

Carbon kinetic isotope effect in the reaction $\text{CH}_4 + \text{Cl}$: a relative rate study using FTIR spectroscopy

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Abstract

The $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effect in the reaction of methane with chlorine atoms ($\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}}$) was investigated at 298 K using photolysis of static $\text{Cl}_2/\text{CH}_4/\text{N}_2$ mixtures, with in-situ analysis of isotopic composition by FTIR absorption spectroscopy. Least squares fitting of composite $^{12}\text{CH}_4/^{13}\text{CH}_4$ spectra to reference spectra obtained at the same temperature, pressure and resolution enabled the relative $^{12}\text{CH}_4/^{13}\text{CH}_4$ content to be measured at a high precision. The result obtained was $\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}}(298\text{ K}) = 1.066 \pm 0.002 (2\sigma)$, in excellent agreement with the single previous experimental determination at this temperature. This result confirms the unexpectedly high fractionation in the title reaction.

1. Introduction

The important role that the atmospheric trace gas methane (CH_4) plays both as a greenhouse gas [1] and in the chemistry of both the troposphere and stratosphere [1,2], is reflected in the scientific effort that has been directed into understanding and characterising its sources and sinks [3,4]. Measurements of the isotopic composition of atmospheric methane can be used to identify and quantify the relative contributions of its various sources, which each carry a distinct isotopic signature, as long as reliable laboratory data on isotopic fractionation in the reactions that remove CH_4 from the atmosphere are available [5–7].

The reaction between Cl-atoms and CH_4 represents an important removal process for stratospheric CH_4 where it may contribute up to 35% of the total CH_4 loss in the middle and upper stratosphere at mid-latitudes, and even more at high latitudes [8]. To date, a single experimental determination of the $^{12}\text{C}/^{13}\text{C}$ fractionation of CH_4 in its reaction with chlorine atoms has been made at this institute [9] and which determined a surprisingly high carbon kinetic isotope effect $\text{KIE}^{12\text{C}/13\text{C}} = 1.066 \pm 0.002$ at 298 K, which increased to 1.075 ± 0.005 at 223 K. For comparison the reaction with OH has a $\text{KIE}_{\text{OH}}^{12\text{C}/13\text{C}} \approx 1.005$ [10]. When incorporated into a 2-D model [8] of the stratospheric chemistry of CH_4 , this large KIE was found to significantly alter $^{12}\text{CH}_4/^{13}\text{CH}_4$ ratios especially in the middle and upper stratosphere, but also in the lower stratosphere, where it brought modelled and measured $^{12}\text{CH}_4/^{13}\text{CH}_4$ ra-

tios closer in agreement [11–14]. The $\text{CH}_4 + \text{Cl}$ reaction produces CO highly depleted in ^{13}C ($\sim -110\%$), leading to significant depletion of CO in the lower Antarctic stratosphere [12,15], as well as during tropospheric ozone depletion events in the Arctic [16]. Furthermore, the reaction $\text{CH}_4 + \text{Cl}$ has a significant impact [17] on the $\delta^{13}\text{C}$ balance of atmospheric CH_4 and may also influence the isotopic composition of CH_4 in the marine boundary layer, where evidence for the presence of Cl atoms has been obtained [18].

Recent theoretical calculations using conventional transition state theory (CTST) [19,20] have predicted a significantly lower $^{12}\text{C}/^{13}\text{C}$ fractionation in the $\text{Cl} + \text{CH}_4$ reaction at room temperature, and have cast some doubt on the accuracy of the experimentally derived KIE, and on the validity of the conclusions of models that have employed these results. During the course of the present investigation a further theoretical study was however published [21], that found that use of CTST resulted in large errors for $\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}}$ but that agreement between theory and experiment was found by use of higher level dynamical calculations. The major thrust of the present experimental study was to resolve the differences in the calculated and measured values of $\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}}$ by performing further experiments using a different analytical and experimental approach.

