1. **12.4(b)** Use the information in Table 12.1 to calculate the moments of inertia and the rotational constants (as frequencies and wavenumbers) of $\mathrm{H}^2\mathrm{Cl}^3\mathrm{Br}$, $(1\mathrm{H}^2\mathrm{Cl}^3\mathrm{Br}^1) = 34.9668\,\text{amu}$, $R(\text{Cl}-\text{Cl}) = 107\,\text{pm}$; $R(\text{Cl}-\text{Br}) = 177\,\text{pm}$; ClCl angle $= 110^\circ$.

   $\mathrm{H}^2\mathrm{Cl}^3\mathrm{Br}$ is a symmetric rotor; its moments of inertia are given by the formulas (Table 12.1)

   \[ I_j = m_j(1 - \cos \theta)R^2 \]

   \[ I_j = \frac{m_j(1 - \cos \theta)R^2}{m} + \frac{m_j(1 - 2\cos \theta)R}{m} \]

   We substitute the following data into the above formulas and then perform the calculation.

   \[ m_1 = 0.1078 \times 1.0078 \times 1.66054 \times 10^{-27} \text{ kg} \]

   \[ m_2 = 34.9668 \times 1.66054 \times 10^{-27} \text{ kg} \]

   \[ m_3 = 12.0000 \times 12.0000 \times 1.66054 \times 10^{-27} \text{ kg} \]

   \[ m = m_1 + m_2 + m_3 = 117.9142 \times 117.9142 \times 1.66054 \times 10^{-27} \text{ kg} \]

   \[ R = 177 \text{ pm} \times 1.77 \times 10^{-10} \text{ m} \]

   \[ \theta = 110^\circ \]

   Since the factor $m$ is common to each term in the formulas, multiplication by its value ends up performed until the end of the calculation. The results are:

   \[ I_1 = 2 \times 34.9668 \times 1.66054 \times 10^{-27} \text{ m}^2 \]

   \[ = 8.88 \times 10^{-20} \text{ kg m}^2 \]

   Substitution of the data in a similar manner into the above formula for $I_2$ gives

   \[ I_2 = \frac{2.54 \times 10^{-20} \text{ kg m}^2}{4 \pi I_1} \]

   We use eqns 12.13 to calculate the rotational constants in wavenumbers

   \[ A = \frac{h}{4 \pi I_1} = 5.74 \text{ m}^{-1} = 0.0574 \text{ cm}^{-1} \]

   \[ B = \frac{h}{4 \pi I_1} = 11.02 \text{ m}^{-1} = 0.1102 \text{ cm}^{-1} \]

   In frequency units we have

   \[ A = \frac{h}{4 \pi I_1} = 1.72 \times 10^4 \text{ s}^{-1} \times \left( \frac{1}{7.22 \times 10^9 \text{ Hz}} \right) \]

   \[ B = \frac{h}{4 \pi I_1} = 3.30 \times 10^4 \text{ s}^{-1} \times \left( \frac{1}{7.22 \times 10^9 \text{ Hz}} \right) \]

   This rotational spectra material was not covered in class and will not be on the final, but it is a good exercise to show how structure and spectra relate. It also may be helpful for those of you in Chem 343.

2. **12.6(b)** If the wavenumber of the $J = 1 \leftarrow 0$ rotational transition of $\mathrm{H}^2\mathrm{Cl}^3\mathrm{Br}$ considered as a rigid rotator is 16.93 cm$^{-1}$, what is (a) the moment of inertia of the molecule. (b) the bond length?

   (a) The wavenumber of the transition is related to the rotational constant by

   \[ \hbar \Delta \nu = \Delta E = \hbar c \Delta F = \hbar c R \left( J(J+1) - (J-1)(J-1) \right) = 2 \hbar c \nu \]

   where $J$ refers to the upper state ($J = 1$). The rotational constant is related to molecular structure by

   \[ R = \frac{\hbar}{4 \pi c I} \]

   where $I$ is moment of inertia. Putting these expressions together yields

   \[ \Delta \nu = \frac{2BJ}{2\pi c I} \]

   so

   \[ I = \frac{\hbar^2}{2BJ^2} \]

   \[ \nu = \nu \left( \frac{1.0546 \times 10^{-34} \text{ J s}}{1.0546 \times 10^{-34} \text{ J s}} \right) \times (1) \]

   \[ I = \frac{3.307 \times 10^{-43} \text{ kg m}^2}{\text{J}} \]

   (b) The moment of inertia is related to the bond length by

   \[ I = m \cdot R^2 \]

   so

   \[ R = \left( \frac{I}{m} \right)^{1/2} \]

   \[ m = m_1 + m_2 + m_3 = 1.60054 \times 10^{-27} \text{ kg} \]

   \[ m = 6.0494 \times 10^{-26} \text{ kg} \]

   and

   \[ R = \left( \frac{1.414 \times 10^{-10} \text{ nm}}{141.4 \text{ pm}} \right) \]

3. **12.18(b)** From the data in Exercise 12.18a, predict the fundamental vibrational wavenumbers of the deuterium halides.

