**Response to the Anonymous Referee #1 Comments for the manuscript "**Reaction between perfluoroaldehydes and hydroperoxy radical in the atmosphere: Reaction mechanisms, reaction kinetics modelling, and atmospheric implications**"**

We sincerely appreciate the time and effort you dedicated to reviewing our manuscript. Your insightful feedback has significantly enhanced both the scientific content and written presentation, elevated the paper's academic value while improved its accessibility and clarity for readers. Below, we provide point-by-point responses to your comments. All corresponding revisions are marked in the tracked-changes version of the updated manuscript, where reviewer comments (RC) appear in black text and author responses (AC) in blue.

**Specific Comments**

**1. Abstract**

**(a) Comment:** the atmospheric lifetimes for $C_2F_5CHO$ and $C_3F_7CHO$, approximately 14.4-31.3 hours and 21.6-51.8 hours by $HO_2$ are much shorter than those via OH radical," it is not validated. (lines 15-16)

**Response:** We thank the reviewer for highlighting the need for validation of the atmospheric lifetime. In the revised manuscript, we define the atmospheric lifetime $\tau$ for linear perfluorinated aldehydes reacting with $HO_2$ as $\tau = 1/(k[HO_2])$, where $k$ is the bimolecular rate constant and $[HO_2]$ represents the concentration of $HO_2$ radicals. The full atmospheric lifetime data are presented in Section 3.3, where atmospheric lifetimes with respect to bimolecular reactions as functions of altitude are list in Table 2.

We revised the sentence "$\tau_1$, and $\tau_2$ are the atmospheric lifetimes of the $HO_2$ reaction with $C_2F_5CHO$ and $C_3F_7CHO$, respectively." to "$\tau_1 = 1/(k_1[HO_2])$ and $\tau_2 = 1/(k_2[HO_2])$ define the atmospheric lifetimes for $HO_2$ reaction with $C_2F_5CHO$ and $C_3F_7CHO$, respectively." on page 13

We also revised the sentence "As illustrated in Table 2, the $HO_2$-mediated elimination pathways for $C_2F_5CHO$ and $C_3F_7CHO$ are characterized by relatively rapid reaction rates within the troposphere (< 10 km), resulting in relatively short atmospheric lifetimes of approximately $5.18 \times 10^4$ - $1.13 \times 10^5$ s (14.4 - 31.3 hours) and $7.78 \times 10^4$ - $1.86 \times 10^5$ s (21.6 - 51.8 hours)." to "The $HO_2$-mediated elimination pathways for $C_2F_5CHO$ and $C_3F_7CHO$ are characterized by relatively rapid reaction rates within the troposphere (< 10 km), resulting in relatively short atmospheric lifetimes of approximately 14.4 - 31.3 hours and 21.6 - 51.8 hours (See Table 2)." on page 12

**2. Introduction**

**(a) Comment:** Alternating use of "perfluoroaldehydes" (in tittle) and "linear perfluoroaldehydes" may confuse readers.

**Response:** We have standardized the terminology to "linear perfluoroaldehydes" throughout the manuscript to avoid ambiguity.

**(b) Comment:** The transition from PFAS's GWP to perfluoroaldehyde sources (lines 25-30) is unclear.

**Response:** We added a transitional sentence to clarify the link between PFASs' environmental impact and the formation of linear perfluoroaldehydes: "During their degradation in the atmosphere, PFASs undergo complex chemical transformations, leading to the formation of linear perfluoroaldehydes. (Alam et al.,2024; Burkholder et al., 2015; David et al., 2021; Wang et al., 2021, 2024)" on page 1

**(c) Comment:** The literature review focuses solely on OH and Cl radicals, omitting potential roles of other oxidants (e.g., $O_3$, $NO_3$). (lines 35-49)

**Response:** We expanded the discussion to acknowledge other oxidants: "Linear perfluoroaldehydes were generally considered to be removed through photochemical reactions (Chiappero et al., 2006; Kelly et al., 2004) and free radical reactions initiated by OH and Cl radicals (Andersen et al., 2004; Chiappero et al., 2010; Wang et al., 2007). Additionally, $NO_3$ may also contribute to their atmospheric degradation. (Burkholder et al., 2015; Ziemann and Atkinson, 2012)" on page 2

**(d) Comment:** The long sentence "Moreover, the rate constant of Cl atoms with $C_nF_{2n+1}CHO$ (1,2, 3, 4) is around 2 × $10^{-12}$ $cm^3$ $molecule^{-1}s^{-1}$, which is slightly faster than that of the OH radical reactions." (lines 46-47) has poor readability and unclear notes.

