



RESEARCH LETTER

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Key Points:

- CF₄ was measured as a primary photolysis product of CF₃C(O)F
- CF₃C(O)F is a degradation product of halocarbons currently in the atmosphere
- Model calculations find photochemical production minor compared to industrial emissions

Supporting Information:

- Tables S1 and S2 and Figures S1–S9

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An atmospheric photochemical source of the persistent greenhouse gas CF₄

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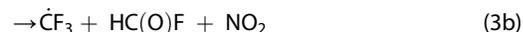
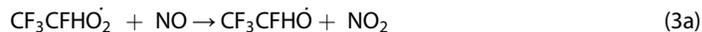
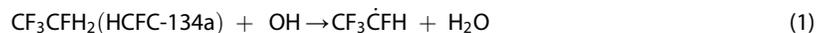
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Abstract A previously uncharacterized atmospheric source of the persistent greenhouse gas tetrafluoromethane, CF₄, has been identified in the UV photolysis of trifluoroacetyl fluoride, CF₃C(O)F, which is a degradation product of several halocarbons currently present in the atmosphere. CF₄ quantum yields in the photolysis of CF₃C(O)F were measured at 193, 214, 228, and 248 nm, wavelengths relevant to stratospheric photolysis, to be $(75.3 \pm 1) \times 10^{-4}$, $(23.7 \pm 0.4) \times 10^{-4}$, $(6.6 \pm 0.2) \times 10^{-4}$, and $\leq 0.4 \times 10^{-4}$, respectively. A 2-D atmospheric model was used to estimate the contribution of the photochemical source to the global CF₄ budget. The atmospheric photochemical production of CF₄ from CF₃CH₂F (HFC-134a), CF₃CHFCl (HCFC-124), and CF₃CCl₂F (CFC-114a) per molecule emitted was calculated to be $(1-2.5) \times 10^{-5}$, 1.0×10^{-4} , and 2.8×10^{-3} , respectively. Although CF₄ photochemical production was found to be relatively minor at the present time, the identified mechanism demonstrates that long-lived products with potential climate impacts can be formed from the atmospheric breakdown of shorter-lived source gases.

1. Introduction

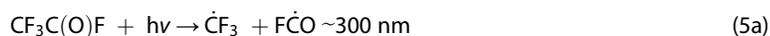
Atmospheric CF₄ and its sources are a concern because of its atmospheric persistence, with an atmospheric lifetime estimated to be 50,000 years, and significant global warming potential of ~6600 on a 100 year time horizon [World Meteorological Organization (WMO), 2014]. That is, CF₄ is an extremely potent and effectively permanent greenhouse gas [Forster et al., 2007; Intergovernmental Panel on Climate Change, 2013; WMO, 2014] that has no significant atmospheric loss process [Ravishankara et al., 1994]. At present, sources of CF₄ are predominantly anthropogenic with the majority of fugitive emissions being associated with aluminum production [Marks et al., 2003; Mühle et al., 2010]. A lesser source of atmospheric CF₄ is via its use, among other perfluorinated compounds, as a plasma etchant [Mühle et al., 2010; WMO, 2014]. CF₄ falls under the directive of the Kyoto protocol, of which a principal aim as stated in Article 2 of the United Nations Framework Convention on Climate Change is to “achieve ... stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system.” As a result, emissions and the atmospheric abundance of CF₄ are under scrutiny.

In this study, the UV photolysis of trifluoroacetyl fluoride, CF₃C(O)F, was examined as a potential atmospheric photochemical source of CF₄. CF₃C(O)F is an atmospheric degradation product of widely used refrigerant halocarbons, e.g., CF₃CFH₂ (HFC-134a), CF₃CFHCl (HCFC-124), CF₃CFCl₂ (CFC-114a), CF₃CFHCF₃ (HFC-227ea), and CF₃CF=CH₂ (HFO-1234yf) [Burkholder et al., 2015]. In the atmosphere, the degradation of hydrofluorocarbons (HFCs) and hydrofluorochlorocarbons (HCFCs) is initiated predominantly by gas-phase reaction with the OH radical, where the haloalkyl radical products formed in the reaction lead to the rapid formation of CF₃C(O)F, i.e., CF₃C(O)F is formed in the same atmospheric region as the precursor removal, e.g., for HCFC-134a



