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High-Resolution Spectroscopy of Stable Atmospheric Molecules

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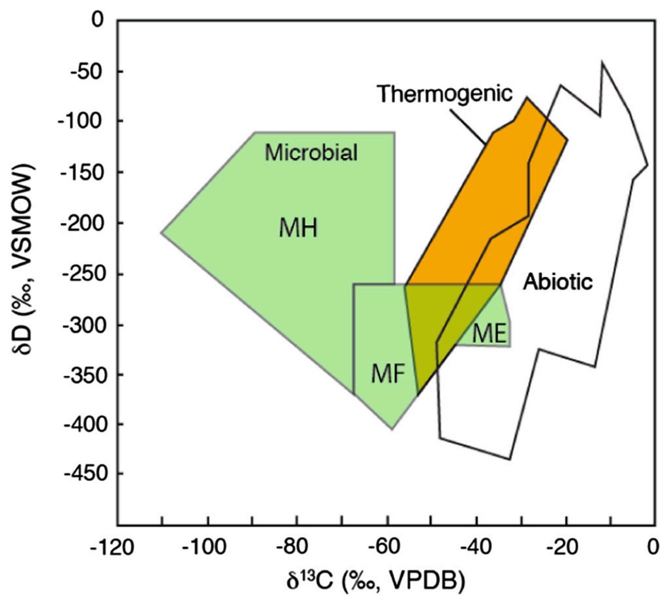
Methane Isotope Chemistry

Isotope-ratio analysis allows for hydrocarbon sources and sinks to be tracked and quantified. This ratio can elicit information on the formation, loss processes, and associated temperatures particular to a gas sample. We focused our work on methane, because it is the most important greenhouse gas behind CO_2, and we sought to characterize the characteristic isotopic signatures different source and loss processes leave on a methane sample.



Isotopic enrichment of ^{13}C and D for different CH_4 sources

(Douglas et al. 2017)

The isotopic signature a reaction imparts is expressed as a kinetic isotope effect (KIE):

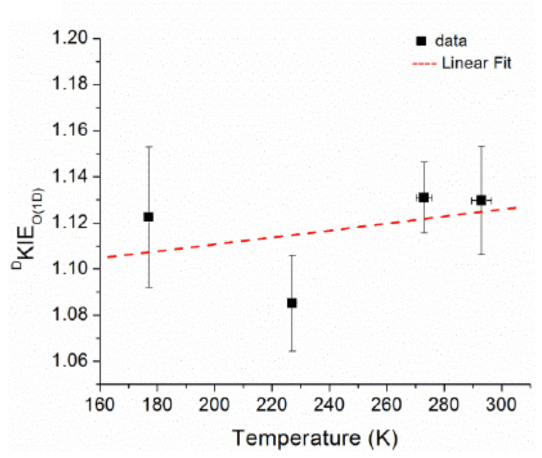
$$KIE = \frac{k_{light}}{k_{heavy}} = \frac{\ln([light]_f/[light]_0)}{\ln([heavy]_f/[heavy]_0)}$$

We studied the effect of substituting ^{13}C for ^{12}C and D for H in CH_4 at 177 – 293 K in the loss reactions:

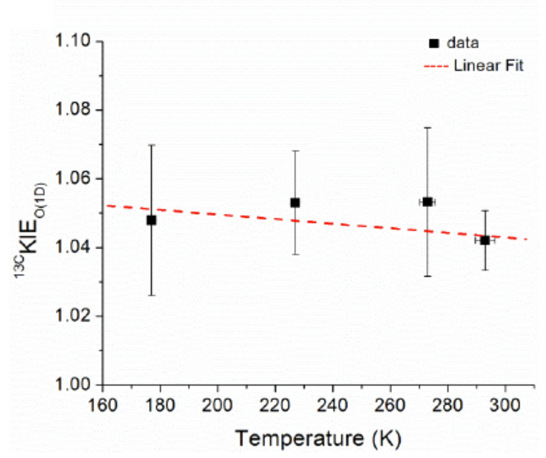
$CH_4 + O(^1D) \rightarrow CH_3 + OH$

$CH_4 + OH \rightarrow CH_3 + H_2O$

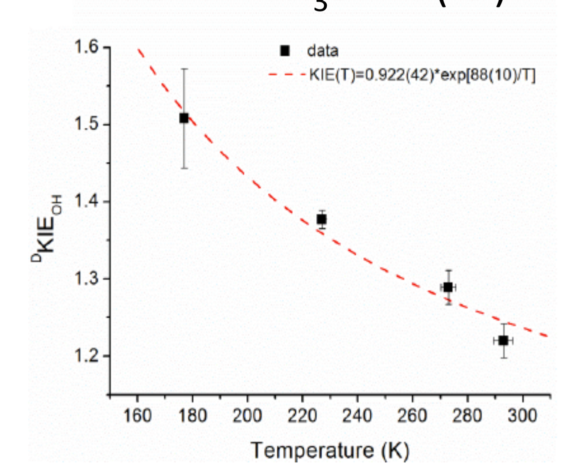
Results



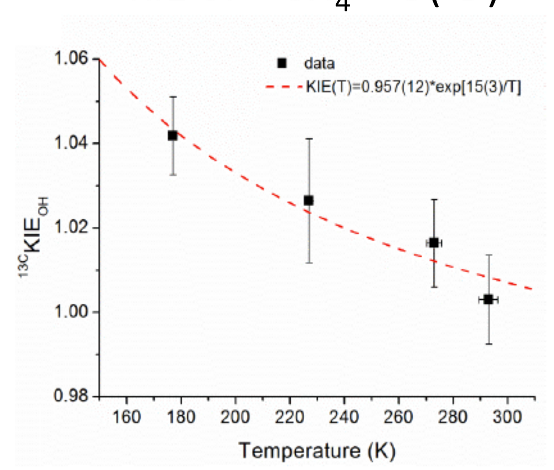
KIE of $^{12}CH_3D + O(^1D)$



KIE of $^{13}CH_4 + O(^1D)$



KIE of $^{12}CH_3D + OH$



KIE of $^{13}CH_4 + OH$

KIE of $CH_4 + O(^1D)$ shows no temperture dependence

KIE of $CH_4 + O(^1D)$ shows larger than expected temperature depedence

Future Work

Perform similar experiments with:

- Cl as an oxidant
- Multiply-substituted clumped isotopes $^{13}CH_3D$ and $^{12}CH_2D_2$

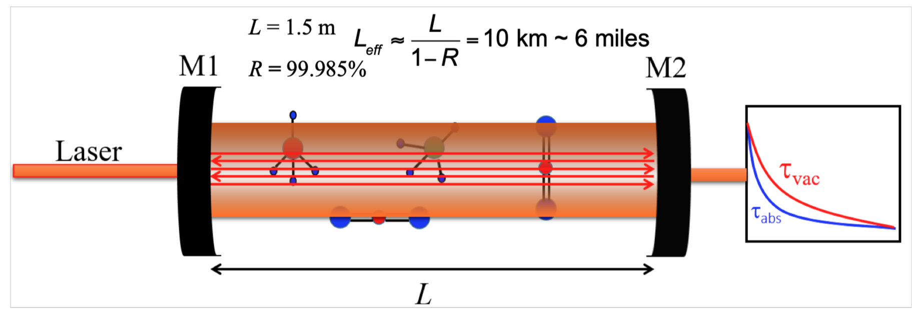
Acknowledgments

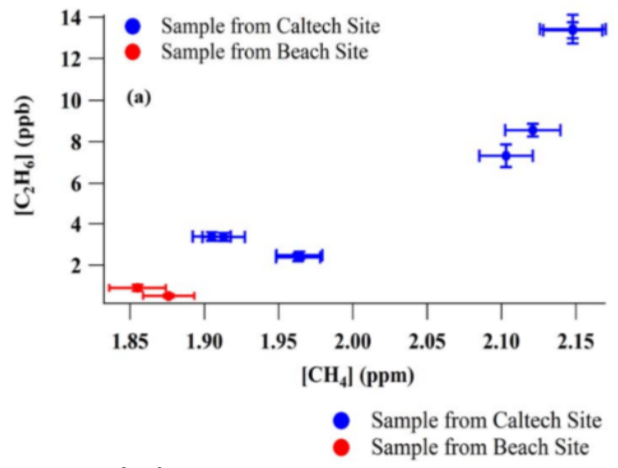
The NASA NESSF fellowship for supporting Linhan Shen and Thinh Bui.
Result plots from Thinh Bui's dissertation.

Atmospheric Ethane Abundance: Identifying Fugitive Emissions

A challenge in identifying fugitive methane emissions, such as industrial gas leaks, is distinguishing them from often neighboring biogenic sources such as livestock, landfills, or wetlands.

Comparing a sample's ratio of methane to higher order hydrocarbons like ethane can identify a hydrocarbon source. Biogenic sources have an ethane/methane enhancement ratio of less than 0.2%, while thermogenic sources typically show enhancement greater than 6%, and have been measured as high as 45%.





