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Fine structure of the amide I band in acetanilide

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The ir absorption spectrum of both single crystals and powdered samples of acetanilide (a model system for proteins) has been studied in the amide I region, where a narrow band has been identified as a highly trapped soliton state. The powder-sample spectra have been decomposed using four Lorentzian bands. A strong temperature dependence has been found for the intensity of two of the subbands, which also show a complementary behavior. Polarization studies performed on thin crystals have shown that the subbands have the same polarization. Low-temperature spectra of partially deuterated samples show the presence of the subbands at the same absorption frequencies found using the fitting procedure in the spectra of nondeuterated samples. The soliton model currently proposed to explain the origin of the anomalous amide I component at 1650 cm^{-1} still holds, but some modification of the model is required to account for the new features revealed by this study.

INTRODUCTION

Recently there has been much experimental¹⁻³ and theoretical⁴⁻⁷ interest in crystalline acetanilide (ACN), a model system for proteins, with emphasis on the temperature-dependent ir absorption band at 1650 cm^{-1} . This is a rather narrow band, detached from the general amide I vibrational excitation, and it has been identified as a highly trapped soliton state^{2,4} in the Davydov model or as a vibronic analog of a small Holstein polaron.^{5,7} The more recent theoretical work⁷ suggests that the shift Δ of this polaron frequency from the unperturbed amide I mode is due to coupling with both acoustic and optical longitudinally polarized lattice modes. Moreover, acoustic coupling is found to contribute to about half of the total observed shift ($\Delta=15\text{ cm}^{-1}$) and to dominate the temperature dependence of the absorption strength of the polaron peak. This last theoretical result⁷ prompted us to look at the fine structure of the unpolarized absorption spectrum in the amide I region, where the absorption profile shows the presence of temperature-dependent unresolved bands in the shoulder of the 1650 cm^{-1} peak (see Fig. 5 of Ref. 2, reprinted as Fig. 2 in Ref. 7).

MATERIALS AND METHODS

Acetanilide, from Sigma Chemicals (St. Louis), was dissolved in reagent-grade ethanol, filtered, and recrystallized. The crystals were then zone refined in a homemade oven. Two methods were employed for obtaining single crystals suitable for ir absorption experiments. A small amount of the zone-refined powder was sealed under 0.8 bar of CO_2 gas in a glass envelope which had a square cross section. The glass envelope was placed on one side on a hot plate set at 80°C . The powder sublimated and condensed on the top cold face, and long needles and flakes of ACN crystals were formed. The glass envelope

was then carefully opened and the flakes, of about $0.5\times 0.5\text{ cm}^2$, were removed and mounted in a holder made of aluminum foil. The crystal holder was clamped to a cell made from oxygen-free high-conductivity copper mounted on a closed-cycle helium refrigerator (Lake Shore Cryotronics, Inc., Columbus, Ohio) equipped with calcium fluoride windows. Single crystals were also grown by melting some ACN powder between two pressed Istran II or CaF_2 windows. Upon cooling, the material crystallized into several wedge-shaped single crystal fingers. The larger single crystal was selected by masking the rest of the material. Abbott and Elliott have shown that this procedure results in crystals preferentially grown along the c axis.⁸ Crystals obtained with this procedure were generally thinner than the crystal flakes, and they were more suitable for the study of the a -direction polarization. Instead, the absorption in the b direction was very weak. Partially deuterated samples were prepared by dissolving ACN in deuterated methyl alcohol and then recrystallized. The amount of water absorbed from the air during the crystallization process was generally sufficient to obtain a low H/D ratio. The deuterium content was estimated from the ratio of the N-D to the N-H stretching-band integrated absorption.

A Mattson 5000 (Cleveland, Ohio) Fourier transform infrared spectrometer equipped with a Perkin Elmer gold-grid polarizer was used for the measurement of the polarized spectra. At least 1000 scans at a resolution of 1.0 cm^{-1} were collected for each polarization direction. The polarizer was then turned 10° and a new spectrum was collected. The intensity of the bands were plotted versus the polarizer angle to determine the direction of the crystal axes with respect to the polarizer vertical.

FITTING PROCEDURE

In the spectral region from 1630 to 1680 cm^{-1} , four Lorentzian bands were fitted to the measured ir spec-

TABLE I. Four-band decomposition using a sum of Lorentzians. T is the temperature (K), A the amplitude (arbitrary units), C the center (cm^{-1}), and W the FWHM (cm^{-1}).

