SUMMARY of SELECTION RULES

all of which are based on:

In order that $\int \psi^*_{initial} \vec{\mu} \psi_{final} d\tau \neq 0$,

$\Gamma_{initial} \otimes \Gamma_{\mu} \otimes \Gamma_{final}$ must contain A_{1g}, or A_1, or ...

ELECTRIC DIPOLE SPECTROSCOPY:

ELECTRONIC transitions: uV-Visible

If, as is usual, the ground state is totally sym.

$\Gamma_{excited\ state} = \Gamma_x$ or Γ_y or Γ_z

accompanied by

Δv : intensity determined by overlap for 0-0 and totally sym. vibrations only

accompanied by

$\Delta J = \begin{cases} +1 & R\ branch \\ -1 & P\ branch \end{cases}$

$\Delta M_J = 0, \pm 1$

VIBRATIONAL transitions: infrared

Ground state ($v = 0$ for all modes) is totally symmetric

$\Gamma_{vib} = \Gamma_x$ or Γ_y or Γ_z

$\Delta v = 1$ most intense, others also observed

accompanied by

$\Delta J = \begin{cases} +1 & R\ branch \\ -1 & P\ branch \end{cases}$

$\Delta J = 0$ Q branch except for $\Sigma - \Sigma$ vibrational transitions e.g. diatomic molecule

$\Delta M_J = 0, \pm 1$

PURE ROTATIONAL transitions: microwave

Many of the lower rotational states are occupied

Molecule must have a permanent electric dipole moment, (i.e., Γ_x or Γ_y or Γ_z is totally symmetric

$\Delta J = 1$ $\Delta M_J = 0, \pm 1$

Raman Spectroscopy

$H^{(1)}(t) = -\vec{\mu}_{induced} \cdot \vec{E}(t)$ $\quad \vec{\mu}_{induced} = \underline{\alpha}\,\vec{E}$

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

For diatomics,

$$\alpha = \alpha_{eq} + \left(\frac{\partial \alpha}{\partial R}\right)_{eq} (R - R_e) + \cdots$$

For polyatomics,

$$\alpha = \alpha_{eq} + \sum_k \left(\frac{\partial \alpha}{\partial Q_k}\right)_{eq} Q_k + \cdots$$

$\left(\frac{\partial \alpha}{\partial Q_k}\right) = 0$ unless Q_k belongs to the same IRREP as that component of α, i.e., α_{xx} or α_{xy} or ... $\Gamma_{Q_k} = \Gamma_\alpha$

Then,

$\left(\frac{\partial \alpha}{\partial Q_k}\right)_{eq} \int \psi^*_{v_k''} Q_k \psi_{v_k'} \, d\tau$ determines the intensity

$\Gamma_{v_k''} \otimes \Gamma_{Q_k} \otimes \Gamma_{v_k'}$ must contain the totally symmetric representation

If this is the ground vibrational state, then $\Gamma_{v_k''}$ is totally symmetric

so that $\Gamma_{v_k'} = \Gamma_{Q_k} = \Gamma_\alpha$

ONLY THOSE VIBRATIONS that belong to the same symmetry species as α_{xx}, α_{xy}, etc. are "RAMAN-active."

For diatomic molecules, $(R - R_e)$ belongs to Γ_α, therefore vibrational Raman spectra will be observed for diatomics

RAMAN SCATTERING SPECTROSCOPY:

VIBRATIONAL RAMAN

$\Gamma_{vib} = \Gamma_{xx}$ or Γ_{xy} or Γ_{xz} or Γ_{yy} or Γ_{yz} or Γ_{zz}

$\Delta V = 1$ most intense, others also observed accompanied by

$\Delta J = 0$ Q branch

$\Delta J = \begin{cases} +2 & S \text{ branch} \\ -2 & O \text{ branch} \end{cases}$

PURE ROTATIONAL RAMAN

$\Delta J = \begin{cases} +2 & S \text{ branch} \\ -2 & O \text{ branch} \end{cases}$

"FORBIDDEN" transitions may be observed when perturbations mix up states. Even in these cases SYMMETRY dictates what mixing is allowed, i.e.,

$\int \psi_a^* h \psi_b \, d\tau \neq 0$ only if $\Gamma_a \otimes \Gamma_h \otimes \Gamma_b$ contains A_{1g}, or A_1, or ...

