Comparisons of measured and requantized classical molecular dynamics calculated line shape of air-broadened isolated transitions of molecular oxygen

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Why molecular oxygen ?

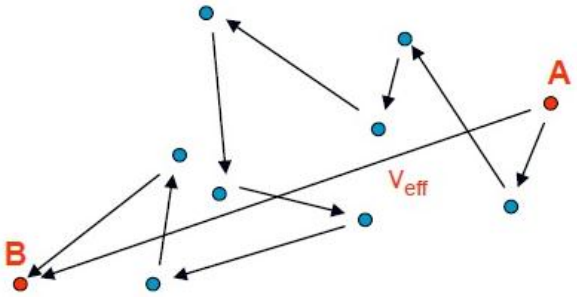
❑ O_2 absorption bands (A, B, γ) are used for a number of remote sensing applications as:

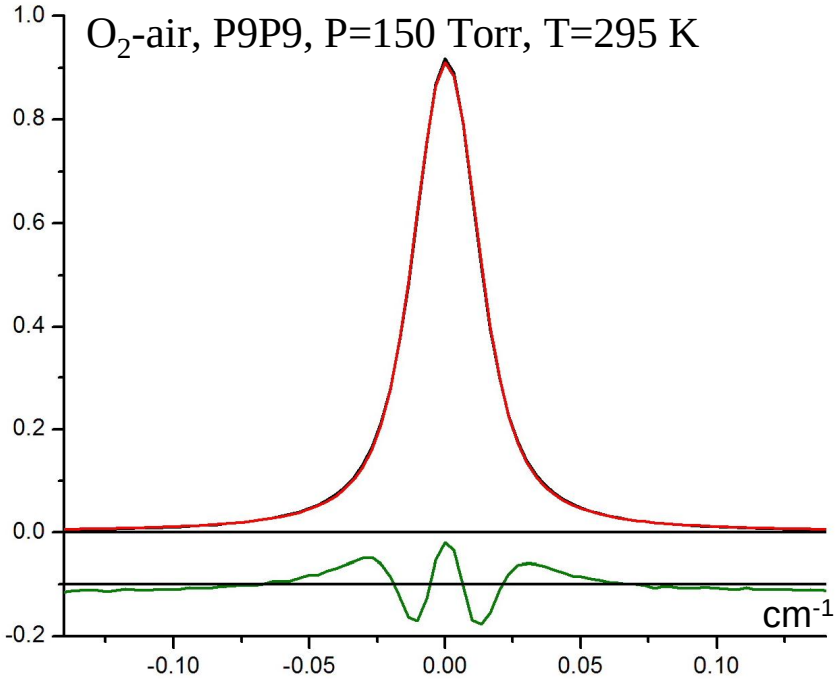
- wind measurements,
- determination of surface pressure, clouds and aerosols proprieties, vertical profiles of pressure and temperature,é

❑ But the Voigt profile, widely used for the analysis, is **inaccurate** as it neglectes:

- *The speed-dependences of the collisionnal widths γ(v) and shifts δ(v)*

-*The velocity changes induced by collisions (Dicke narrowing effect)*





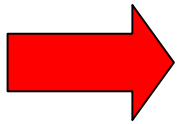
Line shape model beyond the Voigt profile

❑ Recently, a new simplified line shape model (Hartmann-Tran model) has been developed in order to account for the effects neglected by the Voigt profile. This model has been proposed as a standard for the future updates of the spectroscopic databases.
(Tennyson *et al.*, *Pure and Applied Chemistry*, in press (2014))

❑ The parameters involved in this model can be obtained from theoretical spectra obtained from Classical Molecular Dynamics Simulations (CMDS).

❑ These simulations provide (among other quantities) the autocorrelation function of the dipole, yielding to the spectra through a Laplace-Fourier Transform.

❑ They have been successfully applied for line shape predictions for pure CO_2, H_2O, and for one transition (P11P11) of pure O_2.