T	$A(1)$	$C(1)$	$W(1)$	$A(2)$	$C(2)$	$W(2)$	$A(3)$	$C(3)$	$W(3)$	$A(4)$	$C(4)$	$W(4)$
300	7	1645.0	5.5	11	1649.5	5.5	42	1661.1	5.5	40	1666.7	5.5
200	9	1645.0	4.5	26	1649.5	4.5	42	1661.1	4.5	43	1666.2	4.5
100	11	1644.5	3.2	67	1649.5	3.2	30	1661.8	3.2	47	1665.7	3.2
70	13	1644.5	3.1	77	1649.6	3.1	23	1661.9	3.0	49	1665.9	3.0
20	17	1644.5	3.0	89	1649.7	3.0	20	1661.9	2.4	54	1666.2	2.6

trum. A nonlinear least-squares analysis program, based on the Marquard algorithm,⁹ was used to minimize the function

$$\chi^2 = \frac{1}{(n - v - 1)} \times \sum_j \sum_i \left[\left(\frac{A_i v_j}{1 + (v_j - C_i/2W_i)^2} - D_j \right)^2 / \sigma_j^2 \right],$$

where j (1–50) corresponds to the number of data points used, v is the number of free parameters, the index i (1–4) corresponds to the four different Lorentzians, v is the frequency in wave numbers, and the D_j 's and σ_j are the digitized values of the spectrum and the error at each wave number in the region 1630–1680 cm^{-1} . To start the fitting routine, the initial values of the four center frequencies and the width of the bands were fixed at the values obtained by inspection of the low-temperature spectrum. Then the amplitudes only were fitted. Once a good fit for the amplitude was obtained, the band's center, amplitude, and width were simultaneously fitted. For temperatures higher than 70 K the width of the four bands was assumed to be the same in order to reduce the number of independent parameters. The effective number of parameters was 9 at each temperature. The values of the χ^2 were close to 1, except at 20 K, where the χ^2 was about 2 due to the presence of a small band near 1656 cm^{-1} not included in the fit.

RESULTS

Analysis of the amide I bands using Lorentzian components

An analysis of the 1665- and 1650- cm^{-1} bands in terms of superposition of Lorentzian components was performed on the same set of data already reported in Fig. 5 of Ref. 2. At least two components were necessary to describe the shape of the 1650- cm^{-1} band in the entire tem-

perature range investigated. The decomposition of the band centered at 1665 cm^{-1} required also at least two components, but at low temperature the deviation from the recovered shape using two components was quite high, and probably three components must be used (from Fig. 5 of Ref. 2 three components can be distinguished in the region 1655–1667 cm^{-1}). The result of the analysis at several different temperatures [center, amplitude, and full width at half maximum (FWHM) of each of the components] is reported in Table I. The position of the center of the bands did not change with temperature, whereas the width and intensity were temperature dependent. In calculating the area of the bands (Table II), as the product of the FWHM times the amplitude, we first recognized that the total integrated intensity, i.e., the sum of the areas of the four component bands, remained fairly constant in the temperature range from 20 to 300 K. The integrated intensity of the two Lorentzian components in which we decomposed each band had different temperature behavior. The component bands at 1665 cm^{-1} and at 1645 cm^{-1} had similar, but complementary temperature behavior and the total area change due to the sum of these two bands was about 10% of the total area over all the temperature range. Instead, the integrated intensity of the two components bands at 1661 and 1650 cm^{-1} had complementary behavior. The sum of their integrated intensity was constant in the temperature range from 300 to 20 K, but each of them had a strong temperature dependence (Fig. 1). The integrated intensity of each of these two subbands changed about fivefold from 20 to 300 K.

Partially deuterated samples

As we earlier reported,² fully deuterated samples display a different behavior with respect to the unusual temperature dependence of the polaron (or soliton) band at 1650 cm^{-1} . In the experiments reported here, we

TABLE II. Integrated intensities of the component bands.

