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 Secondly, the authors calculate ODPs partly based on outdated values as is described in one of the specific comments below.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.
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> **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.
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> **Text added to the start of section 2.3:**
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> 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.

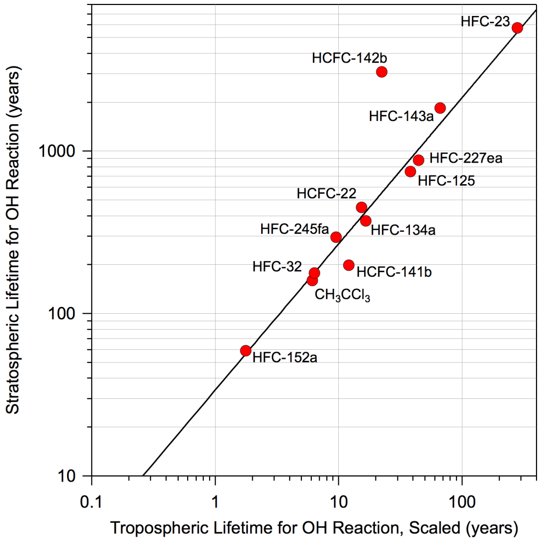
Author Response: Reviewer #1 suggested including "estimates" in the title to help clarify the content of the manuscript.

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:



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 %?

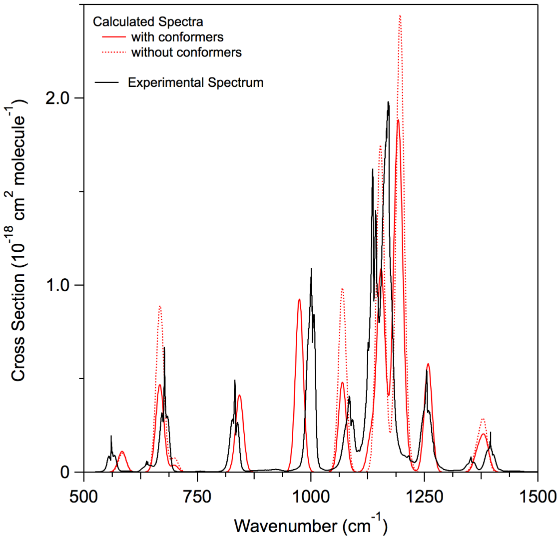
Author Response: This statement was intended to mean the vast majority.

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.



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