Photon Initiated Ice Chemistry: Formation of Iso-halons in Clathrate Hydrates

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Introduction

Halomethanes constitute a category of organic compounds characterized by carbon-halogen bonds. They manifest both naturally, via the biosynthesis by marine organisms predominantly bacteria[1], and synthetically through industrial processes. Notably, halomethanes are notorious for their adverse effects on the Earth's atmosphere, particularly their role in ozone layer depletion. Specific manmade halomethanes known as chlorofluorocarbons (refrigerants, aerosols, and solvents), are well known for their destruction of the ozone layer. When exposed to ultraviolet solar radiation, halomethanes undergo photodissociation, giving rise to halogens and other free radicals which catalyze reactions that contribute to the depletion of the ozone layer[2]. In the condensed phase iso-halons are known to form which are isomeric forms of halomethanes, distinguished by unique halogen-halogen interactions. Our research aims to examine the photon-triggered generation of iso-halons in both amorphous and clathrate hydrates, focusing on the spectroscopic identification of resulting products. Our goal is to gain a comprehensive understanding of iso-halon formation and their subsequent reactivity with common atmospheric components, notably ozone and water, leading to the formation of significant environmental consequences. This includes ozone layer depletion, acid rain, and the generation of free radicals.

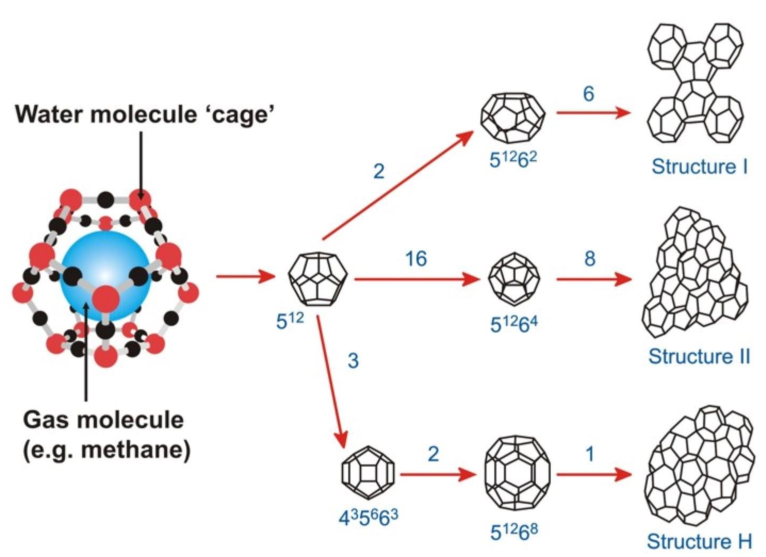

Figure 1: Common gas hydrate structures[3]

$$ClO + ClO \rightarrow Cl_2O_2$$
$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$$
$$ClOO + M \rightarrow Cl + O_2 + M$$
$$2\,(Cl + O_3 \rightarrow ClO + O_2)$$
$$2\,O_3 + h\nu \rightarrow 3\,O_2.$$

Figure 2 Catalytic cycle of ClO and Ozone[4]

Experimental Method

Amorphous State:

1. Initial Deposition at 50K:

- CH2ClI deposited for 2 minutes; IR and UV/vis spectra recorded

2. Cooling and Laser Excitation at 4K:

- Cooled to 4K; excited with 410/390 nm laser for 15 minutes; IR and UV/vis recorded.

3. Warming to 30K:

- Warmed to 30K; spectra taken

4. Re-cooling and Final Spectroscopy at 4K:

- Temperature cooled to 4K; IR and UV/vis spectra recorded

Hydrate State:

1. Initial Deposition and Spectroscopy at 50K:

- CH2ClI deposited for 2 minutes; IR and UV/vis spectra recorded

2. Temperature Increment and Minimization of Boil:

- Temperature raised to 130K in 20K steps.

3. Stabilization and Spectroscopy at 130K:

- Sample held at130K for 2 hours; IR and UV/vis spectra recorded

4. Cooling to 4K:

-Temperature was reduced to 4K.

