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Vibration–rotation levels of water beyond the Born–Oppenheimer approximation

Nickolai F. Zobov [1], Oleg L. Polyansky [1], C. Ruth Le Sueur, Jonathan Tennyson
Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, UK

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Abstract

The value of the adiabatic correction to the Born–Oppenheimer electronic energy is calculated as a function of geometry for water using SCF wavefunctions. A mass-dependent adiabatic function is combined with high-accuracy ab initio electronic structure calculations due to Partridge and Schwenke. Vibrational band origins for H_2O, D_2O, T_2O, HDO, HTO and DTO are analysed. Unlike previous calculations on the H_3^+ system, it is suggested that non-adiabatic effects are more important than adiabatic ones in determining accurate isotope dependence of the vibrational band origins of water. Use of the adiabatic surface and effective masses of the heavy particles intermediate between the nuclear and atomic masses is found to significantly improve predictions of rotational term values. The adiabatic correction is found to be of particular importance for rotational levels with high K_a.

1. Introduction

Water is an important molecule in its own right and one which provides a benchmark for the development of theoretical methods. State-of-the-art ab initio electronic structure calculations are now capable of predicting vibrational band origins of water to within a few wavenumbers, and other spectroscopic properties with similar (~ 0.02 %) accuracy [1,2]. However such calculations are performed within the Born–Oppenheimer approximation which assumes that the electrons relax instantly to any motion of the nuclei. Recent work by Handy and coworkers [3-5] and ourselves [6] has suggested that the Born–Oppenheimer diagonal correction or adiabatic correction can have a significant effect on the accuracy with which spectral properties of hydrogen containing molecules can be predicted. This work has largely focused on vibrational spacings.

The properties of hot water are important for a number of reasons. A good illustration is the well-documented [7,8] but almost totally unassigned infrared sunspot spectrum. The water in the sunspot spectrum has an effective temperature of about 3100 K and has an average line density of nearly 50 lines per cm^{-1}. It is clear that any theoretical attempt to assign or model this spectrum will require high accuracy, an accuracy which cannot be obtained within the Born–Oppenheimer approximation [9].

The electronic structure of water is sufficiently complicated that even the sophisticated ab initio calculations cited above have yet to reach the Born–Oppenheimer limit. Considerably more accurate effective potential energy surfaces can be obtained by

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[1] Permanent address: Institute of Applied Physics, Russian Academy of Science, Uljanov Street 46, Nizhnii Novgorod, Russia 603024.

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directly inverting spectroscopic data using variational rotation-vibration calculations [9,10]. However the fitting procedures used to construct these spectroscopically determined potentials mean that the relative importance of various contributions to the effective potential are masked. In particular it is not possible to determine what, if any, non-adiabatic contributions are included in such potentials.

In particular, fits to data on a single isotopomer give effective potentials which include the adiabatic correction to the Born-Oppenheimer approximation for that isotopomer. Polyansky et al. [10] used their effective $H_2{}^{16}O$ potential to predict fundamental frequencies for $D_2{}^{16}O$, $T_2{}^{16}O$, $HD^{16}O$ and $HT^{16}O$. Their results are illuminating: their potential fitted the $H_2{}^{16}O$ fundamentals to better than 0.1 cm^{-1} and reproduced the ν_2 bending fundamentals to this accuracy for all isotopomers. The ν_1 symmetric stretch for D_2O and T_2O were reproduced to within 0.2 cm^{-1}, errors of $\sim$ 0.6 cm^{-1} were found for ν_1 for the asymmetrically substituted isotopomers. For the ν_3 asymmetric stretch fundamental, the symmetric isotopomers gave errors no greater than 0.3 cm^{-1} and the asymmetric isotopomer predictions were in error by 0.3 and 1.2 cm^{-1} for HDO and HTO respectively. Furthermore, only for ν_3 for HDO and HTO were the calculated values too high.

In subsequent work improving their potential, Polyansky et al. [9] reproduced 3200 $H_2{}^{16}O$ energy levels with a standard deviation of only 0.6 cm^{-1}. They found that they were unable to improve their fit with further adjustments to the potential and concluded that their inability to find a single potential energy function which completely reproduced all the known levels of $H_2{}^{16}O$ was due to non-adiabatic effects. This conclusion was reinforced by similar analysis performed on the spectroscopically simpler H_2S system [11]. In order to extend and improve such calculations it is important to develop an understanding for the relative importance of, say, adiabatic and non-adiabatic corrections to the Born-Oppenheimer approximation.

