

Theoretical treatment of the dielectric response of all-*trans*-polyacetylene

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First-principles electronic-band-structure results for polyacetylene are used to calculate the dielectric function $\epsilon(q, \omega)$ of this material as a function of frequency ω and wave vector q . We find that our theoretical results when compared with the recent experimental results reported by Ritsko describe well many of the dominant features of the electron energy-loss spectra within a self-consistent interband transition linear response model for noninteracting parallel chains. A discussion is provided of other physical effects outside this simple model which may have a measurable effect on the optical and energy-loss spectra of polyacetylene.

A linear plasmon dispersion relation in *trans*-polyacetylene has recently been observed from electron energy-loss spectra observed by Ritsko *et al.*^{1,2} As Ritsko points out,¹ this linear dispersion is anomalous, since for most other systems (such as graphite) with large positive dispersion the momentum dispersion is quadratic. These features of the energy-loss spectra are dependent upon the dielectric

function $\epsilon(q, \omega)$. We present herein a calculation of $\epsilon(q, \omega)$ using the results of first-principles band-structure calculations³ which indicate that the dominant features of the energy-loss spectra can be understood employing a one-electron wave-function model.

In our calculation we use the self-consistent longitudinal dielectric constant $\epsilon(q, \omega)$ derived by Ehrenreich and Cohen⁴:

$$\epsilon(q, \omega) = 1 + \frac{4\pi e^2}{q^2 \Omega} \sum_{m, m', k} \frac{|(m, k | m', k + q)|^2}{\hbar \omega + E_{m', k+q} - E_{m, k}} [f_0(E_{m', k+q}) - f_0(E_{m, k})], \quad (1)$$

where Ω is the volume per C₂H₂ unit and all notation is as that used by Adler.⁵ The sums over m and m' refer to sums over both filled and empty bands. In order to evaluate Eq. (1) at $q = 0$ we employ the identity⁵

$$(m, k | m', k + q) = \hbar q (m, k | p + \hbar k + \hbar q | m', k + q) / [m(E_{m', k+q} - E_{m, k})] \quad (2)$$

for the case of all vectors along the chain axis.

For the one-electron wave functions $|m, k\rangle$ and band energies entering Eq. (1) we use our linear combination of atomic orbitals (LCAO) $X\alpha$ self-consistent one-dimensional band-structure results³ to calculate the longitudinal response for polarizations parallel to the chain axis in an ideal one-dimensionally periodic chain of polyacetylene. Thus no interchain or disorder effects are included in our model. In obtaining our band-structure results we have employed a representative geometry for polyacetylene with C-C bond lengths of 1.35 and 1.45 Å and C-H bond lengths of 1.08 Å. All bond angles were set at 120°. We have found that the resultant occupied valence-band density of states leads to results which are in excellent agreement with x-ray photoelectron spectroscopy experiments. In evaluating Eq. (1) all occupied bands have been shifted down by 0.8 eV to yield a one-dimensional band gap in agreement with experiment of 1.8 eV.⁶ This level shift corrects the well-known tendency of local-density-functional models to underestimate the band gaps⁷ and is an ansatz which simulates the effect of introducing a self-

interaction correction⁸ in an appropriate manner for the purposes of this analysis. For the volume Ω per C₂H₂ unit in Eq. (1) we use the value corresponding to the measured bulk density of 0.4 g/cm³.⁹ Since we are interested in energies for $\epsilon(q, \omega)$ under 10 eV, we consider only the π and π^* bands at the Fermi level as well as the two highest occupied and lowest unoccupied σ bands (which describe all interband excitations across the Fermi level less than 15 eV). As a result of our numerical methods the imaginary part ϵ_2 of the calculated $\epsilon(q, \omega)$ has been broadened by a Gaussian smoothing function of half-width 0.35 eV in order to damp oscillations arising from the numerical algorithms employed. Calculations using less broadening indicated the major features of our results [$\epsilon(0, 0)$ and the plasmon dispersion relation] are relatively insensitive to this amount of broadening. The real part ϵ_1 of the dielectric function was calculated from $\epsilon_2(q, \omega)$ using a Kramers-Kronig analysis.

