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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, 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.

Keywords: Water vapour; Line assignments; Atmospheric radiation; Adiabatic potential energy surface; Rotational nonadiabaticity

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 standard 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 1*s* orbital frozen [20], a core–core and core–valence correlation surface to correct for the frozen 1*s*(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 on the grounds that they had an unacceptably large error, in some cases over 1 cm^{-1}. It is likely that some of these levels actually result from misassigned transitions; for other levels there may be simply too few levels associated with that vibrational mode to properly constrain the fit. Fits which included data on $J = 10$ rotational levels, were also performed. This adds a further 350 energy levels to the data set but has only a small influence on the final standard deviation.

Fits which included all levels with the chosen degree of rotational excitation gave a standard deviation significantly larger than 0.02 cm^{-1}. We therefore decided to perform one fit aimed at producing a very high accuracy fit by excluding data sensitive to poorly determined regions of the potential. This fit also used levels with $J = 0$, $J = 2$, and $J = 5$ but all levels which had a residual larger than 0.07 cm^{-1} were excluded. A new fit was performed and excluded levels which were accurately reproduced were re-introduced into the fit. This process was repeated with an expanding dataset until no further levels could be included without significantly degrading the fit. This fit has a significantly lower σ of 0.028 cm^{-1}, very close to our aim of 0.02 cm^{-1}, for a dataset of just over 1000 levels. This dataset comprises about two-thirds of all the possible levels and spans the entire energy range, up to 25 000 cm^{-1} above the ground state.

2.3. Morphing function

The mass-independent fitting function employed here was of the form of a morphing function [36,37], $f_{\mathrm{morp}}(r_1, r_2, \theta)$, where (r_1, r_2, θ) are the standard bond length, bond angle coordinates of water, for which equilibrium values r_e and θ_e were taken as 1.80965034 a_0 and 1.82404493 rad, respectively. The equilibrium parameters in the mass-independent morphing function are slightly different from our best estimates for these quantities [14], e.g., 1.81007 a_0 and 1.82387 rad for $H_2{}^{16}O$, and also from the corresponding values employed during construction of the correction surfaces of the CVRQD PES [22–24]. Small changes, on the order reported here, do not have a noticable effect on the overall quality of the fits.

The morphing function smoothly distorts the original ab initio potential, $V_{\mathrm{CVRQD}}(r_1,r_2,\theta)$, into the more accurate fitted potential:

$$V_{\mathrm{FIS3}}(r_1, r_2, \theta) = f_{\mathrm{morp}}(r_1, r_2, \theta) V_{\mathrm{CVRQD}}(r_1, r_2, \theta). \tag{1}$$

For our fits the morphing function was expressed as a power series in so-called Jensen coordinates [4]:

$$\begin{aligned} s_1 &= \frac{r_1 + r_2}{2} - r_e \\ s_2 &= \cos\theta - \cos\theta_e \\ s_3 &= \frac{r_1 - r_2}{2} \end{aligned} \tag{2}$$

$$f_{\mathrm{morp}} = c_{000} + \sum_{ijk} c_{ijk} s_1^i s_2^j |s_3|^k \qquad 2 \leqslant i + j + k \leqslant N, \tag{3}$$

where the value of N is known as the order of the fit. The parameters c_{ijk} are determined by least-squares fitting to the experimental data.

We performed many tests with different functions and our final fit utilized that combination of functions which both improved the fit and for which the fit did not diverge. The terms retained in that fit are given in Table 1. In particular we tested all fourth-order ($N = 4$) terms as well as the effect of including fifth-order ($N = 5$) terms.

Symmetry considerations dictate that the potential should be independent of the sign of s_3. The use of $|s_3|$ in Eq. (3) ensures this behaviour but at the possible price of inserting a seam in the potential due to discontinuous derivatives associated with terms with $k = 1$. This form of the function, including odd powers of k, was successfully employed by us to fit both $H_2{}^{16}O$ [11] and $D_2{}^{16}O$ [19] PESs. In the latter case, this fit was performed iteratively as part of the analysis of a hot D_2O emission spectrum. These odd powers were found to be important for representing the behaviour of some of the highly excited stretching states. We performed extensive graphical inspection of potentials which included terms with odd powers of k and failed to find any discernible seam. Our final FIS3 fit, nevertheless, only included even functions of k and required 23 parameters to be varied up to fifth order ($N = 5$). A comparable fit which included terms odd in k required terms only up to fourth order ($N = 4$), but 26 parameters, to give a slightly better fit: $\sigma = 0.071$ against 0.079 cm^{-1} for the FIS3 fit.

