

Laboratory measurements of methanol photolysis branching ratios to guide astrochemical models

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Abstract. Methanol is ubiquitous in star-forming regions, and has recently been detected in a protoplanetary disk. Astrochemical models have shown that methanol photolysis contributes to complex organic chemistry in interstellar ices. While some methanol photolysis branching ratios have been measured, infrared condensed-phase measurements rely on assumptions about the chemistry, and mass spectrometric measurements cannot distinguish structural isomers. To address these challenges, we are using pure rotational spectroscopy to quantitatively probe the methanol photolysis products. We use a VUV laser to dissociate methanol in the throat of a supersonic expansion, and probe the products downstream after cooling is complete. We then use a rotational diagram analysis to determine the relative density of each product relative to methanol. We have detected the methoxy, hydroxymethyl, and formaldehyde photolysis products. We present here the experimental setup and the initial results and discuss these results in the context of interstellar chemistry.

Keywords. astrochemistry, molecular data, molecular processes, ISM: molecules

1. Introduction

Complex organic molecules (COMs) are highly abundant in regions of star formation, but their formation pathways are not well-understood. Gas-phase ion-molecule reactions have been shown to be inefficient for forming some of the most abundant COMs (Horn *et al.* (2004)). Therefore, recent astrochemical models (Garrod *et al.* (2008), Laas *et al.* (2011), Garrod (2013)) have explained COM formation via UV photolysis of icy grain mantles followed by radical-radical recombination reactions on the ice surface during star formation. Methanol is a good test of these proposed formation pathways because of its prevalence in interstellar ices. Methanol is commonly found in the condensed phase in dense molecular clouds, and can compose up to 20% of the ices in these regions (Gibb *et al.* (2004)). Methanol photolysis is therefore thought to be a major source of the organic functional groups that go on to form the backbones of COMs in the ISM. Despite its importance in astrochemistry, the methanol photodissociation mechanism has not been quantitatively determined in full. We therefore seek to provide laboratory measurements of the methanol photolysis branching ratios to guide astrochemical models.

The photolysis of methanol can proceed via multiple reaction pathways, which are overviewed in the reaction energy diagram shown in Figure 1. Two of the products of methanol photolysis, the radicals methoxy (CH_3O) and hydroxymethyl (CH_2OH), are of particular interest in astrochemistry. Further reaction of these radicals with hydroxyl radical (HCO), formed from photolysis of formaldehyde, can produce different structural

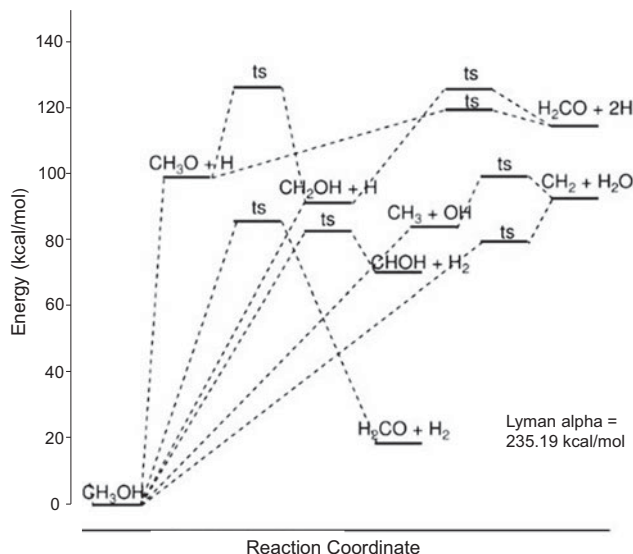


Figure 1. Reaction pathways for methanol photolysis.

isomers of molecules with the formula $C_2H_4O_2$. In the gas-grain model proposed by Garrod *et al.*, hydroxymethyl is linked to the production of glycolaldehyde, and methoxy to methyl formate; therefore, measuring the precise branching ratios of methanol photolysis is of interest to the astrochemical community at large.

