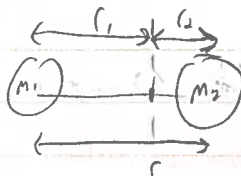


Spectroscopy

Year 2 T1

Rotational Spectroscopy

Rigid Rotor energy levels



$$I = \sum m_i r_i^2$$

$$m_1 r_1 = m_2 r_2$$

$$= m_1 r_1^2 + m_2 r_2^2$$

rotating about
its centre
of mass

$$I = m_2 r_1 r_2 + m_1 r_1 r_2$$

$$I = (m_1 + m_2) r_1 r_2$$

$$\text{using } m_1 r_1 = m_2 (r - r_2) = m_2 (r - r_1) = m_2 r_2$$

$$m_1 r_1 = m_2 (r - r_2)$$

$$I = (m_1 + m_2) r_1 r_2$$

$$m_2 r_2 = m_2 (r - r_1)$$

$$I = \frac{m_1 m_2 r^2}{m_1 + m_2} \rightarrow \mu r^2$$

↳ reduced mass

$$m_1 r_1 = m_2 r - m_2 r_1$$

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

$$r_2 = \frac{m_1 r}{m_1 + m_2}$$

E-levels of rotational states:

$$F(J) = E_{J, hc}$$

$$F(J) = B J(J+1)$$

rotational constant

$$B = \frac{h}{8\pi^2 I_c}$$

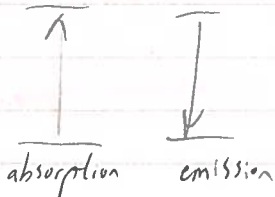
$$F(J) \propto J(J+1)$$

B for small molecules
are in the region $0.1 - 10 \text{ cm}^{-1}$

$B \propto \frac{1}{I} \Rightarrow$ larger molecules have more closely spaced rotational energy levels

1.2 EM spectrum
&
unit conversion

1.2:



1.3 Transition dipole moment (R)

electric dipole moment:

$$\mu = -e\mathbf{r}$$

for QM:

$$R = \int \psi_f^* \hat{\mu} \psi_i d\tau$$

1.4 B.O. approx using QM

ψ is a product of:

- electronic ψ_e
- vibrational ψ_v
- rotational ψ_r

$$E_{tot} = E_e + E_v + E_r$$

Incorporated w/ centrifugal forces

↳ stretches bonds, $\uparrow I$

centrifugal forces stretch

the bond distortion

↳ reduces rotational constant

↳ energy levels smaller gaps

$$F(J) = B J(J+1) - D J^2(J+1)^2$$

$$D = \frac{4B^3}{6e}$$

centrifugal distortion constant

Evaluating transition dipole moment

$$R_{fi} = \int \psi_f^* \mu \psi_i d\tau$$

\uparrow final \uparrow initial

$\neq 0$ for ~~$J \rightarrow J$~~ $\Delta J = \pm 1$

Rotational selection rules
for linear rotors

\hookrightarrow by conservation
of momentum

Wave numbers allowed $J \rightarrow J+1$

$$\begin{aligned}\tilde{\nu}(J+1 \leftarrow J) &= F(J+1) - F(J) \\ &= B(J+1)(J+1) - BJ(J) \\ &= 2B(J+1)\end{aligned}$$

Intensities of lines of rotational spectrum

Intensity lines have a Gaussian-like
distribution

Population of rotational energy level J
given by the Boltzmann expression

$$N_J = N_{g,J} e^{-(E_J/kT)}$$

\uparrow number of molecules in the sample \uparrow degeneracy of level J

Relative Population of rotational level J ,

$$\frac{N_J}{N_0} = (2J+1) e^{-hcBJ(J+1)/kT}$$

Differentiate by parts:

Max population:

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

$$kT \approx 1000 hcB \text{ @ room temp}$$

Vibrational Spectroscopy

We want to calculate the force constant

$$Rmb \quad V(x) = \frac{1}{2} kx^2$$

for Harmonic Oscillator:

$$E_v = \left(v + \frac{1}{2}\right) h\nu \quad v=0,1,2,\dots$$

$$\omega = \sqrt{\frac{k}{\mu}} \Rightarrow \text{vibrational angular frequency}$$

Energy levels of vibrational state:

\hookrightarrow expressed as a vibrational term
or a wavenumber

$$\tilde{\nu} = G(v) = \frac{E_v}{hc}$$

$$= \underbrace{W_e}_{\text{harmonic vibrational wavenumber}} \left(v + \frac{1}{2}\right)$$

$\hookrightarrow W_e$ harmonic vibrational
wavenumber (cm^{-1})

$$W_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

for Anharmonic oscillator:

Real diatomic molecule \neq NOT H.O.

