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Micro-conformational transitions in L-alanine single crystals revisited by low wavenumber Raman spectroscopy

Boris A. Kolesov^{a,b} and Elena V. Boldyreva^{a,c,*}

The properties of the crystalline L-alanine have been attracting attention for a very long time, and there is much controversy in the results already reported. One of the most interesting problems is that of the localization of vibrational energy and the micro-transitions (named 'breathers' by Barthes *et al.* [M. Barthes, H. N. Bordallo, F. Dénoyer, J.-E. Lorenzo, J. Zaccaro, A. Robert, F. Zontone, *Eur. Phys. J.* 2004, **B37**, 375]. In the present study, we have addressed this problem once again, having measured the high-resolution polarized Raman spectra in the temperature range from 4 to 300 K. The wavenumber, bandwidth and intensity of all the modes polarized along the *c*-axis (the axis of the head-to-tail chains of zwitterion in the structure) show discontinuities at 30–50, 100–120 and 180–220 K. We interpret the observed anomalies of spectral characteristics in terms of micro-conformational transitions accompanied by the rearrangement of the hydrogen-bond network and relate them to previously published work. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: L-alanine; amino acids; Raman spectroscopy; hydrogen bonding; micro-transitions

Introduction

Crystalline L-alanine is one of the most extensively studied systems but, nevertheless, many of the numerous published results are controversial and many questions remain open. Although no structural polymorphic transitions in L-alanine have been observed in a wide temperature range from 10 to 300 K, several anomalies have been reported. Thus, the value of the unit cell parameter *c* has been reported to increase on cooling;^[1,2] Barthes *et al.*^[3] have shown this increase to be step-wise. Migliori *et al.*^[4] have described an unusual behavior of the intensities of the low wavenumber modes as 41 and 49 cm⁻¹ on cooling and related them to the occurrence of localized vibrational states. An unusual temperature dependence of the Raman band at ~490 cm⁻¹ corresponding to the NH₃⁺ torsional mode^[5–8] and unusually long (>10 ps) lifetimes for the low wavenumber librations^[9] have been reported.

Vibrational spectra of L-alanine have been studied in Refs [5,7,10–12] by IR and Raman spectroscopy and in Refs [13–17] by inelastic neutron scattering. Raman spectra and density functional theory (DFT) calculation of polycrystalline L-alanine were reported by Williams *et al.*^[18] and DFT calculations of L-alanine in aqueous solution and in the solid state by Tortonda *et al.*^[19] and Chowdhry *et al.*^[20] In our previous work,^[21] we reported the results of a variable-temperature study of the polarized Raman spectra in the high wavenumber spectral range, which revealed several unusual spectral features, in particular, an unusual energy and temperature dependence of the intensity of selected Raman bands in the high wavenumber range.^[21] These results were interpreted assuming that the N–H stretching self-trapped states are formed in the crystals of amino acids, not for any N–H stretching vibrations but exclusively for those related to the N–H...O hydrogen bonds along the head-to-tail chains of the zwitterions. These self-trapped states could be expected to be related to the various anomalies reported earlier for the behavior of crystalline L-alanine, and to manifest themselves not only in

the high wavenumber range but also in the low wavenumber range. The aim of the present study was to measure the polarized Raman spectra from the oriented single crystals of L-alanine at temperatures from 4 to 300 K in the low wavenumber range, in order to check and interpret the occurrence of the anomalies previously reported in the literature in relation to the recent findings in the high wavenumber range. We were interested in a detailed variable-temperature study of band parameters such as the maximum position, half-width and intensity. The polarization of the spectra in this work was used not to establish the symmetry of a vibrational band but to select in the whole spectrum exclusively the vibrational bands corresponding to a crystallographic direction. The spectral range between 30 and 600 cm⁻¹ has been chosen since our primary interest was in the temperature response of the relatively weak intermolecular hydrogen bonds and most of the anomalies reported previously were related to the bands in this spectral range of lattice modes and low wavenumber torsional modes of the molecular fragments.

Materials and Methods

Samples

L-Alanine was crystallized from saturated aqueous solutions by slow evaporation. The orientation of the crystallographic axes of

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the crystals was found using a STOE IPDS-II diffractometer and the X-SHAPE software.^[22] The crystals had the shape of parallelepipeds with typical size 0.2–1 mm and had no visible imperfections when observed under a polarized optical microscope. The Raman spectra measured under ambient conditions from different sites of the crystal agreed well with each other, thus confirming the optical homogeneity of the samples.

Raman spectroscopy

The polarized single-crystal Raman spectra were collected using a LabRAM Horiba single spectrometer with a charge-coupled device (CCD) detector (Symphony) from Jobin-Yvon. The laser line was used for wavenumber calibration of the spectra. The 488 nm line of an Ar⁺ laser (35LAP431 from Melles Griot, USA) was used for the spectral excitation, and the diameter of the laser spot on the sample surface was 5 μm. The laser power at the sample was typically 3 mW. Laser power stability was better than ±0.5%. The incident light was focused and the scattered light was collected by an Olympus MPlan N objective with 10× enhancement and numerical aperture (NA) = sin θ = 0.25. The polarization leakage *L* is:

$$L = \int_{90-\theta}^{90+\theta} \cos^4 \theta \times d\theta$$

For $\theta = \arcsin(0.25)$, $L = 2.7 \times 10^{-4} = 2.7 \times 10^{-2}\%$. The spectra at all temperatures were measured in the backscattering collection geometry with a Raman microscope. A liquid helium ST-500 Microscopy Cryostat from Janis (USA) was used for recording the low-temperature spectra. The alanine crystals were wrapped in indium foil for better thermal contact, keeping an open field at the upper surface accessible for light, and were fixed on a cold finger of the cryostat. The cryostat was also fixed, so that any occasional movements (a shift or rotations) were excluded. The precision of the measured temperatures of the cold finger is 0.1 K, but the true temperature of the sample can differ from the measured one due to some heating of the sample at the laser spot. We estimate this heating to be 4–5 K for transparent crystals. The stability of temperature during measurement was maintained by a temperature controller to better than 0.1 K. All measurements were performed with a spectral resolution of 0.6 cm⁻¹. The experiments were reproduced many times with different L-alanine crystals, in several cryostat loadings and on different days. Sometimes, we had crystals of several compounds (not only L-alanine) loaded simultaneously in the same cryostat. The measurements were highly reproducible.

Raman bands were fitted by PsVoigt1 function to determine their spectral parameters, i.e. wavenumber, bandwidth and integral intensity. The band at 856 cm⁻¹ (not shown in the figures) was used as a reference line for intensity calibration. This mode does not take part in intermolecular motions, and the relatively large energy of the mode makes the dependence of its Raman intensity on temperature negligible.

