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Chapter 4 Raman Spectroscopy

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Interaction

What types of interaction do we expect between radiation and matter ?

Absorption: Excitation of molecules to upper state by absorbing photon.

Emission: Transition of molecules from excited state to lower state.

Deflection: Change the direction of progression.

Scattering (interaction as a particle with molecules):

Rayleigh scattering : Scattering without energy exchange by small particle (molecules). Explain the blue sky and red sunset.

Mie scattering : Scattering without energy exchange by larger particle (large cluster). Explain the white cloud.

Raman scattering : Scattering with energy exchange by small particle (molecules). The wavelength of scattering radiation is different from that of the incident radiation because of energy exchange.

Duality of light: wave and particle. It has both character
because the particle travels like a wave.

4.1 INTRODUCTION

Raman observed the first inelastic scattering from molecules using sunlight.

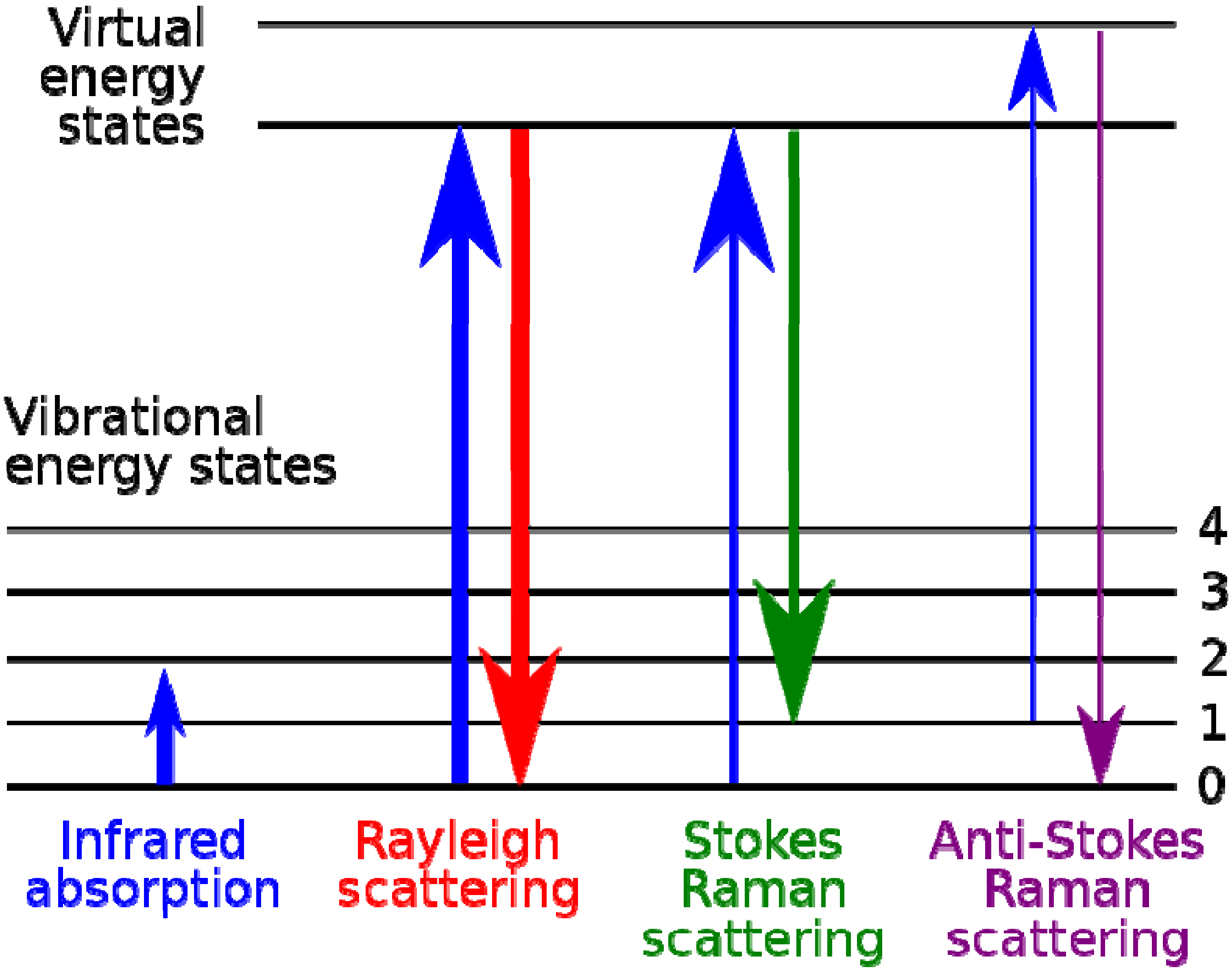
Although the inelastic scattering of light was predicted by Smekal in 1923, it was not until 1928 that it was observed in practice. The Raman effect was named after one of its discoverers, the Indian scientist Sir C. V. Raman who observed the effect by means of sunlight (1928, together with K. S. Krishnan and independently by Grigory Landsberg and Leonid Mandelstam). Raman won the **Nobel Prize in Physics in 1930** for this discovery accomplished using sunlight, a narrow band photographic filter to create monochromatic light and a "crossed" filter to block this monochromatic light. He found that light of changed frequency passed through the "crossed" filter. Subsequently the mercury arc became the principal light source. Currently lasers are used as light sources.

He observed the scattering radiation of different frequencies from that of incident radiation using an optical filter which can block a radiation of a specific frequencies.

About Raman

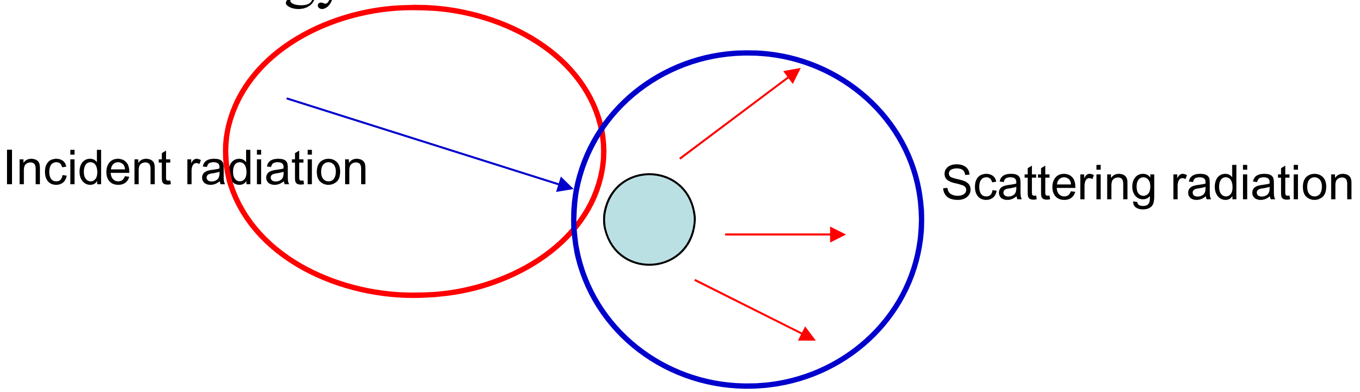
Chandrasekhara Venkata Raman was born on November 7, 1888 in an Iyer family in Tiruchirapalli, Tamil Nadu. He was the second child of Chandrasekhar Iyer and Parvathi Amma. His father was a lecturer in mathematics and physics, so he had an academic atmosphere at home. He won the 1930 Nobel Prize in Physics for his work on the scattering of light and for the discovery of the Raman effect. Raman spectroscopy is based on this phenomenon. His nephew Subramanyan Chandrasekhar, also won a Nobel prize in physics in 1983.

Although Raman effect was discovered in 1930, no development has been made until the development of laser because Raman scattering is too weak to observe. It is about 1 scattering from 10^7 incident radiation. With very strong radiation from laser, it is widely applicable to condensed materials.


Virtual energy states
Vibrational energy states
4
3
2
1
0
Infrared absorption
Rayleigh scattering
Stokes Raman scattering
Anti-Stokes Raman scattering

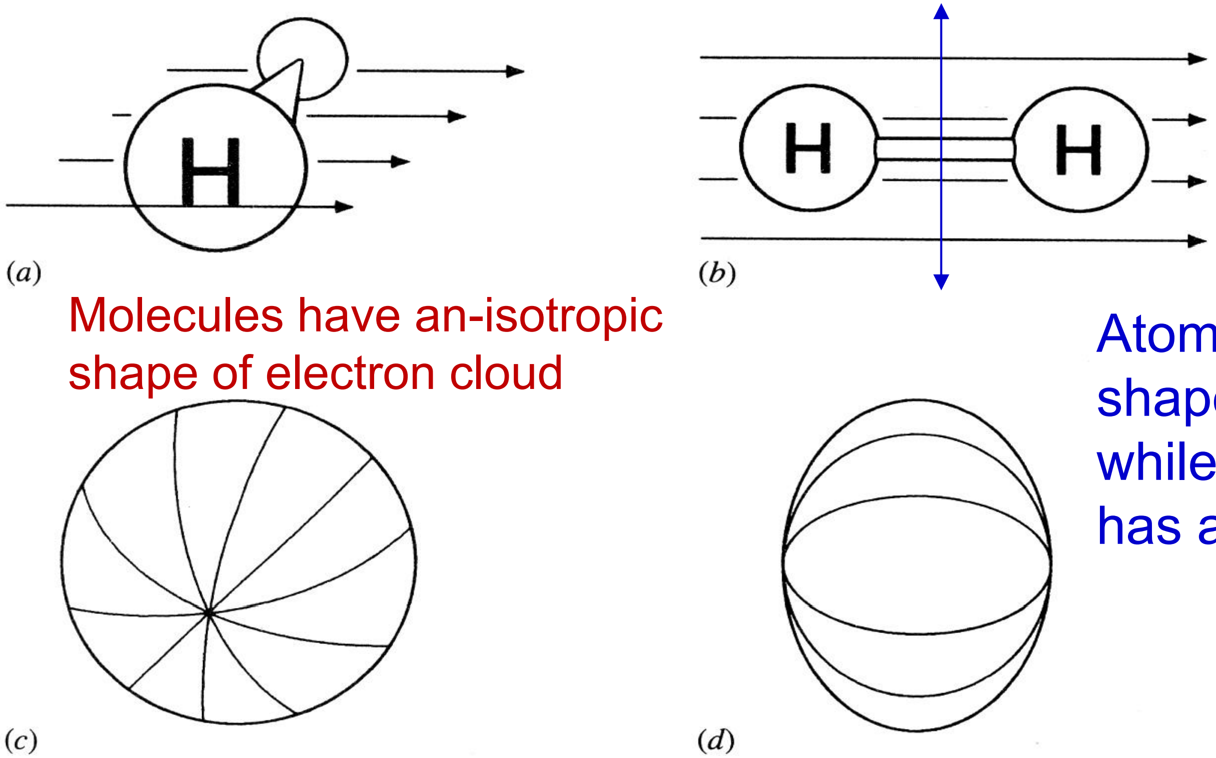
4.1.1 Quantum Theory of Raman Effect Very difficulty

As a stream of **photons collides with a particular molecule** the photons will be deflected without change in energy if collisions are **perfectly elastic**. If energy is exchanged between photon and molecule, the collision is said to be **inelastic**. The molecule can gain or lose discrete amounts of energy in accordance with quantal laws - the energy must coincide with a transition between two molecular energy levels.



Elastic: No exchange of energy : Rayleigh or Mie : No interest to chemists
Inelastic: Energy exchange : Raman : worth to study for molecules

4.1.2 Classic Theory of Raman Effect: Molecular Polarizability



Molecules have an-isotropic shape of electron cloud

Atoms have spherical shape of electron cloud, while hydrogen molecule has a cylindrical shape..

Figure 4.1 The hydrogen molecule in an electric

Absorption/emission : dipole moment
Scattering: polarizability = polarize + ability

The electric field of radiation will polarize the electron cloud of molecules in the direction of incident radiation.

Dipole moment vs. Polarizability

- Dipole moment: Unequal distribution of electric charge
  - Electric dipole moment
    - Permanent dipole moment : Polar molecules
    - Induced dipole moment : Nonpolar molecules
  - Magnetic dipole moment
    - Orbital dipole moment
    - Spin dipole moment Magnetic property
- Polarizability: Distortion ability of electron cloud from equilibrium

  The electron cloud is distorted by an oscillating electric field (radiation), in which the distortion depends on the field strength as well as the size of electron cloud (or cloud density). The soft cloud can be easily distorted but the hard one is not.

  Polarization generates induced dipole moment.

  Polarizability depends on the field direction.

Polarizability ellipsoid

Two axes

Polarizability : Ability to change electron cloud by vibration, etc.

Major axis: difficult to change
Minor axis: easy to change

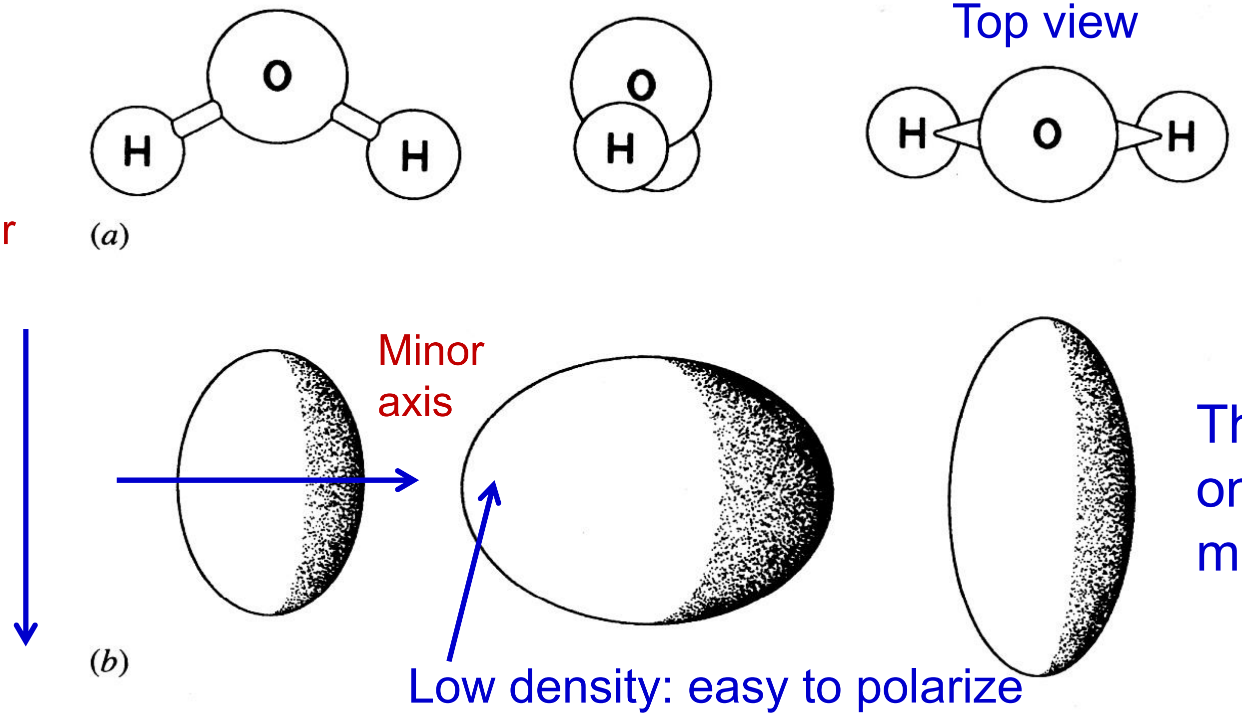
Front view

Side view

Top view

Major axis

Minor axis



Low density: easy to polarize

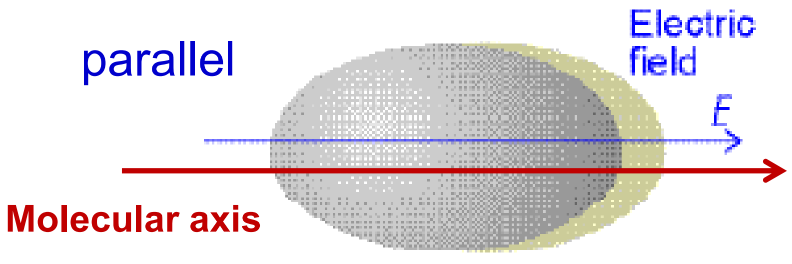
The shape depends on the orientation of molecules.

Figure 4.2 The water molecule and its polarizability ellipsoid, seen along the three main axes.

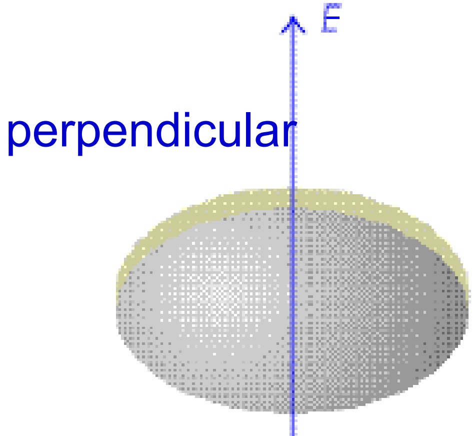
Polarizability has a property of tensor while dipole moment has a property of vector.

Polarizability of molecules

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.



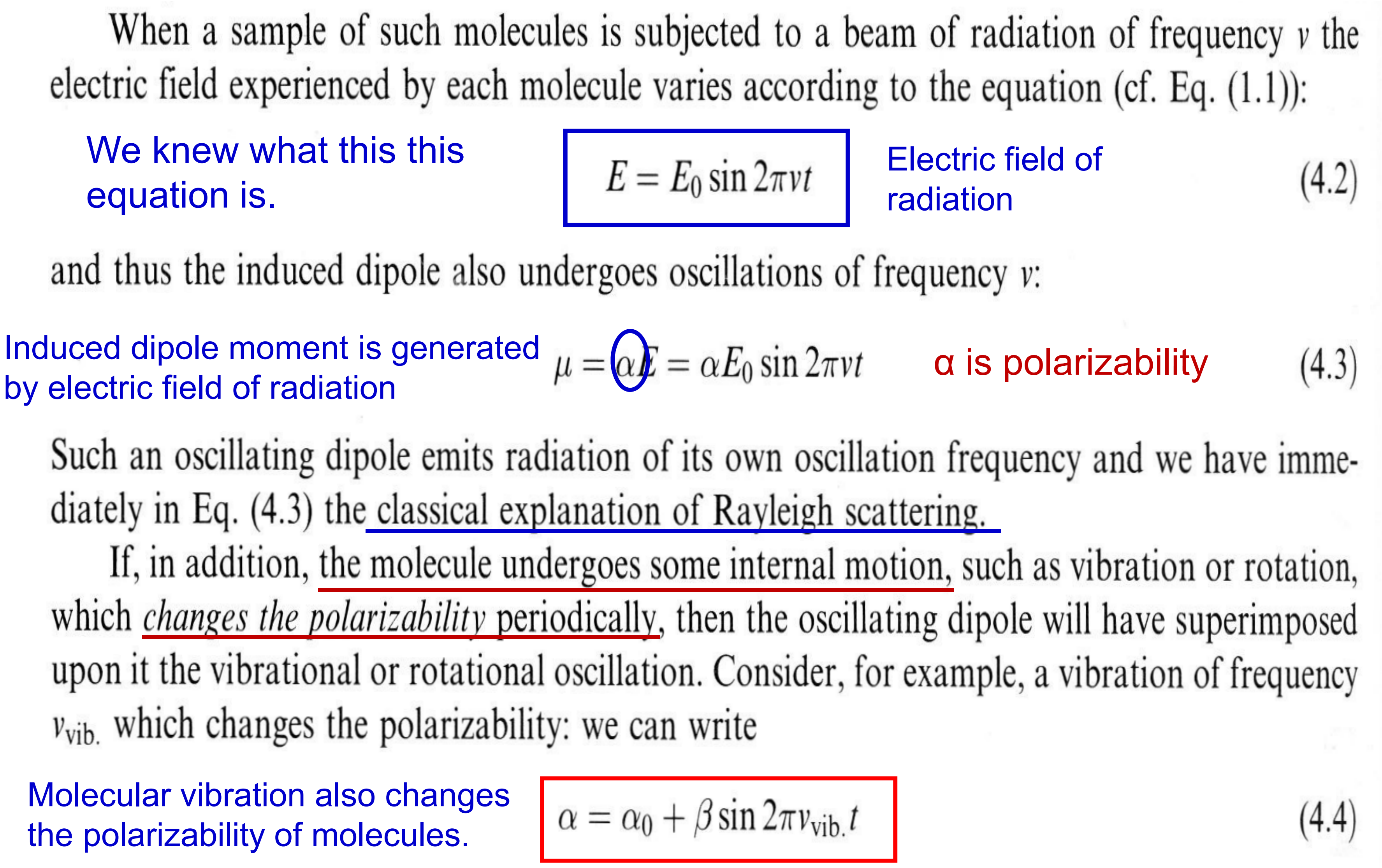
(a)



(b)

Isotropic : same in every direction : independent of direction
Anisotropic : depends on direction

Mathematical Expression



When a sample of such molecules is subjected to a beam of radiation of frequency ν the electric field experienced by each molecule varies according to the equation (cf. Eq. (1.1)):

We knew what this this equation is.

$$\boxed{E = E_0 \sin 2\pi\nu t} \qquad (4.2)$$

Electric field of radiation

and thus the induced dipole also undergoes oscillations of frequency ν:

Induced dipole moment is generated by electric field of radiation

$$\mu = \alpha E = \alpha E_0 \sin 2\pi\nu t \qquad (4.3)$$

α is polarizability

Such an oscillating dipole emits radiation of its own oscillation frequency and we have immediately in Eq. (4.3) the classical explanation of Rayleigh scattering.

If, in addition, the molecule undergoes some internal motion, such as vibration or rotation, which *changes the polarizability* periodically, then the oscillating dipole will have superimposed upon it the vibrational or rotational oscillation. Consider, for example, a vibration of frequency $\nu_{\text{vib.}}$ which changes the polarizability: we can write

Molecular vibration also changes the polarizability of molecules.

$$\boxed{\alpha = \alpha_0 + \beta \sin 2\pi\nu_{\text{vib.}} t} \qquad (4.4)$$

where α_0 is the equilibrium polarizability and β represents the rate of change of polarizability with the vibration. Then we have:

From above two equations

$$\underline{\mu = \alpha E = (\alpha_0 + \beta \sin 2\pi\nu_{\text{vib.}}t)E_0 \sin 2\pi\nu t}$$

or, expanding and using the trigonometric relation:

We know this relation

$$\boxed{\sin A \sin B = \tfrac{1}{2}\{\cos(A - B) - \cos(A + B)\}}$$

we have

Text error (ν)

Raman scattering

Final expression

$$\mu = \boxed{\alpha_0 E_0 \sin 2\pi\nu t} + \boxed{\tfrac{1}{2}\beta E_0\{\cos 2\pi(\nu - \nu_{\text{vib.}})t - \cos 2\pi(\upsilon + \nu_{\text{vib.}})t\}} \qquad (4.5)$$

and thus the oscillating dipole has frequency components $\nu \pm \nu_{\text{vib.}}$ as well as the exciting frequency ν.

