fluorescence will occur (Red-Edge Effect).

The presence of REE in flexible 9MA and 9TBA in nonpolar matrix (3MP) is explained in terms of different conformers that have slightly different absorption energies.

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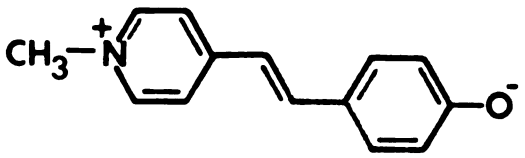
CHAPTER I

INTRODUCTION

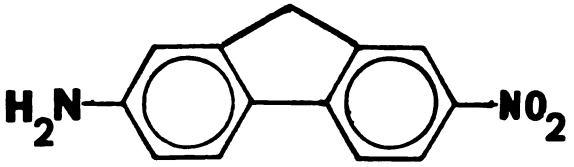
This study deals with solvent effects on absorption and luminescence properties of molecules that undergo large change in dipole moment upon electronic excitation. Changes in quantum yield (ϕ_F) and energy of fluorescence (λ_F) in pure solvents of different polarities and mixed solvents were sought. Our objective is to examine the effects of solvent-cage relaxation on emission spectra of certain molecular systems. From the beginning we suspected that different solvation cages, hence different excitation energies may occur and hence we looked for excitation wavelength dependence of luminescence energy and spectral resolution due to edge excitation (excitation at the red edge of the first absorption band) at low temperatures.

Three types of molecular systems were examined; the first molecular system undergoes a substantial <u>decrease</u> <u>in dipole moment</u> upon electronic excitation. As an example of this molecular system we have studied the optical and luminescence properties of pyridine merocyanine dye which undergoes 5.5D decrease in its dipole moment upon

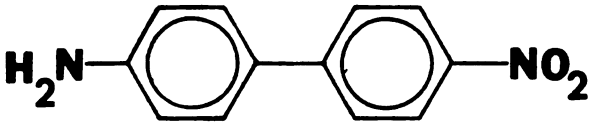


Pyridine merocyanine dye

excitation. The second molecular system undergoes an increase in dipole moment upon excitation: as an example of this system we have studied the optical and luminescence properties of 2-amino-7-nitrofluorene and 4,4' amino nitrodiphenyl (abbreviated as ANF and AND, respectively).

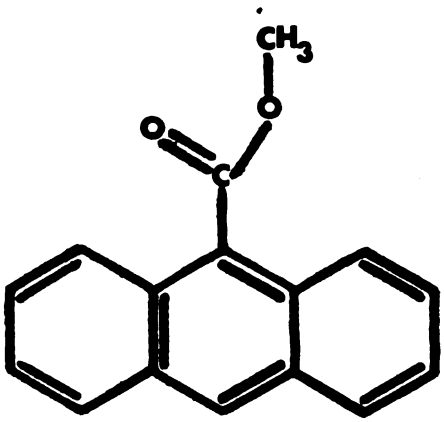


ANF

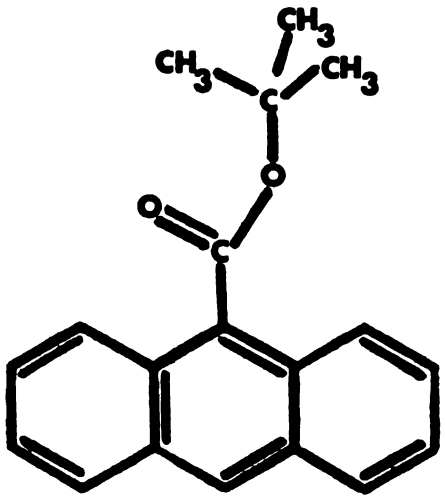


AND

These molecules undergo an increase in their dipole moments by 18D and 12D respectively upon electronic excitation. The third molecular system represents flexible molecules that undergo geometric relaxation in the excited state upon electronic excitation. As an example of this system we have studied 9-methylanthroate (9MA) and 9-tertbutyl anthroate (9TBA).



9-Methyl Anthroate (9MA)



9-Tertbutyl Anthroate (9TBA)

For merocyanine dye we have found a large blue shift in absorption, a small blue shift in emission in more polar solvents. Also the emission undergoes a blue shift upon lowering the temperature of the solution, and the absorption spectra exhibit an "apparent" blue shift upon lowering the temperature of the solution. While no excitation wavelength dependence of the fluorescence (red-edge effect) was observed in fluid media, a large red-edge effect was measured in rigid glass at low temperature and in polymer matrices at room temperature. The red-edge effect observed in rigid glass at low temperature gradually decreases when the concentration of the solute increases. These observations were interpreted in terms of a potential energy diagram built upon the assumption of a statistical distribution of solute polar molecules in different solvation sites. Thus even in a homogeneous condensed phase, solute molecules are expected to occupy a variety of solvation sites at any given time giving rise to different

absorption energies corresponding to the same electronic transitions. Such variation in solute-solvent local interactions which is orientation dependent is responsible for the observed REE and the inhomogeneous broadening of the absorption spectra. The absence of REE at higher concentrations is explained in terms of energy transfer among solute molecules in different solvation sites. ANF and AND offered the converse example of the pyridine merocyanine dye. ANF and AND absorption spectra undergo a red shift in more polar solvents. Their low temperature absorption undergoes a red shift instead of the blue shift observed in the case of merocyanine dyes at low temperatures. The REE observed for ANF and AND in different solvents at 77 K and in polymer matrices at room temperature were explained also in terms of a potential energy diagram that considers the statistical distribution of the solute among different solvation sites. The main difference here with respect to merocyanine is that the most stable solvation site lies at longer wavelength (red edge side) of ANF and AND absorption spectrum and not at shorter wavelength of the spectrum as in the case of pyridine merocyanine dye. This is of course due to the fact that ANF and AND undergo an increase in dipole moment upon excitation and in the case of pyridine merocyanine dye a decrease in dipole moment occurs.

For 9MA and 9TBA, the excitation wavelength

dependence of the fluorescence in 3MP at 77 K was studied. The variation of emission intensities of different vibronic bands of 9TBA at different excitation wavelength at 77 K were studied. The results are interpreted in terms of Shpol'skii effect.

The second chapter gives a detailed review of solvent effects on electronic absorption and emission spectra. The third chapter is a review of the red edge effect phenomenon (REE): different observations and interpretations are given by different authors. Two kinds of REE are distinguished. A related effect, namely the Shpol'skii effect, is also briefly discussed. Chapter IV describes the molecular systems we have studied with their corresponding absorption and emission spectra. The detailed study of pyridine merocyanine dye, ANF, AND, 9MA and 9TBA is presented in Chapter V together with our interpretation. The experimental part that describes the preparation, purifications and spectral measurements is summarized in Chapter VI. In Chapter VII I have discussed the significance of our study together with some suggestions for future work.

CHAPTER II

SOLVENT EFFECT ON ELECTRONIC SPECTRA

I. Solvent Effect on Absorption Spectra:

In the vapor phase at reduced pressure the observed absorption is due to electronic transitions in isolated molecules and high-resolution spectra showing vibrational and rotational structure are observed. Such resolution will decrease under conditions of high pressure due to intermolecular interactions in a molecular collision and this is called pressure broadening. This is similar to the spectrum of a dilute solution where the solute and solvent molecules are in close contact, all rotational structure is eliminated even in inert solvents, e.g., hydrocarbon solvents that are transparent in the region of solute absorption. Intermolecular collisions perturb the vibrational levels causing a blurring of the vibrational structure of the spectrum. Besides such a blurring effect, one may also observe an intensity change as well as a shift in the wavelength of the absorption bands depending on the kind of transition that the solute undergoes and its environment. Thus in the case of polar solutes in polar solvents one usually observes large changes in the position, intensity

and shape of absorption bands.

The interpretation of solvent effect is made difficult because they are sometimes small and thus not easy to measure precisely, and also because they are often the results of several effects which sometimes reinforce one another and sometimes cancel out. There is also some difficulty in the fact that the most easily measured and most often recorded solvent effect is the displacement or shift of the absorption maximum whereas theoretical considerations of electronic energy states refer to the position of (0,0) band, which is not necessarily affected in the same way as the maximum. Since it is practically impossible to locate the (0,0) band in diffuse or structureless solution spectra, the spectral shifts are referred to absorption maxima.

Solvent effects are qualitatively interpreted[1] in terms of dipole polarization and hydrogen-bonding forces between solute and solvent molecules. The following important factors must be considered: a) the momentary transition dipole during the optical absorption; b) Franck-Condon effects; c) the difference in permanent dipole moment between the ground and excited state involved in the electronic transition of the solute; d) properties of the solvent such as its dipole moment, its dielectric constant, its donicity and its ability to interact specifically with solute molecules, i.e., via a hydrogen bond; and d) a

factor to account for the statistical nature of intermolecular forces.[2]

Different intermolecular interactions such as hydrogen bonding, dipole-dipole, dipole-induced dipole and dispersion forces which occur in solutions may cause different shifts* in the electronic spectra depending on the nature of solvent-solute interaction and the electronic transition involved.

When optical absorption occurs, a transition dipole of the solute induces a momentary polarization in the solvent causing a stabilization of the excited electronic state relative to its energy in the vapor phase giving rise to a red shift (few hundred wave numbers, cm^{-1}) in the absorption spectrum. This polarization red shift is a result of dispersion forces and is operative in all solutions, whether the solute and solvent molecules are polar or not. It was found[3] that the magnitude of the polarization red shift increases with the refractive index of the solvent.

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*(Red shift): A shift in absorption and emission to lower energy (i.e., to longer wavelength).

*(Blue shift): A shift in absorption and emission to higher energy (i.e., to shorter wavelength).

In the case of polar solute molecules that undergo a large change in dipole moment (either an increase or a decrease) upon excitation, there will be different interaction energies between the polar solute and the solvent molecules particularly if the latter is also polar. In the case of a non-polar solvent, dipole-induced dipole forces dominate while in the case of polar solvent dipole-dipole interactions play the major role. Solvent molecules will interact with the solute molecules in the ground and excited state to different extents depending on the change in dipole moment of the solute upon excitation.

The Franck-Condon principle plays a major role in solvent effects on absorption and emission spectra. A solute molecule in solution is in equilibrium with the surrounding solvent molecules. The energy of the equilibrium ground state depend on two factors: (a) a packing factor which depends on the geometry of the solute and solvent molecules, and (b) a factor which depends on the degree of mutual orientation interaction if the solute and solvent are polar or if there is hydrogen bonding between them. The geometry, charge distribution, and dipole moment of the solute may be different in the excited state from the ground state; therefore, the equilibrium configuration of the solvent cage would also be different in the excited state from that in the ground state. The Franck-Condon principle states that an optical transition occurs in a

time that is short compared with the period of nuclear motions, therefore at the instant of the transition, the solvent configuration around the excited-state solute molecule is not the equilibrium configuration, but a conformation geometrically identical to the solvated ground state, i.e., a Franck-Condon state configuration. The energy of this configuration is higher than that of the equilibrium configuration in the excited state, which is reached upon relaxation of the system. A time of at least several molecular vibrations (10^{-13} sec) is required for a geometrical rearrangement of the solute molecule and a time of the order of 10^{-11} sec is required for the solvent reorientation. Since the lifetime of an excited singlet state is of the order of 10^{-9} - 10^{-8} sec, there is ample time for excited-state equilibrium to be established before deactivation occurs. In the same manner, the ground-state configuration of the system after fluorescence is not an equilibrium configuration, but a Franck-Condon state whose energy is higher than that of the ground-state equilibrium configuration; the system then relaxes to its equilibrium ground-state. Franck-Condon factors may contribute significantly to the observed shifts in absorption and emission spectra. One may classify the solution spectra into four different cases and consider solvent shifts observed in each case.

Case I: Non-polar Solute in Non-polar Solvent

The transition dipole induces a dipole in the neighboring solvent molecules and the solution spectrum is shifted to the red owing to the polarization effect and the shift depends on the solvent refractive index. The solution spectrum will tend to retain its vibrational structure.

Case II: Non-polar Solute in Polar Solvent:

This is similar to Case I, except there might be a slight packing strain since dipolar and particularly hydrogen bonding forces between the solvent molecules themselves will tend to increase the solvent-cage relaxation time after the transition[4]. A red shift that depends on the solvent refractive index will be observed together with an increase in the blurring of vibrational spectra relative to Case I.

Case III: Polar Solute in Non-polar Solvent:

Depending on whether the excited state dipole moment is smaller or larger than that of the ground state one has two cases:

a. Solute Dipole Moment Decreases Upon Excitation - Since the solvent is non-polar, there will be no orientation strain. Because of dipole-polarization (polarization of the solvent molecules by solute dipoles), the excited state

solvation energy will be less than that of the ground state. This results in a blue shift of the absorption spectrum, the amount of which will be dependent on the refractive index of the solvent. The polarization red shift still occurs and the observed shift will depend on the relative magnitude of the two effects.

b. Solute Dipole Moment Increases Upon Excitation - The increased solute dipole moment in the excited state makes its solvation energy greater than that of the ground state. This results in a red shift in the absorption spectra depending on the solvent refractive index. The red shift adds to the polarization red shift and gives rise to the observed shift in the spectrum.

Case IV: Polar-Solute in Polar Solvents:

In this case, dispersion, dipole-polarization and dipole-dipole forces are operative. In the case of hydrogen-bonding solvents the hydrogen-bonding forces must also be considered.

a. Solute Dipole Moment Increases Upon Excitation - In this case the dipole-dipole forces between the solute and solvent are greater in the excited state than in the ground state and a red shift is expected. Orientation strain in this case is small because the solvent molecules are already partly oriented.

b. Dipole Moment Decreases Upon Excitation - If the dipole moment decreases as a result of excitation the solvation energy is larger in the ground state than in the excited state. The excited solute molecule finds itself in a cage of dipoles whose orientation is that appropriate to the equilibrium ground state. In this case the blue shift resulting from dipole-dipole interaction is due to the greater solvation energy of the ground state and to the orientation strain which contributes a term equal to the energy required to orient solvent dipoles around the excited solute molecule.

The magnitude of the blue shift will depend on several factors, including the magnitude of the change in dipole moment during the transition, the value of the solvent dipole moment, and the sizes of solute and solvent molecules. If the solvent molecules are small, for example, more of them can get close to the solute dipole, and greater interaction will result. The superimposed polarization red shift will usually be dominated by this dipole blue shift. If the dipole moment changes its direction during excitation, one should expect a large orientation strain and hence a large blue shift due to dipole-dipole forces.

The last factor (e) dealing with the statistical nature of intermolecular forces and the fluctuation of all physical characteristics of the liquid resulting from it, accounts for the spectral inhomogeneity inherent in

experimentally observed absorption and emission spectra and represents the superposition of "elementary" spectra corresponding to molecules with different "molecular environment" potentials.

II. Effect of Hydrogen Bonding Solvents

Bayliss and McRae[1] considered hydrogen bonding interactions to be a special case of dipole-dipole interactions. However, Pimentel[5] pointed out that dipole-induced dipole and dipole-dipole interactions produce small solvent shifts compared with those due to hydrogen bond. He discussed the influence of hydrogen bonding formation on electronic transitions in terms of the Franck-Condon principle. Solvent shifts due to hydrogen bonding can be expressed as follows (See Figure 1):

$$\Delta\nu_a = \nu_a - \nu_o = W_g - W_e + w_e \quad \ldots\ldots 1$$

$$\Delta\nu_f = \nu_f - \nu_o = W_g - W_e - w_g \quad \ldots\ldots 2$$

where:

$\Delta\nu_a$ is the energy shift in absorption maximum,

$\Delta\nu_f$ is the energy shift in emission (fluorescence) maximum,

ν_a is the energy of absorption maximum,

ν_f is the energy of emission (fluorescence) maximum,

ν_o is the energy of absorption maximum in the gas phase,

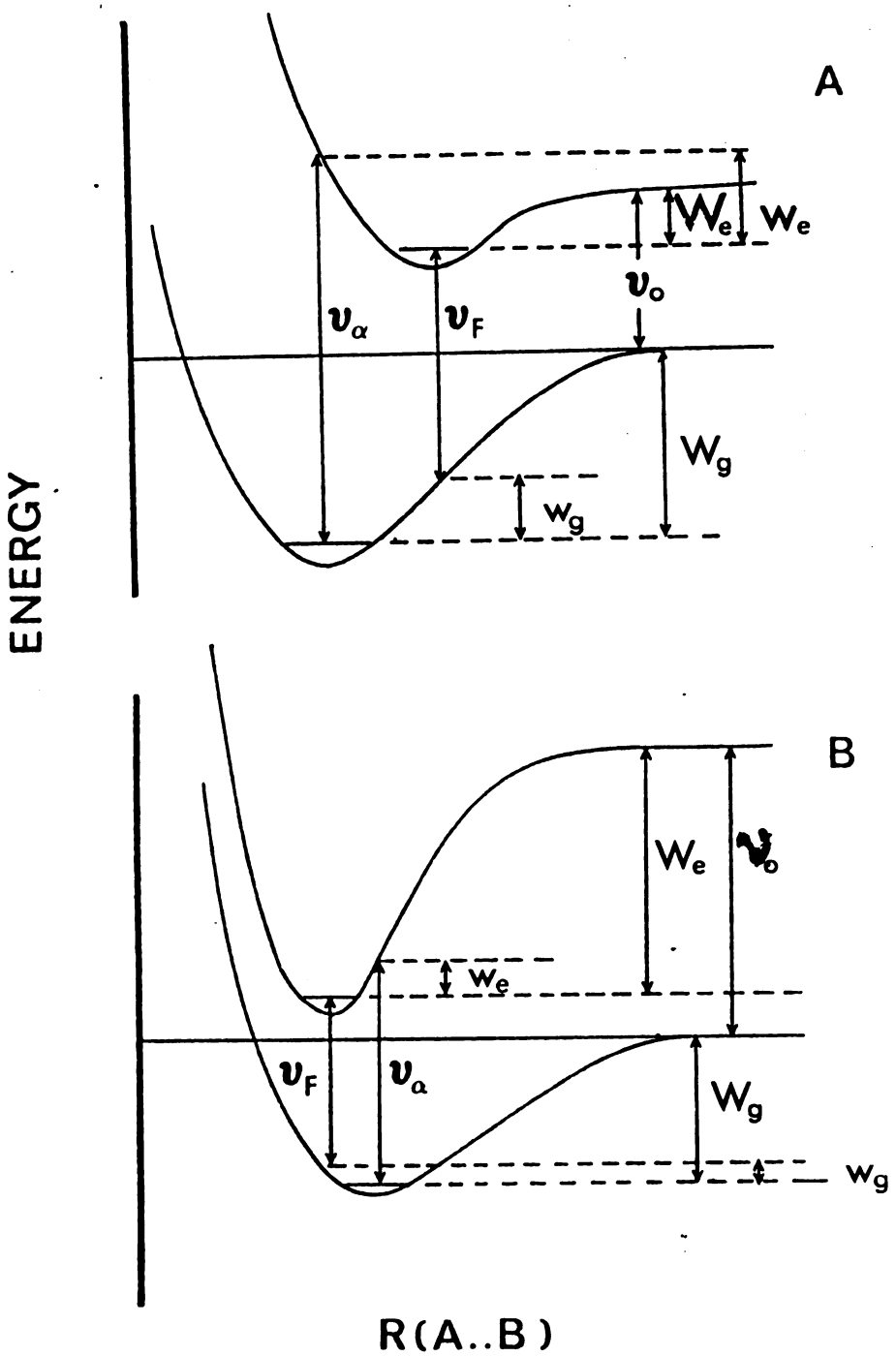


Figure 1. Solvent shifts due to hydrogen bonding. A) Hydrogen bonding is stronger in the ground state. B) Hydrogen bonding is stronger in the excited state.

W_g is the energy in the ground state which results from H-bonding interaction of the solvent with the solute,

W_e is the energy in the excited state which results from hydrogen bonding interaction of the solvent with solute upon excitation.

(w_e and w_g) are the energies implied by the Franck-Condon principle and always positive.

Since w_e and w_g are always positive, the shift in absorption and emission will depend on whether the value of W_g is greater or less than W_e, when

$W_g > W_e$, i.e., the hydrogen bond is stronger in the ground state than in the excited state as shown in Figure 1A. A blue shift in an absorption spectrum which exceeds w_e by a value of W_g-W_e will result. In emission, the shift is less than W_g-W_e by w_g, so that a blue or red shift may be observed depending on W_g-W_e and w_g. However, the shift is small compared to W_g.

If $W_e > W_g$, i.e., the hydrogen bond is stronger in the excited state than in the ground state as shown in Figure 1B, a red shift in the absorption spectrum which is less than W_g-W_e by w_e is expected. In emission, the red shift exceeds W_g-W_e by w_g.

Well characterized hydrogen bonds have energies in the range of 1-7 Kcal/mole (350-2500 cm^{-1}). According to

the above discussion, a blue shift in absorption may exceed the ground state hydrogen bonding energy, hence, the expected blue shift occurs in the range of 350-2500 cm^{-1} or larger than 2500 cm^{-1}. But a red shift in absorption should never exceed W_g, i.e., should not be larger than 2500 cm^{-1}. For $\pi^* \leftarrow n$ transition in hydrogen bonding media, a blue shift in absorption is usually observed.[6,7] This is due to the decrease in charge density on the lone pair atom as a result of lone pair promotion. Thus, the hydrogen bond is always stronger in the ground state.

A red shift in absorption spectrum indicates that hydrogen bonding is stronger in the excited state. This may indicate an increase in the acidity or basicity depending on the functional group at the chromophore involved in hydrogen bonding.

III. Theories of Solvent Spectral Shift:

The general theory which relates spectral shifts to various interactions between the solute and the solvent molecule is incomplete. These spectral shifts are attributed to (a) physical interactions between the solute and solvent molecules and (b) to some important specific effects like: hydrogen bond formation; proton or charge transfer between solvent and solute; and solvent-dependent aggregation; ionization or dissociation and isomerization equilibria.

Ooshika[8] presented a theory of solvent shifts for polar and non-polar solvents. McRae[9] published a similar theory and applied it to dye molecules[10]. He used the same model used by Onsager[11] in his theory of the dielectric constant of polar liquids. By Onsager's theory one calculates the polarization due to one molecule by representing it as a polarizable point dipole in a cavity electric field. All other molecules give rise to a homogeneous dielectric with a dielectric constant equal to the bulk liquid. McRae divided the polarization of the dielectric into two parts: one due to orientation and the other due to electronic polarization of the solvent molecules. The interaction between the polar solute and dielectric was calculated to second order in perturbation theory. Liptay[12] presented a theory of solvent sensitivity and discussed it qualitatively in terms of hydrogen bonding properties of the solvent. Kirkwood-Fröhlich theory[13-15] represents a modification of Onsager's theory that takes into account short-range order in the solvent.

Several other theories by Marcus[16], Abe[17] and Weigang and Wild[18] have also been presented.

The starting point of most theories of the general solvent spectral shift is the presumably known set of wave functions for the unperturbed electronic states of isolated solute and solvent molecules. Second-order perturbation theory was used to develop expressions for the

change of the stationary electronic energy levels and of energy differences or transition energies of a single solute molecule which arise from electric fields due to a particular (but unspecified) configuration of an individual solvent molecule. The resulting shifts were then averaged over all appropriate configurations of the solvent molecules of the solution.

According to the scheme derived by Nicol[19], the appropriate solute-solvent pair distribution function was expressed in terms of the wave functions $|K,i\rangle = |K\rangle|i\rangle$ for the K-th electronic state of an isolated solvent molecule and the unperturbed i-th electronic state of an isolated solute-chromophore. (Solvent index will always precede the solute index and the 0 designates the ground state of either molecule.)

The Hamiltonian $H = H_o + H'$ for this solvent-solute pair was defined in terms of H_o, the sum of the separate, unperturbed Hamiltonians for the isolated solvent and solute molecules, and H', the interaction operator. $|K\rangle$, $|i\rangle$ and H_o were presumed to be known from vapor phase spectra H' was defined in terms of an electric field $\vec{E}_m$ that the solvent medium produces at the site of the solute molecule. E_{Ki} was taken to be the sum of the unperturbed energies of the solvent molecule in state K and the solute in state i while ε_{Ki} represents the corresponding perturbed energy including terms to second order in the perturbation.

If one deals with one particular transition of the solute from state 0 to state 1 then E(00-01) is the unperturbed solute transition energy and equal to $E_{01} - E_{00}$ while ε(00-01) is the corresponding energy for the perturbed (solvated) solute and equal to $\varepsilon_{00} - \varepsilon_{01}$. The shift obtained for this particular configuration was:

$$\Delta\nu(cm^{-1}) = (hc)^{-1}[\Delta E(00\text{-}01)]$$

$$= (hc)^{-1}[\varepsilon(00\text{-}01) - E(00\text{-}01)] \qquad (3)$$

This has been averaged over the configurations of the solvent molecules to obtain expressions for the general solvent spectral shifts.

The perturbed energies of the solute chromophore-solvent pair were written in terms of quantities just defined:

$$\varepsilon_{00} = E_{00} + \langle 00|H'|00\rangle + \sum_{K\neq 0} \frac{|\langle 00|H'|K0\rangle|^2}{E_{00} - E_{K0}}$$

$$+ \sum_{i\neq 0} \frac{|\langle 00|H'|0i\rangle|^2}{E_{00} - E_{0i}} + \sum_{i,K\neq 0} \frac{|\langle 00|H'|Ki\rangle|^2}{E_{00} - E_{Ki}} \qquad (4)$$

$$\varepsilon_{01} = E_{01} + \langle 01|H'|01\rangle + \sum_{K\neq 0} \frac{|\langle 01|H'|K1\rangle|^2}{E_{01} - E_{K1}}$$

$$+ \sum_{i\neq 1} \frac{|\langle 01|H'|0i\rangle|^2}{E_{01} - E_{0i}} + \sum_{\substack{i\neq 1 \\ K\neq 0}} \frac{|\langle 01|H'|Ki\rangle|^2}{E_{01} - E_{Ki}} \qquad (5)$$

The first term of the right hand side of equations (4) and (5) is the zero-order unperturbed energy for the isolated chromophore. The second term in both equations is the first-order term and represent the interaction of the permanent dipole moments of solvent and solute molecules. This contributes to the shift only if both molecules are polar. The three remaining terms in both equations arise in second order and represent respectively:

(a) the third term is the interaction of the permanent dipole moment of the solute with the dipole moment induced in the solvent by the solute dipole. The contribution of this term is zero if the solute is non-polar.

(b) the fourth term is the interaction of the permanent dipole moment of the solvent with the dipole moment induced in the solute by the solvent dipole. This term vanishes for a non-polar solvent.

(c) the fifth term is the interaction of the mutually induced dipoles of the solute and solvent. This term is non-zero in all cases.

The average shift of the transition energy due to

solute-solvent interaction, was obtained by subtracting Equation (4) from Equation (5) and averaging the resulting expression over the appropriate two particle distribution functions for the separation and mutual orientation of a solvent molecule relative to the solute. This was represented[19] as follows:

$$\langle \Delta E(00\text{-}01) \rangle_{Av.} = \langle \varepsilon(00\text{-}01) \rangle_{Av.} - \langle E(00\text{-}01) \rangle_{Av.}$$

$$= [(\langle 01|H'|01\rangle)_{Av.} - (\langle 00|H'|00\rangle)_{Av.}]$$

$$+ \left[\sum_{K\neq 0} \left\{ \frac{(|\langle 01|H'|K1\rangle|^2)_{Av.}}{E_{01} - E_{K1}} - \frac{(|\langle 00|H'|K0\rangle|^2)_{Av}}{E_{00} - E_{K0}} \right\} \right]$$

$$+ \left[\sum_{i\neq 1} \frac{(|\langle 01|H'|0i\rangle|^2)_{Av}}{E_{01} - E_{0i}} - \sum_{i\neq 0} \frac{(|\langle 00|H'|0i\rangle|^2)_{Av}}{E_{00} - E_{0i}} \right]$$

$$+ \left[\sum_{\substack{K\neq 0 \\ i\neq 1}} \frac{(|\langle 01|H'|Ki\rangle|^2)_{Av}}{E_{01} - E_{Ki}} - \sum_{\substack{K\neq 0 \\ i\neq 0}} \frac{(|\langle 00|H'|Ki\rangle|^2)_{Av}}{E_{00} - E_{Ki}} \right] \quad (6)$$

The interaction operator was approximated as follows:

$$H' = -\vec{E}_m \cdot \vec{\mu}_{solute} \quad (7)$$

where $\vec{E}_m$ is an electric field that the solvent medium produces at the site of the solute molecule and $\vec{\mu}_{solute}$ is

the dipole moment operator on the solute coordinates. Wavefunctions for the system that are simple products of isolated molecule wavefunctions were introduced so that each matrix element of the perturbation in Equation (6) is expressed as a product of three terms:

$$\langle 0i|H'|Kj\rangle = \langle 0i|-\vec{E}_m \cdot \vec{\mu}_{solute}|Kj\rangle$$

$$= - \langle 0|E_m|K\rangle\langle i|\mu_{solute}|j\rangle\cos\theta \qquad (8)$$

where

$\langle 0|E_m|K\rangle$ represents the electric field at the site of the solute produced by the u_{0K} th permanent or transition dipole moment of the solvent molecules.

$\langle i|\mu_{solute}|j\rangle$ represents the appropriate permanent or transition dipole moment of the solute; and

$\cos\theta$ represents the effect of mutual orientation of the solvent and solute.

Each of the four terms in Equation (6) was decomposed and related to macroscopic properties: Only the final forms will be given without their mathematical details.

A. Interaction between permanent dipoles of the solute and the solvent is represented by the first term of Equation (6) and is written as

$$[\langle 01|H'|0|\rangle]_{Av} - [\langle 00|H'|00\rangle]_{Av} = D[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}] \quad (9)$$

where

$$D = -[(2d^{-3})(\mu^{o}_{solute})(\mu^{1}_{solute}\cos\beta - \mu^{o}_{solute})] \quad (10)$$

ε, n, represent the dielectric constant and the refractive index of the solution, respectively. μ^{1}_{solute}, μ^{o}_{solute} are the magnitudes of the permanent dipole moment of the excited and ground states, respectively, and β is the angle between them. d is the radius of a solute molecule obtained by approximating it as a spherical particle.

B. Interaction between the permanent solute dipole and induced solvent dipole is represented by the second term of Equation (6) and thus can be written as

$$\sum_{K\neq 0} \{\frac{(|\langle 01|H'|K1\rangle|^2)_{Av}}{E_{01} - E_{K1}} - \frac{(|\langle 00|H'|K0\rangle|^2)_{Av}}{E_{00} - E_{K0}}\} = C[\frac{n^2-1}{2n^2+1}] \quad (11)$$

where

$$C = -[d^{-3}(\mu^{1}_{solute})^2 - (\mu^{o}_{solute})^2] \quad (12)$$

C. Interaction between induced solute dipole and permanent solvent dipole is represented by the third term of Equation (6) and has the following final form:

$$\sum_{i\neq 1} \frac{(|\langle 01|H'|0i\rangle|^2)_{Av}}{E_{01} - E_{0i}} - \sum_{i\neq 0} \frac{(|\langle 00|H'|0i\rangle|^2)_{Av}}{E_{00} - E_{0i}} = B^1 \left[\frac{(\varepsilon - n^2)}{\varepsilon} \frac{(2\varepsilon + n^2)}{(n+2)^2}\right] \qquad (13)$$

where

$$B^1 = -\left[\frac{108\ \ell n^2 (R/d)}{R^3} kT\ (\alpha^1_{solute} - \alpha^0_{solute})\right] \qquad (14)$$

here α^0_{solute} and α^1_{solute} represent the polarizabilities of the initial (ground) and final (excited) states of the solute respectively. R represents the radius of the solvent shell taken from the center of the solute. k, T are the Boltzmann constant and temperature in Kelvin scale.

D. Interaction between mutually induced dipoles of solute and solvent is represented by the fourth term of Equation (6) has the following final form:

$$\left[\sum_{\substack{K\neq 0 \\ i\neq 1}} \frac{(|\langle 01|H'|Ki\rangle|^2)_{Av}}{E_{01} - E_{Ki}}\right] - \left[\sum_{\substack{K\neq 0 \\ i\neq 0}} \frac{(|00|H'|Ki\rangle|^2)Av}{E_{00} - E_{Ki}}\right] = A\left[\frac{n^2-1}{2n^2+1}\right] \qquad (15)$$

where

$$A = -\left[\frac{1}{d^3}\right]\left[\left(\sum_{i\neq 1} A_{1i}(\mu^{1i}_{solute})^2\right)-\left(\sum_{i\neq 0} A_{0i}(\mu^{0i}_{solute})^2\right)\right] \quad (16)$$

where A_{1i} and A_{0i} are weighting factors[9] depending upon the transition frequencies of both the solute and solvent.

The final form of Equation (6) would be then:

$$\langle \Delta E(00\text{-}01)\rangle_{Av} = (A + C)\left[\frac{n^2-1}{2n^2+1}\right] + B^1\left[\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n+2)^2}\right] + D\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \quad (17)$$

The parameters A, B^1, C and D may be viewed either as phenomenological constants to be evaluated from experimental results or as parameters to be calculated from Equations (16, 13, 12 and 10) respectively. Equation (17) is still approximate and similar to Equation (18) found by other authors.[9,20,21]

$$\Delta\nu = \text{dispersion term} + B\left(\frac{n^2-1}{2n^2+1}\right) + C\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) + \text{Stark effect term} \quad (18)$$

Either equation is still approximate and describes only shifts resulting from interactions between the solute and solvent molecules. They do not take care of any specific interactions like, hydrogen-bonding, proton-transfer, etc.

The ability of different terms in Equation (18) to explain solvent shifts in different types of solvent system has been examined for both π-π^* and n-π^* transitions of organic molecules, including dyes.[2,20,21] n-π^* transition energies of C=O and C=S groups in different solvents are found to vary linearly with the stretching frequencies in the same solvents, indicating the importance of ground-state stabilization by solvents.[20,21]

The London dispersion term in Equation (18) (causing red shifts with respect to the gas phase) also involves the function $(n^2-1)/(2n^2+1)$. A plot of spectral shifts of non-polar solutes like aromatic hydrocarbons against $(n^2-1)/(2n^2+1)$ is found to be linear. The linearity is strictly expected for non-polar solvents (aliphatic hydrocarbons and so on). It is not surprising, therefore, that different linear plots are found for different families of solvents, particularly when some of them, like ketones, are quite polar.[18,19] It is noteworthy that solvent shifts of polar solutes in non-polar solvents are also accounted for by the $(n^2-1)/(2n^2+1)$ term, although the observed solvent shift would be due to the combined effect of the first

two terms in Equation (18). One could, in principle, rationalize spectral shift data in different types of solvent by incorporating a dielectric constant or Stark effect term. This has been done by Nicol[19] who derived Equation (17) and found a linear plot of shifts in the absorption maxima of aromatic hydrocarbons in a variety of solvents. This equation also shows that the dispersion effect on the refractive index terms of the solvent alone cannot account for spectral shifts in polar solvents.

Equation (18) can be simplified to study the effect of the dielectric constant term (third term) alone by measuring band shifts in two polar solvents of nearly the same refractive index but different dielectric constant.[20,21] From such a study, one can obtain estimates of the excited-state dipole moments of solute molecules. Diethyl ether ($n = 1.356$ and $\varepsilon = 4.3$) and acetonitrile ($n = 1.344$ and $\varepsilon = 37.5$) seem to make a good pair of such solvents. Basu[22] has given a detailed quantum mechanical treatment of frequency shifts in solutions by considering Onsager's reaction field model. Basu evaluated the stabilization energy of electronic states due to solute-solvent interaction in terms of 2^{nd} order perturbation theory.

Finally, I would like to mention that Kosower[23] has given a solvent polarity scale based on the effects of solvents on the intramolecular Charge-Transfer band of pyridinium iodide. This scale is defined in terms of Z

values of solvents given by the energies in Kcal/mole of the absorption maxima of 4-methoxycarbonyl-1-ethylpyridinium iodide. The solvents listed in this scale vary from non-polar to highly polar and hydrogen bonding solvents. The change in charge-transfer absorption spectra are so large and their measurement so readily made the Z values have been preferred by physical organic chemists over the Y values[24] obtained from solvolysis kinetics of t-butyl-chloride. Charge transfer to solvent spectra of I^- and other systems have been correlated with Z values.[25,26] While such empirical parameters may be useful for correlations, they do not provide the exact mechanism of solvent effects, considering the wide variation in the nature of solvents included in obtaining the scale.

IV. Solvent Shifts as an Aid in Characterizing Electronic States

Measurement of the effect of different solvents on absorption bands is one convenient way of characterizing the electronic states involved. As an example, solvent effect on different types of electronic absorption transitions can be classified as follow:

1. $n \rightarrow \pi^*$ vs $\pi \rightarrow \pi^*$ Transitions

In an $n \rightarrow \pi^*$ transition in a carbonyl group the oxygen atom has less electron density in the excited state, and

the carbonyl group, as well as the molecule as a whole, becomes less polar. In a hydroxylic solvent such as ethanol, hydrogen bonding between the carbonyl group and the solvent is stronger in the ground state than in the excited state.[7] The net result is that n-π^* absorption bands are blue-shifted in hydroxylic solvents relative to non-polar, hydrocarbon solvents. A typical shift may be on the order of 400-800 cm^{-1}.

A more extreme case occurs when a molecule with a non-bonding orbital is dissolved in acid solution. Under these conditions, the atom with the n electrons is protonated, and the energy difference between the ground and excited states becomes much greater than in alcoholic solutions; the solvent shift to shorter wavelengths may be so large that the n-π^* transition appears to vanish completely.

