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ir overtone spectrum of the vibrational soliton in crystalline acetanilide

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The self-trapping (soliton) theory which was recently developed to account for the anomalous amide-I band at 1650-cm^{-1} in crystalline acetanilide (a model system for protein) has been extended to predict the anharmonicity constant of the overtone spectrum. These infrared-active overtones which have been detected at 3250, 4803, and 6304 cm^{-1} yield an anharmonicity constant that is in good agreement with the theory.

Recently, we have proposed that an anomalous band at 1650 cm^{-1} in crystalline acetanilide (ACN), a model system for protein, could be assigned to a self-trapped state[1-3] similar to a Davydov soliton.[4] This assignment has been questioned by several researchers. Blanchet and Fincher have suggested that the existence of a band at 3250 cm^{-1} with the same temperature dependence as the 1650-cm^{-1} band is evidence for an assignment based upon a structural transition.[5] From a more conventional perspective, Johnston and Swanson have argued that the 1650-cm^{-1} band can be assigned to Fermi resonance.[6] In the context of this ongoing controversy, it is interesting to consider the predictive power of the self-trapping theory. Here we show that this theory is able to predict the anharmonicity constant for an overtone spectrum which is in good agreement with independent measurements. The first overtone of this spectrum is at 3250 cm^{-1}.

Consider a single, hydrogen bonded chain of crystalline ACN. The classical Hamiltonian can be written in terms of complex mode amplitudes (a_n) for amide-I vibrations at molecules (indexed by n) along the chain, and the normal coordinates (q_k) for low-frequency optical-phonon modes (indexed by wave number k). Assuming the self-trapped state to be stationary implies $\dot q_k = 0$; thus the Hamiltonian is

$$H=\sum_{n,k}\left[\omega_I|a_n|^2-J(a_{n+1}a_n^*+a_n^*a_{n-1})+\tfrac{1}{2}W_kq_k^2-\chi_{kn}q_k|a_n|^2\right] . \tag{1}$$

Here ω_{I} is the amide-I frequency ignoring phonon interactions, J is the nearest-neighbor dipole-dipole coupling energy, W_k is an harmonic potential for the phonon mode at wave number k, and the χ_{kn} are nonlinear coupling coefficients between the amide-I and phonon modes. Variation with respect to q_k implies that $q_k=(\chi_{kn}/W_k)|a_n|^2$, so the Hamiltonian reduces to

$$H=\sum_n\left[\omega_I|a_n|^2-J(a_{n+1}^*a_n+a_n^*a_{n+1})-\tfrac{1}{2}\gamma|a_n|^4\right] , \tag{2}$$

where (assuming χ_{kn} is independent of n)

$$\gamma=\sum_k\chi_{kn}^2/W_k . \tag{3}$$

Detailed calculations[3] show that $J=3.96\ \mathrm{cm}^{-1}$ and

$$\gamma=44.7\pm1.5\ \mathrm{cm}^{-1} , \tag{4}$$

where the uncertainty arises because peak positions in Ref. 2 are recorded only to the nearest wave number. Since $2J \ll \gamma$, the second term in the summation of (2) can be neglected. This corresponds to assuming that the self-trapped energy is concentrated at a single molecule, as is observed in detailed numerical calculations.[3] Thus the Hamiltonian reduces to a sum of noninteracting terms of the form

$$h=\omega_I|a|^2-\tfrac{1}{2}\gamma|a|^4 , \tag{5}$$

where the subscripts have been dropped for typographical convenience. The most general solution of this classical Hamiltonian is $a=\sqrt{N}\exp[-i(\omega_I-\gamma N)t]$, where N is an arbitrary constant.

Under quantization (5) becomes an operator $\hat h$, defined by the substitutions

$$|a|^2\rightarrow\tfrac{1}{2}(a^\dagger a+aa^\dagger) , \tag{6}$$

and

$$|a|^4\rightarrow\tfrac{1}{6}(a^\dagger a^\dagger a\,a+a^\dagger a\,a^\dagger a+a^\dagger a\,aa^\dagger+a\,a^\dagger a\,a^\dagger+aa\,a^\dagger a^\dagger+a\,a^\dagger a^\dagger a) , \tag{7}$$

where a and $a^\dagger$ are boson annihilation and creation operators with the properties $a|N\rangle=\sqrt{N}|N-1\rangle$ and $\hat a^\dagger|N\rangle=\sqrt{N+1}|N+1\rangle$. The eigenvectors of $\hat h$ are the set $\{|N\rangle\}$ for which the eigenvalues $E_N=\langle N|\hat h|N\rangle$ are readily computed to be

$$E_N=\omega_I(N+\tfrac{1}{2})-\tfrac{1}{2}\gamma(N^2+N+\tfrac{1}{2}) . \tag{8}$$

An overtone spectrum is generated by transitions from the ground state, with energy $E_0=\frac{1}{2}\omega_I-\frac{1}{4}\gamma$ to $|N\rangle$, with energy E_N. Such transitions are induced by anharmonicities that are not included in (5). Thus absorption lines are expected at $\nu(N)=E_N-E_0$, or

$$\nu(N)=\omega_0N-\tfrac{1}{2}\gamma N^2 , \tag{9}$$

where $\omega_0\equiv\omega_I-\frac{1}{2}\gamma$ is the amide-I mode frequency includ-

TABLE I. Comparison of overtone measurements and calculations.

