4.8: Problems

1. For each molecule, calculate the reduced mass (in kg) and the force constant for the bond (in N/m).

Molecule	ω_e (cm $^{-1}$)	μ (kg)	k (N/m)
$^{1}H^{79}Br$	2648.975		
$^{35}Cl_2$	559.72		
$^{12}C^{16}O$	2169.81358		
$^{69}Ga^{35}Cl$	365.3		

2. The typical carbonyl stretching frequency is on the order of 1600-1900 cm^{-1}. Why is this value smaller than the value of ω_e for CO given in the table above?

3. The first few Hermite polynomials are given below.

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2-2$

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

   a. Use the recursion relation to generate the functions H_3 (y) and H_4 (y).
   b. Demonstrate that the first three Hermite polynomials (H_0 (y), H_1 (y) and H_2 (y)) form an orthogonal set.

4. The Morse Potential function is given by

$$U(x) = D_e\left(1 - e^{-\beta x}\right)$$

where $x = (r - r_e)$.

   a. Find an expression for the force constant of a Morse Oscillator bond by evaluating
   b. For $^{1}H^{35}Cl$, $D_e = 7.31 \times 10^{-19} J$ and $\beta = 1.8 \times 10^{10} m^{-1}$. Use your above expression to evaluate k for the bond in HCl.
   c. On what shortcoming of the Harmonic Oscillator model does the Morse Potential improve? What shortcoming does the Morse model share with that of a Harmonic Oscillator?

5. The following data are observed in the vibrational overtone spectrum in $^{1}H^{35}Cl$ (Meyer & Levin, 1929).

$v' \leftarrow v$"	$\tilde{\nu}_{obs}$ (cm^{-1})
$1 \leftarrow 0$	2885.9
$2 \leftarrow 0$	5666.8
$3 \leftarrow 0$	8347.0
$4 \leftarrow 0$	10923.1
$5 \leftarrow 0$	13396.5

From these data, calculate a set of $\Delta G_{v+\frac{1}{2}}$ values. Fit these results to the form

$$\Delta G_{v+\frac{1}{2}} = \omega_e - 2\,\omega_e x_e (v+1)$$

to determine values for ω_e and $\omega_e x_e$ for HCl.

6. The following wavenumber frequencies are reported for the band origins for the $1-v$" bands in an electronic transition of a diatomic molecule. Using the Birge-Sponer method, determine the dissociation energy of the molecule in its ground electronic state.

v"	Wavenumber (cm^{-1})	$\Delta G_{v+\frac{1}{2}}$ (cm^{-1})
	19586.9	
	19522.3	
	19504.8	
	19465.9	
	19418.3	
	19375.1	
	19323.2	
	19275.7	
	19223.8	
	19167.6	
	19111.4	
	19050.9	
	18990.4	
	18925.6	
	18860.7	
	18795.9	
	18722.4	
	18653.3	
	18579.8	
	18506.3	
27	18428.5	
	18342.1	
	18259.9	
	18177.8	
	18091.5	
	17996.3	
	17909.8	
	17814.8	
	17719.7	
	17624.6	