PART – D

SPECTROSCOPIC INVESTIGATIONS

CHAPTER - 1

GENERAL INTRODUCTION

During the past one and a half decades, interest in both theoretical and experimental studies of the electronic spectral properties of aromatic compounds containing strong mesomeric substituent groups has continued to have a deeper understanding of the electronic structure of and also of the radiative and nonradiative properties of such molecules[1-16]. The presence of strong mesomeric substituents, like nitro (NO_2) group, shows a drastic change in the electronic spectra of parent compounds. The situation some times is so complicated that it becomes difficult to analyse the spectra in terms of the electronic states of the parent compounds. The modification in the spectral characteristics results from the presence of new n-π^* and intramolecular charge transfer (CT) states in these substituted molecules. The CT states are suggested to be the primary source of the spectral shift[17] from the parent compounds. The radiative and nonradiative properties of the molecules are severely affected. Some of the nitroaromatics give either fluorescence or phosphorescence only while a few give both emissions. The lack of emission in nitrobenzene is well known[3]. Inspite of a high triplet (t) quantum yield (Φ_t), phosphorescence quantum yield (Φ_p) in nitroaromatic molecules is usually small. Nonradiative process from $^1n-\pi^*$ is observed to be efficient. These problems brought the electronic spectral studies of nitroaromatic compounds in focus recently[1-16].

The present investigation is an effort to provide informations regarding the electronic spectral properties of some nitroaromatic compounds. The electronic spectral data are collected in UV - Visible region at 298°K and also some times at 77°K. In order to analyse the spectra and to assign the electronic transitions, the standard technique depending upon the solvent effect is used. To have a better understanding of radiative and nonradiative processes, emission polarisation and mixed crystal spectra are also studied in some cases.

Adequate theoretical interpretation of the spectral data rests on modern theories. In the following sections of this chapter, we will discuss briefly the LCAO - MO method, the composite molecule method, the theory of solvent effect on the electronic spectra and the radiative and nonradiative processes.

1.2 LCAO - MO method

In molecular orbital (MO) theory, the molecular orbitals are described in terms of the one electron function in is generally extended over the whole molecule and to which the electrons are allocated so as to satisfy the Pauli's exclusion principle. There are two principal approximate methods for obtaining molecular orbitals : the free electron method[18] and the LCAO-MO method.

In LCAO - MO approximation MO's (ψ_m) are expressed as a linear combination of atomic orbitals (χ_i) i.e.

$$\psi_m = \sum_i c_{mi} \chi_i \qquad (1.21)$$

where C_{mi} is the coefficient describing the amount of the i th atomic orbital to be found in m th molecular orbital.

This approximation is based on an expectation that when an electron gets close to a nucleus, the influence of the potential field due to that nucleus becomes predominant and as a consequence MO's in that region resemble to the AO's corresponding to those atoms.

These molecular orbitals are assumed to be an effective one electron Hamiltonian (h) for the equilibrium nuclear configuration of the molecule. So that one will have

$$h \psi_m = E_m \psi_m \qquad (1.22)$$

The orbital energies and the coefficients C_{mi} are obtained using the Variation method if the matrix elements h_{ij} of the Hamiltonian and those S_{ij} of overlap between the atomic orbitals are known. The secular equations are given by :

$$\sum_j C_j (h_{ij} - E S_{ij}) = 0 \qquad (1.23)$$

for each i. If there are n atomic orbitals in the expression for molecular orbitals, there are n secular equations of this type and they will have non trivial solutions only when n th order secular determinant is zero i.e.

$$|h_{ij} - E S_{ij}| = 0 \qquad (1.24)$$

The determination of appropriate numerical values of the matrix elements h_{ij} and S_{ij}'s remains as the only difficult problem. To evaluate these, exact form of h and also the exact form of atomic orbitals are to be known. Let us write few simplifying symbols :

$$\alpha_i = h_{ii}$$

$$\beta_{ij} = h_{ij} = h_{ji} \quad (i \neq j)$$

Here α_i is the coulomb integral of the atomic orbital χ_i. This integral represents the coulomb energy of an electron in the atomic orbital χ_i. β_{ij} is the resonance integral between the atomic orbitals χ_i and χ_j and it amounts to the energy of interaction of the two atomic orbitals. Both α and β correspond to negative energy. If it is assumed that all the atomic orbitals are normalised, the secular equations (1.23) can be rewritten as

$$\sum_{j \neq i} C_j(\beta_{ij} - E S_{ij}) + C_i(\alpha_i - E) = 0 \qquad (1.25)$$

for each i.

It is known that the absorption spectra of aromatic hydrocarbons in the near UV - Visible region are due to transitions of the π - electrons. The approximations to these secular equations for these π - orbitals, called the Huckel approximations, are the following ;[19-22]

1) α_i are taken to be same for each atomic orbital and this is expressed by α .

2) S_{ij} are assumed to be zero for $i \neq j$.

3) β_{ij} are considered to be nonzero only between neighbouring atoms. So $\beta_{ij} \neq 0$ if atom i is bonded to j i.e. ($i \longleftrightarrow j$).

4) All the resonance integrals for neighbouring carbon atoms are assumed to be equal and are denoted by β .

Using these approximations, equation (1.25) becomes :

$$\sum_{j\to i} c_j\beta + c_i(\alpha - E) = 0 \qquad (1.26)$$

for each i.

By dividing equation (1.26) by β and writing

$$(\alpha - E)/\beta = W \qquad (1.27)$$

following simple form is obtained :

$$\sum_{j\to i} c_j + W c_i = 0 \qquad (1.28)$$

for each i.

The secular determinant now has W everywhere on the diagonal, and 1 in the off-diagonal elements of row i and column j if atoms i and j are neighbours, but zero otherwise. Thus we can easily set up the secular determinant for any π - electronic system consisting entirely of the carbon π -centres. The n th order secular determinantal equation can be solved to give n solutions for W. The energy of the m th molecular orbital is given by :

$$E_m = \alpha + W_m (-\beta)$$

That is, W is the orbital energy as expressed in units of ($-\beta$) with reference to α .

$$W_m = (E_m - \alpha) / (- \beta)$$

Since ($-\beta$) is a positive quantity, a negative or positive value of W means a lower or higher energy of the α .

If the molecular orbitals are normalised, use of Huckel approximations leads to

$$E_m = \alpha + 2 \sum_{i \to j} C_{mi} C_{mj} \beta$$

and $W_m = - 2 \sum C_{mi} C_{mj}$

When applying the simple LCAO - MO method to a π - system containing a heteroatom, the difference of the coulomb integrals for the atomic orbitals can be allowed for by expressing the coulomb integrals α_i as ($\alpha + h_i \beta$) where α and β are standard coulomb integral and resonance integral respectively. An appropriate value is assigned to the parameter h_i.

In simple LCAO - MO method distinction between singlet and triplet states can not be made. It is because in this method electronic repulsive interactions have been ignored. When it is considered in advanced MO method[23] (ASMO) antisymmetrized configuration functions are no longer eigenfunctions of the

Hamiltonian. True eigen functions are then made by the method of configuration interaction[24] (ASMO CI). In the self consistent - field molecular orbital method (SCF MO)[25], the required integrals are estimated by the use of assumed forms of the atomic orbitals and no empirical parameters are used. Pariser and Parr[26,27] have developed a method which incorporates empirical elements with the ASMOCI method and is applicable to more complex molecules. In the Pariser - Parr method zero - differencial - overlap approximation is used and some required integral values are determined by empirical and semiempirical method. A set of simplifying approximations have been introduced into the SCF MO method by Pople. Some times, the Pariser-Parr method and the Pople method are combined together commonly known as PPP method.

1.3 Composite - Molecule Method

Method of Simple Composite Molecule[29-31] in the one electron approximation is described which may be used to interpret the electronic absorption spectra of systems where strong mesomeric groups are substituted on the ring. Let us consider a composite conjugate system R - S where, say, for substituted benzene, the ring is taken as R and substituent as S linked to each other by a formally single bond between the atoms 'r' and 's' which belong to R and S resp.

In the LCMO approximation, the π -MO's of the composite system R - S can be obtained as linear combinations of π - orbitals of fragments R and S and their energies can be obtained by solving the proper secular equations based on the π - orbitals of the seperated fragments.

Now let $\phi_{m(R)}$'s $\phi_{n(S)}$'s and $\Psi_{k(RS)}$'s are the π -orbitals of R, S and R - S resp. which are the solutions of the equations :

$$h^R \phi_{m(R)} = \eta_{m(R)} \phi_{m(R)}$$

$$h^S \phi_{n(S)} = \eta_{n(S)} \phi_{n(S)} \qquad (1.31)$$

$$h^{RS} \Psi_{k(RS)} = \varepsilon_{k(RS)} \Psi_{K(RS)}$$

where $h^R = T + V^R$, $h^S = T + V^S$ and $h^{RS} = T + V^R + V^S$ are the effective one electron Hamiltonian operators for R, S and R - S resp. Here, V^R and V^S are the effective potentials acting on the electron in R and S resp. and T is the kinetic energy operator for the electron.

The effective one electron Hamiltonian for the composite system may also be expressed as :

$$h^{RS} = h^o + h' \qquad (1.32)$$

where h^0 is the Hamiltonian for the system of the two seperated fragments and h is the perturbation operator representing, interaction between R and S. Since, $\phi_{m(R)}$'s and $\phi_{n(S)}$'s are localised in R and S regions respectively and V^R and V^S are important in the R and S regions only, the required matrix elements of the operator h^{RS} can be approximately given by :

$$h^{RS}_{m(R),\, u(R)} = h^{R}_{m(R),\, u(R)} = \delta_{mu}\, \eta_{m(R)} \qquad (1.33)$$

$$h^{RS}_{n(S),\, \vartheta(S)} = h^{S}_{n(S),\, \vartheta(S)} = \delta_{n\vartheta}\, \eta_{n(S)} \qquad (1.34)$$

and

$$h^{RS}_{m(R),\, n(S)} = h_{m(R),\, n(S)} = b_{m(R),\, r}\, b_{n(S),\, s} \cdot \beta_{rs} \qquad (1.35)$$

where δ is the kronecker symbol; $b_{m(R),r}$ and $b_{n(S),s}$ are the coefficients of the atomic orbitals χ_r and χ_s in $\phi_{m(R)}$ and $\phi_{n(S)}$ respectively and β_{rs} is the resonance integral between χ_r and χ_s i.e.

$$\beta_{rs} = \int \chi_r\, h^{RS} \chi_s\, d\tau = \int \chi_r\, h' \chi_s\, d\tau \qquad (1.36)$$

In the LCMO approximation, the form and energies of the molecular orbitals of R - S can be obtained by using perturbation theory, instead of solving the secular equations. Thus, if the relation :

$$|h'_{m(R),n(S)}| << |\eta_{m(R)} - \eta_{n(S)}| \qquad (1.37)$$

holds good for any pair of $\phi_{m(R)}$ with one of the $\phi_{n(S)}$'s, one of the molecular orbitals of R – S and its energy can be approximately expressed as follows :

$$\begin{aligned} \psi_{K(RS)} &= N_K\left[\phi_{m(R)} + \sum_{n(S)} \left\{\frac{h'_{m(R),n(S)}}{(\eta_{m(R)}-\eta_{n(S)})}\right\}\phi_{n(S)}\right] \qquad (1.38) \\ &= \phi^{P}_{m(R)} \end{aligned}$$

$$\varepsilon_{K(RS)} = \eta_{m(R)} + \sum_{n(S)} \frac{(h'_{m(R),n(S)})^2}{(\eta_{m(R)}-\eta_{n(S)})}) = \eta^{P}_{m(R)} \qquad (1.39)$$

Thus, if S is regarded as a mesomeric substituent, by the use of perturbation theory, we can express in an analytical form the changes in energies and forms of the molecular orbitals of a molecule R produced by the introduction of the substituent S.

This theory of composite molecule predicts the absorption intensity of a CT band as a function of angle of twist (θ_{rs}) of the bond between r and s. Suzuki[32] has shown that the oscillator strength (f) of a CT band is proportional to $\cos^2\theta_{rs}$. If the molar extinction coefficient at the absorption maxima can be taken to be proportional to f, its proportionality to the cosine square of the angle of twist, i.e. the relation originally assumed by Braude[33] is reached.

Simple composite molecule method essencially has the same limitations in interpreting electronic spectra as simple LCAO-MO has. In advanced composite molecule method, the electronic interactions have been included and the π- electronic states of a conjugated system are described as arising from mixing of electronic configurations expressed in terms of π- orbitals located on its fragments under the correct total π- electronic Hamiltonian for the system[34,35].

1.4 Nitroaromatics as Composite Molecules

A nitroaromatic molecule can be considered as a composite system with two fragments. The first fragment being the aromatic ring (R) while the other one is the nitro group (S). The fragments are linked to each other in R – S by a single bond between atom r (carbon atom) belonging to R and atom s (nitrogen atom) belonging to S. A method of simple composite molecule in the one electron approximation can be used to interpret the electronic absorption spectra of such a system. In this method, the π-MO's of the composite conjugated system (R – S) are regarded as arising from mixing of the π- MO's of the two fragments under the influence of the effective one electron Hamiltonian for the composite system. This method has been developed mainly by Dewar and is known as Simple Composite Molecule method or LCMO method.

1.41 Nitro group

In the planar nitro group, there are four π- electrons : two from the nitrogen atom and one each from the oxygen atoms. The 2 $p\pi$-AO (χ_N) of nitrogen and 2 $p\pi$- AO's of oxygen atoms (χ_{O1} and χ_{O2}) combine to give three π- MO's Φ_{-1} , Φ_0 and Φ_{+1} of the nitro group.

There exists a symmetry plane which is perpendicular to the nitro group plane. It bisects the angle between the two N - O bonds. Thus, the two oxygen atoms O_1 and O_2 are equivalent and the following group orbitals can conveniently be formed from the two oxygen 2 $p\pi$ - AO's :

$$\chi_{O(s)} = (2)^{-1/2} (\chi_{O1} + \chi_{O2}) \qquad 1.411$$

$$\chi_{O(a)} = (2)^{-1/2} (\chi_{O1} - \chi_{O2}) \qquad 1.412$$

The symmetrical group orbitals $\chi_{O(s)}$ interacts with the nitrogen 2 $p\pi$ - AO χ_N and the antisymmetrical group orbital $\chi_{O(a)}$ does not. Therefore, the three π- MO's of the nitro group in the zero-overlap approximation can be expressed as :

$$\phi_{-1} = b_{-1,1}\,\chi_N - b_{+1,1}\,\chi_{O(s)} \qquad 1.413$$

$$\phi_{0} = \chi_{O(a)} \qquad 1.414$$

$$\phi_{+1} = b_{+1,1}\,\chi_N + b_{-1,1}\,\chi_{O(s)} \qquad 1.415$$

J. Tanaka has evaluated the values of the coefficients $b_{-1,1}$ and $b_{+1,1}$ to be equal to 0.7003 and 0.7133 respectively. ϕ_{-1}, ϕ_{0} and ϕ_{+1} are the antibonding, nonbonding and bonding π - orbitals respectively. The antibonding orbital (ϕ_{-1}) remains vacant while the other two lower orbitals ϕ_{+1} and ϕ_{0} are occupied in the ground state.

The highest bonding orbital is designated by + 1 and the lower orbitals in order of decreasing energies are designated by + 2, + 3, ··· and so on in a mesomeric system. Similarly - 1 represents the lowest antibonding orbital and higher orbitals in order of increasing energies are designated as - 2, - 3, ··· and so on.

