Connecting Symmetry, Vibrational Spectroscopy, and Inorganic Chemistry

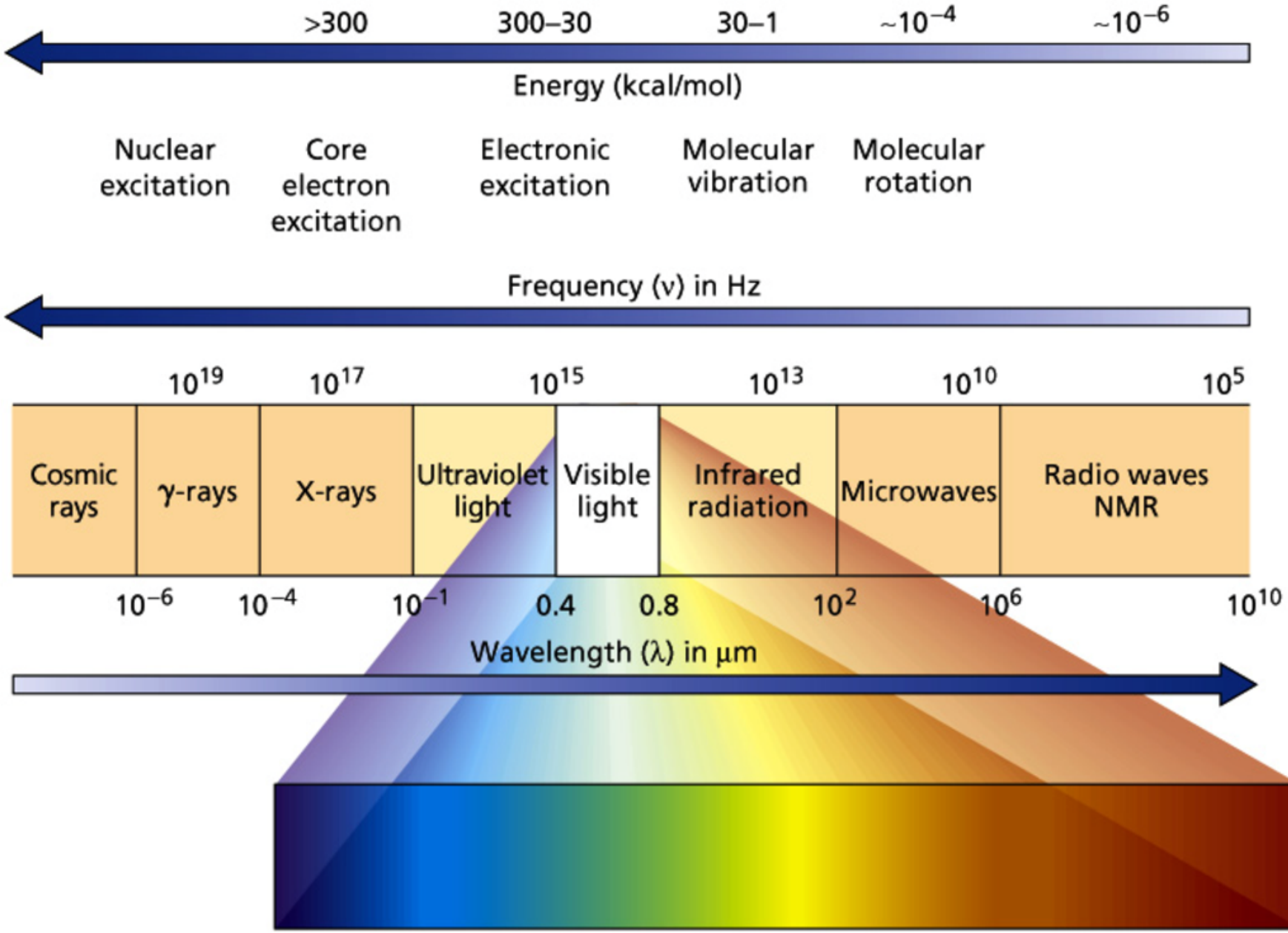
Quote from Eugene Paul Wigner

See also: *Current Science*, vol. 69, no. 4, 25 August 1995, p. 375

From the preface to his book on group theory:

Wigner relates a conversation with von Laue on the use of group theory as the natural tool with which to tackle problems in quantum mechanics. "I like to recall his question as to which results... I considered most important. My answer was that the explanation of Laporte's rule (the concept of parity) and the quantum theory of the vector addition model appeared to me most significant. Since that time, I have come to agree with his answer that the recognition that almost all rules of spectroscopy follow from the symmetry of the problem is the most remarkable result."

