

A DEEPER LOOK 5 Rotational selection rules

The starting point for the identification of rotational selection rules is the general definition of the transition dipole moment between states with wavefunctions ψ_f and ψ_i :

$$\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i d\tau$$

where $\hat{\mu}$ is the electric dipole moment operator, $-e\mathbf{r}$.

(a) Pure rotational selection rules

The procedure involves expressing trigonometric functions and the rotational wavefunctions in terms of spherical harmonics (Table 7F.1) and then using standard integrals to identify the criteria for the integrals to be non-zero.

Step 1 Identify the rotational wavefunctions

For a diatomic molecule the rotational wavefunctions are the spherical harmonics $Y_{J,M}(\theta, \phi)$ (Topic 7F). The transition dipole moment for the spectroscopic transition $f \leftarrow i$ is therefore

$$\mu_{fi} = \int \psi_{\epsilon_i}^* \psi_{\nu_i}^* Y_{J_i, M_i}^* \hat{\mu} \psi_{\epsilon_f} \psi_{\nu_f} Y_{J_f, M_f} d\tau$$

For a pure rotational transition the initial and final electronic and vibrational states are the same, and so $\mu_i = \int \psi_{\epsilon_i}^* \psi_{\nu_i}^* \hat{\mu} \psi_{\epsilon_i} \psi_{\nu_i} d\tau_{e,v}$ can be identified as the permanent electric dipole moment of the molecule in the state i . This equation then becomes

$$\mu_{fi} = \int Y_{J_f, M_f}^* \mu_i Y_{J_i, M_i} d\tau_r$$

The remaining integration, denoted $d\tau_r$, is over the rotational coordinates of the molecule. It follows immediately that the molecule must have a permanent dipole moment in order to have a microwave spectrum: this is the gross selection rule for microwave spectroscopy.

Step 2 Write the dipole moment in terms of spherical harmonics

The three components of the dipole moment can be written in terms of the angles θ and ϕ (Fig. 1)

$$\mu_{i,x} = \mu_0 \sin\theta \cos\phi$$

$$\mu_{i,y} = \mu_0 \sin\theta \sin\phi$$

$$\mu_{i,z} = \mu_0 \cos\theta$$

These trigonometric factors can be written in terms of the three spherical harmonics $Y_{1,0}$, $Y_{1,\pm 1}$ listed in Table 7F.1:

$$\mu_{i,x} \propto \mu_0 (Y_{1,1} - Y_{1,-1}) \quad \mu_{i,y} \propto \mu_0 (Y_{1,1} + Y_{1,-1}) \quad \mu_{i,z} \propto \mu_0 Y_{1,0}$$

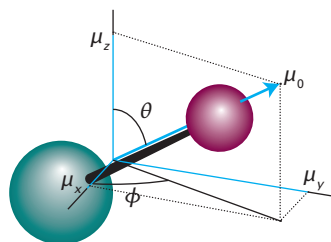


Figure 1 The relation between the three components of the dipole moment and the angles θ and ϕ .

Step 3 Evaluate the integral using a standard result

With these substitutions, the transition moment becomes a sum of terms each of which is an integral over the product of three spherical harmonics of the form

$$\int Y_{J_f, M_f}^* Y_{j, m} Y_{J_i, M_i} d\tau_r$$

with $j = 1$ and $m = 0, \pm 1$, depending on which component is involved. This integral is well known in the theory of angular momentum and is zero unless $M_{J,f} = M_{J,i} + m$ and $J_f = J_i \pm j$. Because $m = 0, \pm 1$ it follows that $\Delta M = M_{J,f} - M_{J,i} = 0$ or ± 1 , and because $j = 1$ it follows that $\Delta J = J_f - J_i = \pm 1$.

(b) Rotational Raman selection rules

Consider a diatomic molecule, with polarizabilities α_{\parallel} and α_{\perp} , and an electric field \mathcal{E} applied in the laboratory Z -direction. The induced dipole moment is parallel to the Z -axis, so $\mu_z = \alpha_{ZZ}\mathcal{E}$.

