Rotational Raman spectroscopy

Raman scattering could also appears when molecule change their rotational energy:

- Pure rotational Raman spectra
- Roto-vibrational Raman spectra

‣ The ***first requirement***: **the polarizability of the molecule must be anisotropic** (it must depend on the orientation of the molecule).

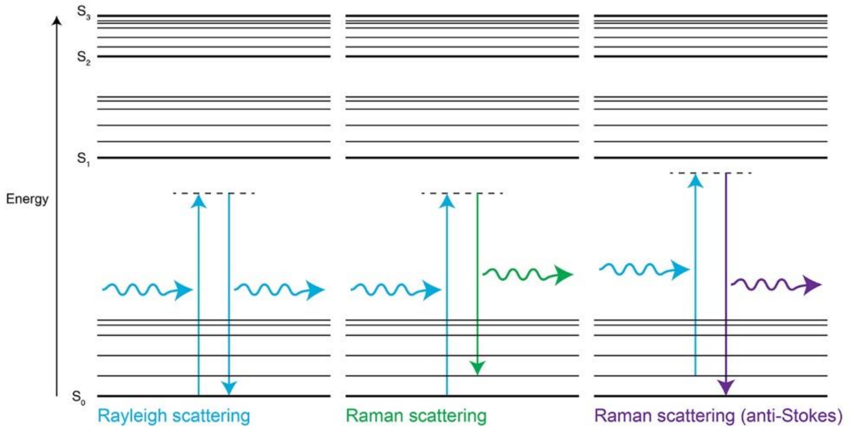
‣ Raman spectroscopy is less restrictive than pure rotational spectroscopy:

Linear symmetric molecules **do have rotational Raman spectra.**

Linear symmetric molecules (CO_2, O_2, N_2) do not have pure rotational spectra (do not possess permanent dipole moments).

‣ **Spherical top molecules** such as CH_4 and SF_6 still **do not have rotational Raman spectra** as they do not have an anisotropic polarizability.

Raman selection rules

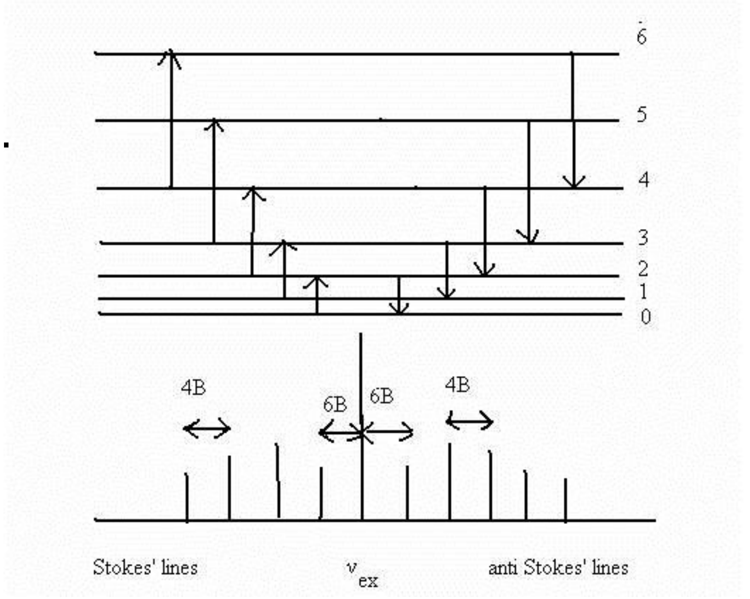


Vibrational Raman:

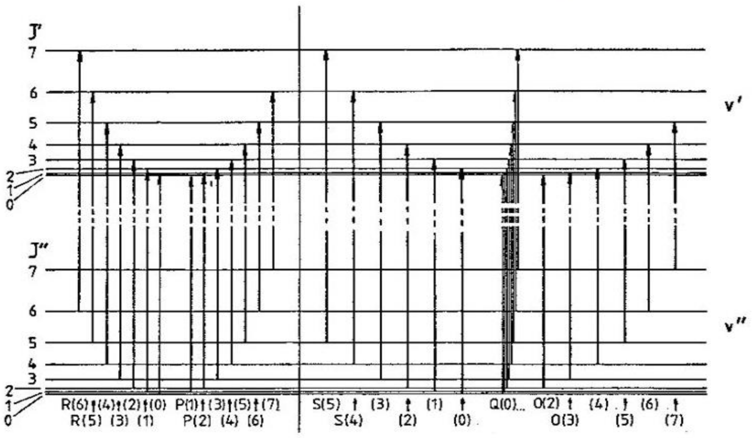
- ► *Polarisability of molecule must change* during a particular vibration (gross selection rule)
- ► **Δv = ± 1** (vibrational quantum number) (specific selection rule)

Rotational Raman:

- ► Anisotropic polarisability: the polarizability of the molecule must depend on the molecule orientation (i.e. molecule must not be spherically symmetric: CH_4, SF_6, ...)
- ► **ΔJ = ± 2** (rotational quantum number) (specific selection rule)



Vibration-Rotation Spectra



Infrared spectrum
ΔJ = ±1

Raman spectrum
ΔJ = 0 , ±2

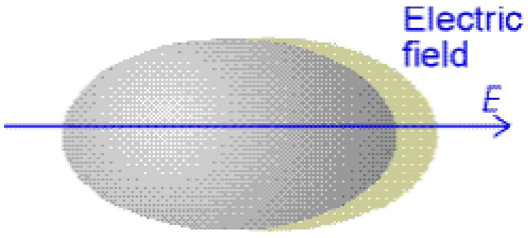
Roto-vibrational Raman:

- ► Combined: anisotropic polarizability which polarizability change during vibration
- ► **Δv = ± 1, ΔJ = 0, ± 2**

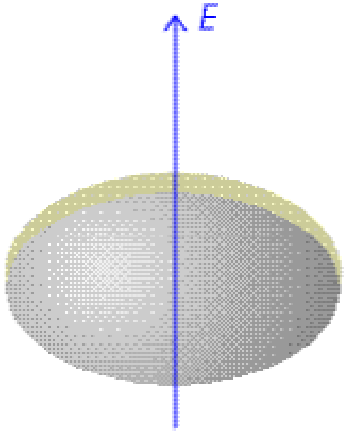
Polarizability of molecules during rotation

- An electric field applied to a molecule results in its distortion, and the distorted molecule acquires a contribution to its dipole moment (even if it is nonpolar initially).

