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Kinetic isotope effects of $^{12}CH_3D + OH$ and $^{13}CH_3D + OH$ from 278 to 313 K

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Abstract. Methane is the second most important long lived greenhouse gas and plays a central role in the chemistry of the Earth's atmosphere. Nonetheless there are significant uncertainties in its source budget. Analysis of the isotopic composition of atmospheric methane, including the doubly substituted species $^{13}CH_3D$ offers new insight on the methane budget as the sources and sinks have distinct isotopic signatures. The most important sink of atmospheric methane is oxidation by OH in the troposphere which accounts for around $84\,\%$ of all methane removal. Here we present experimentally derived methane + OH kinetic isotope effects and their temperature dependence over the range of 278 to 313 K for CH_3D and $^{13}CH_3D$; the latter is reported here for the first time. We find $k_{CH_4}/k_{CH_3D} = 1.31 \pm 0.01$ and $k_{CH_4}/k_{^{13}CH_3D} = 1.34 \pm 0.03$ at room temperature, implying that the methane + OH kinetic isotope effect is multiplicative such that $(k_{CH_4}/k_{^{13}CH_4})(k_{CH_4}/k_{CH_3D}) = k_{CH_4}/k_{^{13}CH_3D}$, within the experimental uncertainty, given the literature value of $k_{CH_4}/k_{^{13}CH_4} = 1.0039 \pm 0.0002$. In addition, the kinetic isotope effects were characterized using transition state theory with tunneling corrections. Good agreement between the experimental, quantum chemical, and available literature values was obtained. The theoretical calculation confirms that the $^{13}CH_3D$ isotope effect is the product of D- and ^{13}C- isotope effects. Based on the results we conclude that the OH reaction (the main sink of methane) at steady-state can produce an atmospheric clumped isotope signal ($\Delta(^{13}CH_3D) = \ln([CH_4][^{13}CH_3D]/[^{13}CH_4][CH_3D])$) of 0.02 ± 0.02. This implies that the bulk tropospheric $\Delta(^{13}CH_3D)$ reflects the source signal with relatively small adjustment due to the sink signal (i.e. mainly OH oxidation).

1 Introduction

Atmospheric methane is the subject of increasing interest from both the climate research community and the public due its impacts on climate change, as reported by the IPCC (2013). The direct radiative forcing of methane is 0.64 $\mathrm{Wm^{-2}}$. Including feedback mechanisms and secondary effects e.g. increased $\mathrm{O_3}$ production, stratospheric water vapor and production of $\mathrm{CO_2}$, methane's radiative forcing becomes 0.97 $\mathrm{Wm^{-2}}$, $2/3$ of the forcing by $\mathrm{CO_2}$ over the same time period (IPCC, 2013, Fig. 8.15).

Atmospheric methane has both natural and anthropogenic sources and the two categories contribute about equally (Ciais et al., 2013, and references therein). Wetlands are the dominant natural source, and agriculture and waste are the largest anthropogenic sources. Fossil fuels make smaller contributions. A majority ($84\,\%$) of atmospheric methane is removed by oxidation by OH in the troposphere:

$$\mathrm{CH_4 + OH \rightarrow CH_3 + H_2O}, \tag{R1}$$

while oxidation in the troposphere by Cl contributes about $4\,\%$ of the total:

$$\mathrm{CH_4 + Cl \rightarrow CH_3 + HCl}. \tag{R2}$$

About $8\,\%$ of methane is removed in the stratosphere by radical oxidation, such as reactions (R2) and (R3):

$$\mathrm{CH_4 + O(^1D) \rightarrow CH_3 + OH}. \tag{R3}$$

The rest ($4\,\%$) is removed by soil (Kirschke et al., 2013).

Carbon and hydrogen isotopic analysis are widely used to distinguish microbial and thermal sources of atmospheric methane (e.g., Lowe et al., 1997; Ferretti et al., 2005; Tyler et al., 2007; Lassey et al., 2007). However, reactions (R1), (R2), and (R3) produce relatively large D/H isotope effects (Saueressig et al., 1995, 1996, 2001; Crowley et al., 1999; Feilberg et al., 2005). Thus, the construction of an accurate top-down methane budget by isotopic analysis must take the isotopic signatures of both sources and sinks into account (Quay et al., 1999; Bergamaschi et al., 2000; Allan et al., 2001a, b). An isotope budget based on methane source (and sink) fractionations is an underdetermined systems (e.g., Pohlman et al., 2009). Recent advances in mass spectrometry (Eiler et al., 2013; Stolper et al., 2014) and laser infrared spectroscopy (Ono et al., 2014; Wang et al., 2015) facilitate measurement of rare double-substituted isotopologues. The abundance of these "clumped" isotopologues (clumped refers to the rare isotopes being clumped together) generally follows a stochastic distribution (i.e. $[^{12}\mathrm{CH_4}][^{13}\mathrm{CH_3D}] = [^{13}\mathrm{CH_4}][^{12}\mathrm{CH_3D}]$). However, small deviations from stochastic distribution can be induced by thermodynamic (Ma et al., 2008; Stolper et al., 2014; Liu and Liu, 2016), kinetic (Joelsson et al., 2014; Wang et al., 2015), and photolytic processes (Schmidt et al., 2013; Schmidt and Johnson, 2015). Analysis of the clumped isotope anomaly in methane will yield

unique constraints for the methane budget. Optical methods, as will be shown in this paper, provide high throughput and accuracy for overcoming the problems of analysis of clumped CH_4. The difference and advantage of this approach is the additional information not available in single isotope analysis, especially regarding the mechanism of formation, independent of the enrichment of D and ^{13}C in the starting material.

