

Spectroscopy

using electromagnetic radiation to study atoms and molecules

- ◆ one of the most important applications of quantum mechanics
- ◆ uses radiation to determine atomic and molecular properties
- ◆ provides molecular structures with extraordinary accuracy
- ◆ monitors molecular events on timescales down to femtoseconds
- ◆ many practical applications, including analytical chemistry

The fundamental idea behind spectroscopy: the energy of absorbed or emitted photons equals the difference between the quantum mechanical energy levels of atoms or molecules involved in the transition

$$h\nu = hc/\lambda = hc\tilde{\nu} = |E_{\text{final}} - E_{\text{initial}}|$$

But there are mysteries!

Example For an absorption transition with $E_{\text{final}} - E_{\text{initial}} = 6.00$ eV, only a photon with energy $h\nu = 6.00$ eV is absorbed. **Why?** Couldn't a 7.00 eV photon be absorbed and a 1.00 eV photon keep on going?

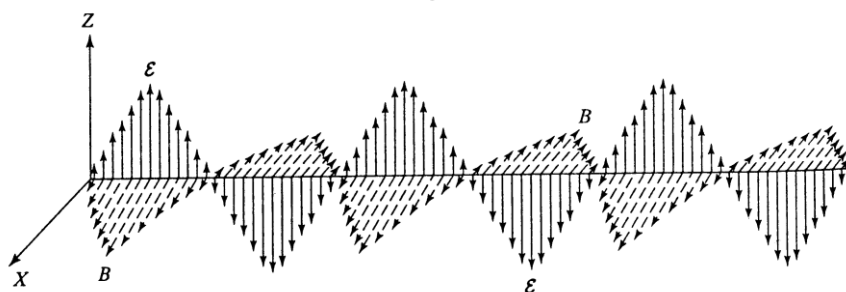
Example In many cases, photons with the correct energy $|E_{\text{final}} - E_{\text{initial}}|$ are never absorbed or emitted. **Why?**

Spectroscopic Selection Rules

The energy levels of atoms and molecules decide the **possible** frequencies and wavelengths of absorbed and emitted radiation for atomic and molecular transitions.

But what transitions are **probable** (most intense)?

Electromagnetic radiation consists of propagating oscillations in the strengths of the electric and magnetic fields.



Atoms and molecules are collections of positively-charged nuclei and negatively-charged electrons. The strength of the interaction between electromagnetic radiation and atoms or molecules is governed the electric **dipole moment operator**

$$\hat{\mu} = \sum q_i \vec{r}_i$$

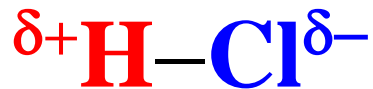
for the distribution of electrical charges q_i at positions \vec{r}_i .

In SI units, an electric dipole is expressed in C m. In practice, the non-SI unit **“Debye”** is often used.

$$1 \text{ Debye} = 1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

Molecules with large permanent dipoles (*i.e.*, *large permanent separation of electrical charge*, such as HCl) therefore interact relatively strongly with radiation

$$\leftarrow \hat{\mu} = 1.08 \text{ D}$$



producing the most intense (most probable) transitions. Molecules and atoms can also have fluctuating (transient) electric dipole moments that can interact with radiation, though more weakly.

Time-Dependent Perturbation Theory

Gives the **spectroscopic selection rules** that decide which transitions between quantum mechanical states are the most intense.

Until now, we've looked at wave functions obtained by solving the **time-independent Schrödinger equation for stationary states**

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

But transitions from one state to another are transient processes described by the **time-dependent Schrödinger equation**

$$\hat{H}\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

To solve this equation for spectroscopic transitions, the time-dependent part of the Hamiltonian operator $\hat{H}^{(1)}$ is treated as a small perturbation superimposed on the time-independent Hamiltonian $\hat{H}^{(0)}$ for isolated atoms and molecules in stationary states.

$$\hat{H}(\vec{r}, t) = \hat{H}^{(0)}(\vec{r}) + \hat{H}^{(1)}(\vec{r}, t)$$

To solve the time-dependent Schrödinger equation

$$(\hat{H}^{(0)} + \hat{H}^{(1)})\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

it's convenient to simplify the equations by assuming the electric field of the electromagnetic radiation oscillates in the z -direction

$$E(t) = E_{0z} \cos(2\pi\nu t)$$

ν is the frequency of the radiation and E_{0z} is the amplitude of the oscillations in the electric field. If μ_z is the dipole moment of a molecule in the z -direction, the energy of interaction between the radiation and the molecule is

$$\hat{H}^{(1)} = -\vec{\mu} \cdot \vec{E} = -\mu_z E_{0z} \cos(2\pi\nu t)$$

If the molecule has no dipole moment in the z -direction, there is no interaction.