Massachusetts Institute of Technology


>300
300–30
30–1
~10^−4
~10^−6
Energy (kcal/mol)
Nuclear excitation
Core electron excitation
Electronic excitation
Molecular vibration
Molecular rotation
Frequency (ν) in Hz
10^19
10^17
10^15
10^13
10^10
10^5
Cosmic rays
γ-rays
X-rays
Ultraviolet light
Visible light
Infrared radiation
Microwaves
Radio waves NMR
10^−6
10^−4
10^−1
0.4
0.8
10^2
10^6
10^10
Wavelength (λ) in μm

Selection Rule for IR Spectroscopy

- The molecular dipole moment may undergo a change during a molecular vibration
- If the vibration or "normal mode" has the same symmetry as x, y, or z, then it involves a change in the molecular dipole moment during the vibration, by symmetry, and otherwise not
- The criterion for absorption of infrared (IR) radiation by resonant excitation of a molecular vibration is that it must involve a change in molecular dipole moment
- This is because the interaction is between the oscillating electric dipole of the electromagnetic radiation and the changing molecular dipole arising from the electron distribution in the vibrating molecule
- The symmetry of the electric dipole operator is the same as x, y, and z as listed in the character tables

Selection Rule for IR Spectroscopy

- The molecular dipole moment may undergo a change during a molecular vibration
- If the vibration or "normal mode" has the same symmetry as x, y, or z, then it involves a change in the molecular dipole moment during the vibration, by symmetry, and otherwise not
- The criterion for absorption of infrared (IR) radiation by resonant excitation of a molecular vibration is that it must involve a change in molecular dipole moment
- This is because the interaction is between the oscillating electric dipole of the electromagnetic radiation and the changing molecular dipole arising from the electron distribution in the vibrating molecule
- The symmetry of the electric dipole operator is the same as x, y, and z as listed in the character tables

Massachusetts Institute of Technology

Selection Rule for IR Spectroscopy

- The molecular dipole moment may undergo a change during a molecular vibration
- If the vibration or "normal mode" has the same symmetry as x, y, or z, then it involves a change in the molecular dipole moment during the vibration, by symmetry, and otherwise not
- The criterion for absorption of infrared (IR) radiation by resonant excitation of a molecular vibration is that it must involve a change in molecular dipole moment
- This is because the interaction is between the oscillating electric dipole of the electromagnetic radiation and the changing molecular dipole arising from the electron distribution in the vibrating molecule
- The symmetry of the electric dipole operator is the same as x, y, and z as listed in the character tables

Massachusetts Institute of Technology

Selection Rule for IR Spectroscopy

- The molecular dipole moment may undergo a change during a molecular vibration
- If the vibration or "normal mode" has the same symmetry as x, y, or z, then it involves a change in the molecular dipole moment during the vibration, by symmetry, and otherwise not
- The criterion for absorption of infrared (IR) radiation by resonant excitation of a molecular vibration is that it must involve a change in molecular dipole moment
- This is because the interaction is between the oscillating electric dipole of the electromagnetic radiation and the changing molecular dipole arising from the electron distribution in the vibrating molecule
- The symmetry of the electric dipole operator is the same as x, y, and z as listed in the character tables

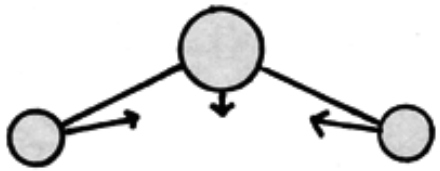
Massachusetts Institute of Technology

Selection Rule for IR Spectroscopy

- The molecular dipole moment may undergo a change during a molecular vibration
- If the vibration or "normal mode" has the same symmetry as x, y, or z, then it involves a change in the molecular dipole moment during the vibration, by symmetry, and otherwise not
- The criterion for absorption of infrared (IR) radiation by resonant excitation of a molecular vibration is that it must involve a change in molecular dipole moment
- This is because the interaction is between the oscillating electric dipole of the electromagnetic radiation and the changing molecular dipole arising from the electron distribution in the vibrating molecule
- The symmetry of the electric dipole operator is the same as x, y, and z as listed in the character tables