VIBRONIC COUPLING: Mix in some bright state

$\Gamma_{Q_k} = \Gamma_{\text{excited elec. state}} \otimes \Gamma_{x,y,z}$ ← bright state and $\Gamma_{vib} = \Gamma_{Q_k}$

SPIN-ORBIT COUPLING: Mix in some singlet state which is either a bright state itself or is vibronically mixed with a bright state.

$\Gamma_{\text{excited elec state (triplet)}} \otimes \Gamma_{R_x, R_y, R_z} = \Gamma_{\text{some singlet state}}$

WHAT MAKES "FORBIDDEN" TRANSITIONS OBSERVABLE?

A. Vibrational-electronic coupling ⇒ "VIBRONIC" transitions

Consider the electric dipole transition probability between the states Ψ_{g0} and Ψ_{exv}

$$M = \int \Psi_{g0}^{*}\, \vec{\mu}\, \Psi_{exv}\, d\tau = \iint \psi_g^{*}(\vec{r},Q)\, \vec{\mu}\, \psi_{ex}(\vec{r},Q)\, d\vec{r}\; \psi_{vib\,0}^{*(g)}(Q)\, \psi_{vib\,v}^{(ex)}(Q)\, dQ$$

$$H_{pert} = \sum_{k=1}^{3N-6} \left(\frac{\partial H_{elec}}{\partial Q_k}\right)_{eq} Q_k$$

H_{pert} can mix the electronic states of the system:

$$\psi_{ex}^{(1)}(\vec{r},Q) = \psi_{ex}^{(0)}(\vec{r},Q) + \sum_{j}^{elec.st.} \sum_{k}^{vib\ modes} \underbrace{\frac{Q_k \int \psi_{ex}^{*(0)} \left(\frac{\partial H_{elec}}{\partial Q_k}\right)_{eq} \psi_j^{(0)}\, d\tau}{E_j^{(0)} - E_{ex}^{(0)}}}_{\text{mixing coefficients}} \psi_j^{(0)}(\vec{r},Q)$$

$$M = \int \psi_g^{(0)*}\, \vec{\mu}\, \psi_{ex}^{(0)}(\vec{r},Q_{eq})\, d\vec{r} \cdot \int \psi_0^{(g)}(Q)\, \psi_v^{(ex)}(Q)\, dQ$$

$$+ \sum_{j \neq ex} \int \psi_g^{(0)*}\, \mu\, \psi_j^{(0)}(\vec{r},Q_{eq})\, d\vec{r} \cdot \sum_k \frac{\int \psi_{ex}^{*(0)} \left(\frac{\partial H_{elec}}{\partial Q_k}\right)_{eq} \psi_j^{(0)}\, d\tau}{E_j^{(0)} - E_{ex}^{(0)}} \cdot \int \psi_0^{(g)} Q_k\, \psi_v^{(ex)}\, dQ$$

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$$H_{vert} = \sum_{k=1}^{3N-6} \left(\frac{\partial H_{elec}}{\partial Q_k} \right)_{eq} Q_k$$

H_{vert} can mix the electronic states of the system:

$$\psi_{ex}^{(1)}(\vec{r};Q) = \psi_{ex}^{(0)}(\vec{r};Q) + \sum_{j}^{\text{elec. st.}} \sum_{k}^{\text{vib modes}} \frac{Q_k \int \psi_{ex}^{*(0)} \left(\frac{\partial H_{elec}}{\partial Q_k} \right)_{eq} \psi_j^{(0)} \, d\tau}{E_j^{(0)} - E_{ex}^{(0)}} \psi_j^{(0)}(\vec{r};Q_{eq})$$

mixing coefficients

$\Gamma_g \otimes \Gamma_{x,y,z} \otimes \Gamma_{ex}$ must be tot. sym.

