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Infrared-active vibrational modes of charged solitons in $(CH)_x$ and $(CD)_x$

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We present a joint experimental and theoretical study of the lattice dynamics of polyacetylene, including both the unperturbed polymer and the doped polymer containing charged solitons at dilute concentrations. A quantitative understanding of the Raman spectra and the soliton-induced infrared absorption in *trans*-$(CH)_x$ and *trans*-$(CD)_x$ has been achieved. The detailed agreement between calculated and experimentally observed infrared-active vibrational modes provides specific experimental evidence of soliton doping in polyacetylene.

I. INTRODUCTION

Solitons in *trans*-$(CH)_x$ are nonlinear conformational excitations of the polymer, extended domain walls across which the sign of the bond alternation is reversed.[1-4] Because of the strong coupling of the π-electron energies to the atomic positions, the formation of a soliton leads to a nonbonding localized electronic state with energy at the center of the energy gap. Within a one-electron theory, acceptor or donor doping of the polymer does not result in hydrogenic impurity states or free carriers in the valence or conduction bands. Rather, it is energetically favorable to generate charged solitons upon doping, with the excess charge in the spinless localized mid-gap soliton state.

As a result of doping, the electrical conductivity increases by many orders of magnitude,[5] whereas the Curie-law contribution to the susceptibility is found to decrease rapidly,[6] consistent with ionization of the localized spin of the neutral soliton defects in *trans*-$(CH)_x$. Moreover, this occurs initially without an associated increase in Pauli susceptibility.[6] Thus, the results of magnetic and electrical measurements imply the existence of spinless charge carriers. Quantitative spectroscopic evidence of the formation of a state at mid-gap has been obtained from *trans*-$(CH)_x$ films at dilute doping concentrations. These results are all consistent with the soliton doping mechanism. Nevertheless, specific experimental evidence bearing a detailed signature of the soliton structure is of clear importance.

The first specific evidence for the formation of charged solitons upon doping appears to be the infrared studies of the donor and acceptor states in lightly doped polyacetylene. In a series of experiments with various dopants Fincher *et al.*[8] found that upon dilute doping two new absorption modes appeared in the ir region, at 1370 cm^{-1} and 900 cm^{-1}, with remarkable intensity. The two modes are primarily polarized parallel to the chain direction, and their intensities grow in proportion to the dopant level, becoming comparable to any of the $(CH)_x$ ir lines at about 0.1%. Thus Fincher *et al.*[8] concluded that the doping-induced ir modes had oscillator strength enhanced by approximately 10^3 and that such a large enhancement must arise from coupling the new vibrational modes (induced by doping) to the electronic oscillator strength of the polyene chain. Fincher *et al.*[8] emphasized the generality of their results; the same modes were observed for iodine and AsF_5 (p type) and for Na doping (n type). Thus these intense absorptions are not due to specific vibrations of the dopant molecules, nor to detailed interactions between the molecules and the polymer chain. The observed generality suggests that the intense ir absorption modes are intrinsic features of the doped $(CH)_x$ chain.

Motivated by these experimental observations, Mele and Rice[9,10] developed a theory of the lattice dynamics of solitons in $(CH)_x$. In the frequency range of vibrational modes they found several internal modes peculiar to the soliton structure. In particular, two of these modes were found to be strongly infrared active, deriving their oscillator strength from interactions with the π electrons. Mele and Rice[10] showed that the dominant motions associated with the infrared-active vibrational modes (IAVM) of a soliton involve an antisymmetric contraction of the single (or double) bonds on one side of the soliton center and an expansion on the other, thus driving charge back and forth across the soliton center. They furthermore pointed out that the expected oscillator strengths of the IAVM of a soliton are large enough to be observable at very dilute doping, consistent with the experimental results, and obtained quantitative agreement with the experimental frequencies and oscillator strengths.

In this work, we report a joint experimental and theoretical study of the vibrational excitations of charged solitons in fully deuterated polyacetylene $(CD)_x$. We find that due to the strong coupling between the π electrons and the normal modes of vibration, the IAVM of solitons are changed significantly upon deuteration, both in their frequencies and relative oscillator strengths. These changes are, however, fully accounted for by the theory with *no* adjustable parameters; the IAVM for solitons in $(CD)_x$ are calculated with the only input to the model being the replacement of the deuteron mass for the proton mass. We also find that the same mass change accounts for the shifts in the frequencies of the resonance-enhanced Raman lines in undoped $(CD)_x$.

