Reconstructed Normal modes of the XY_n reference system in high symmetry

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Contents

1 General rules of reference system in "standard orientation"

The general rules in the geometry of reference system obey the definition of spherical coordinate system.

- Atom X is always the first one, which is located in the center.
- For the n number of Y atoms on the spherical surface,
  1. The Y atoms are grouped by their z coordinates. Atoms in each group have the same z value.
  2. These groups are ordered by the z values. The first group have the largest positive z value.
  3. In each group, the first Y atom should be put on the positive x-axis (if this is allowed by the symmetry) or some other high-symmetry axis, whereas the others should be ordered counterclockwise.
- Search $e^{max} = \max |(x, y, z)_i|$ in the atomic Cartesian coordinates, and one or more elements may be found. If the first extreme element is negative, then the Cartesian coordinates should be multiplied by -1.

The general rules in the normal mode $\boldsymbol{l}_m$ of reference system.

- $\boldsymbol{l}_m$ should be mass-independent (let $m_X = m_Y$), and have been normalized by $\boldsymbol{l}_m^\dagger \boldsymbol{l}_m = 1$.
- Atom X can be distorted only in the last 3 normal modes, which correspond to the relative translations between X and $n\times$ Y in x, y, and z directions. In other normal modes if the contributions from atom X are not zero, they must be projected out.
- Search $e^{max} = \max |(l_m)_i|$ in the $3(n+1)$ elements of $\boldsymbol{l}_m$, and one or more elements may be found. If the first extreme element is negative, then replace $\boldsymbol{l}_m$ by $-\boldsymbol{l}_m$.
- For degenerate normal modes (eg. T, $T^\dagger$, and $T^\ddagger$ in T modes, E and $E^\dagger$ in E modes), they should be rotated, which makes that
  1. In T and E: the distortions in the z direction are zero if possible. Then the zero distortions in the y direction if necessary.
  2. In $T^\dagger$: the distortions in the y direction are zero. Then the zero distortions in the x direction if necessary.
  3. The new $T^\ddagger$ and $E^\dagger$ can be obtained uniquely by the orthonormal condition.
- In general, the normal modes are ordered by degeneracy. Exceptions are
  1. Normal modes with distorted atom X should be the last.
  2. e modes should be the first in pseudo-triplet-degenerate normal modes.
- Before and after the rotation, all the normal modes (including the translational and rotational ones) should be orthogonal.

For most of the XY_n systems, two possible high-symmetric references are given: $O_h/D_{(n-2)h}$ and $C_{(n-1)v}$. However, the XY_4 system has only one high-symmetric reference T_d because C_{3v} is a subgroup of it, and for XY_8 the C_{7v} and D_{6h} references are not often used.

2 XY_4 reference system in T_d symmetry

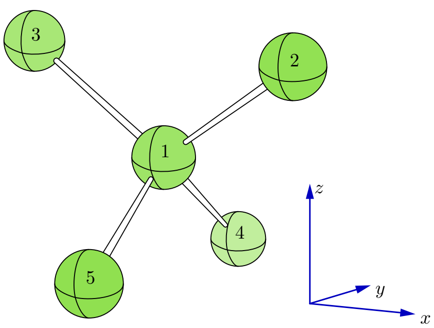
Symbols and constants used in this section:

r_1: radius of the reference sphere.

$\mathscr{C} = 1/\sqrt{3}$, $\mathscr{D} = \sqrt{2/3}$.

$\alpha = \mathscr{C}/2$, $\beta = \mathscr{D}/2$, $\gamma = 2/\sqrt{5}$, $\delta = 1/\sqrt{20}$, $\epsilon = 1/2$, $\zeta = 1/\sqrt{8}$.

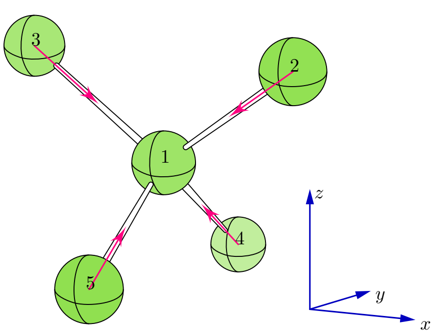
2.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ \mathscr{D}\, r_1 & 0 & \mathscr{C}\, r_1 \\ -\mathscr{D}\, r_1 & 0 & \mathscr{C}\, r_1 \\ 0 & \mathscr{D}\, r_1 & -\mathscr{C}\, r_1 \\ 0 & -\mathscr{D}\, r_1 & -\mathscr{C}\, r_1 \end{pmatrix} \tag{1}$$

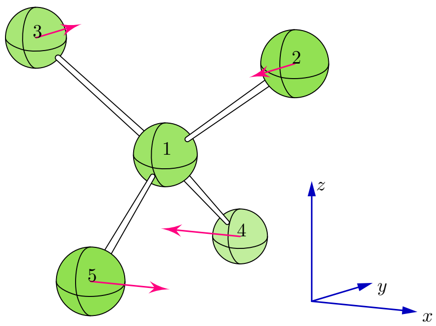
2.2 Reconstructed normal modes

2.2.1 A_1 (breathing)

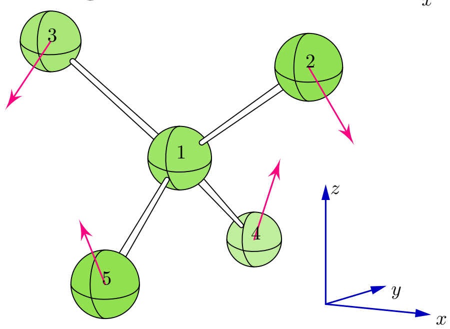


$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & \alpha \\ -\beta & 0 & \alpha \\ 0 & \beta & -\alpha \\ 0 & -\beta & -\alpha \end{pmatrix} \tag{2}$$

2.2.2 E

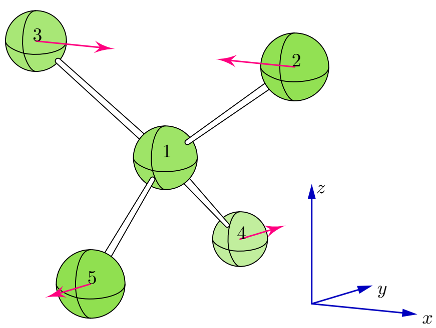


$$\boldsymbol{l}(E) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & -\epsilon & 0 \\ \epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \end{pmatrix} \tag{3}$$

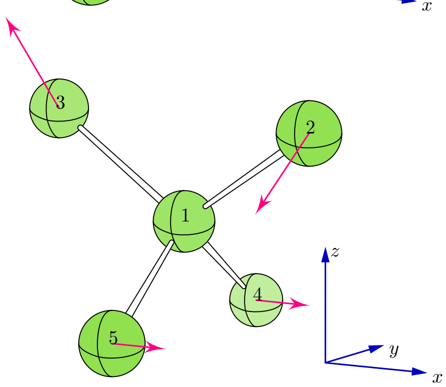


$$\boldsymbol{l}(E^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ -\alpha & 0 & \beta \\ \alpha & 0 & \beta \\ 0 & -\alpha & -\beta \\ 0 & \alpha & -\beta \end{pmatrix}$$

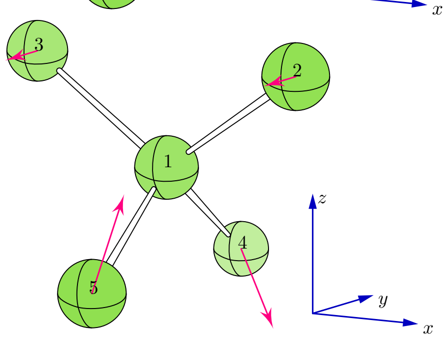
2.2.3 (I) T_2



$$\boldsymbol{l}(T_2) = \begin{pmatrix} 0 & 0 & 0 \\ \epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ 0 & -\epsilon & 0 \\ 0 & \epsilon & 0 \end{pmatrix} \tag{4}$$

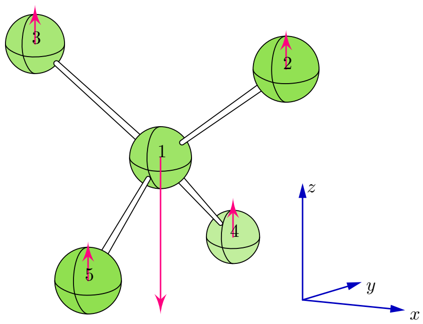


$$\boldsymbol{l}(T_2^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ \zeta & 0 & \epsilon \\ \zeta & 0 & -\epsilon \\ -\zeta & 0 & 0 \\ -\zeta & 0 & 0 \end{pmatrix}$$



$$\boldsymbol{l}(T_2^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \zeta & 0 \\ 0 & \zeta & 0 \\ 0 & -\zeta & \epsilon \\ 0 & -\zeta & -\epsilon \end{pmatrix}$$

2.2.4 (II) T_2 (triplet-degenerate intra-molecular translations between atoms X and 4 $\times Y$)



$$\boldsymbol{l}(T_2) = \begin{pmatrix} \gamma & 0 & 0 \\ -\delta & 0 & 0 \\ -\delta & 0 & 0 \\ -\delta & 0 & 0 \\ -\delta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_2^\dagger) = \begin{pmatrix} 0 & \gamma & 0 \\ 0 & -\delta & 0 \\ 0 & -\delta & 0 \\ 0 & -\delta & 0 \\ 0 & -\delta & 0 \end{pmatrix}, \boldsymbol{l}(T_2^\ddagger) = \begin{pmatrix} 0 & 0 & \gamma \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \end{pmatrix} \tag{5}$$

2.3 Curvilinear parameters of T_d reference and their components

XY_4: T_d reference

```
R1                                  % A1
R2   theta2                         % E
R3   theta3   phi3                  % (I)T2
R4   theta4   phi4                  % (II)T2
```

3 XY_5 reference system in D_{3h} symmetry

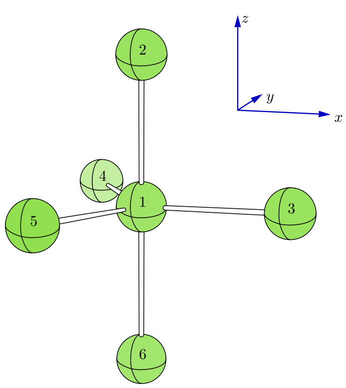
Symbols and constants used in this section:

r_1 radius of the reference sphere.

$\mathscr{C}_n$ $= cos(\frac{2n\pi}{3})$, $\mathscr{S}_n = sin(\frac{2n\pi}{3})$.

α $= \sqrt{1/5}$, $\beta = \sqrt{1/20}$, $\gamma = \sqrt{3/20}$, $\delta = \sqrt{3/10}$, $\epsilon = \sqrt{2/15}$, $\eta = 1/2$, $\theta = \sqrt{1/12}$, $\iota = \sqrt{1/10}$, $\xi = \sqrt{1/3}$, $\pi = \sqrt{1/30}$, $\rho = \sqrt{5/6}$, $\kappa = \sqrt{3/14}$, $\lambda = \sqrt{2/7}$, $\mu = \sqrt{8/21}$, $\nu = \sqrt{2/21}$.

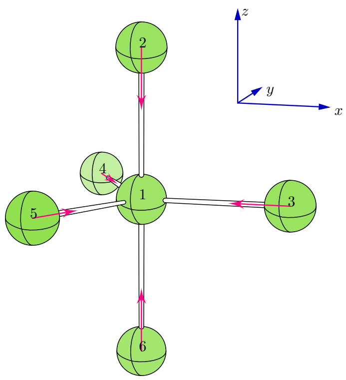
3.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & r_1 \\ r_1 & 0 & 0 \\ \mathscr{C}_1\ r_1 & \mathscr{S}_1\ r_1 & 0 \\ \mathscr{C}_2\ r_1 & \mathscr{S}_2\ r_1 & 0 \\ 0 & 0 & -r_1 \end{pmatrix} \tag{6}$$

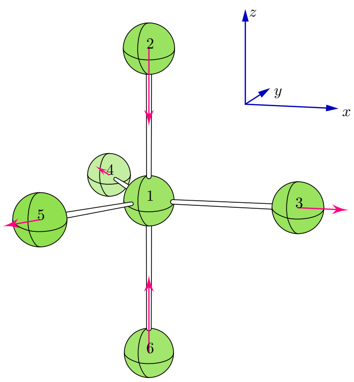
3.2 Reconstructed normal modes

3.2.1 (I) A_1' (breathing)



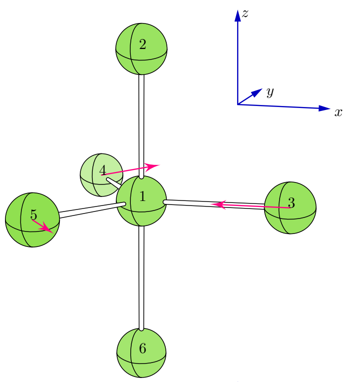
$$\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha \\ \alpha & 0 & 0 \\ -\beta & \gamma & 0 \\ -\beta & -\gamma & 0 \\ 0 & 0 & -\alpha \end{pmatrix} \tag{7}$$

3.2.2 (II) A_1' (anti-breathing)

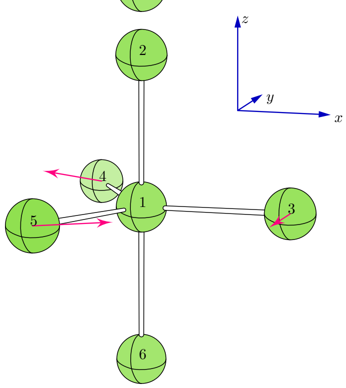


$$\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \delta \\ -\epsilon & 0 & 0 \\ \pi & -\iota & 0 \\ \pi & \iota & 0 \\ 0 & 0 & -\delta \end{pmatrix} \tag{8}$$

3.2.3 (I) E' ((t_1, τ_1) deformation mode of 3-membered ring)

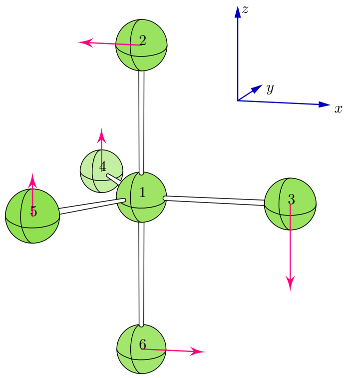


$$\boldsymbol{l}(E') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \xi & 0 & 0 \\ -\theta & -\eta & 0 \\ -\theta & \eta & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{9}$$

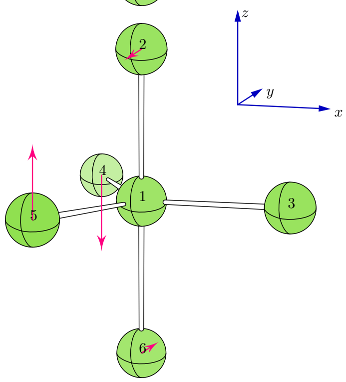


$$\boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \xi & 0 \\ \eta & -\theta & 0 \\ -\eta & -\theta & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

3.2.4 E'' (relative rotation between 2×Y and the 3×Y plane around x- and y- axes)

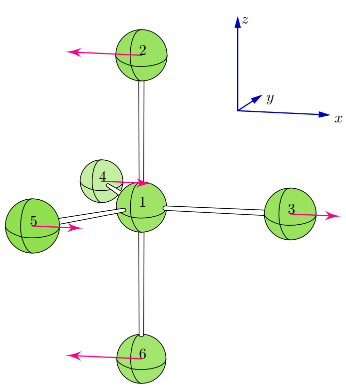


$$\boldsymbol{l}(E'') = \begin{pmatrix} 0 & 0 & 0 \\ \kappa & 0 & 0 \\ 0 & 0 & \mu \\ 0 & 0 & -\nu \\ 0 & 0 & -\nu \\ -\kappa & 0 & 0 \end{pmatrix} \quad (10)$$



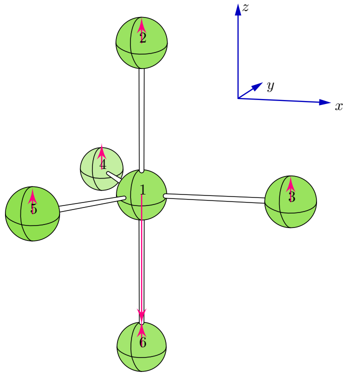
$$\boldsymbol{l}(E''^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \lambda \\ 0 & 0 & -\lambda \\ 0 & -\kappa & 0 \end{pmatrix}$$

3.2.5 (II) E' + (I)A_2'' (pseudo-triplet-degenerate intra-molecular translations between atoms 2 ×Y and 3 ×Y)



$$\boldsymbol{l}(E') = \begin{pmatrix} 0 & 0 & 0 \\ \delta & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ \delta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \delta & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & \delta & 0 \end{pmatrix}, \boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \delta \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & \delta \end{pmatrix} \quad (11)$$

3.2.6 (III)E' + (II)A_2'' (pseudo-triplet-degenerate intra-molecular translations between atoms X and 5 $\times Y$)



$$\boldsymbol{l}(E') = \begin{pmatrix} \rho & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & \rho & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \end{pmatrix}, \boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & \rho \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \end{pmatrix} \quad (12)$$

3.3 Curvilinear parameters of D_{3h} reference and their components

XY_5: D_{3h} reference

```
R1                                          % (I)A1'
R2                                          % (II)A1'
R3   theta3                                 % (I)E'
R4   theta4                                 % E"
R5   theta5   phi5                          % (II)E' + (I)A2"
R6   theta6   phi6                          % (III)E' + (II)A2"
```

4 XY_5 reference system in C_{4v} symmetry

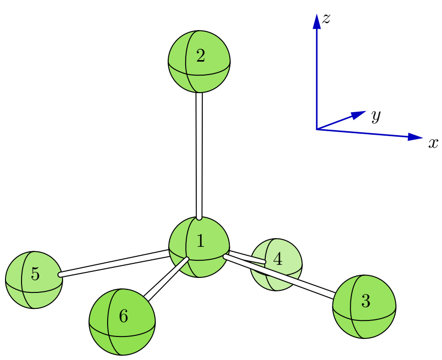
Symbols and constants used in this section:

r_1 radius of the reference sphere.

