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Supporting information for article:

The dehydration process in the dl-phenylglycinium trifluoromethanesulfonate monohydrate crystal revealed by XRD, vibrational and DSC studies

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Supporting information

Table S1   Selected bond lengths (Å), bond angles (°) and torsion angles (°) in the PGTFH and PGTF crystals determined by the XRD measurements

PGTFH

S1A—O1A	1.440 (2)	C1B—C2B	1.523 (3)
S1A—O2A	1.4439 (19)	C2B—N1B	1.503 (3)
S1A—O3A	1.455 (2)	C2B—C3B	1.516 (3)
S1A—C1A	1.825 (3)	C3B—C4B	1.382 (4)
C1A—F1A	1.335 (3)	C3B—C8B	1.389 (4)
C1A—F2A	1.327 (4)	C4B—C5B	1.393 (4)
C1A—F3A	1.326 (3)	C5B—C6B	1.378 (4)
O1B—C1B	1.312 (3)	C6B—C7B	1.385 (5)
O2B—C1B	1.221 (3)	C7B—C8B	1.397 (4)
O1A—S1A—O2A	115.19 (12)	O2B—C1B—C2B	122.8 (2)
O1A—S1A—O3A	114.63 (11)	N1B—C2B—C1B	107.57 (18)

O1A—S1A—C1A	104.11 (13)	N1B—C2B—C3B	110.1 (2)
O2A—S1A—O3A	113.46 (11)	C3B—C2B—C1B	113.4 (2)
O2A—S1A—C1A	104.13 (12)	C4B—C3B—C2B	120.0 (2)
O3A—S1A—C1A	103.42 (12)	C4B—C3B—C8B	120.0 (2)
F1A—C1A—S1A	110.56 (18)	C8B—C3B—C2B	119.9 (2)
F2A—C1A—S1A	110.4 (2)	C3B—C4B—C5B	120.2 (2)
F2A—C1A—F1A	108.3 (2)	C6B—C5B—C4B	119.9 (3)
F3A—C1A—S1A	111.21 (19)	C5B—C6B—C7B	120.2 (3)
F3A—C1A—F1A	108.2 (2)	C6B—C7B—C8B	120.0 (3)
F3A—C1A—F2A	108.1 (2)	C3B—C8B—C7B	119.6 (3)
O1B—C1B—C2B	111.6 (2)	H1W—O1W—H2W	110 (4)
O2B—C1B—O1B	125.6 (2)		
O1A—S1A—C1A—F1A	61.1 (2)	O1B—C1B—C2B—C3B	−58.9 (3)
O1A—S1A—C1A—F2A	−179.15 (19)	O2B—C1B—C2B—N1B	−0.1 (3)
O1A—S1A—C1A—F3A	−59.1 (2)	O2B—C1B—C2B—C3B	121.9 (2)
O2A—S1A—C1A—F1A	−60.0 (2)	C1B—C2B—C3B—C4B	−53.8 (3)
O2A—S1A—C1A—F2A	59.8 (2)	C1B—C2B—C3B—C8B	129.3 (3)

O2A—S1A—C1A—F3A	179.8 (2)	C2B—C3B—C4B—C5B	−176.8 (2)
O3A—S1A—C1A—F1A	−178.83 (19)	C2B—C3B—C8B—C7B	177.1 (3)
O3A—S1A—C1A—F2A	−59.0 (2)	N1B—C2B—C3B—C4B	66.8 (3)
O3A—S1A—C1A—F3A	61.0 (2)	N1B—C2B—C3B—C8B	−110.1 (3)
O1B—C1B—C2B—N1B	179.1 (2)		

PGTF

S1A1—O1A1	1.426 (4)	O2B1—C1B1	1.197 (7)
S1A1—O2A1	1.439 (4)	C1B1—C2B1	1.501 (7)
S1A1—O3A1	1.409 (5)	C2B1—N1B1	1.498 (7)
S1A1—C1A1	1.791 (7)	C2B1—C3B1	1.497 (7)
C1A1—F1A1	1.285 (8)	C3B1—C4B1	1.369 (8)
C1A1—F2A1	1.326 (8)	C3B1—C8B1	1.374 (8)
C1A1—F3A1	1.276 (8)	C4B1—C5B1	1.359 (10)
S1A2—O1A2	1.421 (4)	C5B1—C6B1	1.347 (11)
S1A2—O2A2	1.412 (5)	C6B1—C7B1	1.376 (11)
S1A2—O3A2	1.419 (5)	C7B1—C8B1	1.377 (10)
S1A2—O1X2	1.52 (7)	O1B2—C1B2	1.318 (7)

S1A2—O2X2	1.26 (6)	O2B2—C1B2	1.191 (7)
S1A2—O3X2	1.54 (6)	C1B2—C2B2	1.509 (7)
S1A2—C1A2	1.800 (7)	C2B2—N1B2	1.476 (7)
C1A2—F1A2	1.310 (8)	C2B2—C3B2	1.505 (7)
C1A2—F2A2	1.297 (8)	C3B2—C4B2	1.373 (8)
C1A2—F3A2	1.301 (7)	C3B2—C8B2	1.367 (9)
C1A2—F1X2	1.36 (5)	C4B2—C5B2	1.393 (10)
C1A2—F2X2	1.27 (5)	C5B2—C6B2	1.343 (12)
C1A2—F3X2	1.25 (6)	C6B2—C7B2	1.353 (11)
O1B1—C1B1	1.312 (7)	C7B2—C8B2	1.364 (9)
O1A1—S1A1—O2A1	114.5 (3)	F2X2—C1A2—F1X2	115 (3)
O1A1—S1A1—C1A1	105.5 (3)	F3X2—C1A2—S1A2	101 (3)
O2A1—S1A1—C1A1	104.5 (3)	F3X2—C1A2—F1X2	107 (4)
O3A1—S1A1—O1A1	111.9 (3)	F3X2—C1A2—F2X2	102 (4)
O3A1—S1A1—O2A1	115.4 (3)	O1B1—C1B1—C2B1	112.3 (5)
O3A1—S1A1—C1A1	103.5 (3)	O2B1—C1B1—O1B1	123.9 (5)
F1A1—C1A1—S1A1	112.2 (6)	O2B1—C1B1—C2B1	123.7 (5)

F1A1—C1A1—F2A1	103.2 (7)	N1B1—C2B1—C1B1	107.5 (5)
F2A1—C1A1—S1A1	110.9 (5)	C3B1—C2B1—C1B1	113.1 (5)
F3A1—C1A1—S1A1	114.3 (5)	C3B1—C2B1—N1B1	110.8 (4)
F3A1—C1A1—F1A1	108.3 (7)	C4B1—C3B1—C2B1	120.7 (5)
F3A1—C1A1—F2A1	107.3 (7)	C4B1—C3B1—C8B1	118.1 (6)
O1A2—S1A2—C1A2	103.2 (3)	C8B1—C3B1—C2B1	121.1 (5)
O2A2—S1A2—O1A2	113.8 (3)	C5B1—C4B1—C3B1	122.6 (7)
O2A2—S1A2—O3A2	117.2 (4)	C6B1—C5B1—C4B1	119.1 (7)
O2A2—S1A2—C1A2	103.5 (3)	C5B1—C6B1—C7B1	120.2 (7)
O3A2—S1A2—O1A2	113.0 (3)	C6B1—C7B1—C8B1	120.3 (7)
O3A2—S1A2—C1A2	103.9 (3)	C3B1—C8B1—C7B1	119.7 (7)
O1X2—S1A2—O3X2	105 (4)	O1B2—C1B2—C2B2	109.9 (5)
O1X2—S1A2—C1A2	98 (3)	O2B2—C1B2—O1B2	125.5 (5)
O2X2—S1A2—O1X2	114 (4)	O2B2—C1B2—C2B2	124.5 (5)
O2X2—S1A2—O3X2	103 (4)	N1B2—C2B2—C1B2	108.1 (4)
O2X2—S1A2—C1A2	119 (3)	N1B2—C2B2—C3B2	112.5 (4)
O3X2—S1A2—C1A2	117 (2)	C3B2—C2B2—C1B2	110.3 (5)

