First-principles calculations of collisional effects on molecular gas spectra for planet and exoplanet atmosphere studies

Ha Tran
Laboratoire de Météorologie Dynamique
CNRS, Sorbonne Université, Ecole Polytechnique
htran@lmd.ipsl.fr

1. Main collisional effects on absorption spectra
2. Collisional parameters and exoplanetary atmosphere studies
3. Collisional parameters in Database
4. First-principles calculations of collisional effects on absorption spectra

The optical thickness in radiative transfer calculations

The optical thickness along the line of sight:

$$\tau_\sigma(z) = \sum_i \sum_j \int_0^z S_{\sigma_j}^{N_i}\big(T(z)\big)\emptyset_{LS}\left(\sigma - \sigma_j, P(z), T(z)\right) N_i(z)dz$$

In this equation :

- ***i*** is the index for various absorbing species
- ***j*** is the index for the lines of species ***i***
- $N_i(z)$ is the number density of species ***i***
- $S(T)$ is the integrated line intensity

The spectral density or the line shape $\emptyset_{LS}$ is given by:

$$\emptyset_{LS}(\tilde{\sigma}) = \frac{1}{\pi} Re \int_0^\infty e^{-i\tilde{\sigma}t}\Phi(t)dt$$

$\Phi(t)$ is the dipole autocorrelation function

The basic line-shape parameters

Neglecting collision-induced changes of the molecule velocity and the dependences of the collisional parameters on the molecular speed, one gets, for not too long wavelengths, **the Voigt profile**

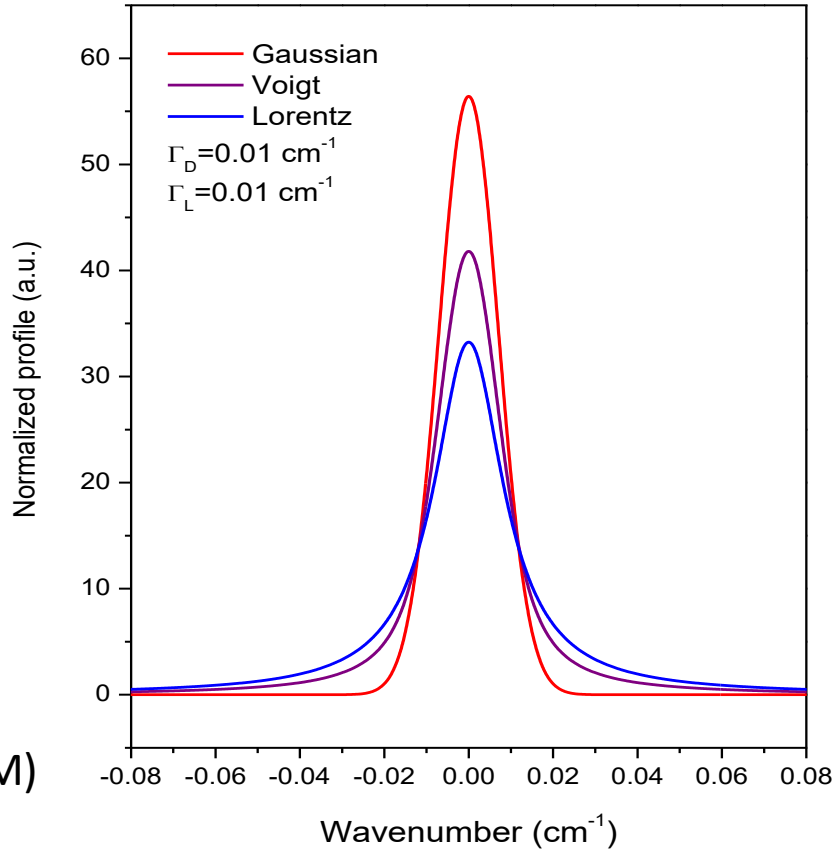
$$\Phi^{Voigt}(\sigma-\sigma_{fi}) = \Phi^{Doppler}(\sigma-\sigma_{fi}) \otimes \Phi^{Lorentz}(\sigma-\sigma_{fi})$$

$$\Phi^{Doppler}(\sigma-\sigma_{fi}) = \frac{\Gamma_D}{\sqrt{\pi}} e^{-\left(\frac{\sigma-\sigma_{fi}}{\gamma_D}\right)^2} \qquad \Gamma_D = \sigma_{fi}\sqrt{\frac{2k_BT}{mc^2}} \quad \text{(HW at 1/e)}$$

$$\Phi^{Lorentz}(\sigma-\sigma_{fi}) = \frac{1}{\pi}\frac{\Gamma_{fi}}{(\sigma-\sigma_{fi}-\Delta_{fi})^2+{\Gamma_{fi}}^2}$$

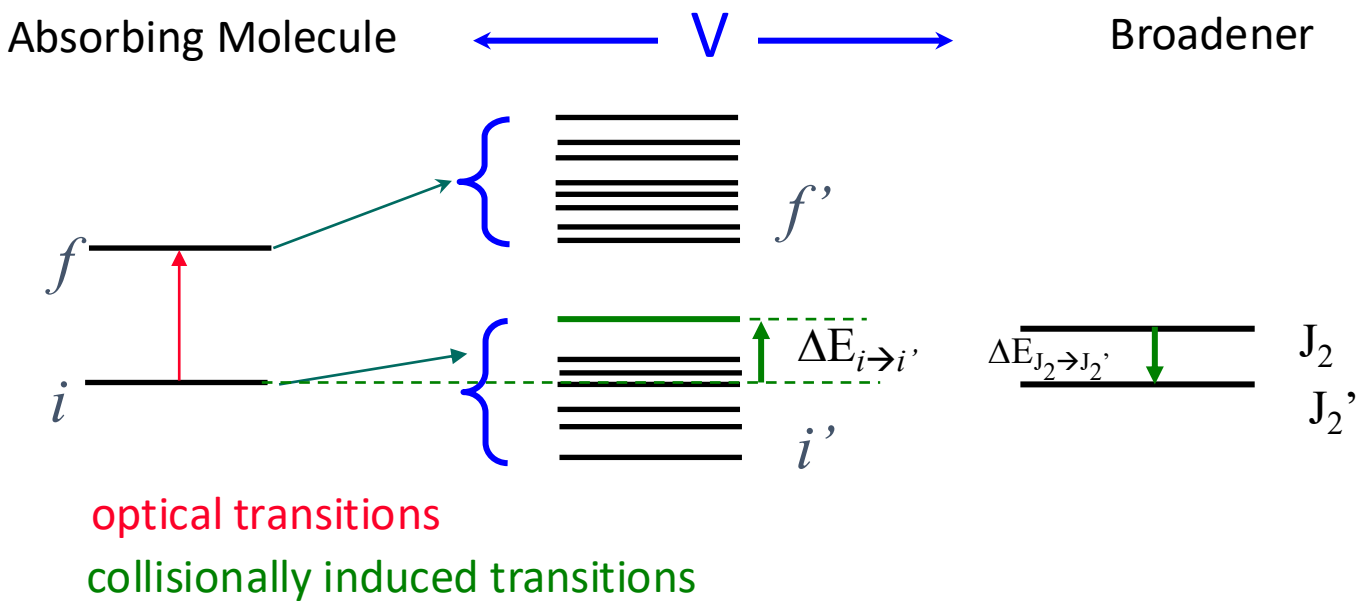
Γ: collisional width (HWHM)
Δ : collisional spectral shift

$\gamma = \Gamma/P$ broadening coefficient (cm^{-1}/atm)
$\delta = \Delta/P$ pressure-shift coefficient (cm^{-1}/atm) → Database such as HITRAN



Comparaison between the Doppler, Lorentz and Voigt profiles.

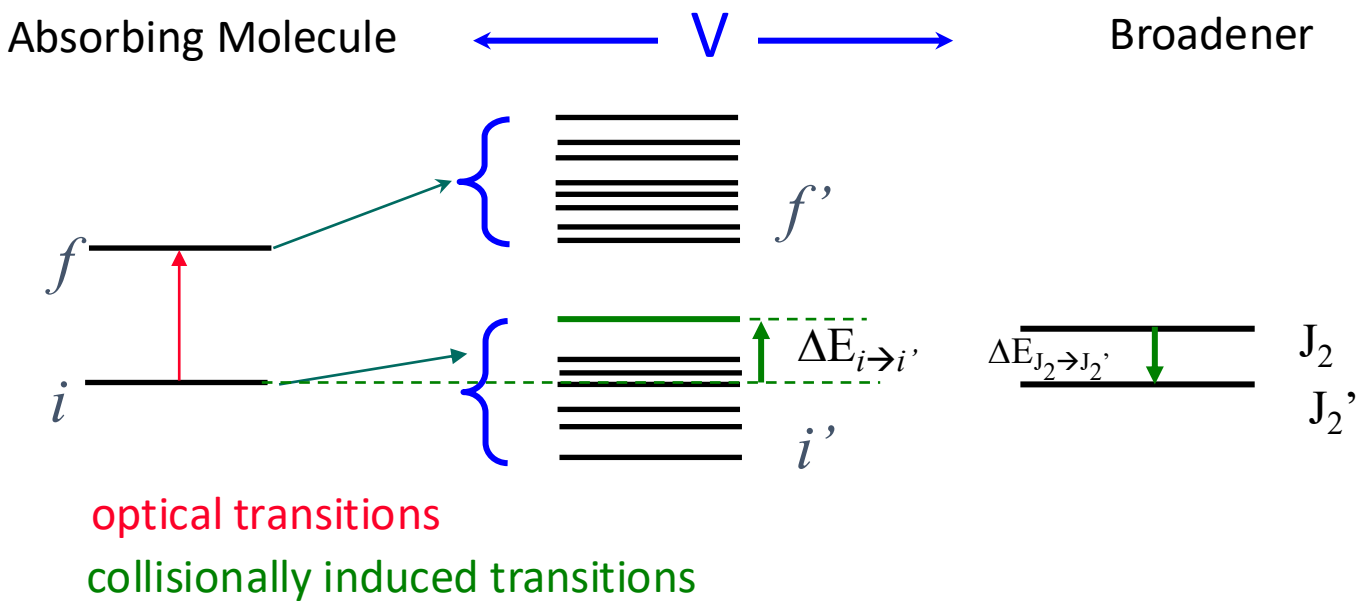
What happens ?



Collisions induce a loss and dephasing of the coherence. The dipole autocorrelation function $\Phi_{fi}(t)$ is thus dephased and damped by successive collisions: $\Phi_{fi}(t) = \Phi_{fi}(0)\ exp[-(\Gamma_{fi} - i\Delta_{fi})t]$

Γ related with the sum of what happens in lower and upper states
Δ related with the difference of what happens in lower and upper states

What happens ?



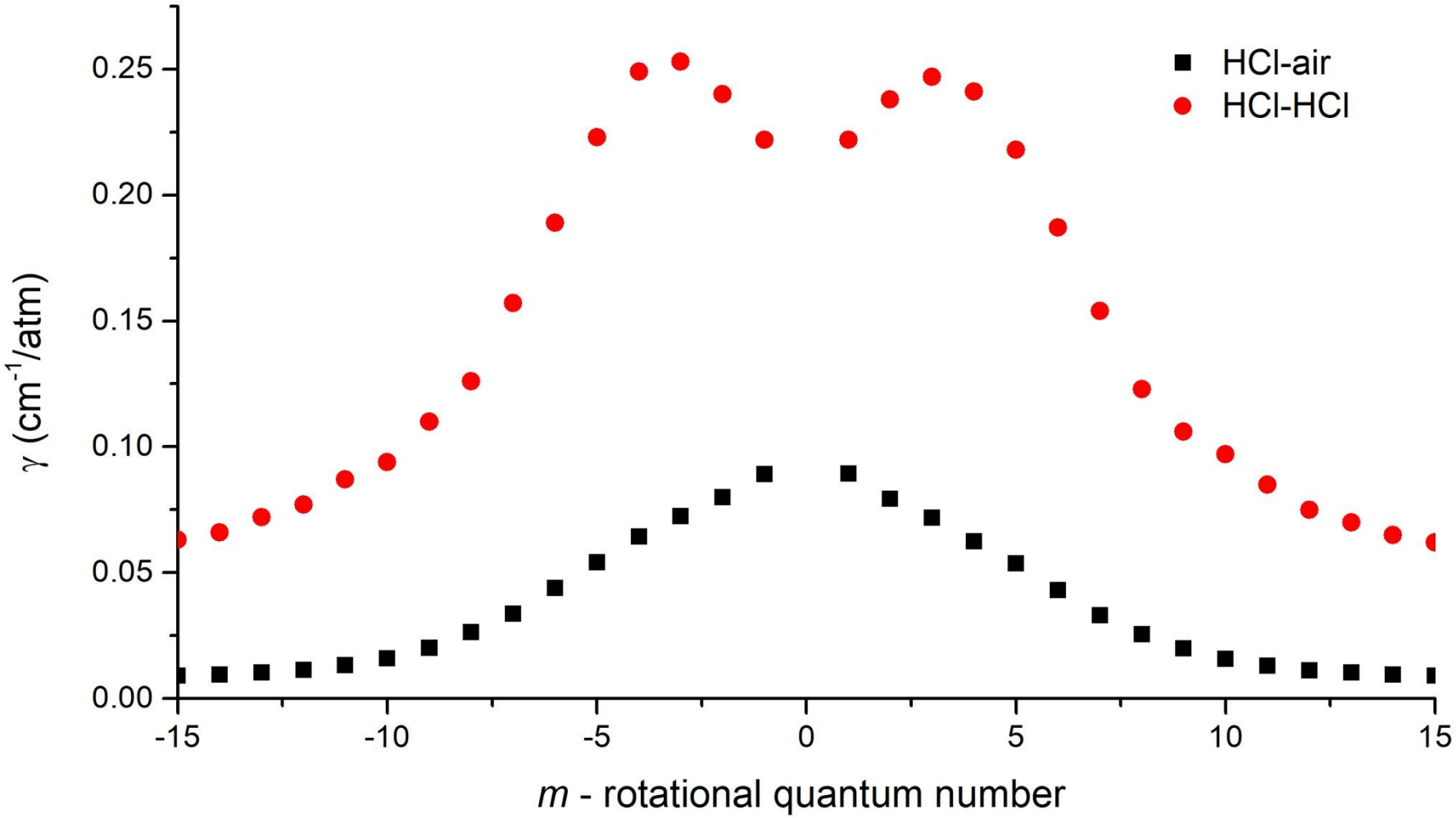
optical transitions

collisionally induced transitions

Collisions induce a loss and dephasing of the coherence. The dipole autocorrelation function $\Phi_{fi}(t)$ is thus dephased and damped by successive collisions: $\Phi_{fi}(t) = \Phi_{fi}(0)\ exp[-(\Gamma_{fi} - i\Delta_{fi})t]$

Γ all the more important that:
- Interactions are strong and at long distances
- Interactions are efficient (closely-spaced levels)
- Collisions are frequent ($\Gamma\uparrow$ with density)

