

## From Quantum Beats to Wavepackets

**Reading:** Chapter 9.2.1-4, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2<sup>nd</sup> Ed., Academic Press, 2004.

Last time:

How to get a glimpse of mechanism: **cause** and **effect**

e.g. The *effect* might be  $\langle \mathbf{N}_1 \rangle_t$  and the *cause* might be  $\langle \mathbf{h}_{12} \rangle_t$ .

$$\frac{d}{dt} \langle \mathbf{N}_1 \rangle = \frac{-d}{dt} \frac{\langle \mathbf{h}_{12} \rangle_t}{\hbar(\omega_1 - \omega_2)} \quad \text{relation between cause and effect}$$

or 
$$i\hbar \frac{d}{dt} \langle \mathbf{N}_1 \rangle_t = \langle \Omega - \Omega^\dagger \rangle_t \quad \text{transfer rate operator}$$

Today: classes of pluck  $\rightarrow$  classes of wavepacket

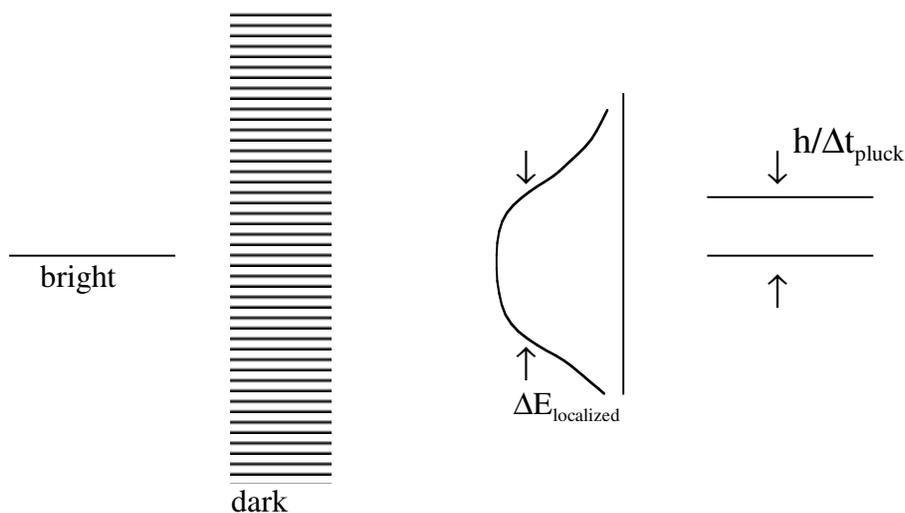
Quantum Beats are usually simple, few-level coherences.

Wavepackets are usually more complex, many-level coherences.

Both are the result of a pluck where  $\Delta t < \frac{\hbar}{\Delta E}$ .

Kinds of pluck:       \* merely short  
                           \* genuinely localized

A localized pluck prepares a zero-order non-eigenstate. The localized state character of this non-eigenstate is distributed (“fractionated”) over eigenstates that span an energy range  $\Delta E_{\text{localized}}$ .



If the pluck is sufficiently short, it prepares an *a priori* known initially localized excitation.

“genuinely localized”

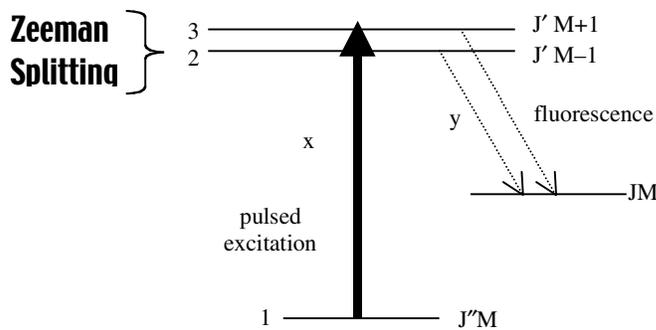
If the pluck is **not** sufficiently short, it prepares an ill-specified coherent superposition

“merely short”

