

Interaction process between gaseous CH₃I and NaCl particles: implication for iodine dispersion in the atmosphere

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Figure S3 DRIFTS spectra of NaCl after 5 hours of CH₃I continuous flow, then under static conditions for 1 hour and finally under 1 hour of continuous Ar flow in the spectral range 1400-900 cm⁻¹. Bands in blue are CH₃I adsorbed on NaCl and in green are gaseous CH₃I near NaCl surface.

Figure S4 DRIFTS spectra of NaCl in the spectral range 1400-900 cm⁻¹ after 1 hour of CH₃I continuous flow, then under static conditions for 4 hours and finally under Ar flow at 23 °C for 1 hour, at 100 °C for 15 minutes, 200 °C for 15 minutes and 400 °C for 15 minutes. Bands in blue are CH₃I adsorbed on NaCl and green are gaseous CH₃I.

Figure S5 Double log curve of rate of $\Sigma\text{CH}_3\text{I}_{\text{adsorbed}}$ versus CH₃I gaseous concentration at 1000, 500 and 200 ppm (experiment series (4)).

Theoretical Calculation

The structure of CH₃I monomer was calculated with the Gaussian16 program using the long range corrected functional $\omega\text{B97X-D}$ with the aug-cc-pVTZ basis set for hydrogen, carbon and oxygen atoms, while the aug-cc-pVTZ-PP basis set was used for the iodine atom that incorporates a small-core relativistic pseudo potential. More details can be found elsewhere ¹.

Tables

Table S1: Experimental conditions of the series of experiments performed in this study.

Salt	Exposure phase				Spontaneous desorption phase (Static condition)	Induced desorption phase (Continuous Ar flow of 108 mL.min ⁻¹)	Activated desorption phase (Continuous Ar flow of 108 mL.min ⁻¹)			Repetition
	Temperature (°C)	[CH ₃ I] _g (ppm)	CH ₃ I/Ar flow (mL.min ⁻¹)	Duration	Duration	Duration	Duration at 100°C	Duration at 200°C	Duration at 350°C	
Experiment series (1)										
NaCl	23	1000	108/0	5 hours	1 hour	1 hour	0	0	0	3
Experiment series (2)										
NaCl	23	1000	108/0	1 hour	4 hours	1 hour	15 min	15 min	15 min	1
Experiment series (3)										
NaCl	23	500	54/54	5 hours	0	0	0	0	0	2
NaCl	23	200	21/87	5 hours	0	0	0	0	0	1
Experiment series (4)										
NaI	23	1000	108/0	1 hours	0	0	0	0	0	1
KBr	23	1000	108/0	1 hours	0	0	0	0	0	1

Table S2: The calculated loss of adsorbed CH₃I between exposure phase and static and Ar flow phases (experiment series 2). A is the sum of the area of 1275, 1244, 1220, 1183, 1073 and 1024 cm⁻¹ bands ($\sum \text{CH}_3\text{I}_{\text{adsorbed}}$). A_{exp} denotes the area at the end of exposure phase, A_{static} denotes the average area of the last 32 minutes in static phase and A_{Ar} denotes the area at different temperature in Ar flow phase.

Spectral Region	Adsorbed CH ₃ I in CH ₃ deformation region
Band area uncertainty	0.37
CH₃I exposure phase	
Duration	1 hour
A _{exp} : after 1 hour	0.46 ± 0.37
Spontaneous desorption phase	
Duration	1 hour
A _{static} : after 4 hour	0.48 ± 0.37
Induced and activated desorption phases	
Duration	2 hours
A _{Ar} : Area at 23 °C	0.42 ± 0.37
A _{Ar} : Area at 100 °C	0.48 ± 0.37
A _{Ar} : Area at 200 °C	0.39 ± 0.37

Table S3: Determination of the total amount of iodine taken up by NaCl using ICP-MS technique and determination of conversion factor.

Using ICP-MS to determine the total number of iodine taken up by solid NaCl in mg using [E-S1]:			
$m_t(\text{I}) \text{ in the solution} = [\text{I}] \text{ in ppb} \times \text{Volume of NaOH (mL)}$ [E-S1]			
Then total mass of iodine taken up by dissolved salt in number of atoms /mg was determined by [E-S2]:			
$m_t(\text{I}) \text{ in dissolved NaCl} = \frac{m_t(\text{I}) \text{ in the solution (mg)}}{m_{\text{NaCl dissolved}} \text{ (mg)}} \times 10^{-3} \times \frac{\text{Avogadro's number}}{\text{Molar mass of Iodine}}$ [E-S2]			
The total amount of iodine taken up total NaCl (number of atoms) is then [E-S3]:			
$m_t(\text{I}) \text{ in total NaCl} = m_t(\text{I}) \text{ in dissolved NaCl (number of atoms /mg)} \times \text{Total } m_{\text{NaCl}} \text{ (mg)}$ [E-S3]			
Experiment series (1) : NaCl exposed to 1000 ppm CH ₃ I for 5 hours	Repeat 1	Repeat 2	Repeat 3
Mass of NaCl in the reactor (mg)	150.0	144.2	146.2
Mass of NaCl (mg) dissolved in NaOH after exposure phase	100.1	100.6	100.3
Volume of NaOH solution (ml)	10	10	10
ICP MS results and determination of iodine concentration on NaCl			
Analyse 1 (ppb)	2.94×10 ²	3.48×10 ²	4.33×10 ²
Analyse2 (ppb)	2.92×10 ²	3.52×10 ²	4.46×10 ²
Analyse 3 (ppb)	2.80×10 ²	3.42×10 ²	4.25×10 ²
Average [I] concentration (ppb)	2.88×10 ²	3.47×10 ²	4.34×10 ²
Total mass of iodine in the NaOH solution (mg)	2.88×10 ⁻³	3.47×10 ⁻³	4.34×10 ⁻³
Mass of iodine taken up (mg/mg of NaCl)	2.88×10⁻⁵	3.45×10⁻⁵	4.33×10⁻⁵
Amount of iodine taken up (number of atoms/mg of NaCl)	1.37×10¹⁴	1.64×10¹⁴	2.05×10¹⁴
Mean of amount of iodine taken up by NaCl (number of atoms/mg of NaCl)		1.69×10¹⁴	
Absolute uncertainty interval at 95% confidence level(+/- number of atoms)		8.6×10¹³	
Total iodine mass taken up by the total mass of NaCl			
Total mass of iodine taken up by <u>total mass</u> of NaCl (mg)	4.32×10⁻³	4.98×10⁻³	6.33×10⁻³
Total amount of iodine taken up by <u>total mass of</u> NaCl (number of atoms)	2.05×10¹⁶	2.36×10¹⁶	3.00×10¹⁶
Absolute uncertainty interval (+/- number of atoms)	1.64×10¹⁵	1.89×10¹⁵	2.40×10¹⁵
Conversion factor of FTIR $\Sigma\text{CH}_3\text{I}_{\text{adsorbed}}$ band area to number of CH₃I absorbed on NaCl			
$\Sigma_{\text{CH}_3\text{I}}$ Band area – pseudo absorbance (a.u.)	2.085	2.069	2.338
absolute area uncertainty (+/- surface unit of integrated area)	0.37	0.37	0.37
Conversion factor (number of I atoms on NaCl/ surface of integrated band)	9.83×10 ¹⁵	1.14×10 ¹⁶	1.28×10 ¹⁶
Conversion factor absolute uncertainty	1.91×10 ¹⁵	2.24×10 ¹⁵	2.28×10 ¹⁵
Mean conversion factor		1.14×10 ¹⁶	
Mean conversion factor uncertainty		3.74×10 ¹⁵	

Figures

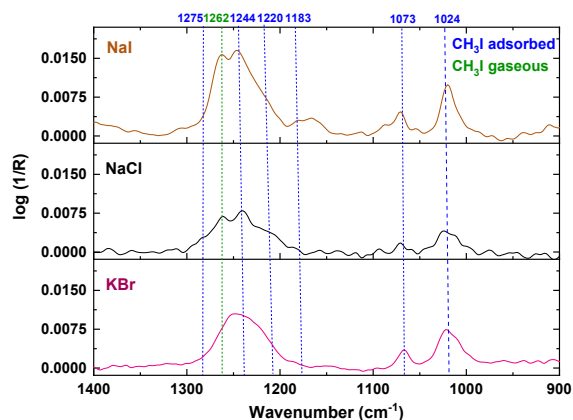


Figure S1: DRIFTS spectra in the 1400-900 cm⁻¹ IR spectral range of NaCl (in black), NaI (in dark yellow) and KBr (in violet) exposed to 1 hour of CH₃I (108mL.min⁻¹, 1000 ppm) continuous flow at 23°C and 1 atm. Bands in blue are adsorbed CH₃I and green are gaseous CH₃I near the surface.

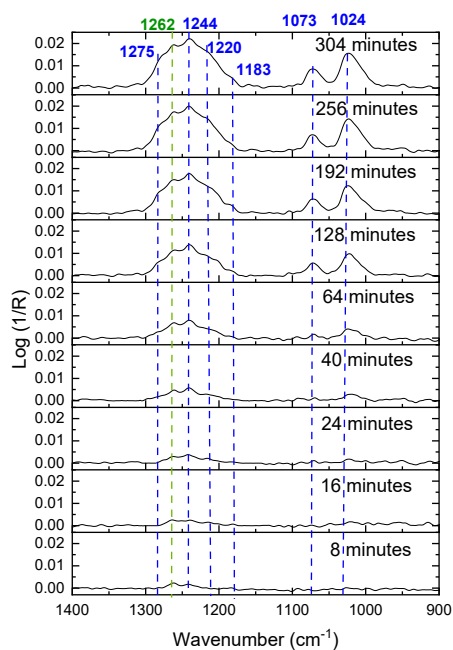


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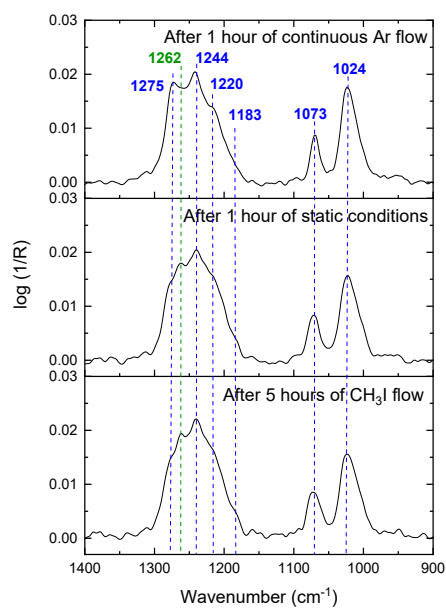


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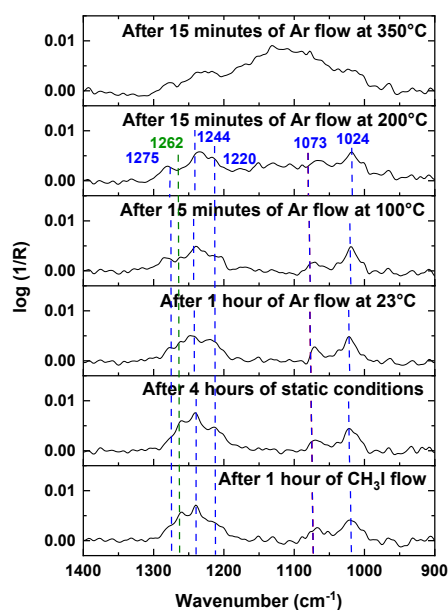


Figure S4: DRIFTS spectra of NaCl in the spectral range 1400-900 cm⁻¹ after 1 hour of CH₃I continuous flow, then under static conditions for 4 hours and finally under Ar flow at 23 °C for 1 hour, at 100 °C for 15 minutes, 200 °C for 15 minutes and 400 °C for 15 minutes. Bands in blue are CH₃I adsorbed on NaCl and green are gaseous CH₃I.

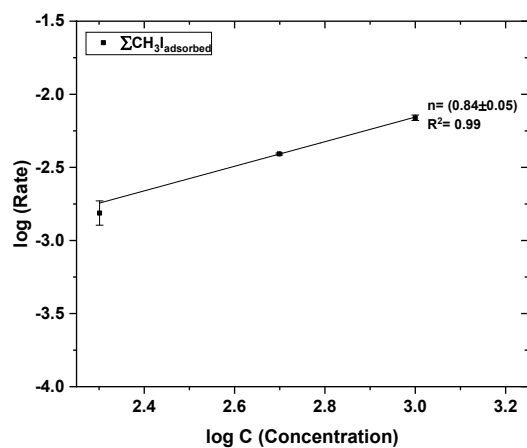


Figure S5: Double log curve of rate of $\Sigma\text{CH}_3\text{I}_{\text{adsorbed}}$ versus CH_3I gaseous concentration at 1000, 500 and 200 ppm (experiment series (4)).

Reference:

¹ S. Sobanska, H. Houjeij, S. Coussan, C. Aupetit, S. Taamalli, F. Louis, L. Cantrel, A. C. Gregoire and J. Mascetti, Infrared matrix-isolation and theoretical studies of interactions between CH_3I and water, *J. Mol. Struct.*, 2021, **1236**, 130342. DOI: 10.1016/j.molstruc.2021.130