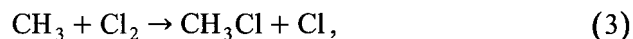
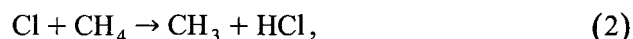
2. Experimental

$\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}}$ was investigated at room temperature by using the relative rate method in static gas mixtures. The experiments were carried out in a ≈ 44 l cylindrical quartz reaction chamber of ≈ 1.5 M length and ≈ 50 cm diameter. Radially mounted around the reaction chamber were a set of fluorescent photolysis lamps (270–370 nm, Phillips TL12) that provide a homogeneous flux of dissociative radiation to initiate chemistry, in this case by the photolysis of Cl_2 (see later). Analysis of the gas-phase in the chamber was by Infrared (IR) spectroscopy. The IR emission from the Globar source of a Bomem DA 008 FTIR spectrometer was coupled into the chamber via KBr windows mounted in stainless steel end plates, that also support a multi-pass White optics system. The analysis light trans-

versed the chamber 28 times to give a total optical path-length of ≈ 32 m, before its intensity (I_0 and I) was measured by a liquid- N_2 cooled MCT detector. Absorption spectra, $\log_{10}(I_0/I)$, were recorded at resolutions (Hamm apodized) of 0.15, 0.075, 0.05 and 0.04 cm^{-1} . Depending on resolution, between 250 and 1000 scans were co-added to achieve a good signal to noise ratio (S/N), requiring an acquisition time of between 0.5 and 1.5 h per spectrum.

Gas mixtures were introduced into the chamber via a glass manifold that ensures homogeneous mixing, and their pressures measured by 10 and 1000 Torr capacitance manometers. Note that due to the kinetic analysis employed, knowledge of absolute concentrations of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ were not necessary. As the reactor is not thermostatted, all experiments were carried out at room temperature (298 ± 2 K) and at a total pressure of 750 Torr N_2 bath gas.

First, reference spectra of $^{12}\text{CH}_4$ (Messer Griessheim, 4.5) and $^{13}\text{CH}_4$ (Air Liquide, 99.6 isotopic purity) samples were obtained by diluting a sample to $\approx 1\%$ in N_2 , and expanding ≈ 1.8 Torr of this mixture into the evacuated reaction chamber, which was then filled to 750 Torr N_2 before IR spectra were obtained at the chosen resolution. Once the $^{12}\text{CH}_4$ spectrum had been corrected for the presence of $\approx 1\%$ $^{13}\text{CH}_4$, the two reference spectra could be used for deconvolution of composite $^{13}\text{CH}_4/^{12}\text{CH}_4$ mixtures. Circa 1.5–2 Torr of a pre-mixed $^{12}\text{CH}_4/^{13}\text{CH}_4/\text{N}_2$ sample were then expanded into the cell, followed by ≈ 1 Torr of pure Cl_2 , and 750 Torr N_2 . The total CH_4 concentration was $\approx 1 \times 10^{15}\text{ cm}^{-3}$. An IR spectrum of this initial composite mixture was then obtained. Following this, a series of photolysis steps were carried out, in which the photolysis lamps were briefly switched on (≈ 1 s) and new spectra were obtained. The chemistry initiated by the TL12 lamps is:



resulting in the catalytic formation of Cl-atoms and destruction of CH_4 . Using this method, $> 99\%$ of the Cl-atoms generated are via reaction 3, rather than by photolysis. The very short photolysis times have the advantage that the cell temperature (and thus the

rotational distribution of CH₄) does not change during the experiment. For this reason experiments were not carried out in air, where reaction 3 is prevented by the formation of CH₃O₂, and all Cl-atoms are generated in reaction (1) only. This requires photolysis over periods of several minutes in order that a sufficient depletion in CH₄ could be observed. Such long photolysis periods result in a warming of the reactor walls, and of the gas mixture by several Kelvin, which is undesirable if the spectrum is rotationally well resolved. As discussed previously at 750 Torr N₂ bath gas pressures, Cl²P_{3/2} and Cl²P_{1/2} are expected to be in thermal equilibrium. In these experiments both Cl₂ containing the natural relative abundance of ³⁵Cl, ³⁷Cl of ≈ 3:1 (Linde 99.5%), and isotopically purified ³⁵Cl₂ (Isotec, 99.66% isotopic purity) were used.

At this point it is instructive to examine the differences (and similarities) between these experiments and those carried out previously by the same authors [9] using tunable diode laser absorption spectroscopy (TDLAS) for analysis of ¹²CH₄/¹³CH₄ ratios. The major difference is that in the present experiments, the reaction with Cl-atoms, the analysis of both the change in concentration and in isotopic composition of CH₄ take place in one chamber, and using one method (FTIR). The TDLAS experiments involved photolysis in a small reactor (≈ 1 l) before gas was transferred through a cold finger to an evacuated glass bulb. This sample was analysed by GC (concentration) and by TDLAS (isotopic composition). For simplicity of handling the FTIR experiment clearly has advantages. We note also that vastly different initial ¹²CH₄/¹³CH₄ ratios were used. In the TDLAS experiments, methane of natural isotopic composition was used (≈ 1% ¹³CH₄ and 99% ¹²CH₄), requiring the analysis of a weak-¹²CH₄ strong-¹³CH₄ line pair. In the FTIR experiments, the initial isotopic mix was ≈ 1: 1. Typical initial CH₄ concentrations were ≈ 1 × 10¹⁵ cm⁻³ in the FTIR experiments, compared to ≈ 5 × 10¹⁶ cm⁻³ in the TDLAS experiments.