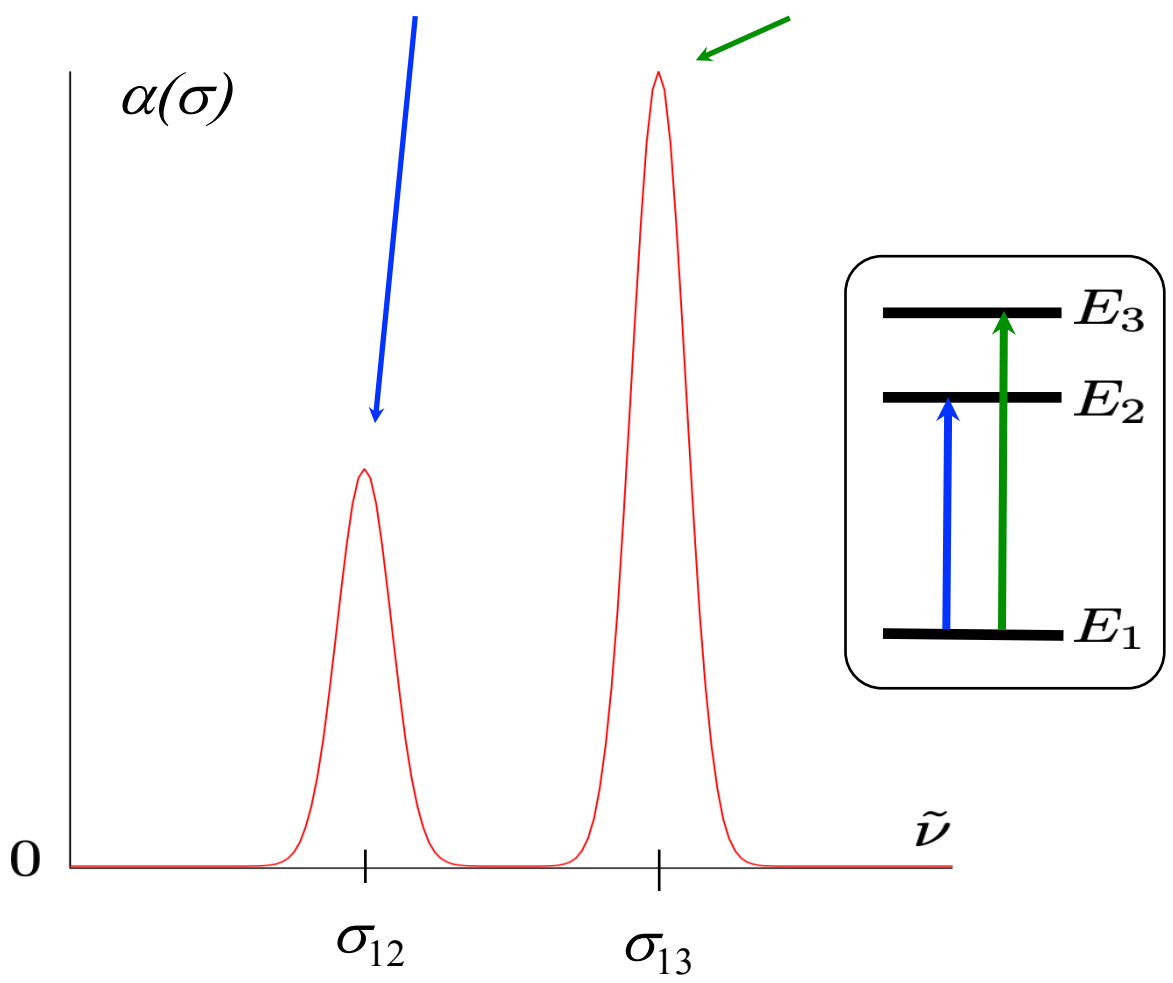
Self- and air-broadening coefficient of HCl

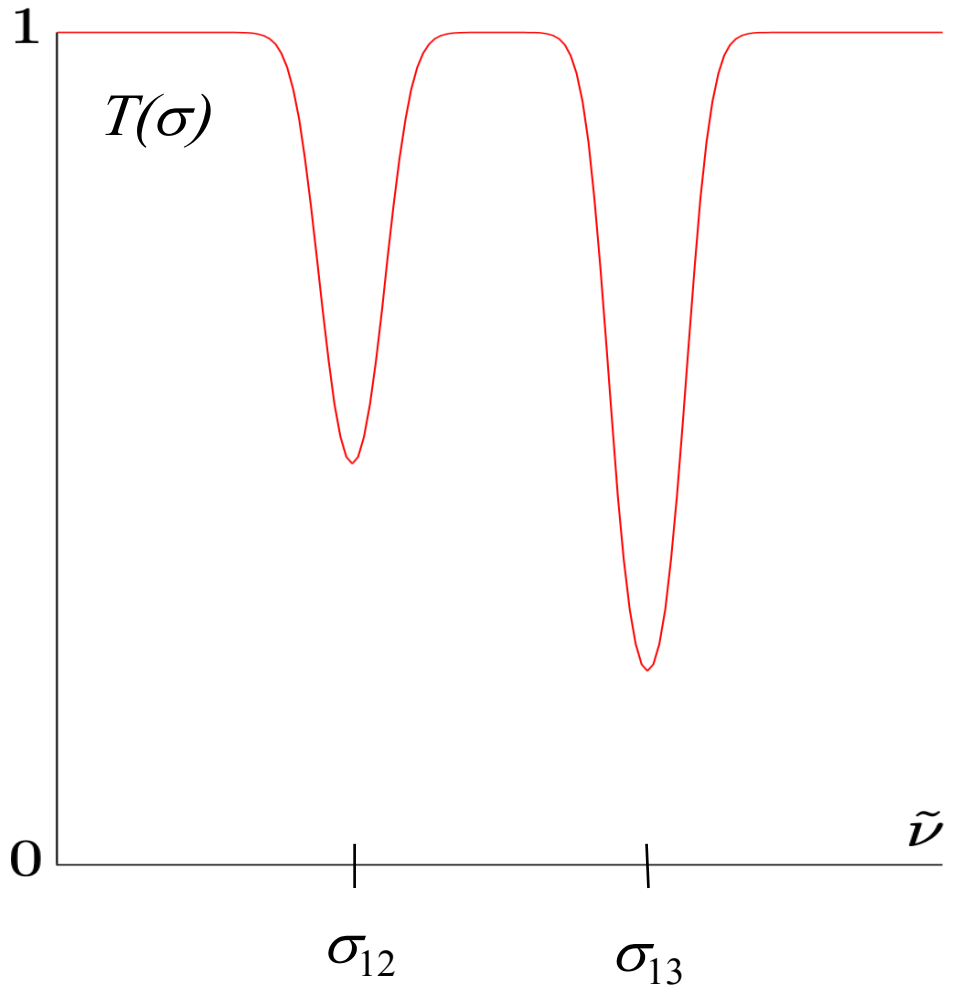


Construction of absorption spectra from isolated lines

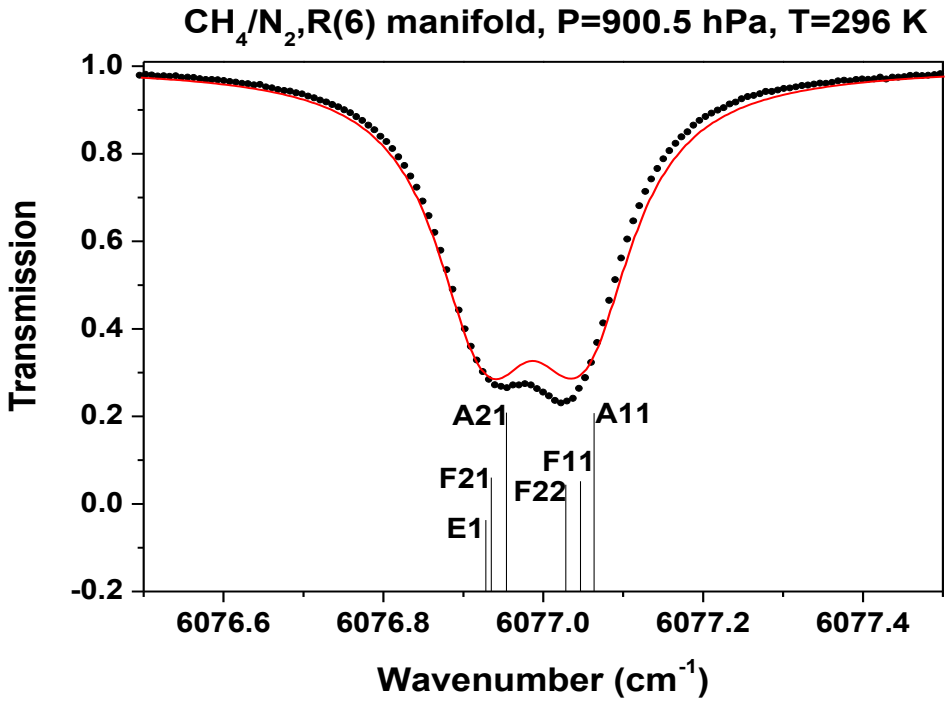
$$\alpha(\sigma) = \alpha_{12}\ \Phi(\sigma-\sigma_{12}) + \alpha_{13}\ \Phi(\sigma-\sigma_{13})$$

$$T(\sigma) = \exp\{-\alpha(\sigma)\ \ell\}$$





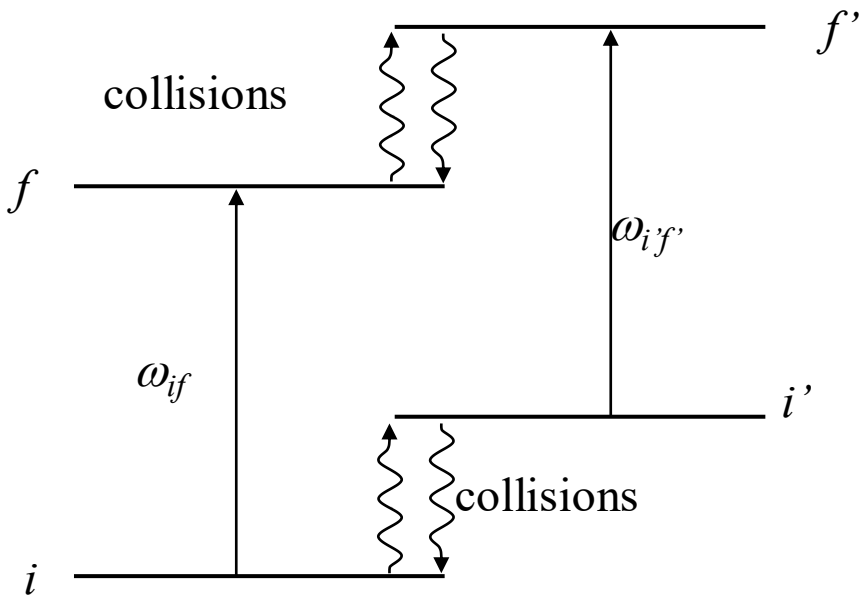
Line mixing



Collisions induce transfers of populations between the levels of the two lines that lead to transfers of intensity between the lines.

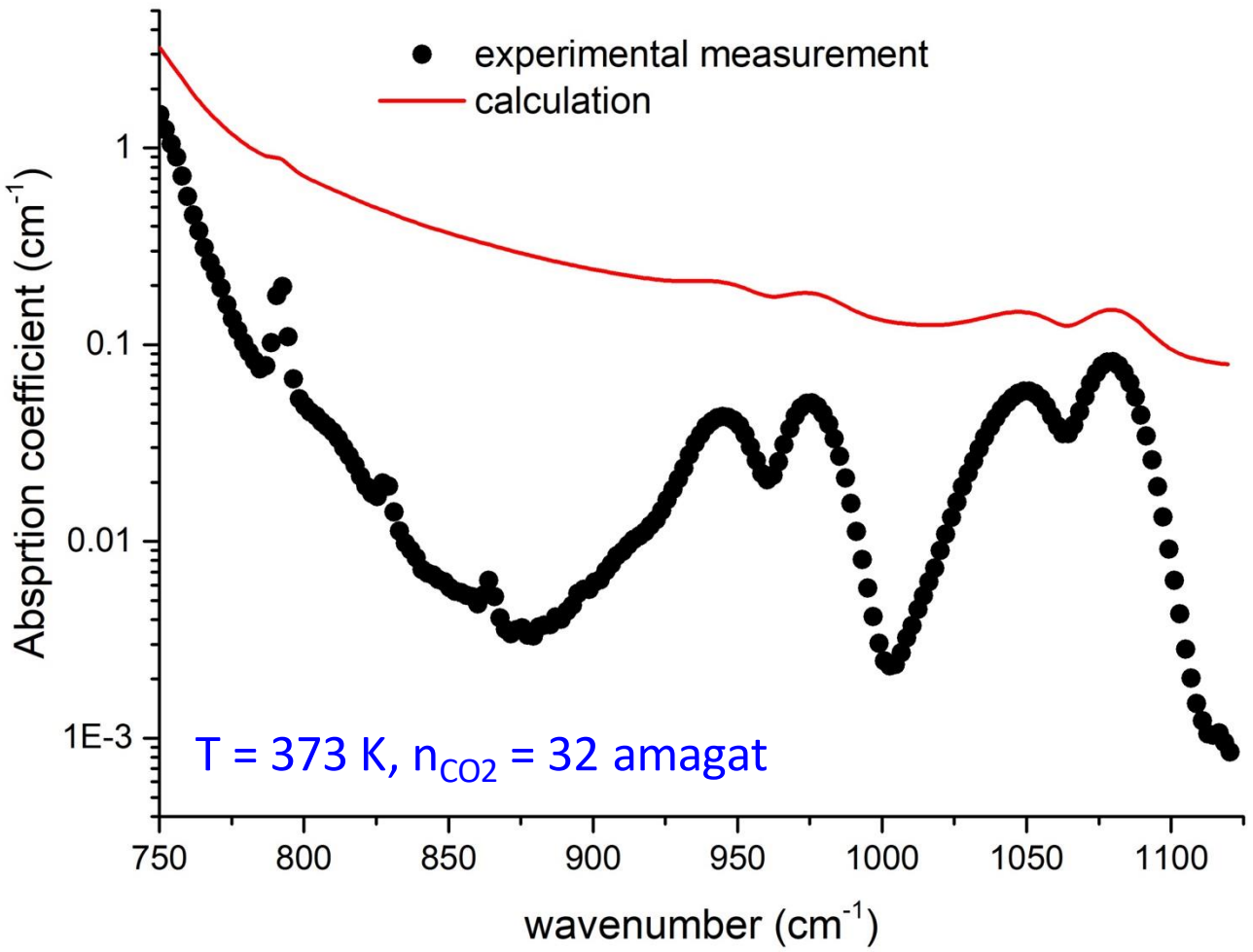
Hartmann et al., "*Collisional effects on molecular spectra*" (2021)

In some cases, for closely spaced lines, the Voigt profile fails when P increases. It predicts shapes that are too broad.



