Authors' responses to referees' comments ACP-2010-569

"An upper limit for water dimer absorption in the 750nm spectral region and a revised water line list" by A. J. L. Shillings, S. M. Ball, M. J. Barber, J. Tennyson, and R. L. Jones.

We thank the referees for their interest in our paper, and for their comments and suggestions for improving the manuscript. We response below.

Referee # 1: A. Campargue (Atmos. Chem. Phys. Discuss. 10, C9896-C9898, 2010)

Comment 1: A great part of the results and conclusion relies on the quality of the monomer database near 740 nm. It leads to the UCL08 line list which is a mixture of experimental and calculated data. My major concern is that the most relevant experimental source in the region was missed by the authors. This source is "ICLAS of water in the 770 nm transparency window (12746-13558 cm-1). Comparison with FTS databases", J. Quant. Spectrosc. Radiat. Transfer 109 (2008) 2832–2845 by A. Campargue, S. N. Mikhailenko, and A. W. Liu. In this paper, we compared the different theoretical and experimental databases in the spectral region of interest, in particular HITRAN, Tolchenov and Tennyson 2008 and BT2!! The sensitivity of the ICLAS technique allowed detecting more than two times the number of transitions in Tolchenov and Tennyson 2008, now adopted in the HITRAN database. This paper following Kassi 2005 was motivated by the same goal: improving the monomer database in the region where Pfeilsticker et al claimed the detection of the WD signature and our conclusion was:" Considering these results and the fact that WD signature at 750 nm could not be confirmed by subsequent measurements, "the first evidence for atmospheric WD detection as reported in Ref. [1 = Pfeilsticker et al., Science, 2003] had to be revoked" [5 = Lotter, PhD thesis, Heidelberg University, 2006]. The Fig. 6 [actually Fig 9] of our paper shows low resolution simulations very similar to those presented in the paper under review. The ICLAS experimental line list should have been used by Shillings et al or at least they should have compared to low resolution simulations obtained with ICLAS and UCL08 line lists to evaluate the "missing" absorption of the ICLAS data in the region of interest.

Response 1: We thank the referee for drawing our attention to the Campargue et al. paper; we apologise for omitting to reference this relevant work in our original manuscript. We now include Campargue et al. at the end of Section 4.1 (together with Kassi et al., 2005) when we discuss the likelihood that some water monomer lines are missing from HITRAN08 around 750 nm. We cite Campargue et al. again in Section 4.2 as a second study that (in addition to Kassi et al.) concluded that the feature originally attributed by Pfeilsticker et al. to a water dimer absorption is more probably a consequence of water monomer lines missing from the version of HITRAN Pfeilsticker et al. used to fit their spectra.

Unfortunately it has not been possible to fit the BBCRDS spectra using absorption cross sections generated from the Campargue et al. line list. As detailed in response 4 below, air-broadening and self-broadening coefficients for the individual water monomer lines are needed to calculate linearised absorption cross sections, and these are not supplied in the Campargue data. Instead, we produce an extra figure for this response, Fig R1, which compares low resolution water monomer spectra generated from the UCL08 and Campargue line lists. This figure is analogous to Fig 9 in the Campargue et al. paper (5 cm^{-1} FWHM Gaussain line shape; 10 Torr water vapour; 296 K), although it extends to higher wave number to incorporate more of the spectral region accessed in our study. Fig R1 shows that the structure in the low resolution spectra generated from the Campargue and UCL08 line lists agree rather well: for example, both spectra contain many similar lines in the weakly-absorbing 12,950-13,150 cm^{-1} (760-772nm) region where HITRAN08 has hardly any lines (see also Fig 9 in Campargue et al.). However, there are still systematic differences between individual features, with the UCL08 spectrum generally showing a greater absorption (lower panel of Fig R1). It seems this is more due to differences in line parameters for individual lines, rather than being due to the numerous additional weak lines included in UCL08, because there is only a marginal difference between the UCL08 spectrum generated using lines up to the same intensity cut-off as Campargue et al. ($S > 1.6 \times 10^{-28}$ cm molecule^{-1}; approx 2500 lines in this region) and the UCL08 spectrum generated with lines down to a cut-off intensity of $S = 1.0 \times 10^{-30}$ cm molecule^{-1} (approx 8500 lines). Except for some larger differences above 13,400 cm^{-1} (presumably caused by differences in a few strong lines), the UCL08–Campargue intensity difference is smaller than 1×10^{-9} cm^{-1}, and so would be below the detection limit of the present BBCRDS study.

