

High pressure as a tool to study intermolecular interactions. Retrospect and prospects.

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High pressure is as important thermodynamic parameter, as **is** temperature. It is widely used to study phase diagrams and thermodynamics of inorganic compounds and minerals. At the same time, pressure is also a powerful tool to study intra- and intermolecular interactions in coordination and organic compounds. By increasing pressure, one can achieve **a** much more pronounced compression than on cooling, so that the corresponding changes in the interatomic distances and angles – directly related to changes in electron density distribution – can be very significant. One can influence both on the thermodynamics and on the kinetics of various processes, ranging from crystallization to chemical reactions, in solution and in the solid state. This can be used to obtain new polymorphs, to understand structure-forming factors, as well as to understand the mechanisms of phase transitions and chemical reactions.

Originally, high-pressure research of coordination and organic compounds was based mainly on spectroscopic studies, in order to estimate activation volumes and to elucidate the mechanisms of the chemical reactions. Pressure-induced high-spin – low-spin phase transitions in solid coordination compounds, often related to pronounced color changes, have been also extensively studied by spectroscopic techniques. In the last decade, the progress in developing hardware and software for high-pressure diffraction experiments made it possible to get detailed information of cell parameters and volumes, **and / or** space symmetry groups, molecular packing, geometry of the hydrogen bonds and other intermolecular contacts, as well as on molecular conformations and intramolecular bonds and angles at high pressures *in situ*. The first examples of successful charge-density studies of coordination and organic compounds have been published. The effect of the detailed compression and decompression strategy on the high-pressure phases is being studied, as well as the effects of fluid phases in contact with the solid sample and of the starting crystal structure (comparing the effect of pressure on different polymorphs of the same compound). A special field is related to comparing the effects of cooling and increasing pressure on the same starting solutions or crystal structures, which are often radically different. These various experimental studies, complemented with theoretical calculations based on different levels of approximations, make it possible to follow the relative roles of different types of non-covalent interactions and their variation with pressure.

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