Band	1	2	3	4	1 + 4	2 + 3	1 + 2 + 3 + 4
T (K)							
300	38.5	60.5	231.0	220.0	258.5	291.5	550.0
200	40.5	117.0	189.0	193.5	234.0	306.0	540.0
100	35.2	214.4	96.0	150.4	185.6	310.4	496.0
70	40.3	238.7	69.0	147.0	187.3	307.7	495.0
20	51.0	267.0	48.0	140.4	191.4	315.0	506.4

FIG. 1. Temperature behavior of the integrated intensity of the 1650- (○) and 1662-cm⁻¹ (●) bands and the sum (scale $\times \frac{1}{2}$) of the integrated intensities of the two bands (×).

prepared partially deuterated samples in which the ratio D/H was about 90%. Upon cooling, some spectral features characteristic of the undeuterated sample appeared in the amide I region. In the partially deuterated sample, we were able to distinguish four small bands at 1667, 1662, 1650, and 1645 cm⁻¹ (Fig. 2), in exact correspondence with the position of the components bands obtained by decomposing the spectrum of the non-deuterated polycrystalline sample using four Lorentzians.

Polarized ir spectra of single crystal of ACN

To further investigate the origin of the component bands in the amide I region, we performed a series of ir absorption experiments using polarized light with the aim of detecting whether there was a different polarization direction of the component bands. The polarization experiments have shown that there was a strong dependence of the band intensity upon the polarization direction, but we were unable to assign uniquely a different polarization direction to the component bands. Due to the sample preparation technique employed, only one crystal orientation was investigated, while in the microcrystalline samples used for the band analysis in terms of Lorentzian components, presumably all the crystal orientations were equally represented.

To determine the crystal orientation, we followed the Abbott and Elliott argument.⁸ A band at 1570 cm⁻¹, assigned to the C—N vibration mode, has a transition-moment direction along the *b* axis of the crystal. This band is 100% polarized in our samples, indicating that the crystal orientation has the *c* axis parallel to the direction of the incident radiation and the *b* axis at 0° with respect to the vertical direction of the polarizer.

The ir spectrum in the 1000–1800 cm⁻¹ region for polarization direction along the *a* axis and *b* axis is different. In the *a* direction, which roughly corresponds to the alignment along the hydrogen-bonded chain, all the ab-

FIG. 2. ir spectra of powder sample of partially deuterated ACN in the temperature range from 10 to 300 K.

sorption bands associated with amide vibrations have a large intensity. In contrast, the spectrum in the *b* direction shows weak absorption bands for the amide modes. The same characteristic features were observed in several different samples of different thickness and size.

Inspection of the amide I region from 1600 to 1700 cm⁻¹ (see Fig. 3) shows the characteristic absorptions of the amide I in ACN at 1665 and 1650 cm⁻¹. These bands are well resolved in the *b* direction. In the *a* direction, broader bands are observed centered at around 1665 and 1650 cm⁻¹ with FWHM on the order of 3 cm⁻¹ at 60 K. In the *b* direction a small red shift of about 1 cm⁻¹ was observed with respect to the *a* direction for the band at

FIG. 3. Polarized ir spectra of a single crystal of ACN in the amide I region at 10 K. *a*, direction of polarization; *b*, direction of polarization. The *c* axis was parallel to the radiation beam.

1667 cm^{-1} . The integrated intensity in the a -direction was much larger than in the b direction, in agreement with the room temperature experiments of Abbott and Elliott.⁸

DISCUSSION

In our previous work,² we tentatively assigned the component bands at 1665, 1662, and 1659 cm^{-1} (partially resolved in the low-temperature spectrum of Fig. 5 of Ref. 2) to the ir-active modes B_{2u} , B_{1u} , and B_{3u} , respectively. These modes should be polarized along the crystal's a , b , and c directions, respectively. We already cautioned² that this assignment was not supported by calculations based on dipole-dipole interactions.¹⁰ The polarization experiments reported here further point out the inadequacy of this explanation. The decomposition of the amide I region into four Lorentzian bands may be questionable. However, the low-temperature spectrum clearly shows a peak at 1667 cm^{-1} and two shoulders at 1662 and 1660 cm^{-1} . In this spectral region we used only two components. At high temperature, the bands are not resolved, and we arbitrarily impose, as a starting point for the fitting procedure, the existence of two bands of Lorentzian shape with the same center position as determined from the low-temperature spectrum. The fitting program then adjusted the position of the bands to give the best fit. In the region from 1650 to 1645 cm^{-1} , the low-temperature spectrum shows only one band which is clearly nonsymmetric. The use of a symmetric Lorentzian shape forced the fitting algorithm to include a band at 1645 cm^{-1} to account for the nonsymmetry of the spectral shape. However, due to the small contribution of this band (less than 10%) to the total intensity and due to the small temperature variation, we have not included this band in the discussion. On the basis of our band decomposition and single-crystal polarized spectra, we observe that the temperature dependence of the integrated area of the band at 1666 cm^{-1} shows a change between 300 and 100 K, but then levels off at lower temperature, while the band at 1661 cm^{-1} shows a much larger and continuous decrease of the integrated intensity as the temperature is lowered (Fig. 1). According to the present proposed explanation for the origin of the 1650- cm^{-1} band,² the intensity of these two subbands should have the same temperature dependence. The band analysis shows that this is not the case and a modification of the proposed model must be introduced for the under-

