Chemistry 332 **Assignment #7** (due Monday 15, March, in class)

Q1. H_3^+ is believed to be the most abundant polyatomic molecule in the universe. But studying the properties of H_3^+ is difficult under lab conditions because the molecule is unstable and decomposes rapidly in collisions with other molecules or with the walls of spectroscopy cells. As a result, the correct structure of H_3^+ (linear or cyclic) was unknown for many years.

For linear H_3^+, the Huckel determinantal equation gives the energy levels:

$$\alpha+\sqrt{2}\beta \qquad \alpha \qquad \alpha-\sqrt{2}\beta$$

[3] For triangular H_3^+, the energy levels are:

$$\alpha+2\beta \qquad \alpha-\beta \qquad \alpha-\beta$$

a) Which H_3^+ structure, linear or cyclic, is predicted to be more stable? Explain.

b) Describe how IR spectroscopy could be used to determine whether H_3^+ is linear or cyclic.

c) Based on experimental evidence, which H_3^+ structure, linear or cyclic, is more stable?

Q2. **a)** Use Huckel theory to calculate the π-electron energy of cyclobutadiene in terms of α and β.

b) Does π-electron delocalization stabilize cyclobutadiene? Justify your answer.

[6] **c)** Is the ground-state cylcobutadiene molecule a singlet state? Or a triplet state? Explain.

d) Estimate the wavelength of the photon required to raise ground state cyclobutadiene to the lowest energy excited π-electron state. Use $\beta = -75$ kJ mol^{-1}.

Q3. In Chem 331, we used the Schrodinger equation $\hat{H}\psi = E\psi$ to develop a basic understanding of the quantum mechanics of free particles, confined particles, harmonic oscillators, rotators, and
[1] hydrogen-like atoms. Why is this Schrodinger equation inadequate for spectroscopic studies?

Q4. In Chem 332, we use $E_{0z}(\mu_z)_{21}\left[\dfrac{1-e^{i(E_2-E_1+h\nu)t/\hbar}}{E_2-E_1+h\nu}+\dfrac{1-e^{i(E_2-E_1-h\nu)t/\hbar}}{E_2-E_1-h\nu}\right]$ to estimate the probability of a spectroscopic transition from state 1 to state 2.

a) How can this result be used to predict absorption frequencies?

b) How can this result be used to predict absorption frequencies?

[2] **c)** What is E_{0z}?

d) What is $(\mu_z)_{21}$?

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Q5. **a)** In Chem 331, we used the **harmonic potential energy** $V(x) = kx^2/2$ to analyze the quantum mechanics of molecular vibration. x is the displacement from the equilibrium bond length and k is the force constant.

To analyze high-resolution vibrational spectra, the **Morse potential** $U(x) = D_e(1 - e^{-\beta x})^2$ is frequently used instead. Show the force constant calculated for a Morse potential is $k = 2D_e\beta^2$.

[4] **b)** In the limit $x \rightarrow \infty$, show $U(x) = D_e$.

c) As $x \rightarrow -\infty$, show $U(x) \rightarrow \infty$.

d) On the same graph, sketch the harmonic potential $V(x)$ and Morse potential $U(x)$. Use the sketch to explain why the Morse potential gives a better representation of the internuclear potential energy and vibrational spectra than the harmonic potential.

Q6. High-resolution vibrational spectroscopy for $H^{35}Cl$ gives

transition	$\tilde{\nu}_{0\rightarrow n}$ / cm^{-1}
$0 \rightarrow 1$ (fundamental)	2885.9
$0 \rightarrow 2$ (first overtone)	5668.0
$0 \rightarrow 3$ (second overtone)	8347.0
$0 \rightarrow 4$ (third overtone)	10,923.1
$0 \rightarrow 5$ (fourth overtone)	13,396.5

a) Give two reasons why the transition frequencies show $H^{35}Cl$ is anharmonic oscillator.

