

# Infrared matrix- isolation and theoretical study of interactions between CH<sub>3</sub>I and water

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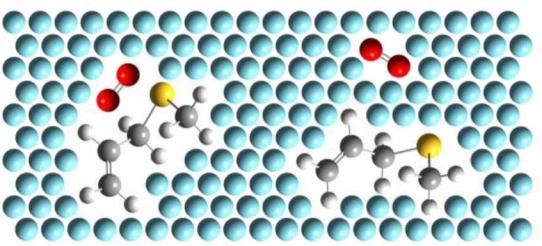
**Hanaa Houjeij**

Supervisors: Sophie Sobanska (ISM/CNRS 5255) / Anne Cecile Gregoire (IRSN/L2EC)

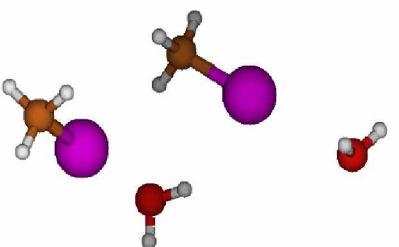
In collaboration with: Joëlle Mascetti (ISM), Christian Aupetit (ISM), Stephane Coussan (PIIM), Florent Louis (PC<sub>2</sub>A), Sonia Taamali (PC<sub>2</sub>A)

# OUTLINE

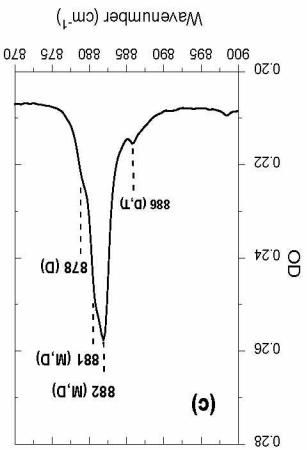
↳ Iodine compounds in nuclear and atmospheric context



↳ Experimental strategy for matrix isolation infrared spectroscopy



↳ DFT calculation for spectral interpretation



↳ Conclusion and perspectives

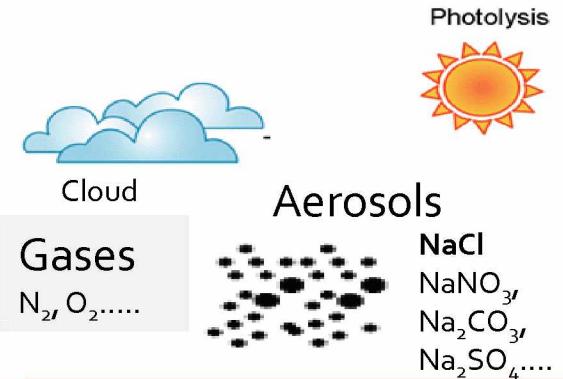
# Context



In case of Severe Nuclear Accident (Fukushima, Chernobyl...)

Modelled by C3X IRSN operational tool without considering reactivity of  $\text{CH}_3\text{I}$

Transportation to the atmosphere



Health effect



Environment contamination

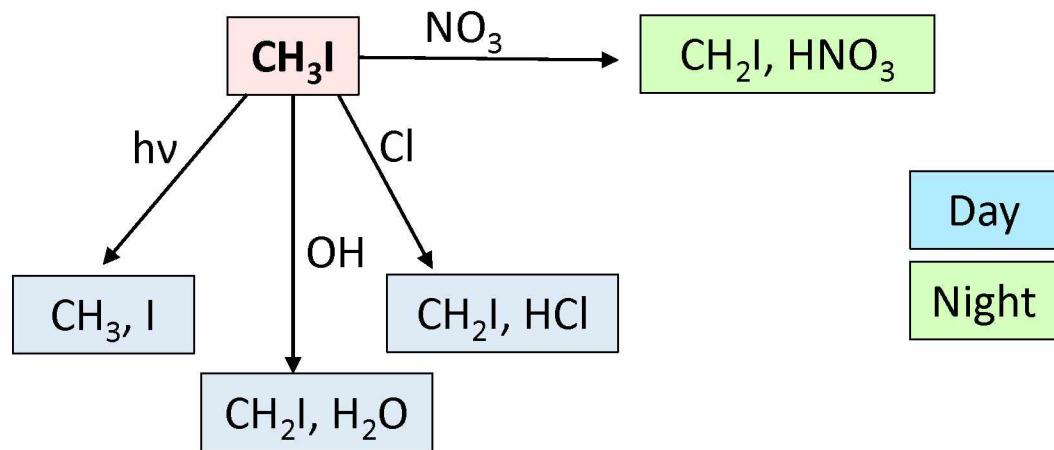


Radioactive Iodine

Aerosols,  
gaseous  
organic iodides  
(e.g.  $\text{CH}_3\text{I}$ )  
and  $\text{I}_2$

# Reactivity of $\text{CH}_3\text{I}$ in the atmosphere

## $\text{CH}_3\text{I}$ homogenous reactivity



## $\text{CH}_3\text{I}$ heterogeneous reactivity

- Quantitative determination of  $\text{CH}_3\text{I}$  uptake by carbonaceous aerosols

W. Wang, *Chem. Phys. Lett.* 440 (2007) 348–351

Y. Shi, *Chinese Sci. Bull.* 53 (2008) 733–738



Mechanism is not known

- $\text{CH}_3\text{I}$  adsorption on ice and influence on photochemistry

A.B. Alekseyev et al., *J. Chem. Phys.* 126 (2007)

G. Li, et al., *J. Phys. Chem. A.* 109 (2005)

S.ZHANG, , *Thèse de Doctorat, Aix-Marseille Université*, 2012

C. FORTIN, *These de Doctorat, Lille université*, 2019

Bai et al., *RSC Adv.*, 2015, 5, 88087

Interaction of  $\text{CH}_3\text{I}$  with atmospheric aerosols is not investigated

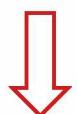
$\text{CH}_3\text{I}$  interaction with water in the atmosphere is not well known