standing of the behavior of the ACN ir spectrum in the amide I region. One possibility that can qualitatively account for the existence of subbands is the existence of a double well structure, which arises from the nonplanarity of the amide group. Two equivalent positions for the N—H bond, corresponding to a deviation of about 0.1 rad from the planar geometry of the amide group, have been proposed by Fillaux and deLoze¹¹ to explain the fine structure of the soft-mode region shown in the Raman spectrum of *N*-methylacetamide. The asymmetry due to the double well potential could be the origin for the nonlinear coupling between the C=O vibration and the N—H bending, which was proposed to explain the amide I anomalous behavior. A Raman doublet at approximately 120 cm^{-1} was identified in the low-temperature spectrum of *N*-methylacetamide and assigned to the torsional mode along the C—N bond. Recently Fillaux suggested¹² that the nonharmonic potential in which the N—H proton is moving is responsible for the formation of the soliton at 1650 cm^{-1} , following Scott's argument.³

As a matter of fact, disregarding the weak and temperature-dependent 1645- cm^{-1} band, one could suppose that the normal amide I band in ACN is split into two components with absorption at 1662 and 1666 cm^{-1} , because of this double well.¹¹ This splitting can arise because of tunneling between the two wells, and only the component at 1662 cm^{-1} gives rise to the anomalous band at 1650 cm^{-1} . This interpretation is based on the sum law shown in Fig. 3 for the 1650- and 1661- cm^{-1} bands.

As a second possibility to account for the fine structure of the amide I bands in ACN, one can postulate that the band at 1650 cm^{-1} is due to a soliton which is stable at high temperature (an excited polaron state in the phonon field, visually a deformation of the trapped charge cloud). Then, still disregarding the weak band at 1645 cm^{-1} , the observed nearly constant intensity of the sum of the band at 1650 and 1662 cm^{-1} could arise from the competition of the two soliton energy levels during the ir absorption. This model requires a treatment of the temperature dependence of the soliton band(s) different from the one initially proposed by Scott *et al.*³

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¹G. Careri, U. Buontempo, F. Carta, E. Gratton, and A. C. Scott, *Phys. Rev. Lett.* **51**, 304 (1983).

²G. Careri, U. Buontempo, F. Galluzzi, A. C. Scott, E. Gratton, and E. Shyamsunder, *Phys. Rev. B* **30**, 4689 (1984).

³A. C. Scott, E. Gratton, E. Shyamsunder, and G. Careri, *Phys. Rev. B* **32**, 5551 (1985).

⁴J. C. Eilbeck, P. S. Lomdahl, and A. C. Scott, *Phys. Rev. B* **30**, 4703 (1984).

⁵D. M. Alexander, *Phys. Rev. Lett.* **54**, 138 (1985).

⁶S. Takeno, *Prog. Theor. Phys.* **75**, 1 (1986).

⁷D. M. Alexander and J. A. Krumhansl, *Phys. Rev. B* **33**, 7172

(1986).

⁸N. B. Abbott and A. Elliott, *Proc. R. Soc. London, Ser. A* **234**, 247 (1956).

⁹P. R. Bevington, in *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).

¹⁰Y. N. Chirgadze and N. A. Nevskaya, *Biopolymers* **15**, 607 (1976); *Dokl. Akad. Nauk SSSR* **208**, 447 (1973) [*Sov. Phys.—Dokl.* **18**, 80 (1973)].

¹¹F. Fillaux and M. deLozé, *J. Raman Spectrosc.* **7**, 224 (1978).

¹²F. Fillaux, in *Proceedings of the International Conference on Microphysics of Enzyme Catalysis*, edited by J. L. Houben and G. Salvetti, Pisa, 1987 (unpublished), p. 69.