Chem 30324, Spring 2017, Homework 7

Due March 24, 2017

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}.

NO goes for a spin

1. 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}.

2. 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 $\hbar$.

3. 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.

4. 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 $\hbar$.

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

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

7. Predict the *relative intensities* of the first 4 lines in the pure rotational spectrum of gaseous $^{14}N = {}^{16}O$ at 298 K. Recall that the intensities depend on the difference in populations of the initial (l) and final (l') states, according to $g(l) \left(e^{-\varepsilon(l)/k_B T} - e^{-\varepsilon(l')/k_B T} \right)$.

NO takes a stretch

8. 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?

9. 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?

10. Predict the positions of the central four lines in the rovibrational spectrum of $^{14}N = {}^{16}O$.

11. NO_2 readily forms from NO in the presence of oxygen. An infrared spectrum of NO_2 has three features, at 1318, 750, and 1618 cm^{-1} . Is NO_2 a linear or bent molecule? Justify your answer.

I see the light!

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

13. 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.