Chem 30324, Spring 2018, Homework 6

Due March 6, 2018

Quantum mechanics of vibrating NO. ¶

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}N= ^{16}O, has a bond length of 1.15077 Å and harmonic vibrational frequency of 1904 cm^{-1}.

1. The ground vibrational wavefunction of N=O can be written

$$\Psi_{\upsilon=0}(x) = \left(\frac{1}{\alpha\sqrt{\pi}}\right)^{1/2} e^{-x^2/2\alpha^2}, \quad x = R - R_{eq},$$
$$\alpha = \left(\frac{\hbar^2}{\mu k}\right)^{1/4}$$

where $x = R - R_{eq}$. Calculate $\langle x \rangle$ and $\langle x^2 \rangle$ for NO in the $\Psi_{\upsilon=0}(x)$ state (you might want to use α as a length unit).

2. Calculate the average potential energy, $\langle V(x) \rangle$, in the ground state, in units of *hv*. Hint: This is trivial to calculate given the answer to question 1!

3. Using conservation of energy and your answer to question 2, calculate the average kinetic energy, $\langle T(x) \rangle$, in the ground state, in units of *hv*. Comment on the relationship between the kinetic and potential energies. This is a general result for all υ, and is a consequence of the virial theorem for the harmonic potential.

4. Calculate the classical minimum and maximum values of the ^{14}N=^{16}O bond length for a molecule in the ground vibrational state. *Hint:* Calculate the classical limits on *x*, the value of *x* at which the kinetic energy is 0 and thus the total energy equals the potential energy.

5. Calculate the probability for a quantum mechanical ^{14}N= ^{16}O molecule to have a bond length outside the classical limits. This is an example of quantum mechanical tunneling.

Statistical mechanics of vibrating NO

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

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

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

8. Use your answer to Question 7 to estimate the vibrational heat capacity (dE/dT) of a mole of ^{14}N=^{16}O in this temperature range. How does your answer compare to the classical estimate, R=8.314 J/mol K?

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

```
In [ ]:
```