Infrared spectra of the hydrogen bond in pimelic acid crystals: Polarization and temperature effects

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Henryk T Flakus

University of Silesia in Katowice

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Infrared spectra of the hydrogen bond in pimelic acid crystals: polarization and temperature effects

Henryk T. Flakus *, Artur Miros

Institute of Chemistry, University of Silesia, 9 Szkolna Street, Pl-40-006 Katowice, Poland

Abstract

This paper deals with the polarized IR spectra of the hydrogen bond in pimelic acid crystals and their quantitative interpretation. The spectra were measured for the v_{O-H} and v_{O-D} band frequency regions, at temperatures of 298 and 77 K, for the 'alpha' crystalline form of pimelic acid. Two kinds of transmission spectra were obtained, for the beam perpendicular to the two different crystalline faces: 'ac' and 'ab'. The spectra of the hydrogen and the deuterium bonded systems were quantitatively reproduced, with sufficient accuracy, on the basis of the 'strong-coupling' model, assuming the $(COOH)_2$ cycles to be the structural units responsible for the basic spectral properties. It was found that the spectra could be reproduced only, when assuming spectral activity in the IR of the totally symmetric proton stretching vibrations in centrosymmetric cyclic dimers of hydrogen bonds. The polarization effects in the crystal spectra were interpreted as directly connected with the hydrogen bond orientation in the crystal. However, in the pimelic acid crystalline spectra there were not observed another polarization effects characteristic for another carboxylic acid crystals, depending on differentiation of the long- and of the short-wave branch properties of each of the v_{O-H} and v_{O-D} bands. The temperature variation only affect the intensity ratio between the lower- and the higher-frequency branches of the v_{O-H} and v_{O-D} bands. These spectral effects were ascribed to less strained hydrogen bond structures in the pimelic acid lattices of the 'alpha' crystalline form and a relatively low concentration of defects in the lattices. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen bond; Molecular crystals; Polarized IR spectra; '*Strong-coupling*' model; Band shape analysis; Model calculations; Linear dichroism effects; Temperature and isotopic effects

1. Introduction

A particular value of IR spectroscopy in hydrogen bond research results from very spectacular spectral effects accompanying hydrogen bond formation in molecular systems. The most important effects are observed in the frequency ranges of the proton stretching vibration bands v_{X-H}, corresponding to the stretching motions of the X–H bonds in the X–H … Y hydrogen bridges [1–3]. Very often the bands exhibit fine structure elements, qualitatively resembling by shapes perturbed *Franck–Condon* progressions from electronic spectra. The latter effects used to be observed in the spectra of medium strength hydrogen bonds [1–3].

Resolving of the v_{X-H} and v_{X-D} band fine structures is the way to understand the hydrogen bond dynamics and by this the very nature of the hydrogen bond. Theoretical models elaborated during the recent 60 years aimed to explain the above listed spectral phenomena considered to be the attributes of hydrogen bonds. So far, the so called '*strong-coupling*' model, based on anharmonic coupling mechanisms between hydrogen bond normal vibrations of different frequencies, provides the only fully quantitative approach, allowing for numerical reconstitution of the even well-developed v_{X-H} and v_{X-D} sharp band fine structures [4–7]. In spite of its relatively simple formalism, the theory succeeded in the quantitative description of the single hydrogen bond system spectra, as well as of the spectra of the hydrogen bond dimers in the gaseous or in the liquid phase [8–10]. In several cases successful efforts were undertaken to quantitatively interpret the IR spectra of the hydrogen bonded molecular crystals, the polarized spectra included [11–16].

In this respect the more recent '*strong-coupling*' model seems to even predominate over the latest and more sophisticated theory, elaborated for interpretation of the vibrational spectra of hydrogen bonds, mainly weak hydrogen bonds, the so called '*relaxation*' or the '*linear response*' theory [17]. In the case of polarized spectra, the '*strong-coupling*' model, although not considering some basic details of the v_{X-H} band forming mechanisms included in the '*relaxation*' theory, however, allows for a quantitative theoretical description of spectral properties of mutually interacting hydrogen bonds within one unit cells [11–16,18]. So far no reports are known, concerning a fully quantitative interpretation of experimental polarized spectra of hydrogen bonded crystals, in the limits of the '*relaxation*' theory [17]. Only recently first efforts were published first to include the *Davydow couplings* in the limits of the '*relaxation*' theory formalism [19–21].

For oriented hydrogen bonds in a crystal, measurements of the polarized spectra can provide a wealth of information about complex fine structures of the v_{X-H} and v_{X-D} bands, the transition moment directions and energy levels of the hydro-

gen bond systems A few recent studies in that area provided a number of new and quite unexpected, highly abnormal polarization, temperature and isotopic effects in the spectra of the hydrogen bonds for a number of model crystals, in the v_{X-H} and v_{X-D} bands. One of the new effects is the breaking of the vibrational dipole selection rules in the IR, for the centrosymmetric dimers of the hydrogen bonds, in the frequency range of the v_{X-H} and v_{X-D} bands [22]. Another one is the '*self-organization*' of the proton and deuteron mixtures in the hydrogen bond systems in molecular crystals [23], or the so called '*long-range*' H/D isotopic effects in the vibrational spectra [24]. Therefore, it seems that those studies are still in the stage of collecting experimental data and of making attempts to partially describe the effects. Therefore, those effects seem to still become a challenge to the contemporary theory of the vibrational spectra of hydrogen bonds.

