CHAPTER 2

Symmetry operations

Exercise 2.1

Give all the symmetry elements of H_2O, NH_3 and CH_4. For each molecule list the symmetry operations which commute.

Solution 2.1

(a) H_2O has 4 symmetry elements,

$$E, C_2, \sigma_v(xz), \sigma_v(yz).$$

They can be seen in Fig 2.1.
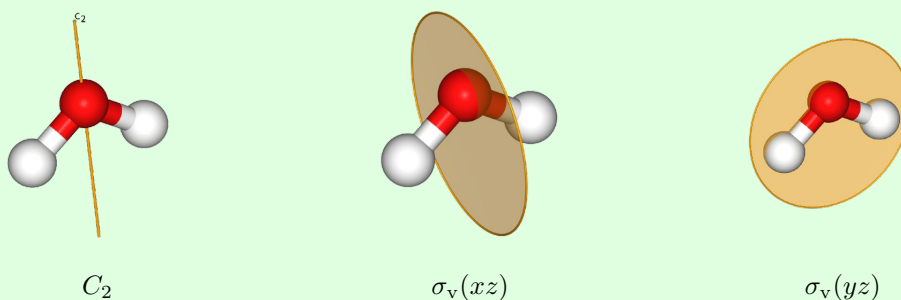

| C_2 | $\sigma_v(xz)$ | $\sigma_v(yz)$ |

Figure 2.1: All symmetry elements of H_2O except the identity E.

For H_2O, all symmetry operations commute with each other. In the next chapter, readers will know that H_2O belongs to the point group $\mathscr{C}_{2v}$, an Abelian group.

(b) NH_3 has 5 symmetry elements,

$$E, C_3, \sigma_v', \sigma_v'', \sigma_v'''.$$

They can be seen in Fig 2.2.

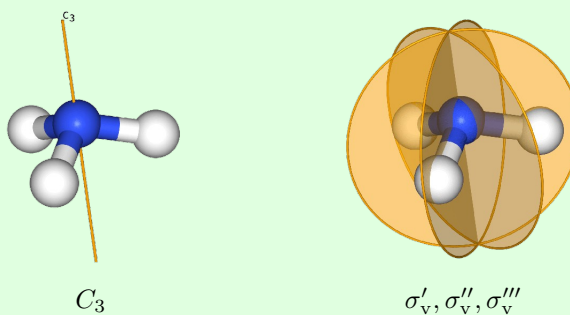| C_3 | $\sigma_v', \sigma_v'', \sigma_v'''$ |

Figure 2.2: All symmetry elements of NH_3 except the identity E.

For NH_3, not all symmetry operations commute with each other. Now we only list the cases where two different elements commute.

- E commute with other symmetry operations.
- C_3 commute with C_3^2.

In the next chapter, readers will know that NH_3 belongs to the point group $\mathscr{C}_{3v}$, a non-abelian group.

(c) CH_4 has 17 symmetry elements,

$$E, 4C_3, 3C_2, 6\sigma, 3S_4.$$

They can be seen in Fig 2.3.

<div align="center">$4C_3$ $3C_2$ 6σ $3S_4$</div>
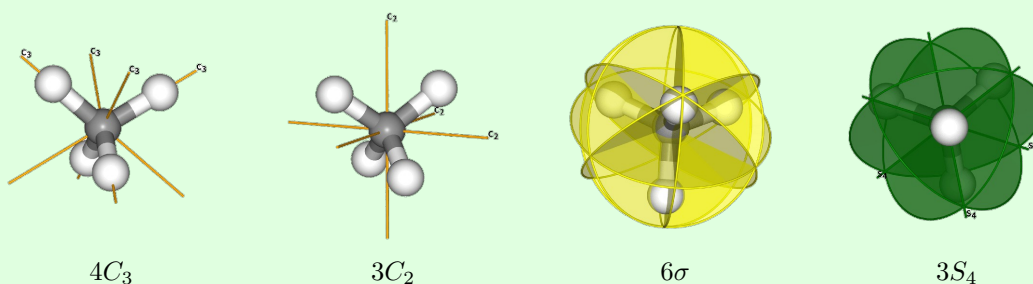
Figure 2.3: All symmetry elements of CH_4 except the identity E.

