National Aeronautics and Space Administration

LABORATORY STUDIES OF THE HETEROGENEOUS UPTAKE OF METHANE IN THE MARTIAN ATMOSPHERE

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Program: RTD-Topic

Project Objective:

- Atmospheric methane (CH_4) on Mars recorded by the SAM/TLS instrument on the Curiosity rover shows seasonal variability in the 0.24-0.65 ppbv range with occasional spikes in the 7 ppbv range.
- The sources of methane may be geochemical, biological or both. While there is no obvious surface biological source, microbes may exist below the surface.
- Perchlorates (ClO_4^-) are present in the Martian soil in large abundances, and may act to chemically oxidize CH_4 and other organics through interactions in the soil.
- The primary objective of this project is to explore chemical mechanisms for methane loss processes on Mars though lab studies focusing on the roles of perchlorate reactions.

Significance of Results:

- Our experimental observations show that volatile chlorine oxides are produced from the photolysis of perchlorate salt from irradiation at 185 and 254 nm, and that the chlorine oxide yields are proportional to the duration of photolysis. In addition, CH_4 react with UV-activated ClO_4^- to form CO_2.This is potentially quite significant for interpreting results from Martian landers and rovers including Viking and MSL.
- Despite recent report of detection of CH_4 and other organics on Mars by MLS, the values are still much lower than expected. Chlorine oxides, which are themselves highly photolabile, may be responsible for oxidizing the available organic carbon to form carbon dioxide, formaldehyde or other simple hydrocarbons which are volatile and can be further oxidized in the atmosphere.

Summary:

- Under UV radiation, perchlorate $Mg(ClO_4)_2$ can be decomposed into $Mg(ClO_3)_2$ and chlorine oxides (ClO_2, Cl_2O_4, Cl_2O_6, Cl_2O_7), which indicates that O and Cl atoms are likely generated.
- CH_4 reacts with UV photolysis products of perchlorate to form CO_2 .
- $^{13}CH_4$ react with UV photolysis products of perchlorate to form $^{13}CO_2$.
- CH_3Cl may be formed in this reaction.

Acknowledgement: We would like to thank Prof. Yuk Yung and Prof. Mitchio Okumura for their helpful discussions.

Results:

The experiment was conducted in a vacuum chamber depicted in Fig. 1. A thin film of magnesium perchlorate ($Mg(ClO_4)_2$) was deposited on a calcium fluoride (CaF_2) window, which was mounted on a cold finger connected to a helium (He) cryostat. The temperature of the window can be adjusted from 4 – 320 K. So far our experiment has been carried out at room temperature. The infrared (IR) absorption spectra of the CaF_2 window along with the gas-phase molecules in the chamber can be collected with a Nicolet Fourier transform infrared (FTIR) spectrometer. Methane can be injected into the chamber. A mercury (Hg) discharge lamp (184 nm (20%) and 254 nm (80%)) was used as the UV source.

Experiments conducted:

1) **ClO_4^- + CH_4 without UV**
   No reaction
2) **ClO_4^- + UV** (reaction, Fig. 2)
3) **ClO_4^- + CH_4 with UV** (reaction, Fig. 3)
4) **ClO_4^- + $^{13}CH_4$ with UV**
   (reaction, slope 0.0019, Fig. 4 and 5)
5) **$^{13}CH_4$ with UV only**
   (less reaction, slope 0.0006)
4) **CH_3Cl production confirmation** (Fig. 6)