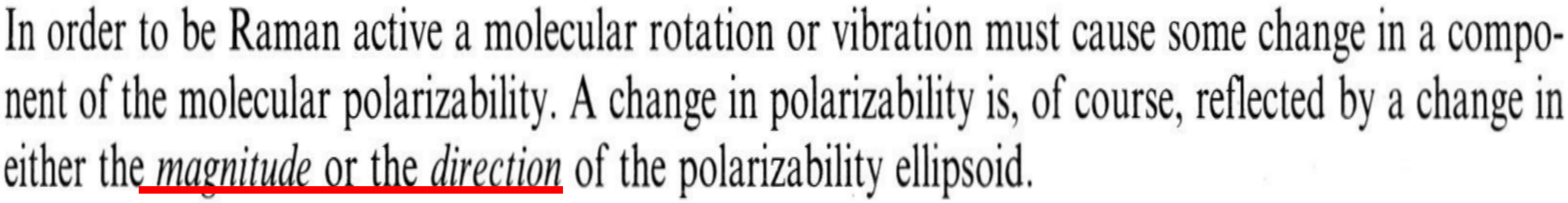
We obtain 3 terms

It should be carefully noted, however, that if the vibration does not alter the polarizability of the molecule (and we shall later give examples of such vibrations) then $\underline{\beta = 0}$ and the dipole oscillates only at the frequency of the incident radiation; the same is true of a rotation. Thus we have the general rule:

Rayleigh scattering

Condition for Raman scattering

Raman scattering



In order to be Raman active a molecular rotation or vibration must cause some change in a component of the molecular polarizability. A change in polarizability is, of course, reflected by a change in either the *magnitude* or the *direction* of the polarizability ellipsoid.

$$\frac{1}{2}\underset{\substack{\uparrow\\ \text{Change of polarizability}}}{\boxed{\beta}}E_0\{\overset{\text{Lose energy}}{\cos 2\pi(\nu - \nu_{\text{vib.}})t} - \overset{\text{Gain energy}}{\cos 2\pi(\nu + \nu_{\text{vib.}})t}\}$$

Reminder: The condition for activity in spectrum

Rotation : Dipole moment (polar molecules)

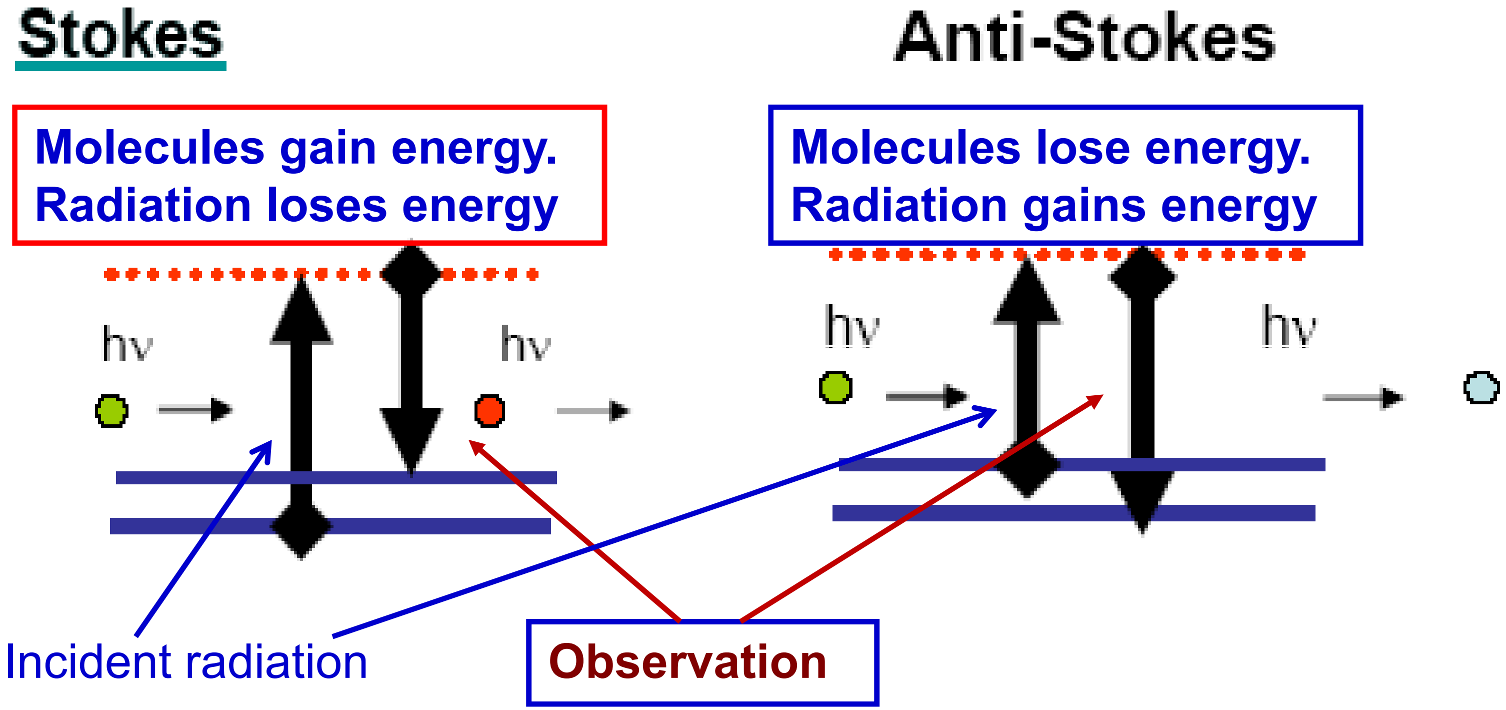
Vibration : Dipole moment change (unsymmetric vibration)

Raman : Polarizability change (unsymmetric polarizability)

Two terms in Raman scattering : Stokes and anti-Stokes

There are two ways of energy exchange process between matter and radiation.

Raman scattering : inelastic collision



Stokes

Molecules gain energy.
Radiation loses energy

Anti-Stokes

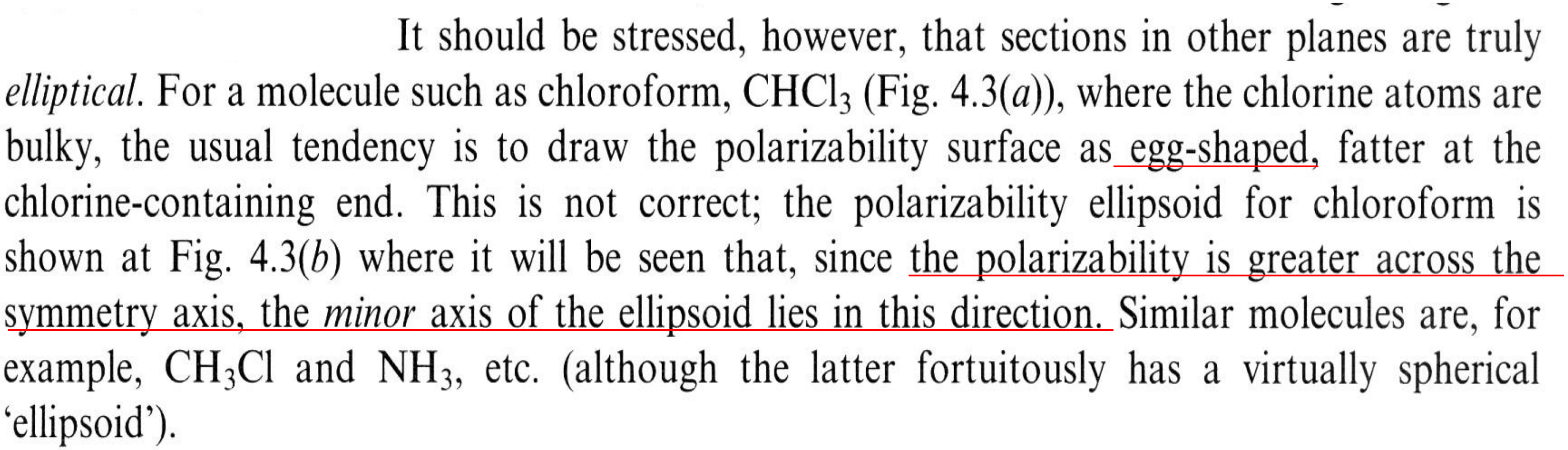
Molecules lose energy.
Radiation gains energy

Incident radiation

Observation

Net change: scattering radiation energy – incident radiation energy

Polarizability ellipsoid



It should be stressed, however, that sections in other planes are truly *elliptical*. For a molecule such as chloroform, $CHCl_3$ (Fig. 4.3(*a*)), where the chlorine atoms are bulky, the usual tendency is to draw the polarizability surface as egg-shaped, fatter at the chlorine-containing end. This is not correct; the polarizability ellipsoid for chloroform is shown at Fig. 4.3(*b*) where it will be seen that, since the polarizability is greater across the symmetry axis, the *minor* axis of the ellipsoid lies in this direction. Similar molecules are, for example, CH_3Cl and NH_3, etc. (although the latter fortuitously has a virtually spherical 'ellipsoid').

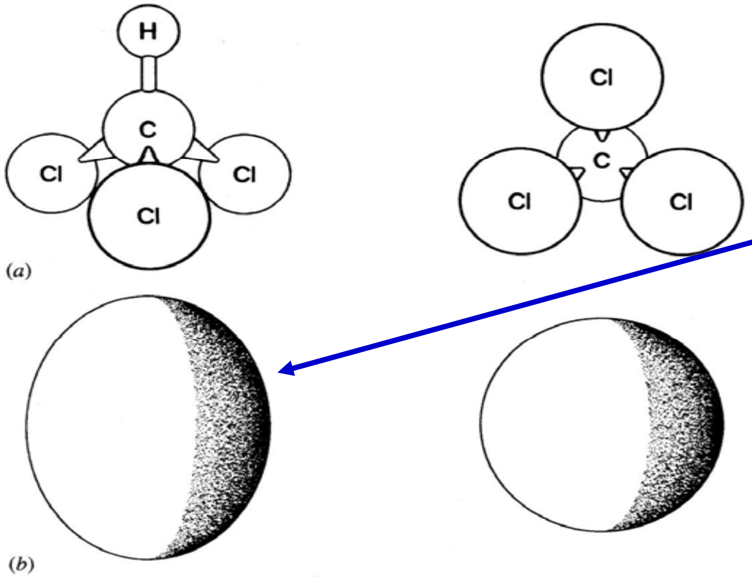
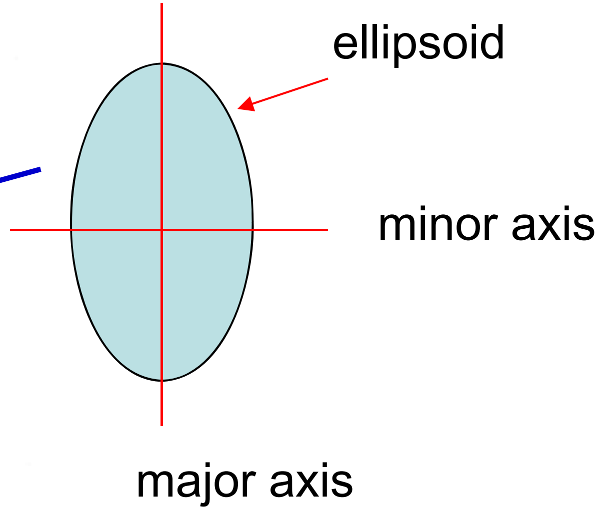


Figure 4.3 The chloroform molecule and its polarizability ellipsoid, seen from across and along the symmetry axis.

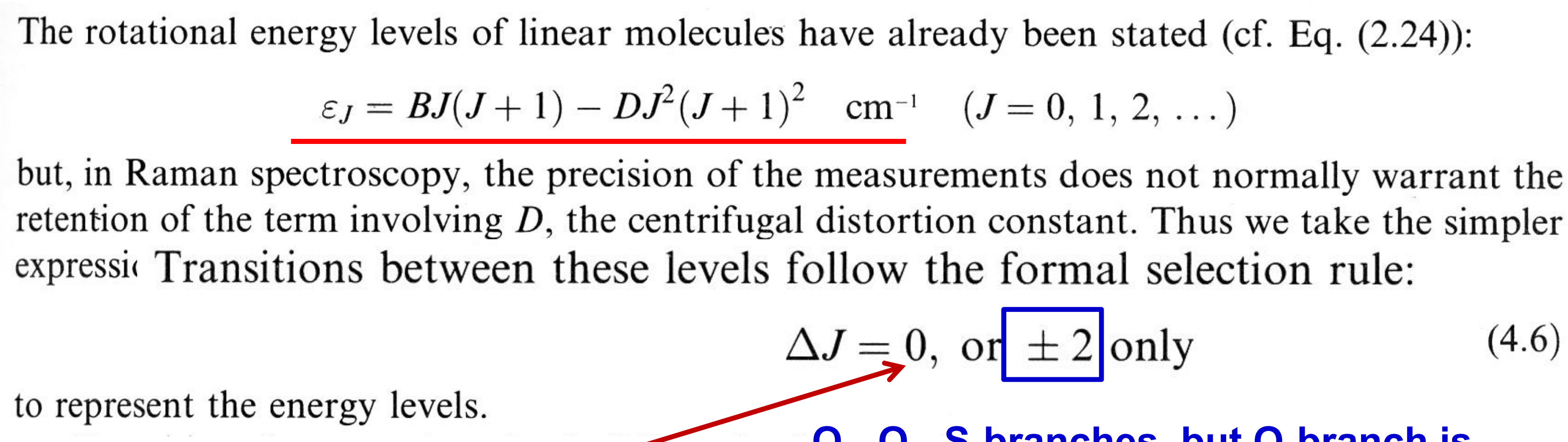


4.2 Pure Rotational Raman Spectra

Rotational Raman spectroscopy is not very popular tool because of resolution problem in spectrum

4.2.1 Linear Molecules

The same molecules, but different point of view. Raman selection rule is different from MW.



The rotational energy levels of linear molecules have already been stated (cf. Eq. (2.24)):

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 \quad \text{cm}^{-1} \quad (J = 0, 1, 2, \ldots)$$

but, in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving D, the centrifugal distortion constant. Thus we take the simpler expressi

Transitions between these levels follow the formal selection rule:

$$\Delta J = 0, \text{ or } \boxed{\pm 2} \text{ only} \tag{4.6}$$

to represent the energy levels.

meaningless

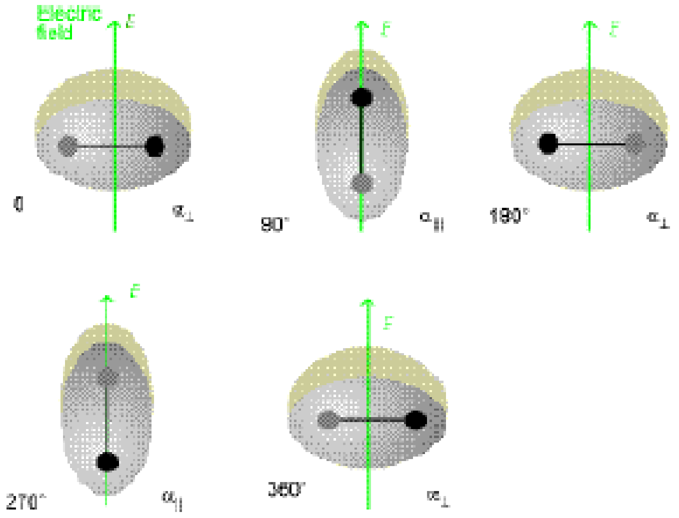
O-, Q-, S-branches, but Q-branch is the same as Rayleigh scattering

Same energy equation, but different selection rule

Rotation of Polarizability

- 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.

Same position in every 180 degree.



The reason of $\Delta J = \pm 2$ is related to rotation of polarizability ellipsoid.

Raman scattering : Stokes (-) and anti-Stokes (+) lines.

Combining, then, $\underline{\Delta J = +2}$ with the energy levels of Eq. (4.6) we have:

Calculation of transition energy

$$\Delta\varepsilon = \varepsilon_{J'=J+2} - \varepsilon_{J''=J} = B(4J+6) \quad \text{cm}^{-1} \tag{4.8}$$

Molecules gain energy. Stokes scattering

Since $\Delta J = +2$, we may label these lines S branch lines (cf. Sec. 3.2) and write

$$\Delta\varepsilon_S = B(4J+6) \quad \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots) \tag{4.9}$$

where J is the rotational quantum number in the *lower* state.

Reminder: Branch is related to J change.

Thus if the molecule gains rotational energy from the photon during collision we have a series of S branch lines to the low wavenumber side of the exciting line (Stokes' lines), while if the molecule loses energy to the photon the S branch lines appear on the high wavenumber side (anti-Stokes' lines). The wavenumbers of the corresponding spectral lines are given by:

Scattering radiation:

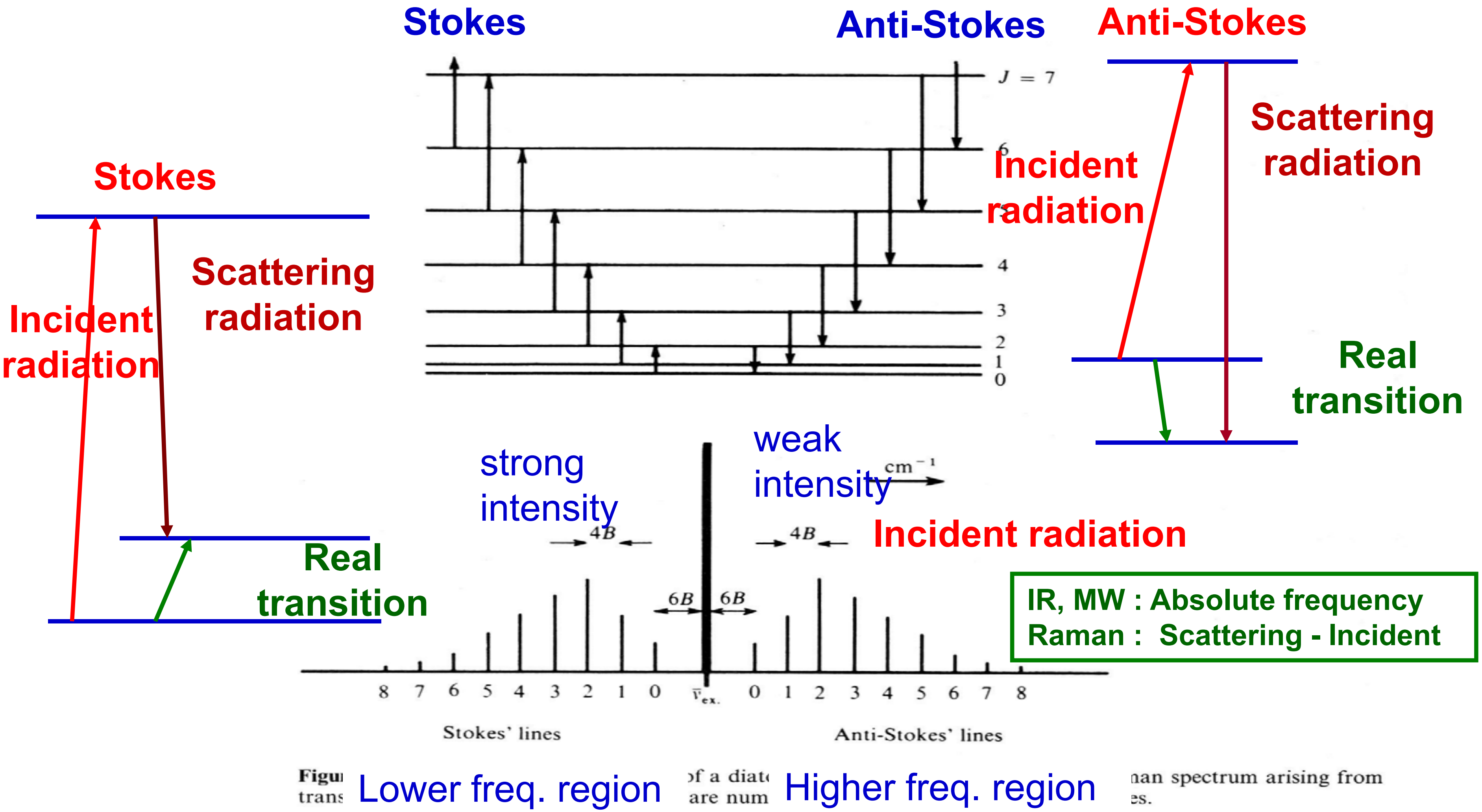
$$\underline{\bar{\nu}_S = \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_S = \bar{\nu}_{\text{ex.}} \pm B(4J+6) \quad \text{cm}^{-1}} \tag{4.10}$$

where the plus sign refers to anti-Stokes' lines, the minus to Stokes' lines, and $\bar{\nu}_{\text{ex.}}$ is the wavenumber of the exciting radiation.

