Review of Manuscript "Global Warming Potentials for the C_1-C_3 Hydrochlorofluorocarbons (HCFCs) Included in the Kigali Amendment to the Montreal Protocol," by D.K. Papanastasiou et al.

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.

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.

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.

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…"

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.

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.

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 [37]Cl isotopomers and ii) the SAR relationships used, as discussed on p. 7., lines 110 to 114.

Minor Suggestions / Errata

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

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…"

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.

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

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?

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

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

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

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.

p. 12 Figure 4: It would be helpful to put the units (cm^2 molecule^{-1} cm^{-1}) directly on the plot of this figure, not just in the legend.

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}, 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.

p. 17 Figure 6: Good Figure-lots of information, which is well presented.

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.

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.

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.

p. 18 line 378: This is not true for the spectral region 700-1300 cm^{-1}.

p. 19 line 382: It might be valuable to emphasize or to provide additional details regarding this phenomenon.

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.

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.

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.

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

Papers Discussing Accuracies of Calculated Gaussian Intensities, esp. for Multiple Conformers

Halls, M. D.; Schlegel, H. B., Comparison of the performance of local, gradient-corrected, and hybrid density functional models in predicting infrared intensities. *The Journal of chemical physics* **1998,** *109* (24), 10587-10593.

Jiménez-Hoyos, C. A.; Janesko, B. G.; Scuseria, G. E., Evaluation of range-separated hybrid density functionals for the prediction of vibrational frequencies, infrared intensities, and Raman activities. *Physical Chemistry Chemical Physics* **2008,** *10* (44), 6621-6629.

Lindenmaier, R.; Williams, S. D.; Sams, R. L.; Johnson, T. J., Quantitative Infrared Absorption Spectra and Vibrational Assignments of Crotonaldehyde and Methyl Vinyl Ketone Using Gas-Phase Mid-Infrared, Far-Infrared, and Liquid Raman Spectra: s-cis vs s-trans Composition Confirmed via Temperature Studies and ab Initio Methods. *The Journal of Physical Chemistry A* **2017,** *121* (6), 1195-1212.

Williams, S. D.; Johnson, T. J.; Sharpe, S. W.; Yavelak, V.; Oates, R.; Brauer, C. S., Quantitative vapor-phase IR intensities and DFT computations to predict absolute IR spectra based on molecular structure: I. Alkanes. *Journal of Quantitative Spectroscopy and Radiative Transfer* **2013,** *129*, 298-307.