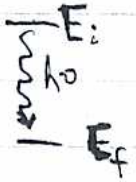
Rotation-Vibration Spectroscopy

Chem. 1410
Oct. 8, 2007

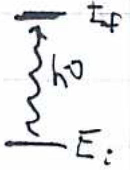
Uses: Determination of molecular structure

Overview of types of optical spectra:

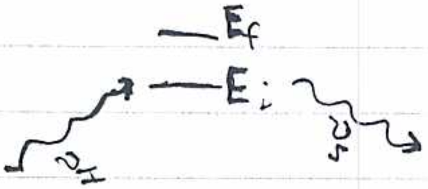
① Emission:



; ② Absorption:



③ Raman scattering:



$h(\nu_s - \nu_I) = E_i - E_f$

Raman notes: (i) $E_f - E_i$ "small" ⇒ need lasers for adequate resolution ("monochromaticity")

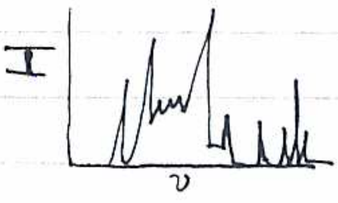
(ii) Stokes: $\nu_s < \nu_I$ [E into molecule]

Antistokes: $\nu_s > \nu_I$ [molec. releases energy]

Spectral Blueprints: Both $E = E(v, J, e_k)$ and $I = I(v, J, e_k)$

v: Vibrational quantum #
J: rotational quantum #
e_k: electronic q.n.
I: Intensity

Hence,



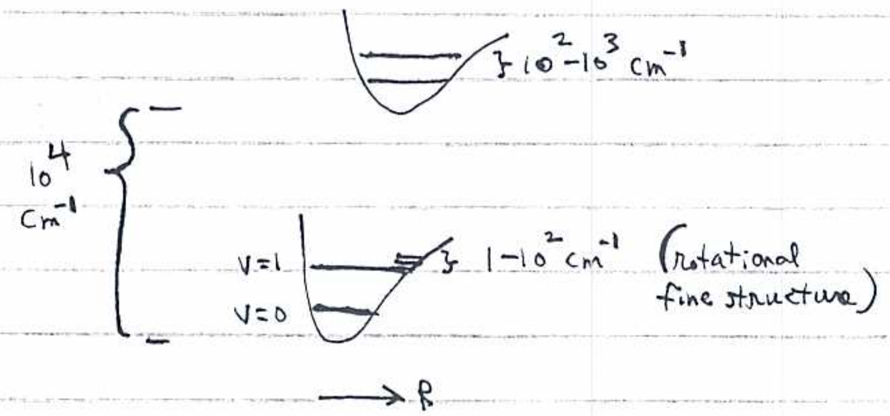
} molecular blueprint(!)

Population + **Intensity** : $N(E) \propto \underset{\substack{\uparrow \\ \text{sample} \\ \text{size}}}{N}\, g\, e^{-E/k_BT}$ ← Boltzmann factor

degeneracy of level E

Hence, $$\frac{I(E)}{I(E')} \sim \frac{N(E)}{N(E')} = \left(\frac{g}{g'}\right) e^{-[E-E']/k_BT}$$

Relevant energy scales for different types of motion:



Note, $k_BT \cong 200$ cm^{-1} at room temperature

Thus: At room temp, spectra are usually electronically, vibrationally cold; rotationally hot (↑ congested)

Selection Rules + Intensity ← determine whether transitions are allowed or forbidden.

Quantum Mech. Statement of selection rules for absorption, emission:

$$\underset{\sim}{\mu}_{fi} = \int d\tau\, \psi_f^* \underset{\sim}{r}\, \psi_i = \text{transition dipole moment} \quad ; \quad \text{Intensity of transition} = \left|\underset{(\sim)}{\mu_{fi}}\right|^2$$

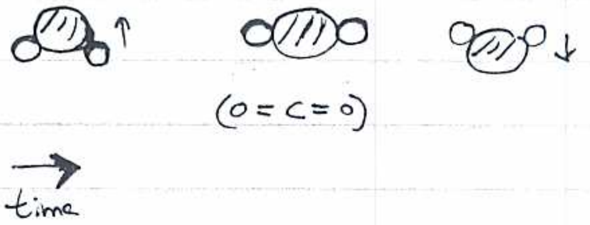
(x, y, z) components ⟺ different E field polarization

Gross Selection Rules : Rotational transitions - non-zero only for molecules w/ permanent dipole moment.

