Spectroscopy Exercises

Solutions to Exercise 4C

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1. For a molecule belonging to the D_{2h} point group, **deduce whether the following vibrational transitions from the ground vibrational state are allowed in the infrared and/or Raman spectrum. State the direction of the transition moment and/or the component of the polarizability involved.**

a. to the v=2 level of a b_{1g} vibration
b. to the v=1 level of an a_u or b_{2u} vibration
c. to the combination level involving v=1 of a b_{1u} and v=1 of a b_{3g} vibration
d. to the combination level involving v=2 of an a_u vibration and v=1 of a b_{2g} vibration.

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a)

General remarks: For a molecule, a transition from ν_1 to ν_2 to be infrared-active(raman)-active, $\Psi_{v2}^*\hat{\mu}\Psi_{v1}$ ($\Psi_{v2}^*\hat{\alpha}_{ij}\Psi_{v1}$) has to be symmetric in order to not vanish upon integration. This is aequivalent to the direct sum of the functions to contain the totally symmetric representation (a consequence coming from group theory). In the case that Ψ_{v1} is the ground state, the direct product $\Psi_{v2}^*\hat{\mu}$ ($\Psi_{v2}^*\hat{\alpha}$) has to contain the totally symmetric representation (since the ground state is totally symmetric). For this to happen, $\Gamma(\Psi_2) = \Gamma(\hat{\mu}_i)(\Gamma(\Psi_2) = \Gamma(\hat{\alpha}_{ij}))$ has to hold for all components i, j.

Operator specific remarks: The dipole moment operator is proportional to the space-operator. Therefore, $\hat{\mu}_i$ possesses B_{1u} , B_{2u} , B_{3u} symmetry for the x,y and z component respectively. For the polarizibility, the following symmetries are given for the different components:

$$\begin{pmatrix} A_g & B_{1g} & B_{2g} \\ B_{1g} & A_g & B_{3g} \\ B_{2g} & B_{3g} & A_g \end{pmatrix}$$

With the above considerations in mind, the transitions are investigated as follows:

a) The symmetry of the niveau $\nu = 2$ of a b_{1g} vibrational mode is $B_{1g} \otimes B_{1g} = A_g$, which is different from any component of $\hat{\mu}$. Therefore, it is IR-forbidden. However, since the components α_{ii} are of symmetry A_g, the transition is Raman allowed.

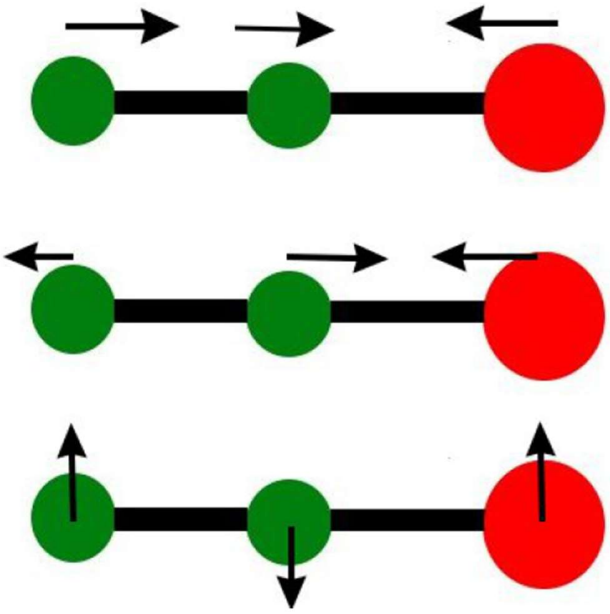
b) Neither the au nor the b_{2u} vibrational mode possesses an adequate symmetry contained in μ or α_{ij} . Therefore these transitions are neither IR nor Raman allowed.

c) The symmetry of the combined vibrational mode is: $B_{1u} \otimes B_{3g} = B_{2u}$. Therefore, this transition is Raman forbidden, but IR allowed with component μ_y.

d) The symmetry of the combined vibrational mode is: $A_u \otimes A_u \otimes B_{2g} = B_{2g}$. Therefore, this transition is Raman allowed with component α_{xz}, but IR forbidden.

