$CFCl_3$ (CFC-11): UV absorption spectrum temperature dependence measurements and the impact on atmospheric lifetime and uncertainty

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Key Points:
* Uncertainty in the CFC-11 photolysis lifetime was reduced from ~25 to 4%
* Previous recommendations overestimated the T-dependence of the UV spectrum
* The lifetime and GWP of CFC-11 are less than previously reported

$CFCl_3$ (CFC-11) is both an atmospheric ozone-depleting and potent greenhouse gas that is removed primarily via stratospheric UV photolysis. Uncertainty in the temperature dependence of its UV absorption spectrum is a significant contributing factor to the overall uncertainty in its global lifetime and, thus, model calculations of stratospheric ozone recovery and climate change. In this work, the CFC-11 UV absorption spectrum was measured over a range of wavelength (184.95–230 nm) and temperature (216–296 K). We report a spectrum temperature dependence that is less than currently recommended for use in atmospheric models. The impact on its atmospheric lifetime was quantified using a 2-D model and the spectrum parameterization developed in this work. The calculated global annually averaged lifetime was 58.1 ± 0.7 years (2σ uncertainty due solely to the spectrum uncertainty). The lifetime is slightly reduced and the uncertainty significantly reduced from that obtained using current spectrum recommendations.

Key Words: Ozone depleting substance, chlorofluorocarbon, photolysis, UV cross section

1. Introduction

Accurate knowledge of the atmospheric lifetimes of ozone depleting substances (ODSs) is important to the understanding of their atmospheric abundance, emissions, and future environmental impacts as well as the calculation of ozone depleting (ODPs) and global warming potentials (GWPs). $CFCl_3$ (CFC-11) is a key long-lived man-made ODS that is also a potent greenhouse gas (GHG) [*WMO*, 2011] whose production was phased out under the Montreal Protocol and its subsequent amendments. CFC-11 is of particular importance due to its atmospheric abundance and the fact that it is the reference substance to which ODPs for all other ODSs are scaled. The atmospheric abundance of CFC-11 is presently decreasing [*WMO*, 2011] from a maximum mixing ratio of ~270 ppt in the early 1990s to a present day value of ~240 ppt; CFC-11 accounts for 22% of the present day stratospheric chlorine. CFC-11 is primarily removed in the stratosphere by UV photolysis at wavelengths between 190 and 230 nm and to a lesser extent by gas-phase reaction with $O(^1D)$ atoms.

The room temperature UV absorption spectrum, $\sigma(\lambda,298\ K)$, of CFC-11 is reasonably well established, ±5%, over the wavelength range most critical to atmospheric photolysis (see *Sander et al.* [2011] and references therein). However, the spectrum temperature dependence, which is key to determining its stratospheric photolysis rate, is less certain and the level of uncertainty contributes substantially to the uncertainty in determining the global lifetime of CFC-11 [*SPARC*, 2013]. The CFC-11 absorption spectrum temperature dependence has been reported in studies by *Bass and Ledford* [1976] (186–230 nm, 222–298 K), *Chou et al*. [1977] (185–226 nm, 213–296 K), *Hubrich et al*. [1977] (158–260 nm, 208 and 298 K), *Simon et al*. [1988] (174–230 nm, 225–295 K), and *Mérienne et al*. [1990] (200–238 nm, 220–296 K) over the range of wavelengths and temperatures given in parentheses. The absorption spectrum parameterization reported in the *Simon et al*. [1988] study is currently recommended for use in atmospheric models in *Sander et al.* [2011] due, in part, to the combined wavelength and temperature range coverage of the dataset. Discrepancies among the available datasets, however, led the recent *SPARC* [2013] lifetime report to recommend a substantial uncertainty in the low-temperature spectrum, i.e., approximately a ±25% uncertainty in $\sigma(\lambda,220\ K)$.

