

# SFB-Workshop 2021 (May 3th-4th)

## Hands-on Session:

### ABC of rotational spectroscopy

How to analyze the rotation vibration spectrum of a molecule with PGopher

In this hands-on session we want to become familiar with the software PGopher, a free general purpose program for simulating and fitting rotational, vibrational and electronic spectra. It uses a standard graphical user interface and has features to make comparison with, and fitting to, spectra from various sources easy. A screenshot of the user interface is given in Figure 1.

#### The session consists of two parts:

In the the first step, we will simulate a rotation vibration spectrum of Carbon Monoxide CO by entering calculated molecular parameters into PGopher. Then, we will fit the simulated spectrum to a measured spectrum to optimize the parameters. Since CO possesses only one moment of inertia, its spectrum resembles the spectrum in section 9 of the introduction.

In the second part, we will analyze the spectrum of the asymmetric rotor molecule HSOH, which possesses three different moments of inertia and thus shows a more complex spectrum, which was shown in section 8 of the introduction.

#### Step by Step guide

##### Part 1

##### Fitting the spectrum of CO

- 1.) Download the file Pgopher.exe from the Internet: <http://pgopher.chm.bris.ac.uk/download>
- 2.) Open PGopher and create a new linear molecule: *File* → *New* → *Linear Molecule*  
Zoom into the spectrum, until you see 4-5 spectral lines in the plot. Then re-define the width of the simulated spectral lines by entering "0.25" in the line width field (Gau:) at the top (see figure 1). This defines the line width in  $\text{cm}^{-1}$  in form of a Gaussian curve. To see the change, redraw the spectrum (*Plot new* in figure 1).
- 3.) To zoom out, click "All". Under *View* → *Constants* you can display the molecular parameters, which define the simulated spectrum. In the beginning, there is a ground state  $v = 0$  and an excited state  $v = 1$  and a transition matrix element between the two states:  
<Excited |  $\mu$  | Ground>.
- 4.) We want to simulate the spectrum of a vibration rotation band of CO. The parameters for the ground state are known, enter them under  $v = 0$ :

$$B = 57626.97 \text{ MHz}$$

$$D = 0.147 \text{ MHz}$$

Make sure that *MHz* is set as unit before entering them (*Convert Units* button in the upper part of the window).

5.) The parameters for the excited state  $v = 1$  are unknown, but as starting point, it can be plausibly assumed, that the rotational constant is similar to that of the ground state. Therefore enter under  $v = 1$ :

$$B = 57000 \text{ MHz}$$

6.) Now we need an experimental spectrum of the CO vibrational band, to determine the parameters for  $v = 1$ . Load the measured spectrum (*COexp.ovr*) into PGopher via Drag and Drop (or via *File* → *Load Overlay*) and click *All*. You can now see the simulated spectrum and the measurement. . You may use the red-green X-plot button which cycles through different plot styles. Most convenient is the plot which has the calculated spectrum pointing downwards and the measured spectrum pointing upwards.

7.) Identify the approximate position of the band origin in the measurement data, enter this value under  $v=1$ , *Origin* and redraw the spectrum. The simulated and measured band should now have approximately the same position.

8.) Now assign lines of the simulated spectrum to the corresponding lines of the measured spectrum: Right-click on a simulated line, then use BOTH mouse buttons to draw a window around the measured line. The assigned line appears in the linelist. Assign about 10 lines in this way. If you made wrong assignments, you can delete the line from the line list and try again.

9.) Fit the parameters of the excited state to the measurement: Set the band origin and the rotational constant B of the excited state to *Float - yes*. Click *Fit* several times in the linelist and observe the change in the spectrum. If there are problems with the fit: Pay attention to equal units in the parameters and in the diagram (e.g.  $\text{cm}^{-1}$  for both or MHz for both). If you messed up your parameters, the *Undo fit* button in the line list window can save your life. :-)

10.) With the improved prediction you can assign and fit more lines. You can now also fit the centrifugal distortion constant D of the  $v=1$  state.

11.) How do B and D in  $v = 1$  differ from the ground state values and does this meet your expectations? Discuss!

12.) Play around: Change the temperature and observe how the intensities of the lines change. Have a look at the Fortrat diagram (the button to the left of *Scale y axis*). Change B and D in both states and see what happens to the spectrum.