$\mathscr{C}$ $= 1/4$, $\mathscr{S} = \sqrt{15/16}$.

α $= 1/2$, $\beta = \sqrt{1/5}$, $\gamma = 1/4$, $\delta = \sqrt{3/5}$, $\epsilon = \sqrt{3/80}$, $\zeta = \sqrt{12/25}$, $\eta = \sqrt{3/100}$, $\pi = \sqrt{1/30}$, $\rho = \sqrt{5/6}$.

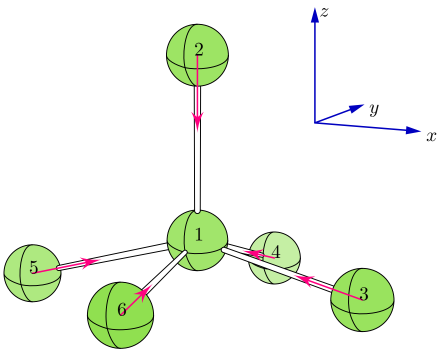
4.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & r_1 \\ \mathscr{S}\ r_1 & 0 & -\mathscr{C}\ r_1 \\ 0 & \mathscr{S}\ r_1 & -\mathscr{C}\ r_1 \\ -\mathscr{S}\ r_1 & 0 & -\mathscr{C}\ r_1 \\ 0 & -\mathscr{S}\ r_1 & -\mathscr{C}\ r_1 \end{pmatrix} \quad (13)$$

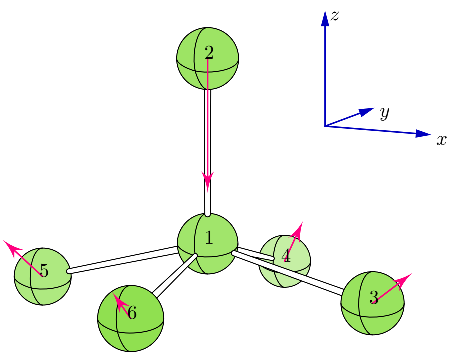
4.2 Reconstructed normal modes

4.2.1 (I)A_1 (breathing mode)



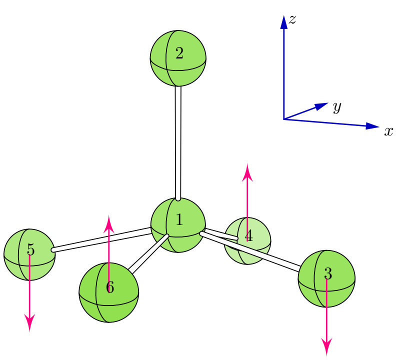
$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \beta \\ \mathscr{S}\ \beta & 0 & -\mathscr{C}\ \beta \\ 0 & \mathscr{S}\ \beta & -\mathscr{C}\ \beta \\ -\mathscr{S}\ \beta & 0 & -\mathscr{C}\ \beta \\ 0 & -\mathscr{S}\ \beta & -\mathscr{C}\ \beta \end{pmatrix} \tag{14}$$

4.2.2 (II)A_1 (anti-breathing mode)



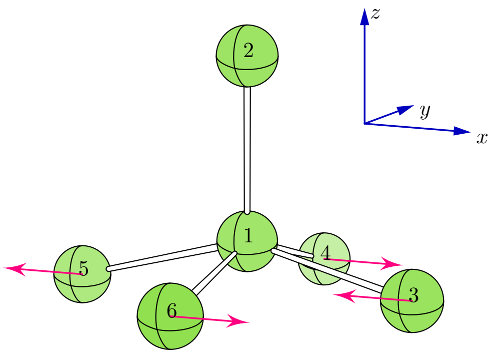
$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \delta \\ -\gamma & 0 & -\epsilon \\ 0 & -\gamma & -\epsilon \\ \gamma & 0 & -\epsilon \\ 0 & \gamma & -\epsilon \end{pmatrix} \tag{15}$$

4.2.3 (I)B_2 (q_2 puckering mode of 4-membered ring)

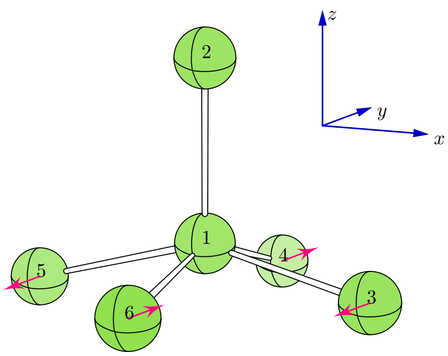


$$\boldsymbol{l}(B_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & \alpha \\ 0 & 0 & -\alpha \end{pmatrix} \tag{16}$$

4.2.4 (I)E ((t_1, τ_1) deformation mode of 4-membered ring)

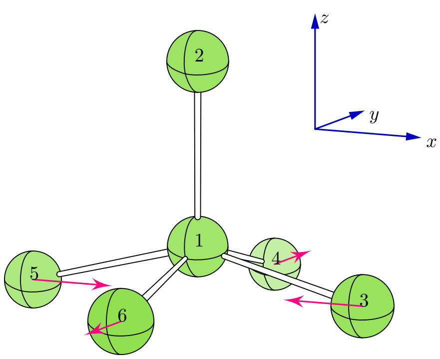


$$\boldsymbol{l}(E) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ \alpha & 0 & 0 \\ -\alpha & 0 & 0 \end{pmatrix} \tag{17}$$

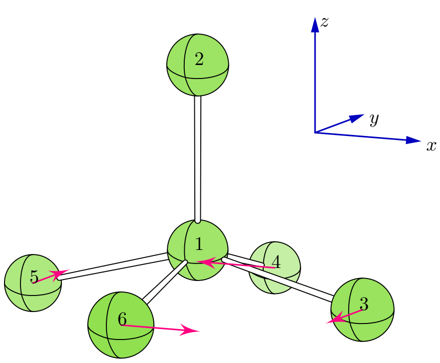


$$\boldsymbol{l}(E^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & \alpha & 0 \\ 0 & -\alpha & 0 \end{pmatrix}$$

4.2.5 (II)$B_2 + B_1$ ((t_2, τ_2) deformation mode of 4-membered ring)



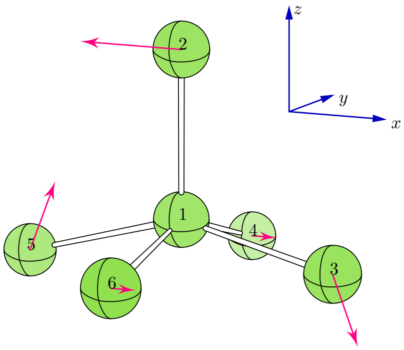
$$\boldsymbol{l}(B_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \alpha & 0 & 0 \\ 0 & -\alpha & 0 \\ -\alpha & 0 & 0 \\ 0 & \alpha & 0 \end{pmatrix} \tag{18}$$



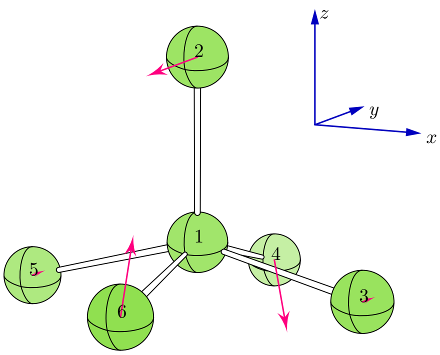
$$\boldsymbol{l}(B_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \alpha & 0 \\ \alpha & 0 & 0 \\ 0 & -\alpha & 0 \\ -\alpha & 0 & 0 \end{pmatrix}$$

4.2.6 (II)E (relative rotation between $Y2$ and the $4\times Y$ plane around x- and y- axes)

Contributions in z column are not zero because of orthogonality to the total rotation modes.

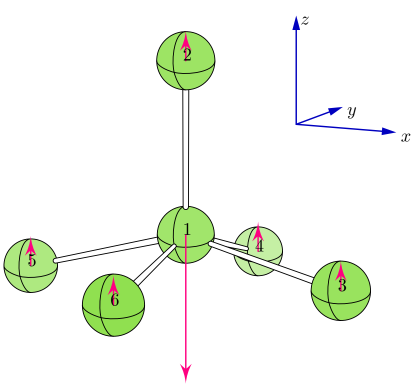


$$
\boldsymbol{l}(E) = \begin{pmatrix} 0 & 0 & 0 \\ \zeta & 0 & 0 \\ -\eta & 0 & \beta \\ -\eta & 0 & 0 \\ -\eta & 0 & -\beta \\ -\eta & 0 & 0 \end{pmatrix} \tag{19}
$$



$$
\boldsymbol{l}(E^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \zeta & 0 \\ 0 & -\eta & 0 \\ 0 & -\eta & \beta \\ 0 & -\eta & 0 \\ 0 & -\eta & -\beta \end{pmatrix}
$$

4.2.7 (III)E + (III)A_1 (pseudo-triplet-degenerate intra-molecular translations between atoms X and 5 $\times Y$)



$$
\boldsymbol{l}(E) = \begin{pmatrix} \rho & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \\ -\pi & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E^{\dagger}) = \begin{pmatrix} 0 & \rho & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \\ 0 & -\pi & 0 \end{pmatrix}, \boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & \rho \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \\ 0 & 0 & -\pi \end{pmatrix} \tag{20}
$$

4.3 Curvilinear parameters of C_{4v} reference and their components

XY_5: C_{4v} reference

```
R1                                      % (I)A1
R2                                      % (II)A1
R3                                      % (I)B2
R4   theta4                             % (I)E
R5   theta5                             % (II)B2 + B1
R6   theta6                             % (II)E
R7   theta7   phi7                      % (III)E + (III)A1
```

Another set of curvilinear parameters of C_{4v} reference: (I)B_2 and (II)B_2 are exchanged to get a turnstil rotation mode of atoms $Y5$ and $Y6$.

XY_5: C_{4v} reference

```
R1                                      % (I)A1
R2                                      % (II)A1
R3                                      % (II)B2
R4   theta4                             % (I)E
R5   theta5                             % (I)B2 + B1
R6   theta6                             % (II)E
R7   theta7   phi7                      % (III)E + (III)A1
```

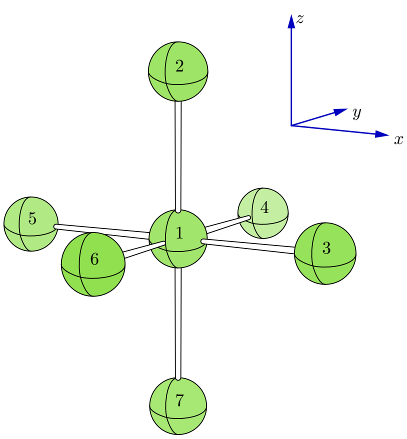
5 XY_6 reference system in O_h symmetry

Symbols and constants used in this section:

r_1: radius of the reference sphere.

$\alpha = 1/\sqrt{6}$, $\beta = 1/2$,$\gamma = 1/\sqrt{3}$, $\delta = \gamma/2$, $\epsilon = \sqrt{6/7}$, $\zeta = \epsilon/6$.

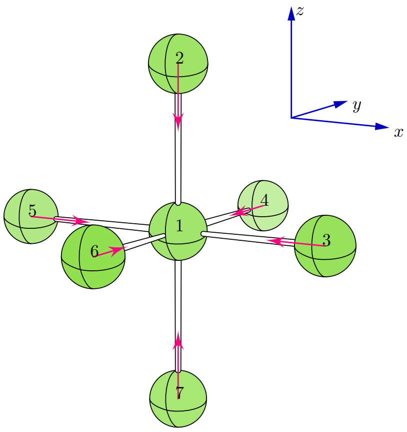
5.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \\ Y7 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & r_1 \\ r_1 & 0 & 0 \\ 0 & r_1 & 0 \\ -r_1 & 0 & 0 \\ 0 & -r_1 & 0 \\ 0 & 0 & -r_1 \end{pmatrix} \tag{21}$$

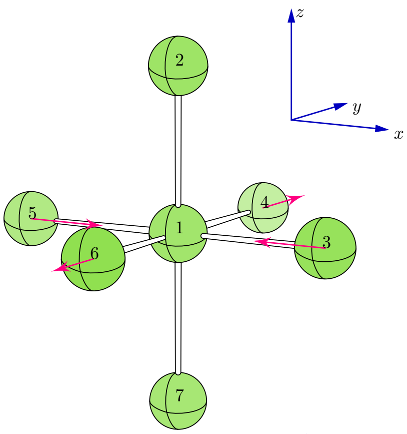
5.2 Reconstructed normal modes

5.2.1 A_{1g} (breathing)

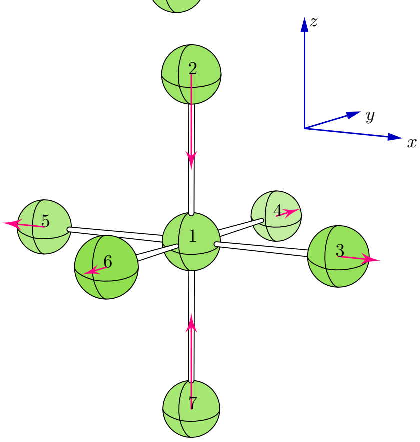


$$\boldsymbol{l}(A_{1g}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha \\ \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ -\alpha & 0 & 0 \\ 0 & -\alpha & 0 \\ 0 & 0 & -\alpha \end{pmatrix} \tag{22}$$

5.2.2 E_g (anti-breathing)

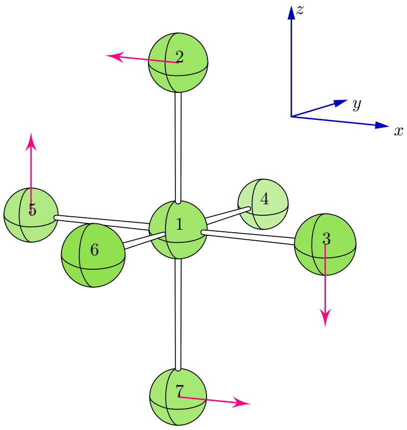


$$\boldsymbol{l}(E_g) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \beta & 0 & 0 \\ 0 & -\beta & 0 \\ -\beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{23}$$



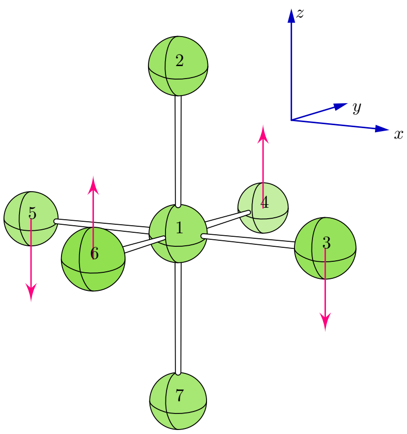
$$\boldsymbol{l}(E_g^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma \\ -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & -\gamma \end{pmatrix}$$

5.2.3 T_{2g} ((t_2, $\tau_2 = 90^o$) deformation modes of three 4-membered rings)



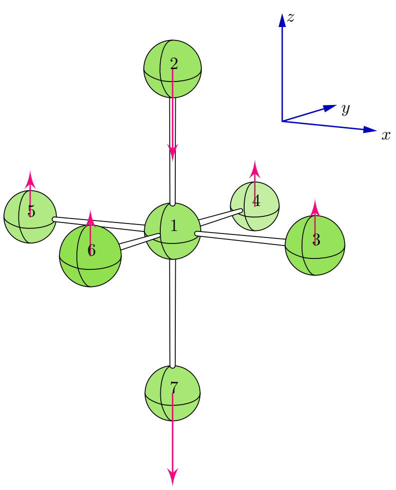
$$\boldsymbol{l}(T_{2g}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \beta & 0 \\ \beta & 0 & 0 \\ 0 & -\beta & 0 \\ -\beta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{2g}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & 0 \\ 0 & 0 & \beta \\ 0 & 0 & 0 \\ 0 & 0 & -\beta \\ 0 & 0 & 0 \\ -\beta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{2g}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \beta \\ 0 & 0 & 0 \\ 0 & 0 & -\beta \\ 0 & -\beta & 0 \end{pmatrix} \quad (24)$$

5.2.4 T_{2u} (q_2 puckering modes of three 4-membered rings)



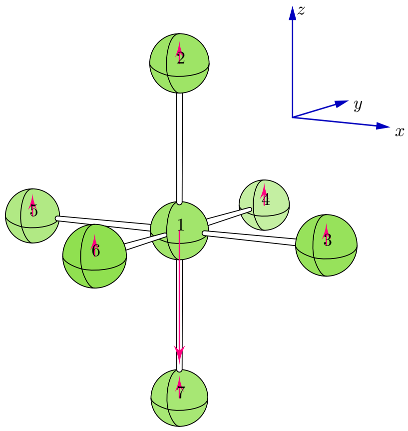
$$\boldsymbol{l}(T_{2u}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & 0 \\ 0 & 0 & 0 \\ -\beta & 0 & 0 \\ 0 & 0 & 0 \\ -\beta & 0 & 0 \\ \beta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{2u}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \beta & 0 \\ 0 & -\beta & 0 \\ 0 & 0 & 0 \\ 0 & -\beta & 0 \\ 0 & 0 & 0 \\ 0 & \beta & 0 \end{pmatrix}, \boldsymbol{l}(T_{2u}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \beta \\ 0 & 0 & -\beta \\ 0 & 0 & \beta \\ 0 & 0 & -\beta \\ 0 & 0 & 0 \end{pmatrix} \quad (25)$$