# Objectives



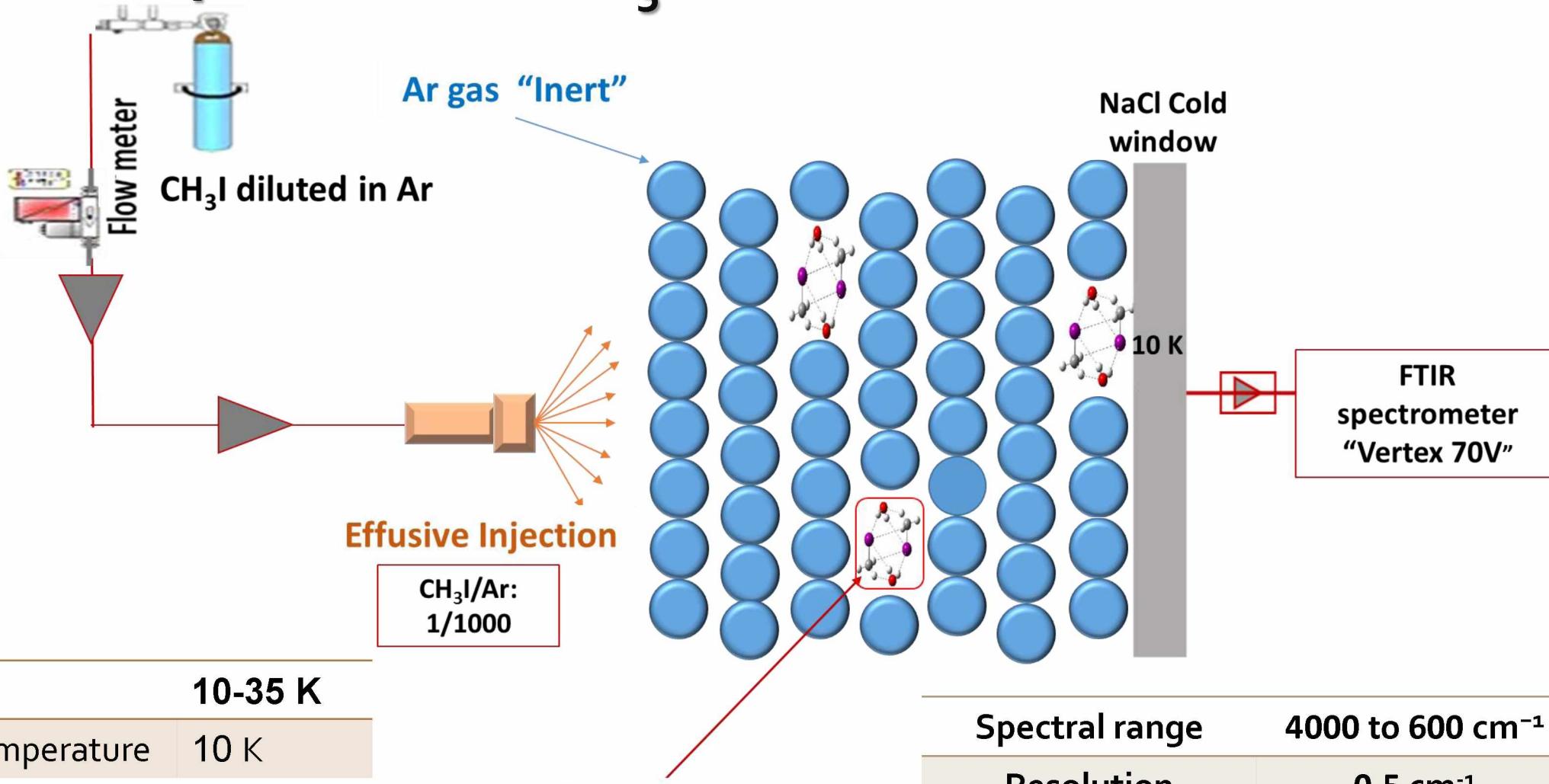
*Influence of water on the reactivity of  $\text{CH}_3\text{I}$  in gas phase:*

- Cloud condensation nuclei (CCN) formation
- Photolysis of  $\text{CH}_3\text{I}$

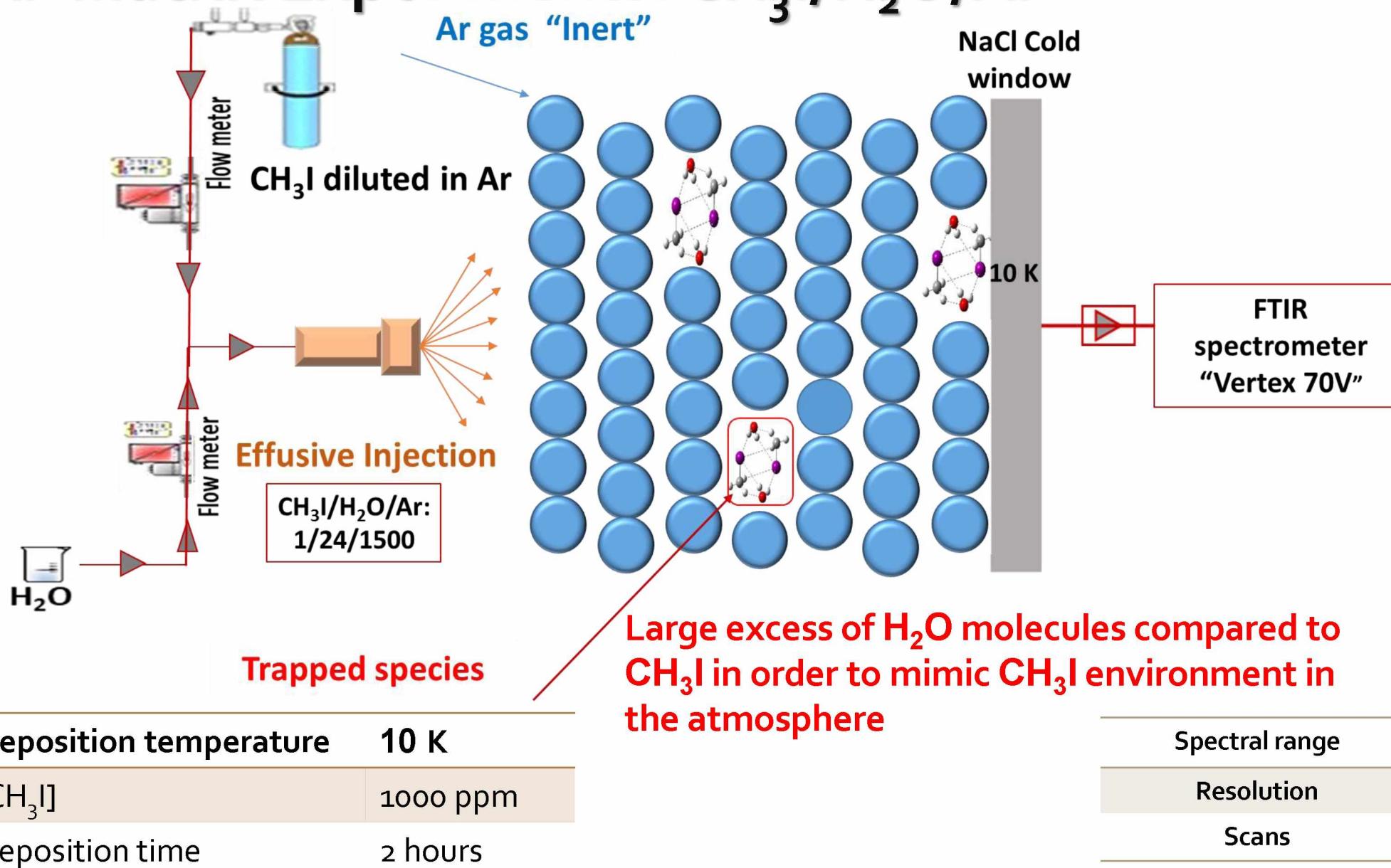


*Investigation of intra and inter-molecular interactions by Matrix Experiments coupled with Fourier transform spectroscopy (FTIR)*

# Ar-Matrix Experiments: $\text{CH}_3\text{I}/\text{Ar}$



# Ar-Matrix Experiments: $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar}$



# DFT calculation methodology

**Objective :** To help in identifying the IR bands of  $(\text{CH}_3\text{I})_n$  clusters and  $(\text{CH}_3\text{I})_n\text{-}(\text{H}_2\text{O})_m$  complexes

