First Detection of Methoxymethanol as a Photolysis Product of Methanol

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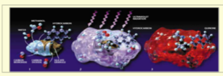
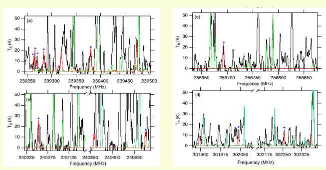
Abstract: We report the first identification of methoxymethanol (CH_3OCH_2OH) as a photolysis product of condensed methanol based on temperature programmed desorption studies conducted following irradiation with photons of energies below the ionization threshold (9.8 eV) of condensed methanol. The first detection of methoxymethanol in the interstellar medium was reported in 2017. In the interstellar medium, UV photolysis of condensed methanol (CH_3OH), contained in ice mantles surrounding dust grains, is thought to be the mechanism that drives the formation of "complex" molecules, such as methyl formate ($HCOOCH_3$), dimethyl ether (CH_3OCH_3), acetic acid (CH_3COOH), and glycolaldehyde ($HOCH_2CHO$). Methoxymethanol was first identified in 1995 as an electron-induced radiolysis product of condensed methanol. Because none of the previous studies identified methoxymethanol as a photolysis product of condensed methanol, methoxymethanol was suggested as a possible tracer molecule for the presence of electron-initiated reactions in interstellar ices. The results presented in this study indicate that methoxymethanol can be formed from both the radiolysis and photolysis of methanol.

Introduction



Methanol is of particular astrochemical interest because of its presence in the interstellar medium (ISM), especially in ices found in dark dense molecular clouds near star-forming regions. It has been proposed that prebiotic molecules found in the ISM may originate via radical-radical reactions involving fragments originating from small molecules (e.g., methanol). Astronomers now believe that these reactions occur in the solid phase of ices deposited on silicate or carbonaceous dust grains in dense interstellar clouds. The ices are constantly bombarded by high-energy photons (e.g., γ rays) and cosmic rays. We propose that the secondary electrons generated when high-energy radiation interacts with matter are an important driving force behind reactions in the ISM.

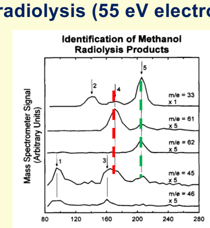
December 2017: Identification of Methoxymethanol in the ISM [~10 quadrillion miles away]



Black: Overall microwave spectrum of NGC 6334I
Red: Simulated rotational spectrum of Methoxymethanol
Green: Simulations of species that are major contributors to the overall spectrum

Brett A. McGuire *et al* 2017 *ApJL* **851** L46; James O. Chibueze *et al* 2014 *ApJ* **784** 114

First identification of Methoxymethanol as a radiolysis (55 eV electrons) product of methanol



1: Dimethyl ether (~95 K)
2: Methanol (~140 K)
3: Ethanol (~160 K)
4: Methoxymethanol (~170 K)
5: Ethylene glycol (~205 K)

C2 O2 H6
2(12) + 2(16) + 6(1) = 62

Arumainayagam et. al., *J. Phys. Chem.*, 1995, 99 (23), 9530-5

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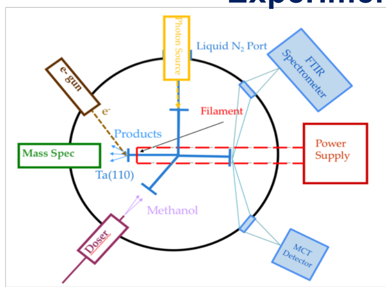
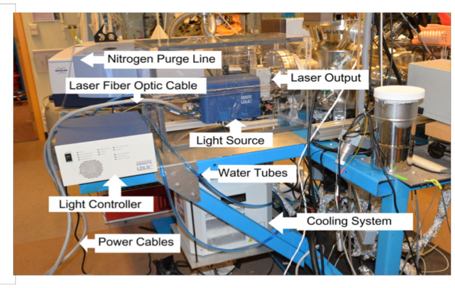
Experimental Procedure





Step 1. Gas-phase methanol is dosed onto the liquid nitrogen-cooled Ta(110) crystal to form a nanoscale thin film.

