Response to reviews of paper

Advancing Halocarbon Radiative Efficiency Estimates by coupling radiative transfer and quantum chemical calculations: impact of updated spectroscopic parameters and low-frequency contributions

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Black plain font = reviewer comment

Blue Italic = author response

In addition to the responses to the reviewer comments, a small number of minor grammatical changes have been made to the paper.

REVIEWER 1

General Comments:

This preprint reports an update to the Pinnock curve reflecting changes in spectral line parameters in the HITRAN2020 database and the updated MT_CKD_4.3 water vapor continuum. The impact of these changes on the shape of the Pinnock curve and radiative efficiency values for 30 halocarbons is discussed. In particular, the manuscript focuses on wavenumbers below 500 cm^{-1} and employs a rigorous anharmonic quantum-chemistry protocol to calculate radiative efficiencies *in silico*.

The content of the preprint is scientifically sound, and the work significantly contributes to the fast calculation of climate metrics (radiative efficiencies and global warming potentials) workflow by updating the Pinnock curve and then providing this curve to the community in the Supplement. The manuscript is well organized and clearly written. It will be ready for publication after addressing the minor revisions listed below.

We thank the reviewer for this thorough and positive assessment to our paper.

Specific Comments:

Introduction

Line #24: The phrase “the greenhouse capacity” is at odds with the following discussion of the RE climate metric in lines #24-26. Generally, the “greenhouse capacity” is associated more with the GWP of a gas. Perhaps a different phrase can be used instead.

We agree, although we are not sure that the phrase is particularly associated with the GWP. We replace “capacity” by “strength”.

Lines #54-57: The phrase "without any other change in the climate system" should be clarified because Shine and Myhre (2020) included the stratospheric temperature adjustment, which does account for some change in the climate system. This could be mentioned at the end of line #57.

Thank you – we think some editing led to this incorrect description. The original Pinnock curve was the pure instantaneous forcing. We modify the text to make the later addition of stratospheric temperature adjustment clear.

Methods

Line #104: The sentence mentions the “most recent updates in the HITRAN and MT_CKD”. This sentence should be rephrased, given the release of HITRAN2024 and the use of HITRAN2020 in this work.

Yes, we agree that this needs rephrasing. To make clear that the changes incorporated in HITRAN2024 are minor compared to those in HITRAN2020, we add the HITRAN2024 curve to Figure 2 (see below) – given this minor impact, and the timing of the release of HITRAN2024, we were not in a position to fully incorporate HITRAN2024 in the final Pinnock curve because this was a substantial computational task. We have altered the text above, and incorporated new text at the end of Section 2.1 to make clear where HITRAN2024 is used and where it is not, in the remainder of the paper. In Section 3.1 we then discuss the (small) impact of HITRAN2024 on our results.

Please also see our response to minor comment #1 from Reviewer 2.

Lines #120-121: The use of different basis sets for C, H, F versus Br stands out and needs to be justified further. While it is understandable that these basis sets are mixed to be computationally cost-effective, the mixing of jun-cc-pV(T+d)Z and aug-cc-pVTZ-PP leads to a basis set imbalance. The resulting C-F and C-Br bonds can be too long/short, directly affecting energy derivatives used to calculate the harmonic and anharmonic spectra. A counterpoint could be that this QC approach yields relatively accurate RE values, as per Alvarado-Jiménez and Tasinato (2024); however, this argument should be made in text.

The use of different basis sets for C,H,F and Br atoms is indeed inherited from the original 2024 paper, where this combination was benchmarked. The choice was motivated by (i) knowledge of the good performances of the jun-cc-pV(T+d)Z basis set for first- and second-row atoms and (ii) the need to include effective core pseudopotentials on Br. For the latter, Petterson’s ECPs were only available for augmented- (aug-cc-pVnZ) and non-augmented (cc-pVnZ) basis sets. In any case, for C, H, and F atoms, the use of the jun-augmented basis sets instead of the aug-augmented counterpart was not expected to impact particularly on the vibrational frequencies and intensities related to the normal modes mainly involving those atoms. For the purpose, we carried out additional tests on $CHBr_3$ and CH_2Br_2, by using the aug-cc-pVTZ basis set for C and H: vibrational frequencies

agree within 5 cm^{-1} (2 cm^{-1} on average), while IR intensities agree within 20% at most (3% on average). With these data, REs obtained by using aug-cc-pVTZ and jun-cc-pVTZ basis sets differ by about 0.0001 W m^{-2} ppb^{-1}. A comment has been added to the methods section.

