5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #10: Transitions II

Last Time

oscillating electric field

$\boxed{\langle i|e\vec{r}|f\rangle_r}$

$$P_{if} \propto \underset{\boxed{\text{Intensity}}}{\varepsilon^2} \left|\sum_{S,b} \langle v_i|M_{b,if}|v_f\rangle_R \langle \Omega_i J_i M_i|\alpha_{Sb}|\Omega_f J_f M_f\rangle_{\theta,\phi}\right|^2$$

all electric dipole transition probabilities

unique radial factor

universal angular factor
- polarization: S, ΔM
- band type: b, ΔΩ
- branch type ΔJ

pure rotation i = f → b = z for diatomic (μ along z)
⇓
$v_i = v_f$ σ(xz) and σ(yz) symmetry
b = z → ΔΩ = 0

$$\langle v|M_{z,ii}(R)|v\rangle_R = \underbrace{M_{z,ii}(R_e)}_{\text{if homonuclear} \to =0} + \left.\frac{dM}{dQ}\right|_{Q=0} Q_{vv} + \frac{1}{2}\left.\frac{d^2M}{dQ^2}\right|_{Q=0} Q_{vv}^2$$

Q_{vv}^n matrix elements in Harmonic Oscillator Basis Set $(Q = R - R_e)$

$$P_{if} \propto [\underset{\mu^2}{\text{const.}} + \underset{(d\mu/dR)^2}{\text{small } v^2} \text{ term}]\left|\langle \Omega J_i M|\alpha_{Zz}|\Omega J_f M\rangle\right|^2$$

Today: finish pure rotation spectrum
Hönl-London Factors
rotation-vibration spectrum Δv = ±1 propensity rule dM/dR ≠ 0
anharmonic and centrifugal correction terms
[PERTURBATION THEORY]
rotation-vibration-electric spectrum all Δv → Franck Condon factors
R-centroid approximation
stationary phase approximation

Final factor is $\left|\langle \Omega J_i M|\alpha_{Zz}|\Omega J_f M\rangle\right|^2$ direction cosine matrix element

Each J consists of 2J + 1 degenerate M-components.

direction cosine matrix elements → sum over M → Hönl-London rotational linestrength factors

[can't do this sum so simply for OODR because initial M's are not equally populated]

see Hougen page 39, Table 7

$$\sum_{M} \left| \left\langle \Omega J_i M \right| \alpha_{Zz} \left| \Omega J_f M \right\rangle_{\theta\phi} \right|^2 \equiv S_{J_i J_f}^{\Omega\Omega} / 3$$

Herzberg Diatomics, page 208

sum rule

$$\frac{2J_f+1}{3} g_f^{el}$$

useful for checking calculations

common final state

$$\begin{cases} = \dfrac{(J_f+\Omega+1)(J_f-\Omega+1)}{3(J_f+1)} \sim \dfrac{J_f}{3} & J_i = J_f + 1 \text{ (R or P)} \\[2ex] = \dfrac{\Omega^2 (2J_f+1)}{3J_f} \sim \dfrac{2\Omega^2}{3J_f} & J_i = J_f \text{ (Q branch weak at high J)} \\[2ex] = \dfrac{(J_f+\Omega)(J_f-\Omega)}{3J_f} \sim \dfrac{J_f}{3} & J_i = J_f - 1 \text{ (P or R)} \end{cases}$$

The increase with J is due to 2J + 1 degeneracy factor being included. These formulas for a common final state do not depend on whether J_i or J_f is upper or lower state. Similar set of formulas for transitions out of common initial state.

These formulas cannot depend on our choice of quantization axis. If we sum over equal X, Y, Z polarized absorption or emission, the factor of 3 must go away because of the isotropy of space and the equivalence of X, Y, Z.

Next case: Rotation-Vibration Spectra (Diatomic or Linear Molecule)

i = f - still have $\Omega_i = \Omega_f \Rightarrow \alpha_{Zz}$

$v_i \neq v_f$

$$P_{if} \propto I\left|\left\langle v_i \middle| M_{z,ii}(R) \middle| v_f \right\rangle_R\right|^2 S^{\Omega\Omega}_{J_iJ_f}$$

exactly the same as for pure rotation spectra

Here the absolute intensity factor is slightly different from that for pure rotation — do the same power series expansion in Q about R_e (i.e. Q = 0).