The *SPARC* [2013] lifetime report recommends a global steady-state (year 2000) lifetime for CFC-11 of 52 years with 2σ uncertainties that lead to lifetimes in the range 43 to 67 years (see discussion in *SPARC* [2013]). The recommended lifetime and range are based on a combination of model calculations and derivations from atmospheric observations. The range in the recommended lifetime has several contributing factors due to uncertainties in both the model and observationally based lifetimes, including the uncertainty in the UV absorption spectrum

[*Minschwaner et al.*, 2013; *Rigby et al.*, 2013; *SPARC*, 2013]. The present level of CFC-11 lifetime uncertainty is significant and directly impacts the ability to model climate change and climate-chemistry coupling scenarios. An objective of the present work was to constrain the UV spectrum of CFC-11 further, particularly at temperatures most relevant to stratospheric photolysis, and, thus, its lifetime and uncertainty.

In this work the UV absorption spectrum of CFC-11 was measured at 216, 235, 254, 274, and 296 K at 24 discrete wavelengths between 184.950 and 230 nm. The present results are compared with previous temperature dependent studies mentioned above and the discrepancies are discussed. A parameterization of $\sigma(\lambda,T)$ was developed from our work for use in atmospheric models. The NASA Goddard Space Flight Center (GSFC) 2-D coupled chemistry-radiation-dynamics model [*Fleming et al.*, 2011] was used to evaluate the atmospheric photolysis, local and global annually averaged lifetimes of CFC-11 as well as the range of lifetimes obtained based solely on the estimated uncertainty in $\sigma(\lambda,T)$.

2. Experimental Details

The apparatus used in this work was similar to that used in recent studies from this laboratory [e.g. *Papadimitriou et al.*, 2013]. In brief, the apparatus consisted of a 30 W deuterium (D_2) lamp, whose output was collimated through a 90.4 ± 0.3 cm long, jacketed absorption cell and directed onto the entrance slit of a 0.25 m monochromator with a photomultiplier tube detector. The beam-path outside of the absorption cell and monochromator were purged with N_2. The monochromator wavelength was calibrated using atomic lamps to ±0.1 nm and the resolution was ~1 nm (FWHM). Additional measurements were made at 184.950, 213.856, and 228.802 nm using Hg, Zn, and Cd atomic lamp light sources, respectively, with a photodiode detector coupled with narrow band-pass filters. The absorption cell temperature was maintained by circulating fluid from a temperature-regulated reservoir through the cell jacket. The gas temperature was measured using a thermocouple inserted at both ends of the absorption cell and was accurate to ~1 K over the temperature range of this study.

Absorption cross sections, $\sigma(\lambda,T)$, were determined using the Beer's law

$$A(\lambda) = -\ln[I(\lambda)/I_0(\lambda)] = \sigma(\lambda, T) \times L \times [\text{CFC-11}] \quad \text{(I)}$$

where A is absorbance at wavelength λ, $I(\lambda)$ and $I_0(\lambda)$ are the measured light intensities in the presence and absence of sample, L is the pathlength of the absorption cell. Measurements were performed under static conditions and [CFC-11] was determined from absolute pressure measurements using the ideal gas law. Absorbance was measured for a range of concentrations, at least 10 concentrations were used in each measurement, and cross sections were determined from a linear least-squares fit of A against [CFC-11]. Signals were stable to better than 0.5% and

$I_0(\lambda)$ values were measured at the beginning and end of an experiment agreed to within 0.5%, corresponding to an absorbance uncertainty of less than ~0.005.

CFC-11 (99.7%) samples were purified in freeze-pump-thaw cycles before use. He (UHP, 99.999%) was used as supplied. Gas mixtures, prepared manometrically in 12 L Pyrex bulbs, with 0.0022, 0.0218, and 0.1836 mixing ratios of CFC-11 in He (accurate to 1%) were used to introduce the sample into the absorption cell. Pressures were measured using calibrated 10, 100, and 1000 Torr capacitance manometers.

