Reviewer #1

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

Author General Comment: Several of the reviewer comments refer to the estimated uncertainties presented in our manuscript. Estimating uncertainties in the atmospheric metrics, although important, has generally been ignored in the literature to date. However, we believe that uncertainties should be a part of the discussion. A major hurdle in such a discussion, however, is that it is difficult to quantitatively estimate uncertainties in estimated quantities. In our manuscript, we have taken the approach of estimating uncertainties based on the performance obtained using the HCFC training dataset, i.e., what we call average behavior. We acknowledge that not all molecules follow "average" behavior, but the intention is that our analysis will provide a general perspective on the issue of metric uncertainty. Note that we emphasize that direct fundamental laboratory studies are preferred. However, in the absence of laboratory data theoretical methods can provide reasonably reliable results.

There was a misinterpretation by this reviewer of the range of GWPs reported in Table 2 as the uncertainty range of our analysis. The reported range is indeed large, which reflects the fact that the isomers of a HCFC family have different properties, while the uncertainties for the individual isomers is estimated to be much less, ~30-50%. This misinterpretation represents a thread for several of the other reviewer comments. We have revised the text in an attempt to avoid this misinterpretation by others.

A general comment from this and other reviewers was a lack of a historical perspective and citations for the development of applying theoretical methods to the quantitative calculation of infrared spectra, which was a major component of our study. To address this issue, we have added text to Section 2.3 that is relevant to the development of the theoretical methods and have cited some of the previous applications from our laboratory as well as from others as examples.

Reviewer Comment: The paper is a study by Burkholder et al. to synthetically estimate atmospheric rate constants (using certain models and approximations to estimate the atmospheric loss processes), as well as to use (*ab initio*) synthetic calculated infrared absorption spectra so as to ultimately derive estimates for the lifetimes and global warming potentials for a series of the C1-C3 hydrochlorofluorocarbons contained in the Kigali amendment to the Montreal protocol.

      Author Comment: A minor point, the theoretical methods in our work used density functional theory (DFT) not *ab initio* methods.

Reviewer Comment: In that amendment, when accounting for all of the C1 to C3 conformers of the HCFCs, there are 274 species of interest, but of these only 15 have both the actual measured relevant kinetic rate constants and requisite quantitative infrared absorption spectra to derive accurate values for the RE and ultimately the associated GWP. It will take many years and more likely many decades until most or all of the experimental data are acquired for these 274 species, so any efforts to derive some interim values using estimates, models and theoretical calculations are clearly justified. Such is the motivation for the present work. The paper thus represents a seminal contribution for estimating the GWP values for these 259 species; it also represents a very great deal of work. To write such a paper requires significant expertise in kinetics, atmospheric chemistry and modelling, IR spectroscopy, quantum chemical calculations, etc. The paper should clearly be published. We thus recommend publication with only minor modification.

      Author Comment: We truly appreciate the reviewer comments. We would like to clarify, however, that the 274 species is the total number of "isomers" for the C1-C3 HCFCs. Each isomer may have a number of "conformers" (i.e., molecular configurations with slightly higher energy), that were included in our metric determinations. We considered

conformers within 2 kcal/mole of the lowest energy geometry, which enables us to account for at least ~98% of the Boltzmann population distribution.

Reviewer Comment: This reviewer does have concerns leading us to criticise certain aspects of the study. Without pointing to a specific paragraph, the overall hue or colour of the narrative gives the reader an impression of the resultant data or GWP values indicate greater precision and accuracy than is perhaps warranted: The phrase "… such estimates are accurate enough for our study" is used quite often. The paper is in essence a (warranted) theoretical study that of necessity involves many approximations or extrapolations to derive certain data which are used with other data to calculate the lifetime and GWP values. Many of these data have non-trivial uncertainties and represent possible sources of significant error. However, in several places phrases to the effect "this study provides reliable policy relevant GWP metrics" imply significant accuracy. For example, inspection of column 5 in their Table 2 manifests their own estimates as the 100-year GWP values with ranges that at first blush appear to vary from 5x to 35x between the lower and upper bounds! While the data are clearly needed, the language should perhaps be modified to recognize the limitations of such calculated data.

Author Response: The reviewer has misinterpreted the range of values for the isomer GWPs presented in column 5 of Table 2 as the uncertainties associated with a given HCFC chemical formula. Second, the reviewer makes a reasonable point that some of the uncertainty statements in our paper are not quantitative. We have made an effort in this manuscript to convey to the reader that the metrics reported in this work are estimates that have uncertainty associated with them (the consideration of uncertainties in this type work is an issue often overlooked, or ignored, in previous studies and assessments). That said, it is not straightforward to assign accurate statistical uncertainties for molecules with "unknown" properties. However, we should be more careful in using phrases such as "suitable for this study", which was meant to imply that these values represent a minor uncertainty in comparison with other sources of uncertainty. In our approach, we have recommended "average" uncertainties based on our comparisons with literature data, i.e., our training dataset. Note that metrics derived from accurate laboratory measurements still will lead to metric uncertainty, which can be substantial, due to the methods used to determine atmospheric lifetimes and radiative properties. For example, the well-mixed radiative efficiency estimation method given in Hodnebrog et al. (2013) is estimated to have a 25% uncertainty associated with the method. These other sources of uncertainty were not included in our analysis.

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 <u>change</u> 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~~ <u>good</u> 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 C_1-C_3 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.

We have revised the use of "accurate" as follows:

Section 2.1: Therefore, this method of accounting for stratospheric loss ~~is acceptably accurate for our purpose~~ leads to only a minor uncertainty in the calculated global lifetime.

Section 2.1: As shown later, the $O(^1D)$ reaction is a minor loss process, <1%, for nearly all the HCFCs included in this study and, therefore, the estimation method used is not critical as this loss process is a minor contributor to the global lifetime ~~are sufficiently accurate for our study.~~

Reviewer Comment: Related to this phraseology aspect is the need for their intro/summary text to point out that more and better experimental data of several different kinds are needed: 1) Experimental measurements of atmospheric lifetimes are clearly needed; the laboratory of Dr. Burkholder and others are known for careful measurement of such rate constants and these are clearly warranted – while the SARs are good approximations, actual experimental data are required. 2) Even for relatively simple molecules such as the smaller HFCFs, the *ab initio* Gaussian calculations still can vary significantly from the measured infrared cross sections (see below), and these IR data need to be measured experimentally as well, including to longer wavelengths as the authors point out. Current experimental IR absorption data can have accuracies of 3% or better. 3) Whilst measurement of such kinetic and IR absorption data for all of the 259 named molecules will likely not occur soon, even increasing the number of species in the training set (Table 1) from 15 to 25 or 35 or ? would obviously increase the accuracy and relevancy of the study. Such considerations need to be suggested in either the introduction or discussion sections, or both. A more appropriate slant to be taken throughout the manuscript would thus be words to the effect: "In the absence of such experimental data, the following study provides estimates of…"

Author Response: We agree with the reviewer sentiment whole heartedly. For compounds of interest direct careful laboratory studies are surely preferred. We have expressed this point of view in both the introduction and conclusion sections of our paper. It is also implicit in our approach that an improved (expanded) training dataset would be beneficial to the analysis presented in our work.

Author Action: None

Reviewer Comment: One other general comment is that in several spots the paper would do better to simply flesh out some of the details as to how the results and approximations are realised. This is especially true for the experimental and calculation sections. However, their error analysis is likely the best approach for a study of this magnitude.

Author Response: The results and approximations used in our work are based on the behavior of the training dataset, which for HCFCs is rather limited. We present our estimated uncertainties based on the "average" behavior (as discussed above) of the training dataset, although outliers are acknowledged. Note that the Betowski et al. study used a much larger training dataset that included a variety of classes of molecules to derive general properties that were applied to HCFCs. We argue that this approach resulted in a bias in their HCFC results (note that their theoretical results and those presented in this work are in good agreement).

Author Action: None

Reviewer Comment: Finally, the section of the manuscript that deserves a bit more attention is section 2.3 where the intensities of the calculated IR spectra are compared to the measured IR spectra over the spectral region 2000-500 cm^{-1}. One initial question is how do the computed LWIR intensities compare with known values? Moreover, while not an expert in the Gaussian calculations, this reviewer fears that the 20% estimate as to the uncertainty in the IR absorbance spectra may perhaps be a bit too generous. The vibrational frequencies can now routinely be calculated with an accuracy of ca. 1 to 2% using such a basis set, and this is sufficient except in those cases where the predicted line frequency (depending on accuracy) is either adjacent to or obscured by an atmospheric absorption bands due to H_2O, CO_2 or O_3. However, the IR absorption intensities are far more difficult to predict with such accuracy - the eigenvalues (frequencies) to the nuclear motion equation are far less susceptible to approximations in the wavefunction than are the vibrational intensities (the eigenvectors). Besides the 20% estimate obtained from the training set, a more extensive discussion of the accuracy of the Gaussian results is likely justified.

Author Response: A thorough discussion of the uncertainties associated with theoretically calculated infrared absorption spectra is relevant to this work, and that of others, but is well beyond the scope of our manuscript. Because of the volume of calculations required in this work, we have used DFT methods that yield reasonable results without too much computing cost. We have based our uncertainty estimates on how well the DFT methods work for the training dataset. Future studies could build on the work presented in this manuscript. We have added text to the beginning of Section 2.3 to provide better perspective for the calculation methods (text given below). The next comment is related to this one.

Reviewer Comment: The authors have used DFT methods (B3LYP/6-31G(2df,p)) to estimate total IR cross sections, and have compared their results with a training set of molecules, to show that they are confident that their estimated cross sections are within about 20% of measured cross sections, for those that have experimental values. Their claimed accuracy would be made stronger if they had also compared their B3LYP method with a few standard small molecules that have been used to assess absolute accuracy of computed IR cross sections, as in Jemenez-Hoyos et al., PCCP, 2008, 6621-6629, and Halls and Schlegel, J Chem Phys, 1998, vol 109, 10587-10593, where the standard deviation of B3LYP computed IR cross section (by individual band) is shown to be about 11 km/mol (conversion to cross section is certainly known by the authors) for a set of molecules whose band strengths extend from less than 10 km/mol to about 90 km/mol. In addition to these, more recent work has shown that for a set of alkanes, the absolute errors for IR band strengths were shown to be less than about 15% for B3LYP/6-31+G(d,p) computation compared to experiment, Williams et al., JQSRT, 2013, vol 129, 298-307.

It would be beneficial for the authors to review / cite some papers that have discussed the accuracy of the IR vibrational intensities, especially those that are conformer dependent. [A quick review of the literature pulled up the references listed below.] A similar discussion as to "quick and dirty estimate" may also be justified for two other areas: i) the neglect of the 37Cl isotopomers and ii) the SAR relationships used, as discussed on p. 7., lines 110 to 114.

Author Response: We had not reviewed the history of theoretical calculations and the application to molecules of atmospheric interest in our original submission. The other reviewers have also requested that this be included in our revised manuscript along with citation of some application papers.

Author Action: We have added "new" text with ample literature citations at the beginning of Section 2.3 "Theoretical Calculations". The text includes the papers suggested by the reviewer as well as additional relevant material and some examples of work from our lab

and others. We have also added the following text to address not including calculations with Cl-atom isotopes (note that including all permutations of Cl-atom isotopes would have expanded the depth of the present work tremendously, while not altering the general conclusions from this work): "In principle, substitution of ^{35}Cl by ^{37}Cl in a heavy molecule would lower the frequency of the C-Cl stretch by ~3%".

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 ±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 CH_2ClF 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).

Minor Suggestions / Errata

Reviewer Comment: Title: Perhaps insert "Estimates" into the title to read: "Global Warming Potential Estimates for the C1-C3 Hydrochlorofluorocarbons (HCFCs)…"

     Author Response: Agee

     Author Action: Title changed as follows: Global Warming Potential <u>Estimates</u> for the C_1-C_3 Hydrochlorofluorocarbons (HCFCs) Included in the Kigali Amendment to the Montreal Protocol

Reviewer Comment: Pg. 3 line 61: Perhaps change first sentence to read "Due to the current dearth of such experimental data, the objective of the present work is to provide a best-effort and comprehensive evaluation…"

     Author Response: We have used the phrase the "in the absence of experimental data…" in our manuscript, which we believe is a concise and accurate description.

     Author Action: None

Reviewer Comment: p. 4. Line 63: Define the acronym GTP. 1, sent.21: In previous studies, emission factors have units of g kg-1, here the emission factors have units of g km-1. Please explicitly define the emission factor that you are estimating somewhere in the manuscript.

     Author Response: GTP is defined on its first use on page 2. We are not addressing or discussing emission factors in our manuscript. So, we don't understand the origin of this comment.

     Author Action: None

Reviewer Comment: p. 7 line 120: Insert "red" between "solid" and "symbols"

     Author Response: This refers to the caption for Figure 1. Red is not necessary as there are only solid and open symbols on the graph.

     Author Action: None

Reviewer Comment: p. 8 line 134 – 148. Almost every sentence in these two paragraphs mentions another source of error. Can the composite uncertainty be estimated at the end of this section 2.1?

     Author Response: There are estimated uncertainties in the lifetimes and calculated infrared absorption spectra that propagate into the metrics as discussed in this text. Therefore, each parameter is considered separately and then combined to obtain an estimated uncertainty in the metric at the end of the discussion. Seeing that the uncertainties are estimated values, we feel that reporting uncertainty values in a table would place too much emphasis on the accuracy of these estimated values.

     Author Action: None

Reviewer Comment: p. 8 line 153: It would be well to not only define FRF, but explain its meaning

     Author Response: We have not included background material on the derivation or meanings of lifetime, ODP, RE, GWP, GTP, and FRF in our manuscript. Instead, we have provided the pertinent references that provide the detail necessary to fully understand these metrics.

     Author Action: None

Reviewer Comment: p. 10 line 206. Is the comparison of experimental and predicted IR spectrum a "typical" result or is this one of the better matches?

Author Response: This comment refers to Figure 3. This result is typical. A comparison of the individual experimentally reported spectra and our calculated spectra for all molecules with experimental data is provided graphically in the SI.

Author Action: We have added the follow text following the introduction of Figure 3: "A comparison of experimental and theoretical spectra for all molecules with experimental data is provided in the SI (see Section 5).".

Reviewer Comment: p. 11 Figure 3: Where do the experimental data come from in this Figure? One of the references?

Author Response: This comment applies to both Figure 3 and 4. The source of the experimental spectra are given in Table 1.

Author Action: We have reiterated the source of the experimental spectra in the captions for Figures 3 and 4 as follows: "… (see Table 1 for the source of the experimental spectrum)".

Reviewer Comment: p. 11 Figure 3: The figure could facilitate a better comparison of predicted v. measured intensities if the y-axis were equally stretched in the two frames such that they were at the same factor, e.g. that 2.0 E-18 units were the same length in the top and bottom panels. While quite weak, it appears there are two small bands in the experimental data near ca. 610 and ca. 1385 cm^{-1} that are missed in the Gaussian calculations.

Author Response: The Gaussian calculation presented here considers only the fundamental vibration frequencies. Therefore, it is possible that weak combination or overtone bands are not included in the calculated spectra. The overall quality of the literature infrared absorption reference spectra was not explored as part of our study. The other reviewers have request that the panels for this figure be combined.
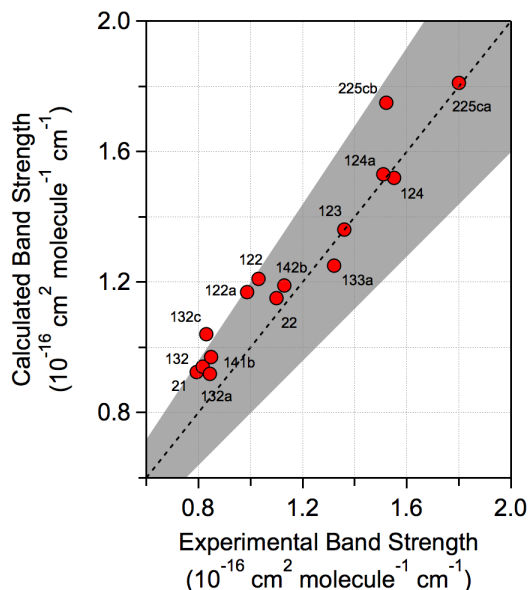
Author Action: Figure revised as follows:
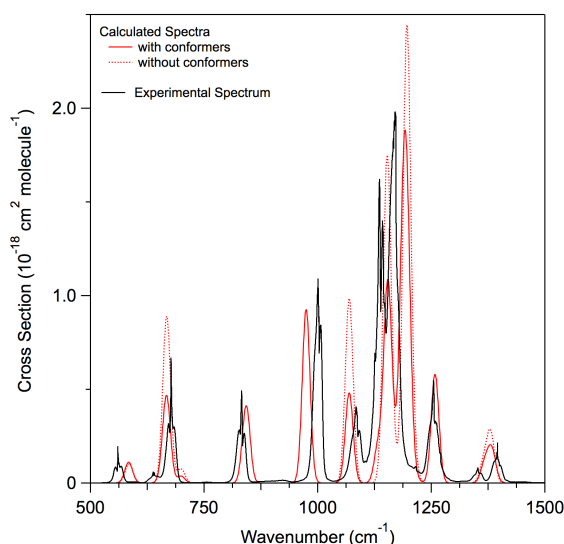
Reviewer Comment: p. 12 Figure 4: It would be helpful to put the units (cm2 molecule-1 cm-1) directly on the plot of this figure, not just in the legend.

Author Response: Okay

Author Action: Units removed from figure caption and figure revised as follows:

5   **Reviewer Comment**: p. 14 line 294: This sentence seems perhaps unjustified: While there are far fewer data for bands below 500 cm^{-1}, it is curious that "the contribution of vibrational bands in this region to the RE is… usually minor, i.e. <1%". While it is true there are often fewer fundamental below 500 cm^{-1}, the ability to act as a greenhouse gas is also a function of the blackbody radiation of the earth and the blackbody curve near 295K maximizes near 1000 cm-1,

10   with very appreciable intensity from 200 to 1000 cm^{-1}. This sentence needs clarification or a reference to more extensive work. It may also suggest the need for more experimental measurements of IR intensities in the far-infrared.

          Author Response: Our results would indicate that an experimental focus on far-infrared absorption bands is not presently warranted for HCFCs. This is because the band

15   intensities in this region are usually much weaker than the C-F stretching region and our calculations show that the contribution to the RE would be small, less than 1% in nearly all cases. Stated another way: we are guiding experimental effort away from an unproductive effort, because it is not easy in the laboratory to go below 500 cm^{-1} in the spectrum measurements.

20   **Author Action**: None

      Reviewer Comment: p. 17 Figure 6: Good Figure-lots of information, which is well presented.
          Author Response: Thanks

25   **Reviewer Comment**: p. 18 line 356: Establishing the reliability of the metrics based on the average behaviour can be quite an approximation. Perhaps include language that acknowledges this approximation.

