Experimental and theoretical studies of line-shape parameters to address the spectroscopic challenges of planetary atmospheres

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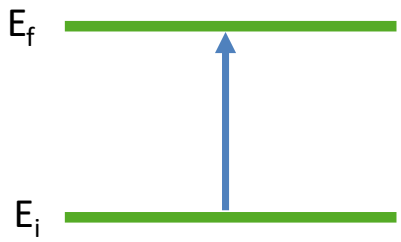
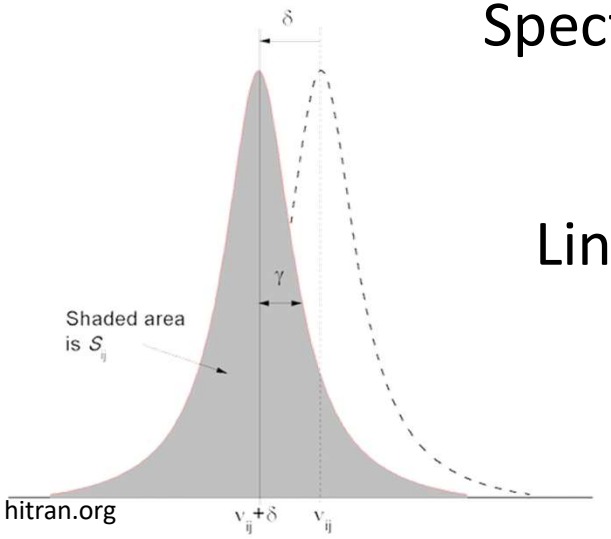
Introduction



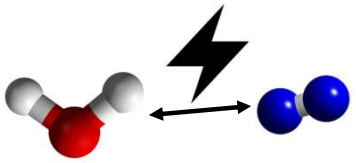
$$I = I_0 e^{-k.L}$$



Spectroscopic parameters

Line-shape parameters

(γ_0, δ_0, …)

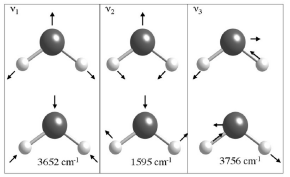


Atmospheric interests

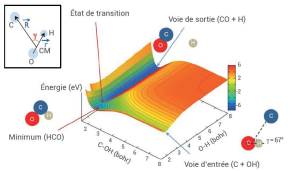
Climat changes

Planetary atmospheres

Fundamental interests



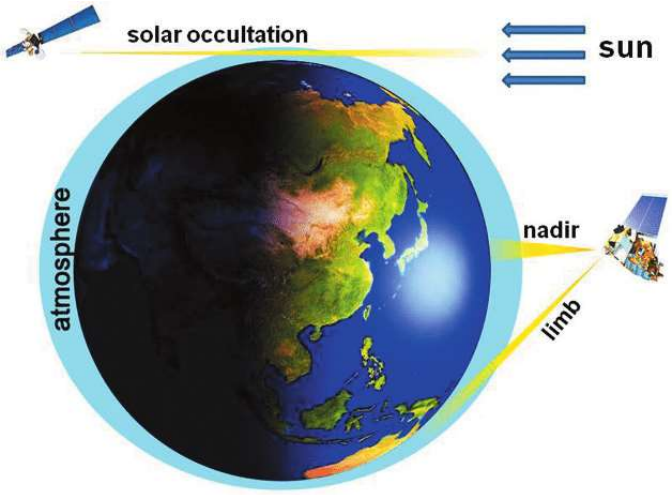
Molecular properties

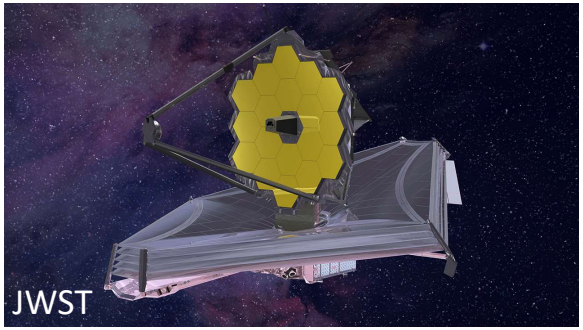


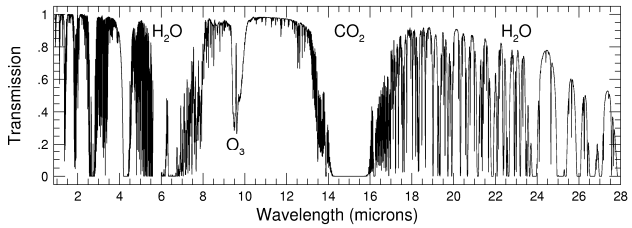
Models

Introduction

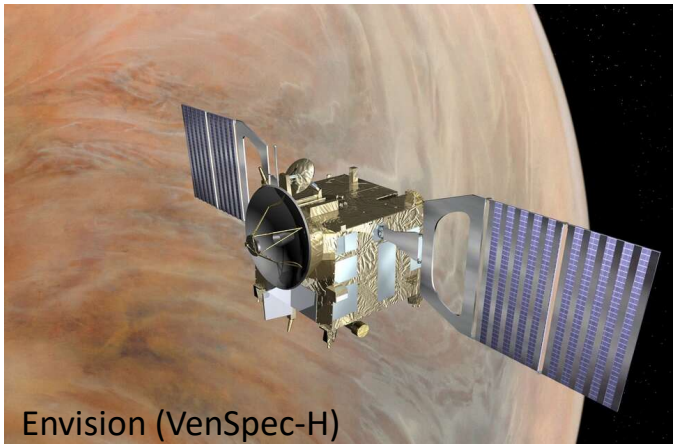
Remote sensing for planetary atmospheres





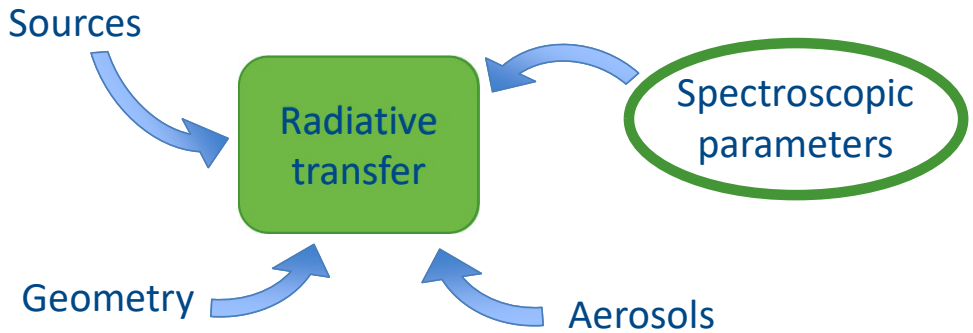


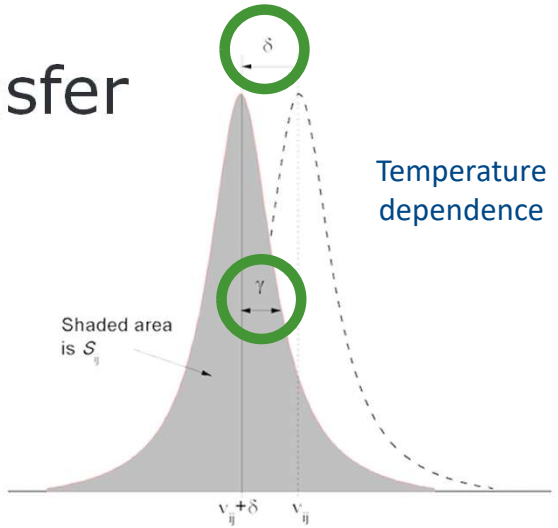
Pressure
Concentration
Temperature
…

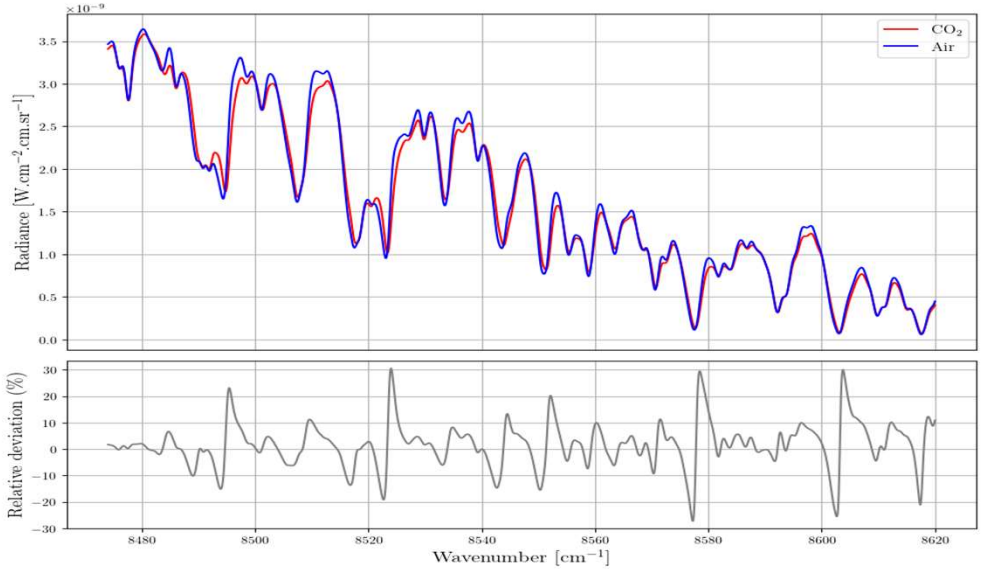


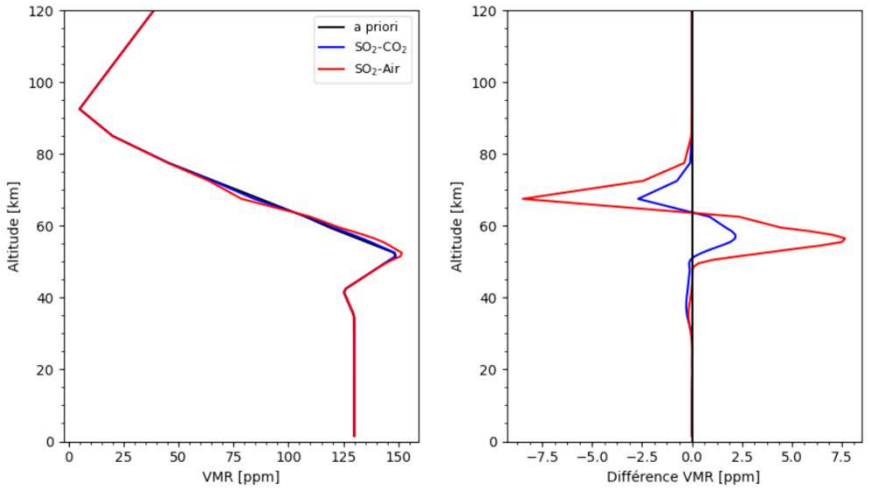
Introduction

Radiative transfer







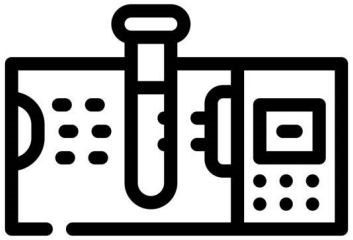


E. Ducreux, private communication

L. Fabris, Master thesis, University of Namur (2022)

Introduction

Spectroscopic challenges



Measurement campaign: weeks, months
Spectra analysis: weeks, months
→ Dozens or hundreds of lines

