Breathers or Structural Instability in Solid L-Alanine: a New IR and Inelastic Neutron Scattering Vibrational Spectroscopic Study

Mariette Barthes,* Aasmund Fahre Vik,[#] Alexandra Spire,[†] Heloisa N. Bordallo,[‡] and Juergen Eckert[§]

G.D.P.C., Université Montpellier II, 34095 Montpellier Cedex 5, France, L.P.M., Université Montpellier II, 34095 Montpellier Cedex 5, France, IPNS, Argonne National Laboratory, Argonne, Illinois 60439, LANSCE−12, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and Materials Research Laboratory, University of California, Santa Barbara, California 93106

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Incoherent Inelastic Neutron Scattering data and new infrared spectra were acquired in order to examine both the external and internal vibrations in crystalline L-alanine. For the first time we observe a splitting of the NH_3^+ torsional band below a temperature of approximately 220 K as well as an overtone of this band. The intensity of both of these bands is strongly dependent on temperature. Birefringence and depolarization measurements performed with single crystals reveal a subtle breaking of symmetry around 220 K perhaps involving the hydrogen bond networks. We show that this instability cannot, however, be the origin of the observed splitting. Instead, the anomalous temperature dependence of the observed intensity and frequency of the torsional mode and its overtone may be explained on the basis of a nonlinear coupling of the NH_3^+ oscillator with lattice phonons. This leads to localization of vibrational energy, a so-called “breather” or “vibrational polaron”.

Introduction

Amino acids are the building blocks for proteins and as such are of special interest in vibrational spectroscopy. In the crystalline state, they serve as models for the examination of a wide range of intermolecular interactions of importance in chemistry and biology.; for example, proton transfer, which is central to catalysis and many biochemical processes;[1] low frequency vibrations, which contain information on weak interactions taking place in enzyme reactions; supramolecular self-assembly and intracellular interactions.[2] Coupled motions of different oscillators are responsible for nonharmonic dynamics and for localization of vibrational energy. Such interactions can create coherent nonlinear structures such as solitons, vibrational polarons, breathers, i.e., intrinsic localized modes (ILM),[3] which can transport charge or energy in biomolecular processes. While the existence of such excitations in crystals has been widely predicted by theories, they are still somewhat controversial and have not yet received an unambiguous, direct experimental confirmation. Nonetheless, they remain the best actual explanation for a large body of anomalous spectroscopic observations in crystals with H-bonded molecular chains.[4,5]

L-Alanine is the smallest naturally occurring chiral amino acid. Our interest in this material stems from earlier observations of nonlinear behavior of two low-frequency Raman modes at 42 and 49 cm^{-1} [6] and continues our studies of ILM in acetanilide and *N*-methylacetamide. Non-harmonic properties of some amide modes have also been reported in two polyalanine compounds.[7] Our new spectroscopic investigation of L-alanine was also initiated as a first step in our program to study such short polypeptides. The properties of crystalline L-alanine have been the subject of extensive investigations. The crystal structure was determined to be orthorhombic (space group $P2_12_12_1$ or $D_2{}^4$) by X-ray diffraction at room temperature[8] and 23 K[9] and by neutron diffraction.[10] The vibrational dynamics have been studied by infrared spectroscopy,[11] Raman scattering,[12] CARS,[13] coherent[14] and incoherent[15] inelastic neutron scattering. Thermal conductivity measurements have been reported for the temperature range of 5−300 K.[16]

Apart from the anomalous intensity of two low-frequency Raman modes, some other unusual properties have been revealed by these investigations. In the crystal, the molecule is zwitterionic ($^+H_3N-C_2H_4COO^-$) and the nitrogen atom is coupled to three networks of intermolecular hydrogen bonds of unequal strength.[8−10] The reduction in volume of the crystal with decreasing temperature is associated with a decrease of two of the lattice parameters (a and b), while the third (c) shows a small increase.[9] This slight negative thermal expansion along the c-axis has been attributed to a coupling between molecular librations and acoustic modes. The measured sound velocity in the direction of the strongest chain of H bonds (along c) is about twice the calculated value.[14] The reported thermal conductivity exhibits low-temperature exponential behavior up to 250 K; the usual hyperbolic temperature dependence and subsequent constant regime is not observed. These results are indicative of strong anharmonic interactions and that part of the thermal conductivity is by optic phonons.[16]

The lifetimes of low-frequency vibrations (librons) have also been determined and found to be very long (>10 pS).[13] The energy of the infrared absorption band related to the torsion of the NH_3 group (485−500 cm^{-1}) was observed to have an unusual temperature dependence which was attributed to the breaking of one or two of the H-bonded networks.[12] The dynamics of the NH_3 group are strongly coupled to the three

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* To whom correspondence should be addressed. G.D.P.C., Universite Montpellier II.

[#] G.D.P.C., Université Montpillier II.

[†] IPNS, Argonne National Laboratory.

[‡] LANSCE-12, Los Alamos National Laboratory.

[§] Materials Research Laboratory, University of California.

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H-bonded networks with several interacting degrees of freedom, and may well behave as a non-linear or a chaotic oscillator. It is therefore a good candidate for the search of non-linear structures such as breathers or polarons.

In this paper we present a new study of the near and far IR spectra of mono- and polycrystalline pure L-alanine $H_3N-C_2H_4-COO$(Ala), on N-deuterated alanine $D_3N-C_2H_4-COO$(Ala-ND3), and $H_3N-C_2D_4-COO$(Ala-CD4) along with INS spectra collected on L-alanine and (Ala-CD4) between 5 K and room temperature, and give special attention to the dynamics of the NH_3 group.

We also performed two kinds of high-resolution birefringence (hereafter called "F" and "2F"[17]) measurements of an L-alanine single crystal, in order to check for the possible occurrence of some structural instability, and to determine the temperature dependence of the transmitted light intensity between crossed polarizers with directions of vibration parallel to the dielectric axes of the single crystal.

Experimental Section

L-Alanine (purity 99,9%) was purchased from Sigma Aldrich Company. Single crystals for the birefringence measurements were either prepared in our lab by evaporation of a water solution, or selected from the small as-grown Aldrich single crystals. Their orientation was determined by X-ray diffraction. Ala-ND_3 used in the IR measurements was also prepared in our lab. The C-deuterated samples (Ala-CD4) used in both INS and IR experiments, were obtained from CDN Isotopes (Interchim).

IR measurements were performed on Bruker IFS-113V and Perkin-Elmer-"Spectrum", spectrometers, both with a resolution of 0.5 cm^{-1}. The samples were cooled to 5 K using an optical Air Liquide circulation cryostat and the temperature was stabilized within one degree for each spectrum collection. The INS data were collected on the FDS time-of-flight spectrometer at the Los Alamos Neutron Science Center (LANSCE), between 300 K and 12 K using a closed-cycle He refrigerator. The energy resolution was approximately 3% of the transferred energy. The FDS spectra were obtained by numerical deconvolution of the instrumental function from the raw data. INS intensity and force field calculations were carried out using the program CLIMAX,[18] which reproduces the INS spectrum of molecular vibrations.

The vibrational frequencies and the atomic displacements are obtained from a normal coordinate analysis using the Wilson-GF method.[19] Intensities of overtones and combinations modes can then be calculated from the fundamentals. The intensity (I) for the i-th mode is obtained from the tensor B_i (representing the mean-square displacement of the scattering atom in the i-th mode)

$$I \propto J_n(QQ{:}B_i)e^{(-QQ{:}A)}$$

where $J_n(x)$ is the n-th order Bessel function (n = 1 for the fundamental, 2 for the first overtone, etc.), Q is the momentum transfer, and $A = \sum B_i$. The structural parameters used in the generation of the G matrix are those given by Destro et al.[9]

Birefringence measurements were performed on a device built in our lab[22] using an electrooptic modulator[17] excited by an AC-voltage at frequency "F",[20] and a Babinet - Soleil compensator.[21] We recall here that the linear birefringence Δn (= ($n_c - n_a$)) of a single crystal of thickness e, is related to the variation of the elastic energy (or of the integral of the specific heat) released when a structural instability occurs. This quantity is sensitive probe of very small lattice distortions that occur over a small range of temperatures, and has been used, for example, to study magnetic or structural phase transitions and associated critical phenomena.[21]

The phase shift per unit path length due to the birefringence of the sample is:

$$\Psi = 2\Pi\Delta n/\lambda$$

The phase shift created by the electrooptic modulator is given by

$$\phi = \phi_{\mathrm{mod}} \sin(2\Pi Ft)$$

With our apparatus the light flux (I_L) coming on the photomultiplier has the following form:

$$I_L = I_0[A + B\sin\Psi \times \sin(2\Pi Ft) + C\sin(2\epsilon) \times \cos\Psi \times \sin(4\Pi Ft)] \quad (1)$$

A, B, and C are factors independent of ψ and ϕ. The second term of the sum gives the contribution to the signal detected at the frequency "F", and is proportional to sin ψ. ψ is kept near zero with the compensator, so that $\sin\psi \approx \Psi$. This term is then directly proportional to the birefringence of the alanine crystal, and hence to its temperature dependence. ϵ is the angle between one orthorhombic crystallographic axis and the direction of the incident light polarization. ϵ is carefully adjusted to zero in the beginning of the experiment so that the third term in equation (1) cancels. In this case there is no detectable signal at frequency "2F".

