A mm/submm Wave Spectrometer to Quantify Astrochemical Reaction Rates

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Motivation

Observational astronomy is becoming "data enabled", and the molecular inventory of ISM is diverse

Herschel (ESA)

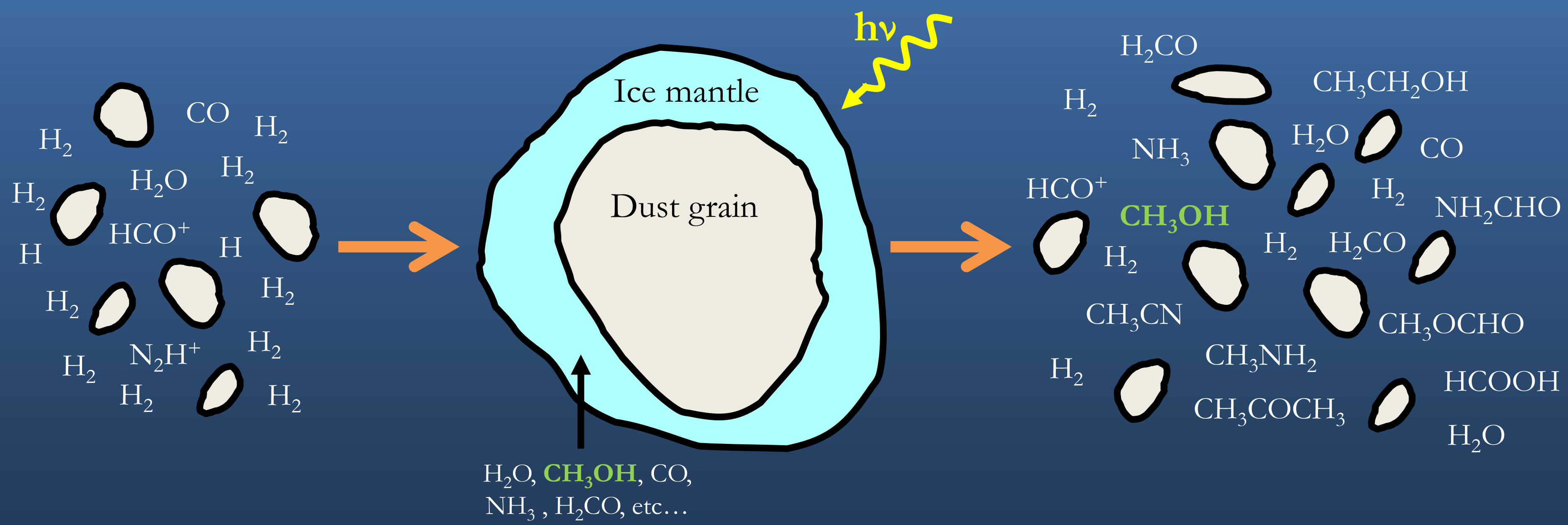
SOFIA (NASA/DLR)

ALMA (ESO/NAOJ/NRAO), photo credit: J. Guarda (ALMA)

Chemical models rely on quantitative rate information

→ **laboratory support plays central role**

Methanol as Case Study



$$CH_3OH \xrightarrow{h\nu} \mathbf{CH_2OH} + H$$
$$\longrightarrow \mathbf{CH_3O} + H$$
$$\longrightarrow \mathbf{CH_3} + OH$$
$$\longrightarrow H_2CO + H_2$$

$$\mathbf{CH_2OH} \xrightarrow{HCO} \mathbf{HCOCH_2OH}$$
$$\mathbf{CH_3O} \longrightarrow \mathbf{HCOOCH_3}$$
$$\mathbf{CH_3} \longrightarrow CH_3CHO \xrightarrow[+OH]{-H} \mathbf{CH_3COOH}$$

Methanol as Case Study

Branching ratios have yet to be quantitatively measured

$$CH_3OH \xrightarrow{h\nu} CH_2OH + H$$
$$\longrightarrow CH_3O + H$$
$$\longrightarrow CH_3 + OH$$
$$\longrightarrow H_2CO + H_2$$

CH_3O & CH_2OH need more laboratory spectral information

$$CH_2OH \xrightarrow{HCO} HCOCH_2OH$$
$$CH_3O \longrightarrow HCOOCH_3$$
$$CH_3 \longrightarrow CH_3CHO \xrightarrow[+OH]{-H} CH_3COOH$$

