

RIGIDITY OF THE MOLECULAR ION 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 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 H_5^+ and its deuterated isotopologues. 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 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.