Homework

- confirm for yourself for homework that $\Gamma_{3N}(H_2O) = 3A_1 + 1A_2 + 2B_1 + 3B_2$

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma'(yz)$
$\Gamma(H_20)$	9	−1	1	3
A_1	1	1	1	1
A_2	1	1	−1	−1

$$n_{A_1} = \frac{1}{4}[(1 \bullet 9 \bullet 1) + (1 \bullet -1 \bullet 1) + (1 \bullet 1 \bullet 1) + (1 \bullet 3 \bullet 1)]$$

$$n_{A_1} = \frac{1}{4}[9 - 1 + 1 + 3] = \frac{12}{4} = 3$$

$$n_{A_2} = \frac{1}{4}[(1 \bullet 9 \bullet 1) + (1 \bullet -1 \bullet 1) + (1 \bullet 1 \bullet -1) + (1 \bullet 3 \bullet -1)]$$

$$n_{A_2} = \frac{1}{4}[9 - 1 - 1 - 3] = \frac{4}{4} = 1$$

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma'(yz)$
$\Gamma(H_20)$	9	−1	1	3
B_1	1	−1	1	−1
B_2	1	−1	−1	1

$$n_{B_1} = \frac{1}{4}[(1 \bullet 9 \bullet 1) + (1 \bullet -1 \bullet -1) + (1 \bullet 1 \bullet 1) + (1 \bullet 3 \bullet -1)]$$

$$n_{B_1} = \frac{1}{4}[9 + 1 + 1 - 3] = \frac{8}{4} = 2$$

$$n_{B_2} = \frac{1}{4}[(1 \bullet 9 \bullet 1) + (1 \bullet -1 \bullet -1) + (1 \bullet 1 \bullet -1) + (1 \bullet 3 \bullet 1)]$$

$$n_{B_2} = \frac{1}{4}[9 + 1 - 1 + 3] = \frac{12}{4} = 3$$

Problem

- determine the symmetry and activity of the vibrational modes of a tetrahedral molecule such as CH_4 or CCl_4
- first find all the symmetry elements of T_d (this was a tutorial problem from the MOs course) I've reproduced some of the material here
- The character table for the T_d point group (**Figure 1**) is shown to the left, and it tells us the key symmetry operations in this group are E, $8C_3$ $3C_2$, $6S_4$ and $6\sigma_d$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	h=24
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	
T_1	3	0	-1	1	-1	
T_2	3	0	-1	-1	1	($T_x T_y T_z$)

Figure 1 T_d character table

- there are three useful ways of thinking about a tetrahedral molecule, each one emphasises a different aspect of symmetry, **Figure 2**
  - (a) the C_2 axes
  - (b) the C_3 axes
  - (c) the cubic structure

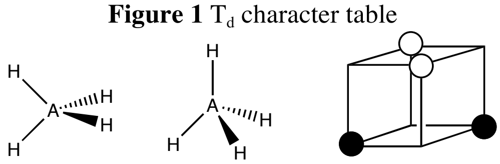


Figure 2 Tetrahedral molecules

- the "cube" may be less familiar to you, think of the H atoms occupying opposite corners of a cube and the central atom A is at the centre
- there are $8C_3$ operations
  - a C_3 axis lies along each bond, one C_3 axis is shown in **Figure 3**, the others are easily predicted because the four H atoms are symmetry equivalent, if one has a C_3 axis passing through it then they all will, hence there are four C_3 axis symmetry <u>elements</u>
  - around each axis there are 3 possible C_3 operations: C_3^1 C_3^2 C_3^3, the last operation $C_3^3 = E$ is equivalent to the identity and so is already counted, there are then two symmetry <u>operations</u> associated with each C_3 axis and thus there are eight distinct C_3 operations in T_d : $8C_3$

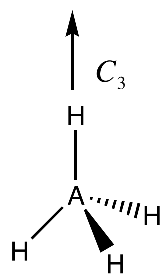


Figure 3 C_3 axis

- there are $3C_2$ operations
  - a C_2 axis lies between each pair of A-H bonds, **Figure 4a**, bisecting each pair of atoms and through the center of each pair of faces in the cube, **Figure 4b**, as there are 3 pairs of faces to each cube, there will be $3C_2$ axes
  - as we associate only one operation with each C_2 axis there are $3C_2$ operations in T_d

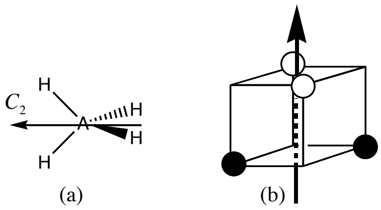


Figure 4 C_2 axis

- there are $6\sigma_d$ operations
  - a σ mirror plane passes through each pair of atoms and contains a C_2 axis, ie two mirror planes cross each pair of faces, **Figure 5**, these are dihedral mirror planes σ_d.
  - as there are 3 pairs of faces each with two mirror planes there are $6\sigma_d$ operations in T_d

