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Raman Tensors of Some Betaine – Acid Crystals: Relation Between Betaine Carboxylate Group Scissoring Mode and Hydrogen Bonds*

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The hydrogen bonds of different strength are formed to the betaine carboxylate group in the crystalline complexes of this amino acid with water, boric acid, orthoarsenic acid and orthophosphoric acid. Their properties are characterized by the Raman tensor calculated for the betaine carboxylate group scissoring modes. The values and orientations of its $\alpha'(\mathrm{R})_{zz}$ principal component strongly depend on the betaine – acid hydrogen bond properties. These results are related to the proton position shift in the considered complexes: from the acidic part of the hydrogen bridge to the betaine carboxylate group.

Key words: betaine – acid crystals, hydrogen bond, Raman tensor, carboxylate group, scissoring mode

The trimethylammonioacetate or shortly betaine, $(CH_3)_3N^+$-CH_2-COO^-, represents the family of permanent zwitterions, $(R_1R_2R_3)N^+$-R_4-COO^-, usually described as betaines. These compounds, owing to their polar carboxylate groups, form hydrogen bond networks with a variety of organic and inorganic acids. The resulting crystals are frequently investigated because of their interesting properties, *e.g.* phase transitions with ferroelectric, antiferroelectric and ferroelastic behaviour as well as the phases with commensurate and incommensurate superstructures [1–4]. Additionally, the betaines are important in many living systems as methyl transfer agents [5], osmoprotectors and osmoregulators [6].

Recently we have presented the classification method of the betaine hydrogen bonds based on X-ray, vibrational and ^{13}C NMR parameters [7]. On this basis five categories of the betaine – acid complexes and their hydrogen bonds are described: (1) MO – the molecular complexes with the bonding protons are not transferred to the betaine; (2) IP – the hydrogen bonded ion pairs with the bonding proton at the betaine oxygen atom; (3) BHB – the homoconjugated betaine complexes with the bonding proton at the central region of the hydrogen bonds; (4) PPD – the MO, IP and BHB complexes with the bonding proton position disorder and (5) LBHB – the PPD complexes with low barrier hydrogen bonds.

In this contribution we present a method of the Raman tensor calculations for chosen vibrations of the betaine complexes as well as the possibilities of its interpretation in terms of the betaine hydrogen bonds properties.

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* Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

EXPERIMENTAL

The Raman spectroscopic data for the Raman tensor calculations were taken from [8–11]. The single crystal samples of cubic shape with their edges parallel to the principal optical directions, *X*, *Y* and *Z*, were prepared for all the systems considered by us. They were oriented by means of the polarizing microscope and using the X-ray method. In all the cases six components of the Raman spectra, namely the *XX*, *YY*, *ZZ*, *XZ*, *YZ* and *XY* ones, were recorded by JOBIN YVON Ramanor U-1000 spectrometer in the wave number region of 3600–10 cm^{-1}, at room temperature and with 1 cm^{-1} resolution. The 514.532 nm line of the Ar^+ ion laser was used as the excitation source. The Raman tensor calculations were performed by means of the computer program prepared by Jan Baran. See below for details of this computational procedure.

RESULTS AND DISCUSSION

The Raman tensor calculation: The Raman tensor considered by us, $\alpha(\mathrm{R})_{ii}$, is defined in a local coordinate system with the principal axes $i = x, y, z$. It was calculated from the intensities of selected Raman bands apparent in the spectra of selected betaine single crystals. These data were related to the crystal coordinate system *X, Y, Z*. The local coordinate system *x,y,z* was determined by two steps:

1. The starting and trial local coordinate system x,y,z was selected by intuition and using the crystal structure data of chosen complex (commonly it is defined by positions of the atoms participating in the vibration considered – see the next part of this discussion).
2. The transformation of the trial system into the local coordinate system with the Raman tensor principal axes (x,y,z → *x,y,z*) was based on the reproduction of the Raman bands intensities. The last procedure is presented below.