} Molecules that lack a perm. dipole moment give no microwave spectrum

Vibrational transitions - must have oscillating dipole moment during vibration

NB: molecule could be nonpolar w/ oscillating dipole induced by vibration



Notes: (i) homonuclear diatoms are vibrationally inactive [E.g. ← (F)—(F) →]
give no infrared spectrum

(ii) Not all modes of complex molecules are vibrationally active ; Eg. in CO_2

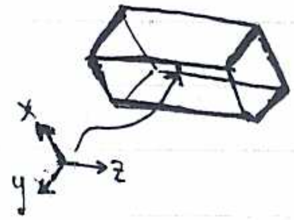
← O=C=O →

symmetric stretch mode has 0 dipole moment at all times.

Rotational Spectra [of Polyatomic Molecules]

Essential Prelude...

Rotational E levels ← Depends intimately on moments of inertia



For any rigid body (e.g. molecule), there exist 3 axes (attached to center of mass), termed "principal axes", of direct importance to rotational inertial energy levels (cf. below); for high-symmetry molecules, principal axes coincide w/ symmetry axes

E.g.

$$I_z = \sum_\alpha m_\alpha (x_\alpha^2 + y_\alpha^2) \text{ , etc.}$$

point masses

ExI: Heteronuclear diatomic:

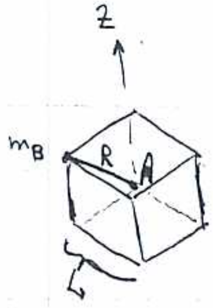
$$I_{\parallel} = \text{“}I_z\text{”} = 0$$

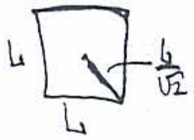
$$I_y = I_x = I_\perp = m_1 \left(\frac{m_2 R}{m_1+m_2}\right)^2 + m_2 \left(\frac{m_1 R}{m_1+m_2}\right)^2$$

$$= \boxed{\frac{m_1 m_2}{(m_1+m_2)} R^2}$$

Note: termed "linear rotor"; special case of a "symmetric rotor" or "symmetric top"

Ex 2: AB_4 tetrahedron [Spherical Top]



Note: 

, Hence $R^2 = \left(\frac{L}{2}\right)^2 + \left(\frac{L}{\sqrt{2}}\right)^2 = \frac{3}{4}L^2$

$$I_x = I_y = I_z = 4\cdot m_B\left(\frac{L}{\sqrt{2}}\right)^2 = 2m_B\underset{\frac{4}{3}R^2}{\underset{\downarrow}{\cancel{L^2}}} = \boxed{\frac{8}{3}m_B R^2}$$

Connection Between Moments of Inertia and Rotational Energies

Classically, $E_{rot} = \frac{1}{2}\left[I_x\omega_x^2 + I_y\omega_y^2 + I_z\omega_z^2\right]$; $\underset{\sim}{\omega}$ = angular velocity w.r.t. principal axes

$$= \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} \xrightarrow[\text{"Quantize"}]{} \boxed{\frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} + \frac{\hat{J}_z^2}{2I_z} = \hat{H}_{rot}}$$

Since ↗

→ $J_x = I_x\omega_x$, etc.

angular momentum

or "Rotor"

(Aside) Classifying rigid bodies: (i) Spherical Tops, $I_x = I_y = I_z$; includes objects in cubic point groups (e.g. SF_6, CH_4)

(ii) Symmetric Top, $I_x = I_y \neq I_z$;
includes objects w/ C_3 or higher axis [e.g. NH_3]

(iii) Linear Rotor: symmetric rotor w/ $I_z = 0$; e.g. $O=C=O$, all diatomics

(iv) Asymmetric Top: $I_x \neq I_y \neq I_z$ [E.g. $H^{\ O}\ H$]

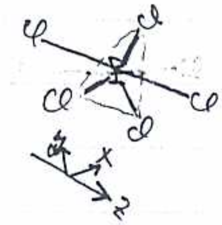
Now...