As noted above, other halocarbons containing the $\text{CF}_3\text{CF-}$ moiety are also capable of leading to the formation of $\text{CF}_3\text{C(O)F}$. For chlorofluorocarbons (CFCs), the initial degradation step involves UV photolysis rather than OH reaction, and $\text{CF}_3\text{C(O)F}$ is formed via the subsequent unimolecular elimination of Cl, e.g., for CFC-114a, $\text{CF}_3\text{CFCIO} \rightarrow \text{CF}_3\text{C(O)F} + \text{Cl}$ [Burkholder *et al.*, 2015].

The region of the atmosphere where $\text{CF}_3\text{C(O)F}$ is formed will influence its degradation and end-product yields, i.e., the potential formation of CF_4 . In the stratosphere, $\text{CF}_3\text{C(O)F}$ is expected to be removed primarily by short-wavelength UV photolysis [Weibel *et al.*, 1992; Bierbrauer *et al.*, 1999; Sander *et al.*, 2011]:



where the photodissociation thresholds at 298 K were calculated using the heats of formation from Sander *et al.* [2011]. In the troposphere, $\text{CF}_3\text{C(O)F}$ will hydrolyze within weeks and produce trifluoroacetic acid, $\text{CF}_3\text{C(O)OH}$, a persistent pollutant [Henne *et al.*, 2012; WMO, 2014; Burkholder *et al.*, 2015].

In the following sections, (1) experimental determinations of the CF_4 quantum yield, $\Phi_{\text{CF}_4}(\lambda)$, in the UV photolysis of $\text{CF}_3\text{C(O)F}$, channel (5d), at 193, 214, 228, and 248 nm are reported and (2) a 2-D atmospheric model was used to calculate the production and distribution of $\text{CF}_3\text{C(O)F}$ from HFC-134a, HCFC-124, and CFC-114a and the subsequent photochemical production of CF_4 using the $\Phi_{\text{CF}_4}(\lambda)$ determined in this work. The contribution of this photochemical source to the global CF_4 budget is discussed within the framework of continued and increased use of HCFCs and HFCs.

2. Experimental Details

The CF_4 quantum yield in the photolysis of $\text{CF}_3\text{C(O)F}$ at four discrete wavelengths, spanning the region most relevant for its stratospheric photolysis, was determined by monitoring the loss of $\text{CF}_3\text{C(O)F}$ and the production of CF_4 by Fourier transform infrared spectroscopy (FTIR) in a closed reaction system. $\Phi_{\text{CF}_4}(\lambda)$ was determined from the slope of a least squares linear regression fit to $[\text{CF}_4]_t$ versus $\Delta[\text{CF}_3\text{C(O)F}]_t$. The experimental methods and procedures used in this work are described briefly below.

The experimental apparatus consisted of a photolysis reactor that was coupled to an absorption cell of a Fourier transform infrared spectrometer (FTIR) for the simultaneous monitoring of reactant loss and product formation, see schematics of the different experimental setups used in this study in Figures S1–S3 in the supporting information and McGillen and Burkholder [2015] for additional detail. $\text{CF}_3\text{C(O)F}$ was introduced into the reactor along with the bath gas (N_2 or He) and, in most cases, a radical scavenger (either Br_2 or O_2). The well-mixed sample was exposed to the photolysis light source over a series of discrete time intervals with infrared spectra recorded following each interval. The infrared spectra were analyzed using standard reference spectra. Photolysis at 193 nm (ArF) and 248 nm (KrF) was performed using the output of a pulsed excimer laser (5–10 Hz and $(0.02\text{--}1.1) \times 10^{16}$ photon cm^{-2} pulse $^{-1}$ for 193 nm; 10 Hz and $(1.8\text{--}2.6) \times 10^{16}$ photon cm^{-2} pulse $^{-1}$ for 248 nm). For photolysis at 214 and 228 nm, atomic lamps (Zn and Cd) were used with setups shown in Figures S2 and S3. A minimum of six photolysis steps were performed per experiment to obtain a precise measurement of $[\text{CF}_4]_t$ versus $\Delta[\text{CF}_3\text{C(O)F}]_t$. Pressure, bath gas, initial $\text{CF}_3\text{C(O)F}$ concentration, radical scavenger concentration, surface-to-volume ratio, photolysis volume, and photon flux were varied over the course of the measurements. Experiments were also conducted in the presence and absence of a radical scavenger and under circulating and static conditions (see Table S1 in the supporting information for a summary of the experimental conditions). Additional test experiments were conducted where CF_3Br was photolyzed or CF_3I was added to the mixture. On the basis of the test measurements, it was concluded that CF_4 was produced only through a primary photolysis process with no measurable contributions from secondary or wall reactions. $\text{CF}_3\text{C(O)F}$ (99%), CF_3Br (99%), CF_3I (99%), O_2 (UHP), He (UHP), and N_2 (99.9998%) were used as received. Br_2 was degassed prior to use.

