Spectroscopy: Tinoco Chapter 10 (but vibration, Ch.9)

Vibrational Spectroscopy (Typical for IR and Raman)

Born-Oppenheimer separate electron-nuclear motion

\[ \psi (rR) = \chi_\nu (R) \phi_{el} (r,R) \] -- product fct. solves sum \( H \)

electronic Schrödinger Equation

\[ H_{el} \phi_{el} (r,R) = U_{el} (R) \phi_{el} (r,R) \]

eigen value \( \rightarrow \) \( U_{el}(R) \) parametric on \( R \)

potential energy for nuclear motion (see below)

Nuclear Schrödinger Equation

\[ H_n \chi (R) = E \chi (R) \]

\[ H_n = -\frac{\hbar^2}{2M} \nabla^2 \chi + V_n (R) \]

\[ V_n(R) = U_{el}(R) + \sum \beta \chi_\nu Z_{\alpha \beta} e^{2/|R_{\alpha \beta}|} \]

Solving this is 3N dimensional – N atom

Simplify \( \rightarrow \) Remove
(a) Center of Mass (Translate)
(b) Orientation of molecule (Rotate)

Results in (3N – 6) coordinates - called internal coord.

– motion of nuclei wrt each other
a) Translation — like atoms – no impact on spectra since continuous (no potential – plane wave)
b) Rotation — also no potential but have angular momentum

kinetic energy associated with rotation – quantized
- no potential, but angular momentum restricted

1. Diatomics (linear) sol’n \( Y_{JM} (\theta, \phi) \) – same as H-atom

\[ E_{JM} = \frac{\hbar^2 J(J+1)}{2I} \]

\[ I = \sum \alpha M_{\alpha} R_{\alpha}^2 \text{ (diatomic I=} \mu R_{\alpha}^2 \) \]

(spectra \( \Delta J = \pm 1, \ \Delta M_J = 0, \pm 1 \) \( \Delta E_J = (J + 1) \frac{\hbar^2}{I} \) )

2. Polyatomics – add coordinate (\( \omega \)) and quantum number (K) for angular momentum
– previously refer \( J,M_J \) to a lab axis, now complex
(this \( K \) is projection of angular momentum onto molecular axis, so internal orientation of molecule)

Rotational Spectra (aside – little impact on Biology)

Diatomic: \( E_{JM}^{rot} = J(J+1)B_{e} \) \( I = \mu R_{e} \mu = M_{A}M_{B}/M_{A}+M_{B} \)

if \( B_{e} = \hbar/(8\pi^2 I_{c}) \) \( E_{JM} = J(J + 1)B_{e} \) in cm\(^{-1}\)
or \( E_{JM}^{rot} = (hc) J(J + 1)B_{e} \)

Note: levels increase separation as J inc.
Transitions allowed by absorption (far-IR or $\mu$-wave / typical $B_0 < 10 \text{cm}^{-1}$).

Selection rules:
$\Delta J = \pm 1$, $\Delta M = 0, \pm 1$, $\Delta E_{J\rightarrow J+1} = (J+1)2B$ (absorb $\Delta J = +1$)

IR or $\mu$-wave

regularly spaced lines, intensity reflect
rise → degeneracy ($\delta_J$)
fall → exponential depopulation
Boltzmann: $n_J = \delta_J n_0 \exp \left[ - J(J+1)B/kT \right]$

Pure Rotational Far-IR spectrum of CO
-- note 1st transition (23 cm$^{-1}$) is for $J=5 \rightarrow J=6$ (I think)
Raman – light scattering experiment \( v_s = v_0 - v_J \)
\( \Delta J = 0, \pm 1, \pm 2 \) in general but \( \Delta J = \pm 2 \) diatomic (K = 0)
diatomic (linear) spacing \(-4B\)

**Figure 8.9.** Rotational Raman spectrum of \( N_2 \), courtesy of Bryan Broocks, Department of Chemistry, University of Idaho.
Rotational Raman spect. of \( N_2 \)
(left) anti-Stokes: \( \Delta J = -2 \)  (right) Stokes: \( \Delta J = 2 \)
Condensed phase – these motions wash out (bio-case)  
(still happen – no longer free translation or rotation ⇒ phonon and libron in bulk crystal or solution)

