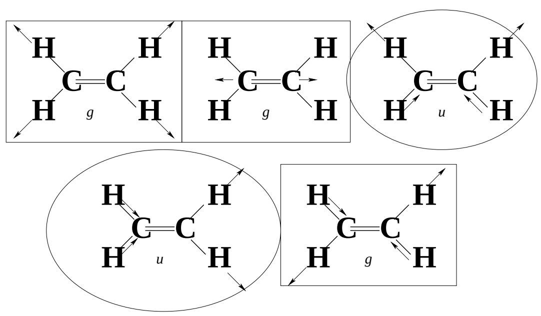
Chemistry 410A **Exam 6** **Spring 2008**

Solutions

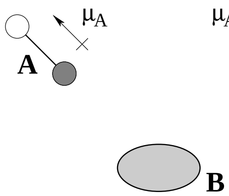
1. The five stretching modes of ethene are illustrated below. Circle the pictures that correspond to modes that are *infrared active* (*i.e.*, that can be excited according to electric dipole selection rules) and draw a rectangle around any that are *Raman active*. **Solution:** The point group is D_{2h}, which has inversion symmetry. We know right away then that only vibrational modes antisymmetric under $\hat{I}$ may be infrared active, and only symmetric modes may be Raman active. In fact, according to the character table, *any* mode with g symmetry is Raman active, and any mode except a_u modes will be infrared active. It isn't necessary to assign the individual representations, except to see if any u modes are symmetric under inversion (and therefore a_u):



2. The rotational constant of $^{12}C^{16}O_2$ is given in Table 8.2 as $0.390\,\mathrm{cm}^{-1}$. Use this to find the C=O bond length in CO_2. **Solution:** We can start from Eq. 8.6 for B in terms of the moment of inertia I, remembering that I depends in turn on the bond lengths:

$$\begin{aligned} B\ (\mathrm{cm}^{-1}) &= \frac{16.858}{I(\text{ amu Å}^2)} \\ I &= \frac{16.858}{B} \\ &= \sum_i m_i a_i^2 = 2m_\mathrm{O} R_\mathrm{CO}^2 \\ R_\mathrm{CO} &= \left(\frac{16.858}{2m_\mathrm{O}B}\right)^{1/2} = \left(\frac{16.858}{2(15.99)(0.390)}\right)^{1/2} = \boxed{1.16\ \text{Å}}. \end{aligned}$$

3. For the arrangement of molecules shown below, write an expression for the total *force* on non-polar molecule B, having polarizability α_B, due to its interaction with two molecules A each with dipole moment μ_A. The distance between A and B is R for both interactions, and the two AB axes form an angle of 90°.



Solution: The effect is the vector sum of two dipole-induced dipole interactions, 90° apart. The force for each interaction is the derivative of the potential energy:

$$F_{2-2^*} = -\frac{d}{dR}u_{2-2^*}(R) = -\frac{24\mu_{\rm A}^2\alpha_{\rm B}}{(4\pi\epsilon_0)R^7}.$$

The total force would be the resultant or vector sum of the individual (and equal) forces $\vec{F}_1$ and $\vec{F}_2$,

$$F_T = \sqrt{F_1^2 + F_2^2} = \sqrt{2}F_{2-2^*} = -\frac{24\sqrt{2}\mu_{\rm A}^2\alpha_{\rm B}}{(4\pi\epsilon_0)R^7}.$$

(The sign here implies that this is an attractive force, working to reduce R.)

4. The Lennard-Jones potential that we introduced is prpoerly called the Lennard-Jones **6-12** potential, because the general form is used for other powers of R as well. For example, in the AMBER molecular mechanics program, hydrogen bonding is represented using a Lennard-Jones **10-12** potential:

$$u_{\rm HB}(R) = \epsilon_{\rm HB}\left[\left(\frac{R_e}{R}\right)^{12} - 2\left(\frac{R_e}{R}\right)^{10}\right].$$

Find the value of R where $u_{\rm HB}(R) = 0$ in terms of R_e. **Solution:**

$$0 = \epsilon_{\rm HB}\left[\left(\frac{R_e}{R_0}\right)^{12} - 2\left(\frac{R_e}{R_0}\right)^{10}\right]$$

$$2\left(\frac{R_e}{R_0}\right)^{10} = \left(\frac{R_e}{R_0}\right)^{12} \qquad R_0^2 = \frac{1}{2}R_e^2 \qquad R_0 = \boxed{2^{-1/2}R_e}.$$

5. The icosohedral or cuboctahedral geometries of a close-packed X_{13} cluster complete a coordination shell around the central X atom. Estimate the cluster size N of a close-packed cluster X_N that exactly completes *two* shells around the central atom. **Solution:** A wide range of values is acceptable here. If we placed one atom at the middle of each of the 20 faces of the icosohedral structure, we'd get too low a value because the gaps between these atoms would be greater than in the first shell. Placing additional atoms at each of the 30 edges would get us closer, estimating about 50 atoms in the second shell for a total cluster size of $\boxed{N = 63}$. The actual "magic number" associated with the completion of the second shell is based on the cuboctahedral geometry, and is $\boxed{N = 55}$.