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Stable carbon isotope fractionation in the UV photolysis of CFC-11 and CFC-12

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Abstract

The chlorofluorocarbons CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) are stable atmospheric compounds that are produced at the earth's surface, but removed only at high altitudes in the stratosphere, where their removal liberates atomic chlorine that then catalytically destroys stratospheric ozone. For such long-lived compounds, isotope effects in the stratospheric removal reactions have a large effect on their global isotope budgets. We have determined the photolytic isotope fractionation for stable carbon isotopes of CFC-11 and CFC-12 in laboratory experiments. $^{13}C/^{12}C$ isotope fractionations (ε) range from (-23.7 ± 0.9) to (-17.5 ± 0.4) ‰ for CFC-11 and (-69.2 ± 3.4) to (-49.4 ± 2.3) ‰ for CFC-12 between 203 and 288 K, a temperature range relevant to conditions in the troposphere and stratosphere. These results suggest that CFCs should become strongly enriched in ^{13}C with decreasing mixing ratio in the stratosphere, similar to what has been recently observed for CFC chlorine isotopes. In conjunction with the strong variations in CFC emissions before and after the Montréal Protocol, the stratospheric enrichments should also lead to a significant temporal increase in the ^{13}C content of the CFCs at the surface over the past decades, which should be recorded in atmospheric air archives such as firn air.

1 Introduction

The chlorofluorocarbons CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) are the most abundant anthropogenic halocarbons in the atmosphere. Before their production was banned under the Montréal Protocol and its amendments, the usage of these compounds as refrigerants, cleansers, aerosol propellants and foam-blowing agents worldwide resulted in significant atmospheric loading; at their peaks in 1990 and 2003, respectively, mean mixing ratios in the troposphere were approximately 260 ppt (ppt = pmole mole^{-1} = 10^{-12} mole mole^{-1}) for CFC-11 and 550 ppt for CFC-12 (Forster et al., 2007; AGAGE, 2010). Due to the buildup of these and other anthropogenic halocarbons, total organic chlorine levels in the troposphere increased from approximately 600 ppt in 1900 to nearly 3350 ppt in 2008. CFC-11 and CFC-12 account for approximately 55 % of the total, outweighing contributions by natural compounds such as methyl chloride, HCl and naturally emitted molecular chlorine (Butler et al., 1999; WMO, 2010).

Chlorofluorocarbons such as CFC-11 and CFC-12 are produced by anthropogenic processes at the earth's surface, but have their only significant sinks in the stratosphere, at altitudes where UV-C radiation ($\lambda < 220$ nm) is sufficiently energetic to dissociate the C-Cl bond: Reaction (R1). A minor sink (approximately 7 %) is due to Cl abstraction by O(^{1}D), which is produced from the photolysis of ozone in the stratosphere: Reaction (R2) (Seinfeld and Pandis, 1998).

$$\mathrm{CF}_m\mathrm{Cl}_4-m+h\nu \xrightarrow{\lambda<220\,\mathrm{nm}} \mathrm{CF}_m\mathrm{Cl}_{3-m}+\mathrm{Cl}\cdot \tag{R1}$$

$$\mathrm{CF}_m\mathrm{Cl}_{4-m}+\mathrm{O}(^1\mathrm{D}) \longrightarrow \mathrm{CF}_m\mathrm{Cl}_{3-m}+\mathrm{ClO}\cdot \tag{R2}$$

These reactions cause the initial release of chlorine to begin the now well-known catalytic decomposition of ozone first proposed by Molina and Rowland (1974).

In addition, CFC-11 and CFC-12 have a significant global warming potential (4750 and 10 900 times that of $\mathrm{CO_2}$ per kg, respectively, over a 100 yr time horizon), resulting together in an atmospheric radiative forcing of approximately 0.233 W m^{-2} in 2005 and thus contributing to anthropogenic climate change (Massie and Goldman, 1992; Forster et al., 2007).

Since the implementation of the Montréal Protocol in 1987, the mixing ratios of CFC-11 and CFC-12 in the troposphere have decreased from their peak values to 240 ppt and 530 ppt, respectively, as sources have decreased in strength and the stratospheric sink has become dominant (Engel et al., 1998; Forster et al., 2007; AGAGE, 2010). However, due to the long atmospheric lifetimes of these compounds (45 and 100 yr for CFC-11 and CFC-12, respectively, WMO, 2010), it is expected that atmospheric effects caused by the presence of these CFCs will persist for decades to centuries (Engel et al., 1998; Forster et al., 2007).

