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THE EFFECT OF VIBRONIC TRANSITION ON THE INTERBAND OPTICAL ABSORPTION IN (CH)$_x$

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Abstract - A model for vibronic transitions in the quasi-one-dimensional semiconductor (CH)$_x$ is described. It appears that the resulting electron-phonon (e-p) coupling parameter is only a fraction of the e-p coupling constant responsible for the gap in (CH)$_x$.

Polyacetylene-(CH)$_x$ is a quasi-one-dimensional semiconductor in which the valence and conduction bands are composed of the carbon $\pi$-$\pi$ orbitals. The interband optical absorption is thus associated with electronic transitions between these orbitals and therefore to a charge redistribution. This charge redistribution changes the strength of the electron-phonon (e-p) interaction and may result in a vibronic structure accompanying the main electronic transition. In a "configuration coordinate" (c.c.) description one may envision such a composite electron-vibration transition as a transition from the ground state to a displaced excited state in which both the electronic and the vibrational states are excited/1/. The intensity of these vibronic transitions are related directly to the displacement of the excited state relative to the ground state. When the displacement is negligible, i.e. when the charge redistribution did not affect the equilibrium position of the atoms, only pure electronic transitions should appear. On the other hand, for a finite displacement the electronic transition is accompanied by vibrational transitions.

The theory of vibronic structure associated with well defined electronic levels of localized defects in solids or of polyatomic molecules is well developed /1,2,3/. However since polyacetylene is, in principle, an infinitely long chain of CH units, the electronic levels are condensed to quasi-continuum bands. The interlevel spacing within these bands is smaller than typical vibration frequencies, hence the absorption spectrum of polyacetylene is a convolution of various electronic transitions with their respective vibronic side bands. It is obvious then that in such long molecules the density of electronic levels must properly be taken into account. In a recent paper/4/ we have developed a formalism for vibronic transitions appropriate for very long chain-like polyatomic molecules like polyacetylene. In our formalism we treat polyacetylene as a quasi one-dimensional semiconductor and calculate the valence to conduction band transition rate in the
presence of the e-p interaction using the adiabatic approximation. Considering only dispersionless optical phonons ($\omega_j$) we obtained in the weak coupling limit for the absorption coefficient at energy $\epsilon_j$ from the ground vibrational state ($|0>\rangle$) in the valence band to a possible excited vibrational state ($|\nu_j>\rangle$) in the conduction band

$$\alpha(\epsilon) = \sum \alpha_0 (\epsilon - \nu_j \omega_j) |<\nu_j|0>\rangle^2$$  \hspace{1cm} (1)

where $\alpha_0$ is the bare electronic absorption coefficient and $\nu_j = 0, 1, 2, \ldots$ This convolution spectrum is shown schematically in Fig. 1. It is important to note two features of eq. (1): The energy dependence of $\alpha$ and the weight of the vibronic side bands. The energy dependence comes both from $\alpha_0$ or the joint density of states - and the lattice matrix elements $<\nu_j|0>\rangle$. It is clear that in solids where the electronic energy levels are dense, the main energy dependence of $\alpha(\epsilon)$ would arise from the joint density of states. Thus, in Fig. 1 the width of each vibronic peak is determined by the joint density of electronic states. Secondly, the weight of each vibronic band is proportional to $|<\nu_j|0>\rangle|^2$. These matrix elements vanish unless (in the c.c. description) the conduction band vibrations are displaced with respect to the valence band vibrations. In other words, the weight of the vibronic bands is a measure of the difference of the linear e-p interaction between the conduction and valence bands. For weak e-p coupling only the first excited vibrational state is important, and the weight is given approximately by $1, 3/.$

$$|<1|0>\rangle|^2 = S^2$$  \hspace{1cm} (2)

where $S$ is the dimensionless Huang-Rhys parameter. It is related to the displacement $\Delta q$ (in the c.c. description) via

$$S = \frac{\Delta q}{2\tilde{q}} = \frac{\Delta \Delta \hbar}{j \hbar}$$  \hspace{1cm} (3)

where $\tilde{q}$ is the zero-point displacement, and $\Delta \Delta$ is the difference of the linear e-p interaction (in units of energy/length) between the valence and conduction bands.

In Fig. 2 we show the absorption spectra of cis-(CH)$_2$ under pressure $1/.$ The decrease of the gap with pressure and the broadening of the absorption leading edge can be understood as primarily the result of the increase in the transverse transfer integral with pressure. The second peak at higher energy is interpreted as a vibronic transition and its behavior with pressure can naturally be accounted for using eq. (1)$1/.$ Fitting the intensity of the second peak to the experimental spectrum at ambient pressure, we obtained $\Delta \Delta = 0.3$ eV/Å, $5/,$ and it is consistent also with relatively large extension range of the electronic wavefunction $1/.$
We conclude that, at least for cis-(CH)\textsubscript{x}, the absorption can be described by the convolution given in eq. (1). Therefore it is not necessary to invoke the existence of localized excitations to account for the vibronic structure as has been suggested previously /6/. Furthermore, contrary to a recent analysis/7/, the parameter $\Delta A$ deduced from the vibronics intensity is only a fraction of the e-p coupling constant responsible for the gap in $(\text{CH})_x$.

Fig. 2. Pressure dependence of the interband absorption.

References