Tutorial on IR Spectroscopy using PGOPHER

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and

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Special thanks to J. Vander Auwera for providing the experimental CO and CO_2 spectra

Goal of Part 1

- ✓ Make a link between the observed and simulated spectra using fitted molecular parameters (spectroscopist's job)

or / and

- ✓ Rely on a spectrum calculated *ab initio* (quantum chemist's job)
- ✓ Rely on a list of lines (database)

Spectroscopy

Hamiltonian model => energy E_1, E_2
Light-matter interaction => selection rules, intensity
Collisions at finite T, P => line-shape

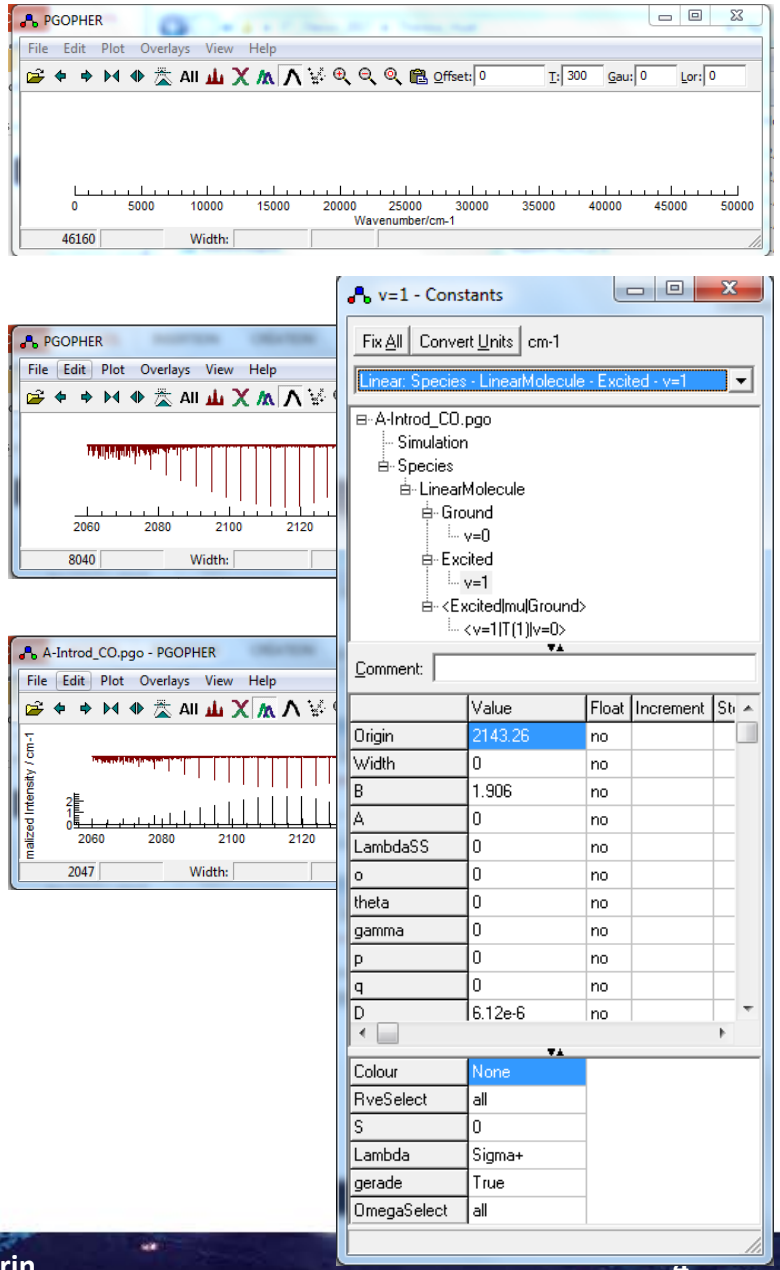
Example 1: PGOPHER

⇒ Open Pgopher.exe: double clic

⇒ Load the observed spectrum:
File / Load overlay:
MyDATA_CO_1-0

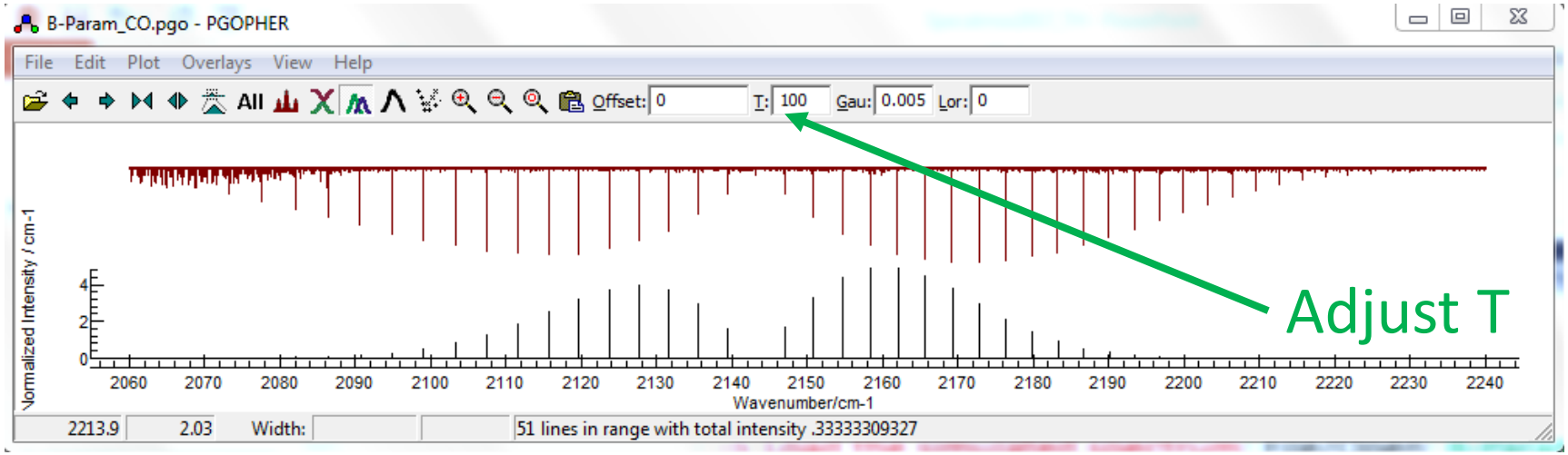
⇒ Load the simulated spectrum:
File / Open: A-Introd_CO.PGO

