

Evidence of Polaron Excitations in Low Temperature Raman Spectra of Oxalic Acid Dihydrate

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ABSTRACT: Low temperature Raman spectra of oxalic acid dihydrate (8K - 300 K) both for polycrystalline and single crystal phase show strong variation with temperature in the interval from 1200 to 2000 cm^{-1} . Previous low temperature diffraction studies all confirmed the stability of the crystal $P2_1/n$ phase with no indications of any phase transition, reporting the existence of a strong hydrogen bond between the oxalic acid and a water molecule. A new group of Raman bands in the 1200 – 1300 cm^{-1} interval below 90 K is observed, caused by possible loss of the centre of inversion. This in turn could originate either due to disorder in hydroxyl proton positions, or due to proton transfer from carboxylic group to water molecule. The hypothesis of proton transfer is further supported by the emergence of new bands centered at 1600 cm^{-1} and 1813 cm^{-1} , which can be explained with vibrations of H_3O^+ ions. The broad band at 1600 cm^{-1} loses intensity, while the band at 1813 cm^{-1} gains intensity on cooling. The agreement between quantum calculations of vibrational spectra and experimentally observed Raman bands of hydronium ions in oxalic acid sesquihydrate crystal corroborate this hypothesis.

INTRODUCTION

The importance of understanding the influence of lattice defects on optical, conduction and transport properties of materials manifests repeatedly in the study of organic photovoltaic materials for solar cells¹ and high -T_c superconductors², while proton dynamics deserves special attention because of the role hydrogen bonding plays in biochemistry. Recent advances in study of voltage gated proton channels revealed the intricate mechanism of membrane depolarization which triggers the proton flow from the cell³ and the role which amino acid vibrations might play in opening and closing of the proton channel⁴.

Here we present the results of low temperature Raman spectroscopic study of oxalic acid dihydrate which demonstrate strong temperature dependence of proton vibrational dynamics. In most stable molecular crystals cooling causes bands to become narrower, revealing multiplet structure called Davydov splitting, while their positions shift to higher wavenumbers. In oxalic acid (OXAC) dihydrate a group of bands between 1200 and 1300 cm⁻¹ emerges below 100 K, while bands between 1300 and 2000 cm⁻¹ shift, broaden and change intensity in the way unexpected for the stable crystal phase. At the same time the number of low frequency phonons remains the same and their positions shift slightly and continuously. Possible loss of inversion centre at the site of oxalic acid molecule might take place, stemming either from the disorder of hydroxyl proton positions or from proton transfer from the carboxylic group to the water molecule. We shall argue that Raman results are supporting the latter hypothesis, and shall corroborate our conclusion with observed and calculated Raman spectra of oxalic acid sesquihydrate, COOHCOO⁻·2H₃O⁺·H₂O.

Oxalic acid (OXAC) dihydrate is an exemplary system displaying strong hydrogen bonding, examined repeatedly by X-ray and neutron diffraction⁵⁻⁹. Early vibrational spectroscopic

studies by Villepin and Novak¹⁰⁻¹² and single crystal far infrared study by Wyncke et al¹³ attracted many other researchers to tackle the dynamics of this crystal using deuterium NMR¹⁴, ac conductivity measurements¹⁵, Raman^{16,17}, high pressure X-ray¹⁸ and neutron diffraction¹⁹, terahertz spectroscopy accompanied with density functional theory calculation²⁰ and Car-Parrinello molecular dynamics simulation²¹.

The stable (COOH)₂ · 2H₂O crystal appears in the α form only, while deuterated (COOD)₂ · 2D₂O can appear both in the α and in the unstable β form. When deuterated β form is cooled below 273 K it spontaneously transforms into the α form¹⁶. Heat capacity measurements of the protonated crystal revealed smooth C_p curve²², which together with low temperature structure determination studies^{6,9} supported the sole existence of the stable α phase having $P2_1/n$, $Z=2$, $a = 6.093 \text{ \AA}$, $b = 3.469 \text{ \AA}$, $c = 11.926 \text{ \AA}$ and $\beta = 105.690$ at 15 K⁶. Recently, Macchi et al.¹⁹ thoroughly investigated the two polymorphs of oxalic acid dihydrate at pressures from 0 to 10 GPa, reporting the proton migration at high pressure.

