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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A semi-empirical potential energy surface and line list for $H_2^{16}O$ extending into the near-ultraviolet" *by* Eamon K. Conway et al.

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(Also provided as attached file) Report on A semi-empirical potential energy surface and line list for H216O extending into the near-ultraviolet by EK Conway et al

This work aims to contribute to the understanding of the strong discrepancy existing between some recent low resolution measurements of water absorption in the UV and calculations of the water absorption spectrum in this region. The paper is pleasant to read and the reported results, although lacking experimental validation, are very convincing and question seriously the origin of the much stronger water absorption measured by Pei et al and Du et al around 300 nm

Conway et al optimized a semi-empirical PES for H216O up to 37000 cm-1 and J= 20 and against empirical energy levels and generate a new line list up to 41200 cm-1. The obtained list is found to increase the UV absorption compared to the previous POKAZATEL list which was questioned by Lampel et al near 363 nm. The new calculations are now consistent with the results of Lampel et al. It is worth noting that according to the authors and in spite of the importance given in the paper to the improved PES, the differences in the DMS used for POKAZATEL and in the present work are mainly responsible of the increased UV absorption. Nevertheless, the obtained increased absorption is far to be sufficient to bring theory in accordance with the above mentioned experimental works: the resulting calculated absorption cross-sections remain between one and three orders smaller than the experimental values by Pei et al and Du et al. As underlined by the authors, new highly sensitive measurements in the region are highly suitable to validate their list.

Below a number of questions and suggestions: - 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 are considering. Could you give details about the adopted procedure to associate the levels. - 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. - 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. 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? Were some empirical energy levels excluded? On which criterion? What about bending levels? In the IUPAC-TG dataset of H216O, 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? - 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? - 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 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 considered set of MARVEL energy levels is unclear. Reference to a submitted paper Furtenbacher et al., 2020 is given. The full significance of the above sentence requires more precision - 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.

- 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 CKAPTEN 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?

- 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. . .

- 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 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)

- 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.

In conclusion, considering, the quality of the reported results obtained using state-of-the art theoretical calculations and the importance of the water absorption for a number of atmospheric applications, I recommend publication of this paper once the above comments and suggestions will have been addressed.

A. Campargue Tuesday, 28 April 2020

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2020-286/acp-2020-286-RC1-supplement.pdf

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