

Spectroscopically determined potential energy surfaces of the H_2^{16}O , H_2^{17}O , and H_2^{18}O isotopologues of water

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Abstract

Adiabatic potential energy surfaces (PESs) for three major isotopologues of water, H_2^{16}O , H_2^{17}O , and H_2^{18}O , are constructed by fitting to observed vibration–rotation energy levels of the system using the nuclear motion program DVR3D employing an exact kinetic energy operator. Extensive tests show that the mass-dependent ab initio surfaces due to Polyansky et al. [O.L. Polyansky, A.G. Császár, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D.W. Schwenke, P.J. Knowles, *Science* 299 (2003) 539–542.] provide an excellent starting point for the fits. The refinements are performed using a mass-independent morphing function, which smoothly distorts the original adiabatic ab initio PESs. The best overall fit is based on 1788 experimental energy levels with the rotational quantum number $J = 0, 2, \text{ and } 5$. It reproduces these levels with a standard deviation of 0.079 cm^{-1} and gives, when explicit allowance is made for nonadiabatic rotational effects, excellent predictions for levels up to $J = 40$. Theoretical linelists for all three isotopologues of water involved in the PES construction were calculated up to 26000 cm^{-1} with energy levels up to $J = 10$. These linelists should make an excellent starting point for spectroscopic modelling and analysis.

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1. Introduction

The concept of the potential energy surface (PES) underlies much of chemical physics and determining accurate PESs is therefore an activity fundamental to the discipline. In principle accurate PESs can be computed using quantum mechanics but for polyatomic molecules the only ab initio surface available which approaches the accuracy demanded by high-resolution spectroscopy experiments is that of the two-electron H_3^+ molecule [1]. For triatomic many-electron systems the use of spectroscopic data and variational nuclear motion calculations has become a stan-

dard technique for determining (effective) potential energy surfaces from which rovibrational transitions of accuracy better than 0.1 cm^{-1} can be computed.

Water is arguably the single most important triatomic molecule. It is therefore unsurprising that there are a number of spectroscopically determined potentials available for this key system [2–11]. A detailed comparison of these surfaces is given in [11]. While the surfaces show a steady improvement in accuracy with time, none can yet reproduce the known spectroscopic data for the system with even close to experimental accuracy. It should also be noted that the improvement of the fitted surfaces is closely related to the improvement of the starting point of the fit, which is generally provided by high-quality ab initio electronic structure calculations.

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In this work, we attempt to produce a PES for water which reproduces the spectroscopic data to close to experimental accuracy for several isotopologues at the same time. Our aim is an average unsigned residual error significantly less than 0.1 cm^{-1} . This value is considerably larger than the quoted statistical errors on experimentally determined energy levels, which are generally 0.002 cm^{-1} or less, see [12]. However, such estimates largely ignore systematic effects. Our experience of using combination differences to analyse various spectra is that the value of about 0.02 cm^{-1} is a considerably more realistic error for much of the data that has been reported. This is the value we are therefore aiming at when trying to produce a PES fitted with “experimental accuracy.”

An important motivation of our attempt to perform a high accuracy fit is the availability of new ab initio adiabatic PESs for water [13], termed CVRQD [14]. These surfaces, which explicitly include many corrections for minor effects such as special relativity, Born–Oppenheimer breakdown, and even quantum electrodynamics (QED), reproduce the observed energy levels of H_2^{16}O and several of its isotopologues to within 1 cm^{-1} , approximately an order of magnitude better than the previous best ab initio treatment of the same problem [10]. The ability to fit data for several isotopologues simultaneously tests the treatment of the non-Born–Oppenheimer behaviour of PESs (see, e.g. [15]). Another reason for performing this study is to aid the analysis of an emission spectrum of H_2^{16}O recorded recently using an oxyacetylene torch [16–18]. This very hot spectrum contains many transitions between states with a high degree of rotational excitation and thus the spectrum also provides severe test of the high- J performance of the fitted PES.

2. Methodological details

There are four ingredients that are necessary for obtaining a good spectroscopically determined potential energy surface:

- (i) a good starting PES,
- (ii) an extensive and reliable set of experimental data,
- (iii) a good functional form for the fit, and
- (iv) an accurate method for determining the experimental observables from the (fitted) potential.

Our general strategy, which has been used successfully before [11,19], is to fit a morphing function which adjusts the starting ab initio potential. Our strategy and the morphing function employed in this study are described below.

2.1. Starting PES

Several test calculations focused on the starting PES of the fitting procedure. All employed the high accuracy CVRQD ab initio PES of Polyansky et al. [13], which consists of a number of component parts: a complete basis set

(CBS) valence-only (V) surface obtained by extrapolating large basis set internally contracted multireference configuration interaction (ICMRCI) calculations keeping the oxygen $1s$ orbital frozen [20], a core–core and core–valence correlation surface to correct for the frozen $1s(\text{O})$ orbital in the ICMRCI calculations (C) [21], relativistic correction surfaces to the electronic kinetic energy and Coulomb interactions (R) [22,23], a quantum electrodynamic (QED) correction surface (Q) [24], and an adiabatic or diagonal Born–Oppenheimer correction (BODC) surface (D) obtained at the aug-cc-pVTZ ICMRCI level [13,15].

Somewhat unexpectedly, fits to $J=0$ data proved to be divergent if only the CV part of the CVRQD potentials of the three isotopologues of water were used. Adding the correction surfaces, i.e., employing the full CVRQD PESs, gave convergent fits. We tested using different combinations of R, Q, and D corrections, as well as different available forms of the BODC correction, since this correction appears to be sensitive to the ab initio method used for its determination [15]. The conclusion of these test calculations was that use of all terms as presented by Polyansky et al. [13,20] gave a starting point at least as good as the other combinations tested, and one which is certainly more justifiable. Therefore, in the final fittings only the full CVRQD PESs of the three isotopologues have been used.

2.2. Experimental data

The observed energy levels of H_2^{16}O [12], H_2^{17}O [25–30], and H_2^{18}O [25–28,31–34] were employed as the spectroscopic data during the fits.

As we performed many trial fits testing both the starting point and the dataset used, initial studies focused on the vibrational band origins (VBOs), i.e., energy levels with $J=0$ only. It is well known [35] that such fits do not give reliable potentials. Nevertheless, our experience shows that they are useful for rapid tests as a prelude to performing considerably more expensive studies which include states with $J>0$.

We attempted to construct a reliable dataset. Tests with all the ‘measured’ band origins rapidly showed that including those VBOs for which the $J=0$ term value had not been directly determined experimentally by observation of a transition to this state significantly worsened the fit. These were therefore excluded from the dataset. Without these it was still not possible to obtain a high accuracy fit, so data were removed until a very tight fit with a standard deviation, σ , of about 0.03 cm^{-1} was achieved. Using this reduced set of data as a starting point the other VBOs were re-introduced into the fit and those which did not lead to a significant deterioration were retained.

From this starting point, a number of fits were performed. Our final fit, which resulted in a PES we call FIS3, standing for fitted surface for three isotopologues, included all data for states with $J=0$, $J=2$, and $J=5$ for H_2^{16}O , H_2^{17}O , and H_2^{18}O . This constituted over 1800 energy levels. From these, about 50 levels were excluded

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