D/H kinetic isotope effect in the reaction CH_4 + Cl

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Abstract. The D/H kinetic isotope effect (KIE^D_{Cl}) in the reaction of CH_4 with Cl has been investigated using a tunable diode laser absorption spectrometer (TDLAS) to measure $^{12}CH_3D/^{12}CH_4$ ratios. A KIE^D_{Cl} of 1.508 ± 0.041 was obtained at room temperature (296 K). Experiments employing Fourier transform infrared measurements of $^{12}CH_3D/^{12}CH_4$ ratios confirmed this result. An investigation of the temperature dependence showed an increase of KIE^D_{Cl} (1.592 ±0.057 at 223 K) with decreasing temperature. This very large D/H fractionation effect affects the overall isotope fractionation in the middle and upper stratosphere, where Cl contributes substantially to the total removal of CH_4.

1. Introduction

Methane can be regarded as one of the most important atmospheric trace gases. It contributes to global greenhouse warming and has a profound influence on the chemistry of the atmosphere. Clearly, an accurate determination of the CH_4 budget is essential to evaluate its global impact [*Lelieveld et al.*, 1993; *Crutzen*, 1995]. Isotope measurements play an increasingly important role in the investigation of atmospheric trace gases such as CO_2, CO, O_3, N_2O, and CH_4. For methane, a variety of $\delta^{13}CH_4$ studies has been performed [*Stevens and Engelkemeir*, 1988; *Quay et al.*, 1991; *Wahlen*, 1993; *Lowe et al.*, 1994], which allow the tropospheric CH_4 budget to be constrained. While the main tropospheric CH_4 sink is the reaction with OH, the reactions CH_4 + Cl and CH_4 + $O(^1D)$ also contribute substantially to methane removal in the stratosphere [*Crutzen and Schmailzl*, 1983]. Very different carbon kinetic isotope effects are associated with these reactions (KIE^{13C}_{OH} = 1.0054 ±0.009 (273-353 K) [*Cantrell et al.*, 1990], $KIE^{13C}_{O(^1D)}$ = 1.001 (297 K) [*Davidson et al.*, 1987] and KIE^{13C}_{Cl} = 1.066-1.075 (297-223 K) [*Saueressig et al.*, 1995]), so that stratospheric $\delta^{13}CH_4$ measurements could, in principal, allow the determination of the partitioning between these removal processes [*Bergamaschi et al.*, 1996]. In addition to $^{13}C/^{12}C$, D/H ratios contain information about the tropospheric and stratospheric cycling of CH_4. Recently

reported δD measurements in the lower and middle stratosphere (15 to 28 km) show an overall D/H kinetic isotope effect in methane of KIE = 1.19 ± 0.02 [*Irion et al.*, 1996]. Available laboratory measurements of KIE^D show poor agreement (KIE^D_{OH} values of 1.192 (277 K) [*DeMore*, 1993], 1.301 (277 K) [*Gierczak et al.*, 1994], and 1.492 (416 K) [*Gordon and Mulac*, 1975]) and they are not complete (no reported measurement for $KIE^D_{O(^1D)}$). For the chlorine sink, KIE^D_{Cl} = 1.36 ± 0.04 (T = 295 ± 2K) has been determined by *Wallington and Hurley*, [1992]. In this paper we report new measurements of KIE^D_{Cl} using two different techniques for the analysis of D/H ratios. In addition the temperature dependence of KIE^D_{Cl} was investigated.

2. Experimental

Two series of measurements were performed employing both tunable diode laser absorption spectroscopy (TDLAS) and Fourier transform infrared (FTIR) absorption measurements for the analysis of the isotopic composition of methane:

TDLAS measurements

The D/H kinetic isotope fractionation factor in the reaction CH_4 + Cl can be obtained if the change in isotopic composition of the sample gas is measured as a function of the amount of methane consumed. This process is described by the Rayleigh equation,
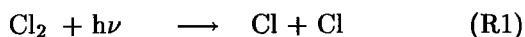
$$R_f = R_i * \left(\frac{C_f}{C_i}\right)^{\left(\frac{1}{KIE^D_{Cl}} - 1\right)} \qquad (1)$$