[4] **b)** The Morse potential gives the energy levels

$$\tilde{E}_n = \tilde{\nu}_e\left(n+\frac{1}{2}\right) - x_e\tilde{\nu}_e\left(n+\frac{1}{2}\right)^2 \qquad n = 0, 1, 2, 3, \ldots$$

an **anharmonic oscillator**. x_e is the anharmonic constant. For the anharmonic oscillator, show the frequency of the $n = 0$ to n transition is

$$\tilde{\nu}_{0\rightarrow n} = n\tilde{\nu}_e - x_e\tilde{\nu}_e n(n+1) \qquad n = 1, 2, 3, \ldots$$

c) Calculate the fundamental frequency $\tilde{\nu}_e$ and the anharmonic constant x_e for $H^{35}Cl$ using the measured transition frequencies. *Suggestion*: Plot $\tilde{\nu}_{0\rightarrow n} / n$ against $n + 1$.

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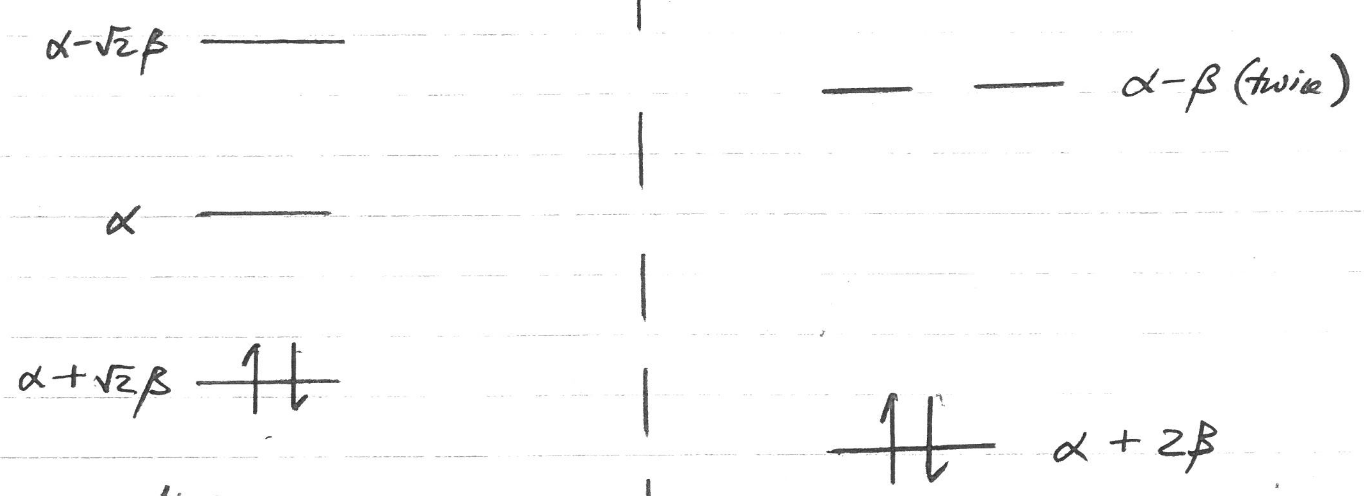
(Q1) a) Linear H_3^+ | Triangular H_3^+



linear
π electron energy
$= 2(\alpha+\sqrt{2}\beta)$

triangular
π electron energy
$= 2(\alpha+2\beta)$

$$E_{linear} - E_{triangular} = 2(\cancel{\alpha}+\sqrt{2}\beta) - 2(\cancel{\alpha}+2\beta)$$

$$= (2\sqrt{2}-4)\beta$$

$$= -1.17\beta \approx -1.17(-75 \text{ kJ mol}^{-1})$$

$$= +87.9 \text{ kJ mol}^{-1}$$

linear H_3^+ is predicted to have higher energy ($\therefore$ less stable)

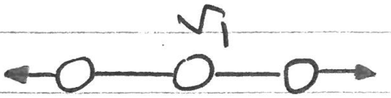
b) IR spectra of H_3^+

if linear: $3N-5 = 3(3)-5 = 4$ normal-mode vibrations (similar to CO_2)

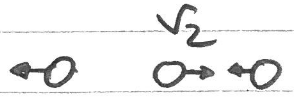
if triangular (nonlinear): $3N-6 = (3)(3)-6 = 3$ normal-mode vibrations (similar to H_2O)

(Q1 b cont.)

linear H_3^+ normal vibration modes (4)