F1A2—C1A2—S1A2	111.9 (5)	C4B2—C3B2—C2B2	119.0 (6)
F2A2—C1A2—S1A2	113.8 (5)	C8B2—C3B2—C2B2	121.9 (5)
F2A2—C1A2—F1A2	105.5 (6)	C8B2—C3B2—C4B2	119.0 (6)
F2A2—C1A2—F3A2	107.0 (6)	C3B2—C4B2—C5B2	118.7 (7)
F3A2—C1A2—S1A2	112.1 (5)	C6B2—C5B2—C4B2	121.5 (7)
F3A2—C1A2—F1A2	106.1 (7)	C5B2—C6B2—C7B2	119.1 (7)
F1X2—C1A2—S1A2	109 (2)	C6B2—C7B2—C8B2	120.9 (8)
F2X2—C1A2—S1A2	121 (2)	C7B2—C8B2—C3B2	120.7 (7)
O1A1—S1A1—C1A1—F1A1	176.1 (6)	O3X2—S1A2—C1A2—F1X2	−54 (4)
O1A1—S1A1—C1A1—F2A1	61.3 (6)	O3X2—S1A2—C1A2—F2X2	170 (4)
O1A1—S1A1—C1A1—F3A1	−60.1 (7)	O3X2—S1A2—C1A2—F3X2	58 (4)
O2A1—S1A1—C1A1—F1A1	54.9 (6)	O1B1—C1B1—C2B1—N1B1	170.0 (5)
O2A1—S1A1—C1A1—F2A1	−59.8 (6)	O1B1—C1B1—C2B1—C3B1	−67.3 (6)
O2A1—S1A1—C1A1—F3A1	178.8 (6)	O2B1—C1B1—C2B1—N1B1	−8.9 (8)
O3A1—S1A1—C1A1—F1A1	−66.2 (7)	O2B1—C1B1—C2B1—C3B1	113.8 (7)
O3A1—S1A1—C1A1—F2A1	179.0 (6)	C1B1—C2B1—C3B1—C4B1	139.3 (6)
O3A1—S1A1—C1A1—F3A1	57.6 (7)	C1B1—C2B1—C3B1—C8B1	−44.0 (8)

O1A2—S1A2—C1A2—F1A2	61.5 (6)	C2B1—C3B1—C4B1—C5B1	178.4 (7)
O1A2—S1A2—C1A2—F2A2	−57.9 (6)	C2B1—C3B1—C8B1—C7B1	−179.1 (7)
O1A2—S1A2—C1A2—F3A2	−179.5 (6)	N1B1—C2B1—C3B1—C4B1	−99.9 (6)
O2A2—S1A2—C1A2—F1A2	−179.6 (6)	N1B1—C2B1—C3B1—C8B1	76.9 (7)
O2A2—S1A2—C1A2—F2A2	61.0 (7)	O1B2—C1B2—C2B2—N1B2	−162.1 (5)
O2A2—S1A2—C1A2—F3A2	−60.6 (7)	O1B2—C1B2—C2B2—C3B2	74.5 (6)
O3A2—S1A2—C1A2—F1A2	−56.6 (6)	O2B2—C1B2—C2B2—N1B2	18.7 (8)
O3A2—S1A2—C1A2—F2A2	−176.0 (6)	O2B2—C1B2—C2B2—C3B2	−104.7 (7)
O3A2—S1A2—C1A2—F3A2	62.4 (6)	C1B2—C2B2—C3B2—C4B2	−128.9 (6)
O1X2—S1A2—C1A2—F1X2	57 (4)	C1B2—C2B2—C3B2—C8B2	49.5 (8)
O1X2—S1A2—C1A2—F2X2	−79 (4)	C2B2—C3B2—C4B2—C5B2	178.3 (6)
O1X2—S1A2—C1A2—F3X2	170 (4)	C2B2—C3B2—C8B2—C7B2	−177.6 (6)
O2X2—S1A2—C1A2—F1X2	−179 (4)	N1B2—C2B2—C3B2—C4B2	110.3 (6)
O2X2—S1A2—C1A2—F2X2	45 (5)	N1B2—C2B2—C3B2—C8B2	−71.2 (7)
O2X2—S1A2—C1A2—F3X2	−66 (5)		

Room temperature vibrational spectra of PGTFH and PGTF

Hydrogen bond vibrations

The PGTFH crystal contains three O–H···O hydrogen bonds. Water molecule act as-proton acceptors ((R(O···O) = 2.632(3) Å) or as protons donors ((R(O···O) = 2.781(3) and 2.771(3) Å). The stretching vibration of the stronger O–H···O (O1B–H1B···O1W) hydrogen bond manifests itself as two broad A, B bands with maxima at 3046 cm^{-1} and 2627 cm^{-1} (Novak, 1974). Additionally these two bands exhibit fine structure with submaxima at 3228, 3164, 3147, 3111, 3042 and 2969 cm^{-1} on the A band and submaxima at 2869, 2776, 2672, 2625, 2602 and 2528 cm^{-1} on the B band. This structure probably derives from the stretching vibrations of the –NH$_3^+$ groups, νNH, that are involved in the second type of hydrogen bonds, N–H···O detected in PGTFH (Table 4 3). In turn, the stretching vibrations of the weaker O–H···O (O1W–H1W···O2A^i and O1W–H2W···O3A) hydrogen bonds are considered as stretching vibrations (asymmetric and symmetric) of water molecule. The broad and intense band at 3361 cm^{-1} apparent in the infrared spectrum has been assigned to ν_{as}H$_2$O vibration. No Raman counterpart of this vibration has been detected.

The bands due to the deformation modes of the strongest O–H···O hydrogen bond, δOH and γOH, are only present in the infrared spectrum of PGTFH and are localized at 1128 and 952 cm^{-1}, respectively.

The bands due to deformation vibration of weaker O–H···O hydrogen bonds in which water molecule is involved, as in the case of stretching vibration, are treated as disturbed deformation vibrations of water molecules. In this case the bands due to the following vibrations should be expected: scissoring (δH$_2$O), twisting (τH$_2$O), rocking (ρH$_2$O) and wagging (ωH$_2$O) (Siamwiza et al., 1975; Tayal et al., 1980; Singh & Khanna, 1986). In the infrared spectra of hydrated crystal only band due to the scissoring vibration, δH$_2$O, at 1652 cm^{-1} and band at 672 cm^{-1} assigned to the one of the libration modes have been observed. These bands have not been observed in the vibrational spectra of anhydrous form of the studied crystal.

From XRD data for the PGTF crystal one can learn that there are two O–H···O hydrogen bonds between carboxylic group of the cation and oxygen atoms of sulfonic group of the anion and six N–H···O hydrogen bonds in the crystal in question and that in general these bonds are weaker than the corresponding one in the PGTFH crystal (Table 3). These findings are proved by infrared spectra of PGTF. The stretching vibration of O–H···O hydrogen bonds, νOH, give rise to the broad and intense band at about 3160 cm^{-1} with very poor define fine structure. And as in the case of the PGTFH crystal, the stretching vibrations of the N–H···O hydrogen bonds, νNH, contribute to the broad band due to the νOH vibrations and are responsible for its very modest fine structure.

