Symmetry and Spectroscopy

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Rm 405 Laby

Resources

Web Resources:

- information on my web-site under "Teaching"

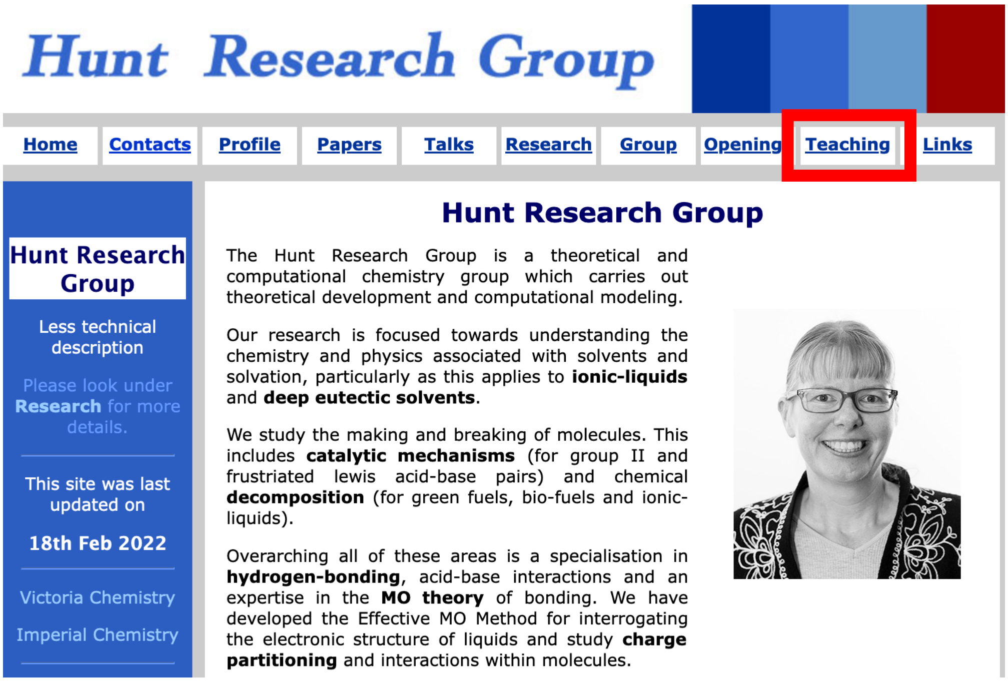


Figure 1 Image from my web-page

Reading Resources:

- Kieran C. Molloy, Group Theory for Chemists, Second edition, Woodhead Publishing, 2011, Cambridge
  - first edition is fine as well and is available electronically via the library
  - https://www.sciencedirect.com/book/9780857092403/group-theory-for-chemists
- PW Atkins and RS Friedman, Molecular Quantum Mechanics, Oxford University Press, Oxford
  - 4th or 5th edition are fine, both books are available in the Library

Additional reading is IMPORTANT

- Other books and optional reading is indicated over the duration of the course
- Some of the additional material is background reading it will support the lectures, and some is to help those having problems with a particular section.
- Some elective reading is advisable. However do not attempt to read everything I suggest, but pick and choose!

Introduction

Molecular Spectra

- light incident on a sample can interact with the molecules within the sample, interrogating the spectra derived from this interaction provides information about the molecules.
- The key relationship is $hc/\lambda = E_a - E_b$ where λ=wavelength of the incident light (c is the speed of light and h is Planks constant), $E_{a/b}$ are quantised energy levels of the molecule
  - frequency is $f = c/\lambda$ (units s^{-1})
  - wavenumber is $\nu = 1/\lambda$ in units cm^{-1} (ie not an SI unit)
- light incident on the molecule is
  - absorbed and emitted immediately (rotational and vibrational spectra (IR) and UV-vis spectra)
  - transmitted (defining an objects colour)
  - reflected (reflectance spectra)
  - scattered (Raman spectra)
  - light can also be emitted some time later (fluorescence spectra)
  - valence or core electrons can be ejected (photoelectron spectra)
- energy quantisation within a molecule has a very large range which cannot be spanned by a single source or detector. Each type of interaction will occur over a very specific energy range.

