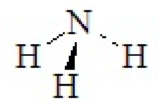
Chapter 6
Answers to Problems

6.1 (a) NH_3

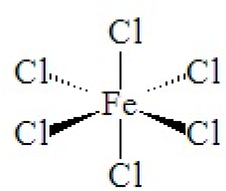


C_{3v}	E	$2C_3$	$3\sigma_v$
N_i	4	1	2
χ_i	3	0	1
Γ_{3n}	12	0	2

$$\Gamma_{3n} = 3A_1 + A_2 + 4E$$
$$\Gamma_{trans} = A_1 + E \quad \Gamma_{rot} = A_2 + E$$
$$\Gamma_{3n\text{-}6} = 2A_1 + 2E = 4 \text{ frequencies}$$

Infrared	4 ($2A_1 + 2E$)
Raman	4 ($2A_1 + 2E$)
Polarized	2 ($2A_1$)
Coincidences	4 ($2A_1 + 2E$)
Silent modes	0

(b) $FeCl_6^{3-}$

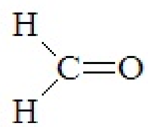


O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
N_i	7	1	1	3	3	1	1	1	5	3
χ_i	3	0	-1	1	-1	-3	-1	0	1	1
Γ_{3n}	21	0	-1	3	-3	-3	-1	0	5	3

$$\Gamma_{3n} = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$$
$$\Gamma_{trans} = T_{1u} \quad \Gamma_{rot} = T_{1g}$$
$$\Gamma_{3n\text{-}6} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u} = 6 \text{ frequencies}$$

Infrared	2 ($2T_{1u}$)
Raman	3 ($A_{1g} + E_g + T_{2g}$)
Polarized	1 (A_{1g})
Coincidences	0
Silent modes	1 (T_{2u})

(c) H_2CO

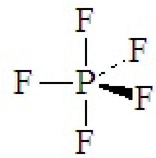


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
N_i	4	2	2	4
χ_i	3	-1	1	1
Γ_{3n}	12	-2	2	4

$$\Gamma_{3n} = 4A_1 + A_2 + 3B_1 + 4B_2$$
$$\Gamma_{trans} = A_1 + B_1 + B_2 \quad \Gamma_{rot} = A_2 + B_1 + B_2$$
$$\Gamma_{3n\text{-}6} = 3A_1 + B_1 + 2B_2 = 6 \text{ frequencies}$$

Infrared	6 ($3A_1 + B_1 + 2B_2$)
Raman	6 ($3A_1 + B_1 + 2B_2$)
Polarized	3 ($3A_1$)
Coincidences	6 ($3A_1 + B_1 + 2B_2$)
Silent modes	0

(d) PF_5

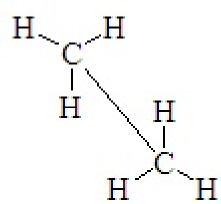


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
N_i	6	3	2	4	1	4
χ_i	3	0	-1	1	-2	1
Γ_{3n}	18	0	-2	4	-2	4

$$\Gamma_{3n} = 2A_1' + A_2' + 4E' + 3A_2'' + 2E''$$
$$\Gamma_{\text{trans}} = E' + A_2'' \quad \Gamma_{\text{rot}} = A_2' + E''$$
$$\Gamma_{3n\text{-}6} = 2A_1' + 3E' + 2A_2'' + E'' = 8 \text{ frequencies}$$

Infrared	5 ($3E' + 2A_2''$)
Raman	6 ($2A_1' + 3E' + E''$)
Polarized	2 ($2A_1'$)
Coincidences	3 ($3E'$)
Silent modes	0

(e) C_2H_6 (staggered configuration)

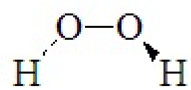


D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
N_i	8	2	0	0	0	4
χ_i	3	0	-1	-3	0	1
Γ_{3n}	24	0	0	0	0	4

$$\Gamma_{3n} = 3A_{1g} + A_{2g} + 4E_g + A_{1u} + 3A_{2u} + 4E_u$$
$$\Gamma_{trans} = A_{2u} + E_u \quad \Gamma_{rot} = A_{2g} + E_g$$
$$\Gamma_{3n\text{-}6} = 3A_{1g} + 3E_g + A_{1u} + 2A_{2u} + 3E_u = 12 \text{ frequencies}$$

Infrared	5 ($2A_{2u} + 3E_u$)
Raman	6 ($3A_{1g} + 3E_g$)
Polarized	3 ($3A_{1g}$)
Coincidences	0
Silent modes	1 (A_{1u})