1.42 Energies and Wave functions of Nitroaromatics

S. Nagakura and Nagakura *et al*[33] calculated the energies and wave functions of π — electronic states of nitrobenzene. They have taken into account eight singlet electron configurations : the ground configuration (V_0 or G), five locally excited (L E) and two CT configurations for nitrobenzene. Of the five LE configurations, four are the configurations corresponding to the α, p, β and β' states of benzene and one is the configuration arising from the $(\pi - \pi^*)$ S - S transition within the nitrogroup i.e. from $\phi_{0'}$ to $\phi_{-1'}$. The energies of these LE configurations E_α, E_p, E_β, $E_{\beta'}$ and E_{NO_2} were determined as 4.89, 6.17, 6.98, 6.98 and 6.26 ev respectively from the observed positions of the corresponding absorption bands of benzene and nitromethane. The CT configurations arising from the one electron transition from ϕ_{+1} to $\phi_{-1'}$ and the another one arising from ϕ_{+2} to $\phi_{-1'}$. The energies of these CT configurations were evaluated as 4.03 and 5.06 ev respectively by the use of the equation

$$E (CT) = I_B - A_{NO_2} - C \qquad (1.421)$$

where I_B and A_{NO_2} are the ionization potential of benzene (9.24 ev) and the electron affinity of nitro group (0.4 ev) respectively and C is the coulomb interaction between the negative charge distributed in the nitrogroup and the positive charge distribution in the benzene ring in the CT configuration. The off-diagonal matrix elements of the total π- electronic Hamiltonian (H) necessary for the calculation of configuration interaction can be evaluated in terms of β^c_{CN}, the core resonance integral between the adjacent carbon and nitrogen $2p\pi$- AO's. The nonzero interaction matrix elements are $\langle LE_p | H | CT_s \rangle$, $\langle G | H | CT_s \rangle$, $\langle LE_\alpha | H | CT_a \rangle$, $\langle LE_{\beta'} | H | CT_s \rangle$ and $\langle LE_\beta | H | CT_a \rangle$. The other off diagonal elements are zero.

It has been shown that in nitrobenzene, the ground state has 93.3% G and 6.6 % CT_s and very little of LE_p and LE_β. The first excited state has 48.5% of both LE_α and CT_a. The second excited state contains 70.3 % of CT_s.

1.5 Solvent Effect on the Electronic Spectra

The electronic spectral changes in the presence of solvent molecules arise due to the introduction of a local field around the solute molecule, which is different than that in a free space and also due to alteration in the charge density of the molecule. In general, changes in both the intensity and the energy of a band are observed[36,37]. In addition, some times, weak or forbidden transitions may also gain intensity. Following are the predominant effects :

1) <u>Dielectric effects</u> : These are the dipolar effects between the solute and the solvent molecules;

2) <u>Dispersive effects</u>: These are due to Vander Waals forces;

3) Short range specific effects: These are developed due to a field introduced by the weak bond formation like hydrogen bond between the solute and solvent molecules;

4) Concentration effect: If the concentration of the solute molecules in solvent is not very small, then the solute - solute interaction may not be avoided. These may cause dimer formation between the two monomer solute molecules; and

5) The long range intermolecular resonance effects: These are very important in the emission studies.

All these effects are to be considered while calculating the spectral energy shift or spectral intensity change.

1.51 Solvent Effect on Transition Energy of an Allowed Transition

Upon absorption the electro-magnetic radiations, the permanant dipole of the molecule in the ground state (μ_g) changes to the dipole moment in the excited state (μ_e). In presence of solvent molecules, owing to the solute solvent interaction, ground and excited states stabilise differently. The change in the stabilisation energy ΔW is given by :

$$\langle \Delta W \rangle = h \Delta \nu^{a} \qquad (1.511)$$

where $\Delta\nu^a$ is the change in the absorption maxima frequency and h is the Planck's constant.

Thus, we see that the study of the solvent shift may reveal various features of the ground and excited states of the molecules. In general $n-\pi^*$ states show blue shift while $\pi-\pi^*$ and CT states show red shifts.

Using quantum mechanical perturbation theories, Ooshika[38] has calculated first time the stabilisation energy of an electronic state due to solute solvent interaction in 1954. The same method was used later by Longuet - Higgins and Pople[39] and by McRae[40].

Here, we will discuss the quantum mechanical theory on the solvent effect on electronic spectra. The proposed theory is the stationary theory where the translational motion of the molecules is neglected completely. The theory will hold only for slow perturbations. The time dependence of Hamiltonian for the absorbing system has also been considered but the complications and difficulties associated with such a theory in evaluating the interaction is obvious.

Let us consider a dilute solution so as to avoid solute - solute interaction. The problem is now to find the appropriate stationary energy states of a system consisting of a single solute surrounded by a set of solvent molecules in a given configuration and then average over all possible configurations. Let Φ_m, ε_n and Ψ_n, E_n are the eigenfunctions and eigenvalues of solute and solvent molecule respectively. Then a set of basic functions $\Psi_{mn} = \Phi_n \Psi_n$ can be used for the interacting pair. The next step is to introduce the perturbation Hamiltonian H, and the interaction energy to second order in H, using perturbation theory which may be written as :

$$W_{mn} = \langle \Phi_m \Psi_n | H' | \Phi_m \Psi_n \rangle + \sum_{n' \neq n} \frac{|\langle \Phi_m \Psi_n | H' | \Phi_m \Psi_n \rangle|^2}{E_n - E_{n'}} + \sum_{m' \neq m} \frac{|\langle \Phi_m \Psi_n | H' | \Phi_m \Psi_n \rangle|^2}{\varepsilon_m - \varepsilon_{m'}} + \sum_{m' \neq m,\, n' \neq n} \sum \frac{|\langle \Phi_m \Psi_n | H' | \Phi_m \Psi_n \rangle|^2}{\varepsilon_m - \varepsilon_{m'} + E_n - E_{n'}} \qquad (1.512)$$

If we assume that H′ represents the electrostatic interaction between the solute and the solvent molecules, then the perturbation operator may be written as :

$$H' = \sum_i \frac{\mu_0 \mu_i}{r_i^3} \Theta_i \qquad (1.513)$$

where μ_0 and μ_i represent the dipole moment of the solute and i th solvent molecule respectively; r_i and Θ_i are the distance and the mutual orientation between the solute and the i th solvent molecule. The above simple dipolar representation of the molecular interaction is not operative in cases where the specific short range forces like hydrogen bonding, charge transfer etc. are present.

Using equations (1.513), equation (1.512) becomes :

$$
\begin{aligned}
W_{mn} = {} & (\langle \Phi_m | \mu_0 | \Phi_m \rangle) \sum_i \frac{\langle \Psi_n | \mu_i | \Psi_n \rangle}{r_i^3} \Theta_i \\
& + \langle \Phi_m | \mu_0 | \Phi_m \rangle^2 \sum_{i,j} \sum_{n' \neq n}^{i} \frac{\langle \Psi_n | \mu_i | \Psi_{n'} \rangle \langle \Psi_n | \mu_j | \Psi_{n'} \rangle}{(E_n - E_{n'})\, r_i^3\, r_j^3} \Theta_i \Theta_j \\
& + \sum_{m' \neq m} \sum_{i,j} \frac{\mu_i \mu_j}{r_i^3\, r_j^3} \Theta_i \Theta_j \frac{\langle \Phi_m | \mu_0 | \Phi_{m'} \rangle^2}{\varepsilon_m - \varepsilon_{m'}} \\
& + \sum_{m' \neq m} \sum_{i,j} \sum_{n' \neq n} \frac{\langle \Phi_m | \mu_0 | \Phi_{m'} \rangle^2 \langle \Psi_n | \mu_i | \Psi_{n'} \rangle \langle \Psi_n | \mu_j | \Psi_{n'} \rangle}{(\varepsilon_m - \varepsilon_{m'} + E_n - E_{n'})\, r_i^3\, r_j^3} \Theta_i \Theta_j
\end{aligned}
\qquad (\ 1.514\ )
$$

The first term arising from the first order perturbation theory. It represents the interaction between two permanent dipoles. The second term corresponds to the permanent dipole of the solute with dipole induced in solvent. The third term represents the interaction of the permanent dipole of solvent with the dipole induced in the solute. The last term represents the second order interaction with states in which both the molecules are excited, corresponds to the dispersive interactions.

In order to make above expression available for any practical use, we will have to assume a specific model for solvent solute system. Direct evaluation of the integrations is not possible due to our lack of knowledge of molecular eigen functions.

The relatively simple Onsager model[41] having broad physical meaning for liquid dielectric is most suitable to simplify expression (1.514) in terms of refractive index (n) and the dielectric constant (D) of the solvent and the polarisability of the solute molecule. In Onsager model, the solute molecule is considered as a point dipole at the centre of a homogeneous spherical solvent dielectric cavity.

In Onsager's theory, the dipolemoment of a solute in solution μ'_m is related to the dipole moment of the isolated solute molecule μ_m , its static polarisability α_m and a suitable reaction field R_i (this field arises from the orientation induction polarisation of the dielectric by the solute dipole), as

$$\mu'_m = \mu_m + \alpha_m R_i \qquad (1.516)$$

where the reaction field due to induction[R_i (ind)]; R_i (ind) $= 2\mu_m/a^3 \, [(n^2-1)/(n^2+2)]$ and reaction field due to orientation[R_i (or)]: R_i (or) $= 2\mu_m/a^3 \left[(D-1)/(D+2) - (n^2-1)/(n^2+2)\right]$. Here, 'a' is the Onsager's cavity radious.

In order to apply this theory, let us imagine a solute molecule surrounded by N solvent molecules. Fixing the solute molecule, let N molecular distribution function be

$$f(1, 2, \quad N) = f_0 + f_1 \qquad (1.516)$$

where f_0 is the hypothetical distribution function when the dipolemoment of the solute molecule is assumed to be zero and f_1 represents the orientation of the solvent molecules by the dipole of the solute molecule in solution. The orientation relaxation time of solvent molecules should be much larger than the time required for light absorption (10^{-16} second) by the solute. Using the statistical concepts, averaging of the various interaction terms in (1.514) over the molecular distribution function can be performed to get the energy change of the solute molecule in the state m due to solvent solute interaction as $\langle W_{mm} \rangle$. The frequency shift of the absorption maximum is the difference between $\langle W \rangle$ for the ground (g) and excited (e) states of the solute molecule, the solvent molecules being in the g - state. The general expression for the solvent shift of a solute molecule in nonpolar solvent is given by :

$$\hbar \Delta \nu^{a} = \langle W_{eg} \rangle - \langle W_{gg} \rangle$$

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

$$\left.(\mu_g^2-\mu_e^2)+\frac{2}{a^3}\left(\frac{n^2-1}{n^2+2}\right)\frac{E}{E+\varepsilon}\left\{|P_{eg}|^2+\varepsilon(\alpha_g-\alpha_e)\right\}\right\} \qquad (1.517)$$

where P_{eg} is the transition moment of solute for the electronic transition between the states 'g' and 'e'. The first term represents the polarisation effects while the second term is the term representing the dispersive effects which exists in all the systems irrespective of the polar character of the solute and the solvent.

In case of polar solvents, one extra interaction term will also be arising. This comes from the orientation - induction effect of solvent dipole on the solute molecule. The shift due to this interaction term is given by :

$$h \Delta \nu^{a} (OR-IN) = \frac{3}{(2D+1)} \cdot \frac{(2D+1)^{2}(D-n)^{2}}{(2D+n^{2})\ \ D} \cdot \frac{kT}{3a^{3}} (\alpha_{e} - \alpha_{g}) + \frac{1}{a^{3}} \left(\frac{2D-2}{D+2} \right)^{2} (\mu_{e}^{2} \alpha_{e} - \mu_{g}^{2} \alpha_{g}) \tag{1.518}$$

From (1.517) and (1.518), it can be noted that this is only the temperature dependent term in the solvent shift expression. Therefore, the informations about this interaction can be obtained by the temperature effect studies on the electronic spectral shift.

1.43 Solvent Effect on the Intensity of Allowed Electronic Transitions

The oscillator strength (f) is related to the transition moment (M_{ij}) corresponding to the absorption band of the molecule and is given by :

$$f \propto \left\{ |M_{ij}|^2 = |\langle i|M|j\rangle|^2 \right\} \qquad (1.431)$$

It is obvious that M_{ij} is sensitive to the exact form of the states 'i' and 'j' which are subject to modifications due to solute - solvent interactions.

According to classical dispersion theory f is given by :

$$f = 4.315 \times 10^{-5} \int \varepsilon(\nu)\, d\nu \qquad (1.432)$$

where $\varepsilon(\nu)$ is the extinction coefficient at wave-number ν . The integration is over the band considered.

The effect of solvent on the unperturbed oscillator strength f_i of solute i has traditionally been accounted for by the Chako's factor $\{(n^2+2)^2/9n\}$ in the expression :

$$f_i \left\{(n^2+2)^2/9n\right\} = K \cdot S = f_s \qquad (1.433)$$

where f_s is the oscillator strength in a very dilute solution.

The solvent correction factor in the brackets of (1.433) arises from the use of the Lorentz local field for the electric field acting on the solute molecule in solution and was first introduced by Chako in 1934[42]. He, however, did not take into account the polarisability changes due to the presence of solvent molecules. The inadequacy of his correction is further accentuated by the fact that the Lorentz field does not take account of the translational fluctuations in the fluid. Chako's factor is always greater than unity and is same for all the solutes in a given solvent. Contrary to this, various authors[43,44] have pointed out that the experimental solvent correction was in cases less than or equal to one and thus the factor has shown its dependence on the properties of both solute and solvent.

Theoretical investigations[45-50] of the problem have generally focused on either the changes in polarisability, often without clearly distinguishing between them. Recently the problem has been thoroughly investigated by S. Abdulnur and B. Linder[51] to show that the Chako's factor is of minor importance as compared to an additional intermolecular force (IMF) factor.

Let us consider a system of N non overlaping nonpolar spherical molecules with centres located at $\bar{R}_1$, $\bar{R}_2 \cdots \bar{R}_N \equiv \bar{R}^N$, where $\bar{R}^N$ is the vector in three dimensional vector space. In presence of field $E(t) = E_0 e^{i\omega t}$, the Hamiltonian of the system can be written as :

$$H = H_e + H^{in} + K + H^{ex} \qquad (1.434)$$

where H_e : Hamiltonian for the electronic motion of free molecules

H^{in} : Interaction between the molecules

K : Kinetic energy operator taking care of the translational fluctuations

H^{ex} : Interactions of the system with the radiation field

The problem is treated by double perturbation theory : time - dependent in the interaction with the field and time independent in the intermolecular interaction. The Hamiltonian may also be written as :

$$H = H^{o} - M.E_o \exp (i\omega t + \xi t) \qquad (1.435)$$

where $H^{o} = H_e + H^{in} + K$ and $M = \sum_j \overline{m}_j = \sum e_n \overline{r}_n$, where n numbers the charges in the molecule and $\overline{r}_n$ is the radious vector of the n th charge with respect to an arbitrary origin. The factor $e^{\xi t}$ insures the adiabatic switching-on of the field. The average induced moment, linear in E_o is given by[61]

$$\langle \overline{M} \rangle = -\frac{i}{\hbar} \int_0^\infty d\tau \; T_r \Big[\overline{M} \Big\{ \exp\Big(-\frac{iH^\circ\tau}{\hbar}\Big) \Big\} (-\overline{M}\cdot\overline{E}_0) \exp\Big(\frac{iH^\circ\tau}{\hbar}\Big) - \Big\{ \exp\Big(-\frac{iH^\circ\tau}{\hbar}\Big) \Big\} (-\overline{M}\cdot\overline{E}_0) \Big\{ \exp\Big(\frac{iH^\circ\tau}{\hbar}\Big) \Big\} \overline{M} \Big] \rho \exp\big\{ (i\omega + \xi)(t - \tau) \big\} . \qquad (1.493)$$

where ρ is the statistical operator of the system of interacting molecules in the absence of the applied field i.e.

$$\rho = \exp(-\beta H^\circ) / T_r \left[\exp(-\beta H^\circ) \right]$$

and $\beta = 1/kT$

At ordinary temperatures, only the ground electronic state is populated in most of the molecules while the partitioning of the molecules among the translational energy levels is classical i.e. within an energy interval kT, the energy levels are densely spaced. Now, in addition, using the fact that the electronic motion is rapid than the nuclear motion, one can obtain an expression for $\langle M \rangle$ which would be independent of kinetic parameters and will be in terms of transition moment between the states considered.

