# Pressure effects on spectral shapes and precise atmospheric remote sensing

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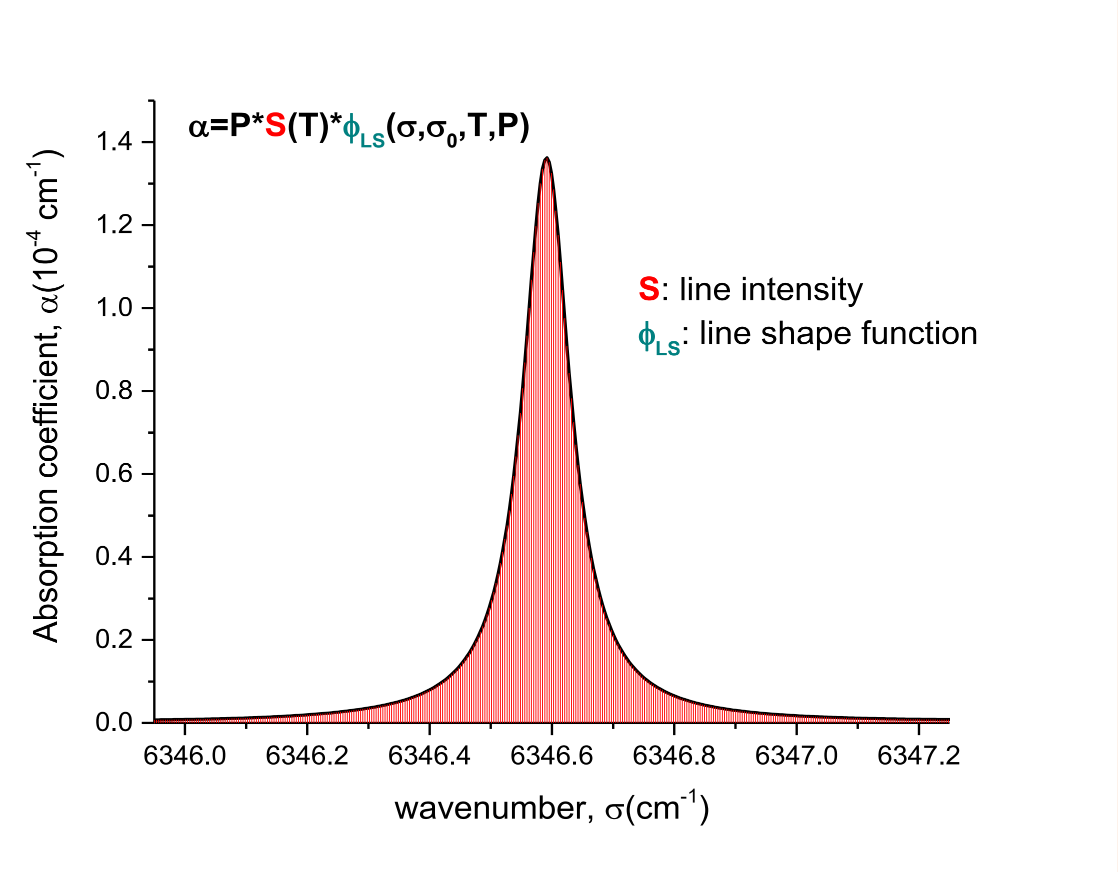
- Introduction
- Isolated line shapes
- Line-mixing effects
- Pressure dependence of the measured line intensity
- Conclusions

# Line shape modeling

- Greenhouse gases remote sensing requires absorption cross-section modeling with unprecedented high accuracy

- Line intensity and shape parameters must be determined with accuracy better than a few per mill



# The optical thickness and the spectral profile

The optical thickness along the line of sight:

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

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 of transition $\emptyset_{LS}$ 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 optical thickness and the spectral profile

$\Phi(t)$ is given by the integral over all velocities of the autocorrelation function $\Phi(\vec{v},t)$ of the dipole moment of molecules having velocity $\vec{v}$ :

$$\Phi(t) = \int d\Phi(\vec{v},t)\, d\vec{v}$$

with $\phi(\vec{v},0) = f_{MB}(\vec{v})$

$\Phi(\vec{v},t)$ satisfies the Boltzmann-Liouville kinetic equation:

$$\frac{\partial\phi(\vec{v},t)}{\partial t} = -\int f(\vec{v}',\vec{v})\phi(\vec{v},t)d\vec{v}' + \int f(\vec{v},\vec{v}')\phi(\vec{v}',t)d\vec{v}'$$
$$+\left(i\omega_0 + i\vec{k}\vec{v} - \Gamma(v) + i\Delta(v)\right)\phi(\vec{v},t)$$

# Isolated line shapes

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→ Doppler profile

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⟹ Voigt profile

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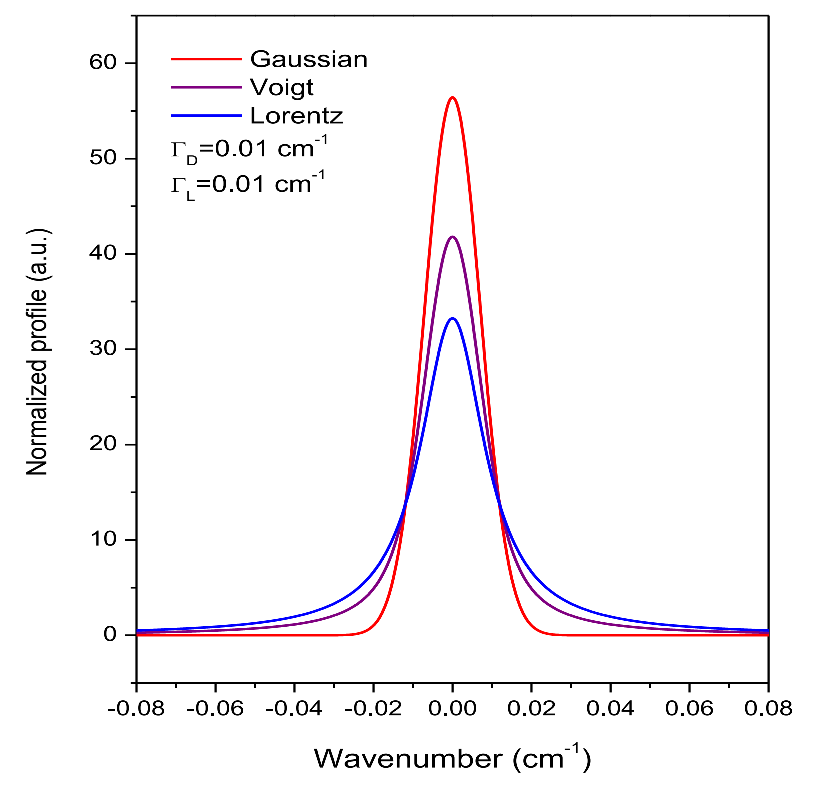

$$I_V(\omega) = \int_{-\infty}^{+\infty} I_D(\omega' - \omega_0)\, I_L(\omega - \omega', \Gamma, \Delta)\, d\omega'$$

$\vec{v}' + \int f(\vec{v}, \cancel{\quad} \vec{v}', t)\,d\vec{v}'$

$+ i\Delta(\cancel{\;})\big)\, \phi(\vec{v}, t)$

$\Longrightarrow$ Voigt profile

*Comparaison between the Doppler, Lorentz and Voigt profiles.*

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Speed dependent hard collision model

# The Hartmann-Tran (HT) profile

HT profile : Speed dependent hard collision model + correlation between velocity- and internal-state-changing collisions

- It can accurately represent isolated line shapes of various systems in atmospheric conditions with an accuracy of 0.1%

- HT profile can be expressed as a combination of Voigt profiles ⇒ comparable computational times

- Equivalent to simplified profiles in different limits ⇒ it can be used with existing data obtained from simplified profiles

- First-order line-mixing can be easily included

**Current accurate spectroscopic measurements exclusively use this profile**

Systems: $CO_2$, $CH_4$, $O_2$, CO, $NO_2$, $N_2O$, HCl,… and $H_2O$

Corresponding data included in databases,
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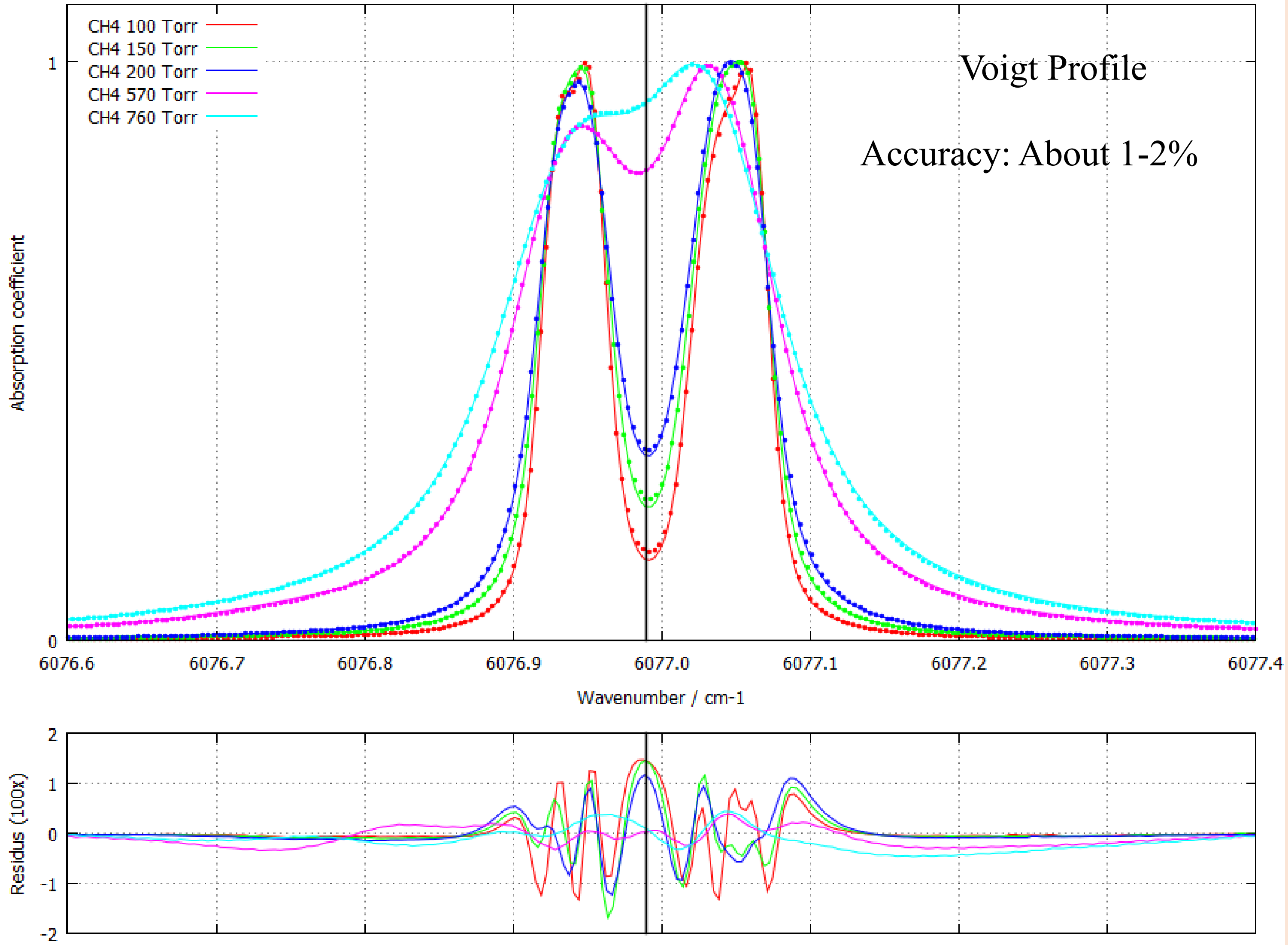

