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SYMMETRY AND OPTICAL ABSORBTION SPECTRA OF POLYMERS

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In Ref 1 symmetry properties of electronic energy bands of polymer molecules were briefly discussed, in particular the selection rules for excitation of electrons by means of a small external time-dependent perturbation. Now we specialize the general conclusions obtained there to an important case of such a perturbation - that of electromagnetic radiation.

To describe the absorbtion of radiation one commonly uses a semiclassical description of the interaction of the EM field with an electron in the polymer molecule under study.[2] (This is satisfactory as we are concerned here with some qualitative features of the absorbtion spectra, but our conclusions hold true in a quantum-electrodynamical treatment as well.) We further restrict ourselves (in first approximation) to one photon processes, so that the transition-inducing perturbation becomes $\hat{H}_{pert} = -(e/mc)\hat{\vec{A}}\cdot\hat{\vec{p}}$, $\hat{\vec{A}}$ being the vector potential of the EM field and $\hat{\vec{p}}$ being the linear momentum of the electron.

For a monochromatic plane wave in the vacuum one has

$$\vec{A}_{\vec{k}}(\vec{r},t) = \exp(i\alpha)\exp\left[i(\vec{k}\vec{r}-\omega t)\right]\left[a_1\vec{e}_1+ia_2\vec{e}_2\right] + \text{compl. conj.}, \quad (1)$$

where $\vec{e}_1$, $\vec{e}_2$ and $\vec{k}/|\vec{k}|$ make a right-handed coordinate frame. For a fixed $\vec{r}$, the end of the vector $\vec{A}_{\vec{k}}$ moves around an ellipse with the main semiaxes $2a_1$ and $2a_2$ satisfying

$$A_1^2/(2a_1)^2 + A_2^2/(2a_2)^2 = 1 \ . \qquad (2)$$

For $a_1 > 0$, $a_2 > 0$ one has the right elliptical polarization, and for $a_1 > 0$, $a_2 < 0$ the left one; $|a_1| = |a_2|$ describes the circular polarizations and $a_1 \neq 0$, $a_2 = 0$ correspond to polarization in a plane.

Retaining only the absorbtion-inducing term of $\vec{A}$ (the first term of the RHS of (1)) and taking the usual dipole approximation $\exp(i\vec{k}\vec{r}) \cong 1$, one arrives at

$$w_{i \to f} \sim \left| \langle f | a_1 \hat{p}_1 + i a_2 \hat{p}_2 | i \rangle \right|^2 \ . \qquad (3)$$

Now $\hat{p}_1$ and $\hat{p}_2$ can be expressed in terms of the irreducible components of $\hat{\vec{p}}$ with respect to the symmetry group Ln_p (cf Ref 1). By applying some group-theoretical considerations one finds[3] these to be $\hat{p}_z$, $\hat{P}_1 = (1/2)(\hat{p}_x - i\hat{p}_y)$ and $\hat{P}_{-1} = (1/2)(\hat{p}_x + i\hat{p}_y)$ transforming according to ${}_0A_0$, ${}_0A_1$ and ${}_0A_{-1}$ respectively.

Let us consider some important special cases (in what follows the fiber axis is always taken to be the z axis).

1. BEAM ALONG THE POLYMER CHAIN: $\vec{e}_1 = \vec{e}_x$, $\vec{e}_2 = \vec{e}_y$
   a. Right circular polarization: $a_x = a_y > 0$; $\mu = -1$ and $w_{i \to f} \sim \left| \langle f | \hat{P}_{-1} | i \rangle \right|^2 = 0$ unless $\Delta m \doteq -1$
   b. Left circular polarization: $a_x = -a_y > 0$, $\Delta m \doteq \mu = +1$
   c. Polarization in a plane (say the xz plane): $a_x > 0$, $a_y = 0$, $\hat{p}_x = \hat{P}_1 + \hat{P}_{-1}$, $\Delta m \doteq \mu = \pm 1$
2. BEAM PERPENDICULAR TO THE POLYMER CHAIN (say along the x axis)
   a. Polarization in the plane xz: $a_1 = 0$, $a_2 = a_z > 0$, $\mu = 0$ $w_{i \to f} \sim \left| \langle f | \hat{P}_0 | i \rangle \right|^2 = 0$ unless $\Delta m \doteq 0$
   b. Polarization in the plane xy: $a_1 = a_y > 0$, $a_2 = 0$, $\mu = \pm 1$ as $\hat{p}_y = \hat{P}_{-1} - \hat{P}_1$, so $\Delta m \doteq \pm 1$.

One has to remember that the energy is also conserved, i.e. that $E_f - E_i = \hbar\omega$, and that each band has its value of m. So (except in some polymers of very low symmetry) it follows that if the transitions from e.g. the valence to the conduction band are allowed for the $\parallel$ polarizations, they are forbidden for the $\perp$ polarized radiation, and vice versa. Hence, one should observe large alterations (dichroism) in the absorbtion spectra of the polarized radiation (in a polymer with at least partially oriented chains) when the plane of polarization is rotated (around the y axis).

With some prerequisite work on the assignation of the band structure, similair and more detailed analysis[3] can be carried through for each given polymer molecule with the purpose to obtain useful information regarding its absorbtion spectrum. Furthermore, new possibilities are opening to some challenging applications, such as selective excitations to obtain interesting EM response of the system to the incident optical signal.

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