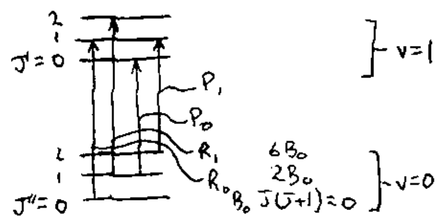
VIBRATION-ROTATION SPECTRA

SUMMARY

Every vibrational energy level has a rotational energy level structure built on it. The rotational part is exactly as in the previous section, but centrifugal distortion can be ignored. For one vibration (e.g. a diatomic), energies G(v) are expressed as:

$$\mathbf{G(v) = (v+½)\omega_e - (v+½)^2\omega_e x_e + \text{(possible higher terms)}}$$

A simple harmonic oscillator (SHO) has only the first term. ω_e and $\omega_e x_e$ are the frequency and anharmonicity for infinitesimal vibration amplitude at the bottom of the potential well.



Selection Rules:

1. For IR, the vibration must cause a change in dipole moment.
2. For Raman, the vibration must change the polarisability.
3. In centro-symmetric molecules, no vibration can be both IR and Raman active.
4. In both IR and Raman, $\Delta v = \pm1$ transitions are by far the strongest. This rule is not strict, because:
   a) a transition dipole can come from higher powers of the vibration coordinate extension, even for SHO.
   b) Anharmonicity removes the symmetry of the vibration wavefunctions. So $\Delta v = \pm2, \pm3\ldots$ transitions are seen weakly.
5. The selection rules for rotational fine structure are $\Delta J = \pm1$ for IR and $\Delta J = 0, \pm2$ for Raman, if no other angular momentum is present. If another angular momentum is present then $\Delta J = 0,\pm1$ for IR and $\Delta J = 0, \pm1, \pm2$ for Raman.

Line Positions:

For $\Delta v = 1$, the vibrational origins ($\Delta J = 0$) are at $\Delta G(v) = \omega_e - 2v\omega_e x_e$, where v is the quantum number of the upper state. Successive origins differ by $2\omega_e x_e$.

IR rotational structure may have P,Q and R branches for $\Delta J = -1,0,+1$ respectively. The B values are different in each vibrational level, written B_0, B_1, etc. Because they are only slightly different, the P and R branches have a line spacing of about $2B_{av}$, but there is a double-sized gap of about $4B_{av}$ at the band origin. Lines close up in the R branch and spread out in P.

Remember that when observing different isotopes (e.g. HCl), the correct ratio (for this example it would be 3:1) is NOT seen, because transmittance is on a logarithmic scale.

The B values are smaller for higher vibration levels, because on average the bonds get extended:

$$B_v = B_e - (v+½)\alpha$$

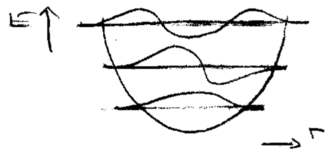
From B values in two levels α can be found ($B_1 - B_0 = \alpha$). B_e is the (theoretical) rotational constant at the bottom of the potential well and gives the equilibrium bond length.
Formally, $B_e = h/(8\pi^2 cI)$ where $I = \mu r_e^2$.
For Raman, with $\Delta J = 0, \pm2$, the structure is analogous.

Intensities:

For the rotational part, populations are as given in the last section. Vibrational energies are >kT, so normally only v=0 is strongly populated. The weak transitions starting from v=1 etc. are called hot bands.

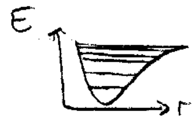
Vibrational Energy Levels

Energy of a molecular vibration depends on internuclear distance.
Harmonic Oscillator + Quantum Mechanics gives:



$E = (v+\tfrac{1}{2})h\nu$

A real diatomic curve diverges at higher energies:



This is anharmonicity. Convergence of energy levels. This is described well by:

$$E = (v+½)h\nu - (v+½)^2 x_e \nu + (v+½)^3 y_e h\nu$$

x_e – small anharmonicity correction term. Further terms are even smaller, usually neglected.

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

Isotopically related molecules (e.g. H_2 and D_2) have identical potential energy curves. Independent of mass. k is thus the same, so can predict energy level spacings. Spacing smaller for the heavier isotopes.
Dissociation Energies are thus different → smaller ZPE for heavier atoms. C-H easier to break than C-D.