Energy Levels: Spherical Rotor $\hat{H} = \frac{1}{2I}(\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2) = \frac{\underset{\sim}{\hat{J}}^2}{2I} \Rightarrow \boxed{E_J = J(J+1)\frac{\hbar^2}{2I} \ ; J = 0, 1, 2, \dots}$

Conventionally, $\boxed{\frac{\hbar^2}{2I} \equiv hcB}$, B = rotational constant

Symmetric Rotor ; Note, 2 types:

(i)



$I_z < I_{x,y}$

"Prolate"

(ii)

$I_z > I_{x,y}$; "Oblate"

Now

$$\hat{H} = \frac{1}{2I_\perp}\underbrace{[\hat{J}_x^2 + \hat{J}_y^2]}_{(\underset{\sim}{J}^2 - J_z^2)} + \frac{1}{2I_\parallel}\hat{J}_z^2 = \frac{\underset{\sim}{\hat{J}}^2}{2I_\perp} + \frac{1}{2}\left(\frac{1}{I_\parallel} - \frac{1}{I_\perp}\right)\hat{J}_z^2 \Rightarrow$$

"$I_{x,y}$" "I_z"

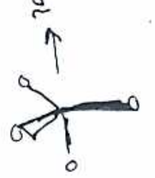
$$\boxed{E_{JK} = \frac{\hbar^2 J(J+1)}{2I_\perp} + \frac{\hbar^2}{2}\left[\frac{1}{I_\parallel} - \frac{1}{I_\perp}\right]K^2 \qquad J = 0, 1, 2, \dots ; \ K = -J, \dots, J}$$

Note: (i) $\hbar K$ = projection of ang. momentum on molecule figure axis.

(ii) $\pm K \cong J$

$\underset{\sim}{J}$ $\rightarrow$ J spinning about figure axis

(iii) $K=0$



∃ tumbling ~~about figure axis~~

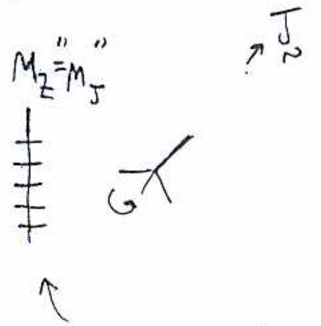
Linear Rotors: $I_{\parallel} \to 0$, no rotation abt. figure axis ⇒ "tumbling only" ⇒ $K=0$ in symmetric rotor E-level formula

Hence:

$$\boxed{E_J = \frac{\hbar^2}{2I} J(J+1)\ ,\ J=0,1,2,\dots}$$

← NB: Not identical to spherical rotor case because of degeneracy issues

Degeneracies:



projection of $\underset{\sim}{J}$ onto lab fixed z axis is quantized, $M_J = (0, \pm 1, \dots, \pm J)\hbar$

Clearly, M_J does not affect $E_{J,K}$ in absence of external (electric) field favoring a particular molecular orientation.

However, these states are distinguishable [← Affects degeneracies, hence level populations, hence intensities]

Count Rotational States: Spherical Rotor, $(2J+1)(2J+1)$ states for each E_J

Symmetric Rotor:

$$\left.\begin{array}{ll} 2(2J+1) & \text{states for each } E_{JK}\ ;\ K=1,\dots,J \\ (2J+1) & \text{states for } E_{J0} \end{array}\right\} \text{total degeneracy of } (2J+1)^2$$

Linear Rotor: $(2J+1)$ states for each E_J

Stark Effect: Can break M_J degeneracy by applying electric field to molecule w/ permanent electric dipole moment [E.g. HCl]; cf. Atkins Sect. 16.4

Rotational Transitions = "E levels" + "selection rules" + "(Boltzmann) population"

Selection Rules: for linear Rotor, $\Delta J = \pm 1$, $\Delta M_J = 0, \pm 1$ [For symmetric rotor same rules, plus $\Delta K = 0$]

Furthermore, $|\mu_{J+1,J}|^2 = \mu^2 (J+1)/(2J+1)$ = Intensity of $J \to J+1$ transition

(for linear rotor)

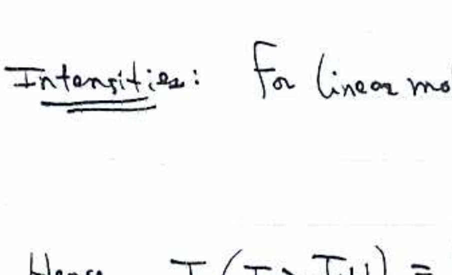
μ ↑ permanent dipole moment

Hence expect absorption frequencies (for linear rotor):

$$h\nu = \underset{\text{"}hcB\text{"}}{\frac{\hbar^2}{2I}} \{J(J+1) - (J-1)J\} = hcB(2J)$$