$\therefore r \rightarrow \infty \Rightarrow$ dissociation into 2 neutral atoms

$\hookrightarrow F = \frac{dV}{dr} = 0 \therefore$ curve flattens

$r \rightarrow 0 \Rightarrow$ +ve charges on the nuclei
cause mutual repulsion

$$\hookrightarrow F = \frac{dV}{dr} \uparrow \uparrow$$

Expressing $V(x)$ as Taylor series:

$$V(x) = V(0) + V'_0 x + \frac{V''_0}{2!} x^2 + \frac{V'''_0}{3!} x^3 + O(x^4)$$

3rd order onwards \rightarrow important for
large displacements

Using Morse Potential

$$V(x) = h c D_e (1 - e^{-ax})^2$$

- D_e : well depth

$$a = \sqrt{\frac{\mu \omega_e^2}{h c D_e}}$$

as required

$$x \rightarrow 0, V(x) \rightarrow 0$$

$$x \rightarrow \infty, V(x) \rightarrow h c D_e$$

Solving for Schrödinger eqⁿ for Morse potential

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

↳ first anharmonic wave number

⊛ as $v \uparrow$

↳ anharmonic term becomes more significant

↳ vib energy lvs become more more closely spaced → until they converge @ the dissociation limit

Pictures see notes online

Selection rules: $\Delta v = \pm 1, \pm 2, \pm 3 \dots$

found by evaluating the transition dipole moment

$$R_v = \int \psi_v'^* \mu \psi_v'' d\tau$$

for a heterodiatomic molecule μ varies with x

$$\mu(x) = \mu_e + \left(\frac{d\mu}{dx}\right)_e x + \frac{1}{2!} \left(\frac{d^2\mu}{dx^2}\right)_e x^2 + O(x^3)$$

↳ $e \rightarrow$ referring to eq^m bond length
↳ subbing the m.b. dip transition dipole moment

$$R_v = \underbrace{\mu_e \int \psi_v'^* \psi_v'' d\tau}_= 0 + \mu_e' \int \psi_v'^* x \psi_v'' d\tau + \dots$$

∴ ∴ orthogonal

$$R_v = \mu_e' \int \psi_v'^* x \psi_v'' d\tau + \dots$$

⊛ non-zero if $\Delta v = \pm 1$

$$\Delta v = \pm 1, \pm 2, \pm 3 \dots$$

fundamental vibrational transitions

(1st 2nd ... vibrational over tones

effect of harmonicity are relatively small
↳ over tones are weaker than fundamental

$$\begin{aligned} \tilde{V}(v+1 \leftarrow v) &= G(v+1) - G(v) \\ &= \omega_e (v + \frac{3}{2}) - \omega_e x_e (v + \frac{3}{2})^2 \\ &\quad - [\omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2] \end{aligned}$$

$$\tilde{V}(v+1 \leftarrow v) = \omega_e - 2\omega_e x_e (v+1)$$

Intensities

↳ depend on vib population

using Boltzmann distribution again

$$\frac{N_v}{N_0} = e^{-\frac{hc[G(v) - G(0)]}{kT}}$$

Normally: $hc[G(v) - G(0)] \gg kT$

∴ ground vibrational state ($v''=0$) is significantly populated @ normal temps

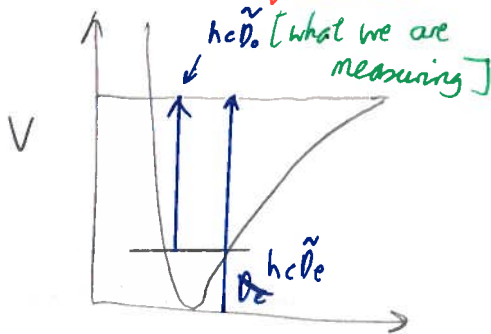
↳ for $v'' \neq 0 \Rightarrow$ referred to hot bands

∴ intensities $\uparrow \uparrow$ w/ temp for these bands

Dissociation energies:

D_0 differs from well-depth D_e

for the zero-pt energy: $G(0) = \frac{1}{2} h\nu_0 - \frac{1}{4} h\nu_0 x_e$



using a Birge-Sponer plot to determine D_0

$$D_0 = \sum_v \Delta G(v)$$

where

$$\Delta G = h\nu_0 - 2h\nu_0 x_e(v+1)$$

Area under the plot of ΔG against $v + \frac{1}{2}$

sum of separations between energy levels

↳ leading to D_0 (see moodle graphs)

