Chapter 27 Problems: Rotational and Vibrational Spectroscopy

1. Calculate the ratio, N_1/N_o, of molecules in the $\upsilon = 1$ and $\upsilon = 0$ vibrational states for carbon monoxide, CO, at 25.0 °C. Assume a harmonic oscillator with $\tilde{v}_e = 2169.8$ cm^{-1} [Hint: at 25.0 °C, kT = 207.2 cm^{-1}]

Answer: The plan is to use the Boltzmann population ratio, Eq. 8.10.8, for a harmonic oscillator with energy $\tilde{G}_\upsilon = \tilde{v}_e(\upsilon + \frac{1}{2})$, Eq. 27.5.2.
   The energy difference in wave numbers is, $\Delta\varepsilon = \tilde{G}_1 - \tilde{G}_o = \tilde{v}_e(1 + \frac{1}{2}) - \tilde{v}_e(0 + \frac{1}{2}) = \tilde{v}_e$. The Boltzmann population ratio, Eq. 8.10.8, gives:

$$\frac{N_1}{N_o} = e^{-\Delta\varepsilon/kT} = e^{-2169.8 \text{ cm}^{-1}/207.2 \text{ cm}^{-1}} = 2.83 \times 10^{-5}$$

A negligible number of CO molecules are in upper vibrational states, giving a large population difference. As a result, IR absorbance is a sensitive method compared to NMR and microwave spectroscopy.

2. Calculate the ratio, N_1/N_o, of molecules in the J = 1 and J = 0 rotational levels for carbon monoxide, CO, at 25.0 °C. Assume a rigid rotor with $\tilde{B}_e = 1.932$ cm^{-1} [Hint: at 25.0 °C, kT = 207.2 cm^{-1}]

Answer: The plan is to use the Boltzmann distribution, taking into account the 2J + 1 degeneracy of the rotational states.
   The energy in wave numbers of a rigid rotor is $\tilde{F}_J = \tilde{B}_e[J(J + 1)]$. Since the J = 0 state of a rigid rotor is at zero in energy, $\Delta\varepsilon = \tilde{F}_1 - \tilde{F}_o = \tilde{B}_e[J(J + 1)]$, in wave numbers. The Boltzmann population ratio, Eq. 8.10.8, gives for any single rotational state with J = 1:

$$\frac{N_1}{N_o} = e^{-\Delta\varepsilon/kT} = e^{-2(1.932 \text{ cm}^{-1})/207.2 \text{ cm}^{-1}} = 0.9815 \qquad \text{for } m_J = -1, 0, \underline{\text{or}} +1$$

The degeneracy of the J = 1 level is $g_J = 2J + 1 = 3$, giving the final ratio as:

$$\frac{N_1}{N_o} = g_J\, e^{-\Delta\varepsilon/kT} = 3\, e^{-2(1.932 \text{ cm}^{-1})/207.2 \text{ cm}^{-1}} = 2.945$$

In other words, there are more CO molecules in the J = 1 level than the J = 0 level, because of the degeneracy. However, the probability of a radiative transition is proportional to the state to state population difference.

3. How does the Doppler width of a transition depend on temperature and the mass of the molecule?

Answer: As the temperature increases the root-mean-squared speed of gas molecules increases, thus increasing Doppler broadening. As the mass of the molecule increases the root mean squared speed decreases, thus decreasing the Doppler broadening.

4. Calculate the Doppler line width of the 83305. cm^{-1} electronic transition of HF at 500.0 K. This temperature is on the order of the temperature in the ionosphere.

*Answer:* The plan is to refer to Example 27.2.1.
    The mass of HF is m = (20.00 g mol^{-1}/N$_A$)(1 kg/1000 g) = 3.321x10^{-26} kg:

$$\Delta\tilde{v}_D = 2\left(\frac{\tilde{v}_o}{c}\right)\sqrt{\frac{2kT \ln(2)}{m}} = 2\left(\frac{83305. \text{ cm}^{-1}}{2.998\text{x}10^8 \text{ m s}^{-1}}\right)\sqrt{\frac{2(1.381\text{x}10^{-23} \text{ J K}^{-1})(500.0 \text{ K}) \ln(2)}{3.321\text{x}10^{-26} \text{ kg}}}$$
$$= 0.298 \text{ cm}^{-1} = 8.94\text{x}10^9 \text{ s}^{-1} = 8.94 \text{ GHz}$$

See example 27.2.1 for a note about the proper units of the speed of light. The broadening is much greater than some interesting interactions involving the nuclei and is also significant relative to rotational fine-structure spacing. Collisional broadening in the ionosphere is negligible, since the pressure is so low.

5. (a). Draw the Fourier transformed spectrum of the function f(t) in Figure 27.3.2 as a histogram, in the same style as the Fourier transforms shown in Figure 27.3.1b for the three Fourier coefficients. (b). The period of the function, L, is 1.00x10^{-3} s. Calculate the lowest frequency Fourier component.

Answer: (a). From Figure 27.3.2, the Fourier coefficients are large for 1 kHz and 2 KHz and zero for 3 kHz:
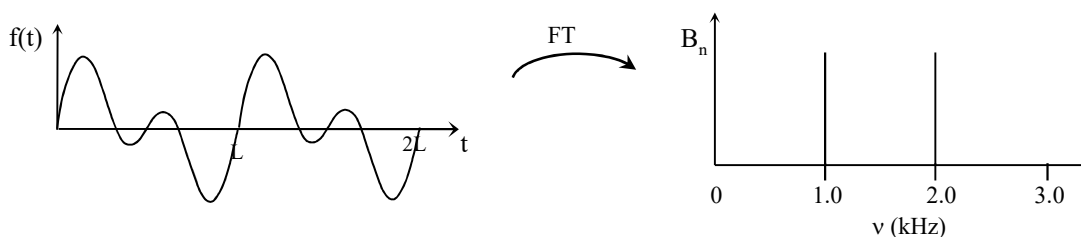
(b). The fundamental Fourier frequency is v_o = 1/L = 1/1.00x10^{-3} s = 1000 s^{-1} = 1.00 kHz. The Fourier components then occur at frequencies nv_o = 1 KHz, 2 kHz, 3 KHz, 4 kHz, ….

6. Many experiments give a time response that decays exponentially in time: $f(t) = e^{-t/\tau}$, where τ is the time constant for the decay. (a). Show that the Fourier transform, using Eq. 27.3.8, is:

$$g(v) = \frac{2\tau}{1 + i2\pi\tau v}$$

(b). The square of the magnitude of a complex function is given using Eq. 23.9.7. Show that:

$$g(v)^*g(v) = \frac{4\tau^2}{1 + 4\pi^2\tau^2 v^2}$$

(c). The result of experiments is often given as a magnitude spectrum, $A^2(v) = g(v)^*g(v)$. Do a quick plot of the magnitude spectrum assuming $\tau = 1$ s.

Answer: (a). The Fourier transform using Eq. 27.3.8 is:

$$g(v) = 2\int_0^\infty e^{-t/\tau}\, e^{-i2\pi vt}\, dt = 2\int_0^\infty e^{-(1/\tau + i2\pi v)t}\, dt = -2\left.\frac{e^{-(1/\tau + i2\pi v)t}}{1/\tau + i2\pi v}\right|_0^\infty$$

$$= -2\left[\frac{e^{-\infty}}{1/\tau + i2\pi v} - \frac{e^0}{1/\tau + i2\pi v}\right] = \frac{2}{1/\tau + i2\pi v} = \frac{2\tau}{1 + i2\pi\tau v}$$

(b). The squared magnitude is given by the complex conjugate multiplied by the original function:

$$A^2(v) = g(v)^*g(v) = \left(\frac{2\tau}{1 - i2\pi\tau v}\right)\left(\frac{2\tau}{1 + i2\pi\tau v}\right) = \frac{4\tau^2}{(1 - i2\pi\tau v)(1 + i2\pi\tau v)} = \frac{4\tau^2}{1 + 4\pi^2\tau^2 v^2}$$

(c). The spreadsheet and plot are given below. The value of $A^2(v)$ is given in cell D5 as:
"=4*\$D\$2/(4*PI()^2*C5^2*\$D\$2^2 +1)"

A1	B	C	D	E
2		tau =	1	s
3				
4		v (s^{-1})	A^2(ω)	
5		0	4.0000	
6		0.025	3.9037	
7		0.05	3.6407	
8		0.075	3.2731	
9		0.15	2.1183	
10		0.225	1.3340	
11		0.3	0.8785	
12		0.375	0.6105	
13		0.45	0.4447	
14		0.525	0.3367	
15		0.6	0.2629	
16		0.675	0.2107	
17		0.75	0.1724	
18		0.825	0.1435	
19		0.9	0.1213	
20		0.975	0.1038	
21		1.05	0.0898	
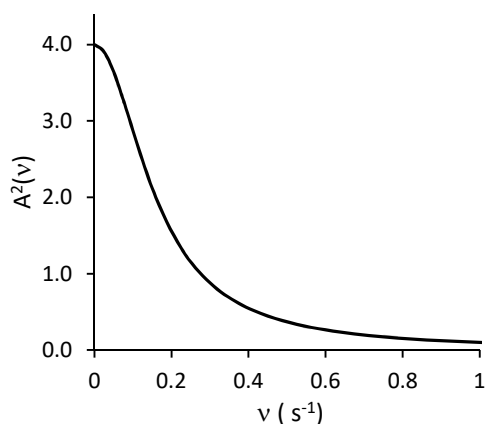
7. Which of the following molecules give pure-rotational absorption spectra? N_2, O_2, NO, CH, CO, CO_2, N_2O, SO_2, C_2H_4, CH_4, and $H_2C{=}O$ (formaldehyde).

Answer: The gross selection rule for rotational absorption is that the molecule must possess a permanent dipole moment. As a result only NO, CH, CO, N_2O, SO_2, and $H_2C{=}O$ are microwave active.

8. Which of the following molecules give vibrational absorption spectra? N_2, O_2, NO, CH, CO, CO_2, N_2O, and SO_2.

Answer: The gross selection rule for vibrational absorption is that the molecule must give a changing dipole moment during the vibration. For the diatomics, only NO, CH, and CO are infrared active. The symmetric stretch of linear triatomics is IR forbidden, but the asymmetric stretch and bending modes are IR active, see Table 27.7.1. As a result, the asymmetric stretch and the two degenerate bending modes of CO_2 are IR active. All normal modes of bent triatomics are IR active; so SO_2 is IR active. All normal modes for asymmetric linear triatomics are IR active, so N_2O is IR active; the symmetric stretch, the asymmetric stretch, and bending modes all present an oscillating dipole moment.

9. Which of the following molecules give vibrational Raman spectra? N_2, O_2, NO, CH, CO, CO_2, N_2O, and SO_2.

Answer: The plan is to note the molecules that have a center of symmetry, that is have an inversion center. Molecules with a center of symmetry are centrosymmetric. The exclusion rule is then applied.

   The short answer is only the asymmetric stretch and the bending vibrations of CO_2 are Raman forbidden. All the other molecules and the symmetric stretch of CO_2 are Raman active.

   The molecules with a center of symmetry are N_2, O_2, and CO_2. No normal mode of a centrosymmetric molecule is both Raman and IR active. Since the homonuclear diatomics and the symmetric stretch of CO_2 are IR forbidden, the stretches must be Raman active.

   For the heteronuclear diatomics, the stretch is both Raman and IR active. Remember that the polarizability is a function of the volume of the molecule. As a result for the heteronuclear diatomics, the polarizability and dipole moment both change during the vibration. Therefore, NO, CH, and CO are Raman active.

   All normal modes for asymmetric linear triatomics and bent triatomics are Raman active, so N_2O and SO_2 are Raman active, see Table 27.7.1.

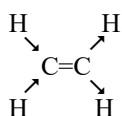10. Which of the following normal modes are infrared active and which are Raman active? The arrows indicate the movement of the exterior atoms. In the asymmetric stretches, the central atoms also move to maintain a fixed center of mass, but that movement is not shown. [Formal group theory is not required for this problem.]
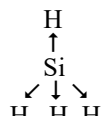
H←C≡C→H
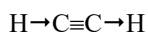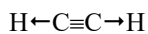
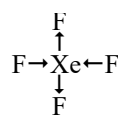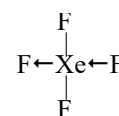H→C≡C→H
*acetylene*
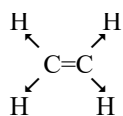
ethylene

ethylene

silane

XeF_4

XeF_4

Answer: The plan is to use the volume change during the vibration to judge the change in polarizability and the asymmetry of the vibration to judge the change in dipole moment. No normal mode of a centrosymmetric molecule is both Raman and IR active.

   None of the molecules has a permanent dipole moment. We need to look for a changing dipole moment during the vibration. Each molecule is centrosymmetric, so if the mode is IR active, then it must be Raman forbidden. For the totally symmetric stretches, all the exterior atom movements are outward, away from the center of mass. The symmetric stretches are all IR forbidden and Raman active, which includes the symmetric modes for acetylene, ethylene, and silane. The asymmetric stretches, where some exterior atoms move inward and some move outward, are all IR allowed and Raman forbidden, which include the asymmetric stretches for acetylene, ethylene, and the second mode for XeF_4. The symmetric stretches all change the volume of the molecule without a net shift of the electron density, relative to the center of mass.

   The difficult case is the first mode for XeF_4. The motion of the F-atoms is symmetrical with respect to the center of mass for the opposite pairs. The mode does not change the dipole moment, so the mode must be IR forbidden and correspondingly Raman active. The mode is symmetric, but not totally symmetric. The question remains as to whether the mode changes the volume of the molecule. Luckily the lack of a dipole moment and the center of symmetry give the Raman activity using the Exclusion Rule. In the table below, *IR* is for IR active and *R* is for Raman active.
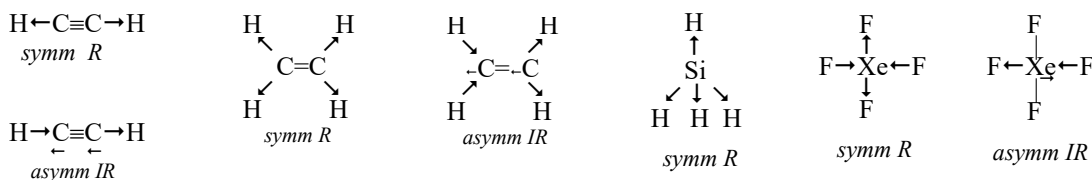
11. The lowest energy transitions in the rotational spectrum of HF are 41.105 and 82.211 cm^{-1}. Calculate the equilibrium bond length of HF, R_o.

Answer: The plan is to note that the spacing between adjacent lines in the rotational absorption spectrum of a diatomic molecule is $2\tilde{B}$, following Example 27.4.1.

   The spacing between rotational transitions for HF is 41.106 cm^{-1}. The rotational constant is $\tilde{B} =$ 41.106 cm^{-1}/2 = 20.553 cm^{-1}. The reduced mass for HF is:

$$\mu_{HF} = \frac{(1.007825)(18.998403)}{1.007825+18.998403} \text{ (g mol}^{-1}) \frac{1}{N_A} \text{ (1kg/1000 g)} = 1.589229\text{x}10^{-27} \text{ kg}$$

For units, the $\tilde{B}$ value can be converted to m^{-1} and then c = 2.99792x10^8 m s^{-1}:

$$\tilde{B} = 20.553 \text{ cm}^{-1} \text{ (100 cm/1 m)} = 2055.3 \text{ m}^{-1}$$

with Eq. 27.4.2: I = $\hbar/(4\pi\tilde{B}c)$ = 1.05457266x10^{-34} J s/[4π(2055.3 m^{-1})(2.997925x10^8 m s^{-1})]
                  = 1.3619$_8$x10^{-47} kg m^2

Alternatively, keeping $\tilde{B}$ in cm^{-1} and the speed of light in cm s^{-1} for the $\tilde{B}$c product:

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266 \times 10^{-34}$ J s/$[4\pi(20.553$ cm$^{-1})(2.997925 \times 10^{10}$ cm s$^{-1})]$
$\qquad\qquad\qquad = 1.36198 \times 10^{-47}$ kg m^2

with Eq. 27.4.2: $R_o = (I/\mu)^{\frac{1}{2}} = 9.2574 \times 10^{-11}$ m $= 0.9257$ Å

<u>12</u>. Two adjacent lines in the rotational absorption spectrum of $^{14}N^1H$ are at 98.036 and 130.714 cm^{-1}. Calculate the equilibrium bond length of HF, R_o, and the rotational quantum numbers of the lower states of the two transitions.

Answer: The plan is to note that the spacing between adjacent lines in the rotational absorption spectrum of a diatomic molecule is $2\tilde{B}$, with the transitions at $\Delta\tilde{F} = \tilde{F}_{J''+1} - \tilde{F}_{J''} = 2\tilde{B}(J''+ 1)$.
   The spacing between rotational transitions for $^{14}N^1H$ is 32.678 cm^{-1}. The rotational constant is $\tilde{B} = 32.678$ cm$^{-1}/2 = 16.339$ cm^{-1}. The reduced mass for $^{14}N^1H$ is:

$$\mu_{NH} = \frac{(1.007825)(14.003074)}{1.007825+14.003074} \text{ (g mol}^{-1}) \frac{1}{N_A} \text{ (1kg/1000 g)} = 1.561174 \times 10^{-27} \text{ kg}$$

For units, the $\tilde{B}$ value can be converted to m^{-1} and then c $= 2.99792 \times 10^8$ m s^{-1}:

$$\tilde{B} = 16.339 \text{ cm}^{-1} \text{ (100 cm/1 m)} = 1633.9 \text{ m}^{-1}$$

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266 \times 10^{-34}$ J s/$[4\pi(1633.9$ m$^{-1})(2.997925 \times 10^8$ m s$^{-1})]$
$\qquad\qquad\qquad = 1.71325 \times 10^{-47}$ kg m^2

Alternatively, keeping $\tilde{B}$ in cm^{-1} and the speed of light in cm s^{-1} for the $\tilde{B}$c product:

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266 \times 10^{-34}$ J s/$[4\pi(16.339$ cm$^{-1})(2.997925 \times 10^{10}$ cm s$^{-1})]$
$\qquad\qquad\qquad = 1.71325 \times 10^{-47}$ kg m^2

with Eq. 27.4.2: $R_o = (I/\mu)^{\frac{1}{2}} = 1.04757 \times 10^{-10}$ m $= 1.0476$ Å

Given Eq. 27.4.3 and the transitions at 98.036 and 130.714 cm^{-1}, the quantum numbers for the lower state, J", are:

$\qquad\quad \Delta\tilde{F} = 98.036$ cm$^{-1} = 2\tilde{B}(J''+ 1) = 2(16.339$ cm$^{-1})(J''+ 1)$ $\qquad$ giving J" $= 2$ i.e. $3\leftarrow2$
$\qquad\quad$ and $\quad 130.714$ cm$^{-1} = 2\tilde{B}(J''+ 1)$ $\qquad\qquad\qquad\qquad\qquad$ giving J" $= 3$ i.e. $4\leftarrow3$

<u>13</u>. Calculate the moment of inertia of water about the z-axis, which is the figure axis. The rotational constant about the z-axis is $\tilde{A} = 14.512$ cm^{-1}. Assume the bond angle is 104.48°.[1] Calculate the O–H bond length.