The space symmetry group of crystalline L-alanine (C₃H₇NO₂) is *P*2₁2₁2₁; there are four molecules per unit cell, which are present as zwitterions, ⁻COO–CH(CH₃)–NH₃⁺. The hydrogen-bonded zwitterions of L-alanine form head-to-tail chains along the crystallographic axis *c*, which are further linked into a three-dimensional framework by several types of N–H···O hydrogen bonds (Fig. 1).^[1,2]

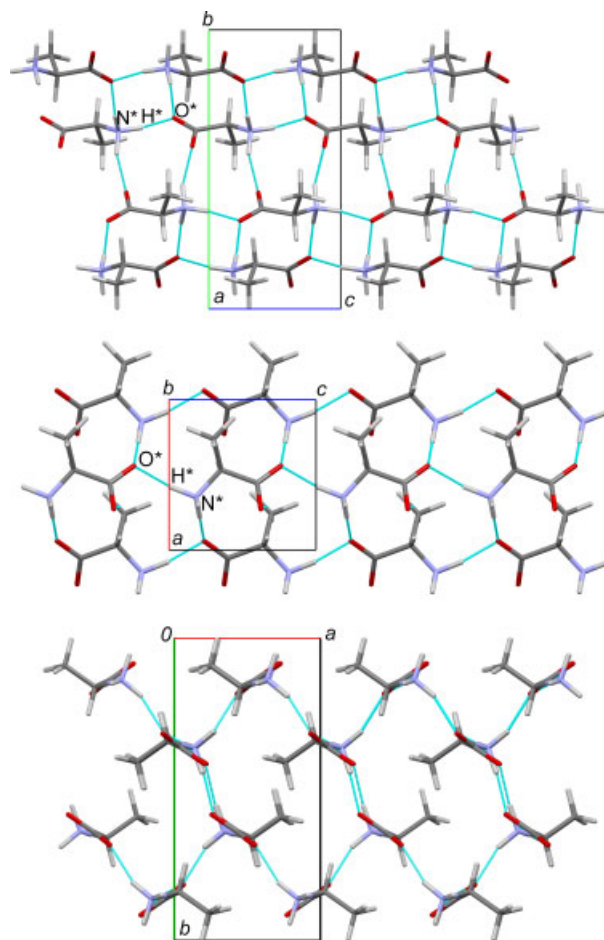


Figure 1. The fragments of the crystal structure of L-alanine (normal to different crystallographic axes). Hydrogen bonds are shown by blue dotted lines. The N⁺–H⁺···O⁻ bonds within zwitterion chains are labelled.

The vibrational representation of the lattice translations is as follows:

$$3A_1(x, y, z) + 2B_1(x, y) + 2B_2(x, z) + 2B_3(y, z).$$

All modes are Raman active. These modes involve the motions of the molecules along each of the crystallographic axes *a*, *b* and *c*, and three of them, *A*₁(*z*), *B*₂(*z*) and *B*₃(*z*), are polarized along the *c*-axis. The same representation is valid for the librational modes as well.

Results

The polarized Raman spectra (30–600 cm⁻¹) of L-alanine single crystals at 4 K (Fig. 2(a)) are in a good agreement with those previously reported in the literature,^[4,7,10] but a better spectral resolution made it possible to resolve several bands, which have been considered as individual bands in Refs [4,7,10]. One can see that two modes at 38 and 41 cm⁻¹ are observed in the *cc* spectrum (Fig. 2(b)) instead of one mode at 40–41 cm⁻¹.^[4,7,10] The mode at 38 cm⁻¹ is at the edge of the notch-filter absorption band and is assigned possibly to plasma line of Ar⁺-laser. Three modes at 48, 49 and 49.5 cm⁻¹ were detected instead of one band at 48 cm⁻¹ in Refs [4,7,10]. The mode at 105 cm⁻¹ splits into two

lines (105.2 and 105.9 cm^{-1}) in the **cc** spectrum and the mode at 110 cm^{-1} in the **bb** spectrum splits into three components (110.9 , 111.5 and 112.2 cm^{-1}) at temperatures below 140 K (Fig. 3(b)). The mode at 121 cm^{-1} (113 cm^{-1} at room temperature) in the **aa** and **bb** spectra also splits into at least two components (121.5 and 122.2 cm^{-1}) but at temperatures below 200 K (Fig. 3(a) and (b)). The mode at 150 cm^{-1} splits into 149.2 and 149.8 cm^{-1} at $T < 60\text{ K}$ (Fig. 3(b)). On heating, the wavenumber of this mode decreases, and the mode overlaps with the other mode at 140 cm^{-1} in the **cc** spectrum and with the modes at 144 cm^{-1} in the **aa** and **bb** spectra. Barthes *et al.*^[3] have also reported this overlapping, but as occurring at 170 K .

A detailed assignment of the low wavenumber vibrational bands is a difficult problem. To the best of our knowledge, there

are no good and reliable quantum mechanical calculations of the low wavenumber part of vibrational spectrum of amino acid crystals. Among the intramolecular vibrations, only the rotation of one part of the molecule relative to another part, or bending of these fragments, can be characterized by low wavenumbers. The molecule of alanine is rather small, and the relative rotation of its fragments is simply a torsional motion of COO , CH_3 or NH_3 , which are characterized by wavenumbers in the range $200\text{--}500\text{ cm}^{-1}$. The same holds for the intramolecular bending. An extra argument supporting the assignment of the bands in the $40\text{--}150\text{ cm}^{-1}$ region as lattice vibrations is that all intramolecular low wavenumber vibrations are hardly polarized in one crystallographic direction, in contrast to the translational modes. The force constant K for a typical $\text{N-H}\cdots\text{O}$

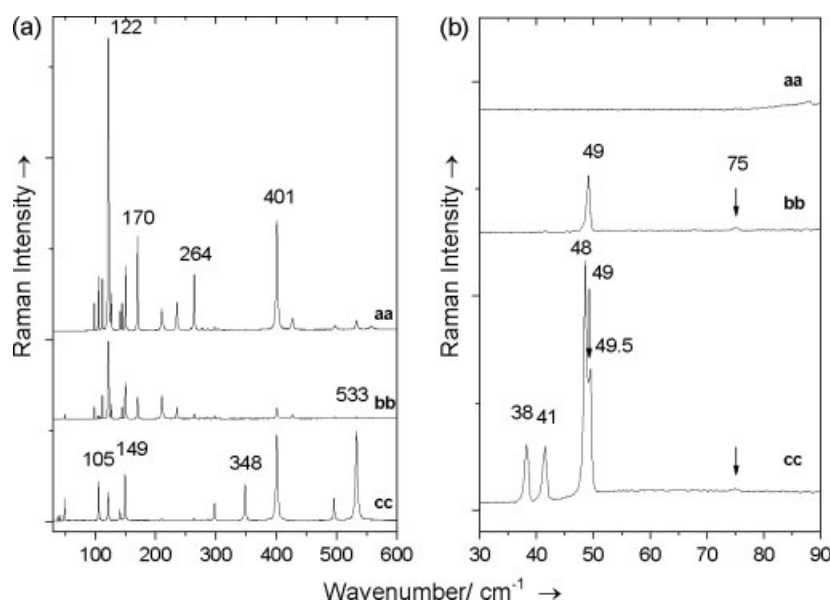


Figure 2. Polarized Raman spectra of L-alanine single crystals at 4 K in the range $30\text{--}600\text{ cm}^{-1}$ (a) and $30\text{--}90\text{ cm}^{-1}$ (b). The definitions **aa**, **bb** and **cc** imply the directions of the polarization vector of the incident (first symbol) and the scattered (last symbol) light with respect to crystal axes.