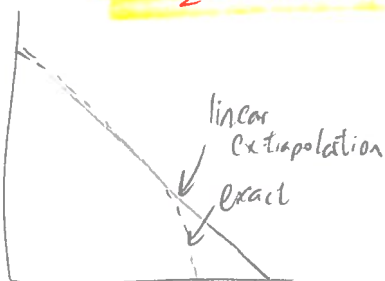
BUT may overestimate

∴ higher order anharmonic terms result in a deviation from linearity as $v \uparrow$

Calculating D_e :

$$D_e = D_0 + G(0)$$

$$= D_0 + \frac{1}{2} h\nu_0 - \frac{1}{4} h\nu_0 x_e$$



$G(v_{max})$:

$$\frac{dG(v)}{dv} = 0$$

$$= h\nu_0 - 2h\nu_0 x_e(v + \frac{1}{2})$$

$$\Rightarrow (v + \frac{1}{2}) = \frac{h\nu_0}{2h\nu_0 x_e}$$

↳ substituting back for $G(v)$

$$= h\nu_0(v + \frac{1}{2})$$

$$G(v_{max}) = \frac{h\nu_0^2}{2h\nu_0 x_e} - h\nu_0 x_e \frac{h\nu_0}{4h\nu_0 x_e^2}$$

$$G(v_{max}) = \frac{h\nu_0^2}{4h\nu_0 x_e} = D_e$$

or

$$D_0 = D_e - G(0) = D_e - (\frac{1}{2} h\nu_0 - \frac{1}{4} h\nu_0 x_e)$$

Vibration-rotational spectroscopy

Rovibr

Rovibrational transitions

=> rotational transitions

accompanying each vibrational transition

-> spectral features referred as

Band Spectra

selection rules: $\Delta v = \pm 1, \pm 2, \dots$

$\Delta J = \pm 1$

Note that ~~delta~~ $\Delta J = 0$ is not observed

-> meaning no observation of pure vibrational transition

if have pure vibrational transition

-> known as Band centre

Exceptions: molecules having their orbital angular momentum about their internuclear axis

-> selection rules: $\Delta v = \pm 1, \pm 2, \dots$

$\Delta J = 0, \pm 1, \dots$

Energy levels (just a sum)

$$S(v, J) = G(v) + F(J)$$

if ignoring anharmonicity

&

Centrifugal distortion

-> rewriting the vibration-rotation term

$$S(v, J) = w_e(v + \frac{1}{2}) + B J(J+1)$$

PQR Branches

-> groups of absorption

$$\Delta J \quad -1 \quad 0 \quad +1$$

Branch P Q R

$$\tilde{\nu}_{\text{branch}}(J) = w_e - 2BJ \quad w_e \quad w_e + 2B(J+1)$$

Transitional wavenumber of lines in each branch can be determined by applying the appropriate ΔJ selection rules

& calculating the difference between the vib-rot terms $\tilde{\nu}[S(v', J') - S(v'', J'')]$

- Q branch, $v+1 \leftarrow v$

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

$$= w_e(v + \frac{1}{2}) + B J(J+1)$$

$$- w_e(v + \frac{1}{2}) - B J(J+1) = w_e$$

* Q branch consist of lines at the harmonic wavenumber, w_e

- R branch, $v+1 \leftarrow v$

$\Delta J = \pm 1$

$$\tilde{\nu}_R(J) = \tilde{\nu}[S(v+1, J+1) - S(v, J)]$$

$$= w_e(v + \frac{3}{2}) + B(J+1)(J+2)$$

$$- w_e(v + \frac{1}{2}) - B J(J+1)$$

$$= w_e + 2B(J+1)$$

* R branch consists of a series of equally spaced lines @ higher wavenumbers than Q branch, $w_e + 2B, w_e + 4B, \dots$

- P branch, $v+1 \leftarrow v$

$\Delta J = -1$

$$\tilde{\nu}_P(J) = \tilde{\nu}[S(v+1, J-1) - S(v, J)]$$

$$= w_e(v + \frac{3}{2}) + B(J-1)J$$

$$- w_e(v + \frac{1}{2}) - B J(J+1)$$

$$= w_e - 2BJ$$

* P Branch consists of a series of equally spaced lines @ lower wavenumbers than Q branch, $w_e - 2B, w_e - 4B$