where R_i, R_f, C_i and C_f refer to initial or final R = $[^{12}CH_3D]/[^{12}CH_4]$ and C = $[CH_4]$ respectivly; KIE^D_{Cl} = $k_{^{12}CH_4}/k_{^{12}CH_3D}$ is the ratio of the rate constants for $^{12}CH_4$ + Cl and $^{12}CH_3D$ + Cl. KIE^D_{Cl} was derived from the slope of the straight line when ln (R_f/R_i) is plotted versus ln (C_i/C_f). The change in mixing ratio was determined by GC analysis, while the change in isotopic composition was measured by the TDLAS technique [*Bergamaschi et al.*, 1994]. A $^{12}CH_3D/^{12}CH_4$ absorption line pair of the sample gas is analysed relative to a standard gas with known $^{12}CH_3D/^{12}CH_4$ ratio (R_i = 1.301*10^{-4} or δD $^{V-SMOW}$ = 164.7 ‰). Two different $^{12}CH_3D/^{12}CH_4$ line pairs (line pair A: 3044.289 cm^{-1} / 3044.170 cm^{-1} and line pair B: 3042.341 cm^{-1} / 3042.221 cm^{-1}) were

employed in order to check for potential cross interferences by species other than methane. The measurements were performed at ≈ 30 hPa total pressure and relative absorptions of a few percent (optical pathlength of 81 or 93 m).

The chemical apparatus and the gas handling procedure were as described in *Saueressig et al.*, [1995]; only essential details are given here. Static $CH_4/Cl_2/N_2$ gas mixtures were irradiated (310-410 nm) for 3-5 minutes to produce Cl radicals via a catalytic reaction sequence:

$$Cl_2 + h\nu \longrightarrow Cl + Cl \quad (R1)$$

$$CH_4 + Cl \longrightarrow CH_3 + HCl \quad (R2)$$

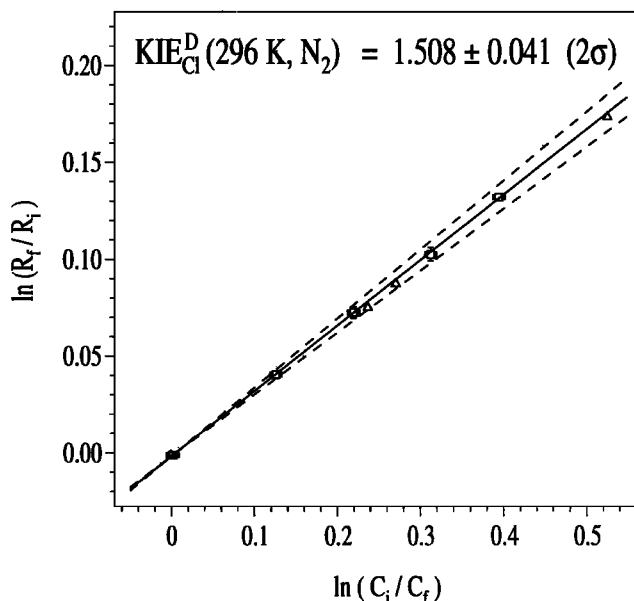$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl \quad (R3)$$

This way 99.9 % of the Cl radicals are produced in reaction (R3). Experiments were also carried out with O_2 present. In this case the CH_3 radicals are rapidly scavenged to produce CH_3O_2 leading to a purely photolytic Cl production (R1) [*Saueressig et al.*, 1995]. The gas mixtures contained 2.1 % CH_4 and 0.3-1.2 % Cl_2 at total bath gas pressure of 500 hPa (N_2 or N_2/O_2) in a 1.3 l reaction vessel. High methane mixing ratios were necessary to ensure sufficiently strong $^{12}CH_3D$ absorptions. Before and after photolysis, gas samples were withdrawn to establish the change in CH_4 mixing ratio and isotopic composition. Prior to the extraction of the samples the gas mixture was circulated in a closed loop containing a glass spiral kept at 90.7 K (Ar^{liq}) for the removal of condensibles such as Cl_2, HCl, and CH_3Cl. Liquid argon was used so that the high methane pressures of 10.5 hPa were still far below the equilibrium vapour pressure ($p_{CH_4}^{eq}$ (90.7 K) ≈ 40 hPa).

FTIR measurements

A second set of experiments was conducted with a FTIR-spectrometer (BOMEM DA-08) interfaced to a cylindrical quartz vessel of 44 l volume that is equipped with multi-pass optics to give an optical pathlength of

Figure 1. The TDLAS measurements (line pair A): change in isotopic composition of CH_4 [$\ln(R_f/R_i)$] plotted versus degree of conversion [$\ln(C_i/C_f)$] at 296 K. The triangles are results with O_2 present. The dashed lines represent the 95% confidence limits of the fit.

