## Molecular Vibrations

Basic quantum mechanical description - harmonic oscillator.
Symmetry properties of normal modes
Selection rules for Absorption Spectroscopy
Combination and overtone bands
Anharmonicity
Experimental Aspects
Raman Spectroscopy

Harmonic Oscillator $\mathrm{F}=-\mathrm{kq}, \mathrm{U}=\frac{1}{2} \mathrm{kq}{ }^{2}$

$$
\overrightarrow{\mathrm{F}}_{\mathrm{el}} \quad \overrightarrow{\mathbf{F}} \quad \text { mola }
$$

Taylor Series expansion of the potential energy:

$$
\mathrm{U}\left(\mathrm{q}_{1}, \mathrm{q}_{2}, \ldots . \mathrm{q}_{N}\right)=\mathrm{U}(0,0 \ldots . .0)+\sum_{1}^{N}\left(\frac{\mathrm{dU}}{\mathrm{dq}}\right)_{0} \mathrm{q}_{\mathrm{j}}+\frac{1}{2!} \sum_{i=1}^{N} \sum_{j=1}^{N}\left(\frac{\mathrm{~d}^{2} \mathrm{U}}{\mathrm{dq}_{\mathrm{i}} \mathrm{dq}}\right)_{0} \mathrm{q}_{i} \mathrm{q}_{j} \quad+\text { more terms }
$$



$$
\mathcal{H}=\frac{\hbar^{2}}{2 \mu} \frac{\partial^{2}}{\partial q 2}+1 / 2 k q^{2}
$$

q = vibrational coordinate,
k = force constant
$\mu=$ reduced mass
Solutions of the Schrödinger equation:

$$
\mathrm{E}_{\mathrm{i}}(\mathrm{n})=(\mathrm{n}+1 / 2) \hbar \omega_{\mathrm{i}} \quad \mathrm{n} \varepsilon \mathrm{~N}_{0} \quad \omega_{\mathrm{i}}=\sqrt{\mathrm{k} / \mu_{\mathrm{i}}}
$$

Eigenfunctions: $\varphi_{n}=N_{n} H_{n}(q) \exp -a q^{2}$

$$
\begin{array}{ll}
H_{n}(q) \text { : Hermite Polynomials: } \\
H_{0}=1 & \\
H_{1}=2 q & \\
H_{2}=4 q^{2}-2 & n=0,2,4, \ldots \text { par } \\
& n=1,3,5 \ldots \text { impar }
\end{array}
$$

$$
H_{3}=8 q^{3}-12 q
$$

$$
H_{4}=16 x^{4}-48 x^{2}+12
$$

## The symmetry of vibrational modes

N atoms in a molecule imply 3 N degrees of freedom of movement. Three of those can be ascribed to translational and three additional ones to rotational motion. Thus there are $3 \mathrm{~N}-6$ vibrational modes for a non-linear molecule For a linear molecule the rotational motion around the bond axis is not activated (energy too large due to the very small moment of inertia. In this case there are $3 \mathrm{~N}-5$ vibrational modes.

Basis chosen: molecular basis: dimension 3Nx3N. In this basis we can describe the effect of all the symmetry operations upon all of the atomic coordinates. Example $\mathrm{H}_{2} \mathrm{O}$ : four $9 \times 9$ matrices

Example $\quad C_{2}$

|  |  |  | \% |  |  | a | , | $y_{\text {a }}$ |  | $\mathrm{X}_{\mathrm{b}}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ( |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | -1 |  |  | 0 | 0 | 0 | $0$ | 0 | 0 | 0 |  |
| $z_{0}{ }^{\prime}$ |  |  | 0 | + | 1 | 0 | 0 | 0 |  | 0 | 0 |  |  |
|  |  | 0 | 0 |  |  | 0 | 0 | 0 |  | -1 |  | 0 | 0 |
| $y^{\prime}{ }^{\prime}$ |  | 0 | 0 |  | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 10 | 0 |
|  |  |  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | + |  |
|  |  |  | 0 |  | - | -1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $\mathrm{yb}^{\prime}$ |  |  |  |  |  |  |  |  | 0 |  | 0 | 0 | 0 |
|  |  | 0 | 0 |  |  |  |  |  |  | 10 |  |  |  |

$$
\chi_{\mathrm{T}}=-1
$$

Analogous matrices can be written for the other three symmetry operations in the group $\mathrm{C}_{2 \mathrm{v}}$. The corresponding characters are: $\chi_{T}(E)=9, \quad \chi_{T}\left(C_{2}\right)=-1, \quad \chi_{T}\left(\sigma_{v}\right)=1, \quad \chi_{T}\left(\sigma_{v}^{*}\right)=3$

## Simplified procedure in finding out the characters: $\chi_{T}(R)$

1) Atoms moved by the symmetry operation contribute nothing
2) Coordinates maintained by the operation on non-moved atoms contribute +1
3) Coordinates inverted by the operation on non-moved atoms contribute -1

In the next step we apply the decomposition formula to find out how often each irreducible representation in the group $\mathrm{C}_{2 \mathrm{v}}$ is realized by the 3 N motional degrees of freedom.

$$
a_{1}=\frac{1}{h} \sum_{R} \chi_{T}(R) \chi^{(1)(R)}
$$

$a_{A 1}=\frac{1}{4}(9 \times 1+(-1) \times 1+1 \times 1+3 \times 1)=3$
$\mathrm{a}_{\mathrm{A} 2}=\frac{1}{4}(9 \times 1+(-1) \times 1+1 \times(-1)+3 \times(-1))=1$
$\mathrm{a}_{\mathrm{B} 1}=\frac{1}{4}(9 \times 1+(-1) \times(-1)+1 \times 1+3 \times(-1))=2$
$\mathrm{a}_{\mathrm{B} 2}=\frac{1}{4}(9 \times 1+(-1) \times(-1)+1 \times(-1)+3 \times 1)=3$

$$
\begin{aligned}
& \Gamma_{\text {total }}=3 \mathrm{~A}_{1}+1 \mathrm{~A}_{2}+2 \mathrm{~B}_{1}+3 \mathrm{~B}_{2} \\
& \Gamma_{\text {trans }}=1 \mathrm{~A}_{1} \\
& \Gamma_{\text {rot }}=\quad 1 \mathrm{~B}_{1}+1 \mathrm{~B}_{2} \\
& 1 \mathrm{~A}_{2}+1 \mathrm{~B}_{1}+1 \mathrm{~B}_{2}
\end{aligned}
$$

|  | Character table $\mathrm{C}_{2 \mathrm{v}}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $E$ | $C_{2}$ | $\sigma_{v}(x z)$ | $\sigma_{v}^{\prime}(y z)$ |  |  |
| $\mathrm{A}_{1}$ | 1 | 1 | 1 | 1 | $z$ | $x^{2}, y^{2}, z^{2}$ |
| $\mathrm{A}_{2}$ | 1 | 1 | -1 | -1 | $R_{z}$ | $x y$ |
| $\mathrm{B}_{1}$ | 1 | $-1$ | 1 | -1 | $x, R_{y}$ | $x z$ |
| $\mathrm{B}_{2}$ | 1 | $-1$ | $-1$ | 1 | $y, R_{x}$ | $y z$ |

irreducible representation of the 3 N degrees of freedom -irreducible representation of the 3 translational modes -irreducible representation of the 3 rotational modes

$$
\Gamma_{\text {vib }}=2 \mathrm{~A}_{1} \quad+1 \mathrm{~B}_{2}
$$

## Vibrational normal modes of $\mathrm{H}_{2} \mathrm{O}$

Asymmetric Stretch $3756 \mathrm{~cm}^{-1}$
$\begin{aligned} & \text { Symmetric Stretch } \\ & 3657 \mathrm{~cm}^{-1}\end{aligned} \quad$ All symmetry,$~$ operations are conserved
only E and $\sigma_{v}{ }^{\prime}$ are conserved
$\mathrm{A}_{1}$
$A_{1}$

$B_{2}$



## Second Example: $\mathbf{S F}_{4}$

Group $\mathrm{C}_{2 \mathrm{w}}$ Total representation:
Set of four $15 \times 15$ matrices.
We expect 3N-6 = 9 vibrational modes and want to know their symmetry types