As part of this process we have computed the adiabatic or Born-Oppenheimer diagonal correction (BODC) for water. Nuclear motion calculations are presented here using this surface and a high-accuracy ab initio potential [2]. These calculations suggest that for water vibrations, unlike those of H_3^+ and its isotopomers which we treated in a similar manner [6,12], non-adiabatic effects are more important than adiabatic ones when moving beyond the Born-Oppenheimer approximation.

2. Calculations

2.1. Electronic motion calculations

The adiabatic correction for water was calculated using the formulation of Handy et al. [3] as implemented as part of the CADPAC [2] program suite [6]. This formulation allows the Born-Oppenheimer diagonal correction (BODC) to be calculated using the expression

$$\Delta V^{ad} = \langle \Psi | - \frac{1}{2} \sum_I \frac{1}{M_I} \nabla_I^2 | \Psi \rangle$$
$$= \sum_I \frac{1}{2M_I} \langle \nabla_I \Psi | \nabla_I \Psi \rangle , \qquad (1)$$

where the sum runs over all $3N$ nuclear coordinates. In this work we use an SCF wavefunction for water expressed in terms of atom centred Gaussian Type Orbitals (GTOs); in this case the wavefunction is translationally and rotationally invariant, and there is no need to consider more complicated forms of the BODC [5].

The BODC was evaluated using SCF wavefunctions obtained with a standard CADPAC basis of (13s8p3d/8s6p3d) on O and (10s3p/6s3p) on each H. The calculations were performed at the 325 points used by Kedziora and Shavitt [1]. This non-uniform grid covers OH bondlengths, r_1 and r_2, in the range 1.45 a_0 - 2.80 a_0 and H$\hat{O}$H bondangle, θ, in the range 0.71 rad - 2.95 rad.

This calculation yields three mass-dependent BODC surfaces, one for each atom. However the symmetry between the two H atoms makes it preferable to express these surfaces in symmetrised displacement coordinates

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[2] The Cambridge Analytic Derivatives Package (CADPAC), Issue 5, Cambridge 1992. A suite of quantum chemistry programs developed by R.D. Amos with contributions from I.L. Alberts, J.S. Andrews, S.M. Colwell, N.C. Handy, D. Jayatilaka, P.J. Knowles, R. Kobayashi, N. Koga, K.E. Laidig, P.E. Maslen, C.W. Murray, J.E. Rice, J. Sanz, E.D. Simandiras, A.J. Stone and M.-D. Su.

$$S_1 = \frac{r_1 + r_2}{2} - r_e ,$$
$$S_2 = \theta - \theta_e ,$$
$$S_3 = \frac{r_1 - r_2}{2} , \qquad (2)$$

where (r_e, θ_e) are equilibrium values taken to be (1.80965 a_0, 1.824045 rad). In these coordinates the adiabatic correction, for isotopomer XYO, has the form

$$\Delta V^{\mathrm{ad}}_{\mathrm{XYO}} = \frac{1}{m_{\mathrm{O}}} f^{\mathrm{S}}_{\mathrm{O}}(S_1, S_2, S_3) + \left(\frac{1}{m_{\mathrm{X}}} + \frac{1}{m_{\mathrm{Y}}}\right) f^{\mathrm{S}}_{\mathrm{H}}(S_1, S_2, S_3) + \left(\frac{1}{m_{\mathrm{X}}} - \frac{1}{m_{\mathrm{Y}}}\right) f^{\mathrm{A}}_{\mathrm{H}}(S_1, S_2, S_3) . \qquad (3)$$

The three surfaces were expressed as power series in the symmetrized displacement coordinates

$$f(S_1, S_2, S_3) = \sum_{i,j,k} c_{i,j,k} S_1^i S_2^j S_3^k , \qquad (4)$$

where symmetric functions, superscripted S, contain only even k and the asymmetric function odd k. Of course this asymmetric function only contributes for asymmetric isotopomers HDO, HTO and DTO.

The coefficients resulting from least square fits to our 325 data points are presented in Table 1. These fits have a standard deviation of $\sim 10^{-6}$ E_h u ($\sim$ 0.2 cm^{-1} u). For $H_2{}^{16}O$, our calculated BODC is typically about 600 cm^{-1}. However over 80 % of this correction arises from the BODC to O. As can be seen from Table 1, once allowance is made for the mass weigthing, the BODC for O is nearly constant as a function of geometry. Indeed the variation $f^{\mathrm{S}}_{\mathrm{O}}$ is so small that its inclusion had little influence on the nuclear motion calculations discussed below, although it was retained for completeness. Conversely the BODC due to the hydrogen atoms is, as in H_2, $\sim$ 100 cm^{-1}, but shows more variation with geometry.