The major similarity is that both experiments employed the same generation scheme for Cl-atoms, though we note that use of air or N₂ as bath gas gave identical results in the TDLAS experiments. The major advantage of the TDLAS experiment is its inherently superior signal to noise ratio (and thus

precision) and its high resolution (≈ 10⁻⁴ cm⁻¹). Generally, FTIR measurements of relative rates yield a precision of ≈ several percent. In order to increase the precision of the measurement to a level where < 0.5 percent effects could be resolved, a spectral deconvolution procedure was used that involved the simultaneous fitting of ≈ 40 rotational lines of ¹²CH₄ and ¹³CH₄ mixtures to obtain accurate partial (relative) concentrations of both isotopomers (see below).

3. Results and discussion

Fig. 1 displays IR absorption spectra of ¹³CH₄ (1a) and ¹²CH₄ (1b) between 1305 and 1355 cm⁻¹ at 0.04 cm⁻¹ resolution. The FWHM of the lines is ≈ 0.15 cm⁻¹, due to pressure broadening in the 750 Torr N₂ bath gas. A set of spectra obtained at 0.075 and 0.15 cm⁻¹ resolution are given in Fig. 2 for comparison. Clearly, the ¹²CH₄ and ¹³CH₄ lines are less well separated at the lowest resolution, although the signal to noise is considerably better due to higher light throughput resulting from the use of larger apertures. Also, as the scan time is considerably reduced for spectra at lower resolutions, a factor 2 to 4 more scans could be co-added without significantly extending the duration of the experiment. Fig. 1c displays a spectrum of the ¹²CH₄/¹³CH₄/Cl₂ mixture prior to photolysis (data points). The relative concentrations of ¹²CH₄ and ¹³CH₄ in this composite spectrum were obtained by least squares fitting of this data to the reference spectra (Fig. 1a and b).

$$\text{Spectrum 1c} = \left\{ \left({}^{12}\text{MF} * \text{spectrum 1b} \right) + \left({}^{13}\text{MF} * \text{spectrum 1a} \right) \right\} \quad (\text{i})$$

where ¹²MF and ¹³MF are multiplication factors for the reference spectra. For spectrum 1c, ¹²MF and ¹³MF were found to be (1.1463 ± 0.0030) and (1.1589 ± 0.0032), respectively, thus defining the initial ¹²CH₄/¹³CH₄ absorption ratio as (0.9891 ± 0.0038). After a total of ≈ 4 s photolysis, ≈ 60% of the methane had been removed by reaction with Cl-atoms and spectrum 1d was obtained, for which a

