

Basic theory of Raman intensity and Raman cross-section: Introduction to the Placzek theory

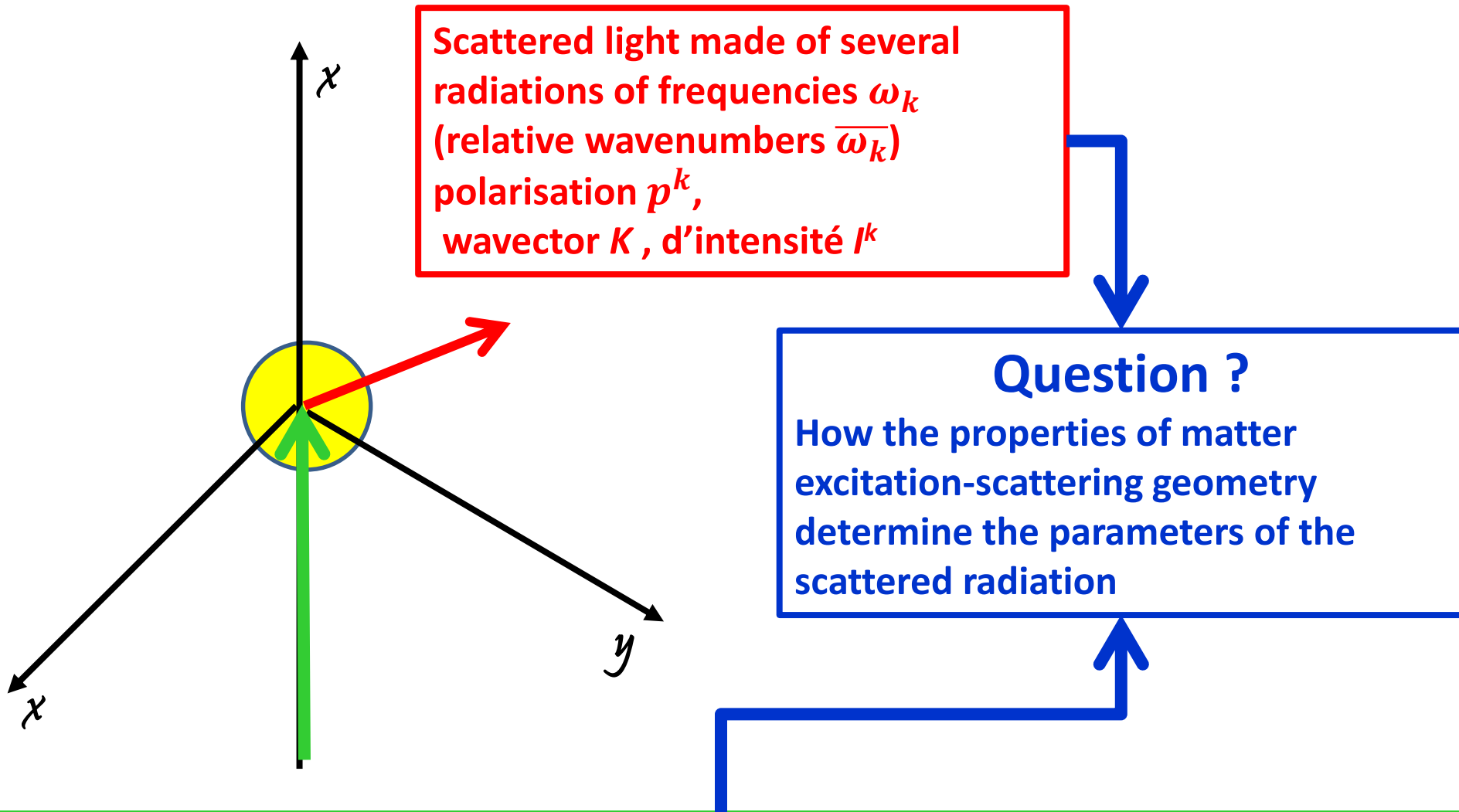
J.Dubessy

UMR GeoRessources, CNRS-UL



UNIVERSITÉ
DE LORRAINE

Raman spectroscopic experiment



Incident monochromatic radiation, characterised by its frequency ν_L (wavenumber $\overline{\nu_L}$), wave-vector, polarisation p^i , intensity-irradiance at the sample

Raman scattering : induced dipoles by the electric field of laser

Induced electric dipole \mathbf{p} : by electric field $\mathbf{E}(t)$ from the exciting radiation:

$$\mathbf{p} = \mathbf{p}^{(1)} + \mathbf{p}^{(2)} + \mathbf{p}^{(3)} \text{ avec } \mathbf{p}^{(1)} \gg \mathbf{p}^{(2)} \gg \mathbf{p}^{(3)}$$

$$\mathbf{p}^{(1)} = \boldsymbol{\alpha} \cdot \mathbf{E}; \quad \mathbf{p}^{(2)} = \frac{1}{2} \boldsymbol{\beta} : \mathbf{E}\mathbf{E}; \quad \mathbf{p}^{(3)} = \frac{1}{6} \boldsymbol{\gamma} : \mathbf{E}\mathbf{E}\mathbf{E}$$

$\mathbf{p}^{(1)}$: (C.m) ; \mathbf{E} : (V.m⁻¹);

$\boldsymbol{\alpha}$: symmetric polarisability tensor ($\alpha_{ij} = \alpha_{ji}$) avec $\alpha_{ij} = 10^{-40}$ C. V⁻¹. m²

$$\alpha_{ij} = (\alpha_{ij})_0 + \sum_k \left(\frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l + \dots$$

For the single normal mode of vibration Q_k :

$$(\alpha_{ij})_k = (\alpha_{ij})_0 + (\alpha'_{ij})_{k,0} Q_k \text{ avec } (\alpha'_{ij})_{k,0} = \left(\frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0 \text{ ou } \boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \boldsymbol{\alpha}'_k Q_k$$

If the oscillator is harmonic: $Q_k = Q_{k,0} \cos((\omega_k t + \delta_k))$ with δ_k , phase / radiation,

$\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \boldsymbol{\alpha}'_k Q_k$ et $\mathbf{E} = \mathbf{E}_0 \cos \nu_L t$, ν_L . From $\mathbf{p}^{(1)} = \boldsymbol{\alpha} \cdot \mathbf{E}$

$$\mathbf{p}^{(1)} = \boldsymbol{\alpha}_0 \mathbf{E}_0 \cos \nu_L t + \boldsymbol{\alpha}'_k \mathbf{E}_0 Q_{k,0} [\cos \nu_L t] \times [\cos((\omega_k t + \delta_k))]$$

Raman scattering : induced dipoles

$$\mathbf{p}^{(1)} = \alpha_0 \mathbf{E}_0 \cos \nu_L t + \alpha'_k \mathbf{E}_0 Q_{k,0} [\cos \nu_L t] \times [\cos((\omega_k t + \delta_k))]$$

$$\cos A \cos B = \frac{1}{2} [\cos(A + B) + \cos(A - B)]$$

$$\mathbf{p}^{(1)} = \mathbf{p}^{(1)}(\nu_L) + \mathbf{p}^{(1)}(\nu_L - \omega_k) + \mathbf{p}^{(1)}(\nu_L + \omega_k)$$