   The relation between vibrational frequency and wavenumber is

   \[ \nu = \frac{h}{2\pi c} \left( \frac{k}{m \cdot \text{v}} \right)^{1/2} \]

   The reduced masses of the hydrogen halides are very similar, but not identical

   \[ m_{\text{H}} = m_{\text{H}} + m_{\text{Cl}} \]

   \[ m_{\text{D}} = m_{\text{H}} + m_{\text{Cl}} \]

   \[ \nu_0 = 4141.3 \text{ cm}^{-1} \quad \text{HF} \; 2988.9 \text{ cm}^{-1} \quad \text{H}^2\text{Cl} \; 2649.7 \text{ cm}^{-1} \quad \text{H}^2\text{Br} \; 2309.5 \text{ cm}^{-1} \quad \text{H}^2\text{I} \]
We assume that the force constants as calculated in Exercise 13.18(a) are identical for the deuterium halide and the hydrogen halide.

For DF

\[ k_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u}^{-1} + 18.9348 \text{ u}^{-1})}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.3071 \times 10^{28} \text{ kg}^{-1} \]

\[ \nu = \frac{(3.3071 \times 10^{28} \text{ kg}^{-1}) \times (967.04 \text{ kg s}^{-2})^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})^{1/2}} = 3002.3 \text{ cm}^{-1} \]

For DCI

\[ k_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u}^{-1} + 34.8668 \text{ u}^{-1})}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.1624 \times 10^{28} \text{ kg}^{-1} \]

\[ \nu = \frac{(3.1624 \times 10^{28} \text{ kg}^{-1}) \times (515.59 \text{ kg s}^{-2})^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})^{1/2}} = 2143.7 \text{ cm}^{-1} \]

For DBr

\[ k_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u}^{-1} + 80.9463 \text{ u}^{-1})}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.0646 \times 10^{28} \text{ kg}^{-1} \]

\[ \nu = \frac{(3.0646 \times 10^{28} \text{ kg}^{-1}) \times (411.75 \text{ kg s}^{-2})^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})^{1/2}} = 1885.8 \text{ cm}^{-1} \]

For DI

\[ k_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u}^{-1} + 126.9048 \text{ u}^{-1})}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.0376 \times 10^{28} \text{ kg}^{-1} \]

\[ \nu = \frac{(3.0376 \times 10^{28} \text{ kg}^{-1}) \times (314.21 \text{ kg s}^{-2})^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})^{1/2}} = 1640.1 \text{ cm}^{-1} \]

4. 12.25(b) Which of the vibrations of an AB₃ molecule are infrared or Raman active when it is (a) trigonal planar, (b) trigonal pyramidal?

(a) A planar AB₃ molecule belongs to the D₃h group. Its four atoms have a total of 12 displacements, of which 6 are vibrations. We determine the symmetry species of the vibrations by first determining the characters of the reducible representation of the molecule formed from all 12 displacements and then subtracting from these characters the characters corresponding to translation and rotation. This latter information is directly available in the character table for the group D₃h. The resulting set of characters are the characters of the reducible representation of the vibrations. This representation can be reduced to the symmetry species of the vibrations by inspection or by use of the little orthogonality theorem.

<table>
<thead>
<tr>
<th>D₃h</th>
<th>E</th>
<th>2C₃</th>
<th>2S₃</th>
<th>3C₂</th>
<th>3σv</th>
</tr>
</thead>
<tbody>
<tr>
<td>χ (translation)</td>
<td>3</td>
<td>0</td>
<td>-2</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Unreduced atoms</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>χ (total)</td>
<td>12</td>
<td>12</td>
<td>-2</td>
<td>-2</td>
<td>2</td>
</tr>
<tr>
<td>χ (rotation)</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>χ (vibration)</td>
<td>6</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

χ (vibration) corresponds to A'₁ + A'₂ + 2E'.

Again referring to the character table of D₃h, we see that E' corresponds to χ and A'₂ to χ; hence A'₁ and E' are IR active. We also see from the character table that E' and A'₁ correspond to the quadratic terms; hence A'₁ and E' are Raman active.

(b) A trigonal pyramidal AB₃ molecule belongs to the group C₃v. In a manner similar to the analysis in part (a) we obtain

<table>
<thead>
<tr>
<th>C₃v</th>
<th>E</th>
<th>2C₃</th>
<th>3σv</th>
</tr>
</thead>
<tbody>
<tr>
<td>χ (total)</td>
<td>12</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>χ (vibration)</td>
<td>6</td>
<td>-2</td>
<td>2</td>
</tr>
</tbody>
</table>

χ (vibration) corresponds to 2A₁ + 2E. We see from the character table that A₁ and E are IR active and that A₁ + E are also Raman active. Thus all modes are observable in both the IR and the Raman spectra.
5. Predict the shape of the nitronium ion, NO$_2^+$, from its Lewis structure and the VSEPR model. It has one Raman active vibrational mode at 1400 cm$^{-1}$, two strong IR active modes at 2360 and 540 cm$^{-1}$, and one weak IR mode at 3735 cm$^{-1}$. Are these data consistent with the predicted shape of the molecule? Assign the vibrational wavenumbers to the modes from which they arise.

The Lewis structure is $\{\text{O}=\text{N}=\text{O}\}^+$. VSEPR indicates that the ion is [linear] and has a center of symmetry. The activity of the modes is consistent with the rule of mutual exclusion; none is both infrared and Raman active. These transitions may be compared to those for CO$_2$ (Fig. 11.40 of the text) and are consistent with them. The Raman active mode at 1400 cm$^{-1}$ is due to a symmetric stretch ($v_1$), that at 2360 cm$^{-1}$ to the antisymmetric stretch ($v_3$), and that at 540 cm$^{-1}$ to the two perpendicular bending modes ($v_2$). There is a combination band, $v_2 + v_3 = 3750$ cm$^{-1} \approx 3735$ cm$^{-1}$, which shows a weak intensity in the infrared.

6. The protein haematin is responsible for binding and carrying O$_2$ in some invertebrates. Each protein molecule has two Fe$^{3+}$ ions that are in very close proximity and work together to bind one molecule of O$_2$. The Fe$^{3+}$ group of oxygenated haematin is coloured and has an electronic absorption band at 500 nm. The resonance Raman spectrum of oxygenated haematin obtained with laser excitation at 500 nm has a band at 844 cm$^{-1}$ that has been attributed to the O-O stretching mode of bound O$_2$. (a) Why is resonance Raman spectroscopy and not infrared spectroscopy the method of choice for the study of the binding of O$_2$ to haematin? (b) Why is the 844 cm$^{-1}$ band arises from a bound O$_2$ species may be obtained by conducting experiments on samples of haematin that have been mixed with O$_3$, instead of O$_2$. Predict the fundamental vibrational wavenumber of the 1$^{16}$O$_2$-D$^{18}$O stretching mode in a sample of haematin that has been treated with O$_3$. (c) The fundamental vibrational wavenumbers for the O-O stretching modes of O$_2$, O$_3$, and O$_2^+$ (peroxide ion) are 1555, 1107, and 878 cm$^{-1}$, respectively. Explain this trend in terms of the electronic structures of O$_2$, O$_3$, and O$_2^+$. Hint: Review Section 10.4. What are the bond orders of O$_2$, O$_3$, and O$_2^+$? (d) Based on the data given above, which of the following species best describes the Fe$^{3+}$ group of haematin: FeFe$^{3+}$NO, FeFe$^{3+}$O$^-$, or FeFe$^{3+}$O$_2^+$? Explain your reasoning. (e) The resonance Raman spectrum of haematin mixed with $^{18}$O$_2$ has two bands that can be attributed to the O-O stretching mode of bound oxygen. Discuss how this observation may be used to exclude one or more of the four proposed schemes (7-10) for binding of O$_2$ to the Fe$^{3+}$ site of haematin.

(a) Resonance Raman spectroscopy is preferable to vibrational spectroscopy for studying the O-O stretching mode because such a mode would be [infrared inactive], or at best only weakly active. (The mode is sure to be inactive in free O$_2$, because it would not change the molecule’s dipole moment. In a complex in which O$_2$ is bound, the O-O stretch may change the dipole moment, but it is not certain to do so at all, let alone strongly enough to provide a good signal.)

(b) The vibrational wavenumber is proportional to the frequency, and it depends on the effective mass as follows:

$$\tilde{v} \propto \left( \frac{k}{m_{\text{eff}}} \right)^{1/2} \quad \text{so} \quad \tilde{v}(^{18}\text{O}_2) = \left( \frac{m_{\text{eff}}(^{18}\text{O}_2)}{m_{\text{eff}}(^{16}\text{O}_2)} \right)^{1/2} = \left( \frac{16.0 u}{18.0 u} \right)^{1/2} = 0.943.$$

and \(\tilde{v}(^{18}\text{O}) = (0.943)(844 \text{ cm}^{-1}) = 796 \text{ cm}^{-1}\).

Note the assumption that the effective masses are proportional to the isotopic masses. This assumption is valid in the free molecule, where the effective mass of O$_2$ is equal to half the mass of the O atom, it is also valid if the O$_2$ is strongly bound at one end, such that one atom is free and the other is essentially fixed to a very massive unit.

(c) The vibrational wavenumber is proportional to the square root of the force constant. The force constant is itself a measure of the strength of the bond (technically of its stiffness, which correlates with strength), which in turn is characterized by bond order. Simple molecular orbital analysis of O$_2$, O$_3$, and O$_2^+$ results in bond orders of 2, 1.5, and 1, respectively. Given decreasing bond order, one would expect decreasing vibrational wavenumbers (and vice versa).

(d) The wavenumber of the O-O stretch is very similar to that of the peroxide ion, suggesting FeFe$^{3+}$O$^-$.

(e) The detection of two bands due to $^{16}$O$^{18}$O implies that the two O atoms occupy non-equivalent positions in the complex. Structures 7 and 8 are consistent with this observation, but structures 5 and 6 are not.

Somehow the numbers are goofed up, 7,8 have equivalent O’s but 9,10 have different O’s, bonded and terminal.
7. Identify the molecular orbitals for F₂ in the images shown here in terms of the designations discussed in Section 16.9, i.e. label them \( \sigma \) or \( \pi \) and bonding or antibonding and \( g \) or \( u \). The molecular axis is the \( z \) axis, and the \( y \) axis is tilted slightly out of the plane of the image.

The upper two images:

The left image has \( \sigma \) symmetry, the AOs are out of phase, and there is a single node between the atoms. Therefore it is the \( 3\sigma_u^* \) or \( \sigma_u^*(2p_z) \) MO. The right image is of \( \pi \) symmetry and has no node in the bonding region. It is the \( 1\pi_u \) or \( \pi_u(2p_x) \) MO.

The lower two images:

The left image shows out of phase AOs with no overlap. Therefore it is the \( 1\sigma_u^* \) or \( \sigma_u^*(1s) \) MO. The right image has \( \sigma \) symmetry with no nodes in the bonding region. Therefore it is the \( 3\sigma_g \) or \( \sigma_g(2p_z) \) MO.

