Response to Reviewer #1

We sincerely thank the reviewer for the thorough, detailed, and constructive evaluation of our manuscript. The comments provided valuable guidance for improving the scientific clarity, methodological rigor, and contextual positioning of this work. In response, we carefully re-examined the manuscript in its entirety, with particular attention to consistency with established literature, transparency of assumptions and limitations, and appropriate presentation of uncertainty and numerical precision.

To adequately address the reviewer's comments, we found that the original structure of the manuscript was not sufficient to clearly separate background context from experimental methodology. Accordingly, the manuscript has been restructured, with the original Introduction reorganized to more clearly distinguish the scientific background and prior literature from the experimental and analytical methodology. This reorganization improves readability and ensures that established knowledge is properly contextualized, while the methodological developments and experimental procedures are presented in a focused and coherent manner.

A major component of the revision involved re-evaluating the absorption cross-section (ACS) and radiative efficiency (RE) of COF_2 following established methodologies reported in the literature, particularly those of Hodnebrog et al. (2020) and Thornhill et al. (2024). This reanalysis resolved discrepancies identified in the original submission and led to revised ACS and RE values that are now in close quantitative agreement with previous studies when evaluated over consistent spectral ranges. We also explicitly report the integrated ACS, clarify differences relative to line-by-line datasets such as HITRAN, and provide a transparent uncertainty assessment based on experimentally determined ACS uncertainties and their propagation to derived quantities. In addition, well-established information not essential to the logical development of the present study has been removed to avoid potential misunderstanding regarding novelty, allowing the revised manuscript to clearly focus on the experimental determination and evaluation of the ACS, radiative efficiency, and GWP of COF_2. **All revisions made in response to the reviewer's comments are highlighted in yellow in the revised manuscript.**

Reviewer Comment #1

Comment:

I am not an atmospheric chemist, but it did not take me long to search for and identify several papers on COF2 atmospheric chemistry that appear directly relevant to this work – these include https://doi.org/10.1021/acs.jpca.9b00899 https://doi.org/10.1007/BF00696901, https://doi.org/10.1016/j.cplett.2004.08.022 and https://doi.org/10.1021/j100033a023. Even the COF2 Wikipedia page presents a structure for the COF2 molecule which is very close to the structure presented here as if it is new science. Other databases such as Pubchem and NIST seem to contain well-established information on COF2.

Response:

We thank the reviewer for this insightful comment. In the revised manuscript, the relevant prior studies on COF_2 hydrolysis and its infrared absorption and radiative impact are now cited explicitly in the Introduction. These include established theoretical investigations of COF_2 hydrolysis (Francisco, 1993; Zachariah et al., 1995; Uchimaru et al., 2004) and recent evaluations of its absorption cross-section and radiative efficiency based on existing spectroscopic datasets (Hodnebrog et al., 2020; Thornhill et al., 2024), as well as reference to the HITRAN database.

At the same time, discussions of molecular structure and other well-established properties that are not required for the logical development or interpretation of the present experimental results have been removed. This revision was made to avoid any possible misunderstanding that previously established knowledge might be interpreted as original to this study. The manuscript now clearly builds upon the existing literature while focusing on the experimental determination and analysis of the ACS, radiative efficiency, and GWP of COF_2.

Manuscript Changes:

Lines 63-67 and 75-84.

Reviewer Comment #2-3

Comment:

I do work in the area of radiative transfer. There is existing data of absorption cross-sections (see the supplementary data of Hodnebrog et al. (2020) (already referred to in the paper) and Thornhill et al. https://doi.org/10.1029/2024JD040912, for the source of this data). There is also line-by-line data for the major COF2 bands, readily available on the HITRAN database HITRANonline (it is Gas ID 29). It is essential that the new measurements in this paper are compared with this earlier work and any differences (and possible reasons for the differences) are discussed. The present paper even lacks a discussion of the integrated cross-section, leaving the reader to guess how the measurements compare with the previous literature. I believe this is also essential.

In addition, both Hodnebrog (in their supplementary information) and Thornhill already present the radiative efficiency for a constant COF2 profile (0.123 and 0.126 W/sq.m/ppb respectively) (although Thornhill's reason for focusing on COF2 is not the same as in this paper). This needs to be acknowledged and some comparison of the new value – which is about 17% higher than these two studies – is necessary, with some possible explanations for this quite large difference.