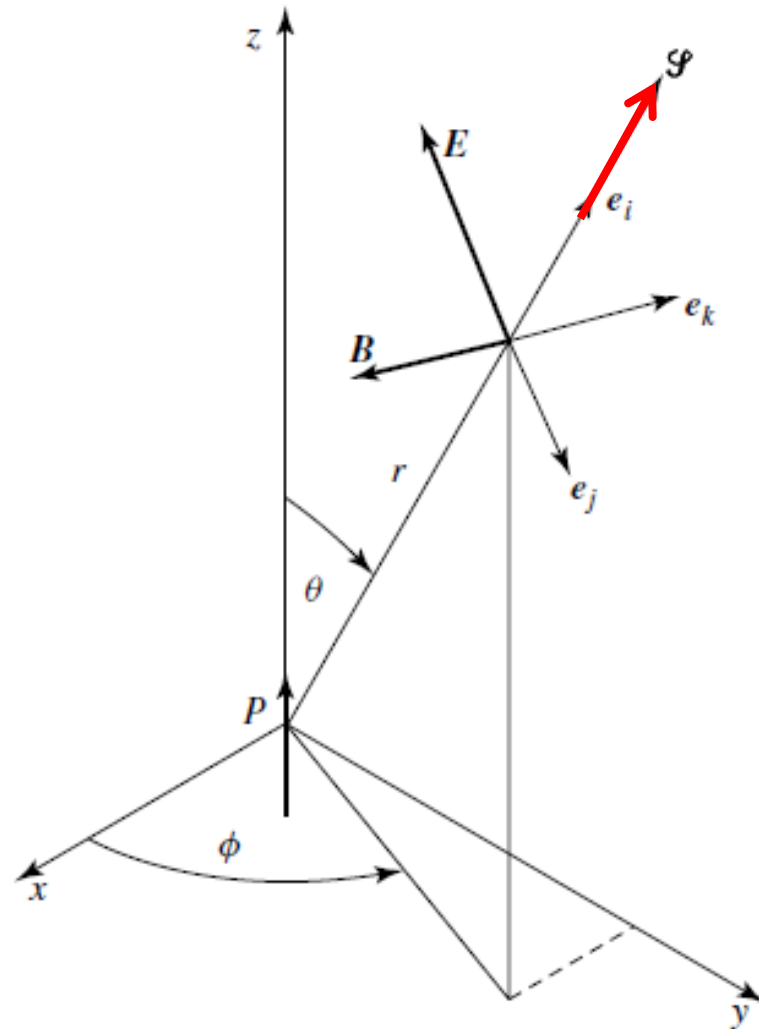
Stokes Raman **Anti-Stokes Raman**

$$\mathbf{p}^{(1)}(\nu_L) = \mathbf{p}_0^{Ray} \cos \nu_L t \text{ avec } \mathbf{p}_0^{Ray} = \alpha^{Ray} \cdot \mathbf{E}_0 \text{ et } \alpha^{Ray} = \alpha_0$$

$$\mathbf{p}^{(1)}(\nu_L \pm \omega_k) = \mathbf{p}_{k,0}^{Ram} \cos\{(\nu_L \pm \omega_k)t \pm \delta_k\}$$
$$\mathbf{p}_{k,0}^{Ram} = \alpha_k^{Ram} \cdot \mathbf{E}_0 \quad \text{avec} \quad \alpha_k^{Ram} = \frac{1}{2} \alpha'_k Q_{k,0}$$

Induced electric oscillatory dipoles

What is the intensity of a radiation originating from an induced electric oscillatory dipole ?



S: Poynting vector: $S = (\mu_0)^{-1} E \wedge B$

In the radiation propagation direction

Energy flux / unit time / surface area = irradiance of electromagnetic radiation

$$S = (\mu_0)^{-1} E_j B_k (e_j \wedge e_k)$$

$$S = (\mu_0)^{-1} E_j B_k e_i$$

$$S = c_0 (\mu_0)^{-1} (B_k)^2 e_i$$

$$S = \epsilon_0 c_0 (E_j)^2 e_i$$

ϵ_0 Vacuum electric permittivity

μ_0 Vacuum magnetic permeability

Oscillatory electric dipole: Average Poynting vector

$$\mathbf{E} = \frac{-\omega^2 p \sin \theta}{4\pi\epsilon_0 c_0^2 r} \mathbf{e}_j$$

$$\mathbf{B} = \frac{-\mu_0 \omega^2 p \sin \theta}{4\pi c_0 r} \mathbf{e}_k$$

$$\mathbf{S} = \left(\frac{1}{16\pi^2 \epsilon_0 c_0^3} \right) \frac{\omega^4}{r^2} p^2 \sin^2 \theta \mathbf{e}_i = \left(\frac{\pi^2 c_0}{\epsilon_0} \right) \frac{\bar{\omega}^4}{r^2} p^2 \sin^2 \theta \mathbf{e}_i$$

$\mathbf{p}(\omega) = p_{k,0} \cos\{\omega t \pm \delta_k\} \Rightarrow$ **instantaneous** Poynting vector

For a **500 nm radiation**, period $\tau = 1/\nu = \lambda/c = 5E - 7 / 3E8 = 1,7E - 15$ s

Detectors only measure averaged energy \Rightarrow only the average Poynting vector

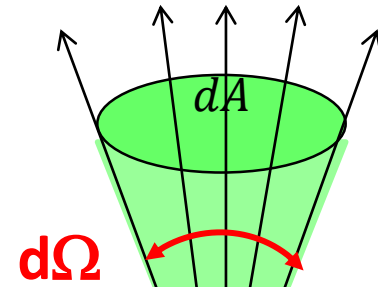
As $(\bar{p})^2 = (1/2)(p_0)^2$:

$$\bar{\mathbf{S}} = \frac{1}{2} \mathbf{S} = \left(\frac{1}{32\pi^2 \epsilon_0 c_0^3} \right) \frac{\omega^4}{r^2} p_0^2 \sin^2 \theta \mathbf{e}_i = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) \frac{\bar{\omega}^4}{r^2} p_0^2 \sin^2 \theta \mathbf{e}_i$$

Oscillatory electric dipole: energy flux from the dipole

Average power per dA area: $d\Phi = |\bar{\mathbf{S}}|dA$

$$d\Phi = \left(\frac{1}{32\pi^2 \epsilon_0 c_0} \right) \frac{\omega^4}{r^2} p_0^2 \sin^2 \theta dA = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) \frac{\bar{\omega}^4}{r^2} p_0^2 \sin^2 \theta dA$$



$dA/r^2 = d\Omega$, thus :

$$d\Phi = \left(\frac{1}{32\pi^2 \epsilon_0 c_0} \right) p_0^2 \omega^4 \sin^2 \theta d\Omega = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) p_0^2 \bar{\omega}^4 \sin^2 \theta d\Omega$$

Oscillatory electric dipole: intensity radiation from the oscillating dipole

Irradiance of electromagnetic radiation = the power per unit solid angle

$$I = \frac{d\Phi}{d\Omega}$$

$$\text{As } d\Phi = \left(\frac{1}{32\pi^2 \epsilon_0 c_0^3} \right) p_0^2 \omega^4 \sin^2 \theta d\Omega = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) p_0^2 \bar{\omega}^4 \sin^2 \theta d\Omega$$

$$I(W.sr^{-1}) = \left(\frac{1}{32\pi^2 \epsilon_0 c_0^3} \right) \omega^4 p_0^2 \sin^2 \theta = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) \bar{\omega}^4 p_0^2 \sin^2 \theta$$

Circular frequency or wavenumber of the oscillatory dipole

Oscillatory electric dipole: number of scattered photons

$$I(\text{W} \cdot \text{sr}^{-1}) = \left(\frac{1}{32\pi^2 \epsilon_0 c_0^3} \right) \omega^4 p_0^2 \sin^2 \theta = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) \bar{\omega}^4 p_0^2 \sin^2 \theta$$

$\bar{\omega}$ radiation wavenumber scattered by the induced dipole

$$I = k'_\omega \omega^4 p_0^2 \sin^2 \theta = k'_\omega \bar{\omega}^4 p_0^2 \sin^2 \theta \quad I$$

$$= 1,671 \times 10^{28} \bar{\omega}^4 p_0^2 \sin^2 \theta$$

Photon number = $I(\text{W}/\text{sr}^{-1})$ / single photon energy:

$$E_{\text{photon}} = h\nu = hc_0\bar{\nu} = 6,62606957 \times 10^{-34} \times 299\,792\,458 \times \bar{\nu} = 1,986 \times 10^{-25} \times \bar{\nu}$$

$$N_{\text{photons}} = 8,414 \times 10^{50} \times \bar{\omega}^3 p_0^2 \times \sin^2 \theta$$

