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Global spectroscopy of the water monomer

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Given the large energy required for its electronic excitation, the most important properties of the water molecule are governed by its ground potential energy surface (PES). Novel experiments are now able to probe this surface over a very extended energy range, requiring new theoretical procedures for their interpretation. As part of this study, a new, accurate, global spectroscopic-quality PES and a new, accurate, global dipole moment surface are developed. They are used for the computation of the high-resolution spectrum of water up to the first dissociation limit and beyond as well as for the determination of Stark coefficients for high-lying states. The water PES has been determined by combined *ab initio* and semi-empirical studies. As a first step, a very accurate, global, *ab initio* PES was determined using the all-electron, internally contracted multi-reference configuration interaction technique together with a large Gaussian basis set. Scalar relativistic energy corrections are also determined in order to move the energy determinations close to the relativistic complete basis set full configuration interaction limit. The electronic energies were computed for a set of about 2500 geometries, covering carefully selected configurations from equilibrium up to dissociation. Nuclear motion computations using this PES reproduce the observed energy levels up to 39 000 cm^{-1} with an accuracy of better than 10 cm^{-1}. Line positions and widths of resonant states above dissociation show an agreement with experiment of about 50 cm^{-1}. An improved semi-empirical PES is produced by fitting the *ab initio* PES to accurate experimental data, resulting in greatly improved accuracy, with a maximum deviation of about 1 cm^{-1} for all vibrational band origins. Theoretical results based on this semi-empirical surface are compared with experimental data for energies starting at 27 000 cm^{-1}, going all the way up to dissociation at about 41 000 cm^{-1} and a few hundred wavenumbers beyond it.

Keywords: Stark coefficients; photodissociation; variational nuclear motion calculations; potential energy surface; water; dipole moment surface

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1. Introduction

As pointed out by Mielke *et al.* [1], there is a very limited set of 'solved problems' in molecular quantum mechanics. These problems all involve small, few-electron hydrogenic systems. The water molecule—with three nuclei and 10 electrons—is much more complicated, but not impossibly so. This means that the goal of finding an accurate, quantum-mechanical solution to the high-resolution spectroscopy of this triatomic molecule is a non-trivial but realistic goal.

Owing to the importance of the spectroscopy of the water molecule and its isotopologues for applications [2,3], its spectra are very well studied experimentally and theoretically up to the blue end of the optical region [4]. Spectra in this region can be computed to spectroscopic accuracy (loosely defined as 'better than $1\,\mathrm{cm}^{-1}$') by a combination of *ab initio* and semi-empirical methods. What prevented a global solution to the water monomer problem was the total lack of experimental information on the states beyond $26\,000\,\mathrm{cm}^{-1}$. Recent experimental and theoretical advances have, however, begun to fill this gap.

There are at least two major reasons for thoroughly studying the spectrum of the water monomer. As water is one of the most abundant molecules on the Earth and in the Universe, applications requiring accurate knowledge of its spectra are numerous. As this issue covers in detail many of these applications, we will not discuss them here. The second reason is that the water molecule represents a benchmark system. It was one of the first polyatomic molecules for which variational calculations were performed by Whitehead & Handy [5]. It was also the first polyatomic and polyelectronic system to be treated with close to spectroscopic accuracy [6]; for which relativistic and quantum electrodynamic (QED) effects were computed [7–10]; and for which very accurate *ab initio* and semi-empirical potential energy surfaces (PESs) were developed. At present, it is one of the few chemically bound polyatomic molecules for which the spectra up to dissociation and above have been observed. An experimental observation of water at dissociation was described as an ultimate goal in a review by Bernath [11]. However, the levels at dissociation are like branches and leaves of a tree, with the root system extending into a conventional study of infrared (IR) and visible spectra. Our exploration of the levels up to and above dissociation is to a large extent based on the knowledge accrued about the spectrum below $26\,000\,\mathrm{cm}^{-1}$—the traditional region for water monomer spectroscopy. This is why, in order to present a coherent picture of global water monomer spectroscopy, a review of the methods and results up to $26\,000\,\mathrm{cm}^{-1}$, some $15\,000\,\mathrm{cm}^{-1}$ below dissociation, is a necessary prelude.

A comprehensive line list represents the final encapsulation of knowledge about a molecule's spectrum. In particular, the data required by applications related to the absorption and emission of radiation by the water monomer can be expressed in the form of a line list with frequencies of the line centres and their intensities, usually augmented by energy level assignments [12,13] and line shape data; the latter two, however, will not be considered here. There are a number of water line lists available, the most comprehensive one, designated as BT2 [14], consisting of over 500 million entries. The BT2 line list was computed using an *ab initio* dipole moment surface (DMS) due to Schwenke & Partridge [15] and a spectroscopically determined PES due to Shirin *et al.* [16]. This line list has been used for various applications, including the recent discovery of water on exoplanet HD189733b [17].

The results presented here represent a significant step towards assembling all the components needed to generate a global, accurate water line list, as these studies provide precise and experimentally validated knowledge about the PES and DMS of water over an extended energy range.

This paper is organized as follows. In §2, we review the analysis of experimental data up to 26 000 cm^{-1}, which, until recently, proved to be the upper limit of accessible energy levels for the water molecule. In §3, we describe recent progress in the analysis of the observed energy levels from 26 000 cm^{-1} up to dissociation at about 41 100 cm^{-1}. These two sections provide the basis for analysing the resonance (quasi-bound) states of water—those whose upper energy levels lie above the first dissociation threshold energy. The results are discussed in §4. Section 5 is devoted to the description of the fitting of a global PES to experimental data. Section 6 briefly describes the determination of a new, global water DMS and calculation of the Stark coefficients using our best PES and DMS. In §7, we present our conclusions.

