Spectroscopy and Characterisation
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Resources

Web
- copies course notes
- download slides
- model answers
- links to good web-sites

Reading

Recommended Texts
- PW Atkins and RS Friedman, Molecular Quantum Mechanics, Oxford University Press, Oxford

Secondary Text

Elective reading
- background material that supports lectures
- specialist material that explains difficult concepts in more detail
- if you are interested in a wider perspective

Molecular Spectra

light -> molecule -> spectra
light incident on a sample interacts with molecules
various spectra are obtained which contain information about the molecules

Key relationship
wavelength / wavenumber
\( f = \frac{c}{\lambda} \) (frequency) \( \nu = \frac{1}{\lambda} \) (wavenumber)
\( \Delta E = \frac{hc}{\lambda} = hf = hc \nu \)
Molecular Spectra

light -> molecule -> spectra
light incident on a sample interacts with molecules
various spectra are obtained which contain information about the molecules

Key relationship
Incident light is:

absorbed (rotational and vibrational spectra and UV-vis spectra)
transmitted (objects colour)
reflected (reflectance spectra)
scattered (Raman spectra)
Molecular Spectra

light -> molecule -> spectra
light incident on a sample interacts with molecules
various spectra are obtained which contain information about the molecules

Key relationship
Incident light is:
absorbed (rotational and vibrational spectra and UV-vis spectra)
transmitted (objects colour)
reflected (reflectance spectra)
scattered (Raman spectra)
emitted later (fluorescence spectra)
eject an electron (photo-electron spectra)

ν(cm⁻¹) E(kJ mol⁻¹)
rotational levels (microwave) ν=10 cm⁻¹ E=0.1 kJ mol⁻¹
vibrational levels (IR) ν=1000 cm⁻¹ E=1 kJ mol⁻¹
electronic levels (UV-vis) ν=10,000 cm⁻¹ E=100 kJ mol⁻¹

This Course

study light interacting with molecules
vibrational and electronic spectroscopy
certain relationships must hold: Selection Rules
these are determined by symmetry!

symmetry is important more generally
chemistry, physics, mathematics
very important in Quantum Mechanics
matrix representation of symmetry operators
perturbation theory

symmetry is important in determining
vibrations of a molecule
selection rules for vibrational spectroscopy (IR and Raman)
nature of the “state” of a molecule
electronic spectrum of a molecule
electronic spectroscopy (colour and UV-vis)

Example

produced Pd(NH₃)₂Cl₂ but which isomer is present cis or trans?
look at the IR spectrum
Pd-Cl stretching mode <350 cm⁻¹
cis-isomer Cᵥ symmetry and will have 2-modes
trans-isomer D₂h symmetry and will have 1-mode

IR Raman
trans D₂h bₐ₁, a₂g a₂g

cis Cᵥ a₁g, b₁g a₂g, b₂g

Fig 3

Orbitals:

**determine symmetry**

under a symmetry operation

orbital maps onto itself $\Rightarrow +1$

or if inverted $\Rightarrow -1$

then compare to the character table to determine symmetry label

hence this orbital $b_1$
Binary Functions

Use the same process for the translation and rotation of the whole molecule.

Important!

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2&lt;/sub&gt;</th>
<th>E</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;</th>
<th>σ&lt;sub&gt;v&lt;/sub&gt;(xz)</th>
<th>σ&lt;sub&gt;v&lt;/sub&gt;(yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>σ&lt;sub&gt;v&lt;/sub&gt;(xz)</td>
<td>σ&lt;sub&gt;v&lt;/sub&gt;(yz)</td>
<td></td>
</tr>
<tr>
<td>d&lt;sub&gt;yz&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ \Gamma \{ d_{yz} \} \rightarrow b \mathbf{B}_2 \]

Symmetry Operators

- **symmetry operations**
- **symmetry elements**
- **symmetry operator**

Mathematical representation of the action (physical operation) operator “acts on” something (hence the brackets)

- molecule
- wavefunction
- banana
- vibration!

Allows us to write an equation for the symmetry operation

\[ \text{operator } C_2 \text{ acts on wavefunction} \]

\[ \text{operator } C_2 \text{ acts on molecule} \]

Matrix Representation

- **we can represent a symmetry operator as a matrix**
- **notation D(R)**
- D stands for Darstellung = representation in German
- R stands for the operator

- **determine D(R) by examining the effect of an operation on the quantity under consideration (the basis)**

- **you have already met several matrix representations of symmetry operators!**

- **go through a number of examples now**

**Point Groups**

- **C<sub>2</sub>, C<sub>4</sub>, C<sub>6</sub>, D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub>, D<sub>6</sub>**

**Quantised**

8 takes on specific values depending on the type of axis

- \( \theta = 0^\circ \) and \( 180^\circ \) for the \( C_2 \)
- \( \theta = 0^\circ, 120^\circ, 240^\circ \) for the \( C_3 \)
- \( \theta = 0^\circ, 90^\circ, 180^\circ, 270^\circ \) for the \( C_4 \)

**C<sub>2</sub>(z) operation:**

\[
D(C_2(z)) = \begin{pmatrix}
\cos(\pi) & -\sin(\pi) & 0 & -1 & 0 & 0 \\
\sin(\pi) & \cos(\pi) & 0 & 0 & -1 & 0 \\
0 & 0 & 1 & 0 & 0 & 1
\end{pmatrix}
\]

\[ \text{Quantised!} \]
Matrix Representation

- Under $C_2$, the $z$ vector is unchanged, and the $x$ and $y$ vectors are rotated and become negative.

$$R(x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & -\sin(\theta) \\ 0 & \sin(\theta) & \cos(\theta) \end{pmatrix}$$

$$R(y) = \begin{pmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{pmatrix}$$

$$R(z) = \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In Class Activity

- Determine the matrix representation for $\sigma_{yz}$.

$$\sigma_{yz}(x') = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$D(\sigma_{yz})$$

$$\sigma_{yz}(y') = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$D(\sigma_{yz})$$

Important!