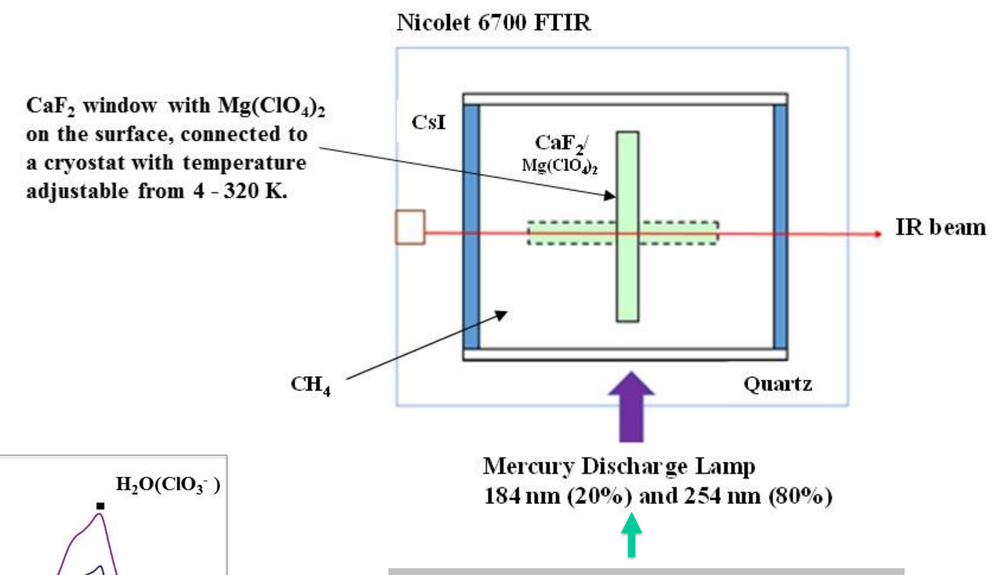


Figure 1. Schematics of the experimental setup.

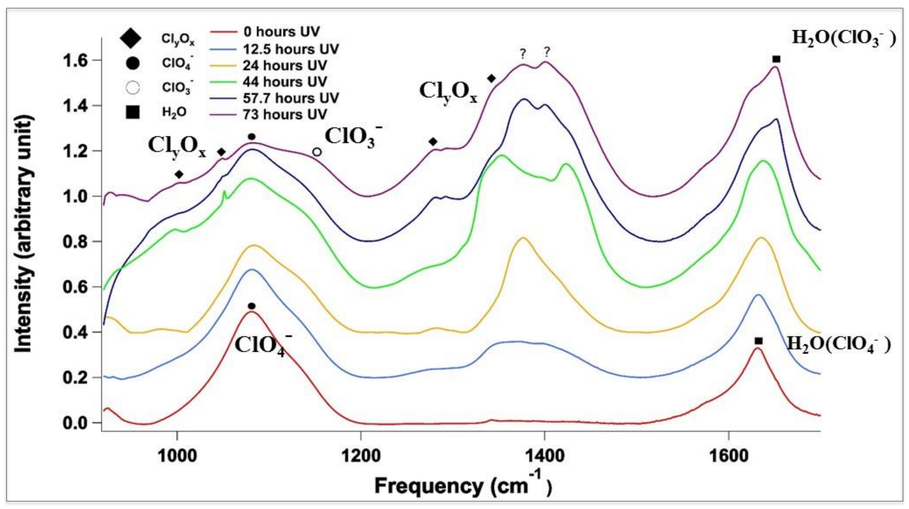
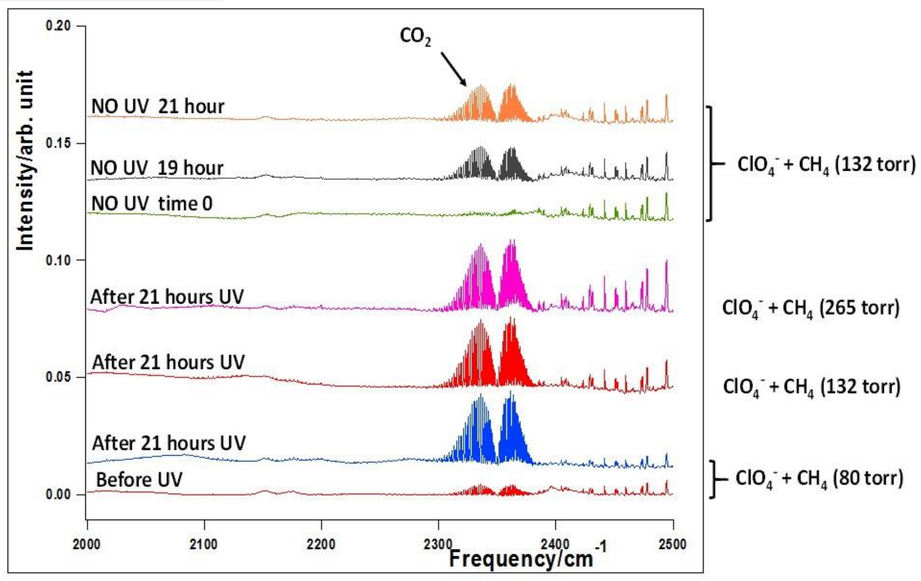
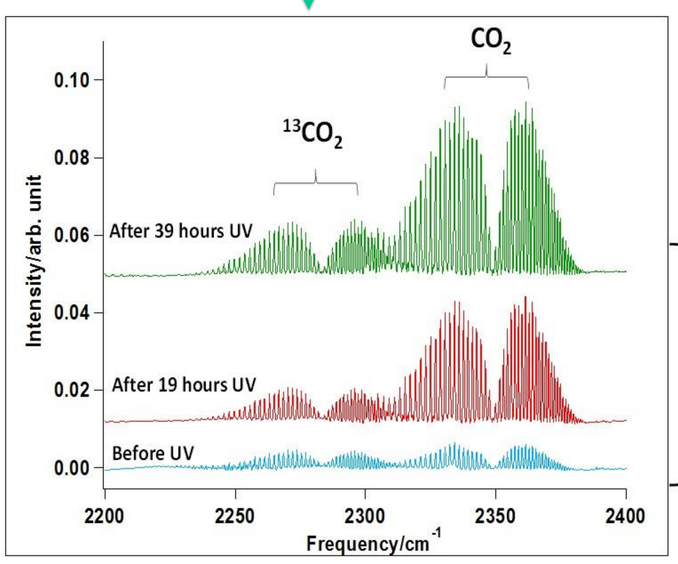