Table 1
Fitted coefficients, c_{ijk}, of the morphing function, see Eq. (3)

$i\ j\ k$	Fit
0 0 0	0.999889690804555
1 1 0	0.001962855624902
2 0 0	0.001827303733462
3 0 0	0.006559311836591
0 0 2	0.002515462972508
4 0 0	−0.028264815761006
0 2 0	−0.001525914350558
0 3 0	0.001747685885798
0 4 0	0.003086854517214
2 1 0	−0.002243900693018
1 2 0	−0.007048218869391
1 0 2	0.004232544985046
0 1 2	−0.006876558429599
0 0 4	−0.015730261187827
3 1 0	−0.001123213540527
1 3 0	0.000479805945951
2 2 0	0.007961636523251
2 0 2	−0.000093232218421
1 1 2	0.069430862743389
0 2 2	0.002207321035815
5 0 0	0.027705184633497
0 5 0	−0.003983265650346
2 1 2	−0.090472927101580

Dimensions are $a_0{}^{-(i+k)}$.

2.4. Nuclear motion calculations

All nuclear motion calculations were performed using Radau coordinates with the ‘bisector’ axis embedding which places the x-axis so that it bisects the bond angle and the z-axis in the molecular plane [38,39]. This axis embedding is the natural one for the three isotopologues of water considered.

The program DVR3D [40] was used with 29 radial grid points for Morse oscillator-like basis functions and 40 angular grid points based on (associated) Legendre polynomials. Vibrational Hamiltonian matrices of final dimension 1500 were diagonalised and for rotational problems these matrices had dimension $300 \times (J + 1 - p)$, where J is the rotational quantum number and p the parity. Nuclear masses have been used for all calculations.

For calculations with $J \leqslant 5$ rotational nonadiabatic effects contribute 0.01 cm^{-1} or less to the rotational energy. Nevertheless, as the effects increase approximately as J^2 [41], it is necessary to consider them for calculations with higher J. Schwenke [15] performed a comprehensive, ab initio treatment of rotational nonadiabatic effects by explicitly treating coupled surfaces. Schwenke also calculated simplified, effective nonadiabatic operators by taking expectation values of these coupling surfaces; these operators have been shown to work well [42].

In this work, the magnitude of the three rotational nonadiabatic operators due to Schwenke [15] were treated as parameters which were determined in separate one-parameter fits of energy levels with $J = 20$. For our FIS3 fit the best results were obtained using 25% of the values given by Schwenke, whereas for the fit which included $J = 10$ levels, the best fit was obtained by taking 18% of these values. All calculations with $J > 10$ presented in this paper use these scaled nonadiabatic operators.

3. Results and discussion

3.1. Low J

Table 1 presents the coefficients of our recommended mass-independent morphing function. The full functional form for the fit, including the underlying CVRQD adiabatic potentials, can be obtained from www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/3mol.

To help gauge the accuracy of our final fit, Table 2 presents an analysis of the errors. This table gives the error in fitting the vibrational band origins plus the error in reproducing the rotation levels within each vibrational state once the VBO error has been removed. Missing entries correspond to data which were omitted from the final fit for reasons discussed in the previous section.

In this paper, we have used a morphing procedure to fit to experimental data in order to improve adiabatic ab initio PESs [13] of three major water isotopologues simultaneously. The underlying Born–Oppenheimer surface, including relativistic and quantum electrodynamic correc-