3. Results and Discussion

Gas-phase UV absorption cross sections, $\sigma(\lambda,T)$, for CFC-11 were determined at 24 discrete wavelengths over the range 184.95–230 nm at 216, 235, 254, 274, and 296 K. $\sigma(\lambda,T)$ values are summarized in Tables S1 and S2 in the supplementary material and plotted in Figure 1. $\sigma(\lambda,T)$ values shown in Figure 1 are average values when multiple measurements were performed. The CFC-11 UV absorption spectrum has continuous absorption from the shortest to the longest wavelength included in this study. $\sigma(\lambda,T)$ decreases toward longer wavelengths from a maximum at 184.950 nm with the decrease nearly exponential at wavelengths greater than ~210 nm. The true spectrum maximum lies at a wavelength shorter than included in this work; *Simon et al*. [1988] report a maximum near 176 nm. However, photolysis at wavelengths less than ~190 nm is relatively unimportant as an atmospheric loss process (Figure 2). The peak transition has been assigned to a (C–Cl)* ← Cl transition [*Sandorfy*, 1976].

A temperature dependence of the CFC-11 absorption spectrum, Figure 1, was observed across much of the absorption spectrum, but was weak near 196 nm. At wavelengths greater than 196 nm, the cross sections decreased with decreasing temperature. At wavelengths less than 196 nm a weak increase in cross section was observed with decreasing temperature. The strongest temperature dependence was observed at the longest wavelengths of this study, e.g. the cross section decreases by ~52% between 296 and 216 K at 230 nm.

The measurement precision was high over the wavelength range studied, typically less than 1% uncertainty. Replicate measurements were made in many cases that included using different sample mixing ratios and different ranges of absorbance as well as different experimental parameters (e.g. light intensity and optical filtering). In each case, the measured absorption obeyed Beer's law. The measurement reliability was also tested by comparing data obtained with the monochromator at the wavelength of the atomic lamps. The 296 K measurements at 213.95 nm (Zn line) agreed to better than 1%, while the difference at 228.802 nm (Cd line) was ~4%, with the Cd lamp measurements being greater.

The uncertainties reported in Table S1 are 2σ from the precision of the Beer's law fits to the data. The overall 2σ uncertainty including estimated systematic errors of the measurement is estimated to be 4% at all wavelengths included in this study.

3.1 CFC-11 UV spectrum parameterization. On the basis of the present σ(λ,T) measurements, a spectrum parameterization was developed using the empirical expression given in Table 1. The fit parameters are given in Table 1 and spectra calculated from this expression are included in Figure 1 for comparison with the experimental data. The parameterization fits the experimental data to within 2% between 192–222 nm, lower panel in Figure 1. The parameterization is valid over the wavelength range 190-230 nm (optimized for 192–230 nm) and over the temperature range (216-296K) of the experimental data. Extrapolation outside the range of the experimental data may lead to systematic errors.

3.2 Comparison with previous studies. The σ(*λ*,296 K) results obtained in this work are in agreement with the recommended room temperature absorption cross section data given in *Sander et al*. [2011] to better than 7% between 190 and 230 nm. Results from all previous temperature-dependent studies are compared with the present results in Figure 1. The *Simon et al*. [1988] study is assumed to supersede the *Vanlaethem-Meurée et al*. [1978] study from the same group. Overall, the agreement among the various temperature dependent studies is rather poor, with differences on the order of ±10–20%. The present results are most consistent with the data of *Chou et al*. [1977], where the agreement is to within 5%, or better, over most of the wavelength range; the differences are somewhat greater for some of the longer wavelength data points, but still agree to within 10%. The work of *Mérienne et al*. [1990] is in reasonable agreement (within 10%) with the present work, but systematic discrepancies are observed for wavelengths <215 nm. The work of *Simon et al*. [1988], *Hubrich et al*. [1977], and *Bass and Ledford* [1976] show the largest disagreement with the parameterization developed in this work. In the case of *Hubrich et al*. [1977] and *Bass and Ledford* [1976], the disagreement is more random and most likely is due to the scatter in their experimental data. *Simon et al*. [1988] report a CFC-11 spectrum temperature dependence that is greater than any of the other studies. (Note: the *Simon et al*. CFC-11 cross section parameterization is currently recommended for use in atmospheric modeling in *Sander et al*. [2011].) As discussed below, the stronger spectrum temperature dependence will lead to a longer atmospheric photolysis lifetime. As shown in Figure 1, significant systematic differences are observed for the spectrum temperature dependence with differences of ~15% at 230 K and 210 nm (i.e., the most critical temperature and wavelength for the atmospheric photolysis of CFC-11). The reasons for the disagreement are unknown. It should also be noted that *SPARC* [2013] reports a systematic error in the

