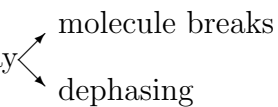


## Lecture 30 and part 31: Electronic Spectroscopy. Franck-Condon.

### Highlights

- “Electronic Structure” and “Dynamics”  
atom → diatomic molecule → small polyatomic → large molecules  
gas phase → condensed phase  
radiative decay → non-radiative decay 
  - molecule breaks
  - dephasing
- Kinds of spectra: rotation, vibration, electronic
- Some ways to record spectra
- Selection Rules
- Franck-Condon Principle  $\Delta\mathbf{R} = 0$ ,  $\Delta\mathbf{P} = 0$   
quantitative and qualitative F-C factors  
diatomic molecule (1 mode) → polyatomic molecule ( $3N - 6$  modes)  
FC “dark” modes, FC “bright” modes
- Absorption and Emission Spectra: gas vs. condensed phase
- Non-radiative decay: “Dynamics”
  1. molecule breaks
  2. 3-level system → quantum beats
  3. vibrational wavepacket: Ehrenfest  $\langle x \rangle_t$ ,  $\langle p \rangle_t$   
diagonal anharmonicity → wavepacket spreads  
intermode anharmonicity → new modes light up

4. Electronic Curve Crossings  $\rightarrow$  new stuff from other electronic state
5. Bixon-Jortner Theory  $\rightarrow$  rapid loss of ability to radiate
6. Photochemistry: photon-induced reactions, unimolecular and bimolecular
7. Förster: Donor  $\rightarrow$  Acceptor processes  $\langle R^{-3} \rangle$

A molecule is a collection of  $e^-$  and nuclei. No analytic solution for  $\geq 3$  bodies

\* Born–Oppenheimer Approximation: clamp the nuclei (no vibration or rotation) and solve for the electronic energy levels at a grid of nuclear geometries:  $E_i(\mathbf{R})$ . connect the dots  $\rightarrow$  potential energy surfaces PES  $V_i(\mathbf{R})$

Understand the relative energies and shapes of the PESs in terms of LCAO–MOs: configurations  $\rightarrow$  Electronic States

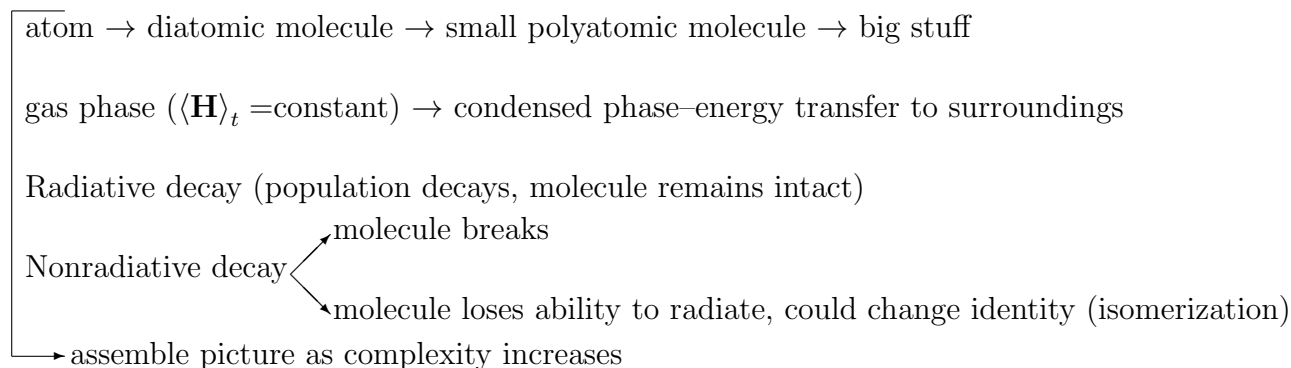
MO's: bonding, nonbonding, antibonding, structure-demanding (e.g.  $\sigma$  vs.  $\pi$  bonds,  $sp^n$  hybridization)

\* Once we have a PES, we solve nuclear Schrödinger Equation for the vibrational levels. The  $3N - 6$  normal mode frequencies “encode” the geometric structures (molecular shape and force constants).

Next we solve semi-rigid rotor for rotational levels and vibration dependence of rotational constants. More encoding of PES in observable energy levels.

$$\Psi_{\text{evv}} = \psi_{\text{el}} \chi_{\text{vib}} \phi_{\text{rot}}$$

From diatomic to polyatomic molecules: there is a lot of information about the spectrum and structures of a polyatomic molecule. How do we organize it?