          Author Response: In general, we agree with this comment, but as discussed in response to other comments we do not feel that a more quantitative analysis is possible at this time

30   for molecules lacking experimental data.
          Author Action: None

Reviewer Comment: p. 18 line 370: This statement seems a bit skeptical and perhaps further explanations are needed to convince the readers that indeed the computed REs are within 10% of experimental values. Furthermore, a discussion of the estimated band strength uncertainty may strengthen the validity of the statement.

Author Response: The estimated RE uncertainty given in our manuscript is based on the average behavior found for the training dataset, which shows roughly a ~10% uncertainty. Sources of uncertainty in the RE calculation arise from the calculated frequencies and band strengths. Combining these with the irradiance profile leads to some cancelation of error, although that is difficult to quantify other than in comparison of the calculated REs with the experimentally determined values. In our error discussion, we have used a 20% RE uncertainty.

Author Action: We have added a figure to the SI that shows the agreement between the lifetime corrected experimental and calculated REs for the training dataset (see below). 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. Note that comparing 'lifetime corrected" REs increases the spread in the correlation between the experimental and calculated values because of differences between experimental and calculated lifetimes and the correction factor. The figure shows the 20% correlation range, which is used in the metric uncertainty analysis. A general discussion of the uncertainties associated with band intensity calculation is now included in the introductory paragraphs to Section 2.3.
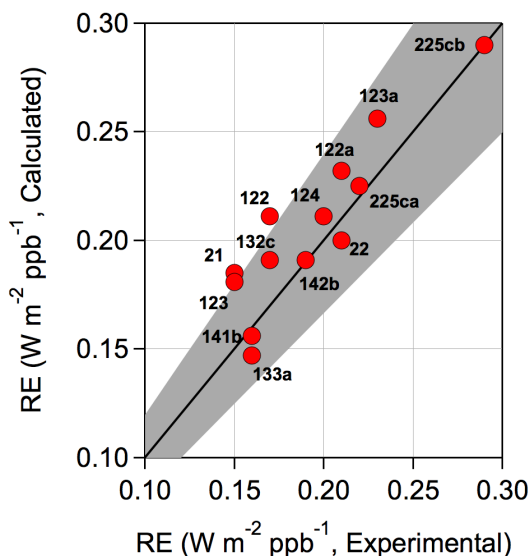
Figure S3: Comparison of experimental and calculated "lifetime corrected" radiative efficiencies (REs) for the training dataset HCFCs. The solid line is the 1:1 correlation. The gray shaded region represents ±20% around the 1:1 line. Note that the spread in REs without applying the "lifetime correction" is ~±10%.

Reviewer Comment: p. 18 line 375-377: Similar to the comment above, this sentence needs to be justified and it may be beneficial to have a discussion regarding the accuracy of the Gaussian results somewhere in the manuscript.

Author Response: We are basing our estimated uncertainties on the level of agreement with the training dataset values, which is pretty good. A comprehensive discussion of the uncertainties associated with the Gaussian calculations, more specifically, the calculations using DFT methods, is beyond the scope of this work. We have addressed this point in the revised Section 2.3 and in an earlier response regarding estimated uncertainties.
Author Action: None

Reviewer Comment: p. 18 line 378: This is not true for the spectral region 700-1300 cm^{-1}.
Author Response: This comment regards the discussion that a change in the vibrational band centers primarily impacts the RE through the overlap with the irradiance profile. What is given in the manuscript is correct. This and the next comment are related.
Author Action: None

Reviewer Comment: p. 19 line 382: It might be valuable to emphasize or to provide additional details regarding this phenomenon.
Author Response: This comment refers to the possibility that the metric uncertainty might be greater if an absorbing molecule's infrared spectrum was near the CO_2 or H_2O absorption features. This issue has been mentioned in the text, but is difficult to quantify in general terms. This is a situation where laboratory studies would be needed.
Author Action: None

Reviewer Comment: p. 19 line 402-403: This sentence may benefit from some clarification. When compared to results from Betowski et al., it appears that the present results are 29% greater, which would suggested that the accuracy of the present results is at least ≥29%. There are many uncertainties presented in this section. It might be helpful to the readers to have a table displaying all of the uncertainty values in the SI.
Author Response: The reviewer has misinterpreted the results that are already included in the text. We actually agree very well with the raw HCFC results from the Betowski et al. study. The 29% difference is due to the band strength scaling factor developed in the Betowski et al. study that was based on an analysis of many classes of compounds. We argue that their band strength analysis yielded biased results for the HCFC class and that the 29% scaling factor should not be applied. This difference is, therefore, not representative of the uncertainty in the analysis.
Author Action: None

Reviewer Comment: p. 19 line 409-411: Might be beneficial to include how the present results compare to other experiments. Including more studies may strengthen this section of the manuscript.
Author Response: We do not agree with this comment. Basically, what the reviewer is suggesting is what was done in the Betowski et al. work. We already compare with all HCFC experiments, so other experiments would mean other classes of compound. We argue that this approach that was used in the Betowski et al. work led to a bias in the HCFC results. So, the approach used in the present work that limits the training dataset to HCFCs is most appropriate.
Author Action: None

Reviewer Comment: p. 20 line 425: The term "policy-relevant" is used in this sentence, yet the present results are off by a factor of 12. Again, adding language that acknowledges the limitations of such calculated data and the need for additional experimental data is likely justified.

> **Author Response**: The present results are not off by a factor of 12. We believe that this comment is based on the misinterpretation of the range of GWPs given in Table 2 as described in a previous comments and responses.
>
> **Author Action**: None

Reviewer Comment: p. 22 line 457: The need for additional laboratory studies is absolutely needed, and we suggest this point be emphasized throughout the paper.

> **Author Response**: We agree that experimental studies are preferred over theoretically calculated or empirically derived values. We have emphasized this point in the most visible Introduction and Conclusion sections.
>
> **Author Action**: None

Reviewer #2

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

Reviewer Comment: This paper describes the derivation of atmospheric lifetimes, ozone depletion potentials, infrared spectra, radiative efficiencies and global warming and temperature potentials for a very comprehensive set of HCFCs. The work is largely based on theoretical approaches but has a strong focus on comparisons with observation- and lab-based data. The paper is generally of sufficient quality and novelty for publication in ACP. I do however have two main concerns: Firstly, previous literature on theoretical calculations of GWPs, ODPs, etc. is largely ignored. Including more references at least for the most important HCFCs would also help the authors to highlight why their approach is superior to previously published works. Secondly, the authors calculate ODPs partly based on outdated values as is described in one of the specific comments below.

Author Comment: The history of using theoretical methods to estimate infrared absorption spectra, which are needed for GWP determinations, dates back decades. Blowers and co-workers provided some of the first studies that applied theoretical methods to greenhouse gases of atmospheric relevance. Other noteworthy studies are the comprehensive works of NIST (Kazakov et al., 2012) and Betowski et al. (2015). We have included Betowski et al. in our discussion, but we could add other citations to provide additional perspective. The focus of our paper is on the application of these proven methods in a comprehensive manner to a class of compounds of interest to the Montreal Protocol, but for which laboratory data are not available. The novelty of this work is in that we have comprehensively addressed the role of conformers, which has been routinely neglected in previous studies, in deriving relevant metrics. We have also made an attempt to address the uncertainties associated with the estimated metrics, another topic frequently neglected. We don't believe our work is necessarily superior to similar previous studies, but it does provide a comprehensive systematic study of a large number of HCFCs of interest to the Montreal Protocol. The results obtained in our work are provided in great detail in the available SI, such that future studies by other research groups can benefit from this work. The semi-empirical ODPs provided in this work use the model lifetime results presented in the SPARC lifetime report, which are currently recommended for atmospheric modeling. We have also applied an empirical formulation, based on the SPARC lifetime results, for the fractional release factors for the many HCFCs that do not have reported values.

Author Action: We have added text to the manuscript in section 2.3 Theoretical Calculations to address the lack of history and citations in the original submission.

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 ±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 CH_2ClF 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).

Reviewer Comment: Title: I think the current title describes the content of the paper insufficiently.

Author Response: Reviewer #1 suggested including "estimates" in the title to help clarify the content of the manuscript.

Author Action: Title changed as follows: Global Warming Potential Estimates for the C_1-C_3 Hydrochlorofluorocarbons (HCFCs) Included in the Kigali Amendment to the Montreal Protocol

Reviewer Comment: Figure S1: HFC-227ea is misspelled and HCFC-22 and HFC-125 appear twice.

Author Response: Thanks, there were typos in the labels.

Author Action: The labeling has been corrected as follows:

Figure: plot of Stratospheric Lifetime for OH Reaction (years) vs Tropospheric Lifetime for OH Reaction, Scaled (years), showing data points labeled HFC-23, HCFC-142b, HFC-143a, HFC-227ea, HFC-125, HCFC-22, HFC-245fa, HFC-134a, HFC-32, HCFC-141b, CH₃CCl₃, HFC-152a.
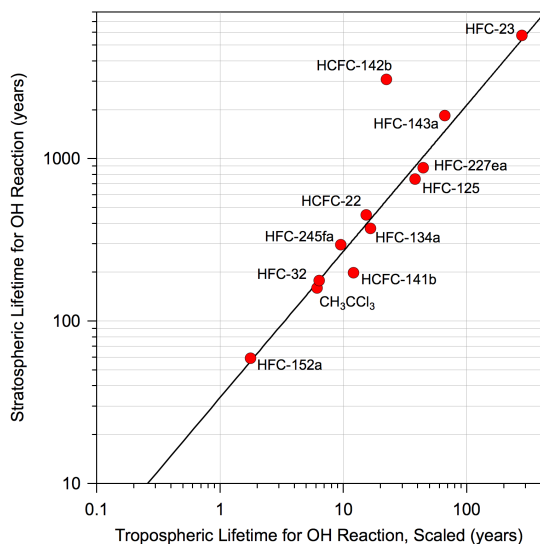
Reviewer Comment: Page 5, line 15-16: This is misleading as only one HCFC seems to have been used.

Author Response: This section addresses the determination of stratospheric lifetimes that, as stated, includes 2 HCFCs (142b was not included in the fit) and 8 HFCs. We are not sure how this was misinterpreted.
Author Action: None

Reviewer Comment: Page 5, line 16-17 and line 19: What does 'in most cases' mean? 51 %?

Author Response: This statement was intended to mean the vast majority.
Author Action: For clarification, the text has been revised as follows: ~~In most cases,~~ The stratospheric loss via the OH reaction accounts for ~≤5% of the total OH loss process for >95% of the HCFCs.

Reviewer Comment: Page 6, line 14-15: The method previously used for calculating fractional release has recently been proved wrong and age-of-air estimates have been improved, both of which have substantial implications for a number of compounds including HCFCs. I am surprised that the editor did not question this as he is an author on all three recent papers (Ostermoeller et al., 2017; Engel et al., 2017; Elvidge et al., accepted, 2018 – all ACP).

Author Response: It is not clear how the results from the cited recent papers would be applied to molecules with unknown lifetimes and no observational data. The empirical approach used in this work to relate the fraction of a molecule removed in the stratosphere to its fractional release is a reasonable estimation method, recommended by several atmospheric modeling groups, for use in the semi-empirical ozone depletion potential (ODP) calculation. The preferred approach to determine ODPs would be to use atmospheric model calculations for each of the 274 HCFCs included in the work to calculate the ODPs. Such calculations were, however, considered beyond the scope of this study.
Author Action: None

Reviewer Comment: Figure 3: It would help to see the experimental and the calculated spectrum 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.

14

Calculated Spectra
— with conformers
····· without conformers
— Experimental Spectrum
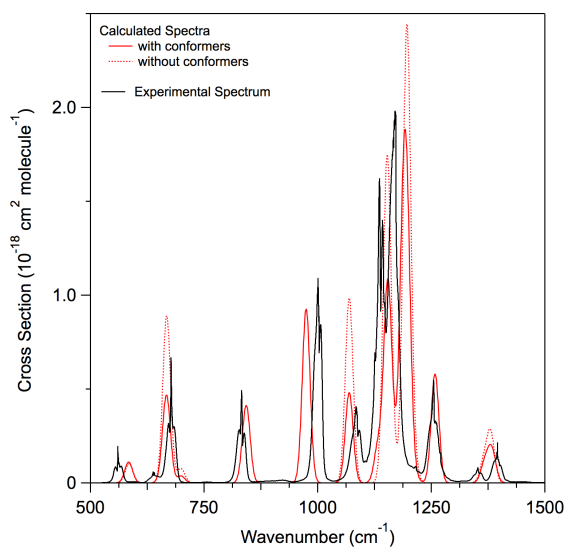
Reviewer Comment: Page 11, line 29-31: I don't think there should be a section for GTPs if it only contains one sentence.

     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 17, line 3-4: Why are these HCFCs of primary interest?

     Author Response: These are the HCFCs identified by the parties as some of the most likely candidates to watch for future use. However, this is not an official policy statement.

     Author Action: None

Reviewer #3

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

5

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
10   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
15   **Author Action**: We have revised the text in the abstract as follows: "The C_1–C_3 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.".

20 **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
25   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
30   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~~
35   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 C_1-C_3 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
40   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
45   **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
50   potentials" throughout the manuscript.

16

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 ±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 CH_2ClF 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.
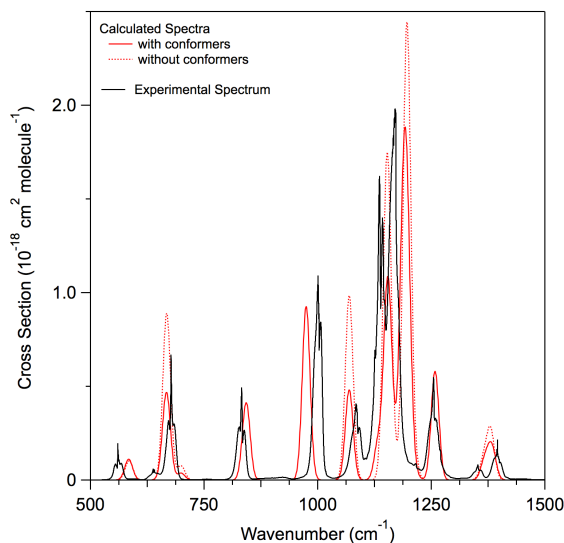
Reviewer Comment: Page 10, line 9-11: Perhaps I missed something, but is it shown somewhere that the broadening leads to better agreement with experimental HCFC spectra? As I interpret Fig. 5, it only shows the difference with and without the broadening and not comparison to experimental data.

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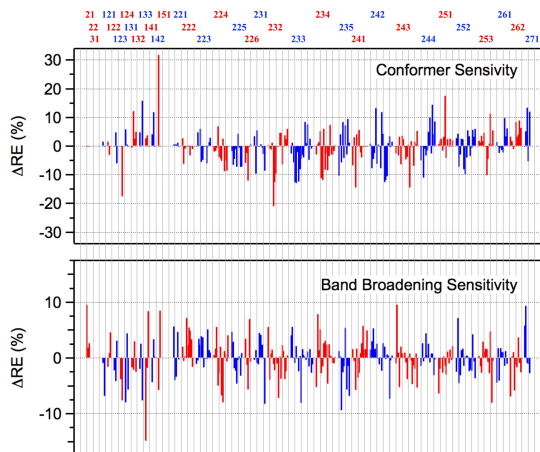
Reviewer Comment: Page 11, line 15: Could you include "(see Section 5)" at the end of the sentence? I started looking for the datasheets in the supplementary information without finding it, before I realized these were only available on a web site.

       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 IntRF_CO2(T) the integrated radiative forcing of CO2? Also, M_HCFC in the formula is not defined, I think.

       Author Response: Agree

       Author Action: Text revised as follows: where $IntRF_{CO2}(T)$ is the <u>integrated</u> radiative forcing of CO_2 <u>and M_{HCFC} is the HCFC molecular weight</u>.

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: <u>A comparison of the experimentally derived REs and the calculated values for the training dataset is given in Figure S3.</u>

20
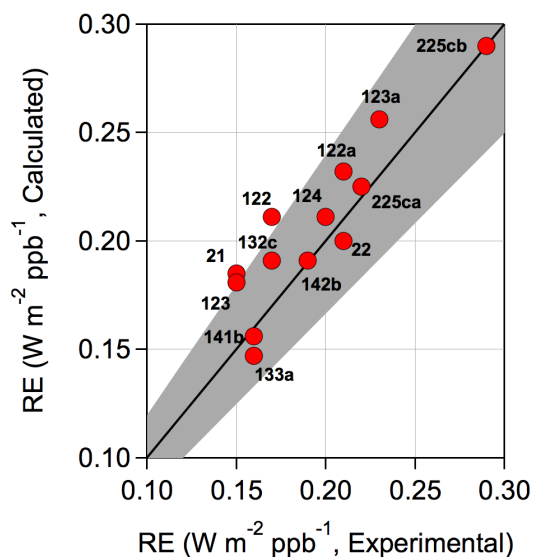
Figure S3: Comparison of experimental and calculated "lifetime corrected" radiative efficiencies (REs) for the training dataset HCFCs. The solid line is the 1:1 correlation. The gray shaded region represents ±20% around the 1:1 line. Note that the spread in REs without applying the "lifetime correction" is ~±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, <u>where</u> the range of 100-year time horizon global warming potentials (GWPs) <u>obtained in this work for various HCFC isomers all with the chemical formula</u> given in the first column <u>is</u> 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.

Global Warming Potential ==Estimates== for the C_1-C_3 Hydrochlorofluorocarbons (HCFCs) Included in the Kigali Amendment to the Montreal Protocol

5

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Abstract. Hydrochlorofluorocarbons (HCFCs) are ozone depleting substances and potent greenhouse gases that are controlled under the Montreal Protocol. However, the majority of the 274 HCFCs included in Annex C of the protocol do not have reported global warming potentials (GWPs) that are used to guide the phase-out of HCFCs and the future phase-down of hydrofluorocarbons (HFCs). In this study, GWPs for all C_1–C_3 HCFCs included in Annex C are

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reported based on estimated atmospheric lifetimes and theoretical methods used to calculate infrared absorption spectra. Atmospheric lifetimes were estimated from a structure activity relationship (SAR) for OH radical reactivity and estimated O(^{1}D) reactivity and UV photolysis loss processes. The ==C_1–C_3== 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. The results from this study provide ~~reliable~~ policy relevant GWP metrics for the

25

HCFCs included in the Montreal Protocol in the absence of experimentally derived metrics.

1 Introduction

Hydrochlorofluorocarbons (HCFCs) are ozone depleting substances (ODSs), the production and use of which are controlled under the Montreal Protocol on Substances that Deplete the Ozone Layer (1987). HCFCs have been used as substitutes for chlorofluorocarbons (CFCs) in various commercial and residential applications, e.g. foam blowing,

30

and refrigerator and air conditioning systems. In addition to being ODSs, HCFCs are also potent greenhouse gases (WMO, 2014).