2. Conventional spectra of the water monomer

The particular characteristics of the water molecule have made it necessary to develop special techniques to be able to analyse its spectra. In what follows, we describe and make use of these tools that were needed to compute the spectrum of water up to and above its first dissociation limit. The special character of water spectroscopy started to emerge in the early analysis of the IR and millimetre-wave (MMW) spectra in the 1960s and 1970s. At that time, the theoretical tools to analyse the high-resolution rovibrational spectra of small molecules were based on perturbation theory (PT), where the harmonic oscillator and the rigid rotor models were used as exactly solvable problems and anharmonicity and non-rigidity were allowed for by PT. In final form, PT-based effective Hamiltonians for asymmetric tops were formulated by Watson [18]. Owing to the lightness and in particular the quasi-linearity of the water molecule [19,20], PT series for water converge very slowly, or indeed sometimes not at all. Unlike other molecules, whose spectra are often fitted to effective Hamiltonians with experimental accuracy, MMW, sub-MMW and IR data on water have never been fitted to a polynomial Hamiltonian to the accuracy of the underlying experiment; a recent demonstration was provided by Furtenbacher & Császár [21].

Various re-summation techniques of PT were used to alleviate this convergence problem [22,23], and significant improvements were achieved. PT summation more or less solved the problem for levels with high rotational angular momentum, J, and high K_a (the projection of J onto the a-axis) within one isolated vibrational state, such as the ground [22] or the first excited vibrational state [24]; some lines belonging to these states were assigned in laboratory spectra of hot water using this technique [25]. However, once highly excited J and K_a levels in many excited vibrational states were observed experimentally, calculating high J, K_a levels in isolation was not sufficient. A very clear example of the problem was given by the spectrum of water in sunspots [26]. Because of the high temperature of

Table 1. Summary of spectroscopically determined potential energy surfaces for the $H_2{}^{16}O$ molecule: σ is the standard deviation of the fitted levels in cm^{-1}, N_{vib} is the number of vibrational levels used in the fit and E_{max} is the maximum energy of the fitted vibrational levels.

reference	σ (cm^{-1})	N_{vib}	E_{max} (cm^{-1})
Hoy *et al.* [32]	214.0	25	13 000
Carter & Handy [33]	2.42	25	13 000
Halonen & Carrington [34]	5.35	54	18 000
Jensen [28]	3.22	55	18 000
Polyansky *et al.* [29] (PJT1)	0.60	40	18 000
Polyansky *et al.* [31] (PJT2)	0.94	63	25 000
Partridge & Schwenke [35]	0.12	42	18 000
Partridge & Schwenke [35]	0.33	105	25 000
Shirin *et al.* [16]	0.10	105	25 000
Shirin *et al.* [36]	0.08	169	25 000
Maksyutenko *et al.* [37] (PES8)	0.03	105	25 000
Shirin *et al.* [38]	0.03	169	18 000
Bubukina *et al.* [39]	0.02	105	25 000
this work	0.09	146	40 000

sunspots, rotational lines belonging to tens of vibrational states interact and must be considered simultaneously. Under these circumstances, it becomes particularly hard to apply effective Hamiltonians.

An alternative approach based on variational nuclear motion computations with exact kinetic energy operators [27] potentially solves this problem. The use of exact kinetic energy operators means that the major issue for the variational nuclear motion computations is the accuracy of the PES. Early water PESs [28] gave results far from experimental accuracy or even the accuracy needed to assign the lines in a water spectrum. A breakthrough was achieved by Polyansky *et al.* [29], who calculated energy levels up to $K_a = 20$ with an accuracy of better than $0.1\,cm^{-1}$ for part of the spectrum. This was already, in principle, good enough to assign spectra of hot water or sunspots [30]. The overall standard deviation for the data fitted by Polyansky *et al.* [29] and in a subsequent improved PES [31] was about $0.5\,cm^{-1}$. Table 1 summarizes the development of spectroscopically determined, ground-state PESs for the water molecule.

The PES of Polyansky *et al.* [29] was obtained purely empirically, by fitting to available experimental data. Partridge & Schwenke [35] showed in a seminal paper that the use of a very accurate *ab initio* PES as a starting point for the fitting could significantly (by about a factor of 5) reduce the standard deviation of the fit. Another important property of *ab initio* PESs was first pointed out by Polyansky *et al.* [26]: even if the absolute deviation between theory and experiment for rotational levels within one vibrational state was significantly higher for *ab initio* PESs than for empirically tuned ones, these discrepancies displayed a much smoother behaviour with respect to the rotational quantum numbers. As a result, it was actually an *ab initio* PES that was used in our computations of energy levels with J and K_a up to 33 in various vibrational states that allowed the assignment of the spectrum of water in sunspots [40].

Apart from the assignment of previously unassignable sunspot spectra, Polyansky *et al.* [26] firmly established the advantage of using variational calculations to analyse and assign high-resolution spectra of polyatomic molecules. A series of papers dealt with assignment of hot and cold laboratory spectra of water vapour [40–51] using variational approaches. These allowed a significant increase in the number of vibrational states observed and in the number of assigned spectral lines with correct rotational and vibrational quantum numbers. For instance, the highest observed value of the bending quantum number, v_2, increased from 4 to 10, and the effect of quantum monodromy, which takes place on highly excited bending states of quasi-linear molecules [52], was observed [50]. We used the assigned observed water lines to create a database of water monomer energy levels [53], which, in turn, has been used to create a set of energy levels used for fitting the PESs; this resulted in a steady improvement in the quality of the PES [16]. Note that a new activity synthesizing experimental water energy levels is currently under way [2,3], based on the MARVEL algorithm of Furtenbacher *et al.* [54].

As high-quality PESs are indispensable for calculating and assigning water spectra just below and above dissociation, which are considered in the following sections, let us provide a few details about our PES computations.