Response:

We thank the reviewer for these detailed and constructive comments. In the original submission, the stratosphere-adjusted radiative efficiency (RE) of COF_2 was approximately 17 % higher than the values reported by Hodnebrog et al. (2020) and Thornhill et al. (2024). Upon re-examination, we identified that this discrepancy arose from the use of a stitched ACS spectrum combining measurements at different concentrations, which introduced partial saturation in some spectral regions and led to an overestimation of the integrated RE.

In the revised manuscript, we have reanalyzed the ACS using a single, unsaturated FTIR spectrum and strictly followed the evaluation procedures described by Hodnebrog et al. (2020) and Thornhill et al. (2024). The integrated ACS is now explicitly reported and compared with existing datasets, showing close agreement (within ~2 %) with the PNNL-based values reported in these studies. Differences relative to HITRAN line-by-line data are discussed in terms of the omission of broadband baseline absorption in line-by-line datasets.

As a result of this re-evaluation, the revised RE value (0.119 W m^{-2} ppb^{-1}) is now within 3–6 % of the literature values. When the literature RE values are recalculated over the same effective spectral range as the present measurements (650–3000 cm^{-1}), the remaining discrepancy is reduced to approximately 1 %, indicating near consistency among the datasets. These points are now clearly discussed in the revised manuscript.

Manuscript Changes:

Lines 230-239 and 261-267.

Reviewer Comment #4

Comment:

There is a lack of discussion of uncertainties, for example on the absorption cross-section and radiative efficiency and, in my view, results are presented with an inappropriate level of precision (e.g., 4 decimal places in the case of RE). Generic estimates of uncertainties (and the source of uncertainties) for this class of gases are available in the two Hodnebrog Rev. Geophys. papers, and I assume similar generic estimates are available for reaction rates.

Response:

We thank the reviewer for emphasizing the importance of uncertainty treatment and appropriate numerical precision. In the revised manuscript, a dedicated Uncertainties section has been added, in which the relative standard uncertainties of the absorption cross-section (ACS) are evaluated based on experimental parameters and propagated consistently to the integrated ACS and radiative efficiency (RE). The reported numerical precision has been revised accordingly to reflect realistic experimental uncertainty. The resulting uncertainty levels for ACS and RE are comparable to those reported for similar gases in Hodnebrog et al. (2013, 2020).

Manuscript Changes:

Lines 331–345 (Uncertainties).

Reviewer Comment #5

Comment:

18: “kinetic decay” – in atmospheric science it is more common to call this the e-folding lifetime.

Response:

We thank the reviewer for this helpful suggestion. The term “kinetic decay” has been replaced with “e-folding lifetime” throughout the manuscript to align with standard atmospheric science terminology.

Manuscript Changes:

Lines 17, 110, and 386.

Reviewer Comment #6

Comment:

*32-34: This definition is incomplete – it is the time-integrated radiative forcing of a 1 kg pulse emission at time t=0 compared to the same mass emission of CO2.

Response:

We thank the reviewer for this valuable clarification. The definition of GWP has been revised to explicitly state that it is the ratio of the time-integrated radiative forcing resulting from a 1 kg pulse emission of gas i at time t = 0 to that from an equivalent 1 kg pulse emission of CO_2 over a specified time horizon.

Manuscript Changes:

Lines 158-160.

Reviewer Comment #7

Comment:

58-61: Very minor, but I am not sure this text is needed. The ACS is the prime property.

Response:

We thank the reviewer for this suggestion and agree that the absorption cross section (ACS) is the primary quantity of interest in this study. Accordingly, the detailed explanation of absorbance has been removed, and the text has been revised to focus directly on the ACS as the fundamental molecular property from which radiative efficiency is derived.

Manuscript Changes:

Lines 174-175.

Reviewer Comment #8

Comment:

77: No explanation is given for the lower wavenumber (649 cm-1) lower limit. Presumably determined by the infrared detector?

