

# 2024 COST/DAN summer school

## Tutorial "Rotational Spectroscopy for Radioastronomy"

### 1 Rotational spectrum of CO

In radioastronomy you observe rotational emission (or absorption) lines of molecules. Each molecule has a very specific rotational fingerprint that can be used for his identification. If several rotational lines of one molecule are observed in the same astronomical source, the observed absolute and relative intensities can be used to derive additional parameters, like the rotational excitation temperature and the abundance of that specific molecule. In order to do so you need to know several intrinsic properties of your molecule, such as its transition frequencies and line strengths as a function of temperature (which are linked to the Einstein coefficients and energy level diagram of the molecule). On the other hand you might want to search for a new molecular species in space knowing its spectroscopic parameters, and would like to predict its likely radioastronomical signal, e.g., its optical depth or brightness temperature, based on a modeled abundance, excitation temperature, and again its molecular parameters.

In this exercise we will learn how to both gather spectroscopic parameters of a molecule (CO in this case) from experimental data, as well as using these spectroscopic parameters then to predict a rotational spectrum and calculate important parameters such as transition frequencies, Einstein coefficients, and partition functions. For this we will use the program PGopher (see instructions for installation in the separate file).

Rotational energies of a diatomic molecule in the rigid rotor approximation can be written as

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

where  $I$  is the moment of inertia and  $J = 0, 1, 2, \dots$  is the rotational quantum number. In rotational spectroscopy it is, however, more common to use units of frequency instead of units of energy, hence instead of rotational energy  $E_J$  the associated rotational term value

$$F(J) = E_{rot}/h = BJ(J+1)$$

is typically found, where  $B = \frac{h}{8\pi^2 I}$  is the rotational constant.

- Derive the SI unit for the rotational constant in the equation for  $F(J)$ .
- Calculate the frequency separation  $\Delta F(J)$  between rotational levels  $J' = J+1$  and  $J'' = J$ . This is the same as the transition frequency  $\nu_{J+1 \leftarrow J} = \nu_{ul} = \Delta F(J)$  for a transition between two rotational levels  $u = J' = J+1$  and  $l = J'' = J$ .
- The following table gives some rotational transitions ( $\nu_{ul}$  in units of MHz) of the CO molecule and its  $\text{C}^{18}\text{O}$  isotopologue that were measured in the laboratory (please note that some transitions are missing):

transition	CO	C <sup>18</sup> O
$J = 1 - 0$	115271.2	109782.1
$J = 2 - 1$	230538.0	219560.4
$J = 3 - 2$	345796.0	329330.6
$J = 4 - 3$	461040.8	439088.8
$J = 5 - 4$	576267.9	548831.0
$J = 9 - 8$	1036912.4	
$J = 11 - 10$	1267014.5	

Derive the rotational constant  $B$  for CO and C<sup>18</sup>O from the transition frequencies. Why is  $B$  smaller for C<sup>18</sup>O?

## 2 Fitting the CO spectrum using Pgopher

You might have noticed in the previous that you get slightly different values for  $B$  of CO when using, e.g., the  $J = 1 - 0$  or  $J = 11 - 10$  transition. This is due to the fact that the distance between the atoms slightly increases when the molecule rotates. It can be described by adding an additional term to the rotational term value caused by this centrifugal distortion

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

where  $D$  is the centrifugal distortion constant. Higher order terms (in  $J^n(J+1)^n$ ) can also be added if needed.

We now want to derive the rotational constant  $B$  and centrifugal distortion constant  $D$  of CO using the program Pgopher. Install the program Pgopher as described in the additional pdf file on the server. Download the .zip file from there and extract the file "CO-linelist.ovr" which contains experimentally derived transition frequencies of the CO molecule (intensities of all lines are set to 1). Open the Pgopher program. Go to "Plot" → "Units" and select "MHz". Go to "File" → "Load Overlay" and select the file "CO-linelist.ovr". You will see the rotational transitions of CO given in the above table as stick diagram. Go to "File" → "New" and select "Linear Molecule". A new panel appears with some random simulated spectrum (it is in fact a ro-vibrational spectrum). We now have to change this simulation for our purpose. Go to "View" → "Constants". In the new window that appears:

- In the left (or top, depending on your computer) panel delete the state "Excited" (right click, in the window that might pop choose "yes, all").
- In the top right, click "convert units" until it shows "MHz"
- Go to "Ground" → "v=0" and enter the value you obtained for  $B$  in (c) as a starting value (in MHz). Check that the entry for "float" is set to "no".
- As a next step we have to tell the program how to calculate transition strengths. Right click on "Linear Molecule" and select "New" → "Transition Moment". Right click on the new item " $\langle \text{Ground} | \mu | \text{Ground} \rangle$ " that appeared and select "New" → "Spherical Transition Moment". Enter in this panel as a "Value" for the "Strength" the permanent dipole moment of CO:  $\mu = 0.11011$  (given in Debye, 1 D =  $3.33564 \cdot 10^{-30}$  Cm).
- Now go back to the main window and press the "Simulate Spectrum" button (that's the button with a red spectrum on it). You will now see in the lower panel the simulated rotational absorption spectrum of CO using the  $B$  value you provided. You might have to change units again by going to "Plot" → "Units" and select "MHz". Please note that the numbers on the frequency axis need to be multiplied by  $10^6$  (or whatever number is given on the far right of the axis) to obtain the real transition frequency in MHz.

