Defects in a Nonlinear Pseudo One-Dimensional Solid

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These infrared studies of acetanilide together with the existence of two equivalent structures for the hydrogen-bonded chain suggest the possibility of a topological defect state rather than a Davydov soliton as suggested previously. Acetanilide is an example of a class of one-dimensional materials where solitons are a consequence of a twofold degenerate structure and the nonlinear dynamics of the hydrogen-bonded network.

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The structure of acetanilide (ACN), with four chains of hydrogen-bonded amide groups running through the crystal, is an interesting model system possessing a one-dimensional array of hydrogen bonds. To understand the hydrogen-bonding mechanism is of crucial importance in polymer physics with direct application to hydrogen-bonded polymers, and of clear biological interest since the hydrogen bond is largely responsible for the structure of the alpha helix of proteins and the double helix of DNA. Acetanilide is a likely candidate to support nonlinear solitonic-type excitations which, in turn, can be studied in the framework of a highly ordered crystalline system.

The first studies of structure[1] and optical properties[2] were in the middle 50's. Recently Careri *et al.*[3] reported anomalous features in the low-temperature infrared (ir) spectra. Their results show that a new band at 1650 cm^{-1} is the only major change that occurs at low temperatures. They associated this band with the formation energy of a soliton and interpreted their results within a model similar to that proposed by Davydov.[4]

We present here Fourier-transform ir studies of acetanilide in the middle- and far-ir regions (4500–30 cm^{-1}). The strong temperature dependence of the spectra is shown by several new bands appearing in the low-temperature regime with the same temperature dependence as reported for the 1650-cm^{-1} mode. ACN is an outstanding example of a nonlinear system which supports strongly self-trapped vibrational excitations in a solid. As a result the key question to ask is not whether solitary excitations exist in ACN, but rather if they are described as topological or nontopological solitons.[5] Our results in combination with a structure that admits a twofold degeneracy clearly opens the possibility for topological solitons.

The experiments were performed in an IBM-98 vacuum Fourier-transform ir spectrometer. The sample was mounted on the cold finger of an Oxford cryostat that allowed the temperature to be varied from 20 to 300 K. Thin polycrystalline acetanilide samples were obtained by melting the material on different substrates; KBr for the middle-ir and polyethylene for the far-ir experiments. Deuterated acetanilide samples were supplied by S. B. Maerov of our laboratories.

The strong nonlinearities of the problem are clearly illustrated by the spectral features of the NH stretching band, shown in Fig. 1 for 20 and 300 K. The nature of the NH mode is complex; the main peak appears at 3306 cm^{-1} at room temperature and it shifts to 3296 cm^{-1} at low temperatures. Numerous satellites, whose origin remained unsolved, appear in the low-energy side of the main NH stretch. Their relative intensities are independent of temperature and depend only weakly on their energy position with respect to the main NH stretch. The inset of Fig. 1 shows that there is a linear correspondence between the peak energy position and sideband number, *n*. The constant

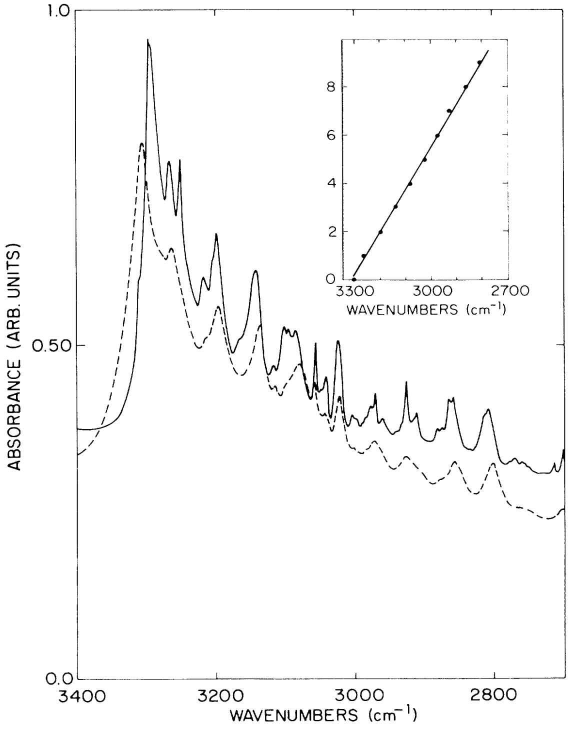

FIG. 1. NH stretching band at 30 K (solid curve) and at 300 K (dashed curve).