Table 2
Summary of fitted energy levels grouped by vibrational excitation

Band	Fit			
	ω	$\Delta\omega$	σ	N
$H_2{}^{16}O$				
000	0.000	0.000	0.003	16
010	1594.746	−0.029	0.010	17
020	3151.630	0.049	0.022	17
100	3657.053	−0.016	0.018	17
030	4666.790	0.103	0.013	17
110	5234.977	−0.116	0.011	17
040	6134.015	−0.011	0.061	15
120	6775.093	−0.079	0.008	17
200	7201.540	0.055	0.026	17
002	7445.045	−0.062	0.023	17
130	8273.976	−0.007	0.009	15
210	8761.582	−0.098	0.023	13
012	9000.136	−0.041	0.015	17
220	10284.367	−0.040	0.070	10
022	10521.800	−0.056	0.053	6
300	10599.686	0.119	0.046	17
102	10868.876	−0.066	0.028	17
230	11767.390	0.064	0.004	10
032	12007.776	−0.112	0.039	15
310	12139.315	−0.087	0.029	17
112	12407.662	−0.085	0.041	17
042	13453.600	−0.093	0.094	10
400	13828.277	0.034	0.057	17
122	13910.896	−0.035	0.022	17
202	14221.161	0.072	0.051	16
004	14537.504	0.082	0.044	16
410	15344.503	−0.154	0.027	15
132	15377.700	−0.001	0.028	8
212	15742.795	−0.034	0.055	17
340	16534.300	0.040	0.029	8
500	16898.400	−0.064	0.051	17
222	17227.300	0.027	0.045	15
402	20533.400	−0.065	0.041	7
700	22529.296	0.081	0.074	8
001	3755.929	0.114	0.027	17
011	5331.265	0.026	0.012	17
021	6871.520	−0.005	0.012	17
101	7249.818	0.150	0.031	17
031	8373.853	0.010	0.014	17
111	8806.999	0.009	0.022	17
041	9833.585	−0.042	0.023	17
121	10328.731	0.017	0.010	17
201	10613.354	0.111	0.041	17
003	11032.406	−0.061	0.033	17
051	11242.800	−0.264	0.100	5
131	11813.207	0.117	0.025	17
211	12151.255	−0.083	0.030	17
013	12565.007	0.100	0.020	17
141	13256.200	0.159	0.040	10
301	13830.938	−0.004	0.035	17
023	14066.194	0.024	0.029	16
103	14318.812	−0.032	0.023	17
151	14648.200	−0.042	0.098	7
231	15119.028	0.144	0.082	17
311	15347.956	−0.175	0.090	17

Experimental band origins, ω, fit errors in the band origin, $\Delta\omega$, and standard deviations for rotational levels within each band, σ, are in cm^{-1}. N stands for the number of rotational levels for that vibrational state included in the fit; note that for all vibrational states except the ground state, where it is 16, $N_{\max} = 1 + 5 + 11 = 17$. A blank entry in ω means that the datum, whether or not available from experiment (see text), was not included in the fit.

(*continued on next page*)

Table 2 (*continued*)

Band	Fit			
	ω	$\Delta\omega$	σ	N
033	15534.709	0.002	0.063	17
113	15832.765	0.055	0.036	17
241	16546.300	0.085	0.037	8
043	16967.500	−0.008	0.163	8
203	17495.528	0.009	0.033	16
331	18265.820	−0.008	0.088	17
411	18393.314	0.036	0.077	13
213	18989.961	0.008	0.039	14
303	20543.137	−0.075	0.041	8
601	22529.441	0.083	0.103	7
240			0.100	6
320			0.058	16
420			0.095	11
221			0.025	15
401			0.068	16
123			0.068	15
302			0.059	16
104			0.084	13
053			0.102	3
510			0.065	8
341			0.151	11
600			0.076	9
142			0.060	7
321			0.088	11
050			0.118	6
133			0.099	6
034			0.147	3
501			0.099	13
223			0.039	5
511			0.102	2
060			0.170	2
330			0.107	3
611			0.313	1
$H_2^{17}O$				
000	0.000	0.000	0.003	15
010	1591.325	−0.021	0.010	17
020	3144.980	0.055	0.020	17
100	3653.142	−0.015	0.017	17
001	3748.319	0.119	0.025	17
011	5320.262	0.051	0.019	11
101	7238.725	0.167	0.011	3
121			0.013	16
300			0.094	14
201			0.093	15
102			0.087	16
003			0.083	15
041			0.038	4
220			0.057	4
$H_2^{18}O$				
000	0.000	0.000	0.002	16
010	1588.276	−0.013	0.007	17
020	3139.050	0.060	0.018	17
100	3649.685	−0.014	0.016	17
030	4648.460	0.087	0.026	17
110	5221.240	−0.120	0.019	17
120	6755.510	−0.072	0.006	17
200	7185.870	0.055	0.023	16
002	7418.720	−0.053	0.016	14
001	3741.567	0.122	0.023	17
011	5310.460	0.048	0.014	17
021	6844.598	0.013	0.012	17
101	7228.880	0.163	0.032	17
041	9795.330	−0.043	0.014	9
131			0.103	15
310			0.089	16
211			0.079	16
112			0.067	16
013			0.102	15
221			0.024	10
320			0.116	6
301			0.051	14
400			0.027	9
040			0.025	9
202			0.059	10
103			0.036	11
220			0.039	3
121			0.022	16
300			0.095	16
102			0.074	15
003			0.079	16
230			0.059	3
201			0.096	15
023			0.053	4
042			0.051	1
141			0.066	1
122			0.081	1

tions, is isotopically independent and the surfaces for different isotopologues differ only in the corresponding BODC corrections [13]. The accurate fits obtained for all three isotopologues, see Table 2, show that correlated-level ab initio BODCs are of high enough quality to correctly represent mass effects.