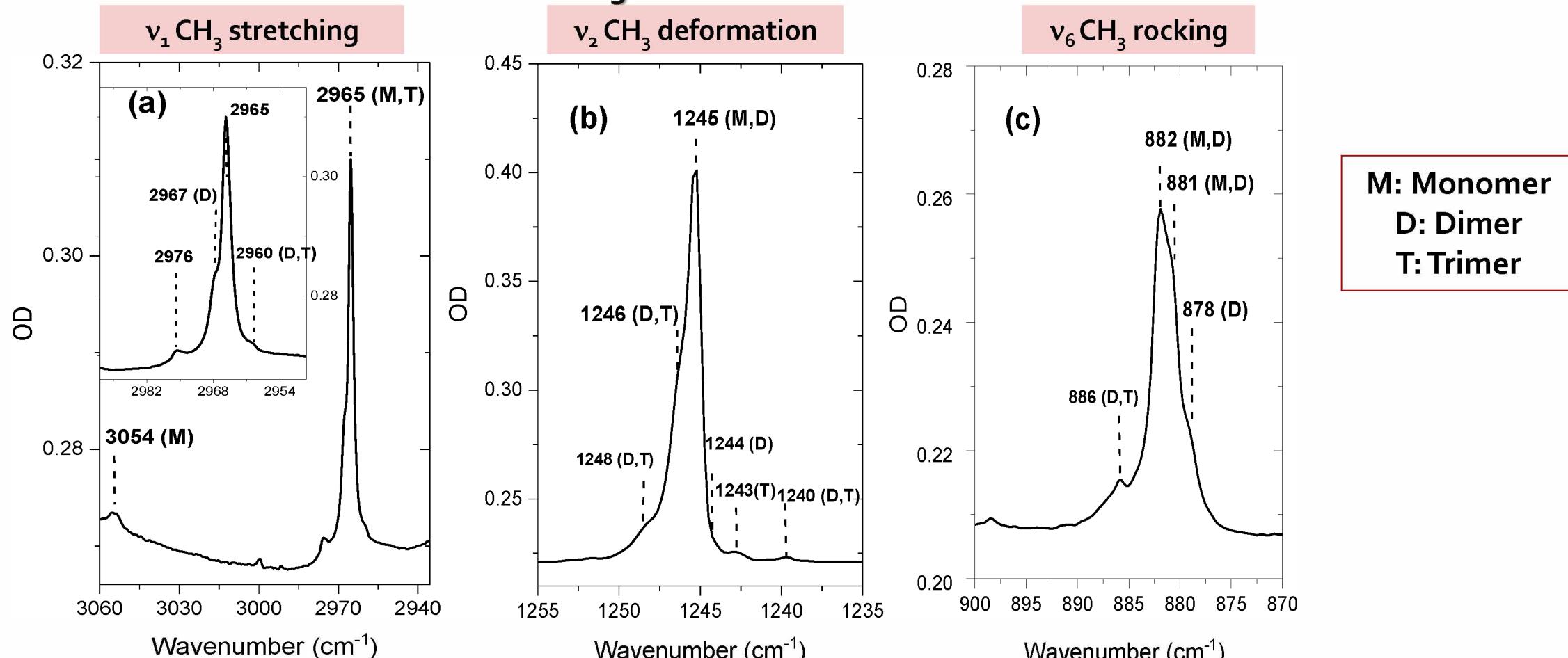
- Prediction of the **isomers** for  $(\text{CH}_3\text{I})_n$  and molecular complex  $(\text{CH}_3\text{I})_n\text{-}(\text{H}_2\text{O})_m$  ( $n = 1, 2, 3$  and  $m = 1, 2, 3$ )
- Optimisation of the geometry** by Gaussian 16 program , using  **$\omega$ B97XD** with the base **aug-cc-pVTZ** for H, O, C and **aug-cc-pVTZ-PP + ECP28** for I (see methodology in [1])
- Calculation of  $\Delta G^\circ_{10K}$**  (not shown).
- Calculation of the **vibrational frequencies** ,  **$\Delta v$**

**Summary of stable geometries**

Structure	Number of stable geometries
$2\text{CH}_3\text{I}$ (Dimer)	2
$3\text{CH}_3\text{I}$ (Trimer)	2
$1\text{CH}_3\text{I}\text{-}1\text{H}_2\text{O}$ (1:1)	2
$1\text{CH}_3\text{I}\text{-}2\text{H}_2\text{O}$ (1:2)	2
$2\text{CH}_3\text{I}\text{-}1\text{H}_2\text{O}$ (2:1)	5
$1\text{CH}_3\text{I}\text{-}3\text{H}_2\text{O}$ (1:3)	4
$2\text{CH}_3\text{I}\text{-}2\text{H}_2\text{O}$ (2:2)	10

[1]: Villard, A. et al.. *Int. J. Quantum Chem.* 119, 1–11 (2019).

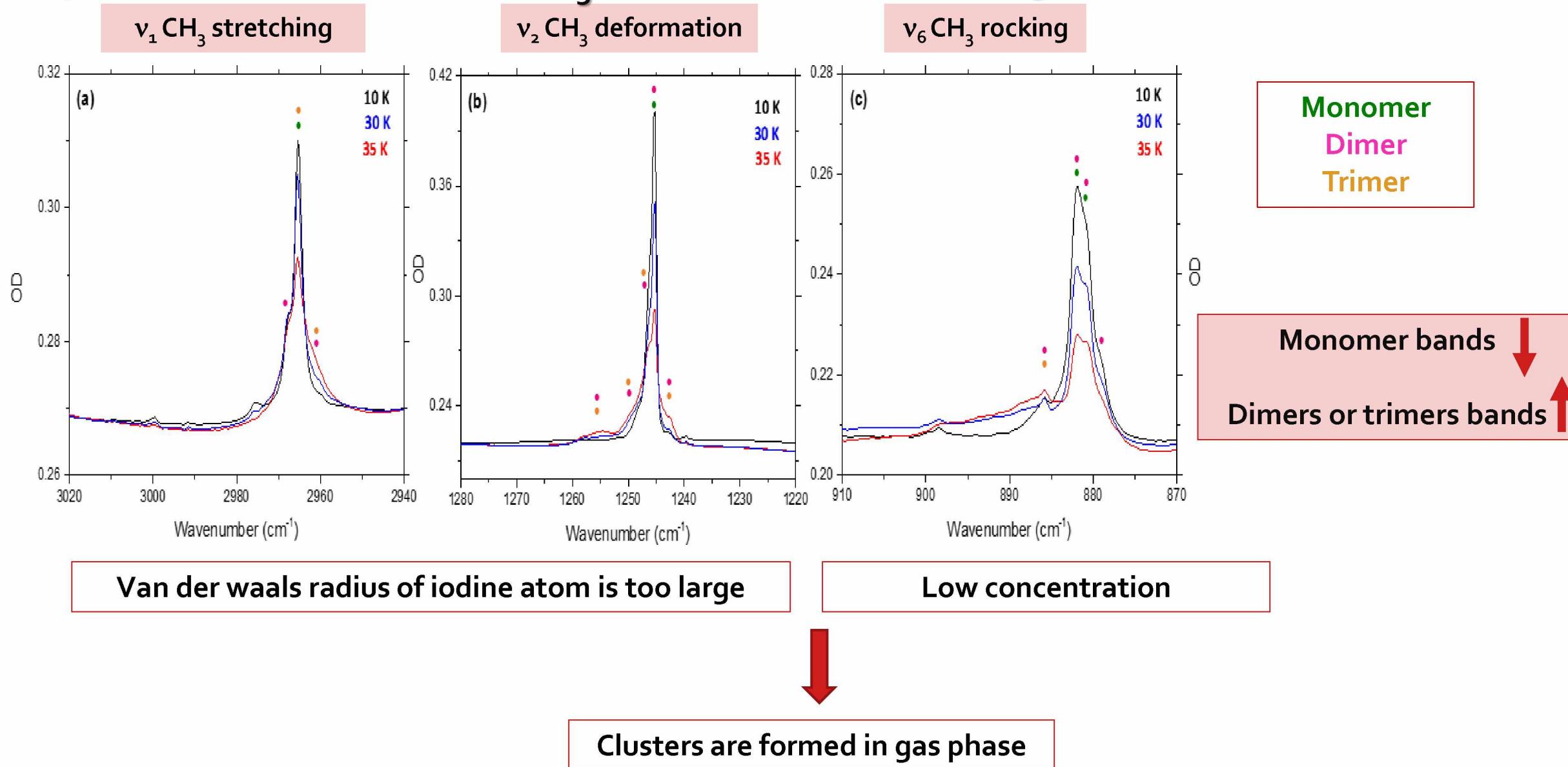
# Experimental results for $\text{CH}_3\text{I}/\text{Ar}:1/1000$ , Deposition at 10 K