Diatomics:

$$G(v) = \frac{E_v}{hc} = (v+\tfrac{1}{2})\omega_e - (v+\tfrac{1}{2})^2\omega_e x_e \qquad v = 0, 1, 2 \ldots$$

$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ vib. freq at $\rightleftharpoons$, in cm^{-1} (μ in kg)

x_e = anharmonicity constant

ZPE ⇒ $v = 0$

Harmonic Oscillator Potential:

$$V(R) = ½\, k\, (R - R_e)^2.$$

Morse Potential:

$$V(R) = D\, [\, 1 - e^{a(R-Re)}\,]^2$$

$a = 2\pi c\omega_e(\mu/2D_e)^{1/2}$.

Dissociation Energy:

$$dG(v) / dv = 0 \text{ at } v = 0$$

$$\frac{D_e}{hc} = G(v_D) = \frac{\omega_e^2}{4x_e\omega_e} \qquad D_0 = D_e - ZPE$$

Polyatomics:
Quanta in normal modes – A,B,C … : v_A, v_B, v_C …
Degeneracy d_A, d_B, d_C…

Ignoring Anharmonicity:

$$G(v_A, v_B \ldots) = (v_A + \tfrac{d_A}{2})\omega_e^A + (v_B + \tfrac{d_B}{2})\omega_e^B + \ldots \qquad /cm^{-1}$$

No simple relationship between bond force constants and vibrational frequencies of normal modes.

Vibration-Rotation Energy Levels

Diatomics:

$$F(v,J) = G(v) + F(J)$$

B varies with vibrational level as:

$$B_v = B_e - \alpha\,(v+½).$$
$$B_e = h/8\pi^2 c\mu r_e^2$$

Symmetric Top Polyatomics –

$$F(v_A, v_B \ldots; J; K) = G(v_A, v_B, \ldots) + F(J,K)$$
$$B_v = h/8\pi^2 c\mu(\langle 1/r^2\rangle_v)$$

Variation due to:

- Anharmonicity
- Intrinsic property of $\langle 1/r^2\rangle$

Infrared Spectroscopy – Vibration-Rotation

Diatomics –

Vibrational Changes:

$$\mu_{el}(R) = \mu(R_e) + \left(\frac{d\mu}{dR}\right)_{R_e}(R-R_e) + \frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{R_e}(R-R_e)^2 + \ldots$$

Only 1st 2 terms ⇒

$$\int \chi_f^*(R)\,\mu(R)\,\chi_i(R)\,dR =$$

$$\underbrace{\int \chi_f^*(R)\,\mu(R_e)\,\chi_i(R)\,dR}_{=0 \text{ unless } \chi_i = \chi_f} + \left(\frac{d\mu}{dR}\right)_{R_e}\int \chi_f^*(R-R_e)\chi_i\,dR$$

Second Term $\neq 0$ if $\left.\frac{d\mu}{dR}\right)_{R_e} \neq 0$ & $\Delta v = \pm 1$

(assuming Simple Harmonic Oscillator wavefunctions)

For real molecules, anharmonicity ➔ $\Delta v = \pm 2, \pm 3 \ldots$
Allowed, but weak.
Also, dipole moment change $\neq 0$, so heteronuclear only.

Populations –

$$N_v/N_o = e^{-G(v)\,hc\,/\,kT}$$

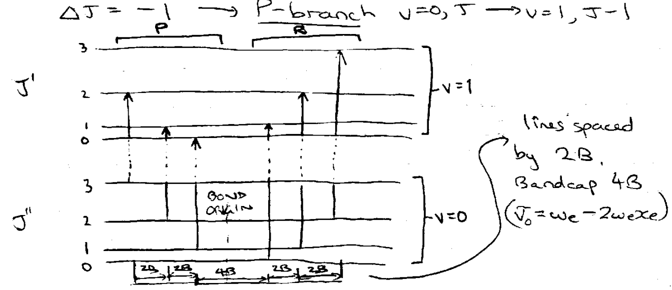
Hence for most diatomics, only see absorption from v = 0 (for room-temp).