5.2.5 (I) T_{1u} (intra-molecular translations between $\mathbf{2}\times Y$ and $\mathbf{5}\times Y$)



$$\boldsymbol{l}(T_{1u}) = \begin{pmatrix} 0 & 0 & 0 \\ -\delta & 0 & 0 \\ \gamma & 0 & 0 \\ -\delta & 0 & 0 \\ \gamma & 0 & 0 \\ -\delta & 0 & 0 \\ -\delta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & -\delta & 0 \\ 0 & \gamma & 0 \\ 0 & -\delta & 0 \\ 0 & \gamma & 0 \\ 0 & -\delta & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \\ 0 & 0 & \gamma \end{pmatrix} \quad (26)$$

5.2.6 (II) T_{1u} (triplet-degenerate intra-molecular translations between atoms X and 6 $\times Y$)



$$\boldsymbol{l}(T_{1u}) = \begin{pmatrix} \epsilon & 0 & 0 \\ -\zeta & 0 & 0 \\ -\zeta & 0 & 0 \\ -\zeta & 0 & 0 \\ -\zeta & 0 & 0 \\ -\zeta & 0 & 0 \\ -\zeta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\dagger}) = \begin{pmatrix} 0 & \epsilon & 0 \\ 0 & -\zeta & 0 \\ 0 & -\zeta & 0 \\ 0 & -\zeta & 0 \\ 0 & -\zeta & 0 \\ 0 & -\zeta & 0 \\ 0 & -\zeta & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\ddagger}) = \begin{pmatrix} 0 & 0 & \epsilon \\ 0 & 0 & -\zeta \\ 0 & 0 & -\zeta \\ 0 & 0 & -\zeta \\ 0 & 0 & -\zeta \\ 0 & 0 & -\zeta \\ 0 & 0 & -\zeta \end{pmatrix} \quad (27)$$

5.3 Curvilinear parameters of O_h reference and their components

XY_6: O_h reference

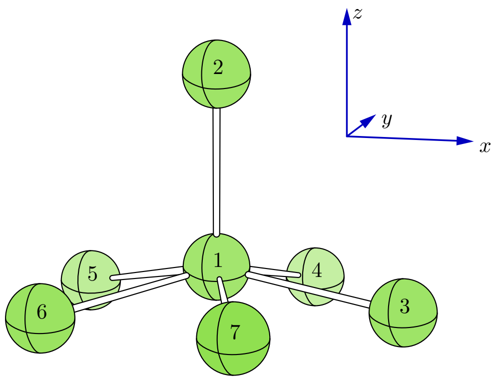
```
R1                                          % A1g
R2   theta2                                 % Eg
R3   theta3   phi3                          % T2g
R4   theta4   phi4                          % T2u
R5   theta5   phi5                          % (I)T1u
R6   theta6   phi6                          % (II)T1u
```

6 XY_6 reference system in C_{5v} symmetry

Symbols and constants used in this section:

- r_1 radius of the reference sphere.
- $\mathscr{C}_n = cos(\frac{2n\pi}{5})$, $\mathscr{S}_n = sin(\frac{2n\pi}{5})$.
- $\alpha = 1/5$, $\beta = \sqrt{24/25}$, $\gamma = \sqrt{1/6}$, $\delta = 2/5$, $\epsilon = \sqrt{1/150}$, $\eta = \sqrt{2/3}$, $\theta = \sqrt{4/150}$, $\iota = \sqrt{1/5}$, $\xi = \sqrt{2/15}$, $\pi = \sqrt{5/9}$, $\rho = \sqrt{1/45}$, $\kappa = \sqrt{2/5}$, $\lambda = \sqrt{6/7}$, $\mu = \sqrt{1/42}$.

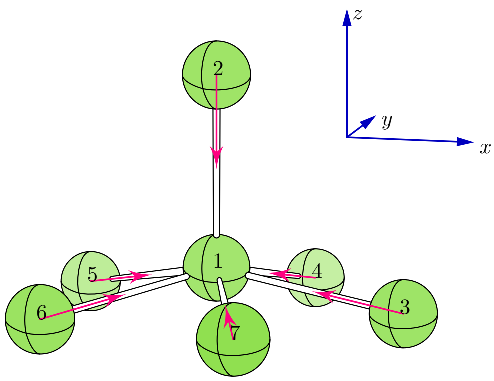
6.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \\ Y7 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & r_1 \\ \beta r_1 & 0 & -\alpha r_1 \\ \mathscr{C}_1\beta r_1 & \mathscr{S}_1\beta r_1 & -\alpha r_1 \\ \mathscr{C}_2\beta r_1 & \mathscr{S}_2\beta r_1 & -\alpha r_1 \\ \mathscr{C}_3\beta r_1 & \mathscr{S}_3\beta r_1 & -\alpha r_1 \\ \mathscr{C}_4\beta r_1 & \mathscr{S}_4\beta r_1 & -\alpha r_1 \end{pmatrix} \tag{28}$$

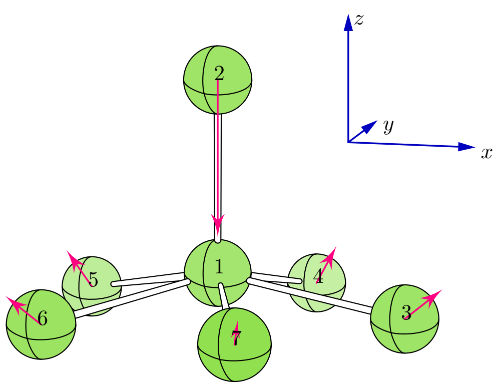
6.2 Reconstructed normal modes

6.2.1 (I) A_1 (breathing mode)



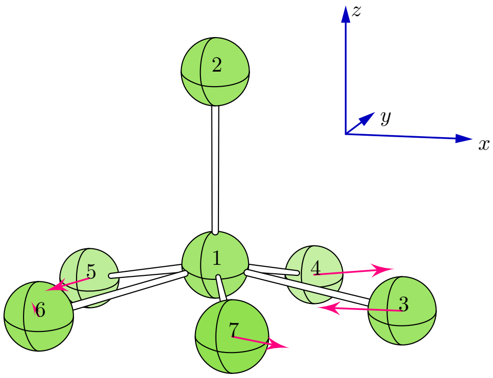
$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma \\ \delta & 0 & -\epsilon \\ \mathscr{C}_1\delta & \mathscr{S}_1\delta & -\epsilon \\ \mathscr{C}_2\delta & \mathscr{S}_2\delta & -\epsilon \\ \mathscr{C}_3\delta & \mathscr{S}_3\delta & -\epsilon \\ \mathscr{C}_4\delta & \mathscr{S}_4\delta & -\epsilon \end{pmatrix} \tag{29}$$

6.2.2 (II) A_1 (anti-breathing mode)

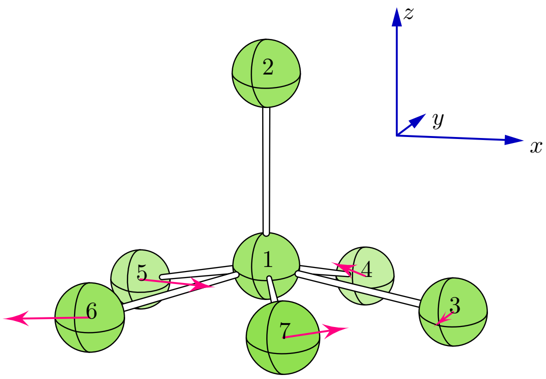


$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \eta \\ -\alpha & 0 & -\theta \\ -\mathscr{C}_1\alpha & -\mathscr{S}_1\alpha & -\theta \\ -\mathscr{C}_2\alpha & -\mathscr{S}_2\alpha & -\theta \\ -\mathscr{C}_3\alpha & -\mathscr{S}_3\alpha & -\theta \\ -\mathscr{C}_4\alpha & -\mathscr{S}_4\alpha & -\theta \end{pmatrix} \tag{30}$$

6.2.3 (I) E_1 ((t_1, τ_1) mode of 5-membered ring)

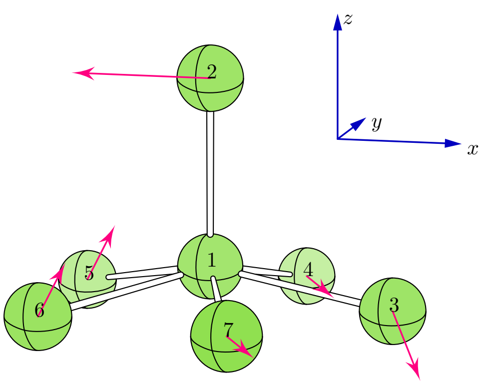


$$\boldsymbol{l}(E_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \iota & 0 & 0 \\ \mathscr{C}_3\iota & \mathscr{S}_3\iota & 0 \\ \mathscr{C}_1\iota & \mathscr{S}_1\iota & 0 \\ \mathscr{C}_4\iota & \mathscr{S}_4\iota & 0 \\ \mathscr{C}_2\iota & \mathscr{S}_2\iota & 0 \end{pmatrix} \tag{31}$$



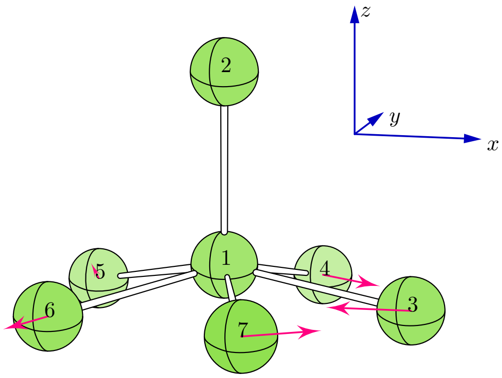
$$\boldsymbol{l}(E_1^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \iota & 0 \\ \mathscr{S}_2\iota & \mathscr{C}_2\iota & 0 \\ \mathscr{S}_4\iota & \mathscr{C}_4\iota & 0 \\ \mathscr{S}_1\iota & \mathscr{C}_1\iota & 0 \\ \mathscr{S}_3\iota & \mathscr{C}_3\iota & 0 \end{pmatrix}$$

6.2.4 (II) E_1 (relative rotation between $Y2$ and the 5$\times Y$ plane around x- and y- axes)

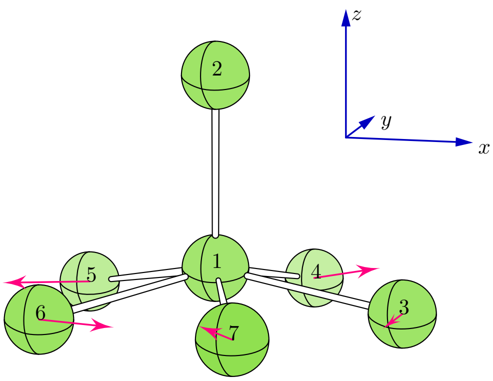


$$\boldsymbol{l}(E_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \pi & 0 \\ 0 & -\rho & 0 \\ 0 & -\rho & \mathscr{S}_1\xi \\ 0 & -\rho & \mathscr{S}_2\xi \\ 0 & -\rho & \mathscr{S}_3\xi \\ 0 & -\rho & \mathscr{S}_4\xi \end{pmatrix}, \boldsymbol{l}(E_1^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ \pi & 0 & 0 \\ -\rho & 0 & \xi \\ -\rho & 0 & \mathscr{C}_1\xi \\ -\rho & 0 & \mathscr{C}_2\xi \\ -\rho & 0 & \mathscr{C}_3\xi \\ -\rho & 0 & \mathscr{C}_4\xi \end{pmatrix} \tag{32}$$

6.2.5 (I) E_2 ((t_2, τ_2) mode of 5-membered ring)

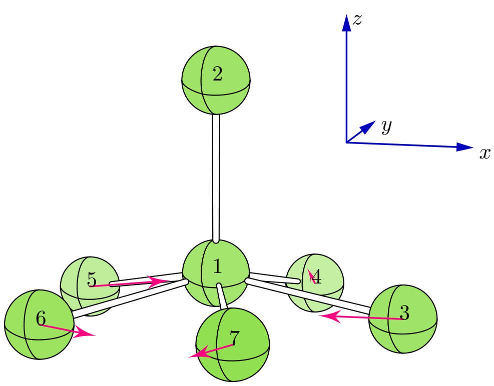


$$\boldsymbol{l}(E_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \iota & 0 & 0 \\ \mathscr{C}_2\iota & \mathscr{S}_2\iota & 0 \\ \mathscr{C}_4\iota & \mathscr{S}_4\iota & 0 \\ \mathscr{C}_1\iota & \mathscr{S}_1\iota & 0 \\ \mathscr{C}_3\iota & \mathscr{S}_3\iota & 0 \end{pmatrix} \tag{33}$$

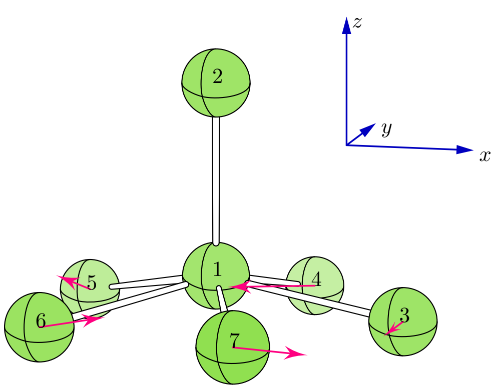


$$\boldsymbol{l}(E_2^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \iota & 0 \\ \mathscr{S}_3\iota & \mathscr{C}_3\iota & 0 \\ \mathscr{S}_1\iota & \mathscr{C}_1\iota & 0 \\ \mathscr{S}_4\iota & \mathscr{C}_4\iota & 0 \\ \mathscr{S}_2\iota & \mathscr{C}_2\iota & 0 \end{pmatrix}$$

6.2.6 (II) E_2 ((t_3, τ_3) mode of 5-membered ring)

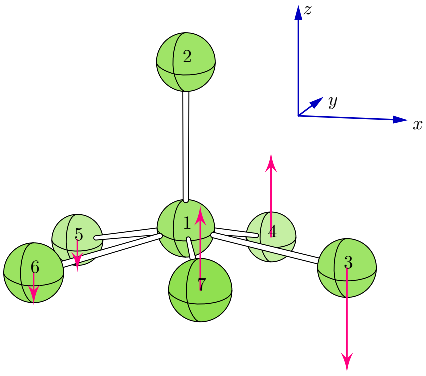


$$\boldsymbol{l}(E_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \iota & 0 & 0 \\ \mathscr{C}_4\iota & \mathscr{S}_4\iota & 0 \\ \mathscr{C}_3\iota & \mathscr{S}_3\iota & 0 \\ \mathscr{C}_2\iota & \mathscr{S}_2\iota & 0 \\ \mathscr{C}_1\iota & \mathscr{S}_1\iota & 0 \end{pmatrix} \tag{34}$$

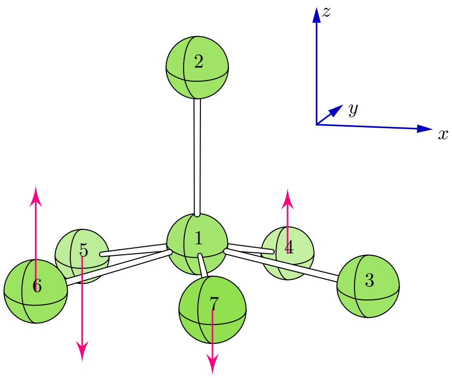


$$\boldsymbol{l}(E_2^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \iota & 0 \\ \mathscr{S}_1\iota & \mathscr{C}_1\iota & 0 \\ \mathscr{S}_2\iota & \mathscr{C}_2\iota & 0 \\ \mathscr{S}_3\iota & \mathscr{C}_3\iota & 0 \\ \mathscr{S}_4\iota & \mathscr{C}_4\iota & 0 \end{pmatrix}$$

6.2.7 (III) E_2 ((q_2, ϕ_2) mode of 5-membered ring)

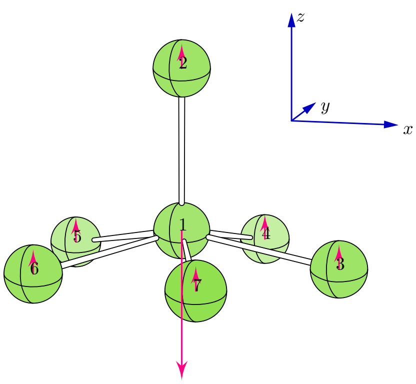


$$\boldsymbol{l}(E_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \kappa \\ 0 & 0 & \mathscr{C}_3\kappa \\ 0 & 0 & \mathscr{C}_1\kappa \\ 0 & 0 & \mathscr{C}_4\kappa \\ 0 & 0 & \mathscr{C}_2\kappa \end{pmatrix} \tag{35}$$



$$\boldsymbol{l}(E_2^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mathscr{S}_3\kappa \\ 0 & 0 & \mathscr{S}_1\kappa \\ 0 & 0 & \mathscr{S}_4\kappa \\ 0 & 0 & \mathscr{S}_2\kappa \end{pmatrix}$$

6.2.8 (III)E_1 + (III)A_1 (pseudo-triplet-degenerate intra-molecular translations between atoms X and 6 $\times Y$)



$$\boldsymbol{l}(E_1) = \begin{pmatrix} \lambda & 0 & 0 \\ -\mu & 0 & 0 \\ -\mu & 0 & 0 \\ -\mu & 0 & 0 \\ -\mu & 0 & 0 \\ -\mu & 0 & 0 \\ -\mu & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E_1^\dagger) = \begin{pmatrix} 0 & \lambda & 0 \\ 0 & -\mu & 0 \\ 0 & -\mu & 0 \\ 0 & -\mu & 0 \\ 0 & -\mu & 0 \\ 0 & -\mu & 0 \\ 0 & -\mu & 0 \end{pmatrix}, \boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & \lambda \\ 0 & 0 & -\mu \\ 0 & 0 & -\mu \\ 0 & 0 & -\mu \\ 0 & 0 & -\mu \\ 0 & 0 & -\mu \\ 0 & 0 & -\mu \end{pmatrix} \tag{36}$$

6.3 Curvilinear parameters of C_{5v} reference and their components

XY_6: C_{5v} reference

```
R1                                  % (I)A1
R2                                  % (II)A1
R3   theta3                         % (I)E1
R4   theta4                         % (II)E1
R5   theta5                         % (I)E2
```

```
R6   theta6                                % (II)E2
R7   theta7                                % (III)E2
R8   theta8   phi8                         % (III)E1 + (III)A1
```

7 XY_7 reference system in D_{5h} symmetry

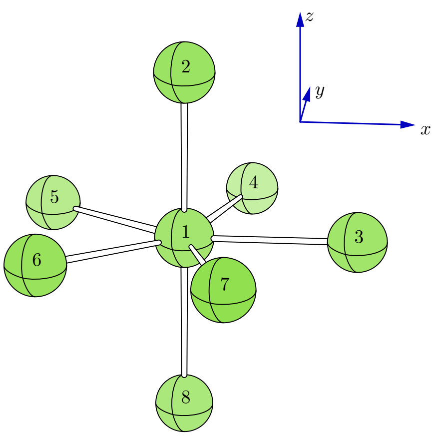
Symbols and constants used in this section:

r_1 radius of the reference sphere.