Hagege *et al.* (1968) determined the gas-phase branching ratios for the main dissociation pathways of methanol at 184.9 nm via mass spectrometry. However, because the radicals hydroxymethyl and methoxy have the same mass, it was impossible to determine separate branching ratios for these two pathways; a total branching fraction for $CH_3O + CH_2OH$ was determined to be $\sim 75\%$. Öberg *et al.* (2009) performed studies in the condensed phase using reflection-absorption infrared spectroscopy (RAIRS). This study also determined that the two radicals of interest made up the majority of the photolysis products; more specifically, this study showed that hydroxymethyl was the main radical produced. However, this conclusion was made not by directly observing the production of radicals on the surface of the ice, but instead by observing the production of COMs from recombination reactions during warm-up. Based on their observations, this information was inferred from a chemical model which only assumed the production and recombination of first generation radicals produced from methanol photolysis.

Our experiment attempts to directly observe the products of methanol photolysis in the gas phase using direct absorption millimeter and submillimeter rotational spectroscopy. Through this technique, we aim to quantify the photolysis branching ratios for as many reaction pathways as possible, with a particular focus on distinguishing – for the first time – the hydroxymethyl and methoxy channels.

2. Experimental Design

The experimental setup can be seen in Figure 2. Argon was used as a carrier gas and was bubbled through liquid methanol. The gas mixture was flowed through a pulsed valve (Parker-Hannafin, Series 9, 1 mm pinhole) into a vacuum chamber held at a background pressure of 12 mTorr. The backing pressure for the valve was maintained at 32 psig, and the valve was operated with a 2 ms opening time at a rep rate of 44 Hz. The sample

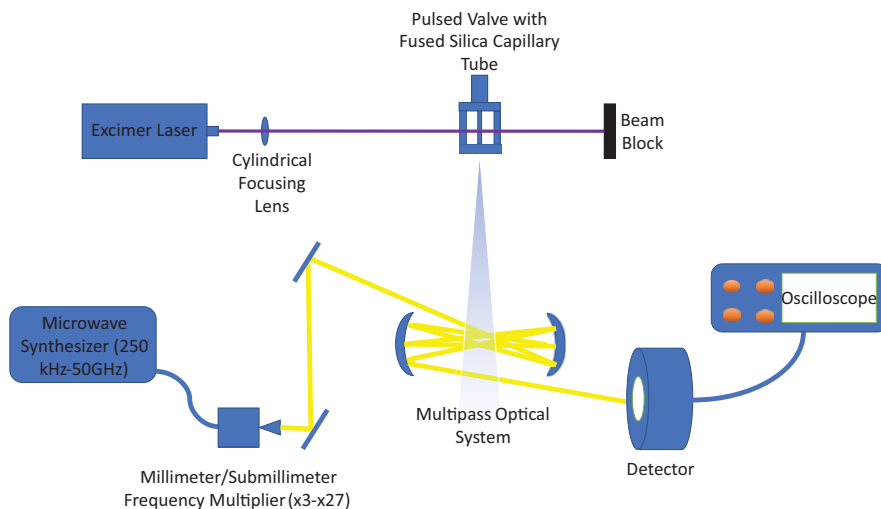


Figure 2. The design of the spectrometer used in conducting the methanol photolysis experiments.

passed through a fused silica tube affixed to the front of the pulsed valve. The output of a UV excimer laser (GAM LASER Inc., EX5 250 Hz) at 193 nm was focused onto the tube using a cylindrical lens. Photolysis occurred in the tube, and the photolysis products were rotationally and vibrationally cooled via supersonic expansion. The expansion was probed with millimeter/submillimeter light, produced from the output of a frequency synthesizer (Agilent Technologies, E8257D PSG with options 1EA, UNU, 550, and UNT) that was then multiplied to the range of 50 - 1000 GHz using frequency multipliers (Virginia Diodes Inc., AMC-S268). The millimeter/submillimeter beam path followed a multipass arrangement that enabled seven passes through the expansion. The output was detected using an InSb hot electron bolometer (QMC Ltd., QFI/XBI) and the resultant time-response of the detector was collected using a digital oscilloscope. From these data, 3D plots of spectral intensity versus frequency and time relative to the firing of the pulsed valve were constructed.

