21GRD04 - isoMET

D4: Report on the analysis of at least two gas mixtures of pure CH_4 of varied clumped isotopic composition value assigned for $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ linked to stochastics by CH_4 equilibration

Organisation name of the lead participant for the deliverable:

Empa

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Deliverable Cover Sheet

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1 Summary

One of the aims of WP2 – "A sustainable metrological infrastructure for a dataset for CH_4 isotope source signature measurements in Europe" of the European isoMET project is to evaluate the potential for source apportionment of rare doubly-substituted $^{13}CH_3D$ and $^{12}CH_2D_2$ isotopologues analysis.

Experimental and theoretical studies suggest that differences in the abundance of rare, doubly-substituted isotopologues of CH_4 provide independent information on the thermogenic or microbial origin of CH_4 source processes as well as mixing of pure CH_4 sources. While high-resolution laser spectroscopic (OIRS) and mass-spectrometric (HR-IRMS) approaches have been developed in recent years, metrological traceability to stochastics has to be realised to improve international compatibility and facilitate uptake for source appointment. First exemplary measurements of doubly substituted CH_4 isotopologues for prominent European source sectors will indicate the potential of $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ for enhanced source apportionment and guide future research in this direction.

In the sections below input from A1.1.3, A2.2.4 and A2.2.5 is provided by Empa, NPL, UU, VTT, UofG as a report on the development of pure CH_4 reference gas mixtures. The main results of this work are:

- NPL established 4 static pure CH_4 standards for use as RMs and validation gases for clumped isotope measurements ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) with different bulk isotopic composition in $\delta^{13}C$-CH_4 (-46.35 to -39.19‰) and $\delta^{2}H$-CH_4 (-202.56 to -182.04‰).
- Empa minimised uncertainty contributions limiting the accuracy of an established OIRS analyser for quantification of $^{13}CH_3D$, $^{12}CH_2D_2$ and $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$ at natural abundance to reach a target precision of 0.2 ‰ for $\delta^{13}CH_3D$ and 0.5 ‰ for $\delta^{12}CH_2D_2$. In addition, Empa optimised the existing analytical procedure towards smaller sample volumes (<10 ml CH_4 STP).
- VTT demonstrated the detection of very rare doubly substituted methane isotopologue in a natural methane sample using CRDS for the first time. In the future, VTT intends to improve the signal-to-noise ratio of the device and target regions where reference $^{13}CH_4$ absorption lines are present, enabling referenced measurements of $^{13}CH_3D$ and express abundances in the established Δ notation.
- The four pure CH_4 standards provided by NPL were analysed by HR-IRMS at UU and UofG and by OIRS at Empa, linked to international scales and stochastics by CH_4 equilibration. For both $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, results obtained at Empa by OIRS and UU by HR-IRMS show good agreement within the analytical uncertainty (within 2σ standard error). In contrast, the values reported by SUERC are significantly lower for both clumped isotopic species, falling outside the range of analytical uncertainty, which needs reassessment of the analytics.

In summary the established four pure CH_4 gases have been values assigned for $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ and are ready to be used by other CH_4 clumped isotope laboratories as future RMs.

2 Preparation of pure CH_4 standards (A113; Ruth Pearce, Emily Hopkinson, Chris Rennick (NPL))

2.1 Objective

NPL, with the support of Empa, UU and UofG, established 4 static pure CH_4 standards by gravimetric blending of CH_4 from different origin and different isotopic composition for use as RMs and validation gases for the clumped isotope measurements ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$). The target uncertainties are 0.05 ‰ for $\delta^{13}C$-CH_4 and of 1 ‰ for $\delta^{2}H$-CH_4.

These CH_4 RMs and validation gases were used as input for A2.2.5, in which they were analysed for $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$.

2.2 Selection of pure CH_4 sources

The high purity CH_4 samples were selected from eight compressed gas cylinders containing fossil-origin CH_4 from several sources: commercially available ultra-high purity CH_4 (CK gases N6.0), from laboratory stocks, and the CH_4 characterised in the EMPIR 19ENV05 STELLAR project (Air Liquide, N6.0). The potential sources were screened for the $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 isotope ratios using an Aerodyne spectrometer and prepared as samples diluted to approx. 550 µmol mol^{-1} in nitrogen. The natural variability between suppliers and batches resulted in a relatively large span of $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4. Due to the fossil origin, none of the samples have $\delta^{2}H$-CH_4 near the highly enriched isotope ratio for atmospheric CH_4, which is around −90‰. Out of the eight screened CH_4 samples, four remained after removing those with similar isotopic signatures, or where there was an insufficient quantity needed for provision of preference materials across the isoMET project and to support future work. The isotope ratios of the selected pure CH_4 sources are given in Table 1.

