ACTION SPECTROSCOPIC STUDY OF $(H_2O\text{-}X)^+$ COMPLEXES IN THE OVERTONE RANGE

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LOUVAIN-LA-NEUVE

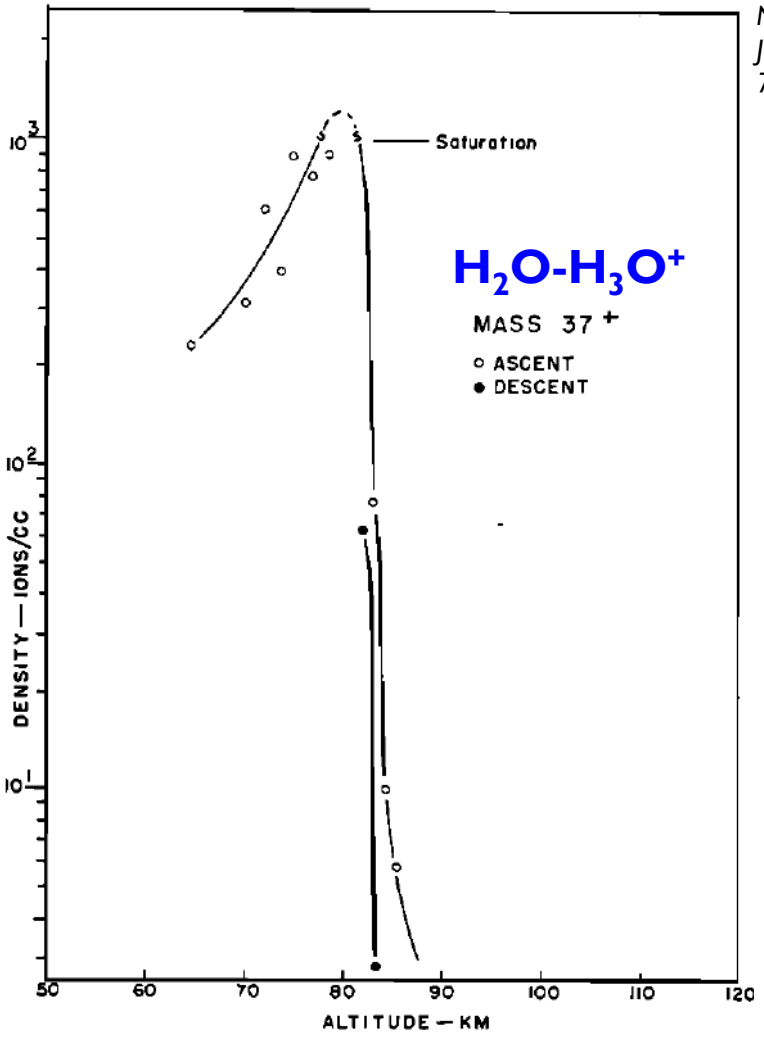
CONGRES GENERAL

150 ANS SOCIETE FRANCAISE DE PHYSIQUE

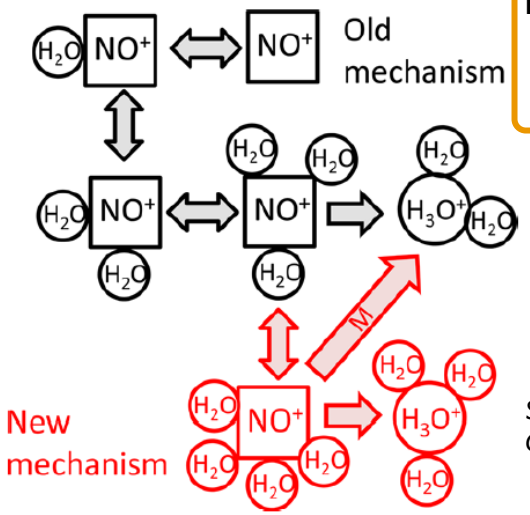
04 JULY 2023

UCLouvain

CHARGED COMPLEXES OF H_2O



Narcisi, R. S., & Bailey, A. D. (1965). Journal of Geophysical Research, 70(15), 3687-3700.



Atmospheric Ion Chemistry

1963 : first positive ion measurements at altitudes from 64 to 84 km

- Detection of the H_2O-H_3O^+ complex
- In fact, ionic water cluster $(H_2O)_n$-H_3O^+ are dominant in this region

How these water cluster are formed and especially H_3O^+ ?

- Charge transfer in positive H_2O complexes

$$O_2^+(H_2O) + H_2O \rightarrow H_3O^+(OH) + O_2$$

Shuman, N. S., Hunton, D. E., & Viggiano, A. A. (2015) Chemical reviews, 115(10), 4542-4570.

COMPLEXATION OF THE H_2O CATION

Neutral complexes → **Cationic complexes**

Already existing in the laboratory

Experimental setup dedicated to high resolution spectroscopy of neutral complexes

- Ro-vibrational spectroscopy
- Comparison with charged complexes…

RESEARCH ARTICLE | JUNE 08 2023

Understanding the high-resolution spectral signature of the N_2–H_2O van der Waals complex in the 2OH stretch region

R. Glorieux ; B. M. Hays ; A. S. Bogomolov ; M. Herman ; T. Vanfleteren ; N. Moazzen-Ahmadi ; C. Lauzin

+ Author & Article Information

J. Chem. Phys. 158, 224302 (2023)

https://doi.org/10.1063/5.0150823 **Article history**

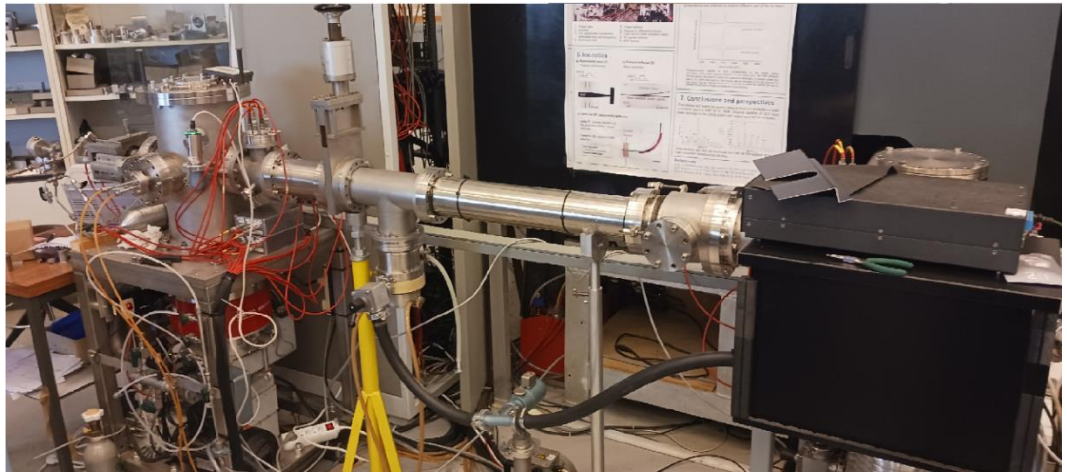
Existing but to be adapted

Stargate setup : UV photo-dissociation spectroscopy

- Ro-vibronic spectroscopy of N_2O^+
- Towards ro-vibrational spectroscopy !

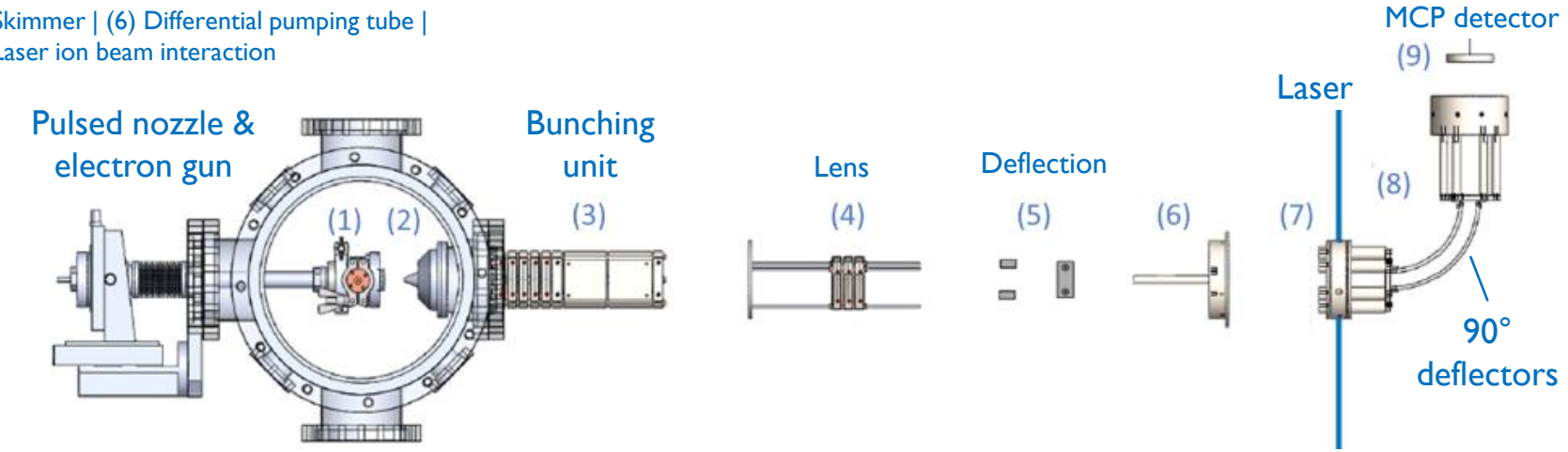
STARGATE

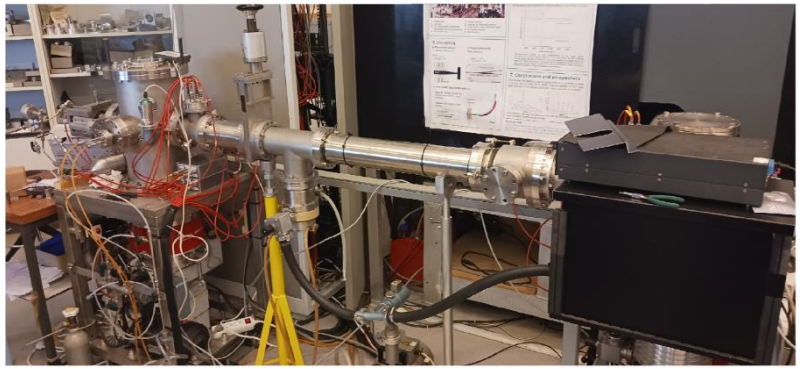
Spectroscopy of **T**ransient **A**nions and **R**adicals by **G**ated and **A**ccelerated **T**ime-of-flight **E**xperiment