Table 1
Fitted coefficients, in μhartree times atomic mass units, of the adiabatic correction to Born–Oppenheimer potential, see Eqs. (3) and (4)

i	j	k	$f^{\mathrm{S}}_{\mathrm{O}}$	$f^{\mathrm{S}}_{\mathrm{H}}$	i	j	k	$f^{\mathrm{A}}_{\mathrm{H}}$
0	0	0	37356.83139	189.65925	0	0	1	−70.67273
1	0	0	85.51687	−53.90300	1	0	1	145.61028
0	1	0	90.00281	23.30821	1	1	1	23.50163
2	0	0	284.70894	67.89052	0	0	3	−56.94870
0	2	0	8.62922	−17.08162	2	0	1	−93.87483
0	0	2	231.64624	76.01110	0	2	1	−11.38221
1	1	0	31.61609	−8.31483	1	1	1	−12.06689
3	0	0	−306.99286	−50.25909				
0	3	0	11.61762	14.02839				
2	1	0	−134.84571	−14.82899				
1	2	0	−15.15433	18.38998				
1	0	2	−927.28925	−181.38649				
0	1	2	−20.21532	−6.92278				
4	0	0	111.10407	5.54128				
0	4	0	37.84844	14.48113				
0	0	4	230.08839	52.91334				
3	1	0	44.62810	−1.77743				
1	3	0	135.54639	13.10338				
2	2	0	161.13736	34.03004				
2	0	2	1152.43962	167.13496				
0	2	2	115.45701	16.46124				
1	1	2	−165.53560	−61.90073				
5	0	0	20.49566	14.20162				
0	5	0	52.39852	17.94321				
4	1	0	76.43377	42.69724				
1	4	0	138.36648	56.83519				
1	0	4	−321.84119	−52.70324				
0	1	4	172.99300	36.17267				
3	2	0	17.04009	6.79350				
3	0	2	−533.64679	−45.48514				
2	3	0	−127.91398	−49.18359				
0	3	2	−391.10482	−49.35202				

2.2. Nuclear motion calculations

Nuclear motion calculations were performed using the DVR3D program suite [13] and previously optimised basis sets [10]. Calculations were performed for all the ^{16}O isotopomers of water for which spectroscopic data is available. A number of calculations were performed testing different combinations of ab initio and spectroscopically determined potentials with and without the mass-dependent adiabatic correction given above, and with various masses. These calculations made extensive comparisons with available experimental data both for all the observed vibrational band origins and for a number of rotationally excited states.

Tables 2 and 3 summarize calculations for the vibrational and rotational levels of the water isotopomers. These calculations were all performed with ab initio Born–Oppenheimer surface of Partridge and Schwenke [2]. The ab initio surface is less accurate than the spectroscopically determined effective potential PJT2 [9], for which we also performed calculations, but the ab initio surface corresponds to the solution of well-defined model which considerably eases interpretation of the results. In fact comparison of the two surfaces showed that the difference between the two of them was a remarkably smooth function showing little structure [2]. This behaviour should be contrasted with the considerable structure found when performing a similar comparison of earlier [10,14] spectroscopically determined potentials.

The most notable result of Table 2 is how insensitive our results are to the inclusion of the BODC. Similar results were found both for higher band origins, where experimental data is available, and for calculations starting from the PJT2 potential. It is clear that the BODC surfaces we calculate do not give a large enough mass-dependent variations to reproduce the non-Born–Oppenheimer behaviour of the fundamentals noted previously [10]; this is in complete contrast to H_3^+ where the BODC accounted for about 90% of this behaviour [6,12].

Conversely the vibrational band origins in general, and ν_3 fundamental in particular, show rather greater sensitivity to the choice of heavy particle masses in the calculation. What constitutes the correct mass to use in high-accuracy calculations at or beyond the Born–Oppenheimer approximation remains a subject of some debate [5,15]. However the remaining uncertainties in the ab initio Born–Oppenheimer potential means that it is not possible to use the vibrational fundamentals computed here to add to this debate.

Table 3 shows the $J = 20$ rotational term values calculated using the same models analysed above for the vibrational fundamentals. Although results are only presented for the vibrational ground state, similar results were obtained for all vibrationally excited states for which $J = 20$ experimental data is available, once allowance was made for overall shifts caused by errors in the vibrational band origin.