Scientific Approach

1. Build mm/submm spectrometer

2. Benchmark spectrometer
   - radical prep/detection
   - sensitivity

3. Spectral support of photodissociation products

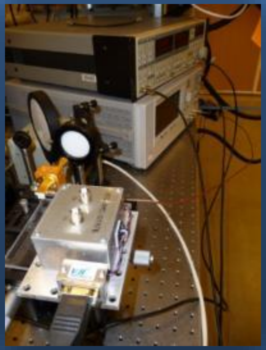
4. Observe and quantify methanol photodissociation products

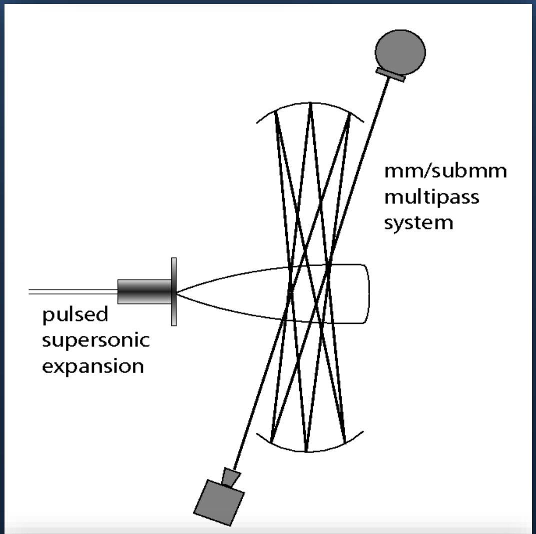
Experimental Design

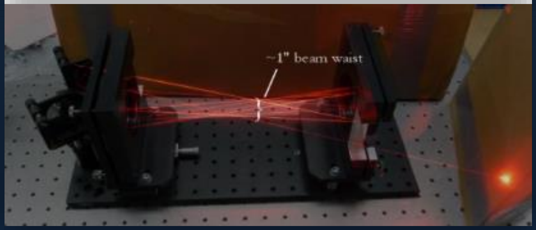
- mm/submm wave source is analog signal generator + frequency multiplier kit to access 50-1000 GHz

- Spectral beam is coupled to multipass optical cell (Perry cell) to give ~7 passes

