

CHAPTER 9

Molecular Vibrations

Problem 9.1

For ethylene:

- determine the point group;
- determine the number and symmetry of the vibrational normal coordinates;
- determine the spectroscopic activity of each fundamental level.

Solution 9.1

(a) Ethylene (C_2H_4) possesses 3 mutually perpendicular C_2 axes and a horizontal mirror plane (σ_h). Consequently, it is assigned to the D_{2h} point group.

(b) The character of Γ^0 is

$R =$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\chi^0(C_i)$	18	0	0	-2	0	6	2	0

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = 3\Gamma^{A_g} \oplus 3\Gamma^{B_{1g}} \oplus 2\Gamma^{B_{2g}} \oplus \Gamma^{B_{3g}} \oplus \Gamma^{A_u} \oplus 2\Gamma^{B_{1u}} \oplus 3\Gamma^{B_{2u}} \oplus 3\Gamma^{B_{3u}}.$$

From the character table of D_{2h} , viz., Table 9.1, we find the decomposition of the translational representation Γ^t and the rotational representation Γ^r :

$$\begin{aligned}\Gamma^t &= \Gamma^{B_{1u}} \oplus \Gamma^{B_{2u}} \oplus \Gamma^{B_{3u}}, \\ \Gamma^r &= \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{B_{3g}}.\end{aligned}$$

Table 9.1: The character table for the D_{2h} point group.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	$x^2; y^2; z^2$
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
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x
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

Hence, we obtain the decomposition of the vibrational representation Γ^v :

$$\Gamma^v = 3\Gamma^{A_g} \oplus 2\Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{A_u} \oplus \Gamma^{B_{1u}} \oplus 2\Gamma^{B_{2u}} \oplus 2\Gamma^{B_{3u}}. \quad (9.1)$$

Therefore, we conclude that there are in total 12 vibrational normal coordinates, and 3, 2, 1, 1, 1, 2, 2 for Γ^{A_g} , $\Gamma^{B_{1g}}$, $\Gamma^{B_{2g}}$, Γ^{A_u} , $\Gamma^{B_{1u}}$, $\Gamma^{B_{2u}}$, $\Gamma^{B_{3u}}$, respectively.

(c) We list all determination of the spectroscopic activity of each fundamental level as follows:

Irreducible representations	Count	Spectroscopic activity
Γ^{A_g}	3	Raman
$\Gamma^{B_{1g}}$	2	Raman
$\Gamma^{B_{2g}}$	1	Raman
Γ^{A_u}	1	inactive
$\Gamma^{B_{1u}}$	1	infra-red
$\Gamma^{B_{2u}}$	2	infra-red
$\Gamma^{B_{3u}}$	2	infra-red

Because ethylene has a center of inversion (*i*), the Rule of Mutual Exclusion, stated in the last paragraph of section 9-11, dictates that no mode can be both infra-red and Raman active.

Problem 9.2

Show on the basis of infra-red and Raman spectra that it is possible to distinguish between the two crown forms of octachlorocyclooctane, one in which the hydrogen atoms are all equatorial (\mathcal{D}_{4d}) and the other in which the hydrogen atoms are alternating between axial and equatorial positions (\mathcal{C}_{4v}).

Solution 9.2

We analyse these two issues separately, and summarize these conclusions in the end.

- Firstly, we list the character tables of the \mathcal{D}_{4d} point group as follows.

Table 9.2: The character table for the \mathcal{D}_{4d} point group.

\mathcal{D}_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C'_2$	$4\sigma_d$	
A_1	1	1	1	1	1	1	1	$x^2 + y^2; z^2$
A_2	1	1	1	1	1	-1	-1	R_z
B_1	1	-1	1	-1	1	1	-1	
B_2	1	-1	1	-1	1	-1	1	z
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(x, y)
E_2	2	0	-2	0	2	0	0	$(x^2 - y^2, xy)$
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	(R_x, R_y)
								(xz, yz)

In the \mathcal{D}_{4d} point group, the irreducible representations of the infra-red active modes and Raman active modes are mutually exclusive:

$$\Gamma^t = \Gamma^{B_2} \oplus \Gamma^{E_1}, \quad (9.2)$$

$$\Gamma^r = \Gamma^{A_2} \oplus \Gamma^{E_3}, \quad (9.3)$$

$$\Gamma^\alpha = 2\Gamma^{A_1} \oplus \Gamma^{E_2} \oplus \Gamma^{E_3}. \quad (9.4)$$

The character of Γ^0 is

$R =$	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C'_2$	$4\sigma_d$
$\chi^0(C_i)$	72	0	0	0	0	-2	12

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = 6\Gamma^{A_1} \oplus 3\Gamma^{A_2} \oplus 3\Gamma^{B_1} \oplus 6\Gamma^{B_2} \oplus 9\Gamma^{E_1} \oplus 9\Gamma^{E_2} \oplus 9\Gamma^{E_3}.$$

