Rotational selection rules

For a heteronuclear diatomic molecule a transition between two states with the absorption or emission of electromagnetic radiation can only occur between certain two states $\psi_{J'M'}, \psi_{J''M''}$, for which the matrix element $\langle \psi_{J'M'} | \mu | \psi_{J''M''} \rangle$ of electric dipole moment operator is not zero. Derive the rotational selection rules $\Delta J = J' - J'' = \pm 1$ and $\Delta M = M' - M'' = 0, \pm 1$ in the rigid rotor approximation, where the rotational wavefunction in spherical coordinates has the form

$$\psi_{JM}(\theta, \phi) = Y_{J,M}(\theta, \phi) = \frac{1}{\sqrt{2\pi}} P_J^M(\cos\theta) \mathrm{e}^{iM\phi},$$

where $Y_{JM}(\theta, \phi)$ are spherical harmonics functions and P_J^M are associate Legendre polynomials.

Utilize both methods suggested below.

Method 1: Express dipole moment in spherical coordinates and utilize the following identities for goniometric functions and for associated Legendre polynomials:

$$\cos\phi = \frac{\mathrm{e}^{i\phi} + \mathrm{e}^{-i\phi}}{2}$$

$$\sin\phi = \frac{\mathrm{e}^{i\phi} - \mathrm{e}^{-i\phi}}{2i}$$

$$(2J+1) z P_J^M(z) = (J+M) P_{J-1}^M(z) + (J-M+1) P_{J-1}^M(z)$$

$$\sqrt{1-z^2} P_J^M(z) = \frac{1}{2J+1} [(J-M+1)(J-M+2) P_{J+1}^{M-1}(z) - (J+M-1)(J+M) P_{J-1}^{M-1}(z)]$$

$$\sqrt{1-z^2} P_J^M(z) = \frac{-1}{2J+1} [P_{J+1}^{M+1}(z) - P_{J-1}^{M+1}(z)]$$

Method 2: The components of the dipole moment can be written as functions of the spherical harmonics:

$$\mu_x = \mu_0 \sin\theta \cos\phi = -\frac{1}{2} \left(\frac{8\pi}{3} \right)^{0.5} \mu_0 (Y_{1,+1} - Y_{1,-1})$$

$$\mu_y = \mu_0 \sin\theta \sin\phi = i \frac{1}{2} \left(\frac{8\pi}{3} \right)^{0.5} \mu_0 (Y_{1,+1} + Y_{1,-1})$$

$$\mu_z = \mu_0 \cos\theta = \left(\frac{4\pi}{3}\right)^{0.5} \mu_0 Y_{1,0}.$$

$Y_{J,M}$ is a member of the basis that spans the irreducible representation $\Gamma^{(J)}$ of the full rotation group. Find the selection rules for ΔJ and ΔM for which the integrand in the term $\langle \psi_{J'M'}|\mu|\psi_{J''M''}\rangle$ spans the completely symmetric irreducible representation.

Solution 1: Components of the electric dipole moment can be expressed in spherical coordinates as follows

$$\begin{aligned}\mu_x &= \mu_0 \sin\theta \cos\phi,\\ \mu_y &= \mu_0 \sin\theta \sin\phi,\\ \mu_z &= \mu_0 \cos\theta.\end{aligned}$$

Spherical harmonics $Y_{J,M}(\theta,\phi)$ can be written as a product of two functions which depend only on one of the angles θ, or ϕ

$$Y_{J,M}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} P_J^M(\cos\theta) e^{iM\phi}$$

which means that the matrix elements can be separated into two independent integrals over θ and over ϕ for each of the dipole moment components.

For μ_z, the matrix element can be expressed as

$$\begin{aligned}\langle \psi_{J',M'}|\mu_z|\psi_{J,M}\rangle &= \int_0^{2\pi}\int_0^{\pi} Y^*_{J',M'}(\theta,\phi)\ \mu_0 \cos\theta\ Y_{J,M}(\theta,\phi)\ \sin\theta d\theta d\phi = \\ &= \frac{\mu_0}{2\pi}\int_0^{2\pi} e^{i(M-M')\phi} d\phi \int_0^{\pi} P_{J'}^{M'}(cos\theta)\cos\theta P_J^M(cos\theta)\sin\theta d\theta\end{aligned}$$

The first integral will only be non-zero for $M = M'$ and using the substitution $z = \cos\theta$ will allow us to use the following identity for associate Legendre polynomials

$$(2J+1) z P_J^M(z) = (J-M+1) P_{J+1}^M(z) + (J+M) P_{J-1}^M(z).$$

If we further use the orthogonality condition for associate Legendre polynomials for fixed M

$$\int_{-1}^{1} P_{J'}^M(z) P_J^M(z) dz = \frac{2(J+M)!}{(2J+1)(J-M)!}\delta_{J,J'}$$

we will be able to fully evaluate the matrix element for μ_z.

