

13.E: Molecular Spectroscopy (Exercises)

These are homework exercises to accompany [Chapter 13](#) of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q13.1

1. Calculate the energy difference for radiation wavenumber of, $\nu = 1.00\text{cm}^{-1}$ including the type of molecular process that absorbs of this radiation corresponding to.
2. Given the wavelength of 3.4×10^{-4} , which molecular process does it fall into?
3. What are other advantages of knowing the spectroscopy of molecules?
4. Do you think the spectroscopy and molecular processes of the molecules have relationship to temperature? Explain.
5. What is other form that you can express in above equation?

Q13.20

The vibrational term of a diatomic molecule is

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2\chi_e\nu_e \quad (13.E.1)$$

Show that the spacing between adjacent levels is given by

$$\Delta G = G(v+1) - G(v) = \nu_e - 2\chi_e\nu_e(v+1)$$

Show that the maximum vibrational quantum number, v_{max} is given by

$$v_{max} = \frac{1}{2\chi_e} - 1 \quad (13.E.2)$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e\chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \quad (13.E.3)$$

Explain how the constants ν_e and χ_e can be evaluated from a plot of ΔG versus $v+1$, called a Birge-Sponer plot. After finding these constants, determine the dissociation energy of the molecule. Use the following experimental data of H_2 to determine the dissociation energy of the molecule.

v	$G(v) / \text{cm}^{-1}$
0	4161.12
1	8087.11
2	11782.35
3	15250.36
4	18497.92
5	21505.65
6	24287.83
7	26830.97
8	29123.93
9	31150.19
10	32886.65
11	34301.83
12	35351.01

v	$G(v) / \text{cm}^{-1}$
13	35972.97

Explain why your plot is not linear for high values of v . How does this dissociation energy differ with the experimental value of 38269.48cm^{-1} .

S13.20

$$\begin{aligned}\Delta G &= G(v+1) - G(v) = \left(v + \frac{3}{2}\right) \nu_e - \left(v + \frac{3}{2}\right)^2 \chi_e \nu_e - \left(v + \frac{1}{2}\right) \nu_e + \left(v + \frac{1}{2}\right)^2 \chi_e \nu_e = \nu_e - \chi_e \nu_e (2v + 2) \\ &= \nu_e - 2\chi_e \nu_e (v + 1)\end{aligned}$$

In the limit that $\Delta G \rightarrow 0$, $v \rightarrow v_{\text{max}}$, solving for v_{max} gives

$$0 = \nu_e - 2\chi_e \nu_e (v_{\text{max}} + 1) \quad (13.E.4)$$

$$2\chi_e (v_{\text{max}} + 1) = 1 \quad (13.E.5)$$

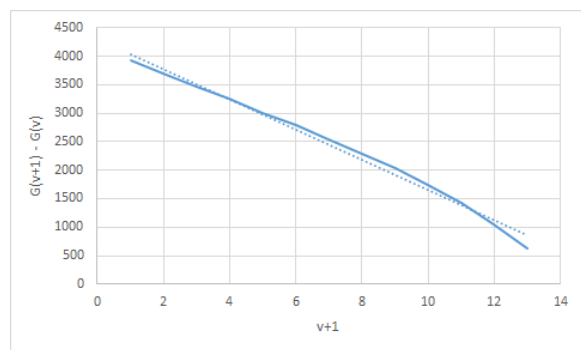
$$v_{\text{max}} = \frac{1}{2\chi_e} - 1 \quad (13.E.6)$$

The molecule dissociates in the limit $\Delta G \rightarrow 0$, so the dissociation energy is given by

$$\begin{aligned}D_e &= G(v_{\text{max}}) = \left(\frac{1}{2\chi_e} - \frac{1}{2}\right) \nu_e - \left(\frac{1}{2\chi_e} - \frac{1}{2}\right)^2 \chi_e \nu_e = \frac{\nu_e}{2\chi_e} (1 - \chi_e) - \frac{\nu_e}{4\chi_e} (1 - \chi_e)^2 \\ &= \frac{\nu_e}{4\chi_e} (2 - 2\chi_e - 1 + 2\chi_e - \chi_e^2) = \frac{\nu_e}{4\chi_e} (1 - \chi_e^2) \approx \frac{\nu_e}{4\chi_e}\end{aligned} \quad (13.E.7)$$

The final step can be made if we assume χ_e to be very small.

