

## HITRAN Exercise

### Introduction

There are many lessons to be learned from the HITRAN data base. Here we look at one or two specific examples. JHAWKS is a java based program that searches the HITRAN data base for the absorption lines of specified compounds and isotopes, and plots the output of the search in a convenient format. PCLnWin, a Windows version of a program called FASCODE, can then be used to calculate transmission and make some radiative transfer calculations. FASCODE also contains data on clouds and aerosols and on real continua (as opposed to line wing continua)

The 2004 HITRAN data base contains almost 1 million vibration-rotation lines of 9 gases, each gas having more than one isotope. There are also data on freons and on some other pollutants. The details of this database are described by Rothman, et al, 2005, "The HITRAN 2004 Molecular Spectroscopic Database, JQSRT, Vol. 96, pp. 139-204, Dec. 2005.

We will use two parts of the JHAWKS program: the Select option, which finds and lists line data, and the Plot option, which represents the line strengths graphically. We shall then use the program PCLnWin to calculate opacity and transmission.

### Exercise 1: JHAWKS – Select

The 15 $\mu\text{m}$  (667  $\text{cm}^{-1}$ ) band of  $\text{CO}_2$  is a prominent feature in the terrestrial infrared spectrum. However, there are not only  $\text{CO}_2$  lines in this spectral region. If you print out all lines between 665 and 667  $\text{cm}^{-1}$ , you will find that there are 1778 from 9 chemical species, not to mention isotopes. For exercise 1.1, use the Select menu option of the JHAWKS program, which can be run by using the Windows explorer to go to the 'C:\JHAWKS' directory and double-clicking on the file runJHawks.bat. The manual is in the same directory in pdf format (hawksman.pdf).

- 1.1 Print out all lines between 665.4490  $\text{cm}^{-1}$  and 665.53819  $\text{cm}^{-1}$ . Print out 170  $\text{CO}_2$  lines between 667 and 668  $\text{cm}^{-1}$  for 296K. Note the wide range of line strengths.

*(Helpful hint: You can convert a JHAWKS output file to a more readable format that automatically decodes molecule numbers. Look under **File, Change Format.**)*

- 1.2 The atmosphere contains  $7.2 \times 10^{21}$   $\text{CO}_2$  molecules  $\text{cm}^{-2}$  in a vertical path through the whole atmosphere. Assume that they are all contained in a horizontal path at a total pressure of 1 bar and temperature 296K. What is the optical path at the center of a Michelson-Lorentz  $\text{CO}_2$  line at 667.661509  $\text{cm}^{-1}$ ? (Section 6.1.1 of the HITRAN manual (see handout) contains some possibly useful information.)
- 1.3 The line strength is proportional to the population of the lower state of the transition. This may be obtained from Boltzmann's law:

$$S(T) \propto n'' = ne^{-(E''/kT)}/Q(T),$$

where  $Q(T) = \sum_{\text{all states}} e^{-E/kT}$  is the partition function or state sum. The two  $\text{CO}_2$  lines at  $667.661509 \text{ cm}^{-1}$  and  $667.80102 \text{ cm}^{-1}$  are examples of small and large lower state energies, and they are for the same molecule and isotope. Calculate the ratio  $Q(200)/Q(296)$  independently for the two bands from data at 200K and 296K, and show that the same value is given by both bands. Note that  $E''$  is given in wavenumbers rather than ergs. Multiply by  $hc$ .

## Exercise 2: JHAWKS – Plot

This exercise is mainly Show and Tell; we restrict ourselves to the region of the  $667 \text{ cm}^{-1}$   $\text{CO}_2$  band. Use the Plot menu option of the JHAWKS program.

- 2.1 Plot the  $\text{CO}_2$  lines, including all isotopes, from  $600$  to  $725 \text{ cm}^{-1}$  on a logarithmic scale at 296K. There are three narrow groups of lines, one in the center and one at each side. These are the three Q-branches that were referred to in Exercise 1.2. Now look at a linear scale for a temperature of 296K. The central Q-branch now stands out, while the two flanking Q-branches are barely visible.

This band has the classical structure of a band of a linear molecule, with a strong and narrow Q-branch flanked by regular arrays of lines known as the P- and R-branches. For some  $\text{CO}_2$  bands the Q-branch is missing.