5. Laser Excitation and Final Spectroscopy:

- Sample excited with a laser for 15 minutes (410 nm or 390 nm); IR and UV/vis spectrum was taken

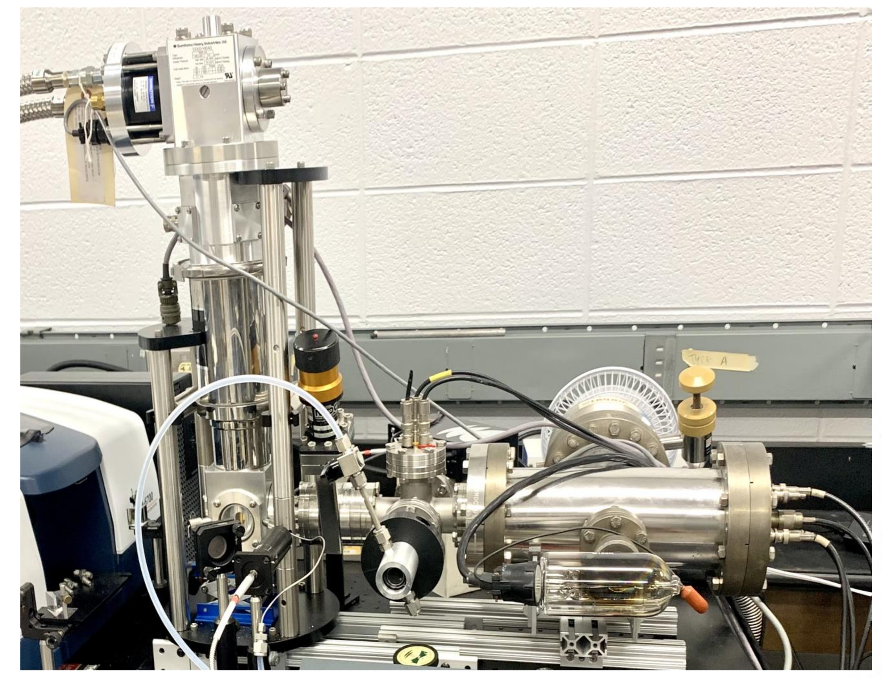

Figure 3: Matrix Isolation Apparatus

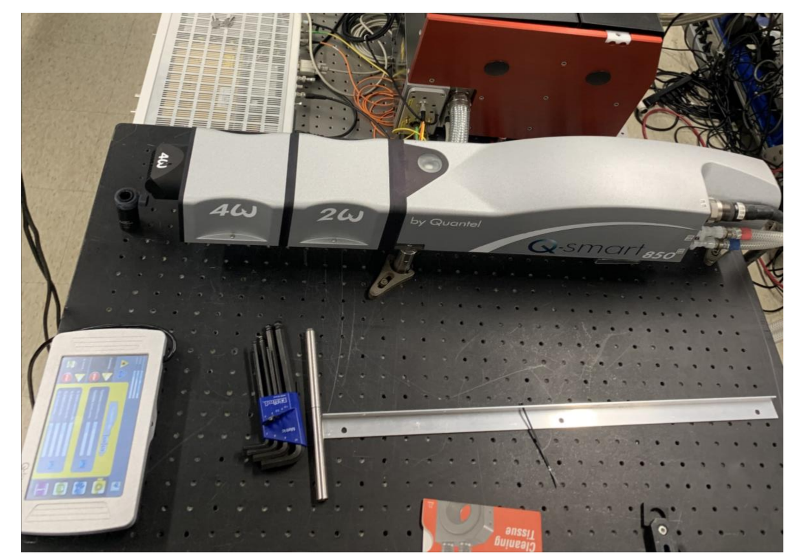

Figure 4: Nd:YAG Dye Laser

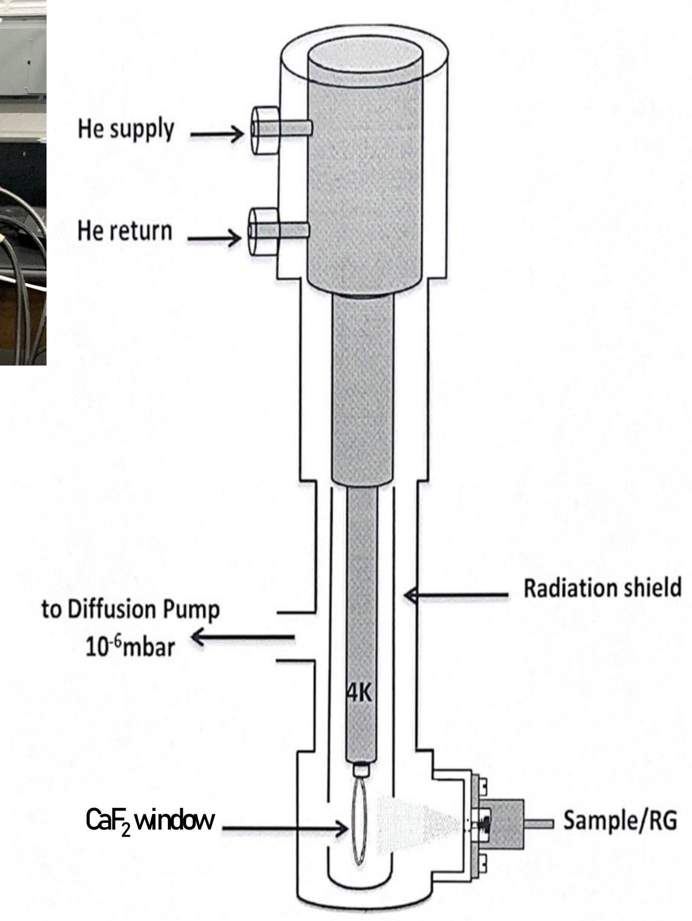

Figure 5: Cryo Schematic

Computational Method

- Optimized ground state structures for CH_2ClI halomethane and iso-halon
- Calculated harmonic vibrational frequencies and vertical excitation energies