$$
\begin{aligned}
\langle\psi_{J',M'}|\mu_z|\psi_{J,M}\rangle &= \frac{\mu_0}{2\pi}2\pi\delta_{M,M'}\int_{-1}^{1}P_{J'}^{M}(z)zP_{J}^{M}(z)dz = \\
&= \mu_0\delta_{M,M'}\int_{-1}^{1}P_{J'}^{M}(z)\frac{1}{2J+1}\left[(J-M+1)P_{J+1}^{M}(z)+(J+M)P_{J-1}^{M}(z)\right]dz \\
&= \mu_0\frac{(J-M+1)}{(2J+1)}\frac{2(J+1+M)!}{(2J+3)(J+1-M)!}\delta_{J+1,J'}\delta_{M,M'} \\
&+ \mu_0\frac{(J+M)}{(2J+1)}\frac{2(J-1+M)!}{(2J-1)(J-1-M)!}\delta_{J-1,J'}\delta_{M,M'}
\end{aligned}
$$

From the expression above, it is clear that the matrix element for μ_z can be non-zero only for transitions for which $M = M'$ and $J = J' \pm 1$ or rather when $\Delta M = 0$ and $\Delta J = \pm 1$.

The matrix elements for μ_x and μ_y can be evaluated similarly with the exception that dipole moment components in x and y directions depend on the angle ϕ too. However expressing the cosine and sine of ϕ in terms of exponential functions

$$
\begin{aligned}
\cos\phi &= \frac{e^{i\phi}+e^{-i\phi}}{2} \\
\sin\phi &= \frac{e^{i\phi}-e^{-i\phi}}{2i}
\end{aligned}
$$

will allow us to follow a similar procedure as we did for μ_z.

For μ_x, we will get

$$
\begin{aligned}
\langle\psi_{J',M'}|\mu_x|\psi_{J,M}\rangle &= \frac{\mu_0}{2\pi}\int_{0}^{2\pi}e^{i(M-M')\phi}\cos\phi d\phi\int_{0}^{\pi}P_{J'}^{M'}(cos\theta)\sin\theta P_{J}^{M}(cos\theta)\sin\theta d\theta \\
&= \frac{\mu_0}{2\pi}\frac{1}{2}\int_{0}^{2\pi}e^{i(M-M'+1)\phi}d\phi\int_{-1}^{1}P_{J'}^{M'}(z)\sqrt{1-z^2}P_{J}^{M}(z)dz \\
&+ \frac{\mu_0}{2\pi}\frac{1}{2}\int_{0}^{2\pi}e^{i(M-M'-1)\phi}d\phi\int_{-1}^{1}P_{J'}^{M'}(z)\sqrt{1-z^2}P_{J}^{M}(z)dz
\end{aligned}
$$

It is clear that the first integral over ϕ will be non-zero only for $M = M' - 1$ and the second for $M = M' + 1$. Using this and the identities

$$
\begin{aligned}
\sqrt{1-z^2}P_{J}^{M}(z) &= \frac{-1}{2J+1}\left[P_{J+1}^{M+1}(z)-P_{J-1}^{M+1}(z)\right] \\
\sqrt{1-z^2}P_{J}^{M}(z) &= \frac{1}{2J+1}\left[(J-M+1)(J-M+2)P_{J+1}^{M-1}(z)-(J+M+1)(J+M)P_{J-1}^{M-1}(z)\right]
\end{aligned}
$$

will allow us to use the orthogonality condition for associate Legendre polynomials for fixed M again.

$$\begin{aligned}
\langle\psi_{J',M'}|\mu_x|\psi_{J,M}\rangle &= \frac{\mu_0}{2}\delta_{M,M'-1}\int_{-1}^{1} P_{J'}^{M+1}(z)\frac{-1}{2J+1}\left[P_{J+1}^{M+1}(z) - P_{J-1}^{M+1}(z)\right] dz \\
&+ \frac{\mu_0}{2}\delta_{M,M'+1}\int_{-1}^{1} P_{J'}^{M-1}(z)\frac{1}{2J+1}\Big[(J-M+1)(J-M+2)P_{J+1}^{M-1}(z) \\
&- (J+M+1)(J+M)P_{J-1}^{M-1}(z)\Big] dz \\
&= \frac{\mu_0}{2}\delta_{M,M'-1}\delta_{J',J+1}\frac{-1}{2J+1}\frac{2(J+M+2)!}{(2J+3)(J-M)!} \\
&+ \frac{\mu_0}{2}\delta_{M,M'-1}\delta_{J',J-1}\frac{1}{2J+1}\frac{2(J+M)!}{(2J-1)(J-M-2)!} \\
&+ \frac{\mu_0}{2}\delta_{M,M'+1}\delta_{J',J+1}\frac{(J-M+1)(J-M+2)}{2J+1}\frac{2(J+M)!}{(2J+3)(J-M+2)!} \\
&+ \frac{\mu_0}{2}\delta_{M,M'+1}\delta_{J',J-1}\frac{(-1)(J+M+1)(J+M)}{2J+1}\frac{2(J+M-2)!}{(2J-1)(J-M)!}
\end{aligned}$$

