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Phase transitions in non-centrosymmetric pyridinium trifluoromethanesulfonate crystal: Vibrational studies



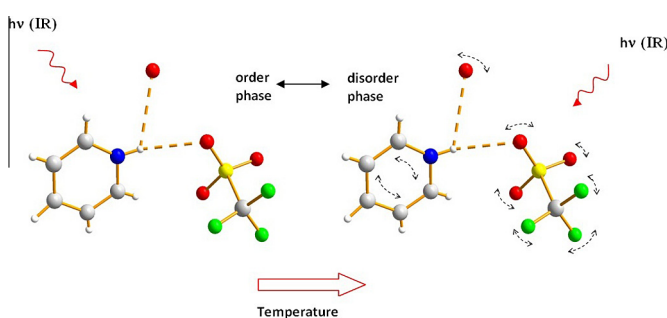
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HIGHLIGHTS

- Multiple structure of νNH band arises from Fermi resonance.
- Internal modes of PyHOTf fulfill selection rules of the factor group in IR spectra.
- PyH^+ cation and ^-OTf anion are involved in the order–disorder phase transitions.
- PyH^+ cation and ^-OTf anion exhibit rotational mobility at high temperature phases.

GRAPHICAL ABSTRACT



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ABSTRACT

Infrared spectroscopy ($4000\text{--}400\text{ cm}^{-1}$) in the wide temperature range, from 11 to 473 K, has been used to investigate the non-centrosymmetric pyridinium trifluoromethanesulfonate crystal, exhibiting several phase transitions. The assignments of the bands observed in the studied spectra have been proposed. The temperature dependence of the wavenumbers and the full width at half maximum (FWHM) of the bands arising from some internal vibrations of the pyridinium cation and the triflate anion have been analyzed in order to achieve a knowledge of whether these both ions are involved in the phase transitions and what is the role of these both ions in these phase transitions. The infrared measurements showed that the both ions, pyridinium cation and triflate anion are involved in the high temperature phase transitions of the order–disorder type, previously reported at 305.1 and 396.7 K. They also revealed that these transitions are governed by a rotational mobility (changes in dynamical states) of both the pyridinium and triflate ions. Our results show that the multiple structures of the νNH and νND bands observed in the studied infrared spectra is due to the Fermi resonance interaction between the stretching vibration of the $\text{N}\text{--}\text{H}\cdots\text{O}$ hydrogen bond and the overtones and combinations of the internal vibrations of the pyridinium cation.

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Introduction

Pyridinium trifluoromethanesulfonate (PyHOTf), universally used as a source of the trifluoromethanesulfonate anion in the diverse chemical reactions, turn out to be very attractive species

for its interesting physical properties. Recently reported Differential Scanning Calorimetry (DSC) has revealed several fully reversible phase transitions in this crystal [1]. According to these data three reversible and well defined solid–solid phase transitions of a first order character at 305.1, 358.7 and 396.7 K and a very weak anomaly at low temperature (at about 205.3 K) of a second order nature in studied crystal were observed. The DSC results were fully supported by X-ray studies [1]. The PyHOTf crystal

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belongs to the non-centrosymmetric $P4_32_12$ space group of tetragonal system [1,2] in two low temperature phases (phase V and IV). The phase transition at 305.1 K (IV \rightarrow III) is accompanied by change of the space group from $P4_32_12$ (in phase IV) to P_2 (in the phase III), and simultaneously, by change of the crystallographic system from tetragonal (phase V and IV) to monoclinic one (phase III). Both intermediate phases (III and II) belong to a monoclinic system. In the high-temperature phase I (prototype phase) the crystal is pseudo-cubic with a slight tetragonal deformation. Additionally, the TGA measurement has shown the thermal stability of the crystal in question up to about 620 K [1]. As follows from DSC data the studied crystal is characterized by a low entropy of melting (about $14 \text{ J mol}^{-1} \text{ K}^{-1}$) and a relatively high melting temperature (about 490 K) [1]. According to Timmermans' criterion for a plastic crystal [3] all these features imply that PyHOTf may appear as a promising high temperature proton conductor.

In this contribution vibrational spectra of the PyHOTf crystal at room temperature and temperature dependent infrared spectra of the PyHOTf crystal in wide temperature range are presented. The temperature dependent infrared spectra can provide information on anomalous dynamical properties of crystals near structural phase transition or on structural changes near structural phase transition. Those data can be easily determined from the evolution of the infrared band shapes as well as from infrared band positions versus temperature. The utility of infrared spectroscopy in the structural phase transition investigations has been written in many publications (see for example ref [4]). Recently reported XRD data show that the low temperature phase transition is accompanied by weakness of one N-H...O hydrogen bond but the high temperature phase transitions are triggered off by the high disordered of pyridinium cations and triflate anions [1]. Our analysis of the temperature dependent infrared spectra was preceded by detailed discussion of the infrared spectra measured at room temperature based on the PyHOTf crystal structure and vibrational spectra of the pyridinium cations, triflate anions and their salts.

Experimental details

PyHOTf was obtained from a saturated aqueous solution containing pyridine and triflic acid in the 1:1 molecular ration at room temperature. The N-deuterated species was prepared by threefold re-crystallization from D_2O solution. The degree of the deuterium substitution at the nitrogen atom has been estimated at ca. 60 per cent on comparing the infrared spectra of the N-deuterated and non-deuterated species.

The infrared spectra for polycrystalline sample of studied crystal were measured for the mulls in Nujol and fluorolube in wide temperature range (473–11 K) in the $4000\text{--}400 \text{ cm}^{-1}$ wavenumbers region with a Bruker IFS-66 and Bruker IFS-88 spectrometer. The resolution was 2 cm^{-1} . The low temperature spectra (11–300 K) were measured with a spectrometer equipped with closed helium cryostat (ARS Displex Model CS202-X1.Al closed cycle cryostat) to which a temperature controller of Scientific

Instruments (Model SI-9700-1) was joint. The high temperature spectra (300–473 K) were recorded with the Specac high temperature cell. The infrared powder spectrum for N-deuterated sample was recorded at room temperature only. The temperature dependent IR spectra were recorded in the following way:

- (i) *The low temperature spectra.* The first spectrum was measured at 11 K. Then the sample was heated step-by-step, up to the room temperature. The maximum temperature variation in one step was 25 K and the waiting time for the temperature stabilization was 20 min. After every step and temperature stabilization the spectrum was measured.
- (ii) *The high temperature spectra.* These spectra were measured from room temperature to 473 K and an analogous step-by-step procedure was applied.

The FT Raman spectra of polycrystalline spectra of both crystals, deuterated and un-deuterated were recorded with a Nicolet IFS-860 instrument with a Raman attachment in the $3500\text{--}200 \text{ cm}^{-1}$ region. The 1064 nm line of a Nd:YAG diode pump laser (power = 400 mW) was used for excitation. The spectral resolution was 2 cm^{-1} .

The programs: GRAMS/386 Galactic Industries and Origin 5.0 were used for the numerical fitting of the experimental data.

Results and discussion

The crystal structure and selection rules for the PyHOTf crystal at room temperature

The crystal of PyHOTf at room temperature is tetragonal and belongs to the $P4_32_12$ space group with eight molecules, occupying the general position, per unit cell [1]. The pyridinium cations (PyH^+) and trifluoromethanesulfonate (^-OTf) anions are arranged in infinite and helical chains in which they are alternately bonded by bifurcated medium strong N-H...O hydrogen bonds of 3.214 and 3.159 Å lengths [1]. The same molecular arrangement is observed in the low temperature phase (below 205 K), however, the N...O distances are shorter (2.929 and 2.925 Å, respectively).

The results of the factor group analysis of studied crystal are summarized in Table 1a. The correlation diagram relating the factor group to the site group is shown in Table 1b. There it is seen that the presence of eight molecules in the unit cell can result in splitting of each internal vibrations into six components. Three of them ($A_2 + 2E$) are predicted in infrared spectrum and five of them ($A_1 + B_1 + B_2 + 2E$) should be Raman active.

Vibrational spectra at room temperature

The vibrational spectra of PyHOTf and its partly N-deuterated species measured at room temperature are shown in Fig. 1. The wavenumbers of the bands observed in these spectra are reported in Table 2.

Table 1a
Formal analysis of the fundamental modes ($k = 0$) for the PyHOTf crystal at 165 K and at room temperature (in the V and IV phase).

D_4	N^a	A	Lattice vibrations		Internal vibrations		Selection rules	
			T	L	$C_5H_5NH^+$	$CF_3SO_3^-$	IR	Raman
A_1	60	0	6	6	30	18		$x^2 + y^2, z^2$
A_2	60	1	5	6	30	18	z	
B_1	60	0	6	6	30	18		$x^2 - y^2$
B_2	60	0	6	6	30	18		xy
E	120	1	11	12	60	36	x, y	xz, yz

^a Used abbreviation: N – total number of modes; A – acoustical modes; T – translational modes; L – librational modes.

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