- $\text{CH}_3\text{I}$  monomer (M) and dimer (D) bands are consistent with literature <sup>1</sup>
- **Trimer (T) bands assignment cannot be excluded**
- Dimer (D) and trimer (T) frequencies are very close to those of monomers (M) because of the weak interaction

1- Ito, F., *Chem. Phys. Lett.* **343**, 185–191 (2001).

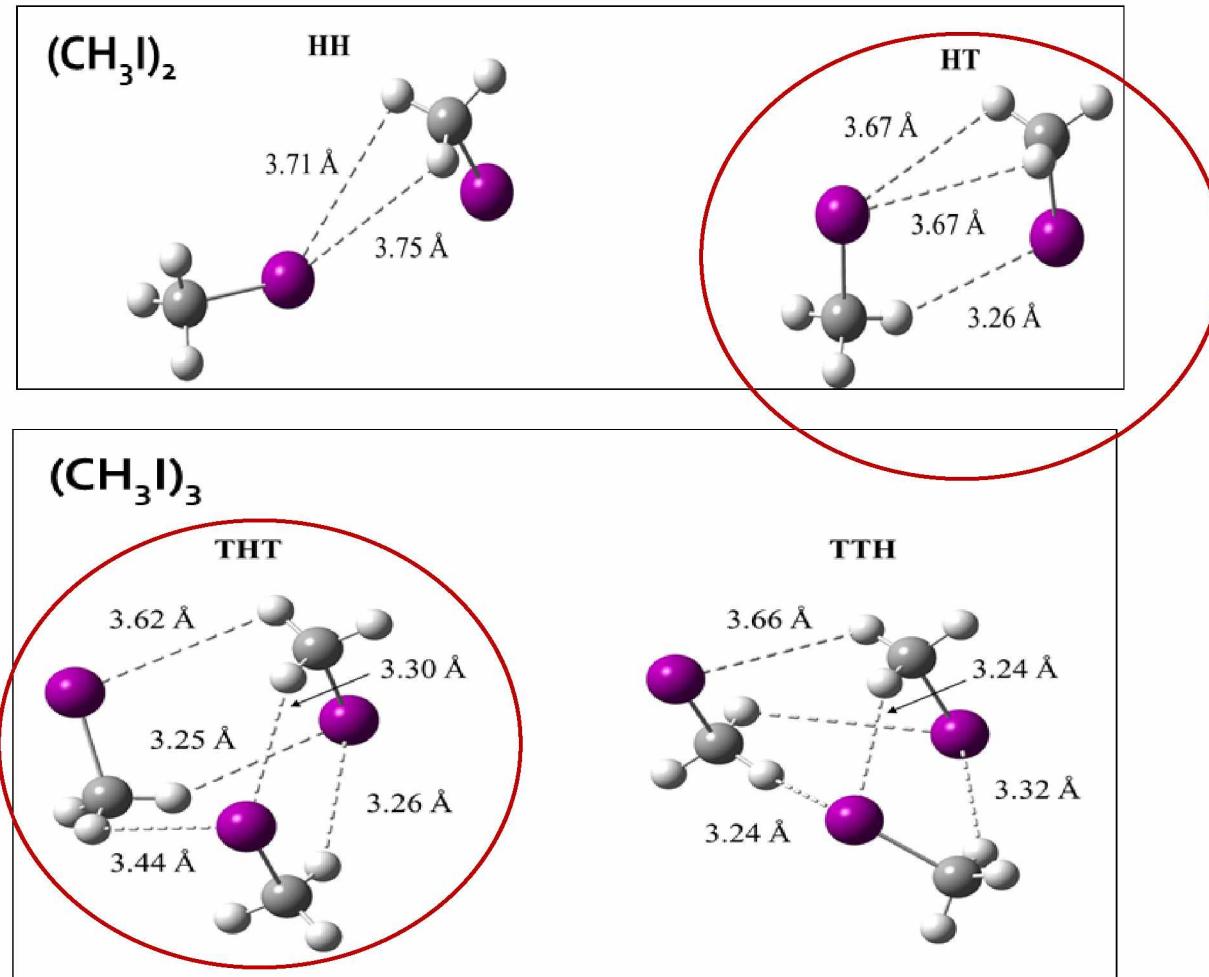
# Experimental results for $\text{CH}_3\text{I}/\text{Ar}:1/1000$ , Annealing 10-35 K



