Lecture #9: The Born-Oppenheimer Approach to Transitions

- Selection Rules
- Relative Intensities

First of 3 lectures illustrating simplest patterns in 3 main types of transitions - mostly for diatomic molecules

permanent $\mu$ pure rotation (microwave) $\Delta v \equiv 0$
change in $\mu$ rotation-vibration (IR) $\Delta v \approx \pm 1$
electronic symmetries rotation-vibration-electronic (UV – VIS) $\Delta v = \text{any}$

How does the Born-Oppenheimer Approximation help us to predict what to expect in the spectrum?

Begin reading Hougen monograph [http://physics.nist.gov/Pubs/Mono115/contents.html](http://physics.nist.gov/Pubs/Mono115/contents.html)
Chapter 6 of Bernath

KEY TOPICS

* Electric dipole transitions: $e \sum_{\alpha} \vec{r}_\alpha \rightarrow \vec{M}_{if}(R)$
  
  integrate over $r$

* DIRECTION COSINES LAB XYZ $\rightarrow$ body xyz
  
  integrate over $\theta, \phi, \chi$

* Selection Rules
  
  symmetry and propensity

* Hönl-London rotational linestrength factors
  
  sum over $M_j$

Last time I was concerned with how to go

$$\hat{H} \rightarrow \hat{H}^\circ + \hat{H}' \rightarrow E_{evJ}$$

exact simplified missing exact

This was mostly formal.
As spectroscopists we care much less about how to compute spectra *ab initio* than how to extract information from real spectra.

The reason the Born-Oppenheimer approximation is so important is that it enables us to simplify our interpretation of spectra.
It is very helpful to think of $E_{evr} = T_i + G_i(v) + F_{i,v}(J)$

and that all electronic properties vary slowly with $R$, and all observable quantities normally vary smoothly with $v,J$.

All non-smooth variations should be explained by resonances in an energy denominator of a perturbation expansion.

Expect to find patterns in spectra that can be represented as power series in $(v + 1/2)$ and $J(J + 1)$.

\[
E_{ivJ} = T^i_e + \sum_{\ell,m} Y_{\ell,m} (v + 1/2)^\ell [J(J + 1)]^m
\]

The $Y_{\ell,m}$ are "molecular constants". They are of no special importance except as intermediate step in $E_{evr} \rightarrow V_{i,j}(R)$.

For the present, we must concentrate on how to go from spectrum $\rightarrow Y_{\ell,m}$.

To do this we need to know what will appear in the spectrum:
* selection rules
* relative intensity patterns

electric dipole transitions

\[
P_{if} \propto |\langle i | \langle v_i | \langle \Omega_i J_i M_i | \vec{E}_L \cdot \vec{\mu}_b | \Omega_f J_f M_f \rangle | v_f \rangle | f \rangle|^2
\]

oscillating electric field in LAB
body (dipole antenna)
body-fixed coordinates of $e^-$ with respect to center of mass.

All of this and next Lecture deals with above equation.
In the spirit of Born-Oppenheimer we get rid of all electronic coordinates by integrating over \( r \).

Only the electronic wavefunctions and \( \sum_{\alpha} \vec{r}_\alpha \) depend on \( r \).

\[
e \left\langle i \left| \sum_{\alpha} \vec{r}_\alpha \right| f \right\rangle \equiv \vec{M}_{if} (R)
\]

\[\text{transition dipole moment function}\]

next we integrate over \( \theta, \phi \): the orientation of body \( z \) with respect to LAB XYZ (for polyatomics we would need 3 Euler angles).

\[\text{DIRECTION COSINES} \quad \vec{e}_L \cdot \vec{\mu}_b = (\varepsilon_x \hat{X} + \varepsilon_y \hat{Y} + \varepsilon_z \hat{Z}) \cdot (M_x \hat{x} + M_y \hat{y} + M_z \hat{z})\]

\[\hat{X} \cdot \hat{x} \equiv \cos (\hat{X}, \hat{x}) \quad \alpha_{\text{LAB}} \text{ a 3 } \times \text{ 3 matrix}\]

\[
\alpha(\theta, \phi) = \begin{pmatrix}
\hat{X}\hat{x} & \hat{X}\hat{y} & \hat{X}\hat{z} \\
\hat{Y}\hat{x} & \hat{Y}\hat{y} & \hat{Y}\hat{z} \\
\hat{Z}\hat{x} & \hat{Z}\hat{y} & \hat{Z}\hat{z}
\end{pmatrix}
\]

It requires 3 Euler angles to define XYZ with respect to xyz, but \( \theta, \phi \) are only 2 needed for a diatomic molecule.
In order to specify $\vec{r}$ in both LAB and body, need one more angle. Phase choice — conventionally used in *ab initio* calculations. Unexpected result below. [Why do we care? Electronic coordinates. Nuclei are by definition on the z axis.] This is the transformation that relates LAB to body (fixed choice of $x = \pi/2$).

$$
\begin{pmatrix}
X \\
Y \\
Z
\end{pmatrix}
= \begin{pmatrix}
-\sin \phi & -\cos \theta \cos \phi & \sin \theta \cos \phi \\
\cos \phi & -\cos \theta \sin \phi & \sin \theta \sin \phi \\
0 & \sin \theta & \cos \theta
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
\alpha(\theta, \phi)
$$

LAB

This is the direction cosine matrix. See Hougen page 18

Does not need to be Hermitian. Needs only to be unitary $\alpha^{-1} = \alpha^\dagger$. Check!

