Methane Source and Sink Attributions Using Cavity Ring-down Spectroscopy

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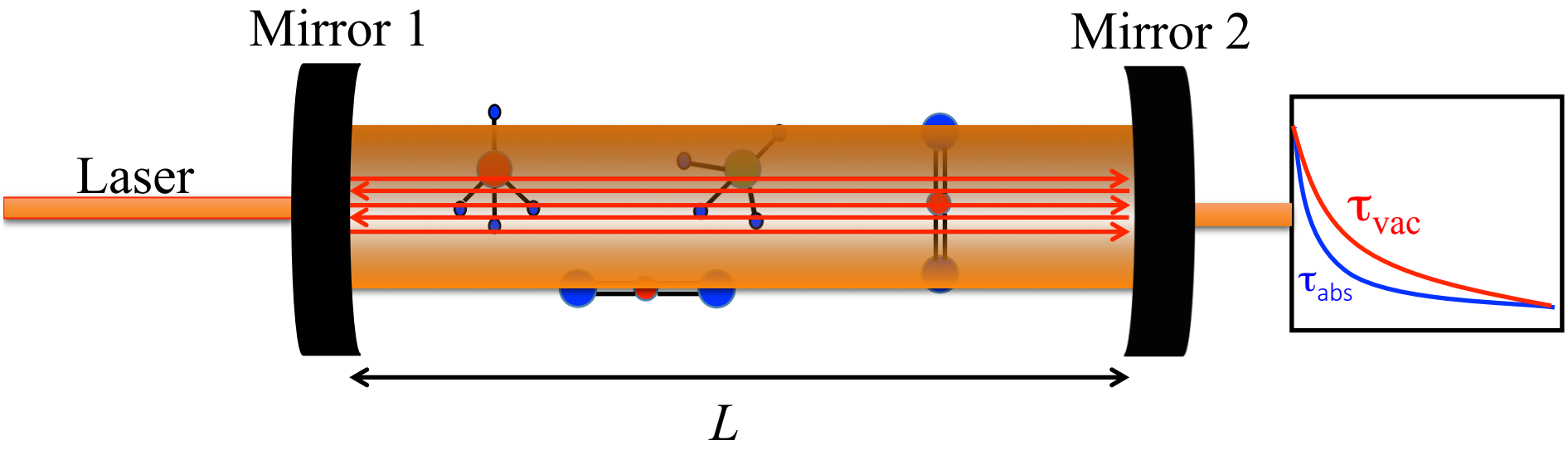
Fundamentals of Cavity & Cavity Ring-down Spectroscopy (CRDS)



- measure absorption without noise from light intensity fluctuation

- increase absorption path length by increasing mirror reflectivity

$L = 20.75$ cm (~ physical length of the TLS)

$R \sim 99.985$ %

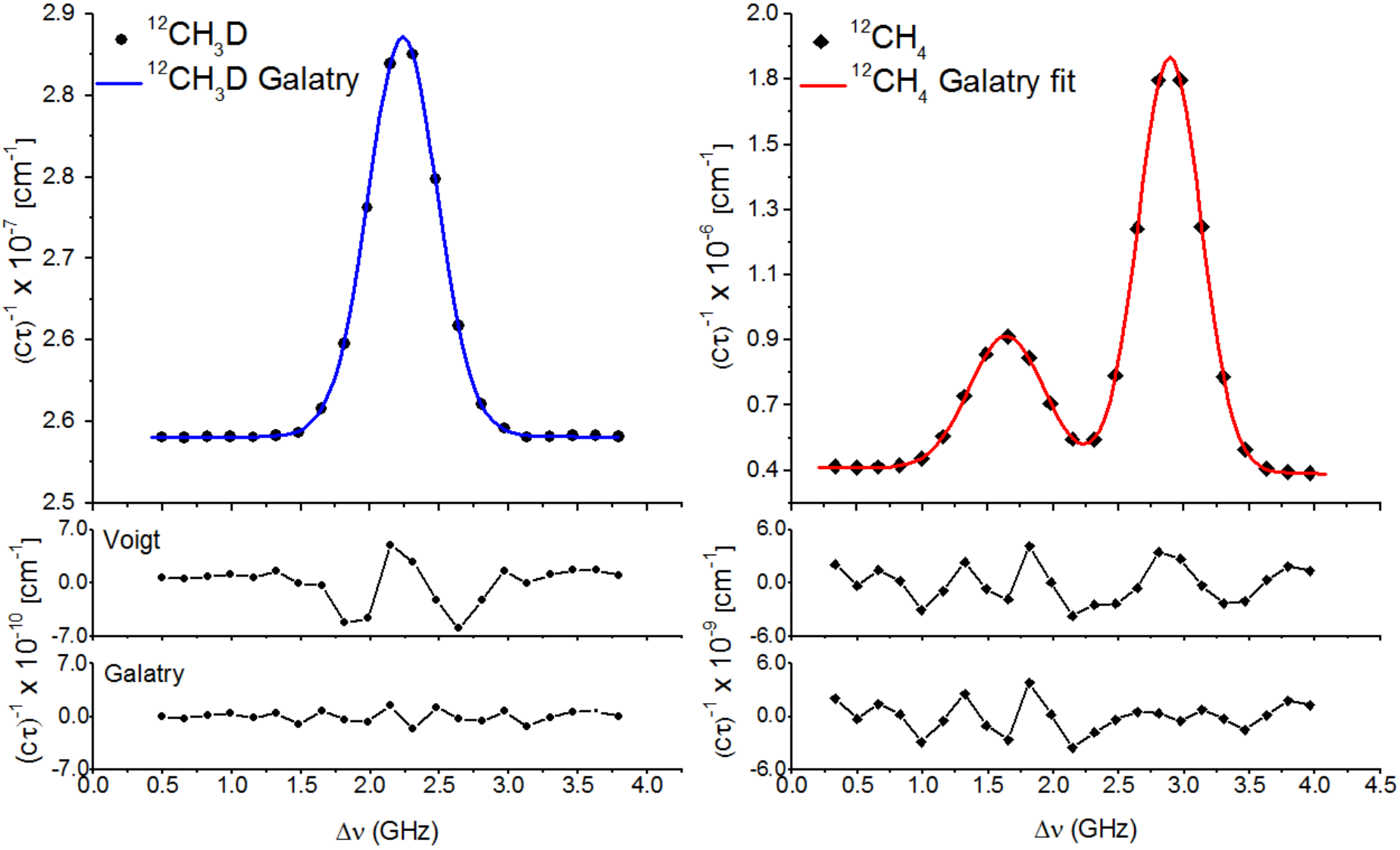
$$L_{eff} \approx \frac{L}{1-R} = 1.38 \text{ km}$$ (16.8 m for TLS)