$\mathscr{C}_n = cos(\frac{2n\pi}{5})$, $\mathscr{S}_n = sin(\frac{2n\pi}{5})$.

$\alpha = \sqrt{1/7}$, $\beta = \sqrt{2/35}$, $\gamma = \sqrt{5/14}$, $\delta = \sqrt{1/5}$, $\epsilon = \sqrt{8/45}$, $\eta = \sqrt{5/18}$, $\theta = \sqrt{2/5}$, $\iota = \sqrt{7/8}$, $\xi = \sqrt{1/56}$.

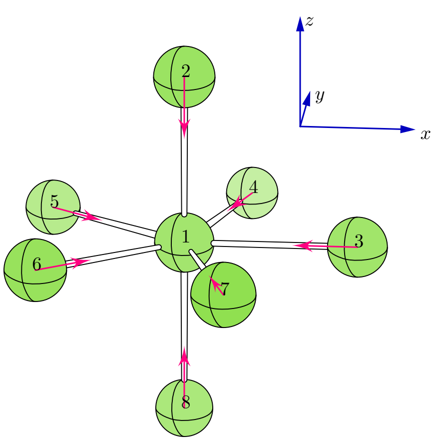
7.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \\ Y7 \\ Y8 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & r_1 \\ r_1 & 0 & 0 \\ \mathscr{C}_1 r_1 & \mathscr{S}_1 r_1 & 0 \\ \mathscr{C}_2 r_1 & \mathscr{S}_2 r_1 & 0 \\ \mathscr{C}_3 r_1 & \mathscr{S}_3 r_1 & 0 \\ \mathscr{C}_4 r_1 & \mathscr{S}_4 r_1 & 0 \\ 0 & 0 & -r_1 \end{pmatrix} \tag{37}$$

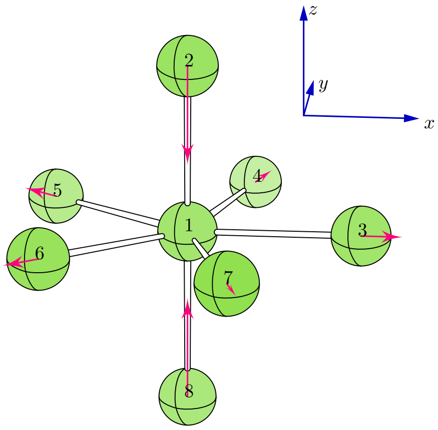
7.2 Reconstructed normal modes

7.2.1 (I) A_1' (breathing mode)



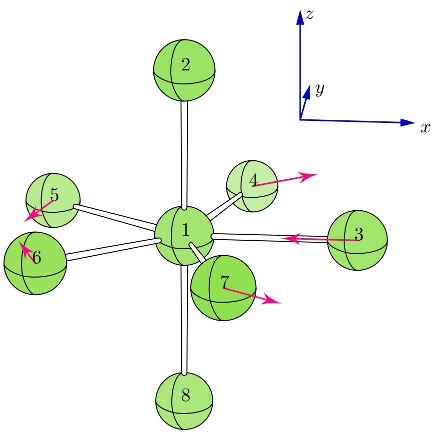
$$\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha \\ \alpha & 0 & 0 \\ \mathscr{C}_1\alpha & \mathscr{S}_1\alpha & 0 \\ \mathscr{C}_2\alpha & \mathscr{S}_2\alpha & 0 \\ \mathscr{C}_3\alpha & \mathscr{S}_3\alpha & 0 \\ \mathscr{C}_4\alpha & \mathscr{S}_4\alpha & 0 \\ 0 & 0 & -\alpha \end{pmatrix} \tag{38}$$

7.2.2 (II) A_1' (anti-breathing mode)

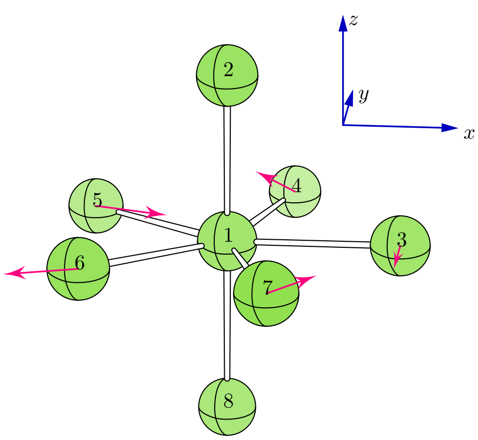


$$
\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma \\ -\beta & 0 & 0 \\ -\mathscr{C}_1\beta & -\mathscr{S}_1\beta & 0 \\ -\mathscr{C}_2\beta & -\mathscr{S}_2\beta & 0 \\ -\mathscr{C}_3\beta & -\mathscr{S}_3\beta & 0 \\ -\mathscr{C}_4\beta & -\mathscr{S}_4\beta & 0 \\ 0 & 0 & -\gamma \end{pmatrix} \tag{39}
$$

7.2.3 (I) E_1' ((t_1, τ_1) mode of 5-membered ring)

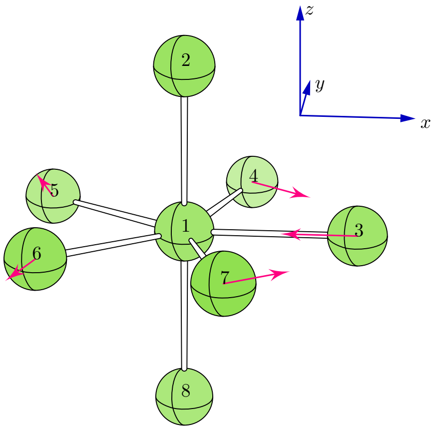


$$
\boldsymbol{l}(E_1') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \delta & 0 & 0 \\ \mathscr{C}_3\delta & \mathscr{S}_3\delta & 0 \\ \mathscr{C}_1\delta & \mathscr{S}_1\delta & 0 \\ \mathscr{C}_4\delta & \mathscr{S}_4\delta & 0 \\ \mathscr{C}_2\delta & \mathscr{S}_2\delta & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{40}
$$

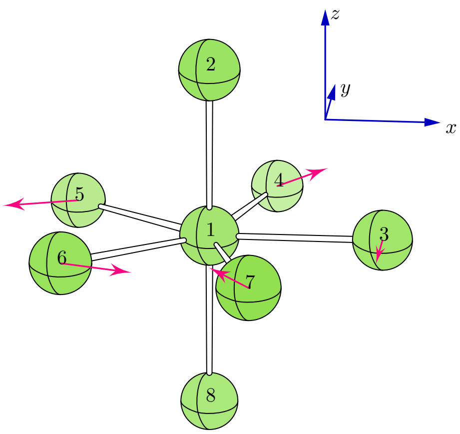


$$
\boldsymbol{l}(E_1'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \delta & 0 \\ \mathscr{S}_2\delta & \mathscr{C}_2\delta & 0 \\ \mathscr{S}_4\delta & \mathscr{C}_4\delta & 0 \\ \mathscr{S}_1\delta & \mathscr{C}_1\delta & 0 \\ \mathscr{S}_3\delta & \mathscr{C}_3\delta & 0 \\ 0 & 0 & 0 \end{pmatrix}
$$

7.2.4 (I) E_2' ((t_2, τ_2) mode of 5-membered ring)

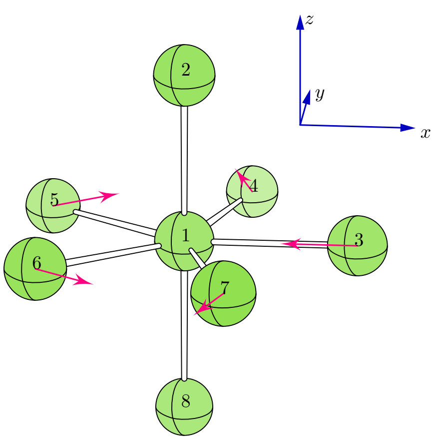


$$\boldsymbol{l}(E_2') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \delta & 0 & 0 \\ \mathscr{C}_2\delta & \mathscr{S}_2\delta & 0 \\ \mathscr{C}_4\delta & \mathscr{S}_4\delta & 0 \\ \mathscr{C}_1\delta & \mathscr{S}_1\delta & 0 \\ \mathscr{C}_3\delta & \mathscr{S}_3\delta & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (41)$$

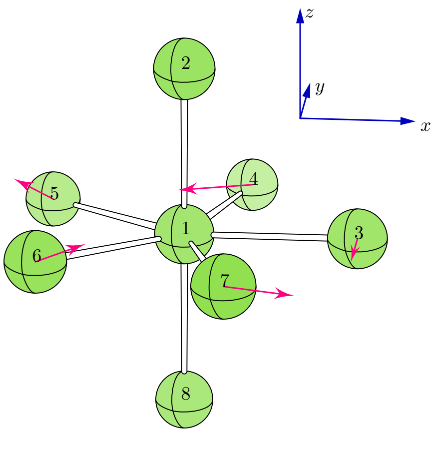


$$\boldsymbol{l}({E_2'}^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \delta & 0 \\ \mathscr{S}_3\delta & \mathscr{C}_3\delta & 0 \\ \mathscr{S}_1\delta & \mathscr{C}_1\delta & 0 \\ \mathscr{S}_4\delta & \mathscr{C}_4\delta & 0 \\ \mathscr{S}_2\delta & \mathscr{C}_2\delta & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

7.2.5 (II) E_2' ((t_3, τ_3) mode of 5-membered ring)

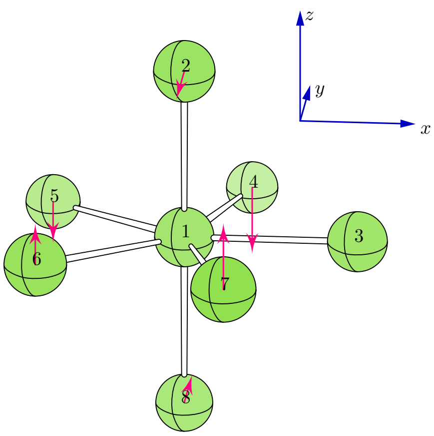


$$\boldsymbol{l}(E_2') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \delta & 0 & 0 \\ \mathscr{C}_4\delta & \mathscr{S}_4\delta & 0 \\ \mathscr{C}_3\delta & \mathscr{S}_3\delta & 0 \\ \mathscr{C}_2\delta & \mathscr{S}_2\delta & 0 \\ \mathscr{C}_1\delta & \mathscr{S}_1\delta & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (42)$$

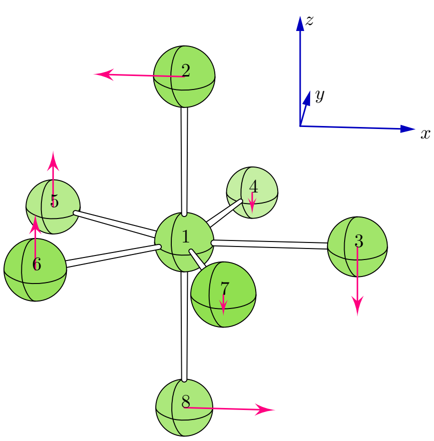


$$\boldsymbol{l}(E_2'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \delta & 0 \\ \mathscr{S}_1\delta & \mathscr{C}_1\delta & 0 \\ \mathscr{S}_2\delta & \mathscr{C}_2\delta & 0 \\ \mathscr{S}_3\delta & \mathscr{C}_3\delta & 0 \\ \mathscr{S}_4\delta & \mathscr{C}_4\delta & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

7.2.6 E_1'' (relative rotation between 2×Y and the 5×Y plane around x- and y- axes)

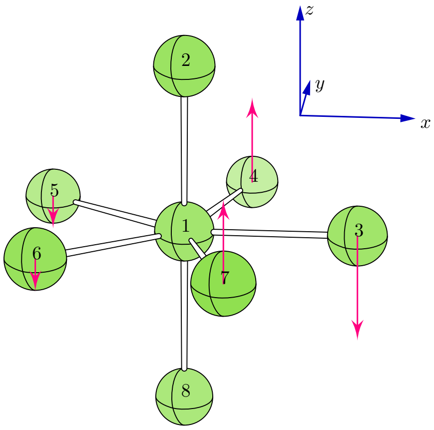


$$\boldsymbol{l}(E_1'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mathscr{S}_1\epsilon \\ 0 & 0 & \mathscr{S}_2\epsilon \\ 0 & 0 & \mathscr{S}_3\epsilon \\ 0 & 0 & \mathscr{S}_4\epsilon \\ 0 & -\eta & 0 \end{pmatrix} \tag{43}$$

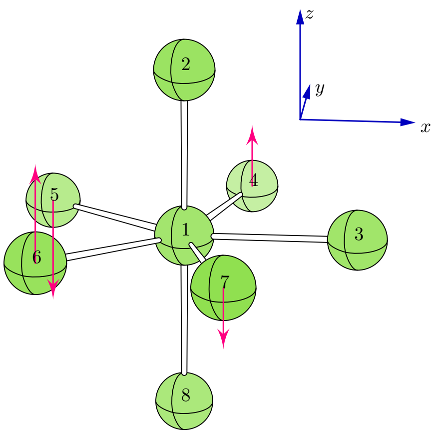


$$\boldsymbol{l}(E_1''^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ \eta & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & 0 & \mathscr{C}_1\epsilon \\ 0 & 0 & \mathscr{C}_2\epsilon \\ 0 & 0 & \mathscr{C}_3\epsilon \\ 0 & 0 & \mathscr{C}_4\epsilon \\ -\eta & 0 & 0 \end{pmatrix}$$

7.2.7 E_2'' ((q_2, ϕ_2) mode of 5-membered ring)

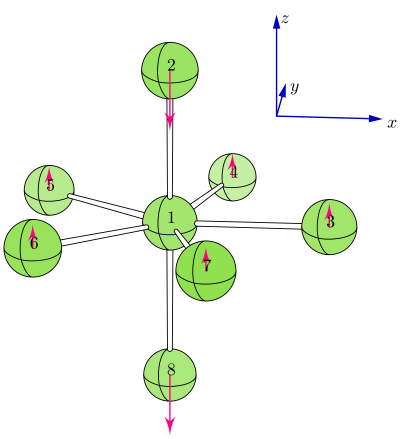


$$\boldsymbol{l}(E_2'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \theta \\ 0 & 0 & \mathscr{C}_3\theta \\ 0 & 0 & \mathscr{C}_1\theta \\ 0 & 0 & \mathscr{C}_4\theta \\ 0 & 0 & \mathscr{C}_2\theta \\ 0 & 0 & 0 \end{pmatrix} \tag{44}$$



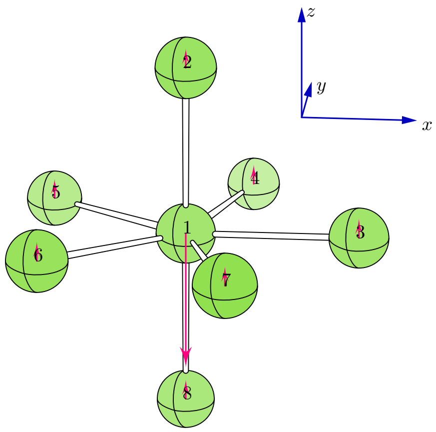
$$\boldsymbol{l}({E_2''}^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mathscr{S}_3\theta \\ 0 & 0 & \mathscr{S}_1\theta \\ 0 & 0 & \mathscr{S}_4\theta \\ 0 & 0 & \mathscr{S}_2\theta \\ 0 & 0 & 0 \end{pmatrix}$$

7.2.8 (II) E_1' + (I) A_2'' (pseudo-triplet-degenerate intra-molecular translations between atoms **2**$\times Y$ and **5**$\times Y$)



$$\boldsymbol{l}(E_1') = \begin{pmatrix} 0 & 0 & 0 \\ \gamma & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ \gamma & 0 & 0 \end{pmatrix}, \boldsymbol{l}({E_1'}^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & \gamma & 0 \end{pmatrix}, \boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & \gamma \end{pmatrix} \tag{45}$$

7.2.9 (III) E_1' + (II) A_2'' (pseudo-triplet-degenerate intra-molecular translations between atoms X and $\mathbf{7}\times Y$)



$$
\boldsymbol{l}(E_1') = \begin{pmatrix} \iota & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \end{pmatrix}, \boldsymbol{l}({E_1'}^{\dagger}) = \begin{pmatrix} 0 & \iota & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \end{pmatrix}, \boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & \iota \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \end{pmatrix} \tag{46}
$$

7.3 Curvilinear parameters of D_{5h} reference and their components

XY_7: D_{5h} reference

```
R1                                           % (I)A1'
R2                                           % (II)A1'
R3    theta3                                 % (I)E1'
R4    theta4                                 % (I)E2'
R5    theta5                                 % (II)E2'
R6    theta6                                 % E1"
R7    theta7                                 % E2"
R8    theta8    phi8                         % (II)E1' + (I)A2"
R9    theta9    phi9                         % (III)E1' + (II)A2"
```

8 XY_7 reference system in C_{6v} symmetry

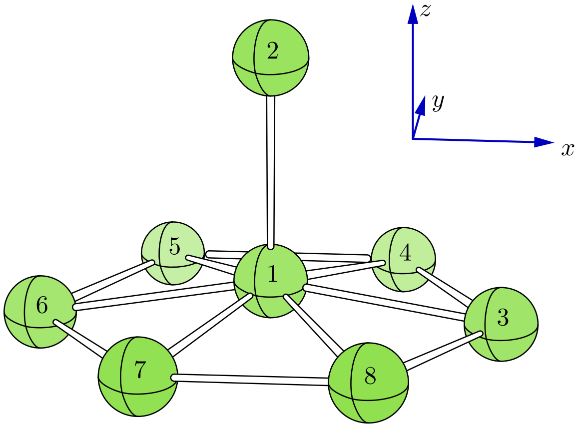
Symbols and constants used in this section:

r_1 radius of the reference sphere.

