

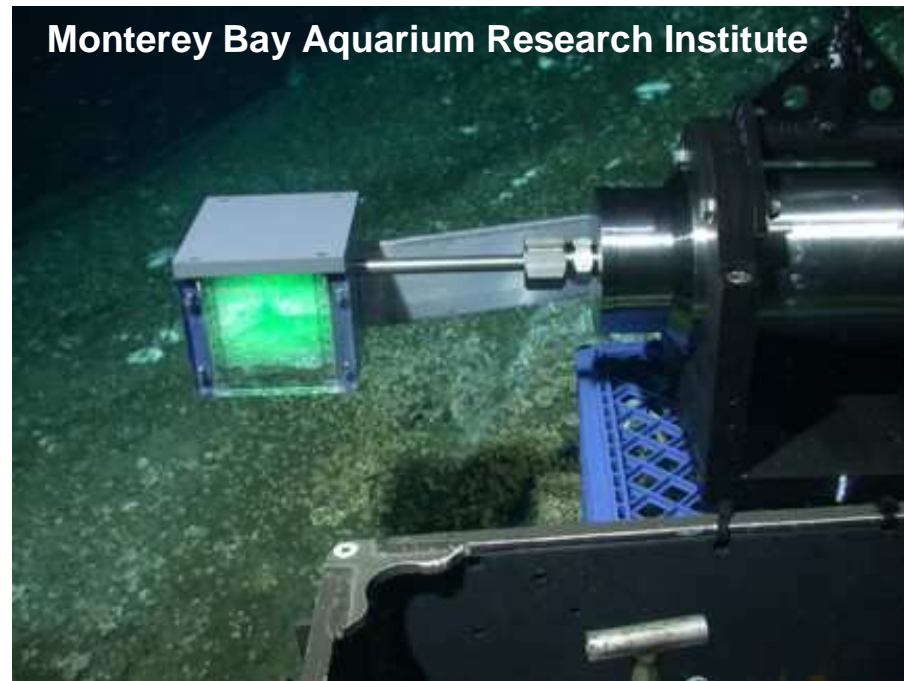
# **RAMAN SPECTROSCOPY OF GASES**

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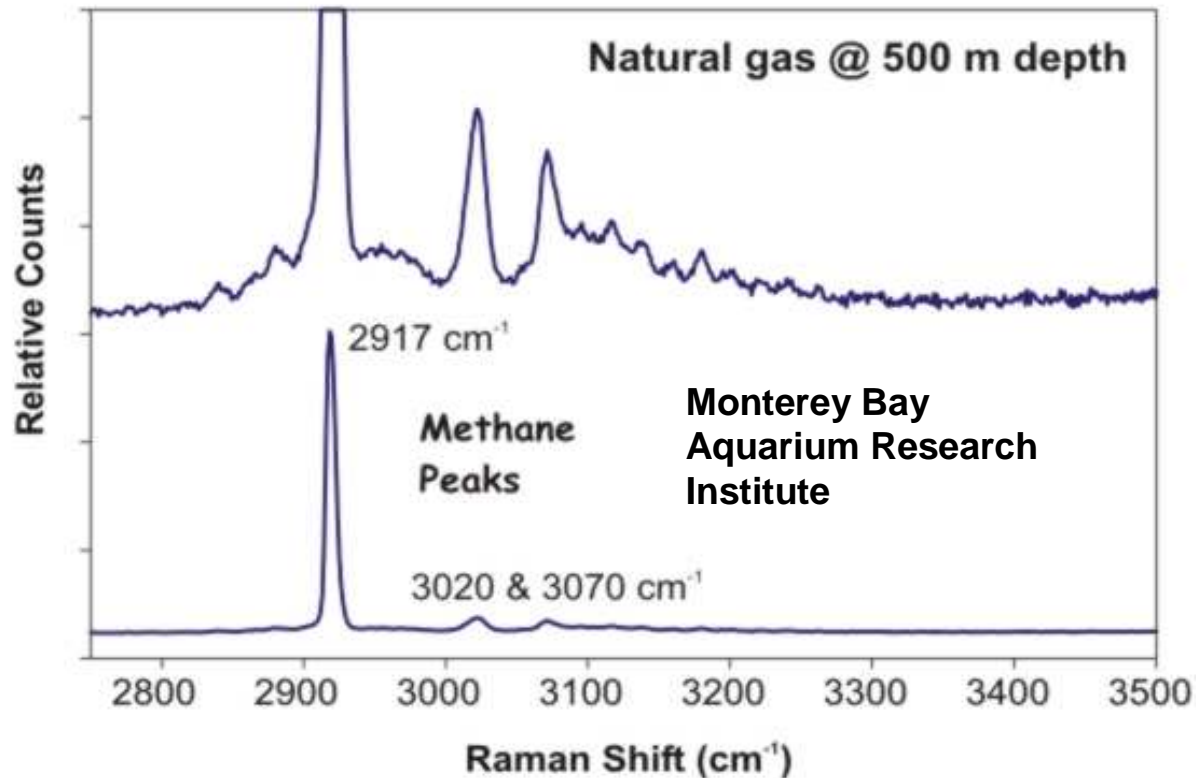
**UMR G2R-CNRS Nancy  
(France)**