Response:

We thank the reviewer for this comment. The lower wavenumber limit is determined by the detector response. The FTIR detector used in this study responds down to approximately 650 cm^{-1}, which sets the lower bound of the measured ACS spectrum. For RE calculations, the ACS data were averaged onto a 10 cm^{-1} grid to match the resolution of the stratospheric-adjusted Pinnock curve, and because this curve is defined up to 3000 cm^{-1}, the RE-relevant ACS spectrum spans 650–3000 cm^{-1}.

Manuscript Changes:

Lines 223-226.

Reviewer Comment #9

Comment:

*79: No source is given for these CO2 reference values and the specification of a single lifetime for CO2 is inappropriate for reasons explained in all the IPCC WG1 assessments. I recommend that the authors simply adopt and cite the IPCC AR6 AGWP(100) for CO2 which is in the supplementary information for https://doi.org/10.1017/9781009157896.009 at https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC_AR6_WGI_Chapter07_SM.pdf

Response:

We thank the reviewer for this valuable comment. We agree that using a single lifetime for CO_2 is inappropriate and have therefore adopted the 100-year absolute global warming potential ($AGWP_{100}$) reference value from the IPCC AR6 Working Group I Supplementary Material (Chapter 7; https://doi.org/10.1017/9781009157896.009). The $AGWP_{100}$ of CO_2 ($0.0895\ pW\cdot m^{-2}\cdot yr\cdot kg^{-1}$) is now used as the reference for all GWP calculations, ensuring consistency with the IPCC methodology.

Manuscript Changes:

Lines 170-171.

Reviewer Comment #10

Comment:

88: “potent” – do you mean in terms of radiative efficiency?

Response:

We thank the reviewer for the comment. The term “potent” was revised for clarity. The sentence now reads: ″F-gases exhibit exceptionally high radiative efficiency values and often possess atmospheric lifetimes ranging from decades to millennia, resulting in GWP values that are thousands to tens of thousands of times higher than that of CO2.”

Manuscript Changes:

Lines 42-43.

Reviewer Comment #11

Comment:

91: “emphasize the need” – this isn’t quite accurate. These protocols, amendments and agreements were posed in terms of CO2-equivalence (and hence why GWP-100 is widely used to provide that equivalence). They did not specifically focus on the need to reduce emissions of particular gases, but provided signatories with the option of doing so. It can also be noted that the Kigali Amendment to the Montreal Protocol https://ozone.unep.org/treaties/montreal-protocol/amendments/kigali-amendment-2016-amendment-montreal-protocol-agreed is perhaps also relevant, although not specifically relevant to the gases mentioned on line 85.

Response:

We thank the reviewer for this helpful comment and agree that the original wording was not sufficiently precise. In the revised manuscript, the text has been corrected to clarify that international climate agreements adopt GWP_{100} as a metric for CO_2-equivalent reporting, rather than explicitly emphasizing the reduction of specific gases. The revised text now accurately reflects the role of GWP_{100} in emissions reporting under the Kyoto Protocol, the Paris Agreement, and related frameworks, and places the discussion of F-gases in this appropriate context.

Manuscript Changes:

Lines 39-41 and 44-46.

Reviewer Comment #12

Comment:

98: “moderately toxic” – all references that I looked at seem to say it is highly toxic. I am not in a position to judge.

Response:

We thank the reviewer for this careful observation. The term “moderately toxic” was cited directly from Mitsui et al. (2004), where COF_2 was described as having toxicity comparable to other fluorinated gases commonly used in semiconductor processes. In that context, the phrase likely referred to its relative handling risk in industrial environments, rather than its absolute toxicity to humans. However, we acknowledge that COF_2 is indeed a highly toxic gas with a molecular structure similar to phosgene, and the use of the term “moderately toxic” could be misleading or open to misinterpretation. As the toxicity classification is not central to the scientific objectives of this study, we have removed the phrase from the revised manuscript to avoid confusion.

Manuscript Changes:

Lines 61-62.

Reviewer Comment #13

Comment:

110: The wavenumber range of the measurements needs to be stated. Presumably this is determined by the detector?

