Spectroscopy in Inorganic Chemistry

Vibration and Rotation Spectroscopy
Symmetry requirement for coupling combination bands and Fermi resonance
$\nu_3$  1505 cm$^{-1}$  (R, IR)   E'   stretches
$\nu_1$  888 cm$^{-1}$  (R)   A$_1'$   stretch
$\nu_2$  718 cm$^{-1}$  (IR)   A$_2''$  bend
482 cm$^{-1}$  (R, IR)   E'   bends
<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( \text{cm}^{-1} )</th>
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<th>( \text{V} )</th>
<th>( E' )</th>
<th>( \text{stretches} )</th>
<th>( \nu_1 + \nu_3 = A_1' \times E' = E' ) (IR)</th>
<th>( 2 \nu_2 = A_2'' \times A_2'' = A_1' ) (R)</th>
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### Vibration and Rotation Spectroscopy

#### Fermi Resonance

\[ V_1 = A_1' \quad (R) \]

**Fermi resonance**

\[ 2 V'_2 = A_2'' \times A_2'' = A_1' \quad (R) \]

#### Vibrational Frequencies

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<tr>
<th>( \nu )</th>
<th>Frequency</th>
<th>Symmetry</th>
<th>Description</th>
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93/02/10 Ferdowsi University of Mashhad
E' stretch

A1' stretch

E' bend

ν₃

ν₁

ν₂

ν₄

E' bend

A₂'' bend
v1 symmetric stretch

v2 out of plane bend

v3 asymmetric stretch

v4 asymmetric bend
Vibrational coupling

- Acetylene

C-C   C-H

C-H  3287 cm\(^{-1}\)   C-D  2427 cm\(^{-1}\)
### Fundamental vibrational modes of C2HD

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<th>Mode</th>
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<td>(v_1)</td>
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### Fundamental vibrational modes of acetylene

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Microwave spectroscopy
Microwave spectroscopy

- Rotational spectroscopy
- Far IR & microwave
- Resolution: microwave $10^{-8}$ cm$^{-1}$ (fingerprint) IR 1 cm$^{-1}$
Microwave spectroscopy

- Fine and hyperfine structures (splittings due to large amplitude motions, quadrupole coupling, spin-spin or spin-rotation interaction)
- Internal motion
- Torisional barrier frequency and energy
- Exact Dipole moment determination
- Low frequency vibrational modes ($C_3$, PAH’s)
- Intervibrational transitions: $C_2H_4$
• Low pressure gas phase experiments: 10 mTorr
• Polar molecules (ground state)
Microwave-generator

Attenuator

Pump and gas inlet

Absorption cell

Detector

Sawtooth-generator

Amplifier

Oscilloscope
Diatomic Molecules

moment of inertia

\[ I_e = \mu r_e^2 \]

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

rigid rotor model

\[ E(J) = B_e J(J+1) \]

\[ B_e = \frac{\hbar}{8\pi^2 c I_e} \]

rotational constant

\[ E = \hbar BJ(J+1) \]

\[ B = \frac{\hbar^2}{2I} \]

nonrigid rotor model

\[ E(J)(cm^{-1}) = B_e J(J+1) - D_e J^2 (J+1)^2 \]
Diatomic Molecules

Using the selection rule $\Delta J = \pm 1$

$$E_R = (2B_e - 4D_e) + (2B_e - 12D_e)J'' - 4D_eJ'^3$$

$$\Delta E = B_e [J'(J' + 1) - J''(J'' + 1)] - D_e [J'^2(J' + 1)^2 - J''^2(J' + 1)^2]$$

nonrigid rotor model

$$E(J)(cm^{-1}) = B_e J(J + 1) - D_e J^2(J + 1)^2$$

the initial rotational energy state

the initial rotational energy state
$E = \hbar BJ(J + 1)$

$J \text{ to } J + 1$

$\Delta E = 2B\hbar(J + 1)$

$E = \hbar \nu$.

$\Delta \nu = 2B(J + 1)$

$B = \frac{\hbar^2}{2I}$
• Selection rules:
dipole moment
$\Delta J = \pm 1$

\[ \Delta v = 2B(J + 1); \]

$J=0$ to $j=1$

\[ \Delta v = 2B = \frac{2\hbar}{8\pi^2 I} \]

$I$: calculated
rigid rotor model

nonrigid rotor model
**Stark effect**

In the presence of a static external electric field the $2J+1$ degeneracy of each rotational state is partly removed. The Stark effect is the shifting and splitting of spectral lines of atoms and molecules due to presence of an external electric field.
• **Zeeman effect**

  splitting a spectral line into several components in the presence of a static magnetic field.
Rotational Raman spectra

- Molecules with anisotropic polarizability show pure rotational Raman spectra
  \[ \text{CH}_4 \quad \text{CH}_3\text{Cl} \]
- The selection rule for rotational Raman Spectra is \( \Delta J = \pm 2 \)
  \[ \Delta E = B\hbar(4J' - 2) \]
- the lines which are at frequencies less than that of exciting line with \( \Delta J = + 2 \) are called as **Stokes** lines
- the lines which are at frequencies higher than that of exciting line with \( \Delta J = - 2 \) are called as **anti-Stokes** lines.
The separation between the Stokes lines becomes:

\[
\Delta \tilde{\nu}_{J,J \pm 2} = \tilde{\nu}_{i} - \tilde{\nu}_i - B(2J + 3) = \tilde{\nu}_i + B(2(J \pm 2) + 3) = -2BJ - 3B + 2BJ + 4B + 3B = 4B
\]
- $O_2$