Carboxylic acid crystals, with centrosymmetric cyclic dimers of hydrogen bonds O–H … O, make particularly interesting model systems for further studies on the crystalline infrared polarized spectra of the hydrogen bond. It is because the spectral properties of the diverse crystalline systems can be confronted with the spectral properties of the carboxylic acid dimers formed in the gaseous phase, when the spectra of the dimers were analyzed in details by the subsequently proposed theoretical models [2–5,8–10]. The dicarboxylic acid molecules form well defined crystalline phases even at the room temperature, in contrast to monocarboxylic acids.

Among the carboxylic acid crystals, those with odd numbers of carbon atoms in a molecule have relatively low melting points compared with the even carbon atom dicarboxylic acids. This is important, when single crystals are to be grown from the melt without thermal decomposition. Also the mutual orientations of neighbouring $(COOH)_2$ cycles are not parallel for the odd series. This fact is expected to be a source of some dichroic effects in the crystal spectra.

In this paper we present polarized single-crystal IR spectra of pimelic acid (HOOC-$(CH_2)_5$-COOH) and its deuterium derivative and their

theoretical interpretation. The molecules of pimelic acid still contain relatively low numbers of the skeleton hydrogen atoms, in relation to one $(COOH)_2$ cycle, when compared with the other, longer carbon chain molecules of the series of compounds, so the v_{C-H} bands should not considerably influence the v_{O-H} band contours.

2. Pimelic acid crystal

In the literature two forms of pimelic acid crystals are described: the α and β forms. The high temperature α form crystallizes in $P2_1/c = C_{2h}^5$, (characteristic for dicarboxylic acids, with odd numbers of carbon atoms) [25–29]. Identity periods for the 'α' form crystals are: $a = 5.68(5)$ Å, $b = 9.71(2)$ Å, $c = 22.45(10)$ Å, $\beta = 136.8(5)°$, ($Z = 4$). [25–29]. The H-bonded molecules of pimelic acid form infinitely long chains in the crystal, which are approximately parallel to the 'c'-axis. In each unit cell there are two kinds of crystallographically non-equivalent centrosymmetric $(COOH)_2$ cycles [29]. Rapidly '*frozen*', the high temperature form α remains stable for more than 2 weeks at room temperature [28].

At 75°C the 'α' form undergoes a phase transition to the β form ($I2_1/c = C_{2h}^6$, $a = 9.84$ Å, $b = 4.89$ Å, $c = 22.43$ Å, $\beta = 130.8°$, $Z = 4$) [25–29].

3. Experimental

Pimelic acid (Sigma-Aldrich) was used without further purification. Pimelic acid crystals were obtained by melting solid samples between two CaF_2 windows, followed by very slow cooling of the melt, while the CaF_2 plates were pressed tightly. The freshly obtained crystals were identified as the α-form by X-ray [30]. In the course of growing between the CaF_2 plates, the crystals develop two kinds of the crystalline planes: 'ac' (010) and 'ab' (001). Under these conditions, very thin crystals, with absorbances < 0.5 were obtained. One of them, developing the 'ac' face had a form of plates, whereas the other one, with the

'ab' plane developed, had the form of flattened needles (oblong plates). The two kinds of monocrystals were recognized by the X-ray. Monocrystalline fragments, suitable for our spectroscopic studies (i.e. having dimensions of at least 2×2 mm), were selected from a polycrystalline mosaic and then spatially oriented under a polarization microscope. For the monocrystalline areas selected by using a diaphragm (with a hole diameter 1.5 mm), the polarized absorption spectra were recorded in transmission with 2 cm^{-1} resolution. Measurements were accomplished at ambient and at liquid nitrogen temperature (77 K), with normal incidence to one of the selected crystalline faces 'ac' or 'ab'. The polarized spectra were measured for two forms of the pimelic acid single crystals and for two orientations of the electric field vector 'E'. For the first form, with developed 'ac' face spectra were measured for 'E' parallel to the 'c'-axis and also parallel to the '$a*$'-axis of the lattice ('$a*$' denotes the vector in the reciprocal lattice). For the other crystalline form, with developed 'ab' face, the spectra were obtained for 'E' parallel to 'a' and also for 'E' parallel to 'b'. For each crystal form, as well for each isotopomer, the measurements were repeated for several crystals.

The deuterium derivative of pimelic acid was obtained by evaporating the pimelic acid solution in D_2O under reduced pressure.

The IR spectra were recorded with the Nicolet Magna 560 FT-IR spectrometer. A good quality spectrum was obtained after 100–200 scans only.

4. Results

We started with the spectra of the polycrystalline isotopomers in KBr disks. The spectral changes relevant for the following discussions are shown in Fig. 1.

Fig. 2 shows polarized single-crystal spectra of pimelic acid, measured at room temperature (incidence perpendicular to the 'ac' plane) and Fig. 3 presents the low-temperature polarized spectra of the same crystal.

In Fig. 4 the low-temperature polarized spectra

of the pimelic acid crystal, taken for the '*ab*' crystalline face are shown. The room-temperature spectra do not considerably differ from them.

