

Fundamentals of Spectroscopy for Optical Remote Sensing
Homework #10 (Molecular Spectroscopy)

1. For nitrogen N_2 and oxygen O_2 molecules
 - (a) Given that the equilibrium distances of the N-N and O-O are $r_e = 1.0940 \text{ \AA}$ and 1.2074 \AA respectively, calculate their moments of inertia.
 - (b) Calculate their rotational constants B_e . The measured spectroscopic rotational constants of N_2 and O_2 are $B_0 = 1.998 \text{ cm}^{-1}$ and 1.438 cm^{-1} respectively. Why is there the difference between B_0 and B_e ?
 - (c) Determine the transitions from $J=0$ to $J=1$ and from $J=1$ to $J=2$ for both molecules in wave numbers, in megahertz, and in eV.

2. The vibrational energy spacings for the hydrogen halides are
 - HF: 3958.4 cm^{-1}
 - HCl: 2989.7 cm^{-1}
 - HBr: 2559.3 cm^{-1}
 - HI: 2230.0 cm^{-1}Calculate the force constant of each hydrogen halide molecule and account for any trend in these force constants.

3. Spectroscopic constants of $^{127}\text{I}^{35}\text{Cl}$ have been measured: $\nu_{\text{vib}} = 384.18 \text{ cm}^{-1}$ and $\nu_{\text{vib}}x_e = 1.465 \text{ cm}^{-1}$. The bond dissociation energy of $^{127}\text{I}^{35}\text{Cl}$ has also been measured to be 2.153 eV .
 - (a) Calculate the wave number of the transition between $v=0$ and $v=1$.
 - (b) Repeat part (a) for the transition between $v=1$ and $v=2$.
 - (c) What is the depth of the molecular potential curve of $^{127}\text{I}^{35}\text{Cl}$ (that is, what is the value of D_e)?

4. Consider the HCl molecule and use the following constants for the $X^1\Sigma^+$ ground state: $\nu_{\text{vib}} = 2989.74 \text{ cm}^{-1}$, $\nu_{\text{vib}}x_e = 52.05 \text{ cm}^{-1}$, $\nu_{\text{vib}}y_e = 0.056 \text{ cm}^{-1}$, $B_e = 10.5909 \text{ cm}^{-1}$, $a_e = 0.3019 \text{ cm}^{-1}$, $r_e = 1.27460 \text{ \AA}$ (the first electronic excited state lies about 77000 cm^{-1} above the ground state).
 - (a) Calculate the rotational constant D_e .
 - (b) Calculate the first six rotational energy levels (consider the molecule as vibrating rotator).
 - (c) Calculate the first six vibrational energy levels.
 - (d) Sketch the vibration-rotation energy levels you have got.

5. Given the following constants for N_2 ,

	$\tilde{\nu}_e$	B_0	B_1	D_0	(cm^{-1})
N_2	2330.7	1.98957	1.97219	5.76E-6	

Where $\tilde{\nu}_e$ is the vibrational frequency, B_0 , B_1 and D_0 are the rotational constants. (All four quantities are in wavenumber (cm^{-1}) unit.) Shine a 532nm laser beam through a Raman cell containing N_2 , and observe the scattering light to an angle perpendicular to the laser beam. Rayleigh, pure rotational Raman, and vibration-rotational Raman scattering lines will occur.

- (1) What is the Rayleigh scattering light wavelength (nm) and corresponding wavenumber (cm^{-1})?
- (2) Take this Rayleigh scattering light as the reference of wavenumber, figure out the relative wavenumber of pure rotation Raman (RR) lines (originated from $v = 0$). Mark the corresponding branch and consider the first 6 lines for each branch.
- (3) Take this Rayleigh scattering light as the reference of wavenumber, figure out the relative wavenumber of vibration-rotational Raman (VRR) lines (only consider $v = 0$ and $v = 1$ vibrational levels and associated rotational levels). Mark the corresponding branch and consider the first 6 lines for each branch.
- (4) For the vibration-rotational Raman lines, calculate the wavelength of the Q-Branch (0-0) transition lines. [(0-0) means from $J = 0$ to $J = 0$]
- (5) Assume the transition matrix elements (transition probability) are equal for the Stokes VRR and anti-Stokes VRR, estimate the intensity ratio between the Stokes and the anti-Stokes VRR lines from the Boltzmann factor.

HW #10 is due on Tuesday, December 3rd, 2013 in class.