Ex: H_2O for VenSpec-H (4 spectral regions)
→ 5760 lines in more than 50 bands

Once interaction potential is known
→ Computations of thousands of lines

- Temperature dependence
- Experimental difficulties

Introduction

Methodology

Measure line shape parameters

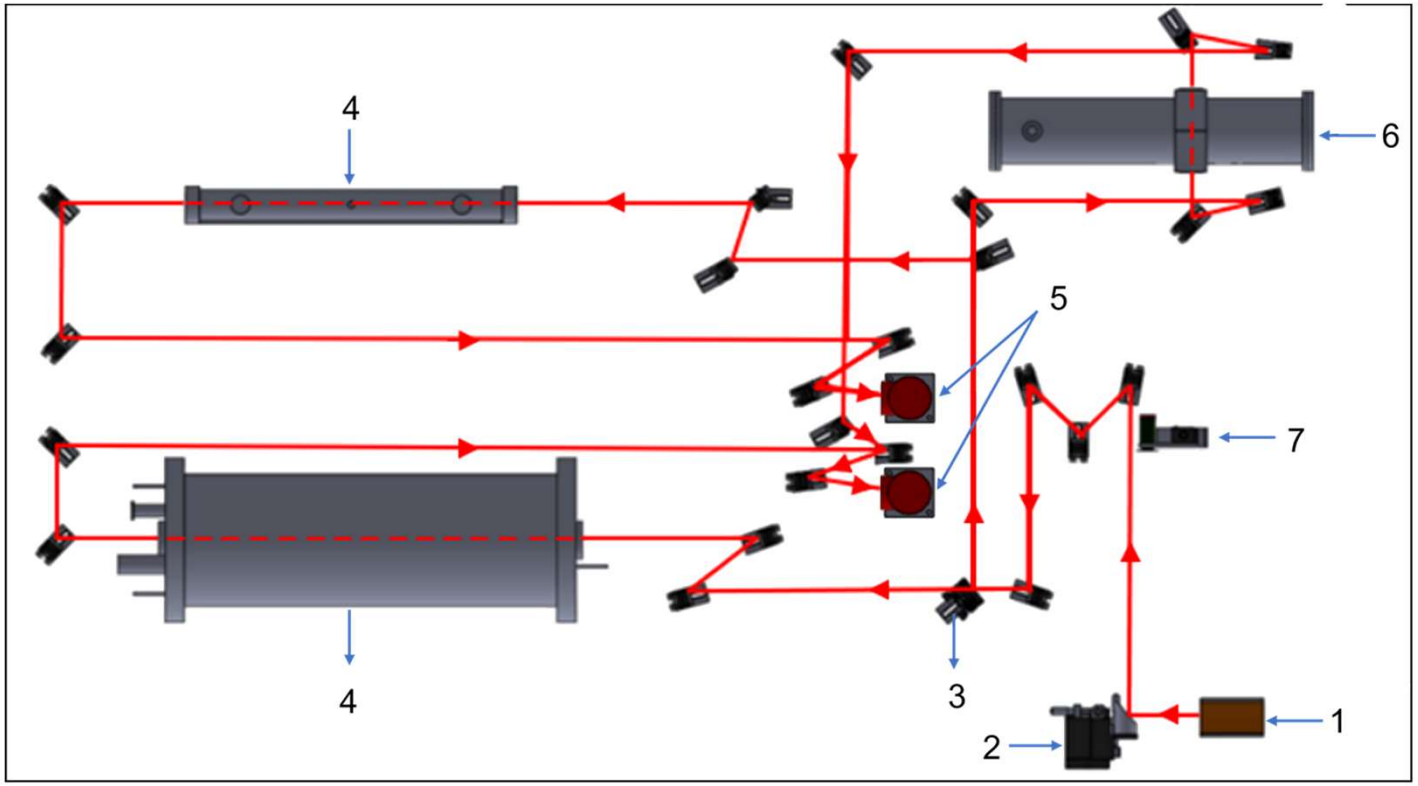
Determine intermolecular potential

Compute line shape parameters for many vibrational bands

(γ_0, δ_0, speed and temperature dependencies)

Laboratory measurements

QCL spectrometer



1. Quantum Cascade Laser
2. Parabolic mirror
3. Beam splitter
4. Absorption cells
5. Detectors
6. Confocal étalon
7. Chopper

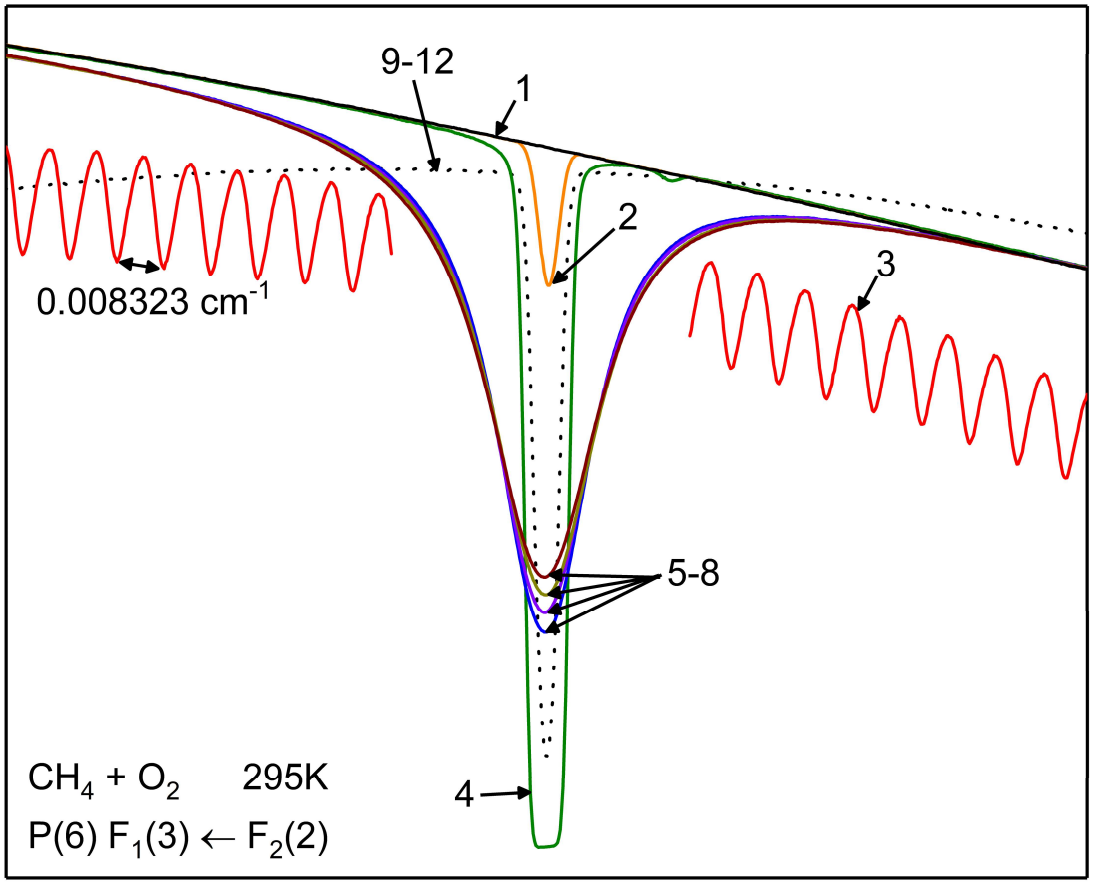
Characteristics

- High-resolution (5 x 10^{-5} cm^{-1})
- Excellent SNR (>2000)
- Spectral range (0.1 - 2 cm^{-1})

T. Roland, Master thesis, University of Namur (2022)
B. Vispoel *et al.*, JQSRT, 328, 109150 (2024)

Laboratory measurements

QCL spectrometer

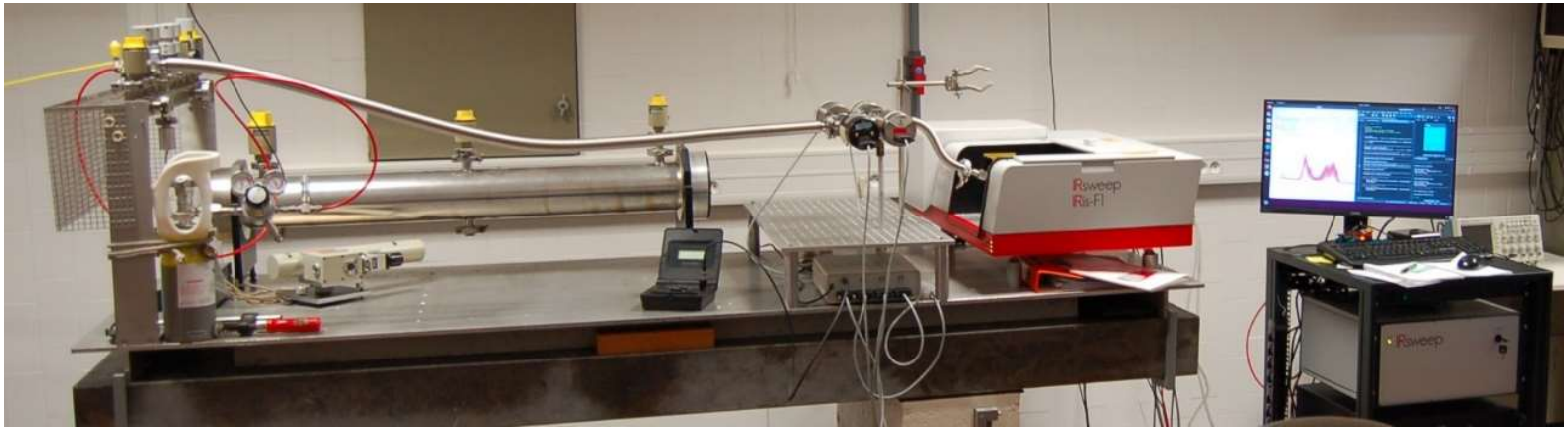


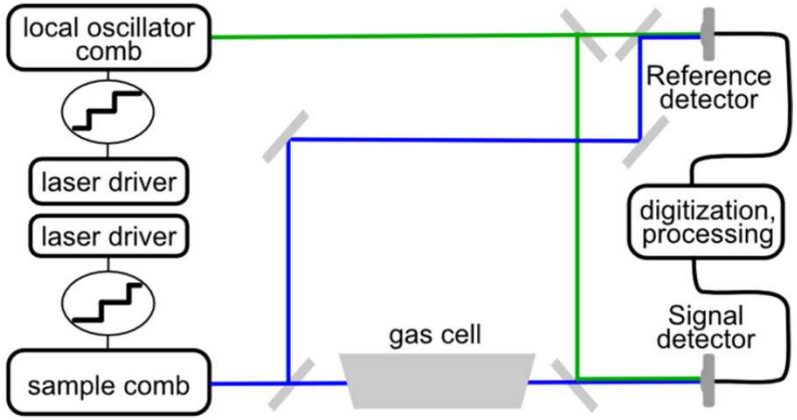
(1) QCL emission profile
(2) Low-pressure pure CH_4 line
(3) Confocal étalon fringes
(4) Saturated line
(5-8) Perturbed line
(9-12) Reference line

Vispoel and Lepère, HRMS 2022, Praha (Czech Republic), 2022
B. Vispoel *et al.*, JQSRT, 328, 109150 (2024)

