

## Abstract of the PhD Thesis

### Temperature-dependent linear dichroic effects in the IR spectra of molecular crystals containing in the crystal lattices chains hydrogen-bonded molecules.

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IR spectroscopy in polarized light is one of the most powerful methods of investigating of inter-hydrogen bond couplings in molecular crystals. The recent experimental studies and the recently proposed theoretical approaches have suggested that a direct relationship between the IR spectral properties and the electronic structure of the molecular systems forming infinitely long hydrogen bond chains of a „zig-zag”-type geometry exists. The electronic structure of the associating molecules determines the way in which the vibrational exciton coupling between hydrogen bonds in the chains occurs.

In the case crystals, in which the associating molecules contain large delocalized  $\pi$ -electronic systems coupled directly with hydrogen bonds, the adjacent hydrogen bonds in a chain are strongly „tail-to-head” (TH) exciton-coupled. The totally symmetric („in-phase”) proton vibrations in the hydrogen bonds generate electric currents oscillating along each individual molecular chain. However, simultaneously a relatively weak „through-space” (SS) exciton coupling in the crystals involves the closely-spaced hydrogen bonds belonging to two adjacent chains in a lattice. This coupling of the „side-to-side”-type occurring via the van der Waals forces is typical for molecular systems with no large  $\pi$ -electronic systems in their structures, where only small  $\pi$ -electronic systems are localized on the carbonyl or thiocarbonyl groups. The relative contribution of the two different types of the *Davydov-coupling* is temperature-dependent.

A strong TH-type *Davydov-coupling*, involving hydrogen bonds in an individual chain, dominates at very low temperatures for molecules containing large  $\pi$ -electronic systems. The relative contribution of the TH-type mechanism in the spectra generation decreases along with the increasing temperature to the benefit of the SS-type coupling. It is due to weakening of the electronic current induced in the individual chains by the oscillating protons, influenced by large-amplitude thermal atomic motions.

The two competing individual exciton coupling mechanisms, i.e., TH and SS, are responsible for the appearance in the polarized spectra of temperature- dependent *Davydov-splitting* effects. They also determine of the temperature-dependent linear dichroic effects differentiating the polarization properties of the two opposite branches of the  $\nu_{X-H}$  and the  $\nu_{X-D}$  bands.