3. Results

To test the performance of the spectrometer and optimize experimental conditions, spectra of methanol were collected at the beginning of each set of measurements. This enabled all measurements to be referenced back to the parent methanol molecule, eliminating the effects of day-to-day fluctuations in valve conditions and sample delivery. Examples of typical methanol spectra are shown in Figure 3.

A Boltzmann diagram analysis was carried out for each molecule detected, and from this analysis the temperature and number density was determined. An example of this analysis for methanol can be seen in Figure 4.

Photolysis of the parent methanol is evidenced by the appearance of a depletion in the methanol absorption signal, shortly after the laser pulse. We time the submillimeter probe to coincide with this methanol depletion signal. A typical methanol depletion signal can be seen in Figure 5.

The first product targeted was formaldehyde; as shown by Hagege *et al.*, it is the most stable molecule produced via methanol photolysis, and was seen as a large percentage of

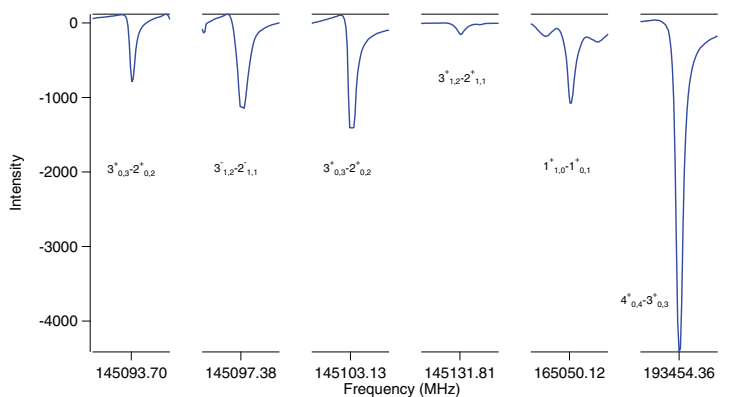


Figure 3. Several methanol lines observed in the experiment.

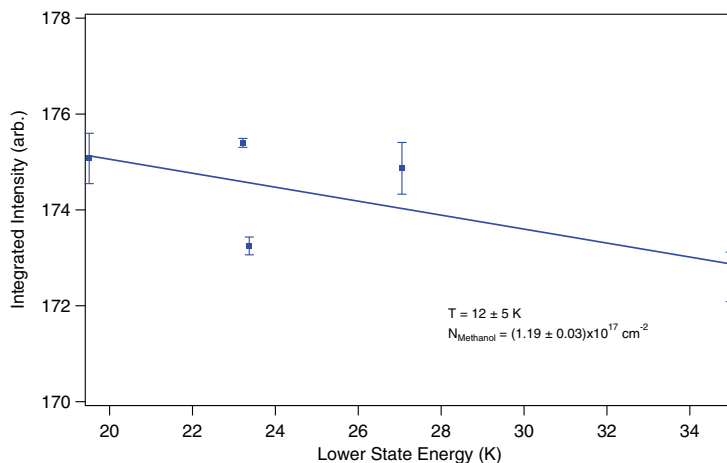


Figure 4. The Boltzmann diagram calculated from the collected methanol spectra.

the total photolysis products measured in that experiment. An example of formaldehyde spectra taken during methanol photolysis can be seen in Figure 6.

We found formaldehyde production was dependent on the position of the laser on the fused silica tube. The further down the tube that the UV light was aimed, the less formaldehyde signal was observed. Our current understanding of this phenomenon stems from the collisions happening in the fused silica tube. As shown in Figure 1, formaldehyde can either form directly from photolysis, or through further reactions of methoxy and hydroxymethyl. Therefore, formaldehyde is produced in greater concentrations when the laser is aimed at the beginning of the tube, allowing collisions between the radical products in the tube or with the walls of the tube that lead to further reactions. This idea is supported by the detection of an increase in observed methoxy radical signal when the laser is near the end of the tube (see Figure 7).

