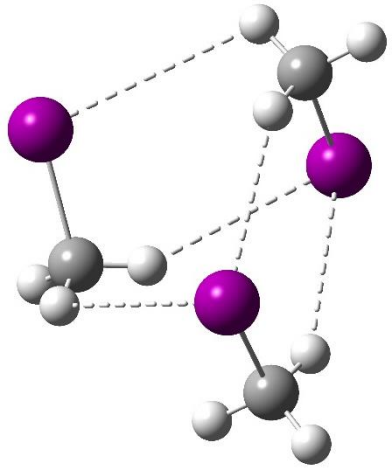
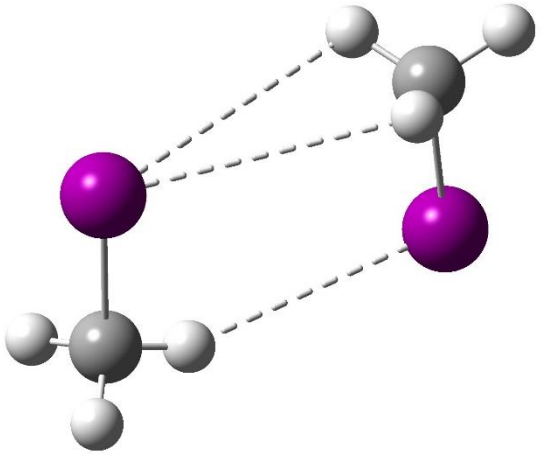
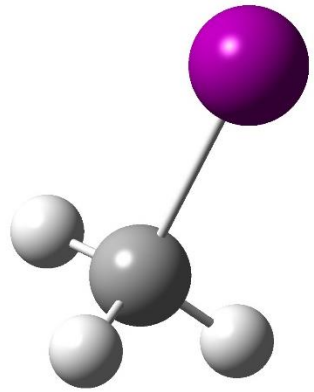
Etude de la photochimie UV de la molécule de CH_3I. Des matrices cryogéniques aux glaces d'eau

S. Coussan, J. Mascetti, S. Sobanska



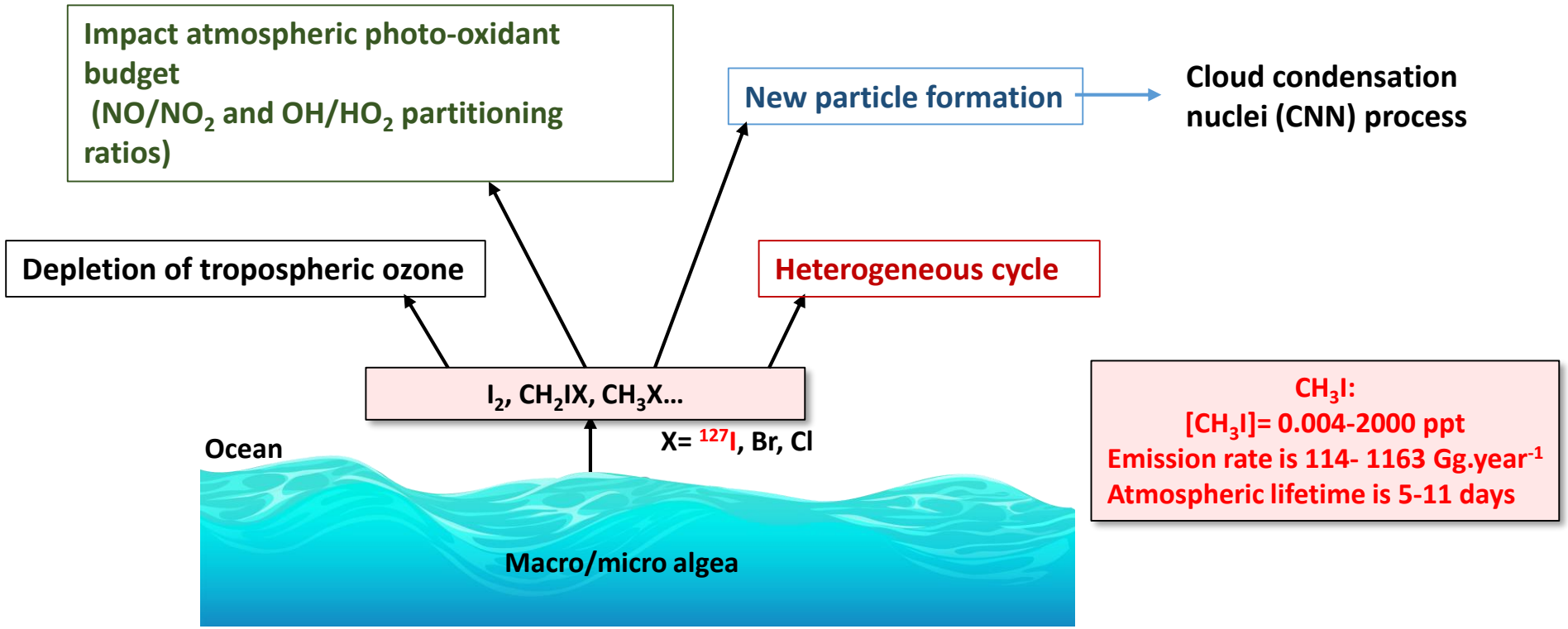




$(CH_3I)_n(H_2O)_m$ trapped in cryogenic matrices / on water ice
Nuclear Risks and Atmospheric Chemistry

S. Sobanska, S. Coussan

Iodine compounds (^{127}I) in the atmosphere



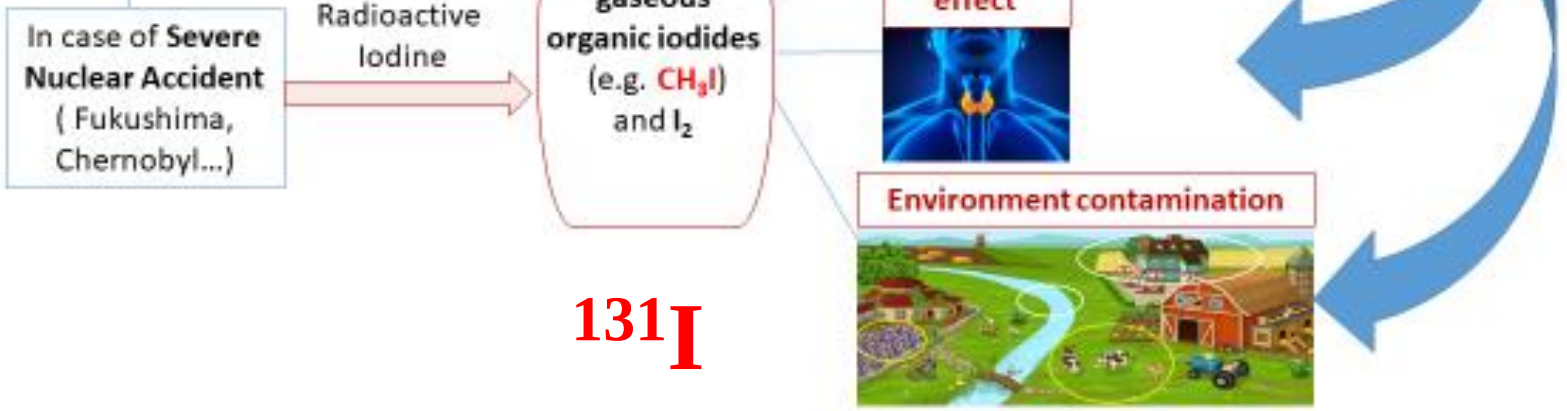
S.Lopez, Chem. Rev. (2012), 1773

$(CH_3I)_n(H_2O)_m$ trapped in cryogenic matrices / on water ice
Nuclear Risks and Atmospheric Chemistry

