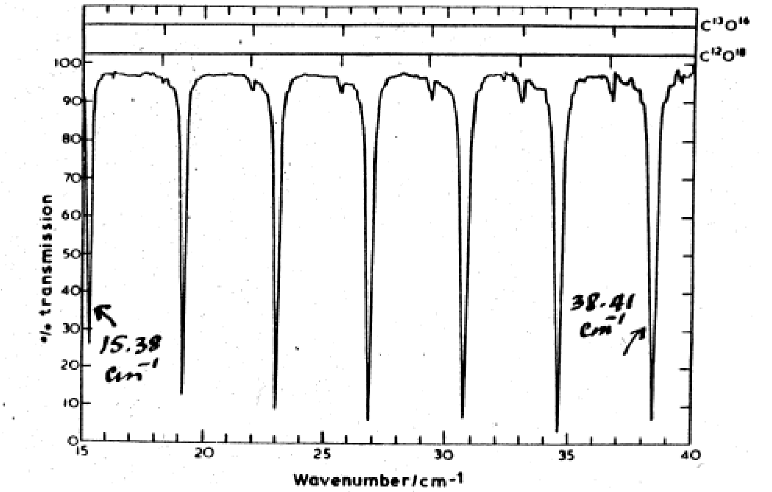
Problem Set 14
On Molecular Spectroscopy

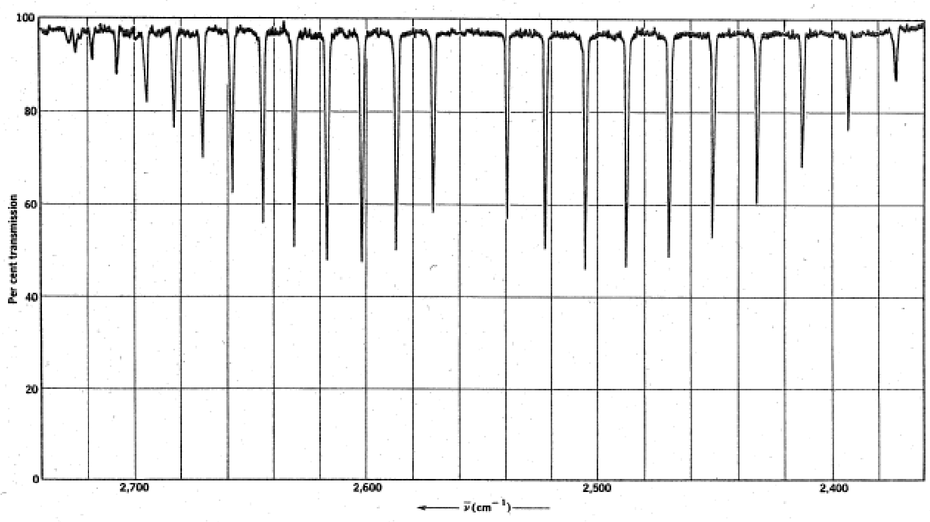
Use the attached formulas (see last page) for the energy of a diatomic molecule in terms of its molecular constants in order to have uniform notation.

Part I

1. Derive an expression in terms of B, D, and J_{lower} giving the energy spacing between adjacent rotational states for a diatomic rotor. Does the deviation from the rigid rotor result increase or decrease as J increases? From your derived expression and the selection rule $\Delta J = \pm 1$, draw a stick diagram of a microwave spectrum for a diatomic molecule, for example CO. Label each peak with values of J_{lower}. From your derived expression, determine the frequency spacing between adjacent peaks in the microwave spectrum of a diatomic molecule. Suppose you have measured the frequencies in the microwave spectrum of the CO molecule. Determine a suitable choice of a straight line plot that would provide directly (from slope and intercept) the molecular or spectroscopic constants that can be extracted from the microwave spectrum. Sketch such a plot and identify what the slope and intercepts are equal to. A portion of the CO microwave spectrum is shown below:

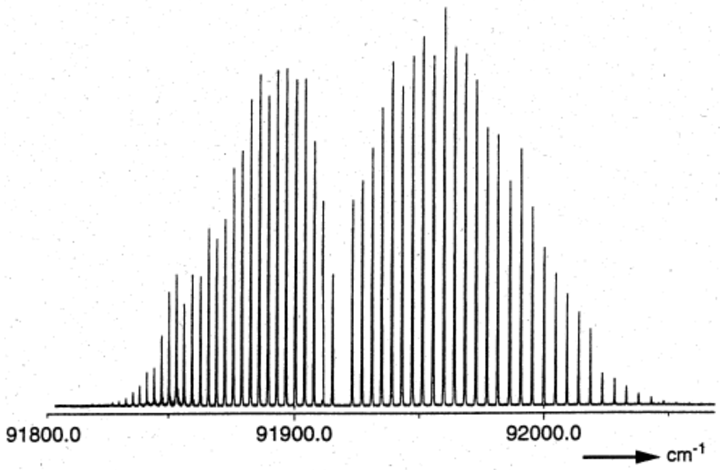


2. Derive an expression in terms of the spectroscopic constants giving the frequencies of transitions between v = 0 and v = 1 accompanied by rotational transitions for a diatomic molecule, for example CO. The selection rule is $\Delta J = \pm 1$, unless the molecule has other angular momentum (non-vanishing net S or net Λ), in which case also $\Delta J = 0$ is allowed. From your derived expression, draw a stick diagram of an infrared spectrum. Label each peak with values of J_{lower}. From your derived expression, determine the frequency spacing between adjacent peaks in the center of the infrared spectrum of a diatomic molecule. Determine the frequency spacing between adjacent peaks in the low frequency side of the infrared spectrum in terms of the spectroscopic constants and J_{lower}. Show one such spacing in your stick diagram, labeled with the appropriate expression frequency spacing for the chosen peaks. Do the same for the high frequency side of the spectrum. Suppose you have measured the frequencies in the infrared spectrum of the CO molecule. Determine a suitable choice of a straight line plot that would provide directly (from slope and intercept) the molecular or spectroscopic constants that can be extracted from the infrared spectrum. Sketch such a plot and identify what the slope and intercepts are equal to. An example of an infrared spectrum is shown below:

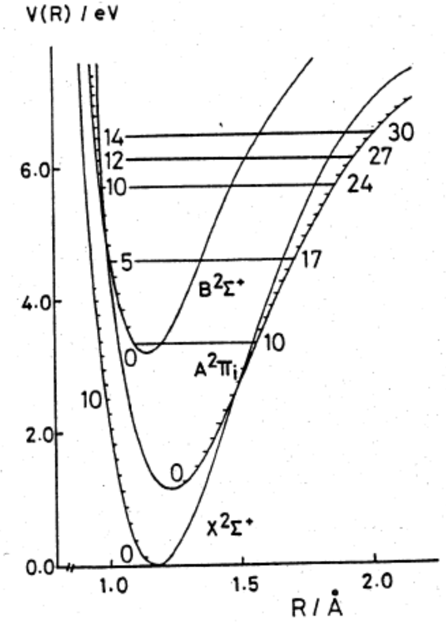


The rotational structure of the v = 0 to v = 1 transition of HBr gas.

3. Derive an expression, in terms of the spectroscopic constants, giving the <u>frequencies of transitions</u> between $v''= 0$ of the ground electronic state of a diatomic molecule and the $v'=0$ of an excited electronic state, accompanied by rotational transitions. An example of such transitions is shown here for CO molecule [from Ubachs et al. J. Mol. Spec. 388-396 (1995)]



Be sure to distinguish the spectroscopic constants of the two electronic states (upper = ′, lower = ″). From your derived expression, determine the <u>frequency spacing between adjacent peaks in the low frequency side of the spectrum in terms of the spectroscopic constants and J_{lower}</u>. Do the same for $v''= 0$ to $v'=1$. CN molecules are found in many extraterrestrial sources such as the Sun, stellar atmospheres, comets, and interstellar clouds. Its violet spectrum (electronic transitions $B^2\Sigma^+ \leftrightarrow$ ground $X^2\Sigma^+$) has also been observed in the laboratory. Suppose you have a list of the measured frequencies in the high resolution (rotational transitions are individually resolved) spectrum of the violet system of CN molecule for $v''= 0$ to $v'=0$, the most intense vibrational progression. Determine a suitable choice of a straight line plot that would provide directly (from slope and intercept) the molecular or spectroscopic constants that can be extracted from this electronic spectrum. Sketch such a plot and identify what the slope and intercepts are equal to. The potential energy curves for the three lowest energy states of CN are shown below: [from Ito et al., J. Mol. Spec. 127, 283-303 (1988)]



Potential energy curves for the $X^2\Sigma^+$, $A^2\Pi_i$, and $B^2\Sigma^+$ states of CN.

