1. The following questions regard vibrational spectroscopy of molecules.
   a) The transition of $^{1}H^{35}Cl$ with $v = 1 \leftarrow 0, J = 6 \leftarrow 7$ occurs at 2842.6358 cm$^{-1}$, and the transition with $v = 1 \leftarrow 0, J = 5 \leftarrow 6$ occurs at 2863.8232 cm$^{-1}$. From this information, calculate the spring constant of the vibrational potential (assuming the harmonic approximation) and the equilibrium length of the HCl bond.
   b) Hydrogen cyanide (HCN) is a linear polyatomic molecule. i) calculate the number of normal modes of the molecule and ii) sketch the vibrational motion for each of these normal modes.
   c) i) Draw energy level diagrams corresponding to: Rayleigh scattering, Stokes Raman scattering, and anti-Stokes Raman scattering. ii) Explain why stimulated Raman spectroscopy can be used to amplify the Raman scattering probability in comparison to spontaneous Raman.

2. The following questions regard general aspects of electronic transitions in molecules.
   a) Explain why the bond lengths of molecules are nearly always longer in an electronic excited state compared to their lengths in the ground electronic state. Frame your explanation in terms of the energies of interactions of electrons and nuclei in various molecular orbitals. 
   b) Write an expression for the average value of the transition dipole moment of a diatomic molecule,
      \[
      \langle \mu_{eg} \rangle = \int_{-\infty}^{\infty} \psi_{e} \hat{\mu} \psi_{g} \, dv ,
      \]
      undergoing an electronic transition from the ground state, $\psi_{g}$, to an excited state, $\psi_{e}$. Let the wavefunction, $\psi$, be given by the product of electronic, $\phi_{elec}$, and vibronic, $V_{vibr}$, functions, $\psi = \phi_{elec} V_{vibr}$. The dipole operator is given by the sum of contributions from electrons and nuclei, $\hat{\mu} = \hat{\mu}_{elec} + \hat{\mu}_{nuc}$. Evaluate the expression by separating the electronic and nuclear coordinates and keeping the integrals in symbolic form remembering that $\hat{\mu}_{elec}$ only operates on $\phi_{elec}$ and $\hat{\mu}_{nuc}$ only operates on $V_{vibr}$. Remember also that the electronic portions of the wavefunctions, $\phi$, are orthogonal such that $\int_{-\infty}^{\infty} \phi_{e} \phi_{g} \, dv = 0$.
   c) i) state the two assumptions made about nuclear motion in the Frank-Condon principle. ii) explain why vibrational progressions are observed in electronic spectra of molecules with excited states that have significantly weaker bonding character than their ground states (Fig. 13.6) even though only one vibrational state of the electronic excited state would seem to have exactly the same nuclear configuration as the ground state (Fig. 13.7).
   d) i.) Sketch the ground and excited state potential energy surfaces of a diatomic molecule in a manner similar to Fig. 13.21 of the text. Be sure to label the axes. ii.) Label the relevant electronic radiative and vibronic non-radiative processes leading to fluorescence. iii.) State explicitly how your sketch is consistent with the Franck-Condon principle and with the tendency for excited states to have less bonding character than ground states. iv.) Use your diagram to explain why the fluorescence spectra of molecules nearly always occur at longer wavelengths compared to their absorption spectra (Fig. 13.22).