(f) H_2O_2

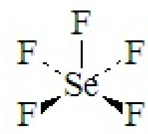


C_2	E	C_2
N_i	4	0
χ_i	3	-1
Γ_{3n}	12	0

$$\Gamma_{3n} = 6A + 6B$$
$$\Gamma_{trans} = A + 2B \quad \Gamma_{rot} = A + 2B$$
$$\Gamma_{3n\text{-}6} = 4A + 2B = 6 \text{ frequencies}$$

Infrared	6 ($4A + 2B$)
Raman	6 ($4A + 2B$)
Polarized	4 ($4A$)
Coincidences	6 ($4A + 2B$)
Silent modes	0

6.2 (a) SeF_5^-

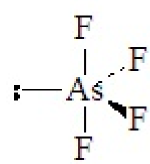


C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
N_i	6	2	2	4	2
χ_i	3	1	-1	1	1
Γ_{3n}	18	2	-2	4	2

$$\Gamma_{3n} = 4A_1 + A_2 + 2B_1 + B_2 + 5E$$
$$\Gamma_{\text{trans}} = A_1 + E \quad \Gamma_{\text{rot}} = A_2 + E$$
$$\Gamma_{3n\text{-}6} = 3A_1 + 2B_1 + B_2 + 3E = 9 \text{ frequencies}$$

Infrared	6 ($3A_1 + 3E$)
Raman	9 ($3A_1 + 2B_1 + B_2 + 3E$)
Polarized	3 ($3A_1$)
Coincidences	6 ($3A_1 + 3E$)
Silent modes	0

(b) AsF_4^-

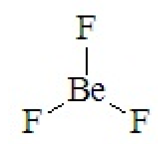


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
N_i	5	1	3	3
χ_i	3	-1	1	1
Γ_{3n}	15	-1	3	3

$$\Gamma_{3n} = 5A_1 + 2A_2 + 4B_1 + 4B_2$$
$$\Gamma_{\text{trans}} = A_1 + B_1 + B_2 \quad \Gamma_{\text{rot}} = A_2 + B_1 + B_2$$
$$\Gamma_{3n\text{-}6} = 4A_1 + A_2 + 2B_1 + 2B_2 = 9 \text{ frequencies}$$

Infrared	8 ($4A_1 + 2B_1 + 2B_2$)
Raman	9 ($4A_1 + A_2 + 2B_1 + 2B_2$)
Polarized	4 ($4A_1$)
Coincidences	8 ($4A_1 + 2B_1 + 2B_2$)
Silent modes	0

(c) BeF_3^-

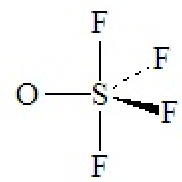


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
N_i	4	1	2	4	1	2
χ_i	3	0	-1	1	-2	1
Γ_{3n}	12	0	-2	4	-2	2

$$\Gamma_{3n} = A_1' + A_2' + 3E' + 2A_2'' + E''$$
$$\Gamma_{\text{trans}} = E' + A_2'' \quad \Gamma_{\text{rot}} = A_2' + E''$$
$$\Gamma_{3n\text{-}6} = A_1' + 2E' + A_2'' = 4 \text{ frequencies}$$

Infrared	3 ($2E' + A_2''$)
Raman	3 ($A_1' + 2E'$)
Polarized	1 (A_1')
Coincidences	2 ($2E'$)
Silent modes	0

(d) OSF_4

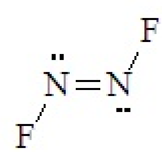


C_{2v}	E	C_2	σ_v	σ_v'
N_i	6	2	4	4
χ_i	3	-1	1	1
Γ_{3n}	18	-2	4	4

$$\Gamma_{3n} = 6A_1 + 2A_2 + 5B_1 + 5B_2$$
$$\Gamma_{trans} = A_1 + B_1 + B_2 \quad \Gamma_{rot} = A_2 + B_1 + B_2$$
$$\Gamma_{3n\text{-}6} = 5A_1 + A_2 + 3B_1 + 3B_2 = 12 \text{ frequencies}$$

Infrared	11 ($5A_1 + 3B_1 + 3B_2$)
Raman	12 ($5A_1 + A_2 + 3B_1 + 3B_2$)
Polarized	5 ($5A_1$)
Coincidences	11 ($5A_1 + 3B_1 + 3B_2$)
Silent modes	0

(e) *trans*-FNNF

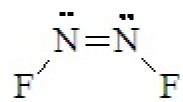


C_{2h}	E	C_2	i	σ_h
N_i	4	0	0	4
χ_i	3	-1	-3	1
Γ_{3n}	12	0	0	4

$$\Gamma_{3n} = 4A_g + 2B_g + 2A_u + 4B_u$$
$$\Gamma_{trans} = A_u + 2B_u \quad \Gamma_{rot} = A_g + 2B_g$$
$$\Gamma_{3n\text{-}6} = 3A_g + A_u + 2B_u = 6 \text{ frequencies}$$

Infrared	3 ($A_u + 2B_u$)
Raman	3 ($3A_g$)
Polarized	3 ($3A_g$)
Coincidences	0
Silent modes	0

(f) *cis*-FNNF

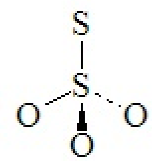


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
N_i	4	0	0	4
χ_i	3	-1	1	1
Γ_{3n}	12	0	0	4

$$\Gamma_{3n} = 4A_1 + 2A_2 + 2B_1 + 4B_2$$
$$\Gamma_{trans} = A_1 + B_1 + B_2 \quad \Gamma_{rot} = A_2 + B_1 + B_2$$
$$\Gamma_{3n\text{-}6} = 3A_1 + A_2 + 2B_2 = 6 \text{ frequencies}$$

Infrared	5 ($3A_1 + 2B_2$)
Raman	6 ($3A_1 + A_2 + 2B_2$)
Polarized	3 ($3A_1$)
Coincidences	5 ($3A_1 + 2B_2$)
Silent modes	0

(g) $S_2O_3^{2-}$

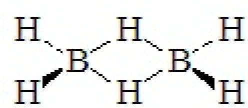


C_{3v}	E	$2C_3$	$3\sigma_v$
N_i	5	2	3
χ_i	3	0	1
Γ_{3n}	15	0	3

$$\Gamma_{3n} = 4A_1 + A_2 + 5E$$
$$\Gamma_{\text{trans}} = A_1 + E \quad \Gamma_{\text{rot}} = A_2 + E$$
$$\Gamma_{3n\text{-}6} = 3A_1 + 3E = 6 \text{ frequencies}$$

Infrared	6 ($3A_1 + 3E$)
Raman	6 ($3A_1 + 3E$)
Polarized	3 ($3A_1$)
Coincidences	6 ($3A_1 + 3E$)
Silent modes	0

(h) B_2H_6

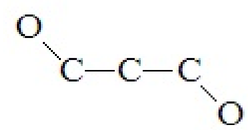


D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
N_i	8	2	2	0	0	2	6	4
χ^i	3	-1	-1	-1	-3	1	1	1
Γ_{3n}	24	-2	-2	0	0	2	6	4

$$\Gamma_{3n} = 4A_g + 2B_{1g} + 3B_{2g} + 3B_{3g} + A_u + 4B_{1u} + 3B_{2u} + 4B_{3u}$$
$$\Gamma_{trans} = B_{1u} + B_{2u} + B_{3u} \qquad \Gamma_{rot} = B_{1g} + B_{2g} + B_{3g}$$
$$\Gamma_{3n\text{-}6} = 4A_g + B_{1g} + 2B_{2g} + 2B_{3g} + A_u + 3B_{1u} + 2B_{2u} + 3B_{3u}$$

Infrared	8 ($3B_{1u} + 2B_{2u} + 3B_{3u}$)
Raman	9 ($4A_g + B_{1g} + 2B_{2g} + 2B_{3g}$)
Polarized	4 ($4A_g$)
Coincidences	0
Silent modes	1 (A_u)

6.3 C_3O_2 as C_{2h}



C_{2h}	E	C_2	i	σ_h
N_i	5	1	1	5
χ_i	3	-1	-3	1
Γ_{3n}	15	-1	-3	5

$$\Gamma_{3n} = 4A_g + 2B_g + 3A_u + 6B_u$$
$$\Gamma_{trans} = A_u + 2B_u \qquad \Gamma_{rot} = A_g + 2B_g$$
$$\Gamma_{3n\text{-}6} = 3A_g + 2A_u + 4B_u$$

Comparing these results with those developed in the text (pp. 190-191):

	C_{2h}	$D_{\infty h}$
Infrared	6 ($2A_u + 4B_u$)	4 ($2\Sigma_u^+ + 2\Pi_u$)
Raman	3 ($3A_g$)	3 ($2\Sigma_g^+ + \Pi_g$)
Polarized	3 ($3A_g$)	2 ($2\Sigma_g^+$)
Coincidences	0	0
Silent modes	0	0

6.4 In the correlation diagrams shown below, only the species of T_d and D_{4h} associated with normal modes are shown on the left. The frequency numbering of the undistorted structure has been retained for the distorted structure, with subscripts (*a*, *b*, *c*) for formerly degenerate modes, to show the fate of individual modes on descent in symmetry.

(a) Distorted tetrahedron (XY_4E) - C_{2v}

	T_d	C_{2v}		
ν_1	A_1	A_1	$\nu_1, \nu_{2a}, \nu_{3a}, \nu_{4a}$	i.r., Raman (pol)
ν_2	E	A_2	ν_{2b}	Raman
ν_3, ν_4	T_2	B_1	ν_{3b}, ν_{4b}	i.r., Raman
		B_2	ν_{3c}, ν_{4c}	i.r., Raman

(b) Slightly squashed tetrahedron - D_{2d}

	T_d	D_{2d}		
ν_1	A_1	A_1	ν_1, ν_{2a}	Raman (pol)
ν_2	E	B_1	ν_{2b}	Raman
ν_3, ν_4	T_2	B_2	ν_{3a}, ν_{4a}	i.r., Raman
		E	ν_{3bc}, ν_{4bc}	i.r., Raman

(c) Square pyramid with X at the apex - C_{4v}

	D_{4h}	C_{4v}		
ν_1	A_{1g}	A_1	ν_1, ν_3	i.r., Raman (pol)
ν_2	B_{1g}	B_1	ν_2, ν_5	Raman
ν_4	B_{2g}	B_2	ν_4	Raman
ν_3	A_{2u}	E	ν_6, ν_7	i.r., Raman
ν_5	B_{2u}			
ν_6, ν_7	E_u			

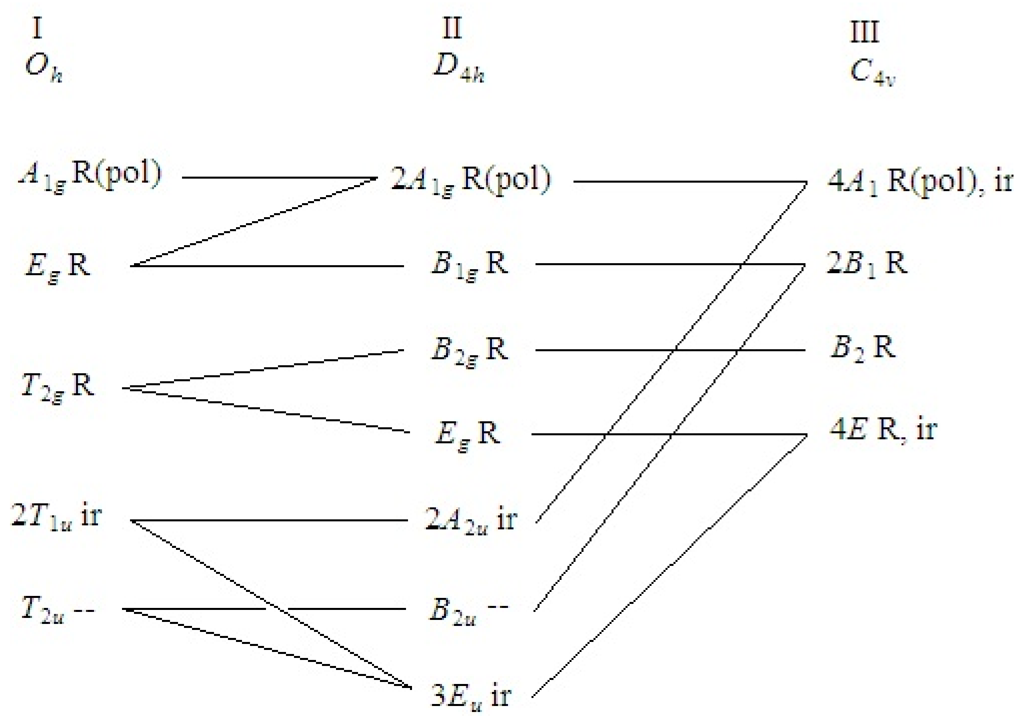
Note that the formerly silent mode, ν_5 (B_{2u}), of the perfect square plane becomes Raman active as a result of this distortion.

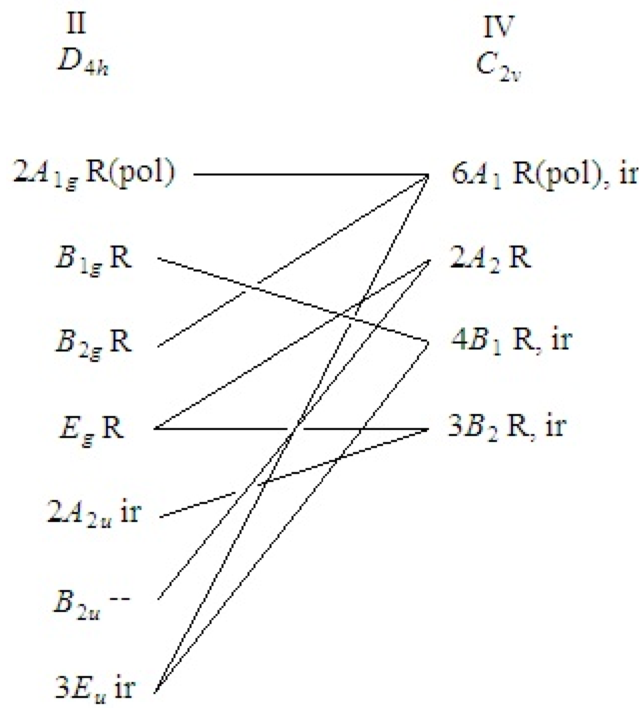
(d) Planar MX_4 with two long *trans* positions - D_{2h} (C_2' of D_{4h} retained)

	D_{4h}	D_{2h}		
ν_1	A_{1g}	A_{1g}	ν_1, ν_2	Raman (pol)
ν_2	B_{1g}			
ν_4	B_{2g}	B_{1g}	ν_4	Raman
ν_3	A_{2u}	B_{1u}	ν_3, ν_5	i.r.
ν_5	B_{2u}			
ν_6, ν_7	E_u	B_{2u}	ν_{6a}, ν_{7a}	i.r.
		B_{3u}	ν_{6b}, ν_{7b}	i.r.

6.5 Direct correlations from structure I to II to III can be made by using the correlation tables in Appendix B. A correlation from III to IV cannot be made in this way. Although C_{2v} is a subgroup of C_{4v}, structure IV is not obtained by retaining pre-existing elements of structure III. Most significantly, the C_2 axis of IV does not exist in III, but rather is newly created. However, it is possible to make a correlation from II (D_{4h}) to IV (C_{2v}), using the correlation in Appendix B in which C_2'' of D_{4h} is retained as the C_2 axis of C_{2v}. If a correlation III (C_{4v}) → IV (C_{2v}) is attempted, using the correlation tables without realizing the inconsistency of axis orientations in the two structures, the incorrect results for IV will be $6A_1$ (R - pol, ir) + A_2 (R) + 4 B_1 (R, ir) + $4B_2$ (R, ir). That the results from the correlation II → IV shown below are correct can be verified by determining the selection rules for IV *de novo*. By contrast, a structure whose selection rules could be determined correctly by direct correlation from III would be *trans*-MA_2B_3C. (Structure IV in Fig. 3.1 may be changed to this in the future.)

In the correlation diagrams shown here (I → II → III, this page, and II → IV, next page) only those symmetry species associated with normal modes are shown. When two or more frequencies occur with the same symmetry, the number of occurrences is indicated in front of the Mulliken symbol.





	I	II
Infrared	2 ($2T_{1u}$)	5 ($2A_{2u} + 3E_u$)
Raman	3 ($A_{1g} + E_g + T_{2g}$)	5 ($2A_{1g} + B_{1g} + B_{2g} + E_g$)
Polarized	1 (A_{1g})	2 (A_{1g})
Coincidences	0	0
Silent modes	1 (T_{2u})	1 (B_{2u})
	III	IV
Infrared	8 ($4A_1 + 4E$)	13 ($6A_1 + 4B_1 + 3B_2$)
Raman	11 ($4A_1 + 2B_1 + B_2 + 4E$)	15 ($6A_1 + 2A_2 + 4B_1 + 3B_2$)
Polarized	4 (A_1)	6 ($6A_1$)
Coincidences	8 ($4A_1 + 4E$)	13 ($6A_1 + 4B_1 + 3B_2$)
Silent modes	0	0

6.6 (a) CO_2 [O=C=O] Use D_{2h} as a working group.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
N_i	3	3	1	1	1	1	3	3
χ^i	3	-1	-1	-1	-3	1	1	1
Γ_{3n}	9	-3	-1	-1	-3	1	3	3

$$\Gamma_{3n} = A_g + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$
$$\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u} \quad \Gamma_{\text{rot}} = B_{2g} + B_{3g} \text{ (not } B_{1g} - R_z)$$
$$\Gamma_{3n\text{-}5} = A_g + B_{1u} + B_{2u} + B_{3u}$$
$$\Rightarrow \text{In } D_{\infty h}, \Gamma_{3n\text{-}5} = \Sigma_g^+ + \Sigma_u^+ + \Pi_u = 3 \text{ frequencies}$$

Infrared	2 ($\Sigma_u^+ + \Pi_u$)
Raman	1 (Σ_g^+)
Polarized	1 (Σ_g^+)
Coincidences	0
Silent modes	0