The stable isotope composition of molecules in the atmosphere can be altered by chemical reactions due to differences in chemical bond strengths ascribed to isotopic substitution, causing fractionation between the different isotopologues of a given molecule (Brenninkmeijer et al., 2003). Isotope values are conveniently expressed in δ notation, in the case of ^{13}C:

$$\delta^{13}\mathrm{C} = \frac{^{13}R_{\mathrm{sample}}}{^{13}R_{\mathrm{standard}}} - 1 \tag{1}$$

where ^{13}R is the $^{13}\mathrm{C}/^{12}\mathrm{C}$ ratio in a sample or standard material, respectively. The internationally accepted reference material for ^{13}C is Vienna Pee Dee Belemnite (VPDB), and the δ value is commonly multiplied by 1000 ‰ to express it in per mille (‰) for readability. Assuming a Rayleigh-type fractionation, the isotope fractionation ε relates the change in δ value and mixing ratio during a photolysis reaction as follows:

$$\ln\left(\frac{\delta^{13}\mathrm{C}+1}{\delta^{13}\mathrm{C}_0+1}\right) = \varepsilon \ln(F) \tag{2}$$

where $\delta^{13}\mathrm{C}_0$ and $\delta^{13}\mathrm{C}$ are the stable carbon isotope ratios of the compound before and after photolysis, respectively, and F is the fraction remaining after photolysis. ε is also commonly expressed in ‰.

CFC-11 and CFC-12 have similar atmospheric cycles as N_2O, which is also long-lived (120 yr lifetime) and has mainly surface sources and stratospheric sinks. In the case of N_2O, laboratory experiments, field measurements and modelling studies have shown strong heavy isotope enrichments in the stratosphere, which have an important effect on the isotopic composition in the troposphere (e.g. Rahn and Wahlen, 1997; Röckmann et al., 2001; Kaiser et al., 2003, 2006; Blake et al., 2003; von Hessberg et al., 2004; Morgan et al., 2004). For CFC-12, recent measurements of the stable chlorine isotope ratio ($^{37}\mathrm{Cl}/^{35}\mathrm{Cl}$) of stratospheric CFC-12 have shown strong ^{37}Cl enrichments. Associated with the well-established decrease in mixing ratio above the tropopause, a progressive increase in the ^{37}Cl/^{35}Cl ratio by up to 27 ‰ relative to tropospheric air was observed over 14–34 km altitude, with an apparent isotope fractionation of $\varepsilon_{\mathrm{app}} = (-12.1 \pm 1.7)$ ‰ (Laube et al., 2010a).

In this study we report the intrinsic carbon (^{13}C/^{12}C) isotope fractionation (ε) in CFC-11 and CFC-12 during UV photolysis at atmospherically relevant temperatures.

2 Method

Photolysis experiments were carried out in March 2011 with a mixture of CFC-11 and CFC-12 in nitrogen, utilizing a photolysis setup at the University of East Anglia in Norwich, UK. The gas mixture used in the experiments was prepared using a custom dilution system with sample loops of 2.5 and 0.1 ml (Laube et al., 2010b). This system is built into a HP5890 GC oven and is maintained at 353 K to ensure that compounds are in the gas phase when they are diluted. It uses a Valco 6-port valve for switching sample loops, Nupro valves for controlling input and extraction of compounds, a scroll pump for evacuation, and oxygen-free nitrogen (BOC Gases Inc.) for dilution.

Using this system, 5 µmol CFC-11 and 0.2 µmol of CFC-12 were mixed in turn with nitrogen into a single 3 l canister at 300 kPa total pressure, which yielded mixing ratios of 13 ppm for CFC-11 and 530 ppb for CFC-12, both with an error of ±10 %. These high mixing ratios were chosen in order to provide adequate material for analysis, while keeping sample volumes small. The use of oxygen-free nitrogen in the mixture excludes the O(^{1}D) reaction described in Reaction (R2) from taking place in the reaction chamber. The gas amount of the prepared mixture was sufficient for all experiments.

Figure 1 shows a diagram of the photolysis setup. The quartz-glass reactor, which has a volume of 125 ml (total system volume including lines is approximately 160 ml), is temperature controlled through an ethanol regulator and cooler. Pressures in the reactor system are measured through an array of pirani, piezo and CMR pressure sensors; evacuation of the entire system is facilitated through a scroll pump. Photolysis of the CFC mixture is induced by a water-cooled 1 kW antimony (hereafter Sb) lamp (mfr. Heraeus, Hanau, Germany) with a continuous emission spectrum from 190 to 225 nm, which is ideal for inducing photolysis in CFCs. This lamp has previously been used for photolysis experiments with N_2O (Röckmann et al., 2001; Kaiser et al., 2002, 2003).

