

The IR spectroscopy provides the most complete data system concerning the complex dynamics of atomic movements in hydrogen bonds. The most valuable and promising results of these studies can be obtained, when the IR spectra of spatially oriented single crystals are measured in a wide temperature range, using polarized radiation. The measurement of the polarized spectra of molecular crystals, characterized by various arrangements of hydrogen bonds in the crystal lattices followed by their quantitative interpretation, allowed revealing novel spectacular spectral effects. The subject of my dissertation was the study of the IR spectral properties of hydrogen-bonded cyclic trimers and tetramers in crystals. The main part of the study depended of the measurement of temperature effects and H/D isotopic “*self-organization*” processes in the hydrogen- bonded cycles. Measurements of the polarized IR spectra were performed at 293 and 77 K in the ν_{X-H} and ν_{X-D} band frequency ranges for molecular crystals containing hydrogen- bonded trimers, tetramers and even hexamers in their crystal lattices. It was proved that the individual crystal spectral properties remain in a close relation with the electronic structure of the two different- size molecular associated systems. A vibronic coupling mechanism involving the hydrogen bond protons and the electronic movements in the π -electronic systems in the associated molecules determines the way in which the vibrational exciton coupling between the hydrogen bonds in the cyclic trimers and tetramers occurs. A strong coupling mechanism involving all hydrogen bonds in a cycle results from a “*tail-to-head*”(TH)-type Davydov coupling widespread via the π -electrons. In turn, a weak “*through-space*” (SS) exciton coupling involves two opposite hydrogen bonds in tetramers or the adjacent in hydrogen bonds in the trimers. The relative contributions of each exciton coupling mechanism, TH and SS, in the spectra of investigated compounds are temperature and the molecular electronic structure dependent. This explains the observed differences in the temperature-induced evolution of the compared spectra. Moreover, the two exciton coupling mechanisms are also dependent of the crystal symmetry and of the kind of the hydrogen isotope atoms in the hydrogen bridges. The mechanism of the H/D isotopic “*self-organization*” processes in the crystals composed of hydrogen-bonded cyclic trimers and tetramers was also analyzed. Taking into account, two different cases of the molecular electronic structure, it may be emphasized that this aspect determines the way in which the discussed processes occur. In molecules with large π -electronic systems identical hydrogen isotope atoms, H or D, exist in the entire hydrogen bond cycles, trimers and tetramers, whereas in the case of molecules with small π -electronic systems, the H/D isotopic “*self-organization*” mechanism involves the opposite hydrogen bonds in the tetramer cycles.