34 m. 5 photolysis lamps (280-360 nm) were mounted radially around the reaction cell in order to provide a homogeneous light flux throughout the volume. CH_4 / Cl_2/N_2 gas mixtures were irradiated in several steps up to a maximum photolysis time of 18 s. The experiments were conducted at 296 K and 1000 hPa total pressure (N_2). An approximately 1:1 mixture of $^{12}CH_4$ and $^{12}CH_3D$ was used ([$^{12}CH_4$] = 53 - 66 $ppmv$ and [$^{12}CH_3D$] = 66 - 78 $ppmv$). The chlorine mixing ratios were between [Cl_2] = 1150 and 1280 $ppmv$.

The IR analysis light was detected by a liquid helium cooled Cu-Ge detector. 256 scans at 0.04 cm^{-1} resolution were co-added over a period of 110 minutes. The reaction vessel was housed in a light-tight aluminium shield and no change in methane mixing ratio was observed over this period. At each step of the photolysis an absorption spectrum between 1100 and 1320 cm^{-1} was recorded. To improve the signal-to-noise-ratio (SNR) the spectrometer was fitted with a filter passing radiation with $\nu \le 1320$ cm^{-1}. A strictly linear relationship was found between optical density (OD) and methane mixing ratio.

The fractionation factor KIE_{Cl}^D was obtained by the relative rate technique. Two ensembles of different absorption lines, 21 lines for $^{12}CH_4$ and 28 for $^{12}CH_3D$, were analysed (Table A). A spectral stripping procedure was used to determine the relative absorption (and thus relative mixing ratio) of each line compared to the pre-photolysis spectrum. KIE_{Cl}^D was calculated as follows:

Table A. The absorption lines used for FTIR analysis at 0.04 cm^{-1} resolution: line positions ν are given according to HITRAN database [*Rothman et al.*, 1992].

$^{12}CH_4$,	ν [cm^{-1}]	$^{12}CH_3D$,	ν [cm^{-1}]
1237.020	1277.473	1102.469	1179.987
1237.272	1281.611	1110.780	1181.391
1238.022	1286.544	1113.949	1184.273
1238.712	1289.684	1114.493	1185.745
1241.949	1292.678	1115.941	1187.263
1243.352	1311.432	1119.025	1188.603
1245.769	1316.827	1141.597	1191.464
1255.000		1143.391	1195.707
1256.602		1144.305	1197.439
1260.811		1144.961	1198.540
1261.650		1145.509	1199.494
1262.228		1148.492	1258.516
1270.785		1150.056	1266.261
1276.844		1150.881	1267.208

$$\ln\left(\frac{OD_{^{12}CH_4}(0)}{OD_{^{12}CH_4}(t)}\right) = \ln\left(\frac{[^{12}CH_4](0)}{[^{12}CH_4](t)}\right)$$

$$= k_{^{12}CH_4} [Cl] t \quad (2)$$

$$\ln\left(\frac{OD_{^{12}CH_3D}(0)}{OD_{^{12}CH_3D}(t)}\right) = \ln\left(\frac{[^{12}CH_3D](0)}{[^{12}CH_3D](t)}\right)$$

$$= k_{^{12}CH_3D}\,[Cl]\,t \qquad (3)$$

By plotting $\ln\left(OD_{^{12}CH_4}(0)/OD_{^{12}CH_4}(t)\right)$ versus $\ln\left(OD_{^{12}CH_3D}(0)/OD_{^{12}CH_4}(t)\right)$ a straight line is obtained whose slope is equal to KIE^D_{Cl}. Note that when $[^{12}CH_4] \gg [^{12}CH_3D]$ the Rayleigh equation (1) and the equations (2)/(3) are equivalent.
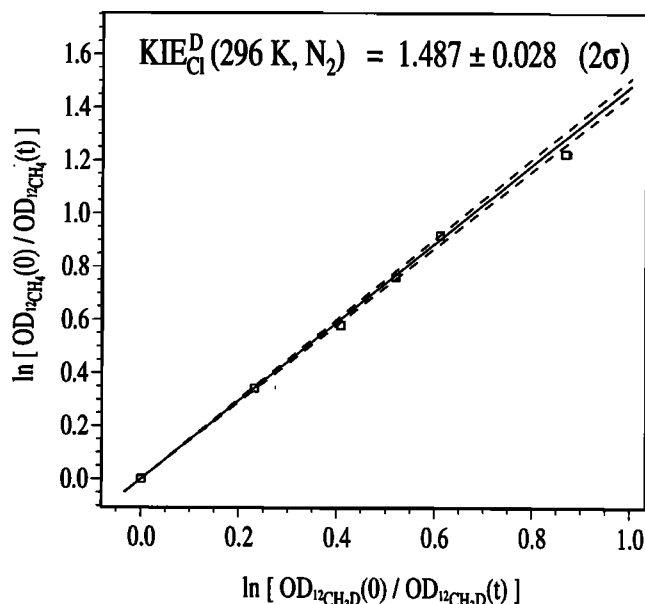
3 . Results

The measurements obtained with the TDLAS spectrometer (line pair A) are summarized in Figure 1. At room temperature both chemical systems (with and without O_2) yielded identical results ($KIE^D_{Cl} = 1.508 \pm 0.041$ (n=4) and 1.496 ± 0.042 (n=3) respectivly (2σ), Table B). This fact confirms that in both systems the distribution between excited $Cl(^2P_{1/2})$ and groundstate $Cl(^2P_{3/2})$ was already in thermal equilibrium (Boltzmann distribution) before the reaction started.

Control experiments (n_o in Table B), comprising the complete gas handling procedure except the photolysis of the gas mixture, showed no change of the initial isotopic compostion (R_i).

The use of linepair B resulted in $KIE^D_{Cl} = 1.536 \pm 0.074$ (2σ, n=3, at 296 K, $CH_4/Cl_2/N_2$) which agrees well with the other measurements at 296 K. Thus we rule out potential interferences of our line pairs due to absorptions of gas phase constituents other than CH_4 . The data from the experiments performed with the FTIR spectrometer are shown in Figure 2. The result $KIE^D_{Cl} = 1.487 \pm 0.028$ (2σ, n = 5, 296 K, $CH_4/Cl_2/N_2$) is in excellent agreement with the TDLAS measurements (Table B). We also performed experiments at low resolution ($0.5\ cm^{-1}$, $[^{12}CH_4] = [^{12}CH_3D] = 90\ ppmv$ at 1000 hPa) and noticed a non Beer-Lambert behavior of the absorption lines. Once corrected for the non-linearity (conversion to mixing ratio using calibration curves) a KIE^D_{Cl} of about 1.5 was obtained in agreement with the result at high resolution.

Table B. D/H kinetic isotope effect (KIE^D_{Cl}) and its temperature dependence measured with the TDLAS spectrometer (line pair A) and the FTIR spectrometer.

|	T[K]	KIE^D_{Cl}	n	n_0	bath gas
TDLAS:	296	1.508 ± 0.041	4	2	N_2
	296	1.496 ± 0.042	3	1	N_2/O_2
	263	1.575 ± 0.051	3	1	N_2
	243	1.587 ± 0.053	3	1	N_2
	223	1.592 ± 0.057	3	1	N_2
FTIR:	296	1.487 ± 0.028	-	-	N_2

ΔKIE^D_{Cl} is given with 2σ standard deviation, n refers to experiments with photolysis, n_0 is the number of control experiments without photolysis.

$$KIE^D_{Cl}(296\ K, N_2) = 1.487 \pm 0.028 \quad (2\sigma)$$

Figure 2. The relative rate technique applied to the reaction of $^{12}CH_4$ and $^{12}CH_3D$ with Cl measured with a FTIR spectrometer. The dashed lines represent the 95% confidence limits of the fit.

Our results are thus considered independent of the experimental setup, the source of Cl atoms, and the analysis method for isotopic composition.

