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Theoretical study of the infrared absorption in *trans*-$(CH)_x$ and *trans*-$(CD)_x$

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A calculation of the vibration spectra of *trans*-$(CH)_x$ and *trans*-$(CD)_x$ is presented; it includes for the first time the out-of-plane motions and the infrared (ir) absorption intensities. To obtain a reliable set of transferable parameters, extensive simultaneous optimizations of both the force constants and the electro-optical parameters were performed to solve the inverse spectral problem for several short polyenes. The calculations evince a novel major effect in *trans*-polyacetylene: The A_u in-plane C—H bending mode is expected to give rise to the strongest ir absorption band at ~ 1300 cm^{-1} but its intensity is in fact dramatically reduced. The same effect is seen in the deuterated polymer. Lowering of the resonant Raman frequencies and the ir band disappearance are both believed to be caused by coupling of the vibrations to the π-electron system. For the ir case this is probably caused by the large dipole moments of the vibrating C—H bonds.

The vibrational spectrum of polyacetylene, the prototype semiconducting polymer, has been studied extensively,[1–16] and it is perhaps surprising that some basic questions concerning undoped *trans*-$(CH)_x$ seem still to be open. First, the assignments of some of the observed spectral features are still uncertain, either because the labels proposed in different (Raman, infrared, computational) studies are not mutually consistent, or else because their origin was simply described as "unclear" or "not identified." Next, the literature seems to ignore a major effect apparent from the infrared (ir) absorption spectra. Namely, the C—H bond stretching, the out-of-plane C—H bending, and the in-plane C—H bending vibrations, characteristic of the methine (=CH—) structural element, cause oscillations of the substantial dipole moment (~ 0.4 D) of the C—H bond along the x, y, and z axes, respectively. Neighboring methine elements vibrate in phase in the modes Q_4, Q_8, and Q_{12} (cf. Fig. 1) which are, therefore, expected to be strongly ir active, with the intensity ratio $I_4 < I_8 \simeq I_{12}$.

The corresponding characteristic ir absorption bands are indeed always observed[17] at roughly ~ 3000 cm^{-1} (medium), ~ 1300 cm^{-1} (strong), and 700—1000 cm^{-1} (strong) in the large family of compounds containing methine segments, including shorter polyenes. However, as seen from Fig. 2, the in-plane C—H bending band at ~ 1300 cm^{-1} is almost completely absent from the experimental ir absorption spectrum of *trans*-$(CH)_x$. Figure 3 shows that a simi-

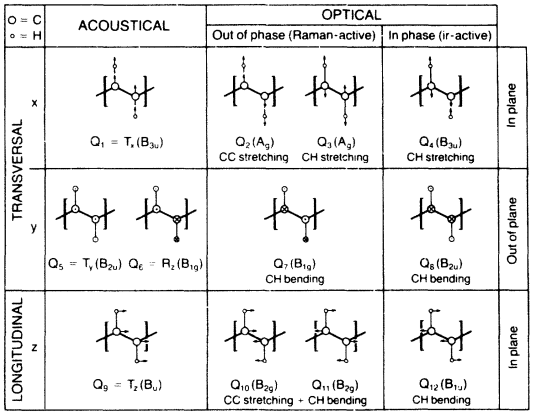

FIG. 1. Symmetry modes of a single, infinite, undimerized *trans*-polyacetylene chain. Dimerization reduces the symmetry and the labels change accordingly: $A_g, B_{2g} \rightarrow A_g$; $B_{1g}, B_{3g} \rightarrow B_g$; $A_u, B_{2u} \rightarrow A_u$; and $B_{1u}, B_{3u} \rightarrow B_u$.

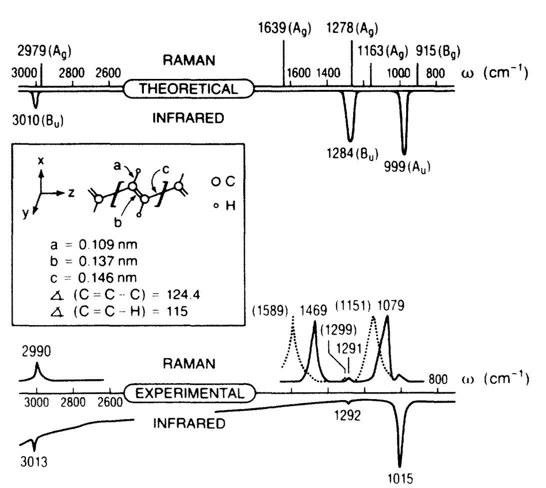

FIG. 2. Infrared and Raman spectra of undoped *trans*-$(CH)_x$, theoretical (upper) and experiental (lower). The Raman intensities have not been calculated, but the longer lines are used to indicate the expected resonance enhancement. The experimental Raman spectrum (Ref. 9) is given for $\lambda_{exc} = 647.1$ nm (solid line) and $\lambda_{exc} = 350.7$ nm (broken line); the former is believed to correspond to long uninterrupted-conjugation segments. The inset shows the periodic model utilized in this calculation; in others the geometry was varied towards the nondimerized model (not shown).

lar effect takes place in *trans*-$(\mathrm{CD})_x$ as well.