Line #132: The "relevant thermal conditions" should be defined by providing a temperature or temperature range used when accounting for conformer populations.

Conformer population analysis was carried out by considering Gibbs free energy evaluated at 298 K. This has been clarified in the text.

Line #133: The phrase "incorporating spectral data" should be qualified by mentioning that it is calculated spectral data.

This has now been specified.

Line #144-46: While it is understandable that using DSDPBEP86-D3 may be computationally impractical for an anharmonic calculation of HFC-43-10mee, the mixing of different levels of theory for the HFC-43-10mee calculation needs to be justified further. Paraphrasing the key points in the "Computational details" section of Alvarado-Jiménez et al. (2026) may help.

Some more details and references have been added.

Line #150: The choice of HWHM of 5 or 30 cm^{-1} should be justified. Is the HWHM chosen to ensure the QC spectrum resembles/matches experimental spectra?

We now specify that the molecular weight was the main driver of the choice. Actually, a HWHM that, according to our experience was a sound approach for the molecular masses, was employed. No attempt was made to tune with respect to experimental band shapes.

Line #165-69: A sentence or two on the exact atmospheric lifetime adjustment (degradation by OH or photolysis in the stratosphere) used for each family of compounds studied should be included.

The lifetime adjustment procedure has been described more clearly in the text, linking the type of adjustment with molecular composition.

Line #173: The sources of error that contribute to the "average uncertainty of about 5%" for QC cross-sections should be outlined. Is this based on the deviation values presented in Table 1 in Alvarado-Jiménez and Tasinato (2024)? If so, this should be clarified.

The error estimate is indeed mainly based on the results from previous paper (and also confirmed by the subsequent studies, including the present one). Following Reviewer suggestions this has now been better clarified.

Results

Line #234: The QC calculations account for anharmonic corrections to wavenumbers; however, there can still be a mismatch between calculated IR absorption wavenumbers and peak locations in experimental data. Since the location of each QC peak affects the integrated band strength (Table 1) and RE values (Table 2), were QC peak locations checked versus available experimental data?

We probably did not fully catch the question. While peak locations do affect the RE (by placing the absorption in a given interval of the discretized Pinnock curve), it does not strongly impact the intensity. Strictly speaking, from a more technical point of view, harmonic (and not anharmonic) wavenumbers enter the perturbative expressions of the transition dipole moments used to obtained intensities beyond the double harmonic approximation. Clearly, there are few insights to be gained in comparing harmonic wavenumbers with respect to experimental values.

In any case, as far as anharmonic wavenumbers are concerned, DSDPBEP86/triple-ζ calculations deliver a mean absolute deviation from experimental data around 8 cm^{-1} (also note that DSDPBEP86 performs the same as, or slightly better than, the rev-DSDPBEP86 functional considered by Barone et al. Front. Chem. 8, 584203, 2020).

Line #283-285: The phrase "the proportion of the total RE" should be clarified. Does the total RE here refer to the value from QC calculations or experimental data? In addition, the statement "(here defined as 0-500 cm^{-1})" conflicts with the lower experimental wavenumber of 150 cm^{-1} in line #282. Perhaps this statement can be moved to the methods section, or the statement "the far-IR region (here defined as 0-500 cm^{-1})" could be replaced with "low-wavenumber region".