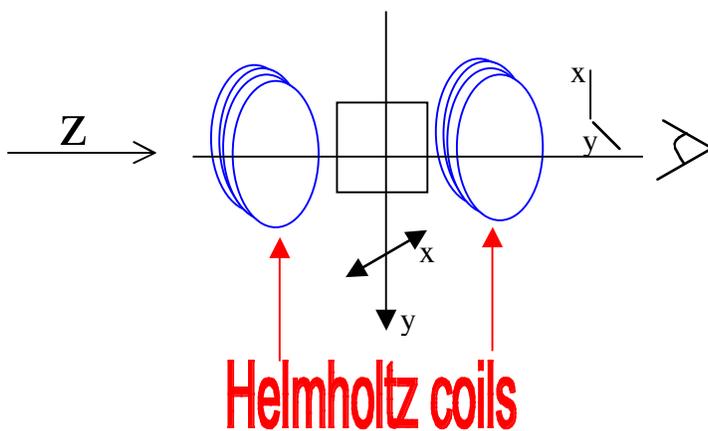
Classes of localization

- \* polarization quantum beats (angularly localized)
- \* population quantum beats (spatially localized or localized in state space, e.g., vibrational wavepacket)

Polarization QB - easiest kind to observe, even with a long excitation pulse. Why?  
 ((Hanle effect))



$$I(t) = \text{Trace} (\mathbf{D} \mathbf{U}(t,0) \mathbf{E} \rho(0) \mathbf{E}^\dagger \mathbf{U}(t,0))$$



DC Magnetic field in z direction

Excite with x polarized light propagating in y direction

Detect light propagating in z direction,  $\frac{I_x - I_y}{I_x + I_y}$ .

see polarization QB as B-field increases from 0.

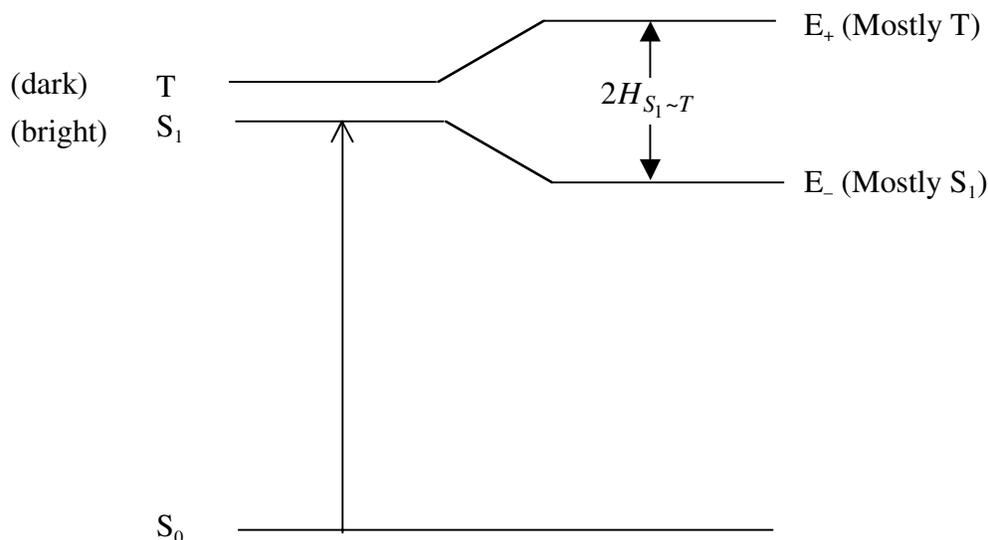
Larmor precession of magnetic moment about z direction. Transition dipole moves because it is attached to the molecule frame and a magnetic moment that is fixed in the molecule frame precesses in the laboratory frame.

Has anyone looked at fluorescence from an atomic  $^1P \rightarrow ^1S$  transition excited by a linearly polarized laser?

If the polarization axis of the exciting radiation is pointing toward you, you see no fluorescence. The transition moment is fixed in space.

- \* can force the transition moment to rotate in external magnetic field
- \* more complicated if there are other nonzero angular momenta
- \* even more complicated if it is a molecule and not an atom

Population QB



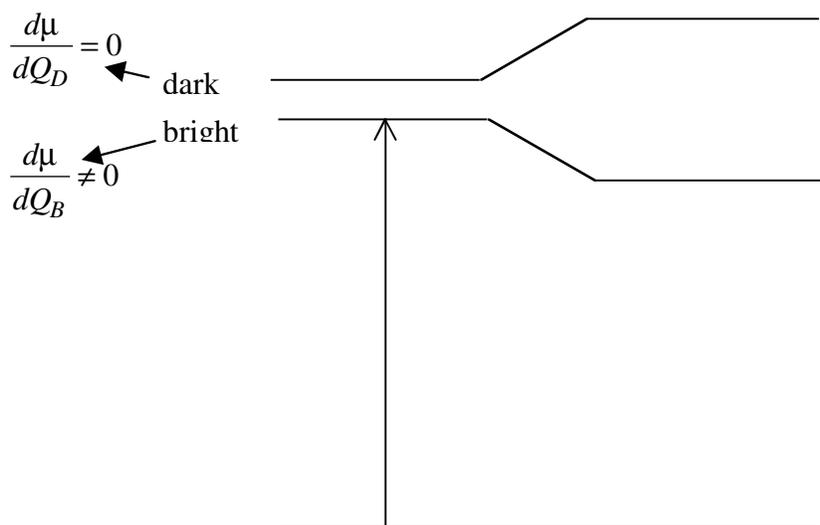
No polarization required. In fact, use geometry in which polarization quantum beat cannot be detected. What is that? Several schemes possible. (Alignment is a  $T_q^2$  second rank tensor quantity.)

At  $t = 0$  prepare  $S_1$  which is not an eigenstate.  $S_1$  is capable of fluorescing.  $T$  is not.

As coherent superposition evolves, becomes predominantly  $T$  in character. Fluorescence rate decreases because  $T$  cannot fluoresce.

It is *as if* population flows back and forth between bright and dark state.

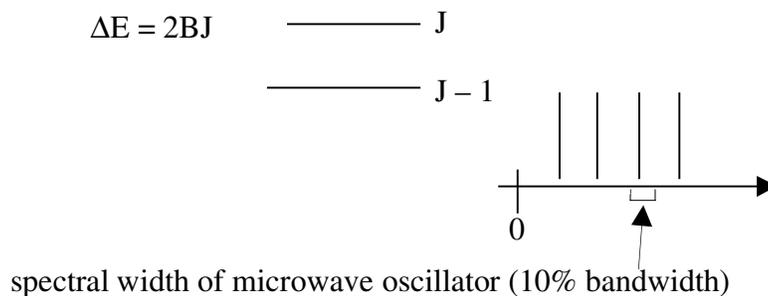
Similarly for anharmonic coupling



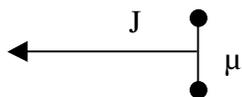
Now it is useful to discuss various kinds of localized excitations that are easily achievable.

Pure rotation spectrum: microwave region (or TeraHertz)

picture of  $I(\omega)$ :



requires a permanent electric dipole moment

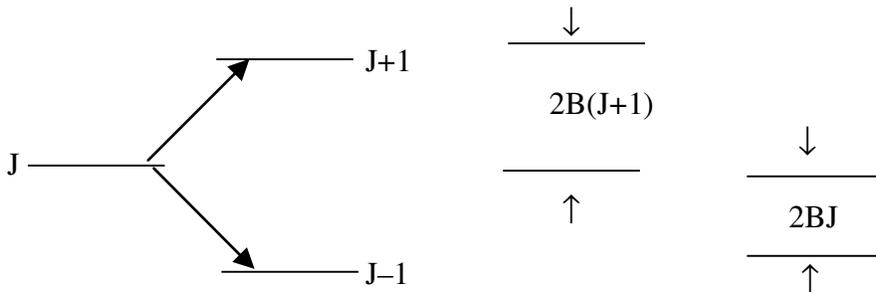
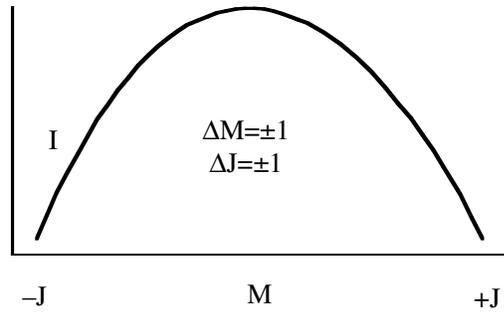
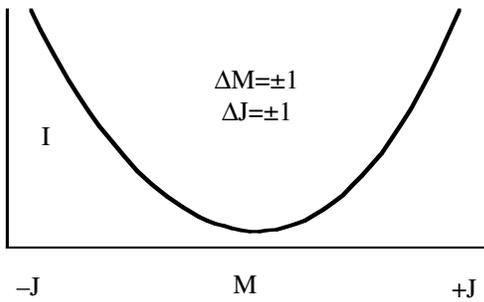


radiation exerts a torque to transfer its 1 unit of angular momentum

molecules with  $\vec{J}$  pointing  $\parallel$  to the radiation propagation direction (call it z) are preferentially excited:  $M = \pm J$

excitation is spatially anisotropic.

