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, 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. 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.

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 at 130K 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

Results & Discussion

• Optimized ground state structures for CH2ClI 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 51^516^2 hydrate with CH2ClI and iso-halon
• Used the Raj High Performance Computing Cluster for computations

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

Current Goals

• Experimentally form CH2ClI in the 51^516^2 hydrate and amorphous state
• Form the iso-halon in the hydrate and amorphous state
• Compare the reaction products of the above

References