**Vibration:** Internal coordinates – solve
— problem $V(R)$ not separable – 3N – 6 coordinates

$$H(R) = - \sum_{\alpha} (\hbar^2/2M_\alpha) v_\alpha^2 + V(R)$$

$V(R)$ has all electrons attract all nuclei, in principle could separate, but all nuclei repel, which is coupled - $R_{\alpha\beta}$

**Harmonic Approximation – Taylor series expansion:**

$$V(R) = V(R_e) + \sum_{\alpha} \frac{\partial V}{\partial R_\alpha} \Big|_{R_e} (R_\alpha - R_e) + \frac{1}{2} \sum_{\alpha} \frac{\partial^2 V}{\partial R_\alpha \partial R_\beta} \Big|_{R_e} (R_\alpha - R_e)(R_\beta - R_e) + ...$$

Expansion in Taylor Series

1\textsuperscript{st} term – constant ⇒ just add to energy
2\textsuperscript{nd} term – zero at minimum
3\textsuperscript{rd} term – 1\textsuperscript{st} non-zero / non-constant term  
harmonic – potential has form of $1/2 kx^2$

**Problem – $R_\alpha$, $R_\beta$ mixed ⇒ $H_n$ not separate**

Solution → New coordinates “Normal coordinates”

$$Q_j = \sum_{i}^{3N} c_{ij} q_i \text{ where } q_i = x_{i\alpha}/(M_\alpha)^{1/2}, y_{i\alpha}/(M_\alpha)^{1/2}, z_{i\alpha}/(M_\alpha)^{1/2}$$

normal coordinates mass weighted Cartesian

analogy – actual problem a little different:

$$H = \sum_{j}^{3N} -\hbar^2/2 \frac{\partial^2}{\partial Q_j^2} + \frac{1}{2} \sum_{j}^{3N} k_{Q_j} Q_j^2 = \sum_{j} \hbar_j (Q_j)$$

See this is summed $H$ → product $\chi = \prod_{j} \chi_j (Q_j)$

summed $E = \sum_{j} E_j$

each one is harmonic oscillator  
(know solution):

$$\hbar_j \chi_j (Q_j) = E_j \chi_j (Q_j)$$

$$H = \sum_{j} \hbar_j(Q_j) \quad E_j = (v_j + 1/2) \hbar_j$$
So for $3N - 6$ dimensions – see regular set $E_j$ levels

$\nu_j = 0, 1, 2, \ldots \infty$ but for each $3N-6$ coordinate $j$

Interpret

go back to diatomic $N = 2$  $3N = 6$
coordinates
remove translation $\rightarrow$ 3 coordinates left
remove rotation (just $\theta, \phi$) $\rightarrow$ 1 coord. vibration bond

model of harmonic oscillator works

$$E = (\nu + 1/2) \hbar \nu = 1/2 \pi \sqrt{\frac{k}{\mu}}$$

$k$ – force constant ,

$$\mu = \frac{M_AM_B}{M_A + M_B}$$

heavier molecules $\rightarrow$ lower frequency

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Frequency cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>$\sim 4000$</td>
</tr>
<tr>
<td>$\text{HCl}$</td>
<td>$\sim 2988$</td>
</tr>
<tr>
<td>$\text{HF}$</td>
<td>$\sim 4141$</td>
</tr>
<tr>
<td>$\text{C–H}$</td>
<td>$\sim 2900$</td>
</tr>
<tr>
<td>$\text{C–D}$</td>
<td>$\sim 2100$</td>
</tr>
<tr>
<td>$\text{F}_2$</td>
<td>892</td>
</tr>
<tr>
<td>$\text{Cl}_2$</td>
<td>564</td>
</tr>
<tr>
<td>I–I</td>
<td>$\sim 214$</td>
</tr>
<tr>
<td>I–Cl</td>
<td>$\sim 384$</td>
</tr>
</tbody>
</table>

stronger bonds $\rightarrow$ higher $k$ - higher frequency

<table>
<thead>
<tr>
<th>Bond</th>
<th>Frequency cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>$\sim 2200$</td>
</tr>
<tr>
<td>C=C</td>
<td>$\sim 1600$</td>
</tr>
<tr>
<td>C–C</td>
<td>$\sim 1000$</td>
</tr>
<tr>
<td>O=O</td>
<td>1555</td>
</tr>
<tr>
<td>N≡O</td>
<td>1876</td>
</tr>
<tr>
<td>N≡N</td>
<td>2358</td>
</tr>
<tr>
<td>C≡O</td>
<td>2169</td>
</tr>
</tbody>
</table>

