DETERMINATION OF METHANOL PHOTOLYSIS BRANCHING RATIOS VIA ROTATIONAL SPECTROSCOPY

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Methanol Photolysis in the Interstellar Medium (ISM)

- Radicals are mobile on grain surfaces at $T > 20$ K and can combine with other radicals.

\[
\begin{align*}
\text{CH}_3\text{OH} & \underset{hv}{\rightarrow} \text{CH}_2\text{OH} + \text{H} \\
& \rightarrow \text{CH}_3\text{O} + \text{H} \\
& \rightarrow \text{CH}_3 + \text{OH} \\
\text{H}_2\text{O}, \text{CO, CH}_3\text{OH}, \text{NH}_3, \text{H}_2\text{CO} & \text{Ice mantle}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{glycolaldehyde} \\
\text{CO} & \rightarrow \text{methyl formate} \\
\text{CH}_3\text{CO} & \rightarrow \text{acetone}
\end{align*}
\]

## Previous Studies of Methanol Photolysis Branching Ratios

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Hagege et al. (1968)</th>
<th>Öberg et al. (2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH $\rightarrow$ CH$_2$OH + H</td>
<td>~75%</td>
<td>~73%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~15%</td>
</tr>
<tr>
<td>$\rightarrow$ CH$_3$O + H</td>
<td>~5%</td>
<td>~12%</td>
</tr>
<tr>
<td>$\rightarrow$ CH$_2$ + H$_2$O</td>
<td></td>
<td>~0%</td>
</tr>
<tr>
<td>$\rightarrow$ CH$_3$ + OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rightarrow$ HCOH + H$_2$</td>
<td>~20%</td>
<td></td>
</tr>
<tr>
<td>$\rightarrow$ CO + 2H$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rightarrow$ H$_2$CO + H$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental Setup

- Excimer Laser
- Cylindrical Focusing Lens
- Pulsed Valve with Fused Silica Capillary Tube
- Beam Block
- Microwave Synthesizer (250 kHz-50GHz)
- Millimeter/Submillimeter Frequency Multiplier (x3-x27)
- Multipass Optical System
- Oscilloscope
- Detector
Multipass Optical Path
Parent Methanol Reference Lines

Intensity

$3^+_{0,3}-2^+_{0,2}$  $3^-_{1,3}-2^-_{1,1}$  $3^+_{0,3}-2^+_{0,2}$  $3^+_{1,3}-2^+_{1,1}$  $1^+_{1,0}-1^+_{0,1}$  $4^+_{0,4}-3^+_{0,3}$

Frequency (MHz)

145093.70  145097.38  145103.13  145131.81  165050.12  193454.36
Rotation Diagram for Parent Methanol

\[ T = 12 \pm 5 \text{ K} \]

\[ N_{\text{methanol}} = (1.19 \pm 0.03) \times 10^{17} \text{ cm}^{-2} \]
Laser Photolysis + Methanol Depletion

![Graph showing detector signal over time with annotations for Laser RFI, Methanol Depletion, Baseline, and Methanol Absorption.]
Formaldehyde Photolysis Product

$T = 19 \text{ K}$

$\frac{N}{N_{\text{methanol}}} = (3.7 \pm 0.4) \times 10^{-5}$
Methanol Dissociation

Lyman alpha = 235.19 kcal/mol

Methoxy Photolysis Product

\[ T = 3.7 \, \text{K} \]

\[ \frac{N}{N_{\text{methanol}}} = (6 \pm 2) \times 10^{-4} \]
Hydroxymethyl Photolysis Product


Caveats:
-- No line strength information included
-- Our fit of the reported lines does not converge

\[
T = 0.6 \text{ K} \\
\frac{N}{N_{\text{methanol}}} = (8.1 \pm 3) \times 10^{-4}
\]
## Methanol Photolysis Branching Ratios

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Hagege et al. (1968)</th>
<th>Öberg et al. (2009)</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH + h$_v$</td>
<td>CH$_3$ + OH</td>
<td>&lt; 5%</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>CH$_3$O + H</td>
<td>~75%</td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td>CH$_2$OH + H</td>
<td>~75%</td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td>H$_2$CO + H</td>
<td>20%</td>
<td>0%</td>
</tr>
</tbody>
</table>

*assumed

Conclusions and Future Work

- Determine optimal laser position on tube
- Try different Ar/CH$_3$OH ratios
- Collect more hydroxymethyl lines, refine fit
- Measure other branching ratios for COMs
- Try other laser wavelengths, compare branching ratio changes
Acknowledgements

- Luyao Zou, AJ Mesko, Kevin Roenitz
- Undergraduates: (on project) Samuel Zinga; (off project) Elena Jordanov, Lindsay Rhoades, Houston Smith
- Past Group Members: Brian Hays and Jake Laas
- NASA Emerging Worlds Award NNX15AH74G
Boltzmann Diagram Analysis

- Formula for integrated line intensities:
  \[
  \int_{-\infty}^{\infty} I_b \, d\nu = \frac{hc^3Ag_u N_T}{8\pi k\nu^3Q(T_{rot})} e^{-E_u/kT_{rot}}
  \]

- Conversion of Einstein A to B coefficient:
  \[
  A_{1\rightarrow0} = B_{1\rightarrow0} \frac{8\pi\hbar\nu^3}{c^3}
  \]

- Y versus X: \[
  \ln[(\int_{-\infty}^{\infty} I_b \, d\nu)(k/(\hbar^2 \nu B_{g_u}))] \text{ versus } E_u = E_1 + h\nu
  \]

- Inverse of slope is proportional absolute \(T_{rot}\) of molecules in supersonic expansion

- The relationship \(e^{y-intercept} Q(T_{rot})\) allows for the determination of relative abundance ratio

<table>
<thead>
<tr>
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<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h)</td>
<td>Planck constant</td>
</tr>
<tr>
<td>(c)</td>
<td>Speed of light</td>
</tr>
<tr>
<td>(A)</td>
<td>Einstein A coefficient</td>
</tr>
<tr>
<td>(g_u)</td>
<td>Upper State degeneracy</td>
</tr>
<tr>
<td>(k)</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Frequency (MHz)</td>
</tr>
<tr>
<td>(N_T)</td>
<td>Number density</td>
</tr>
<tr>
<td>(Q(T_{rot}))</td>
<td>Rotational Partition Function</td>
</tr>
<tr>
<td>(E_u)</td>
<td>Upper State Energy</td>
</tr>
<tr>
<td>(T_{rot})</td>
<td>Rotational Temperature</td>
</tr>
</tbody>
</table>