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Chemistry 6011 [redacted] 54 points

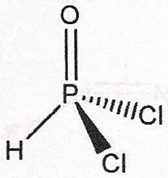
Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds

Problem Set #2

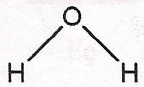
Chapter 4-

1 point each

1. Assign the following molecules to their appropriate point groups. 11 points

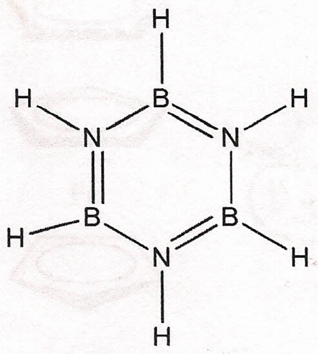


C_∞? no C_n? no σ? Yes C_s



C_∞? no C_n? yes → C_2

$2C_2 \perp C_2$? no S_4? no σ_h? no $2\sigma_v$? Yes C_{2v}

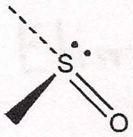


~~C_∞? no C_n? yes → C_3~~

~~$3C_2 \perp C_3$? No S_4? No σ_h? Yes~~

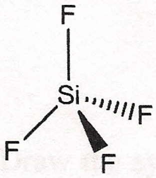
~~As drawn, not delocalized.~~ ~~C_{3h}~~

If delocalized → D_{3h}

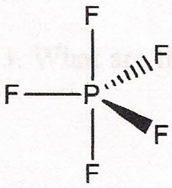


C_∞? no C_n? no σ? ~~no~~ yes ~~i? no~~ ~~C_1 or C_s~~

C_s

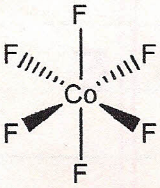


C_∞? no C_n? yes → C_3 → $4C_3$ i? no 6σ? yes T_d



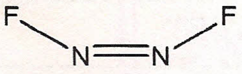
C_∞? no C_n? yes → C_3 → C_3

$3C_2 \perp C_3$? Yes σ_h? yes D_{3h}



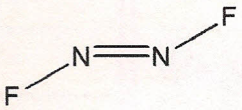
C_∞? no C_n? yes $\rightarrow C_4$ $3C_4$? yes i? yes

O_h



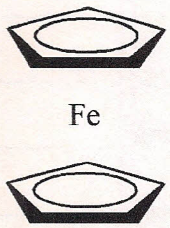
C_∞? no C_n? yes $\rightarrow C_2$ $3C_2 \perp C_2$? no S_4? No
σ_h? No $2\sigma_v$? Yes

C_{2v}

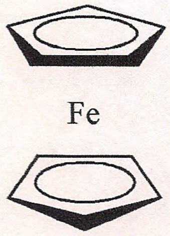


C_∞? no C_n? Yes $\rightarrow C_2$ $2C_2 \perp C_2$? no S_4? no σ_h? yes

C_{2h}



C_∞? no C_n? yes $\rightarrow C_5$ $5C_2 \perp C_5$? Yes σ_h? Yes D_{5h}

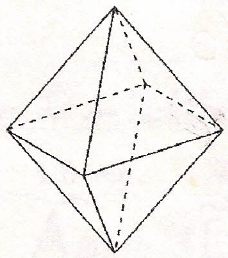


C_∞? no C_n? yes $\rightarrow C_5$ $5C_2 \perp C_5$? yes σ_h? no $5\sigma_v$? yes

D_{5d}

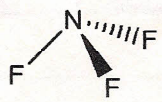
2. Find and draw all of the symmetry elements in an octahedron. 2 points

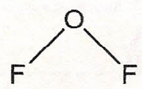
Eliminate



Draw the symmetry elements. You can redraw the molecule a few times so that it easy to see your elements. Also give one example of each type of symmetry element.

3. What are the symmetries of the normal modes of vibration of these molecules? 4 points





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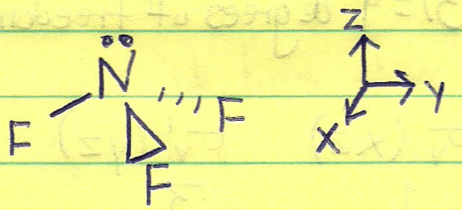
3.  Nonlinear 4 points

$3N = 3(4) = 12$ total degrees of freedom.

Point group? C_{3v}

C_{3v}	E	$2C_3$	σ_v
Unshifted atoms	4	1	2
contributions per atom	3	0	1
Γ_{total}	12	0	2

$A_1 = \frac{1}{6}[12(1)(1) + 0 + 2(3)(1)] = \frac{1}{6}(18) = 3$

$A_2 = \frac{1}{6}[12(1)(1) + 0 + 2(3)(-1)] = \frac{6}{6} = 1$

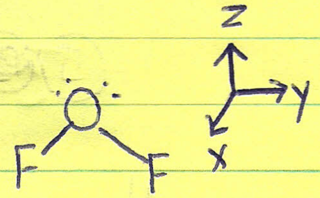
$E : \frac{1}{6}[12(1)(2) + 0 + 2(3)(0)] = \frac{24}{6} = 4$

$\Gamma_{total} = 3\underbrace{A_1}_{\text{1D rep.}} + \underbrace{A_2}_{\text{1D rep.}} + 4\underbrace{E}_{\text{2D-rep.}} \Rightarrow 12$ degrees of freedom

$-\Gamma_{trans} : A_1 + E$ (from x, y, z in character table)