Isotopic effects in the pimelic acid spectra are presented for a crystal having ca. 95% of the protons replaced by deuterons. The spectra cover a wide frequency range, including the ν_{O-D} band, but also the '*residual*' ν_{O-H} band, as well as the ν_{C-H} bands. Fig. 5 shows the polarized room-temperature spectra of the deuterium derivative crystal, ('*ac*' face) and Fig. 6 the low temperature spectra of the same crystal.
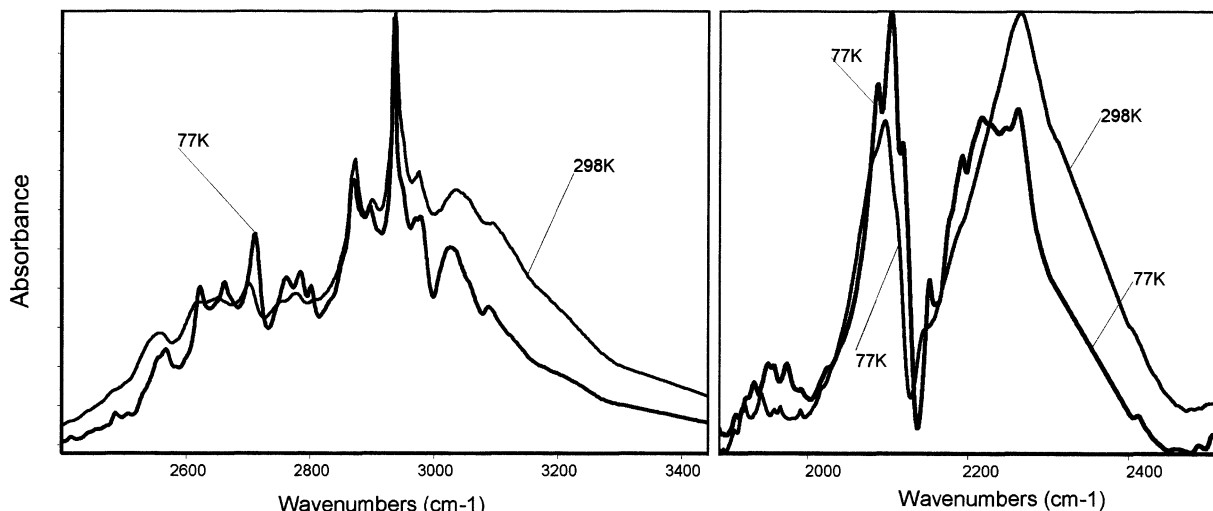

Fig. 1. The IR spectra of pimelic acid polycrystalline samples in the KBr pellets: (a) The ν_{O-H} and ν_{C-H} band frequency ranges from the spectra of $CH_2(CH_2CH_2COOH)_2$; (b) The ν_{O-D} band from the IR spectra of the deuterium derivative of pimelic acid.
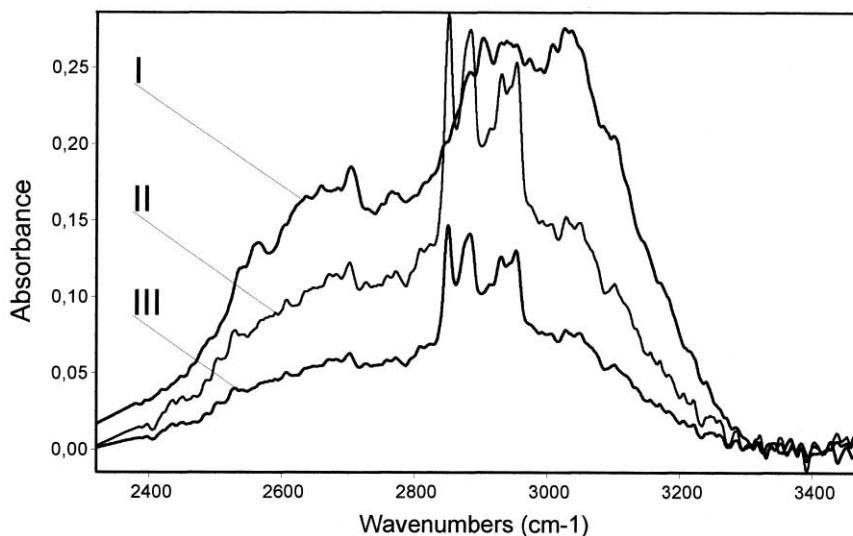

