Localized phonons associated with solitons in polyacetylene: Coupling to the nonuniform mode

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We report the observation of photoinduced infrared absorption due to the recently predicted localized phonons in $trans$-$(CH)_x$ and its deuterated analog $(CD)_x$. The infrared activity results from coupling of the three lattice degrees of freedom to a soliton shape-modulation mode involving nonuniform translation of the soliton. Our results agree with the energies and weak oscillator strengths predicted for these new modes and for the related absorptions which result from coupling to the uniform translation of the soliton. This agreement provides confirmation of the accuracy and applicability of the electron-phonon model in describing the nonlinear soliton excitation in polyacetylene.

In the Su-Schrieffer-Heeger (SSH) model[1] of polyacetylene, which incorporates electron-phonon coupling into a tight-binding Hamiltonian, charges added to a chain (either through charge transfer doping or following photoexcitation) disrupt the dimerization pattern leading to the creation of spinless charged domain walls, or solitons, separating sections of chain with opposite bond alternation. These solitons have a characteristic spectrum of localized vibrational excitations and electronic states which are accessible spectroscopically.[2]

Three vibrational modes with large oscillator strength are observed; in the "amplitude-mode" (AM) formalism due to Horovitz,[3] these correspond to the coupling of the three lattice degrees of freedom of the $(CH)_x$ chain (that modulate the dimerization amplitude and, thus, are resonantly enhanced in Raman scattering[4]) to the zero-frequency uniform translational freedom of the charge. Recently, a series of elegantly performed calculations, based on the SSH Hamiltonian and its continuum version, has predicted infrared activity due to the coupling of these same three lattice degrees to a soliton shape modulation mode, i.e., one having *nonuniform* translation of the soliton.[5-9] In this paper, we report the observation of these extra absorptions in both $(CH)_x$ and its deuterated analog, $(CD)_x$, and we find that our results are in good agreement with the energies and weak oscillator strengths predicted. This agreement provides an important confirmation of the accuracy of the electron-phonon coupling model for describing the nonlinear soliton excitation in polyacetylene.

Steady-state photoinduced absorption experiments were performed as previously described[10] with an IBM instruments (Bruker) vacuum Fourier transform spectrometer. The samples were thin films of either Shirakawa-route or Durham-route[11] polyacetylene; the deuterated samples were prepared from (CD) gas, 99.8% isotopic purity. Simultaneous deposition of the Shirakawa material on three different substrates was followed by use of each sample in the appropriate spectral region with the proper detector: Si substrate, 40–220

cm^{-1}, Ga:Ge bolometer; CsI, 200–450 cm^{-1}, bolometer; and KBr, 400–4500 cm^{-1}, pyroelectric deuterated triglycine sulfate (DTGS). Splining of the resulting curves allowed accurate integration of oscillator strengths. After preparation, the samples were isomerized as appropriate under high vacuum and then transferred to the high vacuum cryostat in the spectrometer without any exposure to air, using a specially designed sample cell. The photoinduced absorption was measured at 80 K; interferograms were collected at 4 cm^{-1} resolution with light from an Ar^+ laser alternately on and off the sample and coadded until a satisfactory signal-to-noise ratio was achieved, typically for 15 to 45 h. The resulting interferograms were Fourier transformed with Happ-Genzel apodization and ratioed to provide the IRAV spectra.

Figure 1 shows the photoinduced absorption spectrum of isomerized Shirakawa $(CH)_x$ between 40 and 4500 cm^{-1}. Most prominent are previously reported features:[10,12] vibrational absorptions centered at 536, 1288, and 1365 cm^{-1} with relative integrated oscillator strengths (OS's) 29, 1.0, and 4.2, respectively, and a broad electronic transition peaking at 3560 cm^{-1}; all of these energies are somewhat sample dependent. A barely noticeable shoulder on the electronic transition, between 1500 and 2000 cm^{-1}, has also been reported. The corresponding data above 200 cm^{-1} for Shirakawa $(CD)_x$ are shown in Fig. 2; the established data[10,13] are the vibrational absorptions at 510, 1045, and 1227 cm^{-1} (OS's: 41, 21, 1.0), the electronic transition at 3560 cm^{-1}, and, again, the shoulder between 1500 and 2000 cm^{-1}. Other sharp features in the spectra having derivative characters are due to thermal modulation of known absorptions in the spectra of the unexcited polymer, e.g., the feature at ~750 cm^{-1} in the $trans$-$(CH)_x$ spectra may be due to a small amount of remnant cis material. The derivativelike feature in the same position in the $(CD)_x$ sample is due to thermal modulation of an absorption of $trans$-$(CD)_x$ at 750 cm^{-1}. Only features having nonderivative character, e.g., the mode at 1034 cm^{-1}, may be considered authentic signatures of a pho-

