AB INITIO PREDICTIONS OF ISOTOPIC SHIFTS IN WATER

DAVID W. SCHWENKE, *NASA Ames Research Center, MS T27B-1, Moffett Field, CA 94035-1000*.

Empirical potential energy surfaces for water have reached the accuracy where break down of the Born-Oppenheimer approximation must be accounted for in order to obtain uniform accuracy for all isotopomers. While it is not yet possible to directly compute a potential energy surface of sufficient accuracy to show this break down, it should now be possible to accurately predict the mass dependence of the Born-Oppenheimer breakdown terms. In this work we use accurate *ab initio* first and second order corrections to the Born-Oppenheimer approximation in conjunction with an empirical potential energy surface calibrated for the principle isotopomer to predict the spectrum of all isotopomers of water. The diagonal Born-Oppenheimer correction is computed using a newly development code for multi-reference configuration interaction wavefunctions, while the adiabatic correction functions are computed using the self-consistent-field/configuration interaction singles method.