Stratospheric CH4 isotopes

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This article is simply an attempt to discuss the proposed observation altitudes for MISO, a Laser Heterodyne Radiometer (LHR) satellite mission proposed to observe CH4 isotopes (^{13}C in CH4 and ^{12}C in CH4) in the UTLS.

ADFA-UNSW are proposing 3 observation altitudes for the satellite, centred at 14, 18 and 22km, giving ~4km vertical resolution. These altitudes are chosen from available absorption lines that provide sufficient absorption at higher altitudes without saturating at lower altitudes, as well as the available wavelength range for the detectors/lasers.

The question at the moment is whether these altitudes are sensible to include in the instrument simulator from a scientific perspective. This article will discuss some of the considerations for those choices. Some points up front:

- We don't know how strictly constrained the possible observation altitudes are.
- This article therefore assumes that any observation range is possible.
- We also do not fully know (remember?) the precision/accuracy of the proposed measurements with the LHR technique, but assume that they are insufficient to resolve the small isotopic signals in the troposphere.
- We are concentrating only on δ^{13}C in CH_4, not on δD (i.e. CH_3D).
- It would be instructive if a calculation of the expected averaging kernels could be provided given the satellite observing geometry, instrument resolution, and selected lines. Have the proposed observing altitudes been selected on the basis of such calculations?

1 Background on methane and its isotopes in the atmosphere

1.1 Troposphere

The troposphere is well-mixed, and the CH_4 mole fraction is determined by the balance between its sources and sinks. Methane is a relatively long-lived gas, meaning that its tropospheric mole fractions are quite stable, with variations arising from seasonal changes in sources and sinks, and a long-term temporal trend from an imbalance between the production and loss. These signals are relatively small compared to the mole fraction.

The isotopic signatures in CH_4 in the troposphere are governed by the contributing processes of the sources and the sinks, including their kinetic fractionation effects. Biogenic sources of CH_4 have an isotopic $\delta^{13}CH_4$ of approximately -60‰compared to nonbiogenic sources, which are relatively less depleted with $\delta^{13}CH_4$ around -40‰. Biogenic sources include wetlands, rice paddies, termites, and ruminant animals, while nonbiogenic sources of CH_4 include gas venting/leakage and coal mining Tyler, Rice, and Ajie (2007).

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The background atmospheric $\delta^{13}CH_4$ is measured at a subset of the background surface in situ observation sites, such as Cape Grim (Australia), Mauna Loa, South Pole, Mace Head and others. The variability is small, with values typically varying by comfortably less than 0.5‰with season, and an interhemispheric gradient of approximately 0.2‰. The detection of isotopic signatures in the troposphere therefore places high demands on measurement precision and accuracy, to levels of performance beyond current and short-term future remote sensing capabilities.

1.2 Stratosphere

In contrast, in the stratosphere the mole fraction of CH_4 changes rapidly with altitude. The only stratospheric methane source is transport from the troposphere. This occurs mainly through the upwelling branch of the Brewer-Dobson circulation in the tropics. In the absence of local sources, CH_4 mole fractions decrease rapidly with altitude as a result of removal via chemical reaction with OH, $O(^1D)$ and Cl.

$CH_4 + OH \rightarrow CH_3 + H_2O$

$CH_4 + O(^1D) \rightarrow OH + CH_3$

$CH_4 + Cl \rightarrow HCl + CH_3$

The first of these means that methane oxidation is a source of water vapour in the stratosphere, and therefore impacts on moistening/drying processes in the UTLS.

Concentrations decrease from approximately 1800 $nmolmol^{-1}$ at the tropopause via these reactions. There are differences in rate constants between $^{13}CH_4$ and $^{12}CH_4$ for these reactions, resulting in kinetic isotope effects (KIE). A lower zero point energy for the larger molecular mass isotope results in a lower rate constant for its reaction. The lighter isotope therefore reacts more quickly, resulting in an isotopic enrichment in the remaining stratospheric CH_4. Consequently, the $\delta^{13}C$ in CH_4 increases with decreasing CH_4 mole fraction and increasing altitude. Röckmann, Brass, Borchers, and Engel (2011) show this with high-altitude balloon measurements of methane and its isotopic composition. Rather than the sub permille variability seen through most of the well-mixed troposphere around values of approximately -47‰, $\delta^{13}C$ in CH_4 in the stratosphere increases with height, with some values reaching higher than -20‰.