Next step : calculation of $\bar{\nu}^3 p_0^2$

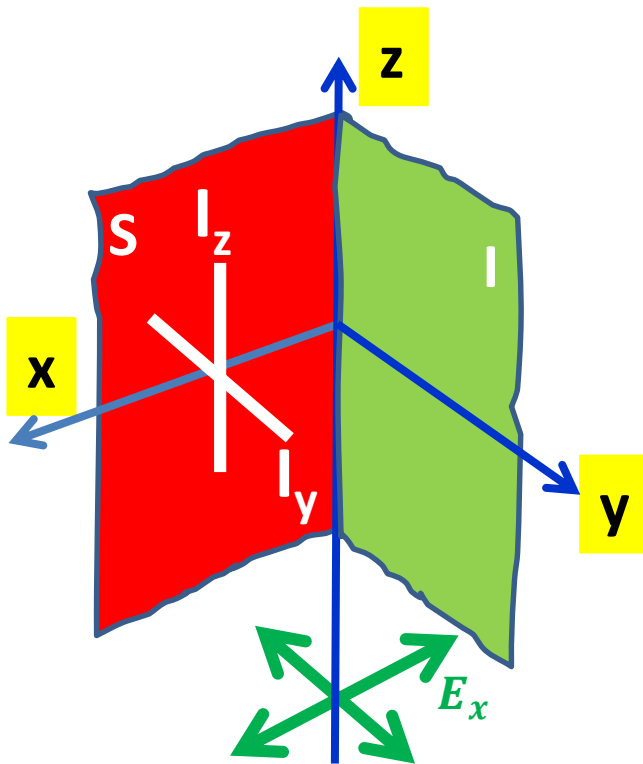
Raman scattering : excitation and scattering geometry

$$p_{k,0}^{Ram} = \alpha_k^{Ram} \cdot E_0 \quad \text{avec} \quad \alpha_k^{Ram} = \frac{1}{2} \alpha'_{k,0} Q_{k,0}$$

$$p^{(1)}(v_L \pm \omega_k)_{x,0} = \left\{ (\alpha'_{xx})_{k,0} E_{x,0} + (\alpha'_{xy})_{k,0} E_{y,0} + (\alpha'_{xz})_{k,0} E_{z,0} \right\} Q_{k,0}$$

$$p^{(1)}(v_L \pm \omega_k)_{y,0} = \left\{ (\alpha'_{yx})_{k,0} E_{x,0} + (\alpha'_{yy})_{k,0} E_{y,0} + (\alpha'_{yz})_{k,0} E_{z,0} \right\} Q_{k,0}$$

$$p^{(1)}(v_L \pm \omega_k)_{z,0} = \left\{ (\alpha'_{zx})_{k,0} E_{x,0} + (\alpha'_{zy})_{k,0} E_{y,0} + (\alpha'_{zz})_{k,0} E_{z,0} \right\} Q_{k,0}$$



Incident radiation (polarized laser): 1 component
 $E_x \perp^i$ perpendicular to incident plane
 or $E_y \parallel^i$ to incident plane : $E_z = 0$

Scattered Raman radiation: 2 components
 $p_{y_0} \perp^s$ scattering plane
 $p_{z_0} \parallel^s$ scattering plane; $I_x = 0$

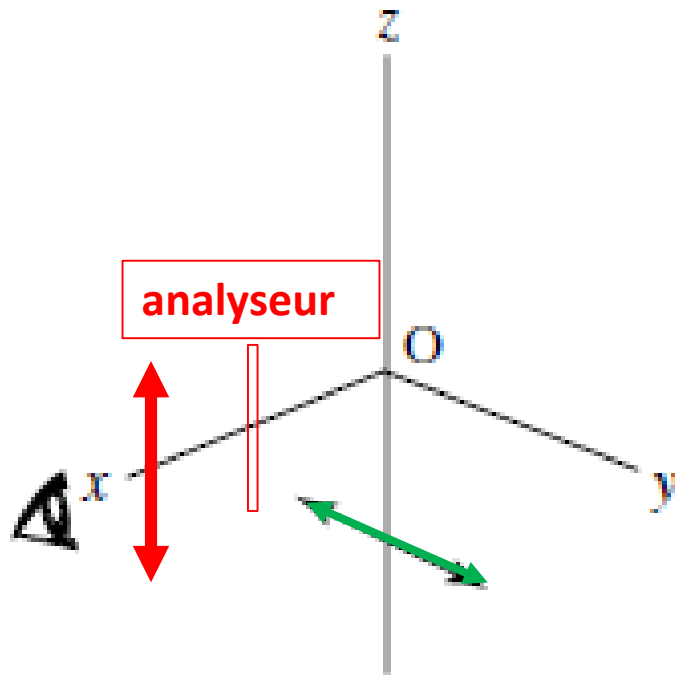
Raman scattering : excitation and scattering geometry

$$p^{(1)}(\nu_L \pm \omega_k)_{x,0} = \left\{ (\alpha'_{xx})_{k,0} E_{x,0} + (\alpha'_{xy})_{k,0} E_{y,0} + (\alpha'_{xz})_{k,0} E_{z,0} \right\} Q_{k,0}$$

$$p^{(1)}(\nu_L \pm \omega_k)_{y,0} = \left\{ (\alpha'_{yx})_{k,0} E_{x,0} + (\alpha'_{yy})_{k,0} E_{y,0} + (\alpha'_{yz})_{k,0} E_{z,0} \right\} Q_{k,0}$$

$$p^{(1)}(\nu_L \pm \omega_k)_{z,0} = \left\{ (\alpha'_{zx})_{k,0} E_{x,0} + (\alpha'_{zy})_{k,0} E_{y,0} + (\alpha'_{zz})_{k,0} E_{z,0} \right\} Q_{k,0}$$

Ox ($\theta = \pi/2$)



Exciting radiation $E_{x,0} = 0; E_{z,0} = 0$

Collection, P(y) absorbed by polarizer:

$$p^{(1)}(\nu_L \pm \omega_k)_{y,0} = 0$$

$$p^{(1)}(\nu_L \pm \omega_k)_{x,0} = \{0\}$$

$$p^{(1)}(\nu_L \pm \omega_k)_{y,0} = \{0\}$$

$$p^{(1)}(\nu_L \pm \omega_k)_{z,0} = \left\{ (\alpha'_{zy})_{k,0} E_{y,0} \right\} Q_{k,0}$$

Raman scattering : excitation and scattering geometry

$$I(W.sr^{-1}) = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) \bar{\nu}^4 p_0^2$$

$$p_0 = \alpha_k \cdot E_0 \quad \text{avec} \quad \alpha_k = \frac{1}{2} \alpha'_k Q_{k,0}$$

Depending on scattering geometry, $p_0 = P_{\sigma,0} = (\alpha'_{\sigma y})_{k,0} E_{y_0} Q_{k,0}$, soit :

$$p_0^2 = \left\{ (\alpha'_{\sigma y})_{k,0} \right\}^2 \left\{ E_{y_0} \right\}^2 \left\{ Q_{k,0} \right\}^2$$
$$I = \left(\frac{\pi^2 c_0}{2\epsilon_0} \right) \bar{\omega}^4 \left\{ (\alpha'_{\sigma y})_{k,0} \right\}^2 \left\{ E_{y_0} \right\}^2 \left\{ Q_{k,0} \right\}^2$$

Irradiance of laser radiation is \mathfrak{S}_L and depends on the electric field value E_{y_0}

$$\mathfrak{S}_L = (1/2)c_0\epsilon_0\{E_{y_0}\}^2 \Rightarrow \{E_{y_0}\}^2 = 2\mathfrak{S}_L/(c_0\epsilon_0)$$

For a single and fixed oscillator

$$I = \left(\frac{\pi^2}{\epsilon_0^2} \right) \bar{\omega}^4 \left\{ (\alpha'_{\sigma y})_{k,0} \right\}^2 \left\{ Q_{k,0} \right\}^2 \mathfrak{S}_L$$

Raman intensity of gas molecules: \mathcal{N} rotating induced dipoles

1 single oscillatory induced dipole $\Rightarrow \mathcal{N}$ oscillatory induced dipoles **freely rotating**.