Using the same procedure we find: $\Gamma_{\text {vih }}=4 \mathrm{~A}_{1}+\mathrm{A}_{2}+2 \mathrm{~B}_{1}+2 \mathrm{~B}_{2}$

## Vibrational normal modes of $\mathrm{SF}_{4}$



## Simplified procedure in finding out the characters: $\chi_{T}(R)$

1) Atoms moved by the symmetry operation contribute nothing
2) Coordinates maintained by the operation on non-moved atoms contribute +1
3) Coordinates inverted by the operation on nonmoved atoms contribute -1

$$
\chi_{\mathrm{T}}(\mathrm{E})=15, \quad \chi_{\mathrm{T}}\left(\mathrm{C}_{2}\right)=-1, \quad \chi_{\mathrm{T}}\left(\sigma_{\mathrm{v}}\right)=3, \quad \chi_{\mathrm{T}}\left(\sigma_{\mathrm{v}}^{\prime}\right)=3
$$

Expressed by a formula

$$
\left.\chi_{\mathrm{T}}(\mathrm{R})=\{(+-) 1+2 \cos \phi)\right\} M
$$

+ for rotations
- for reflections,
$\phi=$ Rotation angle
$M=$ number of atoms not moved


## Selection rule for the fundamental transition $\Psi_{0}->\Psi_{1}$

We need to know the symmetry types of the integrands, To be determined by the direct products: At least one of them must contain $A_{1}$.

$$
\begin{aligned}
& \left|<\psi_{0}\right| x \mid \psi_{1}>1^{2} \\
& \left|<\psi_{0}\right| y \mid \psi_{1}>1^{2} \\
& 1<\psi_{0}|z| \psi_{1}>1^{2}
\end{aligned}
$$

| $\Gamma_{\psi 0} \otimes \Gamma_{x} \otimes \Gamma_{\psi 1}$ |
| :--- |
| $\Gamma_{\psi 0} \otimes \Gamma_{y} \otimes \Gamma_{\psi 1}$ |
| $\Gamma_{\psi 0} \otimes \Gamma_{z} \otimes \Gamma_{\psi 1}$ |

These direct products must be analyzed

1) Symmetry of the vibrational ground state $\psi_{0}=\prod_{i=1}^{3 N-6} \boldsymbol{\varphi}_{\mathrm{o} i}=\prod_{i=1}^{3 N-6} \exp -a i q i^{2}$

Because $\boldsymbol{\varphi}_{\mathrm{o}}(q)=\boldsymbol{\varphi}_{\mathrm{o}}(-q)$ for all normal modes, each symmetry operation turns $\psi_{0}$ into itself.. Thus the vibrational Ground state always belongs to the irreducible representation $\mathrm{A}_{1}$.
2) Symmetry of the first excited state $\quad \psi_{1} \sim \varphi_{1}(\mathrm{j}) \prod_{\mathrm{i} \ddagger \mathrm{j}}^{3 \mathrm{~N}-6} \boldsymbol{\varphi}_{\mathrm{o} i}=2 \mathrm{qj} \prod_{\mathrm{i}=1}^{3 \mathrm{~N}-6} \exp -$ aiqi $^{2}$

Since $q$ is the vibrational coordinate itself the first excited state wavefunction has the same symmetry as the vibrational mode itself.
3) Symmetry of the translation operators $x, y, z$ : depends on the group considered; see character table.

Example $H_{2} O$ : the three vibrational modes $A_{1}, A_{1}, B_{2}$ are all allowed because $z$ belongs to $A_{1}$ and $y$ belongs to $B_{2}$. Example $\mathrm{SF}_{4}$ : the $\mathrm{A}_{2}$ mode is forbidden because none of the translation operators belong to $\mathrm{A}_{2}: 8$ allowed modes

## Selection rules for overtone bands.

$$
\psi_{0}=\prod_{i=1}^{3 N-6} \varphi_{\mathrm{o} i} \quad \Longrightarrow \quad \Psi_{2} \sim \varphi_{2}(\mathrm{j}) \prod_{\mathrm{i} \ddagger \mathrm{j}}^{3 \mathrm{~N}-6} \boldsymbol{\varphi}_{\mathrm{o} i}=\left(4 \mathrm{q}_{\mathrm{j}}^{2}-2\right) \prod_{\mathrm{i}=1}^{3 \mathrm{~N}-6} \exp -\operatorname{aiqi}^{2}
$$

Direct products to be analyzed:

$$
\begin{aligned}
& \Gamma_{\psi 0} \otimes \Gamma_{x} \otimes \Gamma_{\psi 2} \\
& \Gamma_{\psi 0} \otimes \Gamma_{y} \otimes \Gamma_{\psi 2} \\
& \Gamma_{\psi 0} \otimes \Gamma_{z} \otimes \Gamma_{\psi 2}
\end{aligned}
$$

Both $\Psi_{0}$ and $\Psi_{2}$ belong to $\mathrm{A}_{1}$ (totally symmetric). Thus, the transition is group-theoretically allowed if at one of the translation operators $x, y$ or $z$ belongs to $A_{1}$

Despite this prediction, the transition will be weak, however, for a quantum-mechanical reason, which we can see from the following argument:
Remembering $\mathrm{W}_{\mathrm{mn}}=\left|\frac{d}{d t} a_{m}(t)\right|^{2}=|<\mathrm{m}| \mathcal{H}_{1}|\mathrm{n}>|^{2}$ (11) $\quad$ with $\mathcal{H}_{1}(\mathrm{t})=-\mu \mathrm{E}(\mathrm{t})$ where $\mu \sim$ translational operator like the vibrational coordinate q . We can express $\mathrm{W}_{\mathrm{mn}}$ in a Taylor series in the vibrational coordinate q :

$$
<\mathrm{n}|\mu| \mathrm{m}>=\underbrace{\mu_{0}<\mathrm{n} \mid \mathrm{m}>}_{\text {zero }}+\left(\frac{d \mu}{d q}\right)_{0}<\mathrm{n}|\mathrm{q}| \mathrm{m}>+\left(\frac{d^{2} \mu}{d q^{2}}\right)_{0}<\mathrm{n}\left|\mathrm{q}^{2}\right| \mathrm{m}\rangle+ \text { other terms }
$$

For the fundamental transition $\mathrm{n}=0$ and $\mathrm{m}=1 .<\mathrm{n}|\mathrm{q}| \mathrm{m}>$ is non-zero, so group theory can be used to decide if $\left(\frac{d \mu}{d q}\right)_{0}$ is non-zero For the overtone transition we have $\mathrm{n}=0$ and $\mathrm{m}=2$ and $<\mathrm{n}|\mathrm{q}| \mathrm{m}>$ is zero for a harmonic oscillator, and only the third term is different from zero. This results in an overall much smaller transition probability.

$$
<0|\mu| 2\rangle=\underbrace{}_{0}<0|2\rangle+\left(\frac{d \mu}{d q}\right)_{0}<0|q| 2\rangle+\left(\frac{d^{2} \mu}{d q^{2}}\right)_{0}<0\left|q^{2}\right| 2\rangle+\ldots . .
$$

## Selection rules for combination bands.

$$
\psi_{0}=\prod_{i=1}^{3 N-6} \boldsymbol{\varphi}_{\mathrm{o} i} \quad \Longrightarrow \quad \Psi_{2} \sim \boldsymbol{\varphi}_{1}(\mathbf{j}) \boldsymbol{\varphi}_{1}(\mathbf{k}) \prod_{\mathrm{i}+\mathrm{j}, \mathrm{k}}^{3 \mathrm{k}-6} \boldsymbol{\varphi}_{\mathrm{o} i}=4 q j q k \prod_{\mathrm{i}=1}^{3 \mathrm{~N}-6} \exp -\operatorname{aiqi}^{2}
$$

In this case we determine the irreducible representation of the excited state wave function from the direct product of the irreducible representations of the vibrational modes participating in the combination. The mode will be allowed if the combination belongs to one of the irreducible representations of the translation operators (see character table):

Example $\mathrm{SF}_{4}$ : combination band $\mathrm{B}_{1} \otimes_{\mathrm{B}_{2}}=\mathrm{A}_{2}$. Not observed, because none of the translation operators in the group $\mathrm{C}_{2 \mathrm{v}}$ belong to $\mathrm{A}_{2}$.