The kinetic isotope effect ${}^{j}E\alpha$ is a characteristic property of each process:

$$ {}^{j}E\alpha \equiv \frac{k({}^{i}E + OH)}{k({}^{j}E + OH)}, \tag{1} $$

where ${}^{i}E$ is the most abundant (here, the lighter) isotopologue, ${}^{j}E$ the rare (heavy) isotopologue, $k(E + OH)$ is the reaction rate coefficient for the reaction $E + OH$. As a measure of how much of a fractionation of $^{13}CH_3D$ kinetic reactions produce, the apparent clumpiness, γ is used. It is a measure of the effect of the clumped substitution on the reaction rate, as opposed to the combined effect of two single substitutions. It is defined as (Wang et al., 2015):

$$ \gamma \equiv \frac{{}^{13C,D}\alpha}{{}^{13C}\alpha \times {}^{D}\alpha} \tag{2} $$

A related measure is the $\Delta(^{13}CH_3D)$ value that quantifies the extent to which rare isotopes clump together to form a multiply substituted species, as opposed to a stochastic distribution (Ono et al., 2014):

$$ \Delta(^{13}CH_3D) \equiv \ln\left(\frac{[^{13}CH_3D][^{12}CH_4]}{[^{12}CH_3D][^{13}CH_4]}\right), \tag{3} $$

where $[^{13}CH_3D]$, $[^{12}CH_4]$, $[^{12}CH_3D]$ and $[^{13}CH_4]$ represent the concentrations of the different isotopologues.

The kinetic isotope effects for the singly substituted species CH_3D and $^{13}CH_4$ have been studied previously both experimentally and theoretically, see Tables 3 and 4 respectively. The kinetic isotope effect ${}^{13C,D}\alpha$ for the reaction with OH is not described in the existing literature. The related kinetic isotope effect for the $CH_4 + Cl$ reaction was measured at room temperature with the present setup by Joelsson et al. (2014) and found to be 1.60 ± 0.04. The kinetic isotope effects in the doubly substituted methane isotopologue CH_2D_2 for the reaction $CH_4 + Cl$ has been studied previously by Feilberg et al. (2005).

In the present study the kinetic isotope effects ${}^{D}\alpha$ and ${}^{13C,D}\alpha$ are determined using the relative rate method. Species concentrations in the reaction cell are determined using Fourier Transform Infrared (FTIR) spectroscopy. Further, ${}^{D}\alpha$, ${}^{13C}\alpha$, and ${}^{13C,D}\alpha$ are calculated using quantum chemistry and transition state theory.

2 Experimental procedures

16 experiments were conducted, numbered from 1 through 16, see Table 1; eight (Experiments 1–8) for $^{12}CH_3D$ and eight (Experiments 9–16) for $^{13}CH_3D$. The experiments were conducted at four different temperatures ($T = 278, 288, 298, 313\mathrm{K} = 5, 15, 25, 40^{\circ}\mathrm{C}$); two experiments were conducted for each temperature.

2.1 Relative rate method

The experiments were carried out using the relative rate method on a semi-static gas mixture. The decaying concentrations of reactants were measured as a function of the extent of reaction. Considering two bimolecular reactions with second order rate coefficients k_{A} and k_{B},

$$\mathrm{A} + \mathrm{OH} \xrightarrow{k_{\mathrm{A}}} \mathrm{Products}, \tag{R4}$$

$$\mathrm{B} + \mathrm{OH} \xrightarrow{k_{\mathrm{B}}} \mathrm{Products}, \tag{R5}$$

and assuming there were no other loss processes, the following relation holds:

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) = \frac{k_{\mathrm{A}}}{k_{\mathrm{B}}} \ln\left(\frac{[\mathrm{B}]_0}{[\mathrm{B}]_t}\right). \tag{4}$$

Here $[\mathrm{A}]_0$, $[\mathrm{A}]_t$, $[\mathrm{B}]_0$ and $[\mathrm{B}]_t$ represent the concentrations of compounds A and B at times 0 and t respectively. The slope of $\ln([\mathrm{A}]_0/[\mathrm{A}]_t)$ versus $\ln([\mathrm{B}]_0/[\mathrm{B}]_t)$ gives the relative reaction rate coefficient. In these experiments A is $^{12}CH_4$ and B is $^{12}CH_3D$ or $^{13}CH_3D$.

2.2 Photoreactor

Experiments were carried out in the photochemical reactor at the University of Copenhagen, Department of Chemistry. The reactor has been described in detail elsewhere (Nilsson et al., 2009). It consists of a 100 L quartz cell with multi-pass optics surrounded by 16 UV-C fluorescent Hg lamps in a temperature controlled housing. The cell is coupled to a Bruker IFS 66v/S FTIR spectrometer with either a mercury cadmium telluride (MCT) detector (Experiments 1–4) or an indium antimonide (InSb) (Experiments 5–16). The InSb-detector has a better signal-to-noise ratio, the MCT-detector is used in Experiments 1–4 for logistical reasons. Two thermocouple gauges are placed inside the temperature controlled housing to monitor the temperature and a pressure gauge is connected to the cell to monitor pressure inside the cell. The temperatures and the pressures were logged every 0.5 s.