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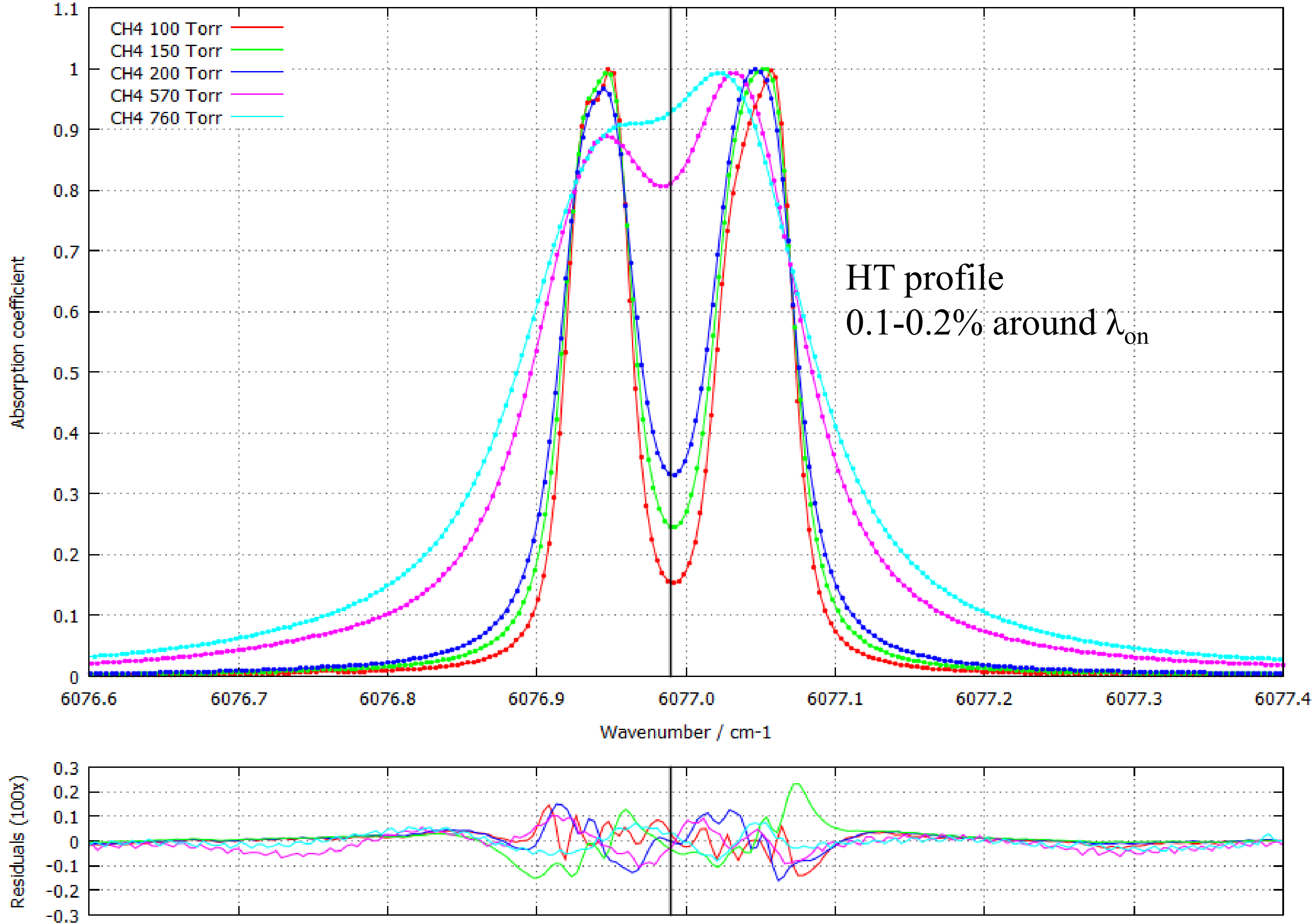

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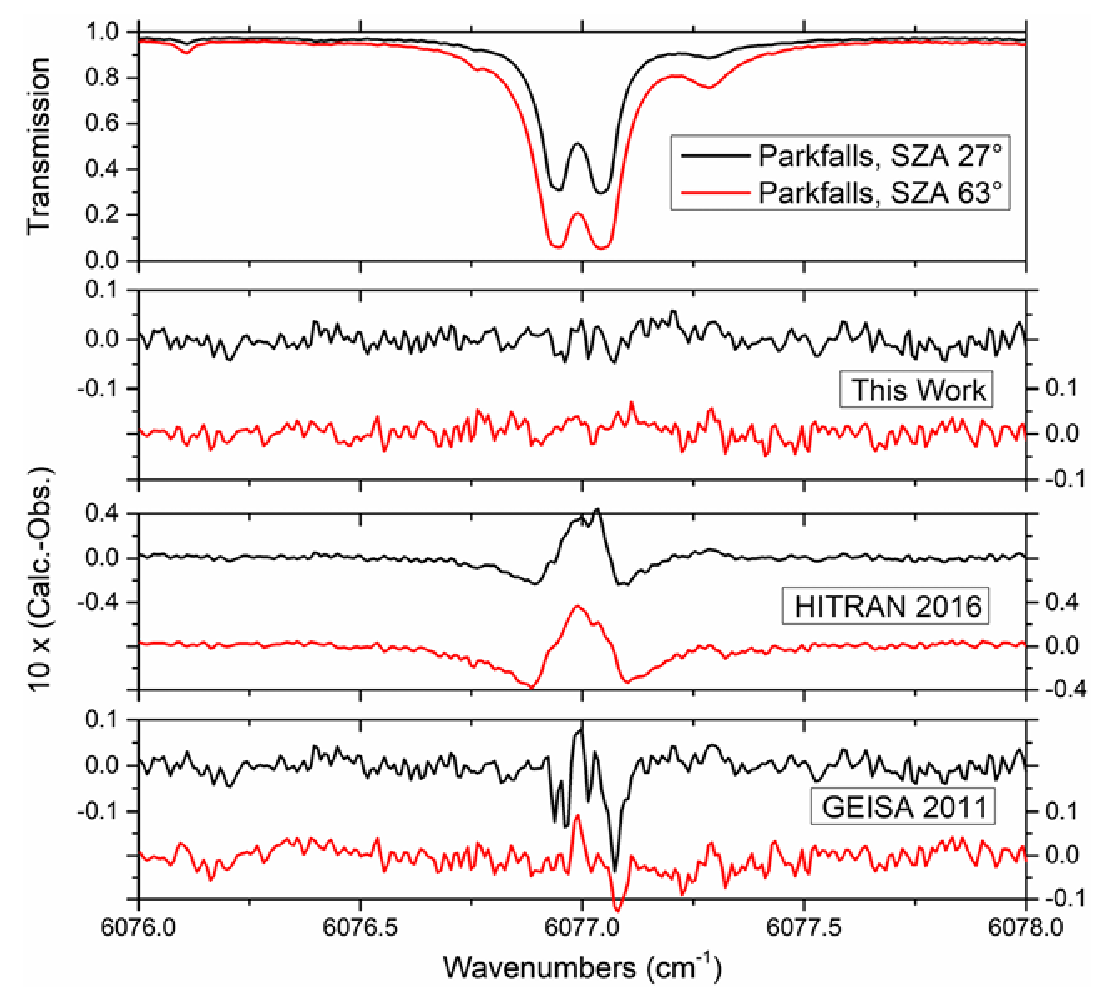

# Isolated line shapes

**Some remaining issues:**

- Few data available for temperatures other than room temperature
- Highly accurate data often cover small spectral ranges only
- First-order line mixing not sufficient for large line-mixing effects (e.g. $O_2$ A band, $CH_4$, $CO_2$ Q-branches)

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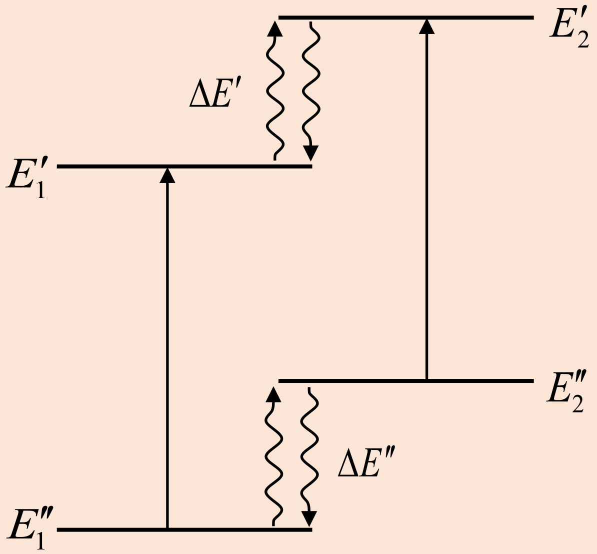
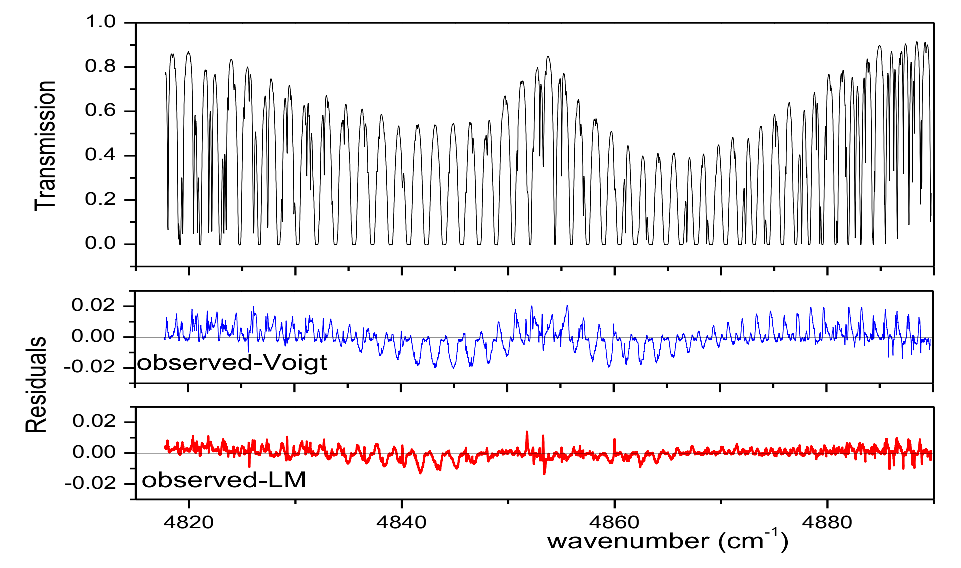


- Modeling of line-mixing effects
- Measurements of LM matrix elements from experimental data

# Line-mixing effects



← Fits of a ground based transmission spectra in the region of the $2\nu_1 + \nu_3$ band of $CO_2$

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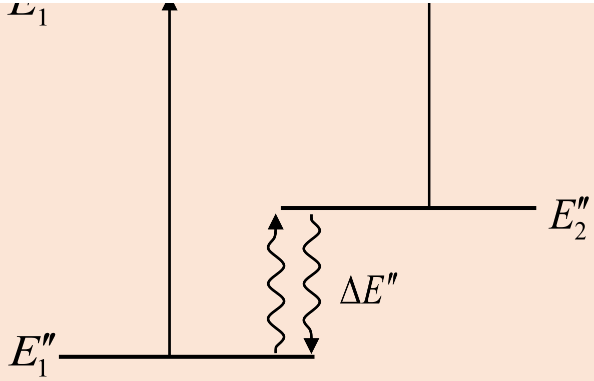

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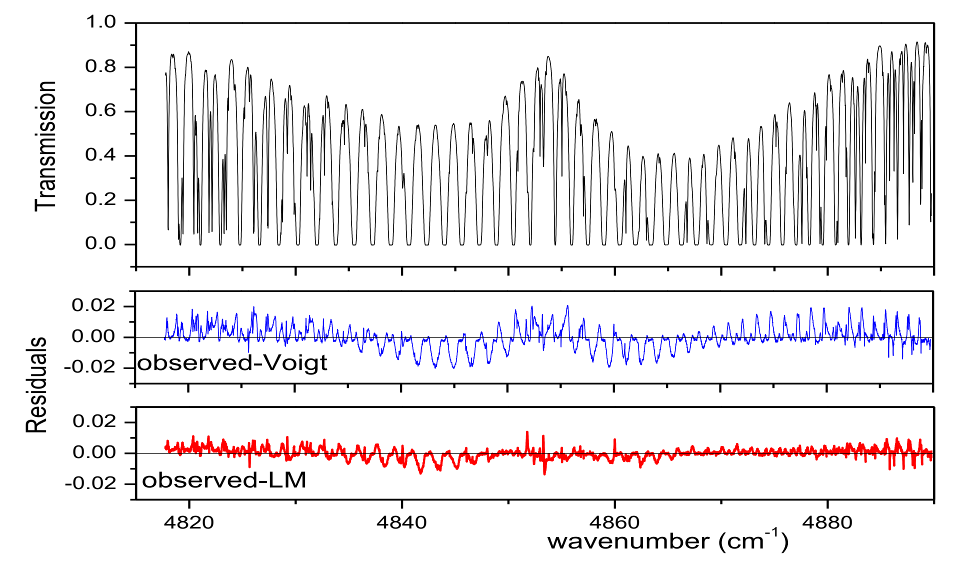

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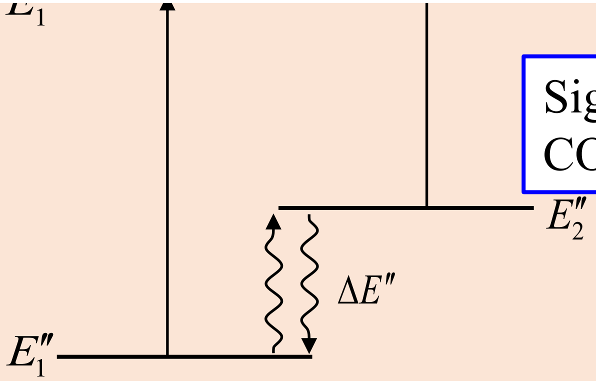
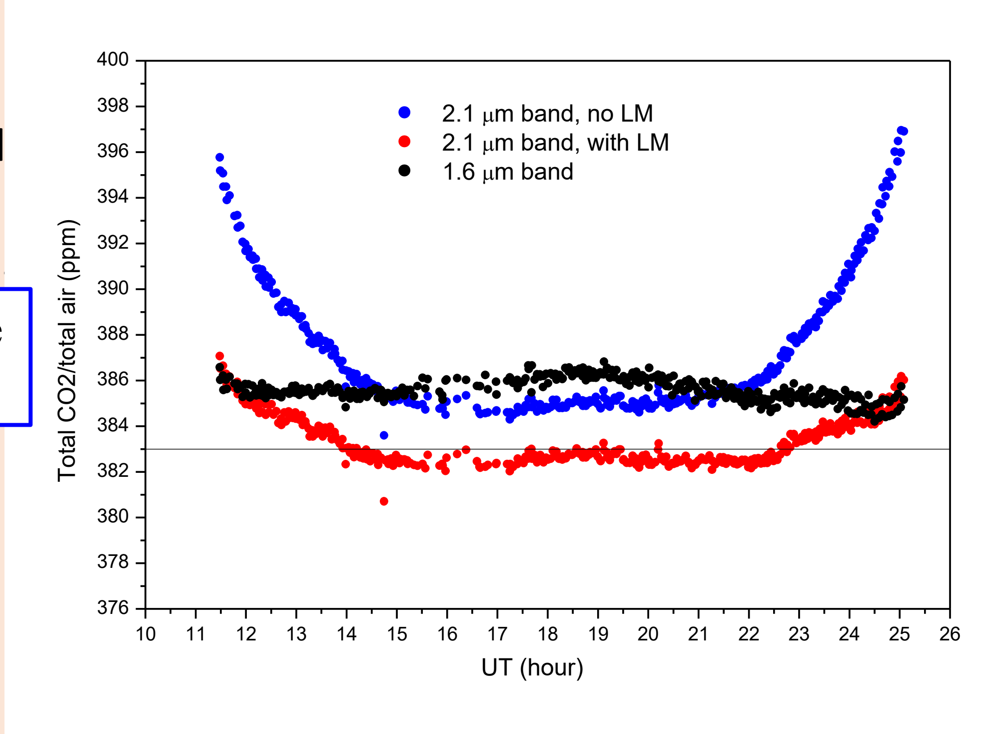


Significant errors (3%) on the $CO_2$ atmospheric amount.



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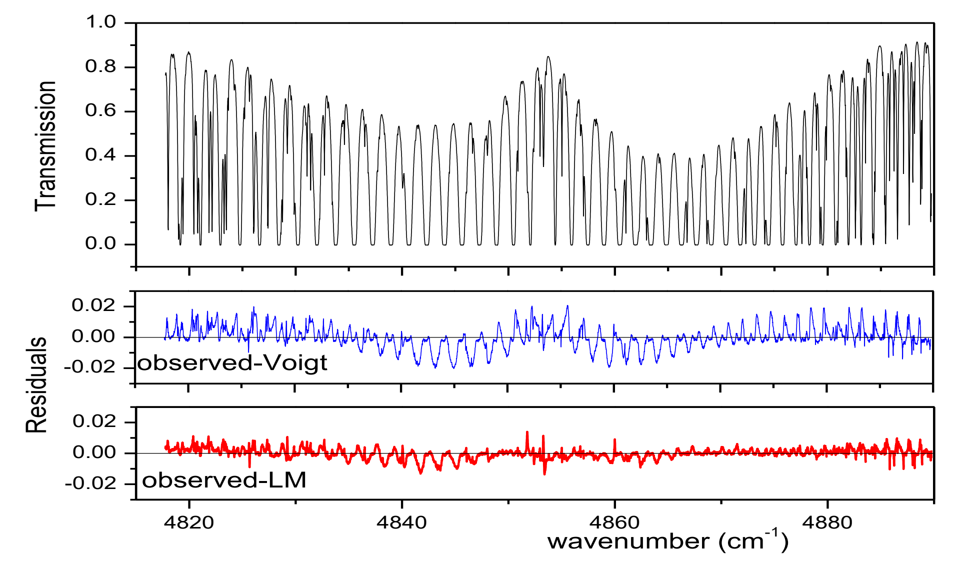

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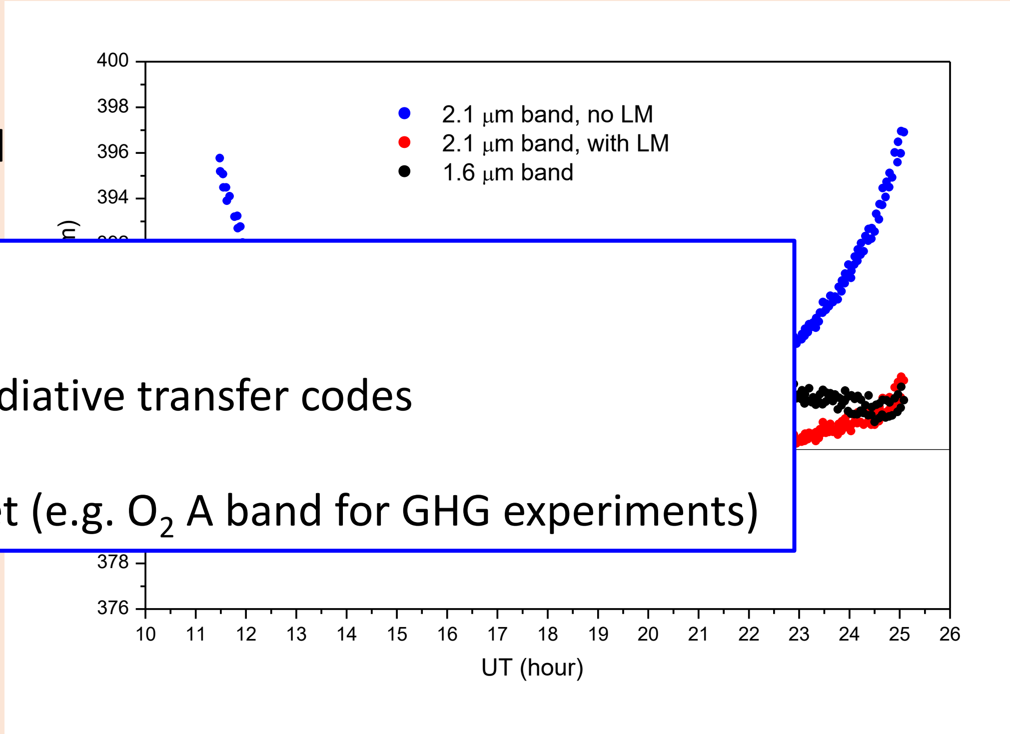
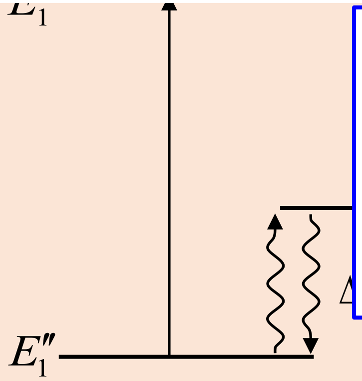




