Chapter 4 - Solutions to Assigned Problems

14. (d) using the reduction formula (note: Γ is used in the text to represent a reducible representation), and noting the order (h) is 8,

$a_{A1}\,(\Gamma_1) = 1/8\,[1\times1\times6 + 2\times1\times0 + 1\times1\times2 + 2\times1\times2 + 2\times1\times2] = 2$
$a_{A2}\,(\Gamma_1) = 1/8\,[1\times1\times6 + 2\times1\times0 + 1\times1\times2 + 2\times(-1)\times2 + 2\times(-1)\times2] = 0$
etc.

therefore, Γ_1 factors into $2\,A_1 + B_1 + B_2 + E$

$a_{A1}\,(\Gamma_2) = 1/8\,[1\times1\times6 + 2\times1\times4 + 1\times1\times6 + 2\times1\times2 + 2\times1\times0] = 3$
...
$a_{E}\,(\Gamma_2) = 1/8\,[1\times2\times6 + 2\times0\times4 + 1\times-2\times6 + 2\times0\times2 + 2\times0\times0] = 0$

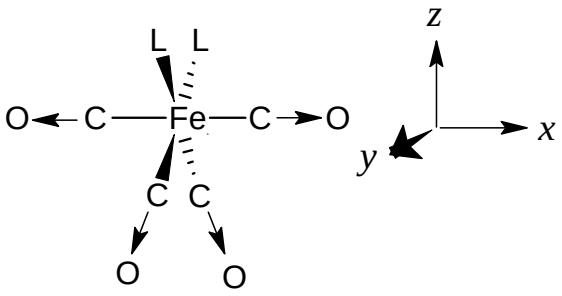
and Γ_2 factors to $3\,A1 + 2\,A_2 + B_1$

15. for $\Gamma_1\,(C_{3v})$, $h = 6$:
$a_{A1} = 1/6\,[1\times1\times6 + 2\times1\times3 + 3\times1\times2] = 3$
$a_{A2} = 1/6\,[1\times1\times6 + 2\times1\times3 + 3\times(-1)\times2] = 1$
$a_{E} = 1/6\,[1\times2\times6 + 2\times(-1)\times3 + 3\times0\times2] = 1$
$\Gamma_1\,(C_{3v})$ factors into $3\,A_1 + A_2 + E$

similarly, $\Gamma_2\,(C_{3v})$ factors into $A_2 + 2\,E$

for O_h, $h = 48$ (!)
$a_{A1g} = 1/48\,[1\times6\times1 + 0 + 0 + 6\times2\times1 + 3\times2\times1 + 0 + 0 + 0 + 3\times4\times1 + 6\times2\times1] = 1$
...
$a_{Eg} = 1/48\,[1\times6\times2 + 0 + 0 + 6\times2\times0 + 3\times2\times2 + 0 + 0 + 0 + 3\times4\times2 + 6\times2\times0] = 1$
$a_{T1g} = 1/48\,[1\times6\times3 + 0 + 0 + 6\times2\times1 + 3\times2\times(-1) + 0 + 0 + 0 + 3\times4\times(-1) + 6\times2\times(-1)] = 0$
...
$\Gamma\,(O_h) = A_{1g} + E_g + T_{1u}$

18. (a) Point group is C_{2v}, I would suggest the following coordinate system:



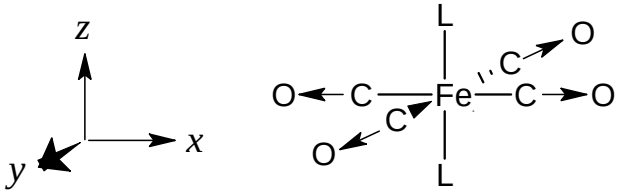
Looking only at the arrows on the bonds, and utilising the same rules (if the arrow moves, it's worth 0; if it stays the same, +1; if it reverses sign, -1)