Using the statistical concepts and by developing the virial expansion for the extinction coefficient, integrated over an allowed band, the following expression is obtained :

$$\left[\frac{(n^2+2)^2}{9n}\right] f_i \left[1+\left(\frac{N_j}{f_i V}\right)\times\int g^{(2)}(\bar{R}_{ij})\, f_{ij}(\bar{R}_{ij})\, d\bar{R}_{ij}\right] = K\cdot\int \qquad (1.437)$$

where (N_j/V) is the number of solvent molecules 'j' per C.C. of the solution; $g^{(2)}$ (R_{ij}) is the ordinary two body distribution function; f_i is the oscillator strength of the isolated unperturbed solute molecule i ; f_{ij} (R_{ij}) is an oscillator strength function of particles 'i' and 'j' and is parametrically dependent upon R_{ij} . The integration of LHS extends strictly over the volume of the solution sample. However, since the fuction f_{ij} drops off very quickly with internuclear distance (R_{ij}^{-6} dependence) the integration can be extended to infinity without introducing much error.

Comparision of (1.433) and (1.437) shows that the former can be reduced to the latter if one neglects the integration. This is only possible in the case of an absorber in a very rarified gas when $(N_j/V) \rightarrow 0$.

The main difficulties arise involving the configurational integration of the LHS of (1.437) in trying to numerical estimates for the solvent correction from that equation. The first stems from a lack of knowledge of accurate wave-functions of the isolated molecules needed to estimate the various matrix elements in the expression for f_{ij}. The second difficulty is to estimate the summation over all the discrete states and the implied integration over the continuum states in each of the various terms of f_{ij}.

1.5 Radiative and Nonradiative Decay Processes

The ground state of most of the stable organic molecules is a singlet and the lowest excited state is a triplet[37]. Although one can observe the spectra due to triplet ⟷ singlet transitions, the very severe multiplicity restriction on the transition is apparent when the observations show that the radiative life time of the t-states of the organic molecules are in the range of 10^{-2} - 1 seconds while those of the lowest singlets are of the order of 10^{-9} - 10^{-6} seconds. The light emission transition between the states with the same spin multiplicity is called fluorescence while that between the states with different multiplicities is called phosphorescence transition. In addition to light emission, there are always various radiationless transitions in polyatomic molecules. A nonradiative transition between the states with same multiplicities is known as 'internal conversion' while that between the states with different multiplicities is known as 'inter system crossing' (ISC). The observed decay time of an excited state depends upon the radiative and nonradiative transition probabilities (K_r and K_{nr} respectively) and is given by

$$\tau = \frac{1}{K_r + K_{nr}} \qquad (1.51)$$

1.51 Radiative processes

The interaction of an electronic system with quantised radiationfield causes emission and absorption of photons. Let H is the Hamiltonian of the total system given by :

$$H = H_{el} + H_{rad} + H_{int} \qquad (1.511)$$

$$= H_o + H_{int}$$

where, H_{el} and H_{rad} are the Hamiltonians corresponding to the electronic system and the radiation field.

The eigen functions Ψ_M of H_0 are the unperturbed stationary states given by :

$$\Psi_M = \Psi_M^{el}(\bar{r}) \cdot \Phi^{ph}_{n_1, n_2, \cdots\cdots n_\lambda} \qquad (1.512)$$

where $\Psi_M^{el}(\bar{r})$ is the m th state of the electronic system with eigen values E_m^{el}, and $\Phi^{ph}_{n_1,n_2\cdots} = \varphi_{n_1} \cdot \varphi_{n_2} \cdots\cdots \varphi_{n_\lambda}$ means that there are n_1 photons of energy E_1^{ph}, n_2 photons of

E_2^{ph} and soon.

The perturbation caused by H_{int} causes the transition to the state

$$\Psi_N = \Psi_n^{el}(\bar{r}) \quad \Phi^{ph}_{n_1' n_2' \ldots} \qquad (1.513)$$

The transition probability is proportional to the square of the matrix element $\langle \Psi_M | H_{int} | \Psi_N \rangle$. Let $E_m^{el} > E_n^{el}$; then assuming radiation field to be in vacuo with respect to matter, the one photon emission probability ω_{MN} for isolated molecules, where the interaction between the molecules is neglected, can be given by :

$$\omega_{MN} = \frac{64\,\pi^4 \nu^3}{3\,h\,c^3} \left| M_{nm} \right|^2 + \frac{8\pi^3}{3\,h^2} \left| M_{nm} \right|^2 \rho(\nu) \qquad (1.514)$$

where $\rho(\nu)$ is the energy density of emitted photons. The first and second terms in equation (1.514) are the spontaneous and the induced emission probabilities respectively.

When molecules are embedded in a fluid or solid solvents and there are no specific interactions between the molecules and the medium, then following formula can be derived :

$$\omega_{MN} = \frac{64\,\pi^4 \nu^3}{3\,h\,c^3\,n} \left| M_{nm} \right|^2 + \frac{8\,\pi^3}{3\,h^2\,n} \left| M_{nm} \right|^2 \rho(\nu) \qquad (1.515)$$

where n is the refractive index of the medium.

Oscillator strength is an important quantity concerning the practical aspects of transition probability. The oscillator strength is related to the spontaneous emission probability as :

$$f_{nm} = \frac{8\pi^2 m\nu}{3 h e^2} \left| M_{nm} \right|^2 \qquad (1.516)$$

The electronic spectra with vibrational structures can be well understood on the basis of Born - Oppenheimer approximation[54] and the Franck - Condon principle. According to Born - Oppenheimer approximation, molecular wave functions can be written in terms of the product of electronic and nuclear parts i.e.

$$\left.\begin{aligned} \Psi_n^{el} &= \Psi_{n\upsilon''} \simeq \Psi_n \cdot \phi_{n\upsilon''} \\ \Psi_m^{el} &= \Psi_{m\upsilon'} \simeq \Psi_m \cdot \phi_{m\upsilon'} \end{aligned}\right\} \qquad (1.517)$$

Using equations (1.517), the expression for oscillator strength can be obtained as :

$$f_{nm} \simeq f_{no,m} = \frac{4\pi mc}{3\hbar} \bar{\nu} \left| Q_{nm}(\bar{R}_e) \right|^2 \cdot \sum_{\upsilon'} \left| S_{no,m\upsilon'} \right|^2 \qquad (1.518)$$

where $e \cdot Q_{n\upsilon'', m\upsilon'}$ represents the relative contribution of the n $\upsilon'' \leftrightarrow$ m υ'' transition to M_{nm}, which is a sum of many vibronic contributions of this type and $S_{n\upsilon'', m\upsilon'} = \int \phi^*_{n\upsilon''}(\bar{R})\, \phi_{m\upsilon'}(\bar{R})\, d\bar{R}$ is the vibrational overlap integral.

Equation (1.518) clearly indicates that the Franck - Condon principle, which states that during the electronic transition the nuclear configuration of a molecule remains approximately at the equilibrium configuration $\bar{R}_e$ of the initial state, plays an important role.

1.511 Forbidden Transitions

Usually the transitions between the states with different multiplicities are forbidden. Let the electronic wave function may be written as a product of space $\Psi_m(r)$ and spin $\Theta_m(S)$ parts i.e.

$$\Psi_m \simeq \Psi_m(r) \cdot \Theta_m(S) \tag{1.5111}$$

The transition moment M_{mn} is thus,

$$\begin{aligned} M_{mn} &= \left\langle \Psi_m(r)\, \Theta_m(S) \middle| M \middle| \Psi_n(r)\, \Theta_n(S) \right\rangle \\ &= \left\langle \Psi_m(r) \middle| M \middle| \Psi_n(r) \right\rangle \cdot \left\langle \Theta_m(S) \middle| \Theta_n(S) \right\rangle \end{aligned} \tag{1.5112}$$

Θ_m (S),Θ_n (S) are orthogonal, if the two states have different multiplicities and then M_{mn} becomes zero. Thus the transition will be multiplicity forbidden. The transition, however, is weakly allowed as the Spin - Orbit (S - O) coupling increases. The S - O interaction can be enhanced not only by the heavy atom in the molecule (internal heavy atom effect) but also by the interaction with other molecules containing heavy atoms (external heavy atom effect)[55]

1.52 Non-radiative Processes

The interaction between the electronic and nuclear motions causes the radiationless transitions. As mentioned earlier the molecular electronic states (Φ) in the Born-Oppenheimer approximation are given by

$$\Phi = \Phi_{mv'}(\bar{R}_i, \bar{r}_j) \simeq \Psi_m(\bar{R}_i, \bar{r}_j) \cdot \Phi_{mv'}(\bar{R}_i) \qquad (1.521)$$

where $\Psi_m(\bar{R}_i,\bar{r}_j)$ is the stationary states of the electronic system in presence of fixed nuclei. Equation (1.521) represents the wave function of the unperturbed Hamiltonian H^0. The transition occurs between the states Φ_i and Φ_f due to the kinetic energy operator of the nuclear motion $H' = T_N$ with the transition probability per unit time as :

$$\omega_{if} = \frac{2\pi}{\hbar} \left| \langle \Phi_f | H' | \Phi_i \rangle \right|^2 \delta(E_f - E_i) \qquad (1.522)$$

where E_i and E_f are the energies of initial and final states Φ_i and Φ_f respectively. $\delta(E_f - E_i)$ is the delta function which represents the conservation of energy in the transition. The transition probability can be obtained by integrating over the final state i.e.

$$\omega = \frac{2\pi}{\hbar} \left| \langle \Phi_f | H' | \Phi_i \rangle \right|^2 \rho(E_f) \tag{1.523}$$

where $\rho(E_f)$ is the level density of the final state. Equation (1.523) is valid only when H is time independent and the final state is continuous. This indeed is the situation in solutions and solids where intermolecular interactions make the level density larger ;

The matrix elements of equations (1.522) and (1.523) may be written as

$$\langle \Phi_f | H' | \Phi_i \rangle = -\hbar^2 \sum_i \langle \Psi_n | \frac{\partial}{\partial \bar{R}_i} | \Psi_m \rangle \langle \Phi_{nv''} | \frac{\partial}{\partial \bar{R}_i} | \Phi_{mv''} \rangle \tag{1.524}$$

The integral in (1.524) may be written using perturbation theory as

$$\langle \Psi_n | \frac{\partial}{\partial \bar{R}_i} | \Psi_m \rangle \simeq \frac{\langle \Psi_n^e(\bar{R}_i) | \left(\frac{\partial H^0}{\partial \bar{R}_i} \right)_e | \Psi_m^e(\bar{R}_i) \rangle}{(E_m^e - E_n^e)} \tag{1.525}$$

Here, the superscript and subscript 'e' represents the quantities in equilibrium nuclear configuration.

The first term in (1.524) corresponds to the electronic transition moment integral of radiative transition and second one is the vibrational overlap, the square of which is the Franck Condon factor. This second term plays an important role in the radiation-less process. The value of this factor depends upon ($E_m^{0} - E_n^{0}$). The transition probabilities of the nonradiative processes $S_3 \rightsquigarrow S_2$, $S_2 \rightsquigarrow S_1$ etc. may be much larger than that of the $S_1 \rightsquigarrow G$ process. The second term in (1.524) will affect the transition probabilities in a similar way because this factor may be larger for the smaller energy gap in general.

When the molecules are dissolved in solvents, the interaction of the solute molecule with the solvent molecules generally enhances the radiationless transition probability. For i th normal mode :

$$\tau_i(m\,n) = \langle \Psi_n | \frac{\partial}{\partial \bar{R}_i} | \Psi_m \rangle$$

where $\Psi_n(\bar{R}_i)$ are the electronic states corresponding to the Hamiltonian : $H = H_0 + H_{S,O}$

where H_0 represents the K. E. and P. E. for electrons, H_{SO} is the spin-orbit interaction operator and both H_0 and H_{SO} contains nuclear coordinates as parameters and so can be expanded in the Taylor series. The wave function is given by

$$\Psi_n(\bar{R}_i) \simeq \Psi_n^e + \sum_{l \neq n} \Bigg[\frac{\langle \Psi_l^e | H_{so}^e + \sum_i \left(\frac{\partial H_0}{\partial \bar{R}_i}\right)_e \bar{R}_i + \sum_i \left(\frac{\partial H_0}{\partial \bar{R}_i}\right)_e \bar{R}_i | \Psi_n^e \rangle}{(E_n^e - E_l^e)}$$

$$+ \sum_{k \neq n} \Bigg\{ \frac{\langle \Psi_l^e | H_{so}^e | \Psi_k^e \rangle \langle \Psi_k^e | \sum_i \left(\frac{\partial H_0}{\partial \bar{R}_i}\right)_e \bar{R}_i | \Psi_n^e \rangle}{(E_n^e - E_l^e)(E_n^e - E_k^e)}$$

$$+ \frac{\langle \Psi_l^e | \sum_i \left(\frac{\partial H_0}{\partial \bar{R}_i}\right)_e \bar{R}_i | \Psi_k^e \rangle \langle \Psi_k^e | H_{so}^e | \Psi_n^e \rangle}{(E_n^e - E_l^e)(E_n^e - E_k^e)} \Bigg\} \Bigg] \Psi_l^e \qquad (1.526)$$

Using (1.526), $\tau_i(mn)$ is given by:

$$\tau_i(mn) \simeq \frac{\langle \Psi_n^e | \left(\frac{\partial H_{so}}{\partial \bar{R}_i}\right)_e | \Psi_m^e \rangle}{(E_m^e - E_n^e)}$$

$$+ \sum_{l \neq m} \Bigg[\frac{\langle \Psi_n^e | H_{so}^e | \Psi_l^e \rangle \langle \Psi_l^e | \left(\frac{\partial H_0}{\partial \bar{R}_i}\right)_e | \Psi_m^e \rangle}{(E_n^e - E_l^e)(E_m^e - E_n^e)}$$

$$+ \frac{\langle \Psi_n^e | \left(\frac{\partial H_0}{\partial \bar{R}_i}\right)_e | \Psi_l^e \rangle \langle \Psi_l^e | H_{so}^e | \Psi_m^e \rangle}{(E_m^e - E_l^e)(E_m^e - E_n^e)} \Bigg] \qquad (1.527)$$

Here the 1st term is the direct compling between the initial and the final state by the spin vibronic interaction. In the 2nd term, the initial state couples with the intermediate state Ψ_1^e through the vibronic interaction and the intermediate state interacts with the final state by the S - O coupling. In the 3rd term, the initial state interacts with the intermediate state through the S - O coupling and the intermediate state couples with the final state through the vibronic interaction.

CHAPTER 2

ELECTRONIC SPECTRA OF 9-NITROANTHRACENE : SOLVENT EFFECT ON $^1A \longrightarrow {}^1L_a$ AND $^1A \longrightarrow {}^1L_b$ TRANSITIONS.

1. Introduction

In aromatic hydrocarbons, four S - S bands are usually observed. In benzene, the lowest singlet state is ^1L_b with the next higher as ^1L_a.

In cata-condensed hydrocarbons as one moves from benzene to higher polyacenes, both ^1L_a and ^1L_b energy levels of benzene move to lower energy. The lowering in energy of ^1L_a is steeper than the ^1L_b. The correlation diagram of Klevens and Platt[56] for the spectra of polyacene series predicts that ^1L_b band should be hidden under the stronger ^1L_a transition in anthracene. Moffitt[57], Pariser[58] and Ham et al[59] also support this prediction from theoretical view point. In an effort to provide direct experimental evidence, Char[60] and Sidman[61] failed to observe ^1L_b band in anthracene molecule. However, the situation is quite different in substituted anthracenes. Strong mesomeric substituents like nitro group in anthracene molecule are expected to show strong effect on the π - electronic states of anthracene owing to their substitutional perturbations. We have chosen 9-nitroanthracene (NA) molecule to see if ^1L_b band appears on nitro group substitution. Intramolecular CT band is expected to be the lowest and should be of very low intensity as this molecule is found to have nonplanar structure. The interplanar angle[62] between the nitro group plane and the anthracene ring plane is as large as 85°. The situation in NA is quite different than that of anthracene and it is quite possible that the ^1L_b band of anthracene may shift to an accessible spectral region in this molecule.

In this chapter, we present the results of our studies on the electronic absorption and emission spectra of NA and show that indeed in this molecule the lowest energy state is having the predominantly π- character and is different from ^1L_a. The effects of various polar and non-polar solvents have also been investigated.

2. Experimental

The compound, a gift from Prof. R. S. Becker, was further purified by repeated recrystallization using purified benzene. Needle shaped yellow crystals having melting point at 146°C were obtained. The spectrograde solvents (BDH and E - merck) were used.