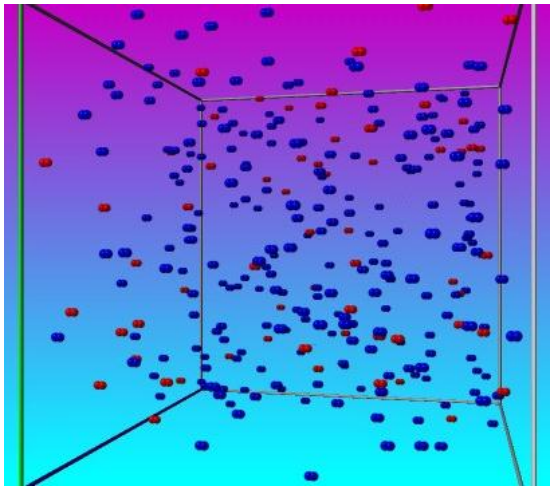


Can we developed a HT model for O_2-air ?

Classical Molecular Dynamics Simulations

❑ **N_M (>10^6) molecules (20% O_2, 80% N_2) treated simultaneously**

- Placed in a cubic box (size determined from N_M and molecular density n)
- Periodic boundary (treated box surrounded by 4096 identical other boxes)
- When a molecule gets out of the box, it comes back-in from the opposite box



❑ **The state of each molecule *m* (linear, rigid rotor) is parameterized by its:**

- Center of mass (CoM) position and velocity
- Molecule orientation
- Molecule rotational speed

❑ **The site-site intermolecular potentials for O_2-O_2, O_2-N_2 et N_2-N_2 have been taken from the literature (as 6-12 Lennard-Jones)**

❑ **The O_2 electronic spin has been neglected in the calculations**

- O_2 transitions are under the form $\Delta N(N'')\,\Delta J(J'')$
- Hence ñPPò and ñPQò transitions types are **equivalent** in the calculations

Classical Molecular Dynamics Simulations

❑ **Initialization (time t=0)**

- Random CoM positions and axis orientations
- CoM velocity and rotation: random orientations, modules from Maxwell-Boltzmann

❑ **Time evolution for all molecules treated sequentially** (with small enough time step ***dt***)

- At each time ***t*** compute force and torque on each molecule from sum of potential gradient of over surrounding neighbors (cut-off sphere of 20 Å)

- Then compute acceleration of CoM and of orientation

- Then compute molecule parameters at ***t+dt*** from those at ***t***

❑ **For each molecule *m*, a requantification procedure is applied based on the correspondence principle:** Associates the rotational quantum number N_m to the rotational speed ω_m by

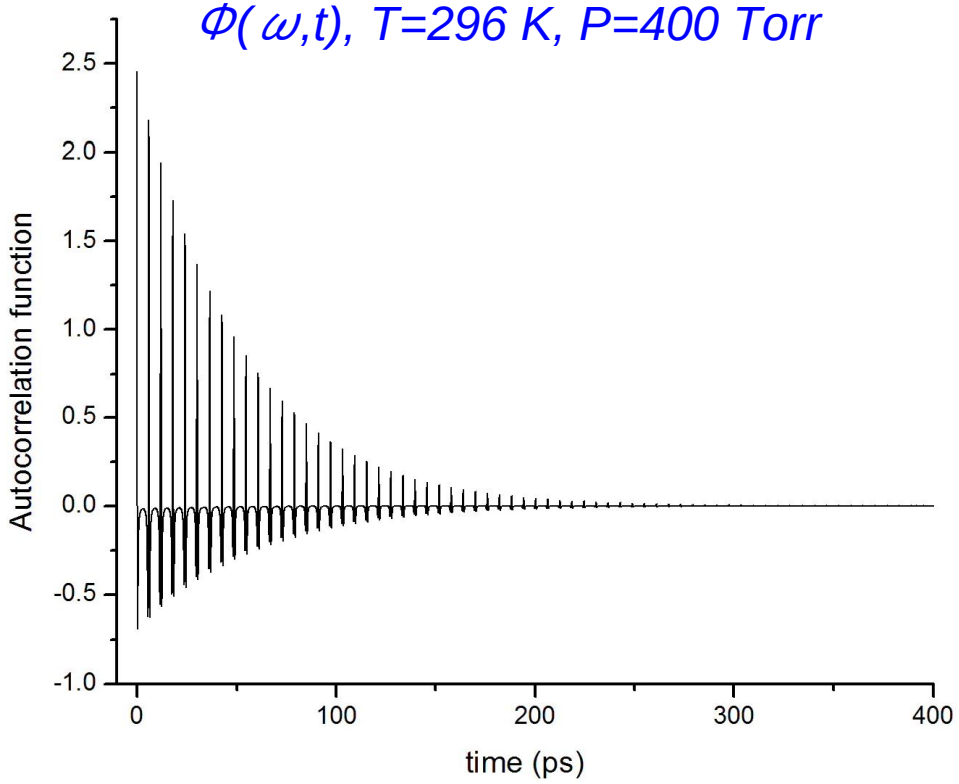
$$\frac{1}{2} I \omega_m^{\,2} \approx \frac{\hbar^2}{2I} N_m (N_m + 1)$$