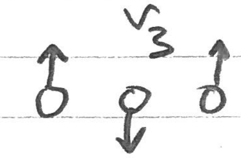


symmetric stretch
(no change in the dipole moment → IR inactive)



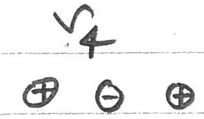
asymmetric stretch

IR active



bending

IR active



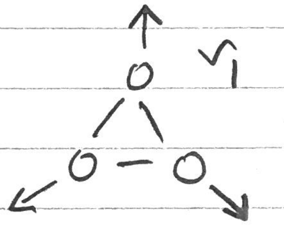
bending (rotated 90°)

IR active

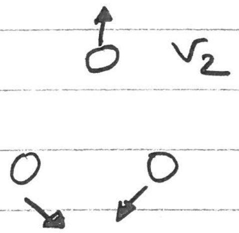
Four normal modes, but ν_1 is IR inactive.
Also, bending vibrations are degenerate $\nu_3 = \nu_4$.

predict: <u>two IR bands</u> ν_2 and $\nu_3 = \nu_4$

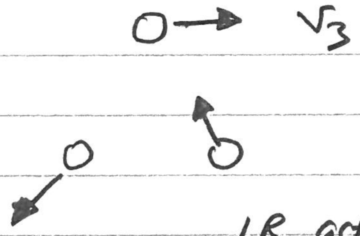
triangular H_3^+ normal vibration modes (3)



IR inactive



IR active



IR active

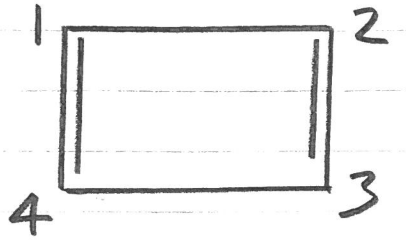
two IR active vibrations ν_2 and ν_3
but degenerate (rotated by 120°): $\nu_2 = \nu_3$

predict <u>one IR band</u> $\nu_2 = \nu_3$

c) In 1980, the IR spectrum of H_3^+ was finally measured.
<u>one band!</u>

∴ triangular

②Q2 Huckel theory for cyclobutadiene



4 p_z orbitals
on carbon atoms
1, 2, 3, 4

determinantal
equation
$\left(x = \frac{\alpha - E}{\beta}\right)$

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

$$0 = x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} . - 1 \begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix}$$

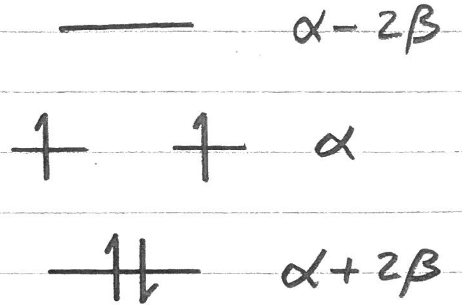
$$0 = x(x^3 - 2x) - (x^2 + 1 - 1) - (1 + x^2 - 1)$$

$$0 = x^4 - 2x^2 - x^2 - x^2$$

$$0 = x^4 - 4x^2 = \underbrace{(x^2 - 2x)}_{\boxed{x = 0, 2}} \underbrace{(x^2 + 2x)}_{\boxed{x = 0, -2}}$$

$$x = \frac{\alpha - E}{\beta} = -2, 0, 0, 2$$ (four roots)

(Q2 a cont.)



π - electron energy

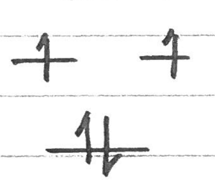
$$E_{\pi} = 2(\alpha + 2\beta) + 2\alpha$$
$$= 4\alpha + 4\beta$$

b) delocalization energy = E_{π}(cyclobut.) − $2E_{\pi}$(ethylene)