togenerated species. The low noise level of the spectra shown here now allows detection of two new features in each spectrum. In $(CH)_x$, absorptions are seen at 1034 (OS, 0.20) and 1438 cm^{-1} (OS, 0.16); in $(CD)_x$, the corresponding absorptions are at 858 (OS, 0.3) and 1340 cm^{-1} (OS, 0.7). It is the presence of these features with their associated oscillator strengths that confirms the validity of the recent calculations and of the model upon which they are based.

After the prediction of intense three-peaked infrared activity of solitons in polyacetylene,[14] Horovitz showed[3] that this activity is characteristic of the coupling of the three lattice degrees of freedom to the translational motion of the added charge. In the presence of a bond-alternation wall, oscillator strength is transferred from the three phonon continua to bound phonons at $k = 0$. Nakahara and Maki[15] (NM) then showed that in the (one-component) continuum version of the SSH Hamiltonian, due to Takayama, Lin-Liu, and Maki (TLM),[16] there are two normal modes of the soliton. The first is the uniform translational (Goldstone) mode of even symmetry, which generates the three absorptions ("T modes") of Horovitz.[3,17] This mode corresponds to uniform displacement of the dimerization wave function of the soliton, as shown in the inset to Fig. 1. The second, the breathing mode or amplitude oscillation of the soliton, also shown in the inset to Fig. 1, has symmetry *opposite* to the first and, thus, would not be expected to generate infrared activity. (The usual symmetry dependence of vibrational wave functions for electric dipole transitions is here reversed due to the opposite sense of
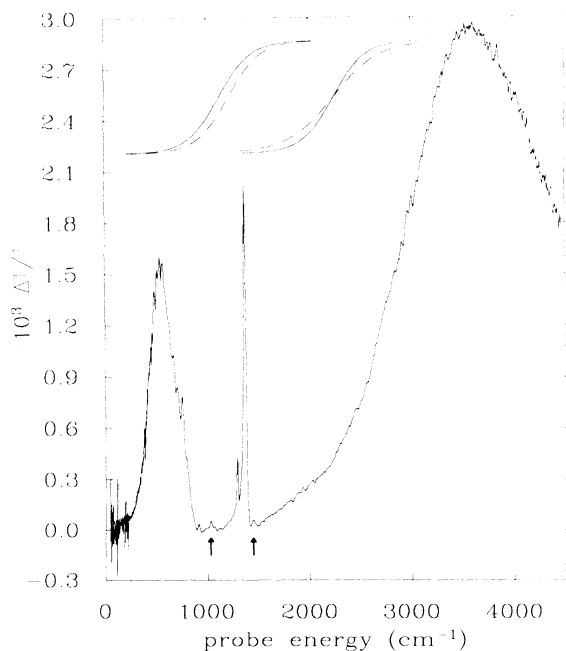
the dimerization on either side of the charged defect.[6]) These are the same two modes that are found for a soliton in the ϕ^4 field theory.

Ito, Terai, Ono, and Wada pointed out[5] that the variational method used by NM to solve the eigenvalue problem for small vibrations around a charged defect could have overlooked the presence of further localized modes. Solving the eigenvalue problem in the one-component TLM model numerically, they found three bound modes for a soliton: the first two corresponding to the two of NM and a third having the same (even) symmetry of the uniform translational mode[5] and, thus, expected to contribute to the infrared conductivity.[6] This nonuniform translational mode is represented in the inset to Fig. 2. More recently, Terai *et al.* have followed the formalism, previously developed by Mele and Hicks,[18] to calculate the results of coupling of the third bound mode to the three lattice degrees of freedom.[9] The third bound mode of the one-component model is thus found to generate three peaks (B modes) in the infrared conductivity. The energies and relative intensities of two of these peaks are in reasonable agreement with the values given above for the newly resolved low-intensity peaks in the photoinduced IRAV spectra of both $(CH)_x$ and $(CD)_x$. The third peak is predicted to have oscillator strength significantly below the other two and, at 1292 cm^{-1} for $(CH)_x$ or 1193 cm^{-1} for $(CD)_x$,[9] would be expected to be absorbed under the stronger translational modes. The origin of the reproducible shoulder at 1320 cm^{-1} in the $(CH)_x$ spectra is thus unclear.