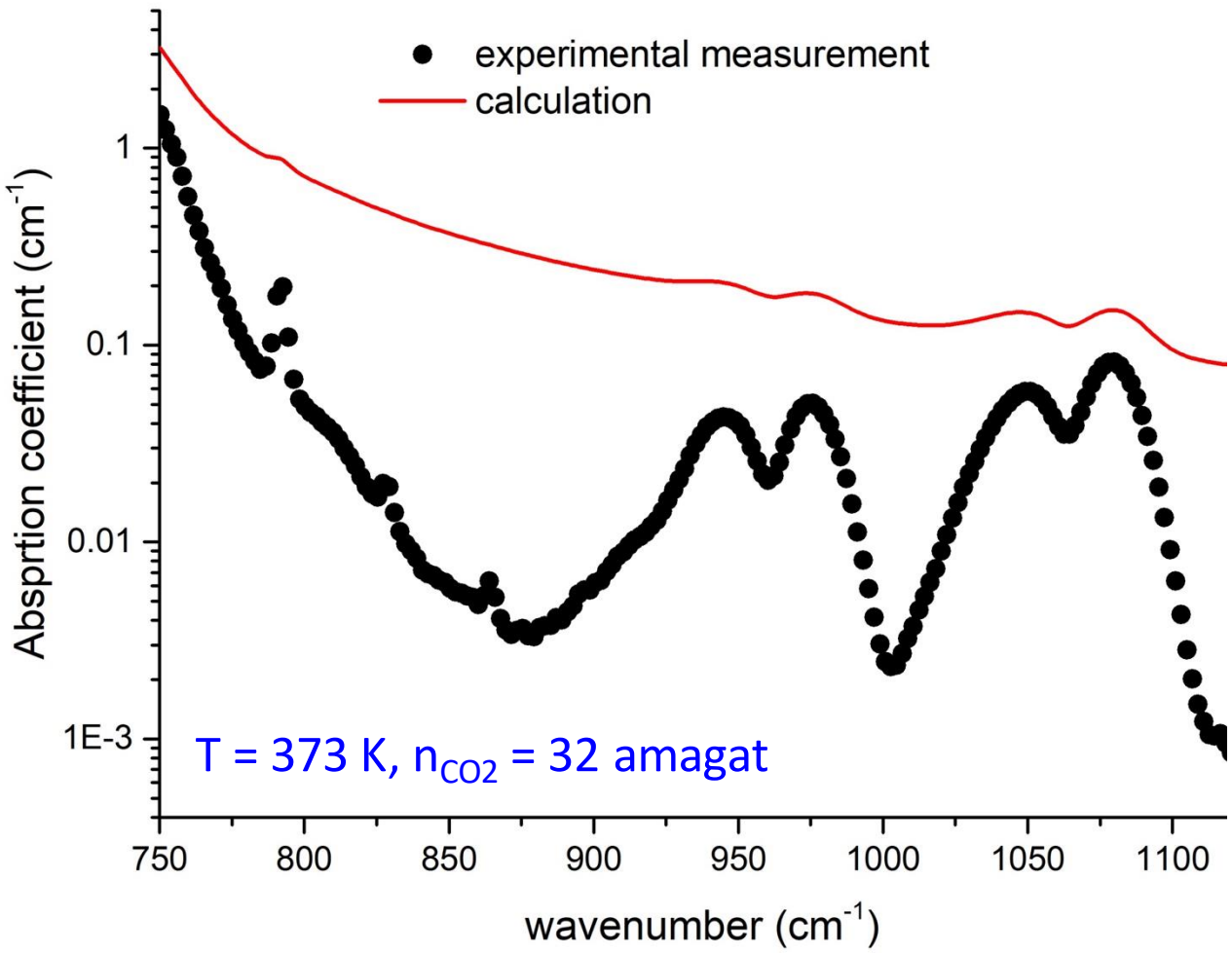
Far-wing absorption

The right wing of the CO_2 ν_2 band



Far-wing absorption

The right wing of the CO_2 ν_2 band



- Line-mixing effects
- Non-impact effects

The impact approximation assumes that :

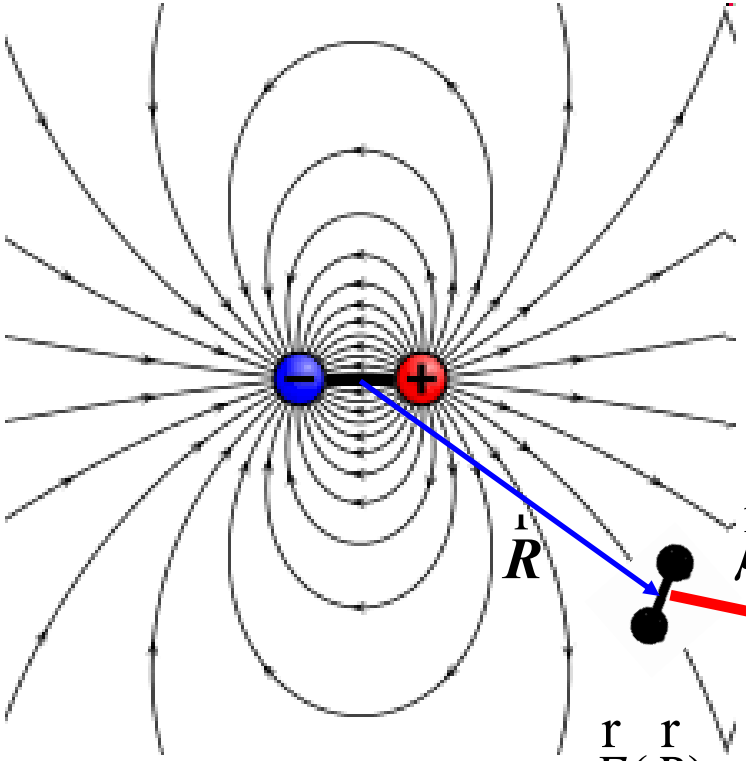
- Collisions are completed: the duration of collisions (τ_c~1 ps) is negligibly small with respect to the interval between successive collisions (~ $1/\Gamma$).

- Negligible influence of the finite duration of collisions: valid only for $|\omega-\omega_0|^{-1} >> \tau_c$ or for $|\sigma-\sigma_0| << (2\pi c\tau_c)^{-1}$

$\Rightarrow$ This is not valid anymore when $|\sigma-\sigma_0|$ is comparable or larger than $(2\pi c\tau_c)^{-1}$ (when $|\sigma-\sigma_0|$ is greater than a few cm^{-1})

Collision-induced absorption

Ex: N_2 in the field of CO dipole



CO permanent dipole

$$\vec{d} = q(\vec{r}_+ - \vec{r}_-)$$

induced dipole in N_2

$$\vec{\mu}(\vec{R}) = \alpha_0 \vec{E}(\vec{R})$$

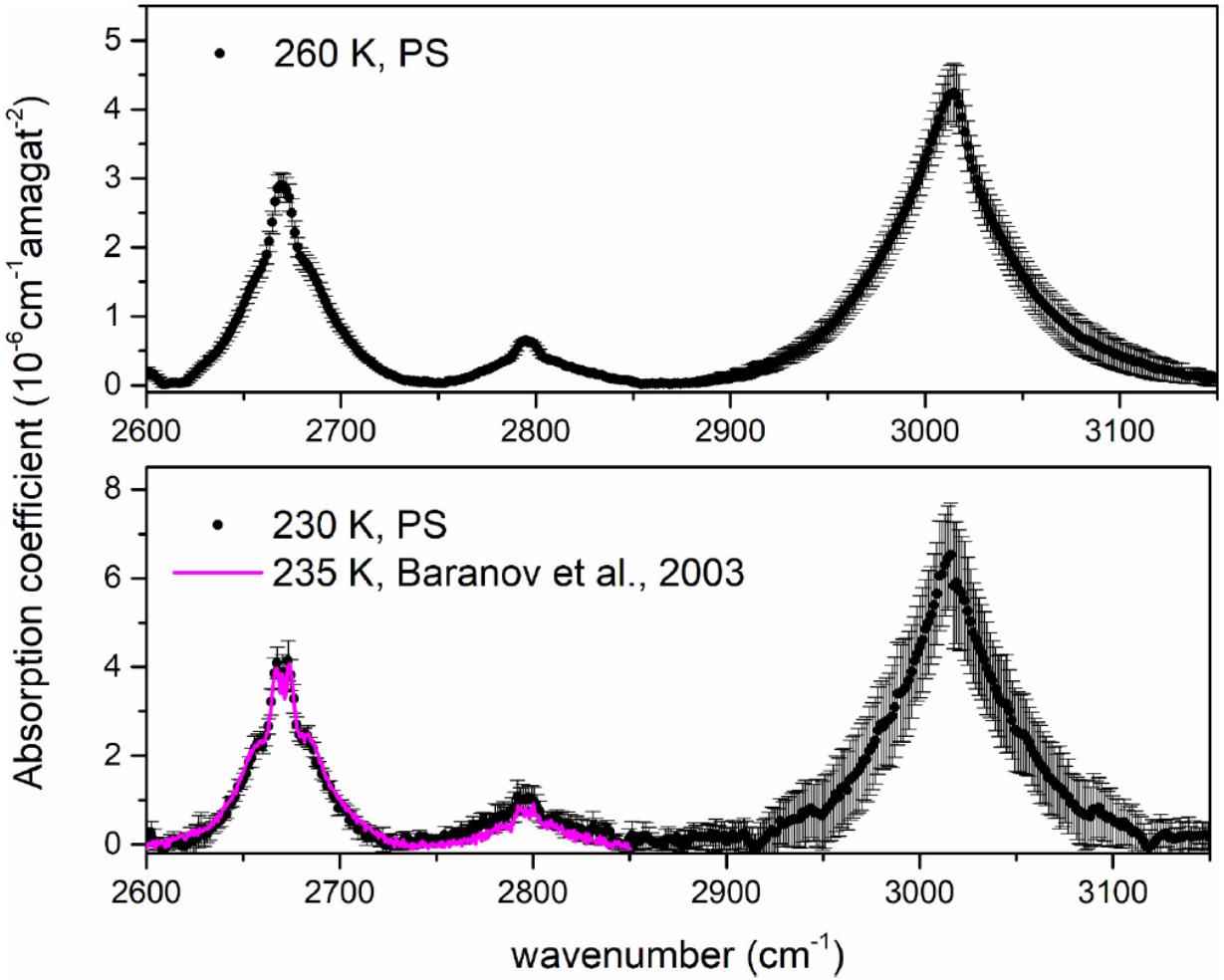
α_0: N_2 polarizability

$$\vec{E}(\vec{R}) = \frac{1}{4\pi\varepsilon_0}\left(3\vec{R}\frac{\vec{d}.\vec{R}}{R^5} - \frac{\vec{d}}{R^3}\right)$$

When two **particles are close to each other**, an instantaneous dipole is induced which leads to a broad and weak absorption spectrum

Collision-induced absorption

Ex: CIA spectrum of pure CO_2



When two **particles are close to each other**, an instantaneous dipole is induced which leads to a broad and weak absorption spectrum

2

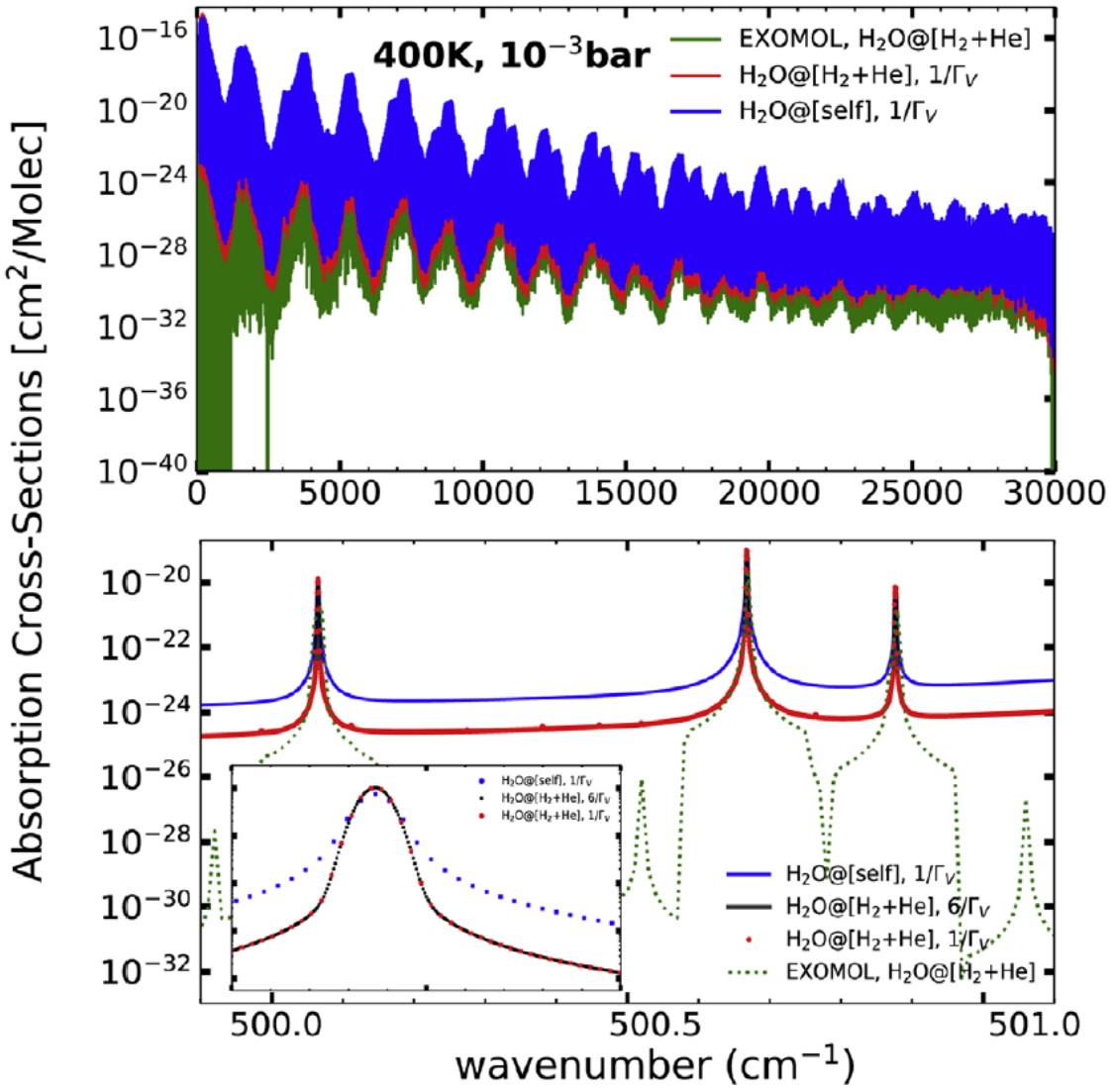
Collisional parameters and (exo)planetary atmosphere studies

"Accurate and sufficiently complete sets of spectroscopic line shape parameters are crucial to atmospheric opacity calculations to aid efforts of exoplanet atmosphere characterization and radiative transfer modeling"

The Need for Laboratory Measurements and Ab Initio Studies to Aid Understanding of Exoplanetary Atmospheres

2019 | Fortney, Jonathan J; Robinson, Tyler D; Domagal-Goldman, Shawn; Genio, Anthony D Del; Gordon, Iouli E; Gharib-Nezhad, Ehsan; Lewis, Nikole; Sousa-Silva, Clara; Airapetian, Vladimir; Drouin, Brian; Hargreaves, Robert J; Huang, Xinchuan; Karman, Tijs; Ramirez, Ramses M; Rieker, Gregory B; Tennyson, Jonathan; Wordsworth, Robin; Yurchenko,… et al.