Additionally, KIE^D_{Cl} was measured at 3 different temperatures using TDLAS (line pair A, $CH_4/Cl_2/N_2$): 263 K (n=3), 243 K (n=3), and 223 K (n=3). The results obtained (Table B) showed an increasing fractionation effect for $^{12}CH_4$ and $^{12}CH_3D$ with decreasing temperature. The temperature dependence of KIE^D_{Cl} expres-
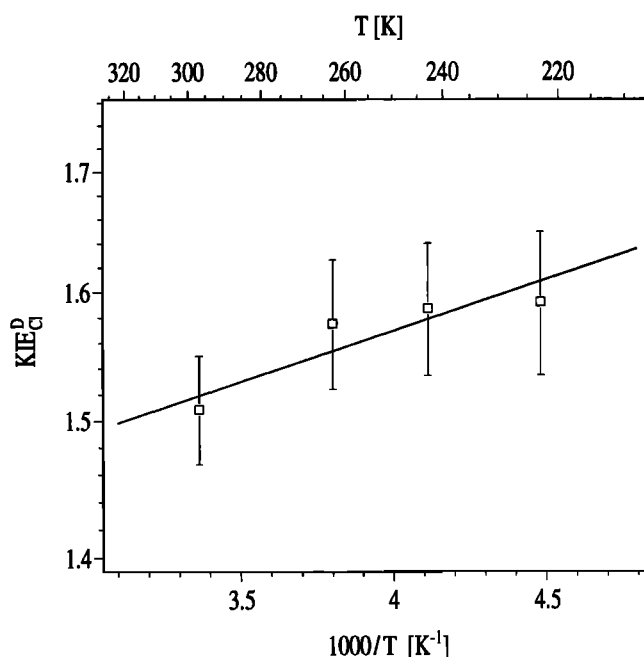
Figure 3. Temperature dependence of KIE^D_{Cl} between 223 K and 296 K: $KIE^D_{Cl}(T) = 1.278\text{*}\exp(51.308/T)$ measured with the TDLAS spectrometer (line pair A).

sed in Arrhenius form, is given by: $KIE^D_{Cl} = (1.278 \pm 0.095)*exp((51.31 \pm 19.08)/T)$ as shown in Figure 3.

4. Discussion

For two different chemical reaction sequences we obtained indistinguishable results for the fractionation effect (KIE^D_{Cl}) of $^{12}CH_3D/^{12}CH_4$ in the reaction with Cl. Other potential removal processes for methane that could have affected our experiment, i.e. $CH_4 + OH$, are unimportant as discussed in *Saueressig et al.*,[1995].
The reported $KIE^D_{Cl} = 1.508 \pm 0.041$ at 296 K is significantly larger than the value of 1.36 ± 0.04 measured by *Wallington and Hurley*, [1992] at T $= 295 \pm 2 K$. After learning of the results of the present work, *Hurley and Wallington* (private communication, 1996) have extended their earlier FTIR investigations and now report a value of $KIE^D_{Cl} = 1.47 \pm 0.09$ (obtained at 0.25 cm^{-1}, 295 K, 933 hPa with $[^{12}CH_4] = 10 - 123$ *ppmv* and $[^{12}CH_3D] = 49 - 90$ *ppmv*) in excellent agreement with our results and consistent within the combined 2σ errors with their published value of 1.36 ± 0.04. Although no evidence was found for problems associated with non-linearity of the IR features used, these authors prefer their most recent value because more data were acquired and the analysis procedures have improved since the early work.
A value for the $KIE^D_{Cl} > 1.33$ (derived from the 4/3 ratio of the number of H atoms in $^{12}CH_4$ and $^{12}CH_3D$ respectively) is at first glance surprising, as it appears to indicate that the reactivity of the C-H bonds towards Cl is decreased by the presence of a D atom. However, it must be noted that the symmetry of $^{12}CH_4$ and $^{12}CH_3D$ are different and that the degeneracy of the normal modes of vibration in $^{12}CH_4$ is lifted in $^{12}CH_3D$ leading to important differences in the transition state for H atom abstraction.
We now compare our result for the fractionation effect (KIE - 1) in the Cl + $^{12}CH_3D/^{12}CH_4$ reaction of 51 % to the value of 19.2 % obtained for OH + $^{12}CH_3D/^{12}CH_4$ [*DeMore*, 1993]. The ratio of the fractionation effects is thus 2.7. This may be compared with the fractionation of $^{13}CH_4/^{12}CH_4$ by Cl and OH whose ratio is 66 ‰ /5.4 ‰ $= 12.2$ [*Saueressig et al.*, 1995; *Cantrell et al.*, 1990]. Therefore the relative influence of the reaction $CH_4 + Cl$ on the stratospheric δD distribution should be less pronounced, compared to its influence on the $\delta^{13}C$ distribution [*Bergamaschi et al.*, 1996].

References

Bergamaschi, P., M. Schupp, and G.W. Harris, High-precision direct measurements of $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$ ratios in atmospheric methane sources by means of a long-path tunable diode laser absorption spectrometer, *Appl. Opt.*, *33*, 7704-7716, 1994.

Bergamaschi, P., C. Brühl, C.A.M. Brenninkmeijer, G. Saueressig, J.N. Crowley, J.U. Grooß, H. Fischer, and P.J. Crutzen, Implications of the large carbon kinetic isotope effect in the reaction $CH_4 + Cl$ for the $^{13}CH_4/^{12}CH_4$ ratio of stratospheric methane, *Geophys. Res. Lett.*, *23*, 2227-2230, 1996.