Following Partridge & Schwenke [35], all the fitted PESs of triatomic molecules start with an accurate *ab initio* PES. The water PES of Partridge & Schwenke [35] was the first *ab initio* PES with an accuracy suitable for high-resolution spectral analysis and one that could serve as a starting point for the fit. For relatively highly excited vibrations, the errors were of the order of $20\,\mathrm{cm}^{-1}$, and it became clear that fitting required a significantly better *ab initio* starting point. Before our recent determination of the global *ab initio* surface, the most accurate *ab initio* PES of the water monomer was obtained by Polyansky *et al.* [6]. At that time, we used the electronic structure package MOLPRO [55] with the internally contracted multi-reference configuration interaction (IC-MRCI) method and an aug-cc-pV6Z Gaussian basis set with complete basis set extrapolation for determining a pure Born–Oppenheimer (BO) PES. Core–core and core–valence correlation [56], adiabatic [57], relativistic [7–9], QED [8] and non-adiabatic energy corrections [58] have also been determined. These corrections were added together to yield a composite PES in the fashion of the focal-point analysis technique [59]. The magnitude of these ‘small correction terms’ on the vibrational levels varies with energy and vibrational state, but is from about $1\,\mathrm{cm}^{-1}$ to about $10\,\mathrm{cm}^{-1}$. This makes it necessary to include these corrections in calculations if high accuracy is to be achieved. Building a high-accuracy composite PES meant that about 20 000 experimentally known levels belonging to five water isotopologues could be matched via a first-principles approach with a standard deviation of $1\,\mathrm{cm}^{-1}$ [6,60]. Again, this work was limited to levels below $26\,000\,\mathrm{cm}^{-1}$, as this limit was determined by the highest energy levels known experimentally at the time. In fact this limit was set more than 25 years ago by Camy-Peyret *et al.* [61] and has proved quite difficult to break.

We used the composite, adiabatic CVRQD *ab initio* PES [6,60] as a starting point during several attempts to improve the accuracy of spectroscopically determined PESs [16,37,39]. The first attempt by Shirin *et al.* [16] gave a standard deviation of $0.08\,\mathrm{cm}^{-1}$ between computed and measured rovibrational energies. The second attempt [37] resulted in a significant reduction of the standard deviation, down to $0.03\,\mathrm{cm}^{-1}$. This PES, designated as PES8 by Maksyutenko *et al.* [37], allowed the first assignment of lines above $26\,000\,\mathrm{cm}^{-1}$ to be made. The most recent attempt to fit the levels below the $26\,000\,\mathrm{cm}^{-1}$ limit resulted in a standard deviation of only $0.022\,\mathrm{cm}^{-1}$ [39].

With the DVR3D [62] program suite, which performs efficient variational nuclear motion computations with an exact kinetic energy operator and a very accurate PES, we are well equipped to attempt to break through this limit of $26\,000\,\mathrm{cm}^{-1}$. In particular, we consider states with $v=9$ up to dissociation, where, for the sake of brevity, we use the notation $v=n$ to represent the local mode doublet states given in normal mode notation by $(n,0,0)$ and $(n-1,0,1)$. This is described in §3.

3. Water spectrum up to dissociation

The studies of the water spectrum up to dissociation were largely driven by experimental developments [63]. The observation of water dissociation using multi-resonance laser spectroscopy and the resulting accurate determination of the first dissociation energy of water [64] opened the door to attempts to fill the gap between the known energy levels below $26\,000\,\mathrm{cm}^{-1}$ and dissociation at about $41\,100\,\mathrm{cm}^{-1}$. Maksyutenko *et al.* [37] made the first steps to fill this gap. The PES8, mentioned earlier, was used to assign the levels of $v=9$, the next overtone band after the $v=8$ band studied by conventional spectroscopy. Assignment of the $v=9$ overtone already presented a serious challenge, as three pairs of levels lie close to each other near $27\,500\,\mathrm{cm}^{-1}$; these states are coupled by accidental resonances, which always make the assignment considerably harder. However, computations using PES8 met this challenge, as they were accurate enough to predict the values of the $v=9$ energy levels to better than $1\,\mathrm{cm}^{-1}$.

The calculations for the $v=9$ band were performed when the experimentally observed values were already known. The real test of the predictive power of our first-principles model was shown when we fitted the newly assigned $v=9$ levels and predicted the $v=10$ levels before the measurements were made. The predictions for $v=10$ were again within $1\,\mathrm{cm}^{-1}$ and usually not much more than a linewidth away from the observations (figure 1). This demonstrated the ability of our fitted PES to extrapolate to the next unfitted v accurately. This procedure was continued up to $v=12$ and experimental levels belonging to 23 new vibrational states up to $v=12$ and $34\,000\,\mathrm{cm}^{-1}$ were assigned.

However, it became clear that for even higher energies, corresponding to vibrational quantum numbers $v>12$, the computations had to be based on a new PES. The grid points used to construct the CVRQD *ab initio* PES [6,60] were not designed for calculations of spectra up to dissociation. Execution of a new set of *ab initio* electronic structure computations was therefore deemed necessary.

In order to expand the *ab initio* PES of Polyansky *et al.* [6], a wider grid of points, covering areas just below and above dissociation, had to be produced. The BO energies at 2000 points, which cover all these energy regions, were calculated by Grechko *et al.* [65]. Test computations suggested that a significant improvement in the accuracy of the PES could be achieved using an all-electron treatment rather than the valence-only plus core–valence correction as performed