The gas mixture, at pressures near 100 kPa, was irradiated with UV light with exposure times varying from 0 to 3 h while the reactor was kept at various temperatures (203, 233, and 288 K): at 203 and 233 K the exposure times were 0–3 h with 0.5 h intervals (7 samples each), and at 288 K the exposure times were 0, 1.5, and 3 h. This gave a total of 17 samples.

After each experiment, the content of the reactor was expanded into a 1.75 l evacuated stainless steel canister. These were subsequently topped up to 200 kPa pressure with oxygen-free nitrogen, to provide adequate volumes and mixing ratios for the analysis system.

The sample canisters were measured in April 2011 in the isotope laboratory of the Institute for Marine and Atmospheric Research Utrecht (IMAU) of Utrecht University (The Netherlands) for mixing ratio and $\delta^{13}C$ using the system described in Zuiderweg et al. (2011). This instrument was originally designed for the measurement of stable carbon isotope ratios of non-methane hydrocarbons. It features a novel method of removing unwanted compounds (e.g. CO_2 and CH_4) by use of a 3 m × 6.35 mm packed Porapak Q pre-column, where compounds to be excluded from analysis are separated from the compounds of interest gas chromatographically. Separation of compounds is accomplished by using a 52.5 m × 0.25 mm Poraplot Q column, the effluent of which is split to (1) a HP 5970 quadrupole MS and (2) a Thermo Finnigan Delta Plus XL isotope ratio mass spectrometer by way of a Pt-Cu-Ni combustor and open split. Peak integration is accomplished through the ISODAT software package. $\delta^{13}C$ results from this instrument are reported relative to the international Vienna Pee Dee Belemnite standard (VPDB) in per mil (‰). Details of calibration procedures are elaborated in Zuiderweg et al. (2011).

This system was tested for measurement capability of C_1 chlorofluorocarbons with a PraxAir Inc. calibration mixture containing approximately (150 ± 8) ppb of both CFC-11 and CFC-12, among other compounds. Testing results with various volumes showed that the isotopic results were volume independent and stable for CFC measurement, with δ^{13}C repeatability ($1\,\sigma$, $n = 30$) of 0.9 and 0.7 ‰ for CFC-11 and CFC-12, respectively, above peak areas of 0.5 Vs (2 ng C equivalent), and mixing ratio measurement precision of ±5 %. Sensitivity of the instrument is approximately 0.25 Vs (ng C) (Zuiderweg et al., 2011). A sample chromatogram demonstrating compound separation can be found in Fig. 2. Daily calibration of the instrument was accomplished by measuring the above standard before the start and after the finish of that day's measurement series. Blank measurements showed no remnant CFC or interfering peaks.

To ensure that peak areas for the samples exposed longest were still above the specified threshold limit of 0.5 Vs, each analysis consumed 1 l (100 kPa, 295 K) of analyte, which allowed for 2 measurements of each of the sample canisters, under normal circumstances.

The theoretical zero photolysis time mixing ratios used for calculating F (the unphotolysed fraction remaining) were established by calculating the number of moles of each CFC in the reactor prior to exposure given a particular reactor temperature. Subsequently, the number of moles of each CFC in the reactor post-exposure was back-calculated from the VMR measurements of each can. All calculations took into account pressure gauge offsets.

3 Results and discussion

The photolysis rate coefficient J is given by:

$$J = -\frac{\ln(F)}{t} \tag{3}$$

and the isotope fractionation ε is given by Eq. (2). Therefore, we have plotted the natural logarithm of fraction remaining, $\ln(F)$, against photolysis time (Fig. 3a, b) and $\ln(\delta^{13}C + 1)$ against $\ln(F)$ (Fig. 3c, d) respectively for both compounds at all three temperatures, in order to obtain J and ε through the slope of linear fits to the data. A summary of least-squares fit parameters for the reaction rate coefficient and isotope fractionation is given in Table 1. For CFC-11, points with $\ln(F) < -3$ have been rejected as interference from a neighbouring peak disturbs the peak integration, leading to incorrect $\delta^{13}C$ and consequently affecting ε obtained from the plotted data. The samples affected and thus omitted have exposure times above 2 h, at 233 and 288 K.