Second example: $\mathrm{PCl}_{3}$, group $\mathrm{C}_{3 v^{*}}$ The vibrational analysis results in the following representations of the 6 normal modes: $\Gamma_{\text {vib }}=2 \mathrm{~A}_{1}+2 \mathrm{E}$
For analyzing the symmetry of a combination band $E \times E$, we first work with the character table to develop a reducible representation and then apply the decomposition formula to get the irreducible representation.


## Anharmonicity:

## The Morse potential (1929)



Internuclear Separation (r)

Instead of the parabolic potental, P. Morse developed an empirical potential that also allows an exact solution to the Schrödinger equation:

## $\mathrm{U}=\mathrm{D}_{\mathrm{e}}(1-\exp -\mathrm{aq})^{2}$ with $\mathrm{a}=\left(\mathrm{k} / 2 \mathrm{D}_{\mathrm{e}}\right)^{1 / 2}\left[\mathrm{~cm}^{-1}\right]$

Solution:

$$
\begin{array}{r}
E_{\text {vib }}(n)=(n+1 / 2) h v_{0}-\frac{h^{2} v_{0}^{2}}{4 D_{e}}(n+1 / 2)^{2} \\
\text { where } v_{0}=\frac{a}{2 \pi} \sqrt{D_{e} / \mu}
\end{array}
$$

## Features, compared to harmonic osc.:

-lower zero-point energy
-energy levels not equidistant -there is a maximum value of $n$. -maximum energy= $D_{e}$
-at the limit: transition from vibration to free translation
-asymmetry of the potential is realistic considering that attraction and repulsion potentials depend differently on internuclear distance.


Philip McCord Morse (1903-1985), MIT

## The Lennard-Jones Potential

(


Univ. Cambridge, ,,father" of Theoretical Chemistry"

Spectroscopic Manifestations of Anharmonicity:


$$
E_{\text {vib }}(n)=(n+1 / 2) h v_{0}-\frac{h^{2} v_{0}^{2}}{4 D_{e}}(n+1 / 2)^{2}
$$



## Dispersive dual-beam IR spectrometer



Source: black-body radiator (1300-1500 ^C) SiC(Globar)
Wavelength selection: grids, prisms, Michelson interferometer
Sample compartment: gases: glass cells ( $5-10 \mathrm{~cm}$ ) with NaCl windows.
liquids: thin films between NaCl plates
solids: suspensions in oils, KBr pellets, fine powders for ATR

Detectors: heat: resistance thermometer, thermocouple photons: IR sensitive semiconductors: $\mathrm{PbSe}, \mathrm{PbTe}$

FTIR spectrometer
(Michelson interferometer)
A.Michelson

1852-1931
U. Chicago,

Nobel prize

If $2(A C-A B)=\frac{2 n+1}{2} \lambda$
If $2(A C-A B)=n \lambda, n \in N_{0}$
extinction enhancement

Mirror moves with velocity $\mathrm{v}_{\mathrm{m}}$.Monochromatic radiation would then result in an oscillatory detector signal
$S(t)$ with period $T=\frac{\lambda / 2}{v_{m}}$
The corresponding frequency is $f=2 v_{m} / \lambda=2 v_{m} v / c$ $\mathrm{f}=\mathbf{2} \mathrm{v} \mathrm{m} / \mathrm{c} \approx \mathbf{1 0}^{-10} \mathrm{v}$ if $\mathrm{v}_{\mathrm{m}} \approx 1.5 \mathrm{~cm} / \mathrm{s}$

Typical conditions: DW =1 ms, 2000 channels, AT $=\mathbf{2 s}$
Attenuated total reflectance (ATR) mode


## Raman Spectroscopy

Predicted 1923, demonstrated 1928
Inelastic scattering of light in the VIS region



Chandrasekara Raman 1888-1970
Univ. Calcutta
Nobel Prize 1930

## Physics of the interaction

The oscillating electric component of the electromagnetic wave produces and oscillating electric dipole moment by interacting with the electrons of the molecule:

Polarizability tensor

$$
\left(\begin{array}{c}
\alpha_{x x} \alpha_{x y} \alpha_{x z} \\
\alpha_{y x} \alpha_{y y} \alpha_{y z} \\
\alpha_{z x} \alpha_{z y} \alpha_{z z}
\end{array}\right)
$$

symmetric, 2nd rank
In non-spherical molecules $\alpha$ is direction dependent, described by a second-rank tensor. The fluctuating electric dipole moment forced upon the molecule by the E vector constitutes emission of an electromagnetic wave. However, because of the tensorial quality the dipole moment is generally not aligned with the $E$ vector. The molecule undergoes vibrations. Owing to these vibrations, the polarizability oscillates as well, with the frequencies $w_{i}$ of all the normal modes $i$ describing the vibrational motion of the molecule: $\mathbf{q}_{\mathbf{i}}=\mathbf{q 0} \boldsymbol{\operatorname { c o s }} \mathrm{w}_{\mathbf{i}} \mathbf{t}$ To describe this, we can expand the polarizability in a Taylor series:
$\alpha=\alpha_{0}+\sum_{i}\left(\frac{d \alpha}{d q_{i}}\right){ }_{0} q i+$ higher terms (neglected) $\mu=\alpha \varepsilon=\alpha_{0} \varepsilon+\left(\sum_{i}\left(\frac{d \alpha}{d q_{i}}\right)_{0} q_{i}\right) \varepsilon$.
Now inserting $\mathcal{\varepsilon}=\varepsilon_{0} \cos \omega_{0} t$ and $\mathbf{q}_{i}=\mathbf{q} 0 \boldsymbol{\operatorname { c o s }} \omega_{i} \mathbf{t}$ the result is:
$\boldsymbol{\mu}=\alpha_{0} \varepsilon_{0} \cos \omega_{0} t+\left(\sum_{i}\left(\frac{d \alpha}{d q_{i}}\right){ }_{0} q_{0} \cos \omega_{i} t\right) \varepsilon_{0} \cos \omega_{0} t$.
$\mu=\alpha \varepsilon=\alpha_{0} \varepsilon_{0} \cos \omega_{0} t+\left(\sum_{i}\left(\frac{d \alpha}{d q_{i}}\right)_{0} q_{0} \varepsilon_{0}\left[\cos \left(\omega_{0}-\omega_{i} t\right)+\cos \left(\omega_{0}+\omega_{i}\right) t\right]\right.$.

Sir George Stokes


1819-1903
Cambridge U


Ninn William Strutt, 3. Baron
Rayleigh 1842-1919
Cambridge U. Nobel prize 1904

## Selection Rules in Raman Spectroscopy

From the latter equation we see that Stokes and Anti-Stokes lines can only be observed if $\left(\frac{d \alpha}{d q_{i}}\right)_{0}$ is different from zero: In words: the polarizability of the molecule has to change during the course of the vibration. Again we can use the group theory formalism to make this assessment. Fór simple molecules this can be done by inspection, as shown by the examples below:

## Normal vibrational modes of $\mathrm{CO}_{2}$


$V_{1}$ Stretch
Change in polarizability No change in dipole moment

Bend
$\mathrm{v}_{2}$
No change in polarizability Change in dipole moment


## Normal vibrational modes of $\mathrm{H}_{2} \mathrm{O}$



Change in both Polarizability and dipole moment

The symmetry properties of the polarizability tensor components are the same as those of binary products $x, y$ and $z$. To show this, we consider a symmetry operation $R$, that converts a vector ( $x, y, z$ ) into a vector ( $x^{\prime}, y^{\prime}, z^{\mathbf{\prime}}$ )

$$
\left(\begin{array}{l}
x \\
y \\
z
\end{array}\right) \xrightarrow{\mathcal{R}}\left(\begin{array}{c}
x^{\prime} \\
y^{\prime} \\
z^{\prime}
\end{array}\right)=\left(\begin{array}{lll}
R_{x x} & R_{x y} & R_{x z} \\
R_{y x} & R_{y y} & R_{y z} \\
R_{z x} & R_{z y} & R_{z z}
\end{array}\right)\left(\begin{array}{c}
x \\
y \\
z
\end{array}\right)
$$