EMU-CNRS International School: Applications of Raman Spectroscopy  
to Earth Sciences and cultural Heritage : 14-16<sup>th</sup> of june 2012

- real-time monitoring of anaesthetic and respiratory gas mixtures during surgery
- process gas analysis
- environmental gas analysis, industrial gas emission monitoring
- gas seeping in sea floor
- palaeofluid analysis contained in fluid inclusions



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- 1) Methane only identified component that has been in the spectra. Other higher hydrocarbons may be present, they are not in high enough concentrations to be detected by Raman analyses. GC analysis on shore verified that methane is present at ~97%.
- 2) Brunsgaard Hansen et al. [2002]: pressure (density) of a methane mixture from the ratio of the 3020 ( $\nu_3$ ) and 3070 cm<sup>-1</sup> ( $2\nu_2$ ) bands]: 0.67 @ 1582 m (~16.1 MPa); 1.75 @ 250 m (~2.6 MPa).

# RAMAN INTENSITY OF GASES

the number of Raman photons vibrational mode  $j$ , with a wavenumber,  $\nu_j$

$$dP_{j,m}^{Raman}(\bar{\nu}_0, \bar{\nu}_j^g, \theta)$$

gas  $m$  excited with a laser radiation at  $\bar{\nu}_0$

$$dP_{j,m}^{Raman}(\bar{\nu}_0, \bar{\nu}_j^m, \theta) = \frac{P^{laser}(\bar{\nu}_0)}{A} \times \frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_j^m, \theta) \times d\Omega(\theta) \times N_m$$

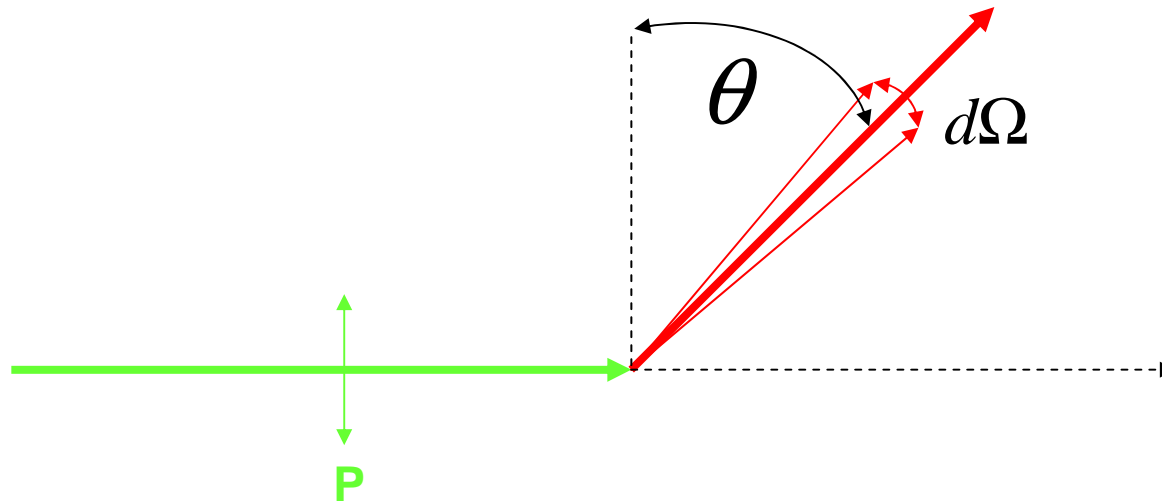
$P^{laser}(\nu_0)$  the number of photons delivered by the laser incoming on the gas sample

A: excited area of the sample by the laser beam

$\frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_j^m, \theta)$  (in  $\text{cm}^2/\text{sr}^{-1}$ ) the differential Raman scattering cross-section of the vibrational mode  $j$  into a direction defined by angle  $\theta$  between the direction of observation without polarization analyzer and the polarization vector of the laser

$d\Omega(\theta)$  (in sr) is the acceptance solid angle of the collection of Raman photons scattered by the sample in the direction of observation