The matrix element for μ_y can be evaluated in the same way, only now it depends on $\sin\phi$ which changes the prefactor by $1/i$ and the sign for the second two terms

$$\begin{aligned}
\langle\psi_{J',M'}|\mu_y|\psi_{J,M}\rangle &= \frac{\mu_0}{2i}\delta_{M,M'-1}\delta_{J',J+1}\frac{-1}{2J+1}\frac{2(J+M+2)!}{(2J+3)(J-M)!} \\
&+ \frac{\mu_0}{2i}\delta_{M,M'-1}\delta_{J',J-1}\frac{1}{2J+1}\frac{2(J+M)!}{(2J-1)(J-M-2)!} \\
&- \frac{\mu_0}{2i}\delta_{M,M'+1}\delta_{J',J+1}\frac{(J-M+1)(J-M+2)}{2J+1}\frac{2(J+M)!}{(2J+3)(J-M+2)!} \\
&- \frac{\mu_0}{2i}\delta_{M,M'+1}\delta_{J',J-1}\frac{(-1)(J+M+1)(J+M)}{2J+1}\frac{2(J+M-2)!}{(2J-1)(J-M)!}.
\end{aligned}$$

In summary, the matrix elements for μ_x and μ_y will only be non-zero for $\Delta M = \pm 1$ and $\Delta J = \pm 1$ and the matrix element for μ_z can be non-zero for $\Delta M = 0$ and $\Delta J = \pm 1$.

Solution 2: Spherical harmonics $Y_{J,M}$ are members of the basis that span the irreducible representation $\Gamma^{(J)}$ of the full rotation group.

Rotations around any axis going through the origin by an angle α are conjugate to each other and together they form a class of the full rotation group which means that, if we want to count the character of the irreducible representation $\Gamma^{(J)}$, we can do so by considering any of the axis going through the origin and the result will be the same.

For simplicity, I will consider rotations around the z-axis, denoted by $\hat{R}_\alpha$. Applying this rotation to spherical harmonics simply yields

$$\hat{R}_\alpha Y_{J,M} = e^{-iM\alpha} Y_{J,M}.$$

The character of the irreducible representation $\Gamma^{(J)}$ can then be expressed as a sum

$$\chi^J(\hat{R}_\alpha) = \sum_{M=-J}^{M=J} e^{-iM\alpha}.$$

Since the components of the electric dipole moment can be expressed in terms of the spherical harmonics

$$\begin{aligned}
\mu_x &= -\frac{1}{2}\sqrt{\frac{8\pi}{3}}\mu_0(Y_{1,1} - Y_{1,-1}) \\
\mu_y &= i\frac{1}{2}\sqrt{\frac{8\pi}{3}}\mu_0(Y_{1,1} + Y_{1,-1}) \\
\mu_z &= \sqrt{\frac{4\pi}{3}}\mu_0 Y_{1,0},
\end{aligned}$$

I will be further interested in the product $Y_{1,m}Y_{J,M}$. This product will be a member of a basis that spans a new representation Γ^{new} which is generally reducible.

To express this new representation in terms of the irreducible representations it is convenient to consider its characters, which will be equal to the product of $\chi^J(\hat{R}_\alpha)$ and $\chi^1(\hat{R}_\alpha)$ characters

$$\chi^{new}(\hat{R}_\alpha) = \left(\sum_{m=-1}^{m=1} e^{-im\alpha}\right)\left(\sum_{M=-J}^{M=J} e^{-iM\alpha}\right)$$

