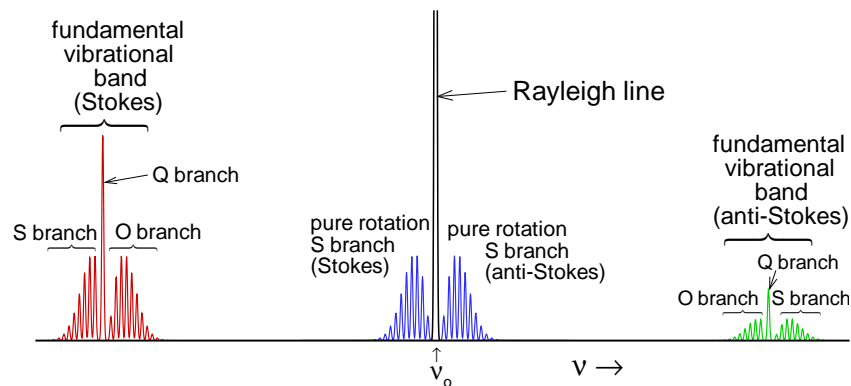
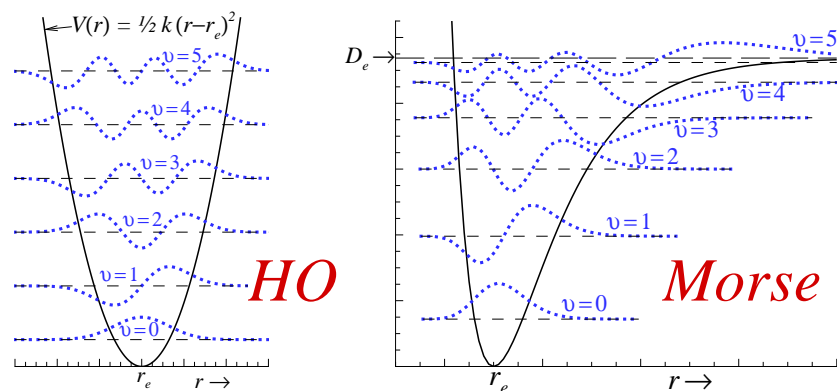
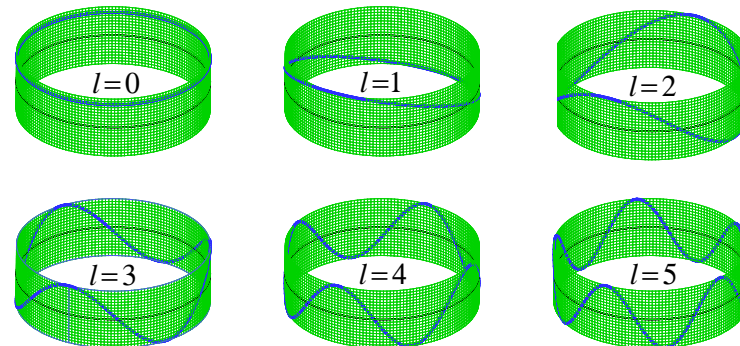
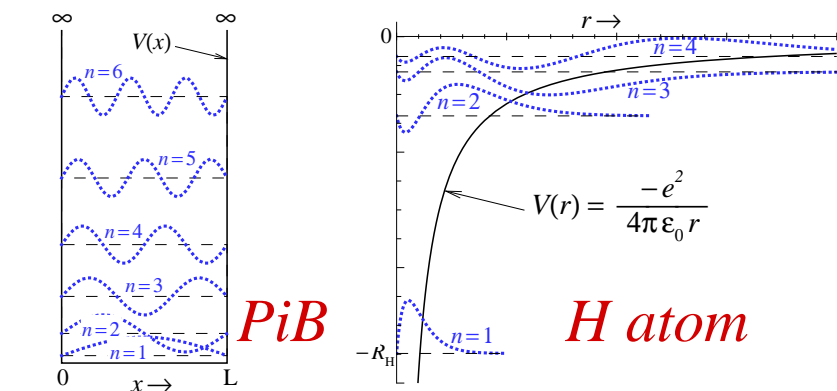


# Spectroscopy for the Masses

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Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada



# *An Introduction to Atomic, Rotational, Vibrational, Raman, Electronic, Photoelectron, and NMR Spectroscopy*

**A general science course for term 1B or 2A**

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*Why did we do this ?*

Conventional curricula normally do not teach a ‘Molecular Spectroscopy’ until year 3 or 4, and it usually presumes a full course in Quantum Mechanics as a pre-requisite.

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This effectively restricted any broad understanding of spectroscopy to the relatively small numbers of students who specialize in Phys. Chem.

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### *Why was this a bad thing ?*

- Students studying, and graduates working in, ***all*** areas of science will encounter or use *some* kind of spectroscopy in their studies or everyday work, and they really should have some understanding of the underlying physical principles.
- Our students in year-2 complained that they were seeing the same low-level “dumbed-down” (typically 2-3 lectures) introducing them to spectroscopic concepts in their intro, analytical, organic, inorganic courses, followed by a leap to a particular application, but never get a view of the overall subject.
- Year-1 courses on most areas of Sciences present much material that students have seen (though often never mastered) in high school, which makes it difficult to motivate them. We felt that presenting *new* material that combined novelty, physical insight, and broad applicability might excite them!

## 1. Light, Quantization, Atoms and Spectroscopy

### 1.1 *Light and the Electromagnetic Spectrum*

#### 1.1.1 The wave properties of light

$$c = \nu \lambda = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$$

$$\tilde{\nu} = \frac{1}{10^2 \lambda} = \frac{\nu}{10^2 c}$$

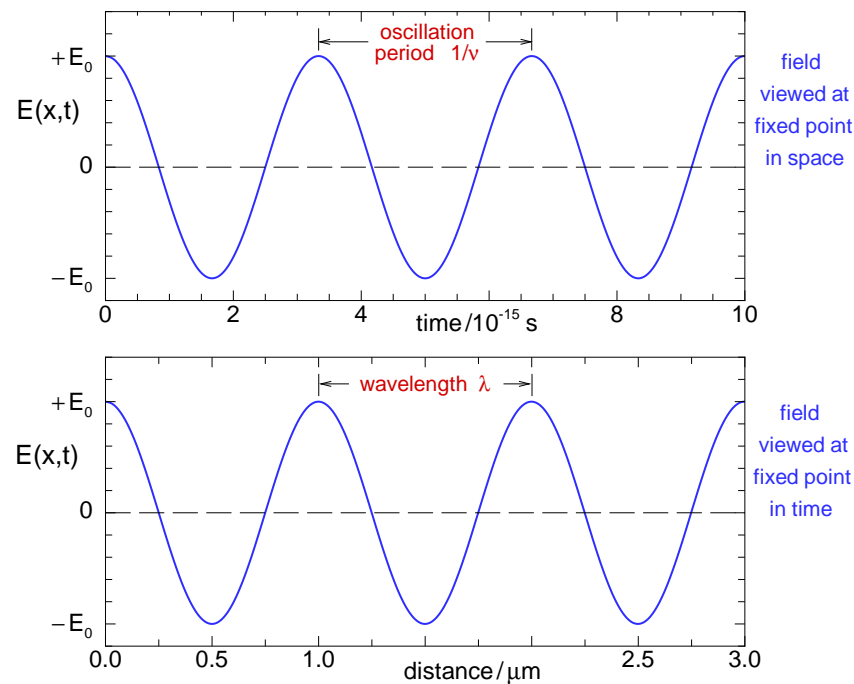


Figure 1: The electric field of light oscillates in space and in time.

$$E(x,t) = E_0 \cos \left( \frac{2\pi\nu}{c} x - 2\pi\nu t + \phi_0 \right)$$

## 1. Light, Quantization, Atoms and Spectroscopy

### 1.1 *Light and the Electromagnetic Spectrum*

#### 1.1.2 The Quantum theory of Light

- Max Planck and ‘black-body’ radiation

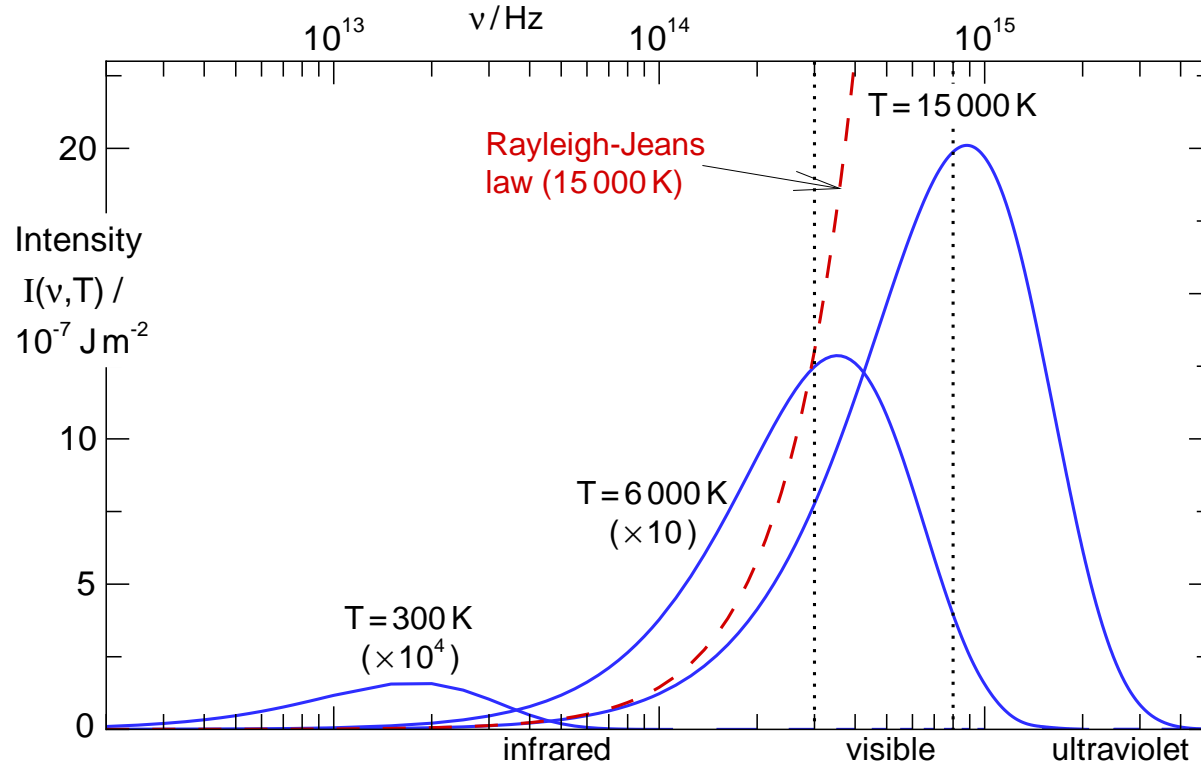


Figure 2: Black-body radiation: observed distributions and the Rayleigh-Jeans law prediction.