Response:

We thank the reviewer for this helpful comment. The wavenumber ranges of the FTIR measurements have now been explicitly stated in the revised manuscript and are determined by the detector type used in each instrument. Specifically, the ACS measurements were performed using a Nicolet iS50 FTIR spectrometer equipped with a DTGS detector (spectral range: 4000–650 cm^{-1}) and a 2.4 m multipass gas cell, while the time-resolved experiments were conducted using an Arcoptix GASEX OEM FTIR spectrometer equipped with a 4-TEC MCT detector (spectral range: 5000–830 cm^{-1}). Because the FTIR detector used for ACS measurements covers 650–4000 cm^{-1} and the stratospheric-adjusted Pinnock curve is defined up to 3000 cm^{-1}, the ACS spectrum relevant for RE calculations spans 650–3000 cm^{-1}, as determined jointly by the detector response and the applicable range of the Pinnock curve.

Manuscript Changes:

Lines 104, 110-111 and 223-226.

Reviewer Comment #14

Comment:

*157-163: Although quite interesting, no motivation is given for presenting these DFT calculations. Why are they needed, when you have measurements and, in terms of integrated cross-sections, how do they compare with the measurements? If it is to allow attribution of bands to specific modes of vibration, that is interesting, but I think this has already been established in the earlier literature – for example, see the papers that are referred to by the HITRAN database for COF2. So, again, more references to the older literature are necessary and the text can be shortened so that it doesn't appear as if the results presented here are original.

Response:

We thank the reviewer for this helpful comment and agree that the DFT calculations were not essential to this study. In the revised manuscript, the DFT calculation results have been removed to avoid potential confusion and to maintain a clear focus on the experimental FTIR measurements and the evaluation of the ACS, RE, and GWP of COF_2.

Manuscript Changes:

Reviewer Comment #15

Comment:

*168-181: Again, this section is presented without any references to earlier work, implying that this is new knowledge. As noted above, the molecular structure presented here is very little different to the COF2 entry on Wikipedia. I am not sure why the authors choose to compare with formaldehyde. This seems to lengthen the paper unnecessarily and can be removed.

Response:

We thank the reviewer for this valuable comment and fully agree with the observation. The discussion comparing COF_2 with formaldehyde and the associated structural description does not add essential scientific value to this study. In the revised manuscript, this section has been removed to maintain focus on the experimental results and to avoid any implication that the structural information represents new findings.

Manuscript Changes:

Reviewer Comment #16

Comment:

Figure 2a: Although I believe Figure 2a is not necessary, note that the angles in the figure and in the caption are slightly different. There is also no need, in my view, to repeat information that is in the figure in the caption.

Response:

We thank the reviewer for this careful observation and fully agree with the comment. Figure 2a and its caption are not essential to the main discussion and may cause unnecessary repetition. In the revised manuscript, Figure 2a has been removed to improve clarity and conciseness.

Manuscript Changes:

Reviewer Comment #17

Comment:

*Figures 2b and 3b: the authors need to revisit how that they handle the low wavenumber noise in the FTIR spectra. The fact that the noise sends the ACS negative is completely unphysical but it is not recommended that these are set to zero whilst retaining positive noise, as this introduces a bias. Many studies simply exclude regions between bands (i.e. set the ACS to zero) where the signal to noise ratio is too low.

Response:

We thank the reviewer for this valuable and technically insightful comment. We fully agree that the low-wavenumber noise in the FTIR spectra should be handled carefully to avoid unphysical negative absorption cross-section (ACS) values and potential bias.

In the revised analysis, the FTIR spectra were averaged onto a 10 cm^{-1} grid prior to ACS calculation. This averaging effectively suppresses random noise, removes negative excursions in low–signal-to-noise regions, and eliminates bias introduced by selectively setting only negative values to zero.

Furthermore, this 10 cm^{-1} grid spacing is directly consistent with the spectral resolution of the the stratospheric-adjusted Pinnock curve used in the RE calculation. Therefore, the averaged ACS data can be applied in a one-to-one correspondence with the Pinnock curve spectral grid, ensuring both numerical consistency and physical validity in the RE evaluation.

Manuscript Changes:

Lines 223-224.

Reviewer Comment #18

Comment:

184-189: Some of this discussion repeats information provided already in Section 2.