Vibrational Transition Energies –

$$G(v+1) - G(v) = \omega_e - 2(v+1)\,\omega_e x_e.$$

For v =0, $= \omega_e - 2\omega_e x_e \approx \nu_o$
This ν_o is the Fundamental vibrational frequency.
First Overtone, $G(2) - G(0) = 2\omega_e - 6\omega_e x_e$.
Note, $D_e = \omega_e^2/4\omega_e x_e$
Rotational Changes – $\Delta J = \pm 1$

$\Delta J = +1 \rightarrow$ R-branch $v=0, J \longrightarrow v=1, J+1$
$\Delta J = -1 \rightarrow$ P-branch $v=0, J \longrightarrow v=1, J-1$



R-branch:
$\nu^R(J) = F(v+1,J+1) - F(v,J) = \nu_o + (B_o+B_1)(J+1) + (B_1-B_o)(J+1)^2$

P-branch:
$\nu^P(J) = F(v+1,J-1) - F(v,J) = \nu_o - (B_1+B_o)J + (B_1-B_o)J^2$
$\nu(J+1) - \nu^P(J) = -(B_1+B_o) + (B_1-B_o)(2J+1)$

Isotope Effects –

$\omega_e \propto 1/\sqrt{\mu}$ $\omega_e x_e \propto 1/\mu$ $B_e \propto 1/\mu$

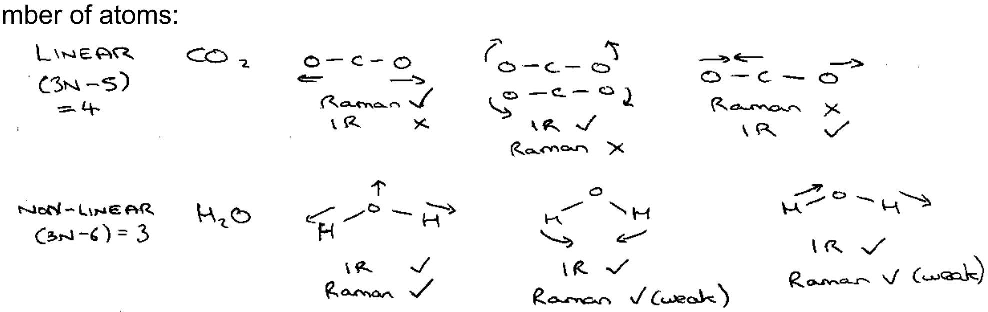
Combination Differences –
In IR vib-rot spectra.

$$\tilde{\nu}^R(J) - \tilde{\nu}^P(J+2) = (4B_o - 6D_o)(J+\tfrac{3}{2}) - 8D_o(J+\tfrac{3}{2})^3$$
$$\approx 4B_o(J+\tfrac{3}{2}) \quad \text{(ignoring centrifugal)}$$

$$\tilde{\nu}^R(J) - \tilde{\nu}^P(J+2) = (4B_1 - 6D_1)(J+\tfrac{1}{2}) - 8D_1(J+\tfrac{1}{2})^3$$
$$\approx 4B_1(J+\tfrac{1}{2}) \quad \text{(ignoring centrifugal)}$$

Normal Modes in polyatomic molecules. Combined motion of several atoms.
Bond vibrations not independent.

What are Normal Modes?
The vibratory motions in a polyatomic molecule can be analysed as a sum of “normal modes”, component vibrations in which all atoms move at the same frequency with sinusoidal displacements.
Normal modes are SHO, independent, and orthogonal – model valid for low quantum numbers only.
N – number of atoms:

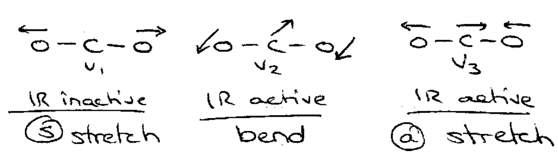


Displacement in MASS-WEIGHTED sum of coordinates Q_i such that all terms of the form $d^2V/dQ_idQ_j = 0$

Linear –

3N – 5 normal modes of vibration.

e.g. CO_2:



$G(v_1, v_2, v_3) = (v_1+½)\omega_1 + (v_2+½)\omega_2 + (v_3+½)\omega_3$
(ignoring anharmonicity)

Infrared Selection Rules –
Dipole moment must change on vibration.
$\Delta J = \pm1$ for parallel vibrations (change parallel to linear molecule xis).
$\Delta J = 0, \pm1$ for perpendicular vibrations (change perpendicular to axis – bending).

Q-branch –

$$G(v_2=1, J) - G(v_2=0, J) = (B_1 - B_o)J(J+1) + v_o.$$

$B_1 - B_o$ small – transitions pile up.
Transition allowed because of double degeneracy.

Symmetry of Rotational Wavefunction – parity.
Designate levels wrt space-fixed inversion.