For example: $x^{\prime}=R_{x x} x+R_{x y} y+R_{x z} z$
Likewise, for the transformation from a binary product such as $x^{2}$ to $x^{\prime 2}$ we have

$$
\begin{aligned}
& x^{2} \xrightarrow{\mathcal{R}} x^{\prime 2}=\left(R_{x x} x+R_{x y} y+R_{x z} z\right)^{2}=R_{x x}^{2} x^{2}+R_{x y}^{2} y^{2}+R_{x z}^{2} z^{2}+2 R_{x x} R_{x y} x y+2 R_{x y} R_{x z} y z+2 R_{x z} R_{x x} z x \quad(A) \\
& x y \xrightarrow{\mathcal{R}} y^{\prime} \text { and transformation of the other elements can be expressed analogously via matrix multiplication }
\end{aligned}
$$

Now we'll have a look at the transformation of the polarizability tensor components.

$$
\begin{aligned}
& \mu=\alpha \mathcal{R} \xrightarrow{\mathcal{R}} \mu^{\prime}=\alpha^{\prime} \mathcal{E}^{\prime} \quad \text { with } \quad \varepsilon^{\prime}=\mathcal{R} \mathcal{E} \\
& \mu=\alpha \mathcal{R} \xrightarrow{\mathcal{R}} \mu=\alpha^{\prime} \mathcal{R} \mathcal{L} \quad \mu^{\prime}=\mathcal{R} \mu \\
& \mathcal{R}^{-1} \mathcal{R} \mu=\mathcal{R}^{-1} \alpha^{\prime} \mathcal{R} \mathcal{E} \\
& \alpha \mathscr{E}=\mathcal{R}^{-1} \alpha^{\prime} \mathcal{R} \mathcal{E}
\end{aligned}
$$

$$
\begin{aligned}
& \left(\begin{array}{l}
\alpha_{x x} \alpha_{x y} \alpha_{x z} \\
\alpha_{y x} \alpha_{y y} \alpha_{y z} \\
\alpha_{z x} \alpha_{z y} \alpha_{z z}
\end{array}\right)=\left(\begin{array}{l}
R_{x x} R_{x y} R_{x z} \\
R_{y x} R_{y y} R_{y z} \\
R_{z x} R_{z y}
\end{array}\right)\left(\begin{array}{l}
\alpha_{x z} R_{x x}+\alpha_{x y} R_{x y}+\alpha_{x z} R_{x z} \\
\alpha_{y x} R_{x x}+\alpha_{y P_{x y}}+\alpha_{y z} R_{x z} \\
\alpha_{z x} R_{x x}+\alpha_{z y} R_{x y}+\alpha_{z z} R_{x z}
\end{array}\right.
\end{aligned}
$$

Only the first column of the product matrix $\mathcal{R} \alpha \mathcal{R}^{-1}$ is shown here. This will be sufficient to calculate the component $\alpha_{x x}$. We obtain

$$
\alpha_{x x}{ }^{\prime}=R_{x x} \alpha_{x x} R_{x x}+R_{x x} \alpha_{x y} R_{x y}+R_{x x} \alpha_{x z} R_{x z}+R_{x y} \alpha_{y x} R_{x x}+R_{x y} \alpha_{y y} R_{x y}+R_{x y} \alpha_{y z} R_{x z}+R_{x z} \alpha_{z x} R_{x x}+R_{x z} \alpha_{z y} R_{x y}+R_{x z} \alpha_{z z} R_{x z}
$$

Combination of the terms in the same colors (considering that the polarizability tensor is symmetric leads to

$$
\begin{align*}
\alpha_{x x}^{\prime} & =R^{2}{ }_{x x} \alpha_{x x}+R^{2}{ }_{x y} \alpha_{y y}+R_{x z}^{2} \alpha_{z z}+2 R_{x x} R_{x y} \alpha_{x y}+2 R_{x x} R_{x z} \alpha_{x z}+2 R_{x y} R_{x z} \alpha_{y z}  \tag{B}\\
x^{\prime 2} & =R_{x x}^{2} x^{2}+R_{x y}^{2} y^{2}+R_{x z}^{2} z^{2}+2 R_{x x} R_{x y} x y+2 R_{x z} R_{x x} z x+2 R_{x y} R_{x z} y z \tag{A}
\end{align*}
$$

This comparison shows that the tensor $\alpha$ transforms under symmetry operations like the binary products of $x, y$ and $z$

Selection rule in Raman spectroscopy: All the modes that belong to the same irreducible representation as one of the binary product operators of $x, y$, and $z$ are Raman active, as the direct products where $\mathbf{i}, \mathbf{j}=\mathbf{x}$ or $\mathbf{y}$ or $\mathbf{z}$ will contain $A_{1}$ or $A^{\prime}$ or $A_{1 g}$

$$
\begin{aligned}
& \Gamma_{\psi 0} \otimes \Gamma_{i j} \otimes \Gamma_{\psi 1} \\
& \Gamma_{\psi 0} \otimes \Gamma_{i j} \otimes \Gamma_{\psi 1} \\
& \Gamma_{\psi 0} \otimes \Gamma_{i j} \otimes \Gamma_{\psi 1}
\end{aligned}
$$

Mutual exclusion rule: For molecules with a center of inversion
All translation operators belong to an irreducible representation of type u (ungerade), while all binary products of translation operators belong to an irreducible representation of type g (gerade). As a consequence the infrared and Raman spectra have no bands in common. Examples $\mathrm{CO}_{2}, \mathrm{~N}_{2}$, trans $\mathrm{N}_{2} \mathrm{~F}_{2}$ (as opposed to cis- $\mathrm{N}_{2} \mathrm{~F}_{2}$ )

## Character table $\mathrm{C}_{2 \mathrm{v}}$

|  | $E$ | $C_{2}$ | $\sigma_{v}(x z)$ | $\sigma_{v}^{\prime}(y z)$ |  |  |
| ---: | :--- | ---: | ---: | ---: | :--- | :--- |
|  | $\mathbf{A}_{\mathbf{1}}$ | 1 | 1 | 1 | 1 | $z$ |
| $\mathbf{A}_{\mathbf{2}}$ | 1 | 1 | -1 | -1 | $R_{z}$ | $x y$ |
| $\mathbf{B}_{\mathbf{1}}$ | 1 | -1 | 1 | -1 | $x, R_{y}$ | $x z$ |
| $\mathbf{B}_{\mathbf{2}}$ | 1 | -1 | -1 | 1 | $y, R_{x}$ | $y z$ |


cis form

trans form

Character table $\mathrm{C}_{2 \mathrm{~h}}$

| $\mathrm{C}_{2 \mathrm{~h}}$ | E | $\mathrm{C}_{2}$ | i | $\sigma_{\mathrm{h}}$ |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{A}_{g}$ | 1 | 1 | 1 | 1 | $\mathrm{R}_{\mathrm{x}}, \mathrm{x}^{2}, \mathrm{y}^{2}, \mathrm{z}^{2}, \mathrm{xy}$ |
| $\mathrm{B}_{\mathrm{g}}$ | 1 | -1 | 1 | -1 | $\mathrm{R}_{\mathrm{s}}, \mathrm{R}_{y}, \mathrm{xz}, \mathrm{yz}$ |
| $\mathrm{A}_{u}$ | 1 | 1 | -1 | -1 | z |
| $\mathrm{B}_{\mathrm{u}}$ | 1 | -1 | -1 | 1 | $\mathrm{x}, \mathrm{y}$ |

no IR and Raman bands in common
$\mathrm{C}_{2 \mathrm{v}}$

$$
\mathrm{C}_{2 \mathrm{~h}}
$$

Structural Information from Vibrational Spectroscopy

Cis $\mathbf{N}_{2} \mathrm{~F}_{2}$

cis form


trans form

Trans $\mathbf{N}_{2} \mathrm{~F}_{\mathbf{2}}$


## Polarization Phenomena in Raman Spectroscopy

......a consequence of the anisotropy of the molecular polarizability
$\mu=\alpha \mathcal{E} \quad$ where $\varepsilon=\varepsilon_{0} \cos \omega_{0}$ t oscillates with the frequency of the incident light
$\alpha\left[\mathrm{Cm}^{2} / \mathrm{V}\right]$ is the polarizability: „ease" with which electrons can be moved within the molecule to create an electric dipole
In non-spherical molecules $\alpha$ is direction dependent, described by a second-rank tensor.