**Response:** We split the sentence for clarity: "Moreover, the rate constant of Cl atoms with $C_nF_{2n+1}CHO$ (n = 1–4) is approximately 2 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. This value is slightly faster than that of the corresponding OH radical reactions under similar conditions." on page 2

**3. Computational Methods**

**(a) Comment:** In section 2.1, the "CCSD(T)-F12a/cc-pVTZ-F12" method is mentioned, but the text fails to demonstrating its applicability to perfluorinated compound systems. (lines 75-78)

**Response:** We added validation references for fluorinated systems: "Furthermore, CCSD(T)-F12a/cc-pVTZ-F12 has been shown good performance for molecules containing fluorine atoms.(Dong et al., 2021; Long et al., 2022; Xia et al., 2024)" on page 3

**4. Results and Discussion**

**(a) Comment:** Figure 1 contains no relevant information. "The result shows that the specific reaction scale factors are 0.955 for TS1 (See Figure 1) and 0.956 for TS2 (See Figure 1)" . (lines 95-96)

**Response:** We corrected the text to reference the correct Table (Table S1 in the Supplement) and clarified the context: "The result shows that the specific reaction scale factors are 0.955 for TS1 (see Table S1) and 0.956 for TS2 (see Table S1), which …" on page 4

**(b) Comment:** Grammatical error in "The torsion of the C-C bond gives produces multiple conformers". (lines 152-153)

**Response:** Corrected to: "Nevertheless, the internal rotation of the C–C bond produces multiple conformers…" on page 6

**(c) Comment:** Figure 3's X-axis label ("Number of alkyl functional groups") is misleading, as the compounds are perfluorinated. (lines 180-185)

**Response:** We appreciate the reviewer's precision feedback and we have revised the label to: "Number of perfluorinated carbon units". The revised Figure 3 is shown below (on page 8):

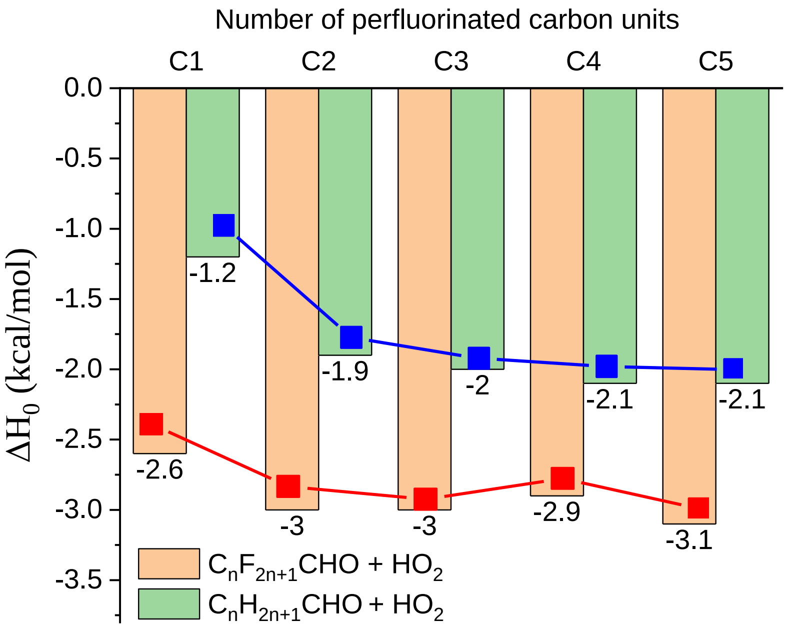

**Figure 3.** The impacts of perfluorinated carbon length on the enthalpies of activation at 0 K in the $C_nH_{2n+1}CHO/C_nF_{2n+1}CHO + HO_2$ reactions. The values for $C_nH_{2n+1}CHO$ (n = 1-5) + $HO_2$ and $C_nF_{2n+1}CHO + HO_2$ are obtained from references (Ding and Long, 2022; Gao et al., 2024) and calculated by using FNO-CCSD(T)-F12a/cc-pVDZ-F12.