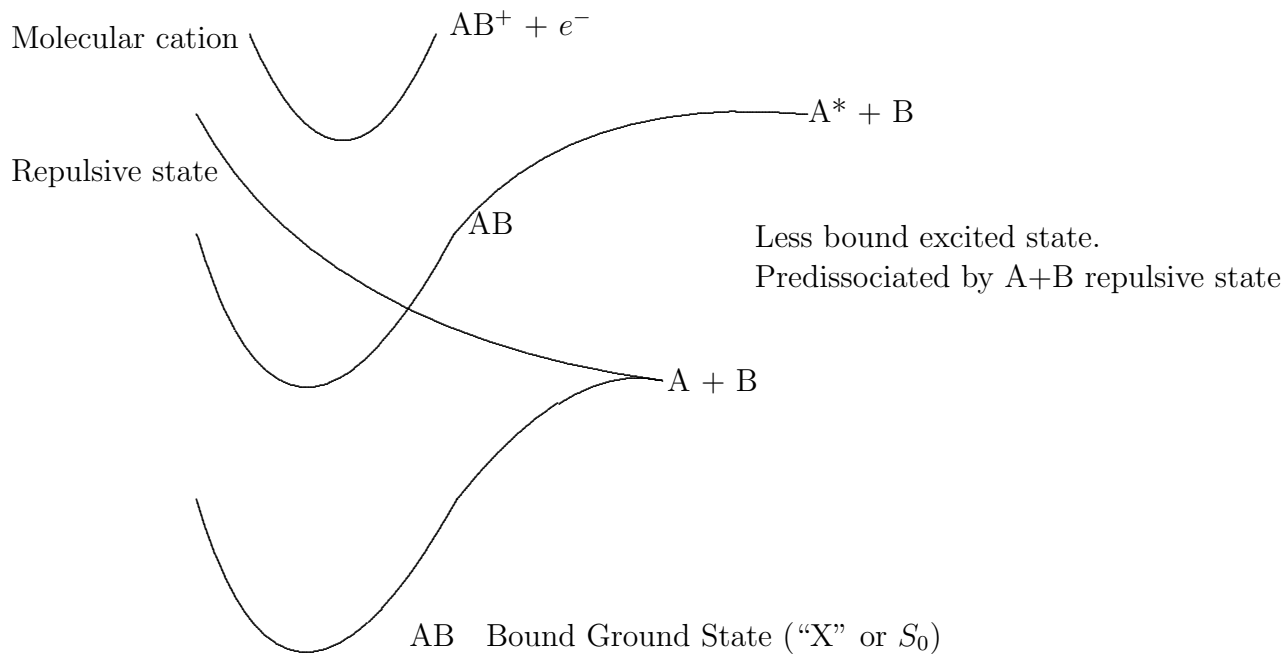


## Kinds of Spectrum

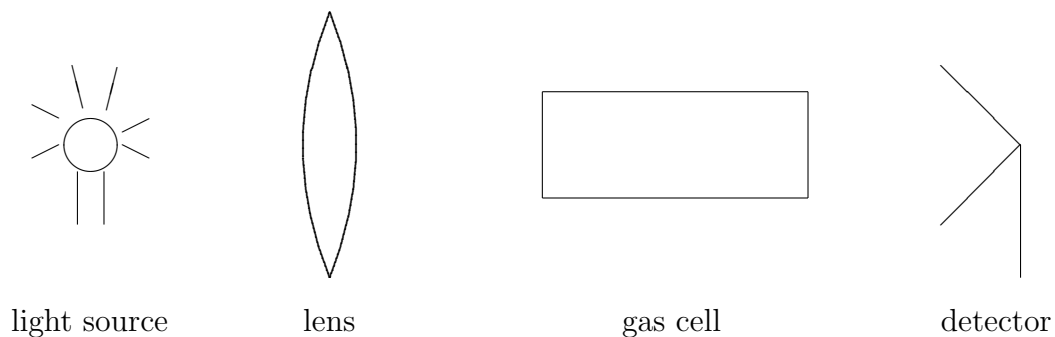
(everything except NMR is based on electric dipole transition moments: typically  $10^3$  times larger than magnetic dipole transition moments).

rotation	microwave	$\mu \neq 0$	[HCl]
vibration	infrared	$\frac{d\bar{\mu}}{dQ_i} \neq 0$	[CO <sub>2</sub> ]
electronic	ultraviolet	$\mu_{e_1, e_2} \neq 0$	transition moment (not zero, even for H <sub>2</sub> )

Kinds of things a diatomic molecule can do:



## Kinds of Spectroscopy



## Methodology

- absorption
- induced fluorescence (using laser)
- multi-photon ionization, resonance enhanced [ions are easier to collect and detect than photons, why?]
- more sophisticated schemes: 2-color, stepwise vs. coherent (STIRAP = Stimulated Raman Adiabatic Passage)

Rules that govern what we can see:

$\vec{\mu}$  is a one- $e^-$  operator

$$\vec{\mu} = \sum_{\text{electron } i} e\vec{r}_i$$

$\psi_{\text{el}}$  = Slater determinant: product of  $1e^-$  spin-orbitals

$\Delta_{\text{so}} = 1$  and  $\alpha \not\leftrightarrow \beta$

for electric dipole:	parity+ $\leftrightarrow$ -
for magnetic dipole:	parity+ $\not\leftrightarrow$ -
total $e^-$ spin	$\Delta S = 0$

Other point group symmetry elements: important for small molecules and metal-centered inorganic complexes [Group Theory]

## Electronic Transitions

Many vibrational bands

Vibrational Band System  $\rightarrow$  a lot of information about the change in shape of PES for excited electronic state (') vs. ground electronic state (").