2.3 Laboratory proceedure

Gas mixes were prepared by expanding H_2O vapor (Milli-Q Ultrapure Water) into the chamber through a glass gas manifold. The two methane isotopologues CH_3D (Experiments 1–8) (purity

$> 98\%$, Cambridge Isotope Laboratories, Inc.) or $^{13}CH_3D$ (Experiments 9–16), and CH_4 (purity $> 99\%$, Aldrich) and O_3 were flushed into the chamber with a N_2 buffer (purity 99.998%, Air Liquide), all at the concentrations given in Table 1. $^{13}CH_3D$ was synthesized using the Grignard reaction, see Joelsson et al. (2014). O_3 was generated from O_2 (purity 99.97 %, Air Liquide) using an ozone generator (Model AC-20, O_3 Technology), preconcentrated before injection on silica gel cooled with ethanol and dry ice to $-67°C$. The desired pressure in the cell (450 hPa) was obtained using N_2 as bath gas. The starting pressure is chosen such that the pressure is high enough for the N_2 to quench $O(^1D)$ radicals, but low enough to keep the final pressure below atmospheric pressure. The gas mixture was left to rest for up to 1.5 $hours$ while several IR spectra were recorded to ensure that no instability or dark chemistry occurs in the gas mix. The UV-C lamps were lit for up to 5 min photolysing at least 75 % of the O_3 according to:

$$O_3 + h\nu \rightarrow O(^1D) + O_2. \quad \text{(R6)}$$

$O(^1D)$ then subsequently reacts with H_2O to yield OH:

$$O(^1D) + H_2O \rightarrow OH + OH. \quad \text{(R7)}$$

Up to 0.2 Pa O_3 was flushed with about 20 hPa N_2 into the chamber to compensate for the loss of ozone with time, mainly due to $O(^3P) + O_3$. A pressure gradient was established and maintained throughout the filling process such that no gas leaked back from the chamber into the gasline. Spectra were recorded at each filling step. The procedure was repeated until the mix had a final pressure of 933 hPa. Two experiments were conducted at each of the temperatures 278, 288, 298, and 313 K for each of the two heavy methane istopologues. Exact temperatures are listed in Table 1. After each experiment a dilution test was performed: 133 hPa was pumped out and the chamber is refilled with 133 hPa N_2. This was repeated 5–6 times. Ideally, concentration calculations from the spectral fits (data analysis described below) of the resulting spectra should give a linear fit with the slope of 1. The slope of these dilution tests are presented in Table 2. In an extra experiment with $^{12}CH_3D$, N_2O (Air Liquide, no purity information available) was added as an $O(^1D)$ tracer. The results from this experiment are used as a benchmark to validate a model that was constructed to investigate the extent of $O(^1D)$ chemsitry, see Sect. 2.5. An example of an experimental plot can be found in Fig. 4 and the full data set in Figs. S1–S8 in the Supplement.

2.4 Data analysis

The experimental IR spectra were analyzed using the program MALT which simulates experimental FTIR spectra (Griffith, 1996) combined with non-linear least squares fitting to best-fit the calculated spectra to measured spectra (Griffith et al., 2012). The MALT program generates a simulated spectrum from initial estimates of the absorber concentrations and instrument parameters. The residual between the experimental and simulated spectra is reduced through iteration. Simulated line-shapes

Table 1. Experimental setup. The experiment numbers are listed in column Exp., the detector in the column Detect., the heavy CH_4 isotopologue included in the experiments are listed in column $[^xCH_3D]$, the mean measured temperatures in the photoreactor are listed in column T, the H_2O-vapour concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[H_2O]_{t=0}$, the mean O_3 concentration after refill (i.e. the "top"-values) as obtain from spectral fitting are listed in column $[O_3]_{\text{top}}$, the $^{12}CH_4$- concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[^{12}CH_4]_{t=0}$, and the heavy CH_4 concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[^xCH_3D]_{t=0}$. Note that for the experiment including CH_3D, the value of initial concentration only refers to $[^{12}CH_3D]_{t=0}$.

Exp.	Detect.	$^xCH_3D$	T /K	$[H_2O]_{t=0}$ /hPa	$[O_3]_{\text{top}}$ /hPa	$[^{12}CH_4]_{t=0}$ /hPa	$[^xCH_3D]_{t=0}$ /hPa
1	MCT	CH_3D	298.2 ± 1.2	7.1	–[a]	0.030	0.054
2	MCT	CH_3D	297.6 ± 0.8	5.6	0.19	0.058	0.042
3	MCT	CH_3D	277.2 ± 0.2	5.2	0.29	0.109	0.046
4	MCT	CH_3D	277.0 ± 0.2	5.1	0.16	0.073	0.035
5	InSb	CH_3D	284.5 ± 0.1	7.2	0.26	0.025	0.033
6	InSb	CH_3D	291.1 ± 0.2	7.4	–[a]	0.052	0.050
7	InSb	CH_3D	313.5 ± 1.3	7.1	0.17	0.025	0.029
8	InSb	CH_3D	312.4 ± 0.9	4.3	–[a]	0.022	0.040
9	InSb	$^{13}CH_3D$	298.5 ± 0.1	5.1	–[a]	0.035	0.026
10	InSb	$^{13}CH_3D$	297.6 ± 0.6	6.4	0.13	0.025	0.033
11	InSb	$^{13}CH_3D$	276.8 ± 0.8	5.4	–[a]	0.024	0.024
12	InSb	$^{13}CH_3D$	277.2 ± 1.3	5.1	–[a]	0.022	0.030
13	InSb	$^{13}CH_3D$	287.4 ± 1.2	5.4	–[a]	0.021	0.028
14	InSb	$^{13}CH_3D$	287.4 ± 0.4	4.5	–[a]	0.016	0.029
15	InSb	$^{13}CH_3D$	314.4 ± 1.0	5.2	0.26	0.023	0.037
16	InSb	$^{13}CH_3D$	313.8 ± 0.8	8.3	0.17	0.025	0.035

[a] Spectra recorded during or after photolysis, $[O_3]_{\text{top}}$ not availible

are generated using HITRAN absorption parameters (version 2008) (Rothman et al., 2009) convolved with an FTIR instrument function simulating the Bruker IFS 66v/S instrument. The InSb detector covers a spectral range from 1800–5000 cm^{-1} and the MCT detector covers a spectral range from 400–5000 cm^{-1}. The concentrations of $^{12}CH_3D$ and $^{13}CH_3D$ were calculated from spectral fits in the region 2140–2302 cm^{-1}, see Fig. 1 and 2. Interference from H_2O, CO_2, and CO was eliminated by including simulated spectra obtained from the HITRAN database in the fit. As there is no HITRAN data available for $^{13}CH_3D$ in this region, the cross sections from 2000–2400 cm^{-1} for this isotopologue were estimated by shifting the spectrum of $^{12}CH_3D$, see Joelsson et al. (2014). Concentrations of $^{12}CH_4$ were calculated from spectral fits in the region 2838–2997 cm^{-1}.