- Spectroscopy is performed 2-2.5 cm downstream from valve

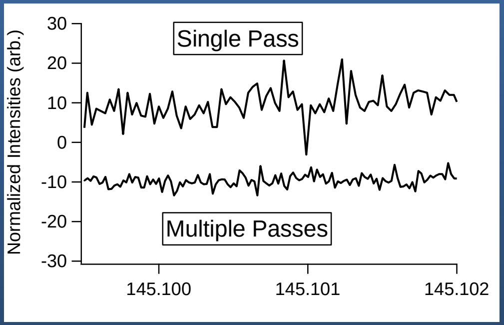




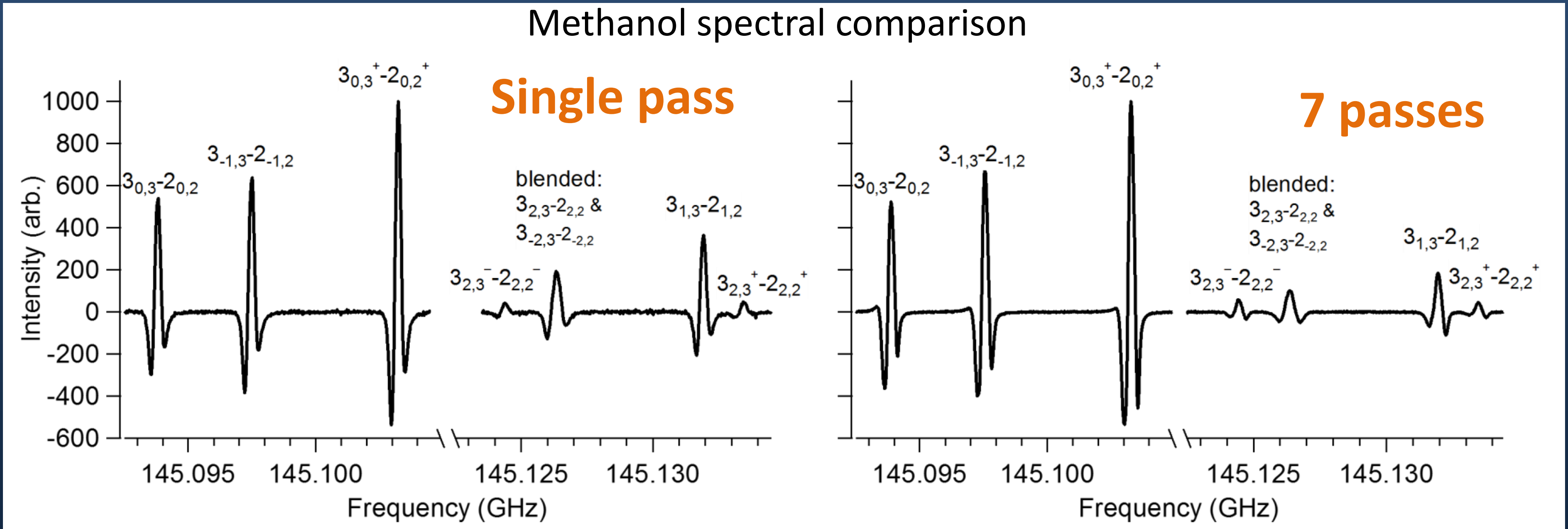


Experimental Design

- Multiple passes enables 3- to 5-fold increase in SNR



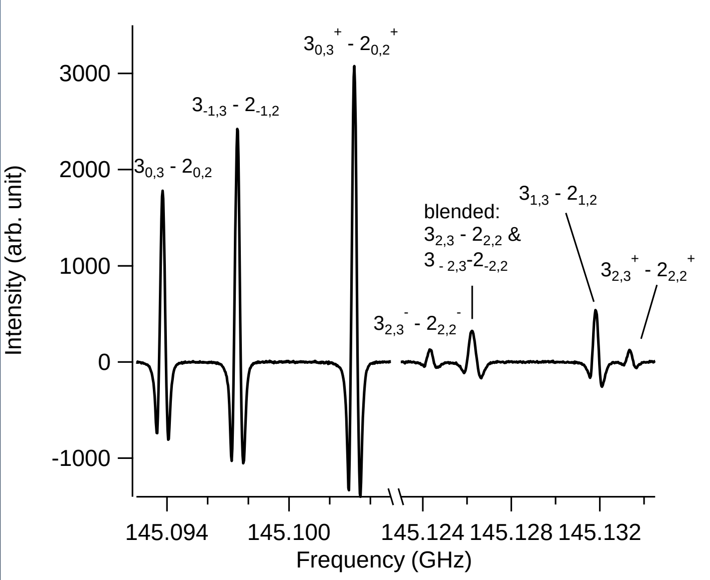
- No other differences
  - both scans show <20 K rot. temp.
  - no line broadening

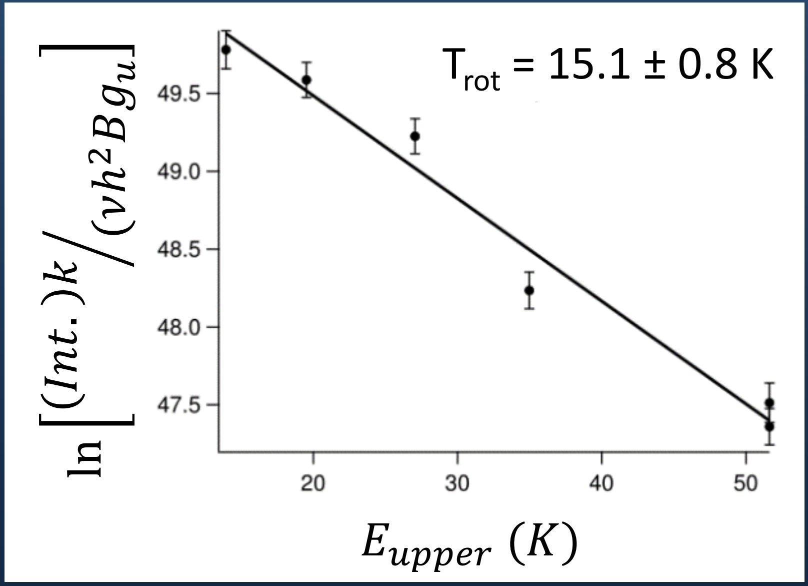


Laas, Hays, & Widicus Weaver 2013, JPC A, online only

Spectral Analysis

- Direct absorption enables quantification of sample (Beer's Law)
- Boltzmann analysis is performed via rotation diagram
  - Uncalibrated integrated intensities preclude absolute, but not relative concentrations
  - Linearity of graph ensures LTE is reasonable approximation