transition	region	$\approx\lambda$ (nm)	$\approx\nu$ (cm^{-1})	$\approx E$ ($kJmol^{-1}$)
pure rotational	microwave	$1\text{-}10*10^7$	1-10	0.01-0.1
ro-vibrational	infrared (IR)	$0.3\text{-}5*10^4$	**200-3500**	2-42
electronic	UV-vis	**300-700**	$1.4\text{-}3*10^4$	170-400

Table 1 Energy units and ranges for the various transitions

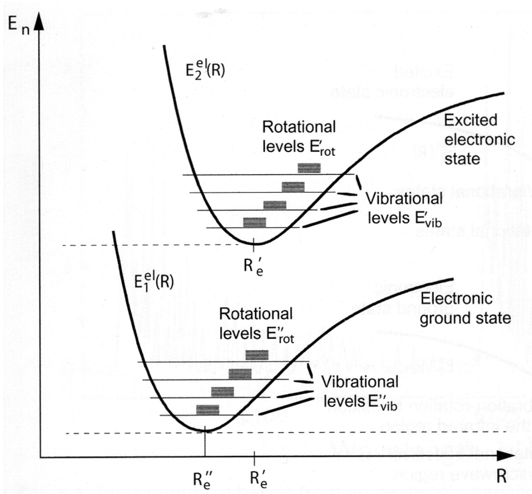


Figure 2 schematic representation of energy level quantisation in a diatomic molecule

- in this short course we will consider only vibrational spectroscopies, however many of the basic principles are transferable to other types of spectroscopy
  - when light interacts with a molecule certain relationships, determined by symmetry (selection rules), must hold before a transition is allowed.
  - symmetry is a very important tool used in mathematics, chemistry and physics. Symmetry it a key component of quantum mechanics.

  - symmetry is used in solving the equations that allow us to compute the vibrational spectrum of a molecule, or to predict the electronic spectrum of a molecule (computational chemistry)
  - symmetry is used to label vibrations, to determine the ground and excited states of molecules, and to predict which transitions are possible.
- we also look at the "bench top" employment of symmetry in the interpretation and prediction of spectra.
  - once something is known about the symmetry of a molecule, spectral features can be predicted (without resorting to extensive computations).
  - from the spectrum of an unknown compound, the symmetry and thus some of the structural features can be determined.
  - for example we may have the experimental spectrum of $Pd(NH_3)_2Cl_2$ and wish to identify which isomer is present. Using symmetry we know the trans isomer (which has D_{2h} symmetry) will exhibit a single Pd-Cl stretching vibration ν(Pd-Cl) around 350 cm^{-1} while the cis isomer (which has C_{2v} symmetry) will exhibit two stretching modes, **Table 2** and **Figure 3**.

	M-X vibrations	
	IR	Raman
trans-isomer D_{2h}	b_{3u}	a_g
cis-isomer C_{2v}	a_1, b_2	a_1, b_2