3.2. High J

To test the ability of the fitted FIS3 potential to reproduce highly excited rotational states we performed a number of comparisons with experimental levels for $J = 20$, as well as newly assigned levels for $J = 39$ and 40 of $H_2^{16}O$ [16]. All high-J levels, except two for $J = 39$ corresponding to (010), reside on the ground vibrational state. As a benchmark these comparisons were repeated using the spectroscopic potential of Partridge and Schwenke [10], called PS hereafter. The results are summarized in Table 3.

All our fits reproduced the observed $J = 20$ levels with an accuracy similar to or better than PS. However, this

Table 3
Summary of predicted energy levels for $H_2^{16}O$ sorted by rotational excitation, J

J	N	σ(FIS3)	σ(PS)	σ(CVRQD)
20	351	0.152	0.268	0.710
20	333	0.128	0.259	0.699
39	10	0.040	0.329	2.282
40	6	0.025	0.382	2.401

N denotes the number of levels used for the comparison. Standard deviations, σ, are in cm^{-1}. The potentials tested include the final PES of this study, FIS3, the spectroscopic PS potential [10], and the ab initio CVRQD potential [14]. For $N = 333$ levels with $v_2 \geqslant 2$ and $K_a > 15$ were removed.

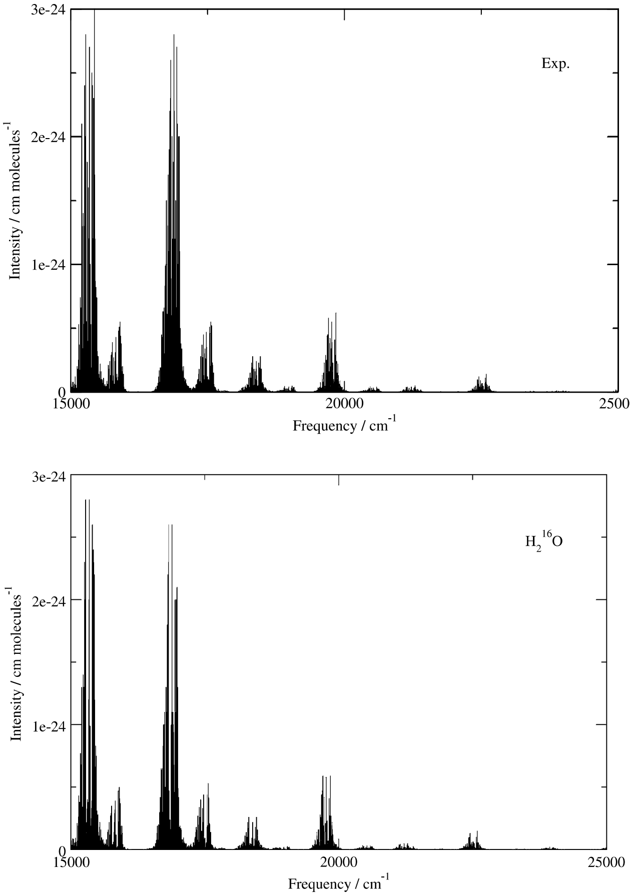

Fig. 1. Comparison of the experimental (upper) [44] and theoretical (lower) spectra for $H_2{}^{16}O$ at 296 K.

comparison masks important details since several of our preliminary fits performed relatively poorly for levels which involved both significant bending and high K_a. Even for our final fit some of this behaviour remains.

It is notable that our FIS3 fit performs significantly better than PS and indeed all our other fits for all the high-J tests. This means that energy levels determined with the new FIS3 potential should provide the best available starting point for analysing the high-J transitions in the oxy-acetylene torch spectrum.

3.3. Linelists

Theoretical linelists for the isotopologues $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$, at a temperature of 296 K, were calculated using the FIS3 PES. These linelists are built upon energy levels up to 26000 cm^{-1} and $J \leqslant 10$. The DVR3D program parameters used were the same parameters as those used for the fits, as described in Section 2. For the intensity calculations, we used the best available dipole moment surface (DMS) of Schwenke and Partridge [43]. The linelists can be downloaded from www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/3mol.

Fig. 1 compares the most recent room temperature experimental spectrum for water vapour in the near infrared and visible [44] with our results generated using the linelist for $H_2{}^{16}O$. Figs. 2 and 3 give theoretical spectra for $H_2{}^{17}O$ and $H_2{}^{18}O$, respectively, using the same frequency range.