2. The infrared spectrum of N_2O has three fundamental bands. Assuming that the structure of N_2O is linear, **explain how this spectrum allows you to distinguish between NNO and NON. Sketch the normal modes.**

With IR spectroscopy one can easily distinguish between NNO and NON, since NNO posesses a permanent dipole, whereas NON does not (assuming a linear structure). Therefore NNO is IR active and NON is not. Furthermore, the 3 fundamental bands can be associated to the following normal modes:



3. **Fill in the table with a YES or a NO to indicate allowed spectroscopic transitions. For vibrational and vibrational Raman transitions, indicate the symmetry species of the vibrational modes to which transitions are allowed.**

General approach:

Purely rotational transitions:

The existence of a permanent dipole moment is investigated: For molecules with a permanent dipole moment, purely rotational transitions are allowed, else not.

Vibrational & vibrational Raman transitions:

For determining the possible vibrational IR and vibrational Raman transitions, the direct product decomposition of the reducible representation of the vibrational part needs to be computed. Since the IR activity is determined by the dipole moment, a mode will be active if the irreducible representation contains a linear part (x, y or z). Similarly, the Raman activity is determined by the polarisability and a mode will be active if the irreducible representation contains a quadratic part (xx,xy, yy, . . .). The irreducible representation can be computed in the following way:

1. Determine the symmetry group G of the molecule
2. If G is an infinite group, then consider a subgroup (for $D_{\infty h}$ this could be D_{2h} for example) and continue solving in that group.
3. Look up (or derive) the character table corresponding to the group
4. For each symmetry element in the group, compute the reducible representation by multiplying the number of unshifted atoms with the contribution per atom 1
5. Obtain the irreducible representation Γ^{irred}_{tot}, by computing the coefficient a_i for each term i using the reduction formula (as also outlined in the lecture notes):

$$a_i = \frac{1}{h} \sum_c \bar{N_c} \chi^i(c) \cdot \chi^{red}(c)$$

6. If the original group was infinite: use (or derive 2) partial correlation tables to map the obtained decomposition back to the infinite group.
7. Subtract the translational and the rotational terms from Γ^{irred}_{tot} in order to obtain Γ^{irred}_{vib}

[1]The contribution per atom depends on the considered symmetry element: a) E. . . 3, b) i. . . -3 c) σ . . . 1 d) $C_n = 1 + 2 \cos (360/n)$ d) $S_n = -1 + 2 \cos (360/n)$

[2]One can easily derive partial correlation tables by matching corresponding functions

H_2O:

H_2O possesses a permanent dipole in z-direction. Therefore, purely rotational transitions are allowed. Furthermore, it belongs to the symmetry group C_{2v}, which possesses the following character table:

C_{2v}	E	C_2	$\sigma_v(x,z)$	$\sigma_v(y,z)$		
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

The character of the reducible representation for H_2O is computed:

- $\chi(E) = 3N_E = 3 \cdot 3 = 9$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 1(1 + 2\cos(180)) = -1$
- $\chi(\sigma_v(x,z)) = N_{\sigma_v(x,z)} = 3$
- $\chi(\sigma_v(y,z)) = N_{\sigma_v(y,z)} = 1$

Since C_{2v} is a finite group (4 group elements), the reduction formula can be applied:

- $a_{A_1} = \frac{1}{4}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 1) = 3$
- $a_{A_2} = \frac{1}{4}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-1) - 1 \cdot 1 \cdot 3 - 1 \cdot 1 \cdot 1) = 1$
- $a_{B_1} = \frac{1}{4}(1 \cdot 1 \cdot 9 - 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot 3 - 1 \cdot 1 \cdot 1) = 3$
- $a_{B_2} = \frac{1}{4}(1 \cdot 1 \cdot 9 - 1 \cdot 1 \cdot (-1) - 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 1) = 2$