Universal notation: Upper state first, single ' for upper state, double " for lower state.

Franck–Condon Principle governs relative intensities of the vibrational bands in an electronic transition

The Franck-Condon principle is based on sudden promotion of one  $e^-$ , so fast that nuclei respond only after the  $e^-$  excitation.

$\Delta \mathbf{R} = 0$  “vertical transitions”

$\Delta \mathbf{P} = 0$  no change in momentum. How is momentum encoded in  $e^{ikt}$ ?  
Transition occurs at value of  $\mathbf{R}$  where spatial oscillation frequency (momentum) is the same in the upper and the lower electronic-vibrational states. “Stationary Phase Approximation” Mostly favors turning point to turning point transitions.

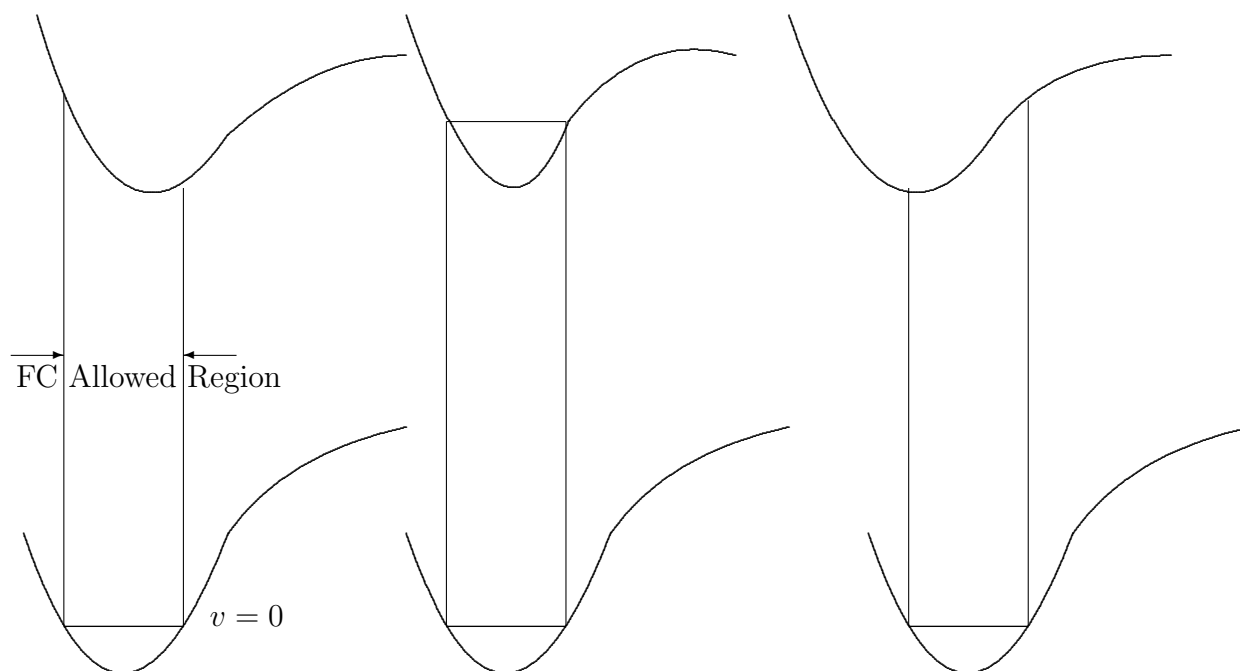
$$\text{FC Factor} = q_{v',v''} \equiv \left[ \int_0^\infty \chi_{v'}(\mathbf{R}) \chi_{v''}(\mathbf{R}) d\mathbf{R} \right]^2$$

This is the square of an overlap integral between initial and final vibrational states.

If you know  $V'(\mathbf{R})$  and  $V''(\mathbf{R})$  you can then compute accurate FC factors. There is no simple formula.

If you do not know  $V'$  and  $V''$ , you can use the vibrational intensity distribution to *qualitatively* describe

$$\Delta V = V'(\mathbf{R}) - V''(\mathbf{R}) \equiv \Delta V(\mathbf{R}).$$



FC allowed region from  $v'' = 0$  is over the range of  $\mathbf{R}$  from turning point to turning point in the  $V'$  potential.

