A selection rule describes how the probability of transitioning from one level to another cannot be zero. It has two sub-pieces: a gross selection rule and a specific selection rule. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field \(E_0 \cos(\omega t)\) that interacts with a transition dipole. The dipole operator is \(\mu = e \cdot \mathbf{r}\) where \(\mathbf{r}\) is a vector pointing in a direction of space.

A dipole moment of a given state is

\[
\mu_z = \int \Psi_1 |^*\mu_z| \Psi_1 |d\tau|
\]

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

\[
(\mu_z)_{12} = \int \Psi_1 |^*\mu_z| \Psi_2 |d\tau|
\]

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If \(\mu_z\) is zero then a transition is forbidden. The selection rule is a statement of when \(\mu_z\) is non-zero.

We can consider selection rules for electronic, rotational, and vibrational transitions.

### Electronic transitions

We consider a hydrogen atom. In order to observe emission of radiation from two states \(\mu_z\) must be non-zero. That is

\[
(\mu_z)_{12} = \int \Psi_1 |^*e \cdot z| \Psi_2 |d\tau| \neq 0
\]

For example, is the transition from \(\Psi_{1s}\) to \(\Psi_{2s}\) allowed?

\[
(\mu_z)_{12} = \int \Psi_{1s} |^*e \cdot z| \Psi_{2s} |d\tau|
\]

Using the fact that \(z = r \cos \theta\) in spherical polar coordinates we have

\[
(\mu_z)_{12} = e \int \int \int e^{-r/a_0}r(2-\frac{r}{a_0})e^{-r/a_0}r^2 \cos \theta \sin \theta \, dr \, d\theta \, d\phi
\]

We can consider each of the three integrals separately.

\[
\int_0^{\infty} e^{-r/a_0}r(2-\frac{r}{a_0})r^2 \cos \theta \sin \theta \, dr \, d\theta \, d\phi
\]
If any one of these is non-zero the transition is not allowed. We can see specifically that we should consider the $q$ integral.

We make the substitution $x = \cos q$, $dx = -\sin q \; dq$ and the integral becomes

$$\int_{-1}^{1} x \; dx = -\frac{x^2}{2} \bigg|_{-1}^{1} = 0$$

which is zero. The result is an even function evaluated over odd limits. In a similar fashion we can show that transitions along the $x$ or $y$ axes are not allowed either. This presents a selection rule that transitions are forbidden for $|\Delta l| = 0$.

For electronic transitions the selection rules turn out to be $|\Delta l| = \pm 1$ and $|\Delta m| = 0$. These result from the integrals over spherical harmonics which are the same for rigid rotator wavefunctions. We will prove the selection rules for rotational transitions keeping in mind that they are also valid for electronic transitions.

### Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the $z$ axis.

$$|\langle \mu_z \rangle_{J,M,J',M'}| = \int_{0}^{2\pi} \int_{0}^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_{J}^{M}(\theta,\phi) \sin \theta \; d\phi, d\theta$$

Notice that $m$ must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_{J}^{M}(\theta,\phi) = N_{JM} P_{J}^{|M|}(\cos \theta) e^{iM \phi}$$

where $\langle N_{JM} \rangle$ is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$|\langle \mu_z \rangle_{J,M,J',M'}| = \mu \; N_{JM} N_{J'M'} \int_{0}^{2 \pi} e^{i(M-M') \phi} \; d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_{J}^{|M|}(x) dx$$

The integral over $f$ is zero unless $M = M'$ so $|\Delta M| = 0$ is part of the rigid rotator selection rule. Integration over $|\phi|$ for $|\Delta M| = M'$ gives $2\pi$ so we have

$$|\langle \mu_z \rangle_{J,M,J',M'}| = 2\pi \mu \; N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_{J}^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$|\langle \mu_z \rangle_{J,M,J',M'}| = 2\pi \mu \; N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_{J}^{|M|}(x) dx$$

Substituting into the integral one obtains an integral which will vanish unless $(J' = J + 1)$ or $(J' = J - 1)$.

$$|\langle \mu_z \rangle_{J,M,J',M'}| = \int_{-1}^{1} P_{J'}^{|M'|}(x) \text{Biggr}(|\frac{\text{Irrac}(J-M+1)}{(2J+1)}| \text{P}_{J+1}^{|M|}(x) + \text{Irrac}(J-M)| \text{P}_{J-1}^{|M|}(x)dx$$

This leads to the selection rule $|\Delta J| = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers $|J|$ and $|M|$ as the total angular momentum and $z$-component of angular
momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1, \Delta m = 0$).

### Vibrational transitions

The harmonic oscillator wavefunctions are

$$\Psi_{\nu}(q) = N_{\nu}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}$$

where $H_{\nu}(a^{1/2}q)$ is a Hermite polynomial and $a = (km/\alpha^2)^{1/2}$.

The transition dipole moment for electromagnetic radiation polarized along the $z$ axis is

$$\langle \mu_z \rangle_{\nu,\nu'} = \int_{-\infty}^{\infty} N_{\nu}N_{\nu'}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}\mu_z(\alpha^{1/2}q)e^{-\alpha q^2/2}dq$$

Note that we continue to use the general coordinate $q$ although this can be $z$ if the dipole moment of the molecule is aligned along the $z$ axis. The transition moment can be expanded about the equilibrium nuclear separation.

$$\mu_z(q) = \mu_0 + \frac{\partial\mu}{\partial q}q + \ldots$$

where $\mu_0$ is the dipole moment at the equilibrium bond length and $q$ is the displacement from that equilibrium state. From the first two terms in the expansion we have for the first term

$$\langle \mu_z \rangle_{\nu,\nu'} = \mu_0 \int_{-\infty}^{\infty} N_{\nu}N_{\nu'}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}dq$$

This term is zero unless $\nu = \nu'$ and in that case there is no transition since the quantum number has not changed.

$$\langle \mu_z \rangle_{\nu,\nu'} = \frac{\partial\mu}{\partial q} \int_{-\infty}^{\infty} N_{\nu}N_{\nu'}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}dq$$

This integral can be evaluated using the Hermite polynomial identity known as a recursion relation

$$xH_{\nu}(x) = \nu H_{\nu-1}(x) + \frac{1}{2} H_{\nu+1}(x)$$

where $x = \sqrt{\alpha}q$. If we now substitute the recursion relation into the integral we find

$$\langle \mu_z \rangle_{\nu,\nu'} = \frac{\partial\mu}{\partial q} \int_{-\infty}^{\infty} N_{\nu}N_{\nu'}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}H_{\nu}(\alpha^{1/2}q)e^{-\alpha q^2/2}dq$$

which will be non-zero if $\nu' = \nu - 1$ or $\nu' = \nu + 1$. Thus, we see the origin of the vibrational transition selection rule that $\nu = \pm 1$. We also see that vibrational transitions will only occur if the dipole moment changes as a function nuclear motion.
Contributors

• Stefan Franzen (North Carolina State University)