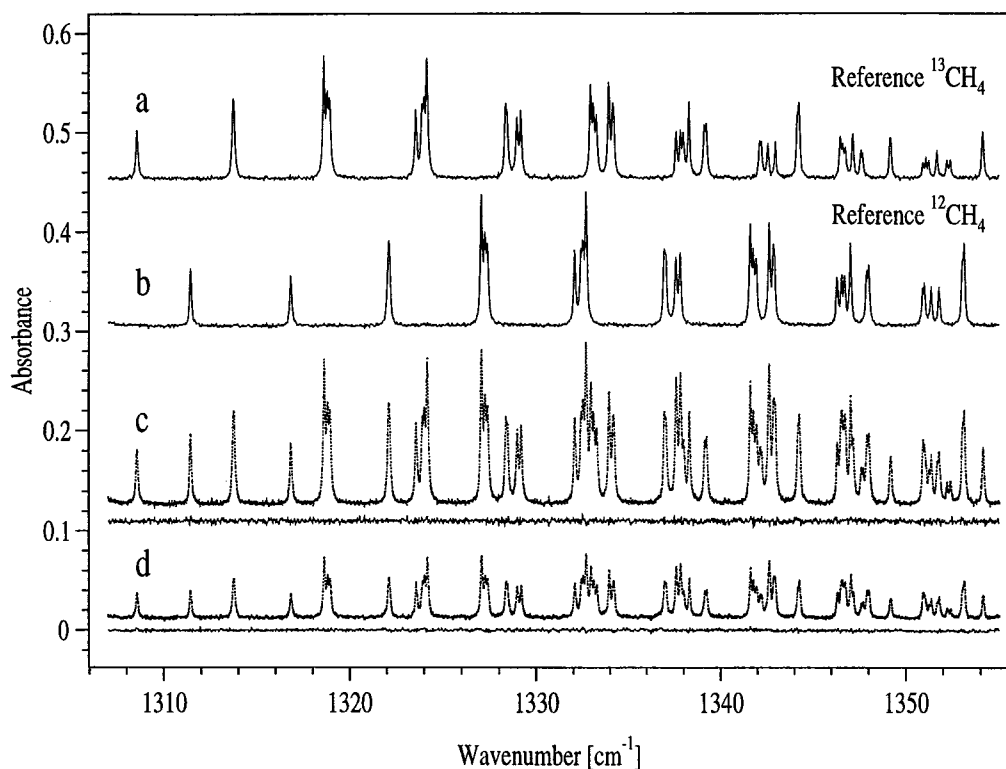


Fig. 1. FTIR absorption spectra of CH_4 at 0.04 cm^{-1} resolution and 750 Torr N_2 . Traces **a** and **b** are the reference spectra used to deconvolute $^{12}\text{CH}_4/^{13}\text{CH}_4$ ratios from composite spectra such as **c** (before photolysis) and **d** (after photolysis). The CH_4 concentration was $\approx 6 \times 10^{14} \text{ cm}^{-3}$. The residuals to the fits of spectra **c** and **d** are also shown. All spectra have been offset for clarity.

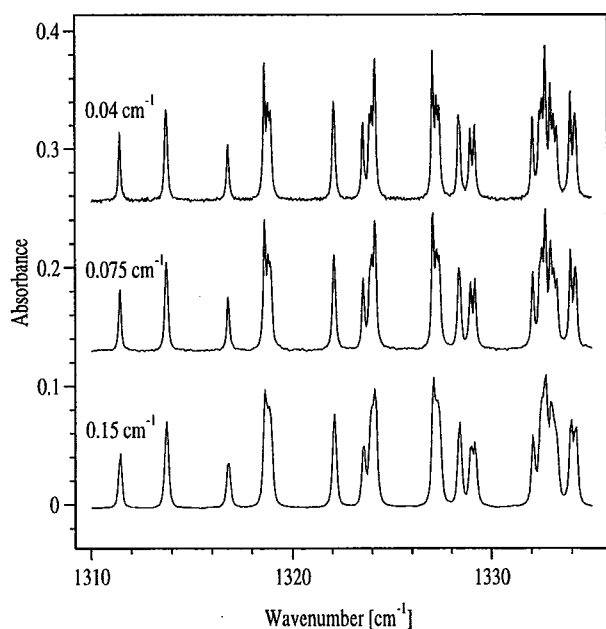


Fig. 2. Composite $^{12}\text{CH}_4/^{13}\text{CH}_4$ spectra ($1310\text{--}1335 \text{ cm}^{-1}$) prior to photolysis, and at three different resolutions. The data obtained at 0.075 and 0.04 cm^{-1} has been offset for clarity.

$^{12}\text{CH}_4/^{13}\text{CH}_4$ absorption ratio of (0.9420 ± 0.0030) was found. This data is listed for each experiment in Table 1. Note that as a relative rate method is used (see below), only relative rates of depletion of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ need to be determined, and, as long as a linearity between absorption and concentration is given, concentrations are not required. For a typical experiment, several photolysis events were interspersed with spectral acquisition and determination of ^{12}MF and ^{13}MF . The errors presented above are 2σ as returned by the linear least squares fit routine which uses a gradient-expansion (Marquardt) algorithm. The high precision of determination of ^{12}MF and ^{13}MF is a consequence of the spectral deconvolution procedure, in which a total of ≈ 40 rotational lines of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ (see Fig. 1c) and a total of > 2500 spectral data points (at 0.04 cm^{-1} resolution) are simultaneously analysed. Individual line analysis, as carried out previously in our relative rate study [22] of Cl-atoms with $^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$ is much less precise, and is suitable only for determination of

Table 1
Multiplication factors (MF) obtained from least squares fitting to $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ reference spectra

