Author's reply to comments from the referee #2 (H. Chen)

We would like to thank H. Chen for his careful reading and comments as well as suggestions. Listed below are our replies to the referee's comments and suggestions. We have revised our manuscript accordingly.

Main comments

(1)

<Referee> Regarding the PBEs of the WS-CRDS CO_2 and CH_4 measurements, one should be aware that a direct way of removing them is to determine the mole fractions of a species of interest from the integrated absorption area instead of from the absorption peak height, which would be practical when the variations in background gases are unavoidable, and cannot be determined easily. Certainly, the measurement would be less precise (when compared to 0.03 ppm for CO_2 and 0.3 ppb for CH_4), but I wonder whether it will be more precise than the measurement determined from the peak height with the estimated PBEs removed based on the method presented in this paper. Can the authors give a comparison of the estimated uncertainties caused by the two different methods?

<Reply> First of all, as you know, WS-CRDS quantifies mole fractions of CO_2 and CH_4 based on the absorption peak height to obtain high precision and excellent long-term stability. We believe that these prominent advantages of WS-CRDS will far outweigh the disadvantages, particularly for the field observations. Our study does not intend to recommend exact correction of the PBEs associated with the matrix gas composition based on our method. We would rather show that such cumbersome bias can be avoided based on our study as well as your study. Although we did not make comparison with other methods (e.g., OA-ICOS instrument), we believe that our study clearly shows WS-CRDS is promising method for the field observation at least.

(2)

<Referee> It may be necessary to reconsider the "accurate measurements" in the context of "transferability" for water vapor corrections for CO_2 and CH_4. The WMO recommended inter-laboratory comparability goal for CO_2 is 0.1 ppm and 0.05 ppm for the northern hemisphere and the southern hemisphere, respectively, and for CH_4 is 2 ppb. I recommend the authors take a different accuracy target than the precision of the measurements when discussing the transferability. Note that the residuals from the fitted water correction functions for the G-1301 (Fig.5), 0.08 ppm for CO_2, and 0.8 ppb for CH_4 are already larger than the precisions. Furthermore, regardless of the transferability of the water vapor corrections, an

alternative way of making high-accuracy measurements of CO_2 and CH_4, rather than performing complete or moderate drying of the air followed by the application of a water vapor correction function, is to develop instrument-specific water corrections as has been done by the authors and researchers in other labs.

<Reply> We have revised the section 5 on the water correction. In the section, we discussed two topics independently: (1) whether the water correction function from one instrument to other instruments is transferable based on our experiments, (2) differences in the water vapor correction values from these functions as well as from past studies (Chen et al. (2010), Winderlich et al. (2010)).

Specific comments

<Referee> P5010, Abstract: It will be helpful to add a sentence like "the pressure-broadening coefficients (PBEs) due to variations in O_2 and Ar for CO_2 and CH_4 are empirically determined, and are linearly correlated with the differences between the mole fractions of O_2 and Ar and their ambient abundances"

Also as mentioned above, I recommended the authors rephrase their conclusions on the transferability and complete/moderate drying of air samples for accurate measurements of CO_2 and CH_4.

<Reply> Thank you for your comments. We have added the sentence in Abstract. We did reanalysis on the water vapor correction according to the comment from the referee #1. As a result, we got the same conclusion with the original one. Please check our revision in section 5.

<Referee> P5011/Line 20, add "measurements of the total" before "column abundances…"

<Reply> We have revised the sentence accordingly.

<Referee> P5012, Please also check WS-CRDS measurements of CO2 (Richardson et al., 2012 in "Journal of atmospheric and oceanic technology")

<Reply> We have added and cited the report by Richardson et al., (2012), and revised accordingly.

<Referee> P5013/Line 23, Change "inverse modeling work" to "further investigation"

<Reply> We have revised the sentence as indicated.

<Referee> P5013/Line 25, Since the impact on synthetic standard gas measurements is only one application, a sentence like "the correlations between the pressure-broadening effects (PBEs) and variations in background gases N_2, O_2, and Ar" will better

describe the section than the original one.

<Reply> We have revised the sentence as indicated.

<Referee> P5014/Line 11-12, "…by adjusting the flow rate using two solenoid valves placed at the inlet and outlet of the cavity" is not true if the WS-CRDS analyzer is a mobile version, which controls a constant flow rate based on a critical orifice. Since the description here is given in general, I would leave out this part of the sentence.

<Reply> We have removed the sentence as indicated.

<Referee> P5018/Line 6, Change "Thus PBEs…" to "Thus the delta coefficients…"

<Reply> We have revised the sentence as indicated.

<Referee> P5018/Line 19-20, what are the precisions of the mass flow controllers? Are the precisions dominating the errors in the calculated dilution effects in Eq. (10)?