EXPERIMENTAL

Single crystals of oxalic acid dihydrate of the $P2_1/n$ symmetry were prepared from saturated MQ water solutions of commercially obtained polycrystalline substance (Fluka, 99.5 % purity) at room temperature. The orientation of crystal axes is depicted in Figure 1. Single crystal of oxalic acid sesquihydrate in the orthorhombic crystal system was obtained as a product of cocrystallization experiment with glutamine. The crystal was oriented on goniometer head on an Oxford Diffraction Xcalibur 3 diffractometer using Mo K_α radiation at room temperature. The unit cell parameters were $a=11.213(9) \text{ \AA}$, $b = 12.203(10) \text{ \AA}$ and $c =$

6.934(9) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 90^\circ$, corresponding to the structure reported by Wenger and Bernstein²³.

Raman spectra were recorded in the triple subtractive configuration of the T64000 Horiba JobinYvon Raman spectrometer using COHERENT INNOVA 400 argon ion laser operating at 515.4 nm as an excitation source. Single crystals were sealed in glass tubes to prevent dehydration upon evacuation of the sample chamber of the Janis Research CCS 350 closed cycle helium cryostat equipped with Lake Shore 331 controller. Phonon spectra (20 – 600 cm^{-1}) were recorded in “single window” mode, while for internal part of the spectra (600 – 3800 cm^{-1}) “multiwindow” mode was chosen. The UV–VIS spectrum was recorded with a Shimadzu UV/VIS/NIR spectrometer (model UV-3600) connected to an integrating sphere. The background was recorded using BaSO₄ supplied by Wako^R, while polycrystalline oxalic acid was mixed with BaSO₄ powder and pressed.

COMPUTATIONAL DETAILS

For both crystal structures, the $P21/n$ ⁷ of the dihydrate and $Pnma$ ²³ of sesquihydrate partial optimization of atomic positions with fixed cell parameters were performed first using density functional theory as implemented in CRYSTAL09 program²⁴. The correlation functional of Lee, Yang and Parr²⁵ with generalized gradient approximation and the exchange functional of Becke²⁶ popularly known as B3LYP functional were used. The crystal structure optimization of oxalic acid sesquihydrate was undertaken by optimizing atoms positions keeping the cell parameters fixed at their experimentally found values and by performing full geometry optimization both of cell parameters and of atoms positions. When the SHRINK keyword defining the grid of k points was set to 2, 4 and 1, the total energy of sesquihydrate crystal was $E_T = -3942,4822265$ Hartree without dispersion correction and $-3942,756056$

Hartree when dispersion correction as described by Grimme²⁷ was taken into account. Full geometry optimization in this case resulted in $E_T = -3942,483064$ Hartree, but shifted to $E_T = -3942,425223$ Hartree when SHRINK factors were 4, 4 and 8, in which case the obtained values for optimized cell parameters were $a = 11.3174 \text{ \AA}$, $b = 12.1685 \text{ \AA}$, and $c = 6.7073 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. The convergence criteria for energy during geometry optimization was set to 10^{-7} Hartree, whereas for calculation of vibrations it was 10^{-10} Hartree. Extra large grid was used. Basis sets for carbon, hydrogen and oxygen of the 6-31G** type were transferred from the study of urea by Gatti et al.²⁸. This basis set has been found adequate for calculations on molecular crystals by Barone²⁹. The calculations were run on HP Z640 workstation equipped with eight processors.

RESULTS AND DISCUSSION

Low frequency Raman spectra of OXAC dihydrate are completely in accord with the existence of a single stable phase (Figure 2). However, Wynncke et al. observed an infrared phonon at 44.5 cm^{-1} at 300 K when electric field was parallel to **a**, whose position shifted to 46.5 cm^{-1} at 223 K and did not shift further on cooling, but whose intensity steadily ceased and which vanished at 80 K¹³.

We would like to point out that temperature dependent Raman spectra in the interval from 1000 to 2000 cm^{-1} require particular attention since the changes observed are quite remarkable. Figure 3 displays Raman spectra of powder and Figure 4 $y(zz)x$ polarized Raman spectrum of a single crystal of protonated oxalic acid dihydrate (OXAC). Supplementary Figure S1 completes the data with $y(zy)x$ polarized spectra. In Porto notation $y(zz)x$ means that we irradiate the crystal with laser light in such a way that the incoming beam enters in y

direction (**b** crystal axes), its incoming linear polarization is along z (crystal **a** axes), the scattered light propagates along x (crystal **c*** axes) and is measured along z. Figures 5 and 6 refer to z(yy)x + z(yz)x polarization. On cooling below 90 K a group of bands below 1300 cm⁻¹ appears in powder spectra and in all polarizations (Figures 3 – 5, Figure S1).

In the previous publication the band assignment was given and polarized Raman spectra of a single crystal presented¹⁷, aided by calculation of phonon transitions based on a harmonic approximation. Most of the bands between 1200 and 1300 cm⁻¹ were assigned as the $\nu(\text{C-O})$ stretching combined with $\delta(\text{C-O-H})$ bending vibrations. However, the majority of them is of ungerade symmetry and are not supposed to be observed if the space group of the crystal is $P2_1/n$. Raman spectra of the deuterated compound follow the same pattern (Supplementary Figure S2a, Figure S2b). Tentatively, an assumption could be made that the centre of inversion existing in oxalic acid is the result of averaging of carboxylic H₁ positions. Indeed, if all carbon and oxygen atoms keep their centrosymmetrical positions, and the disorder starting below 90 K manifests itself mainly through hydroxyl protons, the elementary cell will lose its inversion symmetry element and all previously unobservable infrared transitions would become Raman active. Another important experimental observation of Wyncke et al.¹³ concerns proton displacements along the **a** axis which are strongly coupled with an infrared phonon mode at 46.5 cm⁻¹ existing between 80 K and 223 K¹³ (we assigned it to the bending mode of the hydrogen bond¹⁷). The disappearance of this mode could indicate the disruption of the bond, and the proton transfer from the acid to the water molecule producing H₃O⁺ ion.

The hydrogen bond stretching modes $\nu(\text{OH})$ assigned on the basis of room temperature crystal spectra were observed at 1965 cm⁻¹ (A_g), 2040 cm⁻¹ (B_g), 1943 cm⁻¹ (A_u) and 1850 cm⁻¹ (B_u)¹⁷. Also, 90% of the hydrogen bond stretching modes calculated by Car-Parrinello

molecular dynamics simulation were found to lie in the 1750 – 2250 cm^{-1} interval²¹. Detailed look of the interval 1300 – 2000 cm^{-1} accompanied with careful fit with MINUIT program³⁰ with a minimum number of observed bands reveals nine bands (Figure 6). The minimum close to the 1694 cm^{-1} band is an Evans band. There is a broad central band at 1600 cm^{-1} which on cooling shifts to 1580 cm^{-1} at 8 K (Figure 6.). The origin of this band we attribute to proton polaron, a mode corresponding to the vibration of the defects in the form of $\text{H}_3\text{O}^+ \cdot \text{COOHCOO}^-$. The reason for this we find in comparison of oxalic acid dihydrate spectra with the experimental and calculated Raman spectra of oxalic acid sesquihydrate (Figure 8). The complete list of calculated normal modes is provided in Supplementary material, while in Table 1 a selection of H_3O^+ related modes is given. The H_3O^+ bending modes calculated for fully optimised crystal structure appear as series of transitions in the intervals (1070, 1080 cm^{-1}), (1300 – 1320 cm^{-1}) and (1590 – 1780 cm^{-1}) (Figure 8c) which are assigned to three pronounced bands in the observed spectrum: at 1220 cm^{-1} , 1577 cm^{-1} and 1930 cm^{-1} (Figure 8b). For realistic comparison with the observed spectrum, we note that the calculated frequencies are unscaled and are too high, because carbonyl stretching modes are predicted at 1833 cm^{-1} (B_{1g}), 1838 cm^{-1} (B_{2g}), 1843 cm^{-1} (A_g) and 1848 cm^{-1} (B_{3g}), whereas they are observed at 1706 and 1726 cm^{-1} in the Raman spectrum. We expect carboxyl $\nu(\text{OH})$ stretching modes to be strongly coupled with the stretching modes of the hydronium ion. Both the calculated spectrum with dispersion correction included (Figure 8a) and the one without dispersion correction (Figure 8c) can be inspected by MOLDRAW³¹. Several groups of bands with major involvement of H_3O^+ groups are encircled in red ellipses. Because the calculation was performed in the harmonic approximation, all calculated $\nu(\text{OH})$ stretching modes appear

above 2770 cm^{-1} , whereas in the observed Raman spectrum of oxalic acid sesquihydrate they form a continuous band from 2250 cm^{-1} to 3400 cm^{-1} .

Ever since 1933, when Landau first predicted the self trapping of an electron in crystal lattice³², the study of polarons has been steadily expanding. Pekar³³ and Holstein³⁴ were among the first to model what is now known as large Pekar polaron and small Holstein polaron. The term polaron meaning here both the set of electron coordinates of the electron trapped in the potential well of crystal lattice and the set of lattice coordinates of displaced nuclei. If lattice distortion spreads over many lattice sites, electron trapped in the deformation potential was described in the model of polarized continuum by Fröhlich³⁵ and its binding energy and the effective mass calculated in the strong coupling regime by Feynman³⁶. As pointed out by Emin³⁷, one criterion for judging whether a polaron belongs to the small or large class is the degree of lattice deformation that is present on electron trapping. In the case of small polaron, the equilibrium positions of nuclei do not change, but their vibrational amplitudes alter due to interaction with the electron. On the contrary, when stronger interaction between electrons and nuclei takes place over several elementary cells, ions move to a new set of equilibrium positions and one speaks of a large polaron. In oxalic acid dihydrate a small polaron seems to be more likely, and the previous ac conductivity measurements support this assumption¹⁵.

In the literature, the term “proton polaron” was introduced by Fischer, Hofacker and Ratner for explanation of moving defects in a linear network of hydrogen bonds³⁸.

Krasnoholovets extensively modeled systems exhibiting coherent and incoherent proton tunnelling³⁹ which relate to chains of hydrogen bonds. Such chains in OXAC contain both strong and medium strong H bonds. Yamada used the term “proton polaron” when

discussing the symmetry breaking in at least one of internal coordinate associated with hydrogen bond⁴⁰. Also, Flakus discussed extensively how the anharmonicity of hydrogen bonds causes the loss of the center of inversion⁴¹.

Structural defects which could explain the existence of proton polaron bands are found in the form of $\text{H}_3\text{O}^+ \cdot \text{COOHCOO}^-$ defects. Their geometrical parameters are reported besides oxalic acid sesquihydrate also for $\{\text{H}_3\text{O}^+(\text{HC}_2\text{O}_4^-)(\text{H}_2\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}\}$ crystal obtained by hydrothermal synthesis by Kherfi et al.⁴² The sole symmetry element of that structure is an inversion centre – the space group is $\bar{P}1$, and the infrared band characterizing the bending mode of H_3O^+ is reported at 1590 cm^{-1} ⁴⁰. Fournier et al. studied $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ and $\text{Cs}^+(\text{H}_2\text{O})_{20}$ clusters and reported the umbrella mode of H_3O^+ at 1200 cm^{-1} , while the asymmetric bending of the H_3O^+ was observed around 2000 cm^{-1} ⁴³. Interestingly, the intensity of the corresponding umbrella mode for D_3O^+ around 900 cm^{-1} and asymmetric stretching in the interval $1500\text{-}1700 \text{ cm}^{-1}$ were much weaker than in the protonated case⁴³. This would explain lower intensity of the observed bands in the Raman spectra of $(\text{COOD})_2 \cdot \text{D}_2\text{O}$ (Supplementary Figure S2a and S2b).

In conclusion in Figure 9 UV-VIS spectrum of polycrystalline OXAC dihydrate is shown to illustrate that there are no electronic states present at the energy of the laser used (514.5 nm) which could contribute to the Raman spectrum in the $x(\text{zz})y$ polarization shown in Figure 10.

The great increase in the intensity of the whole spectrum when the measured polarization is along z compared to the spectrum with polarization measured along x displays the spatial inhomogeneity of the defects. The broadness of underlying band in the $x(\text{zz})y$ spectrum is attributed to the electronic polaron state accompanying the proton polaron. Energies of

both are closely centered at approximately 1750 cm^{-1} and 1600 cm^{-1} , but their bandwidths are order of magnitude different: electron polaron spreading over the whole vibrational spectrum ($\Gamma_e \approx 1200\text{ cm}^{-1}$), and proton polaron having bandwidth of $\Gamma_p \approx 200\text{ cm}^{-1}$. The electron polaron bandwidth is close to 0.2 eV , the energy difference between cis and trans conformers of oxalic acid⁴⁴.

CONCLUSIONS

Raman spectra of oxalic acid dihydrate at low temperatures give evidence of growing proton-related disorder below 100 K . The strong temperature dependence of vibrational bands in the $1200\text{-}2000\text{ cm}^{-1}$ interval correlate with loss of the inversion centre and the appearance of $\text{H}_3\text{O}^+ \cdot \text{COOHCOO}^-$ structural defects. The broad bands at 1600 cm^{-1} and the 1813 cm^{-1} are assigned to bending motions of hydronium ions based on the normal modes calculation for $\text{COOHCOO}^- \cdot 2\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ crystal. We describe these excitations as proton polarons because underlying lattice defects are caused by temperature dependent change in proton dynamics.

SUPPORTING INFORMATION

Supplementary Figs. S1, S2a and S2b are available.

The output of quantum mechanical CRYSTAL09 geometry optimization of oxalic acid sesquihydrate together with calculation of its crystal normal modes is provided.

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Table 1. Selection of normal modes of oxalic acid sesquihydrate involving bending motions of H_3O^+ ions calculated after full crystal geometry optimization by CRYSTAL09 program. Complete file is in Supplementary material and can be inspected using MOLDRAW³¹ (i.a. denotes inactive vibration).

calculated (cm^{-1})	symmetry	IR active	Raman active
1070.7	B_{2u}	+	-
1072.0	B_{3g}	-	+
1072.8	A_g	-	+
1075.6	B_{1u}	+	-
1308.4	A_g	-	+
1312.4	B_{3g}	-	+
1313.3	B_{1u}	+	-
1314.7	B_{2u}	+	-
1597.2	A_g	-	+
1605.3	B_{3g}	-	+
1616.5	B_{1u}	+	-
1629.1	B_{2u}	+	-
1638.3	B_{1g}	-	+

1639.1	B_{3u}	+	-
1639.6	B_{2g}	-	+
1680.3	B_{3g}	-	+
1694.6	B_{2u}	+	-
1708.7	B_{3g}	-	+
1715.2	A_g	-	+
1720.8	B_{2u}	+	-
1726.0	B_{2g}	-	+
1728.6	A_u	i.a.	i.a.
1732.1	B_{3u}	+	-
1733.4	B_{1g}	-	+
1739.2	B_{1u}	+	-
1770.1	A_g	-	+
1770.7	B_{2g}	-	+
1774.3	B_{1g}	-	+
1777.0	B_{3u}	+	-
1780.1	B_{1u}	+	-

1780.5	B_{3g}	-	+
1783.6	B_{2u}	+	-
1787.5	A_u	i.a.	i.a.

FIGURE CAPTIONS

Figure 1. The orientation of crystal axes in the single crystal of oxalic acid dihydrate. c^* is the axes perpendicular to a-b plane.

Figure 2. Low frequency Raman spectra of oxalic acid dihydrate in the $z(yy)x + z(yz)x$ polarization. The Porto notation denotes laser beam linearly polarized along y (first letter in brackets) entering along z (letter in front of the brackets). Second letter in brackets indicates the polarization of measured light, and the letter after the brackets the propagation direction of scattered light.

Figure 3. Low temperature Raman spectra of polycrystalline oxalic acid dihydrate.

Figure 4. Low temperature Raman spectra of oxalic acid dihydrate in $y(zz)x$ polarization ($1000 - 2200 \text{ cm}^{-1}$) at 295 K, 270 K, 200 K, 100 K and 8 K. Notice the emerging group of bands at and below 100 K.

Figure 5. Low temperature background uncorrected Raman spectra of oxalic acid dihydrate in $z(yy)x + z(yz)x$ polarization.

Figure 6. Temperature evolution of nine fitted bands in Raman spectra of OXAC in $z(yy)x + z(yz)x$ polarization at 270 K, 190 K, 130 K and 8K (from top downwards). Notice the decrease in the intensity of the broad 1600 cm^{-1} band and the increase in the intensity of the 1813 cm^{-1} band on cooling.

Figure 7. Crystal structure of oxalic acid sesquihydrate is $Pnma$, $Z = 8$. Asymmetric unit is $\text{COOHCOO}^- \cdot 2\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$.

Figure 8. Comparison of the calculated and observed Raman spectra of oxalic acid sesquihydrate. (a) Calculated spectrum including dispersion correction (see Computational section for details). (b) Experimental Raman spectra for two crystal orientations. Modes related to H_3O^+ ions are pointed out by arrows. (c) Calculated spectrum of the fully optimized crystal. The bands involving motions of hydronium ions are encircled in red ellipses.

Figure 9. UV-VIS spectrum of oxalic acid dihydrate. There are no gap states at 514.5 nm (approx. 2 eV, energy of the laser excitation used) that could contribute to Raman spectrum.

Figure 10. Polarized Raman spectra of oxalic acid dihydrate in $x(zz)y$ and $x(zx)y$ orientation.

TOC graphic. The origin of broad Raman bands in oxalic acid dihydrate is attributed to proton polarons arising from $\text{H}_3\text{O}^+ \cdot \text{COOHCOO}^-$ defects.