Molecular Spectroscopy of Small Free Molecules

- "Small" usually means 2-3 atoms
  - Can mean more if there is a lot of symmetry.
- "Free" means no other atoms or molecules close enough to perturb the intramolecular potential.
- Concepts developed can be extended to larger molecules.

Classification of Spectroscopy by Molecular Motions

- We need to be able to describe how molecules move.
- A molecule of N atoms have $3N$ degrees of freedom
  - Translational (three degrees of freedom)
  - Rotational (three degrees of freedom if nonlinear; two degrees of freedom if linear)
  - Vibrational (all remaining degrees of freedom)

Principal Moments of Inertia

- First need the centre of mass.
  - Define coordinates of the centre of mass as (X, Y, Z) such that:

$$\sum_{i=1}^{N} m_i(x_i - X) = 0$$

$$\sum_{i=1}^{N} m_i(y_i - Y) = 0$$

$$\sum_{i=1}^{N} m_i(z_i - Z) = 0$$

  - Then we can treat the translational motion of the molecule as a whole as the motion of a mass $M = \sum_{i=1}^{N} m_i$ located at (X, Y, Z).
- This leaves $3N - 3$ coordinates.

Rotational Motion

- Define a coordinate system $(\overline{x}, \overline{y}, \overline{z})$ through the center of mass and choose the orientation of an axis such that:

$$\sum_{i=1}^{N} m_i \overline{x}_i \overline{y}_i = 0$$

$$\sum_{i=1}^{N} m_i (\overline{x}_i^2 + \overline{y}_i^2) \neq 0$$

  - This is the principal inertial axis system.
  - Usually use (a, b, c) instead of $(\overline{x}, \overline{y}, \overline{z})$
- (a, b, c) is situated in space relative to an external frame of reference with its orientation described by three angles.
- This gives us three principal moments of inertia.

$$I_a = \sum_{i=1}^{N} m_i (b_i^2 + c_i^2)$$

$$I_b = \sum_{i=1}^{N} m_i (a_i^2 + c_i^2)$$

$$I_c = \sum_{i=1}^{N} m_i (a_i^2 + b_i^2)$$

Linear and Nonlinear Molecules

- For a nonlinear molecule, all three of these are nonzero.
  - Therefore $3N - 6$ degrees of freedom still to be accounted for.
- For a linear molecule, only two of these are nonzero.
  - Therefore $3N - 5$ degrees of freedom still to be accounted for.
  - I_a is chosen such that $I_a = 0$. Therefore $b_i = c_i = 0$ and $I_b = I_c$
- The remaining degrees of freedom are internal vibrational degrees of freedom.

The above describes the motion of atoms in terms of classical mechanics.

- Quantum mechanics is used to describe the electronic degrees of freedom and the spin degrees of freedom.
- In spectroscopy we are concerned with the spacing of energy levels.

How are the different types of energy levels spaced?

Spacing of Electronic Energy Levels

- From a quantum mechanical perspective, it is useful to consider electrons belonging to a molecule as particles in a box, where the size of the box is connected to the size of the molecule.
  - This quantum mechanical treatment (see Chpt 12) gives the following formula:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$

  - Thus the spacing of two successive energy levels becomes:

$$\Delta E = E_{n+1} - E_n = [(n+1)^2 - n^2]\frac{\hbar^2 \pi^2}{2mL^2}$$
$$= (2n+1)\frac{\hbar^2 \pi^2}{2mL^2}$$

- Since we are dealing with electrons $m = m_e$
- The molecule can be described by a size parameter R such that:

$$\Delta E_{el} \sim \frac{\hbar^2}{m_e R^2}$$

Sample calculation: when $m_e = 9.1 \times 10^{-31}$ kg, $R = 5$ Å, then $\Delta E = 5 \times 10^{-20}$ J or 30 kJ mol^{-1}.

Spacing of Vibrational Energy Levels

- Consider a diatomic molecule as a harmonic oscillator.
  - For a harmonic oscillator

$$F = -k(x - x_0)$$

$$E = T + V = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}k(x - x_0)^2$$

  - Since doubling a bond length from R to $2R$ usually results in dissociation of a molecule and the energy required for dissociation is approximately the same order of magnitude as that required for electronic excitation, it may be argued that $\Delta E_{el} \sim k(\Delta R)^2$, therefore:

$$k \sim \frac{\Delta E_{el}}{R^2} \sim \frac{\hbar^2}{m_e R^4}$$

  - The energy for the n^{th} level of a harmonic oscillator are given by:

$$E_n = (n + \frac{1}{2})\hbar\omega$$

where:

$$\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{\hbar^2}{m_e R^4 \mu}}$$

.

- Thus:

$$\Delta E_{vib} = \hbar \left(\frac{k}{\mu}\right)^{1/2} = \frac{\hbar^2}{R^2}\left(\frac{1}{m_e \mu}\right)^{1/2}$$

- If the molecule under consideration is a homonuclear diatomic with each atom of mass M then:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{MM}{M+M} = M/2$$

- Then:

$$\Delta E_{vib} = \frac{\hbar^2}{R^2}\left(\frac{2}{m_e M}\right)^{1/2} = \left(\frac{2m_e}{M}\right)^{1/2} \Delta E_{el}$$

Spacing of Rotational Energy Levels

- Assume the diatomic molecule is a rigid rotor.
  - The quantum mechanical treatment of a rigid rotor gives:

    $$E_J = \frac{J(J+1))\hbar^2}{2\mu R^2}$$

    as the energy of the J^{th} energy level.
  - Therefore the spacing between adjacent levels are:

$$\Delta E_{rot} = \left[(J+1)(J+2) - J(J+1)\right]\frac{\hbar^2}{2\mu R^2}$$

$$\Delta E_{rot} = 2(J+1)\frac{\hbar^2}{2\mu R^2}$$

$$\Delta E_{rot} \sim \left(\frac{m_e}{M}\right)\Delta E_{el}$$

$$\boldsymbol{\Delta \mathbf{E}_{\mathbf{el}} : \Delta \mathbf{E}_{\mathbf{vib}} : \Delta \mathbf{E}_{\mathbf{rot}} :: 1 : \left(\frac{\mathbf{m_e}}{\mathbf{M}}\right)^{1/2} : \left(\frac{\mathbf{m_e}}{\mathbf{M}}\right)}$$

Small Molecule Energy Levels - Diatomics

- Must consider first the electronic configuration for the molecular orbitals.
  - This can be described with molecular quantum numbers analoguous to atomic quantum numbers

Molecular	Atomic
Σ	S
Λ	L
Ω	J

  - This time Σ does not represent total spin, but rather that component of spin along the bond axis of the molecule. S is still used for total spin.
  - The same information can be represented in a “Term Symbol”:

$$^{2S+1}\Lambda_{\Sigma+\Lambda}$$

Internal Energy of a Molecule

- Consider diatomic molecule AB in the ground electronic state with a known intramolecular potential $V(R)$ where R is the separation of atom A from atom B.
- Recall the Born-Oppenheimer (B-O) approximation which allows the separation of nuclear and electronic degrees of freedom because nuclei are over three orders of magnitude heavier than electrons.
- The total nuclear energy may be expressed in terms of the Hamiltonian:

$$\hat{H}_{nucl} = -\frac{\hbar^2}{2m_A}\nabla_A^2 \; - \; \frac{\hbar^2}{2m_B}\nabla_B^2 \; + \; V(R)$$

  - The first term is the kinetic energy operator for atom A,
  - The second term is the kinetic energy operator for atom B,
  - The third term is the potential energy operator.

- ∇ is pronounced “nabla” and, for a particle in (x,y,z) space, ∇^2 is:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

  - ∇^2 is also known as “del squared” or the Laplacian operator.

- Now the Hamiltonian needs to be transformed to center-of-mass coordinates for the diatomic AB. This yields:

$$\hat{H}_{nucl} = -\frac{\hbar^2}{2\mu}\nabla_R^2 \ + \ V(R)$$

where

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

or

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

and

$$\nabla_R^2 = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)$$

$$+ \ \frac{1}{R^2}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) \ + \ \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

- The quantum mechanical solution of this equation has the form:

  $$\Psi_N(R,\theta,\phi) = \psi(R)Y_{J,M}(\theta,\phi)$$

  where:

  - $Y_{J,M}(\theta,\phi)$ is the spherical harmonic function and describes the nuclear rotation associated with total angular momentum quantum number J and its projection quantum number M.
  - $\psi(R)$ describes the nuclear vibrational motion.

- When the wavefunction can be factored, the radial and angular components can be solved separately.

  - Thus the radial Schrödinger equation (RSE) can be written for a diatomic molecule:

$$E\psi = -\frac{\hbar^2}{2\mu R^2}\left[\frac{d}{dR}\left(R^2\frac{d\psi}{dR}\right)\right] + \left[\frac{J(J+1)\hbar^2}{2\mu R^2} + V(R)\right]\psi$$

- This equation is of the same form as the radial equation for the H atom (which can be solved exactly):

$$E\Psi = -\frac{\hbar^2}{2\mu r^2}\left[\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right)\right] + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right]\Psi$$

where

$$V(r) = \frac{e^2}{4\pi\epsilon_0 r}$$

- For the diatomic radial equation, the equation can be transformed into a simple form by considering the function $\chi(R) = R\psi(R)$. Thus the equation becomes:

$$E\chi(R) = -\frac{\hbar^2}{2\mu}\frac{d^2\chi(R)}{dR^2} + \left[\frac{J(J+1)\hbar^2}{2\mu R^2} + V(R)\right]\chi(R)$$

- The term inside the brackets can be considered as an effective potential. Each value of J gives a different equation and a different family of mathematical solutions (vibrational energy levels).

Expanding the Potential

- The potential may be expanded into a power series.
  - The variable is:

    $$\rho = R - R_e$$

    where R_e is the equilibrium separation and ρ/R_e is small.
- Then

  $$V(R) = V(R_e) + V'(R_e)\rho + \frac{1}{2}V''(R_e)\rho^2 + \ldots$$

  and

  - $V(R_e) \equiv \ V_e =$ a constant
  - $V'(R_e) \equiv \ (dV/dR)_{R-R_e} = 0$ since R_e is the position of the minimum
  - $V''(R_e) \equiv \ (d^2V/dR^2)_{R-R_e} = k$ where k is the harmonic force constant.
- If ρ is small and the higher order derivatives are small, then:

  $$V(R) = V(R_e) + \frac{1}{2}k\rho^2$$

  This can be recognized as the equation of a parabola and is the **harmonic oscillator** potential. **This is approximation 1.**

- Since $dR = d\rho$ the RSE can be written in terms of ρ:

$$E\chi(\rho) = -\frac{\hbar^2}{2\mu}\frac{d^2\chi(\rho)}{d\rho^2}$$

$$+\left[\frac{J(J+1)\hbar^2}{2\mu(\rho+R_e)^2} + V_e + \frac{1}{2}\rho^2\right]\chi(\rho)$$

  - Now consider:

$$\frac{1}{(\rho+R_e)^2} = \frac{1}{R_e^2}\left[\frac{1}{(1+\rho/R_e)^2}\right]$$

$$\cong \frac{1}{R_e^2}\left[1 - 2\left(\frac{\rho}{R_e}\right) + 3\left(\frac{\rho}{R_e}\right)^2 - \dots\right]$$

  - If $\rho << R_e$, then **a second approximation (rigid rotor)** can be made to keep only the first term. Thus the RSE becomes:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi}{d\rho^2} + \left\{\left[\frac{J(J+1)\hbar^2}{2\mu R_e^2} + V_e - E\right] + \frac{1}{2}k\rho^2\right\}\chi = 0$$

- The vibrational energy E_{vib} is defined as:

$$E_{vib} = E - V_e - \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

  where

  - E = the **total molecular energy** (not including translational energy).
  - V_e = the **total electronic energy plus nuclear repulsion potential energy** at R_e
  - $\frac{J(J+1)\hbar^2}{2\mu R_e^2}$ = the **rotational energy of a rigid rotor diatomic** with quantum number J.

- Thus the RSE becomes:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi}{d\rho^2} + \frac{1}{2}k\rho^2\chi = E_{vib}\chi$$

which is the Schrödinger equation for the harmonic oscillator.

This is the rigid rotor harmonic oscillator approximation

The energy expressions become:

$$E_{rot}(J) = \frac{J(J+1)\hbar^2}{2\mu R_e^2}, \qquad J = 0, 1, 2, 3, \ldots$$

$$E_{vib}(v) = \hbar \left(\frac{k}{\mu}\right)^{1/2} \left(v + \frac{1}{2}\right), \qquad v = 0, 1, 2, 3, \ldots$$

$$E_{el}(n) = V_e \text{ for state } n$$

such that

$$E = E_{el} + E_{vib} + E_{rot}$$

Spectra are full of evidence that molecules are not rigid rotor, harmonic oscillators. Therefore need corrections:

- Recall

  $$V(R) = V(R_e) + V'(R_e)\rho + \frac{1}{2}V''(R_e)\rho^2 + \ldots$$

  - The deviations from the harmonic potential can be treated as **anharmonic corrections**.
  - Vibrational energy level spacing becomes smaller as the vibrational quantum number increases, therefore the anharmonic corrections are negative and are expressed as expansion of $\left(v + \frac{1}{2}\right)$

- Corrections to rotational energy need to include *centrifugal distortion* and *vibration-rotation coupling*.
    - Correction for centrifugal distortion are expressed as a power series in $J(J+1)$.
    - Correction for vibration-rotation coupling is expressed as a power series in terms of $\left(v+\frac{1}{2}\right) J(J+1)$.
- Spectroscopists usually express energy as wavenumbers in units of cm^{-1}
    - Recall that:

$$\overline{\nu} = \frac{1}{\lambda} = \frac{E}{hc}$$

    - Since $h = 6.626 \times 10^{-34}$ Js and $c = 2.998 \times 10^{10}$ cm s^{-1}, the conversion factor is 1.986×10^{-23}J/cm^{-1}.
- Therefore, from this point on, spectroscopic parameters will be considered in units based on cm^{-1}

The Dunham Expansion

- Consider the Dunham Expansion, a general expression of the energy of a diatomic molecule.

$$E(v,J) = Y_{00} + Y_{10}\left(v+\frac{1}{2}\right) + Y_{01}J(J+1)$$

$$+Y_{20}\left(v+\frac{1}{2}\right)^2 + Y_{02}\left[J(J+1)\right]^2$$

$$+Y_{11}\left(v+\frac{1}{2}\right)\left[J(J+1)\right] + Y_{30}\left(v+\frac{1}{2}\right)^3 + \ldots$$

  - The quantum numbers are dimensionless
  - The Y's are in units of cm^{-1}

- This notation is more recent (1932) than the "traditional" spectroscopic notation. It is also more systematic.

Traditional Spectroscopic Notation

- Total energy is written as:

$$E_{vib,rot} = G(v) + F_v(J)$$

where:

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

$$+\omega_e y_e \left(v + \frac{1}{2}\right)^3 + \ldots$$

and:

$$F_v(J) = B_v J(J+1) - D_v \left[J(J+1)\right]^2$$

with:

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) + \ldots$$

and:

$$D_v = D_e + \beta_e \left(v + \frac{1}{2}\right) + \ldots$$

Spectrum of $\mathbf{Na_2}$

(Making sense of table 19.3)

- Information of note:
    - Reduced mass
    - Dissociation energy $D_0$with respect to the zero point energy of the ground state electronic curve.
    - Ionization potential
- Also note that there is missing information.
- Electronic states are listed in descending order, with the ground state at the bottom.
    - T_e is the electronic energy, with reference to the bottom of the potential curves (i.e. $V_e = V(R_e)$).
    - Each row of the table corresponds to a particular electronic state.
    - Spectroscopic constants (cm^{-1}) given in traditional notation, with additional terms (if any) in the footnotes.
    - Then dissociation energy, D_e, with respect to the bottom of the well.
    - And R_e, the equilbrium separation.
    - Followed by notes on allowed transitions and references.

Calculation of Transition Frequencies

- Use the information in the table to calculate the energy associated with the (electronic, vibrational, rotational) state of interest.
- More conventions:
  - $''$(double prime) refers to the state of lower electronic energy.
  - $'$ (single prime) refers to the state of higher electronic energy.
- Consider the transition from $(v'' = 0, J'' = 0)$ of the ground electronic state to $(v' = 0, J' = 0)$ of the first excited electronic state:

$$\nu_{00} = E' - E''$$

$$= T_e' + G'(v' = 0) - [T_e'' + G''(v'' = 0)]$$

$$= (T_e' - T_e'') + \frac{\omega_e' - \omega_e''}{2} - \frac{\omega_e' x_e' - \omega_e'' x_e''}{4}$$

- For higher v or J levels, must consider anharmonicity.

Diatomic Rotational Spectroscopy

- Spectra are simplified considerably by selection rules.
  - Selection rules arise from the dipole transition moment
- For a heteronuclear diatomic, there is a permanent dipole therefore in the ground electronic state, the rotational selection rule is:
  - $\Delta J = J' - J'' = \pm 1$
- For a homonuclear diatomic, there is no permanent dipole, therefore there is no true rotational spectrum.

Predicting a Pure Rotational Absorption Spectrum

- Selection rule is $\Delta J = \pm 1$
- Initial state is the lower state (v'', J'')

$$E(v'', J'') = T_e'' + G(v'') + F_{v''}(J'')$$

- The final state is the upper state (v', J')

$$E(v', J') = T_e' + G(v') + F_{v'}(J')$$

- Since the electronic state and the vibrational state do not change, the observed frequency is:

$$\Delta E = E(J') - E(J'') = F_v(J') - F_v(J'')$$

Example of Calculated Rotational Spectrum

- Assume $v = 0$
  - This is reasonable if the sample is at thermal equilibrium.
- Therefore

$$F_v = B_v J(J+1) - D_v[J(J+1)]^2$$
$$B_v = B_e - \frac{\alpha}{2}$$
$$D_v = D_e + \frac{\beta}{2}$$

- Consider the transition $J = 0 \rightarrow J = 1$

$$\Delta E = 2(B_e - \frac{\alpha}{2}) - 4(D_e + \frac{\beta}{2})$$

- The next line in the spectrum will be $J = 1 \rightarrow J = 2$

$$\Delta E = 4(B_e - \frac{\alpha}{2}) - 32(D_e + \frac{\beta}{2})$$

- And the next line $J = 2 \rightarrow J = 3$

$$\Delta E = 6(B_e - \frac{\alpha}{2}) - 108(D_e + \frac{\beta}{2})$$

- Generally:

$$\Delta E = 2(J'' + 1)(B_e - \frac{\alpha}{2}) - 4(J'' + 1)^3(D_e + \frac{\beta}{2})$$

This gives line positions in the spectrum.

Line Spacings in a Pure Rotational Spectrum

- Consider two adjacent lines for $\Delta v = 0$:

$$\Delta(\Delta E) = 2(J''+2)(B_e - \frac{\alpha}{2}) - 4(J''+2)^3(D_e + \frac{\beta}{2})$$

$$-[2(J''+1)(B_e - \frac{\alpha}{2}) - 4(J''+1)^3(D_e + \frac{\beta}{2})]$$

or

$$\Delta(\Delta E) = 2(B_e - \frac{\alpha}{2})$$

$$-4[(J''+2)^3 - (J''+1)^3](D_e + \frac{\beta}{2})$$

- Thus the lines in the spectrum are nearly evenly spaced, with the deviation due to the centrifugal distortion.
  - Spacing between adjacent lines is approximately $2(B_e - \frac{\alpha}{2})$

To interpret a spectrum, do this “backwards”

- Measure spacing between lines for a particular Δv.
- Fit to equation of appropriate curve to get spectroscopic coefficients.

Interpretation of Vibrational-Rotational Spectra

- Heteronuclear diatomic
- Infrared spectra, therefore a vibrational transition has occurred.
  - Selection rules for strongly allowed transitions are: $\Delta v = \pm 1$; $\Delta J = \pm 1$
  - Weakly allowed transitions are:

    $$\Delta v = \pm 2, \pm 3, \ldots$$

    but with diminished frequency.
- Absorption spectra, therefore final state has a higher energy than the initial state
  - Transitions observed are $\Delta v = 1$; $\Delta J = \pm 1$
  - Initial state is $v = 0$
- Recall energy of a $(0, J'')$ state (neglecting higher order corrections):

$$E(0, J'') = G(0) + F_0(J'')$$

$$= \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + (B_e - \frac{\alpha_e}{2})J''(J''+1)$$

- And energy of a $(1, J')$ state is:

$$E(1, J') = G(1) + F_1(J')$$

$$= \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e + (B_e - \frac{3\alpha_e}{2})J'(J'+1)$$

- Therefore the energy of a line is:

$$E(1, J') - E(0, J'') = \omega_e - 2\omega_e x_e$$

$$+B_e[J'(J'+1) - J''(J''+1)]$$

$$-\frac{3\alpha_e}{2}J'(J'+1) + \frac{\alpha_e}{2}J''(J''+1)$$

- If $\Delta J = 1$ (R branch):

$$E(1, J''+1) - E(0, J'') = \omega_e - 2\omega_e x_e$$

$$+2B_e(J''+1) - \alpha_e((J''^2 + 4J'' + 3)$$

$$= \omega_e - 2\omega_e x_e + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e J''^2$$

  - Defining $m = J'' + 1$ and $\nu_0 = \omega_e - 2\omega_e x_e$, this becomes:

$$\Delta E = \nu_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2$$

- If $\Delta J = -1$ (P branch):

$$E(1, J'' - 1) - E(0, J'') = \omega_e - 2\omega_e x_e$$

$$-2B_e J'' - \alpha_e((J''^2 - 2J'')$$

$$= \omega_e - 2\omega_e x_e + (2B_e - 2\alpha_e)J'' - \alpha_e J''^2$$

  - Defining $m = J''$ and $\nu_0 = \omega_e - 2\omega_e x_e$, this becomes:

$$\Delta E = \nu_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2$$

- Since $\Delta J = 0$ is not allowed, the Q branch is missing.
  - If the Q branch existed, it would be at

$$E(1, J'') - E(0, J'') = \omega_e - 2\omega_e x_e$$

- Line Spacings:
  - R Branch $(\Delta J = 1)$

$$\Delta(\Delta E) = (2B_e - 4\alpha_e) - \alpha_e(2J'' + 1)$$

$$\Delta(\Delta E) = (2B_e - 3\alpha_e) - \alpha_e m$$

- P Branch ($\Delta J = -1$)

$$\Delta(\Delta E) = (2B_e - 2\alpha_e) - \alpha_e(2J'' + 1)$$

$$\Delta(\Delta E) = (2B_e - 3\alpha_e) - \alpha_e m$$

Therefore, a plot of the spacings of adjacent lines against m will give a slope of $-\alpha_e$ and an intercept of $(2B_e - 3\alpha_e)$

Interpretation of Electronic-Vibrational Spectra

- Consider two electronic states of a diatomic molecule:
    - Initial state is the lower state (v'', J'')

$$E(v'', J'') = T_e'' + G(v'') + F_{v''}(J'')$$

    - The final state is the upper state (v', J')

$$E(v', J') = T_e' + G(v') + F_{v'}(J')$$

- The selection rules for electronic transitions do not place restrictions on changes in vibration.

- The limitations of instrumentation means that rotational lines usually are not resolved.
    - Discussion will be restricted to electronic and vibrational changes.

- The likelyhood of vibrational changes is governed by Franck-Condon Principle
    - Electrons are three to four orders of magnitude lighter than are nuclei.
    - Electronic transitions occur so fast that the nuclei do not get a chance to move (Born-Oppenheimer approximation).
    - "Vertical" transitions are favoured.

- The wavenumber associated with a transition is:

$$\begin{aligned}\overline{\nu} = E' - E'' &= T_e' - T_e'' + G'(v') - G''(v'') \\ &= \overline{\nu}_{el} + \omega_e'(v' + \frac{1}{2}) - \omega_e''(v'' + \frac{1}{2}) \\ &\quad -\omega_e' x_e'(v' + \frac{1}{2})^2 + \omega_e'' x_e''(v'' + \frac{1}{2})^2\end{aligned}$$

  - Therefore, just need to assign v' and v'' and fit.
  - But, how do you know when the assignment is correct?
- Consider the spacing of lines within each "family".
  - For a given v'', the spacing between the lines for $v'' \rightarrow v'$ and $v'' \rightarrow v' + 1$ is:

$$\begin{aligned}\Delta\overline{\nu}(v') &= \overline{\nu}(v' + 1, v'') - \overline{\nu}(v', v'') \\ &= \omega_e' - 2\omega_e' x_e'(v' + 1)\end{aligned}$$

  - For a given v', the spacing between the lines for $v'' + 1 \rightarrow v'$ and $v'' \rightarrow v'$ is:

$$\begin{aligned}\Delta\overline{\nu}(v'') &= \overline{\nu}(v', v'' + 1) - \overline{\nu}(v', v'') \\ &= \omega_e'' - 2\omega_e'' x_e''(v'' + 1)\end{aligned}$$

- Therefore can test the line assignments with the Deslandres table.

Construction of the Deslandres Table

- Column label is v''.
- Row label is v'.
- Using figure in lab handout for reference, Look for patterns in your spectrum to make a provisional assignment.
    - Note direction of horizontal axis.
    - Note that spectrum is in terms of wavelength.
- Using a spreadsheet, have three columns for each v'' and two rows for each v'.
    - In the cells corresponding first of the three columns and the first of the two rows, enter the wavelength of the assigned lines.
    - In the next column to each entry, calculate the corresponding wavenumber.
    - In the third column, calculate the difference between successive v'' line positions in wavenumbers.
    - In the second row, second columns (with respect to each spectral line) calculate the difference between successive v' line positions in wavenumbers.
- Inspect the table for anomalies.

What to do About Anomalies

- Anomalies show up as an irregularities in the “pattern”.
  - Expect $\Delta\overline{\nu}(v')$ (or $\Delta\overline{\nu}(v''))$ to become smaller as v' (or v'') gets larger.
  - Anomalies are due to error in peak assignment
  - May also be due to errors in the peak position
- Errors in peak assignments often show up as “jumps” in the pattern.
- Errors in peak position are due to the limitations of the peak-finding algorithm and show up as “zigzags”.

- Once peak assignments are correct, then spectroscopic parameters may be extracted from the Birge-Sponer plots since:

$$\Delta\overline{\nu}(v') = \omega_e' - 2\omega_e' x_e'(v' + 1)$$

$$\Delta\overline{\nu}(v'') = \omega_e'' - 2\omega_e'' x_e''(v'' + 1)$$

- From this, information about the interaction potential may be inferred.
  - Since this is general, $'$ and $''$ are dropped.

Estimation of Dissociation Energy

- At the dissociation energy, the spacing between successive vibrational levels goes to zero.

$$\Delta\overline{\nu}(v_{max}) = \omega_e - 2\omega_e x_e(v_{max} + 1) = 0$$

- Solving for v_{max} gives:

$$v_{max} = \frac{1}{2x_e} - 1$$

and thus

$$G(v_{max}) = \omega_e \frac{(1/x_e - x_e)}{4} = D_e$$

This is the dissociation energy from the bottom of the well.

- For D_0, the dissociation energy from the $v = 0$ state, this must be corrected for the zero point energy, giving:

$$D_0 = \omega_e \frac{(1/x_e - 2)}{4}$$

Determination of Morse Potential

- The Morse potential is a model potential form with the characteristics of an anharmonic oscillator.

$$U(r - r_e) = D_e\{exp\left[-\beta(r - r_e)\right] - 1\}^2$$

  - D_e is the dissociation energy.
  - β is determined from D_e and the harmonic oscillator force constant k_e

$$\beta = \left(\frac{k_e}{2hcD_e}\right)^{1/2}$$

  - The harmonic oscillator force constant k_e is determined from ω_e:

$$k_e = \mu(2\pi c\omega_e)^2$$

- Potential for both electronic states can be determined.

Potential Energy Surfaces

- If the potential is known, then the spectrum can be calculated.
  - But, can the potential be determined from the spectrum?
- Consider a diatomic molecule in the ground electronic state.
  - Potential known to be repulsive at short range and attractive at long range.
  - Choose a functional form that has the desired properties.
  - Morse potential is one such form.

$$V(R) = \mathbf{D}_e \left(1 - e^{-\beta(R-R_e)}\right)^2$$

with only three parameters to be considered.

- How are the spectroscopic coefficients related to the potential?
  - Recall that the harmonic oscillator force constant $k = V''(R_e)$
  - Taking the second derivative of the Morse Potential and evaluating the result at $R = R_e$
    $$\left(\frac{d^2V}{dR^2}\right)_{R_e} = 2\beta^2\mathbf{D}_e = k$$
  - k can be determined from ω_e:
    $$hc\omega_e = \hbar\left(\frac{k}{\mu}\right)^{1/2}$$
- Determination of $\mathbf{D}_e$, depends on how energy levels are considered.
  - Exact QM treatment gives an energy level expression of the form:
    $$G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2$$

  - Solving for $\left(v + \frac{1}{2}\right)$ at the dissociation energy and noting that $\omega_e x_e << \omega_e$, gives

$$\mathbf{D}_e = \frac{\omega_e^2}{4\omega_e x_e}$$

- Now all the information to calculate β is available:

$$\beta = 2\pi c \omega_e \left(\frac{\mu}{2\mathbf{D_e}}\right)^{1/2}$$

- The Morse potential does a reasonable job of representing a diatomic potential but it does have drawbacks
  - Because it has only two additional parameters beside R_e, it can represent only the first anharmonic correction.
  - It does not accurately predict spectral lines.
  - It is too "stiff" as a functional form to fit a real potential.

HERE ENDS
OUR TREATMENT OF SPECTROSCOPY