EXPERIMENTAL SETUP : STARGATE

(2) Skimmer | (6) Differential pumping tube |
(7) Laser ion beam interaction





STARGATE = 3 parts

1) Production of ionic complexes

OH^+ $X_2\text{-}H_2O^+$ $X\text{-}H_2O^+$ H_2O^+ X^+ X_2^+ H_3O^+

X = Ar, N_2O, CO_2, …

2) Mass selection of the complexes

~~$X_2\text{-}H_2O^+$~~ ~~X^+~~ ~~H_2O^+~~ ~~X_2^+~~ ~~OH^+~~ ~~H_3O^+~~

$X\text{-}H_2O^+$

3) Photo-dissociation spectroscopy

$$[X\text{-}H_2O]^+ \xrightarrow{h\upsilon} [X\text{-}H_2O]^{*+} \longrightarrow X + H_2O^+$$

EXPERIMENTAL SETUP : STARGATE

(2) Skimmer | (6) Differential pumping tube |
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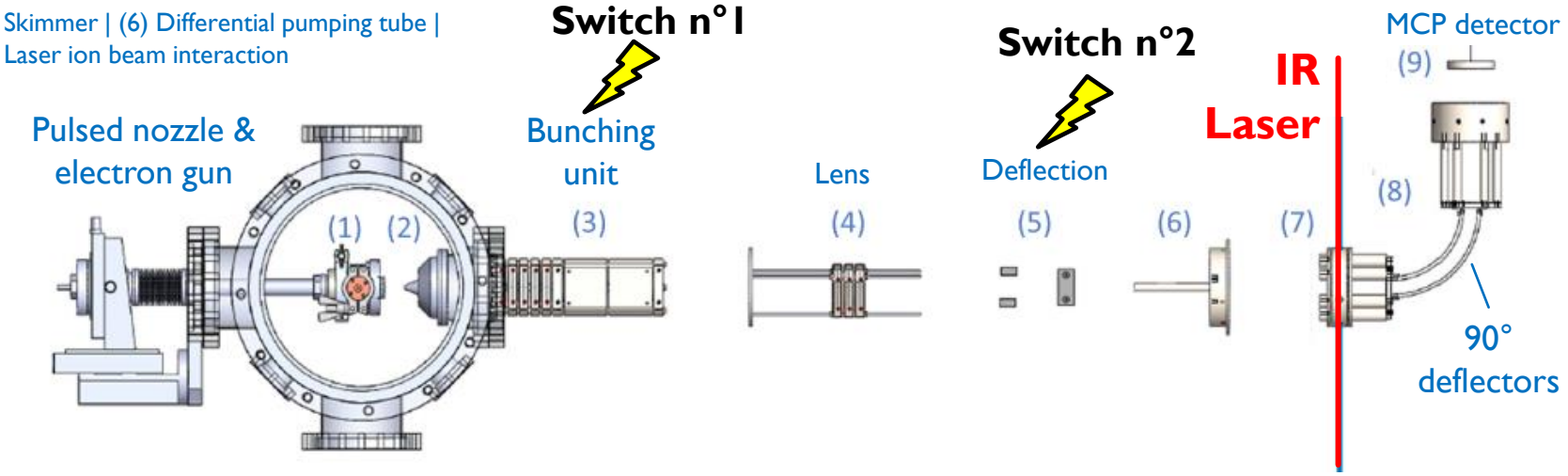
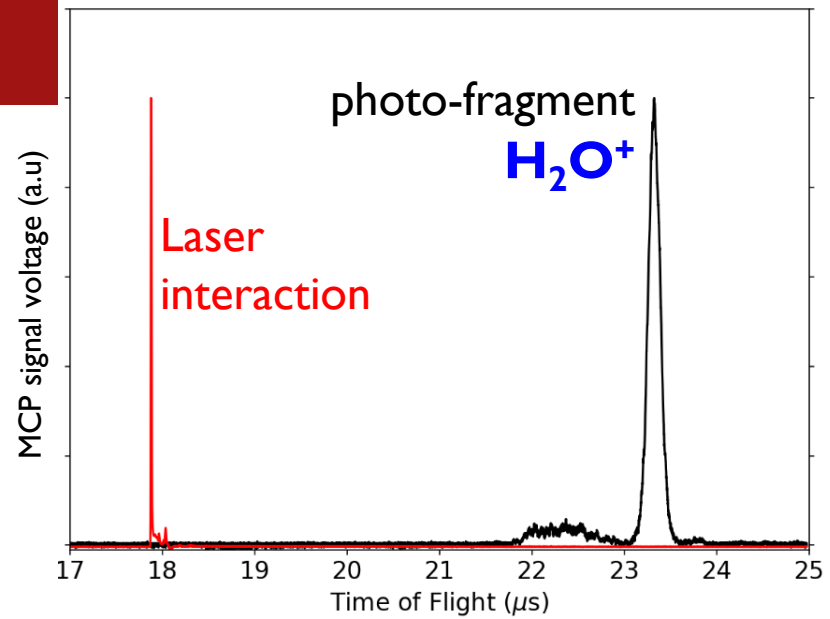
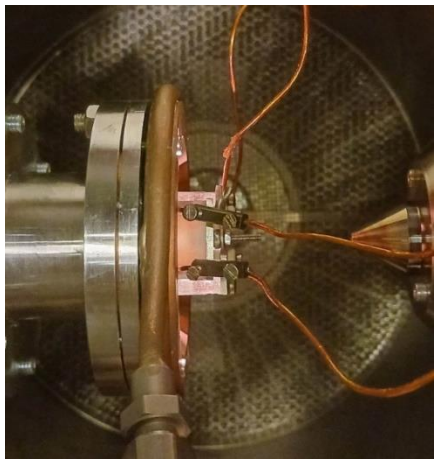




1) Production of ionic complexes

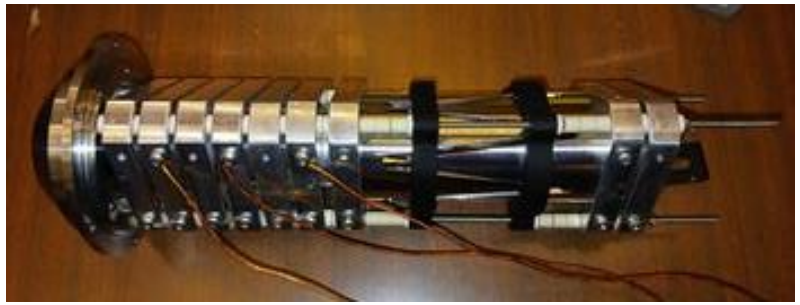
Pulsed supersonic expansion
+
Electron gun



Homemade pulsed valve

2) Mass selection of the complexes

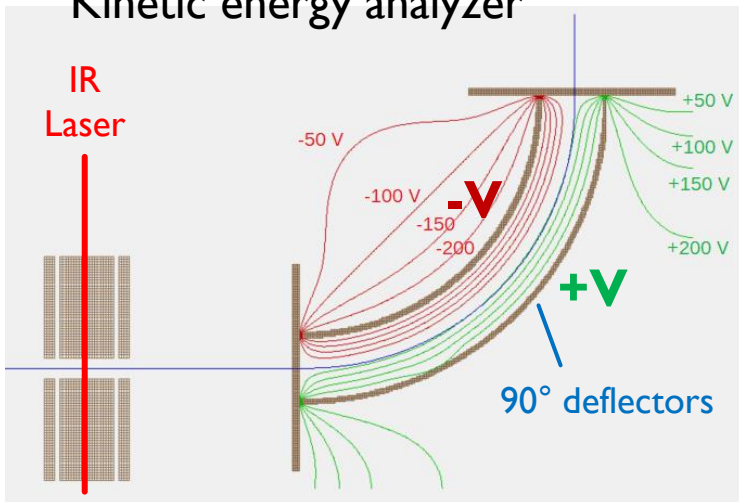
Time of Flight Mass-Spectrometry (ToF-MS)



Bunching unit

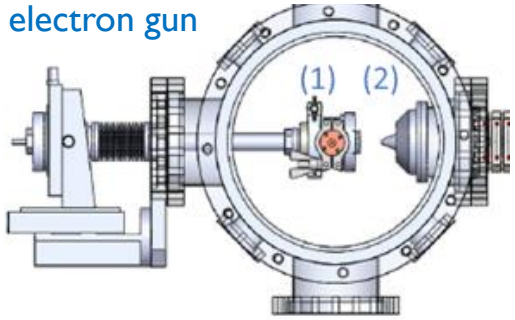
3) Photo-dissociation spectroscopy

Kinetic energy analyzer

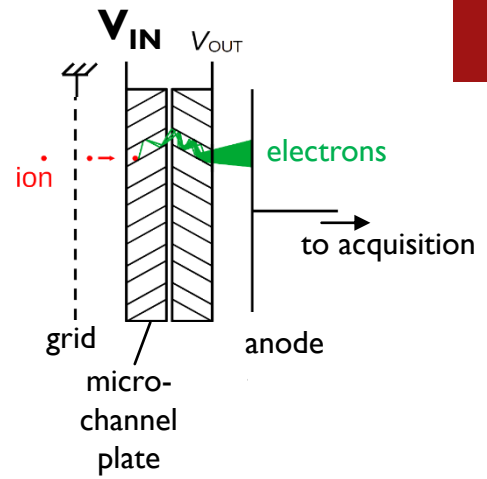


COMPLEXES PRODUCTION OPTIMIZATION

Pulsed nozzle &
electron gun



- Detection of complexes up to 900 amu
- But formation of H_2O complexes with hundred of molecules is expected
  - ➢ Bias due to the detection