Laboratory measurements

Dual comb spectrometer





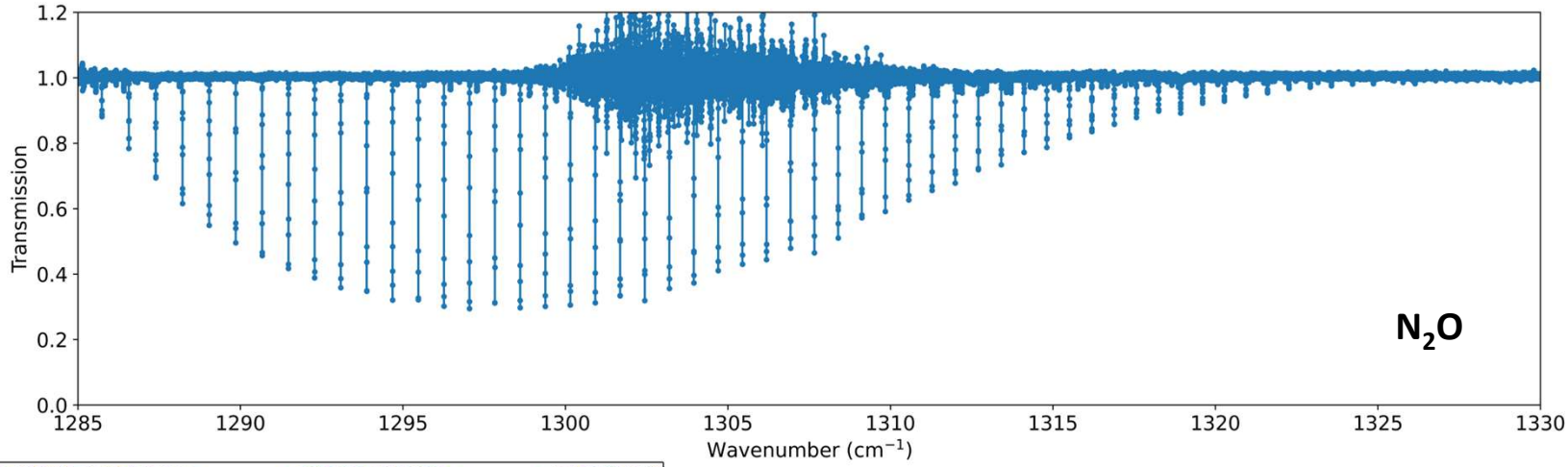
Characteristics

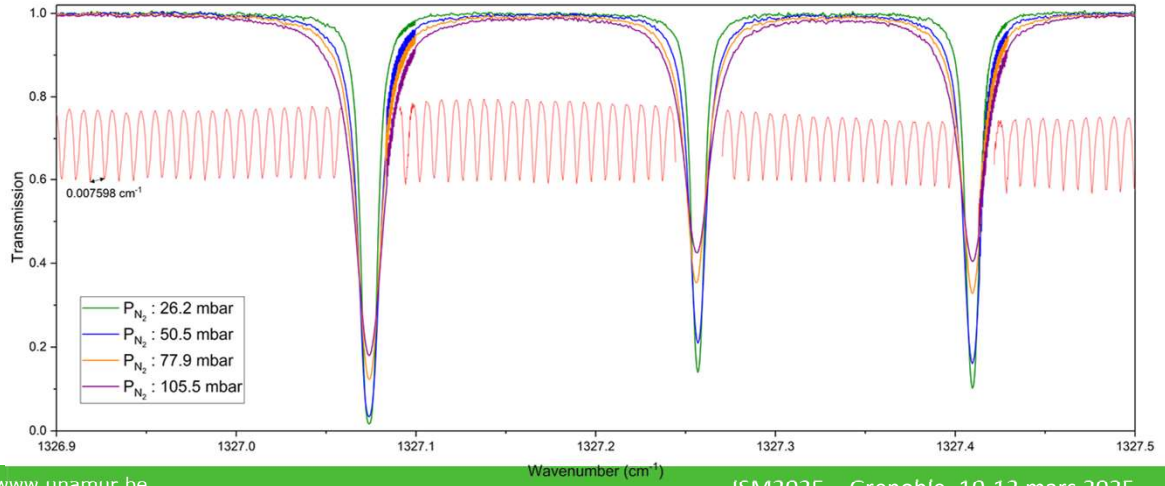
- High-resolution (up to 4 x 10^{-4} cm^{-1})
- Spectral range (60-100 cm^{-1})
- Acquisition time (5-7 min)
- Very good SNR (>650)

Lepère *et al.*, JQSRT, 287, 108239 (2022)
Clément *et al.*, JQSRT, under revision

Laboratory measurements

Dual comb spectrometer

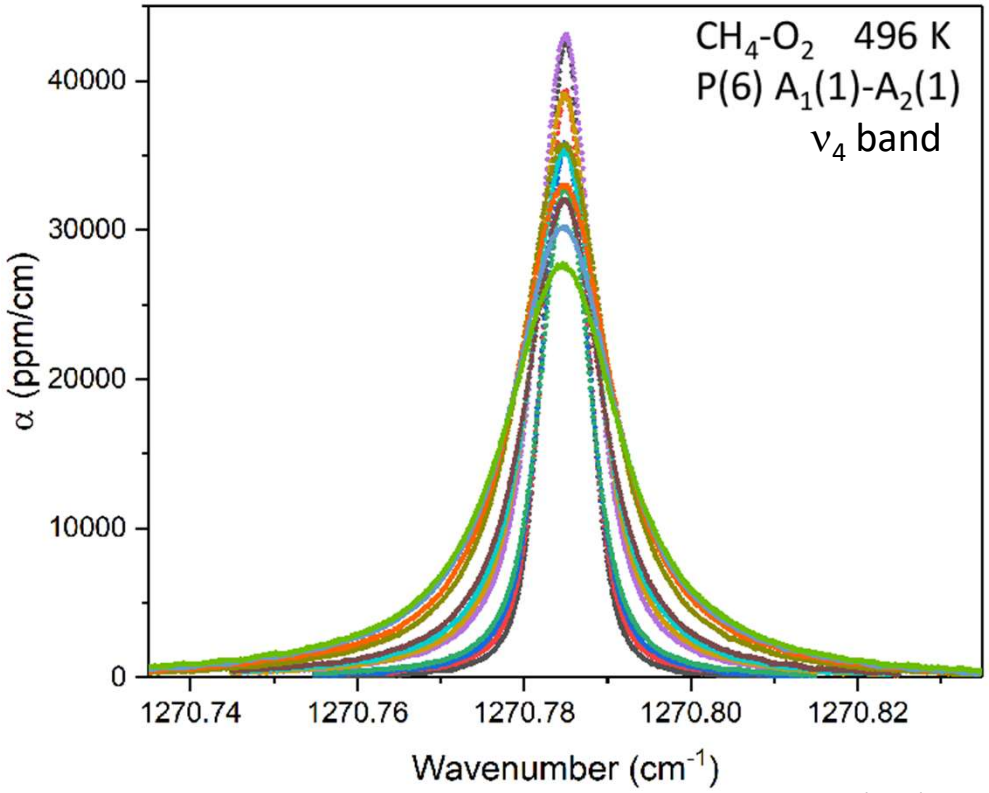


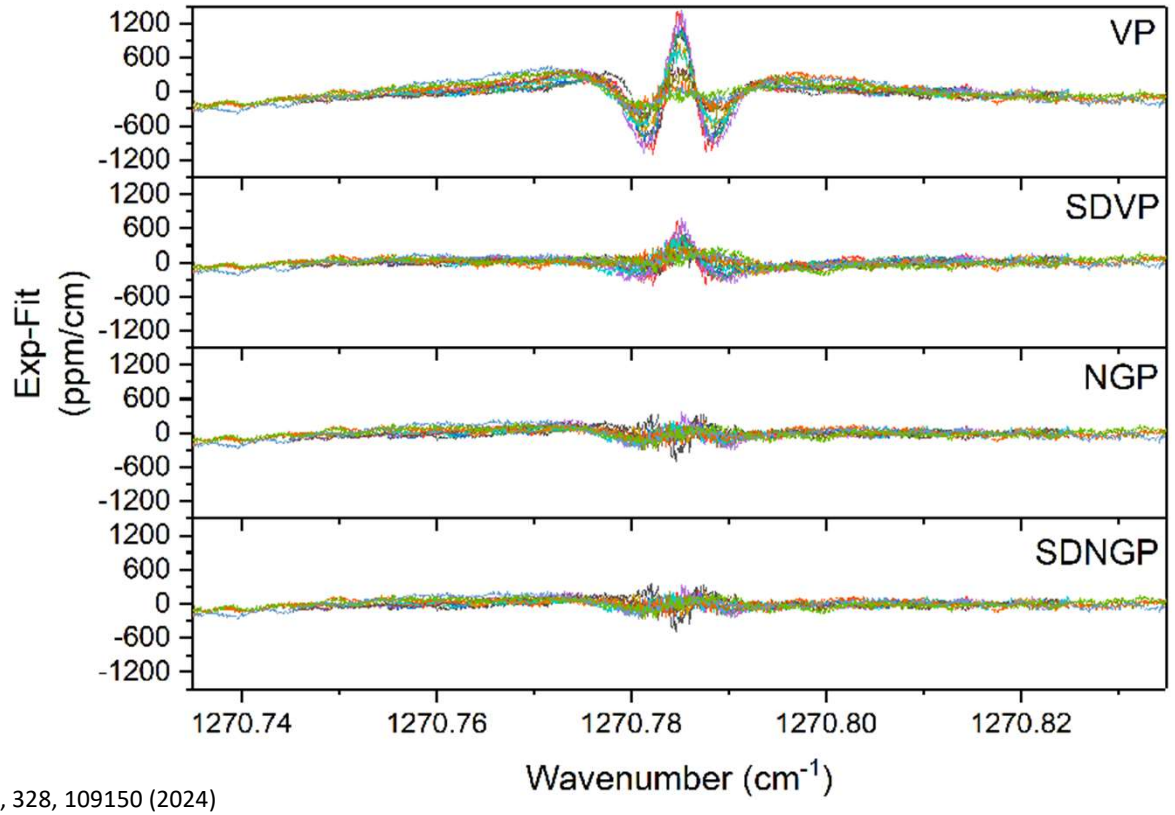


Clément *et al.*, Scientific day & Inauguration of Iris-F1, Namur (Belgium), 2022

Laboratory measurements

Experimental line profile fits



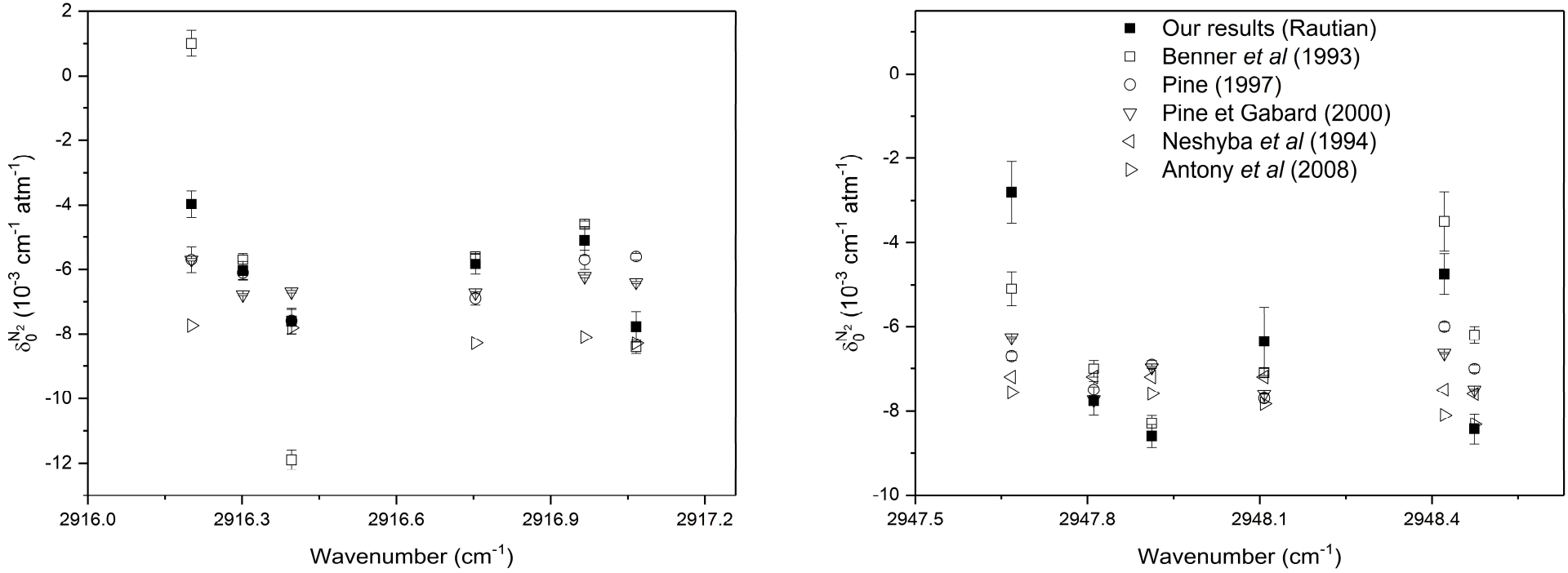


Vispoel *et al.*, JQSRT, 328, 109150 (2024)