<Reply> In this study, we measured the flow rate of the compressed air and the inert gas from the high pressure cylinders with the high precision flow meters, Molbloc while the flows were controlled with the commercially available mass flow controllers. This means that the errors of flow rate are subject to the error of Molbloc, not to that of the mass flow controllers. The manufacturer of the Molbloc guarantees measurement uncertainty less than ±0.02% of the maximum flow rate. On the other hand, the manufacturer of the mass flow controllers guarantees measurement uncertainty less than ±1.5% of maximum flow rate. Thus the Molbloc has high accuracy far beyond that of the mass flow controllers. For example, in this study, errors derived from the dynamic mixing of the compressed air and pure nitrogen is typically less than 0.4% against the excess N_2 mole fraction (e.g., maximum error is estimated to be 20 ppm against 5000 ppm of excess N_2).

<Referee> P5020/Line 6, Change "mixing ratios" to "mole fractions"

<Reply> We have revised the sentence as indicated.

<Referee> P5020/Line 14-18, Here the PBE for N_2 is biggest because the abundance of N_2 is biggest, and that a relative increase of 2.5% of the abundance was considered. Given the same absolute increase for all three species, the PBEs are not very different. Especially for O_2 and Ar, the difference might not be significant. Considering the uncertainties in the pressure-broadening coefficients obtained in Nakamichi et al. 2006, the coefficients (0.067±0.002 and 0.062±0.002) are also very close. Then I have a problem understanding why the delta coefficients for O_2

and Ar (in Table 1) are so different?

<Reply> The pressure broadening coefficients reported by Nakamichi et al. (2006) have different physical dimension from our estimated coefficients, requiring several measured values (FWHM (full width at half maximum), HMDL (half width at half maximum)) which are not shown in their report to compare the coefficients from between Nakamichi et al. (2006) and our experiment under the same dimension. Thus we can’t exactly their values with ours in simple manner. However, the relation of the magnitude of these coefficient values will be the same (N_2>O_2>Ar). Actually this relation is not specific to atmospheric sensing, and the same relationship (N_2>O_2>Ar) suggests validity of our experimental results qualitatively.

<Referee> P5021/Line 26-27, it is acceptable to use purified air for gas standards as long as the potential bias due to the removal of O_2 is quantified. It is certainly preferred to synthetic air, but not as ideal as real ambient air.

<Reply> Absolutely, we think so. However, it is not straightforward to prepare several standard gases with appropriately different mole fraction of CO_2 and CH_4 for atmospheric observation. As an example, we have added preparation of our standard gases using natural ambient air for WS-CRDS calibration in the manuscript.

<Referee> P5021/Line 13, –0.05 ppm for CO_2 is not big, but not negligible. This potential effect should be aware of when making high-accuracy measurements.

<Reply> Because the estimated PBE –0.05 ppm for CO_2 is maximum value, and typical PBEs is estimated to be less than –0.02 ppm for CO_2 according to our O_2 analysis (almost all of O_2 mole fraction is less than ±500 ppm relative to the atmospheric O_2 mole fraction), we described that the impact is negligible. Here, we have rephrased the sentence for revision accordingly.

<Referee> P5023/Line 13, Eq. (14), change ${}^{18}R_{std}$ to ${}^{18}R_{ref}$. And similarly for Eq. (16).

<Reply> We have revised the sentence as indicated.

<Referee> P5026/Line 15, Please specify how was 0.16% (below zero dew point) water vapor achieved.

<Reply> We made small modification on the humidifier. Detail description has been added to the manuscript.

<Referee> P5033/Table 1, what are CO_2x10^7, and CH_4x10^8? If they are the magnification

factors of the coefficients, seem to be too large.

<Reply> Thank you for your indication. These values (10^7 for CO_2 and 10^8 for CH_4) were mistyped during typesetting process. The correct values are 10^{-7} for CO_2 and 10^{-8} for CH_4. Also, please note that units of the variables, C_{target}, δO_2, and δAr in Eq. (6) are ppm while that of PBE is given in ppm for CO_2, and ppb for CH_4.

<Referee> P5041/Fig. 6, I suggest plotting the differences against the reported water vapor, since it is the case in Table 3 as well as in available publications. How was the one sigma calculated here? A calibration of the water vapor scale is given in Winderlich et al. 2010, Page 1118, Eq. (1). How do these water vapor calibrations compare?

<Reply> Thank you for your advice. According to the comment from the referee #1, we did reanalysis on the water vapor correction. In the improved discussion, we evaluated the transferability and difference of water correction function from this study and the previous studies against the reported water vapor. Please check our revision.