Concerning the cited sentence, reference is made to experimental analyses performed on the four molecules, that then were compared to the contribution evaluated by QC calculations. The text has been modified to clarify this point. We also replaced "far-IR region (...)" with "the region below 500 cm^{-1}". In this case, part of the conflict arose because the experimental measurements start at slightly different wavenumbers (around 150 cm^{-1}), while when QC results are used, the full spectral range is available. In this respect, when QC calculations are employed, the low-frequency region is indeed 0 – 500 cm^{-1}. For the four molecules for which the comparison between QC calculations and experiments is possible, we verified, in previous works that the 0 – (c.a.) 150 cm^{-1} contribution accounted for in the QC simulations does not bias the comparison.

Line #285-286: An explicit reference should be made to Table 2 by providing the exact QC calculation low-wavenumber contribution percentages when comparing to experimental percentages mentioned in line #284.

Thank you . We have modified the text to make the comparison with the Table 2 values clearer.

Code and data availability

Thank you for providing the updated Pinnock curve in an easily accessible format. The curve provided is at a resolution of 10 cm^{-1}. If possible, please include an additional file with the Pinnock curve at 1 cm^{-1} resolution (as was done in past iterations of the Pinnock curve).

The incorporation of the new MT_CKD formulations into the line-by-line code used in Shine and Myhre was well beyond the scope of this research and to use the technique we describe at (original) lines 216-218 to modify the 1 cm^{-1} results would be unjustified as the narrow-band model does not possess detail at this higher spectral resolution. Hodnebrog et al. (2013 – their Section 3.3.1 and Figure 6)) demonstrate that, for the vast majority, of molecules tested the 1 and 10 cm^{-1} curves result in radiative efficiencies that agree within 1.5%. This is relatively small compared to other uncertainties discussed at the end of Section 2.3.

Technical Corrections:

Introduction

Line #43: There is a typo "double-**hybdrid**".

Thank you – corrected.

Methods

Line #129: There is an error in the in-text citation "GAUSSIAN 16 (Frisch et al.)" where the year is missing. The Gaussian website (https://gaussian.com/citation/) mentions "year={2016}" under "BibTex Starting Point".

Thank you – corrected.

Conclusions

Line #323: There is a typo "**funtional** in earlier".

Thank you – corrected.

Figures

If possible, please increase the font size for Figures 1-4.

We have increased the font size in all figures. Below is Figure 1.

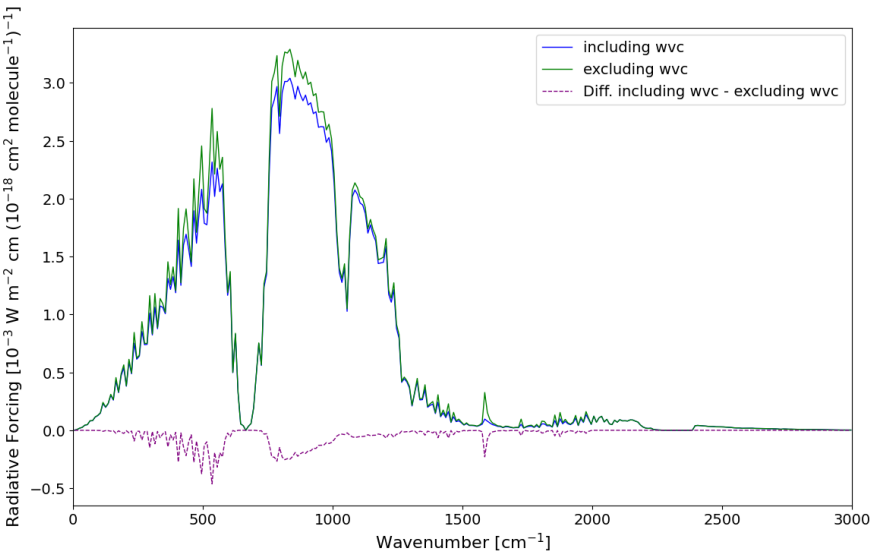


Figure 2: There is inconsistent spacing between MT_CKD and 3.2 or 4.3 in the legend.

Thank you – the new figure is shown below. It also now includes the difference between HITRAN2024 and HITRAN2016 in response to Reviewer 2 Minor Comment 1, and modify the text accordingly to note this addition.