(J=1,2,⋯)

[Holds for symmetric top, too (w/ $I \to I_\perp$), since $\Delta K = 0$]



} haven't addressed intensities yet

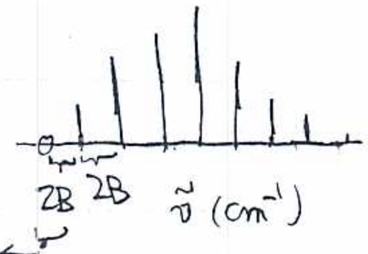
} Rotational (Microwave) Absorption Spectrum

Intensities: For linear molecule, recall:

$$N(E_J) \propto (2J+1)\, e^{-J(J+1)hcB/k_BT}$$

Hence $$I(J \to J+1) = N(E_J) \underbrace{|\mu_{J+1,J}|^2}_{\text{slow variation w/ } J} \sim N(E_J)$$

Hence, typical microwave absorption spectrum:



typically ~ 10 cm^{-1}

Rotational Raman Spectra: Gross Selection Rule: molecule must possess anisotropic polarizability

Polarizability - degree to which electrons + nuclei in an atom or molecule are distorted by an applied electric field

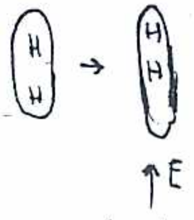
E.g.: Xe

Quite Polarizable

But, for atoms, polarizabilities are isotropic

Similarly for spherical rotors. But, most molecules possess anisotropic polarizabilities [depends on direction of field]

E.g.



highly polarizable

vs.

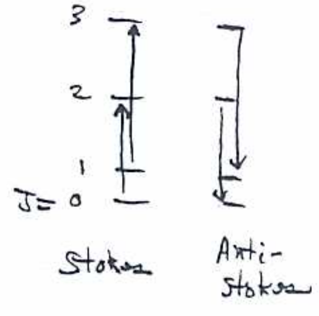
weakly polarizable

Note: <u>All</u> linear molecules have anisotropic polarizabilities [even if permanent dipole moment is zero]

Specific Rotational Raman Selection rule (for linear rotors): $\Delta J = \pm 2$, [0 ← affects only elastic peak]

Thus, Stokes lines $[J \to J+2]$ $\tilde{\nu} - \tilde{\nu}_0 = -B(4J+6)$, $J = 0, 1, 2 \ldots$

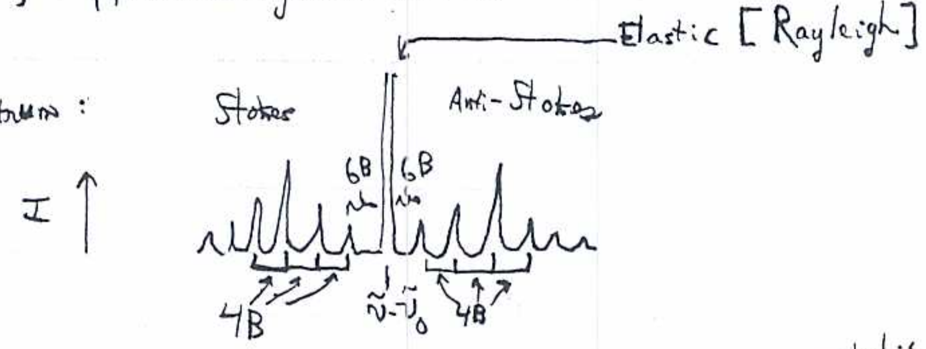
scattered frequency ↑ (on $\tilde{\nu}$); incident frequency ↑ (on $\tilde{\nu}_0$)



Anti-Stokes $[J \to J-2]$ $\tilde{\nu} - \tilde{\nu}_0 = B(4J-2)$, $J = 2, 3, \ldots$

Hence, using $I_{J \to J \pm 2} \cong$ const, and population arguments above ...

Typical Rotational Raman Spectrum :



Vibrations of Diatomic Molecules

Electron → cloud distorts to provide effective restoring force

Vibrational Hamiltonian for Diatomic molec: $\boxed{\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}+V(R)\right]\psi(R)=E\,\psi(R)}$

↑ reduced mass $\mu=\frac{m_1 m_2}{m_1+m_2}$

For small vibrations about the minimum (equilibrium) R_e: $V(R)\cong\frac{1}{2}k(R-R_e)^2 \Rightarrow$

↑ $k=\left.\frac{\partial^2 V}{\partial R^2}\right]_{R=R_e}$

$$\boxed{E_v=\left(v+\tfrac{1}{2}\right)\hbar\omega\ ;\ v=0,1,2,\ldots;\ \omega\equiv\sqrt{k/\mu}}$$

$\psi_v(R)$ = simple harmonic oscillator eigenfunctions centered at R_e

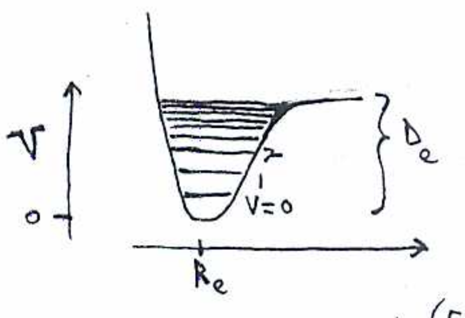
"harmonic" (oscillator) approx.

<u>Anharmonicity</u>: Better representation of $V(R)$ (includes dissociation): Morse potl.,

$$V(R)=D_e\{1-e^{-a(R-R_e)}\}^2$$

↑ well depth

$\omega=\sqrt{2D_e/\mu}\,a$ ← defines vibrational frequency (at) well minimum i.e., $k_{eff}=\mu\omega^2$



(Exact!) Energy levels:

$$\boxed{E_v=\hbar\omega(v+\tfrac{1}{2})-\hbar\omega x_e(v+\tfrac{1}{2})^2}$$

$v=0,1,2,\ldots$; x_e = anharmonicity parameter $=a^2\hbar/2\mu\omega$

Note: Morse well holds finite # of vibrational levels

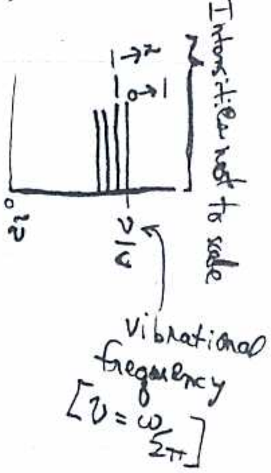
(Infrared)

Vibrational Spectra of Diatomics: Gross Selection Rule - vib. in question must generate [transient] electric dipole moment.

Specific select. rule: $\boxed{\Delta V = \pm 1}$

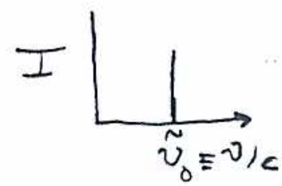
$\Rightarrow$ for h.o. model, $\Delta E = \hbar\omega$ $(V \to V+1)$; for Morse osc. $\Delta E = \hbar\omega - \hbar\omega x_e(2V+2)$

Thus: only 1 absorption line in harmonic approx ; line pattern for anharmonic vibrations

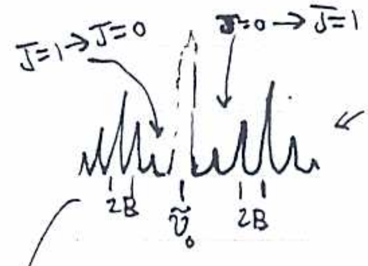


Note: typically vibrational frequencies $\frac{\nu}{c} \sim 1000\ \mathrm{cm}^{-1}$; vs.
room temp $\frac{kT}{hc} \cong 200\ \mathrm{cm}^{-1}$ $\Rightarrow$ only $v=0$ populated
$\Rightarrow$ only see 1 line

(High Resolution) Rotation-Vibration Absorption spectrum



(Low Resolution)



$\tilde{\nu} = \tilde{\nu}_0 + 2B(J+1)$; $J = 0, 1, \ldots$

P Q R Branches

$\tilde{\nu} = \tilde{\nu}_0 - 2BJ$; $J = 1, 2, \ldots$

(High Resolution)

Selection rules: $\Delta J = \pm 1$ $[w/ \Delta v = \pm 1]$; occassionally also $\Delta J = 0$

$\Rightarrow$ P, Q, R branches indicated

Level diagram: