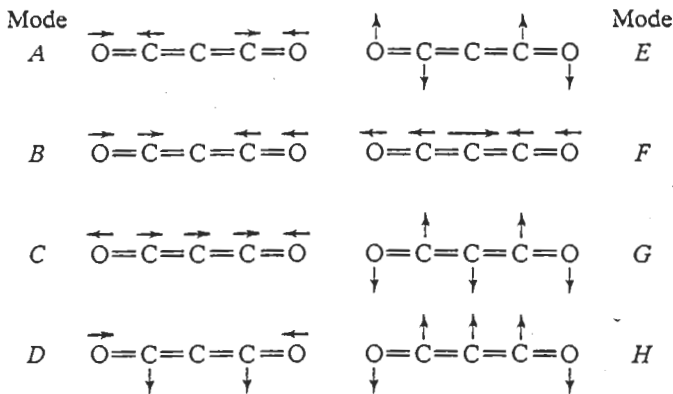


and  $E_z = (v_z + 0.5)h\nu_z$ . Therefore, the coordinates  $x$ ,  $y$ , and  $z$  function as normal-mode coordinates.

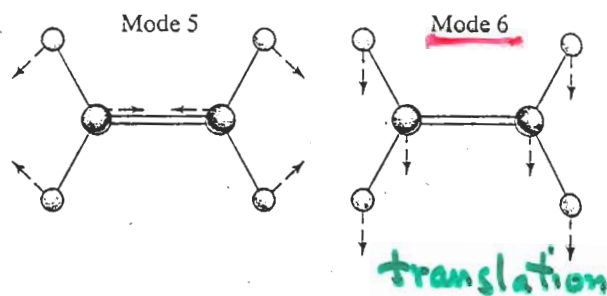
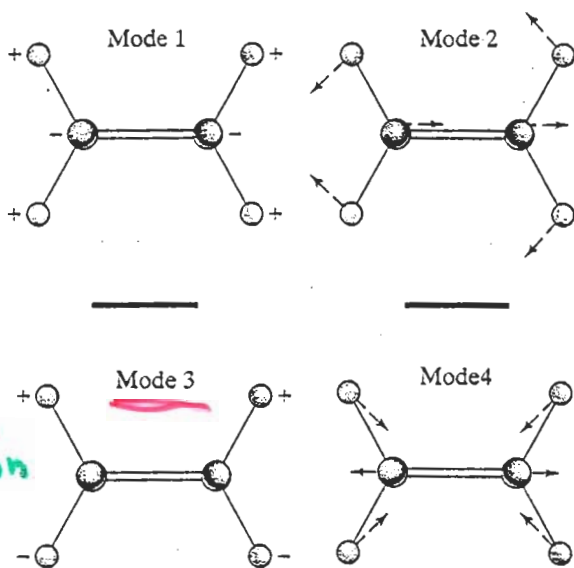
- 15.51 Carbon suboxide is a linear symmetric molecule whose structure is  $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$ . Eight molecular motions of this molecule are shown in the following diagram:



- (A) How many vibrational modes does carbon suboxide have?  
 (B) Which of the molecular motions shown does not correspond to one of the vibrational modes of carbon suboxide?  
 (C) Which of the stretching modes shown above will be IR active? Which will be Raman active?  
 (D) Which of the molecular motions will be doubly degenerate vibrational modes of carbon suboxide? (The arrows show the normal-mode displacements in each mode.)

- 15.52 Consider the ethylene molecule, ( $\text{C}_2\text{H}_4$ ).

- (A) How many vibrational modes does  $\text{C}_2\text{H}_4$  have?  
 (B) The following diagram shows 6 molecular motions of the planar  $\text{C}_2\text{H}_4$  molecule, each of which may be a translation, a rotation, or a vibration:



For each motion, indicate whether it is a translation, rotation, or vibration. In the case of the vibrations the arrows represent the normal-mode displacement coordinates.

(C) Which of the vibrational motions shown would be expected to be IR active? The atoms labeled with the + sign are moving out of the plane of the paper while those labeled with the - sign are moving into the plane of the paper.

- 15.53 Consider the ground state of the  $\text{Li}_2$  molecule.

- (A) What is the appropriate spectroscopic designation for the ground electronic state of this molecule?  
 (B) Suppose we excite  $\text{Li}_2$  into the configuration  $(1s\sigma_g)^2(1s\sigma_u)^2(2s\sigma_g)^1(2s\sigma_u)^1$ . What are appropriate spectroscopic designations for the term states arising from this configuration?

- 15.54 Using the data given in Table 15.7, and referring to the discussion immediately following this table along with the procedure illustrated in Example 12.2, obtain Morse potential fits for the  $X^1\Sigma_g^+$  and the  $B^1\Sigma_u^+$  states of  $\text{H}_2$  and thereby derive Eqs. 15.91 and 15.92.

- 15.55 A spectroscopist measures the vibrational band between the  $X^1\Sigma_g^+$  and the  $B^1\Sigma_u^+$  states of  $\text{H}_2$ . The (02), (03), and (04) bands are found at 11.5043 eV, 11.6577 eV, and 11.8062 eV, respectively. The vibrational wave number and anharmonicity factor for the  $X^1\Sigma_g^+$  ground state are known to be  $4395.2\text{ cm}^{-1}$  and  $117.99\text{ cm}^{-1}$ , respectively. Use these data to determine the vibrational wave number and anharmonicity factor for the  $B^1\Sigma_u^+$  state and the energy spacing between the potential minima of the two states.

- 15.56 Using the rigid-rotor selection rule, derive Eqs. 15.9 and 15.96 for the  $R$  and  $P$  branches of the electron band structure.

- 15.57 The  $A^3\Sigma_u^+$  state of  $\text{O}_2$  has a rotational constant  $B/c = B'_c = 1.05\text{ cm}^{-1}$ . The  $\text{O}_2 X^3\Sigma_g^-$  ground state has  $B_c'' = 1.446\text{ cm}^{-1}$ . Thus, in this case, we have  $B'_c < B_c''$ . At what rotational quantum number will the band head in the  $X^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$  vibrational bands appear? Plot the difference  $(\Delta\omega'_c - \Delta\omega_c)$  versus  $J''$  to show that a Fortrat parabola exists in the  $R$  branch of the spectrum. Is the band head red-shifted or blue-shifted from  $\Delta\omega_c$ ? What does this tell about the equilibrium  $\text{O}_2$  bond length in the two