

Quasistructural Molecules

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The notion of molecules and structures is central to our chemical understanding. One seemingly useful definition of molecules is that they correspond to minima on potential energy surfaces (PES) and the local PES must support at least one bound rovibrational state. The structure of a molecule is usually considered to be the geometry corresponding to the minimum. If a molecule exists and has a structure, it is also commonly accepted that its internal motions can be separated into vibrations and rotations, motions which usually have very different time and energy scales.

Nevertheless, there are chemical systems where both the notion of a molecule, that of a structure, as well as the separation of rotational and vibrational motion can be questioned. The lecture is centered around molecular ions and complexes¹⁻⁵ where the concept of a structure and the separation of vibrations and rotations seems to break down, yielding a quasistructural molecular with associated unusual nuclear dynamics. All of the following characteristics should hold, for a smaller or larger extent, for a molecular system to be considered quasistructural (from a high-resolution spectroscopic point of view): (a) the notion of a static equilibrium structure, corresponding to a minimum on the potential energy surface of the molecule, loses its strict meaning, (b) internal nuclear motions (rotations and vibrations) become dominant, resulting in an effective molecular structure often even qualitatively different from the equilibrium one, (c) separation of the internal nuclear motions breaks down, rotational and vibrational degrees of freedom cannot be separated from each other when interpreting even the lowest rovibrational states of the molecule, resulting in effective rotational constants drastically different from the equilibrium ones even for the ground vibrational state, (d) classification of the rovibrational states requires the use of permutation-inversion symmetry and molecular-symmetry groups, and (e) some of the rovibrational eigenenergies assigned to a vibrational parent state exhibit unconventional (in the most striking cases “negative”) rotational contributions.

Sophisticated tools of the fourth age of quantum chemistry⁶ are able to yield a quantitative understanding of the energy level structure and the high-resolution spectra of quasistructural molecules but it is certainly of interest to develop new models⁷ to aid the qualitative understanding of nuclear motion dynamics of quasistructural molecules.

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