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Calculating the vibration–rotation spectrum of water

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Abstract
The spectrum of water is ubiquitous and therefore the demand for a reliable theoretical model for it remains pressing. The treatment of nuclear motion using methods based on the variational principle has led to a major advance in the development of the model but places great emphasis on the accurate treatment of the underlying potential energy surface. Progress in constructing high-accuracy potentials both *ab initio* and by fitting to spectroscopic data is discussed.

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Water appears to be a small and apparently simple molecule but its study presents tremendous scientific challenges in each of its phases. Ice shows a complexity and subtlety of behaviour that is probably unrivalled, with at least 12 known crystalline phases and several others suspected [1]. Similarly, the anomalous behaviour of liquid water is not readily understood in terms of standard models [2]. In this paper, I discuss the spectroscopy of the gas-phase water molecule and show that it has subtleties hard to anticipate for such a seemingly simple system.

Water is the third most common molecule in the Universe, after H_2 and CO. It is present in a wide variety of astronomical environments including: sunspots [3], the atmosphere of cool stars, circumstellar and star-forming regions (where it is often observed to mase) and cooler objects such as comets. Water is also observed in the interstellar medium. Closer to home, water vapour in our atmosphere is the dominant absorber of incoming sunlight and the most important greenhouse gas. Water vapour is a product of most combustion processes. To take an extreme example: the exhaust of a hydrogen-burning rocket is hot steam.

The importance of the spectrum of water vapour has led to many and continuing laboratory studies. However, its vibration–rotation spectrum is much more complicated than is usual for a small molecule. Its low symmetry means that it has three vibrational modes, all of which are infrared active and have allowed dipole-driven spectra. Similarly, water is an asymmetric top, meaning that it has three distinct rotational constants, yielding a complex series of pure rotation and vibration–rotation transitions. These characteristics are shared with a number of molecules. However, what marks water out is that two of its atoms are hydrogen. The lightness of these atoms leads to two effects. Firstly, the rotational constants of water are large, leading to a spread-out, or open spectrum, which can absorb or emit over very broad regions. Secondly, the hydrogen atoms undergo motions which are very far from harmonic. This means that the harmonic oscillator rule, which states that vibration–rotation transitions only involve changes by a single vibrational quantum, is easily and frequently violated. One further feature of water spectra is that the (near-)resonance between the vibrational frequencies leads to many vibrational bands overlapping into what are called polyads. Both the polyad structure of the water spectrum, which leads to many interactions between different vibrational bands, and the anharmonicity of the underlying potential, which leads to divergence of standard perturbation expansions at rather low values of the rotational quantum number [4], mean that standard theoretical spectroscopic models cannot easily or reliably be applied to water spectra.

The importance of water has led to the application of a variety of alternative theoretical approaches to the study of its vibration–rotation spectra. The most successful of these methods are based on the use of the variational principle for the nuclear motion problem [3, 5], which aims for an, as near as possible, exact solution to the nuclear motion Schrödinger equation of the problem without any assumptions beyond, possibly, that of the Born–Oppenheimer approximation. Variational methods have a number of advantageous features. They treat vibrational and rotational motion at the same time and within the same theoretical framework and can

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Table 1. Summary of spectroscopically determined $H_2{}^{16}O$ potential energy surfaces. σ_{vib} is the standard deviation of the fitted vibrational levels given in cm^{-1}. N_{vib} is the number of vibrational levels used in the fit. $E_{\max}$ is the maximum energy of the fitted vibrational levels given in cm^{-1}.

Reference	Year	σ_{vib}	N_{vib}	$E_{\max}$
Hoy *et al* [11]	1972	214	25	13 000
Carter and Handy [13]	1987	2.42	25	13 000
Halonen and Carrington [14]	1988	5.35	54	18 000
Jensen [15]	1989	3.22	55	18 000
Paulse and Tennyson [16]	1994	3.0	55	20 000
Polyansky *et al* [17]	1994	0.60	40	18 000
Polyansky *et al* [18]	1996	0.94	63	25 000
Partridge and Schwenke [5]	1997	0.33	42	18 000
Shirin *et al* [10]	2003	0.10	106	25 000

treat as many vibrational states as desired, all the way to dissociation if needed [6]. Variational methods give results which can be interpreted in terms of the underlying potential energy surface and, possibly with an allowance for failure of the Born–Oppenheimer approximation, models which are directly transferable between different isotopologues. Variational methods use only rigorous quantum numbers or symmetries; in the case of water, these are J, the rotational-angular momentum, p, the (rotational) parity and q, a quantum number which distinguishes between ortho and para states of the molecule. Use of an exact (within the Born–Oppenheimer approximation) kinetic energy operator means that all interactions between accidentally near-degenerate levels are automatically included.

My group has developed and published variational programs for solving the vibration–rotation problem over a number of years. These programs use either a strictly variational basis set expansion [7] or discrete variable representation (DVR) methods which can behave non-variationally but have many of the attributes of the variational methods. In practice, DVR methods are much more efficient for problems where one wishes to study a large number of levels. Our workhorse is the DVR3D program suite, the most recent edition of which has just been published [8].

For water, a program such as DVR3D can solve the nuclear motion problem for levels of spectroscopic interest and a given potential energy surface to an accuracy better than $0.001\,\mathrm{cm}^{-1}$ [9]. This means that the accuracy of the calculated levels and resulting transition frequencies depends almost entirely on the accuracy of the potential energy surface used in the calculation. Ideally, one should be able to compute a high-accuracy potential *ab initio*. However, despite significant advances in this regard, the best fully *ab initio* procedures still give results far from spectroscopic accuracy [9]. An alternative approach is to start from a good quality *ab initio* potential energy surface and then adjust it by fitting to observed spectroscopic data, see e.g. [5, 10]. This gives what is termed a spectroscopically determined potential. Table 1 compares the accuracy and range of spectroscopically determined potentials derived over the last three decades. Besides the obvious improvement with time of these potentials, the most striking feature of table 1 is the huge improvement obtained when moving from the perturbation theory method of Hoy *et al* [11] to the variational methods used in all the subsequent studies. One important point is not readily obvious from table 1: to get a reliable potential, it is necessary to fit to both vibrationally and rotationally excited levels [12].

Although spectroscopically determined potentials do indeed yield increased accuracy, they are generally much better at representing known data than predicting new levels. Experience has shown [19] that such predictions are more safely made with a completely *ab initio* procedure. For this reason, and because the water spectroscopy problem will only be finally solved with a fully reliable and predictive theoretical model, my group has worked hard at developing a high accuracy *ab initio* model. Our goal of obtaining spectroscopic accuracy, meaning *ab initio* results reliable to about $0.02\,\mathrm{cm}^{-1}$, is still far from being achieved. Indeed, our experience has shown that to break the $1\,\mathrm{cm}^{-1}$ accuracy barrier for water requires consideration of several effects which are traditionally omitted from standard electronic structure calculations, even high accuracy ones.

For better than $1\,\mathrm{cm}^{-1}$ accuracy, ‘minor’ effects that must be considered include corrections to the Born–Oppenheimer approximation, both adiabatic [20, 21] and non-adiabatic [22, 23], the kinetic relativistic motion of the electrons [24, 25], the relativistic effect on the Coulomb potential, known as the Breit effect, [26] and even the radiative correction introduced only by quantum electrodynamics [27]. Once all these effects are considered, there remains the fundamental question of whether the underlying electronic Schrödinger equation can itself be solved to the required accuracy.

Table 2, summarizes the *ab initio* attempts to compute the fundamental frequencies of water. These calculations have clearly improved significantly with time. With the exception of the ‘final’ calculations of Polyansky *et al* [9], all calculations reported only addressed the standard Schrödinger electronic structure problem. Obtaining a precise solution to the quantum mechanical equations which govern the spectroscopy of water is a complicated problem for which one can easily be deceived into thinking one has the correct solution due to a fortuitous cancellation of errors; see the calculation by Martin *et al* [28] for example. An interesting illustration of this is given by the electronic relativistic correction as studied by Csaszar *et al* [24]. Csaszar *et al* started from the *ab initio* multireference configuration interaction (MR-CI) electronic structure surface of Partridge and Schwenke (PS) [5]. In the absence of these relativistic corrections, PS’s surface gives similar errors for bending and stretching motions. However, adding the electronic relativistic correction completely changes this picture: the error for all stretching mode becomes small, whilst that for the bending mode approximately doubles. Subsequent analysis of PS’s calculations [29] showed that it was indeed for the bending coordinate where their potential was poorly converged.

For water, the effects of Born–Oppenheimer approximation are quite large. This means that the task of reproducing energy levels for all isotopically substituted variants of water presents a severe test of any model. Table 3 shows that the calculations of Polyansky *et al* [9], which represent the present state-of-the-art for an *ab initio* treatment of water spectra, manage this with a standard deviation just better than $1\,\mathrm{cm}^{-1}$. This is a good but not spectroscopic accuracy.

Table 2. Summary of *ab initio* calculated fundamental frequencies for water $H_2{}^{16}O$. For a description of each method see the cited references.