S. Sobanska, S. Coussan

Fukushima 2011

Tchernobyl 1986

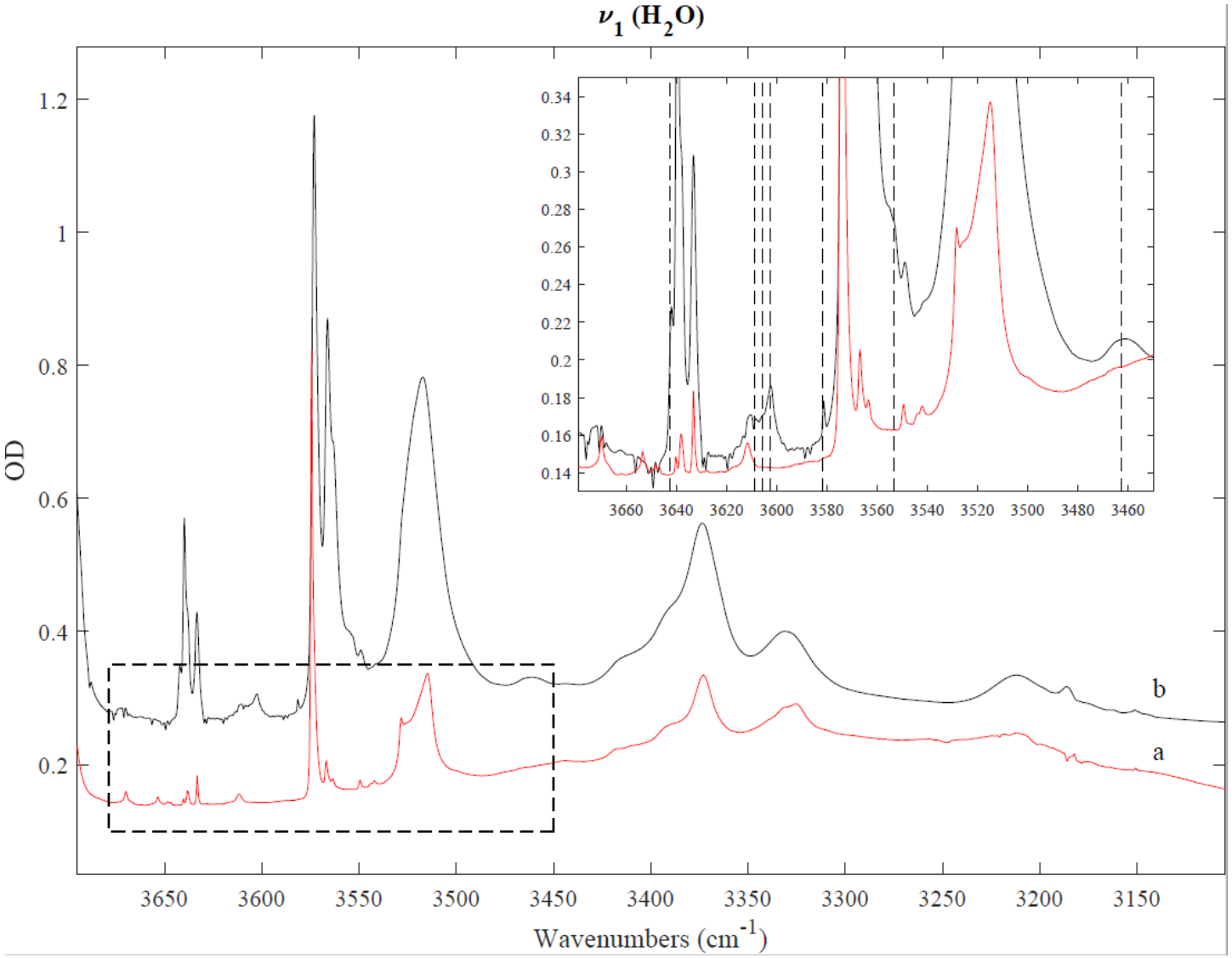


^{131}I

Iodomethane is an **radiotoxic** alkylating agent (which can damage DNA), particularly dangerous for human health.

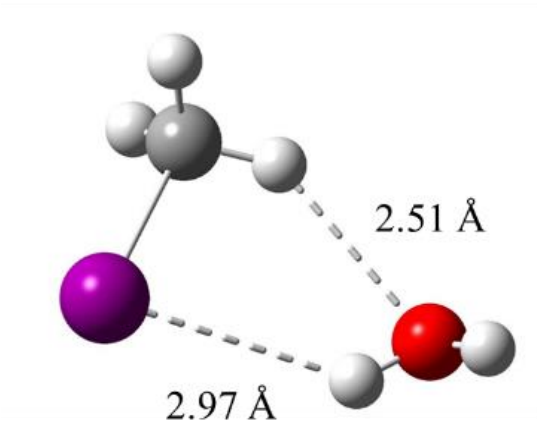
CH_3I-H_2O/Ar

S. Sobanska et al, J. Mol. Struct, 2021, 130342

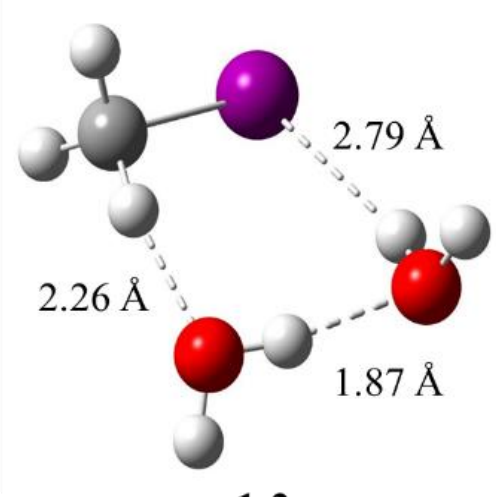


CH_3I-H_2O/Ar

ISM Bordeaux, IRSN CEA Cadarache, PIIM Marseille



1:1a



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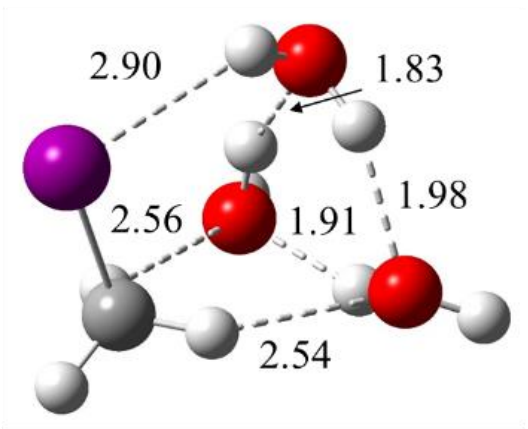
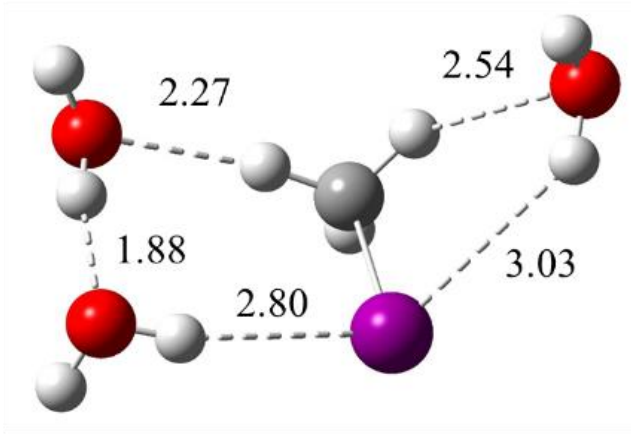


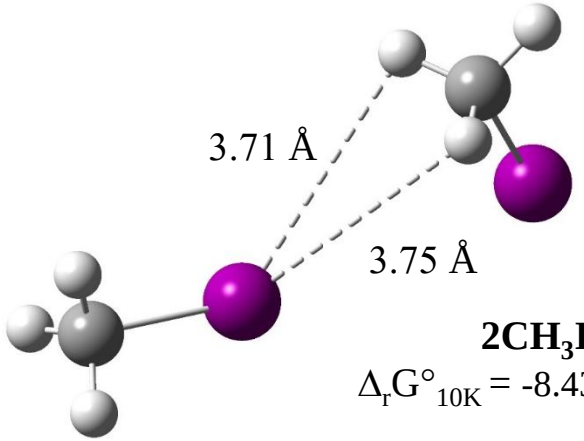
1:3a



1:3c

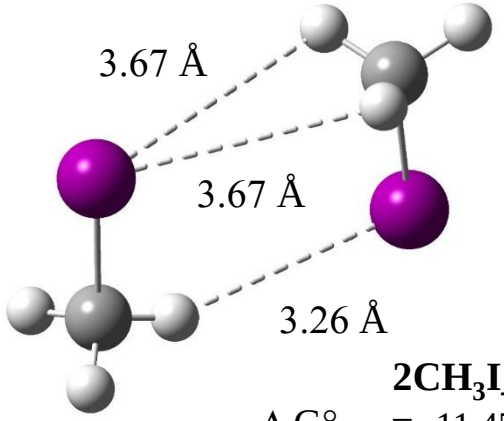
Favors homo-aggregation over hetero-aggregation