With that, the direct product decomposition is: $\Gamma^{irred}_{tot} = 3A_1 + 1A_2 + 3B_1 + 2B_2$
Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma^{irred}_{vib} &= \Gamma^{irred}_{tot} - \Gamma^{irred}_{trans} - \Gamma^{irred}_{rot} \\ &= 3A_1 + 1A_2 + 3B_1 + 2B_2 - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) \\ &= 2A_1 + B_1\end{aligned}$$

This means that 2 vibrational normal modes have A_1 symmetry and 1 normal mode has B_1 symmetry. Considering the character table, A_1 corresponds to z, x^2 , y^2 and z^2 entries, which is associated to a μ_z dipole moment and α_{xx} , α_{yy} and α_{zz} polarisabilities. Similarly, B_1 corresponds to x and xz entries, which is associated to a μ_x dipole moment and an α_{xz} polarisability.

SF_6:

SF_6 possesses no permanent dipole. Therefore purely rotational transitions are not allowed. Furthermore, it belongs to the symmetry group O_h, which has the following character table:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ (C_4^2)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
E_g	2	-1	0	0	2	2	0	-1	2	0		$2z^2-x^2-y^2$, x^2-y^2
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		xy, xz, yz
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x,y,z	

The character of the reducible representation for $SF_6$is computed:

- $\chi(E) = 3N = 3 \cdot 7 = 21$
- $\chi(8C_3) = N_c(1 + 2\cos(360/3)) = 1(1 + 2\cos(120)) = 0$
- $\chi(6C_2) = N_c(1 + 2\cos(360/2)) = 1(1 + 2\cos(180)) = -1$
- $\chi(6C_4) = N_c(1 + 2\cos(360/4)) = 3(1 + 2\cos(90)) = 3$
- $\chi(3C_2) = N_c(1 + 2\cos(360/2)) = 3(1 + 2\cos(180)) = -3$
- $\chi(i) = N_i(-3) = 1 \cdot (-3) = -3$
- $\chi(6S_4) = N_S(-1 + 2\cos(360/4)) = 3(-1 + 2\cos(90)) = -3$
- $\chi(8S_6) = N_S(-1 + 2\cos(360/6)) = 1(-1 + 2\cos(60)) = 0$
- $\chi(3\sigma_h) = N_{\sigma_h} = 5$
- $\chi(6\sigma_d) = N_{\sigma_d} = 3$

Since O_h is a finite group (48 group elements), the reduction formula can be applied to the relevant irreducible terms[3]:

- $a_{A_{1g}} = \frac{1}{48}(1 \cdot 1 \cdot 21 + 8 \cdot 1 \cdot 0 + 6 \cdot 1 \cdot (-1) + 6 \cdot 1 \cdot 3 + 3 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-3) + 6 \cdot 1 \cdot (-1) + 8 \cdot 1 \cdot 0 + 3 \cdot 1 \cdot 5 + 6 \cdot 1 \cdot 3) = 1$
- $a_{E_g} = \frac{1}{48}(1 \cdot 2 \cdot 21 + 8 \cdot (-1) \cdot 0 + 6 \cdot 0 \cdot (-1) + 6 \cdot 0 \cdot 3 + 3 \cdot 2 \cdot (-3) + 1 \cdot 2 \cdot (-3) + 6 \cdot 0 \cdot (-1) + 8 \cdot (-1) \cdot 0 + 3 \cdot 2 \cdot 5 + 6 \cdot 0 \cdot 3) = 1$
- $a_{T_{2g}} = \frac{1}{48}(1 \cdot 3 \cdot 21 + 8 \cdot 0 \cdot 0 + 6 \cdot 1 \cdot (-1) + 6 \cdot (-1) \cdot 3 + 3 \cdot (-1) \cdot (-3) + 1 \cdot 3 \cdot (-3) + 6 \cdot (-1) \cdot (-1) + 8 \cdot 0 \cdot 0 + 3 \cdot (-1) \cdot 5 + 6 \cdot 1 \cdot 3) = 1$

