Motivation

- Photodissociation of simple molecules creates radicals on icy grains:
  
  ![Diagram of icy grains with chemical reactions](image)

- Radical-radical addition reactions on grain surfaces efficiently form complex organic molecules (COMs):

\[
\begin{align*}
\text{CH}_3\text{OH} \xrightarrow{hv} & \text{CH}_2\text{OH} + \text{H} \\
& \text{CH}_3 + \text{OH}
\end{align*}
\]

- Methanol photodissociation is a major source of organic radicals in interstellar ices
- Astrochemical modeling has shown that these photodissociation branching ratios significantly affect relative abundances of C₂H₅O₂ isomers
- Methanol photodissociation branching ratios are not well-known and must be further explored in the laboratory

Photodissociation Laboratory Measurements

- Methanol photodissociation is conducted using VUV discharge lamps in the λ = 120-200 nm range
- Products are stabilized in the gas phase in a seeded supersonic expansion
- Product formation is probed with multipass direct absorption millimeter/submillimeter spectroscopy
- Spectral studies possible at ~50-1200 GHz
- Use of direct absorption detection promises quantitative analysis of branching ratios for reaction dynamics

![Image of multipass optical arrangement](image)

Figure 1. Multipass optical arrangement used for millimeter/submillimeter spectroscopy.

Results

- Products from methanol dissociation in a high-voltage (~600 V) discharge have been detected, verifying the spectrometer’s performance; CH₂O and H₂CO products match literature results
- Upper limits on photodissociation product yields have been determined for formaldehyde & methoxy: ≤0.05% and ≤0.008% w.r.t. methanol, respectively
- No photodissociation products have been detected; further work is being conducted to verify unexpectedly low limits

![Graph showing spectra](image)

Figure 3. Spectra of cold methanol (top) and dissociation products formaldehyde and methoxy (bottom) detected in a discharge experiment.

Ongoing & Future Work

- Laboratory search for photodissociation products is still underway
- Options for increasing spectrometer sensitivity are being explored
- Rotational spectra of methanol photodissociation products will be used to guide interstellar searches
- Observational astronomy data is in-hand for direct comparisons to laboratory data
- Quantitative gas-phase measurements of branching ratios at many wavelengths will be obtained
- Results of photodissociation branching ratios will be incorporated into astrochemical models
- Improved/extended spectral studies of methoxy will be completed; laboratory study of hydroxymethyl’s rotational spectrum is enabled via improved theoretical/experimental studies at other wavelengths
- Experimental scheme is adaptable to other chemical systems of interest

References


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