

Name: KEY

Chemistry 56
Test 3
May 1, 2003

Instructions:

1. Write your name in the space above and on the backs of the other pages.
2. You may use one side of an 8.5" x 11" sheet of paper filled with information as a reference. Please turn this sheet in when you turn in the test.
3. You are allowed to use a calculator, but only for numerical calculations.
4. Your exam booklet should have **nine** pages total, with questions on pages 2-8, and a periodic table and other reference information on p. 9.
5. You have two hours and thirty minutes to work on this exam.

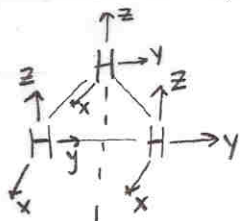
<u>Possible Points</u>	<u>Your Score</u>
Page 2 (14)	
Page 3 (6)	
Page 4 (15)	
Page 5 (14)	
Page 6 (14)	
Page 7 (19)	
Page 8 (18)	
Total (100)	

Low 62
Mean 78
High 89

1. (14 points) One of my academic grandparents, the University of Chicago spectroscopist Takeshi Oka, is famous for his detection of the molecule H_3^+ in outer space. This molecular ion is an equilateral triangle of D_{3h} symmetry. The D_{3h} character table is given below:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Identify the symmetry species (that is, the irreducible representations) of the vibrational modes of H_3^+ using the methods of group theory. Classify each of these modes as IR-active, Raman active, both, or neither.



	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	9	0	-1	3	0	1

$$a_{A_1'} = \frac{1}{12} (1 \cdot 1 \cdot 9 + 2 \cdot 1 \cdot 0 + 3 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot 1 \cdot 1) = 1 \quad \checkmark$$

$$a_{A_2'} = \frac{1}{12} (1 \cdot 1 \cdot 9 + 2 \cdot 1 \cdot 0 + 3 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot (-1) \cdot 1) = 1 \quad \checkmark$$

$$a_{E'} = \frac{1}{12} (1 \cdot 2 \cdot 9 + 2 \cdot (-1) \cdot 0 + 3 \cdot 0 \cdot (-1) + 1 \cdot 2 \cdot 3 + 2 \cdot (-1) \cdot 0 + 3 \cdot 0 \cdot 1) = 2 \quad \checkmark$$

$$a_{A_1''} = \frac{1}{12} (1 \cdot 1 \cdot 9 + 2 \cdot 1 \cdot 0 + 3 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot 3 + 2 \cdot (-1) \cdot 0 + 3 \cdot (-1) \cdot 1) = 0 \quad \checkmark$$

$$a_{A_2''} = \frac{1}{12} (1 \cdot 1 \cdot 9 + 2 \cdot 1 \cdot 0 + 3 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot 3 + 2 \cdot (-1) \cdot 0 + 3 \cdot 1 \cdot 1) = 1 \quad \checkmark$$

$$a_{E''} = \frac{1}{12} (1 \cdot 2 \cdot 9 + 2 \cdot (-1) \cdot 0 + 3 \cdot 0 \cdot (-1) + 1 \cdot (-2) \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot 0 \cdot 1) = 1 \quad \checkmark$$