$$M = \int \psi_g^{(0)*} \vec{\mu} \psi_{ex}^{(0)}(\vec{r};Q_{eq}) \, d\vec{r} \cdot \int \psi_0^{(g)}(Q) \, \psi_v^{(ex)}(Q) \, dQ$$

$$+ \sum_{j \neq ex} \int \psi_g^{(0)*} \mu \psi_j^{(0)}(\vec{r};Q_{eq}) \, d\vec{r} \cdot \sum_k \frac{\int \psi_{ex}^{*(0)} \left(\frac{\partial H_{elec}}{\partial Q_k} \right)_{eq} \psi_j^{(0)} \, d\tau}{E_j^{(0)} - E_{ex}^{(0)}} \cdot \int \psi_0^{(g)} Q_k \psi_v^{(ex)} \, dQ$$

$\Gamma_g \otimes \Gamma_{x,y,z} \otimes \Gamma_j$

non-zero only if $\Gamma_j = \Gamma_x$ or Γ_y or Γ_z

provided the ground electronic state is totally symmetric

$\Gamma_{ex} \otimes \Gamma_{Q_k} \otimes \Gamma_j$

∴ must have $\Gamma_{Q_k} = \Gamma_{ex} \otimes \Gamma_j = \Gamma_{ex} \otimes \Gamma_{x,y,z}$

Q_k cannot be totally symmetric since Γ_{ex} was not Γ_x or Γ_y or Γ_z

$\Gamma_{Q_k} \otimes \Gamma_v$

∴ must have $\Gamma_v = \Gamma_{Q_k}$

In words we say that: The intensity has been stolen or borrowed from the jth electronic state. This has to be accompanied by a change in vibrational state for a NON-TOTALLY SYMMETRIC vibration. (NO 0-0 band observed.)

On the other hand, if the electronic transition is ALLOWED by symmetry, then it is accompanied by a 0-0 band, and a change in vibrational state for TOTALLY SYMMETRIC vibrations ONLY.

B. Spin-orbit Coupling —

This gives singlet ($S=0$) states some triplet ($S=1$) character and gives triplet states some singlet character.

Example a SINGLET STATE:

$$^1\Psi(1,2) = \phi(1)\cdot\phi'(2)\cdot\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}$$

TRIPLET STATE $\cdot\ ^3\Psi(1,2) = [\phi(1)\phi'(2)-\phi'(1)\phi(2)]\cdot$ { $\alpha(1)\alpha(2)$ or $\beta(1)\beta(2)$ or $\frac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{\sqrt{2}}$

$$H_{pert} = \sum_i \zeta(i)\,\vec{l}_i\cdot\vec{s}_i$$

a) The s_z terms INDUCE SINGLET-TRIPLET MIXING:

$$(\zeta(1)\,l_{z_1}\,s_{z_1} + \zeta(2)\,l_{z_2}\,s_{z_2})\,\phi(1)\cdot\phi'(2)\,\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}$$

$$= [\phi'(2)\,\zeta(1)\,l_{z_1}\,\phi(1) - \phi(1)\,\zeta(2)\,l_{z_2}\,\phi'(2)]\,\frac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{2\sqrt{2}}$$

b) The s_x and s_y terms can be written as RAISING and LOWERING operators which will INDUCE SINGLET-TRIPLET MIXING too