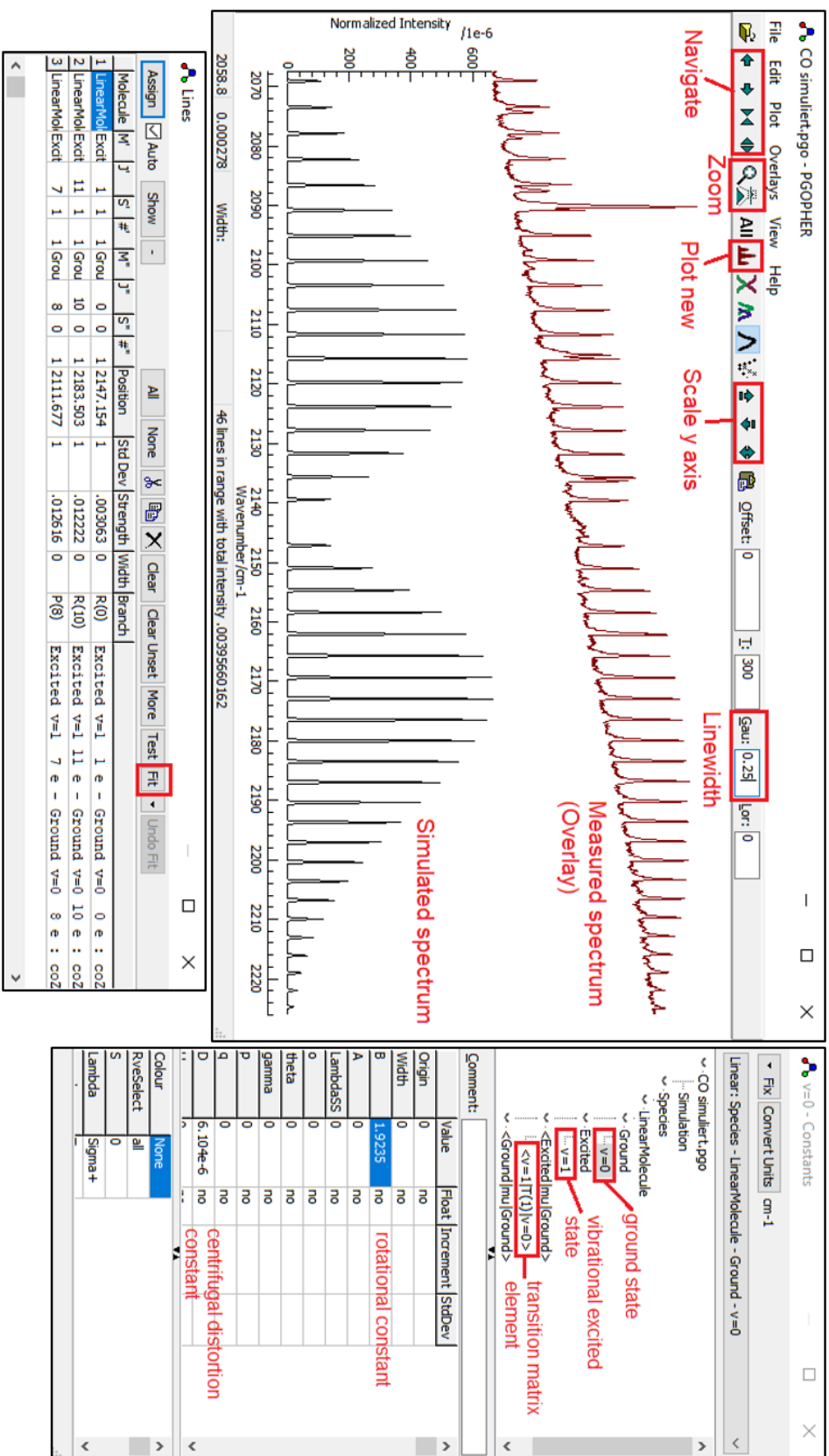


Figure 1: The PGopher user interface: Main window, linelist and constants window

## Part 2

### Fitting the rotational spectrum of HSOH at T = 20 K.

- 1) Open a new PGopher window. In the menu bar in **Plot** set **Units** to **MHz**.
- 2) Drag and drop the HSOH spectrum "HSOH\_measured\_reduced.dat". This is your spectrum up to 2 THz which needs to be analyzed.
- 3) Your colleague from theory has calculated the rotational constants: A = 195 GHz, B = 15 GHz, C = 14 GHz. The  $\mu_c$  dipole component is non-zero and should give a nice c-type spectrum.
- 4) Load the file "HSOH\_Calc.pgo" (drag and drop) which contains the simulated spectrum on the basis of the calculated constants. You should see the calculated spectrum below the measured spectrum and a calculated Fortrat Diagram above your measured spectrum. You may use the X-plot button which cycles through different plot styles. Most convenient is the plot which has the calculated spectrum pointing downwards and the measured spectrum pointing upwards.
- 5) You can use zoom and scroll buttons to get an overview. Try to identify characteristic bands (the Fortrat diagram is very helpful for the assignment of branches).
- 6) Now press **View** and then **constants** to go to the parameter window. Now, you should see the A, B, C constants from theory. (Not too bad 😊)
- 7) Try to assign measured lines to the calculated spectrum (use the procedure you learned when fitting the CO spectrum). Before you can fit the constants you have to set the **Float** value for the constants you want to fit from "no" to "yes".
- 8) Include as many transitions as possible to obtain best results for A, B, C.
- 9) Now your fitted spectrum should look almost perfect. On closer look, however, you can see that some lines are not yet correct. Too bad if you want to perform 3-wave-mixing or any pump-probe experiment with these results. It will definitely fail. 😞.
- 10) Molecules are not really rigid. They change their bond distance through centrifugal forces. Therefore, add the centrifugal distortion parameters DK, DJK, DJ, deltaK, deltaJ, to your fit to see what happens. Check if even higher distortion parameters HK, HKJ, ... PhiK, ... are useful.
- 11) If you reach a perfect match of measured and fitted spectrum the most important part is done.
- 12) Compare the fitted A, B, C with the originally calculated values. How much do they differ?
- 13) Now see if you can reduce the number of used parameters by setting some of them to zero. What is the minimum number of parameters you need for reproducing all transitions of the spectrum within their average line width?
- 14) Finally: Set the temperature to 300 K and see how a room temperature spectrum looks like. That's why we need cooling. 😊.