## 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<sup>-1</sup>.

#### 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:

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

$$\Delta E_{rot} = 2(J+1)\frac{\hbar^2}{2\mu R^2}$$
$$\Delta E_{rot} \sim \left(\frac{m_e}{M}\right)\Delta E_{el}$$

$$\mathbf{\Delta E_{el}}: \mathbf{\Delta E_{vib}}: \mathbf{\Delta E_{rot}}:: \mathbf{1}: \left(rac{\mathbf{m_e}}{\mathbf{M}}
ight)^{\mathbf{1/2}}: \left(rac{\mathbf{m_e}}{\mathbf{M}}
ight)$$

## **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

Atomic
S
L
J

- This time  $\Sigma$  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.

•  $\nabla$  is pronounced "nabla" and, for a particle in (x,y,z) space,  $\nabla^2$  is:

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

- $\nabla^2$  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:

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

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

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

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  $\rho/R_e$  is small.

• Then

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

and

- $V(R_e) \equiv V_e = a \text{ constant}$
- $V'(R_e) \equiv (dV/dR)_{R-R_e} = 0$  since  $R_e$  is the position of the minimum
- $V''(R_e) \equiv (d^2 V/dR^2)_{R-R_e} = k$  where k is the harmonic force constant.
- If  $\rho$  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  $\rho$ :

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

• Now consider:

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

• If  $\rho \ll R_e$ , 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:

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

$$E_{vib}(v) = \hbar \left(\frac{k}{\mu}\right)^{1/2} \left(v + \frac{1}{2}\right), \qquad v = 0, 1, 2, 3, \dots$$
$$E_{el}(n) = V_e \text{ for state } n$$

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

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

- 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  $\rm cm^{-1}$ 
  - 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<sup>-1</sup>, the conversion factor is  $1.986 \times 10^{-23}$  J/cm<sup>-1</sup>.
- Therefore, from this point on, spectroscopic parameters will be considered in units based on  $\rm cm^{-1}$

#### The Dunham Expansion

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

$$E(v,J) = Y_{00} + Y_{10}\left(v + \frac{1}{2}\right) + Y_{01}J(J+1)$$
$$+Y_{20}\left(v + \frac{1}{2}\right)^2 + Y_{02}\left[J(J+1)\right]^2$$
$$+Y_{11}\left(v + \frac{1}{2}\right)\left[J(J+1)\right] + Y_{30}\left(v + \frac{1}{2}\right)^3 + \dots$$

• 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:

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \dots$$

and:

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

with:

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

and:

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

# ${\bf Spectrum \ of \ Na}_2$

(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<sup>-1</sup>) 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 an harmonicity.

## **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 (to first order).

### 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  $\Delta v$ .
- 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:

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

but with diminished intensity.

- 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):

$$E(1, J'' + 1) - E(0, J'') = \omega_e - 2\omega_e x_e$$
$$+2B_e(J'' + 1) - \alpha_e((J''^2 + 4J'' + 3)$$
$$2\omega_e x_e + (2R - 2\omega_e) + (2R - 4\omega_e) I''_e = U''^2$$

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

• 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  $(\Delta J = 1)$

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

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

• P Branch  $(\Delta J = -1)$ 

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

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

Therefore, a plot of the spacings of adjacent lines against m will give a slope of  $-2\alpha_e$  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:

$$\overline{\nu} = E' - E'' = T'_e - T''_e + G'(v') - G''(v'')$$
$$= \overline{\nu}_{el} + \omega'_e(v' + \frac{1}{2}) - \omega''_e(v'' + \frac{1}{2})$$
$$-\omega'_e x'_e(v' + \frac{1}{2})^2 + \omega''_e x''_e(v'' + \frac{1}{2})^2$$

- 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  $v'' \to v'$  and  $v'' \to v' + 1$  is:

$$\Delta \overline{\nu}(v') = \overline{\nu}(v'+1, v'') - \overline{\nu}(v', v'')$$
$$= \omega'_e - 2\omega'_e x'_e(v'+1)$$

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

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

• 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.
- $\beta$  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  $\omega_e$ :

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

• 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  $\omega_e$ :

$$hc\omega_e = \hbar \left(\frac{k}{\mu}\right)^{1/2}$$

- 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  $\omega_e x_e \ll \omega_e$ , gives

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

• Now all the information to calculate  $\beta$  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