Response:

We agree with the reviewer’s observation that the discussion in lines 184–189 partially overlaps with the content already presented in Section 2. In the revised manuscript, the redundant sentences have been removed to avoid repetition and improve the overall conciseness of the text.

Manuscript Changes:

Section 3.1 (Absorption Cross-Section).

Reviewer Comment #19

Comment:

*190-204: Again results are presented without a single reference to previous work in this area. See my comment on 157-163 for where some of earlier papers can be found.

Response:

We agree with the reviewer that the original wording could give the impression that these results were entirely new. In the revised manuscript, this section has been revised to avoid potential misunderstanding, and relevant discussions of previous studies have been consolidated in the Introduction to provide appropriate context and attribution to earlier work.

Manuscript Changes:

Lines 75–84 and Section 3.1 (Absorption Cross-Section).

Reviewer Comment #20

Comment:

*183: This section needs to report the integrated absorption cross-section and to discuss uncertainties in the final value.

Response:

We thank the reviewer for this comment. In the revised manuscript, the integrated absorption cross-section (IACS) is reported as the direct spectral integral of the measured ACS using a constant wavenumber interval. The uncertainty analysis is performed at the ACS level, and the same relative uncertainty therefore applies to both the IACS and the derived radiative efficiency (RE).

Manuscript Changes:

Lines 230–239 (IAC), Table 2, and Lines 331–345 (Uncertainties).

Reviewer Comment #21

Comment:

*217: Is 4 decimal places justified? How does this value compare with previous literature and what are possible reasons for the difference? And what is the estimated uncertainty in the IAC and RE.

Response:

We thank the reviewer for this insightful comment. We agree that the numerical precision of the reported RE value required revision. In the revised manuscript, the number of significant figures for both the integrated absorption cross-section (IAC) and radiative efficiency (RE) has been reassessed based on the underlying measurement precision. Uncertainties associated with IAC and RE are now explicitly described, and the revised values are compared with those reported in previous studies (e.g., Hodnebrog et al., 2013, 2020) to place our results in context and discuss possible sources of differences.

Manuscript Changes:

Lines 230–239 (IAC), Lines 261–267 (RE), Table 2, and Lines 331–345 (Uncertainties).

Reviewer Comment #22

Comment:

*218: "measurable contribution to RF". Without estimates or measurements of the abundance of C2FO it is not possible to make this statement, and I doubt if the RF can be measured as it is so small. The statement should either be better justified, or the authors should stick to RE, which is what they calculate and present.

Response:

We thank the reviewer for this comment and agree that the statement referring to a "measurable contribution to radiative forcing" was not appropriate, as no atmospheric abundance of COF_2 is estimated or measured in this study. In the revised manuscript, this statement has been removed, and the discussion is now restricted to radiative efficiency (RE), which is the quantity explicitly calculated and analyzed in this work.

Manuscript Changes:

The relevant sentence has been removed from the revised manuscript.

Reviewer Comment #23

Comment:

*221-273: Again there is not a single reference to the older literature in the whole of this section, and so the impression is given that this is all new. I believe that the reactions given in Scheme 1 are already well established.

Response:

We thank the reviewer for this comment and agree that references to the established literature were needed in this section. In the revised manuscript, we have added citations to prior theoretical and experimental studies describing the hydrolysis and oxidation pathways of COF_2 (e.g., Francisco, 1993; Zachariah et al., 1995; Uchimaru et al., 2004). These additions clarify that the reaction schemes summarized in Scheme 1 are based on well-established mechanisms, while the present study focuses on a quantitative comparison between O_2-mediated oxidation and H_2O-driven hydrolysis under controlled dry and humid conditions.

Manuscript Changes:

Lines 275–281. Please see Scheme 1.

Reviewer Comment #24

Comment:

226: “negligible”. I am not sure what this means. Its presence is very clear in Figure 4a, but the reader is not told this.

Response:

We thank the reviewer for this careful observation and agree that the term “negligible” was misleading. In the revised manuscript, we clarify that small water-related absorption features are indeed visible and originate from trace amounts of residual moisture in the reaction cell. Although the dehydrated synthetic air contained less than 2 ppm of H_2O, filling the cell to near atmospheric pressure results in a sufficient absolute number of water molecules to produce weak but detectable absorption bands in the FTIR spectrum. This clarification has been added to the text, with the figure reference updated from Fig. 4a in the previous version to Fig. 3a in the revised manuscript.