Incident radiation

ΔJ= -2 : Molecules lose energy: Scattering gains energy: anti-Stokes scattering

Raman and Rayleigh transition



Stokes

Anti-Stokes

Anti-Stokes

Stokes

Incident radiation

Scattering radiation

Real transition

Incident radiation

Scattering radiation

Real transition

strong intensity

weak intensity

Incident radiation

IR, MW : Absolute frequency
Raman : Scattering - Incident

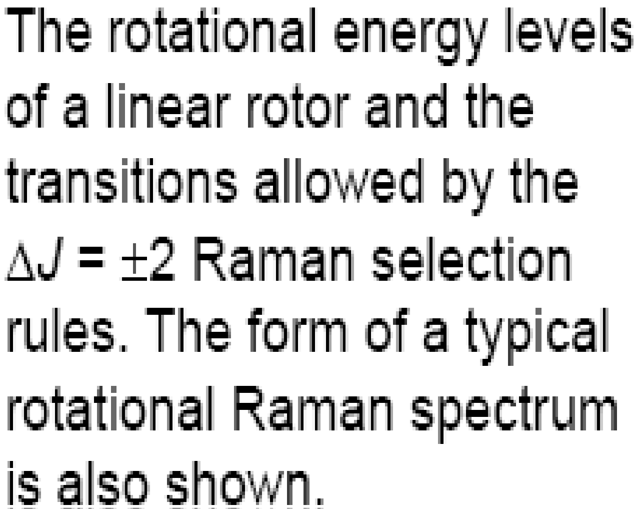
Lower freq. region

Higher freq. region

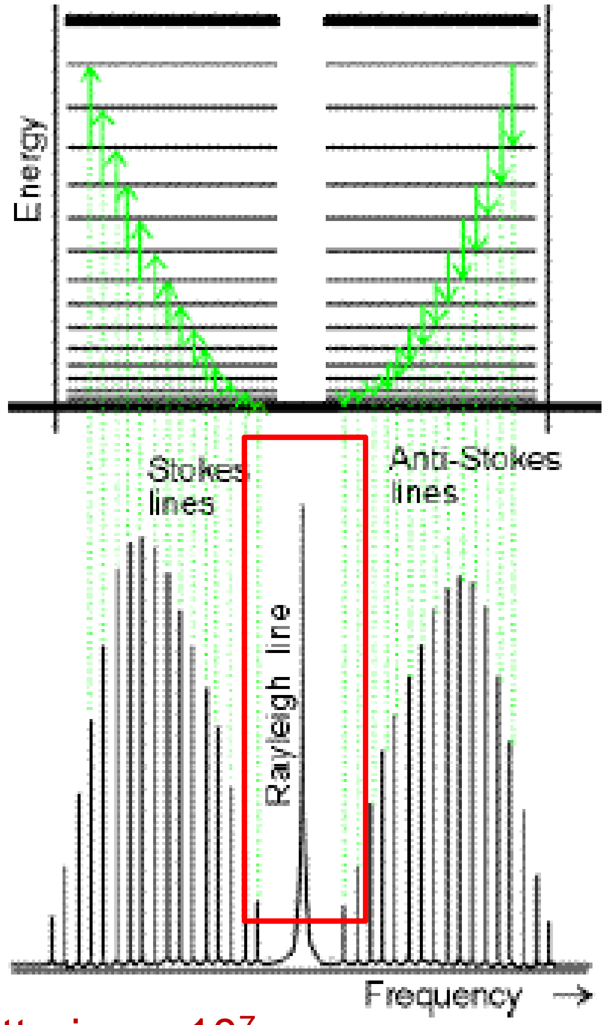
Stokes and anti-Stokes are exactly symmetric about excitation frequency.

Raman and Rayleigh Spectra

We can explain the blue sky in terms of Rayleigh scattering.



The rotational energy levels of a linear rotor and the transitions allowed by the $\Delta J = \pm 2$ Raman selection rules. The form of a typical rotational Raman spectrum is also shown.



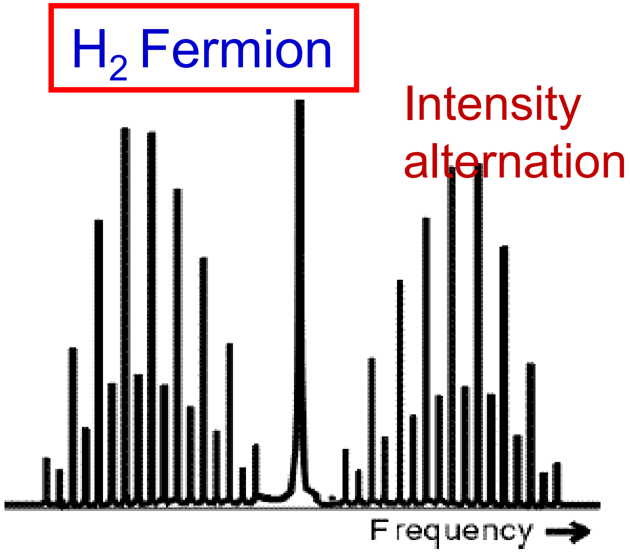
The intensity of Rayleigh scattering is much much stronger than Raman.

Rayleigh scattering = Raman scattering x 10^7

Also, we can see the intensity alternation resulting from nuclear spin statistics.

Raman spectrum of homonuclear diatomic molecules with *I*=1/2

- 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.



The rotational spectrum of H_2 is not observable because it is a nonpolar molecule. But we can see it in Raman spectrum with intensity alternation because of polarizabilty change during rotational motion.

We can see intensity alternation from Raman spectrum due to nuclear spin statistics.

CO_2 molecules: Raman spectrum

- The argument centers around the symmetry of the wavefunctions and the spin on the nuclei of the atoms. Let us consider the case of carbon dioxide as an example. We need only look at the oxygen atoms, since rotation involves only these atoms (the carbon atom is at the center of gravity and does not move). The nuclei of the ^{16}O atoms have a nuclear spin of $I = 0$ (i.e. no spin). (Unfortunately, the symbol for nuclear spin is identical to the symbol for angular momentum, but the context of the discussion should enable you to distinguish the difference.)

^{16}O (I=0) : Boson

- Particles with integral spins are bosons and follow Bose-Einstein statistics. According to the Pauli principle, the total wavefunction for bosons must be symmetric with respect to the interchange of the particles (in this case oxygen nuclei).
- The total wavefunction for the molecule is the product of the electronic wavefunction, the vibrational wavefunction, the rotational wavefunction, and the nuclear spin wavefunction.

Symmetry of wavefunctions

- We now examine the symmetry of the various wavefunctions that make up the total wavefunction.
- The total electronic wavefunction (orbital and spin) is antisymmetric with respect to the interchange of electrons, but it is symmetric with respect to the interchange of oxygen nuclei since nothing changes in the interchange of nuclei. (We are simply interchanging the labels on identical nuclei.)
- The vibrational wavefunction (for the symmetric stretch) is symmetric with respect to the interchange of oxygen nuclei.
- The symmetry of the rotational wavefunction is determined from (-1) raised to the J th power. When $(-1)^J$ is positive, as it must be for even values of J, then the rotational wavefunction is symmetric; when it is negative, as it must be for odd values of J, then the wavefunction is antisymmetric with respect to the interchange of nuclei.

J(even): symmetric, J(odd): anti-symmetric

Nuclear symmetry depends on spin number.

Nuclear Statistics

Fermions: half-integral spin nuclei

$$\frac{Number\ of\ ways\ to\ acheiving\ odd\ J}{Number\ of\ ways\ to\ acheiving\ even\ J}=\boxed{\frac{I+1}{I}}$$

Intensity ratio depends on the I number.

Bosons: integral spin nuclei.

$$\frac{Number\ of\ ways\ to\ acheiving\ odd\ J}{Number\ of\ ways\ to\ acheiving\ even\ J}=\boxed{\frac{I}{I+1}}$$

Intensity ratio depends on the I number.

For hydrogen the ratio is equal to 3, for nitrogen (I=1) it is 1/2

Pure rotational Raman spectrum of CO_2

$C^{16}O_2$, $C^{17}O_2$ show different shapes.

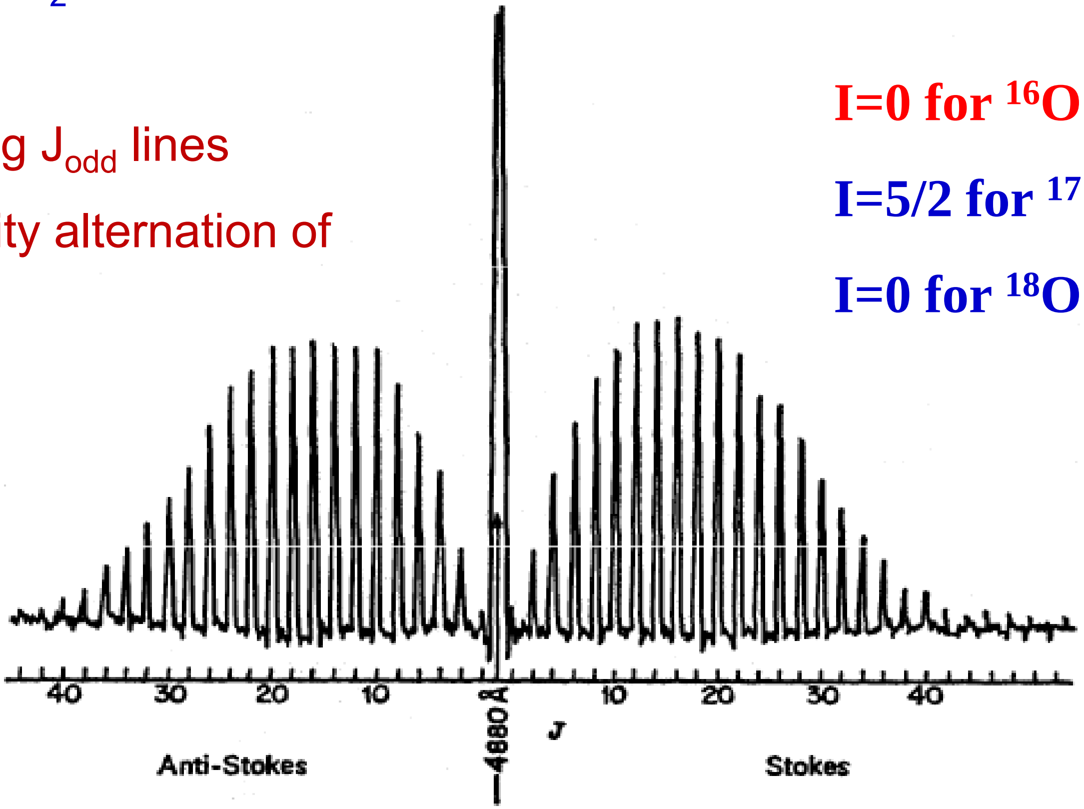
$C^{16}O_2$: missing J_{odd} lines

$C^{17}O_2$: intensity alternation of J_{even} and J_{odd}

I=0 for ^{16}O (Boson)

I=5/2 for ^{17}O (Fermion)

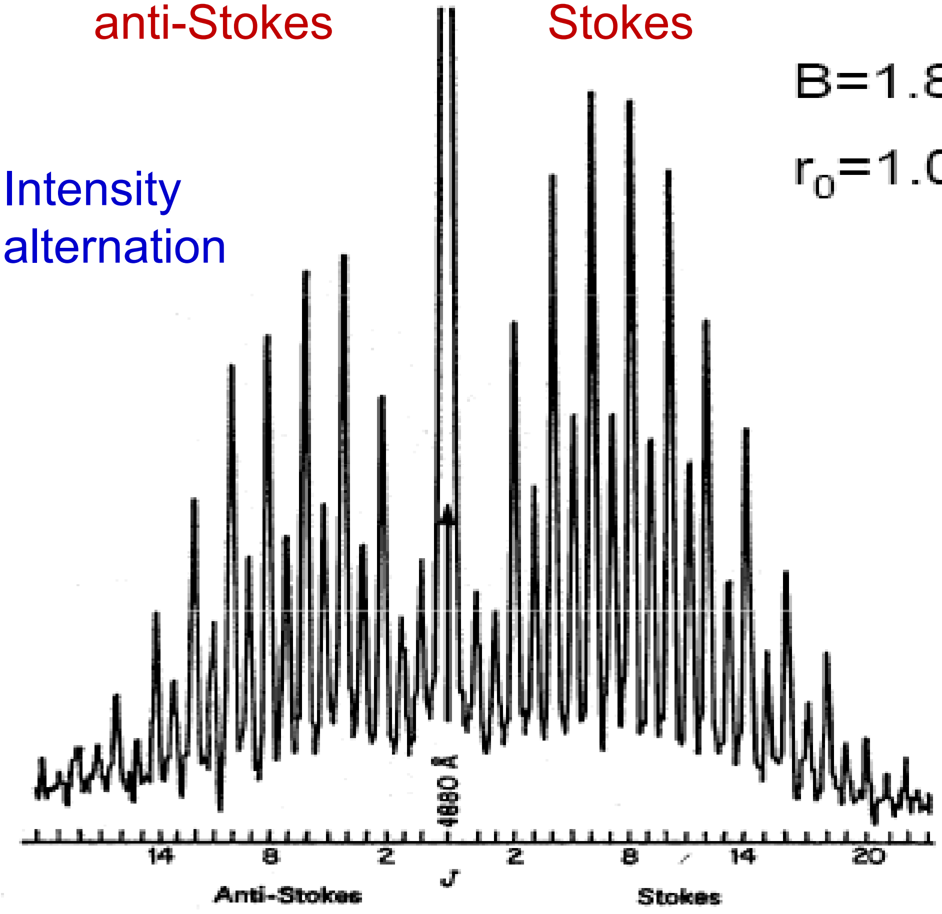
I=0 for ^{18}O



Odd Js disappear for I=0 (Boson) symmetry. Only even Js will be shown.

Thus, the interval between two lines is twice of the molecules with I≠0

Pure Rotational Raman spectra of $^{14}N_2$



Excitation
laser line

anti-Stokes

Stokes

Intensity
alternation

$B = 1.857672 \pm 0.000027\ \text{cm}^{-1}$

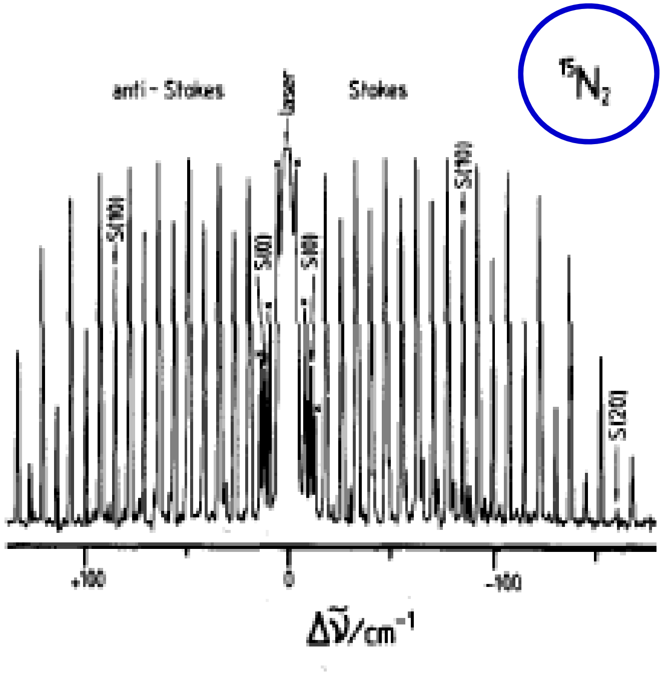
$r_0 = 1.099985 \pm 0.000010\ \text{Å}$

I=1 for ^{14}N (Boson)

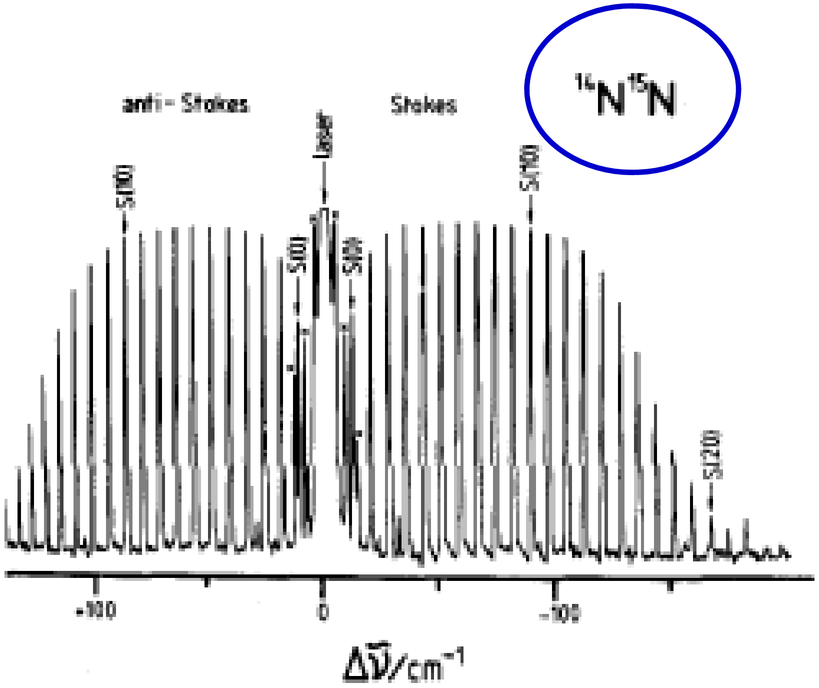
I=1/2 for ^{15}N (Fermion)

Intensity alternation

Center of inversion



No center of inversion



No symmetry law is applied to $^{14}N^{15}N$ because they have different nuclei.

4.2.2 Symmetric Top Molecules

Same energy equation, but different selection rule because it comes from the polarizability change during rotation.

From Eq. (2.38) we have the energy levels:

$$\varepsilon_{J,K} = BJ(J+1) + (A-B)K^2 \quad \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots; K = \pm J, \pm(J-1), \ldots) \tag{4.11}$$

The selection rules for Raman spectra are:

We can observed 5 branches.

$$\left.\begin{aligned} &\Delta K = 0 \\ &\Delta J = 0, \pm 1, \pm 2 \quad (\text{except for } K = 0 \text{ states} \\ &\qquad\qquad\qquad\quad \text{when } \Delta J = \pm 2 \text{ only}) \end{aligned}\right\} \tag{4.12}$$

Additional observation

Meaning less

K, it will be remembered, is the rotational quantum number for axial rotation, so the selection rule $\Delta K = 0$ implies that changes in the angular momentum about the top axis will not give rise to a Raman spectrum—such rotations are, as mentioned previously, Raman inactive. The restriction of ΔJ to ±2 for $K = 0$ states means effectively that ΔJ cannot be ±1 for transitions involving the ground state ($J = 0$) since $K = \pm J, \pm(J-1), \ldots, 0$. Thus for all J values other than zero, K also may be different from zero and $\Delta J = \pm 1$ transitions are allowed.

1. $\Delta J = +1$ (R branch lines)

$$\begin{aligned}\Delta\varepsilon_R &= \varepsilon_{J'=J+1} - \varepsilon_{J''=J} \\ &= 2B(J+1) \quad \text{cm}^{-1} \qquad (J = 1, 2, 3, \ldots \quad (\text{but } J \neq 0))\end{aligned} \tag{4.13a}$$

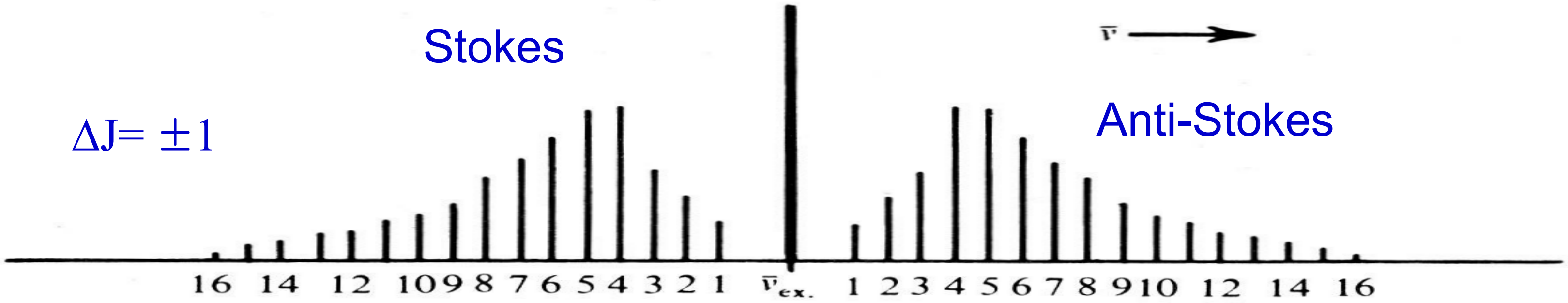
2. $\Delta J = +2$ (S branch lines)

$$\begin{aligned}\Delta\varepsilon_S &= \varepsilon_{J'=J+2} - \varepsilon_{J''=J} \\ &= B(4J+6) \quad \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots)\end{aligned} \tag{4.13b}$$

Thus we shall have two series of lines in the Raman spectrum:

$$\left.\begin{aligned}\bar{\nu}_R &= \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_R = \bar{\nu}_{\text{ex.}} \pm 2B(J+1) \quad \text{cm}^{-1} \qquad (J = 1, 2, \ldots) \\ \bar{\nu}_S &= \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_S = \bar{\nu}_{\text{ex.}} \pm B(4J+6) \quad \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots)\end{aligned}\right\} \tag{4.14}$$

These series are sketched separately in Fig. 4.5(*a*) and (*b*), where each line is labelled with its corresponding *lower* J value. In the R branch, lines appear at $4B$, $6B$, $8B$, $10B$, . . . cm^{-1} from the exciting line, while the S branch series occurs at $6B$, $10B$, $14B$, . . . cm^{-1}. The complete spectrum, shown in Fig. 4.5(*c*) illustrates how every alternate R line is overlapped by an S line. Thus a marked intensity alternation is to be expected which, it should be noted, is not connected with nuclear spin statistics.

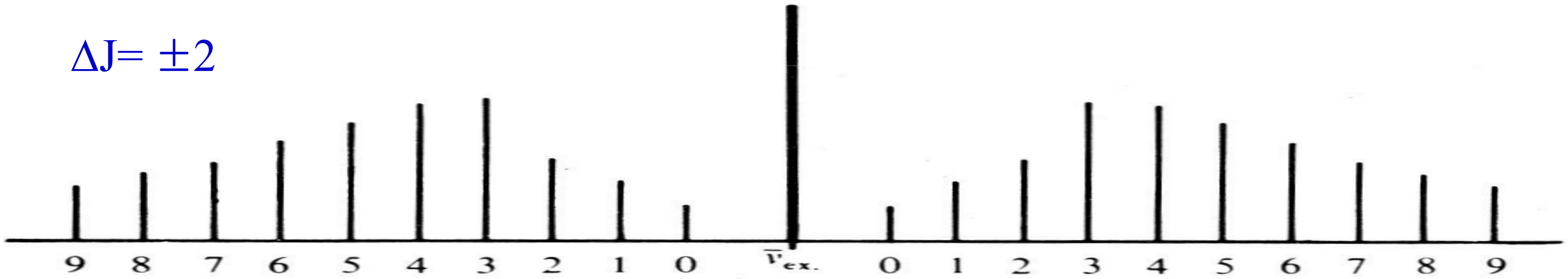


Stokes

$\Delta J = \pm 1$

Anti-Stokes

(*a*) *R* branch



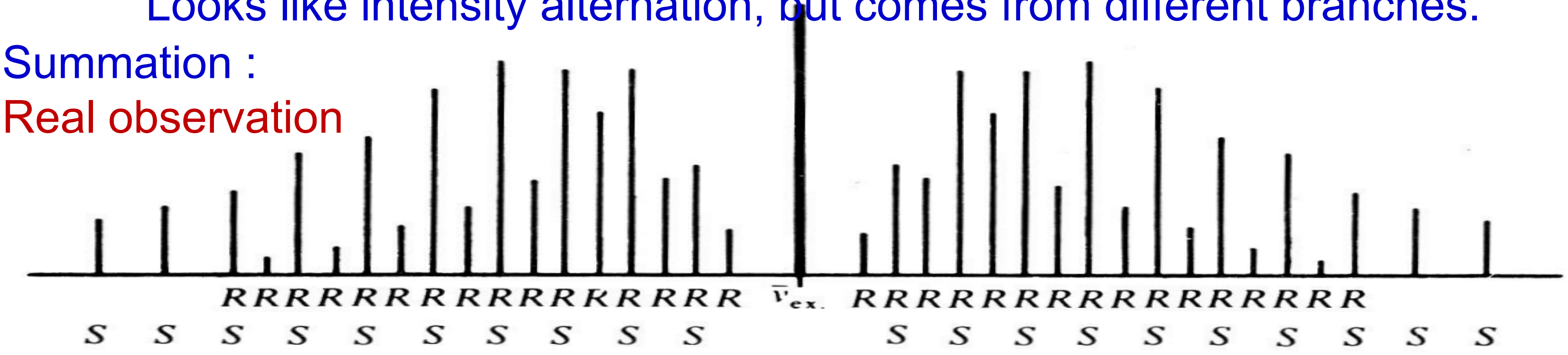
$\Delta J = \pm 2$

(*b*) *S* branch

Looks like intensity alternation, but comes from different branches.