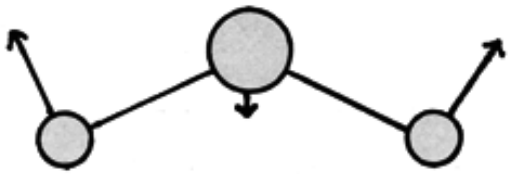
Water Normal Modes of Vibration

(3)(3) − 6 = 3 vibrational modes



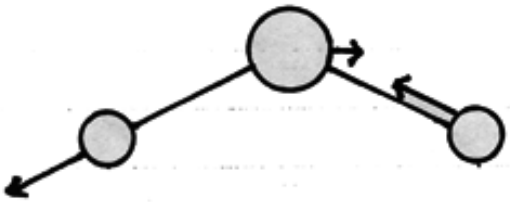
$\bar{\nu}_1 = 3652 \text{ cm}^{-1}$

symmetric stretch



$\bar{\nu}_2 = 1595 \text{ cm}^{-1}$

(mostly) bending mode



$\bar{\nu}_3 = 3756 \text{ cm}^{-1}$

asymmetric stretch

Procedure for IR Vibrational Symmetry Analysis

- Assign the structure to a point group, and refer to the character table
- For each class of symmetry operation, write down the number of atoms unshifted by carrying out the operation
- Note: only unshifted atoms can contribute to the reducible representation we are generating
- Multiply by the characters for x, y, and z, here representing the three degrees of freedom for each atom in the structure; this generates the reducible representation for all $3N$ degrees of freedom
- Subtract the characters for the rotations and translations and you are left with a reducible representation for the $3N - 6$ vibrational degrees of freedom (nonlinear molecule)
- Reduce this reducible representation to find the normal mode symmetries; apply the selection rule

Massachusetts Institute of Technology

Procedure for IR Vibrational Symmetry Analysis

- Assign the structure to a point group, and refer to the character table
- For each class of symmetry operation, write down the number of atoms unshifted by carrying out the operation
- Note: only unshifted atoms can contribute to the reducible representation we are generating
- Multiply by the characters for x, y, and z, here representing the three degrees of freedom for each atom in the structure; this generates the reducible representation for all $3N$ degrees of freedom
- Subtract the characters for the rotations and translations and you are left with a reducible representation for the $3N - 6$ vibrational degrees of freedom (nonlinear molecule)
- Reduce this reducible representation to find the normal mode symmetries; apply the selection rule

Massachusetts Institute of Technology

Procedure for IR Vibrational Symmetry Analysis

- Assign the structure to a point group, and refer to the character table
- For each class of symmetry operation, write down the number of atoms unshifted by carrying out the operation
- Note: only unshifted atoms can contribute to the reducible representation we are generating
- Multiply by the characters for x, y, and z, here representing the three degrees of freedom for each atom in the structure; this generates the reducible representation for all $3N$ degrees of freedom
- Subtract the characters for the rotations and translations and you are left with a reducible representation for the $3N - 6$ vibrational degrees of freedom (nonlinear molecule)
- Reduce this reducible representation to find the normal mode symmetries; apply the selection rule

Massachusetts Institute of Technology

Procedure for IR Vibrational Symmetry Analysis

- Assign the structure to a point group, and refer to the character table
- For each class of symmetry operation, write down the number of atoms unshifted by carrying out the operation
- Note: only unshifted atoms can contribute to the reducible representation we are generating
- Multiply by the characters for x, y, and z, here representing the three degrees of freedom for each atom in the structure; this generates the reducible representation for all $3N$ degrees of freedom
- Subtract the characters for the rotations and translations and you are left with a reducible representation for the $3N - 6$ vibrational degrees of freedom (nonlinear molecule)
- Reduce this reducible representation to find the normal mode symmetries; apply the selection rule

Massachusetts Institute of Technology

Procedure for IR Vibrational Symmetry Analysis

- Assign the structure to a point group, and refer to the character table
- For each class of symmetry operation, write down the number of atoms unshifted by carrying out the operation
- Note: only unshifted atoms can contribute to the reducible representation we are generating
- Multiply by the characters for x, y, and z, here representing the three degrees of freedom for each atom in the structure; this generates the reducible representation for all $3N$ degrees of freedom
- Subtract the characters for the rotations and translations and you are left with a reducible representation for the $3N - 6$ vibrational degrees of freedom (nonlinear molecule)
- Reduce this reducible representation to find the normal mode symmetries; apply the selection rule