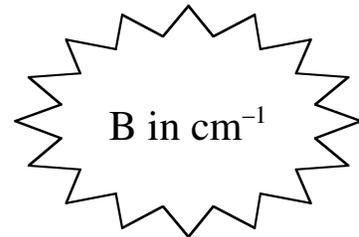
Radiation polarized  $\parallel \mu$  is most effective in exciting molecules



$$T_{ROT} = \frac{1}{2cB(J+1)}$$

and

$$\frac{1}{2cBJ}$$



Is it a physical picture of dipoles rotating or only a mathematical consequence of rephasings in  $e^{-Et/\hbar}$ ?

dipoles rotate relative to lab frame  
**There is a grand rephasing when all dipoles have returned to their original orientation in the lab frame**

$$\Delta T_{\text{grand rephasing}} = \frac{1}{2cB}$$

all J's undergo rephasing an integer number of times  
 each  $\Delta t = \frac{1}{2cB}$

Peter Felker: Rotational Coherence Spectroscopy

based on characteristic grand (and sub-grand) rephasings

$$\text{sym. top } E_{JK} = AK^2 + B[J(J+1) - K^2]$$

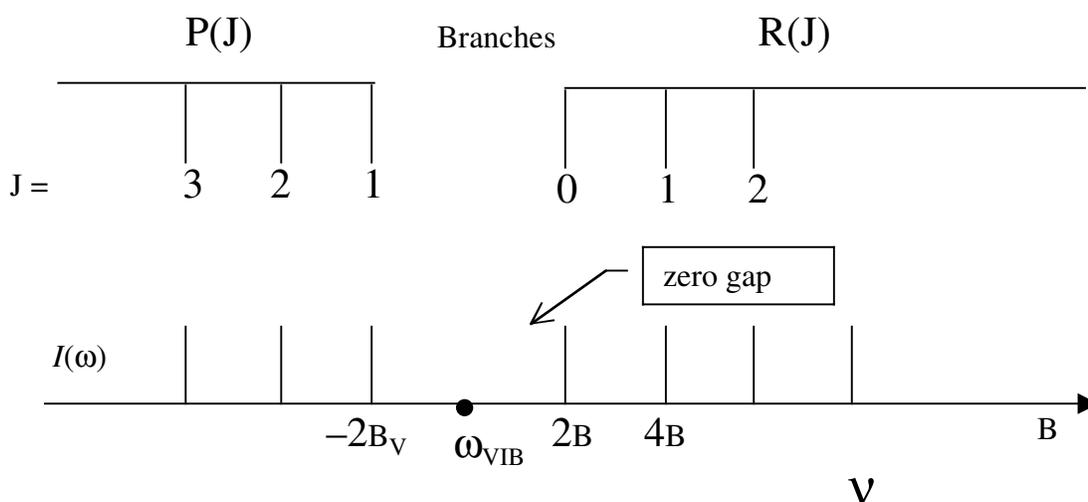
$$A > B$$

short period from A,  
longer period from B.

just a matter of a lot of integer-related rotating dipole antennas.

Pump-probe schemes. Use of polarization in probe to capture grand rephasing.