**(d) Comment:** The calculated high-pressure limit rate constants (e.g., $k_1=5.42\times10^{-14}$-$3.35\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) lack comparison with experimental data or analogous systems (e.g., non-fluorinated aldehydes + $HO_2$), reducing confidence in the results. (lines 204-207)

**Response:** The revised manuscript now includes a comparison of the calculated rate constants for fluorinated aldehydes ($C_2F_5CHO$ and $C_3F_7CHO$) with experimental and theoretical data from non-fluorinated aldehydes ($C_2$H5CHO and $C_3H_7CHO$). This comparison shows that the rate constants for both fluorinated and non-fluorinated aldehydes exhibit similar magnitudes and temperature dependencies, which strengthens the confidence in the calculated results. The revised text is highlighted in the manuscript for easy reference.

Revised to: "Regarding the $C_2F_5CHO$+ $HO_2$ reaction, the rate constant $k_1$ exhibits a decrease from $3.35 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 190 K to $5.42 \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 350 K in Figure 4 and Tables S5-S7. Similarly, the rate constant $k_2$ for the $C_3F_7CHO + HO_2$ reaction also decreases with increasing temperature. These trends are consistent with theoretical studies of non-fluorinated aldehydes such as $C_2H_5CHO$ and $C_3H_7CHO$, where rate constants for reactions with $HO_2$ were reported in the range of $10^{-14}$ to $10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at atmospheric temperatures, indicating similar reactivity between fluorinated and non-fluorinated aldehydes with $HO_2$.(Ding and Long, 2022; Gao et al., 2024)" on page 9

**(e) Comment:** There is inconsistency in the units used for atmospheric lifetimes. Table 2 reports lifetimes in seconds, while the discussion section uses hours. The authors should standardize the units throughout the manuscript to avoid confusion. (lines 250-255)

**Response:** We normalized all lifetime values to hours in the revised manuscript and marked them in the header of Table 2. (on page 13)

**Table 2.** Hydroperoxyl radical concentration (in molecules $cm^{-3}$), rate constants (in $cm^3$ $molecule^{-1}$ $s^{-1}$), and atmospheric lifetimes (in hour) with respect to bimolecular reactions as functions of altitude.

| H (km)[a] | T (K)[a] | P (mbar)[a] | $[HO_2]$[b] | $k_1$ (T, $p$)[c] | $k_2$ (T, $p$)[c] | $\tau_1$[d] | $\tau_2$[d] |
|---|---|---|---|---|---|---|---|
| 0 | 290.2 | 1010 | 1.40E+08 | 1.38E-13 | 9.18E-14 | 1.44E+01 | 2.16E+01 |
| 5 | 250.5 | 496 | 4.90E+07 | 3.44E-13 | 2.30E-13 | 1.65E+01 | 2.47E+01 |
| 10 | 215.6 | 243 | 8.30E+06 | 1.07E-12 | 6.47E-13 | 3.13E+01 | 5.18E+01 |
| 15 | 198 | 119 | 2.30E+06 | 2.21E-12 | 2.98E-13 | 5.47E+01 | 4.05E+02 |
| 20 | 208 | 58.2 | 2.90E+06 | 1.38E-12 | 1.22E-13 | 6.93E+01 | 7.85E+02 |
| 25 | 216.1 | 28.5 | 5.70E+06 | 9.38E-13 | 4.32E-14 | 5.20E+01 | 1.13E+03 |
| 30 | 221.5 | 13.9 | 7.50E+06 | 6.52E-13 | 1.29E-14 | 5.68E+01 | 2.88E+03 |
| 35 | 228.1 | 6.83 | 6.90E+06 | 4.04E-13 | 4.13E-15 | 9.96E+01 | 9.74E+03 |
| 40 | 240.5 | 3.34 | 5.90E+06 | 2.29E-13 | 1.73E-15 | 2.06E+02 | 2.73E+04 |
| 45 | 251.9 | 1.64 | 4.90E+06 | 1.27E-13 | 6.56E-16 | 4.45E+02 | 8.64E+04 |
| 50 | 253.7 | 0.801 | 4.00E+06 | 5.87E-14 | 1.80E-16 | 1.18E+03 | 3.86E+05 |