N	ν_{pred} (cm^{-1})	ν_{meas} (cm^{-1})	FWHM (cm^{-1})	Intensity	Remarks	ν_f (cm^{-1})
1	1650	1650.5 ± 0.5	8	1	ACN microcrystals in KBr at 80 K	1650.1
2	3255 ± 2	3250 ± 1	10 ± 1	0.2 ± 0.01	ACN microcrystals in KBr at 80 K	3250.8
3	4816 ± 5	4803 ± 3	33 ± 2	0.003 ± 0.001	Single crystal at 80 K	4802.1
4	6332 ± 9	6304 ± 5	20 ± 10	0.0002 ± 0.0001	Single crystal at 90 K	6304.0

ing phonon interactions.

Using the value of γ given in (4) and the requirement $\nu(1)=1650$ cm^{-1} determines $\omega_0=1672.4$ cm^{-1}. Then overtones of the 1650 cm^{-1} (soliton) line are predicted to be near the following values: $\nu(2)\approx 3255$ cm^{-1}, $\nu(3)\approx 4816$ cm^{-1}, and $\nu(4)\approx 6332$ cm^{-1}.

In order to experimentally detect the overtone bands predicted by this theory, we have been guided by the following criteria: (a) a soliton overtone must display the same temperature-dependent intensity as the fundamental band at 1650 cm^{-1}, (b) a soliton overtone must be shifted by N^{15} substitution consistently with the isotopic shift displayed by the fundamental band, (c) a soliton overtone must disappear in deuterated ACN, and (d) a soliton overtone must have maximum absorption at the same polarization as the fundamental.

A Nicolet 7000 series FT-IR instrument was used to observe the fundamental and the first two overtones, and a Cary 14 spectrophotometer was used for the third overtone. Our estimates of absolute precision are included in Table I. The samples consisted of single crystals of ACN of appropriate thickness, or of pressed KBr pellets of microcrystalline ACN when the material available was insufficient to grow single crystals.

The theory predicts that the first overtone of the soliton band should be observed near 3255 cm^{-1}. The ir spectrum of ACN in this region displays several bands, most of which can be assigned to overtones enhanced by Fermi resonance with the NH stretching at 3300 cm^{-1}, as is usual with hydrogen bonded amides.[7] This region of the spectrum of ACN has been studied by Abbott and Elliott[8] using dichroism and isotopic dilution methods. However, these authors concluded that "the origin of the structure in the NH and ND stretching modes remains obscure." A band at 3250 cm^{-1} is observed (see Fig. 1) and assigned to the first soliton overtone from the following considerations:

(i) The 3250-cm^{-1} band displays similar temperature dependence as the 1650-cm^{-1} band.

(ii) N^{15} substitution moves the 3250 band to 3246 cm^{-1} with a red shift nearly twice the 2.7 cm^{-1} observed for the fundamental (reported in Fig. 3 of Ref. 1). This shift is seen only for the 3250-cm^{-1} band in this region of the ir spectrum.

(iii) In several runs on partially deuterated samples, not reported here, the intensity of the 1650 band is reduced and the intensity of the 3250-cm^{-1} band is also reduced.

(iv) The 3250-cm^{-1} band has the same dichroism as the 1650-cm^{-1} band.

A complete assignment of the other bands in this region is difficult and beyond the scope of the present work. But we note that the relatively strong band at 3260 cm^{-1} of unknown origin is essentially unaffected by N^{15} substitution and is also temperature independent in the temperature range investigated. In Table I we report the observed frequency and the relative intensity of the first overtone of the soliton band assigned at 3250 cm^{-1}.

The second overtone is predicted by the theory to occur near 4816 cm^{-1}. In this region we found a band at 4803 cm^{-1} which has the required temperature dependence (see Fig. 2), disappears in deuterated samples, and has the correct dichroism. The 4803-cm^{-1} band was observed both in single crystals and in KBr measurements, and it is assigned to the second soliton overtone. The relative intensity of this band is reported in Table I.