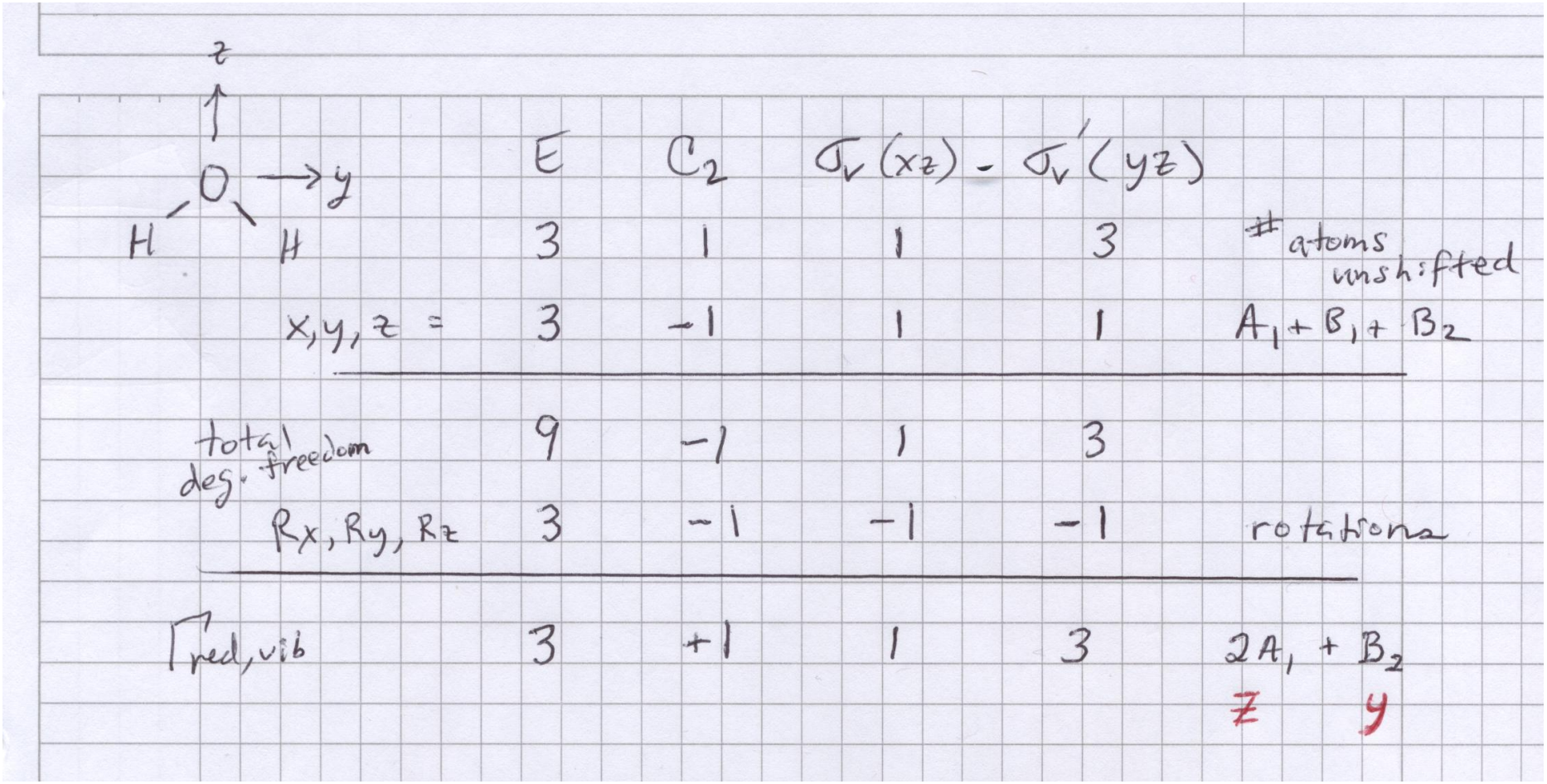
Massachusetts Institute of Technology

Procedure for IR Vibrational Symmetry Analysis

- Assign the structure to a point group, and refer to the character table
- For each class of symmetry operation, write down the number of atoms unshifted by carrying out the operation
- Note: only unshifted atoms can contribute to the reducible representation we are generating
- Multiply by the characters for x, y, and z, here representing the three degrees of freedom for each atom in the structure; this generates the reducible representation for all $3N$ degrees of freedom
- Subtract the characters for the rotations and translations and you are left with a reducible representation for the $3N - 6$ vibrational degrees of freedom (nonlinear molecule)
- Reduce this reducible representation to find the normal mode symmetries; apply the selection rule