Intensity distribution

↳ reflects populations of rotational levels associated w/ the lower vibrational state

However in reality:

R-branch converge

P-branch diverge

For anharmonic oscillator

$$S(v, J) = W_e(v + \frac{1}{2}) + W_e X_e(v + \frac{1}{2})^2$$

$$+ B_v J(J+1)$$

↳ rotational constant depending on vibrational state

$$B \propto \frac{1}{r^2} \Rightarrow v \uparrow, r \uparrow, I \uparrow$$

$$\therefore B \downarrow \text{ as } v \uparrow$$

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

↳ hypothetical value of the rot const. @ bottom of potential well

of potential well

vibration-rotation interaction constant

Determining the transitional wavenumbers:

of lines in each branch of

a vib-rot spectrum of an anharmonic oscillator,

✳ applying appropriate ΔJ selection rules

& calc diff between vib-rot term

for the R branch:

$$\Delta J = +J \quad v+1 \leftarrow v$$

$$J' = J'' + 1 \quad v' \leftarrow v''$$

$$J = J+1$$

$$\tilde{\nu}_R(J) = \tilde{\nu} [G(v+1) - G(v)]$$

$$+ \tilde{\nu} [F(J+1) - F(J)]$$

$$= \tilde{\nu}_{v',v''} + B'(J+1)(J+2) - B''J(J+1)$$

$$\Rightarrow \tilde{\nu}_R(J) = W_e - 2W_e X_e(v+1) + B'(J+1)(J+2) - B''J(J+1) \quad \text{for pure vib transition } v+1 \leftarrow v, \text{ or bandhead}$$

Similarly for P branch, $J' = J'' - 1 \Rightarrow J - 1$

$$v'' = v$$

$$v' = v+1$$

$$\tilde{\nu}_P(J) = \tilde{\nu} [G(v+1) - G(v)]$$

$$+ \tilde{\nu} [F(J-1) - F(J)]$$

$$= \tilde{\nu}_{v',v''} + B'J(J-1) - B''J(J+1)$$

$$= W_e - 2W_e X_e(v+1) + B'J(J-1) - B''J(J+1)$$

✳ P branch lines appear @ lower $\tilde{\nu}$ than pure vib-transition

✳ R branch lines appear @ higher $\tilde{\nu}$ than pure vib-transition

✳ Need to determine B' & B''

using a method \rightarrow combination differences

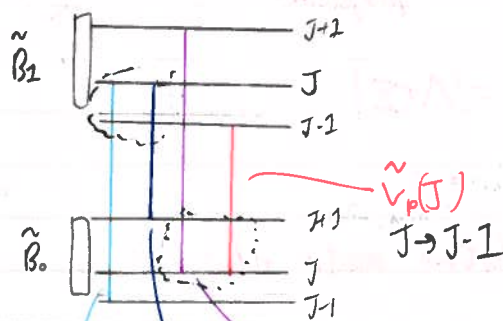
✳ Difference in wavenumber between 2 transitions w/ a common lower vib-rot level

\rightarrow gives us info about energy differences between rot levels in the upper vib-state

similarly $\rightarrow \tilde{\nu}$ diff between 2 transitions w/ a common higher vib-rot level

\Rightarrow gives us info about E-diff between rot levels in the lower vib-state

Combination difference



$$\tilde{\nu}_R(J-1) \quad \tilde{\nu}_P(J+1) \quad \tilde{\nu}_R(J)$$

$$J-1 \rightarrow J \quad J+1 \rightarrow J \quad J \rightarrow J+1$$

$$\left. \begin{array}{l} \tilde{\nu}_R(J-1) \\ - \tilde{\nu}_P(J+1) \end{array} \right\} \text{common higher level - ①} \\ \rightarrow \Delta_2' F(J)$$

① for lower

$$\left. \begin{array}{l} \tilde{\nu}_R(J) \\ - \tilde{\nu}_P(J) \end{array} \right\} \text{common lower level - ②} \\ \rightarrow \Delta_2' F(J) \quad \text{② for upper}$$

$$\begin{aligned} \text{①: } \Delta_2' F(J) &= \tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) \\ &= \tilde{\nu}_{v,v''} + B'(J(J+1)) - B''(J(J-1)) \\ &\quad - \tilde{\nu}_{v,v''} - B'(J(J+1)) + B''(J+1)(J+2) \\ &= B''(J-J^2) + B''(J^2+3J+2) \\ &= B''(J-J^2+J^2+3J+2) \\ &= B''(4J+2) \end{aligned}$$