Transitions in ketones that are classified as π-π^* generally show a slight increase in polarizability in the excited state; the result is a small red shift (usually less than 600 cm^{-1}) of a π-π^* transition in a polar solvent relative to a nonpolar solvent.[27] Transitions in aromatic hydrocarbons which contain no heteroatoms are considerably less affected by polar solvents.[28] Intramolecular charge transfer states in aromatic ketones, by contrast, become much more polar relative to the ground state. Red shifts of 2000 cm^{-1} or more in polar solvents are common,[27] for intramolecular charge transfer bands in aromatic ketones.

The general rule for solvent shifts is that if the excited state is more polarizable than the ground state or has an increased permanent dipole, the spectrum is red-shifted in the more polar solvent; if the reverse applies, the spectrum is blue-shifted.

Kuboyama[29] applied the criteria of solvent shifts in assigning the lowest-energy, singlet-singlet transition in fluorenone, which had long been considered to be an $n \rightarrow \pi^*$ transition, as a $\pi \rightarrow \pi^*$ transition. His results were later substantiated by Yoshihara and Kearns.[30]

2. Locally-Excited States vs Charge-Transfer States

One may classify the electronic states of substituted molecules as being locally excited (L.E.) or charge-transfer (C.T.) states in the zeroth order approximations. A charge-transfer (C.T.) state involves the transfer of an electron between the hydrocarbon and the substituent. Comparing the spectra of a substituted benzene molecule taken in hydrocarbon solvents with those taken in polar solvents will offer a means to identify "C.T." bands. For substituted benzenes, especially those containing a strong donor and a strong acceptor substituent, the dipole moment increases in the same direction in the CT state and thus a red shift is observed whose magnitude depends greatly on the polarity of the solvent and the change in dipole moment during excitation. One should also mention that

the CT bands of chloro, bromo and iodobenzenes are expected to shift to the blue since their dipole moments decrease or may change direction as a result of excitation to CT states.[31,32] Relatively large red shifts are usually characteristic of intramolecular C.T. transitions of substituted benzenes.

Room temperature absorption spectra of p-amino-nitroaniline in methylcyclohexane MCH, acetonitrile CH_3CN and ethylalcohol EtOH are shown in Figure (2).[33] It is clear that the first absorption band is more sensitive than the 2^{nd} band, the first band (CT band) undergoes a red shift of $\sim$4000 cm^{-1} in going from hydrocarbon solvent to ethanol.

As a result of charge-transfer migration from the amino to the nitro group, the dipole moment of p-aminoaniline is expected to increase in the CT state but remain in the same direction as that of the ground state. Larger solvation energies are therefore expected in the CT state compared to the ground state due to the increase in the dipole moment. Also larger hydrogen-bond energies are expected due to the increase of the acidity of the amino group hydrogen atoms and the increase of the nitro group basicity. This explains the red shift observed in polar solvents, particularly hydrogen bonding solvents.

The spectrum of p-nitroaniline in alcohol (Figure 2) shows a shoulder at $\sim$294 and 305 nm corresponding to the $^1B_{2u}$ Locally Excited (LE) benzene transition. Its frequency is

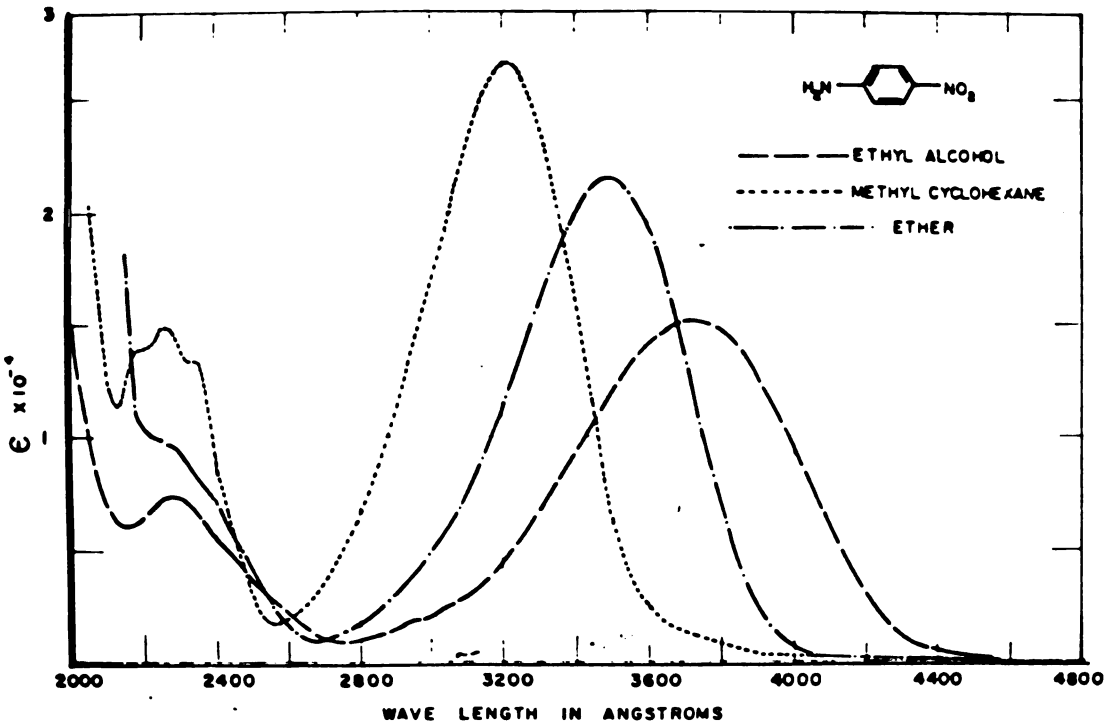


Figure 2. Room temperature absorption spectra of p-nitroaniline in different solvents.[33]

not much affected by change of solvents.

3. Electron-Transfer Transitions

Halogen anions, I^-, Br^- and Cl^- show strong absorption bands in the ultraviolet region.[34a] Their spectra are shown in Figure (3a),[34b] where one can see that the I^- and Br^- exhibit two absorption bands. The spectra of halogen anions were ascribed to electron transfer absorption,[35,36] where an electron was transferred from the halide anion to the solvent.

Strickler and Kasha[37] studied the spectra of halogen anions in acetonitrile, water and ethanol. The spectra of iodine in these solvents are shown in Figure (3b).[37] They[38] have studied the electronic transitions in NO_3^- and NO_2^- ions in solvents of different polarities and differentiated between electron transfer and other internal transitions ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ . . ., etc) in these ions.

Kosower and co-workers[39,40] studied the electronic spectra of N-alkyl-pyridinium iodide in various solvents and found that the spectra are very sensitive to solvent polarity and a large blue shift occurs with increasing solvent polarity. Each absorption band was assigned to the charge transfer band in which an electron is promoted from the iodide ion to the pyridinium ring and therefore the CT state is characterized by a small dipole moment which lies in the plane of the ring.

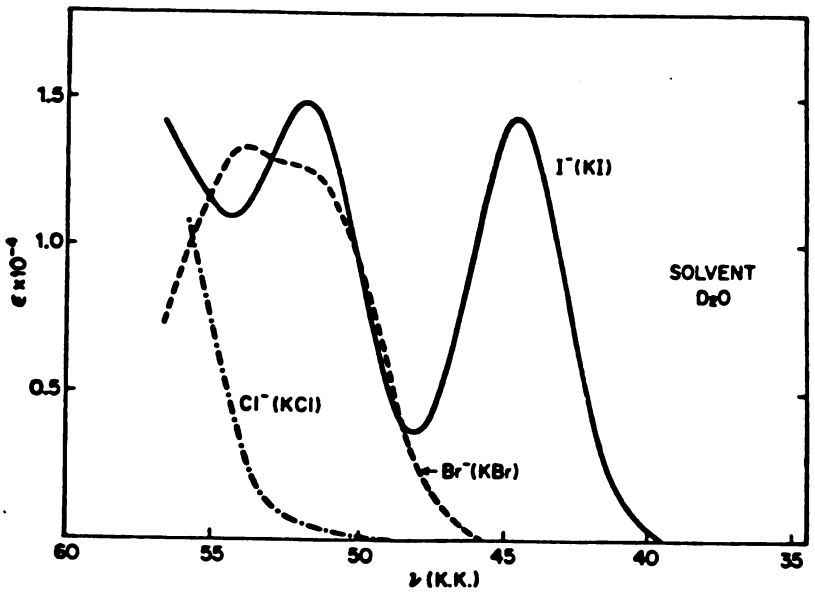


Figure 3a. Room temperature absorption spectra of halogen ions in aqueous solution (D_2O).[34b]

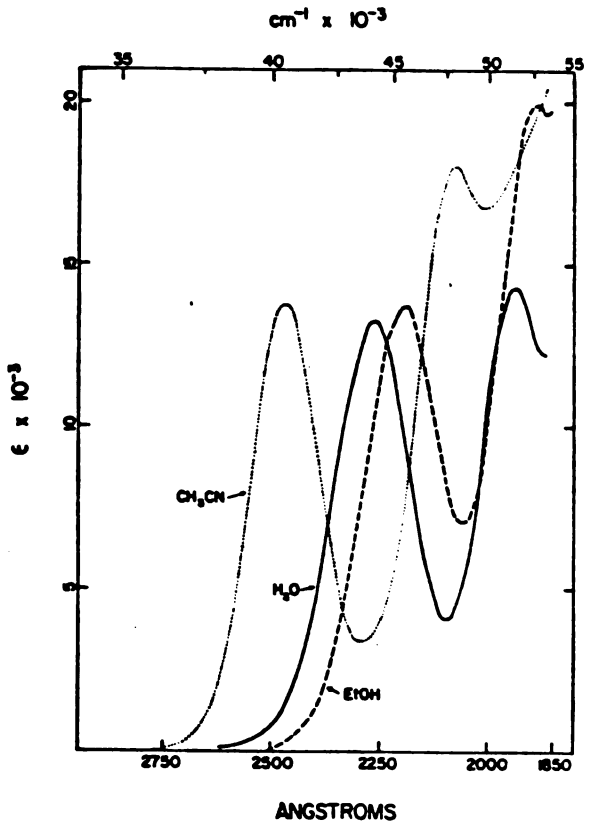
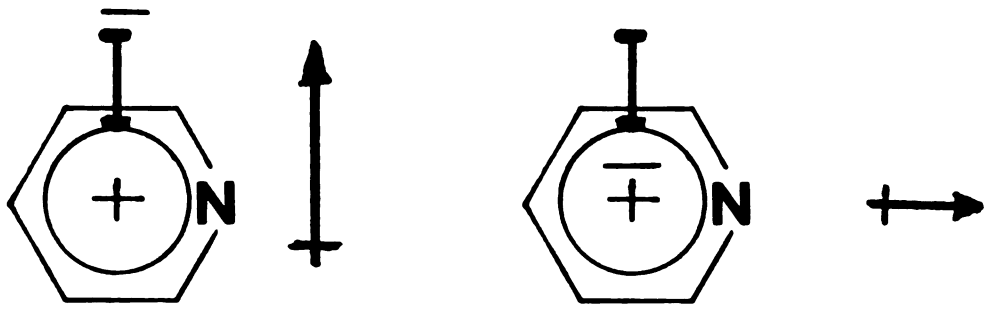


Figure 3b. Room temperature absorption spectra of sodium iodide in acetonitrile, water and ethanol.[37]



μ = 13.1D μ = 8.6D

This is a case where the solvation energy of the ground state is larger than that of the excited state. Moreover, the dipole moment changes its direction as a result of excitation and therefore a large Franck-Condon orientation strain is expected. Both effects contribute to the large observed blue shift in more polar media.

4. Singlet-Triplet Transition

The probability of $T_1 \leftarrow S_0$ transition in organic compounds is a highly sensitive function of the presence of heavy atoms which enhance spin-orbit interactions and increases the intensity of the transition. The spin-orbit interaction is treated quantum mechanically by introducing into the Hamiltonian operator, a term H_{SO} for each electron of the form

$$H_{SO} = \kappa \xi (\hat{\vec{L}} \cdot \hat{\vec{S}}) \qquad (19)$$

where $\hat{\vec{L}}$ is the orbital angular momentum operator, $\hat{\vec{S}}$ is the spin angular momentum operator and ξ is a factor depending on the nuclear field. ξ and therefore H_{SO} is proportional to Z/r^3, i.e., to Z^4 because of the reciprocal relation between Z and r. (Z is the nuclear charge and r is the distance between the electron and the nucleus. Perturbation theory shows that if ψ_S° and ψ_T° are the wavefunctions of "pure" singlet and triplet states, respectively, then the triplet state produced under spin-orbit coupling can be written[41] in the form of the following equation

$$\psi_T = \psi_T^\circ + \sum_K \frac{\langle \psi_{SK}^\circ | H_{SO} | \psi_T^\circ \rangle}{E_T - E_{SK}} \cdot \psi_{SK}^\circ \qquad (20)$$

A similar expression can be written for the singlet state. Thus the effect of spin-orbit coupling is to mix a small amount of singlet character into the triplet states and vice-versa, so that "pure" singlet and triplet states no longer exist. The probability of $S \rightarrow T$ transition increases rapidly with the atomic number and thus solvents with a heavy atom such as iodine will enhance singlet-triplet absorption bands; this will help in their identification.

V. Solvent Effect on Emission Spectra

1. Spectral Shifts

A solute molecule in its ground state is surrounded by solvent molecules in equilibrium in solution. The geometry, charge density and dipole moment of the solute molecule may be different in the excited state; therefore, the equilibrium excited-state configuration of the solvent cage will also be different. The solvent configuration around the excited solute molecule immediately after the electronic transition does not correspond to the equilibrium-excited configuration, but to a configuration geometrically identical to the solvated ground state, i.e., a Franck-Condon state configuration. The relaxation of this configuration occurs to the excited state equilibrium configuration. The time required for solvent reorientation is around 10^{-11} sec in fluid media. Since the life time of an excited singlet state is of the order of 10^{-8} sec, there is enough time for excited state equilibrium to be reached before deactivation occurs if the solvent is not viscous. Also the ground state configuration after fluorescence is not the equilibrium ground state configuration but a state of strain whose energy is higher than that of the ground state equilibrium configuration.

If the dipole moment of the solute changes (in magnitude

and/or direction) upon excitation and the solvent is polar, reorientation of solvent molecules occurs before emission. However, if the solvent is rigid, relaxation times are several order of magnitude larger than the excited state life time, and emission occurs before solvent rearrangement takes place. If however, the polar solvent is fluid, relaxation is much more rapid and emission may occur from the equilibrium excited state where dipole reorientation is completed. Therefore, absorption will occur to the metastable Franck-Condon state ($\bar{\nu}_\alpha$ = absorption frequency in wave numbers cm^{-1}) and emission will occur from the equilibrium state ($\bar{\nu}_\alpha$ = fluorescence emission frequency in wave numbers cm^{-1}). The quantitative expression for $\Delta\bar{\nu}$ in absorption is different from that in emission and the 0-0 band will not coincide. The difference (Stokes' shift) is

$$\Delta_{a-f}\bar{\nu} = \bar{\nu}_\alpha - \bar{\nu}_f$$

$$= \frac{2}{a^3hc}(\mu_e-\mu_g)^2\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] + \frac{2}{a^6hc}$$

$$\left[(\alpha_e-\alpha_g)(3\mu_g^2 - 5\mu_e^2 + 2\mu_g\mu_e)\right]\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] \qquad (21)$$

where a is an effective cavity radius appropriate for the solvent, μ_g, μ_e, D, n, α_e and α_g have their usual meanings.

The second term originates from the dipole-induced

dipole interaction, in many cases can be considered as a second order interaction term and makes a negligible contribution to the shift and the equation is simplified as follows:

$$\Delta_a \bar{\nu}_f = \bar{\nu}_a - \bar{\nu}_f = \frac{2}{a^3 hc} (\mu_e - \mu_g)^2 \left[\frac{(D-1)}{(D+2)} - \frac{(n^2-1)}{(n^2+2)}\right] \qquad (22)$$

The dipole moment difference in ground and excited state can be obtained directly from the Stokes' shift. An estimate of the excited state dipole moment can be made from experimental absorption and emission shift data and the known ground state dipole moment using Equation (22).

In highly viscous solutions this solvent relaxation is slow and fluorescence occurs, but from a non-equilibrium, Franck-Condon state. Since the Franck-Condon state is always higher in energy than the equilibrium excited state, fluorescence in highly viscous solutions is blue shifted with respect to that in solutions of low viscosity. Another consequence of increasing the viscosity of the solution is the increase in the intensity of emission. In fluid media radiationless transitions are very fast in these relaxing systems.[42]

One method of increasing viscosity is to use solvents which form rigid glasses at liquid nitrogen temperature;

a blue shift of the low-temperature fluorescence spectra compared with those at room temperature in the same solvent occurs.

2. Viscous-flow Barriers[43]

Molecules in condensed media always are surrounded by a solvent cage. The cage may be a liquid solvent, a macromolecular enclosure (enzyme site), a lipid membrane, a multi-layer lamellar system, or may be a crystal or surface-adsorption cage. Although photochemical and other kinetic studies have long taken cognizance of the effect of solvent cages on recombination rates, spectroscopic studies of the mechanism of solvent cage action have been neglected in comparison.

The mechanical Viscous- Flow Barrier solvent cage has been analyzed on a quantum-mechanical basis by Dellinger and Kasha.[44,45] Figure (4) indicates schematically the basis of their model. If a molecule upon excitation requires a rather large distortional motion for relaxation, then a large volume of solvent in the cage around the solute must be displaced. For example, in trans-stilbene the torsional relaxation about the double-bond requires that the phenyl groups sweep out a large volume of solvent to reach an equilibrium excited state configuration[45] (upper part, Figure 4). On the other hand,

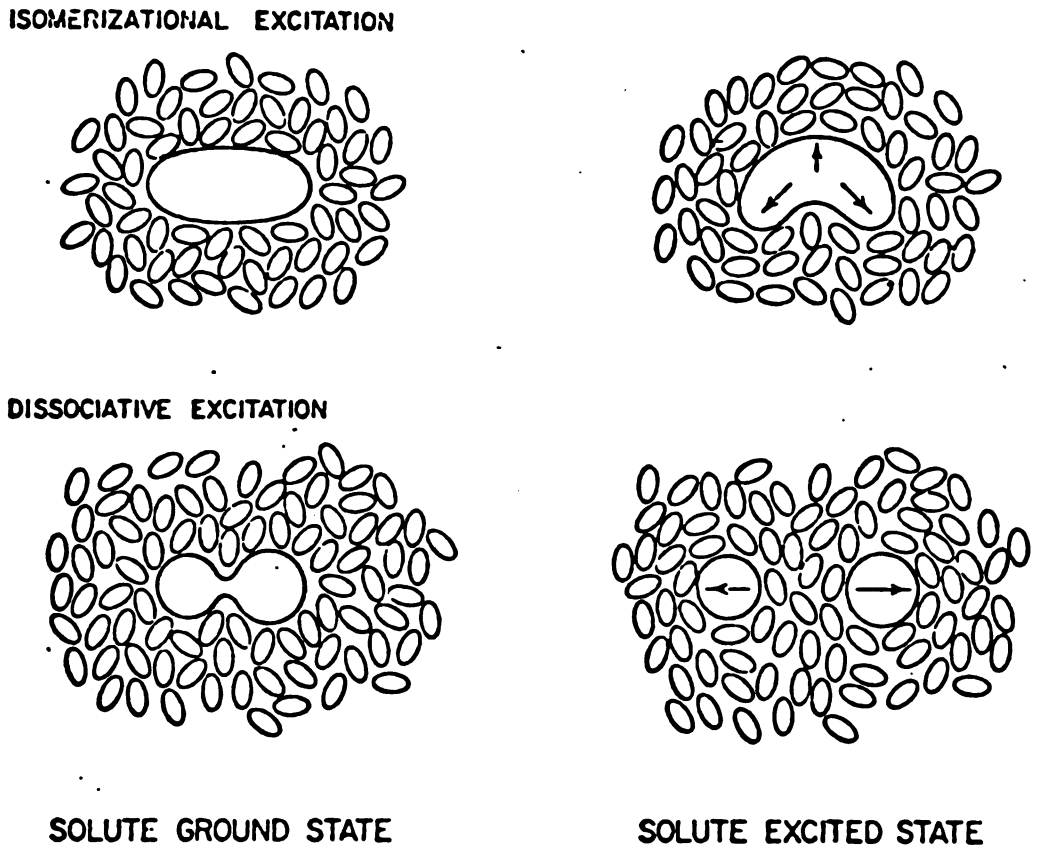
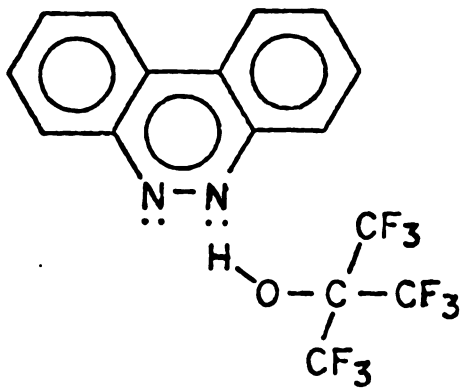


Figure 4. Mechanical viscous-flow-barrier cage proposed by Dellinger and Kasha.[43]

a hydrogen-bonded molecular pair, such as 9,10-diazaphenanthrene complex with t-perfluorobutyl alcohol:



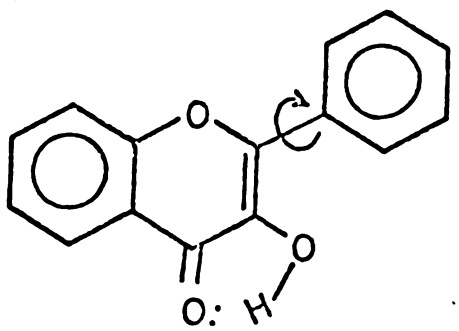
would require displacing a large volume of solvent molecules in the photo-dissociative excitation of this molecular complex.[45]

According to the Dellinger-Kasha model, the solvent cage imposes a barrier to the molecular motion, which appears as a Gaussian-flow barrier added to the potential function where the latter become horizontal, i.e., in the dissociative case, at the dissociative limit. The phenomenological reality of these viscous-flow barriers has been tested by low-temperature spectroscopic studies. Thus, luminescence phenomena reveal that the molecule is trapped in a ground state configuration in rigid glass solvents.

Recently, Mohammadi and Henry[46] have verified the viscous-flow barrier to molecular motion by an entirely

different route. They studied the infrared overtone anharmonicity of C-H vibrations in methylbutanes, and were able to show that the decrease in anharmonicity predicted by the Dellinger-Kasha model was experimentally verified and could be calculated by the Lennard-Jones potential as a quantitative perturbation of Morse potential.[46]

An interesting case of excited state proton transfer spectroscopy was discovered recently in flavones by Sengupta and Kasha.[47] In 3-hydroxy flavone



it was discovered that in hydrocarbon solution at room temperature a green fluorescence was observed, unrelated to the ultraviolet absorption of the molecule. It was deduced that an intramolecular proton-transfer had occurred within the internal H-bond to the carbonyl group, and that a pyrilium-like excited state tautomer yielded the green emission. Upon freezing in a rigid glass solvent, the normal violet-ultraviolet fluorescence could be inhibited by the solvent cage,[47] so that the viscous-flow barrier prevented tautomerization.

3. Solute-Solvent Relaxation in the Nano and Picosecond Range

Molecular relaxation occurring in the "molecule-solvate shell" system after optical excitation is governed by the correlation between radiation lifetime τ_f and environment relaxation time τ_R. The main cases possible here are as follows:[2]

1) $\tau_f >> \tau_R$ - all molecular relaxations are completed within the time τ_f, i.e., the molecule at the moment of deexcitation is in thermodynamic equilibrium with all modes of the "molecule-solvate shell" system;
2) $\tau_f \sim \tau_R$ - molecular relaxations are realized only in part with the result that at the moment of emission the system is not in thermodynamic equilibrium;
3) $\tau_f << \tau_R$ - the case of extreme nonequilibrium, for the relaxations (orientational and translational in particular) do not proceed at all.

Picosecond and nanosecond time resolved spectra are used to measure these relaxation processes.

For a solute that undergoes a large change in dipole moment upon excitation, the study of time dependent spectral shifts will reveal information regarding solvent relaxation. Time dependent emission spectra taken at different delay

times after the excitation pulse are measured.

An example of a time-dependent spectral shift given by the polar molecule ANS (1-Anilino-8-naphthalene sulfonate) in a polar solvent, n-propylalcohol, is shown in Figure (5).[48] Figure (5a) shows the steady-state fluorescence spectra of ANS at room temperature, intermediate temperature and liquid nitrogen temperature. A blue shift of 41 nm is observed. Large time-dependent spectral shifts were observed only in the temperature range from -70° to -170°C in n-propyl alcohol. At higher or lower temperatures the emission spectra are essentially time independent over a time range of 70 nsec. (the lifetime of ANS of approximately 20 nsec places a limit on the length of time available for time-resolved spectral measurements). Figures (5b) and (5c) show the time-resolved spectra in n-propyl alcohol at -90° and -150°C. The indicated delay-time for each spectrum is given relative to the initial rise of the nanosecond flash lamp. It is observed from the figures that the time required to approach the relaxed spectrum (corresponding to the spectrum at room temperature) increases with a decrease in temperature or an increase in viscosity of the solvent.

Ware[48-50] interpreted the phenomenon of time-dependent spectral shift as being due to solvent reorientation about the excited molecule that is required to accommodate the change in dipole moment and moment direction that occurs

Figure 5. (a) Steady-state fluorescence spectra for ANS in n-propyl alcohol at the indicated temperatures.

(b) Time-dependent fluorescence spectra for ANS in n-propyl alcohol at -90°C. A, 0 nsec; B, 2.5 nsec; C, 12.5 nsec; D, 21.5 nsec; E, 31.5 nsec.

(c) Time-dependent fluorescence spectra for ANS in n-propyl alcohol at -150°C. A, 2 nsec; B, 11 nsec; C, 68 nsec.[48]

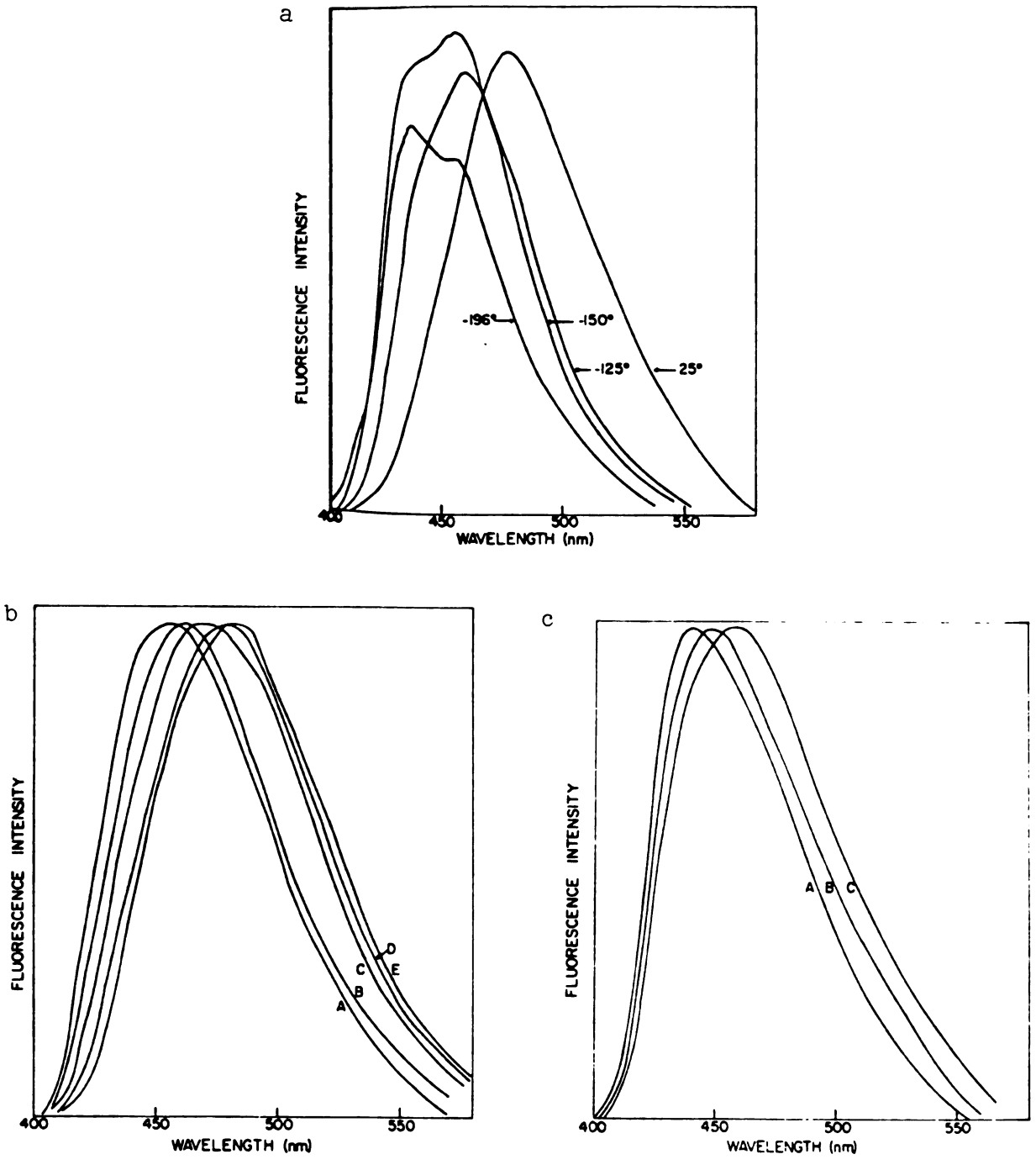

a
FLUORESCENCE INTENSITY
-196°
-150°
-125°
25°
400
450
500
550
WAVELENGTH (nm)
b
FLUORESCENCE INTENSITY
A
B
C
D
E
400
450
500
550
WAVELENGTH (nm)
c
FLUORESCENCE INTENSITY
A
B
C
400
450
500
550
WAVELENGTH (nm)

Figure 5

upon excitation. The extent to which time-dependent spectral shifts are observed is a measure of the degree of relaxation of the excited molecule towards its equilibrium configuration at a given temperature.

Azumi[51] related the time-dependent spectral shift to the edge excitation red shift and interpreted the two phenomena as being due to the same mechanism, which was given by Ware. Naturally the Azumi model based on the above mechanism cannot explain the lack of time-dependent spectral shift and the appearance of REE at 77 K. We believe that the two phenomena have different mechanisms. The time-dependent spectral shift represents spectra corresponding to different stages of relaxation of the bulk continuum at a particular temperature, while the red edge effect represents the spectra corresponding to different solvation sites (different local environments) when excited monochromatically at the red edge of the bulk continuum.

The picosecond light pulse method was used to measure the molecular orientational relaxation times, and time dependence of solute rotation. The principle idea of this laser technique is to induce an anisotropy in the orientational distribution of the solute molecule with a picosecond excitation polarized pulse, and to monitor the return of the system to isotropic distribution with an attenuated picosecond pulse.[52] Due to the induced anisotropy, the absorption of the probe pulse is polarization dependent.

The decay of this dichroism with time, due to thermal molecular motions is determined by measuring the relative transmitted intensities $I_{||}/I_{\perp}$ of the probe light; $I_{||}(t)$ and $I_{\perp}(t)$ are the components, respectively, of the probe light polarized parallel and perpendicular to the excitation light at the time t after the excitation pulse. For rotational motion describable by the rotational diffusion equation, Eisenthal et al.[52] obtained a relation

$$\ell n \frac{I_{||}}{I_{\perp}} \approx \exp[-(6D + 1/\tau)t] \qquad (23)$$

where D is the rotational diffusion constant and τ is the excited state lifetime. The orientational relaxation time is given by $(6D)^{-1}$.

Eisenthal et al.[52] reported the orientational relaxation of rhodamine 6G in a series of normal alcohols, ethyleneglycol, chloroform and formamide together with the effect of hydrogen bonding and the structure of liquids on the molecular rotational motion using picosecond light pulses.

It was found that even though methanol forms a stronger hydrogen bond with rhodamine 6G than chloroform, the relaxation times are found to be equal. The insensitivity of the orientational relaxation of rhodamine 6G to its formation of hydrogen bonded complexes with the molecules of the solvents was explained in terms of the orientational freedom of the hydrogen bond and the fact that the complex

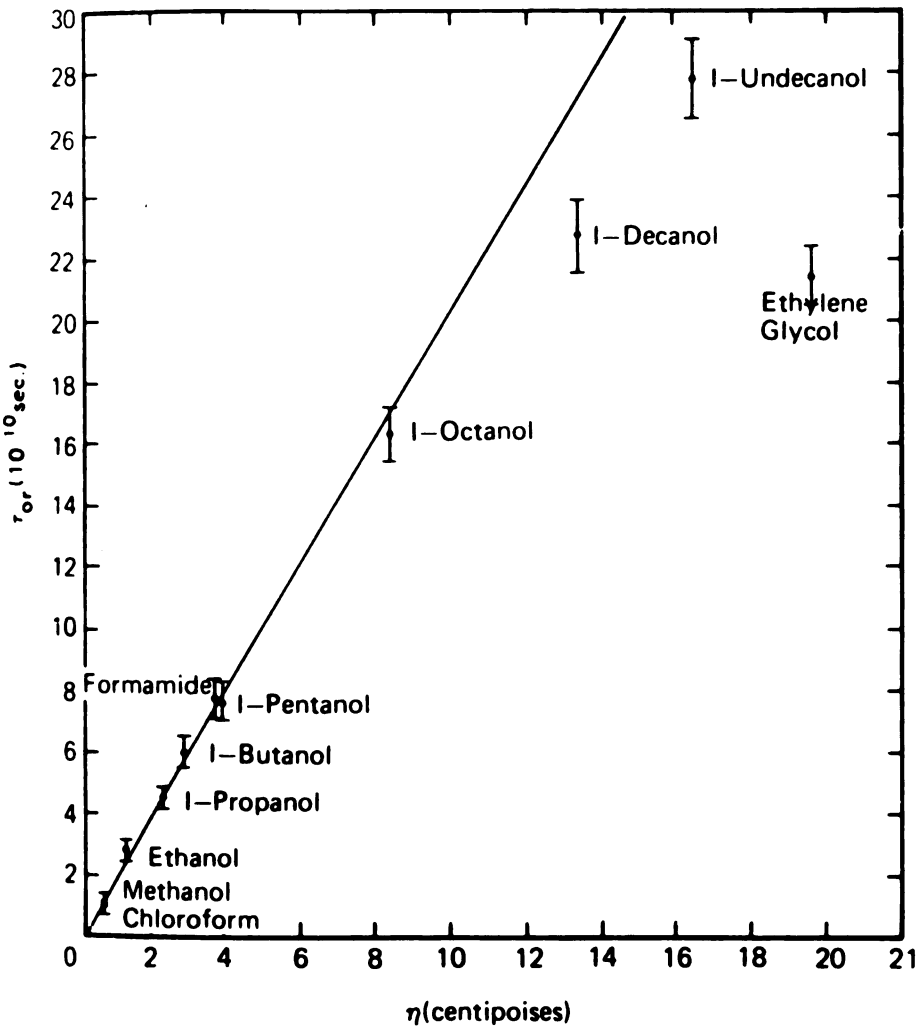


Figure 6. τ_{or} versus solution viscosity for rhodamine 6G in various solvents.[52]

is dynamic in that the solute-solvent hydrogen bonds are breaking and reforming. The same results was found by Levshin et al.,[53,54] for the same solute in formamide and pentanol solvents.

Those observations are clear in Figure (6)[52] and show that the relaxation times of rhodamine 6G in the liquids through octanol vary linearly with the solution viscosity. The departure from linearity in case of decanol and undecanol has been interpreted in terms of greater linear dimension of solvent relative to solute. The deviation of rhodamine 6G in ethyleneglycol may be due to extensive solvent-solvent aggregation by hydrogen bonding interactions.

4. Excited State Level Inversion

If two different excited energy states S_1 and S_2 which have quite different electronic structure lie in close proximity, there is a possibility that the solvent effect will bring about the inversion of two different energy states because the solvent effect on these two excited states may be considerably different. When this kind of inversion occurs in some solvents, a considerable change of fluorescence spectra, intensity, polarization and lifetime is invariably observed, though absorption spectra will remain almost unchanged. The dual fluorescence character of p-cyano-N,N-dimethylaniline (DMAB) in different solvents first pointed out by Lippert

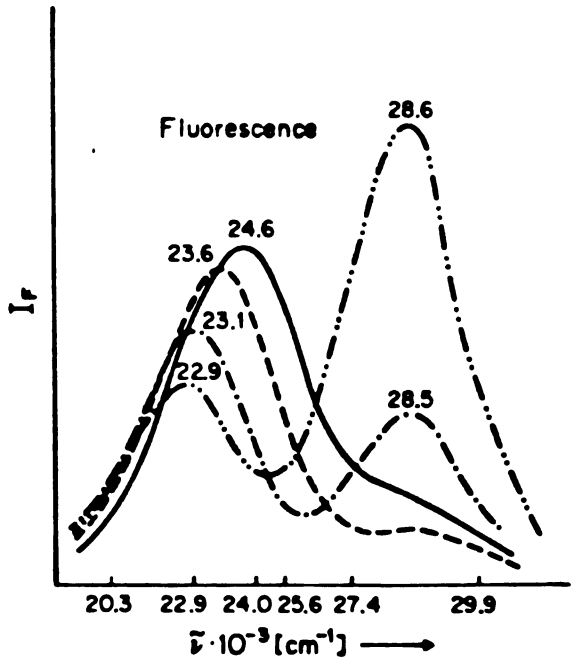
et al.[55,56] is shown in Figure (7a).[55] Such dual fluorescence caused by environmental perturbations has been observed also in indole,[57-60] 1-naphthylamine[61] and 1-naphthol.[62] Suzuki et al.[63] have observed fluorescent level inversion of dual fluorescence in alcoholic solutions of 1-naphthol by a change in temperature only.