Table 1 $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 isotope ratios of the pure CH_4 sources selected after screening. These are nominal isotope ratios that have been measured by OIRS as mixtures in N_2 at c.a. 550 µmol mol^{-1} and used to select the sources with the widest isotopologue ratio range. The Parent column gives the name of the pressurised gas cylinder containing the pure CH_4.

Parent	$\delta^{13}C$-CH_4 / ‰	$\delta^{2}H$-CH_4 / ‰
NG349	−46.35	−182.04
97093072	−43.39	−202.56
97098140	−44.88	−194.72
Stellar	−39.19	−194.52

Subsamples of the selected CH_4 sources were decanted into 100 mL stainless steel sample vessels, filled to between 2 and 30 bar. Individual samples of all CH_4 were sent to Utrecht University, The University of Glasgow and Empa.

3 Spectroscopic developments for $^{13}CH_3D$, $^{12}CH_2D_2$ analysis (A2.2.4; Naizhong Zhang, Joachim Mohn (Empa), Mehr Fatima (VTT))

Using improved data on spectral interferences from A2.2.2, Empa minimised uncertainty contributions limiting the accuracy of an established OIRS analyser for quantification of $^{13}CH_3D$, $^{12}CH_2D_2$ and $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$ at natural abundance to reach a target precision of 0.2 ‰ for $\delta^{13}CH_3D$ and 0.5 ‰ for $\delta^{12}CH_2D_2$. In addition, Empa optimised the existing analytical procedure towards smaller sample volumes (<10 ml CH_4 STP). Results are published in Zhang, Prokhorov [1].

VTT upgraded the prototype spectrometer developed in A2.2.2 to measure $^{13}CH_3D$, and $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$ at natural abundance.

3.1 Rapid High-Sensitivity Analysis of Methane Clumped Isotopes ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) Using Quantum Cascade Laser Absorption Spectroscopy (QCLAS)

Selection of Spectral Windows and Analytical Advances

Using the high-resolution FTIR spectra of $^{13}CH_3D$ and $^{12}CH_2D_2$ obtained in this project (A2.2.1), we were able to identify highly adequate spectral windows for clumped isotope analysis. We selected a $^{12}CH_2D_2$ line at 1076.97 cm^{-1}, with an absorption cross section of 2.9 × 10−18 cm^2/molecule (spectral line intensity of 1.575 × 10^{-27} cm/molecule) and analysed it along with a $^{12}CH3D$ line at 1076.84 cm^{-1}. The spectral line intensity of the selected $^{12}CH_2D_2$ line is about 50% higher than the $^{12}CH_2D_2$ doublet selected by Gonzalez, Nelson [2]. The higher spectral line intensity, along with the improved fitting of an individual line compared to a doublet, enhances sensitivity and precision, as demonstrated below. For $^{13}CH_3D$ analysis, a line at 1163.47 cm^{-1} was selected, with a line intensity of 5.94 × 10^{-26} cm/molecule, similar to the line chosen by Gonzalez, Nelson [2] (1200.26 cm^{-1}). Due to the much higher natural abundance of $^{13}CH_3D$ compared to $^{12}CH_2D_2$, spectral interferences are less critical, and relevant effects can be predicted using spectral simulations. Along with $^{13}CH_3D$, we analysed $^{12}CH_4$ and $^{13}CH_4$ at 1163.49 and 1163.63 cm^{-1}, respectively.

In addition to spectroscopic advances discussed above, our analytical platform incorporates several technological advances, particularly with respect to the inlet system and laser spectrometer. These improvements enable increased sensitivity, facilitating analysis at reduced CH_4 amounts. A key feature of the inlet system is the intermediate gas volume, where sample and reference gases are conditioned for temperature and pressure before injection into the spectrometer's multipass cell. With high-precision pressure measurements and temperature control, we reduced pressure variations in the intermediate volume to ±0.5 Torr, which corresponds to ±0.01 Torr in the spectrometer sample cell. This is an order of magnitude better than the previously described instrument [2]. Especially at lower sample amounts, i.e., low cell pressures, pressure differences between reference and sample gas measurements become the key limiting factor for precision and accuracy and complicated analysis at lower cell pressures/sample amounts in earlier systems. Second, by implementing a two-stage temperature control system, the inlet system is stabilized to ±0.1 K and the spectrometer cell to ±2 mK, minimizing variations in the injected sample amount and reducing spectroscopic artifacts. Third, the dead volume of the spectrometer multipass cell was minimized: the total cell volume, including connecting lines, was reduced to 2.5 L, compared to the 2.8 L reported by Gonzalez, Nelson [2] which corresponds to a ∼10% reduction in CH_4 amount without sacrificing performance.