For the observation of the third overtone (see Fig. 3) a single crystal of approximately 5 mm in length was used in a Cary 14 spectrophotometer. A band at 6304 cm^{-1} with the required temperature behavior was observed. The relative intensity of this band, reported in Table I, was obtained by comparison with other bands which are common to the spectra taken with the Cary 14 and with the Nicolet 7000 FT-IR.

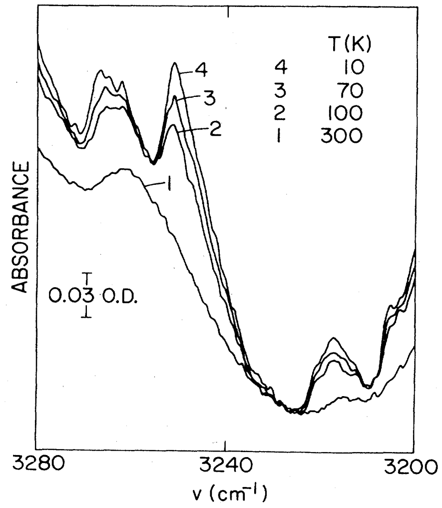

FIG. 1. Absorption spectra of ACN microcrystals in KBr showing the first overtone of the soliton peak. Each curve is the average of 100 scans on a Nicolet 7000 series FT-IR at a resolution of 1 cm^{-1}.

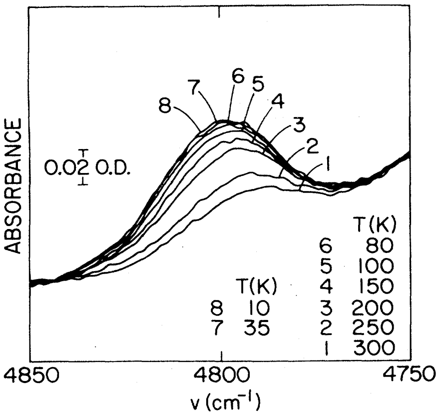

FIG. 2. Absorption spectra of an ACN crystal showing the second overtone of the soliton peak measured as in Fig. 1. The apparent shift in the peak position is caused by a temperature-independent peak at 4780 cm^{-1}. The overtone shift disappears when this peak is subtracted.

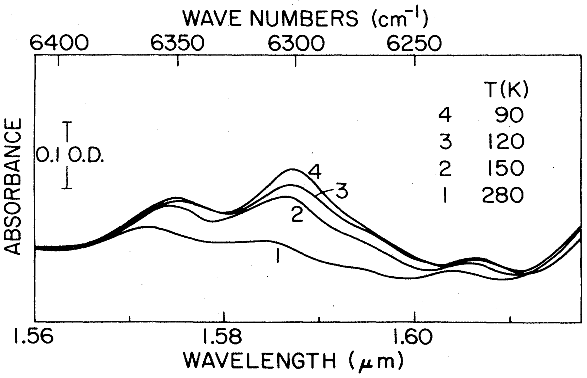

FIG. 3. Absorption spectra of an ACN single crystal (0.5 cm thick) showing the third soliton overtone. The spectra were taken with a Cary 14 spectrophotometer at 1 nm resolution.

Observation of the fourth overtone was not attempted, since the expected intensity, based on extrapolation of the values given in Table I, would require a crystal several centimeters long. We note that a second overtone of the normal amide-1 band has been detected at 4962 cm^{-1} and a third overtone at 6588 cm^{-1}, but with lower intensities with respect to the fundamental. The observed full bandwidths at half maximum (FWHM) for the overtone lines are also reported in Table I. Due to difficulties in subtracting background absorption, only the orders of magnitude of the intensities and bandwidths should be considered significant.

To test Eq. (9) a least-squares fit was made to the measured overtone frequencies by adjusting the parameters ω_0 and γ. In this minimization, terms were weighted by the reciprocal of the squared measurement error. The "fitted" parameters were found parameters were found to be $\omega_{0f} = 1.674.8\ \mathrm{cm}^{-1}$

$$\gamma_f = 49.4\ \mathrm{cm}^{-1}\ , \tag{10}$$

which is in good agreement with the value obtained from detailed numerical calculations[3] and presented in (4). From ω_{0f}, γ_f, and (9), the fitted frequencies ν_f, are calculated in the last column of Table I. The rms difference between measured and fitted frequencies is

$$\left[\frac{1}{4} \sum_{N=1}^{4} (\nu_{\mathrm{meas}} - \nu_f)^2 \right]^{1/2} = 0.6\ \mathrm{cm}^{-1}\ .$$

Since this is well within the accuracy to which the measured frequencies are determined, the data is in excellent agreement with (9).

Our interpretation of the 3250-cm^{-1} band as a two quantum soliton state is of biological significance because it is almost exactly resonant with the 10 kcal/mole of free energy released by the hydrolysis of adenosine triphosphate.

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