- Utilized density functional theory with B3LYP/def2tzvp level of theory
- Computed IR frequencies and UV/vis spectra for the $5^{12}6^2$ hydrate with CH2ClI and iso-halon
- Used the Raj High Performance Computing Cluster for computations

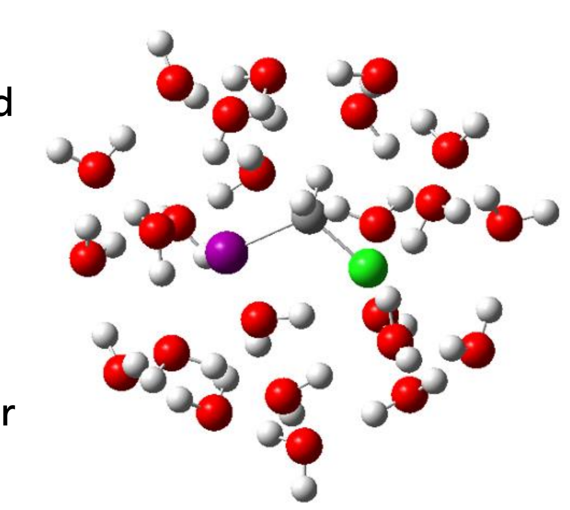

Figure 6: CH_2ClI $5^{12}6^2$ Hydrate Structure

Current Goals

- Experimentally form CH_2ClI in the $5^{12}6^2$ hydrate and amorphous state
- Form the iso-halon in the hydrate and amorphous state
- Compare the reaction products of the above