1.3 Implications

Despite its importance in anthropogenic radiative forcing, much is not yet understood about methane in the atmosphere. For example, there has been ongoing debate over the cause of a cessation of its growth rate between approximately 1999 and 2006, and subsequent resumed atmospheric increase Bousquet et al. (2006); Schaefer et al. (2016). Like for CO_2, most estimates of the global budget of CH_4 come from top down modelling based on global chemical transport modelling. Unlike CO_2, however, the role of the stratosphere is extremely important for the balance of methane. A number of recent studies suggest that there is sensitivity to surface flux estimates dependent on modelling stratospheric methane Ostler et al. (2016); Saad et al. (2016), and that there are considerable differences between models in the stratosphere (Wang et al, in preparation). The causes of these differences is related to a combination of transport and chemistry, with stratosphere-troposphere exchange an important contributor Ostler et al. (2014).

Quantifying both transport and chemistry for methane in the upper troposphere/lower stratosphere (UTLS) therefore has important implications for the global methane budget. Especially of interest are any changes to the transport fluxes between the upper troposphere and lower stratosphere that could occur with changing climate and convective activity. Given the sensitivity of methane and its isotopic signature in the stratosphere, measurements of these could provide powerful constraints on these effects, especially with increased temporal and spatial coverage, such as could be provided by satellite(s). There are currently few measurements of isotopic methane in the stratosphere (e.g. Röckmann et al. (2011)).

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These measurements would be most effective if they spanned the area of greatest variability. Specifically, this would mean encompassing the tropopause and the altitudes above. The proposed satellite observation altitudes of 14 ± 2, 18 ± 2, and 22 ± 2 km would provide measurements across the tropopause in the tropics, which is the region where most upward transport occurs. Contributions to stratosphere-troposphere exchange in the mid-latitudes and the poles, where significant downward transport can occur, would be difficult to capture, as the tropopause heights in these regions would be mostly below the observation altitudes.

2 Validation

Apart from the scientific considerations about sampling across the UTLS, practical validation/calibration options should also be addressed. FTIR ground-based measurements of CH_4 cannot provide adequate vertical resolution to validate CH_4 profiles with 4km resolution (typically two degree of freedom aportioned between stratosphere and troposphere and therefore a vertical resolution of order 10km), and certainly cannot provide validation of isotopic methane. The other options are aircraft or balloon-borne profiles, which are generally expensive, and an empirical validation approach.

One option for obtaining vertical profiles would be to employ a relatively new technique, called AirCore Karion, Sweeney, Tans, and Newberger (2010). This technique has been used to obtain vertically resolved profiles of CO_2, CH_4 and CO. The University of Wollongong group is expanding to develop AirCore measurement capability. With an appropriate analyser, for example a Picarro G2201-*i* or G2132-*i*, this technique could also be applied to methane isotopes as a more cost effective solution than aircraft campaigns, with the advantage of also being able to reach higher altitudes (up to 30km).

An alternative would be to employ an empirical validation approach. Specifically, because the concentration and isotopic ratio of CH_4 in the troposphere is relatively well-known and constant, if the satellite were to measure at one of its altitudes in the troposphere, this knowledge could be used to empirically correct the satellite measurements to match the known tropospheric values.

- Validation
- Latitudinal variability
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2.1 Scientific questions

- Transport (strat-trop exchange, and stratospheric transport itself)
- Climate implications (moistening/drying, for example)

3 Concluding remarks

While the proposed altitudes of 14, 18 and 22km would be useful, if we wish to observe and/or quantify stratosphere-troposphere exchange, having an observation at a lower altitude would be valuable, if it is possible.

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