$N_m$  number of molecules in the irradiated volume seen by the spectrometer



$$\frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_j^m, \theta) = \frac{2^4 \pi^4}{45} \times \frac{(\bar{\nu}_0 - \bar{\nu}_j^m)^4 \times (h/8\pi^2 c \bar{\nu}_j^m)}{1 - \exp(-hc\bar{\nu}_j^m/kT)} \times g_j \times (45a_j^2 + 7\gamma_j^2) \times \frac{2\rho_j + (1 - \rho_j)\sin^2 \theta}{1 + \rho_j}$$

$a_j$  and  $\gamma_j$  are the invariants of the polarizability tensor derived with respect to the normal coordinate of the considered vibration, the linear average and the anisotropy respectively

$\rho_j$  depolarization ratio, a number without dimension, of the considered Raman band

# Relative differential Raman scattering cross-section

- **Why ?** Absolute intensity measurements very difficult to carry out.
- **Consequences:** 1) concentration unit not in mole / (unit volume), but in mole fraction  
 2) Molar density not deduced directly from intensity measurements  
 3) use of a reference gas: N<sub>2</sub> (chemical inertia, abundant)

$$\frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_j^g, \theta) = (5.05 \pm 0.1) \times 10^{-48} \times (\bar{\nu}_0 - 2331)^4 \text{ cm}^6 \cdot \text{sr}^{-1}$$

- Differential Raman scattering cross-section with respect to N<sub>2</sub>

$$\frac{\frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_j^m, \theta)}{\frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_Q^{N_2}, \theta)} = \frac{(\bar{\nu}_0 - \bar{\nu}_j^m)^4}{(\bar{\nu}_0 - \bar{\nu}_Q^{N_2})^4} \times \frac{\bar{\nu}_Q^{N_2}}{\bar{\nu}_j^m} \times \frac{1 - \exp(-hc\bar{\nu}_Q^{N_2}/kT)}{1 - \exp(-hc\bar{\nu}_j^m/kT)} \times \frac{g_j \times (45a_j^2 + 7\gamma_j^2)}{(45(a_Q^{N_2})^2 + 7(\gamma_Q^{N_2})^2)}$$

Schrötter and Klöckner (1979) neglects the term  $1 - \exp(-hc\bar{\nu}_Q^{N_2}/kT)$

# Relative Raman scattering cross-section

Collection angle defined by the planar semi-aperture angle of the microscope

$$\sigma(\bar{\nu}_0, \bar{\nu}_j^m, \Omega_0) = \frac{2^4 \pi^4}{45} \times \frac{(\bar{\nu}_0 - \bar{\nu}_j^m)^4 \times (h/8\pi^2 c \bar{\nu}_j^m)}{1 - \exp(-hc\bar{\nu}_j^m/kT)} \times g_j \times (45a_j^2 + 7\gamma_j^2) \times f(\theta)$$


Extension to the relative Raman scattering cross-section in backcattering geometry using a high N.A. objective

$$\sigma^*(\bar{\nu}_0, \bar{\nu}_j^m) = \frac{(\bar{\nu}_0 - \bar{\nu}_j^m)^4}{(\bar{\nu}_0 - \bar{\nu}_Q^{N_2})^4} \times \frac{\bar{\nu}_Q^{N_2}}{\bar{\nu}_j^m} \times \frac{1 - \exp(-hc\bar{\nu}_Q^{N_2}/kT)}{1 - \exp(-hc\bar{\nu}_j^m/kT)} \times \frac{g_j \times (45a_j^2 + 7\gamma_j^2)}{g_Q^{N_2} \times (45(a_Q^{N_2})^2 + 7(\gamma_Q^{N_2})^2)}$$

$$\sigma(\bar{\nu}_0, \bar{\nu}_j^m, \Omega_0) = \sigma^*(\bar{\nu}_0, \bar{\nu}_j^m) \times \frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_Q^{N_2}, \theta)$$

$$P_{j,m}^{Raman}(\bar{\nu}_0, \bar{\nu}_j^m, \Omega_0) = \frac{P^{laser}(\bar{\nu}_0)}{A} \times \sigma^*(\bar{\nu}_0, \bar{\nu}_j^m) \times \frac{d\sigma}{d\Omega}(\bar{\nu}_0, \bar{\nu}_Q^{N_2}, \theta) \times N_m$$

# Calculation composition

Mole fraction  $x_m = N_m / \sum_{i=1}^{i=n} N_i$    $x_m = \frac{P_{j,m}^{Raman} / \sigma^*(\bar{\nu}_0, \bar{\nu}_j^m)}{\sum_{i=1}^{i=n} [P_{j,i}^{Raman} / \sigma^*(\bar{\nu}_0, \bar{\nu}_j^i)]}$

