Mirdterm Scientific Report

Molecular line shape studies for atmospheric remote sensing

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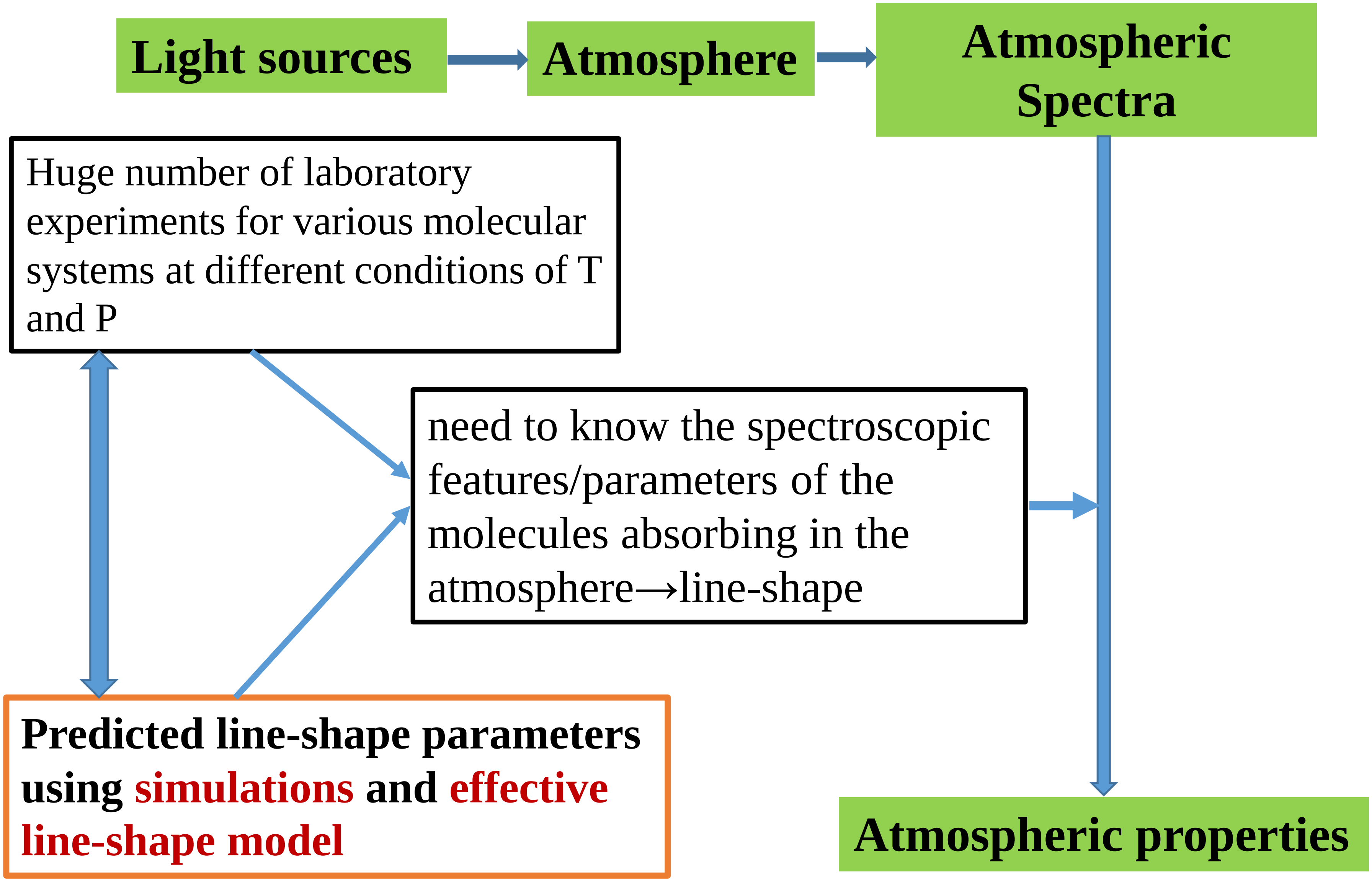
VIETNAM FRANCE UNIVERSITY

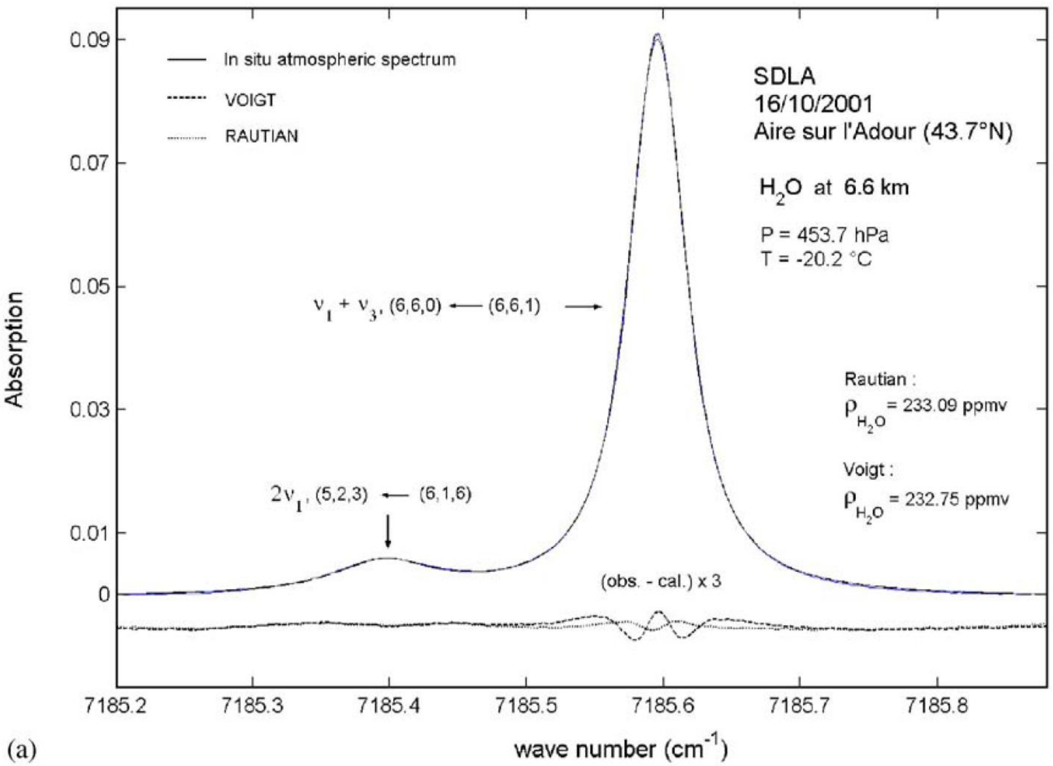
Outline

- Objective of thesis
- Method of research
- rCMDS for CO_2-N_2/O_2 and analysis procedure
- Conclusions and near future working plan
- Scientific activities

The spectroscopy of atmospheric molecules



Line-shape models



In situ absorption spectrum of tropospheric H_2O and its fit using the Voigt profile[1].

[1] G. Durry et al. JQSRT **94** 387–403 (2005).

→ Collision effect - Γ_L

→ Doppler effect - Γ_D

→ Dicke effect: velocity changing collisions

→ Quadratic speed dependence of line width and shift

→ Correlation: velocity-rotational state-changing collisions

Hartmann-Tran profile (HTp)

+ Line mixing

HT + LM profile

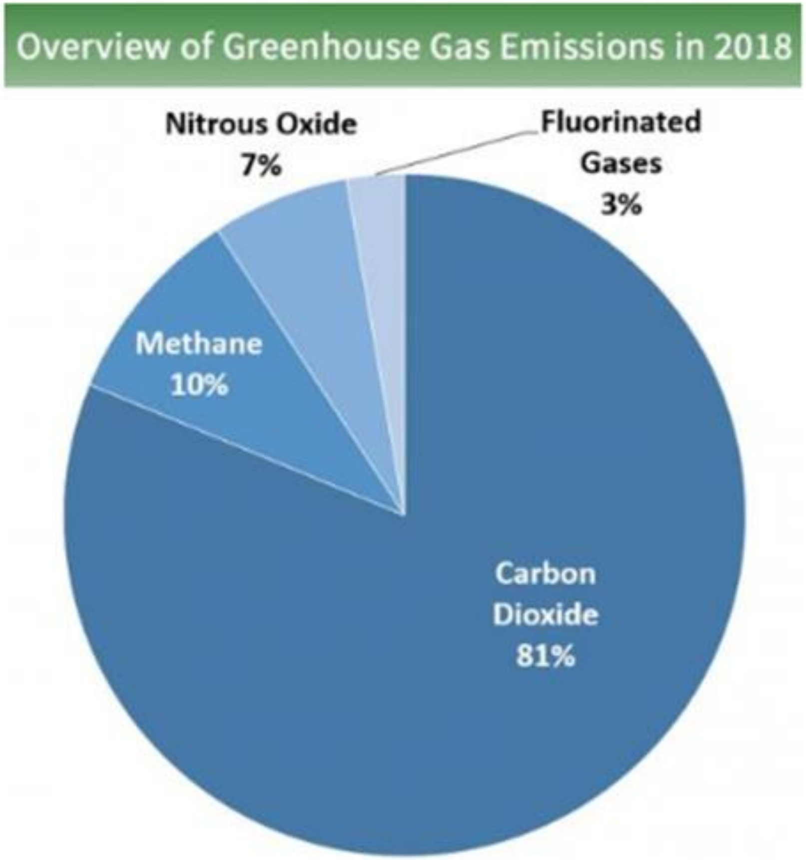
The Hartmann-Tran (HT) profile

→ the new reference line-shape model for high resolution atmospheric remote sensing

→ remaining problems

- Be tested with a limited number of measurements: relevant parameters are not available for many lines of various molecular systems
- Huge amount of works has to be done for laboratory experiments under atmospheric temperature and pressure conditions to deduce HTp parameters for atmospheric applications

Considered molecules



→ CO_2
→ N_2O
→ H_2O

https://www.epa.gov/ghgemissions/overview-greenhouse-gases

Objectives of Research

- Accurate predictions of molecular line shapes for atmospheric pressure and temperature conditions for CO_2 N_2O, CH_3Cl and H_2O

- Combination of simulations and a limited number of measurements to generate parameters of the HTp for high precision remote sensing; The measurements are used to validate the prediction.

