Principles of Molecular Spectroscopy

What variables do we need to characterize a molecule?

> Nuclear and electronic configurations: *What is the structure of the molecule? What are the bond lengths? How strong or stiff are the bonds? What is the symmetry? Where is the electron density?*
> Molecular Behavior: *How much do the nuclei move (vibration/rotation)? How do the structural variables change with time?*
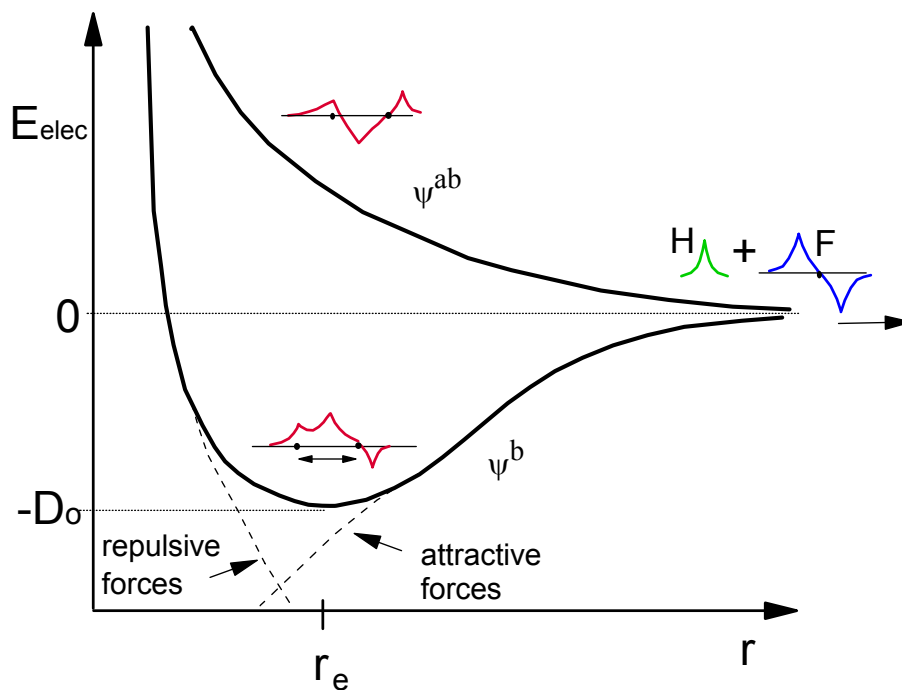
EXAMPLE: H–F

> What is your picture of the structure of this molecule? 2 nuclei + 10 e⁻? Molecular orbitals?

$$\psi^b = c_1 \ \psi^H_{1s} + c_2 \ \psi^F_{2p_z}$$

$$\psi^{ab} = c_2 \ \psi^H_{1s} - c_1 \ \psi^F_{2p_z}$$
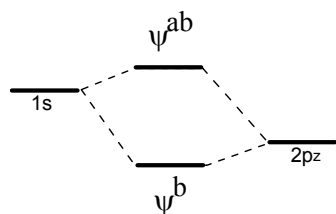
> We quantitatively characterize the structure through the electronic energy as a function of nuclear configuration:

> E_{elec} = electronic energy relative to isolated atoms

If we characterize this energy curve, we have learned much about our molecule:

1) r_e: What is the equilibrium separation between atoms?
2) D_0: What is the strength of the bond? How stable is molecule?
3) Shape of ψ^b or ψ^{ab}: Is r_e fixed? How stiff is bond? How does r_e change if you put energy into bond?
4) Splitting between surfaces: What is the nature and energy of the e^- orbitals involved in bonding?

How can you probe these energy surfaces with light?

- Light resonant with the motion of charged particles such as electrons or nuclei will be absorbed.

- We need rules for the frequency or energy of motion of nuclei and electrons. These will be related to the parameters above.

- What we will find is that different spectroscopies will tell us about different variables:

  Rotational spectroscopy: will tell us where r_e is.

  Vibrational spectroscopy: will tell us how stiff the bond is and about the curvature of potential.