Singly Substituted Methane Abundance Measurement

Laser Type	DFB
Wavelength Range	5999 – 6007 cm^{-1}, 6456 – 6467 cm^{-1}
Physical Cavity Length	90 cm
Absorption Pathlength	30 km
Frequency Stabilization	Yes
Measurement Target	$\delta^{13}C$, δD
α_{min} (cm^{-1} $Hz^{-1/2}$)	1.0×10^{-11}
Peak Line Intensity (cm^{-1} mol^{-1} cm^2)	($^{12}CH_4$) 1.0×10^{-21}

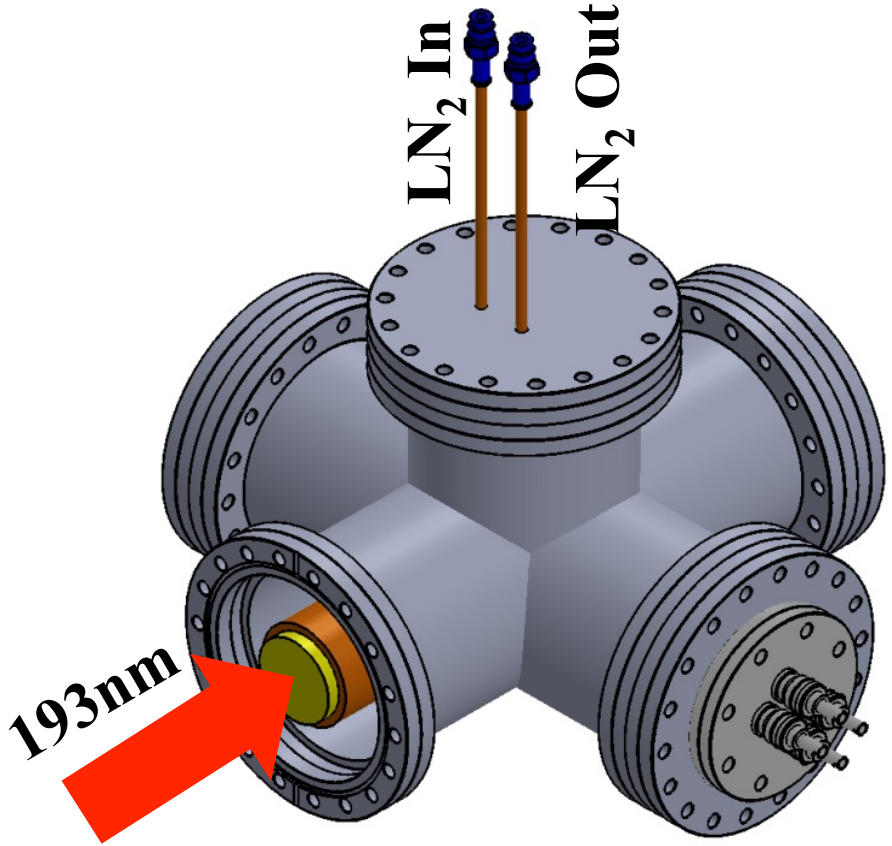
- Most ideal region for $^{12}CH_4$ and $^{13}CH_4$ measurements.
- Sensitivity equivalent to [$^{12}CH_4$] ~ 750 ppt under Martian pressure.