Method of the research

* **Simulations**: Using re-quantized classical molecular dynamic simulations to directly predict the spectral line shapes by Fourier transformation of the dipole auto-correlation function.

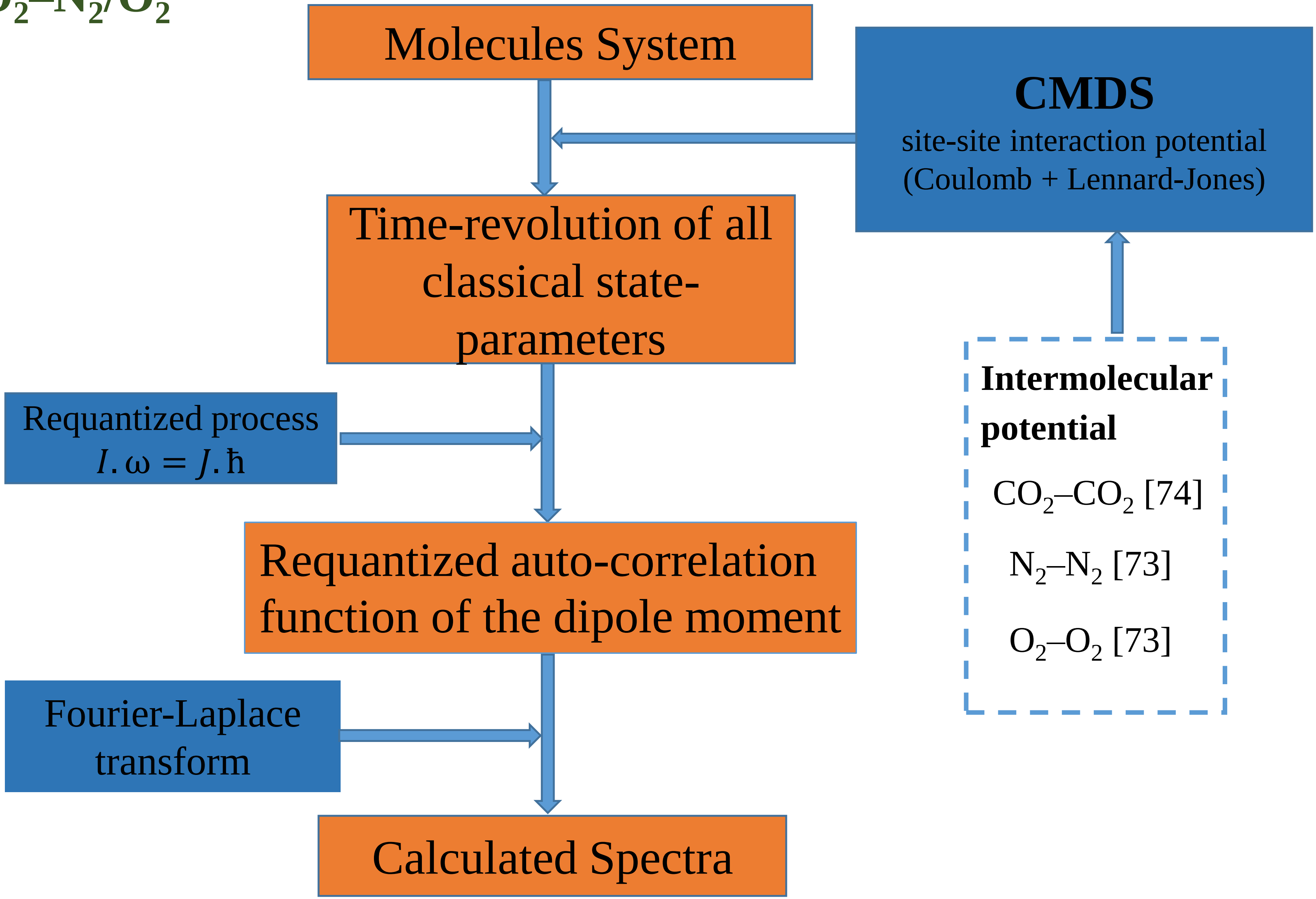
* **Analysis method**: Multi-fitting with HTp and its limited models (Voigt, speed-dependent Voigt, Nelkin–Ghatak, **speed dependent Nelkin–Ghatak**)

* **Comparison** between measured data and predicted parameters $\rightarrow$ strategy to complete HTp data for remote sensing application.

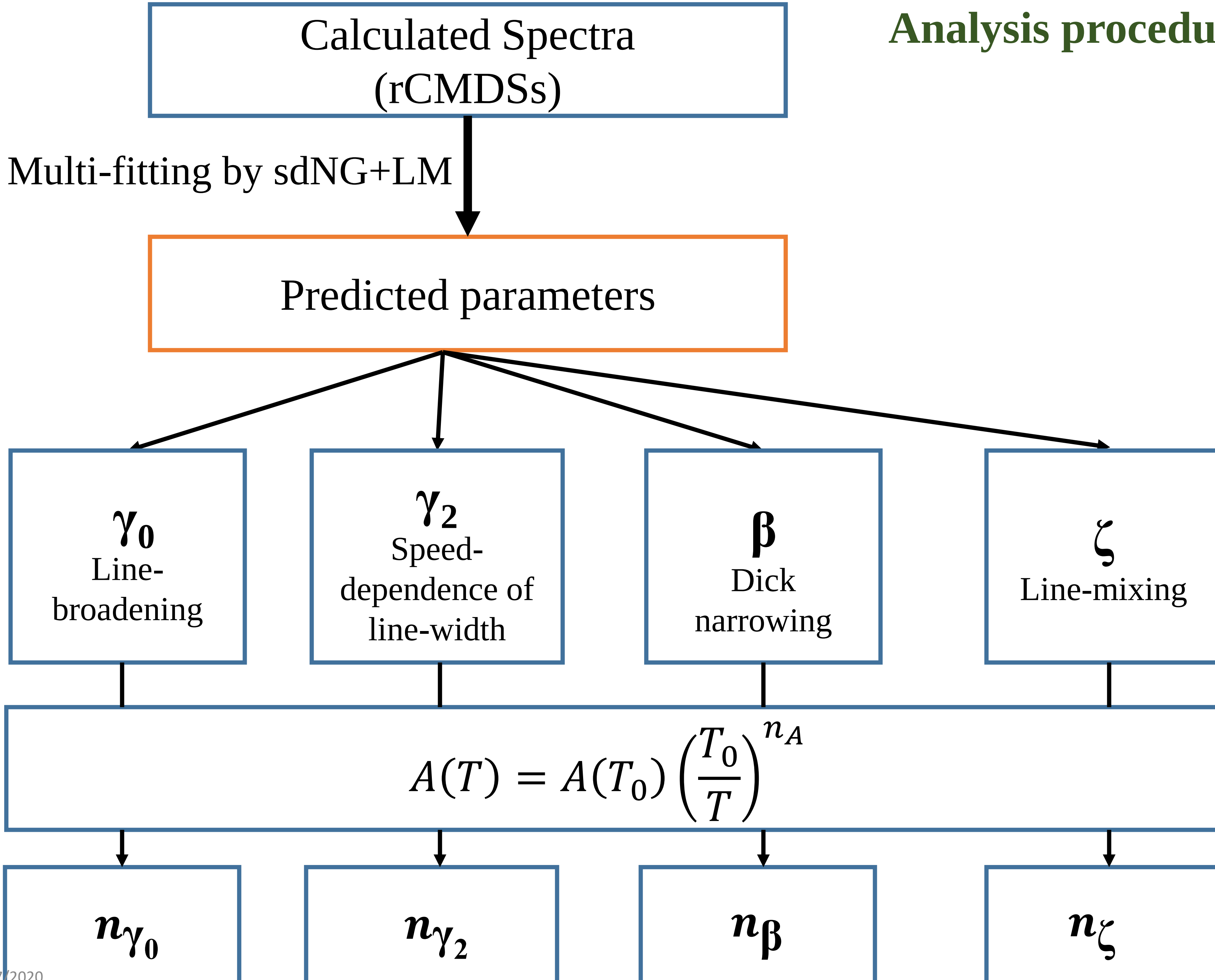
Considered molecular system	**Temperature ranges**	**Pressure**	**Line-shape models used**	**Line-shape parameters**
CO2-N2	200, 250, 296K	1 atm with 50% of CO_2	HTp + LM and its limited line-shape models	- γ_0, γ_2, β, ξ - $n\gamma_0$, $n\gamma_2$, $n\beta$, $n\xi$
CO2-O2	200, 250, 296, 350K			
CO2-air	200, 250, 296K			
N2O-air	200, 250, 296K	1 atm with 50% of N_2O		