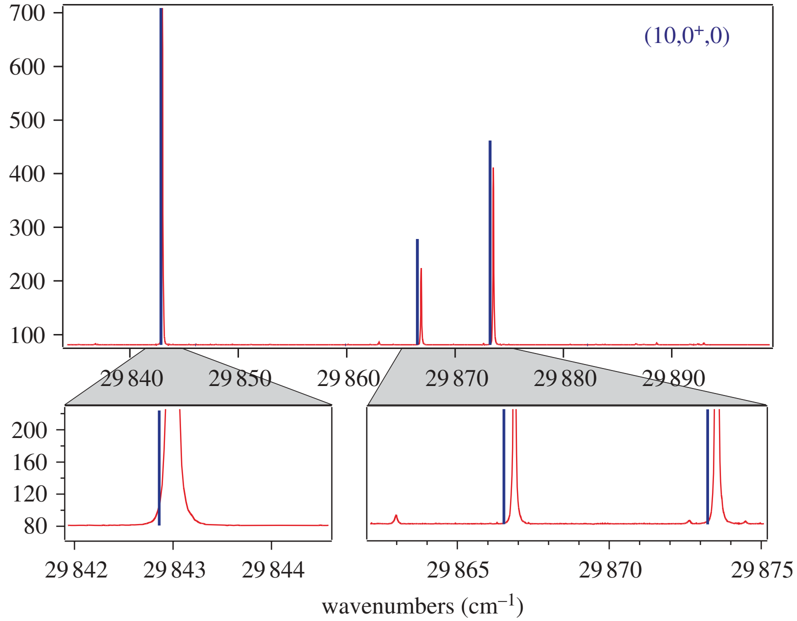

Figure 1. Observed spectrum [37] (solid curve) against prediction (vertical lines) for water overtone states with $v = 10$. The predictions were obtained using PES9, which was fitted to experimental levels up to $v = 9$. (Online version in colour.)

previously [6]. The all-electron aug-cc-pCV6Z Gaussian basis set was chosen for these computations. A second important step was the optimization of the reference space. Tests showed that a significant improvement in accuracy, particularly in the DMS considered below, could be achieved using a larger reference space. The PES of water was therefore recomputed using a complete active space of eight electrons in 10 orbitals.

The computed IC-MRCI(8,10)/aug-cc-pCV6Z energy points were fitted to the analytical PES with a standard deviation of better than $2\,\mathrm{cm}^{-1}$. The resulting PES accurately represents the BO surface up to and above dissociation. As table I of Grechko *et al.* [65] suggests, all the energy levels below $39\,000\,\mathrm{cm}^{-1}$ are calculated with an accuracy better than $10\,\mathrm{cm}^{-1}$. For an *ab initio* calculation in the uncharted territory near dissociation, this is a very encouraging result.

This *ab initio* calculation has been used as the basis for a new PES fit with the aim of accurately representing all states up to dissociation. A comparison of our preliminary vibrational band origin (VBO) results with experiment is given in table 2. This fit reproduces all observed VBOs with a standard deviation of only $0.086\,\mathrm{cm}^{-1}$. This is another encouraging result, but at this stage we should be cautious: so far we have considered states only with $J = 0$ and 2 in the fit.

Another method for assessing the accuracy of any new PES is by comparison with wave functions of states close to dissociation from a previous calculation [66] based upon a different global PES. The computations of Mussa & Tennyson [66] suggested that the states close to dissociation were largely unstructured and chaotic. However, the nuclear motion wave functions obtained by earlier studies [12,65] give a significantly higher proportion of states with regular

Table 2. The vibrational band origins computed up to dissociation with our new fitted PES compared with experiment.

v_1	v_2	v_3	obs.	calc.	obs. − calc.
0	1	0	1594.7463	1594.807	−0.061
0	2	0	3151.6300	3151.712	−0.082
1	0	0	3657.0532	3656.932	0.121
0	3	0	4666.7911	4666.843	−0.052
1	1	0	5234.9748	5234.770	0.204
0	4	0	6134.0148	6134.062	−0.047
1	2	0	6775.0931	6774.944	0.148
2	0	0	7201.5403	7201.608	−0.067
0	0	2	7445.0450	7445.006	0.038
0	5	0	7542.4366	7542.450	−0.014
1	3	0	8273.9773	8273.934	0.043
2	1	0	8761.5820	8761.588	−0.006
0	6	0	8869.9538	8869.907	0.046
0	1	2	9000.1402	9000.103	0.036
2	2	0	10 284.3664	10 284.415	−0.048
0	2	2	10 521.7623	10 521.706	0.055
3	0	0	10 599.6872	10 599.840	−0.153
1	0	2	10 868.8757	10 868.747	0.128
2	3	0	11 767.3890	11 767.472	−0.083
0	3	2	12 007.7757	12 007.753	0.022
3	1	0	12 139.3156	12 139.386	−0.071
1	1	2	12 407.6624	12 407.683	−0.021
4	0	0	13 828.2780	13 828.311	−0.033
1	2	2	13 910.8964	13 910.999	−0.103
2	0	2	14 221.1589	14 221.157	0.001
0	0	4	14 537.5043	14 537.487	0.016
3	3	0	15 108.2386	15 108.031	0.206
4	1	0	15 344.5041	15 344.554	−0.050
2	1	2	15 742.8030	15 742.785	0.017
4	2	0	16 823.3185	16 823.409	−0.091
2	2	2	17 227.3795	17 227.396	−0.017
3	0	2	17 458.2141	17 458.201	0.012
1	0	4	17 748.1067	17 748.099	0.006
5	1	0	18 392.7775	18 392.645	0.132
6	0	0	19 781.3230	19 780.913	0.409
6	1	0	21 221.5688	21 221.533	0.035
7	0	0	22 529.2959	22 529.184	0.111
5	3	2	27 502.6600	27 502.639	0.020
9	0	0	27 540.6900	27 540.742	−0.052
6	1	2	27 574.9100	27 574.896	0.013
9	1	0	28 934.1400	28 934.126	0.013
10	0	0	29 810.8500	29 810.986	−0.136
10	1	0	31 071.5700	31 071.620	−0.050
8	0	2	31 207.0900	31 207.120	−0.030
11	0	0	31 909.6800	31 909.561	0.119
11	1	0	33 144.7100	33 144.702	0.007

(Continued.)