Table 2 Active M-X stretching modes for ML_2X_2 complexes

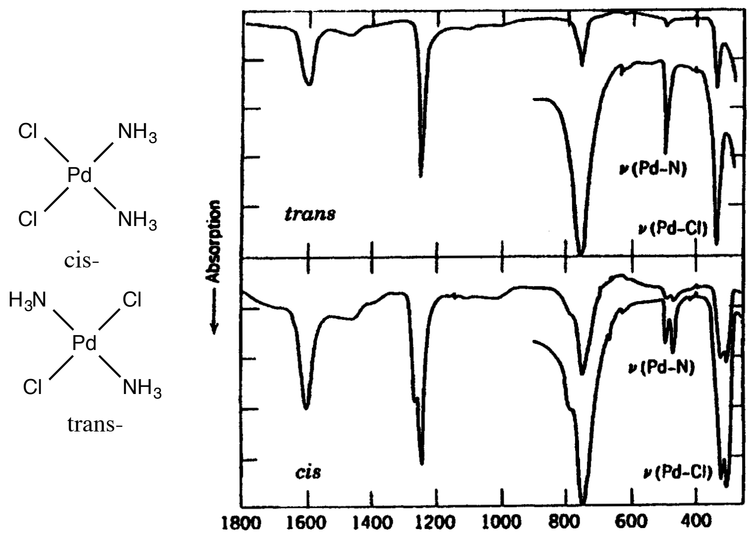


Figure 3 IR spectra of cis and trans $Pd(NH_3)_2Cl_2$.[1]

- we will explore the mathematical and physical foundations of the selection "rules"
  - for example the dipole moment must change before an IR vibration is allowed, and the polarizability must change before Raman scattering is allowed

[1] From Nakamoto Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Edition (1997), John Wiley & Sons, New York, Part B, p10 Fig III-5.

Matrix Representation of Symmetry Operators

Symmetry Operations, Elements and Operators

- **symmetry operations** involve the "physical act" of moving a molecule
  - leave the initial and final states of the molecule *indistinguishable*.
  - only if we label the H atoms in **Figure 4**, do we see that H_a and H_b are exchanged under a C_2 rotation.

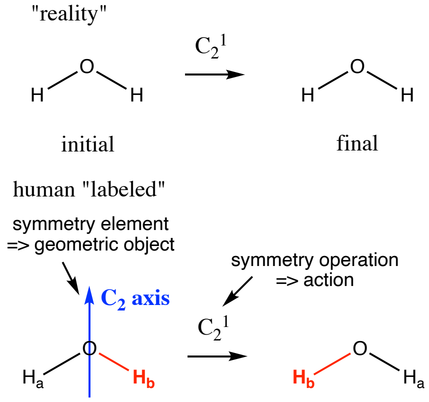


Figure 4 Symmetry operations vs elements

- each symmetry operation has an associated **symmetry element**, symmetry elements are the geometric object about which the operation is executed, thus they are: the axis, the plane, the point, **Figure 5**
  - n-fold rotation (C_n) rotation of $(360/n)^o$ around an n-fold rotation axis
  - reflection in a mirror plane, σ_v, σ_d or σ_h
  - inversion (i) takes a point at (x, y, z) to (-x,-y,-z) through the inversion point (i)
  - improper rotation (S_n) a rotation around an n-fold improper rotation axis (S_n)) followed by reflection in a plane (σ_h) perpendicular to the rotation axis.

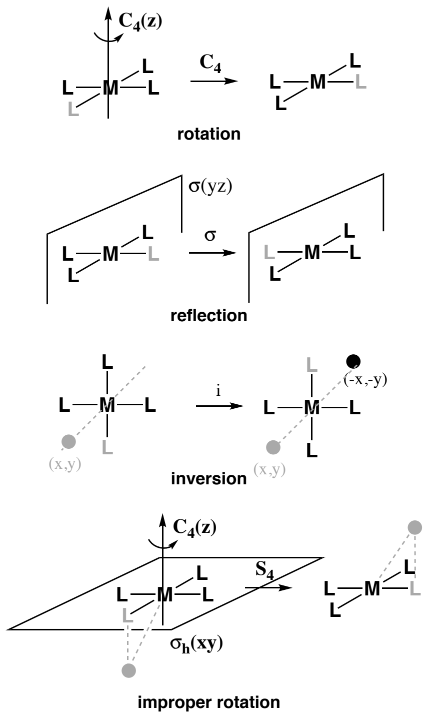


Figure 5 Examples of different symmetry elements

- each symmetry operation also has an associated mathematical operator the **symmetry operator**, which represents the physical act
  - for example the C_2 operator represents the physical action of carrying out a 180° rotation
  - the operator allows us to write a mathematical equation for the action of the operation on a wavefunction or molecule, **Figure 6**
  - here the square brackets or parentheses are used to represent "action on"
    - this can be anything, molecule, atom, wavefunction, a banana or a vibration