$+ \leftrightarrow -$	-	allowed
$+ \leftrightarrow +$ / $- \leftrightarrow -$	-	disallowed

Overtone and Combination Bands (Linear)
Overtone – change of vibrational quantum number by > 1 in one mode.
Combination Band – excitation of 2 different vibrational modes simultaneously.
Example, CO_2

$\tilde{\nu}$

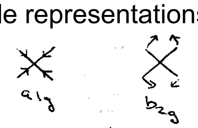
$(0,0,0) \longrightarrow (0,1,0)$	ν_2	fundamental
$(0,0,0) \longrightarrow (0,3,0)$	ν_2	overtone
$(0,0,0) \longrightarrow (1,1,0)$	$[\nu_1+\nu_2]$	combination
$(0,0,0) \longrightarrow (0,0,1)$	ν_3	fundamental
$(0,0,0) \longrightarrow (0,2,1)$	$[\nu_2+\nu_3]$	combination
$(0,0,0) \longrightarrow (1,0,1)$	$[\nu_1+\nu_3]$	combination
$(0,0,0) \longrightarrow (0,4,1)$	$[\nu_2+\nu_3]$	combination
$(0,0,0) \longrightarrow (1,2,1)$	$[\nu_1+\nu_2+\nu_3]$	combination

Selection Rules for Overtones and Combinations:
v_1 – g symmetry.
v_2 – u for odd quanta, g for even.
v_3 – u for odd, g for even.
(0,0,0) – g.
Selection Rule – g $\leftrightarrow$ u.

Vibrational Spectroscopy of Non-Linear Polyatomics

3N – 6 normal modes of vibration.

Characterise by irreducible representations of the molecular symmetry group, e.g.



XeF_4 (D_{4h})

also a_{2u}, b_{1g}, b_{2u}, $2e_u$ – 9 modes (15–6)

Those displayed above ➔ no dipole change. IR inactive.

Vibrational Selection Rules:

$$\langle \psi_i \mid \mu \mid \psi_f \rangle \text{ - totally symmetric.}$$

→ must contain A_1 for allowed transition.
Γ_μ - transforms as x, y, z.
$\Gamma_{\chi i}$ – normally totally symmetric for Ground Level (a_{1g}).
$\Gamma_{\chi f}$ – must transform as x, y or z.
For D_{4h}, a_{2u} and e_u modes active (those with x, y, z in character table).

Rotational Structure in IR Spectra of Polyatomics – Symmetric Top

Selection Rules:
Parallel (allowed by z) –

$\Delta K = 0$ $\Delta J = \pm 1$ for $K = 0$, $\Delta J = 0, \pm 1$ for $K \neq 0$

Perpendicular (allowed by x,y) –

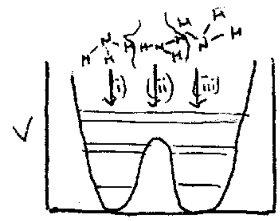
$\Delta K = \pm 1$ $\Delta J = 0, \pm 1$

Overtones and Combination Bands (Polyatomics)
Consider direct product for excited modes. Overtone allowed if product transforms as x,y,z.
e.g. D_{4h} – $b_{1g} \times b_{2u} = a_{2u}$ (allowed).

Hot Bands
Intensity of transitions from vibrationally excited states increases as T increases.

Group Frequencies
Bond vibrations strongly coupled if similar intrinsic frequencies. Some bonds almost completely decoupled ➔ Group Frequency.

Tunnelling and Inversion
When more than one minimum in PE surface ➔ overlap of vibrational wavefunctions possible ➔ tunnelling, e.g. NH_3:



± linear combinations have slightly different energies.
Overlap increases nearer top of the well, hence tunnelling splitting increases.
Tunnelling Splitting Frequency = rate constant for inversion.

Small splittings in other bands also observed due to anharmonic effects, e.g. excitation of other v_i stretching mode causes slight change in bonding potential – different tunnelling frequency.

Broadening in Spectra

a) Lifetime broadening – "natural linewidth".
b) Pressure broadening (collisions)
c) Doppler Effect (effective frequency observed by molecule)
d) Power (saturation) broadening.
e) Unresolved underlying structure.
f) Instrumental resolution.

Lifetime Broadening – if the probability of a system existing in a particular state decays as:

$$|\psi|^2 = |\psi|^2 e^{-t/\tau}$$

This gives rise to an energy uncertainty.