In addition to the detection of the methoxy radical, we have obtained a preliminary detection of the hydroxymethyl radical, shown in Figure 8. Bermudez *et al.* (2017) provided frequencies for rotational transitions of the hydroxymethyl radical that were used to guide our measurements. However, no line strength information was provided in this analysis, and our own fit of their experimental data did not converge. We can therefore only approximate the information needed for the Boltzmann analysis. Nonetheless, the

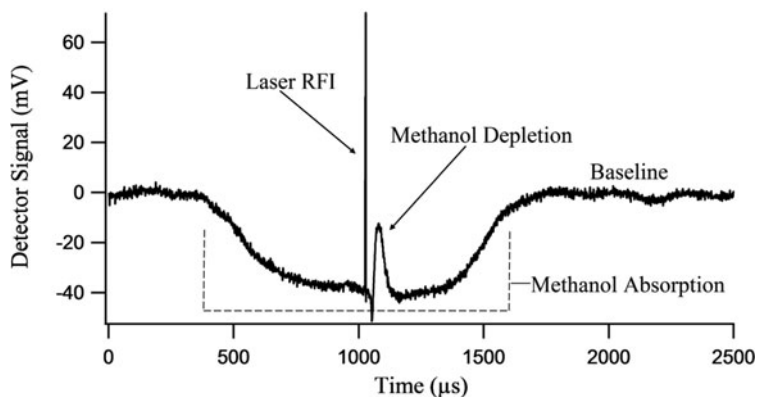


Figure 5. The time response of the methanol absorption feature across a valve pulse, with a depletion feature shortly after the UV laser pulse, taken from McCabe (2016).

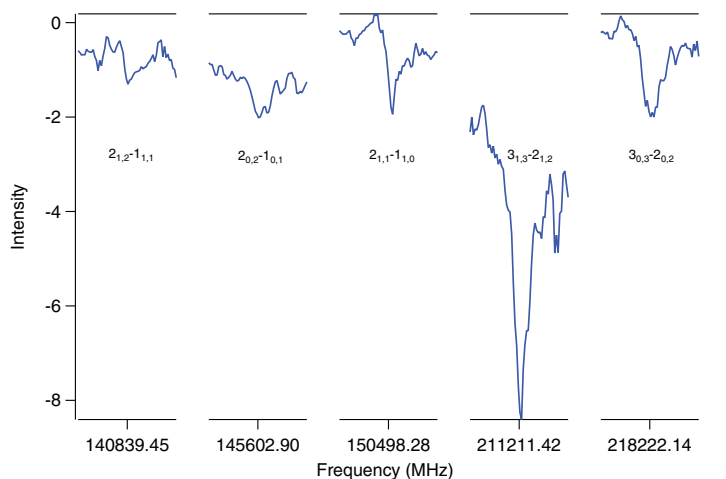


Figure 6. Spectra of formaldehyde produced from methanol photolysis.

lines are clearly present, and we are working to confirm this spectral assignment so that a full quantitative analysis is possible.

In our experiment, we can probe all methanol photolysis channels except OH, the transitions for which lie outside of the range of frequency coverage. For the sake of calculation, we therefore assumed the OH + CH₃ branching ratios determined by both Hagege *et al.* (1968) and Öberg *et al.* (2009). We used the results of the Boltzmann analysis for each product channel, referenced to the parent molecule signal, and calculated a tentative set of branching ratios for methanol photolysis. These ratios are given in Table 1. While these calculations make a number of assumptions, future experiments should help us to determine these branching ratios quantitatively.

Our experimental results can be compared to those of Hagege *et al.* (1968) and Öberg *et al.* (2009). While the results for the methoxy and hydroxymethyl channels are similar to these other studies, the results for formaldehyde are not. Hagege *et al.* (1968) found an order of magnitude larger branching fraction for formaldehyde than we see in our studies. On the other hand, Öberg *et al.* (2009) saw no production of Formaldehyde in their condensed phase work. In our work and that of Öberg *et al.* (2009), the hydroxymethyl channel is the dominant channel. This is in contrast to the results of the model by Laas

