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A further step towards a calculated room temperature line list for $H_2{}^{16}O$ with experimental accuracy[☆]

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ABSTRACT

A water (H_2O) Potential Energy Surface (PES), which reproduces more than 90 % of the experimentally derived rotation-vibration energy levels of $H_2{}^{16}O$ with rotation excitation, J, up to 15 with a standard deviation of only 0.01 cm^{-1} is provided. Only levels with $J \leq 27$ are included in the HITRAN room temperature line list: levels with J between 16 sand 27 are predicted with a standard deviation of about 0.013 cm^{-1}. Line intensity calculations using wavefunctions generated with this PES and a less accurate PES are compared using the same dipole moment surface (DMS) showing differences of up to 1.5%. The importance of using accurate wavefunctions both in terms of convergence of their representation and the reliability of the underlying PES used is discussed.

1. Introduction

The challenge of reaching experimental accuracy in water rovibrational line centers calculation has a long history. When variational nuclear-motion calculations were in their infancy, an accuracy of several cm^{-1} was considered respectable [1], the focus of theoretical calculations was on effective Hamiltonians. Mikhail Tretyakov and his colleagues performed observations of pure rotational water lines in the ground and first excited bending states [2,3], followed by theoretical efforts to improve the convergence of divergent perturbation series of water molecule effective Hamiltonians so that they matched the accuracy of these observations [2–4]. There were two major reasons to study the pure rotational water spectra: developing theoretical methods to match the microwave accuracy of the measured line centers, and trying to observe the qualitative effect of the four-fold clustering of the $K_a = J$ and $K_a = J - 1$ levels of water. However, the failure observe clustering in water was substantiated by the variational calculations performed by Kozin et al. [5]. Nevertheless, four-fold clustering of high K_a levels was measured by Tretyakov and his colleagues for other H_2X type molecules, such as $H_2{}^{32}S$ and $H_2{}^{48}Se$ [6–8]. The observation by Tretyakov and his colleagues of four-fold clustering in these molecules was in line theoretical studies with the Pade/Borel approximation which were used to calculate the line centers. Subsequently, very high K_a levels of water have been observed and analyzed in sunspot spectra [9–13]. These spectra proved to be a turning point the methodology used to calculate water spectra method with from variational calculations demonstrating their increased utility compared to effective Hamiltonians. The first assignment of hot rotational water lines were made using a one-dimensional Padé/Borel approximation to the effective Hamiltonian [14]. However, just as happened in the work of Tretyakov and co-workers [2], the assignment could be done only for the ground and the first excited vibrational states. In this context we note the approach of Coudert [15–17] who has developed effective Hamiltonians which explicitly couple the rotational motion with the bending mode; this approach has proven to be very effective but has so far been limited to low-lying vibrational states.

However, at high temperature such sunspots at about 3200 K, rotational lines belonging to multiple vibrational states can be observed in the spectrum. Water lines in sunspot spectra could only be assigned using variational calculations [10,11], since this theoretical tool allows one to calculate all the vibrational states up to dissociation. The analysis water vapor spectra on the Sun [9] was one of many indicators that the era of variational calculations had arrived and would gradually replace the effective Hamiltonian approach. The main reasons for this substitution was the ability of variational calculations to work from the

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first principles, including the use of *ab initio* potential energy surfaces (PESs) and dipole moment surfaces (DMSs), and the ability to calculate all rovibrational levels of a molecule up to its dissociation energy and even above [18,19]. The main drawback of variational calculations compared with the effective Hamiltonians approach remains the limited accuracy of the underlying *ab initio* PES. This problem can clearly be addressed by fitting the PES to the experimentally derived energy levels. So started a long history of the fitting the PES of water with the aim of achieving experimental accuracy.