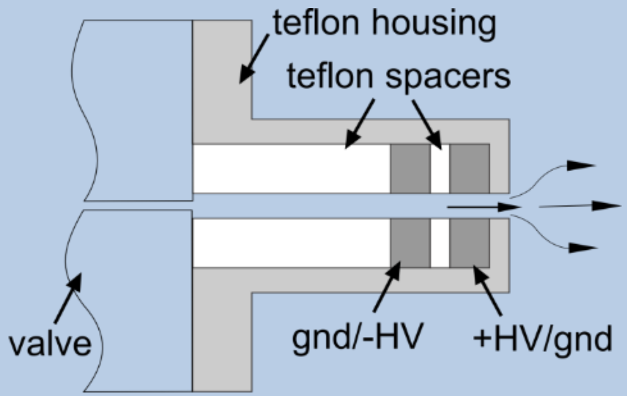


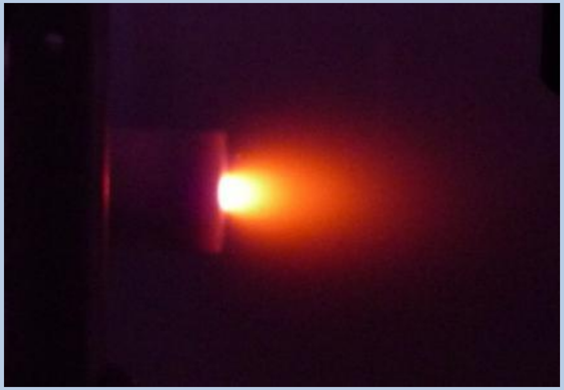


High-Voltage Discharge Study

- A high-voltage plasma discharge was performed on methanol to test ability of spectrometer to prepare, detect, and quantify highly-reactive dissociation products
  - H_2CO and CH_3O as previously reported products (Melnik *et al.*, JCP, 2011)

- Discharge source is based on design by McCarthy *et al.* (2000-present)



