5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

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 μ	pure rotation (microwave)	$\Delta v \equiv 0$
change in μ	rotation-vibration (IR)	$\Delta v \approx \pm 1$
electronic symmetries	rotation-vibration-electronic (UV – VIS)	$\Delta v =$ 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
Chapter 6 of Bernath

KEY TOPICS

* Electric dipole transitions: $e \sum_{\substack{\alpha \\ \text{electrons}}} \vec{r}_\alpha \rightarrow \underbrace{\vec{M}_{if}}_{\substack{\text{vector} \\ \text{in body}}} (R)$

integrate over r

* DIRECTION COSINES LAB XYZ → body xyz

integrate over θ, ϕ, χ

* Selection Rules

symmetry and propensity

* Hönl-London rotational linestrength factors

sum over M_J

Last time I was concerned with how to go

$$\underset{\text{exact}}{\hat{\mathbf{H}}} \rightarrow \underset{\text{simplified}}{\hat{\mathbf{H}}^\circ} + \underset{\substack{\text{missing} \\ \text{stuff}}}{\hat{\mathbf{H}}'} \rightarrow \underset{\text{exact}}{E_{evJ}}$$

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

$$\begin{tikzcd}[column sep=tiny]
E_{evr} = & T_i & + & G_i(v) & + & F_{i,v}(J) \\
& \Phi_i(r;R) \arrow[u] & & \chi_{i,v}(R) \arrow[u] & & |\Omega JM\rangle \arrow[u] \\
& & & V_{i,J}(R) \arrow[u] & &
\end{tikzcd}$$

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 $J(J + 1)$.

BRUTE
FORCE

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

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

$$P_{if} \propto \left|\langle i|\left\langle v_i\left|\left\langle \Omega_i J_i M_i \right|\vec{\varepsilon}_L \cdot \vec{\mu}_b\left|\Omega_f J_f M_f\right\rangle\right| v_f\right\rangle|f\rangle\right|^2$$

oscillating electric field in LAB

body (dipole antenna)
body-fixed coordinates of e^- with
respect to center of mass.

$$\vec{\mu} = e\sum_{\alpha} \vec{r}_{\alpha}$$

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 $\sum\limits_{\substack{\alpha \\ \text{electrons}}} \vec{r}_\alpha$ depend on r.

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

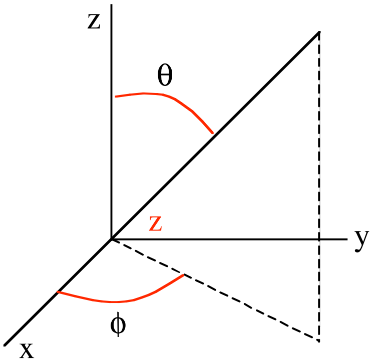
vector in body frame

$x\hat{x} + y\hat{y} + z\hat{z}$ (3 integrals)

3 M_{if} components

transition dipole moment function

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



DIRECTION COSINES

$$\vec{\varepsilon}_L \cdot \vec{\mu}_b = \left(\varepsilon_X \widehat{X} + \varepsilon_Y \widehat{Y} + \varepsilon_Z \widehat{Z}\right) \cdot \left(M_x \hat{x} + M_y \hat{y} + M\right.$$

$$\widehat{X} \cdot \hat{x} \equiv \cos\left(\widehat{X}, \hat{x}\right)$$

$\boldsymbol{\alpha}_{Lb}$ a 3 × 3 matrix

LAB body

$$\alpha(\theta,\phi) = \begin{pmatrix} \widehat{X}\hat{x} & \widehat{X}\hat{y} & \widehat{X}\hat{z} \\ & \ddots & \\ & & \widehat{Z}\hat{z} \end{pmatrix}$$

It requires 3 Euler angles to define XYZ with respect to xyz, but θ, φ 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 $x = \pi/2$).

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

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 θ,ϕ integration.

