IN THE COURSE OF LIGHT/MATTER INTERACTIONS, ANY OF THE QUANTITIES DESCRIBING THE ELECTRIC FIELD MAY CHANGE.

**DIRECTION** \( \vec{E} = \vec{p}/\hbar \)
**WAVELENGTH** \( \lambda = \hbar/\vec{p} \)
**INTENSITY** \( \propto |\vec{E}|^2 \)
**POLARIZATION** (DIRECTIONAL NATURE OF \( \vec{E} \): PLANE OF OSCILLATION)

SOME ASPECTS OF LIGHT-MATTER INTERACTION CAN BE DESCRIBED BY CONSIDERING LIGHT AS PHOTONS, BUT OTHERS CAN ONLY BE UNDERSTOOD BY THINKING OF WAVES.

**LET'S CONSIDER PHOTON PERSPECTIVE FOR A WHILE...**
PHOTONS CAN BE ABSORBED OR CREATED (FLUORESCENCE) AND THEY CAN BE SCATTERED.

* **ELASTIC SCATTERING** \(< \lambda \)
  \( \lambda_{\text{final}} = \lambda_{\text{initial}} \)
  (ONLY DIRECTION CHANGES)

* **INELASTIC SCATTERING** \( \lambda_{\text{final}} \neq \lambda_{\text{initial}} \)
  PHOTON ENERGY INCREASES (ANTI-STOKES)

  \( \lambda_{\text{final}} < \lambda_{\text{initial}} \)

  \( \lambda_{\text{final}} > \lambda_{\text{initial}} \)

  \( \lambda_{\text{final}} \neq \lambda_{\text{initial}} \)
CHEM 4531 FALL 2015

LIGHT/MATTER INTERACTIONS

ΔE REVEALS DIFFERENCES BETWEEN MOLECULAR AND ATOMIC ENERGY LEVELS

ABSORBANCE/TRANSMISSION SPECTROSCOPY IS USUALLY EASIER TO MEASURE BECAUSE THE TRANSITIONS ARE STRONGER (UP TO ALMOST 100% ABSORPTION VS. 10^{-6} / 10^{-7} PHOTONS LIGHT SCATTERING)

\[ \log \left( \frac{I}{I_0} \right) = A = e \chi \] LAMBERT-BEER LAW

MOLECULAR INFORMATION IS CONTAINED IN \( e \) "EXTINCTION COEFFICIENT" ABSORPTION STRENGTH

\[ E = 10^4 - 10^5 \text{ M}^{-1} \text{cm}^{-1} \] VIS/UV ELECTRONIC TRANSITIONS
onto 200-300 nm

\[ E = 1 - 200 \text{ M}^{-1} \text{cm}^{-1} \] IR VIBRATIONAL TRANSITIONS
between 1-1000 nm

\[ E \ll 1 \text{ M}^{-1} \text{cm}^{-1} \] FAR-IR/MICROWAVE ROTATIONAL TRANSITIONS
onto mm

\[ A \]

AT LOW LIGHT INTENSITIES, WE CAN CONSIDER INTERACTION OF A SINGLE PHOTON WITH INITIAL AND FINAL LEVELS (i.e. 2-LEVEL SYSTEM) - EINSTEIN'S MODEL (1917)

\[ \text{ABSORPTION} \quad \text{SPONTANEOUS EMISSION} \quad \text{STIMULATED EMISSION} \]

\[ |1\rangle \quad \rightarrow |1\rangle \quad \rightarrow \quad \downarrow \quad \rightarrow \quad |2\rangle \]

\[ |1\rangle \quad \text{vh} \quad \rightarrow |1\rangle \quad \rightarrow \quad |1\rangle \quad \rightarrow \quad |1\rangle \]

* ABSORPTION: PHOTON IS ANNIHILATED. SYSTEM \( \rightarrow \) HIGHER ENERGY STATE

* SPONTANEOUS EMISSION: PHOTON CREATED. SYSTEM \( \rightarrow \) LOWER ENERGY STATE

* STIMULATED EMISSION: SYSTEM IN \( |2\rangle \) INTERACTS WITH PHOTON OF \( \lambda = h\gamma/\Delta E_2 \) AND NEW PHOTON (ALONG WITH INCIDENT PHOTON) Emitted. SYSTEM \( \rightarrow \) STATE \( |1\rangle \)
EINSTEIN'S MODEL (2 LEVEL SYSTEM)

LET'S ASSUME THE TRANSITION RATE $|1\rangle \rightarrow |2\rangle$
IS PROPORTIONAL TO ENERGY DENSITY OF RADIATION AT THE TRANSITION FREQUENCY

$$W \propto p B_{12}$$

$W = 1 \rightarrow 2$ RATE

$B_{12}$ IS EINSTEIN ABSORPTION COEFFICIENT

EINSTEIN ASSUMED RADIATION SOURCE IS A BLACKBODY (THERMAL) SOURCE $\rho dv$ IS ENERGY DENSITY OF RADIATION IN $[v, v+dv]$ INTERVAL

$$\rho(v) = \frac{8\pi hv^3 c^3}{e^{hv/kT} - 1}$$

THERMAL ENERGY DENSITY OF BLACKBODY (PLANK)

TOTAL RATE OF ABSORPTION $W_{12} = N_1 W = N_1 B_{12} \rho$
WHERE $N_1$ IS # OF MOLECULES IN STATE $|1\rangle$

TWO PROCESSES DEPOPULATE $|2\rangle$:

* SPONTANEOUS EMISSION RATE $W' = A$

COEFFICIENT OF SPONTANEOUS EMISSION, INDEPENDENT OF LIGHT

* STIMULATED EMISSION $W' = B_{21} \rho$

$B_{21}$ IS COEFFICIENT OF STIMULATED EMISSION, RATE IS PROPORTIONAL TO ENERGY DENSITY.

