

## ABSTRACT

The electronic absorption spectra of a few polyenes are studied. It is shown that on adsorption of certain gases on the crystallite surfaces of polyenes like all-trans  $\beta$ -carotene, 15, 15'-cis  $\beta$ -carotene, retinyl alcohol and acetate,  $\beta$ -apo-8'-carotenal and astacene, a new band appears on the low energy side of the intense long wavelength bands of these polyenes. A good mirror image relationship between the new adsorption bands and emission bands of these molecules is also observed. This new band is interpreted to be due to a weak transition to a low-lying  $\pi$ -electronic state ( $1_{Ag}$ ) below the strongly allowed  $1_{B_u}$  state. The significant difference in the solvent behaviour of the intense long wavelength absorption bands and the emission bands of these polyenes confirms that two different excited electronic states are involved in these absorptions and emissions.

The absorption spectra of a series of naphthylpolyenes ( $\alpha, \omega$ -di-1 and  $\alpha, \omega$ -di-2) and anthrylpolyenes ( $\alpha, \omega$ -di-1) in solution and in the crystalline state are studied. It is observed that the naphthylpolyenes have four distinct electronic band systems. The spectral properties indicate that the terminal naphthyl group reduces the symmetry of the short chained polyene molecules to  $C_{2v}$  whereas long naphthylpolyenes retain the usual

conjugated polyene symmetry of  $C_{2h}$ . The spectra of anthryl-polyenes consist of three intense and two weak electronic band systems. Plots of  $\lambda^{-n}$  and  $\epsilon - n$  give a straight line in naphthyl-polyenes and a nearly all-trans form seems to be retained by these polyene chains. In anthrylpolyenes such plots result in a good straight line for lower members only. It is suggested that long anthrylpolyenes are not in all-trans form. Appearance of weak bands ( $1_{A_g} \rightarrow 1_{A_g}$  type) in higher members of anthryl-polyene crystal also support this view. The deviation of the higher members of anthrylpolyenes from all-trans nature is likely in view of the longer chain between the two anthryl terminal groups. It is observed that the highest energy emission and lowest energy absorption bands of naphthyl and anthrylpolyenes show good overlap and identical solvent behaviour. This observation leads to a conclusion that in these polyene molecules the lowest excited state is an allowed  $1_{B_u}$  type, not  $1_{A_g}$  of forbidden type. Some of the absorption bands of naphthyl and anthrylpolyenes in the solid film spectra are explained in terms of factor group split components.

The charge transfer (CT) spectra of polyenes (vitamin A alcohol and acetate) with suitable electron acceptors like chloranil, iodine, iodine monochloride and bromine are observed. It is shown that the CT band of vitamin A alcohol-chloranil

complex is most intense; the intensity of the OF band of complexes formed by other acceptors is comparatively weak. The stability constants of the complexes are also measured. It is suggested that OF mechanism may be involved in some biological processes such as cell division, growth and its regulation by thyroid hormones, pharmacological reaction of iodine and olfactory transduction.

The phosphorescence spectrum of a biphenyl guest - carbazole host mixed crystal with guest concentration  $10^{-2}$  mole/mole is investigated in the temperature range 15 - 90°K. At 15°K the spectrum consists of three superimposed spectra, the most intense one being that of biphenyl guest. The two other spectra are attributed to emission from a shallow trap  $T_1$  and a deep trap  $T_2$ . It is observed that at very low temperature the guest and the two traps are all populated. As the temperature is raised, the shallow trap  $T_1$  is depopulated and emissions from the deep trap  $T_2$  and the guest are observed. On further increase of temperature  $T_2$  is also depopulated and the emission is wholly of biphenyl. A tentative vibrational analysis of the spectra is made. The decay and buildup characteristics of phosphorescence of this mixed crystal are also studied in the temperature range 15-110°. The phosphorescence decay and rise are nearly exponential in the temperature range investigated. It is found that the phosphorescence rise time of biphenyl guest is less than its decay time.

This difference between rise and decay time arises from heterogeneous triplet-triplet annihilation involving a guest triplet and a defect triplet. It is suggested that the delayed fluorescence of annihilative origin is not observed in this mixed crystal owing to a very small fraction of the triplets involved in annihilation. The temperature dependence of the guest phosphorescence lifetime is an intermolecular process and is controlled by the thermally excited process  $T_{1D} \rightarrow T_{1D}^* \rightarrow T_{1H} \rightarrow T_{1G}$ . A kinetic scheme for guest - defect heterogeneous triplet-triplet annihilations is discussed. The thermal energy gap obtained from various Arrhenius plots relevant to the kinetic scheme is in good agreement with the spectroscopic energy difference  $T_{1H} - T_1$ .