$(CH_3I)_n$/Ar



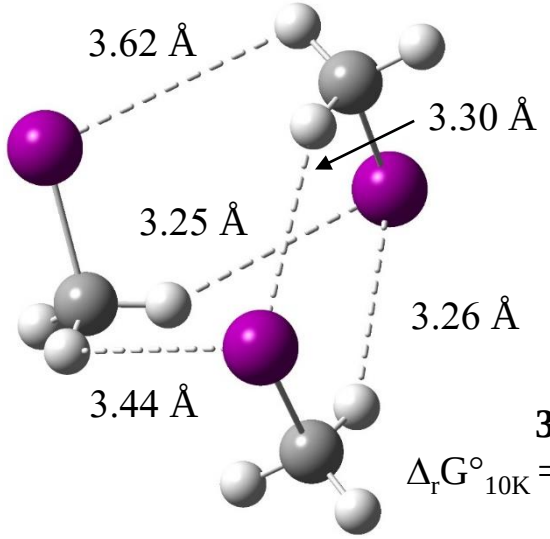
$2CH_3I\_f$

$\Delta_rG°_{10K}$ = -8.43 kJ mol^{-1}



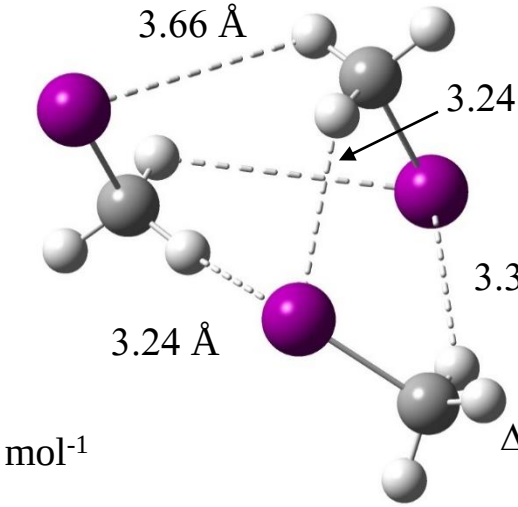
$2CH_3I\_i$

$\Delta_rG°_{10K}$ = -11.45 kJ mol^{-1}



$3CH_3I\_1$

$\Delta_rG°_{10K}$ = -27.73 kJ mol^{-1}



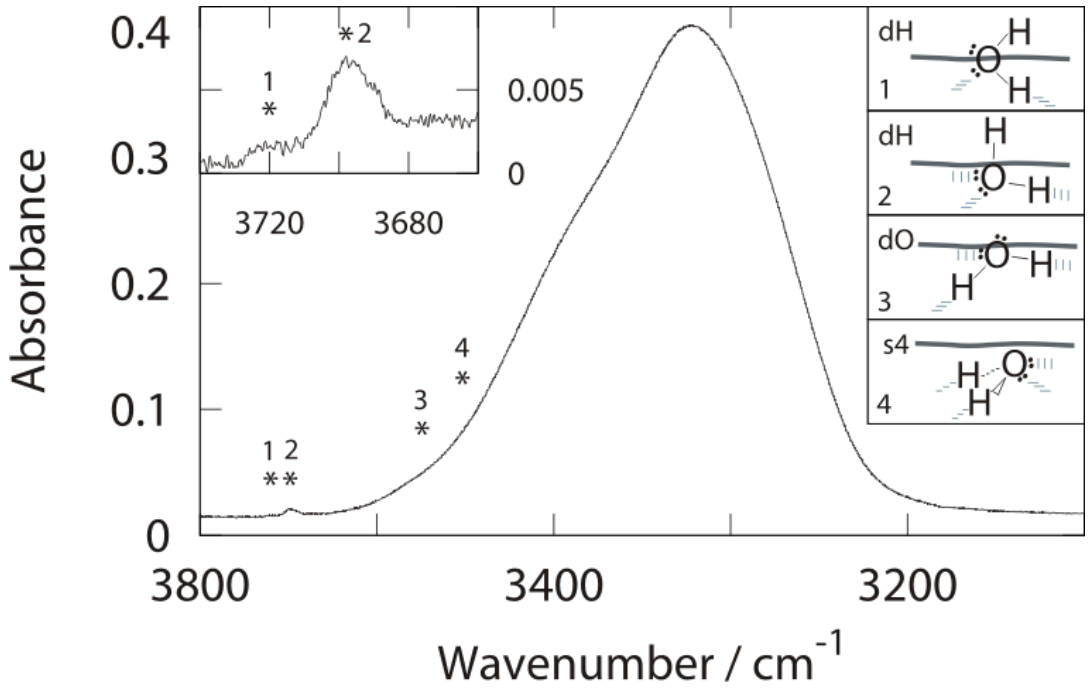
$3CH_3I\_10$

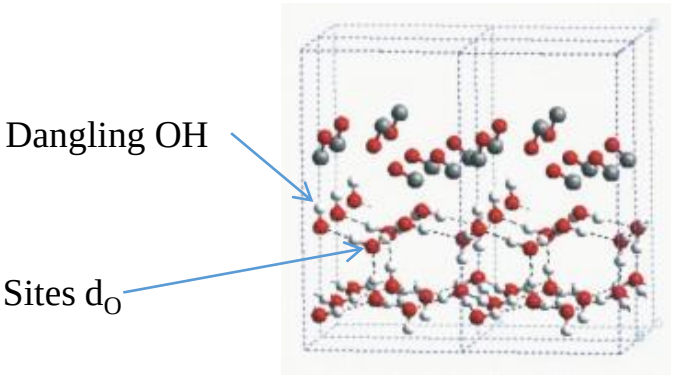
$\Delta_rG°_{10K}$ = -28.28 kJ mol^{-1}

Selectives IR irradiations of Amorphous Solid Water (ASW) – Hydrogen bonded network

- ASW structure changes upon IR irradiation
- Comparison with a global ice warming
- Flip of the surface OH bonds, what about surface reactivity?
- Are those changes irreversible ?
- Vibrational relaxation through OH network ?

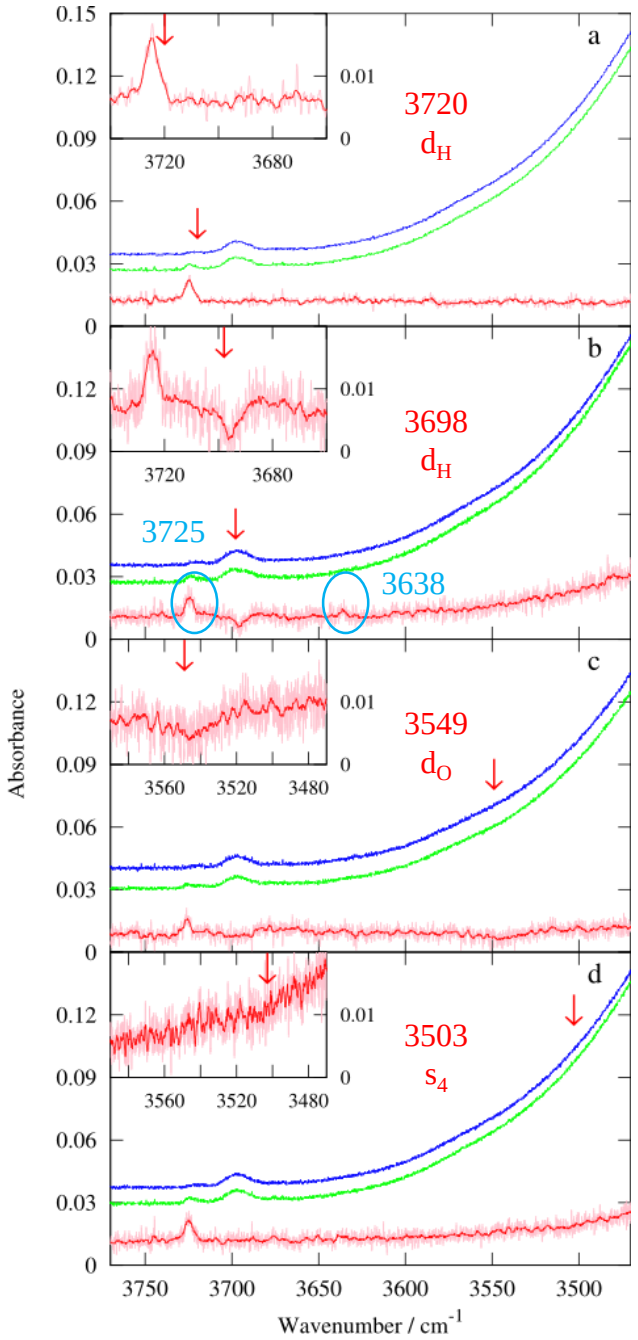
-Vaccuum 10^{-7} mbar
- Beam line dry air purged
- Sample T 3.7 K
- OPO 10 Hz
- Injection through solenoid valve.





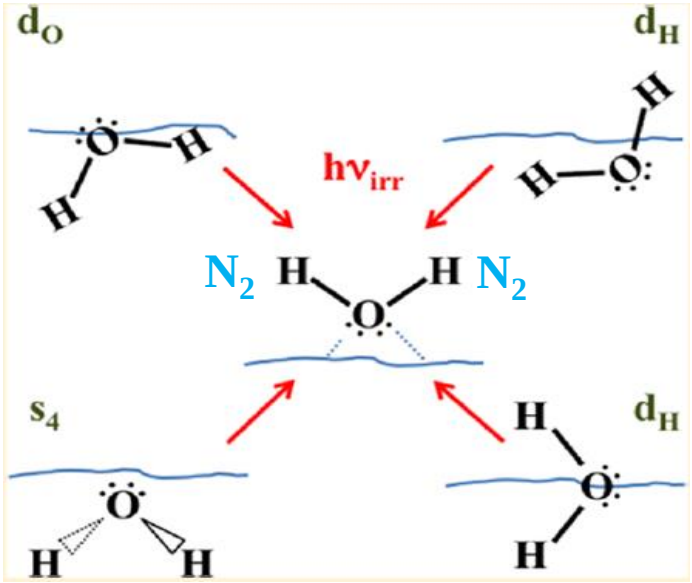
ASW deposited at 50 K and cooled down to 4 K. A QMS is controlling the composition of the remaining vaccum during the experiment.

