Experimental and theoretical study on the capture/desorption of gaseous methyl iodide on sea salt aerosols

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Context

Nuclear

In a **pressurized water reactor**, during a severe accident

Release of ^{131}I (I_2, CH_3I)

I_2 , CH_3I

$O^{\bullet}$, $OH^{\bullet}$ and e-

products of the air radiolysis

Iodine oxides

High temperature
(400, 1000 -1500, … 2500 K)

Atmospheric

In the atmosphere **above oceans**

marine organisms
(macroalgae, phytoplankton)

production

I_2 , CH_3I

hv, O_3

photolyzed
(UV-visible light)
oxidation

Iodine oxides

Tropospheric temperature
(250-300 K)

Key issues

✓ How the methyl iodide **reactivity** is influenced by its environment ?

→ **Reactions** with atmospheric aerosols ?

→ **Influence** of the presence of H_2O ?

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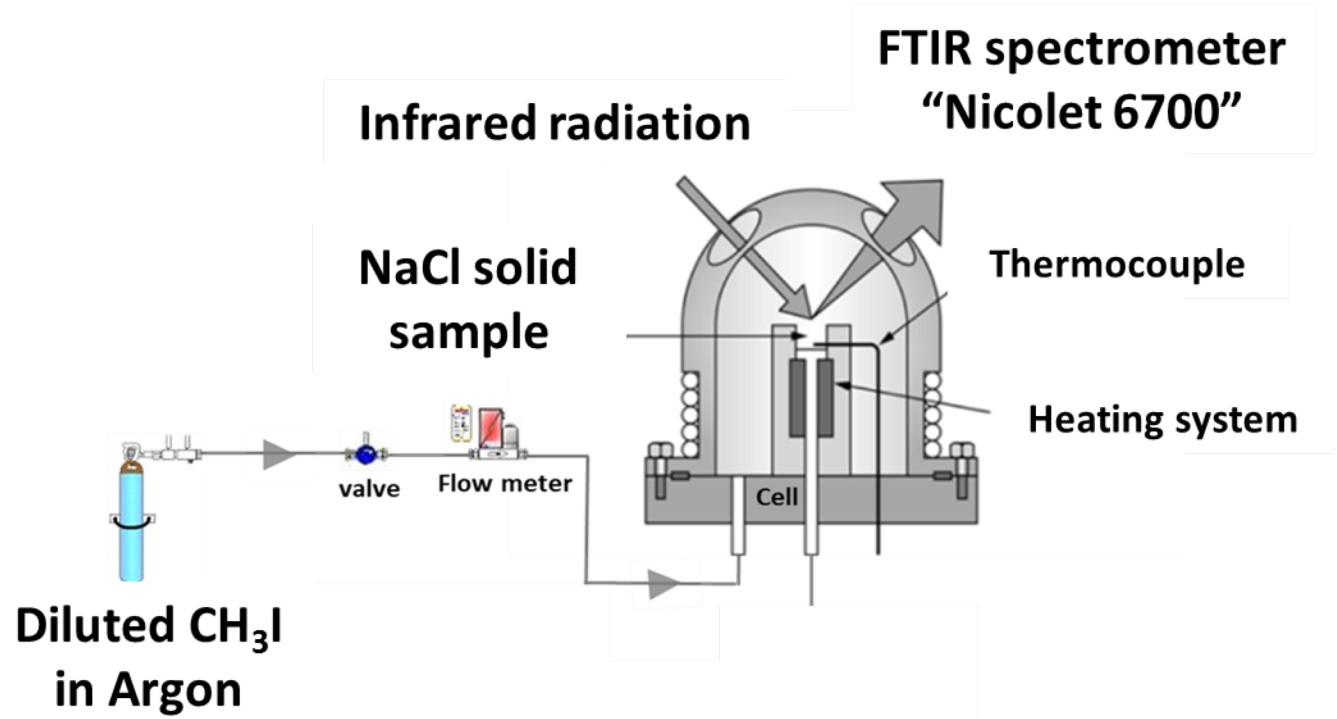
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) experiments

- ✓ To probe Chemical and structural information for solid surfaces exposed to gaseous species
- ✓ Provide semi quantitative analyses for kinetics, adsorption-absorption and surface reaction
- ✓ Reproduce atmospheric conditions (P, T)
- ✓ FTIR spectrum reprocessing in Pseudo absorbance (log(1/R))



Experimental conditions

Salt particles	NaCl (powder)
$[CH_3I]$	1000 ppm
Total flow	100 ml/min
Temperature	Room Temperature
Humidity	~10% at 20°C
Pressure	100 kPa
Total Exposure time	5 hours

Spectral recording conditions

Spectral range	4000 to 700 cm^{-1}
Resolution	8 cm^{-1}
Scans	200
Time for each spectra	8 minutes

The C-I stretching band at 572 cm^{-1} is not accessible, because the spectra is cut in the range below 700 cm^{-1} .

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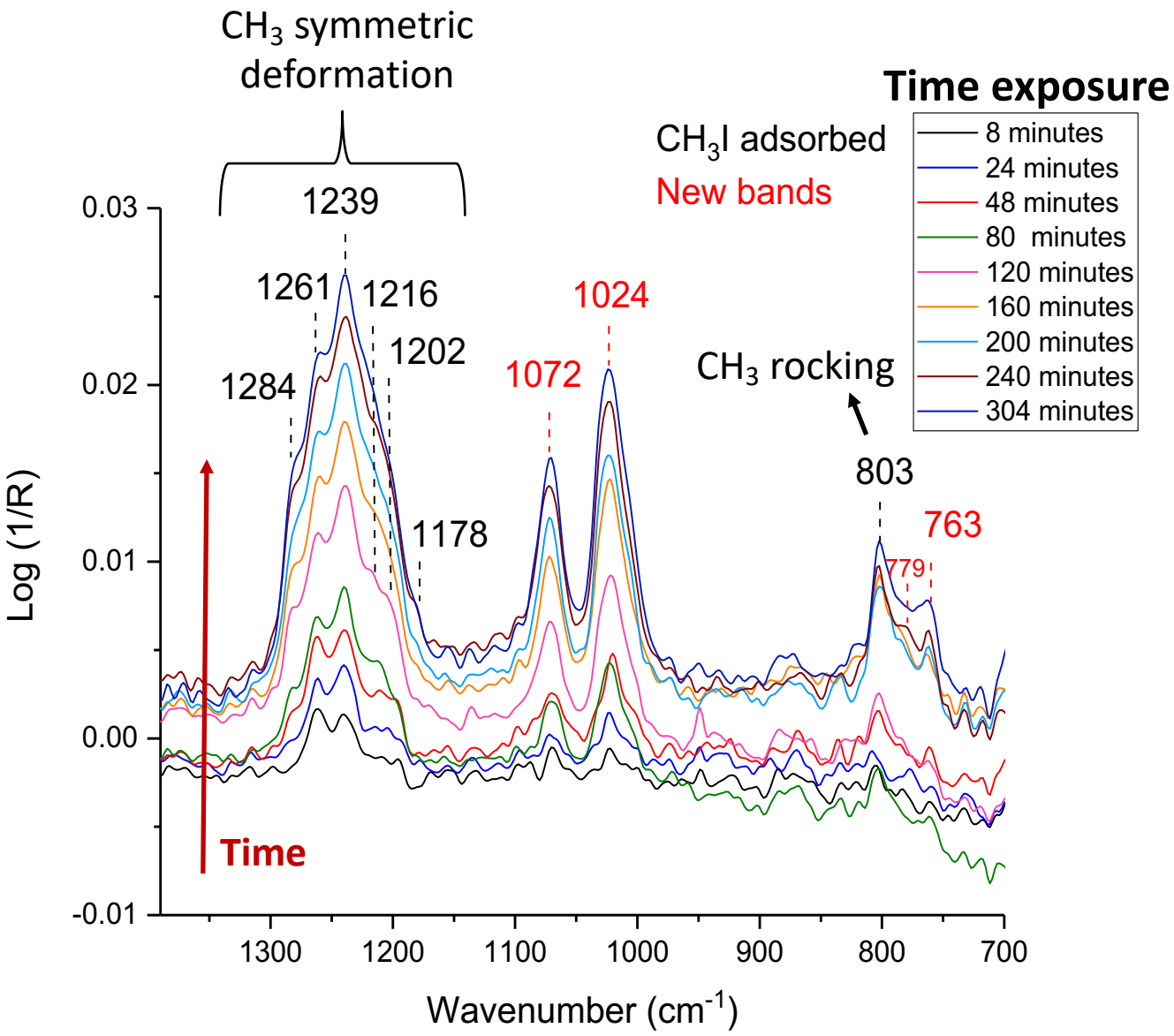
Results: DRIFTS Spectra of NaCl when exposed to CH_3I



- ✓ **CH_3I adsorbed increases as a function of time.**
- ✓ **New IR bands are observed due to CH_3I interaction with NaCl.**
- ✓ **No apparent desorption of CH_3I and new bands are observed when the temperature increased or under Ar flow.**
- ✓ **The kinetic for interaction between CH_3I and NaCl follows a 1st order law.**

Necessity to understand the underlying physico-chemical mechanisms
→ modelling at the molecular scale

CH_3I adsorbed: Chebbi, M., at al., J. Phys. Chem. C 120, 18694–18706 (2016).

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Theoretical study of the CH_3I microhydration

Objective

Quantify CH_3I interaction with water

- A first step to understand its chemistry

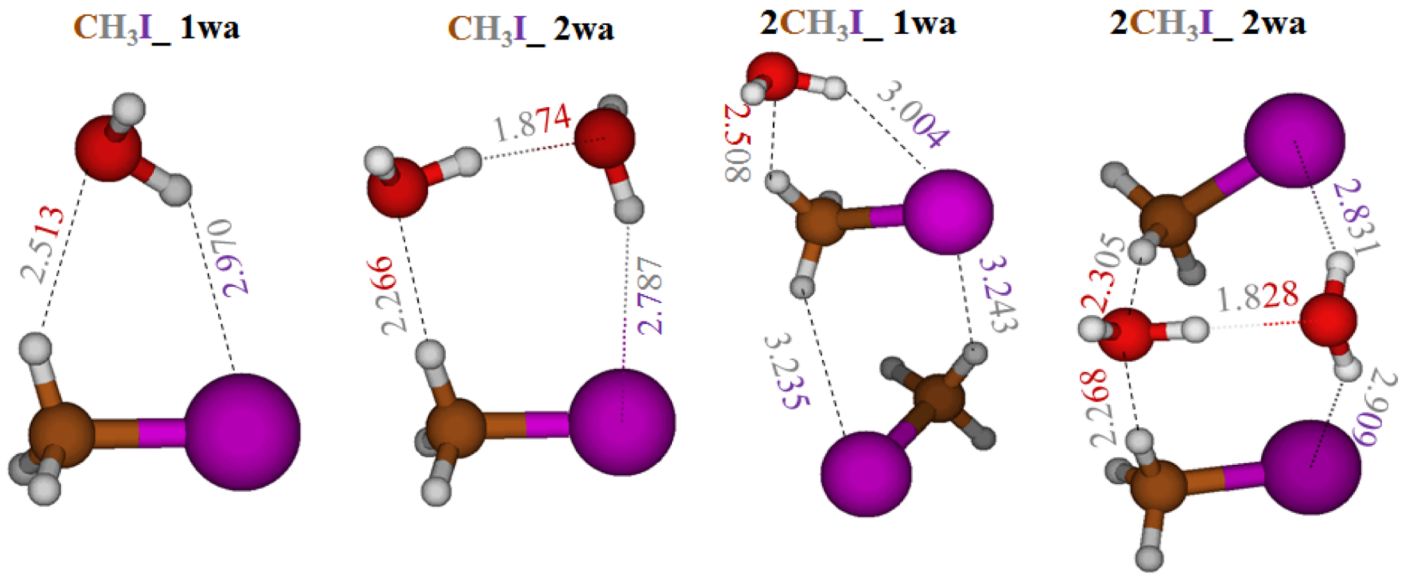
Methods

Quantum Mechanical calculations
(Optimization+ Normal modes analysis)

- ωB97X-D/aug-cc-pVTZ(-PP) level of theory
- Standard reaction enthalpy ($\Delta_r H^\circ_{298K}$)
- Standard Gibbs free reaction energy ($\Delta_r G^\circ_{298K}$)

Results

Weak interaction, in agreement with *Ito et. al.*[1]



Molecular complex	$\Delta_r H^\circ_{298K}$ (kJ mol^{-1})	$\Delta_r G^\circ_{298K}$ (kJ mol^{-1})
CH_3I + 1 H_2O	-8.1	14.8
CH_3I + 2 H_2O	-33.1	25.5
2 CH_3I + 1 H_2O	-14.1	29.9
2 CH_3I + 2 H_2O	-53.3	43.5

[1]Ito, F., et al. *Chem. Phys. Lett.* **343,** 185–191 (2001)

Ongoing: Interaction of CH_3I with a model sea-salt particle

Objective

How CH_3I interacts with NaCl (001) ?
Influence of humidity?

- Support/Explain results from experiment

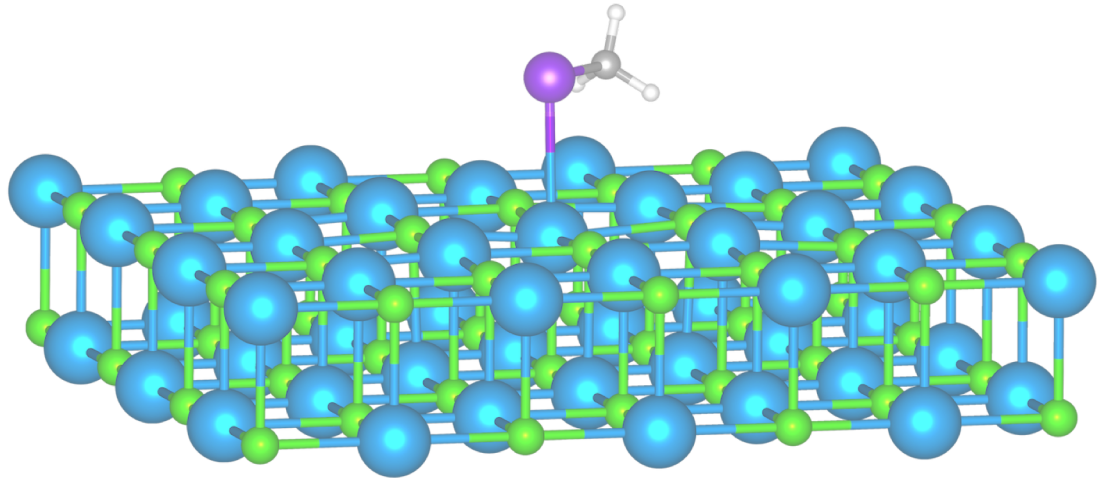
Methods

Quantum Mechanical calculations
(Optimization+ Normal modes analysis)

- QM/QM' ONIOM (DFT/PM7) (Gaussian)
- Periodic plane-wave DFT calculations (Quantum Espresso)

Results

- Benchmark of the gas phase IR spectra
- CH_3I/NaCl interaction competes with CH_3I-H_2O interaction



Optimized DFT geometry of CH_3I adsorbed on a NaCl(100) surface from a QM/QM' ONIOM (DFT/PM7) calculation

Expectations

- AIMD to unravel the reactivity on the surface (diffusion, coverage influence)
- Effect of H_2O on the reactivity/vibrational frequencies
- Other molecules will be also studied (CH_2I_2…)

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