The absorption spectra in various solvents were recorded at 293°K on a Perkin Elmer 202 recording spectrophotometer and also on Spectromom 202 spectrophotometer of Hungarian Optical

Works. Aminco Bowman spectrofluorimeter was used to measure the emission spectrum.

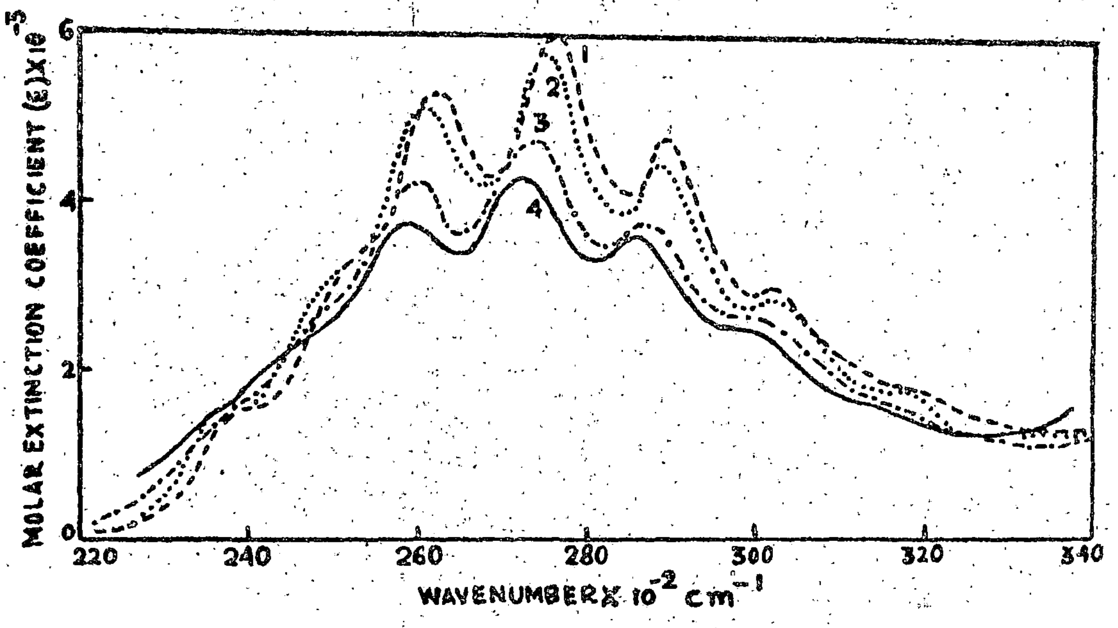
3. Results and Discussions :

The absorption spectra of NA in various nonpolar and polar solvents with the same concentration at room temperature (298 K) are reproduced in Figs. 2.1 and 2.2 respectively. The results of the analysis of the bands are summarised in Tables 2.1, 2.2 and 2.3. In all the solvents, a well defined intense band system at about 26100 cm^{-1} is observed with vibrational structure. In non-polar solvents, however, few more weak bands appear towards the lower energy side of this band system. In polar solvents, these weak bands lose their structure and a general broad weak absorption band is observed in this spectral region.

A close examination of the absorption spectra of NA in various solvents reveals that the strong band system at about 26100 cm^{-1} resembles the lowest energy absorption band of anthracene as shown in Fig. 2.3. The bands on the lower energy side are structurally different from the bands in the intense system and possibly belong to different electronic transition. This deduction has been further substantiated by the vibrational analysis of the spectra in various solvents.

It has been pointed out by Coggeshell and Pozefsky[63] that

Figure - 2.1

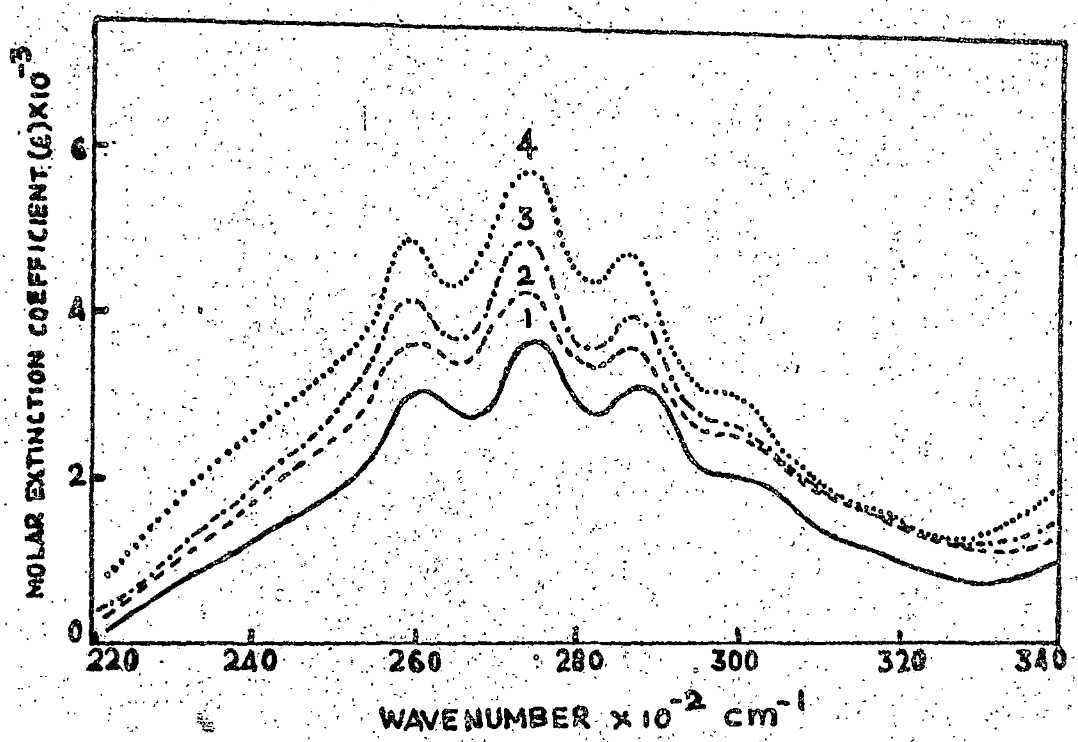


Electronic spectra of 9-nitroanthracene in various nonpolar solvents.

1. n - Hexane;   2. Cyclohexane;

3. Carbontetrachloride;   4. Benzene.

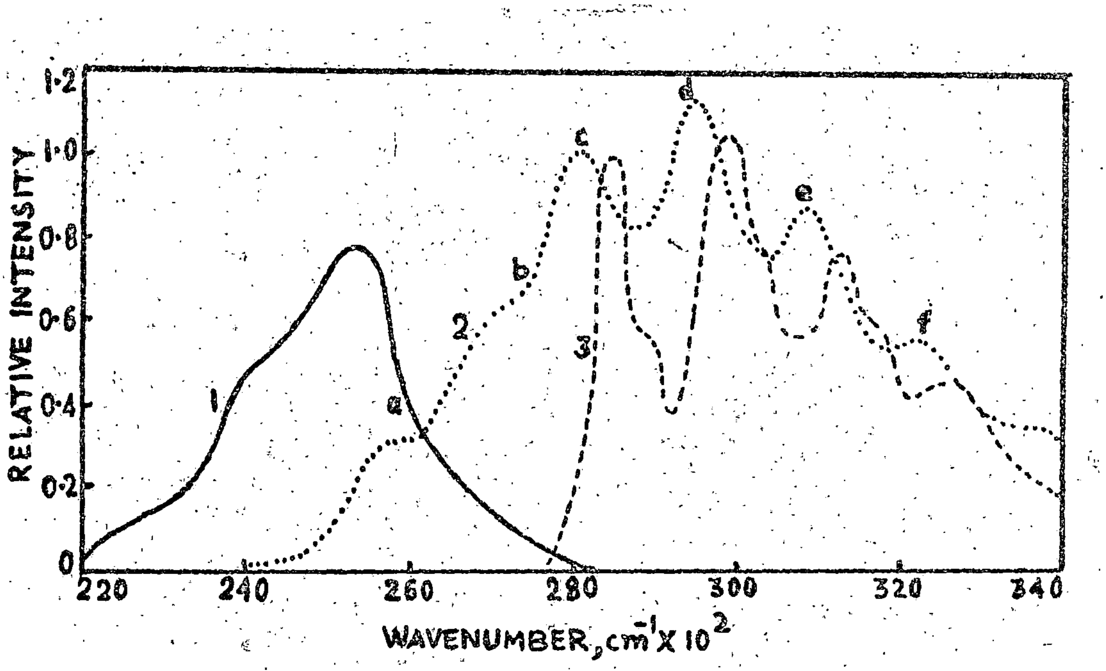
Figure - 2.2



Electronic spectra of 9-nitroanthracene in various polar solvents.

1. Methanol;
2. Tetrahydrofuran;
3. 1, 4 - Dioxane
4. Chloroform.

Figure - 2.3



Emission and absorption spectra in Cyclohexane at room-temperature.

1. Emission spectrum of 9-nitroanthracene;
2. Absorption spectrum of 9-nitroanthracene;
3. Absorption spectrum of anthracene.

Table 2.1 Absorption Bands of 9-Nitroanthracene in Various Non-polar Solvents at Room Temperature.

n - Hexane			Cyclohexane		
Wave number cm^{-1}	Intensity	Tentative assignment	Wave-number cm^{-1}	Intensity	Tentative assignment
24150	w	0_1	24000	w	0_1
25200	vw	$0_1 + 1050$	25000	vw	$0_1 + 1050$
26250	s	0_2	26075	s	0_2
27625	vs	$0_2+1400\pm25$	27475	vs	$0_2 + 1400$
29000	s	$0_2+2x1400 \pm25$	28900	s	$0_2 + 2 x 1400 \pm 25$
30350	w	$0_2+3x1400 \pm25$	30275	w	$0_2 + 3 x 1400 \pm 25$

Contd. .. 2.

Table - 2.1 (contd.)

Carbon tetrachloride			Benzene		
Wave number cm^{-1}	Intensity	Tentative assignment	Wave-number cm^{-1}	Intensity	Tentative assignment
23900	vw	O_1	23700	vw	O_1
24050	vvw	$O_1 + 1050$	24750	vvw	$O_1 + 1050$
25975	s	O_2	25850	s	O_2
27375	vs	$O_2 + 1400$	27250	vs	$O_2 + 1400$
28750	s	$O_2 + 2 \times 1400 \pm 25$	28650	s	$O_2 + 2 \times 1400$
30100	vw	$O_2 + 3 \times 1400 \pm 50$	30000	vw	$O_2 + 3 \times 1400 \pm 50$

w, weak; v, very; s, strong

Table - 2.2 Absorption Bands of 9-Nitroanthracene in Various Polar Solvents at Room Temperature.

Methanol			Tetrahydrofuran		
Wave-number cm^{-1}	Intensity	Tentative assignment	Wave-number cm^{-1}	Intensity	Tentative assignment
Broad and weak absorption in the range $25500 cm^{-1}$ to $22000 cm^{-1}$			Broad and weak absorption in the range $25300 cm^{-1}$ to $22000 cm^{-1}$		
26100	s	0_2	25950	s	0_2
27550	vs	$0_2 + 1400$	27350	vs	$0_2 + 1400$
28925	s	$0_2 + 2 \times 1400$ ± 25	28725	s	$0_2 + 2 \times 1400$ ± 25

Contd.

Table - 2.2 (contd.)

1, 4 - Dioxane			Chloroform		
Wage-number cm^{-1}	Intensity	Tentative assignment	Wave-assignment	Intensity	Tentative assignment
Broad and weak absorption in the range 25500 cm^{-1} to 22500 cm^{-1}			Broad and weak absorption in the range 25000 cm^{-1} to 23000 cm^{-1}		
25900	s	O_2	25875	s	O_2
27300	vs	O_2 + 1400	27275	vs	O_2 + 1400
28700	s	O_2 + 2 x 1400	28575	s	O_2 + 2 x 1400

v, very and s, strong.

Table - 2.3 Experimental Oscillator Strength Values and the X - Factors

Solvent	Oscillator strength	(1 + X)	Solvent	Oscillator strength	(1 + X)
Non-polar			Polar		
n - Hexane	0.1231	0.1044	Methyl alcohol	0.0801	0.0674
Cyclohexane	0.1221	0.0861	Tetrahydrofuran	0.1075	0.0866
Carbon-tetrachloride	0.1130	0.0869	1, 4 Dioxane	0.1141	0.0802
Benzene	0.1070	0.0799	Chloroform	0.1341	0.1048

in benzene and naphthalene spectra, the vibrational spacing involving transitions to a ^1L_a state is of the order of 1400 cm^{-1} and in transition to a ^1L_b state it is of the order of 1000 cm^{-1}. The 1400 cm^{-1} vibration is associated with the C - H in-plane bending whereas the 1000 cm^{-1} vibration is the breathing vibration of the ring.

The spectral analysis of NA shows that the seperation between the bands in the intense system is about 1400 cm^{-1} which possibly is C - H in-plane bending vibration which forms a progression in the absorption spectra of anthracene solution at room temperature. But the seperation between the bands 'b' and 'c' is about 900 cm^{-1} as shown in Fig. 2.3. This observation suggests that 'b' and 'c' belong to two different electronic transitions. The seperation between the bands 'a' and 'b' of the lower energy band system is much less than 1400 cm^{-1} and is about 1050 cm^{-1}. It seems that possibly the breathing vibration of the ring forms the progression in the weak low energy band system. We assign this band system to $^1A \longrightarrow {}^1L_b$ transition.

The emission spectrum of NA in cyclohexane is reproduced in Fig. 2.3. A good overlapping between the observed emission and weak low energy absorption spectrum is observed. Contrary to a previous statement[3], thus, 9-nitroanthracene actually is a weakly fluorescent molecule. This observation is interesting in view of the fact that the luminescence of nitroaromatics is not yet clearly understood. The lowest excited singlet and triplet states of nitroaromatic compounds are usually nearly degenerate and both $\pi-\pi^*$ and $n-\pi^*$ states are present in each molecule. A good overlapping between the lowest energy weak absorption and the emission shows that both initiates from the same states which has a $\pi-\pi^*$ character. It has been suggested by Plotnikov[64] that as the size of the aromatic system increases, $\pi-\pi^*$ state moves to a level lower than the $n-\pi^*$ state energy level. Intramolecular CT character of the low energy state is also expected to increase with the size of the polynuclear nitroaromatics. All these considerations may causes an increase in the ${}^1S_1 \rightarrow S_0$ radiative transition probability.

Thus, we conclude that the lowest excited singlet state in NA is a $\pi-\pi^*$ state and that the system having origin at about 23300 cm^{-1} belongs to ${}^1A \rightarrow {}^1L_b$ and the other having origin at about 26100 cm^{-1} belongs to ${}^1A \rightarrow {}^1L_a$ transition.

