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INS, DFT and temperature dependent IR investigations of dynamical properties of low temperature phase of choline chloride

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ABSTRACT

Within the framework of the research the inelastic neutron scattering and temperature dependent infrared spectroscopy investigations of the low temperature phase of choline chloride were performed. The infra-red spectra in wavenumber region 4000–80 cm^{-1} and in a temperature range 9–300 K were collected. The density functional theory calculations with the periodic boundary conditions for determination and description of the normal modes in the vibration spectra of choline chloride were applied. Bands assigned to the CH_3 torsional vibration were observed at 288 and 249 cm^{-1}. From the analysis of the temperature dependence of the full-width-at-half-maximum the activation energy for CH_3 group reorientation is found to be equal to 1.6 ± 0.2 kcal/mol.

1. Introduction

Choline is a dietary component that can be found in foods as free choline and as esterified forms such as phosphocholine, glycerophosphocholine, sphingomyelin as well as phosphatidylcholine [1]. It functions as a precursor for acetylcholine, phospholipids and the methyl donor betaine [2], it is not only important for the structural integrity of cell membranes, methyl metabolism, cholinergic neurotransmission, transmembrane signaling but also for lipid and cholesterol transport and metabolism [3]. From the chemical point of view choline generally refers to the various quaternary ammonium salts containing the *N*,*N*,*N*-trimethylethanolammonium cation [4].

The organic salt choline chloride $((CH_3)_3NCH_2CH_2OH)^+Cl^-$ exists in two crystalline polymorphs with phase transition of order–disorder type at a temperature of about 351 K [5–7]. The low temperature α form is orthorhombic, with space group $P2_12_12_1$, unit cell dimensions $a = 11.21$, $b = 11.59$ and $c = 5.90$ Å and with four molecules per unit cell [8,9]. The high temperature β form exists in centrosymmetric space group Fm-3 or Fm-3 m with $a = 9.414$ Å and four molecules per unit cell [10]. The calorimetric studies of choline halides [7] indicate that thermally activated molecular reorientation processes may be important for understanding the phase transition.

The proton spin–lattice relaxation time measurements in the Zeeman (T_1) and rotating ($T_{1\rho}$) frames for choline halides were reported [11–13]. It was found that the activation energy for the methyl group motion about the C_3 symmetry axis in the α phase of choline chloride is in the range of 4.5–5.6 kcal/mol, while the activation energy for the motion of N^+Me about the C'_3 axis is equal to 11.0 kcal/mol [13]. In the β phase of choline chloride the activation energies are equal to 6.79 kcal/mol and 4.34 kcal/mol for the general reorientation and for the chain motion, respectively [13]. The ^{13}C and ^2H high-resolution solid-state NMR studies of choline chloride and bromide in their α phases indicate the onset of reorientation motions at the temperatures preceding the transition to their high temperature β phases [14]. These motions are effectively isotropic both below and above the phase transitions. The ^2H and ^{14}N solid-state NMR spectra of polycrystalline choline chloride, bromide, and iodide indicate that the 180° cation flipping motion occurs in all three salts [15]. From the temperature dependence of these spectra, the activation energy for these motions was determined to be equal 5.8 kcal/mol in the iodide salt and 11.0 kcal/mol in the chloride salt [15].

The results of infra-red (IR) investigations in the high temperature phase of choline chloride [7,16,17] are presented. The density functional theory at the B3LYP level (Becke 88 exchange functional [18], three parameter, Lee, Yang and Parr correlation functional [19]) and *ab initio* at the MP2 level (second order Møller–Plesset

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perturbation theory [20]) calculations for trimethylammonium, tetramethylammonium, trimethylethylammonium, choline and acetylcholine cations [21] are reported. The vibrational frequencies and ^{1}H and ^{13}C chemical shifts of choline halides have been calculated using the density functional theory (B3LYP) method with 6−311++G(d,p) (for detailed basis sets nomenclature, consult [22]) and 6–31 G(d,p) basis sets [23].

In this paper we report the inelastic neutron scattering (INS) and temperature dependent infrared experimental data as well as the density functional theory (DFT) calculations for the low temperature phase of choline chloride.

It was shown that the INS technique is particularly useful in the studies on the deformation modes in which the vibrations of hydrogen atoms are involved [24–26]. This is due to the large incoherent scattering cross-section of hydrogen and the high amplitudes of these vibrations. The methyl derivatives became the subject of our interest, since they are characterized by the high intensities of the CH_3 torsional modes. In the focal point reviews [27,28] the application and complementarities of infrared, Raman and INS spectroscopies in the investigation of dynamical properties of materials were presented. In the case of infra-red and Raman spectra the selection rules apply and moreover the intensities of respective bands can be very low. In contrast, such modes in INS spectra are characterized by the high intensities [29–31].

The $S(\mathbf{Q},\omega)$ function (scattering law) for INS as described in [24,27] can be expressed in the form of isotropic harmonic oscillator,

$$S(\mathbf{Q}, n\omega_i) \propto \frac{(QU_i)^{2n}}{n!} \cdot exp(-(QU_{Tot})^2) \quad (1)$$

where ω_i is the ith mode at a frequency ω; $\mathbf{Q}$ is the momentum transfer and U_i is the mean square displacement of the atoms in the ith mode; U_{Tot} is the total root square displacement of all atoms in all modes; $n = 1$ for a fundamental, $n = 2$ for the first overtone or binary combination, etc. This equation is a fundamental expression in the applications of the INS technique in molecular spectroscopy.

The main aims of our studies are the determination and description of the normal modes in the vibration spectra of choline chloride and the application of the DFT calculations with the periodic boundary conditions for an experimental data analysis.

2. Experimental and calculation

The sample of choline chloride with a purity of ⩾99% was bought from Sigma–Aldrich and used in all experiments without additional treatment.

The far and middle infrared absorption measurements were performed using a Bruker 70v vacuum Fourier transform spectrometer. The transmission spectra were collected with a resolution of 2 cm^{-1} and with 32 scans per each spectrum. The standard triglycine sulfate (DTGS) detectors were used. The FT-FIR spectra (525–80 cm^{-1}) were obtained for the sample suspended in APIEZON® apiezon N grease and placed on a polyethylene (PE) disc.

The FT-MIR spectra (4000–500 cm^{-1}) were collected for the sample in a KBr pellet. The temperature measurements were carried out using an Advanced Research System cryostat DE-202A and water cooled helium compressor ARS-2HW operating in a closed cycle mode. The sample was loaded at room temperature and the measurements were performed on cooling down to ca. 9 K in steps of 10 K. Next the measurements were performed on heating from 9 K to 300 K in steps of 25 K. The desired temperature was measured with an accuracy of ±0.1 K and stabilized for ca. 3 min before the measurements were made. The LakeShore 331S temperature controller equipped with a diode sensor was used to control the temperature. The cooling rate between the desired temperatures was ca. 3 K min^{-1}. The PE and thallium bromo-iodide (KRS5) windows were used in the cryostat in the case of FT-FIR and FT-MIR measurements, respectively.

The inelastic neutron scattering experiment was carried out at the pulsed IBR-2 reactor at JINR Dubna (Russia) using the time-of-flight inverted geometry spectrometer NERA [32] at temperature of 20 K. The spectra were converted from neutron per channel to $S(\mathbf{Q}, \omega)$ scattering function per energy transfer. At the energy transfer between 5 and 1200 cm^{-1} the relative INS resolution was estimated to be ca. 3%.

The total energy optimization and the frequency calculations were performed basing on the periodic density functional theory (DFT) using the CASTEP [33] program as a part of the Materials Studio package [34]. The results were obtained for the crystalline state within the generalized gradient approximation (GGA) at PBE

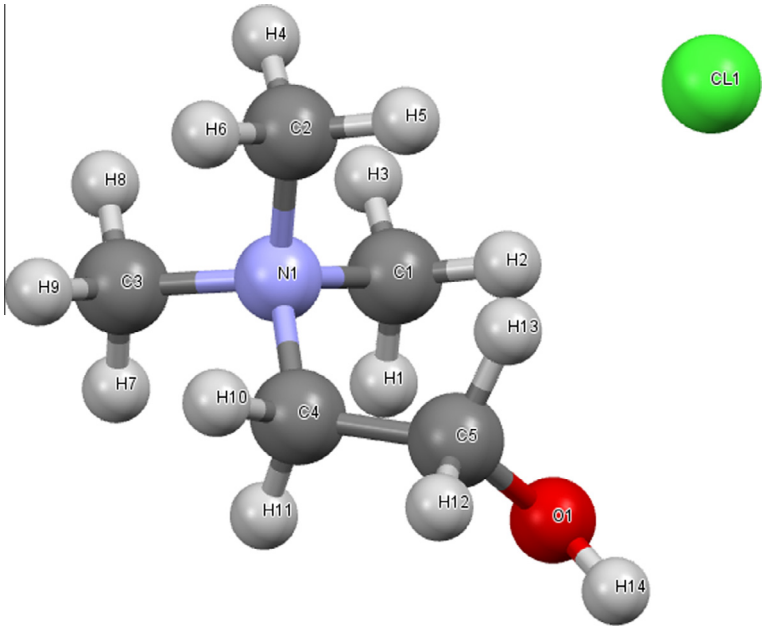

Fig. 1. Scheme of choline chloride molecule with the atom labeling.