With the adoption of the Kigali Amendment (2016) to the Montreal Protocol by the Twenty-Eighth Meeting of the Parties to the Montreal Protocol, parties agreed to the phase-down of hydrofluorocarbons (HFCs), substances that are not ozone depleting but are climate forcing agents. As in the case of HCFCs, the HFC production and consumption

control measures comprise reduction steps from established baselines (see UN Environment OzonAction Fact Sheet (UN, 2017)), which are different for developed and developing countries with an exemption for countries with high ambient temperature parties. Since HFCs are greenhouse gases, baselines and reduction steps are expressed in CO_2 equivalents. The amended Protocol controls eighteen HFCs as listed in Annex F of the Protocol.

5   Although the phase-down steps stipulated in the Kigali Amendment concern only HFCs, the baselines for the reductions are derived through formulae involving both HCFCs and HFCs production and consumption because HFCs are intended to be substitute compounds for HCFCs. This necessitates knowledge of the global warming potentials (GWPs) of all HCFCs involved in the baseline formulae. However, in the amended Protocol, GWPs are available for only 8 HCFCs (HCFCs-21, -22, -123, -124, -141b, -142b, -225ca, and HCFC-225cb) out of the total of 274 HCFCs

10   included in Annex C (274 is the sum of all C_1–C_3 HCFC isomers). Of the 274 HCFCs, only 15 have experimental kinetic and/or infrared absorption spectrum measurements used to determine their GWPs. The majority of the HCFCs listed in Annex C are not currently in use, but the intent of the Protocol was for a comprehensive coverage of possible candidates for future commercial use and possible emission to the atmosphere. For molecules with no GWP available, a provision is included in the Protocol stating that a default value of zero applies until such a value can be included by

15   means of adjustments to the Protocol. Having policy-relevant metrics for these compounds will help guide and inform future policy decisions.

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. The HCFCs that have experimentally measured OH rate coefficients, the

20   predominant atmospheric loss process for HCFCs, and infrared absorption spectra were used as a training dataset to establish the reliability of the methods used to estimate the metrics for the other HCFCs. The training dataset compounds and reference data are listed in Table 1. In the following section, brief descriptions of the methods used to determine the HCFC atmospheric lifetime and ODP are given. Next, the theoretical methods used to calculate the infrared spectra of the HCFCs are described. The infrared spectra are then combined with our estimated global

25   atmospheric lifetimes to estimate the lifetime and stratospheric temperature adjusted radiative efficiency (RE), GWP, and GTP metrics (see IPCC (2013) and WMO (2014) assessments). In the Results and Discussion section, a general overview of the obtained metrics is provided, while the details and results for each of the individual HCFCs are provided in the Supporting Information (SI).

Table 1. Summary of hydrochlorofluorocarbon (HCFC) parameters in the training dataset *

Common Name	Molecular Formula	k_{OH}(298 K) (10^{-14} cm^3 molecule^{-1} s^{-1}) [1]	Atmospheric Lifetime (years)	Stratospheric Lifetime (years)	Infrared Absorption Spectrum Source	Radiative Efficiency (RE) (W m^{-2} ppb^{-1})	Global Warming Potential (GWP) 100-yr time horizon
HCFC–21	$CHFCl_2$	3.0	1.7	~35	Sihra et al. (2001)	0.15	148
HCFC–22	CHF_2Cl	0.49	11.9	161	Sihra et al. (2001)	0.21	1760
HCFC-31	CH_2FCl	4.1	1.2	~35	–	–	–
HCFC–122	$CHCl_2CClF_2$	5.1	–	–	Orkin et al. (2003)	0.17	59
HCFC–122a	$CHClFCCl_2F$	1.6	–	–	Orkin et al. (2003)	0.21	258
HCFC–123	$CHCl_2CF_3$	3.6	1.3	36	Sihra et al. (2001)	0.15	79
HCFC–123a	$CHClFCClF_2$	1.3	4.0	~65	–	0.23	370
HCFC–124	$CHClFCF_3$	0.90	5.9	111	Sihra et al. (2001)	0.20	527
HCFC–124a	CHF_2CClF_2	–	~9.2	~120	Sharpe et al. (2004)	–	–
HCFC–132	$CHClFCHClF$	–	–	–	Sharpe et al. (2004)	–	–
HCFC–132a	$CHCl_2CHF_2$	–	–	–	Sharpe et al. (2004)	–	–
HCFC–132b	$CHCl_2CHF_2$	1.7	–	–	–	–	–
HCFC–132c	CH_2FCCl_2F	1.23	–	–	Orkin et al. (2003)	0.17	338
HCFC–133a	CH_2ClCF_3	1.1 [2]	4.45 [2]	103 [2]	Sharpe et al. (2004) Etminan et al.(2014) McGillen et al.(2015)	0.16 [2]	370 [2]
HCFC–141b	CH_3CCl_2F	0.58	9.4	72.3	Sihra et al. (2001) Sharpe et al. (2004)	0.16	782
HCFC–142b	CH_3CClF_2	0.34	18	212	Sihra et al. (2001)	0.19	1980
HCFC–225ca	$CHCl_2CF_2CF_3$	2.5	1.9	44	Sihra et al. (2001)	0.22	127
HCFC–225cb	$CHClFCF_2CClF_2$	0.89	5.9	101	Sihra et al. (2001)	0.29	525
HCFC–234fb	$CCl_2FCH_2CF_3$	0.080	~45	~85	–	–	–
HCFC–243cc	$CH_3CF_2CFCl_2$	0.24	19.5	~70	–	–	–

* Lifetimes, RE, and GWP values taken from WMO ozone assessment (WMO, 2014) unless noted otherwise.

[1] Rate coefficients taken from NASA evaluation (Burkholder et al., 2015) unless noted otherwise.

[2] Rate coefficient and metrics taken from McGillen et al. (2015) with RE lifetime adjusted and a factor of +1.1 for stratospheric temperature correction applied.

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2 Methods

2.1 Atmospheric Lifetimes

The global atmospheric lifetime (τ_{atm}) is defined as:

$$\frac{1}{\tau_{atm}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{O(^1D)}} + \frac{1}{\tau_{h\nu}}$$

where τ_{OH}, $\tau_{O(^1D)}$, and $\tau_{h\nu}$ are the global lifetimes with respect to OH and $O(^1D)$ reactive loss and UV photolysis, respectively. Other reactive and deposition loss processes for HCFCs are expected to be negligible and not considered in this study. τ_{atm} is also often defined in terms of its loss within the troposphere (τ_{Trop}), stratosphere (τ_{Strat}), and mesosphere (τ_{Meso}) as:

$$\frac{1}{\tau_{atm}} = \frac{1}{\tau_{Trop}} + \frac{1}{\tau_{Strat}} + \frac{1}{\tau_{Meso}}$$

where for example:

$$\frac{1}{\tau_{Strat}} = \frac{1}{\tau_{Strat}^{OH}} + \frac{1}{\tau_{Strat}^{O(^1D)}} + \frac{1}{\tau_{Strat}^{h\nu}}$$

For the HCFCs considered in this study, mesospheric loss processes are negligible and not considered further. The atmospheric loss processes for the HCFCs considered in this study have not been determined experimentally, while τ_{Trop} is predominately determined by the HCFC reactivity with the OH radical. In this work, τ_{Trop}^{OH} was estimated using the CH_3CCl_3 (MCF) relative method (WMO, 2014) where:

$$\tau_{Trop}^{OH} = \tau_{OH}^{HCFC} = \frac{k_{MCF}(272\,K)}{k_{HCFC}(272\,K)}\,\tau_{OH}^{MCF}$$

with the MCF recommended rate coefficient, $k_{MCF}(272\,K) = 6.14 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Burkholder et al., 2015), and tropospheric lifetime, 6.1 years (WMO, 2014).

In the absence of experimental OH reaction rate coefficients, a structure activity relationship (SAR) was used to estimate OH reaction rate coefficients. The SAR of Kwok and Atkinson (1995) and DeMore (1996) were compared with the rate coefficients for the 15 HCFCs (training dataset) for which experimental kinetic measurements are available (Burkholder et al., 2015). The DeMore SAR clearly performed better for these halocarbons and was used in this study. Figure 1 shows the agreement between the experimental 298 K rate coefficient data and the SAR predicted values. For the determination of $k_{HCFC}(272\,K)$ an E/R value of 1400 K was used in the Arrhenius expression, $k(T) = A \exp(-1400/T)$, which is a representative value for the HCFC reactions included in Burkholder et al. (2015). On the basis of the training dataset calculations, we estimate the uncertainty in the SAR 298 K rate coefficients on average to be ~30%. The uncertainty at 272 K will, in some cases, be greater due to our assumption that $E/R = 1400$ K for the unknown reaction rate coefficients. A ~50% uncertainty spread encompasses nearly all the training dataset values at 272 K, see Figure 1. Therefore, we estimate a 50% uncertainty in $k(272\,K)$ for the HCFCs with unknown rate coefficients.
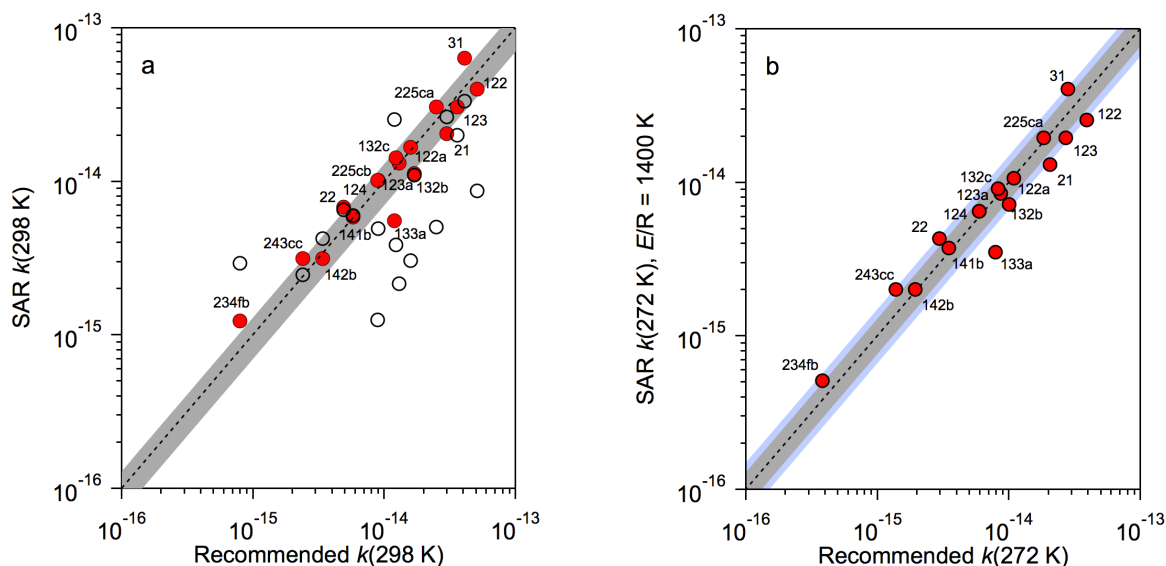
Figure 1: Comparison of structure activity relationship (SAR) OH rate coefficients for the training dataset (Table 1) with rate coefficients recommended in Burkholder et al. (2015). (a) Rate coefficients at 298 K using the SAR of DeMore (1996) (solid symbols) and Kwok and Atkinson (1995) (open symbols). The dashed line is the 1:1 correlation and the shaded region is the ±30% spread around the 1:1 line. (b) Rate coefficients at 272 K using the SAR of DeMore (1996) (solid symbols) with an $E/R = 1400$ K. The dashed line is the 1:1 correlation and the gray shaded region is the ±30% spread and the blue shaded region is the ±50% spread around the 1:1 line.

τ_{Strat} for the HCFCs is determined by a combination of OH and O(^{1}D) reactive loss, and UV photolysis. Presently, there is not a simple means to determine stratospheric lifetimes without the use of atmospheric models. Here, we have estimated stratospheric OH loss lifetimes, τ_{Strat}^{OH}, following a methodology similar to that used in the WMO (2014) ozone assessment, where results from 2-D atmospheric model calculations are used to establish a correlation between tropospheric and stratospheric lifetimes. We have used the lifetimes taken from the SPARC (Ko et al., 2013) lifetime report for 3 HCFCs and 8 HFCs to establish a lifetime correlation, which is shown in Figure S1 in the SI. ~~In most cases.~~ The stratospheric loss via the OH reaction accounts for $\sim\lesssim5\%$ of the total OH loss process for >95% of the HCFCs. Therefore, this method of accounting for stratospheric loss ~~is acceptably accurate for our purpose~~ leads to only a minor uncertainty in the calculated global lifetime.

In most cases, O(^{1}D) reaction and UV photolysis are minor contributors to the global loss of a HCFC. In the absence of experimental data, O(^{1}D) rate coefficients were estimated using the reactivity trends reported in Baasandorj et al. (2013). $\tau_{O(1D)}$ for the HCFCs were based on a comparison with similarly reactive compounds included in the SPARC (Ko et al., 2013) lifetime report. As shown later, the O(^{1}D) reaction is a minor loss process, <1%, for nearly all the HCFCs included in this study and, therefore, the estimation method used is not critical as this loss process is a minor contributor to the global lifetime ~~are sufficiently accurate for our study~~. $\tau_{h\nu}$ was estimated based on the molecular Cl-

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atom content and its distribution within the molecule as follows: each isolated Cl-atom (450 years), each CCl_2 group (80 years), each CCl_3 group (50 years), with a minimum photolysis lifetime of 50 years (Ko et al., 2013). UV photolysis is a minor loss process, with the exception of a few long-lived highly-chlorinated HCFC isomers where photolysis accounts for at most 15% of the global loss.

A minimum stratospheric lifetime of 20 years was applied to approximately account for transport limited stratospheric lifetimes.

2.2 Ozone Depletion Potentials (ODPs)

Semi-empirical ODPs were calculated using the formula:

$$ODP_{HCFC} = \frac{n_{Cl}}{3} \frac{f_{HCFC}}{f_{CFC-11}} \frac{M_{CFC-11}}{M_{HCFC}} \frac{\tau_{HCFC}}{\tau_{CFC-11}}$$

where n_{Cl} is the number of Cl-atoms in the HCFC, M is the molecular weight, f is the molecules fractional release factor (FRF), and τ is the global atmospheric lifetime. The fractional release factor and global lifetime for CFC-11 were taken from the WMO (2014) ozone assessment report to be 0.47 and 52 years, respectively. The fractional release factors for the majority of the HCFCs included in this study have not been reported. The WMO report included 3 year age of air FRFs derived from model studies and field observations for 20 ozone depleting substances (WMO, 2014). In the absence of recommended FRF values, we derived an empirical FRF vs stratospheric lifetime relationship, shown in Figure 2, for the compounds with reported FRFs and the 2-D model stratospheric lifetimes reported in the SPARC (Ko et al., 2013) lifetime report. Table S1 provides the values presented in Figure 2. A fit to the data yielded FRF = 0.06 + 0.875 × exp(-0.0144 × τ_{Strat}), which was used in our calculations.
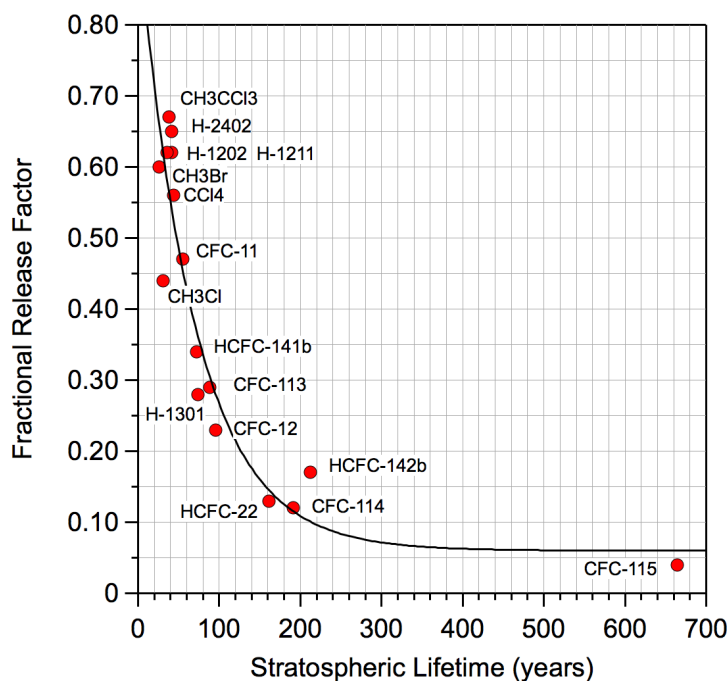
Figure 2: Empirical correlation of fractional release factor (FRF) versus stratospheric lifetime, τ_{Strat}. Stratospheric lifetimes were taken from 2-D model results given in the SPARC (Ko et al., 2013) lifetime report. The FRFs were taken from WMO assessment (WMO, 2014). The solid line is a fit to the data: $FRF = 0.06 + 0.875 \exp(-0.01444 \times \tau_{Strat})$.

2.3 Theoretical Calculations

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 ±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 CH_2ClF the intensity in the region involving C-Cl stretching nevertheless exhibits intensity errors of ~10% (Charmet et al., 2013).

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The large number of molecules considered in this work and the associated geometry optimizations, ~1500 optimizations, required that a cost-effective methodology with reasonable accuracy such as density functional theory (DFT) methods be used. Geometry optimization and vibrational frequencies for all C_1-C_3 HCFCs were carried at the B3LYP/6-31G(2df,p) level using the Gaussian 09 software suite (Frisch et al., 2016). 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. The calculations presented in this work included only the ^{35}Cl isotope because the large number of possible isotopic substitution permutations made the calculation of all combinations prohibitive. In principle, substitution of ^{35}Cl by ^{37}Cl in a heavy molecule would lower the frequency of the C-Cl stretch by ~3%. The level of theory was evaluated based on comparison with available experimental HCFC infrared spectra, see Table 1. Note that our calculations and data available in the NIST quantum chemistry database (2016) obtained using a more costly triple-ζ basis set (aug-cc-pVTZ) showed only minor differences in the calculated frequencies, <1%, and band strengths, <10%, for the molecules in the training dataset.