Manuscript Changes:

Lines 272–273 and 297–300.

Reviewer Comment #25

Comment:

*Table 2: Some values are quoted to 6 significant figures (see also other tables in the paper) without any accompanying uncertainty estimate.

Response:

We thank the reviewer for this comment. In the revised manuscript, the table referred to as Table 2 in the previous version is now presented as Table 3. The values reported in Table 3 are not direct measurement results but parameters obtained from exponential fitting of time-resolved spectral data; thus, the reported digits reflect the numerical output of the fitting procedure rather than measurement precision. For experimentally measured quantities and their derived results, uncertainties are explicitly reported either directly in the corresponding tables or discussed in detail in Section 3.4 (Uncertainties), where relative standard uncertainties associated with the measurements and their propagation are provided. This distinction has been clarified to avoid confusion regarding the apparent numerical precision.

Manuscript Changes:

Please see Table 3, and references to the uncertainty treatment in Section 3.4 (Lines 331-345) have been added.

Reviewer Comment #26

Comment:

*225: More care is needed about such statements as “typical outdoor conditions”. While they may be correct for near-surface conditions where the measurements were made, they may not be appropriate elsewhere. Despite the short lifetimes found in this study, it may be possible for convection to transport some surface emitted C2FO to reach high altitudes and hence lower humidities. Similarly, emissions in high latitudes may not experience such moist conditions. The authors could simply point out that these lifetimes are appropriate to the conditions in which measurements are made, but they may not be appropriate for all locations.

Response:

We agree with the reviewer. In the revised manuscript, we clarify that the reported atmospheric lifetimes and corresponding GWP values are representative of the near-surface humidity conditions under which the measurements were conducted, and that in drier environments, at higher altitudes, or in high-latitude regions, reduced hydrolysis may result in longer effective lifetimes and higher GWP values.

Manuscript Changes:

Lines 374-377.

Reviewer Comment #27

Comment:

*275: The reader should be reminded that these estimates of RE and GWP use the assumption that COF2 is well-mixed, which is highly unlikely given the short lifetime. Although not fully appropriate to the destruction processes for COF2, the Hodnebrog papers present simple methods to adjust the RE (and hence GWP) for gas lifetime. Consequently, the values presented here are likely overestimates. In addition, it should be noted that the GWP for very short lived species is dependent on both the location and time of year of the emissions. A short statement on this may be useful.

Response:

We agree with the reviewer. In the revised manuscript, we explicitly state that COF_2 cannot be considered well-mixed due to its very short atmospheric lifetime and dominant removal by rapid hydrolysis in the presence of water vapor. To maintain consistency with established GWP formulations, a lifetime-dependent correction factor $f(\tau)$ is applied to the radiative efficiency prior to GWP_{100} calculation, following the parameterisation of Hodnebrog et al. (2013, 2020). We also note that lifetime corrections for very short-lived species are associated with increased uncertainty and depend on local atmospheric conditions such as humidity and emission location.

Manuscript Changes:

Relevant discussion has been added in Lines 203–218.

Reviewer Comment #28

Comment:

299-291: This statement is not correct for the AGWP of CO2.

Response:

We agree with the reviewer that the previous statement regarding the AGWP of CO_2 was not correct. In the revised manuscript, the description of AGWP has been corrected to clearly distinguish the definitions of AGWP for CO_2 and COF_2, following the IPCC methodology. The reference value of AGWP for CO_2 is now explicitly adopted from the IPCC AR6 Working Group I Supplementary Material (Smith et al., 2021) and is consistently used as the denominator in the GWP calculation.

Manuscript Changes:

Lines 170–171.

Reviewer Comment #29

Comment:

Supplementary Material: I feel that all the information concerning COH2 should be removed, as its relevance to this study is never established. It is also presented without any reference to the older literature which is extensive for this molecule.