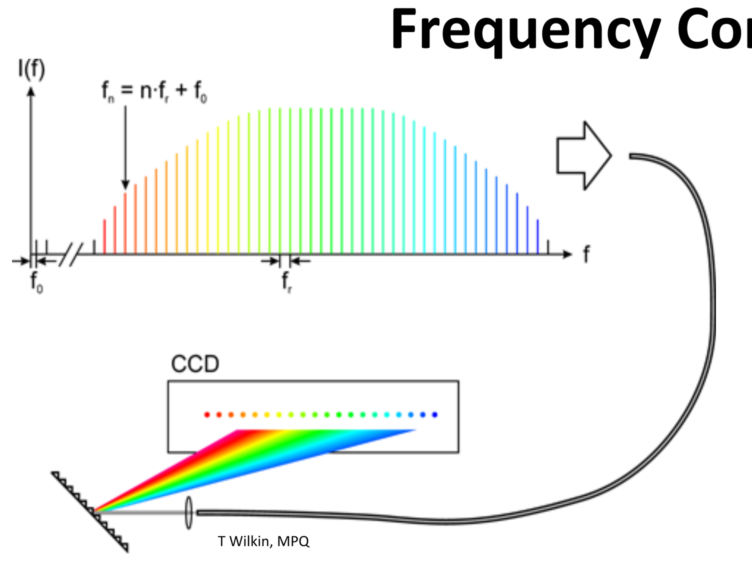
Future Work

- Improve sample purification and frequency stability
- Quantify methane/ethane ratios in various hydrocarbon field sources

Acknowledgements

- The NASA NESSF fellowship for supporting Linhan Shen

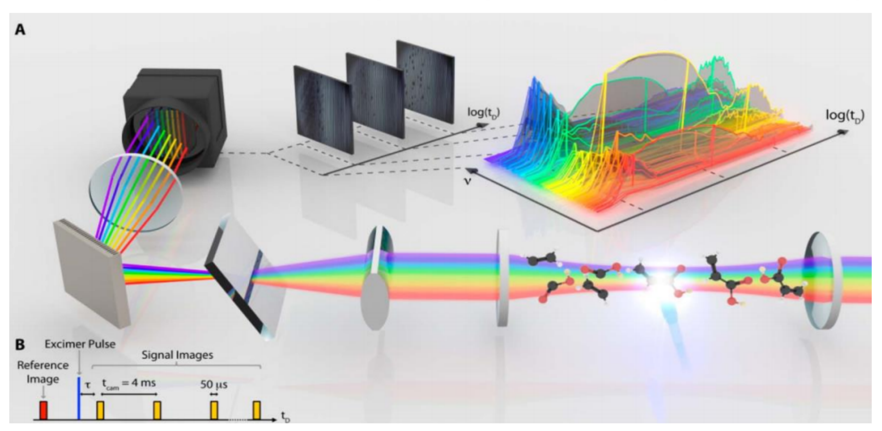
Frequency Comb Spectroscopy



To increase the throughput and number of probe wavelengths available to study complex chemical systems, our group has begun to employ frequency comb spectroscopy. The comb spectrum is a series of equally-spaced probe frequencies, where the frequency of the m^{th} comb tooth = $mf_{rep} + f_0$.

- Measured loss pathways of trans-DOCO, intermediate of OD + CO
- OH + CO kinetics necessary to characterizing radical recycling and ozone formation in the atmosphere

Time-Resolved Frequency Comb Spectroscopy



Fleisher et al. J. Phys. Chem. Lett. (2014), 5 (13), 2241-2246.

Future Work

Construct novel frequency comb systems: using AoD deflectors, microresonator combs, 4 and 10 μm compact diode laser combs.

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- The NASA NESSF fellowship for supporting Thinh Bui
- The Ye lab at JILA, UC Boulder, CO

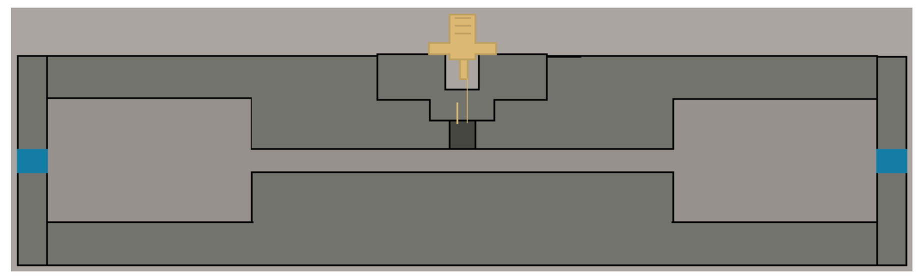
Photoacoustic Spectroscopy of O_2 A-band

In collaboration with NASA's Jet Propulsion Laboratory, we are working to determine OCO-2 spectroscopic parameters for O_2 and CO_2 concentration determination. OCO-2 observes localized CO_2 sources and sinks, with a concentration accuracy goal of ±1 ppm.

