

Exploring conformations and non-covalent interactions in complex molecular systems with rotational spectroscopy

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The flexibility of molecular systems gives rise to complex conformational potential energy surfaces related to the presence of multiple torsional degrees of freedom and different non-covalent interactions occurring within the molecules or with their surroundings.

Accurate data on the structures, the energies and the dynamics of complex organic molecules and small molecular complexes can be obtained by rotational spectroscopy performed in the cold isolated conditions of free jet expansions. These properties can be directly compared to the outcome of accurate quantum mechanical calculations obtained in the same isolated conditions for a very useful and informing benchmarking.

The questions usually addressed regard: the preferred binding sites, the nature of the established interactions, the conformational changes caused by these interactions and finally their driving forces and how they can be influenced. When applied to molecular complexes, answers to these questions allow insight into the molecular interaction process at the molecular level, bridging the gap between gas-phase and bulk properties.

Through chosen examples of flexible organic molecules, bioactive molecules, astrophysical targets and molecular complexes formed in supersonic expansions and characterized by rotational spectroscopy, we will show how non-covalent interactions (strong and weak hydrogen bonds, halogen bond, π - and σ -hole interactions ...) compete to shape the conformational potential energy surface of the complexes, determining their shapes and their dynamics. It will also be shown how these interactions can be drastically changed through substitution (in particular with halogen atoms) or complexation with solvent molecules