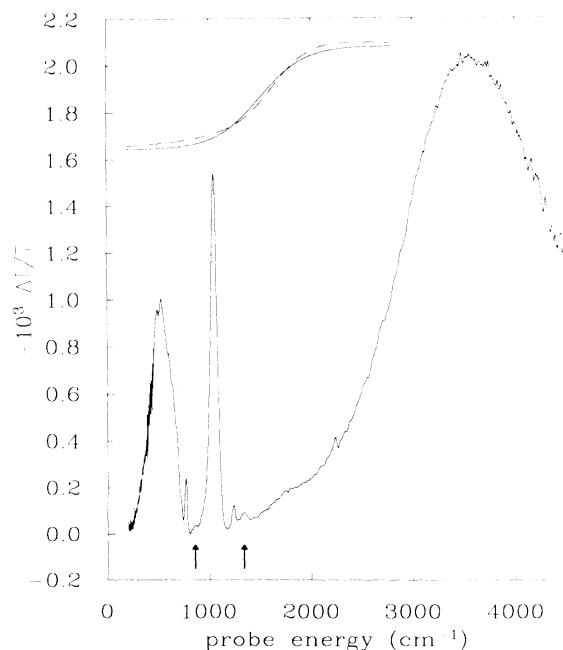Alternative explanations for the newly observed peaks may be considered. Vardeny *et al.* have reported weak

FIG. 1. Photoinduced absorption of *trans*-$(CH)_x$ between 40 and 4500 cm^{-1}. The arrows indicate new absorptions at 1034 and 1438 cm^{-1}. The upper insets are schematic representations of the first (Goldstone) and second (breathing) modes of a soliton.

FIG. 2. Photoinduced absorption of *trans*-$(CD)_x$ between 200 and 4500 cm^{-1}. The arrows indicate new absorptions at 858 and 1340 cm^{-1}. The upper inset is a schematic representation of the third bound mode of a soliton.

absorptions, at energies slightly lower than those of the modes we report here, that disappear upon isomerization of samples.[17] They ascribe these absorptions to the localization of charged solitons near structural defects such as chain ends or *cis* segments. In this case, the structural defect breaks the translational symmetry of the infinite polyacetylene chain; thus, the selection rule[6] preventing ir activity of the second (amplitude oscillation) mode of the soliton would be invalidated. They claim that these weak ir absorptions disappear as isomerization of the sample removes the symmetry-breaking defects.