The majority of the HCFCs have multiple low-energy conformers that have unique infrared absorption spectra. Although only the most stable conformer has been used in most previous theoretical studies, including the individual conformers provides a more realistic representation of the HCFCs infrared spectrum and is expected to improve the accuracy of the calculated radiative efficiency as discussed below. 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. In this work, we have included all conformers within 2 kcal mol^{-1} of the lowest energy conformer. This limit accounts for >98% of the population distribution at 298 K, in most cases. For each HCFC, a relaxed scan was performed to detect all possible conformations. For the C_2 compounds, 3 staggered conformations were examined by rotating the C-C torsional angle by 120°. For the C_3 compounds, 9 possible conformations were calculated by rotating the two torsional angles by 120°. Each stable conformer was then fully optimized at the B3LYP/6-31G(2df,p) level followed by a frequency calculation. Conformer populations were calculated for a 298 K Boltzmann's distribution using the relative energies (including a zero-point correction) from the calculations. Including stable conformers resulted in overlapping vibrational bands and, therefore, more congested spectra which is consistent with the observed spectra for HCFCs. A number of the HCFCs have stereoisomers. Although, the stereoisomers have identical infrared absorption spectra, they were accounted for in the population distribution. Note that for a molecule with a single asymmetrical carbon (a molecule containing a carbon with 4 different groups attached), e.g. HCFC-121a (CHClFCCl$_3$), a pair of stereoisomers exist for each conformation and, therefore, the contribution of stereoisomers to the total population factors out. The entire dataset contains 126 molecules with a single asymmetric carbon and 32 molecules containing 2 asymmetric carbons.

A comparison of the experimental and calculated infrared spectrum of HCFC-124a (CHF₂CClF₂) shown in Figure 3 demonstrates the importance of including conformers in the spectrum calculation. A comparison of experimental and theoretical spectra for all molecules with experimental data is provided in the SI (see Section 5). The calculations found that HCFC-124a has 3 stable conformers at 298 K with the lowest energy conformer having ~50% of the population. The experimental spectrum is characterized by strong absorption features between 1100 and 1500 cm^{-1}, which are mostly associated with C-F bond vibrations, and C-Cl vibrational modes below 1000 cm^{-1}. The comparison with the experimental spectrum shows that the prominent absorption features at ~825, 1000, and 1250 cm^{-1} originate from the higher energy conformers. The calculated spectrum is in good agreement with the experimentally measured spectrum with band positions and total integrated band strengths agreeing to within ~2%. Note that conformer contributions to an infrared absorption spectrum will be different for different molecules. The impact of including conformers in the radiative efficiency calculations is presented later.
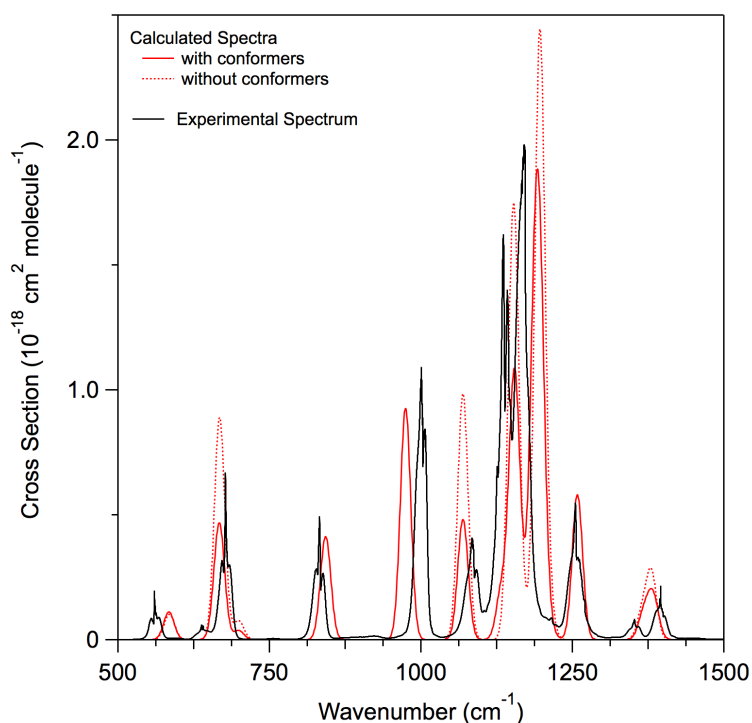
Figure 3: Comparison of experimental and calculated infrared absorption spectrum of HCFC-124a (CHF₂CClF₂). (a) Calculated spectra at B3LYP/6-31G(2df,p) level of theory with (solid) and without (dotted) including stable conformers, and (b) the experimentally measured spectrum (see Table 1 for the source of the experimental spectrum).

Overall, the agreement between experimental and calculated frequencies was good. Figure S2 shows a comparison of experimental vibrational frequencies with the calculated values. There was a systematic overestimation of the calculated vibrational frequencies above 1000 cm^{-1} and an underestimation below 1000 cm^{-1}. An empirical frequency correction, which, in part, accounts for anharmonicity and other approximations used in the level of theory employed,

was derived from this correlation and applied to all the calculated spectra: $\nu_{corrected} = 53.609 + 0.94429 \times \nu_{calculated}$. Using this correction, frequencies around ~1200 cm^{-1} (C-F bond vibrations) and around 800 cm^{-1} (C-Cl bond vibrations) are shifted by only ~1%. The uncertainty associated with the calculated band positions is estimated to be ~1%. The frequency-corrected spectra were used to derive the metrics reported here.

Figure 4 shows a comparison of calculated and experimental band strengths (integrated between 500 and 2000 cm^{-1}) for the training dataset. Overall, the agreement is good for the majority of HCFCs with the calculated band strengths being within 20%, or better, of the experimental values. The calculated band strengths are, however, systematically biased high by ~20%, for band strengths $<$~1.1×10^{-16} cm^2 molecule^{-1} cm^{-1}. A comparison of the training dataset experimental and calculated infrared spectra reveals that the bias originates from a band strength overestimation of bands below 1000 cm^{-1} that are primarily associated with C-Cl bonds. The bias is greatest for molecules containing more than one Cl atom on the same carbon, e.g. CHFCl$_2$ (HCFC-21), CH$_3$CCl$_2$F (HCFC-141b) and CH$_2$FCCl$_2$F (HCFC-132c). ==In fact the intensities of C-Cl stretches are a long-known problem for calculation (Halls and Schlegel, 1998).== Scaling the overall spectrum strength to account for such biases has been applied to decrease the deviation between experimental and theoretical values in an earlier theoretical study by Betowski et al. (2015). However, since the bias is primarily for the bands associated with C-Cl bonds, a scaling of the entire band strength would not be appropriate nor an accurate representation of the experimental spectrum. The spectra reported here do not include a band strength correction, as the prediction of which bands are overestimated is too uncertain without knowledge of the experimental spectrum. Although it is difficult to estimate the uncertainty for the theoretical calculations, an estimated ~20% band strength uncertainty includes nearly all the training dataset values and encompasses the possible systematic bias observed for certain vibrational bands.
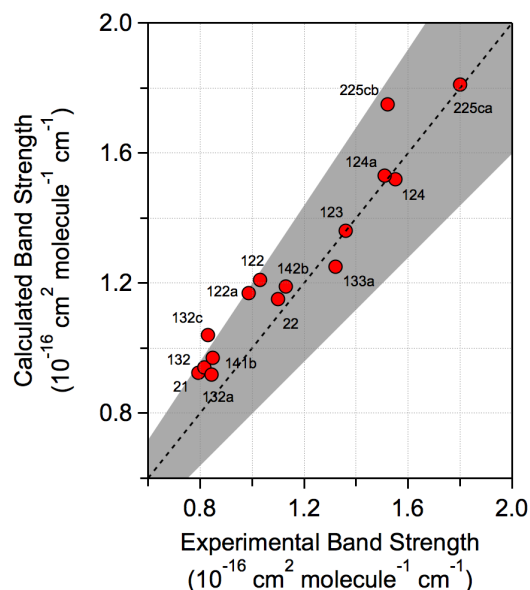
Figure 4: Comparison of experimental and calculated infrared band strengths ~~(in units of 10^{-16} cm² molecule⁻¹ cm⁺)~~ over the 500–2000 cm⁻¹ region for the HCFC training dataset (see Table 1 for the source of the experimental spectra). The dashed line is the 1:1 correlation. The shaded region represents a 20% spread around the 1:1 line.

2.4 Radiative Efficiency

Radiative efficiencies (REs) were calculated using the 298 K infrared absorption spectra calculated theoretically in this work and the Earth's irradiance parameterization given in Hodnebrog et al. (2013). The calculated spectra were broadened using a Gaussian broadening function with a FWHM (full width at half maximum) of 20 cm⁻¹, which reproduces the training dataset spectra reasonably well and provides a more realistic representation of the spectrum and overlap with Earth's irradiance profile. Note that the Gaussian broadening function may not necessarily be an accurate representation of the actual vibrational band shape. Previous theoretical studies of greenhouse gases have applied band broadening as part of their analysis (see Hodnebrog et al. (2013) and references within), although the necessity of broadening has generally not been treated quantitatively. In our work, the calculated bands were broadened to obtain better agreement with available experimental HCFC spectra, which are assumed to be representative of the spectra of the unknown HCFCs, and, in principle, more reliable radiative efficiencies. Figure 5 shows the difference in retrieved REs with and without band broadening. The differences are molecule dependent, but are less than 10% for nearly all the HCFCs. Although the differences are relatively small the use of a realistic broadening function reduces the uncertainty in the RE calculation and should be applied. A comparison of the experimentally derived REs and the calculated values for the training dataset is given in Figure S3.
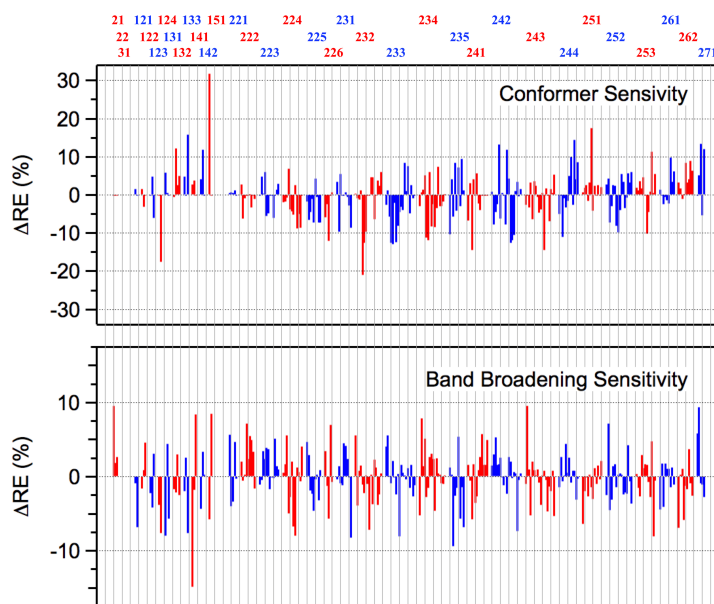
Figure 5: Sensitivity of the calculated HCFC radiative efficiencies in this study to the broadening of the calculated infrared absorption bands, as described in the text, (Lower Panel) and the inclusion of higher energy conformers

(Upper Panel). ΔRE values are relative to the full analysis that includes broadened spectra and all conformers within 2 kcal mole^{-1} of lowest energy conformer.

As illustrated earlier for HCFC-124a, Figure 3, stable HCFC conformers can make a significant contribution to its infrared absorption spectrum. Figure 5 shows the impact of including the conformer population on the calculated RE for each of the HCFCs included in this study. Overall, including conformers increases or decreases the calculated RE by 10%, or less, in most cases. However, there are some HCFCs where a difference of 20%, or more, is observed, e.g. HCFC-124a, HCFC-151, and HCFC-232ba. In conclusion, including the contribution from populated conformers improves the accuracy of the calculated RE values and decreases potential systematic errors in the theoretically predicted RE values.

The strongest HCFC vibrational bands are due to C-F stretches, 1000-1200 cm^{-1}, which strongly overlap the "atmospheric window" region. The molecular geometry of the HCFC determines the exact vibrational band frequencies, i.e., HCFCs and their isomers have unique infrared absorption spectra and REs. Note that the calculated infrared spectra in this work include vibrational bands below 500 cm^{-1}, which is usually the lower limit for experimental infrared absorption spectra measurements. The contribution of vibrational bands in this region to the RE is quantified in our calculations and is usually minor, i.e., <1%.

Lifetime-adjusted REs were calculated using the CFC-11 emission scenario "S" shaped parameterization given in Hodnebrog et al. (2013)**,** which is intended to account for non-uniform mixing of the HCFC in the atmosphere. The adjustment is greatest for short-lived molecules. A +10% correction was applied to all molecules to account for the stratospheric temperature correction (see IPCC (2013) supplementary material section 8.SM.13.4 for the origin of this factor). Well-mixed and lifetime-adjusted RE values are included in the Supporting Information datasheets (see Section 5).

2.5 Global Warming and Global Temperature change Potentials

Global warming potentials on the 20- and 100-year time horizons (T) were calculated relative to CO_2 using the formulation given in IPCC (2013):

$$\mathbf{GWP(T) = \frac{RE\ \tau\ [1 - exp\ (-T/\tau)]}{M_{HCFC}\ Int\ RF_{CO_2}(T)}}$$

where IntRF$_{CO2}$(T) is the integrated radiative forcing of CO_2 and M_{HCFC} is the HCFC molecular weight. The RE used in the calculation was lifetime-adjusted with a stratospheric temperature correction applied. The global lifetimes were estimated as described above in Section 2.1. The CO_2 denominator is consistent with the GWP values reported in the WMO (2014) and IPCC (2013) assessments corresponding to a CO_2 abundance of 391 ppm. Therefore, the values reported in this work can be compared directly to values reported in the WMO and IPCC assessments. A comparison of our training dataset values is given in Figure S3 Figure 6, where the majority of the GWPs agree to within 15%. HCFCs 21, 22, 122, and 123 have larger differences, due primarily to discrepancies between the estimated and literature OH rate coefficients. Our GWP results can be scaled to the 2016 CO_2 abundance of 403 ppm (NOAA, 2017)

by multiplying by 1.03, which accounts for a decrease in the CO_2 radiative efficiency (see Myhre et al. (1998) and Joos et al. (2013)).
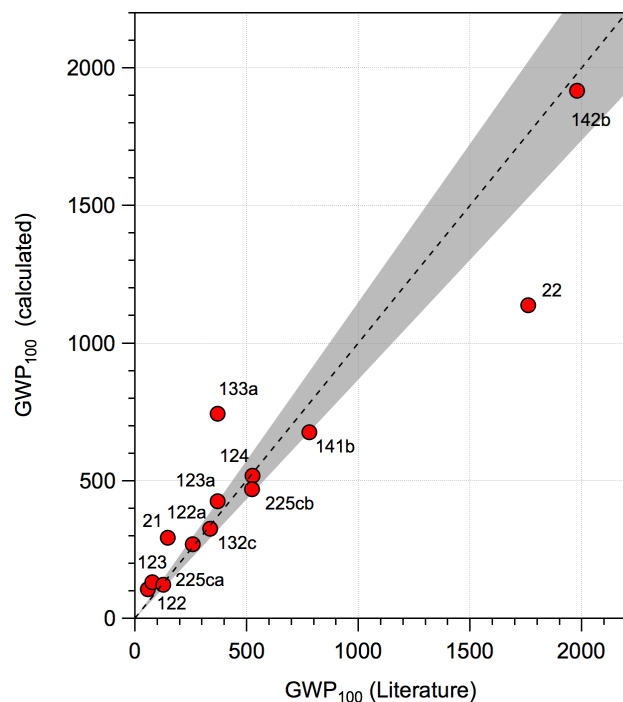
Figure 6. Comparison of 100-year time horizon GWP values reported in the WMO assessment (WMO, 2014) and McGillen et al. (2015) for 133a (with lifetime-adjustment and stratospheric temperature correction applied) and the values calculated in this study. The dashed line represents the 1:1 correlation and the shaded area is a 15% spread around the 1:1 line.

2.6 Global Temperature Potentials

Global temperature change potentials were calculated for the 20-, 50-, and 100-year time horizons using the parameterizations given in the IPCC (2013) supplementary material section 8.SM.11.2.

3 Results and Discussion

Figure 6 7 provides a comprehensive graphical summary of the lifetime, ODP, lifetime and stratosphere stratospheric temperature adjusted RE, GWP, and GTP results obtained in this study and the values that are based on experimental data (in black) where available. The metric values for the individual compounds are available in Table S2 and the individual datasheets in the Supporting Information. A detailed summary of the theoretical results is also included in the datasheets for the individual compounds.

It is clear that the metrics for the C_1-C_3 HCFCs possess a significant range of values with a dependence on the H-atom content as well as the isomeric form for a given chemical formula. In general, an increase in the HCFC H-atom

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content leads to a shorter atmospheric lifetime, e.g. the lifetimes for the HCFC-226 compounds (1 H-atom) are greater than most other HCFCs. However, the HCFC reactivity also depends on the distribution of hydrogen, chlorine, and fluorine within the molecule, i.e., the isomeric form and lifetimes for isomers can vary significantly. For example, the lifetime of HCFC-225ca ($CHCl_2CF_2CF_3$) is 1.9 years, while that of HCFC-225da ($CClF_2CHClCF_3$) is 16.3 years. The highest reactivity HCFCs are short-lived compounds with lifetimes as low as ~0.3 years. The lowest reactivity HCFCs have lifetimes as long as 60 years (HCFC-235fa, $CClF_2CH_2CF_3$).

The trends in the HCFC ODPs follow that of the lifetimes with an additional factor to account for the chlorine content of the HCFC. Overall many of the HCFCs have significant ODPs with 33 HCFCs having values greater than 0.1 and 78 greater than 0.05.