Since C≡O is heteronuclear, no \( g \) or \( u \) designation

8. This is the same sort of question but the images are for C≡O.

(a) (b) (c)

(d) (e) (f)

a: \( 3\sigma_b \) (2p_z).  
b: \( 2\sigma^*(2s) \).  
c\&e: \( 1\pi_b(2p) \)  
d: \( 2\pi_b^* (2p) \)  
f: \( 1\sigma_b(2s) \)
9. P17.3) Use the VSEPR method to predict the structures of the following:

a. BrF$_5$

b. SO$_3^{2-}$

a) BrF$_5$ has 5 ligands and a lone pair. VSEPR predicts that the structure is square pyramidal.

b) SO$_3^{2-}$ has 3 ligands and a lone pair. VSEPR predicts that the structure is pyramidal.

10. P18.14) Calculating the motion of individual atoms in the vibrational modes of molecules (called normal modes) is an advanced topic. Given the normal modes shown in the following figure, decide which of the normal modes of CO$_2$ and H$_2$O have a nonzero dynamic dipole moment and are therefore infrared active. The motion of the atoms in the second of the two doubly degenerate bend modes for CO$_2$ is identical to the first, but is perpendicular to the plane of the page.

All three vibrational modes of water will lead to a change in the dipole moment and are therefore infrared active. The symmetric stretch of carbon dioxide will not lead to a change in the dipole moment and is infrared inactive. The other two modes will lead to a change in the dipole moment and are infrared active.

11. P18.22) Selection rules in the dipole approximation are determined by the integral

$$\mu_{x}^{mn} = \int \psi_{n}^{*}(r) \mu_{x}(r) \psi_{m}(r) dr.$$ If this integral is nonzero, the transition will be observed in an absorption spectrum. If the integral is zero, the transition is “forbidden” in the dipole approximation. It actually occurs with low probability because the dipole approximation is not exact. Consider the particle in the one-dimensional box and set $\mu_{x} = -ex$.

a. Calculate $\mu_{x}^{12}$ and $\mu_{x}^{13}$ in the dipole approximation. Can you see a pattern and discern a selection rule?

You may need to evaluate a few more integrals of the type $\mu_{x}^{1m}$. The standard integral

$$\int x \sin \frac{nx}{a} \sin \frac{nx}{a} dx = \frac{1}{2} \left[ \frac{a^{2} \sin \frac{(n-1)\pi x}{a}}{(n-1)^{2} \pi^{2}} + \frac{ax \sin \frac{(n-1)\pi x}{a}}{(n-1)\pi} \right] - \frac{1}{2} \left[ \frac{a^{2} \sin \frac{(n+1)\pi x}{a}}{(n+1)^{2} \pi^{2}} + \frac{ax \sin \frac{(n+1)\pi x}{a}}{(n+1)\pi} \right]$$

is useful for solving this problem.

b. Determine the ratio $\mu_{x}^{12} / \mu_{x}^{14}$. On the basis of your result, would you modify the selection rule that you determined in part (a)?

a) We first evaluate $\mu_{x}^{12}$.

$$\mu_{x}^{12} = -\frac{2ea}{a} \int x \sin \frac{x}{a} \sin \frac{x}{a} dx = \left[ e \left( \frac{a^{2} \cos \frac{\pi x}{a}}{\pi} + \frac{ax \sin \frac{\pi x}{a}}{\pi} \right) \right]_{0} + e \left( \frac{a^{2} \cos \frac{3\pi x}{a}}{9\pi} + \frac{3ax \sin \frac{3\pi x}{a}}{9\pi} \right)_{0} - e \left( \frac{a^{2} \cos 0}{\pi} + 0 \right) - e \left( \frac{a^{2} \cos 0}{9\pi} + 0 \right)$$

$$= -\frac{e}{a} \left( \frac{a^{2} \cos \pi}{\pi^{2}} + \frac{a \sin \pi}{\pi} \right) + e \left( \frac{a^{2} \cos 0}{\pi} + 0 \right) - e \left( \frac{a^{2}}{9\pi} + 0 \right) = \frac{2ea}{9\pi} - \frac{2ea}{9\pi} = 0$$

$$= -\frac{e}{a} \left( \frac{a^{2}}{\pi^{2}} + 0 \right) - \frac{e}{a} \left( \frac{a^{2}}{9\pi} + 0 \right) = \frac{16e}{9\pi}$$
The result is  
$$
\mu_{x}^{12} = \frac{2e}{a} \frac{8a^2}{9\pi^2} = \frac{16ae}{9\pi^2}
$$

$$
\mu_{x}^{13} = \frac{2e}{a} \int_{0}^{a} x \sin \frac{\pi x}{a} \sin \frac{3\pi x}{a} dx
$$

$$
= \left[ -e^{a^2 \cos 2\pi + 2a \sin 2\pi - \frac{2\pi}{4\pi} + \frac{2\pi x}{4\pi}} + e^{a^2 \cos \frac{4\pi x}{a} + \frac{4a \sin \frac{4\pi x}{a}}{4\pi}} \right]^{a}_{0}
$$

$$
= \left[ -e^{a^2 \cos \frac{2\pi}{4\pi} + 2a \sin 2\pi - \frac{2\pi}{4\pi} + \frac{2\pi x}{4\pi}} + e^{a^2 \cos \frac{4\pi x}{a} + \frac{4a \sin \frac{4\pi x}{a}}{4\pi}} \right]^{a}_{0}
$$

$$
= -e^{a^2 \cos \frac{0}{4\pi} + 0} + e^{a^2 \cos \frac{0}{16\pi} + 0} + e^{a^2 \cos \frac{0}{4\pi} + 0} - e^{a^2 \cos \frac{0}{16\pi} + 0} = 0
$$