3. Results and Discussion

A summary of the experimental data obtained at the four photolysis wavelengths is shown in Figure 1. Independent experiments at each photolysis wavelength yielded consistent results to within the precision

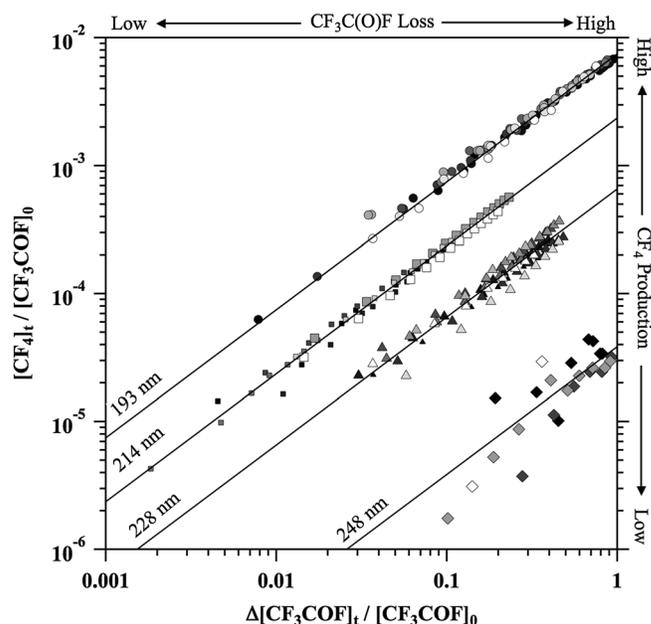


Figure 1. CF_4 formed from the photolysis of $\text{CF}_3\text{C}(\text{O})\text{F}$ at 193 (circles), 214 (squares), 228 (triangles), and 248 nm (diamonds) versus change in $\text{CF}_3\text{C}(\text{O})\text{F}$ concentration normalized by the initial $\text{CF}_3\text{C}(\text{O})\text{F}$ concentration. Shaded markers indicate results obtained in independent experiments. Smaller markers correspond to experiments where $[\text{CF}_3\text{Br}]$ was used as a proxy for $\Delta[\text{CF}_3\text{C}(\text{O})\text{F}]$. Solid lines are least squares fits to the combined data set where the slope is equal to $\Phi_{\text{CF}_4}(\lambda)$.

spectrum of $\text{CF}_3\text{C}(\text{O})\text{F}$ in Figure 2. The 2σ precision of $\Phi_{\text{CF}_4}(\lambda)$ ranged from $\pm 1.3\%$ at 193 nm to $\pm 3\%$ at 228 nm. The CF_4 and $\text{CF}_3\text{C}(\text{O})\text{F}$ reference absorption spectra used in the infrared spectral subtractions have estimated uncertainties of $\pm 3\%$ and $\pm 1.4\%$, respectively [Papadimitriou et al., 2011; Pacific Northwest National Laboratory, 2013], and the precision of the spectral subtraction was estimated to be $\pm 2\%$. The experimental conditions at each photolysis wavelength were varied (see Table S1) to test for possible systematic experimental errors and secondary sources of CF_4 formation. On the basis of the combined uncertainties the absolute (2σ) uncertainty in $\Phi_{\text{CF}_4}(\lambda)$ is estimated to be $\sim 4\%$ at 193 nm, $\sim 7\%$ at 214 nm, and $\sim 16\%$ at 228 nm.