Instrumental Precision

The measurement precision of the QCLAS was evaluated for sample amounts ranging from 3 to 25 mL of pure CH_4 (0.12 to 1.03 mmol CH_4), corresponding to pressures of 1 to 7.5 Torr in the spectrometer multipass cell. The Allan-Werle variance technique [3] was used for precision assessment. Sample measurements were preceded by background spectra correction using a N_2-filled multipass cell, and then conducted over 2 h with a temporal resolution of one second. The calculated Allan deviations are presented in Figure 1 indicate white-noise limited behaviour for approximately 10 s, followed by a steady improvement in precision up to an integration time of 100 to 150 s, at which best precision levels are achieved. For sample amounts larger than 10 mL CH_4 (cell pressure above 3 Torr), the maximum precisions obtained were 0.03‰ for $\delta^{13}C-CH_4$, 0.01‰ for $\delta D-CH_4$, 0.02‰ for $\delta^{13}CH_3D$, and 0.4‰ for $\delta^{12}CH_2D_2$, independent of sample amount. These values are comparable to those reported by [2] for 20 mL CH_4. Since drift effects become significant after 1000 s spectral

averaging, we implemented a standard procedure for a full measurement cycle consisting of background, reference and sample gas measurements with 200 s integration times each.

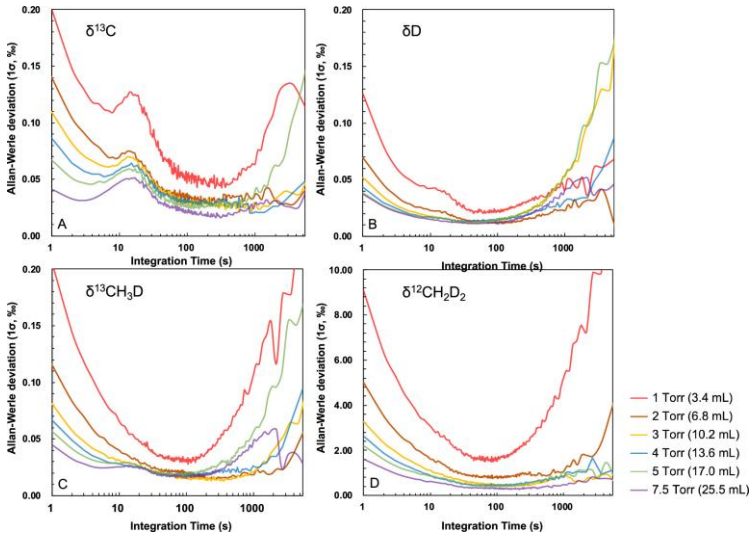

Fig. 1: Allan-Werle deviation for individual isotope deltas at different cell pressures, i.e., methane sample amounts. Reproduced from [1] with permission.

Repeatability for Different CH4 Amounts

While the measurement precision of the laser spectrometer surpasses the precision reported for HR-IRMS, a more important factor with respect to applied performance is its repeatability for consecutive measurements of reference/sample pairs. By applying best practices in HR-IRMS, 1σ standard deviation values (1σ SD, external precision) of ~0.3‰ for $\Delta^{13}CH_3D$ and ~1.5‰ for $\Delta^{12}CH_2D_2$ can be achieved with a sample size of 3−5 mL per measurement. These values were used as a reference for our study.