- $a_{T_{1u}} = \frac{1}{48}(1\cdot 3\cdot 21 + 8\cdot 0\cdot 0 + 6\cdot(-1)\cdot(-1) + 6\cdot 1\cdot 3 + 3\cdot(-1)\cdot(-3) + 1\cdot(-3)\cdot(-3) + 6\cdot(-1)\cdot(-1) + 8\cdot 0\cdot 0 + 3\cdot 1\cdot 5 + 6\cdot 1\cdot 3) = 3$

With that, the direct product decomposition is: $\Gamma^{irred}_{tot} = A_{1g} + E_g + T_{2g} + 3T_{1u} + \ldots$
Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

[3]Remark: Only irreducible terms which are associated to linear or quadratic coordinate terms need to be considered.

$$\begin{aligned}\Gamma^{irred}_{vib} &= \Gamma^{irred}_{tot} - \Gamma^{irred}_{trans} - \Gamma^{irred}_{rot} \\ &= A_{1g} + E_g + T_{2g} + 3T_{1u} + \ldots - (T_{1u}) - (T_{1g}) \\ &= A_{1g} + E_g + T_{2g} + 2T_{1u} + \ldots\end{aligned}$$

This means that one vibrational normal mode has A_1 symmetry, one has E_g symmetry, one has T_{2g} symmetry and two have T_{1u} symmetry. Comparing these terms with corresponding functions in the character table leads to 3 Raman active modes of symmetry A_{1g}, E_g and T_{2g} and two IR active modes of symmetry T_{1u}.

<u>CS_2:</u>
CS_2 possesses no permanent dipole. Therefore purely rotational transitions are not allowed. Furthermore, it belongs to the symmetry group $D_{\infty h}$. Since $D_{\infty h}$ is an ininite group, we consider one of its subgroups - namely D_{2h} [4] , which possesses the following character table:

D_{2h}	E	C_2	$C_2(x)$	$C_2(y)$	i	σ_{xy}	σ_{xz}	σ_{yz}		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	-1	1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	1	-1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	-1	1	-1	1	-1	1	y	
B_{3u}	1	-1	1	-1	-1	1	1	-1	x	

The character of the reducible representation for CS_2 is computed:

- $\chi(E) = N_E \cdot 3 = 3 \cdot 3 = 9$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 3(1 + 2\cos(180)) = -3$
- $\chi(C_2(x)) = N_c(1 + 2\cos(360/2)) = 1(1 + 2\cos(180)) = -1$
- $\chi(C_2(y)) = N_c(1 + 2\cos(360/2)) = 1(1 + 2\cos(180)) = -1$
- $\chi(i) = N_i \cdot (-3) = 1 \cdot (-3) = -3$
- $\chi(\sigma_{xy}) = N_\sigma \cdot 1 = 1 \cdot 1 = 1$
- $\chi(\sigma_{xz}) = N_\sigma \cdot 1 = 3 \cdot 1 = 3$
- $\chi(\sigma_{yz}) = N_\sigma \cdot 1 = 3 \cdot 1 = 3$

[4]The choice of subgroup is in principle arbitrary, yet one of course will appreciate using a subgroup with a decently small numer of elements.