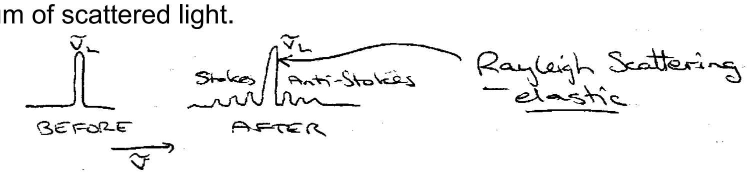
$$\tau\, \delta E \approx \hbar.$$

δE is the full width at half maximum height.

$$\tau\, \delta v = 1/2\pi c$$

Raman Spectroscopy

Monochromatic light, wavenumber v_L (visible).
Measure spectrum of scattered light.

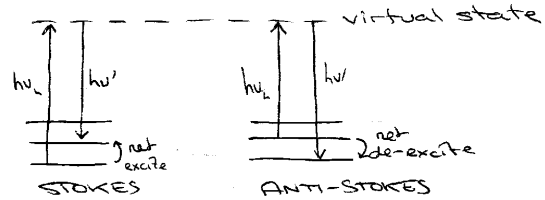


Raman Effect. Inelastic Scattering:

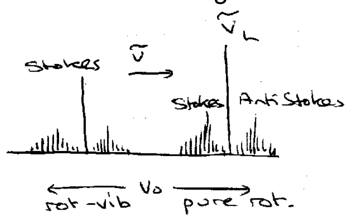
- $v' > v_L$ – Anti-Stokes
- $v' < v_L$ – Stokes

Conservation of Energy: $hv' - hv_L = \Delta E$.

Quantum Picture of Raman –



The "absorption" and "emission" are instantaneous and simultaneous – no transfer of population.
"virtual" state – off-resonant, transient, polarisation induced.
Both pure rotational and vib-rot changes are observed:



No Anti-Stokes vibrational Raman (no population of $v=1$)

Classical description of Raman –
Molecule rotating at frequency ω' – polarisability oscillates with frequency 2ω' → oscillating dipole radiates.

Gross Selection Rules for Raman:
Rotational – molecule must have anisotropic polarisability.

$$\underbrace{\mu_x}_{\text{ind. dipole}} = \alpha_{xx} \underbrace{\mathcal{E}_x}_{\text{field}} \quad \text{(also y \& z)}$$

$$\text{If } \alpha_{xx} = \alpha_{yy} = \alpha_{zz} \text{ – no spectrum}$$

Generally only true for Spherical Top – $I_a = I_b = I_c$.

Vibrational – polarisability change on vibration.

Selection Rules –

$\Delta J = 0, \pm 2$ (rotational and vibrational)

Rotational –

$\Delta J = 0$ (Rayleigh)
$\Delta J = \pm 2$ Stokes / Anti-Stokes

$$\mathbf{F(J+2) - F(J) = B[(J+2)(J+3) - J(J+1)] = (4J+6)B}$$

So Stokes lines at $v_L - (4J+6)B$ $\qquad J = 0,1, \ldots$

$$\mathbf{F(J-2) - F(J) = (4J-2)B}$$

So Anti-Stokes lines at $v_L + (4J-2)B$ $\qquad J = 2,3, \ldots$
Resolution is not normally sufficiently high to include centrifugal distortion.

Vibrational Raman

Rotational Structure –

Q-branch: $\Delta v = 1$, $\Delta J = 0$

$F(v=1,J) - F(v=0,J)$ $\qquad$ [displacement from v_L]
$= v_o + (B_1 - B_o)J(J+1) \approx v_o$ [$= \omega_e - 2\omega_e x_e$]

S-branch: $\Delta v = 1$, $\Delta J = +2$

$F(v=1,J+2) – F(v=0, J)$
$= v_o + B_1(J+2)(J+3) – B_oJ(J+1)$
$= v_o + (B_1+B_o)(2J+3) + (B_1-B_o)(J^2 + 3J + 3)$

O-branch: $\Delta v = 1$, $\Delta J = -2$

$F(v=1,J-2) – F(v=0, J)$
$= v_o + B_1(J-1)(J-2) – B_oJ(J+1)$
$= v_o – (B_1+B_o)(2J-1) +(B_1-B_o)(J^2 – J + 1)$

Rule of Mutual Exclusion – Polyatomic
For molecules with centre of inversion symmetry (i); IR active modes are Raman inactive and vice versa. There may be some modes that are inactive in both.