Figure 2 displays 1σ SD of $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ for repeated (n = 20) analyses of background-reference-sample pairs but using different amounts of CH_4 reference and sample gas. In accordance with Allan-Werle deviation measurements, the CH_4 amount ranged from 3 to 25 mL. Each full analysis was completed within 17 min compared to typically measurement times of HR-IRMS of around 20 h. For both $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ analyses, the repeatability (1σ SD) improved with increasing the amount of gas, but the improvement became negligible beyond ~10 mL STP. Sample volume requirements for $\Delta^{13}CH_3D$ are much more relaxed with repeatability levels of ~0.15‰ for 3 mL CH_4 and ~0.05‰ at 10 mL CH_4 or higher, which is significantly better than the typical performance reported for HR-IRMS (~0.3‰). The effect of sample amount on performance is more apparent for $\Delta^{12}CH_2D_2$, where the target repeatability (<1.5‰) could be reached for sample sizes larger than 10 mL. However, for sample sizes smaller than 10 mL, the 1σ SD increased to ~2‰ (7 mL) and over 4‰ at 3 mL CH_4. In such cases, a recycle-refilling system connected to the current QCLAS system might be applied for 3 to 8 consecutive measurement cycles to achieve satisfactory external precision for $\Delta^{12}CH_2D_2$ analysis. In summary, we confirmed that the CH_4 sample size required for spectroscopic clumped isotope analysis, to reach performance targets of 0.3‰ (or even as good as 0.05‰) for $\Delta^{13}CH_3D$ and 1.5‰ for $\Delta^{12}CH_2D_2$ can be reduced to 3−7 mL CH_4, which is comparable to the sample size required for HR-IRMS analysis.

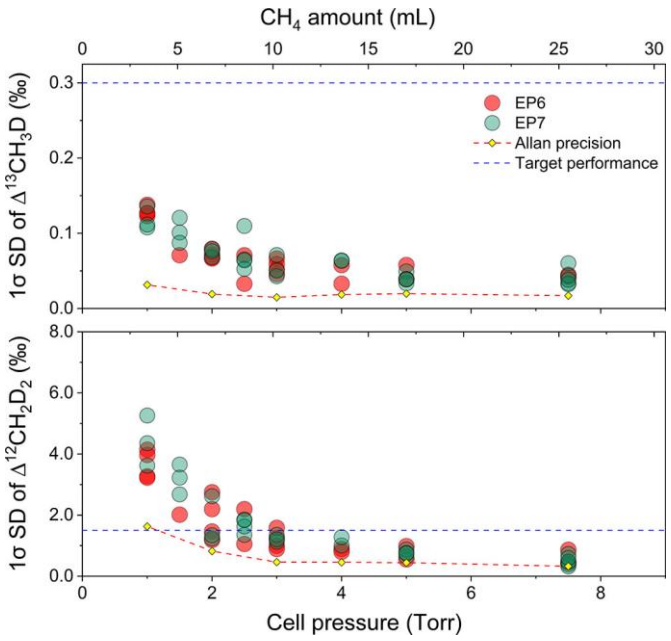

Fig. 2: 1σ standard deviation for repeated sample analysis applying different sample amounts (n = 20). Either EP6 or EP7 was used as the sample gas, while EP6 was used as reference for all analyses. The blue dashed line indicates the target performance, i.e., the 1σ SD (external precision) achieved by HR-IRMS (~0.3‰for $\Delta^{13}CH_3D$ and ~1.5‰ for $\Delta^{12}CH_2D_2$). The red dashed line, along with the yellow diamonds, represents the Allan-Werle precision shown for comparison. Reproduced from [1] with permission.

Heated Gas Calibration

Similar to HR-IRMS, the $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values obtained through spectroscopic analysis are measured and calculated relative to a working reference gas (referred to as EP6). To determine the "true" clumped isotope signatures of samples, the clumped isotope values of the working reference gas must be quantified using equilibrated CH_4 gases. These equilibrated gases can be prepared by heating a CH_4 sample in the presence of a catalyst like Ni or γ-Al_2O_3 in a temperature-controlled and sealed system. In this study, we generated a series of equilibrated methane samples at 70, 150, 200 and 300 °C with varying bulk isotopic compositions. Our observations indicate that the clumped isotope values reach equilibrium after 10 min at 300 °C and 45 min at 220 °C, while the bulk isotope values of the equilibrated CH_4 gases remained consistent throughout the equilibration process.