Collisional parameters and (exo)planetary atmosphere studies



THE ASTROPHYSICAL JOURNAL, 872:27 (8pp), 2019 February 10 https://doi.org/10.3847/1538-4357/aafb7b

The Influence of H_2O Pressure Broadening in High-metallicity Exoplanet Atmospheres

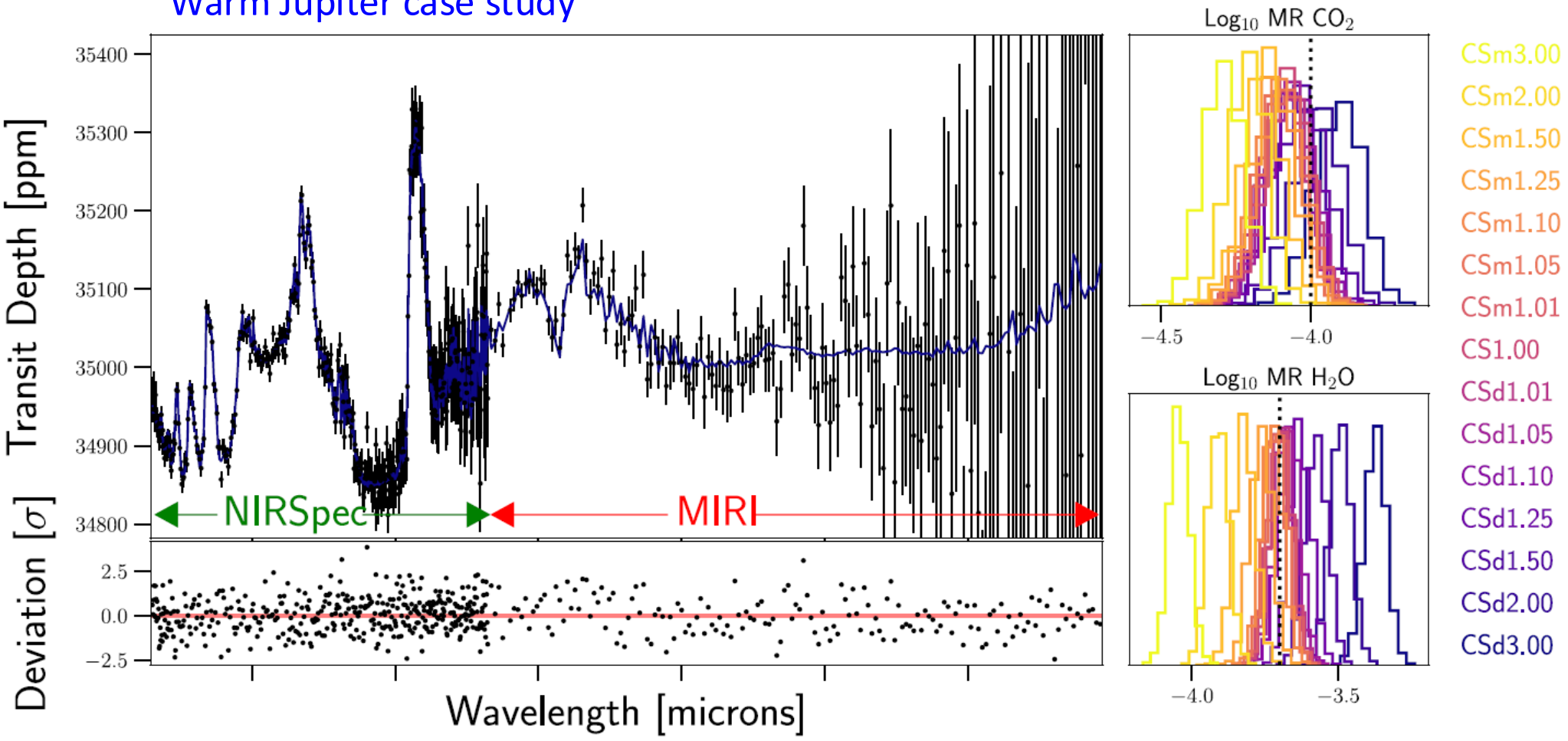
Ehsan Gharib-Nezhad[1] and Michael R. Line[2]
[1] School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA; e.gharibnezhad@asu.edu
[2] School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA
Received 2018 August 13; revised 2018 December 21; accepted 2018 December 21; published 2019 February 7

- H_2/He broadening: Jovian-like atmospheres
- H_2O broadening: high-metallicity or all-steam atmospheres

"The choice of the broadener species can significantly alter the one-dimensional vertical temperature structure of the atmosphere"

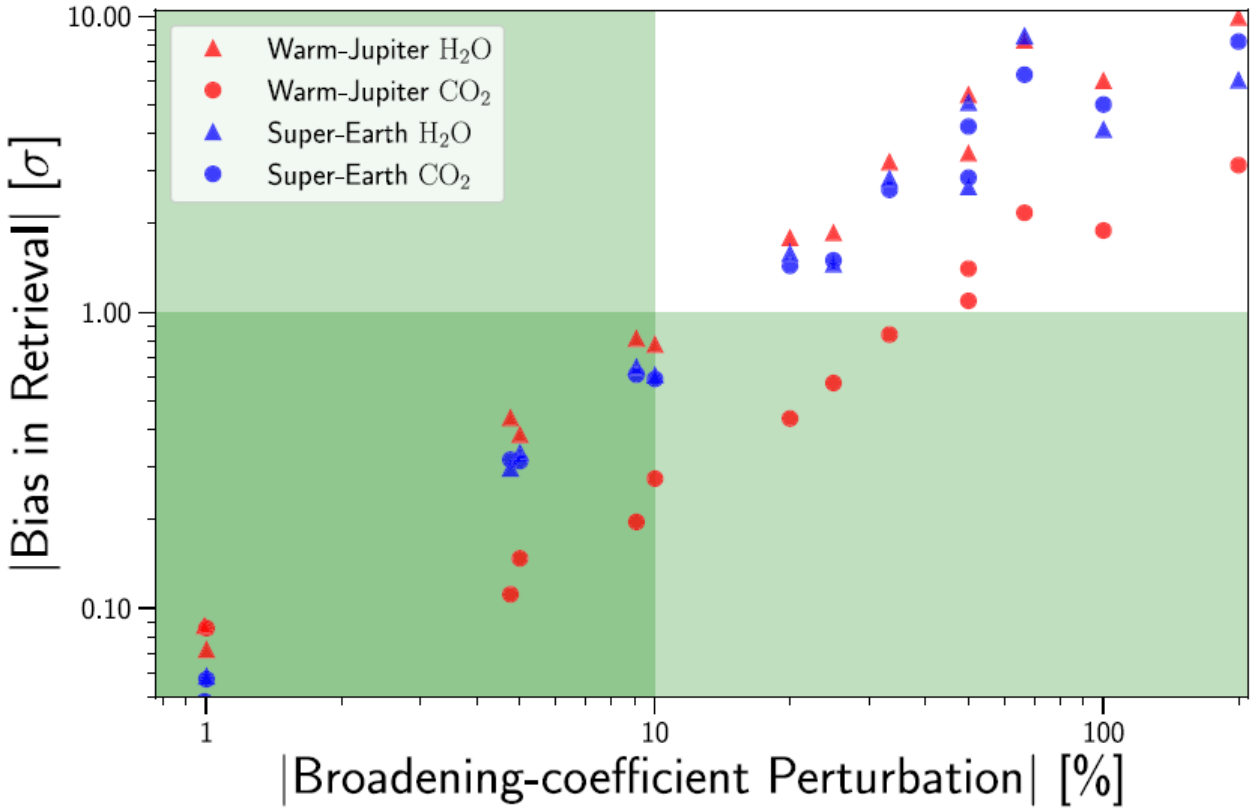
Collisional parameters and (exo)planetary atmosphere studies

Warm Jupiter case study



Wiesenfeld et al., ApJ, 981, 2025

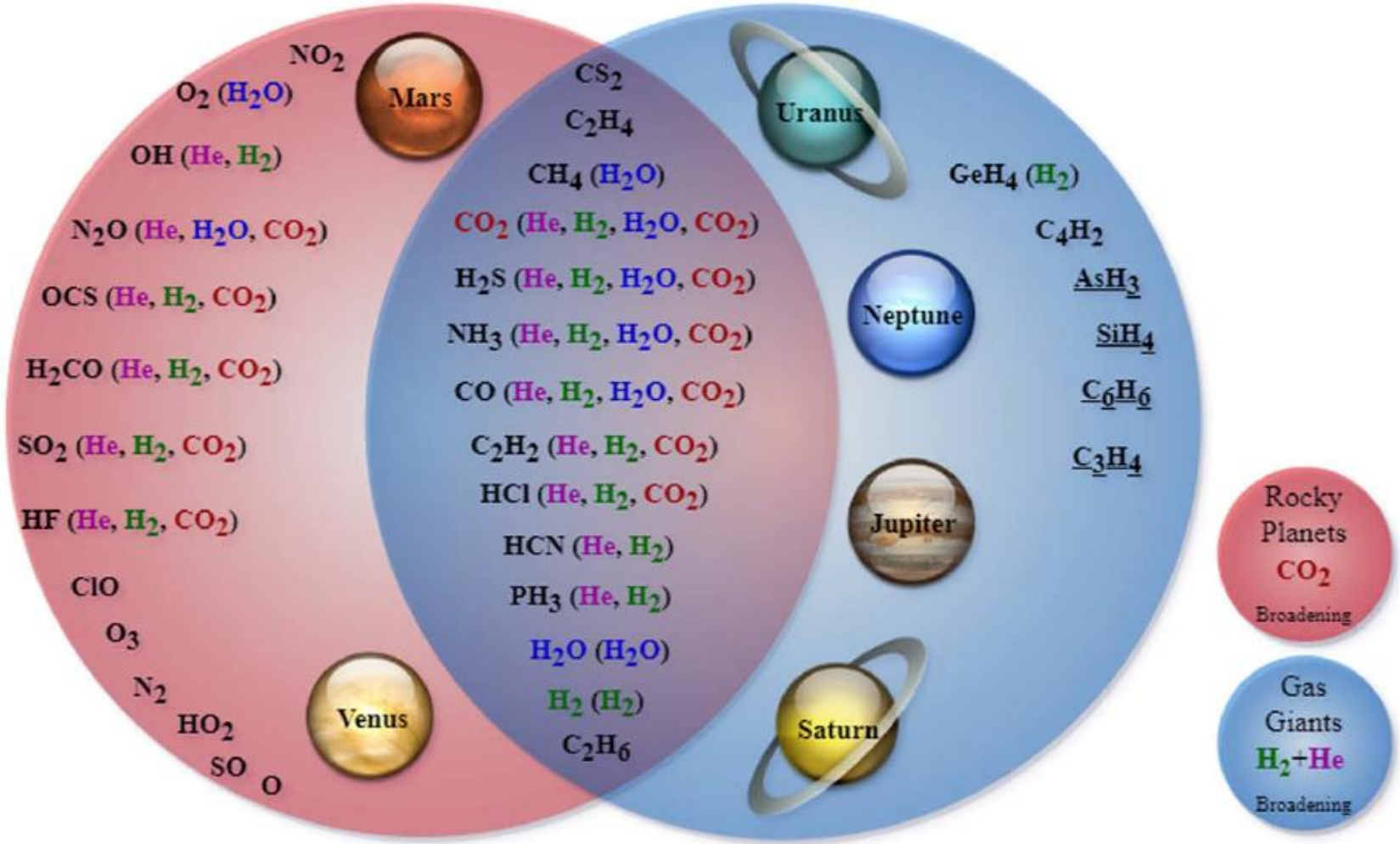
Collisional parameters and (exo)planetary atmosphere studies



- σ: confidence interval on atmospheric interference given by the instrument precision
- Greater than 5σ biases observed among the retrieved water and carbon dioxide abundances
- A precision of about 10% is needed for an acceptable bias range from -1σ to +1σ

Wiesenfeld et al., ApJ, 981, 2025

Situation of collisional parameters in the HITRAN database



Tan et al., The Astrophysical Journal Supplement Series, 262:40, 2022

3 Absorbers and broadeners for which collisional parameters are required

- *N_2 and/or O_2 dominated:* H_2O (N_2, O_2, H_2O); CO_2 (N_2, O_2, CO_2); CH_4 (N_2, O_2, CH_4); O_3 (N_2, O_2), T/P range: 70-500 K, up to ~10 bar
- *CO_2 dominated:* H_2O (CO_2, H_2O); CO_2 (CO_2); CH_4 (CO_2, CH_4), T/P range: 70-2000 K, up to ~100 bar
- *H_2O dominated:* H_2O(CO_2, H_2O); CO_2 (CO_2, H_2O); CH_4 (H_2O, CH_4), T/P range: 70-2000 K, up to ~100 bar
- *H_2 and He dominated:* H_2O, CO, CO_2, CH_4, NH_3, Na, K, Li, Rb, Cs, TiO, VO, HCN, C_2H_2, H_2S, PH_3; T/P range: 70-3000 K, up to 100 bar
- *Vaporized terrestrial:* Radiatively active species: CO_2, H_2O, SO_2, HCl, HF, OH, CO, SiO, KOH, KCl; broadeners: CO_2 and H_2O, T/P range: 700-4000 K, up to ~100 bar

Fortney et al., Astro2020 Science White Paper, https://arxiv.org/abs/1602.06305

3 Absorbers and broadeners for which collisional parameters are required

- *N_2 and/or O_2 dominated:* H_2O (N_2, O_2, H_2O); CO_2 (N_2, O_2, CO_2); CH_4 (N_2, O_2, CH_4); O_3 (N_2, O_2), T/P range: 70-500 K, up to ~10 bar
- *CO_2 dominated:* H_2O (CO_2, H_2O); CO_2 (CO_2); CH_4 (CO_2, CH_4), T/P range: 70-2000 K, up to ~100 bar
- *H_2O dominated:* H_2O(CO_2, H_2O); CO_2 (CO_2, H_2O); CH_4 (H_2O, CH_4), T/P range: 70-2000 K, up to ~100 bar
- ***H_2 and He dominated**:* H_2O, CO**, CO_2**, CH_4, NH_3, Na, K, Li, Rb, Cs, TiO, VO, HCN, C_2H_2, H_2S, PH_3; T/P range: **70-3000 K**, **up to 100 bar**
- *Vaporized terrestrial:* Radiatively active species: CO_2, H_2O, SO_2, HCl, HF, OH, CO, SiO, KOH, KCl; broadeners: CO_2 and H_2O, T/P range: 700-4000 K, up to ~100 bar