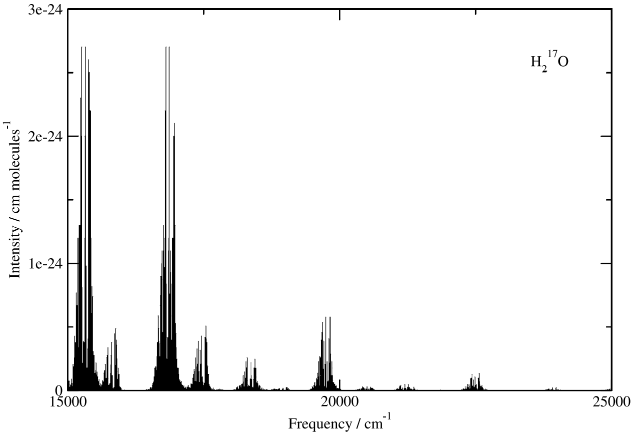

Fig. 2. Theoretical spectrum for $H_2{}^{17}O$ at 296 K.

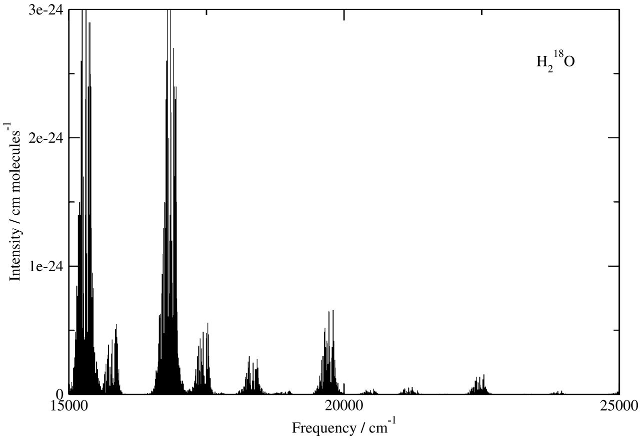

Fig. 3. Theoretical spectrum for $H_2{}^{18}O$ at 296 K.

4. Conclusions

Determination of a Hamiltonian from spectroscopic data by its eigenvalues is not a correctly posed problem. If the Hamiltonian is given, there is only one set of energy levels corresponding to it, but with a finite set of energy levels, such as those obtained from analyses of experimental spectra, there can be many Hamiltonians derived which give these energy levels with a comparable level of accuracy. The question which of these Hamiltonians is correct is in some sense pointless. Of course, different Hamiltonians, describing the same set of experimental data with the same accuracy, can have different extrapolation properties and therefore make very different predictions for yet unknown energy levels (and the corresponding transitions).

Use of an ab initio PES should aid correct extrapolation for energy levels whose values depend strongly on the parts of the PES not determined from existing experimental data. This was one reason why we chose to fit a morphing function, mass independent in the present case, which scaled the high-quality mass-dependent ab initio CVRQD PESs of $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$ [14] to give the fitted potentials. As can be seen from Table 1 all fitted coefficients of the morphing function, with the trivial exception of the first one, are much smaller than unity, which assures smooth and small distortion of the ab initio PESs. Our experience in fitting potential energy surfaces suggests that it is not possible to obtain highly accurate potentials without using a high quality ab initio starting point.

Our final fitted PES, termed FIS3, gives a slightly worse standard deviation for levels with small J than some other, preliminary surfaces we obtained, but it performs significantly better than our other fits and PS's fitted potential [10] for all high J levels, in particular for levels with $J = 39$ and 40. The best overall fit, resulting in the FIS3 potential, is based on 1788 experimental energy levels with $J = 0$, 2 and 5, and it reproduces these levels with a standard deviation of only $0.079\,\mathrm{cm}^{-1}$. The FIS3 PES of $H_2{}^{16}O$ obtained in this study will be of considerable utility for further analysis of high J transitions in the recently reported oxyacetylene torch spectrum [16].

The true magnitude of nonadiabatic corrections to rovibrational levels using PESs remains uncertain. Our final calculations are based on use of 25% of the values given by Schwenke [15], whereas for fits which included levels with $J = 10$, 18% gave the best results. In our previous fitted potential [11] these values varied from plus 80% for J_{xx} and J_{yy} operators to minus 110 % for J_{zz}. Our fits certainly display sensitivity to nonadiabatic effects but it does not appear to be possible to fully determine these effects purely by fitting. A similar situation was found for the study of Born–Oppenheimer-breakdown (BOB) corrections for diatomic molecules by Watson [45], where even using transformed Hamiltonians, which change BOB diatomic functions, leaves one degree of indeterminacy.

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