Now need only to find the non-zero matrix elements of $\vec{l}$ between the electronic space functions:

$$\int \psi_{ex}^{(0)} \vec{l} \, \psi_j^{(0)}(\vec{r}, Q_q) \, d\vec{r}$$

$\vec{l}$: Γ_{R_x} or Γ_{R_y} or Γ_{R_z}

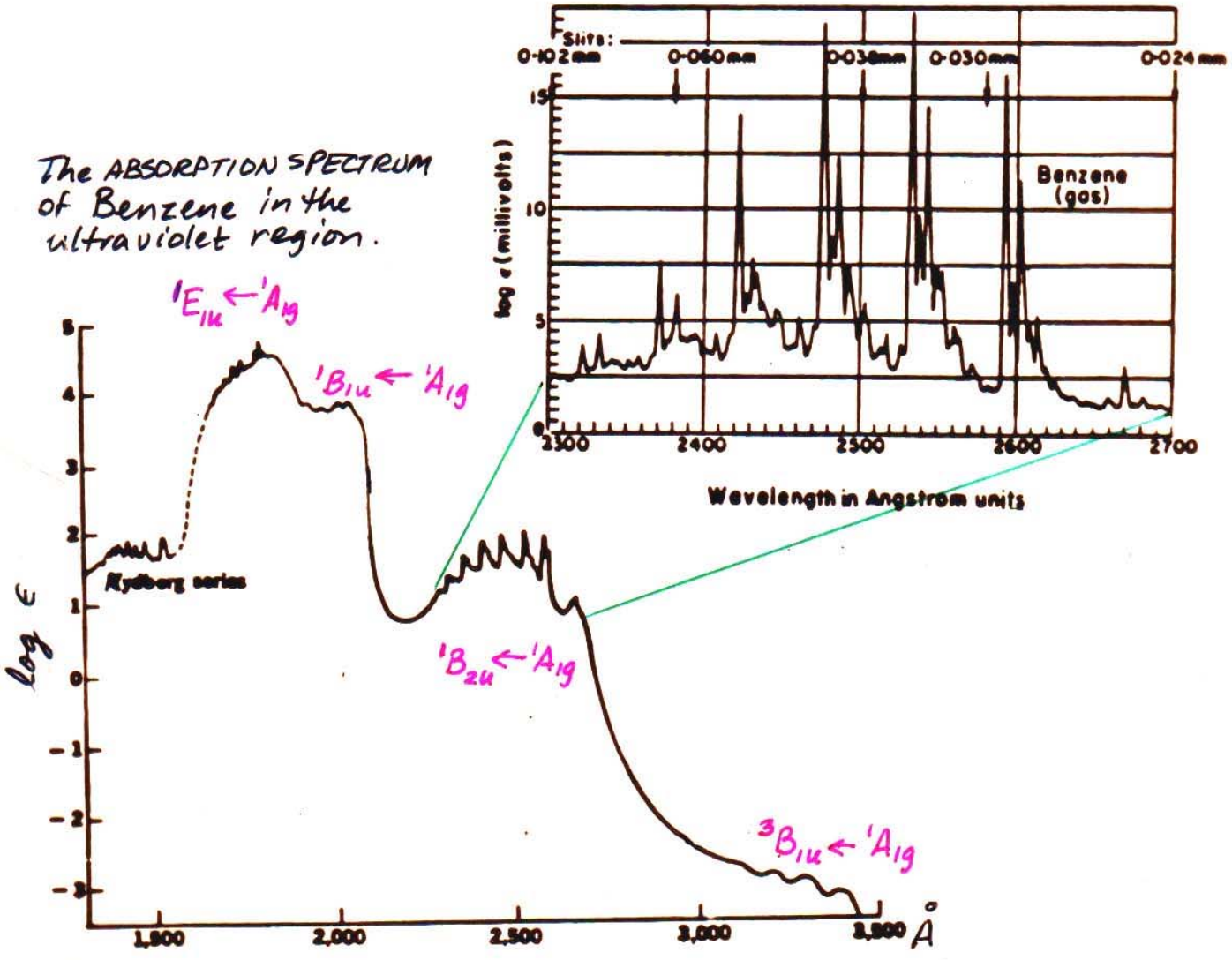
$\Gamma_{ex} \otimes \Gamma_{R_x, R_y, R_z} \otimes \Gamma_j$

In the benzene example, where $\Gamma_{ex} = {}^3B_{1u}$ $\Gamma_{R_x, R_y} = E_{1g}$ $\Gamma_{R_z} = A_{2g}$, Γ_j must therefore be ${}^1B_{2u}$ or ${}^1E_{2u}$.