Hence, we obtain

$$\Gamma^v = 6\Gamma^{A_1} \oplus 2\Gamma^{A_2} \oplus 3\Gamma^{B_1} \oplus 5\Gamma^{B_2} \oplus 8\Gamma^{E_1} \oplus 9\Gamma^{E_2} \oplus 8\Gamma^{E_3}. \quad (9.5)$$

At last, we list all determination of the spectroscopic activity of each fundamental level as follows:

Irreducible representations	Count	Spectroscopic activity
Γ^{A_1}	6	Raman
Γ^{A_2}	2	inactive
Γ^{B_1}	3	inactive
Γ^{B_2}	5	infra-red
Γ^{E_1}	8	infra-red
Γ^{E_2}	9	Raman
Γ^{E_3}	8	Raman

- Firstly, we list the character tables of the the \mathcal{C}_{4v} point group.

Table 9.3: The character table for the \mathcal{C}_{4v} point group.

\mathcal{C}_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2; z^2$
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		xy
E	2	0	-2	0	0	$(x, y); (R_x, R_y)$	(xz, yz)

It is evident that in the \mathcal{C}_{2v} point group, the A_1 and E modes are coincident:

$$\Gamma^t = \Gamma^{A_1} \oplus \Gamma^E, \quad (9.6)$$

$$\Gamma^r = \Gamma^{A_2} \oplus \Gamma^E, \quad (9.7)$$

$$\Gamma^\alpha = 2\Gamma^{A_1} \oplus \Gamma^{B_1} \oplus \Gamma^{B_2} \oplus \Gamma^E. \quad (9.8)$$

The character of Γ^0 is

$R =$	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\chi^0(C_i)$	72	0	0	6	6

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = 12\Gamma^{A_1} \oplus 6\Gamma^{A_2} \oplus 9\Gamma^{B_1} \oplus 9\Gamma^{B_2} \oplus 18\Gamma^E.$$

Hence, we obtain

$$\Gamma^0 = 11\Gamma^{A_1} \oplus 5\Gamma^{A_2} \oplus 9\Gamma^{B_1} \oplus 9\Gamma^{B_2} \oplus 16\Gamma^E. \quad (9.9)$$

At last, we list all determination of the spectroscopic activity of each fundamental level as follows:

Irreducible representations	Count	Spectroscopic activity
Γ^{A_1}	11	infra-red and Raman
Γ^{A_2}	5	inactive
Γ^{B_1}	9	Raman
Γ^{B_2}	9	Raman
Γ^E	16	infra-red and Raman

Therefore, by inspecting whether both the infra-red and Raman spectra appears at the same frequency, inspectors will distinguish the two crown forms of octachlorocyclooctane.

Remark

- Although there is no center of inversion (i), for the \mathcal{D}_{4d} , the symmetry is high enough that no vibration mode can be both infra-red and Raman active.
- In fact, because \mathcal{C}_{4v} is a subgroup of \mathcal{D}_{4d} , their irreducible representations have a relationship. By inspecting the correspondence between two sets of basis functions and rotations, I find the descent

path from \mathcal{D}_{4d} to \mathcal{C}_{4v} , illustrated as the following diagram.

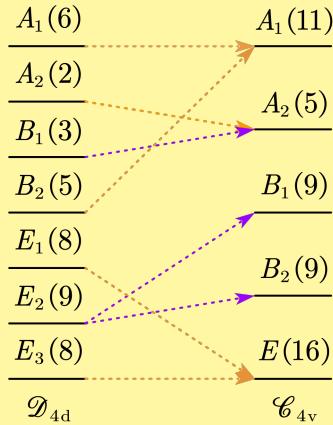


Figure 9.1: Descent paths from \mathcal{D}_{4d} to \mathcal{C}_{4v} . The number in parentheses following the irreducible representations indicates its reduction coefficient in this problem. Orange lines mean that the correspondence are ensured by inspecting the same basis functions or rotations, while purple lines mean the correspondence are confirmed by inspecting the characters of relevant irreducible representations.

- The second paragraph of the reference answer in the textbook at the page 294 is totally wrong. From this answer, I think that the author may only care about the vibrations of all C – Cl bonds. In this way, the answer is

$$\Gamma^{C-Cl} = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 2\Gamma^{B_1} \oplus 2\Gamma^{B_2}.$$

It does have $3\Gamma^{A_1}$, $1\Gamma^{A_2}$ and $2\Gamma^{B_2}$. He might think that since x and y are equivalent, thus he only needs to write one as a representative (i.e., only \mathcal{B} is written). But in group theory reduction, this is illegal! Once a degenerate state splits, both orbitals must be counted simultaneously.