$$\left\langle v_i \middle| M_{z,ii}(R) \middle| v_f \right\rangle = M_{z,ii}(R_e)\left\langle v_i \middle| v_f \right\rangle + \left.\frac{dM_{z,ii}}{dQ}\right|_{Q=0}\left\langle v_i \middle| Q \middle| v_f \right\rangle + \frac{1}{2}\left.\frac{d^2M_{z,ii}}{dQ^2}\right|_{Q=0}\left\langle v_i \middle| Q^2 \middle| v_f \right\rangle$$

$$\left\langle v_i \middle| v_f \right\rangle = 0 \text{ when } v_i \neq v_f \text{ by orthogonality}$$

$$\begin{cases} \left\langle v \middle| Q \middle| v-1 \right\rangle = \left(\dfrac{\hbar}{\mu\omega_e}\right)^{1/2} v^{1/2} \\ \text{requires } \left.\dfrac{dM}{dQ}\right|_{Q=0} \neq 0 \end{cases}$$

for harmonic oscillator
Δv = ±1 <u>propensity rule</u>
amplitude increases $\propto v^{1/2}$
$P_{if} \propto v$

Other contributors to vibrational intensities:

* vibrational anharmonicity: perturbation theory mixes <u>harmonic</u> $v_f = v_i \pm 1$ character into real $v_f \neq v_i \pm 1$ levels

* electrical anharmonicity: next term $\left.\dfrac{d^2M_{z,ii}}{dQ^2}\right|_{Q=0} \neq 0 \Rightarrow \Delta v = \pm 2$

* rotational effects. $|v_i\rangle$ for J is not orthogonal to $|v_f \neq v_i\rangle$ for J ± 1! Then permanent dipole moment, $M_{z,ii}(R_e)$, can contribute to P_{if} for $\Delta v = \pm 1$ transition.

$$|v \pm 1\rangle = \frac{\left\langle v_i \middle| B(R) \middle| v \pm 1 \right\rangle J(J+1)}{\Delta G}|v\rangle^\circ + |v \pm 1\rangle^\circ$$

$$|vJ\rangle = |v0\rangle^\circ + \sum_{v'} \frac{\left\langle v0 \middle| B(R)J(J+1) \middle| v'0 \right\rangle |v'0\rangle^\circ}{E^\circ_v - E^\circ_{v'}}$$

$$B(R) = B(R_e)\left[1 + \frac{Q}{R_e}\right]^{-2}$$

$$= B(R_e)\left[1 - 2(Q/R_e) + \ldots\right]$$

$$|vJ\rangle \approx |v0\rangle^\circ - \left(\frac{2}{R_e}\right) B(R_e) J(J+1)\left[\frac{\left\langle v,0 \middle| Q \middle| v \pm 1,0 \right\rangle}{\mp\hbar\omega}|v \pm 1,0\rangle^\circ + \ldots\right]$$

$$\left\langle v \pm 1J \middle| M(R) \middle| vJ \right\rangle = \frac{\partial M}{\partial Q}v + M(R_e)B_eJ(J+1) \text{ etc.}$$

Herman-Wallis effect. See 3 elegant papers (especially the first one) from David Nesbitt's group:

> D. Nelson, Jr., A. Schiffman, D. Yaron, and D. Nesbitt, "Absolute Infrared Transition Moments for Open Shell Diatomics from *J* Dependence of Transition Intensities: Application to OH", *J. Chem. Phys.* **90**, 5443 (1989);
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> D. Nelson, Jr., A. Schiffman, and D. Nesbitt, "The Dipole Moment Function and Vibrational Transition Intensities of OH", *J. Chem. Phys.* **90,** 5455 (1989);
>
> D. Nelson, Jr., A. Schiffman, J. Orlando, J. Burkholder, and D. Nesbitt, "H + O_3 Fourier-Transform Infrared Emission and Laser Absorption Studies of OH ($X^2\Pi$) Radical: An Experimental Dipole Moment Function and State-To-State Einstein *A* Coefficients", *J. Chem. Phys.* **93**, 7003 (1990).

cross terms give sign of dM/dR with respect to M(R_e).
Add transition amplitudes before taking $|\ \ |^2$.

Non-Lecture: Anharmonic Correction to vibrational wavefunction.

$$|\text{`v'}\rangle = |\text{v}\rangle^\circ + c_{\text{v},\text{v}\pm1}|\text{v}\pm1\rangle$$

$$V(R) = kQ^2/2 + \underbrace{aQ^3}_{\mathbf{H'}}$$

$\omega^{-3/2}$ from Q^3

$$c_{\text{v},\text{v}\pm1} = \frac{\langle \text{v}|aQ^3|\text{v}\pm1\rangle}{\pm\hbar\omega} = a\omega^{-5/2}\mu^{-3/2}\hbar^{1/2}\underbrace{f(\text{v})}\approx \text{v}^{3/2}$$

see perturbation theory
for formulas.