1) Production of ionic complexes

Pulsed supersonic
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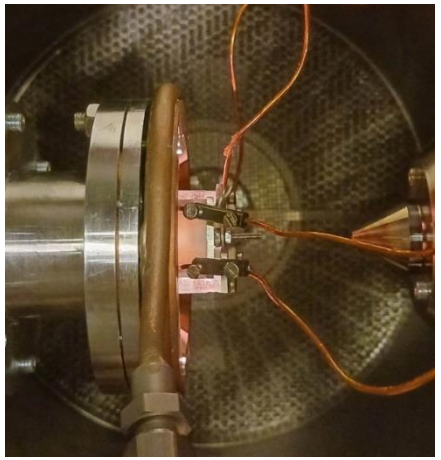
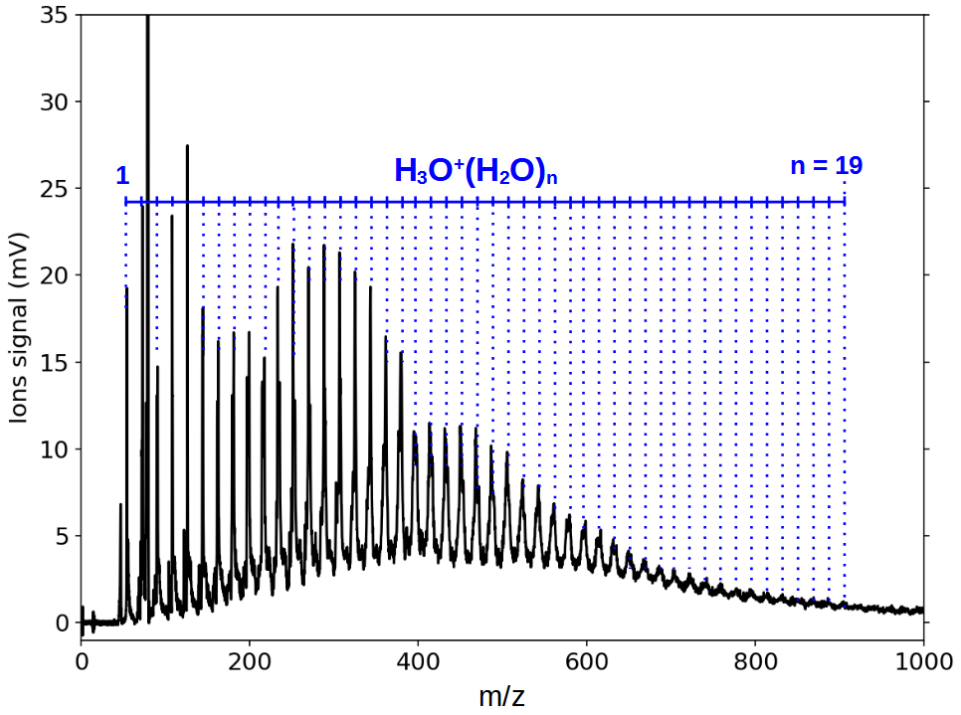
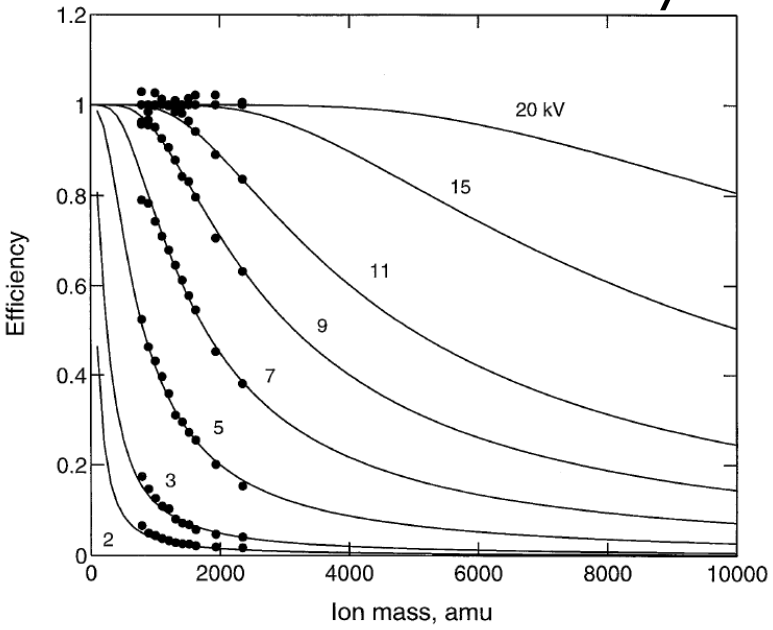
Electron gun



Homemade pulsed valve



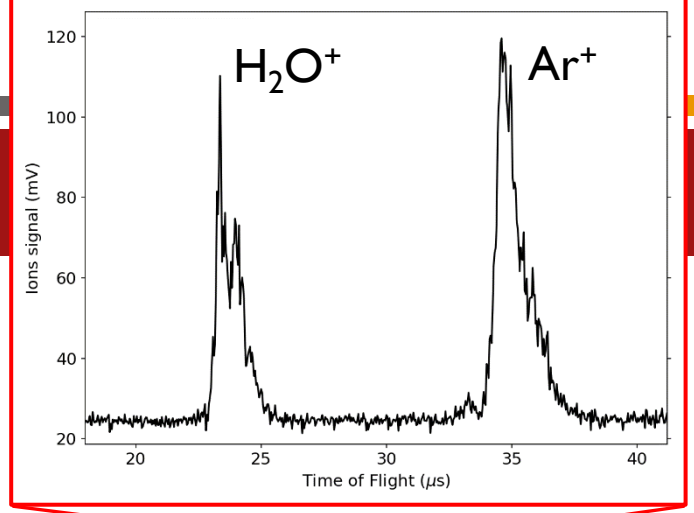
MCP detector efficiency



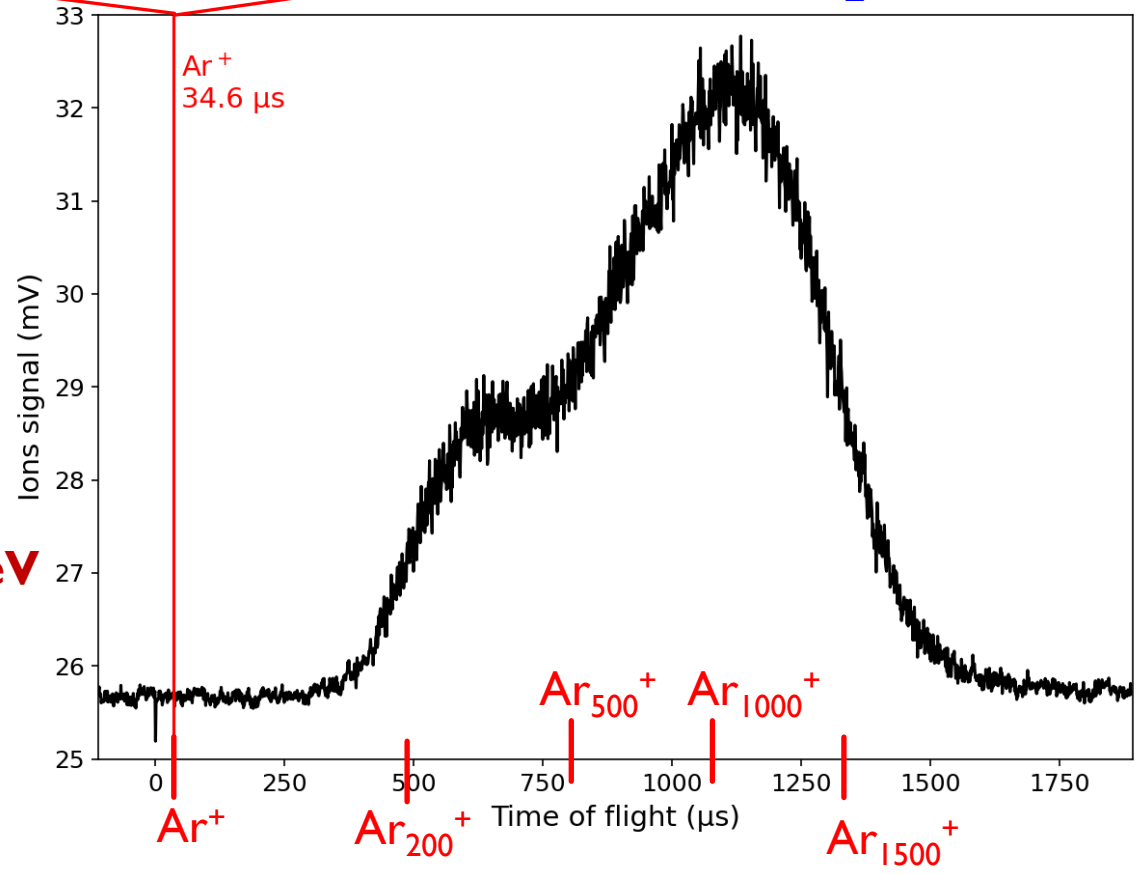
Gilmore, I. S., & Seah, M. P. (2000), International Journal of Mass Spectrometry, 202(1-3), 217-229.