Figure 3a and b show the photolysis behavior of CFC-11 and CFC-12 with exposure time. As expected, the Sb-lamp is very effective in photolyzing CFC-11 and -12, with 95 % and 33 % photolysis of the respective compounds achieved at exposures of 3 h at the coldest reactor temperature of 203 K. At higher temperatures, photolysis occurs faster and thus compound destruction is more complete for a given exposure time. Reaction rates measured range from 3.2×10^{-4} to $4.6 \times 10^{-4}\ \mathrm{s}^{-1}$ for CFC-11 and 4.4×10^{-5} to $9.4 \times 10^{-5}\ \mathrm{s}^{-1}$ for CFC-12 at 203 and 288 K respectively. However, deviations are noted from the linear relationship expected when photolysis data is plotted the manner chosen. These are not the result of the error of the measuring instrument as repeat measurements are very close. Rather, these are ascribed to possible moisture condensation on the reactor (despite ventilation) reducing light intensity and variations in reactor-lamp alignment. Alignment variations can occur in the photolysis setup as the reactor must be occasionally dismounted to remove accumulated bubbles in the reactor cooling fluid.

However, the aforementioned nonlinearity in the data in Fig. 3a and b do not impact the validity of these results for the calculation of ε as the data plotted in Rayleigh fractionation plots (Fig. 3c, d) are extremely well correlated, with least-square r^2 values very close to 1. At all temperatures, isotope fractionations are far larger for CFC-12 than for CFC-11. The strongest fractionations are observed at 203 K, (-69.2 ± 3.4) ‰ for CFC-12 and (-23.7 ± 0.9) ‰ for CFC-11. The magnitude of the isotope fractionations become larger (i.e. ε becomes more negative) towards lower temperatures, similar to the situation with N_2O (Kaiser et al., 2002). It is interesting to note that the CFC-12 fractionations are similar in magnitude to the fractionation in the reaction $CH_4 + Cl$ (Saueressig et al., 1995) or the reaction $CH_3Cl + OH$ (Gola et al., 2005).

In the stratosphere, CFC-11 photodissociates faster than CFC-12 and its atmospheric lifetime is shorter by approximately a factor of 2 (Forster et al., 2007). In our experiments, the photolysis rate of CFC-11 is also faster, but by a factor of 5. Part of the difference can be explained by the fact that the lamp spectrum and the solar actinic flux do not match. In addition, recombination of CFC-12 from photolysis products may occur in our experiments and could potentially be an issue. Model simulations suggest that our derived isotope fractionations could be underestimated by up to 25 % if recombination would be an important factor during our experiments. However, Folcher and Braun (1978) report that due to the quenching effects of balance gas, free radical yield is small (1.5 %) at best, leaving few recombination possibilities. The referenced paper concerns similar photolysis experiments utilizing CO_2-laser photolysed CFC-12 in helium at 11 kPa. Our usage of nitrogen as a balance gas at higher pressures would likely be more effective in limiting free radical yield. Additionally, the linear behaviour observed in the Rayleigh fractionation plots (Fig. 3c, d) provides evidence that the experiments basically mimic a Rayleigh type removal process, i.e. a single stage removal without significant interaction of the products with the reactant.

The present results imply that there should be a strong vertical gradient in $\delta^{13}C$ in the stratosphere for both CFC-11 and CFC-12, similar to the one found for $\delta^{37}Cl$ (Laube et al., 2010a) or $\delta^{13}CH_4$ (Röckmann et al., 2011). The fractionations found here are very large and in particular stratospheric (photolytically aged) CFC-12 is expected to be exceptionally enriched in ^{13}C. For example, sample calculations using the measured fractionations at 203 and 233 K and a stratospheric profile of CFC-12 mixing ratio from Laube et al. (2010a) indicate $\delta^{13}C$ potential enrichments in excess of 60 ‰ compared to tropospheric values at 34 km altitude. However, these are likely to be less due to the effect of atmospheric mixing, which causes apparent (observed) fractionation in the atmosphere $\varepsilon_{\mathrm{app}}$ to be approximately half of the intrinsic (laboratory measured) fractionation (Kaiser et al., 2006; Laube et al., 2010a).