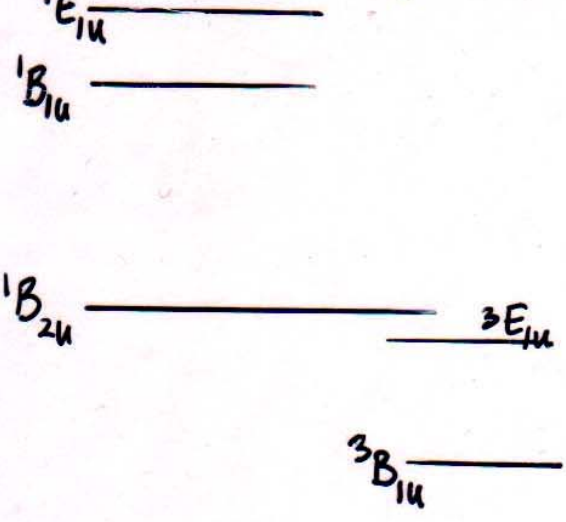
Therefore, the very weak benzene transition ${}^3B_{1u} \leftarrow {}^1A_{1g}$ (7 orders of magnitude less intense than the allowed ${}^1E_{1u} \leftarrow {}^1A_{1g}$.) occurs by ${}^3B_{1u}$ mixing up with a little bit of ${}^1B_{2u}$ (courtesy of the l_x operator) and the intensity is borrowed from the medium weak transition (3 orders of magnitude less intense than the allowed ${}^1E_{1u} \leftarrow {}^1A_{1g}$) ${}^1B_{2u} \leftarrow {}^1A_{1g}$, which in turn is only made possible by vibrational mixing (courtesy of the E_{2g} vibrations)

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

The ABSORPTION SPECTRUM of Benzene in the ultraviolet region.



Benzene energy levels showing low-lying singlet and triplet electronic states.



① $^1E_{1u} \leftarrow {}^1A_{1g}$ "ALLOWED"

$\Gamma_{x,y}$

② $^1B_{1u} \leftarrow {}^1A_{1g}$ "FORBIDDEN"

Need to mix some $^1E_{1u}$ into $^1B_{1u}$:

$B_{1u} \otimes \Gamma_{Q_k} \otimes E_{1u}$ must be A_{1g}

that is, $\Gamma_{Q_k} = B_{1u} \otimes E_{1u} = E_{2g}$

Thus, $^1B_{1u}$ borrows some intensity from $^1E_{1u}$ state by using E_{2g} vibrations.

③ $^1B_{2u} \leftarrow {}^1A_{1g}$ "FORBIDDEN"

Need to mix some $^1E_{1u}$ into $^1B_{2u}$:

$B_{2u} \otimes \Gamma_{Q_k} \otimes E_{1u}$ must be A_{1g},

that is, $\Gamma_{Q_k} = B_{2u} \otimes E_{1u} = E_{2g}$

Thus, $^1B_{2u}$ borrows some intensity from $^1E_{1u}$ state by using E_{2g} vibrations. Mixing coefficient is smaller than for $^1B_{1u}$ since the $(E^{(0)}_{^1E_{1u}} - E^{(0)}_{^1B_{2u}})$ in the denominator is larger than the $(E^{(0)}_{^1E_{1u}} - E^{(0)}_{^1B_{1u}})$ case, thus the intensity obsd. is about two orders of magnitude smaller for the $^1B_{2u} \leftarrow {}^1A_{1g}$ compared to the $^1B_{1u} \leftarrow {}^1A_{1g}$