

# Chem 30324, Spring 2018, Homework 7

Due March 26, 2018 ¶

## NO spectroscopy

The diatomic nitric oxide (NO) is an unusual and important molecule. It has an odd number of electrons, which is a rarity for a stable molecule. It acts as a signaling molecule in the body, helping to regulate blood pressure, is a primary pollutant from combustion, and is a key constituent of smog. It exists in several isotopic forms, but the most common,  $^{14}\text{N} = ^{16}\text{O}$ , has a bond length of  $1.15077 \text{ \AA}$ , a harmonic vibrational frequency of  $1904 \text{ cm}^{-1}$ , and a rotational constant of  $1.7 \text{ cm}^{-1}$ .

1. Predict the *positions* of the four lowest energy lines in the pure rotational spectrum of  $^{14}\text{N} = ^{16}\text{O}$ ,  $\text{cm}^{-1}$ .

2. Predict the *relative intensities* of the first 4 lines in the pure rotational spectrum of gaseous  $^{14}\text{N} = ^{16}\text{O}$  at 298 K. Recall that the intensities depend on the difference in populations of the initial ( $l$ ) and final ( $l'$ ) states, according to

$$g(l) \left( e^{-\varepsilon(l)/k_B T} - e^{-\varepsilon(l')/k_B T} \right).$$

3. Do you expect NO to exhibit an infrared absorption vibrational spectrum? Why or why not? If so, what initial and final vibrational states contribute most significantly to the spectrum?

4. Do you expect NO to exhibit a Raman vibrational spectrum? Why or why not? If so, what initial and final vibrational states contribute most significantly to the spectrum?

5.  $\text{NO}_2$  readily forms from  $\text{NO}$  in the presence of oxygen. An infrared spectrum of  $\text{NO}_2$  has three features, at 1318, 750, and  $1618\text{ cm}^{-1}$ . Is  $\text{NO}_2$  a linear or bent molecule? Justify your answer.

**I see the light!**

6. What is the difference between stimulated absorption and stimulated emission? How do the intrinsic rates of these two processes compare?

7. Under which of Einstein's categories does "fluorescence" belong? Fluorescence is often used to study transitions with energies of a couple eV or more (corresponding to visible or higher energy light), but seldom/never used to study infrared or similar low energy (fractions of an eV) processes. Give a couple reasons why.

## Quantum mechanics of an H atom:

Consider an excited hydrogen atom with a  $2s^1$  electron configuration. The  $2s$  radial wavefunction is given by

$$R_{2,0} = \frac{1}{\sqrt{2a_0^3}}(1 - \rho/2)e^{-\rho/2}, \rho = r/a_0$$

where  $a_0$  = bohr radius. (*Hint:* It's easiest to solve the following using  $a_0$  as the unit of length.)

8. Provide a hand sketch of the 3-D shape of a  $2s$  wavefunction ("orbital"). Be sure to indicate the *sign* of the wavefunction in each region and the location(s) of nodes. How many radial and how many angular nodes does a  $2s$  electron orbital have?

9. Plot the radial probability function  $P_{20}(r) = r^2 |R_{2,0}(r)|^2$ . Be sure to label both axes appropriately. (*Hint: Stick with  $a_0$  as the length unit.*)
10. Determine and indicate on your plot  $\langle r \rangle$ , the expectation value of the distance of the electron from the nucleus.
11. Determine and indicate on your plot  $r_{MP}$ , the most probable distance of the electron from the nucleus.
12. Determine and indicate on your plot the maximum classical distance of the electron from the nucleus in this orbital.
13. What is the probability of finding the electron beyond the classical distance? (Evaluate the necessary integral numerically.)
14. Can a 2s electron undergo an allowed transition to a lower energy electronic state? If so, what frequency (in  $\text{cm}^{-1}$ ) of light would be emitted?