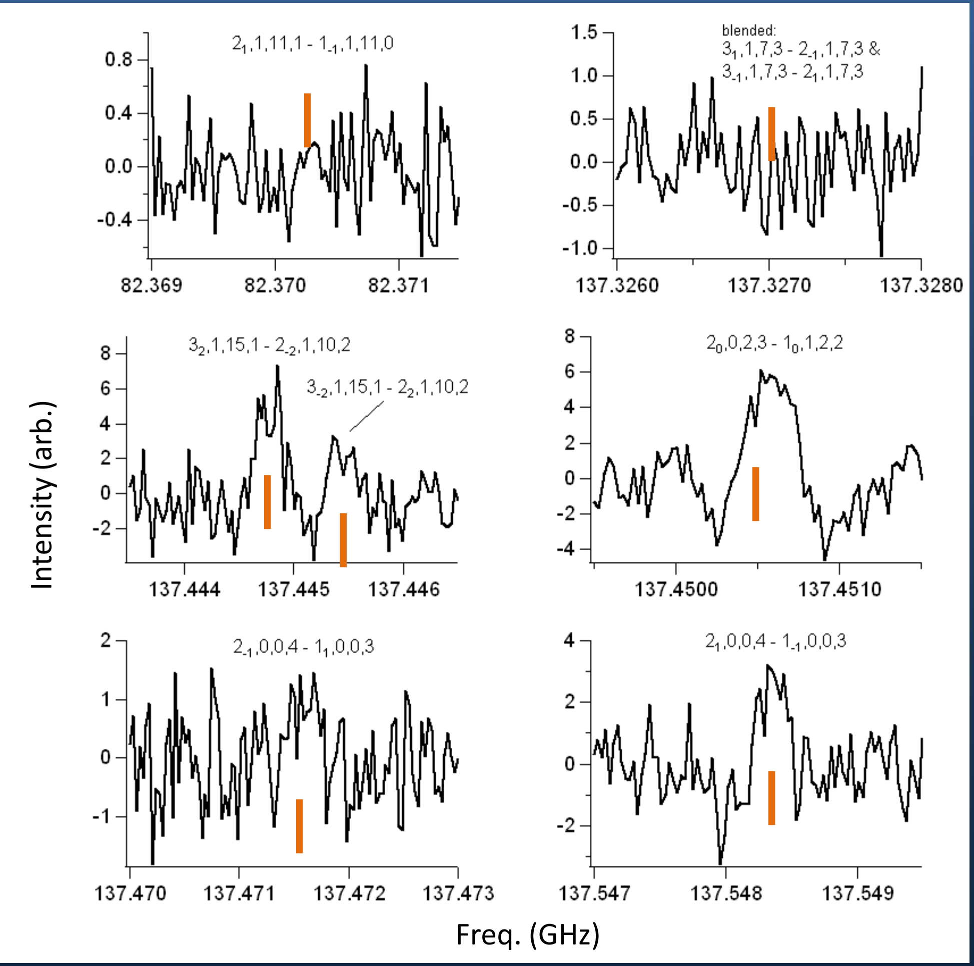


High-Voltage Discharge Study

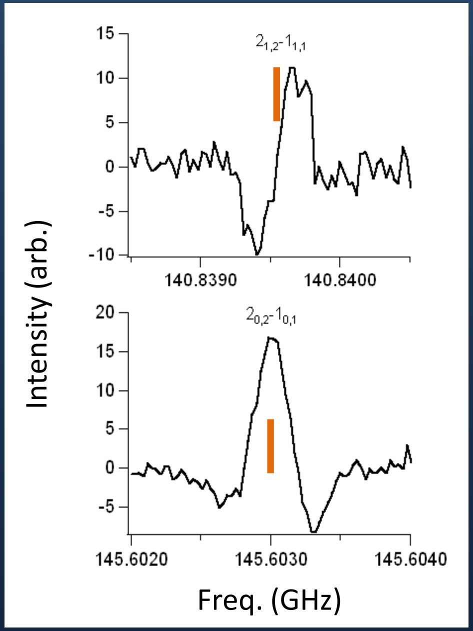
- Both H_2CO and CH_3O have been routinely detected under this scheme
  - +600 HV is applied to front electrode
  - ~1% CH_3OH in Ar

