ABSTRACT

Semiconductive and Spectroscopic Investigations of Some Nitroaromatic Compounds.

Adsorption and desorption of various chemical vapours at different vapour pressures on the crystallite surfaces of 9-nitroanthracene; 2-nitrofluorene; O-, m- and p-nitrobenzoic acids; 1,4-dinitronaphthalene and 1,3,5-trinitrobenzene have been investigated using electrical conductivity as a probe. An exponential dependence of the conductivity upon vapour pressure of the reagent chemical has been obtained. Adsorption and desorption kinetics follow the Roginsky-Zeldovich equation in a modified form. The activation energy for adsorption and desorption is found to depend upon the vapour pressure as well as upon the nature of the chemical vapours. Kinetic analysis data show that in these Vapour-Semiconductor systems, the adsorption is generally a two stage process. In some cases of vapour adsorption on 1,4-dinitronaphthalene and 1,3,5-trinitrobenzene crystal surfaces, a three stage adsorption process is also observed.

The validity of the Compensation effect in various nitroaromatic semiconductors has been examined. The nonbonding electrons of nitrogroup seem to play an important role in the compensation mechanism. A low value of compensation temperature is obtained. Existence of any relationship between the adsorption process and the compensation effect in dark conduction process has been investigated. It has been concluded that the compensation effect is generally observed in cases where the change in the semiconduction activation energy is caused by a two stage adsorption process.

In case where the activation energy is changed by a three stage adsorption process, compensation effect is not observed. All these results are presented in part A of the thesis.

In second part (B) of the thesis, electronic spectral investigations of 9-nitroanthracene, 2-nitrofluorene and 1,4-dinitronaphthalene have been presented.

The electronic spectra of 9-nitroanthracene have been investigated in solution. Two close-lying states have been observed in the low-energy region of the electronic absorption spectra of this molecule. ${}^1A \longrightarrow {}^1L_b$ band which is hidden under the intense ${}^1A \longrightarrow {}^1L_a$ band in anthracene shifts to an accessible spectral region and seperates out from ${}^1L_a$ band in this molecule. The molecule is observed to fluoresc very weakly. A good overlapping between the emission spectra and the ${}^1A \longrightarrow {}^1L_b$ absorption band has been observed. It has been suggested that the low energy excited singlet state is a π-π^* and not n-π^* state as is observed in some other nitroaromatic compounds. The solvent effect on the ${}^1L_a$ band has been explained interms of predominant dispersive interaction and weak dipolar interaction in nonpolar solvents and interms of Orientation-Induction effect and local interactions in polar solvents. The observed change in the oscillator strength of ${}^1L_a$ band is explained interms of intermolecular forces between the solute and the solvent molecules.

Results on the electronic spectral analysis of 2-nitrofluorene are presented in third chapter of part B. Only one intense ${}^1A \rightarrow {}^1L_a$ band system has been observed in the solution electronic absorption spectra of this molecule. The nitro-group perturbation confirms that the ${}^1L_a$ band is long axis polarised. In solution, the ${}^1L_b$ band of fluorene is hidden under the intense band of 2-nitrofluorene. In a mixed-crystal spectra, three band systems have been observed which are assigned as ${}^1A \rightarrow {}^1L_b$, ${}^1A \rightarrow {}^1L_a$ and intramolecular CT bands. The solvent effect on ${}^1A \rightarrow {}^1L_a$ transition energy has also been investigated in various polar and nonpolar solvents.

The electronic absorption and emission spectra of 1,4-dinitronaphthalene have been studied in various protic and nonprotic solvents in various concentrations and at different temperatures. Results are presented in the last chapter of second part B. The low-lying singlet and triplet states have been assigned from solvent effect on the absorption and the emission spectra and also from some luminescent features of this molecule. Phosphorescence polarisation is found to be negative with ${}^1\pi\text{-}\pi^*$ excitation. It has been suggested that the low-lying states in this molecule, in order of increasing energy, are :
$E\ (S_0) < E\ ({}^3\pi\text{-}\pi^*) < E\ ({}^3n\text{-}\pi^*) < E\ ({}^1n\text{-}\pi^*) < E\ ({}^1CT) < E\ ({}^1\pi\text{-}\pi^*)$.
The ${}^3\pi\text{-}\pi^* \rightarrow S_0$ phosphorescence mean life time is significantly low. This has been attributed to strong "proximity effect" i.e. the

vibronic interaction between the close-lying ^3n-π^* and $^3\pi$-π^* states. The luminescence behaviour in protic and nonprotic solvents at 77°K is different. The molecule is nonfluorescent and shows a weak phosphorescence in hydrocarbon media while a weak fluorescence from ^1n-π^* along with the intensification and red shift of the phosphorescence have been observed in protic solvents. The quenching of radiative ^1n-$\pi^* \longrightarrow S_0$ transition in hydrocarbon condensed media, however, has been attributed not to the proximity effect but to some other intermolecular energy transfer process where a different energy transfer route from ^1n-π^* to the excimer state (D^*) resulting in excimer fluorescence emission $D^* \longrightarrow S_0$ is observed. In protic solvents, the local solute-solvent interaction impedes excimer formation and ^1n-$\pi^* \rightsquigarrow D^*$ route is absent. Also the intersystem crossings from ^1CT to ^3n-π^* and $^3\pi$-π^* are enhanced to some extent there.

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