Since D_{2h} is a finite group (8 group elements), the reduction formula can be applied:

- $a_{Ag} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 3) = 1$
- $a_{B1g} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot (-1) \cdot 3) = 0$
- $a_{B2g} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot (-1) \cdot 3) = 1$
- $a_{B3g} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot 1 \cdot 3) = 1$
- $a_{Au} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot (-1) \cdot 3) = 0$
- $a_{B1u} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 3) = 2$
- $a_{B2u} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot 1 \cdot 3) = 2$
- $a_{B3u} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot (-1) \cdot 3)$

giving the following decomposition:
$\Gamma^{irred}_{tot}(D_{2h}) = A_g + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$

Considering now the partial correlation table:
$A_g \rightarrow \Sigma_g^+$, $B_{2g} + B_{3g} \rightarrow \Pi_g$, $B_{1u} \rightarrow \Sigma_u^+$, $B_{2u} + B_{3u} \rightarrow \Pi_u$,

the direct product decomposition in the original infinite group is obtained:
$\Gamma^{irred}_{tot}(D_{\infty h}) = \Sigma_g^+ + \Pi_g + 2\Sigma_u^+ + 2\Pi_u$

Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma_{vib}^{irred} &= \Gamma_{tot}^{irred} - \Gamma_{trans}^{irred} - \Gamma_{rot}^{irred} \\ &= \Sigma_g^+ + \Pi_g + 2\Sigma_u^+ + 2\Pi_u - (\Sigma_u^+ + \Pi_u) - (\Pi_g) \\ &= \Sigma_g^+ + \Sigma_u^+ + \Pi_u\end{aligned}$$

This means that one vibrational normal mode has Σ_g^+ symmetry, one has Σ_u^+ symmetry, one has Π_u symmetry. Comparing these terms with corresponding functions in the character table leads to 1 Raman active mode of symmetry Σ_g^+, E_g and T_{2g} and two IR active modes of symmetry Σ_u^+ and Π_u.

N_2O:

N_2O possesses a permanent dipole. Therefore purely rotational transitions are allowed. Furthermore, it belongs to the symmetry group $C_{\infty v}$. Since $C_{\infty v}$ is an ininite group, we consider one of its subgroups - namely C_{3v}, which possesses the following character table:

C_{2v}	E	C_2	$\sigma_v(x,z)$	$\sigma_v(y,z)$		
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

The character of the reducible representation for N_2O is computed:

- $\chi(E) = N_E \cdot 3 = 3 \cdot 3 = 9$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 3(1 + 2\cos(180)) = -3$
- $\chi(\sigma_v(xz)) = N_\sigma \cdot 1 = 3 \cdot 1 = 3$
- $\chi(\sigma_v(yz)) = N_\sigma \cdot 1 = 3 \cdot 1 = 3$

Since C_{3v} is a finite group (4 group elements), the reduction formula can be applied:

- $a_{A1} = \frac{1}{4}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 3 = 3$
- $a_{A2} = \frac{1}{4}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot 3 + 1 \cdot (-1) \cdot 3 = 0$
- $a_{B1} = \frac{1}{4}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot 3 + 1 \cdot (-1) \cdot 3 = 3$
- $a_{B2} = \frac{1}{4}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot 3 + 1 \cdot 1 \cdot 3 = 3$

giving the following decomposition: $\Gamma^{irred}_{tot}(C_{3v}) = 3A_1 + 3B_1 + 3B_2$
Considering now the partial correlation table:
$A_1 \rightarrow \Sigma^+$, $B_1 + B_2 \rightarrow \Pi$,

the direct product decomposition in the original infinite group is obtained:
$\Gamma^{irred}_{tot}(C_{\infty v}) = 3\Sigma^+ + 3\Pi$

Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma^{irred}_{vib} &= \Gamma^{irred}_{tot} - \Gamma^{irred}_{trans} - \Gamma^{irred}_{rot} \\ &= 3\Sigma_g + 3\Pi - (\Sigma_g + \Pi) - (\Pi) \\ &= 2\Sigma_g + \Pi\end{aligned}$$

This means that two vibrational normal modes have Σ^+ symmetry and one has Π symmetry. Comparing these terms with corresponding functions in the character table leads to all 3 modes to be Raman and IR active.

