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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A semi-empirical potential energy surface and line list for $H_2^{16}O$ extending into the near-ultraviolet" *by* Eamon K. Conway et al.

Anonymous Referee #2

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The manuscript by Conway et al describes a very detailed work on developing a "new" (I would rather say improved or updated) semi-empirical potential energy surface and predicted list of nominally IR but also near IR, optical rovibrational transitions for H2O, with predictions extending all the way up into the near ultraviolet. As water is by far the strongest and most highly populated molecular absorber in the earth's atmosphere, such high quality predictions constitute a topic of undoubtedly high impact for any terrestrial IR, optical, or UV spectroscopic observations. Over the years, Tennyson's group has developed extremely high accuracy methods for solving the exact rovibrational eigenvalues and eigenfunctions for H2O and other small molecules with advanced Hamiltonian methods. Tennyson and his colleague Polyansky are undeni-

ably experts in this field, which the Tennyson group has "plowed" with terrific vigor for many years. I have no doubt about the accuracy and correctness of this paper's scientific contents. Tennyson is extremely good at what he does, in part because he is smart and very good at maths, but also by virtue of having focused on this topic for multiple years if not decades. He has developed many excellent potentials for H2O in particular, each one representing a small yet still significant improvement on the preceding one, and predicting bound states and rovibrational transitions increasingly closer to the 41145 cm-1 dissociation limit. This has resulted in many excellent papers to his name, on a similar topic of improving an already excellent potential energy surface for H2O and making valuable and accurate predictions with it. The reason for this process continuing is not for testing against high level ab initio results (which are likely to be lagging well behind) but for the sheer importance of the resulting numbers. This paper (but more clearly the tables of linelists that he makes available to anyone through HITRAN or email request) will be values and read by any scientist studying spectroscopy of objects through the earth's atmosphere, which is dense with absorbing water vapor and enormous absorption path lengths. This paper in particular focuses on reliable predictions in the UV region, which is a super high order overtone event requiring accurate dipole moment functions, rovibrational wavefunctions, and Born-Oppenheimer corrections. The fact that these predictions indicate only weak absorption features in the UV is certainly to be expected – it is in the tireless quantitation of these absorption spectra that distinguishes Tennyson's contribution and craft.

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