parameterization of the *Simon et al*. [1988] data as their reported spectrum parameterization does not reproduce their reported experimental data to within the quoted accuracy.

4. Atmospheric implications

The GSFC 2-D model was used to quantify the atmospheric loss processes of CFC-11 (photolysis and $O(^1D)$ reaction) and calculate its local and global annually averaged steady-state lifetimes for year 2000 conditions. The photolytic loss of CFC-11 was evaluated in the following wavelength regions: Lyman-α (121.567 nm), 169–190, 190–230, and >230 nm. A unit photolysis quantum yield at all wavelengths was assumed in the calculations. The Lyman-α cross section, 9.8×10^{-17} cm^2 molecule^{-1}, and UV cross sections at wavelengths less than 190 nm and greater than 230 nm were taken from *SPARC* [2013]. Calculations were performed using three σ(λ,T) parameterizations: (1) that developed in this work; (2) the parameterization given in *SPARC* [2013], which corrects a systematic error in the σ(λ,T) parameterization reported in *Simon et al*. [1988]; and (3) the parameterization given in the *Sander et al.* [2011] recommendation (also referred to as *JPL10-6*), i.e., the *Simon et al*. [1988] uncorrected cross section parameterization. The $O(^1D)$ reactive rate coefficient was taken from *SPARC* [2013]. Other kinetic and photochemical parameters were taken from *JPL10-6* unless updated in *SPARC*.

The lifetime was computed as the ratio of the annually averaged global atmospheric burden to the vertically integrated annually averaged total global loss rate [*SPARC*, 2013]. The total global lifetime can be separated by the troposphere (surface to the tropopause, seasonally and latitude-dependent), stratosphere, and mesosphere (<1 hPa) using the total global atmospheric burden and the loss rate integrated over the different atmospheric regions such that

$$\frac{1}{\tau_{\mathrm{Tot}}} = \frac{1}{\tau_{\mathrm{Trop}}} + \frac{1}{\tau_{\mathrm{Strat}}} + \frac{1}{\tau_{\mathrm{Meso}}} \qquad \text{(II)}$$

The 2-D model total global annually averaged lifetimes were calculated to be 58.1 ± 0.7 years for this work, 60.2 ± ~6 years for *SPARC*, and 58.6 ± 4 years for *JPL10-6* (see lifetime summary in Table 2). The significant reduction in the 2σ uncertainty range in the present work reflects the smaller CFC-11 cross section uncertainty (±4%) compared to the *SPARC* (±25%) and *JPL10-6* (±20%) recommendations.

We note that the absolute lifetimes computed here are somewhat greater than the recommended CFC-11 lifetime of 52 years reported in *SPARC* [2013]. The 52 year lifetime was based on a combination of: (1) derivations from various observational datasets, and (2) calculations from seven atmospheric models (including the GSFC 2-D model) which all used the *JPL10-6* recommended kinetic and photochemical parameters. Observationally based lifetimes are subject to a number of uncertainties, see e.g., *Minschwaner et al.* [2013] and *Rigby et al.*

[2013]. The absolute lifetimes computed in models are also dependent on a number of factors and associated uncertainties, including the model transport rates and the UV absorption cross sections of O_2, O_3, as well as CFC-11. The 2-D model lifetime computed using the *JPL10-6* parameters (58.6 years) is somewhat greater than the multi-model mean (55.3 years) reported in *SPARC* [2013], but is very similar to the GEOSCCM 3-D model lifetime (58.3 years). The lifetimes computed here are well within the 2σ uncertainty range (43–67 years) reported in *SPARC* [2013], which is based on the combined effect of the observational and model uncertainties. The CFC-11 lifetimes and uncertainties presented here illustrate the relative changes in these quantities as computed in one particular model due only to the different CFC-11 UV absorption cross sections (this work vs. *SPARC* vs. *JPL10-6*).