$$
\left(\begin{array}{c}
\alpha_{x x} \alpha_{x y} \alpha_{x z} \\
\alpha_{y x} \alpha_{y y} \alpha_{y z} \\
\alpha_{z x} \alpha_{z y} \alpha_{z z}
\end{array}\right)
$$

symmetric, 2nd rank

We remind ourselves again that the forced oscillation the electrons undergo when they feel the fluctuating electric field of the applied electromagnetic wave in itself constitutes the emission of an electromagnetic wave.. In other words when the molecule oscillates like this, it emits an electromagnetic wave - and when there was no energy exchange between the molecule and the electromagnetic wave the emission will be at the same frequency as that of the incident light. With unpolarized light, emission will be generally in all directions.
This is called elastic scattering and corresponds to the Rayleigh emission.

Now, let us use polarized light


Special situation: Molecule is spherically symmetric, and has thus isotropic polarizability; in this case the induced polarization oscillates in the same direction as the electrical field, leading to the re-emission of polarized light


Even using unpolarized light source, we have a superposition of of $A$ and $B$. Scattered light is still polarized in different Ways if we eithre observe in direction x or direction y .

## Light scattered by isotropic molecules is polarized



General case: the molecule is anisotropic. In this case the vectors P and E will not have the same direction. Induced Polarization will be in that direction where the molecule has the largest polarizability.


At each moment the polarized light will be emitted in a different direction. As a result the scattered Light is unpolarized even when using polarized light as the source. Scattering will be observed in both $x$ and $y$ directions

Using an unpolarized light source we will observe both $\mathrm{E}_{\mathrm{x}}$ and $\mathrm{E}_{\mathrm{y}}$ transversal components in both directions


As intensities are proportional to $\mathrm{P}^{2}$
$P_{y}{ }^{2}=\left(\alpha_{y x} \varepsilon_{x}+\alpha_{y y} \varepsilon_{y}\right)^{2}=\alpha_{y x}{ }^{2} \boldsymbol{\varepsilon}_{x}{ }^{2}+\alpha_{y y}{ }^{2} \boldsymbol{\varepsilon}_{y}{ }^{2}$ $P_{z}^{2}=\left(\alpha_{z x} \varepsilon_{x}+\alpha_{z y} \varepsilon_{y}\right)^{2}=\alpha_{z x}{ }^{2} \boldsymbol{\varepsilon}_{x}^{2}+\alpha_{z y}{ }^{2} \boldsymbol{\varepsilon}_{y}{ }^{2}$

For a spherical molecule, however:

Considering natural unpolarized light $\boldsymbol{\varepsilon}_{\mathrm{x}}{ }^{2}=\boldsymbol{\varepsilon}_{\mathrm{y}}{ }^{2}$
Ratio $\rho_{n}=\frac{I_{z}}{I_{y}}=\frac{\alpha_{z x}{ }^{2} \varepsilon_{x}{ }^{2}+\alpha_{z y}{ }^{2} \varepsilon_{y y}{ }^{2}}{\alpha_{y x}{ }^{2} \varepsilon_{x}{ }^{2}+\alpha_{y y}{ }^{2} \varepsilon_{y}{ }^{2}}=\frac{\alpha_{z x}{ }^{2}+\alpha_{z y}{ }^{2}}{\alpha_{y x}{ }^{2}+\alpha_{y y}{ }^{2}}$

$$
\text { Ratio } \rho_{n}=\frac{I_{z}}{I_{y}}=\frac{\alpha_{z \mathrm{x}}{ }^{2}+\alpha_{z \mathrm{y}}{ }^{2}}{\alpha_{y \mathrm{y}}{ }^{2}+\alpha_{y \mathrm{y}}{ }^{2}}=0 \text { as only the } \alpha_{\mathrm{ii}} \text { are non-zero }
$$

We can also choose to use polarized light. Defining the direction of propagation as the z-direction There are two cases:
Case 1: incident light is polarized along y . In this case: $\boldsymbol{\varepsilon}_{\mathrm{x}}=0$. We place the detector along $x$ and measure we observe the scattered light in a direction orthogonal to the polarization plane of the incident light to the oscillation direction of the incident light

$$
\mathrm{P}_{\mathrm{z}}=\alpha_{\mathrm{zy}} \mathrm{E}_{\mathrm{y}} \quad \text { Ratio }=\frac{I_{z}}{I_{y}}=\frac{\alpha_{\mathrm{zy}}{ }^{\mathrm{z}^{=}}}{\alpha_{\mathrm{yy}}{ }^{2}}=\rho_{\perp}
$$



Case 2: incident light is polarized along $x$. In this case: $\boldsymbol{\varepsilon}_{\mathrm{y}}=0$. We place the detector along $x$ and measure we observe the scattered light in a direction parallel to the polarization plane of the incident light to the oscillation direction of the incident light

$$
\begin{array}{lr}
\mathrm{P}_{\mathrm{z}}=\alpha_{\mathrm{zx}} \varepsilon_{\mathrm{x}} \\
\mathrm{P}_{\mathrm{y}}=\alpha_{\mathrm{yx}} \varepsilon_{\mathrm{x}} & \text { Ratio }=\frac{I_{z}}{I_{y}}=\frac{\alpha_{\mathrm{zx}}{ }^{2}}{\alpha_{\mathrm{yx}}{ }^{2}}=\rho_{\|}
\end{array}
$$



These expressions are only valid for scattering by a single molecule fixed in space. In reality, many molecules are present with all kinds of orientations of the polarizability tensor. Considering this distributions the equations a bit more complicated:
Using unpolarized light, the expressions are:
$\rho_{n}=\frac{6 \gamma_{0}{ }^{2}}{45 \alpha_{0}{ }^{2}+7 \gamma_{0}{ }^{2}}$ where $\alpha_{0}=\frac{1}{3}\left(\alpha_{x x}+\alpha_{y y}+\alpha_{z z}\right)$ and $\gamma_{0}{ }^{2}=\frac{1}{2}\left[\left(\alpha_{x x}-\alpha_{y y}\right)^{2}+\left(\alpha_{y y}-\alpha_{z z}\right)^{2}+\left(\alpha_{z z}-\alpha_{x x}\right)^{2}\right]+6\left(\alpha_{x y}{ }^{2}+\alpha_{y z}{ }^{2}+\alpha_{z x}{ }^{2}\right)$

Using polarized light as the incident light source, the expressions are:

$$
\begin{aligned}
& \rho_{\perp}=\frac{3 \gamma_{0}{ }^{2}}{45 \alpha_{0}^{2}+4 \gamma_{0}{ }^{2}} \\
& \rho_{\|}=1
\end{aligned}
$$

These expressions apply to Rayleigh scattering. $\boldsymbol{\alpha}_{\boldsymbol{0}}$ is never zero, because every molecule has electrons. For spherical molecules $\gamma_{0}$ is zero, which means that the depolarization ratios $\rho_{n}=\rho_{\perp}$ are zero
For the general case we have $6 / 7>\rho_{n}>0$ and $3 / 4>\rho_{\perp}>0$
For Raman spectroscopy the Stokes band are relevant: Analogous equations can be developed for $\boldsymbol{\alpha}_{\mathbf{0}^{\prime}}=\frac{d \boldsymbol{\alpha}_{0}}{d q}$ and $\boldsymbol{\gamma}_{\mathbf{0}}{ }^{\prime}=\frac{d \gamma_{0}}{d q}$
$\rho_{n}=\frac{6 \gamma_{0^{\prime}}{ }^{2}}{45 \alpha_{0}{ }^{\prime}+7 \gamma_{0^{\prime}{ }^{2}}}$ where $\alpha_{0}^{\prime}=\frac{1}{3}\left(\alpha_{x x}^{\prime}+\alpha_{y y}^{\prime}+\alpha_{z z}^{\prime}\right)$ and ${\gamma^{\prime}}_{0}{ }^{2}=\frac{1}{2}\left[\left(\alpha_{x x}^{\prime}-\alpha_{y y}^{\prime}\right)^{2}+\left(\alpha_{y y}^{\prime}-\alpha_{z z}^{\prime}\right)^{2}+\left(\alpha_{z z}^{\prime}-\alpha_{x x}^{\prime}\right)^{2}\right]+$ $6\left(\alpha^{\prime}{ }_{x y}{ }^{2}+\alpha^{\prime}{ }_{y z}{ }^{2}+\alpha_{z x}^{\prime}{ }^{2}\right)$

## Depolarization ratios for Raman bands

For each vibrational modes we can write a specific tensor for $\frac{d \alpha_{i j}}{d q}$ with corresponding isotropic and anisotropic components. In this case the isotropic component can be zero. This happens for those modes for which the polarizability does not change during the course of the vibration.