$$\varepsilon = \varepsilon(\nu) = h\nu = hc10^2 \tilde{\nu}$$

$$I(\nu, T) = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

## 1. Light, Quantization, Atoms and Spectroscopy

### 1.1 *Light and the Electromagnetic Spectrum*

#### 1.1.2 The Quantum theory of Light

- Albert Einstein and the photoelectric effect

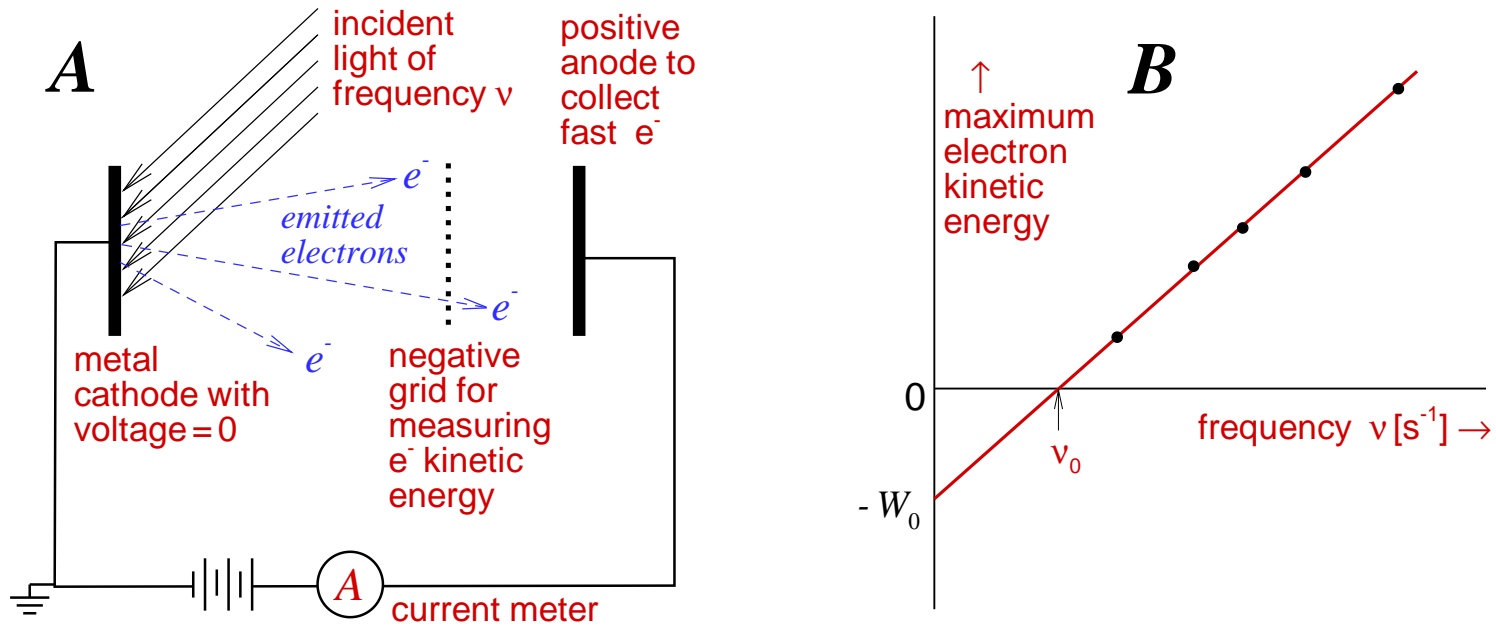


Figure 3: The photoelectric effect: **A**. The experiment; **B**. The observations.

$$\varepsilon(\nu) = h\nu$$

- Arthur H. Compton and “bouncing” photons

$$p_\lambda = h/\lambda$$

## 1. Light, Quantization, Atoms and Spectroscopy

### 1.2 *The Quantum Theory of Matter*

#### 1.2.1 The Spectrum of the Hydrogen Atom

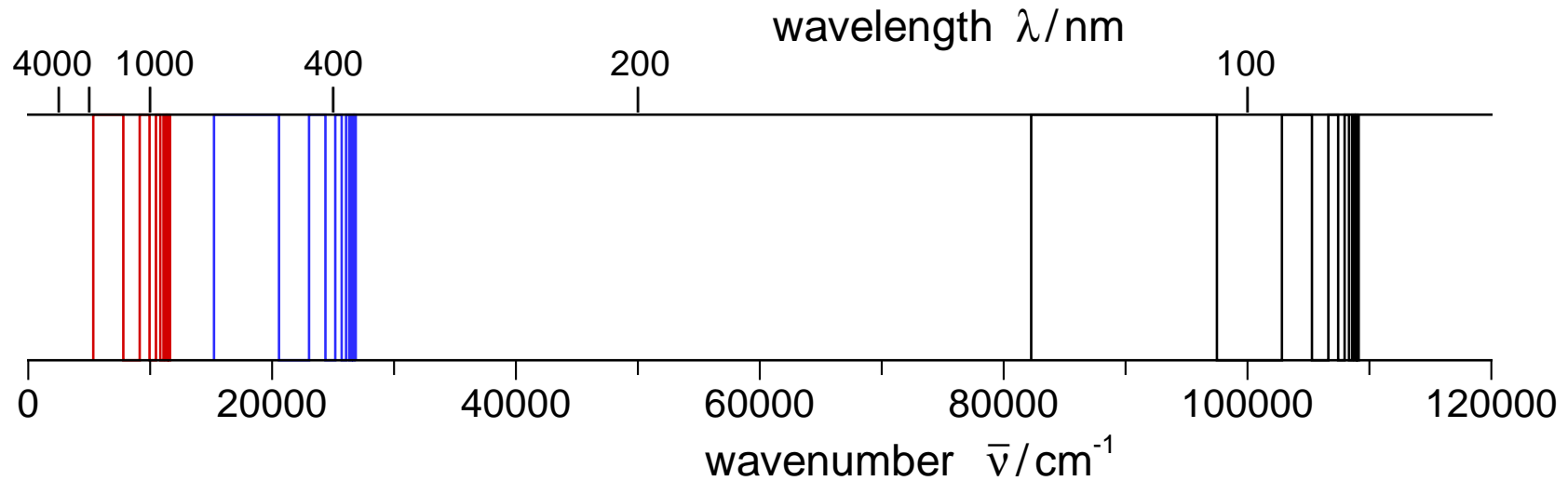


Figure 4: The hydrogen atom emission spectrum. If the emitted light is dispersed by a prism, photons of different frequency cause blackening at different locations on a photographic plate.

$$\tilde{\nu} = \mathbb{R}_H \left( \frac{1}{(2)^2} - \frac{1}{(n_1)^2} \right)$$

# 1. Light, Quantization, Atoms and Spectroscopy

## 1.2 The Quantum Theory of Matter

### 1.2.2 The Bohr Theory of the Atom

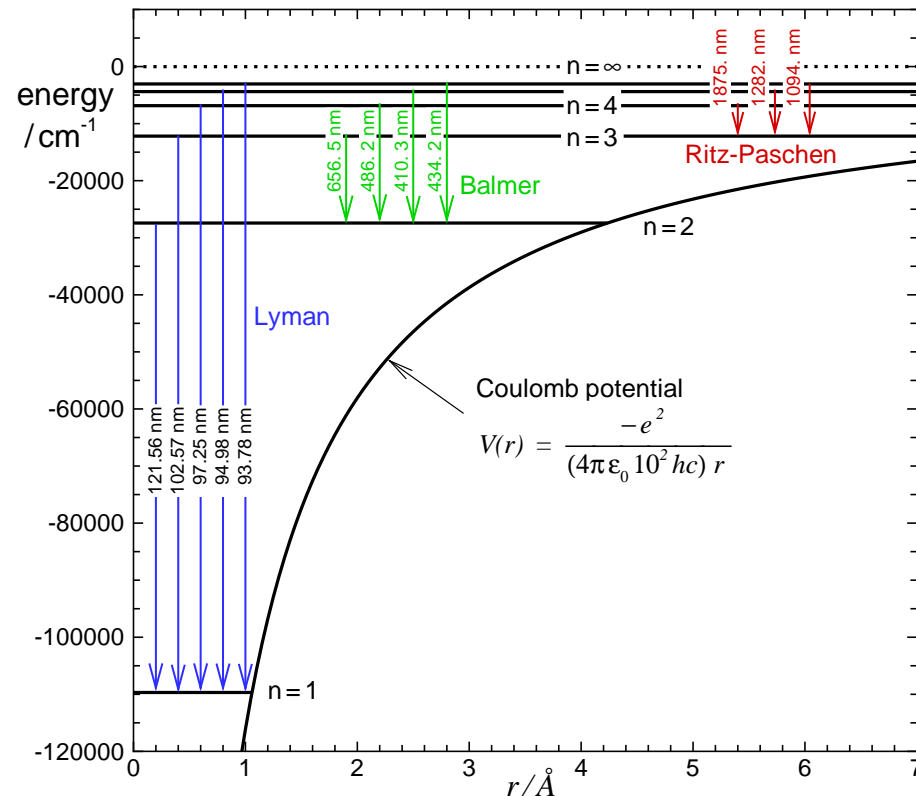


Figure 5: Hydrogen atom energy levels and transitions.

$$\Delta \tilde{E}(n_1, n_2) = \tilde{E}_{n_1} - \tilde{E}_{n_2} = \mathbb{R}_H \left[ \frac{1}{(n_2)^2} - \frac{1}{(n_1)^2} \right] = \tilde{\nu}$$

$$\tilde{E}_n^A = -\mathbb{R}_A \frac{1}{n^2} = -Z^2 \left( \frac{\mu_A}{\mu_H} \right) \mathbb{R}_H \frac{1}{n^2}$$

## 1. Light, Quantization, Atoms and Spectroscopy

### 1.3 Wave Mechanics and the Schrödinger Equation

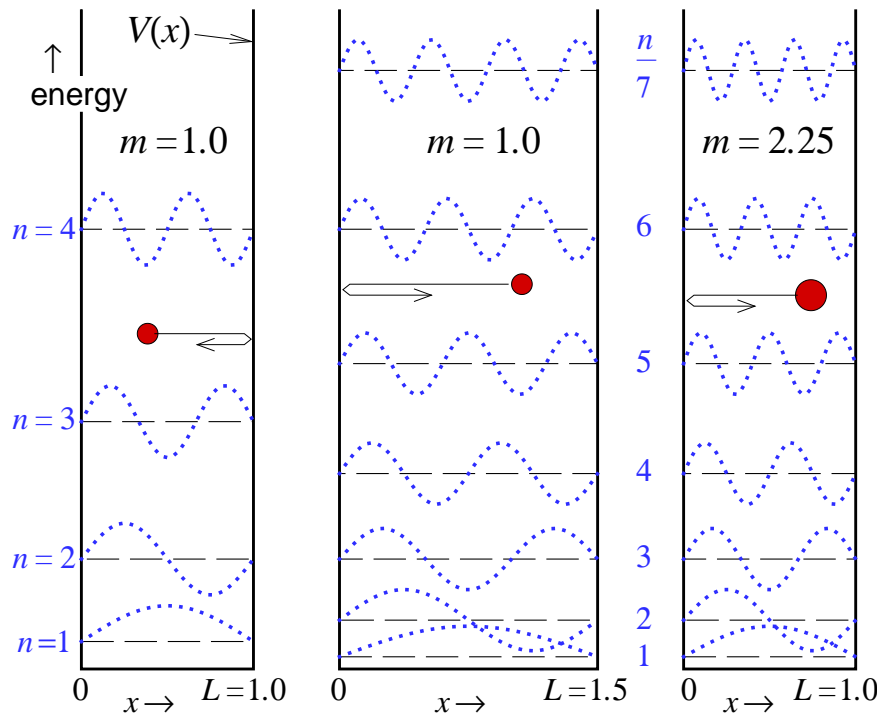
#### 1.3.1 A Particle in a One-Dimensional Box: Schrödinger says ...

$$-\frac{\hbar^2}{2m} \frac{d^2 y(x)}{dx^2} + V(x) y(x) = E y(x) .$$

Inside the box where  $V(x) = 0$ , this becomes

$$\frac{d^2 y}{dx^2} = - \left( \frac{2m E}{\hbar^2} \right) y \quad \text{or} \quad \frac{d^2 y}{dx^2} = - k^2 y \quad \text{where} \quad k^2 = + \frac{2m E}{\hbar^2}$$

with solutions  $y(x) = \sin(k x)$  and  $y(x) = \cos(k x)$



# 1. Light, Quantization, Atoms and Spectroscopy

## 1.3 Wave Mechanics and the Schrödinger Equation

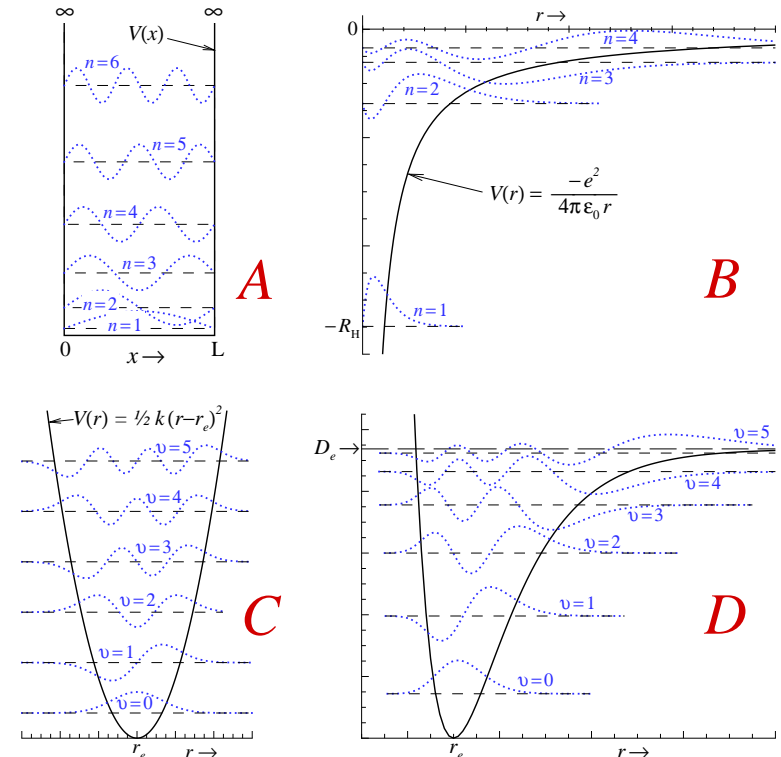
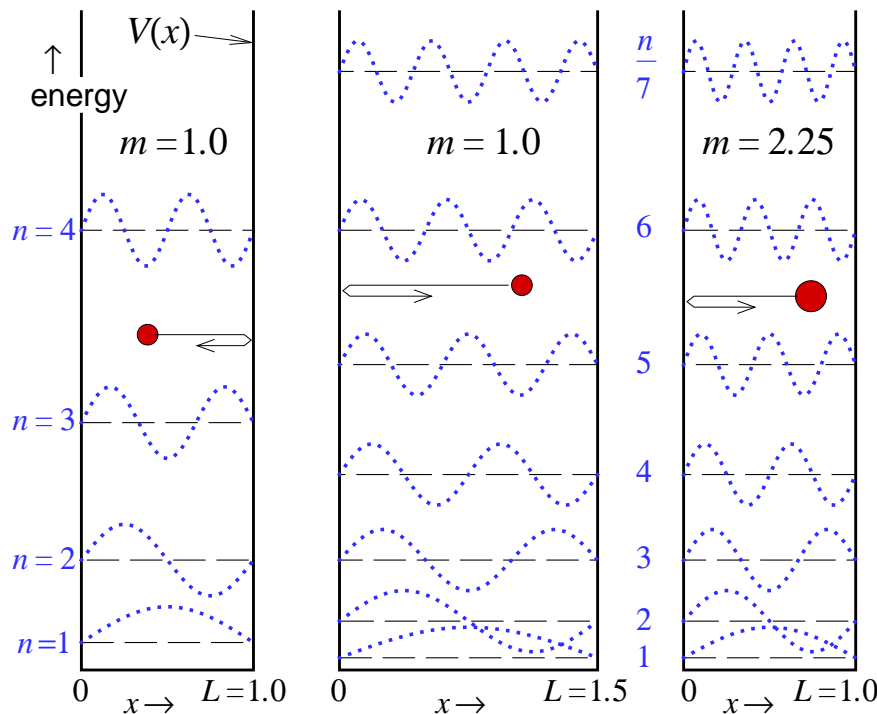
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## 1. Light, Quantization, Atoms and Spectroscopy

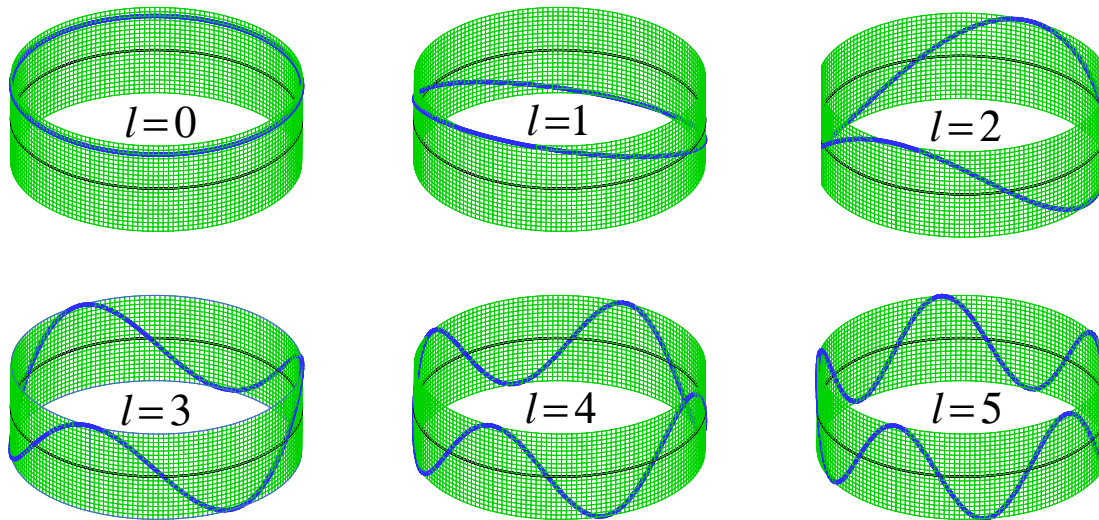
### 1.3 *Wave Mechanics and the Schrödinger Equation*

#### 1.3.2 Orbital or Rotational Motion: A Particle on a Ring

$$-\frac{\hbar^2}{2m r^2} \frac{d^2 \psi(\phi)}{d\phi^2} = E \psi(\phi)$$

or

$$\frac{d^2 \psi(\phi)}{d\phi^2} = - \left( \frac{2m r^2 E}{\hbar^2} \right) \psi(\phi) = -b^2 \psi(\phi)$$



### 1.4 *Electronic Structure of Atoms and Molecules*

#### 1.4.1 Hydrogenic Atomic Orbitals

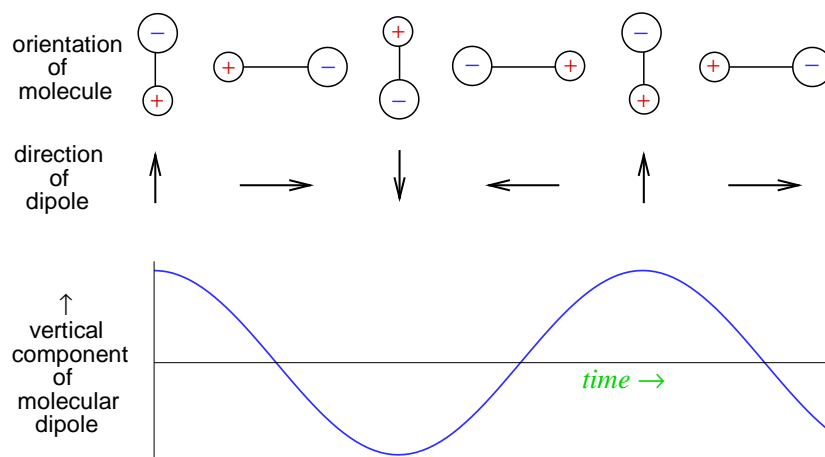
#### 1.4.2 Multi-Electron Atoms and Atomic Spectroscopy

#### 1.4.1 Molecular Energies and the Born-Oppenheimer Approximation

## 2. Rotational Spectroscopy

### 2.1 *Classical Description of Molecular Rotation*

#### 2.1.1 Why Does Light Cause Rotational Transitions?



Behaviour of the vertical component of the dipole field of a polar diatomic molecule rotating clockwise in the plane of the paper.