The result is  
$$
\mu_{x}^{13} = 0.
$$

$$
\mu_{x}^{14} = \frac{2e}{a} \int_{0}^{a} x \sin \frac{\pi x}{a} \sin \frac{4\pi x}{a} dx
$$

$$
= \left[ -e^{a^2 \cos \frac{3\pi x}{9\pi^2} + 3a \sin \frac{3\pi x}{9\pi^2}} + e^{a^2 \cos \frac{5\pi x}{25\pi^2} + \frac{5a \sin \frac{5\pi x}{25\pi}}{25\pi}} \right]^{a}_{0}
$$

$$
= \left[ -e^{a^2 \cos \frac{3\pi}{9\pi^2} + 3a^2 \sin \frac{3\pi}{9\pi^2}} + e^{a^2 \cos \frac{5\pi}{25\pi^2} + \frac{5a^2 \sin \frac{5\pi}{25\pi}}{25\pi}} \right]^{a}_{0}
$$

$$
= -e^{a^2 \cos \frac{0}{9\pi^2} + 0} + e^{a^2 \cos \frac{0}{25\pi^2} + 0} + e^{a^2 \cos \frac{0}{9\pi^2} + 0} - e^{a^2 \cos \frac{0}{25\pi^2} + 0}
$$

$$
= -e^{a^2 \cos \frac{0}{9\pi^2} + 0} + e^{a^2 \cos \frac{0}{25\pi^2} + 0} + e^{a^2 \cos \frac{0}{9\pi^2} + 0} - e^{a^2 \cos \frac{0}{25\pi^2} + 0}
$$

$$
= -e^{a^2 \cos \frac{0}{9\pi^2} + 0} + e^{a^2 \cos \frac{0}{25\pi^2} + 0} + e^{a^2 \cos \frac{0}{9\pi^2} + 0} - e^{a^2 \cos \frac{0}{25\pi^2} + 0} = 0
$$

The result is  
$$
\mu_{x}^{14} = \frac{32ea}{225\pi^2}.
$$

$$
\mu_{x}^{15} = \frac{2e}{a} \int_{0}^{a} x \sin \frac{\pi x}{a} \sin \frac{5\pi x}{a} dx
$$

$$
= \left[ -e^{a^2 \cos \frac{4\pi x}{16\pi^2} + 4a \sin \frac{4\pi x}{16\pi}} + e^{a^2 \cos \frac{6\pi x}{36\pi^2} + \frac{6a \sin \frac{6\pi x}{36\pi}}{36\pi}} \right]^{a}_{0}
$$

$$
= \left[ -e^{a^2 \cos \frac{4\pi}{16\pi^2} + 4a^2 \sin \frac{4\pi}{16\pi}} + e^{a^2 \cos \frac{6\pi}{36\pi^2} + \frac{6a^2 \sin \frac{6\pi}{36\pi}}{36\pi}} \right]^{a}_{0}
$$

$$
= -e^{a^2 \cos \frac{0}{16\pi^2} + 0} + e^{a^2 \cos \frac{0}{36\pi^2} + 0} + e^{a^2 \cos \frac{0}{16\pi^2} + 0} - e^{a^2 \cos \frac{0}{36\pi^2} + 0}
$$

$$
= -e^{a^2 \cos \frac{0}{16\pi^2} + 0} + e^{a^2 \cos \frac{0}{36\pi^2} + 0} + e^{a^2 \cos \frac{0}{16\pi^2} + 0} - e^{a^2 \cos \frac{0}{36\pi^2} + 0} = 0
$$

The result is  
$$
\mu_{x}^{15} = 0.
$$
These results show that the $1 \rightarrow n$ transition is allowed only if $n$ is even, or that the initial and final states have opposite parity with respect to reflection about the center of the box.

\[ \frac{\mu_{12}^2}{\mu_{16}^2} = \frac{16ae}{9\pi^2} \left( \frac{32ea}{225\pi^2} \right) = 12.5. \] It turns out that $\frac{\mu_{12}^2}{\mu_{16}^2} = 45.4$. This means that the transitions from $n = 1$ to $n = 4$ and $6$ are much weaker than the transition from $n = 1$ to $2$. Therefore, effectively, the selection rule is $\Delta n = 1$ for absorption.

12. P18.25) Resonance Raman spectroscopy has been used to study the binding of O$_2$ to oxygen transport proteins like hemerythrin and hemocyanin (T.B. Freedman, J.S. Loehr, and T.M. Loehr, “A Resonance Raman Studies of the Copper Protein Hemcyanin” J. Amer. Chem. Soc. 98:10, 2809–2815). These transport proteins are found in brachiopods and in arthropods, respectively. Hemerythrin binds oxygen to two iron atoms while hemocyanin binds oxygen to two copper atoms. Although O$_2$ is IR inactive, the bond stretch of O$_2$ can be detected by Raman spectroscopy. Assume both iron atoms in deoxyhemerythrin are in the +2 valence state (i.e., Fe$^{2+}$). The oxygen stretch occurs at 845 cm$^{-1}$ in oxyhemerythrin. In contrast free oxygen has a Raman band at 1555 cm$^{-1}$ and peroxide $\left(\text{O}_2^2-\right)$ occurs at 738 cm$^{-1}$. Based on the Raman data, write a scheme for the binding of O$_2$ to the two Fe$^{2+}$ atoms of hemerythrin. Hint: The Raman data indicate that charge transfer accompanies oxygen binding. Include this fact in your reaction scheme.