Raman radiations: distinct δ_k from exciting radiation
 \Rightarrow no interferences and addition of all intensities

$$I(\mathcal{N}) = \mathcal{N} \times I(\mathbf{1})$$

Freely rotating dipole: **term depending on the dipole orientation**

$$I = \left(\frac{\pi^2}{\epsilon_0^2} \right) \bar{v}^4 \left\{ (\alpha'_{\sigma y})_{k,0} \right\}^2 \left\{ Q_{k,0} \right\}^2 \mathfrak{F}_L \times \mathcal{N}$$

$$\text{Average of } \left\{ (\alpha'_{\sigma y})_{k,0} \right\}^2 = \overline{\left\{ (\alpha'_{\sigma y})_{k,0} \right\}^2}$$

$$\alpha' = \begin{bmatrix} \alpha'_{xx} & \alpha'_{xy} & \alpha'_{xz} \\ \alpha'_{yx} & \alpha'_{yy} & \alpha'_{yz} \\ \alpha'_{zx} & \alpha'_{zy} & \alpha'_{zz} \end{bmatrix}; \text{ derivative average polarisability : } \alpha' = \frac{1}{3} [\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz}]$$

derivative anisotropic polarisability:

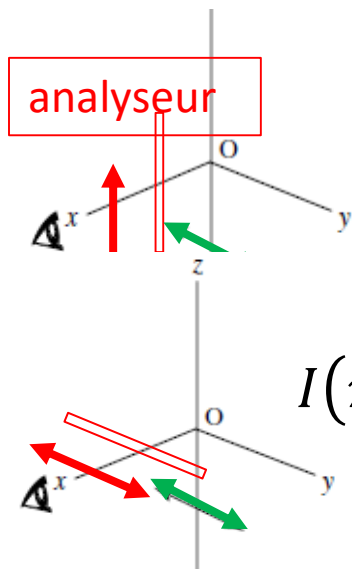
$$(\gamma')^2 = \frac{1}{2} \left[(\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + (\alpha'_{zz} - \alpha'_{xx})^2 + 6 \left((\alpha'_{xy})^2 + (\alpha'_{yz})^2 + (\alpha'_{zx})^2 \right) \right]$$

Raman intensity depends on the orientations of exciting radiation and of the analysed polarization of the scattered radiation.

$$\overline{\alpha'_{xx}}^2 = \overline{\alpha'_{yy}}^2 = \overline{\alpha'_{zz}}^2 = \frac{45a'^2 + 4\gamma'^2}{45} \quad \overline{\alpha'_{yx}}^2 = \overline{\alpha'_{yz}}^2 = \overline{\alpha'_{zx}}^2 = \frac{\gamma'^2}{15}$$

Scattered radiation polarised \parallel scattering plane

Incident radiation \parallel scattering plane



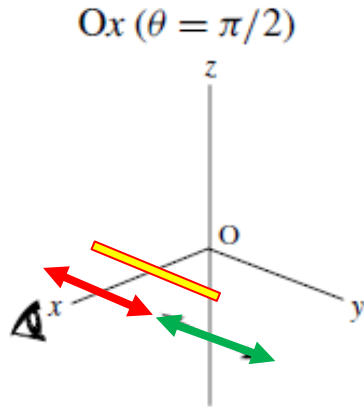
$$I(\pi/2; \parallel^s; \parallel^i) = I = \left(\frac{\pi^2}{\epsilon_0^2} \right) \bar{\omega}^4 \{Q_{k,0}\}^2 \mathfrak{S}_L \times \mathfrak{R} \times \frac{\gamma'^2}{15}$$

$$I(\pi/2; \perp^s; \parallel^i) = I = \left(\frac{\pi^2}{\epsilon_0^2} \right) \bar{\omega}^4 \{Q_{k,0}\}^2 \mathfrak{S}_L \times \mathfrak{R} \times \frac{45a'^2 + 4\gamma'^2}{45}$$

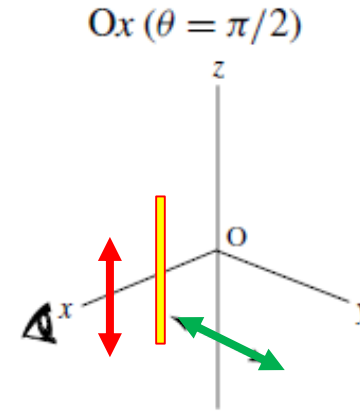
If no analyseur for the collection and for 0° ou 180° geometry

$$I(0 \text{ ou } \pi/; \perp^s + \parallel^s; \parallel^i) = \left(\frac{\pi^2}{\epsilon_0^2} \right) \bar{\omega}^4 \{Q_{k,0}\}^2 \mathfrak{S}_L \times \mathfrak{R} \times \frac{45a'^2 + 7\gamma'^2}{45}$$

Raman intensity of gas molecules: depolarization ratio



$$I(\pi/2; \perp^s; \parallel^i) = I(\parallel)$$



$$I(\pi/2; \parallel^s; \parallel^i) = I(\perp)$$

$$\rho(\pi/2; \parallel^i) = \frac{I(\parallel)}{I(\perp)} = \frac{I(\pi/2; \perp^s; \parallel^i)}{I(\pi/2; \parallel^s; \parallel^i)} = \frac{3\gamma'^2}{45\alpha'^2 + 4\gamma'^2}$$

If normal mode totally symmetric, **totally polarized**, $\gamma' = 0$ and $\rho(\pi/2; \parallel^i) = 0$:
 A1 vibrations of CH₄, N₂, O₂, SO₄²⁻

If Raman band totally **depolarized**, $\alpha' = 0$ et $\rho(\pi/2; \parallel^i) = \frac{3}{4}$

**Depolarisation ratio: a tool for the determination
 of the symmetry class of normal modes**

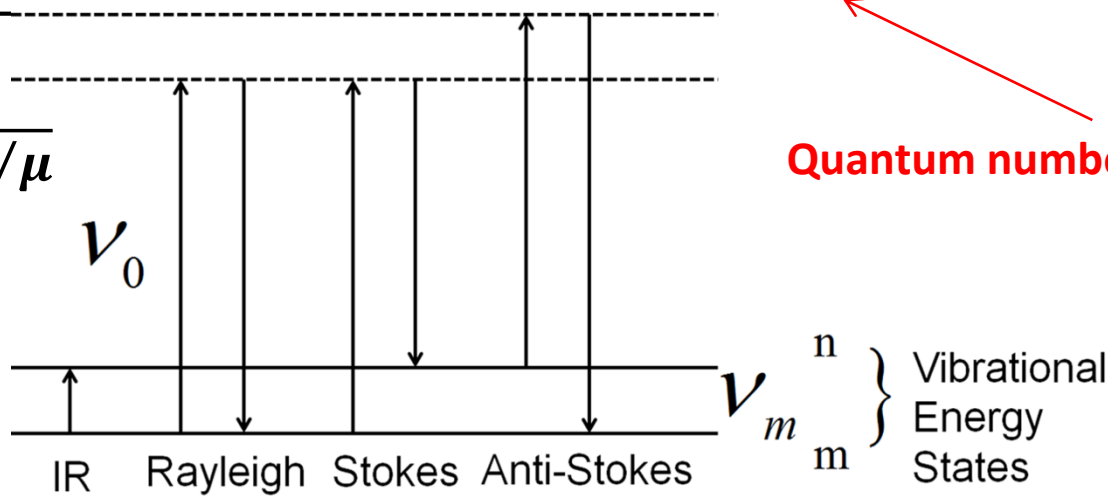
From classical theory of electromagnetism:

- 1) At constant temperature, the intensity of the Stokes line and anti-Stokes line are equal
- 2) The ratio of the Stokes and anti-stokes Raman line of a vibrational mode does not depend on temperature

Quantum mechanics to reconcile theory with experiments

Quantification vibrational energy levels : $E_k(v_k^i) = h\omega_k \times (v_k^i + \frac{1}{2})$

$$\omega_k = (1/2\pi) \times \sqrt{f/\mu}$$



Quantum number of vibration

Number of molecules involved in the Raman transition:

\mathcal{N}_{k,v^i} in initial $E_{v^i k}$

Statistics of Boltzmann

$$\mathcal{N}_{v^i k} = \mathcal{N} \times g_{v^i k} \times \frac{\exp(-E_{v^i k}/k_B T)}{Z_{v,k}}$$

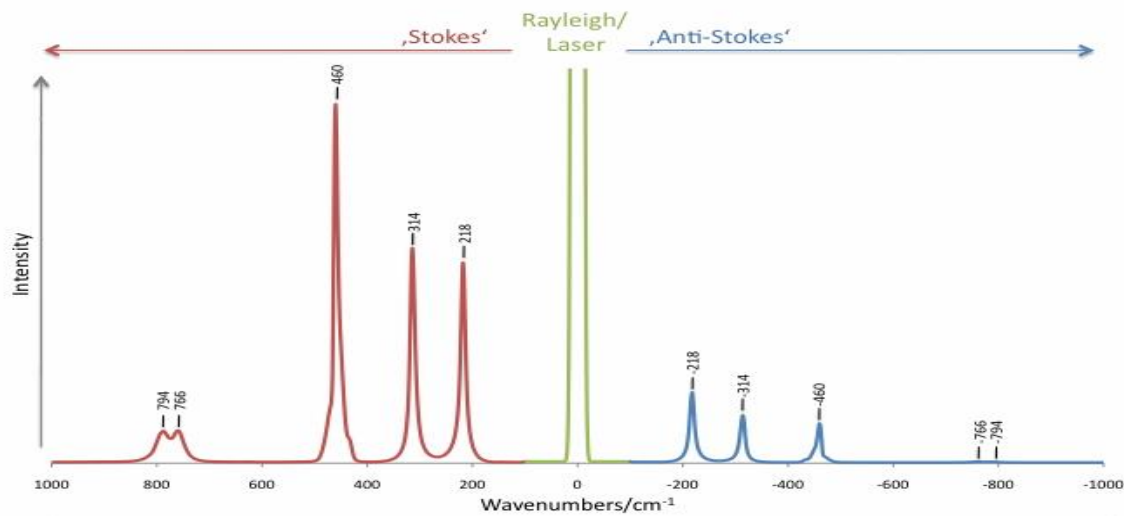
$$Z_{v,k} = \sum_j g_{v^j k} \times \exp(-E_{v^j k}/k_B T)$$

Quantum mechanics : population term

$$f_{v^i_k} = \frac{\exp\{-(v^i_k + 1/2) \times hc_0 \bar{\omega}_k / k_B T\}}{\sum_i \exp\{-(v^i_k + 1/2) \times hc_0 \bar{\omega}_k / k_B T\}} = \frac{\mathcal{N}_{k,v^i}}{\mathcal{N}}$$

$$\frac{I(\text{Stokes})(W sr^{-1})}{I(\text{anti - Stokes})(W sr^{-1})} = \frac{(\bar{\nu}_L - \bar{\omega}_k)^4}{(\bar{\nu}_L + \bar{\omega}_k)^4} \times \exp\{hc_0 \bar{\omega}_k / k_B T\}$$

$$\frac{I(\text{Stokes})(\text{photons. sr}^{-1})}{I(\text{anti - Stokes})(\text{photons. sr}^{-1})} = \frac{(\bar{\nu}_L - \bar{\omega}_k)^3}{(\bar{\nu}_L + \bar{\omega}_k)^3} \times \exp\{hc_0 \bar{\omega}_k / k_B T\}$$



Intensity ratio of Stokes and anti-Stokes lines

$\bar{\nu}_k$ (cm ⁻¹)	10	100	1000
$(\bar{\nu}_L - \bar{\nu}_k)^3 / (\bar{\nu}_L + \bar{\nu}_k)^3$	0,997	0,990	0,853

$h = 6,626 \times 10^{-34}$ J.s; $c_0 = 299792458$ m.s⁻¹; $J. = 2,9998$ 1010m.s⁻¹ $k_B=1,3806 \times 10^{-23}$ K⁻¹

T=300 K

$\bar{\nu}_k = 10$ cm⁻¹, $exp\{hc_0\bar{\omega}_k/k_B T\} = 1,049$;
 $\bar{\nu}_k = 100$ cm⁻¹, $exp\{hc_0\bar{\omega}_k/k_B T\} = 1,613$
 $\bar{\nu}_k = 1000$ cm⁻¹, $exp\{hc_0\bar{\omega}_k/k_B T\} = 119,2$

T= 1300 K

$exp\{hc_0\bar{\omega}_k/k_B T\} = 1,011$;
 $exp\{hc_0\bar{\omega}_k/k_B T\} = 1,12$;
 $exp\{hc_0\bar{\omega}_k/k_B T\} = 3,013$

T (K)	$\bar{\nu}_k$ (cm ⁻¹)	I _S / I _{AS}	T (K)	$\bar{\nu}_k$ (cm ⁻¹)	I _S / I _{AS}
300	10	1,046	1300	10	1,008
300	100	1,603	1300	100	1,109
300	1000	101,7	1300	1000	2,571

Important effect of temperature at high Raman wavenumber

90 ° scattering geometry and non analysed radiation

$$I(\pi/2; \perp^s; \parallel^i) = \left(\frac{h}{8\varepsilon_0^2 c_0 \bar{\omega}_k} \right) (\bar{\nu}_L \pm \bar{\omega}_k)^4 \times \frac{45a'^2 + 4\gamma'^2}{45} \times \frac{\mathcal{U} \times g_{v^i_k}}{1 - \exp\{-hc_0\bar{\omega}_k/k_B T\}} \times \mathfrak{S}_L$$

180 ° scattering geometry and non analysed radiation

Micro-Raman case

$$I(\pi; \perp^s + \parallel^s; \parallel^i) = \left(\frac{h}{8\varepsilon_0^2 c_0 \bar{\omega}_k} \right) (\bar{\nu}_L \pm \bar{\omega}_k)^4 \times \frac{45a'^2 + 7\gamma'^2}{45} \times \frac{\mathcal{U} \times g_{v^i_k}}{1 - \exp\{-hc_0\bar{\omega}_k/k_B T\}} \times \mathfrak{S}_L$$

PLACZEK THEORY ;

Schrötter et Klöckner ,1979); Long (1977; 2002)

Raman scattering cross-sections and gas analysis

$$I_W = \sigma \times \mathfrak{S}_L \times \mathfrak{R} \Rightarrow \sigma = \frac{I_W}{\mathfrak{R} \times \mathfrak{S}_L}$$

Differential Raman cross-section on non-analysed radiation in back-scattering geometry(

$$\begin{aligned} & \frac{d\sigma_k(\bar{\nu}_L, \theta)}{d\Omega} \\ &= (2\pi)^4 \left(\frac{h}{8\pi^2 c_0 \bar{\omega}_k} \right) (\bar{\nu}_L \pm \bar{\omega}_k)^4 \times \frac{45a'^2 + 7\gamma'^2}{45} \times \frac{g_{\nu^i_k}}{1 - \exp\{-hc_0 \bar{\omega}_k / k_B T\}} \times \frac{2\rho_k + (1 - \rho_k) \sin^2 \theta}{1 + \rho_k} \end{aligned}$$

θ : angle between propagation direction of collected Raman radiation with direction polarisation of exciting radiation.