Overall, the CF_4 quantum yields for $\text{CF}_3\text{C}(\text{O})\text{F}$ photolysis at stratospherically relevant wavelengths, < 220 nm, are small with the greatest value of $(75 \pm 1) \times 10^{-4}$ obtained at 193 nm. The atmospheric impact of the photochemical production of CF_4 is evaluated in the next section.

4. Atmospheric Implications

The NOCAR 2-D model [Portmann and Solomon, 2007] was used to evaluate the altitude dependence and global photochemical production of CF_4 in the atmospheric degradation of HFC-134a, HCFC-124, and CFC-114a. At current atmospheric levels, these compounds are expected to be the primary precursors of atmospheric

Table 1. CF_4 Quantum Yields, $\Phi_{\text{CF}_4}(\lambda)$, in the Photolysis of $\text{CF}_3\text{C}(\text{O})\text{F}$ Determined in This Work

Wavelength (nm)	$\Phi_{\text{CF}_4}(\lambda) (10^{-4} \pm 2\sigma)^a$
193	75.3 ± 1
214	23.7 ± 0.4
228	6.6 ± 0.2
248	< 0.4

^aStated errors correspond to the 2σ measurement precision.

of the measurement. No dependence of Φ_{CF_4} was observed with variation of the initial $\text{CF}_3\text{C}(\text{O})\text{F}$ concentration, radical scavenger identity, radical scavenger concentration, photon flux, or surface-to-volume ratio for each of the four photolysis wavelengths tested (see Table S1). A weak negative pressure dependence in $\Phi_{\text{CF}_4}(\lambda)$ of 6 to 15% at 214 and 228 nm was observed between 50 and 650 torr. Further studies are needed to identify and quantify the mechanism of this minor effect.

In the final data analysis for each photolysis wavelength, a linear least squares fit of all experimental data was used to obtain the CF_4 quantum yield, $\Phi_{\text{CF}_4}(\lambda)$. The final values are given in Table 1 where the stated uncertainty is the 2σ precision of the fits. $\Phi_{\text{CF}_4}(\lambda)$ decreased with increasing photolysis wavelength. Due to the greater scatter at 248 nm, we prefer to report an upper limit of $< 0.4 \times 10^{-4}$ for $\Phi_{\text{CF}_4}(248 \text{ nm})$. The $\Phi_{\text{CF}_4}(\lambda)$ values obtained in this work are plotted along with the UV absorption

of $\text{CF}_3\text{C}(\text{O})\text{F}$, whose short-wavelength UV photolysis leads to a photochemical source of CF_4 . An evaluation of the photochemical production of CF_4 requires modeling the precursor compounds' atmospheric abundance, atmospheric distribution, loss processes and regions of loss, and the $\text{CF}_3\text{C}(\text{O})\text{F}$ yield in its degradation. The $\text{CF}_3\text{C}(\text{O})\text{F}$ distribution must be calculated as well using its

