VARIATIONAL ROVIBRATIONAL CALCULATION FOR LINEAR TETRAATOMIC MOLECULES: II. THE B11244 STORY RETOLD

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The linear propynylidynium l-C_3H^+ ($X^1\Sigma^+$) is part of the select group of interstellar cations. Its discovery was accompanied by a controversy in the astrophysical community.[a] Following its initial detection, theoretical calculations questioned the assignment based on 2nd order vibrational perturbation theory (VPT2) calculations. The matter was ultimately resolved by laboratory rotational spectra.[b] The failure of VPT2 was subsequently attributed to a shallow CCC bending potential.[c] Discrete Variable Representation (DVR) calculations[d] later confirmed the D_0/D_e ratio but resulted in a large sextic centrifugal distortion constant H_0 exceeding the astronomical value by an order of magnitude.

Using a new variational method for tetraatomic linear molecules (C8v4; see also P5277), based on Watsons isomorphic Hamiltonian for linear molecules, theory and experiment are reconciled. The C8v4 calculations confirm the small size of H_0 obtained in previous experimental studies. A high-level composite *ab initio* potential energy function (PEF) has been developed, combining explicitly correlated coupled-cluster results with corrections for core-valence correlation, scalar relativistic effects and higher-order correlation as well as the diagonal Born-Oppenheimer correction. Large scale C8v4 calculations using this PEF show excellent agreement with the available experimental rotational[a,c] and vibrational parameters.[e] The presented rotational spectroscopic parameters of excited vibrational states should facilitate forthcoming experimental spectroscopic studies on l-C_3H^+.

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[a] Pety *et al.*, *Astron. Astrophys.* **548**, 68 (2012); Huang *et al.*, *Astrophys. J. Lett.* **768**, 25 (2013).

[b] Brünken *et al.*, *Astrophys. J. Lett.* **783**, 36 (2014).

[c] Botschwina *et al.*, *Astrophys. J.* **787**, 72 (2014).

[d] Mladenović *J. Chem. Phys.* **141**, 224304 (2014).

[e] Brünken *et al.*, *J. Phys. Chem. A* **123**, 8053 (2019).