Photoinduced effects

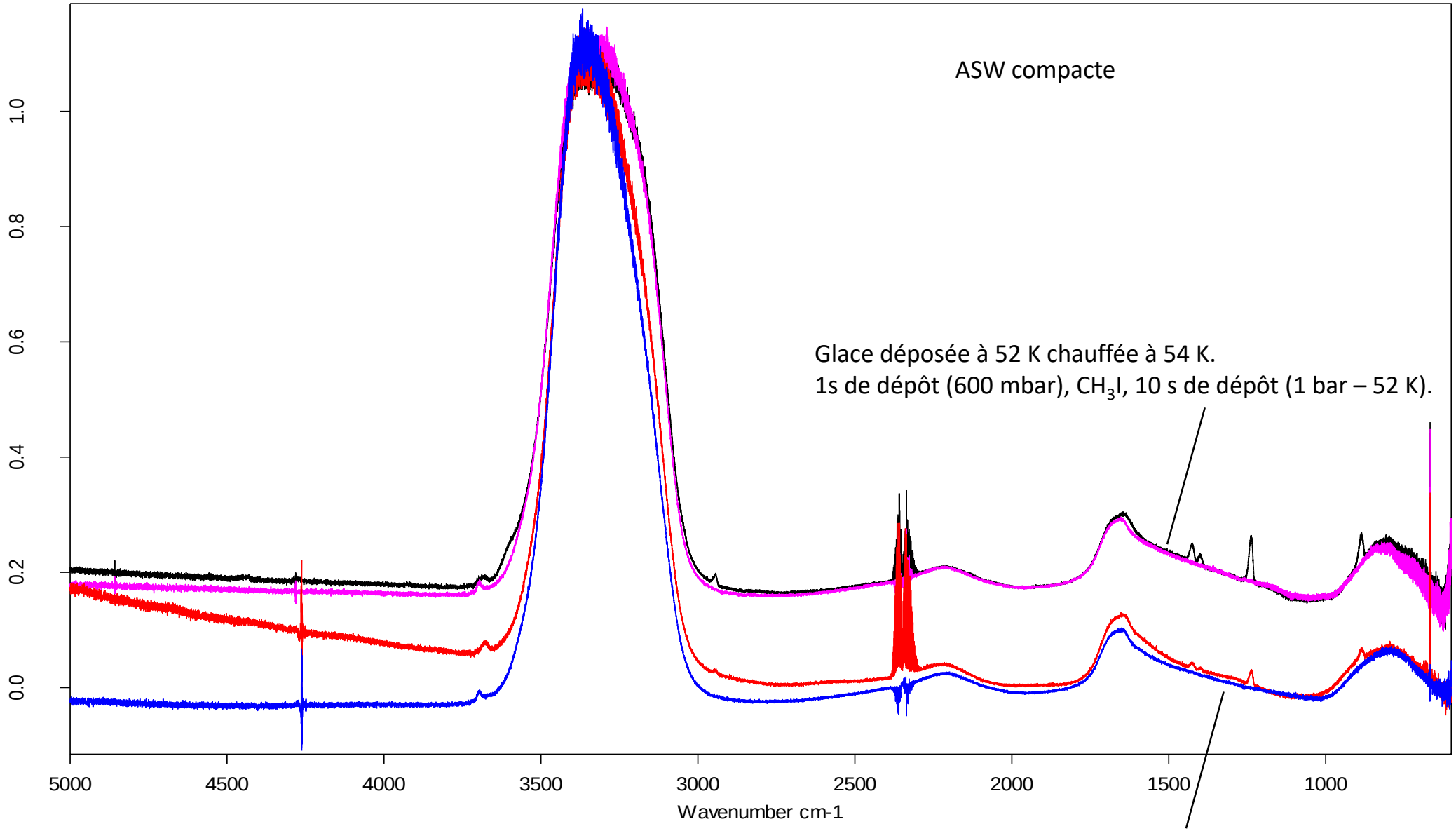


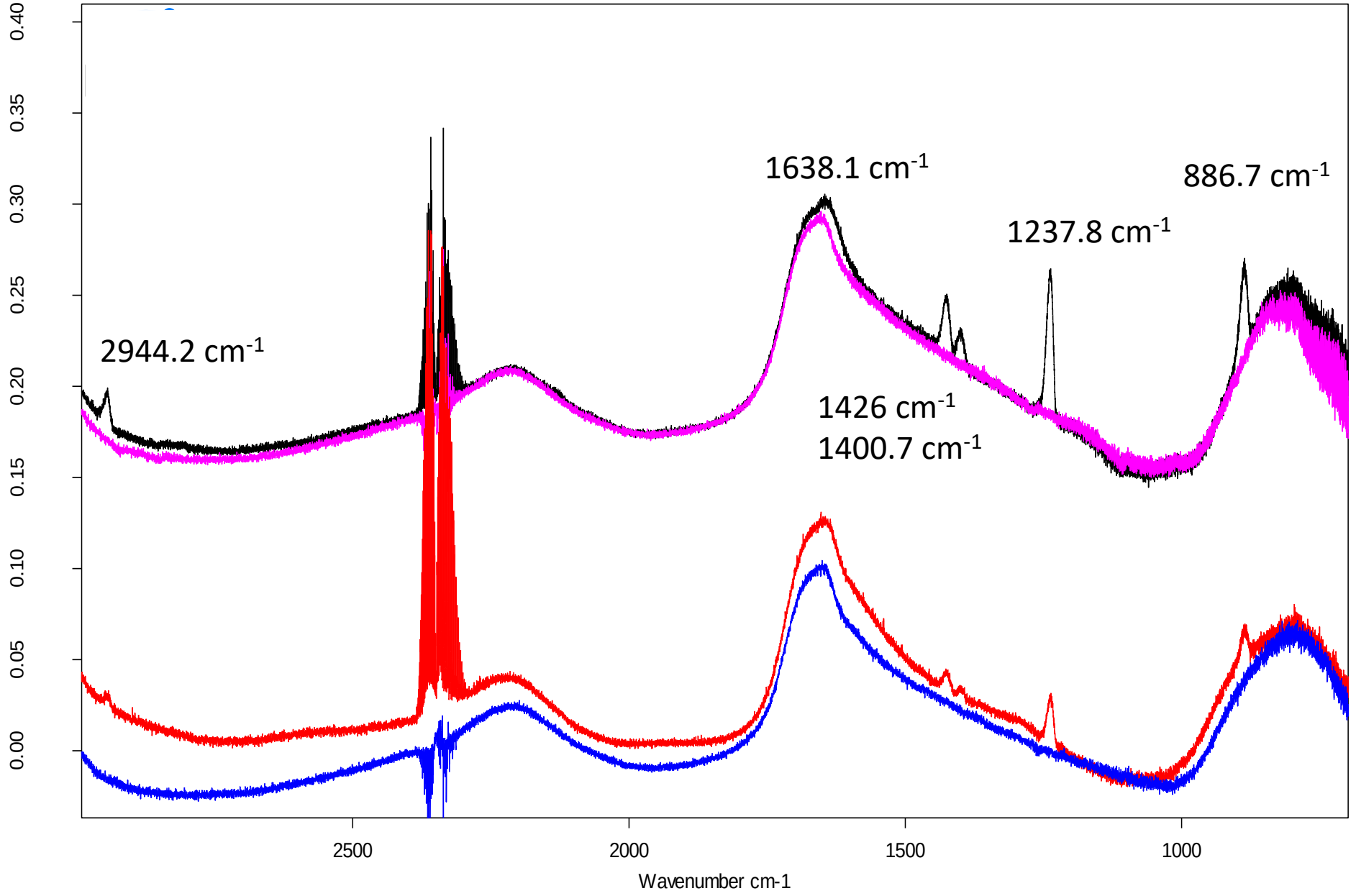
Vibrational mode	Calculated[a] (gas phase)	Observed gas phase[b]	Observed N_2 matrix[c]	Observed H_2O-N_2 complex[a]	Present work
ν_3	3924	3943	3728	3730	3725
ν_1	3822	3832	3635	3640	3638
$\Delta_\nu = \nu_3 - \nu_1$	102	111	93	90	87

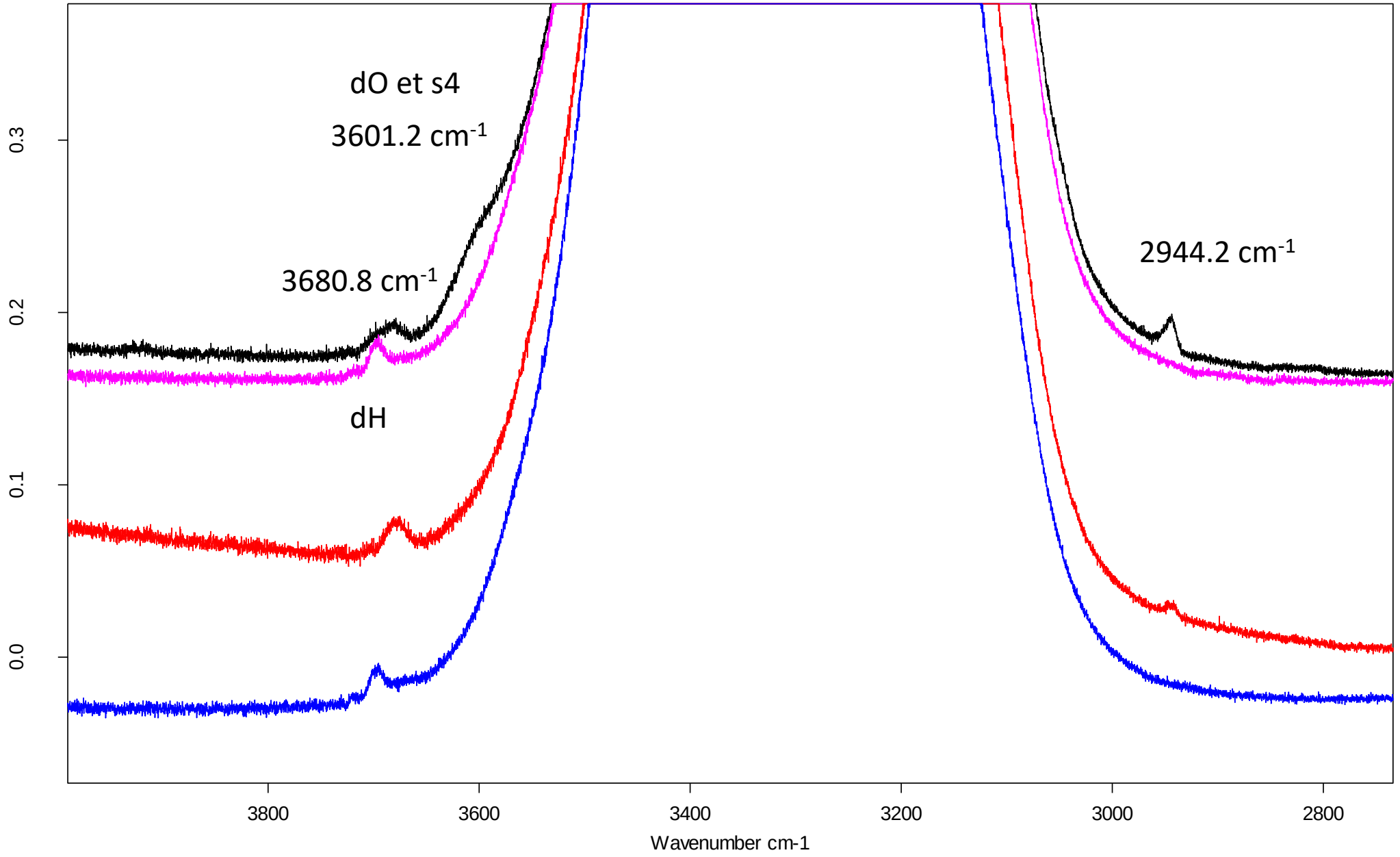
[22] Coussan, S., Loutellier, A., Perchard, J. P., Racine, S., Bouteiller, Y., 1998, J. Molecular Structure, 471, 37
[23] Benedict, W. S., Gaillard, N., Plyler, E. K. 1956, J. Chemical Physics, 24, 1139
[24] Coussan, S., Roubin, P., Perchard, J. P. 2006, Chemical Physics, 324, 527