In addition to HCFC isomers having different reactivity (lifetimes), each isomer also has a unique infrared absorption spectrum and, thus, a unique RE. The HCFC REs range from a low of ~0.03 to a high of ~0.35 W m^{-2} ppb^{-1}. The HCFCs with the highest H-atom content have lower REs, in general, although there are exceptions as shown in Figure 6. As expected, many of the HCFCs are potent greenhouse gases. The GWPs and GTPs also show a strong isomer dependence, e.g. the GWPs on the 100-year time horizon for the 9 HCFC-225 isomers differ by a factor of ~12. The lowest HCFC GWPs in this study are ~10 and the greatest value is ~5400 for HCFC-235fa.
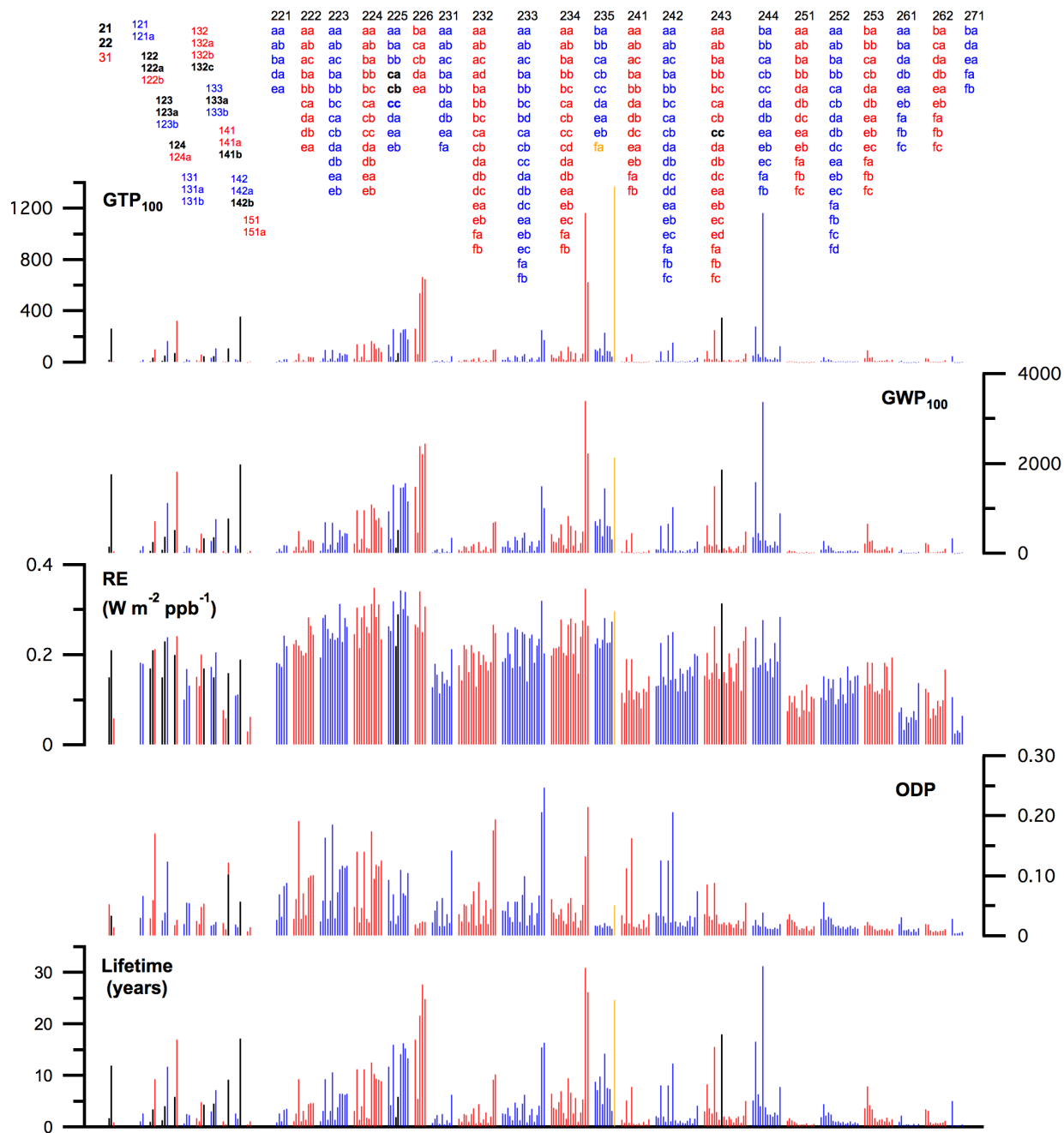
Figure 6 7: Summary of the results obtained in this study for C_1-C_3 HCFCs (red and blue) and the values for which experimentally derived metrics are available (black). The lifetime, GWP, and GTP values for HCFC-235fa ($CClF_2CH_2CF_3$) (gold) have been multiplied by 0.4 to improve the overall graphical clarity.

3.1 Metric Uncertainty

The training calculations have been used to estimate the uncertainties in our atmospheric lifetime estimates and infrared absorption spectra and how these uncertainties propagate through to the key ODP, RE, GWP, and GTP metrics. It is not possible to assign a single uncertainty for all HCFCs for each metric due to their dependence on the individual properties of the HCFCs. To provide a general perspective for the reliability of the metrics reported in this study, we limit our discussion to the average behavior.

The predominant atmospheric loss process for HCFCs was shown to be reaction with the OH radical, while UV photolysis in the stratosphere was found to be a non-negligible loss process for HCFCs with long lifetimes and significant Cl content. The DeMore (1996) SAR predicts the training dataset OH rate coefficients at 298 K to within 25% on average, which directly translates into a 25% uncertainty in the HCFC tropospheric lifetime. A conservative uncertainty estimate in the predicted OH rate coefficients at 272 K would be ~50%, see Figure 1. Including an estimated ~40% uncertainty for the stratospheric UV photolysis and $O(^1D)$ reactive loss processes increases the global lifetime uncertainty by only ~2%.

The semi-empirical ODP uncertainty is directly proportional to the global lifetime uncertainty with an additional factor to account for the uncertainty in the fractional release factor (FRF). For HCFCs with total lifetimes less than 2 years, the total ODP uncertainty is estimated to be 35%, for a 25% uncertainty in the global lifetime. For longer lived HCFCs, the ODP uncertainty is greater, 50% or more.

The theoretically calculated REs for the training dataset agreed to within 10% with the values derived using the experimentally measured spectra, even though our estimated band strength uncertainty is 20%. This method of RE determination is, therefore, expected to provide reliable good estimates of REs in the absence of experimentally based determinations. The accuracy of the lifetime-adjusted RE values depends primarily on the uncertainty in the lifetime, calculated infrared band strengths, and to a lesser degree on the calculated band positions. We estimated the uncertainty in the calculated band strengths to be <20%, although not all vibrational bands are expected to have the same level of uncertainty. The uncertainty in the calculated vibrational band centers primarily impacts the RE through changes in the overlap with the irradiance profile. This sensitivity was estimated by artificially shifting the calculated spectrum in the RE calculation of several representative HCFCs by the estimated band center uncertainty of 1%. The band center uncertainty was found to make less than a 5% contribution to the total RE uncertainty. Note that molecules with strong absorption features near the large CO_2 and O_3 dips in the Earth's irradiance profile would have a greater sensitivity to shifts in the spectrum. The lifetime correction to the RE introduces an additional uncertainty that is dependent on the lifetime of the HCFC and its uncertainty. For compounds with a lifetime of 0.2 to 1 year, i.e., on the steep portion of the lifetime correction profile given in Hodnebrog et al. (2013), an additional ~25% uncertainty is introduced, while for longer-lived HCFCs the lifetime adjustment uncertainty is smaller. A lifetime-adjusted RE uncertainty of ~30% is estimated for the majority of the HCFCs included in this study assuming a 25% uncertainty in the global lifetime.

The overall uncertainty in the GWP and GTP metrics depends on the lifetime and RE uncertainties, with a different dependence on different time horizons. Compounds with lifetimes of less than 1 year have propagated uncertainties of ~55% on average. As the lifetime increases the uncertainty decreases to ~30% on average, or less. The greater uncertainty values for the shorter lived HCFCs is primarily associated with the uncertainty introduced by the lifetime-adjusted RE.

As mentioned earlier, there have been a number of previous studies that have applied methods similar to those used in the present study. The most relevant of these studies is that of Betowski et al. (2015) who reported radiative efficiencies for a large number of the C_1-C_3 HCFCs included in this study. Although they report REs for 178 of the 274 HCFCs included in our work there are significant differences between their REs and those reported here. Figure S4 shows a comparison of the RE values calculated here with those reported in Betowski et al. for the HCFCs common to both studies. The RE values from Betowski et al. are systematically lower than the ones reported here by ~29% on average. A similar systematic underestimation is observed when the Betowski et al. RE values are compared with the available HCFC experimental data used in our training dataset. Betowski et al. used B3LYP/6-31G(d) to calculate the HCFC infrared spectra and applied a band strength correction in their RE calculation. Note that a band strength correction was not applied in the present study as discussed earlier. In addition, Betowski et al. ~~didn't~~ did not use broadened infrared spectra in their RE calculation and included only the lowest energy conformer. These differences can account for some of the scatter in the correlation shown in Figure S4. The average difference between the reported RE values can only partially be explained by the different methods used here, B3LYP/6-31G(2df,p), and in Betowski et al., B3LYP/6-31G(d), as they produce very similar HCFC infrared spectra, i.e., the band strengths obtained with these methods agree to within ~10%.

Betwoski et al. used the available HCFC experimental data and data for a large number of compounds from other chemical classes in their training dataset, e.g. perhalocarbons, haloaldehydes, haloketones, and haloalcohols. On the basis of their analysis, a band strength scaling factor of 0.699, for the B3LYP/6-31G(d) method, was derived. However, for the HCFCs this scale factor introduces a systematic error in the band strength analysis. In Figure 4 we showed that the DFT theoretical methods, without scaling, agree with the available experimental HCFC data to within 20%, or better. Although the HCFC training dataset is relatively small, the band strength scaling factor based on results for other chemical compound classes is most likely not appropriate and introduces a systematic bias for the calculated RE values. Therefore, the infrared spectra reported in the present work and used to derive REs and GWPs were not scaled.

4 Summary

In this study, policy-relevant metrics have been provided for C_1-C_3 HCFC compounds, many of which were not available at the time of the adoption of the Kigali amendment. Table 2 summarizes the results from this study in the condensed format used in Annex C of the amended Protocol where the range of metrics are reported for each HCFC chemical formula. Metrics for the individual HCFCs are given in Table S2 and the data sheets for each of the HCFCs that contain the explicit kinetic parameters and theoretical results obtained in this work.

Table 2. 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 listed ~~given~~ in the first column is given in *italics* *

Group	Substance	Number of isomers	Ozone Depletion Potential***	100-Year Global Warming Potential****
Group I				
CHFCl$_2$	(HCFC-21)**	1	0.04	151
CHF$_2$Cl	(HCFC-22)**	1	0.055	1810
CH$_2$FCl	(HCFC-31)	1	0.02	*47*
C$_2$HFCl$_4$	(HCFC-121)	2	0.01–0.04	*66–158*
C$_2$HF$_2$Cl$_3$	(HCFC-122)	3	0.02–0.08	*105–713*
C$_2$HF$_3$Cl$_2$	(HCFC-123)	3	0.02–0.06	*130–1125*
C$_2$HF$_3$Cl$_2$	(HCFC-123)**	–	0.02	77
C$_2$HF$_4$Cl	(HCFC-124)	2	0.02–0.04	*517–1826*
C$_2$HF$_4$Cl	(HCFC-124)**	–	0.022	609
C$_2$H$_2$FCl$_3$	(HCFC-131)	3	0.007–0.05	*31–175*
C$_2$H$_2$F$_2$Cl$_2$	(HCFC-132)	4	0.008–0.05	*67–441*
C$_2$H$_2$F$_3$Cl	(HCFC-133)	3	0.02–0.06	*273–762*
C$_2$H$_3$FCl$_2$	(HCFC-141)	3	0.005–0.07	*15–676*
C$_2$H$_3$FCl$_2$	(HCFC-141b)**	–	0.11	725
C$_2$H$_3$F$_2$Cl	(HCFC-142)	3	0.008–0.07	*108–1916*
C$_2$H$_3$F$_2$Cl	(HCFC-142b)**	–	0.065	2310
C$_2$H$_4$FCl	(HCFC-151)	2	0.003–0.005	*11–54*
C$_3$HFCl$_6$	(HCFC-221)	5	0.015–0.07	*38–181*
C$_3$HF$_2$Cl$_5$	(HCFC-222)	9	0.01–0.09	*56–495*
C$_3$HF$_3$Cl$_4$	(HCFC-223)	12	0.01–0.08	*56–693*
C$_3$HF$_4$Cl$_3$	(HCFC-224)	12	0.01–0.09	*83–1090*
C$_3$HF$_5$Cl$_2$	(HCFC-225)	9	0.02–0.07	*122–1562*
C$_3$HF$_5$Cl$_2$	(HCFC-225ca)**	–	0.025	122
C$_3$HF$_5$Cl$_2$	(HCFC-225cb)**	–	0.033	595
C$_3$HF$_6$Cl	(HCFC-226)	5	0.02–0.10	*467–2452*
C$_3$H$_2$FCl$_5$	(HCFC-231)	9	0.05–0.09	*17–346*
C$_3$H$_2$F$_2$Cl$_4$	(HCFC-232)	16	0.008–0.10	*26–713*
C$_3$H$_2$F$_3$Cl$_3$	(HCFC-233)	18	0.007–0.23	*38–1496*
C$_3$H$_2$F$_4$Cl$_2$	(HCFC-234)	16	0.01–0.28	*55–3402*
C$_3$H$_2$F$_5$Cl	(HCFC-235)	9	0.03–0.52	*315–5327*
C$_3$H$_3$FCl$_4$	(HCFC-241)	12	0.004–0.09	*10–452*
C$_3$H$_3$F$_2$Cl$_3$	(HCFC-242)	18	0.005–0.13	*29–1027*
C$_3$H$_3$F$_3$Cl$_2$	(HCFC-243)	18	0.007–0.12	*34–1498*
C$_3$H$_3$F$_4$Cl	(HCFC-244)	12	0.009–0.14	*124–3369*
C$_3$H$_4$FCl$_3$	(HCFC-251)	12	0.001–0.01	*9–70*
C$_3$H$_4$F$_2$Cl$_2$	(HCFC-252)	16	0.005–0.04	*24–275*
C$_3$H$_4$F$_3$Cl	(HCFC-253)	12	0.003–0.03	*57–665*
C$_3$H$_5$FCl$_2$	(HCFC-261)	9	0.002–0.02	*7–84*
C$_3$H$_5$F$_2$Cl	(HCFC-262)	9	0.002–0.02	*28–227*
C$_3$H$_6$FCl	(HCFC-271)	5	0.001–0.03	*5–338*

* Typos for HCFC 123 and 124 GWPs entries are corrected here.

** Identifies the most commercially viable substances.

*** The ODPs listed are from the Montreal Protocol, while ODPs derived in This Work for the individual HCFCs are available in the Supporting Material, Table S2.

**** Range of values ~~taken~~ from This Work obtained for the HCFC isomers are given in italics.

We have shown that HCFC isomers have significantly different lifetimes, ODPs, and radiative metrics. Of particular interest are the HCFCs with current significant production and emissions to the atmosphere. Of all the HCFCs listed in Annex C of the amended Protocol, HCFCs -121(2), -122(3), -133(3), 141(3), -142(3), and -225(9) are of primary interest (the values in parenthesis are the number of isomers for that chemical formula). Of these 23 compounds, experimentally based metrics are included in the Kigali amendment only for HCFCs -141b, -142b, -225ca, and -225cb. Therefore, the present work provides policy-relevant information for the other HCFCs.

Although this work has provided ~~reliable~~ a comprehensive set of estimated ~~of key~~ metrics for the C_1-C_3 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. Laboratory measurements of infrared spectra would also provide specific quantitative results to be used in the determination of the RE, GWP, and GTP metrics. It is anticipated that laboratory measurements could yield uncertainties in the reactive and photolysis loss processes of ~10% and the infrared spectrum of ~5%, or better, which are significantly less than the 25% and 20% average estimated uncertainties obtained with the methods used in this work. Therefore, laboratory studies would potentially yield more accurate metrics. Note that the absolute uncertainty in the ODP, RE, GWP, and GTP metrics would also include a consideration of the uncertainties associated with lifetime determination methods and the Earth's irradiance profile approximation used to derive RE values, as well as the uncertainty in CO_2 radiative forcing, which were not considered in this work.

5 Data availability

Figures and tables including the master summary table of metrics for all HCFCs is provided in the supporting material. Data sheets for the individual HCFCs that contain the derived atmospheric lifetimes, ODP, RE, GWP, and GTP metrics and graphs and figures and tables of the theoretical calculation results are available at URL https://www.esrl.noaa.gov/csd/groups/csd5/datasets/.

6 Competing interests

The authors have no financial conflicts.

7 Acknowledgments and Data

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Supporting Information

Global Warming Potentials <mark>Estimated</mark> for the C_1-C_3 Hydrochlorofluorocarbons (HCFCs) Included in the Kigali Amendment to the Montreal Protocol