The ratios of the Raman tensor diagonal components, $r_1 = \alpha(\mathrm{R})_{xx}/\alpha(\mathrm{R})_{zz}$ and $r_2 = \alpha(\mathrm{R})_{yy}/\alpha(\mathrm{R})_{zz}$, as well as the principal axes *x,y,z* were calculated according to the Tsuboi procedure [12,13]. It is based on trial-and-error reproduction of the Raman band intensities ratios, I_{ZX}/I_{YY}, I_{XY}/I_{YY} and I_{YZ}/I_{YY}, for different orientations between the starting x,y,z and crystal *X, Y, Z* coordinate systems. Finally, these two ratios of the Raman tensor components, r_1 and r_2, were used for the calculation of the "normalized" Raman tensor components, $\alpha'(\mathrm{R})_{xx}$, $\alpha'(\mathrm{R})_{yy}$ and $\alpha'(\mathrm{R})_{zz}$, according to our definitions:

$$\alpha'(\mathrm{R})_{xx} = \frac{100}{3}(1 + r_1 + r_1/r_2) = 100\alpha(\mathrm{R})_{xx}\left(\frac{1}{\alpha_{ii}}\right)_{av} \tag{1}$$

$$\alpha'(\mathrm{R})_{yy} = \frac{100}{3}(1 + r_2 + r_2/r_1) = 100\alpha(\mathrm{R})_{yy}\left(\frac{1}{\alpha_{ii}}\right)_{av} \tag{2}$$

$$\alpha'(\mathrm{R})_{zz} = \frac{100}{3}(1 + 1/r_1 + 1/r_2) = 100\alpha(\mathrm{R})_{zz}\left(\frac{1}{\alpha_{ii}}\right)_{av} \tag{3}$$

where: $\left(\frac{1}{\alpha_{ii}}\right)_{av} = \frac{1}{3}\{[\alpha(\mathrm{R})_{xx}]^{-1} + [\alpha(\mathrm{R})_{yy}]^{-1} + [\alpha(\mathrm{R})_{zz}]^{-1}\}$; $i = x, y$ or z; 100 is the scaling factor of the arbitrary chosen value.

Selection of the betaine complexes and the Raman bands: We have selected the following betaine crystals: 1. betaine – water (1:1); 2. betaine – boric acid (1:1); 3. betaine – orthoarsenic acid (1:1); 4. betaine – orthophosphoric acid (1:1).

In all these complexes the molecular hydrogen bonds to the betaine carboxylate group are formed: $(COO^-)\cdots(H\text{-}A)_n$. Table 1 schematically presents properties of these bonds. Our attention is focused on the strongest (the shortest) hydrogen bonds and their distances as the measure of the betaine perturbation degree: $R(O_1\cdots O)_{min}$.

Table 1. Investigated betaine – acid crystalline complexes, the hydrogen bonds to the betaine carboxylate group and the position of the Raman band derived from the betaine δCOO scissoring mode.

No	Betaine – acid crystal and complex name	Directly bonded betaine – acid entities (B – HA)	[1] Hydrogen bonds to betaine CO_1O_2 group	$R(O\cdots O)$ (Å)	δCOO (cm^{-1})	Ref.
1	Betaine – water (1:1)	B – H_2O	$O_1\cdots H–O$ $O_2\cdots H–O$	**2.783** [2] 2.814	732	14, 8
2	Betaine – boric acid (1:1)	B – H_3BO_3	$O_1\cdots H–O$ $O_1\cdots H–O$ $O_2\cdots H–O$	**2.656** [2] 2.716 2.700	729	15, 9
3	Betaine – orthoarsenic acid (1:1)	B – H_3AsO_4	$O_1\cdots H–O$ $O_2\cdots H–O$	**2.501** [2] 2.565	720	16, 10
4	Betaine – orthophosphoric acid (1:1)	B – H_3PO_4	$O_1\cdots H–O$ $O_1–H\cdots O$ $O_2\cdots H–O$	**2.48** [2] **2.48** [2] 2.593	718	17, 11

[1] The hydrogen bonds or contacts with $R(O\cdots X) > 3.000$ Å are omitted.

[2] The shortest bonds (the strongest bonds) $R(O_1\cdots O)_{min}$ are considered in this contribution.

