

Name: KEY

**Chemistry 312**  
**Test 3**  
**May 1, 2008**

Instructions before starting the test:

1. Your exam booklet should have **eight pages** total, with questions on Pages 2-6, a periodic table, equations, and constants on Page 7, and a table of nuclei masses on Page 8. Check to see you have eight pages now. If you do not, ask for another copy of the exam.
2. Write your name in the space above and on the backs of Pages 2-6.
3. You may carefully remove Pages 7-8 from your exam booklet.
4. You may fill both sides of an 8.5" x 11" sheet of paper with whatever information you would like, and refer to it during the exam.
5. You should always demonstrate your thought process in writing unless told not to. You will be awarded credit only for work I can decipher.
6. You have a maximum of **3 hours** to work on this exam.

<u>Page (Possible Points)</u>	<u>Your Score</u>
Page 2 (20)	
Page 3 (18)	
Page 4 (20)	
Page 5 (18)	
Page 6 (24)	
Total (100)	
Average of Tests 1, 2, and 3	
<u>Estimated Grade</u>	

mean 76  
median 78

1. We have considered the biochemical significance of nitric oxide (NO). Imagine a molecule of  $^{14}\text{N}^{16}\text{O}$  lying on the z-axis with its center of mass at  $z = 0$ , with the N at  $z < 0$  and the O at  $z > 0$ . Spectroscopy reveals that  $^{14}\text{N}^{16}\text{O}$  has a rotational constant of  $1.67195 \text{ cm}^{-1}$ .

(a) (20 points) Calculate the coordinates (in Å) of the N and the O nuclei. Assume that the vibrational and rotational states of the molecule have no impact on your calculation.

$$B = \frac{h}{8\pi^2 c \mu R^2} \Rightarrow R = \sqrt{\frac{h}{8\pi^2 c \mu B}}$$

$$\mu = \frac{m_N m_O}{m_N + m_O} = \frac{(14.0031)(15.9949) \text{ u}}{14.0031 + 15.9949} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{\text{u}} \right)$$

$$\mu = 1.239832 \times 10^{-26} \text{ kg}$$

$$\text{so } R = \left[ \frac{(6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(\text{kg m}^2 \text{ s}^{-2} \text{ J}^{-1})}{8\pi^2 (2.99792 \times 10^{10} \text{ cm s}^{-1})(1.239832 \times 10^{-26} \text{ kg})(1.67198 \text{ cm}^{-1})} \right]^{1/2}$$

$$R = 1.162065 \times 10^{-10} \text{ m} = \underline{1.162065 \text{ \AA}}$$

$$\text{and } z_{\text{cm}} = \frac{m_N}{m_N + m_O} z_N + \frac{m_O}{m_N + m_O} z_O = 0 \quad \text{and } -z_N + z_O = R$$

or  $z_N = z_O - R$

$$\text{so } \frac{m_N}{m_N + m_O} (z_O - R) + \frac{m_O}{m_N + m_O} z_O = \frac{m_N + m_O}{m_N + m_O} z_O - \frac{m_N}{m_N + m_O} R = 0$$

$$\Rightarrow z_O = \frac{m_N}{m_N + m_O} R = \frac{14.0031}{14.0031 + 15.9949} (1.162065 \text{ \AA}) = \underline{0.542453 \text{ \AA}}$$

$$\text{and } z_N = 0.542453 \text{ \AA} - 1.162065 \text{ \AA} = \underline{-0.61961 \text{ \AA}}$$

$$\text{so } \boxed{\text{N is at } (0, 0, -0.61961 \text{ \AA})} \quad \text{and} \quad \boxed{\text{O is at } (0, 0, 0.542453 \text{ \AA})}$$

- 1 sig fig error

- 3 didn't use masses on p. 8

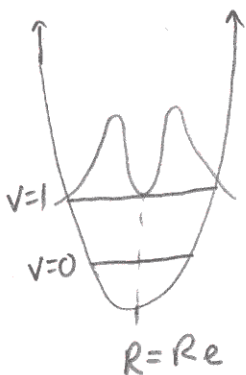
- 4 math error

- 4 Wrong sign

(-6) incorrect solving for  $z_N$  and  $z_O$

[Question 1 continues on the next page.]