Cantrell, C.A., R.E. Shetter, A.H. McDaniel, J.G. Calvert, J.A. Davidson, D.C. Lowe, S.C. Tyler, R.J. Cicerone, and J.P. Greenberg, Carbon kinetic isotope effect in the oxidation of methane by the hydroxyl radical, *J. Geophys. Res.*, *95*, 22455-22462, 1990.

Crutzen, P.J., and U. Schmailzl, Chemical budgets of the stratosphere, *Planet. Space Sci.*, *31*, 9, 1009-1032, 1983.

Crutzen, P.J., On the role of CH_4 in atmospheric chemistry: Sources, sinks and possible reductions in anthropogenic sources, *Ambio*, *24*, 52-55, 1995.

Davidson, J.A., C.A. Cantrell, S.C. Tyler, R.E. Shetter, R.J. Cicerone, and J.G. Calvert, Carbon kinetic isotope effect in the reaction of CH_4 with HO, *J. Geophys. Res.*, *92*, 2195-2199, 1987.

DeMore, W. B. , Rate constant ratio for the reactions of OH with $^{12}CH_3D$ and CH_4 , *Appl. Opt.*, *33*, 7704-7716, 1994.

Gierczak, T., R.K. Talukdar, G.L. Vaghjiani, S. Hedron, and A.R. Ravishankara, Reactions of hydroxyl radicals with methane and deuterated methanes, cited (p 50) *JPL Publication 94-26*, 1994.

Gordon, S., and W.A. Mulac, Reaction of the $OH(X^2\pi)$ radical produced by the pulse radiolysis of water vapor *Int. J. Chem. Kinet., (Symp. 1)*, 289-299, 1975.

Irion, F.W., E.J. Moyer, M.R. Gunson, C.P. Rinsland, Y.L. Yung, H.A. Michelsen, R.J. Salawitch, A.Y. Chang, M.J. Newchurch, M.M. Abbas, M.C. Abrams, and R. Zander, Stratospheric oberservations of $^{12}CH_3D$ and HDO from ATMOS infrared solar spectra: Enrichments of deuterium in methane and implications for HD, *Geophys. Res. Lett.*, *23*, 2381-2384, 1996.

Lelieveld, J, P.J. Crutzen, and C. Brühl, Climate effects of atmospheric methane, *Chemosphere*, *26*, 739-768, 1993.

Lowe, D.C., C.A.M. Brenninkmeijer, G.W. Brailsford, K.R. Lassey, A.J. Gomez, and E.G. Nisbet, Concentration and ^{13}C records of atmospheric methane in New Zealand and Antarctica: evidence for changes in methane sources, *J. Geophys. Res.*, *99*, 16913-16925, 1994.

Quay, P.D., S.L. King, J. Stutsman, D.O. Wilbur, L.P. Steele, I. Fung, R.H. Gammon, T.A. Brown, G.W. Farwell, P.M. Grootes, and F.H. Schmidt, Carbon isotopic composition of atmospheric CH_4: fossil and biomass burning source strengths, *Global Biogeochem. Cycles*, *5*, 25-47, 1991.

Rothman, L.S., R.R. Gamache, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D. Chris Benner, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, and R.A. Toth, The HITRAN molecular database: editions of 1991 and 1992, *J. Quant. Spectros. Radiat. Transfer*, *48*, 469-507, 1992.

Saueressig, G., P. Bergamaschi, J.N. Crowley, H. Fischer, and G.W. Harris, Carbon kinetic isotope effect in the reaction of CH_4 with Cl atoms. *Geophys. Res. Lett.*, *22*, 1225-1228, 1995.

Stevens, C.M., and A. Engelkemeir, Stable carbon isotopic composition of methane from natural and anthropogenic sources, *J. Geophys. Res.*, *93*, 725-733, 1988.

Wahlen, M., The global methane cycle, *Annu. Rev. Earth Planet Sci.*, *21*, 407-426, 1993.

Wallington, T.J., and M.D. Hurley, A kinetic study of the chlorine atoms with CF_3CHCl_2, CF_3CH_2F, $CFCl_2CH_3$, CF_2ClCH_3, CHF_2CH_3, CH_3D, CH_2D_2, CHD_3, CD_4 and CD_3Cl at $295 \pm 2K$, *Chem. Phys. Lett.*, *189*, 437-442, 1992.

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