Answer: The plan is to follow Figure 27.4.2 and Example 27.4.2.
   The geometry is illustrated below with the water molecule in the x-z plane.

Reference to figure, above, shows that $x_2 = -x_3 = R_{OH} \sin(\theta/2)$, where θ is the H-O-H bond angle and R_{OH} is the O–H bond length. The O-atom does not contribute to the moment of inertia about the z-axis, because it lies on the z-axis. Since all the y_i coordinates are zero, the moment of inertia of water about the z-axis is, as in Equation 27.4.25:

$$I_{zz} = \Sigma\, m_i(x_i^2 + y_i^2) = \Sigma\, m_i\, x_i^2 = 2\, m_H\, [R_{OH} \sin(\theta/2)]^2$$

The mass of the H-atom is 1.67353×10^{-27} kg. The moment of inertia is given by Eq. 27.4.2:

$$I_{zz} = \hbar/(4\pi\tilde{A}c) = 1.05457266 \times 10^{-34} \text{ J s}/[4\pi(9.285 \text{ cm}^{-1})(2.997925 \times 10^{10} \text{ cm s}^{-1})]$$
$$I_{zz} = 1.9289 \times 10^{-47} \text{ kg m}^2 = 2\, m_H\, [R_{OH} \sin(104.48/2)]^2$$
$$= 2(1.67353 \times 10^{-27} \text{ kg})[R_{OH}\, (0.79058)]^2$$

Solving for the bond angle gives $R_{OH} = 9.6024 \times 10^{-11}$ m or 0.96024 Å.

14. Use Eqs. 27.4.11 to calculate the three moments of inertia of H_2O. Use units of g mol^{-1} for the masses and Å for the distances. The coordinates of water, aligned with the O-atom at the origin and one O–H bond extending along the x-axis, are:

Atom	x	y	z
O	0	0	0
H	0.9728	0	0
H	-0.2623	-0.9369	0

The coordinates of the center of mass are:

$$x_{cm} = {}^1\!/_m\, \Sigma\, m_i x_i \qquad\qquad y_{cm} = {}^1\!/_m\, \Sigma\, m_i y_i \qquad\qquad z_{cm} = {}^1\!/_m\, \Sigma\, m_i z_i$$

where m_i is the isotope specific mass of atom-i, with coordinates x_i, y_i, z_i, and total molecular mass $m = \Sigma\, m_i$. First, build a spreadsheet to calculate the moment of inertia matrix with the input orientation.[2] Second, the eigenvalues of this matrix are the three moments of inertia. To calculate the eigenvalues use MatLab, Maple, Mathematica, or the "Eigen" matrix diagonalization applet that is on the textbook Web site or on the companion CD. [Hint: The example spreadsheet shown below uses the same geometry for water as given above, but the orientation is chosen as already aligned with the principal axes. For this aligned example, the off-diagonal elements of the moment of inertia matrix should be zero, within round-off error. You should use these values to test your spreadsheet. Your final eigenvalues, starting from the orientation listed above, should give the same results; the final moments of inertia should not depend on the input orientation. The spreadsheet was designed to make the addition of atoms easy for larger molecules.]

A1	B	C	D	E	F	G	H	I
2								
3		*original data:*						
4	atom	mass	x	y	z	mx	my	mz
5	O	15.9949	0	-0.0657	0	0	-1.050865	0
6	H	1.0078	0	0.5222	0.775	0	0.5262732	0.781045
7	H	1.0078	0	0.5222	-0.7752	0	0.5262732	-0.78125
8	sums	18.0105				0	0.0016814	-0.0002
9	com		0	9.33561E-05	-1.11912E-05			
10								
11			$m(x-x_{cm})(y-y_{cm})$	$m(x-x_{cm})(z-z_{cm})$	$m(y-y_{cm})(z-z_{cm})$	$m(x-x_{cm})^2$	$m(y-y_{cm})^2$	$m(z-z_{cm})^2$
12	O	15.9949	0	0	-1.17772E-05	0	0.0692382	2E-09
13	H	1.0078	0	0	0.407794672	0	0.2747216	0.605327
14	H	1.0078	0	0	-0.407888131	0	0.2747216	0.605605
15	sums		0	0	-0.000105236	0	0.6186814	1.210932
16		*Results:*						
17	I =	x	y	z				
18	x	1.82961						
19	y	0	1.210932206					
20	z	0	0.000105236	0.618681357				

The input atomic coordinates are placed in cells D5:F7. The calculated center of mass coordinates, "com", are listed in cells D9:F9, which are then used to form the sums for Eqs. 27.4.11. The resulting moment of inertia matrix is listed in cells C18:E20. The moment of inertia matrix is symmetric, so that only the lower triangular matrix need be listed. In the general case, the moment of inertia matrix will not be a diagonal matrix. The final moment of inertia elements are then input into the "eigen" applet to determine the eigenvalues.

Answer: The spreadsheet with the new orientation is shown below.

A1	B	C	D	E	F	G	H	I
2								
3		*original data:*						
4	atom	mass	x	y	z	mx	my	mz
5	O	15.9949	0	0	0	0	0	0
6	H	1.0078	0.9728	0	0	0.9803878	0	0
7	H	1.0078	-0.2623	-0.9369	0	-0.2643459	-0.944208	0
8	sums	18.0105				0.7160419	-0.944208	0
9	com		0.039756914	-0.052425409	0			
10								
11			$m(x-x_{cm})(y-y_{cm})$	$m(x-x_{cm})(z-z_{cm})$	$m(y-y_{cm})(z-z_{cm})$	$m(x-x_{cm})^2$	$m(y-y_{cm})^2$	$m(z-z_{cm})^2$
12	O	15.9949	-0.03333773	0	0	0.0252817	0.0439608	0
13	H	1.0078	0.049296703	0	0	0.8773598	0.0027699	0
14	H	1.0078	0.269245527	0	0	0.09195	0.7883972	0
15	sums		0.2852045	0	0	0.9945916	0.8351278	0
16		Results						
17	I =	x	y	z				
18	x	0.83513						
19	y	-0.2852	0.994591615					
20	z	0	0	1.82971944				

The input to the "eigen" matrix diagonalization applet appears as below:

0.83513

-0.2852   0.994592

0   0   1.829719

The output agrees with the moments of inertia given in the pre-aligned example and appears as:

```
Eigenvector 1: Eigenvalue=1.829719
0
0
1
-------------
Eigenvector 2: Eigenvalue=1.21095
-0.604517
0.796593
0
-------------
Eigenvector 3: Eigenvalue=0.618698
0.796593
0.604517
0
-------------
```

An on-line applet is available that automatically determines the moments of inertia, spectroscopic rotational constants, symmetry point group, and the contributions of rotation to the entropy and Gibbs energy of a molecule. The "ABC Rotational Constant Calculator" applet is available on the textbook Web site or on the companion CD. The pre-aligned orientation of H_2O is available through the applet as an example, in addition to other examples of larger molecules.

15. Calculate the bond force constant, k_s for $H^{35}Cl$. The fundamental vibration frequency is $\tilde{v}_e = 2990.9$ cm^{-1}.

Answer: The plan is to use Eq. 27.5.4 to calculate the bond force constant. Remember to use isotope specific masses to calculate the reduced mass.

The reduced mass for $H^{35}Cl$ is: $\mu = \left(\dfrac{\mathfrak{M}_1 \mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\dfrac{1}{N_A}$ (1 kg/1000 g)

$\mu = \left(\dfrac{(1.007825)(34.968853)}{(1.007825 + 34.968853)}\right)(\text{g mol}^{-1})\dfrac{1}{6.022137\text{x}10^{23}}$ (1 kg/1000 g)

$= 1.6266526\text{x}10^{-27}$ kg

The bond force constant is given by rearranging Eq. 24.2.1:

$k = 4\pi^2\tilde{v}_e^2c^2\mu = 4\pi^2(2990.9 \text{ cm}^{-1})^2(2.997925\text{x}10^{10} \text{ cm s}^{-1})^2(1.62665\text{x}10^{-27} \text{ kg}) = 516.30$ N m^{-1}

16. Does CH or CO have the greater bond strength? Base your answer on the fundamental vibration frequency for ^{12}CH, which is $\tilde{v}_e = 2860.75$ cm^{-1}, and for $^{12}C^{16}O$, which is 2169.76 cm^{-1}, Table 27.6.1.

Answer: The plan is to calculate the bonds force constants and then compare. Fundamental vibration frequencies cannot be compared directly, especially when the reduced masses are so different.

For ^{12}CH, the reduced mass is: $\mu = \left(\dfrac{\mathfrak{M}_1 \mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\dfrac{1}{N_A}$ (1 kg/1000 g)

$$\mu = \left(\frac{(1.007825)(12.00000)}{(1.007825 + 12.00000)}\right)(g\ mol^{-1})\frac{1}{6.022137\times10^{23}}(1\ kg/1000\ g)$$
$$= 1.5438711\times10^{-27}\ kg$$

The bond force constant for CH is given by rearranging Eq. 24.2.1:

$$k = 4\pi^2\tilde{v}_e^2 c^2\mu = 4\pi^2(2860.75\ cm^{-1})^2(2.997925\times10^{10}\ cm\ s^{-1})^2(1.5438711^{-27}\ kg) = 448.30\ N\ m^{-1}$$

For $^{12}C^{16}O$, the reduced mass is:

$$\mu = \left(\frac{(12.000000)(15.994915)}{(12.000000 + 15.994915)}\right)(g\ mol^{-1})\frac{1}{6.022137\times10^{23}}(1\ kg/1000\ g)$$
$$= 1.138500\times10^{-27}\ kg$$

The bond force constant for CO is:

$$k = 4\pi^2\tilde{v}_e^2 c^2\mu = 4\pi^2(2169.76\ cm^{-1})^2(2.997925\times10^{10}\ cm\ s^{-1})^2(1.138500\times10^{-27}\ kg) = 1901.8\ N\ m^{-1}$$

The larger force constant corresponds to the stronger bond. Even though CH has a higher vibration frequency, CO has a stronger bond. The reversal in order results because the reduced mass of the CH bond is small, which in $g\ mol^{-1}$ is:

for C–H $\quad\mu = 0.9297\ g\ mol^{-1}$ versus for C≡O $\quad\mu = 6.856\ g\ mol^{-1}$

This result is expected since the qualitative bond order in C–H is one and the qualitative bond order in C≡O is three. The molecular orbital filling for CH is given by Figure 26.3.4 with three valence electrons. The correlation of bond strength with force constant is displayed in Figure 26.4.12.

17. The force constant is defined as the second derivative of the vibrational potential function, Eq. 8.11.2. For a non-harmonic potential, such as the Morse potential in Eq. 27.5.8, we must add the stipulation that the second derivative is evaluated at the equilibrium internuclear distance:

$$\left(\frac{d^2V}{dR^2}\right)_{R = R_e} \equiv k$$

Derive the relationship that determines the Morse a-parameter, Eq. 27.5.8, using the following steps: (a). Show that the second derivative of the Morse potential function, Eq. 27.5.7, is:

$$\frac{d^2V}{dR^2} = -2a^2D_e e^{-a(R - Re)} + 4a^2D_e\ e^{-2a(R - Re)}$$

(b). Evaluate the second derivative at the equilibrium internuclear distance, $R = R_e$, and use the definition of the force constant to give:

$$a = \left(\frac{k}{2\ D_e}\right)^{1/2}$$

(c). Use the relationship between the fundamental vibration frequency and the force constant, $\omega_e = 2\pi v_e = \sqrt{k/\mu}$, to give Eq. 27.5.8.

Answer: The Morse potential is given by Eq. 27.5.7: $V(R) = D_e (1 - e^{-a(R - Re)})^2$ with first derivative using the chain rule twice:

$$\frac{dV}{dR} = D_e\, 2(1 - e^{-a(R-Re)})\,(-e^{-a(R-Re)})(-a) = -2aD_e(-e^{-a(R-Re)} + e^{-2a(R-Re)})$$

The second derivative is: $\dfrac{d^2V}{dR^2} = -2aD_e[-e^{-a(R-Re)}(-a) + e^{-2a(R-Re)}(-2a)]$

Gathering terms: $\dfrac{d^2V}{dR^2} = -2a^2D_e e^{-a(R-Re)} + 4a^2D_e\, e^{-2a(R-Re)}$

Evaluating the second derivative at the equilibrium internuclear separation, $R = R_e$, gives:

$$\frac{d^2V}{dR^2} = -2a^2D_e\, e^0 + 4a^2D_e\, e^0 = 2a^2D_e$$

Setting this result equal to the force constant gives $2a^2D_e = k$ and solving for a:

$$a = \left(\frac{k}{2\,D_e}\right)^{1/2}$$

(b). Using $\omega_e = \sqrt{k/\mu}$ gives the force constant as $k = \omega_e^2\,\mu$, which upon substitution into the previous result gives Eq. Eq. 27.5.8.

<u>18</u>. The bond strength parameters for NF are important in validating bond order-bond strength correlations as displayed in Figure 26.4.12. However, the literature bond dissociation energy for NF varies widely depending on the experimental method used. The bond energy from thermochemical measurements is 297 ± 42 kJ mol^{-1} or 3.08 ± 0.44 eV.[3] Determine $\tilde{\nu}_e$, the force constant, zero point energy, and bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for ^{14}NF based on the fundamental vibration frequency $\tilde{\nu}_o = 1123.4$ cm^{-1} and anharmonicity $\chi_e\tilde{\nu}_e = 9.0$ cm^{-1}. Report the bond dissociation energies in cm^{-1}, eV, and kJ mol^{-1}. Compare the spectroscopic bond dissociation energy, as D_o, with the thermochemical value. What effect does using the spectroscopic value have on the bond order-bond strength correlation in Figure 26.4.12?

Answer: The plan is to use Eqs. 27.5.4, 27.5.8, 27.5.11, 27.5.18, and 27.5.12 to "correct for anharmonicity."

For ^{14}NF, the reduced mass is: $\mu = \left(\dfrac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\dfrac{1}{N_A}\,(1\ \text{kg}/1000\ \text{g})$

$\mu = \left(\dfrac{(14.003074)(18.998403)}{(1.007825 + 12.00000)}\right)(\text{g mol}^{-1})\dfrac{1}{6.022137\text{x}10^{23}}\,(1\ \text{kg}/1000\ \text{g})$

$\quad = 1.338617\text{x}10^{-26}$ kg

Based on $\tilde{\nu}_o = 1123.4$ cm^{-1} and $\chi_e\tilde{\nu}_e = 9.0$ cm^{-1}

with Eq. 27.5.11: $\tilde{\nu}_e = \tilde{\nu}_o + 2\chi_e\tilde{\nu}_e = 1123.4$ cm^{-1} + 2(9.0) cm^{-1} = 1141.4 cm^{-1}

with Eq. 27.5.4: $k = 4\pi^2 c^2\tilde{\nu}_e^2\mu = 4\pi^2(2.99792\text{x}10^{10}$ cm s$^{-1})^2(1141.4$ cm$^{-1})^2(1.62668\text{x}10^{-27}$ kg)

$\qquad\qquad\quad k = 618.7$ N m^{-1}

with Eq. 27.5.8: ZPE $= \tilde{G}_o = \tfrac{1}{2}\,\tilde{\nu}_e - \tfrac{1}{4}\,\tilde{\nu}_e\,\chi_e = \tfrac{1}{2}(1141.4$ cm$^{-1}) - \tfrac{1}{4}(9.0$ cm$^{-1}) = 568.44$ cm^{-1}

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (1141.4$ cm$^{-1})^2/(4(9.0$ cm$^{-1}))$

$\qquad\qquad\quad \tilde{D}_e = 36{,}187$ cm^{-1} = 4.49 eV = 433 kJ mol^{-1}

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - ZPE = 36{,}187$ cm^{-1} $- 568.44$ cm^{-1} $= 35618.$ cm^{-1}

$\tilde{D}_o = 4.42$ eV $= 426$ kJ mol^{-1} (spectroscopic)

The spectroscopic and thermochemical dissociation energies differ by 43%. The spectroscopic dissociation energy for NF is in better agreement than the thermochemical value with the dissociation energy for O_2 and falls closer to the extrapolated curve on the plot in Figure 26.4.12.

<u>19</u>. Bond order-bond strength correlations as displayed in Figure 26.4.12 play an important role in understanding the chemical bond. Figure 26.4.12 is based on second period elements. Do the same quantitative correlations hold for third period elements? Consider NCl as an example. Determine $\tilde{\nu}_e$, the force constant, zero point energy, and bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for $^{14}N^{35}Cl$ based on the fundamental vibration frequency $\tilde{\nu}_o = 817.358$ cm^{-1} and anharmonicity $\chi_e\tilde{\nu}_e = 5.300$ cm^{-1}. Report the bond dissociation energies in cm^{-1}, eV, and kJ mol^{-1}. How well do the force constant and bond dissociation energy of NCl agree with the bond order-bond strength correlation in Figure 26.4.12?

Answer: The plan is to use Eqs. 27.5.4, 27.5.8, 27.5.11, 27.5.18, and 27.5.12 to "correct for anharmonicity."

For $^{14}N^{35}Cl$, the reduced mass is: $\mu = \left(\dfrac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\dfrac{1}{N_A}$ (1 kg/1000 g)

$\mu = \left(\dfrac{(14.003074)(34.968853)}{(1.007825 + 12.00000)}\right)$ (g mol^{-1}) $\dfrac{1}{6.022137\text{x}10^{23}}$ (1 kg/1000 g)

$= 1.660378\text{x}10^{-26}$ kg

Based on $\tilde{\nu}_o = 817.358$ cm^{-1} and $\chi_e\tilde{\nu}_e = 5.300$ cm^{-1}

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 817.358$ cm^{-1} $+ 2(5.300)$ cm^{-1} $= 827.958$ cm^{-1}

with Eq. 27.5.4: $k = 4\pi^2c^2\tilde{\nu}_e^2\mu = 4\pi^2(2.99792\text{x}10^{10}$ cm s$^{-1})^2(827.958$ cm$^{-1})^2(1.62668\text{x}10^{-27}$ kg$)$

$k = 403.85$ N m^{-1}

with Eq. 27.5.8: $ZPE = \tilde{G}_o = \frac{1}{2}\,\tilde{\nu}_e - \frac{1}{4}\,\tilde{\nu}_e\,\chi_e = \frac{1}{2}(827.958$ cm$^{-1}) - \frac{1}{4}(5.300$ cm$^{-1}) = 412.654$ cm^{-1}

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (827.958$ cm$^{-1})^2/(4(5.300$ cm$^{-1}))$

$\tilde{D}_e = 32340$ cm^{-1} $= 4.009$ eV $= 386.8$ kJ mol^{-1}

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - ZPE = 32340$ cm^{-1} $- 412.654$ cm^{-1} $= 31923.$ cm^{-1}

$\tilde{D}_o = 3.958$ eV $= 381.9$ kJ mol^{-1} (spectroscopic)

The often listed literature D_o value is the spectroscopic value. The dissociation energy of NCl is in good agreement with the extrapolated curve on the plot in Figure 26.4.12, assuming a doubly-bonded species. However, the NCl force constant, at 404 N m^{-1}, is closer to the force constant for singly-bonded F_2 at 450 N m^{-1} and B_2 at 350 N m^{-1}. Quantitatively, the correlation is poor based on the force constants. However, third period diatomics do show an excellent correlation with qualitative MO bond order, but with weaker bonds overall for a given bond order, compared to the second period diatomics.

