- S7.12 SALCs for sigma bonding in  $O_h$ ?  $A_{1g} + E_g + T_{1u}$ , see Example 7.12 and page 794.
- 7.1 Symmetry elements? (a) a  $C_3$  axis and a  $\sigma_y$  plane in the NH<sub>3</sub> molecule?



(b) a  $C_4$  axis and a  $\sigma_h$  plane in the square-planar [PtCl<sub>4</sub>]<sup>2-</sup> ion?



 $C_4$ 

 $\sigma_{
m h}$ 

C IIIIIII

7.2  $S_4$  or *i*? (a) CO<sub>2</sub>? This linear molecule has a center of inversion. There are only two point groups for linear molecules,  $D \propto_h$  (has *i*) or  $C \propto_v$  (does not have *i*). Therefore, the point group is  $D \propto_i$ .

(b) C<sub>2</sub>H<sub>2</sub>? This linear molecule also has *i*. The point group is  $D\infty_{h}$ .

(c) BF<sub>3</sub>? This molecule possesses neither *i* nor  $S_4$ . It belongs to the  $D_{3h}$  point group.

(d)  $SO_4^{2-2}$ ? This ion has three different  $S_4$  axes, which are coincident with three  $C_2$  axes, but there is no *i*. The point group is  $T_d$ .

7.3 Assigning point groups: (a) NH<sub>2</sub>Cl? The only element of symmetry that this molecule possesses other than E is a mirror plane that contains the N and Cl atoms and bisects the H–N–H bond angle. The set of symmetry elements (E,  $\sigma$ ) corresponds to the point group  $C_s$  (the subscript comes from the German word for mirror, *Spiegel*).



(b)  $CO_3^{2-2}$  The carbonate anion is planar, so it possesses at least one plane of symmetry. Since this plane is perpendicular to the major proper rotation axis,  $C_3$ , it is called  $\sigma_h$ . In addition to the  $C_3$  axis, there are three  $C_2$  axes coinciding with the three C–O bond vectors. There are also other mirror planes and improper rotation axes, but the elements listed so far  $(E, C_3, \sigma_h, 3C_2)$  uniquely correspond to the  $D_{3h}$  point group (note that  $CO_3^{2-}$  has the same symmetry as BF<sub>3</sub>). A complete list of symmetry elements is  $E, C_3, 3C_2, S_3, \sigma_h$ , and  $3\sigma_v$ .



(c) SiF<sub>4</sub>? This molecule has four  $C_3$  axes, one coinciding with each of the four Si–F bonds. In addition, there are six mirror planes of symmetry (any pair of F atoms and the central Si atom define a mirror plane, and there are always six ways to choose a pair of objects out of a set of four). Furthermore, there is no center of symmetry. Thus, the set (E,  $4C_3$ ,  $6\sigma$ , no *i*) describes this molecule and corresponds to the  $T_d$  point group. A complete list of symmetry elements is E,  $4C_3$ ,  $3C_2$ ,  $3S_4$ , and  $6\sigma_d$ .



(d) HCN? Hydrogen cyanide is linear, so it belongs to either the  $D\infty_h$  or the  $C\infty_v$  point group. Since it does not possess a center of symmetry, which is a requirement for the  $D\infty_h$  point group, it belongs to the  $C\infty_v$  point group.

(e) SiFClBrI? This molecule does not possess any element of symmetry other than the identity element, E. Thus it is asymmetric and belongs to the  $C_1$  point group, the simplest possible point group.

(f) BrF<sub>4</sub><sup>-</sup>? This anion is square planar. It has a  $C_4$  axis and four perpendicular  $C_2$  axes. It also has a  $\sigma_h$  mirror plane. These symmetry elements uniquely correspond to the  $D_{4h}$  point group. A complete list of symmetry elements is E,  $C_4$ , a parallel  $C_2$ , four perpendicular  $C_2$ ,  $S_4$ , i,  $\sigma_h$ ,  $2\sigma_v$ , and  $2\sigma_d$ .



The symmetry elements of orbitals? (a) An s orbital? An s orbital, which has the shape of a sphere, possesses an infinite number of  $C_n$  axes where n can be any number from 1 to  $\infty$ , plus an infinite number of mirror planes of symmetry. It also has a center of inversion, *i*. A sphere has the highest possible symmetry.

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1.5

(b) A p orbital? The + and – lobes of a p orbital are not equivalent and therefore cannot be interchanged by potential elements of symmetry. Thus a p orbital does not possess a mirror plane of symmetry perpendicular to the long axis of the orbital. It does, however, possess an infinite number of mirror planes that pass through both lobes and include the long axis of the orbital. In addition, the long axis is a  $C_n$  axis, where n can be any number from 1 to  $\infty$  (in group theory this is referred to as a  $C_{\infty}$  axis).

(c) A  $d_{xy}$  orbital? The two pairs of + and – lobes of a  $d_{xy}$  orbital are interchanged by the center of symmetry that this orbital possesses. It also possesses three mutually perpendicular  $C_2$  axes, each one coincident with one of the three Cartesian coordinate axes. Furthermore, it possesses three mutually perpendicular mirror planes of symmetry, which are coincident with the xy plane and the two planes that are rotated by 45° about the z axis from the xz plane and the yz plane.

(d) A  $d_z 2$  orbital? Unlike a  $p_z$  orbital, a  $d_z 2$  orbital has two large + along its long axis, and a - torus (or doughnut) around the middle. In addition to the symmetry elements possessed by a p orbital (see above), the infinite number of mirror planes that pass through both lobes and include the long axis of the orbital as well as the  $C_{\infty}$  axis, a  $d_z 2$  orbital also possesses (i) a center of symmetry, (ii) a mirror plane that is perpendicular to the  $C_{\infty}$  axis, (iii) an infinite number of  $C_2$  axes that pass through the center of the orbital and are perpendicular to the  $C_{\infty}$  axis, and (iv) an  $S_{\infty}$  axis.