Laboratory measurements

Diode-laser experimental results

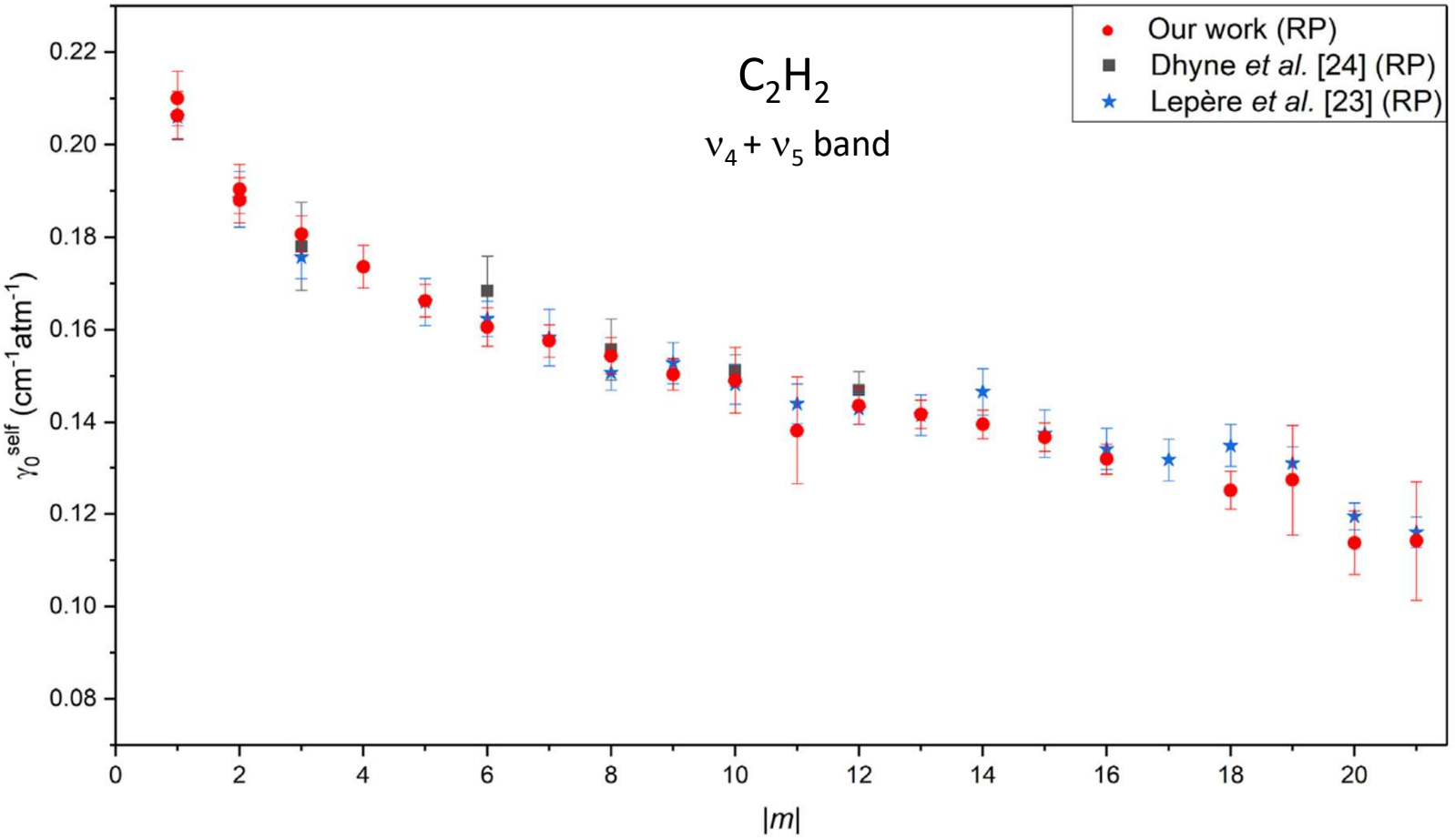
CH_4-N_2 in the ν_3 band



Vispoel, PhD thesis (2016)

Laboratory measurements

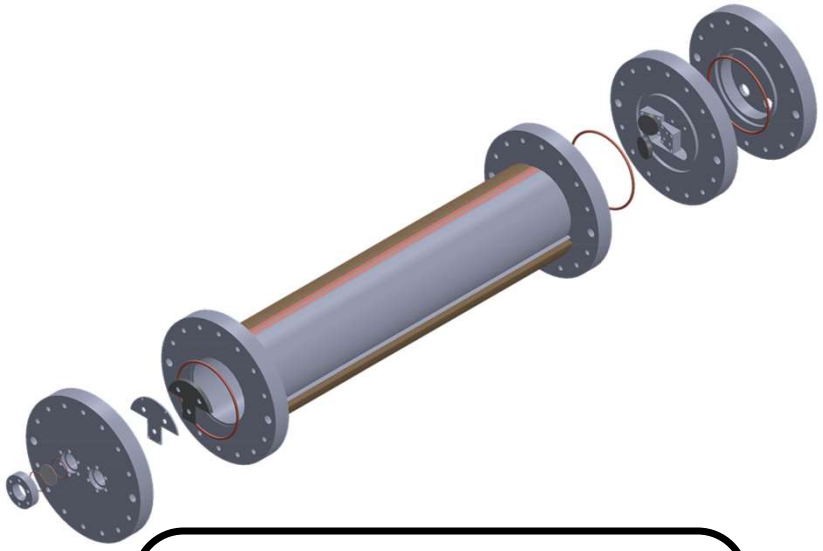
DCS experimental results



Dricot *et al.*, JQSRT, 328, 109149 (2024)

Laboratory measurements

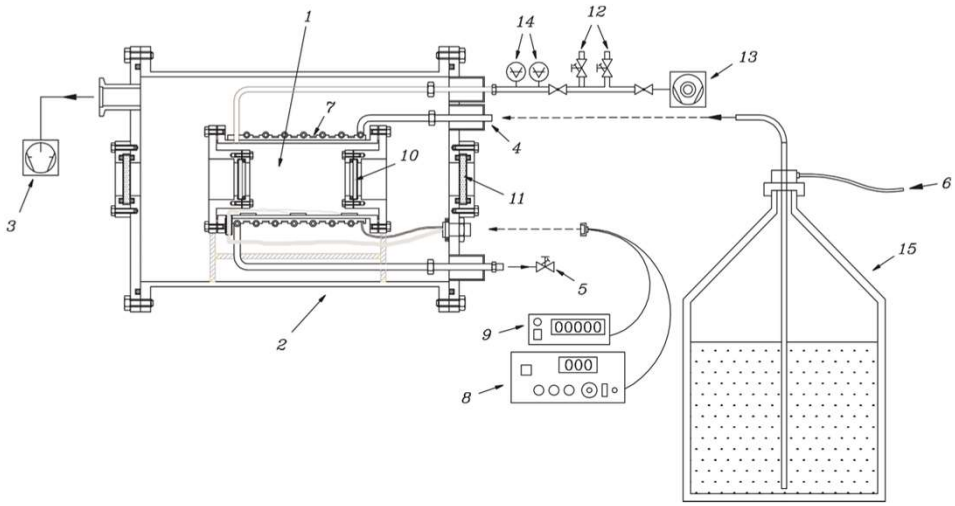
Temperature dependence



- Temperature range: 296 - 1000 K
- Temperature stability: 1 K
- No gradient of temperature
- Single path (0.437 m) and White-type design (2 to 10 m)

Fissiaux *et al.*, JMS (2015), 317, 26
Léonis, PhD thesis (2019)

Temperature range: 100 - 296 K
Temperature stability: 0.1 K
No gradient of temperature
Absorption path: 0.4043 m



Lerot *et al.*, JMS (2003), 219, 329

Laboratory measurements

Temperature dependence

$$\gamma(T) = \gamma(T_0) \left[\frac{T_0}{T}\right]^n \qquad \delta(T) = \delta(T_0) + \delta' \, (T - T_0)$$

Double Power Law

$$\gamma(T) = c_1 \left[\frac{T_0}{T}\right]^{n_1} + c_2 \left[\frac{T_0}{T}\right]^{n_2}$$

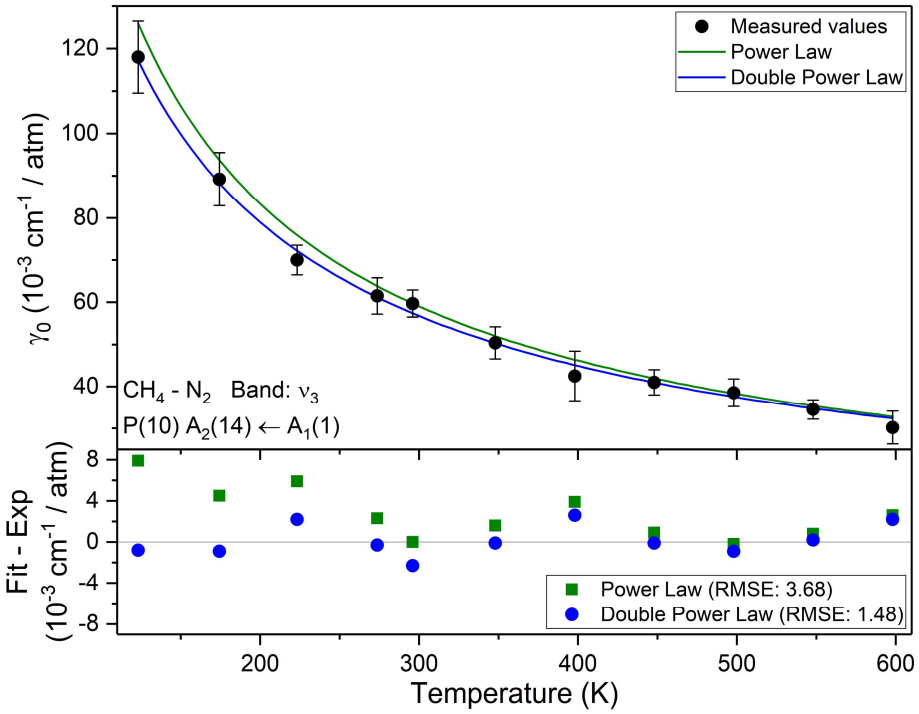
- Physic's based
- Large range of temperature
- Works for half-width, line shift and their speed dependence
- Allow change of sign

Gamache and Vispoel, JQSRT, 217, 440 (2018)

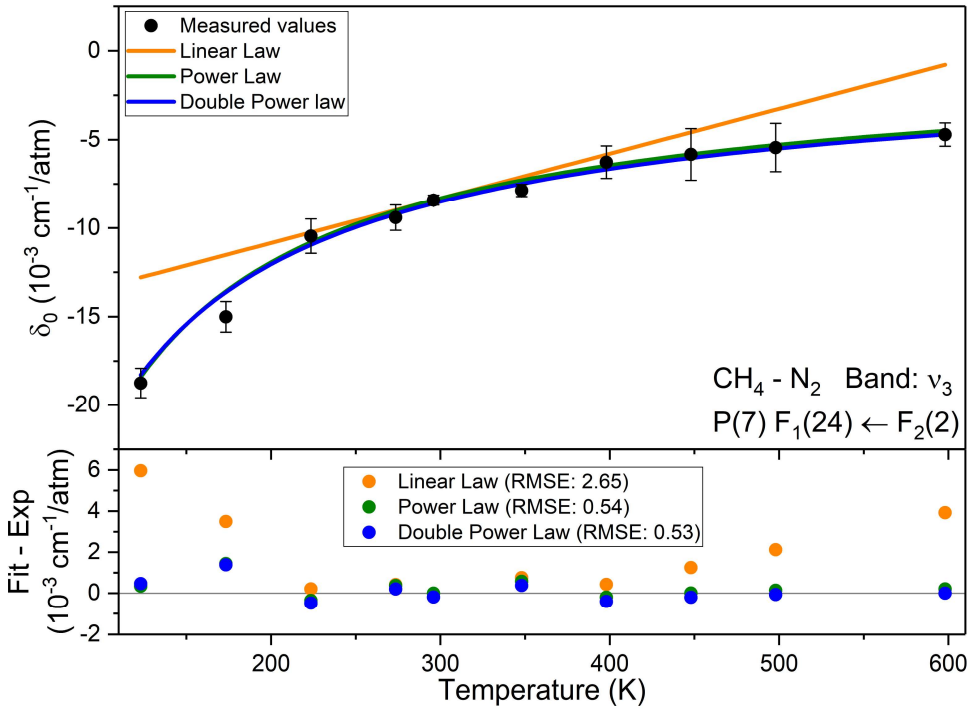
Laboratory measurements

Temperature dependence

$$\gamma(T) = \gamma(T_0)\left[\frac{T_0}{T}\right]^n \qquad \gamma(T) = c_1\left[\frac{T_0}{T}\right]^{n_1} + c_2\left[\frac{T_0}{T}\right]^{n_2} \qquad \delta(T) = \delta(T_0) + \delta'\,(T - T_0)$$