Transition Intensities and Group Theory
Raman effect arises from interaction of the induced dipole moment of the molecule with the EM field.
For a diatomic in an E-field ε polarised in the z-direction, the component of the induced dipole in that direction:

$$\mu_z = \underbrace{\alpha_\perp \varepsilon \sin^2\Theta + \alpha_\parallel}_{\text{polarisabilities } \perp \ \& \ \parallel} \varepsilon \cos^2\Theta$$

2 parts of μ_z transform in $D_{\infty h}$ group in the same way as $x^2 + y^2$ and z^2 (A_{1g}).
Transition Moment (Raman) is of the form:

$$\langle v'J' \mid \mu_z \mid v''J'' \rangle$$

For non-zero transition probability require:
$\Gamma_{v'}, \Gamma_\mu, \Gamma_{v''}$ transforms to A_{1g} (totally symmetric)
x^2, y^2, xy etc → g
x, y, z → u

(Hence mutual exclusion principle above).

Effects of Nuclear Spin Statistics

Pauli Principle:

ψ_{tot} (a) wrt exchange of equivalent FERMIONS
ψ_{tot} (s) wrt exchange of equivalent BOSONS
↳ I = integral
^2D, ^{12}C, ^{16}O, ^{14}N

$\psi = \psi_{el}\psi_{vib}\psi_{rot}\psi_{nuc}\psi_{trs}$

ψ_{tr} — (s) always
ψ_{el} — usually (s), but e.g. O_2 ($^3\Sigma_g^-$) (a)
ψ_{vib} – always (s) in vib. ground state
– always (s) in diatomics
– in polyatomics, may be (a) for odd # of quanta
e.g. CO_2 (v_1, v_2, v_3)
(0,0,0); (1,0,0); (2,0,0) (s)
(0,0,1); (0,0,3) (a)
ψ_{rot} – (s) for even J, (a) for odd J]– for linear

Can thus stipulate (s) of ψ_{nuc}.

Can thus stipulate symmetric of ψ_{nuc}.

Applications to Diatomics (homonuclear) and Linear Molecules

H_2 $\psi_{el}\psi_{vib}\psi_{tr} = s$ $\psi_{tot} = a$

$I = \frac{1}{2}$,

Nuclear Spin:

$$\left.\begin{array}{l}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)] \\ \alpha(1)\alpha(2) \\ \beta(1)\beta(2)\end{array}\right\} 3 \times s$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \} \; 1 \times a$$

NUCLEAR SPIN DEGEN

J even (para) ψ_{nuc} a 1

J odd (ortho) ψ_{nuc} s 3

Populations

$$\text{para: } N_J = N_0(2J+1)\exp(-BhcJ(J+1)/kT)$$

$$\text{ortho: } N_J = 3N_0(2J+1)\exp(-BhcJ(J+1)/kT)$$

Raman of H_2 – there is a 3:1 intensity alternation, in favour of the odd J lines.

D_2 $I = 1$ total ψ is s (bosons)

6 s spin wavefunctions, 3 a

J even – $\psi_{nuc} = s$ 6

J odd – $\psi_{nuc} = a$ 3

2:1 alternation of intensities in favour of even J.

CO_2 – exchange of ^{16}O $I = 0$ ψ_{tot} = symmetric.
ψ_{nuc} can only be symmetric.

For rotational Raman:

Grd vib. state $\psi_{vib}\psi_{el}\psi_{tr} = s$

$\Rightarrow \psi_{rot} = s$ only

Only even J levels exist, so observe transitions:

$$J = 0 \rightarrow 2,\; 2 \rightarrow 4,\; 4 \rightarrow 6$$

$$\text{spacing} \simeq 8B \;(\text{not } 4B)$$

For infrared: for (0,0,1).

ψ_{vib} is a $\Rightarrow \psi_{rot} = a$ only

Only odd J exist $\Rightarrow$ $0 \rightarrow 1$

$2 \rightarrow 3$

(for $(0,0,0) \rightarrow (0,0,1)$) $4 \rightarrow 5$

O_2 $^3\Sigma_g^- \Rightarrow \psi_{el} = a$ $\psi_{vib}\psi_{el}\psi_{tr} = a$

$\Rightarrow \psi_{rot} = s$ only

Only odd J levels exist. Raman: 1 → 3, 3 → 5, …