C_{2v}	E	C_2	σ_v (xz)	σ_v'(yz)
Γ	4	0	2	2

$a_{A1} = 1/4\ [1\times4\times1 + 0 + 1\times2\times1 + 1\times2\times1] = 2$
$a_{A2} = 1/4\ [1\times4\times1 + 0 + 1\times2\times(-1) + 1\times2\times(-1)] = 0$
$a_{B1} = 1/4\ [1\times4\times1 + 0 + 1\times2\times1 + 1\times2\times(-1)] = 1$
$a_{B1} = 1/4\ [1\times4\times1 + 0 + 1\times2\times(-1) + 1\times2\times1] = 1$

Therefore, Γ factors into $2\ A_1 + B_1 + B_2$
All four are IR active (contain x, y, or z), so there are 4 CO stretches in this molecule

18. (b) Point group is D_{4h} (our old friend!), I would suggest using,

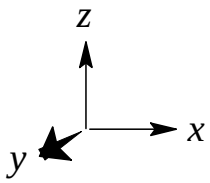


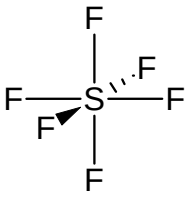
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0	0	0	4	2	0

$a_{A1g} = 1/16\ [1\times4\times1 + 0 + 0 + 2\times2\times1 + 0 + 0 + 0 + 1\times4\times1 + 2\times2\times1 + 0] = 1$
$a_{A2g} = 1/16\ [1\times4\times1 + 0 + 0 + 2\times2\times(-1) + 0 + 0 + 0 + 1\times4\times1 + 2\times2\times(-1) + 0] = 0$
...
$a_{Eu} = 1/16\ [1\times4\times2 + 0 + 0 + 2\times2\times0 + 0 + 0 + 0 + 1\times4\times2 + 2\times2\times0 + 0] = 1$

Therefore, Γ factors into $A_{1g} + B_{1g} + E_u$, of which only E_u is IR active, so this molecule has only 1 IR peak.

19. This problem requires the full solution.





Hints: The C_3 axis is in the middle of an octahedral face
The C_2 axis is along an edge of the octahedron (does not contain S-F bond)
The S_4 axis is coincident with the C_4 (along a F-S-F axis)
The S_6 axis is coincident with the C_3
Remember that σ_d goes between the bonds, so only 3 atoms lie in its plane

Oh	*E*	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	*i*	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	21	0	-1	3	-3	-3	-1	0	5	3

a_{A1g} = 1/48 [21×1 + 0 + (-6)×1 + 18×1 + (-9)×1 + (-3)×1 + (-6)×1 + 0 + 15×1 + 18×1] = 1
a_{A2g} = 1/48 [21×1 + 0 + (-6)×-1 + 18×-1 + (-9)×1 + (-3)×1 + (-6)×-1 + 0 + 15×1 + 18×-1] = 0
a_{Eg} = 1/48 [21×2 + 0 + 0 + 0 + (-9)×2 + (-3)×2 + 0 + 0 + 15×2 + 0] = 1
a_{T1g} = 1/48 [21×3 + 0 + (-6)×-1 + 18×1 + (-9)×-1 + (-3)×3 + (-6)×1 + 0 + 15×-1 + 18×-1] = 1
...
a_{T1u} = 1/48 [21×3 + 0 + (-6)×-1 + 18×1 + (-9)×-1 + (-3)×-3 + (-6)×-1 + 0 + 15×1 + 18×1] = 3
a_{T2u} = 1/48 [21×3 + 0 + (-6)×1 + 18×-1 + (-9)×-1 + (-3)×-3 + (-6)×1 + 0 + 15×1 + 18×-1] = 1

Therefore, Γ reduces to $A_{1g} + E_g + T_{1g} + T_{2g} + 3\ T_{1u} + T_{2u}$
Removing the rotational modes (R_x, R_y, R_z) removes the T_{1g}
Removing the translational modes (x, y, z) removes one T_{1u}
We are left with these vibrational modes: $A_{1g} + E_g + T_{2g} + 2\ T_{1u} + T_{2u}$

Only T_{1u} has an x, y, or z, therefore there are two IR-active vibrational modes.