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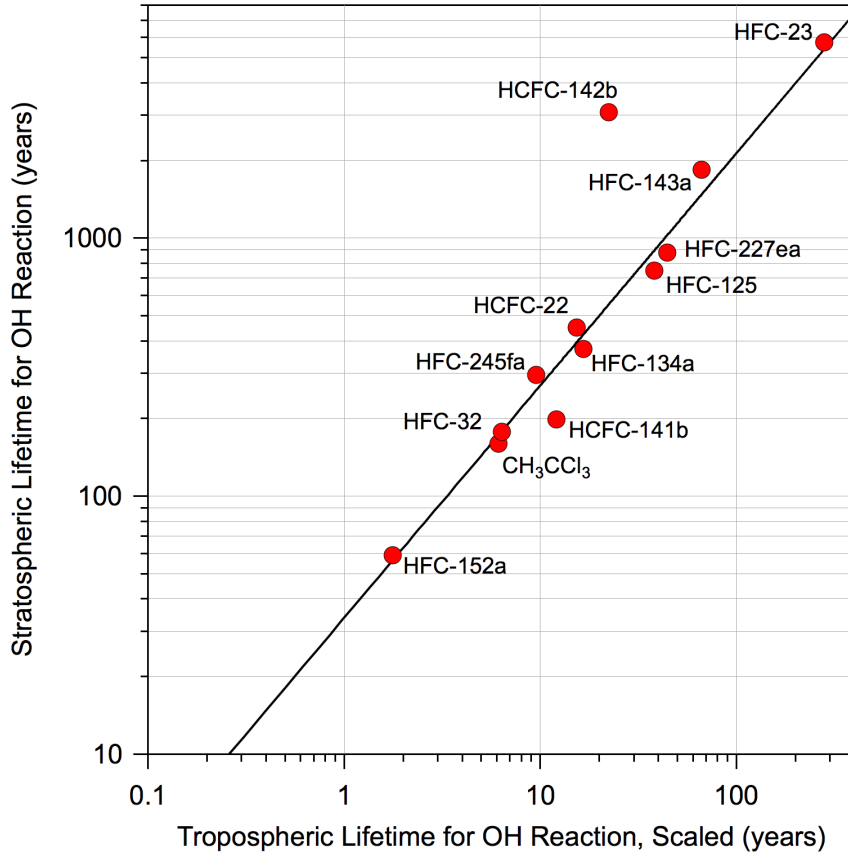
Figure S1. Correlation between the tropospheric and stratospheric lifetimes for OH reactive loss calculated using the 2-D atmospheric model results for the HCFCs and HFCs reported in the SPARC (Ko et al., 2013) lifetime report. The stratospheric lifetime has been corrected for O(^{1}D) reactive loss using reactive rate coefficients reported in Burkholder et al. (2015) and estimated lifetimes as described in the text. The line is a fit to the data, $Log_{10}(\tau_{Strat}^{OH}) = 1.528 + 0.901 \, Log_{10}(\tau_{Trop}^{OH})$. HCFC-142b was not included in the fit. The 2-D model calculated tropospheric lifetimes were scaled to the recommended CH_3CCl_3 tropospheric lifetime of 6.1 years.
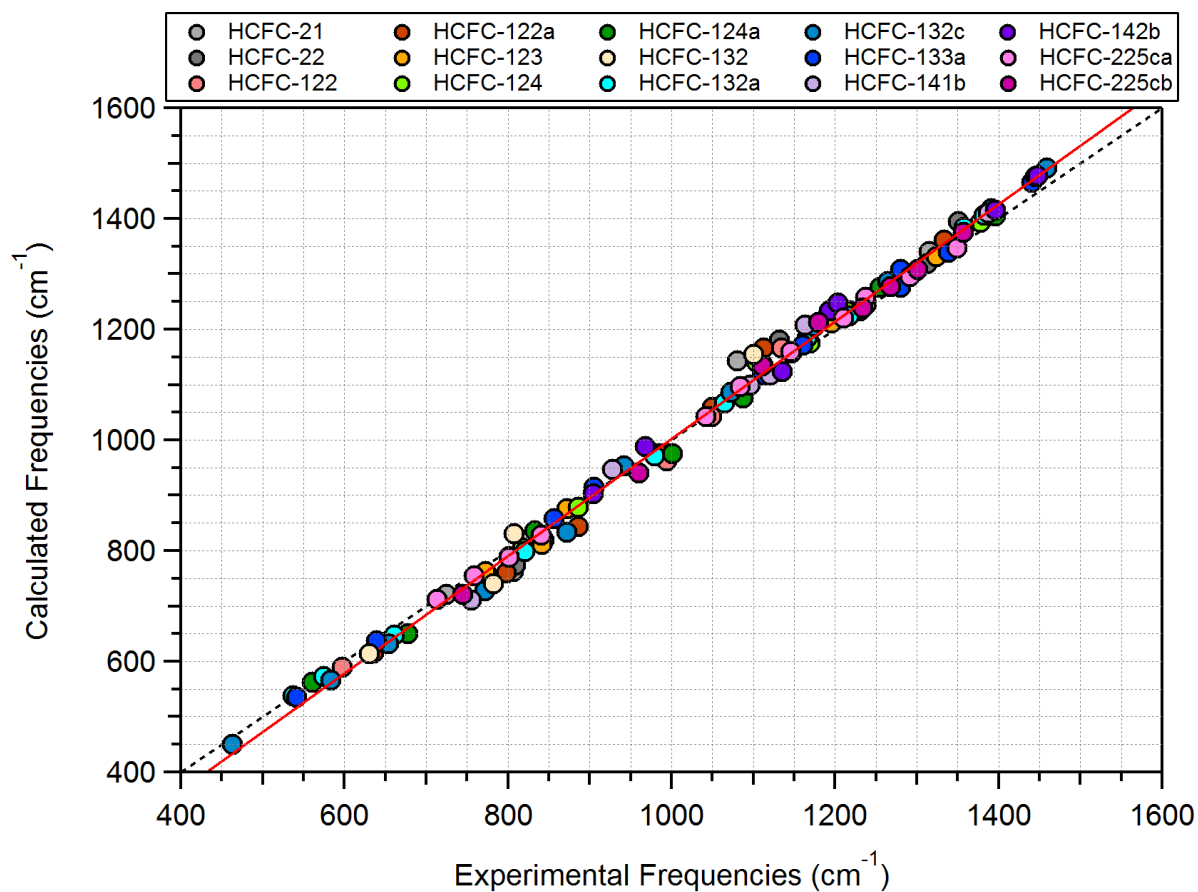
Figure S2. Comparison of experimentally measured and calculated infrared absorption spectrum frequencies for the HCFCs listed in the legend. The dashed line represents a 1:1 correlation. The correlation was used to derive a linear frequency correction (red line) for the calculated HCFC spectra in this study.
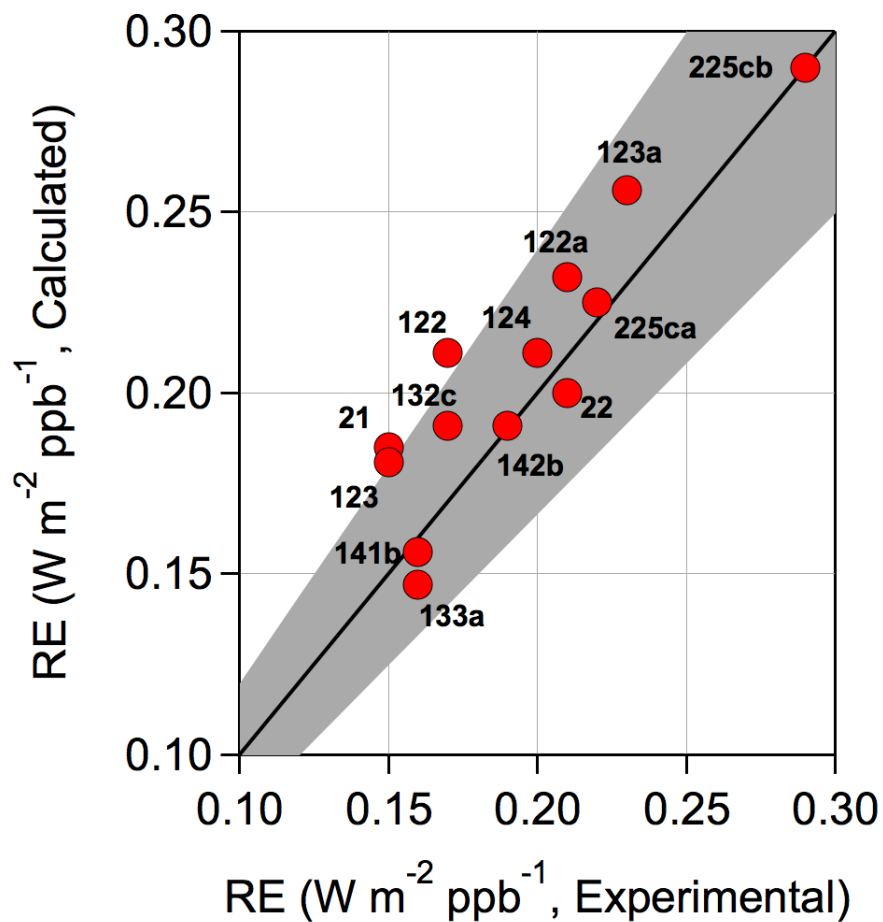
Figure S3: Comparison of experimental and calculated "lifetime corrected" radiative efficiencies (REs) for the training dataset HCFCs. The solid line is the 1:1 correlation. The gray shaded region represents ±20% around the 1:1 line. Note that the spread in REs without applying the "lifetime correction" is ~±10%.

Figure S4. Comparison of radiative efficiencies (RE) (W m^{-2} ppbv^{-1}) calculated in this work and reported in Betowski et al. (2015) The HCFCs that have experimentally derived RE values are shown in blue (rectangles and lines). The dashed line is the 1:1 correlation. The bottom panel shows the percent difference between this work and that of Betowski et al. for each of the HCFCs.

Table S1. Data used to derive the empirical correlation of fractional release factor (FRF) versus stratospheric lifetime, τ_{Strat}. Stratospheric lifetimes were taken from the 2-D model results given in the SPARC (Ko et al., 2013) lifetime report. The FRFs were taken from WMO assessment (WMO, 2014).

Molecule	Fractional Release Factor (FRF)	Stratospheric Lifetime (τ_{Strat}) (years)
CFC-11	0.47	55
CFC-12	0.23	95.5
CFC-113	0.29	88.4
CFC-114	0.12	191
CFC-115	0.04	664
Halon-1202	0.62	36
Halon-1211	0.62	41
Halon-1301	0.28	73.5
Halon-2402	0.65	41
CH_3Cl	0.44	30.4
CCl_4	0.56	44
CH_3CCl_3	0.67	38
HCFC-22	0.13	161
HCFC-141b	0.34	72.3
HCFC-142b	0.17	212
CH_3Br	0.60	26.3

Table S2. Summary of estimated lifetimes, ozone depletion potentials (ODP), radiative efficiencies (REs), global warming potentials (GWPs), and global temperature <mark>change</mark> potentials (GTPs) for the C_1-C_3 hydrochlorofluorocarbons (HCFCs) included in this work. The GWP and GTP values are consistent with the CO_2 radiative forcing used in the IPCC (2013) and WMO (2014) assessments.

HCFC	Formula	Lifetimes (years)								Ozone Depletion Potential (ODP)	Radiative Efficiency (RE) W m^{-2} ppb^{-1}	Global Warming Potential (Time Horizon, years)		Global Temperature change Potential (Time Horizon, years)		
		Global	Total Trop	Total Strat	Total OH Reactive Loss	Trop OH Reactive Loss	Strat OH Reactive Loss	O(^{1}D) Reactive Loss	UV Photolysis Loss			20	100	20	50	100
21	CHFCl$_2$	2.66	2.87	36.4	2.780	2.87	87.2	285	80	0.053	0.185	1078	292	438	53	41
22	CHF$_2$Cl	8.09	8.67	119.8	8.365	8.67	236.2	529	450	0.032	0.2	3847	1138	2661	344	162
31	CH$_2$FCl	0.897	0.927	27.7	0.901	0.927	31.5	463	450	0.015	0.0587	173	47	55	8	7
121	CHCl$_2$CCl$_2$F	1.11	1.17	20.0	1.137	1.17	38.9	185	50	0.030	0.183	244	66	80	11	9
121a	CHClFCCl$_3$	2.67	2.96	27.3	2.863	2.96	89.6	185	50	0.066	0.18	582	158	237	29	22
122	CHCl$_2$CClF$_2$	1.39	1.47	24.5	1.430	1.47	47.8	195	67.9	0.030	0.211	389	105	133	18	15
122a	CHClFCCl$_2$F	3.2	3.54	34.1	3.422	3.54	105.3	195	67.9	0.060	0.232	988	268	434	50	37
122b	CHF$_2$CCl$_3$	9.31	12.6	35.5	12.154	12.6	331.1	195	50	0.170	0.213	2326	713	1702	253	102
123	CHCl$_2$CF$_3$	1.81	1.92	30.8	1.861	1.92	60.7	285	80	0.026	0.181	480	130	173	23	18
123a	CHClFCClF$_2$	4.16	4.45	63.8	4.304	4.45	129.5	285	225	0.038	0.256	1558	425	778	84	60
123b	CHF$_2$CClF$_2$	11.8	15.1	53.8	14.525	15.1	389.0	285	80	0.124	0.24	3394	1125	2694	528	167
124	CHClFCF$_3$	5.47	5.8	98.0	5.600	5.8	164.3	529	450	0.018	0.211	1860	517	1070	114	73
124a	CHF$_2$CClF$_2$	17	19	161.2	18.266	19	478.6	529	450	0.026	0.241	4677	1826	4088	1258	327
131	CHCl$_2$CHClF	0.752	0.786	20.0	0.764	0.786	27.1	185	67.9	0.019	0.101	113	31	36	5	4
131a	CH$_2$ClCCl$_2$F	2.57	2.8	31.4	2.711	2.8	85.3	185	67.9	0.056	0.169	647	175	259	32	24
131b	CH$_2$FCCl$_3$	2.33	2.55	26.2	2.473	2.55	78.5	185	50	0.054	0.132	456	123	176	22	17
132	CHClFCHClF	1.73	1.81	39.1	1.759	1.81	57.7	264	225	0.025	0.152	438	119	156	21	17
132a	CHCl$_2$CHF$_2$	1.12	1.18	23.9	1.144	1.18	39.1	264	80	0.020	0.131	246	67	81	12	9
132b	CH$_2$ClCClF$_2$	4.84	5.21	67.0	5.039	5.21	149.4	264	225	0.048	0.202	1602	441	864	92	62
132c	CH$_2$FCCl$_2$F	3.76	4.14	40.8	4.005	4.14	121.4	264	80	0.054	0.191	1194	325	566	63	45
133	CHClFCHF$_2$	3.07	3.21	67.8	3.109	3.21	96.5	463	450	0.017	0.173	1008	273	434	51	38
133a	CH$_2$ClCF$_3$	9.82	10.6	126.5	10.262	10.6	284.1	463	450	0.026	0.147	2386	743	1782	280	107
133b	CH$_2$FCClF$_2$	7.21	7.71	110.0	7.443	7.71	212.5	463	450	0.024	0.206	2640	762	1736	206	108
141	CH$_2$ClCHClF	1.14	1.19	29.5	1.153	1.19	39.4	247	225	0.022	0.0772	170	46	56	8	6
141a	CH$_2$FCHCl$_2$	0.494	0.51	20.0	0.498	0.51	20.0	247	80	0.011	0.0594	56	15	17	3	2
141b	CH$_3$CCl$_2$F	8.33	10	49.3	9.666	10	269.2	247	80	0.122	0.156	2269	676	1589	211	96
142	CH$_2$ClCHF$_2$	2.61	2.73	60.1	2.643	2.73	83.4	411	450	0.019	0.11	643	174	259	32	24
142a	CH$_2$FCHClF	1.58	1.64	42.3	1.591	1.64	52.7	411	450	0.015	0.113	399	108	139	19	15
142b	CH$_3$CClF$_2$	16.6	18.7	147.6	17.958	18.7	471.3	411	450	0.041	0.191	4969	1916	4319	1291	336
151	CH$_2$ClCH$_2$F	0.487	0.5	20.0	0.488	0.5	20.0	370	450	0.008	0.0306	41	11	12	2	2
151a	CH$_3$CHClF	1.16	1.2	33.2	1.165	1.2	39.7	370	450	0.015	0.0629	199	54	66	9	7
221aa	CHCl$_2$CCl$_2$CCl$_2$F	0.929	0.979	20.0	0.951	0.979	33.1	185	50	0.027	0.183	142	38	46	7	5
221ab	CHClFCCl$_2$CCl$_3$	2.67	2.96	27.3	2.863	2.96	89.6	185	50	0.069	0.181	404	109	164	20	15
221ba	CHCl$_2$CClFCCl$_3$	1.11	1.17	20.0	1.137	1.17	38.9	185	50	0.032	0.174	161	44	53	8	6
221da	CCl$_3$CHClCCl$_2$F	3.29	3.71	29.0	3.592	3.71	110.0	185	50	0.083	0.243	668	181	297	34	25
221ea	CCl$_3$CHFCCl$_3$	3.51	3.99	29.5	3.859	3.99	117.3	185	50	0.088	0.219	644	175	295	33	24
222aa	CHCl$_2$CCl$_2$CClF$_2$	1.11	1.17	20.0	1.137	1.17	38.9	185	50	0.028	0.224	221	60	73	10	8
222ab	CHClFCCl$_2$CCl$_2$F	2.67	2.96	27.3	2.863	2.96	89.6	185	50	0.061	0.234	557	151	226	28	21
222ac	CHF$_2$CCl$_2$CCl$_3$	9.29	12.6	35.2	12.154	12.6	331.1	185	50	0.191	0.221	1616	495	1182	175	71
222ba	CHCl$_2$CClFCCl$_2$F	1.11	1.17	20.0	1.137	1.17	38.9	185	50	0.028	0.21	207	56	68	10	8
222bb	CHClFCClFCCl$_3$	3.15	3.54	28.6	3.422	3.54	105.3	185	50	0.071	0.199	557	151	243	28	21
222ca	CHCl$_2$CF$_2$CCl$_3$	1.38	1.47	21.6	1.430	1.47	47.8	185	50	0.034	0.205	253	68	86	12	10
222da	CCl$_2$FCHClCCl$_2$F	4.48	5.23	31.2	5.055	5.23	149.8	185	50	0.097	0.283	1118	306	580	62	43
222db	CCl$_3$CHClCClF$_2$	4.62	5.42	31.4	5.236	5.42	154.6	185	50	0.100	0.265	1077	296	568	61	41
222ea	CCl$_3$CHFCCl$_2$F	4.68	5.49	31.5	5.306	5.49	156.5	185	50	0.101	0.245	1007	276	534	57	39
223aa	CHCl$_2$CCl$_2$CF$_3$	1.11	1.17	20.0	1.137	1.17	38.9	185	50	0.024	0.195	205	56	68	10	8