Note that, when $\theta = \phi = 0$ (z along Z), we can see unexpected effect of arbitrary phase choice.

$$
\alpha(0,0) = \begin{pmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
$$
i.e. $Y \leftrightarrow x$

X $\leftrightarrow$ $-y$

(extra rotation about Z by $\pi/2$)

OK, now we are ready to do the $\theta, \phi$ integration.

Only factor in $\mathcal{E} \cdot \vec{M}_{if}$ integral that depends on $\theta, \phi$ is $|\Omega J M\rangle$

$|\langle \theta \phi | \Omega J M \rangle|^2$ is probability of finding $z$ pointing in $\theta \phi$ direction with respect to XYZ.

$$
\langle \Omega_i \text{J}_i \text{M}_i | \alpha_{Lb} | \Omega_f \text{J}_f \text{M}_f \rangle_{\theta, \phi}
$$

**Selection rules**

<table>
<thead>
<tr>
<th>BRANCH</th>
<th>$\Delta J = 0, \pm 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TYPE OF BAND</td>
<td>$\Delta \Omega = 0$ for $M_{z,if} \neq 0$ “parallel” or $\Delta \Omega = \pm 1$ for $M_{x,if}$ or $M_{y,if} \neq 0$ “$\perp$”</td>
</tr>
<tr>
<td>POLARIZATION</td>
<td>$\Delta M_J = 0$ for $\epsilon_z \neq 0$ “$\pi$”-polarized, $\Delta M = \pm 1$ for $\epsilon_x$ or $\epsilon_y \neq 0$ “$\sigma$”</td>
</tr>
</tbody>
</table>
So we have
\[ P_{if} \propto \sum_{S,b} \varepsilon_S \left\langle v_i \left| M_{b,if} (R) \right| v_f \right\rangle \left\langle \Omega_{iJiM_i} \left| \alpha_{Sb} \right| \Omega_{fJfM_f} \right\rangle \theta,\phi \]

\[ \text{sum inside of } i \equiv f \]

overall intensity

polarization dependence
rotational selection rules
sub-band selection rule

OK. Now let’s look at specific cases.

**Pure Rotation Spectrum**

\[ i \equiv f \]
\[ v_i \equiv v_f \]

\[ \varepsilon \text{ (only } \Omega = \Lambda) \]

\[ \Delta \Omega = 0 \leftrightarrow M_{i,ii} \neq 0 \]

\[ \text{only possibility} \]

\[ \text{Moreover, if light is linearly polarized, we can choose } Z \text{ as polarization axis, then} \]
\[ \varepsilon_{Z} \neq 0 \leftrightarrow \Delta M = 0 \]

\[ \alpha_{Sb} \text{'s are product of 2 factors: body and LAB} \]

\[ \text{ME's are not so simple for polyatomics} \]

\[ \text{only one component of transition moment is non-zero} \]

So we have simplified it to
\[ P_{if} \propto \sum_{S,b} \varepsilon_S^2 \left\langle v_i \left| M_{z,ii} (R) \right| v_i \right\rangle \left\langle \Omega_{iJiM_i} \left| \alpha_{Zz} \right| \Omega_{fJfM_f} \right\rangle \theta,\phi \]

Next we consider selection rules for 2 factors in this equation.

\[ \bar{\mu} = e \bar{r} \text{ is odd with respect to } i \]

Body-fixed inversion: \[ i \]

[not LAB inversion: \( I \)] which defines parity in atoms

\[ i \Phi_i(r;R) \neq \pm \Phi_i(r;R) \text{ (i on total wavefunction)} \]

not a guaranteed symmetry

**except** for homonuclear molecule

\[ g,u \text{ symmetry} \]

**no pure rotation spectrum for homonuclear** \[ M_i(R) = 0 \]

**yes pure rotation spectrum for heteronuclear** \[ M_i(R) \neq 0 \]
All diatomic molecules have $\sigma_v(xz)$ and $\sigma_v(yz)$ symmetry elements. This means that $M_{x,ii} = M_{y,ii} = 0$ for all diatomic molecules.

So, for diatomic molecule we have only one non-zero component of $\vec{M}(R)$ (unless homonuclear).

Expand in power series about $R_e$ (or some other convenient point)

$$M_{z,ii}(R) = M_{z,ii}(R_e) + \frac{dM}{dR} \bigg|_{R=R_e} (R - R_e) + \frac{1}{2} \frac{d^2M}{dR^2} \bigg|_{R=R_e} (R - R_e)^2$$

Now we can take vibrational matrix elements.

$$\langle v_1 | M_{z,ii}(R) | v_i \rangle_R = M_{z,ii}(R_e) + \frac{dM}{dQ} \bigg|_{Q=0} (Q_{v_1v_i}) + \frac{1}{2} \frac{d^2M}{dQ^2} (Q^2)_{v_1v_i}$$

$Q$ and $Q^2$ matrix elements are trivial in Harmonic Oscillator Basis Set.

$$\langle v | Q | v \rangle = 0$$

$$\langle v | Q^2 | v \rangle = \frac{\hbar}{\mu \omega} (v + 1/2)$$

So this tells us that

* pure rotation $\propto |M_{z,ii}(R_e)|^2$

* varies negligibly with $v$ (intensity $\approx$ const. + small $v^2$ term)

* present treatment ignores $J$-dependence of $V_{ij}(R) \rightarrow \chi_{i,v,J}$ - usually negligible