Water has long been a benchmark system for testing PESs [20]. The fitted PES presented in Refs. [21,22] represented experimentally derived energies with a standard deviation, σ of 0.4 cm^{-1}; breaching the 1 cm^{-1} barrier for the first time. The next breakthrough in the challenge of increasing the accuracy of the water PES was achieved by Partridge and Schwenke (PS) [23] who were able to reach an accuracy of about $\sigma = 0.1\,\text{cm}^{-1}$ for energies up to $15\,000\,\text{cm}^{-1}$. The main improvement of the PS fitting procedure compared to previous attempts was the use a high quality *ab initio* PES as a starting point. Since then, this approach has become the standard method for fitting a molecular PES. This change of approach puts a greater emphasis on developing accurate *ab initio* PESs to provide a good starting point for the fit. The first a really accurate *ab initio* water PES, with $\sigma < 1$ cm^{-1} for all available energy levels and all water isotopologues, was presented in Ref. [9]. This study employed a high level of quantum chemistry modeling and also included relativistic [24], QED [25], adiabatic correction surfaces to allow for corrections to the Born–Oppenheimer approximation, and also a nonadiabatic correction to the exact kinetic energy operator [26] were used in the calculations. An *ab initio* PES was used as the starting point for several fits to water PESs, allowing the standard deviation to gradually decrease towards 0.027 cm^{-1} [27–29]. The calculation of an even better *ab initio* surface [30] facilitated the construction of the PES15k semi-empirical potential which represents the experimental energies below 15 000 cm^{-1} with $\sigma = 0.013$ cm^{-1} [31]. This PES has remained the best available water potential for low-lying energy levels for some time; here we present a new PES which gives a significant improvement both in the standard deviation, achieving an accuracy of $\sigma = 0.010$ cm^{-1}, and coverage of water energy levels.

Given that many energy levels for $H_2{}^{16}O$ are now known empirically to high accuracy [32], another driver for developing an accurate PES for water PES is its role in accurately predicting line intensities. The intensities play a crucial role in the application of spectroscopic studies in a range of remote sensing activities such as monitoring the Earth atmosphere, study of the atmospheres of the solar system planets and the atmospheres of the exoplanets. Recently, high resolution spectroscopic studies of the exoplanets using the Earth based telescopes focused our attention on the further improvement of the knowledge of the intensities of water lines, as they influence the observation of the exoplanetary atmospheres using the radiation of exoplanetary light gone through the Earth atmosphere. Similarly, studies of water in the Earth's atmosphere is important in its own right but good models of water spectra are vital even for weak lines as they often obscure the spectral signatures of important trace species, see Lampel et al. [33] for example. The knowledge of accurate water lines intensities is also of the highest importance for the metrology of humidity [34,35].

Two factors identified in recent studies of line intensities highlight the need for an accurate knowledge of the water PES. First, the possibility of measuring and calculating molecular rovibrational line intensities to an accuracy better than 0.1% [36] or even 0.01% [37] has been demonstrated for other molecules. Second, sensitivity of intensity calculations to the small change in the PES in certain instances has been demonstrated; in particular, changes in the PES which only shifted energy levels by a few units of 10^{-3} cm^{-1} resulted in the change of calculated line intensities of N_2O by 1% or more [38]. Hence, to obtain calculated intensities to better than 0.1%, improvements in the standard deviation with which the PES reproduces the energy levels is important at the 10^{-3} cm^{-1} level.

The paper is organized as follows. In Section 2 the details of the $H_2{}^{16}O$ PES fit to energy levels are given. In Section 3 we consider the predictions of our new PES. Section 4 illustrates the influence of this PES on line intensity calculations. The last section gives our conclusions and considers the implications of the results achieved.

2. Fit of the PES

The need to construct a new potential energy surface was driven by the rather inaccurate extrapolation of our previous surface PES15K [31] to high values of rotational excitation, J. The new surface, which we call PESM, solves this problem by providing high accuracy in calculations of energy levels to high values of the rotational quantum number and at the same time does not degrade the accuracy for low values J. A comparison of the accuracy of the two surfaces for different values J is given in Table 1.

Nuclear motion calculations were performed using DVR3D [39] in Radau coordinates; they used Morse-like oscillators with the values of parameters $r_e = 2.95$, $D_e = 0.3$ and $\omega_e = 0.0085$ in atomic units for both radial coordinates, and associated Legendre functions for the angular coordinate as basis functions. Corresponding DVR grids contained 29, 29 and 40 points for these coordinates, respectively. The final diagonalized vibrational matrices had a dimension of 5500. For the rotational problem, the dimensions of final matrices was set to $400(J+1-p)$, where J is the total angular momentum quantum number and p is the rotationless parity ($p = 0$ for e and 1 for f). The nuclear masses, 15.990526 Da for the oxygen and 1.007276 Da for hydrogen, were used. To ensure good accuracy for high-J levels, we followed the approach of Bubukina et al. [29] and used their model for rotational non-adiabatic effects unchanged.

