

Chem 30324, Spring 2018, Homework 6

Due March 4, 2019

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, $^{14}\text{N}^{16}\text{O}$, has a bond length of 1.15077 \AA and harmonic vibrational frequency of 1904 cm^{-1} .

Spin the NO.

1. Calculate the moment of inertia of $^{14}\text{N}^{16}\text{O}$, in amu \AA^2 , the rotational energy constant, $B = \hbar^2/2I$, in kJ mol^{-1} , and the rotational spectral constant, $\tilde{B} = B/hc$, 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 \tilde{B} , being sure to include appropriate quantum numbers and degeneracies. Also indicate the total rotational angular momentum of each state, in units of \hbar .
3. Whether light can induce an NO to jump from some rotational level m_l to some other one m'_l is determined by whether the transition dipole moment integral $\langle \psi_{m_l} | x | \psi_{m'_l} \rangle$ is zero or non-zero. Find the *selection rule* on Δm_l that make the integral non-zero. Recall that x can be written $r \cos \phi$ in polar coordinates.
4. Use your selection rule to determine the frequencies, in wavenumbers, of the four lowest-energy rotational transitions of an $^{14}\text{N}^{16}\text{O}$ adsorbed flat on a surface.

NO flips

5. 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 \tilde{B} , being sure to include appropriate quantum numbers and degeneracies.

6. Predict the relative populations of the first four rotational quantum states at 298 K. Do you expect one or all of these states to potentially contribute to the rotational spectrum of NO?

7. The selection rule for a molecule rotating freely in space is that $\Delta l = \pm 1$. Predict the frequencies of the four lowest energy transitions in the rotational spectrum of $^{14}\text{N}=^{16}\text{O}$, in cm^{-1} . Could you use rotational spectroscopy to distinguish between NO spinning on a surface and rotating in space?

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

NO takes a stretch

9. One of the selection rules for light to excite a vibration of a molecule is that the dipole moment of the molecule changes as it vibrates. Based on this criterion, do you expect NO to exhibit an infrared absorption vibrational spectrum?

10. Another vibrational absorption selection rule is that $\Delta v = \pm 1$. At ambient temperature, what initial and final vibrational states contribute most significantly to the NO spectrum? Justify your answer.

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

12. 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?

13. NO₂ readily forms from NO in the presence of oxygen. An infrared spectrum of NO₂ has three features, at 1318, 750, and 1618 cm⁻¹. Is NO₂ a linear or bent molecule? Justify your answer.

I see the light!

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

15. 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.