- 2.2 In Exercise 1.3 we looked at the effect of temperature on two specific lines. One line strength increased with temperature while other decreased. See this in a more synoptic context by repeating the linear plot of (2.1) for 200K and comparing the two plots. Rationalize what you observe.
- 2.3 Look more closely at a Q-branch. Plot the lines between  $667$  and  $671 \text{ cm}^{-1}$  on a logarithmic scale between  $10^{-17}$  and  $10^{-26}$ . It appears that a complex structure is repeating itself at least five times. Speculate on the reason for this. (By definition, a line within a Q-branch does not correspond to a rotational *transition*; however, the line is associated with a particular rotational *state*. In this problem, you may assume that the vibrational potential well of the Q-branch is approximately, but not exactly, a harmonic oscillator.)
- 2.4 In band-model theory a distinction is made between “regular” and “random” bands. The P- and R-branches of the  $667 \text{ cm}^{-1}$  band are examples of “regular” or Elsasser bands. Water vapor is the paradigm for “random” bands. Although the spectral region from  $600$  to  $725 \text{ cm}^{-1}$  is far from the center of a water vapor band, the region contains many weak lines of water. Plot them on both linear and logarithmic plots and a maximum line strength of  $10^{-21}$ . It is easy to imagine that the line spacings follow approximately a Poisson distribution, which is what would occur if they were dropped randomly into the spectral interval. The distribution of line strengths has a very long tail.

## Exercise 3: TRANS

In this exercise we examine absorption by CO in the spectral region  $2150$  to  $2190 \text{ cm}^{-1}$ . This spectral region contains 125 lines of five different isotopes. **Print out** the

data from JHAWKS – Select for the principal isotope only. There are 23 lines forming two arrays. The weaker array is an upper-state band and will not concern us. The lines form part of an R-branch (do not get the idea that all vibration-rotation bands are this simple; this band was chosen because it is the simplest available). For 296K (stick to this temperature), the R-Branch maximum is R7.

We shall take the R-branch maximum as representative of a regular array of lines called an Elsasser band. Parameters for this band may be estimated from the mean of the three strongest lines.

Use the program PCLnWin. Click on the desktop icon to start the program. Once inside the program, go to the *Input Data* menu, and choose Select Line File. Choose C:\PCLNWIN\Usr\co\_file.tp3. This file contains the lines for the principal isotope of CO between 2150 and 2190  $\text{cm}^{-1}$ . Next, go to *Input Data, Open* and select the file C:\PCLNWIN\Usr\Test.fsw. From this point you can change parameters with the pull-down menu.

### 3.1 *Strong and weak lines*

Look at a single line by displaying the spectral range 2170 to 2175  $\text{cm}^{-1}$ . The parameter  $u = Sn/2\pi\alpha_L$  is half the optical path at the line center. You can change  $l$  and  $n$  (by adjusting the partial pressure) until  $u \gg 1$  for total  $p = 1$  bar (e.g.  $l = 10$  km and partial pressure =  $2 \times 10^{-6}$  bar – make sure  $u$  is large enough so that weak flanking lines appear). Starting with these initial values each time, make the following modifications. First double the partial pressure and halve  $l$ , keeping  $p$  fixed. Next, double  $p$ , keeping the partial pressure and  $l$  fixed. Next, double the partial pressure, keeping  $p$  and  $l$  fixed. Finally, double  $l$ , keeping the partial pressure and  $p$  fixed. Compare the transmission from these runs. The total transmission is the sum of one strong central line and two weak flanking lines. Discuss how you would expect the transmission from both the strong line and the weak lines to change in the above runs, and compare this to the program results. For the strong line note that a similar effect occurs for doubling the absorbing molecules as for doubling the non-absorbing molecules.

### 3.2 *Elsasser's band model* (OPTIONAL FOR EXTRA CREDIT)

Return to the full range, 2150 to 2190  $\text{cm}^{-1}$ , but consider only the three strongest lines as an example of an Elsasser regular model. The mean transmission (that is, the transmission averaged over several lines) is given in Appendix 8 of Goody and Yung (1989). It is tabulated in terms of  $u$  and  $y = \alpha_L/\delta$ , where  $\delta$  is the spacing between line centers, and  $\alpha_L$  is the Michelson-Lorentz line width. Choose the total pressure so that  $\log_{10} y = -1.2$  for the three strongest lines and vary  $u$  by changing the path length and the partial pressure to cover the full range of absorptions. Estimate the mean transmission by eye, plot against  $\log_{10} u$  and compare to the tabulated Elsasser function.

(*Not required.* If you should be ambitious you might try a similar comparison for a waver vapor band (random model), but selecting the appropriate parameters takes some thought, see Goody and Yung, 1989, 4.6.)

## References

R. Goody and Y. L. Yung, 1989, *Atmospheric Radiation; Theoretical Basics*. New York: Oxford University Press.