$\mathscr{C}_n$ $= cos(\frac{2n\pi}{6})$, $\mathscr{S}_n = sin(\frac{2n\pi}{6})$.

α $= 1/6$, $\beta = \sqrt{35/36}$, $\gamma = \sqrt{1/7}$, $\delta = \sqrt{1/252}$, $\epsilon = \sqrt{5/36}$, $\zeta = \sqrt{5/7}$, $\eta = \sqrt{5/252}$, $\lambda = \sqrt{1/6}$, $\theta = \sqrt{30/49}$, $\iota = \sqrt{5/294}$, $\kappa = \sqrt{2/21}$, $\mu = \sqrt{1/3}$, $\nu = \sqrt{7/8}$, $\xi = \sqrt{1/56}$.

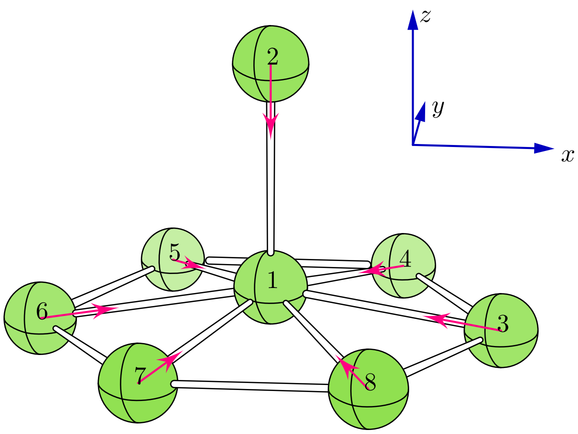
8.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \\ Y7 \\ Y8 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & r_1 \\ \beta r_1 & 0 & -\alpha r_1 \\ \mathscr{C}_1 \beta r_1 & \mathscr{S}_1 \beta r_1 & -\alpha r_1 \\ \mathscr{C}_2 \beta r_1 & \mathscr{S}_2 \beta r_1 & -\alpha r_1 \\ \mathscr{C}_3 \beta r_1 & \mathscr{S}_3 \beta r_1 & -\alpha r_1 \\ \mathscr{C}_4 \beta r_1 & \mathscr{S}_4 \beta r_1 & -\alpha r_1 \\ \mathscr{C}_5 \beta r_1 & \mathscr{S}_5 \beta r_1 & -\alpha r_1 \end{pmatrix} \tag{47}$$

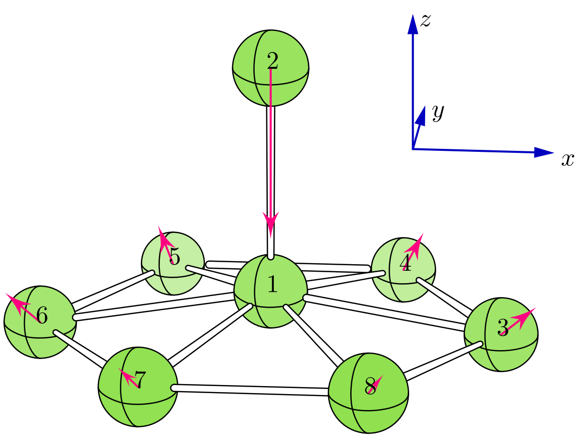
8.2 Reconstructed normal modes

8.2.1 (I) A_1 (breathing mode)



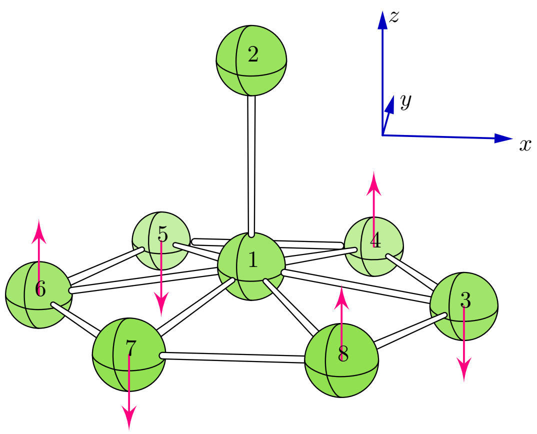
$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma \\ \epsilon & 0 & -\delta \\ \mathscr{C}_1 \epsilon & \mathscr{S}_1 \epsilon & -\delta \\ \mathscr{C}_2 \epsilon & \mathscr{S}_2 \epsilon & -\delta \\ \mathscr{C}_3 \epsilon & \mathscr{S}_3 \epsilon & -\delta \\ \mathscr{C}_4 \epsilon & \mathscr{S}_4 \epsilon & -\delta \\ \mathscr{C}_5 \epsilon & \mathscr{S}_5 \epsilon & -\delta \end{pmatrix} \tag{48}$$

8.2.2 (II) A_1 (anti-breathing mode)



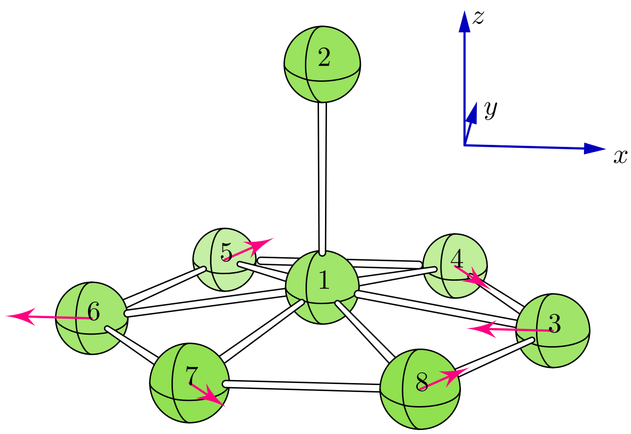
$$\boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \zeta \\ -\alpha & 0 & -\eta \\ -\mathscr{C}_1 \alpha & -\mathscr{S}_1 \alpha & -\eta \\ -\mathscr{C}_2 \alpha & -\mathscr{S}_2 \alpha & -\eta \\ -\mathscr{C}_3 \alpha & -\mathscr{S}_3 \alpha & -\eta \\ -\mathscr{C}_4 \alpha & -\mathscr{S}_4 \alpha & -\eta \\ -\mathscr{C}_5 \alpha & -\mathscr{S}_5 \alpha & -\eta \end{pmatrix} \tag{49}$$

8.2.3 (I) B_2 (q_3 mode of 6-membered ring)

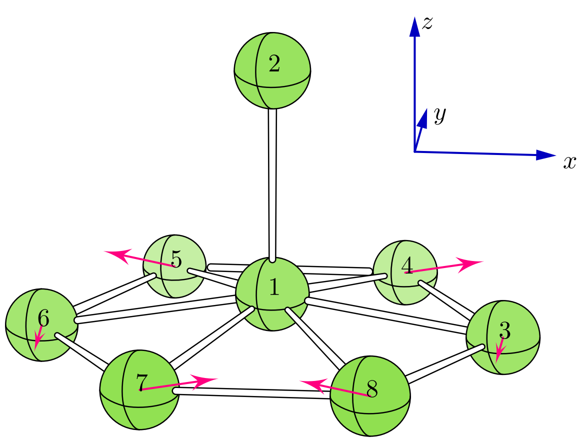


$$
\boldsymbol{l}(B_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \lambda \\ 0 & 0 & -\lambda \\ 0 & 0 & \lambda \\ 0 & 0 & -\lambda \\ 0 & 0 & \lambda \\ 0 & 0 & -\lambda \end{pmatrix} \tag{50}
$$

8.2.4 (I) E_1 ((t_1,τ_1) mode of 6-membered ring)

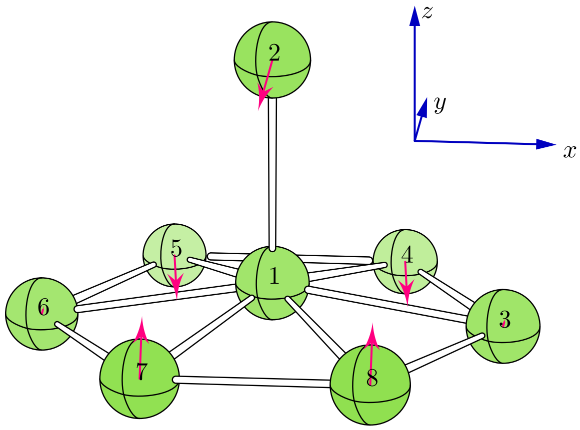


$$
\boldsymbol{l}(E_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \lambda & 0 & 0 \\ \mathscr{C}_2\lambda & \mathscr{S}_2\lambda & 0 \\ \mathscr{C}_4\lambda & \mathscr{S}_4\lambda & 0 \\ \lambda & 0 & 0 \\ \mathscr{C}_2\lambda & \mathscr{S}_2\lambda & 0 \\ \mathscr{C}_4\lambda & \mathscr{S}_4\lambda & 0 \end{pmatrix} \tag{51}
$$

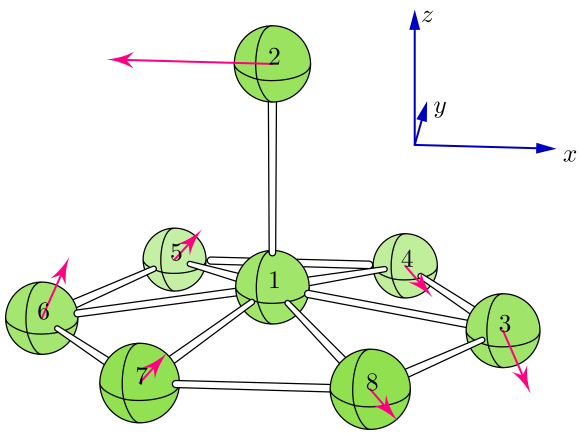


$$
\boldsymbol{l}(E_1^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \lambda & 0 \\ \mathscr{S}_4\lambda & \mathscr{C}_4\lambda & 0 \\ \mathscr{S}_2\lambda & \mathscr{C}_2\lambda & 0 \\ 0 & \lambda & 0 \\ \mathscr{S}_4\lambda & \mathscr{C}_4\lambda & 0 \\ \mathscr{S}_2\lambda & \mathscr{C}_2\lambda & 0 \end{pmatrix}
$$

8.2.5 (II) E_1 (relative rotation between $Y2$ and the $6{\times}Y$ plane around x- and y- axes)

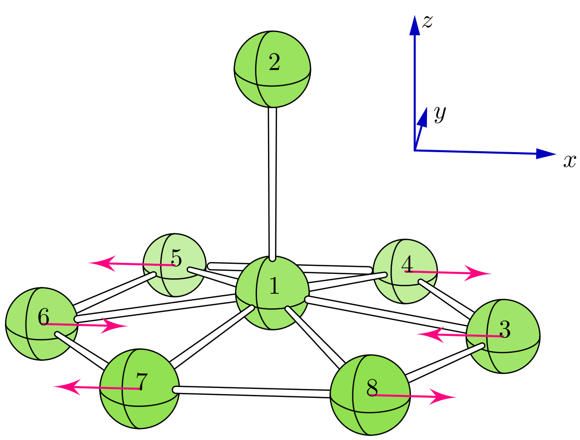


$$\boldsymbol{l}(E_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \theta & 0 \\ 0 & -\iota & 0 \\ 0 & -\iota & \mathscr{S}_1\kappa \\ 0 & -\iota & \mathscr{S}_2\kappa \\ 0 & -\iota & \mathscr{S}_3\kappa \\ 0 & -\iota & \mathscr{S}_4\kappa \\ 0 & -\iota & \mathscr{S}_5\kappa \end{pmatrix} \tag{52}$$

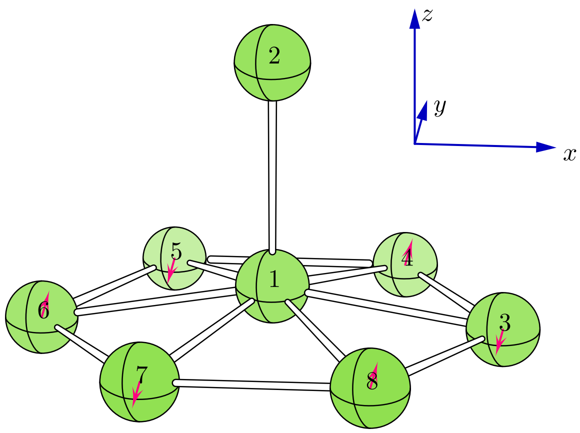


$$\boldsymbol{l}(E_1^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ \theta & 0 & 0 \\ -\iota & 0 & \kappa \\ -\iota & 0 & \mathscr{C}_1\kappa \\ -\iota & 0 & \mathscr{C}_2\kappa \\ -\iota & 0 & \mathscr{C}_3\kappa \\ -\iota & 0 & \mathscr{C}_4\kappa \\ -\iota & 0 & \mathscr{C}_5\kappa \end{pmatrix}$$

8.2.6 (I) E_2 ((t_2,τ_2) mode of 6-membered ring)

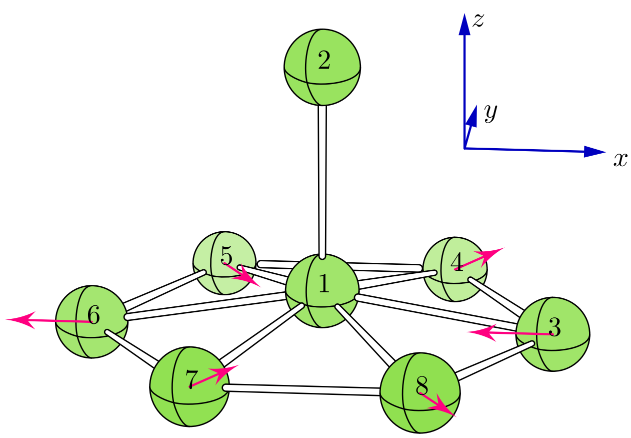


$$\boldsymbol{l}(E_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \lambda & 0 & 0 \\ -\lambda & 0 & 0 \\ \lambda & 0 & 0 \\ -\lambda & 0 & 0 \\ \lambda & 0 & 0 \\ -\lambda & 0 & 0 \end{pmatrix} \tag{53}$$

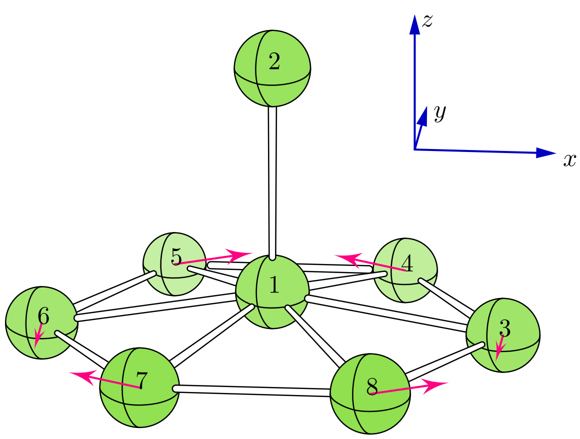


$$\boldsymbol{l}(E_2^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & -\lambda & 0 \\ 0 & \lambda & 0 \\ 0 & -\lambda & 0 \\ 0 & \lambda & 0 \\ 0 & -\lambda & 0 \end{pmatrix}$$

8.2.7 (II) $B_2 + B_1$ ((t_3,τ_3) mode of 6-membered ring)

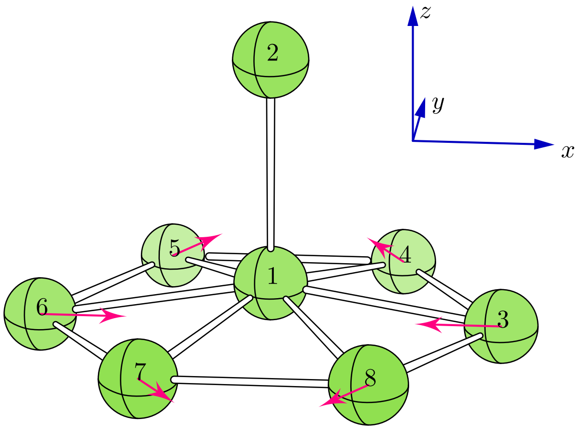


$$\boldsymbol{l}(B_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \lambda & 0 & 0 \\ \mathscr{C}_4\lambda & \mathscr{S}_4\lambda & 0 \\ \mathscr{C}_2\lambda & \mathscr{S}_2\lambda & 0 \\ \lambda & 0 & 0 \\ \mathscr{C}_4\lambda & \mathscr{S}_4\lambda & 0 \\ \mathscr{C}_2\lambda & \mathscr{S}_2\lambda & 0 \end{pmatrix} \tag{54}$$