Internal vibrations of the DL-phenylglycinium cation

Assignments of the bands due to internal vibrations of DL-phenylglycinium cation involved in both studied crystals, PGTFH and PGTF, are listed in the Table 4. Additionally, detailed assignments of the bands due to the internal vibrations of the DL -phenylglycine molecule at both forms, as a cation and as an anion, have been reported in our previous papers (Ilczyszyn *et al.*, 2009a and 2009b; Wołoszyn *et al.*, 2016). As follows from the assignments reported in (Ilczyszyn *et al.*, 2009a and 2009b; Wołoszyn *et al.*, 2016) and presented in Table 4, the corresponding internal vibrations of PG^+ in the various of its compounds give rise to the bands at the same or very close position except for –COOH and $-NH_3^+$ vibrations which are strongly affected by hydrogen bonds in which they are involved. Since of this, only the –COOH and $-NH_3^+$ vibrations and some aromatic ring vibrations will be further discussed. The other vibrations of PG^+ are listed in Table 4 and in our opinion do not require additional comments.

The band due to stretching vibration of the –C=O group has been observed at 1722 cm^{-1} in the infrared spectrum of the PGTFH crystal. Its Raman counterpart has been identified at 1726 cm^{-1}. As expected, the former band is rather broad and intensive, while the latter one exhibits low intensity. In the carbonyl group IR stretching vibrations region of PGTF a broad band at 1742 cm^{-1} and a shoulder at 1764 cm^{-1} have been found. The band at 1742 and the shoulder at 1764 cm^{-1} have been assigned to the stretching vibrations of $vC=O$ of two independent PG^+ cations. Their Raman counterparts have been found at 1748 and 1763 cm^{-1}, respectively. The bands due the $vC=O$ vibrations in anhydrous crystal are observed at higher wavenumbers than corresponding ones in the spectrum of hydrated crystal. This observation shows that hydrogen bonds in which the C=O bond is involved are weaker in the anhydrous form than in the hydrated form and reaffirms the XRD data. The band due to $vC–O(H)$ vibration has been identified in IR spectra, for the hydrated and anhydrous forms at 1237 and 1227 cm^{-1}, respectively. In the Raman spectrum the band due to the $vC–O(H)$ vibration band has been identified only in the anhydrous form, at 1229 cm^{-1}. The bands due to other vibrations of the carboxylic group, δCOO, ωCOO and τCOO, have not been identified in the vibrational spectra of the compound.

The $-NH_3^+$ groups in both crystals are involved in the medium strength N–H···O hydrogen bonds. For this their stretching bands should be shifted to the lower wavenumbers and their intensity should be changed and can be treated as the stretching vibrations of single N–H group involved in the hydrogen bonds of different length. In the hydrated and anhydrous forms, $vN–H$ gives rise to the strong and broad infrared bands at 3046 cm^{-1} (for hydrated crystal) and at 3160 cm^{-1} (for anhydrous crystal). In the Raman spectra only very weak and diffused bands at 3214 and 3165 cm^{-1} (for hydrated crystal) and 3214 and 3150 cm^{-1}

(for anhydrous crystal) have been detected. Out of deformation vibrations of the –NH$_3^+$ groups only band due to the asymmetric deformation vibration δ_{as}NH$_3^+$ at 1582 cm^{-1} in the infrared spectrum of hydrated crystal and symmetric deformation vibration δ_sNH$_3^+$ at 1420 cm^{-1} in the infrared spectrum of anhydrous crystal have been detected (Table 4).

The doublet at 888 and 833 cm^{-1} are observed in the infrared spectrum of hydrated crystal. Its Raman counterpart is apparent at 889 and 833 cm^{-1}. This doublet is due to Fermi resonance between the symmetric ring-breathing vibration ν_1 and the overtone of out-of-plane ring-bending vibration $2\nu_{16a}$ of the aromatic ring (Siamwiza *et al.*, 1975). This doublet in the vibrational spectra of anhydrous crystal is observed at: 885 and 828 cm^{-1} in the infrared and 882 and 825 cm^{-1} in the Raman. Such doublet is observed for a large number of substituted benzenes. For the *p*-phenyl substituted derivatives were found that the intensity ratio of the Fermi resonance doublet is sensitive to many factors, namely "the nature of hydrogen bonding of the phenolic hydroxyl group or its ionization but much less so to the environment of the phenyl ring and the conformation of the amino acid backbone" (Siamwiza *et al.*, 1975). It was found also that the stronger interactions in which phenyl ring (e.g. non-covalent interactions) and /or its side groups (e.g. hydroxyl group) are involved the smaller the differences in the intensity of the component of doublet. So this double, more specifically the intensity ration of its components, can be treated as a pointer of interactions in which molecule that aromatic ring comprises and a qualitative measure of their changes. In the studied crystals the corresponding intensity ratios (I_{higher}:I_{lower}) are equal to about: 10:2.5 (I_{887}:I_{883}) for hydrated form and 10:7.6 (I_{885}:I_{827}) for anhydrous one in the infrared spectra. The corresponding doublet observed in the Raman spectra of both crystals, hydrated and anhydrous, exhibit opposite intensity ratio e.g. 2.3:10 (I_{889}:I_{832}) for the former crystal and 3.6:10 (I_{881}:I_{824}) for the latter one. These values show that differences in the intensity of the components of the doublet are smaller for anhydrous crystal than for hydrated one. This allows to claim that non-covalent aromatic-aromatic ring interactions are stronger in the anhydrous crystal than in hydrated one.

Water vibrations

Water molecule in the PGTFH crystal is involved in the hydrogen bonds network. It acts as a protons donor (O1W–H1W$\cdots$O2A^i and O1W–H2W$\cdots$O3A) and as a protons acceptor (O1B–H1B$\cdots$O1W and N1B–H5B$\cdots$O1W^{iv}). Since the lengths of the hydrogen bonds in which water molecule acts a donor are very similar (R$_{O\cdots O}$ = 2.781(3) Å and 2.771(3) Å) its stretching vibrations, νOH, may couple in-phase and out-of-phase forming two stretching vibrations: ν_sH$_2$O

and $\nu_{as}H_2O$, respectively. Furthermore, the bands due to the scissoring (δH_2O), twisting (τH_2O), rocking (ρH_2O) and wagging (ωH_2O) one should expect in the vibrational spectra of the crystal in question (Tayal *et al.*, 1980; Singh & Khanna, 1986; Lutz, 1988).

The broad and intense band at 3361 cm^{-1} with the shoulder at 3418 cm^{-1} in the infrared spectrum has been assigned to the $\nu_{as}H_2O$ vibration. The band due to the scissoring, δH_2O, has been identified at 1652 cm^{-1}. Libration vibrations of water molecule probably give rise to the weak intense band observed at 672 cm^{-1}. All bands arising from water molecule vibrations have been observed in the infrared spectrum of crystal in question and neither of them has been found in its Raman spectrum.