TOTAL RATE $2 \rightarrow 1$ IS SUM OF RATES

$$W' = A + B_{21} \rho$$

$$W_{21} = N_2 (A + B_{21} \rho)$$

$N_2$ IS # OF MOLECULES IN STATE $|2\rangle$

AT THERMAL EQUILIBRIUM, $N_2 / N_1$ = CONSTANT

RATE UP = $N_1 B_{12} \rho = N_2 (A + B_{21} \rho)$

RATE DOWN

THIS EXPRESSION CAN BE REWRITTEN

(A25EBRA ONLY)
\[ p = \frac{A}{B_{12}} \left( \frac{N_1}{N_2} - \frac{B_{21}}{B_{12}} \right) = \frac{A}{B_{12}} e^{\frac{-\Delta E}{kT}} - \frac{B_{21}}{B_{12}} \]

Where \( \frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}} \)

* Boltzmann Distribution for a system at thermal equilibrium

Compare this expression to Planck's distribution:

\[ \frac{A}{B_{12}} = \frac{8\pi \hbar \nu^3}{c^3} \Rightarrow A = \left( \frac{8\pi \hbar \nu^3}{c^3} \right) B_{12} \]

And \( B_{12} = B_{21} \)

What does this imply?

* Spontaneous emission rate \((A) \propto \nu^3\)

Fluorescence rate very high for UV/visible transitions (electronic excited states)

Emission from excited vibrational and rotational states typically not observed

* If we neglect spontaneous emission \((A \to 0)\)

\[ W_{\text{net}} = N_1 B_{12} \rho - N_2 B_{21} \rho \quad \text{(up-down)} \]

\[ = (N_1 - N_2) B_{12} \rho \]

Absorption \(\propto\) population difference between states

Absorption \(\propto B_{12}\)

**Bottom line:** \(B_{12}\) is the quantity that quantifies strength of the transition

* Note that population inversion \((N_2 > N_1)\)

Cannot be achieved in a two-level system
The value of B comes from a time-dependent Schrödinger equation solution of light-matter interaction.

The detailed solution is too complicated to describe here, but the basic outline is:

* Assume the molecule is a two-level system in ground state at \( t=0 \)

\[
\Psi_1 = \psi_1 e^{-iE_1t/\hbar}, \quad \Psi_2 = \psi_2 e^{-iE_2t/\hbar}
\]

\( \Psi_1, \Psi_2 \)

* Recognize that wavelength of light is \( \approx 10^2 \) nm, which is much larger than size of molecule (\( \approx 1 \) nm), and let's also assume that electric-field interacts with permanent or induced charge dipole in molecule (electric-dipole approximation: magnetic transitions weak)

\[
\hat{H}_{\text{field}}(t) = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}} = -d_x E_0 \cos(2\pi ft)
\]

Assuming E-field amplitude along X-axis

* Solve T.D.S.E. for optical transition rate

\[
(\hat{H}_0 + \hat{H}_{\text{field}}) \phi(x,t) = i\hbar \frac{\partial \phi(x,t)}{\partial t}
\]

\[
\phi(x) = \psi_1(t) \Psi_1 + \psi_2(t) \Psi_2
\]

Initial conditions

\[
|\psi_1(0)|^2 = 1, \quad |\psi_2(0)|^2 = 0
\]

At time \( t \):

\[
|\psi_1(t)|^2 < 1, \quad |\psi_2(t)|^2 > 0
\]

E-field puts system into superposition state of \( \Psi_1 + \Psi_2 \)

* Transition rate - what is \( |\psi_2(t)|^2 \)?

* Substitute \( \phi(x,t) \) into T.D.S.E.

\[
1|\psi_2(t)|^2 = \frac{E_0^2 |d_x|^2}{\hbar^2} \frac{1}{|\Delta E|^2} 
\]

\[
\Delta E = E_2 - E_1
\]
Transition Dipole Moments

\[ M_{x}^{z} = \langle \frac{1}{2} | \hat{M}_{x} | \frac{1}{2} \rangle \]

\[ \hat{M} = M_{x} \hat{x} + M_{y} \hat{y} + M_{z} \hat{z} \]

\[ \hat{M} = \sum_{i} q_{i} \hat{r}_{i} \]

\[ \hat{M} \text{ is Q.M. dipole moment operator.} \]

\[ M_{x} \text{ is the } x\text{-component.} \]

Since we're working with E-field + dipole only along x-axis

The expression for \[ |a_{0}(t)|^{2} \]

shows that population transfer from \[ y_{1} \rightarrow y_{2} \] occurs when

\[ * E_0 \neq 0 \text{ (light is on)} \]

\[ * \Delta E \approx \hbar \nu \text{ (on "resonance")} \]

\[ * M_{x}^{z} 
eq 0 \text{ (transition dipole moment \( \neq 0 \))} \]