Reference	Method	Year	ν_1	ν_2	ν_3
Bucknell and Handy [30]	SCF	1974	4045	1728	4139
Barlett *et al* [31]	MBPT	1979	3702	1610	3789
Knowles *et al* [32]	CASSCF	1982	3691	1645	3794
Martin *et al* [28]	QCISD(T)	1992	3657	1595	3756
Kedziora and Shavitt [33]	MR-CISD	1997	3650.5	1604.6	3746.9
Partridge and Schwenke [5]	MR-CI	1997	3660.5	1597.4	3758.2
Polyansky *et al* [9]	CBS + CV	2003	3660.10	1594.27	3758.76
Polyansky *et al* [9]	Final	2003	3656.33	1595.02	3754.98
Observed [34]			3657.05	1594.75	3755.93

Table 3. Standard deviation (σ) with which the final model of Polyansky *et al* [9] reproduces the vibration–rotation term values for various water isotopologues with rotational excitation $\leqslant J_{\max}$. N(levels) values are considered in each case. Also given is the maximum error for each isotopologue, in cm^{-1}, and the associated value of J. The H_2O isotopologue calculations included rotational non-adiabatic effects.

				Maximum deviation	
Isotopologue	σ (cm^{-1})	$J_{\max}$	N(levels)	obs–calc	J
$H_2{}^{16}O$	1.17	20	9426	6.5	7
$H_2{}^{17}O$	0.56	12	1083	1.4	12
$H_2{}^{18}O$	0.65	12	2460	2.3	6
$D_2{}^{16}O$	0.71	12	2807	3.0	7
$HD^{16}O$	0.47	12	2019	−1.2	11
All	0.95	20	17 795		

It is interesting to consider what would be required to really achieve spectroscopic accuracy. There are probably four aspects of the calculation that should be improved.

1. Undoubtedly the biggest error is still caused by the treatment of the valence correlation problem by extrapolating 4Z, 5Z and 6Z basis to the complete basis set (CBS) limit. A 7Z calculation would greatly improve this but is not technically possible at present. In the longer term, it may well be that explicitly correlated wavefunctions will offer a solution to this problem as they have for H_3^+ [35, 36].
2. The MR-CI model omits some configuration interaction (CI) contributions whose magnitude could be estimated using a full CI calculation. At present, such calculations can only be performed using basis sets too small to make the results useful.
3. The results above used a surface fitted to only 346 *ab initio* points. This is too few and a study using four times this number is nearing completion [37].
4. Non-adiabatic effects have so far been modelled only over a limited energy range [22]; their inclusion over the entire spectroscopic range will probably be important.

One reason for searching for a theoretical solution to the water vibration–rotation problem is that at high temperatures the spectrum becomes too dense to contemplate measuring individual lines in the laboratory. For example, at 3000 K, a temperature important for ‘cool’ oxygen-rich M-dwarf stars, it is necessary to consider a few hundred million water transitions in the infrared alone. For M-dwarfs, these water transitions, and the nearly as dense transitions due to TiO, completely dominate the atmospheric absorptions, giving spectral energy distributions which are unrecognizable as black body functions [38, 39]. Higher resolution astronomical studies, such as those performed for sunspots [3], or indeed laboratory studies at similar temperatures [40], can resolve individual transitions and require models with (near-)spectroscopic accuracy for their interpretation.

Perhaps the most compelling reason for trying to finally nail the water spectroscopy problem is for studies of our atmosphere. Water is responsible for 70% of the known absorption of sunlight by the earth’s atmosphere. Whether there is a significant extra, missing absorption remains controversial [41, 42]; but if there is, then water is likely to be responsible. Recent combined laboratory and theoretical studies have pointed to two possible problems with standard database compilations such as HITRAN. Firstly, weak lines which are hard to see in the laboratory are missing from compilations and may yield significant extra absorption [43]. Secondly, it would appear that many early measurements of the strong lines systematically underestimated their intensity [44]. Atmospheric models [45] suggest that these two effects may contribute as much additional average absorption of solar radiation as 3 and 8 $\mathrm{W\,m^{-2}}$ respectively. These are large amounts compared to estimates of the anthropic greenhouse effect, which are generally less than 1 $\mathrm{W\,m^{-2}}$. Although the 2004 version of HITRAN [46] allows for some of these effects, there are still issues which need to be addressed in the absorption by water.

The water molecule is a seemingly simple three-atom system. Yet its spectrum is dense, complicated, extensive and of extreme importance. The issue of developing a full, reliable, predictive theoretical model for its spectrum is likely to remain a key one for some time to come.

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