Internal vibrations of the $CF_3SO_3^-$ anion

In both crystals, the $CF_3SO_3^-$ anion occupies the position of C_1 symmetry. Because of this, the site symmetry selection rules for the internal vibrations of anion in both crystals are the same (Table S4). The presence of four anions per primitive unit cell in the hydrated crystal and two anions per primitive unit cell in the anhydrous crystal may result in vibrational coupling between internal vibrations of anions. As a result of this coupling, for hydrated crystal, each of A-species in the site group is split into four components; $A_g + B_g + A_u + B_u$; two of them are infrared ($A_u + B_u$) and two are Raman ($A_g + B_g$) active in the factor group (Table 5). In turn in a case of anhydrous crystal, each of A-species in the site group is split into a doublet $A_g + A_u$ with one component infrared active (A_u) and one Raman active (A_g) as a result of coupling (Table 6).

From Table S4 it is seen that a number of bands due to internal vibrations of the $CF_3SO_3^-$ anion observed in the vibrational spectra of both studied crystals generally is well predicted by the site symmetry selection rules. This observation may indicate that in both studied crystals vibrational couplings between four $CF_3SO_3^-$ anions in the unit cell of hydrated form of the crystal in question and between two $CF_3SO_3^-$ anions in the unit cell of anhydrous form of the crystal in question are not present. Moreover the wavenumber of the bands due to anion in question in the vibrational spectra of both studied crystals are very close to that calculated for $CF_3SO_3^-$ anion (Gejji *et al.*, 1993) and observed in the vibrational spectra of the pyridinium trifluoromethanesulfonate crystal (Jesariew & Ilczyszyn, 2015).

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Table S2   The wavenumbers (cm^{-1}) and the infrared intensities of the bands observed in the infrared spectra of polycrystalline sample of the PGTFH/PGTF in the range of temperature 298 K – 373 K (recorded in the nujol mull).

PGTFH/PGTF												
IR(T) [cm⁻¹] (Nujol)												
298 K	333 K	337 K	341 K	345 K	347 K	349 K	353 K	357 K	361 K	365 K	373 K	Assignment[a]
						3498 w sh	3510 m b	3516 m b	3517 m b	3517 m b	3519 m b	$\nu H_2O_{(wet)}$
3412 m sh	3412 m sh	3415 m sh	3415 m sh	3417 m sh	3425 m sh							$\nu_{as}H_2O_{(cryst)}$
3364 m b	3376 m b	3378 m b	3376 m b	3384 m b	3384 m b	3392 m b						$\nu_s H_2O_{(cryst)}$
3228 s	3225 s	3225 s	3225 s	3225 s	3217 w sh							$2x\nu_{8a}(\nu CC)$

												Assignment
						3188 s sh	3189 s	3189 s	3189 s	3189 s	3189 s	νNH···O
3166 s	3166 s	3166 s	3166 s	3166 s	3166 s	3163 s						νNH···O + $\nu_{8a}(\nu CC)$ + $\nu_{19b}(\nu CC)$
3146 s	3146 s	3146 s	3146 s	3146 s	3148 s	3146 s	3148 s	3148 s	3146 s	3146 s	3146 s	νNH···O + $\nu_{8a}(\nu CC)$ + $\nu_{19a}(\nu CC)$
3106 w	3106 w	3106 w	3105 w	3103 w	3098 w	3094 w	3094 w	3094 w	3094 w	3094 w	3094 w	$\nu_{8b}(\nu CC)$ + $\nu_{19a}(\nu CC)$
							3072 w	3072 w	3071 w	3071 w	3072 w	νNH···O
3045 w	3045 w	3045 w	3048 w	3048 w	3048 w	3048 w	3042 w sh	3042 w	3040 w	3041 w	3041 w	$\nu_{7b}(\nu CH)$
2780 vw	2780 vw	2780 vw	2780 vw	2780 vw	2779 vw sh							
							2718 vw	2718 vw	2718 vw	2718 vw	2718 vw	
2667 w	2667 w	2667 w	2667 w	2667 w	2665 w	2665 vw						
2625 w	2623 w	2623 w	2623 w	2623 w	2622 w	2622 w	2622 w	2622 w	2622 w 2602 w	2622 w	2622 w	
2601 w	2600 w	2600 w	2600 w	2600 w	2600 w	2600 w						
1722 s b	1723 s b	1723 s b	1724 s b	1726 s b	1756 w sh 1727 s b	1759 w sh 1734 s b 1732 s b	1764 m sh 1741 s b	1763 m sh 1741 s b	1763 m sh 1741 s b	1763 m sh 1741 s b	1763 m sh 1741 s b	νC=O
1642 w	1642 w	1642 w	1641 w	1641 w	1640 w	1640 w	1639 w	1639 w	1639 w	1640 w	1640 w	$\delta_{as}NH_3^+$
1614 m	1614 m	1614 m	1613 m	1612 m	1611 m	1608 m	1602 m	1602 m	1602 m	1601 m	1601 m	$\nu_{8a}(\nu CC)$

1583 m	1583 m	1583 m	1583 m	1583 m	1583 m	1582 m						$\nu_{8b}(\nu CC)$
2667 w	2667 w	2667 w	2667 w	2667 w	2665 w	2665 vw						
					1548 w	1548 w	1547 w	1547 w	1547 w	1547 w	1547 w	
1501 s	1501 s	1501 s	1501 s	1501 s	1502 s	1502 s	1502 s	1502 s	1500 s	1501 s	1501 s	$\nu_{19a}(\nu CC)$
1401 w	1401 w	1401 w	1401 w	1403 w	1404 w	1416 w	1418 m	1418 m	1417 m	1417 m	1417 m	$\delta_s NH_3^+$
1359 m	1358 m	1358 m	1358 m	1358 w	1358 w	1358 vw	1356 vw	1356 vw	1355 vw	1354 vw	1354 vw sh	δCH
1348 m	1348 m	1348 m	1348 m	1348 w	1348 w	1347 vw						$\gamma CH + \rho NH_3^+$
1307 vw sh												$\nu_3(\delta CH)$
1277 vs	1277 vs	1277 vs	1276 vs	1276 vs	1277 vs	1280 vs	1280 vs sh	1280 vs sh	1279 vs sh	1279 vs sh	1279 vs sh	$\nu_{as}SO_3$
1265 vs	1264 vs	1264 vs	1264 vs	1264 vs	1264 vs	1264 vs	1264 vs b	1264 vs b	1264 vs b	1264 vs b	1264 vs b	$\nu_{as}SO_3$
1236 vs b	1236 vs b	1236 vs b	1237 vs b	1236 vs b	1235 vs b							$\nu C\text{-}O(H)$
1227 vs sh	1227 vs sh	1227 vs sh	1227 vs sh	1227 vs sh	1228 vs sh	1228 vs	1227 vs	1227 vs	1227 vs	1227 vs	1227 vs	$\nu_s CF_3$
1196 m	1195 w	1195 w	1195 w	1195 w	1195 w							$\nu(C\text{-}Cring) + \delta CH + \nu CN$
1182 vs	1182 vs	1182 vs	1182 vs	1181 vs	1180 vs	1178 vs b	1175 vs	1175 vs	1175 vs	1175 vs	1175 vs	$\nu_{9a}(\delta CH)$
1175 vs	1175 vs	1175 vs	1174 vs	1174 vs	1175 vs sh	1178 vs b	1175 vs	1175 vs	1175 vs	1175 vs	1175 vs	$\nu_{as}CF_3$
1160 m	1160 m	1160 m	1159 m	1159 m	1160 m	1159 s	1159 s	1159 s	1159 s	1159 s	1159 s	$\nu_{15}(\delta CH)$
1129 w	1128 w	1127 w	1127 w	1127 w	1128 w	1129 vw sh						δOH