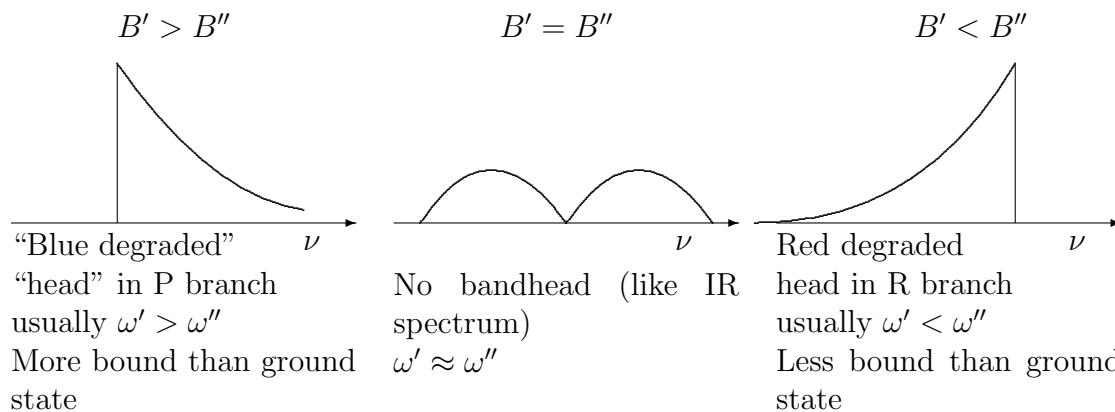
### 3 cases

- Upper state less bound and shifted to larger  $R_e$ : long vibrational “progression” because inner wall is steep.
- Upper state same shape as lower state: only  $\Delta v = 0$  transitions. No progression. Hot bands  $0 - 0$ ,  $1 - 1$ ,  $2 - 2$ : “sequence” structure.
- Upper state *more bound* and shifted to *shorter*  $R_e$ : short progression because outer wall of  $V'$  potential is not steep.

## How do we determine absolute vibrational quantum numbers?

Isotope shifts. Recall that  $\omega = [k/\mu]^{1/2}$  where  $\mu$  is a reduced mass, which depends on isotopologue.

Band shapes: depend on rotational constants



What about FC factors for polyatomic molecules?  $3N - 6$  Vibrational nodes. Benzene has 12 atoms, 30 vibrational modes! Horrible?

Not so bad because many vibrational modes are identical in the upper and lower electronic states.

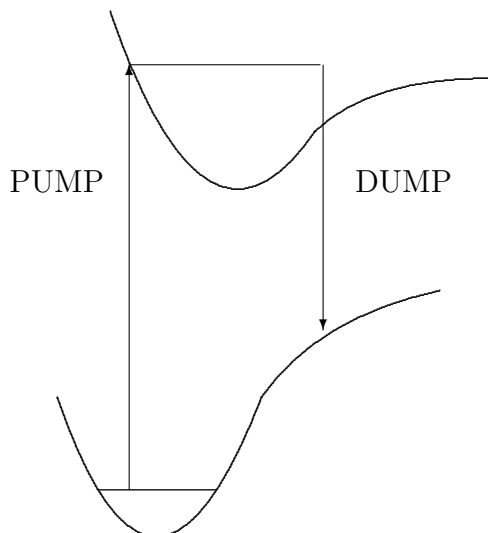
\*When  $\omega' = \omega''$ , those are called “FC dark” modes because they follow the  $\Delta v = 0$  propensity rule.

\*The few modes where  $\omega' \neq \omega''$  are called “FC bright” modes because several  $\Delta v \neq 0$  transitions for that mode are observable. These are the vibrational modes that “generate” the change in geometry between the excited and ground electronic states.

For example, acetylene is linear and with a  $C \equiv C$  bond in the electronic ground state and the first excited singlet state is *trans*-bent with a  $C = C$  bond. The CC stretch and *trans*-bending normal modes are FC bright because they generate the change in geometry.

The vibrational intensity distribution (which modes are FC bright and the  $v'$  distribution of  $q_{v',v''=0}$ ) gives qualitative information about  $\Delta V(\mathbf{R})$ .

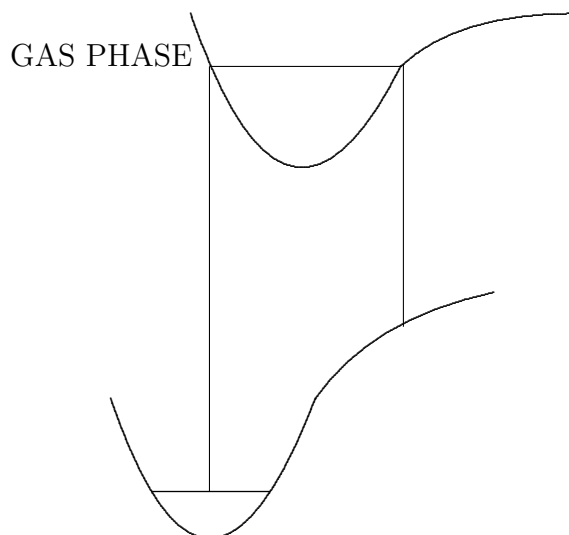
## Stimulated Emission Pumping (“Pump and Dump”)



gives information about highly excited vibrational levels in the electronic ground state. I invented SEP! (Both the experiment and the terminology.)

