Chem 30324, Spring 2018, Homework 6

Due March 7, 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, $^{14}N{=}\,^{16}O$.

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

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

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 hν. 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 $h\nu$. Comment on the relationship between the kinetic and potential energies. This is a general result for all ν, 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?

NO goes for a spin

$^{14}N = {}^{16}O$ has an equilibrium bond length of 1.15077 Å

10. Calculate the moment of inertia of $^{14}N = {}^{16}O$, in amu Å^2, and the rotational energy constant, B, in kJ mol^{-1} and in cm^{-1}.

11. Imagine that the NO 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 moment of each state, in units of $\hbar$.

12. Derive a selection rule for light-induced excitation of the plane-spinning NO molecule. *Hint:* Treat the NO as a 2-D rotor. Find the conditions on Δm_l that make the transition dipole moment integral $\langle \psi_{m_l} | x | \psi_{m_l'} \rangle$ non-zero. Recall that x can be written r cos φ in polar coordinates.

13. Now imagine the NO molecule is free to rotate in three-dimensional space. As in Question 2 above, 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 moment of each state, in units of $\hbar$.

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