Singly Substituted Methane Abundance Measurement



Error in δD ~ 0.24 ‰ (2σ)

Temperature Dependent KIE Measurements of O(^{1}D)/OH + Methane



Cold Chamber (<100K)

$$\frac{\ln([^{12}CH_4]_t / [^{12}CH_4]_0)}{\ln([^{12}CH_3D]_t / [^{12}CH_3D]_0)} = \frac{k_H}{k_D} = \text{KIE}$$

Photochemistry Cell

$[^{13}CH_4]_t$ $[^{12}CH_4]_t$

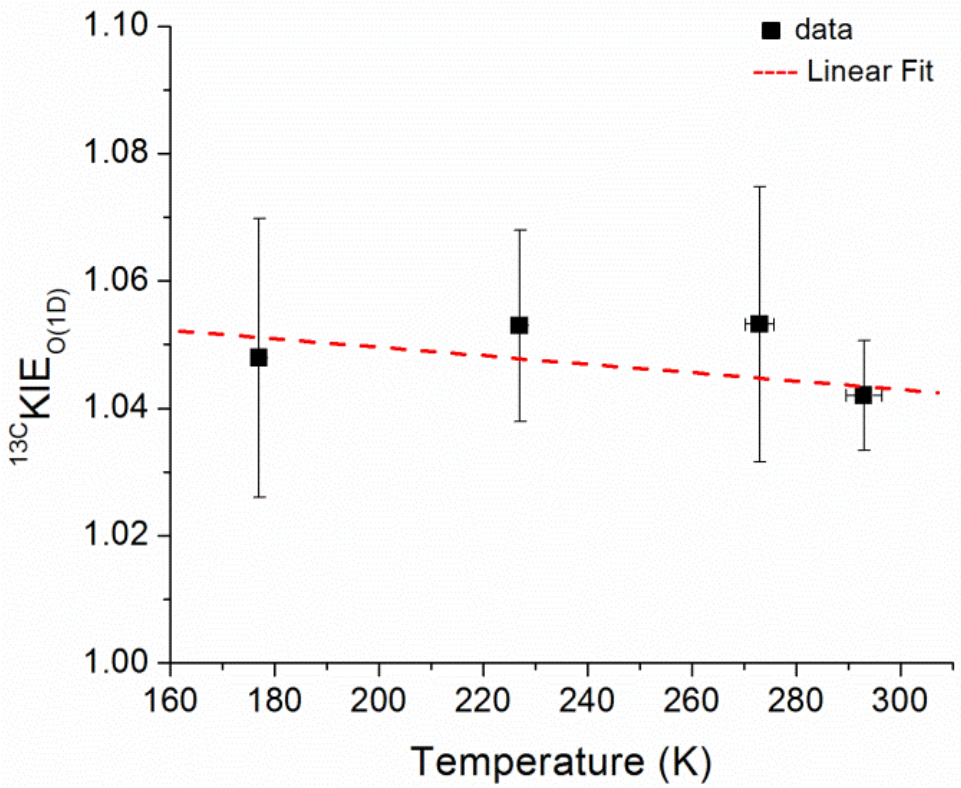
Reference Cell

$[^{13}CH_4]_0$ $[^{12}CH_4]_0$

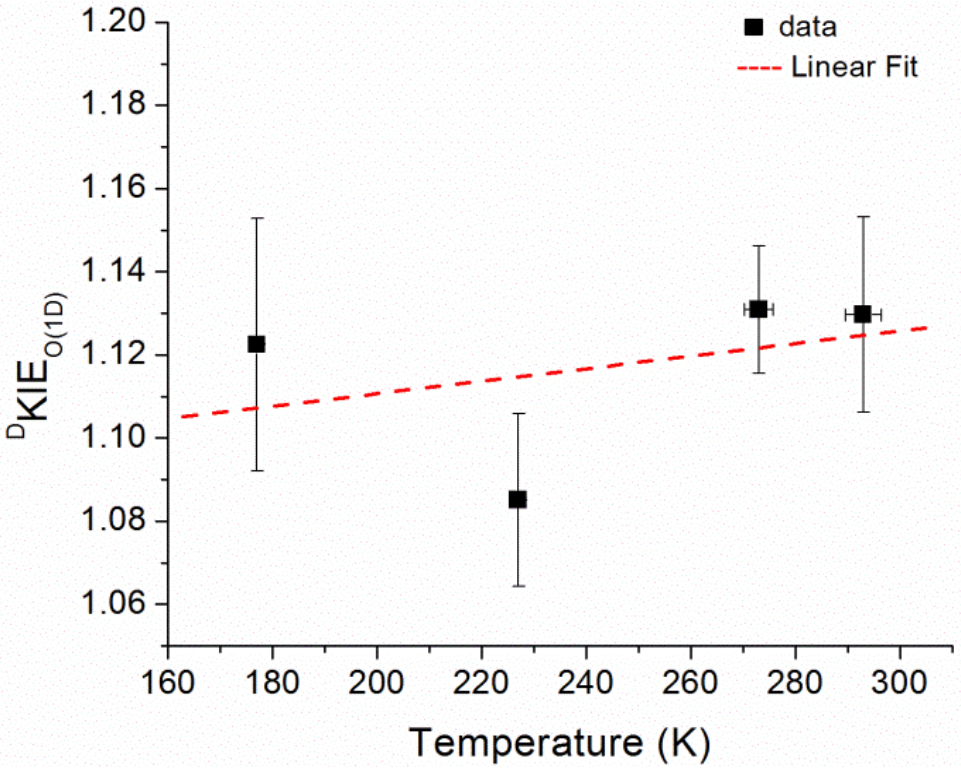
Temperature Dependent KIE Measurements of $O(^1D)$ + Methane

- **Primary CH_4 Depletion Reaction**
  - $N_2O + h\nu \rightarrow N_2 + O(^1D)$
  - $O(^1D) + CH_4 \rightarrow OH + CH_3$ ($k = 1.12 \times 10^{-10}$ $cm^3 molec^{-1} s^{-1}$)
- **Secondary CH_4 Depletion Reaction**
  - $OH + CH_4 \rightarrow H_2O + CH_3$ ($k = 6.3 \times 10^{-15}$ $cm^3 molec^{-1} s^{-1}$)