Results

L-Alanine crystallizes in space group $P2_12_12_1$ with four molecules per unit cell. The precise localization of hydrogen atoms was given in a neutron diffraction study,[10] while X-ray diffraction investigations[8,9] have confirmed that the space group is the same at 23 K and 298 K. With four molecules in the unit cell, we find for the molecular vibrations 153 optical modes: 39 a + 38 b_1 + 38 b_2 + 38 b_3 of which 132 are internal vibrations and 21 lattice modes (6 a + 5 b_1 + 5 b_2 + 5 b_3). Phonons with b symmetry are both IR and Raman active. Normal coordinate analyses have been carried out with different force fields to assign the optical[12] and INS spectra.[15] The factor group splittings have been calculated for the main internal modes, and compared with the spectra.[12]

Inelastic Neutron Scattering. The INS spectra of Ala and Ala-CD4 at different temperatures are presented in figures 1 to 3. The experimental spectra were fitted with the program CLIMAX[18] using a normal coordinate analysis with force constants as variables in such a way that both the calculated frequencies and intensities reproduce the observed spectra.

The molecular vibrations can be described by 38 internal coordinates, which are associated with force constants by means of a constraint matrix. The force constants are defined in terms of locally symmetric groups (CO_2^-, NH_3^+, and CH_3), and in terms of bond stretching and bond-angle bending coordinates for the central core. Initial values of diagonal force constants were taken from the work of Susi and Byler.[12] The observed and calculated INS spectra at 12 K were previously shown[15] and are not reproduced here. A table with the 22 diagonal and 13 interaction force constants, which provided a satisfactory fit of both the intensities and frequencies, is given in the Supporting Information.

TABLE 1: Vibrational Bands (cm^{-1}) and Approximate Assignments for $CH_3CH(NH_3^+)CO_2$

IR	INS	Raman (12)	Calc	PED[a]	approximate description
3090		3080	3105	1(99)	$\nu(\bullet NH_3^+)$
3053		3060	3048	1(99)	$\nu(NH_3^+)$
3034					
3018					
		3003	3002	5(99)	$\nu(CH_3)$
2991		2993	2978	5(95), 9(23)	$\nu(\bullet CH_3^+)$
2966		2962	2959	9(75), 5(24)	$\nu(\bullet C_2{-}H)$
2943		2949	2949	1(99)	$\nu(NH_3^+)$
2884					$\nu(\bullet CH_3)$
		2839	2848	5(100)	$\nu(\bullet CH_3)$
					region of overtones, Fermi resonances and combination bands. More than 20 IR active bands observed
	1760				
	1720				
1660					
1630	1635	1645	1698	12(42)	$\nu(C{-}O)$
1580	1580				
1608	1610	1625	1640	3(39), 2(38)	$\delta(NH_3^+)$, $\rho(NH_3^+)$
1594		1588	1593	2(37), 3(18)	$\delta(NH_3^+)$
1460		1498	1520	6(41), 7(40)	$\delta(CH_3)$, $\rho(CH_3)$
		1459	1477	2(31), 7(18), 6(17)	
1519	1460	1459	1433	2(59), 3(20)	$\delta(NH_3^+)$
1510					
1415	1410	1410	1389	6(24), 10(16)	
1380	1365	1375	1347	6(22)	
1368	1340	1351	1339	6(38), 7(23)	$\delta(\bullet CH_3)$
1312					
		1301	1302	3(19); 10(16)	
	1220	1220	1230	12(13)	
1243	1260				$\rho(NH_3^+)$
1162	1140	1145	1154	3(43), 7(26), 10(15)	$\rho(NH_3^+)$
1120	1110	1110	1103	7(24), 10(19)	
1023	1000	1001	1000	10(27), 7(25), 3(15)	
1017					
972					overtone of $\tau(\bullet NH_3^+)$
	950	964	963	17(26), 3(15)	
921	910	922	918	19(19), 7(18),	
853	820	850	867	12(27), 19(18)	
770	760	775	777	15(63)	γ (CO_2^-)
648	640	653	658		
545	510	527	526	20(19), 14(18), 19(16)	
500	485	480	479	4(62)	$\tau(NH_3^+)$
495					
416	395	404	401	20(26), 14,18(16),	
407					
346	330	325	325	22(48), 15(18)	$\delta(C_1{-}C_2{-}C_3)$
326					
295	300	300	298	21(37)	$\delta(N{-}C_2{-}C_1)$
285					
277		264	265	8(84)	$\tau(CH_3)$
258					
235					
211					
185		192	192	16(93)	$t(CO_2^-)$
	165	165			H-bond stretch
157	154	154			H-bond stretch
143	143	140			H-bond stretch
125		125			
117	116	117			
109	107				
98	95	100			
92					
87	82	85			
74	65	75			librons
		48			
		42			

[a] PEDs were obtained by a normal coordinate analysis.[15] Force constants are given in the Supporting Information. The first number designates the force constant, the second number (in parentheses), its % PED.

TABLE 2: Vibrational Bands (cm^{-1}) and Approximate Assignments for $CD_3CD(NH_3^+)CO_2$

IR	INS	Raman (12)	Calc	PED[a]	approximate description
3142		3120	3145	1(99)	$\nu(\bullet NH_3^+)$
3100		3082	3082	1(99)	$\nu(NH_3^+)$
3080					
3060					
3013		3001	2980	1(100)	$\nu(\bullet NH_3^+)$
2997					region of overtones and combination bands
2977					
2245		2256	2282	5(95)	$\nu(CD_3)$
2237		2245	2251	5(56)	$\nu(CD_3)$
2203		2194	2195	9(60), 5(40)	$\nu(C_2\text{-}D)$
2186					
2049		2050	2035	5(98)	$\nu(CD_3)$
	1750				
1653	1720	1651	1699	12(35)	$\nu(C{-}O)$
1583					
1619	1600	1645	1674	2(54), 3(27)	$\delta(NH_3^+)$
1601	1580	1592	1626	2(33), 12(21)	
1509	1470	1495	1486	2(71)	$\delta(NH_3^+)$
1409	1380	1402	1397	10(25), 2(21), 3(18)	
	1330				
1272	1240	1263	1285	7(25), 17(20)	
1219	1200	1202	1232	6(25); 3(15), 17(12)	
	1170				
1146	1130	1142	1173	7(35), 3(15)	$\rho(CD_3)$
1095	1100	1071	1101	7(31); 6(23)	$\rho(CD_3)$
1068	1060	1053	1084		
1055		1052	1057		
1048					
1036	1025	1019	1014	3(21), 10(17), 6(16)	
1032					
	1000				
970					overtone of $\tau(NH_3^+)$ mode
949	970	945	960	6(36), 12(25)	$\delta(CD_3)$
	945				
906		894	911	3(18), 12(16)	
899					
886					
883					
	865				
821		823	846	10(19), 6(17)	
	815	816	829	6(28), 7(26)	
	795				
745	770	747	745	15(57)	$\gamma(C{-}O)$
	740				
690	715	698	695	19(26), 23(28)	
612	600	630	647	14(19), 18(14)	
530		500	498	19(19), 23(15), 4(16)	
	485				
493		476	476	4(48)	$\tau(NH_3^+)$
386	365	374	376	20(55), 14(15),	$\delta(N{-}C_2{-}C_3)$
315	310	305	307	21(26)	
307					
295					
261	250	261	261	22(44), 21(28)	$\delta(C_1{-}C_2{-}C_3)$
258					
	205				
	192	190	190	16(90)	$\tau(CO_2^-)$
	160	155	156	8(95)	$\tau(CD_3)$
	145				
	138				
	116				
	107				
	100				
	82				
	65				

[a] PEDs were obtained by a normal coordinate analysis.[15] Force constants are given in the Supporting Information. The first number designates the force constant, the second number (in parentheses), its % PED.

