

Spectroscopic studies of polymorphism in 4-methylphenol

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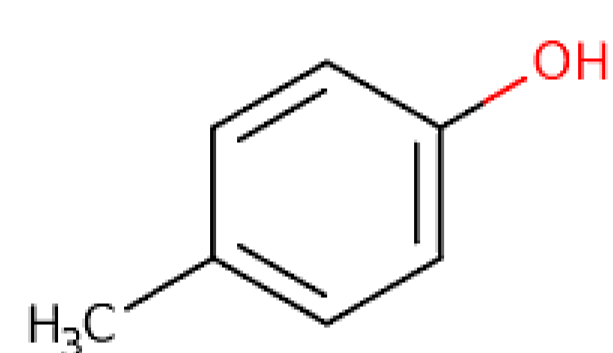
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INTRODUCTION

Polymorphic crystalline phases of 4-methylphenol were investigated earlier using the X-ray diffraction and DSC methods [1]. It has been shown that 4-methylphenol can exist in two polymorphic forms: stable phase (form I) and metastable phase (form II) whose melting temperatures are 309.2 and 307.9 K, correspondingly. The existence of polymorphic forms in 4-methylphenol provides a unique opportunity to study structure-property relationships, since the differences in the vibrational properties between the polymorphs must be due to differences in structure.

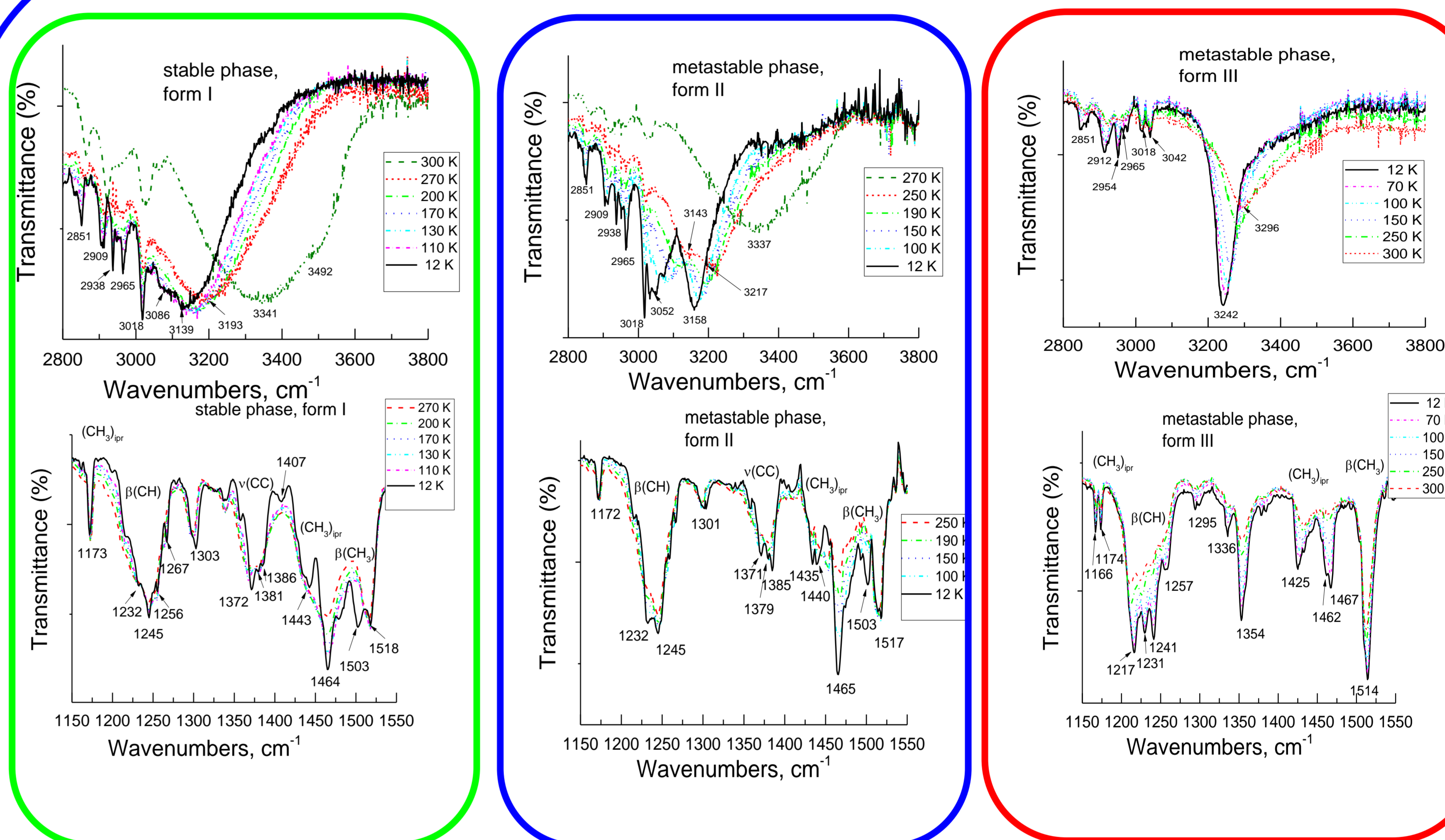
4-methylphenol (*p*-cresol) is an organic compound with the formula $\text{CH}_3\text{C}_6\text{H}_4(\text{OH})$. The molecule structure of 4-methylphenol has a methyl group (CH_3) which is located far from the hydroxyl group (OH) at *para*-position. The hydroxyl groups (OH) are



involved in the formation of an intermolecular hydrogen bonding.

The DSC results show that in addition to the well-known two crystalline phases of 4-methylphenol, which melts at 307.6 and 309.2 K, we discovered the existence of a new crystalline phase (form III), which melts at 302.9 K.

Application of the FT-IR spectroscopy allowed us to obtain for the first time the FT-IR spectra of the stable and two metastable phases of 4-methylphenol and their temperature dependences when the temperature changes from 300 K down to 12 K. We focus on the FT-IR spectra in the most informative 2500-3800 cm^{-1} spectral region of the $\nu(\text{OH})$ stretching vibrations and the methyl group $\beta(\text{CH}_3)$ bending vibrations.



Temperature dependence of the FT-IR spectra of the form I

Temperature dependence of the FT-IR spectra of the form II

Temperature dependence of the FT-IR spectra of the form III

The results indicate :

1. a striking difference in the position and shape of the OH stretching bands in different polymorphs. In form III the position of the OH band has significantly higher wavenumber compared to forms I and II, which indicates that $\text{O-H}\cdots\text{O}$ hydrogen bond is weaker in form III.
2. a striking difference in the position and shape of the bands related to the deformation bending vibrations of the methyl CH_3 groups, when passing from one polymorph to another.

CONCLUSION

The first time we have discovered the new metastable polymorph (form III) of *p*-cresol, which melts at 302.9 K in addition to the well-known two crystalline phases (form I and II) of 4-methylphenol, which melts at 307.6 and 309.2 K, correspondingly.

The first time we have obtained the FT-IR spectra of the stable and two metastable phases of 4-methylphenol and their temperature dependences.

The results obtained allowed us to get information on structure-property relations, since differences in properties among polymorph must be due to differences in structure.