J. A. Noble, C. Martin, H. J. Fraser, P. Roubin, S. Coussan, J. Phys. Chem. C, 2014, 118, 20488-20495.

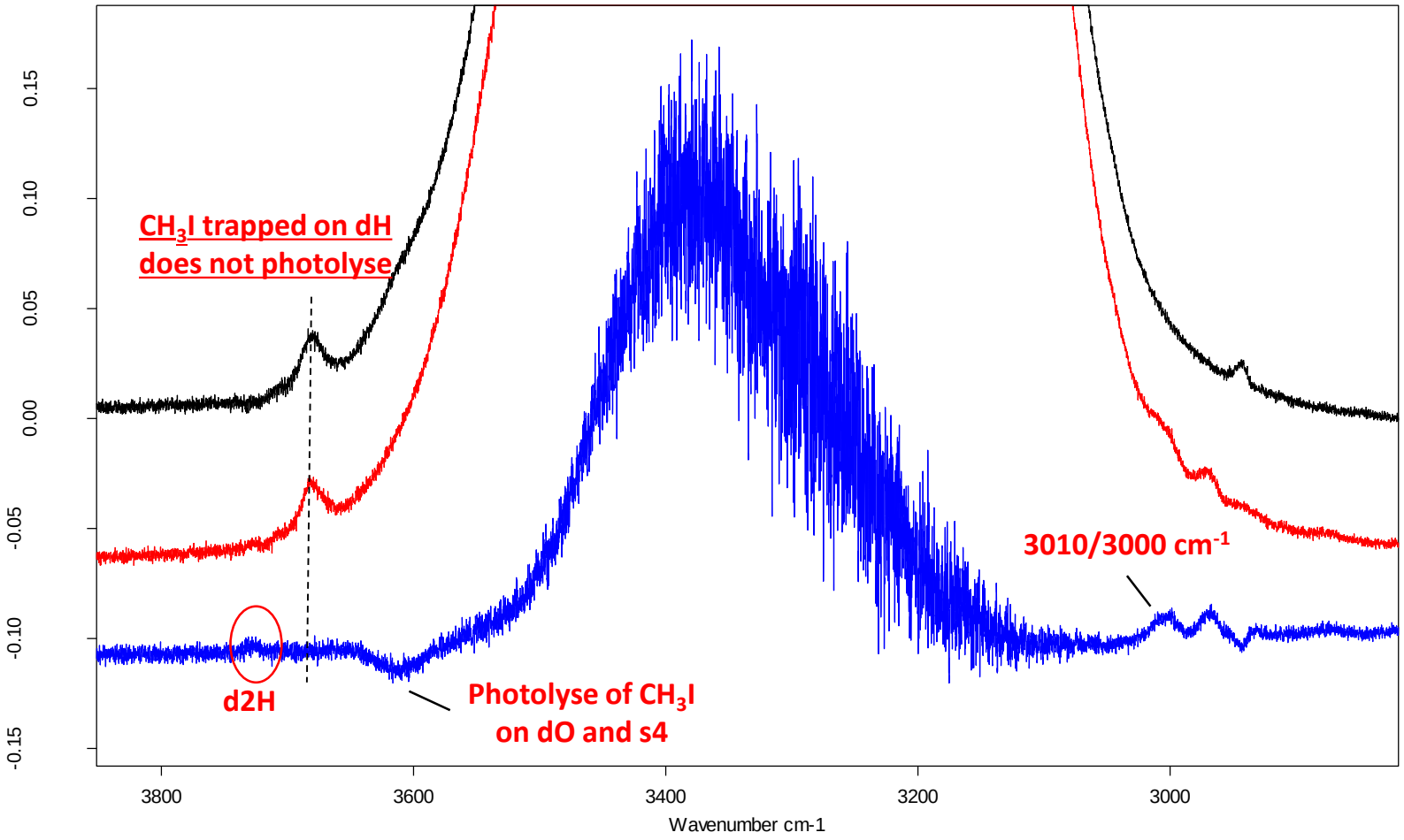

ASW compacte
Glace déposée à 52 K chauffée à 54 K.
1s de dépôt (600 mbar), CH_3I, 10 s de dépôt (1 bar – 52 K).
Glace déposée à 52 K chauffée à 54 K.
1s de dépôt (600 mbar), CH_3I, 500 ms de dépôt (1 bar – 45 K).
0.0
0.2
0.4
0.6
0.8
1.0
5000
4500
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
2944.2 cm-1
1638.1 cm-1
1237.8 cm-1
886.7 cm-1
1426 cm-1
1400.7 cm-1
2500
2000
1500
1000
Wavenumber cm-1


dO et s4
3601.2 cm-1
3680.8 cm-1
dH
2944.2 cm-1
0.0
0.1
0.2
0.3
3800
3600
3400
3200
3000
2800
Wavenumber cm-1

CH_3I on Amorphous Solid Water (ASW)

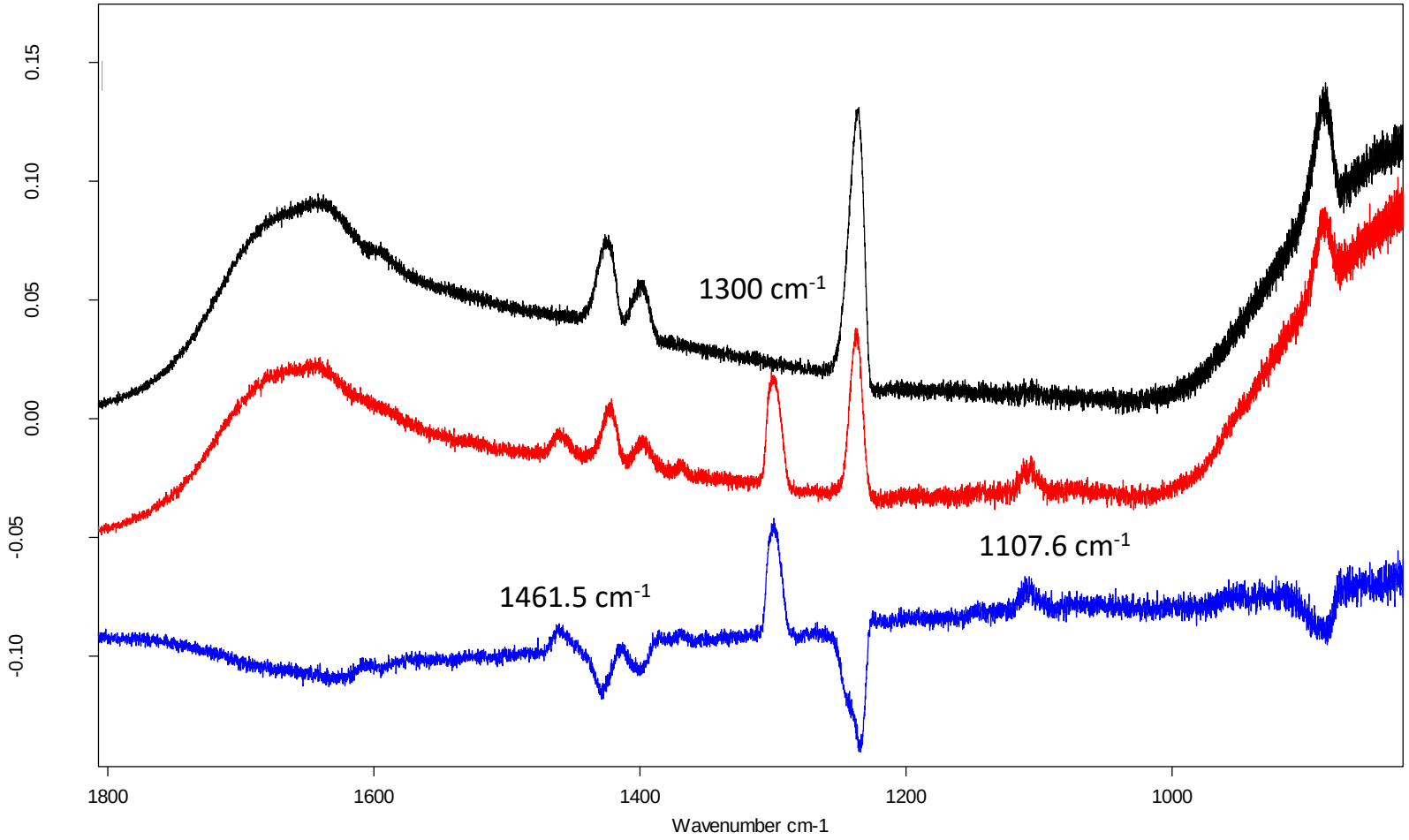
Dr. Sophie Sobanska and Dr. Joëlle Mascetti