![Reaction Scheme](image)

Deoxyhemerythrin contains two ferrous ions bridged by hydroxyl group (A). One iron is hexacoordinate and another is pentacoordinate. The bridging hydroxyl serves as the proton donor for peroxide after O$_2$ binding, resulting in the formation of a single oxygen atom bridge in oxy- and methemerythrin. O$_2$ binds to the pentacoordinate Fe$^{2+}$ at the vacant coordination site (B). Then electrons are transferred from the ferrous ions to generate the binuclear ferric (Fe$^{3+}$,Fe$^{3+}$) center with bound peroxide (C).

13. P18.27) In P18.26 the frequencies of the Raman bands for the bond stretches of $^{16}$O$_2$ and $^{18}$O$_2$ were considered. When $^{16}$O—$^{16}$O is bond to hemacynin, the single Raman band for the O$_2$ bond stretch is split into a doublet. Based on this fact, is the binding geometry of O$_2$ to hemacynin symmetric or asymmetric? Explain your answer. Examples of symmetric and asymmetric binding geometries are given here. Estimate the frequencies of the two bands and state any assumptions you make in your calculation.

![Symmetric and Asymmetric Binding](image)

For vibrational modes to be Raman active, the polarizability of the molecule has to change as it vibrates. This condition is especially applies for the stretching vibration of homonuclear molecules. Therefore, the Raman activity of O$_2$ bound to hemacynin indicates an asymmetric binding arrangement.
14. P18.28) The tautomeric forms of pyrimidine bases in a polynucleotide structure were determined by H. Todd Miles using IR absorption spectroscopy (H. T. Miles (1961) “Tautomeric Forms in a Polynucleotide Helix and their Bearing on DNA Structure” Proc. Natl. Acad. Sci. (USA) 47, 791–802). At issue is whether in the polynucleotide structure the labile proton is located on the amino nitrogen (i.e., structure I) or N3 in the cytosine pyrimidine ring (structure II). To determine this the IR spectra of A) cytidine, B) 1-(b-D-glucopyranosyl-4-dimethylamino-2-pyrimidone), i.e., structure III where R=CH₃, and C) 1,3-dimethylcytosine, i.e., structure IV where R=CH₃, were obtained. It is considered probable that the strong band at 1651 cm⁻¹ is from the vibration of the C“O bond, while the weaker bands are from C“N stretches. Identify the tautomeric form of cytidine in DNA. Explain your answer.

The labile hydrogens of the nucleosides could be attached to either of the two nitrogens in cytidine (I or II) and either oxygen or nitrogen in inosine (see P18.29, V and VI). The function of the alkyl groups in the model compounds is to fix these compounds in structures which are isoelectronic with the possible tautomeric forms of the corresponding nucleoside. The position of the hydrogens is uniquely determined by the laws of valence, and hence, the double bond arrangement can be obtained by comparison of the spectra. The spectrum of cytidine (A) is similar to the spectrum of the model compound III and quite different from that of IV, therefore predicting the structure of cytidine as the amino form I rather than the imino form II.

**Extra Problems**

1. 12.14(b) An object of mass 2.0 g suspended from the end of a spring has a vibrational frequency of 3.0 Hz. Calculate the force constant of the spring.

   The angular frequency is
   \[ \omega = \left( \frac{k}{m} \right)^{1/2} = 2\pi f \quad \text{so} \quad k = (2\pi f)^2 m = (2\pi)^2 \times (3.0 \text{ s}^{-1})^2 \times (2.0 \times 10^{-3} \text{ kg}) \]
   \[ k = 0.71 \text{ N m}^{-1} \]

2. 12.15(b) Calculate the percentage difference in the fundamental vibration wavenumber of ¹HCl and ²HCl on the assumption that their force constants are the same.

   \[ \omega = \left( \frac{k}{m} \right)^{1/2}, \quad \omega' = \left( \frac{k}{m'} \right)^{1/2}, \quad \text{prime} = ²HCl \]
   The force constant, \( k \), is assumed to be the same for both molecules. The fractional difference is
   \[ \frac{\omega' - \omega}{\omega} = \frac{\left( \frac{1}{m'} \right)^{1/2} - \left( \frac{1}{m} \right)^{1/2}}{\left( \frac{1}{m} \right)^{1/2}} = \left( \frac{m}{m'} \right)^{1/2} - 1 \]
   \[ \frac{\omega' - \omega}{\omega} = \frac{m_{Cl}}{m_{HCl}}^{1/2} - 1 = \frac{m_{Cl}}{m_{HCl}} \left( \frac{m_{HCl} + m_{HCl}}{m_{HCl} + m_{Cl}} \right)^{1/2} - 1 \]
   \[ = \left( \frac{1.0078 \text{ u} \times (34.9688 \text{ u})}{(2.0140 \text{ u}) \times (36.9651 \text{ u})} \right)^{1/2} - 1 \]
   \[ = -0.264 \]
   Thus the difference is 28.4 percent
3. **12.16b** The wavenumber of the fundamental vibrational transition of $^{79}\text{Br}^{81}\text{Br}$ is 323.2 cm$^{-1}$. Calculate the force constant of the bond ($m(79\text{Br}) = 78.9183 \text{amu}$, $m(81\text{Br}) = 80.9163 \text{amu}$).