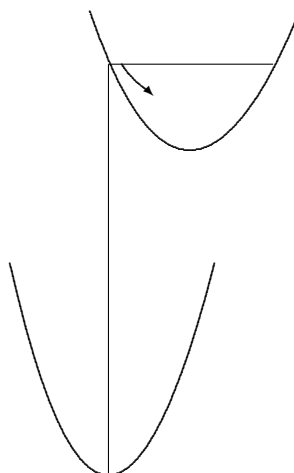
## \*\*Gas Phase vs. Condensed Phase Electronic Spectra

Absorption vs. Emission Spectra.



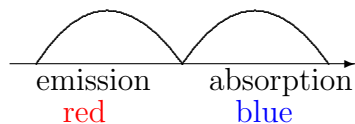
Absorption spectrum is simpler than the emission spectrum because the FC region for *absorption* from  $v'' = 0$  is narrow in energy range and *especially* because in emission from an excited state, the inner and outer turning points on the upper potential curve are far apart.

In condensed phase, the vibrational population in the excited state is rapidly relaxed (by collisions with solvent or lattice) to  $v' = 0$ . Relaxation is always much faster than spontaneous radiative decay.



So in condensed phase, the absorption spectrum is from  $v'' = 0$  and the emission spectrum is from  $v' = 0$ . Get the classic picture of absorption vs. emission spectrum.

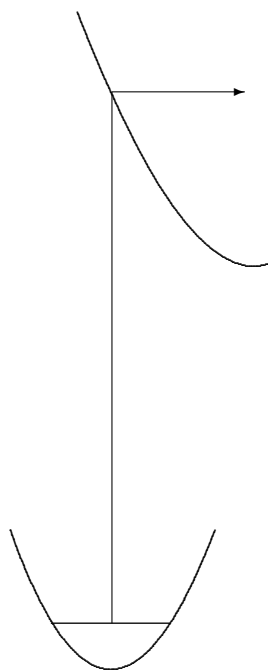




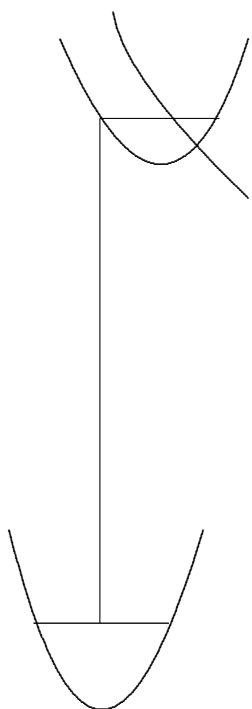
[Herzberg insisted: “red on the right.”]

This gas phase  $\leftrightarrow$  condensed phase difference is due to  $\langle \mathbf{H} \rangle_t = \text{constant}$  (conservation of energy) for gas and  $\langle \mathbf{H} \rangle_t$  rapidly decaying due to intermolecular interactions in condensed phase.

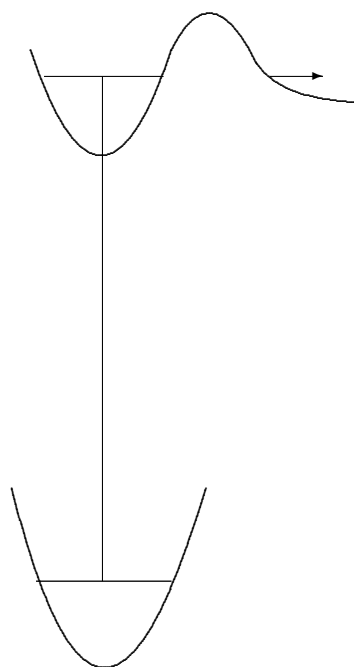
### Collision-Free Dynamics



direct dissociation



predissociation  
via a repulsive state



predissociation by tunneling through a  
barrier on a single potential surface

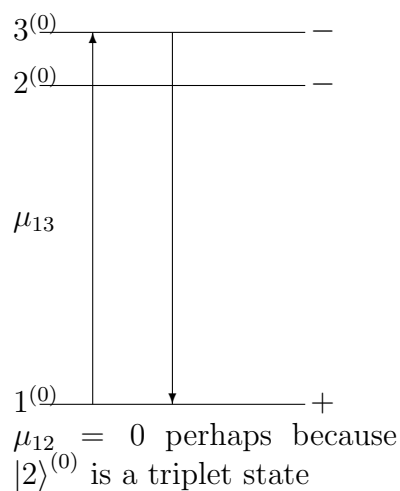
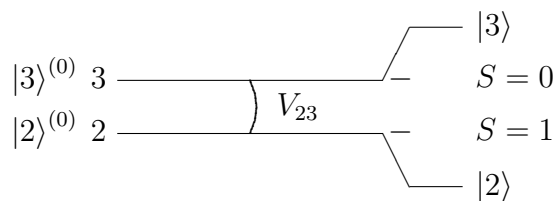
Now let's look beyond the collision-free (no energy removed) non-radiative decay mechanisms as shown in the above figure.

