IMPORTANCE OF RELATIVISTIC CORRECTIONS TO THE SPECTRUM OF WATER AND HYDROGEN SULPHIDE

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The importance of effects as small as minor relativistic corrections in theoretical predictions of energy levels can be as high as few wavenumbers [1]. Two-electron relativistic corrections to the ground-state electronic energy of water and hydrogen sulphide are determined at over 300 (250) geometries. The corrections include the two-electron Darwin term of the Coulomb–Pauli Hamiltonian, and the Gaunt and Breit corrections, calculated perturbationally using four-component variational Dirac–Hartree–Fock wavefunctions. Fitted relativistic correction surfaces are constructed and used with an accurate *ab initio* nonrelativistic Born–Oppenheimer potential to calculate vibrational and rotational levels. The calculations suggest that these two-electron relativistic corrections, which have so far been neglected in rovibrational calculations on light molecules, have a substantial influence on the ro-vibrational levels [2]. The effects considered have markedly different characteristics for the stretching and bending levels.

[1] J. Tennyson, P. Barletta, M.A. Kosten, O.L. Polyansky and N.F. Zobov, *Spectrochimica Acta A* **58** (2002) 663.

[2] H.M. Quiney, P. Barletta, G. Tarczay, A.G. Császár, O.L. Polyansky and J.Tennyson, *Chem. Phys. Lett.* **344** (2001) 413 .