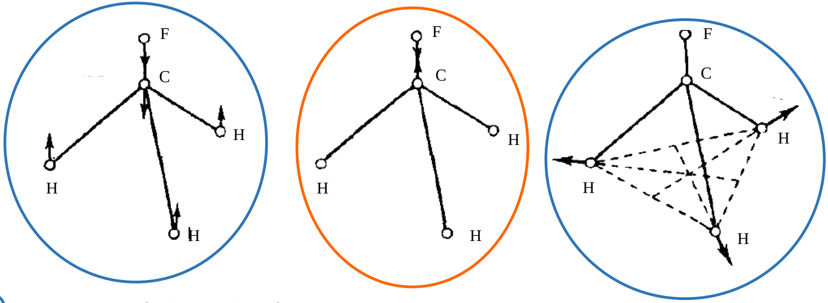
Molecular symmetry group
II. Molecules CH_3F and CH_4

CH_3F

IRs for rotation levels are the same as for NH_3

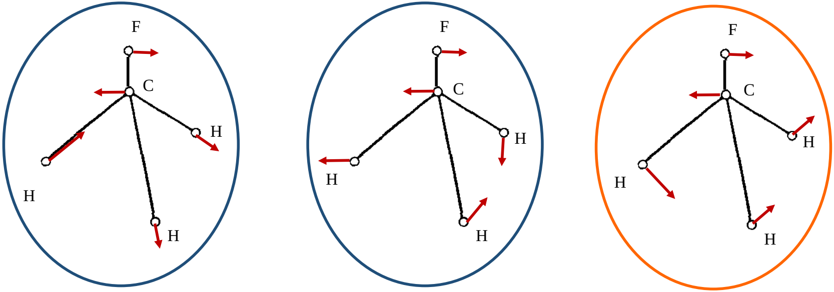
Non-degenerate vibrational modes with normal coordinates transformed ~A_1 of C_{3v}



extension of vibr. modes of NH_3

present in CH_3F, but not in NH_3

Double-degenerate vibrational modes with normal coordinates transformed ~*E* of C_{3v}



For each of these modes, the second linearly independent set of displacements of nuclei is obtained by a rotation over $\pm 2\pi / 3$

CH_4

Point group of the equilibrium configuration (MS group): T_d

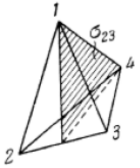
Group of symmetry of a tetrahedron.

All edges have the same length

24 elements: 12 elements of the group T;

6 reflections w. resp. to planes $\sigma_{12}, \sigma_{13}, \sigma_{14}, \sigma_{23}, \sigma_{24}, \sigma_{34}$;

$2 \times 3 = 6$ rotation-reflections s_4, s_4^3 around each of the three 2nd-order axes.



T

e

$4 \times c_3$

$4 \times c_3^2$

$3 \times u_{ik}$

Five classes:

$$\{e\},\ \{c_3^{(i)}, c_3^{(i)\,2}\},\ \{u_{ik}\},\ \{s_4^{(ik)}, s_4^{(ik)\,3}\},\ \{\sigma_{ik}\},$$

# of elements 1 + 8 + 3 + 6 + 6 = 24

with all relevant i, k within a class.

Characters of IRs of T_d

Five classes $\Rightarrow$ five IRs

T_d	e	C_3	u	σ	S_4
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
F_2	3	0	-1	1	-1
F_1	3	0	-1	-1	1

$$1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24$$

Full permutation-inversion group for CH_4

$\mathcal{S}_4 \otimes \mathcal{I}$

48 elements, 10 classes

G_{48}:	E	(123)	(14)(23)	(1423)*	(23)*	E^*	(123)*	(14)(23)*	(1423)	(23)
	1	8	3	6	6	1	8	3	6	6
A_1^+:	1	1	1	1	1	1	1	1	1	1
A_2^+:	1	1	1	−1	−1	1	1	1	−1	−1
E^+:	2	−1	2	0	0	2	−1	2	0	0
F_1^+:	3	0	−1	1	−1	3	0	−1	1	−1
F_2^+:	3	0	−1	−1	1	3	0	−1	−1	1
A_1^-:	1	1	1	1	1	−1	−1	−1	−1	−1
A_2^-:	1	1	1	−1	−1	−1	−1	−1	1	1
E^-:	2	−1	2	0	0	−2	1	−2	0	0
F_1^-:	3	0	−1	1	−1	−3	0	1	−1	1
F_2^-:	3	0	−1	−1	1	−3	0	1	1	−1