Table 1: Information of molecular systems have been considered

Requantized Classical Molecular Dynamics Simulations for CO_2–N_2/O_2



Analysis procedure



Results and discussions

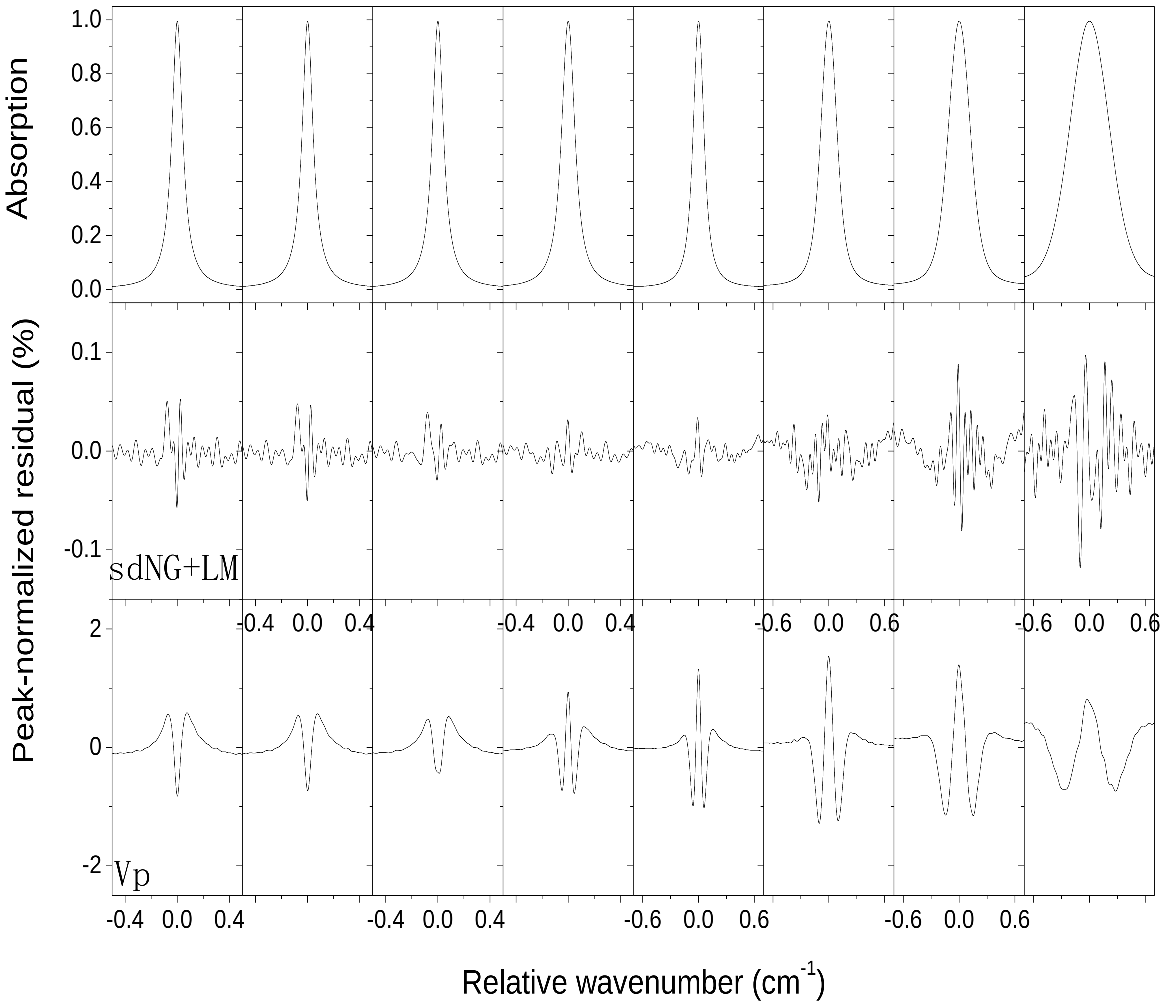
- **rCMDS-calculated spectra**
- **The line-shape parameters and their temperature dependences**

- Line broadening coefficients
- The speed dependence of the line width
- The Dicke narrowing parameter
- The first-order line-mixing parameter