Finally, several calculations of the vibrational spectrum of polyacetylene have already been reported, and although they have provided significant insight into the underlying phenomena, some more detailed and quantitative work is still needed. An agreement with the experimental Raman frequencies—observed[3] at 1020, 1080, and 1474 cm^{-1} for *trans*-$(\mathrm{CH})_x$—was achieved in Ref. 5 through a somewhat unjustified alteration of the force constants. When the constants transferred from "small organic molecules" were used,[10] the corresponding frequencies were found at 1120, 1190, and 1900 cm^{-1}, respectively. With the inclusion of an electron-phonon interaction term and scaling of the coupling constant β, much better values, viz., 1030, 1180, and 1487 cm^{-1}, were obtained[10] for $\beta = 8$ eV/Å. However, 1900 cm^{-1} is much too high for a $\mathrm{C=C}$ vibration that, in conjugated polymers, is not expected[17] to be much higher than 1600–1700 cm^{-1}. (An even higher value, 2110 cm^{-1}, was recently used[12] for an equidistant polyacetylene model.) Furthermore, a subsequent experimental study[13] has indicated that the peak at ~ 1020 cm^{-1} corresponds to an *out-of-plane* vibration, so that frequency matching achieved via fitting in Refs. 5 and 10, in which only *in-plane* degrees of freedom were considered, has to be reexamined.

Motivated by these observations, we have computed the vibration spectrum for a series of *trans*-$(\mathrm{CH})_x$ and *trans*-$(\mathrm{CD})_x$ models, including for the first time the out-of-plane vibrations. We have also computed the ir absorption intensities. The information contained in the theoretical predictions is thus increased; this is essential here since the spectra under study contain relatively few features. Extensive optimizations, in which the frequencies and intensities calculated for *trans*- and *cis*-hexatriene and their deutero-analogs were *simultaneously* matched to experiment, have been performed[18] in order to obtain a stable and reliable set of force constants and electro-optical parameters (i.e., dipole moments and their derivatives). Similar local geometries suggest similar electronic structures and good transferability of the parameters. The method and programs utilized were developed by one of us (L.A.G.) with other collaborators and tested successfully on a great number of molecules and polymers, including some that are very complex.[19] In particular, in our recent study[20] of poly(p-phenylene)—which can be similarly doped to high conductivities—a good agreement between the calculated and the experimental spectra has been found.

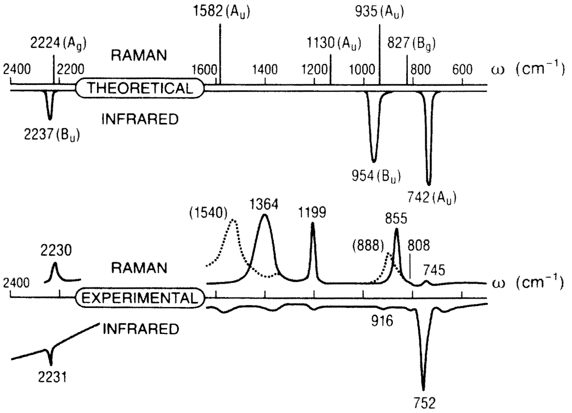

FIG. 3. Infrared and Raman spectra of *trans*-$(\mathrm{CD})_x$ (see caption of Fig. 2).

The results of our computations on *trans*-$(\mathrm{CH})_x$ and *trans*-$(\mathrm{CD})_x$ are presented and compared to the observed ir and Raman spectra in Figs. 2 and 3. For simplicity let us consider first the nondimerized high-symmetry model polyacetylene for which the eigenmodes are easily found (Fig. 1). Dimerization destroys the 2_1 screw axis and the glide-plane symmetry elements, so that line group[21] of the chain lowers from $L2_1/mcm$ onto $L\bar{1}m$. Let $\Delta R = R(\mathrm{C-C}) - R(\mathrm{C=C})$ denote the difference in length of the longer and the shorter carbon-to-carbon distance; we varied it from $\Delta R = 0$ to $\Delta R = 9 \times 10^{-10}$ cm (as found in polyenes); the latter value is used in Figs. 2 and 3. [The value of the dimerization amplitude inferred recently from the x-ray data[22] is $\Delta u = (3 \pm 1) \times 10^{-10}$ cm, corresponding to $\Delta R = (5 \pm 2) \times 10^{-10}$ cm.] Of course, when $\Delta R \neq 0$ one expects some mixing of x and z displacements because of $f_{\mathrm{C-C}} \neq f_{\mathrm{C=C}}$; however, even for $\Delta R = 9 \times 10^{-10}$ cm neither the frequencies nor the mode forms differ much from those of the $\Delta R = 0$ chain. In any case, the correspondence is obvious, and we still may utilize the mode labeling of Fig. 1 in the assignment analysis that follows.