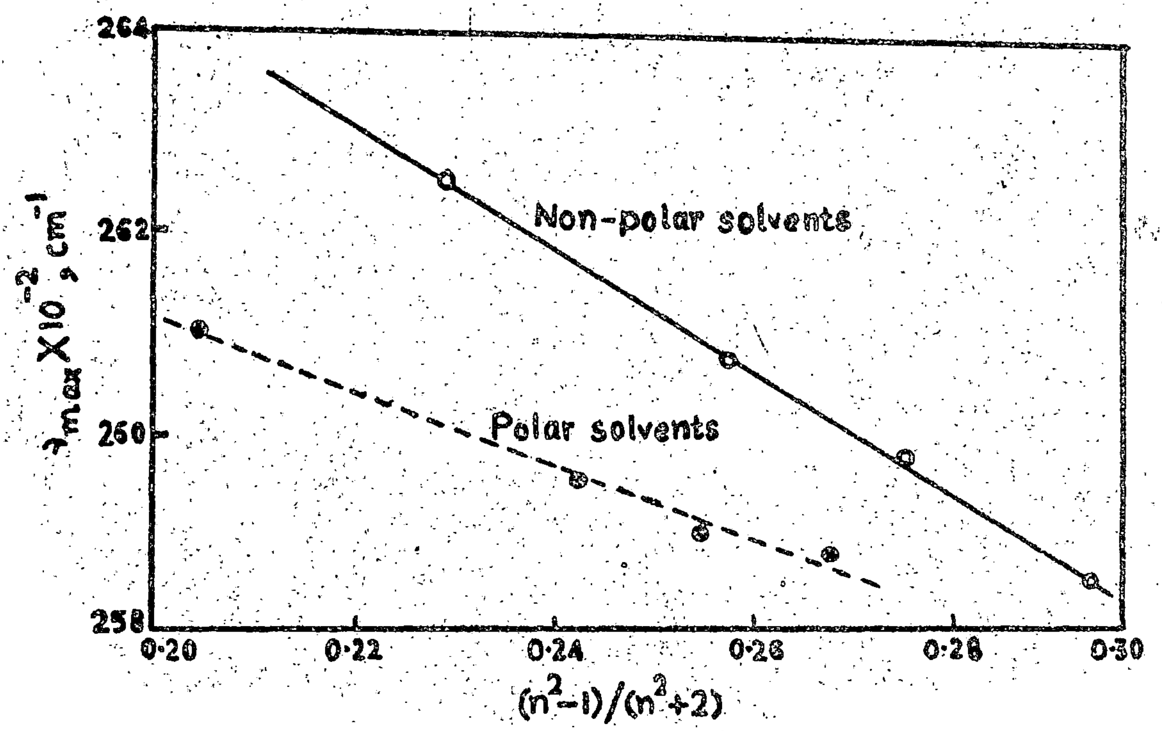
3.2 Solvent Effect

3.21 Solvation energy

In polar solvents like methanol, tetrahydrofuran (THF), 1,4 dioxane and chloroform as shown in Fig. 3.3 though ${}^1A \rightarrow {}^1L_a$ transition shows a vibrational structure, in ${}^1A \rightarrow {}^1L_b$ transition the vibrational structure is not generally observed. In non-polar solvents like n - hexane, cyclohexane, carbontetrachloride and benzene as shown in Fig. 2.1, the vibrational structure of both $^1A \longrightarrow {}^1L_a$ and $^1A \longrightarrow {}^1L_b$ transitions are observed. However the vibrational structure observed in saturated hydrocarbons is appreciably blurred in the solvents like carbontetrachloride and benzene, possibly due to stronger interaction between the solute and solvent molecules.

The solvent effect on the absorption spectra is known to be due to dispersive interaction, dipolar interaction and in case of polar solvents also due to orientation induction effects[12,36] of the solvent dipole on the solute molecule. In addition, local interaction like bond formation etc. may also affect the transition energy. Quantitative estimation of the absorption energy could be made for $^1A \longrightarrow {}^1L_a$ transition only. For both nonpolar and polar solvents, plots of transition energy against the factor $\left[\frac{(n^2 - 1)}{(n^2 + 2)}\right]$ give good straight lines. The linear plot for the polar solvents is, however, on the lower energy range and has a different slope than that for non-polar solvents as shown in Fig. 4. The linear plot in non-polar solvents indicates that the dispersive interactions predominates over the dipolar interactions. For the $^1A \longrightarrow {}^1L_a$ transition of medium intensity, this possibly further suggests that the change

Figure - 2.4



The plot of transition energy of $^1A \longrightarrow {}^1L_a$ band of 9-nitroanthracene against the factor $(n^2 - 1)/(n^2 + 2)$.

in the dipole moment on excitations is small in this molecule. The linear plot in polar solvents is not easy to rationalise. It possibly indicates that the difference in dipole moment in the excited and ground state is small and also the sum total of orientation - induction effect and local interaction is not much dependent on the solvent refractive index. Small refractive index dependence is, however, present giving a different slope of the linear plot. Indeed, 9-nitroanthracene is expected to have strong local interaction with some polar solvents[65-69].

3.22 Oscillator - Strength (f) :

Theoretical studies on the solvent effect on the f - value of an electronic transition in the solute molecule have been mostly concerned with the local field effect[42,45]. The results are always analysed in terms of local field distributions and distortions of electronic charge distribution by the surroundings. 'Chako's Correction Factor' for the spectral intensity change is not sufficient to explain the observed results. Recently, considering long range dispersive forces to be operative, Abdulnur[51,52] has shown that for the conversion of f - value in solution from the corresponding isolated molecular value, Chako's factor is of minor importance compared to an additional 'IMF factor' originating from the intermolecular forces between the solute and the solvent molecules and from the translational fluctuations between the induced moments.

Our results for the f - values in various solvents can not be explained by Chako's factor ($\frac{1}{\gamma}$) alone. Expanding the EMP factor to include local interactions as well, the experimental oscillator strength in solution f_s can be expressed by an empirical relation :

$$\frac{1}{\gamma}(1 + x)\ f_1 = f_s$$

where f_1 is the free molecular oscillator strength. We have estimated the values of (1 + X) f_1 from the experimentally observed oscillator strengths in solution which are presented in Table 2.3. With the increase of n, while in polar solvents the f - value increases, f - value decreases in nonpolar solvents. In case of nonpolar solvents, the dispersive interaction plays a very important role. In going from n - hexane to benzene, the solute solvent dispersive interaction increases. The X - factor increases with the increase of refractive index. Thus, the observed decrease in X - factor indicates a negative value for this factor in nonpolar solvents. In polar solvents the contribution to the X - factor is not only due to dispersive interaction or dipolar interactions but also due to local interactions. Thus, the X - factor in polar solvents will be in the order:

$X_{MeOH} > X_{THF} > X_{Dioxane} > X_{Chloroform}$

The experimentally observed f - values increase in the same order indicating a positive value for the X - factor.

4. Conclusions

The ^1L_b band, which is hidden under the intense ^1L_a band in anthracene, seperates out in 9-nitroanthracene owing to the nitrogroup substitutional perturbation. The molecule (NA) is observed to fluoresc very weakly. The solvent effect on the electronic spectra has been explained interms of the predominant dispersive and other local interactions. Intermolecular forces between the solute and solvent molecules are found to be important.

CHAPTER - 3

ELECTRONIC SPECTRA OF 2 - NITROFLUORENE : SOLVENT EFFECT ON $^1A \longrightarrow {}^1L_a$ TRANSITION.

1. Introduction

In the near UV region, fluorene shows two electronic band systems: one of low intensity at 300 nm is due to the $^1A \longrightarrow {}^1L_b$ transition and the other which is intense appearing at 260 nm is due to the $^1A \longrightarrow {}^1L_a$ transition. According to Platt[70], ^1L_b band is short axis polarised and ^1L_a is long axis polarised. On the other hand, Zwarich[71] concluded, from his polarisation studies of the electronic absorption and the fluorescence spectrum of oriented single crystal that the 300 nm band is long axis polarised.

Substitution of various groups are known to influence the electronic spectra of the parent molecule. The perturbation caused by strong mesomeric substituents is very strong. The complications may arise due to the presence of nonbonding electrons. Appearance of n-π^* and intramolecular CT bands, some times, make the assignment of the observed bands difficult. Thus, the substitution of nitro group at position 2 on fluorene molecule is expected to show a strong perturbation on the long axis polarised transition. The luminescence properties of 2 - nitrofluorene has been investigated by Roy and Becker[10] Khalil et. al[3] and Nagakura et. al.[9]

In this chapter, we present our results on the investigations of the electronic spectra of 2 - nitrofluorene under various conditions and confirm that the $^{1}L_{a}$ band of fluorene is a long axis polarised band. Further, the assignment of the bands and the solvent effect on the electronic absorption spectra of this molecule have also been presented.

2. Experimental

The compound 2-nitrofluorene (NF) from 'Eastman Organic Chemicals' was recrystallised several times from purified ethanol. Solvents of spectrograde quality were used.

Zone-refined biphenyl was used as a host for the mixed crystal spectra. Crystals were glown from the melt with guest concentrations of about 10^{-3}M by slowly lowering the temperature.

The spectra were recorded at room temperature (25°C) on a Spectromom - 202 spectrophotometer.

3. Results and Discussions

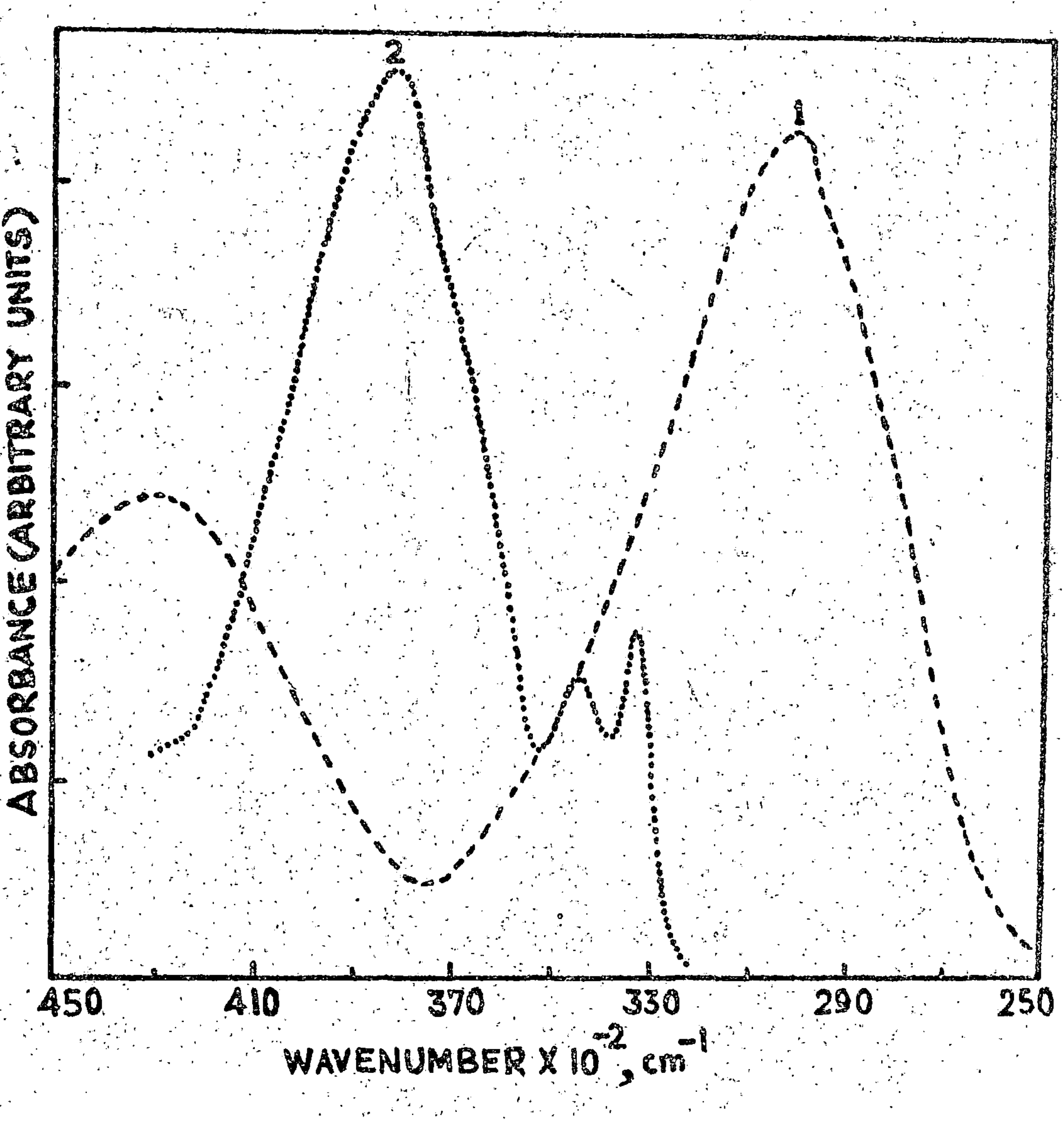
3.1 Spectra and Assignment

In Fig. 3.1, the absorption spectra of fluorene and NF in methanol solution are reproduced. A close examination of the figure reveals that the $^1A \longrightarrow {}^1L_a$ band (33400 cm^{-1}) of fluorene very much resembles the intense band system of NF. But the other band system corresponding to $^1A \longrightarrow {}^1L_b$ band of fluorene is not observed in NF. It seems that as a result of strong nitro group perturbation, the ^1L_a band experiences a larger red shift than ^1L_b band, which appears to be hidden under the intense ^1L_a band. At this point, it may be noted that NO_2 - substitution at second position of the fluorene ring system imparts a strong dipole moment along the C - N bond direction which interacts with the long axis transition dipole moment more strongly than with the short axis transition dipole and thereby perturbs the long axis transition much more. This confirms that 260 nm band of fluorene is a long - axis one but does not confirm that the 300 nm band is a short-axis transition because the oscillator strength value for this transition is one order of magnitude lower than that for the 260 nm band.

Due to the presence of nitro group, as one observes in nitrobenzene[15], in addition to ^1L_a, ^1L_b bands, intramolecular CT and also $^1n\,\pi^*$ transitions may appear in NF.

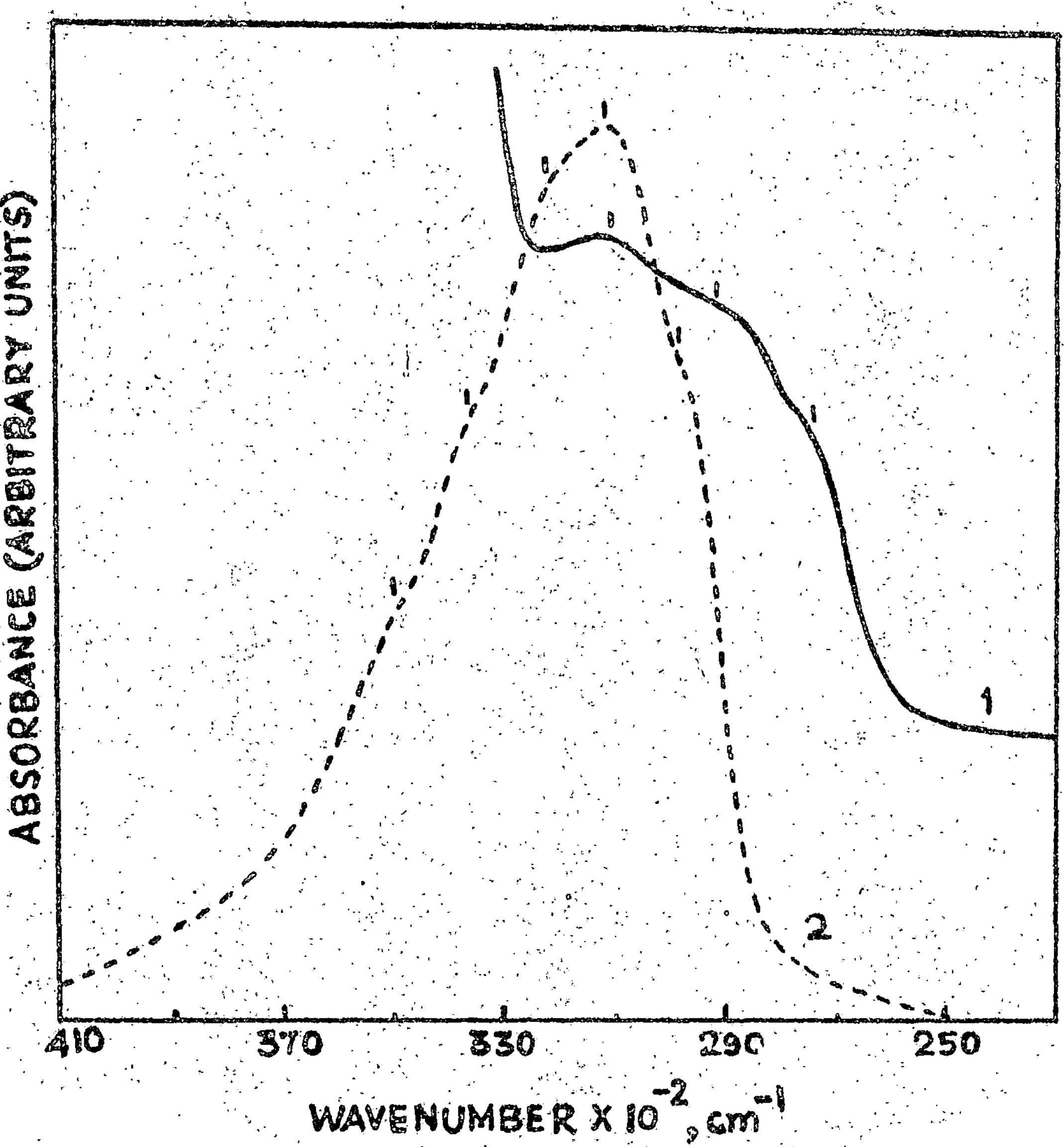
The electronic absorption spectra of the compound in n-hexane are reproduced in Fig. 3.2. The ν_{max} position of the intense band

FIGURE 3.1



Electronic absorption spectra of 2-nitrofluorene (1) and fluorene (2).