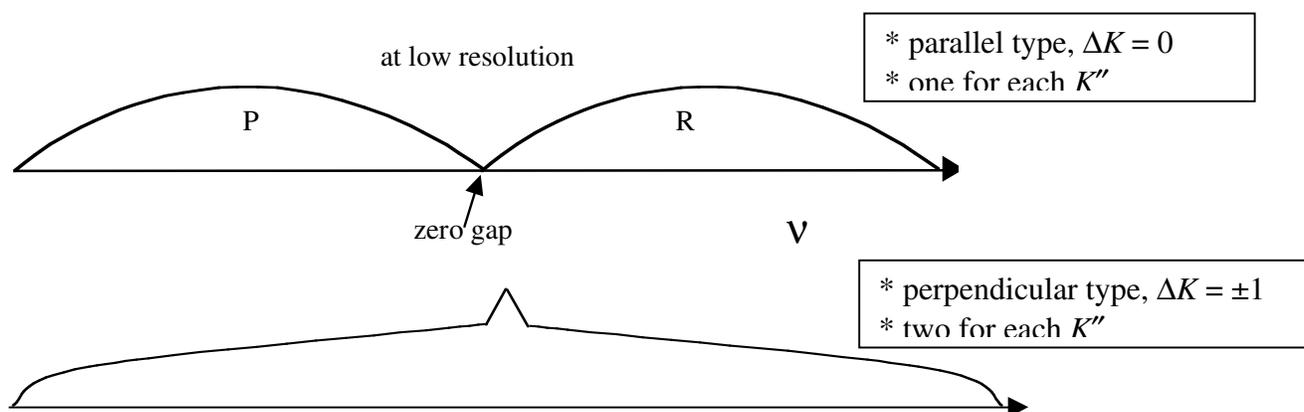
### Vibration-Rotation Spectrum



$$\begin{aligned} R(J) &= B[(J+1)(J+2) - J(J+1)] = B(2J+2) \\ &= 2B(J+1) \quad J = 0, 1, 2 \end{aligned}$$

$$P(J) = B[(J-1)J - J(J+1)] = B(-2J) = -2BJ$$

$$J = 1, 2, 3$$



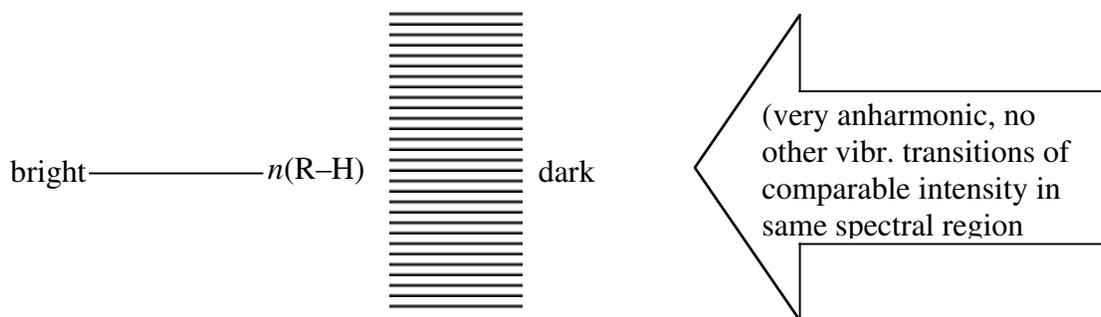
Vibration-Rotation Spectrum: see picture of spectrum,  $I(\omega)$

requires a change in electric dipole moment as molecule vibrates

$$\vec{\mu}(\mathbf{Q}) = \vec{\mu}(\mathbf{Q}_e) + \sum_{j=1}^{3N-6} \frac{\partial \vec{\mu}}{\partial Q_j} (\mathbf{Q}_j - \mathbf{Q}_{je})$$