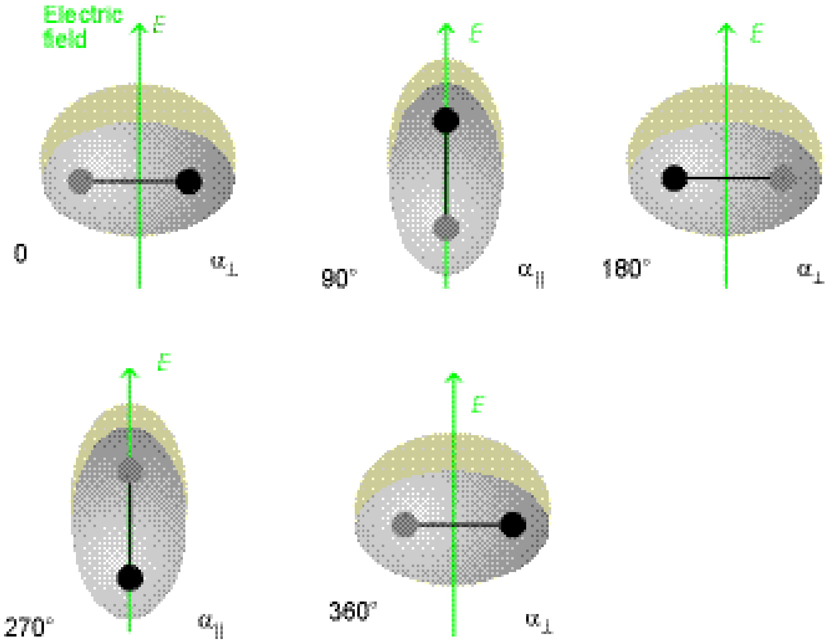
  The polarizability may be different when the field is applied (a) parallel or (b) perpendicular to the molecular axis (or, in general, in different directions relative to the molecule); if that is so, then the molecule has an **anisotropic polarizability**.



(a)



(b)



- *The distortion induced in a molecule by an applied electric field returns to its initial value after a rotation of only 180°* (that is, twice a revolution).

  This is the origin of the $\Delta J = \pm 2$ selection rule in rotational Raman spectroscopy.

Classical theory of rotational Raman spectroscopy

The amplitude of the oscillating electric field can be represented by:

$$E(t) = E_0 \cos \omega t = E_0 \cos 2\pi\nu_{laser} t$$

The variation of polarizability during rotation:

$$\alpha(t) = \alpha_0 + \alpha_1 \cos 2\pi\ (2\nu_{rot})t$$

Dipole moment will change according to:

$$\mu(t) = \alpha(t) \cdot E(t) = [\alpha_0 + \alpha_1 \cos 2\pi\ (2\nu_{rot})t][E_0 \cos 2\pi\nu_{laser} t]$$

Using a trigonometric formula (cos(a) · cos(b) = 1/2[cos(a+b) + cos(a-b)]), the dipole moment can be expressed like:

$$\mu(t) = \underset{\text{Rayleight}}{\alpha_0 E_0 \cos 2\pi\nu_{laser} t} + \underset{\text{Stokes}}{1/2\alpha_1 E_0 \cos 2\pi(\nu_{laser} - 2\nu_{rot})t]} + \underset{\text{Anti-Stokes}}{1/2\alpha_1 E_0 \cos 2\pi(\nu_{laser} + 2\nu_{rot})t]}$$

The rotation of the molecule leads to a periodic modulation of the dipole moment induced by e field of the laser, and those to a modulation of the frequency of the scattered radiation (with $2\nu_{rot}$). The additional lines accompanying the Rayleight signal occurs at spacing corresponding to twice the rotational frequency.

Quantum theory of rotational Raman spectroscopy

The classical explanation for the occurrence of the doubled rotational frequency in the spacing of the rotational Raman lines is reproduced in quantum mechanics in terms of modified selection rules which correspond to a two phonon process.

The quantum-mechanical treatment of rotational Raman effect (inelastic photon scattering, accompanied by the uptake or release of rotational quanta) leads to the selection rule **$\Delta J = \pm 2$** in the case of the linear rotor.

Pure rotational energy levels of **linear molecules** are:

$$E_J = hc[BJ(J+1) - DJ^2(J+1)^2] \quad J = 0, 1, 2, \ldots$$

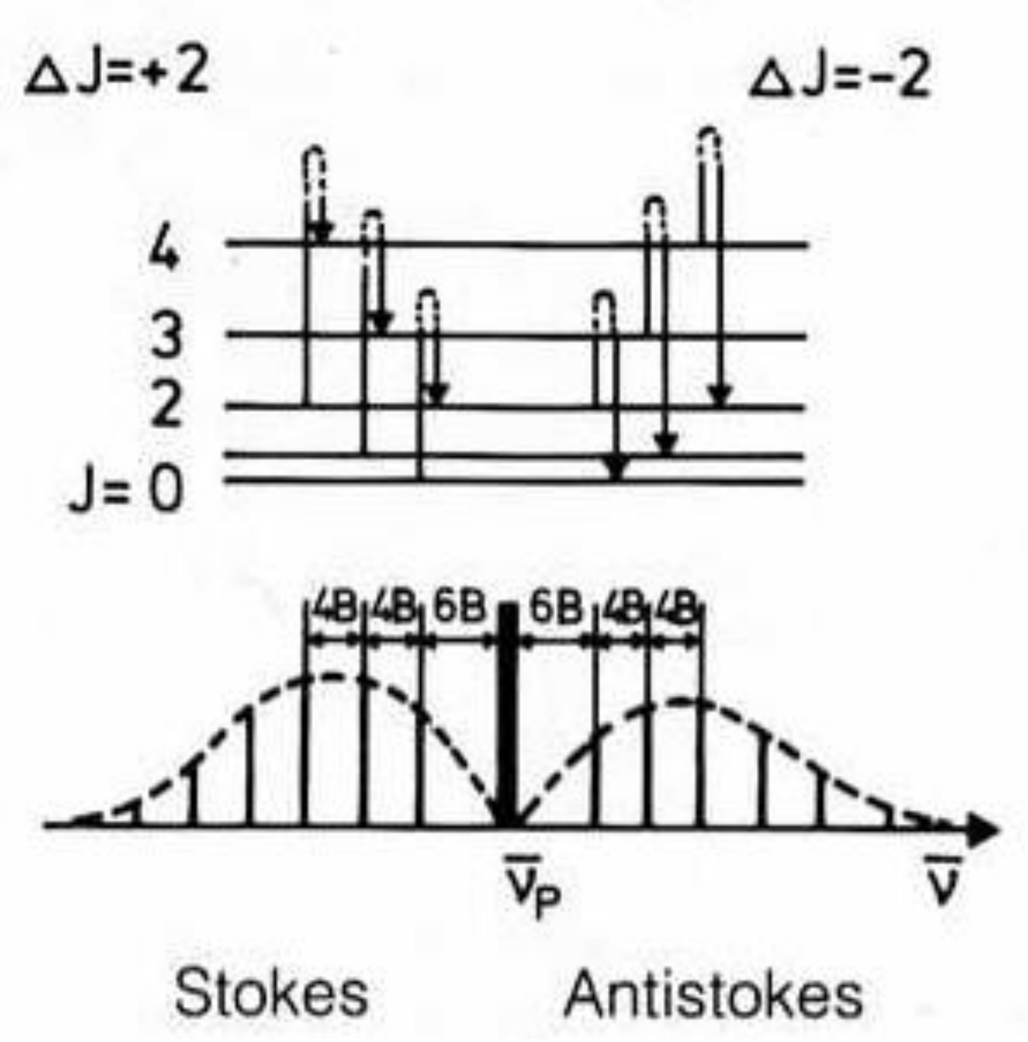
In Raman spectroscopy, *the precision of the measurements does not justify the retention of the term involving D*, the centrifugal distortion constant, so that the above expression simplifies to:

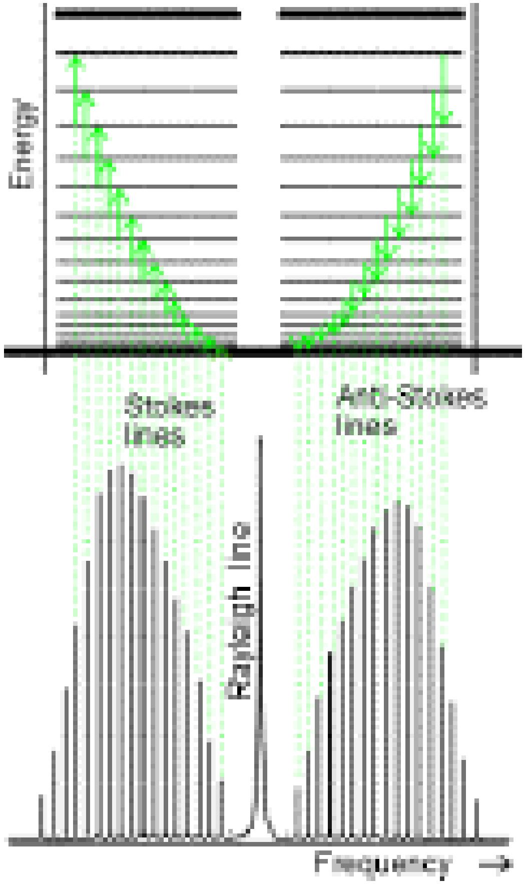
$$E_J = hcBJ(J+1)$$

In rotational Raman, for a linear molecule, the selection rule for J is: **$\Delta J = \pm 2$**
(as opposed to $\Delta J = \pm 1$ in pure rotational spectroscopy)

If $\Delta J = 0$ we obtaine Rayleigh line!

The rotational Raman selection rules: **Δ *J* = ±2**





The form of a typical rotational Raman spectrum.

$$\boxed{E_J = hcBJ(J+1)}$$

Pure rotational Raman spectrum

$E_0 = 0$

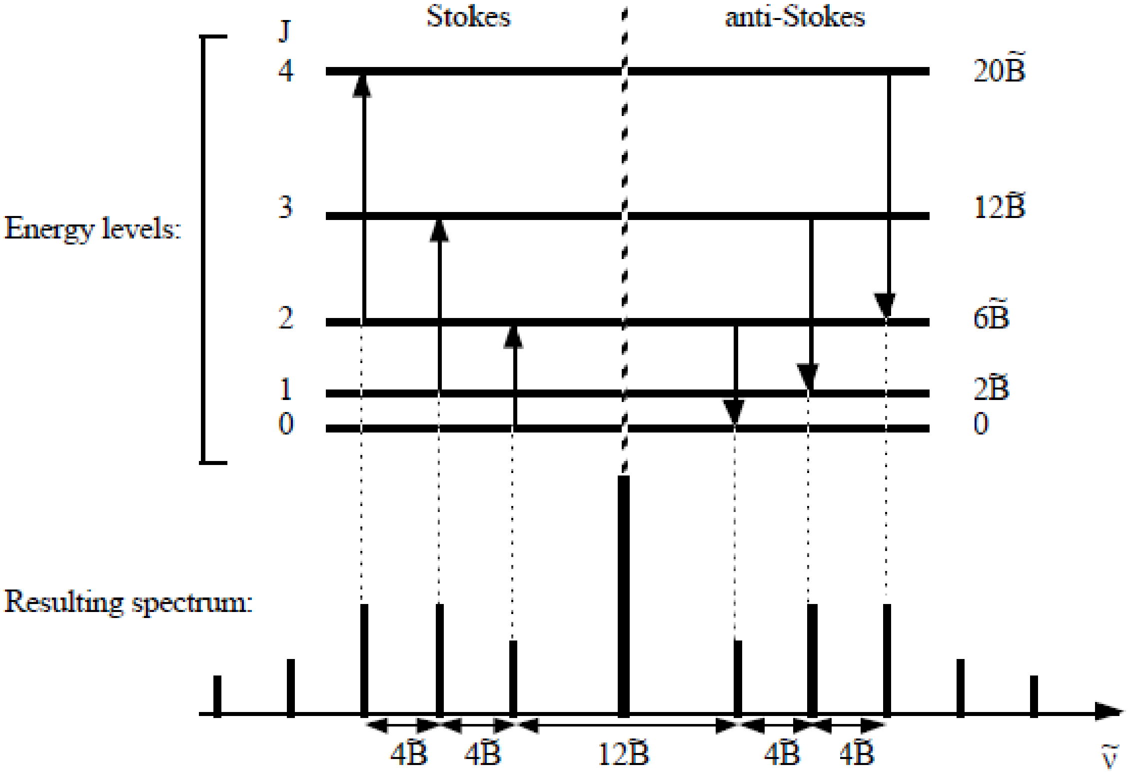
$E_1 = 2Bhc$

$E_2 = 6Bhc$

$E_3 = 12Bhc$

$E_4 = 20Bhc$

$E_5 = 30Bhc$



The lines intensity follow the rotational levels population!

Rayleigh	$\nu_{Ray} = \nu_{laser}$	
Stokes	$\nu_{Stokes} = \nu_{laser} - \nu_{rot}$	the molecule gain rotational energy, $\Delta J = +2$
Anti-Stokes	$\nu_{AntiStokes} = \nu_{laser} + \nu_{rot}$	the molecule lose rotational energy, $\Delta J = -2$

$E_J = hcBJ(J+1)$ J - the rotational quantum number of initial state

The wavenumber of the Raman rotational transition (**Raman Shift**):

Stokes $\bar{\nu}_{Rot} = \frac{1}{hc}(E_{J+2} - E_J) = 2B(2J+3) \quad J = 0,1,2\ldots \quad \Delta J = 2$

Anti-Stokes $\bar{\nu}_{Rot} = \frac{1}{hc}(E_J - E_{J-2}) = 2B(2J-1) \quad J = 2,3,4\ldots \quad \Delta J = -2$

The wavenumber of the Raman rotational **scattered radiation**:

Stokes: $\bar{\nu}_{(J\to J+2)} = \bar{\nu}_{laser} - 2B(2J+3) \quad J = 0,1,2\ldots$

Anti-Stokes: $\bar{\nu}_{(J\to J-2)} = \bar{\nu}_{laser} + 2B(2J-1) \quad J = 2,3,4\ldots$

Stokes:

$\bar{\nu}_0 = \bar{\nu}_{laser} - 6B$

$\bar{\nu}_1 = \bar{\nu}_{laser} - 10B$

$\bar{\nu}_2 = \bar{\nu}_{laser} - 14B$

Anti-Stokes:

$\bar{\nu}_2 = \bar{\nu}_{laser} + 6B$

$\bar{\nu}_3 = \bar{\nu}_{laser} + 10B$

$\bar{\nu}_4 = \bar{\nu}_{laser} + 14B$

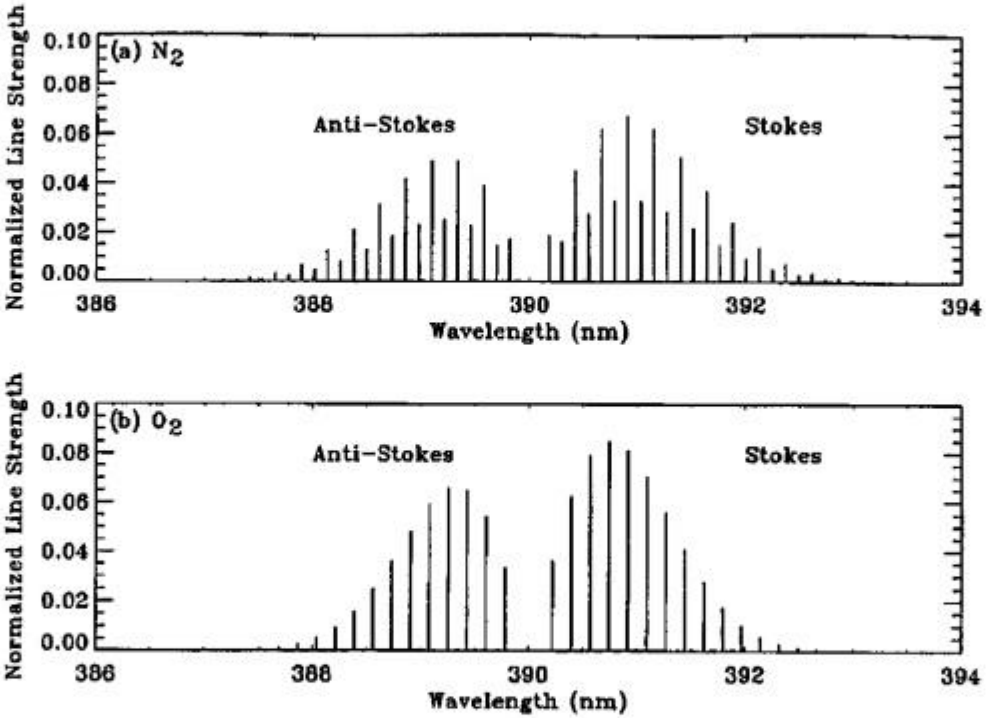
The lines (in Sokes and anti-Stokes branches) are spaced with **4B**!

First lines from Stokes and Anti-Stokes branches are spaced with **6B** relative to Rayleigh line!

Intensity alternation of the rotational Raman lines

- the result of nuclear statistics (sometime missing lines!)

- the result of symmetry



Nuclear spin statistics determine whether or not rotational levels in symmetric molecules actually exist!

The *Pauli Principle*: "*Any acceptable wavefunction must be anti-symmetric with respect to the exchange of two identical fermions* and *totally symmetric with respect to the exchange of two identical bosons*"

If the mass number is even: I is integral such nuclei are Bosons (2k)
odd: I is half-integral such nuclei are Fermions (2k+1)

I - the nuclear quantum number (corresponding to nuclear spin angular momentum).

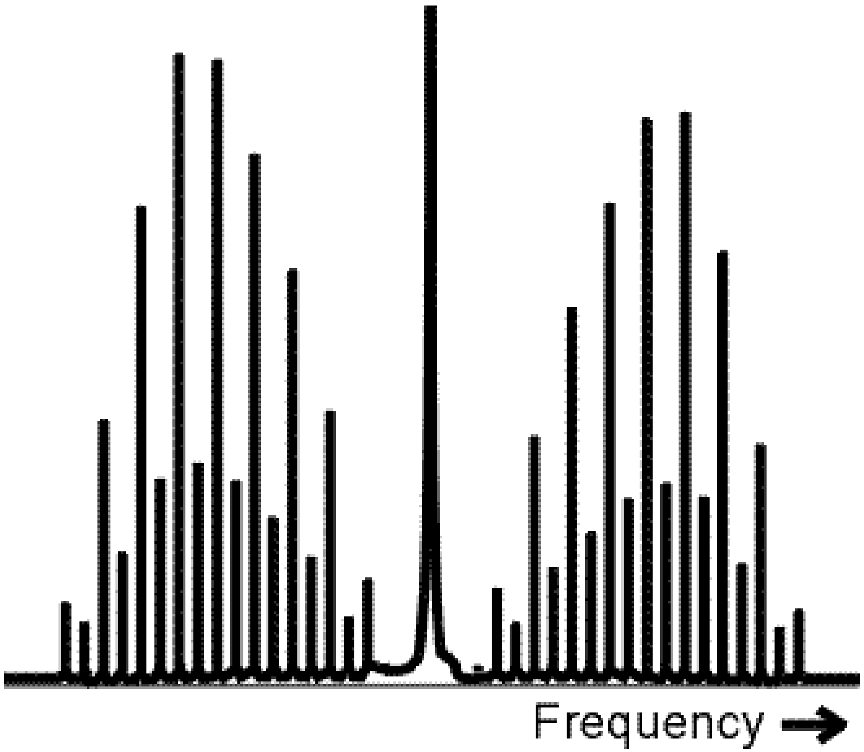
The nuclear spin can have an important influence on the appearance of rotational spectra of **molecules with a center of inversion**.

Nuclear spin statistics must be taken into account whenever a **rotation interchanges identical nuclei**.

Following the Pauli Principle:

a **system of fermions** (particles with half-integer spin) has to be **anti-symmetric** with respect to exchange of the nuclei (negative parity),

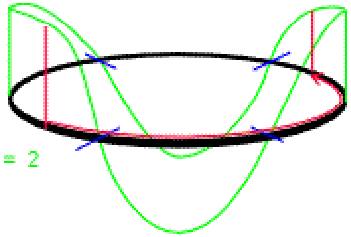
a **system of bosons** (particles with integral spin) has to be **symmetric** with respect to exchange of the nuclei(positive parity).



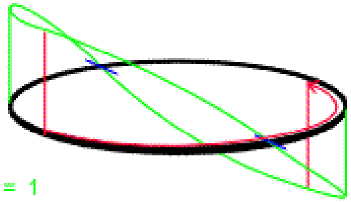
- The rotational Raman spectrum of a diatomic molecule with two identical spin (1/2) nuclei shows an **alternation in intensity** as a result of nuclear statistics.

- For some molecules, in the Raman spectra is **missing every other line**.

Parity of ψ_{rot} :

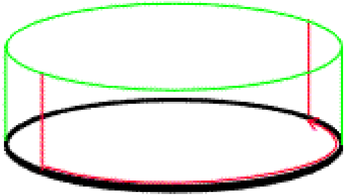

J = 2

ψ_{rot} with J = 0; 2; 4 … corresponds to positive parity,
ψ_{rot} with J = 1; 3; 5 … corresponds to negative parity.


J = 1

Generally, the ratio of symmetric and anti-symmetric states is:

$$\frac{\text{Number of anti-symmetric states (odd J)}}{\text{Number of symmetric states (even J)}} = \begin{cases} \dfrac{I}{I+1} & \text{if} \quad I = 1/2 \\[2ex] \dfrac{I+1}{I} & \text{if} \quad I = 1 \end{cases}$$


J = 0

Examples:

Rotational Raman spectra of $\mathbf{H_2}$: (H → fermion (I=1/2 for individual nuclei)

- the lines corresponding to transitions 0 ---> 2, 2 ---> 4, etc. will be *one-third times* as large as those corresponding to transitions 1 ---> 3, 3 ---> 5, etc.

In H_2 both ψ_{vib} (whatever the value of v) and ψ_{el}, in the ground electronic state, are symmetric to nuclear exchange, so we need to consider only the behaviour of $\boldsymbol{\psi_{rot}}$ **and** $\boldsymbol{\psi_{ns}}$ (the nuclear spin wavefunction).

Ortho- and Para-Forms of H_2

wave function	I_{total}	M_I		
$\uparrow\uparrow$	1	1	Triplet	Ortho - H_2
$\frac{1}{\sqrt{2}}(\uparrow\downarrow+\downarrow\uparrow)$	1	0		
$\downarrow\downarrow$	1	-1		
$\frac{1}{\sqrt{2}}(\uparrow\downarrow-\downarrow\uparrow)$	0	0	Singlet	Para - H_2

For ortho-H_2 (with I = 1 and positive parity of the nuclear spin function) we have rotational states with negative parity, i.e. J = 1; 3; 5, …,
For para-H_2 (with I = 0 and negative parity of the nuclear spin function) we have rotational states with positive parity, i.e. J = 0,2,4, …

For low temperatures only p-H_2 is stable; o-H_2 is metastable

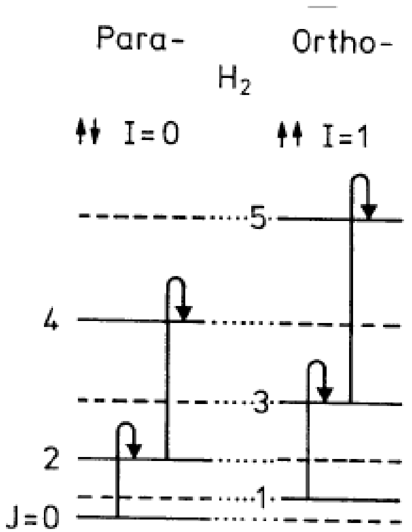
For ^{2}D (with the nuclei being bosons (I = 1 for the individual nuclei), the inverse is true, i.e. at low temperatures only o-$^2D_2$ is stable.

Usually, at higher temperatures, there is thermal equilibrium between the two $^1H_2$ modifications, so H_2 is a mixture of o-H_2 and p-H_2 with a ratio of 3:1.

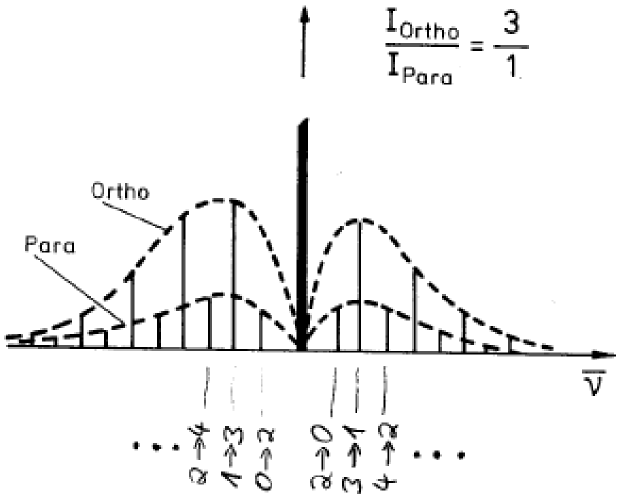
Consequences of nuclear spin

1) There are no transitions with ΔJ = ±1 and thus no rotational transitions in IR absorption. However, for H_2 these are forbidden anyway because of the zero dipole moment.

2) *Rotational Raman lines with ΔJ = ±2 are allowed*. They correspond to (alternating) orto-H_2 and para-H_2. This gives rise to alternating (3:1) intensities.



statistical weight	$g_p = 1$	$g_o = 3$
total statistical weight	$g_p \times (2J+1)$	$g_o \times (2J+1)$



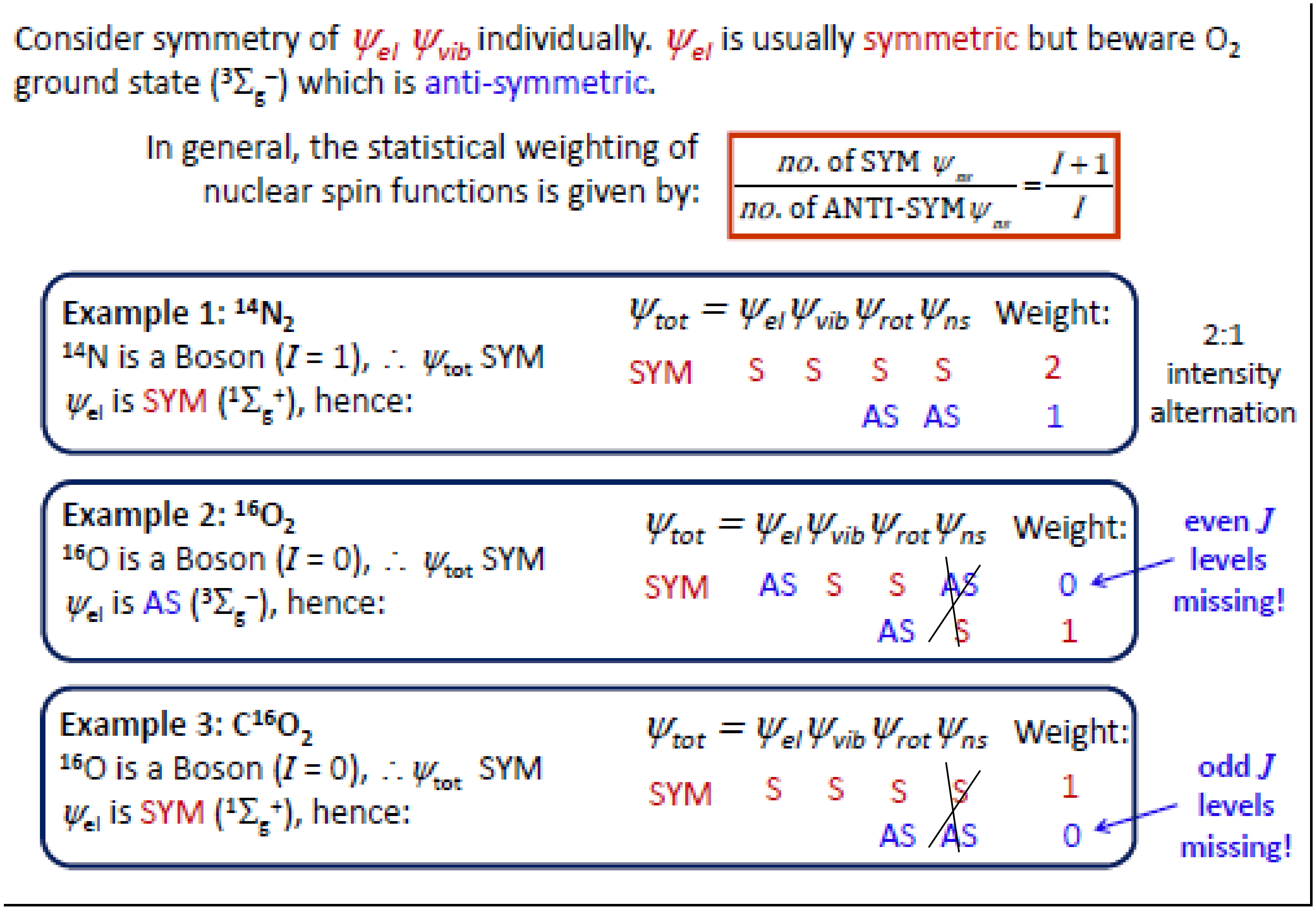
Other molecules

Rotational Raman spectra of $^{19}\mathbf{F}_2$ is similar to $^1H_2$ (ratio 3:1).

Rotational Raman spectra of $^{14}\mathbf{N}_2$ is similar to $^2D_2$ (ratio 2:1).

For $^{16}\mathbf{O}_2$ we have the special case of I = 0,
All rotational levels with even J (0 ,2, 4,..) are completely missing
(the electronic wavefunction in the ground state ($3\Sigma g-$) has negative parity, and in order to obtain the symmetric total wavefunction required for bosons, the rotational levels must have negative parity).
the transitions 1---> 3, 3 ---> 5, 5---> 7 may be seen,
the transitions 0 --- > 2, 2 ---> 4, 4 ---> 6 are missing

Rotational Raman spectra of $\mathbf{CO}_2$:
For $C^{16}O_2$ (triatomic molecule with a centre of inversion) similar arguments apply. The electronic wavefunction in the ground state ($1\Sigma g +$) has positive parity and thus **rotational levels with odd J are missing.**
the transitions 0 --- > 2, 2 ---> 4, 4 ---> 6 may be seen,
the transitions 1---> 3, 3 ---> 5, 5---> 7 are missing



Consider symmetry of ψ_{el} ψ_{vib} individually. ψ_{el} is usually symmetric but beware O_2 ground state ($^3\Sigma_g^-$) which is anti-symmetric.

In general, the statistical weighting of nuclear spin functions is given by:

$$\boxed{\frac{no.\text{ of SYM } \psi_{ns}}{no.\text{ of ANTI-SYM } \psi_{ns}} = \frac{I+1}{I}}$$

Example 1: $^{14}N_2$

^{14}N is a Boson (I = 1), ∴ ψ_{tot} SYM

ψ_{el} is SYM ($^1\Sigma_g^+$), hence:

ψ_{tot}	= ψ_{el}	ψ_{vib}	ψ_{rot}	ψ_{ns}	Weight:
SYM	S	S	S	S	2
			AS	AS	1

2:1 intensity alternation

Example 2: $^{16}O_2$

^{16}O is a Boson (I = 0), ∴ ψ_{tot} SYM

ψ_{el} is AS ($^3\Sigma_g^-$), hence:

ψ_{tot}	= ψ_{el}	ψ_{vib}	ψ_{rot}	ψ_{ns}	Weight:
SYM	AS	S	S	~~AS~~	0
			AS	~~S~~	1

even J levels missing!

Example 3: $C^{16}O_2$

^{16}O is a Boson (I = 0), ∴ ψ_{tot} SYM

ψ_{el} is SYM ($^1\Sigma_g^+$), hence:

ψ_{tot}	= ψ_{el}	ψ_{vib}	ψ_{rot}	ψ_{ns}	Weight:
SYM	S	S	S	~~S~~	1
			AS	~~AS~~	0

odd J levels missing!

If the nuclear spin is zero (I = 0), we can consider that there is no spin wavefunction, thus we can ignore it!

Symmetric top molecule

Only end-over-end rotations produce a change in the polarizability in the case of the symmetric top molecules (a molecule in which two moments of inertia are the same).

The energy levels:

$$E_{JK} = BJ(J+1) - (A-B)K^2 \qquad J = 0, 1, 2, \ldots; K = \pm J, \pm(J-1), \ldots$$

The Raman selection rules for a symmetric top molecule are:

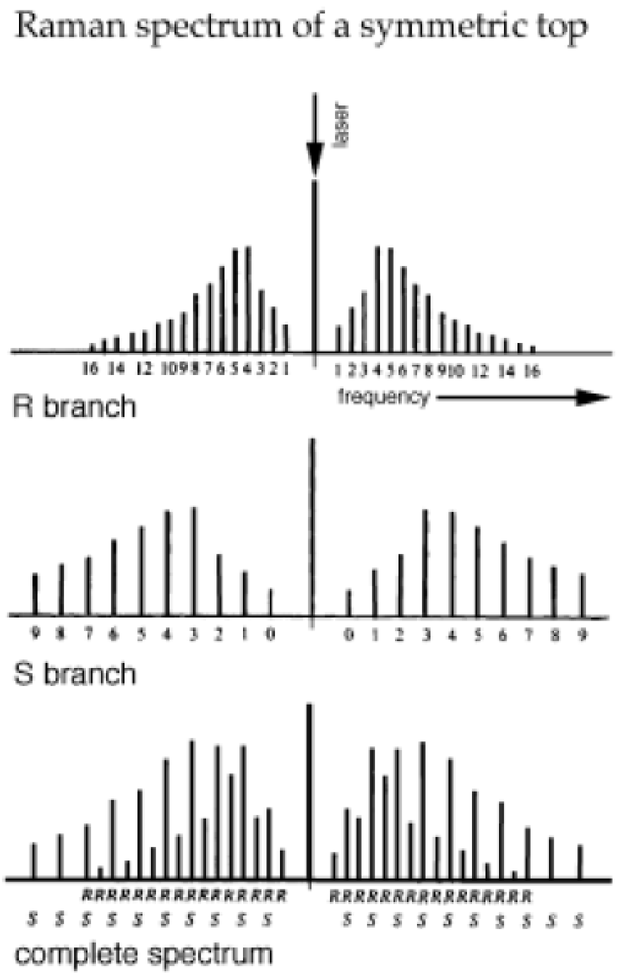
$\Delta K = 0$
$\Delta J = 0, \pm 1, \pm 2$ (except for K = 0 states, when $\Delta J = \pm 2$ only)

A symmetric top molecule has anisotropic polarizability. This selection rule holds for any K. There are two cases:

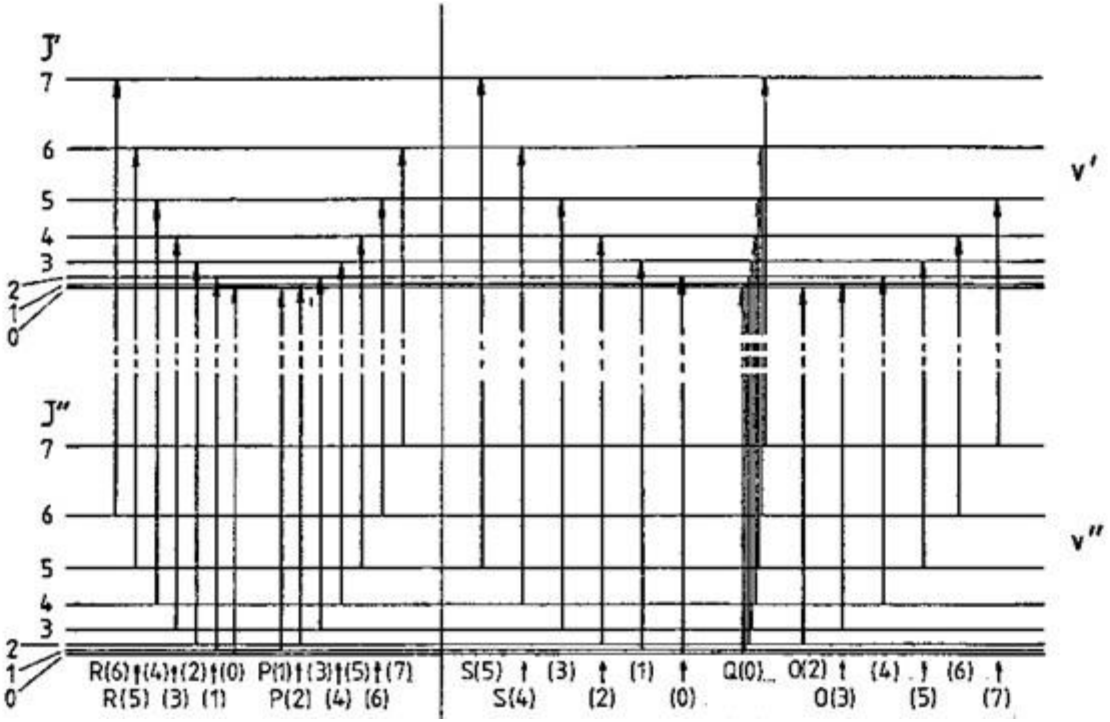
(1) $\Delta J = \pm 1$ (R branch)
Lines at $\Delta E_R = 2B(J+1)$ $J = 1, 2, ..$ but $J \neq 0$

(2) $\Delta J = \pm 2$ (S branch)
Lines at $\Delta E_S = 2B(2J+3)$ $J = 0, 1, 2, ..$

The spectrum shows a complex intensity structure (not to be confused with nuclear spin effects), but the basic line spacing is now 2B, rather than 4B as in the case of linear molecules.


