VARIATIONAL ROVIBRATIONAL CALCULATION FOR LINEAR TETRAATOMIC MOLECULES: I. THE C8V4 APPROACH

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Variational rovibrational calculations for small molecules with up to 3 atoms are nowadays a routine task.[a] By employing accurate potential energy surfaces it is possible to achieve so called "spectroscopic accuracy" of 1 cm^{-1} for small linear molecules.[b] However, rovibrational calculations for linear molecules with more than 3 atoms are still rather scarce.[c] A new variational method (C8v4) will be presented that is able to obtain rovibrational term energies and wave functions of tetraatomic linear molecules based on Watsons isomorphic Hamiltonian for linear molecules.[d] The rovibrational wavefunction is expanded in (symmetrized) products of harmonic oscillator (1D and 2D) and rigid-rotor functions. The intricacies related to the vibrational angular momentum in linear molecules require a careful study of symmetry properties. Kinetic energy matrix elements in the chosen basis set can be evaluated in a fast mixed numerical/analytical fashion. The main computational bottlenecks are the integration of the potential energy matrix and the diagonalisation of the rovibrational Hamiltonian. An efficient hybrid MPI/OMP parallelization has been implemented, exploiting the block structure of the Hamiltonian, that yields a significant reduction of the computational time. The diagonalization employs a K-contraction scheme that reduces the number of basis functions in the final rovibrational Hamilonian by at least an order of magnitude. Example benchmark calculations for acetylene (HCCH) are presented. The converged ($N_{\text{vib}} = 2785$) results for HCCH up to $J_{\text{max}} = 2$ accurately reproduce earlier variational calculations[e] in both g and u symmetry.

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[a] Tennyson, *J. Chem. Phys.* **145**, 120901 (2016).

[b] Schröder and Sebald, *J. Chem. Phys.* **144**, 044307 (2016); Makhnev *et al.*, *J. Phys. Chem. A* **122**, 1326 (2018).

[c] Mladenović, *J. Chem. Phys.* **141**, 224304 (2014); Chubb *et al.*, *J. Chem. Phys.* **149**, 14101 (2018).

[d] Watson, *Mol. Phys.* **14**, 465 (1970).

[e] Bramley and Handy, *J. Chem. Phys.* **98**, 1378 (1993).