Fortney et al., Astro2020 Science White Paper, https://arxiv.org/abs/1602.06305

H_2-broadening coefficients of CO_2 lines in HITRAN

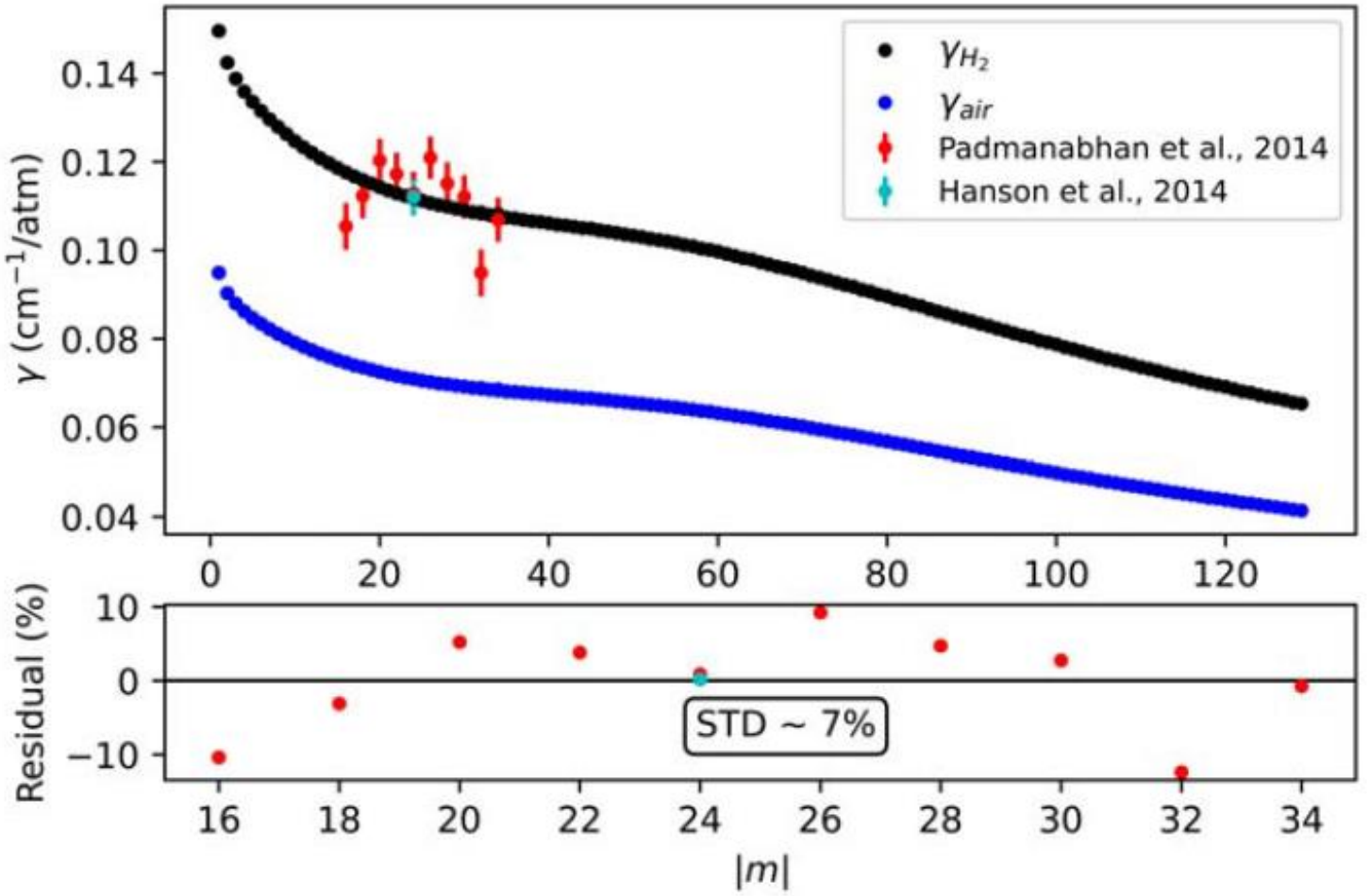
Using a scaling factor from γ_{air}:

$$\gamma_{H2}=1.5767*\gamma_{air}$$

Constant value for the temperature dependence exponent:

$$n=0.58$$

$$\gamma(T)=\gamma(T0)*(T0/T)^n$$



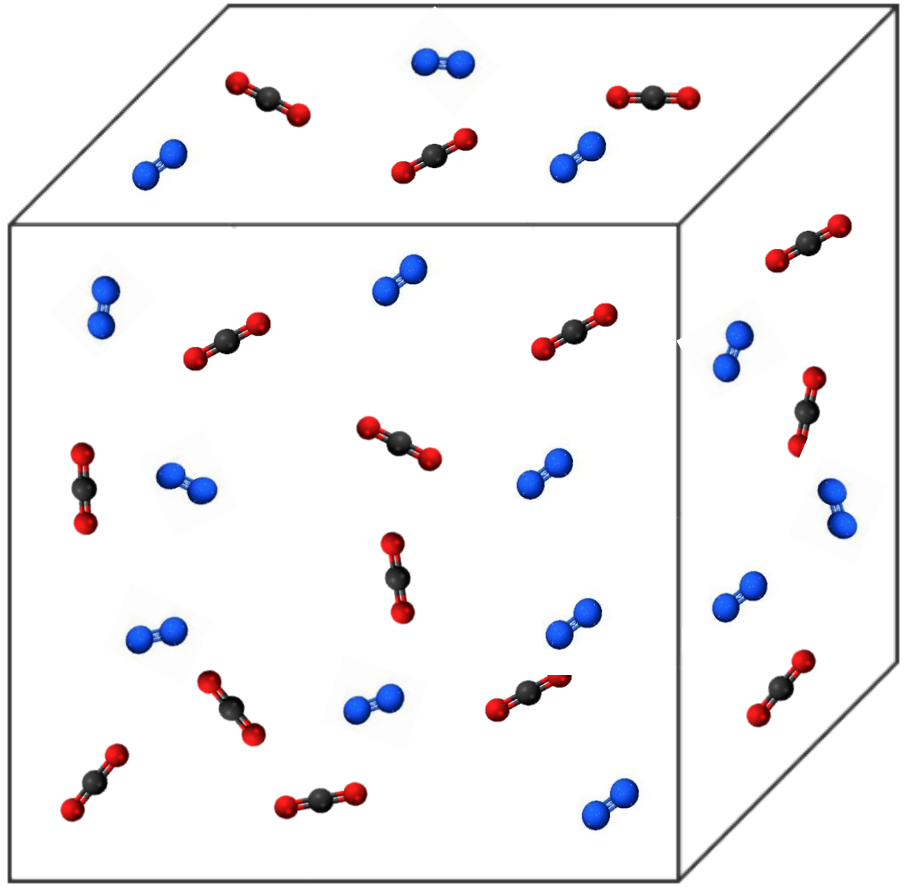
Tan et al., The Astrophysical Journal Supplement Series, 262:40, 2022

Requantized classical molecular dynamics simulations

Principle of rCMDS

- Simulation of a gas: N particles system
- Simulation box with periodic boundary conditions
- Pair potential $\rightarrow$ force and torque
- Equations of motion:

$$m\dot{\vec{v}}_i = \vec{f}_i \quad and \quad I\dot{\vec{\omega}}_i = \vec{\tau}_i$$



$\rightarrow$ This provides the c.o.m. velocities and positions as well as the orientations and angular velocity of all molecules at all times

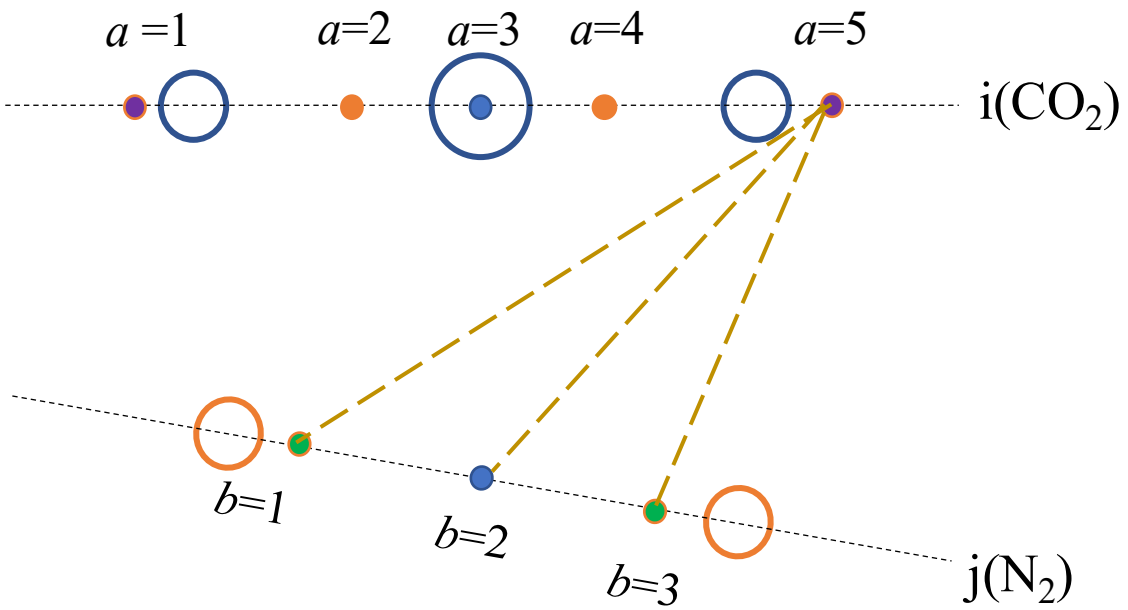
Interaction potential: example for CO_2-N_2

Site-site interaction potential

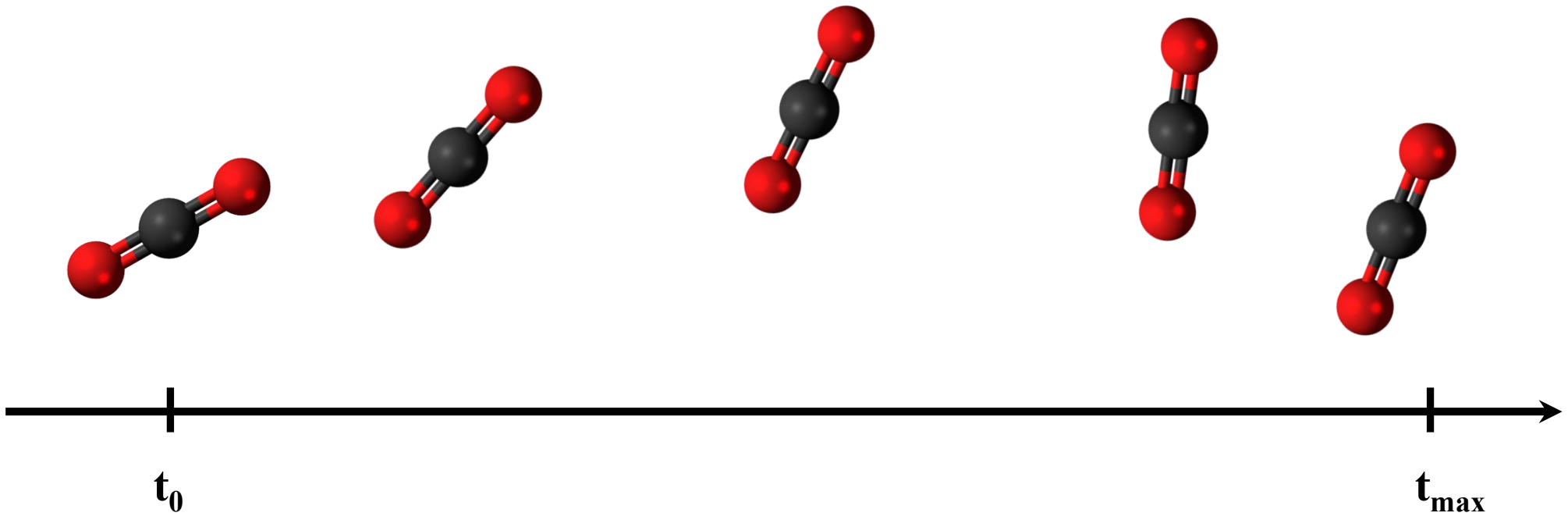
$$V = \sum_{i}\sum_{j>i} V^{C}\left(r_i, r_j\right) + \sum_{i'}\sum_{j'>i'} V^{LN}\left(r_{i'}, r_{j'}\right)$$

Coulombic potential

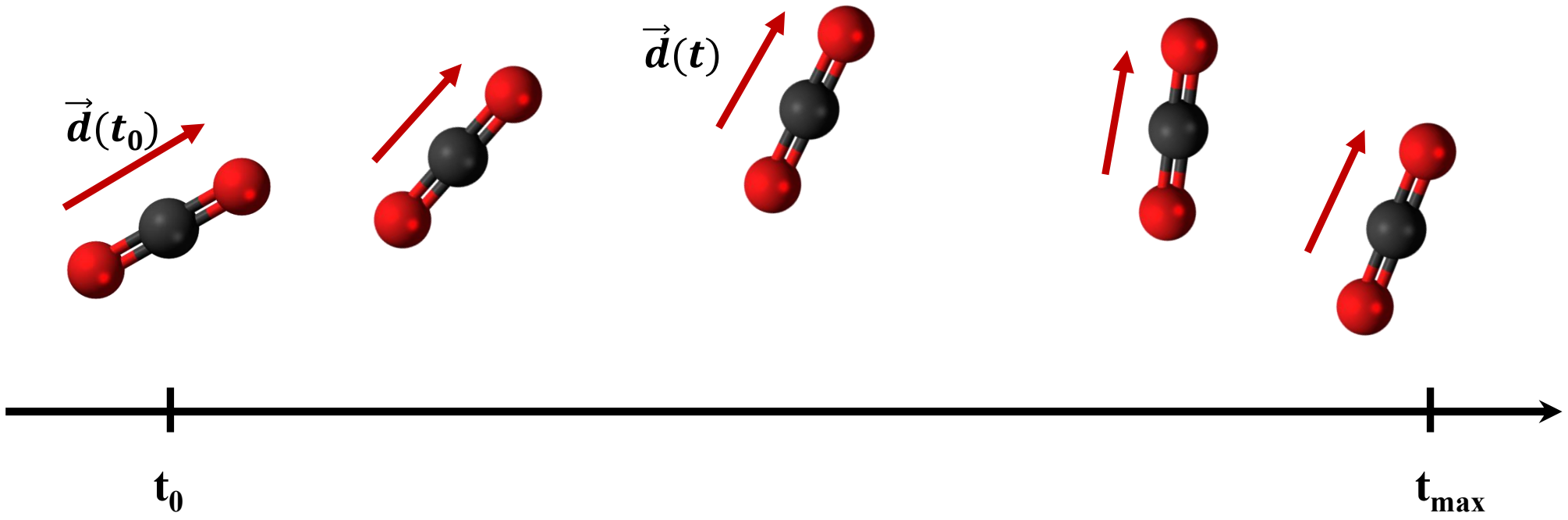
Lennard-Jones potential



From CMDS to the auto-correlation function of the dipole



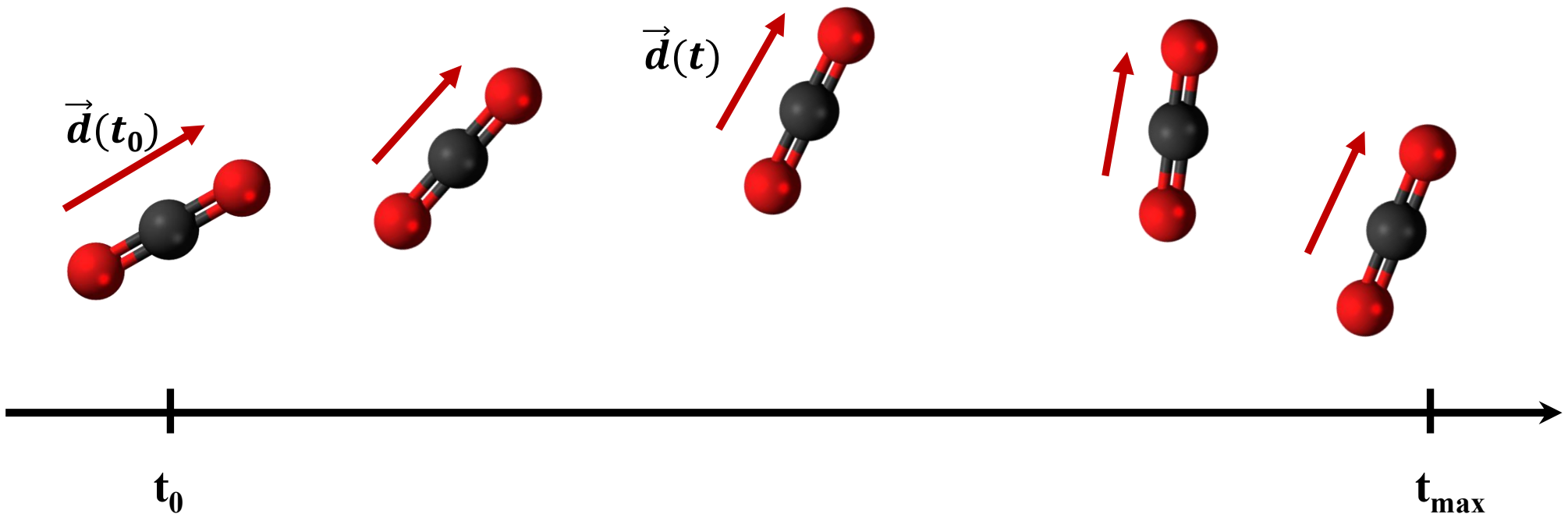
From CMDS to the auto-correlation function of the dipole