Summation :

Real observation



(*c*) Complete spectrum

4.2.3 Spherical Top Molecules: Asymmetric Top Molecules

We cannot observe the rotational spectrum of spherical tops because of no dipole moment.

Spherical top molecules: CH_4, SiH_4 : like a ball

Polarizability ellipsoid is completely spherical, so no change in polarizability.

→ **Raman inactive**

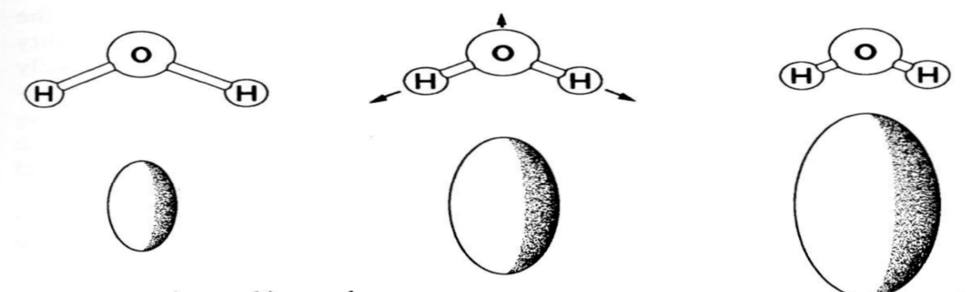
Asymmetric top molecules: All in Raman active. But the spectra are too complicate to analyze.

→ **Raman active**

4.3 VIBRATIONAL RAMAN SPECTRA

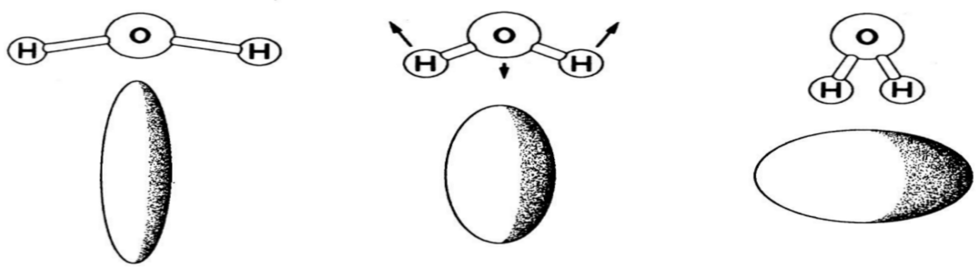
4.3.1 Raman Activity of Vibration

H_2O has 3 modes.



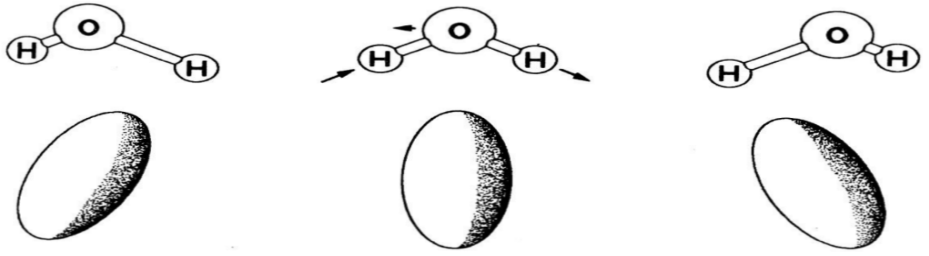
(a) ν_1, symmetric stretching mode

Change in polarizability ellipsoid → Raman active



(b) ν_2, bending mode

Change in polarizability ellipsoid → Raman active

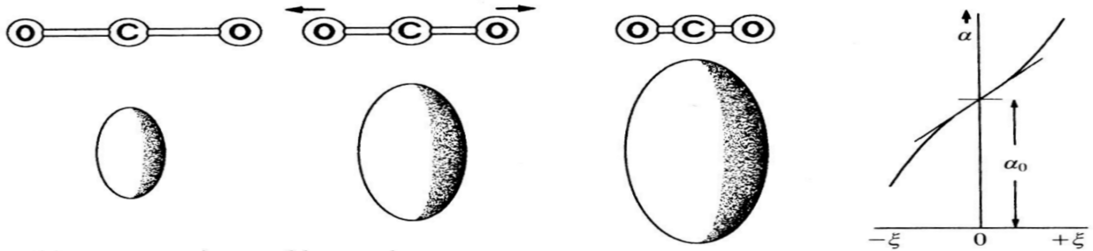


(c) ν_3, asymmetric stretching mode

Change in polarizability ellipsoid → Raman active

Symmetric vibrations give rise to intense Raman lines; non-symmetric ones are usually weak and sometimes unobservable.

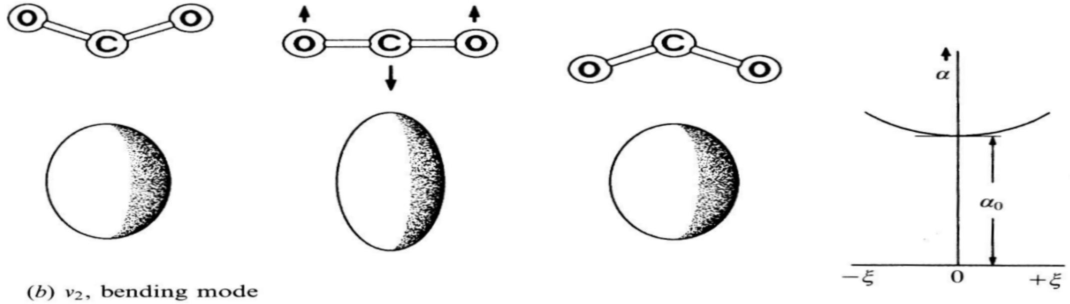
Polarizability change means the slope of variation!!!!



(a) ν_1, symmetric stretching mode

Change in polarizability ellipsoid → Raman active

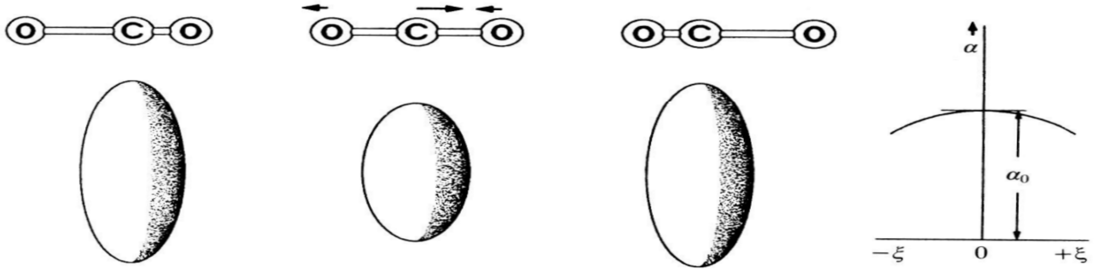
Polarizability change≠0



(b) ν_2, bending mode

Change in polarizability ellipsoid → Raman inactive

Polarizability change=0



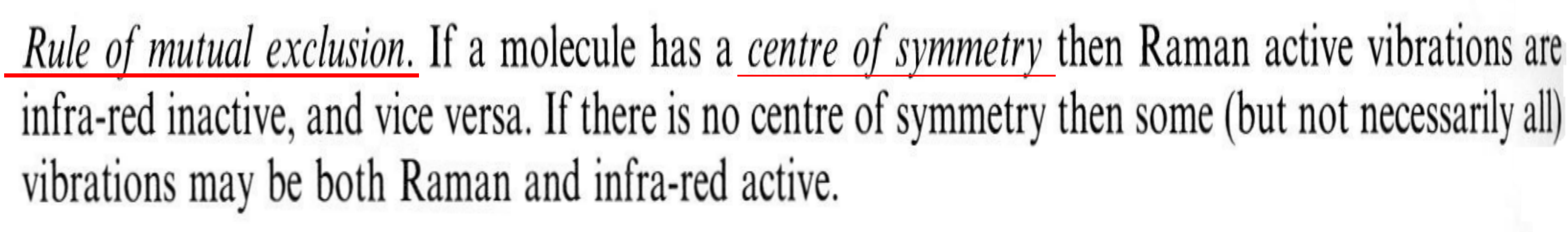
(c) ν_3, asymmetric stretching mode

Change in polarizability ellipsoid → Raman inactive

Polarizability change=0

4.3.2 Rule of Mutual Exclusion

Very important rule in IR and Raman spectroscopy



Rule of mutual exclusion. If a molecule has a *centre of symmetry* then Raman active vibrations are infra-red inactive, and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infra-red active.

Summary of IR and Raman spectra

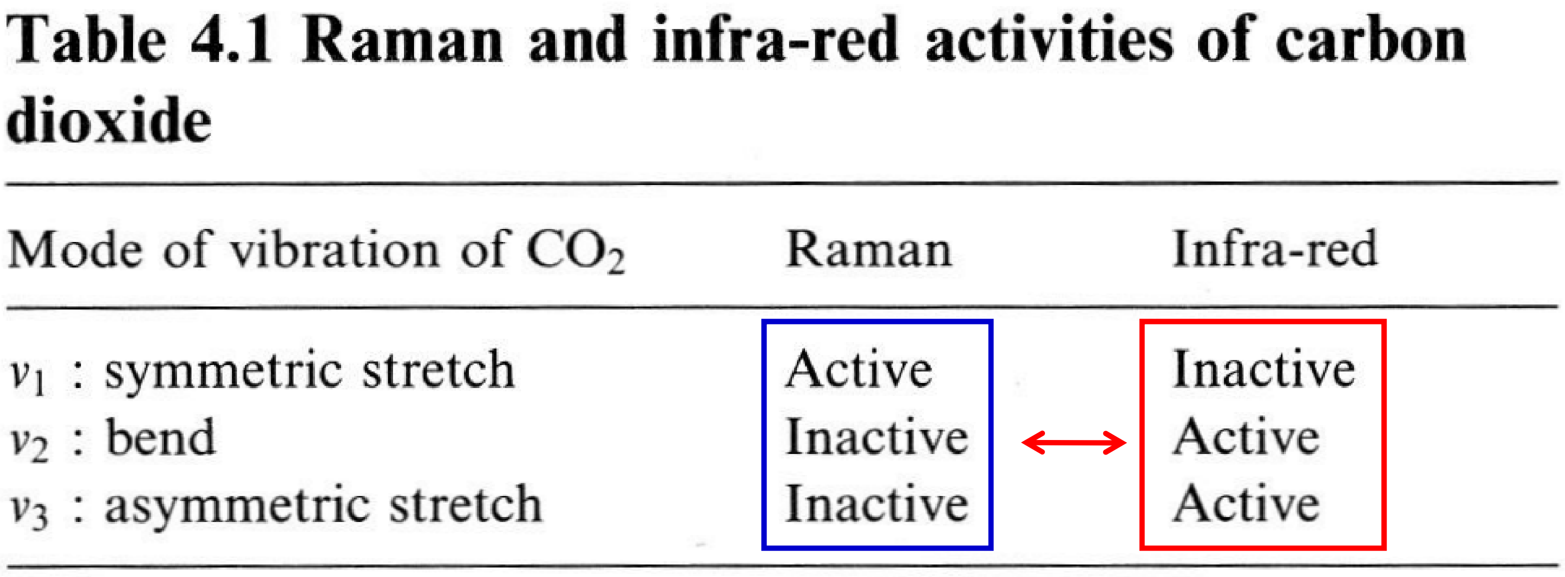
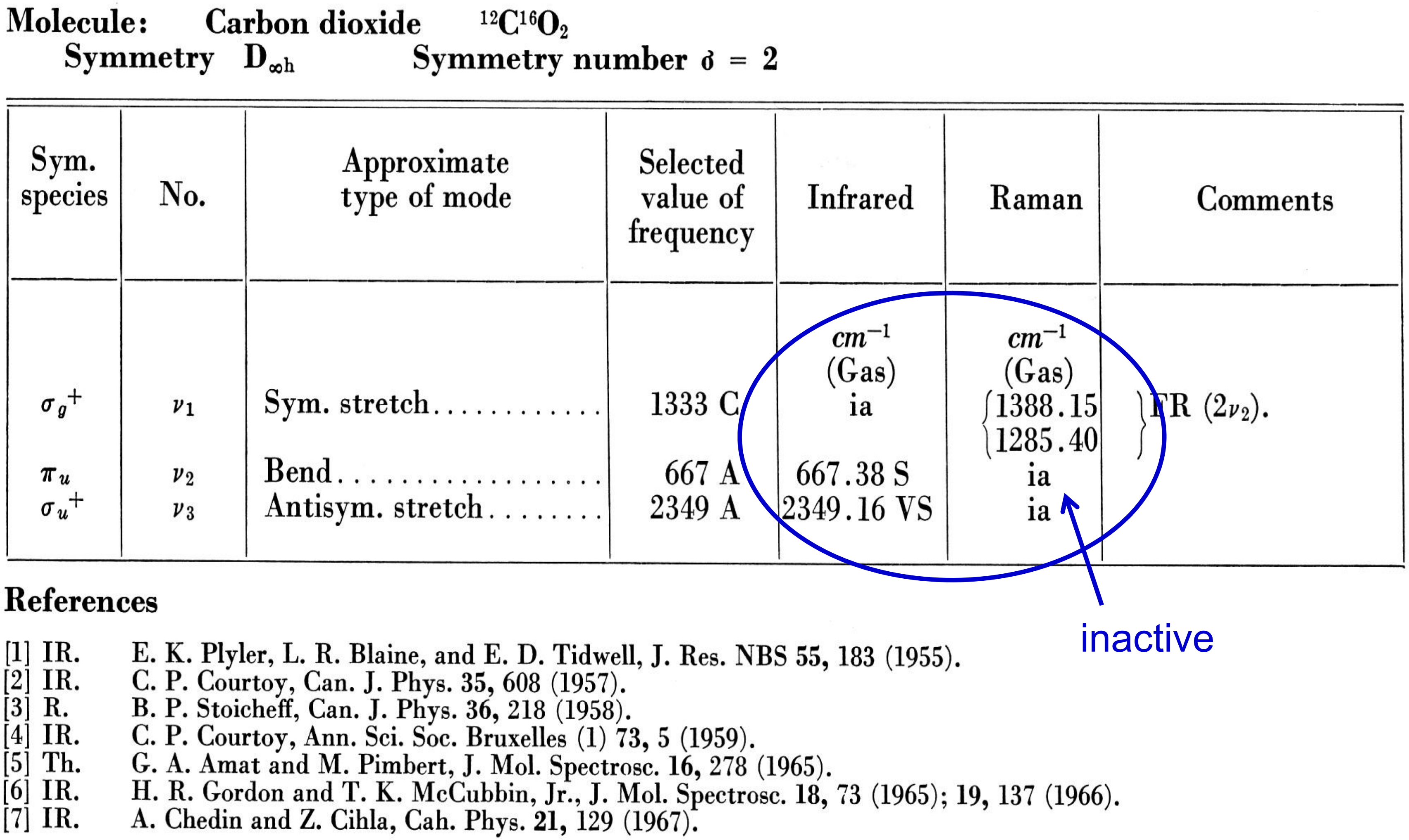


Table 4.1 Raman and infra-red activities of carbon dioxide

Mode of vibration of CO_2	Raman		Infra-red
ν_1 : symmetric stretch	Active		Inactive
ν_2 : bend	Inactive	⟷	Active
ν_3 : asymmetric stretch	Inactive		Active

The rule of mutual exclusion is applied to molecules with center of symmetry only.



Molecule: **Carbon dioxide** $^{12}C^{16}O_2$
Symmetry $D_{\infty h}$ **Symmetry number** $\sigma = 2$

Sym. species	No.	Approximate type of mode	Selected value of frequency	Infrared	Raman	Comments
				cm^{-1} (Gas)	cm^{-1} (Gas)	
σ_g^+	ν_1	Sym. stretch............	1333 C	ia	1388.15 1285.40	FR ($2\nu_2$).
π_u	ν_2	Bend..................	667 A	667.38 S	ia	
σ_u^+	ν_3	Antisym. stretch........	2349 A	2349.16 VS	ia	

inactive

References

[1] IR. E. K. Plyler, L. R. Blaine, and E. D. Tidwell, J. Res. NBS **55,** 183 (1955).
[2] IR. C. P. Courtoy, Can. J. Phys. **35,** 608 (1957).
[3] R. B. P. Stoicheff, Can. J. Phys. **36,** 218 (1958).
[4] IR. C. P. Courtoy, Ann. Sci. Soc. Bruxelles (1) **73,** 5 (1959).
[5] Th. G. A. Amat and M. Pimbert, J. Mol. Spectrosc. **16,** 278 (1965).
[6] IR. H. R. Gordon and T. K. McCubbin, Jr., J. Mol. Spectrosc. **18,** 73 (1965); **19,** 137 (1966).
[7] IR. A. Chedin and Z. Cihla, Cah. Phys. **21,** 129 (1967).

4.3.4 Vibrational Raman Spectra

- Since the Raman spectroscopy shows very weak intensity compared to the ordinary absorption and emission spectroscopy, it can be applied to the condensed phase of materials such as the solid and liquid due to high density.
- Since the transition frequency in Raman spectrum is the difference between the incident and scattered radiation, we can observe vibrational spectra using visible radiation sources. Many excellent visible radiation sources have been developed.
- In order to increase the intensity, many techniques have been already developed using high intensity laser power.
- Finally, Stokes scattering shows much higher intensity than anti-Stokes scattering in Raman spectroscopy. Generally, we observe Stokes scattering only.

The structure of vibrational Raman spectra is easily discussed. For every vibrational mode we can write an expression of the form:

Vibrational energy

$$\underline{\varepsilon = \bar{\omega}_e(v+\tfrac{1}{2}) - \bar{\omega}_e x_e (v+\tfrac{1}{2})^2} \quad \text{cm}^{-1} \qquad (v = 0,\ 1,\ 2,\ \dots) \qquad (4.15)$$

where, as before (cf. Eq. (3.12)), $\bar{\omega}_e$ is the equilibrium vibrational frequency expressed in wavenumbers and x_e is the anharmonicity constant. Such an expression is perfectly general, whatever the shape of the molecule or the nature of the vibration. Quite general, too, is the selection rule:

Vibrational Raman selection rule is the same as IR.

$$\boxed{\Delta v = 0, \pm 1, \pm 2, \dots} \qquad (4.16)$$

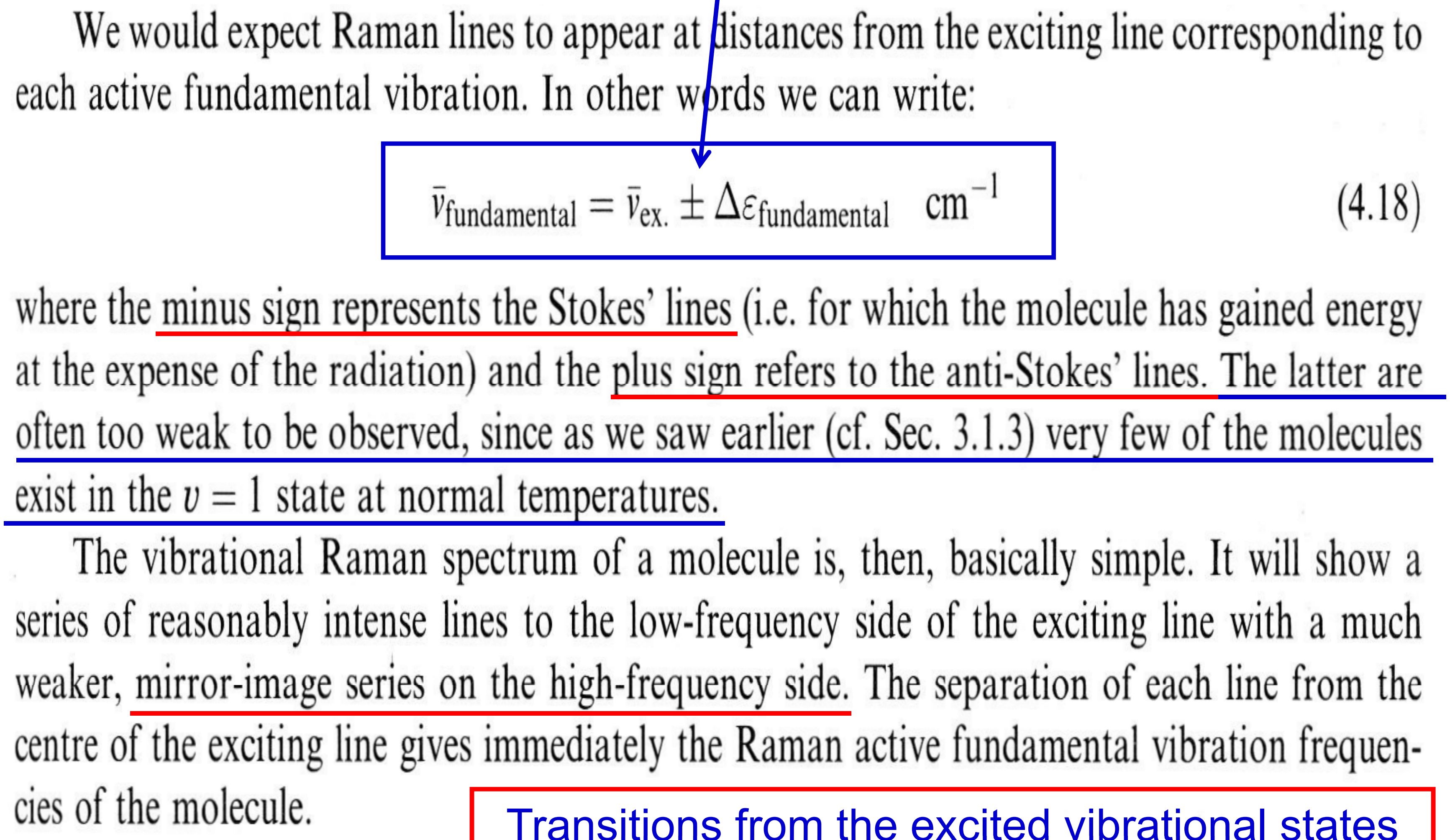
for real molecules

which is the same for Raman as for infra-red spectroscopy, the probability of $\Delta v = \pm 2, \pm 3, \dots$ decreasing rapidly.