Experimental intensities and Raman photons  $I_{j,m}^{Raman} = P_{j,m}^{Raman} \times \xi(\bar{\nu}_0, \bar{\nu}_j^m, \Omega_0) \times t_m$

$\xi(\bar{\nu}_0, \bar{\nu}_j^m, \Omega_0)$  intensity instrumental function at  $\bar{\nu}_0 - \bar{\nu}_j^m$

$$x_m = \frac{I_{j,m}^{Raman} / [\sigma^*(\bar{\nu}_0, \bar{\nu}_j^m) \times \xi(\bar{\nu}_0, \bar{\nu}_j^m, \Omega_0) \times t_m]}{\sum_{i=1}^{i=N} [I_{j,i}^{Raman} / [\sigma^*(\bar{\nu}_0, \bar{\nu}_j^i) \times \xi(\bar{\nu}_0, \bar{\nu}_j^i, \Omega_0) \times t_i]]}$$

gas	CO <sub>2</sub>	CO <sub>2</sub>	CO	H <sub>2</sub> S	SO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	H <sub>2</sub> O
(cm <sup>-1</sup> )	1285	1388	2143	2611	1151	2917	4155	3657
(j)	0.99	1.5	0.99	6.81	5.51	8.7	2.2	2.51

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# Detection limit with a microscope

$$P_{j,m}^{Raman}(\overline{\nu_0}, \overline{\nu_j^m}, \Omega_0) = \frac{P^{laser}(\overline{\nu_0})}{A} \times \sigma^*(\overline{\nu_0}, \overline{\nu_j^m}) \times \frac{d\sigma}{d\Omega}(\overline{\nu_0}, \overline{\nu_Q^{N_2}}, \theta) \times N_m$$

$$N_m = d_m \times A \times L$$

microscope

$$L = \delta z = 4\lambda / (N.A.)^2 \approx 4\lambda = 2\mu\text{m}$$

$$P_{j,m}^{Raman} = P^{laser}(\overline{\nu_0}) \times \sigma^*(\overline{\nu_0}, \overline{\nu_j^m}, \Omega_0) \times \frac{d\sigma}{d\Omega}(\overline{\nu_0}, \overline{\nu_j^m}, \theta) \times d_m \times \delta z$$

For a 100 mW laser at 514.5 nm, the number of photons is  $P^{laser}(\overline{\nu_0}) = 2.5 \times 10^{17}$  photons.s<sup>-1</sup>

$$\frac{d\sigma}{d\Omega}(\overline{\nu_0}, \overline{\nu_j^{N_2}}, \theta) = 44 \times 10^{-32} \text{ cm}^2 \cdot \text{sr}^{-1}$$

For 1 bar pressure  $d_m = N_{Av} / 22400 = 2.7 \times 10^{19}$  molecules.cm<sup>-3</sup>

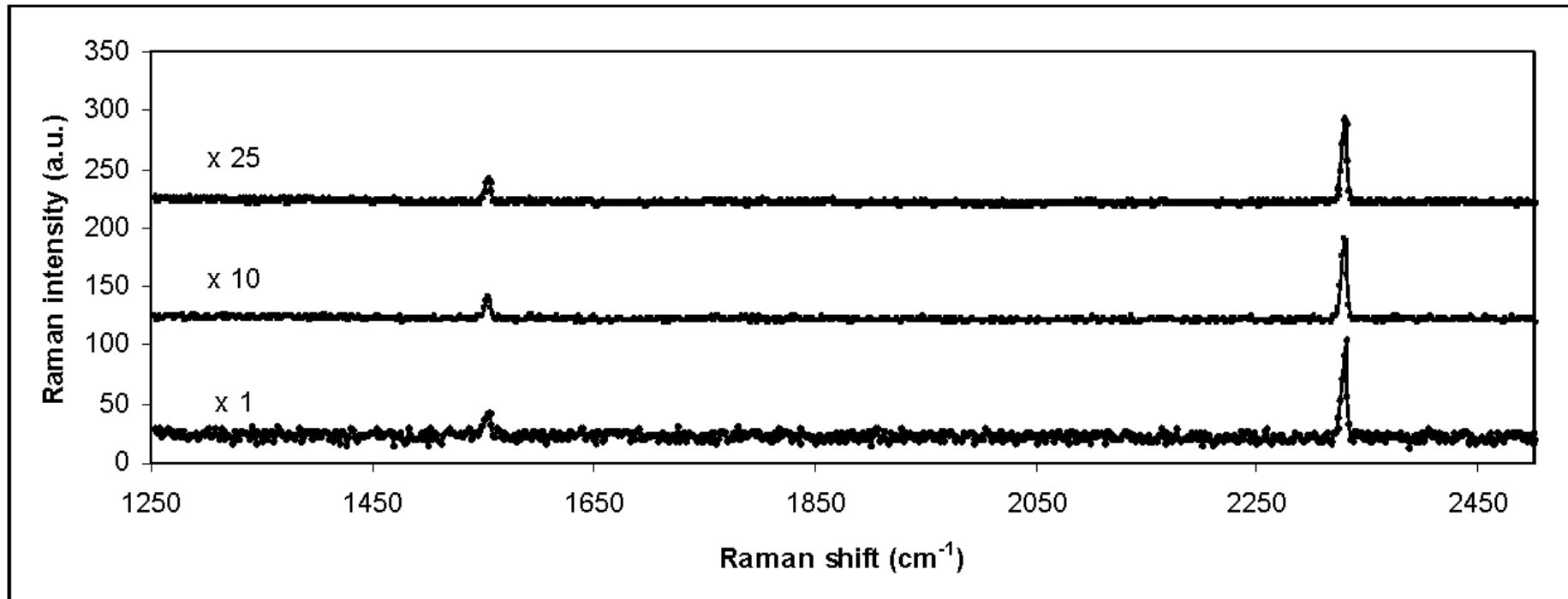
Number of Raman photons.s<sup>-1</sup> is :  $P_{j,m}^{Raman} = 300$  photons.s<sup>-1</sup>

Efficiency of the whole Raman system = 25 %  $P_{j,m}^{Raman}(\text{detector}) = 75$

**Near the detection limit**

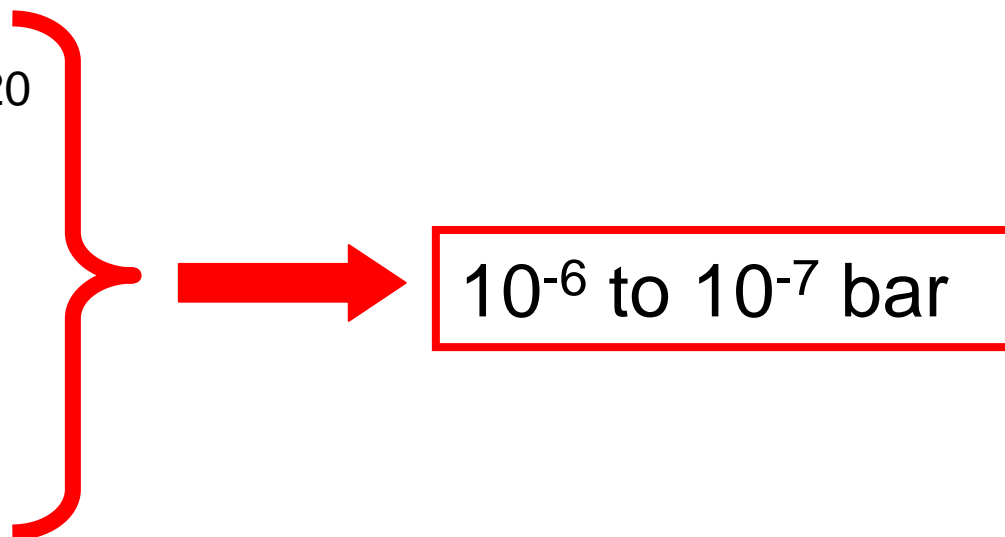
# Detection limit with a microspectrometer

**100 mW, t = 1s, objective x 100**



# Detection limit with a conventional spectrometer

- laser power of several watts: 2 w => x 20
- focus with a lens : L = 1 cm => x 5000
- collection optics with N.A. = 1
- exposure times x 100
- 90 ° scattering geometry



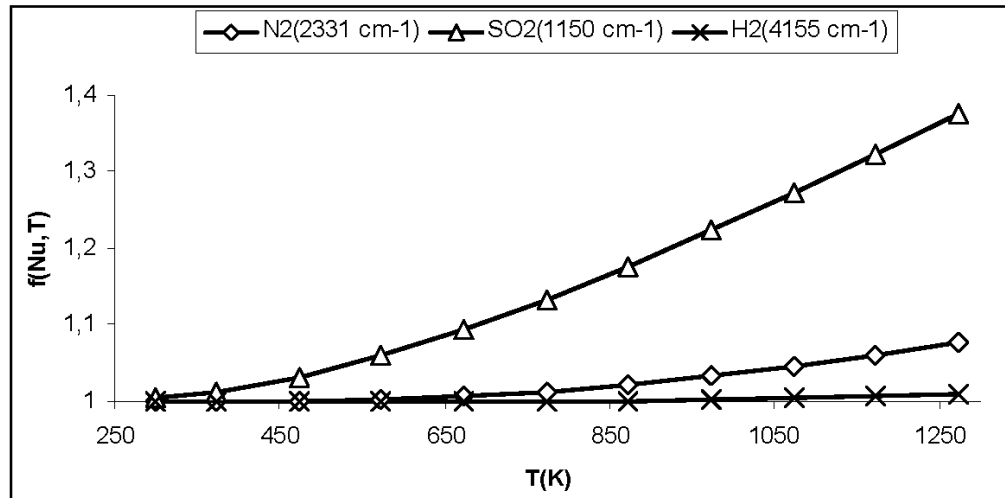
(Tejeda *et al.*, 1997; Avila *et al.*, 1999).

**Raman spectroscopy can be used for monitoring gas composition**

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# Variation of RSCS with temperature

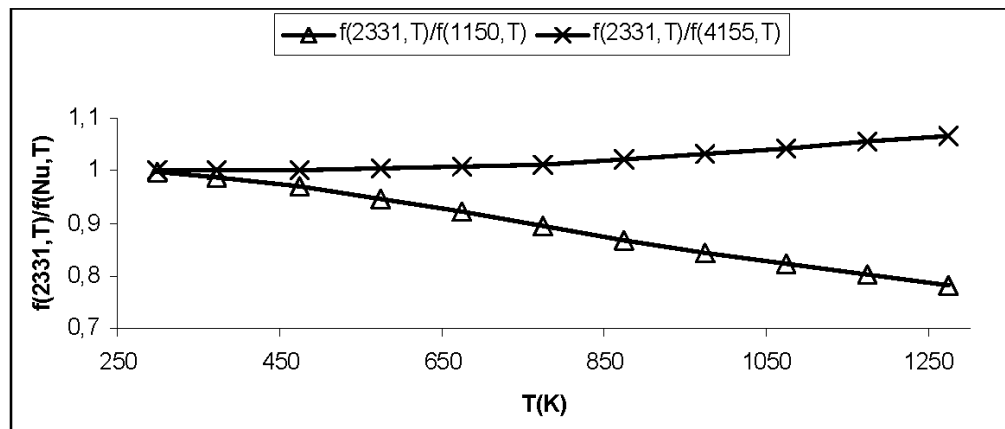
- Each gas RSCS:  $\left[1 / 1 - \exp\left(-hc\overline{\nu}_j^g / kT\right)\right]$  ➔  $\sigma^*\left(\overline{\nu}_0, \overline{\nu}_j^m\right) \propto \frac{1 - \exp\left(-hc\overline{\nu}_Q^{N_2} / kT\right)}{1 - \exp\left(-hc\overline{\nu}_j^m / kT\right)}$



**SO<sub>2</sub>**

**N<sub>2</sub>**

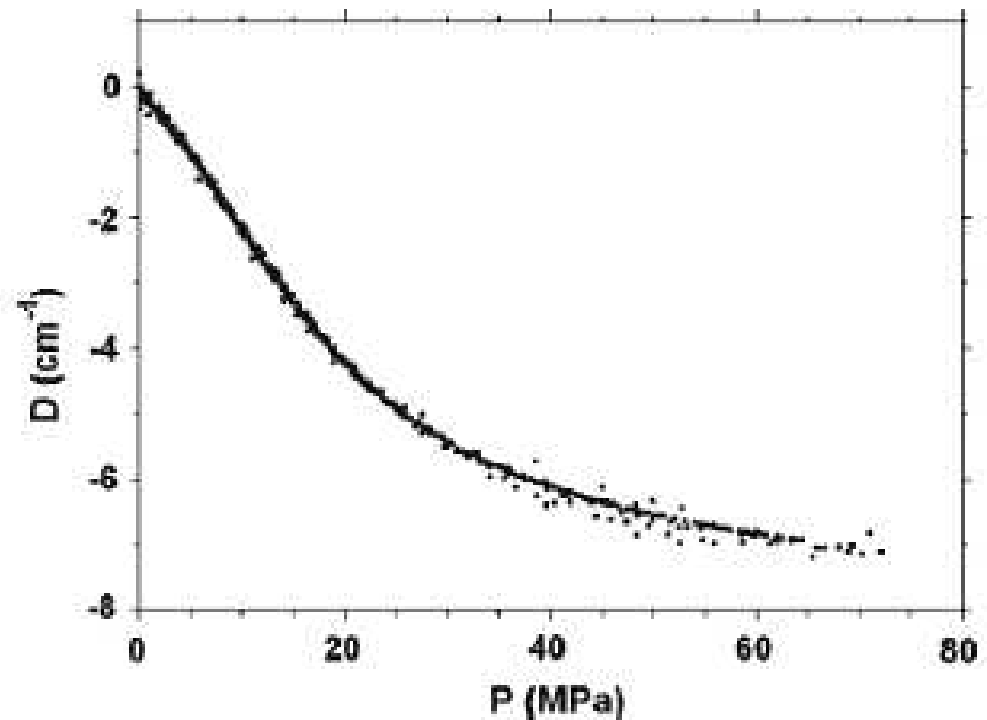
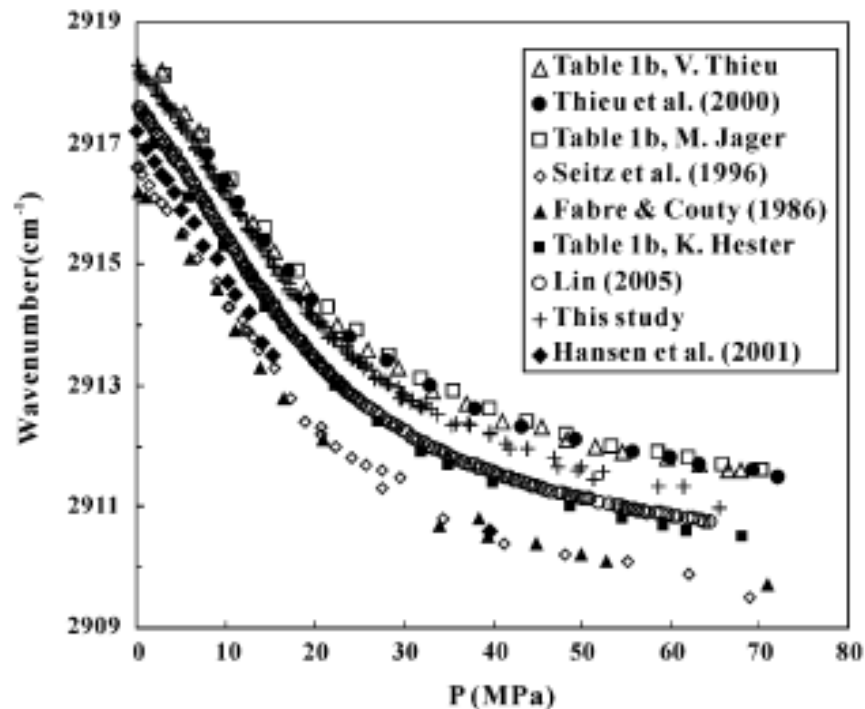
**H<sub>2</sub>**



**N<sub>2</sub>/H<sub>2</sub>**

**N<sub>2</sub>/SO<sub>2</sub>**

# Effect of pressure on peak position



**Lu et al., GCA, 2007,71, 3961-3978**

Several other studies on the pressure effect on  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$

$\text{CH}_4$ - $\text{N}_2$  mixture vs composition

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# Effect of pressure and composition on peak position

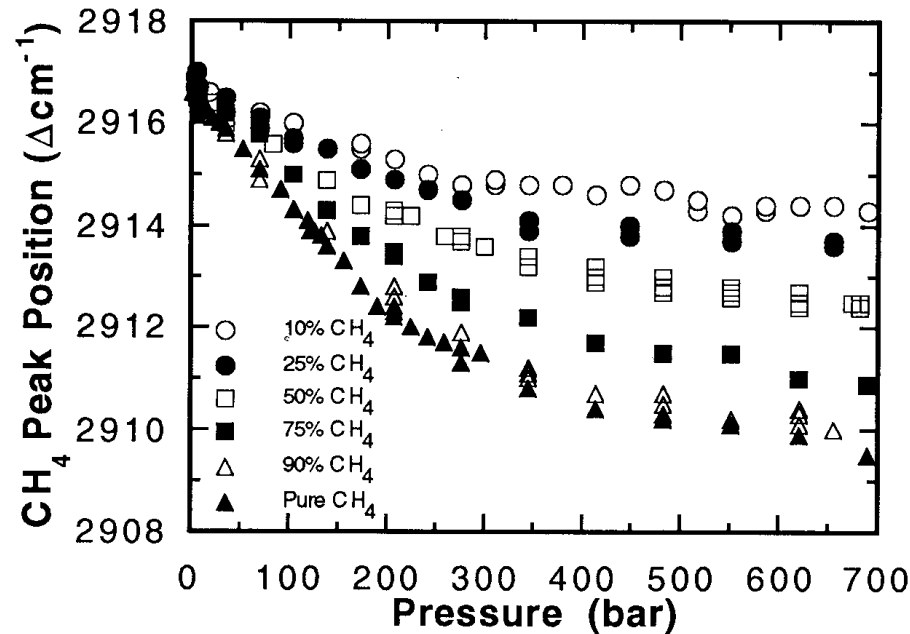


Fig. 3. CH<sub>4</sub> peak position ( $\nu_1$ ) versus total gas pressure for pure CH<sub>4</sub> and various CH<sub>4</sub>-N<sub>2</sub> mixtures (mole percent).

**Seitz, J.C., Pasteris, J.D., & Chou, I.-M. (1993) American Journal of Science, 293, 297–321.**

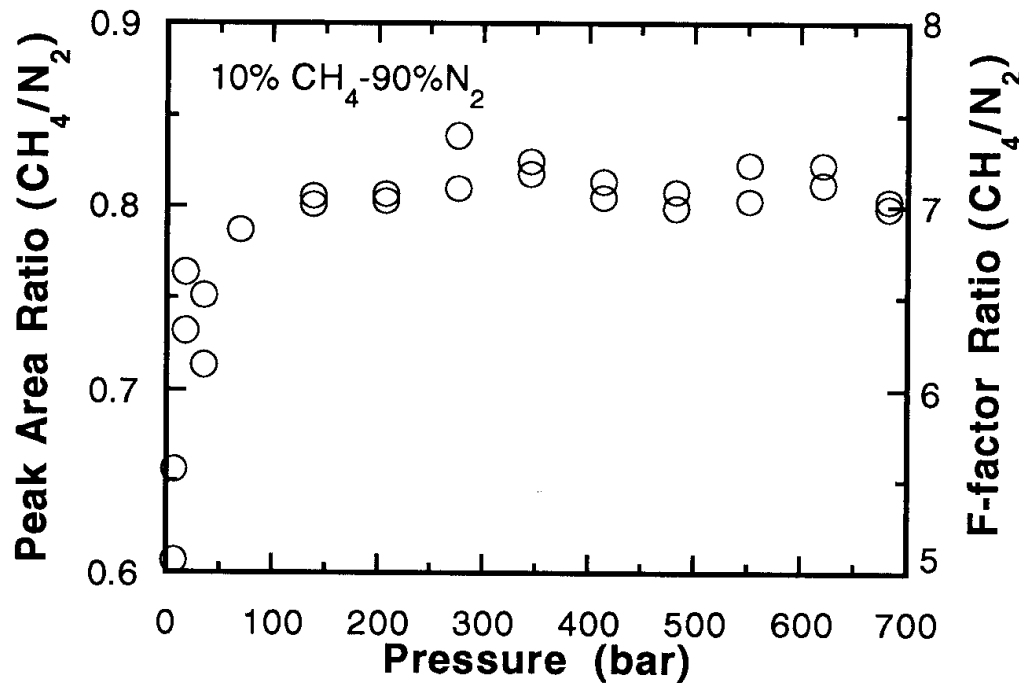
# Variation of RSCS with pressure

$$\Lambda(\overline{\nu_0}, \overline{\nu_j^m}) = \frac{n_s^{j,m} (n_s^{j,m} + 2)^2 (n_0^2 + 2)^2}{81n_0}$$

$$\frac{d\sigma_L}{d\Omega}(\overline{\nu_0}, \overline{\nu_j^m}) = \Lambda(\overline{\nu_0}, \overline{\nu_j^m}) \times \frac{d\sigma_V}{d\Omega}(\overline{\nu_0}, \overline{\nu_j^m})$$

Internal field effect

$$\left[ \frac{\Lambda(\overline{\nu_0}, \overline{\nu_j^m})}{\Lambda(\overline{\nu_0}, \overline{\nu_Q^{N_2}})} \right] \approx 1$$



**Seitz, J.C., Pasteris, J.D., & Chou, I.-M. (1993) American Journal of Science, 293, 297–321.**

Fig. 9. Plot of data for 10 percent CH<sub>4</sub> (90 percent N<sub>2</sub>) mixture; left vertical scale indicates raw peak area ratio (CH<sub>4</sub>/N<sub>2</sub>), and right vertical scale indicates F-factor ratio (CH<sub>4</sub>/N<sub>2</sub>) for the same data. F-factor ratio, related to peak areas, was calculated using eq (3) (see text).