- Zoom in to show only the region 0 – 1500 MHz (Note: To do this press the left mouse button and drag a box around the area you want to see and be sure that the frequency axis is in this box, then click “Change horizontal plot range to selected range”, the symbol showing magnifying glass and spectrum. Be careful to draw the box starting from the left going to the right, otherwise your horizontal/frequency axis will be flipped).
- (a) We now want to fit the rotational constants to the experimental spectrum. For this we need to assign each line in the experimental spectrum (top) to one of the simulated transitions (bottom). Please note that not all rotational transitions were measured, so there are more simulated lines than experimental ones. Right click on one of the peaks in the simulated spectrum that can be assigned to one of the experimental lines, this means a simulated line that has an experimental line very close to it. A “Lines” window will appear, and the simulated lines you chose is listed. Press the right mouse button and drag the mouse over the corresponding experimental peak (upper panel) while keeping the mouse button pressed (you will see a box appearing around the peak). Once you release the mouse you will see a fitted line position and the experimental line position appears in the “Line List Window”, together with a remark from which data-file this is. Repeat this until all experimental lines are assigned. You can delete lines that you accidentally added twice or assigned wrong. In the “Lines” window under “More” → “Sort on” select “Frequency”.

Once you are done click on the button “Fit” in the lines window. Two new window appear giving you some information on your simulation or fit. In the “Residuals” the deviations between your simulated and the experimental lines are shown (in MHz). You will see that there are large residuals for the lines having a higher  $J$  value because we have neglected the centrifugal term.

In fact up to now nothing was fit yet, since we have to tell the program to do so. In a first step we only fit  $B$ . In the “Constants” window change the entry under “Float” for  $B$  to “yes”. Now click on “Fit”. In the “Log” file you find the new and old value for  $B$ , please note them down. You will see that the residuals have improved somewhat, but are still very large.

Go back to the “Constants” window and change the entry under “Float” next to the value for the centrifugal distortion  $D$  to “yes”. Repeat the fit! You will now see that the residuals are much smaller, and that you obtain a changed value for  $B$  and an additional value for  $D$ , please note them down. From the very small deviations we can assume that our fit is good. Congratulations, you have successfully extracted spectroscopic constants from an experimental spectrum! Save your pgopher file.

- (b) Now that we have a good model for the transition frequencies of our CO molecule, let us look at the intensities. Change the temperature  $T$  in the topmost panel to 50 (K). The spectrum now looks different. Explain why! Hint: Think about what we discussed in the lecture! about line intensities and what might be plotted in Pgopher as intensity!
- (c) Under local thermal equilibrium (LTE) the fractional population of a molecule in a rotational level  $J$  is given by

$$p(J) = \frac{g_u}{U(T)} e^{-\frac{E_J}{kT}}$$

where  $U(T)$  is the partition function (also often called  $q(T)$  or  $Z(T)$ ) with

$$U(T) = \sum (2J + 1) e^{-\frac{E_J}{kT}}$$

with the summation over all  $J$ , and  $g_u = 2J + 1$  is the degeneracy of the upper state. It can be shown that for linear molecules the maximum population occurs at  $J_{max} = \sqrt{\frac{kT}{2hB}} - 1/2$ . Calculate  $J_{max}$  for  $T = 300$  K and  $T = 50$  K for CO and check if this relationship holds

using Pgopher. You will notice that the maxima in your spectrum appear at different  $J$ . This is due to the fact that also the line strength  $S$  (and Einstein coefficient  $A$ ) depends on the specific transition, and they also enter into the absorption coefficient. To view the actual level population in Pgopher, click in the “Constant” on “Simulation” and then choose for “IntensityUnits” “NormPopDist” (should have been “Normalized” before). Press simulate. The new plot gives you the population  $p(J)$  of each  $J$  level (y-axis) plotted vs. its frequency (x-axis). Check again if your calculated  $J_{max}$  values agree with the simulation. (Note: if you rightclick on the simulated line with highest intensity, it again appears in the “Lines” window, and you can read off its  $J$  value in the table.