In principle, clumped isotope values should be independent of bulk isotope values. However, a significant nonlinearity effect, primarily influenced by $\delta D-CH_4$ values, has been reported in previous spectroscopic analyses [2]. To address this potential nonlinearity effects, we prepared a suite of in-house standard gases, including three commercially available pure methane gases (EP1, EP6, and EP7), and a $^{12}CH_3D$-spiked sample gas (EP4). CH_4 gases covering $\delta D-CH_4$ values ranging from −204 to −40‰ facilitate to characterize dependencies of $\Delta^{12}CH_2D_2$ and $\Delta^{13}CH_3D$ on $\delta D-CH_4$. Figure 3 illustrates the correlations between apparent clumped isotope values ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) and $\delta D-CH_4$ for four CH_4 samples equilibrated at 300 °C. At a cell pressure of 7.5 Torr, we observed a bias in $\Delta^{13}CH_3D$ of 0.034‰ and in $\Delta^{12}CH_2D_2$ of −0.108‰ for each 1‰ difference in $\delta D-CH_4$ of the sample compared to the reference gas. This effect might be related to imperfect spectral fitting, in particular for the interfering $^{12}CH_3D$ line on $^{12}CH_2D_2$ and/or inaccuracies in baseline corrections. Relationships remain constant over time, unless major adjustments to the spectroscopic setup or spectral fitting are undertaken, which underlines the robustness of our analytical platform. Based on these correlations, the clumped isotope values of the reference gas (EP6) were determined to be 3.58 ± 0.02‰ for $\Delta^{13}CH_3D$ and 8.90 ± 0.23‰ for $\Delta^{12}CH_2D_2$.

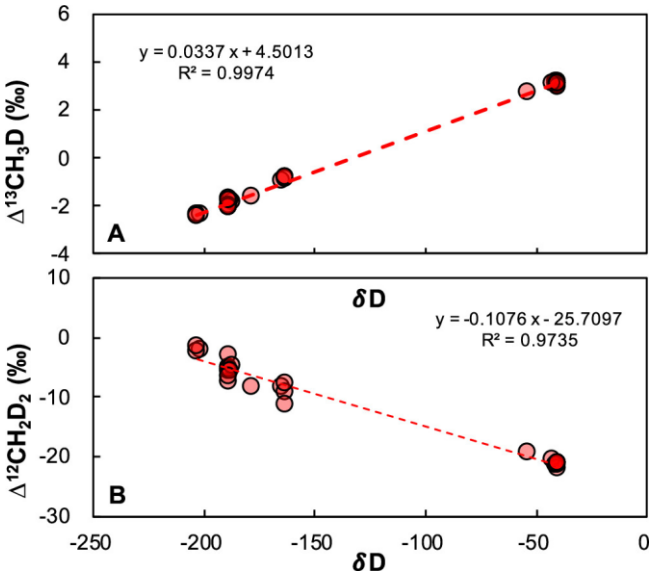

Fig. 3: Apparent (A) $\Delta^{13}CH_3D$ and (B) $\Delta^{12}CH_2D_2$ values for CH_4 gas with varying $\delta D-CH_4$, equilibrated at 300 °C. EP6 was used as the reference for all measurements, while sample gases with different $\delta D-CH_4$ were applied.

3.2 CRDS-based methane clumped isotopologues detection

In this part of the project, we demonstrate a proof-of-concept for the measurement of methane clumped isotopologues using laser spectroscopy, specifically, cavity-ring-down spectroscopy (CRDS) [4]. It measures how long it takes for a laser pulse to decay within a high-reflectivity optical cavity, such that the decay rate will indicate absorption by a target gas. Therefore, it is possible to measure isotopic compositions with a high level of sensitivity and minimum sample preparation.

Selection of Spectral Windows and Analytical Advances

To identify suitable spectral regions for simultaneous measurements of $^{13}CH_3D$ and $^{12}CH_2D_2$ at natural isotope abundance, PTB and Empa reviewed the existing databases, scientific literature and performed additional measurements using Fourier-transform infrared spectroscopy (FTIR) [1]. Through careful analysis, one spectral region was identified as optimal with consideration of several criteria: minimal spectral interference from other molecular species, maximized line strengths for target isotopologues, and the ability to detect two clumped isotopologues. The selected spectral region 2228.4 – 2229.2 cm^{-1} along with the line-data for different molecules and isotopologues are shown in Figure 4.