Results for CO_2/N_2

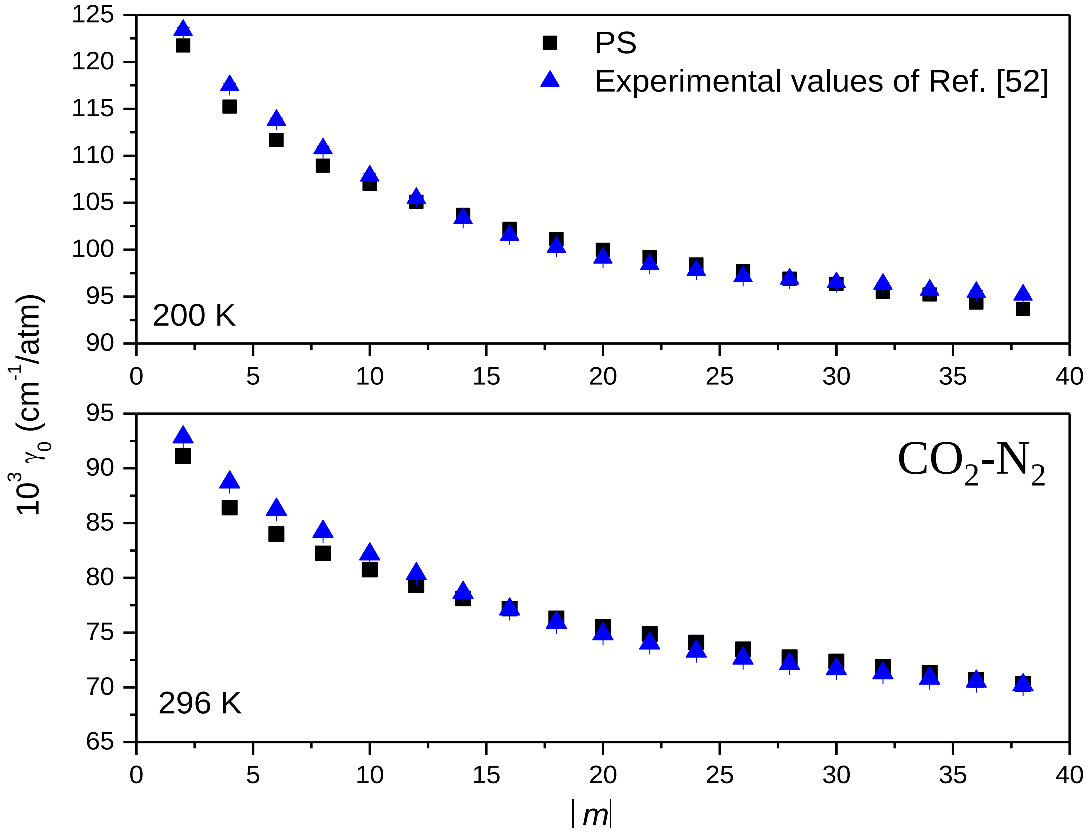
rCMDS-calculated spectra

P(10) of CO_2-N_2 at 200K



very good fits (residual ~ 0.1%)
sdNG+LM can be used to analyze the spectra

The line-broadening coefficient and its temperature dependence

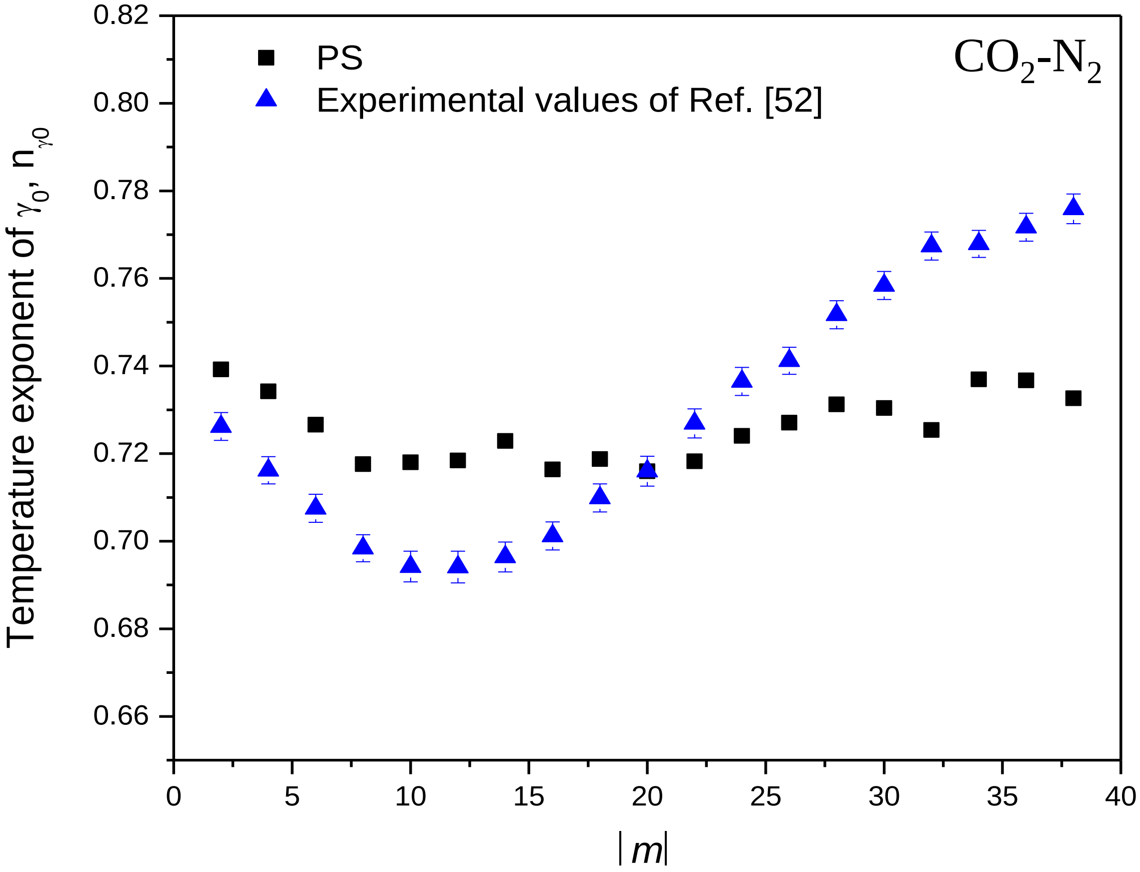


→very good agreement with [52] for both 200 and 296K

→The averaged differences: 0.9 (±0.6) % (at 200 K); 1.1 (±0.8) % (at 296 K)

[52] J. S. Wilzewski, M. Birk, J. Loos, and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer **206**, 296–305 (2018).

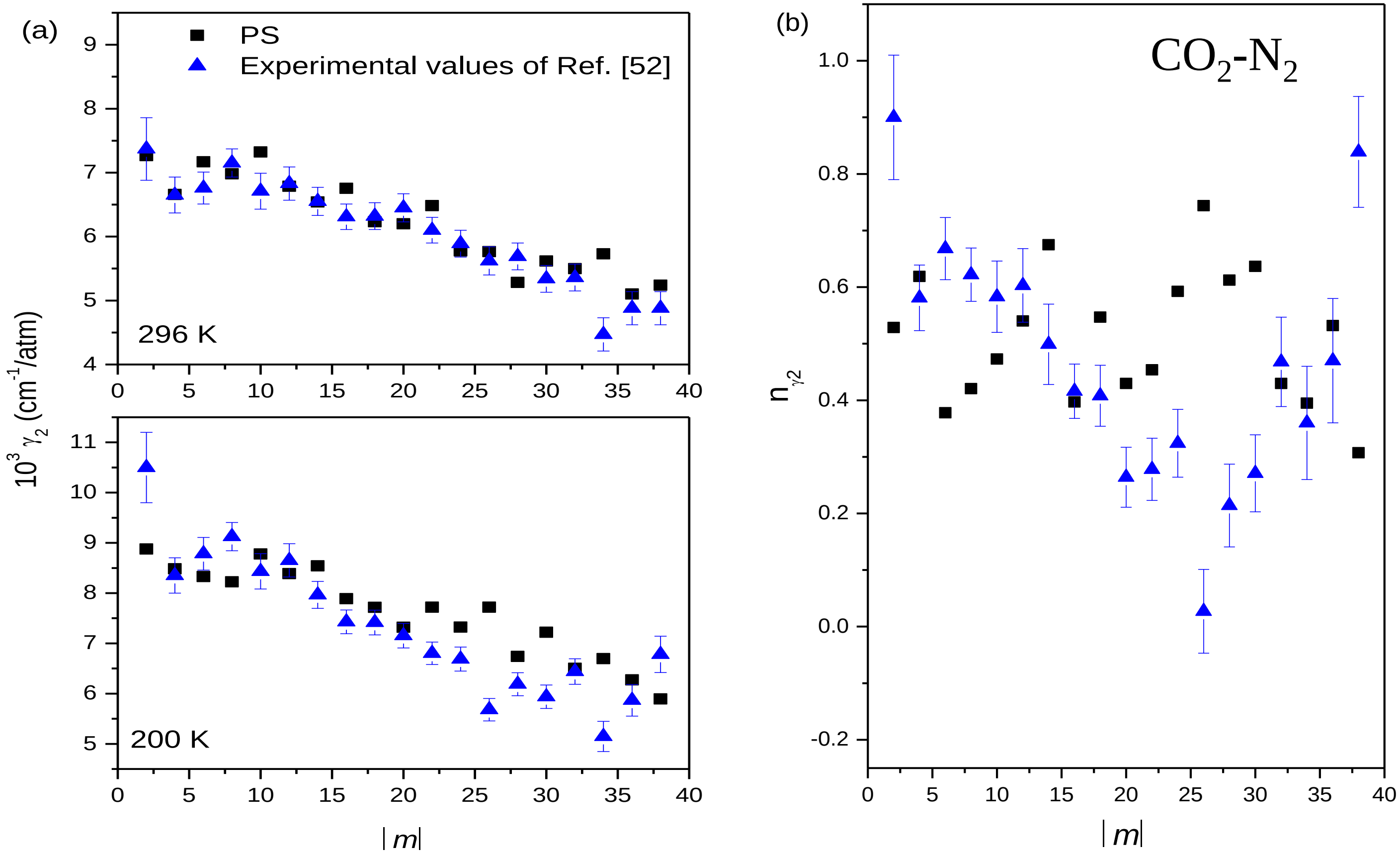
The line-broadening coefficient and its temperature dependence



→ **"non-smooth"** → limited signal-to-noise ratio; considered temperatures

[52] J. S. Wilzewski, M. Birk, J. Loos, and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer **206**, 296–305 (2018).

The speed dependence of the line width and its temperature dependence



→very good agreement with [52]

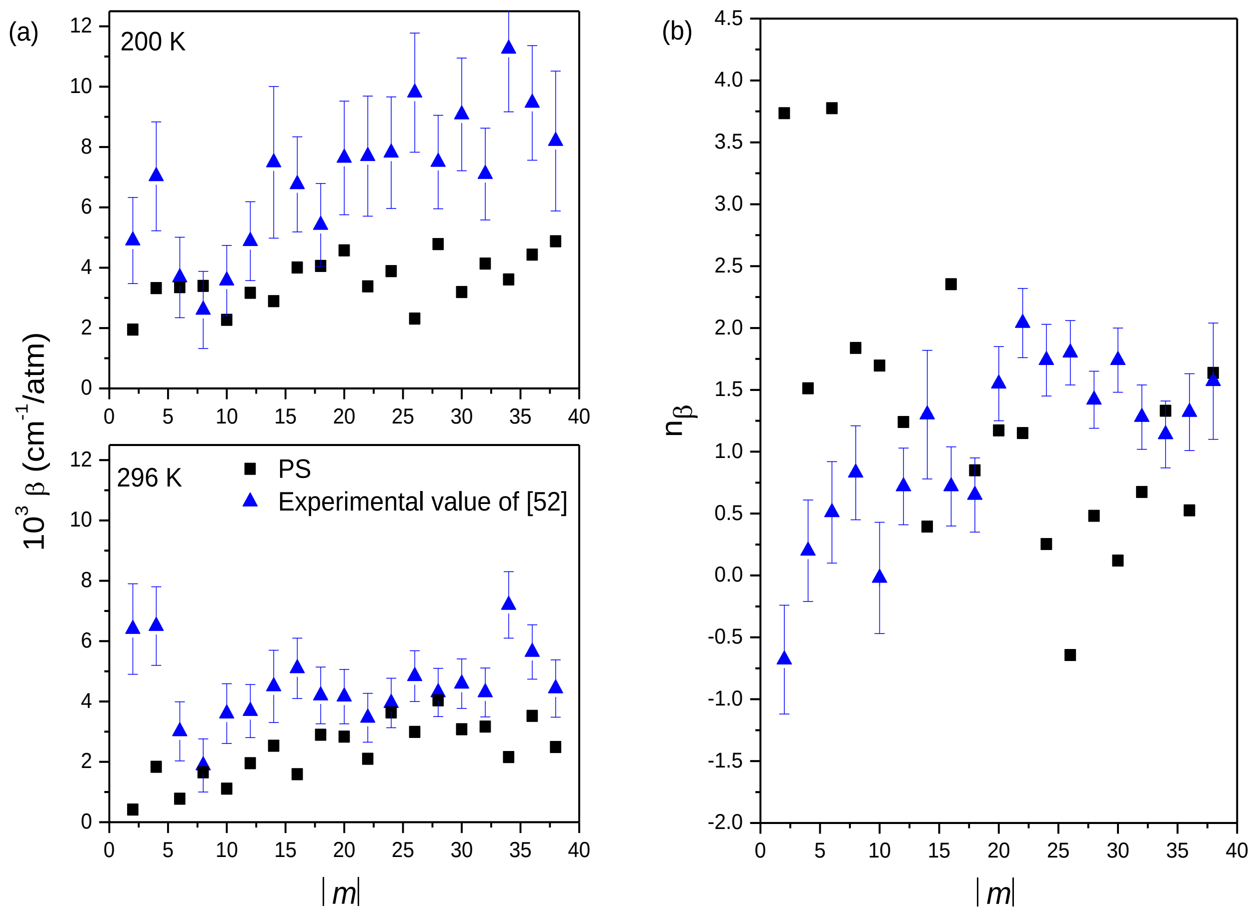
→The averaged differences

*** γ_2: 10% (200 K); 5%(296 K)**

*** $n_{\gamma 2}$: 0.46 (200K); 0.51 (296K)**

[52] J. S. Wilzewski, M. Birk, J. Loos, and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer **206**, 296–305 (2018).