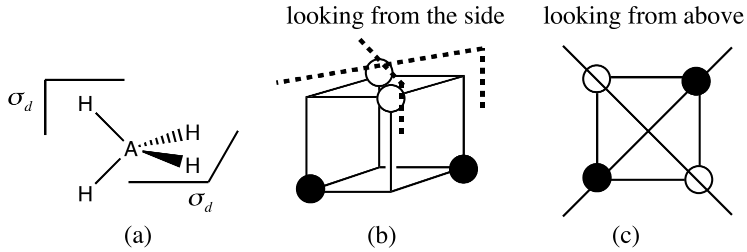


Figure 5 σ_d mirror planes

- there are $6S_4$ operations
  - each C_2 axis has a coincident S_4 axis, consider a rotation of 90º around this axis and then reflection in a plane perpendicular to the axis through the center of the molecule. An example of these elements for the S_4^1 operation is given in **Figure 6**.
  - notice that neither the C_4 nor the σ_h exist within the T_d point group as separate elements!!

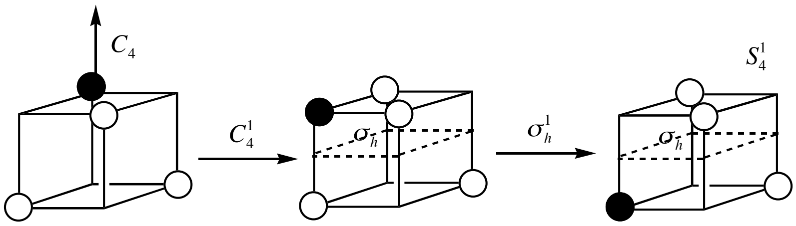


Figure 6 S_4^1 operation

  - S_4^2 (**Figure 7**) is the same as C_2^1 operation and C_2 lies to the left of S_4 and so this operation is not counted with the S_4 operations. In addition the S_4^4 operation is the same as E and so is not counted here either

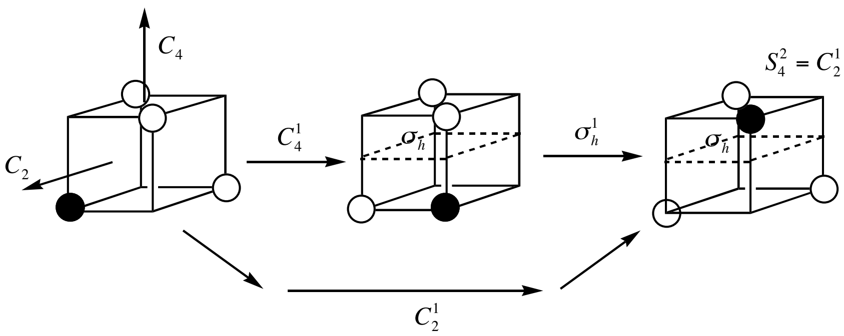
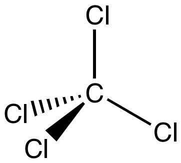


Figure 7 S_4^2 operation

- thus there are $2S_4$ operations per C_2 axis, and as there are $3C_2$ axes there must be $6S_4$ operations in T_d

- Thus we have shown that there are E, $8C_3$ $3C_2$, $6S_4$ and $6\sigma_d$ operations for the Td point group.
- determine the reducible representation, start with the number of atoms lying on symmetry elements, then use the table at the back of your character tables:



T_d	E	C_3	C_2	S_4	σ_d
atoms	5	2	1	1	3
χ(*per atom*)	3	0	−1	−1	1
$\Gamma(CCl_4)$	15	0	−1	−1	3

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma(CCl_4)$	15	0	−1	−1	3
A_1	1	1	1	1	1

$$n_{A_1} = \frac{1}{24}\left[(1 \bullet 15 \bullet 1) + (8 \bullet 0 \bullet 1) + (3 \bullet -1 \bullet 1) + (6 \bullet -1 \bullet 1) + (6 \bullet 3 \bullet 1)\right]$$

$$n_{A_1} = \frac{1}{24}\left[15 + 0 - 3 - 6 + 18\right] = \frac{24}{24} = 1$$

$$n_{A_2} = \frac{1}{24}\left[(1 \bullet 15 \bullet 1) + 0 + (3 \bullet -1 \bullet 1) + (6 \bullet -1 \bullet -1) + (6 \bullet 3 \bullet -1)\right] = \frac{0}{24} = 0$$

$$n_E = \frac{1}{24}\left[(1 \bullet 15 \bullet 2) + 0 + (3 \bullet -1 \bullet 2) + 0 + 0\right] = \frac{24}{24} = 1$$

$$n_{T_1} = \frac{1}{24}\left[(1 \bullet 15 \bullet 3) + 0 + (3 \bullet -1 \bullet -1) + (6 \bullet -1 \bullet 1) + (6 \bullet 3 \bullet -1)\right] = \frac{24}{24} = 1$$

$$n_{T_2} = \frac{1}{24}\left[(1 \bullet 15 \bullet 3) + 0 + (3 \bullet -1 \bullet -1) + (6 \bullet -1 \bullet -1) + (6 \bullet 3 \bullet 1)\right] = \frac{72}{24} = 3$$