Transitions from State 1 to State 2

Consider possible transitions between stationary states 1 and 2 with wave functions ψ_1 and ψ_2 (note: *lower-case* psis!) satisfying the time-independent Schrödinger equations

$$\hat{H}^{(0)}\psi_1(\vec{r}) = E_1\psi_1(\vec{r})$$

$$\hat{H}^{(0)}\psi_2(\vec{r}) = E_2\psi_2(\vec{r})$$

$\hat{H}^{(0)}$ for the stationary states does not depend on the time. As a result, it's relatively easy to show (*try it!*) that the corresponding wave functions (*upper-case* psis!)

$$\Psi_1(\vec{r}, t) = \psi_1(\vec{r})e^{-iE_1t/\hbar}$$

$$\Psi_2(\vec{r}, t) = \psi_2(\vec{r})e^{-iE_2t/\hbar}$$

are solutions of the time-dependent Schrödinger equations

$$\hat{H}^{(0)}\Psi_1(\vec{r}, t) = i\hbar\frac{\partial\Psi_1(\vec{r}, t)}{\partial t}$$

$$\hat{H}^{(0)}\Psi_2(\vec{r}, t) = i\hbar\frac{\partial\Psi_2(\vec{r}, t)}{\partial t}$$

Suppose that the system is initially in state 1, and **the applied radiation field is “turned on” at time $t = 0$** . The subsequent time-evolution of the state of the molecule is then represented by the linear combinations of states 1 and 2

$$\Psi(\vec{r}, t) = a_1(t)\Psi_1(\vec{r}, t) + a_2(t)\Psi_2(\vec{r}, t)$$

with time-dependent mixing coefficients $a_1(t)$ and $a_2(t)$. The system is initially in state 1, so the initial conditions are

$$a_1(0) = 1 \qquad a_2(0) = 0$$

Substituting the expression for $\Psi(\vec{r}, t)$ into

$$(\hat{H}^{(0)} + \hat{H}^{(1)})\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

gives the rather complicated expression

$$\begin{aligned} & a_1(t)\hat{H}^{(0)}\Psi_1 + a_2(t)\hat{H}^{(0)}\Psi_2 + a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 \\ & = i\hbar\Psi_1 \frac{da_1(t)}{dt} + i\hbar\Psi_2 \frac{da_2(t)}{dt} + i\hbar a_1(t) \frac{\partial \Psi_1(\vec{r}, t)}{\partial t} + i\hbar a_2(t) \frac{\partial \Psi_2(\vec{r}, t)}{\partial t} \end{aligned}$$

But wait! The first two terms and the last two terms in this equation cancel (*why?*) to give

$$a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 = i\hbar\Psi_1\frac{da_1(t)}{dt} + i\hbar\Psi_2\frac{da_2(t)}{dt}$$

This equation can be multiplied by Ψ_2^* and integrated over the spatial coordinates τ

$$\begin{aligned} a_1(t)\int\Psi_2^*\hat{H}^{(1)}\Psi_1d\tau + a_2(t)\int\Psi_2^*\hat{H}^{(1)}\Psi_2d\tau \\ = i\hbar\frac{da_1(t)}{dt}\int\Psi_2^*\Psi_1d\tau + i\hbar\frac{da_2(t)}{dt}\int\Psi_2^*\Psi_2d\tau \end{aligned}$$

Ψ_1 and Ψ_2 are normalized and orthogonal (“orthonormal”), and so

$$a_1(t)\int\Psi_2^*\hat{H}^{(1)}\Psi_1d\tau + a_2(t)\int\Psi_2^*\hat{H}^{(1)}\Psi_2d\tau = i\hbar\frac{da_2(t)}{dt}$$

