Structure and dynamics of astructural molecules

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The new algorithms, methods, and codes developed during the fourth quantum age of quantum chemistry [1] allow to address interesting and occasionally strange phenomena related to the motions of the nuclei of molecules exhibiting large-amplitude motions, perhaps over several minima. The nuclear motions and the related high-resolution spectroscopy of the H_n^+ (n = 4, 5, 6, …) systems are simple enough from an electronic structure point of view but are peculiar and highly interesting from a quantum dynamical point of view.

Exhibiting nuclear motions even more complex than those characterizing quasi- and polytopic molecules, an astructural molecule can be characterized with the following properties: (a) the rotational and vibrational energy separations are of the same magnitude; (b) the rigid rotor (RR) and harmonic oscillator (HO) models are unable to yield a reasonable estimate of even the lowest rotational and vibrational energy levels; and (c) simple perturbative treatments based on the RRHO approximation fail already for the lowest nuclear motion states.

The coupling of several large-amplitude motions of H_5^+ and all of its deuterated isotopologues makes this molecular system ideal for the study of phenomena related to astructural molecules. Computing the rovibrational levels of this system accurately presents a considerable challenge. A further challenge is the modelling of the rotation-vibration-tunneling energy levels. Rovibrational energy levels have been computed for $H_nD_{5-n}^+$ (n = 0 – 5) variationally; they show puzzling characteristics [2,3,4] and require models distinctly different from the usually encountered (perturbed) RRHO treatments. The question of the number of deuterated isotopomers of $H_nD_{5-n}^+$ is addressed and solved. Some of the modeling results developed for H_5^+ [3] can be extended to systems containing two weakly coupled internal rotors.

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