- Detected via (2x) LIAs

CH_3O



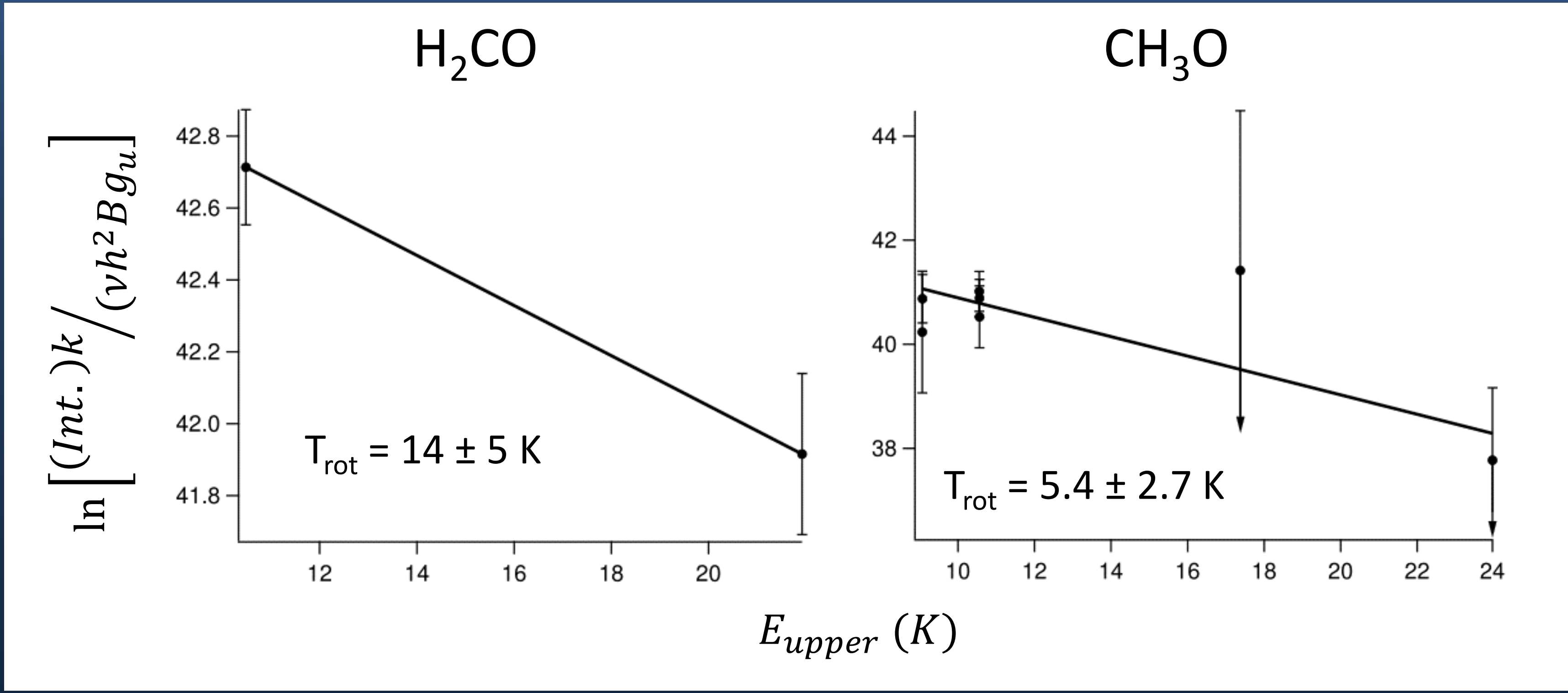
H_2CO



High-Voltage Discharge Study

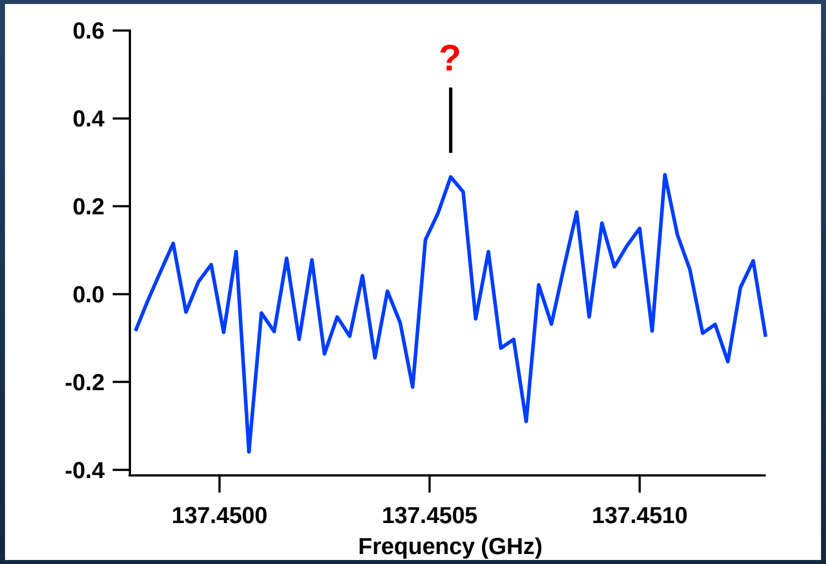
- Line intensities exhibit cold rotational temperature
  - negligible change to methanol with discharge running

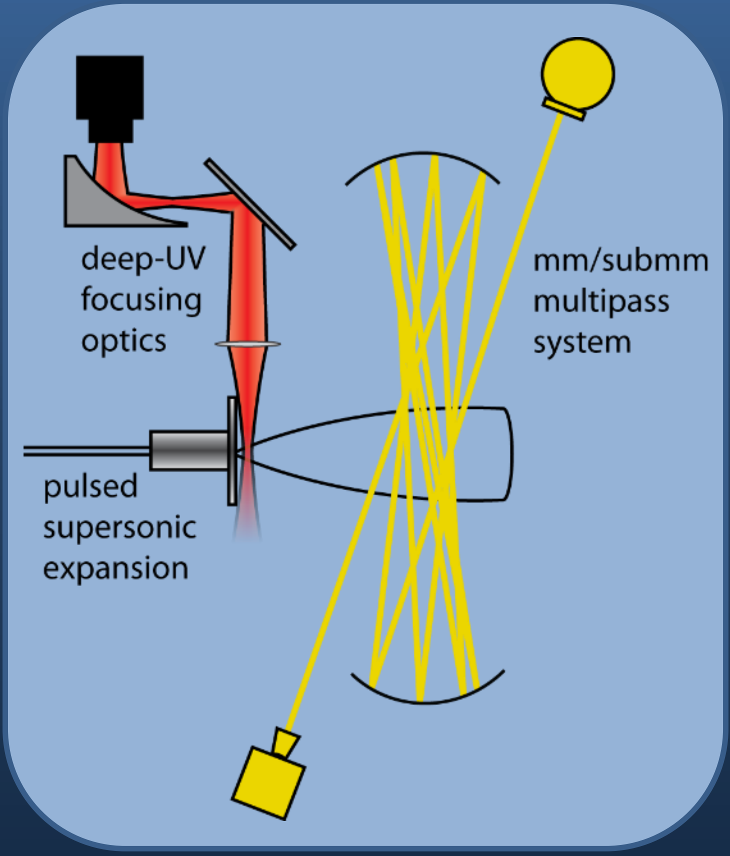
- Dissociation products detected products @ ~0.03% wrt CH_3OH



Ongoing and Future Work: Photodissociation

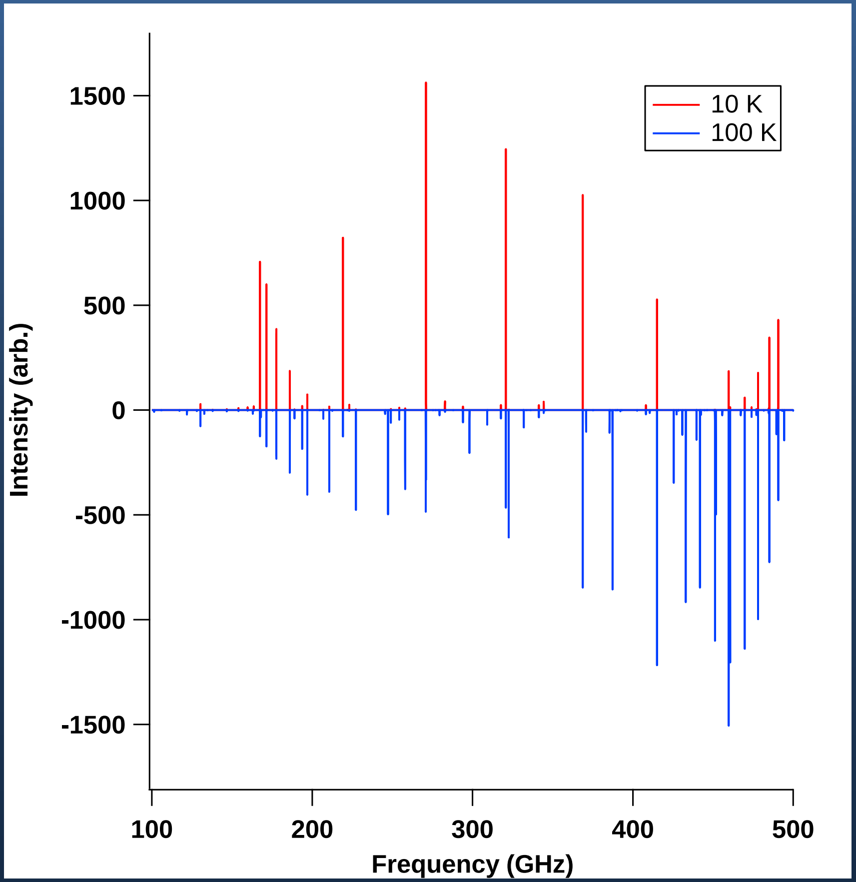
- Astrochemical modeling predicts important role in molecular clouds
- No concrete detection of CH_3O via UV discharge lamp or excimer laser





Ongoing and Future Work: CH_2OH spectral study

- No rotational spectrum yet
- Spectroscopic constants via high-resolution IR study (~0.0005 cm^{-1} accuracy) (Roberts *et al.*, JPC A, 2013)



Ongoing and Future Work

- Experimental setup has been benchmarked and promises to be a powerful tool for lab-astro support
  - spectrometer design is general and versatile for other applications
- Characterize CH_2OH rotational spectrum
- Search for CH_2OH in astronomical data
- Photodissociation via stronger UV source and more spectral data

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