Appendix A

Moment of inertia for a linear triatomic molecule

The inertia tensor $\mathbf{I}$ is a second-rank Cartesian tensor [142],

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}. \tag{A.1}$$

The diagonal elements I_{jj} are called the *moments of inertia*, and the off-diagonal elements I_{jk} are referred to as the *products of inertia*. A particular set of Cartesian coordinates x, y, and z can be chosen such that the axes pass through the center of mass of the body and the *products of inertia* vanish [162]. The moments of inertia about the principle x, y, and z axes are the *principle moments of inertia*, I_{xx}, I_{yy}, and I_{zz}, respectively, and are given as:

$$I_{xx} = \sum_{i=1}^{n} m_i \left[(y_i - y_{c.o.m.})^2 + (z_i - z_{c.o.m.})^2\right] \tag{A.2}$$

$$I_{yy} = \sum_{i=1}^{n} m_i \left[(x_i - x_{c.o.m.})^2 + (z_i - z_{c.o.m.})^2\right] \tag{A.3}$$

$$I_{zz} = \sum_{i=1}^{n} m_i \left[(x_i - x_{c.o.m.})^2 + (y_i - y_{c.o.m.})^2\right] \tag{A.4}$$

where n is the number of atoms and *e.g.* $x_i - x_{c.o.m.}$ is the x component of the vector $\vec{r}_i$ to the ith mass from the center of mass. The total mass of the system, M, is given as the sum over n masses,

$$M = \sum_{i=1}^{n} m_i. \tag{A.5}$$

The three principle moments of inertia are labelled I_{aa}, I_{bb}, and I_{cc}, where by convention, I_{cc} is the largest and I_{aa} is smallest [142]:

$$I_{cc} \geq I_{bb} \geq I_{aa} \tag{A.6}$$

Next, we consider the specific case of a triatomic linear molecule, ABC, whose masses

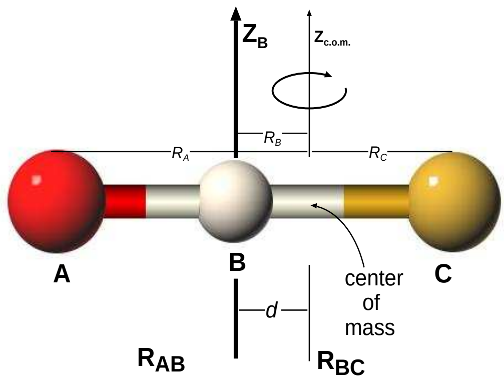

Figure A.1: A linear triatomic molecule ABC with bond lengths R_{AB} and R_{BC} and masses m_{A}, m_{B}, and m_{C}, rotates around an axis $Z_{c.o.m}$ which passes through the center of mass of the molecule.

m_{A}, m_{B}, and m_{C} lie along the molecular axis that rotates about a space-fixed Z axis through the molecule's center of mass, labelled $Z_{c.o.m.}$ (see Figure A.1). Since the masses of the nuclei lie on the a axis, the distance from the ith mass to the a axis is zero, and

$$I_{cc} = I_{bb} > I_{aa} = 0. \tag{A.7}$$

The moment of inertia about the axis through the center of mass is then

$$I_{Z_{c.o.m.}} = m_{\mathrm{A}} R_{\mathrm{A}}{}^2 + m_{\mathrm{A}} R_{\mathrm{B}}{}^2 + m_{\mathrm{A}} R_{\mathrm{C}}{}^2. \tag{A.8}$$

Here, R_{A}, *etc.* are distances from the masses to the center of mass. With help of the *Parallel Axes Thereom*, a transformation can be made to recast Eq. (A.8) in terms of its bond lengths [144]:

Parallel Axes Thereom: *Let the c.o.m. be the center of mass of a rigid body. Let $Z_{c.o.m.}$ be an axis through the c.o.m.. Let Z be another axis parallel to $Z_{c.o.m.}$. Then*

$$I_Z = I_{Z_{c.o.m.}} + Md^2 \tag{A.9}$$

where M is the mass of the body and d is the perpendicular distance between the two axes.

Applying the *Parallel Axes Thereom*, one obtains

$$I_{Z_{c.o.m.}} = \underbrace{m_{\mathrm{A}} R_{\mathrm{AB}}{}^2 + m_{\mathrm{C}} R_{\mathrm{BC}}{}^2}_{I_Z} - Md^2 \tag{A.10}$$

where

$$d = \left(\frac{m_{\mathrm{A}} R_{\mathrm{AB}} - m_{\mathrm{C}} R_{\mathrm{BC}}}{M} \right) \tag{A.11}$$

and

$$M = m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}}. \tag{A.12}$$

Simplifying Eq. (A.10), one obtains,

$$I_{Z_{c.o.m.}} = m_{\mathrm{A}} {R_{\mathrm{AB}}}^2 + m_{\mathrm{C}} {R_{\mathrm{BC}}}^2 - \frac{1}{M} \left(m_{\mathrm{A}} R_{\mathrm{AB}} - m_{\mathrm{C}} R_{\mathrm{BC}} \right)^2 . \tag{A.13}$$

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