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Radical chemistry in atmospheric ice analogs forms persistent trifluoroacetic acid

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Trifluoroacetic acid (TFA, CF₃COOH), the most prevalent per- and polyfluoroalkyl substance (PFAS), is accumulating globally in precipitation, soils, and drinking water, yet its formation remains unresolved. Atmospheric models emphasize gas-phase oxidation of hydrofluorocarbons and hydrofluoroolefins, but measured abundances often exceed predictions, implying missing chemistry. Here, we identify a condensed-phase radical pathway to TFA in cryogenic trifluoromethane/carbon dioxide ice analogs. Energetic processing generates trifluoromethyl (CF₃) and hydroxycarbonyl (HOCO) radicals that undergo barrierless recombination to form TFA. Fourier transform infrared spectroscopy tracks reactive intermediates and carboxylic acid functional groups, while synchrotron vacuum-ultraviolet photoionization reflectron time-of-flight mass spectrometry provides isomer-selective detection of TFA and diagnostic dimer fragments. These results support CF₃–HOCO recombination as a potential condensed-phase route linking fluorocarbon degradation to persistent PFAS formation, highlighting the potential role of ice crystals and cloud particles as chemical reactors in atmospheric fluorine chemistry.

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Introduction

Trifluoroacetic acid (TFA, CF₃COOH, **1**; Fig. 1)—a perfluoroalkyl acid within the broader class of per- and polyfluoroalkyl substances (PFAS)—is currently the most abundant PFAS detected globally. Over recent decades, TFA concentrations have increased by up to three orders of magnitude in precipitation, soils, vegetation, and drinking water.^{1–4} This rapid accumulation has led to its designation as a potential planetary-boundary threat, capable of disrupting freshwater quality, ecosystem functioning, and global chemical pollution boundaries.^{2–9} Moreover, the detection of TFA in food and potable water, coupled with emerging human-health risk assessments, has prompted the establishment of drinking water guideline

values.² Together, these trends underscore the urgent need to resolve the fundamental mechanisms governing TFA formation in natural systems.^{2–4,9–12}

Current theories attribute TFA formation primarily to the oxidation of hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFO), which are widely emitted through refrigeration, air-conditioning, household appliances, and pharmaceutical manufacturing.^{1–4} These key oxidation pathways have been proposed *via* the formation of trifluoroacetyl fluoride (CF₃CFO) or trifluoroacetaldehyde (CF₃CHO), which then undergo bimolecular reactions with molecular oxygen (O₂) and other atmospheric radicals (NO, nitric oxide; NO₂, nitrogen dioxide; HO₂, peroxy),^{4,13–15} or hydrolysis to yield TFA **1** (Fig. 1).^{2–4,16–18} This long-standing view of gas-phase pathways in fluorocarbon degradation has, however, recently come under intense scrutiny. Computational studies indicate that under prevalent atmospheric conditions, key steps in the oxidation of, *e.g.*, 1,1,1,2-tetrafluoroethane (CF₃CH₂F) terminate in the stabilization of the 1,1,1,2-tetrafluoroethylperoxy radical intermediate (CF₃CHFOO),¹⁹ challenging the traditionally assumed sufficiency of hydrofluorocarbon oxidation as the primary source of environmental TFA. Therefore, the inability of HFC oxidation to reproduce observed atmospheric TFA levels could point to the existence of previously unrecognized formation pathways.

Atmospheric aerosols and ice crystals provide plausible alternative environments in which third-body stabilization—unavailable in simple bimolecular gas-phase reactions—can