II. RAMAN SPECTRA FOR *TRANS*-$(CD)_x$: THEORY AND EXPERIMENT

Following the work of Mele and Rice,[9,10] we have constructed a force-field model which consists of two principal parts. First, "bare" nearest-neighbor bond-stretching and bond-bending force constants are chosen by inspecting the characteristic vibrations of small organic complexes containing double and single C–C bonds. We interpolate the dependence of the bond-stretching force constants on bond length to define the force constants appropriate for the infinite polyene, and the force field thus derived is cast into the form of a Keating-model[11] Hamiltonian from which the bare phonons of the polyene chain are calculated. Second, we include a set of delocalized force constants derived from interactions of atomic displacements with the extended π-electronic states. Within the RPA (Ref. 12) we express this effect as a correction to the bare dynamical matrix, $\delta L_{\mu\nu}$, coupling displacements μ and ν with wave vector q given by

$$\delta L_{\mu\nu}(q)=2\sum_k \frac{\langle n,k\,|\,V_\mu^*(q)\,|\,n',k+q\rangle\langle n',k+q\,|\,V_\nu(q)\,|\,n,k\rangle}{E_{n',k+q}-E_{n,k}}, \tag{1}$$

where $V_\mu(q)$ denotes a modulation of the electronic Hamiltonian linear in the displacement $\mu(q)$ and the $|\,n(n'),k\rangle$ are the filled (empty) eigenstates in the π-electron manifold with eigenvalues $E_{n(n')}(k)$. The V_μ are completely defined by the geometry of the chain and a constant, β, the derivative of the nearest-neighbor π-electron transfer integral with respect to bond length.

In Fig. 1(b) we show the effect of the electron-phonon coupling constant β on the in-plane vibrations below 2000 cm^{-1} for *trans*-$(CD)_x$. The dashed curves are the results from the bare-force-field model ($\beta=0$), and the solid curves are the calculated phonons including the coupling to the π electrons through Eq. (1) with $\beta=8$ eV/Å. This value of β was derived from a fit of the calculated zone-center frequencies of gerade modes to the observed Raman lines in *trans*-$(CH)_x$. Since we do not expect a change of the chain geometry in going from $(CH)_x$ to $(CD)_x$ we have used the same force field and the same β for the $(CD)_x$ results shown in Figure 1(b).

Raman scattering experiments were carried out on *trans*-$(CD)_x$ films synthesized as described earlier.[13] The Raman spectra were obtained with a Spex double monochromator, using an argon-ion laser. The Raman spectrum from *trans*-$(CD)_x$ (using the 5146-Å laser line) is shown in Fig. 1(a); the data are in agreement with those published by Kuzmany.[14] We note that the good agreement between the observed zone-center frequencies of the gerade modes and their predicted values for $(CD)_x$ was obtained using no adjustable parameters. The fit to the Raman lines in both $(CH)_x$ and $(CD)_x$ is obtained with $\beta=8$ eV/Å. In a one-dimensional model[1,15] for the polyene chain, this value of β implies a horizontal displacement of ~0.025 Å for the CH unit, or ~0.044 Å for the bond-length change, with an energy gap of 1.4 eV.

The major shifts which occur in the phonon spectrum (Fig. 1) on going from $(CH)_x$ to $(CD)_x$ arise since the increase in mass is sufficiently large compared to the mass of the carbon atom that nontrivial changes occur (i.e., beyond a

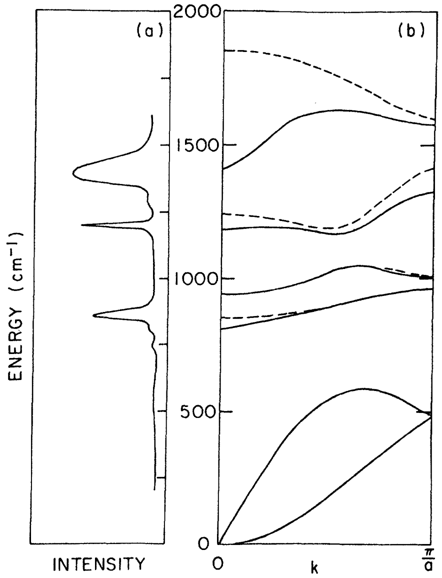

FIG. 1. (a) Experimental Raman spectrum of *trans*-$(CD)_x$ (obtained with 5146-Å radiation). (b) Phonon spectra of *trans*-$(CD)_x$. -----, without electron-phonon screening ($\beta=0$); ——, including effect of electron-phonon interaction with $\beta=8$ eV/Å.