  Electronic spectroscopy: will tell us about where electronic states lie $\rightarrow$ potential energy curves.

Change to a new frame of reference - molecular coordinates

- For any particle (nucleus or electron):

  ➢ Kinetic and potential energy associated with the motion of a particle

  ➢ Translation along *x, y, z* $\rightarrow$ *n* particles
    $\rightarrow$ *3n* degrees of freedom (d.o.f).
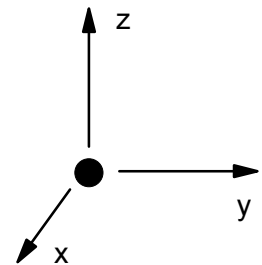
- In a molecule the positions of these particles are linked.

- Choose a molecular frame of reference that originates at the center of mass

$$r_0 = \frac{1}{M} \sum_i m_i r_i$$

***To simplify problem, treat nuclear and electronic motion separately.***

- Electrons are much lighter than nuclei. Therefore, we expect that the electrons will occupy a fixed distribution in space about a nuclear configuration.

- Separate different types of motion based on time-scale or energy of motion.

- 5.61: The basis for drawing potential energy curves is the Born-Oppenheimer Approximation: Motion of electron is much faster than nuclei; doesn't depend on nuclear kinetic energy.

Electrons: The spatial extent motion is described by atomic or molecular orbitals. We will return to this later.

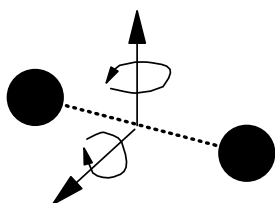***Nuclei:*** Three types of motion for nuclei with respect to the c.o.m. of the molecule:

Consider a diatomic (with 6 d.o.f).
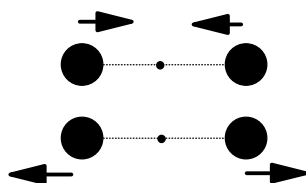
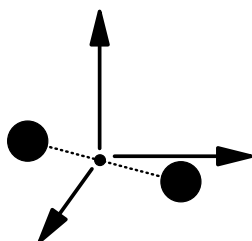   <u>**1) Vibration:**</u> along r.   Displacement of atoms relative to one another / C.O.M. fixed

    <u>**2) Rotation**</u>   Motion about C.O.M. / C.O.M. fixed

    <u>**3) Translation**</u>   move C.O.M.

> **For a polyatomic (n atoms) → 3n degrees of freedom**

	Linear	**Nonlinear**	
Vibrational:	3n−5	3n−6	*Normal Modes*
Rotational:	2	3	
Translational:	3	3	

How are these motions related to the structure of the molecule?
How do these reflect electronic potential?

A classical description allows you to say a lot about spectroscopy, but it doesn't explain experiments very well! We need quantum mechanics!

- The energy that we can add to a molecular system through the motion of one of these degrees of freedom is not continuous, but comes in discrete quantities.

- Energy levels are *quantized*

  Classically, no restriction on the energy in a system. (We can add or remove energy continuously.)

  Quantum mechanics tells us that these energies are not continuous but discrete. We have discrete states with spatial structure, and fixed energy. → These "eigenstates" define the extent of motion of a particle with a unit of energy, and no fractional amount is allowed.

- We represent the state of the system through *quantum numbers*—usually integers. The energy is related to these numbers.

  "Ground State" : configuration of electrons, nuclei, … (a set of quantum numbers) that represent the lowest energy state of the system.

Electronic States:

  We already started this lecture talking about atomic + molecular orbitals, which represent discrete energy states that electrons can occupy. You describe these through discrete quantum numbers, i.e. for atom: *n, l, m, m_s*

  n: principle quantum number; *l*: orb. ang. mom.; *m*: degeneracy; m_s: spin

- These states have definite energy and electron density *distribution* (spatial dimension).

- There is no way for an electron to occupy an intermediate energy between quantized values.

- The energy to move an electron from the ground (lowest energy) state to another is a lot: Typically 20,000-100,000 cm^{-1} = 10-50 kJ/mol. This corresponds to UV and visible light, $\lambda \sim$ 100-500nm

- For polyatomic molecules, we can use linear combinations of atomic orbitals.

