

# Raman transitions and Raman spectroscopy in atoms and molecules

Atomic and Molecular Physics

Aline Sanches Perez

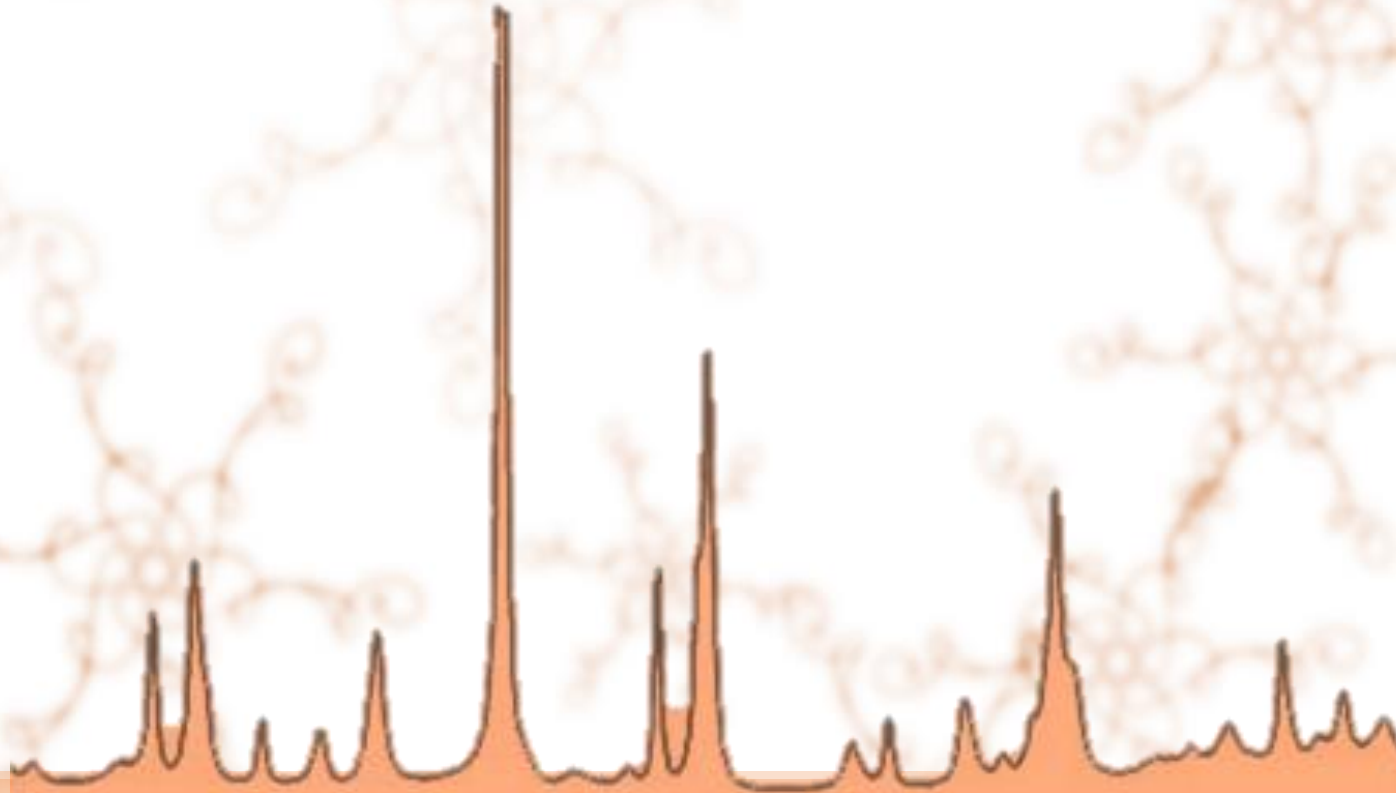
Prof. Philippe W. Courteille

Instituto de Física de São Carlos - USP

2021

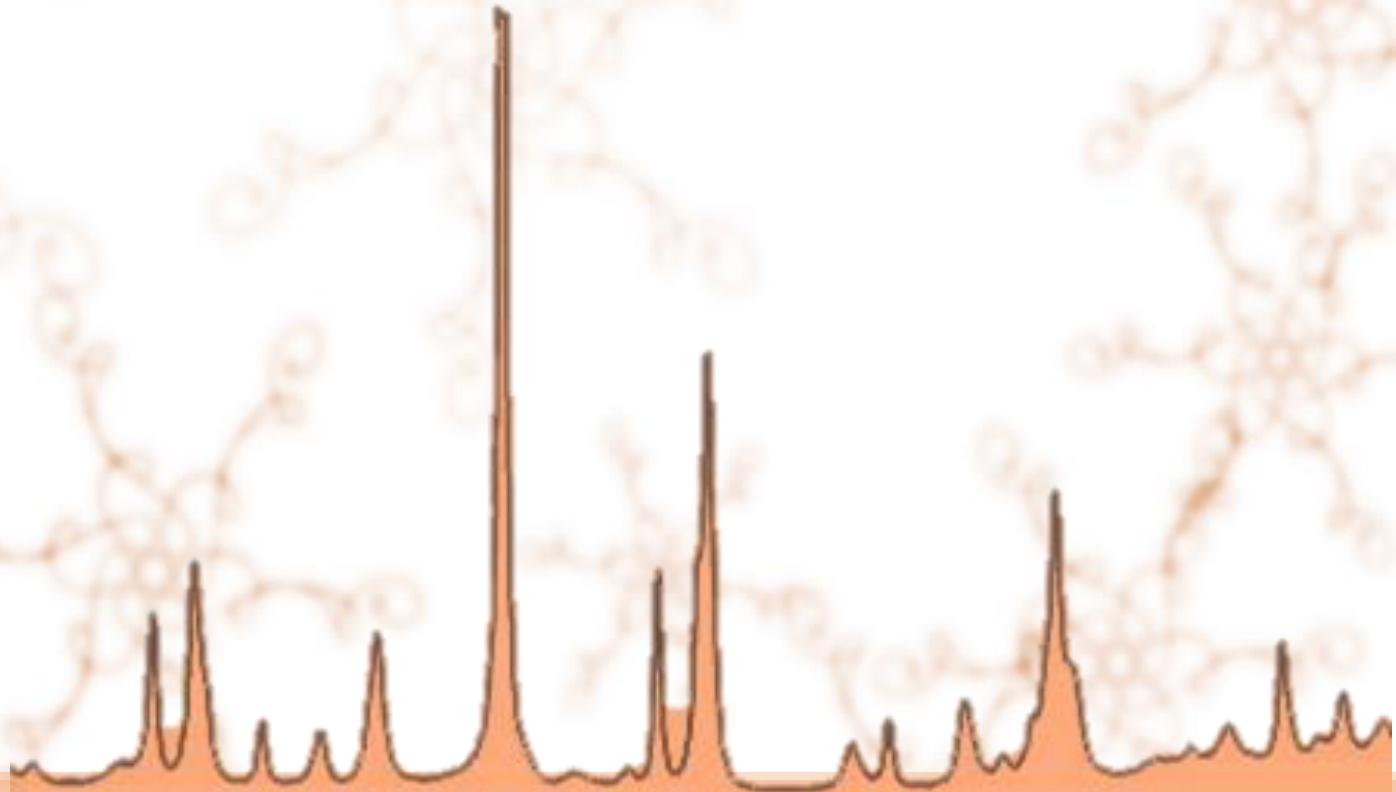
# Outline

- Contextualization