Spectral line shape

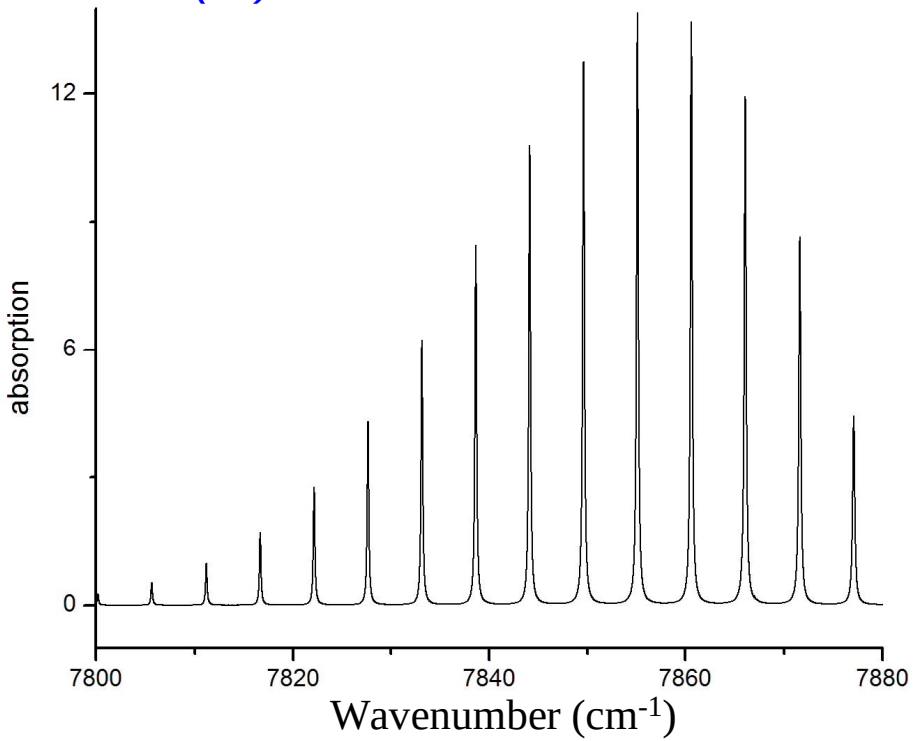
The spectrum $F(\omega)$ is given by the Laplace-Fourier transform of the auto-correlation function (ACF) $\Phi(\omega,t)$