$$C_2[\psi(H_2O)]=\psi'(H_2O)$$

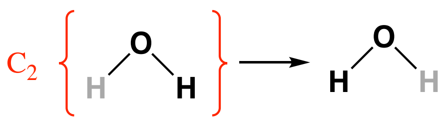
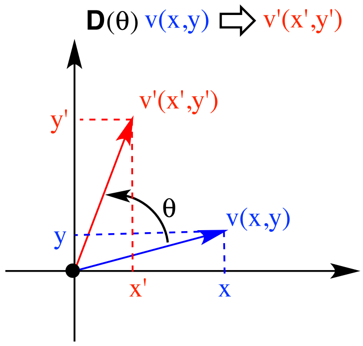


Figure 6 An operator acts on a wavefunction or a molecule

The Matrix Representation of Symmetry Operators

- symmetry operations can be represented by a matrix **operator D(R)**
  - D is for Darstellung=representation in German, R is for operation
  - these are operators in the same way the Hamiltonian is an operator
  - D(R) is determined by examining the effect of the operation on the quantity under consideration (the basis R)
  - R can be anything, atoms, vectors, a molecule or even a banana!
- for example you might have already been introduced to the rotation operator as a matrix. A rotation about the z-axis can be generated by the matrix shown in **Figure 7**

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



z-axis comes out of the page

Figure 7 The rotation matrices for an anticlockwise rotation

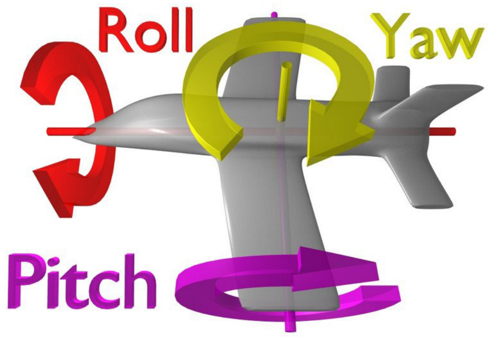
- θ takes on only specific values depending on the type of axis:

  C_2 rotations θ =0° and 180°
  C_3 rotations θ= 0°, 120° and 240°
  C_4 rotations θ= 0°, 90°, 180° and 270°
  and so on for other C_n operations
- notice that the symmetry operator is quantised! Symmetry and quantum numbers (n, l, s etc) are related. Most rotation operators are quantised, however there are a few special symmetry operators that are continuous, for example the C_∞ axis in $C_{\infty v}$ or $D_{\infty h}$
- we take our rotation matrix and operate on a vector, say v(x,y,z) and moving it to a new position v'(x'y',z'), we write this as v'=**D**v
  - the matrix representing the $C_2(z)$ operation is therefore **D**(C_2(z)):

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

Figure 8 The rotation matrix for a C_2 rotation (θ=π)

- real life (macroscopic) applications are all around us!
  - every time you see an object rotating in an app, or an animation or in a computer game, the computer is number crunching through a series of rotation transformation matrices. I have even found a whole book dedicated to just this topic "Matrix transformations for Computer Games and Animation" by John Vince, Springer-Verlag London, 2012
  - the matrices for rotation about the x-axis, y-axis and z-axis are used in flight dynamics, R_X is the roll, R_Y is the pitch and R_Z is the yaw, **Figure 9**



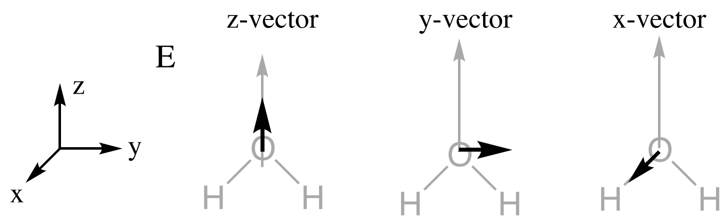
$$R(x)=\begin{pmatrix}1 & 0 & 0\\ 0 & \cos(\theta) & -\sin(\theta)\\ 0 & \sin(\theta) & \cos(\theta)\end{pmatrix}$$

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

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

Figure 9 Graphic and the associated rotation matrices associated with pitch, roll and yaw.[2]

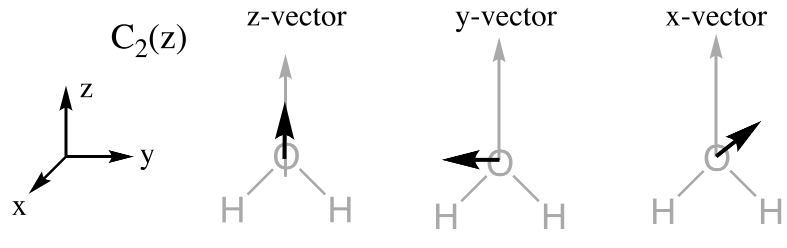
- to determine the matrix operator for a symmetry operation we work out what happens when the operation acts on each unit vector of a system (or atom)
- consider for example operators for the O-atom of H_2O in the C_{2v} point group
  - E leaves the vectors unchanged, **Figure 10**



$$\begin{pmatrix}x'\\ y'\\ z'\end{pmatrix}=\underbrace{\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}}_{D(E)}\begin{pmatrix}x\\ y\\ z\end{pmatrix}=\begin{pmatrix}1x+0y+0z\\ 0x+1y+0z\\ 0x+0y+1z\end{pmatrix}=\begin{pmatrix}x\\ y\\ z\end{pmatrix}$$

Figure 10 matrix representation of the E operation under C_{2v}

  - $C_2(z)$ leaves z unchanged (1), but rotates the x and y vectors which have the values (-1) in the matrix representation, **Figure 11**



$$\begin{pmatrix}x'\\ y'\\ z'\end{pmatrix}=\underbrace{\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}}_{D(C_2(z))}\begin{pmatrix}x\\ y\\ z\end{pmatrix}=\begin{pmatrix}-1x+0y+0z\\ 0x-1y+0z\\ 0x+0y+1z\end{pmatrix}=\begin{pmatrix}-x\\ -y\\ z\end{pmatrix}$$

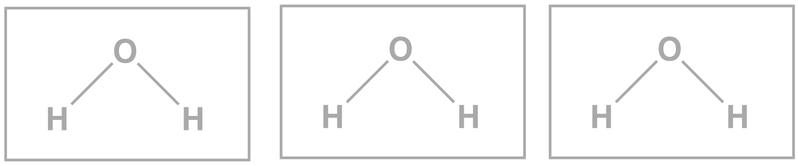
Figure 11 matrix representation of the $C_2(z)$ operation under C_{2v}

[2] Image from:http://en.wikipedia.org/wiki/Flight_dynamics

Activity

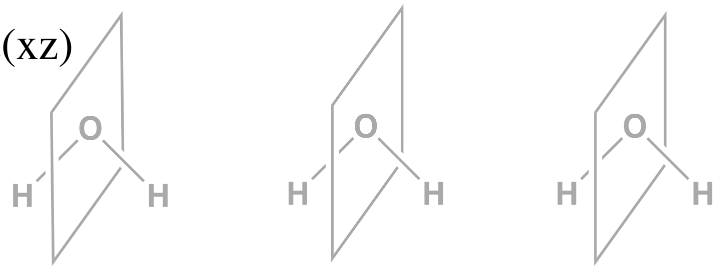
- draw the effect of the operation and determine the matrix representation for the $\sigma_V(yz)$ and $\sigma_V(xz)$ operations

$\sigma_v(yz)$



$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix}}_{D(\sigma_v(yz))} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \end{pmatrix} = \begin{pmatrix} \cdots \\ \cdots \\ \cdots \end{pmatrix}$$

