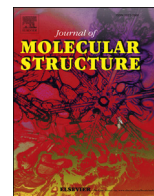




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Vibrational spectroscopic, optical and thermal properties of a hybride pyridazine perchlorate complex—An experimental and theoretical study

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ABSTRACT

Various methods of experiment: differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and infrared (IR) spectroscopy have been used to investigate the phase transitions in pyridazine perchlorate crystal. DSC showed the existence of phase transition at $T = 341$ K. The vibrational IR spectra in Nujol and Perfluorolube mulls were studied in a wide temperature range, from room temperature to 380 K. Special attention was put on the temperatures near the phase transition temperature. The temperature changes of wavenumbers, gravity center and band intensities were analyzed to clarify the phase transition molecular mechanism. Information about hydrogen bonds was obtained. For more detailed band assignment and overall spectral presentation Raman and far infrared (FT–FIR) spectra at room temperature have been carried out. The experimental data interpretation was supported by theoretical calculations based on density functional theory, with the B3LYP method and 6–311++G(d,p) basic set. Some theoretical conformations were analyzed. Calculated normal vibrational modes of the molecule, their frequencies and intensities were compared with these recorded in experiment.

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1. Introduction

Pyridazine perchlorate [(C₄H₄N₂)HClO₄] crystal, abbreviated as PCIO, consists of pyridazinium cations and perchlorate anions. It belongs to organic–inorganic compounds. Pyridazine, a component of the studied crystal, is a heterocyclic aromatic compound with the molecular formula (CH)₄N₂. It contains a six-membered ring with two adjacent nitrogen atoms. Although azines form the basic structures of some of the most important compounds in nature, pyridazines are rare in nature. They are worth researching since they can be found within a number of herbicides and drugs. In solid salts the symmetrical, planar, heteroaromatic cation is involved in interionic hydrogen bonds. The results of the X-ray diffraction method [1,2] indicate that the crystal is monoclinic at room temperature, with the space group P2₁/n and Z = 4. The hydrogen bonds of the C–H···O, N–H···O and N–H···N type [1,2],

which link the ClO₄[−] groups and the pyridazine rings stabilize the crystal structure. Dielectric and optical studies [1] have revealed the first order structural phase transition (PT) at 343 K with thermal hysteresis of about 3 K. The room temperature phase (II) is the ordered one while the phase I above the PT temperature is disordered. At 350 K, at phase I the crystal is trigonal (in Ref. [1] it is described as hexagonal), with the space group R $\bar{3}$ m and Z = 3. The molecules in the crystal are disordered in this phase and the hydrogen bonds are broken [1]. So, the pyridazinium cations and ClO₄[−] anions reveal orientational disorder above the phase transition and hold the rigid crystal lattice at room temperature.

Spectroscopic methods are expected to provide additional, detailed knowledge of any molecular framework. In order to learn more about the nature of the chemical bonds involved, the intermolecular forces and the behavior of normal modes and their connections with the structural phase transition a precise study was made on the IR spectrum of pyridazine perchlorate crystal.

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2. Experimental

Pyridazine perchlorate crystals were grown by slow evaporation method from a saturated aqueous solution of stoichiometric quantities of pyridazine and perchloric acid. The evaporation took place at constant temperature of 303 K.

The temperature dependent infrared spectra were measured with the resolution of 1 cm^{-1} in the range $4000\text{--}400\text{ cm}^{-1}$ by using a Nicolet Nexus FT-IR spectrometer with KBr windows. The measurements were made at several temperatures. The samples were prepared as suspensions of powder obtained from the single crystals in Nujol and Perfluorolube mulls, respectively. The spectra in Perfluorolube mull were recorded in order to point out C–H stretching vibrations, which is impossible in Nujol mull. A Graseby–Specac variable-temperature cell was used to control the temperature. The measured sample temperature was changed in the range of $294\text{--}383\text{ K}$ on heating run. Each spectrum was assembled at constant temperature. The stability of the temperature was $\pm 1\text{ K}$. 128 scans were collected to improve the signal to noise ratio. In the FT-IR interferogram the zero path difference (ZPD) maximum fluctuated between c.a. -5.20 at minimum and c.a. $+7.20$ at maximum. For the spectroscopic data analysis the multifunctional GALACTIC GRAMS/386 program was used. It is worth noting that the band positions obtained by curve fitting may slightly differ from the wavenumbers shown on the observed spectra.

A VERTEX 70 spectrometer was used to record the FT-FIR spectra of the powdered pyridazine perchlorate crystal in Nujol oil in the range of $600\text{--}50\text{ cm}^{-1}$ at room temperature (RT). The crystal in Nujol suspensions were placed between polyethylene windows.

The room temperature spectrum of the compressed pellet made from powdered crystal and KBr was recorded in the range of $4000\text{--}400\text{ cm}^{-1}$ with the use of the same VERTEX 70 spectrometer. The resolution was 2 cm^{-1} .

Raman spectra of a powdered crystal at room temperature were recorded using a Nicolet Magna 860 FT-IR spectrometer, interfaced with a FT-Raman accessory. The Raman spectra were excited with a Nd:YVO₄ laser line at 1064 nm with a power of ca. 290 mW . The measurements were performed in the wavenumber range $4000\text{--}50\text{ cm}^{-1}$ with the resolution of 4 cm^{-1} .

Differential scanning calorimetry (DSC) measurements were carried out using Perkin–Elmer DSC-7 between 113 K and 433 K . The heating/cooling rates of 20 K/min and 10 K/min were carried out. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made on a Setaram SETSYS 16/18 instrument in nitrogen atmosphere, with the heating rate 5 K/min , in the temperature range $300\text{--}670\text{ K}$. The sample mass was 8.51 mg .

DFT calculations at the B3LYP/6-311++G(d,p) level were performed by the Gaussian-03W program [3] tending towards an optimization the frequencies and intensities of the corresponding modes. Theoretically predicted frequencies were scaled down to account for various systematic errors in the theoretical methods. A set of variable scaling factors was used, i.e. factor 0.95 for frequencies above 2000 cm^{-1} and factor 0.98 for frequencies between 1000 and 2000 cm^{-1} .

The Mercury 2.3 program was used for indicating the distances of hydrogen bonds.

3. Results and discussion

3.1. Thermal measurements

The results of differential scanning calorimetry (DSC) measurements for PCIO are presented in Fig. 1a. The crystal was cooled up to 110 K , then heated till 373 K and cooled up to RT. The large

heat anomaly (on cooling and heating) occurs as a result, with the onset at 332 K and the maximum at 341 K (on heating) and can be clearly attributed to the first order phase transition (PT). The temperature hysteresis for the PT is about 4 K . The entropy of the transition equals $-30\text{ J/mol}\cdot\text{K}$ and the phase transition heat -10 kJ/mol .

To verify the crystal stabilization, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out [Fig. 2b] in the temperature range $300\text{--}670\text{ K}$. The anomaly at about 340 K , which takes place without any loss of the sample mass, corresponds to the phase transition detected by the DSC measurements. The next heat anomaly, that is the peak at about 420 K is related to the sample melting. Boetius apparatus was used for the verification. The small anomaly at 460 K is due to the beginning of the sample decomposition. Above 423 K a continuous decomposition of the crystal is visible with a strong endothermic peak placed at about 573 K . The almost complete loss of sample mass is observed above 570 K .

3.2. Vibrational spectra

The infrared spectra and calculated internal vibrations of pyridazine molecule (not ion) were already published [4–7]. The first experiments and calculations did not contain the precise band assignments [as in 4, 5]. Fig. 2a. presents the representative IR spectra obtained in our experiment. These are the spectra recorded in Nujol mull in the range of $4000\text{--}400\text{ cm}^{-1}$ at RT and at 377 K , the spectrum measured in the same range as mentioned above in KBr pellet and the RT FT-FIR spectrum of the powdered pyridazine perchlorate crystal in Nujol oil in the range of $600\text{--}50\text{ cm}^{-1}$. The bands observed in our experiment (in Fig. 2a) arise, in generally, from internal vibrations of C–H stretching ($3100\text{--}3000\text{ cm}^{-1}$), N–H stretching ($3000\text{--}2800\text{ cm}^{-1}$), overtones ($2000\text{--}1665\text{ cm}^{-1}$), C–C stretching in ring ($1600\text{--}1550\text{ cm}^{-1}$), C–C bending in ring ($1500\text{--}1400\text{ cm}^{-1}$), C–H bending ($900\text{--}675\text{ cm}^{-1}$). So called “fingerprint” range extends at $1400\text{--}600\text{ cm}^{-1}$. The lattice vibration modes occur below 450 cm^{-1} . The detailed vibrational assignments to the experimentally observed bands are presented in Table 1. The assignments used as the guidelines in Table 1 are based on the comparison with the IR spectra of pyridazine [8,9], and L-methionine L-methioninium perchlorate monohydrate crystal [10]. In the studied crystal pyridazinium cations (not molecules) and perchlorate anions are considered. Two very broad bands occur at frequencies $3100\text{--}2200\text{ cm}^{-1}$ and $1170\text{--}1050\text{ cm}^{-1}$. These bands appear due to the hydrogen bond modes, stretching and deformation, respectively. In the range $2050\text{--}1900\text{ cm}^{-1}$ overtones appear. The shape of the overtones points to the C–H substitution in the ring, but not at each position.

Detailed temperature analysis and peak fitting to the obtained spectra were done for these bands of the cations and anions internal vibrations for which some significant temperature effects have been observed. The changes evidence especially at temperatures close to the phase transition temperature. In our paper we present some temperature changes connected with wavenumber, intensity and gravity center of bands connected with the structural phase transition in the PCIO crystal. They illustrate the cationic dynamics contribution to the phase transition mechanisms and hydrogen bonds breaking. It is worth noticing that in many cases the wavenumber of the band obtained by the fitted method may be slightly different from the one shown on the measured spectrum.

Raman spectrum at RT is presented in Fig. 2b. The symmetry requirements cause fewer Raman modes active than IR modes. The vibrational assignments to the observed bands are presented in the last column in Table 1. The very strong mode at 990 cm^{-1} is the bending symmetric ClO_4^- characteristic mode.

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