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

$\Phi(\omega,t)$, T=296 K, P=400 Torr

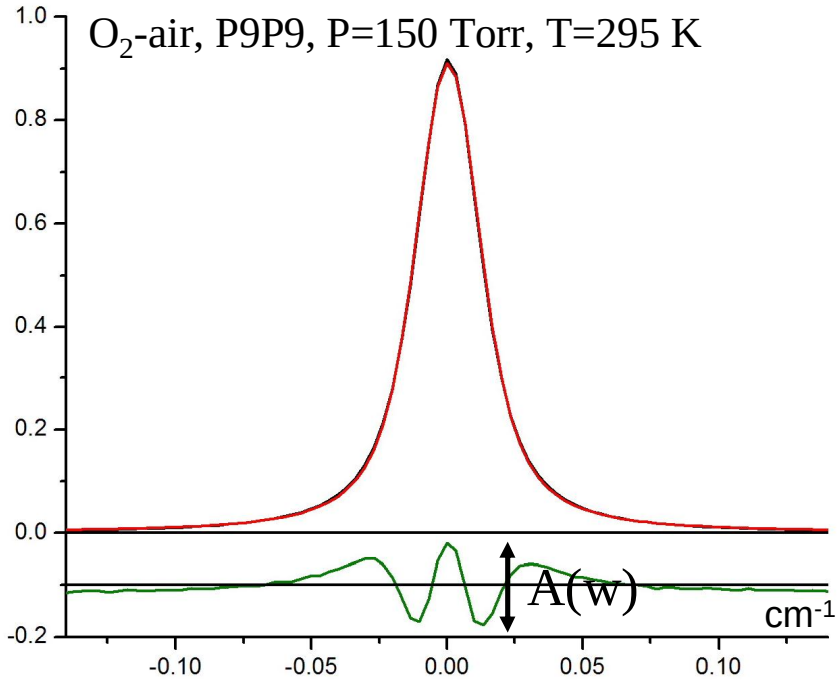


$F(\omega)$, T=296 K, P=400 Torr



Analysis

❑ The effects beyond the Voigt profile can be studied by analyzing the ñWò type signatures in the residuals of the fits.

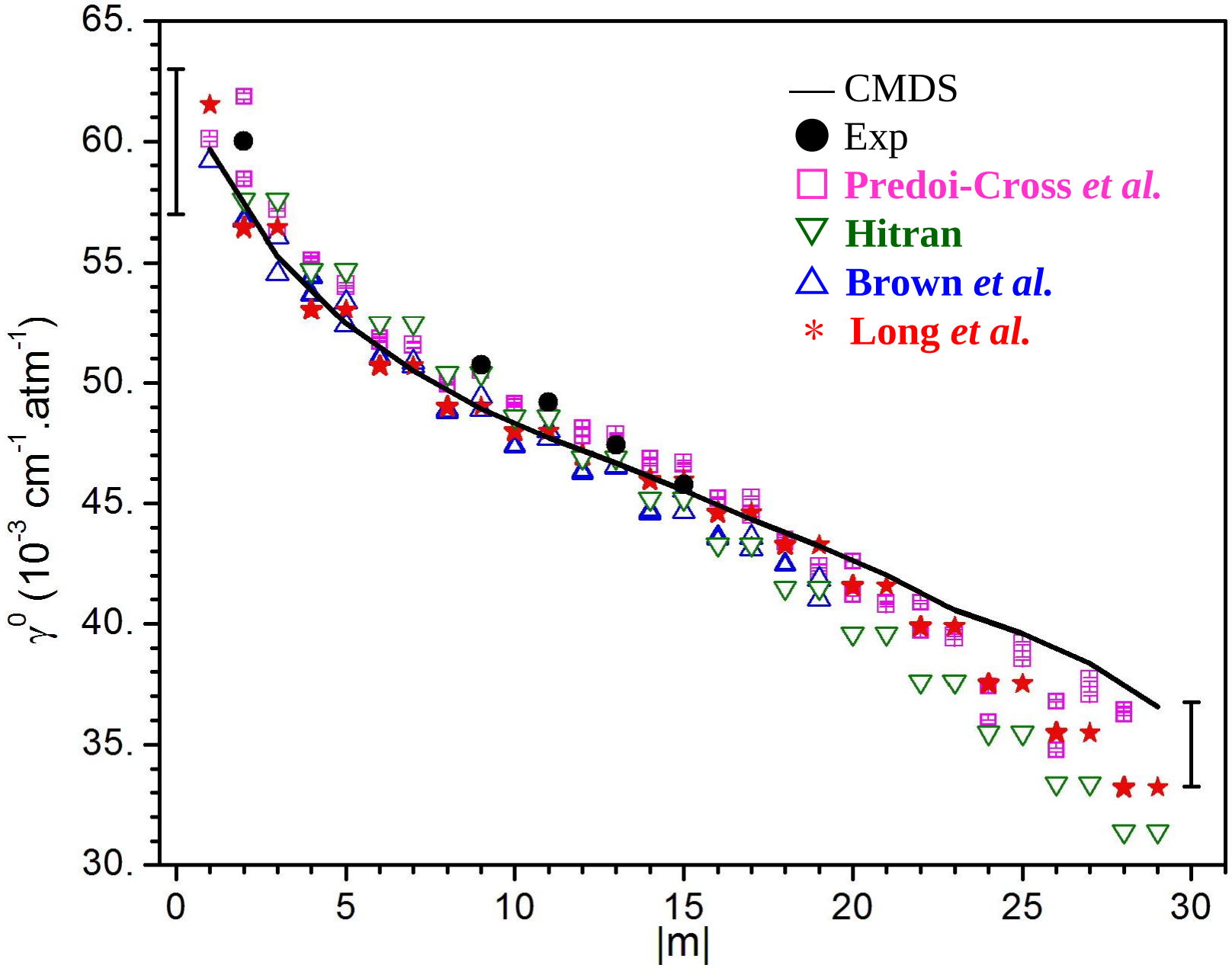


❑ All the studied spectra were adjusted with a Voigt profile:

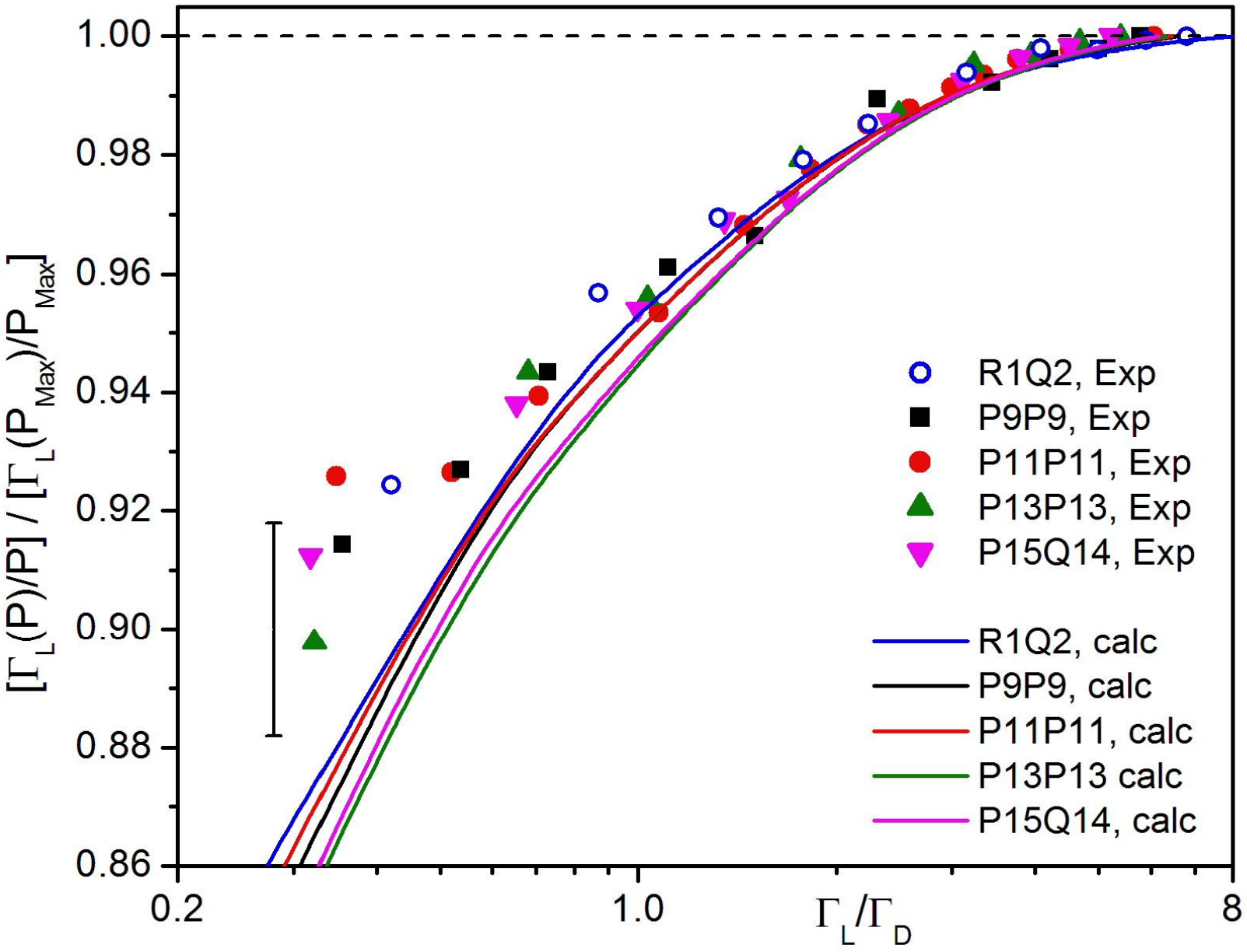
- The Doppler width Γ_D has been **fixed** to its theoretical value,
- The intensity S, the Lorentz width Γ_L have been **adjusted**.