Figure 2 (left panel) shows the global annually averaged vertical profiles of the first-order photolysis and $O(^1D)$ reactive rate coefficients (local lifetimes). CFC-11 is unreactive toward the OH radical with an estimated rate coefficient of $<1 \times 10^{-25}$ cm^3 $molecule^{-1}$ s^{-1} [*SPARC*, 2013], and short wavelength UV radiation only penetrates weakly into the upper-troposphere such that the tropospheric loss of CFC-11 is only a minor global loss process. The tropospheric lifetime was calculated to be ~1550 years (this work), ~1720 years (*SPARC*), and ~1480 years (*JPL10-6*).

Photolysis in the 190–230 nm wavelength region is the dominant loss process in the stratosphere; photolysis in this wavelength region accounts for ~98% of CFC-11 global loss. Figure 2 (middle and right panels) shows the calculated CFC-11 molecular loss rate and mixing ratio vertical profiles. The maximum loss rate is at 22–23 km with significant loss occurring between 18 and 28 km corresponding to temperatures approximately in the range of 208 to 225 K. Photolysis at wavelengths >230 nm is a negligible loss process throughout the atmosphere, while photolysis in the 169–190 nm range is a minor stratospheric loss process, ~0.1%. The $O(^1D)$ reaction is a minor loss process and accounts for ~2% of CFC-11 global loss. The calculated stratospheric lifetimes were 60.4 years (this work), 62.4 years (*SPARC*), and 61.0 years (*JPL10-6*). The *JPL10-6* lifetime differs from the *SPARC* value due to the correction in the *Simon et al*. [1988] cross section parameterization. Fortuitously, the error in the *Simon et al*. parameterization leads to reasonable agreement between the *JPL10-6* lifetime and that reported in this work.

In the mesosphere, short wavelength UV and Lyman-α photolysis are important local loss processes (Figure 2, left panel). At altitudes >65 km, local lifetimes are relatively short, 1 day or less.

The uncertainty (range) in the calculated CFC-11 lifetime due to the uncertainty in the UV absorption cross section data, $\sigma(\lambda,T)$, and the $O(^1D)$ rate coefficient was evaluated using the

2-D model. Model calculations were performed with σ(λ,T) and the $O(^1D)$ rate coefficient increased to the maximum of their 2σ uncertainty limits (fast case, shorter lifetime) and the minimum 2σ limit (slow case, longer lifetime) with all other model input parameters remaining the same. The uncertainties in σ(λ,T) were taken from this work, *SPARC*, and *JPL10-6*, while the $O(^1D)$ rate coefficient uncertainty was taken from *SPARC*. The calculated fast/slow molecular loss rates are included in Figure 2 (middle panel) for comparison with the base case calculation.

A comparison of the photolysis and $O(^1D)$ reaction uncertainty contributions to the overall local first-order loss rate uncertainty (2σ) as a function of altitude is given in Figure 3 for this work and *SPARC*. The horizontal shaded region in Figure 3 highlights the altitude range most critical to the atmospheric loss of CFC-11 and illustrates that UV photolysis in the 190–230 nm region dominates the uncertainty at these altitudes. Figure 3 also shows that the overall uncertainty in the photolytic loss of CFC-11 is significantly reduced in the present work. The 2σ uncertainties (range) of the calculated global annually averaged lifetimes are ±0.7 years. This is greatly reduced from the uncertainty range obtained using the previous photochemical recommendations: ~ ±6 years (*SPARC*) and ~ ±4 years (*JPL10-6*).