Relative: differential Raman cross-section: measured with respect to the one of N_2 :

$$\Sigma^{k,N_2} = \frac{\frac{d\sigma_k(\bar{\nu}_L, \theta)}{d\Omega}}{\frac{d\sigma_{N_2}(\bar{\nu}_L, \theta)}{d\Omega}} \Rightarrow \frac{d\sigma_k(\bar{\nu}_L, \theta)}{d\Omega} = \sigma'_k = Z^{k,N_2} \times \frac{d\sigma_{N_2}(\bar{\nu}_L, \theta)}{d\Omega} = Z^{k,N_2} \times \sigma'_{N_2}$$

$$I_k = Z^{k,N_2} \times \sigma'_{N_2} \times \mathfrak{S}_L \times \mathfrak{R}_k, \text{ pour } k=1 \text{ à } n$$

$$\mathfrak{R}_k = I_{W,k} / (Z^{k,N_2} \times \sigma'_{N_2} \times \mathfrak{S}_L)$$

Raman scattering cross-sections and gas analysis

$$\mathcal{X}_k = I_{W,k} / (Z^{k,N_2} \times \sigma'_{N_2} \times \mathfrak{I}_L) \text{ et } x_k = \frac{\mathcal{X}_k}{\sum_1^n \mathcal{X}_k}$$

$$x_k = \frac{I_{W,k} / (Z^{k,N_2} \times \sigma'_{N_2} \times \mathfrak{I}_L)}{\sum_j I_{W,k} / (Z^{j,N_2} \times \sigma'_{N_2} \times \mathfrak{I}_L)} = \frac{I_{W,k} / (Z^{k,N_2})}{\sum_j I_{W,k} / (Z^{j,N_2})}$$

These expressions are calculated for Raman intensity in watt But CCD = photons:

$$I_{W,k} = I_{photons,k} \times hc_0 (\bar{\nu}_L - \bar{\nu}_k)$$

$$x_k = \frac{I_{photons,k} \times hc_0 (\bar{\nu}_L - \bar{\omega}_k) / (Z^{k,N_2})}{\sum_j I_{photons,j} \times hc_0 (\bar{\nu}_L - \bar{\omega}_j) / (Z^{j,N_2})} = \frac{I_{photons,k} \times (\bar{\nu}_L - \bar{\omega}_k) / (Z^{k,N_2})}{\sum_j I_{photons,j} \times (\bar{\nu}_L - \bar{\omega}_j) / (Z^{j,N_2})}$$

Renormalisation with respect to the wavenumber $\bar{\omega}_{N_2}$ of Q vibration of N_2 :

$$\frac{I_{photons,k} / [Z^{k,N_2} / \{(\bar{\nu}_L - \bar{\omega}_k) / (\bar{\nu}_L - \bar{\omega}_{N_2})\}]}{\sum_j I_{photons,j} / [Z^{j,N_2} / \{(\bar{\nu}_L - \bar{\omega}_j) / (\bar{\nu}_L - \bar{\omega}_{N_2})\}]}$$

We define: $Z^{*j,N_2} = Z^{j,N_2} / \{(\bar{\nu}_L - \bar{\omega}_j) / (\bar{\nu}_L - \bar{\omega}_{N_2})\}$:
 corrections to be done by normalisation / Q(N_2)

Raman scattering cross-sections and gas analysis

$$Z^{*j,N_2} = Z^{j,N_2} / \left\{ \left(\overline{\nu_L} - \overline{\omega_j} \right) / \left(\overline{\nu_L} - \overline{\omega_{N_2}} \right) \right\}$$

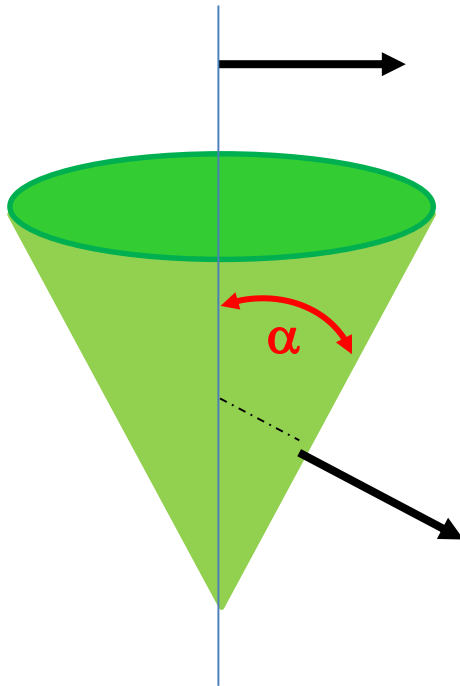
NuL	NuN2	NuL-NuN2	GAZ	Nuj	Zj/N2	NuL-Nuk	correction	Z*j/N2
19435	2331	17104	SO2	1150	5,51	18285	1,069	5,15
19435	2331	17104	CO2	1285	0,99	18150	1,061	0,93
19435	2331	17104	CO2	1288	1,5	18147	1,061	1,41
19435	2331	17104	CO2	2143	0,99	17292	1,011	0,98
19435	2331	17104	H2S	2610	6,81	16825	0,984	6,92
19435	2331	17104	CH4	2917	8,7	16518	0,966	9,01
19435	2331	17104	H2O	3657	2,51	15778	0,922	2,72
19435	2331	17104	H2	4155	2,2	15280	0,893	2,46

Raman scattering cross-sections and gas analysis under microscope

CO₂, CH₄, CO, H₂S, N₂, O₂, H₂, SO₂)

Totally symmetric vibrational modes: $\rho_k = 0$:

$$\frac{2\rho_k + (1 - \rho_k) \sin^2 \theta}{1 + \rho_k} = \sin^2 \theta \quad \Rightarrow \quad \frac{d\sigma_k(\bar{\nu}_L, \theta)}{d\Omega} = \Sigma \times f(\theta)$$



θ varies from 90° to $90^\circ + 2\alpha$

Correction functions $f(\theta)$ are identical of every vibrational bands and cancel in the ratio.

Raman scattering cross-sections in liquids: **internal field effect**

$\epsilon_r > 1$ ou $n > 1 \Rightarrow \nearrow$ by a factor Λ : Onsager's theory

$$\Lambda(\bar{\nu}_L, \bar{\nu}_k) = \frac{n(\bar{\nu}_L - \bar{\omega}_k)}{81 n_{\bar{\nu}_L}} \times \left(n(\bar{\nu}_L - \bar{\omega}_k) + 2 \right)^2 \times \left(n_{\bar{\nu}_L} + 2 \right)^2 \approx 1,29 \text{ for CO}_2$$

$$\sigma'_{k,L} = \sigma'_{k,V} \times \Lambda(\bar{\nu}_L, \bar{\omega}_k) = \sigma'_{k,v} \times \frac{n(\bar{\nu}_L - \bar{\omega}_k) \left(n(\bar{\nu}_L - \bar{\omega}_k) + 2 \right)^2}{81 n_{\bar{\nu}_L}} \left(n_{\bar{\nu}_L} + 2 \right)^2$$

$$\sigma'_{N_2,L} = \sigma'_{N_2,V} \times \frac{n(\bar{\nu}_L - \bar{\omega}_{N_2}) \left(n(\bar{\nu}_L - \bar{\omega}_{N_2}) + 2 \right)^2}{81 n_{\bar{\nu}_L}} \times \left(n_{\bar{\nu}_L} + 2 \right)^2$$

$$\frac{\sigma'_{k,L}}{\sigma'_{N_2,L}} = \frac{\sigma'_{k,V}}{\sigma'_{N_2,V}} \times \frac{n(\bar{\nu}_L - \bar{\omega}_k) \left(n(\bar{\nu}_L - \bar{\omega}_k) + 2 \right)^2}{n(\bar{\nu}_L - \bar{\omega}_{N_2}) \left(n(\bar{\nu}_L - \bar{\omega}_{N_2}) + 2 \right)^2}$$

Very small variations of refractive indices (-0,0005 per 1000 cm⁻¹
for dense CO₂ (1,23 g.cm⁻³)

negligible effects on ratio of relative Raman cross sections

Raman scattering cross-sections and molecular interactions distinct from hydrogen bonds

Molecular interactions may modify α and α' by change of the electron distribution and even of the symmetry.