- (b) (14 points) Say that the  $^{14}\text{N}^{16}\text{O}$  is in the  $v = 1$  state and behaves as a harmonic oscillator. How does this consideration of vibration make your answers in part (a) problematic? Be qualitative but specific, using both words and drawings. (However, your answer does not need to fill this entire space to receive full credit!)



1st, the probability of a given distance btm the nuclei is represented by  $\Psi_v^*(R) \Psi_v(R)$ , as plotted to the left. I.e. there is no 1 precise distance as implied by the calculation in (a).

Moreover, in the  $v=1$  state,  $\Psi_v(R_e) = 0$

(ie there is a node at  $R=R_e$ ), making it impossible that the  $^{14}\text{N}$  and  $^{16}\text{O}$  are ever at the coordinates calculated in (a)

- max  
-12  
for  
all 3  
errors
- (-4) no discussion of node at  $R=R_e$
  - (-4) assertion that  $R_e \uparrow$  from  $v=0$  to  $v=1$  (not true under HO model)
  - (-5) no discussion of uncertainty in  $R$
  - (-4) no plot of  $V(R)$

- (c) (4 points) Draw arrows on the Lewis structure below to represent the vibration of  $^{14}\text{N}^{16}\text{O}$ . Be sure that the "displacement vectors" you draw have the correct relative lengths. You do not need to explain your drawing.



[N moves further because it's lighter]

2. The molecule  $^1\text{H}^{35}\text{Cl}$  has a wavenumber of  $\tilde{\nu} = 2991 \text{ cm}^{-1}$ , an anharmonicity of  $x_e = 1.765 \times 10^{-3}$ , an equilibrium bond length of  $R_e = 1.2746 \text{ \AA}$ , and a well depth of  $D_e = 3.576 \times 10^4 \text{ cm}^{-1}$ . For the following questions, you should assume that  $^1\text{H}^{35}\text{Cl}$  behaves as a non-rigid rotor and a Morse oscillator unless told otherwise.

- (a) (10 points) Consider 1.000 mol of  $^1\text{H}^{35}\text{Cl}$  at  $T = 0 \text{ K}$ . Calculate the minimum amount of energy (in kJ) required to dissociate the entire sample of  $^1\text{H}^{35}\text{Cl}$  into  $^1\text{H}$  and  $^{35}\text{Cl}$  atoms.

$$\begin{aligned}
 D_0 &= D_e - \text{ZPE} = D_e - \left( \frac{1}{2} \tilde{\nu} - \frac{1}{4} x_e \tilde{\nu} \right) \quad (\text{ZPE} \equiv G(v=0)) \\
 &= D_e - \tilde{\nu} \left( \frac{1}{2} - \frac{1}{4} x_e \right) \\
 &= 35760 \text{ cm}^{-1} - (2991 \text{ cm}^{-1}) \left( \frac{1}{2} - \frac{1}{4} (1.765 \times 10^{-3}) \right) \\
 &= (35760 \text{ cm}^{-1} - 1494.2 \text{ cm}^{-1}) \left( \frac{96.485 \text{ kJ mol}^{-1}}{8065.5 \text{ cm}^{-1}} \right) (1.000 \text{ mol})
 \end{aligned}$$

$$\boxed{D_0 = 409.9 \text{ kJ}}$$

-1 sig fig error  
-4 wrong units  
-5 no or incorrect correction for ZPE

-9 wrong model

- (b) (10 points) The most probable "hot band" vibrational transition for HCl is  $v=2 \leftarrow v=1$ . Calculate the wavenumber (in  $\text{cm}^{-1}$ ) of the photon that would drive such a transition.

$$\begin{aligned}
 \tilde{\nu}_{\text{photon}} &= G(2) - G(1) = \frac{5}{2} \tilde{\nu} - \left( \frac{5}{2} \right)^2 x_e \tilde{\nu} - \frac{3}{2} \tilde{\nu} + \left( \frac{3}{2} \right)^2 x_e \tilde{\nu} \\
 &= \tilde{\nu} - \frac{25}{4} x_e \tilde{\nu} + \frac{9}{4} x_e \tilde{\nu} \\
 &= \tilde{\nu} [1 - 4 x_e] \\
 &= 2991 \text{ cm}^{-1} [1 - 4 (1.765 \times 10^{-3})] \\
 &= \boxed{2969.9 \text{ cm}^{-1}}
 \end{aligned}$$

-1 sig fig error

-6 some work

-5 confusion b/tm  $\tilde{\nu}_{\text{molecule}}$  and  $\tilde{\nu}_{\text{photon}}$

[Question 2 continues on the next page.]