From CMDS to the auto-correlation function of the dipole

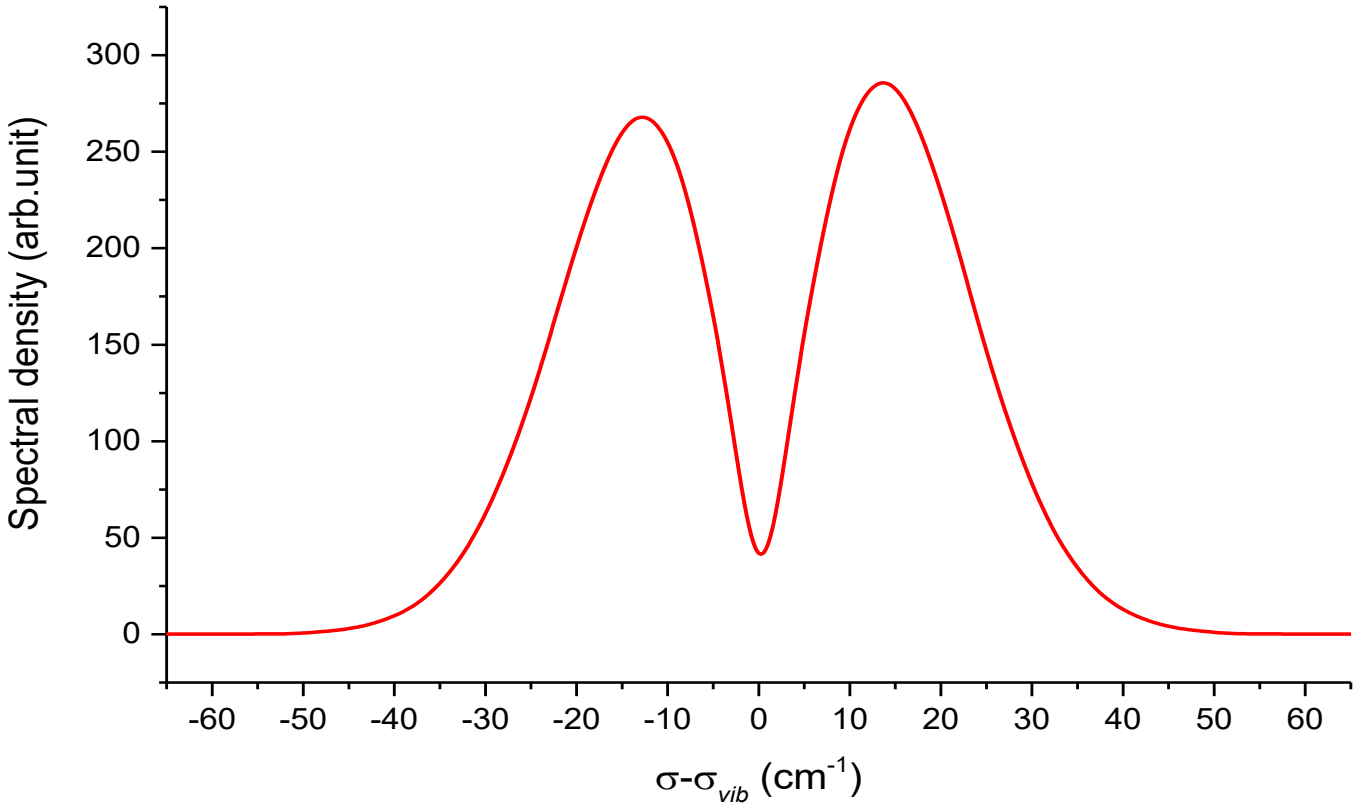
The dipole auto-correlation function Φ(t):

$$\Phi(t) = \frac{1}{N}\sum_{i=1}^{N} \vec{d}_i(t_0) \cdot \vec{d}_i\,(t)$$



From the dipole ACF to the spectral density

$$\Phi(\tilde{\sigma}) = \mathrm{Re}\left\{\frac{1}{\pi}\int_0^{+\infty} \Phi(t) e^{-i\tilde{\sigma}t} dt\right\}$$



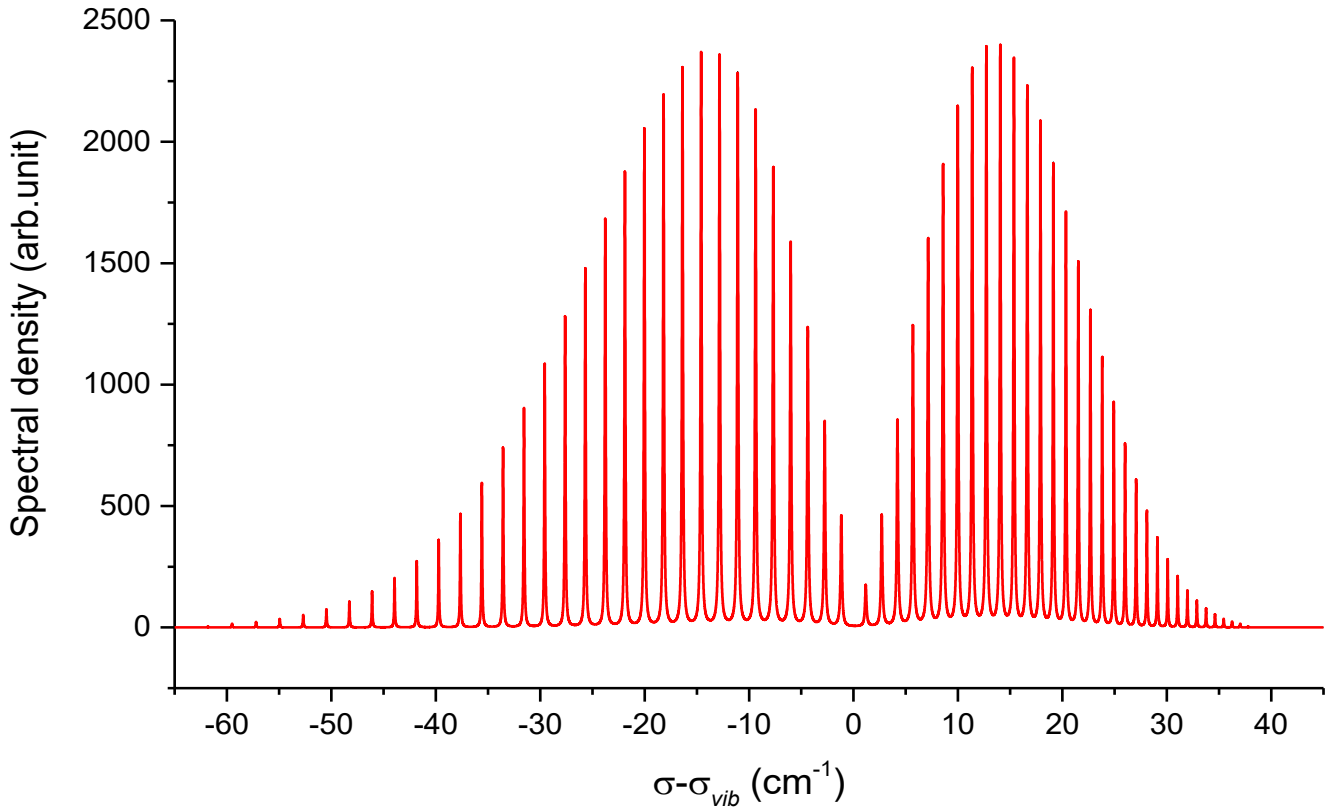
From the dipole ACF to the spectral density: requantization

- For a molecule of classical rotational angular momentum ω_i we find the integer J_i for which $\hbar J_i/I$ is the closest to ω_i.
- Once J_i is found, ω_i is requantized by using the new value $\omega_i^{req} = \hbar J_i/I$ while the orientation of the angular momentum is kept unchanged.

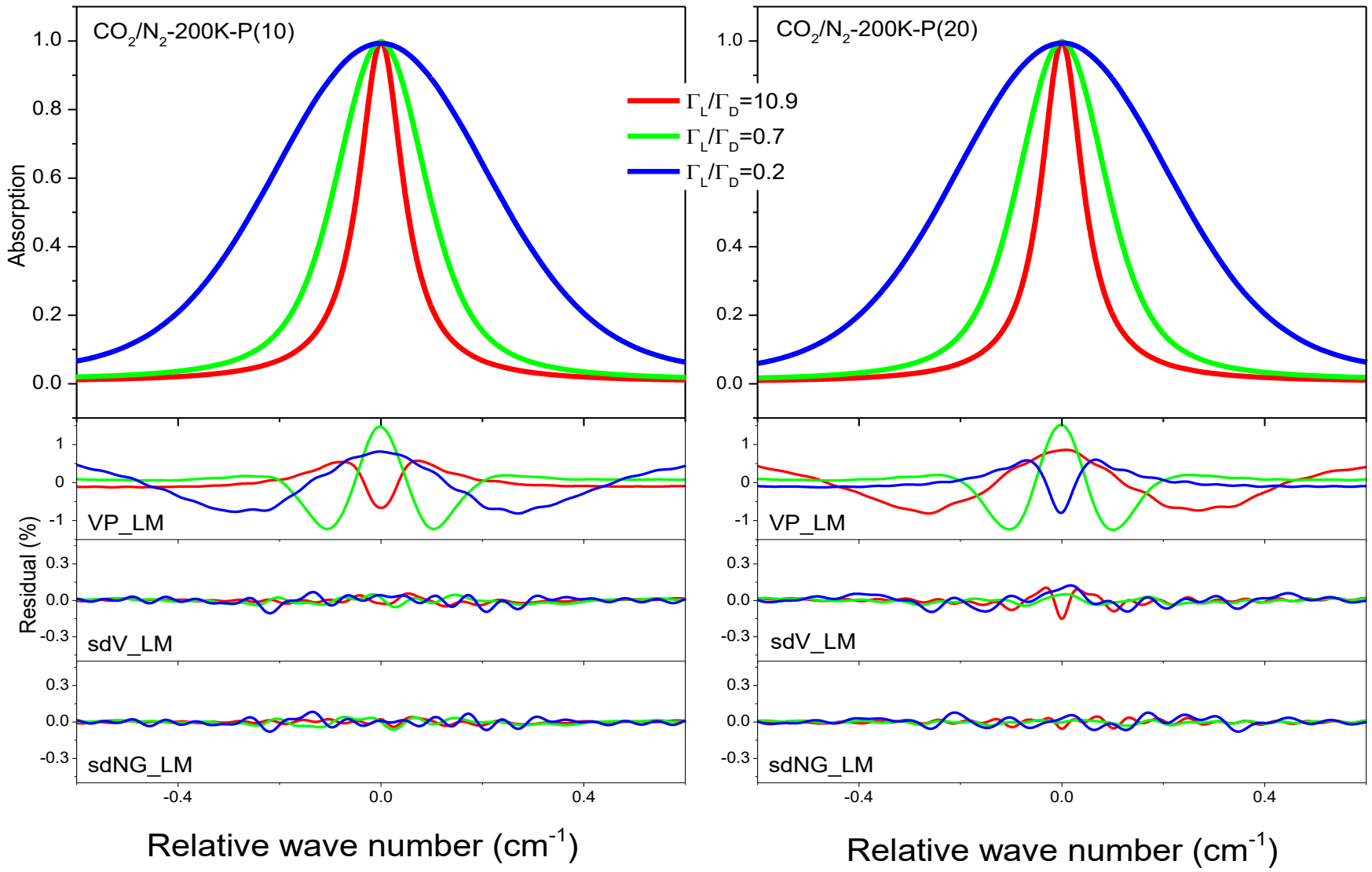
From the dipole ACF to the spectral density: requantization

- For a molecule of classical rotational angular momentum ω_i we find the integer J_i for which $\hbar J_i/I$ is the closest to ω_i.
- Once J_i is found, ω_i is requantized by using the new value $\omega_i^{req} = \hbar J_i/I$ while the orientation of the angular momentum is kept unchanged.

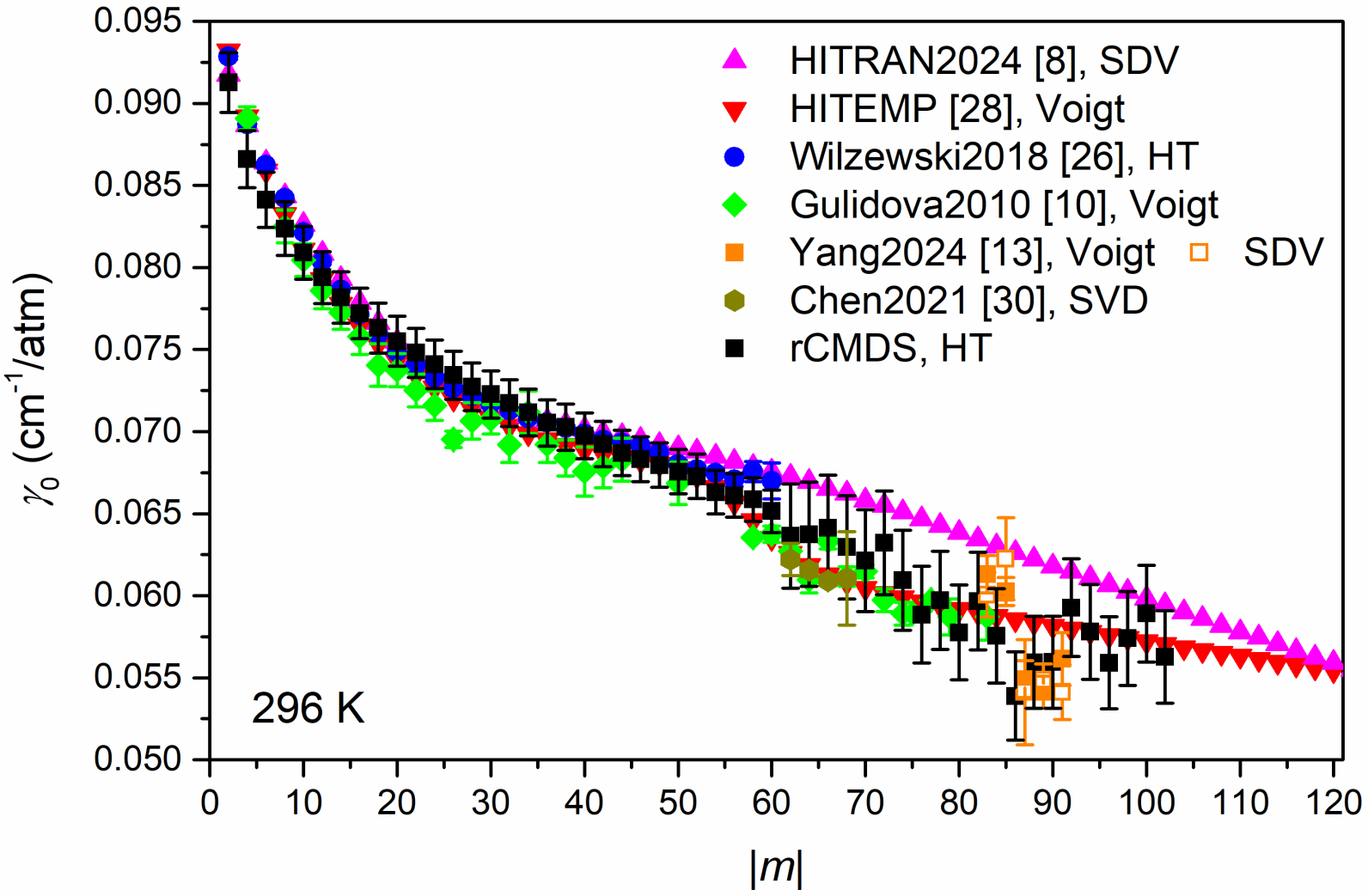
All collisional effects are included, **not a single** parameter has been adjusted