This is key to structural use of IR $\rightarrow$
frequency depends on mass (atom type)  bond strength (type)

Thus frequencies characteristic of structural elements
Called group frequencies:
Typical frequencies for given functional groups

e.g.

$$\text{C} = \text{O}$$  C–OH  C–X

$$\text{C} = \text{O}$$  C–NH  C–X
\[ \psi_1 = \sqrt{2} \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \]
\[ \psi_2 = \frac{1}{\sqrt{2}} \left( \frac{\alpha}{\pi} \right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2} \]
\[ \psi_3 = \sqrt{3} \left( \frac{\alpha}{\pi} \right)^{1/4} \left( 2a x^2 - \frac{3}{2} \right)e^{-ax^2/2} \]
\[ \psi_4 = \frac{1}{\sqrt{6}} \left( \frac{\alpha}{\pi} \right)^{1/4} (2a x^2 - 6ax^2 + 3)e^{-ax^2/2} \]
\[ \psi_5 = \frac{1}{\sqrt{15}} \left( \frac{\alpha}{\pi} \right)^{1/4} \left( 2a^2 x^2 - 10ax^2 + 15 \right)e^{-ax^2/2} \]
\[ \psi_6 = \left( \frac{1}{2^{1/2}} \right)^{1/4} \frac{\alpha}{\pi} H_{\nu}(\alpha^{1/2} x)e^{-\alpha x^2/2}, \quad \alpha = \mu \omega/k \]

Selection rule: \[ \Delta \nu = \pm 1 \]

Figure 7.3. The harmonic oscillator wavefunctions.
<table>
<thead>
<tr>
<th>IR Absorption (cm⁻¹)</th>
<th>Group</th>
<th>Approximate Frequency (cm⁻¹)</th>
<th>Group</th>
<th>Approximate Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>660</td>
<td>C=O</td>
<td>1100</td>
<td>C=O</td>
<td>1600</td>
</tr>
<tr>
<td>690</td>
<td>C=Cl</td>
<td>1570</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>700</td>
<td>C=Br</td>
<td>1680</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>900</td>
<td>N=N</td>
<td>1780</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>1100</td>
<td>N=N</td>
<td>1890</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>1120</td>
<td>S=O</td>
<td>1920</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>1290</td>
<td>O=O</td>
<td>1980</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>2690</td>
<td>C=O</td>
<td>2000</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>3290</td>
<td>O=O</td>
<td>2040</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>3380</td>
<td>N=H</td>
<td>2090</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
<tr>
<td>3600</td>
<td>H=O</td>
<td>2140</td>
<td>C=Cl</td>
<td>1570</td>
</tr>
</tbody>
</table>

Table 3.4: Characteristic Stretching Frequencies of Some Molecular Groups
Transitions \(\rightarrow\) spectra measure change in energy levels
These are caused by interaction of light & molecule

\[ E \rightarrow \text{electric field} \]
\[ B \rightarrow \text{magnetic field} \]
--in phase and \(\perp\)

\[ E \text{ interacts with charges in molecules} \]
- like radio antenna
if frequency of light = frequency of vibration (correspond to \(\Delta E = h\nu = E_i - E_j\))
then oscillating field drives the transition
\(\rightarrow\) leads to absorption or emission

Probability of induce transition
\[ P_{i\rightarrow j} \sim |\int \psi_i^* \mu \psi_j \ d\tau|^2 \]
where \(\mu\) is electric dipole op.
\[ \mu = \sum \sum \left[(Z_\alpha eR_\alpha + e\mathbf{r}_i]\right] = \sum q_rj \rightarrow \text{sum over all charge} \]

Depends on position operator \(r, R \rightarrow \text{electron \& nuclei}\)

Harmonic oscillator: transform \(\mu = \mu(Q_i)\) (norm. coord.)
\[ \int \chi_\nu^*(Q_i) \mu \chi_\nu(Q_i) dQ_i \neq 0 \quad \text{if} \quad \nu_k = \nu_l \pm 1 \]
in addition: \(\frac{\partial \mu}{\partial Q_j} \neq 0\) i.e. \(\Delta \nu = \pm 1\)

Normal mode must change dipole moment
\(\rightarrow\) to have dipole transition
\(\rightarrow\) occur in IR