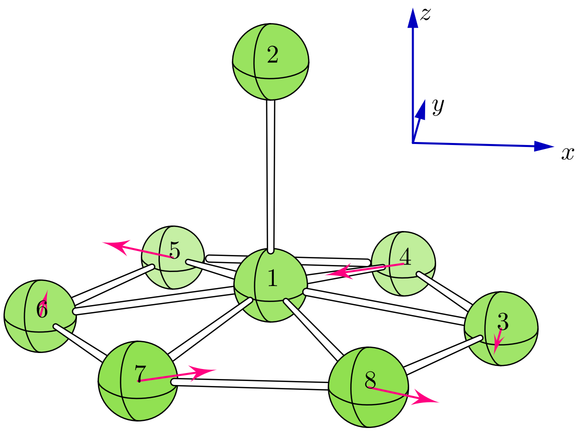


$$\boldsymbol{l}(B_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \lambda & 0 \\ \mathscr{S}_2\lambda & \mathscr{C}_2\lambda & 0 \\ \mathscr{S}_4\lambda & \mathscr{C}_4\lambda & 0 \\ 0 & \lambda & 0 \\ \mathscr{S}_2\lambda & \mathscr{C}_2\lambda & 0 \\ \mathscr{S}_4\lambda & \mathscr{C}_4\lambda & 0 \end{pmatrix}$$

8.2.8 (II) E_2 ((t_4,τ_4) mode of 6-membered ring)

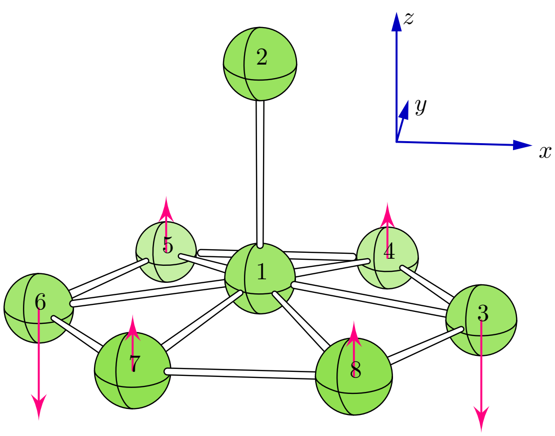


$$\boldsymbol{l}(E_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \lambda & 0 & 0 \\ \mathscr{C}_5\lambda & \mathscr{S}_5\lambda & 0 \\ \mathscr{C}_4\lambda & \mathscr{S}_4\lambda & 0 \\ \mathscr{C}_3\lambda & \mathscr{S}_3\lambda & 0 \\ \mathscr{C}_2\lambda & \mathscr{S}_2\lambda & 0 \\ \mathscr{C}_1\lambda & \mathscr{S}_1\lambda & 0 \end{pmatrix} \tag{55}$$

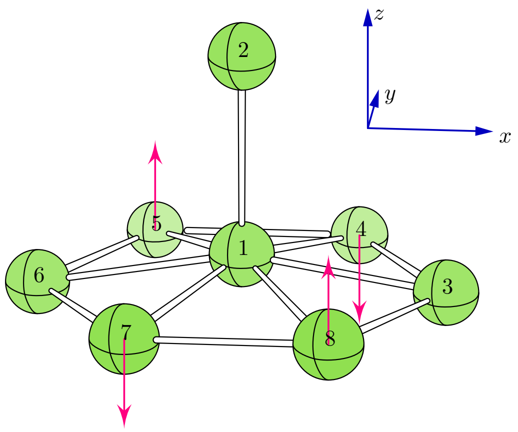


$$\boldsymbol{l}(E_2^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \lambda & 0 \\ \mathscr{S}_1\lambda & \mathscr{C}_1\lambda & 0 \\ \mathscr{S}_2\lambda & \mathscr{C}_2\lambda & 0 \\ \mathscr{S}_3\lambda & \mathscr{C}_3\lambda & 0 \\ \mathscr{S}_4\lambda & \mathscr{C}_4\lambda & 0 \\ \mathscr{S}_5\lambda & \mathscr{C}_5\lambda & 0 \end{pmatrix}$$

8.2.9 (III) E_2 ((q_2,ϕ_2) mode of 6-membered ring)

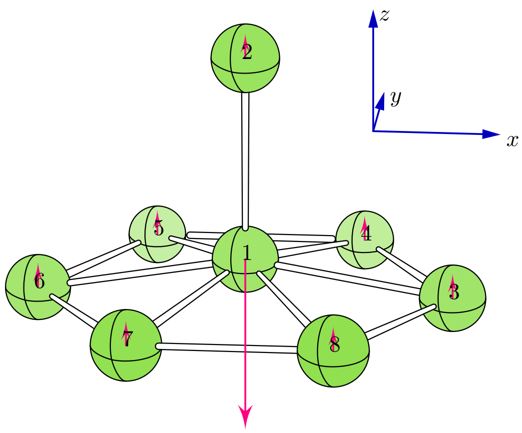


$$\boldsymbol{l}(E_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mu \\ 0 & 0 & \mathscr{C}_2\mu \\ 0 & 0 & \mathscr{C}_4\mu \\ 0 & 0 & \mu \\ 0 & 0 & \mathscr{C}_2\mu \\ 0 & 0 & \mathscr{C}_4\mu \end{pmatrix} \tag{56}$$



$$\boldsymbol{l}(E_2^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mathscr{S}_2\mu \\ 0 & 0 & \mathscr{S}_4\mu \\ 0 & 0 & 0 \\ 0 & 0 & \mathscr{S}_2\mu \\ 0 & 0 & \mathscr{S}_4\mu \end{pmatrix}$$

8.2.10 (III) E_1 + (III) A_1 (pseudo-triplet-degenerate intra-molecular translations between atoms X and $\mathbf{7}\times Y$)



$$\boldsymbol{l}(E_1) = \begin{pmatrix} \nu & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \\ -\xi & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E_1^\dagger) = \begin{pmatrix} 0 & \nu & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \\ 0 & -\xi & 0 \end{pmatrix}, \boldsymbol{l}(A_1) = \begin{pmatrix} 0 & 0 & \nu \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \\ 0 & 0 & -\xi \end{pmatrix} \quad (57)$$

8.3 Curvilinear parameters of C_{6v} reference and their components

XY_7: C_{6v} reference

```
R1                                   % (I)A1
R2                                   % (II)A1
R3                                   % (I)B2
R4   theta4                          % (I)E1
R5   theta5                          % (II)E1
R6   theta6                          % (I)E2
R7   theta7                          % (II)B2+B1
R8   theta8                          % (II)E2
R9   theta9                          % (III)E2
R10  theta10  phi10                  % (III)E1 + (III)A1
```

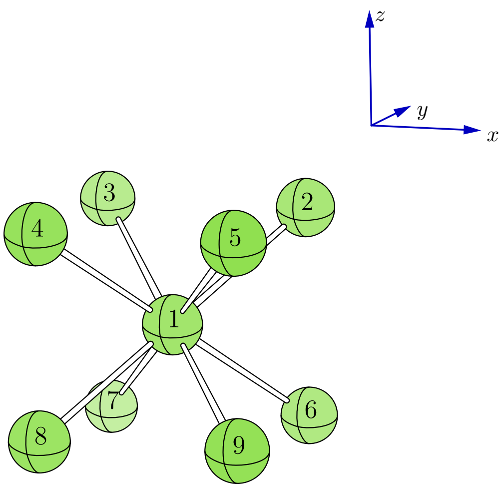
9 XY_8 reference system in O_h symmetry

Symbols and constants used in this section:

r_1: radius of the reference sphere.

$\alpha = \sqrt{6}/12$, $\beta = 1/4$, $\gamma = \sqrt{3}/12$, $\delta = \sqrt{2}/4$, $\epsilon = \sqrt{2}/12$.

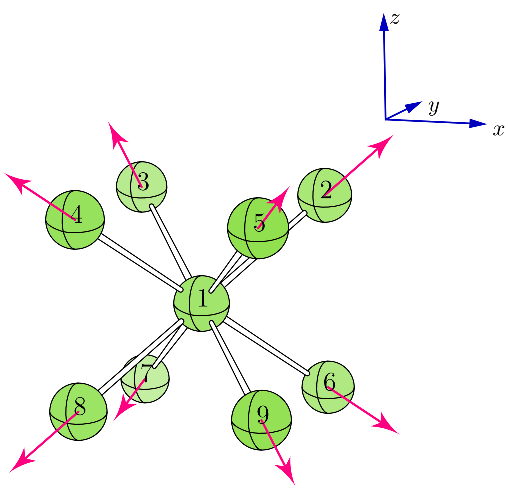
9.1 Cartesian coordinates



$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \\ Y7 \\ Y8 \\ Y9 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ r_1 & r_1 & r_1 \\ -r_1 & r_1 & r_1 \\ -r_1 & -r_1 & r_1 \\ r_1 & -r_1 & r_1 \\ r_1 & r_1 & -r_1 \\ -r_1 & r_1 & -r_1 \\ -r_1 & -r_1 & -r_1 \\ r_1 & -r_1 & -r_1 \end{pmatrix} \quad (58)$$

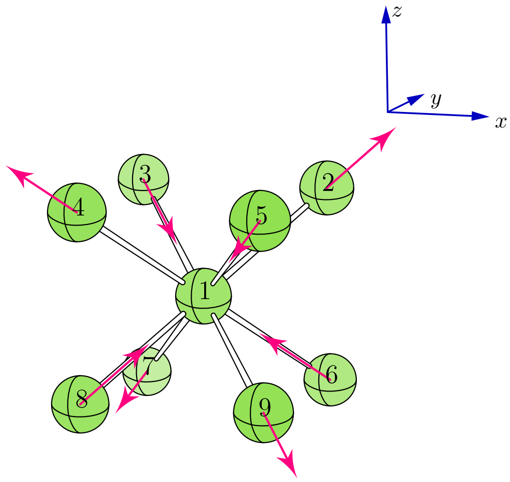
9.2 Reconstructed normal modes

9.2.1 A_{1g} (breathing)



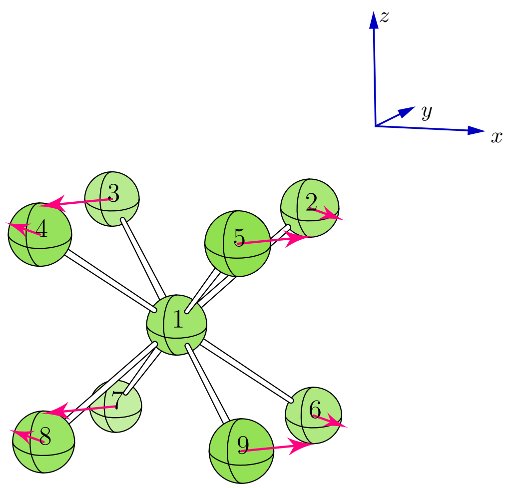
$$\boldsymbol{l}(A_{1g}) = \begin{pmatrix} 0 & 0 & 0 \\ \alpha & \alpha & \alpha \\ -\alpha & \alpha & \alpha \\ -\alpha & -\alpha & \alpha \\ \alpha & -\alpha & \alpha \\ \alpha & \alpha & -\alpha \\ -\alpha & \alpha & -\alpha \\ -\alpha & -\alpha & -\alpha \\ \alpha & -\alpha & -\alpha \end{pmatrix} \quad (59)$$

9.2.2 A_{2u} (anti-breathing)

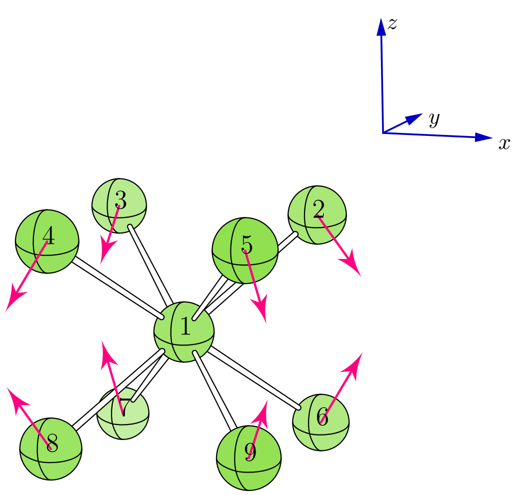


$$\boldsymbol{l}(A_{2u}) = \begin{pmatrix} 0 & 0 & 0 \\ \alpha & \alpha & \alpha \\ \alpha & -\alpha & -\alpha \\ -\alpha & -\alpha & \alpha \\ -\alpha & \alpha & -\alpha \\ -\alpha & -\alpha & \alpha \\ -\alpha & \alpha & -\alpha \\ \alpha & \alpha & \alpha \\ \alpha & -\alpha & -\alpha \end{pmatrix} \tag{60}$$

9.2.3 E_g (relative-translation between two 4-membered rings)

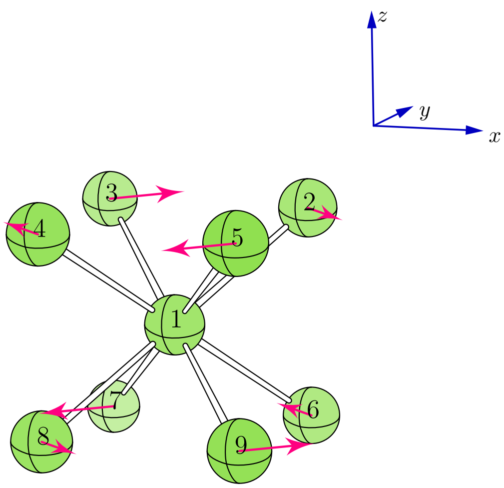


$$\boldsymbol{l}(E_g) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \\ -\beta & \beta & 0 \\ \beta & \beta & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \\ -\beta & \beta & 0 \\ \beta & \beta & 0 \end{pmatrix} \tag{61}$$

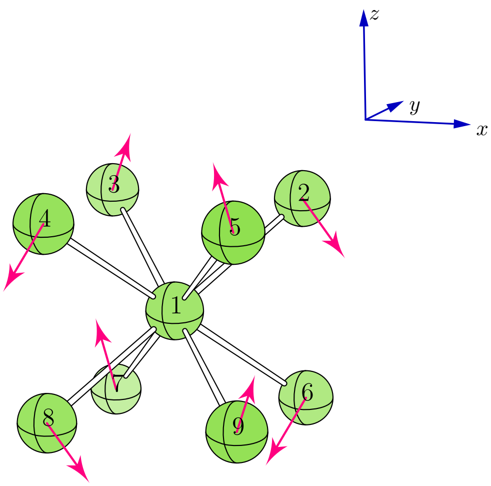


$$\boldsymbol{l}(E_g^\dagger) = \begin{pmatrix} 0 & 0 & 0 \\ -\gamma & -\gamma & 2\gamma \\ \gamma & -\gamma & 2\gamma \\ \gamma & \gamma & 2\gamma \\ -\gamma & \gamma & 2\gamma \\ -\gamma & -\gamma & -2\gamma \\ \gamma & -\gamma & -2\gamma \\ \gamma & \gamma & -2\gamma \\ -\gamma & \gamma & -2\gamma \end{pmatrix}$$

9.2.4 E_u (relative-rotation between two 4-membered rings)

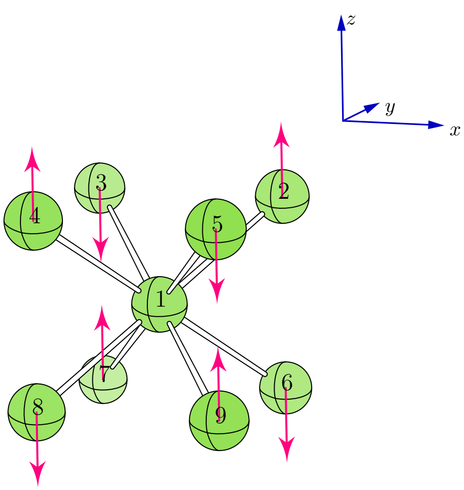


$$\boldsymbol{l}(E_u) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & -\beta & 0 \\ \beta & \beta & 0 \\ -\beta & \beta & 0 \\ -\beta & -\beta & 0 \\ -\beta & \beta & 0 \\ -\beta & -\beta & 0 \\ \beta & -\beta & 0 \\ \beta & \beta & 0 \end{pmatrix} \tag{62}$$



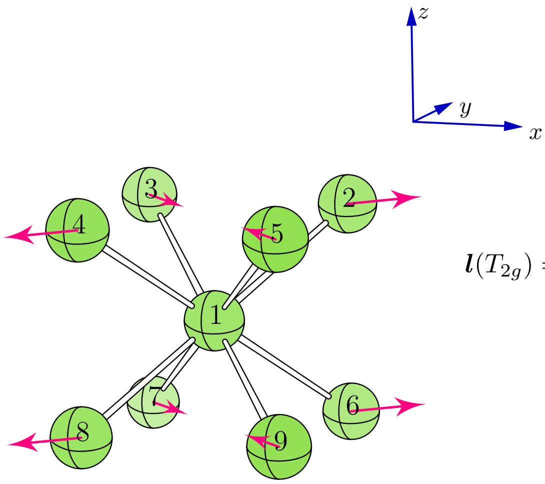
$$\boldsymbol{l}(E_u^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ -\gamma & -\gamma & 2\gamma \\ -\gamma & \gamma & -2\gamma \\ \gamma & \gamma & 2\gamma \\ \gamma & -\gamma & -2\gamma \\ \gamma & \gamma & 2\gamma \\ \gamma & -\gamma & -2\gamma \\ -\gamma & -\gamma & 2\gamma \\ -\gamma & \gamma & -2\gamma \end{pmatrix}$$

9.2.5 (I)T_{2g} (symmetric puckering of two 4-membered rings)