Retrieval of line-shape parameters

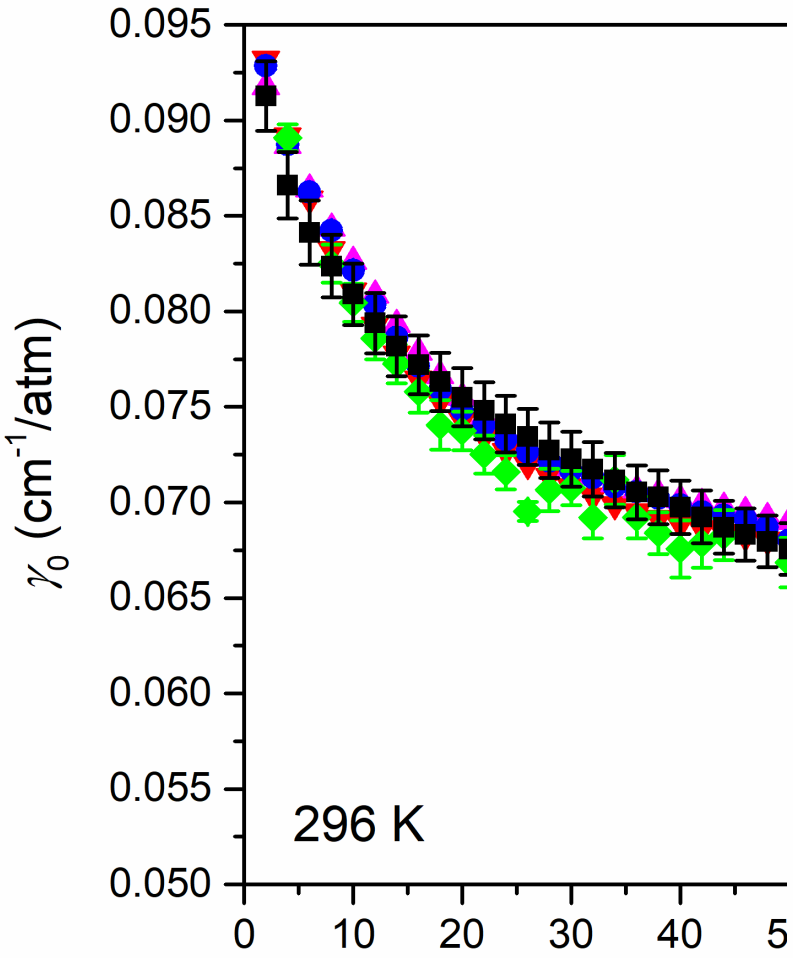


Examples: Results for N_2-broadened CO_2

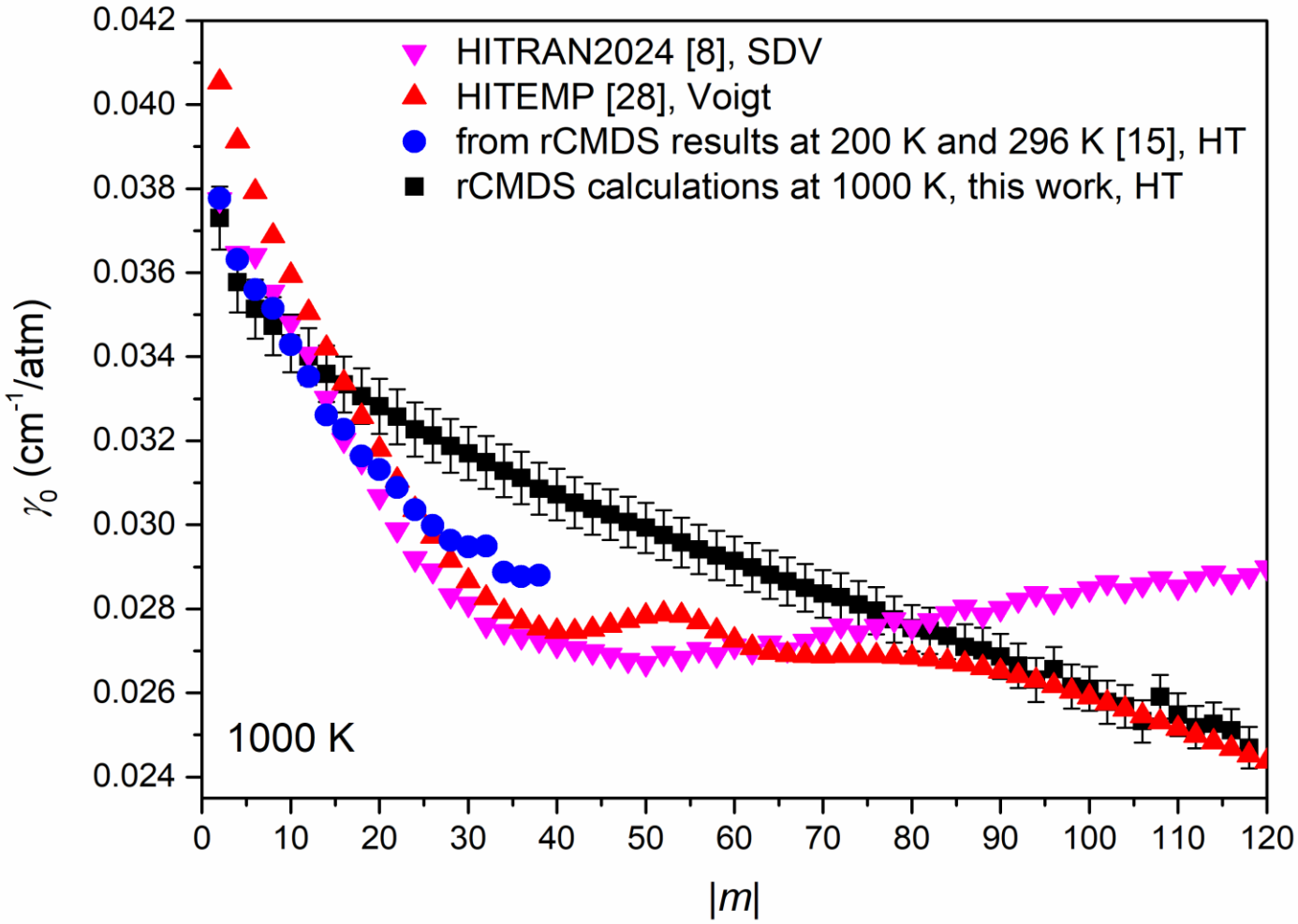


Tran et al., JQSRT, 342, 2025, 109499

Examples: Results for N_2-broadened CO_2

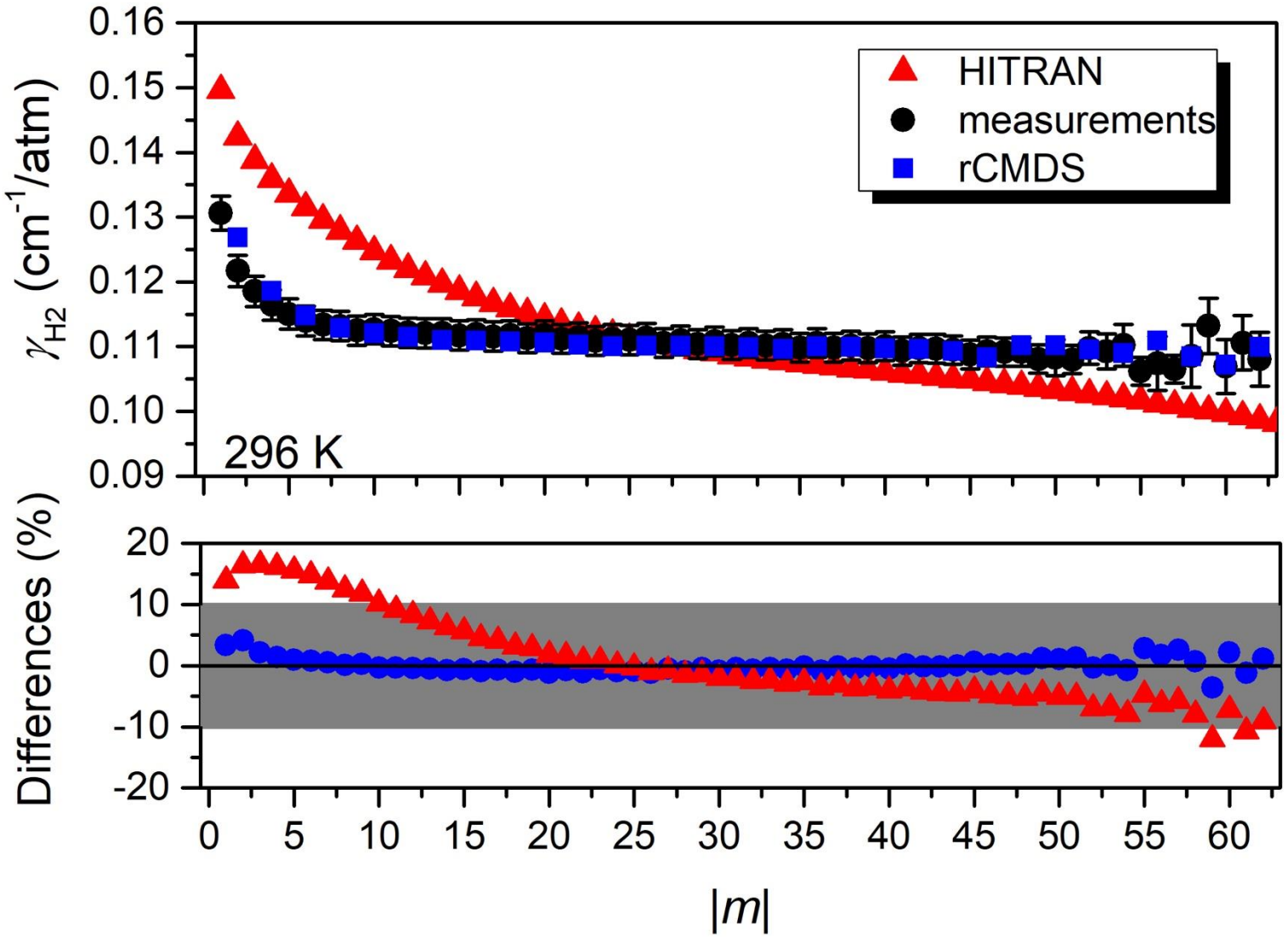


$\gamma(T)=\gamma(T0)*(T0/T)^n$



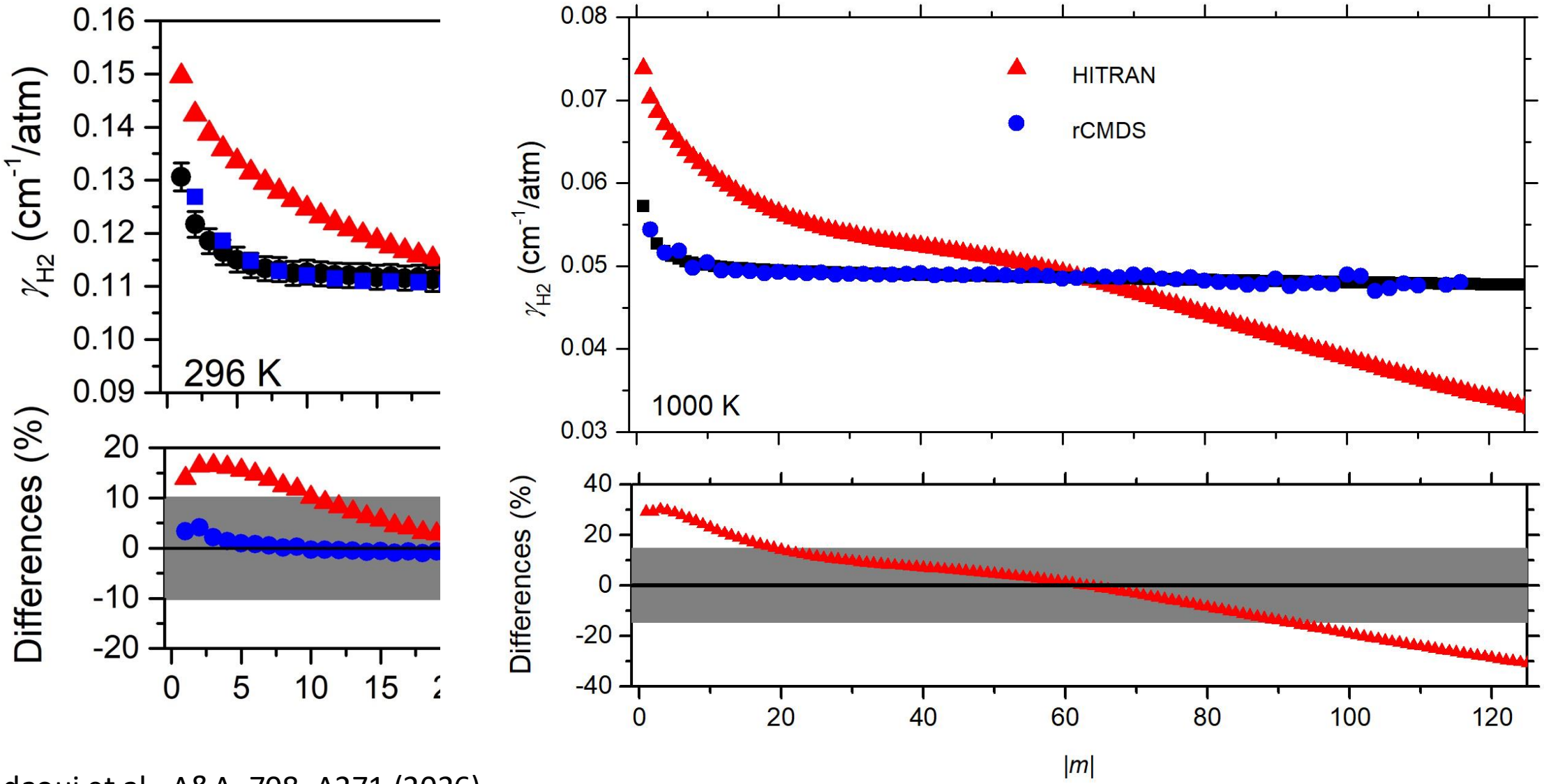
Tran et al., JQSRT, 342, 2025, 109499

Results for H_2-broadened CO_2



Hendaoui et al., A&A, 708, A271 (2026)