Comment 2: I have now some questions about the UCL08 line list: It is always a responsibility to release such database for water. It extends much further than the spectral region of interest and the reader (and potential user) would like to have some more information about the construction of this database: The UCL08 line list includes minor isotopologues, how were obtained line parameters of the isotopologues which may contribute significantly to the absorption in the considered transparency window? The authors give only the BT2 line list as reference for the calculated data but BT2 is limited to the main isotopologue.... How were “mixed“ the experimental line list and the calculated line list? It is a very difficult task as the rovibrational labelling of the calculated line list are not always reliable....

Response 2: The UCL08 line list was compiled as part of the “Continuum Absorption at Visible and Infrared Wavelengths and its Atmospheric Relevance” (CAVIAR) consortium project which involves a series of laboratory experiments and atmospheric observations. The 750-20,000 cm^{-1} range covers most CAVIAR activities, except for some far-IR work where the cut-off levels for HITRAN08 lines are much smaller and HITRAN was considered to be sufficient.

The UCL08 line list was constructed as follows (some of this information was already in the manuscript; however we have revised Section 3 to include all points below). To avoid duplication, lines were matched between the different databases based upon their quantum numbers. Since not all BT2 lines are assigned with a full set of rotational and vibrational quantum numbers, we instead used the parity of the upper and lower states in this case, which can be derived from the rotational and vibrational numbers. The few remaining unmatched lines were checked manually for lines of similar frequency and intensity. Despite this, there remains a possibility of duplicated lines where assignments are radically different. However, these will generally be weak lines and some of these will be offset by corresponding mismatches. When multiple versions of lines are found, they are taken in order of preference from:

1. The experimental papers. (Jenouvrier et al., 2007; Mikhailenko et al., 2007, 2008; Coudert et al., 2008; Tolchenov and Tennyson, 2008). Since none of these include overlapping entries, there’s no need for any ordering within the papers.
2. HITRAN08, except in the 8000-9500 cm^{-1} region.
3. BT2.

In the 8000-9500 cm^{-1} region, we have taken intensities from BT2 instead of HITRAN08 because of the apparent systematic error in HITRAN for that region (see also response 5). Line broadening parameters are taken from HITRAN where available. Otherwise line widths were estimated using a method based on fitting to lines with similar quantum numbers (Voronin et al., 2010): this method has been demonstrated to provide a reasonable fit to known line widths given in HITRAN.

All isotopologues are taken from HITRAN. Ideally, we would have liked to use a theoretical database similar to BT2 to fill these, although most of the missing lines will be rather weak ones. Since the line list was initially prepared in 2008, some later experimental papers have been published containing relevant results not currently included in UCL08. Should a future need arise, it would be relatively easy to incorporate them, however.

The second figure submitted with our responses, Fig R2, shows a comparison of line intensities from the Campargue et al. and the UCL08 lists, distinguishing lines in UCL08 sourced from BT2 and from HITRAN08. This figure suggests that intensities are broadly similar between the two databases.

Comment 3: The discussion about the width of the dimer signature considers that the amplitude of the residuals between the UCL08 simulation and the BBCRDS spectra is a good estimation of the maximum values of the dimer absorption. Nevertheless the uncertainty on the BBCRDS and UCL08 simulations themselves may add additional contributions which should be evaluated and discussed. For instance, as mentioned above UCL08 line list can be compared to ICLAS line list. What is the noise level on the BBCRDS spectra? What is the error which may be induced by the procedure used to linearise the absorption cross sections?

Comment 4: Several comparisons (see for instance Fig. 5) present the BBCRDS spectra of water in air (at 1atm?) compared to a simulation from UCL08 linelist. No information is provided about the way that the UCL08 stick spectrum was convoluted with the BBCRDS apparatus function. This is of major impact for the strong lines. Also, was the pressure broadening taken into account in the UCL08 simulation? Which air broadening coefficients?

