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

J. Hargrove

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Thank you for your consideration of the paper. While your concerns are largely addressed within the paper, the interactive discussion of these issues is likely to be of benefit to the readers. I would like to address your points in detail.

As to the overall merit, the quadratic dependence on water monomer concentration was only the first indication that water dimer might be involved. This was furthered by measuring the extremely broad profile of the absorption (the inferred band-width you mention), and tested successfully for the temperature dependence and resulting equilibrium constant expected for water dimer. The presence of a weaker linear response by deuterated water helped confirm that the absorption was not due to scattering, or other artifacts. This was supported by a similar absorption at 532 nm attributable to $v=6$ and independent measurements by A. Freedman and associates at 440 nm where $v=7$ might be expected. Additionally, measurements at 570 nm found water monomer peaks and a continuum more consistent with self-broadening and a lack of dimer ab-

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sorption.

I agree that the response is approximately 1000 times stronger than one would expect, but your determination is based on a one dimensional potential by Kjaergard et al. and my measurements combined with the broad absorption are 100 times higher than you calculated. Using a three dimensional potential the result increases by a factor of between 100 and 10,000, but still leave much to be desired. Ab initio calciliations of these high overtones in a wildly distorted energy potential are necessarily crude and unreliable. In this case the measurements will have to come first and the theory attempt to find agreement. I have made these measurements and hope that other measurements and calculations will follow.

It is notable that when Kjaergard calculated v=6 he found it to be larger than v=5, and that v=3 and 4 were reduced relative to their expected strength further. This opens the possibility that higher overtones may be enhanced too, but it is a one-dimensional analysis of the hydrogen stretch with insufficient rigor to provide more than a qualitative insight.

To your five points before the main points: a. Instrumental artifacts are unlikely as demonstrated in Hargrove et al, 2006 where NO2 was reliably measured in the same region. b. Contamination in the cell by other absorbers is unlikely because most gas phase species do not absorb at 405 nm, NO2 can be ruled out by the lack of a NO2 signature in the spectrum, and the source water could be shown to be free of contaminants and produce the same absorption as Millipore water by using commercially available Ultrapure water. c. Water vapor overtone lines in the region are not even close to being strong enough to produce this large a continuum absorption. d. Collision induced absorption would contain some response from N2 and O2 with a linear dependence on water, but were not measurable at 405 nm.

Major comment #1: Figure 1 is merely an absorption spectrum of the 405 nm region showing the broad feature with a peak at 409 nm and a valley at 400 nm. That is 600

cm-1 of breadth and I assume it continues further to the red. It is indeed remarkable. It is a composite of four scans in different regions with baseline adjustment made at the endpoints. It does not pretend to show the quadratic behavior. That is in figure 2 and the text. It also does not pretend to show the temperature dependence. That is in figure 4. You seem to understand the nature of figure 3 with a similar style of presentation, though you doubt the limit of detection. The only argument of missing information that can be made about figure 1 is that the measured cross section depends on the equilibrium constant, and I measured that in figure 4 and mentioned it in the text. It would be nice to measure the full spectrum for all of the data but with a YAG pumped dye laser that would take a prohibitively long time and result in less reliable data.

Major comment #2: In the text I clearly state that the noise level in the points that I took at a fixed wavelength were better than in the scans. To infer the noise level from a scan ignores this fact. Also, it is possible for some structure to exist within the noise that would make it appear worse. The noise level was measured carefully and repeatedly and was accepted in the previous publication on NO2 detection without question. The sensitivity needed to measure water dimer can not be determined in advance of the measurements and I will not argue with what you think is likely.

Major point #3: Kjaergard actually predicts a larger v=6 than v=5, and made measurements and calculations on butanediol to show that a cancellation effect exists that could reduce the lower overtones. To say that a measurement is too optimistic suggests that we have some kind of control on the resulting outcome. I will be much more interested in measurements by others than predictive back-of-the envelope calculations. Without publishing this paper it is likely that others making the same measurements initially will not trust their results without making the much more detailed study that I have done. These measurements are possible and need to be encouraged.

Major point #4: Ah yes! Finally some comparison with anticipated measurements. You rightly point out that with a 10 km path-length that a 10-9 cm-1 limit of detection is possible. That is close to what I have. However, differential optical absorption spectroscopy

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(DOAS) cannot measure water vapor independent from the other species present in the air. NO2 has an absorption in this region that is typically larger in polluted atmospheres. Even at 50% saturation of 85 deg C relative humidity as I measured recently the water response is less than 10 ppb of NO2. (It was about 8 ppb equivalent in agreement with the calibration curve.) This would be difficult to observe with the naked eye. Riverside, CA has pollution that is relatively easy to measure and see but the NO2 does not become visibly noticeable until about 30 ppb by my experience, so I doubt your argument about water dimer being clearly visible from my cross section and equilibrium constant. DOAS has been done in this region and I saw a presentation at the Ohio Spectroscopy meeting that contained 10 km data in this region of the spectrum. There was NO2 present and considerable continuum absorption. I questioned the author and he attributed the absorption to significant scattering by particulates. Within the spectrum there was room for both. It may be possible to confirm my measurements with DOAS, but it is more likely that it will be easier to test with cavity ring-down due to the greater control over the content of the sample.

Minor comments at end: Which citations are incorrect? You say 'many' but don't list them and why they are incorrect.

Figure 4 does show the comparison of the enthalpy (slope) and entropy (intercept) agreement between my data and Goldman et al. from which the equilibrium constant is calculated. The values of 0.056 atm-1 for my Keq and 0.051 atm-1 for theirs is listed in the text.

I have addressed the remarkable strength and width of the absorption in figure 1 already, the oscillator strength is an approximation but the order of magnitude result is sufficient to call into question either the ab initio calculations or the measurements. I made the measurements repeatedly over the past three years and trust them.

In figure 2 the error bars are 10-9 cm-1 and as a result are too small to display properly.

Figure 3. I could put in the Hitran data but with only two lines I thought it sufficed to

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say they agree. Your suggestion that the detection limit is not low enough is simply wrong. You said yourself that 10-9 cm-1 was possible at 10 km. I have 6 km of pathlength and the ability to average multiple points. The continuum here at 570 nm is not even suggested to be from water dimer yet it is easily measured. It is not quadratic and has no temperature dependence, so it is not water dimer. For 532 nm, 405 nm 409 nm and 397 nm there is a quadratic dependence and at 405 nm the Van't Hoff plots provide some confirmation. More extensive measurements could be made and I hope that soon they will be made. The best argument I can respond to you with is to look at it yourself and see. Broad sweeping predictions about how something would be impossible do not compare to actual measurements.

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

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