

# HW6

February 26, 2025

## 1 Chem 30324, Spring 2025, Homework 6

## 2 Due March 7, 2025

2.0.1 The diatomic nitric oxide (NO) is an unusual and important molecule. It has an odd number of electrons, which is a rarity for 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,  $^{14}\text{N}=\text{}^{16}\text{O}$ , has a bond length of 1.15077 Å and harmonic vibrational frequency of  $1904\text{ cm}^{-1}$ .

### 2.1 Statistical mechanics of vibrating NO

1. Using your knowledge of the harmonic oscillator and the Boltzmann distribution, complete the table below for the first four harmonic vibrational states of  $^{14}\text{N}=\text{}^{16}\text{O}$ .

Quantum number	Energy (kJ/mol)	Relative population at 400 K	Relative population at 410 K
$v = 0$			
$v = 1$			
$v = 2$			
$v = 3$			

2. Use the table to estimate the average vibrational energy of a mole of  $^{14}\text{N}=\text{}^{16}\text{O}$  at 400 and 410 K.

3. Use your answer to Question 2 to estimate the vibrational heat capacity ( $dE/dT$ ) of a mole of  $^{14}\text{N}=\text{}^{16}\text{O}$  in this temperature range. How does your answer compare to the classical estimate,  $8.314\text{ J/mol K}$ ?

4. Predict the harmonic vibrational frequency of the heavier cousin of  $^{14}\text{N}=\text{}^{16}\text{O}$ ,  $^{15}\text{N}=\text{}^{18}\text{O}$ , in  $\text{cm}^{-1}$ . Assume the force constant is independent of isotope. Do you think these two isotopes could be distinguished using infrared spectroscopy?

## 2.2 Spin the NO.

5. Calculate the moment of inertia of  $^{14}\text{N}^{16}\text{O}$ , in  $\text{amu } \text{\AA}^2$ , the rotational energy constant,  $B = \hbar^2/2I$ , in  $\text{kJ mol}^{-1}$ , and the rotational spectral constant,  $\tilde{B} = B/hc$ , in  $\text{cm}^{-1}$ .

6. Imagine that the  $^{14}\text{N}^{16}\text{O}$  molecule is adsorbed flat on a surface upon which it is free to rotate. Plot out the energies of the four lowest-energy rotational quantum states, in units of  $B$ , being sure to include appropriate quantum numbers and degeneracies. Also indicate the total rotational angular momentum of each state, in units of  $\hbar$ .

7. Now imagine the  $^{14}\text{N}^{16}\text{O}$  molecule is free to rotate in three-dimensional space. As in Question 6, plot out the energies of the four lowest-energy rotational quantum states, in units of  $B$ , being sure to include appropriate quantum numbers and degeneracies. Also indicate the total rotational angular momentum of each state, in units of  $\hbar$ .

8. Use the vector model to sketch the total angular momentum vectors consistent with  $l = 1$ .

9. The gross and specific rotational spectroscopy selection rules are that a molecule must have a dipole and that  $\Delta l = \pm 1$ , respectively. Will  $^{14}\text{N}^{16}\text{O}$  have a rotational spectrum? If so, what will it look like, and why?

## 2.3 Quantum mechanics of an H atom:

2.3.1 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.)

10. Provide a complete set of possible quantum numbers for an electron with the  $2s$  wavefunction.

11. 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  $2s$  wavefunction have?

12. 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.)

13. Determine and indicate on your plot  $\langle r \rangle$ , the expectation value of the distance of the electron from the nucleus. (*Hint:* the course outline gives an expression for this expectation value.)

14. Determine and indicate on your plot  $r_{MP}$ , the most probable distance of the electron from the nucleus.
15. Determine and indicate on your plot the maximum classical distance of the electron from the nucleus in this orbital.
16. (*Extra credit*) What is the probability of finding the electron beyond the classical distance? (Evaluate the necessary integral numerically.)
17. 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?