

University of Silesia  
Faculty of Mathematics, Physics and Chemistry  
Institute of Chemistry  
Department of Chemical Physics

**Jakub T. Hołaj-Krzak**

Thesis  
summary

*“Long-distance” dynamical co-operative interactions involving hydrogen bonds in the lattices of model dicarboxylic acid crystals in the scope of IR spectral studies*

Promoter:

**prof. dr hab. Henryk T. Flakus**

Katowice 2017

The PhD dissertation is devoted to selected problems of the IR spectral properties of hydrogen bonds stabilizing the crystal lattices of model crystals of dicarboxylic acids, with the particular attention paid to the aromatic molecular systems. The investigation results collected by systematic spectral studies of diverse succinic acid isotopomer crystals allowed for the identification of a novel generation mechanism of the inter-hydrogen bond interactions in molecular crystals, namely of the so-called “long-distance” dynamical co-operative interactions. Intensive studies of molecular crystals of the isomeric benzenedicarboxylic acids (i.e. terephthalic, phthalic and isophthalic acid), with their lattices containing infinitely long chains of the molecules linked together by hydrogen bonds, coupled together by the  $\pi$ -electronic aromatic ring systems, prove that in these cases extremely strong co-operative interactions involving the distant hydrogen bond cycles take place. In terms of the proposed theoretical model of the “long-range” dynamical co-operative interactions in a “superdimer” of hydrogen bonds it was possible to interpret non-conventional H/D isotopic effects, depending of a non-random distribution of the protons and deuterons not only in the hydrogen bond cycles but also in longer associate molecule chain fragments. On the basis of the “superdimer” model the effect of the deuterium distribution in the terephthalic acid molecules on to rates of the H/D isotopic exchange in the crystalline hydrogen bonds was explained. The extremely high melting point as well as the extremely low solubility of terephthalic crystals may by also explained on the basis of the model. The theoretical model was also experimentally verified via spectral studies of crystals of mono- and polycyclic dicarboxylic acid crystals of the alicyclic and the alkylaromatic character.

IR spectroscopic studies of crystals of seven isomeric naphthalene dicarboxylic acids have shown that the dynamical co-operative interactions of the “long-range” are not the sole factor determining the H/D isotopic exchange rates. The extremely high passivity of the “1,3” and “1,6” isomers was ascribed to a high energy barrier for the H/D isotopic exchange reaction due to the necessity of the dearomatization of the aromatic rings in the transition states of the reaction in these cases.

The role of the symmetry as the factor determining the susceptibility of the other five isomeric systems (i.e. of the “1,4”, “2,3”, “1,5”, “2,6” and “1,7” naphthalene dicarboxylic acids) on to the H/D isotopic exchange depends on the strong modification of the “long-range” dynamical co-operative interaction energy magnitudes, as the result of the differences in the  $\pi$ -electron density distribution in the naphthalene ring  $\alpha$  and  $\beta$  positions. The relative distances between the carboxyl groups, due their substitution on one or in two different six-membered cycles also determine the H/D isotopic exchange rates in the naphthalene dicarboxylic acid isomers.