We will see now that there are other decay mechanisms that do NOT involve breaking the molecule! “Dynamics”

## Dynamics

Begin with simplest case

- ground state 1
- dark excited state 2  $|2\rangle^{(0)}$
- bright excited state 3  $|3\rangle^{(0)}$



$$\mathbf{H} = \begin{pmatrix} E_1^{(0)} & 0 & 0 \\ 0 & E_2^{(0)} & V_{23} \\ 0 & V_{23} & E_3^{(0)} \end{pmatrix}$$

parity is conserved

$$\boldsymbol{\mu} = \begin{pmatrix} 0 & 0 & \mu_{13} \\ 0 & 0 & 0 \\ \mu_{13} & 0 & 0 \end{pmatrix}$$

$+ \leftrightarrow -$  selection rule

Notice the complementary structures of  $\mathbf{H}$  and  $\boldsymbol{\mu}$ .

Short pulse to excite from  $|1\rangle^{(0)} = |1\rangle$

$$\frac{\hbar}{2\pi\tau} > (E_3 - E_2) \quad \tau \text{ is pulse duration}$$

Uncertainty principle broadened pulse covers the frequencies of both  $E_2 \leftarrow E_1$  and  $E_3 \leftarrow E_1$  transitions.

$$|\Psi(t=0)\rangle = \underset{\substack{\uparrow \\ \text{not an eigenstate}}}{|3\rangle^{(0)}} = (1 - \alpha^2)^{1/2} \underset{\substack{\uparrow \\ \text{eigenstates}}}{|3\rangle} + \alpha \underset{\uparrow}{|2\rangle} \quad \begin{array}{l} \text{due to mixing of zero-order} \\ \text{states by } V_{23} \\ \text{(spin-orbit operator)} \end{array}$$

(This  $\Psi(t)$  is a normalized state.)

$$\alpha = \frac{V_{23}}{E_2^{(0)} - E_3^{(0)}}$$

What is  $\alpha$  in terms of  $E_2^{(0)}$ ,  $E_3^{(0)}$ , and  $V_{23}$ ? You should already know how to derive this!

$$|\Psi(t)\rangle \propto \mu_{13} [(1 - \beta^2)^{1/2} |3\rangle e^{-iE_3t/\hbar} + \beta |2\rangle e^{-iE_2t/\hbar}]$$

These are eigenstates weighted by the bright state  $|3\rangle^{(0)}$  character in each.

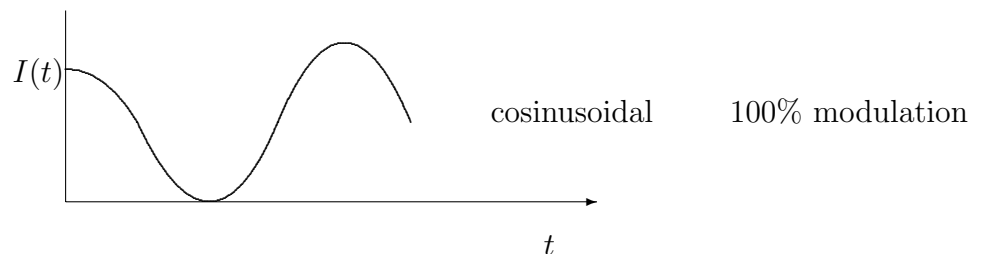
What is  $\beta$ ? What are the values of  $E_2$ ,  $E_3$ ? Again, you already know how to derive these by perturbation theory!

Get Quantum Beats!

$$I(t) \propto \mu_{13}^2 [1 + 2\beta(1 - \beta^2)^{1/2} \cos \omega_{23}t]$$

$$\omega_{23} = (E_2 - E_3)/\hbar$$

If  $\beta = 2^{-1/2}$



Get maximum modulation depth for  $\beta = 2^{-1/2}$ .  $|3\rangle$  and  $|2\rangle$  are 50 : 50 mixed:  $|3\rangle^{(0)} \pm |2\rangle^{(0)}$

This modulation is superimposed on an exponential decay (not shown).

The phase of the modulation is what you expect when you prepare and detect the same “bright state”.

What would  $I(t)$  look like if the  $3 \leftarrow 1$  transition is “bright” for excitation but the  $2 \rightarrow 1$  transition is bright for detection?