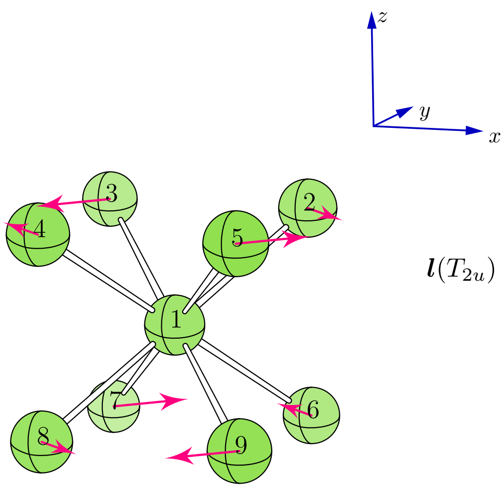
$$\boldsymbol{l}(T_{2g}) = \begin{pmatrix} 0 & 0 & 0 \\ \delta & 0 & 0 \\ -\delta & 0 & 0 \\ \delta & 0 & 0 \\ -\delta & 0 & 0 \\ -\delta & 0 & 0 \\ \delta & 0 & 0 \\ -\delta & 0 & 0 \\ \delta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{2g}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \delta & 0 \\ 0 & -\delta & 0 \\ 0 & \delta & 0 \\ 0 & -\delta & 0 \\ 0 & -\delta & 0 \\ 0 & \delta & 0 \\ 0 & -\delta & 0 \\ 0 & \delta & 0 \end{pmatrix}, \boldsymbol{l}(T_{2g}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \delta \\ 0 & 0 & -\delta \\ 0 & 0 & \delta \\ 0 & 0 & -\delta \\ 0 & 0 & -\delta \\ 0 & 0 & \delta \\ 0 & 0 & -\delta \\ 0 & 0 & \delta \end{pmatrix} \tag{63}$$

9.2.6 (II)T_{2g} (symmetric rhombus modes of two 4-membered rings)



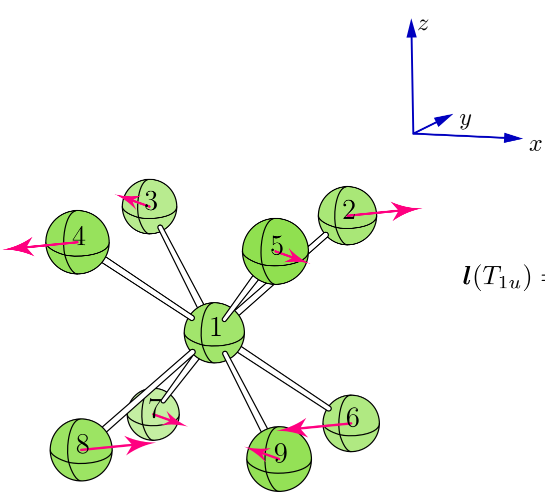
$$\boldsymbol{l}(T_{2g}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & \beta & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \\ -\beta & \beta & 0 \\ \beta & \beta & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \\ -\beta & \beta & 0 \end{pmatrix}, \boldsymbol{l}(T_{2g}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & \beta \\ \beta & 0 & -\beta \\ \beta & 0 & -\beta \\ \beta & 0 & \beta \\ -\beta & 0 & \beta \\ -\beta & 0 & -\beta \\ -\beta & 0 & -\beta \\ -\beta & 0 & \beta \end{pmatrix}, \boldsymbol{l}(T_{2g}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \beta & \beta \\ 0 & \beta & \beta \\ 0 & \beta & -\beta \\ 0 & \beta & -\beta \\ 0 & -\beta & \beta \\ 0 & -\beta & \beta \\ 0 & -\beta & -\beta \\ 0 & -\beta & -\beta \end{pmatrix} \quad (64)$$

9.2.7 T_{2u} (antisymmetric stretching of two 4-membered rings)



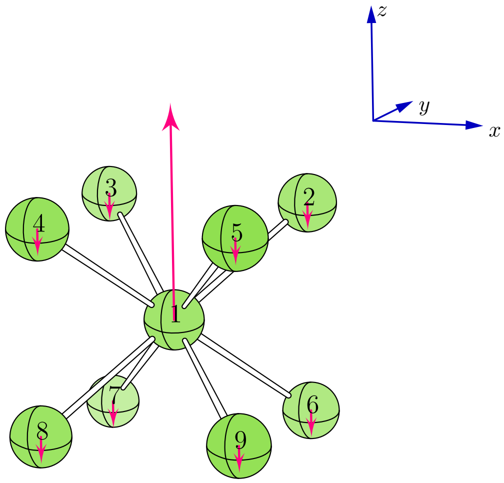
$$\boldsymbol{l}(T_{2u}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \\ -\beta & \beta & 0 \\ \beta & \beta & 0 \\ -\beta & \beta & 0 \\ \beta & \beta & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \end{pmatrix}, \boldsymbol{l}(T_{2u}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & -\beta \\ -\beta & 0 & -\beta \\ \beta & 0 & \beta \\ -\beta & 0 & \beta \\ \beta & 0 & \beta \\ -\beta & 0 & \beta \\ \beta & 0 & -\beta \\ -\beta & 0 & -\beta \end{pmatrix}, \boldsymbol{l}(T_{2u}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \beta & -\beta \\ 0 & -\beta & \beta \\ 0 & \beta & \beta \\ 0 & -\beta & -\beta \\ 0 & \beta & \beta \\ 0 & -\beta & -\beta \\ 0 & \beta & -\beta \\ 0 & -\beta & \beta \end{pmatrix} \quad (65)$$

9.2.8 (I)T_{1u} (antisymmetric breathing of two 4-membered rings)



$$\boldsymbol{l}(T_{1u}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & \beta & 0 \\ -\beta & \beta & 0 \\ -\beta & -\beta & 0 \\ \beta & -\beta & 0 \\ -\beta & -\beta & 0 \\ \beta & -\beta & 0 \\ \beta & \beta & 0 \\ -\beta & \beta & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & \beta \\ -\beta & 0 & \beta \\ \beta & 0 & -\beta \\ -\beta & 0 & -\beta \\ \beta & 0 & -\beta \\ -\beta & 0 & -\beta \\ \beta & 0 & \beta \\ -\beta & 0 & \beta \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \beta & \beta \\ 0 & -\beta & -\beta \\ 0 & \beta & -\beta \\ 0 & -\beta & \beta \\ 0 & \beta & -\beta \\ 0 & -\beta & \beta \\ 0 & \beta & \beta \\ 0 & -\beta & -\beta \end{pmatrix} \quad (66)$$

9.2.9 (II)T_{1u} (intra-molecular translations between atoms X and 8 $\times Y$)



$$\boldsymbol{l}(T_{1u}) = \begin{pmatrix} 8\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \\ -\epsilon & 0 & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\dagger}) = \begin{pmatrix} 0 & 8\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \\ 0 & -\epsilon & 0 \end{pmatrix}, \boldsymbol{l}(T_{1u}^{\ddagger}) = \begin{pmatrix} 0 & 0 & 8\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \end{pmatrix} \tag{67}$$

9.3 Curvilinear parameters of O$_h$ reference and their components

XY_8: O_h reference

```
R1                                       % A1g
R2                                       % A2u
R3    theta3                             % Eg
R4    theta4                             % Eu
R5    theta5    phi5                     % (I)T2g
R6    theta6    phi6                     % (II)T2g
R7    theta7    phi7                     % T2u
R8    theta8    phi8                     % (I)T1u
R9    theta9    phi9                     % (II)T1u
```

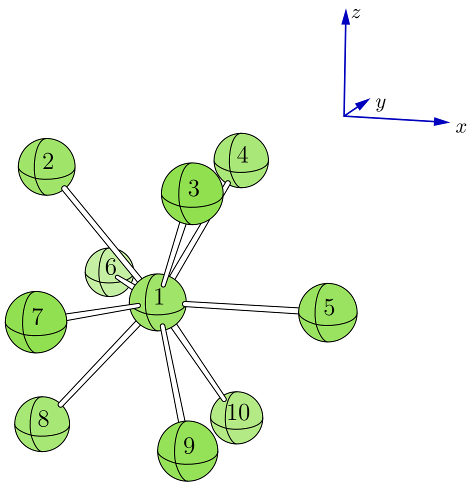
10 XY_9 reference system in D_{3h} symmetry

10.1 Cartesian coordinates

Symbols and constants used in this section:

r_1: radius of the reference sphere.

$\alpha = \sqrt{5/9}$, $\beta = \sqrt{1/3}$, $\gamma = \sqrt{3/4}$, $\delta = 1/3$, $\epsilon = 2/3$, $\eta = 1/2$.



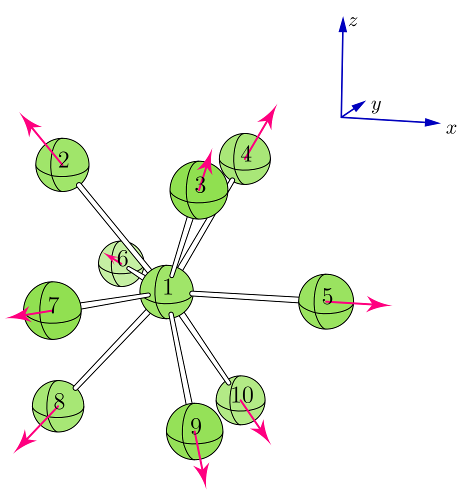
$$\begin{pmatrix} X1 \\ Y2 \\ Y3 \\ Y4 \\ Y5 \\ Y6 \\ Y7 \\ Y8 \\ Y9 \\ Y10 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ -\epsilon r_1 & 0 & \alpha r_1 \\ \delta r_1 & -\beta r_1 & \alpha r_1 \\ \delta r_1 & \beta r_1 & \alpha r_1 \\ r_1 & 0 & 0 \\ -\eta r_1 & \gamma r_1 & 0 \\ -\eta r_1 & -\gamma r_1 & 0 \\ -\epsilon r_1 & 0 & -\alpha r_1 \\ \delta r_1 & -\beta r_1 & -\alpha r_1 \\ \delta r_1 & \beta r_1 & -\alpha r_1 \end{pmatrix} \tag{68}$$

10.2 Reconstructed normal modes

10.2.1 (I)A_1' (breathing)

Symbols and constants used in this section:

$\alpha = \sqrt{5/81}$, $\beta = \sqrt{1/27}$, $\gamma = \sqrt{1/12}$, $\delta = 1/9$, $\epsilon = 2/9$, $\eta = 1/6$, $\theta = 1/3$.

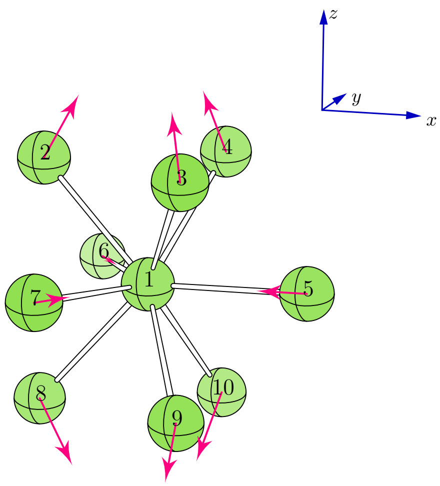


$$\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ -\epsilon & 0 & \alpha \\ \delta & -\beta & \alpha \\ \delta & \beta & \alpha \\ \theta & 0 & 0 \\ -\eta & \gamma & 0 \\ -\eta & -\gamma & 0 \\ -\epsilon & 0 & -\alpha \\ \delta & -\beta & -\alpha \\ \delta & \beta & -\alpha \end{pmatrix} \tag{69}$$

10.2.2 (II)A_1' (anti-symmetric breathing)

Symbols and constants used in this section:

$\alpha = \sqrt{40/1377}$, $\beta = \sqrt{17/162}$, $\gamma = \sqrt{10/153}$, $\delta = \sqrt{10/1377}$, $\epsilon = \sqrt{10/459}$, $\eta = \sqrt{5/306}$, $\theta = \sqrt{5/102}$.

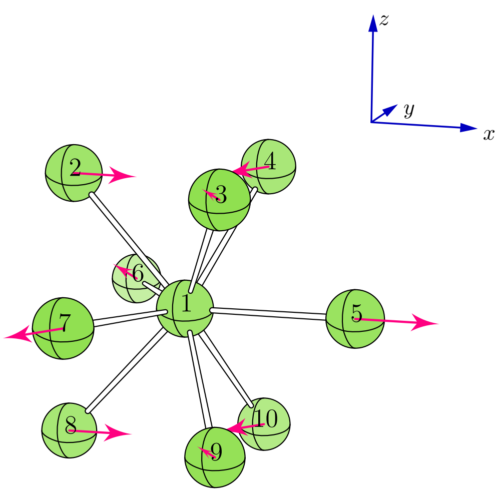


$$\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ \alpha & 0 & \beta \\ -\delta & \epsilon & \beta \\ -\delta & -\epsilon & \beta \\ -\gamma & 0 & 0 \\ \eta & -\theta & 0 \\ \eta & \theta & 0 \\ \alpha & 0 & -\beta \\ -\delta & \epsilon & -\beta \\ -\delta & -\epsilon & -\beta \end{pmatrix} \tag{70}$$

10.2.3 (III)A_1' (anti-symmetric combination of three planar breathing modes)

Symbols and constants used in this section:

$\alpha = \sqrt{8/51}$, $\beta = \sqrt{3/34}$, $\gamma = \sqrt{2/51}$, $\delta = \sqrt{2/17}$, $\epsilon = \sqrt{3/136}$, $\eta = \sqrt{9/136}$.

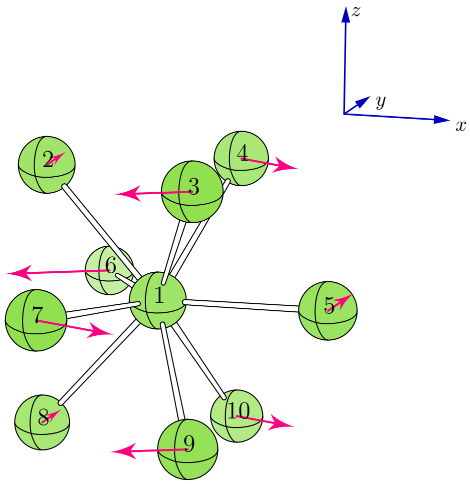


$$\boldsymbol{l}(A_1') = \begin{pmatrix} 0 & 0 & 0 \\ \beta & 0 & 0 \\ -\epsilon & \eta & 0 \\ -\epsilon & -\eta & 0 \\ \alpha & 0 & 0 \\ -\gamma & \delta & 0 \\ -\gamma & -\delta & 0 \\ \beta & 0 & 0 \\ -\epsilon & \eta & 0 \\ -\epsilon & -\eta & 0 \end{pmatrix} \tag{71}$$

10.2.4 A_2' (anti-symmetric combination of three planar rotation modes)

Symbols and constants used in this section:

$\alpha = \sqrt{8/51}$, $\beta = \sqrt{3/34}$, $\gamma = \sqrt{2/51}$, $\delta = \sqrt{2/17}$, $\epsilon = \sqrt{3/136}$, $\eta = \sqrt{9/136}$.

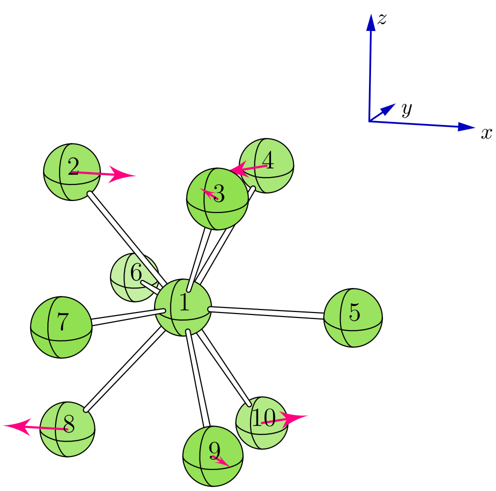


$$\boldsymbol{l}(A_2') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \beta & 0 \\ -\eta & -\epsilon & 0 \\ \eta & -\epsilon & 0 \\ 0 & \alpha & 0 \\ -\delta & -\gamma & 0 \\ \delta & -\gamma & 0 \\ 0 & \beta & 0 \\ -\eta & -\epsilon & 0 \\ \eta & -\epsilon & 0 \end{pmatrix} \tag{72}$$

10.2.5 (I)A_2'' (anti-symmetric combination of two planar breathing modes)

Symbols and constants used in this section:

$\alpha = \sqrt{1/6}$, $\beta = \sqrt{1/24}$, $\gamma = \sqrt{1/8}$.

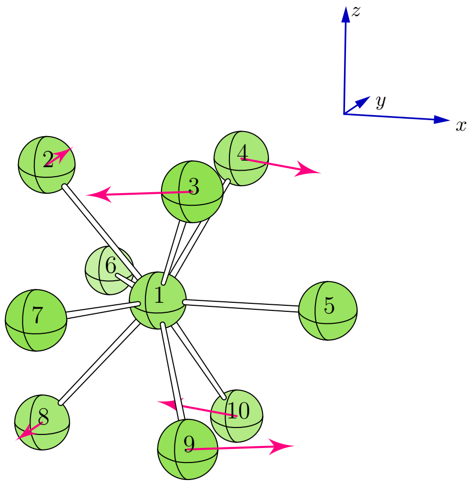


$$\boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & 0 \\ \alpha & 0 & 0 \\ -\beta & \gamma & 0 \\ -\beta & -\gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ -\alpha & 0 & 0 \\ \beta & -\gamma & 0 \\ \beta & \gamma & 0 \end{pmatrix} \tag{73}$$

10.2.6 A_1'' (anti-symmetric combination of two planar rotation modes)

Symbols and constants used in this section:

$\alpha = \sqrt{1/6}$, $\beta = \sqrt{1/24}$, $\gamma = \sqrt{1/8}$.