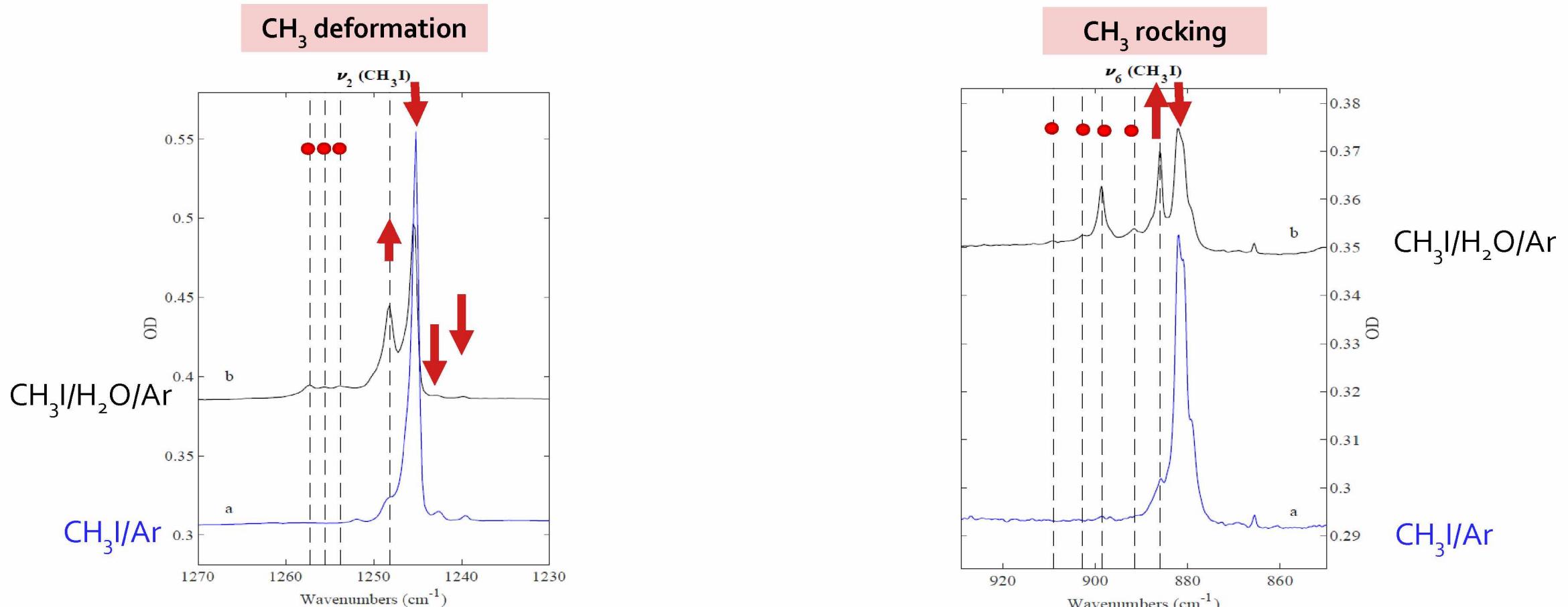
# Experimental results for $\text{CH}_3\text{I}/\text{Ar}$ in dry conditions ( $\text{CH}_3\text{I}/\text{Ar}:1/1000$ ) at 10 K

H: Head  
T: Tail

$\text{CH}_3\text{I}$  stable isomers dimers and trimers:



# Experimental results for $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar}$ : 1/24/1500 at 10 K



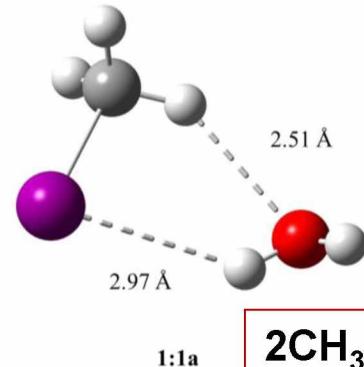
- 1245 (M) and 1243-1240 (D, T)  $\text{cm}^{-1}$  ↓
- 1248  $\text{cm}^{-1}$  (D,T) ↑
- New bands formation (●) at 1257, 1256 and 1254  $\text{cm}^{-1}$
- New bands are blue shifted with respect to 1245  $\text{cm}^{-1}$  (M)

- 882 (M,D) and 881  $\text{cm}^{-1}$  (M,D) ↓
- 886  $\text{cm}^{-1}$  (D, T) ↑
- New bands formation (●) at 909, 903, 899 and 891  $\text{cm}^{-1}$
- New bands are blue shifted with respect to 882  $\text{cm}^{-1}$  (M)

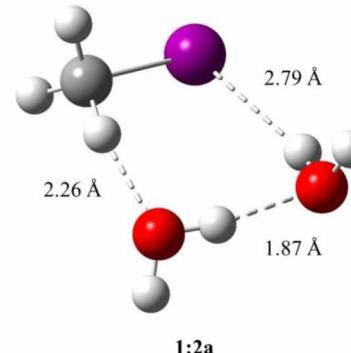
# Experimental results for $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar}$ : 1/24/1500 at 10 K

The new bands shifts in  $\text{CH}_3$  deformation and rocking region match stable isomers of hetero-complexes and aggregates:

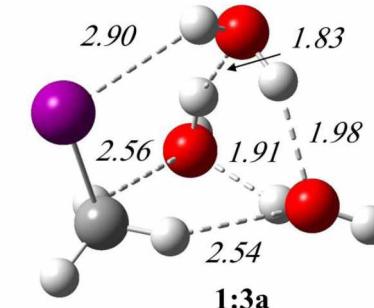
**1 $\text{CH}_3\text{I}-1\text{H}_2\text{O}$  (1:1a)**



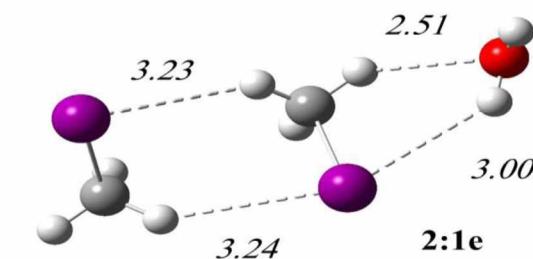
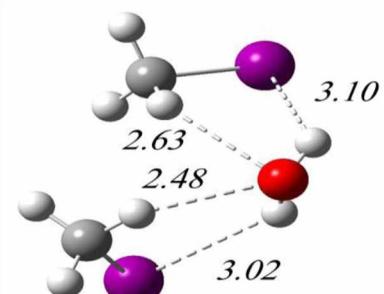
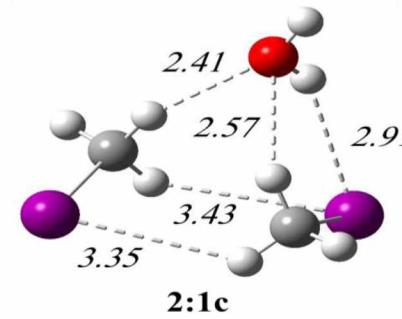
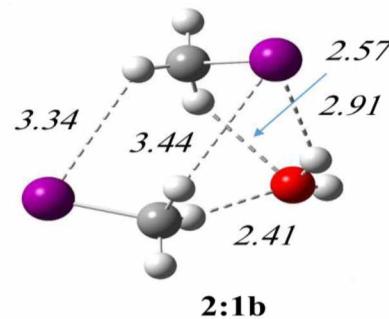
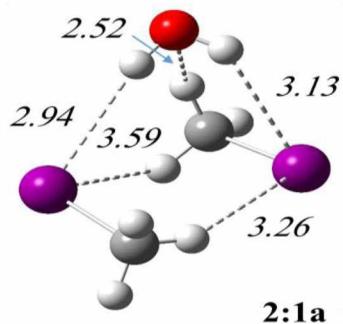
**1 $\text{CH}_3\text{I}-2\text{H}_2\text{O}$  (1:2a)**