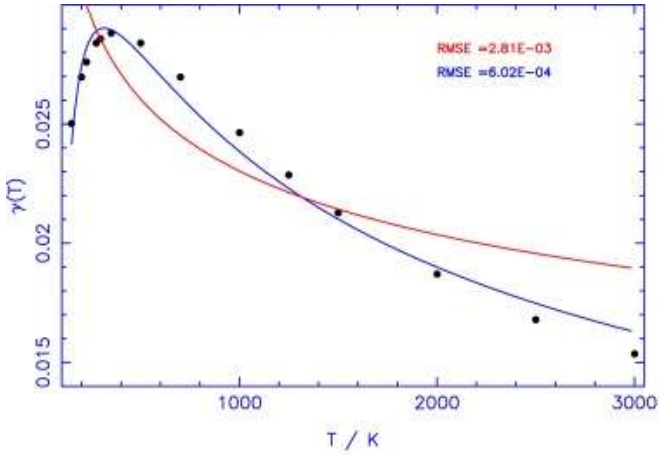


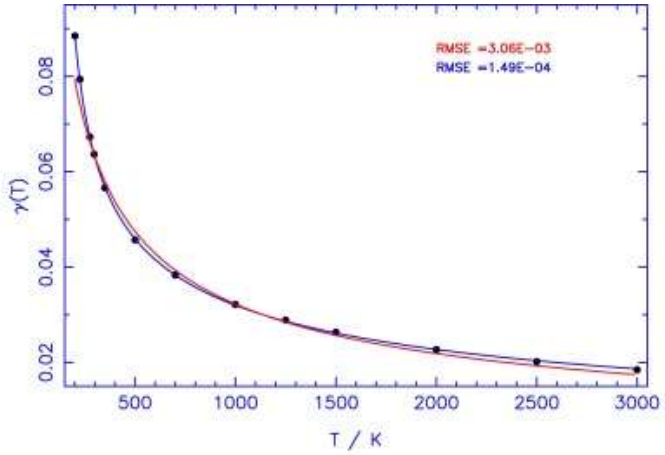
Vispoel and Lepère, Scientific day & Inauguration of Iris-F1, Namur (Belgium), 2022



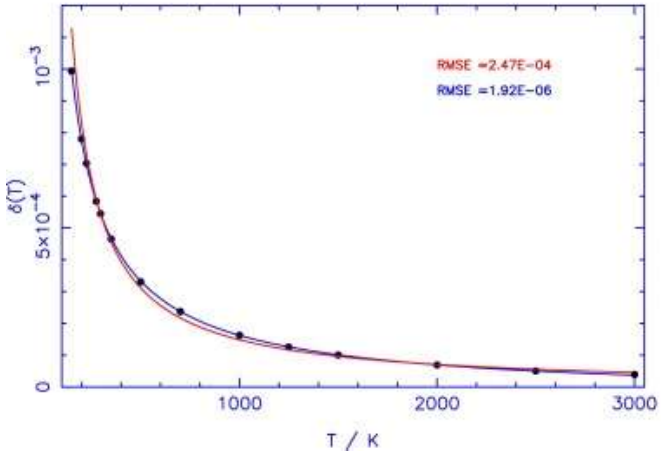
Vispoel and Lepère, JQSRT, 239, 106654 (2019)

Temperature dependence of collisional line shape parameters

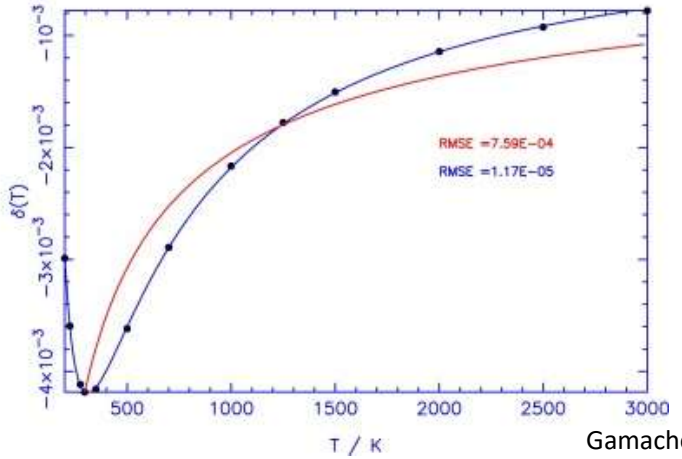




H_2O-N_2 000-000 $15_{1\,15} \leftarrow 14_{0\,14}$



H_2O-H_2 100-000 $8_{6\,3} \leftarrow 7_{5\,2}$



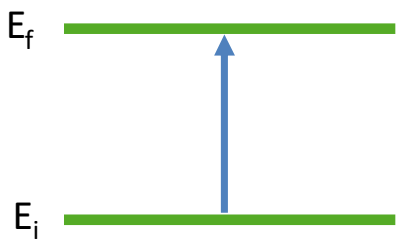
Gamache and Vispoel, JQSRT, 217, 440 (2018)

Line shape calculations

Semi-classical Complex Robert-Bonamy-Ma formalism

Why semi-classical model?

- Accuracy
- Computation resources



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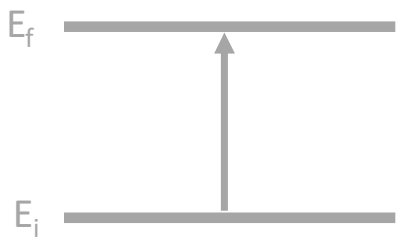
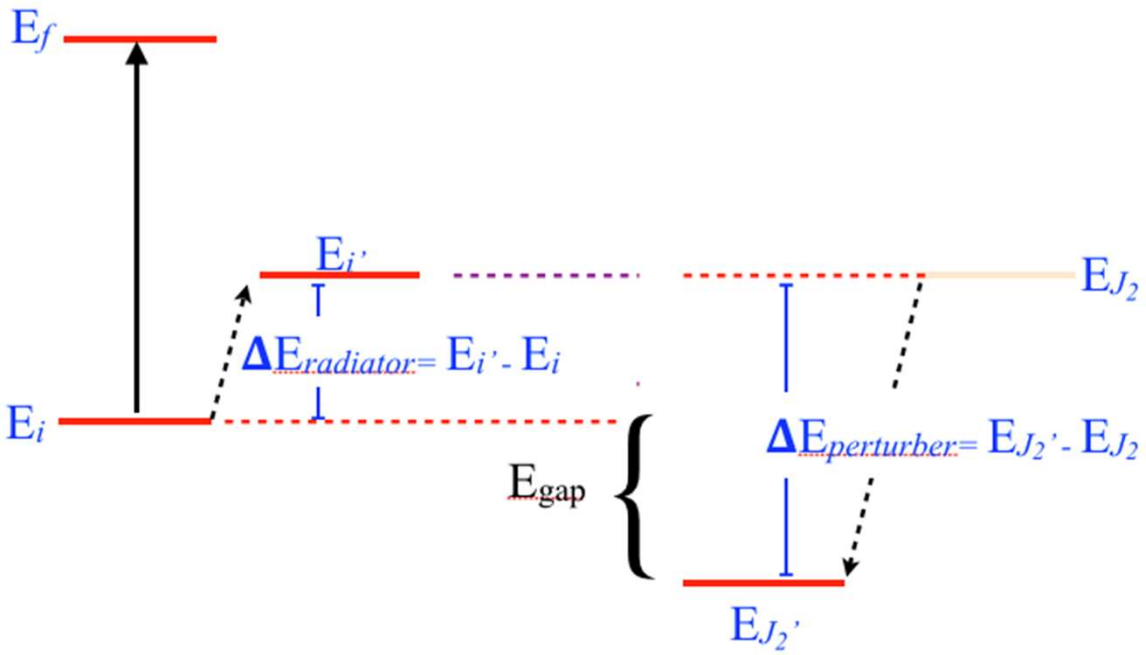




$$E_{gap} = \Delta E_{radiator} - \Delta E_{perturber}$$

R.R. Gamache, private communication

Line shape calculations

Semi-classical Complex Robert-Bonamy-Ma formalism

Semi-classical approach to line shape

$$(\gamma - i\delta)_{f \leftarrow i} = \frac{n_2}{2\pi c} \int_0^{+\infty} v\, f(v)\, dv \int_0^{+\infty} 2\pi\, b\, db \times \left[1 - e^{-i\langle S_1 + \mathrm{Im}\{S_2\}\rangle_{J_2}}\, e^{\langle \mathrm{Re}\{S_2\}\rangle_{J_2}}\right]$$

Classical mechanics

- Trajectory
- Hamilton's equations
- Resonance function
- Explicit integration of the velocity integral

Quantum mechanics

- Internal structure: vibration & rotation
- Probability of collisionally induced transition

Line shape calculations

Intermolecular potential

- Molecular system dependent
- General combination of:
  - Electrostatic components (dipole, quadrupole, octupole, hexadecapole)
  - Atom-Atom components
  - Induction component
  - London dispersion component

$$V = \sum_{l_1\, l_2\, l} \sum_{\substack{n_1\, m \\ m_1\, m_2}} \sum_{w\, q} \frac{U\left(l_1\, l_2\, l, n_1\, w\, q\right)}{R^{q+l_1+l_2+2w}}$$
$$C\left(l_1\, l_2\, l; m_1\, m_2\, m\right) D^{l_1}_{m_1\, n_1}\left(\Omega_1\right) D^{l_2}_{m_2\, 0}\left(\Omega_2\right) Y_{l\, m}\left(\omega\right)$$

4th rank (l_{max} = 4); 20th order ($l_1 + l_2 + 2w$)

G. G. Gray, K. E. Gubbins, Theory of Molecular Fluids, Clarendon Press (Oxford 1984)

Line shape calculations

Intermolecular potential

$$V^{at-at} = \sum_{i=1}^{n}\sum_{j=1}^{m} 4\epsilon_{ij}\left\{\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right\}$$

n and *m*: number of atoms in active molecule and perturber

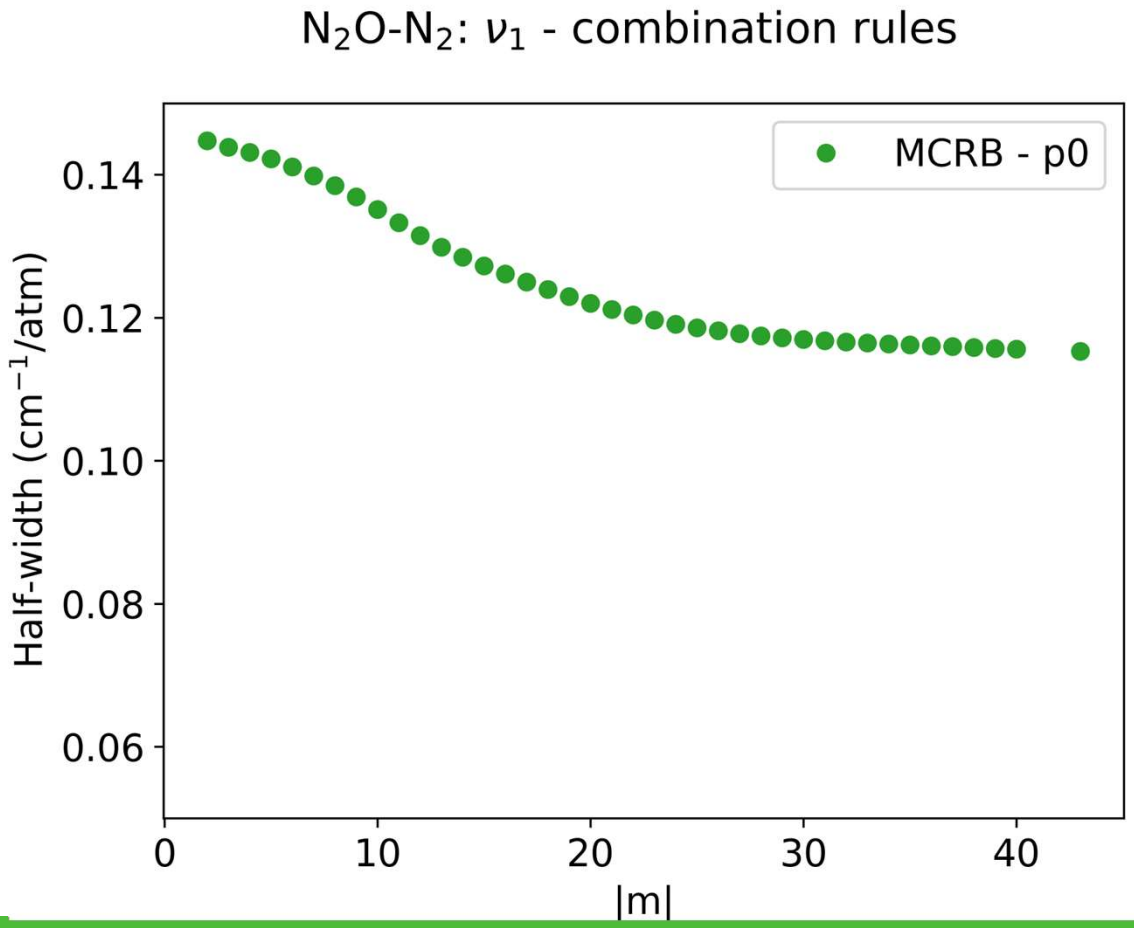
$\boldsymbol{\varepsilon}_{ij}$ and $\boldsymbol{\sigma}_{ij}$: Lennard-Jones parameter for atomic pairs