The PES optimization procedure was based on the method proposed by Yurchenko et al. [40]. We allowed the 246 linear potential parameters of the PES to vary. As a result, we obtained a PES which reproduces a set of 1500 empirical energy levels given by the W2024 MARVEL (measured active rotation vibration energy levels) study [32] with $J = 2, 5, 10$ and 15 for energies up to $15\,000\,\text{cm}^{-1}$. Our fitted PES reproduced these levels with a standard deviation of $0.009\,\text{cm}^{-1}$. About 9% of the energy levels out the total set of available experimental levels in the energy region of interest were excluded from the fit. These levels mostly belong to high v_2 states; treatment of levels within these states requires a separate study, not least because of the effects of monodromy on states with $v_2 \geq 6$ [41,42].

Table 1 presents a rotational-state, J, dependent comparison of the standard deviations due to PESM, obtained in this work, with the best available PESs in the literature, namely PES15K [31], PESC [43] and POKAZATEL [44] for $J \leq 15$. It can be seen that our PESM potential's standard deviations are significantly lower for than PES15K for $J \geq 8$ and much lower than PESC and POKAZATEL for all Js.

Fig. 1 shows a comparison between water energy levels calculated with PESM, PES15K [31] PESC [43] and POKAZATEL [44] as a function of rotational state, J, with W2024 MARVEL empirical levels [32] up to 15000 cm^{-1}; N gives the number of levels considered and σ gives the standard deviation with which they are reproduced, in cm^{-1}.

3. Extrapolations and predictions of higher J levels

To clearly demonstrate the extrapolation properties of PESM, we compared our PESM energy level predictions for $J = 20$ with those of the PESC PES of Conway et. el [43], which were fitted up to $J = 20$ and provide the best current predictions for high J values, while PESM was only fitted up to $J = 15$. The comparison was made with MARVEL energy levels, which have been extensively used in recent HITRAN updates [45,46]. For PESM, the standard deviation (sd) between theory and experiment is 0.014 cm^{-1}, and for Conway et. el PES's - PESC sd = 0.058 cm^{-1}. For comparison, PES15K was fitted to experimental levels with $J = 0, 2, 5$ and gives standard a deviation for $J = 20$ of $0.078\,\text{cm}^{-1}$.

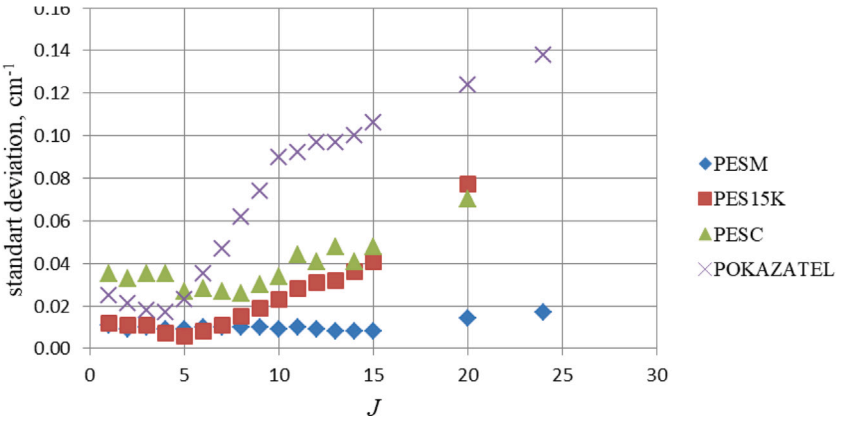

Fig. 1. Comparison of standard deviations of observed minus calculated energy levels for $H_2{}^{16}O$ given using different potential energy surfaces.

Table 1
Comparison of water energy levels calculated with PESM and PES15K [31], PESC [43] and POKAZATEL [44] as a function of rotational state, J, with W2024 MARVEL empirical levels [32] up to 15000 cm^{-1}; N gives the number of levels considered and σ gives the standard deviation with which they are reproduced, in cm^{-1}.