$$\Gamma(CH_4) = A_1 + E + T_1 + 3T_2$$

- determine the irreducible representation of the translation and rotation for the whole molecule

$$\Gamma(T) = T_1$$
$$\Gamma(R) = T_2$$
$$\Gamma(T + R) = T_1 + T_2$$

- subtract the translation and rotation from the reduced representation of 3N to obtain the symmetry of the vibrational modes

$$\begin{aligned}\Gamma_{vib}(CH_4) &= \Gamma(CH_4) - \Gamma(T + R) \\ &= \left(A_1 + E + T_1 + 3T_2\right) - \left(T_1 + T_2\right) \\ &= A_1 + E + 2T_2\end{aligned}$$

- determine the IR and Raman activity of these modes

- IR have the same symmetry as the translational motions

$$\Gamma(T) = T_2$$

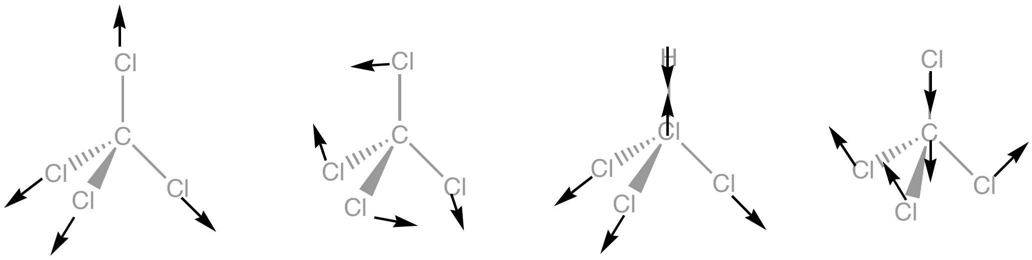
- Raman have the same symmetry as the binary functions

$$\Gamma(f) = A_1 + E + T_2$$

- symmetry and activity of the vibrational modes of CCl_4 are

$$\Gamma_{vib}(CH_4) = A_1(pol) + E(depol) + 2T_2(IR,depol)$$

- the vibrational modes are:



$\nu_1(A_1)$	$\nu_2(E)$	$\nu_{3a}(T_2)$	$\nu_{4a}(T_2)$
symmetric stretch	symmetric bend	degenerate stretch	degenerate bend
≈459cm^{-1}	≈218cm^{-1}	≈793cm^{-1}	≈314cm^{-1}

Figure 8 vibrational modes of methane

- 3N-6=3*5-6=9 and thus there are 9 modes $1(A_1)+2(E)+6(T_2)$
- which produce 4 peaks in the Raman spectrum and 2 peaks in the IR spectrum
- however a number of the IR peaks are outside the range of normal IR spectrometers (400-4000 cm^{-1}).

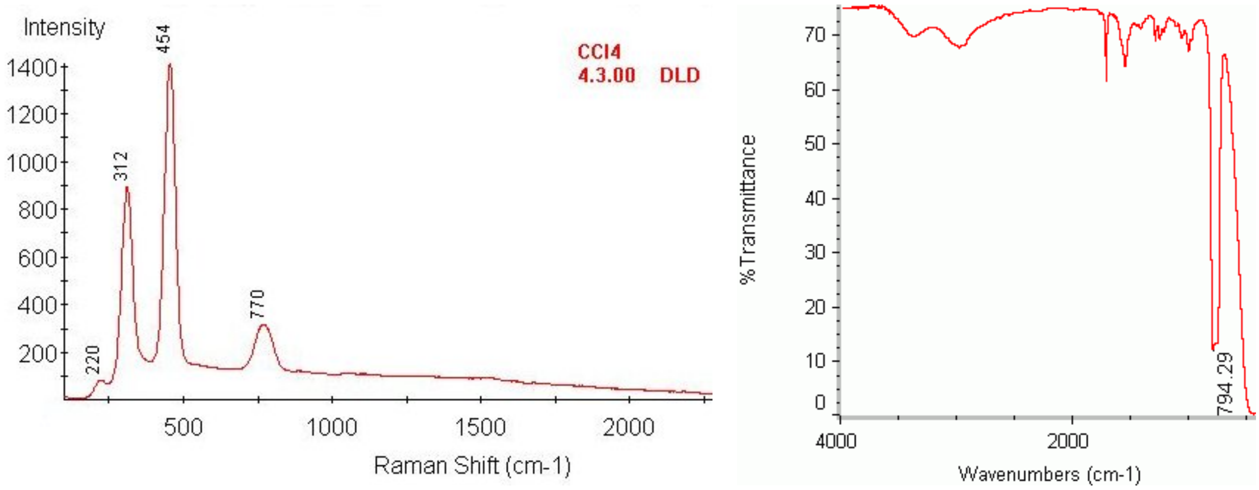


Figure 9 Raman and IR spectra of CCl_4 from web-page: http://ed.augie.edu/~viste/Raman/RamanQuantum.html