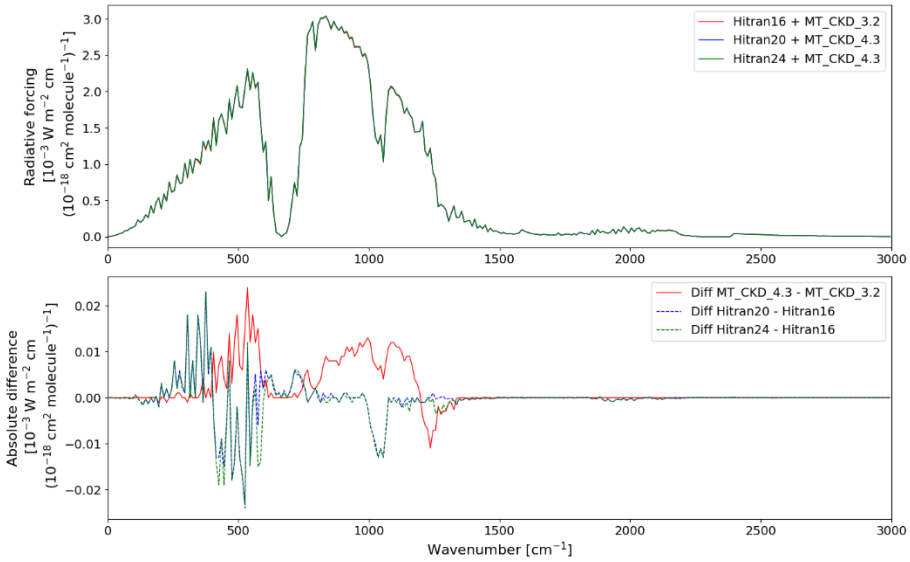
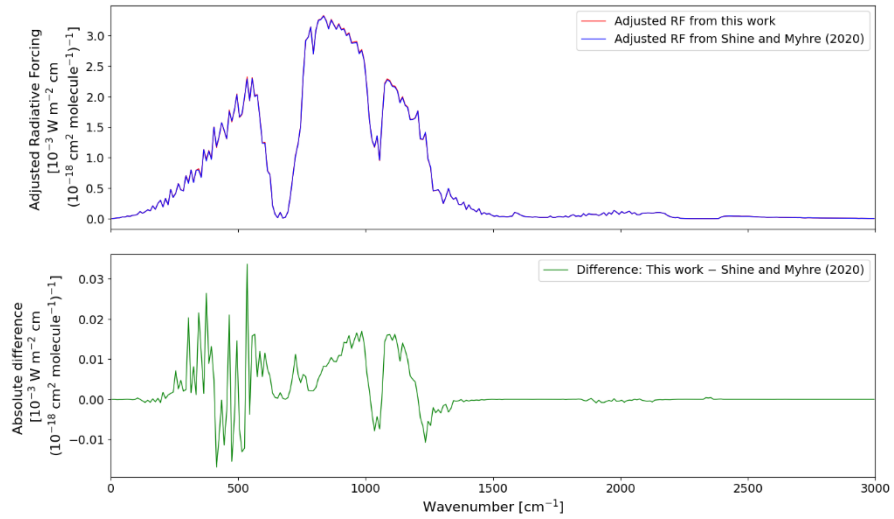


Figure 3: A closing bracket "]" is missing in the top panel y-axis label. Both panels have background grids that are absent in Figures 1 and 2. The lines in both panels seem thicker than those in Figures 1 and 2. Line thickness and background grids should be consistent between figures.