(b) OCN^- $[O–C{\equiv}N]^-$ Use C_{2v} as a working group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
N_i	3	3	3	3
χ_i	3	-1	1	1
Γ_{3n}	9	-3	3	3

$$\Gamma_{3n} = 3A_1 + 3B_1 + 3B_2$$
$$\Gamma_{\text{trans}} = A_1 + B_1 + B_2 \quad \Gamma_{\text{rot}} = B_1 + B_2 \text{ (not } A_2 - R_z)$$
$$\Gamma_{3n\text{-}5} = 2A_1 + B_1 + B_2$$
$$\text{In } C_{\infty v}, \Gamma_{3n\text{-}5} = 2\Sigma^+ + \Pi = 3 \text{ frequencies}$$

Infrared	3 ($2\Sigma^+ + \Pi$)
Raman	3 ($2\Sigma^+ + \Pi$)
Polarized	2 ($2\Sigma^+$)
Coincidences	3 ($2\Sigma^+ + \Pi$)
Silent modes	0

(c) H–C≡C–H Use D_{2h} as a working group.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
N_i	4	4	0	0	0	0	4	4
χ^i	3	-1	-1	-1	-3	1	1	1
Γ_{3n}	12	-4	0	0	0	0	4	4

$$\Gamma_{3n} = 2A_g + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$
$$\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u} \qquad \Gamma_{\text{rot}} = B_{2g} + B_{3g} \text{ (not } B_{1g} - R_z)$$
$$\Gamma_{3n\text{-}5} = 2A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$$
$$\Rightarrow \text{In } D_{\infty h}, \Gamma_{3n\text{-}5} = 2\Sigma_g^+ + \Pi_g + \Sigma_u^+ + \Pi_u = 5 \text{ frequencies}$$

Infrared	2 ($\Sigma_u^+ + \Pi_u$)
Raman	3 ($2\Sigma_g^+ + \Pi_g$)
Polarized	2 ($2\Sigma_g^+$)
Coincidences	0
Silent modes	0

(d) Cl–C≡C–H

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
N_i	4	4	4	4
χ_i	3	-1	1	1
Γ_{3n}	12	-4	4	4

$$\Gamma_{3n} = 4A_1 + 4B_1 + 4B_2$$
$$\Gamma_{\text{trans}} = A_1 + B_1 + B_2 \quad \Gamma_{\text{rot}} = B_1 + B_2 \text{ (not } A_2 - R_z)$$
$$\Gamma_{3n\text{-}5} = 3A_1 + 2B_1 + 2B_2$$
In $C_{\infty v}$, $\Gamma_{3n\text{-}5} = 3\Sigma^+ + 2\Pi = 5$ frequencies

Infrared	5 ($3\Sigma^+ + 2\Pi$)
Raman	5 ($3\Sigma^+ + 2\Pi$)
Polarized	3 ($3\Sigma^+$)
Coincidences	5 ($3\Sigma^+ + 2\Pi$)
Silent modes	0

(e) H–C≡C–C≡C–H Use D_{2h} as a working group.

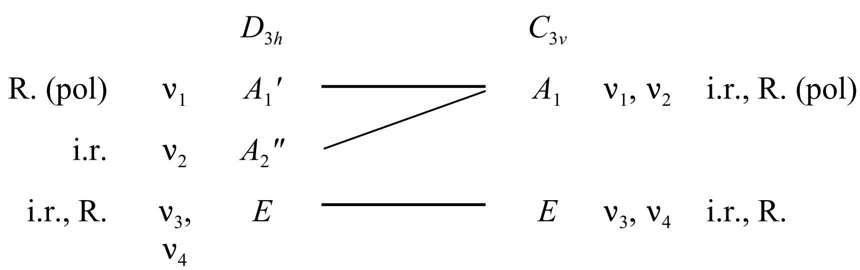
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
N_i	6	6	0	0	0	0	6	6
χ^i	3	-1	-1	-1	-3	1	1	1
Γ_{3n}	18	-6	0	0	0	0	6	6

$$\Gamma_{3n} = 3A_g + 3B_{2g} + 3B_{3g} + 3B_{1u} + 3B_{2u} + 3B_{3u}$$
$$\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u} \quad \Gamma_{\text{rot}} = B_{2g} + B_{3g} \text{ (not } B_{1g} - R_z)$$
$$\Gamma_{3n\text{-}5} = 3A_g + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$
$\Rightarrow$ In $D_{\infty h}$, $\Gamma_{3n\text{-}5} = 3\Sigma_g^+ + 2\Pi_g + 2\Sigma_u^+ + 2\Pi_u = 9$ frequencies

Infrared	$4\ (2\Sigma_u^+ + 2\Pi_u)$
Raman	$5\ (3\Sigma_g^+ + 2\Pi_g)$
Polarized	$3\ (3\Sigma_g^+)$
Coincidences	0
Silent modes	0