Allene:

Allene possesses no permanent dipole. Therefore, purely rotational transitions are not allowed. Furthermore, it belongs to the symmetry group D_{2d}, which possesses the following character table:

D_{2d}	E	$2S_4$	C_2	C_2'	$2\sigma_d$		
A_1	1	1	1	1	1		x^2, y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	(R_x, R_y),(x,y)	(xz,yz)

The character of the reducible representation for allene is computed:

- $\chi(E) = 3N_E = 3 \cdot 7 = 21$
- $\chi(2S_4) = N_s(-1 + 2\cos(360/4)) = 3(-1 + 2\cos(90)) = -3$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 3(1 + 2\cos(180)) = -3$
- $\chi(2C_2') = N_c(1 + 2\cos(360/2)) = 1(1 + 2\cos(180)) = -1$
- $\chi(2\sigma_d) = N_{\sigma_d} = 3$

Since D_{2d} is a finite group (8 group elements), the reduction formula can be applied:

- $a_{A_1} = \frac{1}{8}(1 \cdot 1 \cdot 21 + 2 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-3) + 2 \cdot 1 \cdot (-1) + 2 \cdot 1 \cdot 3) = 2$
- $a_{A_2} = \frac{1}{8}(1 \cdot 1 \cdot 21 + 2 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-3) + 2 \cdot (-1) \cdot (-1) + 2 \cdot (-1) \cdot 3) = 1$
- $a_{B_1} = \frac{1}{8}(1 \cdot 1 \cdot 21 + 2 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot (-3) + 2 \cdot 1 \cdot (-1) + 2 \cdot (-1) \cdot 3) = 2$
- $a_{B_2} = \frac{1}{8}(1 \cdot 1 \cdot 21 + 2 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot (-3) + 2 \cdot (-1) \cdot (-1) + 2 \cdot 1 \cdot 3) = 4$
- $a_E = \frac{1}{8}(1 \cdot 2 \cdot 21 + 2 \cdot 0 \cdot (-3) + 1 \cdot (-2) \cdot (-3) + 2 \cdot 0 \cdot (-1) + 2 \cdot 0 \cdot 3) = 6$

With that, the direct product decomposition is:
$\Gamma^{irred}_{tot} = 2A_1 + 1A_2 + 2B_1 + 4B_2 + 6E$

Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma^{irred}_{vib} &= \Gamma^{irred}_{tot} - \Gamma^{irred}_{trans} - \Gamma^{irred}_{rot} \\ &= 2A_1 + 1A_2 + 2B_1 + 4B_2 + 6E - (E + B_2) - (E + A_2) = \\ &= 2A_1 + 2B_1 + 3B_2 + 4E\end{aligned}$$

This means that 2 vibrational normal modes have A_1 symmetry, 2 have B_1 symmetry, 3 have B_2 symmetry and 4 have E symmetry. Comparing these terms with corresponding functions in the character table leads to all modes being Raman active and 7 modes with symmetry B_2 and E to be IR active.

Cl_2:

Cl_2 possesses no permanent dipole. Therefore purely rotational transitions are not allowed. Furthermore, it belongs to the symmetry group $D_{\infty h}$. Analogously to CS_2, the subgroup D_{2h} will be used to find a decomposition, which will then be mapped to the infinite group using partial correlation tables. The character of the reducible representation for Cl_2 is computed:

- $\chi(E) = N_E \cdot 3 = 2 \cdot 3 = 6$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 2(1 + 2\cos(180)) = -2$
- $\chi(C_2(x)) = N_c(1 + 2\cos(360/2)) = 0(1 + 2\cos(180)) = 0$
- $\chi(C_2(y)) = N_c(1 + 2\cos(360/2)) = 0(1 + 2\cos(180)) = 0$
- $\chi(i) = N_i \cdot (-3) = 0 \cdot (-3) = 0$
- $\chi(\sigma_{xy}) = N_\sigma \cdot 1 = 0 \cdot 1 = 0$
- $\chi(\sigma_{xz}) = N_\sigma \cdot 1 = 2 \cdot 1 = 2$
- $\chi(\sigma_{yz}) = N_\sigma \cdot 1 = 2 \cdot 1 = 2$