The displacements span $A_1' \oplus A_2' \oplus 2E' \oplus A_2'' \oplus E''$

translations span $E' \oplus A_2'' \quad \checkmark$

rotations span $A_2' \oplus E''$

Vibrations span $A_1' \oplus E' \quad \checkmark$

IR-active: $E' \quad \checkmark$

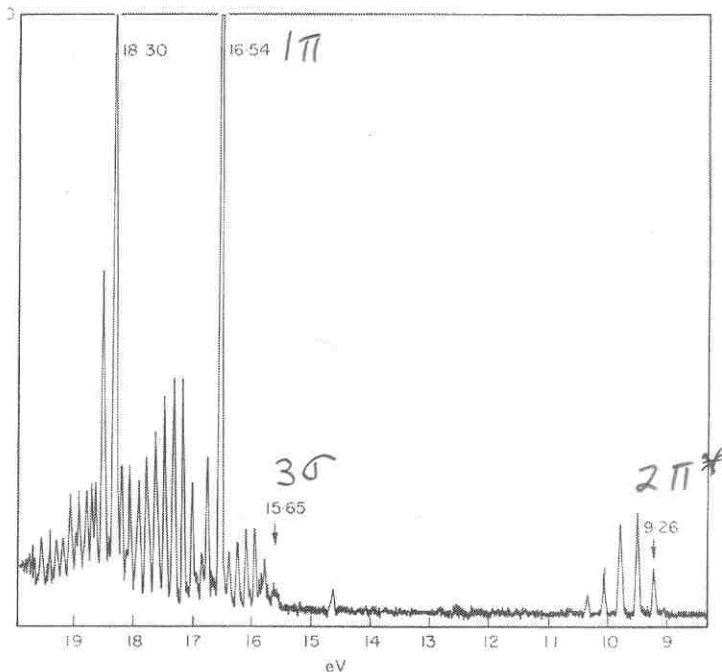
Raman active: $A_1', E' \quad \checkmark$

great!

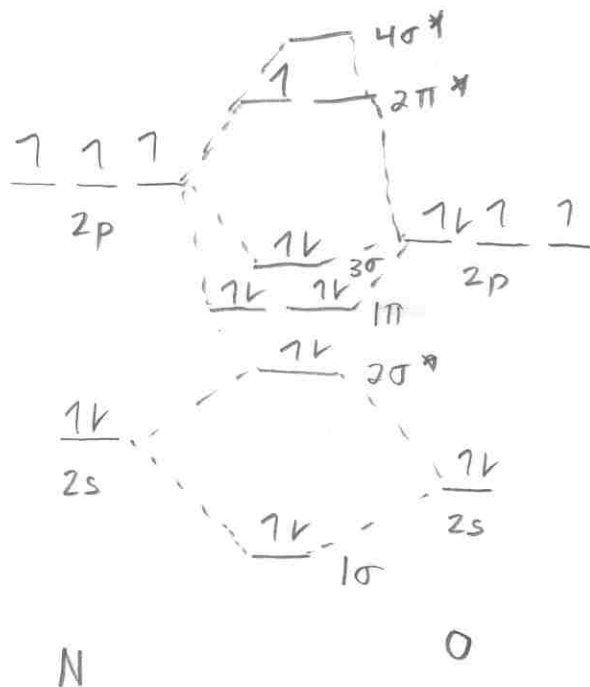
- 4 didn't account for rotations + translations
- 3 didn't know E is 2-dim.
- 3 wrong order
- 4 wrong Γ_{red}

2. (21 points total) The vacuum ultraviolet photoelectron spectrum of nitric oxide (NO) is shown at the right. The x-axis in the spectrum is the ionization energy in eV, and the labeled peaks indicate the four lowest adiabatic ionization energies.

Discuss this spectrum in detail by answering the questions below:



(a) (6 points) Using an energy-level diagram, assign the **three lowest** adiabatic ionization energies to molecular orbitals of NO. (Label the spectrum above.)



-3 1 major error (switched mo's, etc.)
 -1 or -2 1 minor error

[Problem 2 continues on the next page.]

- (b) (7 points) The spacing in the first "system" (that is, the set of five peaks starting at 9.26 eV) is considerably larger than the spacing in the second and third "systems." What does the spacing tell us about the NO^+ cations being formed in this experiment, and why is the spacing in the first system larger?

The spacing in the 1st system is largest because the spacing between vibrational energy levels is largest for that system. The cations formed in the two higher energy transitions are more easily excited vibrationally. This shows that for the two higher energy transitions, the ejected electron is coming from a more bonding orbital. So upon excitation, the bond order decreases for the cation, resulting in a looser, more easily vibrated bond. For the 1st system, losing an electron actually increases the bond order making it harder to vibrate. This NO^+ cation is more energetically favored than the other two.