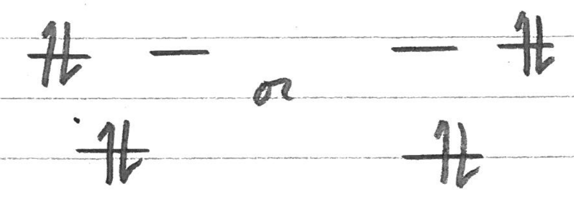
$$= 4\alpha + 4\beta - 2(2\alpha + 2\beta)$$

$$= 0$$

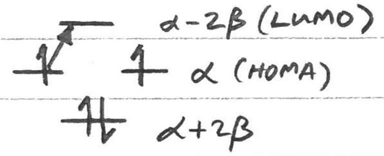
c) using Hund's Rule #1, a triplet (two unpaired electrons) is predicted



lower in energy than



d)



α (HOMO) → α−2β (LUMO)

$$\Delta E = h\nu = -2\beta = \frac{150 \text{ kJ mol}^{-1}}{\text{Avogadro No.}}$$

$$\Delta E = \frac{150 \text{ kJ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.49 \times 10^{-19} \text{ J} = h\nu$$

frequency $\nu = 3.76 \times 10^{14} \text{ s}^{-1}$

wavelength $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8} \text{ m s}^{-1}}{3.76 \times 10^{14} \text{ s}^{-1}} = 798 \text{ nm}$

Ⓠ3 $\hat{H}\psi = E\psi$ applies to systems with constant, time-independent energy E, as in a "stationary" wave.

In spectroscopic transitions, photons can be absorbed or emitted, producing time-dependent wave functions described by the time-dependent Schrodinger equation

$$\hat{H}\,\Psi(\vec{r},t) = i\hbar\,\frac{\partial \Psi(\vec{r},t)}{\partial t}$$

Ⓠ4 the probability of a 1 → 2 transition is proportional to

$$E_{0z}(\mu_z)_{21}\left[\frac{1-e^{i(E_2-E_1+h\nu)t/\hbar}}{E_2-E_1+h\nu} + \frac{1-e^{i(E_2-E_1-h\nu)t/\hbar}}{E_2-E_1-h\nu}\right]$$

a) for absorption, $E_2 > E_1$ and $E_2-E_1-h\nu = 0$ gives ∞ for the second term [$h\nu = E_2 - E_1$]

b) For emission, $E_2 < E_1$ and $E_2-E_1+h\nu = 0$ gives ∞ for the first term [$h\nu = E_1 - E_2$]

c) E_{0z} is the magnitude of the electric field oscillation provided by the radiation at frequency ν

d) $(\mu_z)_{12}$ is the transition dipole moment $\int \psi_2^* \hat{H}^{(1)} \psi_1 \, d\tau$ linking the two states