FIGURE 3.2



Electronic absorption spectra of 2-nitrofluorene :

(1) : 2-nitrofluorene guest-biphenyl host mixed crystal

(2) : solution spectrum in n- hexane.

in different solvents and the results of the spectral analysis (in n - hexane and mixed crystal) are summarised in Table 3.1. An intense band is observed at about 31175 cm^{-1} with a very blurred fine structure. The spectral analysis shows that the spacing between the bands in n - hexane is approximately 1275 cm^{-1} which is possibly the vibrational structure of the $^1A \longrightarrow {}^1L_a$ band. No indication as to the presence of $^1A \longrightarrow {}^1L_b$, CT and $n\pi^*$ bands could be observed. Investigations with other polar and non polar solvents failed to reveal these bands. We have, therefore, studied the spectra of BP in solid state using biphenyl as matrix. The mixed crystal spectrum is also included in Fig. 3.2. The spacing between the bands is of the order of 1800 cm^{-1} which is much larger than 1275 cm^{-1}, the progression - forming vibrational frequency of the molecule. This suggests that these three bands observed in the mixed crystal are three different electronic band systems.

It seems that the weak ^1L_b band appears in the mixed crystal spectra as a result of guest host interaction. It is expected that this interaction is larger for intense $^1A \longrightarrow {}^1L_a$ transition causing more red shift than weak $^1A \longrightarrow {}^1L_b$ transition. The third longest wave length band in the mixed crystal might be either ^1CT or $^1n\pi^*$ transition. But usually the $^1n\,\pi^*$ transitions appear[15] at much longer wavelengths, it is more probable for the longest wave length

TABLE 3.1

Table - 3.1 Spectral Analysis Of The Electronic Spectrum Of 2 - Nitrofluorene.

n - Hexane		Mixed Crystal	
Wavenumber cm^{-1}	Assignment	Wavenumber cm^{-1}	Assignment
29850 (h)	0_2	27397 (msb)	0_1
31175 (vs)	$0_2 + 1275 \pm 25$		
32258 (h)	$0_2 + 2 \times 1275 \pm 50$	29154 (msb)	0_2
33670 (h)	$0_2 + 3 \times 1275 \pm 50$		
34965 (h)	$0_2 + 4 \times 1275 \pm 50$	31055 (msb)	0_3

V, very; m, medium; S, strong; h, hump and b, band mixed crystal band to be the intramolecular CT band.

The fluorescence from this nitro-aromatic could not be detected in any of the solvents used. This possibly suggests that the n π^* transition is the lowest energy singlet-singlet transition in this molecule and is forbidden. The nonradiative decay route from this state to the ground state must be very efficient.

3.2 Solvent Effect

The effect of various solvents has been investigated in the $^1A \longrightarrow {}^1L_a$ band of 2 - nitrofluorene. The non-polar solvents n - hexane, cyclohexane, benzene and carbontetrachloride and polar solvents methanol, ethanol, iso-propanol, tert-butanol, 1, 4 dioxane, tetrahydrofuran (THF), acetone, chloroform and water have been used.

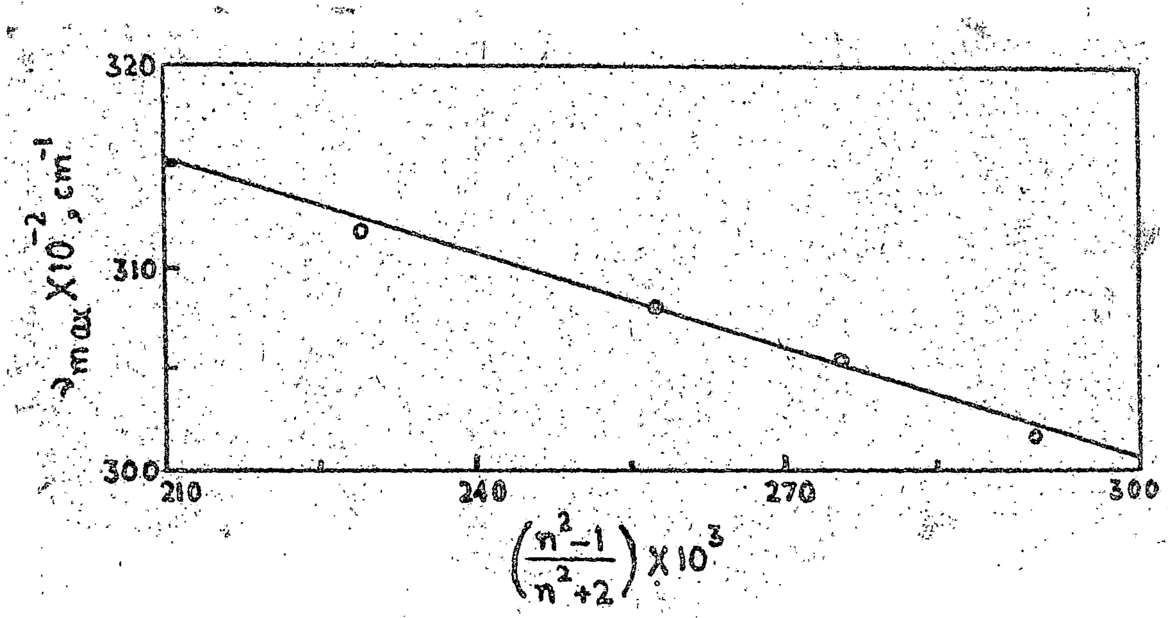
The weak vibrational structure could not be observed in other solvents. In none of the solvents, ^1L_b band system could be seperated out from the intense band and the band maxima gives the ν_{max} for $^1A \longrightarrow {}^1L_a$ transition.

The solvent effect on the absorption spectra is known to be due to dipolar, dispersive and orientation-induction effects[12,36]. In addition, a weak bond formation between the solute and solvent - also contribute to the spectral shift. Evidently, μ_g and μ_e are important as they determine the stabilisation of ground and excited states as a result of dipolar interaction.

For non-polar solvents, the plot of transition energy against the factor f (n) i.e. ($n^2 - 1$)/ ($n^2 + 2$) gives a straight line as shown in Fig. 3.3. Assuming that the solute dipole solvent induced dipole interaction is weak and any significant local interaction is absent, the predominant interaction in these non-polar solvents is the dispersive interaction. This is in confirmity with our experimental observation of bathocromic shift with the increase in n - value and the linear plot of Fig. 3.3.

The electronic absorption spectra of NP in n - hexane solution is increasingly red shifted as the polarity of the solvents is increased. This red shift can be explained by the increase in μ_e which is responsible for the lowering of the excited state energy from the Franck Condon state to the equilibrium state of the Solute molecule. The reorientation of the solvent dipoles is also taking place in the solvation shell during the excited state life time. Thus, the extent to which the spectrum is red shifted depends upon the polarity of the solvent used. However, the examination of Table 3.2 shows that the polar solvents can be classified into two groups according to the magnitude of the shift. In 1, 4 - dioxane, THF, $CH\ Cl_3$ and acetone, the red shift is more than in

FIGURE 3.3



The plot of transition energy of $^1A \longrightarrow {}^1L_a$ band of 2-nitrofluorene against the factor ($n^2 - 1$)/($n^2 + 2$).

TABLE 3.2

Table - 3.2 Solvent Effect on $^1A \longrightarrow {}^1L_a$ Transition of 2 - Nitrofluorene.

Solvent	$_{max}(cm^{-1})$
n - Hexane	31175
Cyclohexane	30800
Carbontetrachloride	30525
Benzene	30150
Methanol	30225
Ethanol	30303
iso-Propanol	30395
tert-Butanol	30441
1, 4 dioxane	30300
THF	30050
$CH\ Cl_3$	29950
Acetone	29850
Water*	22650

* Very sparingly soluble - hot solution

alcohols for equivalent molecular dipole moment values. This is expected in view of the fact that in the above mentioned nonalcoholic polar solvents the solvent absorption band is close to NF band. The results in alcohols and water are different are attributable to the hydrogen bonding and to the resultant erroneous values of the local fields in the solute solvent systems.

Oscillator strength and K - factor[72] calculations for $^1A \rightarrow {}^1L_a$ transition in various solvents could not be made because of the superimposition of other transitions on this intense band.

4. Conclusions

The nitro-group perturbation on position 2 of fluorene molecule confirms that the ^1L_a is long axis polarised. In a mixed crystal spectra three band systems have been observed whereas in solution only the intense ^1L_a band could be observed. The solvent effect on $^1A \longrightarrow {}^1L_a$ transition energy has also been investigated in various polar and nonpolar solvents.

CHAPTER - 4

ELECTRONIC ABSORPTION AND EMISSION SPECTRA OF 1, 4-DINITRONAPHTHALENE

1. Introduction

The electronic absorption and emission spectra of nitroaromatic compounds are of considerable interest and indeed significant amount of work has already been reported[1-18] on some nitroaromatic compounds though clear understanding is still to be achieved. The interest mainly lies in intramolecular charge transfer (CT) band characteristic of the electron donor - acceptor interaction involving the aryl moiety and the nitro group. In addition, the nonbonding electron of the nitro group giving a set of the $n-\pi^*$ states and their interaction with the close lying $\pi-\pi^*$ states affect the radiative and nonradiative processes of the lowest excited states in the nitroaromatic molecules. In Chapter - 2 we have investigated the electronic spectra of 9-nitroanthracene with the aromatic residue comparatively large thus giving the lowest excited states of both singlet and triplet manifold a dominantly $\pi-\pi^*$ character contrary to that observed in nitrobenzene with small aryl moiety[8]. Investigations on the spectroscopic properties of nitronaphthalenes are interesting in view of the fact that the size of the aromatic residue in these molecules is intermediate between that in nitrobenzenes and nitroanthracenes. The electronic spectral properties of 1,4-dinitronaphthalene is not well understood. The assignment of lowest triplet state as $^3n-\pi^*$ by Becker et al[10] is quite doubtful[3]. So, we have investigated the electronic absorption and emission spectra of 1,4-dinitronaphthalene in order to assign low-lying electronic states and to study luminescence characteristics of this molecule. In this chapter, we present our results.

2. Experimental

The compound 1,4-dinitronaphthalene from Eastman Organic Chemicals was recrystallised several times from purified methanol. Solvents used were of spectrograde quality. The absorption spectra in various solvents were recorded at room temperature 298° K on a Shimadzu 210 A spectrophotometer. Emission spectra were recorded on a Perkin Elmer MPF 44A spectrofluorimeter at 77°K. Phosphorescence was isolated by a rotating can phosphorescope. Phosphorescence life time was measured using a ECIL OS 769 oscilloscope display. The emission of the protonated species was studied in a mixture of sulfuric acid with ethanol/methanol (1:1 by volume). Precaution was taken to ensure that no chemical reaction occured in the acid media. The criterion in this regard was that the spectra of the acid solution obtained immediately upon mixing did not there after change in time.

3. Results and Discussions

3.1 Absorption Spectra

The absorption spectrum of 1,4-dinitronaphthalene in methanol at room temperature is shown in Fig. 4.1. In the UV - Vis region, three broad bands with λ_{max} at about 213 nm, 240 nm and 337 nm in decreasing order of intensity are observed. This absorption spectrum is similar to that of 1,5-dinitronaphthalene[1] except that the bands are red shifted in this polar 1,4-dinitronaphthalene molecule. Absorption spectrum of naphthalene in methanol is also shown in Fig. 4.1 for comparison. The absorption spectrum of 1,4-dinitronaphthalene differs considerably from that of naphthalene. Here, we confine our discussion to the low lying states i.e. the broad band in the spectral region 320 nm - 380 nm only. In $H_2 SO_4$ mixture in methanol the broad band is seen to consist of two distinct bands with λ_{max} at 337 nm (Band II) and at 380 nm (Band I) respectively. λ_{max} for the two bands could be easily located for the polar solvents though in nonpolar solvents the significant overlap of the two bands impaired λ_{max} location for the low energy band I. In Table 4.1, solvent effect on the λ_{max} of the two bands is shown. It is observed that the λ_{max} of the low energy band shows a large red shift with solvent polarity and in acidic media this band is almost completely seperated from the high energy band II. This means that the upper state responsible for this band is extremely polar.

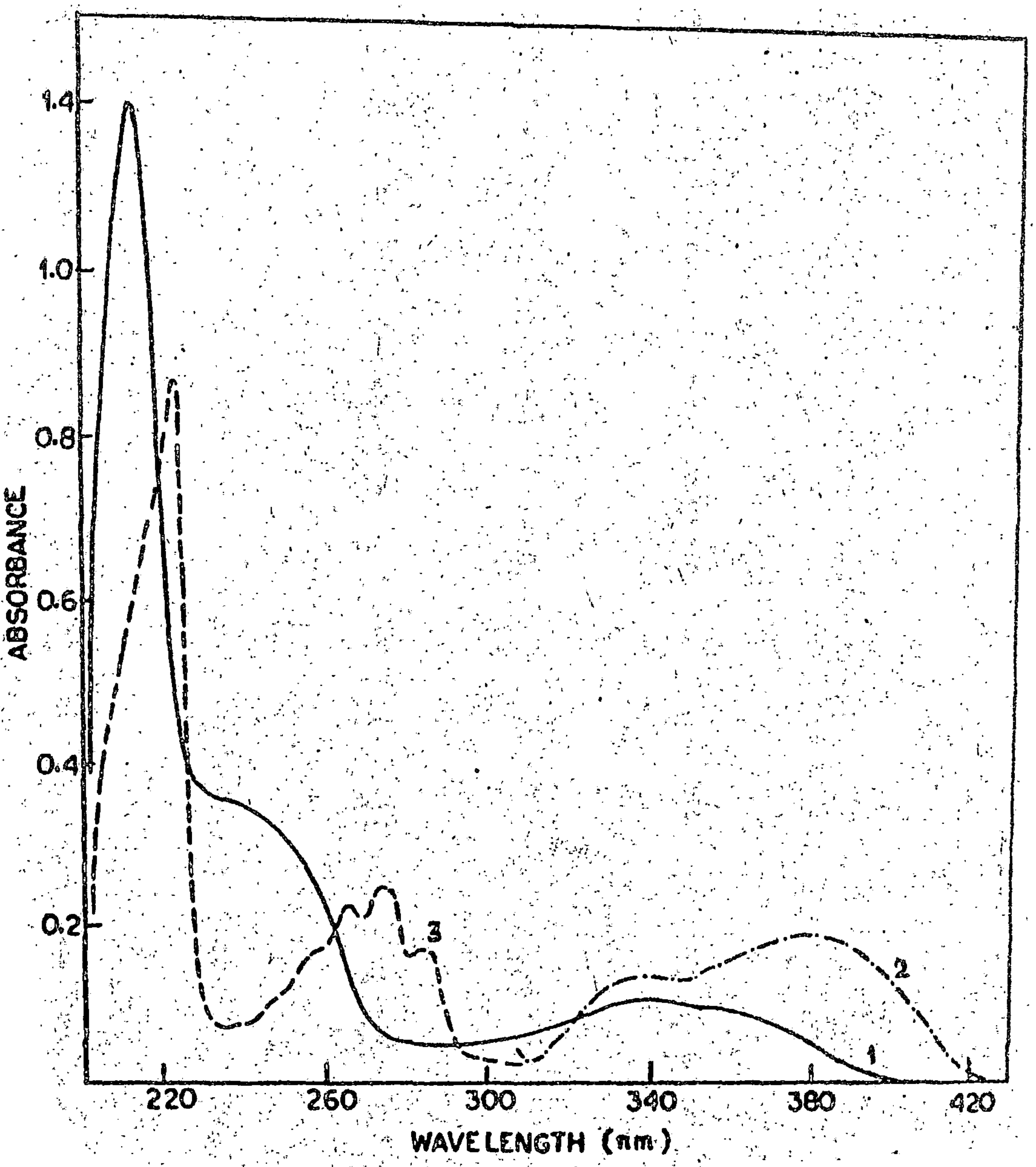


Fig. 4.1 : Electronic absorption spectra of 1,4-dinitronaphthalene at 298°K.