$\sigma_v(xz)$



$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix}}_{D(\sigma_v(xz))} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \end{pmatrix} = \begin{pmatrix} \cdots \\ \cdots \\ \cdots \end{pmatrix}$$

Figure 12 matrix representation of (a) $\sigma_V(yz)$ and (b) $\sigma_V(xz)$ operations under C_{2v}

Some History

- using a matrix to represent a symmetry operator is a particularly powerful way of understanding symmetry because it means that the wealth of experience we have in matrix algebra and matrix mechanics can be used to understand and manipulate symmetry operations.
- Heisenberg (as well as producing the Heisenberg uncertainty principle) developed matrix mechanics. Heisenberg, **Figure 13**, received the Nobel Prize in physics in 1932 when he was 31 "for the creation of quantum mechanics"!

Figure 13 Werner Heisenberg[3]

- Dirac noticed connections between Heisenberg's matrix mechanics and Schrödinger's wave mechanics (**Figure 14**) and reformulated the Schrödinger equation into a matrix notation, which has proven more powerful than that originally proposed by Schrödinger. (He also introduced the bra-ket notation and the delta function.)

Figure 14 Paul Dirac[4] and Erwin Schrödinger[5]

- Paul Dirac and Erwin Schrödinger, shared the Nobel Prize in physics in 1933 "for the discovery of new productive forms of atomic theory."

> The matrix formulation of symmetry **and** the Schrödinger equation were significant breakthroughs. Both can now be treated together and on an equal footing!

[3] photo from the wikipedia web-site: http://en.wikipedia.org/wiki/Werner_Karl_Heisenberg
[4] photo from the wikipedia web-site: http://en.wikipedia.org/wiki/Paul_Dirac
[5] photo from the wikipedia web-site: http://en.wikipedia.org/wiki/Erwin_Schrödinger

<u>Combining Symmetry Elements</u>

- for symmetry operators the method of combination is <u>multiplication</u>
- for example $C_2(z)\sigma_v(xz)\{H_2O\}=\sigma_v(yz)\{H_2O\}$
  - first consider the RHS, show the effect of $\sigma_v(yz)$ acting on vectors of one H, **Figure 15**

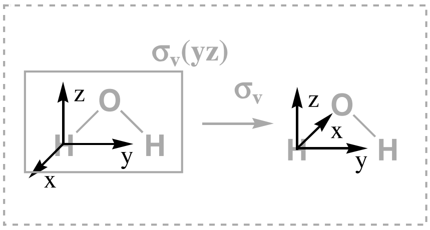


Figure 15 Symmetry operation

  - show the effect of the $\sigma_v(xz)$ operation followed by $C_2(z)$, **Figure 16**:

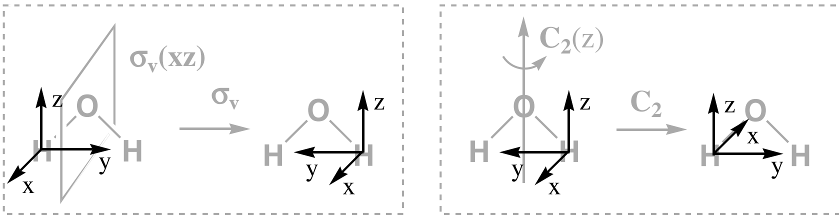


Figure 16 Sequential symmetry operations

IMPORTANT

- the order of operations is important, *and is not what you are used to*
  - the operator $\sigma_v(xz)$ acted on the object within the brackets first, $C_2(z)\sigma_v(xz)\{H_2O\}$
  - and then $C_2(z)$ acts on the result of $C_2(z)[\sigma_v(xz)\{H_2O\}]$
  - for symmetry operators and matrices *start on the inside and work your way out*
- our result the shows that $C_2(z)\sigma_v(xz)\{H_2O\}=\sigma_v(yz)\{H_2O\}$
  - normally the object is assumed and we write the expression as $C_2(z)\sigma_v(xz)=\sigma_v(yz)$ or just simply as $C_2\sigma_v=\sigma_v'$
  - operating with $C_2\sigma_v$ has the same result as simply operating with σ_v'
- how would we express this in a matrix formulation?
  - let us consider the operation $C_2(z)\sigma_v(xz)\{\text{vector}\}$ and $\sigma_v(yz)\{\text{vector}\}$
  - we have already worked out what these matrices look like

