The rovibrational spectroscopy of H_5^+

János Sarka[1,2], Csaba Fábri[2], Attila Császár[1,2]

[1]MTA-ELTE Research Group on Complex Chemical Systems,
1117 Budapest, Pázmány sétány 1/A, Hungary
[2]Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University,
H-1518 Budapest 112, P.O. Box 32, Hungary

The fourth-age quantum chemical code GENIUSH [1-3] 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. [4] The computations are supplemented with one- and two-dimensional analytic results which help to understand the peculiar rovibrational energy-level structure computed correctly for the first time. It is shown that while the 1D "active torsion" model provides proper results when compared to the full, 9D treatment, models excluding the torsion have limited physical significance. The structure of the rovibrational energy levels of H_5^+ proves that this is 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.

References

[1] E. Mátyus, G. Czakó, and A. G. Császár, *J. Chem. Phys.* **130**, 134112 (2009).
[2] C. Fábri, E. Mátyus, and A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).
[3] C. Fábri, E. Mátyus, and A. G. Császár, *Spectrochim. Acta A* **119**, 84 (2014).
[4] C. Fábri, J. Sarka, and A. G. Császár, *J. Chem. Phys.* **140**, 051101 (2014).