

Reviewer #3

We thank the reviewer for their helpful and constructive comments. Our responses and revisions to the manuscript are outlined in detail below.

General reviewer comments:

The paper by Papanastasiou et al. provides estimates of lifetimes, ODPs, REs, GWPs and GTPs for a large number of HCFCs. The study is comprehensive and provides estimates that are very relevant for the recent Kigali Amendment to the Montreal Protocol. Although I recommend publication of the paper, there are some issues that need to be addressed first. Please see detailed comments below.

Reviewer Comment: Abstract: It would be good to include some of the results in the abstract. E.g., give the range of lifetimes and GWP 100-year values.

Author Response: Agree

Author Action: We have revised the text in the abstract as follows: “The C₁-C₃ HCFCs display a wide range of lifetimes (0.3 to 62 years) and GWPs (5 to 5,330, 100-year time horizon) dependent on their molecular structure and H-atom content of the individual HCFC.”.

Reviewer Comment: Page 1, line 23: "Reliable" is too strong in my opinion, considering that the difference from experimentally-derived values can be quite large for some compounds (as shown in Fig. S3).

Author Response: Okay

Author Action: We have removed the subjective “reliable” in several places as follows:
In the Abstract: The results from this study provide ~~reliable~~ policy relevant GWP metrics for the HCFCs included in the Montreal Protocol in the absence of experimentally derived metrics.

In the Introduction: The objective of the present work is to provide a ~~reliable and~~ comprehensive evaluation of the atmospheric lifetimes, ozone depletion potentials (ODPs), GWPs, and global temperature change potentials (GTPs) for the HCFCs listed in Annex C of the amended Protocol.

Section 2.3: Similar approaches have been used in earlier studies for other classes of molecules with ~~reliable~~ good results, see Hodnebrog et al. (2013) and references cited within.

Section 3.1: This method of RE determination is, therefore, expected to provide ~~reliable~~ good estimates of REs in the absence of experimentally based determinations.

Summary: Although this work has provided ~~reliable~~ a comprehensive set of estimated of key metrics for the C₁-C₃ HCFCs that presently do not have experimental data, careful direct fundamental laboratory studies of an intended HCFC would better define the critical atmospheric loss processes (reaction and UV photolysis) used to evaluate atmospheric lifetimes.

Reviewer Comment: Page 2, line 1-2: The sentence looked a bit strange to me. Perhaps better with "an exemption for countries with high ambient temperature"?

Author Response: Agree

Author Action: Text changed as follows: “ which are different for developed and developing countries with an exemption for countries with high ambient temperature parties. ”.

Reviewer Comment: Page 2, line 17: Please change "global temperature potentials" to "global temperature change potentials" throughout the manuscript.

Author Response: Okay

Author Action: Changed in two places in the text and two places in the SI.

Reviewer Comment: Introduction: There are hardly any references to previous work, although I know a lot of work has been done on the topic of calculating absorption spectra and resulting metrics. I do not ask for a review of previous work, but some introduction to the topic on calculated vs. experimental spectra should be included. I also suggest to add references to GWP, ODP and GTP on first use, as all readers may not be familiar with all the terms.

Author Response: Agree

Author Action: We have added text to the introduction to Section 2.3 “Theoretical Calculations” that provides background to the methods applied in this work and also cites literature work that has applied these methods from our laboratory and others.

Text added to the start of section 2.3:

Information about molecular vibrational frequencies, central to the interpretation of infrared spectra, thermodynamics, and many other aspects of chemistry, became amenable to computational determination in the early 1980s. It was recognized that computed harmonic frequencies derived via the second derivative of energy as a function of atomic position were systematically higher than observed fundamentals and scale factors were introduced (Hout et al., 1982; Pople et al., 1981). For Hartree-Fock frequencies these were typically ~0.9 and accounted both for the influence of anharmonicity and deficiencies in the underlying quantum calculations. Frequencies based on methods incorporating electron correlation such as CCSD, CCSD(T) or certain functionals within density functional theory (DFT) often perform well for harmonic frequencies and are scaled by ~0.95 to match fundamental vibrational modes. Such scaling has been updated as more methods appear (Alecu et al., 2010; Scott and Radom, 1996). Rather less information is available concerning the evaluation of absorption intensities for fundamental modes. Within the same harmonic approximation, implemented in popular quantum codes, the intensity is proportional to the square of the derivative of the dipole moment with respect to position. Halls and Schlegel evaluated QCISD results against experiment and their plot indicates deviations of up to around $\pm 20\%$ and then used QCISD as a benchmark to evaluate a range of functionals (Halls and Schlegel, 1998). For B3LYP, they found differences from QCISD of around 10%. More recently, tests of the B3LYP functional found good performance for frequency and intensity (Jiménez-Hoyos et al., 2008; Katsyuba et al., 2013). Some prior work where similar methods have been applied to the infrared absorption for molecules of atmospheric interest include studies of fluoromethanes (Blowers and Hollingshead, 2009), unsaturated hydrofluorocarbons (Papadimitriou and Burkholder, 2016; Papadimitriou et al., 2008b), perfluorocarbons (Bravo et al., 2010), chloromethanes (Wallington et al., 2016), SO_2F_2 (Papadimitriou et al., 2008a), permethylsiloxanes (Bernard et al., 2017), and large survey studies such as by Kazakov et al. (Kazakov et al., 2012) and Betowski et al. (Betowski et al., 2015) to name a few.

Halls and Schlegel noted that real spectra may exhibit the influences of resonances, intensity sharing, and large-amplitude anharmonic modes. These can be partially accounted for in an analysis based on higher derivatives of the energy and the dipole moment, performed for instance within the framework of second-order vibrational perturbation theory (Barone, 2005). Advantages include treatment of resonances among vibrational levels and incorporation of overtones and combination bands. Examples of applications to molecules containing C-H and C-F bonds indicate excellent accord with experiment for band position and intensity, (Carnimeo et al., 2013) but for CH₂ClF the intensity in the region involving C-Cl stretching nevertheless exhibits intensity errors of ~10% (Charmet et al., 2013).

Additional text added within the section:

We are not aware of prior studies of infrared spectra of HCFC conformers, but there have been prior theoretical studies of the conformers of other classes of molecule, such as for validation of observed infrared spectra used to deduce relative energies of carbonyl conformations (Lindenmaier et al., 2017) and comparison with measured infrared intensities for linear alkanes (Williams et al., 2013). The different errors and their trends for the intensities of C-H stretching and HCH bending modes indicate that a simple scaling approach, so successful for frequencies, will not work for intensities.

and

In fact the intensities of C-Cl stretches are a long-known problem for calculation (Halls and Schlegel, 1998).

Reference to metrics included as follows: The infrared spectra are then combined with our estimated global atmospheric lifetimes to estimate the lifetime and stratospheric temperature adjusted radiative efficiency (RE), GWP, and GTP metrics (see IPCC (2013) and WMO (2014) assessments).

Reviewer Comment: Table 1: Where is the IR absorption spectrum for HCFC-123a from? For many of the compounds, absorption spectra are available from several sources (see Table 4 in Hodnebrog et al., 2013). What is the reason for using absorption spectra from (in most cases) only one of the sources? Would be good to briefly state that. Also, in footnote 2 the terms lifetime-adjustment and stratospheric temperature correction have not been defined and could therefore seem confusing for readers not familiar with these. I suggest referring to the appropriate method section where these terms are explained.

Author Response: Typically, the infrared spectra reported from different laboratories are in pretty good agreement and not a source of large uncertainty. The infrared spectra for HCFCs -31, -123a, -132b, -234fb, and -243cc are presently not available in the open literature. These molecules are included in Table 1 because kinetic data is available. There are also a few molecules where infrared data are available, but not kinetic data. In cases where multiple infrared spectrum measurements are available, we have used the spectra we think most reliable, although we have not performed a critical analysis.

Author Action: No change for infrared spectra comment. Citation to IPCC and WMO for terms now given in Introduction (see response above).

Reviewer Comment: Page 5, line 4: As I understand it, these are comparisons to experimental data. I suggest changing to "... for the training dataset with experimental rate coefficients...", just to make that clear.

Author Response: This is a comparison of SAR calculated rate coefficients for the molecules in the training dataset with the available experimental values. Not all molecules in the training dataset have experimental rate coefficient data available (see Table 1).

Author Action: Text revised as follows: Comparison of structure activity relationship (SAR) OH rate coefficients for the training dataset (Table 1) with rate coefficients recommended in Burkholder et al. (2015).

Reviewer Comment: Page 7, line 14-16: Is this shown somewhere? If not, adding "(not shown)" to the end of the sentence would be clarifying.

Author Response: We are quoting the results from our test calculations and the results are given in the text. There is not really anything else to show, or not show.

Author Action: None

Reviewer Comment: Page 8, line 5-6: Differences look larger than 2% in Fig. 3, especially for the band around 1100-1200 cm^{-1} .

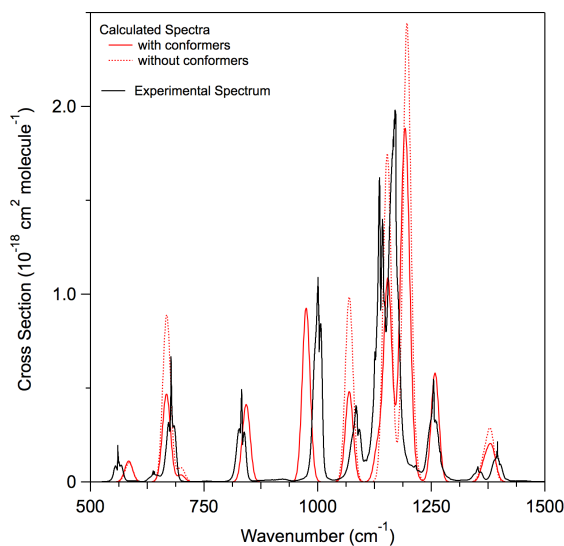
Author Response: There are some discrepancies among individual band strengths, but the total integrated band strengths are in good agreement.

Author Action: Text clarified as follows: The calculated spectrum is in good agreement with the experimentally measured spectrum with band positions and total integrated band strengths agreeing to within ~2%.

Reviewer Comment: Figure 3: It would be much easier to compare the calculated vs. experimental spectra if they were in the same plot.

Author Response: The original figure was split into two panels to minimize congestion. However, this reviewer and another suggested combining the panels.

Author Action: The graph was revised as follows as requested.



Reviewer Comment: Page 10, line 9-11: Perhaps I missed something, but is it shown somewhere that the broadening leads to better agreement with experimental HCFC spectra? As I interpret Fig. 5, it only shows the difference with and without the broadening and not comparison to experimental data.

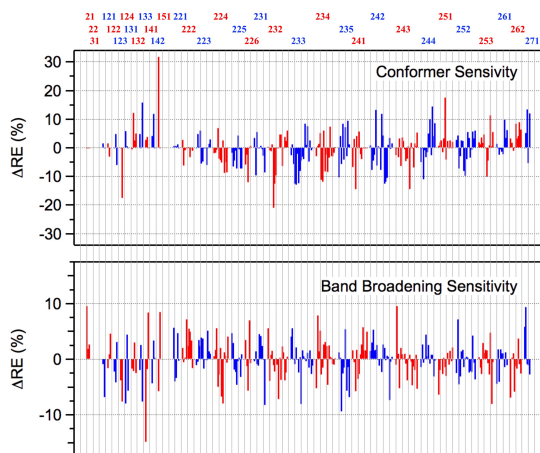
Author Response: Of course, experimental data don't require spectral broadening. Implicit to our discussion of broadening is that a more realistic representation of the actual infrared absorption spectrum should provide a more realistic evaluation of the radiative metrics. Figure 5 was included to illustrate the **sensitivity** of including broadening in our calculations (something ignored in many studies of this type). Note that this does not necessarily mean that including broadening leads to a more accurate metric in our work, although it probably does. Figure 5 shows that in most cases the sensitivity is on the order of 5% for the HCFCs included in this work. We emphasize that this is a sensitivity analysis (as labeled in the figure) not an uncertainty analysis.

Author Action: None

Reviewer Comment: Page 10, line 23: I cannot see that Figure 5 includes all HCFCs studied, when compared to Table 2. Figure 5: I think there is something wrong with the labeling above the plots – compounds HCFC-224 to HCFC-233 are listed twice. A minor point is that it would be more natural to switch the order of the plots, since the broadening sensitivity is discussed first.

Author Response: This figure and its labelling were in error.

Author Action: The figure has been revised as follows:



Reviewer Comment: Page 11, line 15: Could you include "(see Section 5)" at the end of the sentence? I started looking for the datasheets in the supplementary information without finding it, before I realized these were only available on a web site.