Fig. 2. The polarized spectra of the pimelic acid crystal of the '*Alpha*' form, measured at room temperature in the ν_{O-H} band frequency range. The IR beam of normal incidence with respect to the '*ac*' plane was used. The spectra were obtained for the two orientations of the electric field vector '*E*': (I) *E* parallel to the '*c*'-axis; (II) *E* perpendicular to the '*c*'-axis (parallel to the '*a**'-axis); (III) Spectrum (II) renormalized to full scale with spectrum (I).
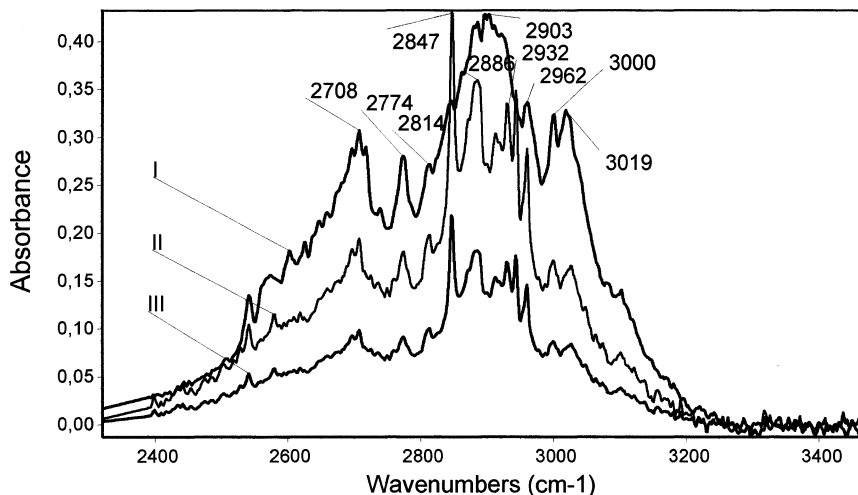
Fig. 3. The polarized spectra of the pimelic acid crystal of the '*Alpha*' form, measured at the temperature of liquid nitrogen, at the frequency range of the v_{O-H} band. Other experimental conditions and the way of presentation of the spectra were identical with those given for Fig. 2.
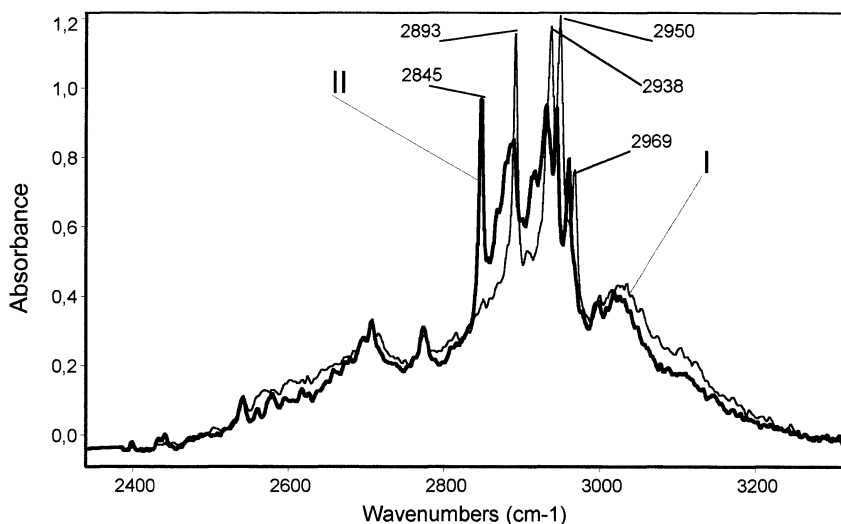

Fig. 4. The polarized spectra of the pimelic acid crystal of the '*Alpha*' form, measured at 77 K, when the IR beam of normal incidence with respect to the '*ab*' crystalline face was used. The spectra were measured for the two orientations of the electric field vector '*E*': (I) *E* parallels to the '*b*'-axis; (II) *E* perpendicular to the '*b*'-axis (parallel to the '*a*'-axis).

Low-temperature spectra of the pimelic acid crystal ('*ab*'-plane) of the D-form are given in Fig. 7.

The spectra from Figs. 1, 5–7 demonstrate the relatively small impact of the v_{C-H} bands onto the v_{O-H} band contour.

5. Discussion

5.1. Model calculations of the v_{O-H} and v_{O-D} band shapes

The v_{O-H} and v_{O-D} band shapes in the spectra

of crystalline pimelic acid are similar to those of other carboxylic acid crystals [16,31,32], and to the gas-phase spectra of hydrogen bonded carboxylic acid dimers [8–10]. This suggests similar structural units, i.e. associated carboxyl groups, in all the cases being the source of the spectral properties of these systems. The hydrogen bonds in the $(COOH)_2$ cycles, treated as centrosymmetric hydrogen bond dimers, can be considered to be the simplest model of the pimelic acid crystalline lattice for interpretation of the spectra. We assume the same spectral properties for the two non-equivalent $(COOH)_2$ cycles [29].
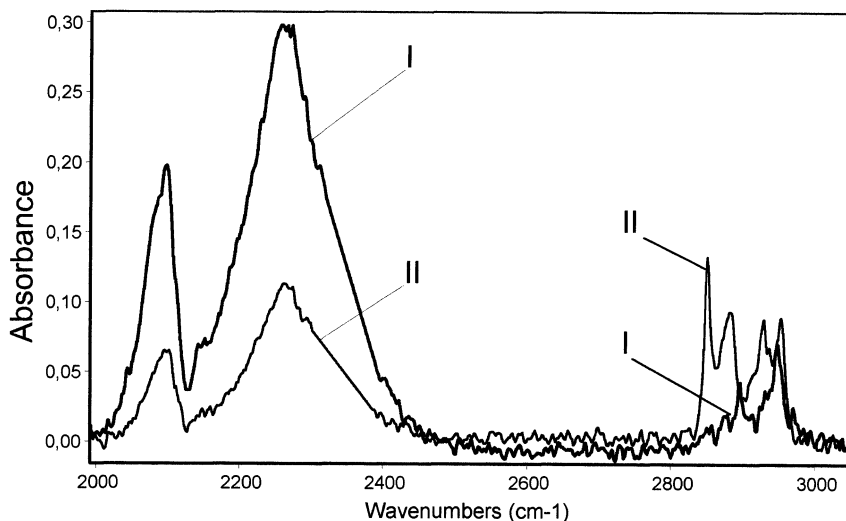
In the limits of the 'strong-coupling' model