For CH_4, not all symmetry operations commute with each other. Now we only list the cases where two different elements commute.

- E commute with other symmetry operations.
- There are 3 C_2-axes, and thus there are 3 C_2 symmetry operations, C_{xy}, C_{yz} and C_{xz}. They are commutative.
- Though there are 4 C_3-axes, $C_3(1)$, $C_3(2)$, $C_3(3)$, $C_3(4)$, there are 8 corresponding symmetry operations, $C_3(1)$, $C_3^2(1) = C_3^{-1}(1)$, $C_3(2)$, $C_3^2(2) = C_3^{-1}(2)$, $C_3(3)$, $C_3^2(3) = C_3^{-1}(3)$, $C_3(4)$, $C_3^2(4) = C_3^{-1}(4)$. Only $C_3(i)$ and $C_3^2(i)$ commute, where $i \in \{1, 2, 3, 4\}$.
- Though there are 3 S_4-axes, S_{4x}, S_{4y}, S_{4z}, there are 6 S_4 symmetry operations (except 3 C_2 symmetry operations), S_{4x}, $S_{4x}^3 = S_{4x}^{-1}$, S_{4y}, $S_{4y}^3 = S_{4y}^{-1}$, S_{4z}, $S_{4z}^3 = S_{4z}^{-1}$. Only S_{4i} and S_{4i}^3 commute, where $i \in \{x, y, z\}$.
- C_{2i} and S_{4i} commute, where $i \in \{x, y, z\}$.
- σ_{xy} and $\sigma_{x\bar{y}}$ commute; likewise, σ_{zx} and $\sigma_{z\bar{x}}$ commute, as do σ_{yz} and $\sigma_{y\bar{z}}$.
- C_{2x} commutes with σ_{yz} and $\sigma_{y\bar{z}}$. Likewise, C_{2y} commutes with σ_{zx} and $\sigma_{z\bar{x}}$. Moreover, C_{2z} commutes with σ_{xy} and $\sigma_{x\bar{y}}$.

In the next chapter, readers will know that CH_4 belongs to the point group $\mathscr{T}_d$, a non-abelian group.

Remark

- Fig 2.1, Fig 2.2 and Fig 2.3 are sourced from https://symotter.org/gallery.
- Comprehensive multiplication tables for various groups are available in reference texts such as *Elements of Group Theory and Multiplication Tables* (Springer, ISBN: 978-981-19-2802-4). Specifically, the tables for the $\mathscr{C}_{2v}$, $\mathscr{C}_{3v}$, and $\mathscr{T}_d$ groups are located in the appendices.
- Figures were cropped to a uniform size on https://www.iloveimg.com.
- Figures was modified by removing the white background using https://www.remove.bg and setting the background color to transparent.

Exercise 2.2

On the basis of symmetry, which of the following molecules cannot have a dipole moment: CH_4, CH_3Cl, CH_2D_2, H_2S, SF_6?

Solution 2.2
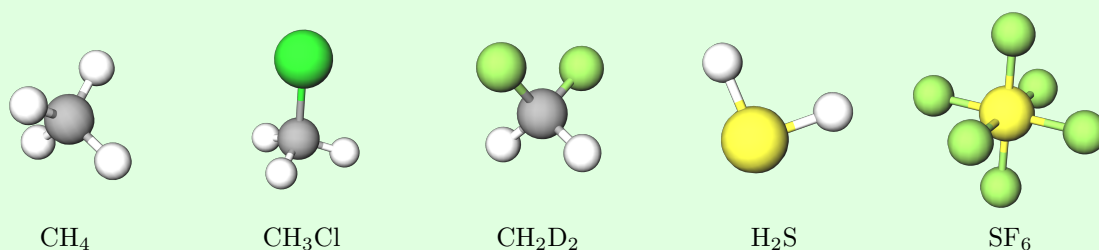
The diagrams of these molecules can be seen in Fig 2.4.

Figure 2.4: Diagrams of CH_4, CH_3Cl, CH_2D_2, H_2S and SF_6.

(a) CH_4 has no dipole moment for its center of symmetry.

(b) CH_3Cl has a dipole moment.