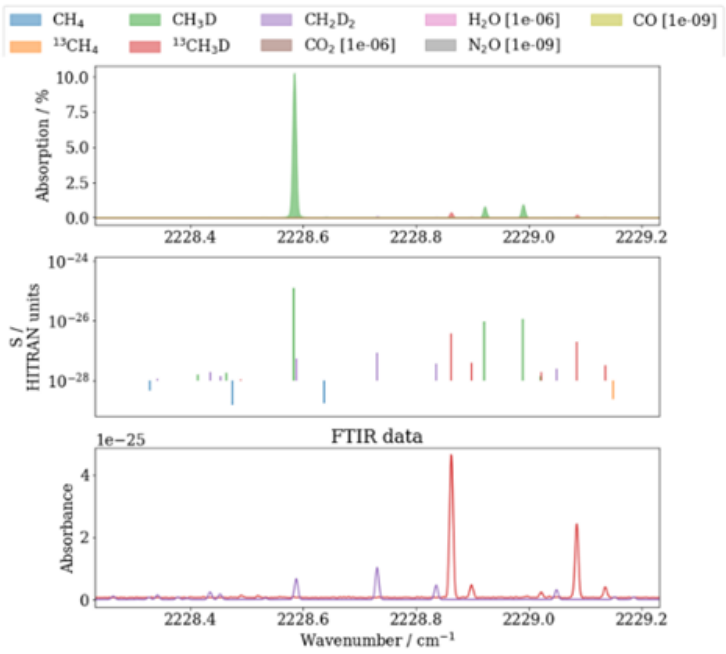

Fig. 4. Simulated absorption spectrum and line strength for CH_4 isotopologues and interfering molecules (H_2O, CO_2, N_2O) are shown on the top and middle panel, respectively. The measured FTIR data for $^{13}CH_3D$ and $^{12}CH_2D_2$ is presented on the bottom panel [1].

Experimental setup

The cavity-ring-down spectrometer developed at VTT, consists of a narrow-linewidth, continuous-wave, tunable quantum cascade laser from Alpes Lasers. This QCL operates at a wavelength of 4.486 µm and can be tuned between 2228 and 2238.9 cm^{-1} by changing laser current and temperature.

The cavity comprises two dielectric-coated ZnSe mirrors, spaced 38 cm apart, with a reflectivity of 99.99% each and 1 m radius of curvature. A Faraday optical isolator with 30 dB isolation is inserted between the two concave mode matching mirrors in order to eliminate optical feedback into the cavity. The alignment of the second mirror is optimized by Physik Instrumente piezo-electric actuators.

Light leaving the cavity is focused on a VIGO HgCdTe photovoltaic detector with the help of a spherical mirror. The signal is then digitized and detected using a compact Red Pitaya STEMlab 125-14 with custom signal conditioning circuits. The same board allows for laser frequency switching by triggering the laser driver after the output reaches a particular threshold. These frequency jumps decouple the laser light from the cavity,

which produces a decaying pulse of light or ring-down event. The custom LabVIEW software fits the ring-down events to an exponential decay signal to calculate the ring-down time. A pump creates a vacuum, and cavity pressure is monitored with a capacitance manometer. The difference of the ring-down time between off-and on-resonance of the absorption lines, is used to calculate the concentration of the sample. We used high-purity (99.9995%) industrial grade methane as a sample for our measurements.

Experimental results

Using the experimental setup described in section 2, we made measurements using pure methane sample at a pressure of 25 mbar. The laser is operated at a temperature of 45°C to target the desired wavenumber range. The spectra are averaged over 1 hour on two days, and the results are shown in Figure 2.

Long-time measurements were recorded, and Allan variance analysis was conducted to estimate the detection limit and stability of our instrument. The results indicated a detection limit of 20‰ for $^{13}CH_3D$ at an averaging time of 60 minutes. Although, this number is higher than that reported by HR-IRMS and TDLAS measurements, the implementation of CRDS in the same wavenumber region as TDLAS could enhance sensitivity by a factor of 52.25, potentially lowering the detection limit to 0.38‰.

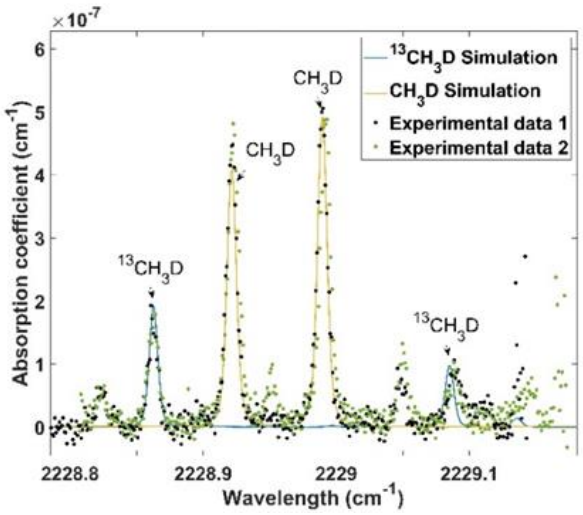

Fig. 5. Experimental spectra of pure CH4 recorded at two different days, plotted with green and black dots. Simulations based on HITRAN for CH_3D and recently published FTIR spectra [1] for $^{13}CH_3D$ are shown for comparison in yellow and blue colours, respectively [4].