Eldering et al. Science (2017), 358.

The absorbance pathlength is determined from measuring the absorbance of the O_2 A-band (759 – 771 nm). Errors in O_2 spectroscopy propagate to the determined CO_2 concentration, and the largest current uncertainties are from line mixing (LM) and collision induced absorption (CIA). Our high-resolution laboratory studies seek to improve understanding of these processes, reducing the uncertaintity in the retrieved CO_2 concentration.

Technique

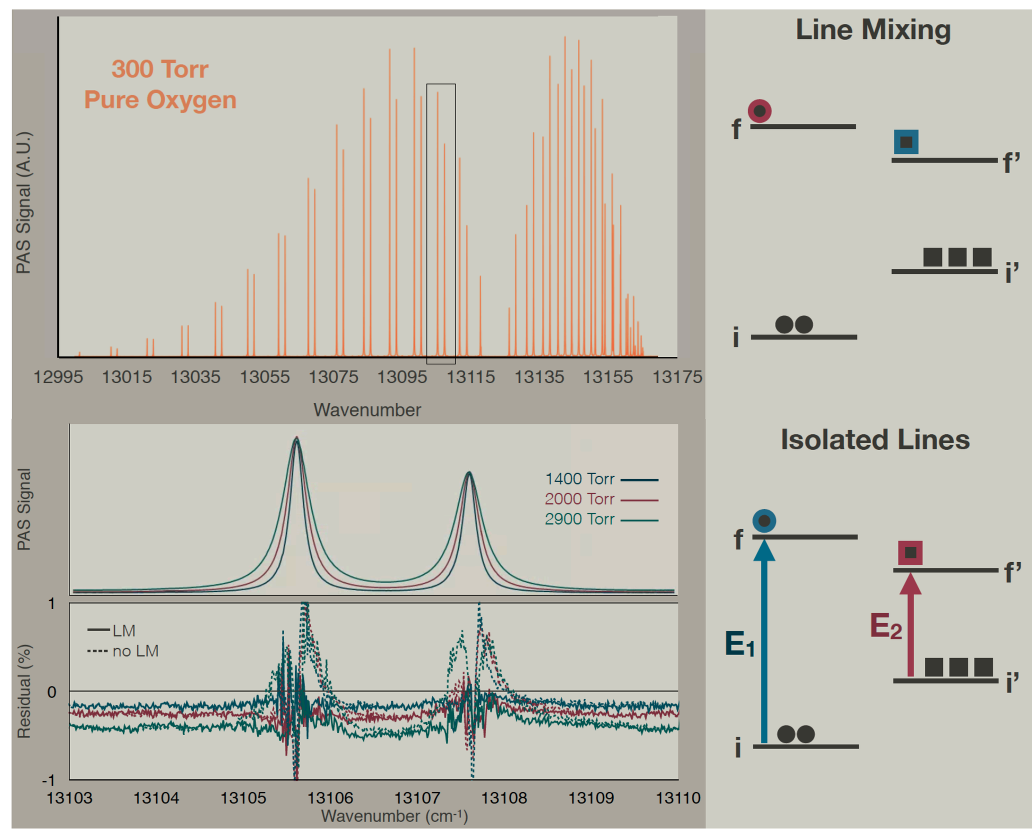


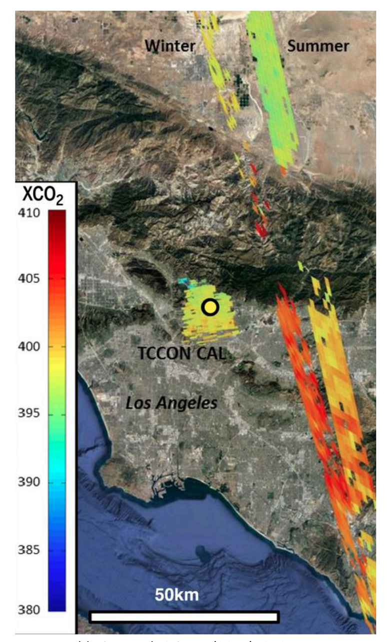
Gillis et al. Rev. Sci. Instr. (2010), 81, 6.

Photoacoustic absorption spectroscopy (PAS) to measure O_2 A-band:

- Has high-sensitivity, zero-background, and large dynamic range
- Tunable laser is intensity-modulated, and when laser is resonant with an O_2 absorption, absorbed energy is transferred to and heats the surrounding bath gas, creating a pressure wave detectable on a microphone.

Results





Eldering et al. Science (2017), 358.

Future Work

- Extend PAS to aerosols
- Understand temperature dependence

Acknowledgements

NASA OCO-2 mission