Interesting is also the case $\gamma_{0}{ }^{\prime}=\frac{d \gamma_{0}}{d q}=0$.
In this case the anisotropy of the polarizability does not change during the course of the vibration. This is the case of a totally symmetric vibrational mode. In this case $\rho_{n}=\rho_{\perp}$ are zero, i.e. the depolarization ratio is zero. If we conduct the Raman spectrocscopy with polarized incident light, the scattered Raman band will also be polarized even if the molecule by itself is not spherically symmetric. But it only applies for the totally symmetric vibrational modes $A_{1}, A_{g}$ or $A_{1 g}$ modes.

The Case $\gamma_{0}{ }^{\prime}=\frac{d \gamma_{0}}{d q} \neq 0 \quad$ applies to any other, not totally symmetric mode. In this case $\rho_{\mathrm{n}}=6 / 7$ invariably.

$$
\frac{6<m\left|\gamma_{0}\right| n>\left.\right|^{2}}{45<m\left|\alpha_{0^{\prime}}\right| n>^{2}+7<m\left|\gamma_{0^{\prime}}\right| n>^{2}}=\frac{6<m\left|\gamma_{0}{ }^{\prime}\right| n>\left.\right|^{2}}{45<m \mid\left(\alpha{ }_{x x}+\alpha_{y y}{ }_{y y}+\alpha_{z z}{ }_{z z}\left|n>^{2}+7<m\right| \gamma_{0^{\prime}} \mid n>^{2}\right.}
$$

$<m\left|\left(\alpha^{\prime}{ }_{x x}+\alpha^{\prime}{ }_{y y}+\alpha_{z z}^{\prime}\right)\right| n>=0$ for all
Vibrational modes that are not totally symmetric

$$
\begin{array}{ll}
x^{2}+y^{2}+z^{2}=r^{2} & \text { smmetric representation } \\
& \text { such as } A_{1}
\end{array}
$$

## Example $\mathrm{CCl}_{4}$


$\mathrm{T}_{\mathrm{d}}$
tetrahedral

$v_{1}$ symm stretch
$\mathrm{a}_{1}\left(\mathrm{R}_{\mathrm{p}}\right)$

$\mathrm{v}_{2}$ bend
$\mathrm{e}\left(\mathrm{R}_{\mathrm{d}}\right)$

$v_{3}$ stretch
$\mathrm{t}_{2}\left(\mathrm{IR}, \mathrm{R}_{\mathrm{d}}\right)$

$v_{4}$ bend $\mathrm{t}_{2}\left(\mathrm{IR}, \mathrm{R}_{\mathrm{d}}\right)$

[^0]
polarized : all bands are observed depolarized The band at $450 \mathrm{~cm}^{-1}$ is missing The band at $450 \mathrm{~cm}^{-1}$ is missing, as it is not depolarized, i.e. there is no z-polarization component in the scattered light emitted in the x-direction. It therefore originates from a totally symmetric mode with $\gamma_{0}{ }^{\prime}=0$.

## Instrumentation

## Dispersive Raman spectroscopy



Typical excitation wavelengths:
408 nm (Ar), 532 nm (YAG frequency doubled), $632 \mathrm{~nm}(\mathrm{He} / \mathrm{Ne}), 785 \mathrm{~nm}$ (semicond) nm using different lasers: $\boldsymbol{I}^{\sim} \nu^{4}$
Preferred for high-temperature work


Wavelength: 1064 nm (Nd:YAG laser) Preferred for sensitive samples, Preferred for fluorescent samples Particularly organic compounds. Not good for HT work

Important experimental variants:

Resonance Raman (involving optical transition)
Dramatically increased signal/noise ratio for those molecules involved in the transition
Surface enhanced Raman (analyte adsorbed on metal clusters) Rotational Raman Spectroscopy

## Chemical applications:

Informational content: frequencies, force constants, reduced masses of the $3 \mathrm{~N}-6$ normal modes Spectra of gases: rotational fine structure, molecular properties

For molecules, it is often possible to decompose the complex vibrational motion into

- Valence modes: one atom vibrates against the remainder of the molecule (bond stretching)
- Framework modes: giving „fingerprint identification!

Valence modes: atom $A$ vibrates against the remainder of the molecule, $R$ : $m_{A} \ll m_{R}$

$$
\omega_{\mathrm{i}}=2 \pi v_{\mathrm{i}}=\sqrt{\mathrm{k}_{\mathrm{i}} / \mu_{\mathrm{i}}} \quad \mu_{\mathrm{i}}=\frac{m_{A} \times m_{R}}{m_{A}+m_{R}} \sim \mathrm{~m}_{\mathrm{A}}
$$

The reduced mass is close to the mass of the single atom.
Isotope effect for identification, based on the mass effect:
$\frac{\mathrm{v}(\mathrm{H})}{\mathrm{v}(\mathrm{D})}=\sqrt{\mathrm{m}_{D} / m_{H}}=\sqrt{2}$
Instead of frequencies, one commonly specifies wave numbers (in $\mathrm{cm}^{-1}$ ): $v=\mathrm{c} / \lambda \rightarrow 1 / \lambda=\frac{\nu}{c}$
Typical valence mode wave numbers in $\mathrm{cm}^{-1}$ (note the mass dependence)

O-H: 3500
C-H; 2900-3100
N-H: 3000
S-H: 2500
$\mathrm{C}=\mathrm{C}: 1600$
C=O: 1500-1750
C=C, C=N: 2200
C=S: 1100

Effect of the
Bond order

## An application: Raman spectra of phosphate glasses



Fig. 4. The unpolarized Raman spectra of sodium ultra- and metaphosphate glasses.

## Hydrogen bond: OH-stretch and O‥O distance




## Water Speciation in Minerals and Glasses by NIR spectroscopy

Near-infrared region: overtone and combination bands


## Raman Spectroscopy of Lithium borate glasses



$1480 \mathrm{~cm}^{-1}$


Boroxol ring
$808 \mathrm{~cm}^{-1}$


Pentaborate unit




Metaborate chain
$1480 \mathrm{~cm}^{-1}$


Diborate unit


Triborate unit
$770 \mathrm{~cm}^{-1}$


Dipentaborate unit


Diborate unit


Tetraborate unit

## IR spectra of gases: rotational fine structure

In the IR spectra of dilute gases one frequently observes multi-peak patterns, which arise from transitions originating from and arriving at different energy levels associated with the rotational motion of the molecules involved. The simplest quantum mechanical model system for this motion is the 3D free rigid rotor. For diatomic molecule the model is called „Particle on a sphere". One atom in the center, the other one on the surface of the sphere. „free" means: no potential energy. Any position on the sphere is equally probable.
"rigid" means: the radius of the sphere is not affected by the rotational energy.
$\hat{H}=-\frac{\hbar^{2}}{2 I}\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial}{\partial \theta}\right)+\frac{1}{\sin ^{2} \theta} \frac{\partial^{2}}{\partial \varphi^{2}}\right]$
$\boldsymbol{I}=\mu \boldsymbol{r}^{\mathbf{2}} \quad$ Moment of inertia of a two-atomic molecule.
Solution of the Schrödinger equation through separation of variables:

## $\Psi=\Theta(\theta) \times \Phi(\phi)$ with the eigenvalues

$$
E(\ell)=\frac{\hbar^{2}}{2 I} \ell(\ell+1)=\frac{L^{2}}{2 I}
$$

This corresponds to the quantization of the angular momentum vector

$$
\begin{aligned}
& \left|\mathrm{L}^{2}\right|=\ell(\ell+1) \hbar^{2} \\
& \mathrm{~L}_{2}=\mathrm{m}_{\ell} \hbar \text {, with } \mathrm{m}_{\ell} \varepsilon\{\ell, \ell-1, \ldots . .-\ell\}
\end{aligned}
$$

## Size quantization <br> Orientation quantization



The eigenfunctions of the rigid rotor are known as the spherical harmonics
TABLE 4.3: The first few spherical harmonics, $Y_{l}^{m}(\theta, \phi)$.

$$
\begin{array}{ll}
Y_{0}^{0}=\left(\frac{1}{4 \pi}\right)^{1 / 2} & Y_{2}^{ \pm 2}=\left(\frac{15}{32 \pi}\right)^{1 / 2} \sin ^{2} \theta e^{ \pm 2 i \phi} \\
Y_{1}^{0}=\left(\frac{3}{4 \pi}\right)^{1 / 2} \cos \theta & Y_{3}^{0}=\left(\frac{7}{16 \pi}\right)^{1 / 2}\left(5 \cos ^{3} \theta-3 \cos \theta\right) \\
Y_{1}^{ \pm 1}=\mp\left(\frac{3}{8 \pi}\right)^{1 / 2} \sin \theta e^{ \pm i \phi} & Y_{3}^{ \pm 1}=\mp\left(\frac{21}{64 \pi}\right)^{1 / 2} \sin \theta\left(5 \cos ^{2} \theta-1\right) e^{ \pm i \phi} \\
Y_{2}^{0}=\left(\frac{5}{16 \pi}\right)^{1 / 2}\left(3 \cos ^{2} \theta-1\right) & Y_{3}^{ \pm 2}=\left(\frac{105}{32 \pi}\right)^{1 / 2} \sin ^{2} \theta \cos \theta e^{ \pm 2 i \phi} \\
Y_{2}^{ \pm 1}=\mp\left(\frac{15}{8 \pi}\right)^{1 / 2} \sin \theta \cos \theta e^{\dot{\Sigma i \phi}} & Y_{3}^{ \pm 3}=\mp\left(\frac{35}{64 \pi}\right)^{1 / 2} \sin ^{3} \theta e^{ \pm 3 i \phi}
\end{array}
$$

## Spherical Harmonics:

## Rotational Spectroscopy

## Rigid free rotor

$$
\begin{aligned}
& \left.E(\ell)=\frac{\hbar^{2}}{2 l} \ell \ell+1\right)=\frac{L^{2}}{2 l} \\
& E(\ell) / h=B \ell(\ell+1)
\end{aligned}
$$

## Non-rigid free rotor (centrifugal distortion)

with $\mathbf{B}=\frac{\hbar}{4 \pi I}$ in units of $\mathrm{s}^{-1}$
with $\mathbf{B}=\frac{\hbar}{4 \boldsymbol{c} \pi \boldsymbol{I}}$ in units of $\mathrm{cm}^{-1}$

$$
\mathrm{E}(\ell) / \mathrm{h}=\mathrm{B} \ell(\ell+1)-\mathrm{D} \ell^{2}(\ell+1)^{2}
$$

Centrifugal distortion $\sim 1 /($ bond rigidity)
i.e. the vibrational force constant

$$
D=4 B^{3} / v_{0}^{2}
$$

Interaction with electromagnetic wave only possible for molecules with permanent electrical dipole

Linear molecule: $\Delta l= \pm 1$, rotation about perpendicular axes Spherical top: no interaction with the electromagnetic wave
Symmetric top: $\mathrm{E}_{\mathrm{rot}} / \mathrm{h}=\mathrm{BJ}(\mathrm{J}+1)+(\mathrm{A}-\mathrm{B}) \mathrm{K}^{2}$

$$
\text { with } \mathrm{B}=\frac{\hbar}{4 \pi I_{b}} \text { and } \mathrm{A}=\frac{\hbar}{4 \pi I_{a}}
$$

$\mathrm{J}=$ quantum number of total angular momentum involving rotation about all axes. K = quantum number of angular momentum describing rotation about the principal axis.

$I_{a}=0, I_{b}=I_{c}$ linear

K can adopt $2 \mathrm{~J}+1$ values within $\{\mathrm{J}, \mathrm{J}-\mathbf{1}, \mathrm{J}-\mathbf{2}, . . . . . \mathrm{J}\}$ (sense of rotation), levels for $\mathrm{K}>0$ are doubly degenerate; $\mathrm{J}=0, \mathrm{~K}=0$ ground state

## Selection rules in rotational absorption spectroscopy:

Transition Probability $\sim{ }^{\sim} Y^{\prime}{ }_{m}(a)|\mu| Y_{m}{ }_{m}(b)>$
$\mu \sim x, y, z$ has odd character
$\quad-\Delta \ell=\ell^{\prime}-\ell= \pm 1$


## Diatomic molecule (rigid rotor)

## Diatomic molecule (non-rigid rotor)

Selection rule: $\Delta \ell=\ell^{\prime}-\ell= \pm 1$


## Spectra of linear triatomic molecules: example $\mathrm{O}=\mathrm{C}=\mathrm{S}$



$$
I=m_{o} r_{0}^{2}+m_{c} r_{c}^{2}+m_{s} r_{s}^{2}
$$

one observable: I (moment of inertia), but two unknowns: $r_{c o}$ and $r_{c S}$

$$
\begin{aligned}
& m_{o} r_{o}+m_{c} r_{c}=m_{s} r_{s} \\
& r_{o}=r_{c o}+r_{c} \\
& r_{s}=r_{c s}-r_{c}
\end{aligned}
$$

$$
m_{o}\left(r_{c o}+r_{c}\right)+m_{c} r_{c}=m_{s}\left(r_{c s}-r_{c}\right)
$$

$$
r_{c}\left(m_{o}+m_{c}+m_{s}\right)=m_{s} r_{c s}-m_{o} r_{c o}
$$

$$
r_{c}=\frac{m_{s} r_{c S}-m_{0} r_{c O}}{m_{0}+m_{c}+m_{s}}=\frac{m_{s} r_{c s}-m_{0} r_{c O}}{M}
$$

$$
I=m_{0} r_{0}^{2}+m_{c} r_{c}^{2}+m_{s} r_{s}^{2}
$$

$$
\begin{aligned}
& \mathrm{I}=\mathrm{m}_{0}\left(\mathrm{r}_{\mathrm{co}}+\mathrm{r}_{\mathrm{c}}\right)^{2}+\mathrm{m}_{\mathrm{c}} r_{\mathrm{c}}{ }^{2}+\mathrm{m}_{\mathrm{s}}\left(\mathrm{r}_{\mathrm{cs}}-\mathrm{r}_{\mathrm{c}}\right)^{2} \\
& I=m_{0}\left(r_{c o}{ }^{2}+2 r_{c o} r_{c}+r_{c}{ }^{2}\right)+m_{c} r_{c}^{2}+m_{s}\left(r_{c s}{ }^{2}-2 r_{c s} r_{c}+r_{c}^{2}\right) \\
& I=M r_{c}^{2}+2 r_{c}\left(m_{o} r_{c o}-m_{s} r_{c s}\right)+m_{o} r_{c o}{ }^{2}+m_{s} r_{c s}{ }^{2} \\
& I=\frac{\left(m_{s} r_{c s}-m_{0} r_{c o}\right)^{2}}{M}+2 \frac{m_{s} r_{c s}-m_{0} r_{c o}}{M}\left(m_{0} r_{c o}-m_{s} r_{c s}\right) \\
& +m_{0} r_{c o}^{2}+m_{s} r_{c s}{ }^{2}
\end{aligned}
$$

$$
\begin{aligned}
& I=\frac{\left(m_{s} r_{c s}-m_{0} r_{c o}\right)^{2}}{M}+2 \frac{\left(m_{s} r_{c s}-m_{0} r_{c o}\right)}{M}\left(m_{0} r_{c o}-m_{s} r_{c s}\right)+m_{0} r_{c o}^{2}+m_{s} r_{c s}^{2} \\
& I=m_{0} r_{c o}^{2}+m_{s} r_{c s}^{2}-\frac{\left(m_{0} r_{c O}-m_{s} r_{c S}\right)^{2}}{M}
\end{aligned}
$$