1111 vw	1111 vw	1111 vw	1112 w	1112 w	1112 w	1112 w	1111 w	1111 w	1111 w	1111 w	1111 w	$\nu_{as}SO_3$
1100 w	1099 w	1099 w	1099 w	1099 w	1099 w	1099 w	1098 vw sh	1098 vw sh	1098 vw sh	1099 vw sh	1099 vw sh	$\nu CN + \nu_{18b}(\delta CH) / \gamma CH$
1074 m	1073 m	1073 m	1073 m	1073 m	1072 m	1072 m	1071 m	1071 m	1071 m	1070 m	1070 m	$\nu_{18b}(\delta CH) + \nu CN$
1031 vs	1031 s	1031 s	1032 s	1032 s	1032 s	1032 s	1033 s	1033 s	1033 s	1033 s	1033 s	$\nu_{s}SO_3$
952 m b	952 m b	945 m b	945 m b	945 w b	945 w b	944 vw b						γOH
921 w	921 w	921 w	921 w	921 w	921 w	921 w	921 w	921 w	920 w	920 w	920 w	$\nu_{17b}(\delta CH)$
888 m	887 m	887 m	886 m	886 m	887 m	885 m	882 m	882 m	882 m	882 m	882 m	$\nu(C\text{-}COO) + \delta COO + \nu(C\text{-}Cring) / \tau CH + \nu(C\text{-}COO)$
833 w	833 w	833 w	832 w	832 m	829 m	828 m	827 m	827 m	827 m	827 m	827 m	$\omega COO + \omega NH_3^+ + \delta CCC$
767 m	766 m	766 m	766 m	766 m	765 m	764 m	762 m	762 m	762 m	763 m	763 m	$\delta_s CF_3$
737 vw							743 vw	743 vw	743 vw	743 vw	743 vw	$\nu_{11}(\delta CH) + \tau COO + \nu_{4}(\delta CC)$

698 s	698 s	698 s	697 s	697 s	697 s	697 s	696 s	696 s	695 s	695 s	695 s	$\delta CCN + \delta COO$
672 w	672 w	671 w	671 w	671 w	671 vw	669 vw sh						
644 s	644 s	644 s	644 s	644 s	644 s	644 s	644 s	644 s	643 s	643 s	643 s	$\delta_s SO_3$
616 w	616 w	616 w	616 w	616 w	616 w	616 w	616 vw	616 vw	616 vw	616 vw	616 vw	$\delta(C_{ring}\text{-}CN) + \nu_{6b}(\delta CC) / \nu_{6a}(\delta CC)$
597 vw	597 vw	597 vw	597 vw	597 vw	597 vw	596 vw sh						$\delta_s SO_3$
574 m	574 m	574 m	574 m	574 m	574 m	574 m	582 m	582 m	582 m	581 m	581 m	$\delta_{as} CF_3$
523 w	523 w	524 w	524 w	524 w	524 w	524 w	526 w	526 w	525 w	525 w	525 vw	$\nu_{16b}(\delta CC) + \gamma(CCC)_{ring}C$
515 s	515 m	514 m	514 m	514 m	514 m	514 m	513 m	513 m	513 m	513 m	513 m	$\delta_{as} SO_3$
					498 vw	498 vw	498 w	498 w	498 w	498 w	498 w	$\delta_{as} SO_3$
484 w	483 w	483 w	482 w	480 w	477 w	477 w	476 w	476 w	475 w	475 w	475 w	$\delta CC=O + \nu CC/skeletal$ vibrations

[a] Used symbols: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad, sh – shoulder; ν – stretching ($_s$ - symmetric, $_{as}$ - asymmetric), δ – bending in plane, γ – bending out of plane, ρ – rocking, τ – torsion, ω – wagging, t – twisting, $_{wet}$ – "free" water molecules, $_{cryst}$ – crystallization water.

Table S3   The wavenumbers (cm^{-1}) and the infrared intensities of the bands observed in the infrared spectra of polycrystalline sample of the PGTFH/PGTF in the range of temperature 298 K – 373 K (recorded in the PCTFE oil).

PGTFH/PGTF												
IR(T) [cm^{-1}] (PCTFE)												
298 K	333 K	337 K	341 K	345 K	347 K	349 K	353 K	357 K	361 K	365 K	373 K	Assignment[a]
							3470 w sh	3473 m b	3503 m b	3515 m b	3520 m b	$\nu H_2O_{(wet)}$
3418 s sh	3416 s sh	3419 s sh	3419 s sh	3419 m sh	3426 m sh	3420 m sh						$\nu_{as}H_2O_{(cryst)}$
3361 s b	3376 s b	3376 s b	3378 s b	3382 m b	3383 m b	3382 m b	3358 m b					$\nu_sH_2O_{(cryst)}$
3227 vs	3223 vs	3223 vs	3223 vs	3221 vs	3220 vs	3220 vs						$2 \times \nu_{8a}(\nu CC)$
							3191 vs	3193 vs	3193 vs	3193 vs	3193 vs	$\nu NH\cdots O$
3165 vs	3165 vs	3165 vs	3165 vs	3165 vs	3165 vs	3165 vs	3163 vs					$\nu NH\cdots O + \nu_{8a}(\nu CC) + \nu_{19b}(\nu CC)$
3145 vs sh	3144 vs sh	3144 vs sh	3142 vs sh	3142 vs sh	3145 vs sh	3145 vs sh	3148 vs sh	3148 vs	3149 vs	3149 vs	3149 vs	$\nu NH\cdots O + \nu_{8a}(\nu CC) + \nu_{19a}(\nu CC)$
3111 w sh	3110 w sh	3107 w sh	3105 w sh	3105 w sh	3101 w sh	3101 w sh	3096 w	3095 vw	3095 vw	3095 vw	3095 vw b	$\nu_{8b}(\nu CC) + \nu_{19a}(\nu CC)$
3045 s	3045 s	3045 s	3048 s	3048 s	3049 s	3049 s	3054 w					$\nu_{7a}(\nu CH)$
							3039 vw	3041 vw	3043 vw	3043 vw	3043 vw	$\nu_{7a}(\nu CH)$
2969 s	2969 s	2969 s	2970 s	2970 s	2970 s	2970 s	2971 m	2978 w	2978 w	2978 w	2978 w	$\nu CC / 2 \times \nu_{19a}(\nu CC)$

