Calculation of rotation–vibration energy levels of the water molecule with near-experimental accuracy based on an *ab initio* potential energy surface

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We argue here that it is becoming possible to achieve near experimental accuracy about 0.1 cm^{-1} from the first principles for water and potentially for other molecules of comparable size [1]. Achieving near experimental accuracy for water would not only show that the behaviour of the water molecule is completely understood from a theoretical perspective but it would also revolutionize the predictive abilities of such calculations.

The *ab initio* calculations were performed using a multi-reference configuration interaction (MRCI) method with aug-cc-pCVnZ (n = Q, 5, and 6) basis sets and basis set extrapolation to CBS limit. Using MRCI+Q *ab initio* points [2], we constructed a new PES by fitting 1260 points lying at energies less than 25 000 cm^{-1} above the equilibrium value. The fit reproduces the ab initio points at standard deviation of only 0.3 cm^{-1}. The BO surface was augmented with a relativistic correction, a QED correction, and an adiabatic correction [3].

An important part of the calculations was the systematic inclusion of the adiabatic, relativistic and quantum electrodynamic (QED) corrections [3]. Each of these corrections was found to contribute significantly to the improved accuracy. The last step was the inclusion of nonadiabatic corrections based on the vibrationally averaged constants given by Schwenke [4].

A purely *ab initio* calculation presented in [1] reproduces some 200 known band origins associated with 7 isotopologues of water ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, HDO, HTO, D_2O and T_2O) with a standard deviation (sd) of about 0.35 cm^{-1} . Introducing three semi-empirical scaling parameters, two affecting the BO PES and one controlling non-adiabatic effects, reduces sd below 0.1 cm^{-1}. Introducing one further rotational non-adiabatic parameter gives sd better than 0.1 cm^{-1} for all observed ro-vibrational energy levels up to J=25.

Ab initio calculations reproducing two semi-empirical scaling parameters for BO PES will be presented at the conference.

We conjecture that the energy levels of closed-shell molecules with roughly the same number of electrons as water, such as NH_3 , CH_4 and H_3O^+, could be calculated to this accuracy using an analogous procedure. This means that *ab initio* calculations are capable of predicting transition frequencies with an accuracy only about a factor of five worse than high resolution experiments.

[1] O.L. Polyansky, R.I. Ovsyannikov, A.A. Kyuberis, L. Lodi, J. Tennyson, N.F. Zobov, Phys. Chem. Chem. Phys., 2013 (in press); dx.doi.org/10.1021/jp312343z.
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