- (c) (8 points) The hot band transition considered in part (b) is not observed in our FTIR experiment. Give one reason why not. (You should be qualitative, but specific.)

For vibrational-sized  $\Sigma$  gaps,  $\frac{n_0}{N} \approx 1$  and  $\frac{n_1}{N} \approx 0$ .

Since virtually no molecules are in the  $V=1$  state at room T, we won't see their excitation to the  $V=2$  state.

-3 vague

-7 blaming computer program systematic error

OK  $\left\{ \begin{array}{l} \Delta J \text{ can't be zero. (Nothing is said about } \Delta J \text{ here)} \\ \text{or the } \underline{v} \text{ vibrational state must change} \end{array} \right.$

-6 Selection rule for  $\Delta V$  violated

- (d) (10 points) Calculate a numerical value for the second derivative of  $^1\text{H}^{35}\text{Cl}$ 's potential energy with respect to  $R$  evaluated at  $R = 1.0 \text{ \AA}$  assuming that  $^1\text{H}^{35}\text{Cl}$  behaves as a harmonic oscillator. Report your answer in units of  $\text{kg s}^{-2}$ .

$$\frac{d^2 V}{dR^2} = k \quad (\text{i.e. not a function of } R!) \quad \text{and} \quad 2\pi c \tilde{\nu} = \sqrt{\frac{k}{\mu}}$$

$$\Rightarrow k = 4\pi^2 c^2 \mu \tilde{\nu}^2$$

$$\text{and } \mu = \frac{(1.0078)(34.9688)}{1.0078 + 34.9688} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{\times} \right) = 1.6266 \times 10^{-27} \text{ kg}$$

$$\text{so } k = 4\pi^2 (2.99792 \times 10^{10})^2 \text{ cm}^2 \text{ s}^{-2} (1.6266 \times 10^{-27} \text{ kg}) (2991)^2 \text{ cm}^{-2}$$

$$k = 516.3 \text{ kg s}^{-2}$$

-2 wrong isotope masses

-4 wrong reduced mass

-7 didn't use HO model

[Problem 2 concludes on the next page.]

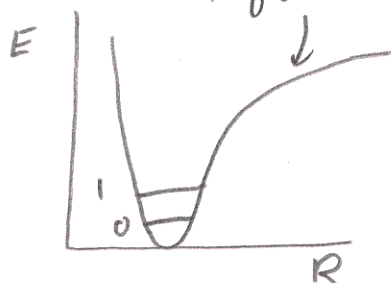
- (e) (10 points) Analysis of a  $v=1 \leftarrow v=0$  rovibrational spectrum of  $^1\text{H}^{35}\text{Cl}$  collected by Sonya Clarkson '03 and Jennifer Lang '04 yielded the results at the right. Explain the trend in these results qualitatively.

Rotational Constant	Value ( $\text{cm}^{-1}$ )
$B_e$	10.593
$B_0$	10.441
$B_1$	10.136

$B_e$  is the rot const at the very bottom of the Morse potential well,  $B_0$  is at  $v=0$  and  $B_1$  is at  $v=1$ .

As you move up the well, the average bond length

increases, and since  $B \sim \frac{1}{R^2}$ ,  $B$  should decrease. due to asymmetry of well



This is consistent with the data.

- 3 no clear statement of why  $\uparrow v$  of a Morse oscillator  $\uparrow \langle R \rangle$
- 6 no discussion of <sup>impact of</sup> vibrational state (i.e. only centrifugal distortion is discussed)
- 3 unclear statement about  $B_e$

- (f) (14 points) Say that instead of a rovibrational absorption spectrum of HCl, we recorded a pure rotational absorption spectrum of HCl. Which branches (P, Q, and/or R) would we observe in this pure rotational spectrum, and why? Be sure to explain the physical origin of any selection rules you invoke.