simple scaling by $M^{-1/2}$) in the normal modes. Our analysis of the character of the modes[16] shows that the two low-frequency vibrations in $(CD)_x$ below 10^3 cm^{-1} involve primarily deuteron motion, whereas the modes near 1200 and 1500 cm^{-1} involve principally (C–C) and (C=C) motions, respectively. The smaller proton mass in $(CH)_x$ leads to a near degeneracy[9] and thus to more mixed character; the three modes below 1400 cm^{-1} involve combined C and H motion while the 1470 mode remains primarily (C=C). The increased intensity of the third Raman line at 1200 cm^{-1} in *trans*-$(CD)_x$ over its weak counterpart[14] near 1300 cm^{-1} in *trans*-$(CH)_x$ can be understood in terms of the character of the modes. In *trans*-$(CH)_x$, the projected motion along the chain direction for this mode primarily involves hydrogen displacement, while in *trans*-$(CD)_x$ the projected motion involves almost entirely carbon displacement. As a result, this mode is more strongly coupled to the electronic structure of the polymer in *trans*-$(CD)_x$, and the enhancement of Raman scattering is considerably stronger.

III. SOLITON-INDUCED INFRARED-ACTIVE VIBRATIONAL MODES: THEORY AND EXPERIMENT

As shown previously for $(CH)_x$, associated with each of the ungerade internal vibrations of a charged soliton there is an induced contribution to the electronic polarizability, an IAVM with large oscillator strength.[10] To study this effect in $(CD)_x$, we first evaluate the phonon density of states (PDS) for the perfect *trans*-$(CD)_x$ polymer chain, and then recalculate the PDS in the presence of a soliton on the chain. To obtain the change in absorption coefficient due to the charged solitons, we follow the earlier procedure[10] and calculate, with the random-phase approximation, the phonon coupling to density fluctuations in the π-electron gas.[12] The results obtained for the ir absorption coefficient (α), associated with a density of 10^{19} cm^{-3} of charged solitons in an unoriented film, are shown in Fig. 2. Comparison of the $(CD)_x$ results [Fig. 2(b)] with the $(CH)_x$ results [Fig. 2(a)] shows a large frequency shift of the two absorptions resulting from the change in the normal mode structure discussed above. The higher-frequency mode in $(CH)_x$ becomes a doublet in $(CD)_x$. Note that the predicted changes ($\delta\nu/\nu \sim 20\%$) are much larger than would be expected from a naive $M^{-1/2}$ shift (~5%) and result directly from specific changes in the lattice dynamics in the vicinity of a soliton domain wall.

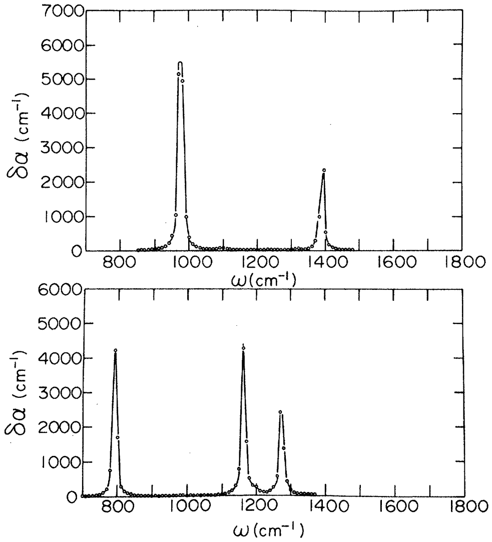

FIG. 2. Soliton-induced infrared-active vibrational modes (theory). (a) *trans*-$CH)_x$; (b) *trans*-$(CD)_x$.