1. Methanol; 2. Acidic ethanol. (Naphthalene in methanol (3) is also shown for comparision)

Table 4.1

Solvent effect on band I and II of 1,4-Dinitronaphthalene.

Solvent	Band I.	Band II
n - Hexane	28409	29705
n - Heptane	28392	29690
Cyclohexane	28323	29650
Methylcyclohexane	28323	29650
Benzene	28039	29240
1,4 Dioxane	28050	29450
Tetrahydrofuran	27920	29660
Ethanol	27855	29720
Methanol	27894	29735
Ethyl acetate	27543	29710
Methanol + 100% H_2SO_4	26315	29720

Band II, on the other hand, shows a little red shift with solvent refractive index (n). These results suggest that Band I is a predominantly CT band where as Band II corresponds mostly to the localised naphthalene ^1L_b band. We, thus, assign band I and band II as ($S_0 \rightarrow {}^1CT$) and ($S_0 \rightarrow {}^1\pi-\pi^*$) respectively. Kojima, Tanaka and Nagakura[1] attributed the broad low energy band (corresponding to our band I and band II) of 1,5-dinitronaphthalene to two overlapping bands, the low energy one corresponding mainly to the ^1L_a of naphthalene mixed to some extent with naphthalene ^1L_b and the ^1CT transition. The high energy band includes the above mentioned three transitions in almost equal proportion. This is appreciably different from what our results of 1,4-dinitronaphthalene as discussed above suggest.

The effect of various solvents on band I and II has been investigated. The nonpolar solvents n - hexane, n - heptane, cyclohexane, methylcyclohexane carbontetrachloride, benzene and polar solvents 1,4-dioxane, tetrahydrofuran, chloroform, ethanol, methanol and ethylacetate have been used.

The solvent effect on the absorption spectrum of a solute molecule is known to be due to dipolar interaction, dispersive interaction and also due to orientation induction effect of the solvent dipoles on the solute molecules[36,12]. Evidently the dipole-moment in the ground (μ_g) and in the excited state (μ_e) are important as they determine the stabilisation of the ground and the excited states as a result of dipolar interaction. In addition a field developed by the local interaction like weak bond formation between the solute and the solvent molecules also attribute to the spectral shift. It is interesting to note that both for polar and non polar solvents plot of transition energy ν_{max} against a factor f (n) i.e. ($n^2 - 1$)/($n^2 + 2$) for band II give good straight line (Fig. 4.2). This indicates that here the dispersive interaction predominates over the dipolar interaction. For the polar molecule 1,4-dinitronaphthalene, this further suggests that the change in the dipolemoment on excitation to the state responsible for this band is small. In some solvents like dioxane, chloroform, carbontetrachloride and benzene, the plot ν_{max} against f (n) for band II though show linearity, form a different straight line and with larger slope than that for other solvents. This possibly is due to these solvents having electronic absorption band close to band II of 1,4-dinitronaphthalene. For band I, such linearity for ν_{max} vs. f (n) plot could not be obtained and this indeed is what one can expect for a highly polar excited state for a CT band where dipolar interactions predominates.

3.2 Emission and Excitation Spectra

The emission spectra of 1,4-dinitronaphthalene in nonprotic and protic solvents at 77°K are shown in Fig. 4.3. The spectral range 350 nm to 475 nm has been recorded without and rest upto 750 nm with a phosphorescence chopper. The phosphorescence spectrum consists of

FIGURE 4.2

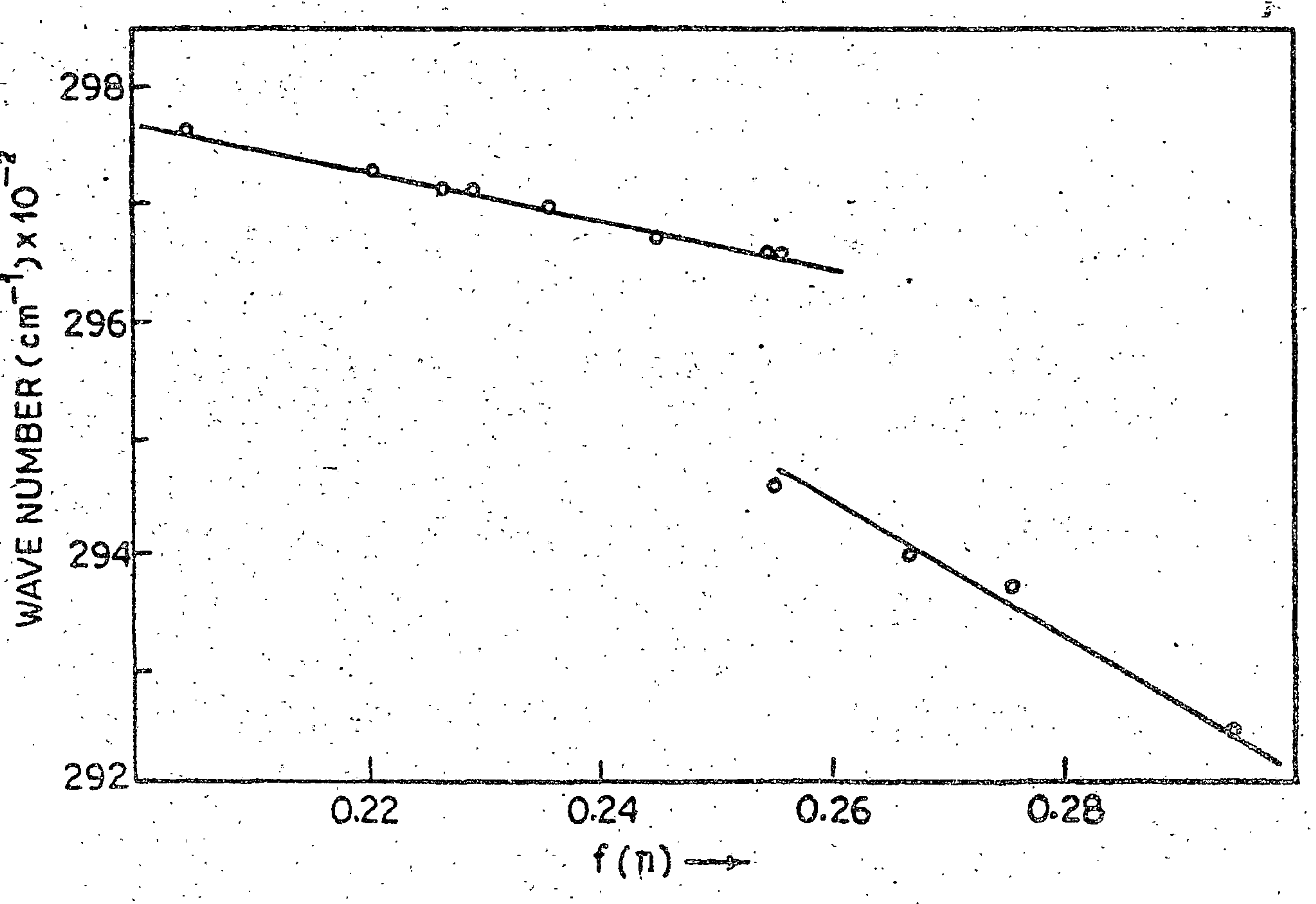


Fig. 4.2 : The plot of transition energy of band II of 1,4-dinitronaphthalene against the function f (n) = (n^2 - 1)/ (n^2 + 2).

FIGURE 4.3

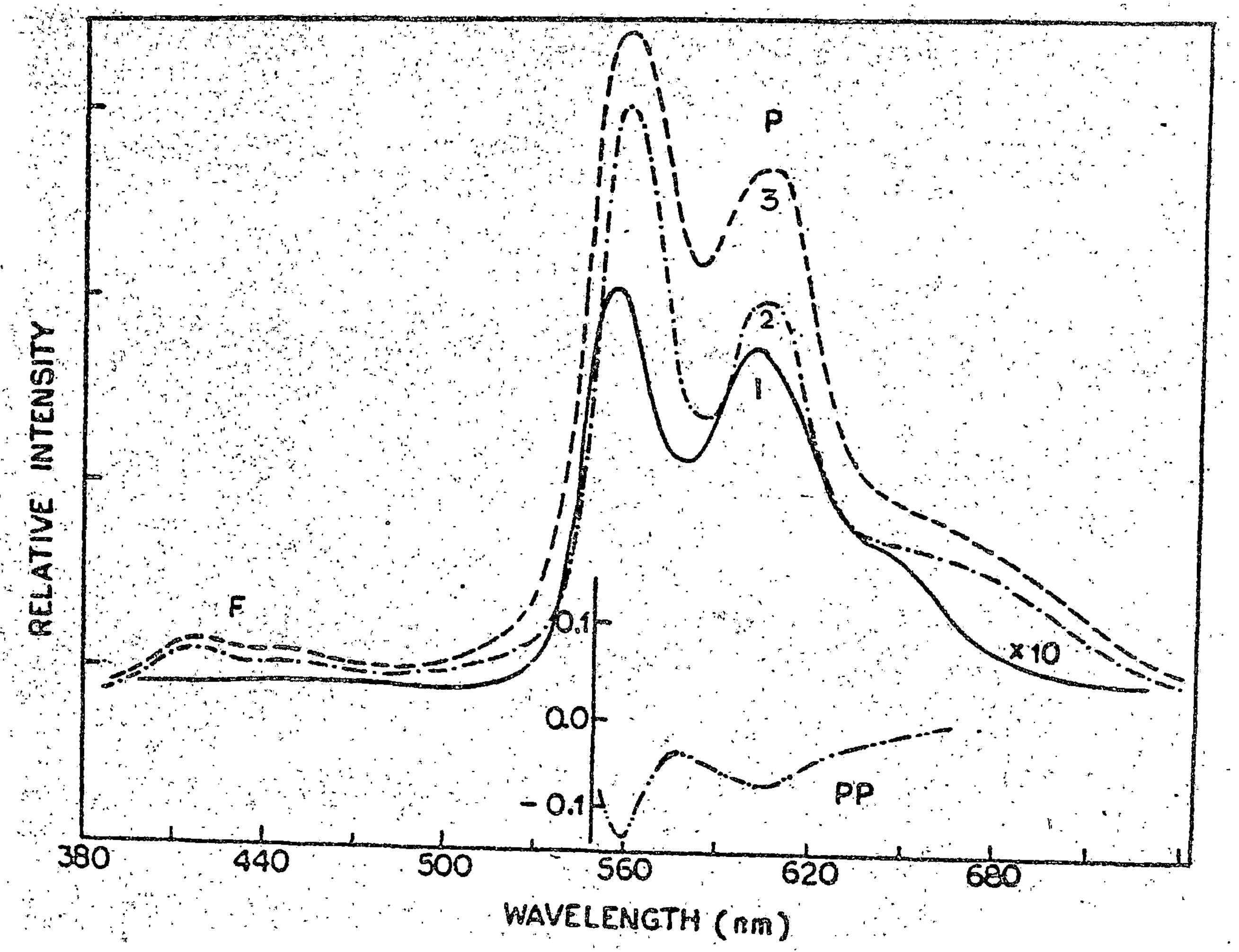


Fig. 4.3 : Emission spectra of 1,4-dinitronaphthalene at 77°K (F - Fluorescence, P - Phosphorescence, PP - Phosphorescence polarisation curve; spectra, 475 nm onwards, are recorded using a phosphorescence chopper) 1. Methylcyclohexane; 2. Ethanol; 3. Acidic ethanol.

three broad bands with the 0 – 0 band at 18050 cm^{-1}, 17955 cm^{-1} and at 17950 cm^{-1} in methylcyclohexane (MCH), ethanol and in acidic ethanol i.e. in H_2SO_4 in ethanol mixture respectively thus showing a red shift in protic solvents. The band positions and a tentative vibrational assignment of the phosphorescence spectrum is shown in Table 4.2. In methylcyclohexane glass at 77°K, the phosphorescence is very weak and no fluorescence is observed even with maximum sensitivity of the fluorimeter indicating a quantum yield $\Phi_F < 10^{-5}$. We estimate the phosphorescence quantum yield in methylcyclohexane $\Phi_P \simeq 10^{-2}$. In protic solvents the phosphorescence intensity is enhanced and in addition weak fluorescence appears in the 400 nm–475 nm region. This behaviour of 1,4-dinitronaphthalene (DNN) molecule is similar to that observed in many polycyclic monoazines such as quinoline, isoquinoline and acridine. However, in monoazines, the triplet quantum yield is small (0.2 for quinoline, 0.3 for isoquinoline[73]) whereas in nitronaphthalenes large triplet quantum yield has generally been observed (0.63 for 1-nitronaphthalene and 0.83 for 2-nitronaphthalene[6,2]). Unfortunately we have not been able to measure the triplet yield for 1,4-dinitronaphthalene molecule and to see if it is really large.

The phosphorescence polarisation has been measured in ethanol glass at 77°K with 337 nm excitation. This is also shown in Fig. 4.3. On $^1\pi\text{-}\pi^*$ excitation, the polarisation degree is negative throughout the whole spectral range and the phosphorescence origin has a negative

Table 4.2

Phosphorescence bands of 1,4-dinitronaphthalene in various glasses at 77K.

Solvent	Band Position (cm^{-1})	Tentative Assignment
Methylcyclohexane	18050	(0, 0)
	16695	0 + 1355
	15380	0 + 2 x 1355 ± 40
Ethanol	17955	(0, 0)
	16610	0 + 1355 ± 10
	15265	0 + 2 x 1355 ± 20
Ethanol + 100% H_2SO_4	17950	(0, 0)
	16610	0 + 1355 ± 15
	15270	0 + 2 x 1355 ± 30

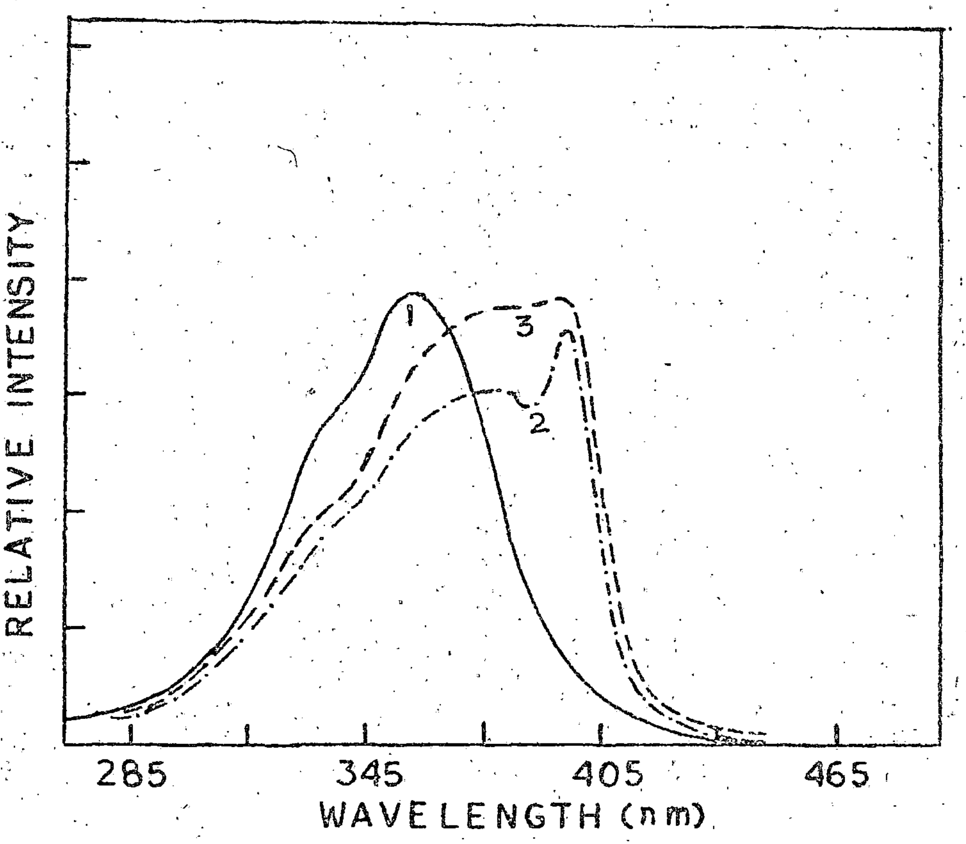
value 0.13. From the solvent behaviour and from the negative polarisation on $^1\pi-\pi^*$ excitation we assign the lowest triplet state as a $^3\pi-\pi^*$ state. This conclusion differs from that of Roy and Becker[10] who assigned the lowest triplet state as $^3n-\pi^*$ state. As has been pointed out by Khalil, Bech and McGlynn[3], their result is quite ambiguous possibly because of the low probability associated with the excitation into the very weak, poorly resolved $^1n-\pi^*$ region. The phosphorescence polarisation of 1 - nitro 4 - methyl naphthalene has been investigated by Krishna et.al.[75], and $^3\pi-\pi^*$ has been shown to be the lowest triplet state. Indeed the structure of the phosphorescence spectrum of the 1,4-dinitronaphthalene molecule is naphthalenic.