 $SO_3^{2-}$  ion? (a) Point group? Using the decision tree shown in Figure 7.9, you will find the point group of this anion to be  $C_{3v}$  (it is nonlinear, it only has one proper rotation axis, a  $C_3$  axis, and it has three  $\sigma_v$  mirror planes of symmetry).

0 5 0 2-

(b) Degenerate MOs? Inspection of the  $C_{3v}$  character table (Resource Section 4) shows that the characters under the column headed by the identity element, E, are 1 and 2. Therefore, the maximum degeneracy possible for molecular orbitals of this anion is 2.

(c) Which s and p orbitals have the maximum degeneracy? According to the character table, the S atom 3s and  $3p_z$  orbitals are each singly degenerate (and belong to the A<sub>1</sub> symmetry type), but the  $3p_x$  and  $3p_y$  orbitals are doubly degenerate (and belong to the *E* symmetry type). Thus the  $3p_x$  and  $3p_y$  atomic orbitals on sulfur can contribute to molecular orbitals that are two-fold degenerate.

7.6 **PF<sub>5</sub>? (a) Point group?** As above, you use the decision tree to assign the point group, in this case concluding that  $PF_5$  has  $D_{3h}$  symmetry (it has a trigonal bipyramidal structure, by analogy with  $PCl_5$ ; it is nonlinear; it has only one high-order proper rotation axis, a  $C_3$  axis; it has three  $C_2$  axes that are perpendicular to the  $C_3$  axis; and it has a  $\sigma_h$  mirror plane of symmetry).

(b) Degenerate MOs? Inspection of the  $D_{3h}$  character table (Resource Section 3) reveals that the characters under the *E* column are 1 and 2, so the maximum degeneracy possible for a molecule with this symmetry is 2.

(c) Which p orbitals have the maximum degeneracy? The P atom  $3p_x$  and  $3p_y$  atomic orbitals, which are doubly degenerate and are of the E' symmetry type (i.e., they have E' symmetry), can contribute to molecular orbitals that are twofold degenerate. In fact, if they contribute to molecular orbitals at all, they *must* contribute to twofold degenerate ones.

- 7.7 **Point groups?** Consult Table 7.2 and Figure 7.9 for decision tree to assign point groups. Using VSEPR theory,  $SnF_4$  has a tetrahedral geometry and the point group is  $T_d$ . Using VSEPR, SeF<sub>4</sub> has a see-saw geometry and the point group is  $C_{2v}$ . Using VSEPR, BrF<sub>4</sub> has a square planar geometry and the point group is  $D_{4h}$ .
- 7.8 AsCl<sub>5</sub> Raman spectrum consistent with a trigonal bipyamidal geometry? From VSEPR, AsCl<sub>5</sub> should be trigonal pyramidal with symmetry  $D_{3h}$ . We first obtain the representation  $\Gamma_{3N}$ :

D <sub>3h</sub>	E	$2C_{3}$	$3C_{2}$	$\sigma_h$	$2S_3$	30,	
3N	18	0	-2	4	-2	4	

 $\Gamma_{3N}$  reduces to:  $2A_1' + A_2' + 4E' + 3A_2'' + 2E''$ ; subtracting  $\Gamma_{trans} (E' + A_2'')$  and  $\Gamma_{rot} (A_2' + E'')$ , we obtain  $\Gamma_{vib}$ :  $2A_1' + 3E' + 2A_2'' + E''$ . Thus we expect 6 Raman bands:  $2A_1'$  (polarized) + 3E' + E'' (note that  $A_2''$  is inactive in Raman since symmetry type does not contain the same symmetry as the function  $x^2 + y^2 + z^2$ ).

7.9 Vibrational modes of SO<sub>3</sub>? (a) In the plane of the nuclei? SO<sub>3</sub> has a trigonal-planar structure. If you consider the  $C_3$  axis to be the z axis, then each of the four atoms has two independent displacements in the xy plane, namely along the x and along the y axis. The product (4 atoms)(2 displacement modes/atom) gives 8 displacement modes, not all of which are vibrations. There are two translation modes in the plane of the nuclei, one each along the x and y axes. There is also one rotational mode around the z axis. Therefore, if you subtract these 3 nonvibrational displacement modes from the total of 8 displacement modes, you arrive at a total of 5 vibrational modes in the plane of the nuclei.

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_{ m h}$	$2S_3$	$3\sigma_v$
$\Gamma_{3N}$	12	0	-2	4	-2	2

 $\Gamma_{3N}$  reduces to:  $A_1' + A_2' + 3E' + 2A_2'' + E''$ . Subtracting  $\Gamma_{trans} (E' + A_2'')$  and  $\Gamma_{rot} (A_2' + E'')$ , we obtain  $\Gamma_{vib} : A_1' + 2E' + A_2''$ .

In the plane:  $A_1'$  is a symmetric stretch; 2E' are modes consisting of (i) mainly asymmetric stretching and (ii) deformation:



0

IF3 02 I - 7e-3F-3x7=2le-20 - 2×6= 12e-40e- or 20 pairs IF. LEWIS DOT 1 F IFI posible Isomers 0 0 00 FN -F F

0

F C2v D3h C3 Most stable, O has double bonds & is bigger than F most stable, O has double bonds & is bigger than F thus it needs more sterically demanding spots > the eg. spots.

-F

F