Atmos. Chem. Phys. Discuss., 7, S6227–S6229, 2007
www.atmos-chem-phys-discuss.net/7/S6227/2007/

Atmospheric Chemistry and Physics Discussions

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

J. Hargrove

Received and published: 23 October 2007

Thank you for your careful and thoughtful consideration of my paper. In response to your comments:

p. 11130 The calculation method was not stated in the paper and could be included in the final version. The estimate was based on the relative bonding of NO2?(H2O)2 and H2O?(H2O)2. It was concluded from relatively crude MP2 calculations that NO2 would be bound more weakly than water and the bonding of water was used as an upper limit for the estimate. The argument is not well established. Since then, our recent measurements on ambient air have consistently showed the same absorption regardless of the NO2 level suggesting that the response is not dependent on the concentration of NO2. This provides better evidence that the NO2 complex is not involved.

p. 11130 Heating the mirrors did not significantly affect the sample temperature. The

mirrors are at one end of a metal buffer chamber that stayed at room temperature when the mirrors were heated independently. The rest of the sample cell also remained at room temperature. There was a change in either the mirror reflectivity or alignment that required a new baseline, but the measured absorptions were unaffected. The buffer chambers were present but not used for most of the experiments, so that was a free flow of gas throughout the light path. As a result the change in temperature from heating the mirrors was not measurable.

p. 11131 Scribano, 2006 is the correct reference. Endnote listed the second authors and I mistakenly split the reference in two instead of deleting the second author. It will be corrected. The likelihood of far-wing continuum absorption is low at this frequency since there are no strong absorptions nearby that could contribute to this level. The theoretical basis for enhanced absorption does not seem to be fully explored at this point, despite much work on the topic. The most recent 9 dimensional calculations by Dr. Bowman?s group seem to come closest to explaining it, but were not developed to the point where they are prepared to publish their results. Apparently the calculations are particularly challenging and potentially uncertain.

p. 11132 I will include the numbers for the Raleigh cross-sections in the discussion. As I recall, the cross section for water vapor is smaller than that for nitrogen and oxygen and at a few percent level has an insignificant effect. I will look up the numbers again. A reference is provided for that estimation.

p. 11132 The oscillator strength was left out of the final version of the paper and should be included. The oscillator strength was taken from the usual calculation from the cross section with a line-width of 1000 cm-1 crudely approximating what was seen in Figure 1 and is sufficient for order of magnitude comparisons. This section can be clarified.

Fig 4. Additional points were attempted between the endpoints but the thermal drift in the alignment of the cell was prohibitive. At this point I don?t have access to the equipment to rerun the experiment as I have completed my Ph.D. The consistency

ACPD

7, S6227–S6229, 2007

between 10 deg C and 15 deg C was sufficient to conclude that the Van't Hoff plot was reasonably linear. To improve on this data would require a more precise temperature measurement such as is available at several other institutions.

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