Step 2. Film is irradiated with low electrons.

Step 3. Temperature programmed desorption (TPD), which involves thermal processing and mass spectrometry, is performed to see what species remain in the film after irradiation.

- UHV chamber is able to do both photolysis and radiolysis.
- The light source is a laser-driven (xenon) plasma with a maximum energy of 7.4 eV. The light source is within a sealed box which we purge with nitrogen so that we don't produce ozone when the source is on.
- Cooling system is used to cool the plasma so that nothing melts.

Results and Discussion

Post-Irradiation Temperature-Programmed Desorption of $^{12}CH_3OH$

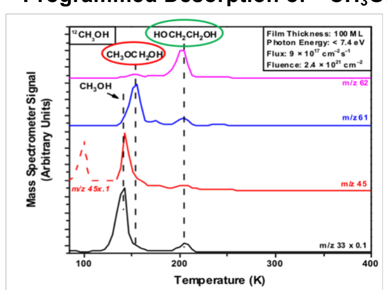


Figure 1. $^{12}CH_3OH$ photolysis experiment with a film thickness of 100 ML, photon energy less than 7.4 eV, flux (# of photons/(cm² x second)) of 9 x 10^{17} cm^{-2} s^{-1}, and fluence (total # of photon incident on thin film) of 2.4 x 10^{21} cm^{-2}. Methoxymethanol and ethylene glycol were detected.

Post-Irradiation Temperature-Programmed Desorption of $^{13}CH_3OH$

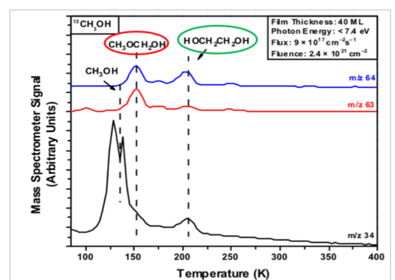


Figure 2. $^{13}CH_3OH$ photolysis experiment with a film thickness of 40 ML, photon energy less than 7.4 eV, flux (# of photons/(cm² x second)) of 9 x 10^{17} cm^{-2} s^{-1}, and fluence (total # of photons incident on thin film) of 2.4 x 10^{21} cm^{-2}. Methoxymethanol and ethylene glycol were also detected.

Methoxymethanol Yield vs. Film Thickness

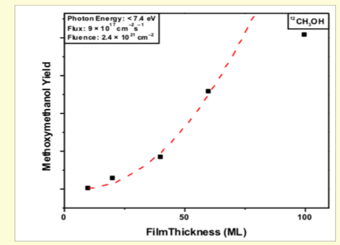
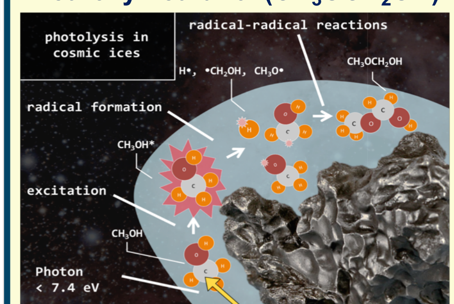


Figure 5. Thinner films were fit with a pure quadratic curve, suggesting a bimolecular reaction mechanism.

Mechanism of Formation for Methoxymethanol (CH_3OCH_2OH)



Radical Formations

$$CH_3OH + e^- \longrightarrow CH_3O\bullet + \bullet H + e^-$$
$$CH_3OH + e^- \longrightarrow \bullet CH_2OH + \bullet H + e^-$$

Radical-Radical Recombination

$$CH_3O\bullet + \bullet CH_2OH \longrightarrow CH_3OCH_2OH$$

Conclusion

Methoxymethanol, which was first identified in the interstellar medium in December 2017, can be formed from both the radiolysis and photolysis of methanol.