Pure rotation requires $M_z(R_e) \neq 0$

Vibration-Rotation mostly due to $\left.\frac{dM_z}{dQ}\right|_{Q=0} \neq 0$

$\boxed{\Delta\text{v} = \pm1 \text{ propensity, } P_{if} \propto \text{v}}$

but also vibrational and electronic anharmonicities and centrifugal distortion

nearly perfect J-independence (except centrifugal effects - hydrides)

$$\text{always}\begin{cases} M_z \neq 0 \quad \text{rotation} \qquad M_x = M_y = 0 \quad \text{“parallel type”} \\ \frac{dM_z}{dQ} \neq 0 \ \text{rotation – vibration} \quad \text{(weak Q branches)} \end{cases}$$

$\boxed{\text{recall Hönl-London factor}}$

(no such restriction to only $M_z \neq 0$ in polyatomic molecules)

$\boxed{\text{can have strong Q branches}}$

Big differences when we consider electronic transitions i ≠ f

- not restricted to only $M_z(R)$ (x,y components also)
- no simple vibrational selection or propensity rules as for the harmonic limit of vibration-rotation because $\{|v_i\rangle\}$ is not orthogonal to $\{|v_f\rangle\}$
- awkwardness about $M_{b,if}(R)$. We would like to express vibrational matrix elements of $M_{b,if}$ as function of $R_{v_i v_f}$ rather than $[M_{b,if}(R)]_{v_i v_f}$.

$\left\{\begin{array}{l}\text{R − centroid approximation}\\ \textbf{stationary phase}\text{, semi-classical Franck-Condon principle}\end{array}\right.$

vibrational intensity distribution provides information about difference in structure

$$P_{if} \propto I_Z \left| \sum_b \langle \Omega_i J_i M | \alpha_{Zb} | \Omega_f J_f M \rangle \langle v_i | M(R)_{b,if} | v_f \rangle \right|^2$$

electronic transition moment

expand M(R) about R′ — some arbitrary value since $R_{ei} \neq R_{ef}$

expand, take ME and divide through by $\langle v_i | v_f \rangle$

$$\frac{\langle v_i | M(R)_{b,if} | v_f \rangle}{\langle v_i | v_f \rangle} = M(R')_{b,if} + \left.\frac{dM}{dR}\right|_{R=R'} \left[\bar{R}_{v_i v_f} - R'\right] + \ldots$$

This looks exactly like $(R - R')^n$ expansion if R is replaced everywhere by the "R-centroid"

$$\boxed{\bar{R}_{v_i v_f} = \frac{\langle v_i | R | v_f \rangle}{\langle v_i | v_f \rangle}}$$

need to look at higher terms in expansion to see the necessity for R-centroids

provided that the R-centroid approximation is valid.

$$\overline{R^{n}_{v_i v_f}} \underset{\substack{\uparrow \\ \text{always true}}}{\equiv} \frac{\langle v_i | R^n | v_f \rangle}{\langle v_i | v_f \rangle} \underset{\substack{\uparrow \\ \text{approximation}}}{\cong} \left(\overline{R}_{v_i v_f}\right)^n$$

This is a very good approximation because of "stationary phase"
(justification for typical type of spectroscopic simplification)

Semi-classical Franck-Condon principle

See:

- * J. Tellinghuisen, "Reflection and Interference Structure in Diatomic Franck-Condon Distributions," *J. Mol. Spectrosc.* **103**, 455 (1984)