4 Analysis of pure CH_4 gases for $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ (A2.2.5; Bibhasvata Dasgupta, Matthieu Clog, Naizhong Zhang (Utrecht University, University of Glasgow, Empa))

UU, UofG and Empa established and optimised individual OIRS / HR-IRMS setups and techniques for equilibration of CH4 at different temperatures between 0 °C and 500 °C to link $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ to stochastics. Completeness of equilibration was assured by spiking with pure $^{13}CH_3D$ and $^{12}CH_2D_2$. Equilibrated CH_4 gases were used to assign $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values to the at least two pure CH_4 gas mixtures established in A1.1.3.

UofG and UU provided their results to Empa to calculate $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values and uncertainties for the pure CH4 gas mixtures for use as calibration/validation gases in A2.2.6, A2.3.4 and A2.3.6, and as potential future reference materials for the clumped CH_4 community.

4.1 Analytics Utrecht University

The analysis at UU was conducted using the Thermo Scientific Ultra high-resolution isotope ratio mass spectrometer (IRMS), which comprises an analytical setup for extraction, sample preparation, and measurement of r extraction, sample preparation, and measurement doubly substituted methane isotopologues such as $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$. The system employs a dual-inlet configuration to alternate between sample and reference gases, ensuring high measurement precision. Methane samples, after purification, are introduced under tightly controlled pressure and flow conditions to maintain consistent ionization. The Ultra IRMS offers the mass resolution necessary to distinguish isobaric interferences, which is crucial for accurate clumped isotope measurements. Each analysis takes about 20 hours: 3 hours for singly substituted CH_3D, followed by 7 sets of $^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, H_3D and $\Delta^{12}CH_2D_2$ which takes 2.5 hours each, allowing for the accumulation of sufficient ion counts to achieve reproducibility levels of ±0.3‰ for $\Delta^{13}CH_3D$ and ±2.4‰ for $\Delta^{12}CH_2D_2$. Calibration is performed using methane equilibrated at known temperatures, and corrections are applied for background signals, linearity, and pressure effects to ensure data accuracy.

Using this setup, we measured 4 IsoMET pure methane gases prepared by NPL, with each measurement repeated to ensure reproducibility. The gases were measured against our in-house pure methane gas AP613 with $\Delta^{13}CH_3D$ = 2.23‰ and $\Delta^{12}CH_2D_2$ = 3.12‰.

4.2 Analytics University of Glasgow

The analysis of methane at the UofG was conducted using a Thermo Scientific Ultra High-Resolution IRMS. A dedicated glass vacuum line equipped with a gas chromatograph and helium-cooled cryostat is used for sample preparation and purification. The Ultra allows for the measurements of methane isotopologues bearing 0, 1 and 2 isotopologues, leading to the measurements of $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$. Our mass spectrometry methods are similar to those of UU (dual inlet mode, tight control of gas pressure during the measurement and of the focusing and ionisation conditions of the gas), but small differences in instrument performance led to slightly different methods. Each analysis uses an aliquot of ~80 micromoles of methane and takes about 22 hours, divided as follows: 4h for the measurement of $^{12}CH_3D$, 5h for the simultaneous measurements of $^{13}CH_4$ and $^{13}CH_3D$ and 12h for the measurement of $^{12}CH_2D_2$. For all measurements the narrowest source slit is used, with the optional aperture ('HR+' mode) to increase resolution for the first two measurements. For measurements of $^{12}CH_3D$ and $^{12}CH_2D_2$ where we use a narrow collector slit, a verification of the peak positions and if necessary, adjustment is applied before every acquisition rather than every block to avoid the effects of instrument drift.