r_{ij}: atom-atom distance

- Many combination rules
- Very different results

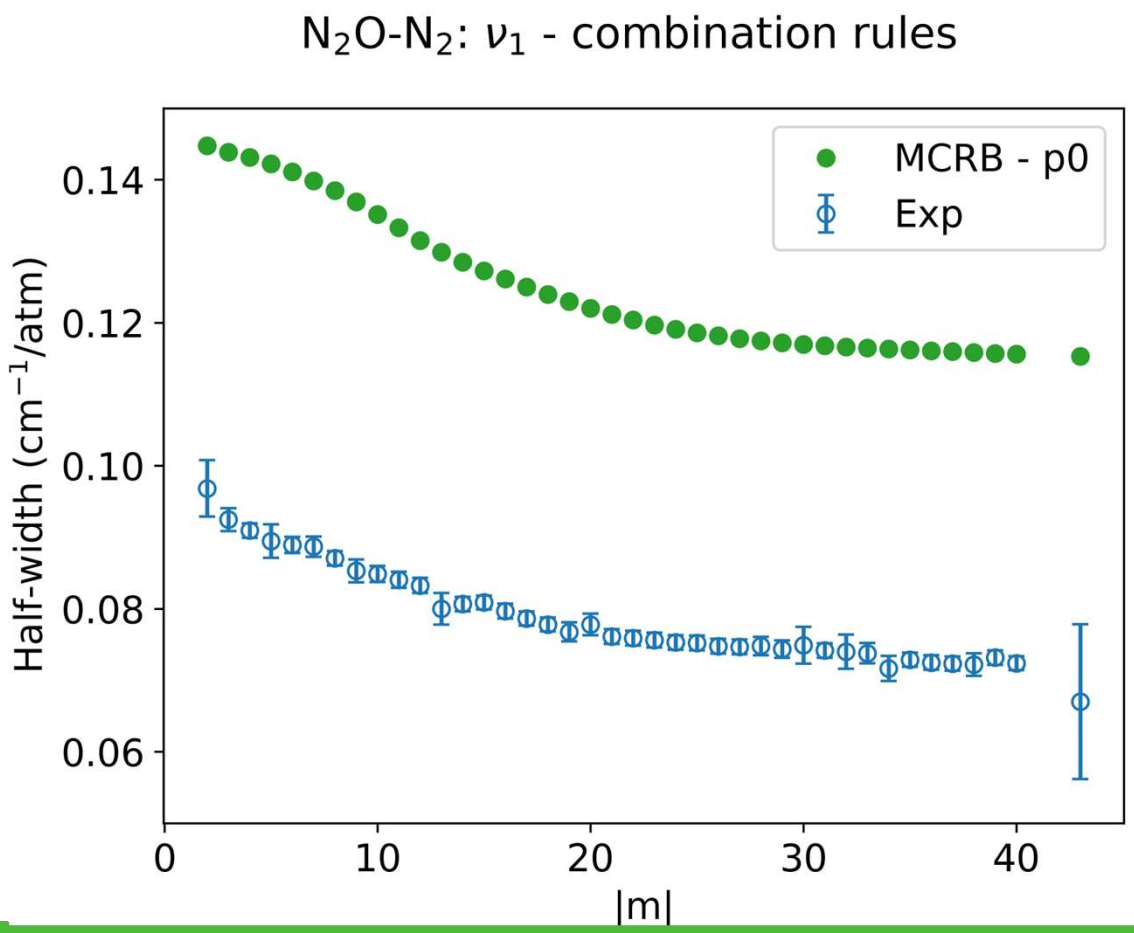
Line shape calculations

Intermolecular potential



Line shape calculations

Intermolecular potential



Line shape calculations

Intermolecular potential

$$V^{at-at} = \sum_{i=1}^{n}\sum_{j=1}^{m} 4\epsilon_{ij}\left\{\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right\}$$

n and *m*: number of atoms in active molecule and perturber

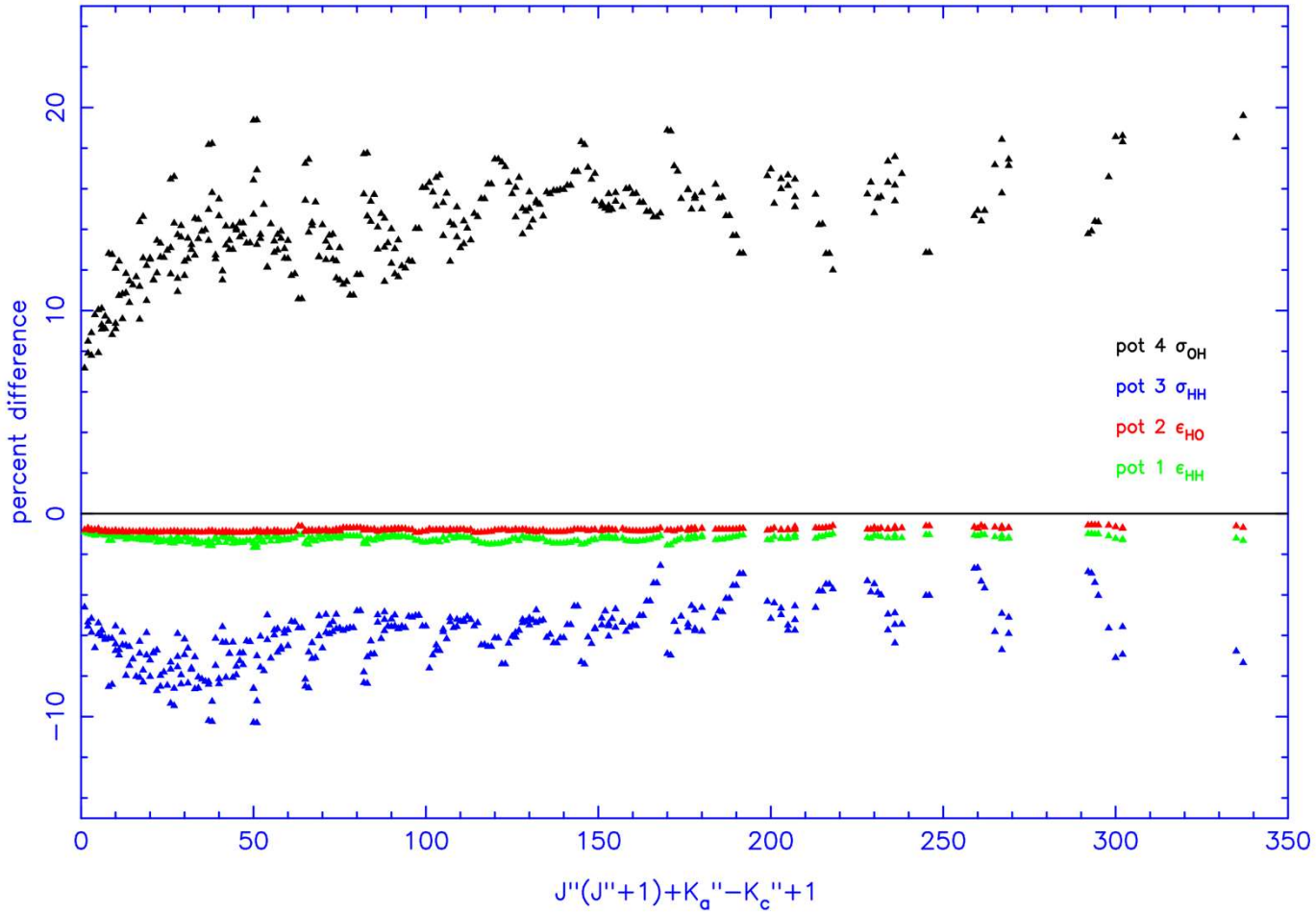
$\boldsymbol{\varepsilon}_{ij}$ and $\boldsymbol{\sigma}_{ij}$: Lennard-Jones parameter for atomic pairs

r_{ij}: atom-atom distance

- Many combination rules
- Very different results
- Adjust at-at parameters to fit reliable experimental data

Line shape calculations

Potential determination (H_2O-H_2)



Renaud *et al.*, Icarus (2018), 306, 275

Line shape calculations

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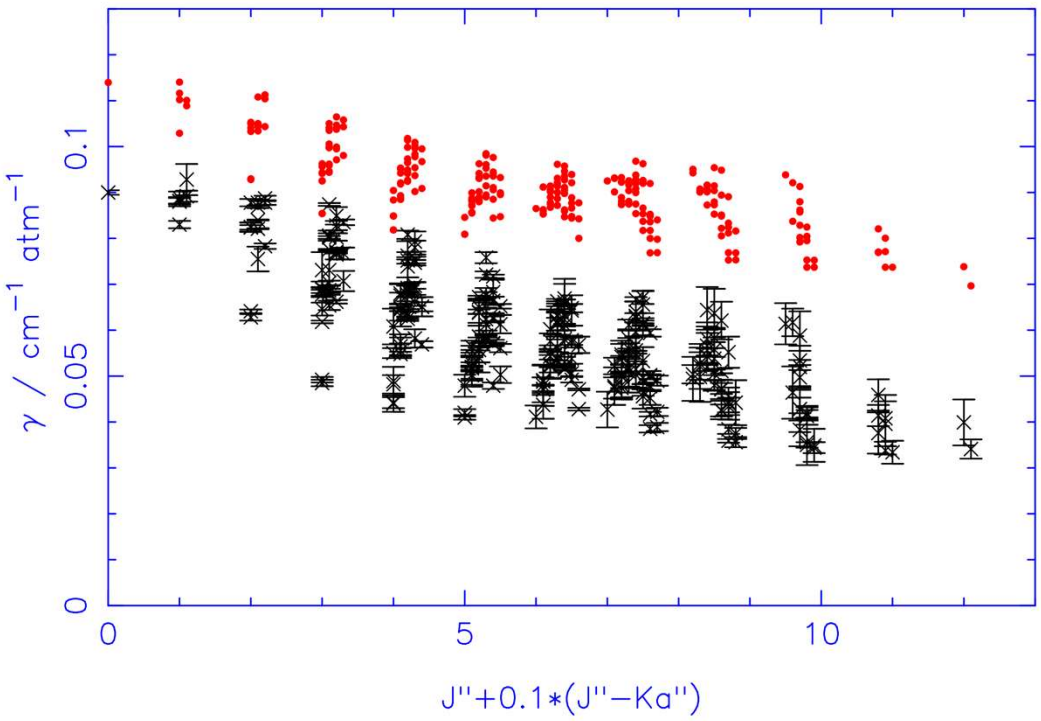
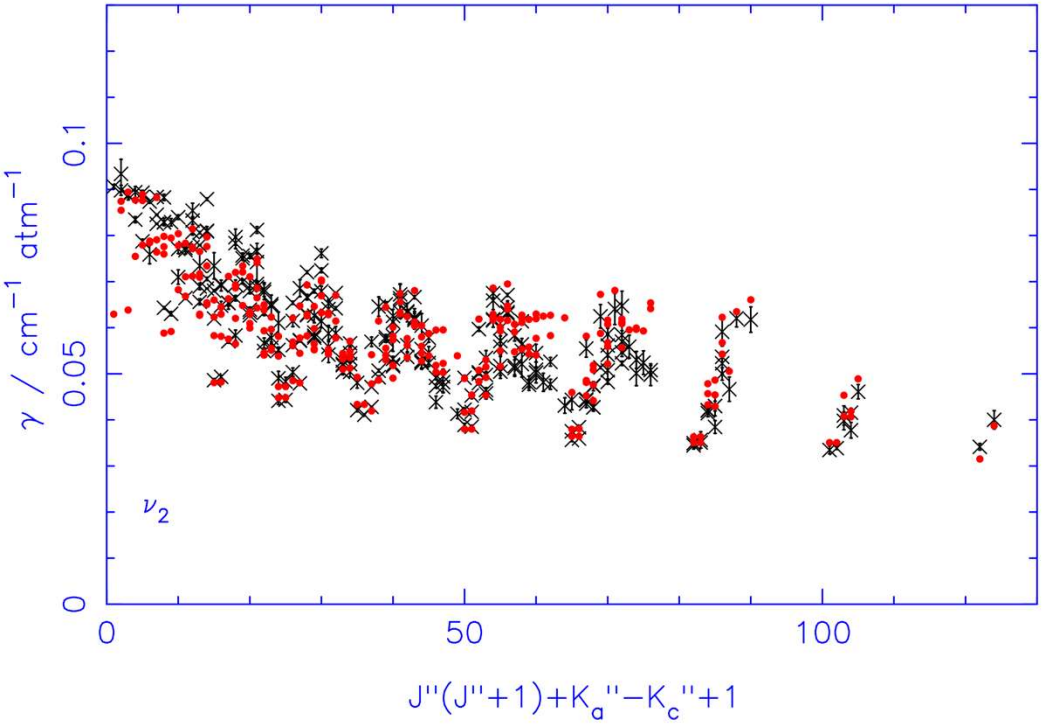