4. The rotational Raman spectrum is obtained under the selection rule $\Delta J = \pm 2$. Derive an expression, in terms of the spectroscopic constants and J_{lower}, giving the frequencies of transitions in the rotational Raman spectrum of a diatomic molecule such as $^{14}N_2$. [Since Raman spectroscopy involves measuring the scattered frequency minus exciting frequency, for "frequencies of transitions" use directly the difference, $\nu_{scattered} - \nu_{exciting}$.] Draw a stick diagram of the spectrum and label each peak with values of J_{lower}. Suppose you have measured the frequencies in the rotational Raman spectrum of the $^{14}N_2$ molecule. Determine a suitable choice of a straight line plot that would provide directly (from slope and intercept) the molecular or spectroscopic constants that can be extracted from the rotational Raman spectrum. Sketch such a plot and identify what the slope and intercepts are equal to. An example of rotational Raman data is in problem 1 of Part II below.

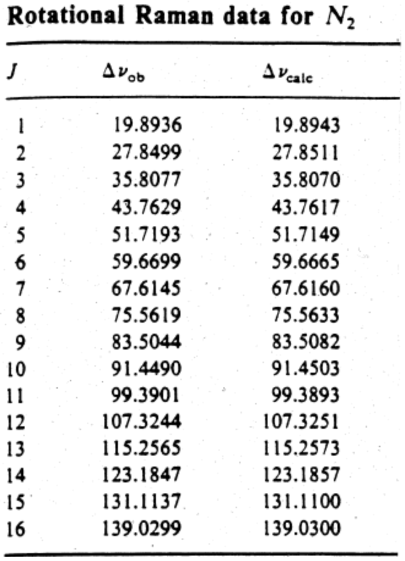
5. The vibrational spacings observed in the emission spectrum of a diatomic molecule from a particular v' ($v'=1$, for example) to various v'' can be used to determine the dissociation energy of the ground electronic state. Draw a sketch of two electronic states with vibrational levels depicted for both. On your sketch, show three electronic transitions, for example $v' = 1$ to $v'' = 2, 3, 4$, measured frequencies are 23549.46 cm^{-1}, 22278.53 cm^{-1}, 21050.85 cm^{-1}. Derive an equation that gives the difference: (23549.46 - 22278.53) cm^{-1}, and another equation that gives the difference (22278.53 - 21050.85) cm^{-1}. Derive the equation that provides the difference $[G_{v''+1} - G_{v''}]$ in terms of the molecular and spectroscopic constants of the molecule and v''. Sketch a plot of such differences (ordinate) against v''(abscissa) from $v'' = 0$ all the way to v''_{max}.

Show on your sketch of two electronic states <u>the sum of all such differences</u> from $v'' = 0$ all the way to v''_{max} .

You will use your derived expressions to find the spectroscopic constants from the observed frequencies in the examples that follow.

Part II

1. Using all the experimental points $\Delta\nu_{ob}$ in the table below, determine B_0 to ± 0.00003 cm^{-1} and D_e to $\pm$ 6x10^{-6} cm^{-1}. $\Delta\nu_{ob} = \nu_{scattered} - \nu_{exciting}$.



Rotational Raman data for N_2

J	$\Delta\nu_{ob}$	$\Delta\nu_{calc}$
1	19.8936	19.8943
2	27.8499	27.8511
3	35.8077	35.8070
4	43.7629	43.7617
5	51.7193	51.7149
6	59.6699	59.6665
7	67.6145	67.6160
8	75.5619	75.5633
9	83.5044	83.5082
10	91.4490	91.4503
11	99.3901	99.3893
12	107.3244	107.3251
13	115.2565	115.2573
14	123.1847	123.1857
15	131.1137	131.1100
16	139.0299	139.0300