-6 something -3 correct line of reasoning, but no mention of vibrations
-3 non-bonding vs. antibonding

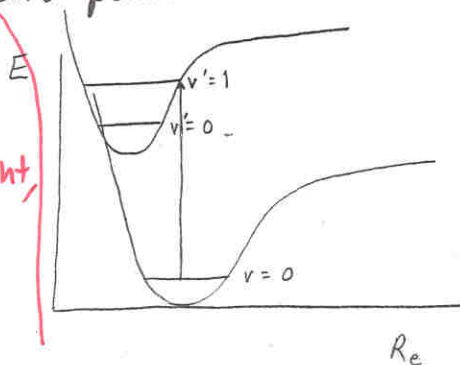
thus the larger vibrational spacing

good 7

- (c) (8 points) Explain in detail (using potential energy curves) why the most intense peak in the first system is not at 9.26 eV.

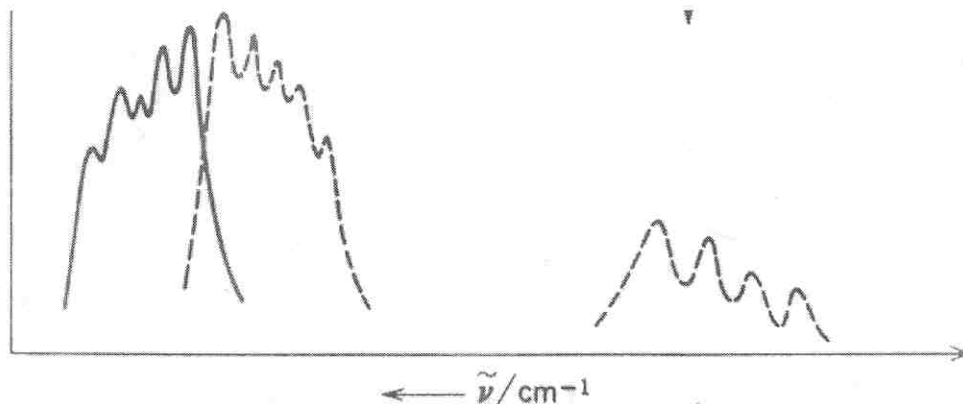
By the Frank-Codon principle, electrons change MOs faster than nuclei. This implies that the most likely transition will not be adiabatic, and lowest in energy, because that requires a change in geometry between the nuclei. The most likely transition, and thus the tallest peak, will instead be at a vertical transition from the center of the zero-point vibrational energy level.

-2 NO^+ curve shifted to the right, or other error



Because an electron is removed from an anti-bonding orbital in this 1st system, the potential energy curve of the resulting NO^+ ion is shifted to the left (higher bond order, therefore lower R_e).
excellent! 8

3. (8 points) Consider the following three spectra of a diatomic molecule:



-2 $E(T_1) < E(S_1)$ not mentioned -2 vibrational relaxation not mentioned

One of these spectra represents absorption, one represents fluorescence, and one represents phosphorescence. Label the three spectra above, and briefly rationalize your assignments below

Absorption and fluorescence are quick transitions with similar energetic transitions, hence them being close together and symmetrical. Absorbance is the most energetic (highest $\tilde{\nu}$) because thermal relaxation lowers the transition energy of the other two. Phosphorescence is much lower because it changes spin as the e^- is excited. This corresponds to a slide into a lower energy curve. So the eventual transition back to ground state is less energetic.

4. (6 points) Explain why describing the rotation of the symmetric rotor NI_3 requires two quantum numbers (J and K), while describing the rotation of a linear molecule like OCS requires only one quantum number (J).

everyone earned full credit

A symmetric rotor possesses two unequal moments of inertia: $I_a \neq I_b = I_c$. Thus two constants are needed - one to express rotation around each I .

A linear rotor, by contrast, possesses only one: $I_a = 0, I_b = I_c$, so only one constant is needed.

good

6

5. (14 points) So-called *hot band* vibrational transitions involve excitation from vibrational quantum states with $\nu > 0$. Although not commonly observed in room-temperature spectra, they are observed for molecules under extreme conditions (such as inside a flame). Take, for example, the molecule HBr, for which $\bar{\nu} = 2649.7 \text{ cm}^{-1}$ and $x_e\bar{\nu} = 45.2 \text{ cm}^{-1}$. Compute the temperature (in K) at which the relative population of the $\nu = 1$ and $\nu = 0$ states is 0.10.