Particularizing, now, to Raman active modes, we can apply the selection rule (4.16) to the energy level expression (4.15) and obtain the transition energies (cf. Eq. (3.15)):

$$\left.\begin{array}{lll}
\text{Strongest intensity} & v=0 \to v=1: \ \underline{\Delta\varepsilon_{\text{fundamental}}} & = \bar{\omega}_e(1-2x_e) \quad \text{cm}^{-1} \\
\text{weak} & v=0 \to v=2: \ \underline{\Delta\varepsilon_{\text{overtone}}} & = 2\bar{\omega}_e(1-3x_e) \quad \text{cm}^{-1} \\
\text{intensity} & v=1 \to v=2: \ \underline{\Delta\varepsilon_{\text{hot}}} & = \bar{\omega}_e(1-4x_e) \quad \text{cm}^{-1} \qquad \text{etc.}
\end{array}\right\} \qquad (4.17)$$

- for Stokes, + for anti-Stokes



We would expect Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibration. In other words we can write:

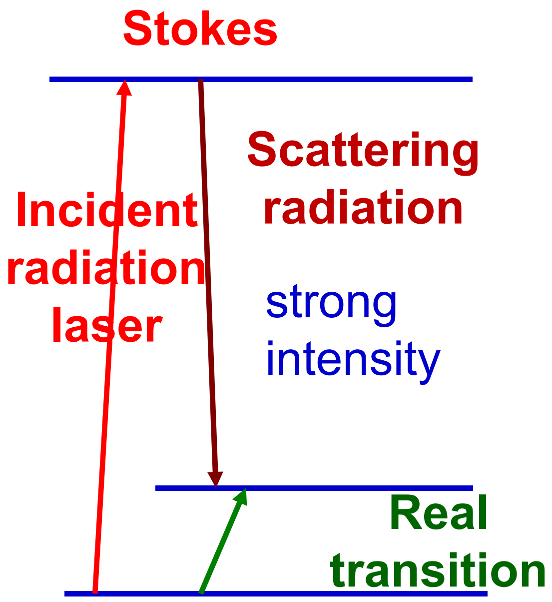
$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_{\text{fundamental}} \quad \text{cm}^{-1} \tag{4.18}$$

where the minus sign represents the Stokes' lines (i.e. for which the molecule has gained energy at the expense of the radiation) and the plus sign refers to the anti-Stokes' lines. The latter are often too weak to be observed, since as we saw earlier (cf. Sec. 3.1.3) very few of the molecules exist in the $v = 1$ state at normal temperatures.

The vibrational Raman spectrum of a molecule is, then, basically simple. It will show a series of reasonably intense lines to the low-frequency side of the exciting line with a much weaker, mirror-image series on the high-frequency side. The separation of each line from the centre of the exciting line gives immediately the Raman active fundamental vibration frequencies of the molecule.

Transitions from the excited vibrational states make anti-Stokes scattering weaker.

Raman and Rayleigh transition



Stokes

Incident radiation laser

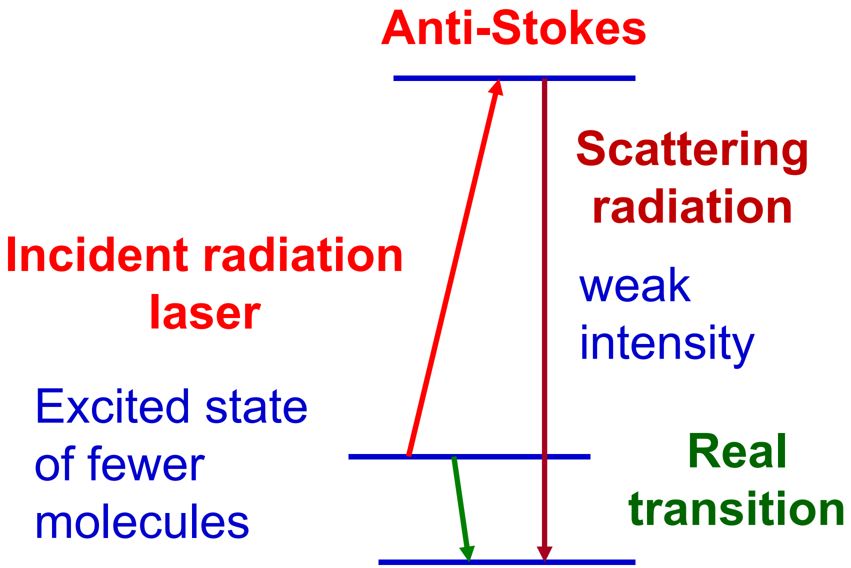
Scattering radiation

strong intensity

Real transition

Ground state of many molecules

Transition from ground state : strong intensity



Anti-Stokes

Incident radiation laser

Scattering radiation

weak intensity

Excited state of fewer molecules

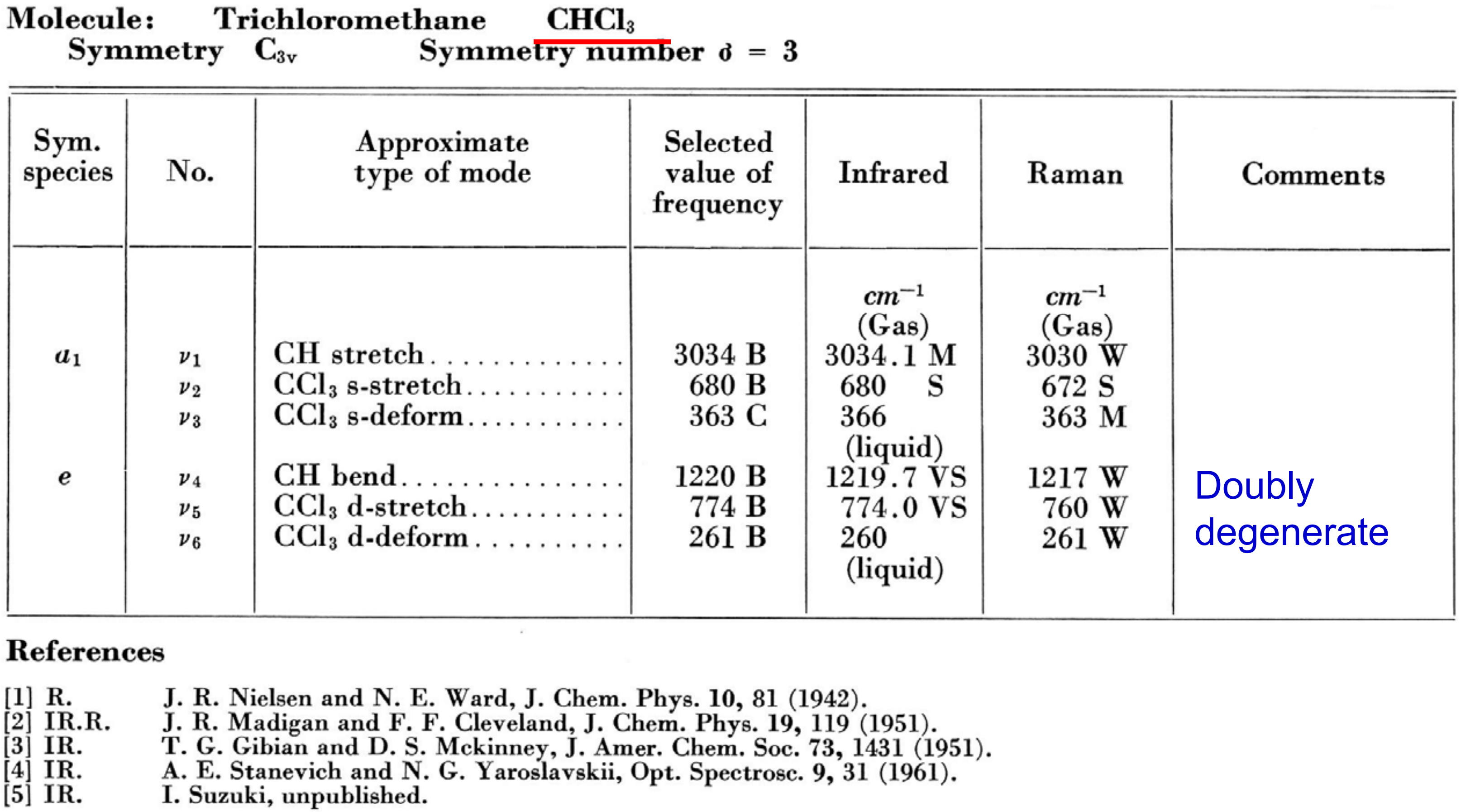
Real transition

Transition from excited states : weak intensity

Stokes and anti-Stokes are exactly symmetric about excitation laser frequency.

Let us apply Raman to $CHCl_3$ (No center of symmetry, IR and Raman)

9 vibrational degrees of freedom, but only 6 modes.

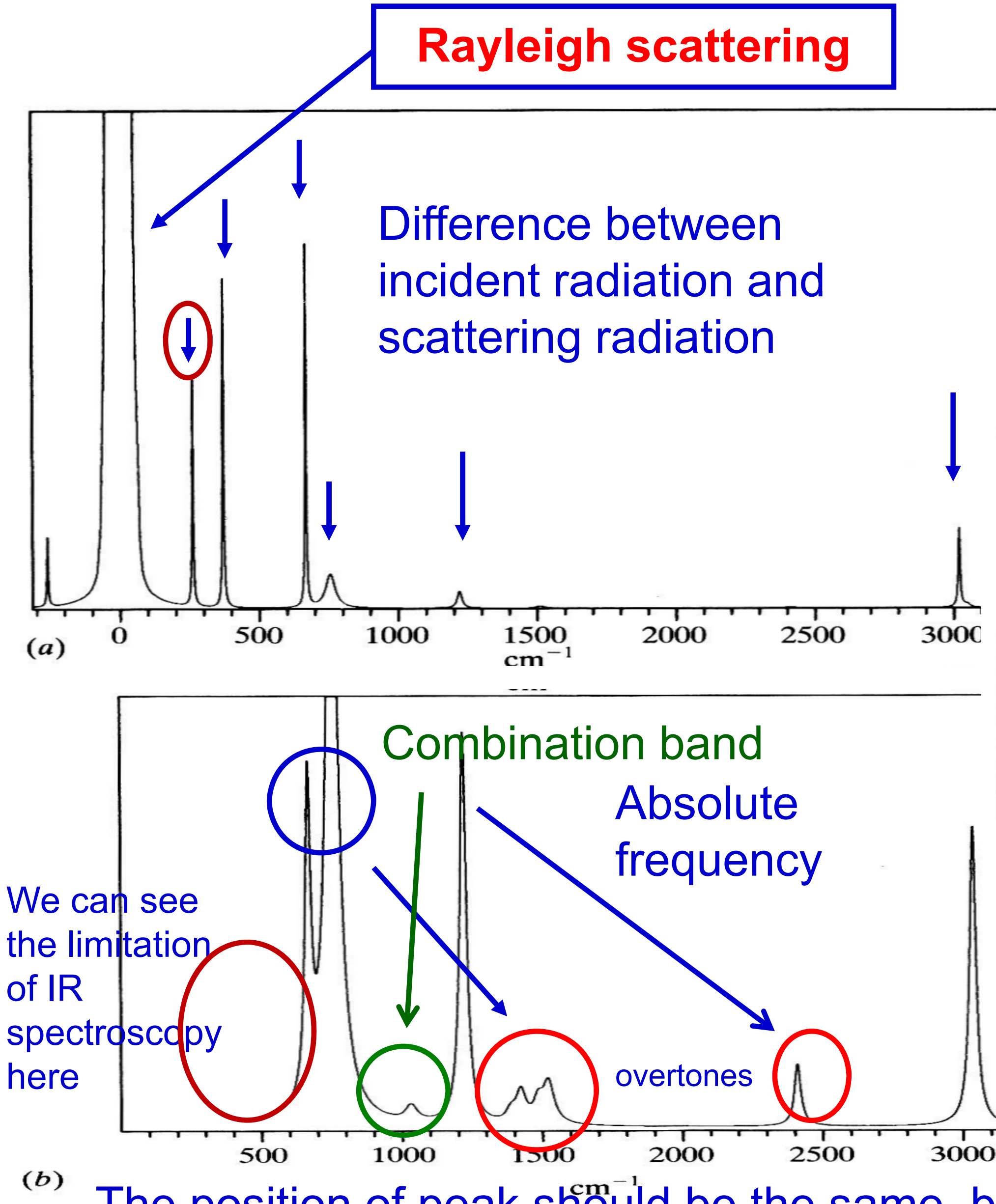


Molecule: **Trichloromethane** **$CHCl_3$**
Symmetry **C_{3v}** **Symmetry number $\sigma = 3$**

Sym. species	No.	Approximate type of mode	Selected value of frequency	Infrared	Raman	Comments
				cm^{-1} (Gas)	cm^{-1} (Gas)	
a_1	ν_1	CH stretch	3034 B	3034.1 M	3030 W	
	ν_2	CCl_3 s-stretch	680 B	680 S	672 S	
	ν_3	CCl_3 s-deform	363 C	366 (liquid)	363 M	
e	ν_4	CH bend	1220 B	1219.7 VS	1217 W	Doubly degenerate
	ν_5	CCl_3 d-stretch	774 B	774.0 VS	760 W	
	ν_6	CCl_3 d-deform	261 B	260 (liquid)	261 W	

References

[1] R. J. R. Nielsen and N. E. Ward, J. Chem. Phys. 10, 81 (1942).
[2] IR.R. J. R. Madigan and F. F. Cleveland, J. Chem. Phys. 19, 119 (1951).
[3] IR. T. G. Gibian and D. S. Mckinney, J. Amer. Chem. Soc. 73, 1431 (1951).
[4] IR. A. E. Stanevich and N. G. Yaroslavskii, Opt. Spectrosc. 9, 31 (1961).
[5] IR. I. Suzuki, unpublished.



Rayleigh scattering

Difference between incident radiation and scattering radiation

Combination band

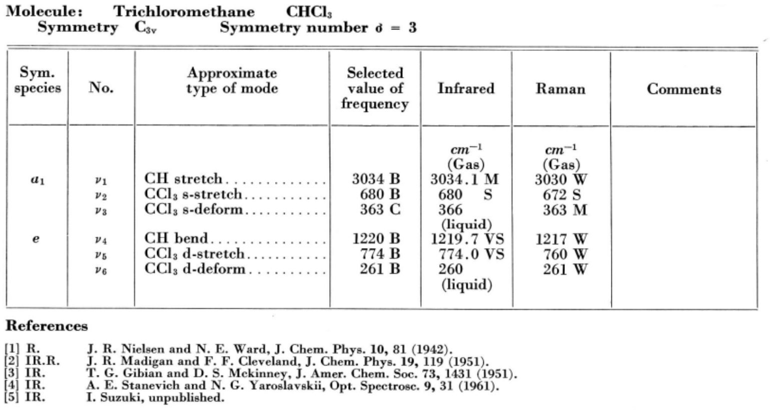
Absolute frequency

We can see the limitation of IR spectroscopy here

overtones

Molecule is active in IR and Raman

Raman spectrum see 6 modes



Molecule: Trichloromethane $CHCl_3$
Symmetry C_{3v} Symmetry number $\sigma = 3$

Sym. species	No.	Approximate type of mode	Selected value of frequency	Infrared	Raman	Comments
				cm^{-1} (Gas)	cm^{-1} (Gas)	
a_1	ν_1	CH stretch	3034 B	3034.1 M	3030 W	
	ν_2	CCl_3 s-stretch	680 B	680 S	672 S	
	ν_3	CCl_3 s-deform	363 C	366 (liquid)	363 M	
e	ν_4	CH bend	1220 B	1219.7 VS	1217 W	
	ν_5	CCl_3 d-stretch	774 B	774.0 VS	760 W	
	ν_6	CCl_3 d-deform	261 B	260 (liquid)	261 W	

References

[1] R. J. R. Nielsen and N. E. Ward, J. Chem. Phys. 10, 81 (1942).
[2] IR.R. J. R. Madigan and F. F. Cleveland, J. Chem. Phys. 19, 119 (1951).
[3] IR. T. G. Gibian and D. S. Mckinney, J. Amer. Chem. Soc. 73, 1431 (1951).
[4] IR. A. E. Stanevich and N. G. Yaroslavskii, Opt. Spectrosc. 9, 31 (1961).
[5] IR. I. Suzuki, unpublished.

IR absorption spectrum see only 5 modes

The position of peak should be the same, but the intensity is not the same because of different transition mechanism.

Coarse structure : vibrational

4.3.5 Rotational Fine Structure

Vibrationally excited but rotationally resolved spectrum

We need not consider in detail the rotational fine structure of Raman spectra in general, if only because such fine structure is rarely resolved, except in the case of diatomic molecules. For the latter we can write the vibration–rotation energy levels (cf. Eq. (3.18)) as:

$$\varepsilon_{J,v} = \underline{\bar{\omega}_e(v+\tfrac{1}{2}) - \bar{\omega}_e x_e(v+\tfrac{1}{2})^2} + \underline{BJ(J+1)} \quad \mathrm{cm}^{-1} \qquad (v = 0, 1, 2, \ldots;\ J = 0, 1, 2, \ldots) \tag{4.19}$$

where, as before in Raman, we ignore centrifugal distortion. For diatomic molecules the J selection rule is $\underline{\Delta J = 0, \pm 2 \text{ (Sec. 2.1)}}$ and, combining this with the vibrational change $v = 0 \rightarrow v = 1$, we have:.

We have already studied this rule.

meaningless

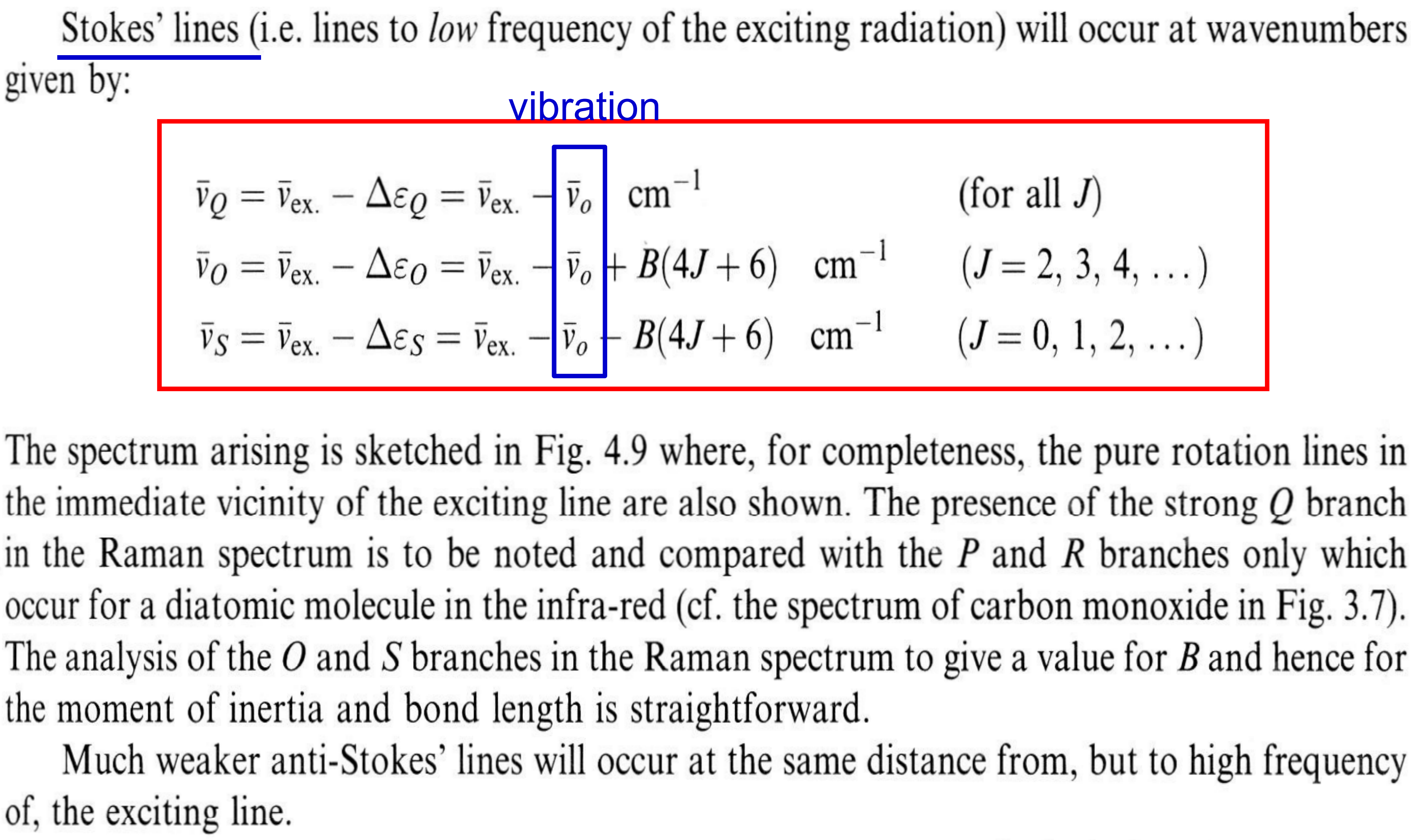
This is important in vibrational

$$\Delta J = 0: \qquad \Delta\varepsilon_Q = \bar{\nu}_o \quad \mathrm{cm}^{-1} \qquad \text{(for all } J) \tag{4.20}$$

$$\left.\begin{array}{ll} \boxed{\begin{array}{ll} \Delta J = +2: & \Delta\varepsilon_S = \bar{\nu}_o + B(4J+6) \quad \mathrm{cm}^{-1} \\ \Delta J = -2: & \Delta\varepsilon_O = \bar{\nu}_o - B(4J+6) \quad \mathrm{cm}^{-1} \end{array}} & \begin{array}{l} (J = 0, 1, 2, \ldots) \\ (J = 2, 3, 4, \ldots) \end{array} \end{array}\right\} \tag{4.21}$$

where we write $\bar{\nu}_o$ for $\bar{\omega}_e(1 - 2x_e)$ and use the subscripts O, Q, and S to refer to the O branch lines ($\Delta J = -2$), Q branch lines ($\Delta J = 0$), and S branch lines ($\Delta J = +2$), respectively.

From now on, let’s ignore anti-Stokes scattering.