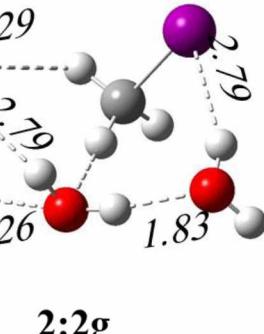
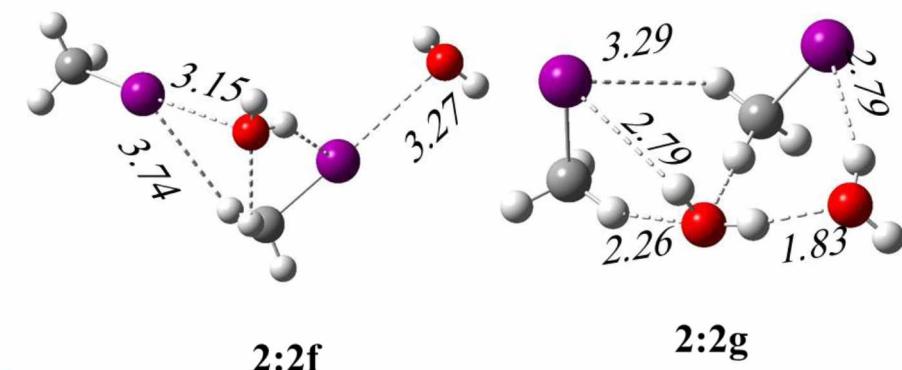
**1 $\text{CH}_3\text{I}-3\text{H}_2\text{O}$  (1:3a)**



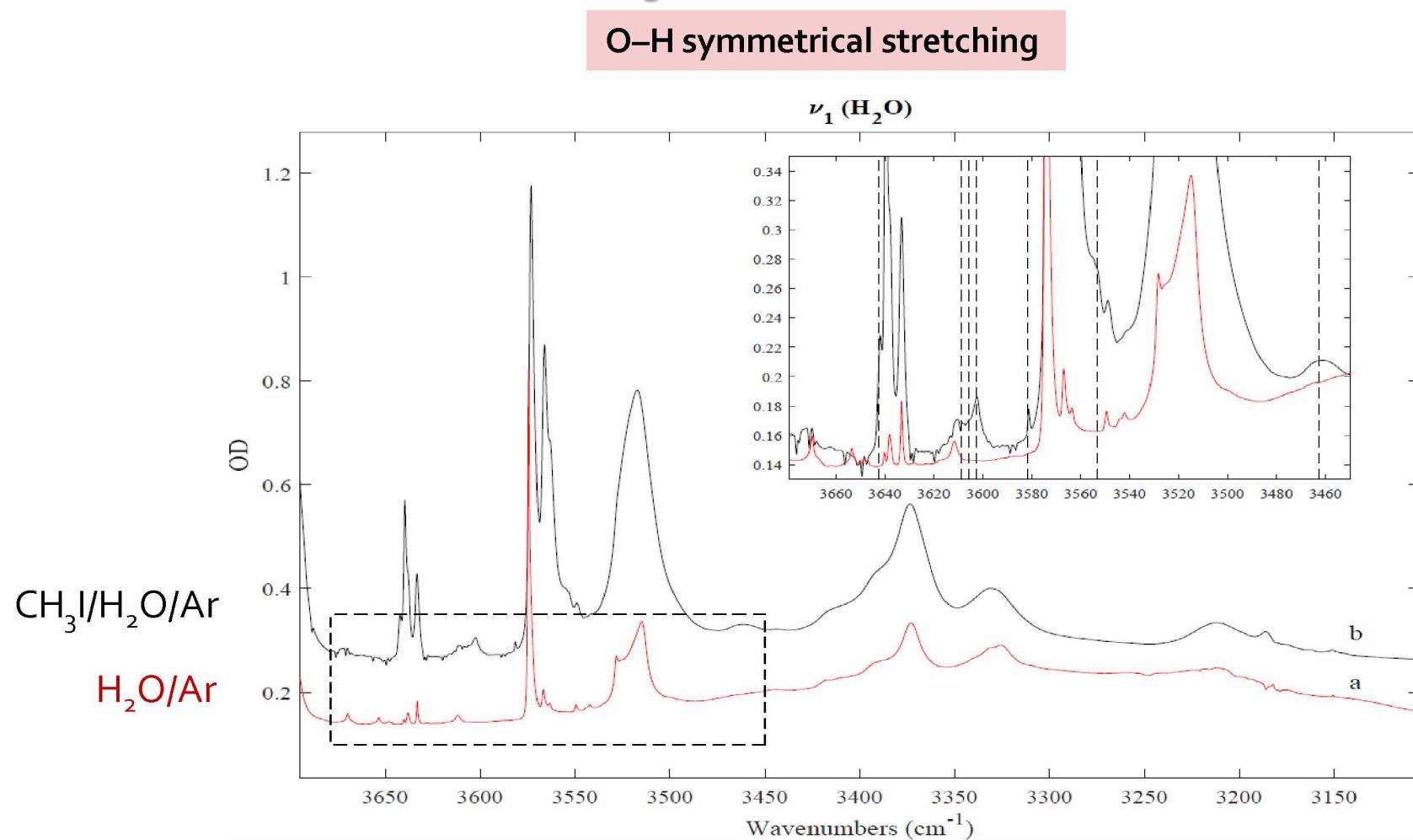
**2 $\text{CH}_3\text{I}-1\text{H}_2\text{O}$  (2:1a - 2:1e)**



**2 $\text{CH}_3\text{I}-2\text{H}_2\text{O}$  (2:2f, 2:2g)**



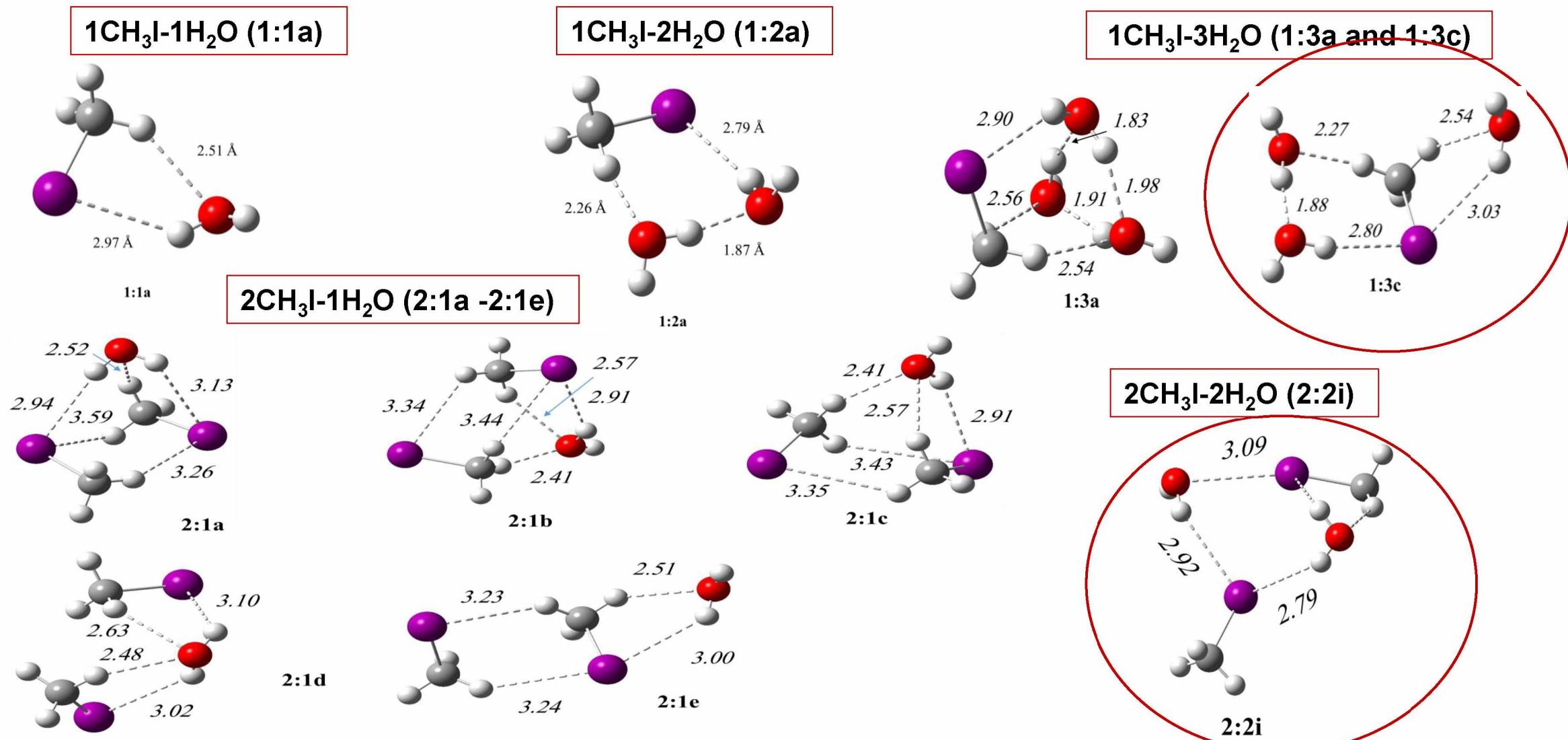
# Experimental results for $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar}$ : 1/24/1500 at 10 K



- Observation of water polymers
- Red and blue shifts which match: 1CH<sub>3</sub>I-1H<sub>2</sub>O (1:1a), 1CH<sub>3</sub>I-2H<sub>2</sub>O (1:2b), 2CH<sub>3</sub>I-1H<sub>2</sub>O (2:1a -2:1e), 1CH<sub>3</sub>I-3H<sub>2</sub>O (1:3a, 1:3c ), and 2CH<sub>3</sub>I-2H<sub>2</sub>O (2:2i)

# Experimental results for $\text{CH}_3\text{I}/\text{Ar}$ in humid conditions ( $\text{CH}_3\text{I}/\text{Ar}/\text{H}_2\text{O}$ : 1/24/1500) at 10 K

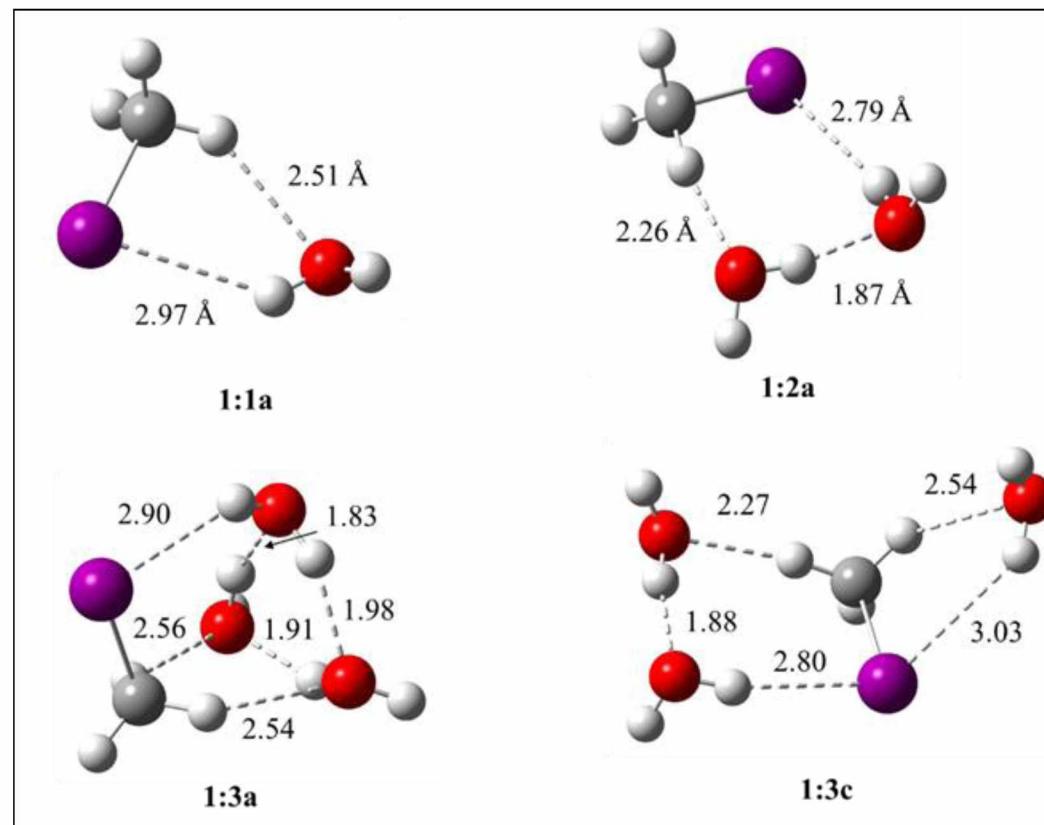
The new bands shifts in  $\text{H}_2\text{O}$  region match stable isomers of hetero-complexes and aggregates:



# Experimental results for $\text{CH}_3\text{I}/\text{Ar}$ in humid conditions ( $\text{CH}_3\text{I}/\text{Ar}/\text{H}_2\text{O}$ ) at 10 K

## Comparing the $\text{CH}_3\text{I}$ and $\text{H}_2\text{O}$ regions

- ❖ We have identified  $1\text{CH}_3\text{I}-1\text{H}_2\text{O}$  (1:1a),  $1\text{CH}_3\text{I}-2\text{H}_2\text{O}$  (1:2a),  $1\text{CH}_3\text{I}-3\text{H}_2\text{O}$  (1:3a, 1:3c)
- ❖ The other complexes such as 2:1 and 2:2 cannot be completely excluded but appear as minor species



# Conclusion and perspectives

- Dimers and trimers of  $\text{CH}_3\text{I}$  are observed despite the high water amount in the initial mixture that may be explained by the **low affinity of  $\text{CH}_3\text{I}$  with water**
- Formation of hetero aggregates of  $\text{CH}_3\text{I}$  and water rather than  $(\text{CH}_3\text{I})_n\text{-}(\text{H}_2\text{O})_m$  complexes
- **Atmospheric implications :**
  - 1-  $\text{CH}_3\text{I}$  will stay in the gas phase rather than be involved in the CCN process
  - 2-  $\text{CH}_3\text{I}$  is not soluble (Henry's constant  $\sim 3 \cdot 10^{-3} \text{ mol.m}^{-3}.\text{Pa}$ ), then not in the water droplets

**BUT** hetero aggregate  $\text{CH}_3\text{I}\text{-H}_2\text{O}$  may influence the photoreactivity of  $\text{CH}_3\text{I}$  in gaseous phase → investigation of the photoreactivity of  $\text{CH}_3\text{I} - \text{H}_2\text{O}$

What about the interaction with iced particles ? (cryogenic experiment is then relevant)

- **Nuclear safety implications :**

$\text{CH}_3\text{I}$  will likely stay in the gas phase but as hetero aggregates with water – that has to be taken into account in the IRSN simulation code

# Acknowledgment



Sophie Sobanska (Thesis supervisor/CNRS)

Joëlle Mascetti Christian Aupetit (Engineer)



Anne Cecile Gregoire (Thesis supervisor)

Laurent Cantrel ( Head of L2EC laboratory)



Florent Louis (Maître de conférences/Lille university)

Sonia Taamali ( Ingenier)



Stéphane Coussan

## Funding Sources

- Institut de radioprotection et de sûreté nucléaire
- Région Nouvelle-Aquitaine
- Centres de calcul de université de Lille



Vibrational Mode	CH <sub>3</sub> I monomer	CH <sub>3</sub> I-H <sub>2</sub> O	Δv	tentative assignments
<b>v<sub>1</sub> CH<sub>3</sub>I</b>	<b>2965</b>	2976	11	CH <sub>3</sub> I
		2968	3	dimer HT
		2965	0	monomer / trimer THT
		2961	-4	dimer HT / dimer HH / trimer THT
		2925		
		2868		
		2855		
		2846		
		2825		
		2819		
<b>v<sub>2</sub> CH<sub>3</sub>I</b>	1246	1257	12	CH <sub>3</sub> I-3H <sub>2</sub> O (1:3a)
	<b>1245</b>	1256	11	CH <sub>3</sub> I-3H <sub>2</sub> O (1:3a)
		1254	9	see text
		1250	5	CH <sub>3</sub> I-2H <sub>2</sub> O (1:2a)
		1248	3	dimer HT / trimer THT / CH <sub>3</sub> I-H <sub>2</sub> O (1:1a)
		1246	1	dimer HT / trimer THT
		1245	0	monomer / dimer HT /
		1243	-2	dimer HH / trimer THT
		1240	-5	CH <sub>3</sub> I
<b>v<sub>6</sub> CH<sub>3</sub>I</b>		909	27	CH <sub>3</sub> I-2H <sub>2</sub> O (1:2a) / CH <sub>3</sub> I-3H <sub>2</sub> O (1:3c)
	<b>882</b>	903	21	CH <sub>3</sub> I-H <sub>2</sub> O (1:1a)
	881	899	17	CH <sub>3</sub> I-2H <sub>2</sub> O (1:2a) / CH <sub>3</sub> I-3H <sub>2</sub> O (1:3a)
		896	14	CH <sub>3</sub> I-3H <sub>2</sub> O (1:3a)
		891	11	CH <sub>3</sub> I-H <sub>2</sub> O (1:1a)
		888	6	see text
		886	4	dimer HT / dimer HH / trimer THT / CH <sub>3</sub> I-3H <sub>2</sub> O (1:3a)
		882	0	monomer / dimer HH
		881	-1	monomer / dimer HH
		879	-2	dimer HH

H <sub>2</sub> O monomer and dimer <sup>29</sup>	H <sub>2</sub> O 4:1000	CH <sub>3</sub> I-H <sub>2</sub> O	Δv	tentative assignments
3776	3777	3777		H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
3757	3756	3756		H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
		3753		H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
		3752	16	see text
		3749	13	see text
3739				H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
3738	3738	3738		H <sub>2</sub> O dimer PA
<b>3736</b>	<b>3736</b>	<b>3736</b>		H <sub>2</sub> O v <sub>3</sub> (nrm)
	3731	3731		H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
3725	3721	3721		H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
		3720	-16	CH <sub>3</sub> I-3H <sub>2</sub> O (1:3c)
3716	3716	3716		H <sub>2</sub> O dimer PD
3711	3711	3711		H <sub>2</sub> O rovibrationnal band v <sub>3</sub>
		3713	-23	CH <sub>3</sub> I-H <sub>2</sub> O (1:1a) / CH <sub>3</sub> I-3H <sub>2</sub> O (1:3c)
3708	3708			H <sub>2</sub> O dimer PD
3670	3670	3670		H <sub>2</sub> O dimer PD / H <sub>2</sub> O rovibrationnal band v <sub>1</sub>
		3662		H <sub>2</sub> O dimer PD
3654	3654	3654		H <sub>2</sub> O dimer PD / H <sub>2</sub> O rovibrationnal band v <sub>1</sub>
	3648	3648		H <sub>2</sub> O dimer PD
	3647	3647		H <sub>2</sub> O dimer PD
		3642	4	see text
	3640	3640		H <sub>2</sub> O dimer PD
<b>3638</b>	<b>3638</b>	<b>3638</b>		H <sub>2</sub> O v <sub>1</sub> (nrm)
3633	3633	3633		H <sub>2</sub> O dimer PA
	3630	3630		H <sub>2</sub> O dimer PD
3628	3628	3628		H <sub>2</sub> O dimer PD
3623				H <sub>2</sub> O rovibrationnal band v <sub>1</sub>
	3617	3617		H <sub>2</sub> O dimer PD
	3612	3612		H <sub>2</sub> O dimer PD
		3609	-29	CH <sub>3</sub> I-H <sub>2</sub> O (1:1a)
3607	3607	3607	-31	H <sub>2</sub> O rovibrationnal band v <sub>1</sub> / see text
		3603	-35	see text
		3582	-56	see text
3574	3576	3574		H <sub>2</sub> O dimer PD
	3567	3567		H <sub>2</sub> O trimer
	3564	3564		H <sub>2</sub> O trimer
	3553	3553	-85	CH <sub>3</sub> I-2H <sub>2</sub> O (1:2a) / CH <sub>3</sub> I-3H <sub>2</sub> O (1:3c)
	3549	3549		H <sub>2</sub> O trimer
	3543	3543		H <sub>2</sub> O trimer
	3528	3528		H <sub>2</sub> O trimer
	3515	3515		H <sub>2</sub> O trimer
		3463	-175	CH <sub>3</sub> I-3H <sub>2</sub> O (1:3a)
	3445	3445		H <sub>2</sub> O tetramer
	3402	3402		H <sub>2</sub> O tetramer
	3392	3392		H <sub>2</sub> O tetramer
	3373	3373		H <sub>2</sub> O tetramer
	3332	3332		H <sub>2</sub> O pentamer
	3325	3325		H <sub>2</sub> O pentamer
	3209	3209		H <sub>2</sub> O High polymer / 2v <sub>2</sub> harmonic