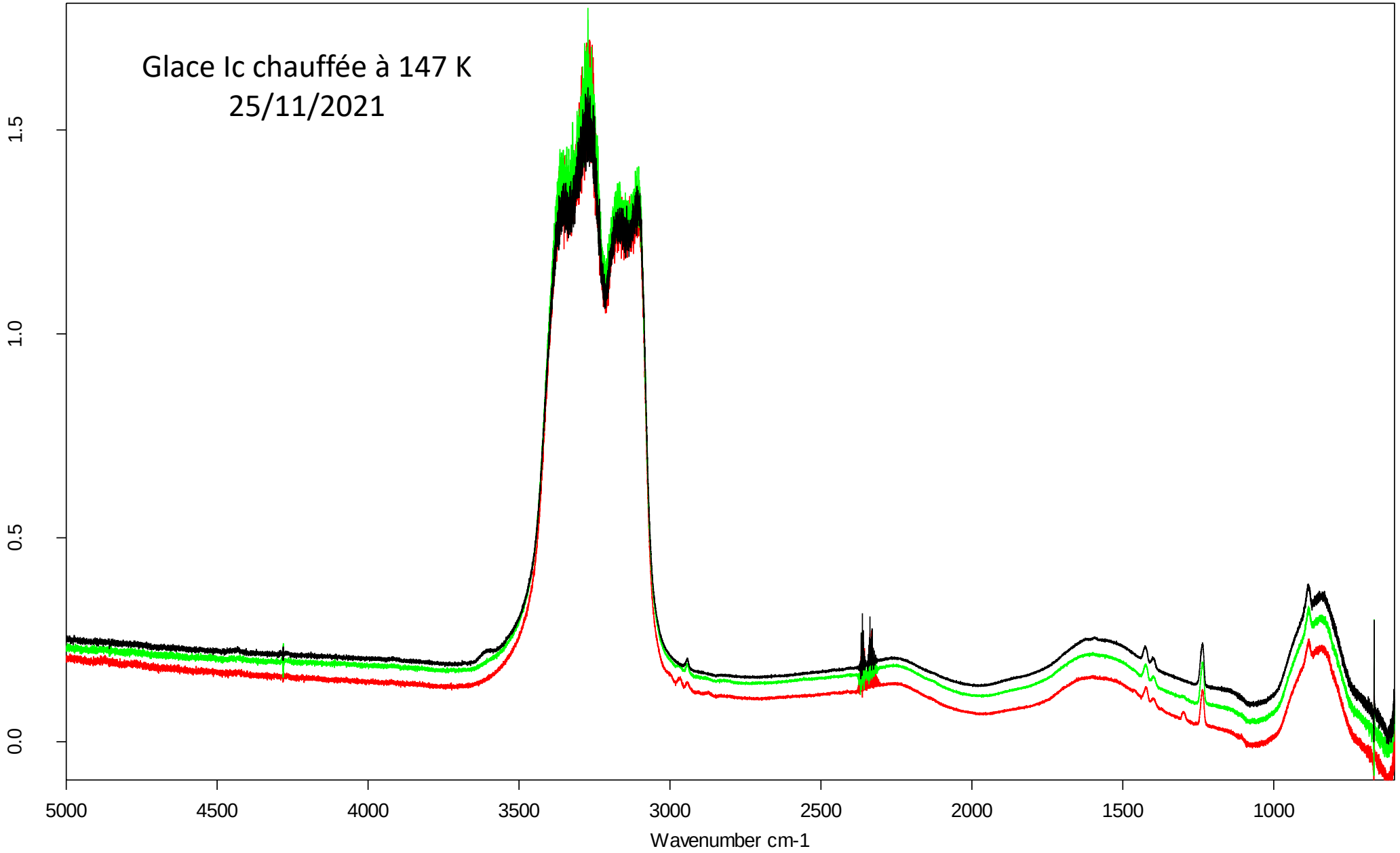


CH_3I dissociation upon broad band UV irradiation

CH_3I on Amorphous Solid Water (ASW)

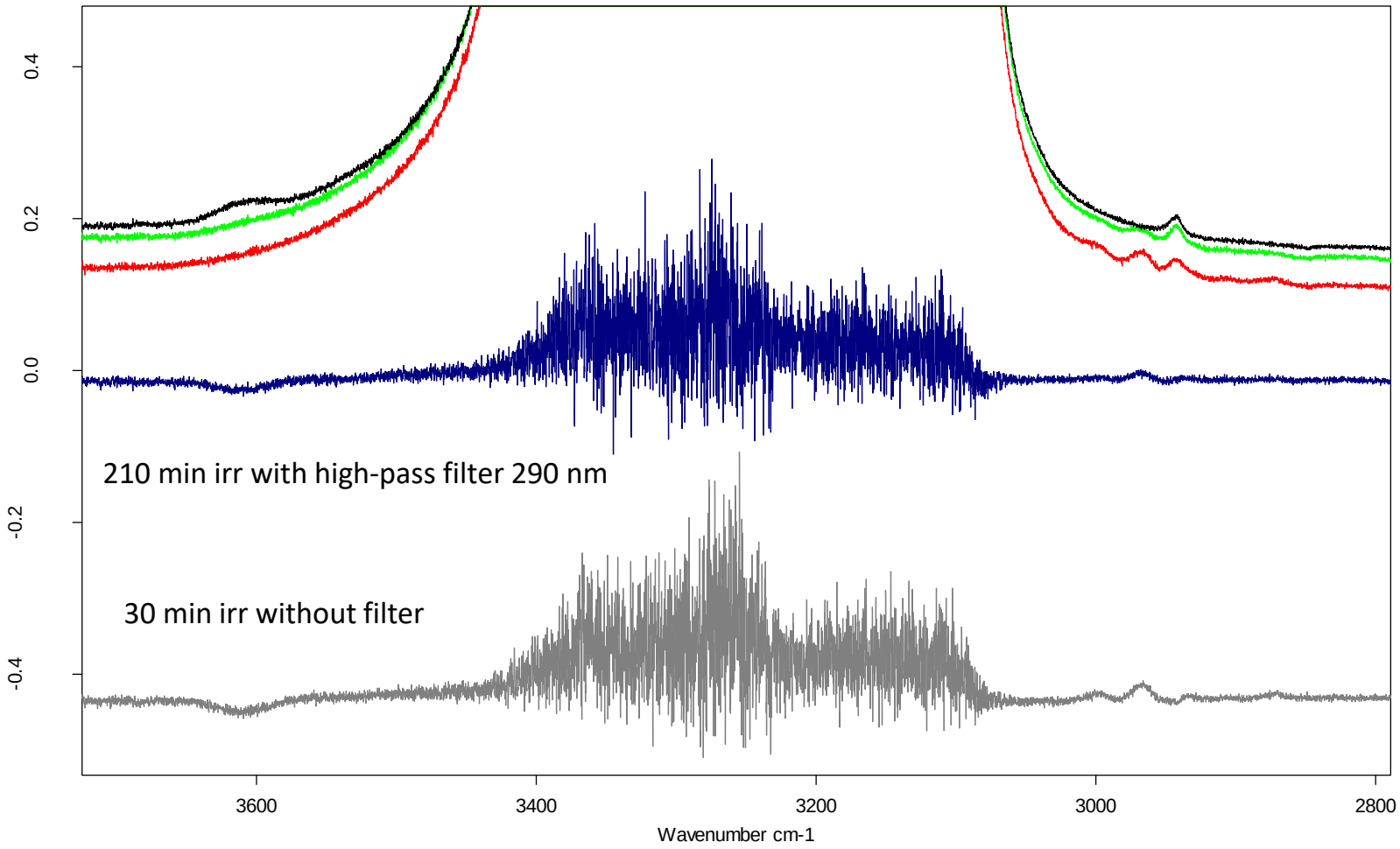
Dr. Sophie Sobanska and Dr. Joëlle Mascetti




Glace Ic chauffée à 147 K
25/11/2021
0.0
0.5
1.0
1.5
5000
4500
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

CH_3I on Cubic Solid Water (Ic)

