Reply to the reviewer 2's comment

We thank the reviewer for their suggestions and comments, which has improved the quality of our manuscript. The manuscript has been rechecked and the necessary changes have been made in accordance with the reviewer's suggestions. The responses to all comments are given below. The revised text in the manuscript has been indicated using blue-coloured font to distinguish it from revisions made in response to the comments of Reviewer #1.

Reviewer #2: In this study, the authors apply metrological techniques to the measurement of radiative efficiencies for select greenhouse gases, which can be used to reduce uncertainties in global warming potentials. The manuscript presents a very detailed uncertainty analysis, going far beyond anything I have previously seen in the determination of radiative efficiencies. It also contains the first radiative efficiency value for PFMEE, a future refrigerant alternative. I recommend this for publication once the following issues are addressed.

(1) Overall I found this a rather difficult manuscript to read through, so it will require editing for English prior to publication. Additionally, the text is riddled with acronyms. I have never seen so many, particularly for simple two-word terms, e.g. atmospheric lifetime (AL) or reference cell (RC). I think such acronyms should be removed for ease of comprehension.

- Thank you for your comments. Regarding the English writing, we had our manuscript proofread by a native speaker. We have also removed the excessive acronyms.

(2) Why did the authors chose to determine the path length of the multipass cell spectroscopically? With a quoted value of 3.169 ± 0.079 m, this gives an overall uncertainty of 2.5 %. Why did the authors not use a laser distance meter? With such an instrument, I have seen path lengths of multipacks cells determined with uncertainties an order of magnitude better than presented in the submitted manuscript.

- Thank you for your comment. We chose a spectroscopic technique because it enhances the simplicity in the calibration of optical path length by using the same spectrometer for absorption cross-section measurement. Additionally, the spectroscopic calibration method reduces potentntial systematic bias between in-spectrometer measurement and external laser distance meter measurement. Owing to substantial uncertainty in the curve-of-growth analysis, one of major uncertainty sources, total uncertainty in the optical path length through spectroscopic calibration appeared to increase further than that of the laser distance measurement. But, this held true only when there was the systematic error arise from the difference in the in-spectrometer and laser-measured optical path length, which is harly assesible.

(3) The path length of the reference cell was determined (mechanically) to be 20.01 ± 0.05 mm. During a measurement using the 125HR spectrometer, however, the IR beam is not collimated through the cell but is focused at the center. This means that the effective optical path length is slightly longer than that determined from a simple mechanical measurement (< ~0.5% longer). Did the authors consider this at all? Simple ray-tracing software could determine this optical path length more accurately.

- Yes, we had considered this, although we did not thoroughly discuss or include it in the uncertainty analysis. This was because we used a rather short reference cell (2 cm) and a smaller aperture size (2 mm). The shorter length and smaller aperture size benefited from a lower potential for error due to the possible path length deviation from the angle of the actual light beam from the optical axis θ.

Discussion regarding this issue with respect to TDLAS experiments has been published in a study by Nwaboh et al. (2014). A conservative approach is to consider that the angle of the actual light beam deviates at the maximum angle from the optical axis $\theta = \theta_{max}$. Figure 1 (below) illustrates the situation when the conservative approach is used. The effective optical path length L_{ref} is a function of the measured length from mechanical measurement L_{cert}, free optical aperture d, and θ_{max}. The relationship between the parameters are $\Delta L = L_{cert} \times (1/\cos\theta - 1)$ with $|\theta| \leq |\theta_{max}|$, and $\tan\theta_{max} = d/L_{cert}$.

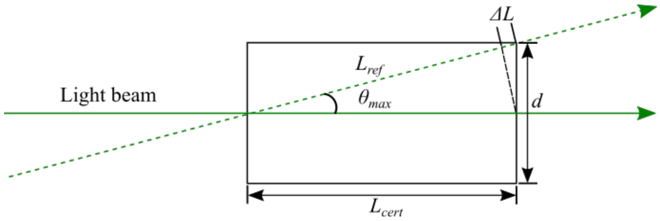

Figure 1. Illustration of the propagation of a light beam inside the reference cell. The effective optical path length is slightly longer than the length determined from a simple mechanical measurement.

For a clear idea of the free aperture size, we simulated the light beam propagation in 3DOptix software (https://design.3doptix.com/). Figure 2 (below) shows the simulation setup. A light source with a diameter of 2 mm was focused using a 400 mm aperture focusing lens. The actual focal length of the FTIR collimator was 418 mm. We were unable to set it to 418 mm due to a software limitation that only allowed for commercially available lenses. The beam was then directed toward two screens, simulating the two faces of the cell window. The distance between two screens was set at 20 mm. The detailed hit image on the screen was then evaluated.

