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Raman spectra of crystalline secondary amides

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Abstract

We present a Raman-spectroscopic study of secondary amides (acetanilide, methacetin, phenacetine, orthorhombic and monoclinic polymorphs of paracetamol) as well as simple amides formanilide and benzanilide. The study was carried out on single crystals and in the temperature range of 5-300 K. The series of compounds with the same molecular fragment - acetamide group – can serve as a model system to study the interrelation between this group and the properties of the intermolecular "peptide-type" NH···O=C hydrogen bonds. For all of the "acetamide family" of the compounds, similar changes in the Raman spectra were observed upon cooling of the samples: emergence of new Amide I(–) and Amide I(+) bands, which are red and blue shifted, respectively, from the conventional Amide-I band by around of 5-10 cm^{-1}. Corresponding changes in the same temperature range were observed for the N-H out-of-plane bending (Amide V) and N-H stretching vibrations of the N-H···O=C hydrogen bond. All of the spectral changes observed upon cooling of the samples can be presumed to result from a delocalization of the Amide-I and N-H modes and appearance of dynamical (Davydov's) splitting at low temperature.

Key words: molecular crystals, Raman spectra, secondary amides, hydrogen bonds, dynamical splitting

Introduction

At the present time much research is dedicated to crystals of small organic molecules. These crystals are also characterized by a network of hydrogen bonds, with any intramolecular motion and conformational changes likely to be in strongly correlation with the cooperative motion of the entire dynamic network. The structures with acetamide group are especially interesting in this respect, since they have in the same molecular fragment a methyl-group, the C=O and N-H groups forming intermolecular hydrogen bonds, similar to those in peptides, thus often called "peptide-type" hydrogen bonds. The acetamide group can be attached to different additional fragments, thus giving rise to the "acetamide family" of compounds, including, among other members, acetanilide (C_8H_9NO), paracetamol ($C_8H_9NO_2$), methacetin ($C_9H_{11}NO_2$), phenacetine ($C_{10}H_{13}NO_2$) (Figure 1). In addition to a possibility of manipulating the environment of the acetamide-groups by modifying molecular structures, one can change juxtaposition of the same molecules in the crystal structure either in a continuous way, adjusting the temperature and pressure within a range of stability of the same phase), or more radically by preparing different polymorphs. In the above-mentioned series, polymorphs were reported for the paracetamol.

We have demonstrated previously [1] on two polymorphs of paracetamol, that variable-temperature polarized Raman spectroscopy of single crystals in several well-defined crystallographic orientations can be extremely informative to study the conformational changes of the molecular backbone in relation to the changes in the crystal structure, in general, and in intermolecular hydrogen bonds, in particular. A state of the acetamide group at the different