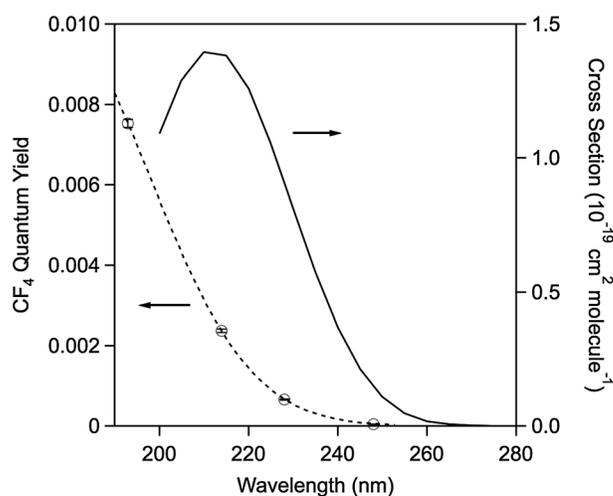


Figure 2. CF_4 quantum yields, $\Phi_{\text{CF}_4}(\lambda)$, in the photolysis of $\text{CF}_3\text{C}(\text{O})\text{F}$ obtained in this work at 193, 214, 228, and 248 nm (symbols) at 296 K. The error bars are 2σ measurement precision. The Gaussian fit of $\Phi_{\text{CF}_4}(\lambda)$ (dashed line) was used in the 2-D model calculations and is given by $\Phi_{\text{CF}_4}(\lambda) = A \exp\left(-\left(\frac{\lambda-\lambda_0}{w}\right)^2\right)$ where $A = 0.0102$, $\lambda_0 = 175.4$ nm, and $w = 31.8$ nm. The 296 K UV absorption spectrum of $\text{CF}_3\text{C}(\text{O})\text{F}$ (solid line) [Sander *et al.*, 2011] is included for perspective.

spheric abundance compared to HCFC-124 and CFC-114a [WMO, 2014] and represents the current primary source of photolytically produced CF_4 .

The $\Phi_{\text{CF}_4}(\lambda)$ results obtained at 193, 214, 228, and 248 nm in this work were fit with a Gaussian expression, as shown in Figure 2, to yield continuous values of $\Phi_{\text{CF}_4}(\lambda)$ across the 190–250 nm wavelength region for use in the 2-D model calculations.

The photodissociation of $\text{CF}_3\text{C}(\text{O})\text{F}$ is strictly a stratospheric loss process because, as shown in Figure 2, $\text{CF}_3\text{C}(\text{O})\text{F}$ has negligible absorption at wavelengths greater than 290 nm. $\text{CF}_3\text{C}(\text{O})\text{F}$ produced in the troposphere will be removed by wet deposition (rainout) and does not lead to the formation of CF_4 . In the 2-D model, a 4 day rain-out rate was used, while the results are not sensitive to the actual rate used. In the stratosphere, the photolysis rate coefficient (J value) for $\text{CF}_3\text{C}(\text{O})\text{F}$ displays an altitude dependence as shown in Figure 3. In the lower stratosphere, the $\text{CF}_3\text{C}(\text{O})\text{F}$ photolysis lifetime is sufficiently long, on the order of years, that transport out of this region is an important removal process that is accounted for in our atmospheric model. The photochemical production of CF_4 will be similar to the $\text{CF}_3\text{C}(\text{O})\text{F}$ photolysis profile. Figure 3 also shows the altitude dependence of the CF_4 yield in the photolysis of $\text{CF}_3\text{C}(\text{O})\text{F}$. The yield decreases with increasing altitude as longer wavelengths, which do not produce CF_4 , contribute more to the total photolysis rate of $\text{CF}_3\text{C}(\text{O})\text{F}$.

The modeled annually averaged production rates of $\text{CF}_3\text{C}(\text{O})\text{F}$ from the atmospheric degradation of HFC-134a, HCFC-124, and CFC-114a were obtained using a 100% $\text{CF}_3\text{C}(\text{O})\text{F}$ yield for HCFC-124 and CFC-114a following degradation and a maximum yield of 20% for HFC-134a degradation, as taken from Wallington *et al.* [1996]. A summary of the model results is given in Table 2 and presented graphically in Figures S4–S9 in the supporting information. For HFC-134a, the CF_4 production per molecule of HFC-134a emitted into the atmosphere was 2.5×10^{-5} molecules. For HCFC-124 and CFC-114a, the CF_4 production per molecule of source gas are 1.0×10^{-4} and 2.8×10^{-3} molecules, respectively. CFC-114a has the greatest per molecule CF_4 production of the three halocarbons modeled due to the sole sink for CFC-114a being stratospheric photolysis. The reaction of CFC-114a with $\text{O}(^1\text{D})$ in the stratosphere is a minor loss process but would also lead to the formation of $\text{CF}_3\text{C}(\text{O})\text{F}$. Thus, the majority of CFC-114a molecules that are lost produce a $\text{CF}_3\text{C}(\text{O})\text{F}$ molecule at altitudes where photolytic CF_4 production occurs.

Using the CF_4 production from the halocarbons and the historical and future emission scenario (RCP4.5) estimates for their emission [O'Doherty *et al.*, 2004; Forster *et al.*, 2007; Mühle *et al.*, 2010], the photolytic

production, loss, and dynamical transport. This allows the altitude dependence of CF_4 production in the degradation of $\text{CF}_3\text{C}(\text{O})\text{F}$ to be estimated in the model.