Stokes’ lines (i.e. lines to *low* frequency of the exciting radiation) will occur at wavenumbers given by:

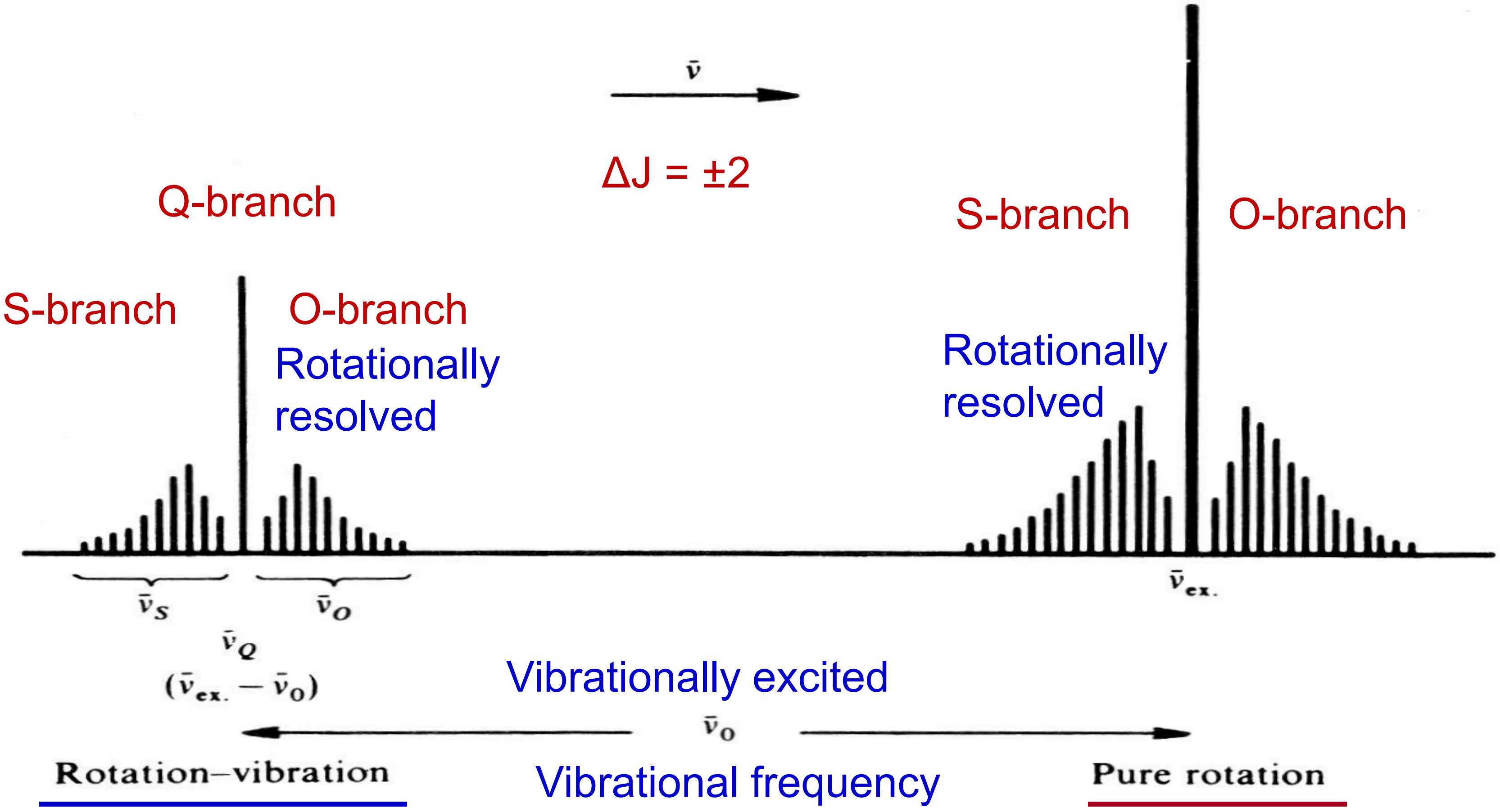
vibration

$$\begin{aligned}
\bar{\nu}_Q &= \bar{\nu}_{\text{ex.}} - \Delta\varepsilon_Q = \bar{\nu}_{\text{ex.}} - \boxed{\bar{\nu}_o} \quad \text{cm}^{-1} && \text{(for all } J\text{)}\\
\bar{\nu}_O &= \bar{\nu}_{\text{ex.}} - \Delta\varepsilon_O = \bar{\nu}_{\text{ex.}} - \boxed{\bar{\nu}_o} + B(4J+6) \quad \text{cm}^{-1} && (J = 2, 3, 4, \ldots)\\
\bar{\nu}_S &= \bar{\nu}_{\text{ex.}} - \Delta\varepsilon_S = \bar{\nu}_{\text{ex.}} - \boxed{\bar{\nu}_o} - B(4J+6) \quad \text{cm}^{-1} && (J = 0, 1, 2, \ldots)
\end{aligned}$$

The spectrum arising is sketched in Fig. 4.9 where, for completeness, the pure rotation lines in the immediate vicinity of the exciting line are also shown. The presence of the strong *Q* branch in the Raman spectrum is to be noted and compared with the *P* and *R* branches only which occur for a diatomic molecule in the infra-red (cf. the spectrum of carbon monoxide in Fig. 3.7). The analysis of the *O* and *S* branches in the Raman spectrum to give a value for *B* and hence for the moment of inertia and bond length is straightforward.

Much weaker anti-Stokes’ lines will occur at the same distance from, but to high frequency of, the exciting line.

Only Stokes lines are shown here



$\Delta J = \pm 2$

Q-branch

S-branch

O-branch

Rotationally resolved

S-branch

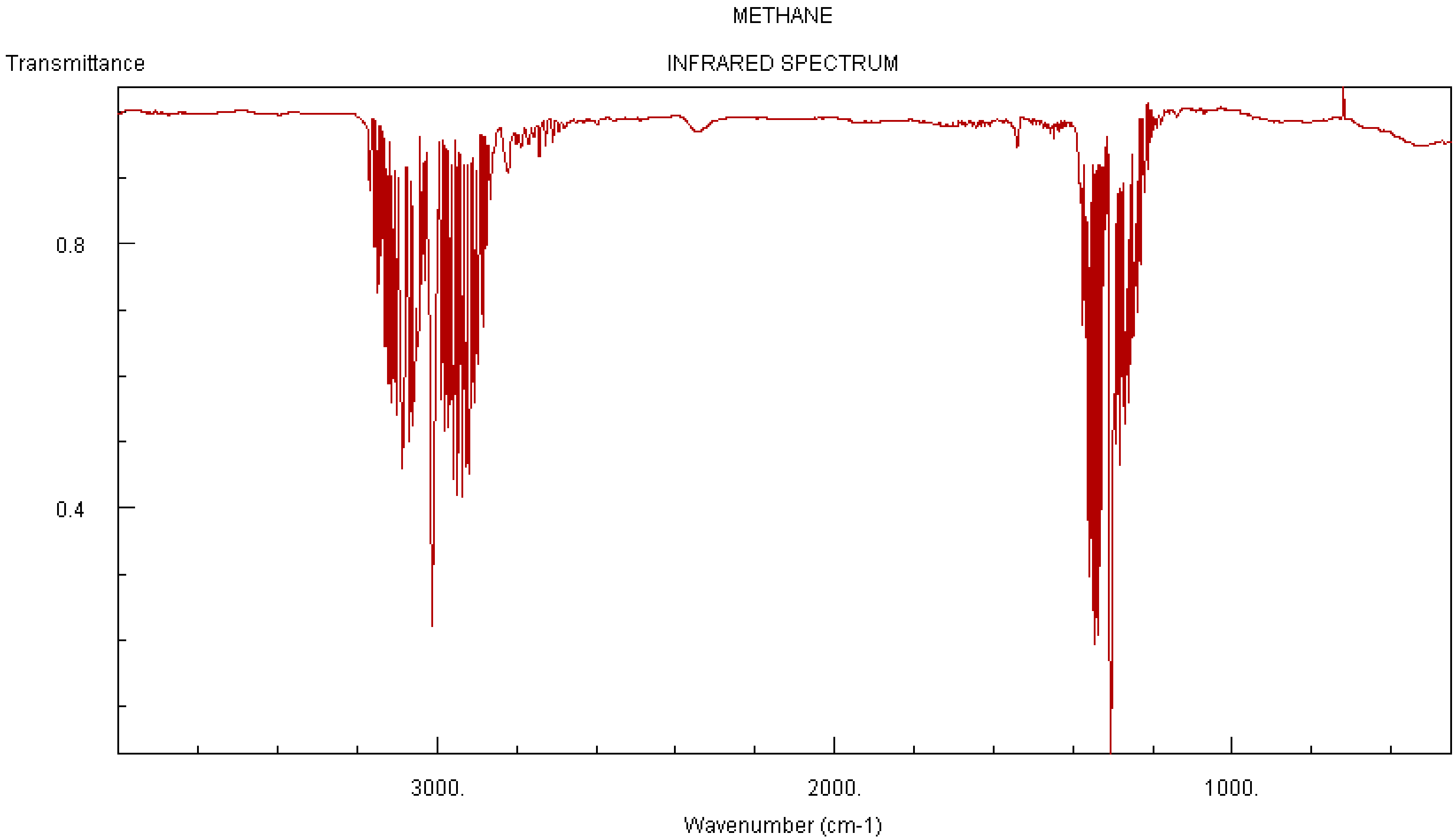
O-branch

Rotationally resolved

Vibrationally excited

Vibrational frequency

Methane



We cannot identify the vibrational modes from IR spectrum. We need Raman spectrum with polarized light source to see the modes.

We can observe the vibrational Raman spectra of nonpolar molecules.

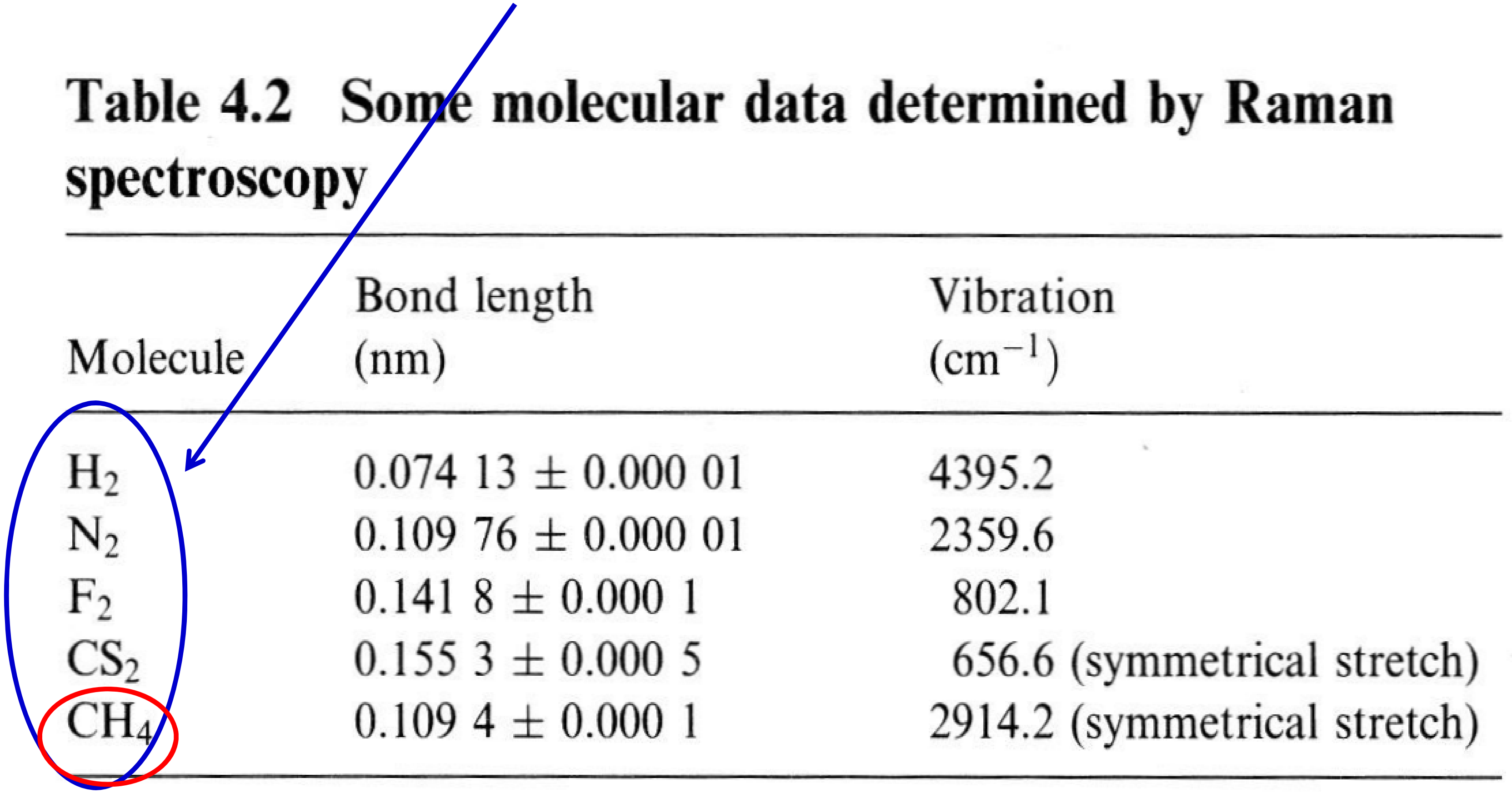


Table 4.2 Some molecular data determined by Raman spectroscopy

Molecule	Bond length (nm)	Vibration (cm^{-1})
H_2	0.074 13 ± 0.000 01	4395.2
N_2	0.109 76 ± 0.000 01	2359.6
F_2	0.141 8 ± 0.000 1	802.1
CS_2	0.155 3 ± 0.000 5	656.6 (symmetrical stretch)
CH_4	0.109 4 ± 0.000 1	2914.2 (symmetrical stretch)

Methane is a spherical-top which is Raman inactive. But the vibrationally excitation is not a spherical-top. (Ball → Rugby ball)

Let’s see the advantage of Raman spectroscopy.

4.4 POLARIZATION OF LIGHT AND THE RAMAN EFFECT

Comparison of IR and Raman Spectroscopy

	IR scheme	Raman scheme
Radiation source	IR	Visible or uv
Frequency	Absolute	Difference between incident and scattered light
Sensitivity	Strong	Extremely weak
Sample	Any phase	Mostly condensed phase
Polarization (Raman advantage)	No effect	Identification of vibrational symmetry

4.4.1 The Nature of Polarized Light

We can easily identify the symmetry of vibrational modes using a polarized light in Raman spectroscopy. Advantage of Raman over IR.

Unpolarized light: Natural light

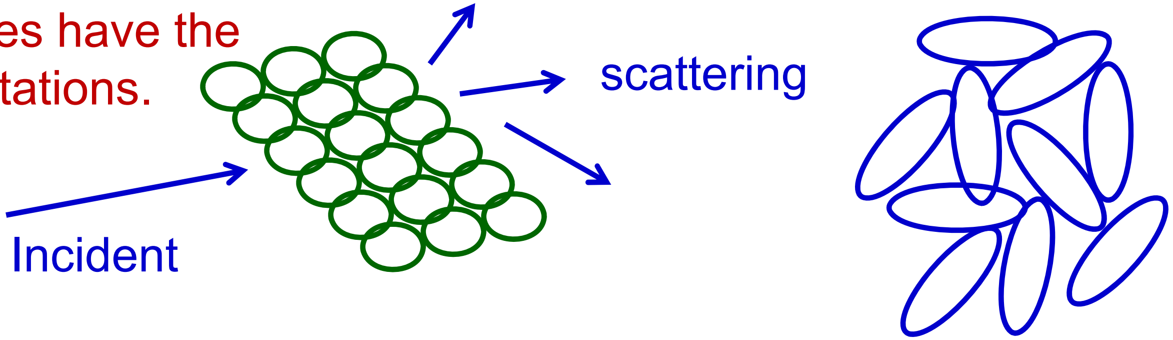
Plane polarized light

Circular polarized light

Ellipsoid polarized light

Matter can rotate the polarization axis in either right-hand or left-hand direction. We understand these molecules as optical isomers.

Suppose there are two types of molecules, spherical and ellipsoidal shape.



Looks like homogeneous even they have random orientation

Looks like heterogeneous for random orientation

All molecules have the same orientations.

scattering

Incident

Molecules have different orientations.

The scattering light shows homogeneous from homogeneous orientation, maintaining the polarization of radiation of ρ = 0.

The scattering light shows heterogeneous from random orientation of ellipsoid, losing the polarization of radiation of ρ = 1.

For most of cases, the degree of depolarization is 0 ≤ ρ ≤ 1. But, we can say which modes are more symmetric from the value of ρ.

We can obtain the information on the vibrational types from the degree of depolarization. This is a real important advantage of Raman over IR.

Difference between natural light and plane-polarized light.

If we use plane-polarized light as an incident radiation, what is happening in the scattering light ?

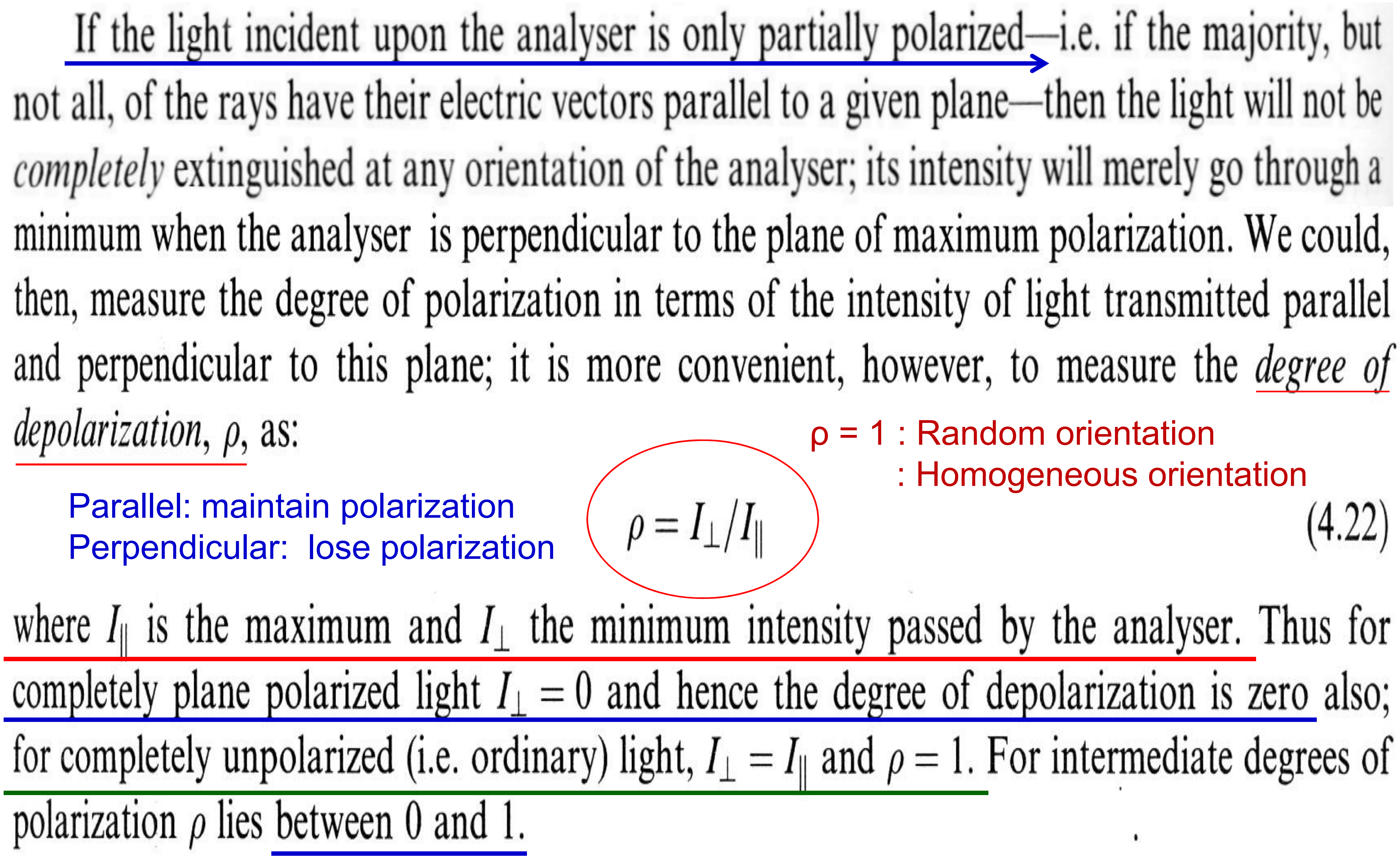
We try to examine the polarity of scattering light by using a polarizer. The polarity of scattering light can be determined by measuring at two different angles. Parallel angle and perpendicular angle.

If the intensity of light at two different angles is exactly same, we say the scattering light is completely depolarized and ρ=1.

If the intensity of light at two different angles is different, we say the scattering light is polarized and $\rho \neq 1$. $0 \leq \rho \leq 1$

Why we can see this kind of difference? We can obtain the information on the vibrational types from the degree of depolarization. This is a real important advantage of Raman over IR.

Polarization (ρ =0) vs. depolarization (ρ=1)



If the light incident upon the analyser is only partially polarized—i.e. if the majority, but not all, of the rays have their electric vectors parallel to a given plane—then the light will not be *completely* extinguished at any orientation of the analyser; its intensity will merely go through a minimum when the analyser is perpendicular to the plane of maximum polarization. We could, then, measure the degree of polarization in terms of the intensity of light transmitted parallel and perpendicular to this plane; it is more convenient, however, to measure the *degree of depolarization*, ρ, as:

$$\rho = I_{\perp}/I_{\parallel} \tag{4.22}$$

where $I_{\parallel}$ is the maximum and $I_{\perp}$ the minimum intensity passed by the analyser. Thus for completely plane polarized light $I_{\perp} = 0$ and hence the degree of depolarization is zero also; for completely unpolarized (i.e. ordinary) light, $I_{\perp} = I_{\parallel}$ and $\rho = 1$. For intermediate degrees of polarization ρ lies between 0 and 1.