sideband spacing of about 55 cm^{-1} is clear throughout the spectra except for complications in the 3060-cm^{-1} region due to the presence of other molecular bands.[6] The low-temperature spectra show a similar sideband spacing and a fine structure develops within each band. A new level appears at 3252 cm^{-1} with the same temperature dependence as reported for the 1650-cm^{-1} mode[3] and red shifted by 16 cm^{-1} from the nearest molecular band. The far-ir spectra show a series of bands at a constant spacing of 41 cm^{-1} and three new peaks, at 128, 80, and 64 cm^{-1}, in the low-temperature regime. Their intensity is dramatically reduced by deuteration.[7] A similar multiple-peak structure near the C-O stretching band can also be observed. However, the presence of numerous other molecular modes[2] in that energy region obscures the effect.

In order to understand the origin of the satellites in the NH stretch we studied the spectra of acetanilide in CCL$_4$ solution. The low-concentration data show two sharp lines; a more intense one at 3609 cm^{-1} associated with the main NH stretch, and a second one at 3060 cm^{-1}, often observed in polymeric materials (nylon-66).[6,8] At very high concentrations the NH stretch suddenly shifts to 3295 cm^{-1}, becomes asymmetric, and shows multiple sidebands. The middle-ir spectra of the melted specimen at 120 °C show that the main stretch barely shifts (3310 cm^{-1}) and satellites do not disappear. These results strongly suggest that the existence of the H-bonded chain is solely responsible for the production of the NH multiple structure. Consequently, it is not surprising that multiple-peak structure in the NH stretch is commonly observed in the spectra of noncrystalline hydrogen-bonded materials such as polyamides and polypeptides.[8]

Figure 2 shows the temperature dependence of the 3252-, 1651-, and 80-cm^{-1} modes. All three bands show the same temperature dependence. Their intensity slowly decreases for temperatures up to 100 K and decreases fairly rapidly thereafter.

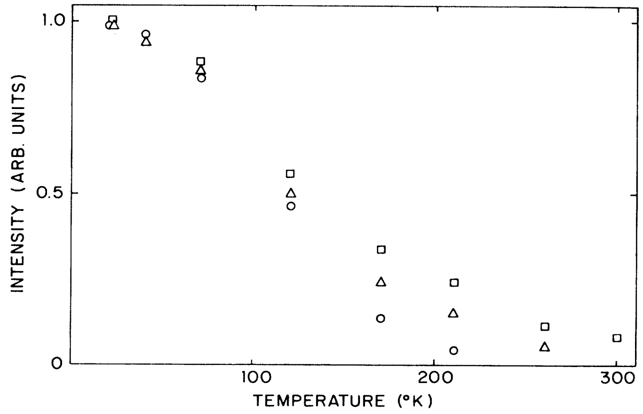

FIG. 2. Temperature dependence of the local modes at 3252 (circles), 1651 (squares), and 80 (triangles) cm^{-1}.

Our results show that several new modes appear in the low-temperature ACN spectra. Careri *et al.*[3] based their interpretation on the existence of a single new mode (1650 cm^{-1}) at low temperatures and associated this band with the formation energy of a Davydov soliton. Our low-temperature spectra show new peaks at 3252, 1651, 118, 80, and 64 cm^{-1}. They all have the same temperature dependence reported for the 1650-cm^{-1} band.[3] Consequently, it seems artificial to choose the 1650-cm^{-1} mode over any of the other new bands as the formation energy of the soliton.

The NH stretching band shown in Fig. 1 represents the key to the understanding of excitations in ACN. Three features of the data delineate the problem: the constant spacing between side bands, the large number of sidebands clearly observable, and the temperature independence of the relative intensity of the sidebands. In general, one might assume that the sideband structure reflects a highly anharmonic potential leading to numerous combination bands. However, such anharmonicities would result in a set of energy levels that were not equally spaced in direct contradiction with the experimental results (inset of Fig. 1). In addition, if the sidebands arose from combination bands (phonon creation with phonon destruction) then the relative intensities would be highly sensitive to temperature, reflecting the change in the Boltzman distribution with temperature. For instance, the intensity of each of the bands at 10 K should be modified by a factor $\exp(-E_0/kT)=e^{-(7.9)l}=(3.7\times10^{-4})^l$ where $E_0=55$ cm^{-1} and l is the peak number away from the absorption at 3300 cm^{-1}.