Results & Discussion

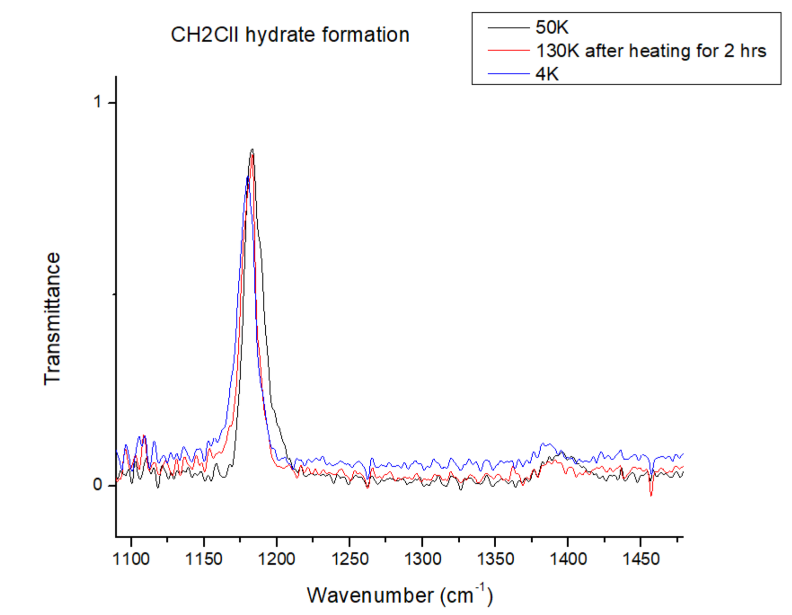

Figure 7a: CH_2ClI Hydrate IR

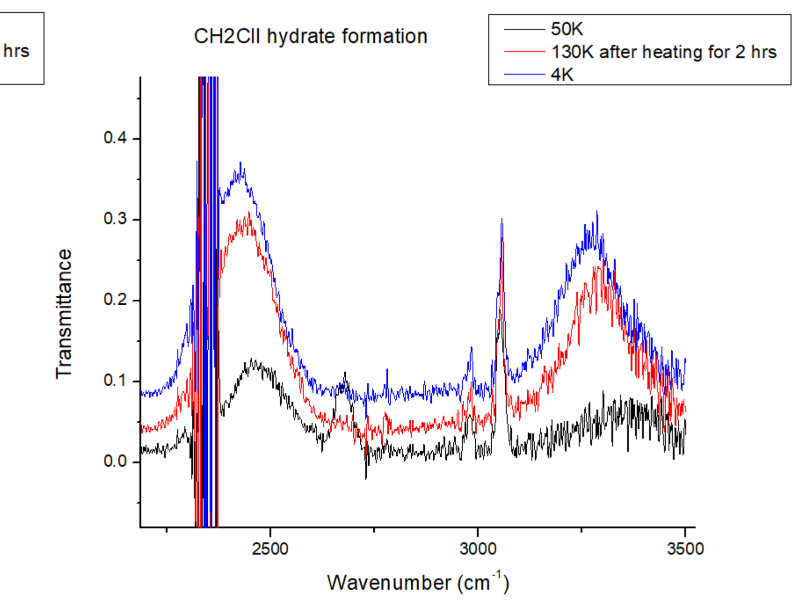

Figure 7b: CH_2ClI Hydrate IR

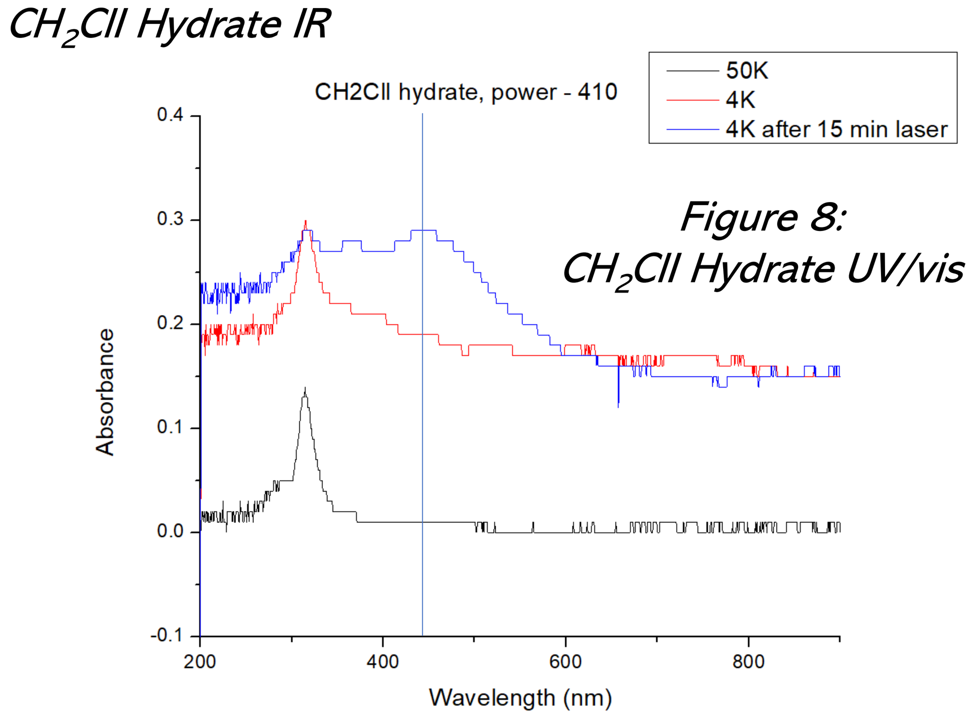

Figure 8: CH_2ClI Hydrate UV/vis

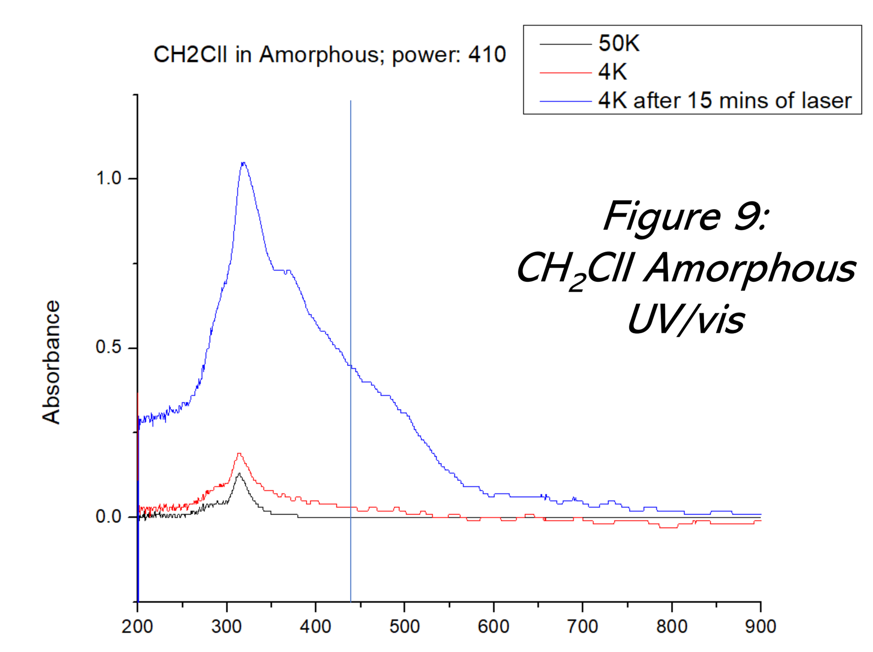

Figure 9: CH_2ClI Amorphous UV/vis

- Figure 7a indicates hydrate formation due to shift of the peak at ~1175 cm^{-1}
- Figure 7b indicates hydrate formation with well structured peaks at ~2400 cm^{-1} and ~3100 cm^{-1}
- Figure 8 identifies iso-halon formation in the matrix at 425 nm at 4K after 15 min laser excitation
- Absence of a peak at 425 nm in Figure 9
  - Indication of a possible chemical reaction product between the iso-halon and water

Future Direction

- Conduct experiment using ozone
- Conduct further experimental trials employing a variety of halomethane and iso-halon systems to investigate potential variations in their reaction chemistries

References

1. Gómez-Consarnau, L., Klein, N.J., Cutter, L.S. and Sañudo-Wilhelmy, S.A. (2021), Growth rate-dependent synthesis of halomethanes in marine heterotrophic bacteria and its implications for the ozone layer recovery. Environmental Microbiology Reports, 13: 77-85.
2. Benavent, N., Mahajan, A.S., Li, Q. et al. Substantial contribution of iodine to Arctic ozone destruction. Nat. Geosci. 15, 770–773 (2022).
3. Koh CA, Sloan ED, Sum AK, Wu DT. Annu Rev Chem Biomol Eng. 2011; 2:237-57
4. Houston, P.L., Chemical Kinetics and Reaction Dynamics, Dover Publications Inc. (2006), 225)