- Raman scattering theory
- Molecular Polarizability
- Energy transfer model
- Raman Spectroscopy
- Applications
- Conclusion



# Objective

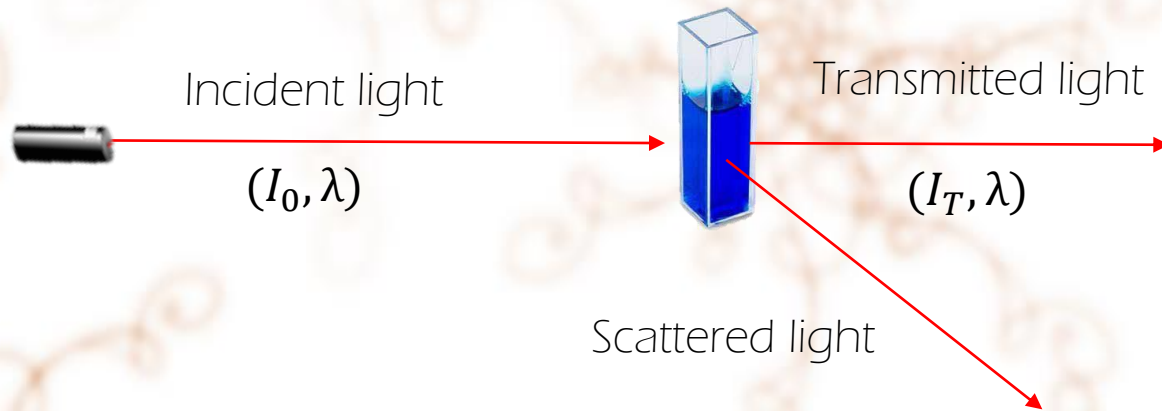
Discuss the basic aspects which support the Raman effect theory and present two distinct application to Raman spectroscopy