Only factor in $\vec{\varepsilon}\cdot\vec{M}_{if}$ integral that depends on θ,ϕ is $|\Omega JM\rangle$

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

$$\langle \Omega_i J_i \underset{\substack{\nearrow \\ M_J}}{M_i} | \alpha_{\underset{\substack{\nearrow \\ XYZ}}{L}\underset{\substack{\nwarrow \\ xyz}}{b}} | \Omega_f J_f M_f \rangle_{\theta,\phi}$$

direction cosine matrix elements

Selection rules

BRANCH	$\Delta J = 0, \pm 1$
TYPE OF BAND	$\Delta\Omega = 0$ for $M_{z,if} \neq 0$ "parallel" or $\Delta\Omega = \pm 1$ for $M_{x,if}$ or $M_{y,if} \neq 0$ "$\perp$"
POLARIZATION	$\Delta M_J = 0$ for $\varepsilon_z \neq 0$ "π"-polarized, $\Delta M = \pm 1$ for ε_x or $\varepsilon_y \neq 0$ "σ"

So we have

$$P_{if} \propto \left| \sum_{S,b} \varepsilon_S \underbrace{\left\langle v_i \middle| M_{b,if}(R) \middle| v_f \right\rangle_R}_{\text{overall intensity}} \underbrace{\left\langle \Omega_i J_i M_i \middle| \alpha_{Sb} \middle| \Omega_f J_f M_f \right\rangle_{\theta,\phi}}_{\substack{\text{polarization dependence} \\ \text{rotational selection rules} \\ \text{sub-band selection rule}}} \right|^2$$

$\boxed{\text{sum inside of } |\ \ |^2}$

OK. Now let's look at specific cases.

<u>Pure Rotation Spectrum</u> $i \equiv f$

$v_i \equiv v_f$

α_{Sb} ME's are product of 2 factors: body and LAB

if we restrict consideration to singlet states, $\Omega_i = \Omega_f$ $\boxed{{}^1\Lambda \text{ (only } \Omega = \Lambda)}$

$\Delta\Omega = 0 \leftrightarrow M_{z,ii} \neq 0$ $\underbrace{M_{x,ii} = M_{y,ii} = 0}$

only possibility

not so simple for polyatomics

$\boxed{\text{only one component of transition moment is non-zero}}$

Moreover, if light is linearly polarized, we can choose Z as polarization axis, then only $\varepsilon_Z \neq 0 \leftrightarrow \Delta M = 0$

So we have simplified it to

$$P_{if} \propto \underbrace{\varepsilon^2}_{\propto \text{Intensity}} \left| \left\langle v_i \middle| M_{z,ii}(R) \middle| v_i \right\rangle_R \left\langle \Omega_i J_i M_i \middle| \alpha_{Zz} \middle| \Omega_i J_f M_i \right\rangle_{\theta\phi} \right|^2$$

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

$\vec{\mu} = e\vec{r}$ is odd with respect to **i**

Body-fixed inversion: **i**
[not LAB inversion: **I**] which defines parity in atoms

i $\Phi_i(r;R) \neq \pm \Phi_i(r;R)$ (**i** on total wavefunction)

not a guaranteed symmetry **except** for homonuclear molecule

g,u symmetry

** no pure rotation spectrum for homonuclear $M_{ii}(R) = 0$
** yes pure rotation spectrum for heteronuclear $M_{ii}(R) \neq 0$

<u>All</u> diatomic molecules have $\overbrace{\sigma_v(xz) \text{ and } \sigma_v(yz)}^{\text{reflection thru plane containing internuclear axis}}$ symmetry elements.
This means that $M_{x,ii} = M_{y,ii} = 0$ for <u>all</u> 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)

The Dipole Moment Function (Permanent)

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

Now we can take vibrational matrix elements.

$$\left\langle v_i \middle| M_{z,ii}(R) \middle| v_i \right\rangle_R = \underbrace{M_{z,ii}(R_e)}_{\substack{\text{permanent dipole} \\ \text{at } R_e}} + \left.\frac{dM}{dQ}\right|_{Q=0} \left(Q_{v_i v_i}\right) + \frac{1}{2}\frac{d^2M}{dQ^2}\left(Q^2\right)_{v_i v_i}$$

Q and $\mathbf{Q}^2$ 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 $\propto \left|M_{z,ii}(R_e)\right|^2$
- * varies negligibly with v (intensity ≈ const. + small v^2 term)
- * present treatment ignores J-dependence of $V_{iJ}(R) \rightarrow \chi_{i,v,J}$ - usually negligible