LARGE CLUSTER DETECTION

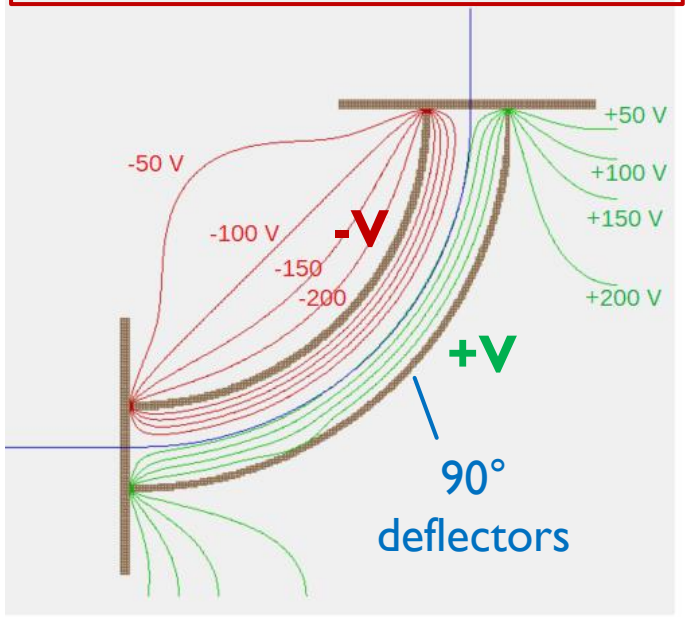
- Switch MCP detector to Daly detector
  - ➢ Detection of large cluster : ~50 000 u (Ar_{1250})
- Confirm by the kinetic energy analyzer



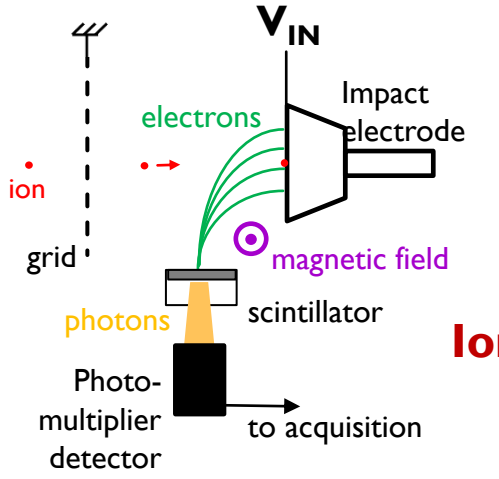
Ar-H_2O cluster



Kinetic energy analyzer

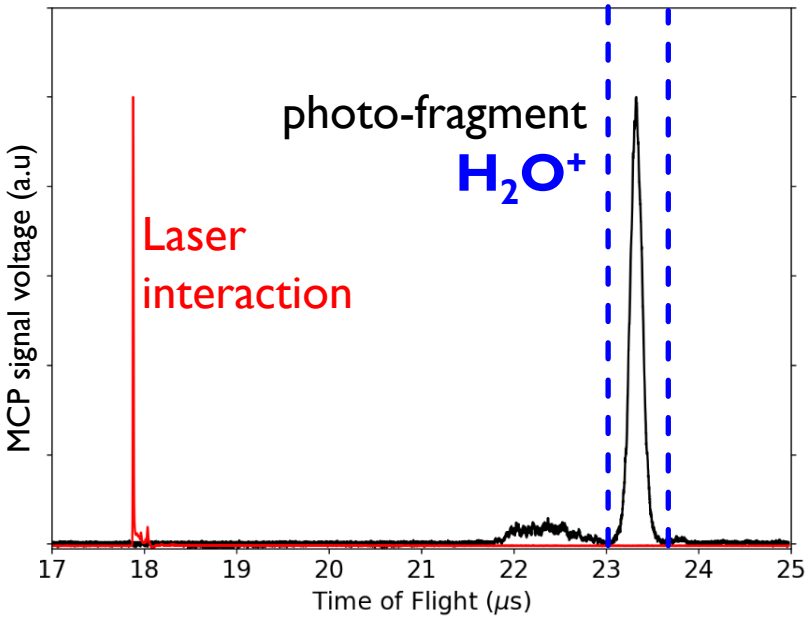


Daly detector

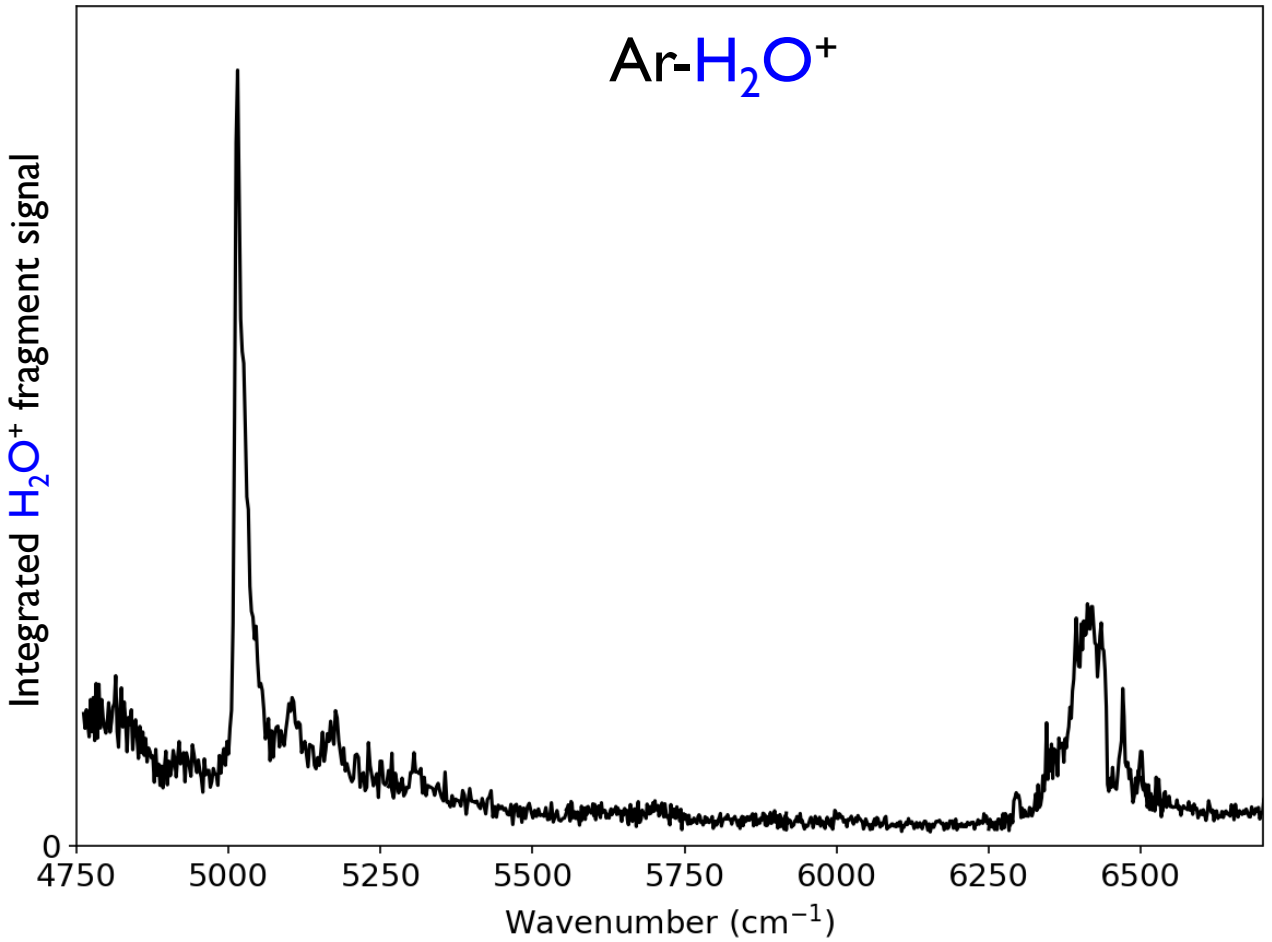


Ions 15 keV

IR SPECTROSCOPY : Ar-H_2O^+



Integrated photo-fragment signal
Vs
Laser wavelength

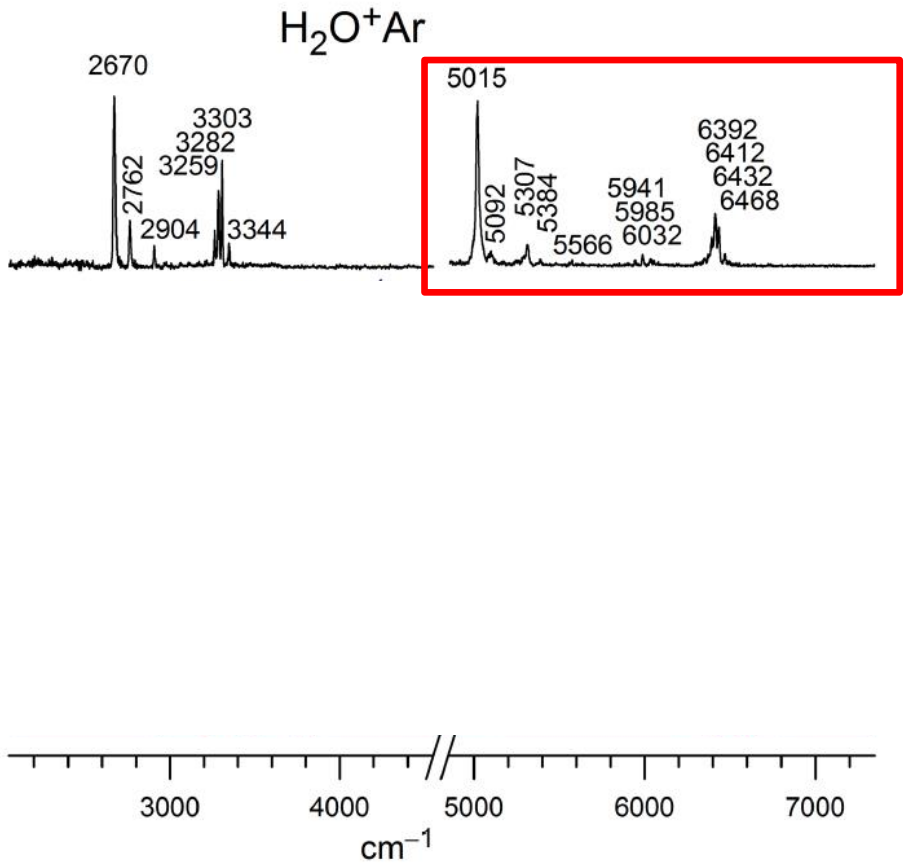


Pulsed IR laser : OPO (Ekspla)