Most observations are Absorption: \(\nu = 0 \rightarrow \nu = 1\)
population \(n_j = n_i \ e^{(E_j - E_i)/kT}\) Boltzmann

\[ \text{The rotational energy levels for two different vibrational states of a diatomic molecule.} \]
Allowed transitions
Diatomic: IR: \( \Delta \nu = \pm 1 \quad \Delta J = \pm 1 \) (i.e. also rotate)
\[ \frac{\partial \mu}{\partial R} \neq 0 \Rightarrow \text{hetero atomic} \]
observe profiles – series of narrow lines separate 2B
– spacing yields geometry: \( \text{B}_e \rightarrow \text{I}_e \rightarrow \text{R}_e \)

\[
\Delta \nu = \pm 1 \quad \Delta J = 0, \pm 2 \\
(\frac{\partial \alpha}{\partial R}) \neq 0 \Rightarrow \text{all molec. change polarizability}
\]

\[\text{Figure 9.7.} \] Vibration-rotation Raman spectrum of \( \text{O}_2 \) in air at atmospheric pressure. The initial quantum numbers of the \( O \) and \( S \) branch lines are indicated, \( \varepsilon \) the \( Q \) branch is off scale.
Diatomic - must be hetero so have dipole
Most common
$\nu = 0 \rightarrow \nu = 1$
$\Delta E = h\nu$

if harmonic
$\nu = 1 \rightarrow \nu = 2$
also $\Delta E = h\nu$
if anharmonic.
$\nu = 1 \rightarrow \nu = 2$ lower freq.
$\nu = 2 \rightarrow \nu = 3$ even lower freq.
get series of weaker transition - lower $\nu$
Also - $\Delta n = \pm 1, \pm 2, \pm 3, \ldots$ possible $\rightarrow$ overtones

Polyatomics - same rules: $\Delta \nu = \pm 1$  $\Delta J = \pm 1$
But include $\Delta J = 0$ for non-linear vibrations (molec.)

e.g. $\leftrightarrow O=\bar{C}=\bar{O} \rightarrow O=C=O$

sym. stretch Raman
asym. stretch IR
linear:
$O=C=O$ symmetric (1354)
$\bar{O}=\bar{C}=\bar{O}$ asymmetric (2396)
$O=C=O$ non-linear bend (673)
**Bends normally ~ \( \frac{1}{2} \nu_e \) of stretches**

If 2 coupled modes, then there can be a big difference

eg. \( \text{CO}_2 \) symm: 1354 asym: 2396 bend: 673
\( \text{H}_2\text{O} \) symm: 3825 asym: 3936 bend: 1654

**Selection rules**

**Harmonic**

\( \Delta \nu_i = \pm 1, \quad \Delta \nu_j = 0 \quad i \neq j \)

**Anharmonic**

\( \Delta \nu_i = \pm 2, \pm 3, \ldots \) overtones
\( \Delta \nu_j = \pm 1 \quad \Delta \nu_i = \pm 1 \) combination band

**IR** – \((\partial \mu / \partial Q_i) \neq 0\)

\( \Rightarrow \) must change dipole in norm.coord.

\( \Rightarrow \) dislocate charge

**Raman** – \((\partial \alpha / \partial Q_i) \neq 0\)

\( \Rightarrow \) charge polarizability

\( \Rightarrow \) typical expand electrical charge

**Rotation:**

\( \Delta J = \pm 1 \) (linear vibration) \( \rightarrow \) P & R branches
\( \Delta J = 0, \pm 1 \) bent or bend linear molec. \( \rightarrow \) Q-band

**HCN linear stretch (no Q) HCN bend mode (Q-band)**

**3N – 6**

**Polyatomic** – \( \chi = \prod_{j=1}^{3N-6} \chi_{\nu_0} (Q_j) \)

Due to **orthogonality** – only one \( Q_i \) can change \( \nu_j \)

\( \Delta \nu_j = \pm 1 \quad \Delta \nu_i = 0 \quad i \neq j \quad (\partial \mu / \partial Q_i) \neq 0 \)

Dipole selects out certain modes

Allow \( \rightarrow \) molecules with symmetry often distort to dipole
IR Intensity → most intense if move charge
e.g. O–H >> C–H
    C–O >> C–C , etc.
In bio systems: -COOH, -COO⁻, amide C=O, -PO₂⁻

Raman – light scattering → $\nu_s = \nu_0 - \nu_{vib}$
caused by polarizability $\Delta \nu = \pm 1$
these tend to complement IR $\partial \alpha / \partial Q_j \neq 0$
    – homo nuclear diatomic
    – symmetrical modes
    -- aromatics, -S-S-, large groups -- most intense


Infrared spectra of (a) cyclohexylamine and (b) methylamine. From Biochem., 7, 1286 (1968).