We have measured the additional absorption (over that of the undoped sample) as a function of frequency for several dilute concentrations of AsF_5 in $(CD)_x$. The experimental details are the same as in the previous work on $(CH)_x$.[8] Figure 3 shows the additional absorption as a function of energy for several successively higher levels of AsF_5 dopant. The highest concentration is expected to be less than 0.1 mole% as inferred from parallel doping studies. Essentially identical results were obtained from *trans*-$(CD)_x$ and from partially isomerized film with mixed *cis*-*trans* content, consistent with the earlier $(CH)_x$ studies.[8] The absorption bands associated with the IAVM of solitons in *trans*-$(CD)_x$ are clearly shown in Fig. 3 as the two strong, broad, peaks at 780 and 1120 cm^{-1}. Although the peak at 1120 cm^{-1} may

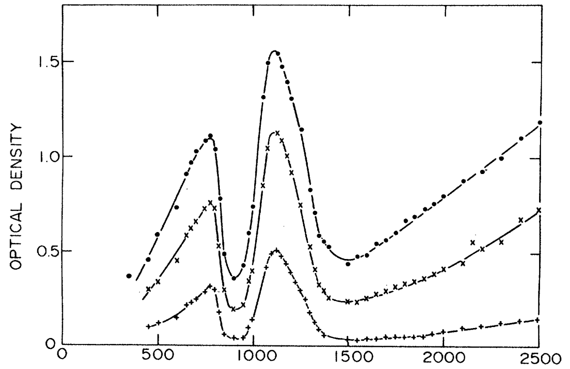

FIG. 3. Experimental results: doping-induced active vibrational modes. The curves represent data from $(CD)_x$ doped with successively higher concentrations of AsF_5; maximum concentration (upper curve) is ~0.1 mole%. Essentially identical results were obtained from *trans*-$(CD)_x$ and from partially isomerized film.

be related to a similar absorption peak at 1088 cm^{-1} observed[17] in heavily doped thin films, the rest of the spectrum is quite different. The slow rise in absorption for energies higher than 0.2 eV is associated with the tail of the strong transition between the valence band and the soliton level at mid-gap.[7]

A comparison of the IAVM of solitons in *trans*-$(CH)_x$ and *trans*-$(CD)_x$ is shown in Fig. 4. The dashed curves are the experimental results for a concentration of approximately 0.1%, and the solid curves are the result of the calculations outlined earlier. Besides the large frequency shifts upon deuteration, the detailed structure of the soliton IAVM that is driven by the higher-frequency stretching oscillations is also changed. First, the absorption is considerably broader and slightly asymmetric, with a shoulder on its high-energy side. The width (measured as full width at half the peak amplitude) of this mode is changed by a factor of 5, from about 50 cm^{-1} in $(CH)_x$ to about 250 cm^{-1} in $(CD)_x$. Secondly, the relative integrated oscillator strengths (Ω) of the two absorption modes are changed. The experimentally determined ratio in $(CH)_x$, $\Omega(900)/\Omega(1370)$, is about $\frac{2}{3}$, whereas the analogous ratio in $(CD)_x$, $\Omega(780)/\Omega(1120)$, is about $\frac{3}{2}$.

As shown in Fig. 4, the calculated infrared absorption associated with the IAVM of solitons is in remarkably good agreement with the experimental results. First, the frequencies are in agreement with the experimental results to an accuracy of a few percent for all the IAVM for both $(CH)_x$ and $(CD)_x$. Secondly, the increased width and asymmetry of the higher-frequency mode in $(CD)_x$ appears to be accounted for by the presence of a third ungerade IAVM at ~1270 cm^{-1} which did not appear in $(CH)_x$. The appearance of this mode is closely related to the presence of a third strong Raman line at 1200 cm^{-1} in *trans*-$(CD)_x$ [see Fig. 1(b)]. These major changes in the vibrational structure of polyacetylene upon deuteration result directly from the change in normal modes due to the heavier deuteron mass. Finally, as is the case for $(CH)_x$, the calculated absolute integrated oscillator strengths correspond to ~20% of the total associated with the added charge, and they agree with the experimental values to within a factor of 2–3. The relative oscillator strengths of the different modes are even more accurate. In $(CH)_x$ the *lower*-frequency mode is more intense by about 3 : 2, whereas in $(CD)_x$ we find that the *higher*-frequency absorption is more intense by ~3 : 2. In both cases the experimental and theoretical intensity ratios are in close agreement.