Fig. 5. The polarized spectra of the deuterium substituted pimelic acid crystal of the 'Alpha' form. Room temperature, the 'ac' crystalline face developed, ca. 95% of D-atoms. Experimental conditions and presentation of the spectra identical with those given for Fig. 2.
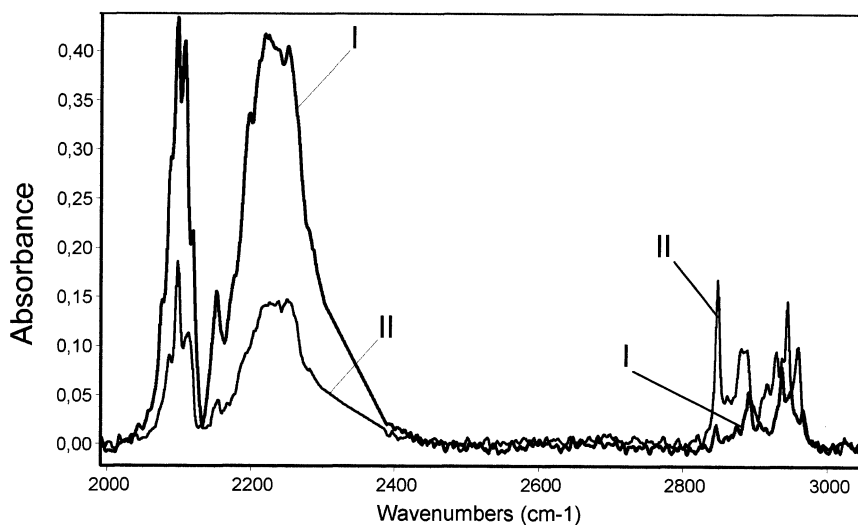

Fig. 6. The polarized spectra of the deuterium substituted pimelic acid crystal of the 'Alpha' form, 77 K. The other experimental conditions and presentation of the spectra identical with those given for Fig. 5.
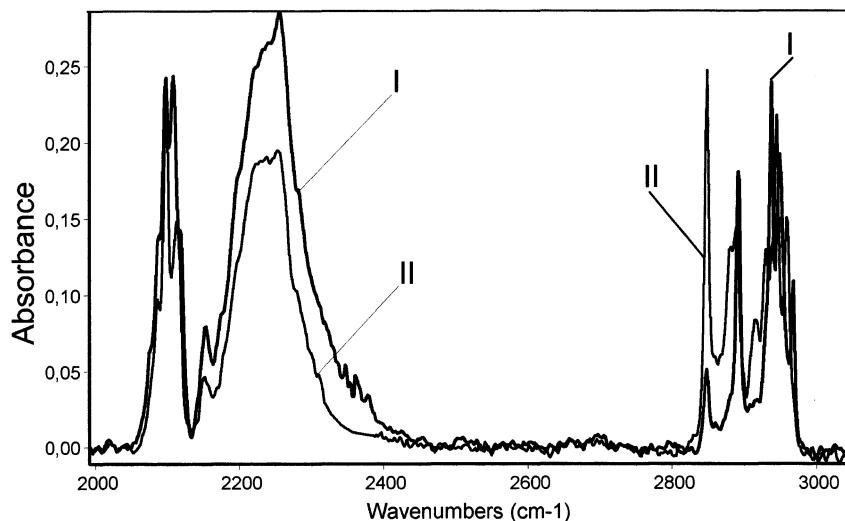
Fig. 7. The polarized spectra of the deuterium substituted pimelic acid crystal of the '*Alpha*' form, 77 K. The '*ab*' crystalline face developed, ca. 95% of D-atoms. The other experimental conditions and the way of presentation of the spectra identical with those given for Fig. 4.

[4,5,11–16] the IR spectra of the dimeric systems of the mutually interacting hydrogen bonds can be reproduced numerically by model calculations. The theoretical spectra depend on the following system of coupling parameters, each having precisely defined physical senses:

1. The distortion parameter of hydrogen bond b_H, describing a change in its equilibrium geometry, upon excitation of the proton stretching vibrations v_{O-H}. For the corresponding deuterium bonds, the theory predicts a distortion parameter $b_D = b_H/\sqrt{2}$ [4,5].
2. The resonance interaction parameters, C_0 and C_1, represent vibrational resonance interactions between the hydrogen bonds in a dimer [4,5,12]. Deuteration effect — diminution of the C_0 and C_1 parameter by 1.0 to times [4,5,12].

In Fig. 8 one can see the theoretically derived spectra of pimelic acid crystals, quantitatively reproducing the v_{O-H} band contour from the crystal spectra.