These results can be interpreted in the following way. These molecules have two electronic states ^1L_b and ^1L_a in the region of their lowest absorption band. The ^1L_a state lies above ^1L_b in free molecules, but these states do lie close to each other. In fluid solutions at room temperature, the solvent molecules around the excited solute molecule will generally have time to reorient themselves before light emission occurs and hence they relax to their preferred equilibrium configuration which is of lower energy. In non polar solvents, the ^1L_a states of these molecules still lie above ^1L_b even in the preferred equilibrium configuration and hence fluorescence occurs from the ^1L_b state. In polar solvents, the interaction between dipole moments of such excited molecules and solvent molecules lowers the energy of the ^1L_a state below that of ^1L_b in their equilibrium configuration and hence fluorescence occurs from the ^1L_a state. The above sequence is shown in Figure (7b).[64] At sufficiently low temperatures and high viscosities the relaxation processes which lead to an equilibrium configuration will not occur to any appreciable

Figure 7. (a) Effect of temperature on the fluorescence spectra of 5×10^{-5} M DEAB (p-diethylaminobenzonitrile) in butylchloride-methylcyclohexane-isopentane mixture (12:3:1 in volume). ———293°K, ------ 234°K, -·-·- 173°K, -··-··- 148°K.[55]

(b) Excited state level inversion caused by mutual interaction between solute in excited state and polar solvent.[64]

a.


Fluorescence
28.6
24.6
23.6
23.1
22.9
28.5
I_F
20.3
22.9
24.0
25.6
27.4
29.9
$\tilde{\nu} \cdot 10^{-3}$ [cm^{-1}]

b.

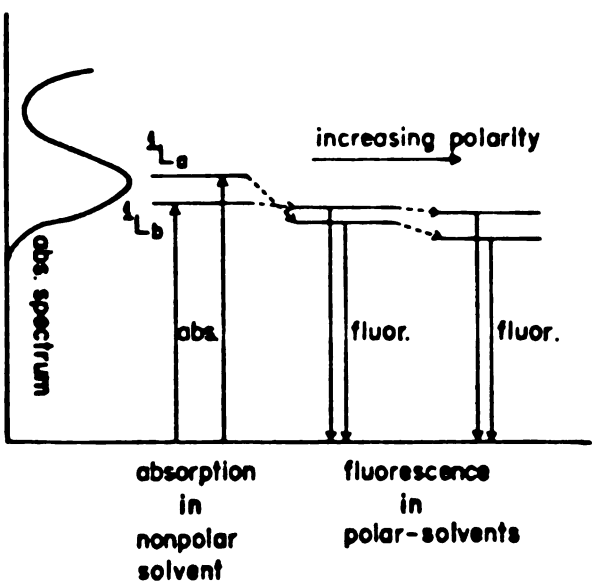

increasing polarity
^1L_a
^1L_b
abs. spectrum
abs.
fluor.
fluor.
absorption in nonpolar solvent
fluorescence in polar-solvents

Figure 7

extent during the lifetime of the excited state and therefore emission will take place from an unrelaxed configuration.

Mataga measured the time-resolved fluorescence spectra and fluorescence decay curves of the ^1L_a and ^1L_b fluorescence of DMAB and demonstrated clearly the relaxation process forming the ^1L_a-solvated state. The ^1L_b fluorescence approaches its intensity maximum after 4 nseconds and ^1L_a fluorescence after about 7 nseconds after the end of a short excitation pulse.

CHAPTER III

THE RED EDGE EFFECT AND A RELATED PHENOMENON

Fluorescence and phosphorescence of some organic molecules exhibit a red shift when excited at the long wavelength edge of the first absorption band. This phenomenon has been termed the red-edge effect[65] (REE), or edge-excitation red shift[66] (EERS) which actually is the difference in wave numbers (cm^{-1}) between the emission maxima obtained on shorter wavelength excitation and excitation at the red edge of the first absorption band.

Narrow band excitation is one of the necessary conditions to be able to observe the REE. This can be accomplished by using a good quality excitation monochromator or recently by using tunable dye lasers. Another condition to observe this phenomenon is the rigidity of the medium such that the life time of the excited state would be in the range of solvation site life time. This condition can be satisfied by lowering the temperature of the solution or by dissolving the material in a polymer matrix (e.g., poly (vinyl alcohol) or polystyrene) at room temperature.

A review of observations of the phenomenon made by different authors during the last two decades is now given.

In 1960 G. Weber reported[67] that concentration depolarization in rigid solutions, which results from singlet-singlet intermolecular energy transfer, failed to occur upon excitation into the red edge of the chromophore absorption band. The emission polarization experiment is represented diagramatically in Figure (8a). The polarization P is defined by the following equation:

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \qquad (24)$$

where $I_{\parallel}$ is the number of photons per unit time (intensity) emitted with their electric vector parallel to the electric vector of the exciting radiation in the laboratory frame of reference and $I_{\perp}$ is the number of photons per unit time (intensity) emitted with their electric vector perpendicular to the direction of the electric vector of the exciting radiation. Polarization reflects anisotropic character and hence lack of energy transfer while depolarization reflects isotropic character and hence an energy transfer. Figure (8b)[67] shows Weber's study of the concentration depolarization of indole in thin propylene glycol films at 220°K. Figure (8b) shows that excitation at the red edge of the absorption band (above 290 nm) resulted in enhanced polarization which indicates that little or no energy transfer occurred under these conditions

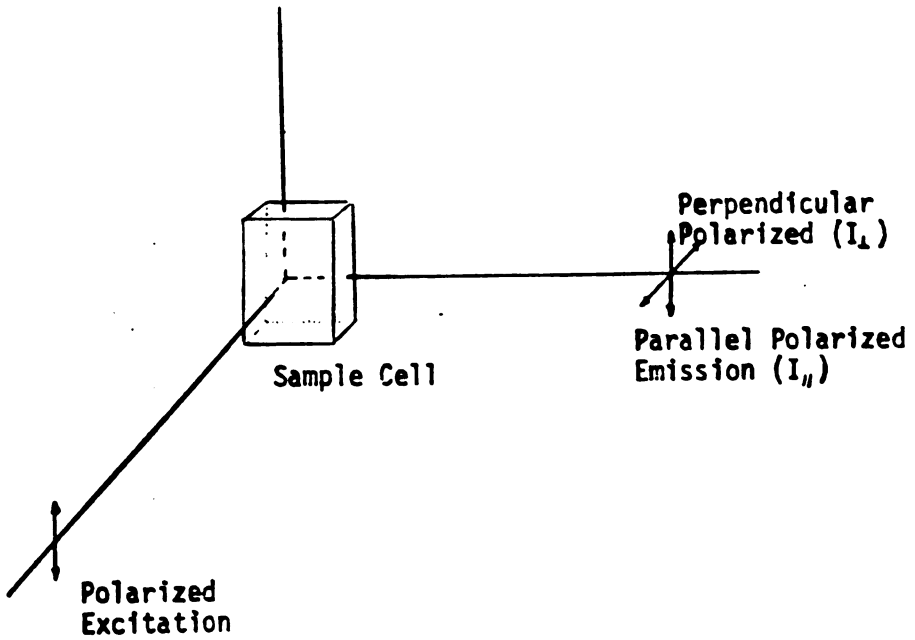


Figure 8a. Diagram showing orientation of parallel and perpendicularly polarized emission with respect to plane of polarization of exciting radiation in the laboratory coordinate system.

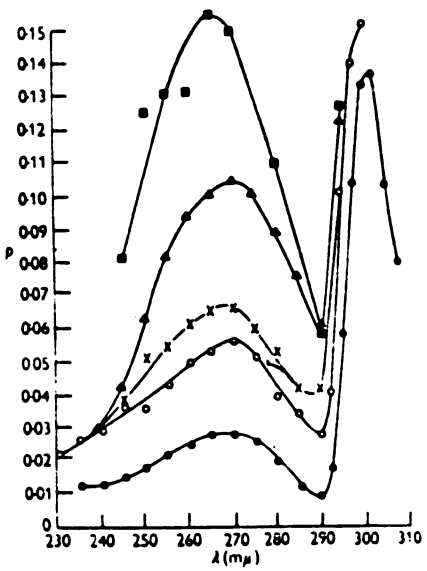


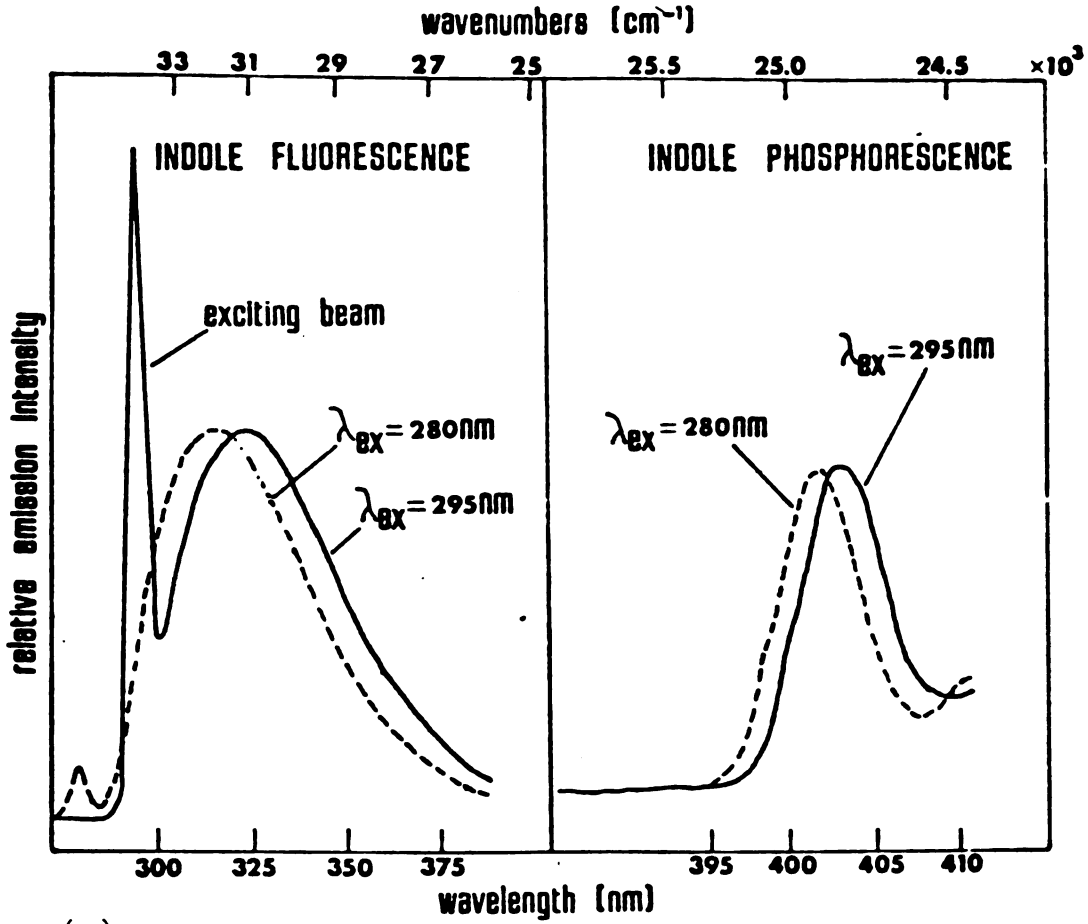
Figure 8b. Excitation polarization spectra of indole in propylene glycol at -70°C. ■, 0.01 M; ▲, 0.05 M; X, 0.1 M; ○, 0.2 M; ●, 0.4 M.[67]

even in concentrated solutions. Other studies[68] by the same author have indicated that this is a general phenomenon in aromatic molecules.

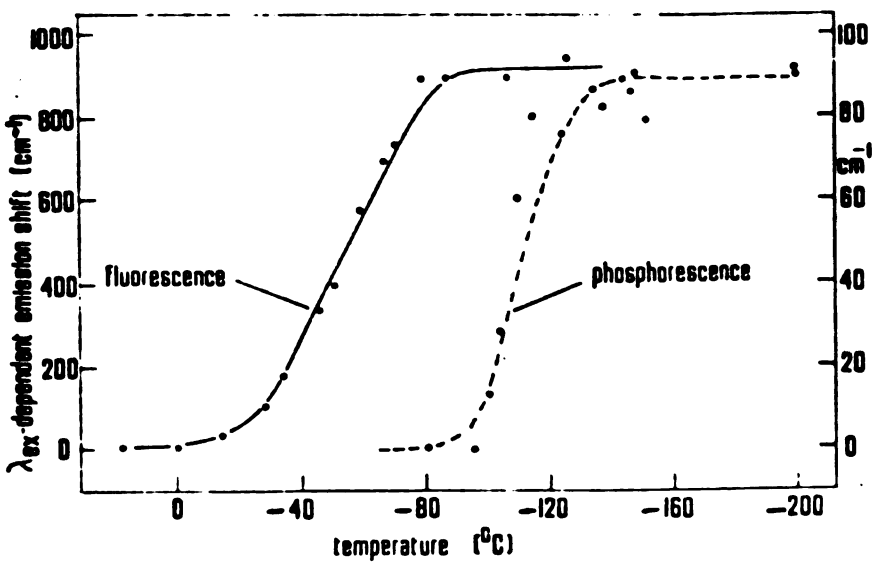
Galley and Purkey[69] measured the excitation wavelength dependence for emission spectra of indole in rigid media. Figure (9a)[69] displays the fluorescence and 0-0 region of the phosphorescence spectra of indole in a 1:1 ethyleneglycol-water glass excited near the center (280 nm) and the red edge (295 nm) of the absorption band. Clearly the emission spectra are not independent of the exciting wavelength as is generally assumed, for the spectra generated at the longer exciting wavelength are red shifted by about 900 cm^{-1} in fluorescence and 90 cm^{-1} in phosphorescence. The emission shift decreases with increasing concentration, at 0.5 M the shift in the fluorescence of indole is 600 cm^{-1} for 280 and 295 nm excitation. An exciting wavelength dependence was not observed for the fluorescence spectra at room temperature. This dependence of the phenomenon on solution "rigidity" is depicted in Figure (9b).[69] The differences in emission wavelength for both the phosphorescence and fluorescence spectra of indole excited at 280 and 295 nm in 4:1 glycerol:water were plotted as a function of temperature. The exciting-wavelength dependence is lost in either case, but the temperature at which the transition occurs for the phosphorescence is much lower than that for fluorescence.

Figure 9. (a) Fluorescence and 0-0 region phosphorescence spectra of 10^{-3} M indole in 1:1 ethylene glycol-water media at 202 and 77 K, respectively, demonstrating the shift between the emission excited at 280 and 295 nm.

(b) Plot of exciting wavelength dependence for the 10^{-3} M fluorescence and phosphorescence spectra versus the temperature of the 4:1 glycerol-water medium. Fluorescence and phosphorescence shifts were measured as the average of the red edge and blue edge differences between the spectra at 280 and 295 nm excitation.[59]


wavenumbers (cm⁻¹)
33
31
29
27
25
25.5
25.0
24.5
×10³
INDOLE FLUORESCENCE
INDOLE PHOSPHORESCENCE
exciting beam
λex=280nm
λex=295nm
λex=280nm
λex=295nm
relative emission intensity
300
325
350
375
395
400
405
410
wavelength (nm)

(a)


1000
800
600
400
200
0
λex-dependent emission shift (cm⁻¹)
fluorescence
phosphorescence
100
80
60
40
20
0
cm⁻¹
0
-40
-80
-120
-160
-200
temperature (°C)

(b)

Figure 9

K. Nagvi et al.[70] showed that the shape of the fluorescence spectrum is sensitive to the exciting wavelength in rigid media. Figures (10a and 10b)[70] shows better resolution in the spectra of P-terphenyl (TP) and P-quaterphenyl (QP) in rigid ethanol when excited at the red edge of the absorption band.

Similar observations to the above were found by us for different systems and are discussed in detail in Chapter V. The phenomenon has been confirmed experimentally by many other authors.[71-79]

Earlier interpretations of the phenomenon will now be given. Weber[71,72] interpreted the phenomenon present in naphthyl amine derivatives as due to the existence of out-of-plane transition moments in absorption and emission, normal to the plane of the aromatic rings, which he thought arose as a result of coupling between out-of-plane nuclear vibrations and in-plane transition moment. His interpretation was based on the measurement of polarization at different wavelengths of excitation and calculation of the rates of in-plane and out-of-plane rotations in aromatic compounds.[71]

Galley[69] interpreted the REE in terms of heterogeneity of solvation sites and emphasized the composite nature of both absorption and emission in rigid solution and provided a simple rationalization for the red edge failure of concentration depolarization obtained by Weber. Excitation

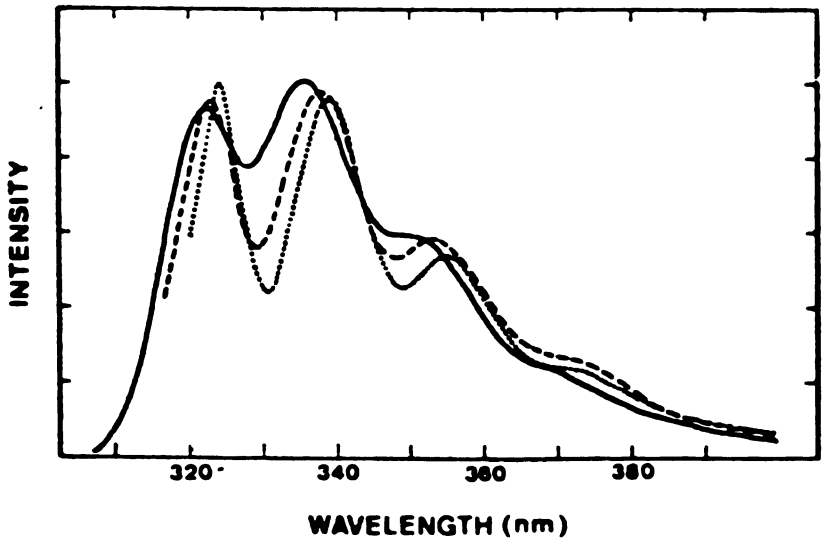


Figure 10a. Fluorescence spectra of $\sim 10^{-5}$ M TP (p-terphenyl) in ethanol at 77 K at different excitation wavelengths. ——— 280 nm; ----- 310 nm; ····· 315 nm.

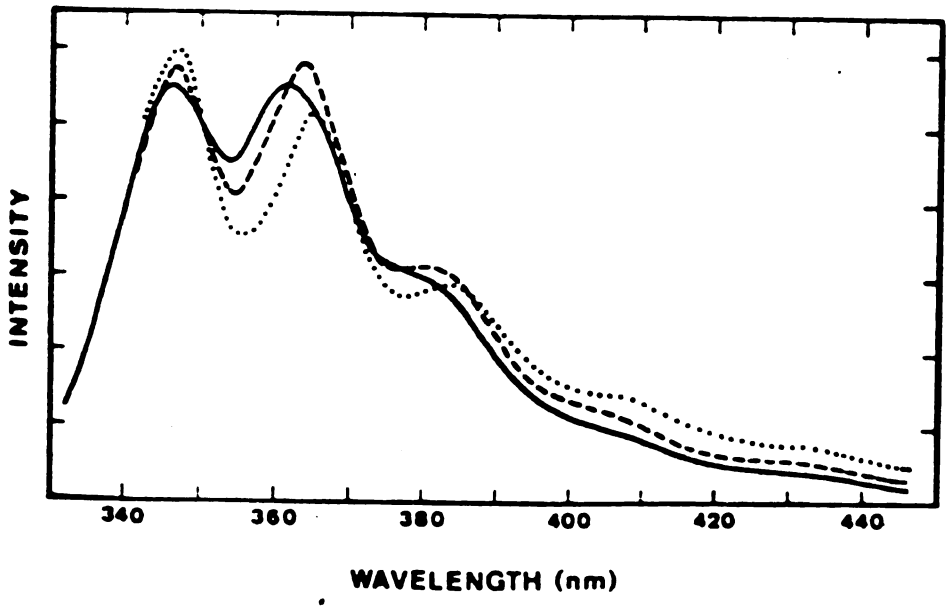


Figure 10b. Fluorescence spectra of $\sim 10^{-5}$ M QP (quaterphenyl) in ethanol at 77 K at different excitation wavelengths. ——— 320 nm; ------ 330 nm; ····· 335 nm.70

into the red edge of the chromophore absorption band selects a certain subpopulation of the solute molecules of small absolute concentration, which by virtue of their particular local environments are characterized by relatively low 0-0 singlet electronic transition energy. Because the bulk of the chromophore molecules in the solution possess 0-0 transitions of higher energy than the subclass of molecules at the red edge, members of the latter subclass have, in general, only neighboring molecules with higher energies. Singlet-singlet energy transfer and, as a result fluorescence depolarization, thus cannot occur for those molecules selectively excited at the red edge of the chromophore absorption band. On the other hand, at shorter exciting wavelengths, molecules of generally higher transition energies are excited and readily undergo energy transfer and fluorescence depolarization. This model of different local environment given by Galley explained the excitation wavelength dependence of the fluorescence in Figure (9a).[69] The results depicted in Figure (9b)[69] were explained by Galley as follows: at -110°C the mobility of the glassy solution is sufficient to randomize the chromophore solvation sites within the triplet-state lifetime of indole (∿7 seconds), whereas a temperature of -53°C is necessary to render the solution fluid enough to average the chromophore local environments within the nanosecond excited singlet state lifetime.

Nagvi[70] interpreted the REE observed in P-terphenyl and P-quaterphenyl as a result of emission from different conformers. Chen[73] interpreted the observation in quinene and 6-methoxyquinoline as a result of emission from more than one electronic states. Tomin[74] and Pavlovich[75] gave an interpretation similar to Galley's model in terms of inhomogeneous spectral broadening. Azumi et al.[51] noted that the mechanism of the REE is similar to the one proposed by Ware et al.[49,50] in interpreting the time-dependent spectral shift.

It may be convenient to distinguish two cases where the solute may assume different conformations: An example of this has been observed in the case of P-terphenyl and P-quaterphenyl in ethanol at 77°K[70] and in the case of the esters of 9-anthroic acid in 3MP at 77°K, Chapter V, observed by us. The other case involves polar solute molecules interacting with various solvation sites in a polar solvent, i.e., a distribution of different solvation sites; an example of this is the case of indole in ethylene glycol-water media at low temperatures[69]. Another example is our recent observation of a large REE in the case of merocyanine dye in polar solvents.[79]

SHPOL'SKII EFFECT

A large number of polyaromatic hydrocarbons exhibit vibronic spectra consisting of a large number of quasilines (i.e., a series of narrow bands which in most cases can be called lines) when present in a frozen n-alkane matrices at 77°K and lower temperatures. This phenomenon has been called "SHPOL'SKII EFFECT" after the Russian physicist E. V. Shpol'skii who discovered it in 1952.[80] The crystallinity and the transparency of the matrix (Shpolskii matrix) is one of the essential conditions to obtain the quasi-linear spectra.[80-84] Temperature as well as the rate of cooling of the matrix are other significant factors in observing Shpol'skii effect. This effect has become a general phenomenon in molecular spectroscopy.[85,86]

A typical example of the Shpol'skii effect is represented by the fluorescence spectrum of coronene in a frozen n-heptane matrix shown in Figure (11).[86] The excitation wavelength dependence of the fluorescence spectrum of benzo[a]-pyrene in n-heptane matrix is also shown. Certain aliphatic alcohols can also be used as solvents for the development of this effect.

To explain the line-like structure one presumes that the aromatic hydrocarbon replaces an aliphatic hydrocarbon at a lattice site and thereby exists in a state that can be described as an oriented gas molecule. Thus the spectra are of unperturbed systems corresponding to the free

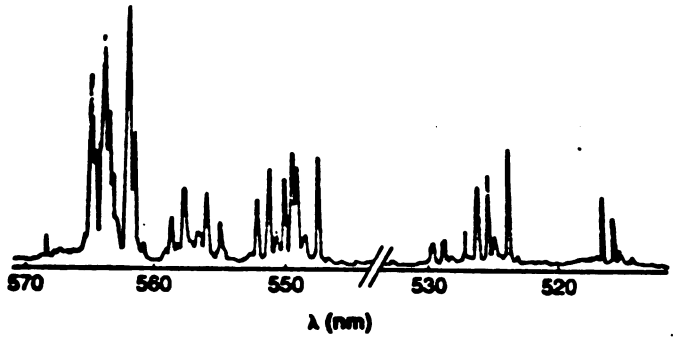


Figure 11a. Fluorescence spectrum of coronene in a frozen n-heptane matrix. The sharp lines arise because of the unique conformation of the coronene in the matrix.

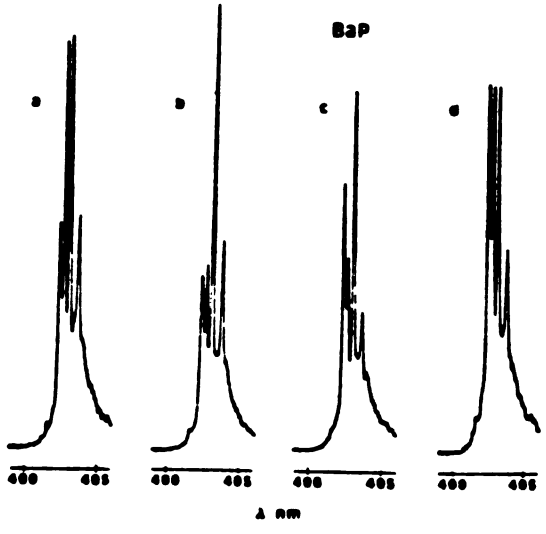


Figure 11b. Variation in the appearance of the 403 nm band system in the fluorescence spectrum of benzo[a] pyrene in heptane matrices at 15 K under dye laser excitation as a function of excitation wavelength: (a) 385.5 nm, (b) 385.7 nm, (c) 385.9 nm, (d) 386.1 nm.[86]

molecule. The ideal situation results when the dimensions of the solute and solvent molecules are comparable so that the solute molecule can occupy a definite position in the host lattice with minimum deformation; for example, the emission spectrum of naphthalene in pentane shows quasi-linear structure, but is more diffuse in hexane and heptane. If the solvent molecule is too small, a similar situation arises. The broader, more diffuse spectra that can result tend to be similar to those obtained in clear, rigid glass solvent systems. These can be a variation in the number of lines and their intensity depending on the solvent, excitation wavelength and temperature. The variations in part appear to originate from the fact that there are local differences in the crystal field surrounding different molecules. Thus, the multiplet structure appears in Figure (11)[86] is explained in terms of a number of distinct sites in the host crystal, in which the guest molecule can reside. Each site will perturb the energy levels to a different extent and so a number of component spectra, each with its own electronic origin, will be produced. Also, the rate of freezing of the mixture is important. Slow freezing results in the loss of some short wavelength components and weakening of some long wavelength components. This probably results from formation of rotational solvent isomers.[82] Under slow freezing it is more likely that a greater proportion of the solvent molecules will be in the

most stable conformation and the spectrum will be simple. Such fine-line spectra can be used to determine structural details of the emitting molecule.[82]

In an amorphous medium (e.g., solution), guest molecules occupy many different microenvironments or "sites" in a low-temperature matrix. Thus, the purely electronic energy levels of different molecules of the same solute are no longer the same and will be shifted to different extent.[87-91] Alternatively, it can be said that guest molecules reside in different "sites" in their "0-0" (purely electronic) absorption frequencies are different.[87] The band width over which these different 0-0 absorption frequencies are found is a measure of the extent of "inhomogeneous broadening" which may contrast with the intrinsic or homogeneous band width of a single molecule. This contrast is clear from Figure (12).[87] Upon monochromatic excitation near the 0-0 absorption band (where the density of vibronic state is small), only those molecules whose absorption bands overlap the laser line will absorb and consequently fluoresce. The resulting emission will therefore exhibit much narrower bandwidths than if a conventional broad-band lamp excitation source is used. This effect is called "site selection", "energy selection", or "fluorescence band narrowing".[87-91]

One of the experimental observations of site selection spectroscopy is shown in Figure (11).[86] It shows the

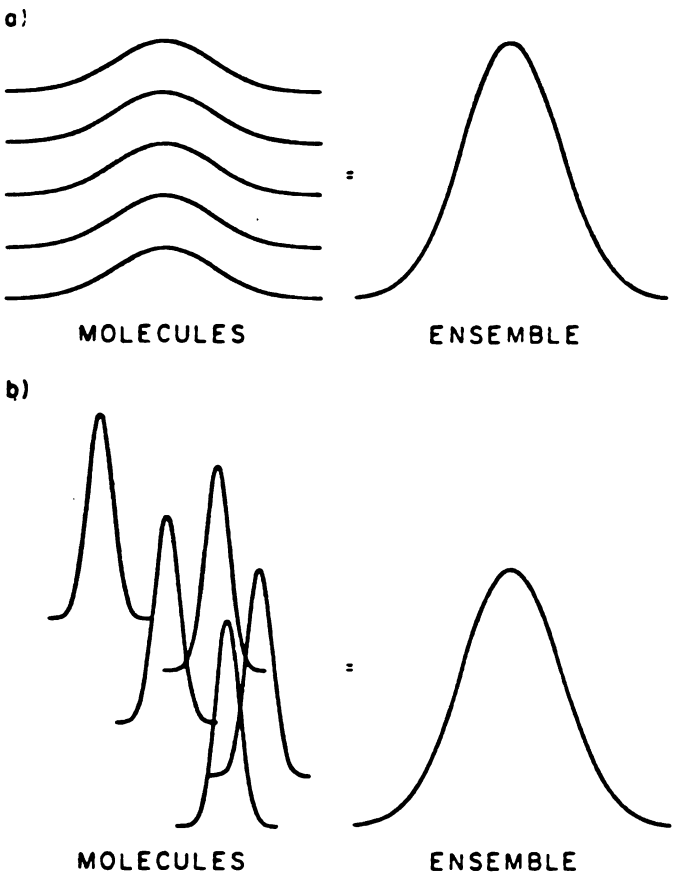


Figure 12. The limiting cases of homogeneous and inhomogeneous broadening. In the homogeneous case (a) the spectrum summed over all molecules in the sample corresponds identically to that for any one of the individual molecules. In the inhomogeneous case, (b), the spectrum summed over all molecules in the sample differs from the spectrum that would be seen for any single molecule.[87]

excitation wavelength dependence of the benzo[a]pyrene emission band in a solid matrix at low temperature. Other examples in the literature show the same concept as being useful in proving either Shpol'skii spectra or the Red Edge Effect discussed in the previous pages.

CHAPTER IV

MOLECULAR SYSTEMS

The goal of our research is to study solvent effects on the absorption and luminescence properties of molecules that undergo large changes in their dipole moment (μ) due to electronic excitations. One can study the change in fluorescence yield and energies as the polarity of the solvent is changed. Such changes can be examined in terms of specific interaction and bulk medium effects. One can also study the effect of solvent cage relaxation on the emission spectra using nanosecond and picosecond time resolved spectroscopy, in fluids as well as in viscous media. Since different solvation cages may exist, different excitation energies may occur in dilute solutions of polar molecules. Thus, it was interesting to study the dependence of luminescence energy, lifetime and spectral resolution on excitation wavelength at low temperatures. The molecular systems which we have studied are also potentially useful as fluorescence probes of biological systems.

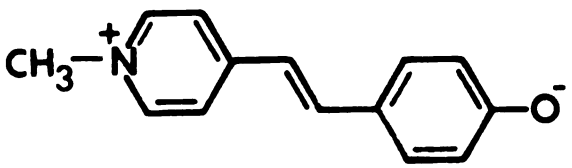
Three categories of molecular systems can be defined:

I. Molecular Systems that Undergo a Large Decrease in Dipole Moment as a Result of Excitation - i.e., $\mu_e < \mu_g$

where μ_g is the dipole moment of the ground state and μ_e is the dipole moment of the excited state.

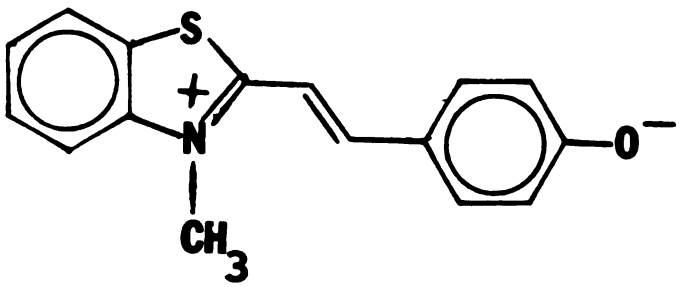
Examples:

1. Merocyanine Dyes



I

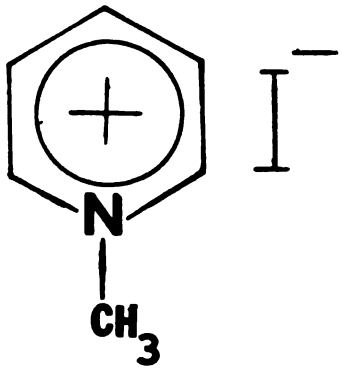
(1-methyl-4-hydroxystyryl)pyridinium betaine or 1-methyl-4-((oxocyclohexadienylidene)-ethylidene-1,4-dihydropyridine.



II

3-methyl-2-((4-oxocyclohexadienylidene)-ethylidene-benzothiazol.

2. Alkyl pyridinium iodides



III

methyl pyridinium iodide.

For Dye I the static dipole moment decreases by 5.5D upon excitation to the first excited singlet state.[92,93] The room temperature absorption spectra of pyridine merocyanine (Dye I) in solvents of different polarities are shown in Figure (13). The absorption maximum in chloroform occurs at 620 nm while in water the maximum occurs at 440 nm, a blue shift of 6500 cm^{-1}. The half-band width of the absorption band increases with the polarity of the solvent. Table (I) shows the absorption maxima, Stokes' shift $\Delta\bar{\nu}$ (cm^{-1}) with respect to chloroform and the half band width (Γ 1/2 cm^{-1}) in some solvents. The fluorescence spectrum of this dye undergoes a much smaller blue-shift as the solvent polarity is increased as shown in Figure (14). These observations are consistent with a dipole moment decrease in the excited state.

Methyl pyridinium iodide is another example which

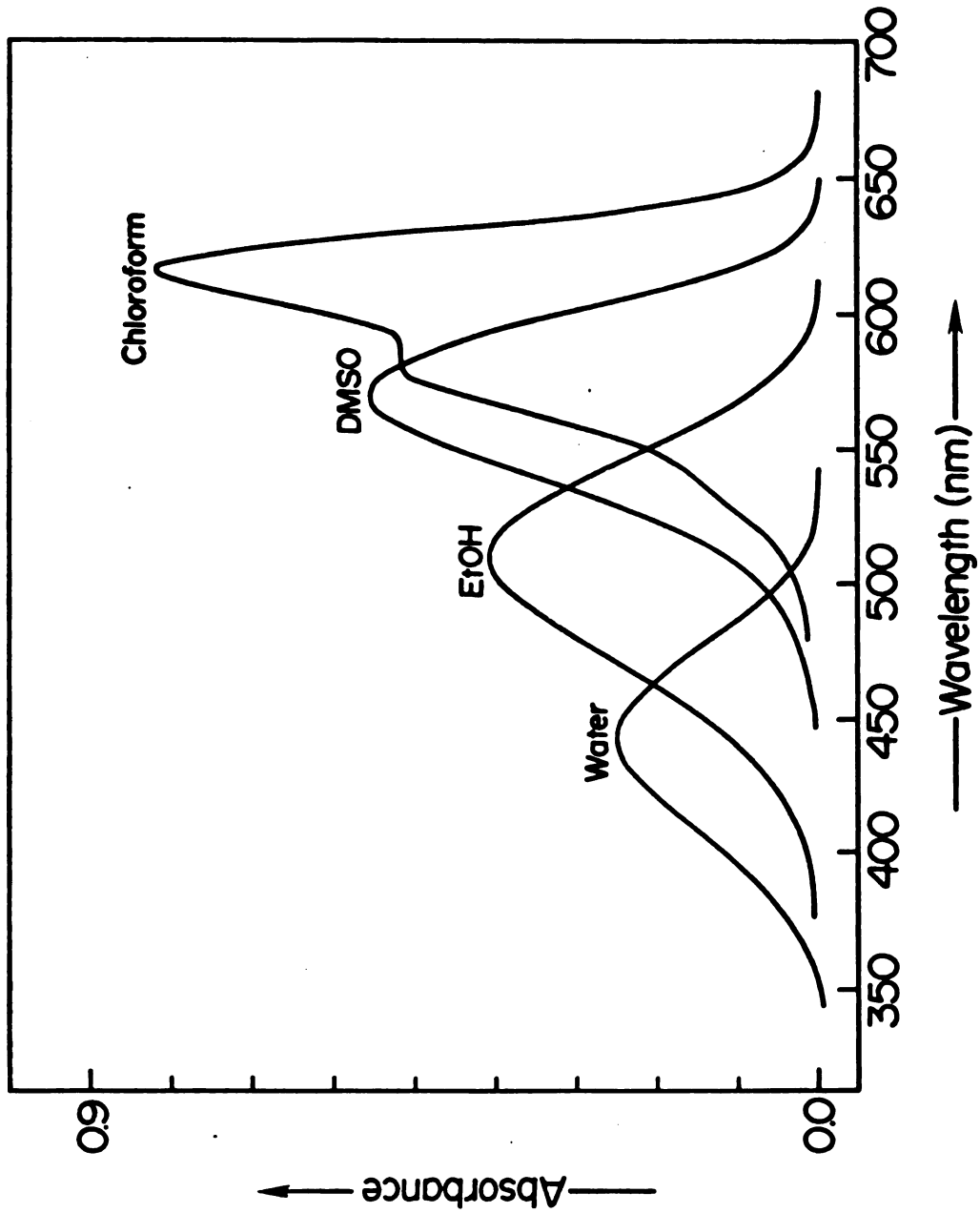


Figure 13. Room temperature absorption spectra of pyridine merocyanine dye in different solvents. DMSO = Dimethyl sulfoxide and EtOH = Ethanol.

