

**Fundamentals of Spectroscopy for Optical Remote Sensing**  
**Homework #8 (Molecular Spectroscopy)**

- For nitrogen  $N_2$  and oxygen  $O_2$  molecules
  - Given that the equilibrium distances of the N-N and O-O are  $r_e=1.0940 \text{ \AA}$  and  $1.2074 \text{ \AA}$  respectively, calculate their moments of inertia.
  - 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  $1.438 \text{ cm}^{-1}$  respectively. Why is there the difference between  $B_0$  and  $B_e$ ?
  - 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.
- The vibrational energy spacings for the hydrogen halides are
  - HF:  $3958.4 \text{ cm}^{-1}$
  - HCl:  $2989.7 \text{ cm}^{-1}$
  - HBr:  $2559.3 \text{ cm}^{-1}$
  - HI:  $2230.0 \text{ cm}^{-1}$Calculate the force constant of each hydrogen halide molecule and account for any trend in these force constants.
- 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  $2.153 \text{ eV}$ .
  - Calculate the wave number of the transition between  $v=0$  and  $v=1$ .
  - Repeat part (a) for the transition between  $v=1$  and  $v=2$ .
  - What is the depth of the molecular potential curve of  $^{127}\text{I}^{35}\text{Cl}$  (that is, what is the value of  $D_e$ )?
- 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  $77000 \text{ cm}^{-1}$  above the ground state).
  - Calculate the rotational constant  $D_e$ .
  - Calculate the first six rotational energy levels (consider the molecule as vibrating rotator).
  - Calculate the first six vibrational energy levels.
  - 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.