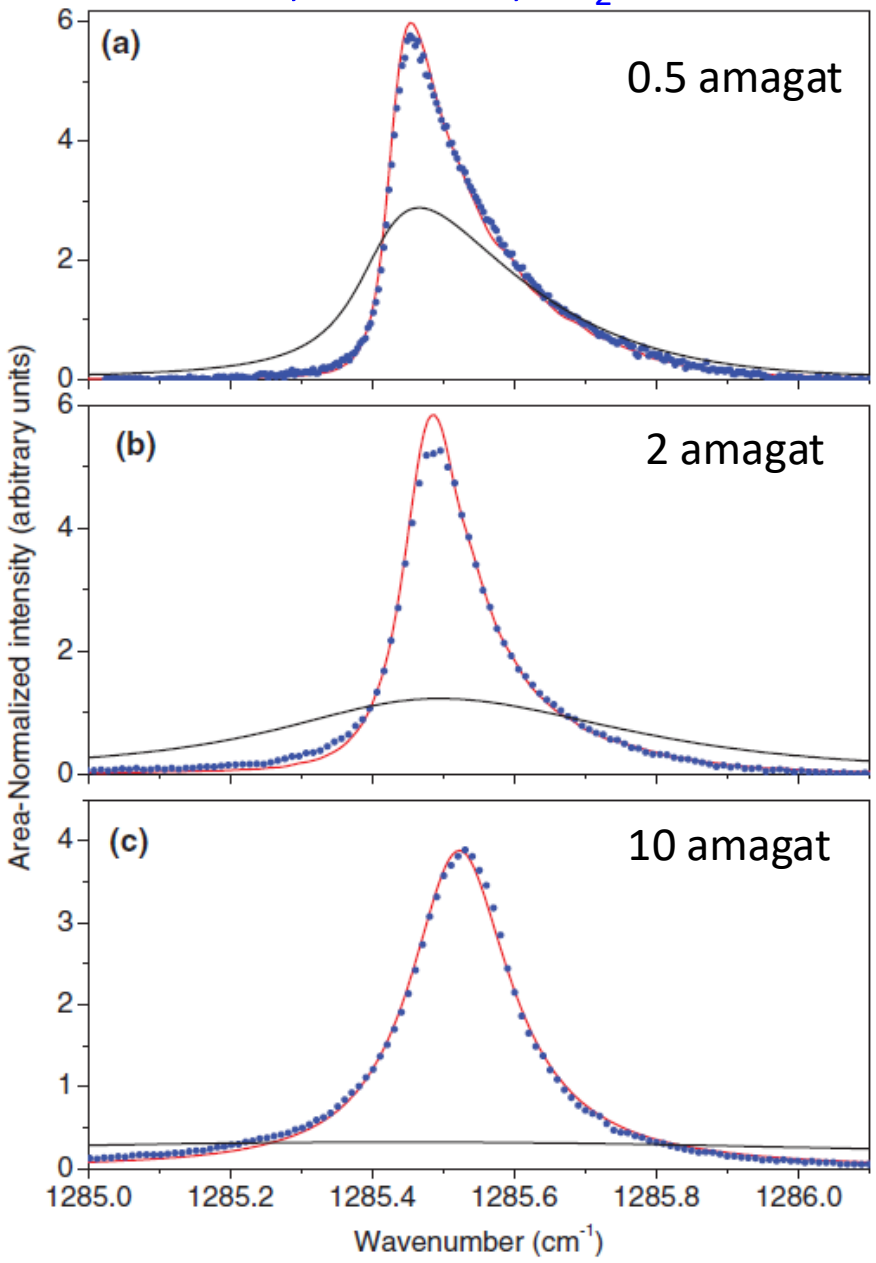
Results for H_2-broadened CO_2



Hendaoui et al., A&A, 708, A271 (2026)

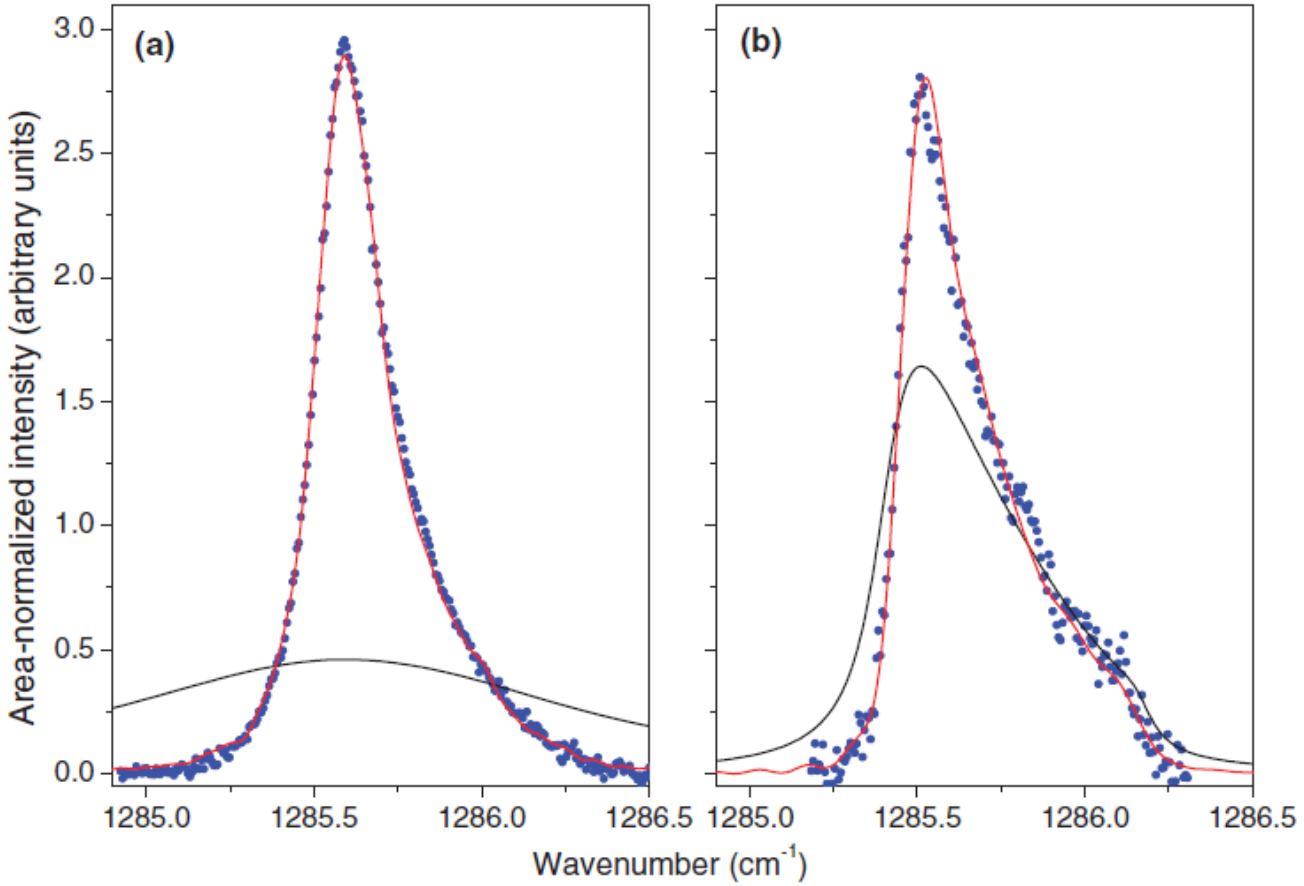
4

self-broadened CO_2
295 K, Q branch, $2\nu_2$ band



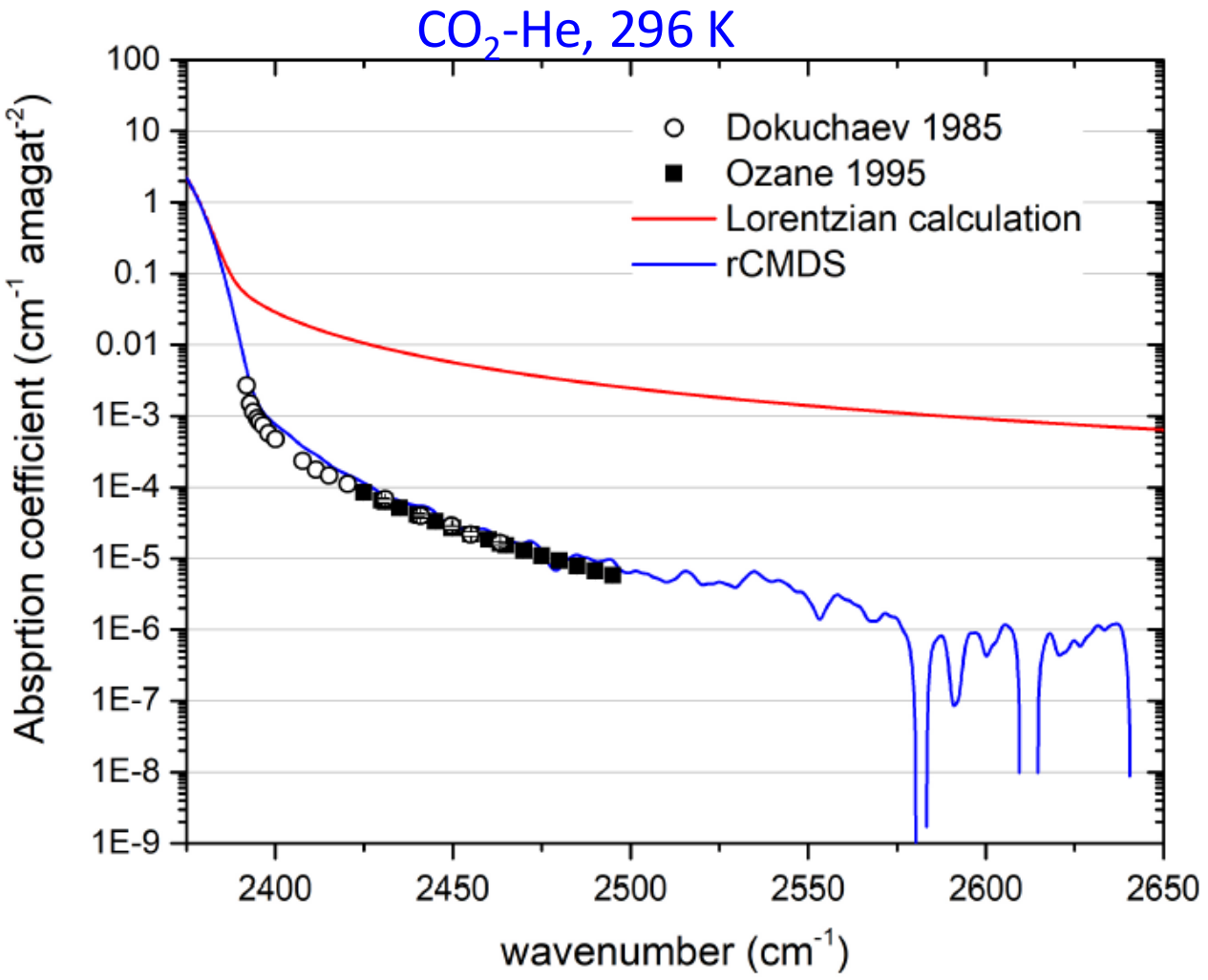
Line-mixing

self-broadened CO_2
700 K, Q branch, $2\nu_2$ band



Lamouroux et al, J Chem Phy, 138, 244310 (2013)
doi: 10.1063/1.4811518

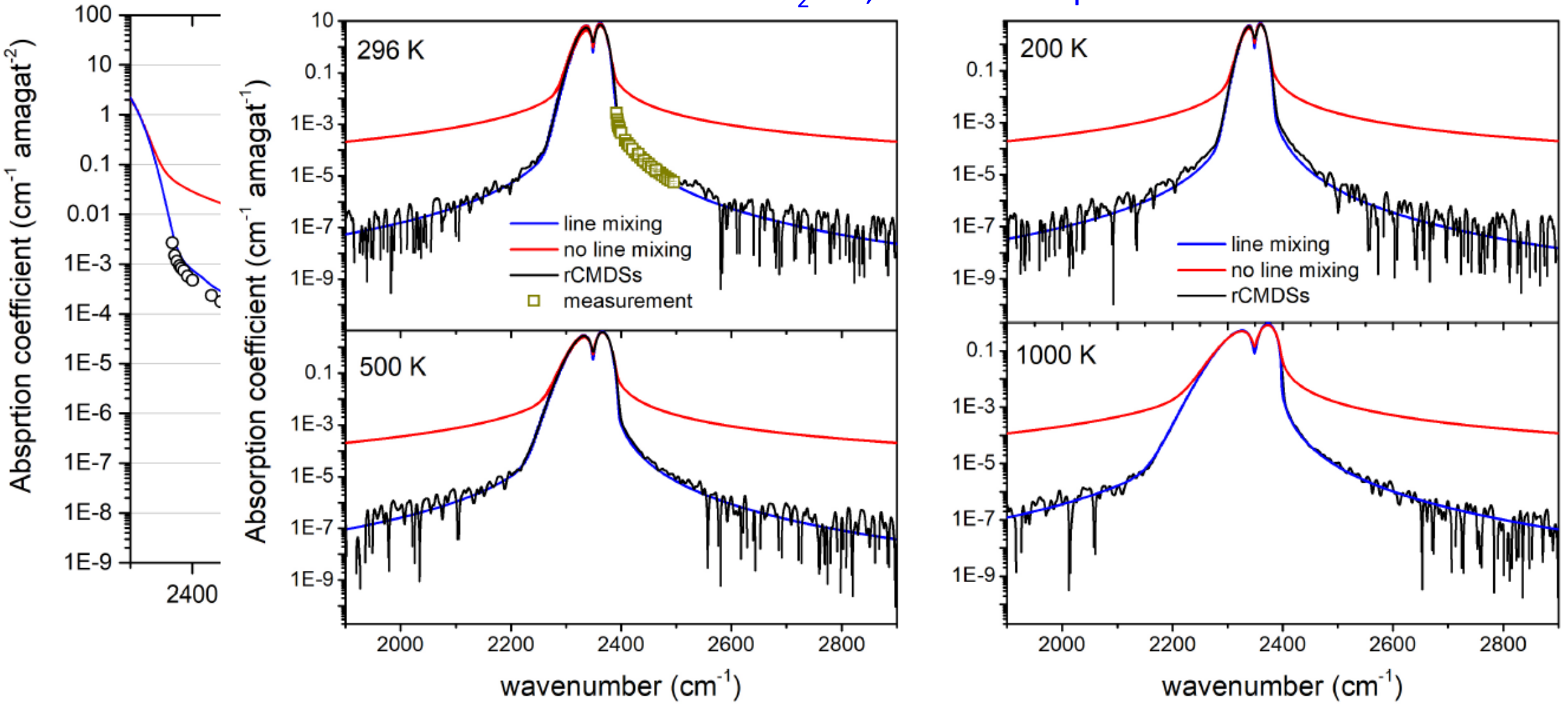
Far-wing absorption



Tran et al., in preparation

Far-wing absorption

CO_2-He, various temperatures



Conclusions

• Collisional effects are a key issue for atmospheric opacity calculations in exoplanet atmosphere characterization and radiative transfer modeling

• Much efforts are needed to measure and predict spectral shape parameters and their temperature dependence, as well as collision-induced absorption, far-wing absorption in P, T conditions relevant to exoplanet atmospheres

• First-principles calculations, based on requantized molecular dynamics simulations are very promising, enabling accurate predictions of various collisional effects on spectra.

• Development and application of such calculations to other molecular systems, including H_2O as active species and broadener

Acknowledgment

Jean-Michel HARTMANN

Ngoc Hoa NGO

Emile DUCREUX

Julien LAMOUROUX

Faten HENDAOUI

Duc Dung TRAN

Christian BOULET

Lee DENIS

Manfred BIRK

Joseph HODGES

Xavier LANDSHEERE

Pascale CHELIN

Marcel SNELS

Iouli GORDON

Gang LI

David JACQUEMART

And many others

Thank you for your attention!

Laboratory studies of line-shape parameters

Measurements: numerous measurements for various absorbing species, pure or diluted in mixtures

- Still relatively few measurements for broadeners other than air
- Efforts needed for temperature and pressure conditions relevant to planet and exoplanet atmospheres

Calculations: various impact models using the intermolecular potential

- Fully quantal Close Coupling models (only possible for simple collisional pairs)
- Semi-classical approaches (Robert Bonamy and followers):

  Generally accurate within 10%, often better

  Some remaining problems for high J
- Classical calculations