To make the result clear, I will write down the first sum explicitly and for

$m = \pm 1$ separate parts with negative and positive exponents

$$\begin{aligned}
\chi^{new}(\hat{R}_\alpha) &= \left(\sum_{M=-J}^{M=J} e^{-i(M+1)\alpha}\right) + \left(\sum_{M=-J}^{M=J} e^{-iM\alpha}\right) + \left(\sum_{M=-J}^{M=J} e^{-i(M-1)\alpha}\right) \\
&= \left(\sum_{M=-J}^{M=-2} e^{-i(M+1)\alpha} + \sum_{M=-1}^{M=J} e^{-i(M+1)\alpha}\right) + \left(\sum_{M=-J}^{M=J} e^{-iM\alpha}\right) \\
&+ \left(\sum_{M=-J}^{M=0} e^{-i(M-1)\alpha} + \sum_{M=1}^{M=J} e^{-i(M-1)\alpha}\right) \\
&= \chi^{J-1}(\hat{R}_\alpha) + \chi^{J}(\hat{R}_\alpha) + \chi^{J+1}(\hat{R}_\alpha).
\end{aligned}$$

It is therefore obvious that our new representation can be written in terms of irreducible representations as follows

$$\Gamma^{(new)} = \Gamma^{(1)} \otimes \Gamma^{(J)} = \Gamma^{(J-1)} \oplus \Gamma^{(J)} \oplus \Gamma^{(J+1)}.$$

The matrix element $\langle \psi_{J'M'} | \mu | \psi_{JM} \rangle$ can be non-zero only if the direct product $[\Gamma^{(J')}]^* \otimes \Gamma^{(1)} \otimes \Gamma^{(J)}$ contains the completely symmetric irreducible representation $\Gamma^{(0)}$. Since we know that $\Gamma^{(0)} \subset [\Gamma^{(a)}]^* \otimes \Gamma^{(a)}$, we can also say that the matrix element can be non-zero only if

$$\Gamma^{(1)} \otimes \Gamma^{(J)} \supset \Gamma^{J'}.$$

And as we have already expressed $\Gamma^{(1)} \otimes \Gamma^{(J)}$ in terms of irreducible representations we can immediately say that the matrix element can be non-zero only when $J = J'$ or $J = J' \pm 1$, or rather when $\Delta J = 0, \pm 1$. In this case, the integrand in the term $\langle \psi_{J',M'} | \mu | \psi_{J,M} \rangle$ spans the completely symmetric irreducible representation $\Gamma^{(0)}$.

The allowed transitions are further restricted by parity. The parity of spherical harmonics is known to be

$$\hat{P} Y_{J,M} = (-1)^J Y_{J,M} \tag{1}$$

which means that the matrix element can be non-zero only when $J' + 1 + J$ is an even number. Combining this result with the previously derived selection rule for ΔJ gives us a new, more strict selection rule, which is $\Delta J = \pm 1$.

To derive the selection rule for ΔM, it is convenient to realise that all the matrix elements will be proportional to $\langle J', M' | 1, m; J, M \rangle$.

We can use the fact that vectors $|1, m; J, M\rangle$ form a basis on the $1 \otimes J$ space, meaning that

$$\mathbb{1}_{1\otimes J} = \sum_{m_1=-1}^{1} \sum_{M_2=-J}^{J} |1, m_1; J, M_2\rangle\langle 1, m_1; J, M_2|.$$

Any vector from this space $|J', M'\rangle$ can be then written as

$$|J', M'\rangle = \sum_{m_1=-1}^{1} \sum_{M_2=-J}^{J} |1, m_1; J, M_2\rangle\langle 1, m_1; J, M_2|J', M'\rangle. \tag{2}$$

Since we know the eigenvalues of the total angular momentum in the z-direction $\hat{J}_z$ to be $\hat{J}_z|J, M\rangle = \hbar M|J, M\rangle$, applying the operator $\hat{J}_z$ to both sides of the equation results in

$$\hbar M'|J', M'\rangle = \sum_{m_1=-1}^{1} \sum_{M_2=-J}^{J} \hbar(m_1 + M_2)|1, m_1; J, M_2\rangle\langle 1, m_1; J, M_2|J', M'\rangle.$$

If we know multiply the equation by the bra-vector $\langle 1, m; J, M|$ and use the orthogonality relation for spherical harmonics, we will get

$$\hbar M'\langle 1, m; J, M|J', M'\rangle = \sum_{m_1=-1}^{1} \sum_{M_2=-J}^{J} \hbar(m_1 + M_2)\delta_{m_1,m}\delta_{M_2,M}\langle 1, m_1; J, M_2|J', M'\rangle$$
$$\hbar M'\langle 1, m; J, M|J', M'\rangle = \hbar(m + M)\langle 1, m; J, M|J', M'\rangle$$

Meaning that for non-zero $\langle 1, m; J, M|J', M'\rangle = \langle J', M'|1, m; J, M\rangle^*$ it must hold that $M' = m + M$, or rather $\Delta M = m$. The selection rule for the matrix element μ_z is then $\Delta M = 0$ and for μ_x and μ_y it is $\Delta M = \pm 1$.