❑ In order to validate the calculations, experimental spectra were recorded at NIST for the R1Q2, P9P9, P11P11, P13P13, and P15Q14 transitions of the $a\ ^1\Delta_g \leftarrow X\ ^3\Sigma_g^-(0,0)$ band, using a frequency-stabilized cavity ringdown spectrometer (FS-CRDS)

Results: Lorentz widths Γ_L

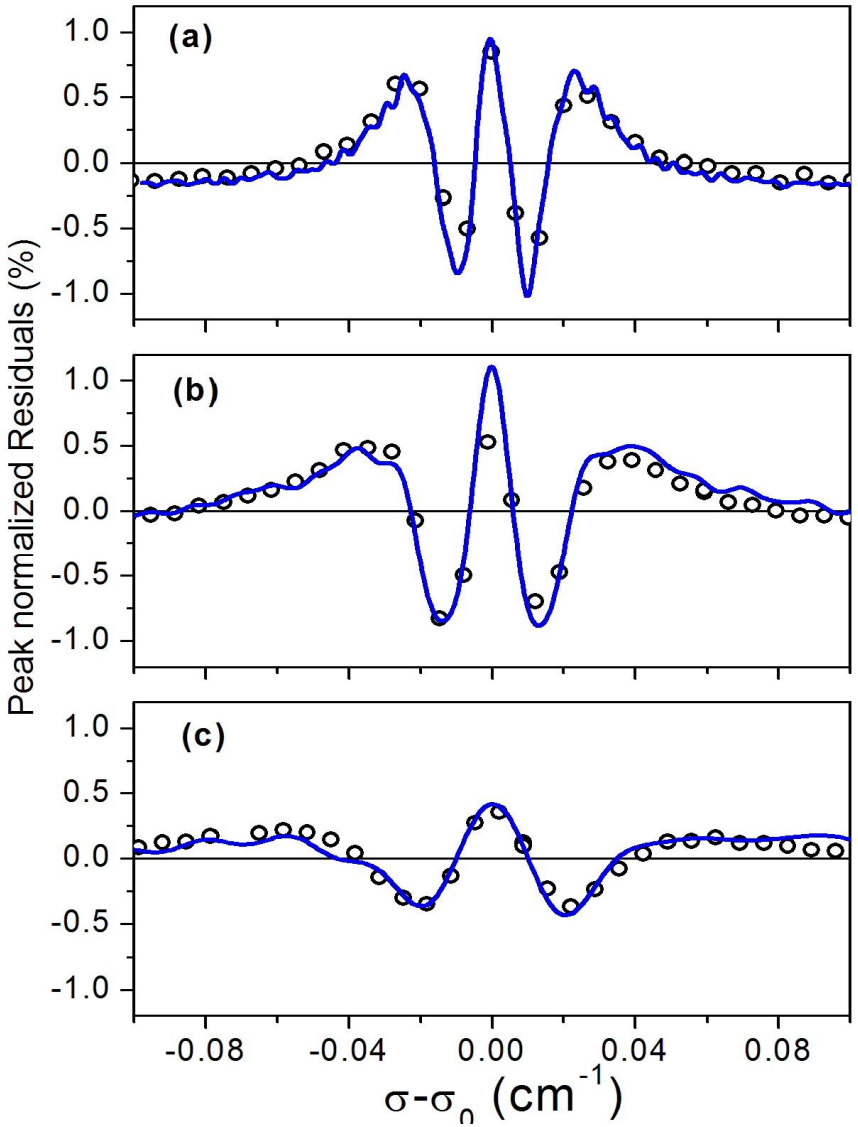


Results: Lorentz widths Γ_L



Results: study of the residuals

Residuals of the fit of theoretical and measured spectra of the P9P9 transition using a Voigt profile.