[a] H denotes altitude (atmospheric scale height); T denotes temperature; p denotes pressure. [b] Data are from ref (Brasseur and Solomon, 2006). [c] $k_1$, $k_2$ are the rate constants of the $HO_2$ reactions with $C_2F_5CHO$ and $C_3F_7CHO$, respectively. [d] $\tau_1$, $\tau_2$ are the atmospheric lifetimes of the $HO_2$ reaction with $C_2F_5CHO$ and $C_3F_7CHO$, respectively

## 5. Atmospheric Implications

**(a) Comment:** The GEOS-Chem simulation results (Lines 273–287) focus on $HO_2$/OH ratios but do not discuss diurnal variation, which could affect the dominance of $HO_2$ pathways.

**Response:** Thank you for your constructive comments. We have added a distribution map of the $HO_2$/OH ratio during the day (see Figure S4) and conducted a detailed analysis. we have added an additional paragraph in the revised manuscript: "Our further analysis of the global distribution of the ratio between $HO_2$ and OH during daytime reveals that $HO_2$ concentrations are generally higher than OH concentrations (see Figure S4). Notably, along the west coast of South America (approximately between 0° and 30°S latitude and 60°W to 120°W longitude), the ratio can reach up to three orders of magnitude. Industrial areas (such as Russia and Malaysia) and certain regions in Africa also exhibit high ratios of 1-2 orders of magnitude. This suggests that in these areas, the concentration of $HO_2$ is significantly higher than that of OH, which may be related to local industrial activities or specific emission characteristics. However, due to the presence of daytime photolysis, the generation and loss pathways of $HO_2$ and OH become more complex, leading to significant uncertainty in interpreting the ratio. For instance, photolysis can alter the formation rates of $HO_2$ and OH, thereby affecting their concentration ratio. Additionally, the high ratios along the eastern coast of North America may be associated with atmospheric transport and regional emission features. Despite these complexities, the high daytime ratios still indicate that in some regions, $HO_2$ may play a role in the oxidation pathways of $C_2F_5CHO$ and $C_3H_7CHO$ both during the day and at night." On page 14