Massachusetts Institute of Technology

Water Vibrational Symmetry Analysis in C_{2v}



Water Vibrational Symmetry Analysis in C_{2v}

Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Representation

Γ	3	1	1	3

Reduced Representation

2	A_1
0	A_2
0	B_1
1	B_2

Water Vibrational Symmetry Analysis in C_{2v}

- We have a mathematical expression for finding out how many times a particular irreducible representation occurs in a reducible one
- It is the same as taking the dot product of two vectors
- $a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$
- h is the group order
- the procedure is to multiply together the characters of the reducible representation and the irreducible representation and take the sum, and then divide by the order of the group
- example: number of times B_2 appears in Γ_{red} 3 1 1 3: $(1 \times 3) + (-1 \times 1) + (-1 \times 1) + (1 \times 3) = 4$, now divide by $h = 4$, so B_2 appears once

Massachusetts Institute of Technology

Water Vibrational Symmetry Analysis in C_{2v}

- We have a mathematical expression for finding out how many times a particular irreducible representation occurs in a reducible one
- It is the same as taking the dot product of two vectors
- $a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$
- h is the group order
- the procedure is to multiply together the characters of the reducible representation and the irreducible representation and take the sum, and then divide by the order of the group
- example: number of times B_2 appears in Γ_{red} 3 1 1 3: $(1 \times 3) + (-1 \times 1) + (-1 \times 1) + (1 \times 3) = 4$, now divide by $h = 4$, so B_2 appears once

Massachusetts Institute of Technology

Water Vibrational Symmetry Analysis in C_{2v}

- We have a mathematical expression for finding out how many times a particular irreducible representation occurs in a reducible one
- It is the same as taking the dot product of two vectors
- $a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$
- h is the group order
- the procedure is to multiply together the characters of the reducible representation and the irreducible representation and take the sum, and then divide by the order of the group
- example: number of times B_2 appears in Γ_{red} 3 1 1 3: $(1 \times 3) + (-1 \times 1) + (-1 \times 1) + (1 \times 3) = 4$, now divide by $h = 4$, so B_2 appears once

Massachusetts Institute of Technology

Water Vibrational Symmetry Analysis in C_{2v}

- We have a mathematical expression for finding out how many times a particular irreducible representation occurs in a reducible one
- It is the same as taking the dot product of two vectors
- $a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$
- h is the group order
- the procedure is to multiply together the characters of the reducible representation and the irreducible representation and take the sum, and then divide by the order of the group
- example: number of times B_2 appears in Γ_{red} 3 1 1 3: $(1 \times 3) + (-1 \times 1) + (-1 \times 1) + (1 \times 3) = 4$, now divide by $h = 4$, so B_2 appears once

Massachusetts Institute of Technology

Water Vibrational Symmetry Analysis in C_{2v}

- We have a mathematical expression for finding out how many times a particular irreducible representation occurs in a reducible one
- It is the same as taking the dot product of two vectors
- $a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$
- h is the group order
- the procedure is to multiply together the characters of the reducible representation and the irreducible representation and take the sum, and then divide by the order of the group
- example: number of times B_2 appears in Γ_{red} 3 1 1 3: $(1 \times 3) + (-1 \times 1) + (-1 \times 1) + (1 \times 3) = 4$, now divide by $h = 4$, so B_2 appears once

Massachusetts Institute of Technology

Water Vibrational Symmetry Analysis in C_{2v}

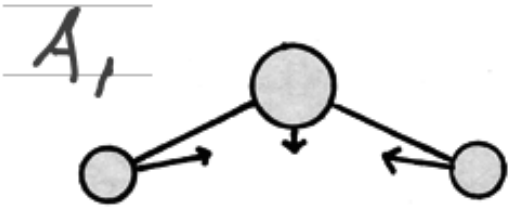
- We have a mathematical expression for finding out how many times a particular irreducible representation occurs in a reducible one
- It is the same as taking the dot product of two vectors
- $a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$
- h is the group order
- the procedure is to multiply together the characters of the reducible representation and the irreducible representation and take the sum, and then divide by the order of the group
- example: number of times B_2 appears in Γ_{red} 3 1 1 3: $(1 \times 3) + (-1 \times 1) + (-1 \times 1) + (1 \times 3) = 4$, now divide by $h = 4$, so B_2 appears once

Massachusetts Institute of Technology

Water Normal Modes of Vibration

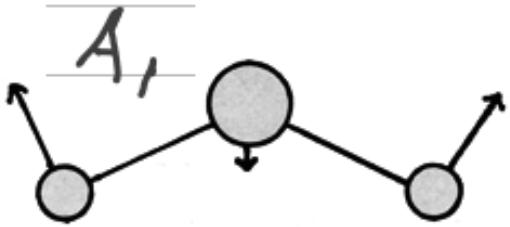
The point group is maintained during the course of a totally symmetric vibration

