

CHM 3411, Dr. Chatfield, Spring 2018

Problem Set 11

Due Wednesday, April 18

Suggested “warmups” (not to turn in): Discussion Questions 12A.1,2, 12B.1,2, 12C.1-3; Exercises [all (b)] 12A.2,11,12, 12B.1,3-5, 12C.2-5, 7-9 (12C.1,6 are good, too, but they are used as problems below)

This problem set covers microwave and infrared (IR) spectroscopy. Additional problems may be added to the problem set later in the week.

1. Atkins Exercise 12B.1(b)
2. Atkins Exercise 12B.3(a), 12.B4(a)
3. Atkins Exercise 12.B5(a)
4. The following two rotational transitions are observed in the microwave spectrum of  $^{12}\text{C}^{16}\text{O}$  in the region 500 Hz to 700 GHz. (1 GHz =  $10^9$  Hz =  $10^8$  s $^{-1}$ . Herz (Hz) is a unit of frequency ( $\nu$ ) and is used as an alternative “energy unit” to wavenumber ( $\tilde{\nu}$ , cm $^{-1}$ ) for measuring rotational transitions. To convert between the two, multiply or divide by  $c$ , the speed of light.)

<u>transition</u>	<u>relative intensity</u>
579.01 GHz	1.00
694.81 GHz <sup>?</sup>	1.19

No other transitions are seen in the above frequency range. Assume that  $r_e$  is independent of isotopic composition (a reasonable assumption). The following information will be useful:

$^{12}\text{C}$  12.0000 amu     $^{16}\text{O}$  15.9949 amu     $^{14}\text{C}$  14.0033 amu

- a. What is the value of  $B$ , the rotational constant, for  $^{12}\text{C}^{16}\text{O}$ ? Give your answer both in units of GHz and cm $^{-1}$ .
  - b. From the value of  $B$ , calculate the equilibrium bond length,  $r_e$ .
  - c. Assign the rotational transitions above (that is, give the initial and final values of  $J$  for each transition).
  - d. From the relative line intensities, estimate the temperature at which the spectrum was taken.
  - e. Calculate the frequencies (in GHz) of the corresponding rotational transitions for  $^{14}\text{C}^{16}\text{O}$ .
5. Atkins Exercise 12D.2(b)
  6. Atkins Exercise 12D.3(b)
  7. Atkins Problem 12D.8
  8. Atkins Problem 12D.10

9. Atkins Exercise 12E.2(b)

10. Atkins Problem P12E.2

In addition to the Atkins problem, do a Spartan calculation on  $\text{NO}_2$ . Are the in agreement with the conclusion you reached from the data in the problem. For the calculation:

- Use the B3LYP/6-31G\* method
- Do an equilibrium geometry calculation, and click on “IR spectrum” and “vibrational modes.” This will first optimize the geometry, and then calculate the vibrational modes.
- Before you start the calculation, set the bond angle to just a little more or less than  $180^\circ$ . This is because if you start it at  $180^\circ$ , you might be “trapped” there even if the optimum geometry is at a different angle ( $180^\circ$  might be an energy maximum, so the force would be zero even though the geometry was not optimized; with zero force, the computer will not find the energy minimum).

You should discuss the shape of the molecule compared to the expectation from VSEPR theory, and observe the vibrational modes. Does the list of which ones are “IR active” agree with what you expected?