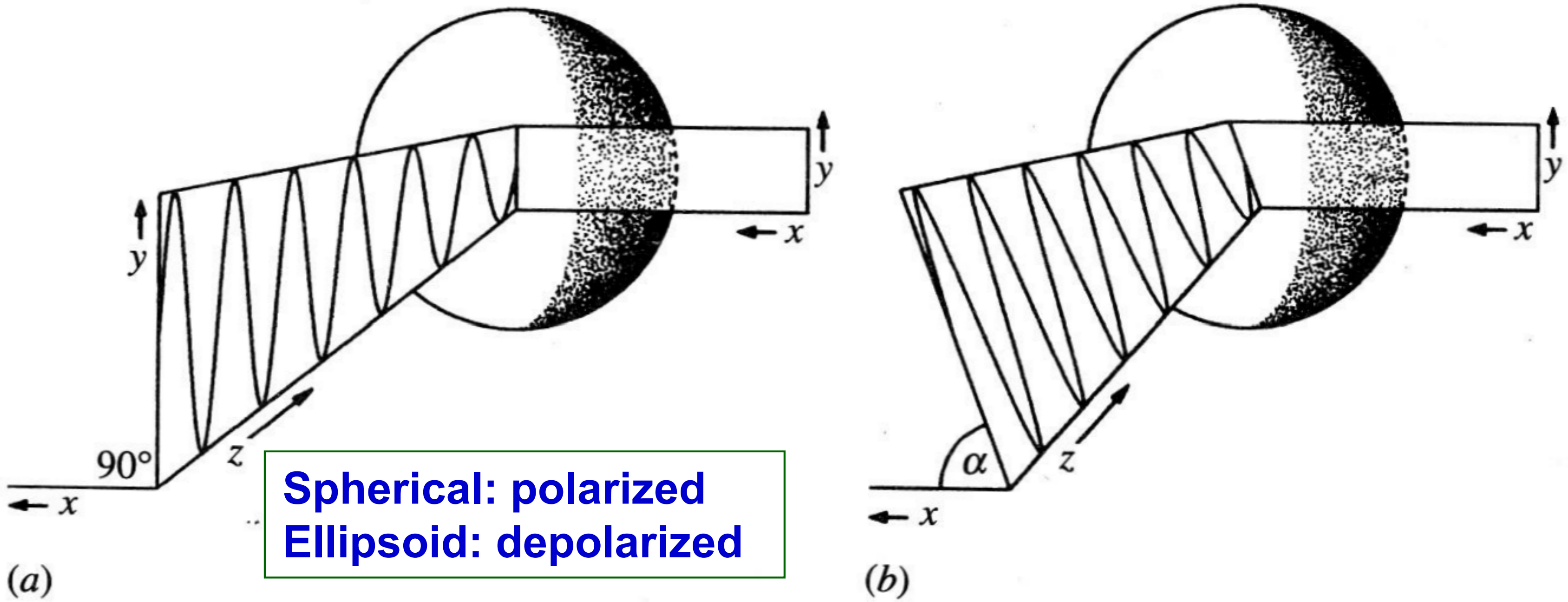
ρ = 1 : Random orientation
: Homogeneous orientation

Parallel: maintain polarization
Perpendicular: lose polarization

Incident light: polarized, Scattered light : polarized : polarized scattering
Incident light : polarized, Scattered light : depolarized : depolarized scattering

Polarization of scattering light

Observation of scattering should be perpendicular to incident radiation to minimize the effect of incident radiation.

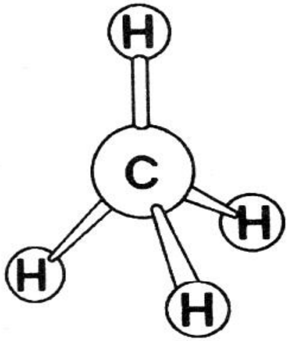


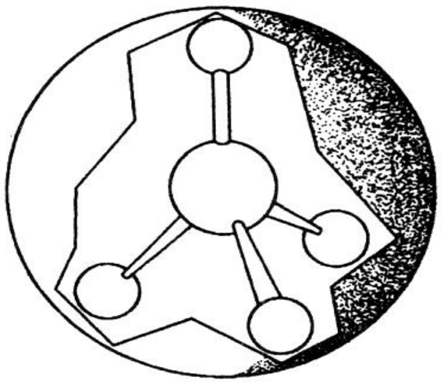
Spherical: polarized
Ellipsoid: depolarized

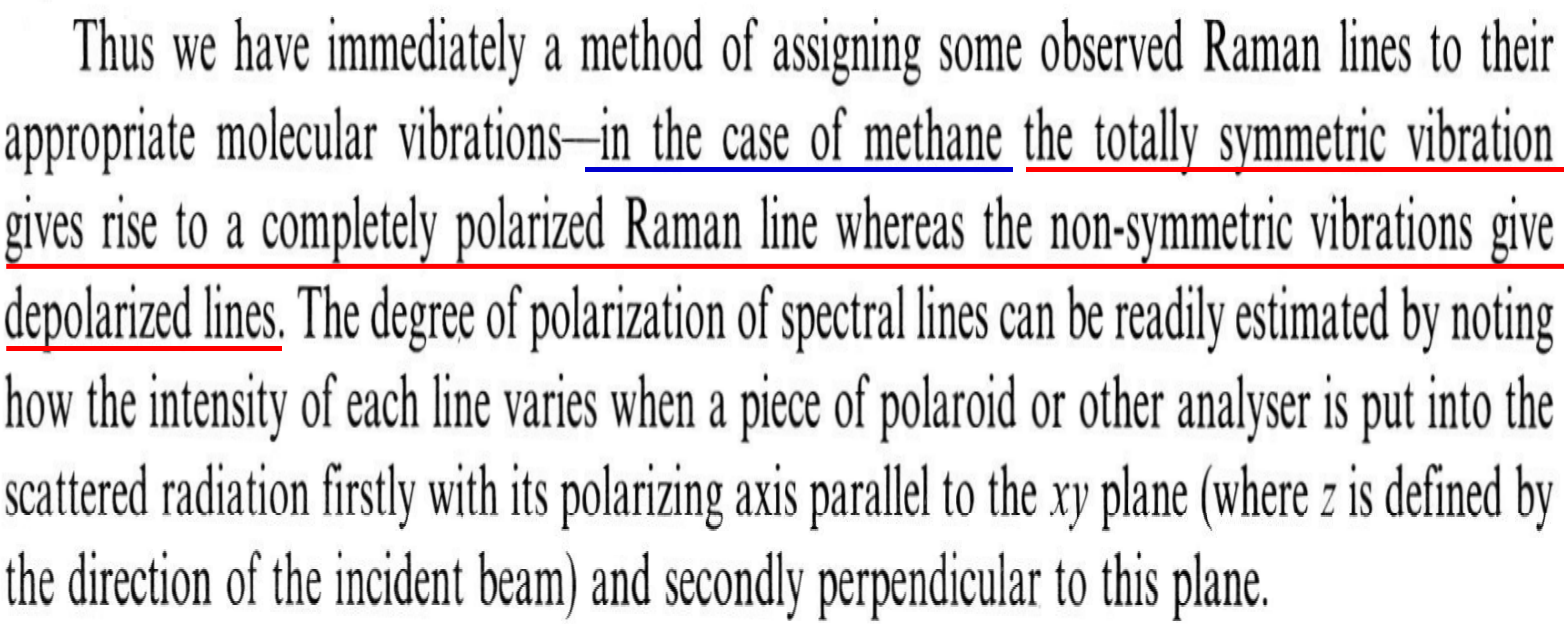
Plane of electric field

Incident light: yz-plane
Observation of scattering light: xy-plane (polarized light)
Observation of scattering light: xz-plane (depolarized light)

4.4.2 Vibrations of Spherical Top Molecules







Thus we have immediately a method of assigning some observed Raman lines to their appropriate molecular vibrations—in the case of methane the totally symmetric vibration gives rise to a completely polarized Raman line whereas the non-symmetric vibrations give depolarized lines. The degree of polarization of spectral lines can be readily estimated by noting how the intensity of each line varies when a piece of polaroid or other analyser is put into the scattered radiation firstly with its polarizing axis parallel to the *xy* plane (where *z* is defined by the direction of the incident beam) and secondly perpendicular to this plane.

Totally symmetric vibrational modes maintains spherical shape.
But non-symmetric vibrational modes make ellipsoid shape.

Try to analyze N_2O using IR and Raman

4.4.3 Extension to Other Types of Molecule

Nitrous oxide : N_2O

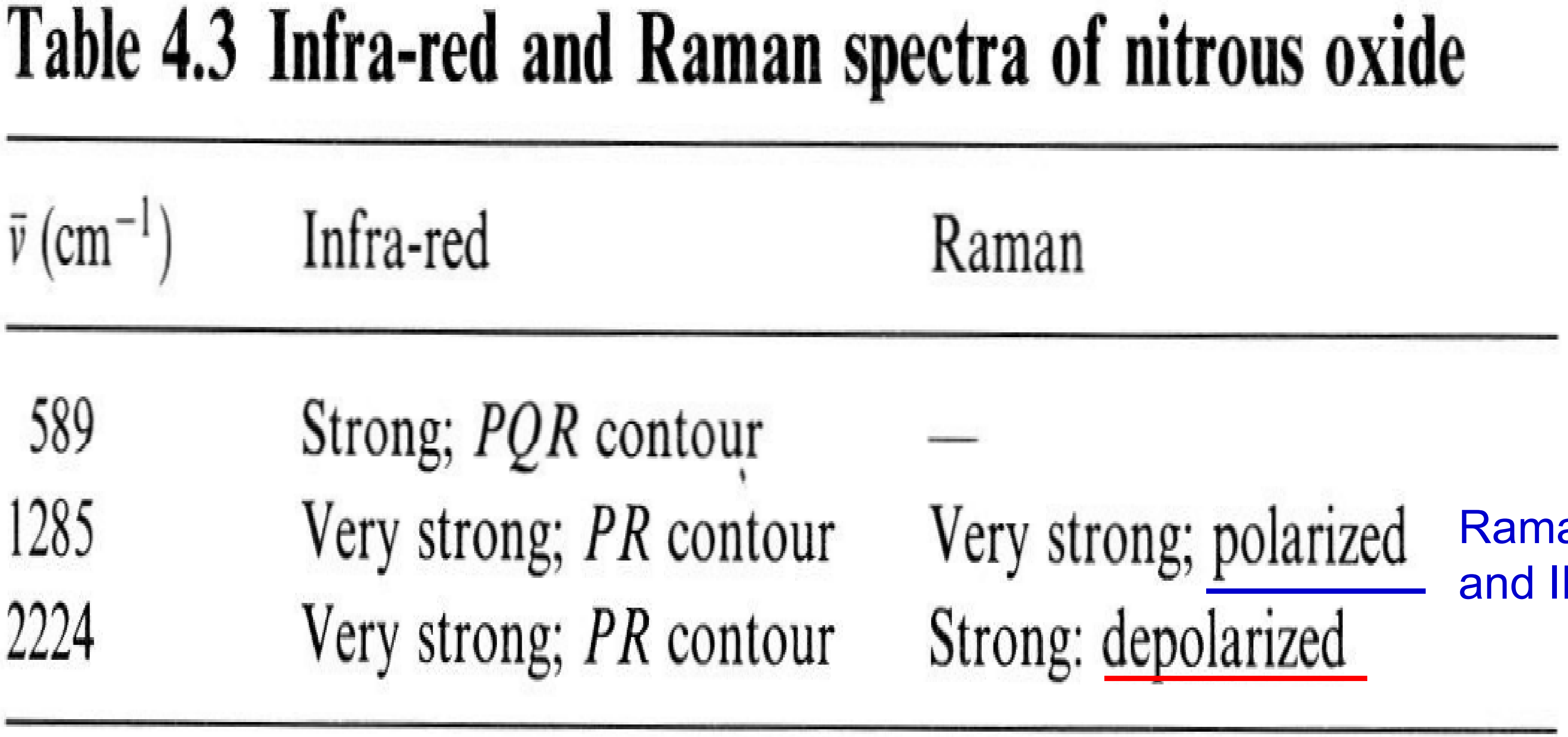


Table 4.3 Infra-red and Raman spectra of nitrous oxide

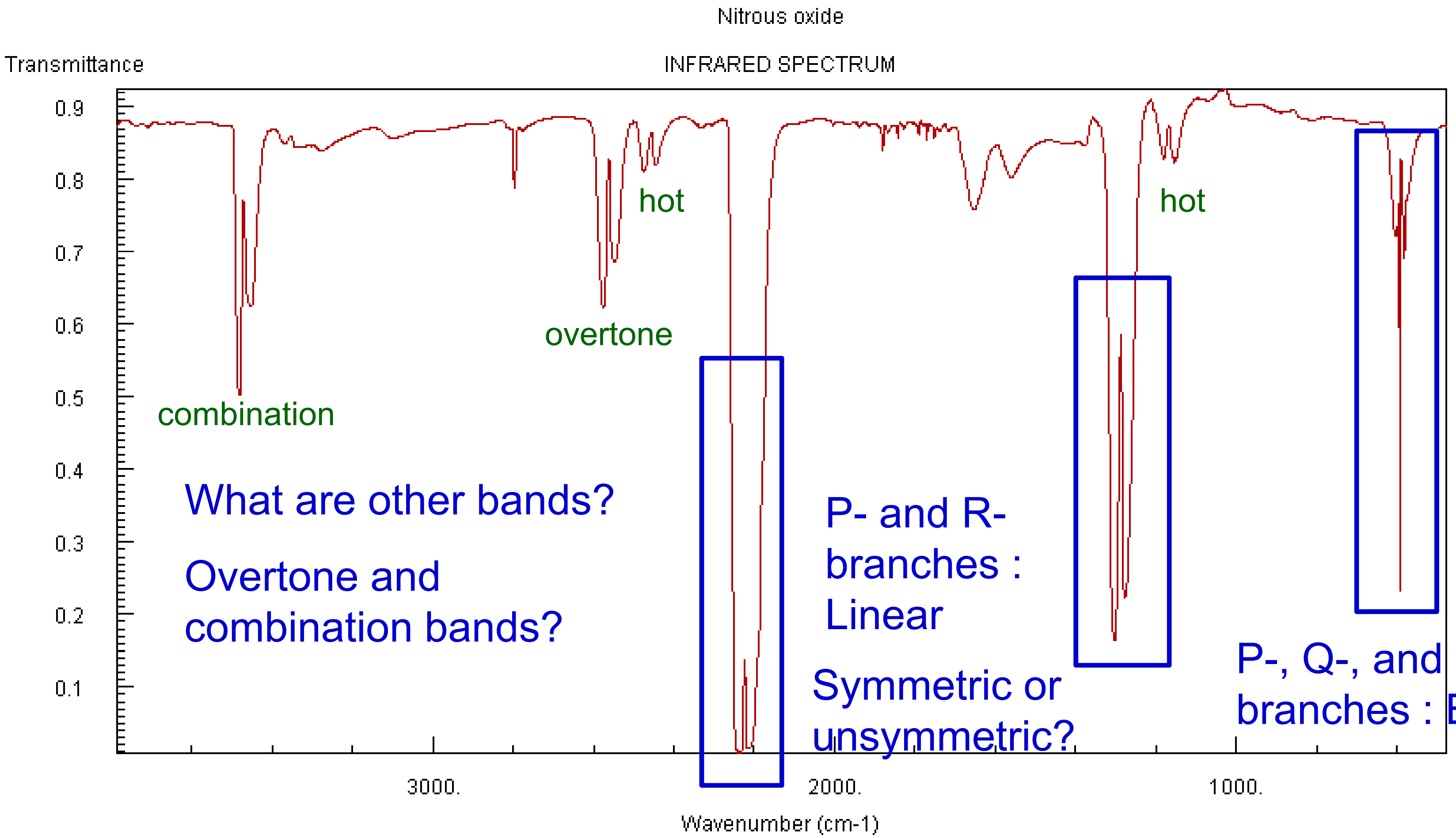
$\bar{\nu}$ (cm^{-1})	Infra-red	Raman
589	Strong; *PQR* contour	—
1285	Very strong; *PR* contour	Very strong; polarized
2224	Very strong; *PR* contour	Strong: depolarized

Raman and IR

Linear structure : P- and R-branches

Polarized : symmetric vibration
Depolarized : unsymmetric

Low resolution spectrum of N_2O



What are other bands?

Overtone and combination bands?

P- and R- branches : Linear

Symmetric or unsymmetric?

P-, Q-, and R- branches : Bent

Analysis of IR/Raman Spectra

- Structure : Linear or Bent structure
- Arrangement of atoms in N_2O : NNO or NON
- Number of vibrational modes : 3
- Assignment of each vibrational mode to IR/Raman spectra.
- IR spectra :
  - Stretching vibration ; $\Delta J = \pm 1$
  - Bending vibration ; $\Delta J = 0, \pm 1$
- Raman spectra :
  - Symmetric vibration : polarized
  - Antisymmetric vibration : depolarized

4.5 STRUCTURE DETERMINATION FROM RAMAN AND INFRARED SPECTROSCOPY

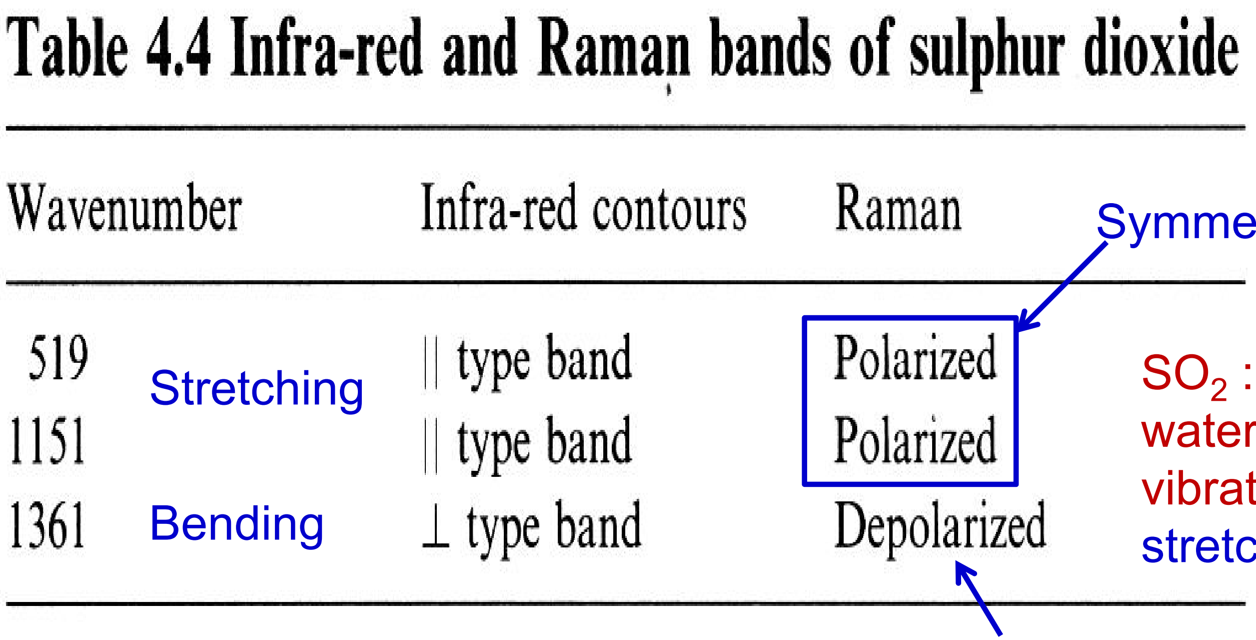


Table 4.4 Infra-red and Raman bands of sulphur dioxide

Wavenumber	Infra-red contours	Raman
519	∥ type band	Polarized
1151	∥ type band	Polarized
1361	⊥ type band	Depolarized

Stretching

Bending

Bent structure

Symmetric

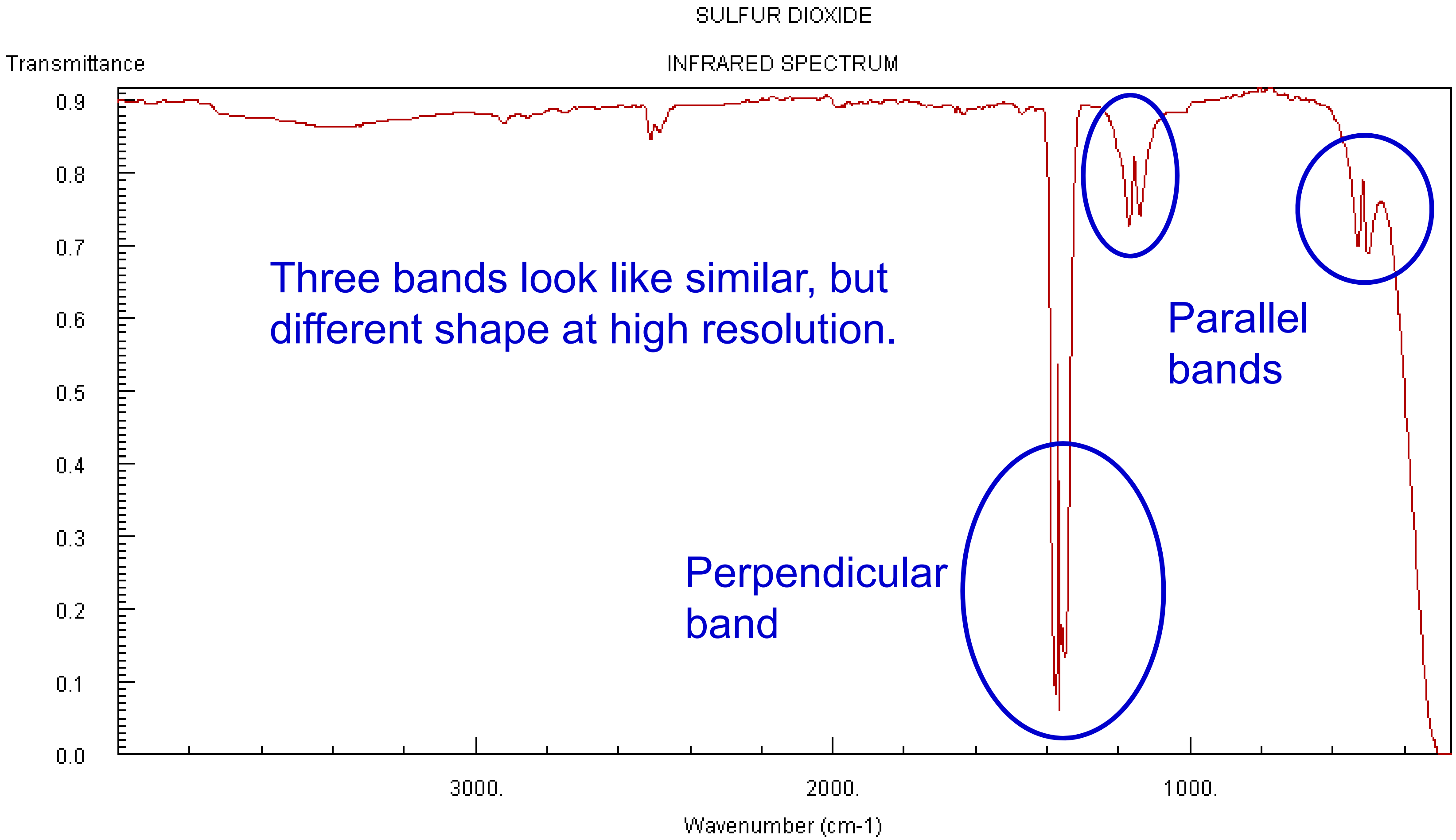
Unsymmetric

SO_2 : Bent structure like water molecule. It has 3 vibrational modes, 2 stretching and 1 bending.

