ADVANCES IN THE THEORETICAL SPECTROSCOPY OF WATER VAPOR: POTENTIALS, DIPOLES AND COMPUTED SPECTRA

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A new semi-empirical potential energy surface for H$_2$O has been refined to over 14000 measured energy levels below 37000 cm$^{-1}$, including all rotational states below 21. A standard deviation of 0.028 cm$^{-1}$ is obtained and there is room for improvement. Combined with the latest available dipole moment surface, new theoretical calculations in the visible show good agreement with atmospheric observation in the 22249-22685 cm$^{-1}$ window (Harder, J. W., and Brault, J. W. (1997), J. Geophys. Res., 102). The absorption feature considered does not strongly interfere with those from other molecules in our atmosphere, which makes it an ideal candidate for accurately retrieving water vapor. Combining theoretical predictions with experimental data, the HITRAN2016 database will be updated to agree with observation. Spectra from this particular PES and DMS will also greatly improve many regions of HITEMP2010.

Computing highly accurate finite field dipoles for even the lightest of molecules such as water is difficult. At the 6Z level, MRCI calculations for this ten electron system in a (8,2) active space configuration requires over 140000 seconds, i.e almost two days. It is not practical to approach calculations involving heavier molecules such as O$_3$ in this way. We present a novel yet simple strategy in which 6Z dipoles can be calculated in a fraction of the time, thus providing means of improving theoretical spectra for many molecules.