In Fig. 3 we compare the photoinduced IRAV spectrum at the same pump intensity for a 15% *trans* Shirakawa sample with that of the same sample after isomerization for 20 min at 165 °C. The percentage of *trans* in the *cis* rich sample was determined from its infrared absorption spectrum;[19] the *cis* content of the isomerized sample was below the detection limit (1%) of the experiment. While the frequencies of the T modes are unchanged by isomerization, the intensities of both T modes and electronic midgap absorptions are higher for the *cis*-rich sample,[20] indicating that the concentration of long-lived photogenerated charges is higher. This complicates direct comparison between the two curves; however, the absorption from the small modes is clearly seen in both samples. It is thus unclear whether the divergence of our results from those of Vardeny *et al.* is due to differences in sample preparation, isomerization, or handling, or rather to the difference between the time scale of their measurements (~ 100 Hz) and ours (0.1 Hz).
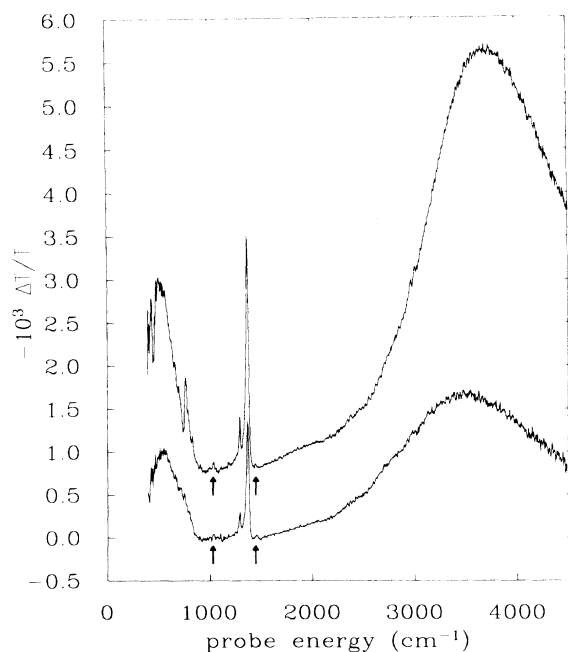
A second possibility is that these modes are an artifact of the synthetic route, perhaps related to impurities or structural imperfection introduced during the synthesis. We have shown in Fig. 4 the photoinduced IRAV spectrum of a thin-film sample of unoriented Durham precursor route $(CH)_x$ both after thermal conversion from the precursor polymer (35% *trans*) and after full isomerization. $(CH)_x$ prepared in this way preserves the disordered conformation of the solution-cast precursor polymer film which is thermally transformed to $(CH)_x$. The straight chain sequences are necessarily short and are terminated by chain bends or twists which raise the band gap but still allow soliton, or single kink, states on the chain.[11] All the absorption features are raised to higher energies in this material; in particular, the electronic "midgap" absorption band peaks at above 4000 cm^{-1}. However, the small vibrational absorptions are still present at 1037 and 1458 cm^{-1} in the partially *cis* sample, thus confirming that they are intrinsic to the polymer; the thermal modulation of the strong *trans* absorption at 1010 cm^{-1} obscures the lower absorption in the fully isomerized sample but the higher one is still present. The reason for the shift of the highest mode from 1438 cm^{-1} in Shirakawa to 1458 cm^{-1} here is not understood in detail. Although some sensitivity of the internal modes of solitons to pinning would be expected, the observed shift of this B mode (20 cm^{-1}) is greater than the shift (8 cm^{-1}) for the corresponding T mode.

These comparisons demonstrate that the small absorptions are intrinsic to charged soliton defects in *trans*-polyacetylene. We thus assign them as the B modes generated by the nonuniform translation of the soliton, as predicted by Terai *et al.* While infrared activity has previously been attributed to non-Goldstone modes in
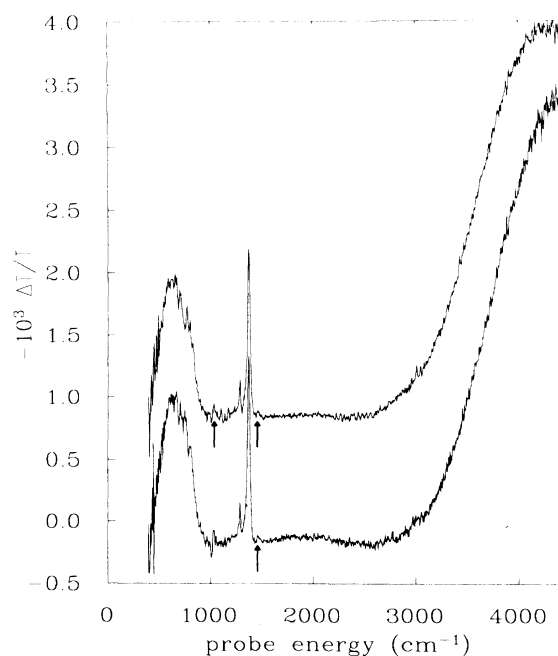

FIG. 3. Comparison of photoinduced absorption of 15% (upper) and fully (lower) Shirakawa *trans*-$(CH)_x$ samples. The 15% *trans* sample shows thermal modulation of the intrinsic *cis* absorptions at 450 and 740 cm^{-1}.

FIG. 4. Comparison of photoinduced absorption of 50% (upper) and fully (lower) Durham *trans*-$(CH)_x$ samples.

polythiophene,[21] the complexity of that system may have allowed some uncertainty; here, the identification is unambiguous.