The Dicke narrowing parameter and its temperature dependence

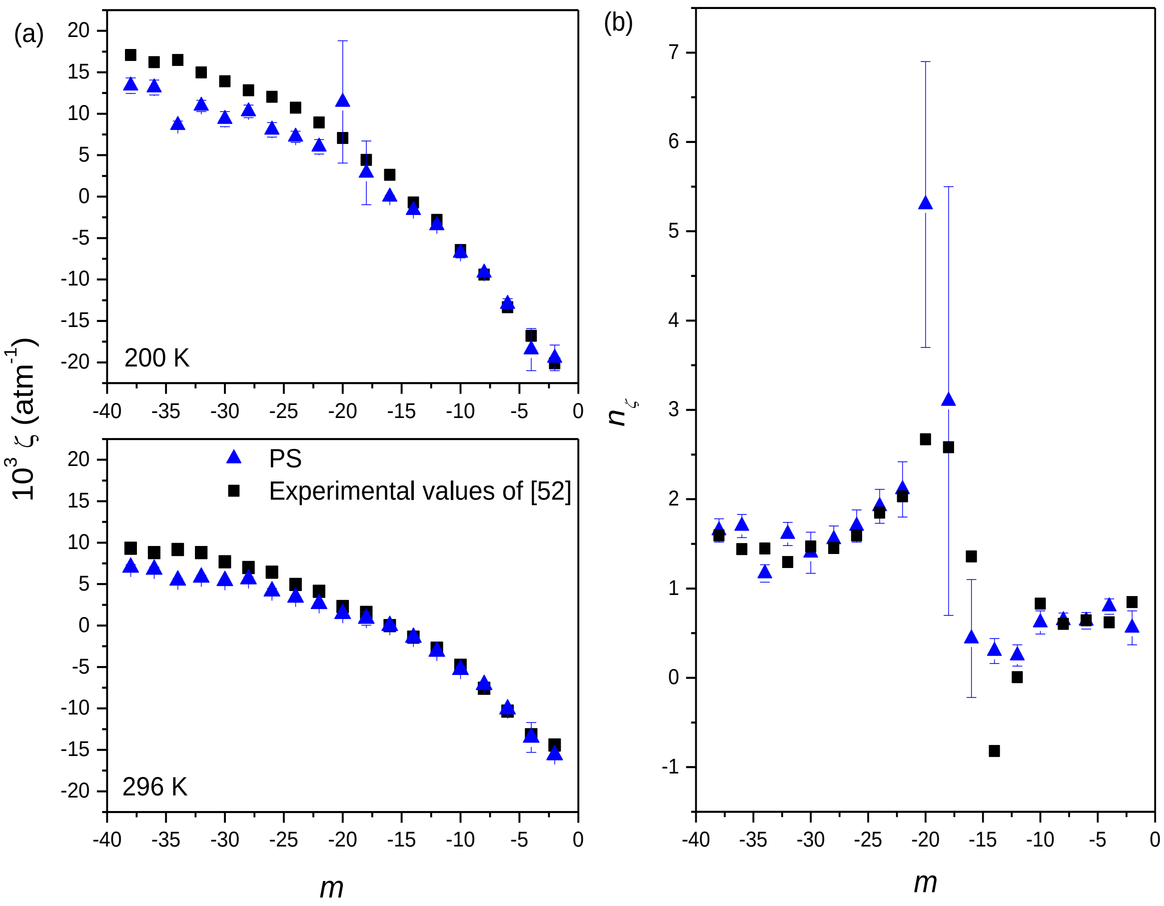


→ $\beta_{cal} < \beta_{[52]}$

→ **rather in good agreement.**

[52] J. S. Wilzewski, M. Birk, J. Loos, and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer **206**, 296–305 (2018).

The first-order line-mixing parameter and its temperature dependence



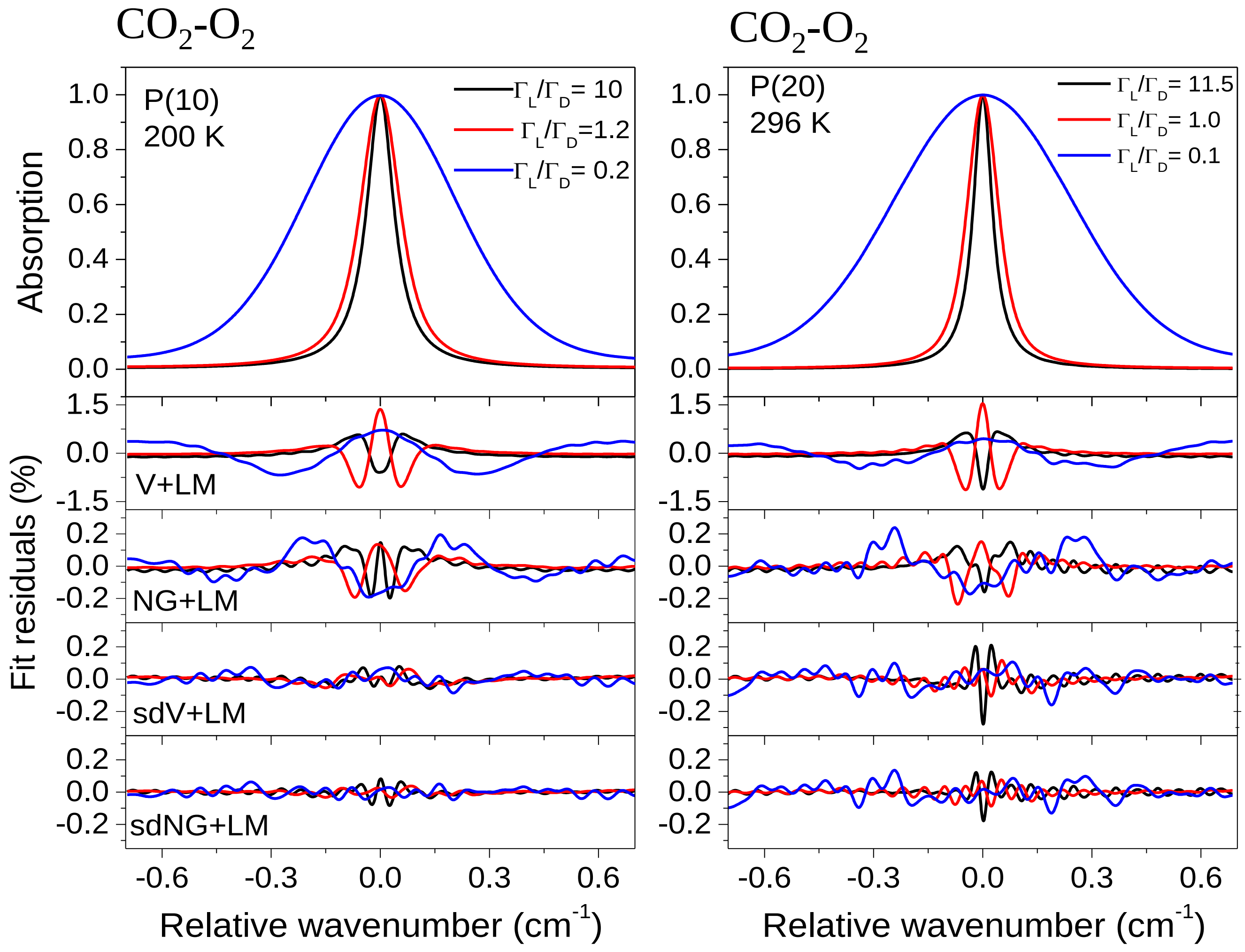
→very good agreement with [52]

12/17/2020

[52] J. S. Wilzewski, M. Birk, J. Loos, and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer **206**, 296–305 (2018).