D-KIE $O(^1D)$



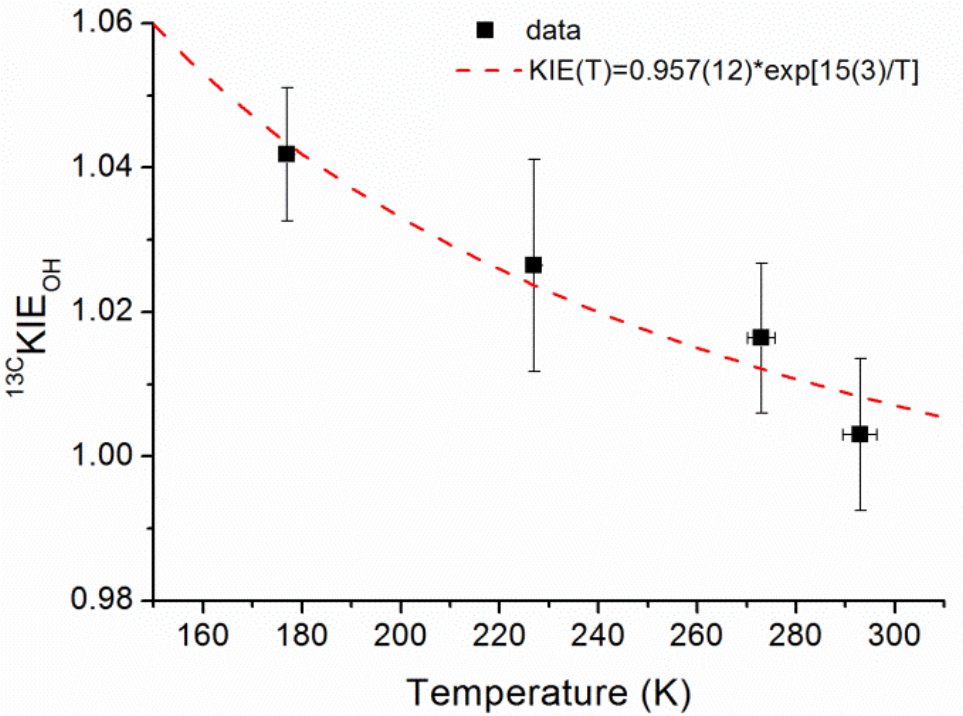
^{13}C-KIE $O(^1D)$



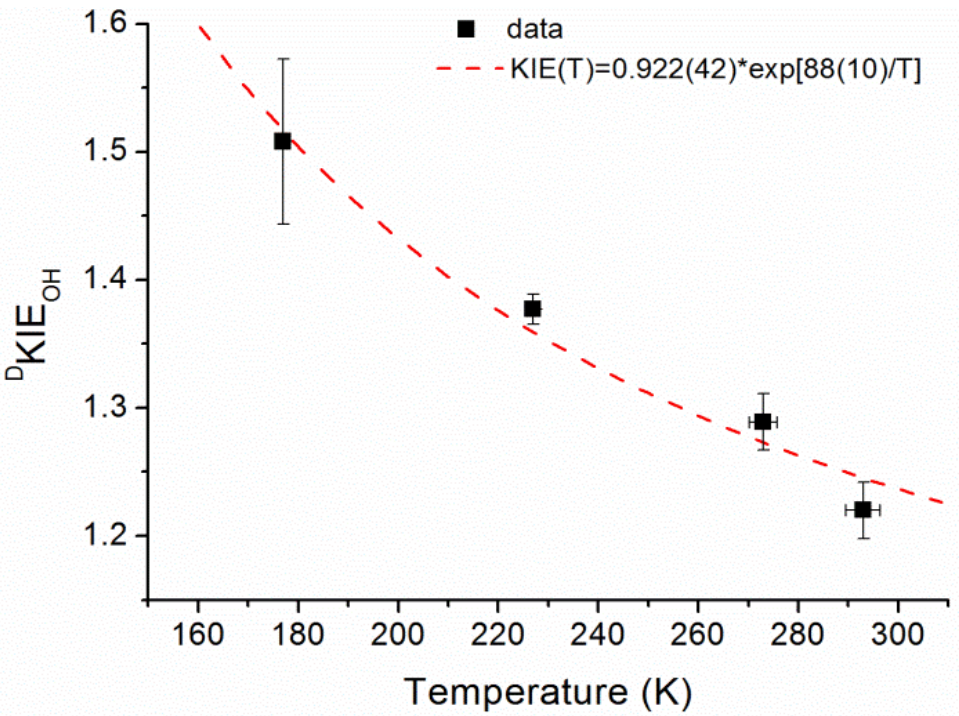
Temperature Dependent KIE Measurements of OH + Methane

- **Primary CH_4 Depletion Reaction**
  - $N_2O + h\nu \rightarrow N_2 + O(^1D)$
  - $O(^1D) + H_2 \rightarrow OH + H$ ($k = 1.1 \times 10^{-10}$ $cm^3molec^{-1}s^{-1}$)
  - $OH + CH_4 \rightarrow H_2O + CH_3$ ($k = 6.3 \times 10^{-15}$ $cm^3molec^{-1}s^{-1}$)
- **Secondary CH_4 Depletion Reaction**
  - $O(^1D) + CH_4 \rightarrow OH + CH_3$ ($k = 1.12 \times 10^{-10}$ $cm^3molec^{-1}s^{-1}$)