Author Response: Okay. It was necessary to place these files on a web site because they exceeded the memory limits for the journal SI.

Author Action: Text added: "Well-mixed and lifetime-adjusted RE values are included in the Supporting Information datasheets (see Section 5)."

Reviewer Comment: Page 11, line 20: Isn't the $\text{IntRF}_{\text{CO}_2}(\text{T})$ the integrated radiative forcing of CO_2 ? Also, M_{HCFC} in the formula is not defined, I think.

Author Response: Agree

Author Action: Text revised as follows: where $\text{IntRF}_{\text{CO}_2}(\text{T})$ is the integrated radiative forcing of CO_2 and M_{HCFC} is the HCFC molecular weight.

Reviewer Comment: Page 11, line 24-25: In my opinion, Figure S3 is important enough to be in the main manuscript instead of the supplementary. In addition it would be good with a table or figure comparing the calculated REs with those from the training dataset.

Author Response: The GWP values are already given in Table 1 and Table S1. A RE correlation figure has been added to the SI.

Author Action: We have moved the GWP correlation figure into the main body of the manuscript, new Figure 6.

Reviewer Comment: Page 11, line 29-31: The section on GTP is very short. I suggest to merge it with section 2.5?

Author Response: Okay.

Author Action: Sub-section title has been removed and GTP added to the preceding sub-section title. “**2.5 Global Warming and Global Temperature change Potentials**”

Reviewer Comment: Page 14, line 18-19: Where is the comparison of REs between calculated and experimental section shown?

Author Response: We did not show a plot of calculated vs experimental REs in our original submission because of the similarity to the infrared spectrum correlation.

Author Action: The figure below that compares the lifetime corrected REs has been added to the SI. The following text was added to Section 2.4: A comparison of the experimentally derived REs and the calculated values for the training dataset is given in Figure S3.

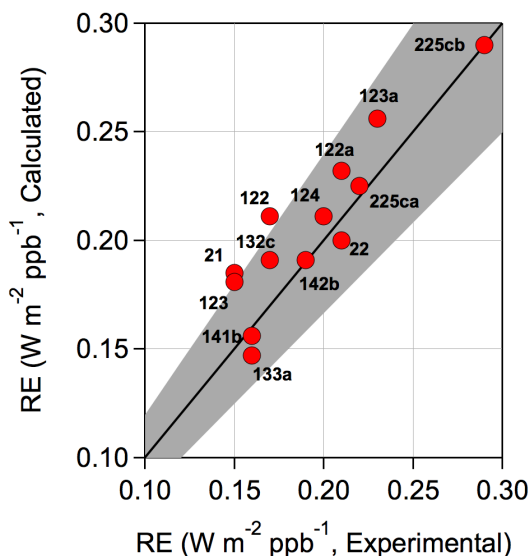


Figure S3: Comparison of experimental and calculated “lifetime corrected” radiative efficiencies (REs) for the training dataset HCFCs. The solid line is the 1:1 correlation. The gray shaded region represents $\pm 20\%$ around the 1:1 line. Note that the spread in REs without applying the “lifetime correction” is $\sim \pm 10\%$.

Reviewer Comment: Table 2: I suggest stating that the range in GWP100 values is due to different isomers, so that the range is not misinterpreted as uncertainty due to the method.

Author Response: Agree. Reviewer #1 misinterpreted the reported range in values as the uncertainty, which makes this comment even more relevant.

Author Action: Table title revised as follows: “The Annex C HCFC table provided in the Kigali amendment to the Montreal Protocol, where the range of 100-year time horizon global warming potentials (GWPs) obtained in this work for various HCFC isomers all with the chemical formula given in the first column is given in *italics* *”.

Reviewer Comment: Page 11, line 21: "as described above" -> "as described in Section 2.1" ?

Author Response: Agree

Author Action: Text added

Reviewer Comment: Page 12, line 2: "stratosphere-adjusted" -> "stratospheric temperature adjusted"

Author Response: Agree

Author Action: Text revised.

Reviewer Comment: Page 15, line 15: "didn't" -> "did not"

Author Response: Okay

Author Action: Changed text to “did not”.

Reviewer Comment: Supplementary Fig. S1: "Burkholder et al." is listed twice in the caption.

Author Response: Agree

Author Action: Authors name has been suppressed in citation.