Few experimental data: due to difficulties (solid angles of collection, reflection, reference,...)

In the system CH_4 (90 mole %)- N_2 (10 mole %): variation of 30% of RCS ratio of CH_4 and N_2 , $1\text{bar} < P < 1000\text{ bar}$ (Seitz et al., 1996).

In other systems (CCl_4 , CHCl_3 , CDCl_3 , CH_2Cl_2 , CD_2Cl_2 ; C_6H_6): variations $< 20\%$, depending on the vibrational modes (Schrötter et Klöckner, 1979).

Raman intensity in aqueous solutions: **unit concentrations**

$$I_{phot,i}^{\nu_k} = \sigma_i^{\nu_k} \times \mathfrak{N}_i \times \mathfrak{S}_L = \sigma_i^{\nu_k} \times [C_i] \times V \times \mathfrak{S}_L$$

$[C_i]$: **Molarity: mole i .dm⁻³**; V : collected excited emitting volume

$$[C_i] = (1000\rho - \sum_j [C_j] \overline{M}_j) \times m_i / 1000; \quad \rho : \text{specific mass of solution (g.cm}^{-3}\text{)}$$

m_i : **molality: mole i .kg⁻³ H₂O** \overline{M}_j : molar mass of solute j

$$I_{phot,H_2O}^{\nu_R} = \sigma_{H_2O}^{\nu_R} \times \mathfrak{N}_{H_2O} \times \mathfrak{S}_L = \sigma_{H_2O}^{\nu_R} \times [C_{H_2O}] \times V \times \mathfrak{S}_L$$

$$[C_{H_2O}] = \frac{(1000\rho - \sum_j [C_j] \overline{M}_{H_2O})}{\overline{M}_{H_2O}}$$

$$\frac{I_{phot,i}^{\nu_k}}{I_{phot,H_2O}^{\nu_R}} = \frac{\sigma_i^{\nu_k}}{\sigma_{H_2O}^{\nu_R}} \times \frac{\overline{M}_{H_2O}}{1000} \times m_i = f(\sigma_i^{\nu_k}, \sigma_{H_2O}^{\nu_R}) \times m_i$$

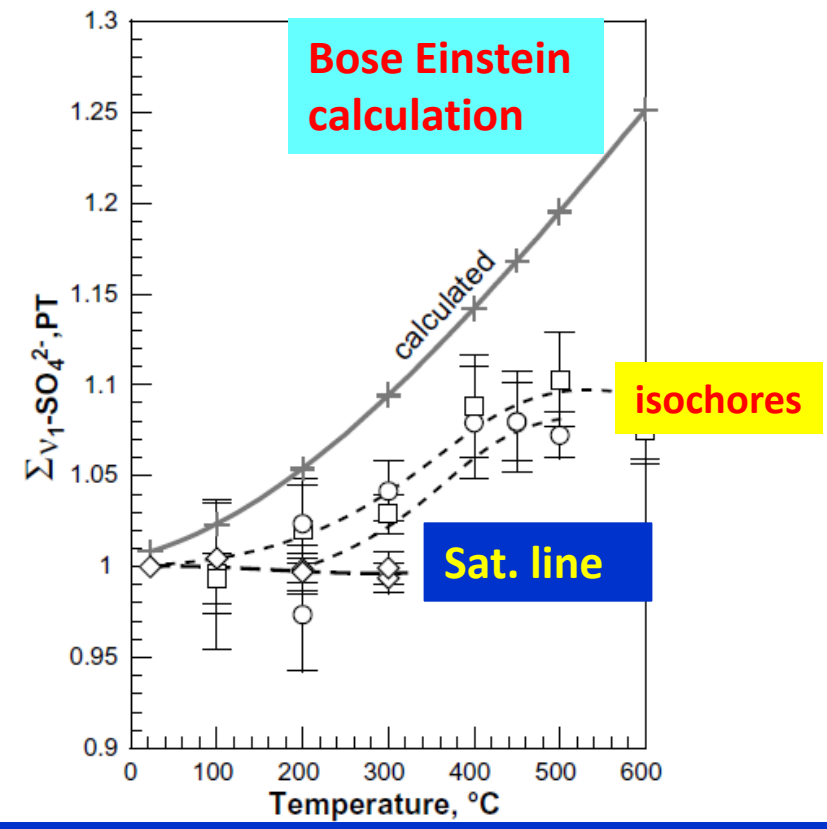
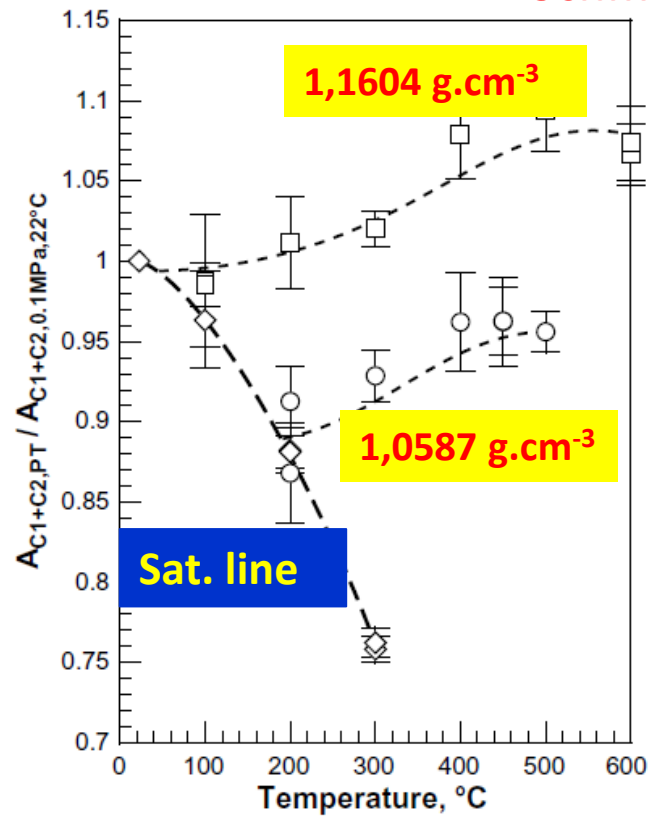
The intensity ratio of a Raman band of a solute and a vibrational band of water is proportional to the solute concentration in the molality scale.

Requires $(\sigma_i^{\nu_k} / \sigma_{H_2O}^{\nu_R})$ is constant versus solute concentration.

Requires constant P, T and constant fluid bulk chemistry except for solute i.

Raman cross section of a solute $f(T,P)$: sulfate in water , A_1 mode

Schmidt (2009). GCA, 73, 425-437



Saturation line: intensity decrease follows density decrease

High density isochores: different behaviour

Saturation line: near constant RRCS because bond expansion.

Positive correlations with pressure/density < than calculated. Anharmonic vibration ?