The calculated and observed fundamental frequencies for Ala and Ala-CD4 are given in Tables 1 and 2, respectively, along with the potential energy distributions (PED) and group frequency assignments. Generally only contributions to the PED greater than 15% are included, and a group frequency description

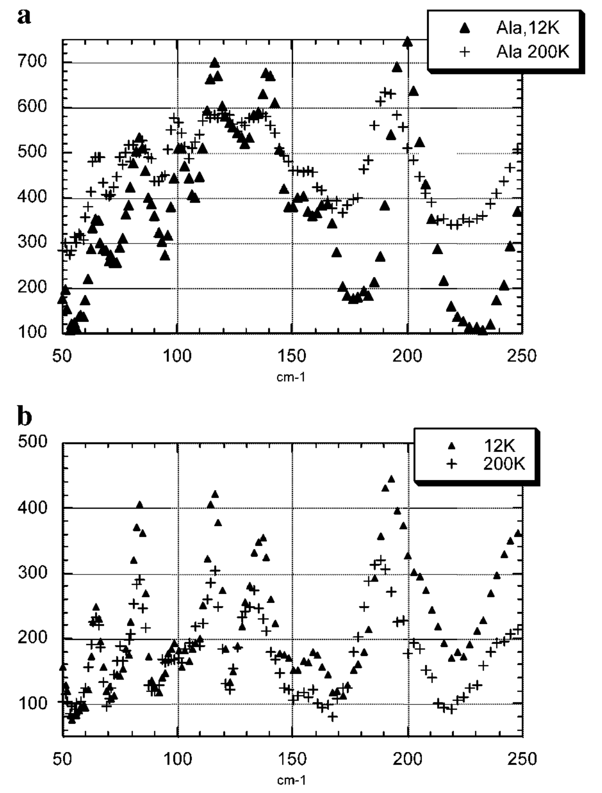

Figure 1. INS spectra (50−250 cm^{-1}) of: a) L-Alanine ; b) L-Alanine -CD4 at 12 K (filled triangle) and 200 K (cross).

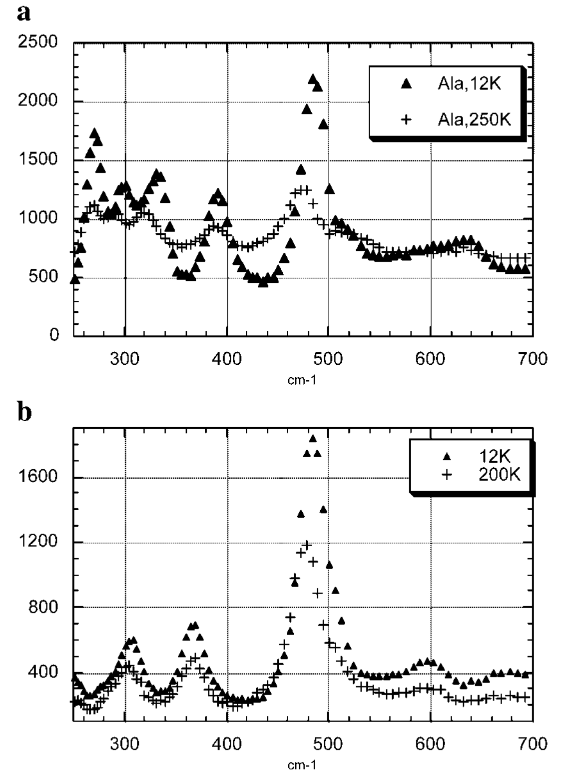

Figure 2. INS spectra (250−700 cm^{-1}) of: a) L-Alanine ; b) L-Alanine -CD4 at 12 K (filled triangle) and 200 K (cross).

is given only if it has a PED contribution is over 35%. Despite the asymmetry of the molecule, a certain number of fundamental frequencies may be described approximately as group vibrations.

Strong peaks are observed at ≈ 50, 65, 82, 100 cm^{-1} in the low-frequency range of the INS spectra (Figure 1), and these are assigned to phonons and librons, while bands at ≈ 118 and 140 cm^{-1} exhibit larger broadening and a decrease in intensity with increasing temperature. Previous analyses[11,12] suggest mainly H bond stretching contributions mixed with the CO_2 torsion for the mode at ≈ 140 cm^{-1}. This is also in agreement with our observation in the far IR of a stronger temperature dependence of the position of these peaks when compared to that of the lattice modes below 100 cm^{-1}. The temperature dependence of the peaks at ≈155 and ≈165 cm^{-1} is less pronounced although they were also assigned to H bond stretching.

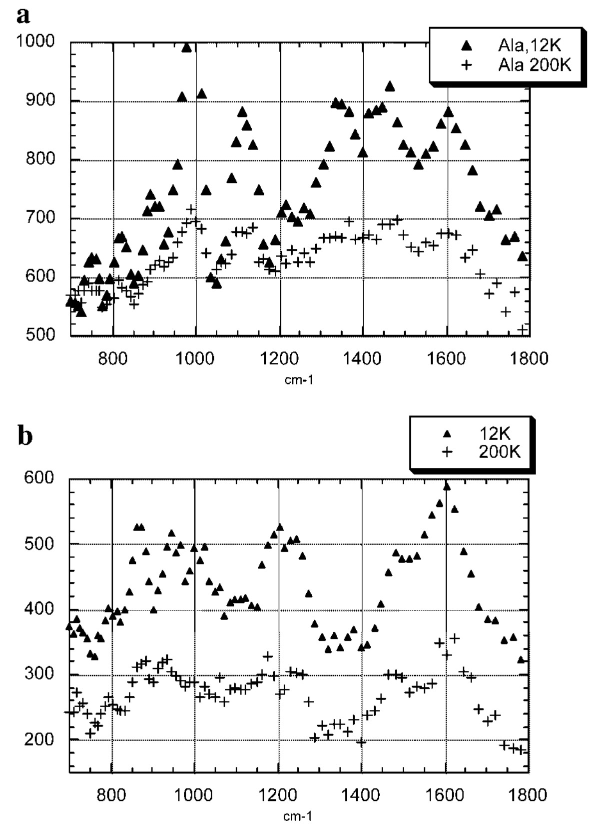

Figure 3. INS spectra (700−1800 cm^{-1}) of: a) L-Alanine ; b) L-Alanine -CD4 at 12 K (filled triangle) and 200 K (cross).

The intense peaks at 275 and 325 cm^{-1} are absent in the spectra of Ala-CD4 and can therefore be clearly assigned as CH_3 torsions. This is in agreement with the IR study of Bandekar et al.[11] as well as our far IR data, but not with the earlier Raman scattering study.[12] We also find that the large factor group splitting (≈ 116 cm^{-1}) calculated for the CH_3 torsions[12] was overestimated as the observed splitting is approximately 50 cm^{-1}.

The band at about 305 cm^{-1} in INS spectra of Ala and Ala-CD4 shows weak temperature dependence, and is also observed in IR spectra of Ala and Ala-ND3 near 320 cm^{-1}. It may therefore be assigned to a skeletal deformation. This peak has not been observed in Raman spectra,[11] even though it is formally Raman-active. The NH_3 torsion at 480 cm^{-1} is the most intense band in the INS spectrum, and its peak position is strongly temperature dependent (Figure 4). The energy resolution is, however, insufficient to observe any splitting in this band.

Peaks at 650, 1160, 1340, and 1410 cm^{-1} are absent in spectra of the Ala-CD4 compound. They are assigned to bending and deformation modes of the methyne and methyl groups, in agreement with our IR spectra, while the broad band around 1600 cm^{-1} contains the $\delta(NH_3)$ vibrations in agreement with the IR data.