2871 m b	2871 w b	2872 w b	2872 w b	2872 w b	2861 w b	2861 m b	2854 vw b					
2776 w	2776 w	2776 w	2776 w	2776 w	2776 w	2776 w	2778 vw					
2671 w	2671 w	2671 w	2671 w	2671 w	2672 w	2672 w	2686 w	2705 w	2711 w	2711 w	2711 w	
2623 m	2622 m	2622 m	2621 m	2621 m	2621 m	2621 m	2621 w	2619 w	2612 w	2612 w	2612 w	
2600 m	2600 m	2600 m	2600 m	2600 m	2600 m	2600 m	2602 w	2600 w				
1722 vs b	1724 vs b	1725 vs b	1725 vs b	1726 vs b	1757 w sh	1760 w sh	1764 m sh	1764 m sh	1764 m sh	1764 m sh	1764 m sh	$\nu C=O$
					1726 vs b	1727 vs b	1730 vs b	1739 vs b	1742 vs b	1742 vs b	1743 vs b	
1651 w	1647 w	1647 w	1645 w	1645 w	1643 w	1643 w	1641 vw	1639 vw sh	1638 vw sh	1638 vw sh	1638 vw sh	$\delta_{as}NH_3^+$
1615 m	1614 m	1614 m	1613 m	1612 m	1612 m	1610 m	1605 m	1602 m	1602 m	1602 m	1602 m	$\nu_{8a}(\nu CC)$
1582 w	1582 w	1582 w	1582 w	1582 w	1582 w	1582 w	1583 w	1583 vw sh				$\nu_{8b}(\nu CC)$
1502 vs	1501 vs	1501 vs	1501 vs	1501 vs	1500 vs	1500 vs	1501 vs	1501 vs	1502 vs	1503 vs	1503 vs	$\nu_{19a}(\nu CC)$
1462 m	1462 m	1462 m	1461 m	1461 m	1461 m	1461 m	1461 m	1461 w	1459 w	1460 w	1460 w	
			1420 vw	1420 w	1419 w	1419 w	1419 m	1419 m	1419 m	1419 m	1419 m	$\delta_s NH_3^+$
1393 vw	1393 vw	1393 vw	1392 vw	1392 vw	1392 vw	1393 vw						$\nu_3(\delta CH)$ / δCH
1358 vw	1358 vw	1358 vw	1357 vw	1357 vw	1357 vw	1357 vw	1357 vw	1356 vw	1354 vw	1355 vw	1355 vw	δCH
1347 m	1347 m	1347 m	1346 w	1346 w	1346 w	1346 w	1346 w	1344 vw sh				$\gamma CH + \rho NH_3^+$

[a]Used symbols: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad, sh – shoulder; ν – stretching ($_s$ - symmetric, $_{as}$ - asymmetric), δ – bending in plane, γ – bending out of plane, ρ – rocking, τ – torsion, ω – wagging, t – twisting, $_{wet}$ – "free" water molecules, $_{cryst}$ – crystallization water.

Table S4   Correlation diagram of the internal vibrations of the trifluoromethanesulfonic anion in the PGTFH and PGTF crystals

	Vibration	Isolated anion C_{3v}	Site symmetry C_1	Factor group C_{2h}	IR [cm^{-1}]	Raman [cm^{-1}]
PGTFH	ν_1 ($\nu_s CF_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + B_g(R) + A_u(IR) + B_u(IR)	1227 vs	1228 (14)
	ν_2 ($\nu_s SO_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + B_g(R) + A_u(IR) + B_u(IR)	1031 vs	1037 (56)
	ν_3 ($\delta_s CF_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + B_g(R) + A_u(IR) + B_u(IR)	766 s	766 (38)
	ν_4 ($\delta_s SO_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + B_g(R) + A_u(IR) + B_u(IR)	643 s	652 (3), 585 (9)
	ν_5 (νCS)	A_1(IR,R)	A(IR,R)	A_g(R) + B_g(R) + A_u(IR) + B_u(IR)		318 (22)
	ν_6 ($\nu_{as} SO_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2B_g$(R) + $2A_u$(IR) + $2B_u$(IR)	1277 vs, 1266 vs, 1112 vw	1268 (9), 1111 (3)
	ν_7 ($\nu_{as} CF_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2B_g$(R) + $2A_u$(IR) + $2B_u$(IR)	1175 s	1174 (6)
	ν_8 ($\delta_{as} CF_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2B_g$(R) + $2A_u$(IR) + $2B_u$(IR)	573 s	577 (9)
	ν_9 ($\delta_{as} SO_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2B_g$(R) + $2A_u$(IR) + $2B_u$(IR)	514 s	513 (5) b
	ν_{10} (ρSO_3)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2B_g$(R) + $2A_u$(IR) + $2B_u$(IR)		349 (37)
	ν_{11} (ρCF_3)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2B_g$(R) + $2A_u$(IR) + $2B_u$(IR)		206 (4)
	ν_{12} (τCS)	A_2(-)	A(IR,R)	A_g(R) + B_g(R) + A_u(IR) + B_u(IR)		
PGTF	Vibration	Isolated anion C_{3v}	Site symmetry C_1	Factor group C_i	IR [cm^{-1}]	Raman [cm^{-1}]

|					
ν_1 ($\nu_s CF_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + A_u(IR)	1220 vs sh	1213 (22)
ν_2 ($\nu_s SO_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + A_u(IR)	1034 vs	1039 (85)
ν_3 ($\delta_s CF_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + A_u(IR)	766 w sh, 761 m	767 (52)
ν_4 ($\delta_s SO_3$)	A_1(IR,R)	A(IR,R)	A_g(R) + A_u(IR)	643 s, 637 s sh, 585 m	646 (17), 584 (23)
ν_5 (νCS)	A_1(IR,R)	A(IR,R)	A_g(R) + A_u(IR)		322 (40)
ν_6 ($\nu_{as} SO_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2A_u$(IR)	1275 vs sh, 1250 s, 1111 m	1270 (19), 1251 (19), 1111 (18)
ν_7 ($\nu_{as} CF_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2A_u$(IR)	1176 vs sh	1172 (19)
ν_8 ($\delta_{as} CF_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2A_u$(IR)	574 m	575 (20)
ν_9 ($\delta_{as} SO_3$)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2A_u$(IR)	512 m	514 (17), 511 (16)
ν_{10} (ρSO_3)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2A_u$(IR)		352 (36) sh, 348 (39)
ν_{11} (ρCF_3)	E(IR,R)	$2A$(IR,R)	$2A_g$(R) + $2A_u$(IR)		205 (10)
ν_{12} (τCS)	A_2(-)	A(IR,R)	A_g(R) + A_u(IR)		
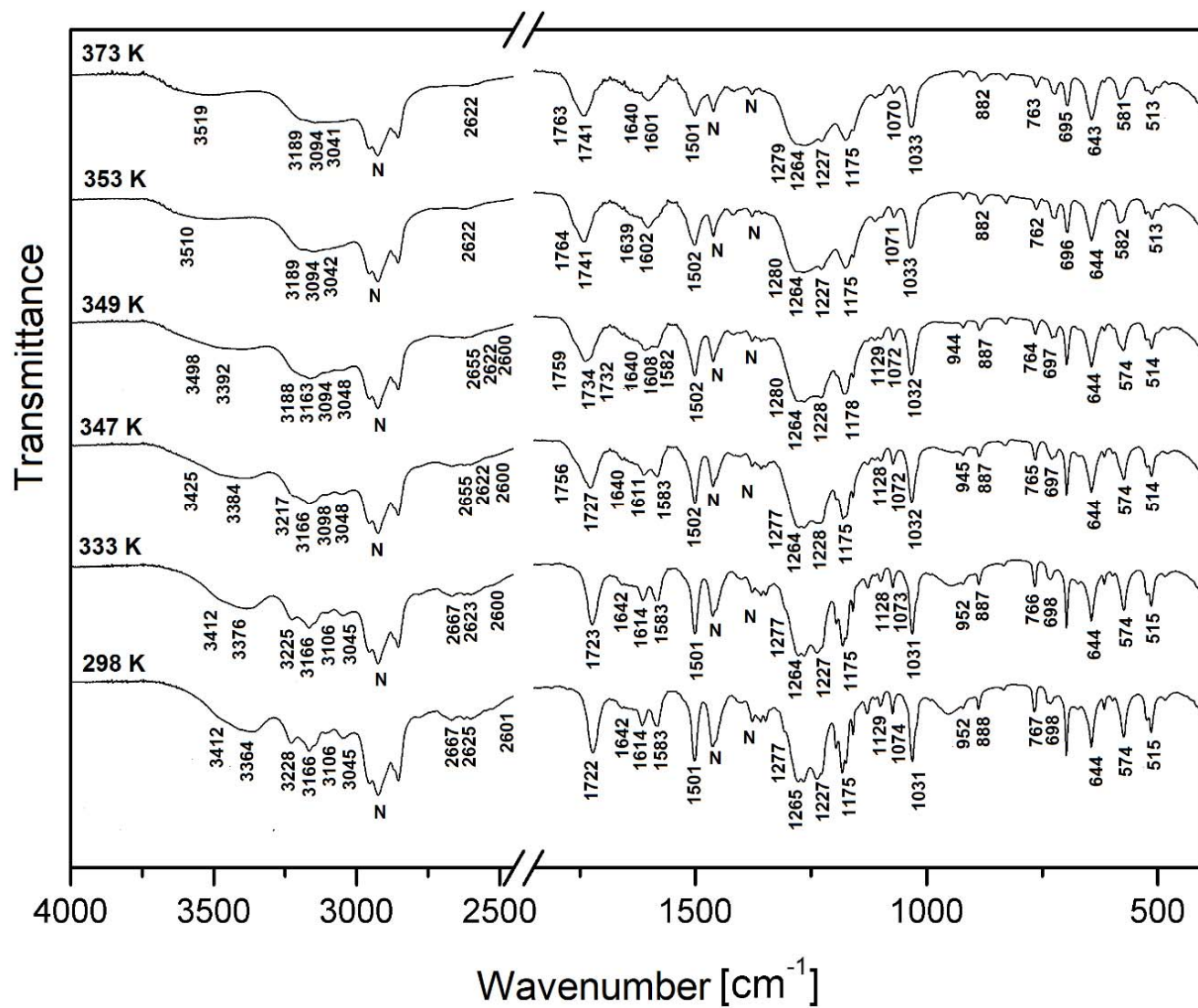
Figure S1 Infrared spectra of the polycrystalline sample of the PGTFH in nujol mull, recorded in the function of temperature (above room temperature).
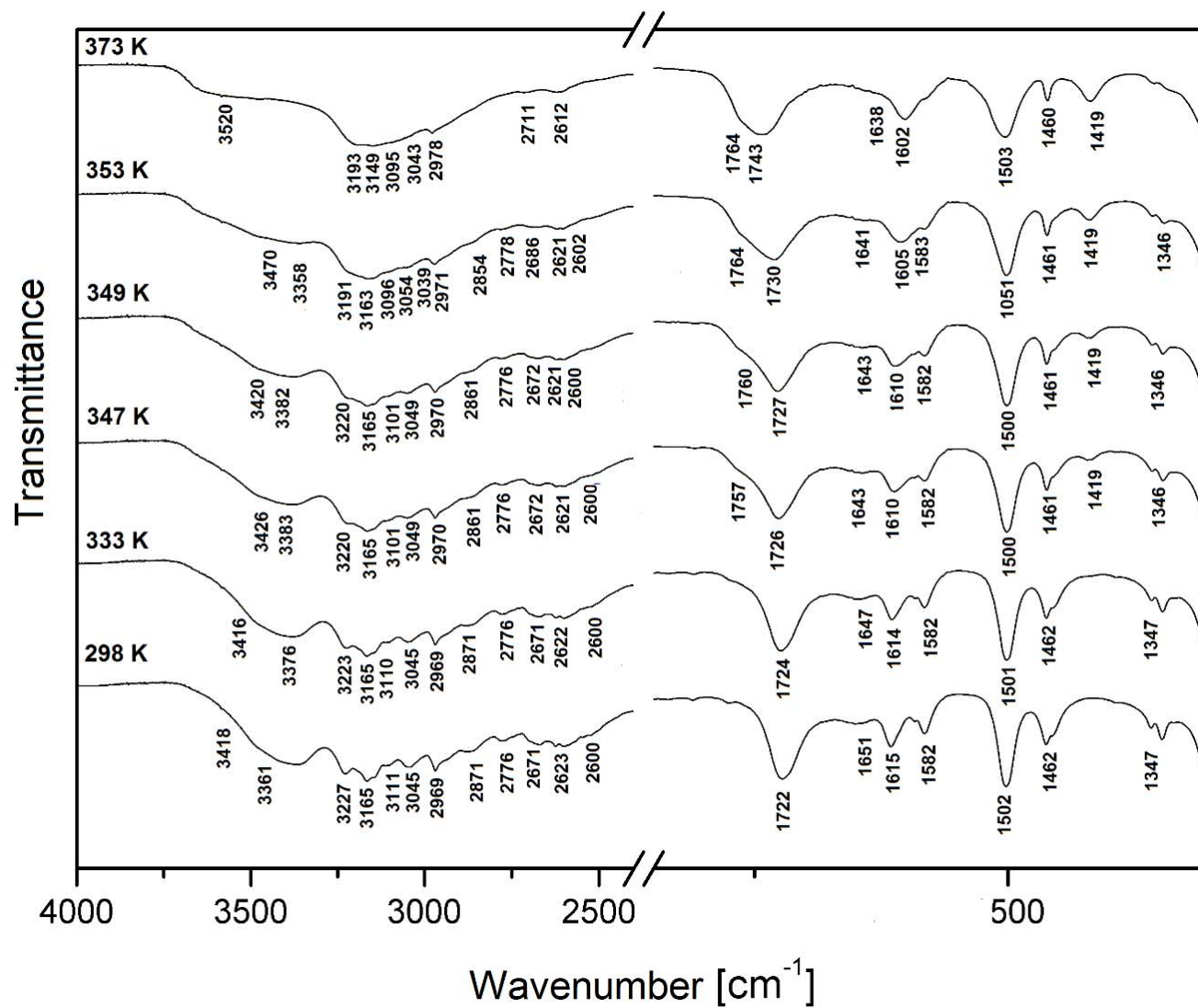
Figure S2 Infrared spectra of the polycrystalline sample of the PGTFH in the PCTFE oil, recorded in the function of temperature (above room temperature).
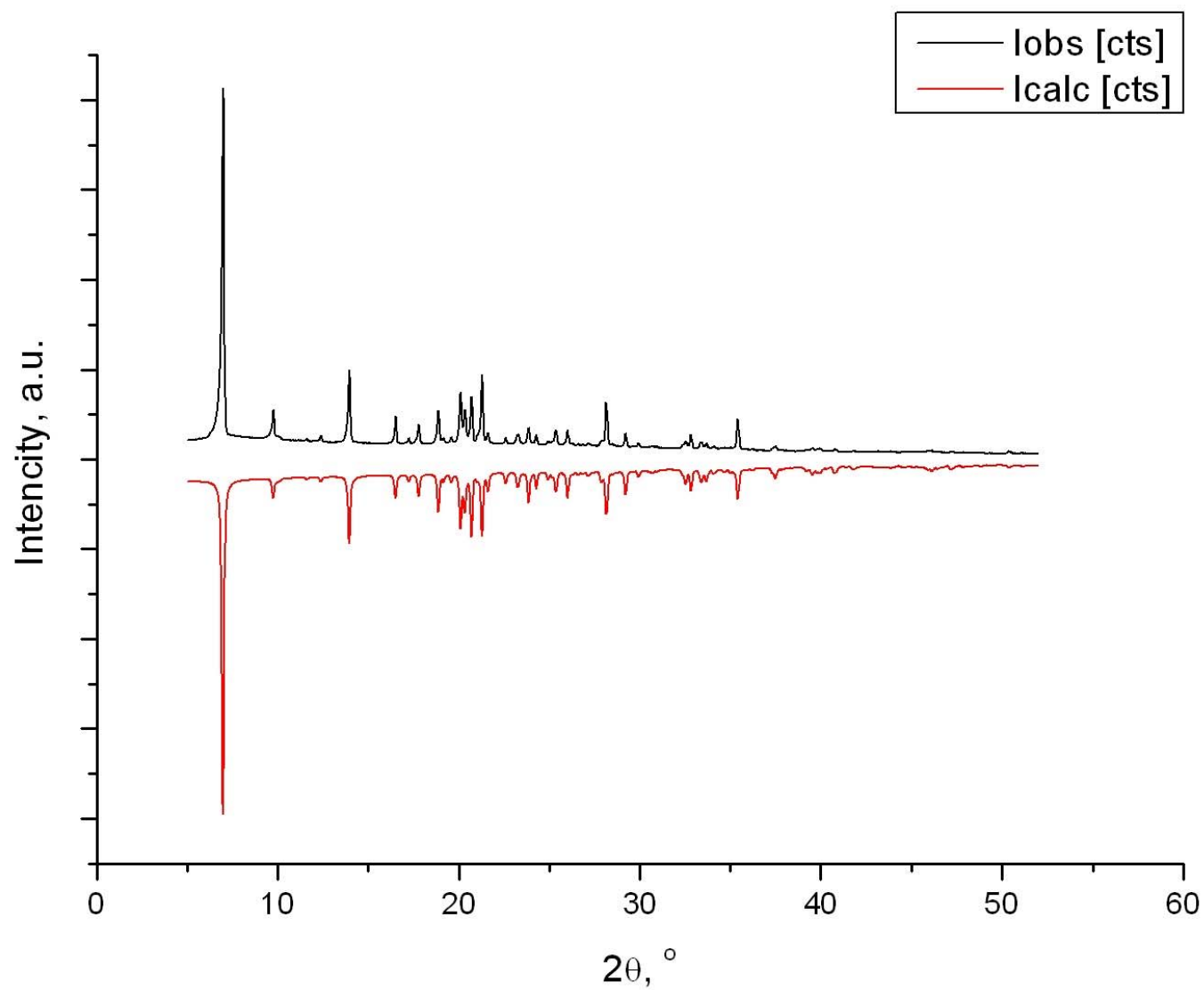
Figure S3 Observed and calculated diffracting pattern of the annealed polycrystalline sample of the PGTF.
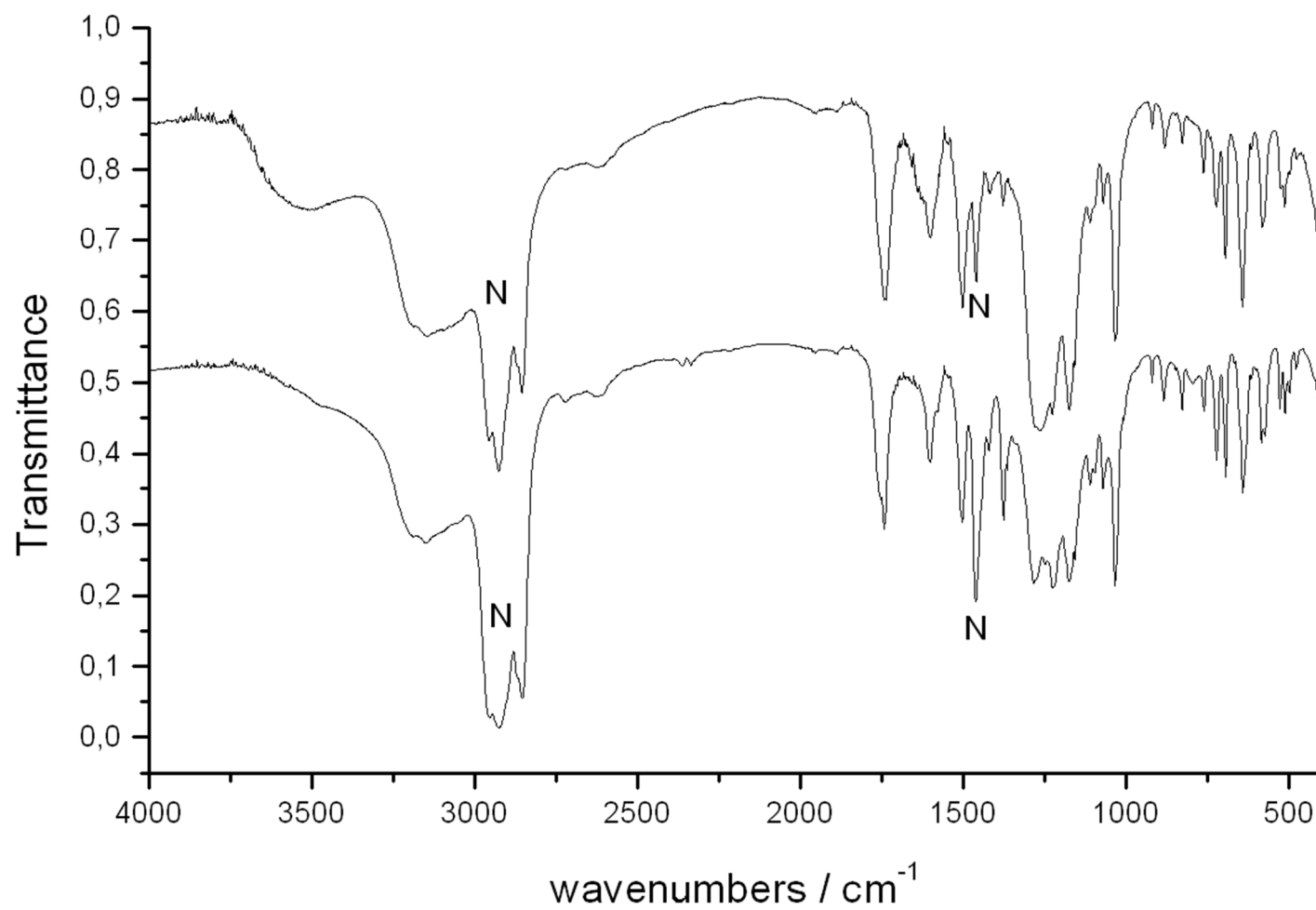
Figure S4 The spectra of dehydrated PGTF crystal recorded in-situ (at 100 °C in the cryostat, upper spectrum) and at room temperature (sample was obtained by drying the hydrated sample under sodium lamp at a temperature about 373 K, lower spectrum).

There are only slight differences between the IR spectrum of desolvated material, PGTF, recorded at room temperature and IR spectrum of the material desolvated in-situ above the water escape temperature (spectrum recorded at 100 ºC) (Fig. S4). These observations apply also to the bands arising from hydrogen bond vibrations. The band due to the stretching vibration of O–H···O hydrogen bond in both spectra is broad, has the same position and shape. The subtle changes one can observe for the bands due to deformation modes: the $\delta_s NH_3^+$ band is observed at 1420 cm^{-1} in the spectrum recorded at room temperature and at 1416 cm^{-1} in the spectrum recorded at 100 ºC; the band due to γOH is observed only in the spectrum recorded at room temperature. Some bands due to aromatic ring and triflate anion vibrations observed in the 550-480 cm^{-1} region are better resolved in the PGTF spectrum recorded at room temperature than in the spectrum recorded in-situ (at 100 ºC) what results from temperature effect.