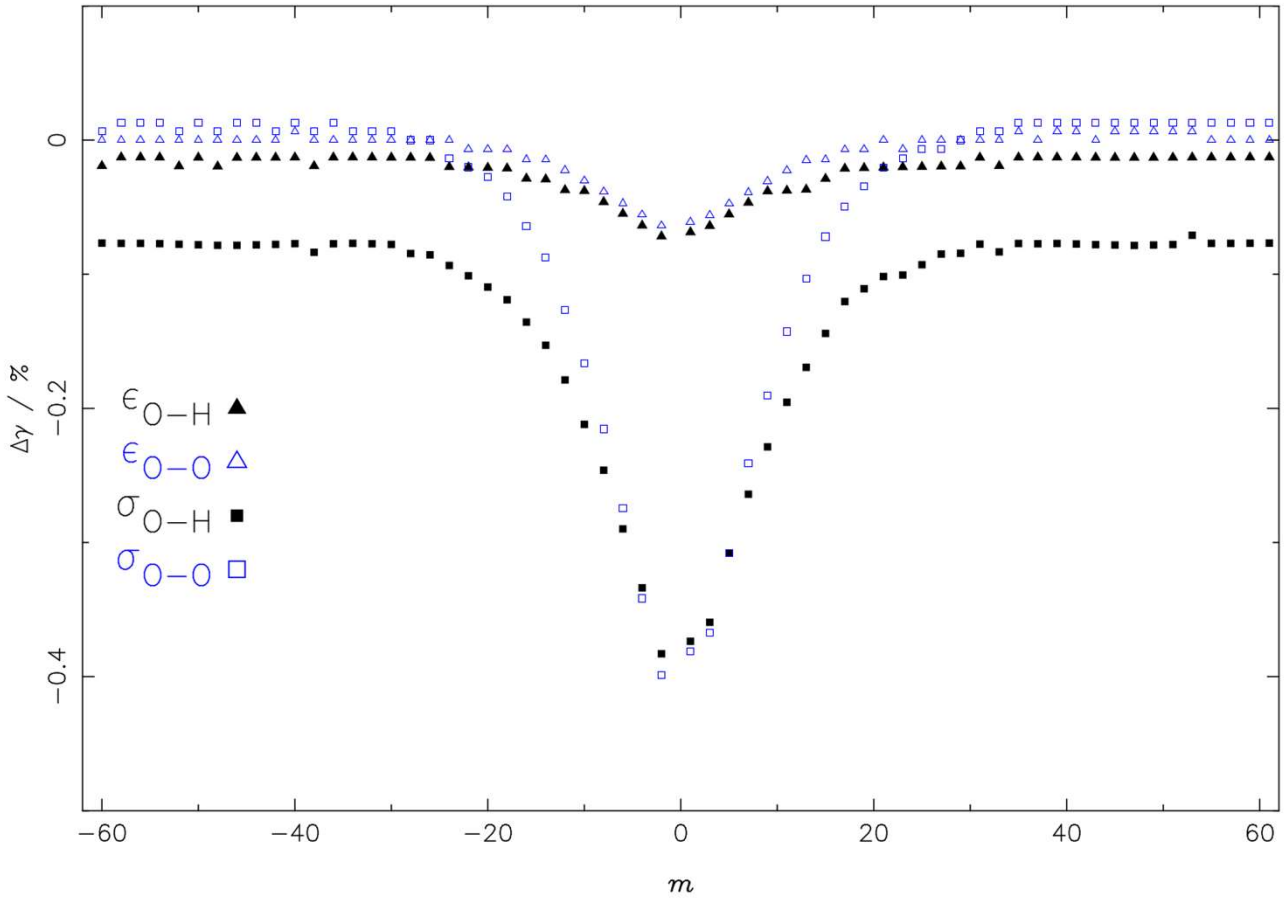


APD: -59.12% → APD: 0.57% (SD: 6.16%)

Renaud *et al.*, Icarus (2018), 306, 275

Line shape calculations

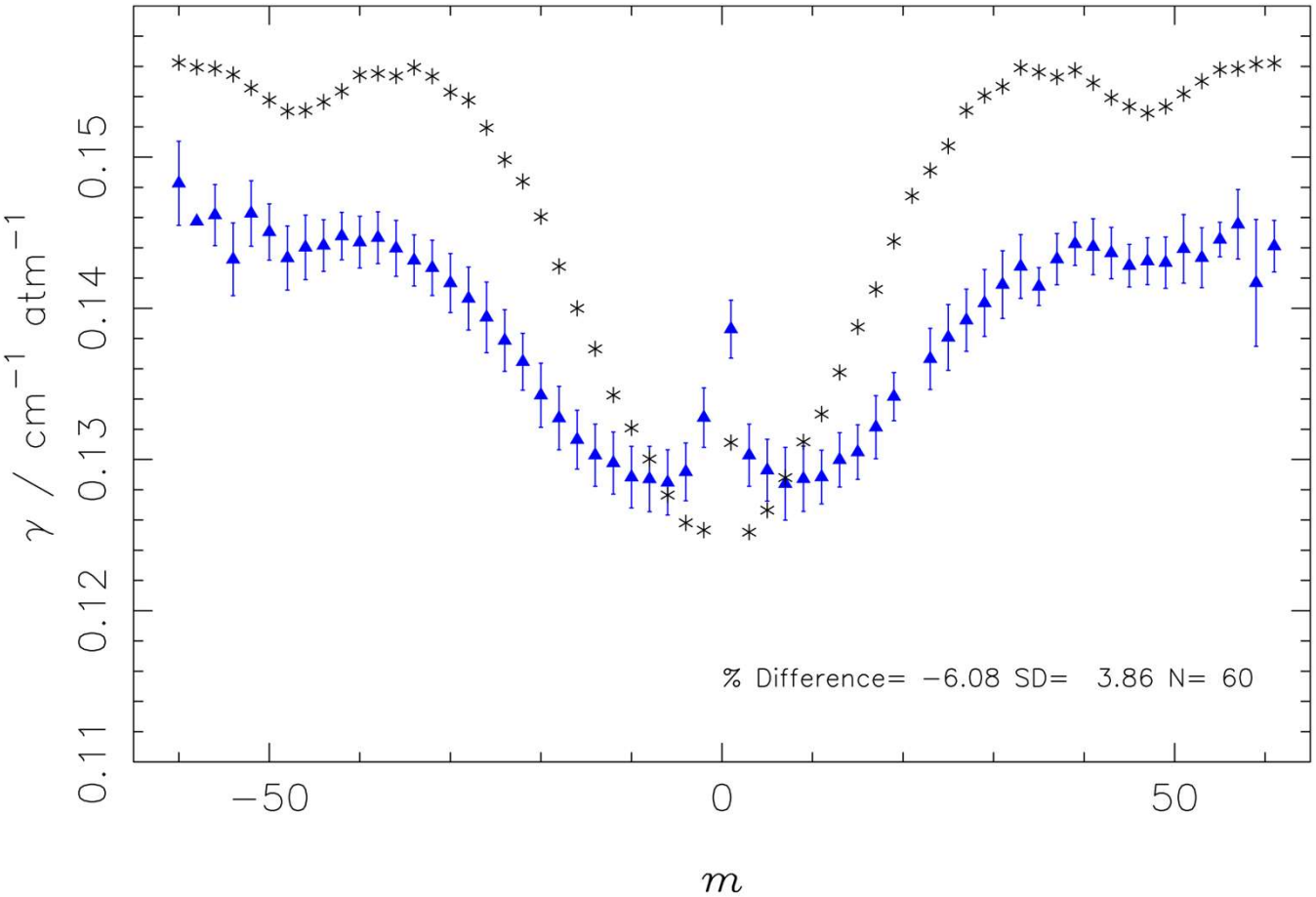
Potential determination (CO_2-H_2O)



Vispoel & Gamache, JQSRT, 316, 108896 (2024)

Line shape calculations

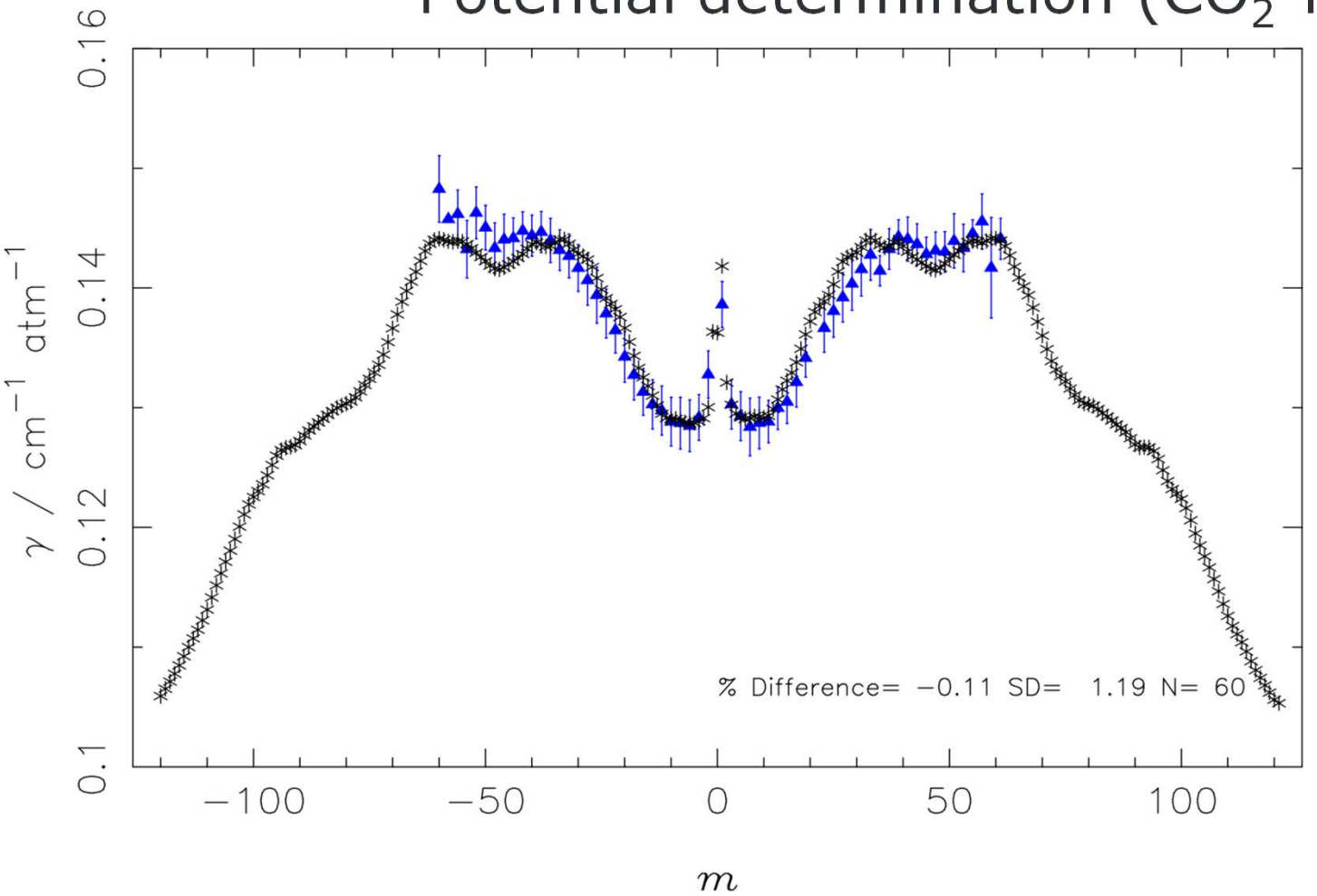
Potential determination (CO_2-H_2O)



Vispoel & Gamache, JQSRT, 316, 108896 (2024)