20. Determine $\tilde{\nu}_e$, the force constant, anharmonicity, zero point energy, and the bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for H_2. The fundamental and overtones for H_2 are listed below.

υ	1	2	3	4	5	6	7	8
$\tilde{\nu}_{\upsilon\leftarrow 0}$ (cm^{-1})	4161.14	8087.11	11782.35	15250.36	18491.92	21505.65	24287.83	26830.97

Answer: The plan is to follow Example 27.5.1 by doing a Birge-Sponer plot, Eq.27.5.20, and using the relationship between the anharmonicity and the bond dissociation energy based on the Morse potential, Eq. 27.5.18.

A Birge-Sponer plot based on Eq. 27.5.20 is implemented in the following spreadsheet.

υ	$\tilde{\nu}_{\upsilon\leftarrow 0}$ (cm^{-1})	$\Delta\tilde{\nu}_\upsilon$ (cm^{-1})
1	4161.14	3925.97
2	8087.11	3695.24
3	11782.35	3468.01
4	15250.36	3241.56
5	18491.92	3013.73
6	21505.65	2782.18
7	24287.83	2543.14
8	26830.97	

slope	-229.603	4156.96	intercept
±	0.809909	3.622021	±
r^2	0.999938	4.285633	s(y)
F	80368.15	5	df
ss$_{reg}$	1476094	91.83325	ss$_{resid}$
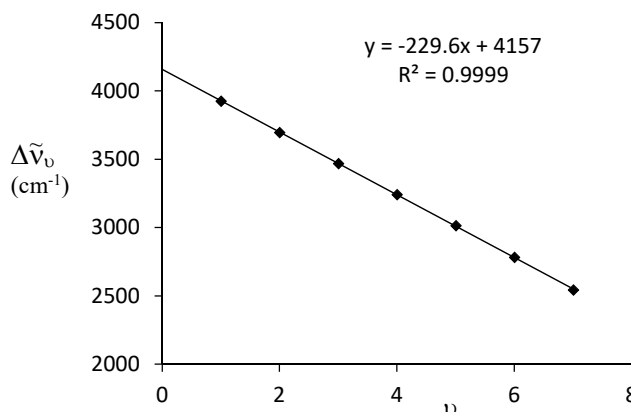
The curve fit gives the anharmonicity as $\chi_e\tilde{\nu}_e = 229.603/2 = 114.80 \pm 0.40$ cm^{-1}. The difference between the intercept and the experimental fundamental of 4161.14 cm^{-1} is caused by deviations from the Morse potential form and experimental error. The final spectroscopic constants are:

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 4161.14$ cm^{-1} + 2(114.80) cm^{-1} = 4390.74 cm^{-1}

with Eq. 27.5.4: $k = 4\pi^2 c^2 \tilde{\nu}_e^2 \mu = 4\pi^2(2.99792\times10^{10}$ cm s$^{-1})^2(4390.74$ cm$^{-1})^2(1.62668\times10^{-27}$ kg)
$k = 1113.$ N m^{-1}

with Eq. 27.5.8: ZPE $= \tilde{G}_o = \frac{1}{2}\tilde{\nu}_e - \frac{1}{4}\tilde{\nu}_e\chi_e = \frac{1}{2}(4390.74$ cm$^{-1}) - \frac{1}{4}(114.80$ cm$^{-1}) = 2166.7$ cm^{-1}

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (4390.74$ cm$^{-1})^2/(4(114.80$ cm$^{-1}))$

$\tilde{D}_e = 41{,}982$ cm^{-1} = 5.205 eV = 502.2 kJ mol^{-1}

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e -$ ZPE $= 41{,}982$ cm^{-1} $- 2166.7$ cm^{-1} = 39816. cm^{-1}

$\tilde{D}_o = 4.937$ eV = 476.3 kJ mol^{-1}

The literature values are $\tilde{\nu}_e = 4401.2$ cm^{-1}, $\chi_e\tilde{\nu}_e = 121.34$ cm^{-1} and $\tilde{D}_o = 4.4774 \pm 0.0004$ eV = 432.00 ± 0.04 kJ mol^{-1}, Table 27.6.1. The literature values include the second anharmonicity

correction giving greater accuracy. The need for accuracy in the bond dissociation energy of H_2 is nicely exemplified by Figure 26.2.2.

<u>21</u>. The fundamental and first two overtones in the vibrational spectrum of the OH radical are 3569.8, 6974.6, and 10217.8 cm^{-1}, respectively. Determine $\tilde{v}_e$, the force constant, anharmonicity, zero point energy, and the bond dissociation energies, $\tilde{D}_e$ and $\tilde{D}_o$.

Answer: The plan is to follow Example 27.5.1 by doing a Birge-Sponer plot, Eq.27.5.20, and using the relationship between the anharmonicity and the bond dissociation energy based on the Morse potential, Eq. 27.5.18.
  The successive differences between the transitions is plotted as a function of the overtone. The fundamental transition is included as the value for $\upsilon = 0$ in the following spreadsheet.

υ	$\tilde{v}_{\upsilon \leftarrow 0}$ (cm^{-1})	$\Delta\tilde{v}_{\upsilon}$ (cm^{-1})
0	3569.8	3569.8
1	6974.6	3404.8
2	10217.8	3243.2

slope	-163.30	3569.233	intercept
⬚	0.981495	1.267105	⬚
r2	0.999964	1.388044	s(y)
F	27681.89	1	df
SS$_{reg}$	53333.78	1.926667	SS$_{resid}$
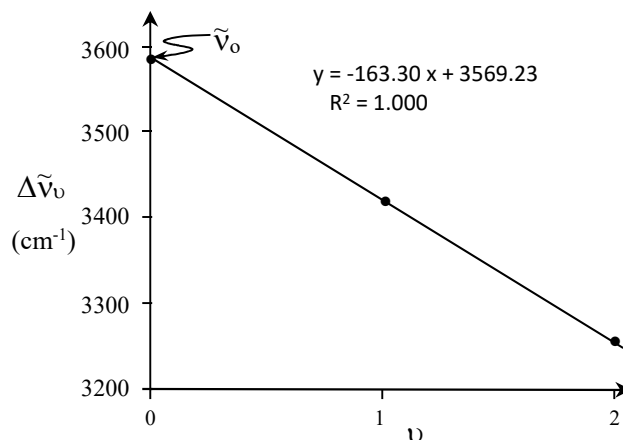
The curve fit gives the anharmonicity as $\chi_e\tilde{v}_e = 81.65 \pm 0.5$ cm^{-1}. The final spectroscopic constants are:

with Eq. 27.5.11: $\tilde{v}_e = v_o + 2\chi_e\tilde{v}_e = 3569.8$ cm^{-1} + 2(81.65) cm^{-1} = 3733.1 cm^{-1}

with Eq. 27.5.4: $k = 4\pi^2c^2\tilde{v}_e^2\mu = 4\pi^2(2.99792\times10^{10}$ cm s$^{-1})^2(3733.1$ cm$^{-1})^2(1.62668\times10^{-27}$ kg)
            $k = 804.3$ N m^{-1}

with Eq. 27.5.8: ZPE = $\tilde{G}_o$ = ½ $\tilde{v}_e$ – ¼ $\tilde{v}_e\chi_e$ = ½(3733.1 cm^{-1}) – ¼(81.65 cm^{-1}) = 1846.14 cm^{-1}

with Eq. 27.5.18: $\tilde{D}_e = \tilde{v}_e^2/4\chi_e\tilde{v}_e$ = (3733.1 cm$^{-1})^2$/(4(81.65 cm^{-1}))

            $\tilde{D}_e = 42,670$ cm^{-1} = 5.29 eV = 510.4 kJ mol^{-1}

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e$ – ZPE = 42,670 cm^{-1} – 1846.14 cm^{-1} = 40824. cm^{-1}

            $\tilde{D}_o = 5.06$ eV = 488.4 kJ mol^{-1}

The literature values are $\tilde{v}_e = 3737.76$ cm^{-1}, $\chi_e\tilde{v}_e = 84.88$ cm^{-1} and $\tilde{D}_o = 4.40$ eV = 424. kJ mol^{-1}, Table 27.6.1. The literature values include the second anharmonicity correction giving greater accuracy and averaging with thermochemically derived values.

22. Calculate the Morse a-parameter for the diatomic molecule Na_2. The fundamental vibration frequency is $\tilde{\nu}_e = 159.13$ cm^{-1} and the dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 5886.54$ cm^{-1}. The most useful final units for a are Å^{-1}. [Hint: the units of $(\mu/(2D_e))^{1/2}$ are (s m^{-1}), so you will need to convert to Å^{-1} using 1 Å $= 1\times10^{-10}$ m. Typical values of a are in the range of ~ 0.5-3 Å^{-1}.]

Answer: The plan is to convert $\tilde{\nu}_e$ to the corresponding radial frequency and $\tilde{D}_e$ into joules.

In s^{-1}: $\omega_e = 2\pi\tilde{\nu}_e c = 2\pi(159.13$ cm$^{-1})(2.99792\times10^{10}$ cm s$^{-1}) = 2.99736\times10^{13}$ s^{-1}

The reduced mass is: $\mu = \left(\dfrac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\dfrac{1}{N_A}(1$ kg/1000 g)

$$= (22.98977 \text{ g mol}^{-1}/2)/6.022137\times10^{23}(1 \text{ kg}/1000 \text{ g}) = 1.908772\times10^{-26} \text{ kg}$$

The dissociation energy in joules is:

$$D_e = \tilde{D}_e \, hc = 5886.54 \text{ cm}^{-1}(6.626076\times10^{-34} \text{ J s})(2.997925\times10^{10} \text{ cm s}^{-1}) = 1.169330\times10^{-19} \text{ J}$$

Using Eq. 27.5.8, the Morse a-parameter is:

$$a = \omega_e\left(\frac{\mu}{2D_e}\right)^{1/2} = 2.99736\times10^{13} \text{ s}^{-1}\left(\frac{1.908772\times10^{-26} \text{ kg}}{2(1.169329\times10^{-19} \text{ J})}\right)^{1/2} = 8.56313\times10^9 \text{ m}^{-1}$$

$$= 8.56313\times10^9 \text{ m}^{-1}(1\times10^{-10} \text{ m}/1 \text{ Å}) = 0.856313 \text{ Å}^{-1}$$

A note about units: In the ratio $\mu/(2D_e)$, you can use the reduced mass in kg mol^{-1} and the dissociation in J mol^{-1}, since the per mol units cancel. Then the conversion factor 1 cm^{-1} = 11.962658 J mol^{-1} is handy. Once again:

$$a = 2\pi\tilde{\nu}_e c \left(\frac{\mu}{2D_e}\right)^{1/2}$$

$$= 2\pi(159.13 \text{ cm}^{-1})(2.99792\times10^{10} \text{ cm s}^{-1})\left[\frac{11.49489 \text{ g mol}^{-1}(1 \text{ kg}/1000 \text{ g})}{2(5886.54 \text{ cm}^{-1})(11.962658 \text{ J mol}^{-1})}\right]^{1/2}$$

$$= 8.56313\times10^9 \text{ m}^{-1}(1\times10^{-10} \text{ m}/1 \text{ Å}) = 0.856313 \text{ Å}^{-1}$$

23. Calculate the Morse a-parameter for $H^{35}Cl$ in Å^{-1}. The fundamental vibration frequency is $\tilde{\nu}_e = 2990.925$ cm^{-1} and the dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 37270.$ cm^{-1}. [Hint: The conversion 1 cm^{-1} = 11.96266 J mol^{-1} is handy. The units of $(\mu/(2D_e))^{1/2}$ are (s m^{-1}), so you will need to convert to Å^{-1} using 1 Å $= 1\times10^{-10}$ m. Typical values of a are in the range of ~ 0.5-3 Å^{-1}.]

Answer: The plan is to convert $\tilde{\nu}_e$ to the corresponding radial frequency and $\tilde{D}_e$ into J mol^{-1}. See the previous problem for comments on the units.

The reduced mass is:

$$\mu = \frac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2} = \frac{(1.007825)(34.968853)}{1.007825 + 34.968853} = 0.979593 \text{ g mol}^{-1}$$

Using Eq. 27.5.8 and $\omega_e = 2\pi\tilde{\nu}_e c$, the Morse a-parameter is:

$$a = 2\pi\tilde{\nu}_e c \left(\frac{\mu}{2D_e}\right)^{\frac{1}{2}}$$

$$= 2\pi(2990.925 \text{ cm}^{-1})(2.99792\text{x}10^{10} \text{ cm s}^{-1})\left[\frac{0.979593 \text{ g mol}^{-1}(1 \text{ kg}/1000 \text{ g})}{2(37270 \text{ cm}^{-1})(11.962658 \text{ J mol}^{-1})}\right]^{\frac{1}{2}}$$

$$= 1.867\text{x}10^{10} \text{ m}^{-1}(1\text{x}10^{-10} \text{ m}/1 \text{ Å}) = 1.867 \text{ Å}^{-1}$$

24. Plot the vibrational potential energy function for Na_2. Assume a Morse potential function. The dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 5886.54 \text{ cm}^{-1}$, the Morse a-parameter is $a = 0.8563 \text{ Å}^{-1}$, and the equilibrium bond length is $R_e = 3.079 \text{ Å}$. [See Problem 22 for the calculation of a.]

Answer: The plan is to write a spreadsheet based on Eqs. 27.5.7-27.5.8.

The Morse function in cell D11 is given as: "=D\$7*(1-EXP(-D\$8*(\$C11-D\$6)))^2".

A1	B	C	D	E
5	vibration freq.	n_e	159.1245	cm^{-1}
6	bond length	R_e	3.07887	Å
7	dissociation energy	D_e	5886.54	cm^{-1}
8	Morse a	a	0.8563	
10		R (Å)	V(R) cm^{-1}	
11		2	13581.22	
12		2.15	8694.26	
13		2.4	3658.84	
14		2.65	1159.12	
15		2.9	161.27	
16		3.15	20.55	
17		3.4	340.24	
18		3.65	880.69	
19		3.9	1501.03	
20		4.15	2121.75	
21		4.4	2701.01	
22		4.65	3219.58	
23		4.9	3671.42	
24		5.15	4057.81	
25		5.4	4383.85	
26		5.65	4656.24	
27		5.9	4882.13	
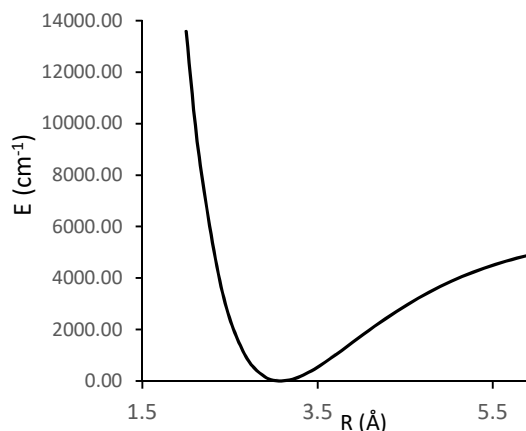
25. Plot the Morse and harmonic vibrational potential energy functions for $H^{35}Cl$. Assume the fundamental vibration frequency $\tilde{\nu}_e = 2990.9 \text{ cm}^{-1}$, dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 37270 \text{ cm}^{-1}$, the Morse a-parameter is $a = 1.867 \text{ Å}^{-1}$, and the equilibrium bond length is $R_e = 1.275 \text{ Å}$. [See Problem 23 for the calculation of a.]

Answer: The plan is to use Eq. 27.5.4 to calculate the bond force constant and then write a spreadsheet based on Eqs. 24.2.1 and 27.5.7-27.5.8.

The reduced mas for $H^{35}Cl$ is: $\mu = \left(\dfrac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\dfrac{1}{N_A}$ (1 kg/1000 g)

$$\mu = \left(\frac{(1.007825)(34.968853)}{(1.007825 + 34.968853)}\right)\frac{1}{6.022137\text{x}10^{23}}(1 \text{ kg}/1000 \text{ g}) = 1.6266526\text{x}10^{-27} \text{ kg}$$

The bond force constant is given by rearranging Eq. 24.2.1:

$$k = 4\pi^2\tilde{v}_e^2 c^2\mu = 4\pi^2(2990.9 \text{ cm}^{-1})^2(2.997925\text{x}10^{10} \text{ cm s}^{-1})^2(1.62665\text{x}10^{-27} \text{ kg}) = 516.30 \text{ N m}^{-1}$$

The cell D4 gives this calculation: "=4*PI()^2*D3^2*(2.99792E+10)^2*D2"

A1	B	C	D	E
2	reduced mass	μ	1.627E-27	kg
3	vibration freq.	v_e	2990.9	cm^{-1}
4	force constant	k	516.29563	N m^{-1}
5	bond length	R_e	1.275	Å
6	dissociation energy	D_e	37270	cm^{-1}
7	Morse a	a	1.867	Å^{-1}
8				
9		R (Å)	V(R) cm^{-1}	V(Harm)
10		0.8	75937.6	31031.7
11		0.95	25954.8	14527.3
12		1.1	5565.2	4212.1
13		1.25	85.1	86.0
14		1.4	1614.7	2149.0
15		1.55	6009.7	10401.2
16		1.7	11181.3	24842.6
17		1.85	16146.3	45473.1
18		2	20502.1	72292.7
19		2.15	24138.7	105301.5
20		2.3	27083.8	144499.5
21		2.45	29422.1	189886.6
22		2.6	31253.4	241462.9
23		2.75	32674.2	299228.3
24		2.9	33768.8	363182.8
25		3.05	34608.1	433326.5
26		3.2	35249.1	509659.4
27		3.35	35737.5	592181.4
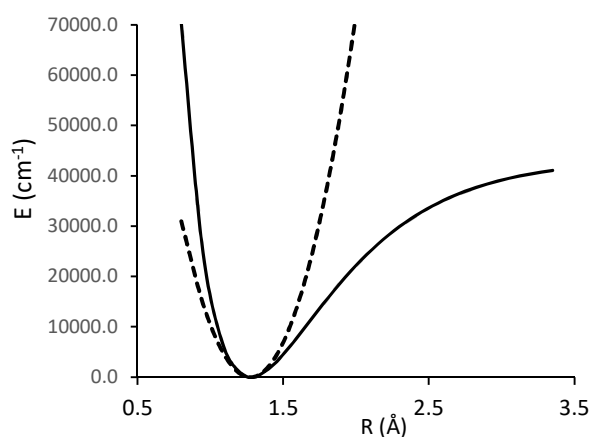
The Morse function in cell D10 is:

"=D$6*(1-EXP(-D$7*($C10-D$5)))^2".