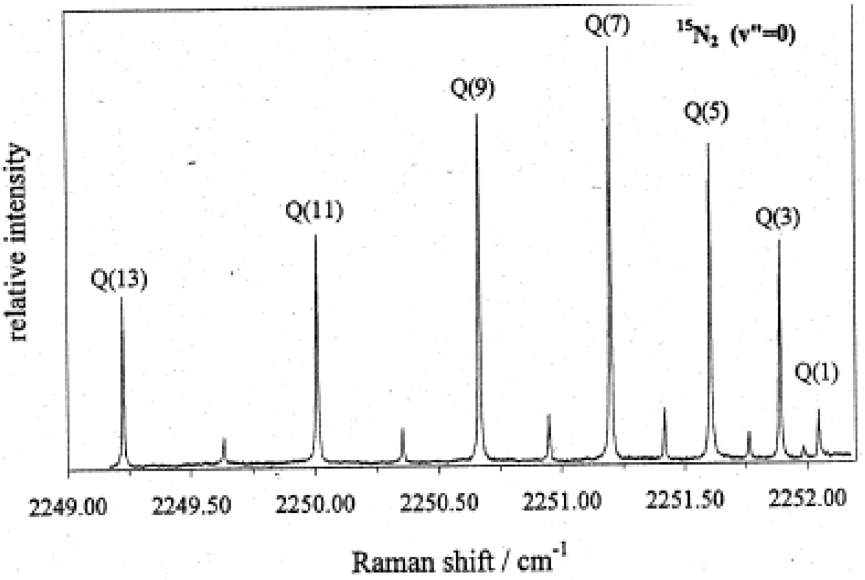
2. The band origins of the $v' - v''$ = 0-1, 0-2, 0-3, ... bands of the Ångstrom system, the spectrum corresponding to the ($B^1\Sigma^+ \leftrightarrow A^1\Pi$) electronic transition in CO molecule, in particular the heavy isotopomer $^{13}C^{18}O$, are shown below, expressed relative to the v = 0 level of the $A^1\Pi$ electronic state, which is 718.43 cm^{-1} above the minimum of the potential energy curve of state $A^1\Pi$. In turn, $A^1\Pi$ is T_e = 65 075.77 cm^{-1} above the ground electronic state of CO. [T_e is measured from the bottom of the ground potential surface to the bottom of the $A^1\Pi$ potential surface.] The rotational constants for each vibrational level is also given.

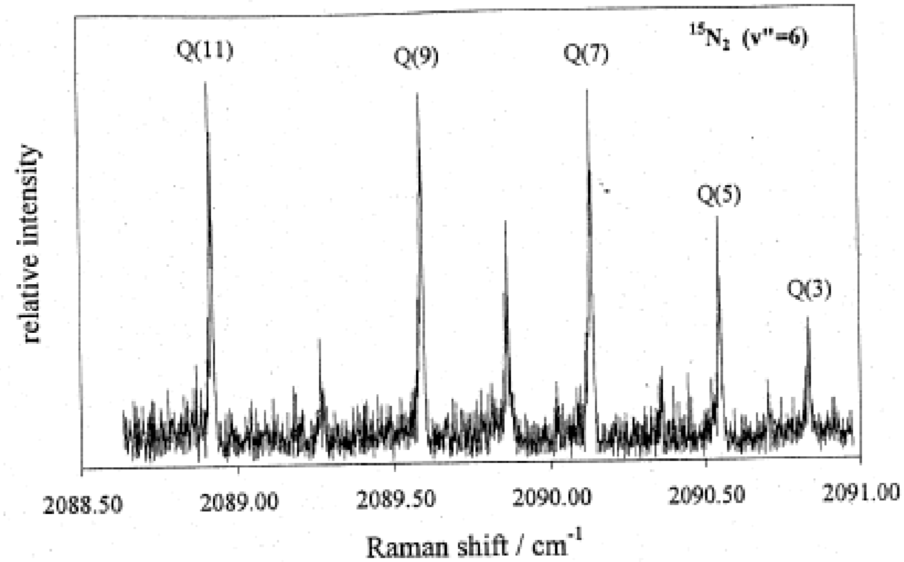
vibrational level	vibrational term cm^{-1}	rotational constants cm^{-1}
0	0.0	1.4574(3)
1	1406.51(4)	1.4366(1)
2	2788.17(4)	1.4173(2)
3	4139.71(4)	1.3931(3)
4	5458.41(4)	1.3772(1)
5	6745.52(4)	1.3561(2)

Data from Prasad and Reddy, J. Mol. Spec. 130, 62-68 (1988)

Make the appropriate fits to straight lines in order to obtain from intercepts and slopes as many precise values of spectroscopic constants from these numbers as you can.