#### 2.1.2 Relative Motion and the Reduced Mass

$$\begin{aligned}\text{KE}_{\text{tot}} &= \frac{1}{2}m_1 \left| \vec{R}_{\text{cm}} - \frac{m_2}{m_1 + m_2} \vec{r} \right|^2 + \frac{1}{2}m_2 \left| \vec{R}_{\text{cm}} + \frac{m_1}{m_1 + m_2} \vec{r} \right|^2 \\ &= \frac{1}{2}(m_1 + m_2) \left| \vec{R}_{\text{cm}} \right|^2 + \frac{1}{2} \left( \frac{m_1 m_2}{m_1 + m_2} \right) \left| \vec{r} \right|^2 = \text{KE}_{\text{cm}} + \text{KE}_{\text{rel}}\end{aligned}$$

#### 2.1.3 Motion of a Rotating Body

$$\text{KE}_{\text{rot}} = \frac{L^2}{2\mathbb{I}} \quad \text{where} \quad \mathbb{I} = \sum_{i=1}^N m_i (d_i^\perp)^2 \longrightarrow \mu(r_e)^2$$

## 2. Rotational Spectroscopy

### 2.1 Quantum Mechanics of Molecular Rotation

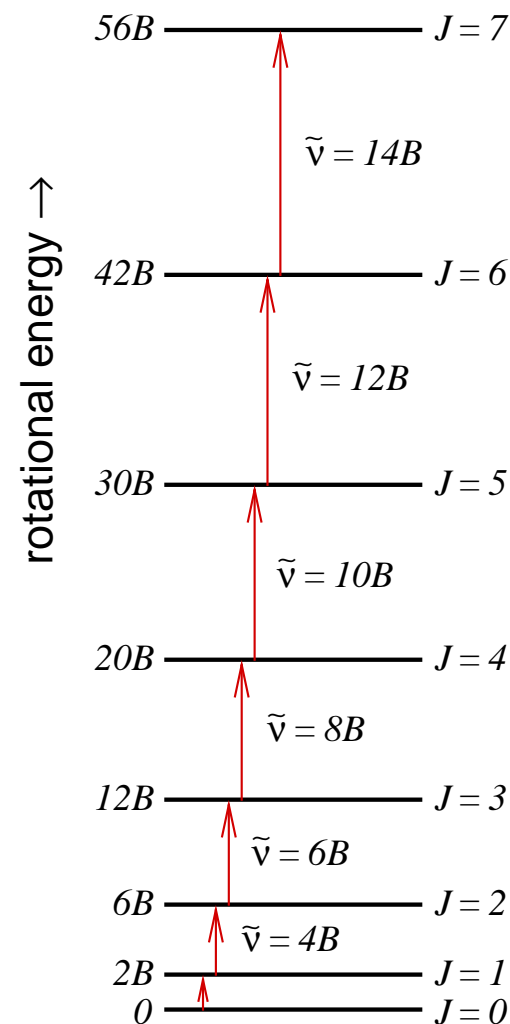
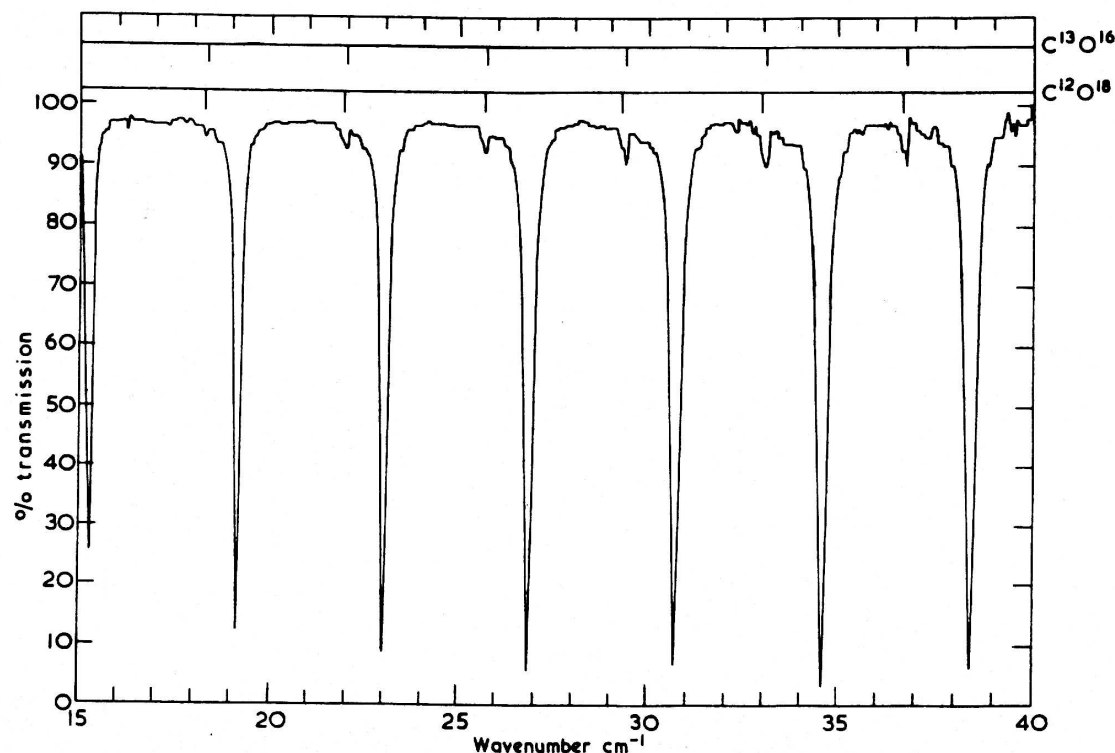
#### 2.1.1 The Basics

$$E_{\text{rot}}(J) = \frac{\hbar^2}{2I} [J(J+1)] = B [J(J+1)]$$

#### 2.1.2 Energy Levels, Selection Rules, and Transition Energies

$$\tilde{\nu}_J^{\text{rot}} = \Delta F(J) = F(J+1) - F(J) = 2B(J+1)$$

$$\Delta \tilde{\nu}_J^{\text{rot}} \equiv \tilde{\nu}_J^{\text{rot}} - \tilde{\nu}_{J-1}^{\text{rot}} = \dots = 2B$$

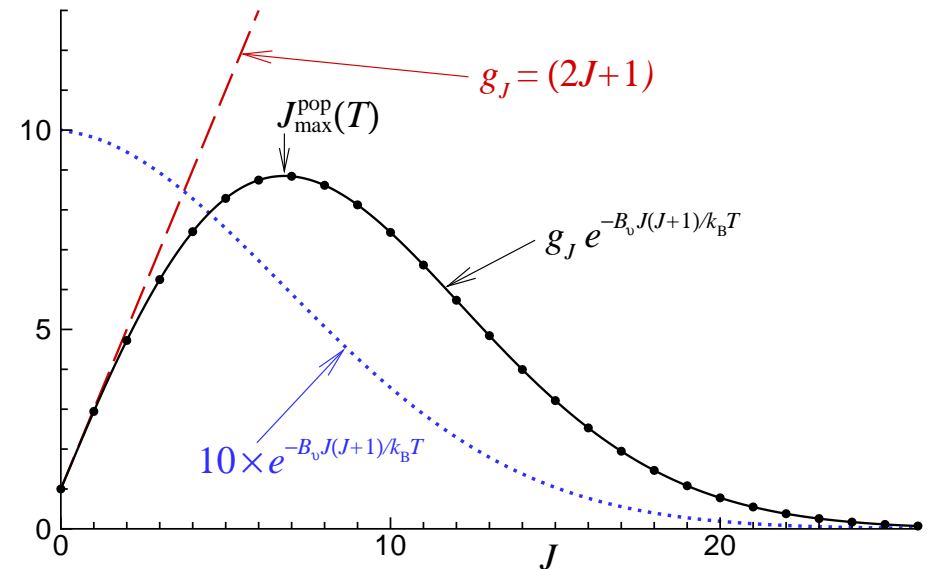
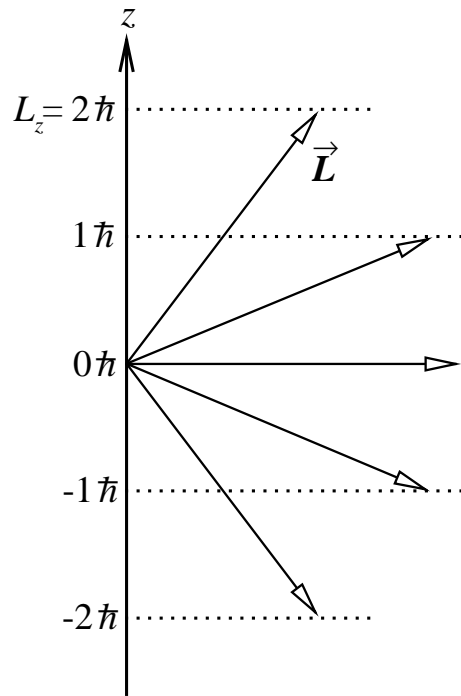


## 2. Rotational Spectroscopy

### 2.3 Complications!

- \* Complication #1: Isotopologues
- \* Complication #2: Vibrational Stretching and Vibrational Satellites
- \* Complication #3: Rotational Stretching or Centrifugal Distortion: Non-Rigid Rotors

### 2.4 Degeneracies and Intensities



$$f_J(T) = (2J + 1) e^{-F_v(J)/k_B T} / Q(T)$$

## 2. Rotational Spectroscopy

### 2.5 Rotational Spectra of Polyatomic Molecules

#### 2.5.1 Linear Molecules are (Relatively) Easy to Treat!

**Case A:** A Diatomic Molecule.

$$\mathbb{I} = \frac{m_1 m_2}{m_1 + m_2} d^2 = \mu d^2 = \mathbb{I}_d$$

**Case B:** A Symmetric Triatomic Molecule.

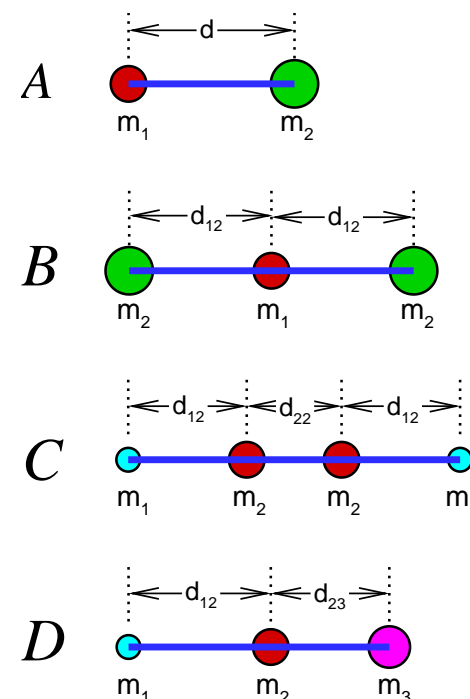
$$\mathbb{I} = m_2(-d_{12})^2 + m_1(0)^2 + m_2(d_{12})^2 = 2m_2(d_{12})^2$$

**Case C:** A Symmetric Tetra-atomic Molecule.

$$\mathbb{I} = 2m_1(d_{12} + \frac{1}{2}d_{22})^2 + 2m_2(\frac{1}{2}d_{22})^2$$

**Case D:** An Asymmetric Triatomic Molecule.

$$\mathbb{I} = m_1(d_{12})^2 + m_3(d_{23})^2 - \frac{(m_1 d_{12} - m_3 d_{23})^2}{(m_1 + m_2 + m_3)}$$

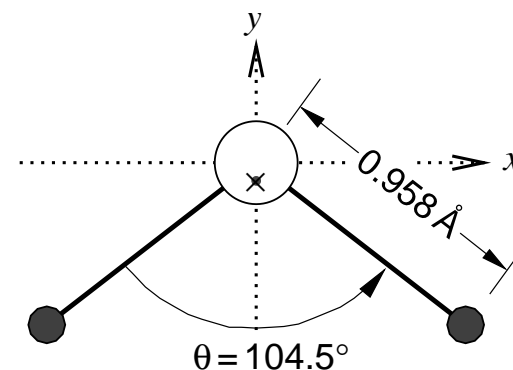


#### 2.5.2 Non-Linear Polyatomic Molecules are More Difficult ...

$$\mathbb{I}_x = \dots = 0.6158 [\text{u } \text{\AA}^2] \equiv \mathbb{I}_A$$

$$\mathbb{I}_y = \dots = 1.1566 [\text{u } \text{\AA}^2] \equiv \mathbb{I}_B$$

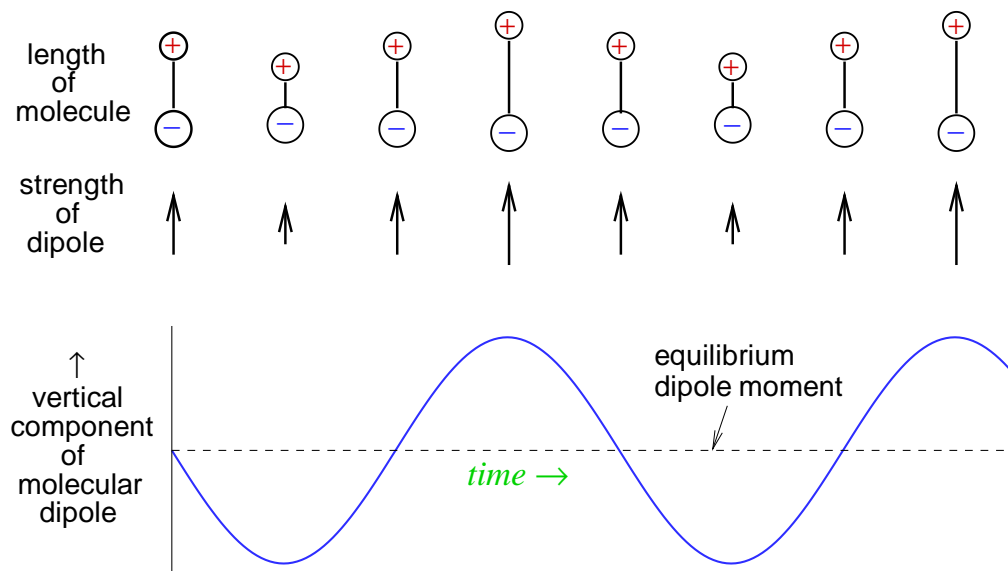
$$\mathbb{I}_z = \mathbb{I}_x + \mathbb{I}_y = 1.7724 [\text{u } \text{\AA}^2] \equiv \mathbb{I}_C$$



### 3. Vibrational Spectroscopy

#### 3.1 *Classical Description of Molecular Vibrations*

##### 3.1.1 Why Does Light Cause Vibrational Transitions?



Dipole moment of a vibrating polar diatomic molecule  
which is fixed and aligned in space.

##### 3.1.2 The Centre of Mass and Relative Motion

##### 3.1.3 The Classical Harmonic Oscillator

$$V_{\text{HO}}(r) = \frac{1}{2} k(r - r_e)^2$$

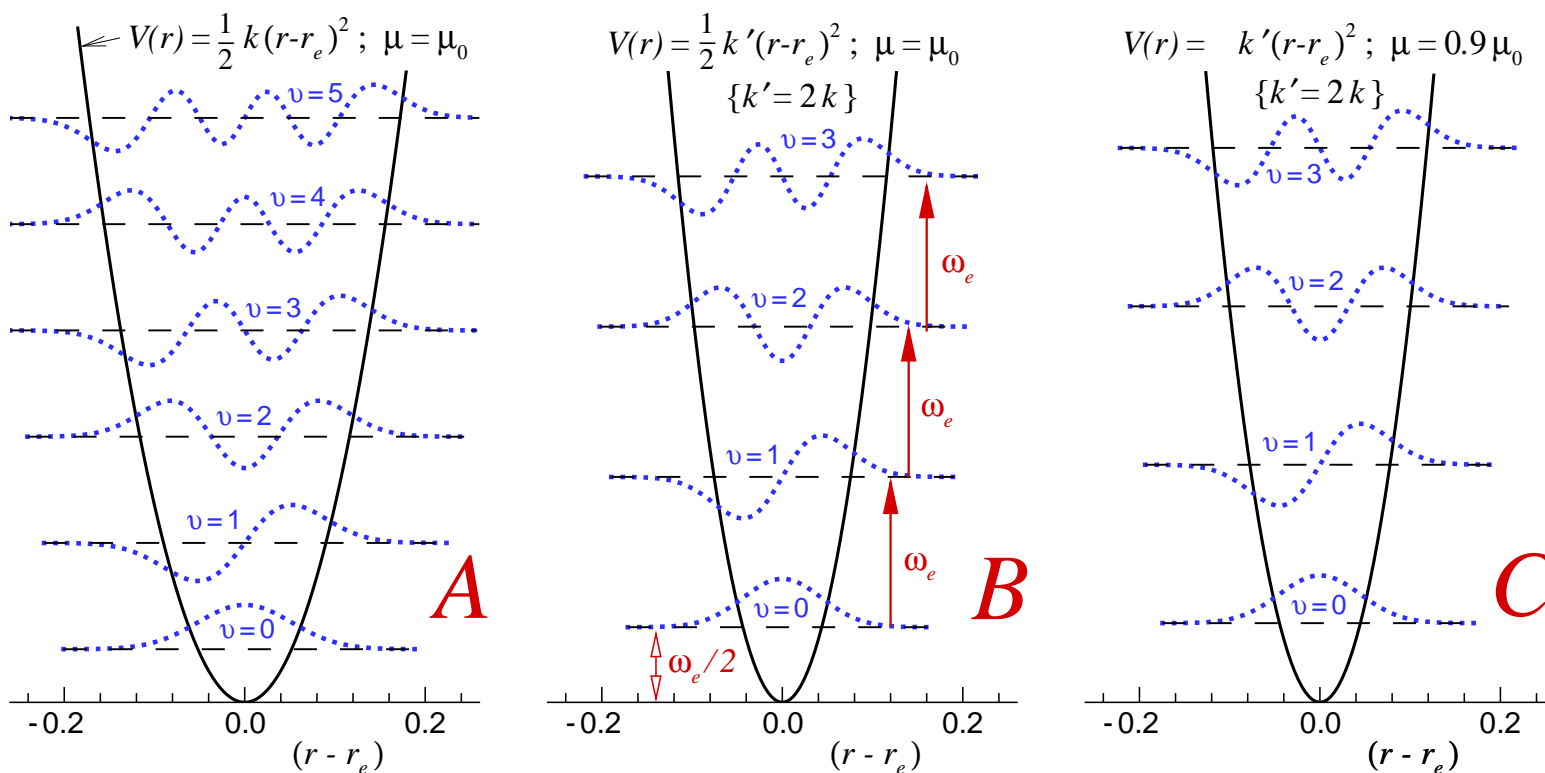
### 3. Vibrational Spectroscopy

#### 3.2 Quantum Mechanics of Molecular Vibration and the Harmonic Oscillator

$$\hat{\mathcal{H}}_{\text{vib}} \psi(r) = -\frac{\hbar^2}{2\mu} \frac{d^2 \psi(r)}{dr^2} + V(r) \psi(r) = E_{\text{vib}} \psi(r)$$

$$G^{\text{HO}}(v) \equiv E_{\text{vib}}^{\text{HO}}(v) / (10^2 hc) = \omega_e (v + 1/2) \text{ [cm}^{-1}\text{]}$$

$$\Delta G_{v+1/2}^{\text{HO}} \equiv G^{\text{HO}}(v+1) - G^{\text{HO}}(v) = \omega_e$$



### 3. Vibrational Spectroscopy

#### 3.3 Anharmonic Vibrations and the Morse Oscillator

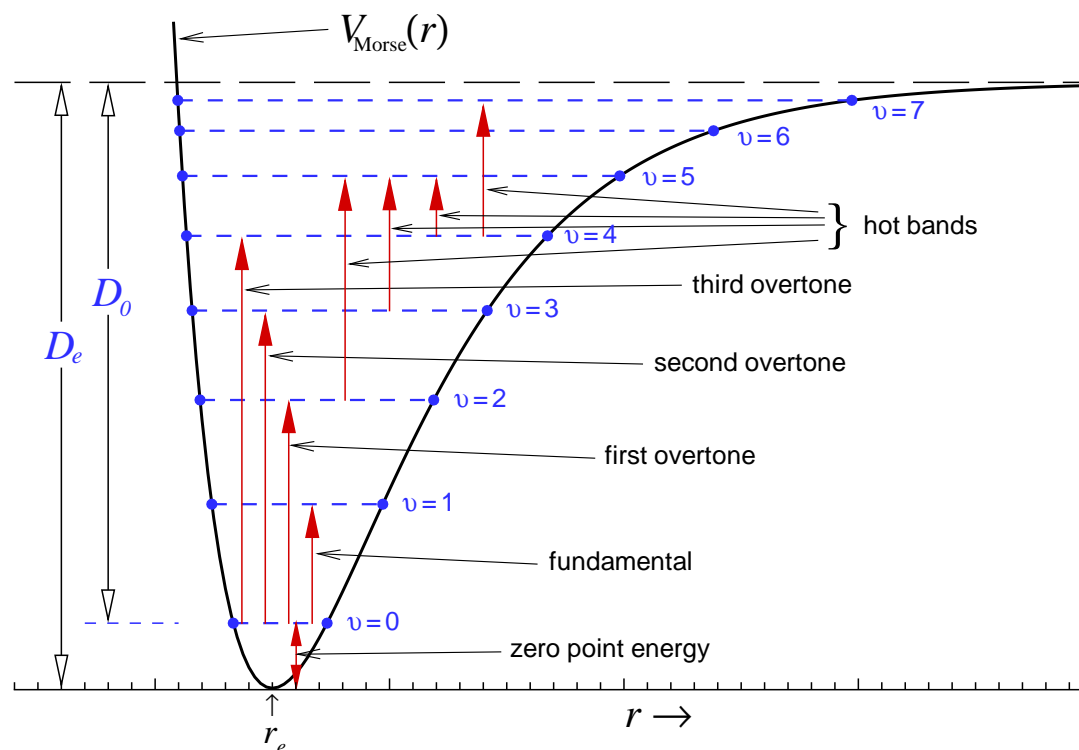
##### 3.3.1 Eigenvalues and Properties of the Morse Potential

$$V_{\text{Morse}}(r) = \mathfrak{D}_e \left[ 1 - e^{-\beta(r-r_e)} \right]^2 = \mathfrak{D}_e \left[ e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)} + 1 \right]$$

$$G^{\text{Morse}}(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$$

$$\omega_e = \hbar \sqrt{\frac{2\mathfrak{D}_e\beta^2}{\mu}} \frac{1}{10^2 hc} \quad \text{and} \quad \omega_e x_e = \beta^2 \frac{\hbar^2}{2\mu} \frac{1}{10^2 hc}$$

$$\mathfrak{D}_e^{\text{Morse}} = (\omega_e)^2 / 4\omega_e x_e$$



### 3. Vibrational Spectroscopy

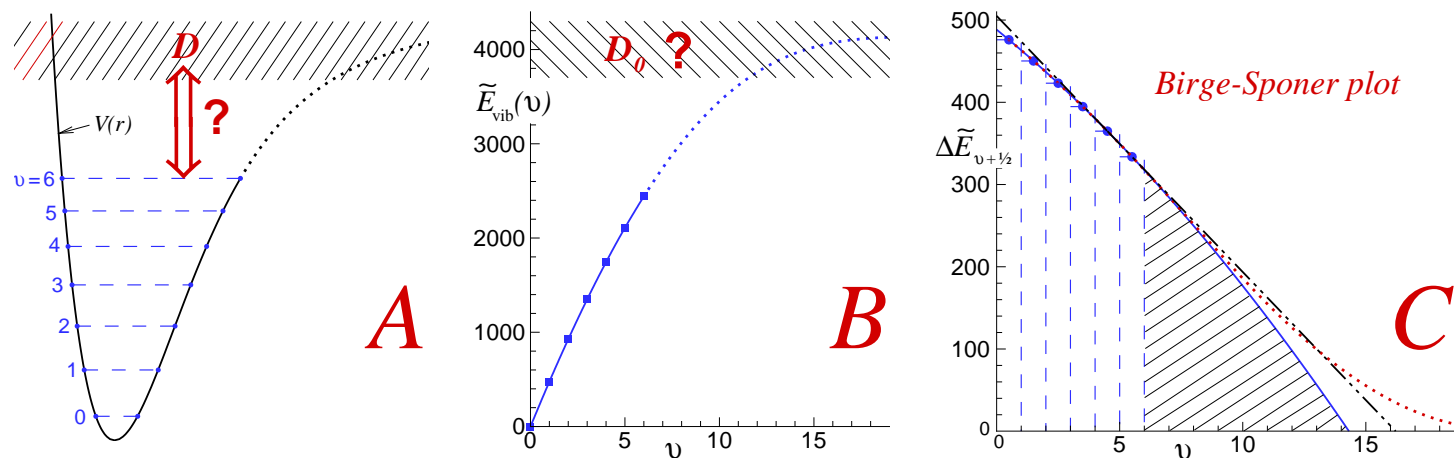
#### 3.3 Anharmonic Vibrations and the Morse Oscillator

##### 3.3.2 Overtones and Hot Bands

##### 3.3.3 Higher-Order Anharmonicity and the Dunham Expansion i

$$\begin{aligned} G(v) &= \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \omega_e z_e(v + 1/2)^4 + \dots \\ &= Y_{1,0}(v + 1/2) + Y_{2,0}(v + 1/2)^2 + Y_{3,0}(v + 1/2)^3 + Y_{4,0}(v + 1/2)^4 + \dots \end{aligned}$$

#### 3.4 Bond Dissociation Energies and Birge-Sponer Plots

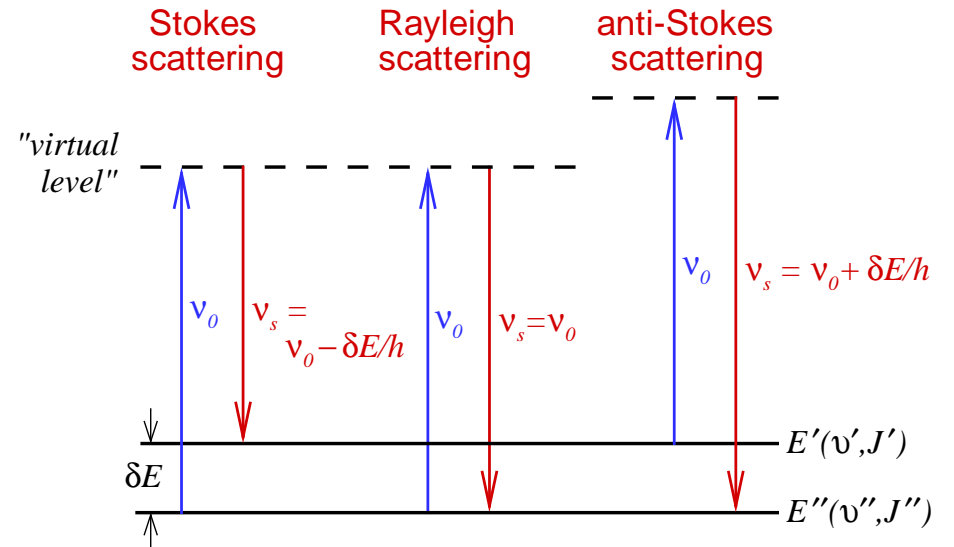
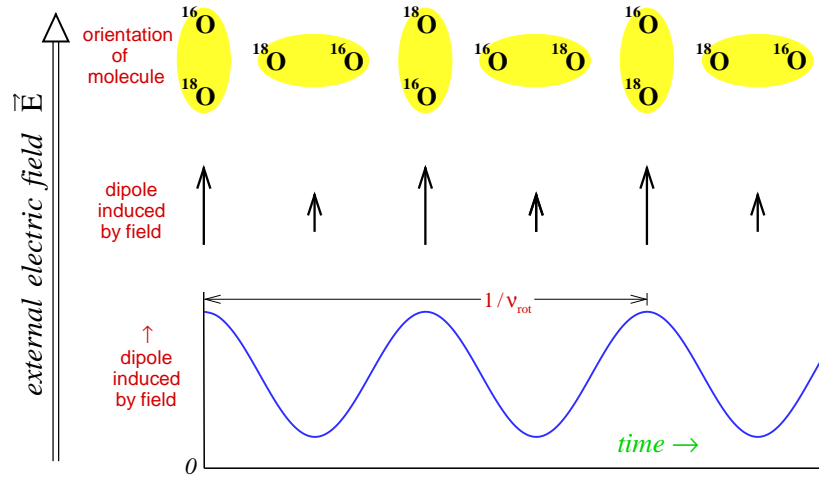


#### 3.5 Vibrations in Polyatomic Molecules

#### 3.6 Rotational Structure in Vibrational Spectra of Diatomics

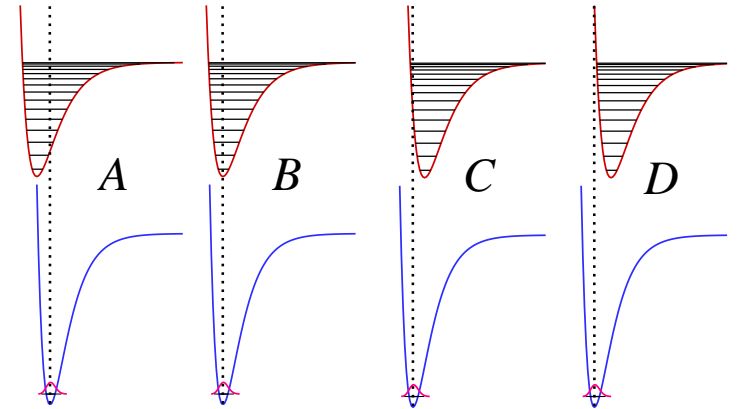
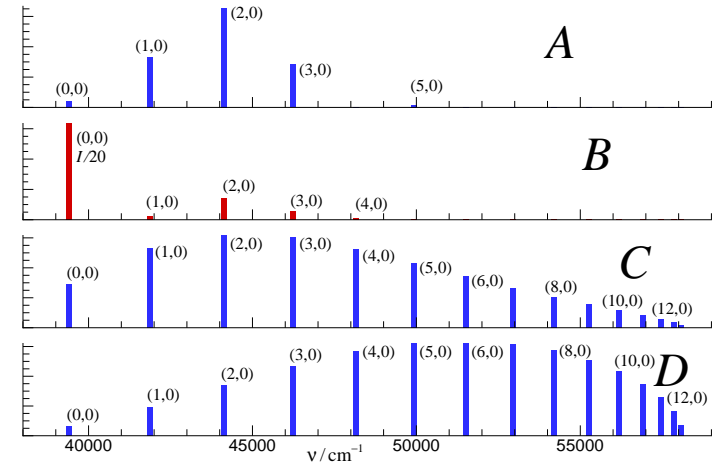
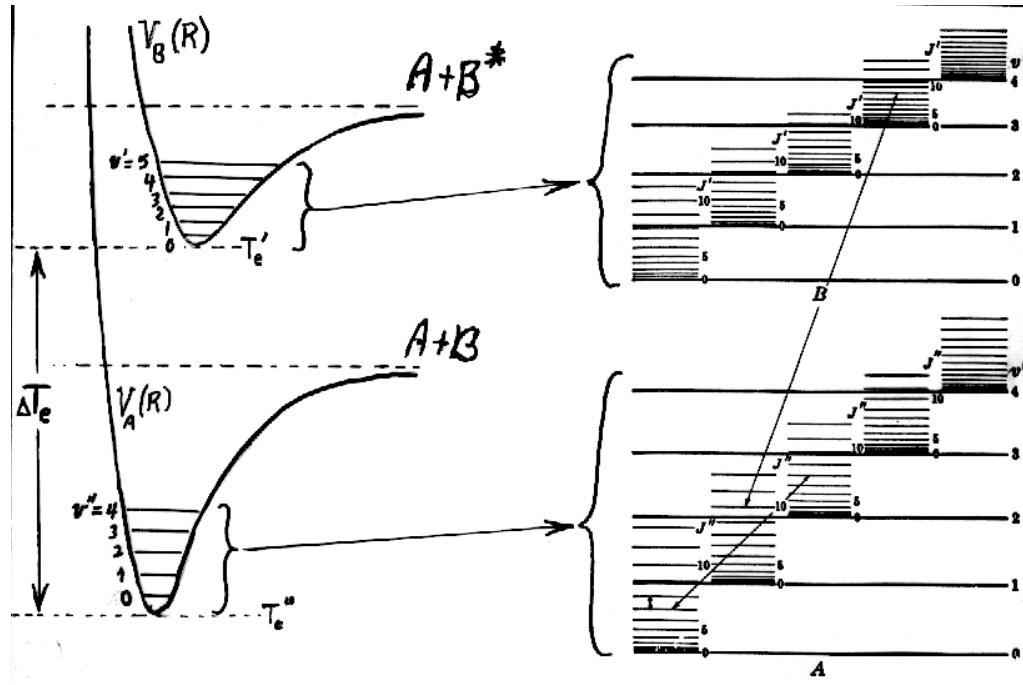
$$\begin{aligned} \tilde{\nu}_P(J'') &= \tilde{E}(v', J') - \tilde{E}(v'', J'') = \tilde{E}(v', J'' - 1) - \tilde{E}(v'', J'') \\ &= \{G(v') + F_{v'}(J'' - 1)\} - \{G(v'') + F_{v''}(J'')\} = \{\text{ignoring centr. distortion}\} \\ &= \tilde{\nu}_0(v', v'') - [B_{v''} + B_{v'}](J'') - [B_{v''} - B_{v'}](J'')^2 \approx \tilde{\nu}_0(v', v'') - \dots \end{aligned}$$

## 4. Raman Spectroscopy



$$\begin{aligned}
 \tilde{\nu}_O^{\text{Stokes}}(J) &= \tilde{\nu}_0 - \left\{ \tilde{E}(v', J-2) - \tilde{E}(v'', J) \right\} \\
 &= \tilde{\nu}_0 - \left\{ [G(v') - G(v'')] + [F_{v'}(J-2) - F_{v''}(J)] \right\} = \dots \\
 &= \tilde{\nu}_0 - \left\{ [G(v') - G(v'')] - (B_{v''} + B_{v'})(2J-1) - (B_{v''} - B_{v'})(J^2 - J + 1) \right\} \\
 \tilde{\nu}_Q^{\text{Stokes}}(J) &= \tilde{\nu}_0 - \left\{ \tilde{E}(v', J) - \tilde{E}(v'', J) \right\} \\
 &= \tilde{\nu}_0 - \left\{ [G(v') - G(v'')] + [F_{v'}(J) - F_{v''}(J)] \right\} \\
 &= \tilde{\nu}_0 - \left\{ [G(v') - G(v'')] - [B_{v''} - B_{v'}]J(J+1) \right\} \\
 \tilde{\nu}_S^{\text{Stokes}}(J) &= \tilde{\nu}_0 - \left\{ \tilde{E}(v', J+2) - \tilde{E}(v'', J) \right\} \\
 &= \tilde{\nu}_0 - \left\{ [G(v') - G(v'')] + [F_{v'}(J+2) - F_{v''}(J)] \right\} = \dots \\
 &= \tilde{\nu}_0 - \left\{ [G(v') - G(v'')] + (B_{v''} + B_{v'})(2J+3) - (B_{v''} - B_{v'})(J^2 + 3J + 3) \right\}
 \end{aligned}$$

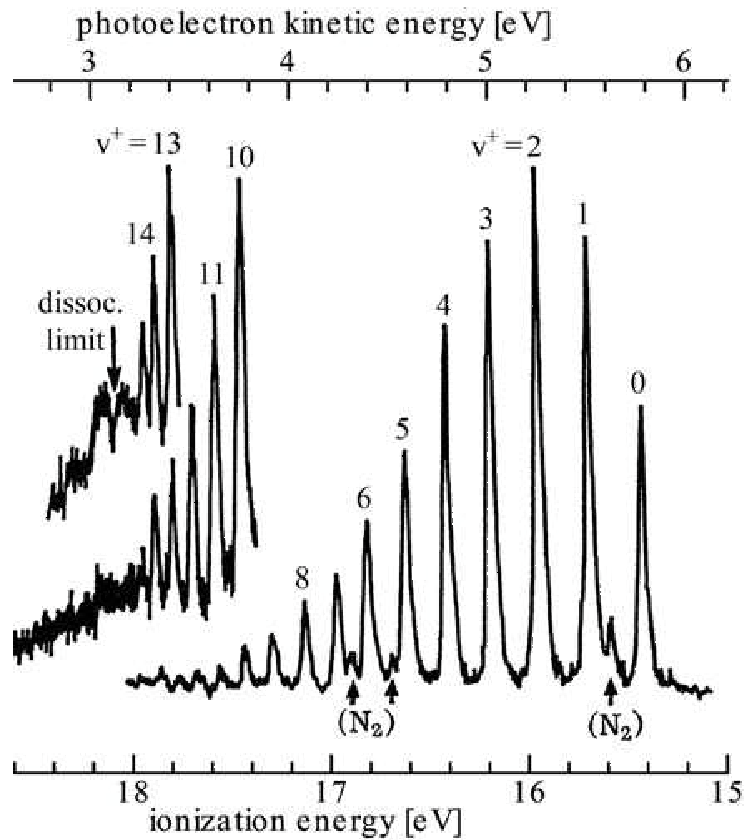
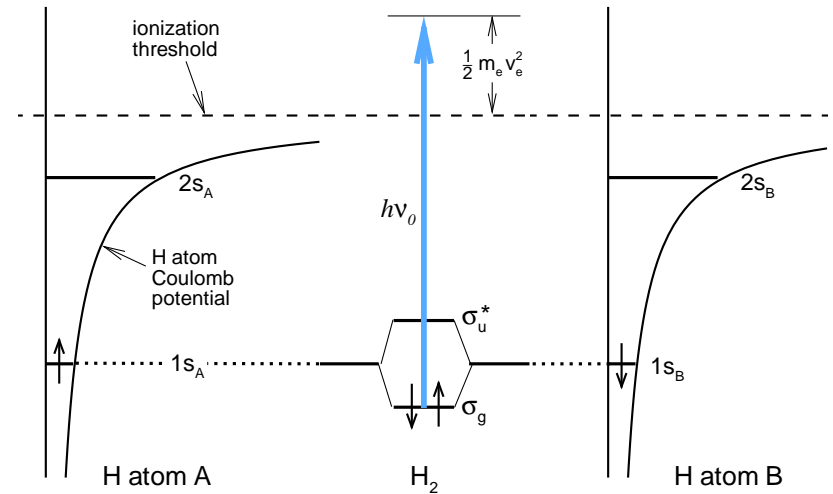
## 5. Electronic Spectroscopy



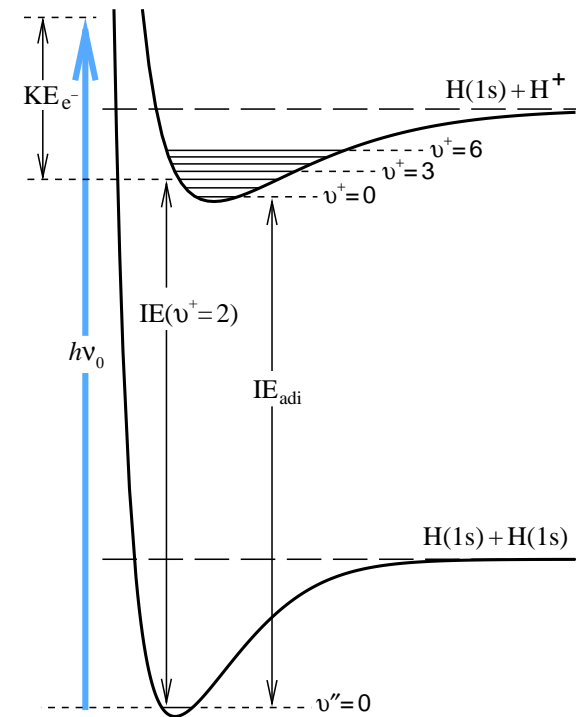
$$\begin{aligned}
 \tilde{\nu}_P(J'') &= \tilde{E}'(v', J') - \tilde{E}''(v'', J'') = \tilde{E}(v', J'' - 1) - \tilde{E}''(v'', J'') \\
 &= \tilde{\nu}_0(v', v'') - [B''_{v''} + B'_{v'}](J'') - [B''_{v''} - B'_{v'}](J'')^2 \\
 \tilde{\nu}_R(J'') &= \tilde{E}'(v', J') - \tilde{E}''(v'', J'') = \tilde{E}(v', J'' + 1) - \tilde{E}''(v'', J'') \\
 &= \tilde{\nu}_0(v', v'') + [B''_{v''} + B'_{v'}](J'' + 1) - [B''_{v''} - B'_{v'}](J'' + 1)^2 \\
 \tilde{\nu}_Q(J'') &= \tilde{E}'(v', J') - \tilde{E}''(v'', J'') = \tilde{E}(v', J'') - \tilde{E}''(v'', J'') \\
 &= \tilde{\nu}_0(v', v'') - [B''_{v''} - B'_{v'}]J''(J'' + 1)
 \end{aligned}$$

## 6. Photoelectron Spectroscopy

$$IE = h\nu_0 - KE_{e^-} = h\nu_0 - \frac{1}{2} m_e (v_e)^2$$



$$h\nu_0 = KE_{e^-} + IE_{adi} + [G^+(v^+) - G^+(0)]$$



## 7. NMR Spectroscopy

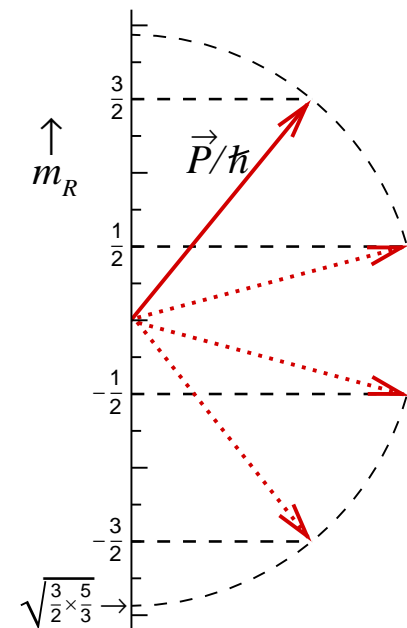
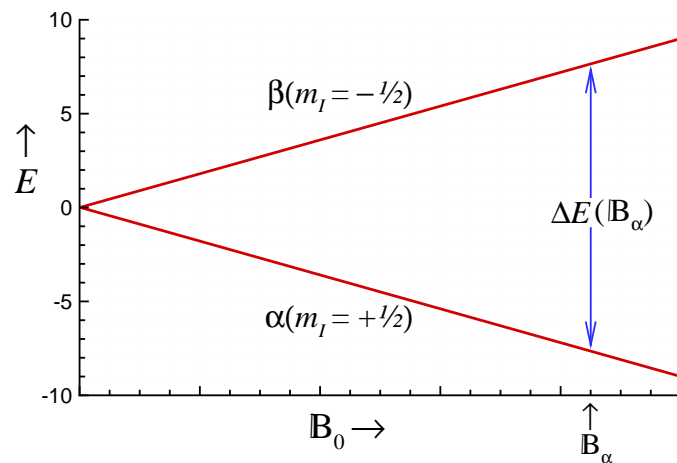
### 7.1 Basics of NMR Spectroscopy

$$|\vec{P}| = \hbar \sqrt{R(R+1)}$$

$$m_R = -R, -R+1, -R+2, R+3, \dots, R-1, R$$

$$\mu = \gamma |\vec{I}| = \gamma \hbar \sqrt{I(I+1)}$$

$$E = E(m_I) = -\mu_z B_0 = -(\gamma I_z) B_0 = -\gamma m_I \hbar B_0$$

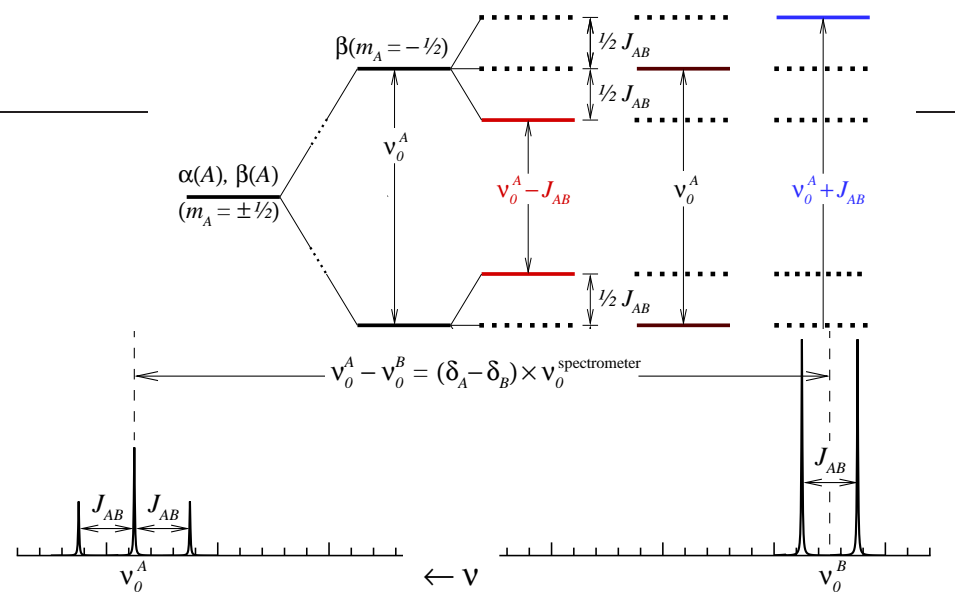
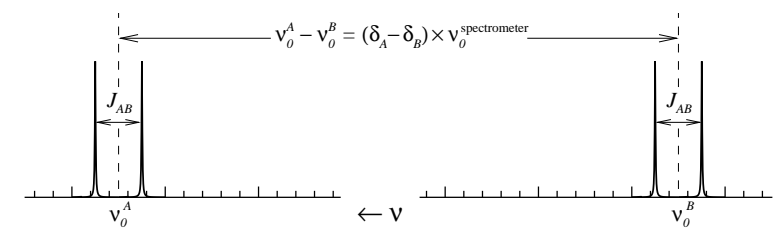
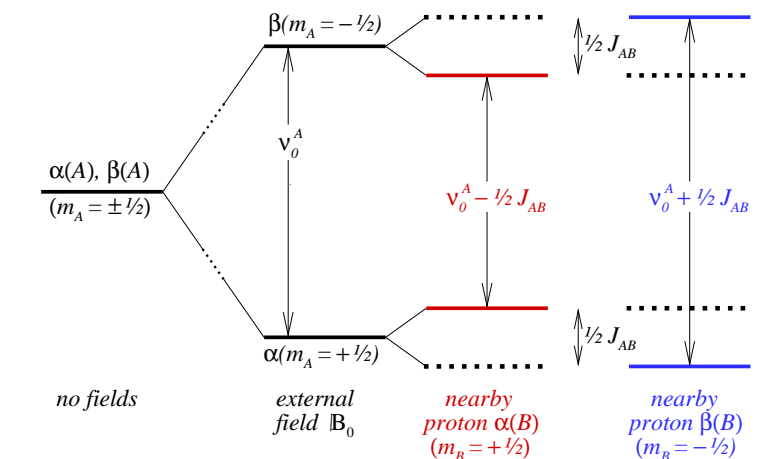


### 7.2 Chemical Shifts

$$\delta_A(\text{in molecule}) = \left( \frac{\nu_0^A(\text{in molecule}) - \nu_0^A(\text{in reference species})}{\nu_0^A(\text{in reference species})} \right) \times 10^6 \text{ [ppm]}$$

## 7. NMR Spectroscopy

### 7.2 Spin-Spin Coupling



# What do we expect them to know ?

Chem 209 Data Sheet: Exam Dec. 18, 2010

- all formulae given on a data sheet
- be able to recognize and understand the symbols in those equations
- be able to recognize, understand, and use those equations

## Formulae

$$c = \lambda \nu$$

$$\tilde{\nu} = \frac{1}{10^2 \lambda} = \frac{\nu}{10^2 c}$$

$$\epsilon(\nu) = h \nu = h c / \lambda$$

$$\text{KE}_{\text{max}}(e^-) = \frac{1}{2} m_e (v_e^{\text{max}})^2 = h \nu - W_0$$

$$p_\lambda = h / \lambda$$

$$\tilde{E}_n = -Z^2 \left( \frac{\mu_{\text{A}}}{\mu_{\text{H}}} \right) \frac{\mathbb{R}_{\text{H}}}{n^2}$$

$$\tilde{\nu} = \mathbb{R}_{\text{H}} \left( \frac{1}{(n_2)^2} - \frac{1}{(n_1)^2} \right)$$

$$\lambda_p = h / m v = h / p$$

$$\tilde{E}_n = \left( \frac{\pi^2 \mathbb{C}_{\text{u}}}{m [\text{u}] (L [\text{\AA}])^2} \right) n^2$$

$$\tilde{E}_\ell = \left( \frac{\mathbb{C}_{\text{u}}}{m [\text{u}] (r [\text{\AA}])^2} \right) \ell^2$$

$$\vec{R}_{\text{cm}} = \left( \sum_i m_i \vec{r}_i \right) / \left( \sum_i m_i \right)$$

$$\mathbb{I} = \sum_i m_i (d_i^\perp)^2$$

$$\mathbb{I}_{\text{d}} = \mu (\bar{r})^2 = \left( \frac{m_1 m_2}{m_1 + m_2} \right) (\bar{r})^2$$

$$E_{\text{rot}} = \frac{1}{2} \mathbb{I} \omega^2 = L^2 / 2 \mathbb{I}$$

$$L = \hbar \sqrt{J(J+1)}$$

$$F(J) = B [J(J+1)] \quad \text{or} \\ = B [J(J+1)] - D [J(J+1)]^2$$

$$\tilde{\nu}_J = \Delta F(J) = F(J+1) - F(J) \\ = 2 B (J+1) \quad \text{or} \\ = 2 B (J+1) - 4 D (J+1)^3$$

$$B [\text{cm}^{-1}] = \frac{\hbar^2}{2 \mathbb{I}} \frac{10^{20}}{10^2 \hbar c} = \frac{\mathbb{C}_{\text{u}}}{\mathbb{I} [\text{u} \cdot \text{\AA}^2]}$$

$$B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2$$

$$\bar{r}_v(J) = \bar{r}_v(J=0) \left/ \left[ 1 - 2[J(J+1)] \frac{D_v}{B_v} \right] \right|^{1/2}$$

$$f_{\text{J}}(T) \propto (2J+1) e^{-F_{\text{v}}(J)/k_{\text{B}} T}$$

$$J_{\text{max}}^{\text{eq}}(T) = \sqrt{\frac{k_{\text{B}} T}{2 B}} - \frac{1}{2}$$

$$V_{\text{HO}}(r) = \frac{1}{2} k (r - r_e)^2$$

$$G^{\text{HO}}(v) = \omega_e (v + \frac{1}{2})$$

$$\omega_e^{\text{HO}} = \sqrt{2 \mathbb{C}_{\text{u}} \tilde{k} [\text{cm}^{-1} \text{\AA}^{-2}] / \mu [\text{u}]}$$

$$V_{\text{Morse}}(r) = \mathfrak{D}_{\text{e}} \left[ 1 - e^{-\beta(r-r_e)} \right]^2 \\ = \mathfrak{D}_{\text{e}} \left[ e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)} + 1 \right]$$

$$G^{\text{Morse}}(v) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2$$

$$\Delta G_{v+1/2}^{\text{Morse}} = G^{\text{Morse}}(v+1) - G^{\text{Morse}}(v) = \omega_e - 2\omega_e x_e (v+1)$$

$$\omega_e^{\text{Morse}} = \sqrt{4 \mathbb{C}_{\text{u}} \mathfrak{D}_{\text{e}} [\text{cm}^{-1}] (\beta [\text{\AA}^{-1}])^2} / \mu [\text{u}]$$

$$\omega_e x_e^{\text{Morse}} = \mathbb{C}_{\text{u}} (\beta [\text{\AA}^{-1}])^2 / \mu [\text{u}]$$

$$\mathfrak{D}_{\text{e}}^{\text{Morse}} = (\omega_e)^2 / (4 \omega_e x_e)$$

$$\tilde{\nu}_R(J) = \tilde{\nu}_0(v', v'') + [B_{v''} + B_{v'}](J+1) - [B_{v''} - B_{v'}](J+1)^2$$

$$\tilde{\nu}_P(J) = \tilde{\nu}_0(v', v'') - [B_{v''} + B_{v'}] J - [B_{v''} - B_{v'}] J^2$$

$$\tilde{\nu}_Q(J) = \tilde{\nu}_0(v', v'') - [B_{v''} - B_{v'}] J(J+1)$$

$$\tilde{\nu}_0(v', v'') = [T_e' + G'(v')] - [T_e'' + G''(v'')]$$

$$\tilde{\nu}^{\text{Stokes}} = \tilde{\nu}_0 - \Delta \tilde{E}_{\text{int}} = \tilde{\nu}_0 - [\tilde{E}(v', J') - \tilde{E}(v'', J'')]$$

$$\tilde{\nu}^{\text{anti-S}} = \tilde{\nu}_0 + \Delta \tilde{E}_{\text{int}} = \tilde{\nu}_0 + [\tilde{E}(v', J') - \tilde{E}(v'', J'')]$$

$$\Delta \tilde{E}_{\text{int}}^O(J) = [G(v') - G(v'')] - (B_{v''} + B_{v'})(2J - 1) \\ - (B_{v''} - B_{v'})(J^2 - J + 1)$$

$$\Delta \tilde{E}_{\text{int}}^Q(J) = [G(v') - G(v'')] - (B_{v''} - B_{v'})J(J+1)$$

$$\Delta \tilde{E}_{\text{int}}^S(J) = [G(v') - G(v'')] + (B_{v''} + B_{v'})(2J + 3) \\ - (B_{v''} - B_{v'})(J^2 + 3J + 3)$$

$$h \nu = \text{KE}_{e^-} + \text{IE}_{\text{adiabatic}} + [G^+(v^+) - G^+(0)] \\ = \text{KE}_{e^-} + \{[T_e^+ + G^+(v^+)] - [T_e'' + G''(v'')]\}$$

$$E(m_I) = -\mu_z \mathbb{B} = -\gamma m_I \hbar \mathbb{B} [J]$$

$$\Delta E = \gamma_{\text{A}} \hbar \mathbb{B} = h \nu_0 [J]$$

$$\nu_0 = \gamma_{\text{A}} \mathbb{B} / 2 \pi [\text{s}^{-1}]$$

$$\nu_0^{\text{A}}(\text{molecule}) = \frac{\gamma_{\text{A}} \mathbb{B}_{\text{eff}}}{2 \pi} = \frac{\gamma_{\text{A}} \mathbb{B}_0}{2 \pi} (1 - \sigma_{\text{A}})$$

$$\delta_{\text{A}} [\text{ppm}] = \frac{\nu_0^{\text{A}}(\text{sample}) - \nu_0^{\text{A}}(\text{reference})}{\nu_0^{\text{A}}(\text{reference})} \times 10^6$$

For Physical Constants, conversion factors,  
and properties of nuclei ...  
see over