Response 3 & 4: All BBCRDS spectra were obtained in air at a total pressure of 1 atmosphere. The following text has been added to the penultimate paragraph of Section 2. “Briefly, the linearised absorption cross sections were produced as follows. High resolution absorption cross sections of the water monomer (appropriate to the temperature of each experiment) were generated from a line-by-line calculation using line intensities, ground state energies and air- and self-broadening coefficients from the UCL08 line list (Voigt line shapes; 0.0005 nm wavelength grid). These cross sections were used to calculate high resolution transmission spectra though representative column amounts of water vapour traversed by the light whilst confined inside the ringdown cavity. Typically 350 such transmission spectra were generated, spanning the time evolution of the ringdown event as recorded on the clocked CCD camera. A hygrometer (Vaisala HMT 330) provided a measurement of the water vapour concentration inside the ringdown cavity to inform the relative amounts of air- and self-broadening used in calculating the high resolution cross sections, and the range of water columns used to calculate the various high resolution transmission spectra. The high resolution transmission spectra were then degraded to the instrument resolution by convolving them with the instrument function (measured using essentially monochromatic lines from an atomic emission lamp). The low resolution transmission spectra were converted to spectra of optical depth, and the optical depth at the central wavelength of each pixel of the CCD camera was plotted as a function of water column amount. For pixels viewing wavelengths where the sample remains optically thin for all column amounts sampled during the ringdown event, the plot is a straight line with a gradient equal to the absorption cross section of water vapour at the resolution of the BBCRDS spectrometer. However, the plot of optical depth versus column amount is curved for pixels sampling wavelengths that include strong absorption lines that saturate at the large water column amounts probed towards the end of the ringdown event. But crucially the curvature of the plot is the same as the curvature of the (natural logarithm of the) ringdown signal versus time, and thus a linearised cross section derived from a linear regression of the column-dependent optical depth represents the average cross section (at the spectrometer’s resolution) presented by water molecules during the multi-exponential ringdown decay. Linearised cross sections were generated in the same way starting from the HITRAN08 dataset in order to test fitting the BBCRDS spectra with this line list too.”

Further comment: The effective use of linearised absorption cross sections relies on having accurate knowledge of (i) the spectroscopy of the narrowband absorber (line positions, intensities, widths etc), and (ii) the spectrometer's instrument function. In practice, it is difficult to separate the errors introduced by imperfect knowledge of these two. Necessarily, stronger lines produce the most curvature in the plots of optical depth versus column amount and thus provide the sternest test of the linearisation approach. However, strong lines in the water monomer spectrum tend to occur close-by other strong lines, and so errors in the parameters of neighbouring lines (within the spectrometer's instrument function) affect the linearised cross section calculated for the line of interest, even if its own line parameters are known accurately. Errors in the shape or width of the instrument function would affect the extent to which neighbouring lines are incorporated into the linearised cross section. The minimum detectable absorption signal of the present BBCRDS instrument is around 2×10^{-9} cm^{-1}, as exemplified by the baseline noise in spectral regions containing only very weak monomer absorptions (Panels 1B and 2B of Figure 6). The BBCRDS residuals are clearly larger than this towards shorter wavelengths where imperfectly fitted water monomer absorption is greatest, particularly for large monomer amounts (e.g. bottom panel of Fig 5). But for the reasons given above, it is difficult to apportion the increased residual structure (over and above the instrument sensitivity) between the various error contributions. It should be said that the water monomer concentrations retrieved from fitting the BBCRDS spectra with the linearised cross sections agreed well with the water concentrations measured by the hygrometer.

Comment 5: Fig.4 looks very strange with an intensity weighted average strongly different than the average intensity values. Does it mean that the problem on the HITRAN values affects mostly the strongest lines? A plot of the ratio versus the intensities in the 8000-9500 cm-1 region would be instructive.

Response 5: As requested, a second panel has been added to Figure 4 showing a plot of the ratio of UCL08 (= BT2 in the 8000-9500 cm^{-1} region) to HITRAN08 intensities as a function of line intensity. The strong lines, which necessarily dominate the intensity-weighted average, typically have ratios around 1.2. A majority of the weaker lines also show intensity ratios between 1.0 and 1.2, suggesting a systematic difference (see also response 2).