The 2-D model calculations of total ozone showed miniscule changes over most of the globe when using the CFC-11 cross sections presented here compared with those computed using *SPARC* [2013]. However, minor changes of a few Dobson units were simulated during the winter polar Southern Hemisphere. Further studies are needed to evaluate the impact of these small changes on the computed ODPs for ODSs since CFC-11 is used as a reference compound in these calculations.

5. Conclusions

This study reports accurate measurements of the UV absorption spectrum of $CFCl_3$ (CFC-11) as a function of temperature between 184.95 and 230 nm. On the basis of 2-D model calculations, the CFC-11 cross section data presented here leads to a faster loss rate and a shorter global annually averaged lifetime (58.1 years) compared to calculations using the recommended cross section data using *SPARC* [2013] (60.2 years) and *JPL10-6* [*Sander et al*., 2011] (58.6 years) photochemical and kinetic recommendations. Although these lifetimes are somewhat greater than the 52 year lifetime recommended in *SPARC* [2013], they are within the *SPARC* 2σ uncertainty range (43–67 years), and illustrate the relative lifetime changes calculated using the different cross section parameterizations.

The present work results in a significant reduction in the CFC-11 photolysis rate 2σ uncertainty, 4%, compared to 25% in *SPARC* and 20% in *JPL10-6*. The reduction in the 2σ

lifetime uncertainty is also significant: ±0.7 years (this work), ±6 years (*SPARC*), and ±4 years (*JPL10-6*). The model simulated total ozone showed minor changes in the winter polar Southern Hemisphere as a result of the updated cross sections presented here, compared to *SPARC* [2013], and these changes may impact the calculation of ozone depletion potentials for the ozone depleting substances. Also, a decrease in the CFC-11 lifetime will decrease its global warming potential (GWP). Although this work has reduced the uncertainties associated with the UV absorption spectrum of $CFCl_3$ (CFC-11) considerably, substantial uncertainty still remains in its atmospheric lifetime due to other uncertainties in observationally derived and model calculated lifetimes as discussed in *SPARC* [2013].

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303 **Table 1.** $CFCl_3$ (CFC-11) UV Absorption Spectrum Parameterization from This Work Valid Over the
304 Wavelength Range 190 to 230 nm for Temperatures Between 216 and 296 K.

$$\log_{10}\left(\sigma(\lambda, \mathrm{T})\right) = \sum_i A_i(\lambda_i - 200)^i + (\mathrm{T} - 273)\sum_i B_i(\lambda_i - 200)^i$$

i	A_i	B_i
0	-18.1863	0.0002656
1	-0.0528	4.228×10^{-5}
2	-0.001126	1.4027×10^{-6}
3	-3.0552×10^{-5}	6.44645×10^{-7}
4	2.24126×10^{-6}	-3.8038×10^{-8}
5	-3.2064×10^{-8}	5.99×10^{-10}

305

306 **Table 2**. Summary of Global Annually Averaged Lifetimes and Uncertainties (Ranges) Calculated Using
307 the GSFC 2-D Model (see text) with Input from This Work, *SPARC* [2013], and *Sander et al*. [2011].

	Lifetime (years)		
	Sander et al.	*SPARC*	This Work
Total	58.6 ± 4	60.2 ± 6	58.1 ± 0.7
Tropospheric	1480	1720	1550
Stratospheric	61.0	62.4	60.4
Mesospheric	$>1 \times 10^6$	$>1 \times 10^6$	$>1 \times 10^6$

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310 **Figure Captions:**

311 **Figure 1.** $CFCl_3$ (CFC-11) UV absorption spectrum. Top: Present measurements (symbols) and
312 parameterized spectra (lines, see Table 1). Bottom: Ratio of measured values to
313 parameterization. Results from previous studies are included for comparison (see legend).

314 **Figure 2**. $CFCl_3$ (CFC-11) 2-D model results: Left: Global annually averaged loss rate
315 coefficient (local lifetime) and contributions (see legend). Middle: Molecular loss rate and
316 uncertainty limits; the slow and fast profiles were calculated using the 2σ uncertainty estimates
317 in the CFC-11 UV absorption spectrum from this work. Right: CFC-11 concentration profile.

318 **Figure 3.** $CFCl_3$ (CFC-11) loss process contribution to the overall local uncertainty (2σ)
319 calculated using the 2-D model (see text). Left: Results obtained from this work. Right:
320 Results obtained using model input from *Sander et al*. [2011] and updates in *SPARC* [2013].

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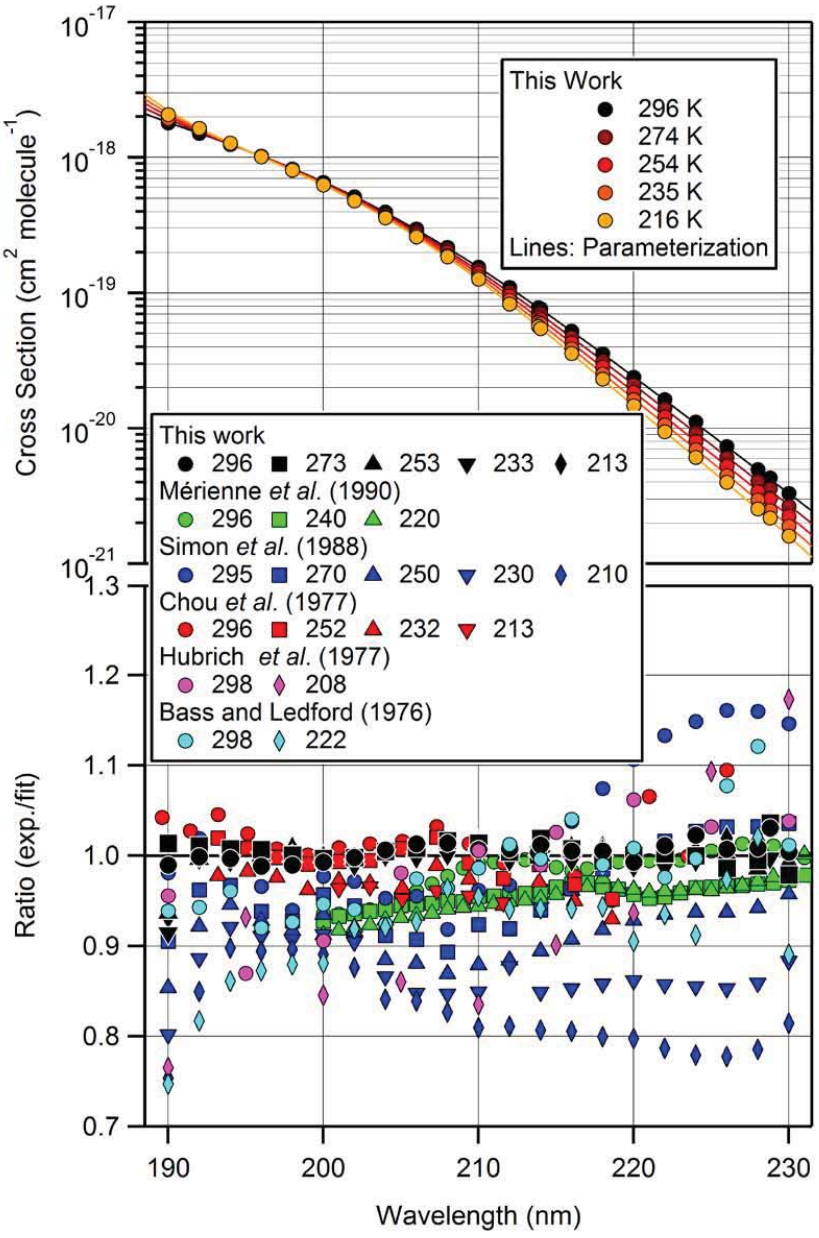