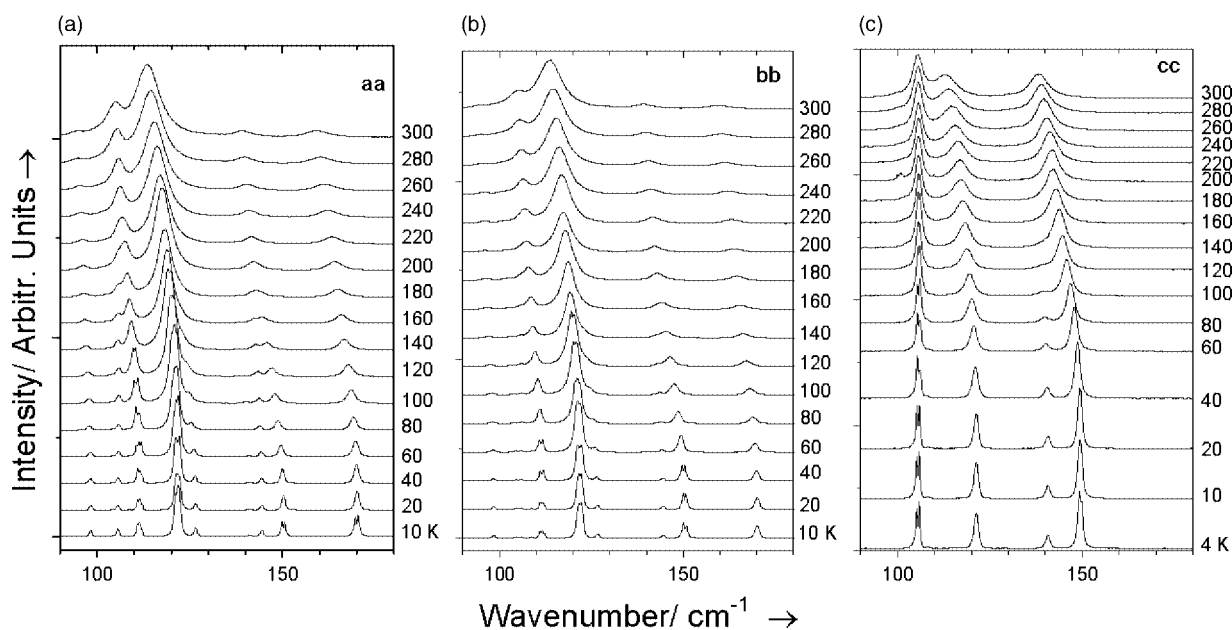


Figure 3. High-resolution polarized spectra at different temperatures in the range $90\text{--}180\text{ cm}^{-1}$.

hydrogen bond is around 13 N/m. In the case of alanine molecules, the force constant responds to the wavenumber of intermolecular vibrations of $\sim 100\text{ cm}^{-1}$. The intense **a** and **b** modes at $115\text{--}130\text{ cm}^{-1}$ can be assigned rather definitely to lattice translations.

The wavenumbers, bandwidths (full width at half height (FWHH)) and the integral band intensities of all the modes in the **cc** spectra measured in the $100\text{--}600\text{ cm}^{-1}$ range *versus* temperature are plotted in Figs 4–6. The temperature-dependent bandwidths were fitted whenever possible by the expression

$$\Gamma(T) = \Gamma(0) \left[1 + \frac{1}{\exp\left(\frac{\hbar\omega_1}{kT}\right) - 1} + \frac{1}{\exp\left(\frac{\hbar\omega_2}{kT}\right) - 1} \right] \quad (1)$$

describing the decay of a phonon with the wavenumber ω into two other phonons ω_1 and ω_2 of lower energy.^[23]

The wavenumbers of all the modes demonstrate discontinuity at approximately 100 and 180–220 K. The bandwidths of all the modes show discontinuities at the same temperature as well, with the mode at 150 cm^{-1} as the only exception, but this mode ‘absorbs’ two other modes at ~ 140 and $\sim 145\text{ cm}^{-1}$, and its bandwidth can be distorted by this ‘absorption’. These unusual features suggest that the mechanism of phonon decay changes at two temperature points.

The integral intensities of the modes *versus* temperature show the most surprising behavior (Fig. 6). A theoretical expression

for the temperature-dependent part of the Raman intensity (Refs [24,25])

$$I(T) = \text{const} \times (n + 1), \quad (2)$$

where n is the thermal population of a phonon state:

$$n = (e^{\hbar\omega/kT} - 1)^{-1} \quad (3)$$

fits roughly the experimentally observed $I(T)$ curves for two modes only – those at 401 and 533 cm^{-1} . As can be seen from Fig. 4, the low temperature bandwidth for all the bands is in the range of $1\text{--}3\text{ cm}^{-1}$. Thus, we deal with a normal crystalline state, where Raman scattering occurs in the centre of Brillouin zone ($k = 0$). At this point phonon dispersion $d\omega/dk = 0$ by definition, selection rules for wave vector are valid, density of states does not change with temperature, but population of phonon states changes exponentially. For all the considered modes, the ω^4 -rule of Raman intensity is about $10^{-3}\text{--}10^{-5}$ of the observed intensity changes, and thus is negligible. The other experimental dependences deviate significantly from the fitting curve based on Eqns (2) and (3). Four modes, i.e. 140 , 297 , 348 and 496 cm^{-1} , show the inverse trend in the intensity changes on increasing temperature. To make the description of the mode intensity behavior more complete, we have plotted the total integral intensity of the three modes at 48 , 49 and 49.5 cm^{-1} from the **cc** spectra (Fig. 7(a)) and the total integral intensity of the modes at $115\text{--}130\text{ cm}^{-1}$ from the **bb** spectra (Fig. 7(b)). The individual bands in this range overlap to a large extent at high temperatures. The intensity of the lattice modes polarized in the **b** direction rises considerably faster