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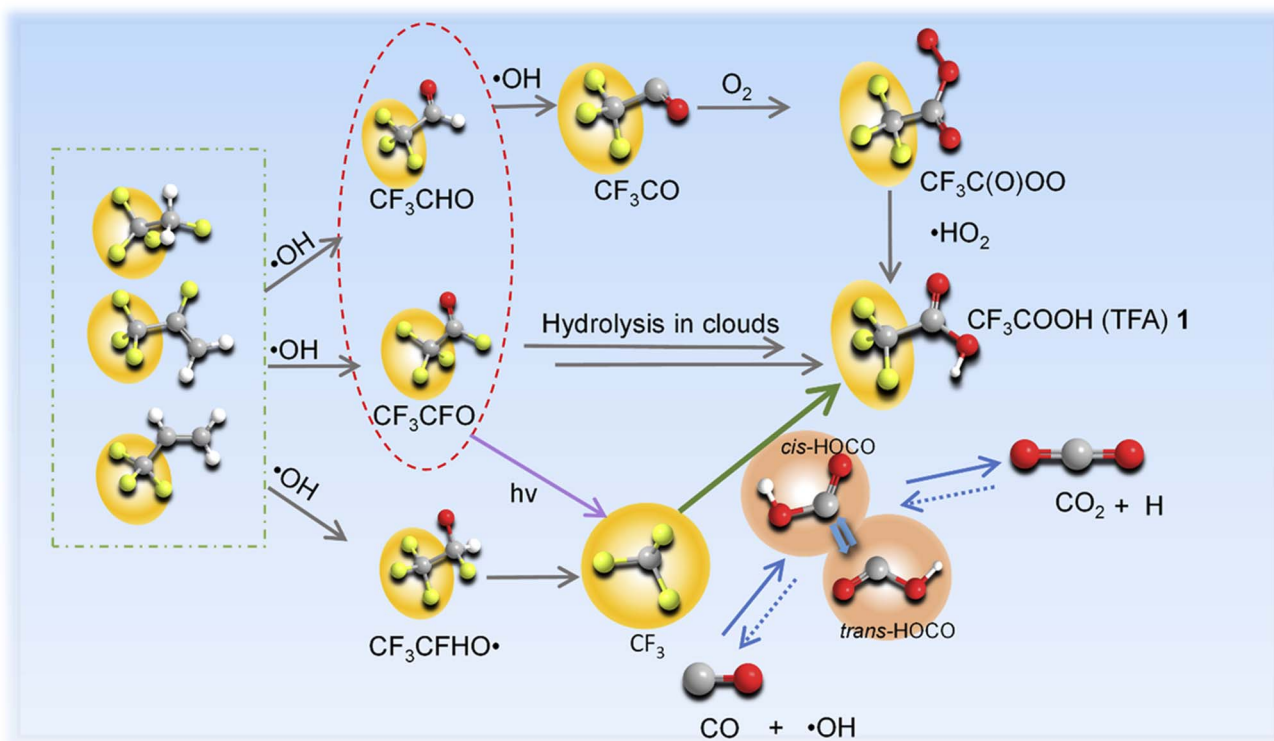


Fig. 1 Atmospheric reaction network involving hydrofluorocarbons (HFCs) to form trifluoroacetic acid (TFA, **1**) and carbon cycling reactions involving carbon monoxide (CO) and carbon dioxide (CO₂). HFCs such as 1,1,1,2-tetrafluoroethane (CF₃CFH₂), 2,3,3,3-tetrafluoropro-1-pene (CF₃CFCH₂), and 3,3,3-trifluoropro-1-pene (CF₃CHCH₂), can be oxidized by hydroxyl (OH) radicals and produce intermediates which generate TFA or trifluoromethyl (CF₃) radicals in the atmosphere.

substantially alter reaction pathways in the upper troposphere.^{19–24} Ice crystals may effectively act as natural chemical reactors, serving as reservoirs for unstable radicals, and could play a role in TFA production.^{19,25–29} These ices could house critical intermediates such as trifluoromethyl radical (CF₃) or provide a surface for multiphase chemical processing. CF₃ radicals are known to be produced from a variety of CF₃ containing compounds, such as 1,1,1,2-tetrafluoroethane,³⁰ trifluoroacetaldehyde,³¹ trifluoroacetylfluoride (CF₃C(O)F),²⁵ and trifluoromethyl sulfur pentafluoride (SF₅CF₃)²⁶ under atmospheric conditions. Thus, a mechanistic investigation of HFC degradation and CF₃ radical reactions under condensed-phase conditions is essential to resolve these discrepancies.

Here, we report on condensed-phase chemistry involving the simplest hydrofluorocarbon, trifluoromethane (CF₃H; HFC-23) and carbon dioxide (CO₂) in cryogenic ice analogs, revealing a previously unrecognized pathway to TFA formation *via* barrierless carbon–carbon recombination of the trifluoromethyl (CF₃) and hydroxycarbonyl (HOCO) radicals. Both the trifluoromethyl and hydroxycarbonyl radicals are critical atmospheric transients, providing insight into atmospheric chemical networks,^{25,27–29,31,32} with trifluoromethyl accessible *via* tropospheric degradation of, *e.g.*, CF₃CFO and CF₃CHO through photolysis or reactions with hydroxyl (OH) radicals.^{30,31,33,34} In this work, trifluoromethyl (CF₃) and hydroxycarbonyl (HOCO) radicals are produced *in situ* in cryogenic trifluoromethane–carbon dioxide (CF₃H/CO₂) model ices *via* non-equilibrium

energetic processing under ultra-high vacuum (UHV) conditions. These radicals can recombine to form TFA **1** within the condensed phase and during warm-up (SI). Supported by isotopic studies, the chemical modification of the ices and the development of functional groups were probed by a Fourier transform infrared (FTIR) spectrometer. After the processing of the ices, the samples were heated to 320 K *via* temperature-programmed desorption (TPD). During TPD, individual subliming molecules were singly ionized *via* vacuum ultraviolet (VUV) photoionization and mass resolved in a reflectron time-of-flight mass spectrometer (PI-ReToF-MS) (SI). Isomer identification was based on computed adiabatic ionization energies (IEs) along with characteristic fragment ions of TFA dimers. Collectively, these results demonstrate that condensed-phase radical chemistry in ice analogs can produce TFA **1**.

Results and discussion

Fourier transform infrared (FTIR) spectroscopy

Prior to the irradiation, the FTIR spectrum of the CF₃H/CO₂ ice (Fig. 2A) reveals vibrational modes connected to CF₃H, such as the symmetric C–F stretching mode (ν_2 ; 1206 cm^{−1}) and the degenerate asymmetric C–F stretching modes (ν_5 ; 1158 cm^{−1}), while CO₂ can be identified predominantly *via* the ν_3 asymmetric stretching mode at 2345 cm^{−1}. A comprehensive list of the vibrational assignments is compiled in Table S1.^{35–38} During the irradiation, new peaks emerge (Fig. 2B). To aid in the

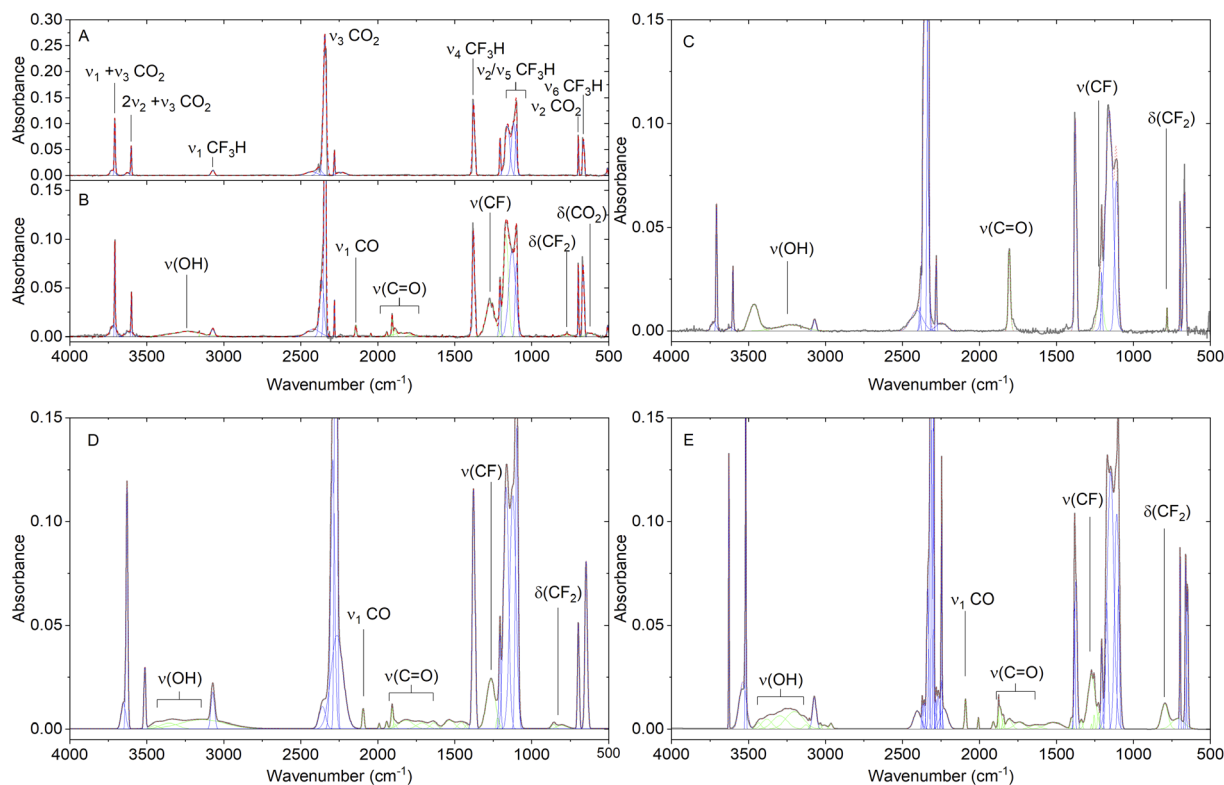


Fig. 2 Fourier transform infrared (FTIR) spectra of the $\text{CF}_3\text{H}/\text{CO}_2$ ices at 10 K (A) before irradiation and (B) after irradiation by 5 keV electrons at a current of 100 nA for 1 h. These FTIR spectra are compared with the (C) $\text{CF}_3\text{H}/\text{CO}_2/1\%$ TFA unirradiated ice, the (D) $\text{CF}_3\text{H}/^{13}\text{CO}_2$ ice after irradiation, and the (E) $\text{CF}_3\text{H}/\text{C}^{18}\text{O}_2$ ice after irradiation. The resulting spectra were deconvoluted to show vibrational absorptions of the reagents (blue), new products (green), and summed (dashed red) to fit the original spectra (gray).

identification of new functional groups, the infrared spectrum was deconvoluted (see SI). The formation of small molecules such as carbon monoxide (CO), carbon trioxide (CO_3), and carbonic difluoride (COF_2) is evident through the infrared absorptions at 2143 (ν_1), 2045 (ν_1), and 1943 cm^{-1} ($\nu(\text{C}=\text{O})$), respectively.^{39–41} Additionally, the *cis*-HOCO radical is observed *via* the prominent $\nu(\text{C}=\text{O})$ at 1797 cm^{-1} , revealing the formation of reactive radicals necessary to produce the carboxylic acid moiety within the ice (Fig. S1).^{42,43} The CF_3 radical is tentatively supported by the C–F stretching mode at 1251 cm^{-1} ; however, this band may overlap with vibrational modes such as of C–O and C–F originating from, *e.g.*, TFA and/or tetrafluoromethane (CF_4).⁴⁴ The formation of the COOH moiety⁴⁴ is supported through the detection of the C–O stretching at 1269 cm^{-1} , the C=O stretching at 1791 cm^{-1} , and the broad absorption originating from the OH stretching at 3241 cm^{-1} . A comparison of these new absorption features with an FTIR spectrum of unprocessed $\text{CF}_3\text{H}/\text{CO}_2$ ice doped with 1% TFA reveals an excellent match with pure TFA **1** (Fig. 2C and Table S2).⁴⁵ The processing of isotopically labelled $\text{CF}_3\text{H}/^{13}\text{CO}_2$ and $\text{CF}_3\text{H}/\text{C}^{18}\text{O}_2$ ices provides further support for the identification of key functional groups of TFA (Fig. 2D, E, Tables S3 and S4). The peaks associated with TFA become evident after sublimation of the reagents (CF_3H and CO_2). The spectra at 160 K detail two key vibrations that show red-shifting: C–O bond and C=O bond (Fig. S2, Tables S5 and S6). Here, in the $\text{CF}_3\text{H}/^{13}\text{CO}_2$ ice, the vibrational mode shifts from 1477 cm^{-1} to 1458 cm^{-1} (19 cm^{-1})

exactly matching the theoretical frequency red shift of 19 cm^{-1} . The $\text{CF}_3\text{H}/\text{C}^{18}\text{O}_2$ ice also shows similar shifting where the C=O vibration shifts from 1770 cm^{-1} to 1732 cm^{-1} (38 cm^{-1}) and the theoretical shift of 46 cm^{-1} . It should be noted that no shifting was observed for the C–F and O–H vibrations consistent with the behavior of unlabeled CF_3H . From quantum chemical calculations at the B3LYP/cc-pVTZ level of theory, the $\nu(\text{C}=\text{O})$ fundamental has a band strength of 4.68×10^{-17} cm per molecule.⁴⁶ Together with the experimentally integrated absorption at 1770 cm^{-1} this yields an estimated TFA **1** column density of 1.1×10^{16} molecules per cm^2 . Applying the experimentally derived band strength for the 1378 per cm CF_3H feature before and after irradiation provides the amount of CF_3H consumed, corresponding to an estimated conversion efficiency from consumed CF_3H to TFA **1** of 2.1%. Based on the incident electron fluence of 5.5×10^{14} electron per cm^2 , this corresponds to approximately 20 TFA **1** molecules per electron or 0.40 molecules per 100 eV of incident electron energy. Finally, time-dependent FTIR was exploited to monitor the development of functional groups associated with TFA **1** (Fig. S3). The absorption at 1216 cm^{-1} , associated with C–F stretching and C–O stretching, increases with a temporal profile similar to the C=O stretching at 1797 cm^{-1} , indicating a common carrier. While these data are consistent with the formation of TFA **1**, the potential overlap with chemically more complex fluorinated carboxylic acids, precludes an

unambiguous assignment. Thus, additional instrumentation is required to confirm TFA **1**.

Photon ionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS)

PI-ReToF-MS during the TPD phase of the irradiated ices to 320 K represents a unique approach for detecting gas-phase molecules isomer-selectively *via* soft photoionization based on their distinct adiabatic ionization energies (IEs) by systematically tuning the photon energies above and below the IE of the isomer(s) to be identified.^{47–52} This results in the identification of, *e.g.*, the parent ions at well-defined mass-to-charge ratios (*m/z*). Therefore, additional PI-ReToF-MS experiments were conducted exploiting

synchrotron vacuum ultraviolet (SVUV) light to selectively ionize the subliming products. In principle, the $\text{CF}_3\text{H}/\text{CO}_2$ system can lead to the formation of four structural isomers: trifluoroacetic acid (TFA, **1**, CF_3COOH) and 2,2-difluoroacetic hypofluorous anhydride (**2**, CF_2HCOOF) along with their enol-type structures 2-fluoroethene-1,1-diyl dihypofluorite (**3**, $\text{CFHC}(\text{OF})_2$), and 2,2-difluoro-1-hydroxyvinyl hypofluorite (**4**, $\text{CF}_2\text{C}(\text{OF})\text{OH}$); their IEs along with the structures are compiled in Fig. 3. The first experiment was conducted by photoionizing the subliming products at 12.10 eV, which can photoionize all isomers **1** to **4**. A successive experiment at 11.50 eV only ionizes—if present—**3** and **4**, but neither **1** nor **2**.

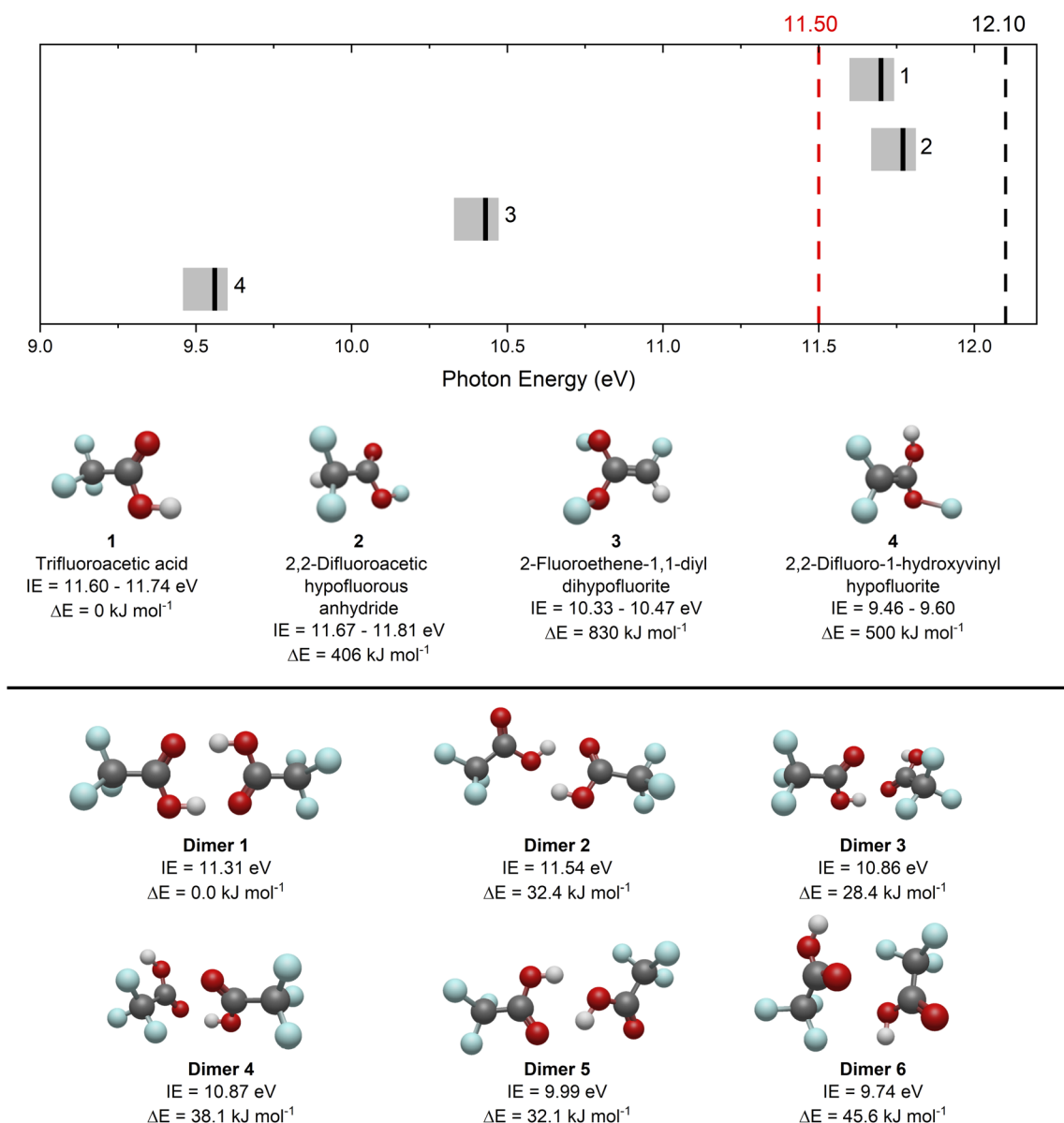


Fig. 3 The isomers of the $\text{C}_2\text{F}_3\text{O}_2\text{H}$ system with calculated relative energies (ΔE), adiabatic ionization energies (IEs, black solid line), and error ranges of the monomeric isomers (gray area) after computational error analysis and correction for the Stark effect at the CCSD(T)/VQZ-F12//B2PLYP-D3BJ/def2-TZVPP level (see Materials and methods). Two photon energies (dashed lines) were used to photoionize sublimed molecules during temperature-programmed desorption. Trifluoroacetic acid **1** dimers (**Dimer 1**–**6**) were calculated with IEs from 9.74–11.54 eV using the CCSD(T)-F12B/cc-pVDZ-F12//B2PLYP-D3BJ/def2-TZVPP level of theory.

As the $\text{CF}_3\text{H}/\text{CO}_2$ ice warms, at the 12.10 eV experiment, a sublimation event was observed at $m/z = 114$ corresponding to the $\text{C}_2\text{F}_3\text{O}_2\text{H}^+$ ion with a peak desorption temperature at 161 K (Fig. 4A). This sublimation event is not observable during the blank experiment, *i.e.* an experiment in which the non-processed $\text{CF}_3\text{H}/\text{CO}_2$ ice sublimates. This indicates that signal at $m/z = 114$ can be attributed to the non-equilibrium processing of the $\text{CF}_3\text{H}/\text{CO}_2$ ice. Recall that at this photon energy, all isomers (1–4) can be ionized. In contrast, when the photon energy was tuned to 11.50 eV, only isomers 3 and 4 are energetically accessible. Under these conditions, no signal is observed for $m/z = 114$, indicating isomer 1 and/or 2 are responsible for the sublimation event in the 12.10 eV experiment; isomers 3 and 4 are absent. Unfortunately, the ionization energies of 1 and 2 overlap within the error limits, thus hindering an identification of 1 *versus* 2.

To distinguish between isomers 1 and 2, we exploit the unique property of TFA to form hydrogen-bonded dimers in the gas phase (Fig. 3). Carboxylic acids such as acetic acid (CH_3COOH) are well-known to form hydrogen-bonded dimers.^{53–56}

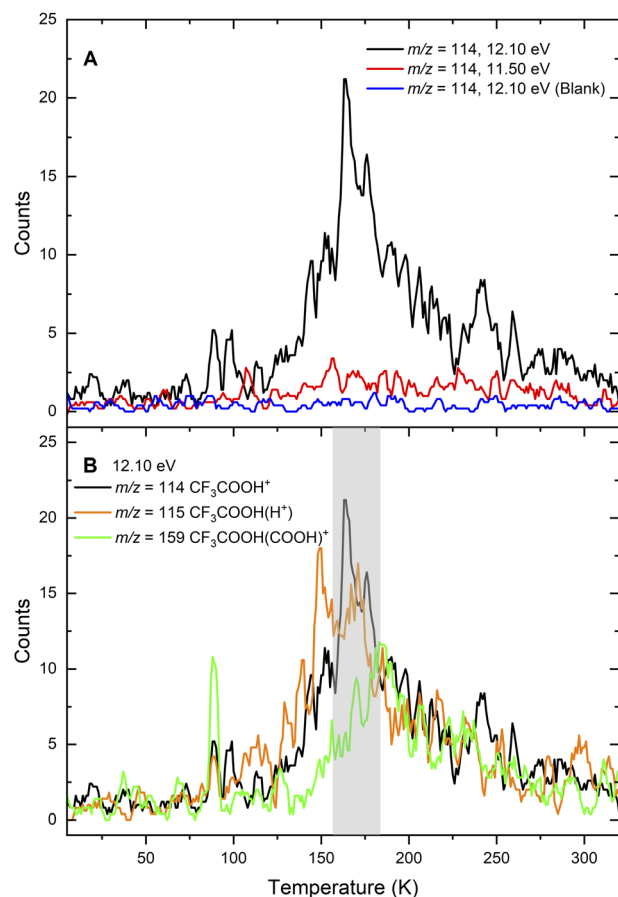
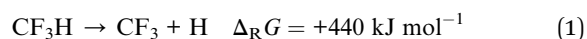


Fig. 4 PI-ReToF-MS profiles of the $\text{CF}_3\text{H}/\text{CO}_2$ ices during TPD. The irradiated $\text{CF}_3\text{H}/\text{CO}_2$ ices ((A) black and red) are compared with the non-irradiated $\text{CF}_3\text{H}/\text{CO}_2$ ices in the same mass-to-charge ratio (m/z) ((A) blue). The masses associated with TFA ((B) black), $\text{CF}_3\text{COOH}(\text{H})^+$ ((B) orange, $m/z = 115$), and $\text{CF}_3\text{COOH}(\text{COOH})^+$ ((B) green, $m/z = 159$) were found utilizing 12.10 eV photons. The gray area marks overlapping signal correlating to co-sublimation of TFA and dimeric TFA (Dimers 1–6) fragments.

Upon photoionization, this results in the formation of characteristic fragment ions, including protonated monomers ($(\text{CH}_3\text{COOH})\text{H}^+$) and ions retaining the hydrogen-bonded acidic moiety ($(\text{CH}_3\text{COOH})\text{COOH}^+$)^{53–56} (Fig. 5). Due to the lack of an acetic proton in 2, only TFA 1 can form hydrogen-bonded dimers in the gas phase, but not 2.^{57,58} The TFA dimers produce protonated TFA 1 ($(\text{CF}_3\text{COOH})\text{H}^+$; $m/z = 115$) and the corresponding carboxylic acid fragment ($(\text{CF}_3\text{COOH})\text{COOH}^+$; $m/z = 159$) upon ionization and dissociation (Fig. 5). Consistent with this assignment, at 12.10 eV, sublimation events are also observed at 161 K with overlapping TPD profiles at $m/z = 115$ and $m/z = 159$, indicative of sublimation and fragmentation of TFA dimers upon photoionization (Fig. 4B). Although naturally occurring $^{13}\text{C}_1$ -TFA (1%) contributes to $m/z = 115$, the $m/z = 115$ signal reaches 83% of the TFA 1 ($m/z = 114$) and therefore cannot be explained by natural ^{13}C abundance alone. Taken together, we can conclude that at least TFA along with its dimer is observed thus strengthening the assignments of TFA 1 based on FTIR and QMS data.

The present $\text{CF}_3\text{H}/\text{CO}_2$ ice provides a simplified model to isolate elementary radical chemistry as a necessary step toward understanding complex bulk compositions contained within atmospheric cloud particles. Indeed, atmospheric condensed phases are dominated by H_2O and are subjected to additional species such as O_2 , NO , and other reactive constituents. These species inherently affect the reaction branching within ices or particulates; however, these results provide more targeted insight into radical production and product formation. In particular, they provide direct access to the CF_3 and HOCO radicals as a way to probe their interaction within ices. Importantly, CO_2 can interact and become trapped at water-ice surfaces,^{59,60} while fluorocarbon species like CF_3 generated in the gas-phase can transiently interact with ice surfaces.⁶¹

Since isomer 1 (TFA) is identified, we next consider possible mechanistic pathways responsible for its formation. Mechanistic insight is derived from the identification of reactive intermediates in the FTIR spectra, products observed in the mass spectra, and established principles of non-equilibrium cryogenic ice chemistry. Given the complexity of the chemistry occurring in irradiated ices, this pathway may represent only one of several possible reaction channels and is proposed here as a plausible mechanism based on the experimentally observed intermediates. Following deposition, the $\text{CF}_3\text{H}/\text{CO}_2$ ice is irradiated with energetic electrons, which can induce bond cleavage in CF_3H to generate the CF_3 radical and atomic hydrogen (Reaction (1)).



Reaction (1) is highly endoergic and cannot proceed thermally at 5–10 K. CF_3 formation is inferred from the expected C–H bond cleavage of CF_3H induced by irradiation while spectroscopically is only tentatively supported by FTIR because its absorption overlaps with other C–F vibrational modes. However, electron irradiation deposits excess energy into the ice matrix, producing suprathermal hydrogen atoms capable of

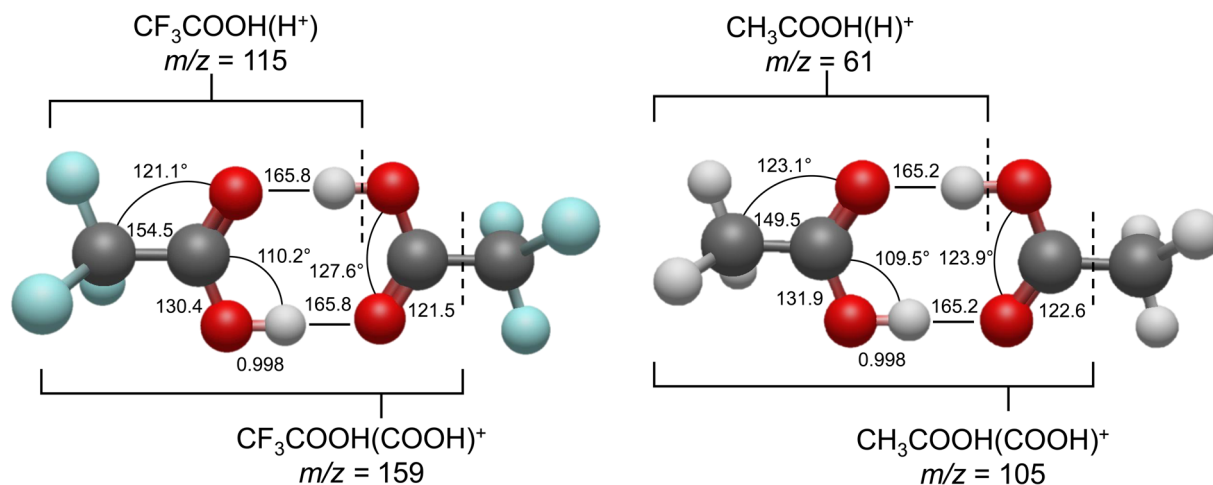
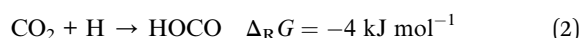
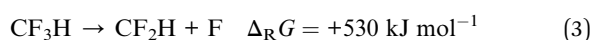


Fig. 5 Calculated geometry of Dimer 1 (left) compared with Socha and Dračinský⁵³ geometry of acetic acid dimer (right) calculated at the MP2/aug-cc-pVQZ level of theory. The dashed lines represent bond cleavage toward characteristic fragments observed for acetic acid and predicted for TFA dimers. Bond lengths are in picometers.

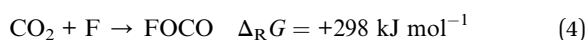
overcoming reaction barriers.^{62–65} These energetic hydrogen atoms can add to CO₂ to form the HOCO radical (Reaction (2)).



The process of forming the HOCO radical is observed in the ice. Time-dependent FTIR spectra (Fig. S4) reveal the rapid formation and destruction of HOCO, which is well fit by the consecutive reaction sequence following Reaction (2) and HOCO destruction towards products. In contrast, reaction pathways involving fluorine atom production and subsequent reactions with CO₂ are strongly suppressed in the ice. Although CF₃H can undergo C–F bond cleavage to yield CF₂H and F atoms (Reaction (3)), based on calculations at the CCSD(T)-F12B/VQZ-F12 level of theory, this reaction is more endoergic than Reaction (1) (Fig. S5 and Reaction (3)).



Further, calculations here show the addition of atomic fluorine to CO₂ to form the fluoroformyloxy radical (FOCO) is strongly endoergic and associated with a large barrier (+305 kJ mol^{−1}) (Reaction (4) and Fig. S6).



This endoergic and the associated barrier of Reaction (4) render fluorine-initiated CO₂ chemistry much less competitive relative to hydrogen addition (Reaction (2)). Once formed, neighboring CF₃ and HOCO radicals can undergo barrierless radical–radical recombination on the singlet-coupled surface forming TFA(CF₃COOH, **1**; Reaction (5)), which is exoergic by 385 to 393 kJ mol^{−1} depending on the configuration of the HOCO radical.^{66–68}



Upon formation, TFA **1** can be stabilized by the surrounding ice matrix. This stepwise radical-mediated pathway involving

CF₃ and HOCO represents a condensed or multiphase mechanism for TFA **1** production. In atmospheric contexts, such chemistry could occur within ice particles and aerosols in the upper troposphere and lower stratosphere, initiated by ultraviolet photons. Although cryogenic ices are employed here as a proof of concept to isolate radical processes, particulate-phase TFA **1** is well documented, suggesting atmospheric aerosols and cloud particles could provide the condensed-phase environment necessary to stabilize the recombination forming TFA **1** (Reaction (5)).¹

In the absence of condensed-phase stabilization, gas-phase formation of TFA **1** *via* CF₃ and HOCO would require efficient third-body stabilization. In this case, the lifetime of the CF₃–HOCO entrance complex becomes critical. The analogous CH₃–HOCO complex is predicted to be relatively long-lived, with an estimated lifetime of 4500 picoseconds, indicating that collisional stabilization in the gas phase may be feasible under atmospheric conditions.^{27,69,70} This suggests that both condensed-phase and gas-phase third-body assisted pathways may contribute to TFA **1** formation.¹⁹

Although this work outlines decomposition of CF₃H as a primary role in formation of TFA **1**, the production of the CF₃ radical is readily known in reaction networks to derive from intermediate species such as CF₃CHO, CF₃CFO and CF₃CFHO, with CF₃CHO decomposition alone proceeding predominantly (>80%) towards CF₃.^{14,30,31,33,34} Reasonably, these reactions could begin by the photolysis of CF₃CHO (Reaction (6)) or CF₃CFO (Reaction (7)) or CF₃CFHO (Reaction (8)), and continue with recombination with the HOCO radical (Reaction (5)).



Overall, these experiments demonstrate that trifluoroacetic acid (TFA **1**) can form in cryogenic condensed phase ices *via*

a pathway consistent with barrierless radical–radical recombination between CF_3 and HOCO . In the context of atmospheric chemistry, this pathway provides a potential multiphase mechanism linking hydrofluorocarbon degradation to persistent PFAS formation. Ultimately, this work identifies a previously overlooked link between short-lived fluorocarbon oxidation intermediates and TFA 1, providing mechanistic and quantitative benchmarks for future investigations of atmospheric fluorine chemistry and persistent PFAS formation.

Conclusions

These findings expand the reactive landscape governing fluorocarbon degradation by introducing a condensed- and multiphase-accessible route to TFA 1. Incorporation of the radical–radical recombination of CF_3 and HOCO into atmospheric models could help reconcile discrepancies between observed and predicted TFA 1 abundances, while highlighting the potential importance of radical multiphase chemistry occurring on or within aerosols and cloud particulates. Ultimately, this work identifies a previously overlooked link between short-lived fluorocarbon oxidation intermediates and TFA 1, with implications for atmospheric fluorine budgets, carbon cycling, and assessments of persistent PFAS formation.^{2–4,32,35,71,72}

Author contributions

Conceptualization: R. I. K. Methodology: R. I. K., R. S., T. Y. Investigation: M. M., K. M., Y. L., N. W. M., P. C., X. B., J. L., B. S., X. W., A. B. Visualization: M. M., K. M., S. B. Supervision: R. I. K., A. M. T. Writing – original draft: M. M., K. M. Writing – review & editing: R. I. K., M. M., K. M., Y. L., X. B., A. M. T., S. B., R. S., T. Y.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data generated in this research are provided in the article and supplementary information (SI) and are available upon request from the corresponding author(s). Source data are provided with this paper. Supplementary information is available. See DOI: <https://doi.org/10.1039/d6sc05084k>.

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