Infrared spectrum of cholesterol as a function of (a) concentration in CCl₄ solution. The sharp band near 3620 cm⁻¹ is assymmetric species while broad bands near 3500 and 3350 cm⁻¹ are assiliated dimers and trimers, respectively. Reproduced from F.S. Parker and M.C. Caserio Basic Principles of Organic Chemistry.

Bio-Applications of Vibrational Spectroscopy

Biggest field – proteins and peptides

a) Secondary structure

Amide modes

\[
\begin{align*}
\text{I} & : & \text{II} & : & \text{III} \\
\text{CN} & : & \text{O} & : & \text{CN} & : & \text{O} & : & \text{CN} & : & \text{O} \\
\text{H} & : & \text{H} & : & \text{H} & : & \text{H} \\
\end{align*}
\]

\begin{align*}
\sim 1650 & : & \sim 1550 & : & \sim 1300 \\
\end{align*}

IR – coupling changes with conform (typ. protein freq.)

\begin{align*}
\text{I} & : & \text{II} \\
\text{helix} & : & \sim 1650^+ & : & 1550 \\
\text{sheet} & : & \sim 1630^* & : & 1530 \\
\text{coil} & : & \sim 1640-50 & : & 1520-60 \\
\end{align*}

Raman - see I, III – III has characteristic mix with $C_\alpha H$

Depends on $\psi$ angle, characterize 2nd struct.

b) Active sites - structurally characterize, selective

i) difference spectra – e.g. flash before / after - kinetic amides – $\text{COO}^- / \text{COOH}$ – functional group

ii) Resonance Raman – intensify modes coupled to chromophore (e.g. heme)

Nucleic Acids – less

a) – monitor ribose conformation

b) – single / duplex / triplex / quad – H-bond

Sugar – little done, spectra broad, some branch appl.

Lipids – monitor order – self assemble - polarization
Peptide Primary and Secondary Structure
Proteins are polymers of amino acids (20 natural)—Peptides more

Pro-Ala-Val-His-Ala-Ser-Leu-Asp-Lys-Phe-Leu-Ala-Ser-
Val-Ser-Thr-Val-Leu

**Primary structure** — sequence of residues (amino acids) in chain—charged, polar, hydrophobic, steric constraints

**Secondary Structure** — stereochemical relation of residues in chain—near neighbor repeat

Helix — side-on

Helix — end-on

Tertiary and Quaternary Structure

**Tertiary** — fold/packing of secondary structure segments in one chain—hydrophobic, S—S, salt bridge, ligand, etc.

**Quaternary** — interaction of subunits or separate components (not covalently bound)

Mb

Hb

[4 subunits]
Amino Acids

Side chains determine secondary structure

Major contribution—IR - charged

Raman - aromatic (Tyr, Trp), S-S, S-H, chromophores: heme, retinal, etc.

Characteristic Amide Vibrations

A - often obscured by solvent

I - Most useful;
IR intense, less interference (by solvent, other modes, etc)
Less mix (with other modes)
Also Raman

II - IR intense
Not Raman, unless RR

III - Raman Intense
Weak IR Multiple bands

IV - VII - difficult to detect, discriminate
IR absorbance and Raman spectra of selected model polypeptides

<table>
<thead>
<tr>
<th>H₂O solution</th>
<th>D₂O solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LKKL)ₙ helix</td>
<td>(LK)ₙ sheet</td>
</tr>
<tr>
<td>polyK Coil (3₁)</td>
<td></td>
</tr>
<tr>
<td>L=Leu</td>
<td>K=Lys</td>
</tr>
</tbody>
</table>

Wavenumbers (cm⁻¹)

Raman spectra of poly-L-lysine in three different conformations

Note: β-sheet amide I, opposite band is intense (high ν)
Amide III large frequency shift, mixing with CαH
Example Protein/H$_2$O IR spectra:

High $\alpha$-helix, 'no' $\beta$-sheet
- Myoglobin
- Hemoglobin
- Cytocrome C
- Citrate Synthase