Problem 9.3

Discuss how the *cis* and *trans* isomers of N_2F_2 can be distinguished by infra-red and Raman measurements.

Solution 9.3

- cis*- N_2F_2 has a C_2 axis and two σ_v and thus belongs to the \mathcal{C}_{2v} point group. Similar to Problem 9.2, first of all, we list the character tables of the \mathcal{C}_{2v} point group as follows.

Table 9.4: The character table for the \mathcal{C}_{2v} point group.

\mathcal{C}_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
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

In the \mathcal{C}_{2v} point group, the irreducible representations of the infra-red active modes and Raman active modes have the same irreducible representations Γ^{A_1} , Γ^{B_1} and Γ^{B_2} :

$$\Gamma^t = \Gamma^{A_1} \oplus \Gamma^{B_1} \oplus \Gamma^{B_2}, \quad (9.10)$$

$$\Gamma^\alpha = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^{B_1} \oplus \Gamma^{B_2}. \quad (9.11)$$

Consequently, *cis*- N_2F_2 exhibits coincident bands in its infra-red and Raman spectra, appearing at the same vibrational frequencies.

- trans*- N_2F_2 has a C_2 axis and a σ_h and thus belongs to the \mathcal{C}_{2h} point group. Then, we list the character tables of the \mathcal{C}_{2h} point group as follows.

Table 9.5: The character table for the \mathcal{C}_{2h} point group.

\mathcal{C}_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	$x^2; y^2; z^2; xy$
B_g	1	-1	1	-1	$R_x; R_y$	$xz; yz$
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	$x; y$	

In the \mathcal{C}_{2h} point group, the irreducible representations of the infra-red active modes and Raman active modes are mutually exclusive:

$$\Gamma^t = \Gamma^{A_u} \oplus 2\Gamma^{B_u}, \quad (9.12)$$

$$\Gamma^\alpha = 4\Gamma^{A_g} \oplus 2\Gamma^{B_g}. \quad (9.13)$$

Although there is no center of inversion (i), the symmetry is high enough that no vibration mode can be both infra-red and Raman active. In other words, *trans*-N₂F₂ does not exhibit coincident bands in its infra-red and Raman spectra, appearing at the same vibrational frequencies.

Problem 9.4

What will be the infra-red and Raman activity of the four fundamental levels of CO₃²⁻?

Solution 9.4

Similar to Problem 9.1, we should solve the current problem in 3 steps.

- Determine the point group: CO₃²⁻ has a C_3 axis and 3 C_2 axes perpendicular to this C_3 axis. Moreover, it has a σ_h . Therefore, it belongs to the \mathcal{D}_{3h} point group.
- Determine the number and symmetry of the vibrational modes. It is clear that from the following character table for the \mathcal{D}_{3h} point group,

$$\Gamma^t = \Gamma^{E'} \oplus \Gamma^{A''_2}, \quad (9.14)$$

$$\Gamma^r = \Gamma^{A'_2} \oplus \Gamma^{E''}, \quad (9.15)$$

$$\Gamma^\alpha = 2\Gamma^{A'_1} \oplus \Gamma^{E'} \oplus \Gamma^{E''}. \quad (9.16)$$

Table 9.6: The character table for the \mathcal{D}_{3h} point group.

\mathcal{D}_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
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	$(x, y) \quad (x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1	
A''_2	1	1	-1	-1	-1	1	z
E''	2	-1	0	-2	1	0	$(R_x, R_y) \quad (xz, yz)$

The character of the Γ^0 is

$R =$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\chi^0(C_i)$	12	0	-2	4	-2	2

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = \Gamma^{A'_1} \oplus \Gamma^{A'_2} \oplus 3\Gamma^{E'} \oplus 2\Gamma^{A''_2} \oplus \Gamma^{E''}.$$

Hence, we obtain

$$\Gamma^v = \Gamma^{A'_1} \oplus 2\Gamma^{E'} \oplus \Gamma^{A''_2}. \quad (9.17)$$

Therefore, we conclude that there are in total 6 vibrational normal modes, and 1, 4, 1 for $\Gamma^{A'_1}$, $\Gamma^{E'}$, and $\Gamma^{A''_2}$, respectively.

3. We list all determination of the spectroscopic activity of each fundamental level as follows:

Irreducible representations	Count	Spectroscopic activity
$\Gamma^{A'_1}$	1	Raman
$\Gamma^{E'}$	2	Raman and infra-red
$\Gamma^{A''_2}$	1	infra-red

Problem 9.5

Determine χ^0 and carry out the reduction of Γ^0 for the following molecules:

- (a) NH_3 (\mathcal{C}_{3v}),
- (b) XeOF_4 (\mathcal{C}_{4v}),
- (c) PtCl_4^{2-} (\mathcal{D}_{4h}),
- (d) *trans*-glyoxal (\mathcal{C}_{2h}).