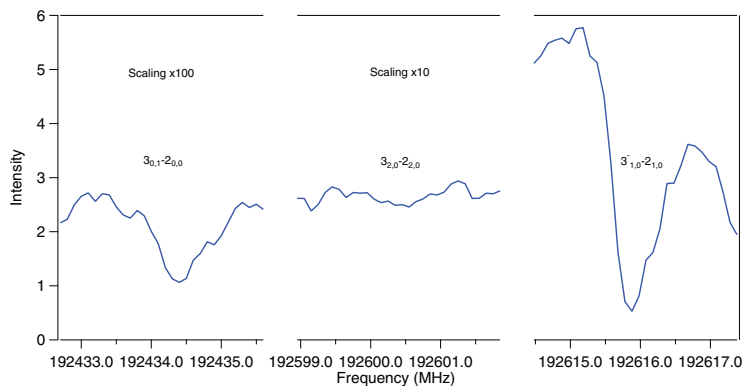


Figure 7. Spectra of methoxy radical produced from methanol photolysis.

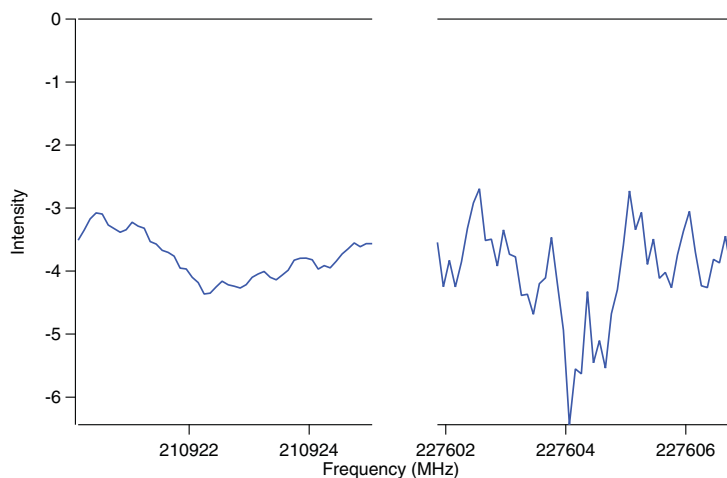


Figure 8. Spectra of hydroxymethyl radical produced from methanol photolysis.

Table 1. Tentative branching ratios calculated for methanol photolysis. The branching fraction for the $\text{CH}_3 + \text{OH}$ channel are assumed from previous studies.

Photolysis Products	Hagege <i>et al.</i> (1968) (gas phase)	Öberg <i>et al.</i> (2009) (condensed phase)	Our Work (assuming $\text{CH}_3=5\%$)	Our Work (assuming $\text{CH}_3=12\%$)
CH_2OH	75% (+ CH_3O)	73%	53%	49%
CH_3O	75% (+ CH_2OH)	15%	39%	36%
CH_3	<5%	12%	5%	12%
H_2CO	20%	0%	2%	2%

et al. (2011), which indicates that the methoxy radical channel is predominant on the surface of ices in interstellar clouds. However, for some COMs the observed abundances indicate that hydroxymethyl may in fact be the dominant branching fraction. Additional studies that fully quantify this channel, as well as that of $\text{CH}_3 + \text{OH}$, are required before direct comparison with observations can be made.

4. Conclusions and Future Work

The branching ratios for methanol photolysis have been investigated. Tentative branching ratios have been extrapolated from experimental measurements presented here, and compared to previous literature values from Hagege *et al.* (1968) and Öberg *et al.* (2009). In the future, we will maximize radical production and find the optimal position for the laser photolysis to occur on the tube so that additional reactions are minimized. We will then finalize our measurements and determine quantitative branching ratios. To do so, we will further investigate the spectrum of hydroxymethyl radical and obtain the line strength information needed for a proper Boltzmann diagram analysis. We will also acquire a higher frequency multiplier and obtain the branching fraction for the $\text{CH}_3 + \text{OH}$ channel. Once the experiment has been completed at 193 nm, we will measure the branching ratios using other UV wavelengths. These results can be used to refine models for chemistry on the surface of interstellar grains, and provide insight into the observations obtained by astronomers.

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