D-KIE OH



^{13}C-KIE OH

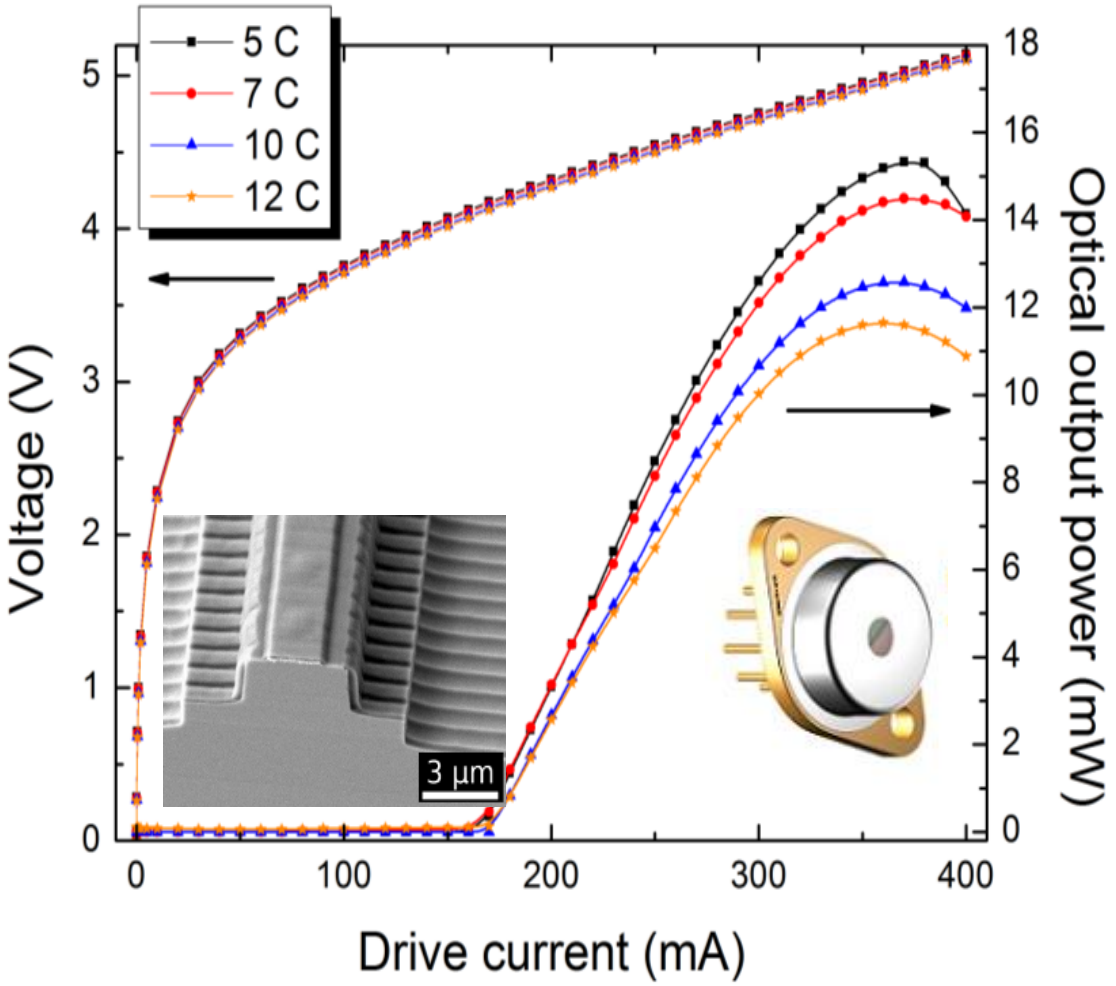


Ethane to Methane Ratio Measurement

Laser Type	IC Laser
Wavelength Range	2972 - 2984 cm^{-1}
Physical Cavity Length	80 cm
Absorption Pathlength	4 km
Frequency Stabilization	No
Measurement Target	$[C_2H_6]$:$[CH_4]$
α_{min} (cm^{-1})	3.5×10^{-10}
Peak Line Intensity (cm^{-1} mol^{-1} cm^2)	($^{12}CH_4$) 1.2×10^{-19}

- Most ideal region for $^{12}CH_4$ and $^{12}C_2H_6$ measurements.
- Sensitivity equivalent to [$^{12}CH_4$] ~ 220 ppt under Martian pressure.
- Sensitivity equivalent to [$^{12}C_2H_6$] ~ 2.2 ppb under Martian pressure.

High Power ICL Manufactured by JPL Microdevices Laboratory (MDL)