Raman spectrum of a symmetric top

Roto-vibrational spectroscopy



Infrared spectrum

Δ v = 1; ΔJ = ±1,

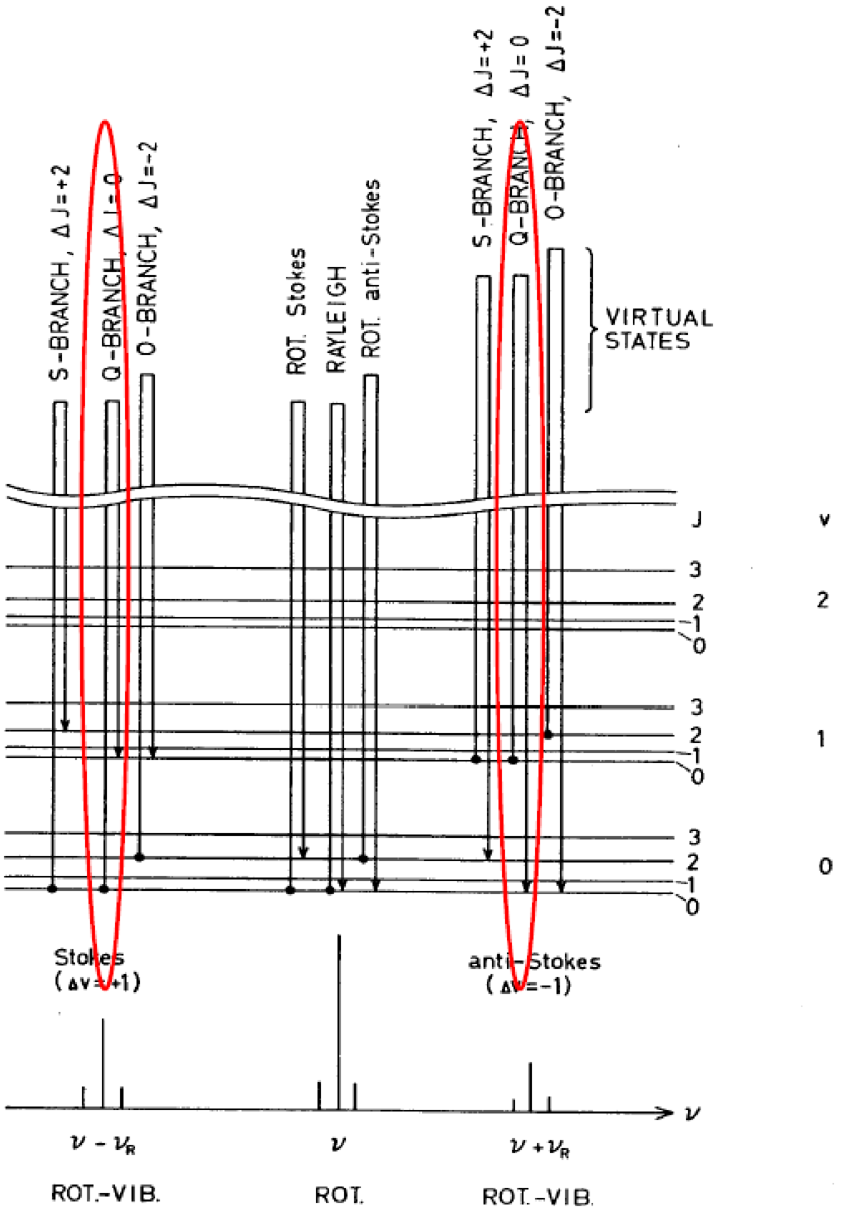
P, Q, R branches

Raman spectrum

Δ v = 1; ΔJ = 0, ±2

O, Q, S branches

Roto-vibrational Raman Spectra



O-Branch, J → J-2

Q-Branch, J → J

Pure vibration

S-Branch, J → J+2

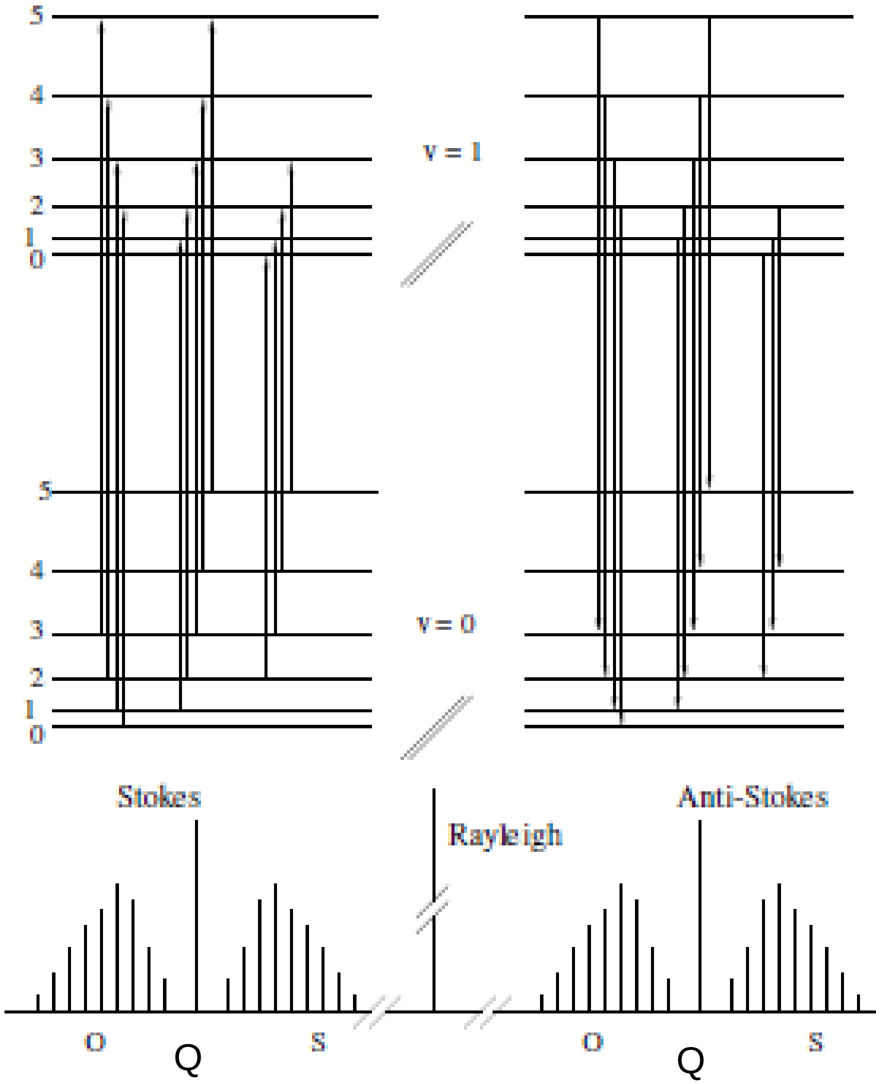
Diatomic molecule (linear)

Selection rule: $\Delta J = 0, \pm 2$ $\Delta v = 1$

$\Delta J = 0$ Q branch (ν_{vibr})

$\Delta J = -2$ O branch: lose rotational energy

$\Delta J = +2$ S branch: gain rotational energy



Stokes
(inelastic)

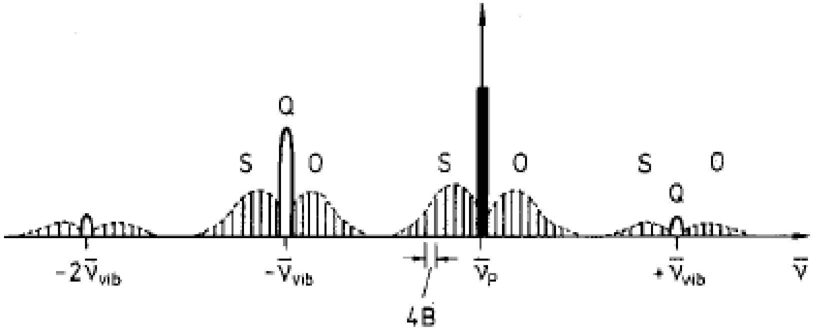
Rayleigh
elastic scattering of molecule and photon

Anti-Stokes
(inelastic)

$\nu' < \nu_{primary}$

$\nu' = \nu_{primary}$

$\nu' > \nu_{primary}$



O and S branch will apear in Stokes and anti-Stokes part of the Raman spectrum!

Stokes domain!

$$\bar{\nu}_{O(\Delta v=1,\Delta J=-2)} = hc(E_{(v=1,J-2)} - E_{(v=0,J)}) = \bar{\nu}_v - B(4J-2)$$ Raman shift

$$\bar{\nu}_{Osc} = \bar{\nu}_{exc} - \bar{\nu}_v + B(4J-2)$$ wavenumber of scattered radiation

$$\bar{\nu}_{Q(\Delta v=1,\Delta J=0)} = hc(E_{(v=1,J)} - E_{(v=0,J)}) = \bar{\nu}_v$$ Raman shift

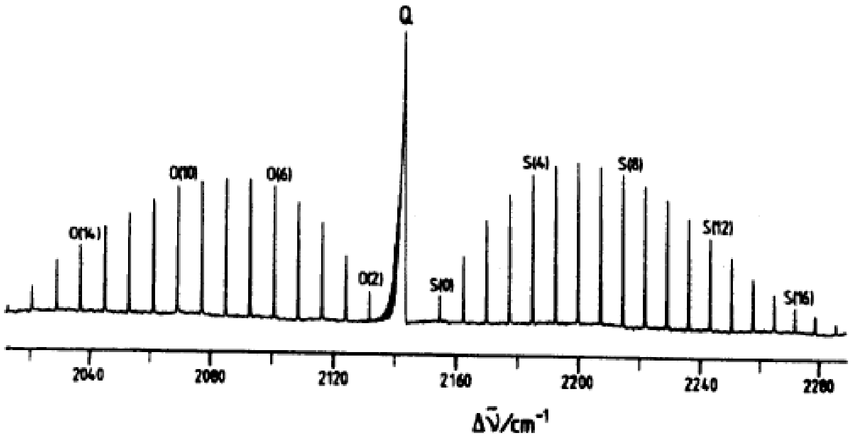
$$\bar{\nu}_{Qsc} = \bar{\nu}_{exc} - \bar{\nu}_v$$ wavenumber of scattered radiation

$$\bar{\nu}_{S(\Delta v=1,\Delta J=2)} = hc(E_{(v=1,J+2)} - E_{(v=0,J)}) = \bar{\nu}_v + B(4J+6)$$ Raman shift

$$\bar{\nu}_{Ssc} = \bar{\nu}_{exc} - \bar{\nu}_v - B(4J+6)$$ wavenumber of scattered radiation

selection rules: $\Delta v = \pm 1, \quad \Delta J = 0, \pm 2$

If vibrational tranzition occurs simultaneously with rotational transitions: O, Q and S branches will be obtained:



The 1–0 Stokes vibrational Raman spectrum of CO showing the *O*-, *Q*-, and *S*-branch rotational structure

Problems

1. For the ICl molecule the following spectroscopic constant are known: $\overline{\nu}_0$ = 385 cm^{-1}; x_e = 0.05 cm^{-1}; B = 5 cm^{-1}.

Calculate wavelengths of S(0) and O(2) lines in the Raman spectrum (Stokes domain) excited by the argon laser with wavelength of 500 nm.

2. The wavenumber of the incident radiation is 20000 cm^{-1}. What is the wavenumber of the scattered Stokes radiation for the J = 0 → 2 transition of $^{14}N_2$. The equilibrium bond length is 110 pm.

3. Explain why in the pure rotational Raman spectrum of CO_2, the displacement from the Rayleigh line of the first observed line is 6B and the separation of successive lines is 8B, whereas for O_2 the corresponding figures are 10B and the separation of successive lines is 8B, where B are the appropriate rotational constants.

4. Lines in the pure rotational Raman spectrum of oxygen are observed at 14.381, 25.876, 37.369, 48.855, 60.337, 71.809, 83.267, 94.712, 106.143, 117.555, 128.949 cm^{-1}. Assign the lines and determine the ground state rotational constant and the bond length of oxygen.