HCFC	Formula	Lifetimes (years)								Ozone Depletion Potential (ODP)	Radiative Efficiency (RE) W m^{-2} ppb^{-1}	Global Warming Potential (Time Horizon, years)		Global Temperature <mark>change</mark> Potential (Time Horizon, years)		
		Global	Total Trop	Total Strat	Total OH Reactive Loss	Trop OH Reactive Loss	Strat OH Reactive Loss	O(^{1}D) Reactive Loss	UV Photolysis Loss			20	100	20	50	100
223ab	CHClFCCl$_2$CClF$_2$	3.18	3.54	31.4	3.422	3.54	105.3	185	59	0.059	0.282	854	232	374	43	32
223ac	CHF$_2$CCl$_2$CCl$_2$F	9.29	12.6	35.2	12.154	12.6	331.1	185	50	0.164	0.289	2262	693	1654	245	99
223ba	CHCl$_2$CClFCClF$_2$	1.39	1.47	23.1	1.430	1.47	47.8	185	59	0.029	0.258	341	92	116	16	13
223bb	CHClFCClFCClF$_2$F	3.18	3.54	31.4	3.422	3.54	105.3	185	59	0.059	0.235	713	193	312	36	27
223bc	CHF$_2$CClFCCl$_3$	10.6	15.1	35.7	14.525	15.1	389.0	185	50	0.185	0.249	2135	682	1638	282	99
223ca	CHCl$_2$CF$_2$CCl$_2$F	1.38	1.47	21.6	1.430	1.47	47.8	185	50	0.029	0.234	308	83	105	15	12
223cb	CHClFCF$_2$CCl$_3$	3.88	4.45	30.2	4.304	4.45	129.5	185	50	0.073	0.238	877	239	422	46	33
223da	CCl$_2$FCHClCClF$_2$	6.48	7.86	37.1	7.582	7.86	216.1	185	59	0.111	0.313	1849	525	1157	130	74
223db	CCl$_3$CHClCF$_3$	6.47	8.02	33.4	7.742	8.02	220.2	185	50	0.117	0.229	1351	383	844	94	54
223ea	CCl$_2$FCHFCCl$_2$F	6.28	7.74	33.2	7.467	7.74	213.1	185	50	0.114	0.282	1619	457	997	110	64
223eb	CCl$_3$CHFCClF$_2$	6.46	8.02	33.4	7.734	8.02	220.0	185	50	0.117	0.262	1545	438	966	108	62
224aa	CHClFCCl$_2$CF$_3$	3.15	3.54	28.9	3.422	3.54	105.3	195	50	0.049	0.247	796	216	347	40	30
224ab	CHF$_2$CCl$_2$CClF$_2$	11.3	15.1	44.6	14.525	15.1	389.0	195	67.9	0.141	0.306	2935	957	2298	426	141
224ba	CHCl$_2$CClFCF$_3$	1.39	1.47	24.5	1.430	1.47	47.8	195	67.9	0.023	0.215	307	83	105	14	12
224bb	CHClFCClFCFClF$_2$	4.1	4.45	51.2	4.304	4.45	129.5	195	150	0.047	0.283	1182	322	585	64	45
224bc	CHF$_2$CClFCCl$_2$F	11.3	15.1	44.6	14.525	15.1	389.0	195	67.9	0.141	0.308	2962	966	2319	430	142
224ca	CHCl$_2$CF$_2$CClF$_2$	1.79	1.92	27.5	1.861	1.92	60.7	195	67.9	0.028	0.262	483	131	173	23	18
224cb	CHClFCF$_2$CCl$_2$F	1.57	1.64	35.0	1.593	1.64	52.8	195	225	0.022	0.248	400	108	139	19	15
224cc	CHF$_2$CF$_2$CCl$_3$	12.5	19	36.7	18.266	19	478.6	195	50	0.174	0.314	3213	1090	2598	549	165
224da	CClF$_2$CHClCClF$_2$	10.4	12.3	67.1	11.813	12.3	322.7	195	150	0.096	0.349	3176	1006	2418	405	146
224db	CCl$_2$FCHClCF$_3$	9.39	12	43.4	11.546	12	316.1	195	67.9	0.119	0.285	2416	743	1775	266	107
224ea	CCl$_2$FCHFCClF$_2$	9.16	11.6	43.3	11.200	11.6	307.5	195	67.9	0.117	0.312	2601	794	1892	276	114
224eb	CCl$_3$CHFCF$_3$	8.88	11.9	35.3	11.435	11.9	313.3	195	50	0.126	0.235	1915	580	1376	194	83
225aa	CHF$_2$CCl$_2$CF$_3$	11.8	15.1	53.8	14.525	15.1	389.0	285	80	0.094	0.264	2818	934	2237	438	139
225ba	CHClFCClFCF$_3$	4.2	4.45	74.3	4.304	4.45	129.5	285	450	0.025	0.254	1172	320	588	64	45
225bb	CHF$_2$CClFCClF$_2$	15.9	19	99.5	18.266	19	478.6	285	225	0.069	0.319	4033	1526	3475	992	260
225ca	CHCl$_2$CF$_2$CF$_3$	1.81	1.92	30.8	1.861	1.92	60.7	285	80	0.020	0.225	451	122	162	22	17
225cb	CHClFCF$_2$CClF$_2$	5.36	5.8	71.2	5.600	5.8	164.3	285	225	0.034	0.29	1685	468	959	102	66
225cc	CHF$_2$CF$_2$CCl$_2$F	14.1	19	55.2	18.266	19	478.6	285	80	0.110	0.344	4081	1458	3412	840	232
225da	CClF$_2$CHClCClF$_2$	16.3	19.5	100.0	18.753	19.5	490.1	285	225	0.071	0.302	3858	1476	3342	980	256
225ea	CClF$_2$CHFCClF$_2$	15.3	18.1	98.7	17.447	18.1	459.1	285	225	0.068	0.34	4211	1562	3594	977	260
225eb	CCl$_2$FCHFCF$_3$	13.4	17.7	54.8	17.053	17.7	449.8	285	80	0.105	0.287	3306	1154	2725	627	179
226ba	CHF$_2$CClFCF$_3$	17	19	161.2	18.266	19	478.6	529	450	0.019	0.267	3792	1480	3314	1020	265
226ca	CHClFCF$_2$CF$_3$	5.47	5.8	98.0	5.600	5.8	164.3	529	450	0.013	0.261	1681	467	967	103	66
226cb	CHF$_2$CF$_2$CClF$_2$	21.6	24.7	173.6	23.763	24.7	607.2	529	450	0.022	0.341	5370	2388	4920	1976	539
226da	CF$_3$CHClCF$_3$	27.7	32.6	185.2	31.292	32.6	778.8	529	450	0.025	0.251	4323	2216	4111	2081	667
226ea	CClF$_2$CHFCF$_3$	24.9	28.8	180.2	27.695	28.8	697.4	529	450	0.023	0.307	5095	2452	4771	2193	649
231aa	CHCl$_2$CCl$_2$CHClF	0.799	0.839	20.0	0.815	0.839	28.8	185	50	0.022	0.128	98	27	31	5	4
231ab	CH$_2$ClCCl$_2$CCl$_2$F	1.61	1.73	23.0	1.674	1.73	55.2	185	50	0.042	0.18	278	75	97	13	10
231ac	CH$_2$FCCl$_2$CCl$_3$	2.33	2.55	26.2	2.473	2.55	78.5	185	50	0.058	0.156	348	94	135	17	13
231ba	CHCl$_2$CClFCHCl$_2$	0.561	0.586	20.0	0.570	0.586	20.8	185	50	0.015	0.114	62	17	19	3	2
231bb	CH$_2$ClCClFCCl$_3$	2.54	2.8	26.9	2.711	2.8	85.3	185	50	0.063	0.163	397	108	158	20	15
231da	CHCl$_2$CHClCCl$_2$F	0.535	0.557	20.0	0.542	0.557	20.0	185	50	0.015	0.136	70	19	22	3	3
231db	CHClFCHClCCl$_3$	1.34	1.43	21.3	1.390	1.43	46.6	185	50	0.036	0.144	186	50	63	9	7
231ea	CHCl$_2$CHFCCl$_3$	0.762	0.799	20.0	0.777	0.799	27.6	185	50	0.021	0.131	96	26	30	4	4
231fa	CCl$_2$FCH$_2$CCl$_3$	6.26	7.71	33.2	7.443	7.71	212.5	185	50	0.143	0.213	1226	346	755	83	49
232aa	CHClFCCl$_2$CHClF	1.65	1.77	24.9	1.715	1.77	56.4	185	59	0.036	0.177	303	82	107	14	11
232ab	CHCl$_2$CCl$_2$CHF$_2$	1.01	1.07	20.0	1.041	1.07	35.9	185	50	0.024	0.143	150	41	49	7	6
232ac	CH$_2$ClCCl$_2$CClF$_2$	2.56	2.8	29.3	2.711	2.8	85.3	185	59	0.053	0.222	587	159	235	29	22
232ad	CH$_2$FCCl$_2$CCl$_2$F	2.33	2.55	26.2	2.473	2.55	78.5	185	50	0.050	0.213	513	139	198	25	19
232ba	CHCl$_2$CClFCHClF	0.988	1.04	20.0	1.010	1.04	35.0	185	59	0.023	0.162	165	45	54	8	6

HCFC	Formula	Lifetimes (years)								Ozone Depletion Potential (ODP)	Radiative Efficiency (RE) W m^{-2} ppb^{-1}	Global Warming Potential (Time Horizon, years)		Global Temperature change Potential (Time Horizon, years)		
		Global	Total Trop	Total Strat	Total OH Reactive Loss	Trop OH Reactive Loss	Strat OH Reactive Loss	O(^{1}D) Reactive Loss	UV Photolysis Loss			20	100	20	50	100
232bb	CH$_2$ClCClFCCl$_2$F	2.56	2.8	29.3	2.711	2.8	85.3	185	59	0.053	0.222	587	159	235	29	22
232bc	CH$_2$FCClFCCl$_3$	3.64	4.14	29.7	4.005	4.14	121.4	185	50	0.075	0.205	766	208	357	40	29
232ca	CHCl$_2$CF$_2$CHCl$_2$	0.704	0.737	20.0	0.716	0.737	25.6	185	50	0.017	0.13	95	26	30	4	4
232cb	CH$_2$ClCF$_2$CCl$_3$	4.47	5.21	31.2	5.039	5.21	149.4	185	50	0.090	0.208	951	260	492	53	37
232da	CHCl$_2$CHClCClF$_2$	0.82	0.859	20.0	0.835	0.859	29.4	185	59	0.019	0.178	151	41	48	7	6
232db	CHClFCHClCCl$_2$F	1.51	1.61	24.0	1.558	1.61	51.7	185	59	0.033	0.2	312	84	108	15	12
232dc	CHF$_2$CHClCCl$_3$	2.83	3.15	27.8	3.048	3.15	94.8	185	50	0.060	0.184	539	146	224	27	20
232ea	CHCl$_2$CHFCCl$_2$F	0.829	0.872	20.0	0.847	0.872	29.8	185	50	0.019	0.165	142	38	45	7	5
232eb	CHClFCHFCCl$_3$	2.04	2.22	25.1	2.154	2.22	69.3	185	50	0.045	0.183	387	105	144	19	15
232fa	CCl$_2$FCH$_2$CCl$_2$F	9.23	12.5	35.2	12.050	12.5	328.5	185	50	0.176	0.267	2254	689	1644	242	99
232fb	CCl$_3$CH$_2$CClF$_2$	10.2	14.4	35.6	13.828	14.4	372.1	185	50	0.194	0.249	2260	713	1712	282	103
233aa	CHClFCCl$_2$CHF$_2$	2.63	2.87	31.6	2.774	2.87	87.1	185	67.9	0.043	0.185	542	147	219	27	20
233ab	CH$_2$ClCCl$_2$CF$_3$	2.57	2.8	31.4	2.711	2.8	85.3	185	67.9	0.042	0.194	556	151	223	27	21
233ac	CH$_2$FCCl$_2$CClF$_2$	3.71	4.14	35.3	4.005	4.14	121.4	185	67.9	0.057	0.25	1030	280	485	54	39
233ba	CHClFCClFCHClF	2.1	2.23	37.8	2.157	2.23	69.4	185	150	0.031	0.202	475	129	178	23	18
233bb	CHCl$_2$CClFCHF$_2$	1.27	1.34	23.3	1.303	1.34	44.0	185	67.9	0.023	0.171	242	66	81	11	9
233bc	CH$_2$ClCClFCClF$_2$	4.75	5.21	53.3	5.039	5.21	149.4	185	150	0.057	0.261	1365	375	729	78	53
233bd	CH$_2$FCClFCCl$_2$F	3.71	4.14	35.3	4.005	4.14	121.4	185	67.9	0.057	0.257	1058	288	498	55	40
233ca	CHCl$_2$CF$_2$CHClF	1.27	1.34	23.3	1.302	1.34	43.9	185	67.9	0.023	0.174	247	67	83	12	9
233cb	CH$_2$ClCF$_2$CCl$_2$F	4.57	5.21	37.3	5.039	5.21	149.4	185	67.9	0.069	0.25	1264	347	663	71	49
233cc	CH$_2$FCF$_2$CCl$_3$	6.26	7.71	33.2	7.443	7.71	212.5	185	50	0.100	0.246	1651	466	1016	112	66
233da	CHCl$_2$CHClCClF$_3$	0.896	0.939	20.0	0.913	0.939	31.9	185	67.9	0.017	0.142	142	38	45	7	5
233db	CHClFCHClCClF$_2$	2.37	2.52	40.1	2.443	2.52	77.6	185	150	0.034	0.238	630	171	245	31	24
233dc	CHF$_2$CHClCCl$_2$F	3.55	3.96	34.8	3.827	3.96	116.5	185	67.9	0.055	0.245	969	263	447	50	37
233ea	CHCl$_2$CHFCClF$_2$	0.982	1.03	20.4	1.002	1.03	34.7	185	67.9	0.019	0.183	201	54	65	9	8
233eb	CHClFCHFCCl$_2$F	2.32	2.51	30.2	2.428	2.51	77.2	185	67.9	0.038	0.221	571	155	221	28	22
233ec	CHF$_2$CHFCCl$_3$	4.13	4.77	30.6	4.614	4.77	137.9	185	50	0.068	0.236	1081	295	537	58	41
233fa	CCl$_2$FCH$_2$CClF$_2$	15.4	23.3	45.7	22.386	23.3	575.3	185	67.9	0.207	0.321	4017	1496	3434	942	250
233fb	CCl$_3$CH$_2$CF$_3$	16.4	29.3	37.3	28.157	29.3	707.9	185	50	0.247	0.204	2636	1011	2286	676	176
234aa	CHF$_2$CCl$_2$CHF$_2$	6.51	7.54	47.4	7.281	7.54	208.3	264	80	0.062	0.198	1499	426	940	105	60
234ab	CH$_2$FCCl$_2$CF$_3$	3.76	4.14	40.8	4.005	4.14	121.4	264	80	0.039	0.215	979	267	464	51	37
234ba	CHClFCClFCHF$_2$	3.39	3.61	56.9	3.489	3.61	107.1	264	225	0.028	0.215	883	240	398	45	34
234bb	CH$_2$ClCClFCF$_3$	4.84	5.21	67.0	5.039	5.21	149.4	264	225	0.035	0.218	1264	348	682	73	49
234bc	CH$_2$FCClFCClF$_2$	7.01	7.71	77.3	7.443	7.71	212.5	264	225	0.045	0.279	2244	645	1457	170	91
234ca	CHClFCF$_2$CHClF	2.74	2.9	51.0	2.806	2.9	88.0	264	225	0.025	0.205	684	185	281	34	26
234cb	CHCl$_2$CF$_2$CHF$_2$	1.65	1.74	29.2	1.691	1.74	55.7	264	80	0.020	0.199	399	108	140	19	15
234cc	CH$_2$ClCF$_2$CClF$_2$	9.46	10.6	85.1	10.262	10.6	284.1	264	225	0.054	0.267	2709	834	1995	301	120
234cd	CH$_2$FCF$_2$CCl$_2$F	6.64	7.71	47.6	7.443	7.71	212.5	264	80	0.063	0.281	2159	615	1367	155	87
234da	CHClFCHClCF$_3$	2.67	2.82	50.3	2.731	2.82	85.9	264	225	0.024	0.203	658	178	268	33	25
234db	CHF$_2$CHClCClF$_2$	5.69	6.18	71.5	5.964	6.18	173.9	264	225	0.039	0.271	1819	508	1067	115	71
234ea	CHCl$_2$CHFCF$_3$	1.06	1.11	23.1	1.076	1.11	37.0	264	80	0.014	0.158	204	55	67	10	8
234eb	CHClFCHFCClF$_2$	2.88	3.04	52.4	2.947	3.04	92.0	264	225	0.026	0.241	842	228	353	42	32
234ec	CHF$_2$CHFCCl$_2$F	5.32	6.04	45.1	5.829	6.04	170.4	264	80	0.052	0.276	1748	485	991	106	68
234fa	CClF$_2$CH$_2$CClF$_2$	31	43.4	108.4	41.582	43.4	1007.2	264	225	0.132	0.347	6220	3402	5999	3323	1166
234fb	CCl$_2$FCH$_2$CF$_3$	26.2	47.6	58.1	45.576	47.6	1094.4	264	80	0.215	0.264	4499	2230	4245	2043	627
235ba	CHF$_2$CClFCHF$_2$	8.8	9.5	120.7	9.156	9.5	256.3	463	450	0.018	0.225	2371	716	1698	238	102
235bb	CH$_2$FCClFCF$_3$	7.21	7.71	110.0	7.443	7.71	212.5	463	450	0.017	0.237	2139	618	1407	167	87
235ca	CH$_2$ClCF$_2$CF$_3$	9.82	10.6	126.5	10.262	10.6	284.1	463	450	0.018	0.215	2451	764	1830	288	110
235cb	CHClFCF$_2$CHF$_2$	4.45	4.7	85.2	4.540	4.7	135.9	463	450	0.014	0.234	1376	377	711	76	53
235cc	CH$_2$FCF$_2$CClF$_2$	14.2	15.7	145.8	15.157	15.7	404.3	463	450	0.021	0.282	4040	1448	3384	838	231
235da	CHF$_2$CHClCF$_3$	7.55	8.09	112.5	7.804	8.09	221.8	463	450	0.017	0.227	2128	620	1429	175	88