With the appropriate unit conversions, \[ B = \frac{|M_{x}^{z}|^{2}}{\hbar \epsilon_0 c^{2}} \]

\[ M_{x}^{z} \text{ is a measure of charge redistribution.} \]

Photons can be created or destroyed only if charge is redistributed by the transition \[ y_{1} \rightarrow y_{2} \]

E-field does work on molecule if photon absorbed if charge distribution in molecule in \[ y_{1} \rightarrow y_{2} \] differs, the E-field causes an oscillating dipole. If the oscillation frequency matches frequency of E-field \[ \rightarrow \text{ absorption or emission occurs} \]

Requirement for \[ M_{x}^{z} 
eq 0 \rightarrow \text{ selection rules} \]
FOR ATOMIC TRANSITIONS:

\[ \hat{\mu} = q \cdot \hat{r} \]

is the dipole operator using radial coordinate \( z = r \cos \theta \) so \( \mu_2 = q r \cos \theta \).

Consider a \( 1s \rightarrow 2s \) transition. You already learned that this would be forbidden because \( \Delta \ell = 0 \)

\[ \mu^{21} = \langle \psi_{2s} | \hat{r} | \psi_{1s} \rangle \]

For H: \( \psi_{1s} \approx e^{-r/a_0} \); \( \psi_{2s} \approx (2 - \frac{r}{a_0}) e^{-r/2a_0} \)

Remember that \( \hat{r} \) is a vector with \( x, y, z \) components.

Let's only look at \( M_z \) component — in spherical coordinates, \( z = r \cos \theta \) so \( M_z = q r \cos \theta \)

\[ M_z = q \int_0^1 \int_0^{2\pi} \int_0^\pi \sin \theta \phi \psi_{2s}^* r \cos \theta \psi_{1s} \]

So \( M_z = 0 \) for \( \Delta \ell = 0 \) as expected.

Symmetry arguments can be used to determine which of these expressions vanish when evaluating transition dipole.

S.A.B. 13.3

NOW WE'RE IN A POSITION TO DISCUSS INDIVIDUAL SPECTROSCOPES THAT PROBE MOLECULAR MOTIONS, BUT LET'S FIRST LOOK AT HOW THEY FIT TOGETHER:

WE USED BORN-OPPENHEIMER APPROXIMATION TO OBTAIN

\[ E_e(R) = \text{potential energy as a function of } R \]

FOR EACH ELECTRONIC STATE \( e \).

FOR NUCLEAR MOTION, WE ARE LEFT WITH

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla_R^2 + E(R) \]

DROP "E" LABEL FOR ELECTRONIC STATES

KINETIC ENERGY OF ROT, VIBRATION, TRANSLATION
Chem 453 Fall 2015

Nuclear Motion

As a consequence, we now have a separable problem:

\[ H = H_{\text{TR}} + H_{\text{VIB}} + H_{\text{ROT}} \]

Translation + Rotation only kinetic energy

Vibration contains \( E(R) \)

So, within B.O. approximation:

\[ \psi_{\text{TOTAL}} = \psi_{\text{TR}} \psi_{\text{ROT}} \psi_{\text{VIB}} \]

\( \psi \)'s and \( E \)'s can be obtained by solving time-independent Schrödinger equations - Free particle

Approximations for molecular motions

Rotational Spectroscopy

Diatomic. For photon absorption to cause a transition

\[ J, M \rightarrow J', M' \]

Quantum numbers for molecular rotation

\[ E_{\text{ROT}} = \frac{J^2}{2I} J(J+1) \]

Rigid rotor levels \( J \)

\( M = -J \ldots 0 \ldots +J \) degenerate

Selection Rules?

For a molecule to transition from \( \psi_{\text{e, v, JM}} \rightarrow \psi_{\text{e, v, J'M'}} \)

\[ \psi_{\text{JM}} = \langle \psi_{\text{e, v, JM}} | \psi_{\text{e, v, J'M'}} \rangle \]

So

\[ \psi_{\text{JM}} = \langle \psi_{\text{e, v, JM}} | \hat{M} | \psi_{\text{e, v, JM}} \rangle \]

\[ M = M_0 \langle \psi_{\text{JM}} | \hat{M} | \psi_{\text{JM}} \rangle \]

\( M_0 \) is permanent dipole moment for electronic state \( (\psi_{\text{JM}}) \)

So \( M_0 \neq 0 \) "gross selection rule"

Polar molecules only!

\( \langle \psi_{\text{JM}} | \hat{M} | \psi_{\text{JM}} \rangle \) can be evaluated with \( \psi_{\text{JM}} \) as spherical harmonics

\[ \Delta J = \pm 1 \]

\[ \Delta M = 0, \pm 1 \]
Rotational transitions occur when photons in far-IR or microwave spectral regions are absorbed.

Molecules rotate about each of their 3 axes in space with nonzero moments of inertia (only 2 rotations for linear molecules).

Since the specific selection rule is \( \Delta J = \pm 1 \) and \( E_J = \frac{\hbar^2}{2I} J(J+1) \), we can see that

\[
E_{J+1} - E_J = \frac{\hbar^2}{2I} [ (J+2)(J+1) - J(J+1) ] = \frac{\hbar^2}{I} (J+1)
\]

\[ \rightarrow \text{Spacing } \Delta E \text{ increases as } J \text{ increases.} \]

Spectroscopists define "rotational constant" \( B \) as

\[
B = \frac{\hbar}{8\pi^2 I} \text{ in Hz (s\(^{-1}\)) or } B = \frac{\hbar}{4\pi^2 c I} \text{ in cm}^{-1}\]

So \( \Delta E = \hbar \nu_{\text{photon}} = \frac{\hbar^2}{2I}(J+1) \rightarrow \nu = \frac{\hbar}{4\pi^2 I} (J+1) \)

\[ \rightarrow \nu_{J \rightarrow J+1} (\text{Hz}) = 2B (J+1) \text{ or } \nu_{J \rightarrow J+1} (\text{cm}^{-1}) = 2B (J+1) \]

Which means that a rotational spectrum of a diatomic \(*\) consists of a set of absorption peaks spaced by \( 2B \) (see slide) Chem4551-31.ppt.

The value of \( B \) or \( \hat{B} \) from a rotational spectrum can be used to obtain bond length, \( r_0 \):

\[
I = \sum M_i r_i^2 \quad M = \frac{m_1 m_2}{m_1 + m_2}
\]
CONSIDER THESE MOLECULES:

\[ \text{H}_2 \quad \text{HF} \quad \text{HCl} \quad \text{HBr} \quad \text{HI} \]

\[ \begin{align*}
\text{E} & \quad 74 \quad 92 \quad 129 \quad 141 \quad 161 \quad (\text{pm}) \\
\text{B} & \quad 60.86 \quad 20.96 \quad 10.58 \quad 8.47 \quad 6.51 \quad (\text{cm}^{-1})
\end{align*} \]

\[ \rightarrow \text{INCREASING} \ I \ (\text{DECREASING} \ B) \]

Heavier molecules have smaller rotational constants.

EXAMPLE CASE:

MICROWAVE SPECTRUM OF \text{^{12}C^{16}O} shows lines with 3.845 cm\(^{-1}\) separation. Calculate bond length.

\[ 2B = 3.845 \text{ cm}^{-1} \quad B = 1.923 \text{ cm}^{-1} \]

\[ I = \frac{\hbar}{8\pi^2 B^2} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{8\pi^2 (1.923 \text{ cm}^{-1})(3 \times 10^{10} \text{ cm}^2/\text{s})} = 1.46 \times 10^{-45} \text{ kg} \cdot \text{m}^2 \]

\[ \mu = \frac{m_c m_0}{m_c + m_0} = \frac{(12 \cdot 16)}{12 + 16}(1.661 \times 10^{-27} \text{ kg}) = 1.139 \times 10^{-26} \text{ kg} \]

\[ r = \sqrt{I/\mu} = \sqrt{1.46 \times 10^{-45} \text{ kg} \cdot \text{m}^2 / 1.139 \times 10^{-26} \text{ kg}} = 1.13 \times 10^{-0.9} \text{m} \\
(113 \text{ pm}, 1.13 \text{ Å}) \]

CHECK CALCULATIONS: \[ I \approx 10^{-45} \text{ to } 10^{-46} \text{ kg} \cdot \text{m}^2 \]

\[ \mu \approx 10^{-25} \text{ to } 10^{-26} \text{ kg} \]

AT HIGH ROTATIONAL STATES, CENTRIFUGAL DISTORTION CAUSES LENGTHENING OF BOND e.g., FOR HCl:

\[ r = 1.283 \text{ Å} \text{ at } J=3 \rightarrow 4; \quad r = 1.293 \text{ at } J=10 \rightarrow 11 \]

WE'VE CONSIDERED THE SIGNIFICANCE OF THE ROTATIONAL LINES—HOW ABOUT THE INTENSITIES OF THESE LINES?
Typical spectrum is a series of lines:

Absorption intensity increases with \(J\) (initial rotational quantum number) passes through max, then tails off...

Recall that absorption intensity is proportional to population difference between states.

This profile is result of thermal distribution of population in rotational levels - similar to Maxwell-Boltzmann speed distribution in gas.

\[ \text{LEVEL} \leftrightarrow \text{ALL QUANTUM STATES AT SAME ENERGY} \]

Population \(N_j\) of molecules in state \(i\) with energy \(E_i\):

For a system at temperature \(T\) is given by Boltzmann distribution

\[
\frac{N_j}{N_{tot}} = \frac{g_j e^{-E_j/kT}}{\sum_j g_j e^{-E_j/kT}} = \frac{g_j e^{-E_j/kT}}{\rho_{rot}}
\]

\(N_j/N_{tot}\): Fraction of molecules in initial level \(j\)

\(g_j = (2j+1)\) degeneracy of states at energy level \(j\)

\(g\) is sum over all thermally accessible states

"partition function" - # of accessible states at temperature \(T\)

\(g=1\) \(\leftrightarrow\) all molecules in one state (low temp)

\(g \sim 10-100\) for small molecule rotational states at 298K
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WIDTH OF THE ROTATIONAL ENVELOPE & PEAK OF DISTRIBUTION

depends on temperature - useful for astronomy & combustion research

To find \( J_{\text{max}} \) (peak) treat \( J \) as a continuous variable

\[ \frac{dN_j}{dJ} = 0 \quad \text{at maximum} \quad N_j(T) \]

\[ J_{\text{max}} = \left( \frac{k_BT}{2\hbar^2C_B} \right)^{1/2} = \frac{1}{2} \]