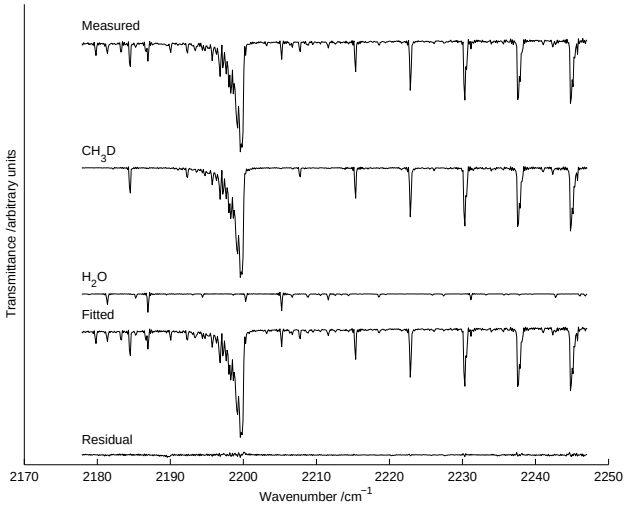

Figure 1. A typical spectral fit in the region where $[^{12}CH_3D]$ is obtained (Experiment 5). Experimental data are shown by the topmost line, followed by the fitted (synthetic) partial spectra of the most dominant absorbers (CH_3D and H_2O), the resulting fitted (synthetic) spectrum (also including CO_2 and CO), and the residual between the measured and fitted spectra is shown by the bottom line.

Interference from $^{13}CH_3D$ was reduced by including temperature adjusted reference spectra in the fit, and interference from $^{12}CH_3D$, H_2O, and H_2CO was by including simulated spectra obtained from the HITRAN database in the fit, see Fig. 3. The spectral windows were sometimes adjusted to exclude saturated lines.

After $[^{x}CH_3D]$ (where $x = 12$ or $x = 13$) and $[^{12}CH_4]$ were obtained from the spectral analysis, $\ln([^{x}CH_3D]_0/[^{x}CH_3D]_t)$ was plotted against $\ln([^{12}CH_4]_0/[^{12}CH_4]_t)$ as described in Sect. 2.1. A straight line was fitted to these data points using a weighted total least squares routine (York et al., 2004). The fitting procedure takes uncertainties in both dimensions into account. The uncertainty $\sigma(\ln([A]_0/[A]_t))$ was calculated using standard error propagation:

$$\sigma(\ln([A]_0/[A]_t)) = \sqrt{\left(\frac{\sigma([A]_0)}{[A]_0}\right)^2 + \left(\frac{\sigma([A]_t)}{[A]_t}\right)^2} \quad (5)$$

where $\sigma([A]$ was obtained as output from MALT. The fitting proceedure, performed using a MATLAB script (York et al., 2004), also yields an error estimation which is defined as the uncertainty of the kinetic isotope effect $\sigma(\alpha)$. An example of a straight line fit can be found in Fig. 4 and the full data set in Figs. S1–S8 in the Supplement. In the temperature dependence curve fitting procedure, the parameters A and B are from a linearized version of the Arrhenius equation:

$$\ln(k) = \ln(A) + B \cdot T^{-1} \quad (6)$$

are adjusted to match experimental. Also here, the method of York et al. (2004) was used. The temperature in the cell was taken as the spatial average of the measurements from two thermocouples

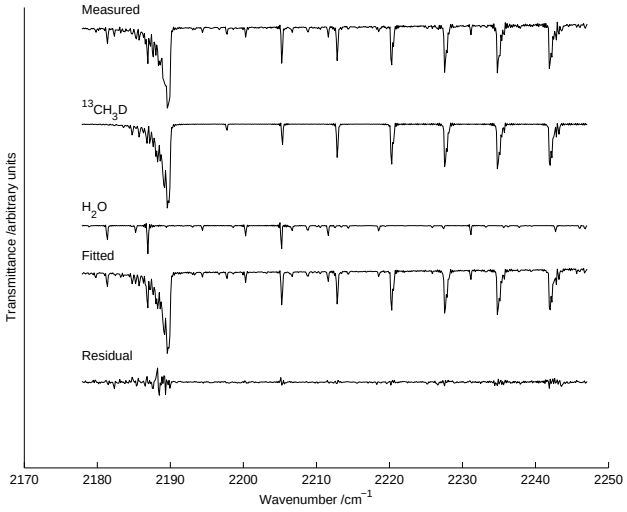

Figure 2. A typical spectral fit in the region where [$^{13}CH_3D$] is obtained (Experiment 10). Experimental data are shown by the topmost line, followed by the fitted (synthetic) partial spectra of the most dominant absorbers ($^{13}CH_3D$ and H_2O), the resulting fitted (synthetic) spectrum (also including CO_2 and CO), and the residual between the measured and fitted spectra is shown by the bottom line.