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HCFC	Formula	Lifetimes (years)								Ozone Depletion Potential (ODP)	Radiative Efficiency (RE) W m^{-2} ppb^{-1}	Global Warming Potential (Time Horizon, years)		Global Temperature change Potential (Time Horizon, years)		
		Global	Total Trop	Total Strat	Total OH Reactive Loss	Trop OH Reactive Loss	Strat OH Reactive Loss	O(^{1}D) Reactive Loss	UV Photolysis Loss			20	100	20	50	100
235ea	CHClFCHFCF$_3$	7.36	7.88	111.1	7.605	7.88	216.7	463	450	0.017	0.227	2088	605	1386	167	86
235eb	CHF$_2$CHFCClF$_2$	3.18	3.33	69.4	3.225	3.33	99.8	463	450	0.012	0.274	1163	315	509	59	44
235fa	CClF$_2$CH$_2$CF$_3$	61.7	88.6	203.8	84.644	88.6	1916.2	463	450	0.051	0.297	6787	5327	6941	5741	3434
241aa	CH$_2$ClCCl$_2$CHClF	1.43	1.52	23.5	1.479	1.52	49.3	185	59	0.035	0.116	187	51	64	9	7
241ab	CH$_2$FCCl$_2$CHCl$_2$	0.765	0.803	20.0	0.780	0.803	27.7	185	50	0.020	0.0937	81	22	25	4	3
241ac	CH$_3$CCl$_2$CCl$_2$F	5.18	6.18	32.1	5.970	6.18	174.1	185	50	0.112	0.191	1091	302	610	65	42
241ba	CH$_2$ClCClFCHCl$_2$	0.788	0.826	20.0	0.802	0.826	28.4	185	59	0.020	0.121	108	29	34	5	4
241bb	CH$_3$CClFCCl$_3$	7.76	10	34.3	9.666	10	269.2	185	50	0.163	0.191	1543	452	1049	131	64
241da	CHCl$_2$CHClCHClF	0.558	0.581	20.0	0.566	0.581	20.7	185	59	0.014	0.1	63	17	19	3	2
241db	CH$_2$ClCHClCCl$_2$F	0.528	0.549	20.0	0.534	0.549	20.0	185	59	0.014	0.119	71	19	22	3	3
241dc	CH$_2$FCHClCCl$_3$	0.75	0.786	20.0	0.764	0.786	27.2	185	50	0.019	0.115	97	26	31	5	4
241ea	CHCl$_2$CHFCHCl$_2$	0.416	0.429	20.0	0.420	0.429	20.0	185	50	0.011	0.0812	38	10	12	2	1
241eb	CH$_2$ClCHFCCl$_3$	1.05	1.11	20.0	1.078	1.11	37.1	185	50	0.027	0.125	147	40	48	7	6
241fa	CHCl$_2$CH$_2$CCl$_2$F	0.533	0.555	20.0	0.540	0.555	20.0	185	50	0.014	0.117	70	19	22	3	3
241fb	CHClFCH$_2$CCl$_3$	1.48	1.59	22.2	1.540	1.59	51.1	185	50	0.037	0.152	254	69	87	12	10
242aa	CHF$_2$CCl$_2$CH$_2$Cl	2.13	2.29	29.3	2.220	2.29	71.2	185	67.9	0.039	0.131	341	92	128	17	13
242ab	CH$_2$FCCl$_2$CHClF	1.78	1.91	27.3	1.849	1.91	60.4	185	67.9	0.034	0.132	288	78	103	14	11
242ac	CH$_3$CCl$_2$CClF$_2$	8.09	10	41.9	9.666	10	269.2	185	67.9	0.125	0.227	2061	610	1426	185	87
242ba	CHClFCClFCH$_2$Cl	1.99	2.11	36.7	2.042	2.11	66.0	185	150	0.033	0.151	371	100	137	18	14
242bb	CHCl$_2$CClFCH$_2$F	1.03	1.09	21.0	1.056	1.09	36.4	185	67.9	0.021	0.133	169	46	55	8	6
242bc	CH$_3$CClFCCl$_2$F	8.09	10	41.9	9.666	10	269.2	185	67.9	0.125	0.244	2221	657	1537	199	93
242ca	CHCl$_2$CF$_2$CH$_2$Cl	1.09	1.15	21.6	1.116	1.15	38.2	185	67.9	0.022	0.144	193	52	63	9	7
242cb	CH$_3$CF$_2$CCl$_3$	12.3	18.7	36.3	17.958	18.7	471.3	185	50	0.206	0.251	3043	1027	2450	508	155
242da	CHClFCHClCHClF	1.32	1.38	29.2	1.338	1.38	45.1	185	150	0.024	0.147	237	64	80	11	9
242db	CHCl$_2$CHClCHF$_2$	0.729	0.761	20.0	0.739	0.761	26.4	185	67.9	0.015	0.119	106	29	33	5	4
242dc	CH$_2$ClCHClCClF$_2$	1.2	1.25	27.6	1.217	1.25	41.4	185	150	0.023	0.17	251	68	83	12	9
242dd	CH$_2$FCHClCCl$_2$F	0.832	0.871	20.0	0.846	0.871	29.8	185	67.9	0.017	0.159	162	44	52	8	6
242ea	CHCl$_2$CHFCHClF	0.724	0.756	20.0	0.735	0.756	26.2	185	67.9	0.015	0.119	106	29	33	5	4
242eb	CH$_2$ClCHFCCl$_2$F	1.24	1.31	23.0	1.267	1.31	42.9	185	67.9	0.025	0.167	253	68	84	12	10
242ec	CH$_2$FCHFCCl$_3$	1.7	1.84	23.5	1.780	1.84	58.3	185	50	0.034	0.174	363	98	129	17	14
242fa	CHCl$_2$CH$_2$CClF$_2$	0.735	0.768	20.0	0.746	0.768	26.6	185	67.9	0.015	0.153	138	37	43	6	5
242fb	CHClFCH$_2$CCl$_2$F	1.61	1.71	26.1	1.662	1.71	54.8	185	67.9	0.031	0.203	400	108	140	19	15
242fc	CHF$_2$CH$_2$CCl$_3$	4.14	4.78	30.6	4.625	4.78	138.2	185	50	0.075	0.198	997	272	496	54	38
243aa	CHF$_2$CCl$_2$CH$_2$F	2.99	3.25	37.3	3.145	3.25	97.5	247	80	0.036	0.154	619	168	264	31	23
243ab	CH$_3$CCl$_2$CF$_3$	8.33	10	49.3	9.666	10	269.2	247	80	0.085	0.205	2091	623	1465	195	89
243ba	CHF$_2$CClFCH$_2$Cl	3.63	3.88	58.0	3.748	3.88	114.3	247	225	0.033	0.146	713	194	332	37	27
243bb	CHFClCClFCH$_2$F	2.67	2.82	49.7	2.733	2.82	85.9	247	225	0.027	0.161	578	157	235	29	22
243bc	CH$_3$CClFCF$_2$Cl	15.6	18.7	94.2	17.958	18.7	471.3	247	225	0.088	0.264	4005	1498	3431	952	252
243ca	CH$_2$ClCF$_2$CHClF	2.89	3.14	36.9	3.038	3.14	94.5	247	80	0.035	0.182	708	192	297	35	27
243cb	CHCl$_2$CF$_2$CH$_2$F	1.46	1.54	27.3	1.491	1.54	49.7	247	80	0.020	0.147	289	78	99	14	11
243cc	CH$_3$CF$_2$CFCl$_2$	13.8	18.7	53.5	17.958	18.7	471.3	247	80	0.134	0.284	4057	1437	3374	809	226
243da	CHF$_2$CHClCHFCl	1.97	2.07	41.9	2.009	2.07	65.0	247	225	0.022	0.162	430	116	158	21	16
243db	CH$_2$ClCHClCF$_3$	1.44	1.51	34.5	1.461	1.51	48.8	247	225	0.018	0.138	268	73	92	13	10
243dc	CH$_2$FCHClCF$_2$Cl	2.03	2.13	42.6	2.066	2.13	66.7	247	225	0.023	0.203	556	151	206	27	21
243ea	CHFClCHFCHFCl	1.57	1.64	36.3	1.587	1.64	52.6	247	225	0.019	0.172	363	98	127	17	14
243eb	CHCl$_2$CHFCHF$_2$	0.898	0.938	20.9	0.911	0.938	31.8	247	80	0.014	0.141	170	46	55	8	6
243ec	CH$_2$ClCHFCF$_2$Cl	1.7	1.78	38.3	1.728	1.78	56.8	247	225	0.020	0.182	417	113	148	20	16
243ed	CH$_2$FCHFCFCl$_2$	2.03	2.17	31.9	2.101	2.17	67.7	247	80	0.026	0.215	587	159	218	28	22
243fa	CHCl$_2$CH$_2$CF$_3$	0.78	0.813	20.0	0.790	0.813	28.0	247	80	0.012	0.12	126	34	40	6	5
243fb	CHFClCH$_2$CF$_2$Cl	2.24	2.36	45.1	2.283	2.36	73.0	247	225	0.024	0.231	699	189	267	34	26
243fc	CHF$_2$CH$_2$CFCl$_2$	5.07	5.73	44.0	5.532	5.73	162.5	247	80	0.056	0.263	1759	486	973	103	68

HCFC	Formula	Lifetimes (years)								Ozone Depletion Potential (ODP)	Radiative Efficiency (RE) W m^{-2} ppb^{-1}	Global Warming Potential (Time Horizon, years)		Global Temperature change Potential (Time Horizon, years)		
		Global	Total Trop	Total Strat	Total OH Reactive Loss	Trop OH Reactive Loss	Strat OH Reactive Loss	O(^{1}D) Reactive Loss	UV Photolysis Loss			20	100	20	50	100
244ba	CH$_2$FCClFCHF$_2$	5.17	5.49	90.5	5.299	5.49	156.3	411	450	0.017	0.173	1308	362	731	78	51
244bb	CH$_3$CClFCF$_3$	16.6	18.7	147.6	17.958	18.7	471.3	411	450	0.027	0.238	4130	1592	3590	1073	279
244ca	CH$_2$ClCF$_2$CHF$_2$	6.39	6.82	100.9	6.586	6.82	190.3	411	450	0.018	0.173	1577	447	980	109	63
244cb	CH$_2$FCF$_2$CHFCl	4.02	4.24	78.6	4.097	4.24	123.9	411	450	0.015	0.178	1061	289	520	57	41
244cc	CH$_3$CF$_2$CF$_2$Cl	31.2	38.1	173.3	36.563	38.1	896.6	411	450	0.039	0.277	6130	3369	5918	3300	1166
244da	CHF$_2$CHClCHF$_2$	3.88	4.09	77.0	3.954	4.09	120.0	411	450	0.015	0.182	1053	287	507	56	40
244db	CH$_2$FCHClCF$_3$	2.44	2.54	57.4	2.464	2.54	78.2	411	450	0.012	0.164	596	162	234	29	23
244ea	CHF$_2$CHFCHFCl	2.39	2.5	56.6	2.417	2.5	76.9	411	450	0.012	0.191	684	185	267	33	26
244eb	CH$_2$ClCHFCF$_3$	2.04	2.12	50.8	2.059	2.12	66.5	411	450	0.011	0.151	460	124	171	22	17
244ec	CH$_2$FCHFCF$_2$Cl	2.88	3.01	64.0	2.918	3.01	91.1	411	450	0.013	0.226	974	264	408	49	37
244fa	CHFClCH$_2$CF$_3$	2.37	2.48	56.3	2.399	2.48	76.4	411	450	0.012	0.185	658	178	256	32	25
244fb	CHF$_2$CH$_2$CF$_2$Cl	7.76	8.35	110.7	8.055	8.35	228.3	411	450	0.020	0.285	3053	895	2076	260	127
251aa	CH$_2$FCCl$_2$CH$_2$Cl	1.26	1.34	23.3	1.296	1.34	43.8	185	67.9	0.028	0.0752	129	35	43	6	5
251ab	CH$_3$CCl$_2$CHFCl	1.73	1.85	26.9	1.795	1.85	58.8	185	67.9	0.037	0.11	260	70	93	12	10
251ba	CH$_2$ClCClFCH$_2$Cl	1.34	1.4	29.4	1.359	1.4	45.7	185	150	0.027	0.0951	173	47	59	8	7
251bb	CH$_3$CClFCHCl$_2$	1.02	1.07	20.9	1.042	1.07	35.9	185	67.9	0.023	0.109	152	41	49	7	6
251da	CH$_2$ClCHClCHFCl	0.693	0.719	20.0	0.699	0.719	25.1	185	150	0.016	0.0821	77	21	24	4	3
251db	CH$_2$FCHClCHCl$_2$	0.404	0.416	20.0	0.408	0.416	20.0	185	67.9	0.009	0.0631	35	9	11	2	1
251dc	CH$_3$CHClCFCl$_2$	0.515	0.535	20.0	0.521	0.535	20.0	185	67.9	0.012	0.122	85	23	26	4	3
251ea	CH$_2$ClCHFCHCl$_2$	0.473	0.489	20.0	0.478	0.489	20.0	185	67.9	0.011	0.0776	50	14	15	2	2
251eb	CH$_3$CHFCCl$_3$	0.678	0.709	20.0	0.690	0.709	24.8	185	50	0.016	0.134	124	34	39	6	5
251fa	CHClFCH$_2$CCl$_2$H	0.331	0.339	20.0	0.333	0.339	20.0	185	67.9	0.008	0.0739	33	9	10	2	1
251fb	CH$_2$ClCH$_2$CCl$_2$F	0.452	0.467	20.0	0.457	0.467	20.0	185	67.9	0.011	0.107	66	18	20	3	2
251fc	CH$_2$FCH$_2$CCl$_3$	0.646	0.676	20.0	0.657	0.676	23.7	185	50	0.015	0.103	91	25	28	4	3
252aa	CH$_2$FCCl$_2$CH$_2$F	1.94	2.07	31.0	2.007	2.07	65.0	231	80	0.029	0.105	307	83	113	15	12
252ab	CH$_3$CCl$_2$CHF$_2$	4.41	4.93	41.9	4.762	4.93	141.9	231	80	0.056	0.153	1006	275	517	55	39
252ba	CH$_2$ClCClFCH$_2$F	2.19	2.31	44.0	2.236	2.31	71.7	231	225	0.027	0.0992	329	89	125	16	12
252bb	CH$_3$CClFCHClF	2.87	3.04	50.9	2.941	3.04	91.8	231	225	0.032	0.147	637	173	266	32	24
252ca	CH$_2$ClCF$_2$CH$_2$Cl	2.47	2.61	47.0	2.525	2.61	80.0	231	225	0.029	0.126	470	127	186	23	18
252cb	CH$_3$CF$_2$CHCl$_2$	1.19	1.25	24.4	1.215	1.25	41.3	231	80	0.019	0.146	263	71	87	12	10
252da	CH$_2$ClCHClCHF$_2$	0.999	1.04	26.7	1.007	1.04	34.9	231	225	0.016	0.0897	135	37	44	6	5
252db	CH$_2$FCHClCHClF	1.15	1.2	29.4	1.162	1.2	39.7	231	225	0.017	0.101	176	48	58	8	7
252dc	CH$_3$CHClCClF$_2$	0.771	0.799	22.2	0.776	0.799	27.6	231	225	0.013	0.149	173	47	55	8	7
252ea	CH$_2$ClCHFCHClF	1.02	1.06	27.2	1.033	1.06	35.7	231	225	0.016	0.112	174	47	57	8	7
252eb	CH$_2$FCHFCHCl$_2$	0.645	0.67	20.0	0.652	0.67	23.5	231	80	0.011	0.0922	90	24	28	4	3
252ec	CH$_3$CHFCCl$_2$F	0.845	0.882	20.0	0.857	0.882	30.1	231	80	0.015	0.175	223	60	71	10	8
252fa	CHClFCH$_2$CHClF	1.15	1.19	29.4	1.158	1.19	39.5	231	225	0.017	0.143	248	67	82	12	9
252fb	CHCl$_2$CH$_2$CHF$_2$	0.657	0.684	20.0	0.665	0.684	23.9	231	80	0.011	0.114	113	31	35	5	4
252fc	CH$_2$ClCH$_2$CClF$_2$	0.937	0.972	25.5	0.945	0.972	32.9	231	225	0.015	0.153	216	59	70	10	8
252fd	CH$_2$FCH$_2$CCl$_2$F	0.703	0.732	20.0	0.712	0.732	25.5	231	80	0.012	0.155	164	45	52	8	6
253ba	CH$_2$FCClFCH$_2$F	3.66	3.86	72.9	3.730	3.86	113.8	370	450	0.017	0.131	814	221	381	42	31
253bb	CH$_3$CClFCHF$_2$	7.85	8.46	108.1	8.164	8.46	231.0	370	450	0.024	0.184	2265	665	1547	195	94
253ca	CH$_2$ClCF$_2$CH$_2$F	4.23	4.47	79.3	4.324	4.47	130.1	370	450	0.018	0.135	964	263	485	52	37
253cb	CH$_3$CF$_2$CHClF	3.48	3.66	70.8	3.544	3.66	108.7	370	450	0.017	0.183	1077	293	492	56	41
253da	CH$_2$FCHClCHF$_2$	1.67	1.74	43.6	1.684	1.74	55.5	370	450	0.012	0.118	335	91	118	16	13
253db	CH$_3$CHClCF$_3$	1.02	1.06	30.2	1.027	1.06	35.5	370	450	0.009	0.12	209	57	68	10	8
253ea	CH$_2$ClCHFCHF$_2$	1.44	1.5	39.1	1.452	1.5	48.5	370	450	0.011	0.113	277	75	95	13	10
253eb	CH$_2$FCHFCHClF	1.5	1.56	40.4	1.516	1.56	50.4	370	450	0.011	0.125	320	87	111	15	12
253ec	CH$_3$CHFCClF$_2$	1.13	1.17	32.7	1.139	1.17	38.9	370	450	0.009	0.183	352	95	116	16	13
253fa	CHClFCH$_2$CHF$_2$	1.83	1.9	46.4	1.843	1.9	60.2	370	450	0.012	0.175	542	147	196	26	20
253fb	CH$_2$ClCH$_2$CF$_3$	1.05	1.09	30.8	1.054	1.09	36.3	370	450	0.009	0.121	216	58	70	10	8

HCFC	Formula	Lifetimes (years)								Ozone Depletion Potential (ODP)	Radiative Efficiency (RE) W m⁻² ppb⁻¹	Global Warming Potential (Time Horizon, years)		Global Temperature <mark>change</mark> Potential (Time Horizon, years)		
		Global	Total Trop	Total Strat	Total OH Reactive Loss	Trop OH Reactive Loss	Strat OH Reactive Loss	O(^{1}D) Reactive Loss	UV Photolysis Loss			20	100	20	50	100
253fc	$CH_2FCH_2CClF_2$	1.48	1.54	39.9	1.489	1.54	49.6	370	450	0.011	0.194	487	132	168	23	18
261aa	$CH_3CCl_2CH_2F$	1.06	1.11	22.7	1.080	1.11	37.1	218	80	0.020	0.0727	132	36	43	6	5
261ba	$CH_3CClFCH_2Cl$	2.19	2.31	43.5	2.237	2.31	71.7	218	225	0.031	0.0827	312	84	118	15	12
261da	$CH_2ClCHClCH_2F$	0.45	0.462	20.0	0.452	0.462	20.0	218	225	0.009	0.0338	26	7	8	1	1
261db	$CH_3CHClCHClF$	0.465	0.478	20.0	0.467	0.478	20.0	218	225	0.009	0.0625	50	14	15	2	2
261ea	$CH_2ClCHFCH_2Cl$	0.536	0.554	20.0	0.539	0.554	20.0	218	225	0.010	0.0493	45	12	14	2	2
261eb	$CH_3CHFCHCl_2$	0.309	0.315	20.0	0.310	0.315	20.0	218	80	0.006	0.0618	33	9	10	2	1
261fa	CH_2ClCH_2CHClF	0.572	0.591	20.0	0.575	0.591	21.0	218	225	0.011	0.0746	73	20	23	3	3
261fb	$CH_2FCH_2CHCl_2$	0.332	0.339	20.0	0.333	0.339	20.0	218	80	0.006	0.0557	32	9	10	1	1
261fc	$CH_3CH_2CCl_2F$	0.614	0.638	20.0	0.621	0.638	22.5	218	80	0.012	0.137	145	39	45	7	5
262ba	$CH_3CClFCH_2F$	3.41	3.59	68.6	3.469	3.59	106.6	336	450	0.020	0.125	837	227	378	43	32
262ca	$CH_3CF_2CH_2Cl$	3.17	3.33	65.6	3.219	3.33	99.6	336	450	0.019	0.117	724	196	316	37	27
262da	$CH_2FCHClCH_2F$	0.924	0.956	27.7	0.929	0.956	32.4	336	450	0.009	0.0587	107	29	34	5	4
262db	$CH_3CHClCHF_2$	0.642	0.662	20.8	0.644	0.662	23.3	336	450	0.007	0.0813	103	28	32	5	4
262ea	$CH_2FCHFCH_2Cl$	0.828	0.856	25.4	0.831	0.856	29.3	336	450	0.009	0.0657	107	29	34	5	4
262eb	$CH_3CHFCHFCl$	0.663	0.685	21.3	0.666	0.685	24.0	336	450	0.007	0.0982	128	35	40	6	5
262fa	$CH_2ClCH_2CHF_2$	0.801	0.828	24.8	0.804	0.828	28.4	336	450	0.008	0.0858	135	37	43	6	5
262fb	CH_2FCH_2CHFCl	0.873	0.902	26.5	0.877	0.902	30.7	336	450	0.009	0.0991	170	46	54	8	6
262fc	$CH_3CH_2CF_2Cl$	1.19	1.24	33.7	1.202	1.24	40.9	336	450	0.011	0.168	394	107	131	18	15
271ba	$CH_3CClFCH_3$	5.05	5.37	83.4	5.190	5.37	153.4	308	450	0.028	0.106	1224	338	675	72	47
271da	$CH_3CHClCH_2F$	0.273	0.278	20.0	0.274	0.278	20.0	308	450	0.004	0.0261	17	5	5	1	1
271ea	CH_3CHFCH_2Cl	0.297	0.302	20.0	0.298	0.302	20.0	308	450	0.004	0.033	23	6	7	1	1
271fa	$CH_2ClCH_2CH_2F$	0.339	0.345	20.0	0.339	0.345	20.0	308	450	0.004	0.0284	22	6	7	1	1
271fb	CH_3CH_2CHClF	0.492	0.506	20.0	0.494	0.506	20.0	308	450	0.007	0.0652	75	20	23	3	3

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