(3)(3) − 6 = 3 vibrational modes



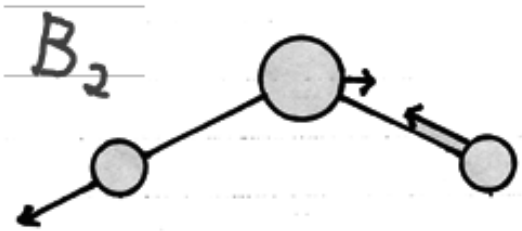
$\bar{\nu}_1 = 3652\ cm^{-1}$

symmetric stretch



$\bar{\nu}_2 = 1595\ cm^{-1}$

(mostly) bending mode



$\bar{\nu}_3 = 3756\ cm^{-1}$

asymmetric stretch

Massachusetts Institute of Technology

IR Spectroscopy as a Structural Tool

- Different point group geometries for a given molecular formula may lead to the prediction of differing numbers of IR-Active bands
- Procedure: carry out vibrational symmetry analysis for various reasonable geometries and note the predictions
- Find out which structure(s) is/are consistent with the experimental data
- We will consider the SF_6 molecule in three different geometries

IR Spectroscopy as a Structural Tool

- Different point group geometries for a given molecular formula may lead to the prediction of differing numbers of IR-Active bands
- Procedure: carry out vibrational symmetry analysis for various reasonable geometries and note the predictions
- Find out which structure(s) is/are consistent with the experimental data
- We will consider the SF_6 molecule in three different geometries

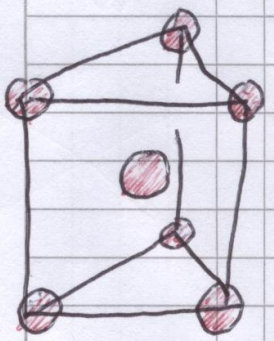
IR Spectroscopy as a Structural Tool

- Different point group geometries for a given molecular formula may lead to the prediction of differing numbers of IR-Active bands
- Procedure: carry out vibrational symmetry analysis for various reasonable geometries and note the predictions
- Find out which structure(s) is/are consistent with the experimental data
- We will consider the SF_6 molecule in three different geometries

IR Spectroscopy as a Structural Tool

- Different point group geometries for a given molecular formula may lead to the prediction of differing numbers of IR-Active bands
- Procedure: carry out vibrational symmetry analysis for various reasonable geometries and note the predictions
- Find out which structure(s) is/are consistent with the experimental data
- We will consider the SF_6 molecule in three different geometries

SF_6 Vibrational Analysis in D_{3h}: 5 IR-Active Bands



	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
# atoms unshifted	7	1	1	1	1	3	
x, y, z	3	0	−1	1	−2	1	$= E' + A_2''$
all deg.	21	0	−1	1	−2	3	
R_x, R_y, R_z	3	0	−1	−1	2	−1	$= A_2' + E''$
$\Gamma_{red,vibs}$:	15	0	1	1	−2	3	

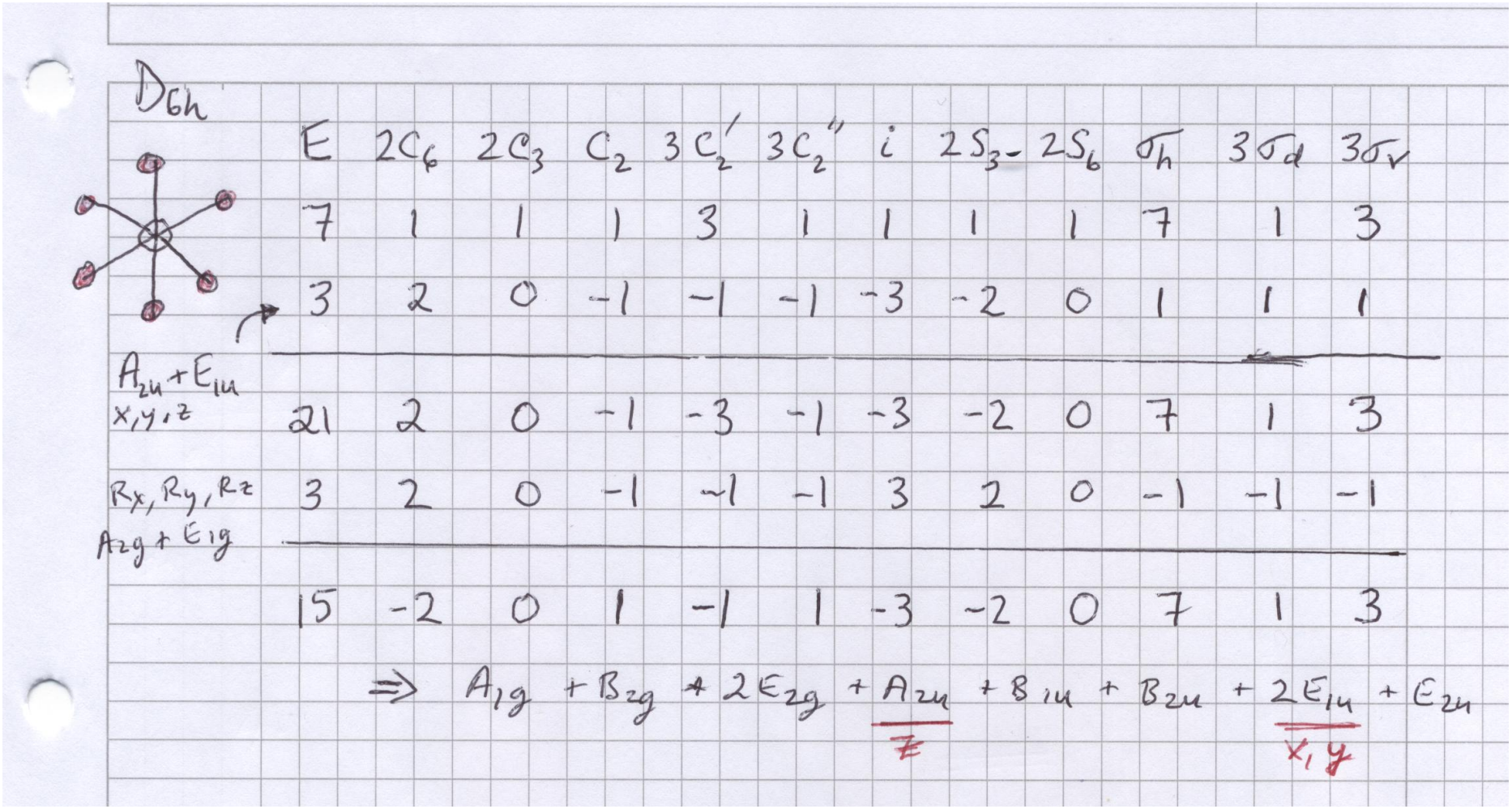
$$= 2A_1' + 3E' + 1A_1'' + 2A_2'' + 2E''$$

$3E'$: x, y; $2A_2''$: z

SF_6 Vibrational Analysis in D_{3h}: 5 IR-Active Bands

	A	B	C	D	E	F	G	H	I	J	K
1	**Character Table**										
2											
4			D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
5			A_1'	1	1	1	1	1	1		x^2+y^2, z^2
6			A_2'	1	1	-1	1	1	-1	R_z	
7			E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
8			A_1''	1	1	1	-1	-1	-1		
9			A_2''	1	1	-1	-1	-1	1	z	
10			E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)
11											
12	**Representation**										
13			Γ	15	0	1	1	-2	3		
14											
15	**Reduced Representation**										
16		2	A_1'								
17		0	A_2'								
18		3	E'								
19		1	A_1''								
20		2	A_2''								
21		2	E''								