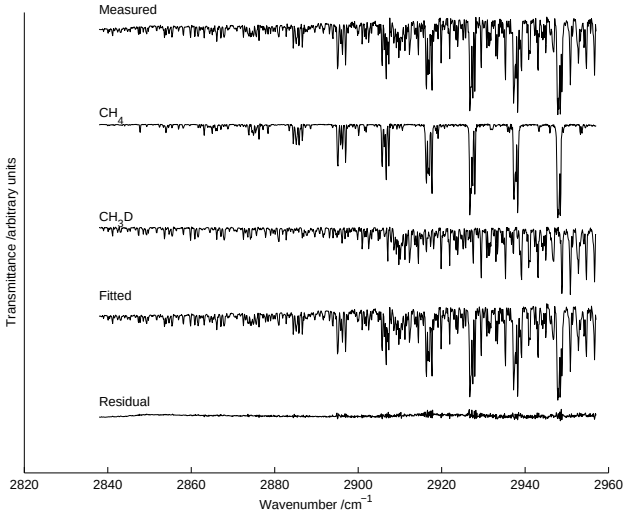

Figure 3. A typical spectral fit in the region where [$^{12}CH_4$] is obtained (Experiment 5). Experimental data are shown by the topmost line, followed by the fitted partial (synthetic) spectra of the most dominant absorbers (CH_4 and CH_3D), the resulting fitted (synthetic) spectrum (also including H_2O), and the residual between the measured and fitted spectra is shown by the bottom line.

inside the temperature housing. The experiment temperature was defined by the temporal mean of the spatially averaged temperature measurement series and the uncertainty of the experiment temperature was the standard deviation of the spatially averaged temperature measurement series.

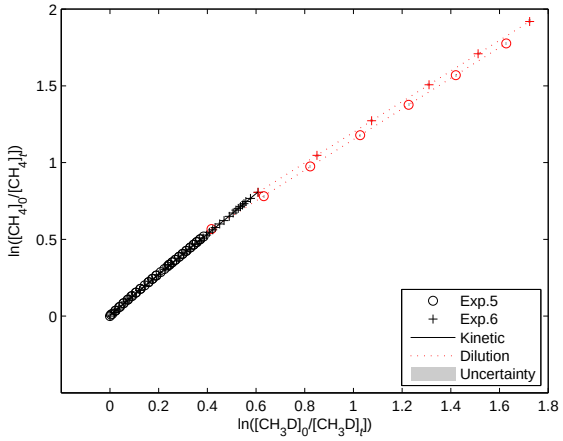

Figure 4. A typical experimental outcome, Experiment 5 and 6: CH_3D, $T = 288$K. Experimental data are shown using black open circles (Exp. 5) and black plus signs (Exp. 6). Corresponding dilution test points are shown using red symbols. A linear fit of the experimental points is shown using a black solid line and linear fit of the subsequent dilution test are represented by a red dotted line, uncertainties for each point are represented by gray areas.

2.5 Kinetic model

A kinetic model was used to determine the influence of $O(^1D)$, reaction (R3), which rivals Reaction (R1).The model is previously described and was used by Nilsson et al. (2012). However, only the methane reaction subset and associated (O_x and HO_x) chemistry were used here. The Kintecus program (Ianni, 2003), simulates the photolysis of O_3 and the following oxidation chain of CH_4. To model ozone photolysis accurately, the modeled O_3 was matched to the measured value by adjusting the photolysis rate, then the model was verified by comparing the decrease of CH_4 and the increase of H_2O during the experiment. The model was run for each refill of O_3, where the reaction rates of Reactions (R1) and (R3) were obtained. The model was designed for room temperature; experiments at other temperatures were not modeled. Experiment 2 was thus modeled: 4.4% of CH_4 was estimated to be lost to Reaction (R3). In an additional experiment N_2O was introduced in the chamber as an $O(^1D)$-tracer. Since N_2O does not react with OH and is not photolyzed at the wavelengths present (Nilsson et al., 2009), the decreased of N_2O should be only due to Reaction (R8):

$$N_2O + O(^1D) \rightarrow \text{products.} \tag{R8}$$

The amount of CH_4 lost by reaction (R3) can therefore be approximated by:

$$1 - \frac{[CH_4]_t}{[CH_4]_0} = 1 - \exp\left(-k_{(R3)}[O(^1D)]t\right) = 1 - \frac{[N_2O]_t}{[N_2O]_0}^{(k_{(R8)}/k_{(R3)})}, \tag{7}$$

where $k_{(R8)} = 1.27 \times 10^{-10} \mathrm{cm}^{-3}\mathrm{s}^{-1}$ and $k_{(R3)} = 1.75 \times 10^{-10} \mathrm{cm}^{-3}\mathrm{s}^{-1}$ (Sander et al., 2010). This gives 2.3% $[CH_4]$ lost by oxidation of $O(^1D)$, Reaction (R3). The kinetic model described above estimated that 4.7 % $[CH_4]$ were lost by Reaction (R3) for this additional experiment. Both methods agree that $O(^1D)$ loss is a minor channel. No correction is applied, and the possible deviation is included in the estimated error.

3 Theoretical procedure

Rate constants and kinetic isotope effects for $CH_4 + OH$ were calculated using a procedure similar to that employed by Joelsson et al. (2014).

3.1 Computational chemistry calculations

The geometries of reactants, products and transition states were determined using a geometry optimization procedure based on the unrestricted MP2 method (Møller and Plesset, 1934) and the aug-cc-pVQZ orbital basis set (Dunning Jr., 1989; Woon and Dunning Jr., 1993). Harmonic vibrational frequencies for all relevant isotopologues of reactants, products, and transition states were obtained at the same level of theory. The calculations were carried out using the Gaussian 09 program package (Frisch et al., 2009).

The electronic energy of the optimized structures were refined using the CCSD(T) method (Watts et al., 1993; Knowles et al., 1993, 2000) with aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets. The results from the different basis sets were used to extrapolate the electronic energy at the complete basis set limit following the approach of Halkier et al. (1998) as described by Joelsson et al. (2014).