Results for CO_2-O_2/air

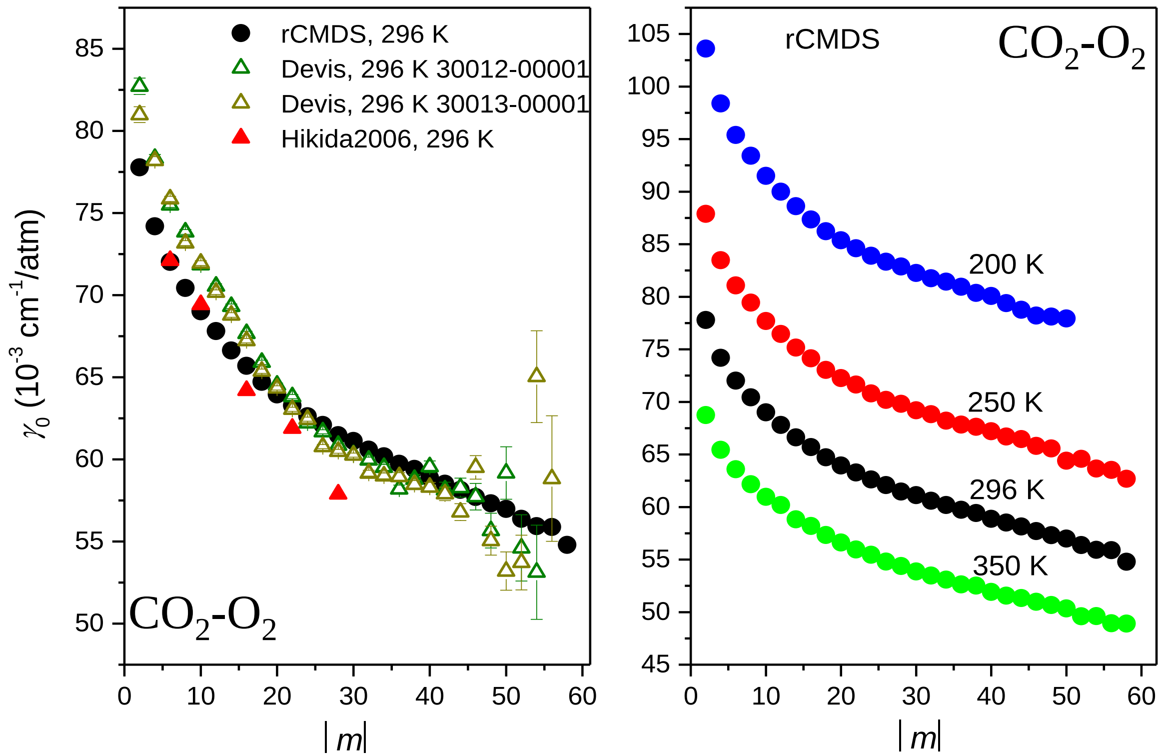
rCMDS-calculated spectra



sdNG+LM can be used to analyze the spectra

Results for CO_2-O_2/air

The line-broadening coefficient and its temperature dependence



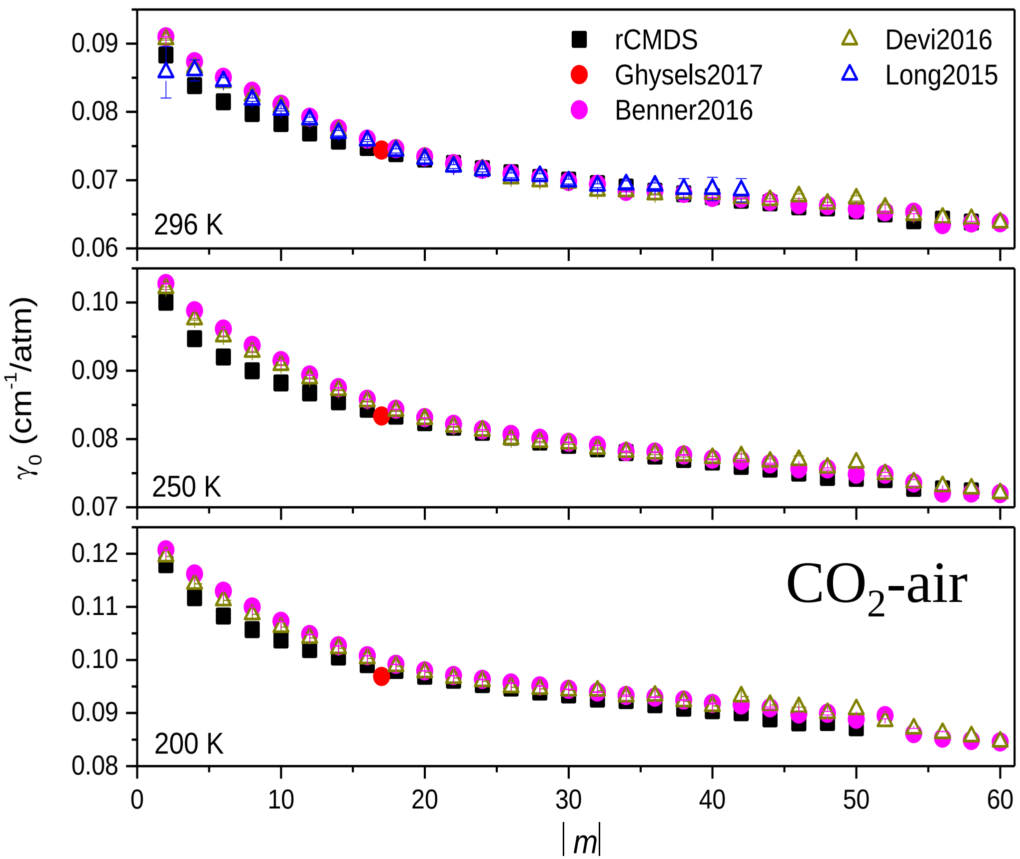
→**rather good agreement with measured results**

(average difference ~ 2%)

→ **the difference: due to the different used models**

[77] Devi VM, Benner DC, Miller CE, Predoi-Cross A. J Quant Spectrosc Radiat Transf 2010;111:2355–69.
[78] Hikida T, Yamada KMT. J Mol Spectrosc 2006;239:154–9.

The line-broadening coefficient and its temperature dependence

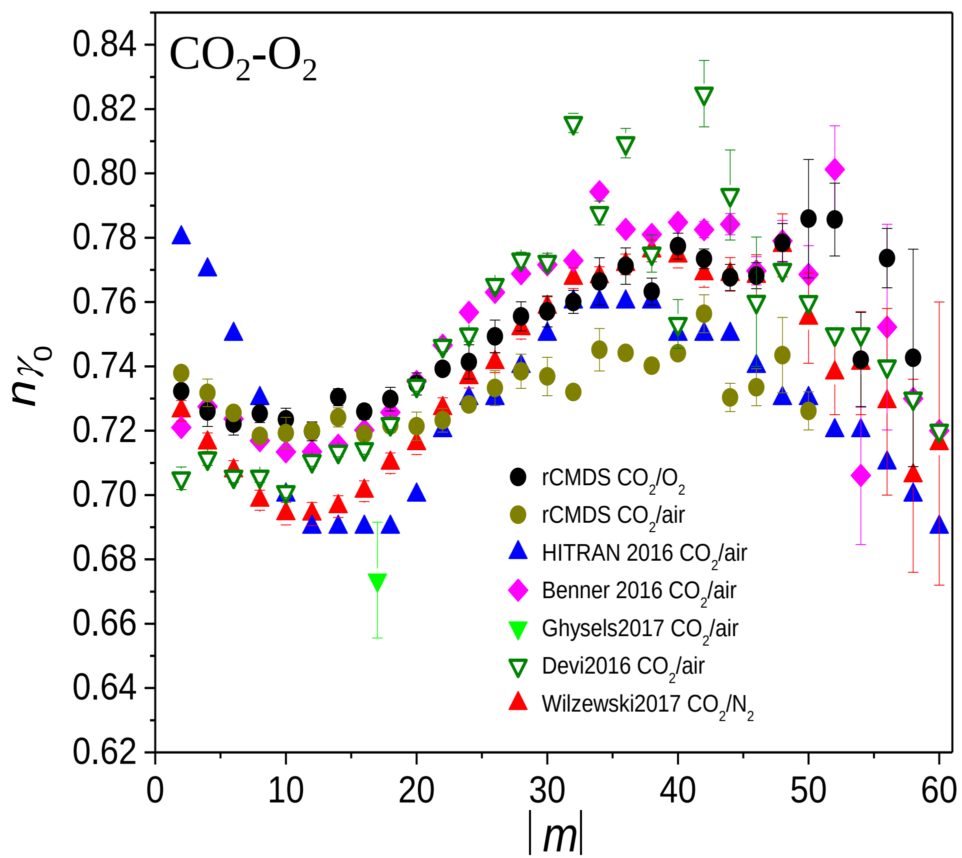


$$\gamma_0^{air}(T) = 0.79\gamma_0^{N2}(T) + 0.21\gamma_0^{O2}(T)$$

→good agreement with the predictions

[56] V. M. Devi, D. C. Benner, K. Sung, L. R. Brown, T. J. Crawford, C. E. Miller, B. J. Drouin, V. H. Payne, S. Yu, M. A. H. Smith, A. W. Mantz, and R. R. Gamache, J. Quant. Spectrosc. Radiat. Transfer **177**, 117 (2016).
[65] Long DA, Wojtewicz S, Miller CE, Hodges JT. J Quant Spectrosc Rad Transf 2015;161:35–40.
[66] Benner DC, Devi VM, Sung K, et al. J Mol Spectrosc 2016;326:31–47.
[68] Ghysels M, Liu Q, Fleisher AJ, Hodges JT. Appl Phys B 2017;123-124:1–13.

The line-broadening coefficient and its temperature dependence



→ predicted values O_2: quite close to air-broadening values

→ air-broadening: good agreement (7-8%)

→rCMDS can be fully used to predict the temperature dependences

[56] V. M. Devi, D. C. Benner, K. Sung, L. R. Brown, T. J. Crawford, C. E. Miller, B. J. Drouin, V. H. Payne, S. Yu, M. A. H. Smith, A. W. Mantz, and R. R. Gamache, J. Quant. Spectrosc. Radiat. Transfer **177**, 117 (2016).

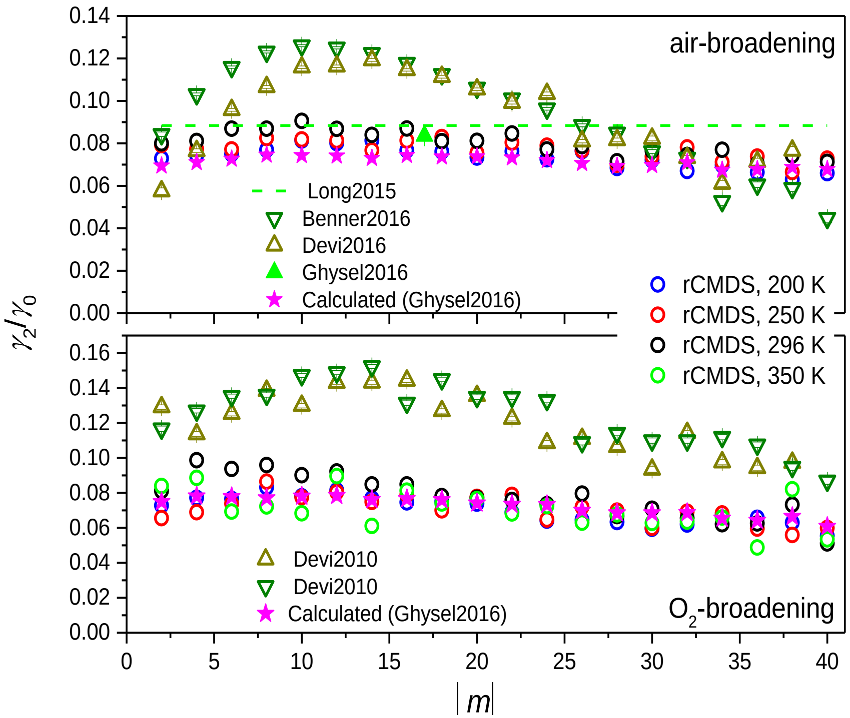
[66] Benner DC, Devi VM, Sung K, et al. J Mol Spectrosc 2016;326:31–47.

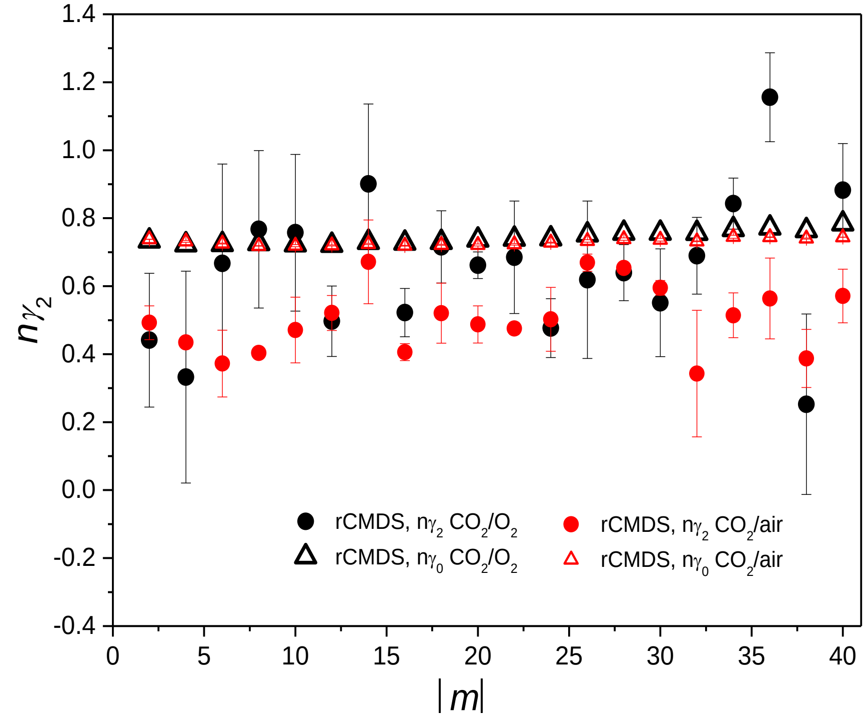
[68] Ghysels M, Liu Q, Fleisher AJ, Hodges JT. Appl Phys B 2017;123-124:1–13.

[69] Wilzewski JS, Birk M, Loos J, Wagner G. J Quant Spectrosc Rad Transf 2018;206:296–305.

[79] Gordon IE,…The HITRAN2016 molecular spectroscopic database. J Quant Spectrosc Radiat Transf 2017;203:3–69. doi:10.1016/j.jqsrt. 2017.06.038.

The speed dependence of the line width and its temperature dependence





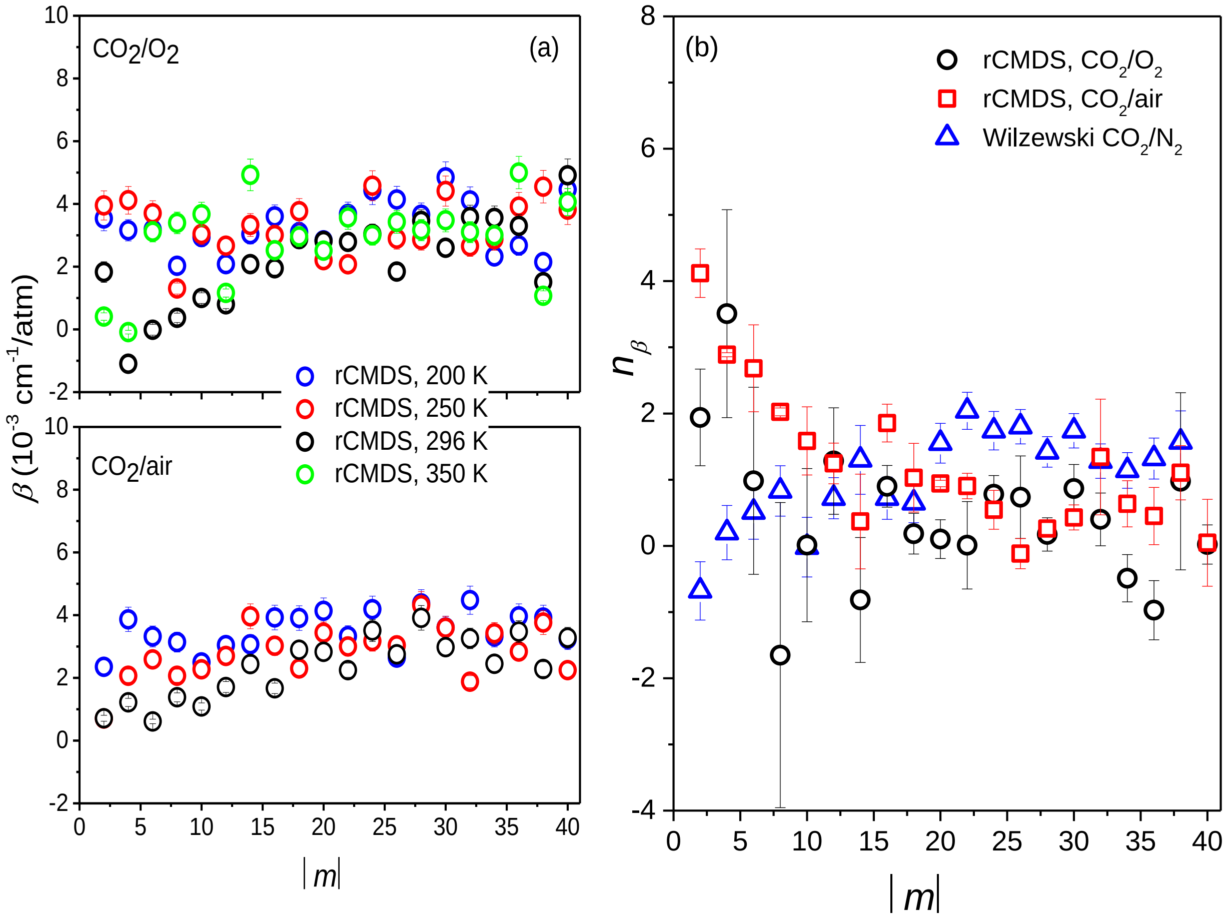
→ CO_2/O_2: rather good agreement

→ CO_2-air: $n_{\gamma 2} < n_{\gamma 0}$

→ CO_2/air: slightly underestimates

Results for CO_2-O_2/air

The Dicke narrowing parameter and its temperature dependence

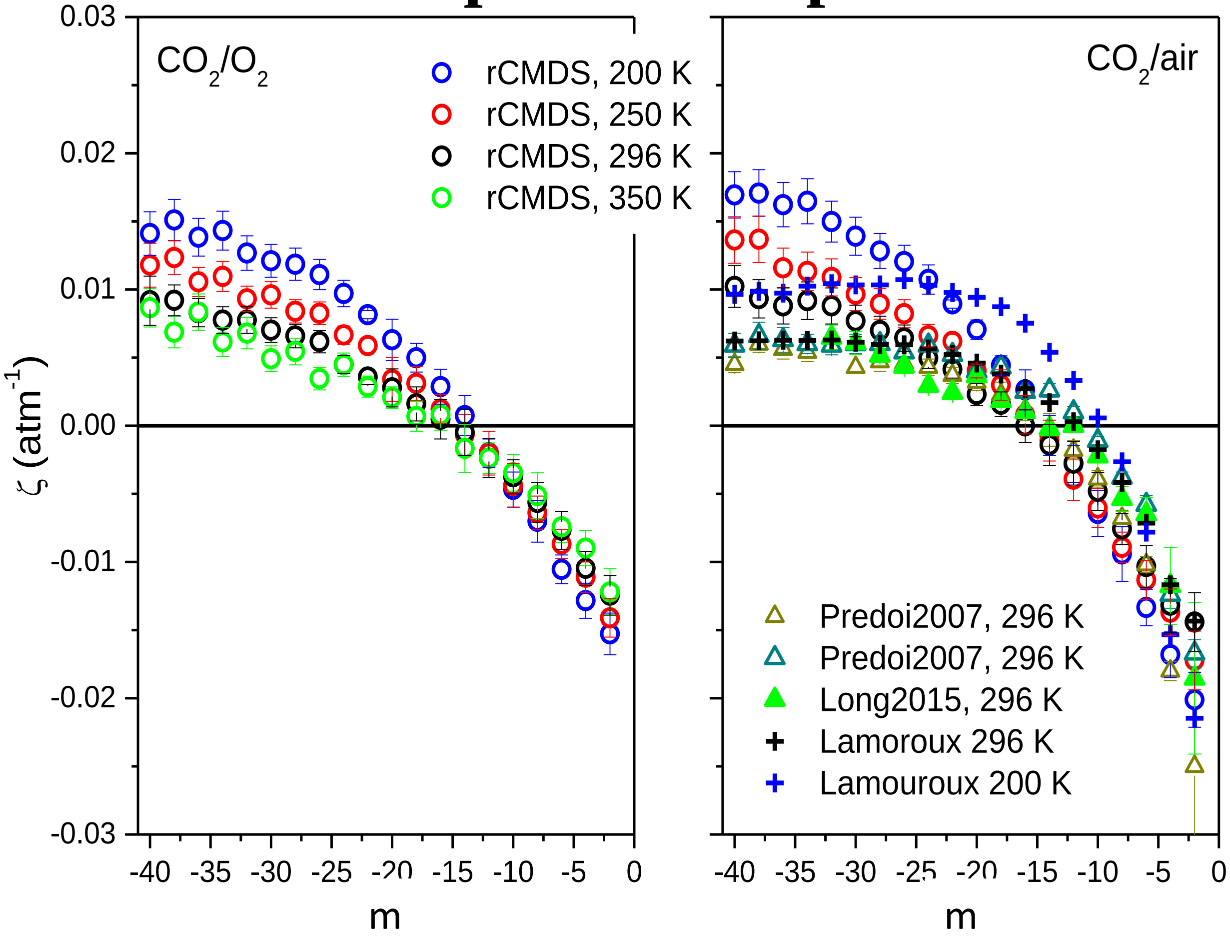


→ $\boldsymbol{\beta}$**: rather small compared to γ_0 and γ_2**→ be influenced by the signal to noise ratio

→ $\boldsymbol{n_\beta}$**: large error bars**

[69] Wilzewski JS, Birk M, Loos J, Wagner G. J Quant Spectrosc Rad Transf 2018;206:296–305.

The first-order line-mixing parameter and its temperature dependence

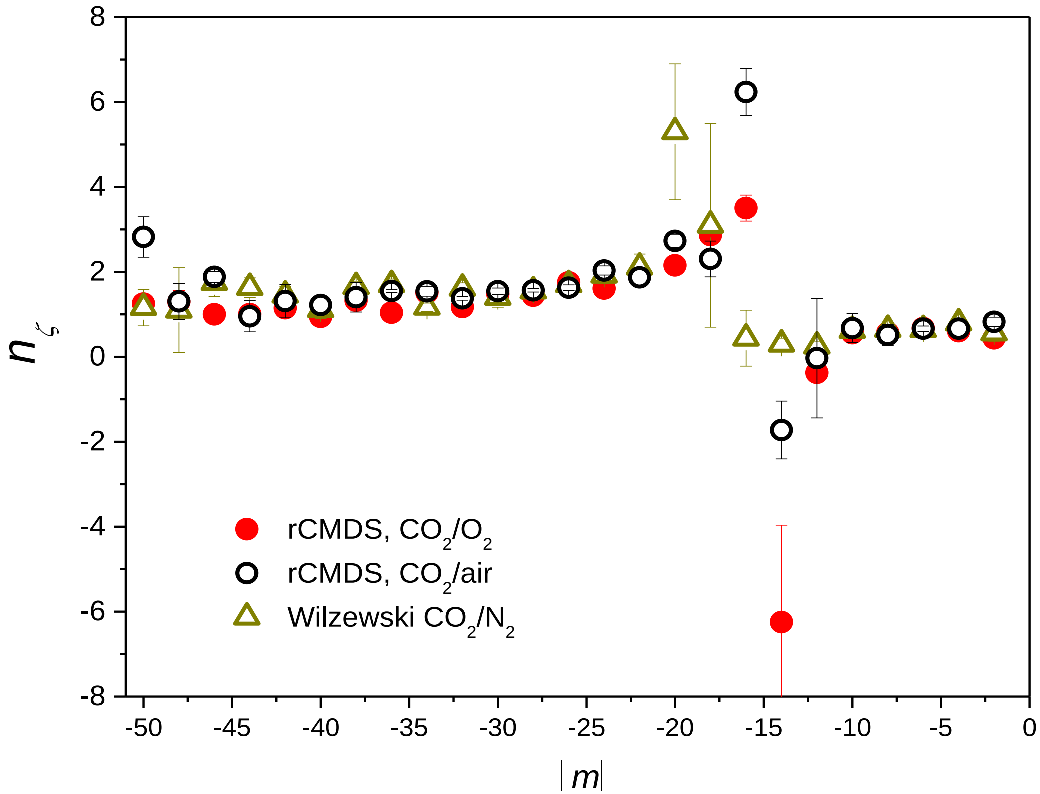


→ $|m| \leq 30$: **very good agreement**

→ **higher $|m|$:, the rCMDS > measured/calculated values**

→ **The difference:** due to **requantization scheme**

The first-order line-mixing parameter and its temperature dependence



→ no significant difference between n_ζ for O_2- and air-broadening

→ good agreement with [69] for CO_2-N_2

Conclusions

- Using rCMDS to simulate spectra of molecular systems for CO_2
- Using HTp and its limited models to analyze simulated spectra
- Obtained parameters are good agreement with other results from measured data
- This method can be use to predict line-shape parameters for other linear molecules
- Similar study on N_2O-air have been considered; a paper has been prepared
- Continue working with CH_3Cl and H_2O in the near future

Scientific activities

1. Vietnam School of Earth Observation 2018 – Recontres du Vietnam-USTH-CNES (2018)

Poster: "Precise predictions of H2O line shapes over a wide pressure range using simulations corrected by a single measurement"

2. The 10th international conference on photonics and applications (**ICPA-10**)

Poster:

- "New intensity measurements of Carbon Dioxide in the 1.6μm region"
- "Model Keilson-Storer and the spectroscopic parameters in the near-infrared of the pure water vapor with Hartmann-Tran profile"

3. Doctoral Day 2019-USTH

Oral talk: "Precise modelling of the infrared spectra of carbon dioxide and of water vapor for atmospheric remote sensing"

4. HRMS 2019, 2019 - Dijon, France

Poster:

- "Precise predictions of H_2O line shape over a wide pressure range using simulations corrected by a single measurement"
- "Prediction of line shape parameters and their temperature dependences for CO_2-air using molecular dynamics simulations"

5. The 11th international conference on photonics and applications (**ICPA-11**)

Poster: "Prediction of air-broadened N_2O lines using classical molecular dynamics simulations**"**

Papers published

1. N.H. Ngo, **H.T. Nguyen**, H. Tran, *Precise predictions of H_2O line shapes over a wide pressure range using simulations corrected by a single measurement*, Journal of Quantitative Spectroscopy & Radiative Transfer 207 (2018) 16–22.

2. H. T. Nguyen, N. H. Ngo, and H. Tran. *Prediction of line shapes parameters and their temperature dependences for CO2-N2 using molecular dynamics simulations*, J. Chem. Phys. 149, 224301 (2018)

3. **H. T. Nguyen**, N. H. Ngo, and H. Tran. *Line-shape parameters and their temperature dependences predicted from molecular dynamics simulations for O_2- and air-broadened CO_2 lines*, J. Chem. Phys. 242, 106729 (2020)

02 papers on ICPA-10

1. Nguyen Thi Huyen Trang, Le Cong Tuong, Ngo Ngoc Hoa; *Model Kelson-Storer and the spectroscopic paramters in the near-infrared of pure water vapor.* Advances in Optics Photonics Spectroscopy and Applications X; 2019; 125

2. Ngo Ngoc Hoa, P.Chelin, X. Landsheere, M. Schwell, **Nguyen Thi Huyen Trang**, Le Cong Tuong. *New measurements of Carbon Dioxide absorption in the 1.6micrometer region.* Advances in Optics Photonics Spectroscopy and Applications X; 2019; 25

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