Rotational Raman scattering $O_2$ in gas cell

$\lambda_{\text{laser}} = 5145 \, \text{Å}$, shows on SPEX at $5148 \, \text{Å}$

2 sec. integration time, slits set to 200 $\mu$m

(values for $j$ are initial values for Stokes, and final values for anti-Stokes)

- 4th Stokes line ($j = 7$ to $j = 9$)
- 4th anti-Stokes line ($j = 9$ to $j = 7$)
Application of IR and Raman spectroscopy

**IR**

- **FTIR:**
  - Fast scanning process
  - Measuring all of the infrared frequencies *simultaneously*
  - Employed a very simple optical device called an *interferometer*
  - Low cost
  - Without filter
  - Mechanical Simplicity
  - Sensitivity
Vibration and Rotation Spectroscopy

\[ r_1 = r_2^{\text{ave}} \]
\[ \Delta r = 0 \]

\[ r_2 = r_2^{\text{ave}} + \frac{\lambda}{4} \]
\[ r_2^{\text{ave}} + \frac{\lambda}{2} \]

180 out of phase

Constant velocity

But frequency of signal at detector is

\[ f = 2Vm \cdot \frac{\nu}{C} \]

\[ \lambda = \frac{C}{\nu} \]

T : as the time required for mirror to move distance of \( \frac{\lambda}{2} \)

f: Interference frequency

\[ Vm \cdot T = \lambda / 2 \]

\[ S_0 \cdot T = \lambda / 2 Vm \]
Michelson Interferometer

Diagram showing the components of a Michelson Interferometer:
- Movable mirror
- Beam splitter
- Stationary mirror
- Incident radiation
- In phase radiation directed towards detector
Interferograms ➔ FFT Calculations ➔ Spectrum

Polystyrene run as film

Wavenumbers (cm⁻¹):

%T
Vibration and Rotation Spectroscopy

Polystyrene measured as a film
Mon May 12 09:13:08 1997
Detector: DTGS KBr
Beamsplitter: KBr
Source: IR

Data points

Wavenumbers (cm⁻¹)
- Absorbance IR
- Transmission IR
- Reflectance IR: specular reflectance, diffuse reflectance
- IR-External reflection spectroscopy
- Photoacoustic Fourier transform infrared spectroscopy (PAS)
Absorbance IR

range of IR frequencies

5.15 x 10^{13} \text{ Hz} \rightarrow \text{sample}

5.15 \times 10^{13} \text{ Hz light is absorbed by sample}

detector
Transmission IR can be used\textsuperscript{(20)} to study surfaces of solids that have transparent windows in the infrared, \textit{e.g.,} oxides of silica and alumina. High surface area materials should be used so that the spectra have an appreciable contribution from the surface as opposed to the bulk. These samples can be pressed into discs and inserted into the beam path.

Transmission IR spectrometers (21) are designed to accommodate these discs.
Reflectance IR:
specular reflectance  diffuse reflectance

- **diffuse reflectance**
  Solids and powders, diluted in a IR transparent matrix if needed
  Information provided is from the **bulk matrix**.

- **specular reflectance**
  Sample must be reflective or on a reflective surface
  Information provided is from the **thin layers**
IR-External reflection spectroscopy
Photoacoustic Fourier transform infrared spectroscopy (PAS)

surface molecules

carbon black saturated reference
reduced signal amplitude and delayed in phase
Gaseous samples usually exhibit rotational fine structure.

In liquid and solid the collision cause to elimination of fine structure. (collision occur before rotation)

IR, near IR, UV, Vis

Lattice vibrations in solids. **phonon modes**

translational and torsional motions of the molecules in the lattice.

**molecular symmetry**

**calcite** \(D_3\)

**CaCO_3** \(CS\)

**aragonite** \(D_{3h}\)

**CO_3^{2-} ion**
CaCO$_3$  

- **calcite**  
  - $D_3$

- **aragonite**  
  - $C_s$

- **CO$_3^{2-}$ ion**  
  - $D_{3h}$

\[ \begin{array}{cccc}
  & v_1 & v_2 & v_3 & v_4 \\
  D_{3h} & A_1'(R) & A_2''(IR) & E'(IR, R) & E'(IR, R) \\
  D_3 & A_1(R) & A_2(IR) & E(IR, R) & E(IR, R) \\
  C_s & A'(IR, R) & A''(IR, R) & A'(IR, R) + A'(IR, R) & A'(IR, R) + A'(IR, R) \\
\end{array} \]
Matrix isolation experiments combined with infrared and Raman studies have led to interesting developments. Unstable compounds, radicals, and intermediates are trapped in an inert or reactive solid matrix by co-condensing the matrix (e.g., argon) and the species to be studied at low temperatures (often 4.2 to 20 K). Uranium, platinum, and palladium carbonyls have been prepared\(^{(29a,b)}\) by allowing controlled diffusion of CO into an argon matrix of the metal. The compounds LiO\(_2\), NaO\(_2\), KO\(_2\), RbO\(_2\), and LiN\(_2\) have also been made\(^{(29c)}\) and investigated by infrared. The findings are consistent with C\(_{2v}\) symmetry. Several interesting species containing bound O\(_2\), CO, and N\(_2\) have been made.\(^{(29d)}\)