3.2 Rate constant calculations

The abstraction of a CH_4 hydrogen atom by OH can occur at four different sites. Depending on the methane isotopologue in question, these sites are either distinguishable or indistinguishable. Microscopic rate constants are calculated for hydrogen abstraction at each site using classical transition state theory with a tunneling correction factor,

$$k^{(i)}_{\mathrm{micro}} = \eta^{(i)}_{\mathrm{tun}} \frac{k_b T}{h} \frac{Q^{(i)}_{\mathrm{TS}}}{Q_{\mathrm{reac}}} \exp\left(-\Delta E^{(i)}/RT\right) \tag{8}$$

where $\Delta E^{(i)}$ is the reaction barrier height (including the zero point vibrational energy) for the i'th reaction path. $\eta^{(i)}_{\mathrm{tun}}$ is a tunneling correction factor obtained using the Wigner tunneling correction (Wigner, 1932). $Q^{(i)}_{\mathrm{TS}}$ and Q_{reac} are the partition functions for the transition state and reacting pair, respectively. The total rate constant is obtained by summing over the microscopic rate constants.

Table 2. Results. The experiment numbers are listed in column Exp., the heavy CH_4 isotopologue included in the experiments are listed in column $^{x}CH_3D$, the mean measured temperatures in the photoreactor are listed in column T, the kinetic isotope effect corresponding to the isotopologue are listed in column α, and the result of the dilution experiments are listed in column k_{dil}.

Exp.	$^{x}CH_3D$	T/K	α	k_{dil}
1	CH_3D	298.2 ± 1.2	1.302 ± 0.038	1.011 ± 0.048
2	CH_3D	297.6 ± 0.8	1.314 ± 0.020	–[a]
3	CH_3D	277.2 ± 0.2	1.294 ± 0.017	0.962 ± 0.037
4	CH_3D	277.0 ± 0.2	1.335 ± 0.017	–[a]
5	CH_3D	284.5 ± 0.1	1.334 ± 0.012	0.999 ± 0.009
6	CH_3D	291.1 ± 0.2	1.323 ± 0.010	0.998 ± 0.010
7	CH_3D	313.5 ± 1.3	1.301 ± 0.007	1.006 ± 0.031
8	CH_3D	312.4 ± 0.9	1.338 ± 0.010	–[a]
9	$^{13}CH_3D$	298.5 ± 0.1	1.359 ± 0.022	1.000 ± 0.029
10	$^{13}CH_3D$	297.6 ± 0.6	1.314 ± 0.007	0.990 ± 0.064
11	$^{13}CH_3D$	276.8 ± 0.8	1.357 ± 0.046	1.016 ± 0.031
12	$^{13}CH_3D$	277.2 ± 1.3	1.344 ± 0.013	1.008 ± 0.030
13	$^{13}CH_3D$	287.4 ± 1.2	1.346 ± 0.025	1.009 ± 0.022
14	$^{13}CH_3D$	287.4 ± 0.4	1.342 ± 0.015	1.011 ± 0.019
15	$^{13}CH_3D$	314.4 ± 1.0	1.316 ± 0.016	1.003 ± 0.038
16	$^{13}CH_3D$	313.8 ± 0.8	1.331 ± 0.033	1.001 ± 0.034

[a] No dilution test performed

4 Results and Discussion

The results of the 16 individual experiments (eight for each isotopologue) are tabulated in Table 2. The resulting $^{\text{D}}\alpha$, $^{13\text{C}}\alpha$, and $^{13\text{C,D}}\alpha$ values from the experimental and theoretical studies are tabulated in Tables 3, 4, and 5 along with previous experimental and theoretical results. The results are also shown in Fig. 5 and 6 for reactions of CH_3D and $^{13}CH_3D$ respectively.

The exponential curve fits yielded the parameters presented in Tables 3 and 5 giving $^{\text{D}}\alpha_{\text{Arr}} = 1.32 \pm 0.13$ and $^{13\text{C,D}}\alpha_{\text{Arr}} = 1.32 \pm 0.20$ at $T = 298\text{K}$. The mean of results of room temperature experiments Experiments 1 and 2, and Experiments 9 and 10 is $^{\text{D}}\alpha_{\text{exp}} = 1.31 \pm 0.01$ and $^{13\text{C,D}}\alpha_{\text{exp}} = 1.34 \pm 0.03$ respectively. It follows that $\gamma_{\text{exp}} = 1.02 \pm 0.02$ at $T = 298\text{K}$, using $^{13\text{C}}\alpha_{\text{exp}} = 1.0039 \pm 0.0002$ (Saueressig et al., 2001), meaning that the clumped isotope might react slower relative to what would be predicted based on the kinetic isotope effects of CH_3D and $^{13}CH_4$. However, if the Arrhenius parameters are used to calculate the kinetic isotope effects at $T = 298\text{K}$, $\gamma_{\text{Arr}} = 1.00 \pm 0.18$ (i.e. the reaction has no clumping effect). All uncertainties are given as one standard deviation (σ). The theoretical results gives $\gamma_{\text{theory}} = 1.00$ at $T = 298\text{K}$.

Table 3. Experimental and theoretical studies of ${}^{\mathrm{D}}\alpha$. The temperature dependence studies are presented in the Arrhenius form ${}^{\mathrm{D}}\alpha(T) = A(T/298\mathrm{K})^n \exp(BT^{-1})$, where A, n, and B are tabulated, T is the given temperature range, and ${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$ is the resulting kinetic isotope effect at $T = 298\mathrm{K}$. Where no B coefficient is presented A can be taken as ${}^{\mathrm{D}}\alpha(T)$ for the given temperature range. All uncertainties are given as one standard deviation (σ).