Figure 2. IR spectra of $Mg(ClO_4)_2$ following UV irradiation for the indicated time periods.

Figure 3. IR spectra of $Mg(ClO_4)_2$ + CH_4 with and without UV at indicated time periods.

Figure 4. IR spectra of $Mg(ClO_4)_2$ + $^{13}CH_4$ with UV at indicated time periods.





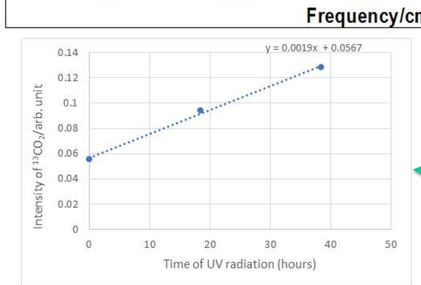


Figure 5. $^{13}CO_2$ progression with UV radiation time for $Mg(ClO_4)_2$ + $^{13}CH_4$ + UV.

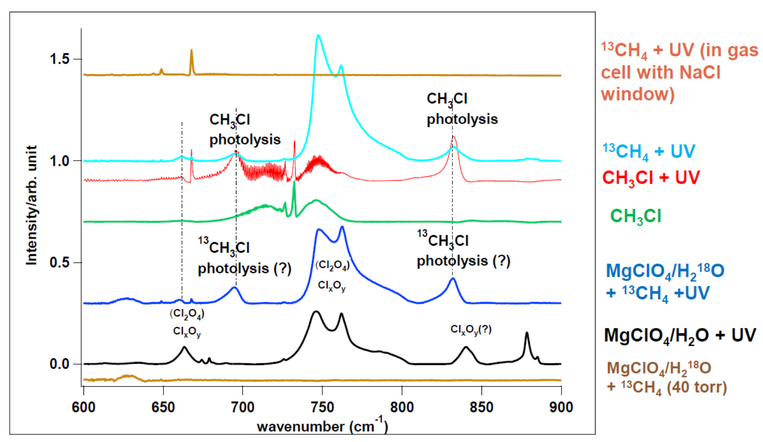


Figure 6. IR spectra of different reactions for confirmation of CH_3Cl production.

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