Table 2
Band origins, in cm^{-1}, for the ^{16}O isotopomers of water. Results calculated using Born–Oppenheimer (BO) and Born–Oppenheimer Diagonal Correction (ΔV^{ad}) are given as observed − calculated

	Obs [a]	BO	BO + ΔV^{ad}		
		atomic [b]	atomic [b]	nuclear [c]	mid [d]
H_2O					
ν_2	1594.7	−2.2	−1.6	−2.0	−1.8
ν_1	3657.1	−2.9	−2.8	−3.8	−3.3
ν_3	3755.9	−1.8	−1.9	−2.8	−2.4
D_2O					
ν_2	1178.4	−1.6	−1.4	−1.6	−1.5
ν_1	2671.7	−2.2	−2.2	−2.6	−2.4
ν_3	2787.7	−1.6	−1.6	−2.0	−1.9
T_2O					
ν_2	995.4	−1.3	−1.2	−1.3	−1.3
ν_1	2237.2	−1.9	−1.9	−2.1	−2.0
ν_3	2366.6	−1.4	−1.4	−1.7	−1.6
HDO					
ν_2	1403.5	−1.8	−1.7	−2.0	−1.8
ν_1	2723.7	−1.9	−2.0	−2.4	−2.2
ν_3	3707.5	−2.3	−2.4	−3.3	−2.9
HTO					
ν_2	1332.5	−1.6	−1.6	−1.9	−1.7
ν_1	2299.8	−1.6	−1.7	−1.9	−1.8
ν_3	3716.6	−2.5	−2.5	−3.4	−3.0

[a] Observed fundamentals from Refs. [20-30].
[b] Calculations performed with atomic masses.
[c] Calculations performed with nuclear masses.
[d] Calculations performed with nuclear masses for O and other masses as average between atomic and nuclear mass.

The rotational term values show smaller relative errors when compared to experiment than the vibrational band origins, however rotational levels appear more sensitive to the addition of the BODC than the vibrations. In particular calculations using atomic masses and the BO potential only perform well for levels with low K_a but poorly for those with high K_a. When the BODC is included in the calculation using atomic masses, the levels are reproduced more uniformly, although the average error is similar. In particular, this calculation gives significantly better results for levels

Table 3
Rotational term values, in cm^{-1}, for the vibrational ground state of $H_2{}^{16}O$. Results calculated using Born-Oppenheimer (BO) and Born–Oppenheimer Diagonal Correction (ΔV^{ad}) are given as observed – calculated. See Table 2 for explanation of the masses used

	Obs [a]	BO	BO + ΔV^{ad}		
		atomic	atomic	nuclear	mid
20_{020}	4048.252	0.6	0.9	−1.2	−0.17
20_{120}	4048.252	0.6	0.9	−1.2	−0.16
20_{119}	4412.317	0.6	1.0	−1.3	−0.16
20_{219}	4412.317	0.6	1.0	−1.3	−0.16
20_{218}	4738.624	0.5	1.0	−1.4	−0.21
20_{318}	4738.636	0.5	1.0	−1.4	−0.20
20_{317}	5031.796	0.5	1.1	−1.4	−0.26
20_{417}	5031.977	0.5	1.1	−1.5	−0.26
20_{416}	5292.096	0.4	1.0	−1.7	−0.35
20_{516}	5294.035	0.4	1.0	−1.7	−0.33
20_{515}	5513.266	0.1	1.0	−1.7	−0.47
20_{615}	5527.046	0.3	1.0	−1.8	−0.39
20_{614}	5680.787	0.2	0.8	−2.1	−0.64
20_{714}	5739.232	0.3	1.0	−1.9	−0.42
20_{713}	5812.074	0.2	0.9	−2.2	−0.65
20_{813}	5947.327	0.5	1.2	−1.9	−0.38
20_{812}	5966.827	0.3	1.0	−2.0	−0.48
20_{912}	6167.909	0.8	1.5	−1.9	−0.32
20_{911}	6170.964	0.7	1.4	−1.9	−0.34
20_{1011}	6407.084	1.1	1.3	−1.8	−0.25
20_{1010}	6407.446	1.0	1.4	−1.9	−0.25
20_{1110}	6664.138	1.3	1.5	−1.9	−0.20
20_{119}	6664.172	1.4	1.5	−1.9	−0.21
20_{129}	6935.425	1.6	1.6	−1.9	−0.19
20_{128}	6935.428	1.6	1.6	−1.9	−0.19
20_{138}	7217.560	1.9	1.7	−1.9	−0.19
20_{137}	7217.560	1.9	1.7	−1.9	−0.19
20_{147}	7507.575	2.0	1.7	−2.0	−0.22
20_{146}	7507.575	2.0	1.7	−2.0	−0.22
20_{156}	7802.700	2.2	1.7	−2.1	−0.27
20_{155}	7802.700	2.2	1.7	−2.1	−0.27
20_{165}	8100.292	2.3	1.7	−2.2	−0.33
20_{164}	8100.292	2.3	1.7	−2.2	−0.33
20_{174}	8397.625	2.4	1.5	−2.4	−0.48
20_{173}	8397.625	2.4	1.5	−2.4	−0.48
20_{183}	8691.916	2.4	1.5	−2.6	−0.63
20_{182}	8691.916	2.4	1.5	−2.6	−0.63
20_{192}	8979.854	2.5	1.3	−2.7	−0.82
20_{191}	8979.854	2.5	1.3	−2.7	−0.82
20_{201}	9257.408	2.5	1.1	−3.1	−1.06
20_{200}	9257.408	2.5	1.1	−3.1	−1.06