Substituting the spatial (ψ_i) and time-dependent ($e^{-iE_it/\hbar}$) factors

$$\begin{aligned} a_1(t)\int(\psi_2e^{-iE_2t/\hbar})^*\hat{H}^{(1)}\psi_1e^{-iE_1t/\hbar}d\tau \\ + a_2(t)\int(\psi_2e^{-iE_2t/\hbar})^*\hat{H}^{(1)}\psi_2e^{-iE_2t/\hbar}d\tau = i\hbar\frac{da_2}{dt} \end{aligned}$$

leads to further simplification

$$a_1(t) e^{-i(E_1 - E_2)t/\hbar} \int \psi_2^* \hat{H}^{(1)} \psi_1 d\tau + a_2(t) \int \psi_2^* \hat{H}^{(1)} \psi_2 d\tau = i\hbar \frac{da_2}{dt}$$

For weak perturbations, relatively few atoms or molecules make the transition out of the initial Ψ_1 state. The term proportional to $a_2(t)$ can therefore be neglected, at least initially, but *not* the term proportional to da_2/dt (*why?*), to give

$$e^{-i(E_1 - E_2)t/\hbar} \int \psi_2^* \hat{H}^{(1)} \psi_1 d\tau = i\hbar \frac{da_2}{dt}$$

The derivative da_2/dt is especially interesting for spectroscopy. It gives the rate at which the population of molecules in state Ψ_2 builds up as a result of the transition from the initial state Ψ_1 .

The time-dependent perturbation Hamiltonian $\hat{H}^{(1)}$ is proportional to the product of the electric dipole moment and the oscillating electric field (assumed for convenience to be along the z axis)

$$\hat{H}^{(1)} = -\mu_z E_{0z} \cos(2\pi\nu t) = -\mu_z E_{0z} \left(e^{i2\pi\nu t} + e^{-i2\pi\nu t} \right)$$

So the expression for da_2/dt becomes

$$\begin{aligned}
i\hbar \frac{da_2}{dt} &= -e^{-i(E_1-E_2)t/\hbar} \int \psi_2^* \mu_z E_{0z} (e^{i2\pi\nu t} + e^{-i2\pi\nu t}) \psi_1 d\tau \\
&= -(e^{-i(E_1-E_2-h\nu)t/\hbar} + e^{-i(E_1-E_2+h\nu)t/\hbar}) E_{0z} \int \psi_2^* \mu_z \psi_1 d\tau
\end{aligned}$$

Defining the **dipole transition moment between states Ψ_1 and Ψ_2**

$$(\mu_z)_{21} = \int \psi_2^* \mu_z \psi_1 d\tau$$

gives

$$\frac{da_2}{dt} \propto E_{0z} (\mu_z)_{21} (e^{-i(E_1-E_2-h\nu)t/\hbar} + e^{-i(E_1-E_2+h\nu)t/\hbar})$$

Integrating between time $t = 0$ (when a_2 for the amplitude of the final state is zero) and time t gives

$$a_2(t) \propto E_{0z} (\mu_z)_{21} \left[\frac{1 - e^{i(E_2-E_1+h\nu)t/\hbar}}{E_2 - E_1 + h\nu} + \frac{1 - e^{i(E_2-E_1-h\nu)t/\hbar}}{E_2 - E_1 - h\nu} \right]$$

Why bother to do all this?

The results are fundamentally important for all spectroscopy:

1. For **absorption spectroscopy** (the final state has higher energy, $E_2 > E_1$) the important resonance denominator $E_2 - E_1 - h\nu$ causes the second term to be relatively large determining $a_2(t)$ when

$$E_2 - E_1 = \Delta E = h\nu \quad \text{absorption}$$

2. For **emission spectroscopy** (the final state has lower energy, $E_2 < E_1$) the resonance denominator $E_2 - E_1 + h\nu$ causes the first term to be relatively large when

$$E_1 - E_2 = \Delta E = h\nu \quad \text{emission}$$

This are the famous **Bohr frequency conditions**:

When a system makes a transition from one state to another, it absorbs (or emits) a photon whose energy is equal to the difference in the energies of the two states.

3. There is no absorption or emission if the dipole transition moment (decided by the stationary initial and final states) is zero.

4. The strength of the absorption is proportional to the dipole transition moment and the amplitude of the oscillating electric field.

Spectroscopic Selection Rules: Diatomic Harmonic Oscillators

To illustrate the selection rules for **molecular vibration**, time-dependent perturbation theory is applied to the diatomic molecules.