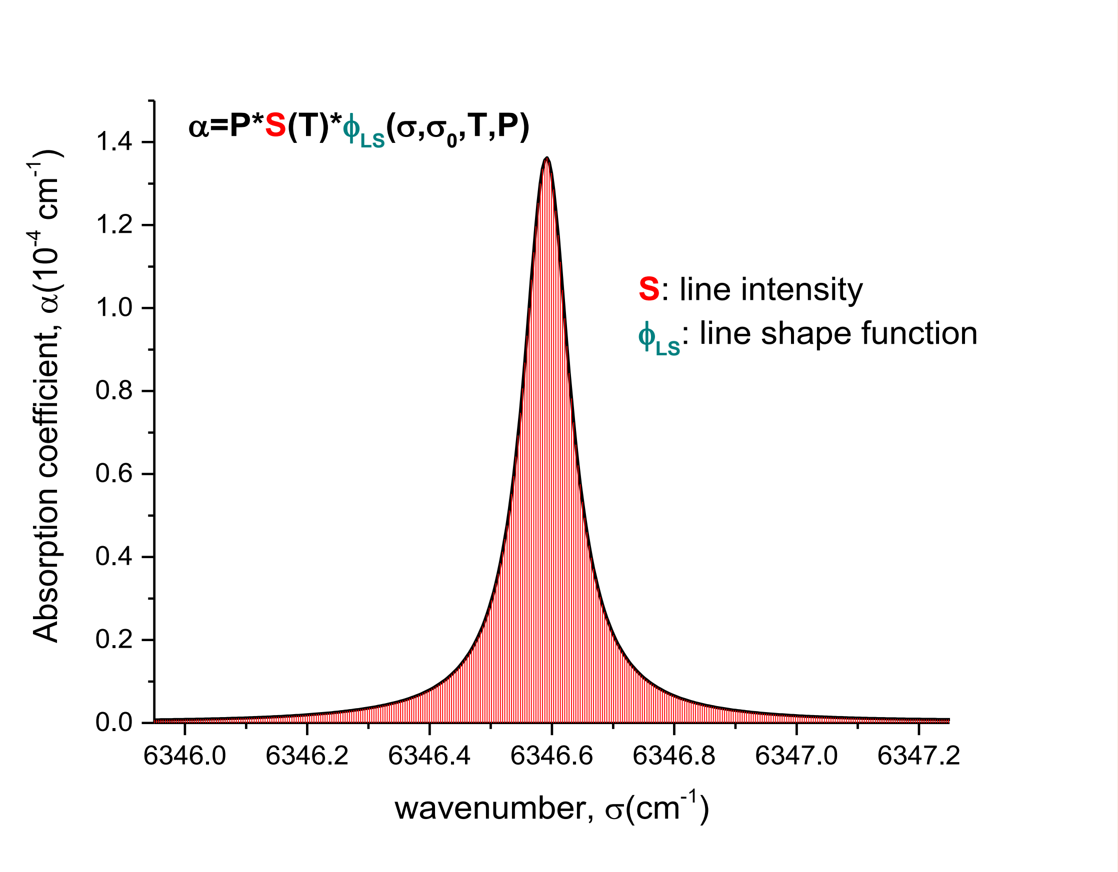
Remaining issues:

- Complexity in incorporating into radiative transfer codes
- Not reach accuracy requirement yet (e.g. $O_2$ A band for GHG experiments)

# Line shape modeling and line intensity

- Greenhouse gases remote sensing requires absorption cross-section modeling with unprecedented high accuracy

- Line intensity and shape parameters must be determined with accuracy better than a few per mill



- **Line intensity, S** is typically determined from fit of measured spectrum assuming a line-shape function. S is always assumed to be independent of pressure.

- **Line-shape function, $\phi_{LS}$:**

- Simplest case: Voigt profile (Doppler and pressure broadening), but leads to large deviation from the measured spectrum.

- Sophisticated profiles account for the speed dependence of collisional broadening and shifting; collision-induced velocity changes; collisional line mixings.

- HTp leading to good agreement (within a few per mill) with the measured spectrum in the central region of line for most molecular systems.

# The impact approximation

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

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

The impact approximation assumes that :

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

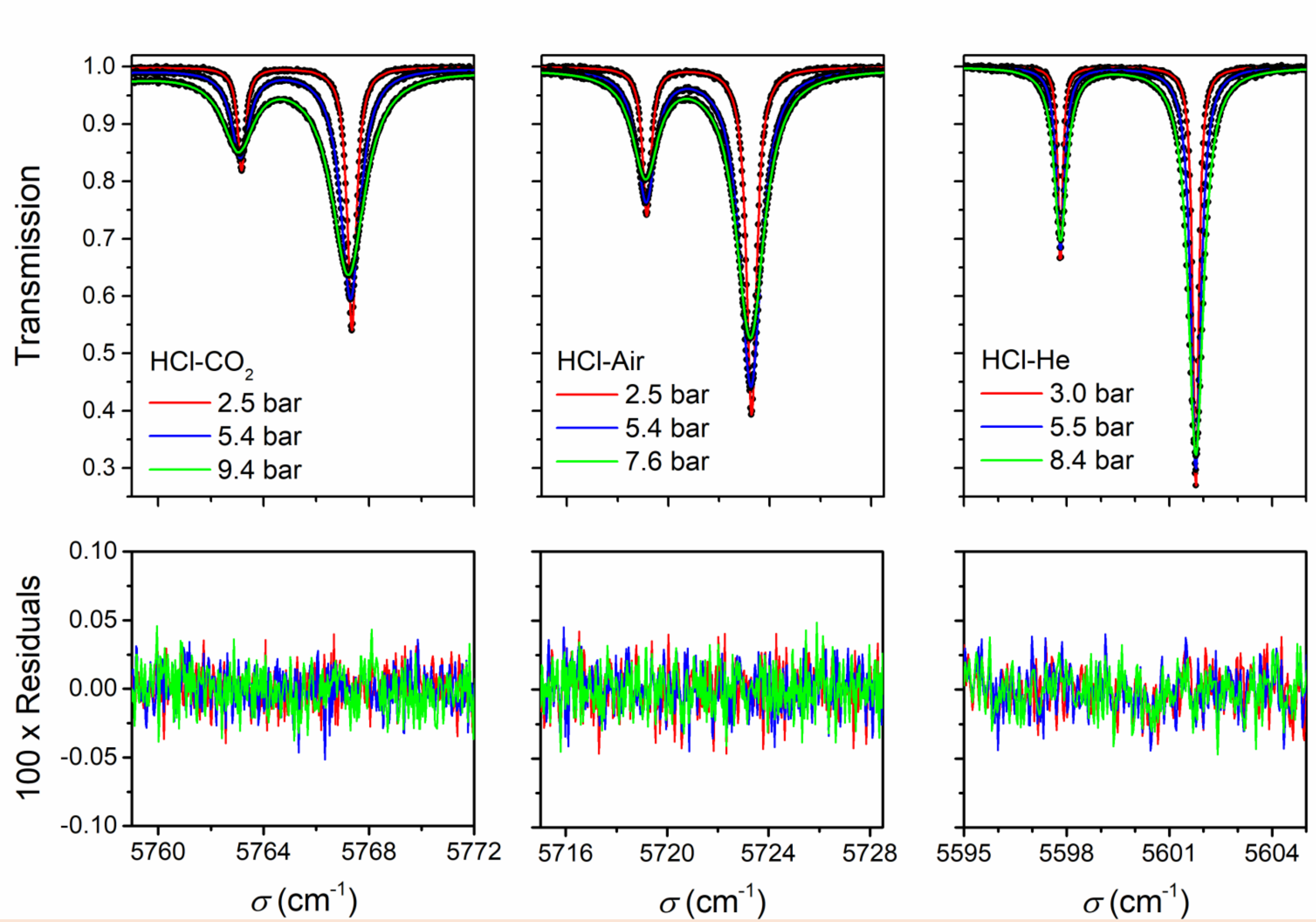
- Negligible influence of the finite duration of collisions: valid only for $|\omega-\omega_0|^{-1} >> \tau_c$ or for $|\sigma-\sigma_0| << (2\pi c\tau_c)^{-1}$

⇒ 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$^{-1}$)

Impact line-shape models fail to reproduce measured spectrum in the line wings. This can lead to significant consequences on the retrieved line intensity and the spectrum modeling!