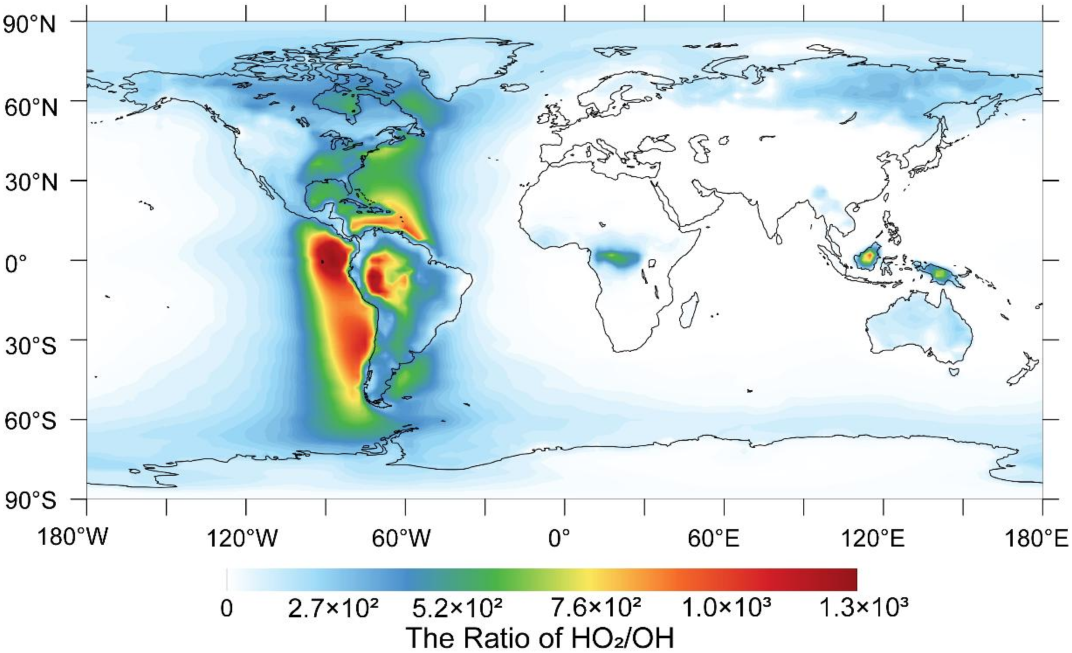

Figure S4. The annual average ratio of $HO_2$/OH during the day globally.

**(b) Comment:**

The prospect for future research is somewhat brief and doesn't adequately take into account the current study's limitations and possible areas for expansion. (lines 321-325)

**Response:** Thanks to the reviewer, we expanded the discussion to highlight limitations and future directions: "While the present investigation establishes the $HO_2$-mediated degradation pathway for linear perfluoroaldehydes ($C_2F_5CHO$/$C_3F_7CHO$), it simultaneously highlights critical gaps in our understanding of their atmospheric lifetimes. Notably, the current work focuses on gas-phase $HO_2$ reactions. However, the roles of heterogeneous interfacial processes (e.g., on aerosol surfaces or cloud droplets) remains unexplored.(Zhang et al., 2024) The potential for $HO_2$-driven defluorination to generate reactive $CF_3$ radicals, which could initiate secondary reactions (e.g., with $O_3$ or $NO_2$), requires systematic investigation to assess implications for atmospheric oxidizing capacity and secondary aerosol formation. Additionally, the study focuses on radical-driven pathways but acknowledges that photolysis is a competing sink for linear perfluoroaldehydes. Future work should quantify photolysis rates under stratospheric UV conditions (e.g., 200–300 nm) to reconcile discrepancies between modeled and observed atmospheric lifetimes.(Thomson et al., 2025) Addressing these limitations will require integrating advanced experimental techniques (e.g., synchrotron-based photoionization mass spectrometry) with multi-scale modeling frameworks, while prioritizing under sampled environments like the upper troposphere and polar regions where $HO_2$ reactivity anomalies could profoundly alter PFAS degradation trajectories.(Alam et al., 2024; Zhou et al., 2024) Such efforts are critical for refining environmental risk assessments of emerging HFOs and guiding the design of next-generation chemicals with minimized atmospheric persistence.” On page 16

**6. References**

**(a) Comment:**

Some of the cited references are incomplete or incorrect.

Lee, B. H., Munger, J. W., Wofsy, S. C., Rizzo, L. V., Yoon, J. Y. S., Turner, A. J., Thornton, J. A., and Swann, A. L. S.: Sensitive Response of Atmospheric Oxidative Capacity to the Uncertainty in the Emissions of Nitric Oxide (NO) From Soils 450 in Amazonia, Geophysical Research Letters, 51, 1-10, https://doi.org/10.1029/2023GL107214, 2024. (lines 448-450)

Long, B., Bao, J. L., and Truhlar, D. G.: Rapid unimolecular reaction of stabilized Criegee intermediates and implications for atmospheric chemistry, Nature Communications, 10, 1–8, https://doi.org/10.1038/s41467-019-09948-7, 2019. (lines 473-474)

Xia, D., Zhang, H., Ju, Y., Xie, H., Su, L., Ma, F., Jiang, J., Chen, J., and Francisco, J. S.: Spontaneous Degradation of the “Forever Chemicals” Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) on Water Droplet Surfaces, https://doi.org/10.1021/jacs.4c00435, 2024. (lines 548-550)