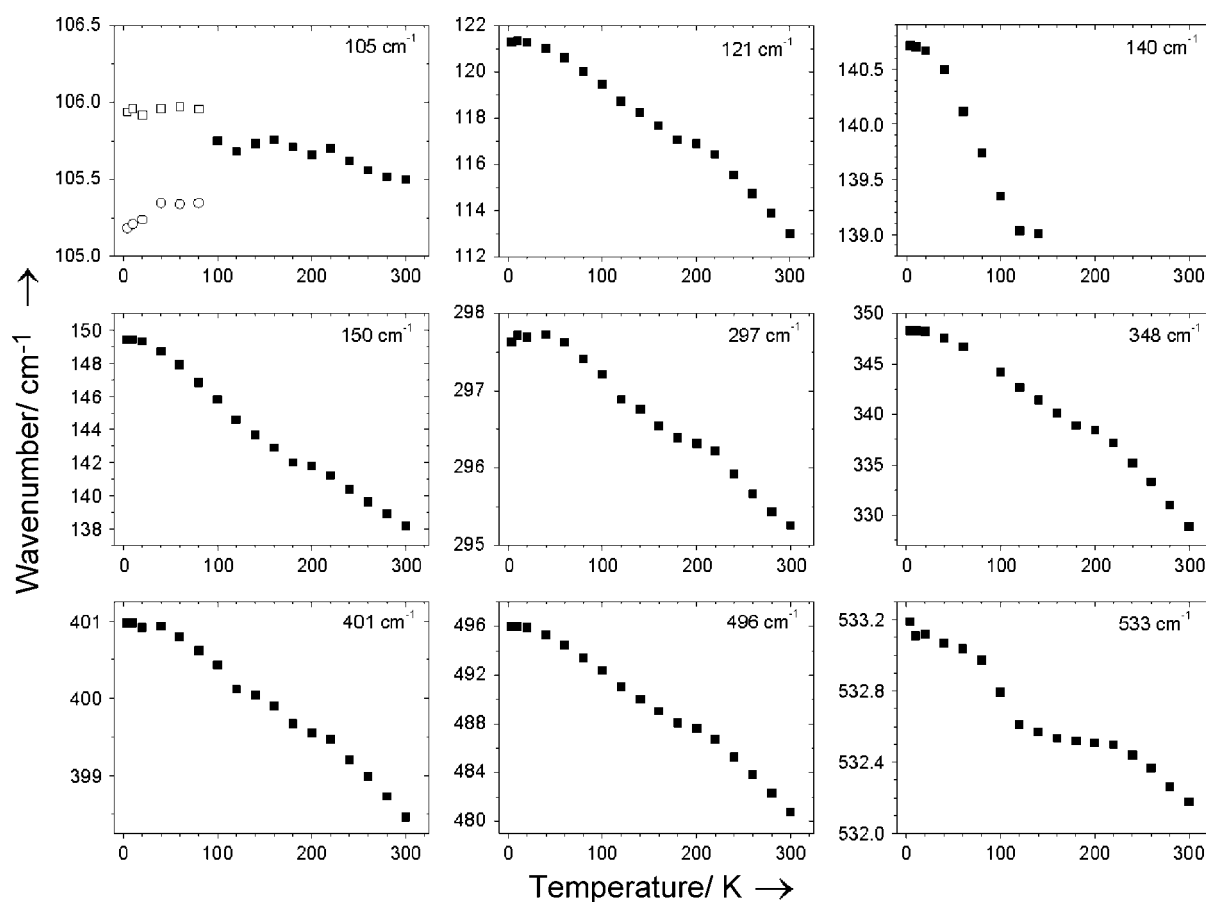


Figure 4. Wavenumbers of different modes *versus* temperature.

with temperature as compared to the theoretically predicted rate (Fig. 7(b)). The c -polarized modes demonstrate a slight increase in the excess intensity and additional fluctuations on heating (Fig. 7(a), and the plots of the intensity of modes at 105, 121 and 150 cm^{-1} in Fig. 6).

Discussion

The peculiar features of the temperature dependences of the spectral characteristics of all the modes (i.e. the wavenumber, bandwidth and the integral intensity) at 100–120 and 180–220 K (and, possibly, also at 30–50 K) can be a consequence of some changes either in the individual molecules or in the crystal cell. To understand the nature of these changes, we shall try to analyze first the intensity changes *versus* temperature, since these dependences deviate the most from the theoretically expected ones. This analysis is also helpful for the assignment of the observed bands.

The temperature dependence of the intensity of the lattice modes ($40\text{--}150\text{ cm}^{-1}$) is one of the most interesting phenomena observed in the spectra of L-alanine (Figs 6 and 7(a)). One can see that intensity of all c modes deviates from the curves calculated using Eqns (2) and (3). The low wavenumber modes in the cc spectra are related to translational motions in the c -direction and thus to the modulation of the $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bond.

However, the O^* and N^* atoms are involved not only in the $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bond but also in other hydrogen bonds (Fig. 1). The parameters of all the hydrogen bonds in which the N^* and O^* atoms are involved are coupled, since the formation of the zwitterions itself would be impossible without the 'extra' hydrogen bonds between the chains.^[21] In order to interpret the changes observed in the cc spectra, one needs to analyze the translational motions along the other crystallographic axes as well.

Figure 7(b) represents the experimental integral intensity of the b modes at $115\text{--}130\text{ cm}^{-1}$ (filled squares) and the thermal population of the mode with a mean wavenumber 120 cm^{-1} (solid curve). The figure shows that the experimental intensity grows with temperature much faster than predicted by Eqns (2) and (3). The difference between the experimental and the predicted intensities, i.e. the 'extra intensity', is shown in the same plot by open squares. One can see that the extra intensity increases linearly with temperature (dashed curve). The behavior of the b -mode intensity is apparently a direct consequence of the ability of the $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bond to respond to the changes in the interactions of the N^* and O^* atoms also with other atoms in the crystalline environment with which they form additional hydrogen bonds. However, a clear elucidation of the effect will be available only after a detailed quantum mechanical calculation of the system.

The temperature dependence of the c -polarized lattice modes is even more complicated. In this case, in addition to the general

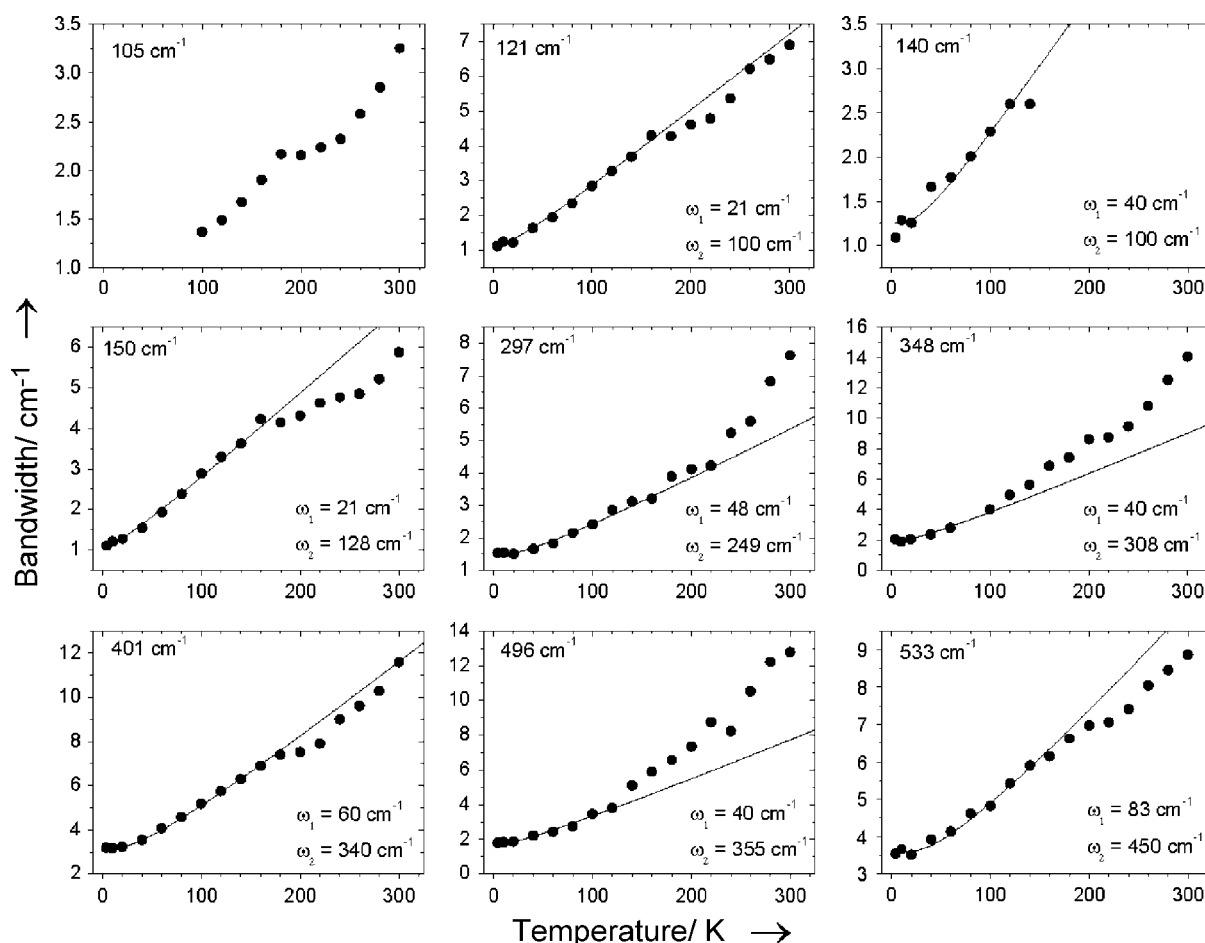


Figure 5. Bandwidth (FWHM) of different modes *versus* temperature. The fitting (solid curves) was made with Eqn (1). Parameters ω_1 and ω_2 are indicated at the figure.

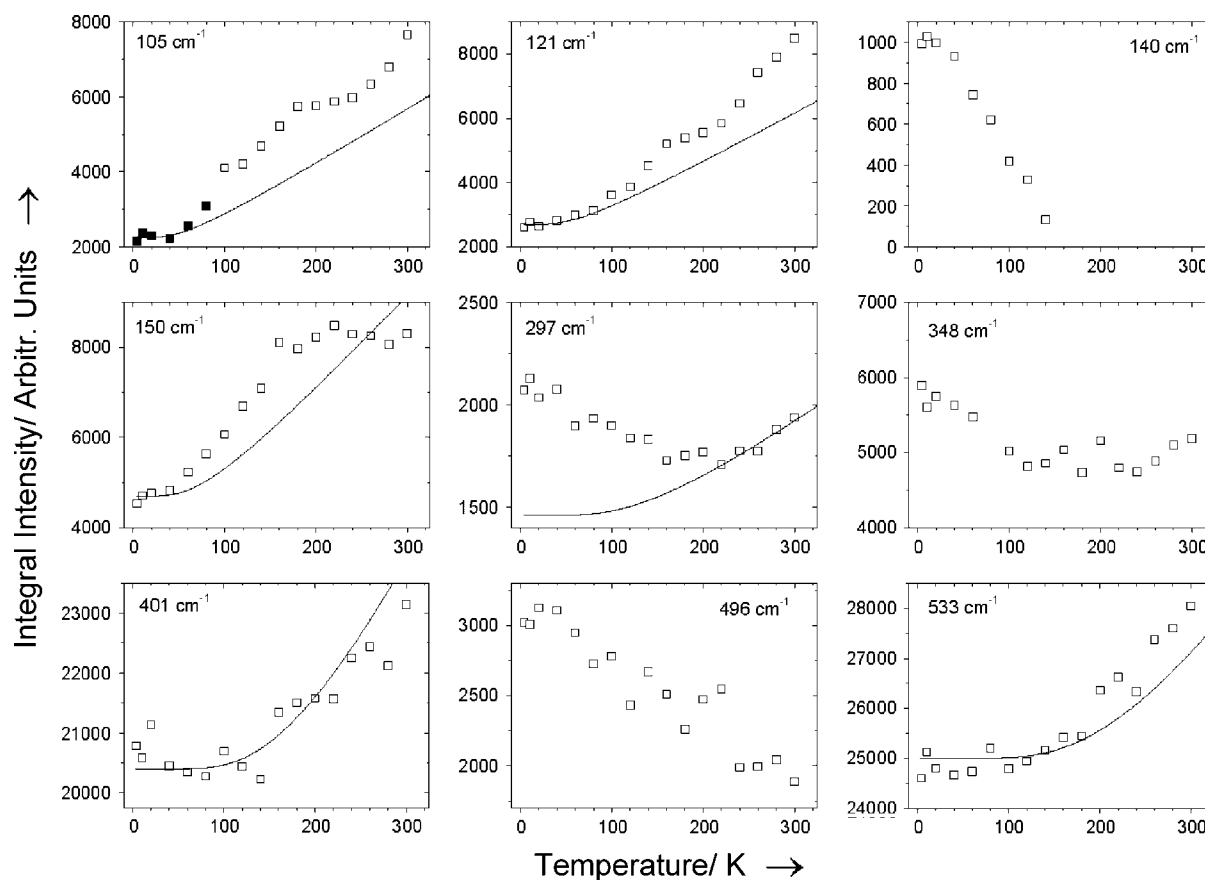


Figure 6. Integral intensity of the modes *versus* temperature. The fitting (solid curves) was made with Eqns (2) and (3). Filled squares on the dependence of the mode at 105 cm^{-1} are the sum of integral intensity of two modes at 105.2 and 105.9 cm^{-1} into which the main mode splits at $T < 100\text{ K}$.

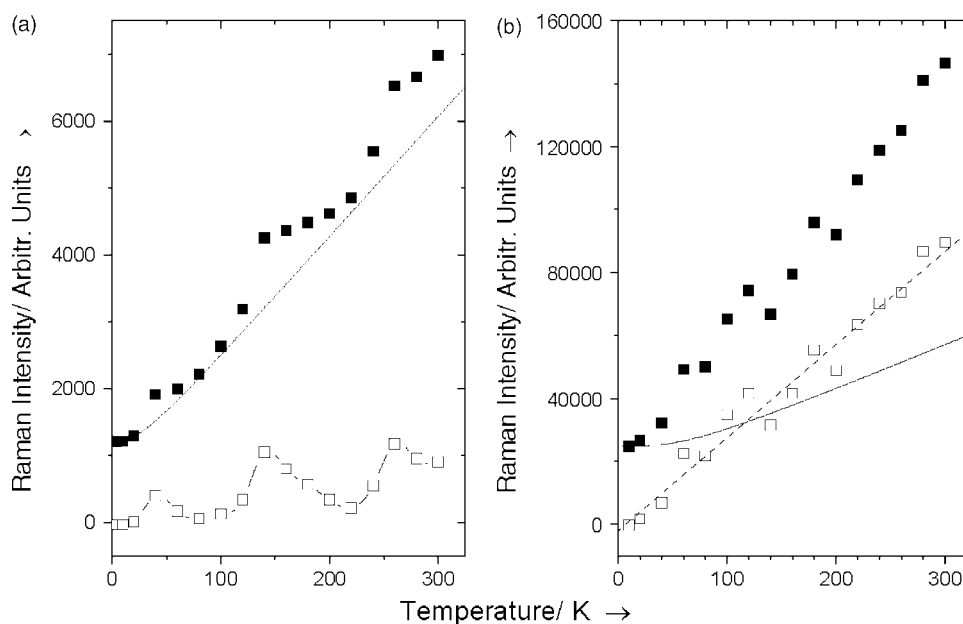


Figure 7. Summarized integral intensity of the bands at 48 , 49 , and 49.5 cm^{-1} from *cc* spectra (a) and bands in the range of $115\text{--}130\text{ cm}^{-1}$ from *bb* spectra (b) at different temperatures. Filled squares – experiment; solid curves – fitting by Eqns (2) and (3); open squares – difference between the experiment and fitting.

increase in the extra intensity, one can see clearly a pulsation of intensity (Fig. 7(a)), which belongs to the most complicated phenomena observed in the **c** spectra of L-alanine. The general increase in the intensity is similar to that observed for the **b**-polarized modes (Fig. 7(b)), but is much weaker; it can result from an increase of the **b**-component contribution to these bands on heating. The vibrational normal coordinates change slightly with temperature, since the temperature dependence of the force constants is not the same for different intermolecular interactions. So, an increase in the **b**-component contribution to a lattice vibration should result also in an increase in its Raman intensity. One can suppose this effect to account for the increase in the intensity of the mode at 41 cm^{-1} on heating reported by Migliori *et al.*^[4] We can see that even a phonon polarized mainly along **c** changes its intensity slightly with temperature because of the growing contribution of the **b** component. The scattering conditions in the experiments described by Migliori *et al.*^[4] do not allow one to assign a definite polarization to a phonon, and therefore the contribution of the **b** component to the measured band can be quite large.

One can suggest that the pulsations of the intensity (Figs 6 and 7(a)) is a consequence of the conflict between (1) an increase in the amplitudes of the vibrations of all the atoms in a molecule and a corresponding expansion of the cell parameters on heating and (2) a simultaneous strengthening of the intermolecular hydrogen bond $\text{N}^*-\text{H}^*\cdots\text{O}^*$ within a head-to-tail chain, resulting from the weakening of the hydrogen bonds between the chains as **a** and **b** expand, which induces a contraction of the cell parameter **c**. In fact, the decrease in **c** inevitably results in the shortening of all the intermolecular contacts along the crystallographic **c** direction, contradicting the general tendency of their lengthening due to the increased vibrational amplitude. One can suppose that the stress, which increases on heating because of this conflict, relaxes periodically with temperature, provoking micro-conformational transitions – relatively small changes in the intramolecular geometry – at some selected temperatures. A similar conflict can occur also in a selected intermolecular $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bond, when the position of the H^* atom (determined by the $\text{N}^*-\text{H}^*-\text{O}^*$ angle) becomes less and less 'optimal'. The 'non-optimum' position of the hydrogen atom can either relax from time to time on its own, or be interrelated with the conformational changes. The periodic relaxation of the H-atom position and micro-conformational transitions can account for the step-wise changes in the **c** parameter observed in Ref. [3]. The temperature values at which this stress relaxation occurs, and the frequency of the relaxation events in a temperature range, should depend, among other parameters, on the crystal size as well as the heating/cooling rate, which are usually different from experiment to experiment, especially if different physical properties are measured. This can explain the large dispersion of the effects and discrepancy in the data reported in the literature. The diffraction experiment described in Ref. [3] is probably the most time consuming among all the experiments described thus far, and therefore the 'steps' observed in that experiment are the most pronounced. The pulsations of the intensities of the lattice modes in the Raman spectra (Figs 6 and 7(a)) must depend strongly on the contribution of the **b** components in the mode. The stress that accumulates in the structure and its subsequent relaxation result in the modulation of the contribution of the **b** component to the mode, and this, in turn, leads to the pulsation of its intensity. The contribution of the **b** component and its temperature dependence are not the same for different lattice modes; therefore, each lattice

mode shows its unique temperature change, and the pulsations of the intensity are observed at different temperature points.

The hypothetical micro-conformational transitions manifest themselves in the temperature dependence not only of intensity but also of other parameters of spectral bands, such as wavenumber and half-width. The dependence of the wavenumber of all the modes in the spectral range $30\text{--}600\text{ cm}^{-1}$ in the **c** spectra versus temperature shows steps at $30\text{--}50$, $100\text{--}120$ and $180\text{--}220\text{ K}$. Besides, some modes in the $100\text{--}150\text{ cm}^{-1}$ range, which can be assigned to lattice vibrations (translations and librations of molecules), split into components (Figs 2 and 3), as if structural transitions have occurred. The changes in the slopes of the curves describing the temperature dependence of the half-widths of all the bands in the temperature ranges $100\text{--}120$ and $180\text{--}220\text{ K}$ (Fig. 5) indicate that the decay of the phonons into the lower energy vibrations changes at these temperatures, i.e. all the phonon–phonon interactions undergo changes. These effects are most probably caused by a change in the hydrogen-bond network in the crystal – either an H-donor 'switches' to another acceptor, or additional bonds are formed so that hydrogen bonds become bifurcated, multicentred. The changes that can account for the anomalies observed in L-alanine on variation of temperature concern only the hydrogen-bond network, whereas the crystal structure is basically preserved, with just small changes in molecular conformations and mutual orientation and juxtaposition of the neighbouring molecular fragments. If these small structural distortions are large enough to be measurable at all, a special (single crystal neutron diffraction?) experiment done at multiple temperature points with a very small step in temperature would be very helpful to test this hypothesis. Although the crystal structure of L-alanine has been analyzed many times,^[1,2,26–29] refinement has been usually done either at one or two temperatures, or at several points with rather large temperature steps between them. The most detailed variable-temperature study has been carried out by Barthes *et al.*^[3] However, although very careful data on the lattice parameter **c** versus temperature have been published in Ref. [3], there was no detailed analysis of the changes in the intra- and intermolecular bond lengths and angles.

One more interesting phenomenon in the spectra is related to the changes of Raman intensity of the modes at 140 , 297 , 348 and 496 cm^{-1} versus temperature (Fig. 6), which are unusual (inverse to normal) compared to the common behavior. The mode at 496 cm^{-1} is assigned to the torsional motion of the NH_3^+ group,^[7,15] whereas the modes at 297 and 348 cm^{-1} should be assigned to the dynamically split torsional motion of the CH_3 group. Numerous investigations of the methyl group vibrations (Ref [30]) showed that in solids their wavenumber is around 300 cm^{-1} . The amplitude of the torsional motions of methyl groups in the crystals of L-alanine is very large because of the small reduced mass of the vibrating atoms (a small moment of inertia of the $-\text{CH}_3$ group considered as a top). Methyl groups in the structure of L-alanine are close to each other, and this makes the dynamic splitting of the $-\text{CH}_3$ torsion quite probable. The high wavenumber mode at 348 cm^{-1} (i.e. the rotation of the neighbouring methyl group tops towards each other) increases by 20 cm^{-1} on cooling from 300 to 4 K as a consequence of the shortening of the distance between the neighbouring molecules, whereas the low wavenumber mode at 297 cm^{-1} (the rotation of the two groups in the same direction) increases by only 2 cm^{-1} under the same conditions (Fig. 3). These spectral changes support the proposed assignment of the modes at 297 and 348 cm^{-1} . The

mode at 140 cm^{-1} can be assigned also to the torsional vibration of the COO^- fragment. This suggestion can be supported by the following arguments: The torsional motions of the COO^- and the NH_3^+ fragments must be interrelated, and their force constants can be expected to be the same, since they are determined by the characteristics of the same $\text{N-H}\cdots\text{O}$ hydrogen bonds linking the two groups. The frequencies of the torsion vibrations of the COO^- and the NH_3^+ fragments should be related to each other as the square root of the inverse ratio of their moment of inertia \mathfrak{I} :

$$\frac{\omega_{\text{tors}}(\text{NH}_3^+)}{\omega_{\text{tors}}(\text{COO}^-)} \cong \sqrt{\frac{\mathfrak{I}_{\text{CO}_2}}{\mathfrak{I}_{\text{NH}_3}}} = 3.65 \quad (4)$$

From Eqn (4), the expected wavenumber of the $\omega_{\text{tors}}(\text{COO}^-)$ is $495/3.65 = 136\text{ cm}^{-1}$.

Thus, each of the mentioned four modes is related to the restricted rotations of the symmetric- COO^- (mode at 140 cm^{-1}), $-\text{CH}_3$ (modes at 297 and 348 cm^{-1}) and $-\text{NH}_3^+$ (mode at 496 cm^{-1}) tops; their Raman intensity decreases on heating. A similar decrease in intensity *versus* temperature was observed for symmetric tops also in other solids (Ref [29]), and is an intrinsic property of top's torsional motions.

The nature of this phenomenon is not clear. At this stage, we can suppose that it is related to the effect of temperature on the contacts of the tops with their neighbours in the crystal. A shift of the hydrogen atoms in the course of the torsional vibration of a top does not change noticeably the length of the C-H and N-H bonds and thus the polarizability of the $-\text{CH}_3$ or the $-\text{NH}_3^+$ groups. In the gas-phase Raman spectra of molecules, no torsional vibrations of the methyl group with a change in the vibration quantum number $\Delta\nu = 1$ are observed, but the overtones with $\Delta\nu = 2$ can be registered.^[31] Even if a weak change in the polarizability of the top occurs, it is not temperature-dependent, since the eigenvector of the vibration does not change with temperature. However, in the Raman spectra of crystals, the main tones ($\Delta\nu = 1$) of the torsional vibrations can be observed, and their intensity depends on the temperature.^[29] This difference between the gas-phase and crystalline-state spectra can be due to the presence of the crystal field and hydrogen bonds with the environment, in which a top can be involved in the crystal. In contrast to the intramolecular bond lengths within a top itself (C-O , C-H , N-H), the distances between a top and the neighbouring atoms in the crystalline environment are changed considerably in the course of a torsional vibration, and, what is even more important, these distances do change with temperature, increasing on heating. This increase in the intermolecular distances on heating may be the main reason of a decrease in the intensity of the torsion vibrations of the $-\text{COO}^-$, $-\text{CH}_3$ and $-\text{NH}_3^+$ tops. In this respect, it is worth noting that the DFT calculations confirm a strong effect of the environment on the structure of L-alanine zwitterions.^[30]

The change in the band intensity *versus* temperature is nonlinear (Fig. 7). The process can be roughly modelled if one supposes that the vibrational system is excited on heating from state A (characterized by the intensity I_A) to the state B (with the intensity I_B). In this case, the experimental intensity I_{exp} is:

$$I_{\text{exp}} = [I_A(1 - e^{-\Delta E/kT}) + I_B e^{-\Delta E/kT}] \times n, \quad (5)$$

where ΔE is the energy gap between the states A and B, k is Boltzmann constant and n is the thermal population of

the corresponding vibration (i.e. the Boltzmann factor n in the common expression for Raman intensity, described by Eqn (3)). At high temperature, all states A are excited to states B, and the distribution ratio $B/A \gg 1$, so that the observed intensity at $T = \infty$ is determined only by I_B . From Eqn (5), one can obtain also Eqn (6):

$$-\Delta E/(kT) = \ln \frac{I_A - I_{\text{exp}}/n}{I_A - I_B} \quad (6)$$

The temperature dependence of I_{exp}/n shows saturation at low and high temperatures (Fig. 8(a)), which corresponds to I_A and I_B , respectively. The energy gap ΔE calculated from Eqn (5) is $\sim 100\text{ cm}^{-1}$ within the experimental error for three of the four modes (with the exception of the mode at 140 cm^{-1}) (Fig. 8(b)). This value is too small compared to the expected height of the barrier between the potential walls of the threefold symmetric top ($\sim 2000\text{ cm}^{-1}$), and too large for the splitting of the ground and excited torsion states which the quantum mechanical tunnelling through the barrier could account for ($\sim 1\text{ cm}^{-1}$). The energy ΔE , identical for the different tops, CH_3 and NH_3^+ , is of the same order of magnitude as the wavenumber of the translational and rotational lattice modes. Thus, the expansion of the intermolecular hydrogen bonds as well as the methyl environment contacts as a consequence of the thermally generated lattice vibrations is presumably the main reason of the decrease in the Raman intensity of the torsional modes.