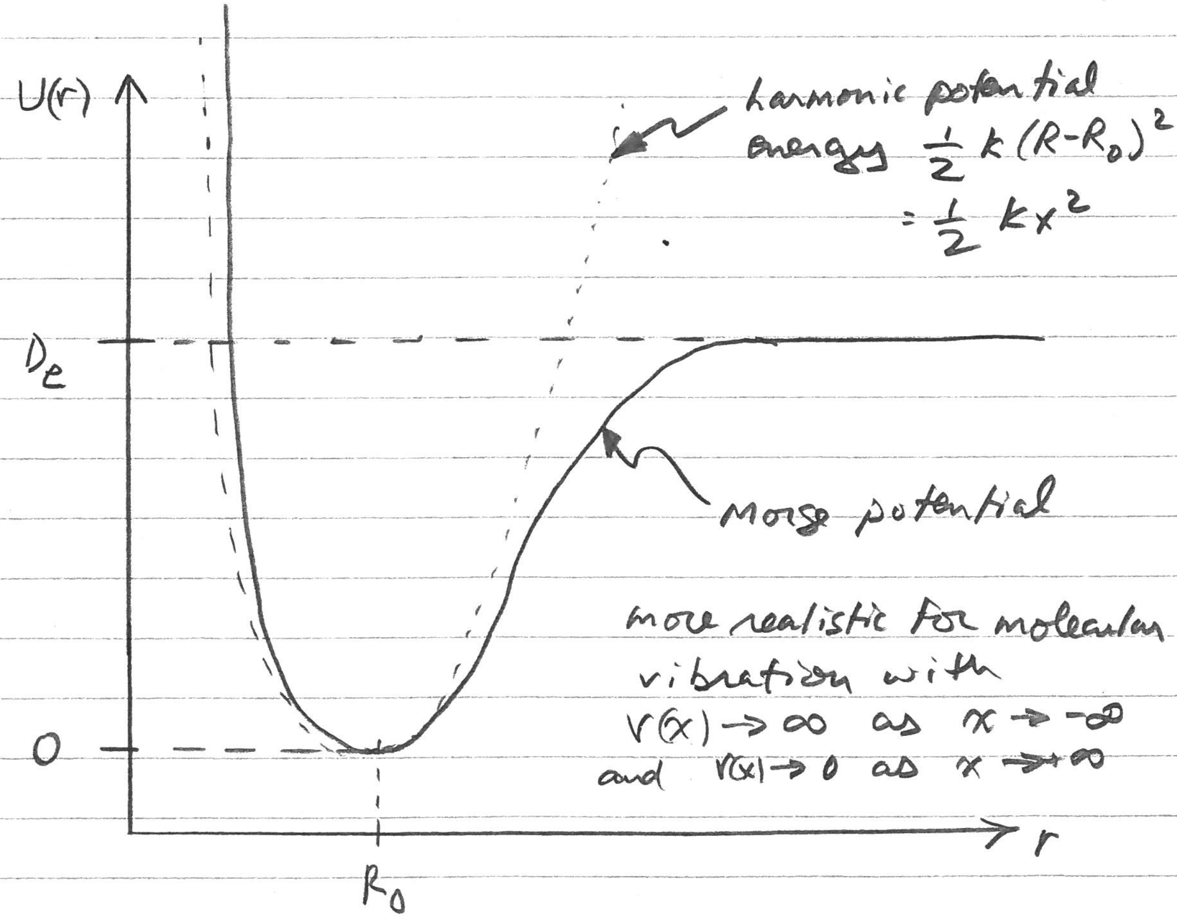
Ⓠ5 a) the harmonic potential energy $V(x) = \frac{1}{2}kx^2$ is an approximation (a pretty good one!) when applied to the vibration of molecules

b) Morse potential energy $U(r) = D_e\left(1 - e^{-\beta x}\right)^2$

as $x \to +\infty$, $e^{-\beta x} \to 0$ and $U \to D_e$

c) as $x \to -\infty$, $e^{-\beta x} \to \infty$ and $U \to \infty$

d)



harmonic potential energy $\frac{1}{2}k(R-R_0)^2$
$= \frac{1}{2}kx^2$

Morse potential

more realistic for molecular vibration with
$V(x) \to \infty$ as $x \to -\infty$
and $V(x) \to 0$ as $x \to +\infty$

gives energy spacing $h\nu$

Q6 a) for harmonic oscillators:

the energy levels are $E_n = (n+\frac{1}{2})h\nu \qquad n=0,1,2,3,\ldots$

and the <u>selection rule</u> for absorption is $\Delta n = 1$

#1 n = 0 to n = 1 is allowed, but the observed overtones (0→2, 0→3, 0→4, 0→5) are forbidden for a harmonic oscillator

#2 the energy levels of a harmonic oscillator are equally spaced, but for $H^{35}Cl$:

a) $\tilde{\nu}_{0\to1} = 2885.9 \text{ cm}^{-1}$

$\tilde{\nu}_{1\to2} = \tilde{\nu}_{0\to2} - \tilde{\nu}_{0\to1} = 5668.0 - 2885.9 = 2782.1 \text{ cm}^{-1}$

energy levels for $H^{35}Cl$ are not equally spaced

b) $$\tilde{E}_n = \tilde{\nu}_e\left(n+\frac{1}{2}\right) - x_e\tilde{\nu}_e\left(n+\frac{1}{2}\right)^2$$

$$\tilde{\nu}_{0\to n} = \tilde{E}_n - \tilde{E}_0 = \tilde{\nu}_e(n+1/2) - x_e\bar{\nu}_e\left(n+\frac{1}{2}\right)^2 - \nu_e\frac{1}{2} + x_e\tilde{\nu}_e\left(\frac{1}{2}\right)^2$$

$$= n\tilde{\nu}_e - x_e\bar{\nu}_e\left[\left(n+\frac{1}{2}\right)^2 - \left(\frac{1}{2}\right)^2\right]$$

$$= n\tilde{\nu}_e - x_e\tilde{\nu}_e(n^2+n)$$

$$= n\tilde{\nu}_e - x_e\tilde{\nu}_e\, n(n+1)$$

(Q6 cont.)