# The case of HCl transitions

Fitting the measured spectra with an “impact” line shape: sdV+LM



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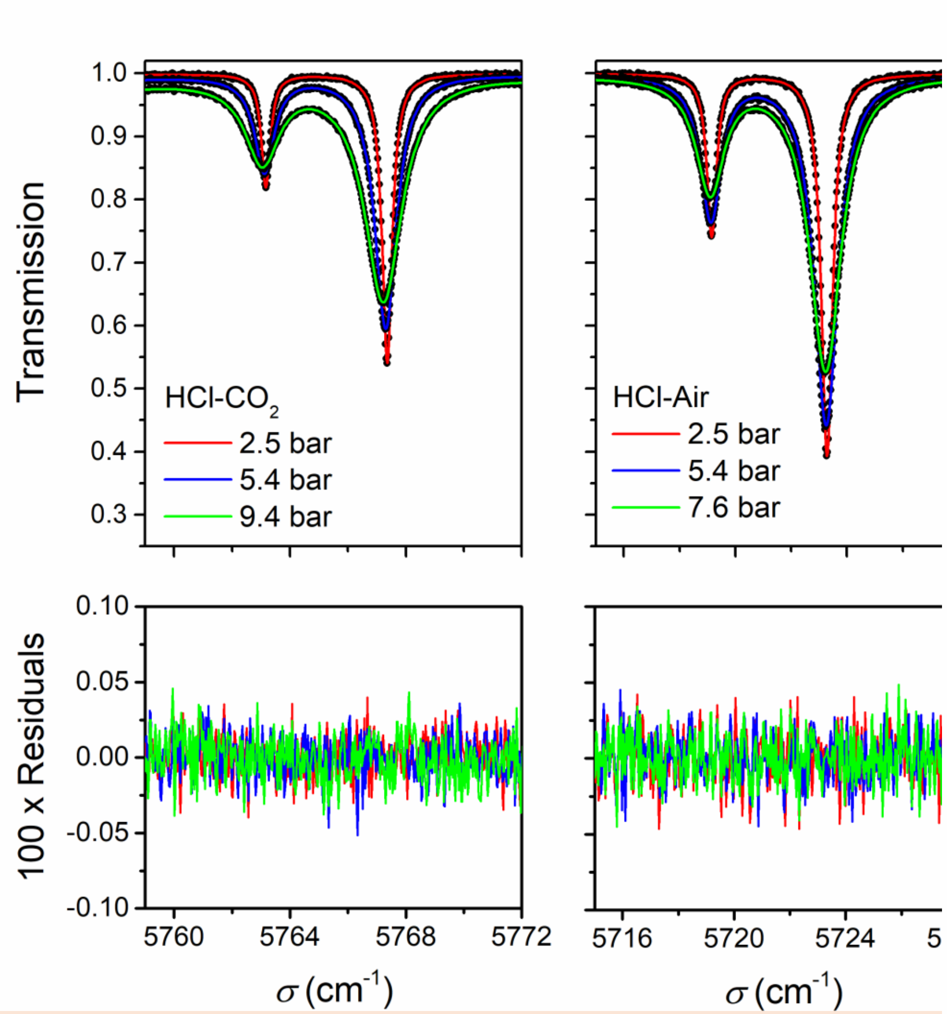
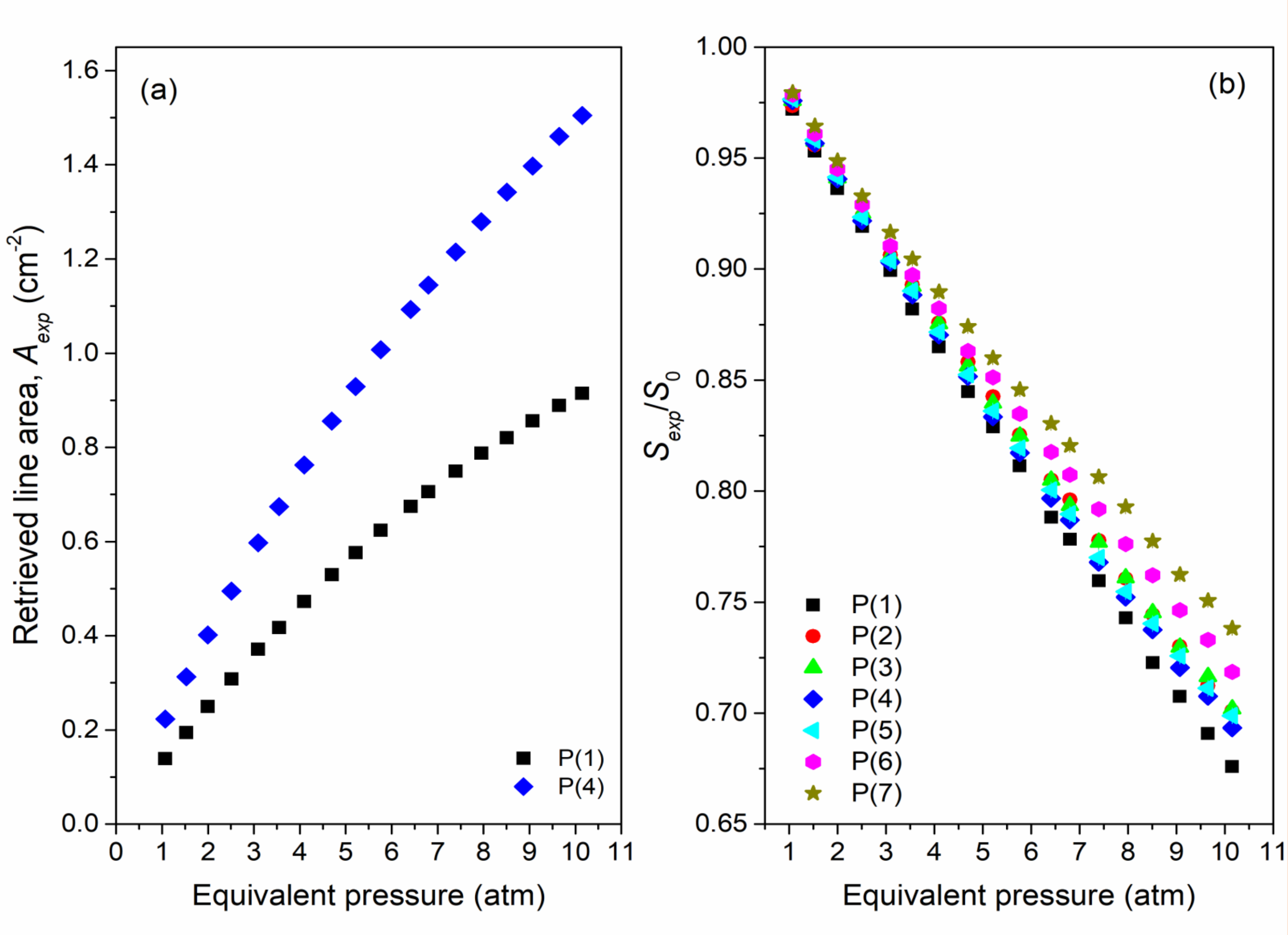


The retrieved intensity depends on the pressure!



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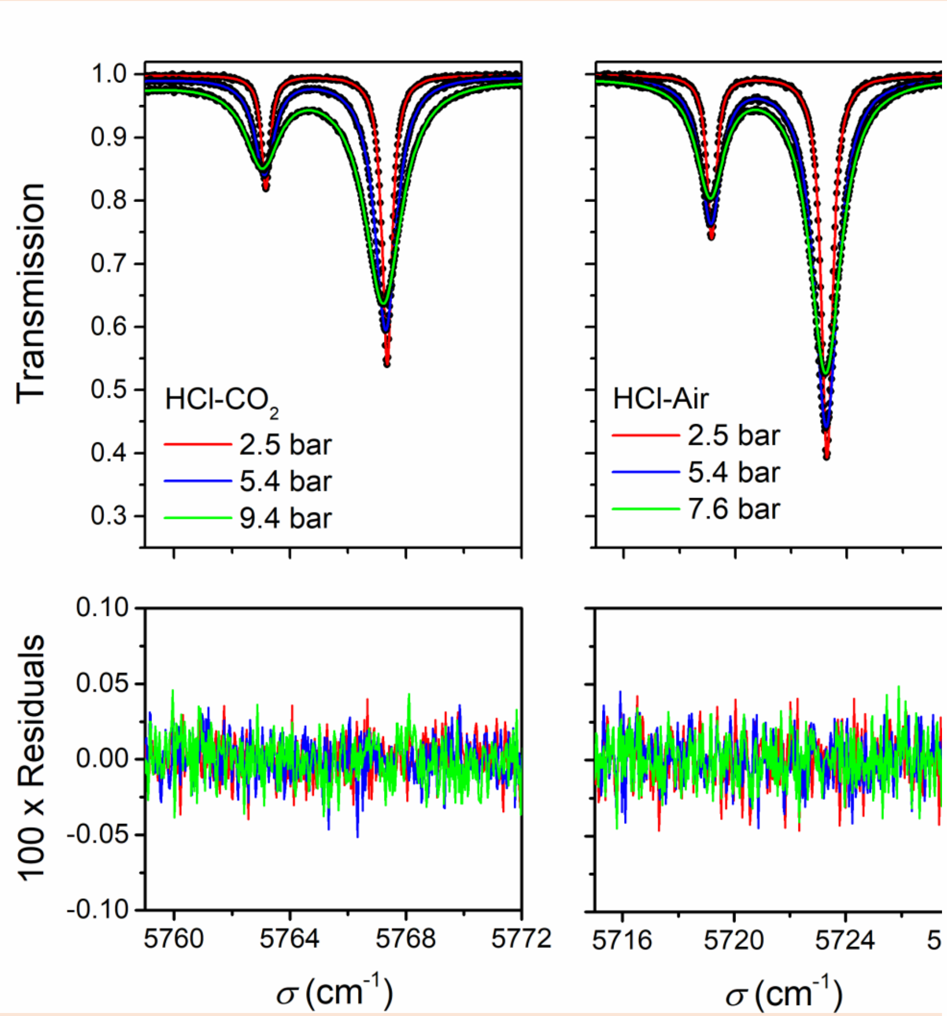