**Response:**

All references have been reformatted to comply with journal guidelines (AGU style) and updated with missing details:

Lee, B. H., Munger, J. W., Wofsy, S. C., Rizzo, L. V., Yoon, J. Y. S., Turner, A. J., Thornton, J. A., and Swann, A. L. S.: Sensitive Response of Atmospheric Oxidative Capacity to the Uncertainty in the Emissions of Nitric Oxide (NO) From Soils 450 in Amazonia, Geophysical Research Letters, 51, e2023GL107214, https://doi.org/10.1029/2023GL107214, 2024. (lines 519-521)

Long, B., Bao, J. L., and Truhlar, D. G.: Rapid unimolecular reaction of stabilized Criegee intermediates and implications for atmospheric chemistry, Nature Communications, 10, 2003, https://doi.org/10.1038/s41467-019-09948-7, 2019. (lines 547-548)

Xia, D., Zhang, H., Ju, Y., Xie, H., Su, L., Ma, F., Jiang, J., Chen, J., and Francisco, J. S.: Spontaneous Degradation of the “Forever Chemicals” Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) on Water Droplet Surfaces, Journal of the American Chemical Society, 146, 11266–11271, https://doi.org/10.1021/jacs.4c00435, 2024. (lines 631-633)

**References (in revised manuscript)**

Alam, M. S., Abbasi, A., and Chen, G.: Fate, distribution, and transport dynamics of Per- and Polyfluoroalkyl Substances (PFASs) in the environment, Journal of Environmental Management, 371, 123163, https://doi.org/10.1016/j.jenvman.2024.123163, 2024.

Andersen, M. P. S., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Stevens, J. E., Martin, J. W., Ellis, D. A., and Mabury, S. A.: Atmospheric chemistry of n-$C_xF_{2x+1}CHO$ (x = 1, 3, 4): Reaction with Cl atoms, OH radicals and IR spectra of $C_xF$

$_{2x+1}C(O)O_2NO_2$, Journal of Physical Chemistry A, 108, 5189–5196, https://doi.org/10.1021/jp0496598, 2004.

Brasseur, G. and Solomon, S.: Aeronomy of the middle atmosphere: chemistry and physics of the stratosphere and mesosphere., Springer Science & Business Media, 617–627 pp., https://doi.org/10.1007/1-4020-3824-0, 2006.

Burkholder, J. B., Cox, R. A., and Ravishankara, A. R.: Atmospheric Degradation of Ozone Depleting Substances, Their Substitutes, and Related Species, Chemical Reviews, 115, 3704–3759, https://doi.org/10.1021/cr5006759, 2015.

Chiappero, M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., and Buck, R. C.: Atmospheric chemistry of perfluoroaldehydes ($C_xF_{2x+1}CHO$) and fluorotelomer aldehydes ($C_xF_{2x+1}CH_2CHO$): Quantification of the important role, of photolysis, Journal of Physical Chemistry A, 110, 11944–11953, https://doi.org/10.1021/jp064262k, 2006.

Chiappero, M. S., Argüello, G. A., Hurley, M. D., and Wallington, T. J.: Atmospheric chemistry of n-$C_6F_{13}CH_2CHO$: Formation from n-$C_6F_{13}CH_2CH_2OH$, kinetics, and mechanisms of reactions with chlorine atoms and OH radicals, Journal of Physical Chemistry A, 114, 6131–6137, https://doi.org/10.1021/jp101587m, 2010.

David, L. M., Barth, M., Höglund-Isaksson, L., Purohit, P., Velders, G. J. M., Glaser, S., and Ravishankara, A. R.: Trifluoroacetic acid deposition from emissions of HFO-1234yf in India, China, and the Middle East, Atmospheric Chemistry and Physics, 21, 14833–14849, https://doi.org/10.5194/acp-21-14833-2021, 2021.

Ding, D. P. and Long, B.: Reaction between propionaldehyde and hydroxyperoxy radical in the atmosphere: A reaction route for the sink of propionaldehyde and the formation of formic acid, Atmospheric Environment, 284, 119202, https://doi.org/10.1016/j.atmosenv.2022.119202, 2022.