c) $\frac{\tilde{\nu}_{0\to n}}{n} = \tilde{\nu}_e - x_e \tilde{\nu}_e (n+1)$

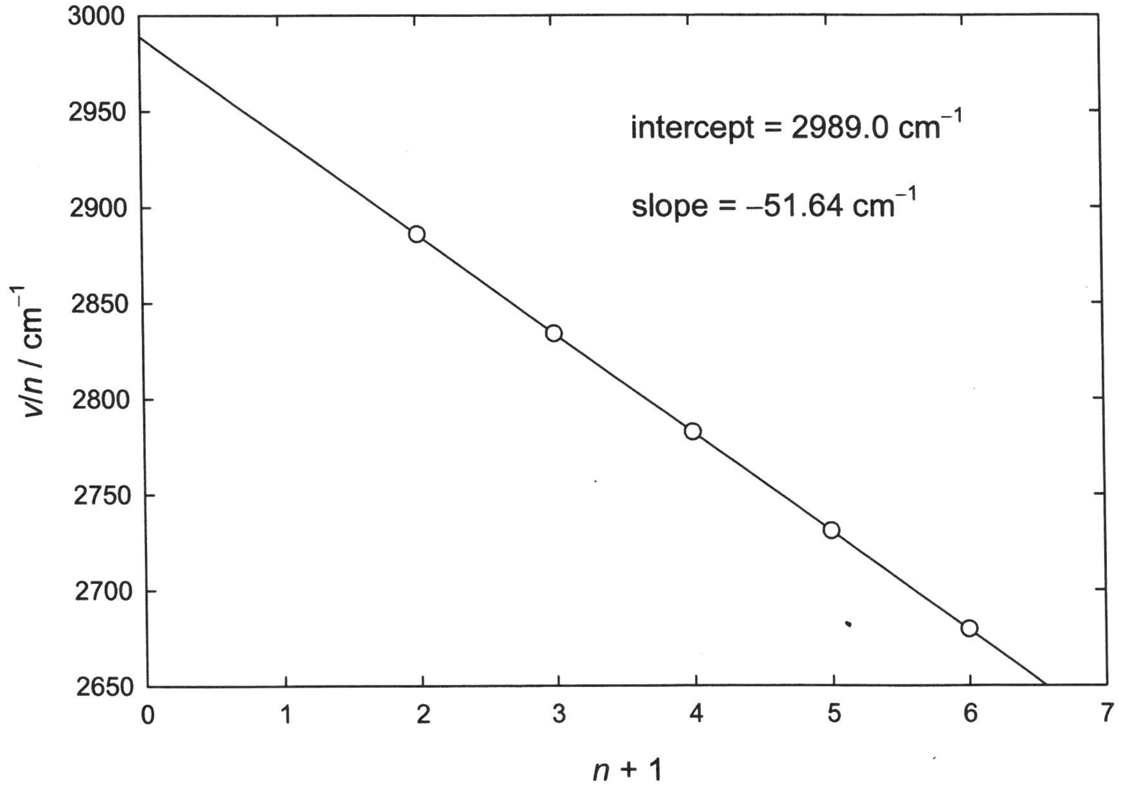
plot $\frac{\tilde{\nu}_{0\to}}{n}$ against n, should be a linear plot

with intercept $\tilde{\nu}_e$ and slope $-x_e \tilde{\nu}_e$

find intercept $= \tilde{\nu}_e = 2989.0 \text{ cm}^{-1}$

slope $= -x_e\tilde{\nu}_e = -51.64 \text{ cm}^{-1}$

anharmonic parameter $x_e = -\frac{\text{slope}}{\tilde{\nu}_e} = \frac{51.64 \text{ cm}^{-1}}{2989.0 \text{ cm}^{-1}} = 0.0173$


intercept = 2989.0 cm^{-1}
slope = –51.64 cm^{-1}
v/n / cm^{-1}
3000
2950
2900
2850
2800
2750
2700
2650
0
1
2
3
4
5
6
7
n + 1