Photolysis step	$^{12}\text{MF} \pm 1\sigma^a$	$^{13}\text{MF} \pm 1\sigma^a$	Resolution cm^{-1}
0	1.0047 ± 8.2	0.9078 ± 7.8	0.15
1	0.7042 ± 13	0.6478 ± 12	
2	0.4976 ± 13	0.4696 ± 12	
3	0.3823 ± 13	0.3646 ± 11	
4	0.2890 ± 12	0.2825 ± 11	
0	0.9955 ± 8.5	0.8990 ± 8.1	0.075
1	0.7562 ± 12	0.6926 ± 11	
2	0.6319 ± 12	0.5868 ± 12	
3	0.4717 ± 12	0.4488 ± 12	
4	0.3556 ± 11	0.3451 ± 11	
0	0.8915 ± 9.1	0.7792 ± 8.3	0.04
1	0.5868 ± 9.9	0.5253 ± 9.0	
2	0.4534 ± 9.0	0.4105 ± 8.2	
3	0.3493 ± 8.0	0.3248 ± 7.3	
4	0.2978 ± 7.8	0.2786 ± 7.2	
0	1.1463 ± 15	1.1589 ± 16	0.05
1	0.8398 ± 14	0.8693 ± 15	
2	0.6982 ± 13	0.7238 ± 14	
3	0.5821 ± 12	0.6134 ± 13	
4	0.4611 ± 10	0.4894 ± 11	
5	0.2569 ± 8.8	0.2863 ± 9.3	
0	0.9654 ± 11	1.1187 ± 11	0.05
1	0.7701 ± 10	0.9019 ± 10	
2	0.5941 ± 10	0.7119 ± 11	
3	0.4585 ± 9	0.5595 ± 10	
4	0.3562 ± 9	0.4397 ± 9	
5	0.2781 ± 8	0.3489 ± 9	
0	0.8185 ± 10	0.9542 ± 11	0.05
1	0.6530 ± 10	0.7742 ± 10	
2	0.5037 ± 9	0.6023 ± 9	
3	0.3446 ± 8	0.4205 ± 9	
4	0.2756 ± 8	0.3425 ± 8	

^a1σ errors are multiplied by 1×10^4 . Each photolysis step corresponds to ≈ 1 s irradiation period.

larger KIEs. Note also that the residuals to the fits in Fig. 1 are without structure, showing that absorption of products in this spectral window is insignificant. This also shows that no significant change in temperature is taking place during the experiment to alter the relative rotational populations, and that absorbance, $\log_{10}(I_0/I)$, scales with concentration in this region, i.e., are linear in the Beer-Lambert sense.

The relative rate constant, for Cl-atoms with $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ is given by:

$$\frac{k(^{12}\text{CH}_4)}{k(^{13}\text{CH}_4)} = \ln\left(\frac{(\text{MF}^{12})_0}{(\text{MF}^{12})_t}\right) \div \ln\left(\frac{(\text{MF}^{13})_0}{(\text{MF}^{13})_t}\right) = \frac{\text{DF}^{12}}{\text{DF}^{13}} \quad (\text{ii})$$

where $(\text{MF})_0$ and $(\text{MF})_t$ are the multiplication factors before photolysis and after t -seconds of photolysis, respectively. ^{12}DF and ^{13}DF are thus defined as the depletion factors for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$, respectively. Fig. 3 displays a relative rate plot according to Eq. (ii). The plot contains data obtained at resolutions of 0.04, 0.075, 0.15 cm^{-1} ($^{35}\text{Cl}^{37}\text{Cl}$) and 0.05 cm^{-1} ($^{35}\text{Cl}_2$). Individual analysis of each data set gave $\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}} = 1.068 \pm 0.004$ ($^{35}\text{Cl}^{37}\text{Cl}$, 0.15 cm^{-1} , 10 data points), 1.066 ± 0.005 ($^{35}\text{Cl}^{37}\text{Cl}$, 0.075 cm^{-1} , 5 data points), 1.064 ± 0.005 ($^{35}\text{Cl}^{37}\text{Cl}$, 0.04 cm^{-1} , 6 data points), and 1.066 ± 0.003 ($^{35}\text{Cl}_2$, 0.05