Looking at the equation for ΔG , we conclude that a plot of ΔG versus $v + 1$ will have an intercept of ν_e and a slope of $-2\chi_e \nu_e$. The experimental data points for H_2 can be plotted as such:



If we use a best linear fit, we determine that the intercept is $\nu_e = 4164.4 \text{cm}^{-1}$ and the slope is $-2\chi_e \nu_e = -232.01 \text{cm}^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400 \text{cm}^{-1} \quad (13.E.8)$$

The plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function.

Q13.21

An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule Na_2 gives $\tilde{\nu}_e = 159.125 \text{cm}^{-1}$ and $\tilde{\nu}_e \tilde{x}_e = 0.7255 \text{cm}^{-1}$. Suggest an experimental method that can be used to determine these spectroscopic parameters. Use

$\nu_{\text{max}} = \frac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2 .

S13.21

First solve for \tilde{x} :

$$\tilde{x} = \frac{0.7255 \text{ cm}^{-1}}{159.125 \text{ cm}^{-1}} = 4.5593 \times 10^{-3} \text{ cm}^{-1} \quad (13.E.9)$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3} \text{ cm}^{-1}} - 1 = 109.67 \text{ cm}^{-1} \quad (13.E.10)$$

There are 109 bound vibrational levels for the ground state of Ne_2 .

Q13.22

A Morse potential is a decent representation of internuclear potential and is modeled by

$$U(q) = D_e(1 - e^{-\beta q})^2 \quad (13.E.11)$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \quad (13.E.12)$$

If $D_e = 6.23 \times 10^{-19} \text{ J} \cdot \text{Molecule}^{-1}$ and $\beta = 1.37 \times 10^{10} \text{ m}^{-1}$ for a given compound, calculate the force constant for that compound.

S13.22

Using a Maclaurin series expansion of the Morse potential, the formula can be rewritten

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2} O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \quad (13.E.13)$$

We know that

$$U(q) = \frac{kq^2}{2} \quad (13.E.14)$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \quad (13.E.15)$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} \text{ J} \cdot \text{Molecule}^{-1})(1.37 \times 10^{10})^2 = 234 \text{ N} \cdot \text{m}^{-1} \quad (13.E.16)$$

Q13.23

Given that $D_e = 7.33 \times 10^{-19} \text{ J} \cdot \text{molecule}^{-1}$, $\tilde{\nu}_e = 1580.0 \text{ cm}^{-1}$, and $R_e = 121 \text{ pm}$, find k and β for $^{16}\text{O}_2$.

S13.23

Assuming a harmonic oscillator model, we can use the equation:

$$\tilde{\nu}_e = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \quad (13.E.17)$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{\nu}_e)^2 \mu \quad (13.E.18)$$

$$= [2\pi(3 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})(1580.0 \text{ cm}^{-1})]^2 (7.9975 \text{ amu})(1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1}) \quad (13.E.19)$$

$$= 1176.3 \text{ N} \cdot \text{m}^{-1} \quad (13.E.20)$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e} \right)^{1/2} \quad (13.E.21)$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 \text{ N} \cdot \text{m}^{-1}}{2(7.33 \times 10^{-19} \text{ J})} \right]^{1/2} \quad (13.E.22)$$

$$= 2.84 \times 10^{10} \text{ m}^{-1} \quad (13.E.23)$$

Q13.24

The fundamental line in the IR spectrum of $^{12}\text{C}^{16}\text{O}$ is 2143.0 cm^{-1} , and the first overtone occurs at 4260.0 cm^{-1} . Find $\tilde{\nu}_e$ and $\tilde{x}_e\tilde{\nu}_e$ for $^{12}\text{C}^{16}\text{O}$.