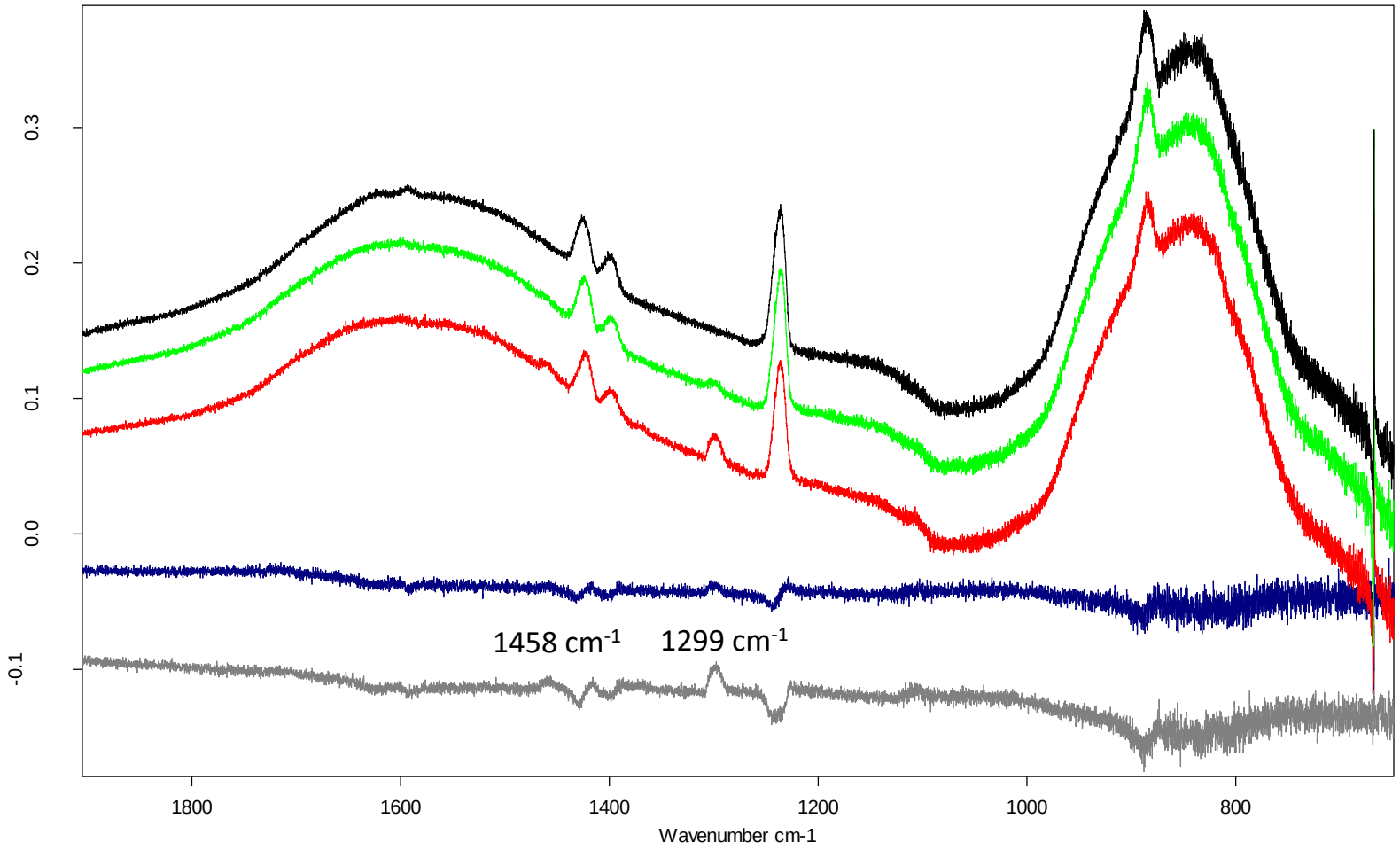
Dr. Sophie Sobanska and Dr. Joëlle Mascetti



CH_3I dissociation upon broad band UV irradiation

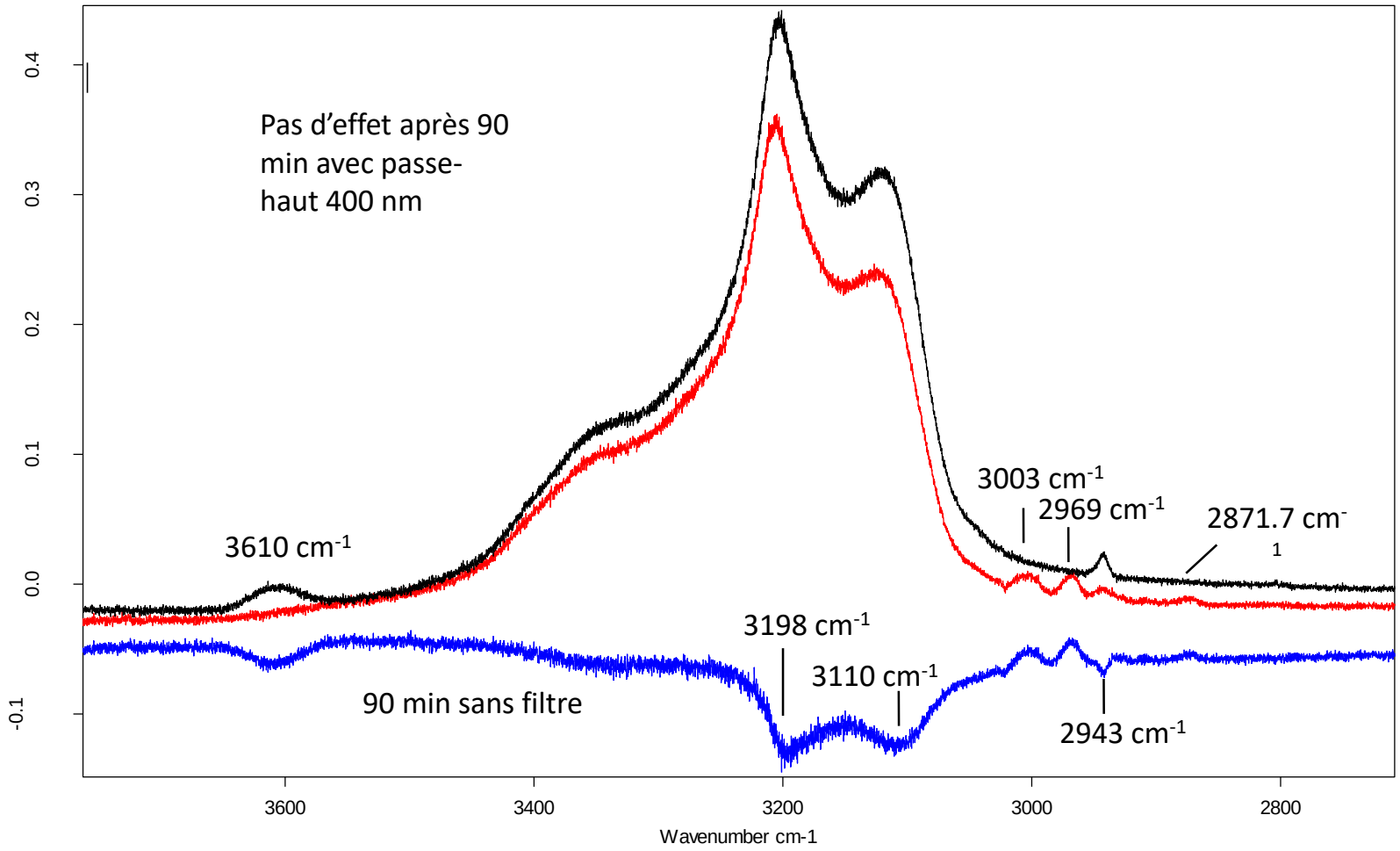
CH_3I on Cubic Solid Water (Ic)

Dr. Sophie Sobanska and Dr. Joëlle Mascetti



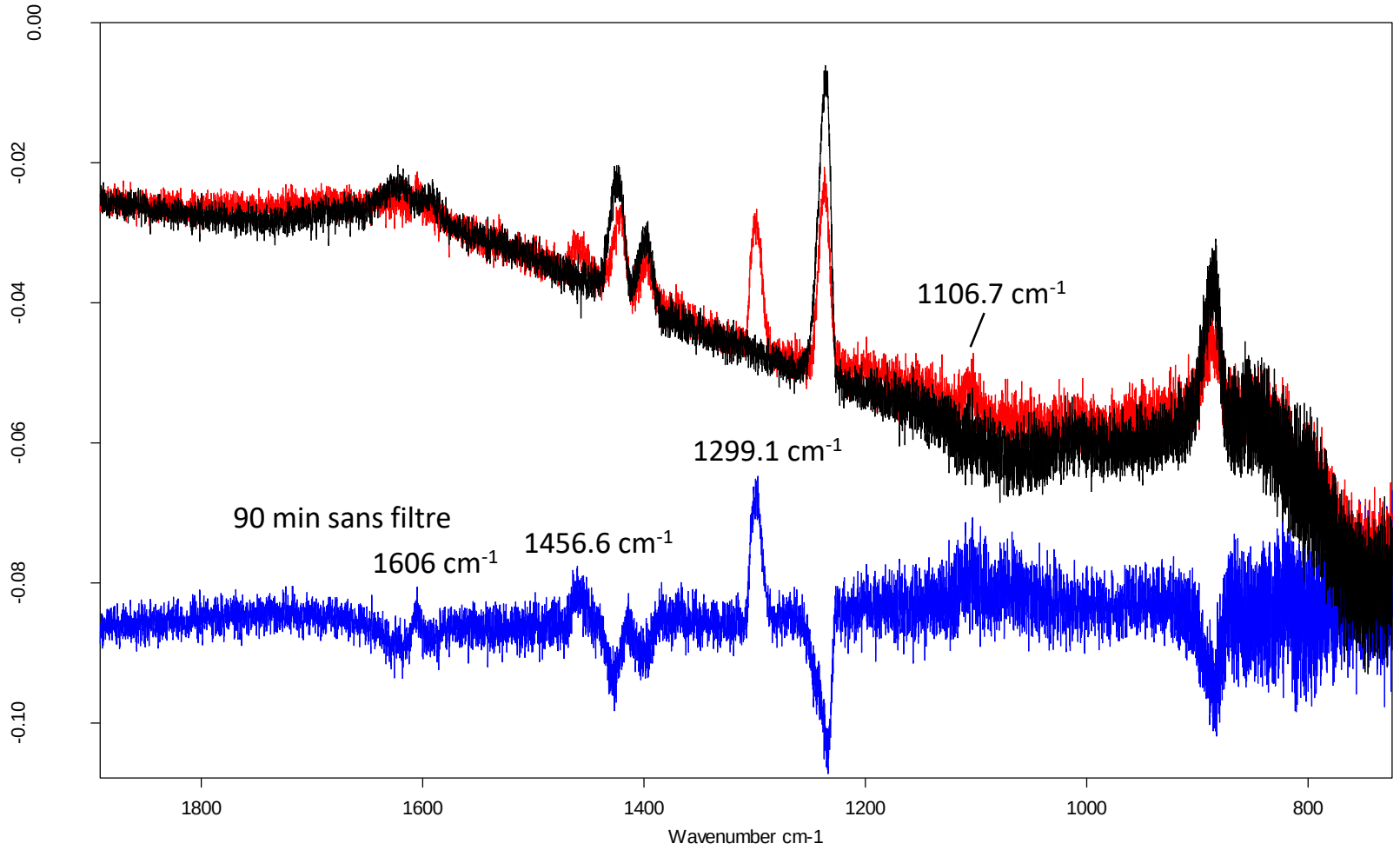
CH_3I on Hexagonal Solid Water (Ih)