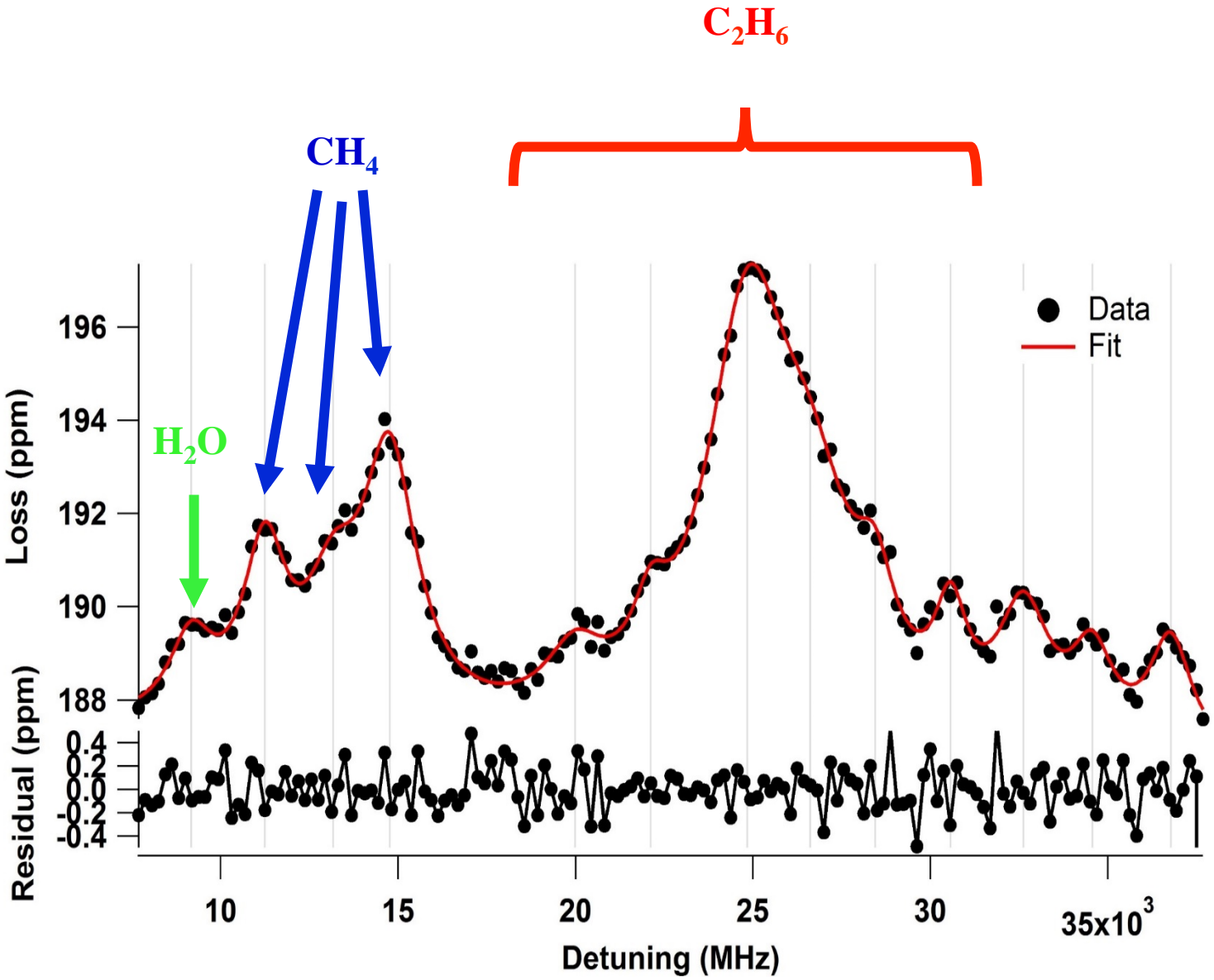


- **Laser line center: 2977 cm^{-1}**
- **Tunable range: 2972 cm^{-1} to 2984 cm^{-1}**
- **Peak power: > 15 mW**
