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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Water dimer absorption of visible light" *by* J. Hargrove

Anonymous Referee #2

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Overall merits:

The paper claims on the detection of water dimer (WD) by visible light at wavelengths around 405 (24691 cm-1) nm. The major argument put forward by the author in favour of WD overtone detection is the apparent quadratic dependence of the observed absorption features with the water vapour partial pressure observed in a CRDS instrument. A closer inspection, however of mostly theoretical and the few available experimental studies on WD overtone detection published in the past, indicate that the inferred absorption at 405 nm is at least a factor of 1000 larger than one can reasonably expect for WD overtone absorption. Since no other robust arguments are further provided in favour of WD overtone detection (which could be inferred from (a) the observed band shape and width, (b) agreement of the observed absorption with theoretical calculations of the band strengths, or (b) up-dated ab-initio calculations of WD vibrational modes combined with (d) conceivable physical arguments which indicate

an extra large band strength for the 8th overtone as compared to the other overtones, and (e) refined estimates of the equilibrium constant for WD formation, et cetera) other interpretations of the observation appear to be more likely. These may include (a) instrumental artifacts, (b) contamination of the cell by any other UV visible absorber, (c) self-broadening of water vapour overtone lines and/or (d) collisional induced absorption of water vapour, et cetera. All these possibilities have to be addressed in much more detail than in the present version of manuscript. I'm also very curious about the implicit claim that the detected 'WD absorption' overtone band may have a band width in excess of 600 wavenumbers (if Figure 1 is indicating this), or if the reverse is true (but then I miss any indication of a band like absorption feature in Figure 1). In view of my criticism that is more substantiated below, I feel that the manuscript needs more than a major revision before it is worth to be reviewed again, and hence it is rejected.

Major comments:

1. Figure 1 does not give the necessary information it pretends to provide on the observation or finding. For any readers familiar with optical absorption measurements, it appears necessary to provide information on the extinction measured/inferred (a) with an empty cell, (b) the cell floated with a buffer gas, and (c) the cell filled with a buffer gas and the targeted gas (H2O and D2O), all documented as a function of T and gas concentration. Since this information is not provided, it is impossible to finally judge on the quality of the present measurements as well as on the possible reasons for observed measured extinction/absorption.

2. By using estimates of the WD equilibrium constants (e.g., inspect the appropriate figure in Ptashnik et al., Q J Royal Meteorol Soc. 2004,130: 2391-2408, and the following studies of Ptashnik et al.,) and calculated line strength (e.g., Schofield and Kjaergaard, 2003, Schofield et al., 2007), it turns out that any optical instrumentation suitable for WD overtone detection (Dn ^{3} 4) should have detection limits better than 2Œ10-10/cm (or better), whereas you claim a detection limit a factor of 10 worse for your CRDS instrument. In fact, by inspecting the peak to peak noise around 24950

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cm-1 (Ds = 1Œ10-22 cm2 inferred from Figure 1, which I take in your favour as the typical 5Œs ! noise level), it turns out that your detection limit cannot be better than 5Œ10-8/cm for saturated air at room temperature (for all the assumed numbers see also 4.). This is a factor of 25 larger than your claim and it is likely a factor of 250 worse than needed for any reasonable attempt for WD overtone detection!

3. Theoretical work has shown that the oscillator strength (or line strength) for WD stretch and bend vibrations are likely to decrease by a factor of 5 per overtone number increase (e.g., Kjaergaard et al.,). Accordingly the absorption is expected to decrease by a factor 125 when going from the 5th (which is probably accessible by present instrumentation) to the 8th overtone. Moreover, if you need to argue on absorption band widths of the order of several 100 wavenumbers (see Figure 1), then the maximum optical depth (OD) will accordingly decrease (e.g., by a factor of 5 to 10 when assuming a typical WD band width of 50 cm-1 vs $>$ 600 cm-1 as indicated in your Figure 1). In conclusion by putting together all information available from the literature, the identification of the apparent 405 nm absorption band as being due to WD overtone absorption is at least a factor of 1000 too optimistic!

4. Finally, your interpretation of WD detection at 405 nm can also be tested by inspection of atmospheric long-path absorption measurements operated either in the active mode using lamps or passive mode using the Sun or the Moon as light sources. For these, typical detection limits in terms of optical thickness are OD $<$ 10-3 and path length up to l = 10 km are common (but l's up to 30 km are possible). Taking your inferred WD data (Keq = 0.056 atm-1 at 300 K and s = 3Œ10-22 cm2) and a pH2O = 20 mbar would give an of OD = lŒsŒKeqŒ(pH2O)2 = 0.15 ! Clearly such a large ODs, caused by any atmospheric species would have been easily discovered by suitable instrumentation in the past (or already by bare eye when inspecting the sky light received from near the horizon). In fact, state of the art long path absorption measurements are easily able to detect ODs smaller than 10-3 throughout the whole UV/visible and near-IR spectral range which for a path length of l = 10 km leads to a detection

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limit of 1Œ10-9/cm!. Unfortunately none of these atmospheric measurements have yet unambiguously identified WD overtone absorption in this spectral range, a fact that you may use to infer an upper limit for any WD overtone absorption at 405 nm.

In conclusion, the arguments put together above (1. - 4.) provide a large body of evidence that the interpretation of your measurements cannot be true. Accordingly, I reject the manuscript as it stands now. I will be willing, however, to review it again if you are to find any other reasonable interpretation to your observation.

Specific/Minor comments:

In the introduction, there are many of incorrect citations, or worse attribution of findings to authors that you will need to correct for.

Compared inferred water dimer equilibrium constant with value from the literature somewhere in the manuscript (possibly in a Figure).

Here more point could be mentioned !

Figure 1: Here it is important to show (a) different absorption spectra (traces) as a function of water vapour partial pressure, (b) indicate where you suspect the WD absorption, (c) and to put forward arguments in the text why the apparent absorption band is wider than the shown spectral interval. In fact, I cast doubt as to whether the WD band width can be larger than the shown interval of 800 wavenumbers. In fact, if the WD absorption would have a width in excess of 800 wavenumbers, than the oscillator strength (or line strength) should be even much larger than assumed by the author,

Figure 2: Show error bars.

Figure 3: Include a comparison of measured and modelled (from the latest HITRAN compilation) water vapour absorption here. Another, the conclusion that could be draw from Figure is that in fact a too large detection limit of your instrument caused this baseline shift.

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