The fundamental vibrational frequency is

$$\omega = \left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = 2\pi v = 2\pi c \nu$$

So

$$k = (2\pi c \nu)^2 m_{\text{eff}}$$

We need the effective mass

$$m_{\text{eff}} = m_1^{-1} + m_2^{-1} = (78.9183 \text{ u})^{-1} + (80.9163 \text{ u})^{-1} = 0.0250298 \text{ u}^{-1}$$

$$k = \frac{2\pi(2.998 \times 10^{10} \text{ cm s}^{-1}) \times (323.2 \text{ cm}^{-1})^2 \times (166054 \times 10^{-27} \text{ kg u}^{-1})}{0.0250298 \text{ u}^{-1}}$$

$$= 245.9 \text{ N m}^{-1}$$

4. **12.23b** Which of the following molecules may show infrared absorption spectra: (a) CH$_2$CH$_3$, (b) CH$_4$, (c) CH$_3$Cl, (d) N$_2$?

See Section 13.10. Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The infrared active compounds are:

(a) CH$_3$CH$_2$, (b) CH$_4$, (c) CH$_3$Cl

5. **12.24b** How many normal modes of vibration are there for the following molecules: (a) C$_2$H$_6$, (b) C$_2$H$_5$CH$_3$, (c) HC≡C=CH?

A nonlinear molecule has $3N - 6$ normal modes of vibration, where $N$ is the number of atoms in the molecule; a linear molecule has $3N - 5$.

(a) C$_2$H$_6$ has 3(12) - 6 = 36 normal modes.

(b) C$_2$H$_5$CH$_3$ has 3(16) - 6 = 42 normal modes.

(c) HC≡C=CH is linear; it has 3(6) - 5 = 13 normal modes.

6. **12.26b** Consider the vibrational mode that corresponds to the boat-like bending of a benzene ring. Is it (a) Raman, (b) infrared active?

(b) The boat-like bending of a benzene ring clearly changes the dipole moment of the ring, for the moving of the C–H bonds out of the plane will give rise to a non-cancelling component of their dipole moments. So the vibration is **IR active**.

(a) Since benzene has a centre of inversion, the exclusion rule applies: a mode which is IR active (such as this one) must be **Raman inactive**.

7. **12.16** Consider the molecule CH$_3$Cl. (a) To what point group does the molecule belong? (b) How many normal modes of vibration does the molecule have? (c) What are the symmetries of the normal modes of vibration for this molecule? (d) Which of the vibrational modes of this molecule are infrared active? (e) Which of the vibrational modes of this molecule are Raman active? **11.7**

(a) Follow the flow chart in Fig. 12.4 of the text. CH$_3$Cl is not linear; it has a C$_3$ axis (only one), it does not have $C_2$ axes perpendicular to $C_3$, it has no $C_3$, but does have 3 mirror planes; so it belongs to $C_{3v}$.

(b) The number of normal modes of a non-linear molecule is $3N - 6$, where $N$ is the number of atoms. So CH$_3$Cl has 9 normal modes.

(c) To determine the symmetry of the normal modes, consider how the Cartesian axes of each atom are transformed under the symmetry operations of the $C_{3v}$ group: the 15 Cartesian displacements constitute the basis here. All 15 Cartesian axes are left unchanged under the identity, so the character of this operation is 15. Under a $C_3$ operation, the H atoms are taken into each other, so they do not contribute to the character of $C_3$. The z axes of the C and Cl atoms, are unchanged, so they contribute 2 to the character of $C_3$; for these two atoms

$$x \rightarrow \frac{x}{2}, \quad \frac{3\sqrt{2}}{2} y$$

$$y \rightarrow \frac{y}{2} + \frac{3\sqrt{2}}{2} x,$$

so there is a contribution of $-1/2$ to the character from each of these coordinates in each of these atoms. In total, then, $x = 0$ for $C_3$. To find the character of $C_3$, call one of the $x$ axes the $x_1$ plane; its $y_1$ plane; its $z_1$ plane; its $C_1$ plane; and one H atom. The $x$ and $y$ coordinates of these three atoms are unchanged, but the $x$ coordinates are taken into their negatives, contributing $6 - 3 = 3$ to the character for this operation; the other two atoms are interchanged, so they contribute nothing to the character. To find the irreducible representations that this basis spans, we multiply its characters by the characters
8. **Q16.16)** Explain why $s$–$p$ mixing is more important in Li$_2$ than in F$_2$.

Atomic orbitals mix to a greater degree if the difference of their orbital energies is small. The difference in the $2s$ and $2p$ orbital energies increases in the sequence Li → F, so the degree of mixing decreases along this sequence.

9. **Q16.22)** Consider the molecular electrostatic potential map for the BH$_3$ molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?

It is an electron acceptor, because the red color around the H indicates a negative value for the electrostatic potential which results from an excess of electron charge.

10. **Q16.23)** Consider the molecular electrostatic potential map for the NH$_3$ molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?

It is an electron donor, because the blue color around the H indicates a positive value for the electrostatic potential which results from a deficiency of electron charge.

11. **P17.1)** Use the VSEPR method to predict the structures of the following:
   a. PF$_3$
   b. CO$_2$
   a) PF$_3$ has 3 ligands and a lone pair. VSEPR predicts that the structure is pyramidal.
   b) CO$_2$ has 2 double-bonded ligands and no lone pairs. VSEPR predicts that the structure is linear.