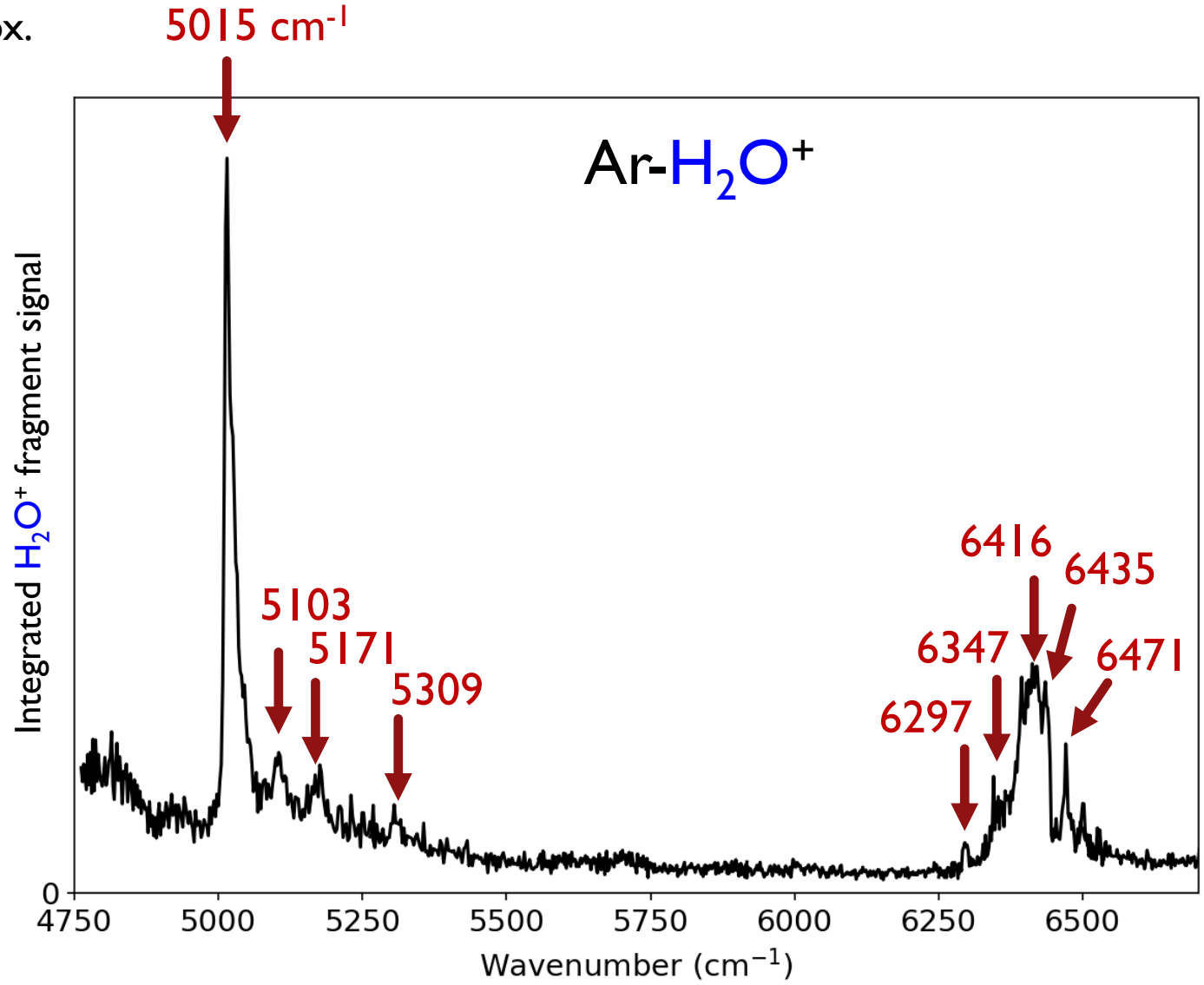
- Idler beam (~ 300 µJ / pulse)
- Pulse repetition rate 30 Hz
- Spectral resolution : few cm^{-1}
- 10 ns pulse duration

$Ar\text{-}H_2O^+$

- Main transitions at 5015 cm^{-1} and 6420 cm^{-1} approx.
- Bands positions similar to the literature
  - ➡ Validation of the setup

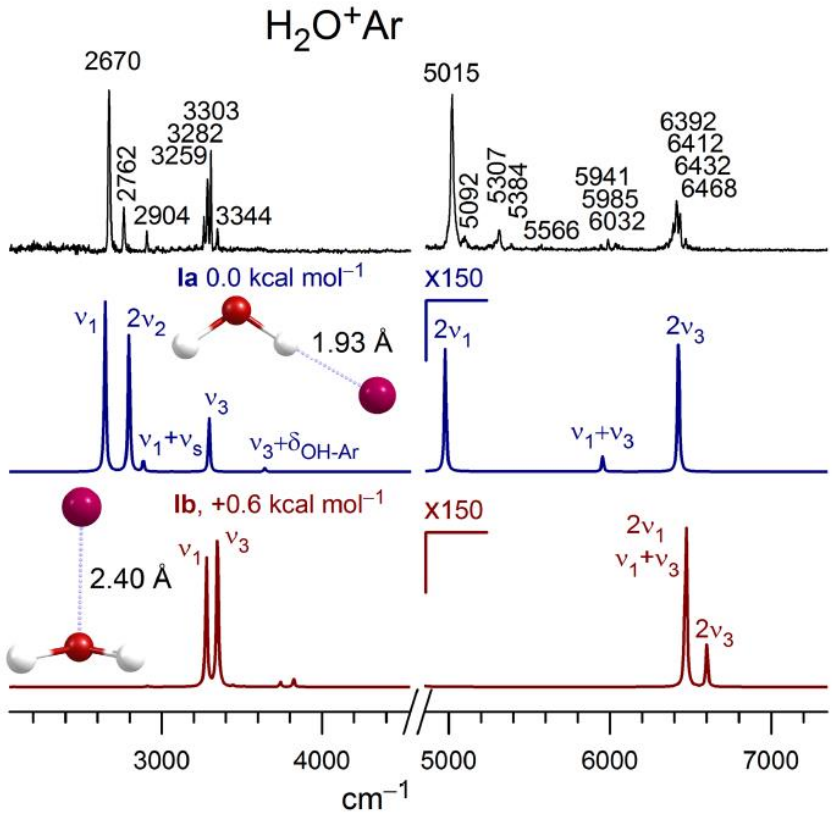


Wagner, J. P., McDonald, D. C., & Duncan, M. A. (2017) *JCP*, *147*(10), 104302.



Ar-H_2O^+

- Both bands : OH stretching modes
- Large energy difference between υ_1 and υ_3
  - ➢ Dominated by the H-bonded isomer
- Bands assigned to overtones $2\upsilon_1$ and $2\upsilon_3$
  - ➢ Anharmonicity of few 100 cm^{-1}