Now, it is quite likely that the next higher triplet state might be the $^3n-\pi^*$ state. If it is so, then owing to the "proximity effect"[74], vibronic interaction between the close-lying triplet states would be important and the radiative and nonradiative decay processes must be affected. A low value of phosphorescence quantum yield can reasonably be attributed as an immediate consequence of it. We have also measured the phosphorescence life time monitoring the decay of both the 557 nm and 602 nm peaks. The mean phosphorescence life time in ethanol glass is 10 ms. This value is significantly less than that of naphthalene which is 2 sec. It has been shown by Lim[74] that a close-lying $^3n-\pi^*$ state can shorten the $^3\pi-\pi^* \rightarrow S_0$ phosphorescence life times significantly due to the vibronic interaction between $^3n-\pi^*$ and $^3\pi-\pi^*$ states.

The position of the CT state, among others, determine the rate of intersystem crossing (ISC) in nitroaromatics[9]. ^1CT state in 1-nitronaphthalene has been shown to be at higher energy than the lowest singlet state which is $^1n\text{-}\pi^*$ state and the initial state of ISC is $^1n\text{-}\pi^*$ where as the final state is $^3\pi\text{-}\pi^*$. From our absorption spectra, we have observed the state with predominantly CT character at 360 nm range and we have not observed any $^1n\text{-}\pi^*$ state though in nitroaromatic molecules $^1n\text{-}\pi^*$ is accepted as the lowest singlet state[3,8]. The weak fluorescence emission we have observed in protic solvents originates at about 395 nm where no absorption band is observed and which quite on the red side of the lowest absorption band I ($^1CT \longleftarrow S_0$) observed. It is quite likely that the $^1n\text{-}\pi^*$ state is located in this spectral region and the observed fluorescence is due to $^1n\pi^* \rightarrow S_0$ transition.

To determine the initial state of ISC, we have studied the Phosphorescence excitation spectra in protic and nonprotic solvents. This is shown in Fig. 4.4. It is interesting to note that in methylcyclohexane, the excitation spectrum is a broad band with λ_{max} at about 354 nm i.e. the CT band we have observed in absorption. In protic solvents, however the excitation spectrum looks complex and in addition to the broad band some overlapping relatively sharp bands with the origin at 395 nm are observed. These results show that in nonprotic solvents, the initial state of ISC is ^1CT state whereas in protic solvents another state with the origin at 395 nm, which we

FIGURE 4.4



Phosphorescence excitation spectra of 1,4-dinitronaphthalene at 77°K.

1. Methylcyclohexane;
2. Ethanol;
3. Acidic ethanol.

think is the ${}^1n-\pi^*$ state, is principally the initial state for ISC though some amount of energy is also transferred from the ${}^1CT$ state. Thus, we conclude that the leveling scheme for the low lying states in 1,4-dinitronaphthalene molecule is

$$E(S_0) < E({}^3\pi-\pi^*) < E({}^3n-\pi^*) < E({}^1n-\pi^*) < E({}^1CT) < E({}^1\pi-\pi^*)$$

Now the questions naturally arise why firstly in MCH the initial state of ISC is ${}^1CT$ and not the ${}^1n-\pi^*$ state and secondly no fluorescence from there. Seperation between the ${}^1CT$ and ${}^1n-\pi^*$ is more in nonprotic solvents than in protic solvents and as such the nonradiative decay route ${}^1n-\pi^* \rightsquigarrow S_0$ due to 'proximity effect' in hydrocarbon solvents is expected to be less efficient. This suggests that there is some other decay route from the ${}^1n-\pi^*$ state.

We have recorded the total luminescence spectra in various solvents without the phosphoroscope. The luminescence spectra in ethanol and in MCH glass ($77^\circ K$) are shown in Fig. 4.8. In ethanol, usual phosphorescence bands as shown in Fig. 4.3 are observed. In MCH, however, an intense broad band with λ_{max} at about 540 nm is observed along with the phosphorescence bands appearing very weak in the tail of the spectrum. As the concentration of DNN decreases, the intensity of the broad band decreases and at 10^{-7} M this band does not appear. We have looked into the temperature dependence of this broad

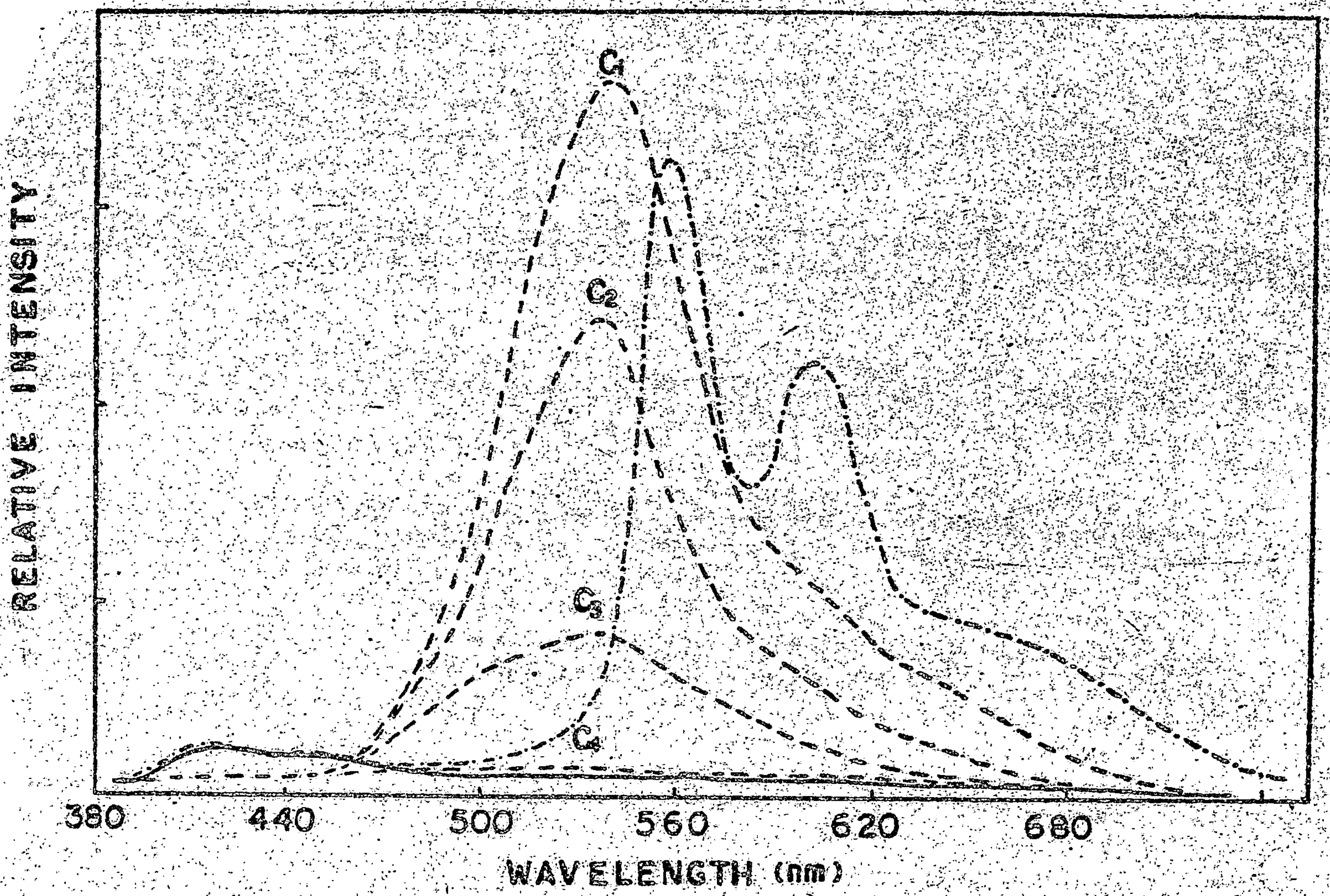
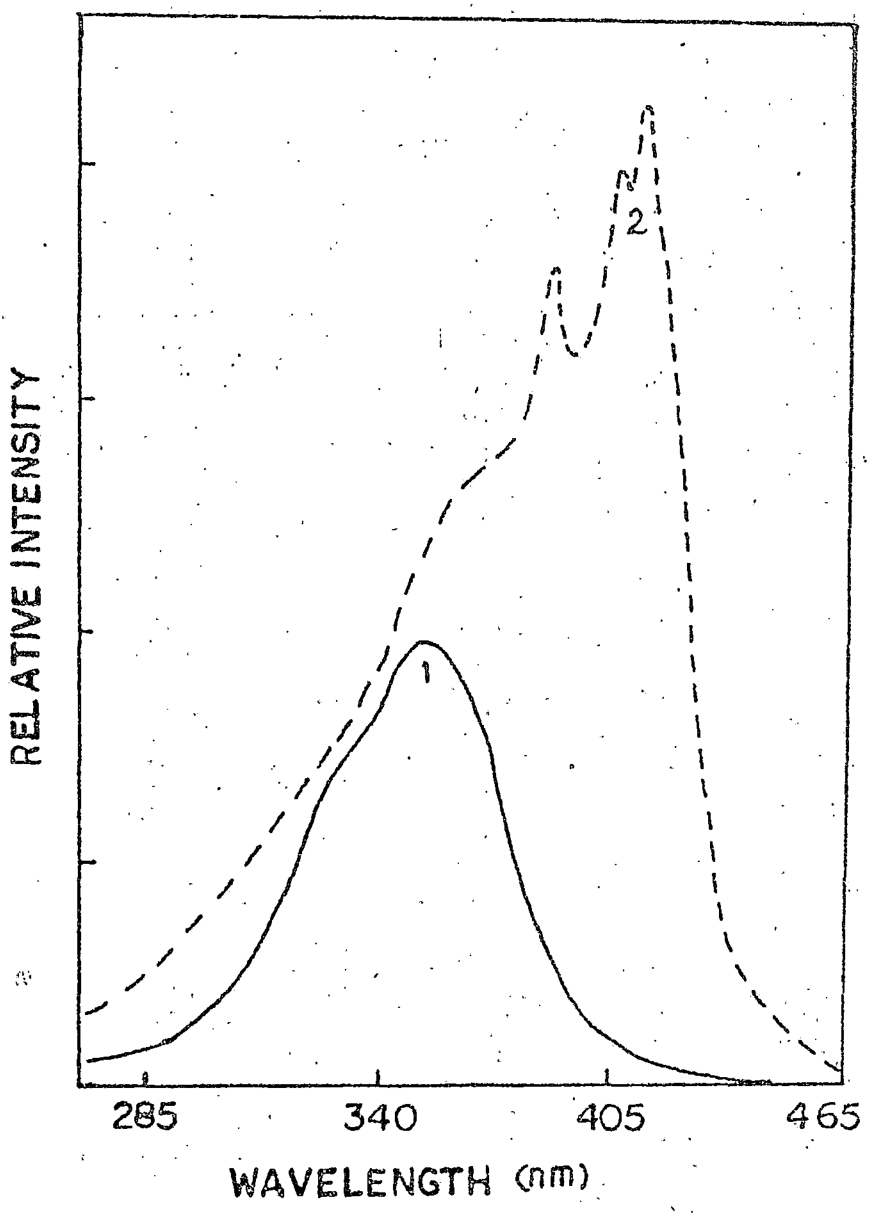


Fig. 4.5 : Total luminescence spectra of 1,4-dinitronaphthalene without chopper(The intensities of the spectra in different solvents are not normalised; concentrations $C_1 = 0.65\times10^{-4}$ M; $C_2 = 0.65\times10^{-5}$ M; $C_3 = 0.65\times10^{-6}$ M and $C_4 = 0.65\times10^{-7}$ M) in ethanol at 77°K (-.-.--); in methylcyclohexane at 303°K (————); in methylcyclohexane at 77°K (- - - - -).

band. Intensity of this broad band decreases with the temperature and at room temperature this emission disappears and a weak fluorescence of DMN is observed. The broad emission band in MCH does not seem to be a solvent associated impurity emission as similar spectra are observed at 77K in other hydrocarbon solvents we have examined like n-pentane, n-hexane, iso-pentane and iso-octane. Absence of this emission in protic solvents excludes its being due to solute associated impurity emission. We have examined the absorption spectrum of concentrated solution of DMN in hydrocarbon solvents at 77K. No absorption band in the spectral region 410 nm - 550 nm is observed. This suggests that the broad emission band is not due to dimer emission. All these observations clearly indicate about the involvement of some new state, which in all probability is the excimer state (D*) in hydrocarbon condensed media at low temperature. With decrease in concentration, the intensity of the broad excimer emission decreases while that of phosphorescence increases.

The phosphorescence and the excimer excitation spectra are different (Fig. 4.6). From the solvent effect on absorption spectra, the band at about 354 nm is found to have predominantly CT character. The phosphorescence in MCH is mainly due to ^{1}CT excitation, the initial state of ISC is ^{1}CT and the final state may be either $^3\pi-\pi^*$ or $^3\eta-\pi^*$. The excitation spectra corresponding to the excimer emission looks complex where, in addition to the broad ^{1}CT absorption band, some sharp bands with origin at about 23900 cm^{-1} are observed.

FIGURE 4.6



Excitation spectra of 1,4-dinitronaphthalene in methyl cyclohexane at 77°K.

1. Phosphorescence excitation spectra;
2. Excimer excitation spectra.

Those sharp bands, in our opinion, are due to $^1n-\pi^*$ excitation. Indeed, the weak fluorescence observed from DNN originates from this $^1n-\pi^*$ state.

The absence of fluorescence and the presence of a weak phosphorescence in hydrocarbon solvents at low temperature is evidently due to the efficient $^1n-\pi^* \rightsquigarrow D^*$ energy transfer which makes the $^1n\pi^* \rightsquigarrow {}^3n\pi^*$ ISC less probable.

Such an excimer emission is not observed in protic solvents. Nitroaromatic molecules in protic solvents are known to form a hydrogen bonding in which oxygens of the nitro group are proton acceptors while the solvent is proton donor[67-69]. This type of local solute-solvent interaction may result in a low probability of D* formation. Thus, in protic solvents $^1n-\pi^* \rightsquigarrow D^*$ route is absent and $^1n \longrightarrow S_0$ fluoresence is observed with low intensity because of the efficient $^1n-\pi^* \rightsquigarrow S_0$ nonradiative process.

4. Conclusions

The low-lying singlet and the triplet states have been assigned from solvent effect on the absorption and the emission spectra and also from polarisation, decay and excitation spectra studies of the phosphorescence emission.

Strong 'proximity effect' between the close lying $^3\pi-\pi^*$ and $^3n-\pi^*$ states has been observed. The quenching of the radiative $^1n-\pi^* \longrightarrow S_0$

transition in hydrocarbon glasses, however, has been attributed not to the proximity effect but to the efficient ${}^{1}n\text{-}\pi^{*} \rightsquigarrow D^{*}$ route resulting in the excimer fluorescence emission. In protic solvents, excimer(D^{*}) formation could not be observed because of the local solute-solvent interactions.

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