CHAPTER 2

Symmetry Operations

Exercise 2.1

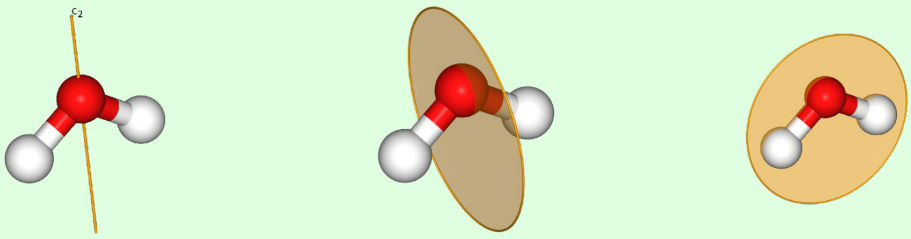
Give all the symmetry elements of H_2O, NH_3 and CH_4. For each molecule list the symmetry operations which commute.

Solution 2.1

(a) H_2O has 4 symmetry elements,

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

They are illustrated in Fig 2.1.



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

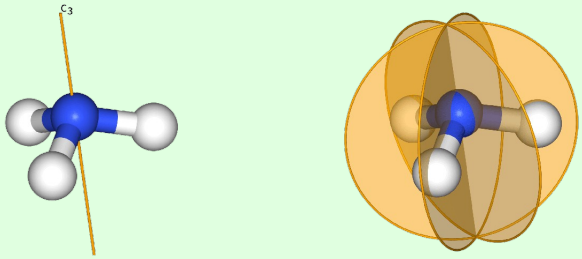
Figure 2.1: All symmetry elements of H_2O except the identity E.

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 are illustrated 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 symmetry operations commute.

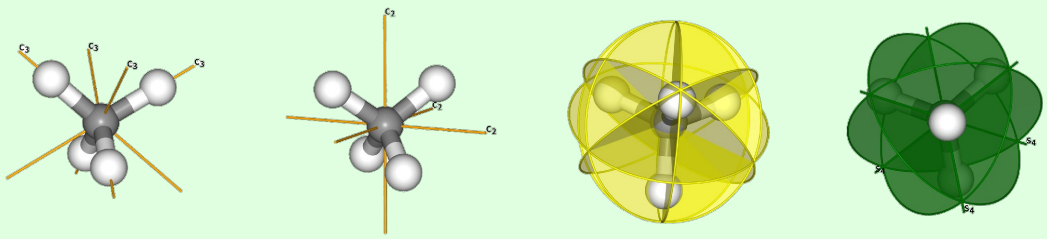
- E commute with other symmetry operations.
- C_3 commute with C_3^2.

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,

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

They are illustrated in Fig 2.3.



$4C_3$ $3C_2$ $6\sigma_d$ $3S_4$

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 symmetry operations commute. Given the high symmetry of the system, we can align a right-handed Cartesian coordinate system with the 3 C_2 axes to define the x, y, and z directions.

- 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, $C_3(i)$, $C_3^2(i) = C_3^{-1}(i)$, where $i \in \{1,2,3,4\}$. 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_{4i}, $S_{4i}^3 = S_{4i}^{-1}$, where $i \in \{x,y,z\}$. Only S_{4i} and S_{4i}^3 commute, where $i \in \{x,y,z\}$. Moreover, $C_{2i} = S_{4i}^2$ commutes with S_{4i} and S_{4i}^3, 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

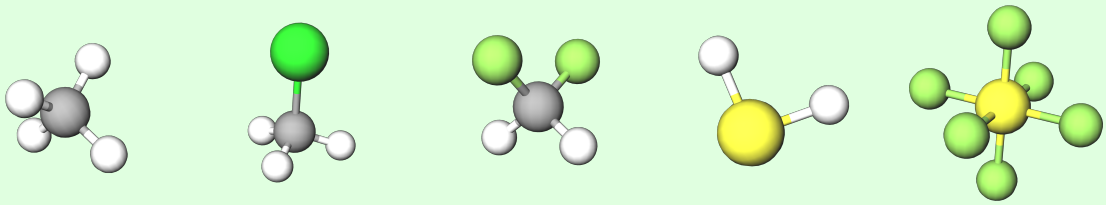
- Fig 2.1, Fig 2.2 and Fig 2.3 are generated from https://symotter.org/gallery.
- Group tables for various groups are available in reference texts such as *Symmetry Representations of Molecular Vibrations* (Springer, ISBN: 978-981-19-2802-4). Specifically, the group tables of $\mathscr{C}_{2v}$, $\mathscr{C}_{3v}$, and $\mathscr{T}_d$ are located in the appendices.
- All figures were cropped to a uniform size on https://www.iloveimg.com.
- All figures were rendered and post-processed for background transparency using https://www.remove.bg.