Comment 6: Finally, as far as I understand, the present title is not the most appropriate: instead of "An upper limit for water dimer absorption . . .." , I will propose "An upper limit on the band width of water dimer absorption. . .

Response 6: We are content to keep the current title, although we acknowledge that the main conclusion of the experimental part our study concerns the width of the dimer absorption feature, rather that its band intensity. Note that our results suggest that the 750 nm dimer band should be very wide, and thus provide a lower limit on the dimer's bandwidth.

Anonymous Referee #2, Atmos. Chem. Phys. Discuss., 10, C11129–C11131, 2010.

Comment: It seems to me that the water dimer upper limit and the new line list are two different topics and could be presented in separate papers. Fig 4 is not in the 750 nm region and could be left out.

Response: We disagree. This paper is a product of the collaboration between our research groups within the CAVIAR Consortium. This work has benefitted from, and been informed by, collaboration with other groups in the CAVIAR Consortium who also use UCL08 for their own work (see also response 2 to Referee #1).

As discussed in our paper, an accurate water monomer database is vital to account for and remove the water monomer structure in spectra attempting to record the dimer's absorption signals. Conversely, the BBCRDS spectra provide an observational test of the UCL08 line list, albeit over a limited spectral range accessed in the present work. There is a natural synergy to keeping this as a single paper. The apparent systematic difference between UCL08 and HITRAN08 shown in Figure 4 will be of interest to other groups beyond CAVIAR who use water vapour line lists in the 8000-9500 cm^{-1} region.

Comment: I think the results are nice and can stand alone without the need for section 4.2. The results of Pfeilsticker have been shown to be in error and the authors have reported this in Lotter's thesis, which is also referenced in this paper. I would delete section 4.2 and fig 6 and would rewrite without repeated reference to Pfeilsticker 2003. The reference to Pfeilsticker could be done in the introduction in a sentence.

Response: In hindsight, we agree that we placed too much emphasis on analysing the BBCRDS spectra for evidence of a Pfeilsticker absorption feature (PAF) – an early motivation for our work was to attempt to repeat the Pfeilsticker et al. study under laboratory conditions using the BBCRDS method. However, we do not believe that Section 4.2 should be deleted. Figure 6 serves a useful purpose because it demonstrates that performing experiments on the high water vapour concentrations available at elevated temperatures ought to produce sufficient water dimer concentrations to yield a dimer band many times stronger than the baseline noise in the BBCRDS spectra, assuming the theoretical line strengths and dimer equilibrium constants are broadly correct. Section 4.2 has now been shortened and re-written to place the emphasis on searching the BBCRDS spectra in Fig 6 for a 25 cm^{-1} HWHM dimer absorption signal expected from theory (like the dimer bands shown in Fig 2). Discussion of the PAF is retained for comparison purposes, but at a greatly reduced level.

Comment: The width of the OH_b stretching transition is likely wide, based on the present work and also the Garden calculation. Overtone spectra recorded of diols with increasing carbon chain length also suggest that these transitions become wider as the hydrogen bond becomes stronger. J. Phys. Chem. A, 110, 10245-10250 (2006).

Response: We thank the referee for alerting us to the above study. Rather than the strength of intra-molecular hydrogen bonds changing with increasing carbon chain lengths, the most relevant result from the above study is that the line width of the diols' hydrogen-bonded OH stretch was observed to increase with increasing excitation. This provides supporting evidence that the high overtone of the water dimer targeted in our work should also be wider than has been observed for the lesser excitations between 1,200 and 8,000 cm^{-1}. We have added a sentence to this effect in Section 5: Discussions (line 7 on page 23365).

Comment: In the figures, make the x-axis point in the same direction, e.g. from low to high wavenumbers.

Response: The x-axis in Fig 3 has been reversed and changed to wavelength (wave number is shown on the secondary x-axis above the figure). Fig 3 now runs in the same direction as the other figures.

Comment: Introduction: 23347, As far as I remember the Hill&Jones and Daniel papers, they were in different regions and not regions where one would expect the OH_b water dimer signal.

Response: The 650-1000 nm wavelength range of the Hill & Jones study includes the predicted positions of several dimer bands. The narrower 624-686 nm range of the Daniel et al. study includes the predicted position of the (albeit weak) $|0\rangle_f|4\rangle_b|1\rangle$ dimer transition.