The atmospheric abundance, lifetimes, and the $\text{CF}_3\text{C}(\text{O})\text{F}$ yields in the degradation of these source gases are given in Table S2. HFC-134a and HCFC-124 are removed by reaction with the OH radical, predominantly in the troposphere, in addition to photolysis in the stratosphere. Therefore, only a fraction of HFC-134a and HCFC-124 released into the atmosphere at the surface is removed in the stratosphere at altitudes where short-wavelength UV photolysis of $\text{CF}_3\text{C}(\text{O})\text{F}$ is an important loss process. CFC-114a, on the other hand, is removed almost exclusively in the stratosphere by short-wavelength UV photolysis since it has no significant tropospheric loss process. Even so, HFC-134a has a much greater atmo-

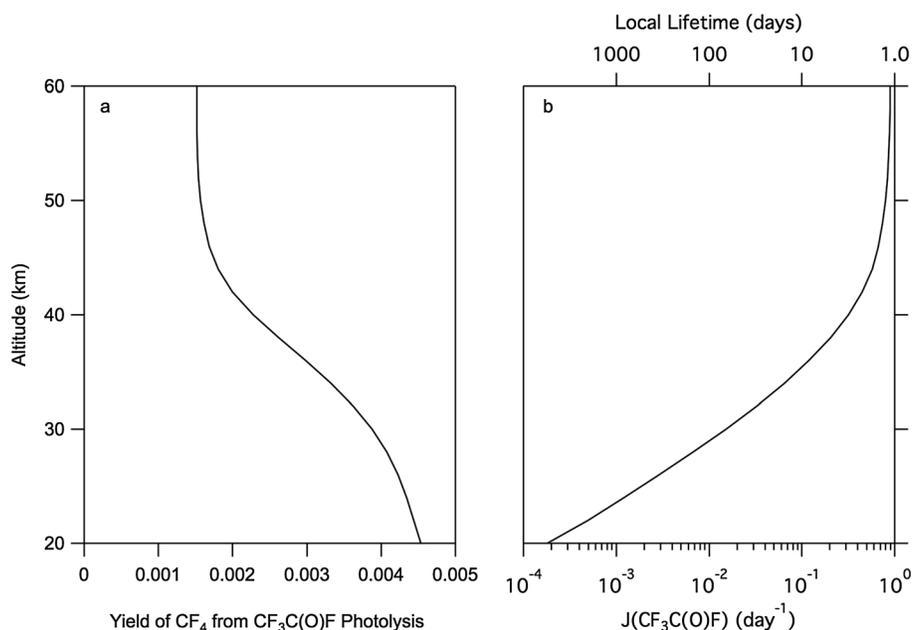


Figure 3. The NOCAR 2-D model calculated altitude dependence of (a) the CF₄ yield in the photolysis of CF₃C(O)F, (b) the CF₃C(O)F photolysis rate coefficient, J , and local lifetime. Both are annual averages calculated at the equator.

production of CF₄ per year was determined. Of these three halocarbons, HFC-134a is found to be the greatest photochemical source of CF₄ due to its much higher current and predicted atmospheric abundance. HCFC-124 and CFC-114a are presently at low levels, and their atmospheric abundance is not expected to increase in the future. As shown in Figure 4, CF₄ produced via CF₃C(O)F photolysis due to HFC-134a degradation is expected to increase in the future to $\sim 9 \text{ t yr}^{-1}$ by the year 2100. This photochemical CF₄ production is currently minor and is expected to remain a minor fraction relative to the direct emissions of CF₄ to the atmosphere, which are currently $\sim 11 \text{ kt yr}^{-1}$ [Möhle *et al.*, 2010].

