

Interactive comment on “A semi-empirical potential energy surface and line list for H₂¹⁶O extending into the near-ultraviolet” by Eamon K. Conway et al.

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We thank the reviewer Alain Campargue for taking the time to read our article thoroughly and for providing a very constructive review. We have tried to address the comments to the best of our ability, and we believe the quality and clarity of the article has been improved by the comments. Below, we address each comment individually and highlight such changes in the article.

1. *When comparing energy levels calculated from different PES (eg Fig. 1) is it straightforward to identify the same energy levels in the different data sets using only the rigorous labels (J, parity, symmetry) in particular in the high energy range that you*

C1

are considering. Could you give details about the adopted procedure to associate the levels.

The rigorous quantum numbers alone are not enough to match a calculated state to the correct corresponding state in MARVEL. We needed to supplement the rigorous quantum labels with energy differences, which is where it becomes difficult and very often non-trivial, particularly in the near-UV with the high density of states to identify the correct match. We added new J states only after the potential surface was optimized to the previous J states considered. This helped keep the energy differences low enough in the next J to make a match more accurately/reliably. For example, we would refine J=0, then pre-calculate J=2 states with this PES and identify the J=2 states. Next, refine J=0 and 2. Calculate J=5 states, then match the J=5 states. Then refine J=0, 2, 5, etc. We now explain this in the text.

2. *Concerning this Fig. 1, it seems that deviations larger than 0.5 cm⁻¹ was excluded below 25000 cm⁻¹? Could you comment? Little is said in the text about this Fig.*

For the Figure, there is indeed a 0.5 cm⁻¹ threshold for matching states below 26 000 cm⁻¹. To make this figure, and to facilitate an equal comparison, we calculated all states with the new PES, POKAZATEL PES and PES15K for 0 ≤ J ≤ 20. Next, the same algorithm was used to match all calculated states from each PES to a respective state in MARVEL. This helped to ensure the calculated energies would be matched via the same procedure and facilitate an equal comparison and accurate RMS comparison. The energy threshold was set to 0.5 cm⁻¹ for E < 26000 cm⁻¹, and 1 cm⁻¹ for states above this limit. Clearly, our PES states do not really need the 0.5 cm⁻¹ cut off, but those states calculated with the POKAZATEL PES do, else if it was lower, less states would be matched from POKAZATEL. This is explained in the text.

3. *Table 1 should be converted in a Fig and this long series of numbers (with rms values with 6 digits!) could be provided as Supplementary Material.*

C2

We agree that figures would be preferable to tables. We have added three subfigures to represent $E < 15000 \text{ cm}^{-1}$, $E \leq 26000 \text{ cm}^{-1}$ and $E \leq 37000 \text{ cm}^{-1}$. We have moved the tables to the supplementary material.

4. *On the other side, I am missing information: the authors refined their PES against $J = 0, 2, 5, 10, 15$ and 20 , representing approximately 4 000 states while Table 1 applies to all their MARVEL levels, correct?*

We did indeed refine to approximately 4000 states, which were in $J=0, 2, 5, 10, 15, 20$. The table represents the residuals for states in MARVEL both refined to ($J=0, 2, 5, 10, 15, 20$) and not refined to ($J=1, 3, 4, 6, 7, 8, 9, 11, 12, 13, 14, 16, 17, 18, 19$). It is important that the PES has a 'smooth' behavior and can accurately predict the states between the Js that have not been fit. Hence, we calculated the residuals for those states in the un-refined Js to further promote its accuracy. The table has been moved to the supplementary.

5. *Were some empirical energy levels excluded? On which criterion? What about bending levels?*

Some states were indeed excluded from the refinement. States were removed if their residuals appeared to be abnormally higher than other J states in the same vibrational band which showed low average residuals. We expect residuals to be similar in the same vibrational band. The high bending states, i.e. $\nu_2 > 4$ were difficult to fit and some were removed for the reason previously mentioned: abnormally high residuals for some states in the same band. Often, those bands with very few states were also outliers. Text has been added to the article to explain why and when states were removed.

6. *In the IUPAC-TG dataset of H_2^{16}O , about 18500 levels were determined. Here the total numbers appearing in Table 1 are significantly lower (10500?) Could you explain? In principle all the IUPAC-TG levels (in fact even more with the recent new observations) should be considered. Could you mention/discuss the levels which were excluded?*

I can indeed explain the 10526 in (now supplementary) Table 1. This number represents the number of states with energy $\leq 15000 \text{ cm}^{-1}$ (see top of table, above $J=0$

C3

averaged results) and $J \leq 20$ that were matched with MARVEL using our calculated states, the remaining have higher energies or larger Js. One can see we compared with 14030 states with $E \leq 26000 \text{ cm}^{-1}$ and $J \leq 20$. There are a total of 10651 states in the latest edition of MARVEL used here that have $J \leq 20$ and $E \leq 15000 \text{ cm}^{-1}$. This means that 125 were not matched to at all: either quantum labels are different, and/or the energy deviations are greater than 0.5 cm^{-1} . But the full set of MARVEL was considered.

7. *The $J = 0, 2, 5, 10, 15$ and 20 levels were used to refine the PES. Does it mean that the rms values given in Table 1 for $J = 0, 2, 5, 10, 15$ and 20 correspond to the same set of levels as those included in the fit?*

Yes, the residuals in Table 1 (for this PES) reflect the fitted states for $J=0, 2, 5, 10, 15, 20$ (minus outliers). Table is in the supplementary now so no line has been added to the paper.

8. *Line 285 : "For energy levels in $J = 20$, our new surface predicts MARVEL states with an RMS error of 0.056 cm^{-1} , a significant improvement to the 0.13 cm^{-1} RMS error obtained with the POKAZATEL (Polyansky et al., 2018) PES." I am wondering to which extend this statement is informative: POKAZATEL was only refined to states in $J = 0, 2$ and 5 while the present PES use levels in $J = 0, 2, 5, 10, 15$ and 20 . The reader does not know if the quoted rms applies for the same set of levels, which ones were excluded. (Note that Line 49, the value of the POKAZATEL rms is as 0.118 cm^{-1}).*

The 0.118 cm^{-1} is the number quoted by Polyansky et al. that reflects their fitted RMS for MARVEL states in their $J=0, 2, 5$. This has been noted in the article. The 0.13 cm^{-1} RMS and the 0.056 cm^{-1} RMS indeed refer to the same states, i.e (supplementary) Table 1, $E < 15000 \text{ cm}^{-1}$, $J=20$ averaged energies. These large differences are due to the insufficient coverage of Js considered for the refinement of the POKAZATEL PES and show how our PES is significantly more suited toward the generation of high temperature spectra that necessitates the use of high J transitions for completeness.

9. *The considered set of MARVEL energy levels is unclear. Reference to a submitted*

C4

paper Furtenbacher et al., 2020 is given. The full significance of the above sentence requires more precision.

We have added the respective reference: J. Phys. Chem. Ref. Data 49, (2020); 10.1063/5.0008253, which recently appeared online. This is the latest MARVEL 2020 data release.

10. *In the conclusion, the references attached to the MARVEL energy levels are (Császár et al., 2007; Furtenbacher and Császár, 2012) which are related to the MARVEL procedure and do not provide the used empirical levels. This “MARVEL washing” of huge experimental efforts should be avoided. In this context, probably Tennyson2013 is a better reference.*

We have replaced these references with the citation to the latest MARVEL2020 article here, as it just appeared online) (and where necessary in the article that references MARVEL energy level comparisons).

11. *Figure 2 should be improved: it seems that continuous lines were used for the plot while sticks or, better, dots should be used. Due to overlapping POKAZATEL CK-APTEN is not visible and there are many other issues. May be restrict the range to 20000-40000 cm⁻¹ and plot only the envelopes of the different lists to allow to distinguish them. Several panels?*

Figure 2 has been modified to use dots over joined lines. Also, a zoomed in region of 22500-40000 cm⁻¹ is included within the figure for clarity in the near-UV.

12. *Line 308-309 “This line list will form basis for the HITRAN2020 line list in the visible and UV . . .”. I am wondering if, as a principle, such announce should not be validated by the HITRAN scientific committee. May be “This line list will be proposed for the HITRAN2020 line list in the visible and UV. . .”*

Yes. Perhaps this was an ambitious assumption. We have addressed it.

13. *Figure 3. I am surprised by the poor correlation between the 0.03 cm⁻¹ and 1 nm resolution spectra. Of course, it could be due to the variation of the density of lines*

C5

which makes the cross section so different compared to the envelope of the 0.03 cm⁻¹ spectrum (for instance near 300 nm). Could you check and increase the sampling of the 1nm spectrum in order to have a smooth line instead of this ugly broken red line (by the way increase its width to make it more visible)

Yes, we can see how the low 1 nm resolution can appear ‘ugly’. We removed the 1 nm comparison and instead add a 0.2 nm resolution comparison to the upper limit from Lampel et al. (2017) deduced from observations at a 0.7 nm resolution. A 0.7 nm resolution spectrum is again very coarse, hence why we choose 0.2 nm: it maintains the band structure while still agreeing with their upper limit.

14. *I am surprised to find no mention and comparison to the high quality CRDS measurements of individual absorption lines near 25300 cm⁻¹ by Dupré et al JCP 2005 doi.org/10.1063/1.2055247. To the best of my knowledge, this is the highest frequency measurements of absorption line intensities.*

We have added a citation to the article of Dupré et al. JCP 2005 in our introduction, and in the conclusion we mention it will be proposed to be added in future releases.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-286>, 2020.

C6