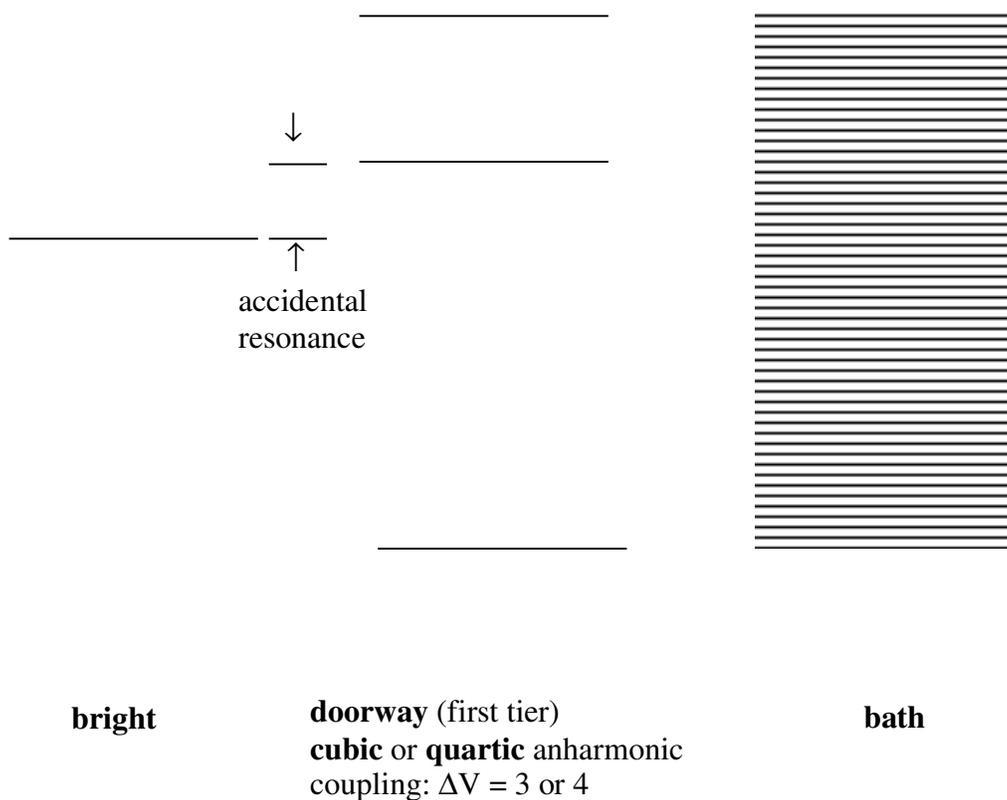
		<u>IR Active?</u>	
linear $\text{CO}_2$	sym. stretch		$Q_1$
	bend (doubly degenerate)		$Q_2$
	antisym stretch		$Q_3$
bent $\text{NO}_2$	sym. stretch		$Q_1$
	bend (non-degenerate)		$Q_2$
	antisym stretch		$Q_3$
$\Delta l = \pm 1$	strong	fundamental	$\frac{d\mu}{dQ}$
$\pm 2$	weak	overtone	both $\frac{d^2\mu}{dQ^2}$ and mechanical
$\pm 3$	very weak		anharmonicity

high overtones, especially for R-H stretches ( $n \times 3000 \text{ cm}^{-1}$ )



Statistical limit Intramolecular Vibrational Redistribution

(see supplement on Heller's Fractionation Index, 10S-5)



IVR, tiers

Bright, doorway, dark (bath)

CH stretch: C–C–H bend 2:1 resonance (cubic anharmonicity, e.g.  $k_{122}Q_1Q_2^2$ ) — usually important. If there are several near resonant coupling mechanisms, get multiple competing pathways.

Doorway state sometimes can “dissolve” in dark bath.

useful tools:

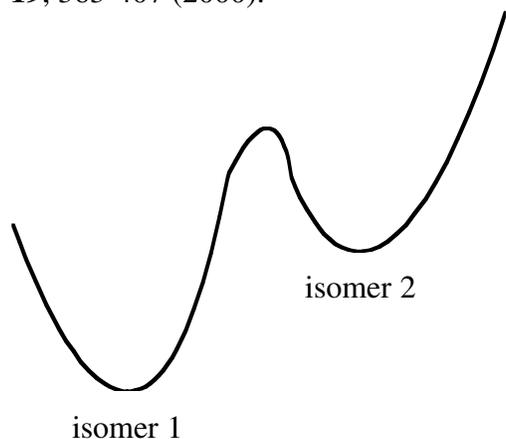
$$\left\langle \mathbf{a}_{RH}^\dagger \mathbf{a}_{RH} \right\rangle \approx \left| \langle \Psi(t) | \Psi(0) \rangle \right|^2$$

$$\left\langle \mathbf{a}_{\text{doorway}}^\dagger \mathbf{a}_{\text{doorway}} \right\rangle$$

There will always be rotational recurrences in a pulse-excited vibration rotation spectrum. Do the rotational recurrences dephase when vibrational bright state dephases? Dispersion of B-values? Depends on nature of detection scheme.

Problem set #8.