'No' $\alpha$-helix, high $\beta$-sheet
- Coonanavlin-A
- Lectin
- Superoxide Dismutase

Fourier Self deconvolved Amide I – Ribonuclease S
Band fit result to Lorentzian shapes, assign, analyze

More sheet than helix, helix probably 2 types, turns not quantitative

(Protein/H$_2$O IR spectra examples (full page))
DNA Base IR

Differentiation of Cytidine (a,b) and methyl derivatives with FTIR

FTIR spectroscopy of Nucleic Acids

I: in-plane base double-bond vibrations - sensitive to base pairing
II: base-sugar bending motions, sensitive to variation in glycosidic torsion angle
III: phosphate group vibrations
IV: phosphate-sugar backbone vibrations, sensitive to sugar puckering
Optical Spectroscopy - Processes Monitored
UV/ Fluorescence/ IR/ Raman/ Circular Dichroism

**Diatomic Model**

**Excited State (distorted geometry)**

**Ground State (equil. geom.)**

**Absorption**

\[ h\nu = E_{\text{grd}} - E_{\text{ex}} \]

**Fluorescence**

\[ h\nu = E_{\text{ex}} - E_{\text{grd}} \]

**Raman**

\[ \Delta E = h\nu_0 - h\nu_s = h\nu_{\text{vib}} \]

**Infrared**

\[ \Delta E = h\nu_{\text{vib}} \]

**Analytical Methods**

**UV** vs absorb. & Fluorescence. move e\(^{-}\) (change electronic state) high freq., intense

**CD** – circ. polarized absorption, UV or IR

**Raman** – nuclei, inelastic scatter very low intensity

**IR** – move nuclei low freq. & inten.
Discussed Diatomic Vibrations at length

Polyatomics

a) expand

\[ V(q) = V(q_0) + \sum_i \frac{\partial V}{\partial q_i} q_i + \sum_{i,j} \frac{\partial^2 V}{\partial q_i q_j} q_i q_j \]

b) diagonalize

\[ V(q) \rightarrow V(Q) \]

\[ Q_i = \sum_{i,j} c_{ij} q_j \]

linear combination x y z on each atom; \( \alpha, \beta \ldots \)

Normal coordinates

6 – Transitions, rotation → no potential \( E \)

→ eigen value “0” {diagonalize potential}

(3N – 6) – vibrations → internal nuclear motion

examples: Triatomics

\[ \rightarrow O = C = O \rightarrow \]

linear symmetric (1354)

\[ \bar{O} = \bar{C} = \bar{O} \rightarrow \]

asymmetric (2396)

\[ \rightarrow O = C = O \downarrow \]

\[ O = \bar{C} = \bar{O} \uparrow \]

bend (673)

\[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{O} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{H} \\
\text{O} \\
\text{H} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{H} \\
\text{O} \\
\text{H} \\
\text{H}
\end{array} \]

\[ 3825 \quad 3936 \quad 1654 \]
Fig. 3.6: Some transitions between the rotational-vibrational energy levels of a diatomic molecule together with the spectrum arising from them.

Fig. 3.6(a): The fundamental absorption (centred at about 2145 cm\(^{-1}\)) and the first overtone (centred at about 4290 cm\(^{-1}\)) of carbon monoxide. The structure of the P branch in the fundamental is partially resolved. (Gas pressure 850 mm Hg in a 10 cm cell.)

Fig. 3.6(b): The centre of the fundamental band of carbon monoxide under higher resolution than in (a). (Gas pressure 100 mm Hg in a 10 cm cell.) The lines are labelled according to the \( J' \) values. The P branch is complicated by the presence of a band centred at about 2100 cm\(^{-1}\) due to the 1\% of \(^{13}\)CO in the sample. Some of the rotational lines from this band appear between P branch lines, others are overlapped by a P branch line and give it an enhanced intensity. P \( \rightarrow \) D.
Fig. 3.12: The rotational energy levels for two vibrational states showing the effect on the spectrum of transitions for which $\Delta J=0$.

Fig. 3.12: Spectrum of the symmetric stretching vibration of the HCN molecule showing the P and R branch lines.

Fig. 3.14: Spectrum of the bending mode of the HCN molecule showing the PQR structure. The broad absorption centred at 800 cm$^{-1}$ is due to unpairing.