5. Conclusions

Once emitted into or formed in the atmosphere, CF₄, a potent greenhouse gas, essentially remains there permanently [Möhle *et al.*, 2010; WMO, 2014]. In this study, the production of CF₄ from the short-wavelength UV photolysis of CF₃C(O)F, which is a degradation product of several halocarbons presently in the atmosphere, was measured at 193, 214, 228, and 248 nm. The CF₄ quantum yield, $\Phi_{\text{CF}_4}(\lambda)$, was found to be wavelength dependent over the critical wavelength range for atmospheric photolysis, with the greatest, albeit small, quantum yield of $(75.3 \pm 1) \times 10^{-4}$ observed at the shortest wavelength, 193 nm. Two-dimensional atmospheric model calculations were used to estimate the photochemical production of CF₄ from the emission and atmospheric degradation of HFC-134a, HCFC-124, and CFC-114a. The photochemical production of CF₄ was in the range $(1\text{--}2.5) \times 10^{-5}$ per molecule emitted into the atmosphere for HFC-134a. The range is due to the uncertainty in the CF₃C(O)F yield in the atmospheric degradation of HFC-134a. HFC-134a was determined to be the greatest halocarbon photochemical source of CF₄ due to its high emission level. The

Table 2. Summary of 2-D Model Results for the Production and Loss Processes for CF₃C(O)F and the CF₄ Production, All in %

Species	CF ₃ C(O)F	CF ₃ C(O)F Loss		CF ₄
	Production	Photolysis	Rainout ^a	Production
HFC-134a	20	4.5	95.5	0.0025
CFC-124	100	3.8	96.2	0.010
CFC-114a	100	90.6	9.4	0.28

^aBased on a 4 day rainout rate in the troposphere.

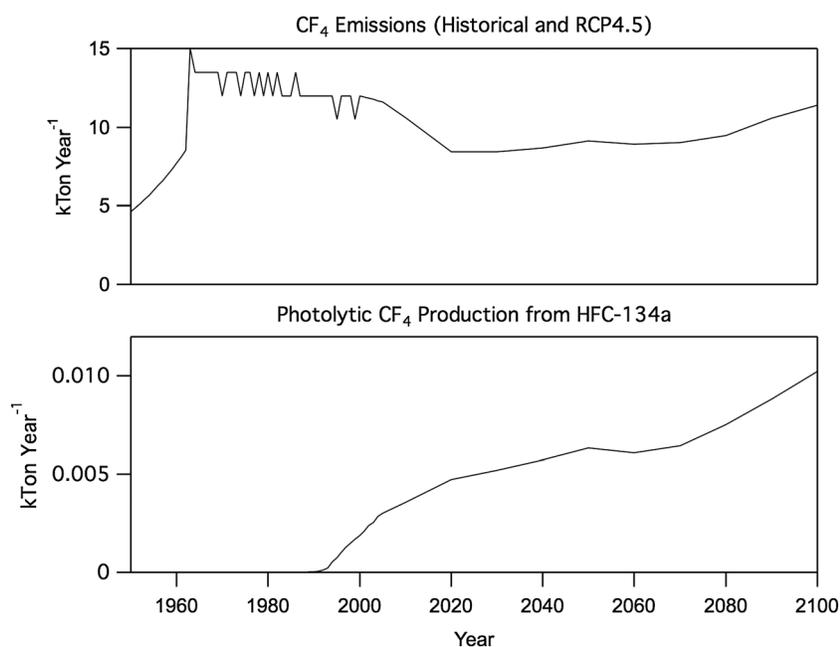


Figure 4. Photochemical production of CF_4 calculated using the NOCAR 2-D model, $\Phi_{\text{CF}_4}(\lambda)$ values from this work, and HFC-134a emissions from the RCP4.5 scenario. Note that the production of CF_4 would occur over the lifetime of HFC-134a (~13 years) but is shown in the year of emission. Historical and projected industrial emissions are included in the top panel for comparison.

total photochemical production of CF_4 was estimated to be ~9 t per year in year 2100. This CF_4 photochemical production is minor compared to the direct anthropogenic emissions. It, however, represents a previously uncharacterized source of CF_4 to the atmosphere. Considering the current and projected increase of halocarbon replacement compound use it was important to quantify this photochemical CF_4 source. It is rather unusual for first-generation end-products to be formed that are much longer lived and stable than the source compound, but this study provides an important example of this occurring. This study also illustrates that the stable end-products formed in the atmospheric degradation of halocarbon replacement compounds requires thorough study to characterize the potential production of environmentally harmful products.

Acknowledgments

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