3. In the Raman spectrum of $^{14}N_2$ and $^{15}N_2$ in the electronic ground state, $\Delta J = 0$ (Q bands) and $\Delta J = -2$ (S bands) have been observed [Orlov et al., J. Mol. Spec. 185, 128-141 (1997). Shown below are portions of the Q branch of the $v' \leftarrow v''$: $1 \leftarrow 0$ and $7 \leftarrow 6$, respectively.



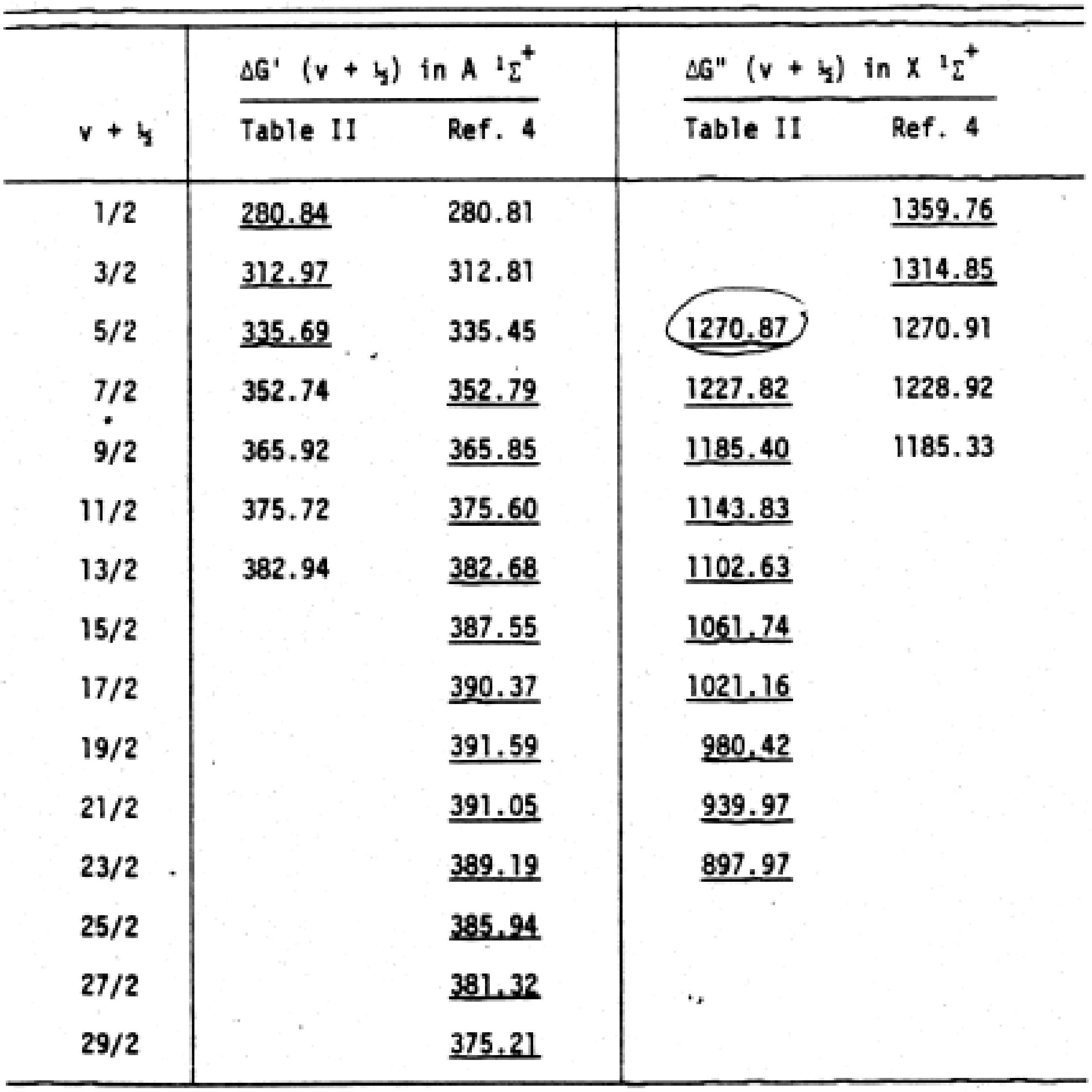


Make an energy level diagram for the energy levels involved and indicate on your diagram the transitions shown in the spectra above, labeling each level with the v and J quantum numbers, and labeling each transition with the same label used by Orlov et al., e.g., Q(11). Discuss why, for $^{15}N_2$ molecule Q(12), Q(10), Q(8), Q(6), Q(4) and Q(2) are so much smaller intensity than the adjacent peaks in the top spectrum ($1 \leftarrow 0$). Ditto for Q(10), Q(8), Q(6), Q(4) and Q(2) in the bottom spectrum ($7 \leftarrow 6$). What do you expect for $^{14}N_2$ molecule? [HINT: Use the Pauli exclusion principle.] Sketch the spectrum for $^{14}N_2$ corresponding to the portion of ($7 \leftarrow 6$) shown for $^{15}N_2$ above.

4. The experimental vibrational spacings $\Delta G'$ and $\Delta G''$ (in cm^{-1}) are given in Table III below for the electronic states $A^1\Sigma^+$ and $X^1\Sigma^+$ of ^{7}LiH. Making use of your answers to no. 5 of Part I of this problems set, make the appropriate plot that will allow you to determine the dissociation energy of the ground $X^1\Sigma^+$ state of ^{7}LiH. You will have to extrapolate your plot because not all the vibrational spacings have been observed. Specify whether you are reporting dissociation energy as D_0 (from the $v'' = 0$ level) or D_e (from the bottom of the potential well).

TABLE III

Average Experimental Vibrational Spacings $\Delta G'$ and $\Delta G''$ (in cm^{-1}) in the $A^1\Sigma^+$ and $X^1\Sigma^+$ States of ^{7}LiH



	$\Delta G'(v+\frac{1}{2})$ in $A\,^1\Sigma^+$		$\Delta G''(v+\frac{1}{2})$ in $X\,^1\Sigma^+$	
$v+\frac{1}{2}$	Table II	Ref. 4	Table II	Ref. 4
1/2	280.84	280.81		1359.76
3/2	312.97	312.81		1314.85
5/2	335.69	335.45	1270.87	1270.91
7/2	352.74	352.79	1227.82	1228.92
9/2	365.92	365.85	1185.40	1185.33
11/2	375.72	375.60	1143.83	
13/2	382.94	382.68	1102.63	
15/2		387.55	1061.74	
17/2		390.37	1021.16	
19/2		391.59	980.42	
21/2		391.05	939.97	
23/2		389.19	897.97	
25/2		385.94		
27/2		381.32		
29/2		375.21		

Note. **Recommended values are underlined.**

How to obtain molecular constants from spectroscopic constants

(1) *If B_e is given in cm^{-1} and masses in amu, how to find the R_e in Å ?*

$$E_{rot} = B_e J(J+1) \quad \text{where } B_e = \frac{\hbar^2}{2\mu R_e^2}$$

$$hcB_e = \frac{\hbar^2}{2} \bullet \frac{1}{\mu R_e^2}$$

$$\underset{\text{cm}^{-1}}{B_e} = \frac{h}{8\pi^2 c} \bullet \underset{\text{amu Å}^2}{\frac{1}{\mu R_e^2}}$$

$$\frac{h}{8\pi^2 c} = \frac{6.62618\text{x}10^{-34}\text{ J s}}{8\pi^2 \text{ x } 3\text{ x}10^8\text{ ms}^{-1}} \bullet \frac{\text{m}^2\text{ kg s}^{-2}}{\text{J}} \bullet \left\lceil \frac{10^{10}\text{ Å}}{1\text{ m}} \right\rfloor^2$$

$$\bullet \frac{6.0224\text{x}10^{23}\text{ amu}}{1\text{ g}} \bullet \frac{10^3\text{ g}}{1\text{ kg}} \bullet \frac{1\text{ m}}{10^2\text{ cm}}$$

$$\frac{h}{8\pi^2 c} = 16.846\text{ amu Å}^2\text{ cm}^{-1}$$

$$\underset{\text{cm}^{-1}}{B_e} = (16.846\text{ amu Å}^2\text{ cm}^{-1}) \bullet \underset{\text{amu Å}^2}{\frac{1}{\mu R_e^2}}$$

