

Interactive comment on “Water dimer absorption of visible light” by J. Hargrove

Anonymous Referee #1

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Overall, I found this paper to be constructive and mostly well thought out. The paper focuses on several probable water dimer absorption bands, with particular focus on the absorption at 405 nm. It is based on this absorption that the equilibrium constant and other thermodynamic properties are determined and comments on relevant atmospheric consequences are made. The 405 nm absorption was determined to purely water dimer based on the quadratic monomer concentration dependence, temperature dependence, and strong comparison to theoretically calculated thermodynamic properties. Although I found the author's thought process and logic sound for the most part, there were several issues that need clarification before publication can be made. Thus I recommend that the paper be tentatively accepted pending revisions.

More specifically:

p. 11130: It not entirely convincing that the 405 nm absorption could not be due

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to NO₂-2H₂O. The author states that the abundance of this species is calculated to be ~1800 times less than that of the water dimer. How was this calculation made? The author needs to provide a reference or at least explain how the estimate was made. Regardless, even if the NO₂-2H₂O species is much less abundant than the water dimer, who is to say that it doesn't have an abnormally high absorption? This is certainly true for the water dimer at 405 nm, which the author himself agrees is orders of magnitude higher than expected.

p. 11130: I did not fully understand the discussion about how the 405 nm absorption could not be due to a thin film. Wouldn't heating the mirrors effect the sample temperature? Hence, wouldn't one expect that heating the mirrors to 40 C should have some effect on the measured absorption?

p. 11131: First, there is an incorrect reference – Goldman2006 does not exist. Second, the author states that the equilibrium constant and cross section might be due to the density of states above dissociation. However, this assertion (Schenter2002) is based on a rigid-rotor harmonic oscillator model. More rigorous results based on a spectroscopic potential (Goldman2004) show that in fact these pre-dissociative states have little effect on the calculated equilibrium constant, and do not likely play a large role in the measured absorption. Consequently, the author thus far has not given a good explanation for this surprising result, which begins to make one wonder whether in fact the absorption at 405 nm is due to far wing continuum absorption or experimental contamination (although the latter seems improbable). Thus, a more thorough explanation for the abnormally high absorption results needs to be given.

p. 11132: I found the discussion that rules out the possibility of Rayleigh and Mie scattering to be too sparse. Comparing Rayleigh cross section numbers for water vapor, N₂ and O₂, as well as an additional sentence explaining the relevance would help.

p. 11132: The discussion of oscillator strengths is very confusing. Explicit reference

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to the experimentally measured water dimer oscillator strength would help put things in context. Also, the justification that the author's results for the absorption are likely accurate because accurate results have been obtained for NO₂ at similar conditions is rather weak. Again, the author needs to spend more time analyzing possible reasons for the absorption in question.

FIG. 4: The linear fit to the results at 10 degrees is essentially made to only two points, since the first two points are nearly identical. It seems reasonable to provide one more temperature measurement at this dew point at the very least.

Minor comments:

1. There are a few typos in the manuscript. Be sure to spell check more thoroughly!
2. FIG. 2 is very difficult to read. A larger font for the figure axes would be greatly appreciated.
3. Be sure to check all references. I caught one mistake, mentioned above.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11123, 2007.

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