Huge experimental and theoretical works to be done

$$\frac{d\sigma_k(\bar{\nu}_L, \theta)}{d\Omega} =$$
$$(2\pi)^4 \left(\frac{h}{8\pi^2 c_0 \bar{\nu}_k} \right) (\bar{\nu}_L \pm \bar{\nu}_k)^4$$
$$\times \frac{g_{v^i_k}}{1 - \exp\{-hc_0 \bar{\nu}_k / k_B T\}} \times$$
$$\frac{45a'^2 + 7\gamma'^2}{45}$$

MOLECULAR INTERACTIONS: SOLVATION, HYDROGEN BONDS

Huge experimental and theoretical works to be done

Reduced Raman spectrum

$$\text{Raman intensity (photons/s): } I_{\text{photons}}(\nu) = C \times (\nu_L - \omega_k)^3 \times \frac{1}{\omega_k} \times \frac{1}{B(T)} \times S_k$$

C , instrument factor,

ν_L frequency of laser radiation, ω_k Raman frequency

$1/B(T)$, Bose Einstein factor, $1/B(T) = (1 - \exp(-hc\bar{\omega}_k/k_B T))^{-1}$

S_k , molar activity of Raman scattering for vibrational mode k at frequency ν_k

Frequency part $(\nu_L - \omega_k)^3 \times \frac{1}{\omega_k}$ and temperature part superimpose to the intrinsic value of intensity within S_k , especially at $< 1000 \text{ cm}^{-1}$.

Reduced Raman spectrum:

$$R_{\text{photons}}(\nu) = I_{\text{photons}}(\nu) \times (\nu_L - \omega_k)^{-3} \times \omega_k \times B(T)$$

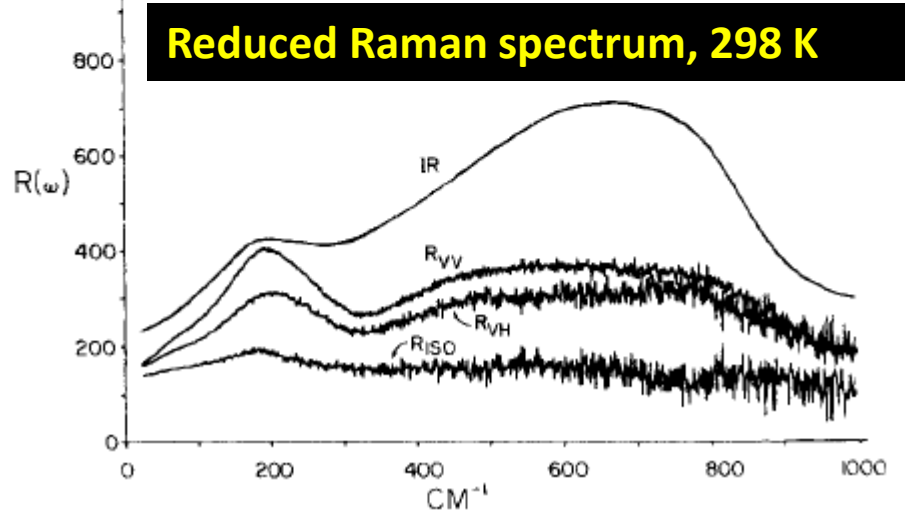
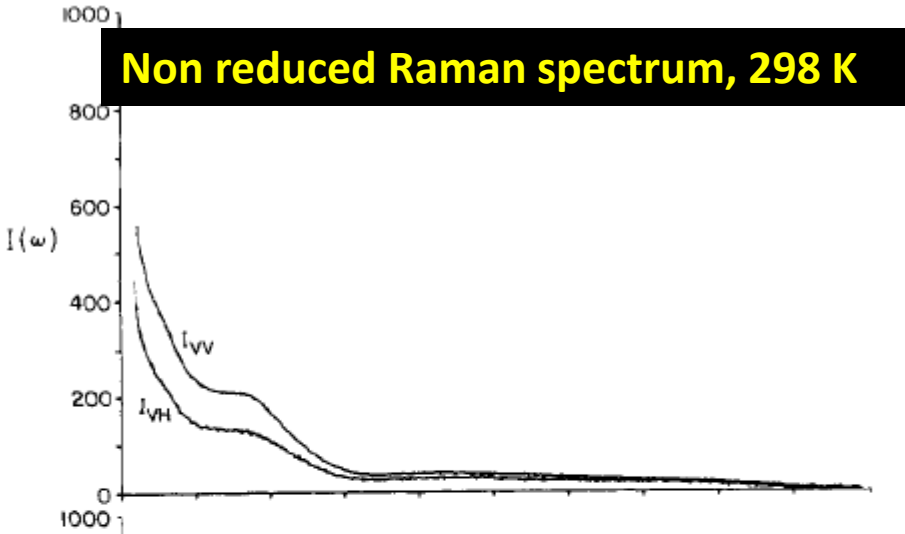
Integrated intensity of ω_k Raman band = transition moment or $(\partial\alpha/\partial Q_k)^2$

Reduced spectrum can be compared to Infrared spectrum

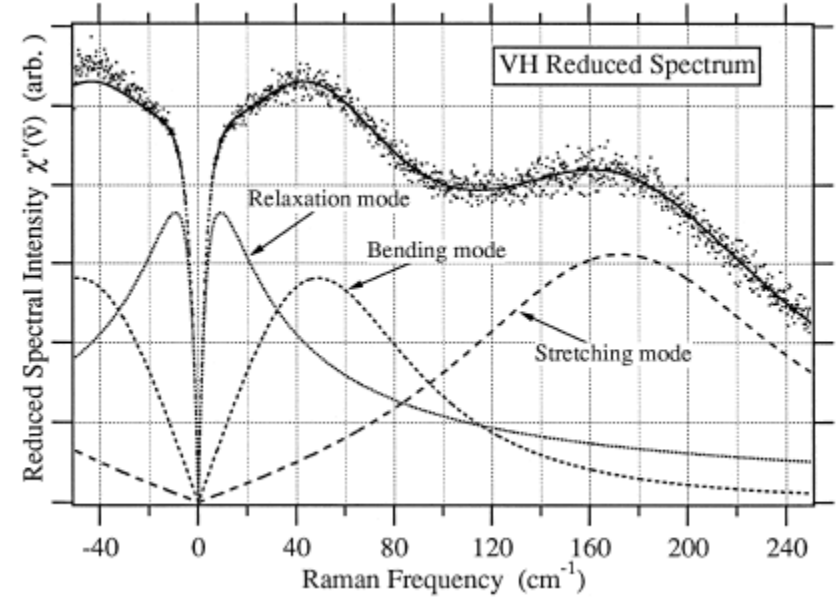
Intensity of reduced spectrum is independent on temperature

Useful for disordered solids, glasses in the $100\text{-}200 \text{ cm}^{-1}$

Reduced Raman spectrum: water study, intermolecular modes



Brooker et al. (1988). JRS, 19, 71-78.



Tominaga et al (1998) Fluid Phase Equilibria, 144, 323-330

Two damped oscillators of a transient distorted tetrahedron of 5 water :

- 194 cm^{-1} : stretching
- 69.1 cm^{-1} : bending

Creation-annihilation mode of hydrogen bond à 8 cm^{-1}

Some references :

D.A. Long (1977). Raman Spectroscopy. McGraw-Hill International Book Company

H.W. Schrötter, & H.W. Klöckner (1979): Raman scattering cross sections in gases and liquids. Pp 123-166 in: *Raman Spectroscopy of Gases and Liquids* (A. Weber editor). Topics in Current Physics. Springer-Verlag.

D.A. Long (2002). The Raman effect. John Wiley and Sons.

J. Dubessy, M.-C. Caumon, F. Rull (2012). Raman Spectroscopy applied to Earth Sciences and cultural Heritage. European Mineralogical Union, EMU Notes 12.