Table I. Optical Properties of Pyridine Merocyanine Dye in Various Solvents.

Solvent	$\Gamma_{1/2}$ cm^{-1}	λ_{max}, nm	$\Delta\bar{\nu}$, cm^{-1}
Water	1900	440	6600
Ethanol	1500	508	3500
Dimethyl sulfoxide	1000	570	1400
Chloroform	400	620	----

$\Gamma_{1/2}$ is the width of the absorption band at half absorbance. $\Delta\bar{\nu}$ (cm^{-1}) is the shift of the absorption maximum with chloroform taken as reference.

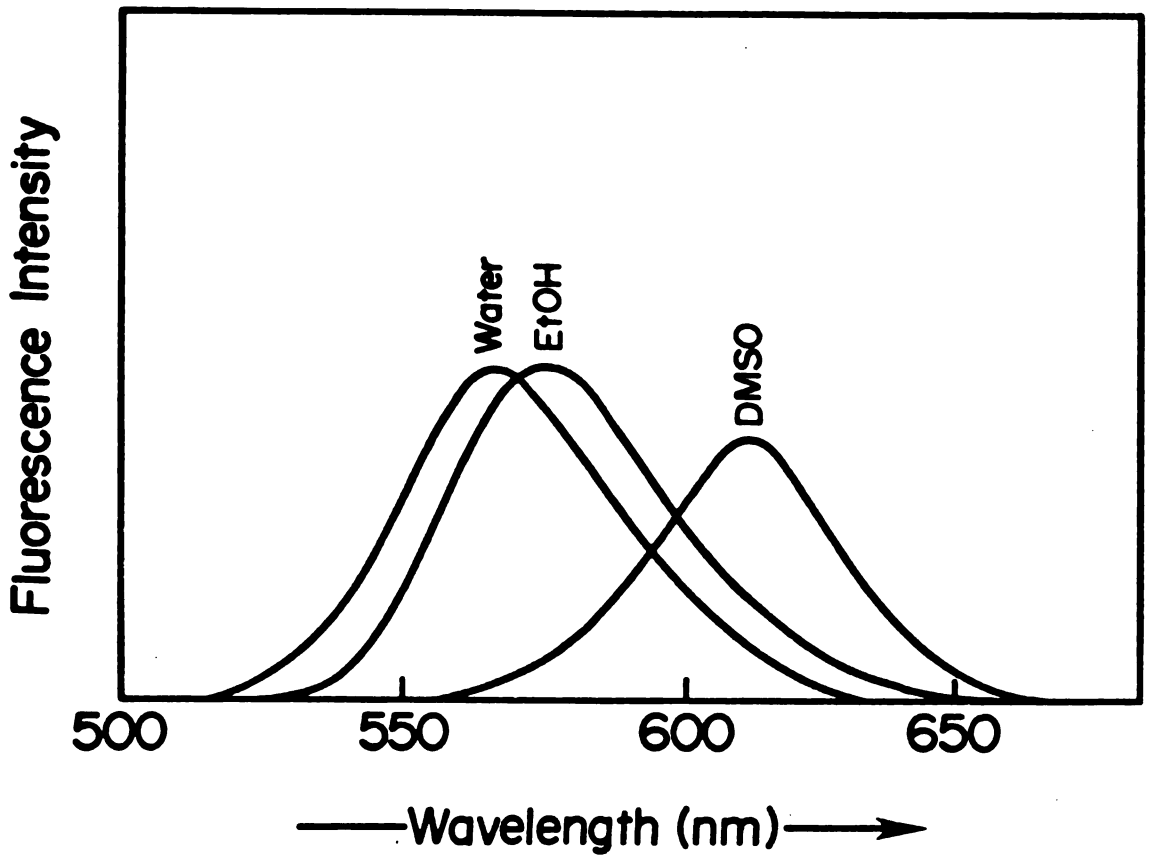


Figure 14. Room temperature fluorescence spectra of pyridine merocyanine dye in different polar solvents.

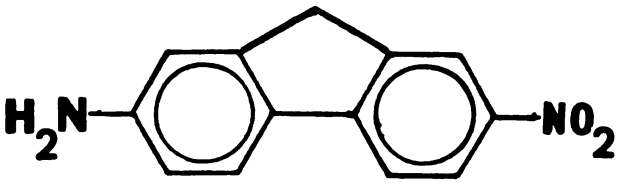
undergoes a large blue shift (20000 cm^{-1}) in polar solvents.[94] The first absorption band corresponds to a charge transfer transition where I^- acts as the electron donor and the pyridinium acts as the electron acceptor. In the excited state, the intermolecular distance between the neutral component is increased. Dramatic relaxations involving the solvent cage as well as the two components solute will occur.

In this category ($\mu_e < \mu_g$), we have studied in detail the pyridine merocyanine (Dye I).

II. Molecular Systems that Undergo a Large Increase in Dipole Moment as a Result of Excitation - i.e., $\mu_e > \mu_g$

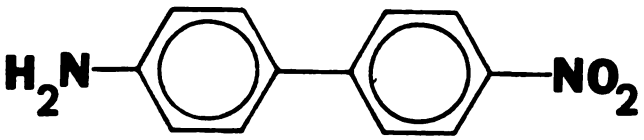
Examples

1. 2-Amino-7-Nitro Fluorene



ANF

2. 4,4' Amino Nitro Diphenyl



AND

The static dipole moment increases[95] upon excitation to the first excited singlet state by 18D for the case of ANF and by 12D for the case of AND.

The room temperature absorption spectra of ANF and AND in solvents of different polarities are shown in Figures (15) and (16), respectively. The absorption maximum for ANF in 3MP (3-methyl pentane) occurs at 365 nm while in ethanol the maximum occurs at 385 nm, a red shift of 1400 cm^{-1}. The red shift in the AND spectra is about 2300 cm^{-1} in going from 3MP to ethanol. The fluorescence spectra of these molecules undergo a larger red shift as the solvent polarity increases as shown in Table II.[96] These observations are consistent with a dipole moment increase in the excited state. Both of these molecular systems were studied in detail.

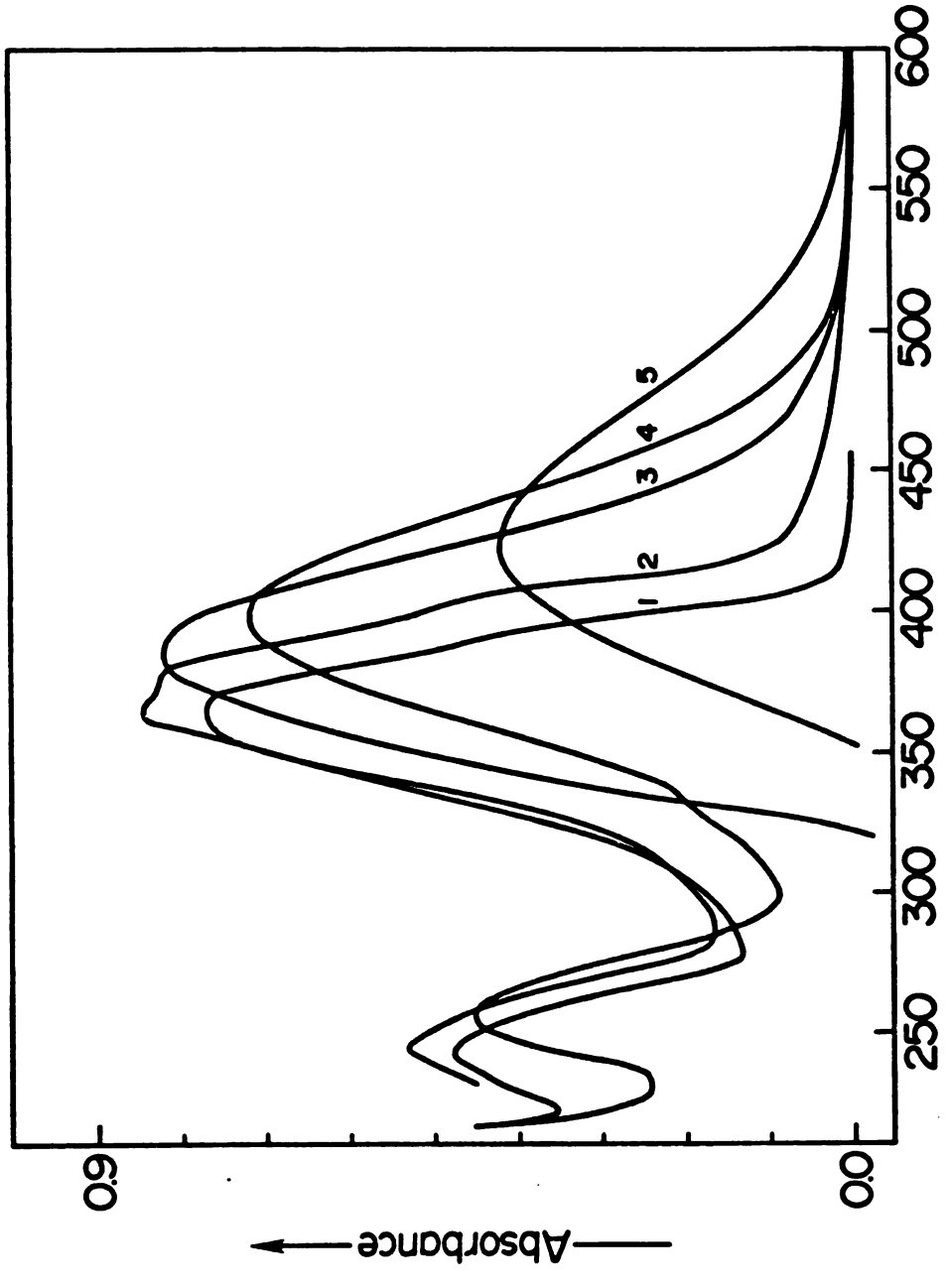


Figure 15. Room temperature absorption spectra of ANF in different solvents: (1) 3MP, (2) Paraffin Oil, (3) Polystyrene film, (4) Ethanol, (5) Polyvinyl alcohol film.

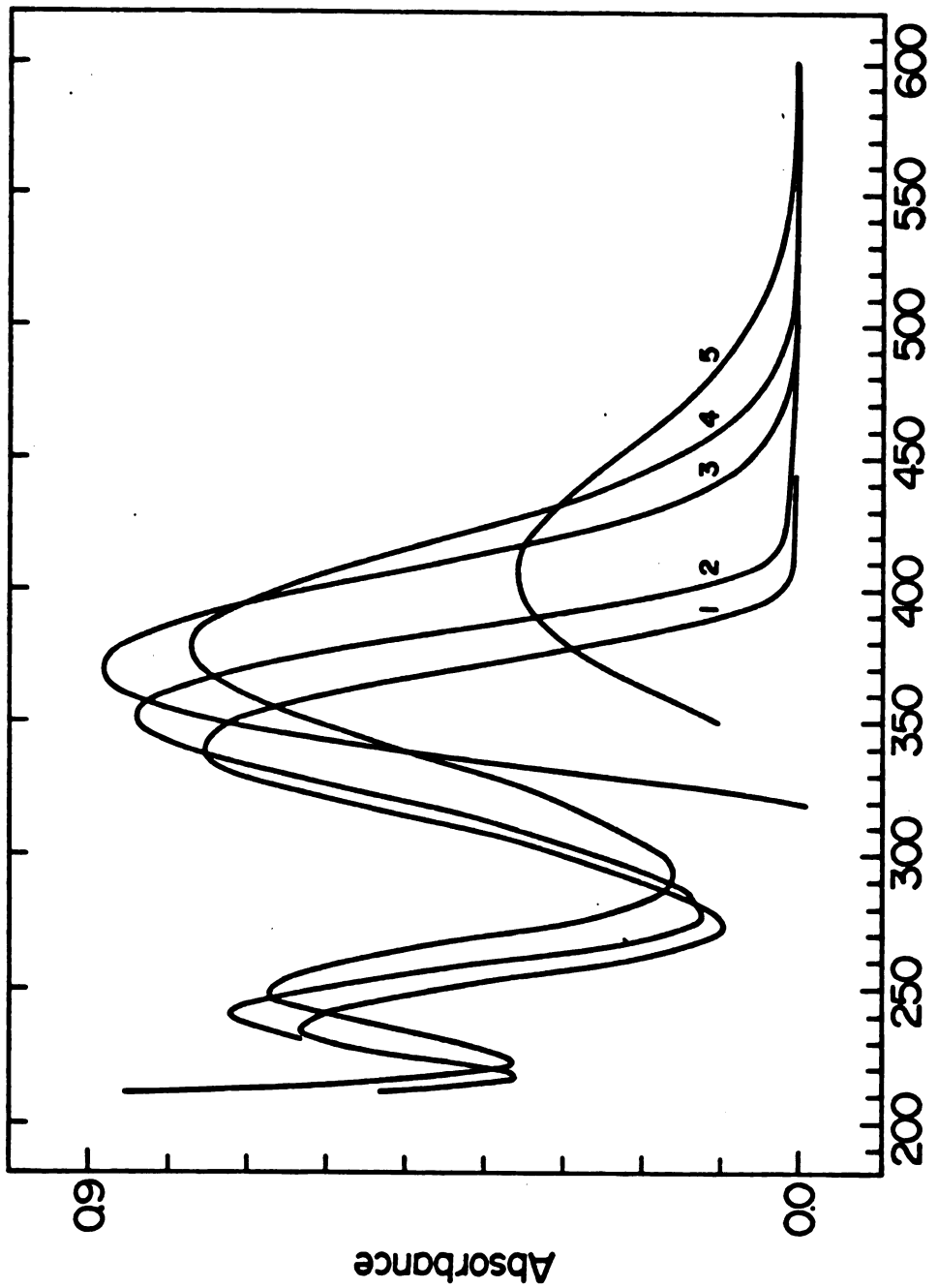


Figure 16. Room temperature absorption spectra of AND in different solvents: (1) 3MP, (2) Paraffin Oil, (3) Polystyrene film, (4) Ethanol, (5) Polyvinyl alcohol film.

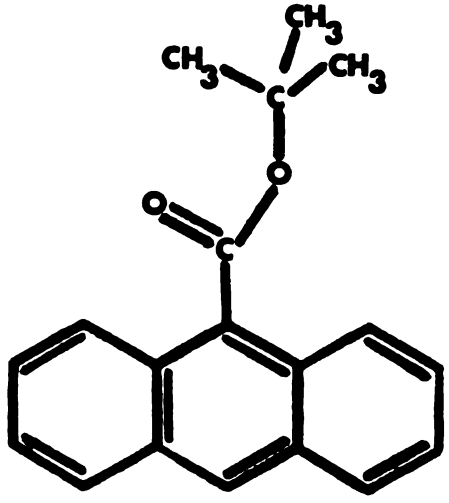
Table II. Fluorescence Properties of ANF (2-Amino-7-Nitrofluorene) in Various Solvents.[96]

Solvent	λ_{max}, nm Absorption	$\Delta\tilde{\nu}$ (cm^{-1})	Fluorescence	$\Delta\tilde{\nu}$(cm^{-1})
Benzene	388	---	515	----
Diethylether	394	400	532	620
1-Propanol	400	800	687	4800
Methanol	397	600	752	6100

III. Flexible Molecules that May Undergo a Change in Equilibrium Geometric Configuration Upon Excitation -

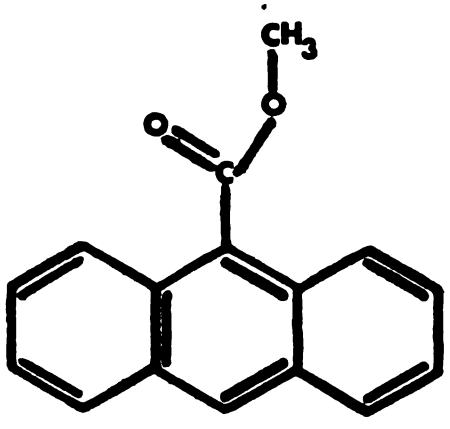
Examples:

1. 9-tertbutylanthroate: (tertbutylester of 9-anthroic acid)



9-Tertbutyl Anthroate (9TBA)

2. 9-methylanthroate (methylester of 9-anthroic acid)



9-Methyl Anthroate (9MA)

These molecular systems undergo geometric relaxation to different equilibrium positions in the excited state depending on the size of the ester group, viscosity and polarity of the solvent matrix. The room temperature absorption and fluorescence at room temperature and at 77°K of 9TBA and 9MA in 3MP are shown in Figures (17) and (18), respectively. The excitation wavelength dependence of the fluorescence spectra in rigid media has been studied for both anthroate esters.[97]

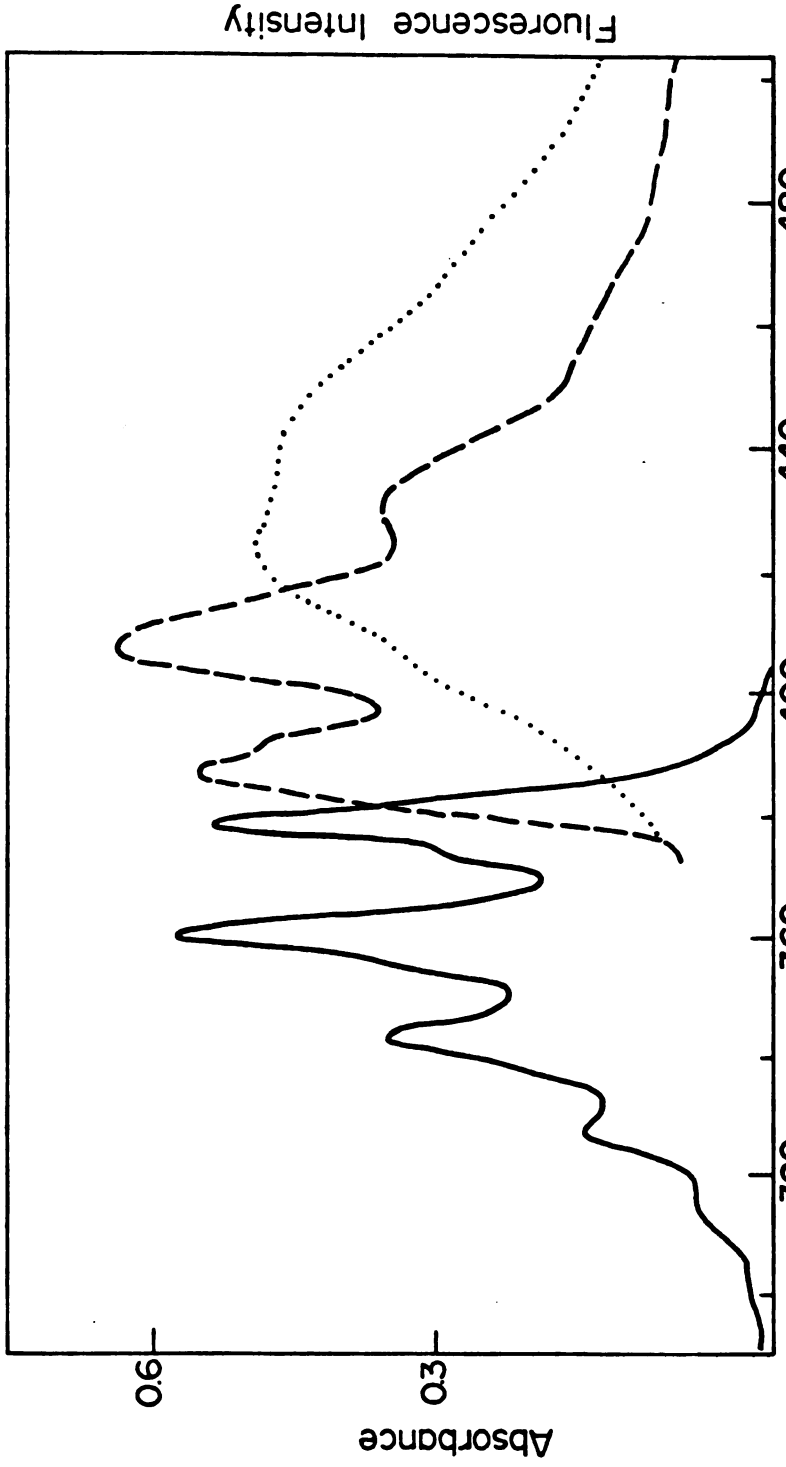


Figure 17. Room temperature absorption spectrum of (7×10^{-5} M) 9TBA and its fluorescence spectra at room temperature (....) and at 77 K (----) in 3MP.

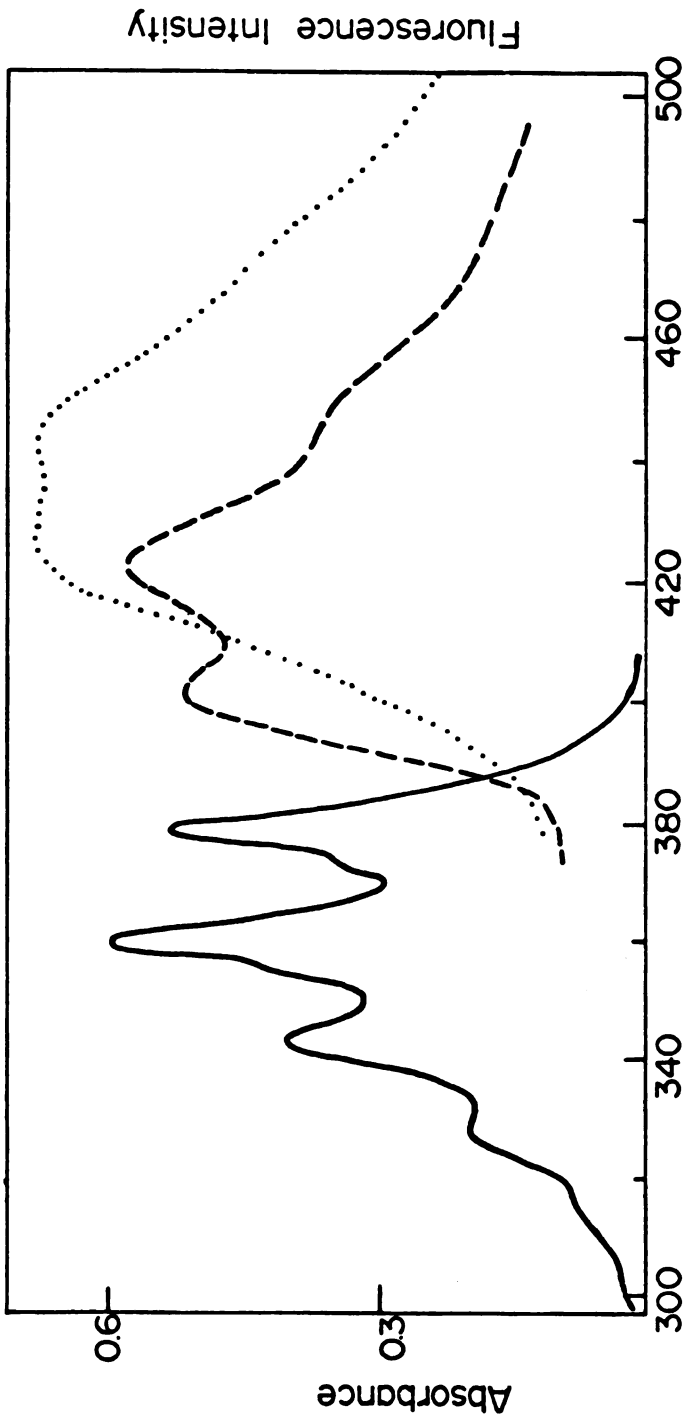


Figure 18. Room temperature absorption spectrum of (7×10^{-5} M) 9MA and its fluorescence spectra at room temperature (····) and at 77 K (----) in 3MP.

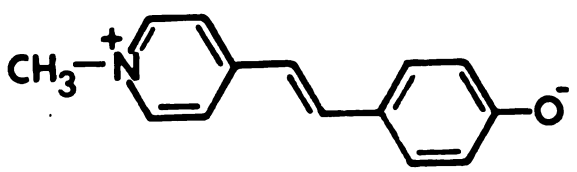
CHAPTER V

RESULTS AND DISCUSSION

I. Molecular Systems that Undergo a Large Decrease in Dipole Moment as a Result of Excitation

A. Pyridine-Merocyanine Dye

As an example of these molecular systems we have studied in detail the absorption, emission and excitation wavelength dependence of the fluorescence of pyridine merocyanine I ($\Delta\mu \simeq -5.5$D upon excitation)[98] in solvents of different polarities at different temperatures as well



I

as at different viscosities.

The electronic absorption spectrum of this merocyanine dye is pH dependent as shown in Figure (19).[99] The protonated form of the dye undergoes cis-trans isomerization as shown in Figure (20),[99] however, the trans form

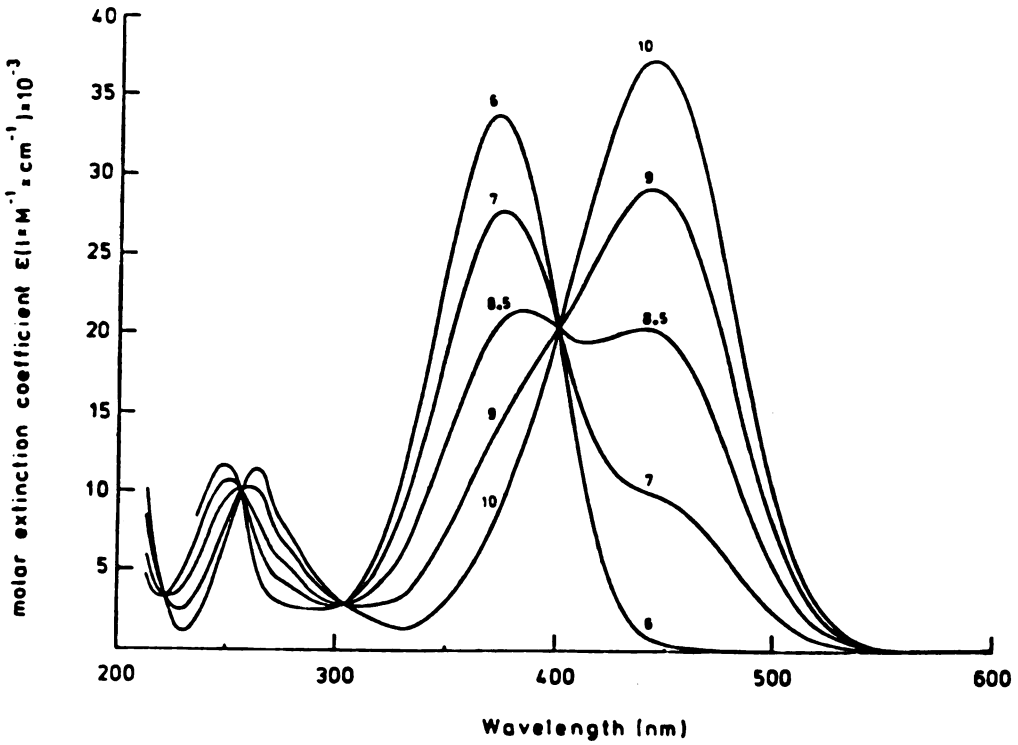


Figure 19. Room temperature absorption spectra of aqueous solutions of pyridine merocyanine dye (2 x 10^{-5} M) at different pH.99

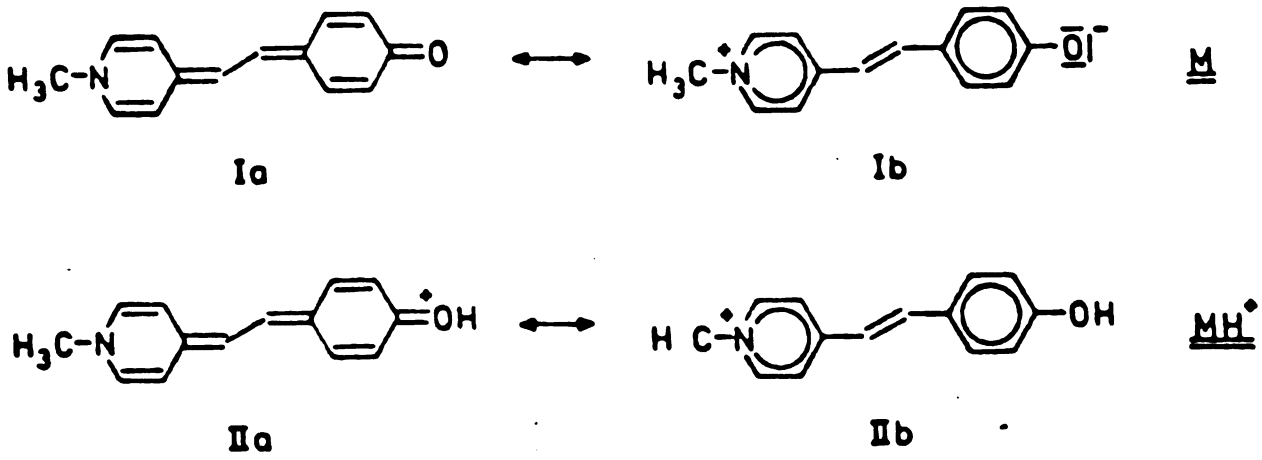


Figure 20a. Resonance structure of pyridine merocyanine dye in its neutral and acidic form.99

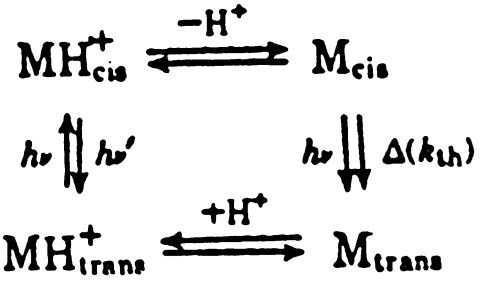


Figure 20b. Photochemical cycle of pyridine merocyanine dye and its cis-trans isomerization.99

is photochemically stable in basic media. All our spectroscopic measurements were made in a basic media by adding either piperidine or potassium hydroxide to the solutions.

The room temperature absorption and emission spectra in solvents of different polarities are demonstrated in Figures (13) and (14), respectively. The absorption spectrum of this dye exhibits a large blue shift in media of increasing polarity. The absorption maximum in chloroform occurs at 620 nm while in water the maximum occurs at 440 nm, a blue shift of $\approx$6500 cm^{-1} as shown in Table I. The half band width of the absorption increases with the polarity of the solvent. The room temperature fluorescence spectra in Figure (14) shows a much smaller blue shift as the solvent polarity is increased. These observations are consistent with a dipole moment decrease in the excited state.

Earlier investigations of merocyanine dyes were limited to their absorption spectra in solvents of different polarities and in solvent mixtures. This particular dye I was synthesized by Brooker and co-workers[100] who proposed it as an indicator of solvent polarity. They explained[100,101] the results similar to those obtained in Figure (13) in terms of a large ground state dipole moment which is significantly reduced upon excitation[92,102]. The work of Balyiss and McRae[103] has established that the solvent

shifts of the merocyanine dyes are only substantial in the case of specific solvent interaction with both the oxygen and nitrogen atoms; in other words the bulk dielectric effect of the solvent has a small effect on the spectrum. Benson and Murrel[104] used an SCF π-electron theory with bond length optimization to calculate the effect of solvent polarity on the structure and spectroscopic properties of the pyridine-merocyanine dye. McRae applied his theory of solvent shift[9] to merocyanines.[10] He considers the dye to be a polarizable dipole in a cavity in a homogeneous dielectric. The magnitude of the electric reaction field from the cavity due to orientational polarization is given by

$$R = \frac{2\mu}{a^3}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \qquad (25)$$

where R is the magnitude of the orientational cation field, μ the dipole moment of the dye in the ground state, ε the dielectric constant of the solvent, n the refractive index of the solvent and a the cavity radius. The maximum absorption energy of the dye, $\bar{\nu}_{max}$, is expected on the basis of McRae's theory to vary regularly with the term in parentheses of the above equation. This term is referred to as F by McRae. Hydrogen bonding solvents show much

larger shifts of $\bar{\nu}_{max}$ than do non-hydrogen bonding solvents for comparable values of F.[10] Campas[105] considers the interaction between the dye and the solvent as a dipole-dipole interaction between the dye molecule and a small number of solvent molecules near the dye. The total dipole moment of the solvent molecules is calculated using the theory of polar liquids developed by Kirkwood[13,14] and modified by Frölich.[15] In Onsager's theory of the dielectric constants of liquids, one considers a single molecule contained in a cavity in a homogeneous dielectric.[11] In the Kirkwood-Fröhlich theory one assumes there are M molecules in the cavity and the limit is taken as M becomes large. A statistical mechanical average over the orientations of the M molecules is performed in two steps; first one molecule is considered fixed and an average is performed over all orientations of the other M-1 molecules. Then an average is taken over all orientations of the one remaining molecule. The total dipole moment of the M molecules with one held fixed tends to a limit as M becomes large enough to encompass the short range order around the molecule which is held fixed. This limiting dipole moment $\bar{\mu}$ is different from the dipole moment μ of the fixed molecule. Kirkwood expressed $\mu \cdot \bar{\mu} = g\mu^2$ and estimated g from X-ray diffraction data on coordination numbers in liquids. From those g values he calculated dielectric constants of water and several alcohols in reasonable agreement with

experiment.[13] Campas used Fröhlich's modification of Kirkwood's theory.[111] Fröhlich considered the M molecules as M non-polarizable point dipoles imbedded in a sphere with dielectric constant n^2, the index of refraction squared. The dipole moment of the molecule in the liquid, μ, is increased by a factor of $(n^2+2)/3$ over the dipole moment of the molecule in the gas phase, μ_o. Fröhlich obtained the result

$$g\mu_o^2 = \frac{9\,K\,T(\varepsilon-n^2)(2\varepsilon+n^2)}{4\pi N\varepsilon(n^2+2)} \qquad (26)$$

where g is the Kirkwood correlation factor, μ_o the dipole moment of the molecule in the gas phase, K the Boltzmann constant, T the absolute temperature, ε, n, defined as before and N the number of molecules per unit volume. Equation (26) reduces to Onsager's equation for g = 1. The problem of the undetermined Kirkwood correlation factor was handled[98] by assuming that the short-range order around the merocyanine is the same as the short-range order in the bulk liquid. Since the above investigations were limited to absorption studies, we decided to study the fluorescence spectra under various conditions.