Study	A	n	B/K	T/K	${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$
Experimental studies					
Present study[a]	1.23 ± 0.08	0	21 ± 21	[278,313]	1.31 ± 0.01[h]
Saueressig et al. (2001)[b]	1.294 ± 0.009	–	–	296	–
Gierczak et al. (1997)[c]	1.09 ± 0.05	0	49 ± 11	[220,415]	1.25 ± 0.07
DeMore (1993)[a]	0.91	0	75	[298,360]	1.17
Gordon and Mulac (1975)[d]	1.50	–	–	416	–
Gordon and Mulac (1975)[d,i]	1.06	–	–	416	–
Theoretical studies					
Present study[e]	1.314	0	6.354	[200,300]	1.339
Sellevåg et al. (2006)[f]	$[1.30, 1.00]$	–	–	[200,1500]	1.27
Masgrau et al. (2001)[g,j]	1.00	-0.02	50.5	[200,1500]	1.25

[a] Fourier transform infrared spectroscopy - relative rate
[b] Tunable diode laser absorption spectroscopy - isotope ratio mass sectrometer
[c] Pulsed photolysis - pulsed laser-induced flourescence
[d] Pulse radiolysis
[e] Transition state theory with Wigner tunneling correction
[f] Canonical unified statistical theory
[g] Multicoefficient correlation method
[h] Average room temperature value, not obatined from curve fit
[i] Re-evaluated by DeMore (1993)
[j] Arrhenius parameters available at (NIST, 2015)

The present experimental room temperature results for ${}^{\mathrm{D}}\alpha$ agree, to within the error bars, with the previous experimental studies, with the exception of DeMore (1993). DeMore (1993) used FTIR spectroscopy with a slow flow setup where the two methane isotopologues were measured seperately with a common reference compound. The low ${}^{\mathrm{D}}\alpha$ value in DeMore (1993) may be explained by interference from $\mathrm{O}(^1\mathrm{D})$ radicals: OH radicals were produced by photolysis of $\mathrm{O_3}$ at 254 nm in the presence of $\mathrm{H_2O}$, as in the present study. A relatively high rate of reaction (R3) would reduce the final kinetic isotope effect, since the kinetic isotope effect for oxidation with $\mathrm{O}(^1\mathrm{D})$ is smaller than the kinetic isotope effect for the oxidation of OH (Saueressig et al., 2001). The present experimental results of ${}^{\mathrm{D}}\alpha$ are also in good agreement with Masgrau et al. (2001) and Sellevåg et al. (2006). The theoretical calculations of ${}^{\mathrm{D}}\alpha$ give a slightly higher value than the experimental results, although they are in good agreement with the best Arrhenius curve fit at $T = 298\mathrm{K}$.

Table 4. Experimental and theoretical studies of ${}^{13\mathrm{C}}\alpha$. The temperature dependence studies are presented in the Arrhenius form ${}^{13\mathrm{C}}\alpha(T) = A\exp(BT^{-1})$, where A and B are tabulated, T is the given temperature range, and ${}^{13\mathrm{C}}\alpha(T = 298\mathrm{K})$ is the resulting kinetic isotope effect at $T = 298\mathrm{K}$. Where no B coefficient is presented A can be taken as ${}^{13\mathrm{C}}\alpha(T)$ for the given temperature range. All uncertainties are given as one standard deviation (σ).

Study	A	B/K	T/K	${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$
Experimental studies				
Saueressig et al. (2001)[a]	1.0039 ± 0.0002	–	296	–
Cantrell et al. (1990)[b]	1.0054 ± 0.0005	–	[273, 353]	1.0054 ± 0.0005
Rust and Stevens (1980)[c,i]	1.003	–	–	–
Theoretical studies				
Present study[d]	1.0137	-1.219	[200,300]	1.0094
Sellevåg et al. (2006)[e]	$[1.014, 1.00]$	–	[200,1500]	1.003
Gupta et al. (1997)[f]	1.010	–	300	–
Melissas and Truhlar (1993)[g,h]	$[1.005, 1.001]$	–	[223,416]	1.005
Lasaga and Gibbs (1991)[h]	[1.0036,1.0076]	–	[150,350]	–

[a] Tunable diode laser absorption spectroscopy - isotope ratio mass sectrometer

[b] Gas chromatography - mass spectrometry

[c] Isotope ratio mass spectrometry

[d] Transition state theory with Wigner tunneling correction

[e] Canonical variational transition state theory

[f] Conventional transition state theory

[g] Interpolated variational transition state theory with centrifugal-dominant, small-curvature tunneling coefficients

[h] Ab initio calculations

[i] No temperature information available

Table 5. Experimental and theoretical studies of ${}^{13\mathrm{C,D}}\alpha$. The temperature dependencies are presented in the Arrhenius form ${}^{13\mathrm{C,D}}\alpha(T) = A\exp(BT^{-1})$, where A and B are tabulated, T is the given temperature range, and ${}^{13\mathrm{C,D}}\alpha(T = 298\mathrm{K})$ is the resulting kinetic isotope effect at $T = 298\mathrm{K}$. All uncertainties are given as one standard deviation (σ).

Study	A	B/K	T/K	${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$
Experimental study[a]	1.18 ± 0.10	38 ± 26	[278,313]	1.34 ± 0.03[c]
Theoretical study[b]	1.328	5.301	[200,300]	1.349

[a] Fourier transform infrared spectroscopy - relative rate

[b] Transition state theory with Wigner tunneling correction

[c] Average room temperature value, not obatined from curve fit

The experimental room temperature result for ${}^{13\mathrm{C,D}}\alpha = 1.34 \pm 0.03$ agrees to within the error bar with both the theoretical value and the best estimate of the Arrhenius curve fit at $T = 298\mathrm{K}$.