After application of the reduction formula, the following decomposition is found:

- $a_{Ag} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 3) = 1$
- $a_{B1g} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot (-1) \cdot 3) = 0$
- $a_{B2g} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot (-1) \cdot 3) = 1$
- $a_{B3g} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot 1 \cdot 3) = 1$
- $a_{Au} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot (-1) \cdot 3) = 0$
- $a_{B1u} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot 1 \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 3) = 2$
- $a_{B2u} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot (-1) \cdot (-1) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot 1 \cdot 3) = 2$
- $a_{B3u} = \frac{1}{8}(1 \cdot 1 \cdot 9 + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot (-1) + 1 \cdot (-1) \cdot (-1) + 1 \cdot (-1) \cdot (-3) + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot (-1) \cdot 3)$

giving the following decomposition:

$\Gamma^{irred}_{tot}(D_{2h}) = A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$

Considering now the partial correlation table:

$A_g \rightarrow \Sigma_g^+$, $B_{2g} + B_{3g} \rightarrow \Pi_g$, $B_{1u} \rightarrow \Sigma_u^+$, $B_{2u} + B_{3u} \rightarrow \Pi_u$,

the direct product decomposition in the original infinite group is obtained:
$\Gamma^{irred}_{tot}(D_{\infty h}) = \Sigma_g^+ + \Pi_g + \Sigma_u^+ + \Pi_u$

Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma_{vib}^{irred} &= \Gamma_{tot}^{irred} - \Gamma_{trans}^{irred} - \Gamma_{rot}^{irred} \\ &= \Sigma_g^+ + \Pi_g + \Sigma_u^+ + \Pi_u - (\Sigma_u^+ + \Pi_u) - (\Pi_g) \\ &= \Sigma_g^+\end{aligned}$$

This means that Cl_2 possesses one vibrational normal mode with symmetry Σ_g^+ which is Raman active.

4. For the molecules BF_3 (D_{3h} symmetry) and cis-diimide HN=NH (C_{2v} symmetry): a,b)
Determine the number and symmetries of the normal modes of vibration. Determine which of these modes will appear in an infrared spectrum and which will appear in a Raman spectrum.

In analogy to problem 3, the number and symmetries of the normal modes of vibration are found.

BF_3:
The point group D_{3h} possesses the following character table:

$\mathbf{D_{3h}}$	**E**	**2C$_3$**	**3C$_2'$**	$\sigma_h(xy)$	**2S$_3$**	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz, yz)

The character of the reducible representation for BF_3 is computed:

- $\chi(E) = N_E * 3 = 4 * 3 = 12$
- $\chi(2C_3) = N_c(1 + 2\cos(360/3)) = 1(1 + 2\cos(120)) = 0$
- $\chi(3C_2') = N_c(1 + 2\cos(360/2)) = 2(1 + 2\cos(180)) = -2$
- $\chi(\sigma_h(xy)) = N_\sigma * 1 = 4 * 1 = 4$
- $\chi(2S_3) = N_s(-1 + 2\cos(360/3)) = 1(-1 + 2\cos(120)) = -2$
- $\chi(3\sigma_v) = N_\sigma * 1 = 2 * 1 = 2$

Since D_{3h} is a finite group (12 group elements), the reduction formula can be applied:

- $A_1' = \frac{1}{12}(1\cdot1\cdot12 + 2\cdot1\cdot0 + 3\cdot1\cdot(-2) + 1\cdot1\cdot4 + 2\cdot1\cdot(-2) + 3\cdot1\cdot2) = 1$
- $A_2' = \frac{1}{12}(1\cdot1\cdot12 + 2\cdot1\cdot0 + 3\cdot(-1)\cdot(-2) + 1\cdot1\cdot4 + 2\cdot1\cdot(-2) + 3\cdot(-1)\cdot2) = 1$
- $E' = \frac{1}{12}(1\cdot2\cdot12 + 2\cdot(-1)\cdot0 + 3\cdot0\cdot(-2) + 1\cdot2\cdot4 + 2\cdot(-1)\cdot(-2) + 3\cdot0\cdot2) = 3$
- $A_1'' = \frac{1}{12}(1\cdot1\cdot12 + 2\cdot1\cdot0 + 3\cdot1\cdot(-2) + 1\cdot(-1)\cdot4 + 2\cdot(-1)\cdot(-2) + 3\cdot(-1)\cdot2) = 0$
- $A_2'' = \frac{1}{12}(1\cdot1\cdot12 + 2\cdot1\cdot0 + 3\cdot(-1)\cdot(-2) + 1\cdot(-1)\cdot4 + 2\cdot(-1)\cdot(-2) + 3\cdot1\cdot2) = 2$
- $E'' = \frac{1}{12}(1\cdot2\cdot12 + 2\cdot(-1)\cdot0 + 3\cdot0\cdot(-2) + 1\cdot(-2)\cdot4 + 2\cdot1\cdot(-2) + 3\cdot0\cdot2) = 1$

giving the following decomposition:
$\Gamma^{irred}_{tot}(D_{3h}) = A_1' + A_2' + 3E' + 2A_2'' + E''$

Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma^{irred}_{vib} &= \Gamma^{irred}_{tot} - \Gamma^{irred}_{trans} - \Gamma^{irred}_{rot} \\ &= A_1' + A_2' + 3E' + 2A_2'' + E'' - (E' + A_2'') - (A_2' + E'') \\ &= A_1' + 2E' + A_2''\end{aligned}$$

This means that BF_3 possesses 1 vibrational normal mode with symmetry A_1' which is Raman active, 2 normal modes of symmetry E' which are both IR and Raman active and another mode with symmetry A_2'' which is IR active.

HN=NH:
The point group C_{2v} possesses the following character table:

- $\chi(E) = N_E * 4 = 3 * 4 = 12$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 0(1 + 2\cos(180)) = 0$
- $\chi(\sigma_v(xz)) = N_\sigma * 1 = 0 * 1 = 0$
- $\chi(\sigma_v(yz)) = N_\sigma * 1 = 4 * 1 = 4$

The character of the reducible representation for HN=NH is computed:

C_{2v}	E	C_2	$\sigma_v(x,z)$	$\sigma_v(y,z)$		
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

Since C_{2v} is a finite group (4 group elements), the reduction formula can be applied:

- $\chi(E) = N_E * 4 = 3 * 4 = 12$
- $\chi(C_2) = N_c(1 + 2\cos(360/2)) = 0(1 + 2\cos(180)) = 0$
- $\chi(\sigma_v(xz)) = N_\sigma * 1 = 0 * 1 = 0$
- $\chi(\sigma_v(yz)) = N_\sigma * 1 = 4 * 1 = 4$

giving the following decomposition:
$\Gamma^{irred}_{tot} = 4A_1 + 2A_2 + 2B_1 + 4B_2$

Subtracting the translational and rotational modes, the irreducible representation of the vibrational part is obtained:

$$\begin{aligned}\Gamma^{irred}_{vib} &= \Gamma^{irred}_{tot} - \Gamma^{irred}_{trans} - \Gamma^{irred}_{rot} = \\ &= 4A_1 + 2A_2 + 2B_1 + 4B_2 - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) = \\ &= 3A_1 + A_2 + 2B_2\end{aligned}$$

This means that cis-diimide possesses three vibrational normal modes with symmetry A_1 which are both IR and Raman active, 1 normal mode of symmetry A_2 which is Raman active and 2 normal modes with symmetry B_2 which are both IR and Raman active.