IVR and Isomerization á la Brooks Pate (J. Keske, D. McWhorter, and B. H. Pate, *Int. Revs. Phys. Chem.* **19**, 363-407 (2000)).



isomer 1 has typical A, B, C rotational constants  
 isomer 2 has different typical A, B, C rotational constants

IVR might cause pure rotation spectrum to be broadened

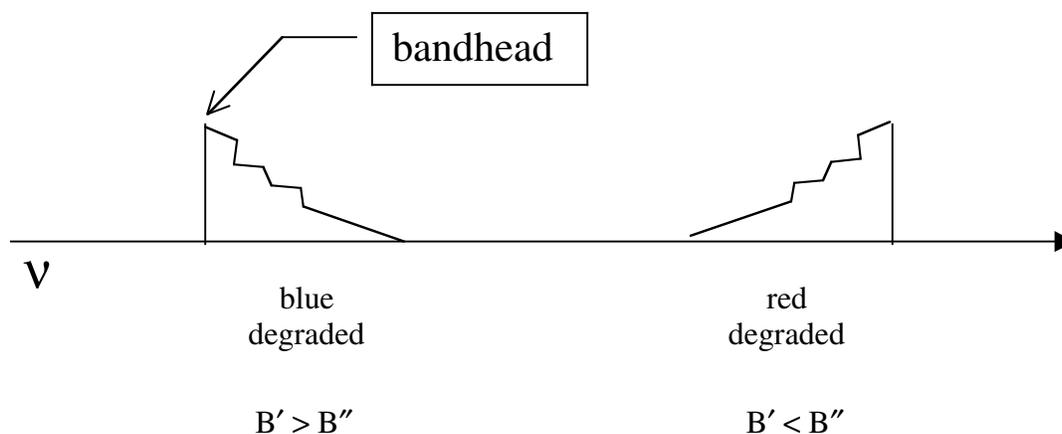
Isomerzation might cause two broadened rotational clusters to merge and narrow  
 “motional narrowing” in NMR (Problem Set #8)

Electronic Spectrum: visible, UV

two flavors

- \* valence states — widely spaced
- \* Rydberg states — often very close together

requires non zero electronic transition moment - joint property of two electronic states. Can be perpendicular to bond axis, even for a diatomic molecule. ( $\parallel$  and  $\perp$  type transitions, weak and strong Q-branch)



electronic-vibration-rotation spectrum

Franck-Condon factors

Classical Franck-Condon:  $\Delta R = 0, \Delta P = 0$   
(see supplement on stationary phase, 10S-1)

In one vibrational band, could have

- rotational coherences
- polarization coherences

If excitation covers several bands, could have vibrational wavepacket with rotational coherences superimposed. Vibrational coherence can be "genuinely localized" or "merely short pulse" excitation.

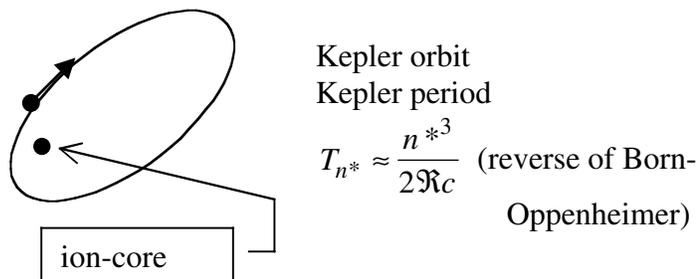
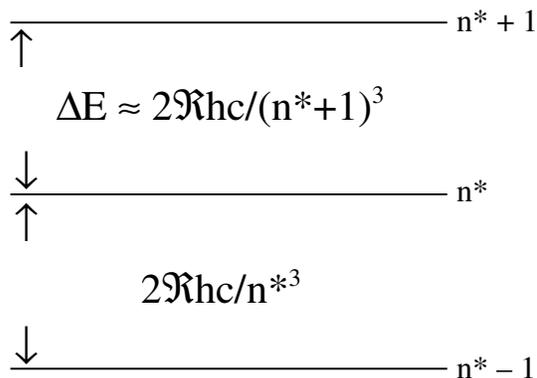
Genuinely localized electronic coherences are rare, except for Rydberg states.

Rydberg Series

$$E_{n^*} = IP - \mathfrak{R}c/n^{*2}$$

$$n^* = n - \delta$$

quantum defect  $\delta$



transition amplitude originates in inner loop of wavefunction, the amplitude of which scales as  $n^{*-3}$ .  
scaling laws on  $\Delta n^*$  and  $\Delta \ell$  but no vertical transfer of entire electronic wavefunction onto the excited state.  
See stationary phase supplement for electronic Franck-Condon-like effects, 10S-1,2.