S13.24

The equations for the fundamental frequency and the overtone are

$$\tilde{\nu} = \tilde{\nu}_e - 2\tilde{x}_e\tilde{\nu}_e \quad (13.E.24)$$

and

$$\tilde{\nu} = 2\tilde{\nu}_e - 6\tilde{x}_e\tilde{\nu}_e, \quad (13.E.25)$$

respectively.

We can set the fundamental frequency equal to 2143.0 cm^{-1} and the first overtone equal to 4260.0 cm^{-1} which is given from the problem statement. Then, we want to solve for $\tilde{x}_e\tilde{\nu}_e$.

Multiply the fundamental frequency by 3 and subtract the overtone.

$$\tilde{\nu}_e = [3(2143.0) - 4260.0] \text{ cm}^{-1} = 2169.0 \text{ cm}^{-1} \quad (13.E.26)$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{\nu}_e = 13.0 \text{ cm}^{-1} \quad (13.E.27)$$

Q13.24

Which of the following molecules exhibit a microwave rotational absorption spectrum: BF_3 , SO_2 , C_2F_2 , NO_3^-

S13.24

SO_2

notes: microwave rotational absorption correlates to the rotation of polyatomic molecules. Would BF_3 and NO_3^- also fall in this range?

Q13-25 Slightly Incorrect

Calculate the fundamental and the first two overtones of

$$\text{H}^{35}\text{Cl} \quad (13.E.28)$$

given

$$\tilde{\nu}_e = 2990.946 \text{ cm}^{-1} \quad (13.E.29)$$

$$\tilde{x}_e\tilde{\nu}_e = 52.819 \text{ cm}^{-1} \quad (13.E.30)$$

S13-25

Use equation,

$$\nu_{\text{obs}} = \tilde{\nu}_e\nu - \tilde{x}_e\tilde{\nu}_e\nu(\nu + 1) \quad (13.E.31)$$

with $\nu = 1, 2, \dots$

The fundamental frequency is given by $\nu=1$ and the first two overtones are given by $\nu=2$ and $\nu=3$.

Fundamental:

$$\tilde{\nu}_{obs} = \tilde{\nu}_e - 2\tilde{x}_e\tilde{\nu}_e = 2990.946\text{cm}^{-1} - 2(52.819\text{cm}^{-1}) = 2885.308\text{cm}^{-1} \quad (13.E.32)$$

First overtone:

$$\tilde{\nu}_{obs} = 2\tilde{\nu}_e - 6\tilde{x}_e\tilde{\nu}_e = 2990.946\text{cm}^{-1} - 6(52.819\text{cm}^{-1}) = 5664.978\text{cm}^{-1} \quad (13.E.33)$$

Second overtone:

$$\tilde{\nu}_{obs} = 3\tilde{\nu}_e - 12\tilde{x}_e\tilde{\nu}_e = 3(2990.946\text{cm}^{-1}) - 12(52.819\text{cm}^{-1}) = 8339.01\text{cm}^{-1} \quad (13.E.34)$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \quad (13.E.35)$$

versus

$$(\nu + 1) \quad (13.E.36)$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \quad (13.E.37)$$

and

$$x_e\nu_e \quad (13.E.38)$$

for

$$H^35Cl \quad (13.E.39)$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu + 1) \quad (13.E.40)$$