Table 2. (*Continued.*)

v_1	v_2	v_3	obs.	calc.	obs. − calc.
12	0	0	33 835.2500	33 835.072	0.177
13	0	0	35 585.9600	35 586.028	−0.068
12	2	0	36 179.3200	36 179.305	0.014
13	1	0	36 684.0500	36 684.048	0.001
14	0	0	37 122.7000	37 122.863	−0.163
12	3	0	37 311.2800	37 311.196	0.083
13	2	0	37 765.6500	37 765.686	−0.036
14	1	0	38 153.2500	38 153.217	0.032
15	0	0	38 462.5200	38 462.442	0.077
14	2	0	39 123.7700	39 123.750	0.019
15	1	0	39 390.2600	39 390.244	0.016
16	0	0	39 574.5500	39 574.502	0.048
16	1	0	40 370.5500	40 370.538	0.011
17	0	0	40 437.2300	40 437.244	−0.014
0	0	1	3755.9287	3755.916	0.012
0	1	1	5331.2668	5331.279	−0.013
0	2	1	6871.5204	6871.499	0.021
1	0	1	7249.8185	7249.811	0.007
0	3	1	8373.8519	8373.781	0.070
1	1	1	8806.9998	8807.010	−0.010
0	4	1	9833.5844	9833.479	0.104
1	2	1	10 328.7270	10 328.729	−0.002
2	0	1	10 613.3644	10 613.429	−0.064
0	0	3	11 032.4046	11 032.455	−0.051
1	3	1	11 813.2048	11 813.255	−0.050
2	1	1	12 151.2533	12 151.352	−0.099
0	1	3	12 565.0070	12 565.012	−0.005
2	2	1	13 652.6584	13 652.740	−0.081
3	0	1	13 830.9368	13 830.988	−0.052
0	7	1	13 835.3735	13 835.421	−0.048
0	2	3	14 066.1956	14 066.179	0.016
1	0	3	14 318.8130	14 318.794	0.018
1	5	1	14 647.9766	14 647.976	0.000
2	3	1	15 119.0309	15 119.116	−0.085
3	1	1	15 347.9578	15 347.955	0.002
0	3	3	15 534.7069	15 534.814	−0.107
1	1	3	15 832.7805	15 832.830	−0.049
2	4	1	16 546.3186	16 546.384	−0.066
3	2	1	16 821.6344	16 821.601	0.033
4	0	1	16 898.8419	16 898.772	0.069
1	2	3	17 312.5513	17 312.552	−0.001
2	0	3	17 495.5280	17 495.596	−0.068
3	3	1	18 265.8212	18 265.865	−0.044
4	1	1	18 393.3146	18 393.225	0.089
1	3	3	18 758.6334	18 758.564	0.069
2	1	3	18 989.9599	18 989.895	0.064
3	4	1	19 679.1925	19 679.081	0.111

(*Continued.*)

Table 2. (*Continued.*)

v_1	v_2	v_3	obs.	calc.	obs. − calc.
5	0	1	19 781.1029	19 781.250	−0.147
4	2	1	19 865.2847	19 865.165	0.118
2	2	3	20 442.7774	20 442.721	0.055
3	0	3	20 543.1286	20 543.137	−0.009
5	1	1	21 221.8273	21 221.926	−0.098
4	3	1	21 314.4482	21 314.588	−0.139
6	0	1	22 529.4399	22 529.505	−0.065
7	0	1	25 120.2771	25 120.364	−0.087
9	0	1	29 810.8740	29 811.005	−0.131
11	0	1	33 835.2200	33 835.072	0.147
9	0	3	35 509.6800	35 509.644	0.035
12	0	1	35 586.0100	35 586.181	−0.171
13	0	1	37 122.7200	37 122.847	−0.127
11	3	1	37 309.8500	37 309.845	0.004
13	1	1	38 153.3100	38 153.296	0.013
14	0	1	38 462.5400	38 462.443	0.096
14	1	1	39 390.2200	39 390.256	−0.036
15	0	1	39 574.5400	39 574.557	−0.017
14	2	1	40 226.3100	40 226.317	−0.007
15	1	1	40 370.8300	40 370.838	−0.008
16	0	1	40 437.2600	40 437.260	0.000

structures. These structures continue analogous structures shown by states at lower energies. Figures 2 and 3 show sample wave functions that can be identified as bending and stretching overtone states at low, intermediate and near-dissociation energies. Although many vibrational states in the near-dissociation region appear irregular and quantum numbers cannot easily be assigned to them [12], the figures illustrate that series of overtone states are discernible at all energies. This is true even above the dissociation threshold [67].

With such an excellent PES at our disposal, we performed nuclear motion calculations using the DVR3D code. Although the absolute accuracy up to 39 000 cm^{-1} is about 10 cm^{-1}, from the point of view of line assignment the predictive accuracy is about 1 cm^{-1}. The reason for this, as exploited during the analysis of sunspot spectra [26,40], is the smooth behaviour of excited rotational levels within a given vibrational state. In assigning lines up to $J = 5$, as long as the vibrational state could be determined, it was possible to predict the position of yet unassigned lines with an accuracy of about 1 cm^{-1} using the smooth variation of the computed results.

It is clear from the present computations that, as far as the accuracy is concerned, there are two distinct regions. Whereas the results up to 39 000 cm^{-1} are very satisfactory, much larger discrepancies between experiment and theory are observed in the region from 39 000 cm^{-1} to dissociation at 41 100 cm^{-1} and also for a few hundred wavenumbers above dissociation, where quasi-discrete spectra have been observed [68]. These discrepancies, which are up to 60 cm^{-1}, represent the last remaining challenge for the computation of the ground

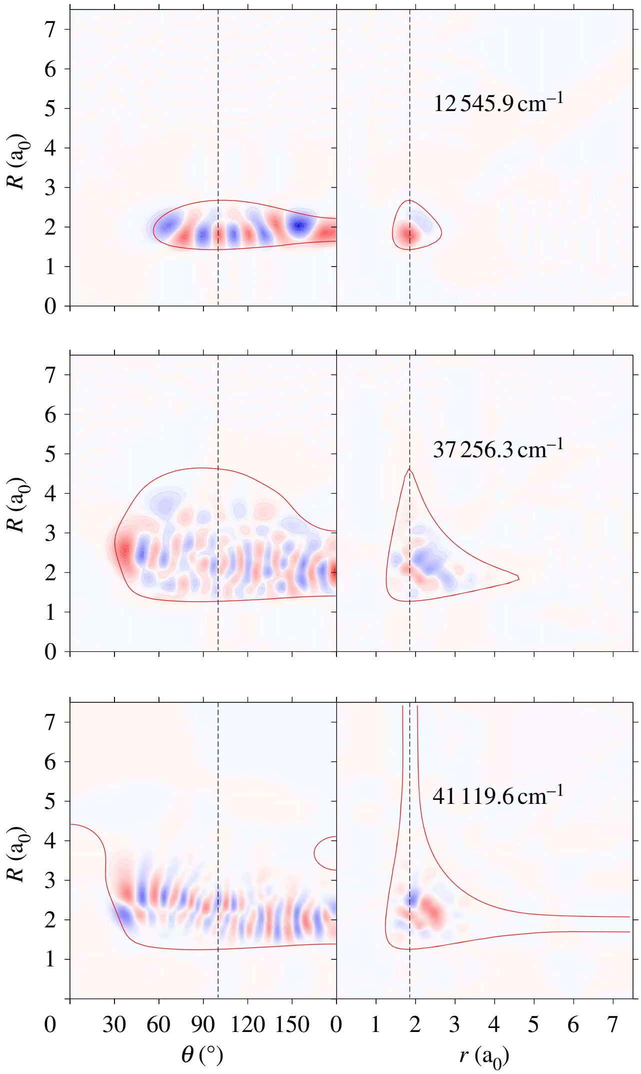

Figure 2. Representative wave functions for bending overtone states. The left-hand plot is for a cut of the OH stretch against the bending angle with the other OH stretch frozen; the right-hand plot is for one OH stretch against the other OH stretch with a frozen angle. The vertical line in each plot gives the value of the frozen coordinate used to make the cut in the partner plot; in general, this line goes through the maximum of the wave function. The outer contour in each plot is the classical turning point for the relevant state whose energy is indicated within the plot.

electronic state PES of water. As corrections for high-order correlation effects and relativistic correction have become incorporated into the PES [12] and the QED correction is likely to be at least an order of magnitude smaller than these, removing the remaining discrepancy between experiment and theory must rely on better treatments of the adiabatic and non-adiabatic corrections to the BO approximation and inclusion of spin–orbit coupling effects [65].

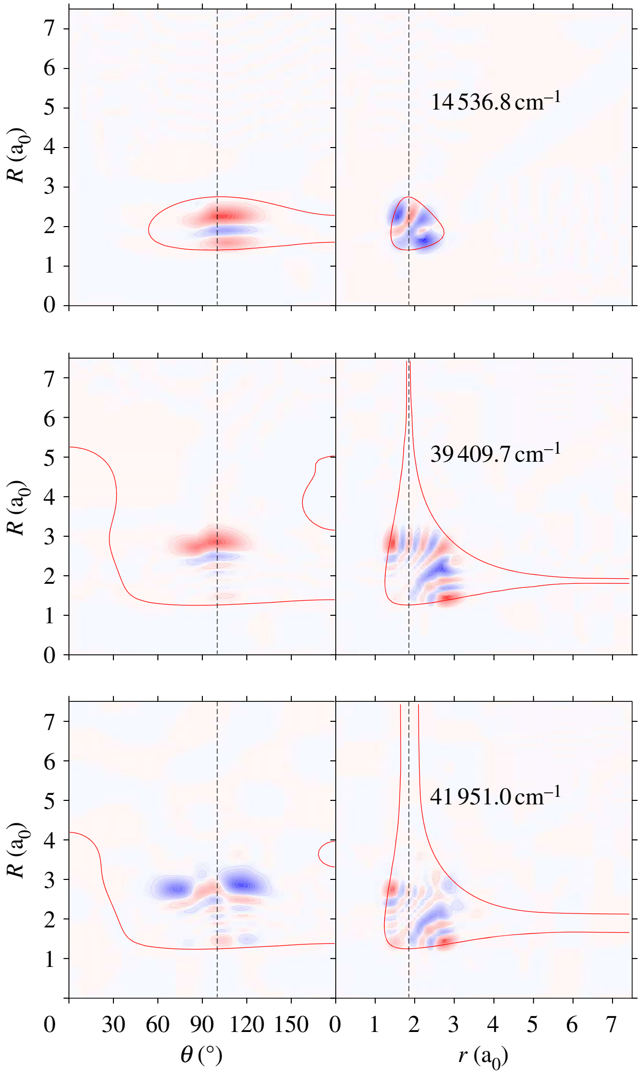

Figure 3. Representative wave functions for asymmetric overtone states. The left-hand plot is for a cut of the OH stretch against the bending angle with the other OH stretch frozen; the right-hand plot is for one OH stretch against the other OH stretch with a frozen angle. See figure 2 for details.

As pointed out by Császár *et al.* [12], the existing high-accuracy DMSs [15,69] are also inadequate for the calculation of intensities of bands at dissociation. This point is addressed in §6, where a new, much more accurate DMS suitable for the intensity calculations at dissociation is discussed.

4. Resonances above dissociation

Vibration–rotation states below and above dissociation could, in principle, be so different that the states above dissociation cannot be subject to high-resolution spectroscopy. It all depends on the lifetime of the possible quasi-bound or resonant states present in the nuclear motion continuum. As experiments showed [68], the spectrum of water above dissociation consists of a set of narrow resonances that appear similar to the lines of the discrete spectrum below dissociation, as well as some much broader features, superimposed on an absorption continuum. Examples of such spectra are given by earlier studies [63,67,68].

Analysis of these above-dissociation lines presents a triple challenge in comparison with the analysis of lines even just below dissociation. First, the accuracy of the BO PES we use for the calculations is worse than that for the surface below 39 000 cm^{-1} by a factor of 5. Second, the basis set required to converge the nuclear motion calculations should consist of many more functions than is needed for calculations below dissociation. Third, the Hamiltonian becomes complex, as we use a complex absorbing potential (CAP) [70] and a modified version of DVR3D [71] for the calculations. A CAP is the minimum possible modification required by the above-dissociation nature of the problem, as more accurate methods involving scattering calculations are much more computationally challenging.

Meeting these challenges allowed Zobov *et al.* [67] to produce a theoretical model of the experimental spectrum (see fig. 1 of [67]); this allowed lines in the observed spectrum belonging to three types of resonances to be identified. Some of the lines just above dissociation belong to the class of shape resonances, whose vibrational ($J = 0$) states lie below dissociation and resonances occur due to the rotational barrier. Observation of higher J values of these states would lead to their expansion further beyond the dissociation energy limit. The second type of resonance is Feshbach resonances. Their energy is partially trapped in a non-dissociative bending state, resulting in their relatively narrow linewidths. The third and most striking feature is the direct photodissociation to the continuum. This strong feature appears at the energy where our calculations predict the dissociative $v = 20$ state would lie. This feature has a large width of about 40 cm^{-1}, which is very much broader than all the other resonance features.

Further improvements in the agreement between theory and experiment for the quasi-bound states also require improvement of the PES. This can be achieved via a joint *ab initio* and spectroscopic fitting procedure, which is described in §5.

5. Global fit of the water potential energy surface

Our principal aim is to derive a global PES for use in the variational calculations of rovibrational energy levels with close to experimental accuracy—about 0.1 cm^{-1}. As discussed earlier, the most accurate *ab initio* calculations still produce errors of about 60 cm^{-1} for levels close to dissociation. To achieve an accuracy of 0.1 cm^{-1} purely *ab initio* seems at present to be impossible. Thus, to obtain a PES that would extrapolate to the levels beyond dissociation and to higher J values with an accuracy better than 1 cm^{-1} and would reproduce known levels with an accuracy close to experimental, the only viable solution is to fit the PES using the experimental levels.

The most accurate empirical PES of $H_2{}^{16}O$ up to 26 000 cm^{-1}, which reproduces the known experimental levels with a standard deviation of 0.022 cm^{-1}, was obtained from an *ab initio* PES by fitting to the available experimental term values up to $J = 5$. In this refinement, the fitted PES was constrained [72] to follow closely the shape of the initial *ab initio* PES. This was achieved by simultaneously fitting the refined PES constants to the *ab initio* points and to the experimental energy levels. This procedure guarantees that the PES retains a physically correct overall shape, which is of special importance for describing the high-energy regions of the PES. Moreover, it allows all potential parameters to be varied irrespective of the usual incompleteness of experimental data. Here, we apply the same procedure to construct a global, empirical PES of H_2O up to $39\,000\,\mathrm{cm}^{-1}$ and hope to extend it to higher energies in the near future.

Our strategy is to include in the fit only rovibration energy levels below $39\,000\,\mathrm{cm}^{-1}$ and see how well the resulting PES extrapolates for higher energy levels. So far, only experimental data for $J = 0$ and 2 are included in the fit. We have obtained a PES that gives a standard deviation of about $0.1\,\mathrm{cm}^{-1}$ for the data included in the fit and extrapolates well to higher energies for the $J = 0$ states. However, as shown by Schryber *et al.* [73], the inclusion in the fit of only $J = 0$ levels can result in a PES that reproduces the VBOs excellently but has discrepancies of up to $100\,\mathrm{cm}^{-1}$ for rotationally excited states. The inclusion in our fit of levels with $J = 2$ helps us to avoid such a catastrophe, but our experience shows that inclusion in the fit of the levels with J at least equal to 5 is necessary to ensure a PES that extrapolates well to higher rotational states. This work is currently in progress.

6. Accurate global dipole moment surface and Stark coefficient calculations

Every model of absorption by water vapour, whether it is in the Earth's atmosphere, in the atmosphere of planets or cool stars or in a cold or hot laboratory environment, is based on calculation of the one-photon absorption spectrum. For this transition, intensities as well as line frequencies are required.

Intensities can be computed within the framework of variational calculations; however, this requires not only an accurate knowledge of the PES, but also that of the DMS. *Ab initio* computation of the DMS has characteristics that differ from those needed for the determination of a PES. The DMS, like the PES, is generally obtained by fitting *ab initio* points to a certain analytical form. For the PES, the standard deviation with which the analytical surface reproduces the calculated points serves as a good measure of the accuracy of a fit. For the DMS, this is not always true.

A clear illustration is the PS and SP DMSs of water due to Schwenke & Partridge [15,35], where the introduction of a dense grid of artificially generated points was necessary to remove oscillation in the analytic, fitted surface between the *ab initio* points used for the fit [15]. Such oscillations lead to spuriously intense high-overtone transitions. Another problem with the DMS is that, if one aims for correct behaviour at high excitations, special care must be taken to ensure the correct asymptotic behaviour. A third difference is that attempts to fit the DMS to experimental data in order to improve the accuracy of intensity calculations have generally resulted in the improvements in the intensity of the lines used in the fit and in a significant deterioration in the predicted intensities for other lines. The accepted strategy here is always to use *ab initio* DMS and not to attempt to improve it by fitting to experimental data [74].

In order to be able to calculate the Stark coefficients of the levels close to dissociation, a very accurate global PES and a similarly accurate DMS are needed. There are very high-quality DMSs published in the literature [15,69]; however, at least two issues remain unsolved with these DMSs. They were not aimed for global spectroscopy and their predicted line intensities were accurate to only about 2–3 per cent. Recently, Lisak *et al.* [75] made very accurate measurements of intensities of some water lines, achieving an accuracy of 1 per cent.

Lodi *et al.* [76] recently produced an *ab initio* DMS that satisfies very stringent requirements of accuracy and globality. The *ab initio* calculations were performed with the MOLPRO package and the aug-cc-pCV6Z basis set in the all-electron IC-MRCI model. Dipole moments were calculated using finite field perturbation at almost 3000 geometries. The resulting DMS reproduces the intensities of high-precision measurements [75] to better than 1 per cent, and to better than 10 per cent for 20 000 strong and medium-strength lines from HITRAN [77]. These results are a significant improvement on the published DMSs of Schwenke & Partridge [15] and Lodi *et al.* [69]. This new DMS paves the way for accurate calculation of the global line list of water isotopologues.