A broad band as in Fig. 1 may also be viewed as indicative of a transition to an excited vibrational state in which the equilibrium value of a second degree of freedom at low frequency is shifted with respect to its value in the ground state. This type of response is not surprising in highly nonlinear systems, where large relaxational effects are expected. Let us denote this as-yet undefined degree of freedom as "relaxational." One can then associate the structure of the NH stretching mode with a vibrational–relaxation-mode band in which the NH in the excited vibrational state relaxes by coupling to low-energy modes. Although the origin of the low-energy relaxational mode needs further investigation, we tentatively assign it to an optical phonon based on low-frequency optical data. While our far-ir studies did not show a mode at the energy of the NH sideband spacing, an intense band appears at about 50 cm^{-1} in Raman data.[3] A similar effect, observed in alkali halides and semiconductors, has been associated with exciton-phonon interactions.[9-11] For those systems, phenomena such as phonon sidebands accompanying exciton peaks, self-trapping of holes and excitons, and temperature dependence of the exciton line shape have been described in detail. Analogous to these systems, the sidebands in ACN are indicative of a large phonon–relaxational-mode coupling. Within the adiabatic approximation, the wave function can be factored into the product of vibrational and relaxational components with the result that for each vibrational energy level there is an associated manifold of librational energy levels. Then, analogous to the Franck-Condon principle, the relaxational transitions that are associated with a vibrational transition are the ones that take place between those relaxational levels with the same configuration in both vibrational states. Thus each peak within the NH stretching band can be associated with a different relaxational transition within a single vibrational excitation. If we denote the initial state of the system by $|n,m\rangle$ where n represents the number of NH vibration quanta and m the number of quanta in the 55-cm^{-1} state, then, the l satellite in the NH band can be represented by the transition

$$|n=0,m=0\rangle \rightarrow |n=1,l\rangle .$$

$E_l = E_1 + l\hbar\omega$, where $E_1 = 2810$ cm^{-1} and $\hbar\omega = 55$ cm^{-1}. In ACN, as in the alkali-halide case, we should think that the zero-phonon line is located at E_1, the lower-energy side of the exciton peak with quite negligible oscillator strength. This indicates that the excited-state well has relaxed by about 500 cm^{-1} and the configuration coordinate has shifted to a new minima of nonzero value by distorting the lattice. Therefore, the NH excitation must be either localized or trapped. The self-trapping can be thought of as analogous to that observed for excitons in polarizable media. This is fully consistent with the existence of sideband structure at about $T = 400$ K, above the melting point of acetanilide. These surprising results, along with the understanding of the origin of the multiple sidebands, proves that ACN is truly a pseudo one-dimensional hydrogen-bonded solid. Above the melting point this system can be thought of as an H-bonded polymer melt.

The most important point is purely based on an experimental fact: The temperature dependence of the 3252-, 80-, and 64-cm^{-1} modes are essentially the same as the temperature dependence of the 1650-cm^{-1} mode. This result substantially negates the model proposed in Ref. 3 and subsequent variants for the temperature dependence due to an optical mode. Although at this time we can only speculate on the nature of the relaxational mode, its low frequency and Raman activity suggest some kind of libronic motion. We believe that these data suggest the possibility that nonlinear trapping of a vibronic excitation may lead to localized geometric kinks or polaronlike distortions in the ACN chains.

Finally, we believe acetanilide as a model system is a good starting point to study nonlinear excitations in solids. ACN belongs to a whole new class of pseudo one-dimensional materials that naturally supports nonlinear solitonic excitations. Although the relaxation-vibration coupling in ACN is different from the electron-phonon coupling in conducting polymers, these materials will have not only the clear advantage of crystallinity but also the different competing interactions that can be modified by proper selection of the molecular entities.

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