For typical small molecule, \( \tilde{B} \ll 1 \text{ cm}^{-1} \)

Eg, for DCS, \( \tilde{B} = 0.2 \text{ cm}^{-1} \)

At 298 K, \( k_BT = 257 \text{ cm}^{-1} \times 1000 \text{ mcB} \)

\[ J_{\text{max}} = 22 \]

VIBRATIONAL SPECTROSCOPY (§ 5.6)

Molecular vibrations are often modeled as harmonic oscillators

At low energies, 3N-6 (nonlinear) or 3N-5 (linear) vibrational modes per molecule. Consider selection rule for absorption

(diatomic, 1-D harmonic):

\[ M_i = \langle \frac{1}{2} | \hat{\mu}_i | \frac{1}{2} \rangle \]

Think of dipole as arising from partial charges \( \pm e_0 \) separated by \( \hat{R} = R_0 + \hat{x} \)

\( R_0 \) - equilibrium bond length

\( x \) - displacement \( (V = \frac{1}{2}kx^2) \)

\[ \hat{\mu} = \hat{R} \hat{e}_0 = R_0 \hat{e}_0 + \hat{x} \hat{e}_0 = \mu_0 + \hat{x} \hat{e}_0 \]

\[ \frac{d\mu}{dx} = \hat{e}_0 \quad \text{and} \quad \mu_0 \text{ is permanent dipole moment} \]

For a transition, \( i \rightarrow f \)

\[ M_i = \langle \frac{1}{2} | \mu_0 + \hat{x} \hat{e}_0 | \frac{1}{2} \rangle = \mu_0 \langle \frac{1}{2} | \frac{1}{2} \rangle + \hat{e}_0 \langle \frac{1}{2} | x \frac{1}{2} \rangle > \]

\[ M_i = \hat{e}_0 \langle \frac{1}{2} | x \frac{1}{2} \rangle > = \left( \frac{\partial \mu}{\partial x} \right) \langle \frac{1}{2} | x \frac{1}{2} \rangle > \]
\[
\frac{\partial V}{\partial x} = 0 \quad \text{only if dipole moment changes with bond length (heteronuclear \, \text{diatomics}) \, \text{CO, HCl, N}_2, H_2}
\]

\[
\langle \psi'_f | \frac{\partial}{\partial x} | \psi'_i \rangle \neq 0 \quad \text{for Hermite polynomials only if} \quad \Delta \nu = \pm 1
\]

**Energies of Transitions?** We saw that
\[
E_v = (v + \frac{1}{2}) \hbar \nu = (v + \frac{1}{2}) \hbar \omega
\]

with \( \omega = \sqrt{\frac{k}{\mu}} \)

Harmonic systems have \( E_{v+1} - E_v = \hbar \nu = \hbar \omega \)

So each vibrational mode \( \rightarrow \) one vib. transition

Frequency/energy of transition is sensitive to force constant, thus bond strength \( \nu = \frac{1}{2} k x^2 = \frac{1}{2} \mu \omega^2 x^2 \)

\( k \) has units of \( N/m \) (\( k \, \text{erg/cm}^2 \) spring constant)

Consider CO
\[
M = \frac{12 \cdot 15.99 + 16 \cdot 1.008}{12 + 16} \times 1.66 \times 10^{-27} \text{ kg} = 1.139 \times 10^{-26} \text{kg}
\]

\( \nu = 0 \rightarrow 1 \) transition \( \Delta E = \frac{1}{2} \hbar \omega_0 = 2170 \text{ cm}^{-1} \) (431 \text{ v} \text{.} \text{J})

\( \omega_0 = 4.08 \times 10^{14} \text{ s}^{-1} \)

\( \nu = 4.08 / 2 \pi \times 10^{14} \text{ s}^{-1} \)

\( = 6.49 \times 10^{13} \text{ s}^{-1} \)

\[
T = \frac{1}{\nu} = 15.4 \text{ fs} \quad \text{fast!}
\]

\[
\Delta E = \frac{1}{2} \hbar \omega_0 = \frac{\hbar}{2\pi} \sqrt{\frac{k}{\mu}} \rightarrow k = \frac{\hbar}{\mu} \left( \frac{2\pi \Delta E}{\hbar} \right)^2
\]

\[
k_0 = 1.139 \times 10^{-26} \text{kg} \left( \frac{2\pi \cdot 1.3 \times 10^{-20} \text{J}}{6.626 \times 10^{-34} \text{J} \cdot \text{s}} \right) = 1900 \text{ N/m}
\]

**Typical force constants**
- \( k_0 = 553 \text{ N/m} \) (\( H_2 \)) single \( \text{H} \) bond
- \( 2300 \text{ N/m} \) (\( N_2 \)) bond

Vibrational transitions are mostly in range from
- 200 \text{ cm}^{-1} \rightarrow 3000 \text{ cm}^{-1} \quad \text{set by force constant} \& \text{ masses}

**Isotope Substitution:** \( \omega_0 = \sqrt{\frac{k}{\mu}} \quad k \text{ doesn't change but reduced mass changes} \)
EXAMPLE OF FREQUENCY CHANGES FOR ISOTOPE SUBSTITUTION:

\( \text{H}_2 \), \( \nu_0 = 4401 \text{ cm}^{-1} \)

\( \text{H}_2^\text{D} : \quad \nu_{\text{HD}} = \frac{m_\text{H} m_\text{D}}{m_\text{H} + m_\text{D}} = \frac{2}{3} \nu_\text{H} \)

\( \nu_{\text{H}_2} = \frac{7m_\text{H}}{2m_\text{H}} = \frac{7}{2} \nu_\text{H} \)

\( \nu_{\text{HD}} = \frac{4}{3} \nu_{\text{H}_2} \quad \omega_0 = \sqrt{\frac{K}{\mu}} \quad \text{so} \quad \omega_0 \sqrt{\mu} \)

so \( \nu_0 (\text{HD}) = \frac{3}{2} \nu_0 (\text{H}_2) \cdot \sqrt{\frac{3}{4}} = 3811 \text{ cm}^{-1} \)

\( \text{D}_2 : \quad \nu_{\text{D}_2} = 2m_\text{H} = 2 \nu_\text{H}_2 \quad \Rightarrow \quad \frac{1}{2} \nu_0 (\text{D}_2) = \frac{1}{2} \nu_0 (\sqrt{2}) = 3112 \text{ cm}^{-1} \)

HEAVIER ISOTOPE \( \rightarrow \) SMALLER VIBRATIONAL ENERGY SPACING

ANHARMONICITY - HARMONIC APPROXIMATION IS ONLY REASONABLE AT THE BOTTOM OF THE POTENTIAL WELL (CHM 4531-15.PPT)

REAL BONDS BREAK AT HIGH ENERGY, AND VIBRATIONAL FREQUENCIES "SOFTEN" AT HIGH ENERGIES, BEFORE BREAKAGE.

\( \Rightarrow \) REALISTIC POTENTIAL WIDENS AT HIGH ENERGY.

"MORSE POTENTIAL" IS MORE REALISTIC

\[ V(r) = D_0 \left[ 1 - e^{-\alpha (r-r_0)} \right]^2 \quad \alpha = \frac{\nu_0}{D_0} \sqrt{\frac{\mu}{2}} \]

\[ E = \frac{\nu_0}{2} (\nu + \frac{1}{2}) - \frac{1}{2D_0} \left[ (\nu_0)^2 (\nu + \frac{1}{2})^2 \right] \]

* NOTE THAT \( D_0 \) IS THE DISSOCIATION ENERGY MEASURED FROM THE BOTTOM OF THE POTENTIAL, WHICH IS NOT THE SAME AS THE SPECTROSCOPIC DISSOCIATION ENERGY \( (D_0) \)

\( D_0 - D_0 = \frac{1}{2} \nu_0 \) (S.A.B. Fig. 13.3)

* MORSE POTENTIAL HAS FINITE \# OF BOUND STATES

* ANHARMONICITY INCREASES WITH \( V \)

\( \Rightarrow E_{\nu+1} - E_{\nu} \) DECREASES
VIBRATIONAL ABSORPTION LINES OF SMALL MOLECULES IN GAS PHASE

Show fine structure due to rotational motions excited simultaneously with vibrational excitation. Why?

Vibrational excitation leads to abrupt change in bond length, which changes moment of inertia, due to conservation of angular momentum, there is a change in J-state.

*(Show Aprili's rules)*

The energies of vibrational-rotational transitions can be written as a sum of harmonic oscillator + rigid rotor terms:

$$E_{v',J} = (v + \frac{1}{2})\hbar\omega + B\hbar\sqrt{J(J+1)}$$

$$B = \frac{\hbar}{2I'n}$$

**Selection rules:**
- Gross selection rule same as IR absorption for vibrations (dipole moment changes w/coord.)
- Specific selection rule: combination of pure rotational + pure vibrational rules

$$\Delta v = \pm 1; \Delta J = \pm 1$$

Spectral lines appear at $\Delta E$ between lower $(v'',J'')$ and upper $(v',J')$ levels:

$$\Delta E = h\nu = (v''-v')h\omega + B\hbar [J'(J'+1) - J''(J''+1)]$$

To convert to cm$^{-1}$, $E/hc \rightarrow \tilde{\nu}$

$$\tilde{\nu} = (v''-v')\frac{\nu_0}{V} + \frac{B}{\nu_0} [J'(J'+1) - J''(J''+1)]$$

*Let's only consider $v'' = 0 \rightarrow v' = 1$ transition and apply $\Delta J = \pm 1$ selection rules: Transitions fall into 2 "branches"

**P-branch** ($\Delta J = -1$)

$$\tilde{\nu} = \nu_0 - 2J'B$$

**R-branch** ($\Delta J = +1$)

$$\tilde{\nu} = \nu_0 + 2J'B$$
VIB/ROT SPECTRA

There is a gap between P/R branches:

P: \( J'' = 1, J' = 0 \)
R: \( J'' = 0, J' = 1 \)

\[ \tilde{v}_p = \frac{\nu_0 - 2\tilde{B}}{\hbar c} \]
\[ \tilde{v}_r = \frac{\nu_0 + 2\tilde{B}}{\hbar c} \]

So 4\( \tilde{B} \) separation between branches

(SHOW HCL SPECTRUM)

The P/R intensity envelopes are determined by thermal population considerations - same as for rotational spectra:

- \( 2J+1 \) degeneracy for each \( J \) value increases with \( J \)
- \( e^{-\frac{E_j}{kT}} \) population term decreases with \( J \)

So overall, \( \frac{N_j}{N_{total}} = \frac{(2J+1)e^{-\frac{E_j}{kT}}}{9} \)

Vibrational frequencies of diatomics range from \( \nu \leq 215 \text{ cm}^{-1} \) for \( ^{12} \text{I}_2 \) to \( 4400 \text{ cm}^{-1} \) \( (\text{H}_2) \). For polyatomics, the low end may extend to \( \ll \text{100 cm}^{-1} \) for bending motions.