Response:

We agree with the reviewer that the information related to COH_2 is not essential to the scope of the present study. Accordingly, all COH_2-related content has been completely removed from the revised Supporting Information. The Supporting Information now exclusively focuses on data and analyses directly relevant to the experimental determination of the absorption cross-sections, radiative efficiency, and GWP of COF_2.

Manuscript Changes:

All COH_2-related figures, tables, and descriptions have been removed from the Supporting Information. Please see the revised Supporting Information.

Response to Reviewer #2

We sincerely thank Reviewer #2 for the careful and insightful evaluation of our manuscript. The comments raised important questions regarding the motivation for new measurements, the relationship to existing spectroscopic datasets, the treatment of experimental uncertainties, and the scope of the study with respect to atmospheric relevance. In response, we have substantially revised the manuscript to clarify these points and to improve its scientific transparency and focus.

In particular, we clarified that the purpose of the present work is not to replace existing COF_2 spectroscopic datasets such as HITRAN or PNNL, but to provide an independent experimental validation under well-controlled laboratory conditions and to assess uncertainty sources relevant to radiative efficiency (RE) and GWP calculations. Comparisons with previous studies have now been made explicit, and a dedicated Uncertainties section has been added to quantitatively evaluate ACS uncertainties and their propagation to derived quantities. We also clarified the roles of dilution, path length uncertainty, gas composition, and potential wall effects in the experimental design.

Finally, we removed content that does not directly contribute to the evaluation of RE and GWP, including all DFT-related material, and clarified the distinction between stratospherically produced COF_2 and COF_2 directly emitted from industrial sources. As a result, the revised manuscript more clearly focuses on the experimental determination and interpretation of ACS, RE, and GWP of COF_2 within a framework that is consistent with existing literature and directly relevant to atmospheric and climate applications. **All revisions made in response to the reviewer's comments are highlighted in green in the revised manuscript.**

Reviewer Comment #1
Comment: It is unusual that the authors provide no discussion or even recognition of COF_2 present in the atmosphere as a degradation product of halogen species such as CFC-12 and HCFC-22. There have been studies of this, e.g., https://doi.org/10.5194/acp-14-11915-2014. Presumably this upper atmosphere COF_2 contributes to the RE and GWP, but has not been considered.
Response: We thank the reviewer for this valuable comment and agree that COF_2 is present in the atmosphere as a secondary degradation product of halogenated compounds such as CFC-12, HCFC-22, and CFC-113. Previous studies have shown that COF_2 acts as a major reservoir of inorganic fluorine in the stratosphere and can contribute to radiative forcing and the effective GWP of its precursor halocarbons (Harrison et al., 2014; Harrison, 2020; Thornhill et al., 2024). In the revised manuscript, we now explicitly acknowledge this stratospheric context. At the same time, we clarify that the present study focuses on COF_2 that may be directly emitted from anthropogenic industrial processes, particularly semiconductor and display manufacturing, rather than COF_2 formed secondarily in the stratosphere. Accordingly, our experimental evaluation of absorption cross-section, radiative efficiency, atmospheric lifetime, and GWP_{100} is restricted to controlled near-surface conditions relevant to direct emissions. This distinction has been added to clearly define the scope of the study and to avoid potential misunderstanding regarding the atmospheric origin considered in our GWP analysis.
Manuscript Changes: Lines 68-74.

Reviewer Comment #2

Comment:

I would like to see a rationale for why new measurements of COF2 were needed, and why they are better than previous spectroscopic measurements. There are spectroscopic data for this molecule in the HITRAN database in the form of line parameters. There are existing cross sections in the literature, e.g. in the PNNL database. Comparisons need to be made.

There is no uncertainty evaluation for the new COF2 ACS. What is the pathlength uncertainty? How accurate is the COF2 composition of the gas cylinder mixture? What contribution does the dilution make to the error budget? What about COF2 adsorption on the walls of the sample cell?

Response:

We thank the reviewer for this detailed and important comment. Below, we address each point raised regarding the motivation for new measurements, comparison with existing datasets, and the evaluation of experimental uncertainties.

(i) Rationale for new COF_2 measurements and comparison with existing spectroscopic data.

Spectroscopic information for COF_2 is indeed available in the HITRAN database in the form of line-by-line parameters and in the literature as experimental absorption cross sections, most notably in the PNNL database. The purpose of the present study was not to replace or improve these datasets, but to independently verify their reproducibility under well-controlled laboratory conditions and to assess potential sources of experimental uncertainty relevant to radiative efficiency (RE) and GWP calculations. HITRAN line parameters primarily represent the strongest vibrational transitions and do not include broadband baseline absorption captured in experimental FTIR spectra, while the PNNL dataset represents a single experimental realization that has been widely adopted in subsequent RE and GWP assessments. Our measurements therefore provide an independent experimental validation of the existing cross-section data.

(ii) Comparison with previous ACS and RE values.

Following the evaluation framework used by Hodnebrog et al. (2020) and Thornhill et al. (2024), the integrated absorption cross-section obtained in this study (1.58×10^{-16} cm molecule^{-1}) agrees within approximately 2 % with the PNNL-based value (1.55×10^{-16} cm molecule^{-1}). The resulting stratosphere-adjusted RE (0.119 W m^{-2} ppb^{-1}) is within 3–6 % of the values reported in these studies. When the literature RE values are recalculated over the same effective spectral range as the present measurements (650–3000 cm^{-1}), the remaining discrepancy is reduced to approximately 1 %, indicating close consistency among the datasets. These comparisons are now explicitly discussed in the revised manuscript.

(iii) Uncertainty evaluation of the ACS.

A dedicated Uncertainties section has been added. The ACS uncertainty was evaluated by propagating uncertainties associated with optical path length (2.4 ± 0.0065 m for the ACS cell), gas composition (3360 ± 67 ppm, $k = 2$), regression procedures, and FTIR baseline noise. For kinetic measurements, a separate 5.0 ± 0.01 m gas cell was used. The combined relative standard uncertainty of the ACS is approximately 2.1 %, which is comparable to uncertainty levels reported for similar halogenated species (Hodnebrog et al., 2013, 2020). Because both the integrated ACS and the RE are linear spectral integrals of the ACS, this relative uncertainty applies directly to both quantities.

(iv) Effect of dilution on uncertainty.

No dilution-related uncertainty applies to the ACS measurements. The ACS was determined using a single, well-defined COF_2/N_2 gas mixture without in situ dilution during spectral acquisition, and the concentration uncertainty of this mixture is already included in the ACS uncertainty budget. For the e-folding lifetime experiments, dilution occurs naturally after sample injection as dry synthetic air or ambient air is introduced to near-atmospheric pressure. However, these experiments rely on the relative temporal decay of the COF_2 absorption signal rather than on absolute concentration values. The lifetime is extracted from the normalized decay profile, such that dilution affects only the initial signal amplitude and not the exponential time constant. Consequently, the influence of dilution on the derived lifetime is expected to be negligible.

(v) Potential adsorption of COF_2 on the cell walls.
The total duration of each FTIR measurement was typically less than 13 h, during which no systematic signal decay or concentration loss indicative of wall adsorption was observed. While longer-term adsorption effects cannot be completely ruled out, their influence during the measurement window relevant to this study appears negligible.

Overall, the primary objective of the present measurements is to provide an independent experimental validation of existing COF_2 spectroscopic datasets under different laboratory conditions. This cross-verification strengthens confidence in the reliability and representativeness of the PNNL-based spectrum and supports its continued use in radiative forcing and GWP assessments.

Manuscript Changes:
Lines 68-74, 75-85, 103, 110-111, 127-129, 331-345.

Reviewer Comment #3

Comment:
What is the purpose of the DFT calculation of COF2? The comparison with the ACS is poor. I don't understand the rationale here. Unless this calculation is intrinsic to the RE/GWP calculations, I don't think its inclusion is warranted for an atmospheric journal.

Response:
We fully agree with the reviewer's comment. The DFT calculations were originally included to provide a comprehensive perspective on COF_2's molecular and spectroscopic characteristics within a single study. However, we recognize that this section does not present new findings and overlaps with previously published results. Therefore, we will remove the DFT-related content from the revised manuscript to maintain focus on the experimental results directly relevant to RE and GWP evaluation.

Manuscript Changes: