Methanol Photodissociation and its Effects on Complex Chemistry in the ISM

Jacob C. Laas and Susanna L. Widicus Weaver
Department of Chemistry, Emory University, Atlanta, GA, 30322, USA

Motivation
- Photodissociation of simple molecules creates radicals in grain mantle ices:

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\begin{align*}
\text{CH}_3\text{OH} \xrightarrow{h\nu} & \text{CH}_2\text{OH} + \text{H} \\
& \text{CH}_2\text{O} + \text{H} \\
& \text{CH}_3 + \text{OH}
\end{align*}
\]
- Radical-radical addition reactions on grain surfaces efficiently form complex organic molecules (COMs):

\[
\begin{align*}
\text{CH}_3\text{OH} \xrightarrow{h\nu} & \text{CH}_2\text{OH} + \text{H} \\
& \text{HCQ} \xrightarrow{} \text{glycolaldehyde} \\
& \text{CH}_3\text{O} + \text{H} \xrightarrow{} \text{methyl formate} \\
& \text{CH}_3 + \text{OH} \xrightarrow{} \text{acetaldehyde}
\end{align*}
\]
- Methanol photodissociation is a major source of organic radicals in interstellar ices
- Astrochemical modeling has shown that these photodissociation branching ratios significantly effect COM relative abundances
- Methanol photodissociation branching ratios are not well-known and need to be experimentally measured

Laboratory Investigation of the Methanol Photodissociation Mechanism

Objective:
- Accurately determine gas-phase methanol photodissociation branching ratios

Experimental Approach:
- Methanol photodissociation is conducted using a vacuum-UV plasma discharge lamp in the 120-200 nm wavelength range
- Products are stabilized using a supersonic expansion
- Methanol depletion and product formation is probed with direct absorption millimeter/submillimeter spectroscopy
- Spectroscopy using a multipass setup (Figures 1 & 2) enables spectral detection of the photodissociation products
- Depletion of methanol signal is quantified and enhancement of photodissociation product signals is monitored

Results
- Methanol signal depletion is achieved at 184.9 nm (Figure 3), with photolysis efficiencies ≤25%

- No change in rotational temperature or vibrational excitation is observed when the lamp is in use, indicating that methanol photodissociation is the dominant depletion process
- Recent astrochemical modeling suggests that CH$_3$O should be the major photodissociation product from methanol, yet non-detection of CH$_3$O in these experiments gives an upper limit of <10% on the branching ratio for this channel
- No OH rotational lines can be detected using this setup based on the weak line intensities expected at these low temperatures
- Search for CH$_3$OH rotational lines using predictions based on rotational constants from IR studies is underway
- Higher detection sensitivity may be necessary for detecting products from minor photodissociation channels

Ongoing and Future Work
- Searches for rotational lines of CH$_3$OH are underway
- Methanol photodissociation branching ratios will be quantified at several photolysis wavelengths
- Wavelength-dependent methanol photodissociation branching ratios will be incorporated into astrochemical models
- Interstellar COM abundances determined from radioastronomical observations will be benchmarked against results from laboratory measurements and models
- Complete spectral coverage from 100 GHz – 1 THz will be obtained for methanol photodissociation products, enabling their direct interstellar detection

References

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