So considering thermal populations:

\( kT/\hbar c \approx 207 \text{ cm}^{-1} \rightarrow e^{-\frac{E_{vibr}}{kT}} \ll 1 \) Usually much less!

Thermal population of vibrational levels above \( \nu'' = 0 \) is typically rather small, so it's reasonable to assume that only ground state level is populated at \( T = 298 \text{K} \).

For rotations, I introduced the "partition function" \( q \)

\[ q_v = \sum_{\nu = 0}^{\infty} q_{v=\nu} e^{-\frac{E_v}{kT}} \] For a diatomic with a single vibrational mode, \( q_v = 1, E_v = (\nu + \frac{1}{2})\hbar \omega \)

\[ q_v = \frac{1}{1 - e^{-\frac{\hbar \omega}{kT}}} \] because for \( x < 1, \frac{1}{1-x} = 1 + x + x^2 + \ldots \)

\[ q_v = 1 - 1/0 \text{ per vibrational mode (one for diatomics)} \]

\( q_v \) increases with size of molecule \( (3N-6 \text{ vibrations}) \)
CHEM 4531  FALL 2015  ELECTRIC SPECTROSCOPY (MOLECULES)

VISIBLE TO UV-WAVELENGTH PHOTONS CAN BE ABSORBED BY
MOLECULES TO CAUSE ELECTRONIC TRANSITIONS 1-10 eV
\( \lambda < 1000 \text{ nm} \)

THESE OPTICAL TRANSITIONS CAN BE VERY STRONG, AND GIVE RISE TO
THE INTENSE COLORS OF MANY MATERIALS E.G., CHLOROPHYLL IN PLANTS
HOMES IN BLOOD/TISSUES

ELECTRONIC STRUCTURE OF MOLECULES CAN BE VERY COMPLICATED
BECAUSE OF THE NUMBER, DIVERSITY OF ATOMIC ORBITALS COMPRISING A
MOLECULE, AND ALSO BECAUSE MANY MOLECULES DON'T HAVE HIGH
ENOUGH SYMMETRY FOR SIMPLE SELECTION RULES TO APPLY AS WE SAW FOR
ATOMIC SPECTRA, SO, WE'LL TAKE A MORE QUALITATIVE VIEW

WITHIN THE B.O. APPROXIMATION, WE CAN CALCULATE THE ENERGY OF
EACH ELECTRONIC STATE AS A FUNCTION OF NUCLEAR GEOMETRY. AS
A RESULT, THIS IS THE PICTURE: (FOR 1-DIMENSION)

\[ E \]
\[ \text{ELECTRONIC POTENTIAL ENERGY} \]
\[ \text{SURFACE FOR EACH STATE} \]

\[ R_0 \]
\[ R \]

\[ \Delta E \] FOR ELECTRONIC TRANSITIONS IS TYPICALLY >> \( k_T \), SO
EXCEPT IN UNUSUAL CIRCUMSTANCES, MOLECULES ARE INITIALLY
IN THE GROUND ELECTRONIC STATE, AT BOND LENGTH \( R_0 \).
IMMEDIATELY AFTER A PHOTON IS ABSORBED, THE
MOLECULE FINDS ITSELF IN A GEOMETRY WHERE IT IS USUALLY
NOT AT THE MINIMUM, SO THE BOND LENGTH MUST
CHANGE, AND VIBRATION IS EXCITED. IN GAS PHASE,
ROTATIONAL EXCITATION ALSO OCCURS
CHEM 4531 FALL 2015

To explain vibrational structure & shapes of electronic spectra of molecules, we apply the "Franck-Condon" principle - nuclei are so massive compared to e- that electronic transitions occur much faster than nuclear geometry can respond

→ electronic transitions are "vertical" picture

Considering the vibrations - let's assume molecule is in ground electronic state, ground vibrational state (harmonic oscillator wavefunction), probability of making a transition at a particular photon energy depends on amplitude of the excited state vibrational wavefunction at the initial bond length (R_i) - show picture

→ depending on the displacement of the two curves, transitions may occur to several excited state vib. levels.

Consider the transition dipole moment for the excitation:

\[ M_{fi} = \langle \psi_f | \hat{\mu} | \psi_i \rangle \]

\[ \psi_i: \text{electronic WF} \]

\[ \psi_f: \text{vibrational} \]

Within the B.D. approximation, \( M_{fi} \) can be factored:

\[ M_{fi} = \langle \psi_f | \hat{\mu} | \psi_i \rangle \langle \psi_i | \psi_i \rangle \]

Assume dipole moment is not strong function of \( R \)

Electric dipole transition moment for redistribution of e- in i → f transition

Overlap integral between ground \( (\psi_i) \) and excited electronic state \( (\psi_f) \) wavefunctions

\[ M_{fi} = M_{fe} | S(\psi_f, \psi_i) | \]

Recall that transition intensity \( B = |M_{fi}|^2/6\varepsilon_h^{2} \)

\[ \text{So} \rightarrow \text{absorption } \propto |S(\psi_f, \psi_i)|^2 \]

\( S \) is the "Franck-Condon factor"
FRANCK-CONDON FACTORS

\( \* \) THE STRENGTH OF THE ABSORPTION TRANSITION IS PROPORTIONAL TO THE SQURED OVERLAP BETWEEN GROUND + EXCITED STATE VIB. WAVEFUNCTIONS

THE FRANCK-CONDON PRINCIPLE EXPLAINS "VIBRATIONAL PROGRESSIONS"

(\# show ch04-4531-34.ppt) VIBRATIONAL STRUCTURE IN ABSORPTION SPECTRA.

OTHER POTENTIAL IS USUALLY DISPLACED TO LARGER \( \text{Re} \) VALUE BECAUSE EXCITED STATES OFTEN HAVE MORE ANTBONDBING CHARACTER THAN GROUND STATE

"DISPLACEMENT" \( |\text{Re} - \text{Re}_0| = \Delta \)

SMALL \( \Delta \) : TRANSITIONS OCCUR TO A FEW EXCITED "VIBRONIC LEVELS -> NARROW SPECTRUM

LARGE \( \Delta \) : TRANSITIONS OCCUR TO SEVERAL EXCITED VIBRONIC LEVELS -> WIDE SPECTRUM OF LOWER PEAK INTENSITY

\* SEPARATIONS OF VIBRONIC LINES IN ABSORPTION SPECTRA DEPENDS ON EXCITED STATE VIBRATIONAL LEVELS

\* FLUORESCENCE (SPONTANEOUS EMISSION) SPECTRA ARE SHIFTED TO LOWER ENERGY (STOKES SHIFT) AND THE SPECTRAL SHAPE IS SIMILARLY CONTROLLED BY FRANCK-CONDON FACTORS FOR EACH EXCITED GROUND STATE VIBRONIC TRANSITION

SCHEMATIC DESCRIPTION OF STOKES SHIFT

\( \Delta \lambda = \lambda_{\text{em}} - \lambda_{\text{abs}} \)

IN MORE DETAIL ORDER OF EVENTS

\[ \begin{align*}
\text{Abs.} & \rightarrow \Delta \text{E} \\
\text{Em.} & \rightarrow \lambda_{\text{em}} \\
\lambda_{\text{abs}} & \rightarrow \Delta \text{E}
\end{align*} \]
1. Molecules are most probably excited to vibrational levels significantly above the "0-0" transition, due to Franck-Condon principle.

2. Vibrational energy in excited state is redistributed among all vibrational modes in molecule, or to solvent molecules via collisions. (Converted to heat!)
   - Energy loss occurs on ps ($10^{-12}$ sec) timescales so molecule drops to lowest vibrational level of excited state "vibrational relaxation"

3. Molecule emits from lowest level of excited state to excited-vibrational levels of ground state (controlled by Franck-Condon factors) on ns timescale

* If ground + excited electronic state curves are very similar → same vib. energy levels → fluorescence spectrum is mirror-image of absorption spectrum

These events are depicted in a diagram
- Show slide

* If excited-state structure greatly differs from ground state, shapes of absorption/emission spectra will significantly differ because energy levels differ
  - No mirror-image symmetry

* Large displacement ($\Delta$) but same energy levels, → mirror image absorption/emission curves show larger stokes shift
PHOTOPHYSICAL PROCESSES ARE OFTEN DEPICTED IN A "JABLONSKI DIAGRAM," WHICH IS BASICALLY LIKE A POTENTIAL ENERGY DIAGRAM WITHOUT AN EXPLICIT COORDINATE AXIS ON THE BOTTOM.

SINGLET STATES VERTICALLY SHIFTED, ABOVE EACH OTHER, LEFT-MOST TRIPLET STATES, QUINTET STATES SHIFTED PROGRESSIVELY TO THE RIGHT — STATES OF SAME MULTIPLICITY STACKED VERTICALLY.

VERTICAL DISPLACEMENT CORRESPONDS TO ΔE FOR ELECTRONIC EXCITATION.
VIBRATIONAL LEVELS ALSO DRAWN

- **S₀**
- **S₁**
- **S₂**
- **T₁**

**VIBRATIONAL RELAXATION**

**FLUORESCENCE**

**PHOSPHORESCENCE**

* **IC:** "INTERNAL CONVERSION" — RELAXATION BETWEEN STATES OF SAME MULTIPLICITY

* **ISC:** "INTERSYSTEM CROSSING" — BETWEEN STATES OF DIFFERING MULTIPLICITY

* FLUORESCENCE/SPIRITUAL EMISION: Sₙ → S₀ (PHOTON EMISSION)
  * USUALLY S₁ → S₀ (NS LIFETIMES)

* PHOSPHORESCENCE: T₁ → T₀ (PHOTON EMISSION (μSEC-MSEC))