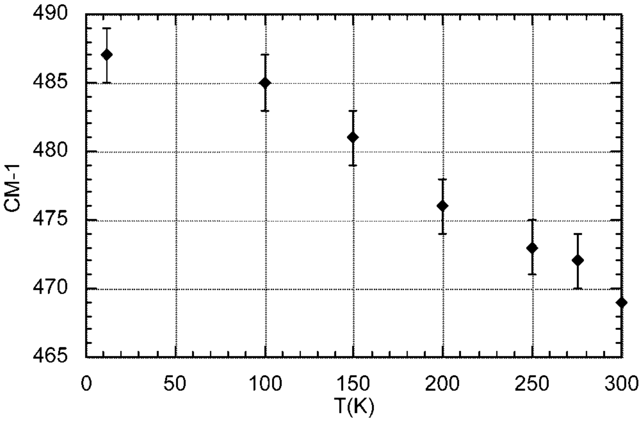

Figure 4. Frequency of the torsional mode of the NH_3^+-group versus temperature.

Infrared Absorption. A representative set of the large number of IR spectra of L-alanine and Ala-ND3 collected at various temperatures is shown in Figures 5 to 7. The frequency of the main absorption peaks are reported in Tables 1 and 3, respectively. The somewhat more limited data for Ala-CD4 are listed in Table 2.

L-***Alanine*****.** Because of the low symmetry of the alanine zwitterion, and in some cases, large factor group splittings,[12] the number of observable vibrational modes (from above 3000 cm^{-1} to low-frequency optical phonons around 74 cm^{-1}) is rather large. Quasiharmonic internal vibrations of the zwitterion tend to show only small shifts of frequency with temperature, i.e., a. fractional frequency shift ($\Delta\nu/\Delta T$ divided by the low-temperature frequency of the band) of about 10^{-4} K^{-1} for internal modes. Fractional frequency shifts for external modes are generally larger, since the effect of temperature on the crystal structure is expected to be greater than on the molecular geometry. For most of the lattice modes, the peak frequency changes by less than 5 cm^{-1} over the whole temperature range. Vibrations involving stretching of the hydrogen bonds show an increase in frequency of about 10 cm^{-1} upon cooling to 10 K, which corresponds to a fractional increase of about 4×10^{-4} K^{-1}.

A few bands with anomalous temperature dependence were observed at about 340, 490 (NH_3^+-torsional mode), and 950 cm^{-1} (possible overtone of the mode at 490 cm^{-1}?) and they all show a marked increase in both frequency and intensity (generally larger than 20%) upon cooling. The mode at 490 cm^{-1} appears to split at around 220 K, and its width also shows unusual temperature dependence.

N-Deuterated L-*Alanine* . The central issue of the present IR study is the nature of the NH_3^+-torsional mode, its possible overtones, as well as coupling with other vibrations. It is for this reason that we collected complete data sets of the IR spectra of Ala-ND3 for reference. The NH_3^+-torsional mode near 490 cm^{-1} is indeed absent in this compound, we observe instead the ND_3^+-torsion at 352 cm^{-1} (at 10 K). This band also exhibits an anomalous increase of intensity upon cooling. The overtone of this mode is not readily identified, but could be in the form of a weak shoulder appearing at about 640 cm^{-1}. The band at 345 cm^{-1} (at 10 K) has been assigned to a C_1–C_2–C_3 skeletal deformation[12] and indeed is present in normal and N-deuterated L-alanine. The INS spectra (Figure 2) show that it contains considerable motions of the methyl protons because of it is not observed in C-deuterated L-alanine but is strong in Ala.

C-Deuterated L*-Alanine*. The anomalous band at ≈ 950 cm^{-1} is also observed to have a strong temperature-dependent intensity in this isotopomer.

TABLE 3: Vibrational Bands (cm^{-1}) and Approximate Assignments for $CH_3CH(ND_3)CO_2$

IR	Raman (12)	approximate description [12]
2998	3003	$\nu_a(CH_3)$
2989	2990	$\nu_a(CH_3)$
2985		
2969	2972	$\nu(CH)$
	2917	$\nu_s(CH_3)$
2340	2293	
2310		
2274		
2225		
	2160	$\nu_s(ND_3^+)$
		region of overtones and combination bands
1623	1591	$\nu(C-O)$
1589		
1459	1461	$\delta_a(CH_3)$
1416	1407	
1374	1376	$\delta(CH_3)$; $\delta(CH)$
1350	1355	$\delta(CH_3)$; $\delta(CH)$
1297	1299	
1196	1189	$\delta_a(ND_3^+)$
1184	1182	$\delta_a(ND_3^+)$
1160	1159	
1142	1148	$\delta_s(ND_3^+)$
1104	1098	
1059	1057	
919	916	$\rho_{\|\|}(CH_3)$
902		
884	874	$\rho_{\wedge}(CH3)$
864	863	$\rho_{\|\|}(ND_3^+)$
828	825	$\rho_{\wedge}$ (ND_3^+)
769	771	$\gamma(C-O)$
620	621	
523	514	$\rho(C-O)$
393	377	$\delta(N-C_2-C_3)$
386		
379		
352	335	τ (ND_3^+)
345		$\delta(C_1-C_2-C_3)$
277	273	
268		
251	258	$\delta(N-C_2-C_1)$
311	211	$\tau(CH_3)$
283		
227		
203		
183	184	$\tau(CO_2^-)$
155		H (D) − bond stretch
142		H (D) − bond stretch
137		
131		
122		
116		
108		
86		
73		

Assignments of IR Vibrations. As our assignments are in general accord with previous work,[11,12,13] we highlight primarily those results that pertain to the question addressed in this paper, as well as a few differing assignments obtained by inclusion of INS spectra. Symmetric (3090 cm^{-1}) and antisymmetric (3018, 3034, and 3053 cm^{-1}) NH_3^+ stretching are identified in L-Ala and in the region between 2200 and 2400 cm^{-1} for Ala-ND3. The N-deuterated sample readily reveals the $\nu(CH)$ modes at 2969, 2985, 2989, and 2998 cm^{-1}. Two such bands are also observed in Ala at 2966 and 2991 cm^{-1}.

A broad band at 3111 cm^{-1} with a strong increase in intensity upon cooling is only present in L-Ala, and not in Ala-ND3 or Ala-CD4, which may be attributable to a combination involving

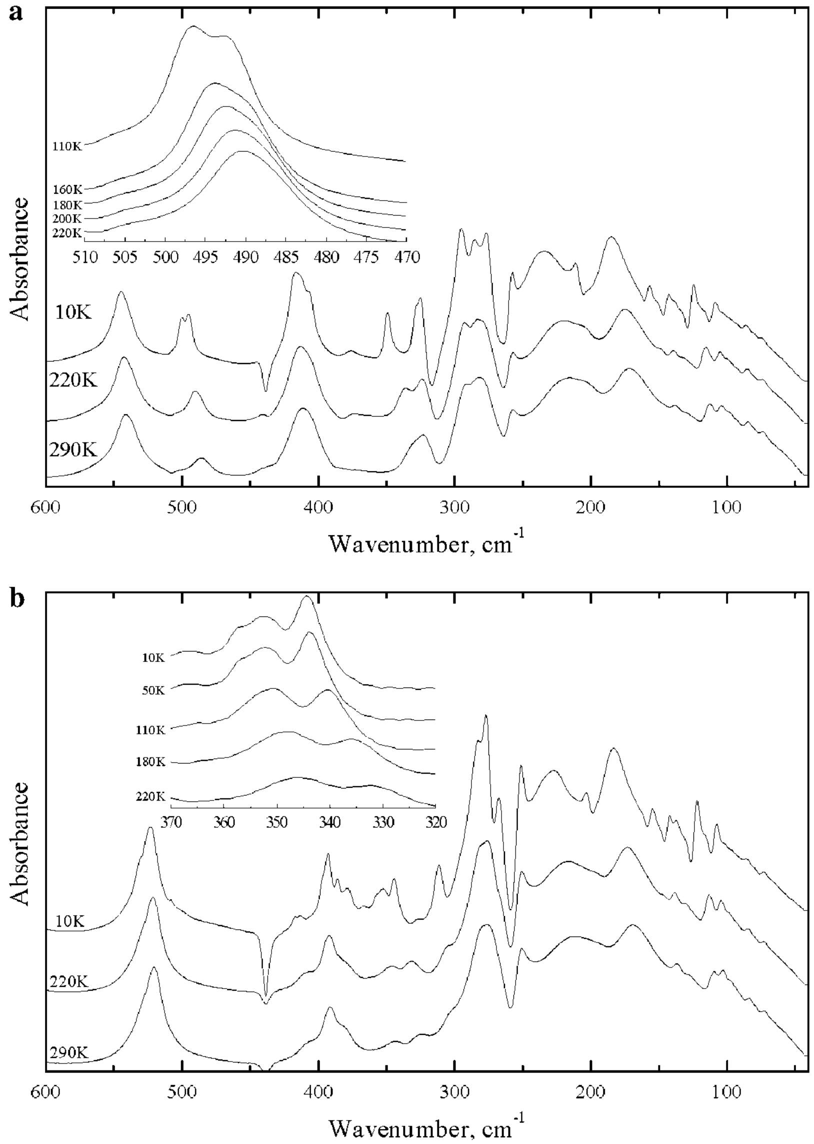

Figure 5. a: IR spectra of polycrystalline L-alanine at different temperatures. A few artifacts are present because of somewhat poor background compensation. A KBr matrix was used for these measurements, and its low transmission in this region results in seemingly negative absorptions at 438 and 511 cm^{-1}. The inset shows the evolution of the NH_3^+-torsional mode versus temperature. **b:** IR spectra of polycrystalline N-deuterated L-alanine at different temperatures. A few artifacts are present because of somewhat poor background compensation. A KBr matrix was used for these measurements, and its low transmission in this region results in seemingly negative absorptions at 438 and 511 cm^{-1}. The inset shows the evolution of the ND_3^+-torsional mode versus temperature.

some “N−H” and “C−H” modes. While we did not observe any decrease of frequency on cooling in the group of bands around 3000 cm^{-1}, as is usually observed for the N−H stretch in Amide systems, we did so for several of the bands in the range 2500 to 2900 cm^{-1}. These may be due to overlapping overtones and combination bands as suggested by Byler and Susi.[12]

The methyl torsions should be assigned at 285 and 335 cm^{-1}, instead of ≈ 200 and ≈ 390 cm^{-1},[12] as a reference to the INS spectra makes apparent. It is also clear from the strong intensity of the respective INS bands in both Ala and Ala-CD4 that the CO_2^- torsion assigned at around 190 cm^{-1} involves strong coupling with the ammonium protons.

The peaks at 124 and 157 cm^{-1} (at 10 K) show shifts of about 10 cm^{-1} from 290 to 10 K (i.e. a fractional frequency shift: $(3-4) \times 10^{-4}$ K^{-1}). These are assigned to H-bonded strains and may be observed in the INS spectra at ≈ 118 and ≈ 155 cm^{-1}, respectively. The corresponding bands at 122 and 150 cm^{-1} of Ala-ND3 have similar temperature behavior. The band at ≈ 144 cm^{-1} has a smaller shift with temperature, and has been assigned to a mixing of H-bond stretching and CO_2^- torsion.[11] The third band at 165 cm^{-1} (INS) is possibly hidden by the broad absorption band at 185 cm^{-1} (L-Ala) and 183 cm^{-1} (Ala-ND3) in the IR spectra. For comparison, the two lattice modes at 75 and 87 cm^{-1} (73 and 86 cm^{-1} in L-Ala-ND3) show only minor shifts in frequency (less than 10^{-4} K^{-1}) on cooling, i.e., smaller than that of the mode at 109 cm^{-1} ($\approx (1-2) \times 10^{-4}$ K^{-1}).

Strongly Anharmonic Bands. The above-mentioned anomalous temperature dependence of certain bands (large changes in integrated intensity of more than 20% and/or frequency (more than 10 cm^{-1})) may be viewed as a sign of anharmonic behavior. As it is often is difficult to establish a baseline for the bands, and hence obtain a reliable value for the integrated intensity, we do not consider those bands with an intensity change ion of less than 20% variations to show evidence for nonlinearity. Figure 8 shows the frequencies of the NH_3^+ torsions (495 and 500 cm^{-1} at 10 K) as a function of temperature obtained in

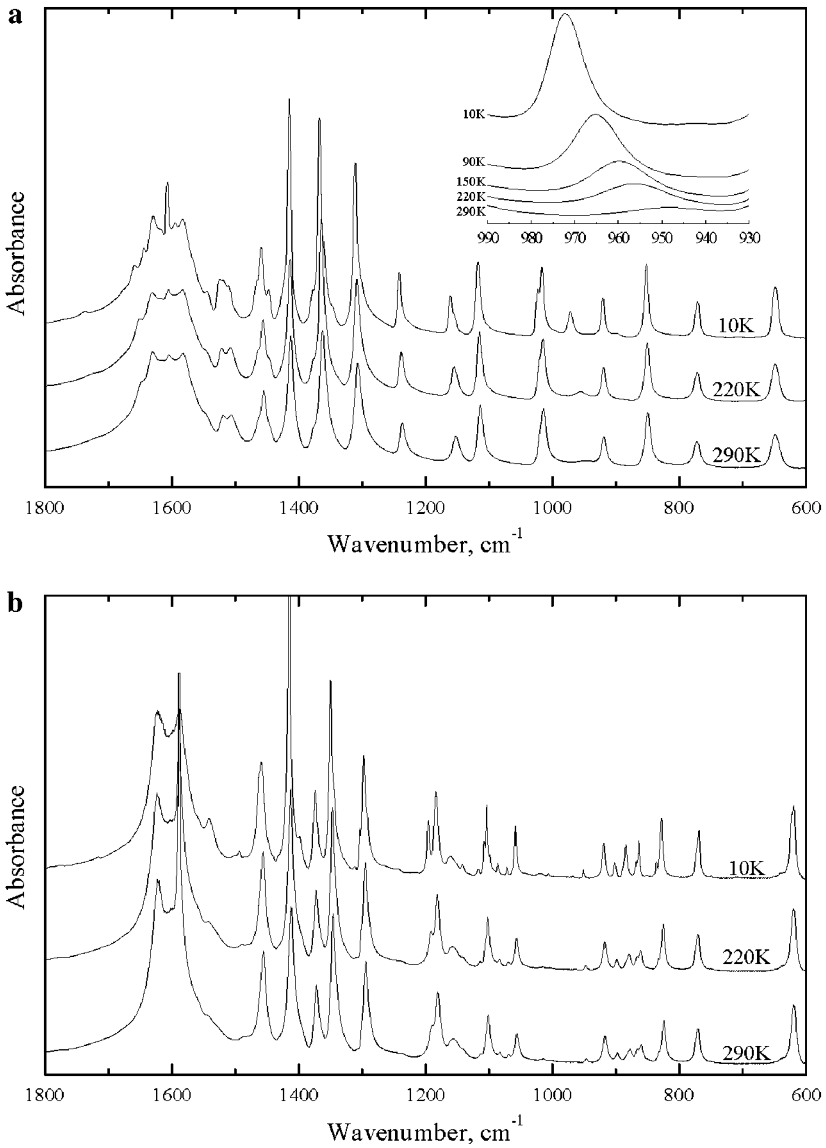

Figure 6. a: IR spectra in polycrystalline L-alanine at different temperatures. The inset shows the evolution of the overtone (of the NH_3^+-torsional mode) versus temperature. **b:** IR spectra in polycrystalline N-deuterated L-alanine at different temperatures.

two different sets of experiments. Only one broad peak is observed at room temperature, but a sideband appears when cooling below 200 K as is shown in the inset in Figure 5a. The band shifts by 14 cm^{-1} from about 486 cm^{-1} at 290 K to 500 cm^{-1} at 10 K. A sideband appears at 488 cm^{-1} (note the large standard deviation in this value due to the low intensity of the band) at a temperature of about 200 K and shifts to 495 cm^{-1} at 10 K. The splitting of these two peaks (some 3−5 cm^{-1}) seems to increase slightly upon cooling. Our spectra do not allow us to determine unambiguously if the latter is a new band that appears below 200 K, or if the splitting between two components increases at this temperature. This splitting has not been observed in previous studies. The full-width-at-half-maximum (fwhm) of the peak at 500 cm^{-1} is shown in Figure 9 as a function of temperature. The band is narrow at 10 K and increases very slightly in width up to about 230 K, at which point the mode begins to broaden appreciably. This result is similar to that reported by Wang and Storms.[12]

Figure 10 shows the integrated intensities (normalized to their values at 10 K) of the torsional NH_3^+ mode and of the band at 972 cm^{-1} as a function of temperature. The latter band is observed for the first time in Ala and cannot be assigned to the methyl rock since it is absent in Ala-ND_3. It must therefore be attributed to motion of the NH_3^+ group, and indeed is also found in the spectrum of Ala-CD4. Its intensity (Figure 10), increases strongly with decreasing temperature which is accompanied by a frequency shift of 24 cm^{-1} (Figure 11). This shift is about twice that of either of the two bands of the NH_3^+ torsion, and may therefore be an indication that this band is to be assigned to the first overtone of $\tau(NH_3^+)$, and reflects the non-linear character of this mode in analogy with the observed overtones of the “polaron” band in ACN.[23] The width of this likely overtone shows (Figure 9) a marked difference to that of τ-(NH_3^+) itself as it rises linearly with temperature above 100 K.

The ND_3^+ torsion may be assigned at 352 cm^{-1} (10 K) in Ala-ND_3 as this band is absent in the spectrum of Ala. It shows less of a frequency shift with temperature than $\tau(NH_3^+)$, i.e., to 344 cm^{-1} at 270 K, while its intensity is difficult to measure because it overlaps with a band at 345 cm^{-1}. A shoulder that appears on cooling at 358 cm^{-1} may well be of a similar origin as that for the NH_3^+ torsion. The band at 345 cm−1 in Ala-ND3, or 349 cm^{-1} in Ala, and may be attributed to the skeletal C_1–C_2–C_3 deformation mixed with the methyl torsion. This band

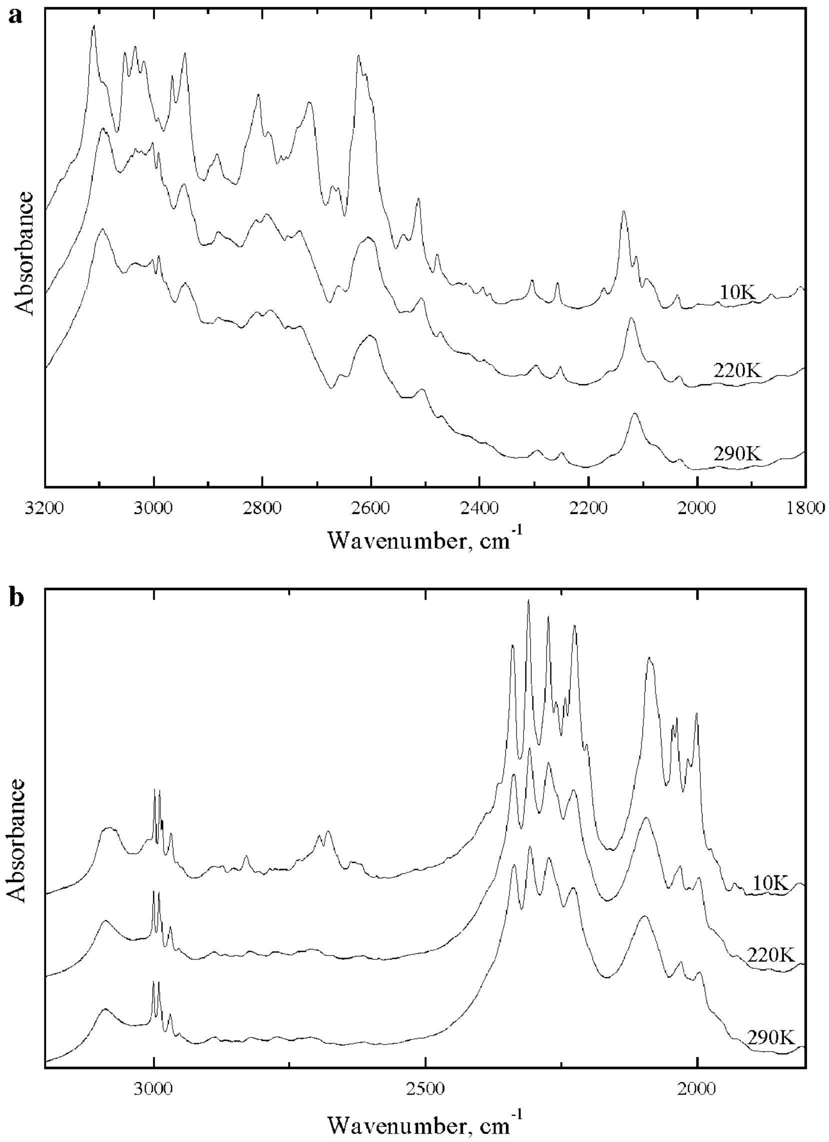

Figure 7. a: IR spectra in polycrystalline L-alanine at different temperatures. **b:** IR spectra in polycrystalline N-deuterated L-alanine at different temperatures.

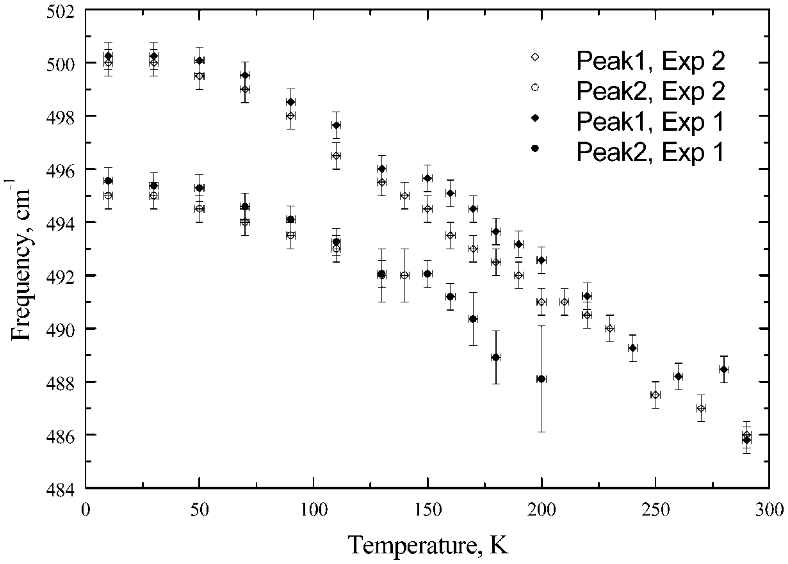

Figure 8. Peak frequencies of the torsional NH_3^+ doublet as a function of temperature.

also shows a significant increase of intensity and a frequency shift of about 16 cm^{-1} on cooling from 290 to 10 K.

Birefringence "F" and "2F". The anomalous behavior of the NH_3^+-torsion, as well as the nonclassical temperature

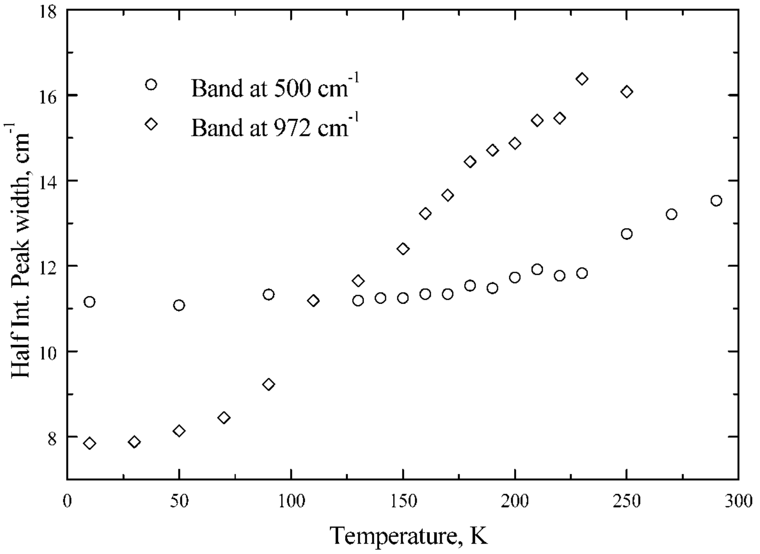

Figure 9. fwhm of the NH_3^+ torsion and its possible first overtone as a function of temperature.