Our results for $\epsilon(0, \omega)$ are presented in Fig. 1. The calculated value of the dielectric constant $\epsilon(0, 0)$ of 4.0 is in good agreement with experimental results from optical-absorption data⁹ on all-*trans*-poly-

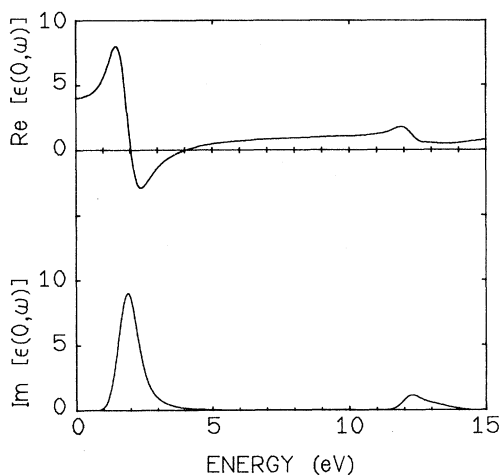


FIG. 1. Calculated optical dielectric function $\epsilon(0, \omega)$ vs energy for all-*trans*-polyacetylene.

acetylene at the density we use in our calculations. The shape of $\epsilon(q, \omega)$ in Fig. 1 for energies less than 4 eV is consistent with those from previous experimental data⁹ and from earlier tight-binding approaches.¹⁰ Our results (not shown) also indicate a large longitudinal response with little dispersion in q for polarization perpendicular to the chain axis around 8–9 eV.

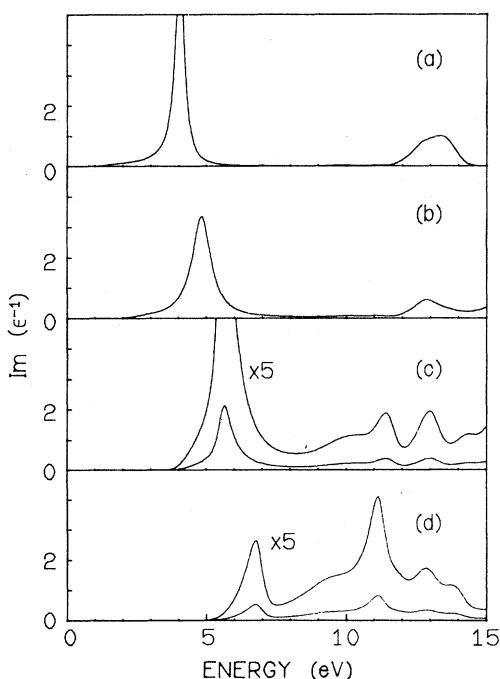


FIG. 2. Predicted electron energy-loss spectra as a function of electron momentum q for the values of q : (a) 0, (b) 0.26 \AA^{-1} , (c) 0.52 \AA^{-1} , and (d) 0.78 \AA^{-1} .

In order to examine the momentum dependence of the dielectric constant we have calculated $\epsilon(q, \omega)$ for the range of ω between 0 and 15 eV and for the discrete set of q values (where q is the magnitude of the propagating wave vector parallel to the chain axis) of 0, 0.26, 0.52, and 0.78 \AA^{-1} . Figure 2 presents our calculated results for the energy-loss spectra of polyacetylene at these values of q . As can be seen from Fig. 1, the peak in ϵ_2 for $q=0$ in Fig. 2(a) at 4.0 eV can be interpreted as a plasmon, since ϵ_1 is zero and ϵ_2 is small and decreasing in this region. This is also true of the peaks in Figs. 2(b) and 2(c) (q equal to 0.26 and 0.52 \AA^{-1}) but not so for $q=0.78 \text{ \AA}^{-1}$ in Fig. 2(d), since our results imply that ϵ_1 for this value of q (not shown) is everywhere positive for energies under 15 eV. A comparison of our calculated plasmon positions with those of the experimental energy-loss spectra^{1,2} is depicted in Fig. 3. In this figure, we see that for all values of q other than 0.78 \AA^{-1} our results predict a linear relationship for the plasmon peaks in excellent agreement with experiment. The exact amount of agreement with experiment that we indicate in Fig. 1 is somewhat fortuitous, since our results are dependent upon the volume Ω per CH unit. Good agreement is maintained with experiment, however, for values of Ω within 20% of the above-mentioned value. Our results indicate that the linear plasmon dispersion is primarily due to the π and π^* bands being basically parallel (in the sense of being collinear across the Brillouin-zone edge at π/a in an unfolded Brillouin-zone scheme) in the region of the energy gap, which