While we defer[20] a detailed discussion of the sample dependence of the IRAV spectra, we here make two observations based upon the AM formalism which provides a useful description of the T modes.[3,4] First, the ratio of the oscillator strengths of the electronic transition to that of the T modes is directly proportional to the dynamic mass of the defect;[13] thus, Fig. 3 shows that the defect mass is decreased by full isomerization of the Shirakawa sample and Fig. 4 shows that the defect mass is highest in the "short chain" unoriented Durham sample. We note that the dynamic masses for the fully isomerized $(CH)_x$ and $(CD)_x$ samples shown in Figs. 1–3 are lower than reported elsewhere in the literature. We consider this to be an important indicator of chain perfection and completeness of isomerization in the vicinity of the charged soliton. Second, the exact energies of the peaks and, in particular, the displacement of the lowest-energy absorption from zero frequency are accounted for by a phenomenological pinning parameter.[3,4] Thus, the unusual width of this mode shown here clearly for the first time may indicate a distribution of pinning parameters. Recently, however, Gammel and Hicks[22] have suggested that the width is due to the coupling of the translational mode to acoustic phonons. A comparison of the frequencies of this mode in Fig. 1 (536 cm^{-1}) and Fig. 4 (625 cm^{-1}) as well as other data[20] shows that the peak position is sample dependent. Nevertheless, both show a shoulder on the blue side which shifts with the peak position, as might be suggested by the acoustic coupling argument.

There is one unanticipated reward of the sample dependence of the spectra. The blue shift of the edge of the electronic transition in the Durham sample has allowed the previously observed shoulder between 1500 and 2200 cm^{-1} to be resolved from that transition (Fig. 4). Horovitz[3] suggested that in the presence of a charged defect, in addition to bound vibrations, extended phonons associated with the three lattice degrees should be weakly infrared active but probably unobservable. Ito and Ono later calculated that the absorption of these extended phonons with the proper (even) symmetry should be observable at energies above that of the associated bound mode.[6] We hence attribute this broad feature, with oscillator strength of 3.0 with respect to the 1287 cm^{-1} mode, to the highest-energy extended phonons. The other two sets of extended phonons are expected to have lower energy, and, thus, their absorption may lie below the stronger T modes.

The observation of infrared absorption, due to both the third bound mode (which is absent in the ϕ^4 field theory solitons) and the extended phonons as predicted by Wada et al., is a confirmation of the accuracy of the SSH and TLM models in describing polyacetylene. That the electron-phonon interaction rather than electron-electron interactions is the principal cause of the semiconducting gap in polyacetylene has been subject of debate. Clearly, some experimental evidence, in particular electron-nuclear double resonance results,[23] implies that

Coulomb correlations are of some importance in polyacetylene. Our point, however, is that the normal-mode calculations of Wada and co-workers,[5–9] using a nonlocal electron polarization that omits Coulomb terms, has managed to accurately predict extremely subtle structure in the infrared absorptions of solitons.

Since the calculation of Ito et al.,[5] there have been further calculations of the bound modes of solitons in both the TLM and SSH models.[8,24–26] While the selection of the proper parameters and boundary conditions used in these calculations is not totally straightforward, it does seem that the number of bound modes of either soliton or polaron defects depends critically upon the value chosen for the dimensionless electron-phonon coupling coefficient[7] λ. The significance of λ is that in the Peierls model the band gap is given by $2\Delta = 2W \exp(-1/2\lambda)$, where W is the total π electron bandwidth; physically, the measured bandwidth of 12.5 eV and band gap of 1.7 eV correspond to $\lambda = 0.19$. It is unclear whether two or three modes are bound by a soliton in the TLM model with this value; Ito et al. used $\lambda = 0.12$ in their calculations. However, both Hicks and Gammel[22] and Terai and Ono[8] have shown that in calculations beginning with the discrete lattice (SSH) model choosing $\lambda = 0.19$, i.e., using the physically observed W clearly provides the three bound modes (plus an unobservable staggered bound mode at the Brillouin-zone edge). This may be because the cosine electronic band structure of the SSH model is a more accurate representation of the band structure than the linearized structure of the TLM model.[22]

The prediction of four total bound modes of a soliton, two of which, as observed, are infrared active, suggest that the observation of the bound modes has provided a spectroscopic identification of the charged defect. However, while the polaron, a spin-$\frac{1}{2}$ defect, is predicted to have seven bound modes,[8] again two of these are infrared active.[27] Thus, in absence of a firmly based expectation of different relative oscillator strengths or energies of the T versus B modes for the two defects, this identification, which is clear otherwise from measurement of ESR and electronic transitions, is not made.

In conclusion, we have observed and identified weak photoinduced infrared absorption due to localized phonons associated with the nonuniform translation motion of solitons and due to the extended phonons associated with the solitons. Our results are in excellent agreement with the predicted energies and weak oscillator strengths. This agreement has provided a detailed confirmation of the accuracy of the electron-phonon model in describing the excited states of polyacetylene.

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