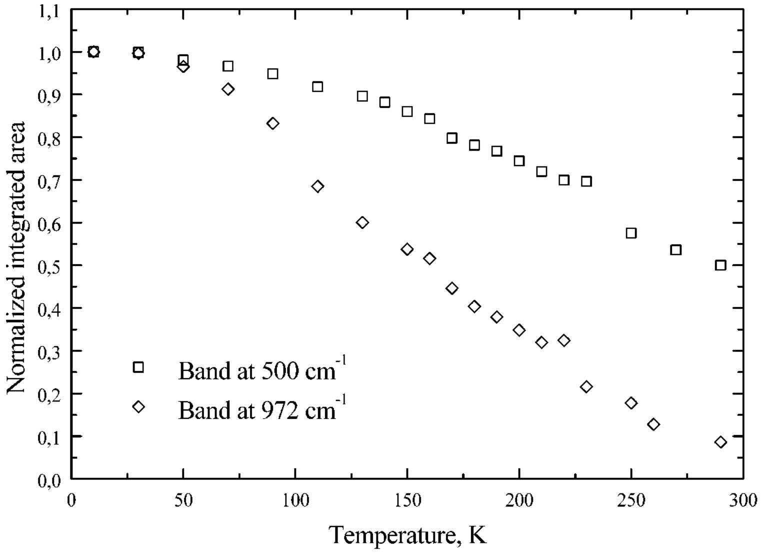

Figure 10. Normalized integrated intensity of the NH_3^+ torsion and its possible first overtone as a function of temperature.

dependence of the low-frequency Raman modes[6] might suggest that a structural instability occurs around 200 K, even though X-ray and neutron diffraction data do not give any such evidence. Nonetheless, we undertook birefringence measurements to look into such a possibility.

The birefringence $\Delta n = (n_c - n_a)$, in the (a, c) plane (detected at the frequency "F" of the electrooptics modulator) is shown in Figure 12. The signal has a monotonic variation with the temperature, and could be fitted with a Debye model which predicts a linear behavior in this temperature range ($T \geq \theta_D$). No discontinuity is observed at any temperature, which could have indicated a structural instability. This is in agreement with all previous crystallographic studies, and confirms that there is no structural phase transition at around 220 K.

The transmitted light intensity detected at the frequency "2F" (Figure 13), which is zero at room temperature, does however increase significantly below 250 K. To rule out any possible parasitic effects from birefringence of the cryostat windows, or small changes in orientation of the sample holder upon cooling, the measurements were repeated in the same manner, first without any sample, and then with a reference orthorhombic single crystal (acetanilide) known to undergo no structural change. No "2F" signal was observed either case.

The existence of a transmitted light intensity at the frequency "2F", below 250 K, requires that:

$$I(2F) = I^0 C \sin(2\epsilon) \times \cos(\Psi) \times \sin(4\Pi F t) \neq 0$$

This indicates that the angle ϵ is no longer equal to zero (although still very small), i.e., that a very slight distortion in the crystallographic axes occurs in this range of temperatures. Such effect was previously observed in the incommensurate system $BaMnF_4$ by "2F" birefringence, and later confirmed by γ-ray diffraction.[24] It is conceivable that the thermal contraction of the crystal structure could result in a very slight monoclinic distortion (with an angle $90° - \epsilon \approx 90°$) with two types of domains because of the unequal strength of the three types of intermolecular H bonds. To confirm the appearance of a nonzero "2F" signal below 250 K the transmitted light between crossed polarizers (without the compensator) was also measured. Since L-alanine is orthorhombic there is a total extinction when the direction of vibration passed by the polarizer coincides with one of the dielectric axes of the crystal,[25] and when the analyzer is perpendicular. Figure 14 shows that the extinction set at room temperature remains about 250 K, and that below this temperature the transmitted light intensity progressively increases.

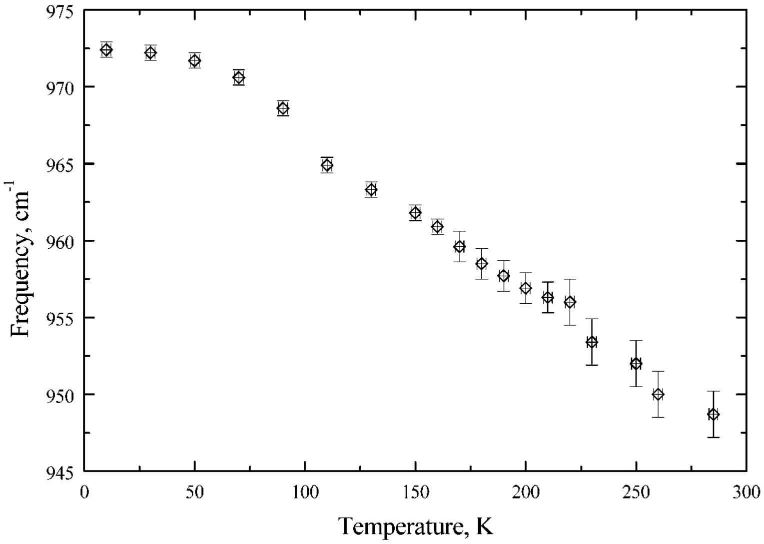

Figure 11. Peak frequency of the possible overtone (of the NH_3^+ torsion) as a function of temperature.

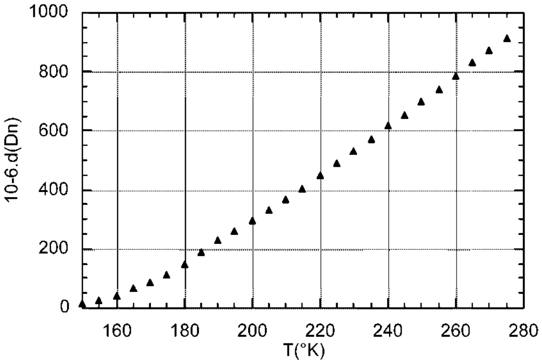

Figure 12. Linear birefringence in the (a, c) plane of a single crystal of L-alanine in the range 100−300 K. No structural instability is observed.

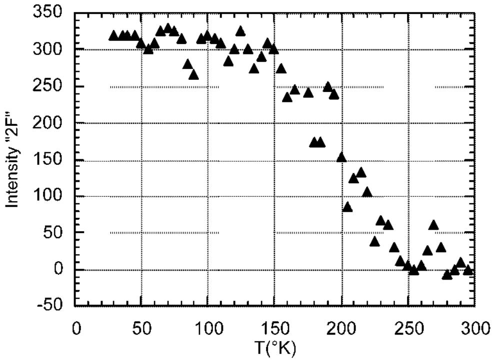

Figure 13. Transmitted light intensity detected at the "2F" frequency. The increase below 250 K indicates that a slight lattice distortion occurs. (The ϵ angle is no longer equal to zero).

Another possible explanation of these unexpected transmitted light intensities would be an increase of the rotary polarization (which is negligible at room temperature) on cooling, and its combination with birefringence. But this would require a deformation of the molecule, which is less probable than a small structural distortion of the lattice as indicated by the very small increase in the c parameter at 20 K.

Discussion

The two main observations of the present study of L-alanine have been the following:

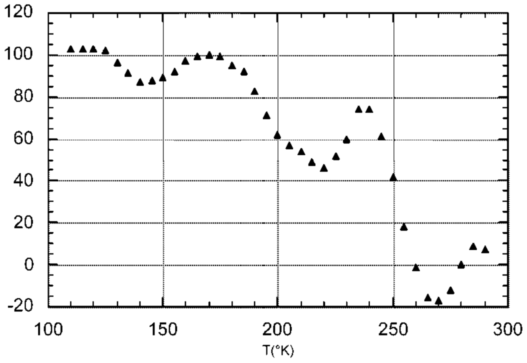

Figure 14. Transmitted light intensity between crossed polarizers having their direction of vibration parallel to the crystallographic a and c axes of the L-alanine single crystal.

(1) The unusual and previously observed temperature evolution of the frequency of the NH_3^+ torsion[11,12] has in fact its origin in a splitting into two bands which becomes apparent below about 220 K. This splitting increases to about ≈ 5 cm^{-1} at 10K. The increase of the fwhm with temperature is also unusual and has a pronounced change in slope at about 220 K, while the integrated intensity changes by more than 50%. A new band with strongly temperature-dependent intensity is observed at 972 cm^{-1} and assigned to the first overtone of the anomalous $\tau(NH_3)$ mode.