(2) *If vibrational frequency ν_e and the U(R) potential energy function are given in cm^{-1} and masses in amu, how to find the second derivative of U(R) at the equilibrium bond length in units of cm^{-1} Å^{-2} ?*

$$hc\nu_e = (h/2\pi)\,[\, U''(R_e) / \mu \,]^{½}$$

$$U''(R_e) = \left\lceil \frac{\partial^2 U(R)}{\partial R^2} \right\rfloor_{R_e} = 4\pi^2\mu c^2 \nu_e^2 \qquad \text{U(R) in joule per molecule}$$

$$\underset{\text{J Å}^{-2}}{U''(R_e)} = \underset{\text{amu (cm}^{-1})^2}{4\pi^2\mu\nu_e^2} \bullet (3\text{x}10^8\text{ m s}^{-1})^2 \bullet \frac{1\text{ kg}}{6.022\text{x}10^{26}\text{ amu}} \bullet \left\lceil \frac{1\text{ cm}}{10^8\text{ Å}} \right\rfloor^2$$

If U(R) is in cm^{-1} , then we want U"(R$_e$) in units of cm^{-1} Å^{-2}. To get this,

$$\underset{\text{cm}^{-1}\ \text{Å}^{-2}}{U''(R_e)} = \frac{4\pi^2\mu\nu_e^2}{hc}$$

$$= \underset{\text{amu cm}^{-1}}{4\pi^2\mu\nu_e^2} \bullet (3\times10^{8}\ \text{m s}^{-1})^2 \bullet \frac{1\ \text{kg}}{6.022\times10^{26}\ \text{amu}} \bullet \left[\frac{1\ \text{cm}}{10^{8}\ \text{Å}}\right]^2 \bullet \frac{1}{6.62618\times10^{-34}\ \text{J s} \times 3\times10^{10}\ \text{cm s}^{-1}} \bullet \frac{1\ \text{J}}{\text{m}^2\ \text{kg s}^{-2}}$$

$$\underset{\text{cm}^{-1}\ \text{Å}^{-2}}{U''(R_e)} = (\ 0.029681\ \text{amu}^{-1}\ \text{cm Å}^{-2}\ ) \bullet \underset{\text{amu}}{\mu}\ \ \underset{(\text{cm}^{-1})^2}{(\nu_e)^2}$$

(3) *If the vibrational-rotational coupling constant frequency α_e is given in cm $^{-1}$ and masses in amu, how to find the third derivative of U(R) at the equilibrium bond length in units of cm $^{-1}$ Å^{-3} ?*

$$\alpha_e = -\frac{2B_e^2}{h\nu_e} \bullet \left[3 + \frac{2B_e\ U'''(R_e)\ R_e^3}{(h\nu_e)^2}\right]$$

Rearrange to find

$$\underset{\text{cm}^{-1}\ \text{Å}^{-3}}{U'''(R_e)} = \left[\frac{\partial^3 U(R)}{\partial R^3}\right]_{R_e} = \underset{\text{dimensionless}}{\left[-\frac{\alpha_e\,\nu_e}{2B_e^2} - 3\right]} \bullet \underset{\text{dimensionless}}{\left[\frac{\nu_e}{2B_e}\right]} \bullet \underset{\text{cm}^{-1}\ \text{Å}^{-3}}{\left[\frac{\nu_e}{R_e^3}\right]}$$

Some conversion factors

$$\underset{\text{J per molecule}}{\Delta E} = h\nu = 6.62618\times10^{-34}\ \text{J s} \bullet \underset{\text{s}^{-1}\ \text{or Hz}}{\nu}$$

$$\underset{\text{J per molecule}}{\Delta E} = 6.62618\times10^{-34}\ \text{J s} \bullet \frac{\text{s}^{-1}}{\text{Hz}} \bullet \frac{10^{6}\ \text{Hz}}{1\ \text{MHz}} \bullet \underset{\text{MHz}}{\nu}$$

$$\underset{\text{J per molecule}}{\Delta E} = hc(1/\lambda) = 6.62618\times10^{-34}\ \text{J s} \bullet 3\times10^{8}\ \text{m s}^{-1} \bullet \frac{10^{2}\ \text{cm}}{1\ \text{m}} \bullet \underset{\text{cm}^{-1}}{(1/\lambda)}$$

1 eV = 8065.46 cm^{-1} 1 eV per molecule = 96, 485 J mol^{-1}