⇒ The interactive model:
View / Constants



Example 2: Look at the parameters impact

⇒ Load the simulated spectrum: File/Open: B-Param_CO.PGO



⇒ « Zoom » on a line: vary the Gaussian & Lorentz shapes

⇒ Back to the **All** spectrum: vary B_0 or B_1 constants

⇒ Etc, …

Example 3: symmetry effects / Intensity alternation

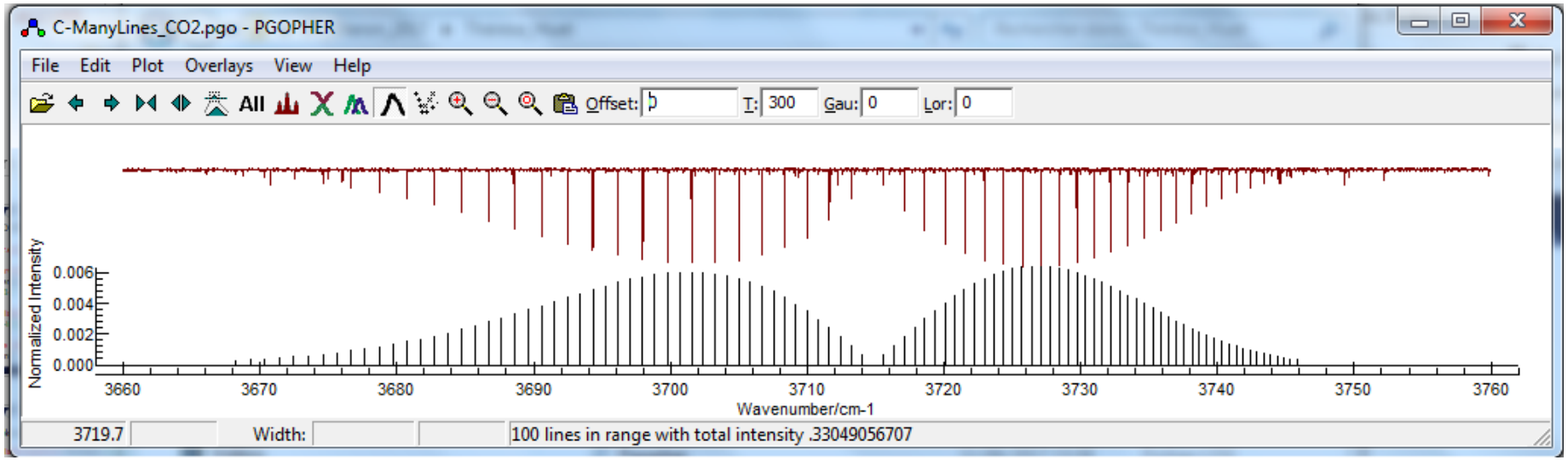
⇒ Load the observed spectrum:

File / Load overlay: MyDATA_CO2_dlco2dz4

⇒ Load the simulated spectrum:

File / Open: C-ManyLines_CO2.PGO

« too many lines ?! » … constants are correct => ??



Example 3: answer is the Pauli principle

The total molecular wavefunction $\psi_{tot}^{i} = \psi_{se}^{i}.\psi_{sn}^{i}.\psi_{e}^{i}.\psi_{v}^{i}.\psi_{r}^{i}$

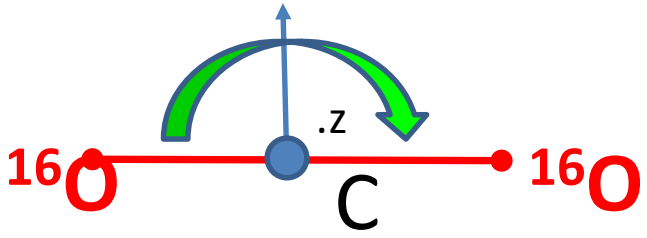
must be symmetric or antisymmetric accordingly to the permutation operation P_{12} *between two identical particles, which are bosons or fermions:*

$$P_{12}\psi_{tot} = \pm\psi_{tot}$$

This principle must be satisfied for electrons and for nuclei (here for ^{16}O).

⇒ Some sublevels (nuclear spin) may be forbidden.

⇒ On the spectrum: missing lines or intensity alternation



⇒ Load the simulated spectrum:

File / Open: D-True_CO2.PGO

AsymWt and SymWt parameters adjusted => Correct