The harmonic potential is $V(R) = \frac{1}{2} k(R - R_e)^2$, however to convert from joules to wave

numbers is given by $\tilde{V}(R) = V(R)/(hc)$ where R is in meters, as given in cell E10:

"=$D$4*((C10-$D$5)/1E10)^2/2/6.2608E-34/2.99792E10"

26. Plot the Morse potential energy function for ^{7}LiH. See Table 27.6.1 for the spectroscopic constants. Superimpose on the potential energy surface the 15 lowest vibrational energy levels, including the effects of anharmonicity. [Hints: See Problem 22 for hints on calculating the Morse a-parameter. A few rows of an example spreadsheet for Na$_2$ are given below. The calculation of the Morse potential, rows B and C, is independent of the calculation of the vibrational energy

levels, rows D and E. However, you can use the R values as a dummy variable to superimpose the vibrational energy levels on top of the potential energy curve. In other words, use columns B, C, and E to construct your scatter plot. Join the potential energy data points with a curve, but leave the vibrational levels as dots. The horizontal position of the vibrational level data points will be meaningless, but the vertical position gives the vibrational energies. You can draw in the horizontal lines representing the vibrational levels by hand.]

For Na₂: Na₂

A1	B	C	D	E
2	reduced mass	μ	11.495	g mol⁻¹
3	vibration freq.	νₑ	159.125	cm⁻¹
4	anharmonicity	νₑχₑ	0.725	cm⁻¹
5	bond length	Rₑ	3.079	Å
6	dissociation E	D₀	0.720	eV
7	dissociation E	Dₑ	5887	cm⁻¹
8	Morse *a*	*a*	0.856	Å⁻¹
9				
10	R (Å)	V(R) cm⁻¹	υ	G(υ) cm⁻¹
11	2.3	5293.9	0	79.4
12	2.5	2423.6	1	237.1
13	2.75	622.8	2	393.3
14	3	28.7	3	548.0
15	3.25	109.4	4	701.4
16	3.5	539.6	5	853.2
17	3.75	1124.8	6	1003.7
18	4	1752.3	7	1152.6
19	4.25	2360.0	8	1300.1
20	4.5	2916.4	9	1446.2
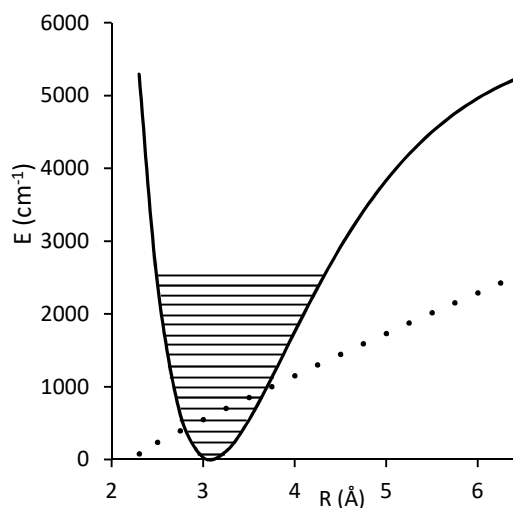
Answer: The plan is to use Eq. 27.5.8 to calculate the Morse *a*-parameter and then write a spreadsheet based on Eqs. 27.5.7 and 27.5.9. The units work out if the reduced mass is given in kg mol⁻¹ and the dissociation energy is converted to J mol⁻¹ using 1 cm⁻¹ = 11.9627 J mol⁻¹.

The reduced mas for ^{7}LiH is: $\mu = \left(\dfrac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right) = \left(\dfrac{(1.007825)(6.015122)}{(1.007825 + 6.015122)}\right) = 0.8632$ g mol⁻¹

Using constants from Table 27.6.1 the dissociation energy from the bottom of the potential energy well using Eq. 27.5.12 is:

$$\tilde{D}_e = \tilde{D}_o + \tfrac{1}{2}\,\tilde{\nu}_e - \tfrac{1}{4}\,\tilde{\nu}_e\,\chi_e$$
$$= 2.429 \text{ ev}(8065.5 \text{ cm}^{-1}/1 \text{ eV}) + \tfrac{1}{2}(1405.498 \text{ cm}^{-1}) - \tfrac{1}{4}(23.168 \text{ cm}^{-1}) = 20288. \text{ cm}^{-1}$$

Using the discussion in Problem 22, the Morse *a*-parameter is:

$$a = 2\pi\tilde{\nu}_e c\left(\dfrac{\mu}{2D_e}\right)^{1/2}$$

$$= 2\pi(1405.498 \text{ cm}^{-1})(2.99792 \times 10^{10} \text{ cm s}^{-1})\left[\dfrac{0.8632 \text{ g mol}^{-1}(1 \text{ kg}/1000 \text{ g})}{2(20288. \text{ cm}^{-1})(11.9627 \text{ J mol}^{-1})}\right]^{1/2}$$

$$= 8.56313 \times 10^9 \text{ m}^{-1}(1 \times 10^{-10} \text{ m}/1 \text{ Å}) = 1.116 \text{ Å}^{-1}$$

Spreadsheet cell D8 does this calculation for the *a*-parameter:

=2*PI()*D3*2.998E10*SQRT(D2/1000/2/(D7*11.9627))*1E-10

The spreadsheet to generate the potential energy surface and the vibrational energies and the corresponding plot are listed below. Cell C11 for the Morse function is:

=D$7*(1-EXP(-D$8*($B11-D$5)))^2

Cell E11 for the anharmonicity corrected vibrational energy levels is:

=$D$3*(D11+0.5)-$D$4*(D11+0.5)^2

A1	B	C	D	E
2	reduced mass	μ	0.863	g mol^{-1}
3	vibration freq.	ν_e	1405.498	cm^{-1}
4	anharmonicity	$\nu_e\chi_e$	23.168	cm^{-1}
5	bond length	R_e	1.596	Å
6	dissociation E	D_o	2.429	eV
7	dissociation E	D_e	20288	cm^{-1}
8	Morse a	a	1.116	Å^{-1}
9				
10	R (Å)	V(R) cm^{-1}	υ	G(υ) cm^{-1}
11	0.98	19826.5	0	697.0
12	1.25	4501.3	1	2056.1
13	1.5	258.0	2	3368.9
14	1.75	508.1	3	4635.4
15	2	2677.1	4	5855.6
16	2.25	5450.8	5	7029.4
17	2.5	8197.3	6	8156.9
18	2.75	10645.8	7	9238.0
19	3	12710.2	8	10272.8
20	3.25	14393.3	9	11261.3
21	3.5	15736.0	10	12203.5
22	3.75	16791.4	11	13099.3
23	4	17612.6	12	13948.7
24	4.25	18246.8	13	14751.9
25	4.5	18734.0	14	15508.6
26	4.75	19106.8	15	16219.1
27	5	19391.2	16	16883.2
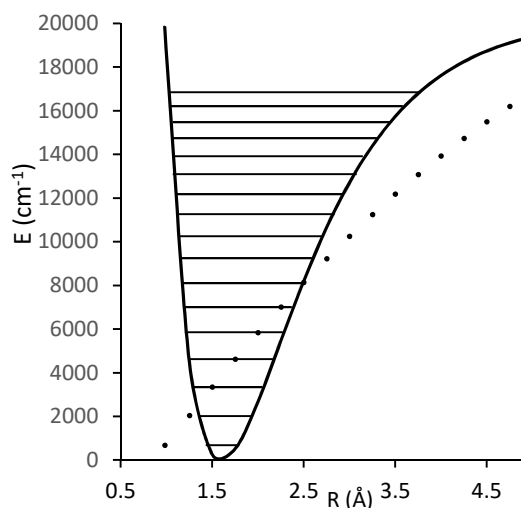
The conclusion is that the illustrations in text books usually overemphasize the effects of anharmonicity. There are typically many more vibrational levels before the dissociation limit than are often depicted, for example Figure 27.5.2.

27. The overtone wave numbers are given directly by Eq. 27.5.8 for the transition $\upsilon'\leftarrow 0$:

$$\tilde{\nu}_{\upsilon'\leftarrow 0} = \tilde{G}_{\upsilon'} - \tilde{G}_0 = \tilde{\nu}_e(\upsilon'+\tfrac{1}{2}) - \chi_e\tilde{\nu}_e(\upsilon'+\tfrac{1}{2})^2 - \tilde{\nu}_e(0+\tfrac{1}{2}) + \chi_e\tilde{\nu}_e(0+\tfrac{1}{2})^2$$

$$= \tilde{\nu}_e\upsilon' - \chi_e\tilde{\nu}_e(\upsilon'^2 + \upsilon' + \tfrac{1}{4}) + \tfrac{1}{4}\chi_e\tilde{\nu}_e$$

$$= -\chi_e\tilde{\nu}_e\,\upsilon'^2 + (\tilde{\nu}_e - \chi_e\tilde{\nu}_e)\upsilon' \qquad\qquad\qquad \text{(Morse, } \upsilon'\text{:upper)}$$

Rather than plotting adjacent differences in a Birge-Sponer plot, this last equation can be used in least squares curve fitting. The result is essentially equivalent, but the process and the associated uncertainties are more direct. Use the data in Example 27.5.1 and a quadratic fit to determine $\tilde{\nu}_e$ and $\chi_e\tilde{\nu}_e$ for H^{35}Cl. Compare to the results in the example.

Answer: The overtone data can be directly input into the "Nonlinear Least Squares Curve Fitting" applet on the textbook Web site or companion CD. The result using the fit function "ax^2 + bx + c" with c fixed at c = 0 is shown below:

```
==================== Results ========================
a= -51.568 +- 0.0528
b= 2937.055 +- 0.22
_____ Output Data _____
    x            y         y(fit)       residual
   1.0       2885.98   2885.48658      0.49342
   2.0       5667.98   5667.83714      0.14286
   3.0       8346.78    8347.05168    -0.27168
   4.0       10922.83  10923.13019    -0.30019
   5.0       13396.32  13396.07267     0.24733
-----------------------------------------------------------
sum of squared residuals= 0.489
stand. dev. y values= 0.4037
correlation between a & b= -0.9696
```

The fit anharmonicity, $\chi_e\tilde{\nu}_e = 51.568 \pm 0.053$ cm^{-1}, differs by 0.3% from the Birge-Sponer value in Example 27.5.1, which is certainly not significant. The fundamental vibration frequency is given by:

$$b = (\tilde{\nu}_e - \chi_e\tilde{\nu}_e)$$

or $\tilde{\nu}_e = b + \chi_e\tilde{\nu}_e = (2937.055 \pm 0.22) + (51.568 \pm 0.053)$ cm$^{-1} = 2988.62 \pm 0.23$ cm^{-1}

which also differs from the result in Example 27.5.1 by an insignificant amount. One advantage of this direct method is that we can see that the between-parameter correlation coefficient is unacceptably large at -0.9696. This warning suggests that the second anharmonicity correction needs to be taken into account for an accurate representation of the data. The same conclusion can be drawn by noticing that there is some systematic curvature in the final curve fit results, rather than a random scatter of points about the curve fit polynomial. The choice of using the Birge-Sponer method or the quadratic curve fit is a matter of preference.

28. Often only the fundamental and first overtone vibration frequencies are observable in infrared spectra. The experimental values for the fundamental and the first overtone are sufficient to obtain a rough estimate of the anharmonicity and the bond dissociation energy. We can use H^{35}Cl as a good test case. Determine $\tilde{\nu}_e$, the force constant, anharmonicity, zero point energy, and the bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for H^{35}Cl. The fundamental and first overtone for H^{35}Cl are 2885.98 and 5667.98 cm^{-1}.

Answer: The first-overtone adjacent difference is $\Delta\tilde{\nu}_1 = 2782.10$ cm^{-1}. Using just the fundamental and first overtone with Eq. 27.5.21 gives:

$$\chi_e\tilde{\nu}_e = (\tilde{\nu}_o - \Delta\tilde{\nu}_1)/2 = (2885.98 - 2782.10)/2 \text{ cm}^{-1} = 51.90 \text{ cm}^{-1}$$

The final spectroscopic constants are:

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 2885.98$ cm$^{-1} + 2(51.90)$ cm$^{-1} = 2989.78$ cm^{-1}

with Eq. 27.5.4: $k = 4\pi^2 c^2 \tilde{\nu}_e^2 \mu = 4\pi^2(2.99792\times10^{10} \text{ cm s}^{-1})^2(2989.78 \text{ cm}^{-1})^2(1.62668\times10^{-27} \text{ kg})$
$$k = 515.9 \text{ N m}^{-1}$$

with Eq. 27.5.8: $\text{ZPE} = \tilde{G}_o = \frac{1}{2}\tilde{\nu}_e - \frac{1}{4}\tilde{\nu}_e\chi_e = \frac{1}{2}(2989.78 \text{ cm}^{-1}) - \frac{1}{4}(51.90 \text{ cm}^{-1}) = 1481.92$ cm^{-1}

with Eq. 27.5.18: $\tilde{D}_e = \tilde{v}_e^2/4\chi_e\tilde{v}_e = (2989.78 \text{ cm}^{-1})^2/(4(51.90 \text{ cm}^{-1}))$

$\tilde{D}_e = 43{,}058 \text{ cm}^{-1} = 5.339 \text{ eV} = 515.1 \text{ kJ mol}^{-1}$

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - \text{ZPE} = 43{,}058 \text{ cm}^{-1} - 1481.92 \text{ cm}^{-1} = 41576. \text{ cm}^{-1}$

$\tilde{D}_o = 5.155 \text{ eV} = 497.3 \text{ kJ mol}^{-1}$

In this case the results are remarkably close to the Birge-Sponer extrapolated value in Example 27.5.1. In all honesty, the agreement with only a single observed overtone and more carefully obtained values is rarely so close. Factor of two errors can occur between values obtained using different extrapolation methods and between methods based on other experimental techniques (e.g. thermochemical values or values from mass spectrometry appearance potentials).

<u>29</u>. A schematic rotational-vibrational absorption spectrum of a diatomic molecule is shown below. The bond length is assumed to be the same in the two vibrational states. Sketch the resulting spectrum if, in the absence of any other changes, (a) the bond length of both vibrational states is increased, (b) the bond force constant is increased, (c) the temperature is increased, and (d) the bond length of just the upper vibrational state is increased.

$\leftarrow \tilde{v}$ (cm^{-1})
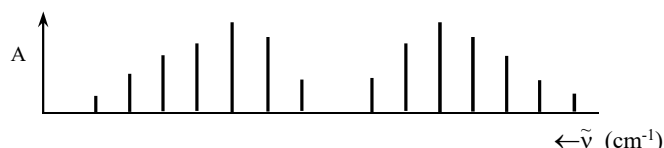
Answer: The plan is to note that the missing, forbidden transition is at $\tilde{v}_o = \frac{1}{2\pi}\sqrt{k/\mu}$ and the peak-to-peak spacing, assuming equal bond lengths in the two vibrational states, is $2\tilde{B}$.
(a). Increasing the bond length decreases the rotational constant $\tilde{B}$, moving the peaks closer together.
(b). Increasing the bond force constant increases the fundamental vibration frequency, $\tilde{v}_o$, which shifts all the transitions to higher frequency. Higher wave number, higher energy, higher frequency, and bluer are all towards the left.
(c). Increasing temperature has no effect on the spectroscopic constants. However, increasing temperature does increase the population of higher rotational states, Figure 27.6.7. As a consequence the rotational transition of maximum intensity is a higher J state.
(d). Increasing the bond length of just the upper vibrational state decreases the $\tilde{B}'$ value. With $\tilde{B}' < \tilde{B}''$, each line moves to lower wave number in proportion to the J''^2 value, Eqs. 27.6.8-27.6.9. In other words, lines further away from $\tilde{v}_o$ move more than lines closer to $\tilde{v}_o$. The R-branch lines get closer together and the P-branch lines get further apart.
The effects are diagrammed below.
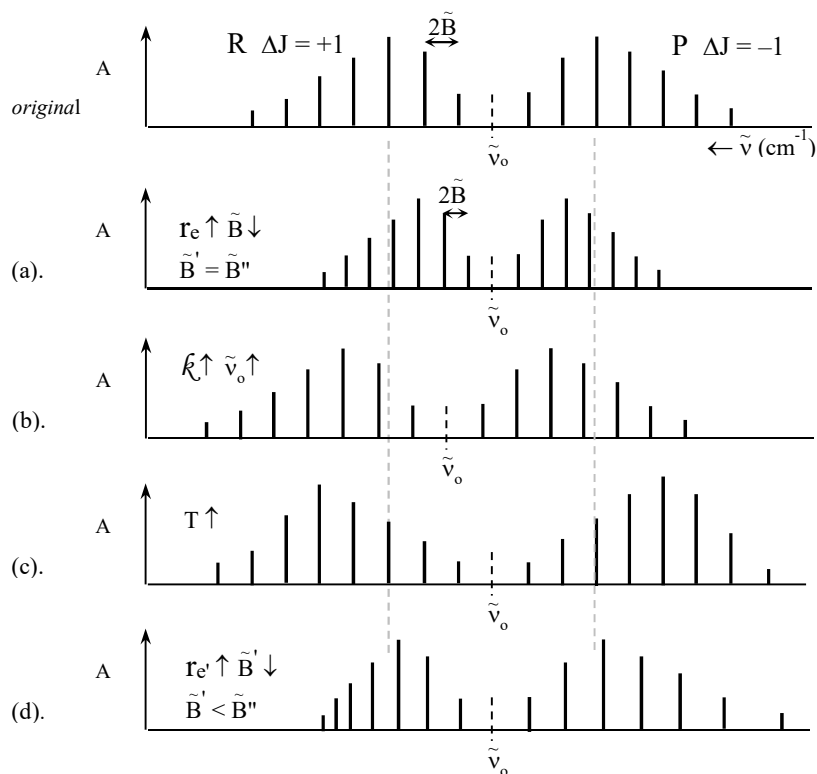
30. Write a spreadsheet to simulate the rotational-vibrational infrared spectrum of ^{12}CH for the $1 \leftarrow 0$ fundamental vibrational transition at 25°C. Use the spectroscopic constants in Table 27.6.1. Include six R-branch and six P-branch transitions. The relative intensity of the transitions is proportional to the Boltzmann weighting factors of the initial rotational levels for the $\upsilon = 0$ vibrational state: $p(J'') \propto (2J'' + 1)\, e^{-\tilde{B}'' J''(J''+1)/kT}$. To emphasize the differences caused by $\tilde{B}' < \tilde{B}''$, compare the appearance for α_e equal to zero, the literature value, and three times the literature value. [Hints: Display your results as an unconnected scatter plot of relative intensity, $p(J'')$, versus the transition wave number. You won't get a "stick" spectrum as in the previous problem, but you can draw lines by hand from each data point to the horizontal axis to sketch the spectrum. Remember that $kT = 207.2$ cm^{-1} at 25°C.]

Answer: The plan is to use Eqs. 27.5.12, 27.6.5, and 27.6.6 to calculate the wave number of each transition. The intensity is proportional to the Boltzmann probability of occupation of each of the ground vibrational state energy levels. The ground state of CH is a doublet, so spectra of CH include Q-branches, which we neglect in this problem.

Using Eq. 27.5.12, the center of the rotational-vibrational band, which is the observed fundamental vibration frequency, is at:

$$\tilde{v}_0 = \tilde{v}_e - 2\chi_e\tilde{v}_e = 2731.87 \text{ cm}^{-1}$$

The rotational constants for the $\upsilon'' = 0$ and $\upsilon' = 1$ states are calculated from α_e using Eq. 27.6.5. The spreadsheet is reproduced below.

A1	B	C	D	E	F
2					
3	ν_0	2731.87	cm⁻¹		
4	B_e	14.46	cm⁻¹		
5	α_e	0.536	cm⁻¹		
6	B"	14.192	cm⁻¹	υ=0	
7	B'	13.656	cm⁻¹	υ=1	
8					
9	J"	J'	F(J") cm⁻¹	ν cm⁻¹	p(J")
10	6	7	168.672	2900.542	0.732
11	5	6	147.792	2879.662	1.409
12	4	5	125.84	2857.71	2.287
13	3	4	102.816	2834.686	3.077
14	2	3	78.72	2810.59	3.315
15	1	2	53.552	2785.422	2.616
16	0	1	27.312	2759.182	1.000
17	1	0	-28.384	2703.486	2.616
18	2	1	-57.84	2674.03	3.315
19	3	2	-88.368	2643.502	3.077
20	4	3	-119.968	2611.902	2.287
21	5	4	-152.64	2579.23	1.409
22	6	5	-186.384	2545.486	0.732

With $\alpha_e = 0.536$ cm⁻¹:
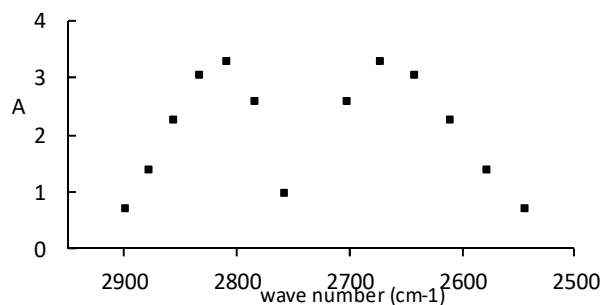
With $\alpha_e = 3(0.536$ cm⁻¹):
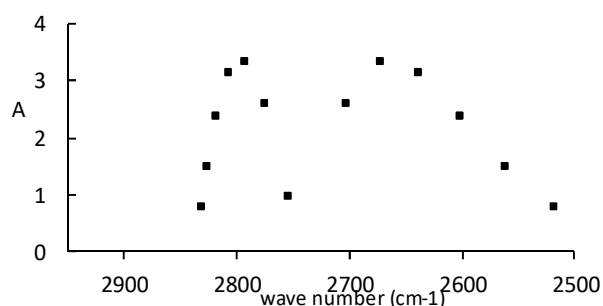
Cell C3 to calculate the observed fundamental frequency is: "=2860.75-2*64.44"

Cell C6 to calculate the rotational constant in the υ" = 0 vibrational state is: "=C4-C5/2"

Cell C7 to calculate the rotational constant in the υ' = 1 vibrational state is: "=C4-3*C5/2"

Cell D10 for the first rotational term value is: "=$C$7*(C10)*(C10+1)-$C$6*B10*(B10+1)"

Cell F10 to find the Boltzmann weighting factor for the J" state is:

$$=(2*B10+1)*EXP(-\$C\$6*B10*(B10+1)/207.2)$$

The first transition wave number in cell E10 just adds the observed fundamental vibration wave number to the rotational term value: "=$C$3+D10"

Note that $\tilde{B}' < \tilde{B}"$ as expected, since the vibration-averaged bond length increases with vibrational quantum number thus decreasing the corresponding rotational constant. The effect of $\tilde{B}' < \tilde{B}"$ is that all transitions move to smaller wave number, but the transitions for high J" shift more than low J" transitions. As a result the R-branch transitions are closer together and the P-branch transitions are further apart. Only when $\tilde{B}' = \tilde{B}"$ is the adjacent peak spacing $2\tilde{B}_0$.

31. The experimental fundamental vibration frequencies in infrared absorption for N_2O are 2224 cm⁻¹, 1285 cm⁻¹, and 588 cm⁻¹. Assuming N_2O is linear, determine if the bonding configuration is NNO or NON.

Answer: The plan is to use the three observed fundamentals and the expected number of IR active normal modes for a linear diatomic, symmetric or asymmetric, to determine the symmetry.

A linear triatomic has 3N – 5 = 3(3) – 5 = 4 normal modes. In order of expected decreasing wave number, the normal modes are an asymmetric stretch, a symmetric stretch, and a degenerate bend. For a symmetric linear triatomic, such as CO_2, the symmetric stretch is IR

forbidden, giving two distinct fundamental frequencies. For an asymmetric linear triatomic, such as H–C≡N, the symmetric stretch gives a changing dipole moment, resulting in three distinct fundamental frequencies. Since N_2O has three observed frequencies, the molecule must be asymmetric, arranged as NNO.

32. The experimental fundamental vibration frequencies in infrared absorption for BCl_3 are 985 cm^{-1}, 462 cm^{-1}, and 243 cm^{-1}. The experimental Raman frequencies are 985 cm^{-1}, 471 cm^{-1}, and 243 cm^{-1}. With reference to Table 27.7.1, determine if BCl_3 is planar or trigonal pyramidal. Assign the observed frequencies to the distinct frequencies, ν_1 - ν_4.[4,5]

Answer: The plan is to count the number of distinct vibration frequencies that are expected for the two different geometries, based on Table 27.7.1.

The asymmetric stretches and asymmetric bends are doubly degenerate in both planar and trigonal pyramidal XY_3 molecules. Doubly degenerate normal modes have the same vibration frequency. For a <u>planar</u> XY_3 molecule, there are three distinct IR vibration frequencies and three distinct Raman frequencies. For a <u>trigonal</u> pyramidal XY_3 molecule, all modes are IR and Raman active giving four distinct IR and four distinct Raman frequencies. Given the three observed IR and three observed Raman frequencies in BCl_3, the molecule must be planar.

We can take the analysis a step further to confirm our conclusion. Assuming the asymmetric stretches occur at higher wave number than the symmetric stretches and the asymmetric bends occur at higher wave number than the symmetric bends, using the IR and Raman activities listed in Table 27.7.1 gives the following schematic appearance in the spectra. The sticks are the predictions using symmetry arguments and the experimental wave numbers are then assigned to the expected pattern based on IR or Raman activity:

	IR				← $\tilde{\nu}$
mode	ν_3	ν_1	ν_4	ν_2	
mode	*asymm str*	*symm str*	*asymm bend*	*symm bend*	
exp.	985		462	243 cm^{-1}	

	Raman				← $\tilde{\nu}$
mode	ν_3	ν_1	ν_4	ν_2	
mode	*asymm str*	*symm str*	*asymm bend*	*symm bend*	
exp.	985	471	243		
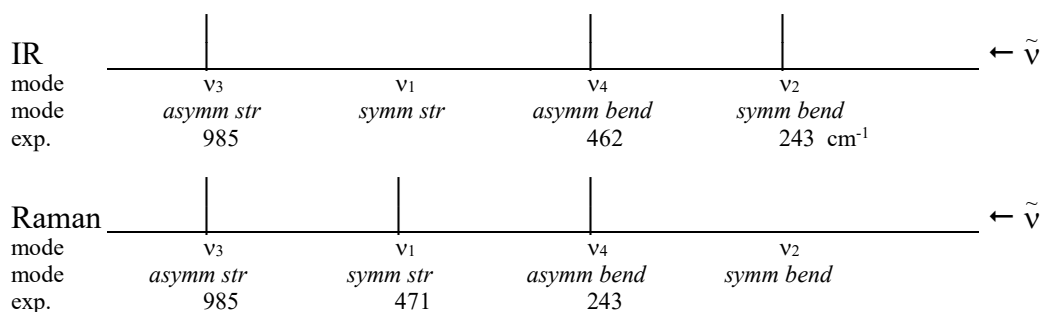
The two repeated transitions didn't match up as expected. However, the pattern of three present and one missing is apparent. Consider the following assignments, which give consistent results for the two repeated frequencies:

	IR				← $\tilde{\nu}$
mode	ν_3	ν_1	ν_2	ν_4	
mode	*asymm str*	*symm str*	*symm bend*	*asymm bend*	
exp.	985		462	243 cm^{-1}	

	Raman				← $\tilde{\nu}$
mode	ν_3	ν_1	ν_2	ν_4	
mode	*asymm str*	*symm str*	*symm bend*	*asymm bend*	
exp.	985	471		243	
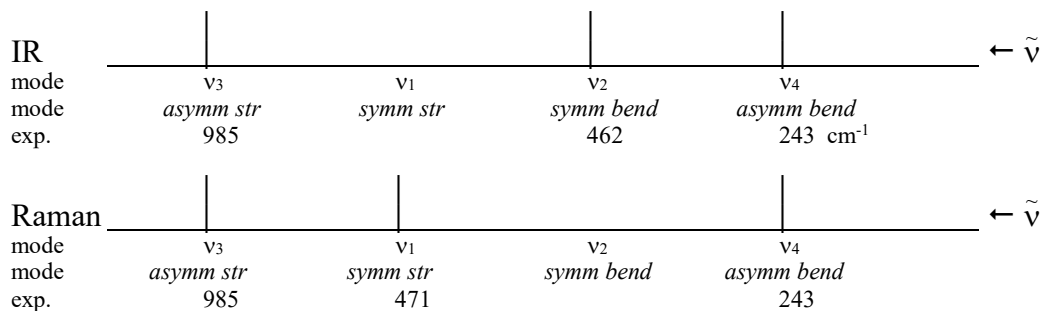
The similar wave number of the symmetric stretch and symmetric bend is surprising. Molecular orbital calculations at the Hartree-Fock and B3LYP levels with a 6-311+G(2d,p) basis set give ~11.5 cm^{-1} difference between these two modes. The difference at HF/6-31G* and HF/6-311G* is ~14 cm^{-1}. The agreement between theory and experiment helps to validate the assignment.

<u>33</u>. The carbonyl stretch for ketones is active in both IR and Raman spectroscopy. Assume a carbonyl stretch occurs at 1800. cm^{-1}. Calculate the wave lengths of the Stokes and anti-Stokes transitions in the Raman spectrum assuming laser excitation using a helium-neon laser at 632.8 nm.

Answer: The plan is to convert to wave numbers to find the transitions and then finally to convert back to wave lengths.

The laser excitation is at: $\tilde{\nu} = 1/\lambda = \dfrac{1}{632.8 \text{ nm } (1\text{x}10^{-9} \text{ m/1nm})(100 \text{ cm/1 m})} = 15803. \text{ cm}^{-1}$

The Stokes transition is at 15803. cm^{-1} – 1800. cm^{-1} = 14003 cm^{-1}
Converting to meters and then inverting gives the wave length of the transition:

$$\lambda = 1/\tilde{\nu} = \dfrac{1}{14003 \text{ cm}^{-1}(100 \text{ cm/1 m})} = 7.141\text{x}10^{-9} \text{ m} = 714.1 \text{ nm} \qquad \text{(Stokes)}$$

The anti-Stokes transition is at 15803. cm^{-1} + 1800. cm^{-1} = 17603 cm^{-1}
Converting to meters and then inverting gives the wave length of the transition:

$$\lambda = 1/\tilde{\nu} = \dfrac{1}{17603 \text{ cm}^{-1}(100 \text{ cm/1 m})} = 5.6808\text{x}10^{-9} \text{ m} = 568.1 \text{ nm} \qquad \text{(anti-Stokes)}$$

<u>34</u>. Name three advantages of Raman spectroscopy over infrared absorption. Name a disadvantage.

Answer: (1). Raman spectra occur in the near-infrared or visible region, depending on the laser used for excitation, which allows the use of glass or plastic cell windows. Raman spectra can be acquired through the containers of personal care products. Mid-infrared cell windows are usually hygroscopic and fragile. Expensive NaCl and KBr salt crystals are typically used for infrared cell windows. (2). Water is a poor Raman scatterer, so Raman spectra in aqueous solvents is common. Special techniques are required for aqueous infrared spectra, such as attenuated total reflection, ATR. (3). Raman is complementary to IR, which allows the determination of normal modes that are forbidden in the infrared. (4). Raman spectrometers can be easily configured as battery powered hand held devices. (5). Raman microscopes are more easily designed with higher spatial resolution than infrared microscopes, since the wave length for Raman scattering is bluer making the optics easier and giving a smaller diffraction limit.
    The main disadvantage of Raman is poor sensitivity compared to infrared absorption.

<u>35</u>. Identifying the point group of a molecule is done using Table 27.8.1 or using a flow chart such as Figure P27.1.

Start

Linear ? → Yes → $C_{\infty v}$ or $D_{\infty h}$

No

Find Principle Axis

None → C_s, C_i or C_1

More than one C_n with $n \geq 3$ → Cubic T, O, I

C_n is the principal axis*

n C_2 perpendicular to C_n ?

Yes → σ_h ? → Yes → D_{nh}

σ_h ? → No → n σ_d ? → No → D_n

n σ_d ? → Yes → D_{nd}

No → S_{2n} collinear with C_n ?

S_{2n} collinear with C_n ? → Yes → n σ_v ? → Yes** → D_{nd}

n σ_v ? → No → S_{2n}

S_{2n} collinear with C_n ? → No → σ_h ? → Yes → C_{nh}

σ_h ? → No → n σ_v ? → Yes → C_{nv}

n σ_v ? → No → C_n

i – inversion: C_i,
C_{nh} - n even,
D_{nh} - n even,
D_{nd} - n odd, $D_{\infty h}$,
S_6, some cubic groups

Figure P27. 1: Flow chart to identify the point group of a molecule. * If there are three mutually perpendicular axes, choose the principal axis perpendicular to the axis that passes through the most atoms or the heaviest atoms. ** There are n perpendicular C_2 axes, but they may not be obvious.[6]

Determine the point group for the following species: (a) SO_2; (b) CO_3^{2-}; (c) C_2H_4, ethylene; (d) *trans*-1,2-$C_2H_2Cl_2$, *trans*-1,2-dichloroethylene; (e) *cis*-1,2-$C_2H_2Cl_2$, *cis*-1,2-dichloroethylene; (f) ClF_3 (T-shaped); (g) NH_3; and (h) C_2H_6, staggered ethane.

Answers: The plan is to note that for nonlinear molecules the first step is to find the highest-fold rotational axis. If the highest-fold rotational axis is unique, then that axis is the principal axis, which gives the value of n, for example in C_{nv} or D_{nh}.

   In displaying the symmetry elements of molecules, several standard symbols are used. Reflection planes are depicted as dotted lines or shaded planes and rotational axes are depicted as listed below. Solid symbols depict C_n axes and hollow symbols are for S_n axes. For molecules with higher symmetry, finding all the symmetry elements is usually not necessary. Instead, the characteristic symmetry operations as listed in Table 27.8.1 are sufficient.
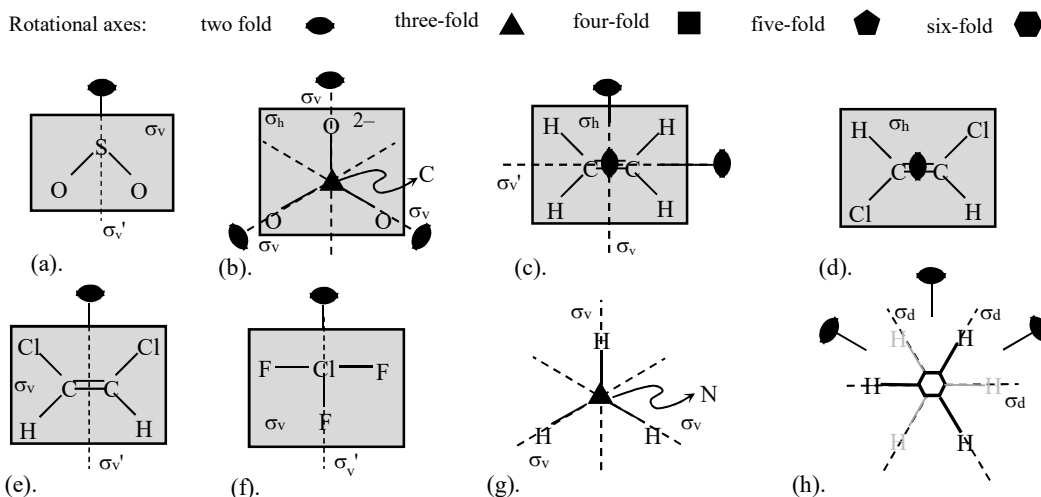
(a). SO_2 is bent: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n} [see Part (h) for an example], no σ_h (which would be perpendicular to the principal axis), but with two σ_v planes: giving C_{2v}.

(b). CO_3^{2-} is trigonal planar: The highest-fold axis is the C_3 axis perpendicular to the plane of the atoms, with three perpendicular C_2 axes, and a σ_h: giving D_{3h}. Note that atoms are not required to lie above and below the σ_h plane; all atoms can lie in the σ_h plane.

(c) C_2H_4, ethylene is planar: The highest-fold axis is a C_2 axis, with two perpendicular C_2 axes, and a σ_h: giving D_{2h}. Since there are three mutually perpendicular C_2 axes, the principal axis is chosen as the C_2 that is perpendicular to the C_2 axis that includes the C-atoms. However, there are two such C_2-axes; the C_2 that is perpendicular to the plane that contains the most atoms is chosen as the principal axis.

(d) *trans*-1,2-$C_2H_2Cl_2$ is planar: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n}, but with a σ_h: giving C_{2h}.

(e) *cis*-1,2-$C_2H_2Cl_2$ is planar: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n}, no σ_h, but with two σ_v planes: giving C_{2v}.

(f) ClF_3 is T-shaped: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n}, no σ_h, but with two σ_v planes: giving C_{2v}.

(g). NH_3 is trigonal pyramidal: The highest-fold axis is the C_3 axis, with no perpendicular C_2 axes, no S_{2n} , no σ_h, but with three σ_v planes: giving C_{3v}.

(h). Staggered C_2H_6 has two tetrahedral centers: The drawing, above, is a Newman projection looking down the C-C axis. A hand-held model is really useful for this discussion. The S_6

improper axis requires some explanation. Rotation about the C–C bond by $360/6 = 60°$ brings a H-atom on the front face of the molecule above a H-atom on the back face. These front-face and back-face atoms are related by a reflection across a plane perpendicular to the S_6 axis. Next considering the vertical planes, the vertical reflection planes bisect the C_2 axes, so they are officially σ_d-dihedral planes. Following the chart then, the highest-fold pure rotational axis is the C_3 axis, with three perpendicular C_2 axes, an S_6 improper axis, and three vertical σ_d-planes: giving D_{3d}. The perspective drawing, below, shows another view of the C_2-axes.
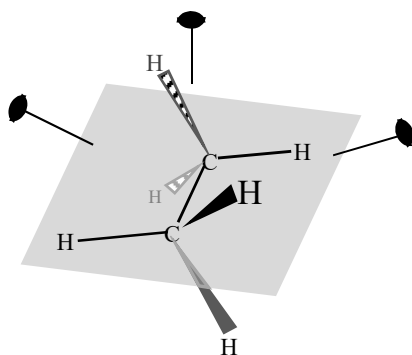
36. Determine the point group for the following species: (a) $PtCl_4^{2-}$ (square planar); (b) PF_5 (trigonal bipyramidal).

Answer: The plan is to follow Table 27.8.1 or the flow chart, Figure P27.1.
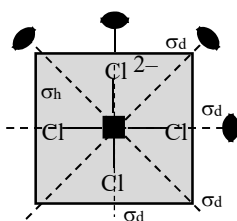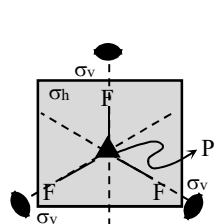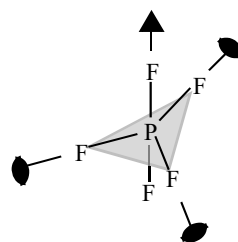
(a).   (b).   Projection on σ_h perspective drawing

(a). $PtCl_4^{2-}$: The highest-fold axis is the C_4 axis perpendicular to the plane of the atoms, with four perpendicular C_2 axes, and a σ_h-plane: giving D_{4h}.
(b) PF_5: The highest-fold axis is the C_3 axis perpendicular to the trigonal-plane of atoms, with three perpendicular C_2 axes, and a σ_h-plane: giving D_{4h}.

37. Determine the irreducible representations for the x, y, and z-components of the transition electric dipole moment in the point group whose character table is given below. The symmetry operations are three mutually perpendicular C_2-axes, which are aligned along the x, y, and z-axes.

	E	$C_2(z)$	$C_2(y)$	$C_2(z)$
A	1	1	1	1
B_1	1	1	-1	-1
B_2	1	-1	1	-1
B_3	1	-1	-1	1

Answer: The plan is to use atomic p_x, p_y, and p_z orbitals as a visual expedient for determining the symmetry relationships for the three C_2-rotations. The components of the transition dipole transform in the same ways as the corresponding atomic orbitals.

   The p_z, p_y, and p_x atomic orbitals are shown below aligned along the z, y, and x-axes, which correspond to the rotational axes in this point group. The identity operation, E, is included for completeness. If the orbital changes phase the "character under rotation" is listed as "–". For no change in phase the listing is "+".
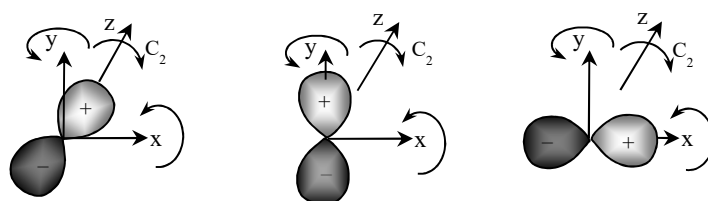
	p_z	p_y	p_x
E	+	+	+
$C_2(z)$	+	–	–
$C_2(y)$	–	+	–
$C_2(x)$	–	–	+
	B_1	B_2	B_3

Reading down the columns of the table reproduces the characters (read across) for the corresponding irreducible representation. The p_z-orbital and the z-component of the transition electric dipole moment transform as B_1. The p_y-orbital and the y-component of the transition electric dipole moment transform as B_2. The p_x-orbital and the x-component of the transition electric dipole moment transform as B_3. Any normal mode that transforms according to B_1, B_2, or B_3 is allowed in infrared absorption. As a check, notice that the given character table is for the D_2 point group, data section Table 27.8.2.

38. (a). Determine the symmetry species, which is the irreducible representation, of the following normal modes of ethylene, C_2H_4. (b). Determine the IR and Raman activity of each mode.

(a).	(b).	(c).	(d).
stretch	stretch	bend	twist
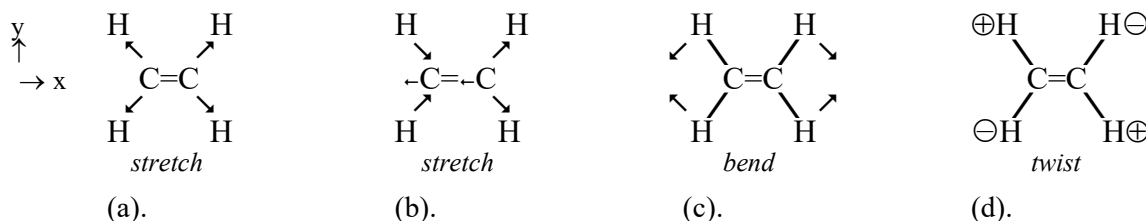
The transformation properties of out-of-plane motions might require some clarification. The progress of the $C_2(x)$ rotation, viewed from the top and along the C=C bond is shown below.

top view: *side view, along C=C:*

H⊖
/
=C   H▶C◀H → <image with C₂> → H▶○◀H   symmetric
\
H⊕

H⊕
/
=C   H▶C◀H → <image with C₂> → H▶○◀H   anti-symmetric
\
H⊕
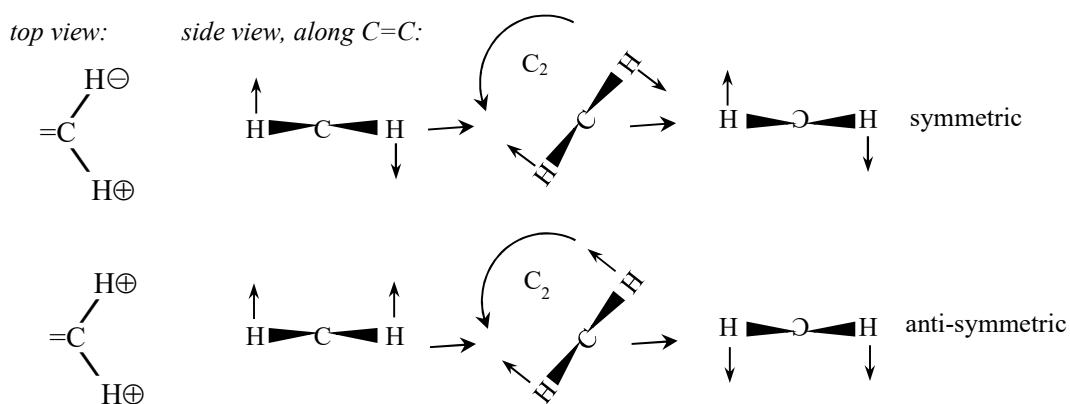
Answer: The plan is to determine the symmetric or anti-symmetric behavior of the normal modes under the symmetry operations of the point group for ethylene, D_{2h}. The D_{2h} character table is given below.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

The symmetry under the operations of the point group and the corresponding irreducible representations are:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_v(yz)$	χ	activity
(a)	1	1	1	1	1	1	1	1	a_g	R
(b)	1	-1	-1	1	-1	1	1	-1	b_{3u}	IR
(c)	1	1	1	1	1	1	1	1	a_g	R
(d)	1	1	1	1	-1	-1	-1	-1	a_u	

   The character table lists the IR active modes as transforming according to the B_{1u}, B_{2u}, and B_{3u} point groups. As a result only mode-b is IR allowed. The character table lists the Raman active modes as transforming according to the A_g, B_{1g}, B_{2g}, and B_{3g} point groups. As a result mode-a and mode-c are Raman allowed. The Exclusion Rule applies because the group includes the inversion operation; as a result no mode is active in both in IR absorption and Raman scattering. Note that mode-d is not active in either form of vibrational spectroscopy. However, this mode is observable in electronic absorption and emission, since there are no symmetry restrictions on vibrational modes in electronic spectroscopy.

39. (a). Use group theory to determine the symmetry species of the normal modes of H_2O, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. (b). Determine which irreducible

representations correspond to stretches and which to bending vibrations. (c). Determine the modes that are IR and Raman active.

Answer: The plan is to use the C_{2v} character table to decompose the reducible representation of the normal modes. We will find $3N - 6 = 3$ normal modes and expect two stretching vibrations, since there are two bonds.

   The geometry and character table for C_{2v} are shown below. The σ_v-plane is perpendicular to the plane of the paper; see also Figure 27.8.7. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x + \Gamma_y + \Gamma_z = A_1 + B_1 + B_2$, and the rotations, $\Gamma_{rot} = A_2 + B_1 + B_2$, are appended to the end of the character table.

C_{2v}	E	C_2	σ_v	$\sigma_v{}'$	h = 4	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	-1	-1	xy	R_z
B_1	1	-1	1	-1	y, yz	R_x
B_2	1	-1	-1	1	x, xz	R_y
Γ_{trans}	3	-1	1	1	$\Gamma_{trans} = A_1 + B_1 + B_2$	
Γ_{rot}	3	-1	-1	-1	$\Gamma_{rot} = A_2 + B_1 + B_2$	

(a). The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below.

C_{2v}	E	C_2	σ_v	$\sigma_v{}'$	Γ	a_i
station. atoms	3	1	1	3		
Γ_{trans}	3	-1	1	1	product	
Γ_{tot}	9	-1	1	3		
Γ_{trans}	3	-1	1	1	subtract	
Γ_{rot}	3	-1	-1	-1	subtract	
Γ_{vib}	3	1	1	3	$\Gamma_{tot} - \Gamma_{trans} - \Gamma_{rot}$	
A_1	1	1	1	1		$1/h(\Gamma_{vib} \cdot A_1) = 8/4 \rightarrow 2A_1$
A_2	1	1	-1	-1		$1/h(\Gamma_{vib} \cdot A_2) = 0$
B_1	1	-1	1	-1		$1/h(\Gamma_{vib} \cdot B_1) = 0$
B_2	1	-1	-1	1		$1/h(\Gamma_{vib} \cdot B_2) = 4/4 \rightarrow B_2$

For example, the decomposition for the A_1 irreducible representation is based on Eq. 27.8.2:

$$a_1 = {}^1/_h \sum_{j=1}^{4} \chi_j^{vib} \chi_{i,j}^{irr} C_{i,j}^{irr} = \frac{1}{4} [3(1)(1) + 1(1)(1) + 1(1)(1) + 3(1)(1)]$$

$$= 8/4 \qquad\qquad \text{giving that } A_1 \text{ appears twice in } \Gamma_{vib}$$

The decomposition for the A_2 irreducible representation is:

$$a_2 = \tfrac{1}{4}\,[3(1)(1) + 1(1)(1) + 1(-1)(1) + 3(1)(-1)]$$
$$= 0 \qquad \text{giving that } A_2 \text{ does not appear in } \Gamma_{vib}$$

The normal modes decompose as $\Gamma_{vib} = 2A_1 + B_2$, giving three modes with three distinct vibration frequencies (no degeneracies). All the normal modes are both IR and Raman active, which confirms Table 27.1.1. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.

(b). The molecule is redrawn with double-headed arrows replacing each bond. The number of <u>arrows</u> that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for H_2O is listed below.
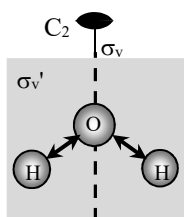
D_{3h}	E	C_2	σ_v	σ_v'	a_i
stationary arrows: Γ_{str}	2	0	0	2	
A_1	1	1	1	1	$1/h(\Gamma_{str}\!\cdot\!A_1) = 4/4 \to A_1$
A_2	1	1	-1	-1	$1/h(\Gamma_{str}\!\cdot\!A_2) = 0$
B_1	1	-1	1	-1	$1/h(\Gamma_{str}\!\cdot\!B_1) = 0$
B_2	1	-1	-1	1	$1/h(\Gamma_{str}\!\cdot\!B_2) = 4/4 \to B_2$

The decomposition for the A_1 irreducible representation is:

$$a_1 = \tfrac{1}{h}\sum_{j=1}^{4} \chi_j^{str}\chi_{i,j}^{irr}\,C_{i,j}^{irr} = \tfrac{1}{4}\,[2(1)(1) + 0(1)(1) + 0(1)(1) + 2(1)(1)]$$
$$= 4/4 \qquad \text{giving that } A_1 \text{ appears once in } \Gamma_{str}$$

The stretching normal modes are $\Gamma_{str} = A_1 + B_2$, giving two stretching modes with two distinct vibration frequencies. Since all the modes include $\Gamma_{vib} = 2A_1 + B_2$, the remaining is a bending mode of A_1 symmetry. These results agree with Figure 27.8.7.

(c). Referring to the C_{2v} character table, the x, y, and z-components of the transition dipole moment transform as B_2, B_1, and A_1, respectively. The quadratic products, such as z^2 and xy, cover all four irreducible representations, giving all the normal modes as possibly Raman active. As consequence, all the normal modes are both IR and Raman active, which confirms Table 27.1.1.

40. Use group theory to determine the symmetry species of the normal modes of BF_3, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. Determine which irreducible representations correspond to stretches and which to bending vibrations. [Hint: for determining the symmetry of a trigonal planar molecule, the S_3 improper rotations act just like C_3 proper rotations, since all atoms lie in the σ_h-plane.]

Answer: The plan is to use the D_{3h} character table to decompose the reducible representation of the normal modes. We will find $3N - 6 = 6$ normal and expect three stretching vibrations, since there are three bonds.

The geometry and character table for D_{3h} are shown below. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x + \Gamma_y + \Gamma_z = A_2'' + E'$, and the rotations, $\Gamma_{rot} = A_2' + E''$, are appended to the end of the character table.
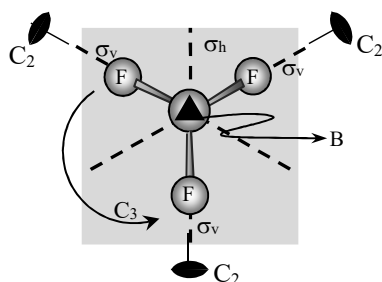
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	$h = 12$	
A_1'	1	1	1	1	1	1	x^2+y^2, z^2	
A_2'	1	1	-1	1	1	-1		R_z
E'	2	-1	0	2	-1	0	$(x, y),(xy, x^2-y^2)$	
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(xz, yz)	(R_x,R_y)
Γ_{trans}	3	0	-1	1	-2	1	$\Gamma_{trans} = A_2''+E'$	
Γ_{rot}	3	0	-1	-1	2	-1	$\Gamma_{rot} = A_2'+E''$	

The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below. Note that once you reach six total modes, you can stop. So the decomposition for E" is not necessary, but we included it for practice.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Γ	a_i
station. atoms	4	1	2	4	1	2		
Γ_{trans}	3	0	-1	1	-2	1	product	
Γ_{tot}	12	0	-2	4	-2	2		
Γ_{trans}	3	0	-1	1	-2	1	subtract	
Γ_{rot}	3	0	-1	-1	2	-1	subtract	
Γ_{vib}	6	0	-4	4	-2	2	$\Gamma_{tot}-\Gamma_{trans}-\Gamma_{rot}$	
A_1'	1	1	1	1	1	1		$1/h(\Gamma_{vib}\cdot A_1') = 12/12 \to A_1'$
A_2'	1	1	-1	1	1	-1		$1/h(\Gamma_{vib}\cdot A_2') = 0$
E'	2	-1	0	2	-1	0		$1/h(\Gamma_{vib}\cdot E') = 24/12 \to 2E'$
A_1''	1	1	1	-1	-1	-1		$1/h(\Gamma_{vib}\cdot A_1'') = 0$
A_2''	1	1	-1	-1	-1	1		$1/h(\Gamma_{vib}\cdot A_2'') = 12/12 \to A_2''$
E''	2	-1	0	-2	1	0		$1/h(\Gamma_{vib}\cdot E'') = 0$

For example, the decomposition for the A_1' irreducible representation is based on Eq. 27.8.2:

$$a_1 = \frac{1}{h} \sum_{j=1}^{6} \chi_j^{vib} \chi_{i,j}^{irr} C_{i,j}^{irr} = \frac{1}{12} [6(1)(1) + 0(1)(2) + (-4)(1)(3) + 4(1)(1) + (-2)(1)(2) + 2(1)(3)]$$

$$= 12/12 \qquad \text{giving that } A_1' \text{ appears once in } \Gamma_{vib}$$

The decomposition for the A_2' irreducible representation is:

$$a_2 = \frac{1}{12} [6(1)(1) + 0(1)(2) + (-4)(-1)(3) + 4(1)(1) + (-2)(1)(2) + 2(-1)(3)]$$

$$= 0 \qquad \text{giving that } A_2' \text{ does not appear in } \Gamma_{vib}$$

The normal modes decompose as $\Gamma_{vib} = A_1' + 2E' + A_2''$, giving six modes with four vibration frequencies, as listed in Table 27.7.1. Because E normal modes are doubly degenerate, the two different A_1-modes and the two different sets of E'-modes give six total normal modes as expected from the 3N-6 rule. The A_1' mode is Raman active, the E' modes are both IR and Raman active, and the A_2'' mode is IR active. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.

The molecule is redrawn with double-headed arrows replacing each bond. The number of arrows that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for BF_3 is listed below.
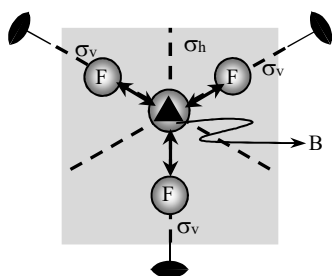
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	a_i
stationary arrows: Γ_{str}	3	0	1	3	0	1	
A_1'	1	1	1	1	1	1	$1/h(\Gamma_{str} \cdot A_1') = 12/12 \rightarrow A_1'$
A_2'	1	1	-1	1	1	-1	$1/h(\Gamma_{str} \cdot A_2') = 0$
E'	2	-1	0	2	-1	0	$1/h(\Gamma_{str} \cdot E') = 12/12 \rightarrow E'$
A_1''	1	1	1	-1	-1	-1	$1/h(\Gamma_{str} \cdot A_1'') = 0$
A_2''	1	1	-1	-1	-1	1	$1/h(\Gamma_{str} \cdot A_2'') = 0$
E''	2	-1	0	-2	1	0	$1/h(\Gamma_{str} \cdot E'') = 0$

The decomposition for the A_1' irreducible representation is:

$$a_1 = \frac{1}{h} \sum_{j=1}^{6} \chi_j^{str} \chi_{i,j}^{irr} C_{i,j}^{irr} = \frac{1}{12} [3(1)(1) + 0(1)(2) + (1)(1)(3) + 3(1)(1) + (0)(1)(2) + 1(1)(3)]$$

$$= 12/12 \qquad \text{giving that } A_1' \text{ appears once in } \Gamma_{str}$$

The stretching normal modes are $\Gamma_{str} = A_1' + E'$, giving three stretching modes with two vibration frequencies. Since all the modes include $\Gamma_{vib} = A_1' + 2E' + A_2''$, the remaining bending modes are $E' + A_2''$. This result verifies the listing in Table 27.7.1.

<u>41</u>. (a). Use group theory to determine the symmetry species of the normal modes of T-shaped ClF_3, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. (b). Determine which irreducible representations correspond to stretches and which to bending vibrations. (c). Can the number of IR and Raman active bands distinguish between trigonal-planar and T-shaped geometries for ClF_3? [Hint: Use Table 27.7.1 for the symmetry species of a trigonal planar XY_3 moleucle.]

Answer: The plan is to use the C_{2v} character table to decompose the reducible representation of the normal modes. We will find $3N - 6 = 6$ normal and expect three stretching vibrations, since there are three bonds.

The geometry and character table for C_{2v} are shown below. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x+\Gamma_y+\Gamma_z = A_1+B_1+B_2$, and the rotations $\Gamma_{rot} = A_2+B_1+B_2$, are appended to the end of the character table.

C_{2v}	E	C_2	σ_v	σ_v'	$h = 4$	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	-1	-1	xy	R_z
B_1	1	-1	1	-1	y, yz	R_x
B_2	1	-1	-1	1	x, xz	R_y
Γ_{trans}	3	-1	1	1	$\Gamma_{trans} = A_1+B_1+B_2$	
Γ_{rot}	3	-1	-1	-1	$\Gamma_{rot} = A_2+B_1+B_2$	

(a). The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below.

C_{2v}	E	C_2	σ_v	σ_v'	Γ	a_i
stationary atoms	4	2	2	4		
Γ_{trans}	3	-1	1	1	product	
Γ_{tot}	12	-2	2	4		
Γ_{trans}	3	-1	1	1	subtract	
Γ_{rot}	3	-1	-1	-1	subtract	
Γ_{vib}	6	0	4	2	$\Gamma_{tot}-\Gamma_{trans}-\Gamma_{rot}$	
A_1	1	1	1	1		$1/h(\Gamma_{vib}\cdot A_1) = 12/4 \rightarrow 3A_1$
A_2	1	1	-1	-1		$1/h(\Gamma_{vib}\cdot A_2) = 0$
B_1	1	-1	1	-1		$1/h(\Gamma_{vib}\cdot B_1) = 8/4 \rightarrow 2B_1$
B_2	1	-1	-1	1		$1/h(\Gamma_{vib}\cdot B_2) = 4/4 \rightarrow B_2$

For example, the decomposition for the A_1 irreducible representation is based on Eq. 27.8.2:

$$a_1 = \frac{1}{h} \sum_{j=1}^{4} \chi_j^{vib}\chi_{i,j}^{irr} C_{i,j}^{irr} = \frac{1}{4}[6(1)(1) + 0(1)(1) + 4(1)(1) + 2(1)(1)]$$

$$= 12/4 \qquad \text{giving that } A_1 \text{ appears three times in } \Gamma_{vib}$$

The decomposition for the A_2 irreducible representation is:

$$a_2 = \frac{1}{4}[6(1)(1) + 0(1)(1) + 4(-1)(1) + 2(1)(-1)]$$

$$= 0 \qquad \text{giving that } A_2 \text{ does not appear in } \Gamma_{vib}$$

The normal modes decompose as $\Gamma_{vib} = 3A_1 + 2B_1 + B_2$, giving six modes with six vibration frequencies. All the normal modes are both IR and Raman active. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total. (b). The molecule is redrawn with double-headed arrows replacing each bond. The number of <u>arrows</u> that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for ClF_3 is listed below.
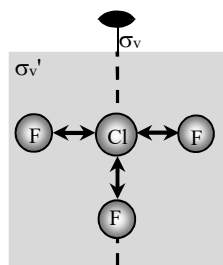
C_{2v}	E	C_2	σ_v	σ_v'	a_i
stationary arrows: Γ_{str}	3	1	1	3	
A_1	1	1	1	1	$1/h(\Gamma_{str}\cdot A_1) = 8/4 \to 2A_1$
A_2	1	1	-1	-1	$1/h(\Gamma_{str}\cdot A_2) = 0$
B_1	1	-1	1	-1	$1/h(\Gamma_{str}\cdot B_1) = 0$
B_2	1	-1	-1	1	$1/h(\Gamma_{str}\cdot B_2) = 4/4 \to B_2$

The decomposition for the A_1 irreducible representation is:

$$a_1 = \frac{1}{h} \sum_{j=1}^{4} \chi_j^{str}\chi_{i,j}^{irr} C_{i,j}^{irr} = \frac{1}{4}[3(1)(1) + 1(1)(1) + 1(1)(1) + 3(1)(1)]$$
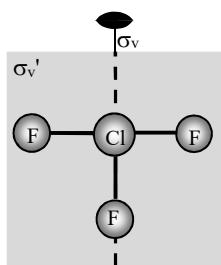
$$= 8/4 \qquad \text{giving that } A_1 \text{ appears twice in } \Gamma_{str}$$

The stretching normal modes are $\Gamma_{str} = 2A_1 + B_2$, giving three stretching modes with three vibration frequencies. Since all the modes include $\Gamma_{vib} = 3A_1 + 2B_1 + B_2$, the remaining bending modes are $A_1 + B_1 + B_2$. Note that formaldehyde, $CH_2{=}O$, is also planar tetra-atomic C_{2v} and therefore gives the same normal mode results.
(c). Referring to the C_{2v} character table, the x, y, and z-components of the transition dipole moment transform as B_2, B_1, and A_1, respectively. The quadratic products, such as z^2 and xy, cover all four irreducible representations, giving all normal modes as possibly Raman active. As a consequence, all the normal modes are both IR and Raman active.

Yes, the number of IR and Raman active bands does distinguish between trigonal-planar and T-shaped geometries for ClF_3. From Table 27.7.1, for trigonal-planar D_{3h} XY_3 molecules there

are three IR and three Raman transitions. From the analysis above, all normal modes of C_{2v} XY_3 molecules are both IR and Raman active.

42. (a). Use group theory to determine the symmetry species of the normal modes of square-planar XeF_4, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. (b). Determine which irreducible representations correspond to stretches and which to bending vibrations. (c). Determine the IR and Raman activity of the modes. The projection of the symmetry operations of the D_{4h} point group upon XeF_4 is shown below. [Hints: There are two C_4 axes, one for clockwise and one for counterclockwise rotation. The C_2 axis is coincident with the C_4 axis, while the C_2' and C_2'' are perpendicular to the C_4 axes. The C_2 axis is required for mathematical completeness and is equivalent to two successive C_4 rotations in the same direction. For determining the symmetry of a square-planar molecule, the S_4 improper rotations act just like C_4 proper rotations, since all atoms lie in the σ_h-plane.]
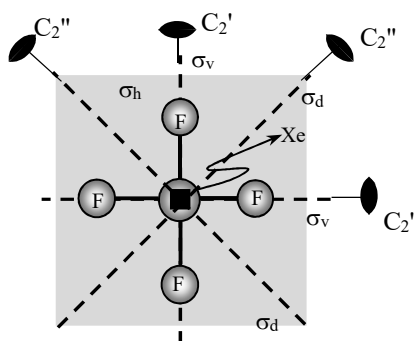
Answer: The plan is to use the D_{4h} character table to decompose the reducible representation of the normal modes. We will find $3N - 6 = 9$ normal modes and expect four stretching vibrations, since there are four bonds.

(a). The character table for D_{4h} is shown below. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x + \Gamma_y + \Gamma_z = A_{2u} + E_u$, and the rotations, $\Gamma_{rot} = A_{2g} + E_g$, are appended to the end of the character table.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$h = 16$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		R_z
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	(x^2-y^2)	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy	
E_g	2	0	-2	0	0	2	0	-2	0	0	(xz, yz)	(R_x, R_y)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x,y)	
Γ_{trans}	3	1	-1	-1	-1	-3	-1	1	1	1	$\Gamma_{trans} = A_{2u} + E_u$	
Γ_{rot}	3	1	-1	-1	-1	3	1	-1	-1	-1	$\Gamma_{rot} = A_{2g} + E_g$	

The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	a_i
stat. atms	5	1	1	3	1	1	1	5	3	1	
Γ_{trans}	3	1	-1	-1	-1	-3	-1	1	1	1	←product
Γ_{tot}	15	1	-1	-3	-1	-3	-1	5	3	1	
Γ_{trans}	3	1	-1	-1	-1	-3	-1	1	1	1	←subtract
Γ_{rot}	3	1	-1	-1	-1	3	1	-1	-1	-1	←subtract
Γ_{vib}	9	-1	1	-1	1	-3	-1	5	3	1	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$1/h(\Gamma_{vib}\cdot A_{1g}) = 16/16 \rightarrow A_{1g}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{2g}) = 0$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$1/h(\Gamma_{vib}\cdot B_{1g}) = 16/16 \rightarrow B_{1g}$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	$1/h(\Gamma_{vib}\cdot B_{2g}) = 16/16 \rightarrow B_{2g}$
E_g	2	0	-2	0	0	2	0	-2	0	0	$1/h(\Gamma_{vib}\cdot E_g) = 0$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{1u}) = 0$
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	$1/h(\Gamma_{vib}\cdot A_{2u}) = 16/16 \rightarrow A_{2u}$
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	$1/h(\Gamma_{vib}\cdot B_{1u}) = 0$
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	$1/h(\Gamma_{vib}\cdot B_{2u}) = 16/16 \rightarrow B_{2u}$
E_u	2	0	-2	0	0	-2	0	2	0	0	$1/h(\Gamma_{vib}\cdot E_u) = 32/16 \rightarrow 2E_u$

For example, the decomposition for the A_{1g} irreducible representation is based on Eq. 27.8.2:

$$a_1 = {}^1\!/_h \sum_{j=1}^{10} \chi_j^{vib} \chi_{i,j}^{irr} C_{i,j}^{irr}$$

$$= {}^1\!/_{16} [9(1)(1) + (-1)(1)(2) + 1(1)(1) + (-1)(1)(2) + 1(1)(2) + (-3)(1)(1) + (-1)(1)(2) +$$
$$5(1)(1) + 3(1)(2) +1(1)(2)]$$

$= 16/16$ giving that A_{1g} appears once in Γ_{vib}

The decomposition for the A_{2g} irreducible representation is:

$$a_2 = {}^1\!/_{16} [9(1)(1) + (-1)(1)(2) + 1(1)(1) + (-1)(-1)(2) + 1(-1)(2) + (-3)(1)(1) + (-1)(1)(2) +$$
$$5(1)(1) + 3(-1)(2) +1(-1)(2)]$$

$= 0$ giving that A_{2g} does not appear in Γ_{vib}

The normal modes decompose as $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$, giving nine vibration frequencies. Because the E_u normal modes are doubly degenerate, the two different sets of E_u-modes give nine total normal modes as expected from the 3N-6 rule. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.

(b). The molecule is redrawn with double-headed arrows replacing each bond. The number of arrows that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for XeF_4 is listed below.
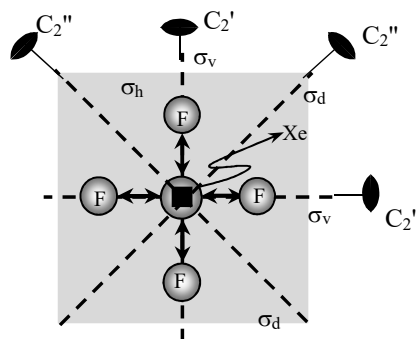
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	a_i
stationary arrows	4	0	0	2	0	0	0	4	2	0	$\leftarrow \Gamma_{str}$
A_{1g}	1	1	1	1	1	1	1	1	1	1	$1/h(\Gamma_{vib}\cdot A_{1g}) = 16/16 \rightarrow A_{1g}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{2g}) = 0$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$1/h(\Gamma_{vib}\cdot B_{1g}) = 16/16 \rightarrow B_{1g}$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	$1/h(\Gamma_{vib}\cdot B_{2g}) = 0$
E_g	2	0	-2	0	0	2	0	-2	0	0	$1/h(\Gamma_{vib}\cdot E_g) = 0$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{1u}) = 0$
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	$1/h(\Gamma_{vib}\cdot A_{2u}) = 0$
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	$1/h(\Gamma_{vib}\cdot B_{1u}) = 0$
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	$1/h(\Gamma_{vib}\cdot B_{2u}) = 0$
E_u	2	0	-2	0	0	-2	0	2	0	0	$1/h(\Gamma_{vib}\cdot E_u) = 16/16 \rightarrow E_u$

The decomposition for the A_{1g} irreducible representation is:

$$a_1 = \frac{1}{h}\sum_{j=1}^{10} \chi_j^{str}\chi_{i,j}^{irr} C_{i,j}^{irr} = \frac{1}{16} [4(1)(1) + 0(1)(2) + 0(1)(1) + 2(1)(2) + 0(1)(2) + 0(1)(1) +$$

$$0(1)(2) + 4(1)(1) + 2(1)(2) + 0(1)(2)]$$

$$= 16/16 \qquad \text{giving that } A_{1u} \text{ appears once in } \Gamma_{str}$$

The stretching normal modes are $\Gamma_{str} = A_{1g} + B_{1g} + E_u$, giving four stretching modes with three vibration frequencies. Since all the modes include $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$, the remaining bending modes are $B_{2g} + A_{2u} + B_{2u} + E_u$.

(c). The x, y, and z-components of the transition dipole moment transform as E_u, E_u, and A_{2u} respectively. The quadratic products, such as z^2 and $(x^2 - y^2)$, transform as A_{1g}, B_{1g}, B_{2g}, and E_g. Note that for a molecule with a center of symmetry, the x, y, z-components of the transition dipole all transform as "u" irreducible representations while the polarizability components transform as "g" irreducible representations, verifying the Exclusion rule. As a consequence, the A_{2u} and both E_u normal modes are possibly infrared active, while the A_{1g}, B_{1g}, and B_{2g} are possibly Raman active. The B_{2u} is forbidden in both infrared absorption and Raman scattering.

<u>43</u>. The normal mode vibrations of a square-planar XY_4 molecule transform as $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$. The normal mode vibrations of a tetrahedral XY_4 transform as $\Gamma_{vib} = A_1 + E + 2T_2$. For molecules such as CH_4 or XeF_4, are square-planar XY_4 and tetrahedral XY_4 geometries distinguishable on the basis of the number of IR and Raman active modes?

Answer: The plan is to use the D_{4h} and T_d character tables, Table 27.8.2 in the data section, to determine if each normal mode is IR or Raman active. This decision is based on the transformation properties of alternatively: the x, y, z-components of the electric transition dipole moment for IR and the quadratic components of the polarizability for the Raman transitions.

   Note that E-modes are doubly degenerate, while T-modes are triply degenerate. Each mode within the degenerate set have the same transition frequency.

   For square-planar D_{4h} molecules, the x, y, and z-components of the transition dipole moment transform as E_u, E_u, and A_{2u} respectively. The quadratic products, such as z^2 and $(x^2 - y^2)$, transform as A_{1g}, B_{1g}, B_{2g}, and E_g. With overall $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$, the A_{2u} and both doubly-degenerate E_u normal modes are possibly infrared active, while the A_{1g}, B_{1g}, and B_{2g} are possibly Raman active. The B_{2u} is forbidden in both infrared absorption and Raman scattering.

   For tetrahedral T_d molecules, the x, y, and z-components of the transition dipole moment transform as T_2. The quadratic products, such as xy and $(x^2 - y^2)$, transform as A_1, E, and T_2. With overall $\Gamma_{vib} = A_1 + E + 2T_2$, both triply-degenerate T_2 normal modes are possibly infrared active, while all nine modes are possibly Raman active. The B_{2u} is forbidden in both infrared absorption and Raman scattering.

   The results for a square-planar XY_4 and a tetrahedral XY_4 are distinguishable on the basis of the number of IR and Raman active modes and the corresponding distinct frequencies:

Geometry XY$_4$	IR active (possibly)	Raman active (possibly)	IR & Raman forbidden
square-planar	5 modes / 3 $\tilde{v}$s	3 modes / 3 $\tilde{v}$s	1
tetrahedral	6 modes / 2 $\tilde{v}$s	9 modes / 4 $\tilde{v}$s	0

Since square-planar molecules have a center of symmetry, no normal mode is both IR and Raman active, the transition frequencies are mutually exclusive. However, for tetrahedral molecules the T_2-modes are both IR and Raman active. For tetrahedral molecules two different frequencies can possibly occur in both the IR and Raman.

<u>44</u>. *Challenge Problem*: Determine the equilibrium bond length R_e, dissociation energy $\tilde{D}_e$, Morse *a*-parameter, fundamental vibration frequency $\tilde{v}_e$, and anharmonicity for HF using molecular structure calculations at the CCSD(T)/cc-pVTZ level. Assume the potential energy surface is in the Morse form with Eq. 27.5.7 giving the fundamental vibration frequency and Eq. 27.5.19 giving the anharmonicity. Calculate the dissociation energy, $\tilde{D}_e$, using separate calculations of the atomic energies of H- and F-atoms. Compare the theoretical spectroscopic constants with experimental literature values. [Hint: you will need to do calculations for HF at the geometry optimized bond length and two other values of the internuclear separation, use $R_e - 0.10$ Å and $R_e + 0.15$ Å. Then fit your three data points to a Morse potential in a spreadsheet.]

Answer: The plan to note that the bond dissociation energy is for the process
HF $\rightarrow$ H (^{2}S) + F(^{2}P) with the $\tilde{D}_e$ calculated as the difference in energy of the products and reactants.

The minimized bond length for HF was 0.917 Å with the energy -100.3383563 H. The values for the two additional bond lengths and the H- and F-atoms are listed in the spreadsheet, below. The spreadsheet was developed to compare the electronic structure energy values to Morse potential values based on the calculated $\tilde{D}_e$, R_e, and a guessed value for the Morse a-parameter. The Morse a-parameter, cell G3, is varied to minimize the sum of squared residuals, cell H11, between the electronic structure calculation data points, cells F7:F9, and the fit Morse curve, cells G7:G9. Goal search can be used, but because of convergence problems, we had to finish by hand to achieve four significant figures in a. The final fit curve is shown in the plot below. The electronic structure values are the solid black triangles and the Morse curve values are in hollow squares. The derived fit is not perfect because the potential energy curve is not exactly a Morse potential.

A1	B	C	D	E	F	G	H	I	J
2		*Atoms*	E (H)		D_e	9.51E-19	J	5.937132	eV
3		H	-0.499809811		a	2.2804	Å^{-1}	2.280E+10	m^{-1}
4		F	-99.62036076		R_e	0.917	Å		
5		*Molecule*							
6		HF R (Å)	E (H)	E-E$_{min}$ (H)	E-E$_{min}$ (J)	Morse (J)	residual^2		
7		0.817	-100.323722	0.01463	6.38E-20	6.24E-20	1.95E-42		
8		0.917	-100.3383563	0	0.00E+00	0	0		
9		1.067	-100.3203793	0.01798	7.84E-20	7.98E-20	2.12E-42		
10									
11						ssr*1E40 =	0.040649		

	C	D	E
12			
13	$\mathcal{M}_1$	1.007825	g mol^{-1}
14	$\mathcal{M}_2$	18.998403	g mol^{-1}
15	μ	1.59E-27	kg
16	ν_e	1.26E+14	s^{-1}
17	ν_e	4187.455392	cm^{-1}
18	k	989.3258205	N m^{-1}
19	$\chi_e\,\nu_e$	91.57056	cm^{-1}
20			
21	1H =	2625.4974	kJ mol^{-1}
22	N$_A$=	6.02E+23	
23	c=	3.00E+10	cm s^{-1}
24	h=	6.63E-34	J s
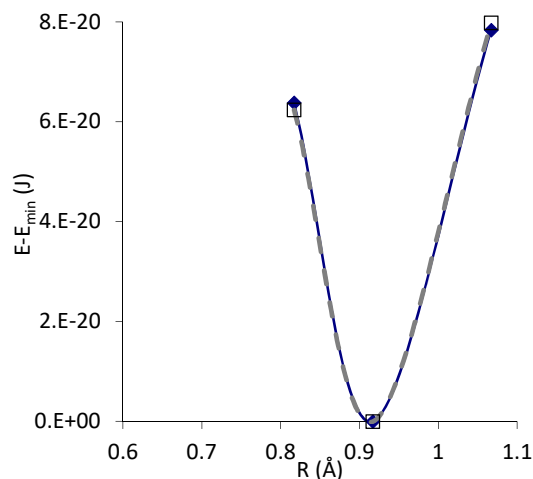
Cell G2 for the dissociation energy is: "=(D3+D4-D8)*D21/D22*1000"
Cell G7 for the Morse curve is: "=$G$2*(1-EXP(-$G$3*(C7-$G$4)))^2"
Cell H7 for the first squared residual is: "=(F7-G7)^2"
Cell H11 sums the squared residuals and multiplies by a fixed factor of 10^{40} to provide a convenient scale for the fit evaluation: "=SUM(H7:H10)*1E40"
Cell G3 is adjusted to minimize cell H11, which at the same time provides a better fit in the plot.
   Once the Morse a-parameter is obtained by manual curve fitting the remaining spectroscopic parameters are calculated. The reduced mass for HF is:

$$\mu_{HF} = \frac{(1.007825)(18.998403)}{1.007825+18.998403}\ (g\ mol^{-1})\frac{1}{N_A}\ (1kg/1000\ g) = 1.589229 \times 10^{-27}\ kg$$

With Eq. 27.5.7, a must be converted to m^{-1} from Å^{-1} to match joule units for D_e:

rearranging $a = \omega_e \left(\dfrac{\mu}{2D_e} \right)^{1/2}$ gives:

$$\nu_e = \frac{a}{2\pi} \left(\frac{2D_e}{\mu} \right)^{1/2} = \frac{2.2804 \times 10^{10} \text{ m}^{-1}}{2\pi} \left(\frac{2(9.51234 \times 10^{-19} \text{J})}{1.589229 \times 10^{-27} \text{ kg}} \right)^{1/2} = 1.25573 \times 10^{14} \text{ s}^{-1}$$

$\tilde{\nu}_e = \nu_e/c = 4187.5 \text{ cm}^{-1}$

With Eq. 27.5.18, rearranging gives:

$$\chi_e \tilde{\nu}_e = \frac{a^2 h}{8\pi^2 \mu c} = \frac{(2.2804 \times 10^{10} \text{ m}^{-1})^2 \, 6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 (1.589229 \times 10^{-27} \text{ kg})(2.99879246 \times 10^{10} \text{ cm s}^{-1})} = 91.571 \text{ cm}^{-1}$$

Comparison with the experimental literature values shows gratifying agreement. Using Eq. 27.5.12, in the form $\tilde{D}_o = \tilde{D}_e - \frac{1}{2} \tilde{\nu}_e + \frac{1}{4} \chi_e \tilde{\nu}_e$, to put the calculated and experimental dissociation energies on the same basis:

Parameter	CCSD(T)/cc-pVTZ	Experimental
R_e	0.917 Å	0.91681 Å
D_o	5.680 eV	5.86 eV
$\tilde{\nu}_e$	4187.5 cm^{-1}	4138.385 cm^{-1}
$\chi_e \tilde{\nu}_e$	91.571 cm^{-1}	89.943 cm^{-1}

45. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). Doppler line broadening for UV transitions is greater than for microwave transitions.
(b). As molecules increase in size, rotational constants decrease.
(c). The wave number for vibrational transitions increases with temperature.
(d). In Raman scattering, the anti-Stokes lines are more intense than the Stokes lines.
(e). Two states with the same energy always mix and transitions to the two states can share intensity even if otherwise forbidden.

Answers:
(a). True: The Doppler broadening in wave numbers or frequency is given as a fraction of the transition frequency, Eq. 27.2.2.
(b). True: For example, for a diatomic molecule the $\tilde{B}$ value is inversely proportional to the bond length. In general the moment of inertia increases with increasing size, which decreases the rotational constant.
(c). False: Vibrational frequencies depend only on the quantum spacing of the energy levels, which does not depend on temperature. The Boltzmann population of excited states increases with temperature giving a change in transition intensity. As a result hot bands are more intense with increasing temperature. Doppler and collisional broadening increase with temperature.
(d). False: Anti-Stokes lines originate in an excited vibrational state, which by the Boltzmann distribution have a much smaller population than the ground state.
(e). Not quite true: To interact the two states must have the same symmetry. For example, anti-symmetric stretches can only interact with overtones or combinations that are also anti-

symmetric. As a consequence Fermi resonances aren't as common as they would be without the symmetry restriction. However, the remainder of the statement is correct; with an interaction, transitions to the two states can share intensity even if otherwise forbidden.

46. The selection rule $\Delta\upsilon = \pm 1$ for harmonic vibrations can also be motivated by using the odd or even symmetry of the integrand in the transition dipole moment integrals, Eqs. 27.9.13. Note that the harmonic oscillator wave functions alternate between even or odd for increasing υ, Table 24.1.1 and Figure 24.2.3b. (a). Assume υ'' for the lower level is even, use the overall even/odd symmetry of the integrand to note if the transition dipole vanishes for $\Delta\upsilon = -2, -1, 0, +1, +2$. (b). Assume υ'' for the lower level is odd, use the overall even/odd symmetry of the integrand to note if the transition dipole vanishes for $\Delta\upsilon = -2, -1, 0, +1, +2$.

Answer: The plan is to note that the harmonic oscillator wave functions are purely odd or even, while the x, y, or z-component of the extension operator is odd.
   The harmonic oscillator wave functions alternate between even and odd for increasing υ. The transition electric dipole moment is proportional to the integral given by Eqs. 27.9.13:

$$\int \chi_{\upsilon'} (R - R_e) \, \chi_{\upsilon''} \; dR$$

The integrand factors into three functions: the final harmonic oscillator wave function, the extension operator $(R - R_e)$, and the initial harmonic oscillator wave function. The extension operator is purely odd around the equilibrium position.

(a). With υ'' even, the final state is υ' as given by the following table:

υ'	parity	integrand	overall parity	transition dipole
$\upsilon''-2$	even	even odd even	odd	forbidden
$\upsilon''-1$	odd	odd odd even	even	allowed
υ''	even	even odd even	odd	forbidden
$\upsilon''+1$	odd	odd odd even	even	allowed
$\upsilon''+2$	even	even odd even	odd	forbidden

(b). With υ'' odd, the final state is υ' as given by the following table:

υ'	parity	integrand	overall parity	transition dipole
$\upsilon''-2$	odd	odd odd odd	odd	forbidden
$\upsilon''-1$	even	even odd odd	even	allowed
υ''	odd	odd odd odd	odd	forbidden
$\upsilon''+1$	even	even odd odd	even	allowed
$\upsilon''+2$	odd	odd odd odd	odd	forbidden

This method doesn't work for odd $\Delta\upsilon$ greater than +3 or less than –3. The general integral result in Eq. 27.9.15 resolves those cases.

<u>47</u>. The "ABC Rotational Constant Calculator" applet determines the moments of inertia, spectroscopic rotational constants, symmetry point group, and the contributions of rotation to the entropy and Gibbs energy of a molecule. The applet is available on the textbook Web site or on the companion CD. Extensive collections of molecular coordinates are available on-line and from molecular mechanics or electronic structure calculations. While many electronic structure packages determine the point group of an input molecule, the "ABC" applet has an adjustable tolerance that allows the point group to be determined in cases where other programs fail. Use the following coordinates to determine the point group and rotational constants for ethane:

```
8
ethane
C        -0.7704  0.0003 -0.0010
C         0.7707 -0.0002 -0.0001
H        -1.1734  1.0280 -0.0004
H        -1.1725 -0.5129 -0.8919
H        -1.1740 -0.5148  0.8883
H         1.1736 -1.0279 -0.0013
H         1.1742  0.5154 -0.8891
H         1.1728  0.5124  0.8911
```

The list is in xyz-format. The first line is the atom count. The second line is a comment. The subsequent lines list the atom and the coordinates.

Answer: The given coordinates are from a density functional minimized structure with the cc-pTZP basis set. The above data was entered into the "ABC" applet (you need to know your ABC's, afterall). The output appears as shown below.

```
Moments of Inertia
Ix =   25.7705 g mol-1 Ang2  or 0.42793e-45 kg m2
Iy =   25.7693 g mol-1 Ang2  or 0.42791e-45 kg m2
Iz =    6.3882 g mol-1 Ang2  or 0.10608e-45 kg m2
_____
 Rotational constants
Ae = 0.65414 cm-1 or 19.611 GHz or 0.94117 K
Be = 0.65418 cm-1 or 19.612 GHz or 0.94121 K
Ce = 2.6389 cm-1 or 79.111 GHz or 3.7968 K
Point group D3d
_____
 Thermodynamics
qr=829.26 with sigma=6
Rotational Entropy=68.35 J mol-1 K-1
Translational Entropy=151.2944 J mol-1 K-1
Trans+Rotation Gibbs Free Energy=-55.571 kJ mol-1
=============================================

 Coordinates in Principal Coordinates Frame
_____
8
ethane (pBP/TZVP in pcf
C      0.0000     0.0000   -0.7705
C      0.0000    -0.0000    0.7705
H      0.5134     0.8902   -1.1738
H     -1.0279    -0.0004   -1.1730
H      0.5139    -0.8902   -1.1734
H     -0.5138    -0.8898    1.1737
H     -0.5133     0.8905    1.1734
H      1.0279    -0.0001    1.1730
```

The point group is correctly recognized as D_{3d} with the default tolerance; see Problem 35h. The moment of inertia calculations are presented in Problem 14. We will have much more to say about the thermodynamic values, which are for an ideal gas, in the statistical mechanics chapter. Translation and rotation make a significant contribution to the Gibbs energy of formation of a molecule.

48. Bending vibrations are characterized as one of four basic types of movements, Figure P27.2.

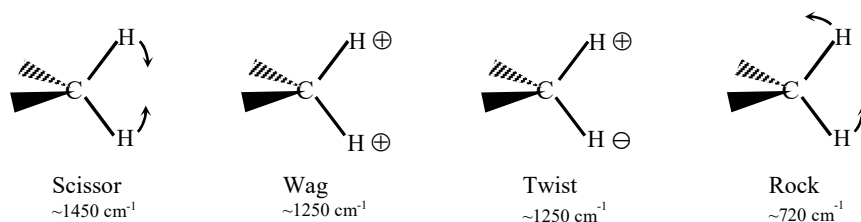| Scissor	Wag	Twist	Rock
~ 1450 cm^{-1}	~ 1250 cm^{-1}	~ 1250 cm^{-1}	~ 720 cm^{-1}

Figure P27.2: Bending vibrations of methylene. Typical frequencies for small hydrocarbons of normal modes dominated by the given type of bend are given.

Determine the normal modes of formaldehyde using an electronic structure calculation at the HF/6-31G* level (or equivalently HF/6-31G(d)). Display the "raw" numerical output files to find the symmetry designations. The experimental frequencies are given in Table P27.1.[7] Formaldehyde has C_{2v} symmetry, the symmetry properties for which are given in Figure 26.6.4. The totally symmetric group, a_1, contains the most symmetrical vibrations. The b_1 and b_2-groups are less symmetrical in the atom movements, b_1 is symmetrical with respect to reflection across the vertical plane that runs through the C=O bond. The b_1 and b_2 designations may be switched in the calculation listing; some authors switch the symmetry labels. Compare the calculated and experimental frequencies, Table P27.1. Animate the normal modes to help compare the modes. Frequencies from *ab initio* calculations are normally multiplied by 0.9 to compare with experimental frequencies. This factor adjusts for anharmonicity. Multiply your frequencies by 0.9; does the scaling improve the agreement with the experimental values?

Table P27.1. Experimental Frequencies of the Normal Modes of Formaldehyde.7

Symmetry of mode	Type of mode	Frequency (cm^{-1})
a_1	CH_2 symmetric stretch	2783 strong
	CO stretch	1746 very strong
	CH_2 scissor	1500 strong
b_1	CH_2 wag	1167 strong
b_2	CH_2 asymmetric stretch	2843 very strong
	CH_2 rock	1249 strong

Answer: The Spartan results are given below. The b_1 and b_2 symmetry labels are switched from the given data. The output also lists the thermodynamic parameters from the calculation. We will discuss these thermodynamic calculations in the statistical mechanics chapter.

```
      Standard Thermodynamic quantities at 298.15 K and 1.00 atm

              Term      ZPE     Enthalpy  Entropy    Cv      % in
                       cm-1    kJ/mol    kJ/mol   J/mol.K  J/mol.K  Ground IR Int.
         --   ----------  -------  -------  -------    ----
      1  B2    1335.821    7.9900   0.0254   0.0984   0.5498    99.84   0.37
      2  B1    1383.128    8.2729   0.0209   0.0807   0.4689    99.87  23.15
      3  A1    1679.553   10.0460   0.0061   0.0229   0.1651    99.97   8.67
      4  A1    2027.134   12.1250   0.0014   0.0051   0.0449    99.99 150.10
      5  A1    3159.409   18.8975   0.0000   0.0000   0.0005   100.00  49.69
      6  B1    3230.997   19.3257   0.0000   0.0000   0.0003   100.00 135.93
         --   ----------  -------  -------  -------    ----
       Total Vibrations   76.6569   0.0538   0.2070   1.2295

             Ideal Gas             2.4789
           Translation             3.7184 151.1751   12.4716
              Rotation             3.7184  66.6145   12.4716
           ----------            -------  -------   -------
                Totals            86.6265 217.9967   26.1727

      Vibrational(v) Corrections:
         Temp. Correction    Hv     86.6265
       Entropy Correction (Hv-TSv)  21.6308
```

The results from the full Gaussian output are shown below. The normal mode displacements are listed below each normal mode. These displacements are the basis of the normal mode animation, see Sec. . The IR and Raman relative intensities and the extent of Raman polarization are also listed. Notice that the non-totally symmetric normal modes are depolarized.

```
      Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
       activities (A**4/AMU), depolarization ratios for plane and unpolarized
       incident light, reduced masses (AMU), force constants (mDyne/A),
       and normal coordinates:
                         1                      2                      3
                        B1                     B2                     A1
      Frequencies --  1335.9812              1383.2798              1679.6943
      Red. masses --     1.3690                 1.3442                 1.1042
      Frc consts  --     1.4396                 1.5154                 1.8355
      IR Inten    --     0.3667                23.1572                 8.6538
      Raman Activ --     0.7661                 4.5093                12.8713
      Depolar (P) --     0.7500                 0.7500                 0.5902
      Depolar (U) --     0.8571                 0.8571                 0.7423
      Atom AN      X      Y      Z       X      Y      Z       X      Y      Z
        1   6    0.17   0.00   0.00    0.00   0.15   0.00    0.00   0.00   0.00
        2   8   -0.04   0.00   0.00    0.00  -0.08   0.00    0.00   0.00   0.08
        3   1   -0.70   0.00   0.00    0.00  -0.25  -0.65    0.00  -0.35  -0.61
        4   1   -0.70   0.00   0.00    0.00  -0.25   0.65    0.00   0.35  -0.61
                         4                      5                      6
                        A1                     A1                     B2
      Frequencies --  2027.9363              3160.0193              3231.6842
      Red. masses --     7.2382                 1.0491                 1.1206
      Frc consts  --    17.5385                 6.1721                 6.8951
      IR Inten    --   150.1652                49.7347               135.9693
      Raman Activ --     8.0997               137.6328                58.3200
      Depolar (P) --     0.3279                 0.1828                 0.7500
      Depolar (U) --     0.4938                 0.3090                 0.8571
      Atom AN      X      Y      Z       X      Y      Z       X      Y      Z
        1   6    0.00   0.00   0.58    0.00   0.00   0.06    0.00   0.10   0.00
        2   8    0.00   0.00  -0.41    0.00   0.00   0.00    0.00   0.00   0.00
        3   1    0.00  -0.46  -0.19    0.00   0.61  -0.35    0.00  -0.60   0.37
        4   1    0.00   0.46  -0.19    0.00  -0.61  -0.35    0.00  -0.60  -0.37
```

The frequencies as wave numbers are compared with and without scaling by 0.9 below:

Symm.	Type	Experiment (cm^{-1})	HF/6-31G*	0.9*HF/6-31G*	% difference
a1	CH$_2$ symm. Str.	2783	3160.0	2844.0	2.2
	CO stretch	1746	2027.9	1825.1	4.5
	CH$_2$ scissor	1500	1679.7	1511.7	0.8
b1	CH$_2$ wag	1167	1336.0	1202.4	3.0
b2	CH$_2$ asymm. Str.	2843	3231.7	2908.5	2.3
	CH$_2$ rock	1249	1383.3	1245.0	-0.3

The factor of 0.9 scaling, which takes into account anharmonicity, improves the agreement. More precise scaling factors are available for specific *ab initio* levels. If you have covered the group theory section, notice that all the modes are both IR and Raman active as expected from the C$_{2v}$ symmetry. However, the predicted intensity of the 1167 cm^{-1} wag is smaller than expected compared to the experimental spectrum.

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