"Non-realizable" operations

Omitting "non-realizable elements": $A_1^{\pm} \mapsto A_1$ and so on

Rotational states for CH_4

Spherical rotor

$|JKM\rangle$ states are degenerate not only w.r.t. M, but also w.r.t. K

For a given M: $(2J+1)$-fold degeneracy w.r.t. K

J	Γ_r
$12n$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1$
$12n+1$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus F_1$
$12n+2$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus E \oplus F_2$
$12n+3$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_2 \oplus F_1 \oplus F_2$
$12n+4$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus E \oplus F_1 \oplus F_2$
$12n+5$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus E \oplus 2F_1 \oplus F_2$
$12n+6$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus A_2 \oplus E \oplus F_1 \oplus 2F_2$
$12n+7$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_2 \oplus E \oplus 2F_1 \oplus 2F_2$
$12n+8$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus 2E \oplus 2F_1 \oplus 2F_2$
$12n+9$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus A_2 \oplus E \oplus 3F_1 \oplus 2F_2$
$12n+10$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus A_2 \oplus 2E \oplus 2F_1 \oplus 3F_2$
$12n+11$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2$

Normal vibrational modes for CH_4

CH_3F: three non-degenrate and three double-degenerate vibration modes

F⟶H: degeneracy “redistributed”

Number	ν_i (cm^{-1})	Description	IR
1	2917	sym. stretch	A_1
2	1534	sym. bend	E
3	3019	asym. stretch	F_2
4	1306	asym. bend	F_2

$$1 + 2 + 3 + 3 = 9$$

Nuclear spin functions

Co-ordinate w.f. $\sim (\{\lambda\} \otimes \mathfrak{g}) \oplus (\{\tilde{\lambda}\} \otimes \mathfrak{u})$
The total (co-ordinate and nuclear-spin) w.f.
$\sim (\{\lambda\}_c \otimes \{\lambda\}_s \otimes \mathfrak{g}) \oplus (\{\tilde{\lambda}\}_c \otimes \{\tilde{\lambda}\}_s \otimes \mathfrak{u})$ for bosonic nuclei;
$\sim (\{\lambda\}_c \otimes \{\tilde{\lambda}\}_s \otimes \mathfrak{g}) \oplus (\{\tilde{\lambda}\}_c \otimes \{\lambda\}_s \otimes \mathfrak{u})$ for fermionic nuclei.

For protons ($s = \frac{1}{2}$) there is one-to-one correspondence between the total nuclear spin I and the IR of the permutation group (the same I may appear several times, the states differing in other quantum numbers that reflect the coupling scheme).

For higher s, we need to perform analysis as follows.

Total nuclear spin for deuterium in CD_3F

Characters of IRs of $\mathcal{S}_3$

	e	(ij)	(ijk)
$\{3\}$	1	1	1
$\{2,1\}$	2	0	-1
$\{1,1,1\}$	1	-1	1

$M_I = 3$: a single w.f. $|1,1,1\rangle$, which corresponds to the highest possible spin $I = 3$ and is invariant under any permutation, i.e. $\sim\{3\}$

$M_I = 2$: three w.f.'s $|1,1,0\rangle$, $|1,0,1\rangle$, $|0,1,1\rangle$
Characters of the corresponding reducible representation T_2:

	e	(ij)	(ijk)
$\chi_2(P)$	3	1	0

According to the character theorem, $T_2 = \{3\} \oplus \{2,1\}$
$\{3\}$ corresponds to $I = 3$ (obtained from $|3,3\rangle$ by lowering M_I by 1)
$\{2,1\}$ corresponds to $I = 2$, which appears here twice ($d_{\{2,1\}} = 2$)

$M_I = 1$: vector space consisting of two subspaces,

$|1,0,0\rangle,\ |0,0,1\rangle,\ |0,1,0\rangle$

and $|1,1,-1\rangle,\ |1,-1,1\rangle,\ |-1,1,1\rangle$

$T_1 = 2T_2$, the table of characters for T_2 see above $\Rightarrow$

$$T_1 = 2\{3\} \oplus 2\{2,1\}$$

1st w.f. $\sim \{3\}$ corresponds to $I = 3$

1st w.f. $\sim \{2,1\}$ corresponds to $I = 2$ (twice!)

2nd w.f. $\sim \{3\}$ corresponds to $I = 1$

2nd w.f. $\sim \{2,1\}$ corresponds to $I = 1$ (twice!)

$M_I = 0$: vector space consisting of two subspaces,
$|1,-1,0\rangle,\ |-1,0,1\rangle,\ |0,1,-1\rangle, |1,0,-1\rangle,\ |0,-1,1\rangle,\ |-1,1,0\rangle$
and $|0,0,0\rangle$ (invariant against permutations)

$$T_0 = T_0' \oplus \{3\}$$

Characters of T_0'

	e	(ij)	(ijk)
$\chi_0'(P)$	6	0	0

$$T_0' = \{3\} + 2\{2,1\} + \{1,1,1\}$$

$$T_0 = 2\{3\} + 2\{2,1\} + \{1,1,1\}$$

$\{3\}$ corresponds to $I = 3$ and $I = 1$
$\{2,1\}$ corresponds to $I = 2$ (twice) and $I = 1$ (twice)
$\{1,1,1\}$ corresponds to $I = 0$
$M_I < 0$: the same structure as for $|M_I|$

$$\sum_{\{\lambda\}} \sum_I (2I+1) = (2s+1)^n, \quad 7 + 2\times 5 + 3\times 3 + 1 = 3^3$$