In absorption, see only R branch (i.e.  $\Delta J = +1$ ).

This is because each photon has spin angular momentum of  $S=1$ , and this angular momentum must be conserved as photon disappears upon absorption. Having the absorbing molecule spin 1 unit faster (i.e.  $\Delta J = +1$ ) does this conservation.

- 4 Could see P branch (or Q branch since  $\Delta M_J = 0$ )
- 6 No discussion of photon spin ang. mom. (-3 if vague)
- 6 all branches allowed

$$X_{\text{CM}} = \frac{m_1}{m_1 + m_2} X_1 + \frac{m_2}{m_1 + m_2} X_2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad I = m_1 R_1^2 + m_2 R_2^2 = \mu R^2$$

$$\frac{E_{\text{rot}}}{hc} = F(J) = BJ(J+1) \quad \text{or} \quad \frac{E_{\text{rot}}}{hc} = F(J) = B_v J(J+1) - D_v J^2(J+1)^2$$

$$B = \frac{h}{8\pi^2 c \mu R^2} \quad \text{or} \quad B_v = \frac{h}{8\pi^2 c \mu R_v^2} \quad D_v = \frac{4B_v^3}{\tilde{\nu}^2}$$

$$N_i = (\text{constant}) g_i \exp(-E_i / kT) \quad g_{\text{rot}} = 2J + 1$$

$$\frac{E_{\text{vib}}}{hc} = G(v) = \left(v + \frac{1}{2}\right) \tilde{\nu} \quad \text{or} \quad \frac{E_{\text{vib}}}{hc} = G(v) = \left(v + \frac{1}{2}\right) \tilde{\nu} - \left(v + \frac{1}{2}\right)^2 x_e \tilde{\nu}$$

$$\omega = 2\pi\nu = 2\pi c \tilde{\nu} = \sqrt{\frac{k}{\mu}} \quad x_e = \frac{\tilde{\nu}}{4D_e}$$

$$V = \frac{1}{2} k(R - R_e)^2 \quad V = hcD_e \{1 - \exp[-a(R - R_e)]\}^2 \quad a = \sqrt{\frac{\mu\omega^2}{2hcD_e}}$$

$$h = 6.62608 \times 10^{-34} \text{ J s} \quad \hbar = 1.05457 \times 10^{-34} \text{ J s} \quad c = 2.99792 \times 10^{10} \text{ cm s}^{-1}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \quad 1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg} \quad 1 \text{ eV} = 96.485 \text{ kJ mol}^{-1} = 8065.5 \text{ cm}^{-1}$$

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 †Ac 227.03	Note: The <i>f</i> block has been omitted for the sake of space. You will not need to refer to them during this exam!														

Masses and natural abundances of selected nuclides

Nuclide	$m/u$	Abundance/%
H	$^1\text{H}$	1.0078
	$^2\text{H}$	2.0140
He	$^3\text{He}$	0.000 13
	$^4\text{He}$	100
Li	$^6\text{Li}$	7.42
	$^7\text{Li}$	92.58
B	$^{10}\text{B}$	19.78
	$^{11}\text{B}$	80.22
C	$^{12}\text{C}$	12*
	$^{13}\text{C}$	13.0034
N	$^{14}\text{N}$	14.0031
	$^{15}\text{N}$	15.0001
O	$^{16}\text{O}$	15.9949
	$^{17}\text{O}$	16.9991
	$^{18}\text{O}$	17.9992
F	$^{19}\text{F}$	18.9984
P	$^{31}\text{P}$	30.9738
S	$^{32}\text{S}$	31.9721
	$^{33}\text{S}$	32.9715
	$^{34}\text{S}$	33.9679
Cl	$^{35}\text{Cl}$	34.9688
	$^{37}\text{Cl}$	36.9651
Br	$^{79}\text{Br}$	78.9183
	$^{81}\text{Br}$	80.9163
I	$^{127}\text{I}$	126.9045