Recall that the **harmonic oscillator wave functions** are

$$\psi_n(x) = N_n H_n(\alpha^{1/2}x) e^{-\alpha x^2/2} \quad n = 0, 1, 2, 3, \dots$$

N_n is a normalization factor, **x is the displacement** of the positions of nuclei 1 and 2 from the equilibrium bond length R_0 (stretched: $x > 0$, compressed: $x < 0$)

$$x = x_2 - x_1 - R_0$$

and α is an abbreviation for

$$\alpha = \sqrt{k\mu/\hbar^2}$$

k is the force constant (a measure of the “stiffness” of the bond), μ is the reduced mass.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$H_n(\xi)$$

$$\xi = \alpha x^{1/2}$$

is the n th **Hermite polynomial** in

$$H_0(\xi) = 1 \quad (\text{even})$$

$$H_1(\xi) = 2\xi \quad (\text{odd})$$

$$H_2(\xi) = 4\xi^2 - 2 \quad (\text{even})$$

$$H_3(\xi) = 8\xi^3 - 12\xi \quad (\text{odd})$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \quad (\text{even})$$

$$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi \quad (\text{odd})$$

Etc.

The energy levels for a harmonic oscillator are equally spaced

$$E_n = \hbar \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right) \quad n = 0, 1, 2, 3, \dots$$

with $E_{n+1} - E_n = \Delta E = (h/2\pi)(k/\mu)^{1/2}$.

Experiments show that homonuclear diatomics, such as N_2 , have no vibrational spectra of significant intensity.

For heteronuclear diatomics, such as CO, only one relatively intense vibrational frequency (the **fundamental frequency**) is observed:

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Why? Shouldn't there be an infinite number of $n \leftrightarrow n'$ transitions $1 \leftrightarrow 2, 1 \leftrightarrow 3, 1 \leftrightarrow 4, \dots, 2 \leftrightarrow 3, 2 \leftrightarrow 4, 2 \leftrightarrow 5, \dots$ with frequencies $\nu_0, 2\nu_0, 3\nu_0, 4\nu_0, \dots$?

To see if transitions between different vibrational states are allowed (*i.e.*, probable), time-dependent perturbation theory suggests that we look at the dipole transition moment $(\mu_z)_{n,n'}$ between the different vibrational states

$$n \rightarrow n' \quad \text{transition}$$

The degree of charge separation, and therefore the dipole moment along the bond axis (assumed to be the z -axis), can change as the bond length oscillates, so the dipole moment, in general, is a function of q (the deviation from the equilibrium bond length).

Harmonic Oscillator Dipole Transition Moment

$$\begin{aligned}(\mu_z)_{n,n'} &= \int \psi_{n'}^*(x) \mu(x) \psi_n(x) dx \\ &= \int N_{n'} H_{n'}(\alpha^{1/2} x) e^{-\alpha x^2/2} \mu(x) N_n H_n(\alpha^{1/2} x) e^{-\alpha x^2/2} dx\end{aligned}$$

The dipole moment can be expanded in a Taylor series about the value μ_0 at the equilibrium bond length ($x = 0$)

$$\mu_z(x) = \mu_0 + \left(\frac{d\mu}{dx} \right)_0 x$$

to give

$$(\mu_z)_{n,n'} = \int N_{n'} H_{n'}(\alpha^{1/2} x) \left(\mu_0 + \frac{d\mu}{dx} x \right) N_n H_n(\alpha^{1/2} x) e^{-\alpha x^2} dx$$

which is equivalent to the two integrals

$$\begin{aligned}(\mu_z)_{n,n'} &= N_{n'} N_n \mu_0 \int H_{n'}(\alpha^{1/2} x) H_n(\alpha^{1/2} x) e^{-\alpha x^2} dx \\ &\quad + N_{n'} N_n \frac{d\mu}{dx} \int H_{n'}(\alpha^{1/2} x) x H_n(\alpha^{1/2} x) e^{-\alpha x^2} dx\end{aligned}$$

Because wave functions for the harmonic oscillator are orthogonal, the first integral is zero.