SF_6 Vibrational Analysis in D_{6h}: 3 IR-Active Bands



SF_6 Vibrational Analysis in D_{6h}: 3 IR-Active Bands

Character Table

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

Representation

Γ	15	-2	0	1	-1	1	-3	-2	0	7	1	3

Reduced Representation

1	A_{1g}
0	A_{2g}
0	B_{1g}
1	B_{2g}
0	E_{1g}
2	E_{2g}
0	A_{1u}
1	A_{2u}
1	B_{1u}
1	B_{2u}
2	E_{1u}
1	E_{2u}

setts
f
Technology

SF_6 Vibrational Analysis in O_h: 2 IR-Active Bands

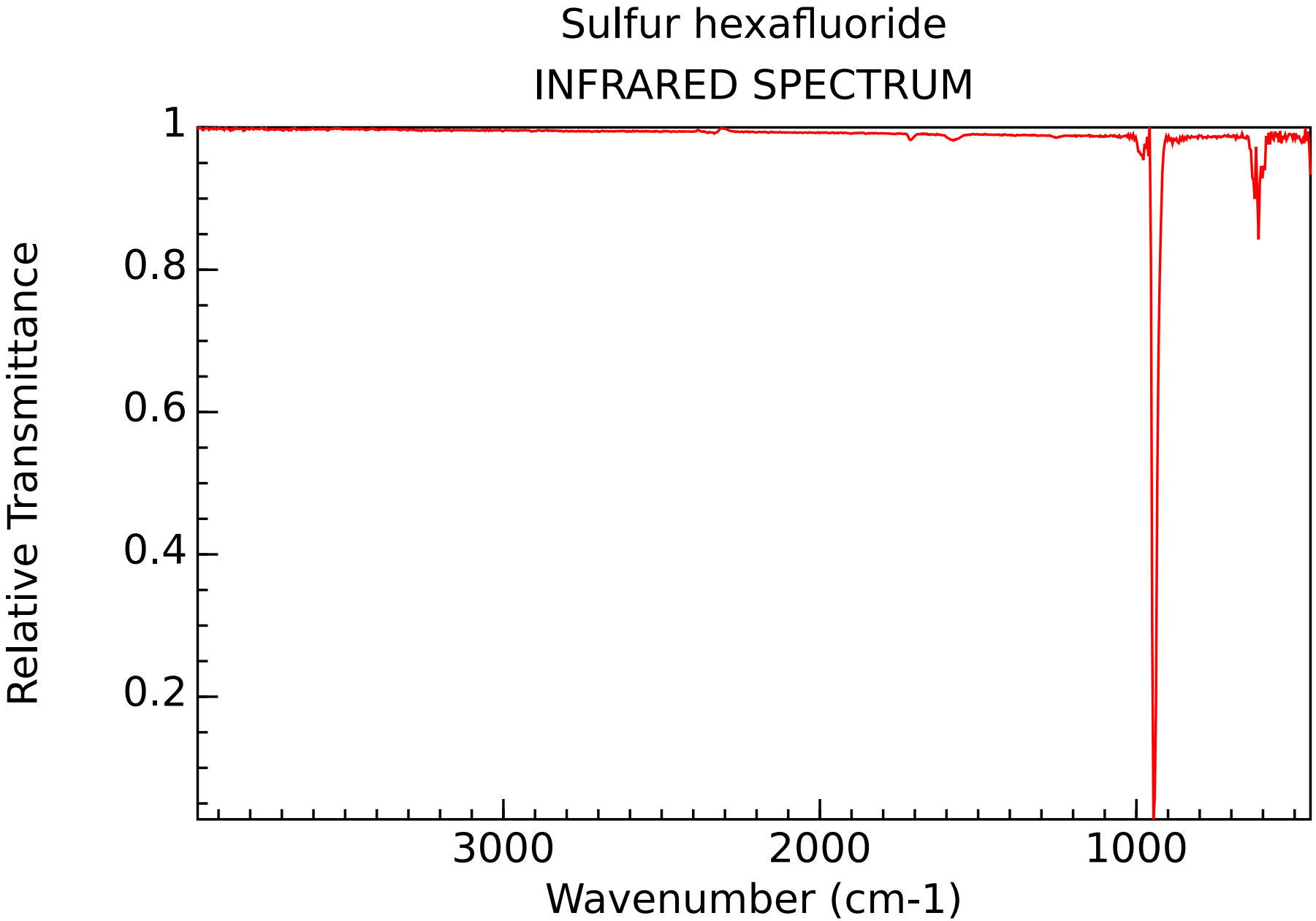
SF_6 (O_h)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	$-i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
1. Atoms unshifted	7	1	1	3	3	1	1	1	5	3
2. x,y,z (T_{1u})	3	0	−1	1	−1	−3	−1	0	1	1
	21	0	−1	3	−3	−3	−1	0	5	3
3. −trans, rot ($T_{1g}+T_{1u}$)	6	0	−2	2	−2	0	0	0	0	0
$\Gamma_{red,vib}$	15	0	1	1	−1	−3	−1	0	5	3

4. $= A_{1g} + E_g + T_{2g} + 2T_{1u} + 1T_{2u}$

SF_6 Vibrational Analysis in O_h: 2 IR-Active Bands

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	**Character Table**														
2															
4			O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
5			A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
6			A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
7			E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
8			T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
9			T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
10			A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
11			A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
12			E_u	2	-1	0	0	2	-2	0	1	-2	0		
13			T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
14			T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		
15															
16	**Representation**														
17			Γ	15	0	1	1	-1	-3	-1	0	5	3		
18															
19	**Reduced Representation**														
20		1	A_{1g}												
21		0	A_{2g}												
22		1	E_g												
23		0	T_{1g}												
24		1	T_{2g}												
25		0	A_{1u}												
26		0	A_{2u}												
27		0	E_u												
28		2	T_{1u}												
29		1	T_{2u}												

Massachusetts Institute of Technology



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)