$-\Gamma_{rot} = A_2 + E$ (from R_x, R_y, R_z in table)

$\Gamma_{vib} = 2A_1 + 2E$ ($3N-6 = 6$ degrees of freedom) 6 normal modes



C_{2v}

$3N = 3(3) = 9$ degrees of freedom

	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
U.A.	3	1	1	3
Cont. per atom.	3	-1	1	1
	9	-1	1	3

$A_1: \frac{1}{4}[9(1)(1) + -1(1)(1) + 1(1)(1) + 3(1)(1)] = \frac{12}{4} = 3$

$A_2: \frac{1}{4}[9(1)(1) + -1(1)(1) + 1(1)(-1) + 3(1)(-1)] = \frac{4}{4} = 1$

$B_1: \frac{1}{4}[9(1)(1) + -1(1)(-1) + 1(1)(1) + 3(1)(-1)] = \frac{8}{4} = 2$

$B_2: \frac{1}{4}[9(1)(1) + -1(1)(-1) + 1(1)(-1) + 3(1)(1)] = \frac{12}{4} = 3$

$\Gamma_{total} = 3A_1 + 1A_2 + 2B_1 + 3B_2$

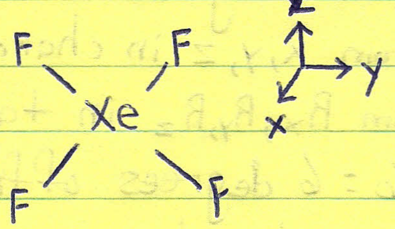
$-\Gamma_{trans} = A_1 + B_1 + B_2$

$-\Gamma_{rot} = A_2 + B_1 + B_2$

$\Gamma_{vib} = 2A_1 + B_2$ Three degrees of freedom

$3N - 6 = 3$

4.



Point group? D_{4h} 2 points

$3N - 6 = 15 - 6 = 9$

Because it has five atoms, we expect 9 vibrational modes, four of which will be stretching modes (because there are 4 bonds) and five of which will be bending modes.

$3(5) = 15$ degrees of freedom

Γ	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
U.A.	5	1	1	3	1	1	1	5	3	1
C/A	3	1	-1	-1	-1	-3	-1	1	1	1

A_{1g}: $\frac{16}{16} = 1$ $\quad A_{2u} = 2$

A_{2g}: $\frac{16}{16} = 1$ $\quad B_{1u} = 0$

B_{1g}: $\frac{16}{16} = 1$ $\quad B_{2u} = 1$

$E_u = 3$

B_{2g}: $\frac{16}{16} = 1$

E_g: $\frac{16}{16} = 1$

$A_{1u} = 0$

$\Gamma_{tot} = 1A_{1g} + 1A_{2g} + 1B_{1g} + 1B_{2g} + 1E_g + 2A_{2u} + 1B_{2u} + 3E_u$

$-\Gamma_{trans} =$ A_{2u}

$-\Gamma_{rot} =$ $+E_g$ $+E_u$

$\Gamma_{vib}: 1A_{1g} + \underbrace{1B_{1g} + 1B_{2g} + 1A_{2u} + 1B_{2u}}_{\text{9 vibrations}} + 2E_u$

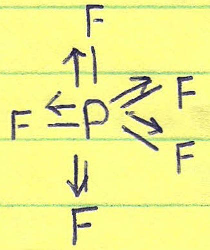
$A_{2u} + E_u$: IR active; transforms like x, y, z

$A_{1g}, B_{1g} + B_{2g}$: Raman active; transform like quadratic functions ~~of~~ of x, y, + z + linear combinations of them

B_{2u}: Neither IR nor Raman

Since this molecule has i, the IR + Raman active modes would be different.

5.



$P: 1s^2 2s^2 2p^6 \overbrace{3s^2 3p^3}^{n=3;\ \text{has d-orbitals}}$

Point group: D_{3h} 4 points

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{total}	5	2	1	3	0	3

$A_1' = 2$
$A_2' = 0$
$E' = 1$
$A_1'' = 0$
$A_2'' = 1$
$E'' = 0$

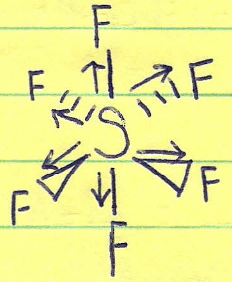
$\Gamma_{red}: 2A_1' + E' + A_2''$

A_1' orbitals: s, d_{z^2}
E' orbitals: p_x, p_y, $d_{x^2-y^2}$, d_{xy}
A_2'': p_z

Possible combinations:

$s, d_{z^2}, p_x, p_y, p_z$ — dsp^3
$s, d_{z^2}, d_{x^2-y^2}, d_{xy}, p_z$ — d^3sp

5 atomic orbitals → 5 hybrid orbitals



S: [Ne]$3s^2 3p^4$ has d-orbitals

Point group: O_h

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_r	6	0	0	2	2	0	0	0	4	2

$A_{1g} = 1$ $\quad E_u = 0$ $\quad \Gamma_{red} : A_{1g} + E_g + T_{1u}$

$A_{2g} = 0$ $\quad T_{1u} = 1$ $\quad A_{1g}$ orbitals: s

$E_g : 1$ $\quad T_{2u} = 0$ $\quad E_g$ " : d_{z^2}, $d_{x^2-y^2}$

$T_{1g} = 0$ $\quad T_{1u}$ " : p_x, p_y, p_z

d^2sp^3 only possible combination

$T_{2g} = 0$

$A_{1u} = 0$

$A_{2u} = 0$