The room temperature fluorescence of fluid dilute solutions ($<10^{-5}$ M) of the dye is excitation wavelength

independent. Once these solutions are made rigid, excitation wavelength dependence, i.e., a Red Edge Effect (REE) is observed. We have observed a large REE for this dye in solvents of different polarities (ethanol, 1-propanol, 1-butanol, 1-hexanol, glycerol, glycerol-water mixture, dimethyl sulfoxide, pyridine and polyvinyl alcohol polymer matrix) at 77 K and in rigid polymer matrices at room temperature. The fluorescence spectra of dilute solutions ($\approx 10^{-6}$M) of the dye in ethanol, 1-propanol, 1-hexanol and polyvinyl alcohol (PVA) film at 77 K as a function of the excitation wavelength are shown in Figures (21-24), respectively. A large red shift of $\approx$1200 cm^{-1} in ethanol, 1-propanol and PVA and 3000 cm^{-1} in 1-hexanol has been observed as the excitation wavelength is increased from the absorption maximum (the number at top left of Figures cited) at 77 K to the red edge of the absorption band (the number at top right of the Figures cited). The magnitude of this red edge effect is viscosity dependent. For example, when the temperature in ethanol is higher than -62°C an insignificant REE is observed. However, below this temperature the viscosity of ethanol solution becomes large, and the REE gradually increases reaching its maximum value at 77 K. Figure (25) shows such observations in ethanol where the REE increases from $\approx$200 cm^{-1} at -119°C to $\approx$1200 cm^{-1} at 77 K. The shape of fluorescence spectra as a function of excitation wavelength at -135°C is shown in

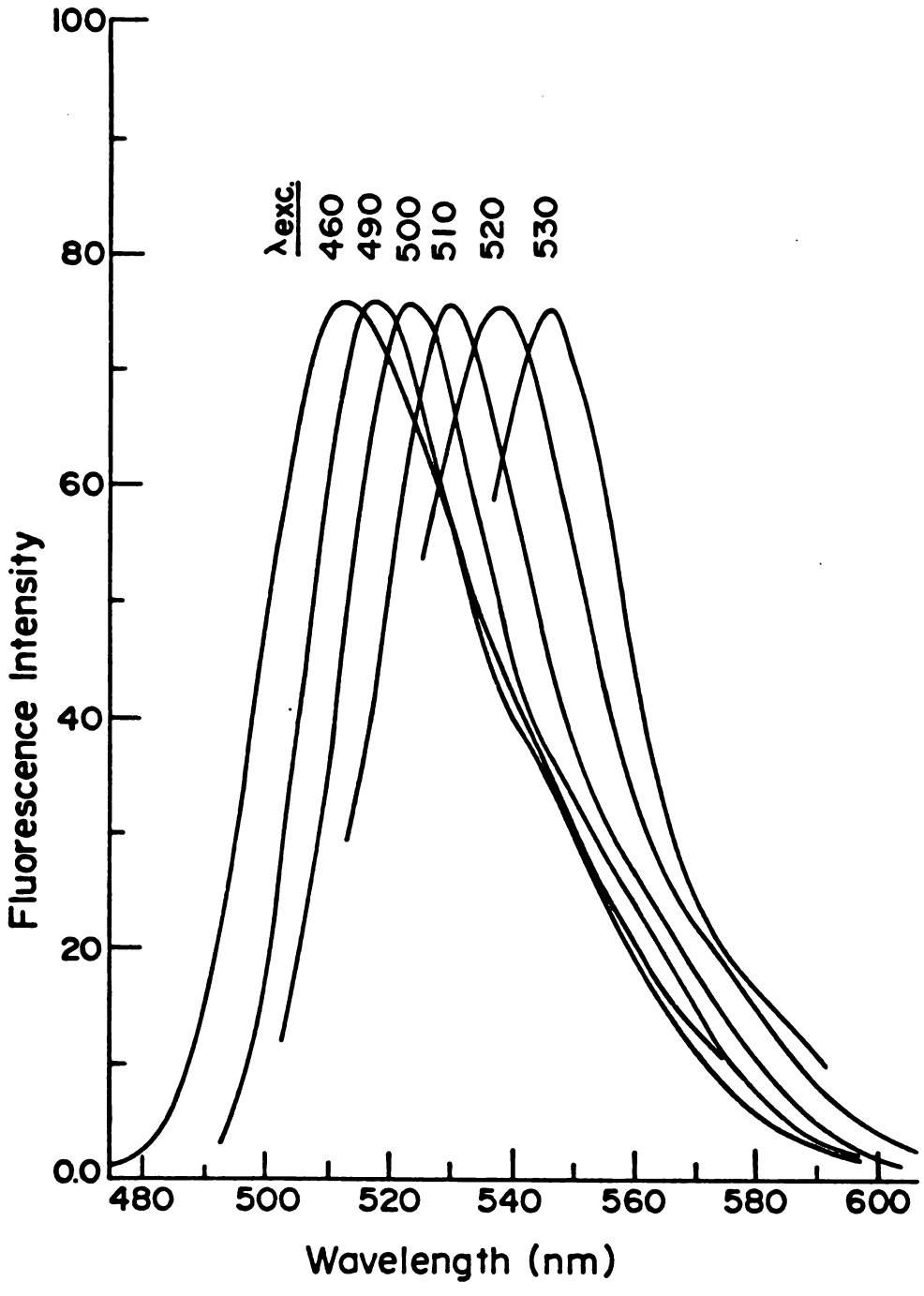


Figure 21. Fluorescence spectra of a dilute solution ($<10^{-5}$ M) of pyridine merocyanine dye in ethanol at 77 K as a function of excitation wavelengths.

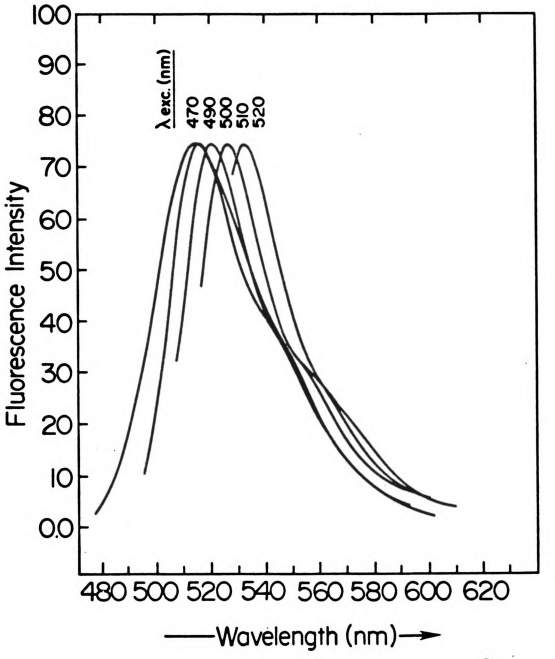


Figure 22. Fluorescence spectra of a dilute solution of pyridine merocyanine dye in 1-propanol at 77 K as a function of excitation wavelengths.

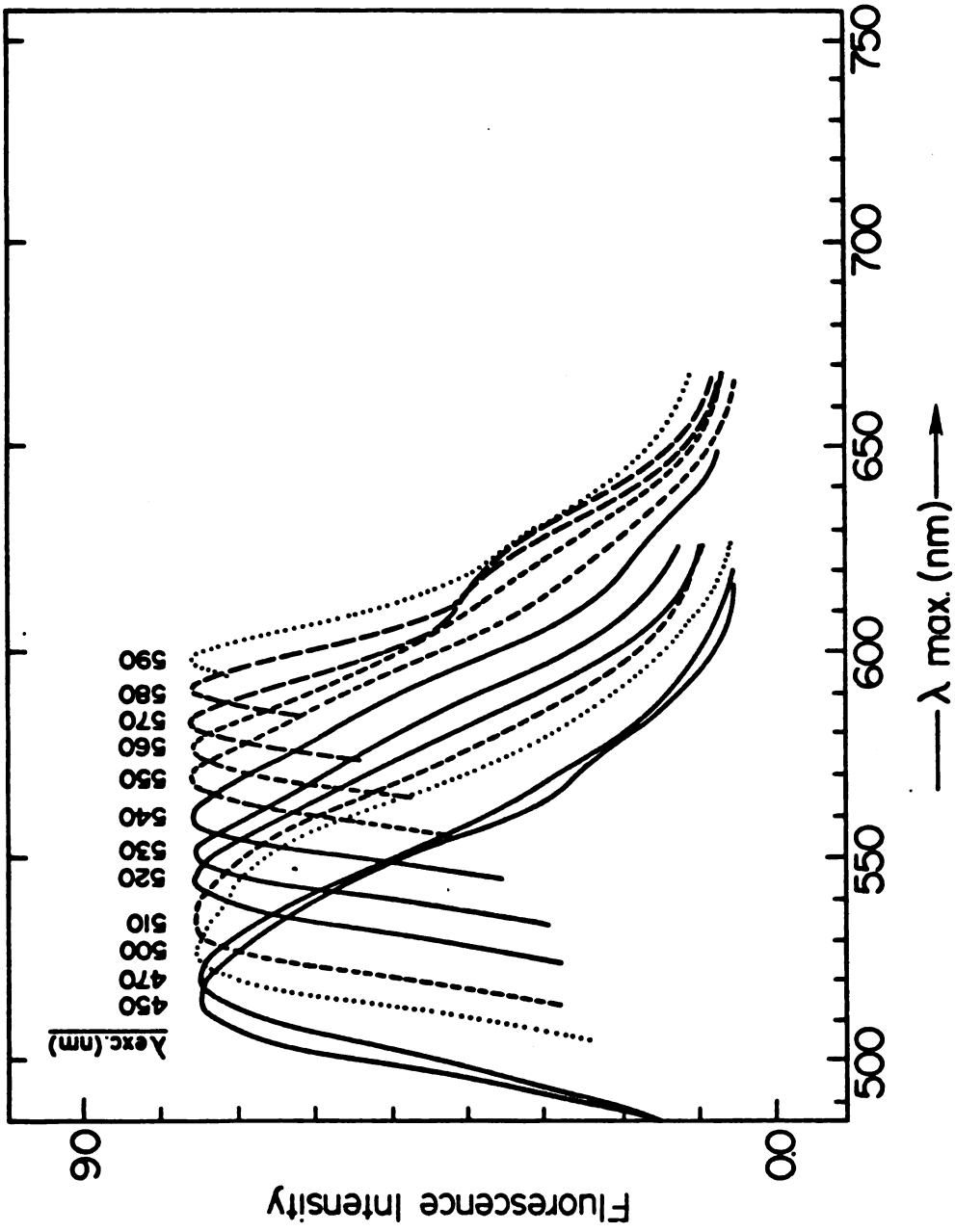


Figure 23. Fluorescence spectra of a dilute solution of pyridine merocyanine dye in 1-hexanol at 77 K as a function of excitation wavelengths.

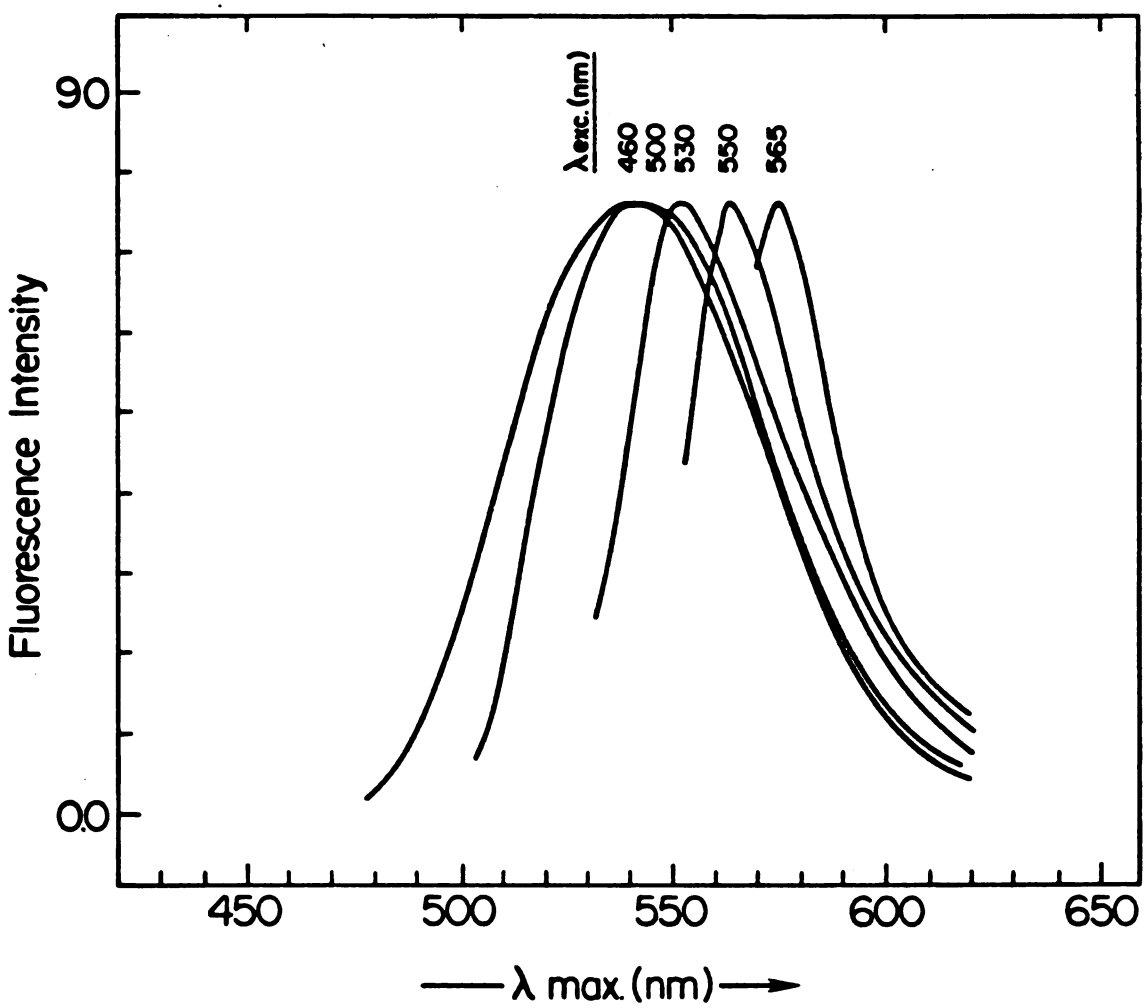


Figure 24. Fluorescence spectra of pyridine merocyanine dye in PVA (polyvinyl alcohol) thin film at 77 K as a function of excitation wavelengths.

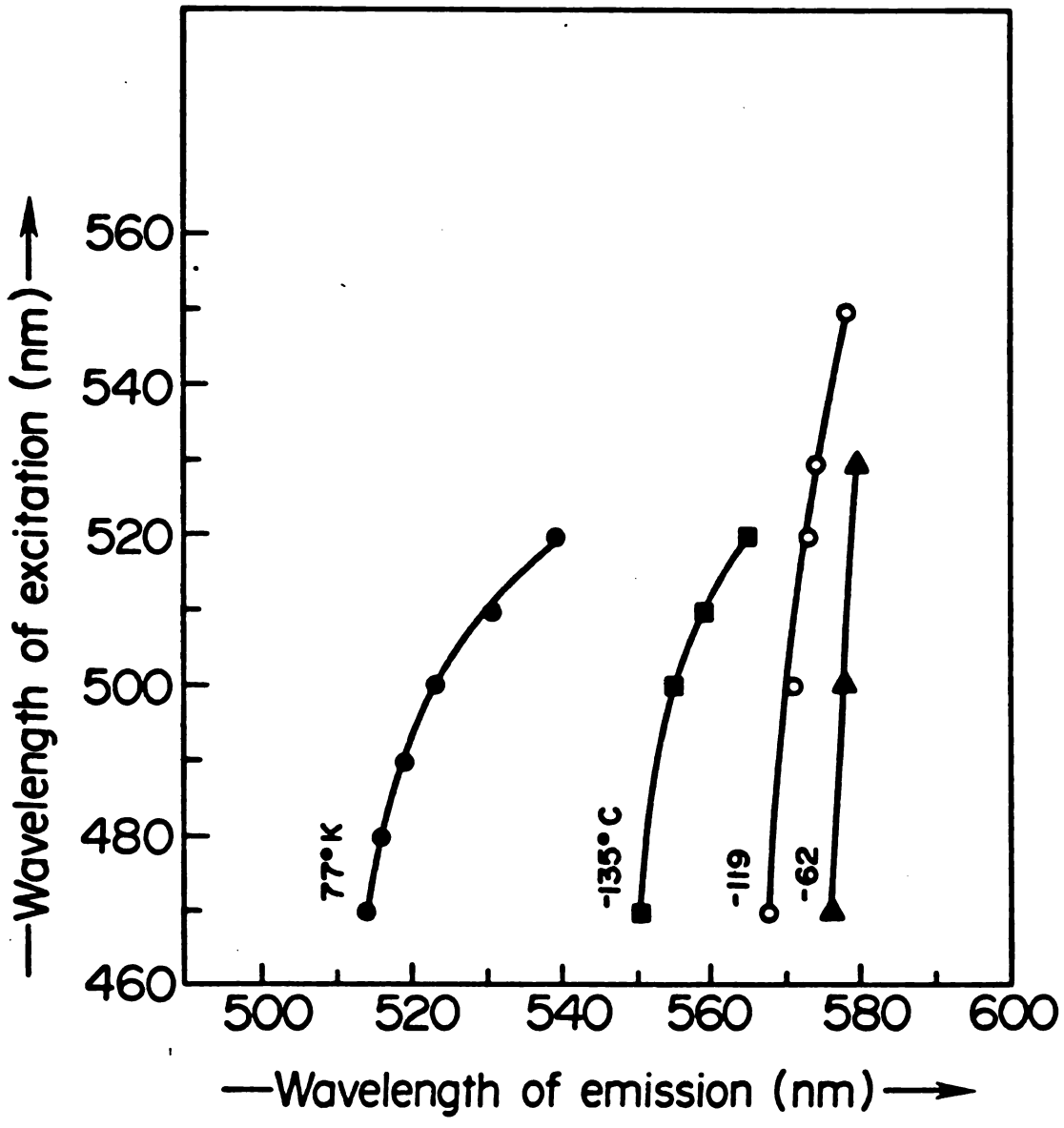


Figure 25. Temperature dependence of fluorescence edge excitation red shift of pyridine merocyanine dye in ethanol.

Figure 26. Another example of viscosity dependence, the magnitude of REE in 1-propanol at -108°C and in glycerol at 0°C are equal (≈400 cm^{-1} in both solvents) proving the significant role of viscosity in this phenomenon as shown in Figure (27).

Careful inspection of Figures (21-23) and (26) shows that the shape of the fluorescence spectrum is highly dependent on the excitation wavelength. As the excitation wavelength is changed toward the red edge of the absorption band a shoulder is observed. The viscosity of the medium as well as the length of the alcohol chain affect the shape of the spectrum. In a longer aliphatic chain alcohol solvent a more defined shoulder appears in the spectrum.

We have also studied the REE as a function of the concentration of the dye. In Figure (28) the emission of 10^{-5}, 10^{-4}, 10^{-3} and 2×10^{-3} M of the dye in ethanol at 77 K, is shown; all solutions are excited at the same wavelength, namely the absorption maximum 460 nm. A red shift of ≈1000 cm^{-1} is observed when the concentration is increased from 10^{-5} M to 2×10^{-3} M. The 1000 cm^{-1} shift represents the decrease in the magnitude of the REE as the concentration is increased, since no REE is observed for the concentrated solution (2×10^{-3} M) and its emission is identical to less concentrated solutions excited at the red edge.

Besides the observation of a REE at low temperatures, we

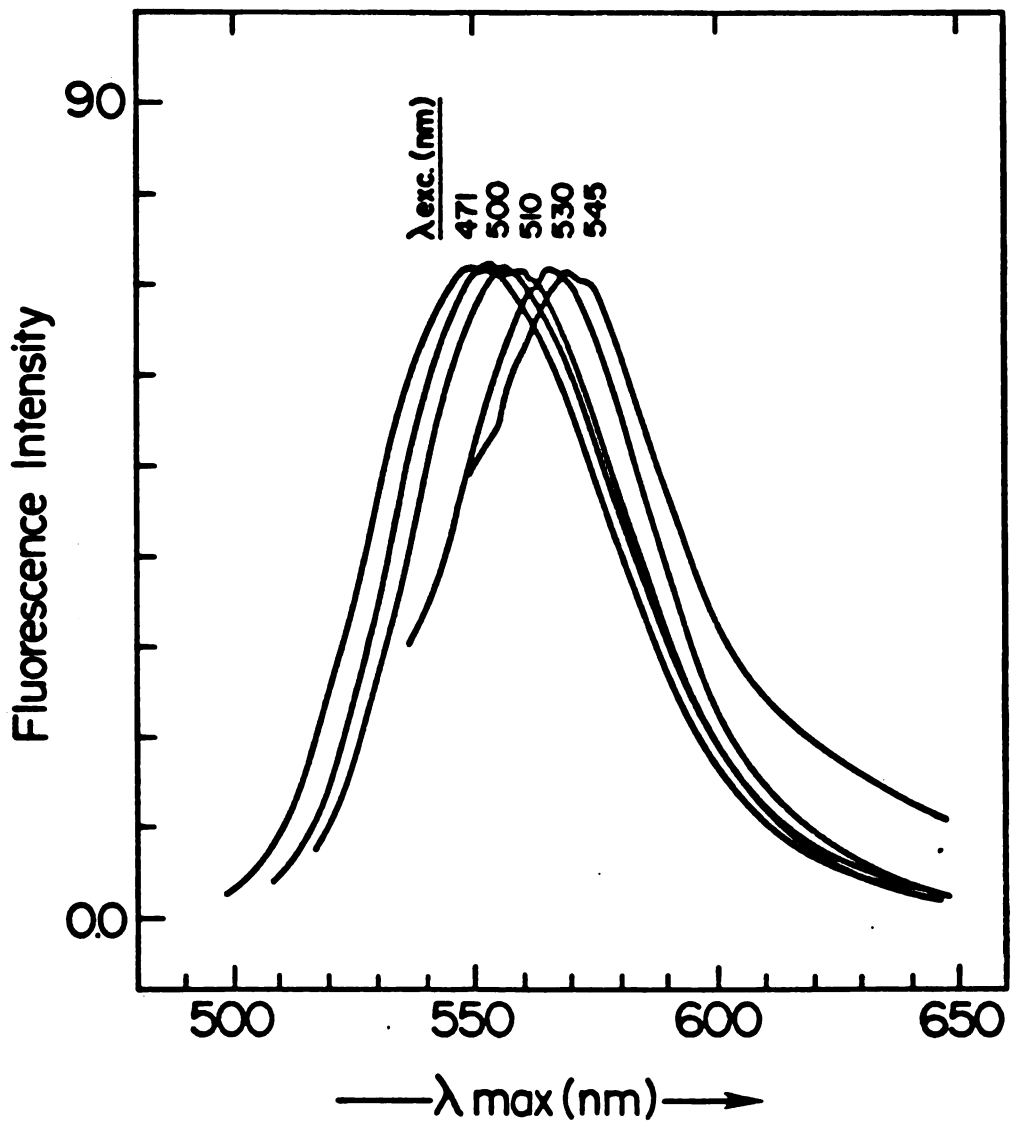


Figure 26. Fluorescence spectra of a dilute solution of pyridine merocyanine dye in ethanol at -135°C as a function of excitation wavelengths.

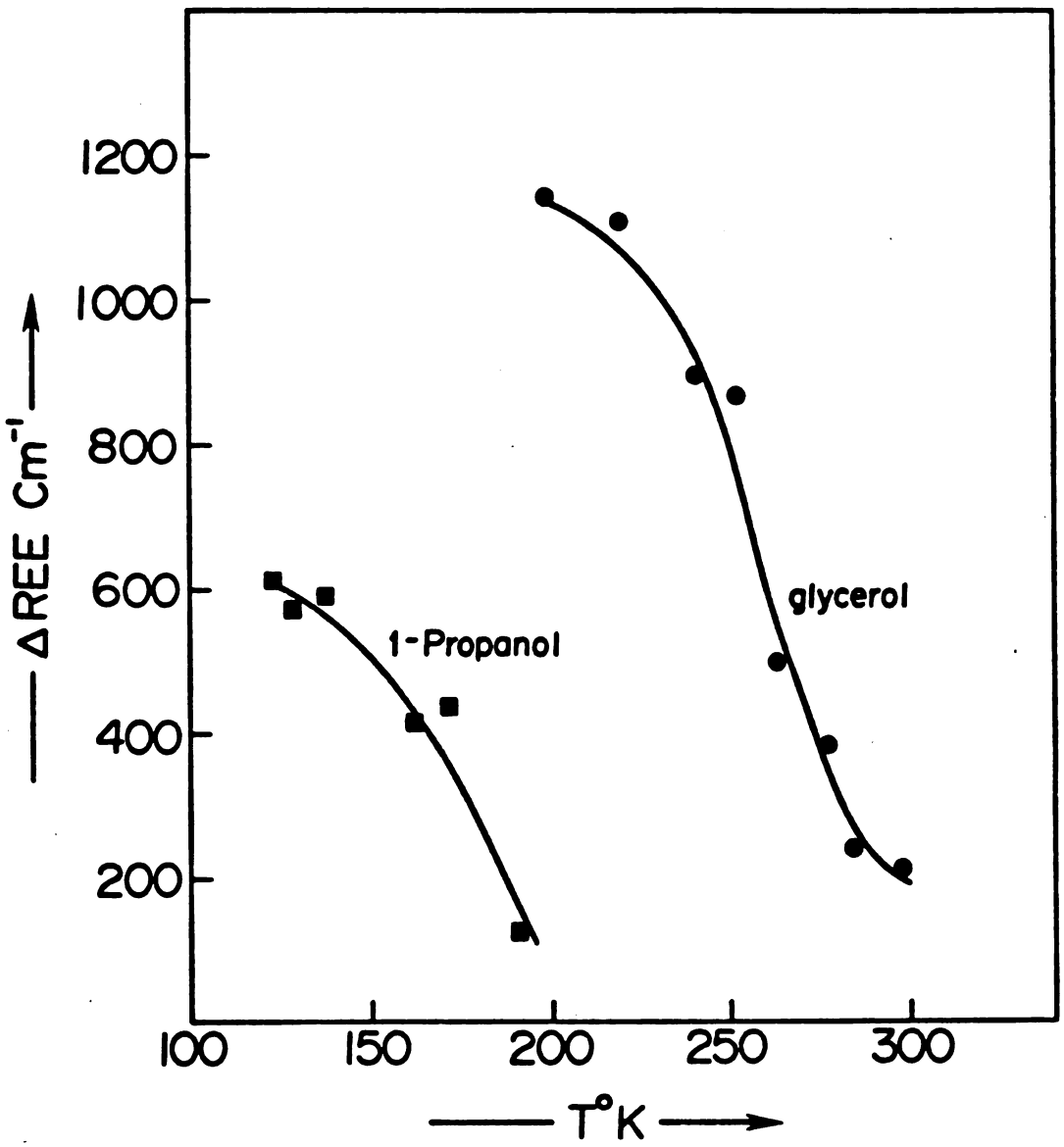


Figure 27. Temperature variation of REE (Red Edge Effect) for pyridine merocyanine dye in two different solvents.

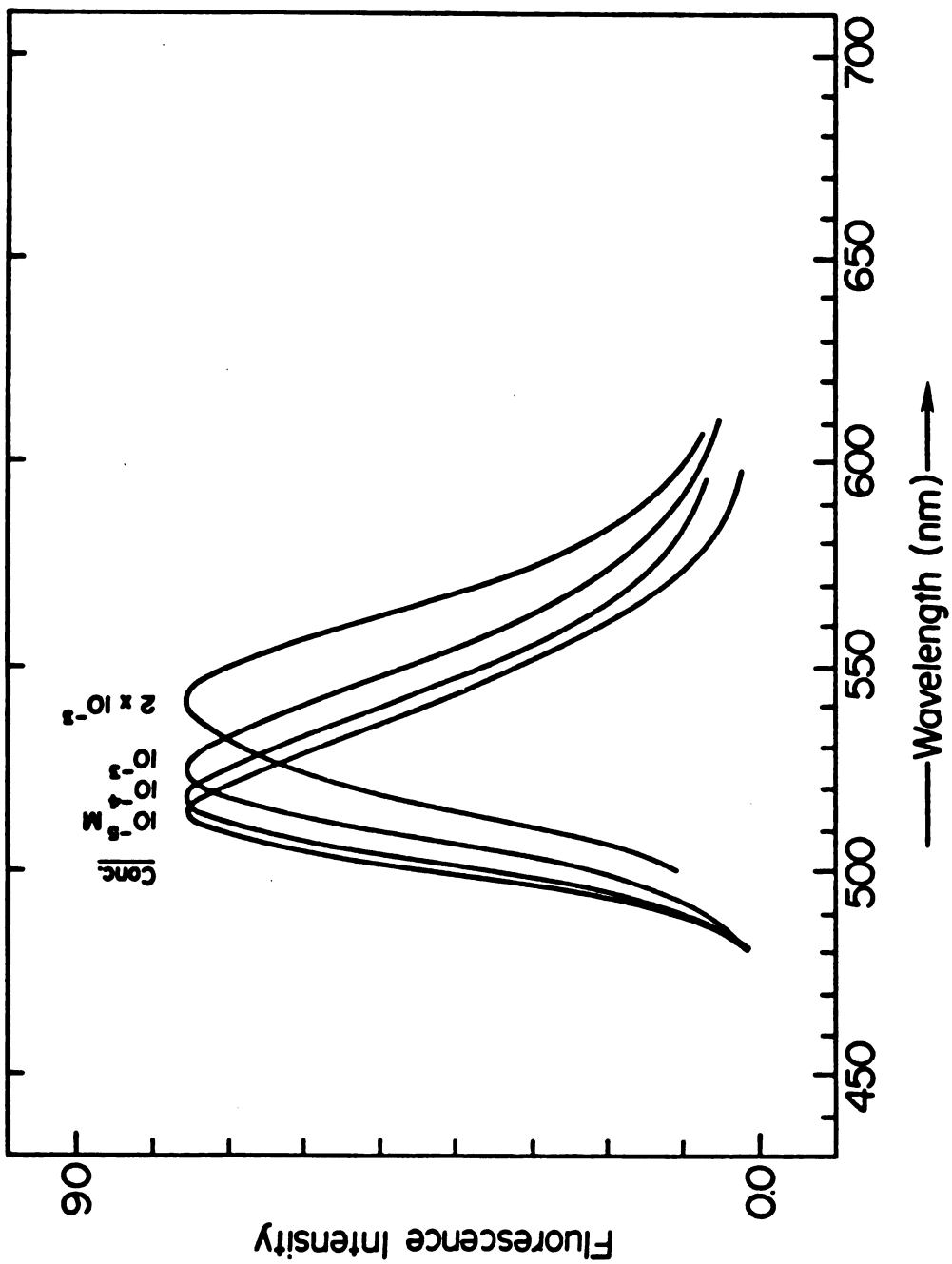


Figure 28. Fluorescence spectra of pyridine merocyanine dye of different concentrations in ethanol at 77 K at fixed excitation wavelength (the absorption maximum at 77 K ∿470 nm).

have also observed a REE in rigid media at room temperature. The results for the pyridine-merocyanine dye in PVA polymer matrix is shown in Figure (29). The magnitude of the REE at room temperature was about ≈450 cm^{-1} compared to ≈1200 cm^{-1} at 77 K.

The fluorescence spectrum of the dye undergoes a blue shift of 2100 cm^{-1} as the temperature is lowered to 77 K. This observation is demonstrated in Figures (30, 31) for ethanol and glycerol solutions, respectively; all solutions were excited at the absorption maximum.

The absorption spectra of the dye in ethanol (10^{-5} M) as a function of temperature are shown in Figure (32). A blue shift of ≈2100 cm^{-1} in going from room temperature to 77 K is observed. Only a small (≈500 cm^{-1}) blue shift in absorption is observed for the dye in PVA thin film as shown in Figure (33).

So far we have made the following experimental observations: first, the absence of a REE in fluid media; second, a large REE as the medium becomes rigid; third, the appearance of shoulders in the emission spectrum when the media become more rigid or when working with long chain alcohol solvents; fourth, the appearance of REE at room temperature in polymer films; fifth, the gradual decrease of the REE as the concentration is increased; sixth, the blue shift of the emission spectrum as the temperature is lowered, and seventh, the blue shift of the absorption spectrum

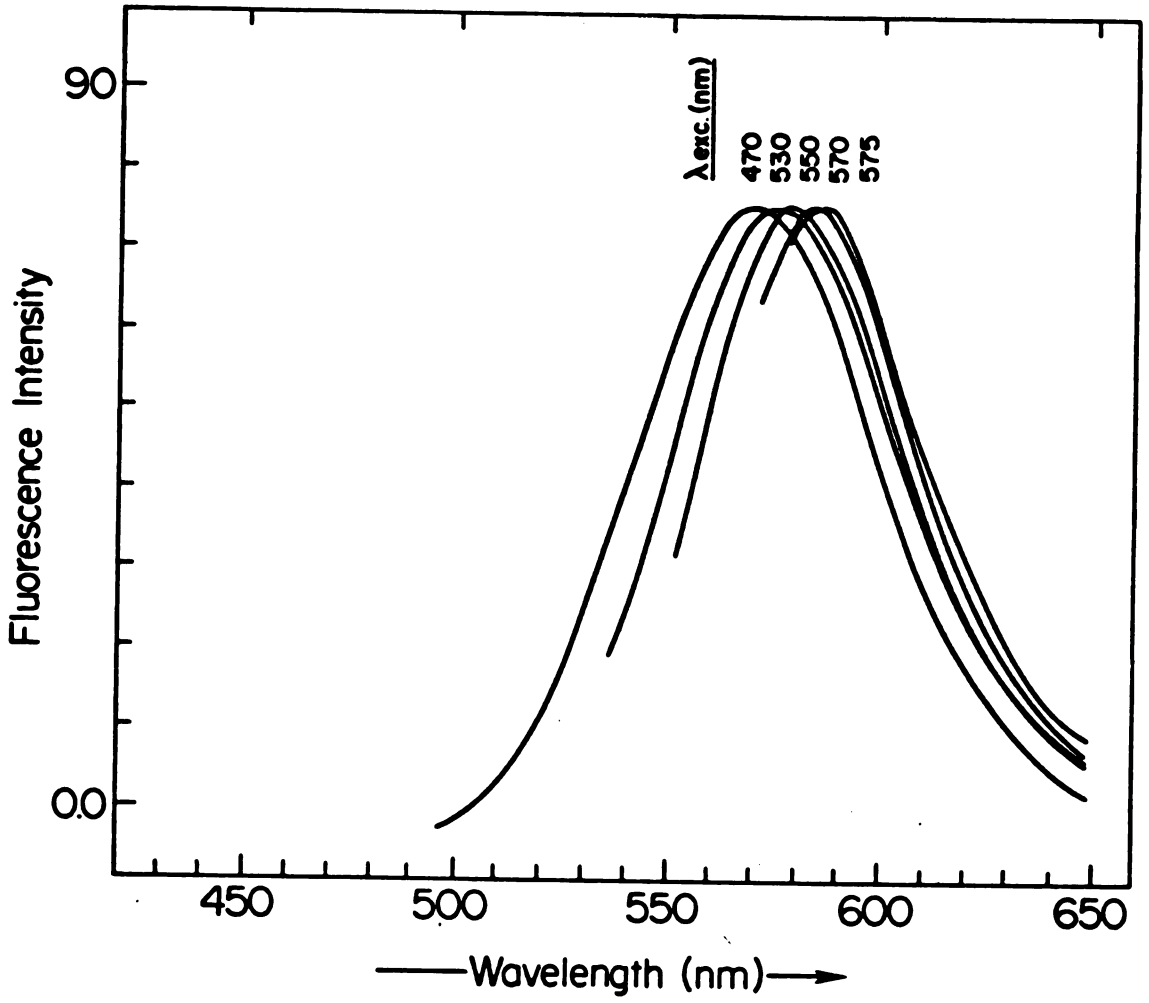


Figure 29. Fluorescence spectra of pyridine merocyanine dye in PVA (polyvinyl alcohol) thin film at room temperature as a function of excitation wavelengths.

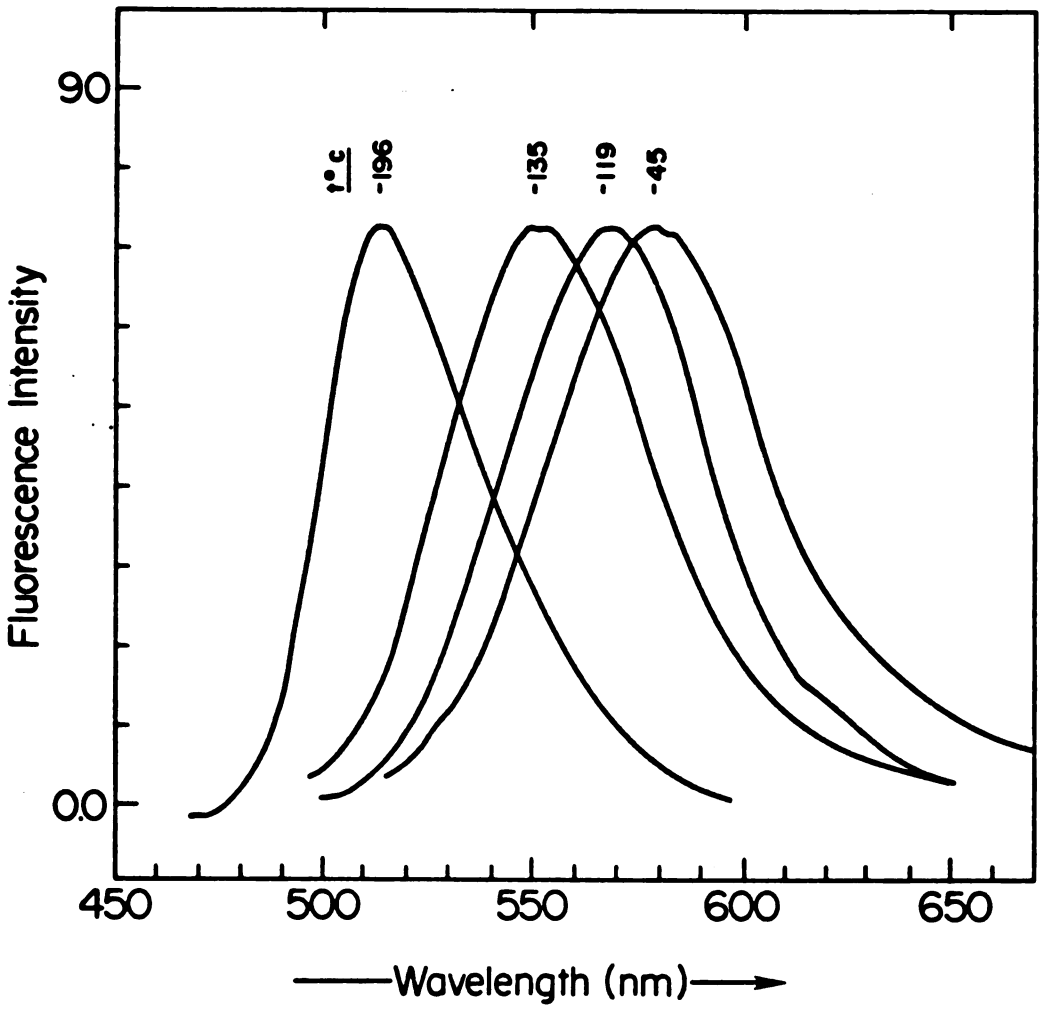


Figure 30. Fluorescence spectra of ($<10^{-5}$ M) pyridine merocyanine dye in ethanol at different temperatures. (The excitation wavelength was the absorption maximum at each temperature.)