- **Side-mode attenuation: 25dB**

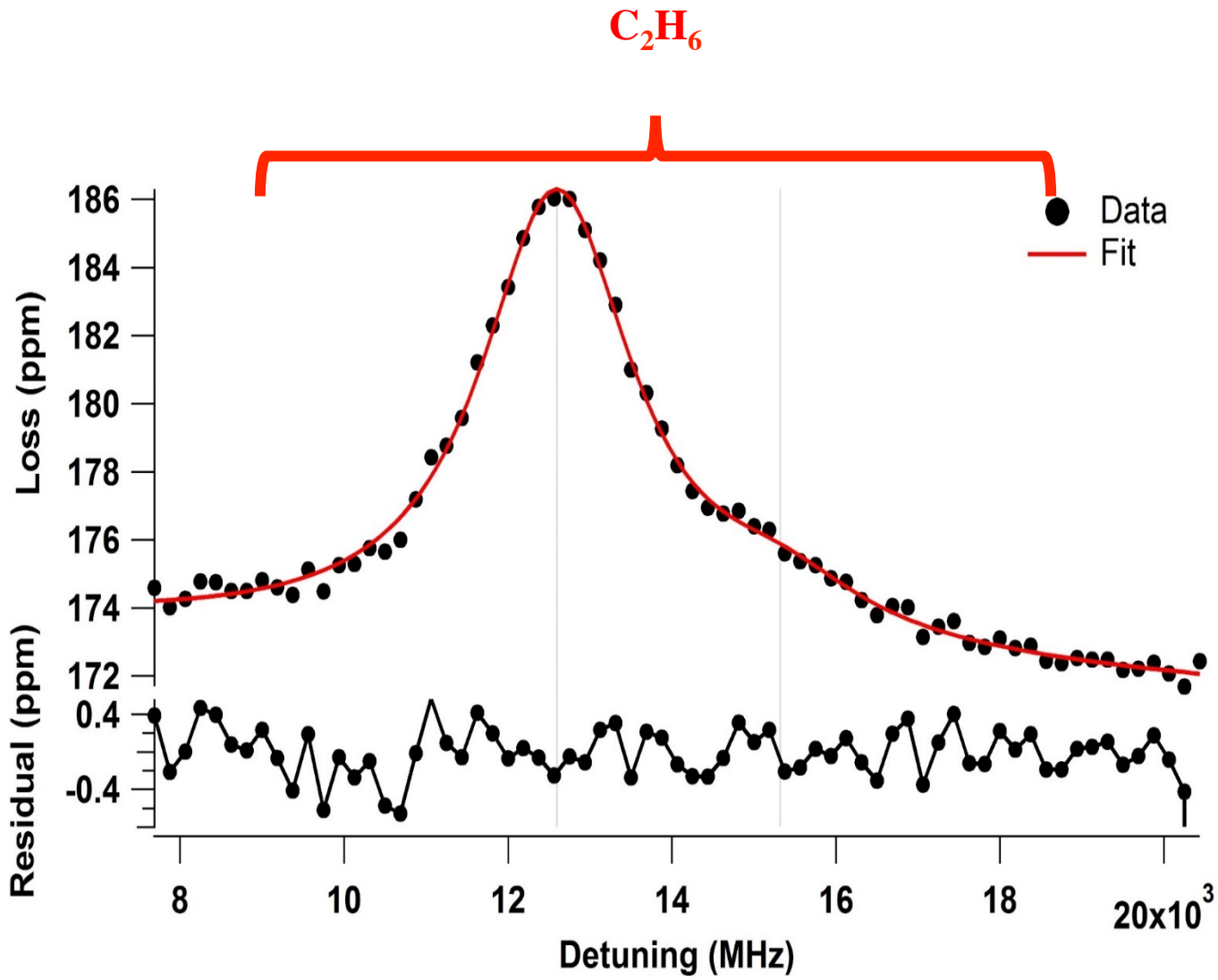
National Aeronautics and Space Administration
Jet Propulsion Laboratory
California Institute of Technology