Our calculations suggest that the band is a superposition of two component bands, each of a different origin. The component bands are assigned transitions to the excited states of the proton vibrations in the centrosymmetric cyclic dimer of the different symmetries. The so-called

'Plus' band [4,5,12], the shorter-wave branch of the experimental v_{O-H} band, is due to the symmetry allowed excitation of the *ungerade* proton vibration in the centrosymmetric dimer of hydrogen bonds. In the experimental spectra it corresponds to the frequency range between 2800 and 3200 cm^{-1}. This part of the observed spectra is to some extent perturbed by the v_{C-H} bands (between 2900 and 3000 cm^{-1}).

When quantitatively interpreting the crystal spectral properties we introduced, however, an unorthodox assumption, concerning breaking of the vibrational dipole selection rules in the IR for the centrosymmetric dimers of the hydrogen bonds. The *gerade* proton vibrations in centrosymmetric dimers of the hydrogen bonds become spectrally active in the IR thanks to a vibronic promotion mechanism [22]. This mechanism can be considered to be a kind of reversion of the familiar *Herzberg–Teller* mechanism from the electronic molecular spectroscopy. Without making the assumption concerning spectral activity in the IR of the totally symmetric proton vibrations in the centrosymmetric dimers, the pimelic acid crystal spectra (particularly the longer-wave part of the v_{O-H} band) cannot be, even approximately, reproduced in the way of the

model calculations. That part of the spectrum (between 2400 and 2800 cm^{-1}) is satisfactorily reproduced by the dimeric 'Minus' band, ascribed to the forbidden vibrational transition [4,5,12,22]. The longer-wave part of the v_{O-H} band reminds by shape a non-regular *Franck–Condon*-type progression. This non-regularity effect cannot be reproduced by our calculations in the limits of our simple model. Such a spectral effect, however, was not observed in the spectra of other homologous molecular systems — adipic and glutaric acids [16,31,32], for which the longer-wave branch of the band was represented by a regular *Franck–Condon*-type progression of a low-frequency.

Fig. 9 shows the results of the model calculations performed to quantitatively reconstruct the v_{O-D} band contour of the crystalline spectra.

These results suggest a generally similar mechanism of the v_{O-D} band generation as for the v_{O-H} band. In spite of its very simple fine structure, the v_{O-D} band is also considered to be of a complex nature, due to contributions of two component bands 'Plus' and 'Minus' [4,5,12,22]. Our calculations also yields the distortion parameter ratio b_H/b_D considerably higher than $\sqrt{2}$, predicted by the simplest version of the '*strong-coupling*' theory [4,5]. Such a value was deduced for isolated hydrogen and deuterium bond systems. In the crystal phase couplings between proton or deuteron stretching vibrations and low energy lattice vibrations can strongly influence the distortion parameter values. The b_H/b_D ratio found is most likely a result of a more effective coupling of the deuteron vibrations with lattice phonons, when compared with the proton vibration cases.
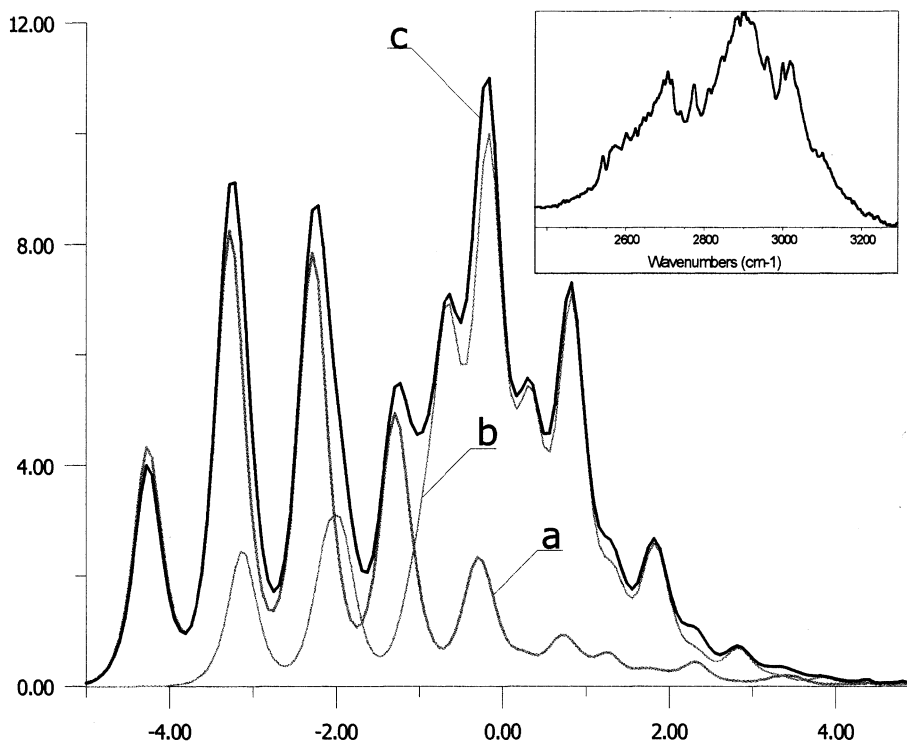