$$\Delta_2' F(J) = 4B''(J+\frac{1}{2})$$

$$\begin{aligned} \text{②: } \Delta_2' F(J) &= \tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) \\ &= \tilde{\nu}_{v,v''} + B'(J(J+1)) - B''(J(J+1)) \\ &\quad - \tilde{\nu}_{v,v''} - B'(J(J-1)) + B''(J(J+1)) \\ &= B'(J^2+3J+2 - J^2+J) \\ &= B'(4J+2) \end{aligned}$$

$$\Delta_2' F(J) = 4B'(J+\frac{1}{2})$$

Eg. $\tilde{\nu}_R(0)$ & $\tilde{\nu}_P(1)$ determination

for $^1\text{H}^{35}\text{Cl}$

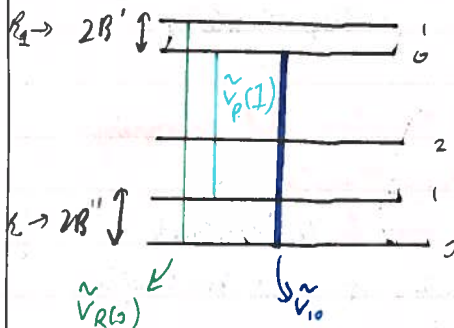
$$B_0 = 10.44 \text{ cm}^{-1}$$

$$B_1 = 10.13 \text{ cm}^{-1}$$

$$\tilde{\nu}_{01} = 2886.04 \text{ cm}^{-1}$$

determination
determine wavenumbers
of the first members
of the P & R branches

in the vib-rot spectrum



$$\tilde{\nu}_R(J) = \tilde{\nu}_{v,v''} + B'(J+1)(J+2) - B''(J)(J+1)$$

$$\tilde{\nu}_R(0) = \tilde{\nu}_{01} + 2B_1 - B_0(0)(1)$$

$$= \tilde{\nu}_{01} + 2B_1$$

$$= 2886.04 + 2(10.13) = 2906.3 \text{ cm}^{-1}$$

$$\tilde{\nu}_P(1) = \tilde{\nu}_{v,v''} + B'(1)(2) - B''(1)(2)$$

$$\tilde{\nu}_P(1) = \tilde{\nu}_{01} + B_1(1) - 2B_0$$

$$= 2886.04 - 2 \times 10.44$$

$$= 2865.16 \text{ cm}^{-1}$$

$$\Rightarrow \tilde{\nu}_{01} = \tilde{\nu}_R(0) - 2B_1 = \tilde{\nu}_P(1) + 2B''$$



by Bojila

Electronic Spectroscopy

- electronic transition occurs:

- ↳ electron distribution changed,
- ↳ nuclei no longer in their equilibrium positions
- ↳ they vibrate

* vibrational transitions that accompany an electronic transition

↳ give rise to the vibrational structure of an electronic transition

→ structure can be resolved in a gas-phase, but is unresolved in liquid

1. Terms symbols: classifying the projection of electronic angular momenta along the molecular axis

in a many-e⁻ molecule:

- Orbital angular momenta of e⁻s are coupled together to give a resultant momentum: L

- all spins are coupled together to give a resultant: S

in H-atom: $j = |l-s| \dots |l+s|$

in molecule: coupling between L & S is usually much less than coupling between L & internuclear axis
- between S & internuclear axis

↳ projections of L & S along the internuclear axis

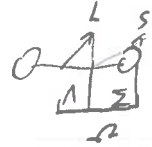
↳ Λ & Σ

are well defined

giving a total angular momentum projection:

$$\Omega = |\Lambda + \Sigma|$$

for diatomic molecules:
 $2s+2$
 $\Lambda_{g/u, \pm}$



2. Electronic selection rules:

* Fermi's golden rule
& Energy Conservation

Spin angular momentum

$$\Delta S = 0$$

Orbital angular momentum

$$\Delta \Lambda = 0, \pm 1$$

Symmetry

$$g \leftrightarrow u; g \leftrightarrow g; u \leftrightarrow u$$

If both states are Σ

$$+ \leftrightarrow +; - \leftrightarrow -; + \leftrightarrow -$$

Transitions between multiplet components

$$\Delta \Sigma = 0, \Delta \Omega = 0, \pm 1$$

$$\text{eg. } N_2 (\sigma_g 1s)^2 (\sigma_g^* 1s)^2 (\sigma_g 2s)^2 (\sigma_g^* 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^2$$