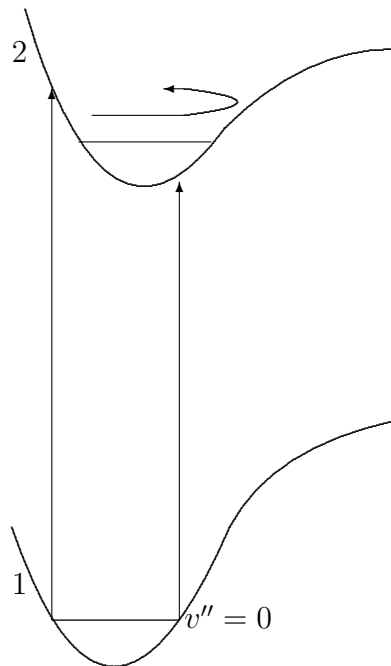
Now we are ready to consider a “wavepacket” built from several vibrational levels of the same electronic state. Again we use a short excitation pulse out of electronic state 1 to create a coherent superposition state in one bright vibrational level of electronic state 2.

$$\mathbf{H} = \begin{pmatrix} E_1 & 0 & 0 & 0 & 0 & \dots \\ 0 & E_2 & 0 & 0 & 0 & \dots \\ 0 & 0 & E_2 + \hbar\omega & 0 & 0 & \dots \\ 0 & 0 & 0 & E_2 + 2\hbar\omega & 0 & \dots \\ 0 & 0 & 0 & 0 & E_2 + 3\hbar\omega & \dots \end{pmatrix}$$

The state with  $E = E_2 + n\hbar\omega$  is denoted  $|2, n\rangle$ . The transition moment  $\langle 1, 0 | \mu | 2, n \rangle \equiv \mu_{10,2n}$ .

$$\boldsymbol{\mu} = \begin{pmatrix} 0 & \mu_{10,20} & \mu_{10,21} & \mu_{10,22} & \mu_{10,23} & \dots \\ \mu_{10,20} & 0 & 0 & 0 & 0 & \dots \\ \mu_{10,21} & 0 & 0 & 0 & 0 & \dots \\ \mu_{10,22} & 0 & 0 & 0 & 0 & \dots \\ \mu_{10,23} & 0 & 0 & 0 & 0 & \dots \end{pmatrix}$$

This gives a vibrational wavepacket



\*Many vibrational levels of electronic state 2 are “coherently” excited.

\*Wavepacket starts at inner turning point of electronic state 2.

\* $\langle x \rangle_t$  and  $\langle p \rangle_t$  follow Newton’s Laws

If upper potential curve is harmonic but  $\omega' \neq \omega''$ , wavepacket remains localized and oscillates at  $\omega' = [k/\mu]^{1/2}$ .

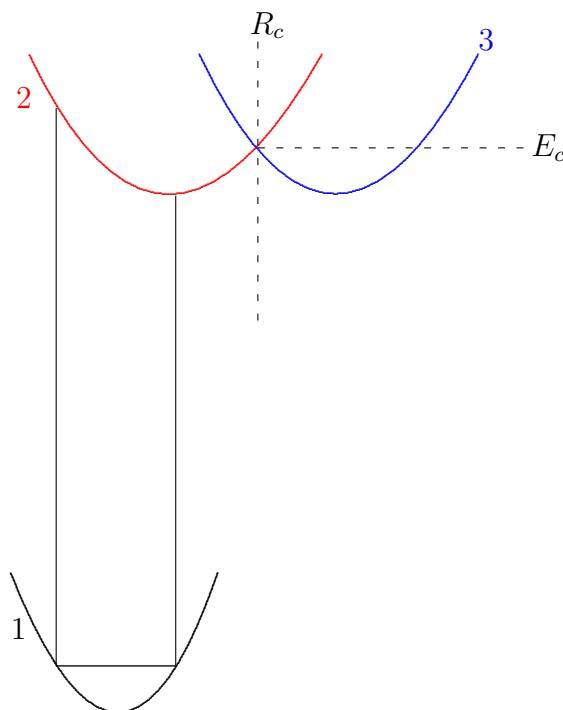
The phases of the eigenstates in the wavepacket are such that the ability of the  $\Psi(t)$  to fluoresce to the  $|1, 0\rangle$  state oscillates at  $\omega$ .

Now add some anharmonicity in the electronic state 2 potential curve.

- Wavepacket continues to oscillate where  $\langle x \rangle_t$  and  $\langle p \rangle_t$  follow Newton's Laws, but the wavepacket spreads out (dephases).
- The total population decay rate from state 2 is unaffected, but the ability to fluoresce into the  $|1, 0\rangle$  state decreases.
- This decrease is superimposed on the oscillations at near  $\omega$ .

Now add intermode anharmonic interactions (Intramolecular Vibrational Redistribution, IVR) in electronic state 2. Begin to see Fourier components in the fluorescence oscillations associated with the harmonic frequencies of the other dark modes in electronic state 2.

Now add a curve crossing between the potential surfaces of electronic states 2 and 3.



Curves 2 and 3 cross at  $R_c, E_c$ .

The wavepacket prepared on state 2 from the  $|1, 0\rangle$  ground state  $v = 0$  level contains a coherent superposition of several vibrational states. Each of these vibrational states “crosses”

into state 3 at  $R \approx R_c$ , which is the stationary phase region. The most efficient crossing is for the states that have the smallest momentum at  $R_c$ . These are the states with energy near  $E_c$ . Some amplitude of the wavepacket on state 2 leaks into state 3 each time the wavepacket crosses through the  $R = R_c$  region. This produces a train of mini-packets spaced in time by the period of oscillation in state 2 at  $E$  near  $E_c$ .