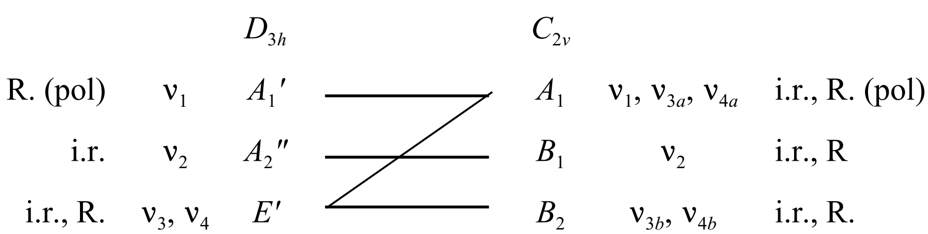
6.7 (a) $\Gamma_{3n\text{-}6} = A_1' + A_2'' + 2E' = 4$ frequencies $\Rightarrow$ $\nu_1\ (A_1')$, $\nu_2\ (A_2'')$, $\nu_3\ (E')$, $\nu_4\ (E')$
The systematic assignment of frequency numbers labels nondegenerate modes before degenerate modes, even though E' is listed before A_2'' in the current D_{3h} character table.

(b) Association along the C_3 axis of the NO_3^- ion causes its symmetry to descend to C_{3v}. The changes in spectra can be predicted from the following correlation diagram.



The descent does not lift any degeneracies, but the spectroscopic activities change significantly. The totally symmetric stretching mode, ν_1, becomes infrared active. The out-of-plane deformation mode, ν_2, becomes a Raman-active polarized mode.

In-plane association causes the NO_3^- ion's symmetry to descend to C_{2v}. The changes in spectra can be predicted from the following correlation diagram.



In this case the E' degeneracies of both ν_3 and ν_4 are lifted. Thus, both ν_3 and ν_4 may split into two frequencies each, with C_{2v} symmetries A_1 and B_2, giving a total of six frequencies active in both the infrared and Raman spectra.

The predictions for both modes of association are summarized in the table below.

	D_{3h}	C_{3v}	C_{2v}
Infrared	3 ($A_2'' + 2E'$)	4 ($2A_1 + 2E$)	6 ($3A_1 + B_1 + 2B_2$)
Raman	3 ($A_1' + 2E'$)	4 ($2A_1 + 2E$)	6 ($3A_1 + B_1 + 2B_2$)
Polarized	1 (A_1')	2 ($2A_1$)	3 ($3A_1$)
Coincidences	2 ($2E'$)	4 ($2A_1 + 2E$)	6 ($3A_1 + B_1 + 2B_2$)
Silent modes	0	0	0

(c) The data are consistent with the predictions of the C_{2v} model of association.

(d) The 830 cm^{-1} frequency is ν_2 (A_2''), which is infrared active but Raman inactive for the "free" ion. The first overtone, $2\nu_2$, has A_1' symmetry in D_{3h}, which is a Raman active species. This fundamental becomes Raman active in either the C_{2v} or C_{3v} models of association. Regardless of the mode of association, the overtone would be Raman active, since all first overtones of nondegenerate modes are totally symmetric and therefore Raman active. Failure to observe ν_2 in the Raman spectrum of 0.3-2.3 M $Al(NO_3)_3$ solutions might seem to suggest that there is no cation-anion or solvent-anion association. However, association cannot be ruled out, because the fundamental, although Raman allowed by association, might be very broad and have too weak an intensity to be observed above the instrumental background.

6.8 (a) True. All even-number direct products of a nondegenerate species give the totally symmetric representation. Thus, all even-number overtones will belong to the totally symmetric representation, which is always Raman allowed.

(b) Not always true. Molecules belonging to point groups C_1, C_s, C_n, and C_{nv} have at least one unit vector transforming as the totally symmetric representation. In these groups, the even-number overtones will be infrared allowed, as well as Raman allowed. Also, in groups with degenerate representations, the direct products will be reducible representations, which may contain an irreducible representation allowing infrared activity.

(c) True. All odd-number direct products of any irreducible representation will be or contain the original representation. If a vibrational mode is active as a fundamental, it follows that all its odd-number overtones will be infrared allowed, too.

(d) True. The direct product of any irreducible representation with the totally symmetric representation is the non-totally symmetric representation. The symmetry-based selection rules for the non-totally symmetric mode will apply to any combination $\nu_s \pm \nu_i$, because the symmetry of the combination is the same as ν_i.

(e) True. All first overtones belong to or contain the totally symmetric representation. The product of the totally symmetric representation with itself is, of course, totally symmetric. Therefore combinations of the type $\nu_s \pm 2\nu_i$ will be Raman allowed.