Quantization of nuclear degrees of freedom:

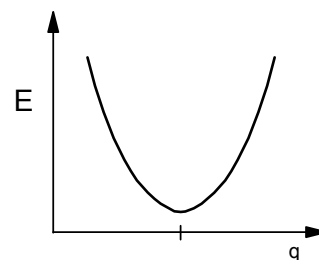The vibration, rotation, and translation of the *3n* nuclear d.o.f. of a molecule are also quantized.

Vibrations:

__Classically__ I can put any energy I want into vibrational motion $\rightarrow$ moves energy levels to higher displacement. For a harmonic oscillator:
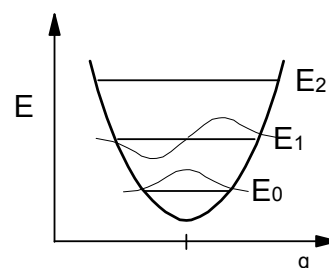
$$E = V + T = \frac{1}{2}kQ^2 + \frac{p^2}{2m}$$

$$Q(t) = A \sin \omega_0 t$$

__Quantum mechanics__ says there are discrete vibrational
energy levels corresponding to specific vibrational states (wave functions).

Each vibrational state has a probability distribution that tells me the probability of finding nuclei in particular position. (Similar to electronic states)

For a quantum mechanical harmonic oscillator, (the simplest quantum mechanical model for a vibration), the energies of these discrete vibrational energy levels is:

$$E_v = E_{vib} = \hbar\omega_0 \left(v + \tfrac{1}{2}\right) \qquad \omega_0 = \sqrt{\frac{k}{m_R}} = 2\pi\nu_0 \qquad \bar{\nu}_0 \cong 3000 - 300 \text{ cm}^{-1}$$

λ typically 3-30 μm (Mid-IR)

- v is the vibrational quantum number, v = 0,1,2…

- Even in lowest state $E_0 = h\nu_0 / 2$.

- Spacing between vibrational levels uniform

$$\Delta E = E_v - E_{v-1} = h\nu_0$$

- The proportionality constant between vibrational frequency and energy is Planck's constant $h = 6.626 \times 10^{-34} \text{ J s}$

- So if we can measure $E_v \rightarrow$ determine $\omega_0 \rightarrow$ determine k.

Rotation: …

Classically, rotation of a free object is governed by angular momentum $L = I\omega_A$ (equiv. to *p=mv* of linear motion)
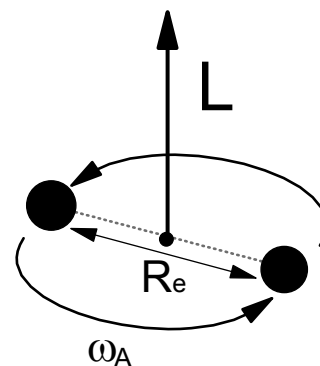
ω_A is the angular velocity ($\omega_A = 2\pi v$)

Moment of Inertia: $I = m_R R_e^2$ or $I = \sum_i m_i r_i^2$

The energy of free rotational motion is all kinetic:

$$E = \tfrac{1}{2}mv^2 = \frac{p^2}{2m} \quad \longleftarrow \quad \text{linear motion}$$

$$E = \tfrac{1}{2}I\omega_A^2 = \frac{\bar{L}^2}{2I} \quad \longleftarrow \quad \text{angular motion}$$

- Classically, the more energy I put into a rigid rotor, the faster it rotates
  $\rightarrow$ higher angular momentum.

- **Quantum mechanically** rotational angular momentum is quantized.

$$E_{rot} = \frac{\overline{L}^2}{2I} \qquad \text{still holds, but } L \text{ is quantized}$$

$$|L| = \hbar\sqrt{J(J+1)} \qquad J = 0,1,2,3\ldots \text{ (rotational angular momentum quantum number)}$$

$$E_{rot} = \frac{\hbar^2}{2I}J(J+1) = \frac{h}{8\pi^2 I}J(J+1) \equiv hc\overline{B}J(J+1)$$

$$\overline{B} = \frac{h}{8\pi^2 cI} \qquad \text{(in cm}^{-1}\text{)}$$

Typically 0.1-10 cm^{-1}
(far infrared/μwave)

- Rotational levels are not equally spaced.

- Rotational levels have degeneracy. $M_J = 0\ldots\pm J$; $g(J) = (2J+1)$

- Rotational spectroscopy: measure $E_{rot} \rightarrow$ determine $\overline{B} \rightarrow I \rightarrow R_e$!

TRANSLATION: (motion of center of mass)

Quantum mechanically: Energy levels given by particle-in-a-box

One-dimension: $\quad E_{trans} = \frac{n^2 h^2}{8ma^2} \quad n = 1,2\ldots \qquad a$: length of box

- This only matters for *very* small boxes.

- Free space: $a \rightarrow \infty$; energy levels are continuous.

Quantum mechanical energies are summed over all degrees of freedom:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} + E_{nuclear} + ...$$

$$\dfrac{E_{trans}, E_{nuclear}, E_{spin}}{\nearrow}$$

low E

$$E = E_{elec} + \hbar\omega_0\left(v + \tfrac{1}{2}\right) + hc\overline{B}J(J+1) + ...$$

$\Delta E \cong 50{,}000 \text{ cm}^{-1}$ $\sim 1{,}000 \text{ cm}^{-1}$ $\sim 1\text{-}10 \text{cm}^{-1}$ $v = 0,1,2...$
                                                               $J = 0,1,2...$

- specify energy through a set of quantum numbers, and characteristic vib./rot./etc. constants

Electronic   **Vibrational**   **Rotational**
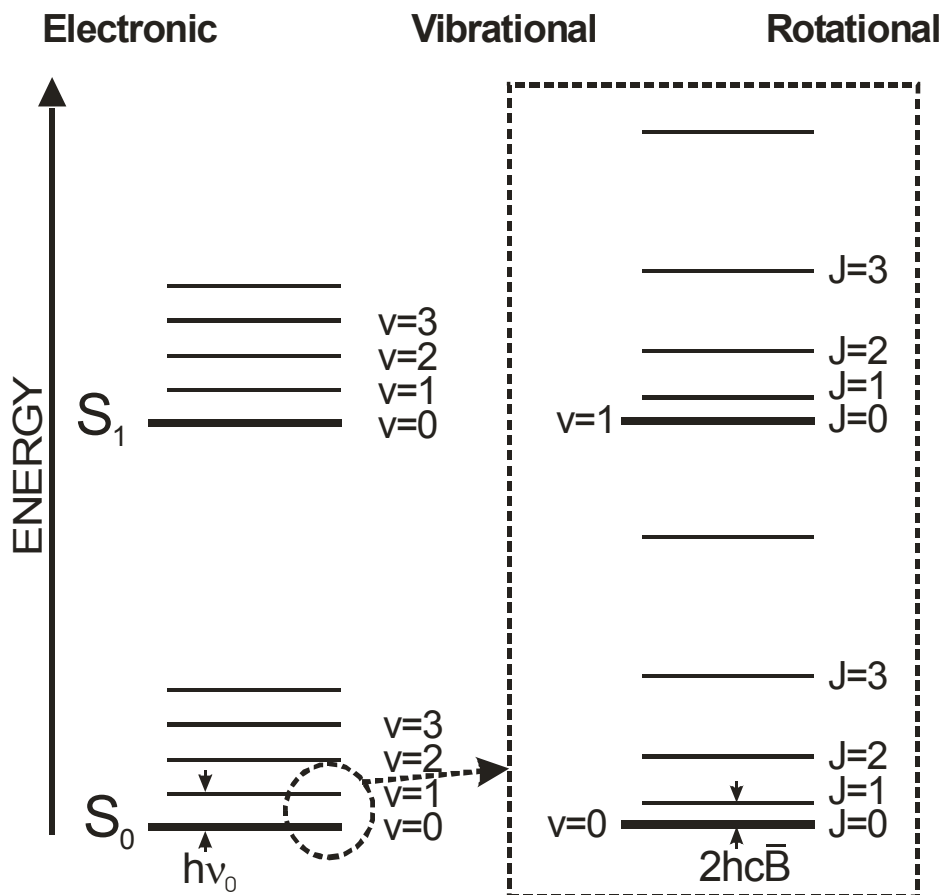
LIGHT:

Classically we talked about a light field driving a classical H.O. The external field allows us to drive the H.O. to higher displacement, the efficiency of displacing the oscillator depended on resonance: $\omega = \omega_0$

How is this compatible with quantum energy levels?

To drive a quantum H.O. to higher amplitude $\rightarrow$ higher energies $\rightarrow$ higher V $\rightarrow$ transitions are discrete!

- Light drives transitions between discrete states.

- Transition requires resonance.

- Light is also quantized: $E = h\nu = \hbar\omega$

    Resonance $\leftrightarrow$ Energy conservation

    Energy of light $=$ Energy difference between initial (i) and final (f) states

    $$E = E_f - E_i$$

    $$\omega = \frac{E_f - E_i}{\hbar} = \frac{\Delta E}{\hbar} \equiv \omega_{fi}$$

- **<u>Absorption features related to energy level splittings!</u>**

    These transitions can be between different electronic, vibrational, rotational states:

    $$E_{field} = \Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot} + \ldots$$

	<u>Spectroscopy</u>	**<u>Light Freq.</u>**	**<u>Transitions</u>**
	Electronic	UV/Vis 10^4-10^5 cm^{-1}	electronic ($+$ vib $+$ rot)
Rot-vib.:	IR/Raman	$10^2 - 10^3\,cm^{-1}$	vibrational ($+$ rot)
pure rot.:	FIR/µwave	$10^{-1} - 10\,cm^{-1}$	rotational

initial state: v'', J''	(double primed)
final state: v', J'	(single primed)

In a quantum system . . . what does light do to quantum states?

Quantum eigenstates are time-independent (stationary). There is no motion.
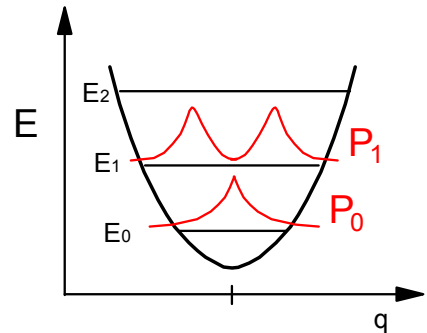
We shouldn't think of absorption as taking molecules from one eigenstate and putting it in another—that's not quite correct. Rather, the light couples these two states together.

What happens after turning on the light field?

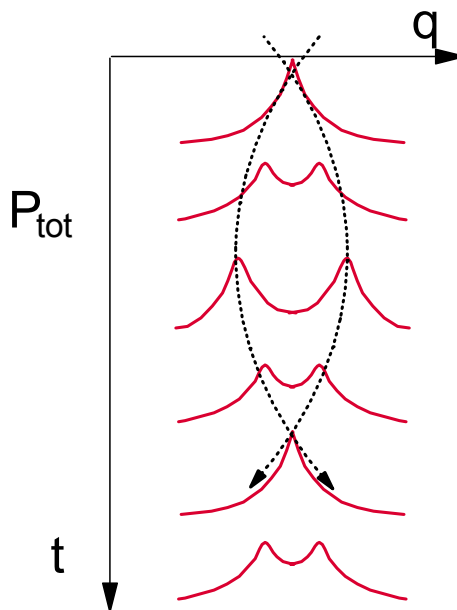$$\psi(t) = c_0(t)\, \psi_0 + c_1(t)\, \psi_1$$

$$P_1 = \left| c_1(t) \right|^2 \quad \propto \quad \sin^2\left(E_1 - E_0\right) t / \hbar$$

$$P_0 = 1 - \left| c_1(t) \right|^2 \quad \propto \quad \cos^2\left(E_1 - E_0\right) t / \hbar$$

The probability of finding the system in one state
     oscillates back and forth.

$P_{tot} = P_1 + P_0$

Intensity of Absorption Lines

What influences the strength of a line?

1) *Population*

Classically: Beer's Law absorbance to number of molecules, *N*, or concentration.

Quantum mechanically: For absorption, what really matters is the population difference between the two quantum states!

$$\Delta N = N_f - N_i$$

- The population of a quantum state – the fraction of molecules occupying that state – is dictated by the temperature.

- For many molecules, the particles distribute themselves through quantum states.

- Lowest E state is most probable. At T = 0 K all molecules are in the ground state—lowest electronic state, $v = 0, J = 0$.

- The equilibrium thermal energy of a collection of molecules has is characterized by the temperature.

$$\langle E \rangle \propto T$$

- The fraction of molecules occupying a quantum level of energy E_i at a temperature T is described by the

Boltzmann distribution (a probability function):

$$N_j = \frac{1}{q} g_j \exp(-E_j / k_B T)$$

- N_j is the fraction of molecules in state j.

- g_j is the degeneracy of the jth state.

- q, the partition function, is a sum over the population of all states

$$q = \sum_j g_j \exp(-E_j / k_B T).$$

- k_B is the Boltzmann constant (1.38×10^{-23} J/K).

- $hc/k_B = 1.44$ cm^{-1} K
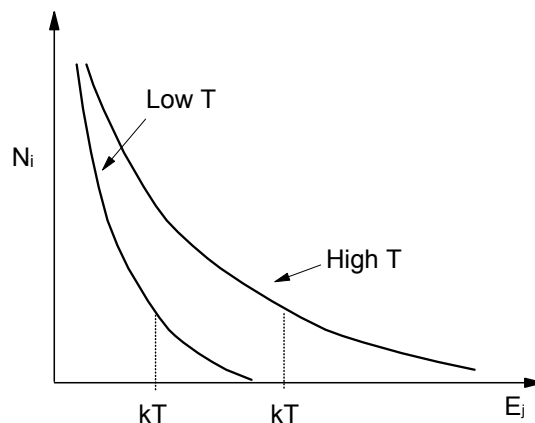
At room temperature (300 K), $k_B T/hc = 208$ cm^{-1}. This means that energy states near or below 200 cm^{-1} will have thermal population at room temperature. These are typically only rotational states in the ground vibrational and ground electronic state.

2) *Transition dipole moment*

The strength of the transition is dictated by the change in the dipole moment with coordinate.

Dipole moment → selection rules!

Selection rules tell you whether absorption or more generally a quantum transition is allowed.

Classically: Absorption requires change of dipole moment

a) $\dfrac{\partial \overline{\mu}}{\partial Q} \rightarrow vibration$

b) Rotation requires polar molecule!

Quantum: Transition dipole moment. The probability of transition is

$$P_{i \rightarrow f} = \left| \int \psi_{final}^{*} \hat{\mu} \psi_{initial} dr \right|^2 \qquad\qquad \hat{\mu} = \sum_{i} q_i \hat{r}_i \text{ is dipole operator}$$

Requires change of parity $(g \leftrightarrow u \text{ symmetry})$.

Vibrations: For a quantum H.O. : $\Delta v = \pm 1$ $\qquad (\dfrac{\partial \overline{\mu}}{\partial Q} \text{ parallel to symmetry axis})$

$$\int \psi_{v'}^{*} q \,\hat{x}\, \psi_{v''} dx \neq 0 \qquad \text{if } v' = v'' \pm 1$$

Anharmonic oscillator Δv relaxed.

Rotations: For quantum rigid rotor: $\Delta J = \pm 1$

$$\int \psi_{J',M_J'}^{*} q \,\hat{x}\, \psi_{J'',M_J''} dx \neq 0 \ \ \text{if } J' = J'' \pm 1$$

(Together with vibrational transition with $\partial \mu / \partial q \perp$ to symmetry axis $\Delta J = -1, 0, +1$).