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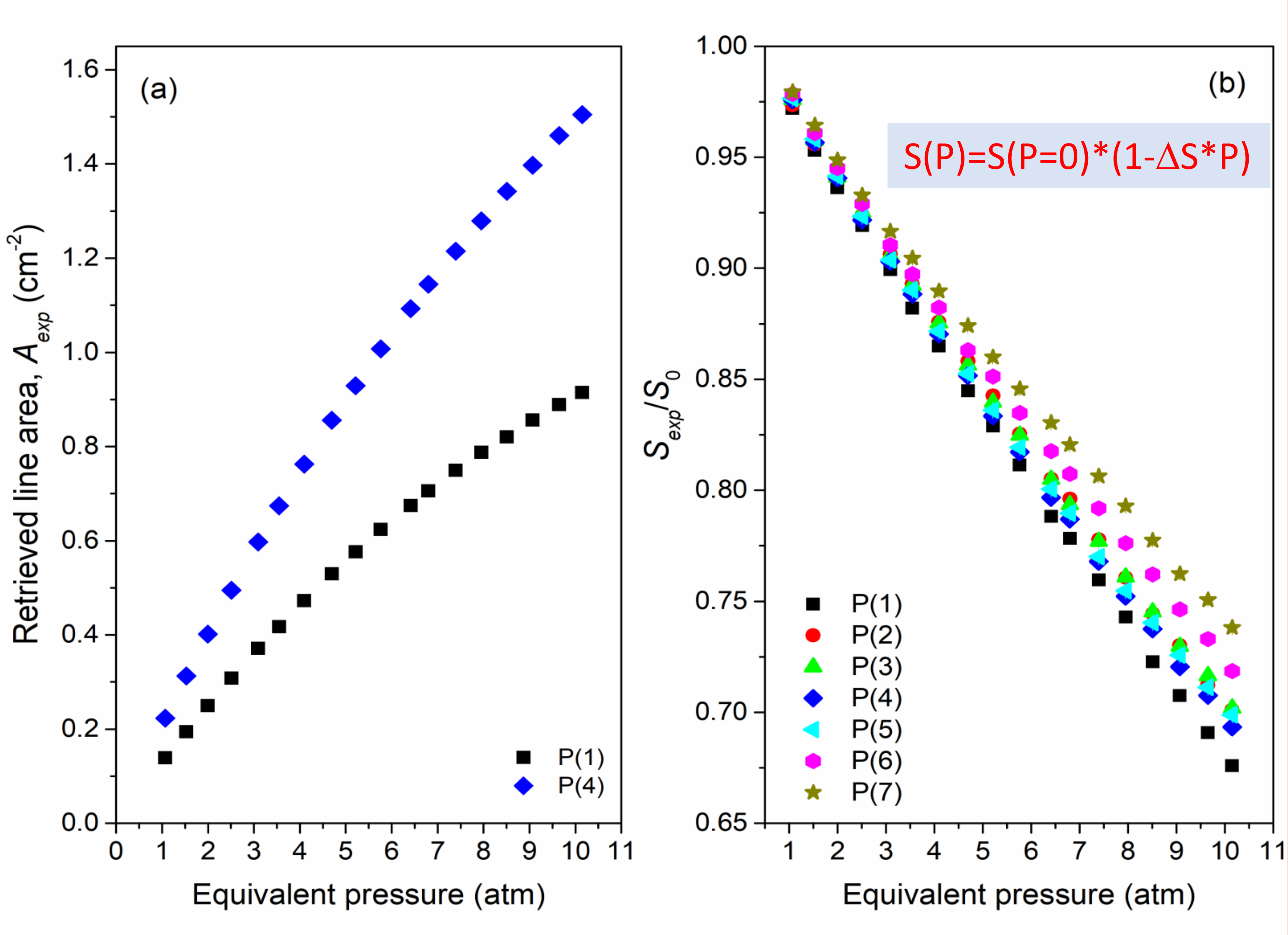
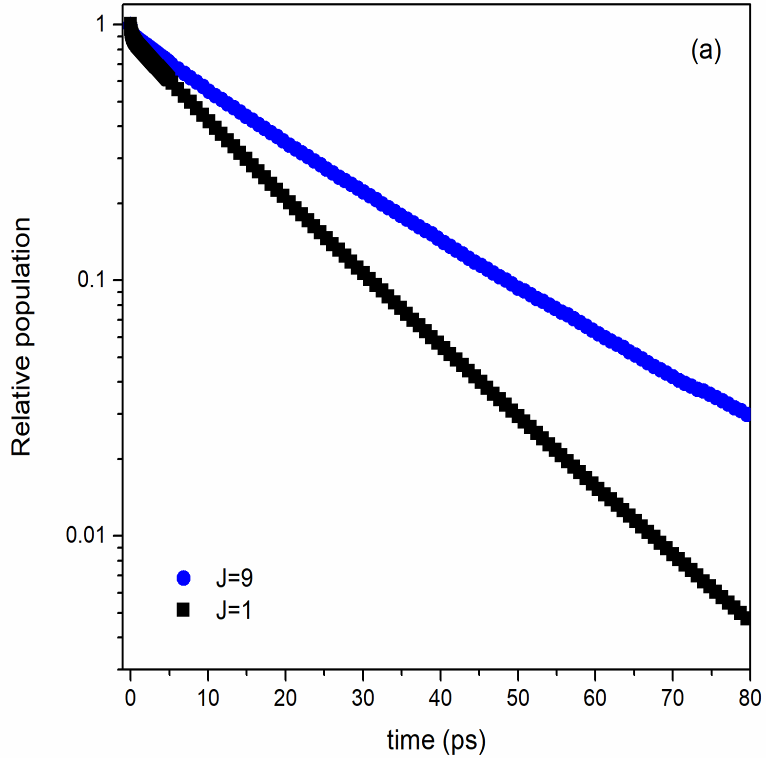
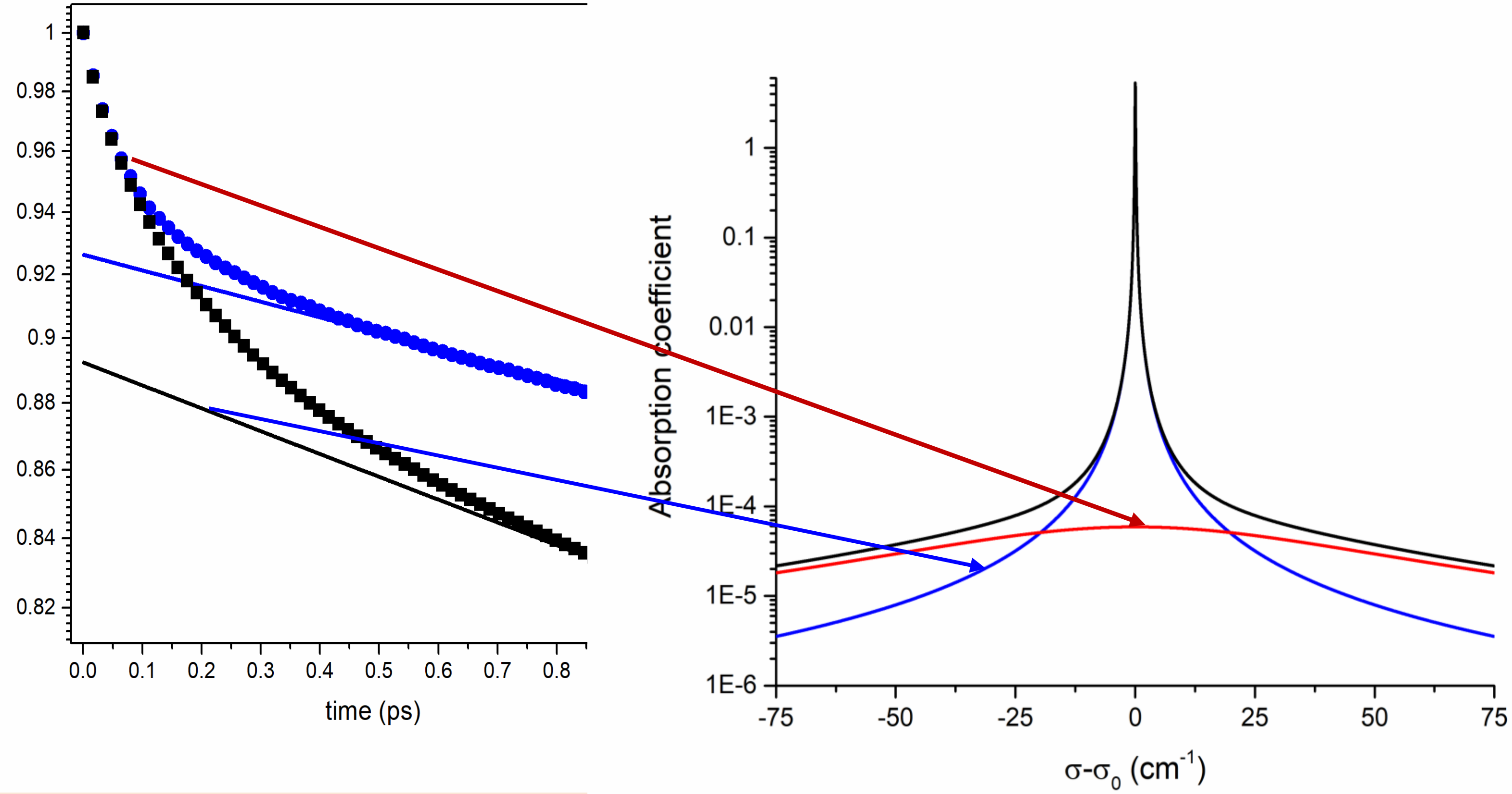


$S(P)=S(P=0)*(1-\Delta S*P)$

# Influence of ongoing collisions

$$\rho_m(t)/\rho_m(0) = (1\text{-}Pa_m)e^{-Pt/\tau_m^{\infty}} + Pa_m e^{-t/\tau_m^{0}}$$

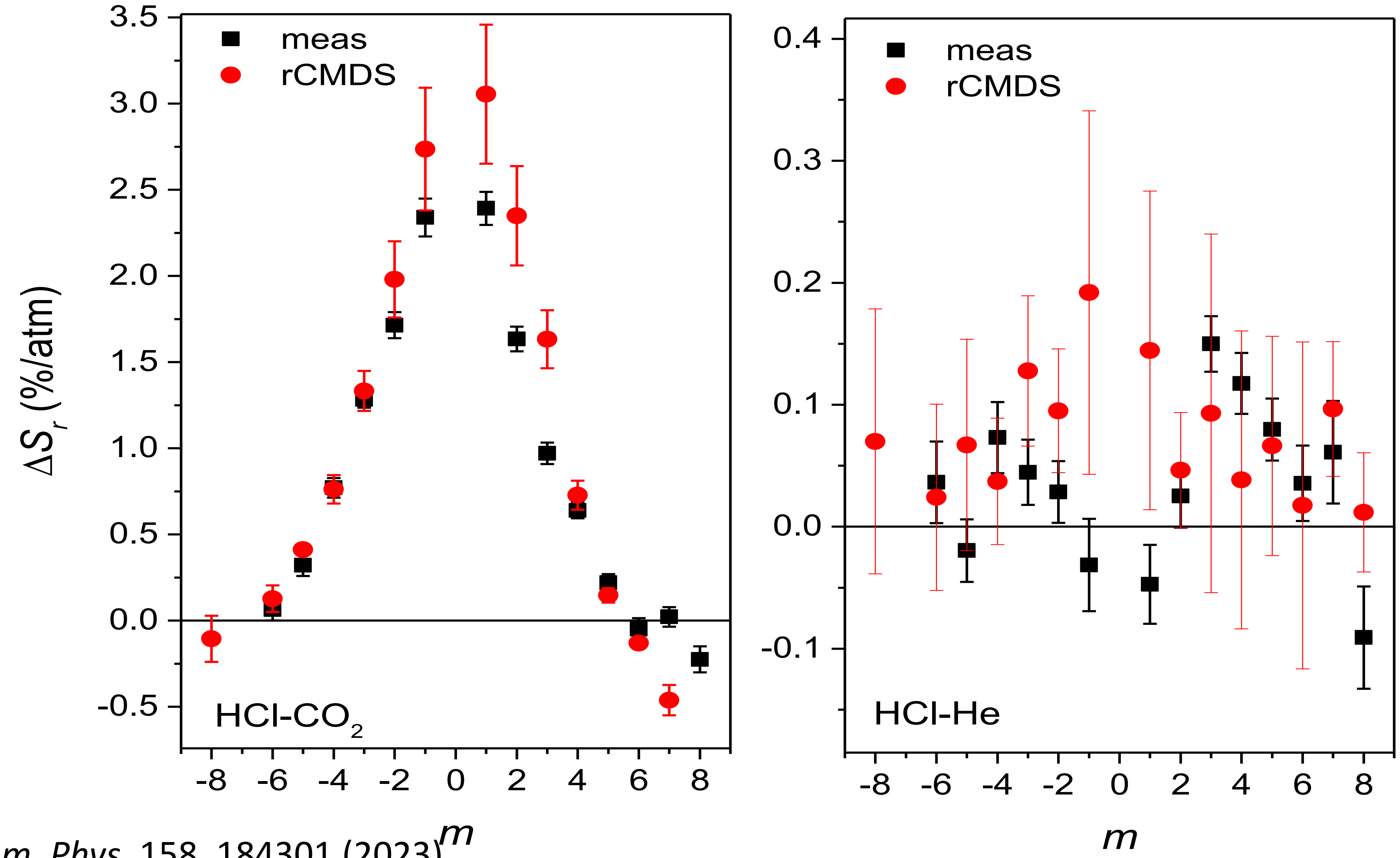




The total spectrum can be modeled as a sum of two contributions:

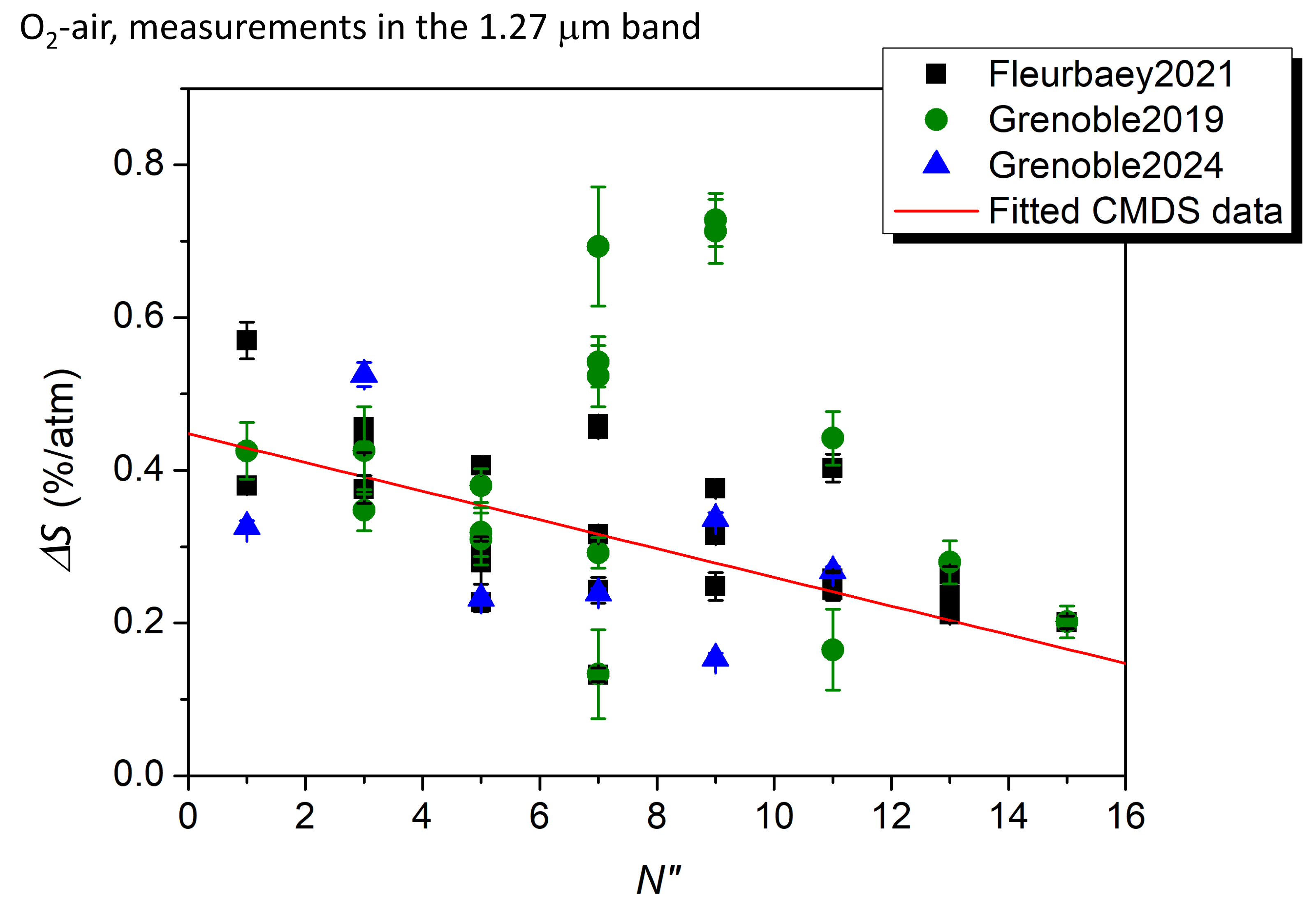
- An intense and narrow Lorentzian at the center of the line
- A weak and large Lorentzian whose magnitude increases with pressure

# Intensity depletion predicted by rCMDS

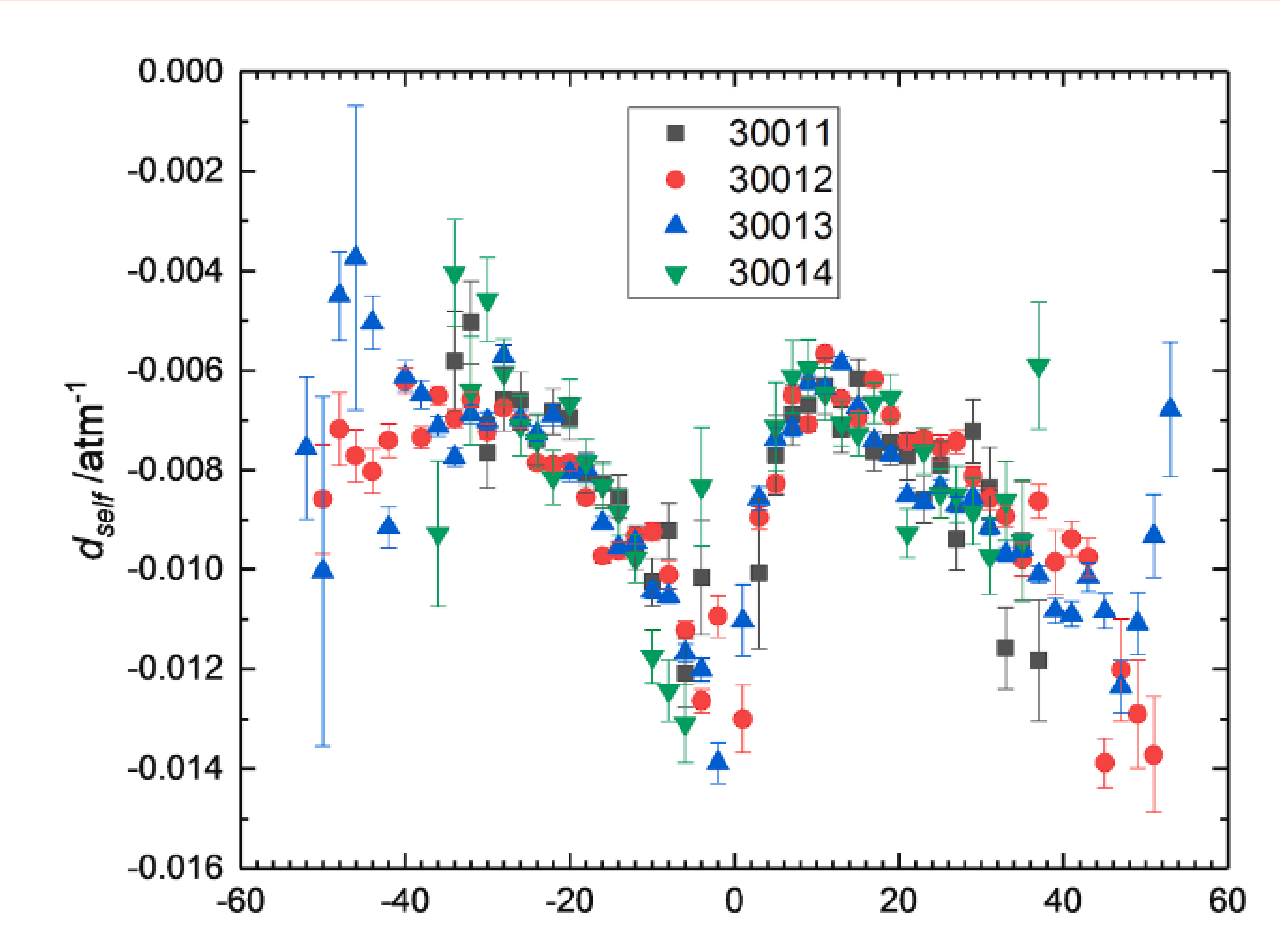


*J. Chem. Phys.* 158, 184301 (2023)

# Preliminary results on $O_2$



# Intensity depletion measured for $CO_2$



*JQSRT* 324, 109055 (2024)