C. Borgentun, C. Frez, R. M. Briggs, M. Fradet, S. Forouhar, Optics Express, ***23,*** *2446-2450 (2015)*

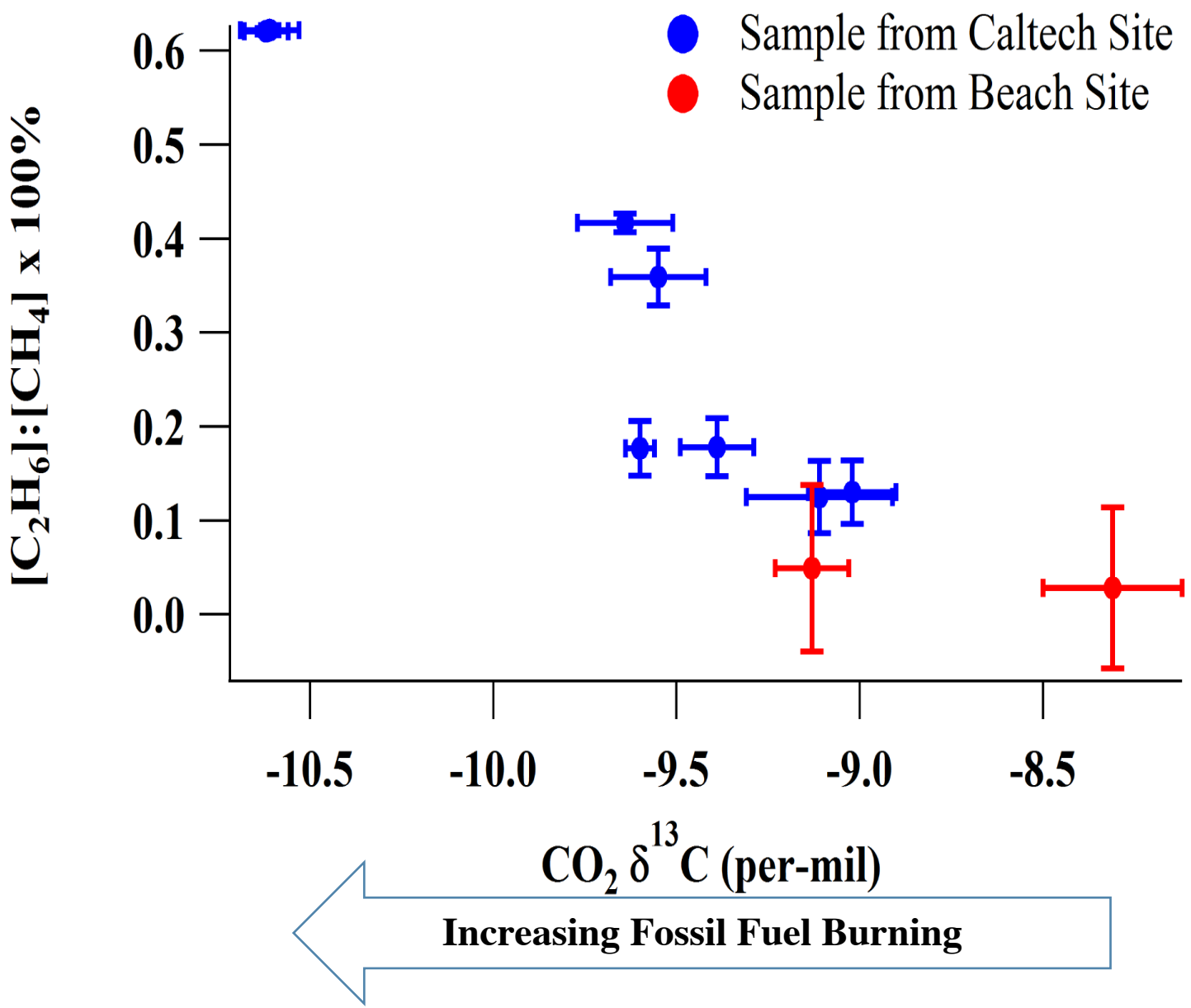
Ethane to Methane Ratio Measurement



Ethane to Methane Ratio Measurement



Ethane to Methane Ratio Measurement



Summary

	NIR Isotopes	Ethane:Methane
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