	PESM		PES15K [31]	PESC [43]	POKAZATEL [44]
J	N	σ	σ	σ	σ
1	148	0.011	0.012	0.035	0.025
2	249	0.009	0.011	0.033	0.021
3	356	0.010	0.011	0.035	0.018
4	457	0.009	0.007	0.035	0.017
5	539	0.009	0.006	0.027	0.023
6	624	0.010	0.008	0.028	0.035
7	665	0.010	0.011	0.027	0.047
8	699	0.010	0.015	0.026	0.062
9	705	0.010	0.019	0.030	0.074
10	688	0.009	0.023	0.034	0.090
11	668	0.010	0.028	0.044	0.092
12	632	0.009	0.031	0.041	0.097
13	591	0.008	0.032	0.048	0.097
14	538	0.008	0.036	0.041	0.100
15	504	0.008	0.041	0.048	0.106

Fig. 1 shows that the PESM potential energy surface of this work not only presents the most accurate standard deviations for the levels up to the fitted values of J =15, but demonstrates excellent agreement with the experimental values up to the highest J levels, present in the room temperature line lists. Thus, PESM solves the problem of the high J calculations significantly better than either of the recent, accurate [31,43] as well as the most widely used [44] surfaces.

A detailed comparison of HITRAN2020 [45] and our new PESM line lists in the range 0–27 000 cm^{-1} is given in the supplementary materials.

4. Comparison of intensities of PESM and PES15K

To check the intensity changes when one uses a more accurate PES, PESM instead of PES15K, we calculated intensities with both these PESs for transitions between levels with J = 4 and 5, J = 10 and 11. All calculation used the accurate CKAPTEN DMS [47]. This allows intensity differences due to the PES/wavefunctions used to be directly identified.

Table 2 presents the average difference in intensities calculated using different surfaces. It is noteworthy that even within the same vibrational band, there can be a significant variation in the intensities calculated with different surfaces. This is illustrated by the example of transitions between levels with J = 4 and 5; our results for calculations with J = 10 and 11 are broadly similar. The differences in line intensities produced with two very accurate PESs and the same DMS indicate, that the intensity predictions can change by up to one percent, and that very many lines display difference in the range 0.1% to 0.5%.

Recent advances in the reliable determination of CO lines intensities with better, than 0.1% level of accuracy gives hope that the lines of the important water molecule will be determined with that accuracy soon. At this stage we do not guarantee, that the PESM potential gives more accurate values for the line intensities than the previously published PESs; the final validation of the accuracy of these theoretically calculated line intensity should be provided by correspondingly accurate measurements. However, the differences shown in the Table 2 allow us to state, that if our aim is a calculation of better than 0.1%, improvements of the PES are of utmost importance.

As a consequence of this result a new goal arises — to determine the accuracy of the PES required for intensity calculations which do not differ from the calculated intensities obtained using an experimentally accurate PES by more than a given value such as 0.1% or 1%. Here we define an experimentally accurate PES as one which reproduces the energy levels within an experimental uncertainty. At present this problem cannot be solved for polyatomic molecules, there are no molecules for which experimentally accurate PESs have been obtained. However, this situation can be modeled by comparing intensity calculations performed using basis sets with the different levels of convergence for the energies. The convergence of energy levels as function of the change of basis set, and indeed several variational nuclear motion programs, were thoroughly investigated recently for the CO_2 molecule [48]. In the next section we use comparisons with this molecule in an attempt to answer the question of how different can the PES be to provide a given convergence for intensity calculation. We note in this context that different rules will apply in the case states undergoing accidental resonance interactions [49,50].

5. New goal for the required accuracy of the PES, dictated by the line intensity accuracy

The required accuracy of line intensities in general and especially those of the water molecule is about 10^{-3} % for metrology and 10^{-2} % for atmospheric modeling and, perhaps, 0.1% for studies planetary and exoplanetary atmospheres, it becomes important to quantify how accurate the PES used must be to meet these requirements. We present below such analysis for water and carbon dioxide.

The accuracy of the intensity calculations depends on the quality of the PES, which we characterize by the standard deviation of the energy levels calculated using compared the experimentally derived levels. We cannot produce, and it is likely we will not be able to do it for in the foreseeable future, a PES which reproduces the experimentally derived energy levels to about 10 kHz (3×10^{-7} cm^{-1}), which is needed to benchmark the analysis we perform below. However, a proxy for modeling the PESs with a range of accuracies is to vary the convergence

Table 2
Intensities (I in cm molecule^{-1}) calculated with PESM and the CKAPTEN dipole moment surface and percentage difference for a calculation using PES15K for transitions with $J = 4$ and 5 for different vibrational bands denoted $v_1v_2v_3$.

band	$\tilde{\nu}$(cm^{-1})	I	ΔI(%)	J'	K'_a	K'_c	J''	K''_a	K''_c
010	1434.689787	1.360E−24	−0.16	5	1	5	4	4	0
	1695.931135	2.821E−19	0.06	5	0	5	4	1	4
	1976.191645	1.219E−22	0.07	5	4	2	4	1	3
020	3214.678609	1.452E−23	0.20	5	2	4	4	3	1
	3403.721024	1.641E−22	0.05	5	3	3	4	2	2
	3593.381307	2.352E−24	0.19	5	4	2	4	1	3
001	3677.357713	1.276E−23	0.20	5	2	4	4	4	1
	3864.317302	1.148E−20	0.21	5	3	2	4	3	1
	4019.476205	1.123E−21	0.31	5	3	3	4	1	4
100	3661.671101	1.713E−23	−0.14	5	1	5	4	2	2
	3853.575886	2.016E−20	−0.05	5	3	2	4	2	3
	4031.397907	2.622E−22	−0.06	5	4	1	4	1	4
030	4986.202421	1.915E−24	−0.04	5	3	2	4	2	3
	5190.624673	2.706E−24	0.24	5	5	0	4	4	1
110	5493.485183	2.544E−23	−0.09	5	4	2	4	3	1
	5601.836247	3.751E−24	0.01	5	4	2	4	1	3
	5710.809043	1.368E−25	−0.13	5	5	1	4	2	2
011	5575.779157	1.554E−22	0.01	5	3	2	4	1	3
	5647.408008	4.285E−23	0.10	5	4	1	4	2	2
	5723.775385	3.577E−23	0.09	5	5	1	4	3	2
120	6881.457691	5.637E−24	−0.70	5	1	4	4	2	3
	7162.193223	2.450E−24	0.70	5	5	1	4	4	0
101	7160.659981	4.100E−24	−0.09	5	2	4	4	4	1
	7341.900441	5.053E−21	−0.29	5	0	5	4	0	4
	7562.122742	3.130E−24	−0.46	5	5	0	4	3	1
021	7116.940577	1.800E−24	−0.20	5	2	3	4	0	4
	7339.781288	1.265E−24	1.50	5	5	0	4	3	1
200	7290.116027	1.418E−21	0.01	5	0	5	4	1	4
	7400.446054	2.447E−23	0.66	5	4	2	4	3	1
	7508.797118	3.570E−24	−0.32	5	4	2	4	1	3
002	7345.273854	4.351E−23	−0.17	5	1	4	4	4	1
	7461.383644	9.780E−25	−0.48	5	2	4	4	3	1
	7630.485113	3.164E−23	−0.14	5	3	2	4	2	3
031	8475.942379	1.059E−23	−0.50	5	0	5	4	0	4
	8477.642865	3.185E−23	−0.47	5	1	5	4	1	4

of the variational calculations as a function of the size of the basis set and the total matrix. In this section, we model this dependence by replacing the quality of the PES with the convergence of the vibrational-rotational wave functions, regulated by the DVR3D parameter which controls the size of final Hamiltonian matrix, MAX3D. We test this for the example of CO_2 [48] and water.

Table 3 shows the dependence of the average deviation (error) of CO_2 energy levels up to 7000 cm^{-1} with $J = 2$, $J = 3$ and related Einstein A coefficients on the size of the Hamiltonian matrix diagonalized. These energy differences are computed relative to a converged calculation with MAX3D=2000. Table 3 also shows the average relative error in the calculated Einstein coefficients A for all R(2) and P(3) transitions between the levels. Table 3 shows that for line intensities accurate to about 0.001%, an accuracy of 2×10^{-6} cm^{-1} or 60 kHz for computed levels is needed.

Table 4 shows the corresponding dependence of the average deviation (error) in the H_2O energies below 10,000 cm^{-1} for $J = 2$, $J = 3$, and the total deviation for $J = 2$ and 3. Here the energy deviation is calculated relative to a converged calculation MAX3D=5500.

We conclude from Tables III and IV that in the case of poor convergence in region of 1 cm^{-1}, the model of the differently converged calculations does not capture the behavior of the different PES. For example, for CO_2, see Table 3, convergence to 0.1 cm^{-1} results in 480% difference in intensities. However, for better converged situations, this model can give good estimation of the necessary accuracy of the PES for obtaining a certain quality of intensity calculation. In this context it is interesting to highlight recent studies on the CO molecule, for which intensities have been measured with exquisite accuracy. Our recent calculations (to be published), compares potential energy curves which gives states with an accuracy of 300 kHz (10^{-5} cm^{-1}) [51] compared to one which gives an accuracy of 50 kHz (just over 10^{-6} cm^{-1}) [52]. These showed that the more accurate potential improved the agreement with experimental intensities by up to 0.1 % for low overtone ($v \le 5$) and up 0.5% for higher overtones.