Solution 9.5

After Problem 9.1 and Problem 9.4, I believe that readers are familiar with the whole solution processes. I tend to demonstrate only the important intermediate results rather than the whole processes. And whatever, in all issues, we have

$$\Gamma^0 = \Gamma^{t,r} \oplus \Gamma^v = \Gamma^t \oplus \Gamma^r \oplus \Gamma^v. \quad (9.18)$$

- (a) The character table for the \mathcal{C}_{3v} point group is below, and we obtain

$$\Gamma^t = \Gamma^{A_1} \oplus \Gamma^E, \quad (9.19)$$

$$\Gamma^r = \Gamma^{A_2} \oplus \Gamma^E. \quad (9.20)$$

Table 9.7: The character table for the \mathcal{C}_{3v} point group.

\mathcal{C}_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2; z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y); (R_x, R_y)$	$(x^2 - y^2, xy); (xz; yz)$

The character of the Γ^0 is

$$R = \begin{array}{|c|ccc|} \hline & E & 2C_3 & 3\sigma_v \\ \hline \chi^0(C_i) & 12 & 0 & 2 \\ \hline \end{array}$$

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 4\Gamma^E.$$

Hence, we obtain

$$\Gamma^v = 2\Gamma^{A_1} \oplus 2\Gamma^E. \quad (9.21)$$

Therefore, our result are eqn (9.19), eqn (9.20), eqn (9.21) and eqn (9.21).

- (b) The character table for the \mathcal{C}_{4v} point group can be seen in Table 9.3 and we obtain

$$\Gamma^t = \Gamma^{A_1} \oplus \Gamma^E, \quad (9.22)$$

$$\Gamma^r = \Gamma^{A_2} \oplus \Gamma^E. \quad (9.23)$$

The character of the Γ^0 is

$$R = \begin{array}{|c|ccccc|} \hline & E & 2C_4 & C_2 & 2\sigma_v & 2\sigma_d \\ \hline \chi^0(C_i) & 18 & 2 & -2 & 4 & 2 \\ \hline \end{array}$$

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = 4\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 2\Gamma^{B_1} \oplus \Gamma^{B_2} \oplus 5\Gamma^E. \quad (9.24)$$

Hence, we obtain

$$\Gamma^v = 3\Gamma^{A_1} \oplus 2\Gamma^{B_1} \oplus \Gamma^{B_2} \oplus 5\Gamma^E. \quad (9.25)$$

Therefore, our result are eqn (9.22), eqn (9.23), eqn (9.24), and eqn (9.25).

(c) The character table for the \mathcal{D}_{4h} point group is below, and we obtain

$$\Gamma^t = \Gamma^{A_{2u}} \oplus \Gamma^{E_u}, \quad (9.26)$$

$$\Gamma^r = \Gamma^{A_{2g}} \oplus \Gamma^{E_g}. \quad (9.27)$$

Table 9.8: The character table for the \mathcal{D}_{4h} point group.

\mathcal{D}_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2; z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)

The character of the Γ^0 is

$R =$	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\chi^0(C_i)$	15	1	-1	-3	-1	-3	-1	5	3	1

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = \Gamma^{A_{1g}} \oplus \Gamma^{A_{2g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_g} \oplus 2\Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus 3\Gamma^{E_u}. \quad (9.28)$$

Hence, we obtain

$$\Gamma^v = \Gamma^{A_{1g}} \oplus \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{A_{2u}} \oplus \Gamma^{B_{2u}} \oplus 2\Gamma^{E_u}. \quad (9.29)$$

Therefore, our result are eqn (9.26), eqn (9.27), eqn (9.28), and eqn (9.29).

(d) The character table for the \mathcal{C}_{2h} point group can be seen in Table 9.5 and we obtain

$$\Gamma^t = \Gamma^{A_u} \oplus 2\Gamma^{B_u}, \quad (9.30)$$

$$\Gamma^r = \Gamma^{A_g} \oplus 2\Gamma^{B_g}. \quad (9.31)$$

The character of the Γ^0 is

$R =$	E	C_2	i	σ_h
$\chi^0(C_i)$	18	0	0	6

Solving the system of linear equations like in Problem 7.1, we obtain

$$\Gamma^0 = 6\Gamma^{A_1} \oplus 3\Gamma^{A_2} \oplus 3\Gamma^{B_1} \oplus 6\Gamma^{B_2}. \quad (9.32)$$

Hence, we obtain

$$\Gamma^v = 5\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 2\Gamma^{B_1} \oplus 4\Gamma^{B_2}. \quad (9.33)$$

Therefore, our result are eqn (9.30), eqn (9.31), eqn (9.32), and eqn (9.33).