FITTING OF POTENTIAL ENERGY SURFACES OF WATER ISOTOPOMERS

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A potential energy surfaces for some major isotopomers of water were constructed by fitting to observed vibration-rotation energy levels of the system using the exact kinetic energy operator nuclear motion program DVR3D [1]. The starting point for the fit is the *ab initi*o Born-Oppenheimer surface and corrections to it: both one- and two-electron relativistic effects, allowance for the Lamb shift and the inclusion of both adiabatic and non-adiabatic non-Born-Oppenheimer corrections [2]. Fits are made by scaling the starting potential by a morphing function, the parameters of which are optimized [3].

Three separate fits were made. *Ab initio* Born-Oppenheimer surface and corrections to it were optimized using experimental data for $H_2{}^{16}O$, $H_2{}^{17}O$ and $H_2{}^{18}O$ molecules together.

Fit 1 included all data for states with J=0, J=2 and J=5. This constituted 1788 energy levels. From these about 60 were excluded on the grounds that they had a unacceptably large error, in some cases over 1 cm^{-1}. This fit reproduced the data with sigma = 0.071 cm^{-1}.

Fit 2 augmented the data used in Fit 1 with J=10 rotational levels For calculations with J>0 in this fit non-adiabatic effects were used. The best fit was obtained by taking 18% of the values given by Schwenke [4]. Use of the J=10 levels added another 350 levels to the dataset used for Fit 1 and worsened sigma slightly to 0.077 cm^{-1}.

Fit 3 started the data used in Fit 1. From this we excluded all levels which had a residual larger than 0.07 cm^{-1}. A new fit was performed and excluded levels which were accurately reproduced were re-introduced into the fit. This process was repeated with expanded dataset until no further levels could be included without significantly degrading the fit. This fit has a significantly lower sigma of 0.028 cm^{-1} for a dataset of just 1004 levels. This dataset comprises about two-thirds of all the possible levels and spans the entire energy range, up to 25000 cm^{-1} above the ground state.

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