To evaluate the second integral, the recursion formula for Hermite polynomials

$$\xi H_n(\xi) = nH_{n-1}(\xi) + \frac{1}{2}H_{n+1}(\xi)$$

is helpful. Defining $\xi = \alpha^{1/2}x$ gives (ξ is the Greek letter xi, not to be confused with ζ , the Greek letter zeta!)

$$(\mu_z)_{n,n'} = \frac{N_{n'}N}{\alpha} \left(\frac{d\mu}{dx} \right)_0 \int H_{n'}(\xi) \left[nH_{n-1}(\xi) + \frac{1}{2}H_{n+1}(\xi) \right] e^{-\xi^2} dx$$

The Hermite polynomials are orthogonal, so the dipole transition moment is zero unless

$$\mathbf{n' = n - 1} \quad \mathbf{or} \quad \mathbf{n' = n + 1}$$

This gives the important selection rule for the allowed transitions for the harmonic oscillator:

Rule #1. $\Delta n = \pm 1$

In addition, the factor $(d\mu/dx)_0$ in the expression for the dipole transition moment gives

Rule #2. The dipole moment of the molecule must vary during a vibration.

Can you use the second rule to understand why homonuclear diatomics are infrared inactive? Does this mean homonuclear diatomics are not vibrating?

Carbon dioxide (O=C=O) has no permanent dipole, but it is strongly infrared active. (Go ask the environmentalists). Why?

Transitions with $\Delta n = \pm 2$ (called **overtones**), forbidden by rule #1, are in fact routinely observed, though relatively weak in intensity. Can you explain this? Is quantum mechanics wrong?

Spectroscopic Selection Rules for Diatomic Rigid Rotors

The time-dependent perturbation theory of spectroscopic transitions combined with the properties of spherical harmonics can be used to derive the selection rules for **linear rigid rotors**. These rules give the observed rotational spectra of diatomics and other molecules.

The wave functions for rigid rotors are spherical harmonics $Y_J^M(\theta, \phi)$

$$\hat{H}Y_J^M(\theta, \phi) = E_J Y_J^M(\theta, \phi)$$

with rotational energies

$$E_J = \frac{J(J+1)\hbar^2}{2I} \quad J = 0, 1, 2, 3, \dots$$

I is the moment of inertia

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

Spherical harmonic functions are also eigenfunctions of the operator for the square of angular momentum

$$\hat{L}^2 Y_J^M(\theta, \phi) = \hbar^2 J(J+1) Y_J^M(\theta, \phi)$$

and the operator for the z -component of the angular momentum

$$\hat{L}_z Y_J^M(\theta, \phi) = \hbar M Y_J^M(\theta, \phi)$$

with respective eigenvalues $\hbar^2 J(J+1)$ and $\hbar M$. The energy of the rotor and the corresponding squared angular momentum differ only by a factor of $I/2$ (*why?*).

But what about the spectroscopy?

To see if transitions between different rotational states are allowed (*i.e.*, probable), time-dependent perturbation theory suggests that we look at the **dipole transition moment** between the different states

$$M', J' \rightarrow M, J$$

Using $\mu_z = \mu \cos \theta$, for the electric field from the radiation, we get

$$\begin{aligned} (\mu_z)_{JM, J'M'} &= \iint Y_{J'}^{M'}(\theta, \phi)^* \hat{\mu} Y_J^M(\theta, \phi) \sin \theta d\theta d\phi \\ &= \mu \iint Y_{J'}^{M'}(\theta, \phi)^* Y_J^M(\theta, \phi) \sin \theta \cos \theta d\theta d\phi \end{aligned}$$

Notice: the dipole moment μ must be nonzero for the transition moment to be nonzero. So, according to the rigid rotor model:

Rule #1. A diatomic must have a permanent electric dipole to have a rotational spectrum.

Why? It is instructive to think about what happens when a diatomic molecule is placed in an electric field (assumed to be in the z -direction).

To generate an energy change, and therefore an interaction between the electric field and the molecule, there must be a separation of charge along the z axis.