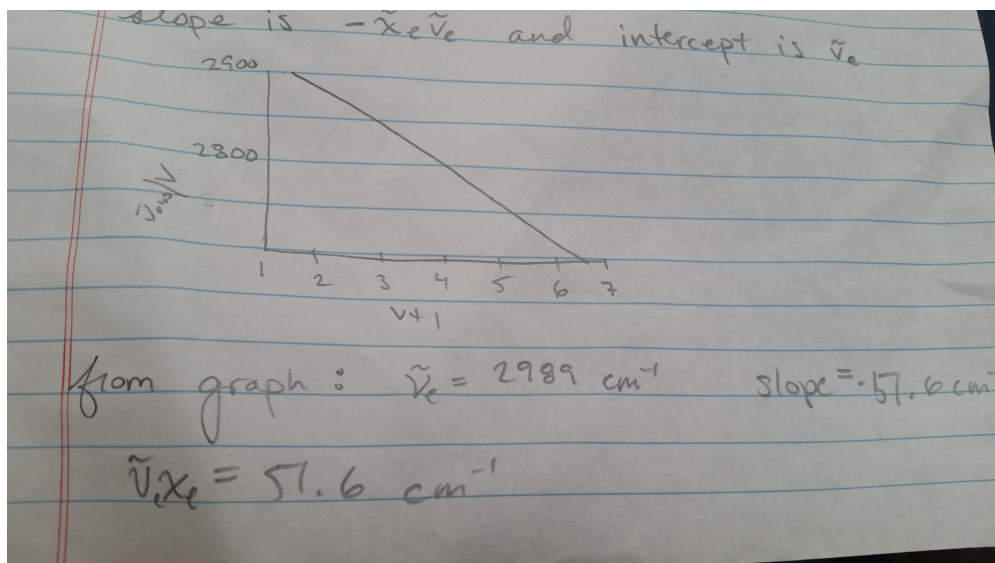
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu + 1) \quad (13.E.41)$$

The slope is

$$-x_e\nu_e \quad (13.E.42)$$

and the intercept is

$$\nu_e \quad (13.E.43)$$



The problem is nice and straight forward. It would be great for an explanation of why the slope is negative for an insight of the graph

Q13.31

Phosphorus nitride (PN) is a heteronuclear diatomic molecule that is similar to N_2 with a triple bond, although is substantially weaker because P is a larger atomic radius than N . Using the following data, calculate $\tilde{\nu}_e'$ and $\tilde{\chi}_e' \tilde{\nu}_e'$ for PN .

IR Transition	$\nu_{abs} [cm^{-1}]$
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\nu_{abs} = \nu_{0,0}' + \tilde{\nu}_e' \nu' - \tilde{\chi}_e' \tilde{\nu}_e' \nu'(\nu' + 1) \quad (13.E.44)$$

Plugging in the appropriate values of ν' , we get:

According to your table $\nu_{0,0}'$ should be 39,699.10 not 29,699.10.

- $\nu' = 0$:

$$\nu_{0,0}' = 39,699.10 \text{ cm}^{-1} \quad (1)$$

- $\nu' = 1$:

$$\nu_{0,0}' + \tilde{\nu}_e' - 2\tilde{\chi}_e' \tilde{\nu}_e' = 40,786.80 \text{ cm}^{-1} \quad (2)$$

- $\nu' = 2$:

$$\nu_{0,0}' + 2\tilde{\nu}_e' - 6\tilde{\chi}_e' \tilde{\nu}_e' = 41,858.90 \text{ cm}^{-1} \quad (3)$$

Solving as a system of equations, we subtract:

$$(2) - (1) = (4), (3) - (1) = (5), \text{ and finally } (5) - 2 \times (4) = (6)$$

Equation (6) can be solved for $\tilde{\chi}_e' \tilde{\nu}_e'$, and then plugged back in to equation (4) or equation (5) to solve for $\tilde{\nu}_e'$. The answer is:

$$\tilde{\chi}_e' \tilde{\nu}_e' = 1103.3 \text{ cm}^{-1} \quad (13.E.45)$$

and

$$\tilde{\nu}_e' = 7.80 \text{ cm}^{-1} \quad (13.E.46)$$

from my calculations $\tilde{\nu}_e' = 1103.3$ and $\tilde{\chi}_e' \tilde{\nu}_e' = 7.80$ it looks like you had them switched