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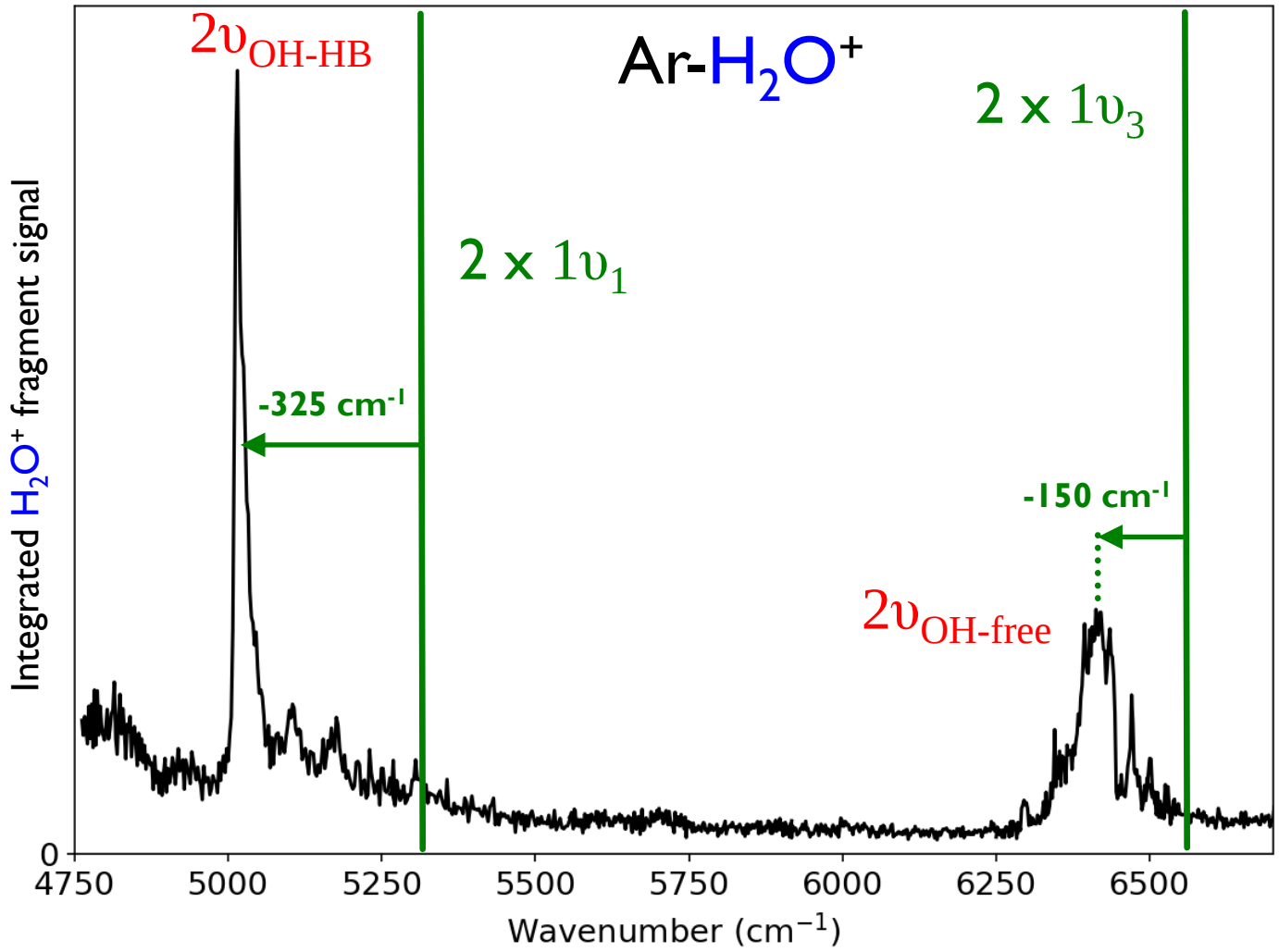
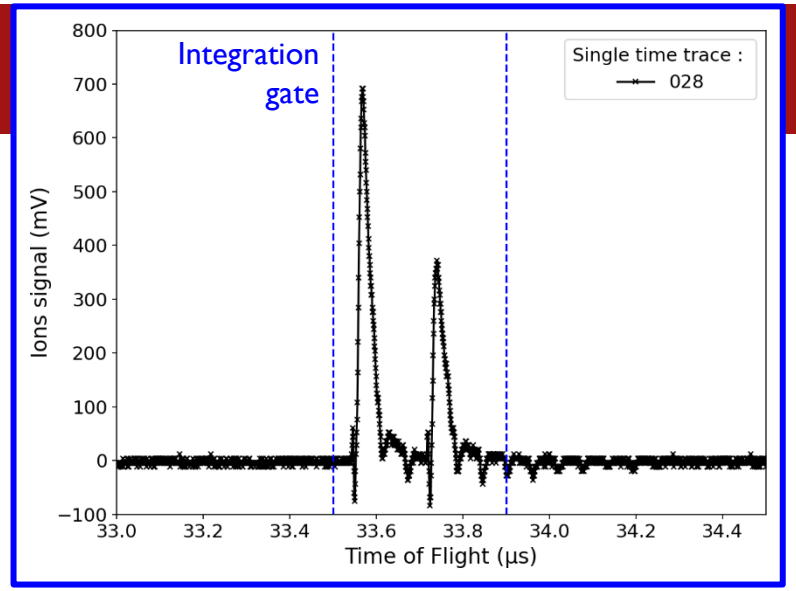
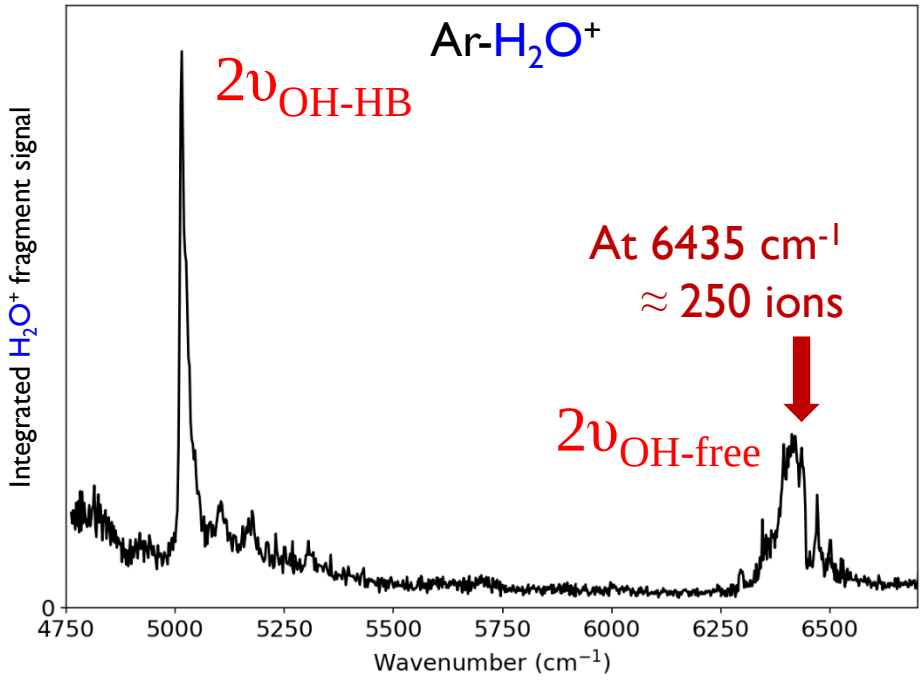


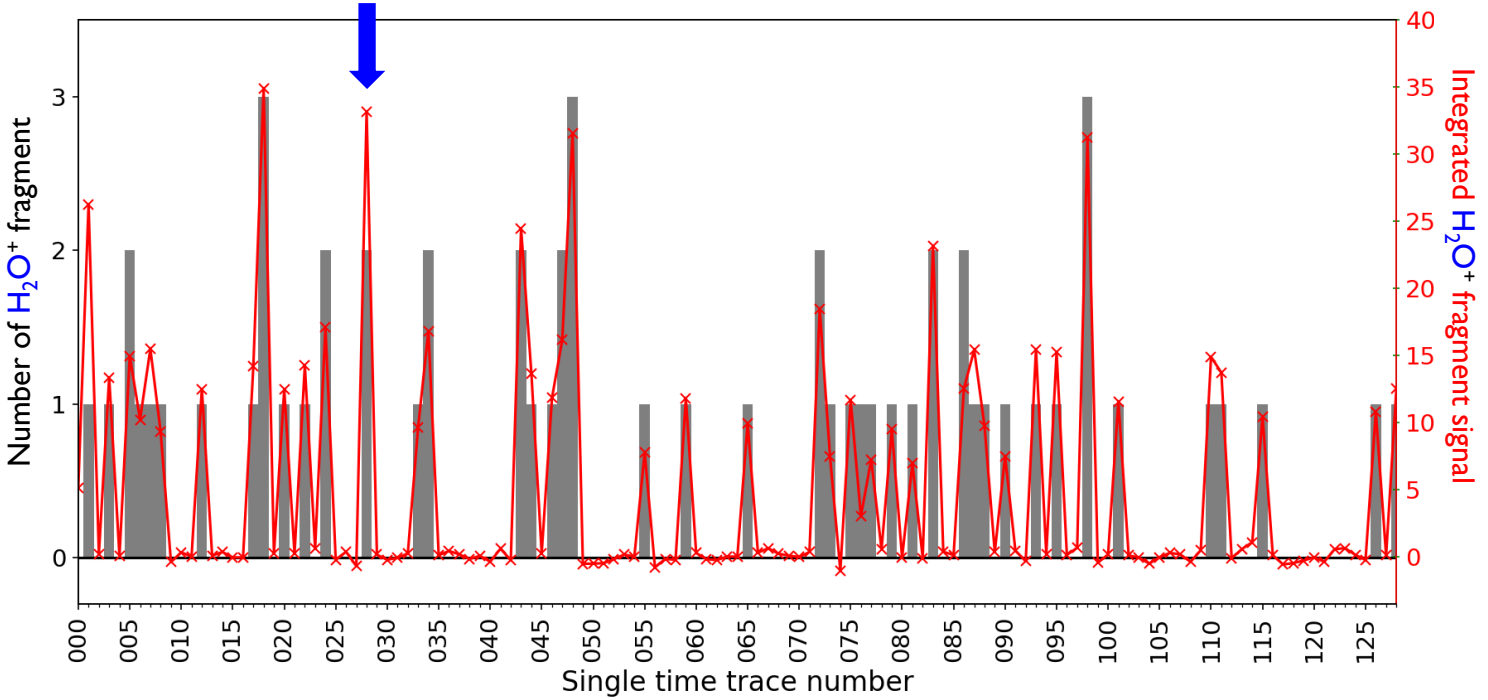
Ar-H_2O^+

Characterization of the setup sensibility

- Optimization of ions detection
- Mean number of ions detected at 6435 cm^{-1} for Ar-H_2O^+ :
  0.5 ions / laser pulse

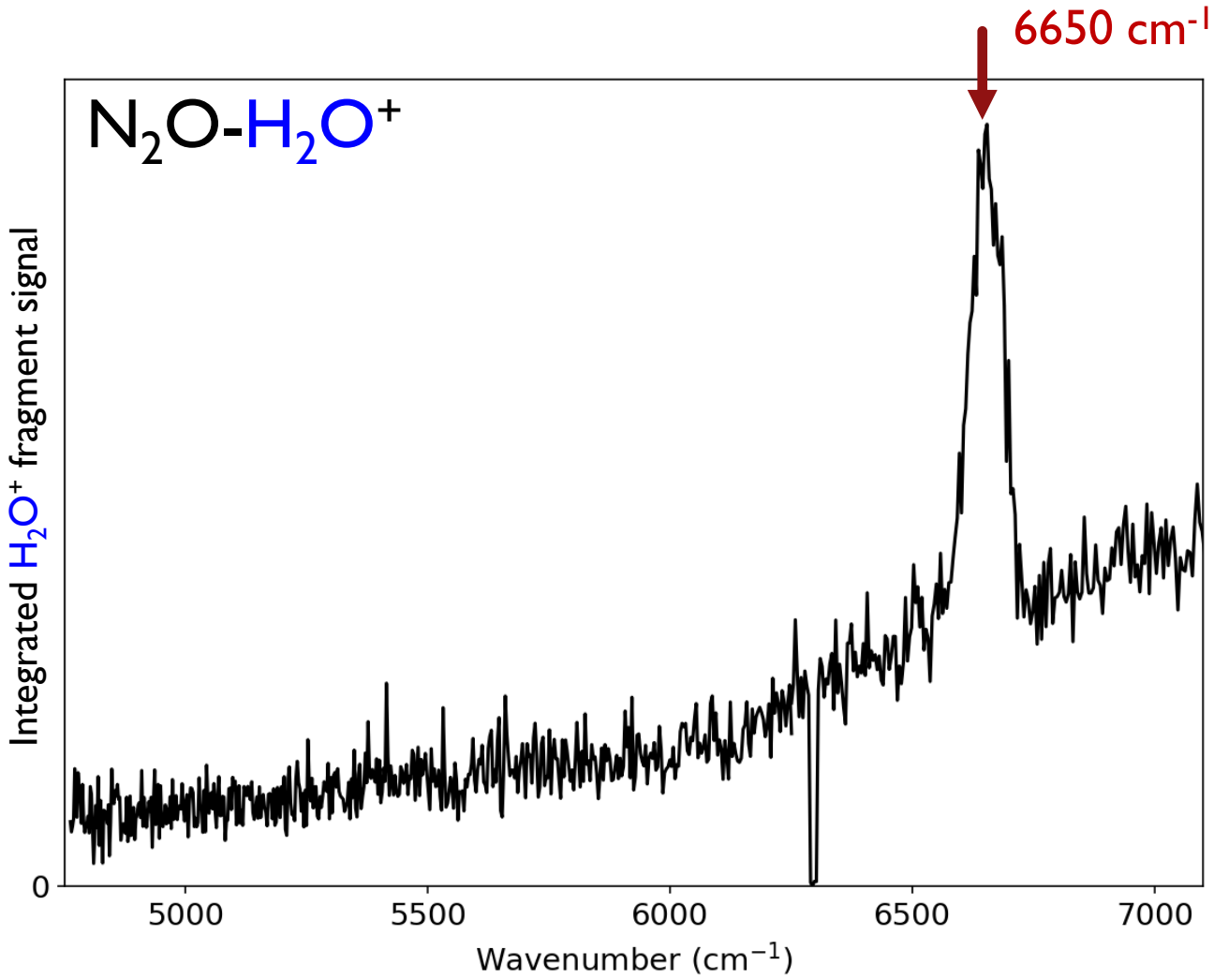






N_2O-H_2O^+

- Main transitions at 6650 cm^{-1}
- No band at 5000 cm^{-1}
- No report in the literature



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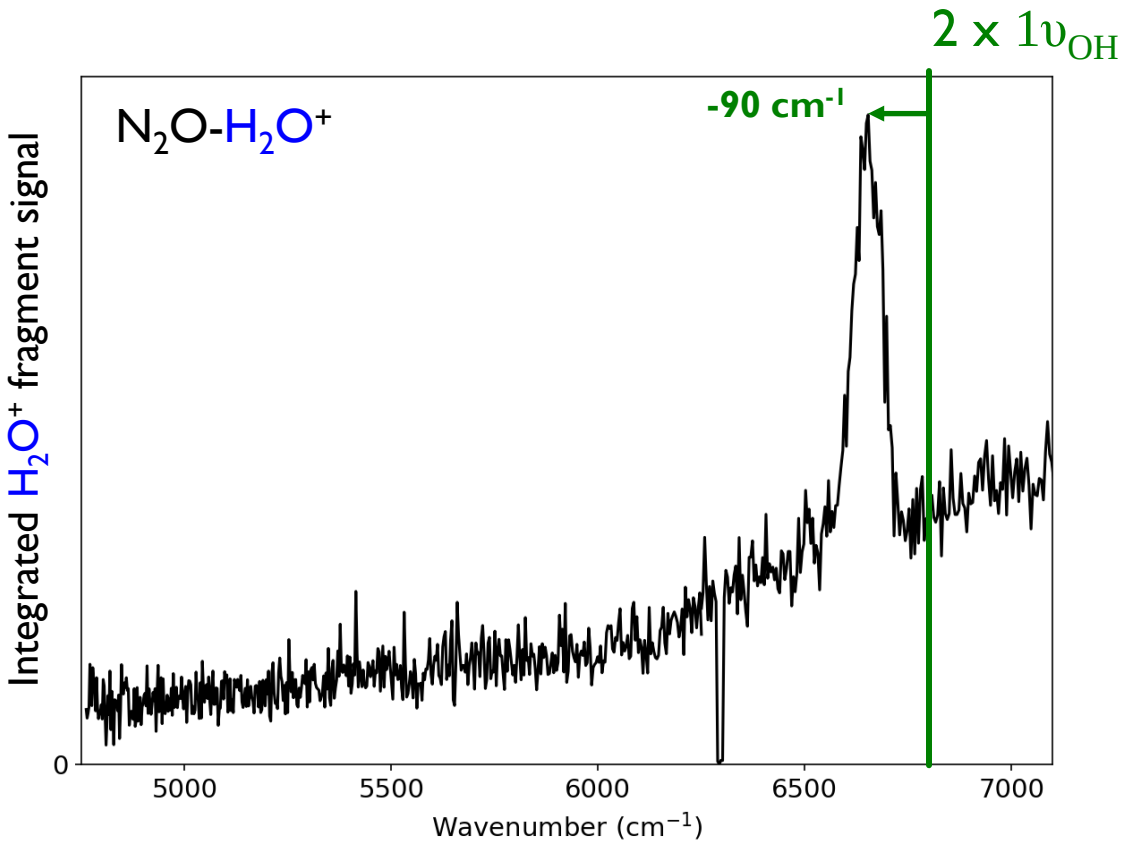
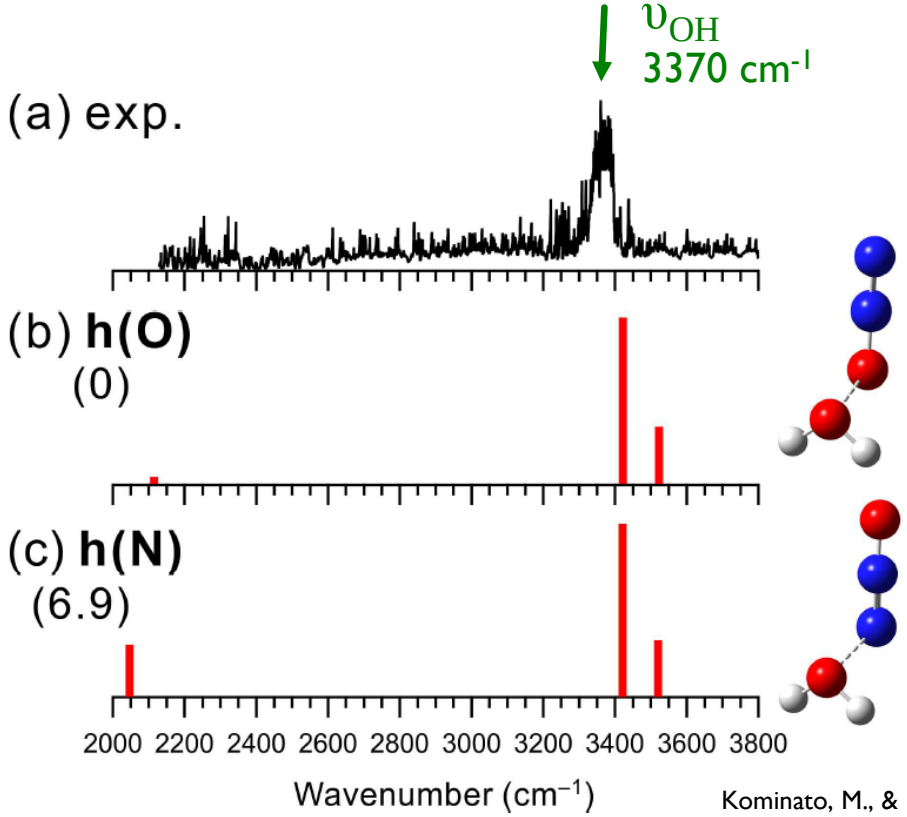


Fundamental modes in the literature

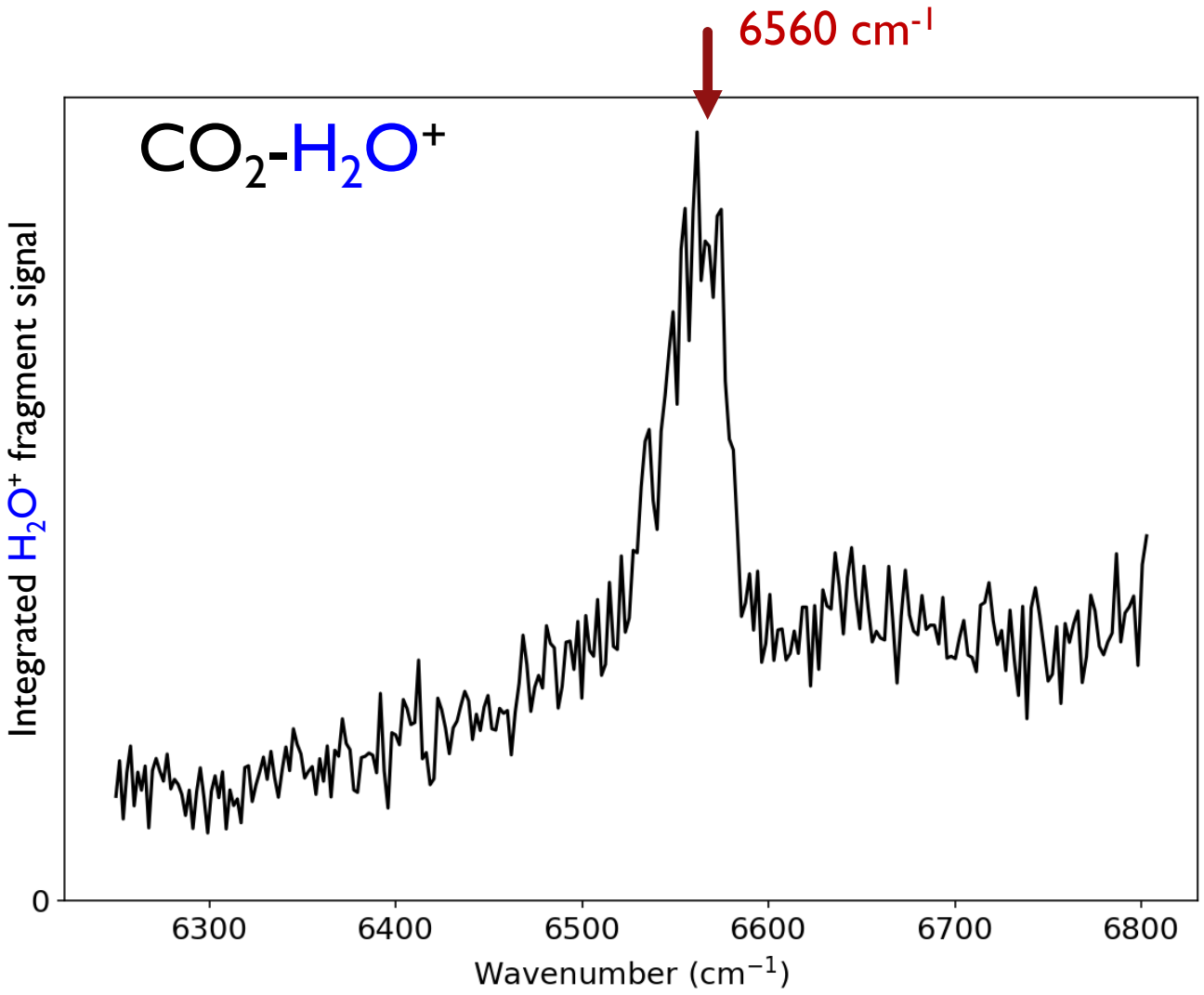
- OH stretching υ_{OH} mode observed at 3370 cm^{-1}
  - The new band is assigned to $2\upsilon_{OH}$ overtone
  - Anharmonicity shift similar to Ar-H_2O^+
- Isomer assignment is elusive



Kominato, M., & Fujii, A. (2023). PCCP, *25*(21), 14726-14735.

CO_2-H_2O^+

- Main transitions at 6560 cm^{-1}
- No band at 5000 cm^{-1}
  - Our laser range : 4760 cm^{-1} to 10 000 cm^{-1}
- No report in the literature of this band



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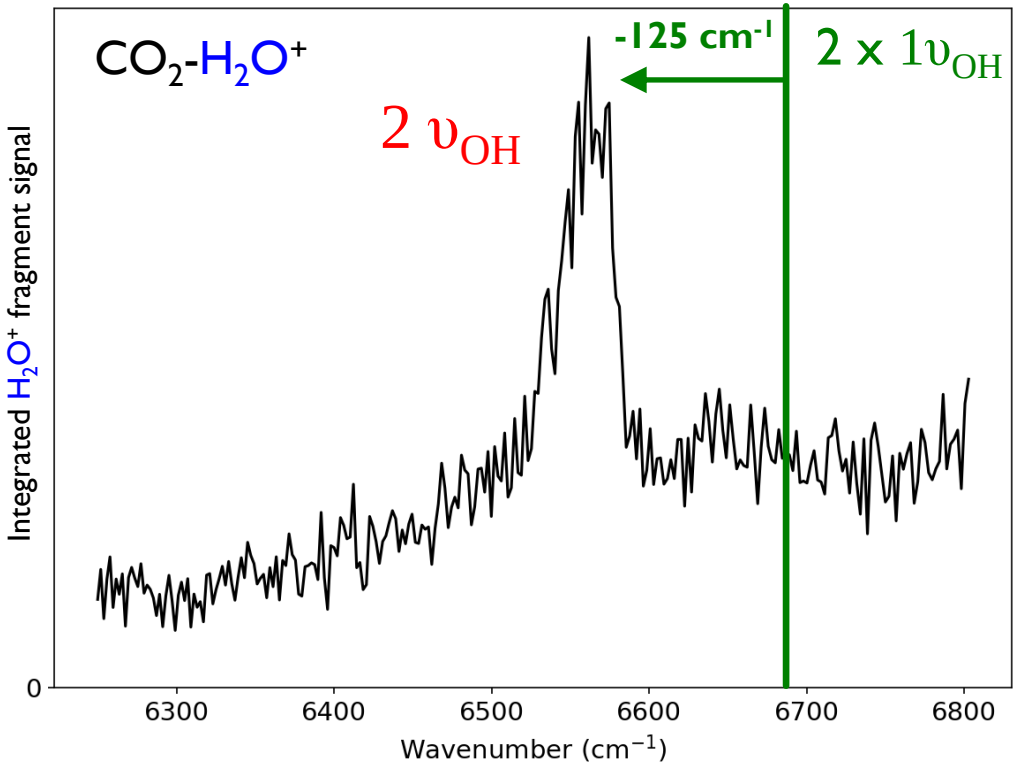
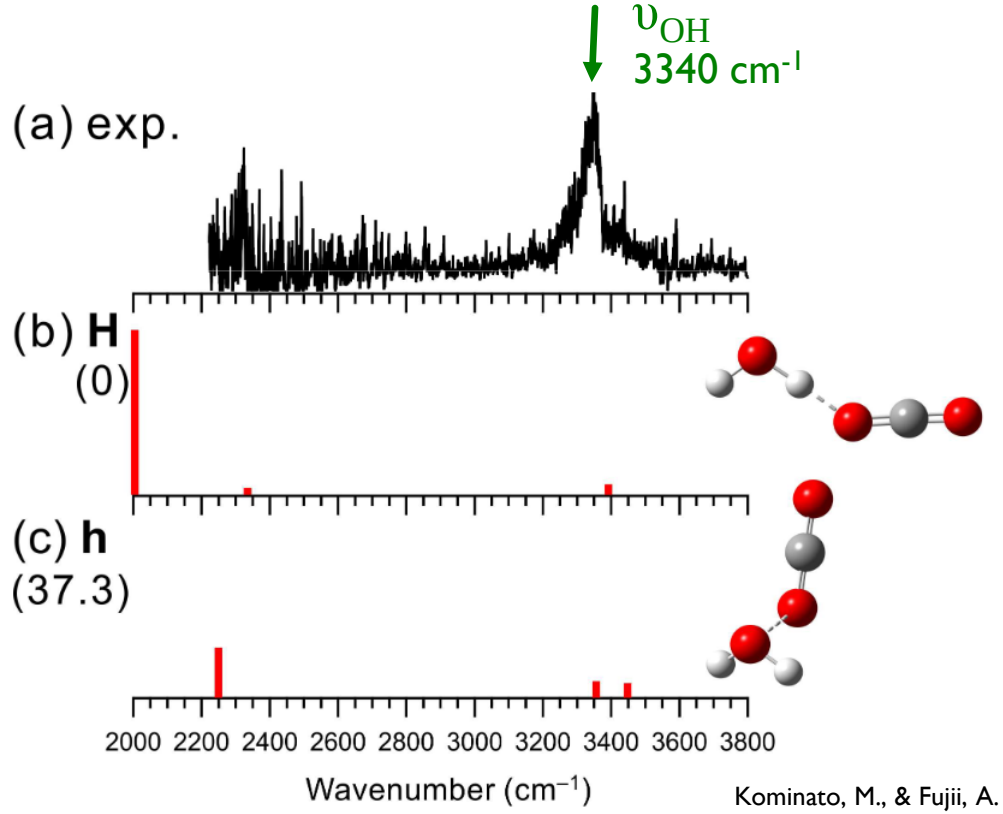


Fundamental modes in the literature

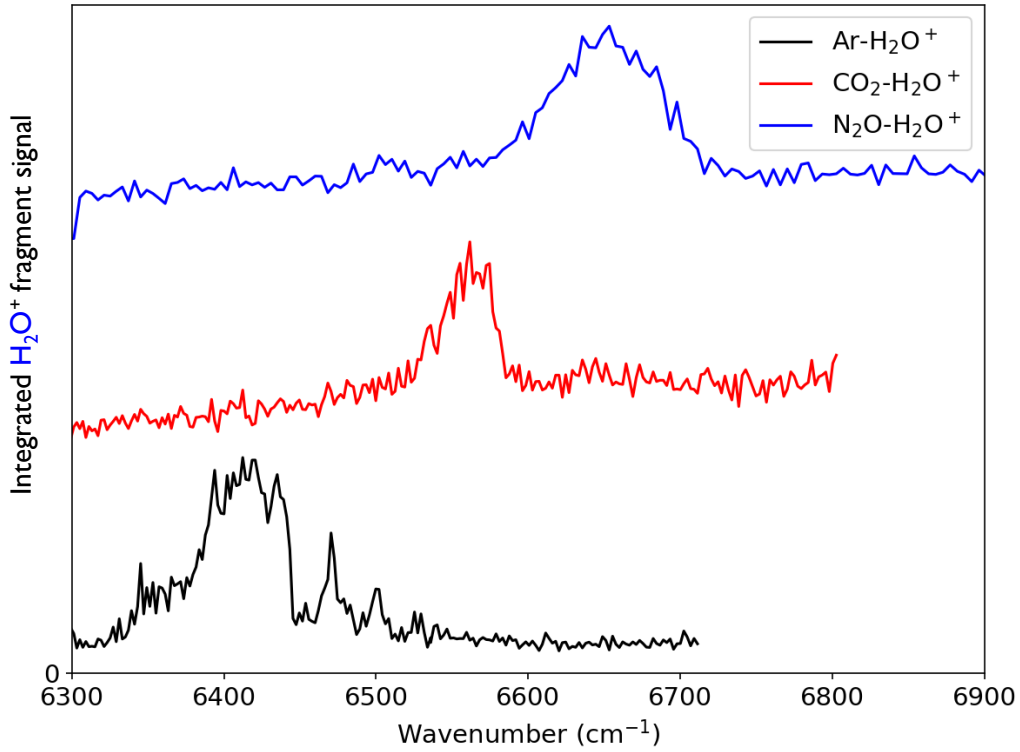
- OH stretching υ_{OH} mode observed at 3340 cm^{-1}
  - The new band is assigned to $2\upsilon_{OH}$ overtone
  - Anharmonicity shift similar to Ar-H_2O^+ and Ar-N_2O^+
- Isomer assignment is elusive



Kominato, M., & Fujii, A. (2023). PCCP, *25*(21), 14726-14735.

CONCLUSION

- STARGATE setup photodissociation action spectroscopy
  - ➢ High sensitivity setup
- Overtones measurement of OH stretching mode of H_2O^+ complexes :
  - ➢ Ar-H_2O^+
  - ➢ CO_2-H_2O^+
  - ➢ N_2O-H_2O^+



Future works

- Determination of the molecular structure for CO_2-H_2O^+ and N_2O-H_2O^+
  - ➢ High resolution spectroscopy of these band (Difference Frequency Generation)
- Extend H_2O^+ complexes investigation : NO-H_2O^+ , O_2-H_2O^+ or N_2-H_2O^+