6.9 (a) The ν_6 frequency arises from three degenerate T_{2u} modes, which are inactive in both the infrared and Raman spectra. They are silent modes.

(b) O_h is centrosymmetric, so the rule of mutual exclusion precludes infrared-active modes from being Raman-active, and vice versa.

(c) $2\nu_4$ This should occur at approximately 2 x 262.7 cm^{-1} = 525.4 cm^{-1}. The observed frequency (531 ± 3 cm^{-1}) is a little high, but not unreasonably so. The symmetry of this overtone is T_{1u} x $T_{1u} = A_{1g} + E_g + T_{1g} + T_{2g}$, making it Raman allowed on the basis of A_{1g}, E_g, and T_{2g}.

$\nu_4 + \nu_6$ This should occur at approximately 262.7 cm^{-1} + 117 cm^{-1} = 379.7 cm^{-1}, which is good agreement with the observed 380 ± 3 cm^{-1}. The symmetry of this combination is T_{1u} x $T_{2u} = A_{2g} + E_g + T_{1g} + T_{2g}$, making it Raman allowed on the basis of E_g and T_{2g}.

$2\nu_6$ If the band at 233 ± 2 cm^{-1} is assigned as $2\nu_6$, then ν_6 is approximately 117 cm^{-1}. As shown above, this is consistent with the assignment of the 380 ± 3 cm^{-1} band to $\nu_4 + \nu_6$. The symmetry of the $2\nu_6$ overtone is T_{2u} x $T_{2u} = A_{1g} + E_g + T_{1g} + T_{2g}$, making it Raman allowed on the basis of A_{1g}, E_g, and T_{2g}. [Note: The symmetry of T_{2u} x T_{2u} is identical to T_{1u} x T_{1u}, as shown for $2\nu_4$ above.] The observed polarization is consistent with the A_{1g} component.

$\nu_1 + \nu_3$ This should occur at approximately 741 cm^{-1} + 739 cm^{-1} = 1480 cm^{-1}, which is good agreement with the observed 1479.4 ± 0.5 cm^{-1}. The symmetry of this combination is A_{1g} x $T_{1u} = T_{1u}$, making it infrared allowed on the basis of T_{1u}.

$\nu_2 + \nu_3$ This should occur at approximately 652 cm^{-1} + 739 cm^{-1} = 1391 cm^{-1}, which is good agreement with the observed 1386.9 ± 0.5 cm^{-1}. The symmetry of this combination is E_g x $T_{1u} = T_{1u} + T_{2u}$, making it infrared allowed on the basis of T_{1u}.

$\nu_2 + \nu_4$ This should occur at approximately 652 cm^{-1} + 263 cm^{-1} = 915 cm^{-1}, which is good agreement with the observed 913.1 ± 0.5 cm^{-1}. ± 0.5 cm^{-1}. The symmetry of this combination is E_g x $T_{1u} = T_{1u} + T_{2u}$, making it infrared allowed on the basis of T_{1u}.

(d) The combination and overtones observed in the Raman spectrum have *gerade* symmetry, and the combinations observed in the infrared spectrum have *ungerade* symmetry. Consistent with the rule of mutual exclusion, the Raman-active frequencies cannot be infrared-active, and vice versa.

(e) In order to be infrared allowed, a combination would have to be or contain T_{1u}. The possible combinations with ν_6, their symmetries, and whether infrared allowed are shown below.

Combination	Symmetries	Allowed?
$\nu_1 + \nu_6$	$A_{1g} \text{ x } T_{2u} = T_{2u}$	No
$\nu_2 + \nu_6$	$E_g \text{ x } T_{2u} = T_{1u} + T_{2u}$	Yes
$\nu_3 + \nu_6$	$T_{1u} \text{ x } T_{2u} = A_{2g} + E_g + T_{1g} + T_{2g}$	No
$\nu_4 + \nu_6$	$T_{1u} \text{ x } T_{2u} = A_{2g} + E_g + T_{1g} + T_{2g}$	No
$\nu_5 + \nu_6$	$T_{2g} \text{ x } T_{2u} = A_{1u} + E_u + T_{1u} + T_{2u}$	Yes

The predicted frequencies for the allowed combinations are:

$$\nu_2 + \nu_6 \approx 652 \text{ cm}^{-1} + 117 \text{ cm}^{-1} = 769 \text{ cm}^{-1}$$

$$\nu_5 + \nu_6 \approx 317 \text{ cm}^{-1} + 117 \text{ cm}^{-1} = 434 \text{ cm}^{-1}$$

Although allowed, these combinations apparently have too weak intensities to be observed.