[a] Observed rotational term values from Refs. [31,32].

with high K_a which are shifted by up to 1.4 cm^{-1} on inclusion of the adiabatic correction.

Again we found significant variations between calculations employing different masses. Interestingly the sign of these errors is completely systematic and changes between calculations performed using atomic and nuclear masses. We note that the calculations are not particularly sensitive to the mass of ^{16}O employed but that best results are obtained by using hydrogenic masses intermediate between atomic and nuclear ones.

Illustrative calculations using the average of these two masses are given in Table 3. We found that this mid masses model yielded excellent results for a wide range, in both J and vibrational level, of rotational term values. Indeed calculations based on this model are presently being used to assign transitions in the spectrum of hot water [16].

Of course the mid-mass rotational term values in Table 3 are still systematically somewhat too high suggesting that closer agreement with experiment could be obtained by use of masses slightly closer the atomic value. Even with this ‘optimal’ mass however, it will not be possible to account for non-adiabatic effects at an accurate enough level to, for example, model the sunspot spectrum. Adjusting the masses of course amounts to scaling the kinetic energy operators. More sophisticated analysis suggests that to model these effects properly scaling factors which affect different parts of the kinetic energy operator and are symmetry dependent will be necessary [17].

3. Discussion and conclusions

Our results suggest that the adiabatic or Born–Oppenheimer diagonal correction (BODC) is not the dominant non-Born–Oppenheimer effect for water vibrations. Conversely changing the heavy particle masses between atomic and nuclear gave rise to significant changes in both our vibrational and rotational term values. The use of atomic masses instead of nuclear masses, or masses intermediate between the two as discussed below, can be justified on the grounds that this model allows for the effects of electrons following the nuclei. For systems with only high-lying excited electronic states, this is the dominant non-adiabatic correction [5]. From our results it appears that for spectroscopic calculations on water beyond the Born–Oppenheimer approximation, non-adiabatic effects are more important than adiabatic ones. Indeed Polyansky et al. [9] recently concluded that the omission of non-adiabatic effects was the leading error in their attempts to obtain a spectroscopically determined (effective) potential for water.

We have already noted above that for H_3^+, the adiabatic correction has been found to be the leading one to the Born–Oppenheimer approximation. Notably similar conclusions have been drawn for rotation–vibration levels of H_2^+ [5,18] and H_2 [5,19]. It would therefore appear that for all (not just H_2 as stated in [5]) purely hydrogenic species the adiabatic correction is particularly important.

Conversely the present work and calculations by Handy and Lee [5] on HF found that the adiabatic correction yielded little, but the use of atomic masses instead of nuclear, i.e. the non-adiabatic approximation, is a significant factor in determining vibrational band origins. Two examples may be too few to generalize from, but it would at least seem plausible that for systems containing hydrogens bound to heavy atoms this may generally be the case.

It has been recently suggested [5] that because the electrons follow the vibrating nuclei, use of atomic masses instead of nuclear masses is preferable for calculations including the adiabatic correction. Our calculations suggest that for the hydrogenic atoms in water a value intermediate between these two may be more appropriate. This is hardly surprising when one considers the electronic structure of water which involves considerable electron transfer away from the hydrogen atoms.

Finally the most surprising, to us at least, result of our calculations is the strong dependence on the adiabatic surface shown by the high-K_a rotational term values. These levels have always been notoriously difficult to model, but to our knowledge it has never been suggested that they should show enhanced sensitivity to adiabatic effects.

In conclusion, we have calculated the adiabatic or Born–Oppenheimer diagonal correction for water as function of geometry. The resulting surfaces have been used to study both the vibration and rotation levels of H_2O and its deuterated and tritiated isotopomers. These calculations suggest that the adiabatic correction to these levels is less important than that given by non-adiabatic contributions to the Born–Oppenheimer approximation. Inclusion of non-adiabatic effects in our rotation–vibration calculations by mass scaling and by the use of more exact formulations [17,33] will be the subject of future work.

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