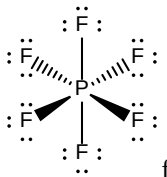
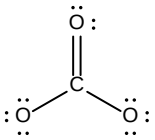
CHM 501
Exam 1
March 5, 2016

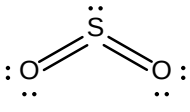
1. (15 pts) Predict the electron configuration for the following: a) Ti; b) Ti^{+}; c) Ti^{2+}; d) Ti^{3+}; e) Ti^{4+}. What is the trend in the ionization energies for this series of ions. Explain your reasoning.

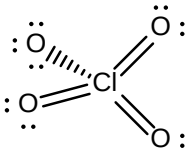
   a) Ti: [Ar] $4s^2 3d^2$
   b) Ti^{+}: [Ar]$3d^3$
   c) Ti^{2+}: [Ar]$3d^2$
   d) Ti^{3+}: [Ar]$3d^1$
   e) Ti^{4+}: [Ar]$3d^0$
   As the charge on the ion increases the ionization energy increases significantly. The IE for Ti^{4+} is especially high since the n = 3 electrons will be removed.

2. (40 pts) Draw the lowest energy Lewis dot structure for each of the following, give the formal charge and the oxidation number for each atom, indicate the molecular geometry, and give the point group: a) PF_6^-; b) CO_3^{2-}; c) SO_2; d) ClO_4^-.

   a)  formal charge: F, 0; P, –1. oxidation number: F, –1; P, +5. Octahedral geometry. O_h.

   b)  plus resonance structures formal charge: O, –2/3; C, 0. oxidation number: O, –2; C, +4. Trigonal planar geometry. D_{3h}.

   c)  formal charge: O, 0; S, 0. oxidation number: O, –2; S, +4. bent planar geometry. C_{2v}.

   d)  formal charge: O, –1/4; Cl, 0. oxidation number: O, –2; Cl, +7. Tetrahedral geometry. T_d.

3. (30 pts) Find the irreducible representations for the vibrations in SF_4. Indicate which of these are predicted to be IR active. Also find the irreducible representations of the σ bonds and lone pairs. What hybrid must be used?

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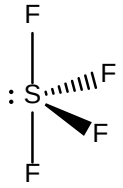

The point group is C_{2v}. The total reps for each part of the problem are:

	E	C_2	σ_v	σ_v'
All degrees of freedom	15	-1	3	3
Sigma bonds plus lone pair	5	1	3	3

The degrees of freedom transform as $5a_1 + 2a_2 + 4b_1 + 4b_2$. Translations transform as $a_1 + b_1 + b_2$ and rotations transform as $a_2 + b_1 + b_2$, which leaves the vibrational degrees of freedom as $4a_1 + a_2 + 2b_1 + 2\ b_2$. The a_1, b_1, and b_2 vibrations are IR active.

The sigma bonds plus lone pair transform as $3a_1 + b_1 + b_2$. This is a sp^3d hybrid.

4. (15 pts) For a general spectroscopic transition, quantum mechanics says the integral $\int \psi^* \hat{o}\hat{p}\psi d\tau$ must be nonzero for the transition to be observed. While group theory cannot be used to evaluate the integral, it can be used to predict whether the value is zero or nonzero. This is done using the inner product. The ground state (ψ) is always the totally symmetric representation so can be ignored. The operators for IR or UV-vis transitions are x, y, or z, however they transform in the group, and ψ^* is the excited state, with its associated representation. From your results from question 3, select 1 vibration that you determined not to be IR allowed (however, not the totally symmetric vibration) and show that the inner product with the irreducible representation for x is zero. Likewise, select one IR allowed vibration (again, not the totally symmetric vibration) and show that the inner product with the corresponding operator representation is equal to the order of the group.

The one non-IR active vibration is a_2. The inner product with b_1 (for example, IR allowed in the x direction) is (1)(1) + (1)(-1) + (-1)(1) + (-1)(-1) = 0. An IR active vibration is b_1. The inner product with b_1 is (1)(1) + (-1)(-1) + (1)(1) + (-1)(-1) = 4, which is the order of the group.

C_{2v}	E	C_2	σ_v	σ_v'		
a_1	1	1	1	1	z	x^2, y^2, z^2
a_2	1	1	-1	-1	R_z	xy
b_1	1	-1	1	-1	x, R_y	xz
b_2	1	-1	-1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
a_1	1	1	1	z	x^2+y^2, z^2
a_2	1	1	-1	R_z	
e	2	-1	0	$(x, y)\ (R_x, R_y)$	$(x^2-y^2, xy)\ (xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
a_1	1	1	1	1	1	z	x^2+y^2, z^2
a_2	1	1	1	-1	-1	R_z	
b_1	1	-1	1	1	-1		x^2-y^2

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b_2	1	-1	1	-1	1		*xy*
e	2	0	-2	0	0	*(x, y) (R_x, R_y)*	*(xz, yz)*

D_{4h}	*E*	$2C_4$	C_2	$2C_2'$	$2C_2''$	*i*	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
a_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
a_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
b_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
b_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		*xy*
e_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	*(xz, yz)*
a_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
a_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	*z*	
b_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
b_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
e_u	2	0	-2	0	0	-2	0	2	0	0	*(x, y)*	