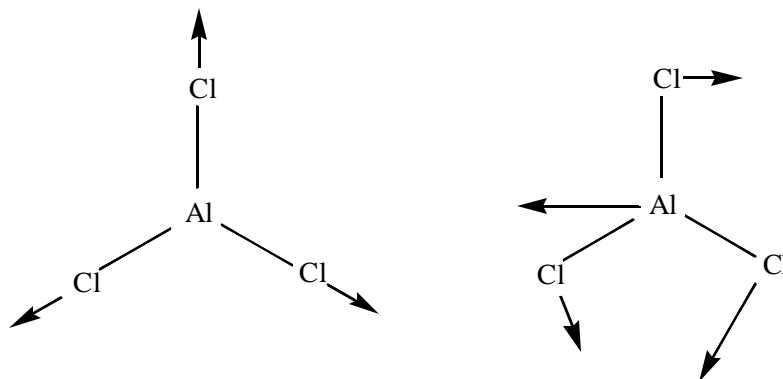


- In the infrared spectrum of  $\text{H}^{79}\text{Br}$ , there is an intense line at  $2559\text{ cm}^{-1}$ . Calculate the force constant of  $\text{H}^{79}\text{Br}$  and the period of vibration of  $\text{H}^{79}\text{Br}$ .
- The force constant of  $^{79}\text{Br}^{79}\text{Br}$  is  $240\text{ Nm}^{-1}$ . Calculate the fundamental vibrational frequency and the zero-point energy.
- The conjugate variables in the uncertainty principle are energy and time. Since  $\Delta E \Delta t = h/4\pi$ , there is a lifetime broadening to an excited electron state. Imagine that the  $\text{H}_2^+$  molecular ion is excited to the dissociative potential energy surface and flies apart. If this process occurs in 50 fs what is the linewidth for the absorption process? How does this time compare with the vibrational period of  $\text{H}_2^+$  if we assume that the vibrational wavenumber is  $3330\text{ cm}^{-1}$ ?
- We have learned that infrared activity depends on a change in the dipole moment of a molecule as it vibrates and that Raman activity results from a change in the polarizability of the molecule as it vibrates. Determine whether the following vibrational normal modes will be infrared or Raman active or both. Describe the motivation for your answer in terms of the dipole moment change of the molecule given the molecular symmetry.
  - The symmetric stretch of  $\text{CO}_2$ .
  - The asymmetric stretch of  $\text{CO}_2$ .
  - The bend of  $\text{H}_2\text{S}$ .
  - The symmetric breathing mode of  $\text{CH}_4$ . A breathing mode consists of four simultaneous stretches in the C-H bonds.
  - The following modes of  $\text{AlCl}_3$ .



5. Polyenes can be treated as a particle-in-a-box problem. The longer the polyene molecule the closer the energy spacing and therefore the smaller the transition energy. This corresponds experimentally to the observation that the absorption spectra shift to lower energies (smaller wavenumber) as the length increases. Demonstrate the trend by calculating  $h^2/8mL^2$  for the four polyenes shown given C-C = 154 pm and C=C = 135 pm. Note that the length of the box includes all of the bonds in the molecule plus one more C-C bond to account for the radius of carbon atoms at the end of the molecule.

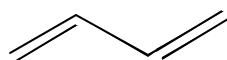
The distances are calculated as follows:

$$L(\text{butadiene}) = 2(\text{C}=\text{C}) + 2(\text{C}-\text{C}) = 2(135 \text{ pm}) + 2(154 \text{ pm}) = 578 \text{ pm}$$

$$L(\text{hexatriene}) = 3(\text{C}=\text{C}) + 3(\text{C}-\text{C}) = 3(135 \text{ pm}) + 3(154 \text{ pm}) = \dots$$

Note that in each case the number of  $\pi$  electrons is equal to the number of carbon atoms and that according to the Pauli principle two electrons occupy each level of the "box".

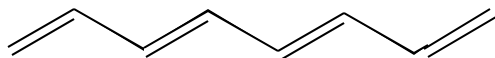
- a.) Using this model calculate the transition energy for each of the four polyenes.  
 b.) How many nodes are predicted for the HOMO of each of these molecules based on the particle in a box wave function?



Butadiene



Hexatriene



Octatetraene



Decapentaene