Fig. 8. Numerical reproduction within the limits of the dimeric model of the v_{O-H} band shape at low temperature from the pimelic acid crystal spectra: (a) The '*Plus*' band; (b) The '*Minus*' band; (c) The superposition of the '*Plus*' and the '*Minus*' bands, reconstituting of v_{O-H} band shape with **E** parallel to the '*c*'-axis. The coupling parameter values: $b_H = 1.5$, $C_0 = 1.0$, $C_1 = -0.3$. Transition energies were calculated with respect to the center of gravity of the pimelic acid monomeric O–H ... O bond spectrum. Coupling parameters and transition energies are in the $v_{O ... O}$ vibration quantum units. On the right upper edge of the figure is the v_{O-H} experimental band contour.
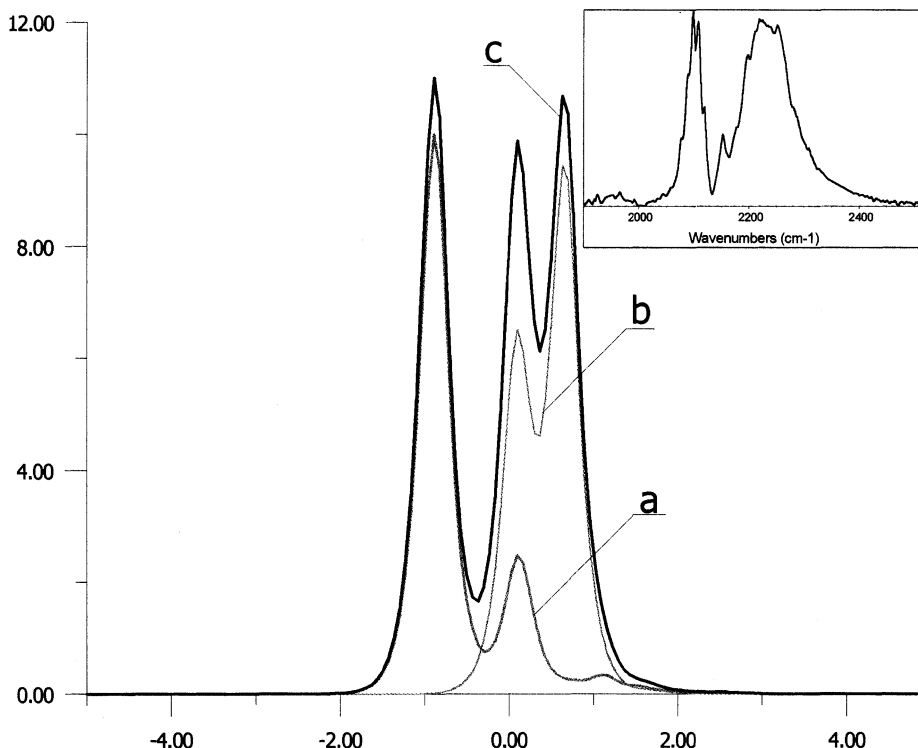
Fig. 9. Numerical reproduction of the low temperature ν_{O-D} band shape, from the D-pimelic acid crystalline spectra in the dimeric model approximation: (a) The '*Plus*' band; (b) The '*Minus*' band; (c) The superposition of the '*Plus*' and the '*Minus*' bands, reconstituting of ν_{O-D} band shape with $\boldsymbol{E}$ parallel to the '*c*'-axis. The coupling parameter values: $b_D = 0.4$, $C_0 = 0.5$, $C_1 = -0.3$. Transition energies were calculated with respect to the center of gravity of the pimelic acid monomeric $O-D \ldots O$ bond spectrum. Coupling parameters and transition energies are in the $\nu_{O \ldots O}$ vibration quantum units. On the right upper edge of the figure is the ν_{O-D} experimental band contour.

5.2. Polarization effects in the spectra

A good correlation between the basic spectral properties of the crystals and the lattice symmetry is found. As the molecular chains spread out parallel to the '*c*'-axis ([001]) of the crystalline lattice, the O–H bonds, seen along [010] (the '*b*'-axis), are also almost parallel to [001] (the '*c*'-axis) [25–29]. This means that the transition moments for the ν_{O-H} vibrations have a strong component as along [001]. Thus the polarized ν_{O-H} band component, with $\boldsymbol{E}//c$, is much more intense when compared with the other component with $\boldsymbol{E}//a^*$ (Figs. 2 and 3). This band remains almost non-influenced by the ν_{C-H} bands. In the latter case in the spectrum relatively low-intensive ν_{C-H} bands appear, as the beam of the normal

incidence with regard to the '*ac*' plane of the lattice excites the C–H bond stretching vibrations.

At incidence of the beam normal with respect to the '*ab*' plane (Fig. 4) the vibrations ν_{C-H} are to be excited, as these normal vibrations have the transition moment strongest components in the '*ab*' plane [25–29].

When carefully analyzing the spectra from Figs. 2 and 3, however, one can find a lack of another kind of polarization effect, recently identified in the spectra of carboxylic acid crystals [16,31,32]. That kind of polarization effect (effect of the '*second kind*') used to be much less pronounced, when compared with the much stronger polarization effects resulting solely from molecular orientations in the lattice. The latest effect depends on a noticeable mutual differentiation of the polar-

ization properties of the two spectral branches of the v_{O-H} band — of the longer- and the shorter-wave branch ones. It can be found relatively easily that the component band intensity ratio remain almost unchanged in the entire v_{O-H} band frequency range of the pimelic acid crystalline spectra (after subtraction of the v_{C-H} bands from the weaker polarized component of the spectrum).