First, for a single $(\mathrm{CH})_x$ chain, the lowest four modes are acoustic. (The fourth mode is the Q_6 mode which for $k = 0$ describes free rotation of the polymer along its axis; when the interchain interaction is turned on it becomes a low-lying optical mode.) The ir band at ~ 1015 cm^{-1} was related early[2] to the out-of-plane C—H bending on the basis of comparison with analogous systems; our calculations support this conclusion. The second, Raman-active mode Q_7 was related[13] to a weak feature observed at $\sim 1015 - 1020$ cm^{-1}. However, disorder breakdown of the selection rules may make the Q_8 mode (notice the frequency coincidence) weakly Raman active, and Q_7 would then correspond to the unidentified[13] weak feature at 878 cm^{-1}. (A distribution of effective conjugation lengths seems to exist[8,9,13] in *trans*-polyacteylene, the shorter segments departing more from the ideal line-group symmetry.) The two highest-frequency (~ 3000 cm^{-1}) C—H bond-stretching modes are also easily identified, and hence, our discussion centers on the modes Q_2, Q_{10}, Q_{11}, and Q_{12}.

The calculated frequency, 1284 cm^{-1}, for the ir-active mode Q_{12} agrees well with the observed frequency, 1292 cm^{-1}. The strong Raman band at 1461–1596 cm^{-1} corresponds to Q_{11}, calculated to be at 1639 cm^{-1}. The second resonant Raman band, at 1064–1151 cm^{-1}, probably arises from the Q_{10} mode predicted at 1278 cm^{-1}; namely, considerable $R(\mathrm{C-C})$ and $R(\mathrm{C=C})$ changes of opposite phases take place in Q_{10} and Q_{11}, which are therefor expected[5,10] to be strongly Raman active (and strongly coupled to the π-electron system, which causes the frequency lowering).

Finally, the Q_2 mode is expected to be weakly Raman active, and it corresponds to one of the two observed[8,13] weak Raman features, at 1170–1175 cm^{-1} and at 1291–1299 cm^{-1}. The calculations give $\nu_2 = 1163$ cm^{-1};

the second feature might originate from the Raman activation of Q_{12}.

The assignment of the Raman and the ir absorption spectra of the fully deuterated polyacetylene (Fig. 3) is performed analogously. The change in geometry of the Q_2 mode was understood[5] to cause the increased Raman activity and coupling to the π electrons.

Several important questions, such as the role of electron-phonon coupling and of symmetry breaking (bond alternation), the disappearance of an ir absorption band, etc., can be discussed now. First, Figs. 2 and 3 show a good agreement of the calculated and the observed frequencies, except for ν_{10}, ν_{11} of *trans*-$(\mathrm{CH})_x$ and for $\nu_2, \nu_{10}, \nu_{11}$ of *trans*-$(\mathrm{CD})_x$, i.e, exactly for the modes for which the geometry suggests significant electron-phonon coupling. Frequency lowering is considerable, 10–15%; notice that the position of these Raman bands depends on the excitation, and the comparison has to be made to the lower-limit frequencies which correspond to the longest conjugation lengths. However, we find lowering to be about 2 times smaller than in Ref. 10; instead of their $\beta = 8$ eV/Å, our estimate for the electron-phonon coupling constant would be much closer to $\beta = 4.1$ eV/Å, the value chosen in Ref. 23. (To avoid misunderstanding, let us stress that our set of force constants is based on hexatrienes, and it includes more interactions than the "short-range force constant" set of Ref. 10, so that this discrepancy is partly semantic; however, our model *is* indeed adiabatic and harmonic.)

One normally can describe vibrations of a polymer assuming that some appropriate structural units have been concatenated without essential changes; however, *trans*-polyacetylene departs strongly from such a description. In this respect it thus differs essentially even from closely related systems such as *cis*-polyacetylene, poly(*p*-phenylene) or shorter polyenes. Another exclusive effect is seen in the ir absorption spectra: The calculated relative intensities are $I_4 = 0.4$, $I_8 = 3.1$, and $I_{12} = 3.3$ for *trans*-$(\mathrm{CH})_x$, and $I_4 = 0.2$, $I_8 = 1.3$, and $I_{12} = 1.8$ for *trans*-$(\mathrm{CD})_x$, while the observed I_{12} are drastically lower in both the normal and the deuterated polymer, cf. Figs. 2 and 3. Furthermore, I_{12} saturates quickly with the average segment length increase in the *cis*-to-*trans* isomerization process[4,14]; therefore, the observed weak absorption at $\sim 1300\ \mathrm{cm}^{-1}$ probably comes from shorter segments and disappears completely in very long chains.

It is natural to ask now how this exceptional behavior relates to another unique feature of *trans*-polyacetylene, namely, its degenerate broken-symmetry ground state. We have, therefore, recalculated the whole phonon spectrum for a series of *trans*-$(\mathrm{CH})_x$ models, varying the carbon-to-carbon bond difference from $\Delta R = 9\times 10^{-10}$ cm to $\Delta R = 0$, restoring gradually the full $L2_1/mcm$ symmetry. (The force constants were scaled accordingly.) However, neither the ir intensities nor the frequencies exhibited major changes: $\nu_{11} = 1639\ \mathrm{cm}^{-1}$, $\nu_{10} = 1278\ \mathrm{cm}^{-1}$, $\nu_{11} = 1284\ \mathrm{cm}^{-1}$, and $\nu_2 = 1163\ \mathrm{cm}^{-1}$ for $\Delta R = 9\times 10^{-10}$ cm, and $\nu_{11} = 1599\ \mathrm{cm}^{-1}$, $\nu_{10} = 1246\ \mathrm{cm}^{-1}$, $\nu_{12} = 1297\ \mathrm{cm}^{-1}$, and $\nu_2 = 1163\ \mathrm{cm}^{-1}$ for $\Delta R = 0$. The undimerized model surprisingly gives better values, but the discrepancy with the experimental data remains too large. (Nor were variations of the force constants and the electro-optical parameters, within reasonable limits, sufficient to match the lowering of Raman frequencies and ir intensities, and a proper description has to include some electron-phonon coupling.)

Frequent misunderstandings make a few remarks necessary at this point. First, when $\Delta R = 0$ the $L2_1/mcm$ line-group symmetry requires all the phonon branches (and all the electron bands as well) to stick together at the Brillouin-zone boundary: $\omega_1(k = \pi/a) = \omega_2(k = \pi/a)1i, \ldots, \omega_{11}(k = \pi/a) = \omega_{12}(k = \pi/a)$. When $\Delta R \neq 0$ the branches open at $k = \pi/a$, and this was called "the phonon analog of the Jahn-Teller effect." There is little analogy in fact; it is the π-electron band degeneracy at the Fermi level that produces asymmetric forces on the nuclei, so that the symmetry reduces from $L2_1/mcm$ into $L\bar{1}m$. All the phonon branches open as a consequence at $k = \pi/a$, but so do all the electron bands, regardless of the actual cause of the symmetry reduction. Next, the ϵ_F electrons have $k = \pi/a$, and the selection rules allow them to couple only to $k = 0$ phonons; in particular, no $k = \pi/a$ phonons lead towards the Peierls distortion.

Let us finally consider the disappearance of the ir absorption by the in-plane C—H bending mode. The following facts have to be taken into account: (i) in the Q_{12} mode hydrogen atoms oscillate in phase along the chain axis with large amplitudes, (ii) each C—H bond has a significant dipole moment, (iii) the π-electron system is very polarizable, and (iv) the ground state is degenerate. Hence one could expect the π-electron charge-density distribution to couple to and move along with the oscillating system of dipoles. It is interesting also to analyze the effects of the presence of a (neutral) soliton on the chain; notice that the soliton has a very low effective mass ($\sim m_e$), large diffusion length ($\sim 10^3$ Å), and diffusion constant $D \simeq 2\times 10^{-2}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$ at relevant temperatures.[24] More detailed studies of this problem are in progress.

In conclusion, the harmonic approximation and careful transfer of the force constants and electro-optical parameters generally provide an adequate description of the vibrational spectra of polymers. Exceptionally, in *trans*-polyacetylene one observes a significant lowering of (a) *the frequencies* of the resonant Raman modes and (b) *the intensity* of ir absorption of the in-plane C—H deformation mode. Couping of the vibrations to the π electrons is believed to cause both effects, although the 8-eV/Å value of the coupling constant, accepted in several recent studies, is probably an overestimate.

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