start with the LHS

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(C_2)} \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(\sigma_v(xz))} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

first evaluate $D(\sigma_v(xz))\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$

then operate with $D(C_2)$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(C_2)} \begin{pmatrix} x \\ -y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

then the RHS

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(\sigma_v(yz))} \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

thus

$$C_2(z)\sigma_v(xz) = \sigma_v(yz)$$

Figure 17 multiplying matrices

- in the case of a matrix formulation we use **matrix multiplication**
  - thus we can achieve the same result by determining the product of matrix multiplication between $C_2(z)\sigma_v(xz)$:

$$\underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(C_2)} \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(\sigma_v(xz))} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{D(\sigma_v(yz))}$$

Figure 18 multiplying matrices

- thus we have shown that:
  - not only are the symmetry operations related to matrices, but that simple algebra performed on operations is directly paralleled by similar algebra performed on matrices
  - **this is an exceptionally powerful conclusion!**

IMPORTANT

- the symmetry operations of the C_{2v} point group and the matrix representations of these symmetry elements are related, ie have a one-to-one relationship (the technical term is *isomorphic*)

$$C_{2v}\left\{E \quad C_2^1 \quad \sigma_v(yz) \quad \sigma_v(xz)\right\}$$
$$C_{2v}\left\{E \quad D(C_2) \quad D(\sigma_v) \quad D(\sigma_v')\right\}$$

- the physical symmetry operations of a point group are directly related to the matrix representations of the symmetry operation
  - we can relate a symmetry operation (R) to a matrix representation, D(R)
  - we can mathematically manipulate the matrices and be confident that if we did the same thing physically we would get the same answer

Activity

- determine $C_2(z)\sigma_v(yz)$ using (a) diagrams (b) matrices and show that:
  - the operators: $C_2(z)\ \sigma_v(yz)=\sigma_v(xz)$
  - and the matrices $\mathbf{D}(C_2(z))\mathbf{D}(\sigma_v(yz))=\mathbf{D}(\sigma_v(xz))$

Key Points

- be able to list the different processes that occur when light is incident on a sample and be able to identify the related spectroscopic techniques
- be able to draw a schematic representation of the energy levels associated with vibrational and electronic transitions, and to be able to identify the unit of measurement associated with each spectroscopy
- be able to explain why symmetry is important
- revision: be able to:
    - write a definition for, and distinguish between a "symmetry element", "symmetry operation" and "symmetry operator"
    - list the key symmetry elements and draw an example of each
    - determine the point group of a given molecule
    - draw **clear** diagrams showing symmetry *elements* on a molecule
- be able to draw **clear** diagrams showing the action of a symmetry *operations* on a molecule
- be able to generate the rotation matrices using trigonometry (cf Figure 7, Figure 8)
- be able to generate the matrix representation of a symmetry operator for a given basis of Cartesian basis vectors (cf Figures 10-12)
- be able to discuss the important relationship between physical operations and mathematical operators
- be able to use diagrams and matrix mechanics to form symmetry operator and symmetry matrix products

Self-Study Problems

- using the set-up given in **Figure 7** show that the components of the rotation matrix are $x'=\cos(\theta)x-\sin(\theta)y$ and $y'=\sin(\theta)x+\cos(\theta)y$
- determine $\sigma_v(yz)C_2(z)$ using (a) diagrams and (b) matrices
- compare your result to the in-class activity, does $\sigma_v(yz)C_2(z)= C_2(z)\sigma_v(yz)$?