12. **P17.5)** Use the VSEPR method to predict the structures of the following:
   a. PCl$_3$
   b. SO$_2$
   a) PCl$_3$ has 5 ligands and a lone pair. VSEPR predicts that the structure is a distorted trigonal bipyramid.
b) SO\(_2\) has 2 ligands and a lone pair. VSEPR predicts that the structure is bent.

13. P17.10) Show that two of the set of four equivalent orbitals appropriate for \(sp^3\) hybridization, 
\[
\psi_a = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z})
\]
and 
\[
\psi_b = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z})
\]
are orthogonal. 

To show that \(\psi_a = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z})\) and \(\psi_b = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z})\) are orthogonal, we must evaluate 
\[
\int \psi_a^{\ast} \psi_b \, d\tau = \frac{1}{4} \left( \int (\phi_{2s})^2 \, d\tau + \int \phi_{2s} \phi_{2s} \, d\tau + \int \phi_{2s} \phi_{2s} \, d\tau - \int \phi_{2s} \phi_{2s} \, d\tau \right)
\]
\[
-\int \phi_{2p_x} \phi_{2p_x} \, d\tau - \int \phi_{2p_x} \phi_{2p_x} \, d\tau - \int \phi_{2p_y} \phi_{2p_y} \, d\tau + \int \phi_{2p_y} \phi_{2p_y} \, d\tau
\]
\[
-\int \phi_{2p_z} \phi_{2p_z} \, d\tau - \int \phi_{2p_z} \phi_{2p_z} \, d\tau - \int \phi_{2p_z} \phi_{2p_z} \, d\tau + \int \phi_{2p_z} \phi_{2p_z} \, d\tau
\]
Because the atomic orbitals are orthonormal, each integral containing two different atomic orbitals has the value zero, and the value one if the two atomic orbitals are identical.

\[
\int \psi_a^{\ast} \psi_b \, d\tau = \frac{1}{4} [1 - 1 - 1 + 1] = 0
\]

14. P18.10) Greenhouse gases generated from human activity absorb infrared radiation from the Earth and keep it from being dispersed outside our atmosphere. This is a major cause of global warming. Compare the path length required to absorb 99\% of the Earth’s radiation near a wavelength of 7 \(\mu\)m for CH\(_3\)CCl\(_3\) \(\varepsilon(\lambda) = 1.8 \text{ (cm atm)}^{-1}\) and the chlorofluorocarbon CFC-14 \(\varepsilon(\lambda) = 4.1 \times 10^3 \text{ (cm atm)}^{-1}\) assuming that each of these gases has a partial pressure of 2.0 \(\times 10^{-6}\) bar.

Rearranging the Beer-Lambert equation, we have for CH\(_3\)CCl\(_3\)
\[
l = -\frac{1}{M \varepsilon(\lambda)} \ln \left( \frac{I(\lambda)}{I_0(\lambda)} \right) = -\frac{1}{1.8 \text{ (cm atm)}^{-1} \times 2.0 \times 10^{-6} \text{ atm}} \times \ln 0.01 = 1.28 \times 10^6 \text{ cm}
\]
For CFC-14 we have
\[
l = -\frac{1}{M \varepsilon(\lambda)} \ln \left( \frac{I(\lambda)}{I_0(\lambda)} \right) = -\frac{1}{4.1 \times 10^3 \text{ (cm atm)}^{-1} \times 2.0 \times 10^{-6} \text{ atm}} \times \ln 0.01 = 5.61 \times 10^2 \text{ cm}
\]

15. P18.26) If the bond stretch for \(^{16}\text{O}_2\) in hemicyanin occurs at 845 cm\(^{-1}\), calculate the frequency of the Raman band expected for the bound stretch of \(^{18}\text{O}_2\) in hemacyanin.

Using the equation for the wave number:
\[
\nu = \frac{1}{\lambda} = \frac{k}{2\pi c} \sqrt{\mu}
\]
one can obtain the ratio:
\[
\frac{\nu^{^{16}\text{O}_2}}{\nu^{^{18}\text{O}_2}} = \sqrt{\frac{k}{\mu^{^{18}\text{O}_2}}} \mu^{^{18}\text{O}_2} = \frac{m^{^{18}\text{O}_2}^2}{m^{^{16}\text{O}_2}^2} = \frac{m^{^{18}\text{O}_2}}{m^{^{16}\text{O}_2}}
\]
\[ \tilde{\nu}(^{16}O_2) = \frac{18u}{16u} = 1.125 \]

And therefore:

\[ \tilde{\nu}(^{18}O_2) = \frac{\tilde{\nu}(^{16}O_2)}{1.125} = \frac{845cm^{-1}}{1.125} = 751.1cm^{-1} \]

16. P18.29) The IR study by H. T. Miles of tautomeric forms of bases in polynucleotide helices described in P18.28 was also applied to purine bases. Inosine, for example, a labile proton may be attached to N1 (V) or to the oxygen bonded to C6 (VI). Compare the IR spectra of inosine (G), 1-methylinosine (VII), and 6-methyloxy-9-β-D-ribofuranosylpurine (VIII) and determine the tautomeric form of inosine.

In analogy to the solution to P18.28, inosine was found to exist in the keto form, V, because of the close similarity of its spectrum with that of model compound VII and its very different spectrum as compared to model compound VIII.