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INFLUENCE OF PERMANENT ELECTRIC MOMENT ON THE ABSORPTION SPECTRA OF POLAR ORGANIC MOLECULES IN THE CRYSTALLINE STATE

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ABSTRACT Expressions for the energies of interaction of the three components of the transition moment of a polar molecule along three rectangular axes in the crystal with the permanent dipoles of the nearest neighbours have been derived. It has been shown that as these energies of the three components are different from each other the absorption band is expected to be split up into three components, as observed experimentally in many cases.

INTRODUCTION

It has been pointed out earlier (Sirkar, 1961) that the ultraviolet absorption spectra of many aromatic polar molecules in the crystalline state show splitting of individual bands into three components. It was suggested that this splitting might be due to interaction between the transition moment of the molecule and the permanent dipoles of the surrounding molecules. An attempt has been made in this note to explain in more detail how such splitting originates.

In Davydov's theory (Davydov, 1948) of factor group splitting in the case of crystals like those of anthracene or naphthalene belonging to the space group C^5_{2h} with two centrosymmetrical molecules per unit cell, two wave functions of the unit cell are given by

$$\gamma^a = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$$

$$\gamma^\beta = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2),$$

where ψ_1 and ψ_2 are respectively the wave functions of the crystal when the first and the second molecule in a particular unit cell are excited.

The wave function of the whole crystal is built up with the help of γ^a and γ^β for individual unit cells using the expression given by Seitz (1936) as the suitable representation of the translational group. Denoting the wave function of the k-th representation by $\phi^{a,\beta}(k_a, k_b, k_c)$ corresponding to $\gamma^{a,\beta}$, we have

$$\phi^{a,\beta}_{(k_a, k_b, k_c)} = \frac{1}{\sqrt{N/2}} \sum_{\mu\nu\omega} e^{i(k_a a\mu + k_b b\nu + k_c c\omega)} \gamma^{a,\beta}_{(\mu, \nu, \omega)} \quad \dots \quad (2)$$

where k_a, k_b, k_c are the resolved parts of the wave vector along the crystal axes and μ, ν, ω are the number of translations along a, b, c axes required to reach the unit cell under consideration. Here the summation is to be taken over the unit cells in the crystal. Putting this expression for $\phi^{a\mu}(k_a, k_b, k_c)$ in the Schrödinger equation and obtaining suitable Hermitian scalar products, the expression for the excitation energy of the crystal corresponding to the wave function ϕ^a of the crystal is given by

$$\Delta E'^a = w'_p - w_p + D + C + \Sigma e^{ik(\overrightarrow{p} - \overrightarrow{l})} \phi'_p \phi_l \,|\, V_{pl} \,|\, \phi_p \phi'_l$$
$$= \Delta w_p + D + C + I_{pl} \tag{3}$$

where

$$D = \sum_l \{\phi'_p \phi_l \,|\, V_{pl} \,|\, \phi'_p \phi_l - \phi_p \phi_l \,|\, V_{pl} \,|\, \phi_p \phi_l\}, \tag{4}$$

I_{pl} is the resonance interaction integral, w'_p and w_p are the excited state and ground state energies of the p-th molecule in the vapour state, all the other molecules being in the ground state, ϕ'_p and ϕ_p are the corresponding wave functions of the molecule, V_{pl} is the potential energy operator for the interaction between the p-th and l-th molecules, the summation being taken over all the molecules except the p-th one, and C is the energy of interaction between the two molecules of the unit cell.

Similarly,

$$\Delta E^\beta = w'_p - w_p - C + D + I_{pl}' \tag{5}$$

So,

$$\Delta E^a - \Delta E^\beta = 2C + I_{11} - I'_{pl} \tag{6}$$

In Davydov's theory applied to the crystal of anthracene it has been assumed (Craig and Hobbins, 1955) that the transition moment in the plane of the molecule in the unit cell can be resolved along the b-axis and in the ac plane of the crystal, respectively and that the former component corresponds to the wave function ϕ^β and the latter to ϕ^a. The splitting between these two components is given by Eqn.(6). It has been pointed out earlier (Sirkar, 1961) that when the value of the oscillator strength f is very small the fourth term in Eqn. (3) produces the splitting only with a shifted component having negligible intensity.

A attempt is now made to calculate the interaction of neighbouring permanent dipoles on the transition moment of polar molecules in the crystalline state by applying Davydov's theory in a modified form.

Davydov's theory extended to polar molecules

According to Davydov's theory the second term D in the expression for the excitation energy (Eqn. 3) gives the difference between the integral of interaction of a molecule in the excited state with all the other unexcited molecules in the crystal and the interaction between the molecule in the ground state and all other

unexcited molecules. The value of D remains the same for both the wave functions ϕ^α and ϕ^β. Hence, the corresponding components of the band being shifted by the same amount by this term, no splitting is produced by these interactions. If it is assumed that the molecules in the crystal have permanent dipoles, the interaction between the transition moment of any molecule and all other molecules in the lattice is to be taken into consideration. As pointed out earlier (Sirkar, 1961) the expression for the interaction between two transition moments can be modified to obtain the interaction between a neighbouring permanent moment and the transition moment. This interaction I is given by

$$I = \frac{-e\,|M_k|\,\mu_l}{r_{kl}{}^3} \{2 \cos\,\theta_{lx} \cos\theta_{kx} - \cos\theta_{ly} \cos\theta_{ky} - \cos\theta_{lz} \cos\theta_{kz}\} \qquad (7)$$

where μ_l and $|M_k|$ are respectively the permanent moment of the l-th molecule and the transition moment of the k-th molecule, r_{kl} is the distance between the molecules $\theta_{lx}, \theta_{ly}, \theta_{lz}$ are the angles made by the dipole with r_{kl} and two other rectangular axes perpendicular to r_{kl} and $\theta_{kx}, \theta_{ky}, \theta_{kz}$ are the angles made by transition moment with r_{kl} and two other axes parallel to the y and z axes mentioned above.

Taking the case of a monoclinic crystal with the dimensions a, b, c and β of the unit cell and assuming that the transition moment can be resolved into three components $|M_x|$, $|M_y|$ and $|M_z|$ along the directions of $a \cos \beta$, b- and c-axes, the interaction I_x between $|M_x|$ and the permanent dipoles of the nearest translationally equivalent molecules calculated from Eqn. (7) is given by

$$I_x = -e\,|M|\,\mu \cos\theta_1 \cos\theta_1{}' \left\{ \frac{2\cos^2(\beta - 90°)}{a^3} - \frac{1}{b^3} - \frac{1}{c^3} \right\} \qquad \ldots \quad (8)$$

Here θ_1, θ_2 and θ_3 are the angles made by the transition moment and $\theta_1{}'$, $\theta_2{}'$ and $\theta_3{}'$ are those made by the permanent dipole with the directions of $a \cos \beta$, b-axis and c-axis respectively. Similarly, the interaction between the component of $|M_y|$ along the b-axis and the nearest neighbouring dipoles is given by

$$I_y = -e\,|M|\,\mu \cos\theta_2 \cos\theta_2{}' \left\{ \frac{2}{b^3} - \frac{1}{a^3} - \frac{1}{c^3} \right\} \qquad \ldots \quad (9)$$

and

$$I_z = -e\,|M|\,\mu \cos\theta_3 \cos\theta_3{}' \left\{ \frac{2}{c^3} - \frac{1}{a^3} - \frac{1}{b^3} \right\} \qquad \ldots \quad (10)$$

It is evident from Eqns.(8), (9) and (10) that the interactions of the different components of the transition moment with the permanent dipoles of the nearest neighbours are different from each other. Hence, these components in the ab-

sorption spectra are expected to be separated from each other, the magnitude of separation depending on the differences of the axial lengths of the unit cell and the orientations of $|M|$ and μ with respect to the axes.

If there be two molecules in the unit cell, the interactions I'_x I'_y and I'_z between the components $|M_x|$, $|M_y|$ and $|M_z|$ of the first molecule with the permanent dipole of the second molecule are to be added to I_x, I_y and I_z respectively and it is evident that interactions $(I_x+I'_x)$, $(I_y+I'_y)$ and $(I_z+I'_z)$ will be quite different from each other.

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