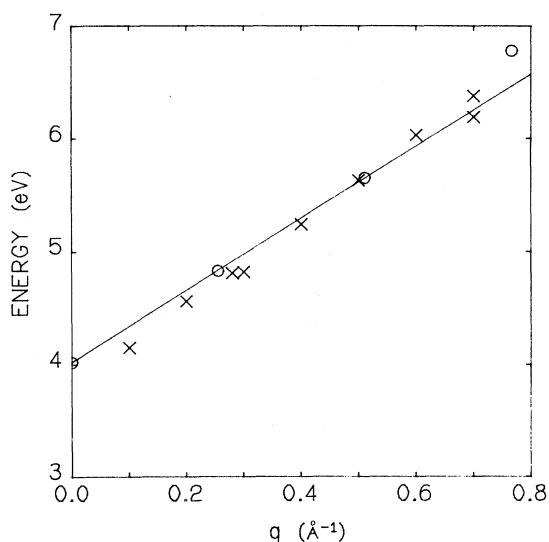


FIG. 3. Calculated and experimental plasmon peaks from electron energy-loss spectra vs electron momentum. Cross marks (x) indicate the experimental results by Ritsko *et al.* (Refs. 1 and 2) and circles (o) indicate our calculated plasmon-peak locations as a function of q .

is the region having most effect on ϵ_2 . This is consistent with the previous interpretation of this mechanism by Ritsko² based on a tight-binding analysis.

Figure 1 shows that our calculated results predict only two major peaks in ϵ_2 . At $q=0$ these peaks correspond to a π - π^* transition at 2 eV and a transition between σ bands at 12 eV. Ritsko² reports an essentially dispersionless experimental peak at about 9 eV which he assigns to σ -band backbone excitations and if so our results imply that this peak may represent a σ -band exciton. In addition, however, our results indicate that there is a strong longitudinal response with little dispersion for polarizations perpendicular to the chain axis around 9 eV arising from σ - π -band transitions across the Fermi level which could partially account for the 9-eV peak as a consequence of lack of orientation of the polyacetylene crystallites.

Ritsko also observes a peak at 2.4 eV which is not predicted by our model. We think that there are three reasonable causes of the peak at 2.4 eV in the large q spectra, with any combination of the three possible. The first possibility is an excitonic enhancement of the absorption edge as described by Ritsko.² A discussion of this mechanism has been presented by Ritsko and we shall not dwell on it here as our analysis presents no significantly new information on this process. The second process is a broadening of ϵ_2 owing to lack of orientation of the crystallites, which will in effect cause ϵ_2 to be a spatial average over all orientations of q where the effective value of q is given by the component of q parallel to the chain axis. Ritsko² indicates this as a possible mechanism but points out that this mechanism would require very strong matrix element effects to describe the experimental data. Our results, however, indicate the matrix elements for excitations across the fundamental gap are indeed large and may well be a source of the 2.4-eV peak in addition to excitonic enhancement.

The third process is a phonon-assisted transition

which allows transitions from band wave vector \vec{k} to $\vec{k} + \vec{q} + \vec{Q}$, where \vec{Q} is the phonon wave vector. These processes would cause a general broadening of $\epsilon_2(q, \omega)$ toward that expected from the joint density of states (JDOS). As Ritsko² has pointed out, the experimental 2.4-eV peak cannot be well described with the use of the JDOS and we do not believe that this mechanism is the predominant one for the 2.4-eV peak. However this mechanism could well increase $\epsilon_2(q, \omega)$ in regions where our interband transition model predicts ϵ_2 to be small due to matrix element effects but the JDOS is of reasonable magnitude. This results in a broadening of our predicted plasmon peaks, which are proportional to $\text{Im}(1/\epsilon)$. If this mechanism is indeed effective in polyacetylene, as our results and the strong electron-phonon coupling expected from the Su, Schrieffer, and Heeger model¹⁰ indicate it may be, then one expects a strong temperature dependence of the sharpness of the plasmon peaks.

In this paper we have presented a theoretical description of the dielectric properties of all-*trans*-polyacetylene using first-principles local-density-functional wave functions and band energies in an interband transition model. These results yield excellent agreement with the experimental plasmon dispersion results of Ritsko *et al.*^{1,2} We have also discussed several other mechanisms and how they influence the results from the basic interband transition model. These results indicate that the one-electron band-structure model is a reasonable starting approximation for predicting the dielectric properties of all-*trans*-polyacetylene.

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