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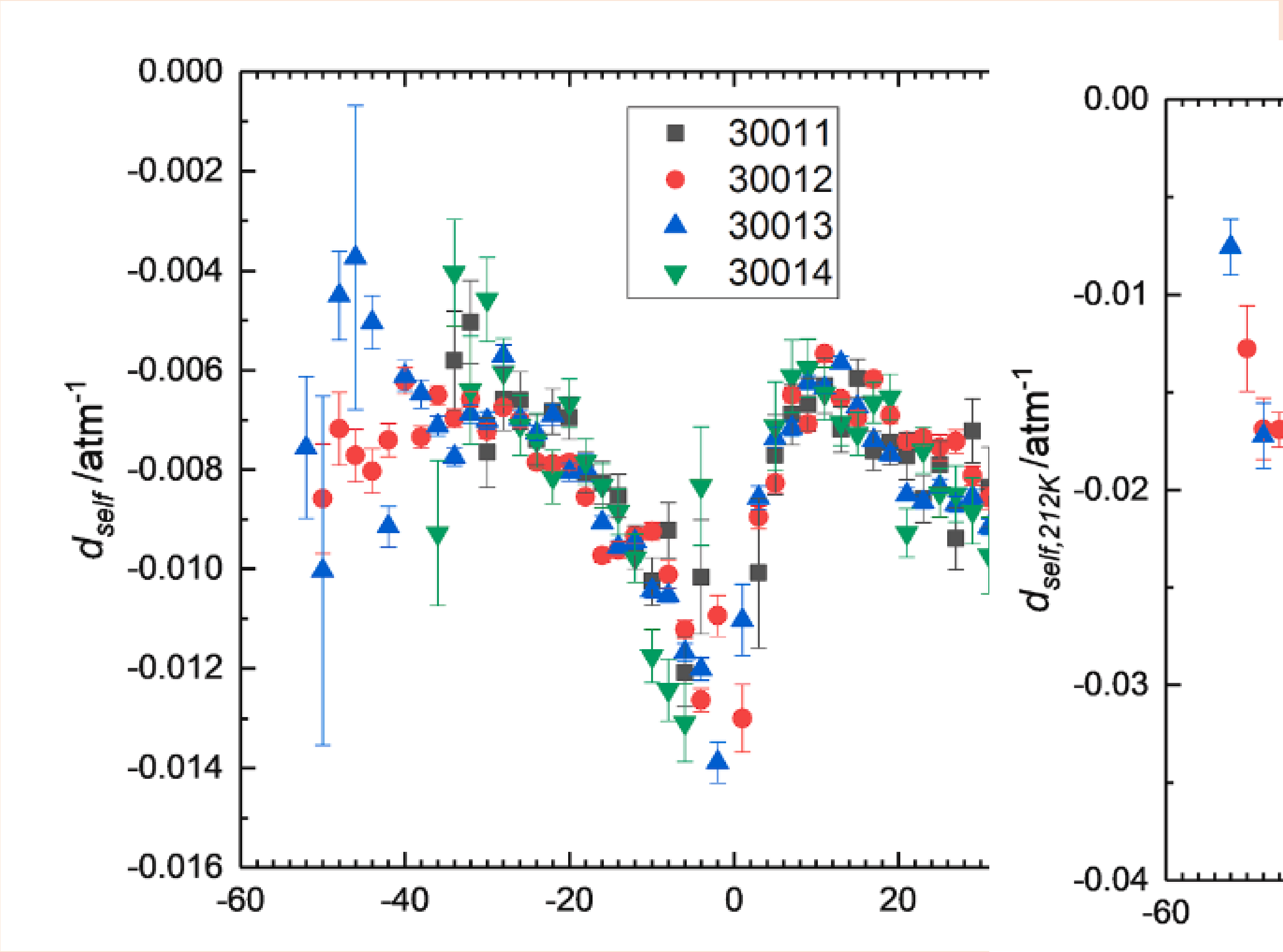

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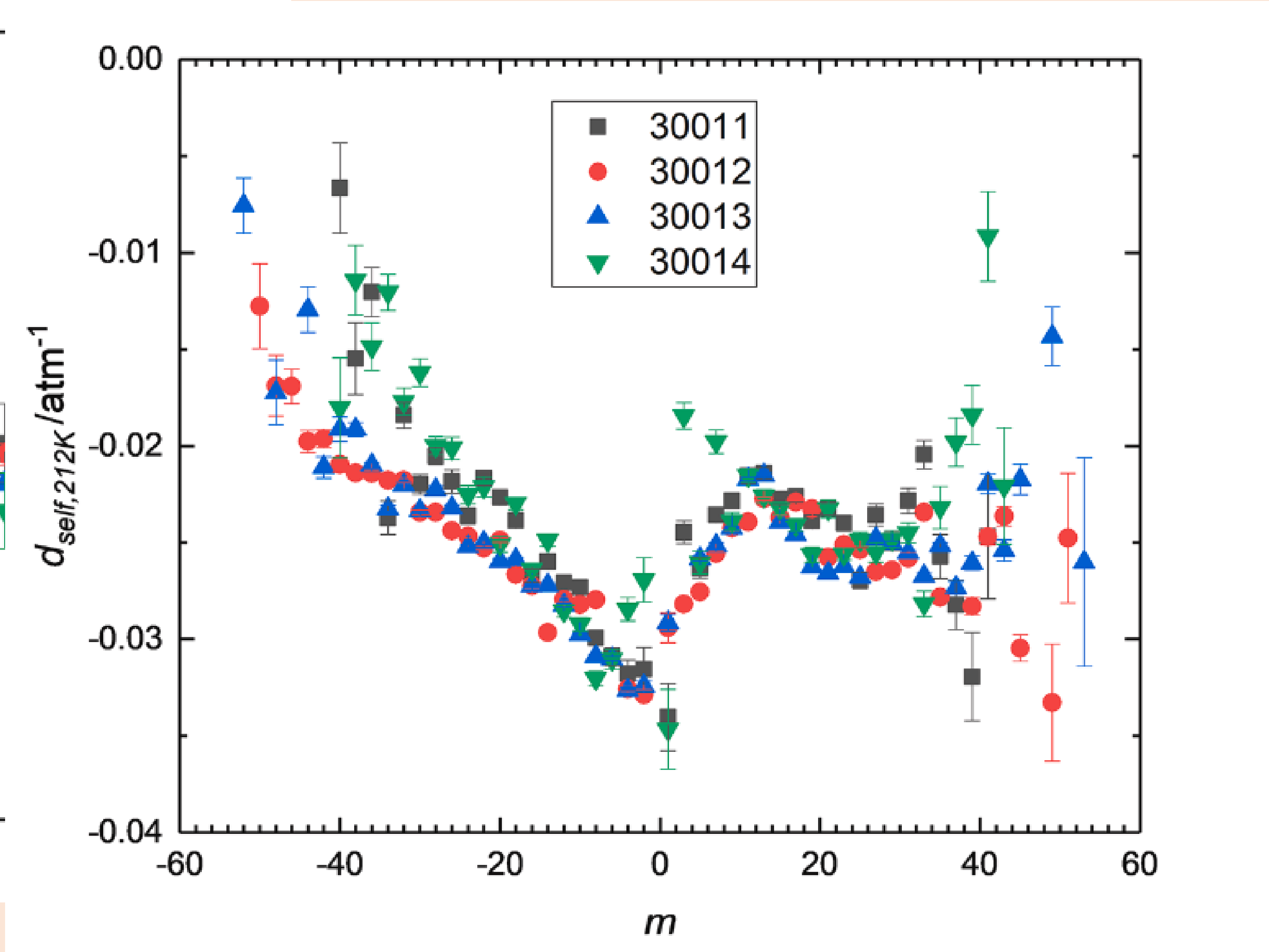

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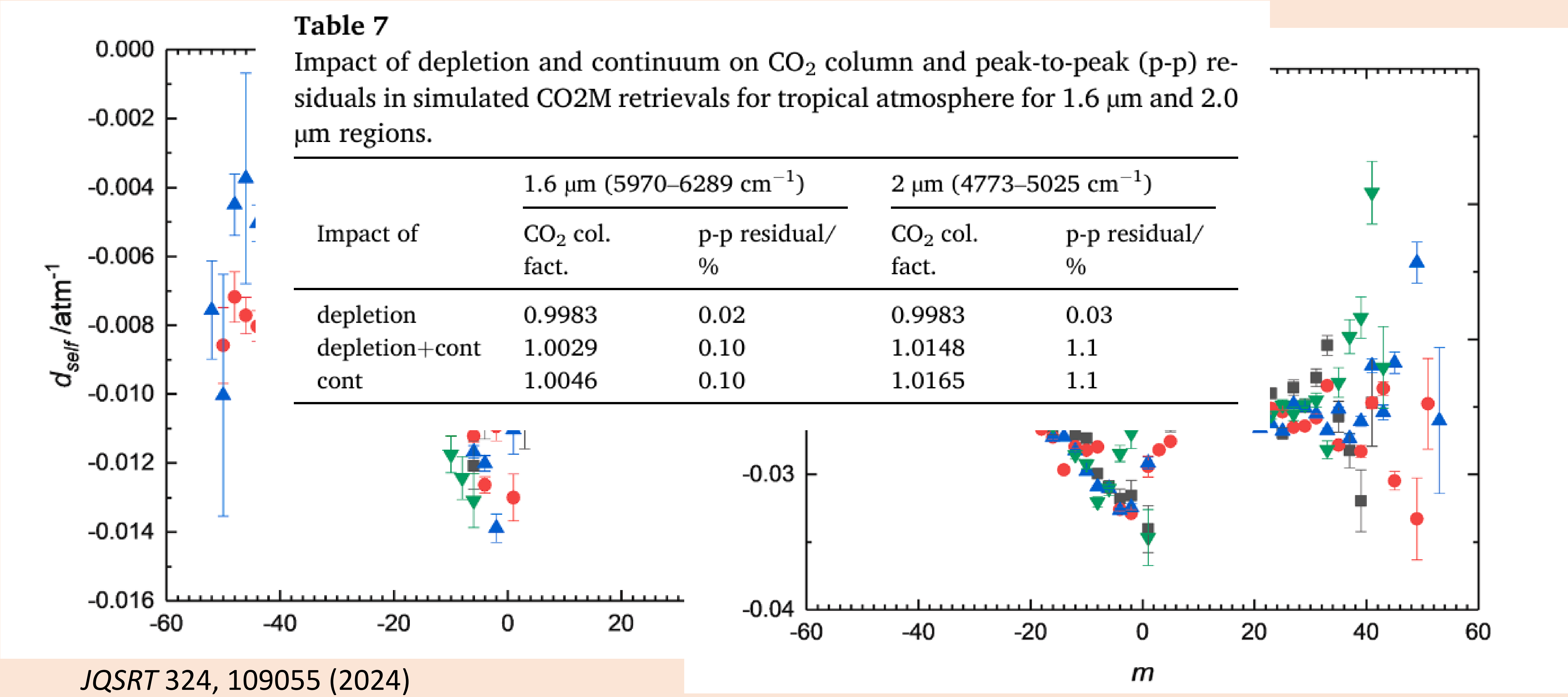

**Table 7**

Impact of depletion and continuum on $CO_2$ column and peak-to-peak (p-p) residuals in simulated CO2M retrievals for tropical atmosphere for 1.6 µm and 2.0 µm regions.

| | 1.6 µm (5970–6289 cm$^{-1}$) | | 2 µm (4773–5025 cm$^{-1}$) | |
|---|---|---|---|---|
| Impact of | $CO_2$ col. fact. | p-p residual/ % | $CO_2$ col. fact. | p-p residual/ % |
| depletion | 0.9983 | 0.02 | 0.9983 | 0.03 |
| depletion+cont | 1.0029 | 0.10 | 1.0148 | 1.1 |
| cont | 1.0046 | 0.10 | 1.0165 | 1.1 |

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# Conclusions and future studies

**Spectral shape is a key issue for high precision remote sensing**

- **When line is isolated, the Voigt profile fails to model isolated line-shape, velocity effects must be considered**
- **When lines are closely spaced, line-mixing should be accounted for**
- **Intensity depletion: A new parameter quantifying the pressure dependence of the retrieved intensity and its temperature dependence for each line of each active molecule / collision-partner**

- **What will be the consequences for applications?**
- **Determine the contribution of molecular complexes to the observed depletion?**
- **Contribution of the far line wings in the continuum?**