$$\nu = 1 : \nu = 0$$

$$1 : 10$$

$$\frac{N_{\nu=1}}{N_{\nu=0}} = 0.10 = \frac{g_{\nu=1}}{g_{\nu=0}} e^{-\Delta E/kT} = e^{-\Delta E/kT}$$

-8 wrong approach
-3 wrong 3.130
-4 wrong ΔG formula

$$e^{-\Delta E/kT} = 0.10$$

$$\frac{-\Delta E}{kT} = \ln 0.1$$

$$T = \frac{-\Delta E}{k \cdot \ln 0.1} = \frac{0.43429}{k} \Delta E$$

$$\Delta G = (G(\nu=1) - G(\nu=0)) = \bar{\nu} - 2x_e\bar{\nu} = 2649.7 \text{ cm}^{-1} - 2(45.2 \text{ cm}^{-1}) = 2559.3 \text{ cm}^{-1}$$

$$\Delta E = hc\Delta G = (6.6261 \cdot 10^{-34} \text{ J s}) (2.9979 \cdot 10^8 \text{ m s}^{-1}) \left(\frac{2559.3}{\text{cm}} \right) \left(\frac{100 \text{ cm}^{-1}}{\text{m}^{-1}} \right) = 5.084 \cdot 10^{-20} \text{ J}$$

$$T = \frac{0.43429}{1.3807 \cdot 10^{-23} \text{ JK}^{-1}} \cdot 5.084 \cdot 10^{-20} \text{ J} = 1599 \text{ K}$$

6. (10 points) If we assume that a diatomic molecule spins like a rigid rotor and vibrates like a harmonic oscillator, its rovibrational term (in cm^{-1}) is given by

$$S(\nu, J) = \left(\nu + \frac{1}{2}\right)\bar{\nu}_0 + BJ(J+1)$$

Let us also assume that initially, $\nu = 0$ and $J = J''$. We then excite rovibrational transitions in the molecule using a FTIR spectrometer. Using the above expression (and results you can derive from it), prove that in the *R* branch ($\Delta J = +1$), the transition wavenumber increases with J'' , but that in the *P* branch ($\Delta J = -1$), the transition wavenumber decreases with J'' .

$$S(\nu, J) = \left(\nu + \frac{1}{2}\right)\bar{\nu}_0 + BJ(J+1)$$

if $\Delta J = +1$: $\left(\nu + \frac{1}{2}\right)\bar{\nu}_0 + BJ(J+1) - \left(\nu + \frac{1}{2}\right)\bar{\nu}_0 + B(J+1)(J+2)$

$$\nu = 0$$

$$S(0, J) = \frac{1}{2}\bar{\nu}_0 + BJ(J+1)$$

$$S(0, J+1) = \frac{1}{2}\bar{\nu}_0 + B(J+1)(J+2)$$

$$= \boxed{\nu + 2B(J+1)}$$

$$\Rightarrow \nu_R(J) = \nu + 2B(J+1)$$

if $\Delta J = -1$: $S(\nu, J-1) = \left(\nu + \frac{1}{2}\right)\bar{\nu}_0 + B(J-1)J$

-2 if $\Delta \nu = +1$
was neglected
-7 wrong approach

$$S(0, J) = \frac{1}{2}\bar{\nu}_0 + BJ(J+1)$$

$$S(0, J-1) = \frac{1}{2}\bar{\nu}_0 + B(J-1)J$$

$$= \boxed{\nu - 2BJ}$$

$$\Rightarrow \nu_P(J) = \nu - 2BJ$$

7. (9 points) Consider the following nuclei and their putative spin states. If a particular state is not allowed for the given nucleus, circle it and explain why.

(A) ${}^7\text{Li}$ with $m_I = +1/2$

(B) ${}^{32}\text{S}$ with $m_I = +1$

16 p^+ , 16 n (both even) $\Rightarrow I = 0 \Rightarrow m_I = 0$ only

(C) ${}^{14}\text{N}$ with $m_I = -1/2$

7 p^+ , 7 n (both odd) $\Rightarrow I = \text{integer} \Rightarrow m_I = \text{integer}$ only

+3 per right answer

8. (18 points) Explain in detail the predictions of classical physics and quantum mechanics for the following phenomena:

- (i) The energy of a magnetic dipole moment in a constant magnetic field.
- (ii) The torque experienced by a magnetic dipole moment in a constant magnetic field.