Similar to the situation for other long-lived trace gases, the fractionations in the removal reactions affect the tropospheric isotope budgets. This is because stratospherically processed air is transported down to the troposphere again after partial removal and corresponding isotope enrichment of the CFCs. In addition, a particular atmospheric signal is expected after the introduction of the Montreal protocol. As the emissions from sources have decreased significantly since 1990 (Forster et al., 2007), the isotope effect in the stratospheric removal reactions should be continuously enriching the entire tropospheric reservoir. This should continue for the coming decades as atmospheric CFC levels are decreasing and should also be observable in atmospheric air archives or polar firn air and eventually in ice cores, similar as to what has been ascertained in firn air for N_2O nitrogen and oxygen stable isotopes (Röckmann et al., 2003).

4 Conclusions

The stable carbon isotopic fractionations in the UV photolysis reactions for CFC-11 and CFC-12 have been determined. Strong isotope enrichments are associated with UV photolysis at environmentally relevant temperatures. The fractionations increase from (-17.5 ± 0.37) ‰ and (-49.4 ± 2.3) ‰ at 288 K to (-23.7 ± 0.89) ‰ and (-69.2 ± 3.4) ‰ at 203 K for the respective compounds. These fractionations imply that strong heavy isotope enrichments should be found in the stratosphere. Expected effects are isotope gradients with CFC removal (e.g. vertical and polewards) in the stratosphere (as have already been ascertained for chlorine isotopes through balloon samples), and a change of the stable carbon isotopic ratio of these compounds in the atmosphere over time.

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Table 1. Summary of reaction rates and isotope fractionations from fits in Fig. 3.

	CFC-11			CFC-12		
Temp (K)	288	233	203	288	233	203
J (s^{-1})	4.6×10^{-4}	3.9×10^{-4}	3.2×10^{-4}	9.4×10^{-5}	6.5×10^{-5}	4.4×10^{-5}
ε (‰)	-17.5 ± 0.37	-23.2 ± 1.1	-23.7 ± 0.89	-49.4 ± 2.3	-55.0 ± 3.0	-69.2 ± 3.4
ε fit r^2	1	0.992	0.992	0.996	0.984	0.986

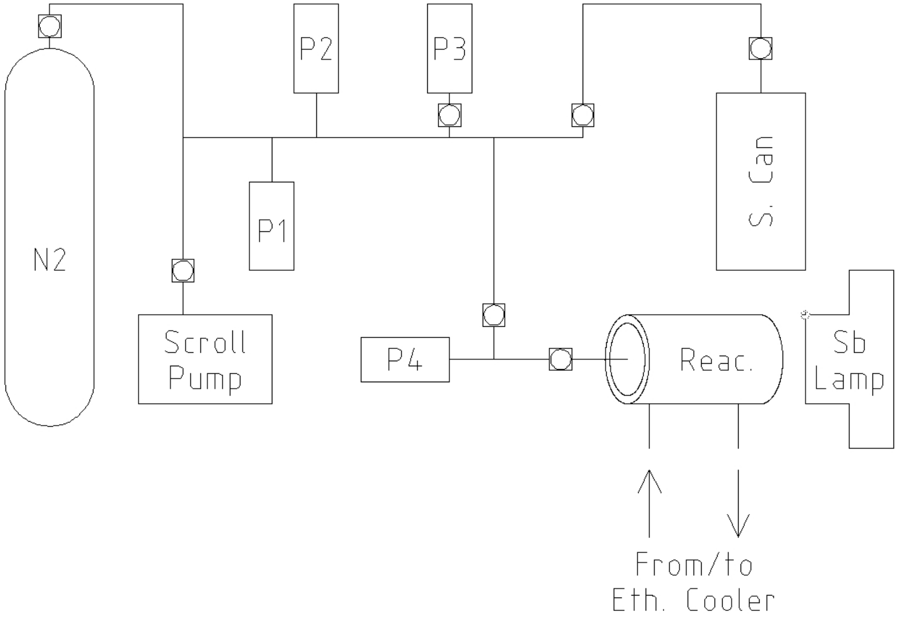

Fig. 1. Diagram of the photolysis setup at the School of Enviromental Sciences at the University of East Anglia. P1–P4 indicate pressure sensors, S. Can the sample canister. During filling of the reactor, the source canister containing the unphotolyzed CFC-mixture is installed in place of the sample canister.

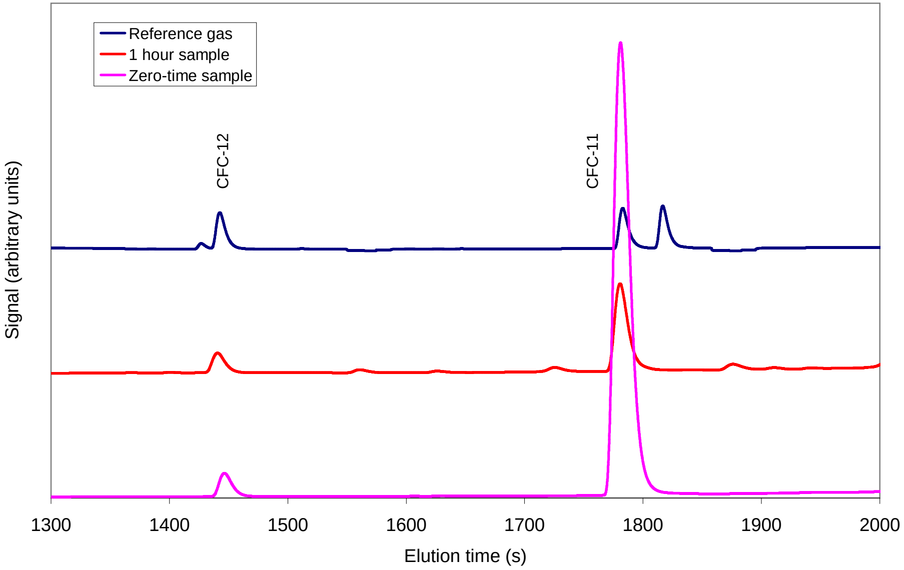

Fig. 2. Example chromatogram from instrument of the Praxair calibration mixture (0.1 l), 1 h exposure sample at 233 K (1 l), and zero-time exposure sample at 233 K (1 l) respectively, demonstrating separation performance.

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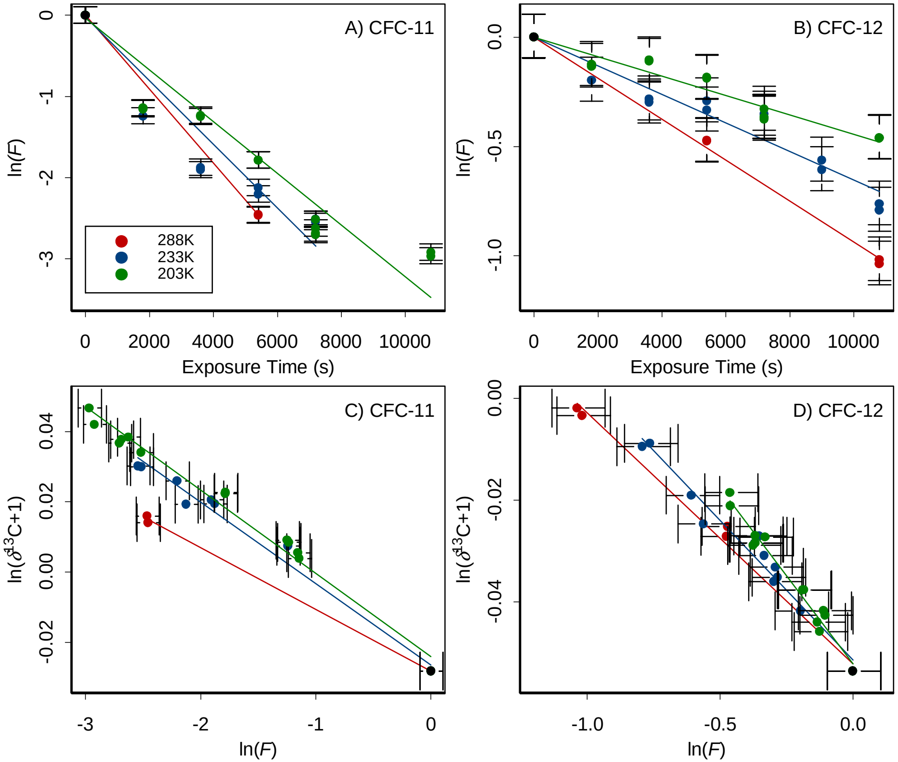

Fig. 3. Plots of ln(F) vs. exposure time in seconds (**a** and **b**) and ln(δ^{13}C + 1) vs. ln(F) (**c** and **d**) for samples at different exposures and temperatures for CFC-11 and -12 with least-squares fits to obtain J and ε. The instrument used has ±10 % uncertainty for mixing ratio measurement, and its δ^{13}C (1 σ) error is 0.9 and 0.7 ‰ for CFC-11 and -12 respectively. Summary of J and ε values from fits in Table 1.