Table 3
CO_2 energy levels (in cm^{-1}) for states up to 7000 cm^{-1} and related Einstein coefficients as an average difference compared to the converged levels a function of final matrix size, MAX3D.

MAX3D	1000	500	400	300	200
$\Delta E_{J=2}$	3.8×10^{-12}	6.8×10^{-8}	1.3×10^{-6}	1.2×10^{-4}	1.3×10^{-2}
$\Delta E_{J=3}$	1.1×10^{-10}	2.8×10^{-7}	6.1×10^{-5}	4.0×10^{-4}	0.29
$\Delta E_{J=2,3}$	6.6×10^{-11}	1.7×10^{-6}	3.7×10^{-5}	2.5×10^{-3}	0.18
$\Delta A/A_{\mathrm{conv}}$	0.00020%	0.0016%	0.035%	2.5%	480%

Thus, when the required accuracy of the intensity is in the range 0.003% to 0.1%, 4×10^{-5} cm^{-1} (or 1 MHz) accuracy of the PES is necessary; this is a strong requirement which is hard to reach for triatomic systems at present. The accuracy of the PES, which has been reached for benchmark triatomics N_2O, CO_2 and water results in intensities which may only be accurate to 2% for some of the lines. We conclude from this that the new goal for fitted PESs and thus the experimental accuracy of the determination of the line centers changes from 30 MHz (0.001 cm^{-1}), which has long been the aim of PES fit [21]. The new goal and paradigm for reproducing measured line centers becomes closer to 1 MHz for intensities accurate to 0.1% and 60 kHz (2×10^{-6} cm^{-1}) for 0.001% accuracy. These are very challenging goals with current techniques.

6. Conclusions

The importance of the water molecule requires the steady improvement of the accuracy and completeness of the quintessence of the study of water spectrum — its line list. Here we present a fitted water

Table 4
H_2O energy levels (in cm^{-1}) for states up to 10000 cm^{-1} and related Einstein coefficients as an average difference compared to the converged levels a function of final matrix size, MAX3D.

MAX3D	1000	500	400	300
$\delta E_{J=2}$	6.1×10^{-8}	5.7×10^{-4}	2.0×10^{-3}	5.6
$\delta E_{J=3}$	2.6×10^{-6}	2.2×10^{-4}	9.8×10^{-4}	0.0056
$\delta E_{J=2} - \delta E_{J=3}$	4.4×10^{-6}	3.9×10^{-4}	1.5×10^{-3}	2.9
$\Delta A/A_{\text{conv}}$	0.01%	1.05%	9.45%	19.33%

potential energy surface (PES) which provides energy levels which reproduce empirical values with a standard deviation of $\sigma = 0.01$ cm^{-1} for levels with $J \leq 15$ and energies below 15 000 cm^{-1}. The predictions for levels with $J \leq 27$ are only slightly less accurate, $\sigma = 0.013$ cm^{-1}. This constitutes the next important step to the experimental accuracy within the variational calculations.

A still unsolved problem is the line positions and line intensities of the excited bending vibrational states. We had to remove many of them from the set of the fitted energies in order to achieve extremely accurate line centers and wavefunctions of the remaining energy levels. Our major goal is to achieve the same accuracy for the excited bending states and transitions as we have done for the other levels and line positions.

The improvement of the PES and the wavefunctions influences significantly the accuracy of the line intensity calculations, which represent very important practical use for the various applications. Our tests show that high accuracy predictions of line intensities also require wavefunctions generated using high accuracy PESs, meaning that further improvements in the fits to potentials of key molecules such as water are required.

CRediT authorship contribution statement

Mikhail An. Rogov: Writing – review & editing, Software, Methodology, Investigation, Data curation. **Nikolai F. Zobov:** Supervision, Investigation, Funding acquisition, Data curation. **Irina I. Mizus:** Funding acquisition, Formal analysis, Data curation. **Roman I. Ovsyannikov:** Software, Investigation, Formal analysis, Data curation. **Jonathan Tennyson:** Writing – review & editing, Software, Funding acquisition. **Oleg L. Polyansky:** Writing – original draft, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jqsrt.2026.109863.

Data availability

The data associated with this article are provided in the paper and the supplementary materials.

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