- Work out what happens to unit vectors placed on the center of an atom.

$$\sigma_{yz}(z') = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$D(\sigma_{yz})$$

$$\sigma_{yz}(z') = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$D(\sigma_{yz})$$
In Class Activity

determine the matrix representation for \( \sigma_v(yz) \)

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
D(\sigma_v(yz))
\]

Matrix Representation

each symmetry operation can be represented by a matrix

VERY powerful technique
allows us to use matrix algebra and matrix mechanics on symmetry operators

Werner Heisenberg developed matrix mechanics
as well as the Heisenberg uncertainty principle
Nobel prize in physics in 1932 when he was 31
“for the creation of quantum mechanics”

Matrix Representation

reformulate Schrödinger’s equation in a matrix notation

MUCH more powerful form of the equation

Paul Dirac
noticed connections between Heisenberg’s matrices and Schrödinger’s wave mechanics
also introduced bra-ket notation and the delta function
shared the Nobel Prize in physics with Schrödinger in 1933 for “the discovery of new productive forms of atomic theory”

Important!
symmetry and Schrödinger equation now on equal footing: both in matrix formulation

The Basis

previous basis: AOs/MOs or Cartesian vectors

other basis sets are possible, determine the matrix:

work out what happens to the basis item under each symmetry operation

a range of examples using D\(_3\) components of D\(_{3h}\) point group for BH\(_3\)
the Boron atomic orbitals s and p
individual H atoms
single bonding MO

Important!
comparing the $D(R)$ of $D_3$ components of $D_{3h}$ point group

extra notes on the web-site if you cannot see how these matrices are generated

<table>
<thead>
<tr>
<th>$D_3$</th>
<th>$E$</th>
<th>$C_3(z)$</th>
<th>$C_3^{-1}(z)$</th>
<th>$C_2(a)$</th>
<th>$C_2(b)$</th>
<th>$C_2(c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_i(s)$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B(p_x)$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B(p_x,p_y)$</td>
<td>(1 0)</td>
<td>(1 0)</td>
<td>(0 -1)</td>
<td>(0 -1)</td>
<td>(0 1)</td>
<td>(1 0)</td>
</tr>
<tr>
<td>$(H_x,H_y,H_z)$</td>
<td>(1 0)</td>
<td>(0 1)</td>
<td>(0 0 1)</td>
<td>(1 0 0)</td>
<td>(0 0 1)</td>
<td>(1 0 0)</td>
</tr>
<tr>
<td>$(s_z+s_y+s_x)$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Combining Symmetry Operations

element: $C_2(z)\sigma_v(xz)\{H_2O\} = \sigma_v(yz)\{H_2O\}$

show using diagrams

for the RHS:
Combining Symmetry Operations

**Example:**

\[ C_2(z) \sigma_v(xz) \{H_2O\} = \sigma_v(yz) \{H_2O\} \]

Show using diagrams:

- For the LHS: operate FIRST with \( \sigma_v \) THEN \( C_2 \)
- For operators always work from the “inside out” not all operators commute
- You cannot change the order

![Diagram](image1)

**Important!**

Final structures are the same

\[ \text{RHS} = \text{LHS} \]

Using Matrices

**Example:**

\[ C_2(z) \sigma_v(xz) \{H_2O\} = \sigma_v(yz) \{H_2O\} \]

Show using diagrams:

- For the LHS:

\[
\begin{pmatrix}
 x' \\
y' \\
z'
\end{pmatrix} =
\begin{pmatrix}
 -1 & 0 & 0 \\
 0 & -1 & 0 \\
 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
 x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
 y \\
z \\
x
\end{pmatrix}
\]

\[ D(C_2) \]

\[ D(\sigma_v(xz)) \]

- For the RHS:

\[
\begin{pmatrix}
 x' \\
y' \\
z'
\end{pmatrix} =
\begin{pmatrix}
 -1 & 0 & 0 \\
 0 & 1 & 0 \\
 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
 x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
 -y \\
z \\
y
\end{pmatrix}
\]

\[ D(\sigma_v(yz)) \]

Final vectors are the same!
Combining Symmetry Operations

The final vectors are the same

\[ C_2(z)\sigma_v(xz)\{H_2O\} = \sigma_v(yz)\{H_2O\} \]

Using matrix multiplication:

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
= \begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

algebra on operations parallels algebra on matrices!

Important!

In Class Activity:

Show using diagrams and then matrices

\[ C_2(z)\sigma_v(yz)\{H_2O\} = \sigma_v(xz)\{H_2O\} \]

Key Points

- Be able to list the processes light incident on a sample undergoes and identify the related spectroscopic techniques
- Be able to draw a schematic representation of the energy levels associated with various transitions, and identify the relevant wavelengths of light
- Be able to define the components of a character table
- Be able to draw clear diagrams showing symmetry operations
- Be able to generate the matrix representation of a symmetry operator for a given basis
- Be able to discuss how matrix representations change for different basis’
- Be able to use diagrams and matrix mechanics to form symmetry operation and symmetry matrix products
- Be able to discuss the important relationship between physical operations and mathematical operators
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