Line shape calculations

Potential determination (CO_2-H_2O)

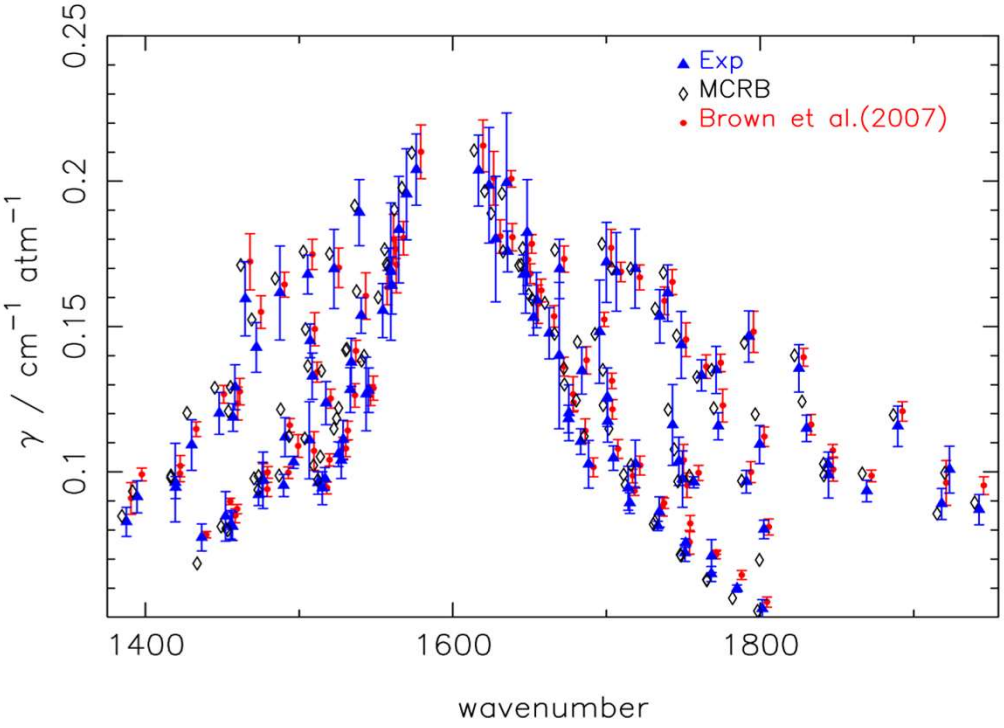


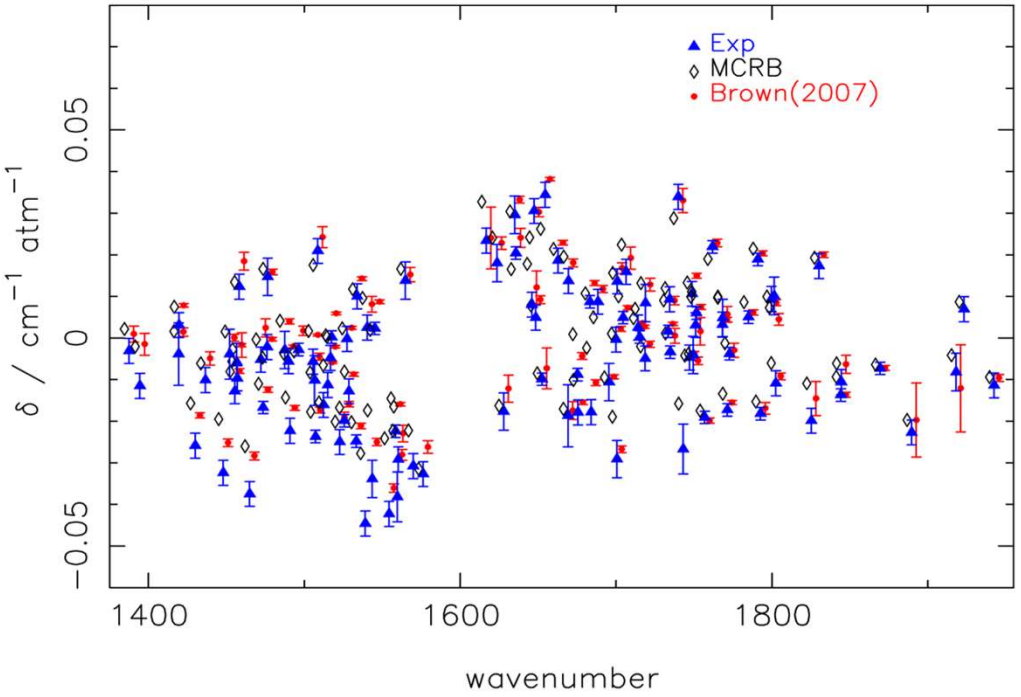
Vispoel & Gamache, JQSRT, 316, 108896 (2024)

Line shape calculations

Potential determination

H_2O-CO_2





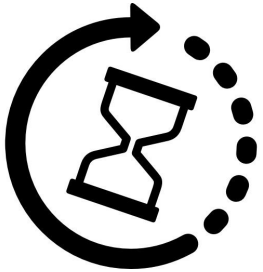
Régalia *et al.*, JQSRT, 231, 126 (2019)

Line shape calculations

What next ?

HITRAN 2020 (H_2O)

- 319 887 transitions
- 555 different vibrational bands



- Make calculations for selected bands
- Develop a physic's-based prediction algorithm

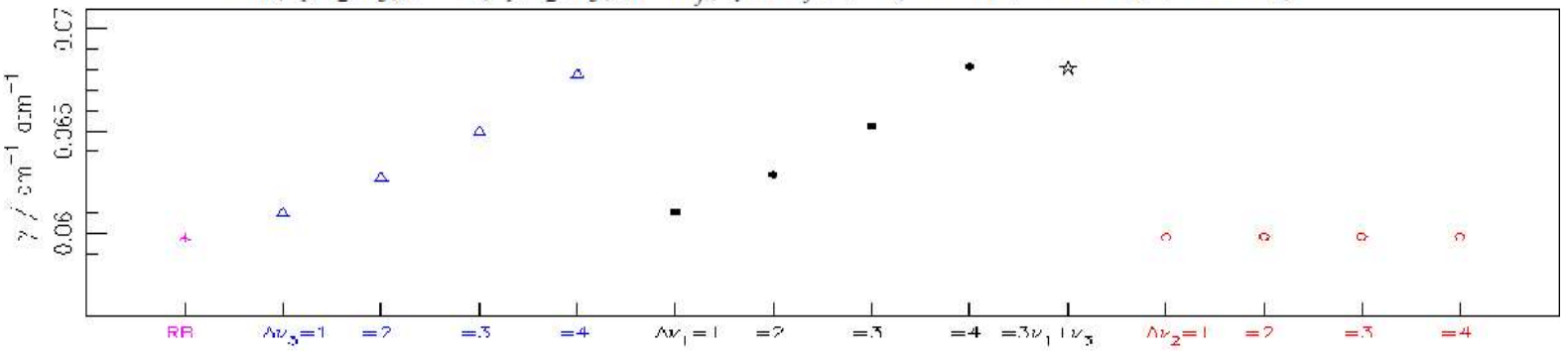
Line shape calculations

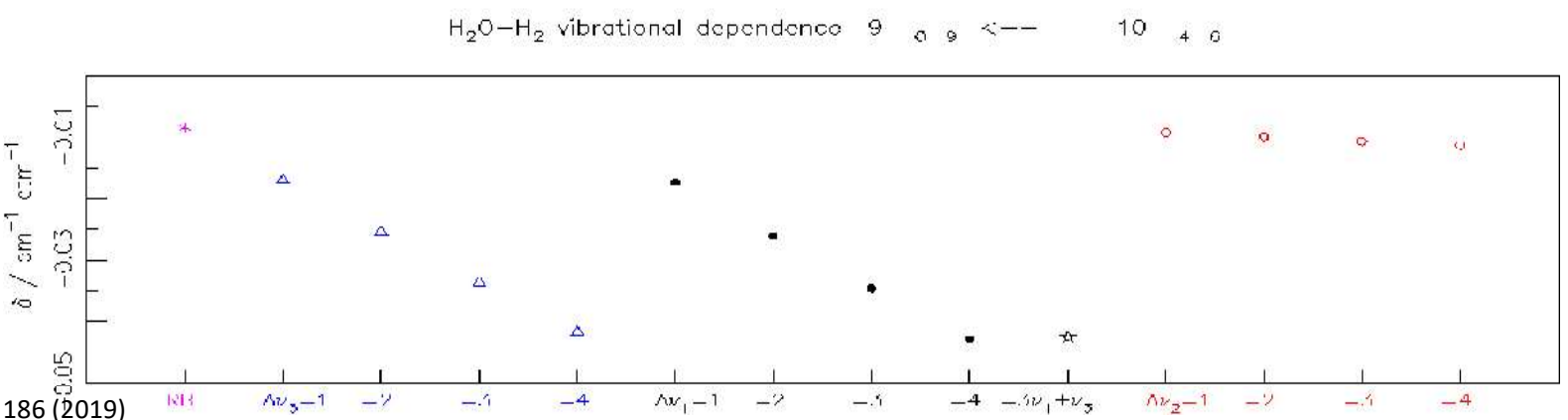
Vibrational dependence – Prediction routine

H_2O-H_2

$$\gamma[(v_1', v_2', v_3')f \leftarrow (v_1'', v_2'', v_3'')i] = \gamma^0_{f\leftarrow i} + A_{f\leftarrow i} \times (0.3\Delta v_1 + 0.07\Delta v_2 + 0.3\Delta v_3)^2,$$

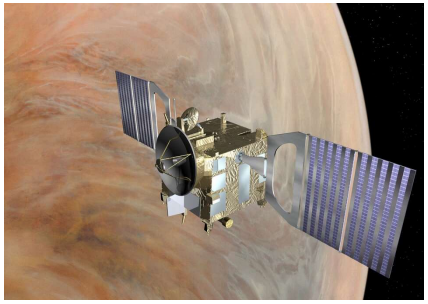
$$\delta[(v_1', v_2', v_3')f \leftarrow (v_1'', v_2'', v_3'')i] = \delta^0_{f\leftarrow i} + B_{f\leftarrow i} \times (0.3\Delta v_1 + 0.07\Delta v_2 + 0.3\Delta v_3).$$

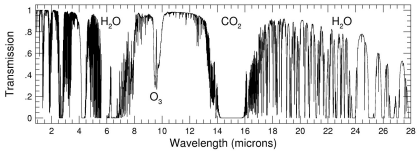




Gamache *et al.*, Icarus, 326, 186 (2019)

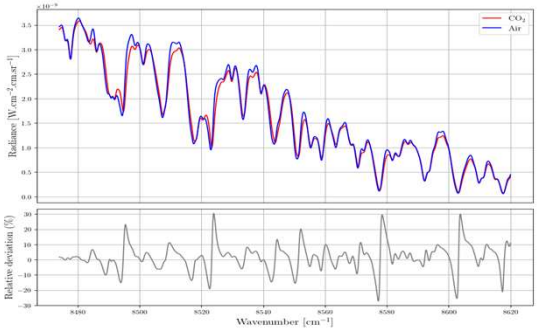
Summary



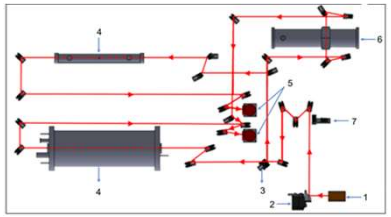


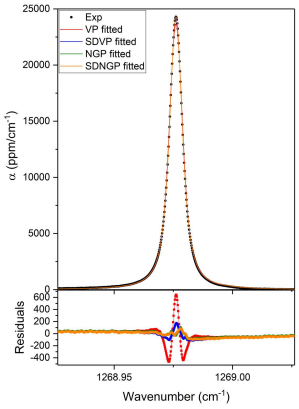
Spectroscopic parameters

Improve radiative transfer



Experimental measurements





Line shape calculations

$$(\gamma - i\delta)_{f\leftarrow i} = \frac{n_2}{2\pi c} \int_0^{+\infty} v\, f(v)\, dv \int_0^{+\infty} 2\pi\, b\, db \times \left[1 - e^{-i\langle S_1 + \mathrm{Im}\{S_2\}\rangle_{J_2}}\, e^{\langle \mathrm{Re}\{S_2\}\rangle_{J_2}}\right]$$

- CRBM calculations
- Prediction routine

WHO is WHO?

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Thank you for your attention