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 molecular structures of CH_4, CH_3Cl, CH_2D_2, H_2S, SF_6 are illustrated in Fig 2.4.



CH_4 CH_3Cl CH_2D_2 H_2S SF_6

Figure 2.4: Molecular structures 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.

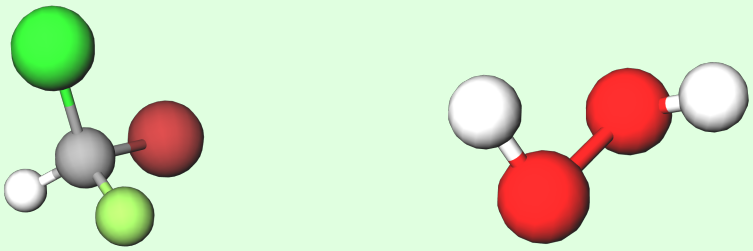
(e) SF_6 has no dipole moment for its center of symmetry.

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 geometries of CHFClBr and H_2O_2 are presented in Fig 2.5, while the various cobalt complexes, including $[Co(en)_3]^{3+}$ and the isomeric $[Co(en)_2(NH_3)_2]^{3+}$, are depicted in Fig 2.6 and Fig 2.7.



CHFClBr H_2O_2

Figure 2.5: Molecular structures 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.

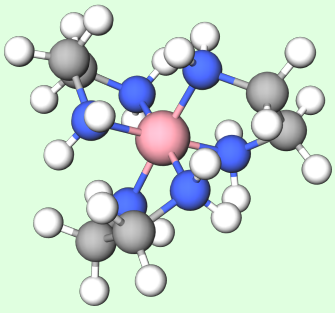
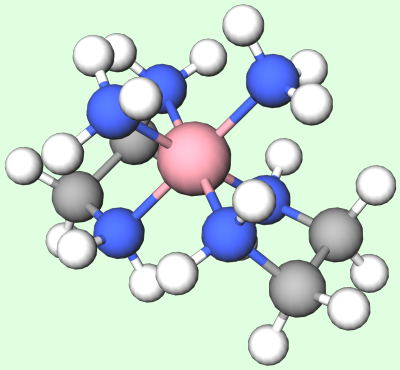
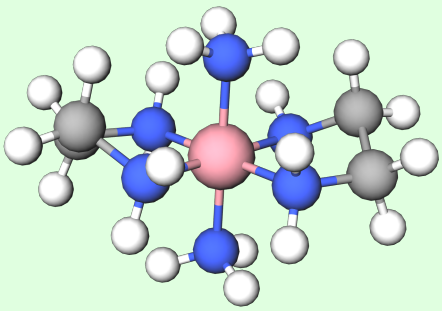


Figure 2.6: Molecular structure of $[Co(en)_3]^{3+}$.

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



cis-$[Co(en)_2(NH_3)_2]^{3+}$



trans-$[Co(en)_2(NH_3)_2]^{3+}$

Figure 2.7: Molecular structures of *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ and *trans*-$[Co(en)_2(NH_3)_2]^{3+}$.

(d) *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ belongs to the point group $\mathscr{C}_2$, which is optically active.

(e) *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ belongs to the point group $\mathscr{D}_2$, which is optically inactive.

Importantly, in the equilibrium geometries of these complexes, $[Co(en)_3]^{3+}$, *cis*-$[Co(en)_2(NH_3)_2]^{3+}$, and *trans*-$[Co(en)_2(NH_3)_2]^{3+}$, each ethylenediamine ligand must be considered non-planar. Thus, for example, *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ belongs to $\mathscr{D}_2$ rather than $\mathscr{D}_{2h}$.