A stringent test for a global DMS is to calculate Stark coefficients for the near-dissociation energy levels and to compare these coefficients with experimentally measured values. We note that accurate measurements of line intensities near dissociation remains an unsolved problem. Furthermore, Stark coefficients can be measured with an accuracy of 0.1 per cent or better [78], whereas the accuracy of intensity measurements is often not much better than 10 per cent for water. Thus, validation of the DMS against Stark coefficients could result in intensity predictions better than average experimental accuracy.

Callegari *et al.* [79] measured and calculated Stark coefficients for water for states up to $v = 8$. We compute Stark coefficients for $J = 1$ of the energy levels of Callegari *et al.* [79] belonging to the (301), (401) and (800) vibrational states (table 3). The wave functions of these levels were calculated using the DVR3D nuclear motion code with the fitted PES12 PES [37]. These wave functions were used as input data for a program computing line strengths using both the published CVR DMS [69] and our new DMS given by Lodi *et al.* [76]. The line strengths, together with line positions, are used to obtain the calculated values of the Stark coefficients. In table 3, Stark coefficients are listed that were computed in Callegari *et al.* [79] using the SP DMS with an average absolute accuracy of 2.8 per cent. They are compared with our latest calculations, which use the new LTP2011 DMS, whereby an average absolute accuracy of 0.84 per cent is achieved. Thus, the ultimate goal of computing a DMS accurate to better than 1 per cent seems to have been achieved. The experimental accuracy of the measured Stark coefficients is estimated by Callegari *et al.* [79] to be 0.5 per cent. Thus, experimental accuracy is almost achieved. Moreover, the systematic character of discrepancies up to 16 000 cm^{-1} opens the way for the possible further improvement of the DMS.

Verification of a DMS for higher-lying levels requires experimental measurements, which are challenging, but it turns out to be possible using the recently developed triple resonance vibrational overtone excitation scheme of Grechko *et al.* [65]. The measurement of Stark coefficients up to $v = 17$ is

Table 3. Observed and calculated Stark coefficients for water in units of Hz $(\mathrm{V\,cm^{-1}})^{-2}$. The percentage difference is defined as (obs. − calc.)/obs. This work uses the dipole moment surface of Lodi *et al.* [76].

						Callegari *et al.* [79]		this work	
vibrational	J	K_a	K_c	E_{obs}	C_{obs}	C_{calc}	% difference	C_{calc}	% difference
$(4,0)^-$	1	0	1	13 853.27	0.4372	0.4413	−0.95	0.4320	1.19
$(4,0)^-$	1	1	1	13 864.28	0.3160	0.2871	9.15	0.3122	1.18
$(4,0)^-$	1	1	0	13 869.39	0.5097	0.5060	−0.72	0.5050	0.90
$(5,0)^-$	1	0	1	16 920.93	0.4277	0.4343	−1.54	0.4248	0.67
$(5,0)^-$	1	1	1	16 932.30	0.3032	0.2849	6.04	0.2995	1.22
$(5,0)^-$	1	1	0	16 937.39	0.5077	0.4996	1.60	0.5057	0.39
$(8,0)^+$	1	0	1	25 140.60	0.4953	0.5058	−2.12	0.5002	−0.98
$(8,0)^+$	1	1	1	25 150.12	0.4250	0.4154	2.26	0.4249	0.26
$(8,0)^+$	1	1	0	25 154.61	0.6657	0.6667	−0.15	0.6706	−0.73
absolute average					2.76		0.84		

currently under way at Laboratoire de Chimie Physique Moleculaire in Lausanne. Preliminary comparison of these experimental values with the calculated Stark coefficients shows excellent agreement [80].

7. Conclusions

Experimental and theoretical work on H_2O monomer spectra has been the subject of numerous reviews [11]. Extending earlier work, we present a consistent picture on studies of the water monomer spectrum across the whole energy range from the bottom of the potential well to its first dissociation asymptote. The main focus of this paper is the recent theoretical developments in the near-dissociation spectroscopy of the water molecule.

Determination of an accurate global *ab initio* PES for $H_2{}^{16}O$ allowed us to assign hundreds of lines belonging to more than 40 vibrational states up to and above dissociation. An accuracy of 10–50 $\mathrm{cm^{-1}}$ in the first-principles rovibrational energy level computations was sufficient for assigning part of the experimental spectra, although this accuracy is very far from the experimental accuracy. Improving this accuracy, particularly in the near-dissociation region, will require treatment of both spin–orbit and non-adiabatic effects. At least for the second of these issues, there are simple model treatments available [81]. However, as these have yet to be tested for triatomics, it makes more sense to try them initially for H_3^+ for which ultra-high-accuracy *ab initio* results are available [82].

Notwithstanding these concerns, the present state-of-the-art *ab initio* results produced a base for further improvement in the accuracy of global calculations for the water monomer spectra. In particular, the fitting procedure developed allowed us to fit the band origins of the water monomer up to 40 000 $\mathrm{cm^{-1}}$ to an accuracy of 0.086 $\mathrm{cm^{-1}}$, close to the experimental one, as a first stage of the fitting of the global water PES with excited rotational energy levels J up to 2. The global LTP2011 DMS calculated by Lodi *et al.* [76] allows both extremely accurate calculations of intensities of conventional spectral lines up to 26 000 cm^{-1} and calculations of Stark coefficients of the levels up to dissociation. The preliminary results of such calculations show excellent agreement with experiment. These two developments represent the key ingredients necessary to give a highly accurate global line list of water rotation–vibration transitions. Such a line list would capture all theoretical knowledge on the spectroscopy of the water monomer in its ground electronic state with an accuracy close to that achievable experimentally.

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