Step 1 Express the component in the molecular frame

In the molecular frame, the components of the dipole moment are μ_x , μ_y , and μ_z , and from Fig. 2 it follows that

$$\mu_z = \mu_x \sin\theta \cos\phi + \mu_y \sin\theta \sin\phi + \mu_z \cos\theta$$

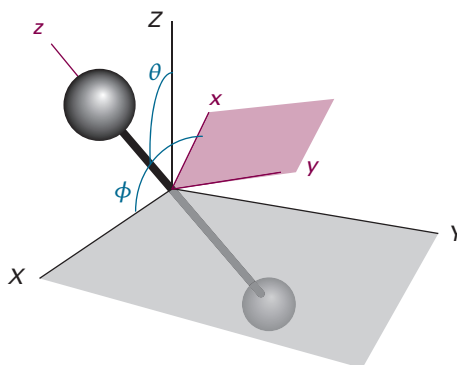


Figure 2 The components of the dipole moment μ_x , μ_y , and μ_z in relation to the laboratory frame.

Similarly, the components of the electric field are

$$E_x = E \sin \theta \cos \phi \quad E_y = E \sin \theta \sin \phi \quad E_z = E \cos \theta$$

Step 2 Express the induced components of the dipole moment in the molecular frame

Because the component of the induced electric dipole moment in the molecular frame, $q = x, y, z$, is related to the component of the electric field in that frame by $\mu_q = \alpha_{qq} E_q$, it follows that

$$\begin{aligned} \mu_z &= \overbrace{\alpha_{xx}}^{\alpha_{\perp}} E_x \sin \theta \cos \phi + \overbrace{\alpha_{yy}}^{\alpha_{\perp}} E_y \sin \theta \sin \phi + \overbrace{\alpha_{zz}}^{\alpha_{\parallel}} E_z \cos \theta \\ &= \alpha_{\perp} E \sin^2 \theta \cos^2 \phi + \alpha_{\perp} E \sin^2 \theta \sin^2 \phi + \alpha_{\parallel} E \cos^2 \theta \\ &\quad \downarrow \text{cos}^2 x + \text{sin}^2 x = 1, x = \phi \\ &= \alpha_{\perp} E \sin^2 \theta + \alpha_{\parallel} E \cos^2 \theta \\ &\quad \downarrow \text{cos}^2 x + \text{sin}^2 x = 1, x = \theta \\ &= \alpha_{\perp} E + (\alpha_{\parallel} - \alpha_{\perp}) E \cos^2 \theta \end{aligned}$$

Step 3 Express the angles in terms of spherical harmonics

The mean polarizability is defined as

$$\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$$

The anisotropy of the polarizability is defined as

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$$

Now note from Table 7F.1 that

$$Y_{2,0}(\theta, \phi) = \left(\frac{5}{16\pi} \right)^{1/2} (3\cos^2 \theta - 1)$$

so

$$\cos^2 \theta = \frac{1}{3} \left\{ 1 + 4 \left(\frac{\pi}{5} \right)^{1/2} Y_{2,0}(\theta, \phi) \right\}$$

It then follows that

$$\mu_z = \left\{ \alpha + \frac{4}{3} \left(\frac{\pi}{5} \right)^{1/2} \Delta\alpha Y_{2,0}(\theta, \phi) \right\} E$$

Step 4 Evaluate the transition dipole moment

Finally, consider the integral that defines the transition moment:

$$\begin{aligned} \mu_{fi} &= \int Y_{J_f, M_{f,i}}^* \mu_z Y_{J_i, M_{j,i}} d\tau_r \\ &= \alpha E \int Y_{J_f, M_{f,i}}^* Y_{J_i, M_{j,i}} d\tau_r + \frac{4}{3} \left(\frac{\pi}{5} \right)^{1/2} \Delta\alpha E \int Y_{J_f, M_{f,i}}^* Y_{2,0} Y_{J_i, M_{j,i}} d\tau_r \end{aligned}$$

The first term is zero if $J_f \neq J_i$ and $M_{j,f} \neq M_{j,i}$ and so does not contribute any off-diagonal elements: it is responsible for the unshifted Rayleigh line. The second term gives a contribution only if both $\Delta\alpha$ and the integral do not disappear. The former requirement implies that the polarizability must be anisotropic; the latter requires $J_f = J_i \pm 2$ and $M_{j,f} = M_{j,i}$.