In addition to corrections for background, it is necessary to correct for a small contribution from the tails of $^{13}CH_3D$ and $^{13}CH_5$ (formed in the ion source) on the $^{12}CH_2D_2$ peak. This is accomplished by characterizing the tail of the peak from the background H_2O before measuring the abundance of $^{12}CH_2D_2$, and applying a correction that takes into account the measurement position relative to the centre of the $^{13}CH_3D$ and $^{13}CH_5$ peaks, the intensity of these peaks and the measured intensities for the H_2O peak and its tail. Our working gas was calibrated against aliquots of methane equilibrated over catalysts at temperatures ranging from 200 to

500ºC. We have measured the 4 IsoMET gas samples prepared by NPL and each measurement was replicated at least twice.

4.3 Analytics Empa

Approximately 40 mL of CH_4 gas was transferred into a ~11.5 mL stainless steel cold finger at a pressure of 4 bar. The cold finger was then connected to the gas inlet system prior to initiating a 20-minute measurement script. The measurement was preceded by a background spectrum measurement of N_2 collected at 1.5 times the target reference/sample pressure to compensate for the different refractive index between gases. Next, the laboratory working reference gas (EP6) was analysed at the target pressure (200 s), followed by the measurement of the sample gas at the same pressure (200 s). Optimal spectral averaging times and maximum time gaps between sample and reference gas measurements were chosen based on the results of Allan-Werle deviation measurements. During background, reference or sample preparation, gas was expanded into the intermediate volume until a target pressure is reached (15.5 Torr per mL CH_4), controlled using a 0−1000 Torr manometer (Baratron AA02A, MKS) and a critical orifice. The repeatability of pressure readings for the intermediate volume is better than 0.5 Torr (1 σ standard deviation). For the pure CH4 standard provided by NPL, the gas was expanded into the multipass cell to reach a pressure of approximately 7.5 Torr. Each sample was measured four times.

4.4 Results

The four pure CH_4 standards provided by NPL cover a range of 4.1‰ and 20.9‰ for $\delta^{13}C$ and δD-CH_4, respectively (Figure 4). Overall, a systematic discrepancy in bulk isotope values was observed, with the $\delta^{13}C$-CH_4 values measured by Empa are approximately 0.8‰ higher than those measured at NPL, while the δD-CH_4 values measured at NPL are about 11‰ lower than those measured by UU. These discrepancies can be attributed to differences between the laboratories in referencing measurements to international isotope ratio scales [5].

For both $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, the results obtained at Empa and UU show good agreement within the analytical uncertainty (within 2σ standard error). In contrast, the values reported by SUERC are significantly lower for both isotopologues, falling outside the range of analytical uncertainty (Figure 6).

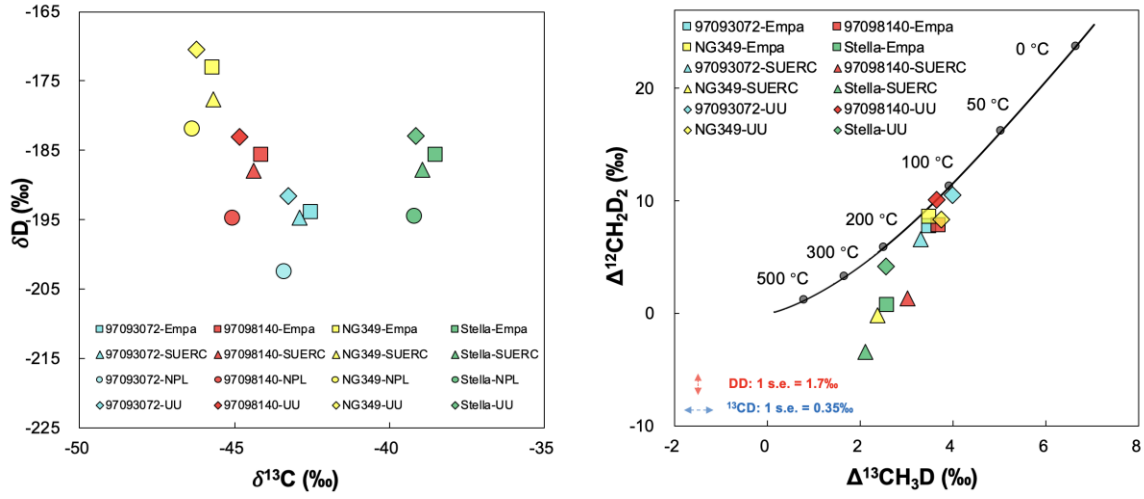

Fig. 6. Comparison of methane bulk (left panel) and clumped (right panel) isotope analyses performed in different laboratories (Empa, NPL, UU: Utrecht University, SUERC: University of Glasgow)

5 References

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