Q13.32

The frequencies of the first few vibronic transitions to an excited state of NaCl* are as follows:

Vibronic Transitions	0 → 0	0 → 1	0 → 2
$\tilde{\nu}_{obs}/\text{cm}^{-1}$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{\nu}_e \tilde{\chi}_e$ for the excited state of NaCl

S13.32

$$A = \tilde{\nu}_e', B = \tilde{\nu}_e' \tilde{\chi}_e'$$

$$12376 = \tilde{\nu}_0, 0$$

$$89706 = \tilde{\nu}_0, 0 + \tilde{\nu}_e' - 2\tilde{\nu}_e' \tilde{\chi}_e' - 12376 = \tilde{\nu}_0, 0 = 77330 = +\tilde{\nu}_e' - 2\tilde{\nu}_e' \tilde{\chi}_e' \quad (1)$$

$$15219 = \tilde{\nu}_0, 0 + 2\tilde{\nu}_e' - 6\tilde{\nu}_e' \tilde{\chi}_e' - 12376 = \tilde{\nu}_0, 0 = 2843 = 2\tilde{\nu}_e' - 6\tilde{\nu}_e' \tilde{\chi}_e' \quad (2)$$

$$77330 + 2B = A \quad (1a)$$

$$2843 = 2A - 6B \quad (2a)$$

$$77330 + 2B = A$$

$$2843 - 154660 = -2B$$

$$B = 75908.5 \text{ cm}^{-1} = \tilde{\nu}_e'$$

$$A = 229147 \text{ cm}^{-1} = \tilde{\nu}_e' \tilde{\chi}_e'$$

Q13.33

Determine the number of translational, rotational, and vibrational degrees of freedom in

- Xe
- HCl
- CS₂
- hemoglobin containing 9272 molecules

The total number of degrees of freedom is $3N$, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N - 5$ vibrational degrees of freedom and a nonlinear molecule has $3N - 6$ vibrational degrees of freedom.

S13.33

The number of translational degrees of freedom is 3, the number of rotational degrees of freedom is 2 for linear molecules and 3 for non-linear molecules. Therefore, the remaining degrees of freedom, which is equal to $3N - 5$ for linear molecules or $3N - 6$ for non-linear molecules, is equal to the number of vibrational degrees of freedom.

	Translation	Rotation	Vibration	Total
Xe	3	0	0	3
HCl	3	2	1	6
CS₂	3	2	4	9

	Translation	Rotation	Vibration	Total
hemoglobin	3	3	27810	27816

Q13.36

Classify each of the following molecules as either a prolate or an oblate symmetric top: XeF_4 , $ClCH_3$, NH_3 , and C_6H_6 .

S13.36

- XeF_4 :oblate
- $ClCH_3$:prolate
- NH_3 :prolate
- C_6H_6 :oblate

Q13.37

Solve for the components of the moment of inertia of a trigonal planar molecule if all the masses are m , the bond lengths are unit length, and all bond angles are 120° .

S13.37

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(\sin^2 30^\circ) = \frac{3}{2}m \quad (13.E.47)$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(\cos^2 30^\circ) = \frac{3}{2}m \quad (13.E.48)$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \quad (13.E.49)$$

Q13.38

This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. Consider a molecule where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively.

Show that

$$I_{xx} = 2 \cos^2 \theta + 8 \sin^2 \theta \quad (13.E.50)$$

$$I_{yy} = 8 \cos^2 \theta + 2 \sin^2 \theta \quad (13.E.51)$$

$$I_{xy} = -6 \cos \theta \sin \theta \quad (13.E.52)$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \quad (13.E.53)$$

and compare the result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and coordinate system such that $\theta = 180^\circ$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 90^\circ$?