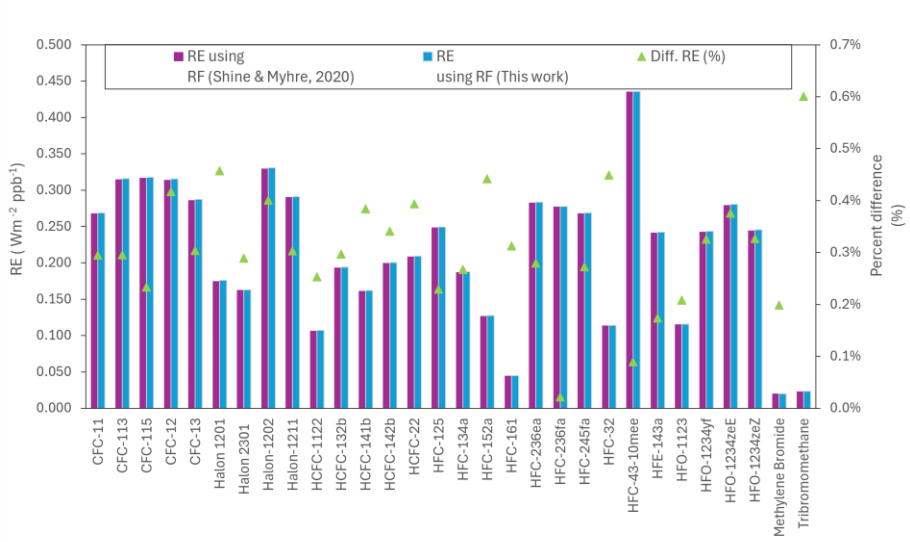
Thank you – we have made the requested change and made all figures consistent.



183

184 Figure 4: The gray border around this figure should be removed. The green line is
185 distracting; perhaps disconnected green markers could be used instead. The "Diff.
186 RE(%)" text is too close to the "Methylene Bromide" label.

187 *Thank you for these very helpful suggestions. We have altered Figure 4, as shown below,*
188 *to take them all in to account*



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190 **Tables**

191 Table 2: Ideally, each table should be independent of the main text. As such, please
192 provide the wavenumber range for the "total RE" in the table caption. The column labels
193 "RE (this work)" and "REThis work / REVan Hoomissen" should explicitly indicate that
194 these columns are restricted to the low-wave number region to avoid confusion with RE
195 values in the last column at an initial glance.

196 *We thank the reviewer for the suggestion. Column title, header and footnotes have been*
197 *modified to make the table self-consistent.*

REVIEWER 2

This is an excellent paper that assesses quantitatively and qualitatively

1. How do HITRAN2020 and MT_CKD4.3 affect the Pinnock curve?

2. Do the new data noticeably alter halocarbon radiative efficiencies?

3. How important is the typically neglected 0–500 cm^{-1} region?

The authors apply a systematic approach, isolating the effects of HITRAN and MTCKD changes and then assessing the combined effect. Figure 2 is very telling. The FIR region discussion is important as it shows that although the contribution is small, it is molecule-dependent, reaching 3% for some species. I believe the paper should be published.

We thank the reviewer for their positive assessment of our paper.

I only have some minor comments:

1. What would be the potential changes with HITRAN2024? I expect minor, but it may be good to speculate a little

We agree – we have now incorporated a discussion of HITRAN2024 in the instantaneous radiative forcing results where, as the reviewer anticipated, we show that its impact is minor. Please also see the response to the comment of Reviewer 1 at our (original) Line #104 and the new Figure shown in our response to Reviewer 2 above.

2. I liked the discussion of the uncertainties, but maybe a table with approximate relative contributions of spectroscpy, MTCKD, atmospheric profiles, etc. will be useful

Thank you for this suggestion – after consideration, we believe the discussion in the text at the end of Section 2.3 is a concise summary of the much more detailed discussion (and Table) which can be found in Hodnebrog et al. (2013) and updated in Hodnebrog et al. (2020). In the revised version we have added reference Hodnebrog et al. (2020) to this sentence, as this seemed appropriate.

3. Change "this differences" to "these differences" on page 12

Thank you – corrected.

4. "...performed by adopting the *in silico* protocol to climate metrics..." on Page 9 and "...The REs exerted by the low wavenumber region..." on page 14 sound a little awkward

We have slightly re-worded both sentences so that they are, hopefully, less awkward.

5. Page 14 ""...gives further confidence on the applicability..." use "in" instead of "on"

Thank you – now changed.