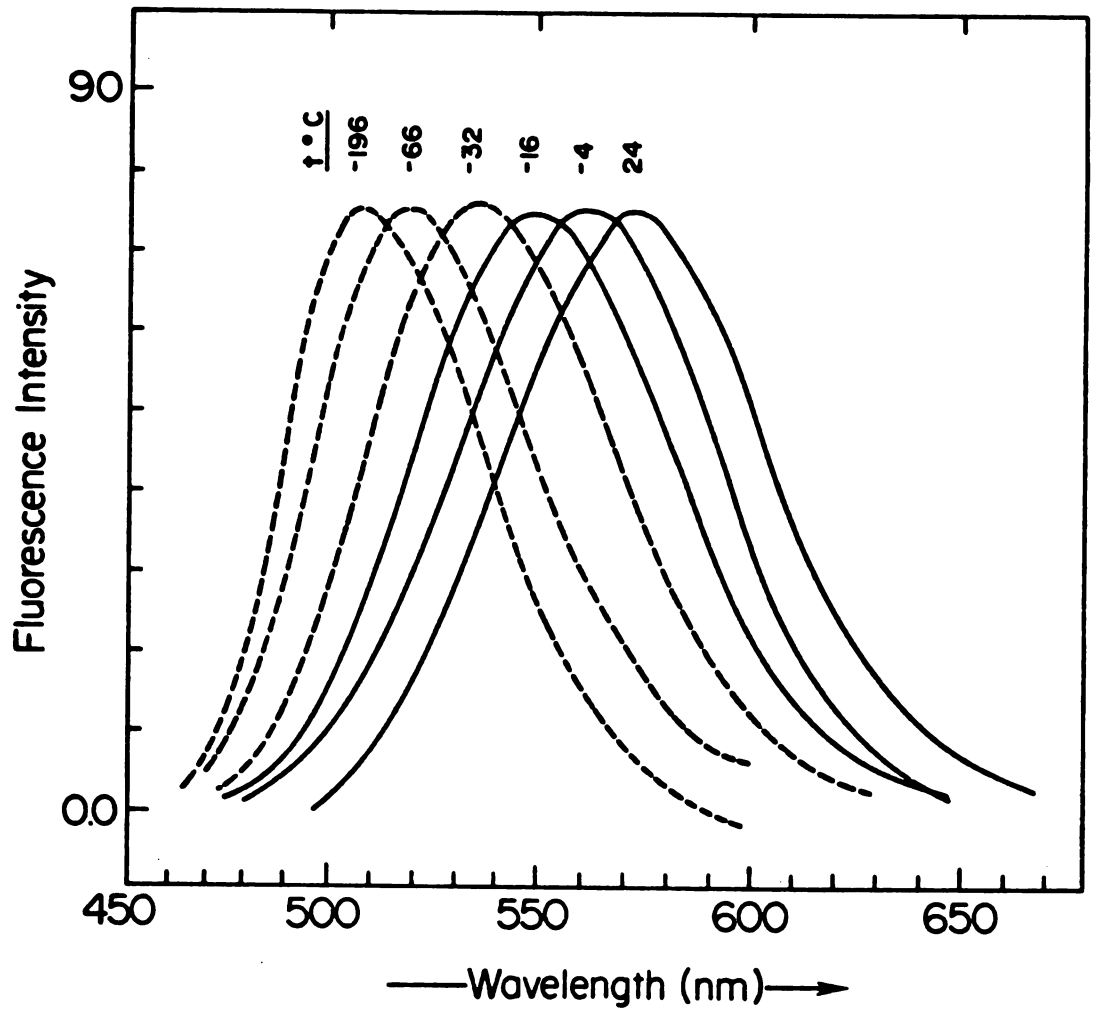


Figure 31. Fluorescence spectra of a dilute solution of ($<10^{-5}$ M) pyridine merocyanine dye in glycerol at different temperatures. (The excitation wavelength was the absorption maximum at each temperature.)

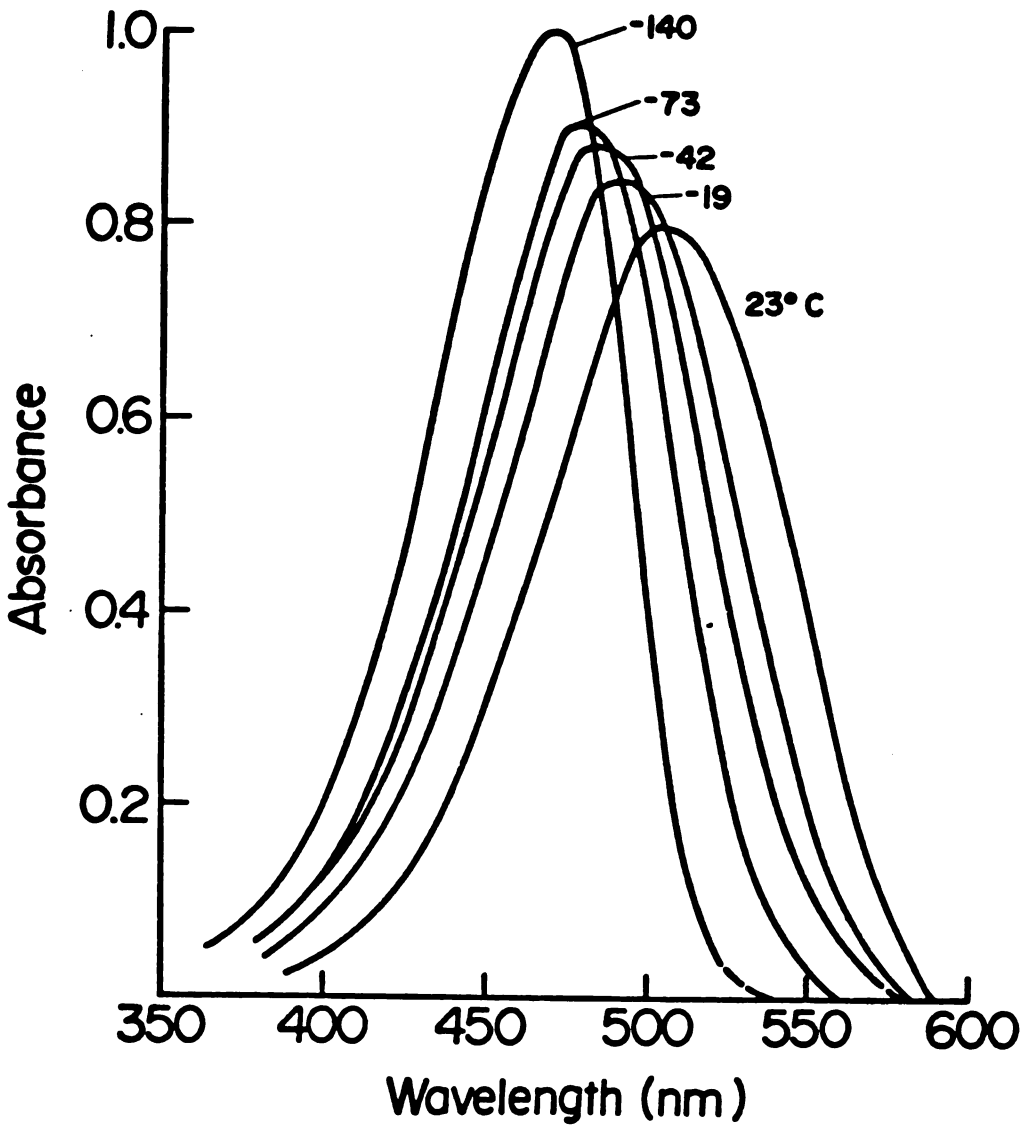


Figure 32. Absorption spectra of pyridine merocyanine dye in ethanol ($\sim 10^{-5}$ M) as a function of temperatures. The temperature in °C is indicated on each spectrum.

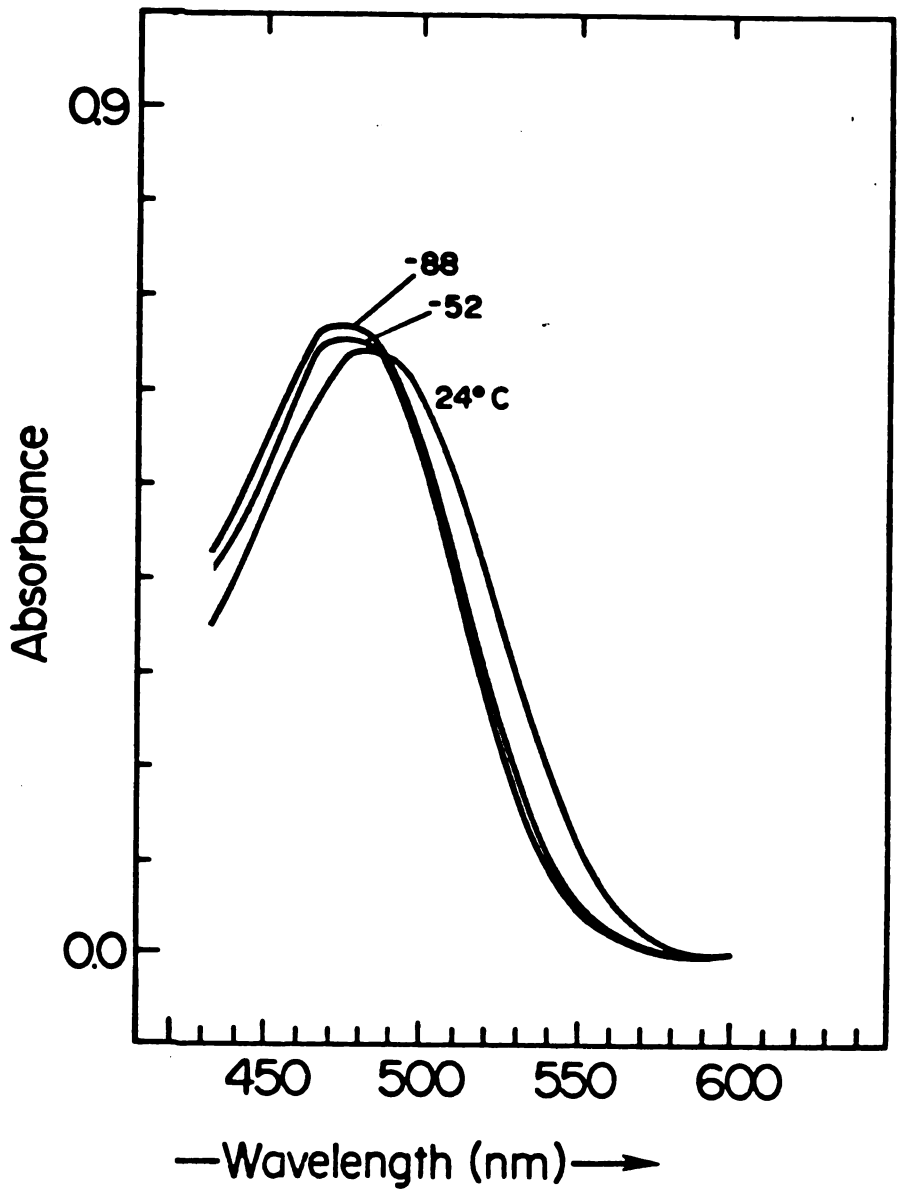


Figure 33. Absorption spectra of pyridine merocyanine dye in PVA (polyvinyl alcohol) thin film as a function of temperature.

as the temperature is lowered.

In order to interpret most of these observations we[79] assume a statistical distribution of the solute among different solvation sites. Thus, even in a homogeneous condensed phase the polar solute molecules are expected to occupy a variety of solvation sites at any given time giving rise to different absorption energies corresponding to the same electronic transitions. A qualitative potential energy diagram representing the interaction of the dye molecule in its ground and excited states with a particular solvation site a is shown in Figure (34). The interaction energy is assumed to depend on two coordinates, one representing the orientation of the polar solvent molecules with respect to the solute dipole symbolized by θ. The other is a translational coordinate, R, representing the intermolecular separation between the solute and the solvent molecules. The dependence of the interaction energy with respect to θ and R is drawn in two perpendicular planes. In the excited state, the magnitude of the interaction energy of the equilibrium configuration is smaller than that of the ground state reflecting a decrease in the dipole moment of the solute upon excitation. Excitation results in a sudden decrease of the solute dipole moment giving rise to a strained Franck-Condon state which will relax along the translational coordinate, R, to the equilibrium excited-state configuration followed by emission. Emission leads

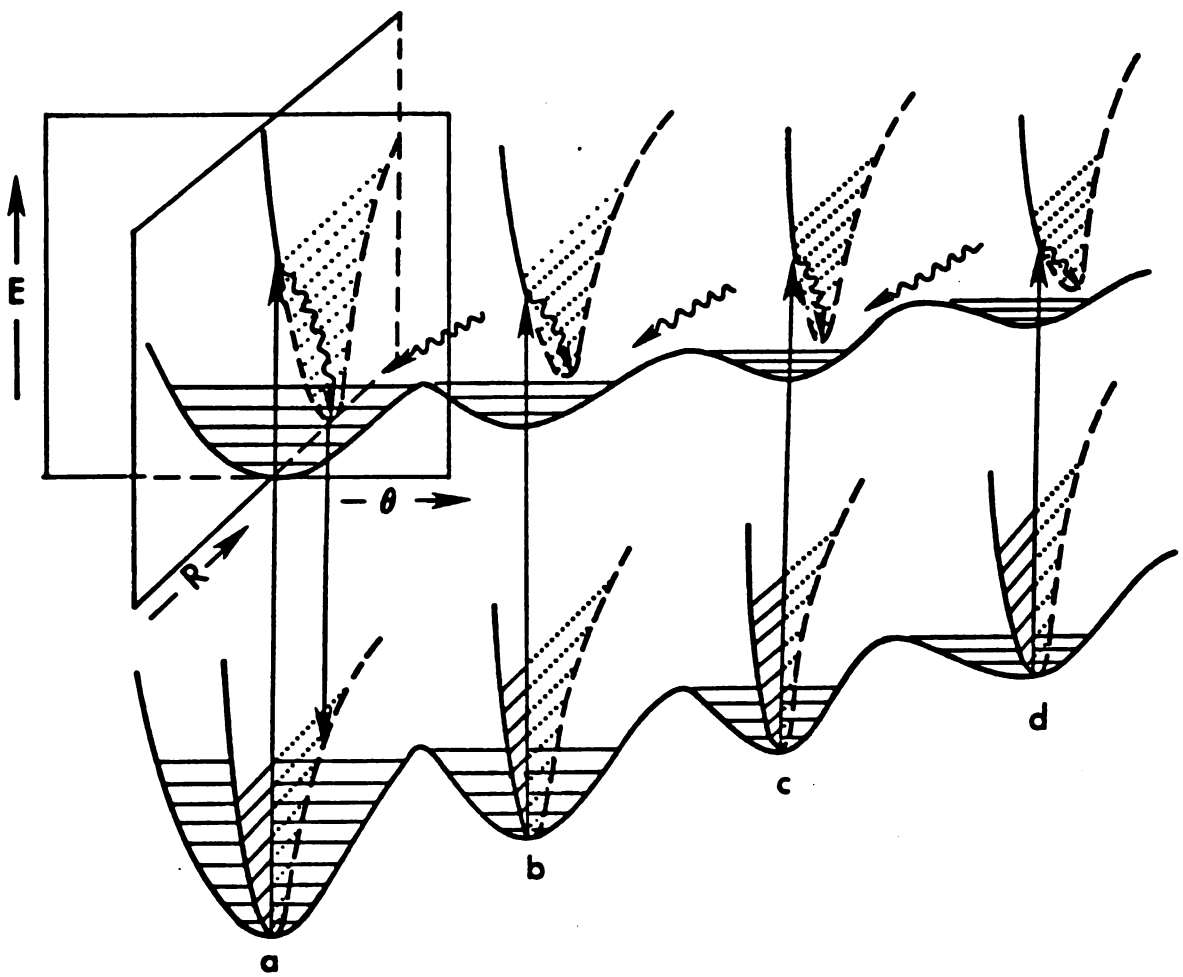


Figure 34. Ground and excited state potential energy curves for a molecular system in which the dipole moment decreases as a result of excitation. Solvation sites, a, b, c and d differ in the orientation of the solvent molecules, θ, but are assumed to have the same intermolecular separation R for simplicity. Solvation site a represents the most stable orientation.

to a sudden increase in the dipole moment of the solute giving rise to a strained Franck-Condon ground state which will relax along R to the equilibrium ground state. The solute may occupy different solvation sites differing in the orientation of the solvent molecules, θ, as well as the intermolecular separation R. In Figure (34), we have represented different solvation sites a, b, c and d having different θ's and the same R for simplicity. Solvation site a represents the most favorable orientation with the largest interaction energy while site d represents the least favorable orientation. In a fluid medium the lifetime of the various solvation sites is short compared to the excited-state lifetime and a dynamic equilibrium exist. One may think of viscosity-dependent barriers between these sites[43] the heights of which depend on the rigidity of the medium. Excitation of the solute dye molecule in site d will lead to a fast relaxation along the R coordinate as well as the θ coordinate and emission originates from the equilibrium excited-state configuration corresponding to the most stable solvation site, i.e., site a. Emission will occur at the same wavelength independent of the excitation wavelength. This accounts for the lack of REE in fluid media represented by the first observation where a dynamic equilibrium exists among the various solvation sites. If the medium is made rigid so that the relaxation rate constant along θ and R is smaller than the fluorescence

rate constant, emission will occur from a Franck-Condon excited state corresponding to the solvation site specifically excited. In rigid media the dynamic equilibrium between different solvation sites is lost, and excitation of the solute in a given solvation site will lead to an emission of the solute in that solvation site. In this case, an excitation wavelength dependence of the fluorescence energy results, i.e., a REE is observed and is experimentally observed in Figures (21-24).

The observation of shoulders in the emission spectra as shown in Figures (21-23 and 25) as the medium becomes rigid and as the alcohol chain becomes longer is explained in terms of inhomogeneous broadening and is similar to the Shpol'skii effect.[80] The inhomogeneous broadening results from the statistical distribution of solute molecules among the different solvation sites that become static in rigid media. The presence of different local environments gives rise to the excitation wavelength dependence of the emission and the appearance of shoulders in the emission spectra particularly in long-chain alcohols.

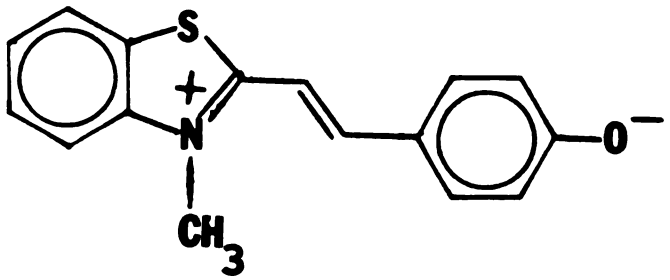
The appearance of REE at room temperature in PVA polymer film, Figure (29) is explained in terms of a matrix that is rigid enough at room temperature to prevent complete equilibrium between different solvation sites. However the REE will be less than that observed at 77 K (Figure 24).

The decrease in the emission dependence upon excitation wavelength at higher concentration as shown in Figure (28) is anticipated as a consequence of singlet-singlet non-radiative transfer from molecular subclasses of higher transition energies to those of lower energy emissions. As a result, emission obtained by excitation into the middle of the chromophore absorption band becomes red-shifted at higher concentrations, which decreases the observed exciting wavelength dependence. In the high concentration limit it is expected that only long wavelength emission (corresponding to solvated dye molecules with lowest transition energies) would be observed at all exciting wavelengths.

The blue shift of the emission spectrum upon lowering the temperature (Figures 30 and 31) is explained in terms of the relaxation rates of the solvent. In fluid media, solvent-shell relaxation around solute molecules occurs fast enough before chromophore emission, i.e., emission will occur from an equilibrium excited state configuration. In a rigid media, solute molecules emit radiation long before solvent cage relaxation, i.e., from a non-equilibrium excited state configuration, the strained Franck-Condon state. Hence emission will be blue shifted relative to the room temperature emission. The lifetime of the excited solute and the relaxation time of the solvent cage become comparable at intermediate temperatures, i.e., at intermediate viscosities. Hence, emission will occur from

intermediate states which will be red shifted relative to emission in rigid media, or blue shifted relative to room temperature (fluid) emission. The blue shift of the absorption at low temperatures (Figures 32 and 33) is explained in terms of temperature-dependent inhomogeneous spectral broadening. Lowering the temperature will change the statistical distribution in favor of solute molecules occupying the most stable solvation sites which absorb at shorter wavelengths. This leads to an apparent blue-shift of the absorption as one lowers the temperature.

B. Benzothiazole Merocyanine



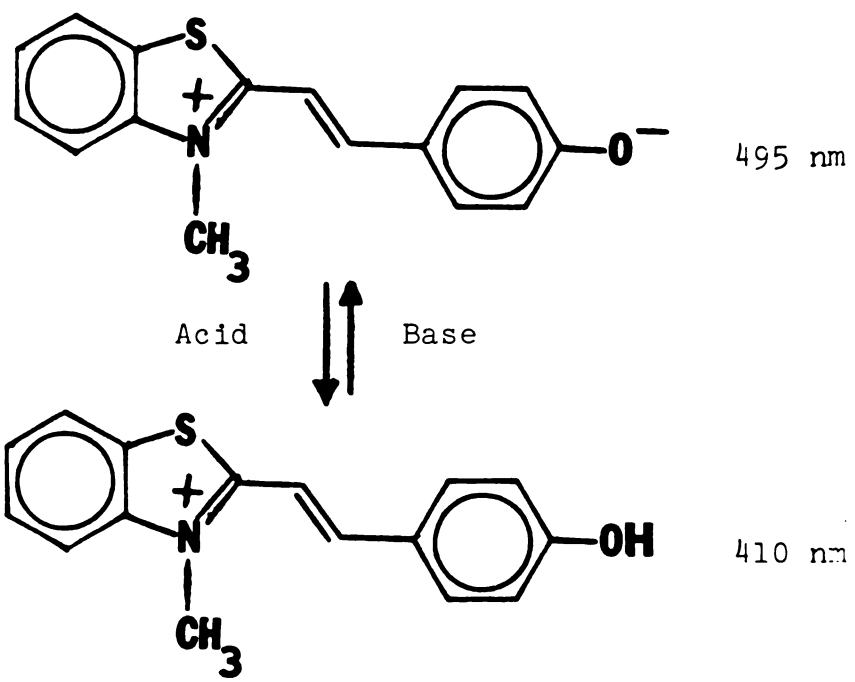
This system undergoes a decrease in dipole moment upon excitation. We have prepared this particular merocyanine dye and have measured its absorption and emission in solvents of different polarities. Its absorption spectra was already measured by McRae.[10]

Like that of pyridine merocyanine, its absorption spectrum is pH dependent and it probably undergoes cis-trans isomerization. The longest wavelength absorption band of the

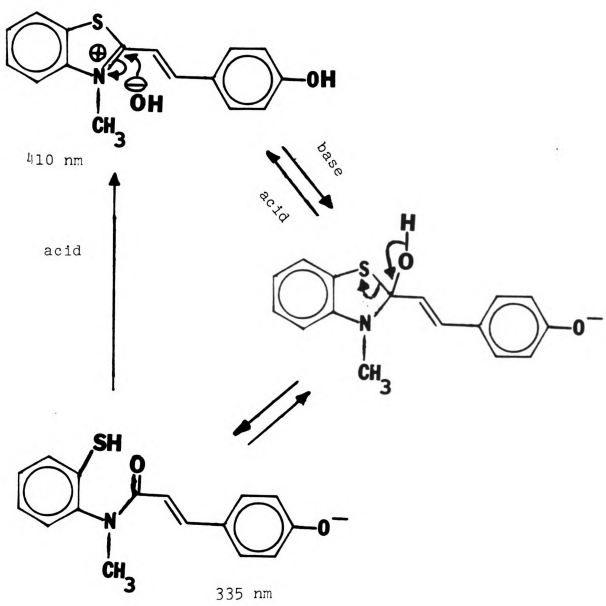
dye in aqueous solution occurs at 495 nm in basic media. The acidic form of the dye absorb at 410 nm in H_2O. Both forms are present at intermediate pH values. We have observed the disappearance of the color of the dye solutions after leaving them overnight, and another absorption at 335 nm was obtained. Adding acid generates the 410 nm band absorption which gives the 495 nm absorption when excess base was added.

Our experiments show that the 335 nm absorption band is a result of chemical reaction of the dye with the base. Private communication with Professor Reusch[106] helped in the elucidation of the basic hydrolysis of the dye at the C-S bond:

Scheme I in water



Scheme II

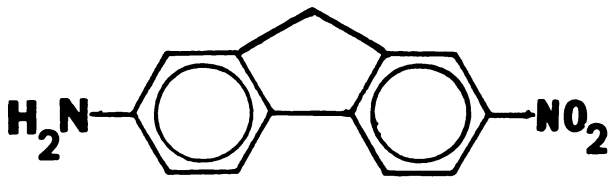


The photochemical reactions that occur in this system made it difficult to study its emission and optical properties. Since many authors have worked with this dye, it seems important to report our findings especially because similar dyes are used in membrane probe studies in aqueous media.

II. Molecular Systems That Undergo a Large Increase in Dipole Moment as a Result of Electronic Excitation

As an example of these molecular systems we have studied the absorption, emission and excitation wavelength dependence of the fluorescence of 2-amino-7-nitrofluorene (ANF) and 4,4'-amino-nitrodiphenyl (AND). These molecules undergo a dipole moment increase[92] by 18D and 12D, respectively upon electronic excitation.

A. 2-Amino-7-nitrofluorene (ANF)



ANF

The room temperature absorption spectra and emission maxima of ANF in solvents of different polarities are shown in Figure (15) and Table (II).[92,96,107] The absorption spectrum of ANF exhibits a red shift in media of increasing polarity. The absorption maximum in 3MP (3-methylpentane) occurs at 365 nm while in ethanol the maximum occurs at 398 nm, a red shift of $\approx$2300 cm^{-1}. The room temperature fluorescence spectra in Table (II)[92,96,107] show a much larger red shift as

the solvent polarity is increased. It undergoes ≈6000 cm^{-1} red shift in going from benzene to methanol. These observations are consistent with a dipole moment increase in the excited state.

Earlier investigations of ANF include the work of Lippert, et al.[92,107-109] who has made observations of the fluorescence shift as a function of temperature and solvent mixture. Their conclusions were that in viscous media (or alcoholic solvents at low temperatures) the fluorescence spectrum undergoes a blue-shift because the rate constant of dielectric relaxation becomes comparable to the fluorescence decay time. Thus, the fluorescence originates from progressively less relaxed states as molecular motion is inhibited. The work of Topp, et al.[96,110,111] indicates that the shape of the spectra and the fluorescence quantum yields also depend on the solvent indicating the presence of some dynamic processes which are in the picosecond range. Thus, they used special techniques to obtain the fluorescence time profiles and emission spectra of the molecule in different states of solvation. This is similar to the nanosecond time resolved spectroscopy technique developed by Ware, et al.[48] for ANS and has been discussed in Chapter II. They showed[96,110,111] that the Stokes' shift of ANF can be time-resolved in a picosecond laser experiment and gives information about the rate of solvent polarization by the excited state dipole. They

have shown that this rate is faster in both 2-propanol and O-dichlorobenzene than the calculated T_2 relaxation time measured by microwave absorption. They also measured the time profile at different places in the fluorescence spectrum of ANF by varying the relative concentration of benzene and 2-propanol in mixed solutions. The delay profiles measured at 490 and 680 nm were found to be exponential. What they found also is that in hydrogen bonded solvents such as 2-propanol, the rate of dielectric polarization is fast enough that at room temperature they could not resolve the shift from their pulse duration. However, when 2-propanol was diluted by benzene the rate of the shift decreased proportionately and the extent of the shift could no longer be explained by the bulk dielectric properties of the solvent. In conclusion, they showed that the environmental Franck-Condon relaxation is complete before relaxation decay occurs, the differential in rates being about one order of magnitude. They proved that the actual position of the fluorescence spectrum observed by time-integrated measurements does not result from a competition between the two processes as suggested by Lippert.[1]

The room temperature fluorescence of fluid dilute solutions of ANF in different polar solvents is hardly fluorescent. Our excitation wavelength dependence of the fluorescence was studied in rigid media at 77 K and in polymer matrices at 77 K and room temperature. Under

these circumstances we have observed a large red edge effect (REE) for ANF. The fluorescence spectra of dilute solutions of ANF in ethanol, PVA (poly(vinyl)alcohol) film and polystyrene film at 77 K as a function of excitation wavelength are shown in Figures (35-37), respectively. A large red shift of ≈900 cm^{-1} in ethanol, ≈1300 cm^{-1} in PVA film and ≈1600 cm^{-1} in polystyrene film was observed as the excitation wavelength was increased from the absorption maximum at 77 K (the number at the top left of figures cited) to the red edge of the absorption band (the number at the top right of figures cited). Such observations were accompanied by the appearance of shoulders in the emission spectra as the excitation wavelength was moved to the red. As in the case of pyridine merocyanine dye, the magnitude of this REE is viscosity dependent. It is decreased by warming up the solutions and it disappears in fluid media at room temperature. The magnitude of the REE in PVA film is ≈600 cm^{-1} at room temperature compared to ≈1300 cm^{-1} at 77 K. Similarly the REE in polystyrene film at room temperature is ≈850 cm^{-1} compared to ≈1600 cm^{-1} at 77 K. These observations are illustrated in Figures (38 and 39) respectively.

The absorption spectra of ANF in different polar solvents undergo red shifts when the temperature is reduced. Figure (40) shows the absorption spectra of dilute solution of ANF in ethanol at different temperatures. A

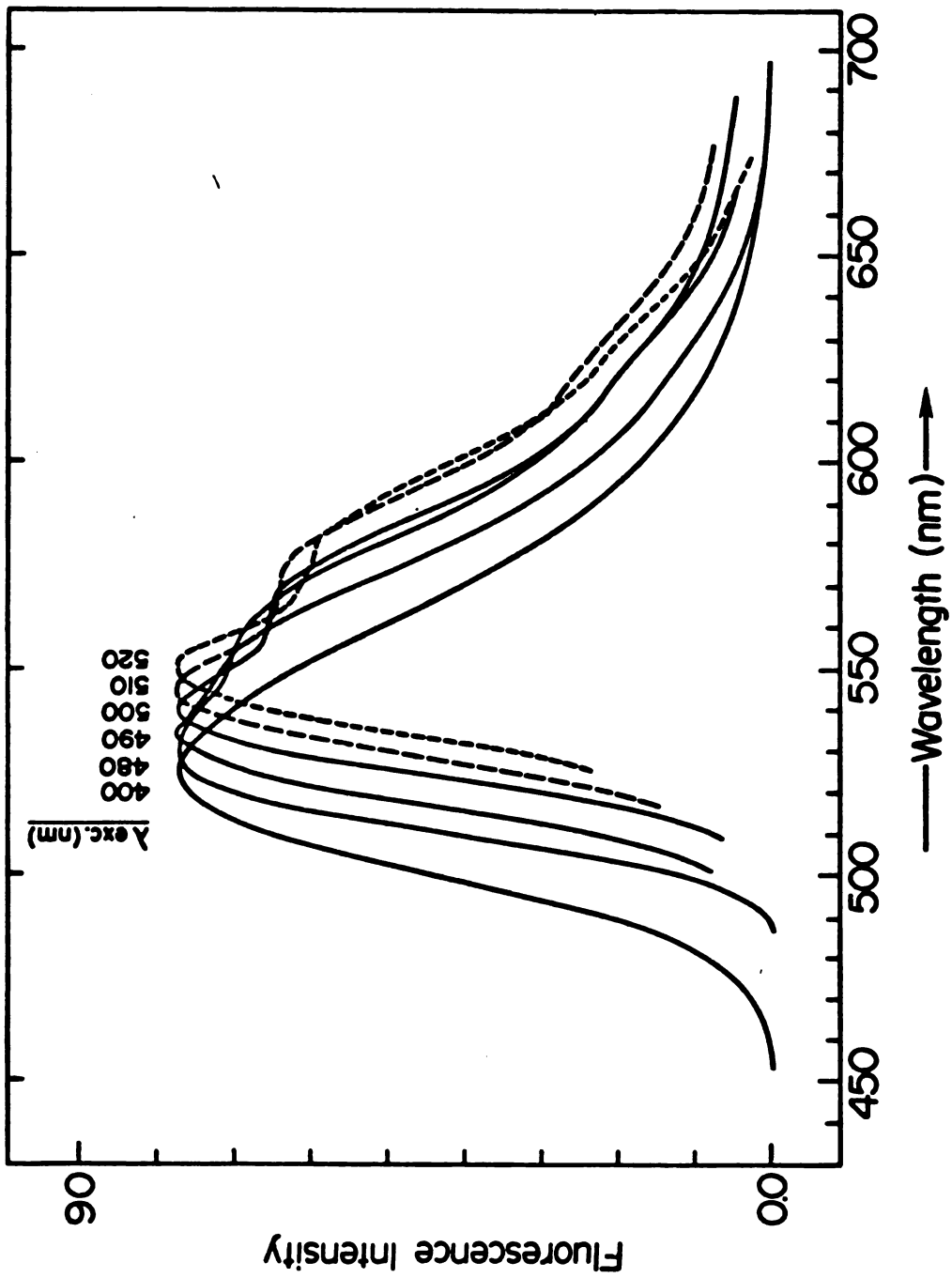


Figure 35. Fluorescence spectra of a dilute solution of ANF in ethanol at 77 K as a function of excitation wavelengths.

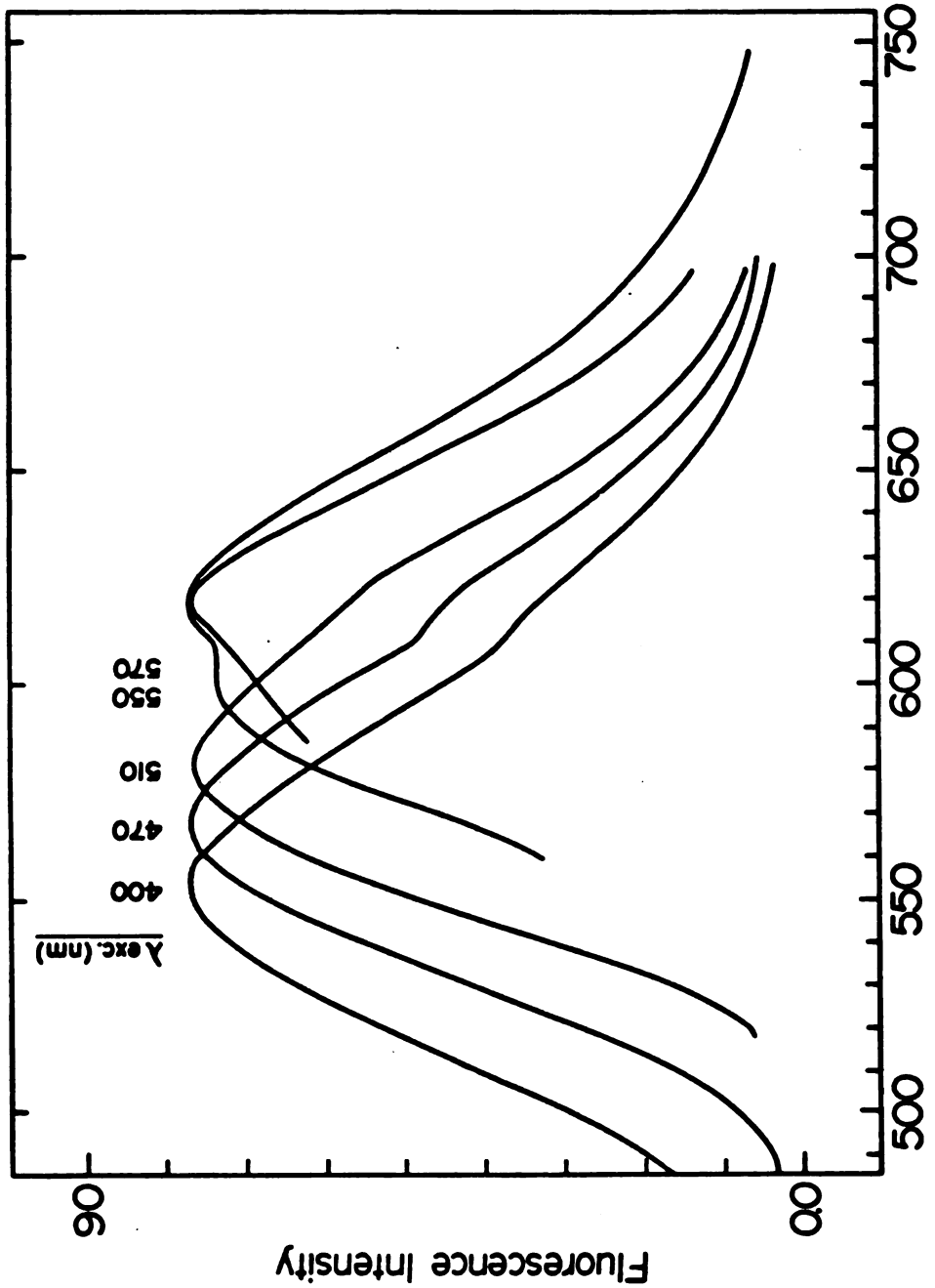


Figure 36. Fluorescence spectra of ANF in PVA thin film at 77 K as a function of excitation wavelengths.