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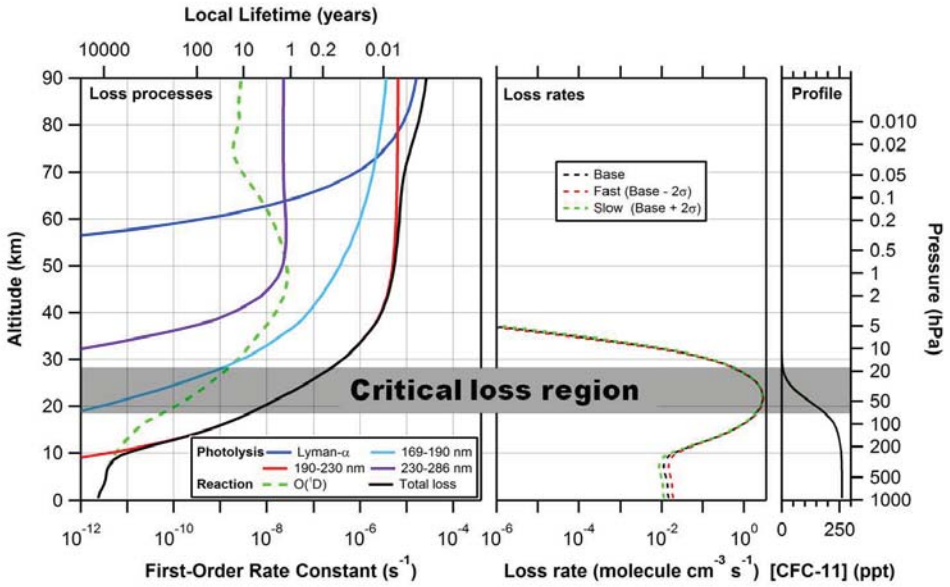

Figure 2. $CFCl_3$ (CFC-11) 2-D model results: Left: Global annually averaged loss rate coefficient (local lifetime) and photolysis and reaction contributions (see legend). Middle: Molecular loss rate and uncertainty limits; the slow and fast profiles were calculated using the 2σ uncertainty estimates in the CFC-11 UV absorption spectrum from this work. Right: CFC-11 concentration profile.

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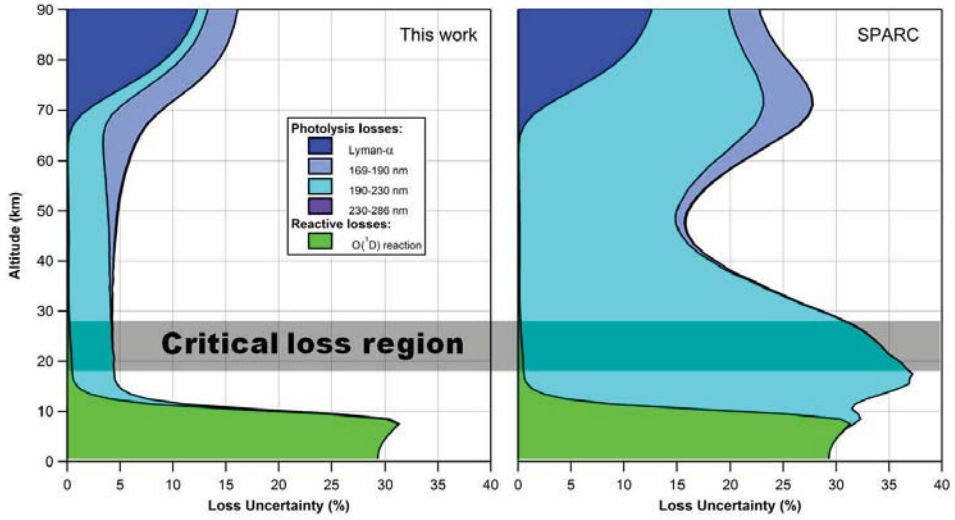

Figure 3. $CFCl_3$ (CFC-11) loss process contribution to the overall local uncertainty (2σ) calculated using the 2-D model (see text). Left: Results obtained from this work. Right: Results obtained using model input from *Sander et al.* [2011] and updates in *SPARC* [2013].

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