Abstract

Isosymmetric phase transitions (IPTs) are solid-state transformations that are challenging to detect as the same space group is maintained throughout the transition despite significant changes in molecular configuration, hydrogen-bond topology, and thermodynamic stability. Understanding IPTs is crucial for solid-state chemistry and medicinal chemistry, given that small polymorphic changes might affect the physicochemical properties of molecular crystals.

The aim of this doctoral dissertation was to study IPTs in selected molecular crystals and determine the structural and thermodynamic factors that lead to their occurrence through molecular modelling methods. Sulfamic acid, resorcinol, and L-serine were selected as model systems exemplifying various types of IPT behaviour. Periodic density functional theory (DFT) calculations were utilized to investigate the selected systems, including structural optimisation, pressure-dependent lattice energy analysis, phonon calculations, and Raman spectrum simulation.

The findings indicated that IPTs should be considered as true first-order phase transitions rather than minor distortions within a single crystal structure. In all analysed systems, the transitions involved changes in thermodynamic stability, discontinuities in lattice parameters, and energetic barriers between closely related phases.

The accurate identification of IPTs requires a comprehensive approach, including molecular modelling methods. A methodological framework for predicting IPTs using periodic DFT methods was proposed based on the obtained results. This approach strengthens the understanding of subtle solid-state transformations and may facilitate future research on molecular crystals.

Keywords: isosymmetric phase transitions, molecular crystals, polymorphism, periodic DFT