Comment: 23348, line 3, add ref to Lotter that says Pfeilsticker's results are not correct.

Response: Agreed.

Comment: 23348, Line 18, why is M necessary?

Response: M is a third body collision partner that acts to remove the energy released when the hydrogen bond is formed between colliding two monomers, thereby stabilising the newly-formed dimer molecule. We have now deleted M from Equation 1a, partly because it is not relevant to the present work, and partly because there is some debate in the literature about how much of water's self-continuum is due to "true-bound" stable dimers (which require a third body for their formation), or "quasi-bound" metastable dimers or "free-pair states" that persist for the duration of a single collision (neither of which requires a third body) [Ptashnik et al, J. Quant. Spectrosc. Rad. Transfer, doi:10.1016/j.jqsrt.2011.01.012, in press].

Comment: 23350, line 26, delete Pfeilsticker reference.

Response: We didn't wish to imply that Pfeilsticker et al. had observed a water dimer feature; rather that they had chosen to conduct their field observations in the 750 nm region in order to target a red-shifted water dimer feature that was spectrally removed from the water monomer band. We have improved the manuscript's wording to make the later meaning clear.

Comment: 23351, line 20. The 20 cm^{-1} is similar to widths observed in OH-stretching overtone spectra of other molecules e.g. phenol, methanol, and seems like a reasonable minimum.

Response: We add a sentence "The OH-stretching overtones in gas phase spectra of other molecules such a phenol (Ishiuchi et al., J. Chem. Phys. A, 110, 7345-7354, 2006) also have bandwidths around 20 cm^{-1} HWHM." We also add a sentence after line 19 "Ptashnik et al. (J. Quant. Spectrosc. Rad. Transfer, doi:10.1016/j.jqsrt.2011.01.012, in press) have recently reviewed the various experimental observations of the water self-continuum in the near-IR, and conclude that the widths of individual water dimer bands are 50-60 cm^{-1} FWHM (25-30 cm^{-1} HWHM)."

Comment: 23353, what is the possible range of the spectrometer; i.e. could spectra have been recorded at lower or higher wavelengths than the ones presented?

Response: In principle, it is possible to access any wavelength region for which broadband pulsed light can be generated (e.g. by changing the dye in the broadband laser) and for which suitable high reflectivity cavity mirrors are available. The clocked CCD camera has usable quantum efficiencies for 350-1000nm. The BBCRDS spectrometer has been used in atmospheric field work to quantify molecular iodine in the marine boundary layer using wavelengths around 560-570 nm (Bitter et al., 2005; Leigh et al., Atmos. Chem. Phys., 10, 11823-11838, 2010) and NO_2 and NO_3 around 660 nm (Bitter et al., 2005; Fuchs et al., Atmos. Meas. Tech., 3, 21-37, 2010).

Comment: 23360, the high temp that gives the most dimer also gives more water for interference; ie possible error in simulation. Is the self-broadening of lines an issue?

Response: Self-broadening of water monomer lines is accounted for when calculating the linearised absorption cross sections used to fit the BBCRDS spectra (see above). However we agree that higher water densities give rise to stronger narrowband absorption lines that saturate at shorter times into the ringdown event, and thereby lead to a greater curvature in the multi-exponential ringdown decay. Thus there is the potential for inaccuracies in the water dimer spectral databases (and the instrument line shape) to produce larger errors in the analysis of high temperature/high water concentration BBCRDS spectra.

Comment: 23360, a width of 2 cm^{-1} is not realistic. Why was this used in simulation?

Response: Agreed 2 cm^{-1} HWHM is too narrow for the water dimer absorption. The simulations include 2 cm^{-1} HWHM because this is the minimum line width observable for our BBCRDS spectrometer's instrument function. In the final paragraph of the Introduction (and elsewhere in the paper), we state that previous studies suggest that the bandwidth of dimer absorptions is likely to be around 20 cm^{-1} HWHM.

Comment: 23364, line 2, I would mention here that Kjaergaard et al, J. Phys. Chem. A. 112, 4324-4335 (2008) shows that even with different vibrational models similar overtone intensities (only done for v=2 in the paper) are obtained, thus further supporting the range of intensity values used in the present study.