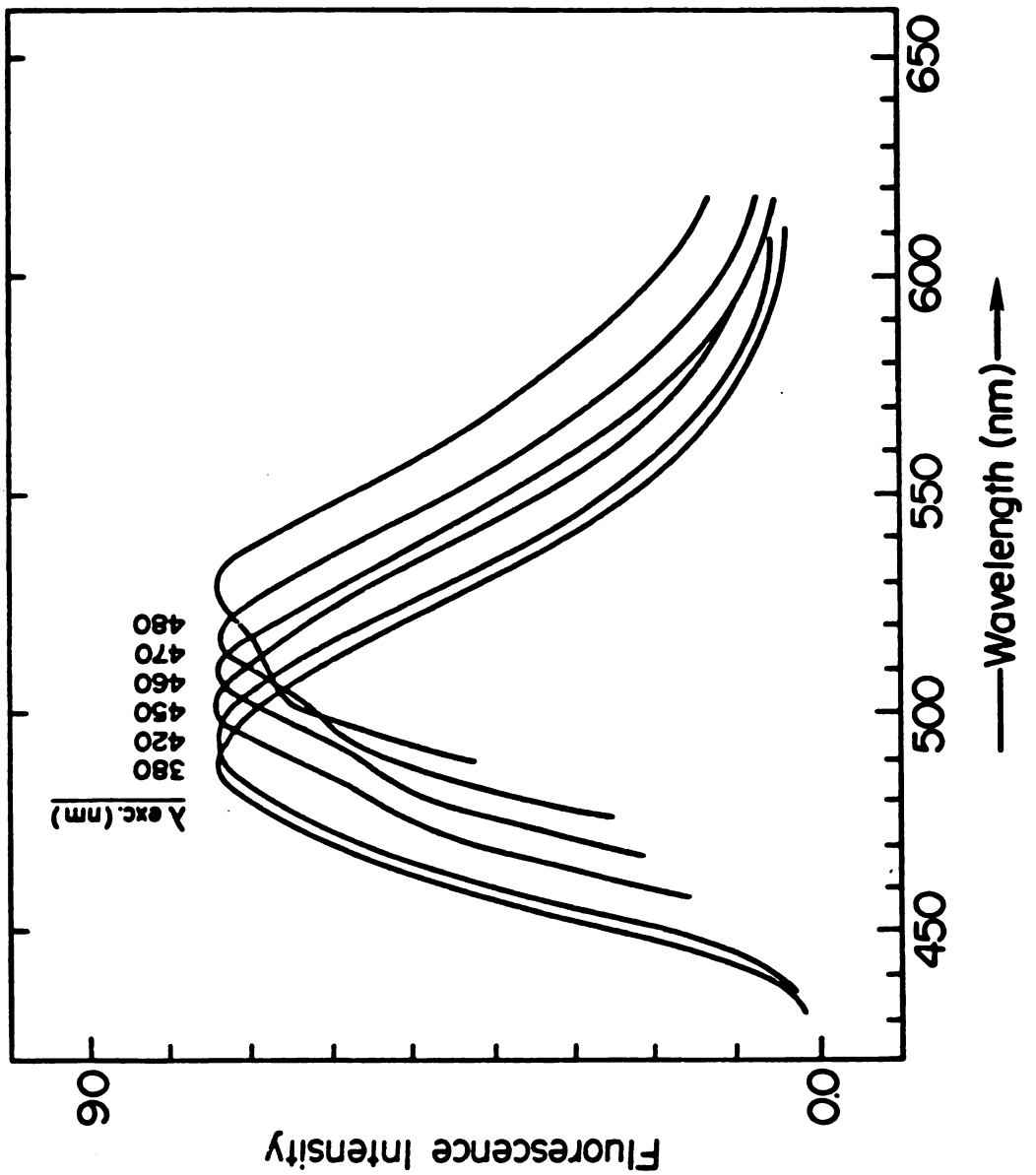


Figure 37. Fluorescence spectra of ANF in polystyrene thin film at 77 K as a function of excitation wavelengths.

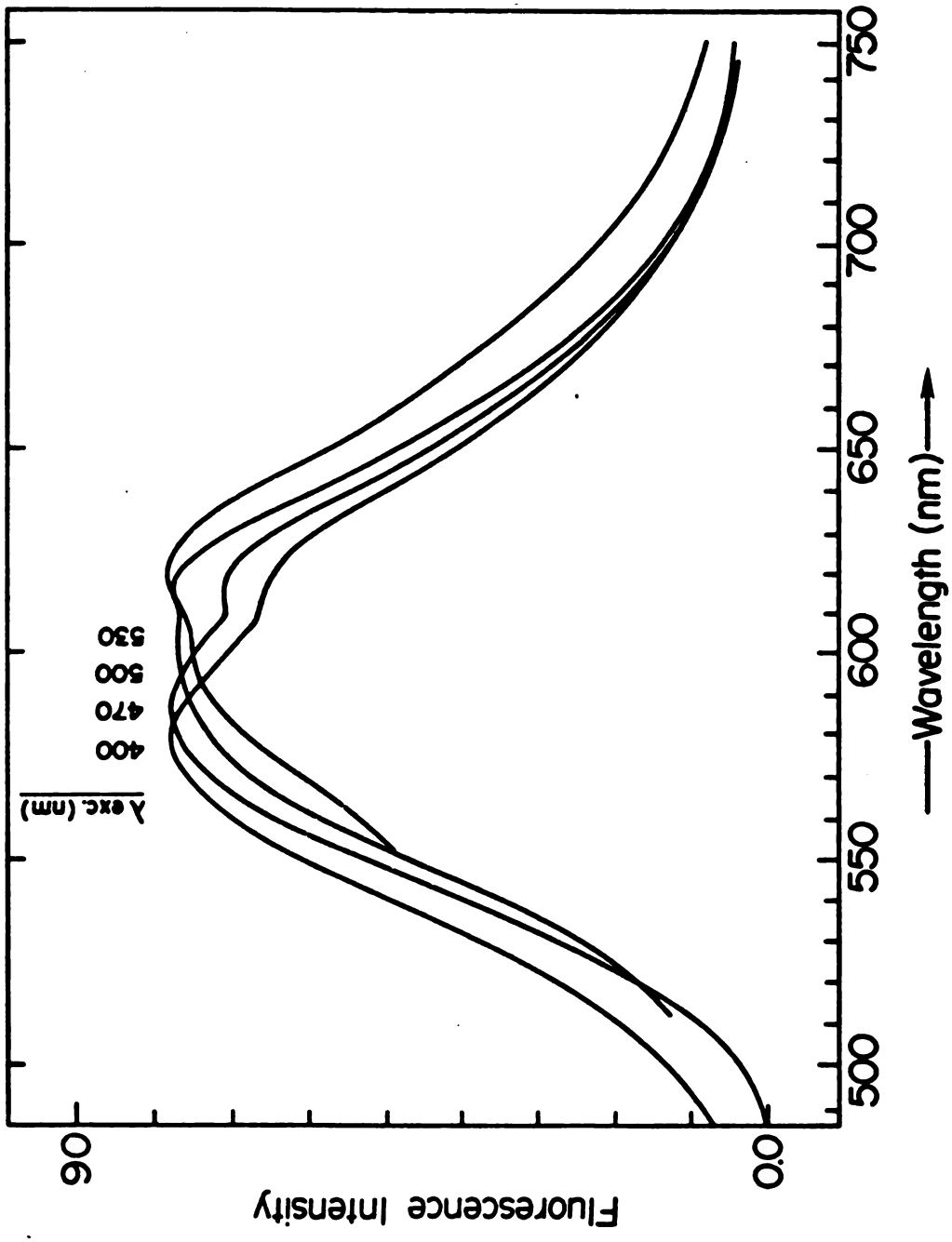


Figure 38. Fluorescence spectra of ANF in PVA thin film at room temperature as a function of excitation wavelengths.

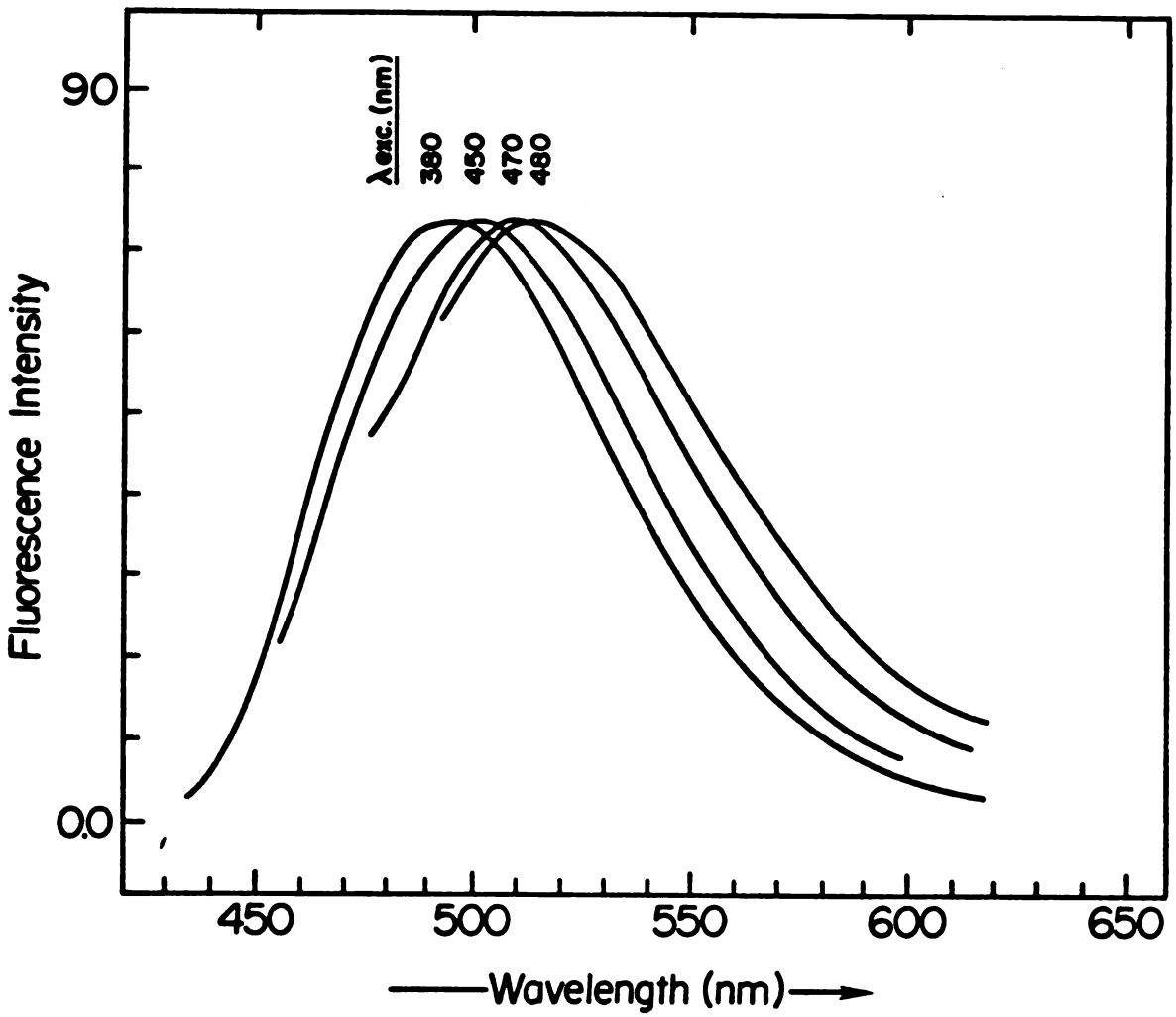


Figure 39. Fluorescence spectra of ANF in polystyrene thin film at room temperature as a function of excitation wavelengths.

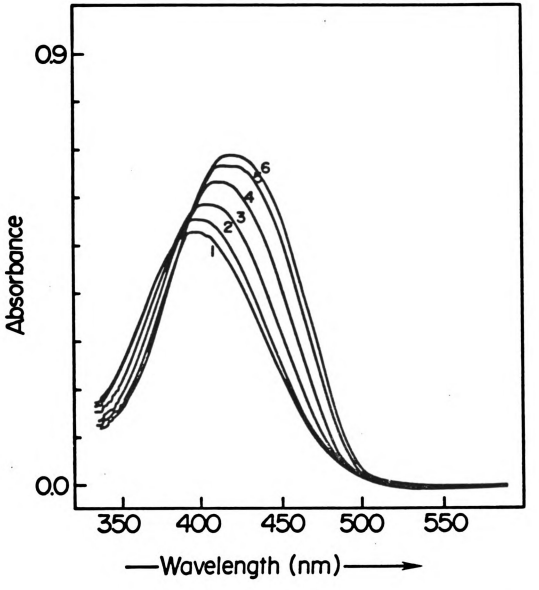


Figure 40. Absorption spectra of ANF in ethanol (3×10^{-5} M) as a function of temperature: (1) 24°C, (2) 0°C, (3) -36°C, (4) -78°C, (5) -104°C, (6) -115°C.

red shift of ≈1500 cm^{-1} was observed upon lowering the temperature to ≈-115°C.

So far we have made the following experimental observations: the absence of a REE in fluid media, a large REE in rigid solvents at 77 K and in polymer matrices at room temperature and 77 K, the appearance of shoulders in the emission spectra when exciting at the red edge, and the red shift of the absorption spectrum as the temperature is lowered.

In comparing these observations with those in the case of pyridine merocyanine dye, one should recall that for ANF the dipole moment is increased in the excited state. A statistical distribution of the solute among different solvation sites is assumed. Thus even in a homogeneous condensed phase, the polar ANF molecules are expected to occupy a variety of solvation sites at any given time, giving rise to different absorption energies corresponding to the same electronic transition. A qualitative potential energy diagram representing the interaction of the ANF molecule in its ground and excited states with a particular solvation site a is shown in Figure (41).

In the excited state, the magnitude of the interaction energy of the equilibrium configuration is greater than that of the ground state, reflecting an increase in the dipole moment of the solute upon excitation. Excitation results in a sudden increase of the solute dipole moment,

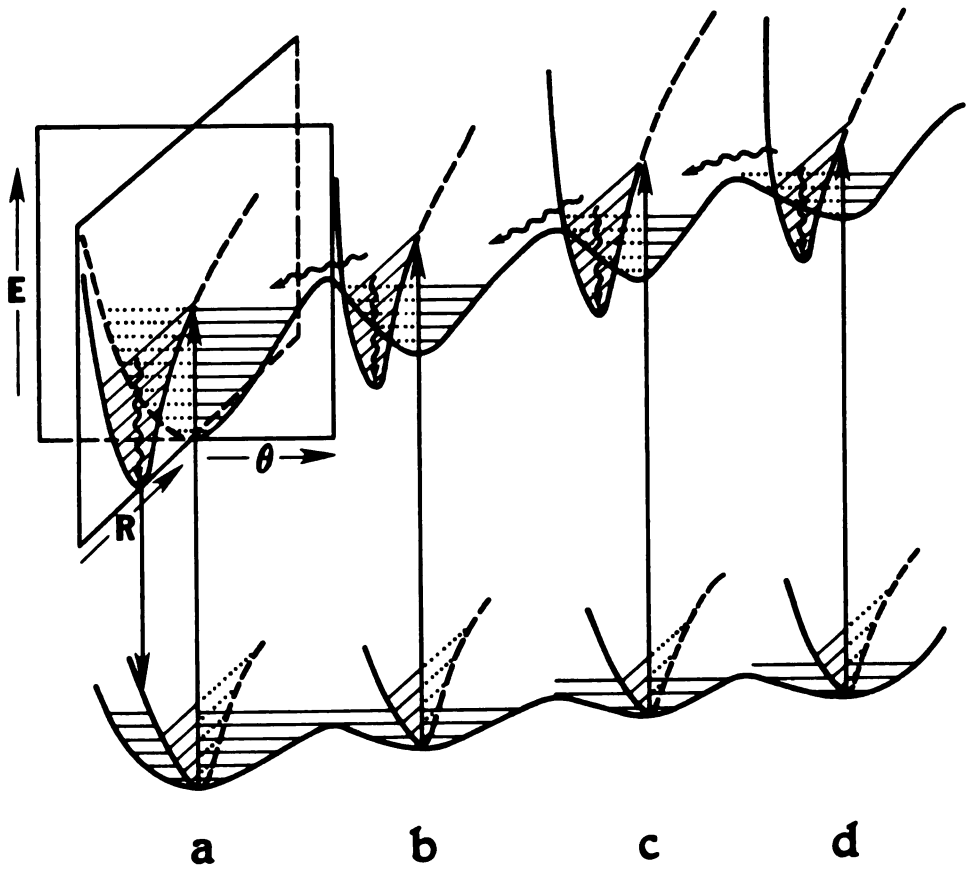


Figure 41. Ground and excited state potential energy curves for a molecular system in which the dipole moment increases as a result of excitation. Solvation sites, a, b, c and d differ in the orientation of the solvent molecules, θ, but are assumed to have the same intermolecular separation R for simplicity. Solvation site a represents the most stable orientation.

giving rise to a strained Franck-Condon state which will relax along the translational coordinate, R, to the equilibrium excited state configuration followed by emission. Emission leads to a sudden decrease in the dipole moment of the solute giving rise to a Strained Franck-Condon ground state which will relax along R to the equilibrium ground state. The solute may occupy different solvation sites differing in the orientation of the solvent molecules, θ, as well as the intermolecular separation R. In Figure (41) we represented different solvation sites a, b, c, and d having different θ's and the same R for simplicity. Solvation site a represents the most favorable orientation with the largest interaction energy and the least transition energy while site d represents the least favorable orientation with the highest transition energy. In fluid medium the lifetime of the various solvation sites is short compared to the excited-state lifetime and a dynamic equilibrium exists. One may think of a viscosity-dependent barrier[44,45] between these sites, the height of which depends on the rigidity of the medium. Excitation of the solute molecule in site d will lead to a fast relaxation along the R coordinates as well as the θ coordinate and emission originating from the equilibrium excited-state configuration corresponding to the most stable solvation site, i.e., site a. Emission will occur at the same wavelength independent of the excitation wavelength, i.e., no

REE is observed in fluid media. If the medium is made rigid such that the relaxation rate constant along θ and R is smaller than the fluorescence rate constant, emission will occur from a Franck-Condon excited state corresponding to the solvation site specifically excited. In rigid media the dynamic equilibrium between different solvation sites is lost, and excitation of the solute in a given solvation site will lead to an emission of the solute in that solvation site. In this case, an excitation wavelength dependence of the fluorescence energy results, i.e., a REE is expected and is experimentally observed, cf. Figures (35,37).

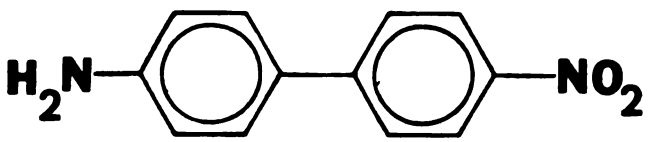
The observation of shoulders in the emission spectra as shown in Figure (35) as the medium becomes rigid and as the wavelength of excitation move to the red are explained in terms of inhomogeneous spectral broadening which results from the statistical distribution of solute molecules among the different solvation sites that become static in rigid media.

The appearance of REE at room temperature in PVA polymer film and polystyrene film of Figures (38 and 39) is explained in terms of matrices that are rigid enough at room temperature to prevent complete equilibrium between different solvation sites. However, the REE is less than that observed at 77 K (Figures 36,37).

The red shift of the absorption at low temperatures (Figure 40) is explained in terms of temperature-dependent

inhomogeneous spectral broadening. Lowering the temperature will change the statistical distribution in favor of solute molecules occupying the most stable solvation site which absorb at longer wavelengths. This leads to an apparent red-shift of the absorption as one lowers the temperature.

B. 4,4'-Amino Nitro Diphenyl (AND)



The room temperature absorption spectra of AND in different solvents are shown in Figure (16). Its absorption exhibits a red shift as the case of ANF in media of increasing polarity. The absorption maximum in 3MP (3-methyl-pentane) occurs at 339 nm while in ethanol the maximum occurs at 377 nm, a red shift of $\approx$3000 cm^{-1}. The absorption spectra of AND in different solvents are blue shifted relative to the ANF absorption spectra in the same solvents as shown in Figures (16 and 15), respectively. Such observations are expected from ground state geometries of these molecules. Conjugation and hence more π-interaction is expected in the ground state of ANF relative to AND because of the carbon bridge in the former making it more planar. Thus ANF absorbs at lower energy than AND in different solvents.

In the excited state the two phenyl groups of AND will be at a smaller angle relative to each other and the Stokes shift of the emission is expected to be large even in

hydrocarbon solvents. However, the excited state dipole moment is increased and a large red shift in the emission is expected to occur as the polarity of the solvent is increased. Inspection of Figures (15 and 16) reveals the absorption spectrum of ANF is more resolved than that of AND. This is consistent with a planar rigid ANF and a flexible AND molecule.

We have observed a large REE for AND in different polar solvents at 77 K as well as in polymer matrices at room temperature and at 77 K.

The fluorescence spectra of dilute solutions of AND in ethanol, 1-propanol, PVA polymer film and polystyrene polymer film at 77 K as a function of excitation wavelength are shown in Figures (42-45), respectively. A large red shift of $\approx$1200 cm^{-1} in ethanol, $\approx$750 cm^{-1} in 1-propanol, $\approx$1400 cm^{-1} in PVA film and $\approx$1300 cm^{-1} in polystyrene film were observed as the excitation wavelengths were increased from the absorption maximum at 77 K (the number at top left of figures cited) to the red edge of the absorption band (the number at the top right of figures cited). Such observations are accompanied by the appearance of shoulders in the emission spectra in ethanol as the excitation wavelengths were moved to the red or by changing the solvent to 1-propanol. As is the case of ANF, the magnitude of these REE are viscosity dependent. At -126°C in ethanol, the REE is $\approx$200 cm^{-1} as shown in Figure (46).

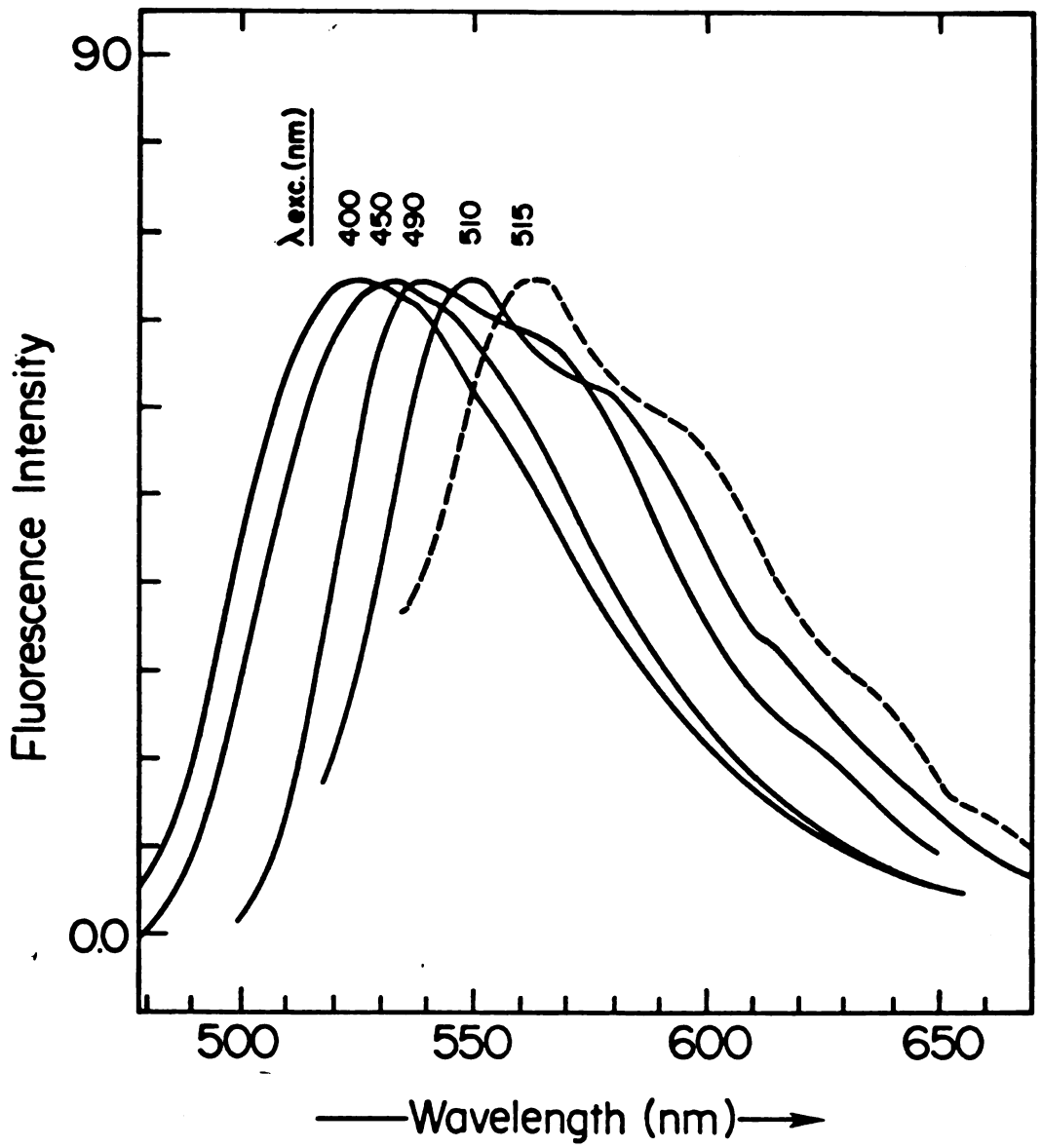


Figure 42. Fluorescence spectra of a dilute solution of AND in ethanol at 77 K as a function of excitation wavelengths.

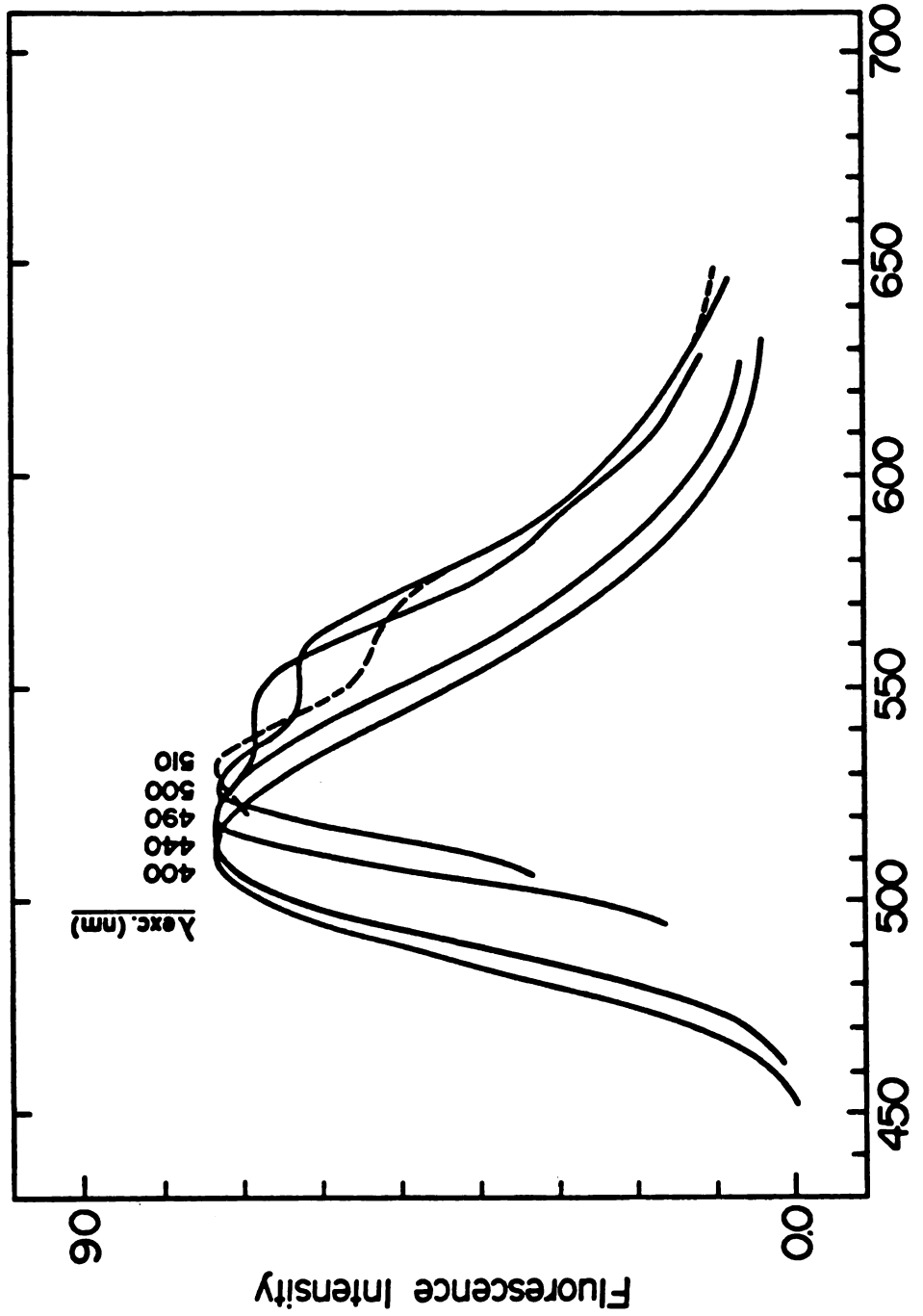


Figure 43. Fluorescence spectra of a dilute solution of AND in 1-propanol at 77 K as a function of excitation wavelengths.

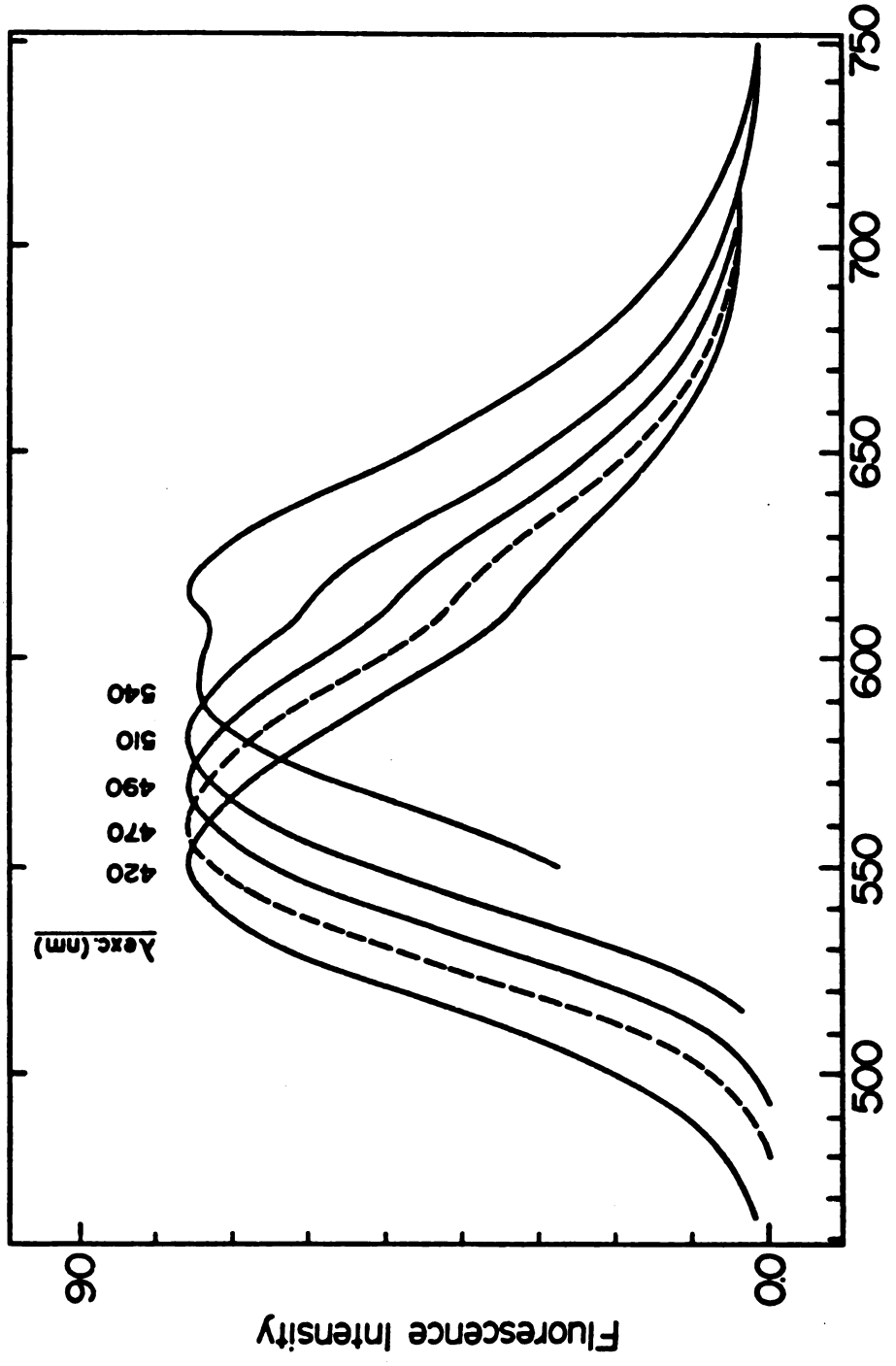


Figure 44. Fluorescence spectra of AND in PVA thin film at 77 K as a function of excitation wavelengths.

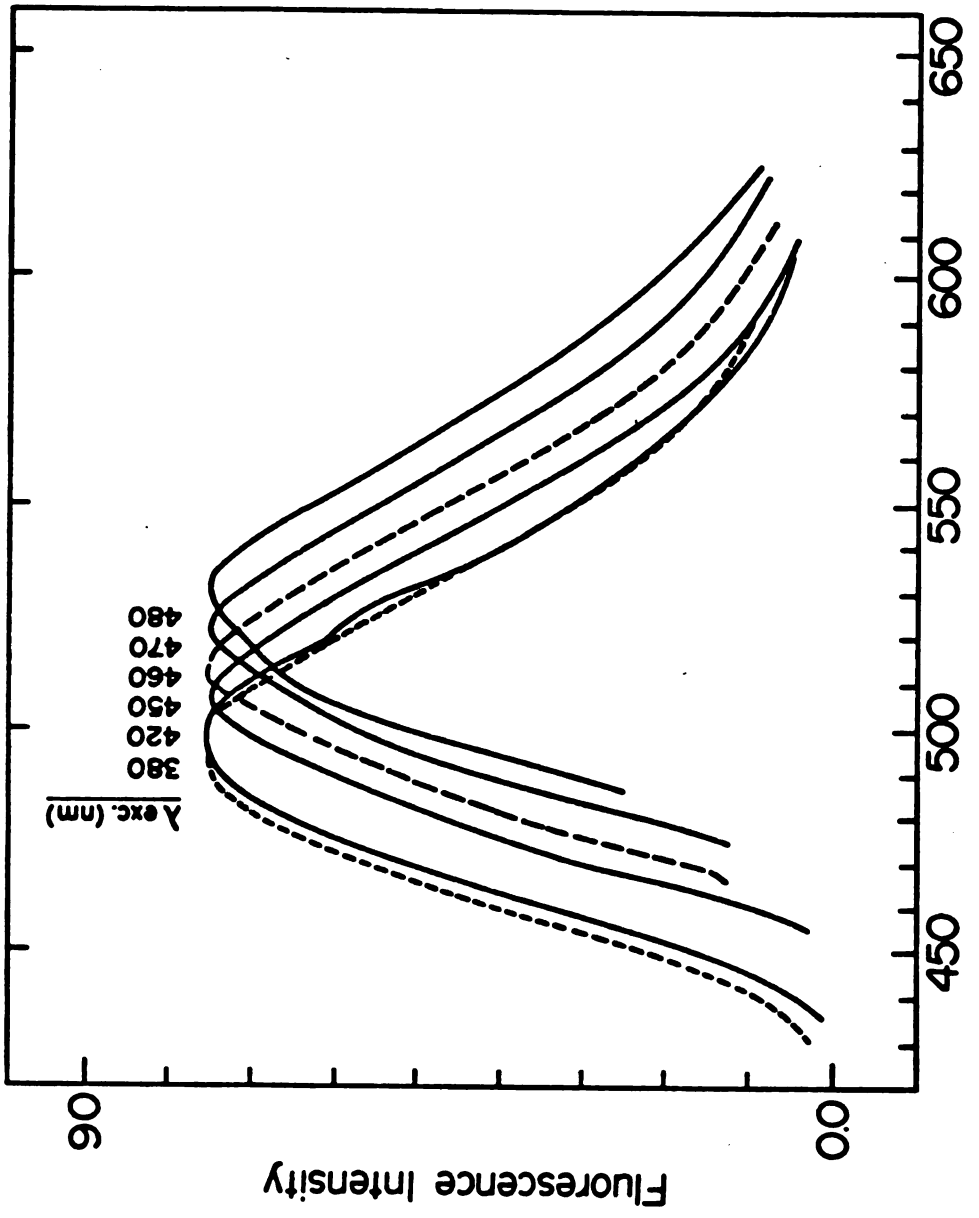


Figure 45. Fluorescence spectra of AND in polystyrene thin film at 77 K as a function of excitation wavelengths.

