Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2022-139

Anonymous Referee #2

Referee comment on "Cavity ring-down spectroscopy of water vapor in the deep-blue region" by Qing-Ying Yang et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-139-RC2, 2022

Yang et al. describe a new cavity-ringdown instrument for high spectral resolution measurement of water vapour absorption around 415 nm. Despite the atmospheric abundance and radiative importance of water vapour, the experimental measurement of its absorption in the blue/near-UV spectral regions has proved surprisingly challenging. This work fills an important gap in our understanding of this key atmospheric species.

The spectral measurements reported here are a significant advance on earlier experimental studies which were limited by a lack of sensitivity. The work of Yang et al. provides indirect evidence that experimental studies showing strong near-UV absorption by water vapour need to be treated with caution. The results of the study are also relevant to recent theoretical work to inform the HITRAN database. The study provides a full quantum assignment to a number of the observed transitions. This work also points to the need to continue both theoretical and (especially) experimental investigations in the blue/near-UV absorption spectrum of water.

Comments:

- This paper describes spectra around 415 nm and labels this the “near-UV”. 415 nm is firmly in the visible spectrum which extends from 400 to 700 nm according to most definitions. The generally accepted definition of near-UV extends up to 400 nm (e.g., UV-A: 315-400 nm). Their use of “near-UV” in referring to their measurements is therefore misleading. I recommend that the terminology throughout the manuscript, including in the title, be changed to reflect this distinction, for example, by replacing “near-UV region” with “at deep blue wavelengths” or something similarly appropriate

elsewhere.

- Further experimental detail is needed. What is the frequency or period for acquisition between individual ringdown measurements? What is the wavelength interval and laser linewidth?
- Attribution of the interference fringes to the cavity mirrors seems reasonable but speculative. There are other system components that could give rise to the same effect, including the ½ wave plate and lenses. A more definitive identification of the source of the fringes should be provided.
- 4: "minimum detectable absorption coefficient of about 4*10−10 cm−1". This statement seems to confuse the standard deviation (precision) with a limit of detection (usually a specified factor of 2 or 3 greater than the measurement precision). Using the label "standard deviation of the residual", or the measurement precision, would be more correct.
- The same reasoning should be applied to the "minimum detectivity of the cross section around 1.5*10−27 cm2 molecule−1" and the criterion for identifying a minimum line intensity should be stated explicitly.
- 113: The authors attribute the main intensity uncertainty to exchange between the gas phase and container walls. Is this not just the uncertainty in pressure during the measurement? The main uncertainty seems to be the measurement precision relative to the signal (peak) size (alluded to in l.116). The dominant source of absorption uncertainty should be clarified.
- In this regard, it would be helpful to see example spectra of absorption lines in the B & C uncertainty category, not just type A absorption lines as shown in Fig. 2.
- 172: Although measurements of water vapour could affect the absorption spectra and retrieval of other trace gases, this and other studies of water vapour measurements imply that such potential interferences are unlikely — at least, at the current absorption sensitivities of atmospheric instrumentation.

Minor textual issues

- Citation style in the manuscript text should follow the standard AMT style and enclose citations in brackets. It is confusing to have references appear in the middle or end of sentences without any distinction between sentence text and citation text.
- 90: It is unclear what is meant by "pressure on dates".
- 174 (Table 1). Add "to": "correspond TO fractional uncertainties of 5-10%, 10-30% and > 40%,"