

RIGIDITY OF THE MOLECULAR ION  $\text{H}_5^+$ 

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The in-house fourth-age quantum chemical code GENIUSH is used for the variational determination of rotational-vibrational energy levels corresponding to reduced- and full-dimensional models of  $\text{H}_5^+$ , a molecular ion exhibiting several strongly coupled large-amplitude motions and strong coupling between its vibrations and rotations. The quantum chemical computations are supplemented with simplified modeling efforts, including one- and two-dimensional exactly solvable models. These models help to understand the peculiar rovibrational energy-level structure computed for  $\text{H}_5^+$  and its deuterated isotopologues. One of the unusual aspect of the results is that the canonical Eckart-embedding of molecule-fixed axes, a cornerstone of the computational spectroscopy of semirigid molecules, seems to provide an inadequate description in this particular case. Furthermore, it is shown that while a 1D “active torsion” model provides proper rovibrational levels when compared to the full, 9D treatment, models excluding the torsion have limited physical significance due to the extremely strong coupling between the torsion and one of the rotations. The role the choice of the internal coordinates and the embedding of the rotational axes play in obtaining converged rovibrational results is discussed in detail. The structure of the rovibrational energy levels of  $\text{H}_5^+$  proves that it is useful to view this ion as a prototypical astructural molecule: the rotational and vibrational level spacings are of the same order of magnitude and the level structure drastically deviates from that computed via perturbed rigid-rotor and harmonic-oscillator models.

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**Time required:** 15 min

**Session Categories (Keywords) by Relevance:** Theory and Computation — Small molecules — Large amplitude motions, internal rotation — Comparing theory and experiment

**Mini-Symposia Requested:** Beyond the Mass-to-Charge Ratio: Spectroscopic Probes of the Structures of Ions — None

**Competing for Rao Prize?** No

**Competing for Miller Prize?** No