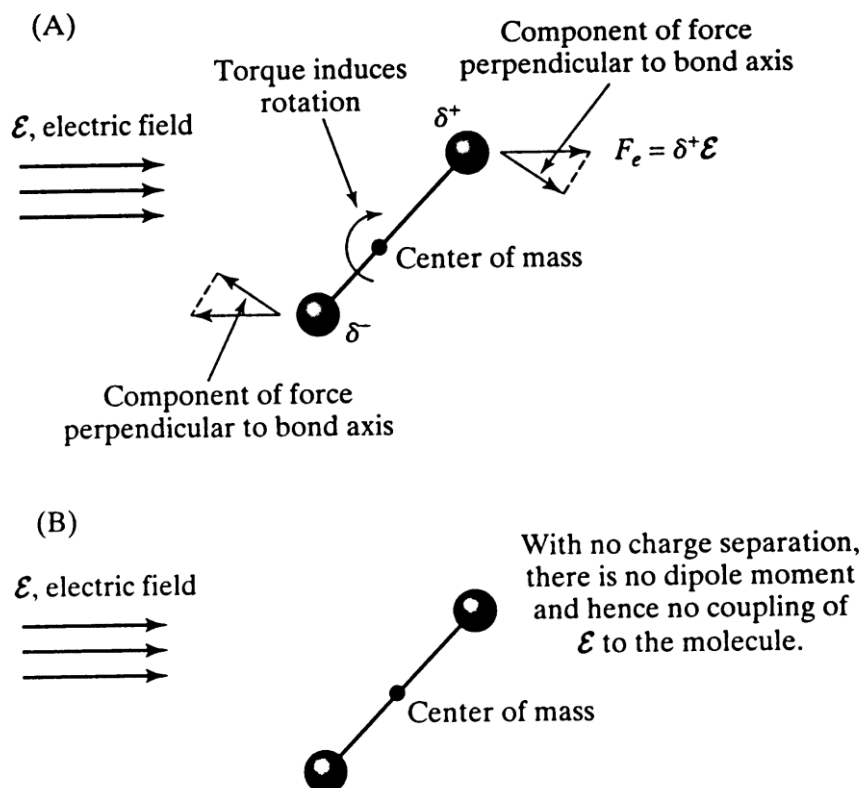
$$\text{electric potential energy} = -\vec{\mu} \cdot \vec{E}$$

Why is there a minus sign? The electric field is defined as the negative gradient in the electric potential. It gives the direction in which a mobile positive charge would move.

$$\vec{E} = -\nabla\phi$$

So a positive electric field combined with a positive dipole has negative potential energy.

Interaction of an Electric Field with a Diatomic Molecule



Next we ask: for what values of the quantum numbers M' , J' , M , J is the transition moment nonzero? From our treatment of a three-dimensional rotor

$$Y_J^M(\theta, \phi) = N_{M,J} P_J^{|M|}(\cos \theta) e^{iM\phi}$$

where $N_{M,J}$ is a normalization constant and $P_J^{|M|}(\cos \theta)$ is a Legendre function. Letting $x = \cos \theta$ and noting that $dx = -\sin \theta d\theta$, the expression for the transition moment dipole becomes

$$(\mu_z)_{JM, J'M'} = \mu N_{J'M'} N_{JM} \int_0^{2\pi} e^{i(M-M')\phi} d\phi \int_{-1}^1 x P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral in ϕ vanishes unless $M = M'$. This condition gives selection rule #2:

$$\boxed{\#2. \quad \Delta M = 0}$$

Why? Notice from the diagram above that the electric field exerts a twisting force (torque) on the molecule affecting its rotation in a plane *parallel to the z axis*, so there is no change in the z-angular momentum (*rotation perpendicular to the z-axis*).

Integration over ϕ for $M = M'$ gives a factor of 2π :

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

To complete the selection rules for diatomics, we can substitute result from the recursion rule for Legendre functions

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

into the integral for the transition dipole moment to get

$$(\mu_z)_{JM, J'M} = 2\pi\mu N_{J'M} N_{JM} \int_{-1}^1 \left[\frac{J - |M| + 1}{2J + 1} P_{J+1}^{|M|} + \frac{J + |M|}{2J + 1} P_{J-1}^{|M|} \right] P_{J'}^{|M|}(x) dx$$

The $P_J^{|M|}(x)$ functions are orthonormal, so integrals over $P_{J+1}^{|M|}(x)$, $P_J^{|M|}(x)$ and $P_{J-1}^{|M|}(x)$ will be nonzero only if $J' = J + 1$ or $J' = J - 1$, respectively. This result gives the final selection rule for the rotational transitions for diatomics:

$$\boxed{\#3. \quad \Delta J = \pm 1}$$

Spectroscopic Selection Rules for the Hydrogen Atom

(electronic transitions)

principal quantum number

$$\boxed{\Delta n \text{ unrestricted}}$$

angular momentum quantum number

$$\boxed{\Delta l = \pm 1}$$

m quantum number

$$\boxed{\Delta m = 0, \pm 1}$$