This observation remains in an essential discrepancy with the analogous spectral properties of other crystalline systems, (adipic acid [31,33], glutaric acid crystal [16]). The analyzed polarization effects in the pimelic acid crystalline spectra seem to indicate a negligible concentration of a particular type of structural defect, i.e. random hydrogen bond deformations in the cyclic systems, particularly of the *out-of-plane* random bending '*up*' or '*down*', with respect to the cycle planes. Such defects, generated during crystallization from the melt in the non-equilibrium conditions, were considered recently to be responsible for the polarization effects of the '*second kind*' [13]. Similar kinds of polarization effects, as those found in the v_{O-H} band range, can be also measured for the v_{O-D} band range, in the spectra of the deuterated compound crystals.

For the v_{O-D} bands some effects of spectral line splitting can be recognized. The narrow and intensive spectral line placed near 2100 cm^{-1} manifests

a doublet structure (10 cm^{-1} split), with the two components strongly differing by their polarization properties. This splitting most likely results from very weak exciton couplings [33,34] between the non-equivalent hydrogen bond cycles in each unit cell. In the other v_{O-D} band fragments similar splitting effects are hard to be identified, probably due to the blurring of the component lines. Perhaps a similar situation might take place for the v_{O-H} band range due to the component band lines strong diffusion.

All the polarization effects seem to prove that the $(COOH)_2$ cycle units as the source of the crystalline spectral properties. With no correlation field effects pronounced, the *oriented-gas-model* seems to be sufficient for interpretation of the spectra. On the other hand, such an approach seems to be the only way to quantitatively interpret the crystal spectra. For this kind of lattice (with two independent $(COOH)_2$ cycle systems and with $Z = 4$), fully quantitative interpretation of the spectra would be a much more complex problem.

6. Temperature effects

The temperature-induced changes rather depend on almost proportional changes of the inten-
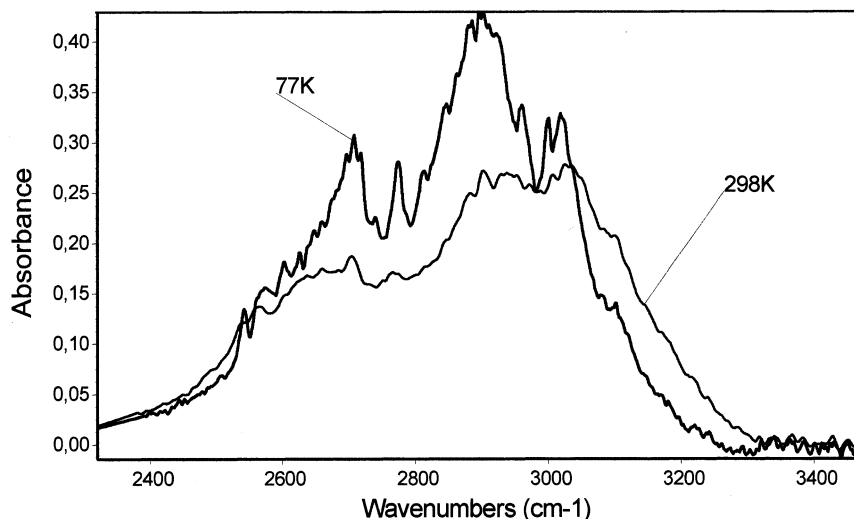

Fig. 10. Temperature impact onto the most intensive component of the v_{O-H} band. The '*ac*' crystalline face, $\boldsymbol{E}//c$. Common scale.

sity in the entire frequency ranges of the v_{O-H} and v_{O-D} bands. Particularly, there are no noticeable changes in the intensity ratios between the longer- and the shorter-wave branches of these bands (Fig. 10).

In each temperature the integral intensity ratio of the longer- to the shorter-wave branch of the v_{O-H} band strongest component is equal to 0.6.

A quite different effect was found in the spectra of the glutaric and the adipic acid crystals [16,31,32]. It seems that lack of such temperature effects for pimelic acid could be connected with a more pronounced stable, relaxed structures of the O–H ... O bonds in the crystalline lattice of pimelic acid, when compared with the lattice properties of the other recently investigated dicarboxylic acid crystals [25–29]. Therefore, no strong spectral effects were noticed, ascribed to the thermal averaging of the hydrogen bond structures. In such a way temperature should not essentially effect the forbidden transition promotion mechanisms, responsible for generation of the longer-wave branches of the v_{O-H} and v_{O-D} bands. For the 'α' phase, stable at room temperature, the lattice is most likely well relaxed, although the hydrogen bonds were found noticeably bent [25–29].

7. Conclusion

The reported studies have proved that the centrosymmetric dimers of the O–H ... O hydrogen bonds, formed in the $(COOH)_2$ cycles, are the source of the basic pimelic acid crystal spectral properties. The crystal spectral properties most probably result from relaxed crystalline lattice structures of pimelic acid, with low concentration of structural defects in the cycles. Relatively small line splitting effects, observed in the spectra of the deuterium isotopomer crystal, prove very weak correlation couplings between the different $(COOH)_2$ cycles in crystalline unit cells of pimelic acid.

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