$^1\Sigma_g^+$ as the corresponding term symbol

→ promoting an electron from the

$$(\sigma_g 2p)^2 \text{ or } (\pi_u 2p)^2 \text{ M.O. to the } (\pi_g^* 2p) \text{ orb.}$$

$$\rightarrow (\sigma_g 2p)^1 (\pi_u 2p)^1 (\pi_g^* 2p)^1$$

$$\rightarrow (\sigma_g 2p)^2 (\pi_u 2p)^1 (\pi_g^* 2p)^1$$

are:

$$\left. \begin{array}{l} ^{1,3}\Pi_g \\ ^{1,3}\Sigma_u^\pm \\ ^{1,3}\Delta_u \end{array} \right\} \text{ (circled)}$$

only state accessible by single-photon absorption from the $^1\Sigma_g^+$ ground state

↳ is the $^1\Sigma_u^+$

Vibrational structure of electronic transitions

→ no restrictions on the change of quantum number associated w/ an electronic transition

$$R_{ev} = \int \psi_e'^* \hat{\mu} \psi_e'' d\tau \quad \psi_{ev} = \psi_e \psi_v$$

$$= \int \psi_e'^* \hat{\mu} \psi_e'' d\tau \int \psi_v' \psi_v'' d\tau$$

$$= \text{Re} \int \psi_v'^* \psi_v'' d\tau$$

electronic transition dipole moment

Frank-Condon overlap integral
vibrational overlap integral

∴ e-transitions occur much more rapidly than v-trans

Frank-Condon principle:

- e-transition takes place on the potential energy surfaces that lie on a vertical line

∴ it is required for the nuclei to be in the same position b4 & after an electronic transition

- Vibronic transitions:

↳ vib-trans accompanied by e-trans

- Vibronic trans give rise to bands

- Band system: set of bands associated w/ a particular electronic transition

Progression: group of transitions w/ a common lower & upper vibrational level

Sequence: group of transitions w/ same Δv

Progressions from $v'' > 0$ are only

visible in absorption

WHEN the harmonic vibration

wavenumber is small, such as in the B-X band system of I_2

Vibronic transition wavenumber:

total energy T of a molecule in a particular electronic, vibrational, & rotational state is written as:

$$T = T_e + G(v) + F(J)$$

Wavenumber of a vibronic transition [excluding rotation]

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

$$= \overset{1}{T_e'} - \overset{2}{T_e''} + \overset{3}{W_e'(v' + \frac{1}{2})} - \overset{4}{W_e''(v'' + \frac{1}{2})} - \overset{5}{W_{ex}''(v'' + \frac{1}{2})^2}$$

5 variables used to calculate

↳ min of 5 lines needed to be measured

→ we can use combination difference to obtain the separations of vibrational levels from the observed transition wavenumbers

→ we can use Reslender's table to better organize the vibrational transition energies

∴ the intensity distribution of the vibrational

components of an electronic transition depends on the relative positions of two electronic potential curves

Dissociation energies

[derived from electronic spectra]

Recalling:

D_0 : energy required to dissociate the molecule in a given electronic state from the lowest vibrational level of that state

Re: Energy from the eq^{ry} geometry;
from the bottom of the P.E well
to the dissociation limit

determining D_0 :

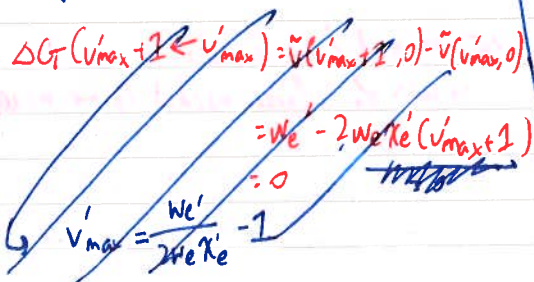
by determining 1. the wavenumber of the $v''=0$ progression limit

$$2. \tilde{v}(v'_i, 0)$$

7. The 0-0 transition from a spectrum:
with ref to the graph

$$\tilde{V}(V'_{max}, 0) = \tilde{U}(0, 0) + D_0'$$

@ The progression limit:



Recalling the Morse oscillator:

$$\frac{d\tilde{G}_v}{dv} = 0 \quad \text{@ the dissociation limit } (v + \frac{1}{2})_{\text{max}}$$

$$\frac{d\tilde{c}_1}{dv} = w_e - 2w_e x_e'(v_{\text{int}}) \cdot 0$$

$$V_{\max} = \frac{W_e'}{2W_e \eta_e'} - 1$$

$$\tilde{v}(v'_{max}, 0) = T_e' - T_e'' + W_e'(v'_{max} + \frac{1}{2})$$

$$-w_e \chi_e' (v_{max} + \frac{1}{2})^2$$

$$- \left[\frac{1}{2} w e'' - \frac{1}{4} w e \kappa e'' \right]$$

Determining ν_0' if the 0-0 transition is known

$$D_\theta' = \tilde{V}(v'_{max}, 0) - \tilde{V}(0, 0)$$

∴ few vibrational levels are populated

if the wavenumber difference between the atomic fragments is known :

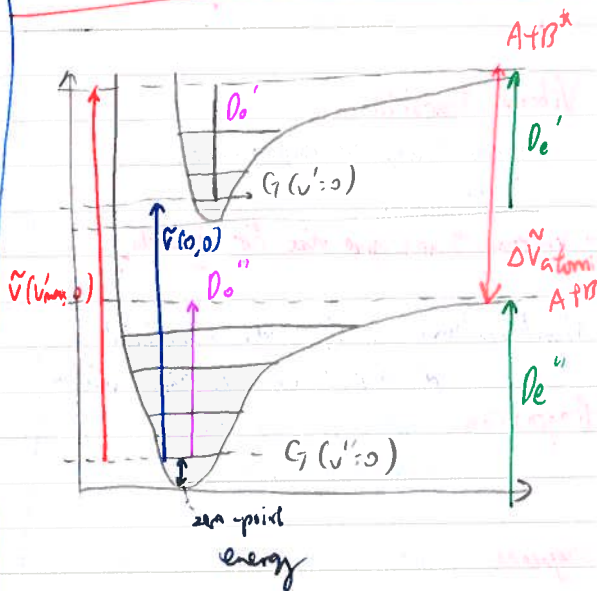
$$Q_3'' = \tilde{v}(v'_{\max}, 0) - \Delta \tilde{v}_{\text{atomic}}$$

$$D_e'' = D_0'' + G''(t_0)$$

$$D_e = \tilde{G}_{V_{max}} = \frac{We^2}{4We_{ke}}$$

$$\hookrightarrow De'' = \frac{We''}{4We''x_e''}$$

$$D_0'' = \frac{W_e''^2}{4W_e x_e''} + G''(c_0)$$



Rotational fine structure

For every vibronic transition; there is a set of accompanying transitions between the stack of rotational levels associated w/ the upper & lower vibronic states

[similar to infrared rovibrational spec]

★ important difference:

B' & B'' can be much larger than in IR spec

↳ we are rearranging e/s

Recalling
Rotational selection rules:

$${}^1\Sigma \rightarrow {}^1\Sigma : \Delta J = \pm 1$$

$${}^1\Pi \rightarrow {}^1\Sigma : \Delta J = 0, \pm 1$$

lines are given individually by:

$$\begin{aligned} (J', J'') &= \tilde{\nu}_0 + B'J'(J'+1) - B''J''(J''+1) \end{aligned}$$

upper
lower

Band origin:

$$\tilde{\nu}_0 = T' - T'' + G'(v') - G''(v'')$$

Branch

$$\begin{aligned} \tilde{\nu}_P(J-1, J) &= \tilde{\nu}_0 + B'(J-1)J \\ &\quad - B''J(J+1) \\ &= \tilde{\nu}_0 + (B' - B'')J^2 - (B' + B'')J \end{aligned}$$

$$\begin{aligned} \tilde{\nu}_Q(J, J) &= \tilde{\nu}_0 + B'J(J+1) - B''J(J+1) \\ &= \tilde{\nu}_0 + (B' - B'')J(J+1) \end{aligned}$$

$$\begin{aligned} \tilde{\nu}_R(J+2, J) &= \tilde{\nu}_0 + B'(J+2)(J+1) - B''J(J+1) \\ &= \tilde{\nu}_0 + (B' - B'')(J+1)^2 + (B' + B'')(J+1) \end{aligned}$$

Band head: when the diff of B' & B'' become so large, one or other branches may end up turning round on itself

if $B' < B''$ P diverge, R converge

$$\tilde{\nu}_R(J+1, J) = \tilde{\nu}_0 + (B' - B'')J^2 + (B' + B'')J + 2B'$$

$$\frac{d\tilde{\nu}_R}{dJ} = 2J(B' - B'') + (B' + B'') = 0$$

$$J_{\text{head}} = -\frac{(B' + B'')}{2(B' - B'')}$$

if $B' > B''$ P converge, R diverge

$$\tilde{\nu}_P(J-1, J) = \tilde{\nu}_0 + (B' - B'')J^2 - (B' + B'')J$$

$$\frac{d\tilde{\nu}_P}{dJ} = 2J(B' - B'') - (B' + B'') = 0$$

$$J_{\text{head}} = \frac{(B' + B'')}{2(B' - B'')}$$

For $\Sigma \rightarrow \Sigma$ transitions:

$\Delta J = \pm 1 \Rightarrow$ only P & R branches observed

For $\Pi \rightarrow \Sigma$ transitions:

$\Delta J = 0, \pm 1 \Rightarrow$ all PQR branches are observed

³¹P N

V''	0	1	2	3	4
$V' = 2$	41859.1	40536.2		37832.9	36652.5

$$\tilde{V}(2, v'') - \tilde{V}(2, v'+1) = W_e'' - 2W_e x_e'' (v''+1)$$

for $v' = 0$

$$41859.1 - 40536.2 = W_e'' - 2W_e x_e'' \quad - \textcircled{1}$$

$$37832.9 - 36652.5 = W_e'' - 2W_e x_e'' (3+1) \quad - \textcircled{2}$$

$$1322.9 = W_e'' - 2W_e x_e'' \quad - \textcircled{1}$$

$$1280.4 = W_e'' - 8W_e x_e'' \quad - \textcircled{2}$$

$$47.5 = 6W_e x_e''$$

$$W_e'' = 1322.9 + 2(7.08)$$

$$W_e x_e'' = 7.08 \text{ cm}^{-1}$$

$$= 1337.1 \text{ cm}^{-1}$$

$$\mu = \frac{14.003 \times 30.970}{14.003 + 30.970} = 1.602 \times 10^{-26} \text{ kg}$$

$$k'' = 4\pi^2 c^2 \mu W_e''^2$$

$$= 1016 \text{ N m}^{-1}$$

$$D_e'' = \frac{W_e^2}{4W_e x_e''}$$

$$= 63130 \text{ cm}^{-1}$$

$$D_0'' = D_e'' - \left(\frac{1}{2} W_e'' - \frac{1}{4} W_e x_e'' \right)$$

$$= 63130 - \left(\frac{1337.1}{2} - \frac{7.08}{4} \right)$$

$$= 62460 \text{ cm}^{-1}$$

D_e'' won't change significantly. it defines the well depth, which is not expected to change upon isotopic substitution. the electronic structure (bonding) does not change

	0	1	2	3	4	5
$\nu'' = 0$:	17080	17126	17167	17203	17234	17260
	46	41	36	31	26	

$$\Delta G(\nu', \nu'' = 0) = W_e' - 2W_e x_e' (\nu' + 2)$$

Plotting ΔG against $(\nu' + 2)$ and fit a straight line

$$\text{gradient} = -5 = -2W_e x_e'$$

$$W_e x_e' = 2.5 \text{ cm}^{-1}$$

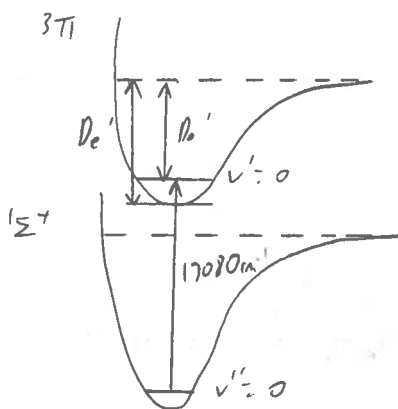
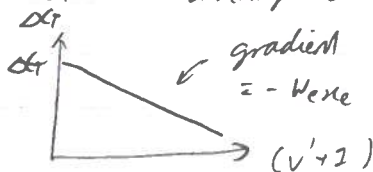
$$\text{Intercept} = 51 \text{ cm}^{-1}$$

$$W_e' = 51 \text{ cm}^{-1}$$

$$D_e = \frac{W_e'^2}{4W_e x_e'}$$

$$= \frac{(51)^2}{4(2.5)}$$

$$= 260.1 \text{ cm}^{-1}$$



$$D_0' = D_e' - \left(\frac{1}{2} W_e' - \frac{1}{4} W_e x_e' \right)$$

$$= 235 \text{ cm}^{-1}$$

$$\text{Dissociation limit} = 17080 + 235 = 17315 \text{ cm}^{-1}$$

$$\tilde{\nu}(\nu_{\text{max}}, 0)$$