For each phenomenon, be sure to identify at least one difference in the classical and quantum-mechanical predictions.

i) Classical: $E = -\vec{\mu} \cdot \vec{B} = -\frac{q}{2m} L_z B_0$ where L_z can vary continuously from

$+|\vec{L}|$ to $-|\vec{L}|$. (θ can vary from 0 to π)



Schematic diagram

-1 minor error
-2 needed more detail on I
-5 no discussion of E

QM: $E = \frac{g\mu_B}{2m} I_z B_0 = -\gamma m_I \hbar B_0$, $m_I = I, I-1, \dots, -I$

Differences: Classical says that E is continuous because L_z can vary continuously. QM says that E is quantized. For example, if $I = \frac{1}{2}$, $m_I = \pm \frac{1}{2} \Rightarrow$ only two different E, $\frac{\gamma \hbar B_0}{2}$ and $-\frac{\gamma \hbar B_0}{2}$. Classical says $\vec{\mu}$ can point in same direction as \vec{B} b/c θ can equal 0. QM says $\vec{\mu}$ can't point in same direction as \vec{B} . excellent

9

ii) Classical:

$\Omega = \Delta L$

Ω = particle orbiting about \vec{L}

Ω = precession

$\vec{\tau} = \frac{q}{2m} \vec{L} \times \vec{B}$

$\Delta \vec{L} \approx \vec{\tau} \Delta t$

-3 no discussion of classical vs. QM
-4 incorrect/missing discussion of precession



* Right hand rule $\Rightarrow \Delta \vec{L} \perp \{\vec{\mu}, \vec{B}\}$ plane \Rightarrow rotation of particle about \vec{B} (precession)

precessional freq, $\nu_p = \frac{1}{2\pi} \frac{q}{2m} B_0$

Ω remains constant $\Rightarrow L_z$ and E remain constant, L_y & L_x change over time

QM: $\nu_p = \frac{1}{2\pi} \gamma B_0$ = Larmor frequency

Ω, I_z, E remain constant, I_x & I_y not known (Heisenberg Uncertainty)

Differences:

ν_p differ by a factor of g. QM predicts ν_p to be a multiple of g (2.00 for e-) so QM places restrictions on ν_p . For classical, we can possibly relate L_x & L_y by some kind of relationship. QM predicts that I_x & I_y can't be known, i.e. no relationship.

Possibly Useful Information

$$h = 6.6261 \times 10^{-34} \text{ J s}$$

$$\hbar = 1.0546 \times 10^{-34} \text{ J s}$$

$$c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

$$m_e = 9.1094 \times 10^{-31} \text{ kg}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

$$k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$$

$$I = \sum_{i=1}^n m_i r_i^2$$

$$F(J, K) = BJ(J+1) + (A-B)K^2$$

$$A = \frac{\hbar}{4\pi c I_{\parallel}}$$

$$B = \frac{\hbar}{4\pi c I_{\perp}}$$

$$F(J) = BJ(J+1)$$

$$B = \frac{\hbar}{4\pi c I}$$

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

$$D = \frac{4B^3}{\bar{v}^2}$$

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-\Delta E/kT}$$

$$G(v) = \left(v + \frac{1}{2}\right) \bar{v}$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m}$$

$$G(v) = \left(v + \frac{1}{2}\right) \bar{v} - \left(v + \frac{1}{2}\right)^2 x_e \bar{v}$$

$$\Delta E = h\nu = h \frac{c}{\lambda} = hc\bar{v}$$

$$\bar{\mu} = \frac{q}{2m} \vec{L}$$

$$\bar{\mu} = \gamma \vec{I}$$

$$E = -\bar{\mu} \cdot \vec{B}$$

$$\vec{\tau} = \bar{\mu} \times \vec{B}$$

$$\vec{\tau} \cong \frac{\Delta \vec{L}}{\Delta t}$$

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															

* 58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
† 90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)