Dong, Z. G., Xu, F., Mitchell, E., and Long, B.: Trifluoroacetaldehyde aminolysis catalyzed by a single water molecule: An important sink pathway for trifluoroacetaldehyde and a potential pathway for secondary organic aerosol growth, Atmospheric Environment, 249, 118242, https://doi.org/10.1016/j.atmosenv.2021.118242, 2021.

Gao, Q., Shen, C., Zhang, H., Long, B., and Truhlar, D. G.: Quantitative Kinetics Reveal that Reactions of $HO_2$ are a Significant Sink for Aldehydes in the Atmosphere and may Initiate the Formation of Highly Oxygenated Molecules via Autoxidation , Physical Chemistry Chemical Physics, 26, 16160–16174, https://doi.org/10.1039/d4cp00693c, 2024.

Kelly, T., Sidebottom, H., Nielsen, C. J., and Sellevag, S. R.: A study of the IR and UV-Vis absorption cross-sections, photolysis and OH-initiated oxidation of $CF_3CHO$ and $CF_3CH_2CHO$, Physical Chemistry Chemical Physics, 1243–1252, 2004.

Long, B., Xia, Y., and Truhlar, D. G.: Quantitative Kinetics of $HO_2$ Reactions with Aldehydes in the Atmosphere: High-Order Dynamic Correlation, Anharmonicity, and Falloff Effects Are All Important, Journal of the American Chemical Society, 144, 19910–19920, https://doi.org/10.1021/jacs.2c07994, 2022.

Thomson, J. D., Campbell, J. S., Edwards, E. B., Medcraft, C., Nauta, K., Pérez-Peña, M. P., Fisher, J. A., Osborn, D. L., Kable, S. H., and Hansen, C. S.: Fluoroform (CHF

3 ) Production from $CF_3CHO$ Photolysis and Implications for the Decomposition of Hydrofluoroolefins and Hydrochlorofluoroolefins in the Atmosphere, Journal of the American Chemical Society, 147, 33–38, https://doi.org/10.1021/jacs.4c11776, 2025.

Wang, Y., Liu, J. yao, Yang, L., Zhao, X. lei, Ji, Y. M., and Li, Z. sheng: Theoretical studies and rate constant calculations of the reactions $C_2F_5CHO$ with OH radicals and Cl atoms, Journal of Molecular Structure: THEOCHEM, 820, 26–34, https://doi.org/10.1016/j.theochem.2007.06.001, 2007.

Wang, Y., Wang, Z., Sun, M., Guo, J., and Zhang, J.: Emissions, degradation and impact of HFO-1234ze from China PU foam industry, Science of the Total Environment, 780, 146631, https://doi.org/10.1016/j.scitotenv.2021.146631, 2021.

Wang, Y., Liu, L., Qiao, X., Sun, M., Guo, J., Zhao, B., and Zhang, J.: Atmospheric fate and impacts of HFO-1234yf from mobile air conditioners in East Asia, Science of the Total Environment, 916, 170137, https://doi.org/10.1016/j.scitotenv.2024.170137, 2024.

Xia, Y., Long, B., Liu, A., and Truhlar, D. G.: Reactions with criegee intermediates are the dominant gas-phase sink for formyl fluoride in the atmosphere, Fundamental Research, 4, 1216–1224, https://doi.org/10.1016/j.fmre.2023.02.012, 2024.

Zhang, W., Issa, K., Tang, T., and Zhang, H.: Role of Hydroperoxyl Radicals in Heterogeneous Oxidation of Oxygenated Organic Aerosols, Environmental Science & Technology, 58, 4727–4736, https://doi.org/10.1021/acs.est.3c09024, 2024.

Zhou, Y., Wang, X., Wang, C., Ji, Z., Niu, X., and Dong, H.: Fate of ‘forever chemicals’ in the global cryosphere, Earth-Science Reviews, 259, 104973, https://doi.org/10.1016/j.earscirev.2024.104973, 2024.

Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chemical Society Reviews, 41, 6582–6605, https://doi.org/10.1039/c2cs35122f, 2012.