# *Spectroscopic and calorimetric investigation of plastic orientationally disordered crystal cyclohexanol*

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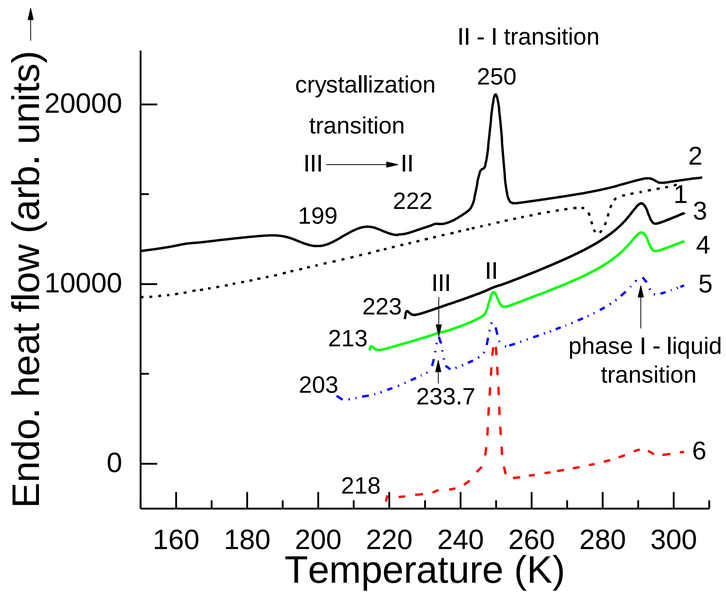
## INTRODUCTION

The present study has intended to investigate polymorphism in cyclohexanol. Cyclohexanol, is an alcohol that consists of cyclohexan bearing a single hydroxy substituent with the formula $CH_3C_6H_4(OH)$. At room temperature it is a orientationally disordered, plastic crystal, which has translation order but not orientational order. Cyclohexanol has at least four crystalline phases; one of them is a orientationally disordered state, (phase I), and three low temperature crystalline modifications: one stable – phase II, and two metastable phases III and III'. The aim of the present investigation is to study the thermodynamic behavior of different phases of cyclohexanol using differential scattering calorimetry technique and IR spectroscopy, which can give new information about their conformational compositions.

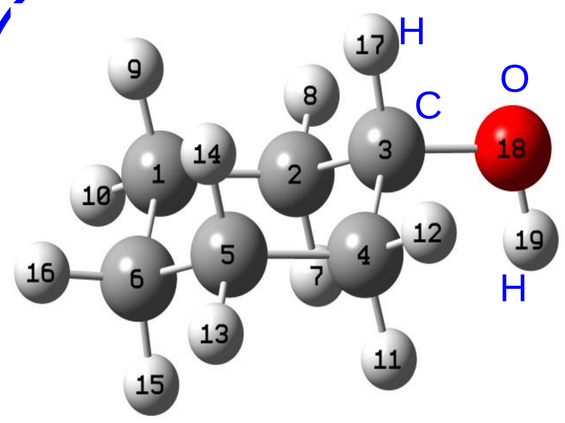
## DSC RESULTS




1. For the first time, we determined the temperature of III – I transition, which occurs at 233.7 K. The temperature of II – I transition is at 250 K.

2. The nucleation process of the metastable phase III develops at 203 K, and of the stable phase II at 213 K. At temperatures higher than 213 K only stable phase nucleate.

3. The fraction of the stable phase II can be increased by annealing at 218 K.




The structure and the numbering scheme of atoms.

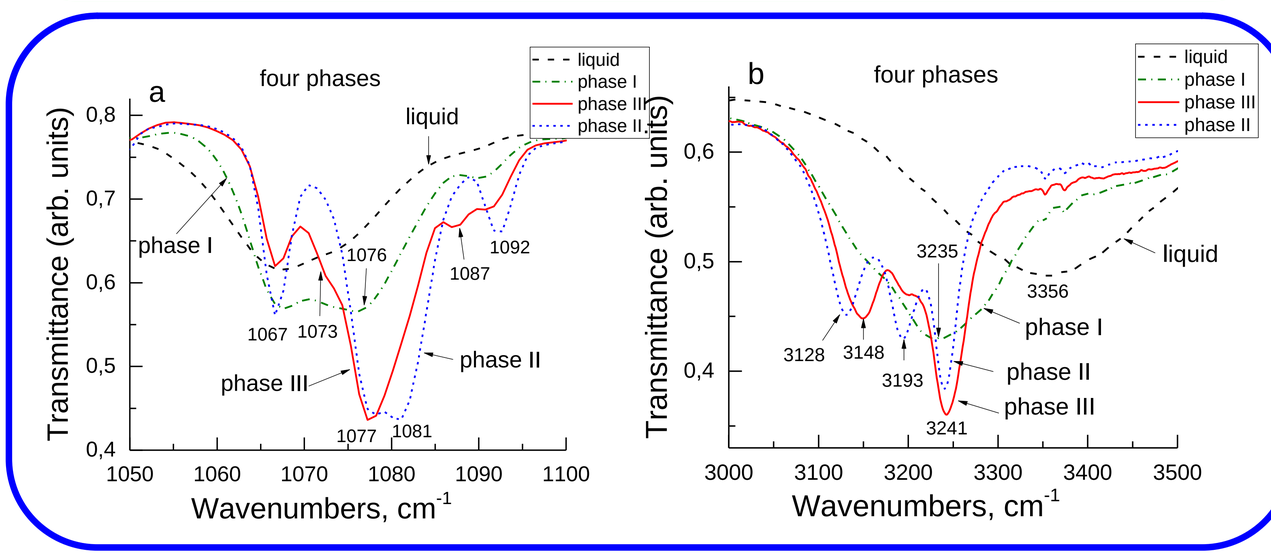
Structural differences between phases mainly concern the fragments located near the OH···O hydrogen bridge. The changes in the C-O and O-H bond lengths and in the values of the angles H-C-O and dihedral angles H-O-C-H lead to changes in ν(OH) stretching and bending β( H-C-O) and χ(H-O-C-H) frequencies.

In type 1 conformer the hydrogen group is in an equatorial out-of-plane conformation with its dihedral angle $H_{19}$-$O_{18}$-$C_3$-$H_{17}$ equal to ~64° and angle $H_{17}$-$C_3$-$O_{18}$ equal to ~110° In type 2 conformer the hydrogen group is in an equatorial in-plane conformation with its dihedral angle $H_{19}$-$O_{18}$ -$C_3$-$H_{17}$ equal to ~180° and angle $H_{17}$-$C_3$-$O_{18}$ equal to ~104° [1].

## INFRARED SPECTRA

The main task is to relate the changes in the structure in cyclohexanol phases recorded during phase transitions between liquid, orientationally disordered and crystalline phases to changes in the infrared spectra (IR).

We will monitor the ν(OH) stretching vibrations and bending vibrations β( H-C-O) and χ( H-O-C-H) that gives us the opportunity to analyze in real time the structural evolution during phase transitions.




The calculation of the IR spectra of conformers [1] showed that the presence of the OH group leads to the appearance of an intense band corresponding to the plane bending vibrations $H_{17}$-$C_3$-$O_{18}$. In type 1 conformer (equatorial in-plane), this band is observed at 1094 $cm^{-1}$, and in type 2 conformer (equatorial out-of-plane) at 1074 $cm^{-1}$. The experimental spectrum of the phase II contains the bands at 1092, and 1077 $cm^{-1}$, which indicates the presence of type 1 and 2 conformers. In the experimental spectrum of the phase III there are small band at 1092 $cm^{-1}$ and strong band at 1077 $cm^{-1}$, which indicates that type 2 conformer predominate in phase III. Phase I is a mixture of conformers of both types.

## CONCLUSION

Phase transitions were studied in cyclohexanol by the DSC method and IR spectroscopy in the ν(OH) stretching vibrations and bending vibrations β( H-C-O) and χ( H-O-C-H) regions. The DSC experiments have shown that the nucleation process of the metastable phase III develops at 203 K, and of the stable phase II at 213 K. At temperatures higher than 213 K only stable phase nucleate. We first established the temperature of the transition III - I at 233.7 K. The transition II – I occurs at 250.0 K. The localization of the orientational glass transition *Tg* is at ~ 163.5 K. Both the orientational glass transition and nucleation of the phases II and III occur in the solid orientationally disordered state.

Based on a comparison of the obtained IR spectra of the phase II and III of cyclohexanol with the calculated spectra for type 1 and type 2 conformers from B3LYP/6-31G(d) [1] we made conclusion that in the stable and metastable phases, different conformers predominate. In the metastable state, phase III type 2 conformer dominate and in the stable state, phase II types 1 and 2 are present. In type 1 conformer the hydrogen group is in an equatorial in-plane conformation. In type 2 conformer the hydrogen group is in an equatorial out-of-plane conformation.

[1]. L.M. Babkov, N.A. Davydova, E.A. Moisejkina. IR spectra of cyclohexanol, structural-dynamic models of molecule // Saratov University Bull. Ser. Physics – 2012 – V. 12. p. 55-62.