❑ **Results:**

-Typical ñWò-shaped residuals

-Both amplitudes and widths of the ñWò are in good agreement between the calculations and the measurements

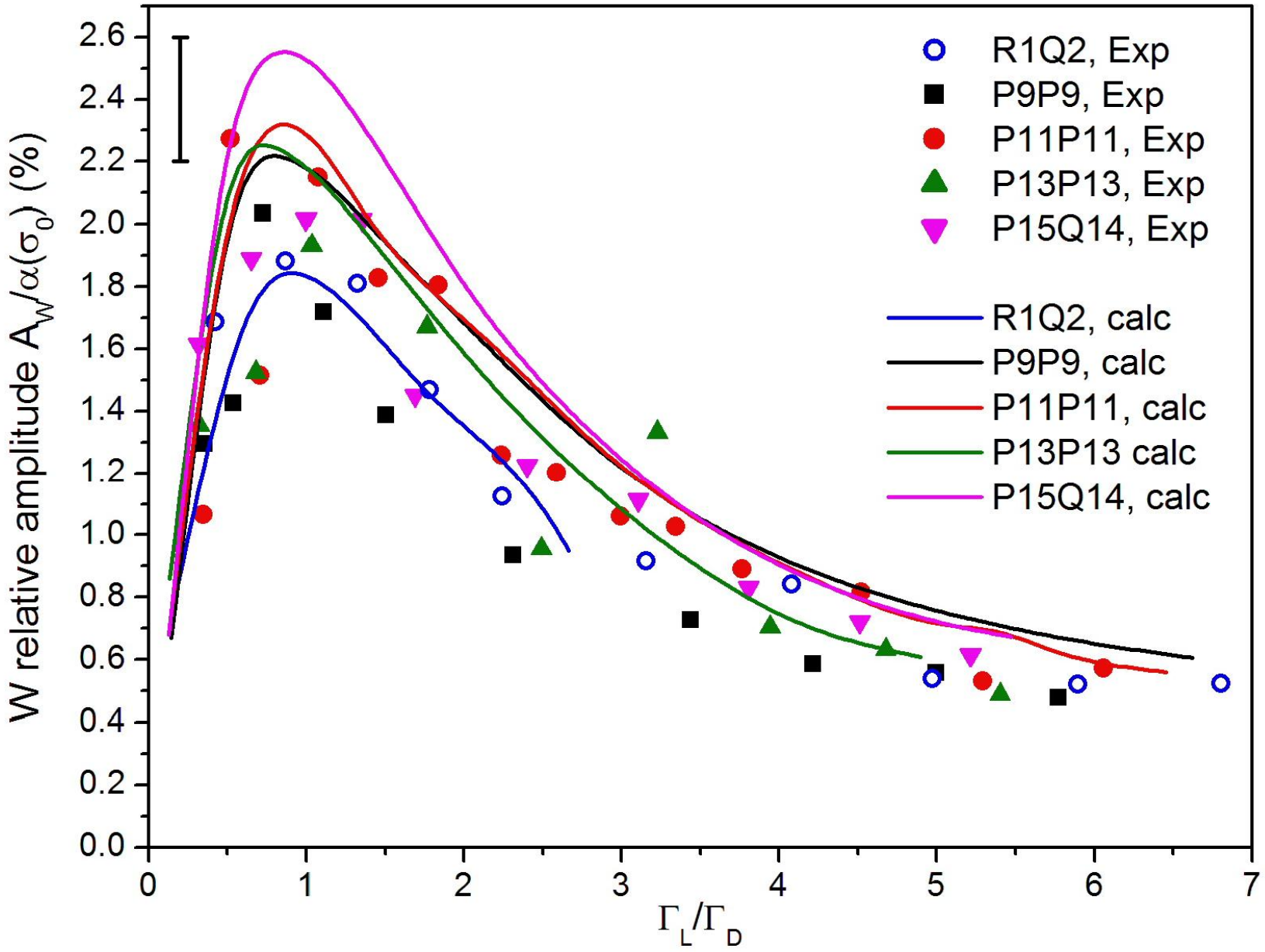
- As seen for other systems (H_2O, CO_2):

For $\Gamma_L/\Gamma_D=1$, *the amplitude is maximum*

For $\Gamma_L/\Gamma_D \to 0$, *the amplitude goes to 0*

For $\Gamma_L/\Gamma_D \to +\infty$, *the amplitude goes to an asymptotique value*

Results: study of the residuals



Conclusion and future work

- The comparison of theoretical and experimental spectra trhough their fits by a Voigt profile demonstrates that the CMDS can be used as a prediction of the (small) deviations to the Voigt profile.

- The results presented here validate the first step of this work that aims at understanding the physical processes that affect the isolated line shapes of molecular oxygen.

- The next step will aim to determinate the parameters describing the velocity changes induced by collisions from the CMDS spectra described here.

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