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Atmospheric Chemistry and Physics Discussions

Interactive comment on "UV and Infrared Absorption Spectra, Atmospheric Lifetimes, and Ozone Depletion and Global Warming Potentials for CCl2FCCl2F (CFC-112), CCl3CClF2 (CFC-112a), CCl3CF3 (CFC-113a), and CCl2FCF3 (CFC-114a)" *by* Maxine E. Davis et al.

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We thank the referee for their constructive comments.

Response to Anonymous Referee #2

This is a very good manuscript reporting UV and IR spectra of four previously understudied chlorofluorocarbons in the atmosphere as well as deriving relevant properties with regard to global warming and stratospheric ozone depletion. I recommend it for

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Discussion paper

publication once the points below have been addressed, in particular the two major concerns on the discussion of IR data and on model uncertainties.

Referee Comment: L49: Should be “atmospheric loadings”. Besides, given in the following are actually not loadings but mole fractions.

Author Response: Okay

Action Taken: In the first paragraph of the Introduction we have changed “atmospheric loading” and “atmospheric abundance” to “atmospheric mixing ratio”.

Referee Comment: L50-51: ppt and ppb not explained

Author Response: Okay

Action Taken: We have included “(part per trillion)” and “(part per billion)” after the first appearance of ppt and ppb, respectively.

Referee Comment: L73-74 What is missing from the introduction is an overview of the current literature on the IR spectra of these CFCs (and in particular their shortcomings), such as the papers mentioned in these two lines.

Author Response: Such a review is not necessary at this stage of the paper. However, we could clarify which molecules were included in the Olliff and Fischer and Etminan et al. studies.

Action Taken: We have revised the text as follows: “... previous infrared studies of Olliff and Fischer (1992; 1994) (CFCs 112, 112a, 113a, and 114a) and Etminan et al. (2014) (CFC-113a) where possible.

Referee Comment: L82-83: Why was this range chosen?

Author Response: The temperature range of the spectrum measurements was chosen in an attempt to represent stratospheric temperatures where these compounds would photolyze. The elevated temperature was included to improve the spectra parameteri-

zations, as stated in the text.

Action Taken: The text was revised as follows: “Absorption measurements were made at 10 discrete wavelengths at temperatures between 207 and 323 K to enable spectrum parameterizations appropriate for stratospheric conditions.”.

Referee Comment: L109: Please define “co-adds”. Also, the make of the FTIR, the cell material and the detector type are not given.

Author Response: “co-adds” is a standard Fourier transform spectroscopy terminology that does not require definition. We do not endorse manufactures in our work and therefore do not include make and model of commercial instruments. We should, however, identify the material of the cell and detector.

Action Taken: The text in this section has been revised as follows: “Measurements were made using a 15 cm single pass Pyrex absorption cell and a MCT detector at a resolution of 1 cm-1 with 100 co-adds. ”.

Referee Comment: L144-49 It needs to be made clearer how equation 2 was used to correct for isomeric impurities, especially since that same equation is later on used for CFC-113a and -114a.

Author Response: There is nothing too complicated done here. It is basically solving two linear equations for two unknowns.

Action Taken: None

Referee Comment: L161 It would be useful to explain to the reader which temperatures are “atmospherically relevant” and why.

Author Response: This was addressed in our revisions above (L82 comment).

Action Taken: None

Referee Comment: L179-180 No discussion of IR spectra in any detail. For instance,

which features of the spectra can be assigned to certain functional groups? And which agree best with other recorded spectra? In which spectral region are the biggest differences and what could be causing this?

Author Response: A detailed comparison of the present results with the available previous work is provided in the supplement. The agreement with the Olliff and Fischer studies and the Etminan et al. study for CFC-113a is relatively good. Therefore, there is not a need for too much discussion. A discussion of the fundamental infrared spectroscopy of CFCs might be of interest to some readers, but was not the focus of the present work.

Action Taken: None

Referee Comment: L198-206 Given that there is a published data set of observed stratospheric mole fractions, which the authors refer to repeatedly I am surprised that no comparison between measurements and model have been attempted at all.

Author Response: The observations are for the surface concentrations only, and we have used these as surface mixing ratio boundary conditions input into the model. However, to our knowledge there are no observations of the vertical profiles of these newly-detected compounds to compare with the model.

Action Taken: We have added text in section 4 to state that the model uses the observed surface concentrations as input boundary conditions.

Referee Comment: L209-210 Which definitions were used to define those regions?

Author Response: Our definitions of the troposphere, stratosphere, and mesosphere are stated in the text as is and are also defined in the referenced Ko et al. SPARC (2013) lifetime report and Fleming et al. (2011) paper.

Action Taken: None

Referee Comment: L215-218 It seems very surprising that the atmospheric model

should introduce no uncertainty at all. This is probably the main reason why the uncertainty ranges in the lifetimes given in Table 5 are so small, and in fact probably too small. One idea how to approach this problem would be to compare the loss rates derived by this model with observations for other more well-known molecules with similar loss distributions. Referee Comment: L245-247 This is related to my previous comment. The small range is not caused by the small uncertainty in the UV spectra but due to not including the probably substantially larger model uncertainties. This creates the impression that the lifetimes and ODPs estimated here are far superior to previous work; which they might be, but this is currently not proven.

Author Response: We appreciate the reviewers' suggestion. However, such a comparison is beyond the scope of the present paper. We have clarified the text to emphasize that we are only addressing the uncertainty in the kinetic and photochemical data in the present paper. Considering uncertainty from other processes is beyond the scope of this paper.

Action Taken: See response to Referee #1s general comment for revisions to the text.

Referee Comment: L256-257 The term "fractional release factors" is explained nowhere in this manuscript. Why would they make a difference to the ODPs?

Author Response: We have added text to define this term, and provided context as to why this is important.

Action Taken: We have added the following text and appropriate references to the end of section 4.1: "The semi-empirical ODPs are dependent on observationally-based fractional release factors for a given stratospheric mean age of air, i.e., the fractional amount of a CFC that has been dissociated at a given point in the stratosphere (and the subsequent release of inorganic chlorine), relative to the amount of a CFC that entered at the tropopause (e.g. Schauffler et al., 2003; Newman et al., 2007; Daniel et al., 2007; Douglass et al., 2008; Laube et al., 2013). Differences in the semi-empirical vs. model ODPs in Table 6 are due, at least in part, to differences in the observationally based

fractional release factors taken for mid-latitude conditions compared to the global model calculations. Differences in the ODPs may also arise from differences in the Ko et al. (2013) lifetimes used for the semi-empirical ODPs vs. the model lifetimes, although these lifetime differences are small."

Referee Comment: L258-266 Again, the IR spectra derived in this work are not discussed at all. In this case it is not even mentioned that they were used in this calculation. Also, a comparison with published REs and GWPs would be useful here as well as in Table 6.

Author Response: We should acknowledge that we used our infrared spectra in the calculation. We should also have acknowledged the previous values for CFC-113a reported in the Etminan et al. (2014) study.

Action Taken: Text revised as follows: "Table 6 summarizes the radiative efficiencies (REs) for the CFCs calculated using the methods described in Hodnebrog et al. (2013) and the global warming potentials (GWPs) for the 20, 100, and 500-year time-horizons using the lifetimes and infrared spectra from this work. ".

The flowing sentence has been added: "Etminan et al. (2014) reported a RE of 0.23 W m-2 ppb-1 for CFC-113a and a GWP100 of 3310 using a lifetime of 51 years. These values are in reasonable agreement with the present results."

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