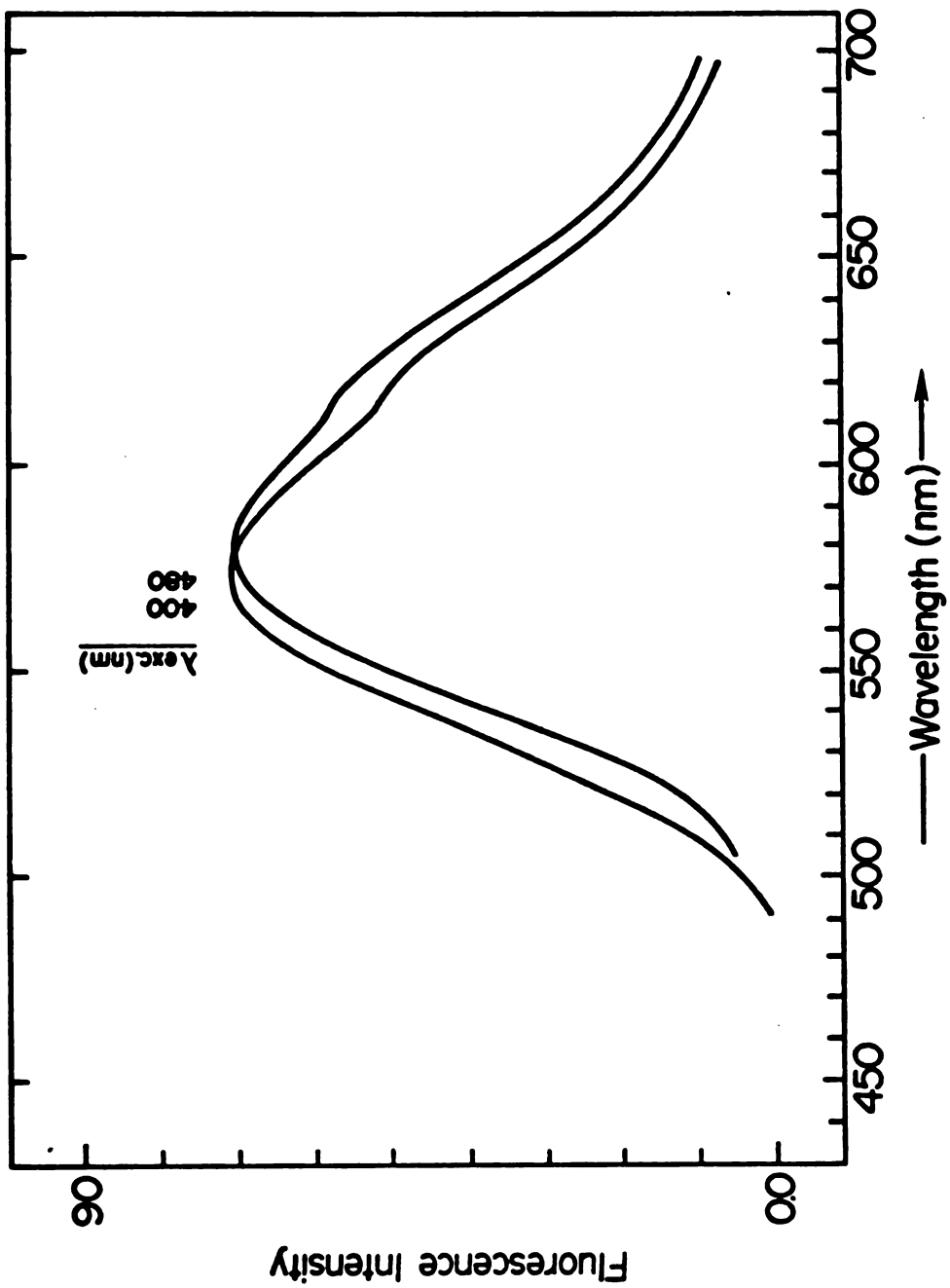


Figure 46. Fluorescence spectra of a dilute solution of AND in ethanol at -126°C as a function of excitation wavelengths.

The values of AND REE's in PVA film and polystyrene film at room temperature are ≈500 cm^{-1} and ≈400 cm^{-1}, respectively. Their corresponding spectra are shown in Figures (47 and 48).

The absorption spectra of AND in different polar solvents undergo red shifts when the temperature is reduced. Figure (49) shows the absorption spectra of a dilute solution of AND in ethanol at different temperatures. A red shift of ≈1500 cm^{-1} was observed upon lowering the temperature to -120°C.

Since AND undergoes an increase in dipole moment upon excitation and also has the same functional groups as ANF, one can explain the above experimental observations as in the case of ANF.

III. Flexible Molecules That May Undergo a Change in Equilibrium Geometric Configuration Upon Excitation

This kind of molecular system is exemplified by the methyl and tertbutylesters of 9-anthroic acid I and II whose ground and excited state geometries were studied earlier.[97] Their room temperature absorption and emission spectra, together with their emission spectra at 77 K in 3MP (3-methylpentane), are shown in Figures (17 and 18) respectively. It was concluded that the ground state

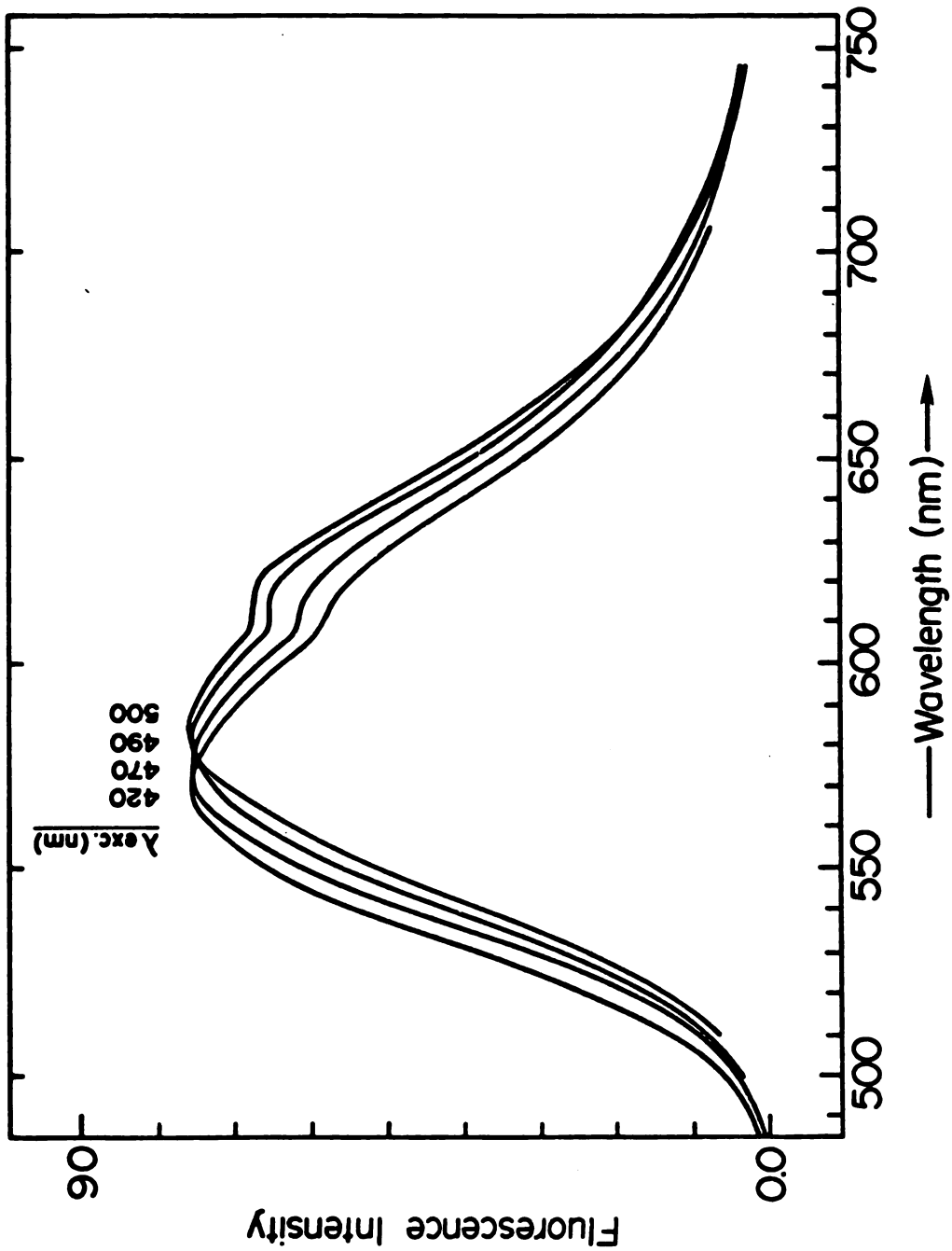


Figure 47. Fluorescence spectra of AND in PVA thin film at room temperature as a function of excitation wavelengths.

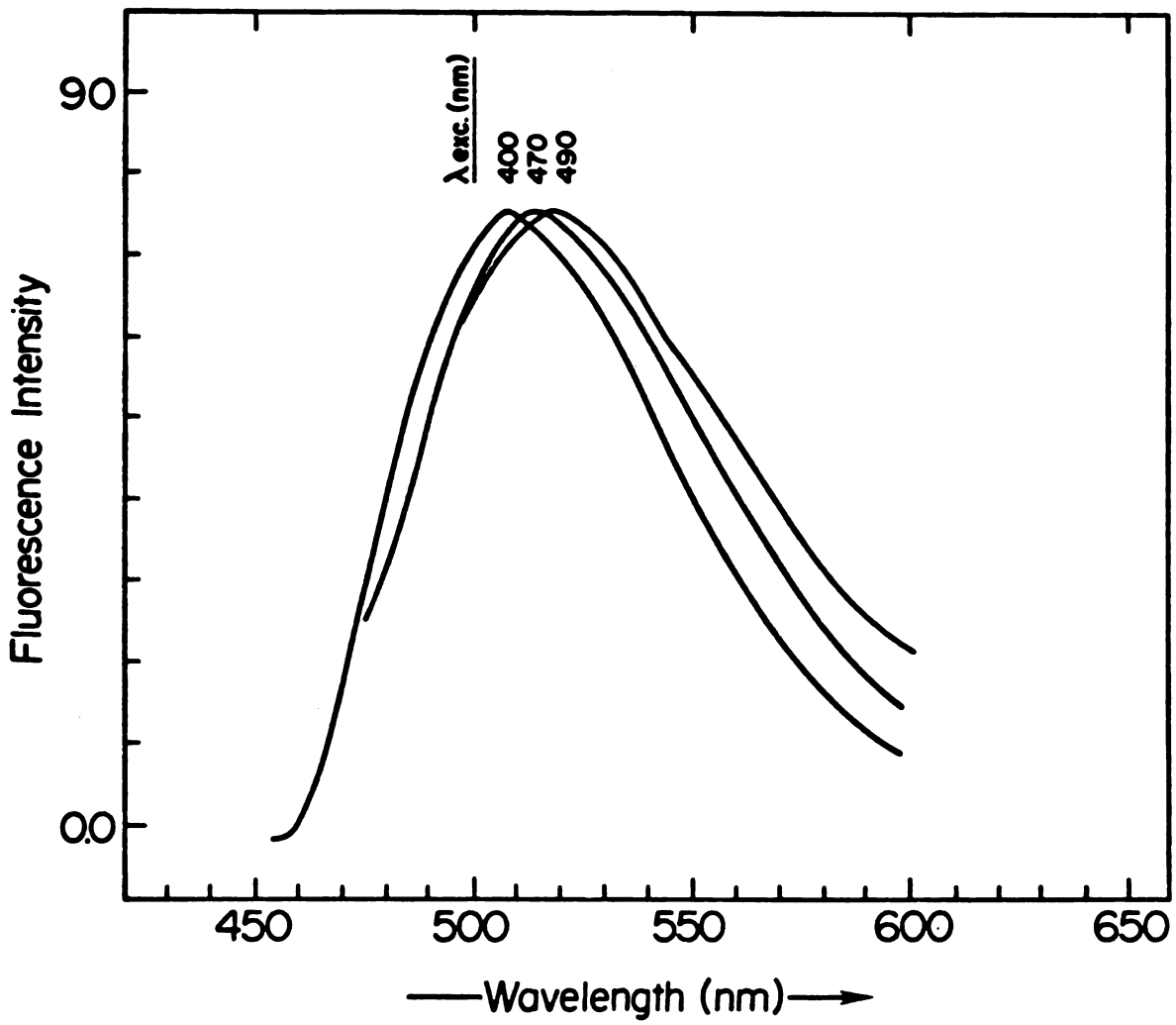


Figure 48. Fluorescence spectra of AND in polystyrene thin film at room temperature as a function of excitation wavelengths.

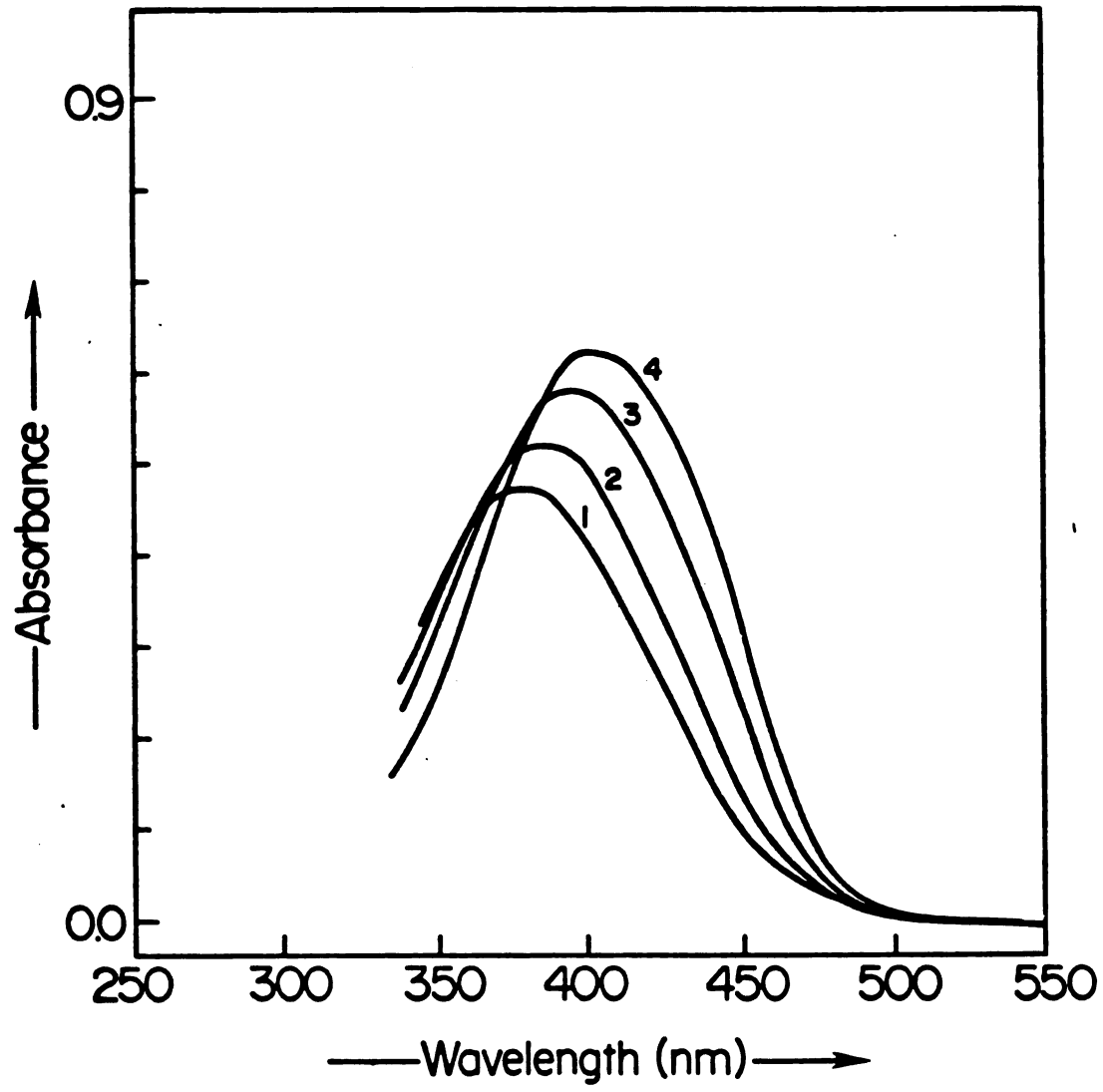
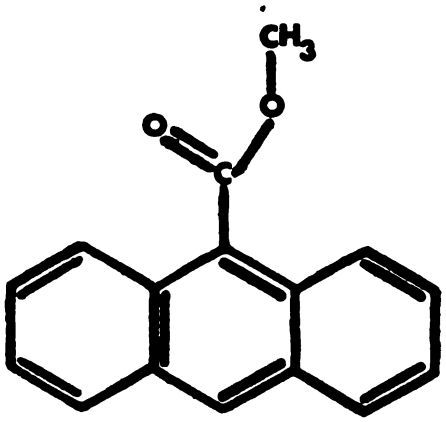


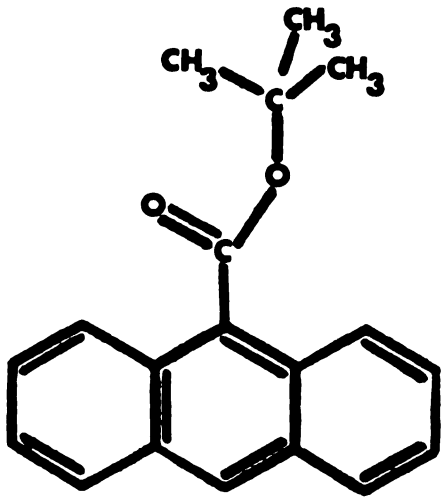
Figure 49. Absorption spectra of AND in ethanol ($\sim 10^{-4}$ M) as a function of temperature. (1) 24°C, (2) -23°C, (3) -86°C, (4) -120°C.

geometries of these molecules are similar to each other



9-Methyl Anthroate (9MA)

I



9-Tertbutyl Anthroate (9TBA)

II

with the carboxyl group out of plane, perhaps of 90° with respect to the anthracene ring, indicating no interaction between the two moieties.[112] A greater interaction between the carboxyl group and the ring in the excited state is expected. Such interactions depend on the size of the ester group, viscosity, structure and polarity of the solvent matrix. While a near-coplanar configuration between the carboxyl group and the ring in the excited state of 9MA is expected, a less planar configuration is expected in the excited state of 9TBA. It was shown[97] that 9MA relaxes to its equilibrium excited state configuration even in a rigid glass hydrocarbon (3MP), while 9TBA does not relax under the same conditions. The

branched tertbutyl group is interlocked in the rigid solvent matrix while the methyl ester group can undergo some relaxation in the same solvent matrix. It should be noted that rigid parafin oil at -80°C does not prevent excited state relaxation of 9-anthroic esters. The structure of the solvent matrix around the anthroic ester molecule is such that there is enough free volume for the ester group to relax during the excited state lifetime.

An excitation wavelength dependence of the fluorescence was carried out for 9MA and 9TBA solutions in a 3MP matrix element at 77 K. Figure (50) shows a red shift of ≈600 cm^{-1} when the excitation wavelength was increased from 385 nm to the far red edge (≈397 nm) of the first absorption band of 9TBA in 3MP. Exciting at the far red edge is accompanied with a highly resolved fluorescence spectrum. The shifts observed in the case of 9MA in 3MP matrix were very small. As Figure (51) shows, a red shift of only ≈200 cm^{-1} was observed when exciting at the far edge of the first absorption band of 9MA. Such shift was not accompanied by more resolution as in the case of 9TBA.

The above experimental observations were interpreted in terms of a red edge effect. The flexibility of these molecules allow the presence of different conformers which are unstable in fluid media. Upon freezing the solution, some of these conformers are trapped in certain configurations. Their lifetimes in the excited state will be

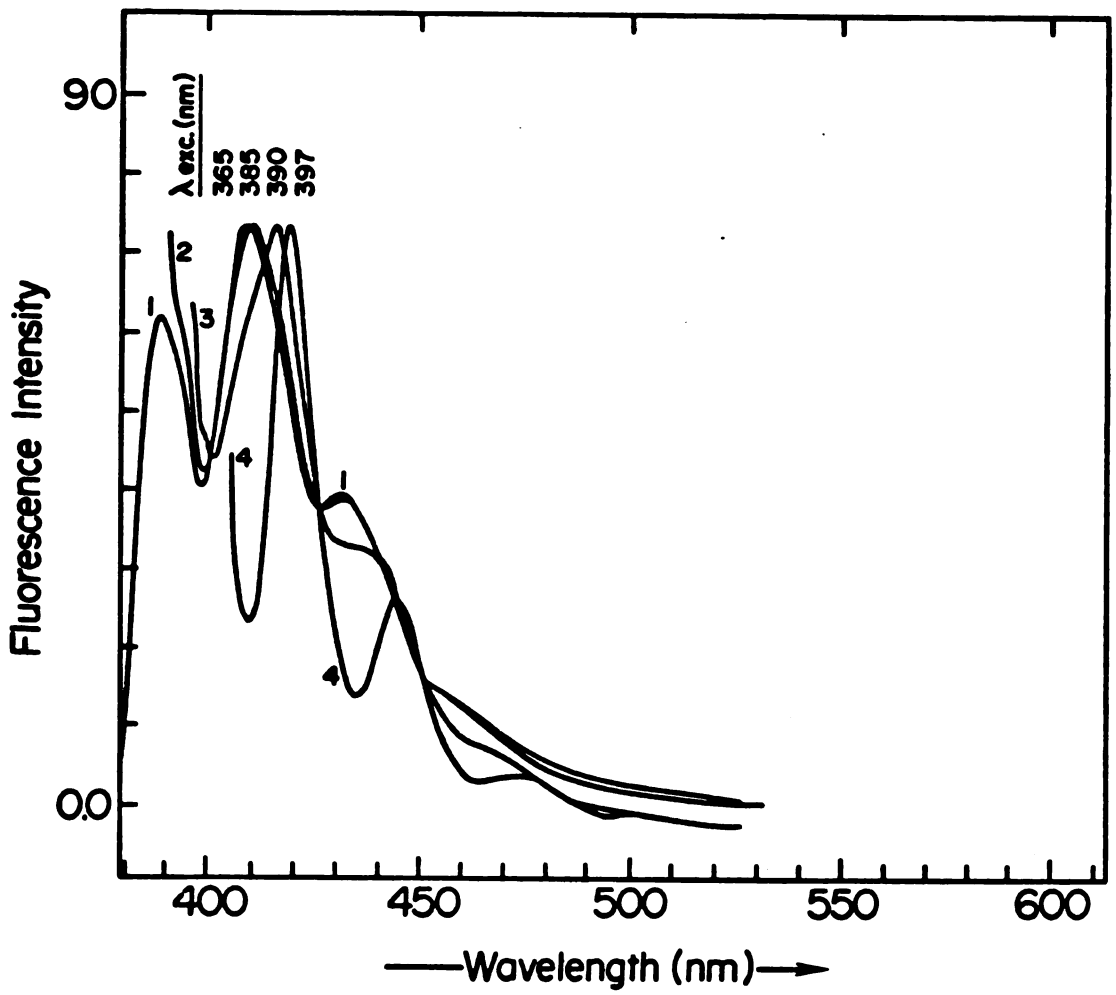


Figure 50. Fluorescence spectra of (7×10^{-5} M) 9TBA in 3MP at 77 K as a function of excitation wavelengths. (Spectrum # 1 corresponds to 365 nm excitation and #4 corresponds to 397 nm excitation.)

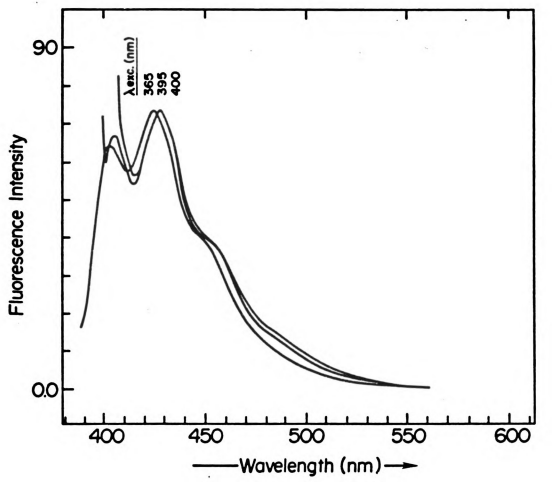


Figure 51. Fluorescence spectra of (7×10^{-5} M) 9MA in 3MP at 77K as functions of excitation wavelength.

dependent on the degree of the medium rigidity as well as the size of the ester group.

Different conformers of 9TBA are being trapped in certain configurations which can't relax in their excited state, i.e., they have a long lifetime compared to the fluorescence life time. The large tertbutyl ester group does not have enough free volume to rotate in the solid matrix. As proposed by Dellinger and Kasha,[43] "if a molecule upon excitation involves a rather large distortional motion for equilibrium relaxation, then a large volume of solvent in the cage around the solute must be displaced". Our interpretation is similar to the "Shpol'skii Effect"[80] where heterogeneity in the local environment of rigid matrices gives rise to solute molecules absorbing at slightly different energies.

Irradiation at the red edge of the first absorption band excites a subclass of molecules (conformers) which are more planar and hence absorb at lower energy than other solute molecules. The emission from this subclass will be red shifted relative to the bulk emission. Selective excitation produces a highly resolved emission spectrum result. However, the extent of resolution of the emission spectrum of 9TBA in 3MP at 77 K did not change regularly with excitation wavelength. Careful inspection of Figure (50) shows that the emission spectrum

excited at 390 nm was less resolved than the emission spectrum excited at 385 nm. More detailed results shown in Figure (52) confirm this observation.

One must point out that it is only in the case of red-edge excitation that we select certain conformers that absorb at that energy. At shorter wavelengths one will excite a mixture of conformers, and the proportion in the mixture varies irregularly with excitation wavelength.

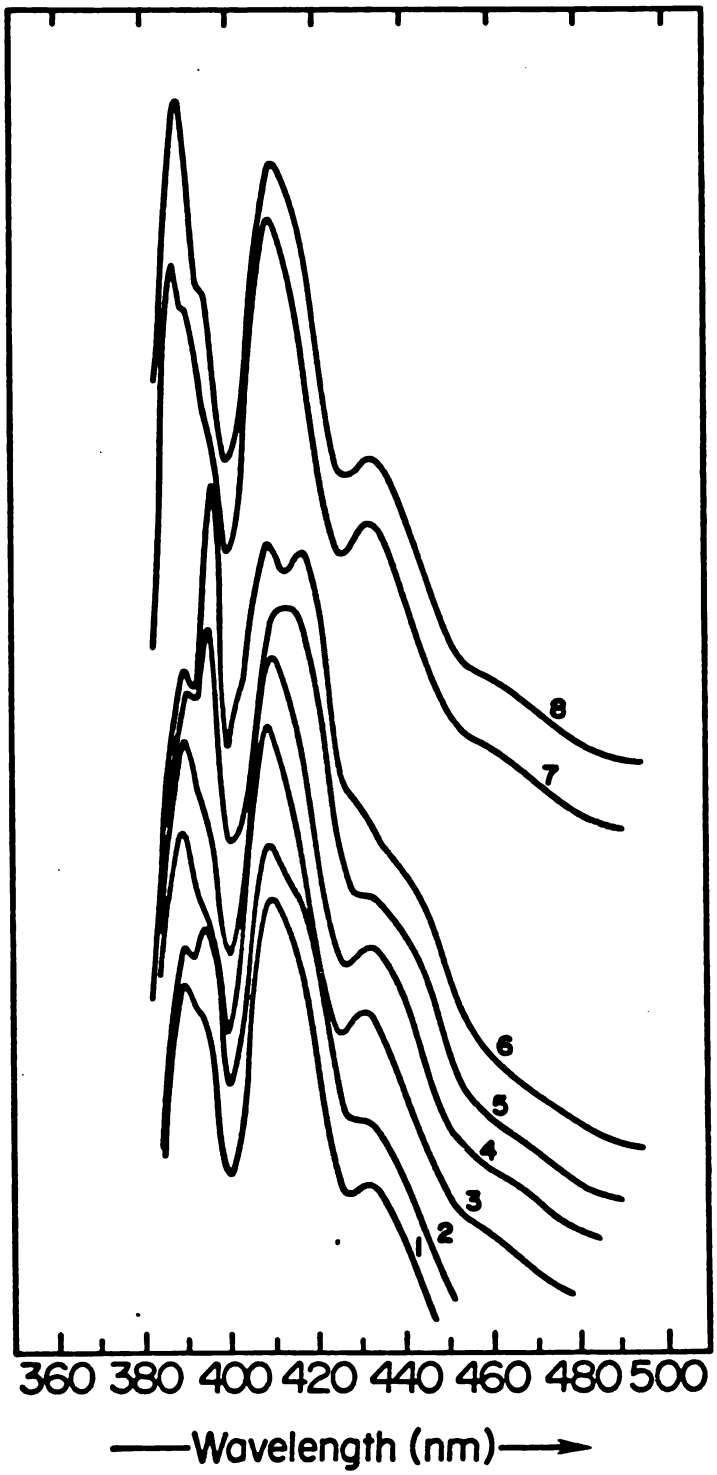


Figure 52. Variation of fluorescence intensity and resolution of vibronic band of (7×10^{-5} M) 9TBA in 3MP at 77 K at different excitation wavelengths which are: (1) 350 nm, (2) 355 nm, (3) 360 nm, (4) 365 nm, (5) 370 nm, (6) 375 nm, (7) 383 nm, (8) 386 nm.

CHAPTER VI

EXPERIMENTAL

A. Materials

I. Purification of Solvents

1. Ethanol:

200 proof ethanol was fractionally distilled at a rate of five drops per minute. Portions of about 50 ml were collected and the absorption spectrum taken in a 10 cm cell to check for benzene. Distillation was continued until the characteristic benzene UV absorption was no longer apparent. Ethanol was then distilled and used as needed.

2. 3-methyl Pentane (3MP)

The Philips pure grade 3MP was mixed with nitric acid and sulfuric acid, then stirred for two days. Then it was separated and washed with base and water. After drying with sodium sulfate for one night, the solution was refluxed over sodium wires for two days and distilled. The vapor passed through a four foot vacuum jacketed column and condensed at a speed of two drops per minute. The purity

was checked by obtaining the absorption spectrum.

3. Water was doubly distilled in our laboratory.

4. 1-Propanol, 1-butanol, glycerin and DMSO

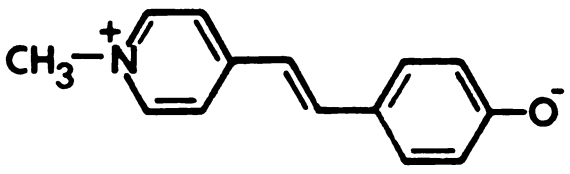
(Dimethyl Sulfoxide) - from Fisher Scientific Company and chloroform from Mallinckrodt were used without further purification.

5. Paraffin Oil from Mc/B, Piperidine and Polystyrene from Aldrich Chemical Company, 1-hexanol from Eastman and Poly(vinylalcohol) [PVA] from Polyscience, Inc. (Cat. No. 2815, 99-99.8 Mole %) were also used without further purification.

II. Preparation and Purification of Chemical Compounds

1. Merocyanine Dyes:

1-Methyl-4-hydroxystyryl)peridinium betaine whose structure is



was prepared using the general procedure described by Brooker[100] and others.[104,113] The merocyanine was purified by repeated recrystallization in methanol and dried under vacuum. The benzothiazol merocyanine dye was synthesized in the same general procedure used by Brooker[100] and described in detail by Kampas.[98]

2. ANF(2-Amino-7-Nitro Fluorene)

ANF was obtained from K & K Laboratories, Inc. and was purified by repeated recrystallization in ethanol.

3. AND (4-Amino-4'-Nitro Diphenyl)

AND was obtained from K & K Laboratories, Inc. and was purified by repeated recrystallization in ethanol.

4. 9MA and 9TBA (Methyl and Tertbutyl Esters of 9-Anthroic Acid)

9MA and 9TBA were prepared from the purified 9-anthroic acid according to the method of Parish and Stock[114] and purified by repeated recrystallization from ethanol.

III. Preparation of Polymer Films

1. Poly(vinylalcohol) PVA Films

PVA (molecular weight 133,000-99% mole hydrolyzed Polyscience Cat. #2815) was combined with water in a ratio of 0.125 gram/ml. The mixture was heated over a steam bath and was stirred occasionally (to prevent dehydration at the surface for 20 minutes. The solution was then permitted to cool to room temperature in a moist environment (a desiccator with water in it works well). The dye solution (1 ml of 10^{-4} M in ethanol for each 1.5 gm PVA) was added to the cool PVA water solution, mixed very well, and put back in a moistened environment for about one hour. The dye solution in PVA was then transferred into a small flexible centrifuge tube and centrifuged at the speed of 15,000 round per minute for about 10-15 minutes (this will remove any dehydrated polymer). The dye solution was then poured into clean, dry molds (molds were prepared by pouring melted paraffin in glass dishes to a depth of 8 mm. After solidification, 4 cm x 4 cm squares were cut out with a razor blade to form the molds). The films were then dried by directing air at them at a very slow rate for about 70 hours at room temperature. Then the films were removed from the molds and the needed measurements made.

2. Polystyrene Films

A few billets of polystyrene were dissolved in the chloroform solution of the dye. The contents were then poured into a flat dish and let to dry slowly in a clean atmosphere. These films were very thin and had an absorbance of about 0.1.

B. Spectral Measurements:

1. Absorption Spectra

All reported absorption spectra were run on Cary 15 and Cary 17 spectrophotometers.

2. Emission Spectra

Fluorescence spectra were recorded on a multicomponent system used in this laboratory consisting of a 500 W Xenon light source, 500 mm Bausch & Lomb excitation monochromator (which provides a narrow excitation band width), McPherson Model 235 Emission Monochromator and EMI Model 9558QB Phototube. Noise reduction and amplification of the PMT signal is achieved by using a Princeton Applied Research Model HR-8-LOCK IN Amplifier and appropriate chopping apparatus. Some of the room temperature emission spectra were recorded by using Aminco-Keirs and Aminco-Bowman spectrofluorometers. The phosphorescence spectra were

obtained with these instruments equipped with a rotating can phosphoroscope.

3. Temperature Variation System

A quartz dewar with flat quartz excitation and emission windows and a narrow glass tube for the samples were used. (A 0.1 cm absorption cell connected to a long pyrex tube was used for low temperature absorption). The temperature of the sample was controlled by boiling liquid nitrogen using a power resistor and allowing the N_2 gas to flow into the sample dewar. The temperature of the sample was monitored through a thermocouple (copper, constantan) dipped inside the solution in the sample tube immediately above the point of excitation or absorption. The lowest stable temperature which can be reached by such a system is around -160°C. Low temperature absorption or emission studies with polymer films were performed by hanging the films vertically in the dewar through a wire and a glass tube. For 77 K measurements the films were dipped directly in the liquid nitrogen.

CHAPTER VII

CONCLUSION AND FUTURE WORK

One of the interesting applications of merocyanine dyes in particular and dyes in general is their extensive use in biology and photography. In biology, merocyanines have been found to be useful in measuring membrane potentials.[115] Membrane potential sensitive dyes have been useful for studying rapid electrical activity in single nerve and muscle cells, in collections of individual cell bodies and in single cells in tissue culture. Dyes have also been used to determine changes in the membrane potential level of cells, organelles and vesicles in suspension and of single cells in conjunction with fluorescence activated cell sorters. Merocyanines have been recently[116] used with lipid bilayer membranes in which the trans-membrane potential can be rapidly and accurately controlled. Potential-dependent changes in the fluorescence and absorption spectra of these dyes were obtained along with the polarization dependence of these properties. In photography[117,118] a stable positive image which is not thermally erasable below 70-80°C was produced from merocyanines[119] when irradiation of a recording paper took place. It leads to the reprography

of transparent documents and also produces continuous tone printing. This process requires no subsequent development, is dry, is an autoprocessor and can be realized with a relatively simple technology.

Besides their importance in measuring membrane potentials and this application in photography, these dyes (merocyanines, ANF and AND) could be used as probes to study the dynamic behavior of liquids and could be potentially used in photography storage.

Since these molecular systems (Chapter IV) are sensitive to polarity and structure of the solvent found from their absorption, emission and the significant role of REE, they could be used to further investigate the following important phenomena in the previous chapter: Shpol'skii effect, site selection spectroscopy, inhomogeneous spectral broadening, time dependent emission spectroscopy and viscous flow barriers.

Some of the studies that could be suggested are now summarized.

I. Pyridine Merocyanine:

1. The room temperature emission spectra of pyridine merocyanine undergoes a gradual red shift upon increasing its concentration in ethanol. Such observations in other systems[120-123] were interpreted in terms of energy migration between molecules whose energy levels differ in position

as a result of inhomogeneous spectral broadening. Careful investigation of the concentration effect in the pyridine merocyanine dye is needed.

2. The REE phenomenon we observed requires further study. Thus polarization experiments at different excitation wavelengths at different temperatures in different solvents may reveal polarization enhancement at red edge excitation. Lifetime measurements in the picosecond range could be performed at room temperatures in different solvents and at different excitation wavelengths at low temperatures should be made. Excitation wavelength dependence could be performed using a tunable dye laser which will enable us to select solute molecules with the same solvent environment.

II. ANF and AND

1. The suggested experimental investigations of pyridine merocyanine should be extended to these dyes.

2. We have observed a large REE in the phosphorescence spectra of these molecules in paraffin oil, polystyrene and polyvinyl alcohol at low temperatures. Detailed steady state and time-resolved study of the solvation of the solute in its triplet state would be very interesting.

III. 9MA and 9TBA

It would be very interesting to study the lifetimes of 9MA and 9TBA in hydrocarbon at 77 K using different excitation wavelengths.

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