S13.38

We use trigonometric functions to find the x and y components

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2 \sin \theta)^2 + 2(1) \left[\sin\left(\frac{\pi}{2}\right) - \theta \right]^2 = 8 \sin^2 \theta + 2 \cos^2 \theta \quad (13.E.54)$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2 \cos \theta)^2 + 2(1) \left[\cos\left(\frac{\pi}{2}\right) - \theta \right]^2 = 8 \cos^2 \theta + 2 \sin^2 \theta \quad (13.E.55)$$

$$I_{xy} = - \sum m_i x_i y_i = -(2 \cos \theta)(2 \sin \theta) - 2 [\cos(\pi) + \theta] [\sin(\pi) + \theta] - \left[\sin\left(\frac{\pi}{2}\right) - \theta \right] \left[\cos\left(\frac{\pi}{2}\right) - \theta \right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta \right] \left[\sin\left(\frac{\pi}{2}\right) + \theta \right] \quad (13.E.56)$$

$$= -6 \cos \theta \sin \theta$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8 \sin^2 \theta + 2 \cos^2 \theta - \lambda & -6 \cos \theta \sin \theta \\ -6 \cos \theta \sin \theta & 8 \cos^2 \theta + 2 \sin^2 \theta - \lambda \end{vmatrix} = 0 \quad (13.E.57)$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin^2 \theta + \cos^2 \theta) + 16(\sin^2 \theta + \cos^2 \theta)^2 \quad (13.E.58)$$

$$0 = \lambda^2 - 10\lambda + 16 \quad (13.E.59)$$

$$\lambda = 5 \pm 3 \quad (13.E.60)$$

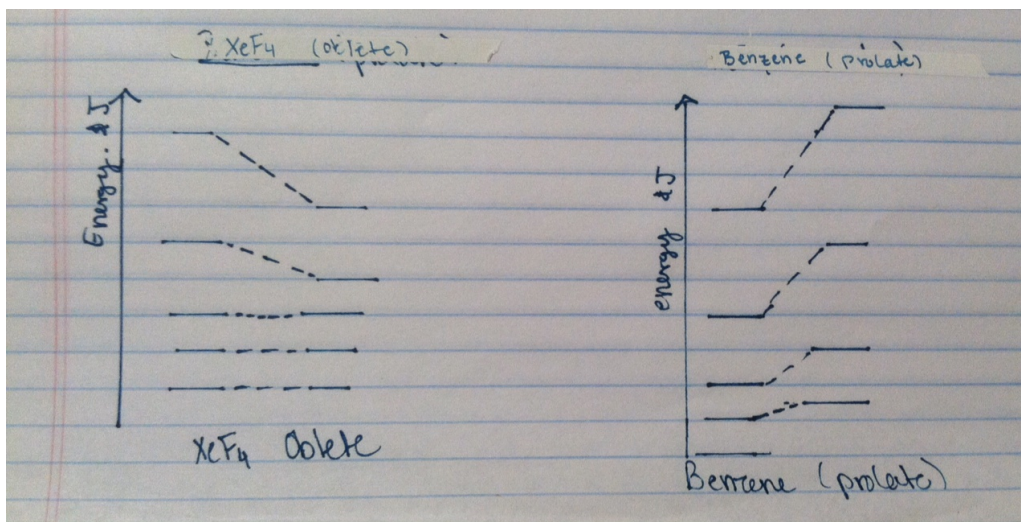
If $\theta = 180^\circ$ then $I_{xx} = 2$, $I_{yy} = 8$, and $I_{xy} = 0$. If $\theta = 90^\circ$ then $I_{xx} = 8$, $I_{yy} = 2$, and $I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

Q13.39

Sketch the energy level diagram of NH_3 (a prolate symmetric top molecule) and XeF_4 (an oblate symmetric top). How do they differ?

S13.39

The energies increase as the J levels increases for the prolate symmetry and the energies decrease as J increases for the oblate symmetry



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