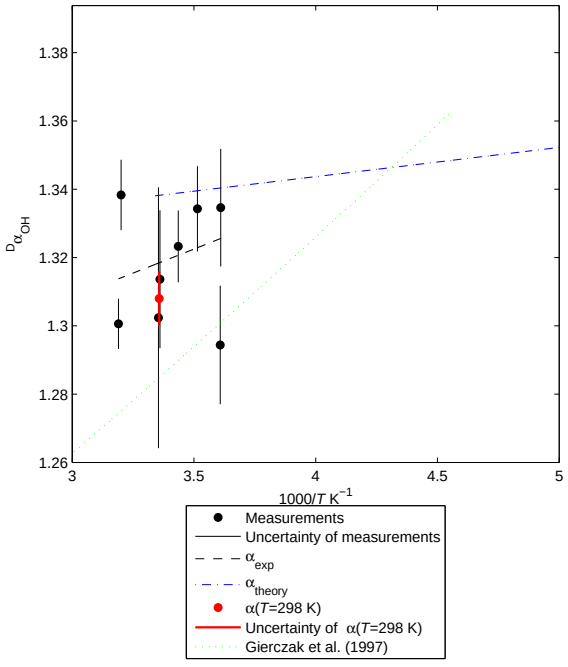

Figure 5. The individual measurements of ${}^{\mathrm{D}}\alpha$, are represented by black points; the accompaning individual error bars are represented by thin black solid lines; the experimental Arrhenius curve fit is represented by a black dashed line; the theoretical Arrhenius curve fit is represented by a blue dashed-dotted line; the mean of the room temperature measurements are represented by a red solid circle; the uncertainty of the room temperature measurements are represented by a thick red solid line; the result from Gierczak et al. (1997) (which is included for comparison) are represented by a green dotted line. All uncertainties are given as one standard deviation (σ).

The theoretical calculations show a very small temperature dependence; the variability in the experimental data is large compared to the value of the slope, making a quantification of the temperature dependence uncertain. Furthermore, the theoretical analysis revealed that the primary cause for the kinetic isotope effect is the substantially reduced reactivity of the D atom, which, in turn, can be explained by a significant increase in reaction barrier due to changes in vibrational zero point energy and to a lesser extent tunneling.

4.1 Atmospheric implications

At steady state, assuming no clumping in emissions, $\Delta(^{13}\mathrm{CH_3D}) = \ln(\gamma)$. It follows that $\Delta(^{13}\mathrm{CH_3D}) = 0.02 \pm 0.02$ implying that the clumped isotope effect of the OH reaction is small. Wang et al. (2015) have studied a variety of natural samples and found $\Delta(^{13}\mathrm{CH_3D})$ values that vary from

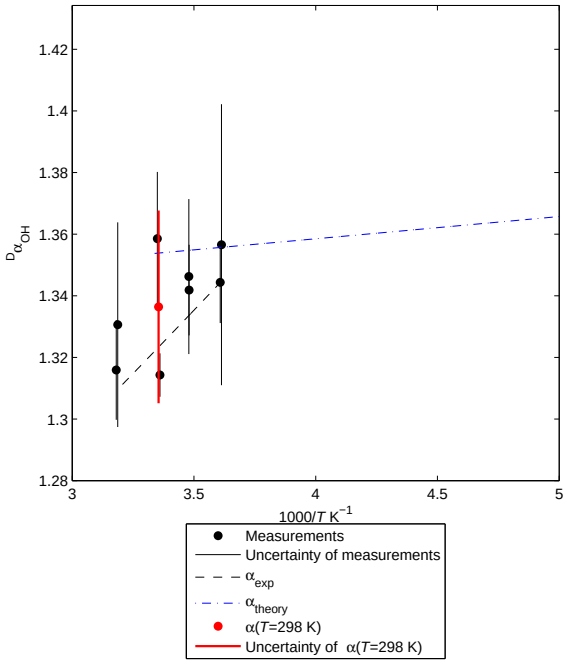

Figure 6. The individual measurements of ${}^{13\mathrm{C,D}}\alpha$, are represented by black points; the accompaning individual error bars are represented by thin black solid lines; the experimental Arrhenius curve fit is represented by a black dashed line; the theoretical Arrhenius curve fit is represented by a blue dashed-dotted line; the mean of the room temperature measurements are represented by a red solid circle; the uncertainty of the room temperature measurements are represented by a thick red solid line. All uncertainties are given as one standard deviation (σ).

$(-3.36 \pm 1.42)‰$ for samples of bubbling gases from The Cedars, Cazadero, California, USA, to $(6.17 \pm 0.34)‰$ for samples from gas voids and hydrates in sediment cores from the Northern Cascadia Margin. Methanogenic bacteria in the laboratory ranged from $-1.34‰$ to $2.29‰$. Natural gas was found to vary from $2.53‰$ to $5.18‰$. Given these natural variations in $\Delta(^{13}\mathrm{CH_3D})$ values of the sources, it is clear from isotopic mass balance that the fractionation from atmospheric oxidation by OH will likely have little effect on the observed $\Delta(^{13}\mathrm{CH_3D})$ value of tropospheric methane. Rather, this number will reflect the relative contributions of the sources. $\Delta(^{13}\mathrm{CH_3D})$ would therefore be a more straightforward tracer for tracking methane sources than conventional isotopic analysis. Further field studies are clearly needed to characterize $\Delta(^{13}\mathrm{CH_3D})$ values of microbial and thermal methane.

5 Conclusions

We present experimentally derived $CH_4 + OH$ kinetic isotope effects and their temperature dependence for CH_3D and $^{13}CH_3D$; the latter is reported for the first time. We find $^{D}\alpha = 1.31 \pm 0.01$ and $^{13C,D}\alpha = 1.34 \pm 0.03$ at room temperature, implying that the kinetic isotope effect is multiplicative such that $(k_{CH_4}/k_{^{13}CH_4})(k_{CH_4}/k_{CH_3D}) = k_{CH_4}/k_{^{13}CH_3D}$ to within the experimental uncertainty. We compare our experimental results to theoretical estimates derived using transition state theory with tunneling correction and kinetic isotope effects reported in the literature. We find good agreement between theoretical and literature values. Based on these experiments we find that the OH reaction (the main sink of methane) at steady-state has a clumped $\Delta(^{13}CH_3D) = 0.02 \pm 0.02$.

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