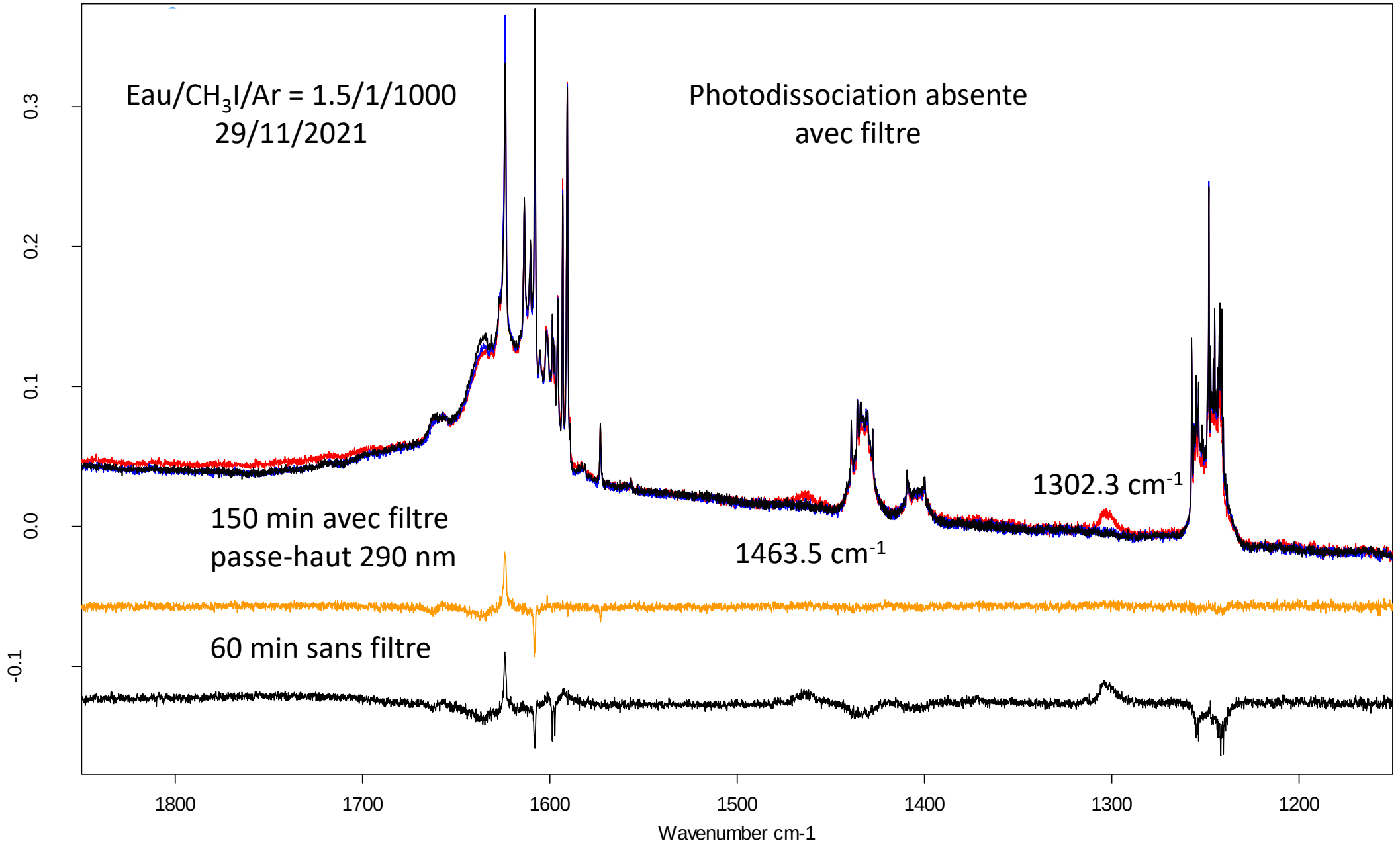
Dr. Sophie Sobanska and Dr. Joëlle Mascetti

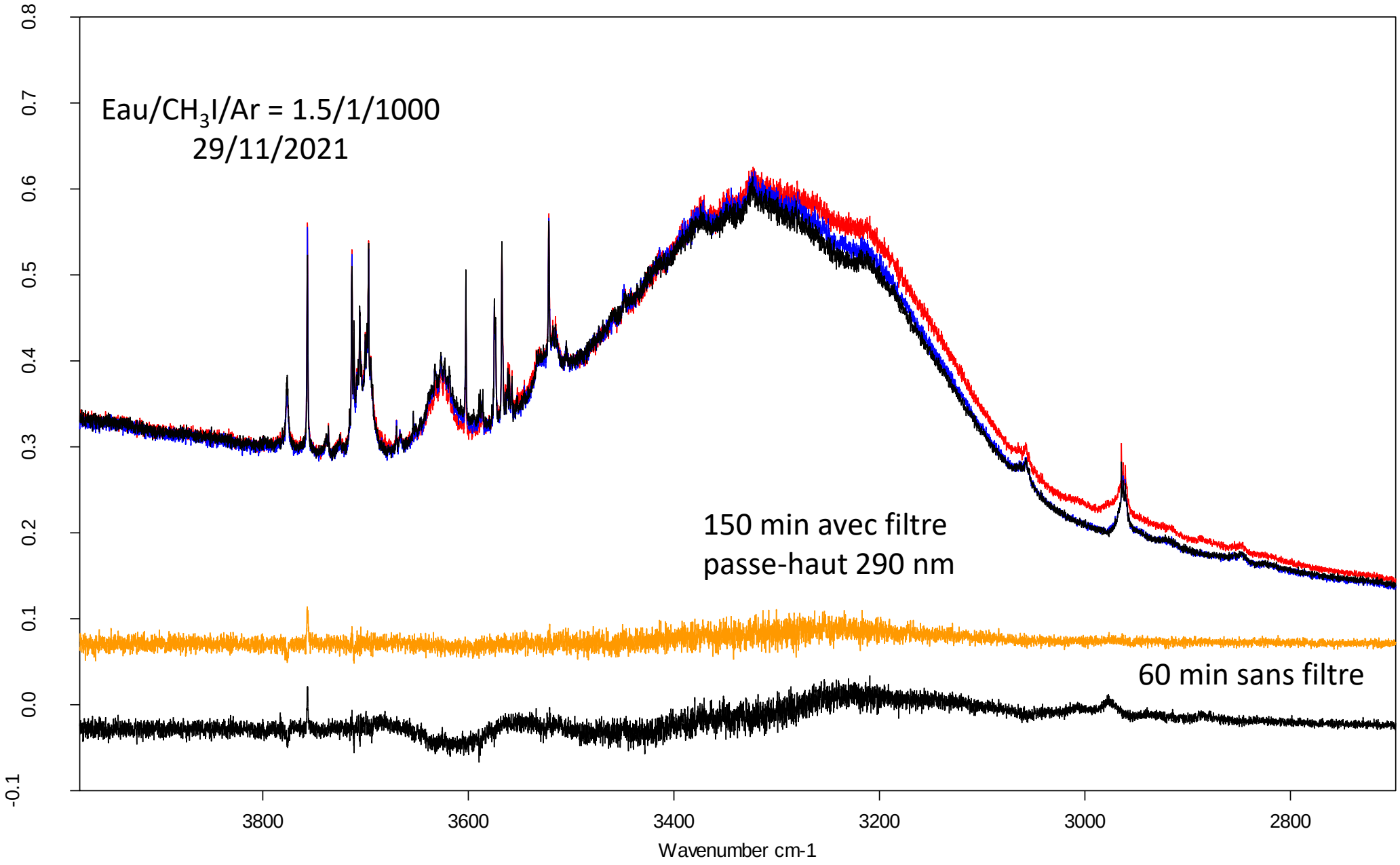


CH_3I on Hexagonal Solid Water (Ih)

Dr. Sophie Sobanska and Dr. Joëlle Mascetti




Eau/CH3I/Ar = 1.5/1/1000
29/11/2021
Photodissociation absente
avec filtre
1302.3 cm-1
150 min avec filtre
passe-haut 290 nm
1463.5 cm-1
60 min sans filtre
0.3
0.2
0.1
0.0
-0.1
1800
1700
1600
1500
1400
1300
1200
Wavenumber cm-1


Eau/CH3I/Ar = 1.5/1/1000
29/11/2021
150 min avec filtre
passe-haut 290 nm
60 min sans filtre
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
3800
3600
3400
3200
3000
2800
Wavenumber cm-1

Conclusions

- Whatever the medium : ASW, Ic, Ih water ices or cryogenic matrices, upon UV broad band or high-pass filtered UV light, CH_3I fragments.
- The fragmentation is directly related to the nature of interaction :
  - If CH_3I is trapped on dH bonds, no fragmentation
  - If CH_3I is trapped on dO or s4 bonds, fragmentation
- ASW, Ic or Ih, do not catalyse fragmentation (the fragmentation rate is the same whatever the ice)