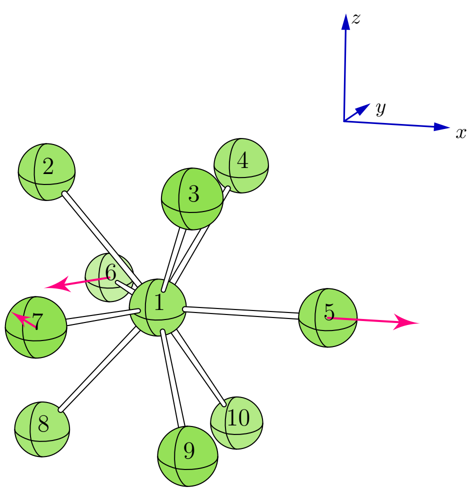


$$\boldsymbol{l}(A_1'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \alpha & 0 \\ -\gamma & -\beta & 0 \\ \gamma & -\beta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & -\alpha & 0 \\ \gamma & \beta & 0 \\ -\gamma & \beta & 0 \end{pmatrix} \tag{74}$$

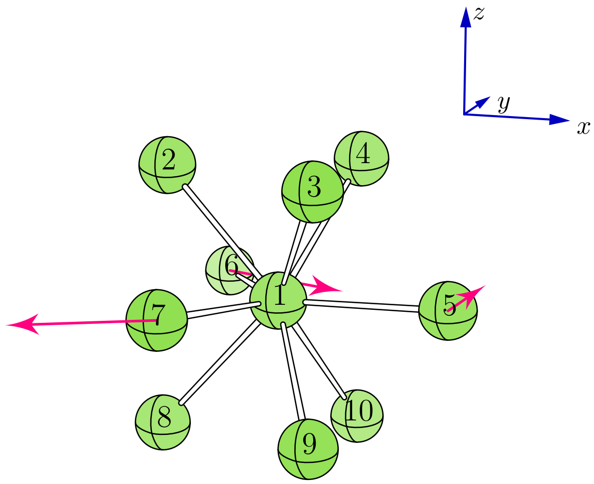
10.2.7 (I)E' (planar deformation of the middle 3-membered ring)

Symbols and constants used in this section:

$\alpha = \sqrt{1/3}$, $\beta = \sqrt{1/12}$, $\gamma = 1/2$.



$$\boldsymbol{l}(E') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \alpha & 0 & 0 \\ -\beta & -\gamma & 0 \\ -\beta & \gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{75}$$

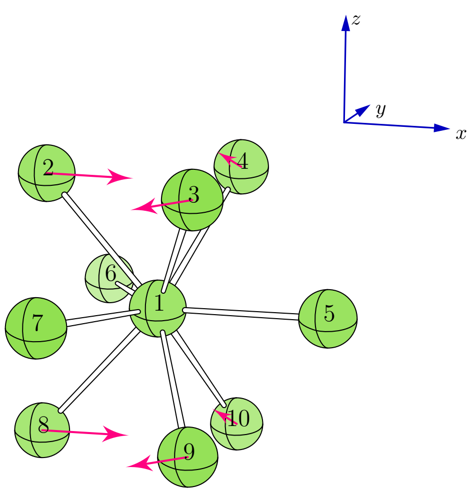


$$\boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \alpha & 0 \\ \gamma & -\beta & 0 \\ -\gamma & -\beta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{76}$$

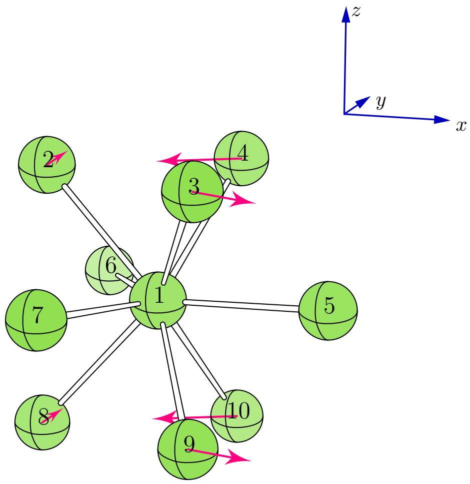
10.2.8 (II)E' (symmetric combination of two planar deformation modes in the top and bottom 3-membered rings)

Symbols and constants used in this section:

$\alpha = \sqrt{1/6}$, $\beta = \sqrt{1/24}$, $\gamma = \sqrt{1/8}$.



$$\boldsymbol{l}(E') = \begin{pmatrix} 0 & 0 & 0 \\ \alpha & 0 & 0 \\ -\beta & -\gamma & 0 \\ -\beta & \gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \alpha & 0 & 0 \\ -\beta & -\gamma & 0 \\ -\beta & \gamma & 0 \end{pmatrix} \tag{77}$$

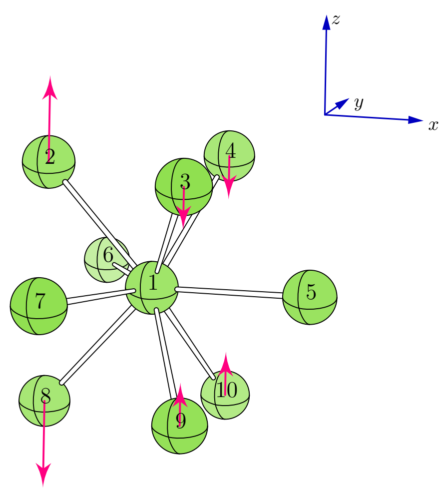


$$\boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \alpha & 0 \\ \gamma & -\beta & 0 \\ -\gamma & -\beta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \alpha & 0 \\ \gamma & -\beta & 0 \\ -\gamma & -\beta & 0 \end{pmatrix} \tag{78}$$

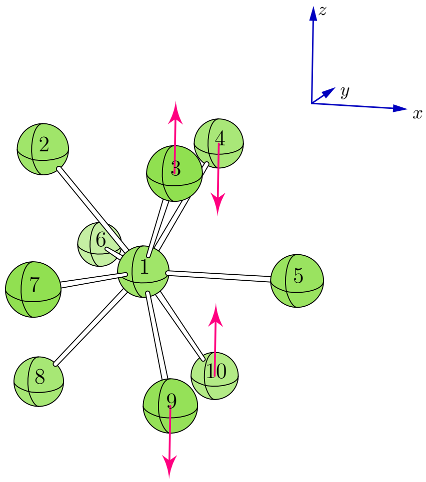
10.2.9 (III)E' (combination of puckering deformation modes in the top and bottom 3-membered rings)

Symbols and constants used in this section:

$\alpha = \sqrt{1/3}$, $\beta = \sqrt{1/12}$, $\gamma = 1/2$.



$$\boldsymbol{l}(E') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\alpha \\ 0 & 0 & \beta \\ 0 & 0 & \beta \end{pmatrix} \tag{79}$$

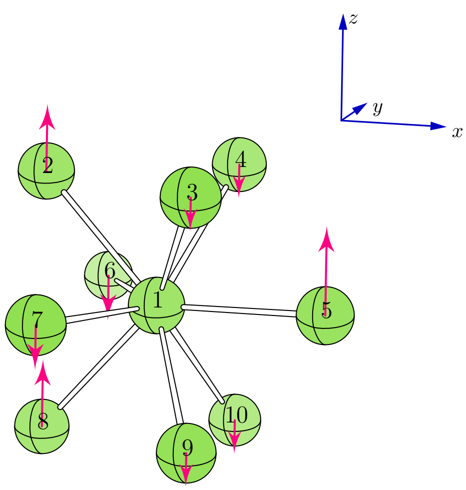


$$\boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \gamma \\ 0 & 0 & -\gamma \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\gamma \\ 0 & 0 & \gamma \end{pmatrix} \tag{80}$$

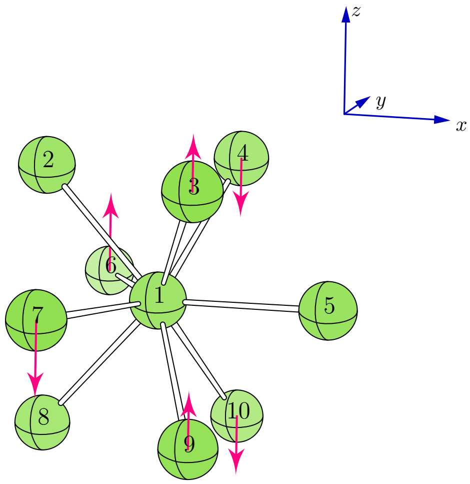
10.2.10 (I)E'' (combination of puckering deformation modes in the three 3-membered rings)

Symbols and constants used in this section:

$\alpha = \sqrt{16/51}$, $\beta = \sqrt{3/17}$, $\gamma = \sqrt{4/51}$, $\delta = \sqrt{4/17}$, $\epsilon = \sqrt{3/68}$, $\eta = \sqrt{9/68}$.



$$\boldsymbol{l}(E'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \beta \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \\ 0 & 0 & \alpha \\ 0 & 0 & -\gamma \\ 0 & 0 & -\gamma \\ 0 & 0 & \beta \\ 0 & 0 & -\epsilon \\ 0 & 0 & -\epsilon \end{pmatrix} \tag{81}$$

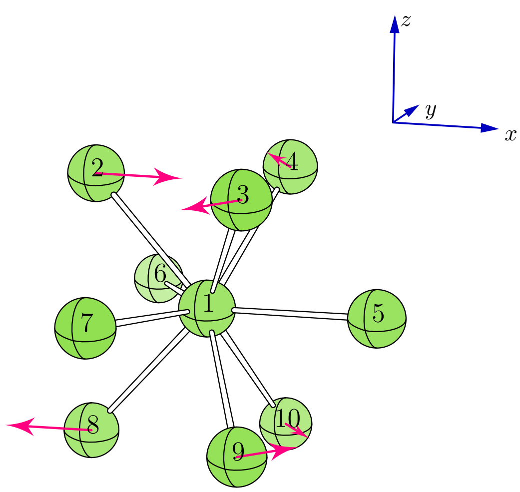


$$\boldsymbol{l}(E''^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \eta \\ 0 & 0 & -\eta \\ 0 & 0 & 0 \\ 0 & 0 & \delta \\ 0 & 0 & -\delta \\ 0 & 0 & 0 \\ 0 & 0 & \eta \\ 0 & 0 & -\eta \end{pmatrix} \quad (82)$$

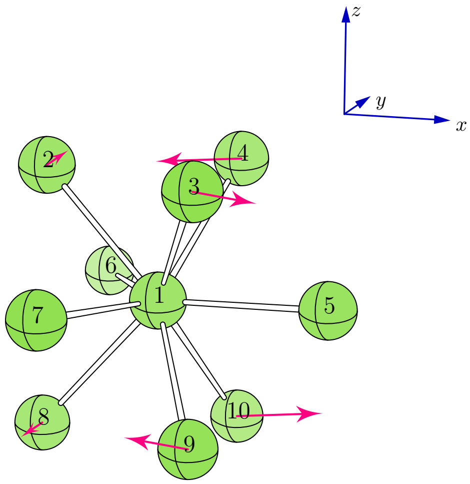
10.2.11 (II)E'' (anti-symmetric combination of two planar deformation modes in the top and bottom 3-membered rings)

Symbols and constants used in this section:

$\alpha = \sqrt{1/6}$, $\beta = \sqrt{1/24}$, $\gamma = \sqrt{1/8}$.



$$\boldsymbol{l}(E'') = \begin{pmatrix} 0 & 0 & 0 \\ \alpha & 0 & 0 \\ -\beta & -\gamma & 0 \\ -\beta & \gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ -\alpha & 0 & 0 \\ \beta & \gamma & 0 \\ \beta & -\gamma & 0 \end{pmatrix} \quad (83)$$

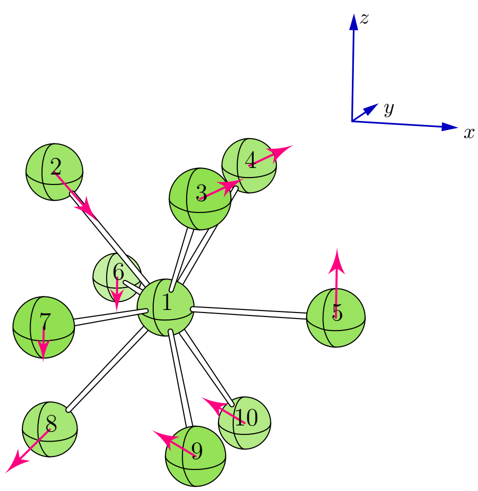


$$\boldsymbol{l}(E''^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \alpha & 0 \\ \gamma & -\beta & 0 \\ -\gamma & -\beta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & -\alpha & 0 \\ -\gamma & \beta & 0 \\ \gamma & \beta & 0 \end{pmatrix} \tag{84}$$

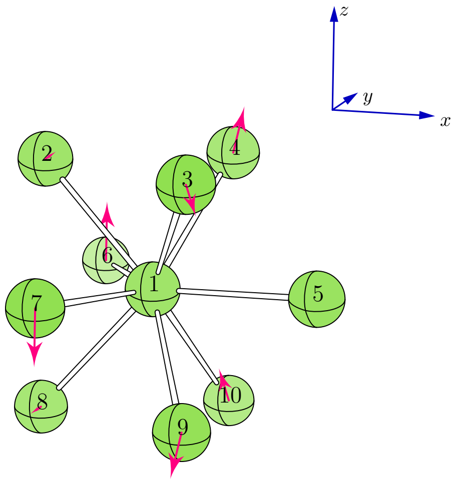
10.2.12 (III)E'' ("seesaw" modes)

Symbols and constants used in this section:

$$\alpha = \sqrt{120/629},\ \beta = \sqrt{160/1887},\ \gamma = \sqrt{30/629},\ \delta = \sqrt{90/629},\ \epsilon = \sqrt{40/1887},\ \eta = \sqrt{40/629},\ \theta = \sqrt{17/222}.$$



$$\boldsymbol{l}(E'') = \begin{pmatrix} 0 & 0 & 0 \\ \theta & 0 & -\beta \\ \theta & 0 & \epsilon \\ \theta & 0 & \epsilon \\ 0 & 0 & \alpha \\ 0 & 0 & -\gamma \\ 0 & 0 & -\gamma \\ -\theta & 0 & -\beta \\ -\theta & 0 & \epsilon \\ -\theta & 0 & \epsilon \end{pmatrix} \tag{85}$$

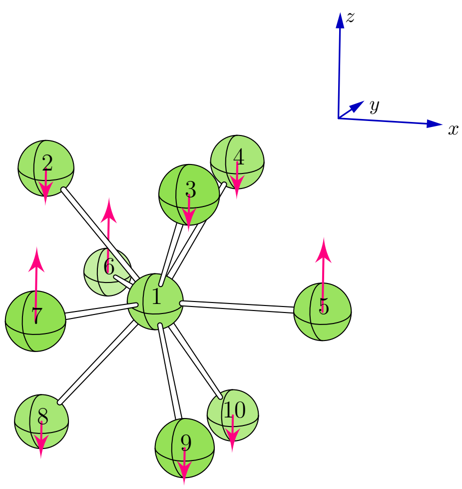


$$\boldsymbol{l}(E''^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \theta & 0 \\ 0 & \theta & -\eta \\ 0 & \theta & \eta \\ 0 & 0 & 0 \\ 0 & 0 & \delta \\ 0 & 0 & -\delta \\ 0 & -\theta & 0 \\ 0 & -\theta & -\eta \\ 0 & -\theta & \eta \end{pmatrix} \tag{86}$$

10.2.13 (IV)E' + (II)A_2'' (relative translations between the top/bottom and middle 3-membered rings)

Symbols and constants used in this section:

$\alpha = \sqrt{2/9}$, $\beta = \sqrt{1/18}$.

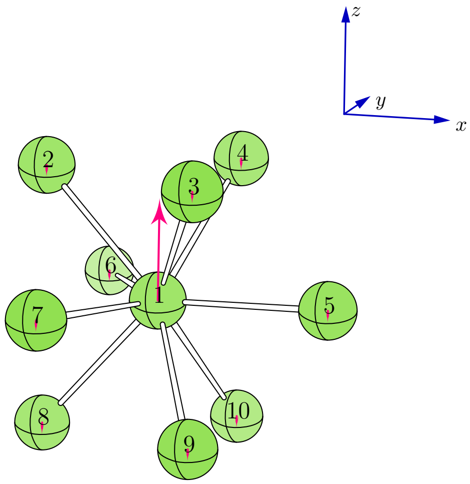


$$\boldsymbol{l}(E') = \begin{pmatrix} 0 & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ \alpha & 0 & 0 \\ \alpha & 0 & 0 \\ \alpha & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \\ -\beta & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & \alpha & 0 \\ 0 & \alpha & 0 \\ 0 & \alpha & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \\ 0 & -\beta & 0 \end{pmatrix}, \boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & \alpha \\ 0 & 0 & \alpha \\ 0 & 0 & \alpha \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \\ 0 & 0 & -\beta \end{pmatrix} \tag{87}$$

10.2.14 (V)E' + (III)A_2'' (intra-molecular translations between atoms X and 9 $\times Y$)

Symbols and constants used in this section:

$\alpha = \sqrt{1/90}$.



$$\boldsymbol{l}(E') = \begin{pmatrix} 9\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \\ -\alpha & 0 & 0 \end{pmatrix}, \boldsymbol{l}(E'^{\dagger}) = \begin{pmatrix} 0 & 9\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \\ 0 & -\alpha & 0 \end{pmatrix}, \boldsymbol{l}(A_2'') = \begin{pmatrix} 0 & 0 & 9\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \\ 0 & 0 & -\alpha \end{pmatrix} \quad (88)$$

10.3 Curvilinear parameters of D_{3h} reference and their components

XY_9: D_{3h} reference

```
R1                                          % (I)A1'
R2                                          % (II)A1'
R3                                          % (III)A1'
R4                                          % A2'
R5                                          % (I)A2"
R6                                          % A1"
R7   theta7                                 % (I)E'
R8   theta8                                 % (II)E'
R9   theta9                                 % (III)E'
R10  theta10                                % (I)E"
R11  theta11                                % (II)E"
R12  theta12                                % (II)E"
R13  theta13  phi13                         % (IV)E'+(II)A2"
R14  theta14  phi14                         % (V)E'+(III)A2"
```