The intensity of the COO^- torsional vibration decreases on heating much more rapidly (and practically down to zero) than those of the $-\text{CH}_3$ and NH_3^+ torsion modes. One can suppose that the effective charges of the oxygen atoms may change with increasing temperature, as a result of the shift of the hydrogen atom H^* in the direction from N^* to O^* along the $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bond.

Conclusion

A detailed analysis of the effect of temperature not only on the band wavenumbers but also on the band intensities and half-widths in the high wavenumber^[21] and in the low wavenumber (this work) range has revealed very interesting features in the temperature dependence of the Raman spectra of L-alanine single crystals. These new experimental findings and the previous observations on various anomalies in response of the crystalline L-alanine to variations in temperature can be interpreted in a self-consistent way, assuming that the $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bonds within a chains of zwitterions in the crystal structure have unusual properties, as compared with those of 'ordinary' hydrogen bonds between the chains. An $\text{N}^*-\text{H}^*\cdots\text{O}^*$ hydrogen bond is formed between the NH_3^+ and the COO^- groups after a proton moves from the COOH -group of one amino acid molecule in a chain to the NH_2 -group of another molecule, and zwitterions are formed instead of a neutral molecules. The mechanism of its formation makes the properties of the $\text{N}^*-\text{H}^*\cdots\text{O}^*$ bond unusual as compared to other 'ordinary' $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, which are not related to a proton transfer from one species to another by their origin: when an 'ordinary' hydrogen bond expands (the distance between a donor N and an acceptor O increases), the proton shifts in the direction of the donor atom, so that the N-H distance decreases, and the wavenumber of the NH stretching vibration increases. This does not hold, however, for an $\text{N}^*-\text{H}^*\cdots\text{O}^*$ bond. In a hypothetical extreme situation, when the distance between

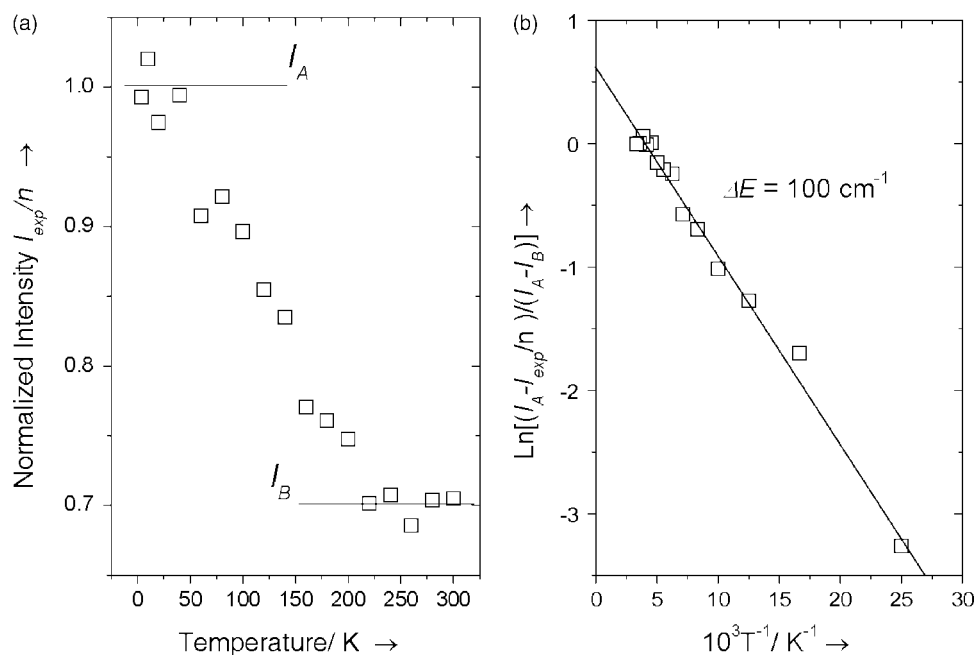


Figure 8. The numerical modelling of intensity decrease of the mode at 297 cm^{-1} (see text). (a) experimental intensity divided by thermal population of mode 297 cm^{-1} ; (b) logarithm $(I_A - I_{\text{exp}}/n)/(I_A - I_B)$ versus inverse temperature (see Eqn (5)).

the molecules in a chain is large enough to exclude the interaction between the alanine molecules in a chain, the H^* atom would be back at the carboxylic group, and the molecules would be no longer zwitter ionic ($\text{NH}_2\text{--CH}(\text{CH}_3)\text{--COOH}$), i.e. on the extension of a $\text{N}^*\text{--H}^*\cdots\text{O}^*$ bond, the proton would move from N^* to O^* . By compressing or expanding the structure, one can influence on the shift of the H^* atom along the $\text{N}^*\text{--H}^*\cdots\text{O}^*$ bond. The inequivalence in the C–O bond lengths in the carboxylic group may serve as a measure of the completeness of the H^* -atom transfer between the two alanine molecules within a chain. Interestingly, in contrast to some other crystalline amino acids, in L-alanine the two C–O bonds in the COO–group are not absolutely equal, which was confirmed also by several independent X-ray and neutron diffraction studies, including very precise ones.^[1–3,26–28] This suggests that the proton transfer from the COOH–head of one alanine molecule to the NH_2 –tail of another alanine molecule, which results in the formation of zwitterions, is not absolutely complete at any temperature at ambient pressure (recently it was shown that the two C–O bonds in L-alanine become almost equal at high pressure, what gives evidence of a more complete H-transfer from the carboxylic group of one molecule to the amino-group of another molecule^[32]).

An important feature of the $\text{N}^*\text{--H}^*\cdots\text{O}^*$ hydrogen bond is that its strength depends to a large extent on the state of the additional hydrogen bonds of N^* and O^* ions with the neighbouring molecules in the structure: as the additional bonds between the chains weaken, the interactions within a chain get stronger and vice versa.^[21] For this reason, the thermal expansion of **a** and **b** lattice parameters in L-alanine crystals provokes a simultaneous contraction of the third parameter **c** along which the head-to-tail chains of zwitterions are directed, and this can explain the negative thermal expansion of L-alanine along this axis.^[1–3] There are therefore two opposite trends in the structural strain along the **c**-axis on heating: extension because of the increased amplitudes of the anharmonic thermal vibrations, and contraction because of the strengthening of the $\text{N}^*\text{--H}^*\cdots\text{O}^*$ bonds within a chain

accompanying the weakening of the $\text{N--H}\cdots\text{O}$ hydrogen bonds between the chains. This conflict provokes a series of micro-conformational transitions accompanied by a periodic subtle rearrangement of the hydrogen-bond network, which give rise to the various ‘anomalies’ reported for the response of crystalline L-alanine to variation in temperature.

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