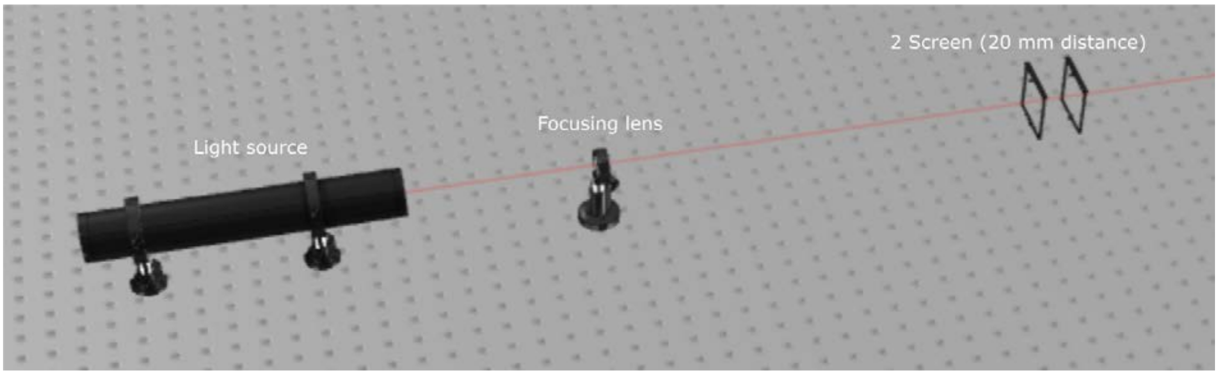

Figure 2. Simulation setup to check for a possible deviation of the actual optical path length from the mechanically measured path length.

Figure 3 (below) shows the simulation result of the beam hitting the surface of the reference cell. The beam hit with a diameter of approximately 0.44 mm, as seen in the first screen. As the beam travels through the cell, its diameter expands to 0.6 mm. Thus, we can estimate d, θ_{max}, and ΔL according to the simulation result. We considered d=0.3 mm (half of the beam size in the second detector screen), thus resulting in θ_{max} = 0.8589° and ΔL=0.002249 mm. This result is equal to a relative expanded uncertainty $U(\Delta L)$= 0.011%, that can be negligible compared to the uncertainty from mechanical measurement.

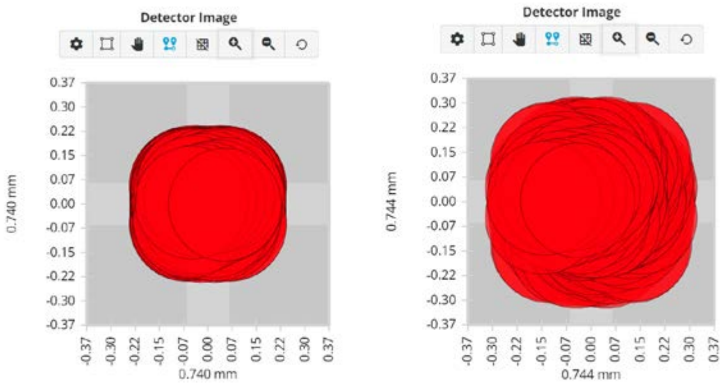

Figure 3. Simulation result of the beam hit at (left) the first detector screen, and (right) the second detector screen.

(4) What is the contribution of the Bruker non-linearity correction to the uncertainties? This doesn't appear to have

been discussed. The correction has the potential to introduce errors in the spectrometer's "zero transmission" level, which will bias the analyses.

- Thank you for your comment. The Bruker nonlinearity correction helps eliminate the ghost spectrum, which is the observation of a ghost signal outside the sensitive spectral range (out-of-band) of spectrometer detectors. We did not explain this in detail in the paper because the ghost spectrum for MCT detectors typically occurs at wavenumbers below 500 cm^{-1}, as reported in the following study:

https://www.researchgate.net/profile/Richard-Lachance/publication/308400303_Non-linearity_correction_of_FTIR_instruments/links/57e2c33c08ae0e3158a6b6a4/Non-linearity-correction-of-FTIR-instruments.pdf.

In addition to the nonlinearity correction, the ghost spectrum was eliminated from our measurement setup by applying a 500 cm^{-1} cut-off frequency. Therefore, the uncertainty due to zero-level offset could be avoided. If "zero transmission" did exist, it would have been cancelled during the process of the absorption spectra being generated by a ratio between I (with absorber) and I_0 (without absorber) spectra. Imperfect correction can be accounted by the uncertainty of the responsivity drift

(5) The authors need to define the term "responsivity drift".

- We have added the definition of the term "responsivity drift" to the main text. The responsivity drift of the FTIR spectrometer occurred as a variation of the measured radiance of the light source. This drift can occur owing to various causes, such as the temporal variation in radiant intensity of the light source, and the detectection sensitivity..

Technical corrections:

line 17: path length, not pass length

- This has been corrected as suggested.

line 76: Voigt, not Voight. Note that Voigt is spelled incorrectly throughout - please correct.

- This has been corrected throughout the manuscript, as suggested.