

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

*Note: Problems #1, 5 and 6 are mandatory while you may choose one from problems #2-4  
Choosing more than one among #2-4 will get extra credits*

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  $1.2074 \text{ \AA}$  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  $1.438 \text{ cm}^{-1}$  respectively. Why 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. For HCl, the internuclear distance is  $r_e=0.12746 \text{ nm}$ . For this molecule (ignore the difference between  $r_e$  and  $r_0$ )
  - (a) Calculate its moment of inertia.
  - (b) Calculate its rotational spectroscopic constant  $B_e$ , in units  $\text{cm}^{-1}$  and MHz.
  - (c) Calculate the energies of rotational energy levels with  $J = 0, 1, 2, \dots, 10$ .
  - (d) Calculate the relative populations of the first ten levels at 300K.
3. 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.

4. 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  $2.153 \text{ eV}$ .
  - (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  $D_e$ )?

5. Consider the HCl molecule and use the following constants for the  $X^1S^+$  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).
- (1) Calculate the rotational constant  $D_e$ .
  - (2) Calculate the first six rotational energy levels (consider the molecule as vibrating rotator).
  - (3) Calculate the first six vibrational energy levels.
  - (4) Sketch the vibration-rotation energy levels you have got.

6. Given the following constants for  $O_2$ ,

|       | $\tilde{\nu}_e$ | $B_0$   | $B_1$   | $D_0 \quad (\text{cm}^{-1})$ |
|-------|-----------------|---------|---------|------------------------------|
| $O_2$ | 1556.4          | 1.43768 | 1.42188 | 4.85E-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 ( $\text{cm}^{-1}$ ) unit. Shoot a 355-nm laser beam (tripled Nd:YAG laser) through a Raman cell containing  $O_2$ , 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 ( $\text{cm}^{-1}$ )?
- (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) 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.