We then can get the two unknown interatomic distances by studying different isotopologues of the molecule, for Example by measuring samples with different O isotopes; the distances are mass -independent

$$
\left.\begin{array}{ll}
I(O C S)=m_{0} r_{c o}^{2}+m_{s} r_{c s}{ }^{2}-\frac{\left(m_{0} r_{c c}-m_{s} r_{c s}\right)^{2}}{M} & \text { Experiment with oxygen-16 } \\
I(O C S)=m_{0} r_{c 0}^{2}+m_{s} r_{c s}^{2}-\frac{\left(m_{0} r_{c 0}-m_{s} r_{c s}\right)^{2}}{M} & \text { Experiment with oxygen-18 }
\end{array}\right] \begin{aligned}
& \begin{array}{l}
\text { 2 equations with 2 } \\
\text { unknowns }
\end{array}
\end{aligned}
$$

## Symmetric top molecule (rigid rotor)

$E_{\text {rot }} / h=B J(J+1)+(A-B) K^{2}$ with $B=\frac{\hbar}{4 \pi I_{b}}$ and $A=\frac{\hbar}{4 \pi I_{a}}$

- $\mathrm{J}=$ quantum number of total angular momentum involving rotation about all axes.
- $K$ = quantum number of angular momentum describing rotation about the principal axis (defined by $I_{a}$ ).
- K can adopt $2 \mathrm{~J}+1$ values within $\{\mathrm{J}, \mathrm{J}-1, \mathrm{~J}-2, . . . .-\mathrm{J}\}$ (sense of rotation)


## Selection rule: $\Delta \mathrm{J}=\mathrm{J}$ - $\mathrm{J}= \pm 1$ <br> $$
\Delta K=0
$$

## $\Delta \mathrm{E}(\mathrm{J}) / \mathrm{h}=2 \mathrm{~B}(\mathrm{~J}+1)$

$\Delta K=0$ means that the rotation around the top axis cannot interact with the electromagnetic wave. This is because there is no dipole moment of the molecule (and no change thereof) when rotation occurs $\perp$ rotation axis

## Rotational Raman spectra

$$
\text { Transition Probability } \sim<Y_{m}^{\prime}(a)|\alpha| Y_{m}^{\prime}(b)>
$$

Linear molecules: the allowed transitions are with $\Delta \ell=0, \pm 2$
Symmetrical top molecules: $\Delta \mathrm{J}=0, \pm 1, \pm 2, \Delta \mathrm{~K}=0$
$\Delta J= \pm 2$, for rotational states $K=0$
Stokes and anti-Stokes lines have comparable intensities
Spherical top molecules: no Rotation Raman effect observed, as the rotation does not create a change in polarizability.


Symmetrical top




As the polarizability tensor has totally symmetric transformation properties, only even-> even and odd-> odd transitions are allowed: $\Delta \mathrm{J}= \pm \mathbf{2}$
$\Delta K=0$ means that the rotation around the top axis cannot interact with the electromagnetic wave.
$\Delta \mathrm{J}=0$ signifies the Rayleigh band.

## Generation of electromagnetic waves

General principle: oscillation of charges -> emission of electromagnetic waves $m \ddot{\mathrm{x}}+\mathrm{fx}=\mathbf{0}->$


Ro-vibrational energy levels (in frequency units)
$E(n, \ell) / h=(n+1 / 2) v_{0}+B \ell(\ell+1)$
For the fundamental vibrational transition we have the selection rules $\Delta \mathrm{n}=\mathbf{1}$

$$
\Delta \ell=\ell^{\prime}-\ell= \pm 1
$$

R-branch: $\Delta \ell=1$
$\Delta \mathrm{E}(\mathrm{n}, \ell) / \mathrm{h}=\mathrm{v}_{0}+2 \mathrm{~B}(\ell+1)$
Q-branch: $\Delta \ell=0$ forbidden
P branch: $\Delta \ell=-1$
$\Delta E(n, \ell) / h=v_{0}+-2 B \ell$


This leads to a multi-peak pattern
$510 \times 564$ with peaks spaced at 2B


Intensity distribution follows the Boltzmann law $I(I)=(2 \ell+1) \exp -E_{\ell} / \mathrm{K}_{\mathrm{B}} \mathrm{T}$. Band with maximum intensity depends on temperature


Differences in the vibrational frequencies of $\mathrm{H}-{ }^{35} \mathrm{Cl}$ and $\mathrm{H}_{-}{ }^{37} \mathrm{Cl}$ detectable
The different line spacings between the P - and the R -branch are a Consequence of the vibrational anharmonicity (breakdown of the Born-Oppenheimer approximation).

## Complications and special cases

1. Centrifugal distortion: The value of $B$ decreases with increasing quantum number $\ell$ This complication is treated by a power expansion of Energy in terms of $\ell$. $E(\ell) / h=B \ell(\ell+1)-D \ell^{2}(\ell+1)^{2}$ Spacing between adjacent peaks decreases with increasing $\ell$.
2. Breakdown of the Born-Oppenheimer Approximation: The value of $B$ depends on the vibrational state; due to bond lengthening (anharmonicity) in the $\mathrm{n}_{\mathrm{v}}=1$ state: $B_{1}<B_{0}$ Peaks of the R-branch are more closely spaced than those of the P-branch.
3. Anharmonicity of vibrations necessitates more in-depth analysis.
4. Concentrated samples (high pressure): loss of resolution due to intermolecular collisions („Bjerrum band")

## Linear polyatomic molecules:

Selection rules depend on the direction of vibration relative to the $\mathrm{C}_{\infty}$ axis


Figure 3.12 Spectrum of the symmetric stretching vibration of the HCN molecule showing the $P$ and $R$ branch lines.
perpendicular


Figure 3.14 Spectrum of the bending mode of the HCN molecule showing the $P Q R$ structure. The broad absorption centred at $800 \mathrm{~cm}^{-1}$ is due to an impurity
C.N. Banwell, Fundamentals of Molecular Spectroscopy, Mc. Graw Hill 1983

## Non-linear Molecules




Figure 3.17 The parallel stretching vibration, centred at $1251 \mathrm{~cm}^{-1}$, of the symmetric top molecule methyl iodide, $\mathrm{CH}_{3} \mathrm{I}$, showing the typical $P Q R$ contour.

Symmetric top molecule: $\mathrm{E}_{\mathrm{rot}} / \mathrm{h}=\mathrm{BJ}(\mathrm{J}+1)+(\mathrm{A}-\mathrm{B}) \mathrm{K}^{2}$ with $\mathrm{B}=\frac{\hbar}{4 \pi I_{b}}$ and $\mathrm{A}=\frac{\hbar}{4 \pi I_{a}}$ In this description J is the quantum number of total angular momentum involving rotation about all axes While $K$ is the quantum number of angular momentum describing rotation about the principal axis. $K$ can adopt $2 \mathrm{~J}+1$ values within $\{\mathrm{J}, \mathrm{J}-1, \mathrm{~J}-2, . . . .-\mathrm{J}\}$.
a) Vibration || to the symmetry axis: $\Delta \mathrm{J}=0, \pm 1, \Delta \mathrm{~K}=0$ (no change in rotational state): regular PQR branch spectrum
b) Vibration $\perp$ to the symmetry axis: $\Delta J=0, \pm 1, \Delta K= \pm 1$ : complex spectrum, $Q$-branch exhibits splitting


[^0]:    * IR is infrared active, R is Raman active, p is polarized, and d is depolarized, e modes are doubly degenerate, t modes are triply degenerate.