We have chosen the δCOO symmetrical, scissoring mode of the betaine carboxylate group represented by reasonably intense and separate Raman bands in the 719–730 cm^{-1} frequency range. This vibration is treated by us as the next parameter for measuring of the betaine perturbation degree by the acids considered: water, boric acid, orthoarsenic acid and orthophosphoric acid. The z axis of the starting trial local coordinate system is defined by the vector parallel to the sum of two vectors parallel to the $C–O_1$ and $C–O_2$ bonds (respectively) in the betaine carboxylate group: $-CO_1O_2^-$. The y axis is perpendicular to the z axis and parallel to the COO^- plane, the x axis is perpendicular to the COO^- plane. Tables 2–4 present the results of our calculations: Table 2 – orientations of the calculated local coordinate systems x,y,z; Table 3 – the Raman bands intensity ratios I_{ZX}/I_{YY}, I_{XY}/I_{YY} and I_{YZ}/I_{YY} as well as the Raman tensor ratios $r_1 = \alpha(R)_{xx}/\alpha(R)_{zz}$ and $r_2 = \alpha(R)_{yy}/\alpha(R)_{zz}$; Table 4 – values of the normalized Raman tensor components $\alpha'(R)_{ii}$ calculated by Eq. (1–3). Fig. 1 schematically shows orientations of the principal directions y and z relative to the betaine carboxylate bonds in the **2–4** crystals.

Table 2. Direction cosines of the local coordinates *x,y,z* (the Raman tensor principal directions) in the crystal coordinate system *X,Y,Z* and the φ angle between the *z* principal axis and the carboxylate C–O$_1$ bond direction [1].

Crystal	Direction cosines of the local coordinate system									φ[2] (°)
	$x(X)$	$x(Y)$	$x(Z)$	$y(X)$	$y(Y)$	$y(Z)$	$z(X)$	$z(Y)$	$z(Z)$	
1	0.1363	0.9891	–0.0534	–0.3049	–0.0094	–0.9525	–0.9426	0.1462	0.3002	72
2	1.0000	0.0000	0.0000	–0.0001	–0.5254	0.8507	0.0000	–0.8500	–0.5254	63
3	0.0992	0.0598	0.9932	–0.9647	–0.2393	0.1106	0.2442	–0.9693	0.0340	5.5
4	0.0078	–0.9999	0.0142	0.4366	0.0163	0.8993	–0.8996	–0.0009	0.4368	0

[1] The longest C–O bonds engaged in the strongest hydrogen bonds C–O$_1$···H–O are considered here.

[2] For the crystals **2, 3** and **4** the *z* axis lies in the carboxylate group plane, for the crystal **1** it significantly deviates from this plane (45°).

Table 3. The observed and calculated intensity ratios of the δCOO Raman bands (I_{XX}/I_{YY}, I_{ZX}/I_{YY}, I_{ZZ}/I_{YY}, I_{XY}/I_{YY} and I_{YZ}/I_{YY}) and the calculated ratios of the Raman tensor components ($r_1 = \alpha(R)_{xx}/\alpha(R)_{zz}$ and $r_2 = \alpha(R)_{yy}/\alpha(R)_{zz}$) for different betaine crystals.

Crystal	Observed					Calculated			r_1	r_2
	I_{XX}/I_{YY}	I_{ZZ}/I_{YY}	I_{ZX}/I_{YY}	I_{XY}/I_{YY}	I_{YZ}/I_{YY}	I_{ZX}/I_{YY}	I_{XY}/I_{YY}	I_{YZ}/I_{YY}		
1	0.000	0.417	0.594	0.000	0.000	0.100	0.028	0.003	–10.606	–7.438
2	0.444	0.291	0.000	0.000	0.301	0.000	0.000	0.519	0.519	0.199
3	21.630	4.680	0.248	1.136	0.000	0.096	1.336	0.001	2.818	6.517
4	0.183	1.008	0.157	0.004	0.000	0.134	0.009	0.000	4.007	4.737

Table 4. The normalized Raman tensor components[1] of the δCOO Raman bands for different betaine crystals.

Crystal	$\alpha'(R)_{xx}$	$\alpha'(R)_{yy}$	$\alpha'(R)_{zz}$
1	–273	–191	26
2	138	53	266
3	142	328	50
4	195	231	49

[1] Calculated using r_1 and r_2 values as well as Eqn (1–3).

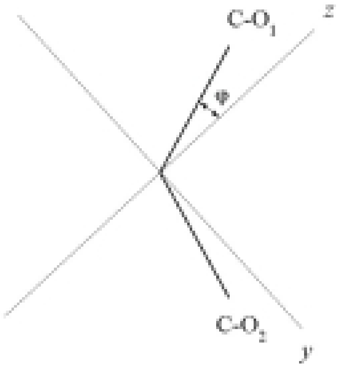

Figure 1. Schematic presentation of the carboxylate C–O$_1$ and C–O$_2$ bonds directions as well as the *z* and *y* principal directions of the Raman tensor calculated for the scissoring mode δCOO of the betaine – acid crystals: **2**, betaine – boric acid (1:1); **3**, betaine – orthoarsenic acid (1:1); **4**, betaine – orthophosphoric acid (1:1). In the betaine – water (1:1) crystal (**1**) the *z* and *y* principal axes significantly deviate from the carboxylate plane.

Relation between the Raman tensor and the betaine hydrogen bonds: The hydrogen bonds in the crystals studied can be treated as the weak, intermediate and strong ones: $R(O\cdots O) \geq 2.7$, $R(O\cdots O) \approx 2.7–2.6$, $R(O\cdots O) \approx 2.6–2.4$ Å, respectively, according to Novak classification [18]. Our attention is focused on the shortest hydrogen bond distances (the strongest bonds) in the complexes considered by us (Table 1): $R(O\cdots O)_{min}$. Among these systems the betaine – water interactions are the weakest and, on the opposite side, the betaine – orthophosphoric acid hydrogen bonds are the strongest. In the last complex the shortest hydrogen bond is characterized by the proton disorder predicted by the X-ray studies [17] as well as by our recent spectroscopic investigations [7].

The hydrogen bond strength variations in the systems studied can be monitored by the Raman tensor calculated for the Raman bands of the δCOO scissoring vibration. These bands, contrary to the symmetric stretching vibration bands of the betaine carboxylate group, are available for a relatively large group of structurally similar betaine crystals [8–11]. We attend to analyse the values of this tensor normalized components (Table 4), as well as the orientations of its principal directions (Fig. 1, Table 2).

The results collected in Table 2 show that in the strong and intermediate betaine complexes (the **4**, **3** and **2** ones) the *z* and *y* principal axes are placed almost exactly in the betaine COO$^-$ plane. The *z* principal direction appears to be especially interesting for two reasons:

1. It is oriented to the betaine C–O$_1$ carboxylate bond, participating in the strongest betaine – acid bond, with different φ angle (Fig. 1). In the betaine – orthophosphoric acid complex the *z* principal axis is parallel to the C–O$_1$ direction, in the betaine – orthoarsenic acid $\varphi = 5°$ and in the betaine – boric acid system it is placed symmetrically between the betaine C–O$_1$ and C–O$_2$ bonds and $\varphi = 63.1°$ (Fig. 1 and Fig. 2).

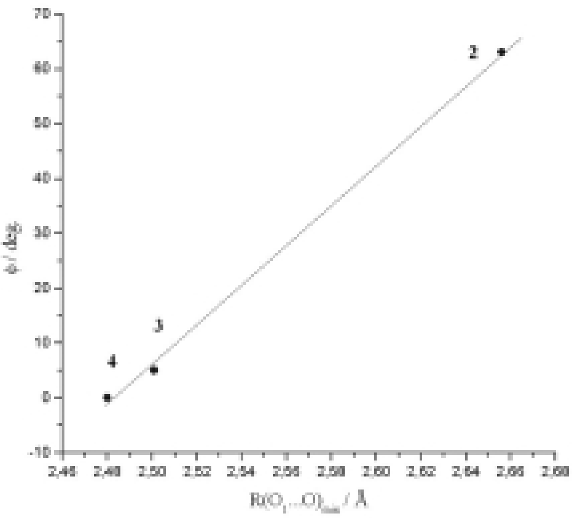

Figure 2. Relation between the shortest hydrogen bond distance $R(O_1\cdots O)_{min}$ and the φ angle between the carboxylate C–O1 bond and the Raman tensor principal z direction in the betaine – acid crystals: **2**, betaine – boric acid (1:1); **3**, betaine – orthoarsenic acid (1:1); **4**, betaine – orthophosphoric acid (1:1). The betaine – water (1:1) crystal (**1**) is not considered here because its z principal direction significantly deviates from the carboxylate plane.

2. The C–O$_1$ carboxylate bond is involved in the strongest betaine – acid hydrogen bonds. Their distances, $R(O_1\cdots O)_{min}$, correlate with the considered φ angle (Fig. 1 and Fig. 2).

We conclude that the strongest betaine – acid hydrogen bond C–O$_1\cdots$H–O is responsible for the z principal axis orientation, relative to the betaine C–O$_1$ direction. This correlation degree strongly increases with the betaine – acid hydrogen bond strength. In the betaine weakest complex, the betaine – water (1:1), the weakest hydrogen bonds are formed and the considered correlation disappears: the z and y axes are at 45° and 11° relative to the COO$^-$ plane, respectively (Table 2).

The real values of the Raman tensor components are not available from our experiments, because their $r_1 = \alpha(R)_{xx}/\alpha(R)_{zz}$ and $r_2 = \alpha(R)_{yy}/\alpha(R)_{zz}$ ratios are only calculated. For this reason the normalized Raman tensor components $\alpha'(R)_{ii}$ were obtained by (1–3) with the multiplier 100 treated as the scaling factor (1–3). Generally, the Raman tensors of different crystals should be characterized by different scaling factors, but we assume its common value for the considered structurally similar systems. According to this simplified assumption, the Raman tensor in the z principal direction, $\alpha'(R)_{zz}$, rapidly decreases, when the shortest betaine – acid hydrogen bond distance $R(O_1\cdots O)_{min}$ decreases (Fig. 3).

This last observation can be related to the betaine hydrogen bonds properties. Raman tensor components $\alpha(R)_{ii}$ are the first derivatives of the molecular polarizability tensor components (α_{ii}), taken with respect to the normal coordinate q of the

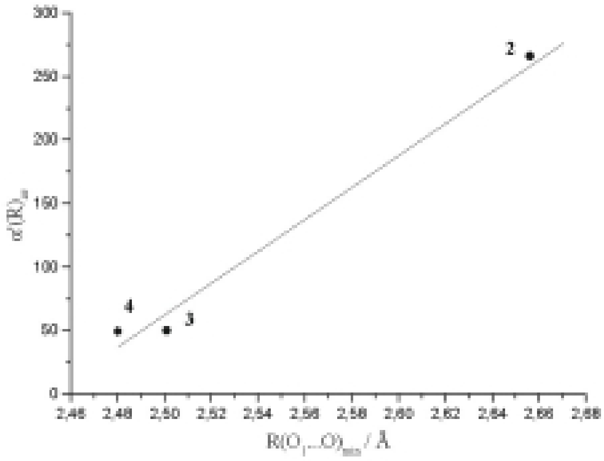

Figure 3. Relation between the shortest hydrogen bond distance $R(O_1\cdots O)_{min}$ and the Raman tensor $\alpha'(R)_{zz}$ component in the betaine – acid crystals presented in Fig. 1.

betaine δCOO scissoring vibration – q is determined by the carboxylate group angle – and calculated for q = 0. Thus, the $\alpha'(R)_{zz}$ quantities presented in Table 4 indicate the sensitivity of the molecular polarizability α_{zz} on q variations, when they are detected in the *z* principal direction. This sensitivity is obviously lower when the stronger hydrogen bonds are formed. For the betaine – water (1:1) crystal, with the weakest hydrogen bonds, the Raman tensor is probably strongly dependent on other factors and its $\alpha'(R)_{zz}$ component does not reveal correlation with this bonds properties (Fig. 2 and Fig. 3).

CONCLUSIONS

1. The method of the Raman tensor calculations, for chosen vibrations in the structurally similar crystalline complexes, is presented. This procedure was used to describe the normalized Raman tensor in selected betaine – acid crystals: values of its principal components $\alpha'(R)_{ii}$ as well as the orientations of its principal axes. These calculations were performed for the scissoring vibrations of the betaine carboxylate group.
2. The Raman tensor component $\alpha'(R)_{zz}$ reveals high sensitivity on the hydrogen bonding to the betaine carboxylate group. Its value as well as its orientation strongly depends on the strongest hydrogen bond distance $R(O_1\cdots O)_{min}$ in the considered crystals. In the betaine – orthophosphoric acid complex this tensor component is parallel to the carboxylate C–O_1 bond and the lowest $\alpha'(R)_{zz}$ value is recorded. It corresponds to the proton delocalization: $O_1\cdots H{-}O \leftrightarrows O_1{-}H\cdots O$ in this crystal $(O_1\cdots O)_{min}$ bond.

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