Response: We have noted this in the revised manuscript, and added a reference to the above paper.

Comment: 23366, line 13, the $\mathrm{OH_b}$ stretching transition has not been measured in the first overtone region, like due to its low intensity.

Response: Agreed, the theoretical studies predict that the v=2 $\mathrm{OH_b}$ stretch is weak. Note that there is observational data in this region: Paynter et al. (2009) have recorded the water self-continuum around 7200 cm^{-1} that underlies the v=2 OH stretching bands of the water monomer, although assignment of the self-continuum's band structure has yet to be performed (see also Ptashnik et al., JQSRT, in press). [We apologies for an error in the title of the Paynter 2009 reference as given in the original manuscript: the correct title is "Laboratory measurements of the water vapour continuum in the 1200–8000 cm^{-1} region between 293 K and 351 K".]

Comment: 23366, the width of the water dimer bands are important for its absorption of sunlight.

Response: We have noted this important effect in the manuscript.

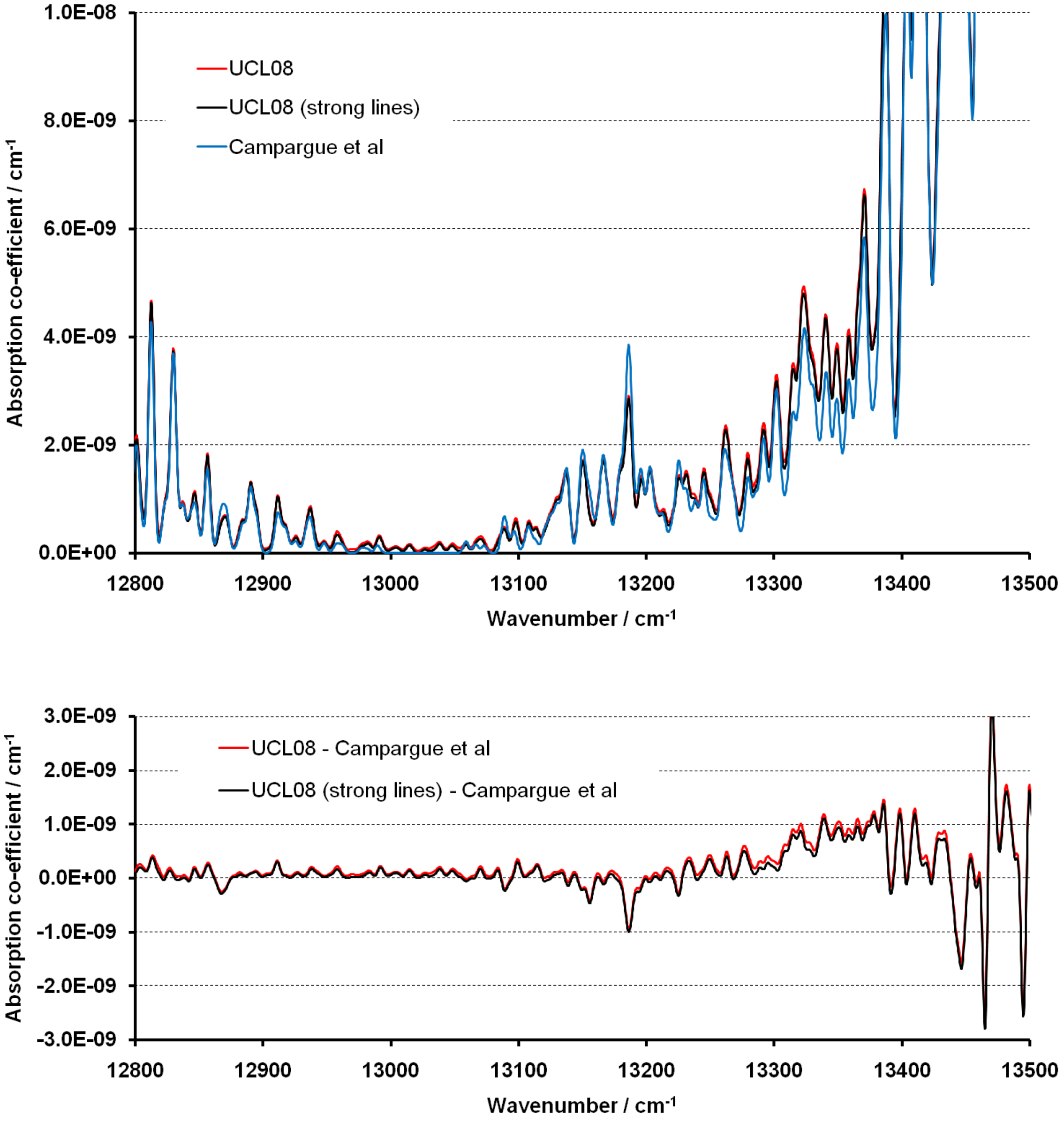

Figure R1: Top panel: Absorption spectra calculated for 10 Torr of water vapour (296 K) using the UCL08 and Campargue et al. (2008) line lists and an assumed Gaussian instrument function of 5 cm^{-1} FWHM. The spectrum shown in black and labelled “UCL08 (strong lines)” uses only the stronger lines from the UCL08 list with a cut-off intensity of $S > 1.6 \times 10^{-28}$ cm $molecule^{-1}$, corresponding to the minimum intensity of lines in the Campargue et al. data. The spectrum shown in red and labelled “UCL08” was generated with lines down to a cut-off intensity of $S = 1.0 \times 10^{-30}$ cm $molecule^{-1}$. Bottom panel: the differences between the UCL08 spectra and the Campargue et al. spectrum.

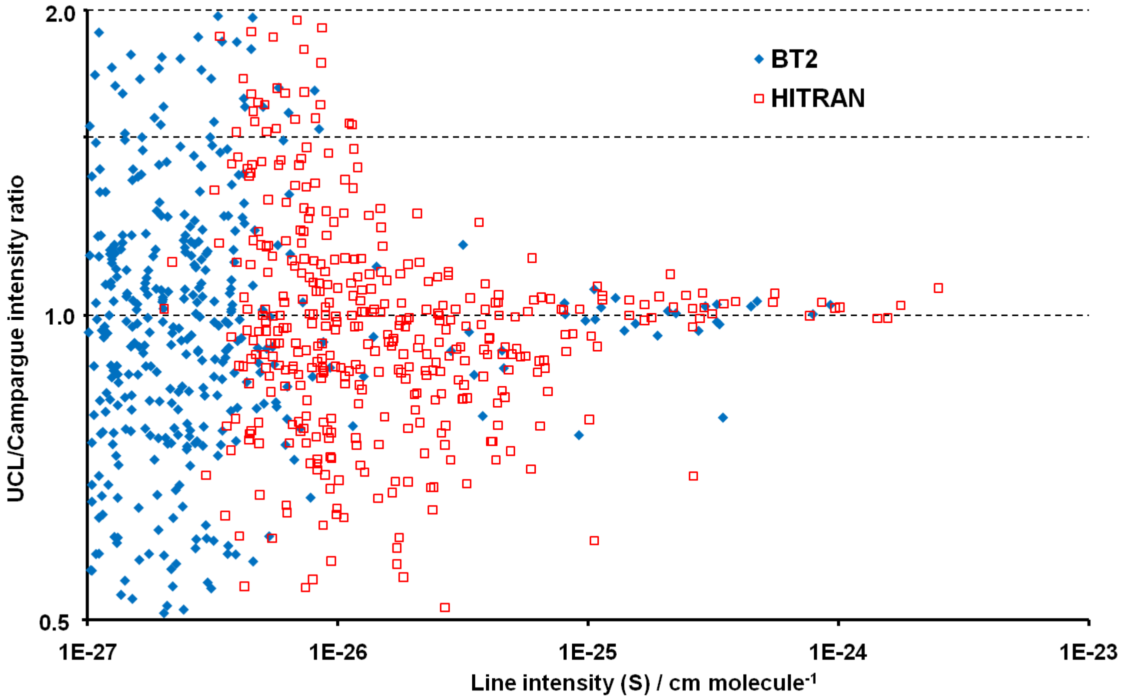

Figure R2: A plot of the ratio of line intensities for lines present in both the Campargue et al. (2008) and UCL08 lists. Red squares and blue diamonds represent line parameters from UCL08 that were sourced from the HITRAN08 and BT2 databases, respectively.