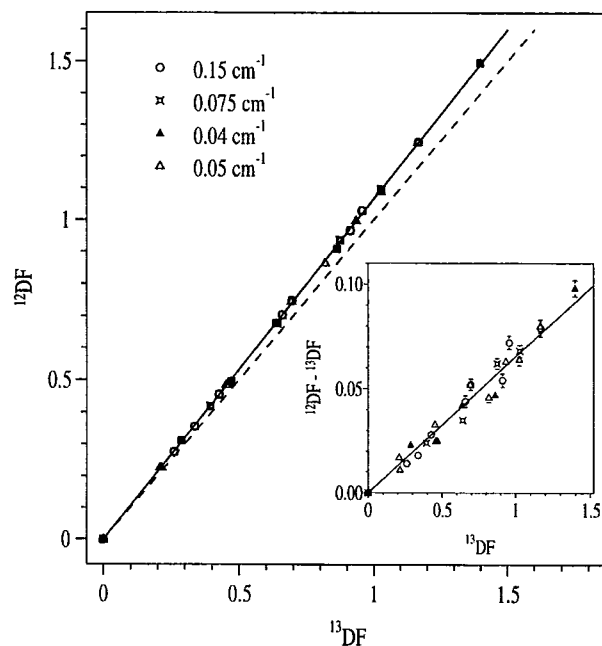


Fig. 3. Plot of ^{12}DF versus ^{13}DF for all experiments at 0.04, 0.05, 0.075 and 0.15 cm^{-1} resolution, and using both $^{35}\text{Cl}^{37}\text{Cl}$ and $^{35}\text{Cl}_2$. The slope defines the ratio: $k(^{12}\text{CH}_4)/k(^{13}\text{CH}_4) = \text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}} = 1.066 \pm 0.02$ (2σ). The dashed line represents a KIE of 1 (i.e. no fractionation). The inset is a plot of $^{12}\text{DF} - ^{13}\text{DF}$ versus ^{12}DF , to show the scatter of the data about the value of $\text{KIE}_{\text{Cl}}^{12\text{C}/13\text{C}} = 1.066$ more clearly.

cm⁻¹, 11 data points). There is therefore no significant, systematic difference between the data obtained at the various resolutions used, or related to the use of ³⁵Cl³⁷Cl or ³⁵Cl₂, and we quote an average $KIE_{Cl}^{12C/13C} = 1.066 \pm 0.002$ at 298 K (2σ errors). This can be confirmed by inspection of the inset to Fig. 3, in which the data, plotted as ¹²DF versus ¹²DF - ¹³DF, is clearly statistically distributed around the 66‰ line.

This result is now compared to previous experimental and theoretical studies of the same reaction. Saueressig et al. obtained $KIE_{Cl}^{12C/13C} = 1.066 \pm 0.02$ (2σ) at 297 K using the TDLAS instrument with a resolution of $\approx 10^{-4}$ cm⁻¹ and two ¹²CH₄/¹³CH₄ line pairs close to 3003 and 3007 cm⁻¹. This result is in excellent agreement with the present determination by FTIR at the same temperature. Although the two experimental studies were conducted at the same institute, we emphasise that completely different experimental set-ups pertaining to the method of analysis of ¹²CH₄/¹³CH₄ ratios and depletion factors, initial ¹²CH₄/¹³CH₄ ratios and concentrations and even reactor size and pressure give the same result, and provide confidence in their independence and their accuracy.

For comparison, the theoretical studies at the CTST level [19,20], return a much lower average $KIE_{Cl}^{12C/13C} \approx 1.030$. CTST is therefore unable to reproduce the absolute size of the kinetic isotope effect, though we note that the slight negative temperature dependence is correctly predicted [20], as is the much lower kinetic isotope effect in the reaction of CH₄ with OH [20,23,24]. Very recent calculations [21] using a higher level of dynamical theory (Variational Transition State Theory, VTST) derived a KIE at 298 K of 1.06, increasing to 1.07 at 243 K, in good agreement with the (now) well characterised experimental result. The convergence of theory and experiment for $KIE_{Cl}^{12C/13C}$ suggests that similar theoretical studies of mass dependent KIE's in atmospheric reactions, especially those which are difficult to access by laboratory experiments, are highly desirable.

4. Conclusions

The carbon kinetic isotope effect in the reaction of Cl-atoms with CH₄ ($KIE_{Cl}^{12C/13C}$) at 298 K was

determined as 1.066 ± 0.002 (2σ), confirming the result of a separate, independent experimental study from the same institute. The confirmation of a large KIE for this reaction substantiates previous conclusions [8] regarding the important role of the title reaction in modifying the atmospheric isotopic composition of methane.

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