- (d) Let us finally see how we can determine Einstein  $A$  coefficients and the rotational partition function  $U(T)$  with Pgopher. To obtain  $A$  you simply change the “IntensityUnits” to “EinsteinA”. Simulate the spectrum again. When you now right click on the transition you can read of the Einstein coefficient in the “Lines” window under strength (for this you have to clear your line list first - make sure you have saved your file!). Check if the Einstein coefficient you find in Pgopher is similar to the one you used for  $\text{C}^{18}\text{O}$  in last weeks tutorial. Why could there be small differences?

Pgopher can calculate the partition function of your molecule at a certain temperature. Simply go to the “Constants” window, right click on “Linear Molecule” and choose “Partition Function Table”. The results will appear in the “Log” window. Check if  $U(10\text{ K})=4$  as used in the last tutorial for  $\text{C}^{18}\text{O}$  is a good approximation. Why could the partition function be different for the two molecules?

## Bonus exercise: Simulating the spectrum of the symmetric top rotor $\text{CH}_3\text{CN}$

(please look at Chapter 10.1 and 10.3 in the book ”Introduction to Astrochemistry” by Satoshi Yamamoto for more details)

Methyl cyanide (or acetonitrile,  $\text{CH}_3\text{CN}$ ) is a prolate symmetric rotor. In this case the moment of inertia around the  $b$  and  $c$  principal axis are the same  $I_c = I_b (> I_a)$ .

- (a) Make a sketch of the  $\text{CH}_3\text{CN}$  molecule and indicate and label the principal axes. Along which axis/axes does this molecule have a permanent dipole moment?
- (b) The rotational term values of a prolate symmetric rotor (including centrifugal distortion) can be expressed by introducing a new quantum number  $K$  ( $K = 0, 1, \dots, J$ ) representing the projection of the total angular momentum onto the symmetry axis (which is always  $a$  for a prolate top), and using rotational constants  $A$  and  $B$  around the  $a$  and  $b$  principal axes:

$$F(J) = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

where  $D_i$  denote the (now three) quartic centrifugal distortion terms. Higher order centrifugal distortion terms (called  $H_i$ ,  $L_i$ , ... for sextic, octic terms ) can be added if very high  $J$  transitions were measured.

The spectroscopic parameters for  $\text{CH}_3\text{CN}$  are [H. Müller et al., A&A 506 (2009) 1487-1499]:

constant	$\text{CH}_3\text{CN}$ [MHz]
$A$	158099.0
$B$	9198.899134
$D_K$	2.851
$D_{JK}$	0.17740796
$D_J$	$3.807528 \cdot 10^{-3}$

Make a new pgopher file by “File” → “New” and select “Symmetric Top”. Open the constants window and delete again the excited state. Fill in the spectroscopic constants of CH<sub>3</sub>CN for the  $v = 0$  state from the above table (Note, in pgopher  $C$  is always used for the symmetry axis; since this is the  $a$  axis in our case, fill in here the value for  $A$ ). Right click on “Symmetric Top”, select “New” → “Transition Moments”. Right click on the new “ $\langle \text{Ground}|\mu|\text{Ground} \rangle$ ” entry and select “Add new” → “Spherical Transition Moment”. Click on the new entry “ $\langle v = 0|T(1)|v = 0 \rangle$ ” and add the dipole moment of CH<sub>3</sub>CN (along the  $\mu_a$  axis, see above) of 3.922 D.

Change “Units” to “MHz” in the “Plot” menu and press simulate and then “All”. The simulated spectrum of CH<sub>3</sub>CN appears. You see a spectrum with evenly spaced “lines”. Zoom into one of these “lines”. You see that each of these “lines” are in fact multiple transitions, with decreasing intensity to lower frequencies.

Can you explain this structure by taking into consideration the expression for  $F(J)$  from above and the additional information that only transitions with  $\Delta J = 1$  and  $\Delta K = 0$  are allowed?

- (c) We now want to compare our simulation to an actual experimental spectrum (from H. Müller, private communication).

Go to “File” → “Load Overlay” and select the file “MeCN.xz”, that was also in the .zip file on the server (you need to change to “All Files (\*.\*)” in the selection window.). This is a real experimental spectrum as coming from an absorption spectrometer. If you zoom into one particular line, you see that it has a very peculiar lineshape. This comes from the detection methods used in the experiment. The real transition frequency is the center of the upward peak.

Zoom in on the leftmost block of experimental transitions. Would you judge the spectroscopic constants sufficient to describe the experimental spectrum? What could you do to improve the match? For practice, you can do the same procedure as described in Exercise 3 and assign several of the lines and try to improve the fit. Be careful to have a sufficient number of transitions assigned before you put any of the rotational constants to “float” (always more transitions than constants!). You can also try to include higher order centrifugal distortion terms like  $H_i$ . Note: The  $A$  (or  $C$  in Pgopher) and  $D_K$  constants cannot be fitted with this experimental data, see (b) above.

- (d) You might have noticed that there are many transitions in the experimental spectrum that do not match any of the simulated transitions. What could be possible reasons for this?