One can use femtosecond pump/probe schemes to view this train of pulses entering the electronic state 3. This is similar to what A. H. Zewail pioneered in his study of the dynamics associated with the ionic-covalent curve crossing in NaI [*J. Chem. Phys.* **88**, 6672 (1988)].

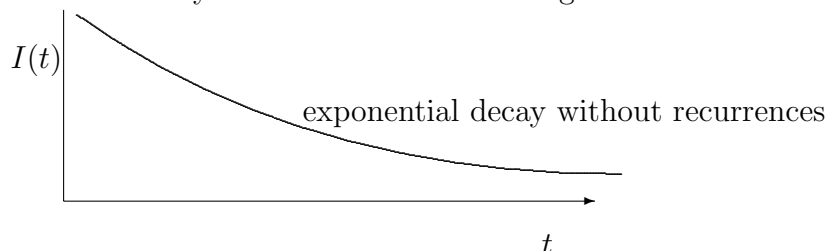
### Bixon–Jortner Theory of Non-radiative Decay [*J. Chem. Phys.* **48**, 715 (1968)].

This answers the question: why do large molecules exhibit fast decay of UV fluorescence which does not involve either breaking of the molecule or actual decay of the total amount of energy in the molecule. The basic idea is that the molecule loses the ability to radiate in the UV because a single bright state is mixed with many near-degenerate dark states (triplets and high vibrational levels of the electronic ground state).

$$\mathbf{H} = \begin{pmatrix} E_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \{E_i^{(0)}\} & & & & \\ 0 & \{H_{ij}^{(1)}\} \neq 0 & & & & \\ 0 & & & & & \\ 0 & & & & & \end{pmatrix}$$

$$\boldsymbol{\mu} = \begin{pmatrix} 0 & \mu_{12} & \mu_{13} & \mu_{14} & \dots & \mu_{1N} \\ \mu_{12} & 0 & 0 & 0 & 0 & \dots \\ \mu_{13} & 0 & 0 & 0 & 0 & \dots \\ \mu_{14} & 0 & 0 & 0 & 0 & \dots \\ \vdots & 0 & 0 & 0 & 0 & \dots \\ \mu_{1N} & 0 & 0 & 0 & 0 & \dots \end{pmatrix}$$

We get MANY 2-level quantum beats, all “phased up” at  $t = 0$ . But each quantum beat is at a different  $\omega_{1n}$ . They get out of phase so that the ability to fluoresce goes away much more rapidly than the radiative decay rate of each individual eigenstate.

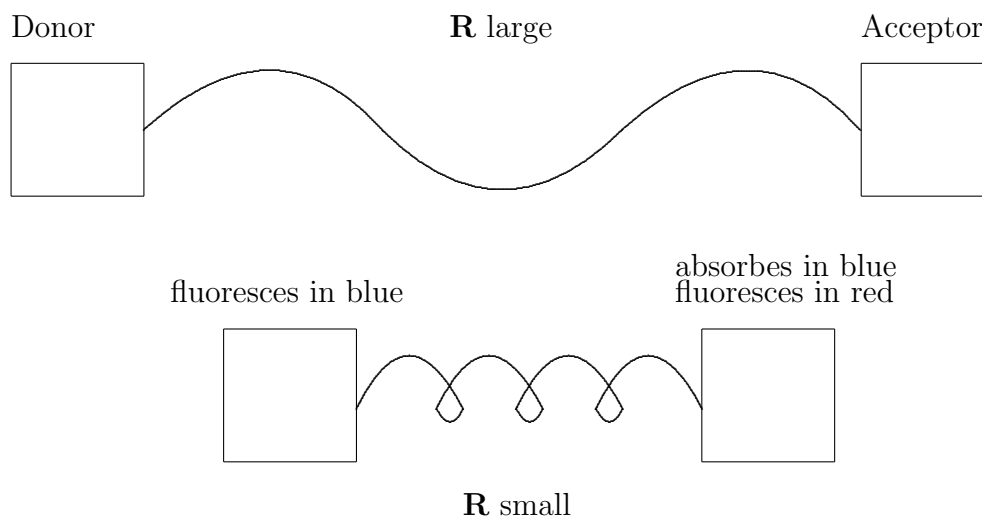


Ability to radiate goes away but  $\langle \mathbf{H} \rangle_t$  remains constant (excited state population does not decay rapidly).

This can be biologically useful

Photochemistry in electronically excited states can be very destructive, but fast *cis-trans* isomerization or intramolecular energy transfer can be protective, thus biologically useful.

## Förster energy transfer



We have Donor as an oscillating (radiating) dipole and Acceptor as an efficient dipole (receiving) antenna.

$$\text{Dipole-dipole interaction energy} \propto \frac{1}{R^3}$$

Used to measure rates of biological processes that involve change in  $R$  between Donor and Acceptor.

Many books on Electronic Dynamics remain to be written.

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5.61 Physical Chemistry  
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