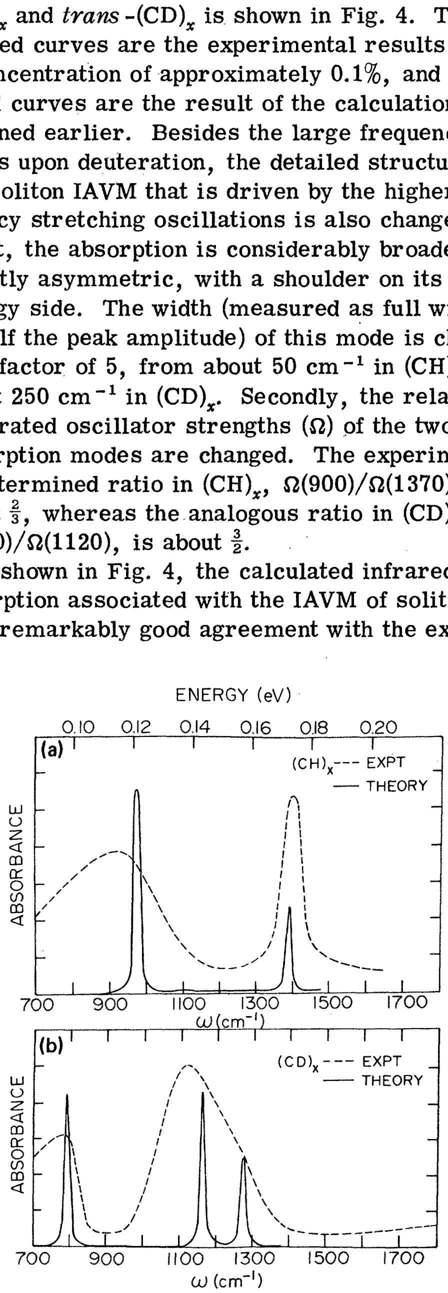

FIG. 4. Soliton-induced infrared-active vibrational modes (IAVM); see text for discussion of absolute intensities and integrated oscillator strengths. (a) *trans*-$(CH)_x$. -----, experiment; ——, theory. (b) *trans*-$(CD)_x$. -----, experiment; ——, theory.

The origin of the induced infrared-active modes differs fundamentally from that proposed by Rabolt *et al.*[17] They attributed the absorption to Raman-active Ag modes, originating from pristine $(CH)_x$, which have become activated in the ir because of the interaction with collective charge oscillations parallel to the chain axis. However, the experimental results are inconsistent with the simple vibronic mode interpretation.[17] In that picture, frequency shifts (relative to the pure polymer) would be expected in proportion to the doping from a combination of bond-weakening and doping-activated turn-on of the coupling to the π electrons.[18] The observation (see Ref. 8 and Fig. 3 of this paper) that in the dilute limit the IAVM intensities are proportional to the dopant concentration, whereas the frequencies of the observed modes are concentration independent, shows that the absorption arises from localized rather than collective modes of the doped polymer chain. The results presented in this paper and Ref. 10 demonstrate that the IAVM originate from the bond distortions associated with the structure of the soliton. These bond distortions seriously perturb the π-electron states and consequently create *new* vibrational modes which are not simply related to the modes of the perfect chain. Thus, the assignment[17] of the strongly ir-active modes in the heavily doped polyacetylene films as vibronic modes must be reconsidered in light of our present findings. In particular, the results shown in Fig.

4 demonstrate that the large isotope shifts observed in the IAVM of solitons are expected, and result directly from the normal mode changes due to the heavier deuteron mass. Contrary to their assertions, the observation by Rabolt *et al.*[17] that the strongly-ir-active modes in *heavily* doped polyacetylene also shift in frequency upon deuteration does not rule out the soliton model, but rather suggests that it might be applicable even at relatively high concentrations. However, studies extending the data to higher concentrations are required to clarify the effect of the semiconductor-metal transition on the soliton IAVM.

IV. CONCLUSION

In conclusion, we have been able to achieve a quantitative understanding of the Raman frequencies and the soliton-induced infrared absorption in *trans*-$(CH)_x$ and *trans*-$(CD)_x$. The success of the theory implies the basic validity of the one-electron approach, with Coulomb interactions playing only a relatively minor role. The detailed agreement between the calculated and experimentally observed infrared-active vibrational modes provides specific experimental evidence of soliton doping in polyacetylene. This remarkably accurate verification of the soliton model, achieved without adjustable parameters, is possible in spite of the apparent complex morphology of these polymers because of the inherent simplicity of the polyene chain structure.

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