(c) CH_2D_2 has a dipole moment.

(d) H_2S has a dipole moment.

(e) SF_6 has no dipole moment for its center of symmetry.

Exercise 2.3

Which of the following molecules cannot be optically active: CHFClBr, H_2O_2, $[Co(en)_3]^{3+}$, *cis*-$[Co(en)_2(NH_3)_2]^{3+}$, *trans*-$[Co(en)_2(NH_3)_2]^{3+}$?

Solution 2.3

The diagrams of these molecules can be seen in Fig 2.5, Fig 2.6 and Fig 2.7.
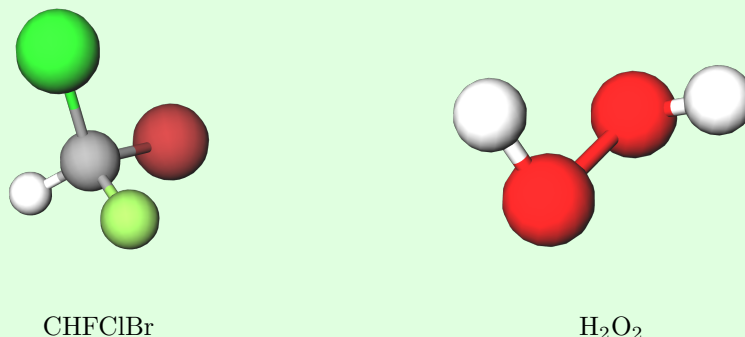

Figure 2.5: Diagrams of CHFClBr and H_2O_2.

(a) CHFClBr belongs to the point group $\mathscr{C}_1$, which is optically active.

(b) H_2O_2 belongs to the point group $\mathscr{C}_2$, which is optically active.
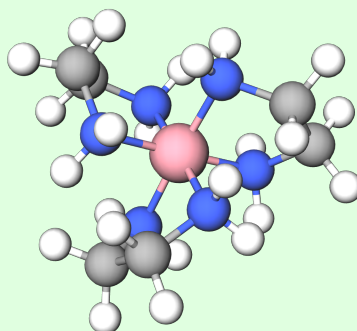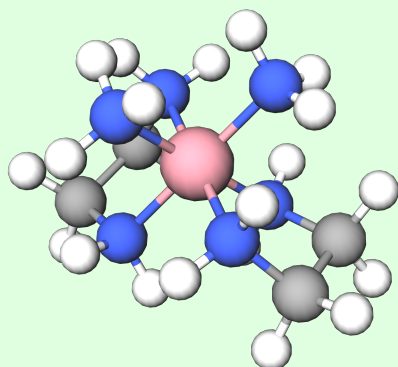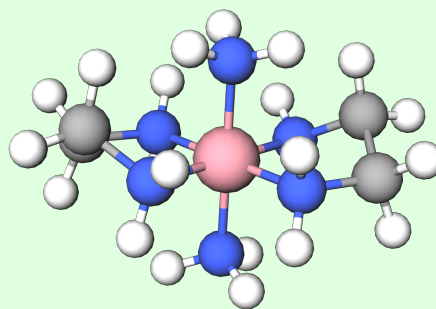

Figure 2.6: Diagrams of $[Co(en)_3]^{3+}$.

(c) $[\text{Co(en)}_3]^{3+}$ belongs to the point group $\mathscr{D}_3$, which is optically active.

$\textit{cis-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$ $\textit{trans-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$

Figure 2.7: Diagrams of $\textit{cis-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$ and $\textit{trans-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$.

(d) $\textit{cis-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$ belongs to the point group $\mathscr{C}_2$, which is optically active.

(e) $\textit{trans-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$ belongs to the point group $\mathscr{D}_2$, which is optically inactive.

Importantly, in the equilibrium geometries of these complexes, $[\text{Co(en)}_3]^{3+}$, $\textit{cis-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$, and $\textit{trans-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$, each ethylenediamine ligand must be considered non-planar. Thus, for example, $\textit{trans-}[\text{Co(en)}_2(\text{NH}_3)_2]^{3+}$ belongs to $\mathscr{D}_2$ rather than $\mathscr{D}_{2\text{h}}$.