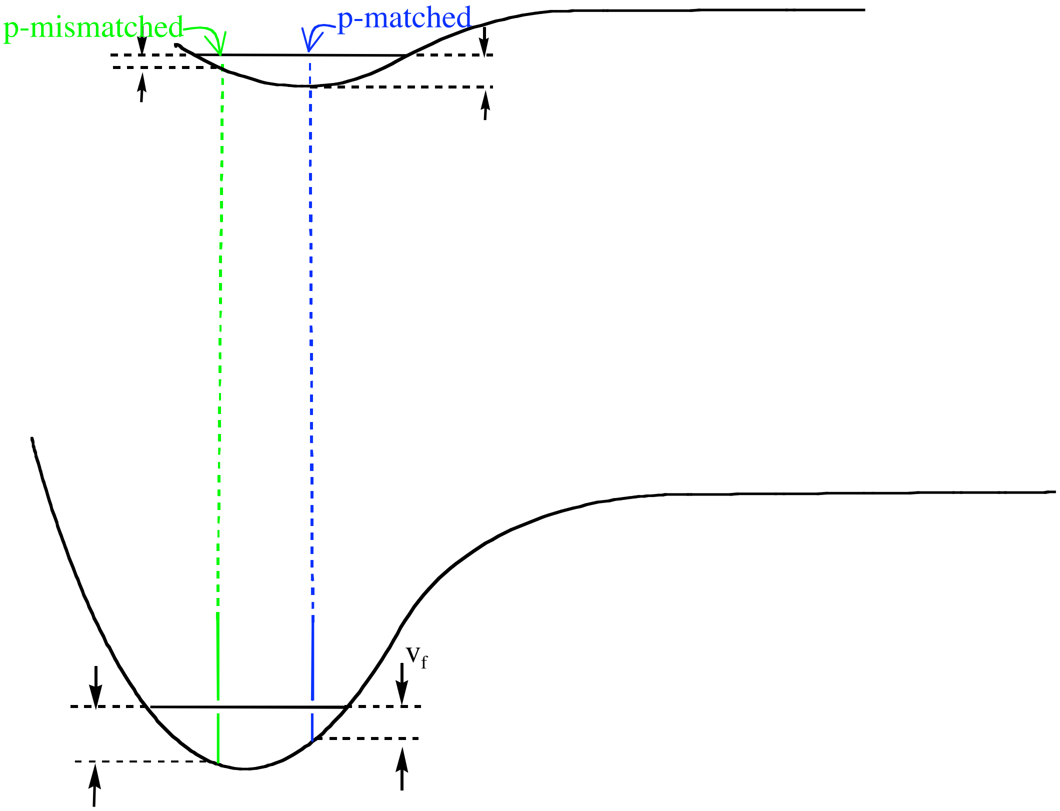
- * C. Noda and R. N. Zare, " Relation Between Classical and Quantum Formulations of the Franck-Condon Principle: The Generalized *r*-centroid Approximation," *J. Mol. Spectrosc.* **95**, 254 (1982)

This R-centroid approximation is convenient because we can think of M(R) as a simple function of a single variable $\overline{R}_{v_i v_f}$ (which usually turns out to be a monotonic function of the wavelength of the transition, λ)

In the R-centroid approximation

$$P_{ij} \propto I \underbrace{q_{v_i v_f}}_{\substack{\text{Franck-Condon factor} \\ \text{(overlap squared)}}} \left| M\left(\overline{R}_{v_i v_f}\right)_{b,if} \right|^2 S^{\Omega_i \Omega_f}_{J_i J_f}$$

Now what is "stationary phase" approximation?
How is it related to semi-classical F-C principle?
vertical * ΔR = 0
no impulse * ΔP = 0

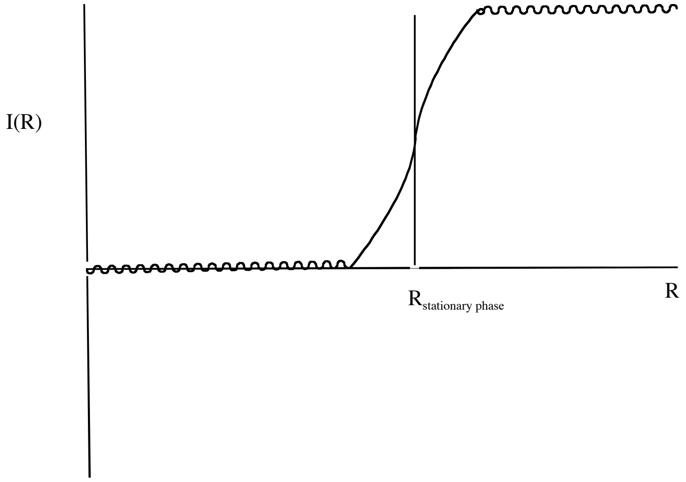


Transition is vertical ($\Delta R = 0$) and "occurs" at that R where $p_{upper} = p_{lower}$. This means that wavefunctions are oscillating at the same spatial frequency.

$$I(R) = \int_{r_<(v_f)}^{R} \chi^*_{v_i}(R')\chi_{v_f}(R')dR'$$

This shows how F–C overlap integral accumulates.

Spatial oscillations of χ given by de Broglie $\lambda = \frac{h}{p}$.



<u>All</u> R^n integrals accumulate near stationary phase point.