(2) A continuous and microscopic deformation of the lattice is observed below about 220 K by depolarization and "2F" birefringence measurements. No phase transition exists, however, as shown in previous crystallographic studies[8,9] and our first birefringence ("F") curve. These effects nonetheless suggest some kind of symmetry breaking. In analogy with "2F" birefringence data in incommensurate $BaMnF_4$,[21] and by considering the apparent shear stress created by the packing forces on cooling, the system could undergo a slight monoclinic structural distortion with close to a 90° angle and two types of domains.

Tentative Interpretation of the Anomalous NH_3 Torsion. The temperature-dependent splitting of the torsion below 200 K into bands at 495 and 500 cm^{-1}could, in principle, be a factor group splitting, which allows three components b_1, b_2, and b_3 separated by gaps of several cm^{-1} (Machida et al.[12]) to be IR active. The

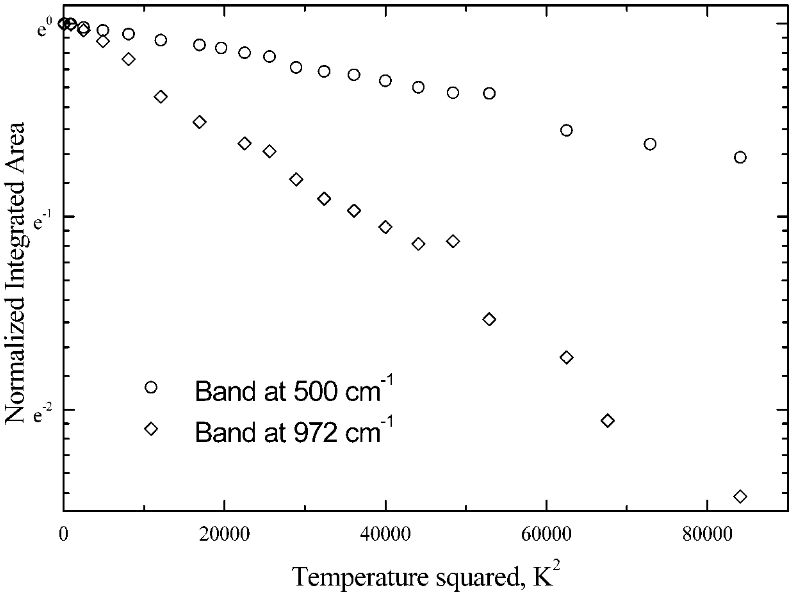

Figure 15. Log of the normalized integrated intensity of the NH_3^+ torsion and its overtone vs T^2. A temperature dependence proportional to exp[$-T^2/\theta^2$] predicted by the vibrational polaron model is obeyed below about 250 K.

individual components should, however, have the same evolution on cooling, have little variation of the intensity, and have the splitting remain approximately constant. Such a factor group splitting also does not provide for the presence of the overtone and its increasing intensity with decreasing temperature.

The presence of two types of domains resulting from a slight monoclinic distortion of the crystal could also explain this splitting under the assumption that both domains are not perfectly symmetric, e.g. if some internal stress is stronger in one type of domain. Such a hypothesis cannot, however, account for the overall change in intensity of the torsional bands with temperature or the existence of the forbidden overtone with an increase of intensity. A monoclinic distortion would furthermore require absorption bands in addition to the NH_3 torsion split in the same range of temperature, which is not observed.

Wang and Storms[12] previously provided a tentative interpretation of the anomalous properties of $\tau(NH_3)$ by assuming that H bonds in two of the H-bonded networks break with increasing temperature, and treated the NH_3^+-librating group as a damped harmonic oscillator. The broadening should then be a thermally activated process, but the activation energy deduced from a comparison with experiment is only half of what would normally be expected. Moreover, the significant increase of intensity observed upon cooling does not fit the expected behavior of a damped harmonic oscillator. On the other hand, the strong anharmonicity in this Raman band[12] is in accord with our observations of the temperature dependent changes in frequency, intensity and fwhm of $\tau(NH_3)$ in the IR. The existence of the overtone of this mode also suggests an interpretation involving nonlinear excitations, which was also proposed as an explanation of the unusual properties of low-frequency Raman modes,[6] or for the unconventional Amide-1 mode in Acetanilide.[4] An ILM can result in Ala from the coupling of the NH_3^+ group torsion to one or more of the three H bonds stretching modes. The low energy sideband of the NH_3^+ torsion at 500 cm^{-1} may then be tentatively assigned to the ILM, i.e., a breather, or vibrational polaron.

The "polaron" theory[26,4] predicts that the temperature dependence of the intensity of the absorption is related to the localized mode in the following way:

$$I(T) \approx I_0 \times \exp(-T^2/\Theta^2) \tag{2}$$

The gap in energy between the "exciton" and the polaron isthen given by:

$$\Delta E = \nu_e - \nu_p = \chi^2/2w - 2J$$

where χ is the exciton−phonon coupling, w is the H bond elastic constant and J is the dipole coupling. Moreover, using the χ value so deduced, it is possible to calculate the frequency of the N-th overtone $\nu(N)_p$ using the theoretical model developed by A.Scott et al.[24]

$$\nu(N)_p = \nu_0 \times N - \frac{1}{2}\gamma N^2 \tag{3}$$

with $\gamma = \chi^2/w$, and ν_0 the internal mode frequency without any coupling with phonons. This value should then be comparable to the experimentally measured frequency of the band at 970 cm^{-1}, that we assumed to be the first overtone of the localized mode.

To compare the observed temperature dependence of the intensity of the torsional band with the polaron model using equation {2}, we fitted the equation $I(T) \approx \exp(-T^2/\Theta^2)$ to the data shown in Figure 11. The reasonable fit gives a Debye temperature Θ of about 80 K, which is quite reasonable for this type of crystal.

We can obtain a value for the anharmonic ratio γ by using our experimental value of $\Delta E = 5$ cm^{-1}, (where we assume that the polaron frequency is $\nu_p = 495$ cm^{-1}, the exciton frequency $\nu_e = 500$ cm^{-1} and the overtone frequency $\nu(2)_p = 970$ cm^{-1}) and a value for the dipole coupling $J \approx 1.5$ to 4 cm^{-1} (as in ACN), with the result that $\gamma = \chi^2/w \approx 16$ to 26 cm^{-1}. If we then take $\chi \approx 6 \times 10^{-11}$ N (again as in ACN), the H bond average force constant, w, can be estimated to be about 8 N/m, which is slightly higher than in ACN and consistent with the shorter H bond distances in Ala.

Finally equation {3} along with the above value of γ can be used to predict the frequency of the overtone estimated to be 964 $cm^{-1} < \nu(2)_p < 974$ cm^{-1}, which is in good agreement with the experimental value of 970 cm^{-1}.

Conclusion

While our new IR spectra, obtained with improved resolution, in conjunction with INS spectra provide vibrational assignments in general agreement with previous studies, they also make it possible to differentiate between quasi-harmonic lattice modes and the H bond strain vibrations of the three H-bonded networks. In addition, the splitting of τ(NH3) along with the other anomalous temperature-dependent properties of this mode suggests the possible existence of nonlinear excitations, and our calculations show that a self-trapped mode provides a reasonable account of the observed behavior. This also applies for the anomalous temperature dependence of the intensity and frequency of the overtone. The self-trapped mode could be an NH_3^+ torsion coupled to one or more phonons, such as for example one of the H bond stretching modes.

A possible structural change, which also could also have explained the splitting of τ(NH3), was investigated by means of birefringence and depolarization experiments. The results can be interpreted to definitively rule out the existence of a conventional phase transition (in agreement with previous structural investigations), but have revealed a subtle and continuous symmetry breaking that occurs below about 250 K. This could be related to the shear stress created by the unequal shrinking of the three H-bonded networks, and to the small increase of lattice parameter c at low temperature.

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Supporting Information Available: Force constants for L-alanine from a normal coordinate analysis and refinement to INS vibrational spectra, has been provided for this journal article. This material is available free of charge via the Internet at http://pubs.acs.org.

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