P-, R- : linear molecules

Parallel and perpendicular : Nonlinear

Parallel and perpendicular bands can be obtained from nonlinear molecules.



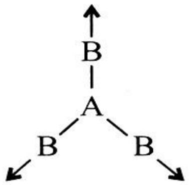
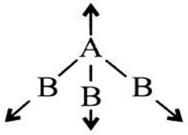
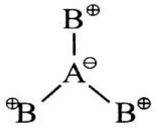
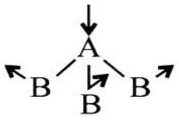
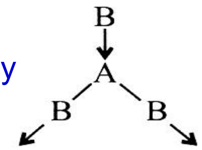
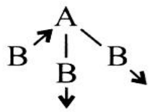
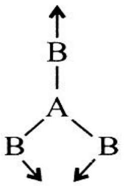
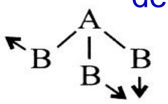
Three bands look like similar, but different shape at high resolution.

Parallel bands

Perpendicular band

What can we expect from two different structures for AB_3 molecules?

Table 4.5 Activities of vibrations of planar and pyramidal AB_3 molecules

Symmetric planar	Activity (*R* = Raman, *I* = infra-red)	Vibration	Pyramidal	Activity (*R* = Raman, *I* = infra-red)
BF_3 	*R*: active (pol.) strong *I*: inactive	ν_1 symmetric stretch	NH_3 	*R*: active (pol.) strong *I*: active ||
 (⊕ = upwards ⊖ = downwards)	*R*: inactive *I*: active ||	ν_2 out-of-plane symmetric deformation		*R*: active (pol.) medium *I*: active ||
Doubly degeneracy 	*R*: active (depol.) weak *I*: active ⊥	ν_3 asymmetric stretch	Doubly degeneracy 	*R*: active (depol.) weak *I*: active ⊥
Doubly degeneracy 	*R*: active (depol.) weak *I*: active ⊥	ν_4 asymmetric deformation	Doubly degeneracy 	*R*: active (depol.) weak *I*: active ⊥

4 atomic molecules, 6 vibrational degrees of freedom, but only 4 vibrational modes because of doubly degeneracy of bending vibration.

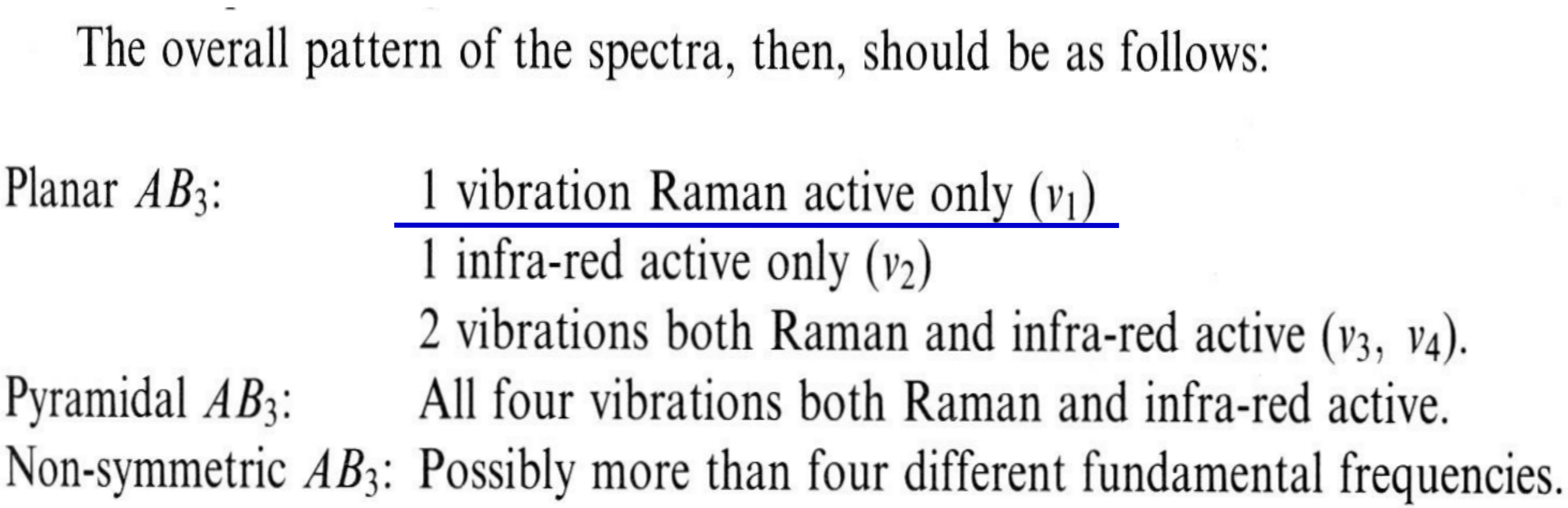
Both molecules have a similar electronic configurations, but they show different structures. We can identify this difference from IR and Raman spectra.

Table 4.6 Infra-red and Raman spectra of NO_3^- and ClO_3^-

Planar	Nitrate ion (NO_3^-)		Pyramidal	Chlorate ion (ClO_3^-)	
Raman (cm^{-1})	Infra-red (cm^{-1})	Assignment	Raman (cm^{-1})	Infra-red (cm^{-1})	Assignment
690 (depol.)	680 ⊥	ν_4	450 (depol.)	434 ⊥	ν_4
—	830 ∥	ν_2	610 (pol.)	624 ∥	ν_2
1049 (pol.)	—	ν_1	940 (depol.)	950 ⊥	ν_3
1355 (depol.)	1350 ⊥	ν_3	982 (pol.)	994 ∥	ν_1

Observation of 3 bands in IR and Raman

Observation of 4 bands in IR and Raman



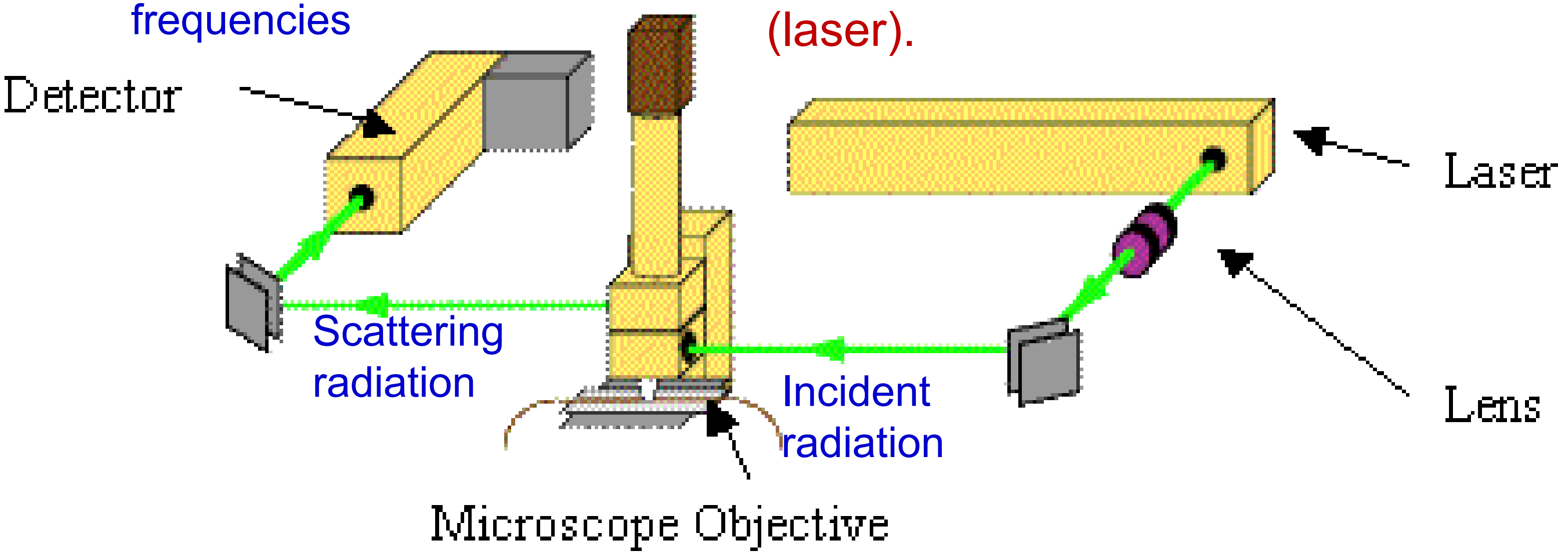
The overall pattern of the spectra, then, should be as follows:

Planar AB_3: 1 vibration Raman active only (ν_1)
1 infra-red active only (ν_2)
2 vibrations both Raman and infra-red active (ν_3, ν_4).
Pyramidal AB_3: All four vibrations both Raman and infra-red active.
Non-symmetric AB_3: Possibly more than four different fundamental frequencies.

Lack of symmetry : Degeneracy is removed to give more bands.

4.6 TECHNIQUES AND INSTRUMENTATION

Monochromatic radiation is passed through a gaseous or liquid sample, the light is scattered and detected



Analyzing frequencies

Need high power incident radiation (laser).

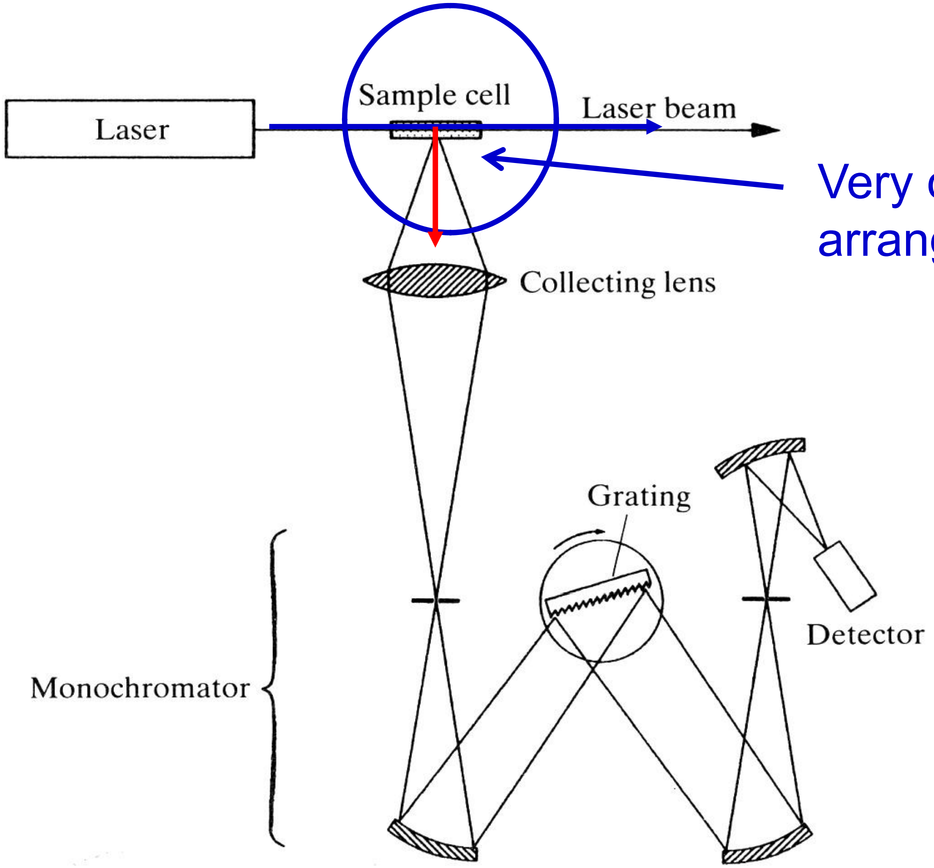
Scattering radiation

Incident radiation

Focusing here

Fig 1.1: Schematic representation of a laser Raman microscope

Observation should be at the perpendicular angle to the incident radiation to reduce the effect of incident radiation.



Very critical arrangement

Figure 4.12 Schematic diagram of a Raman spectrometer.

- The incident radiation source:
- The rotational Raman spectrum is inherently weak, so high intensity light and sensitive detectors are required.
- Lasers produce a narrow, highly monochromatic, coherent beam which can be focused very finely onto a small sample.
- Continuous lasers routinely have powers of up to several watts. but with good detectors, Raman spectra can be observed even using He/Ne lasers.
- Rare gas lasers (based on Ar^+ or Kr^+, for example) which are often used in Raman experiments, can produce light a million times more intense than sunlight.

- Microscope Objective
- This focuses incoming laser light onto the sample and collects the scattered light. This outgoing light includes both Rayleigh and Raman scattered light.

- **Detector**
- **At the spectrometer incoming radiation is dispersed with a grating, and then detected using diodes, a camera or another type of detector. Detectors may be cooled in liquid nitrogen to reduce thermal noise.**

- **Advantages of Raman Spectroscopy**

  -We can extend the vibrational region to less than 500 cm^{-1} region which is difficult to obtain from IR radiation source.

  - We can use visible/uv radiations to obtain vibrational spectrum because the difference between incident and scattering radiations indicates the IR region.

  - Identification of vibrational symmetry using a plane-polarized radiation sources.

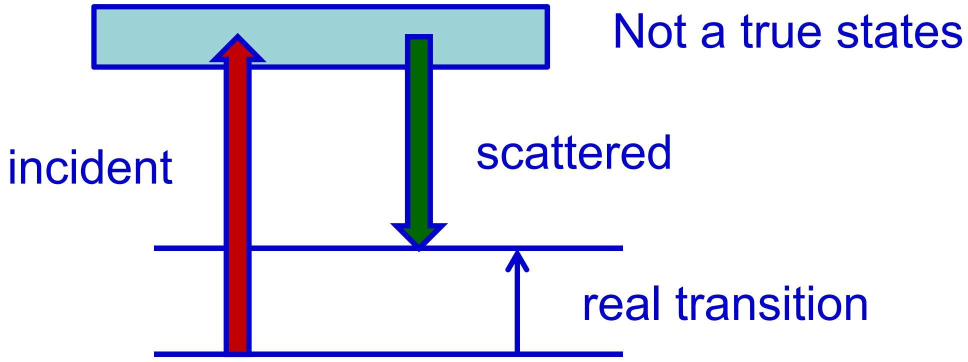
- **Disadvantages**

  - Extremely weak intensity of Raman scattering.

  Many techniques have been developed to improve the intensity of Raman scattering. What are these?

  - High-powered lasers may lead to decomposition of the sample.

Ordinary Raman scattering:


Not a true states

incident

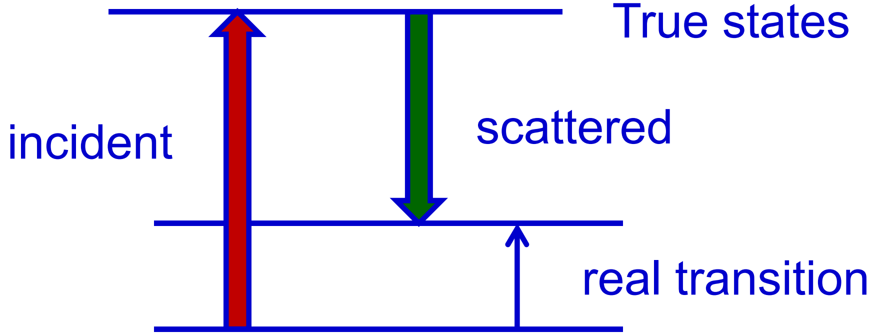
scattered

real transition

Intensity : 1 / 10^7

Intensity increases by an order of 3.

Resonance Raman scattering:


True states

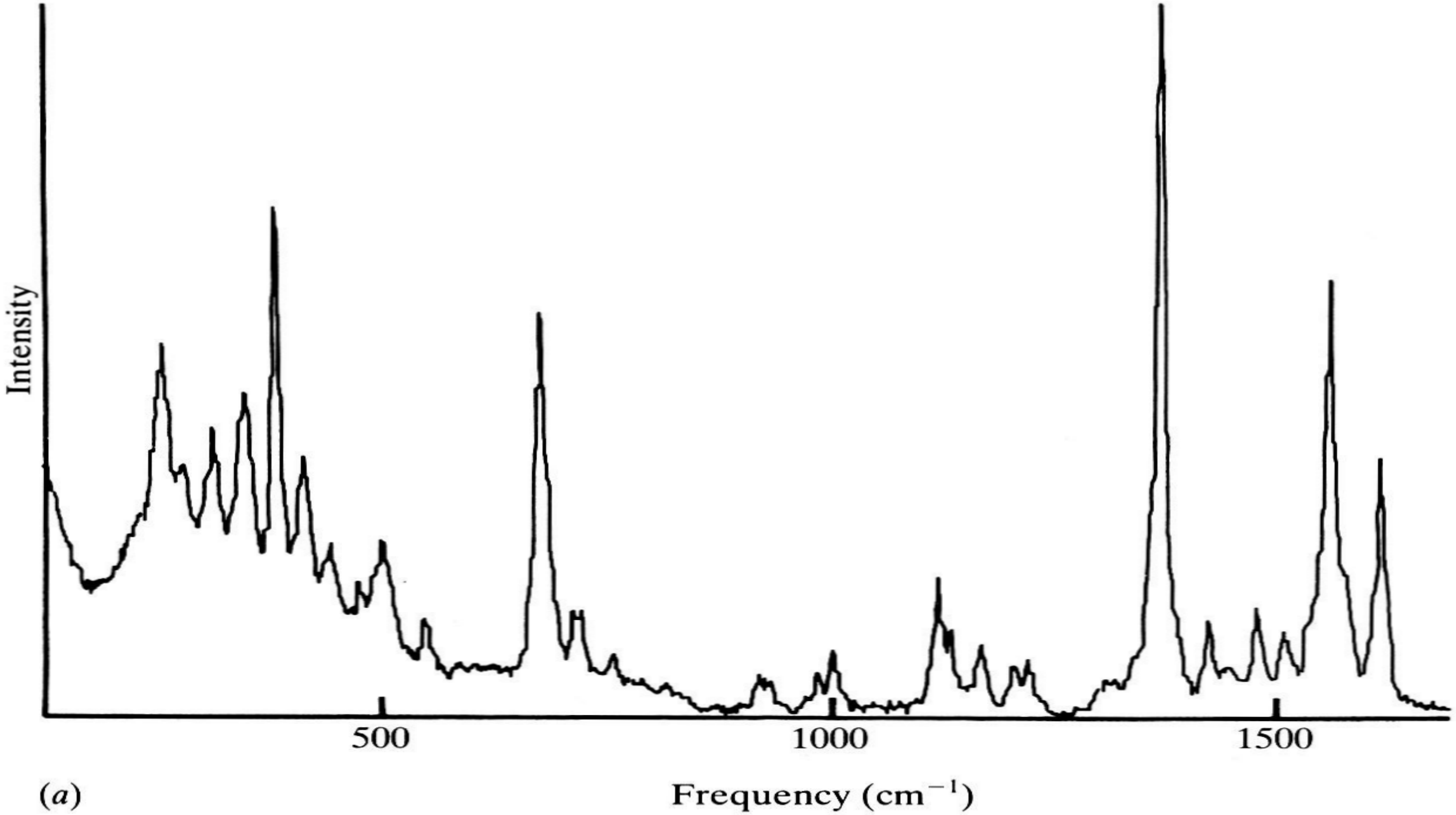
incident

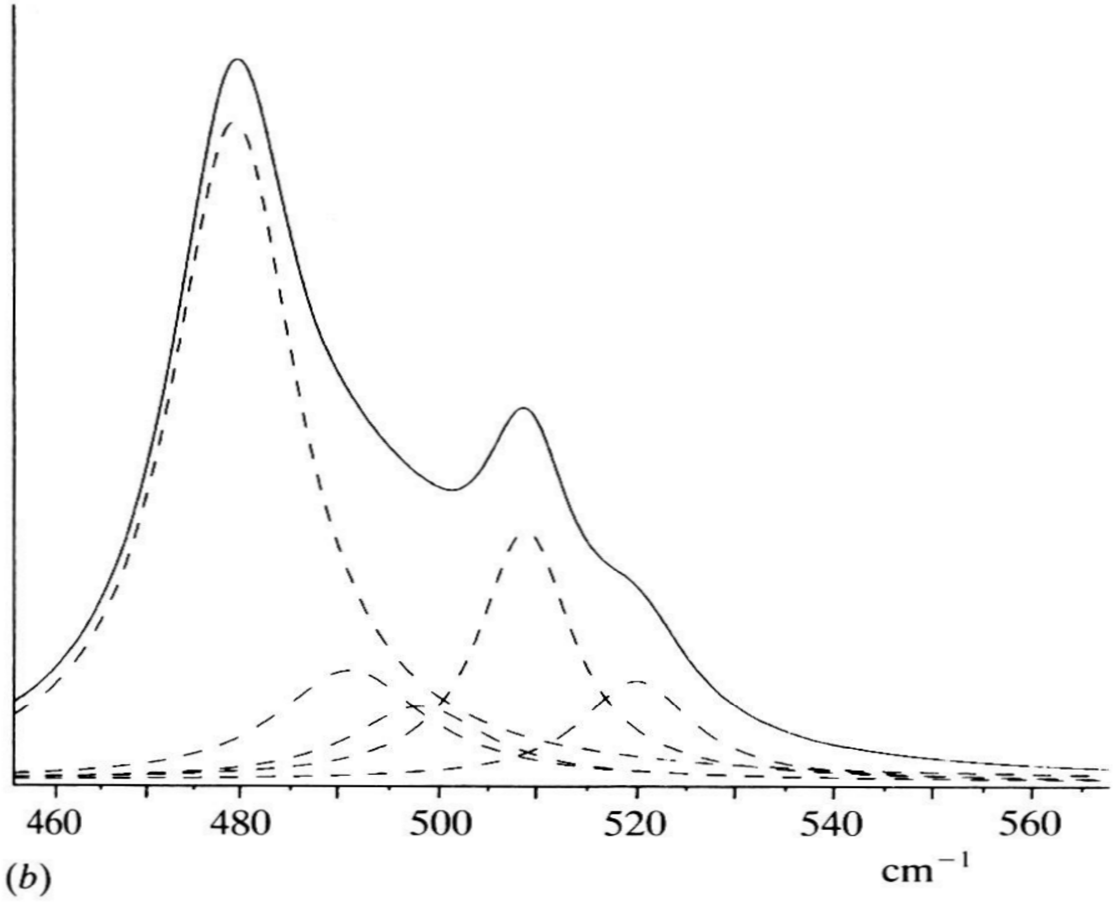
scattered

real transition

Intensity : 1 / 10^4

In resonance Raman scattering, the frequency of incident radiation should be the same as the molecular transition energy, giving much improved Raman intensity.


Intensity
500
1000
1500
(a)
Frequency (cm^{-1})


460
480
500
520
540
560
cm^{-1}
(*b*)

4.7 NEAR-INFRARED FT-RAMAN SPECTROSCOPY