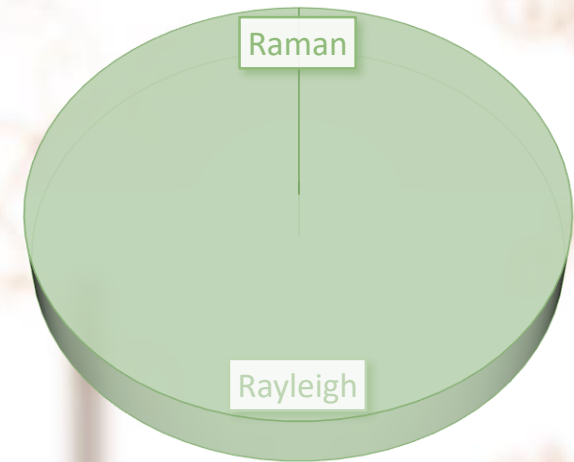
# Contextualization

## Light-matter interaction



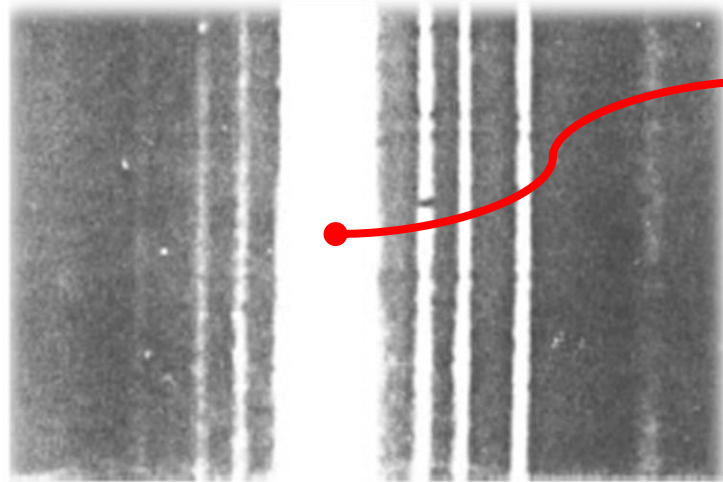
$(I_S, \lambda)$ : Rayleigh Scattering

$(I_S, \lambda')$ : Raman/Brillouin Scattering

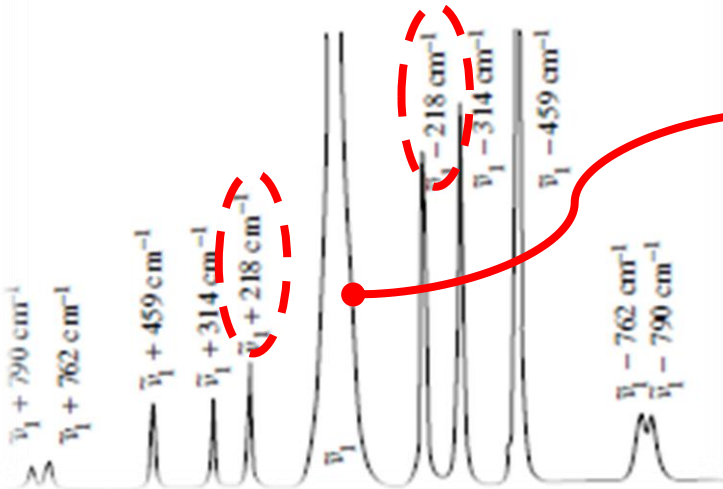


# Contextualization

Espectro: Tetracloreto  
de Carbono



Rayleigh Scattering (XIX)



435,83 nm - Lâmpada de  
Mercúrio (região do azul)

This spectra is facsimiles of spectra reported by Raman and Krishnan (1929) and were photographically recorded

# Contextualization

502

NATURE

[MARCH 31, 1928

shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation *in vacuo*) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the

Atlantic the salmon generally leaves such colonisation to the trout, and itself forms fresh-water colonies only in exceptional circumstances, either in very large lakes with abundance of fishes, or in rivers or lakes with such quantities of parr-food that it is tempted to prolong the parr life. In America, when there are no trout, the salmon form fresh-water colonies more readily.

C. TATE REGAN.

British Museum (Natural History),  
S.W.7, Mar. 17.

## Anomalous Groups in the Periodic System of Elements.

In a paper which will shortly appear in the *Rend. Accad. Lincei*, I have calculated the distribution of the electrons in a heavy atom. The electrons were considered as forming an atmosphere of *completely degenerated* gas held in proximity to the nucleus by the attraction of the nuclear charge screened by the electrons. Formulae were given for the density of the electrons and the potential as functions of the distance  $r$  from the nucleus.

In continuation of the previous work, I have applied the same method to the study of the formation of anomalous groups in the periodic system of elements. From the densities of the electrons and

demonstrable.

210 Bowbazar Street,  
Calcutta, India,  
Feb. 16.

C. V. RAMAN.  
K. S. KRISHNAN.

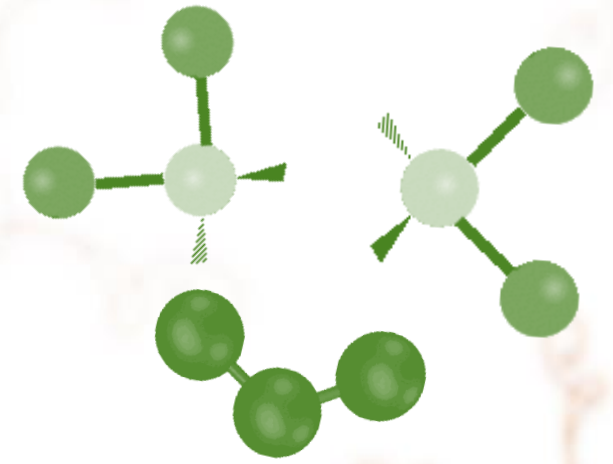
“Se assumirmos que o espalhamento de raios-X do tipo 'não modificado' observado pelo Prof. Compton corresponde ao estado normal ou médio dos átomos e moléculas, enquanto o espalhamento 'modificado' de comprimento de onda alterado corresponde às suas flutuações daquele estado, seguir-se-ia que deveríamos esperar também no caso da luz comum dois tipos de espalhamento, um determinado pelas propriedades ópticas normais dos átomos ou moléculas, e outro representando o efeito de suas flutuações em relação ao seu estado normal. Portanto, torna-se necessário testar se este é realmente o caso. (...)” – Tradução livre.



Nobel -1930



# Molecules



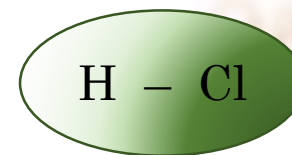
Molecules not only translate, but also vibrate and rotate.

Modes of vibration are mostly dependent on atomic/molecular composition and its temperature.

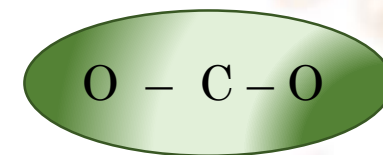
# Molecules

## Induced dipole moment and Resulting dipole moment

1. H – Cl (Hydrogen Chloride) is a linear, electronegatively unbalanced molecule, and therefore has a resulting dipole moment  $\neq 0$ .



2. O – C – O (Carbon Dioxide) is also linear, however it has a resulting dipole moment = 0.





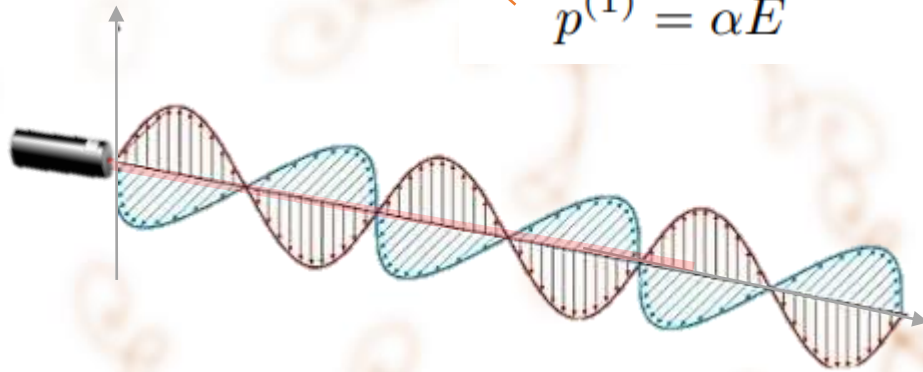
# Raman scattering theory

**Polarizability** usually refers to the tendency of matter, when subjected to an electric field, to acquire an electric dipole moment in proportion to that applied field.

Momento de dipolo induzido

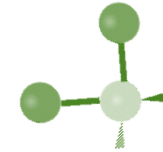
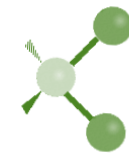
$$p^{(1)} = \alpha E$$

(3.1)



A - A

# Molecular polarizability



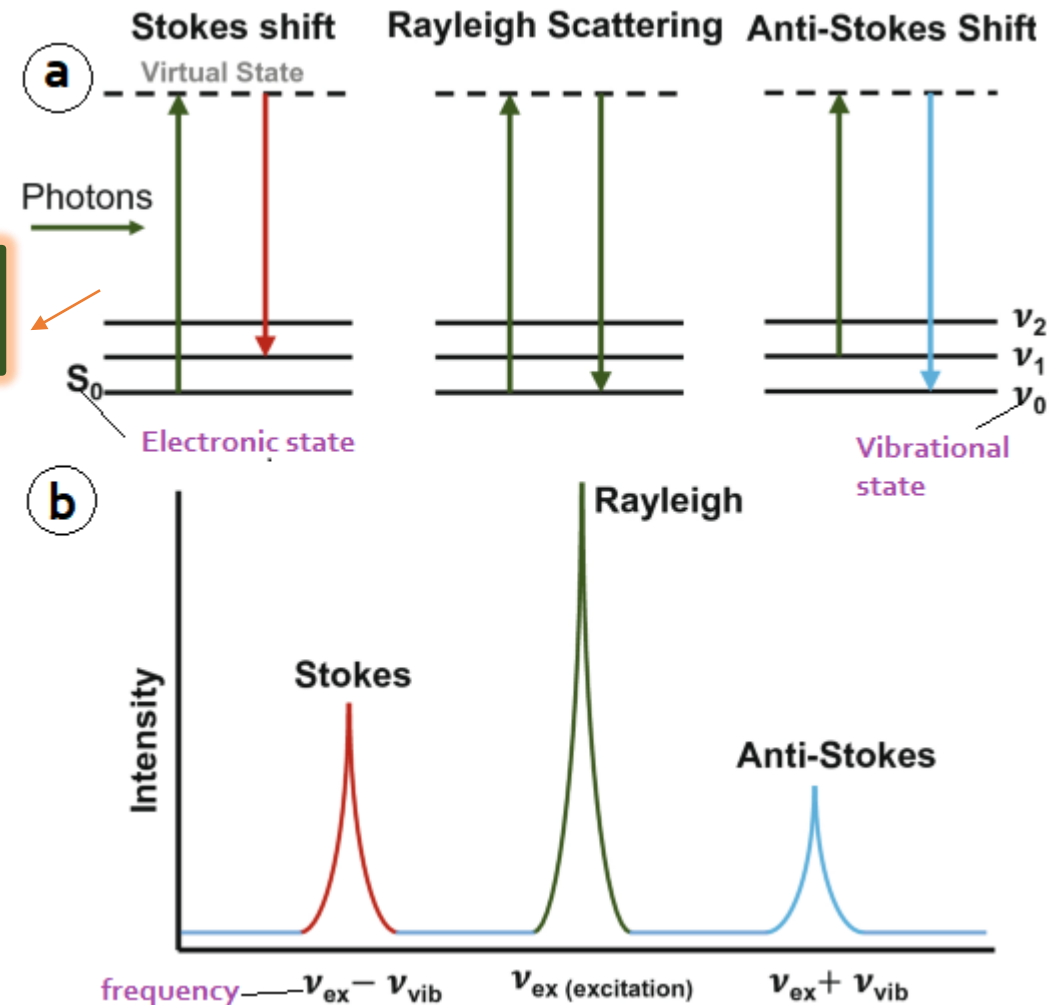
De-excitações de estados vibracionais/rotacionais

## Jablonsk Diagram

Rayleigh Scattering

Raman Scattering

Excitações de estados vibracionais/rotacionais



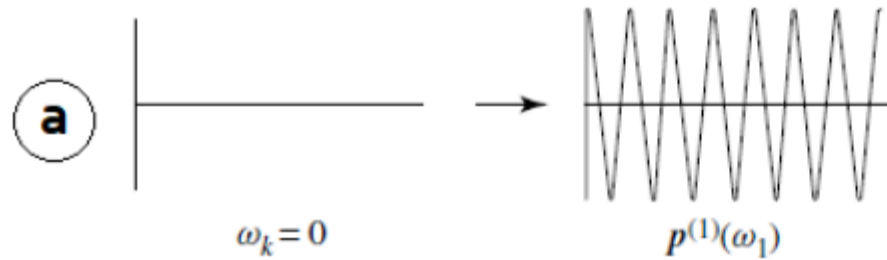
$$p^{(1)} = p^{(1)}(\omega_1) + p^{(1)}(\omega_1 - \omega_k) + p^{(1)}(\omega_1 + \omega_k) \quad (3.2)$$

$$(p^1)_{fi} = \langle \psi_f^{(1)} | \hat{p} | \psi_i^{(0)} \rangle + \langle \psi_f^{(0)} | \hat{p} | \psi_i^{(1)} \rangle \quad (3.6)$$

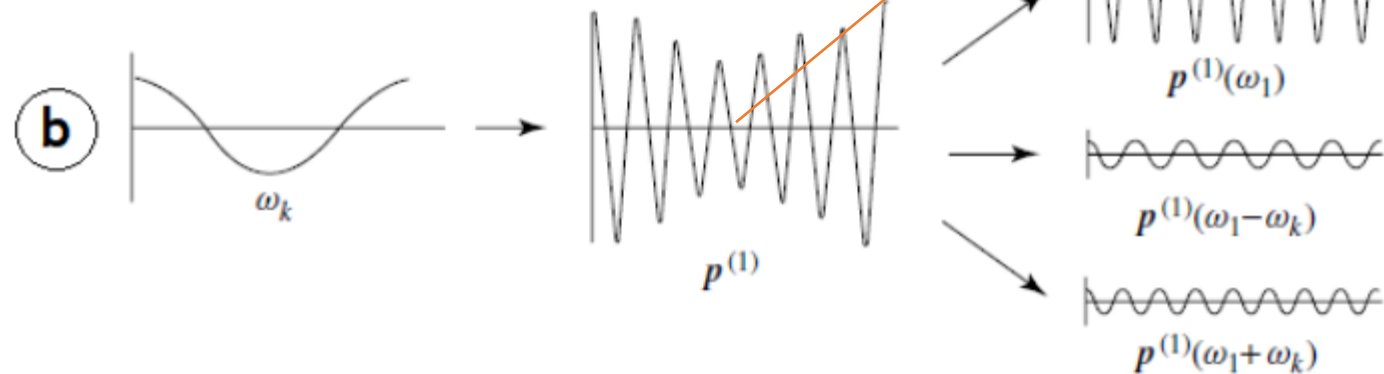
Electric dipole moment operator.

# Raman scattering theory

Linear induced dipoles  $p_1$



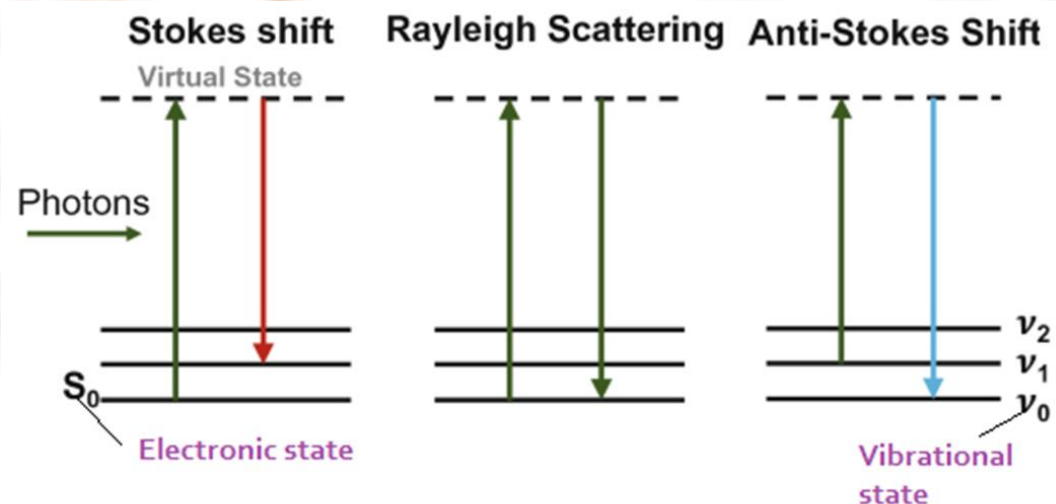
Time dependence of the linear induced dipoles  $p_1$  produced by electromagnetic radiation of frequency  $\omega_1$





# Energy Transfer Model

The incident photon is not absorbed, no conservation of energy in this stage of the process.



$$(\alpha_{\rho\sigma})_{e^f v^f R^f; e^g v^i R^i} = \langle R^f | l_{\rho\rho'} l_{\sigma\sigma'} | R^i \rangle \langle v^f | \langle e^f | \alpha_{\rho'\sigma'} \hat{\alpha}(e^r, v^r) | e^i \rangle | v^i \rangle \quad (3.3)$$

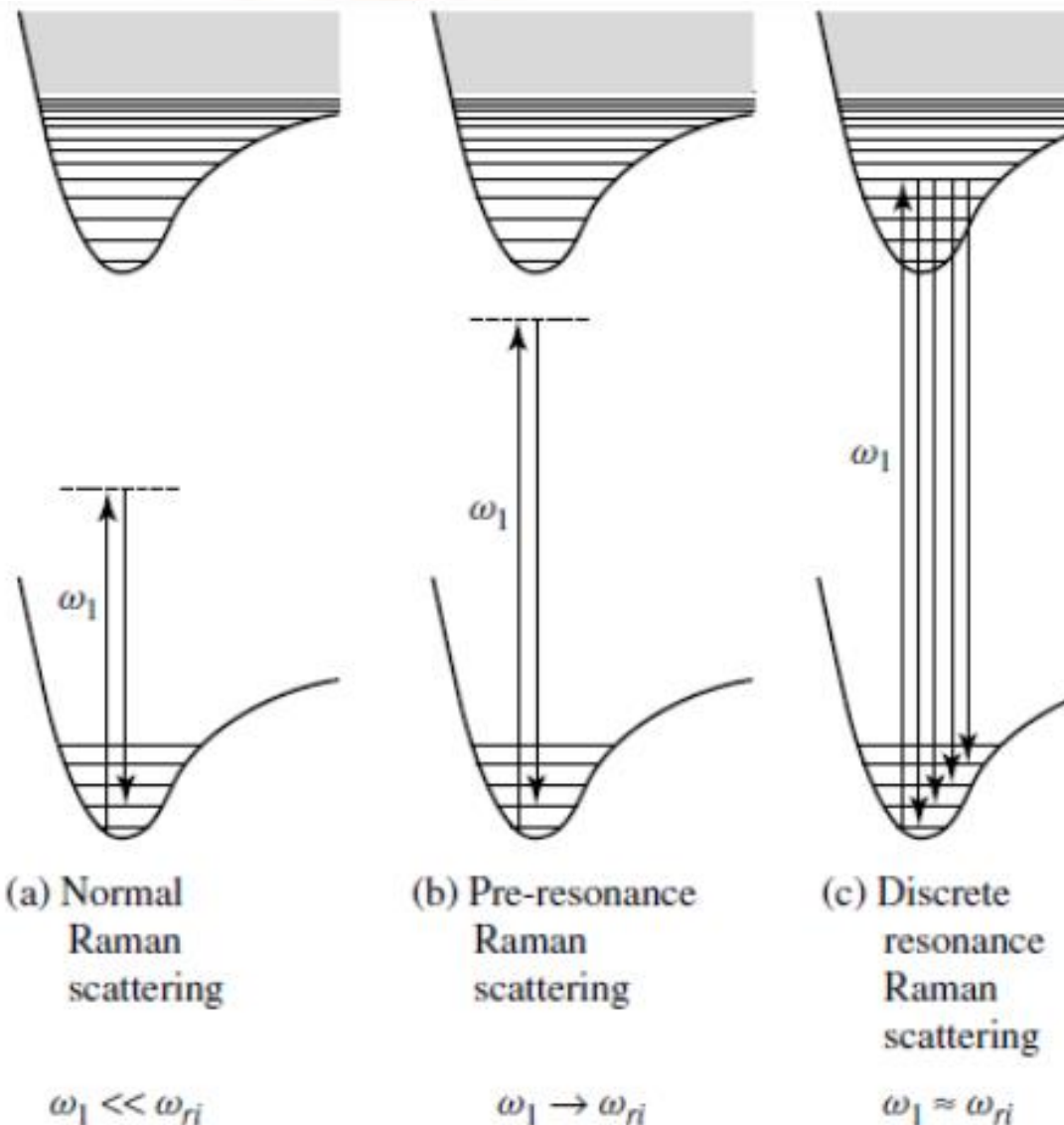
The role of the incident radiation is rather to perturb the molecule and open the possibility of spectroscopic transitions other than direct absorption.

# Raman Resonance

It is possible to amplify the Raman signal



$$(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar} \sum_{r \neq i,f} \left\{ \frac{\langle f | \hat{p}_\rho | r \rangle \langle r | \hat{p}_\sigma | i \rangle}{\omega_{ri} - \omega_1 - i\Gamma_r} + \frac{\langle f | \hat{p}_\sigma | r \rangle \langle r | \hat{p}_\rho | i \rangle}{\omega_{rf} + \omega_1 + i\Gamma_r} \right\}$$

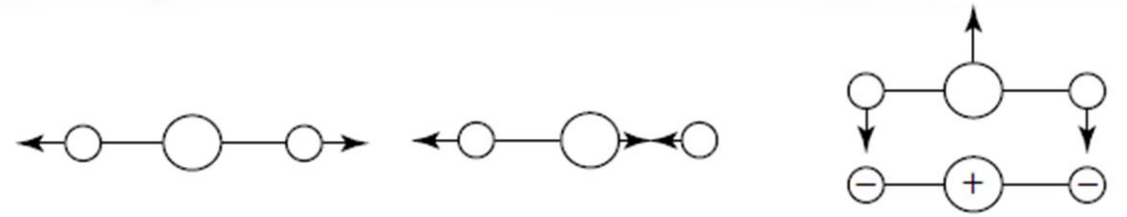


# Raman Activity

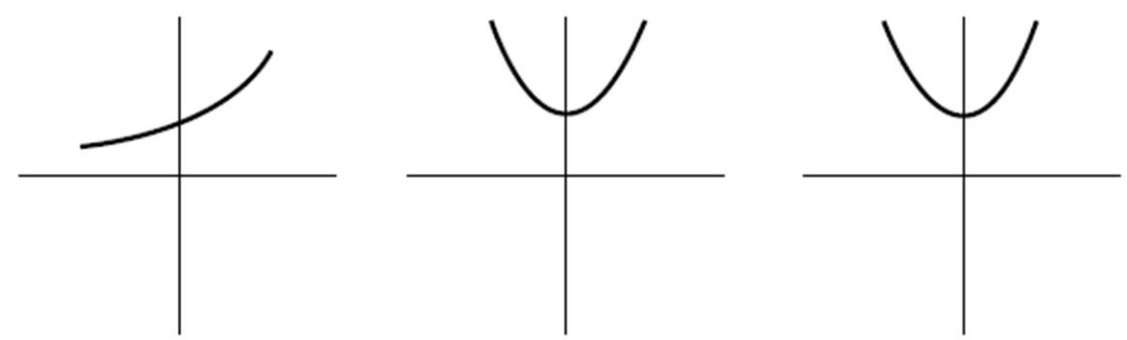
$$(\alpha_{\rho\sigma})_{e^f v^f R^f; e^g v^i R^i} = \langle R^f | l_{\rho\rho'} l_{\sigma\sigma'} | R^i \rangle \langle v^f | \langle e^f | \alpha_{\rho'\sigma'}(e^r, v^r) | e^i \rangle | v^i \rangle \quad (3.3)$$

Polarizability derivative at position equilibrium position

Mode of vibration



Variation of polarizability with normal coordinate (schematic)



Polarizability derivative at equilibrium position

≠ 0

= 0

= 0

Raman activity

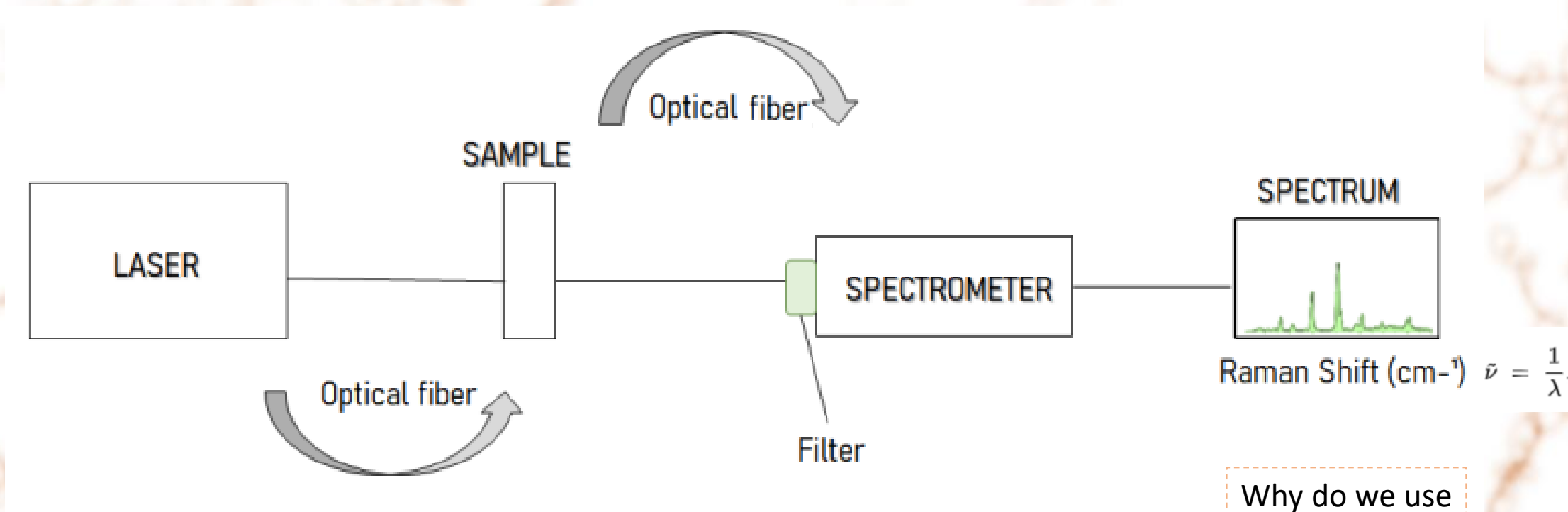
Yes

No

No



# Raman Spectroscopy



Why do we use wavenumber ?

$$\Delta E \sim \frac{1}{cm}$$

# Application: Carbon nanotubes



Respiração Radial (entre 100 e 400  $\text{cm}^{-1}$ )



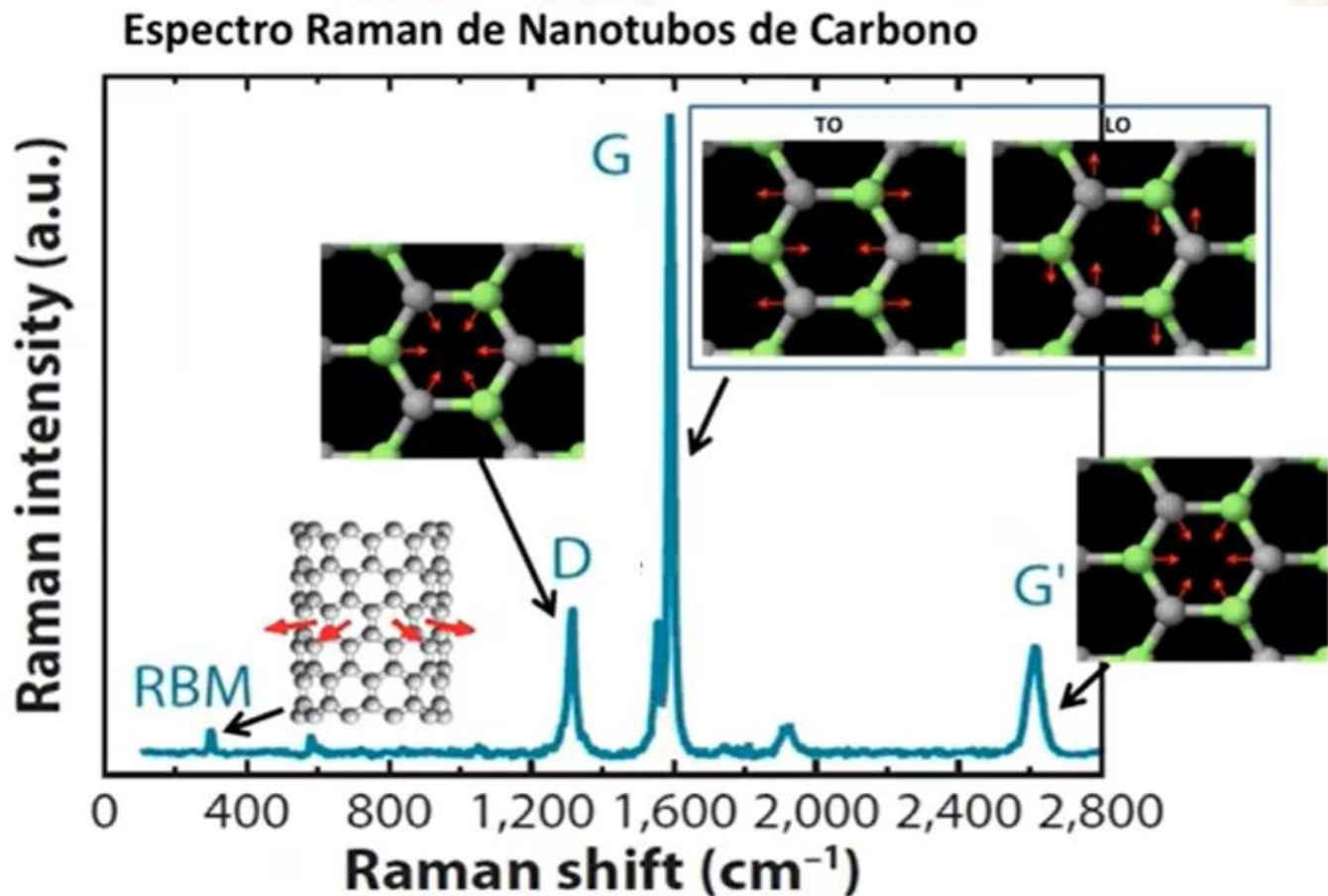
Modo de vibração: banda D  
“Defeitos”



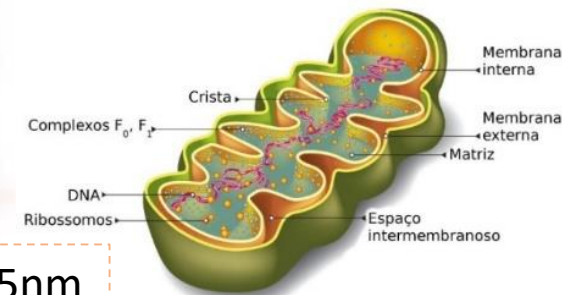
Modo de vibração: banda G



Modo de vibração: banda G'  
Segundo harmônico



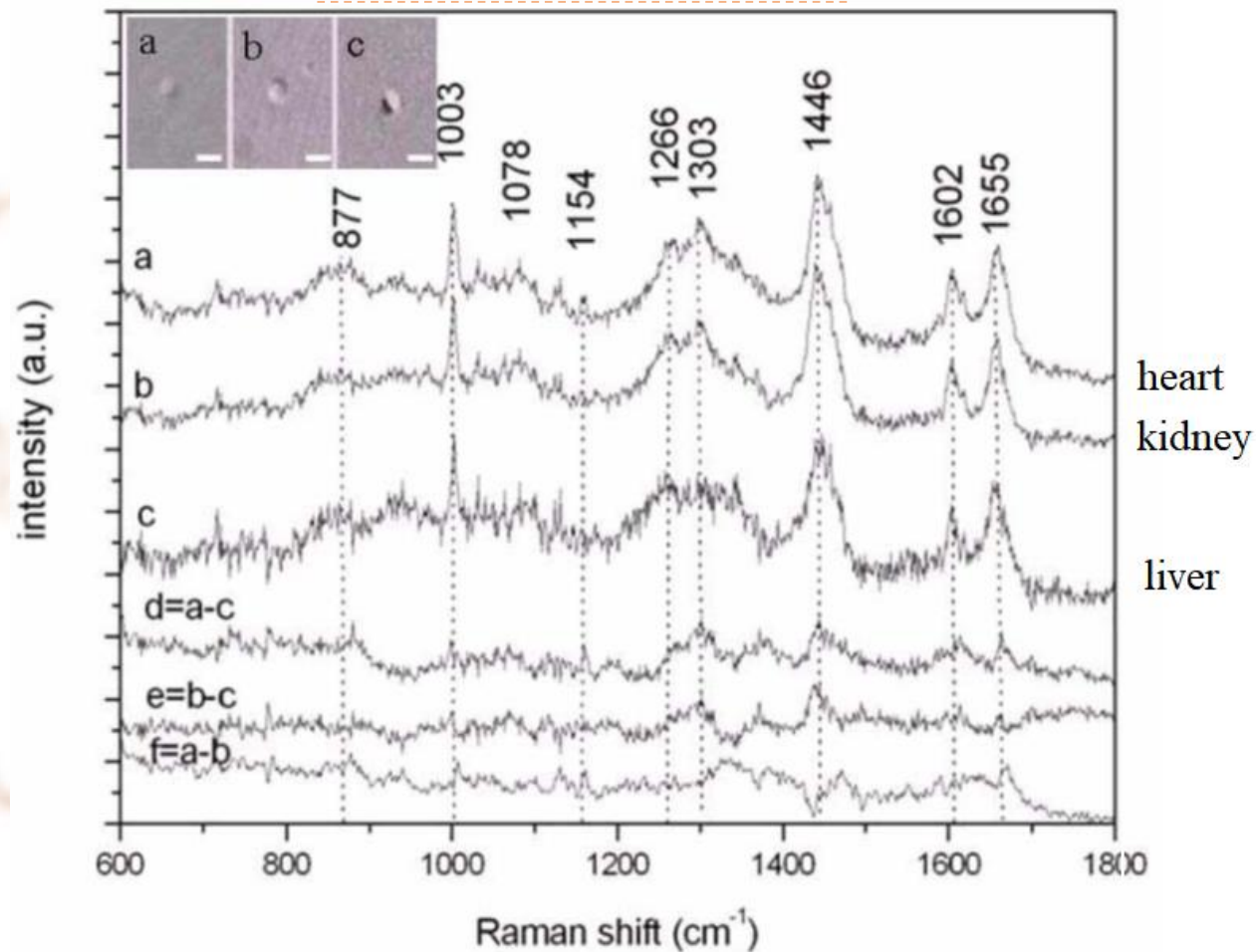
# Application: Mitochondria



Raman spectra at 785nm

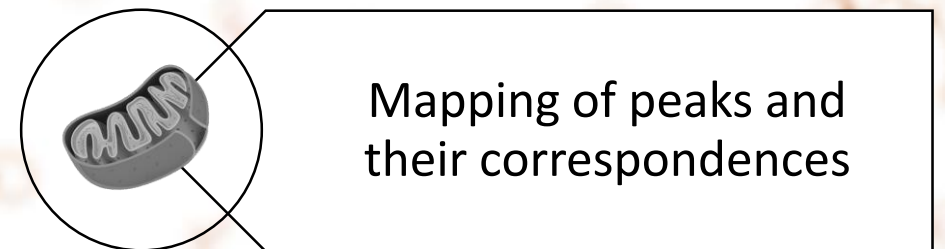
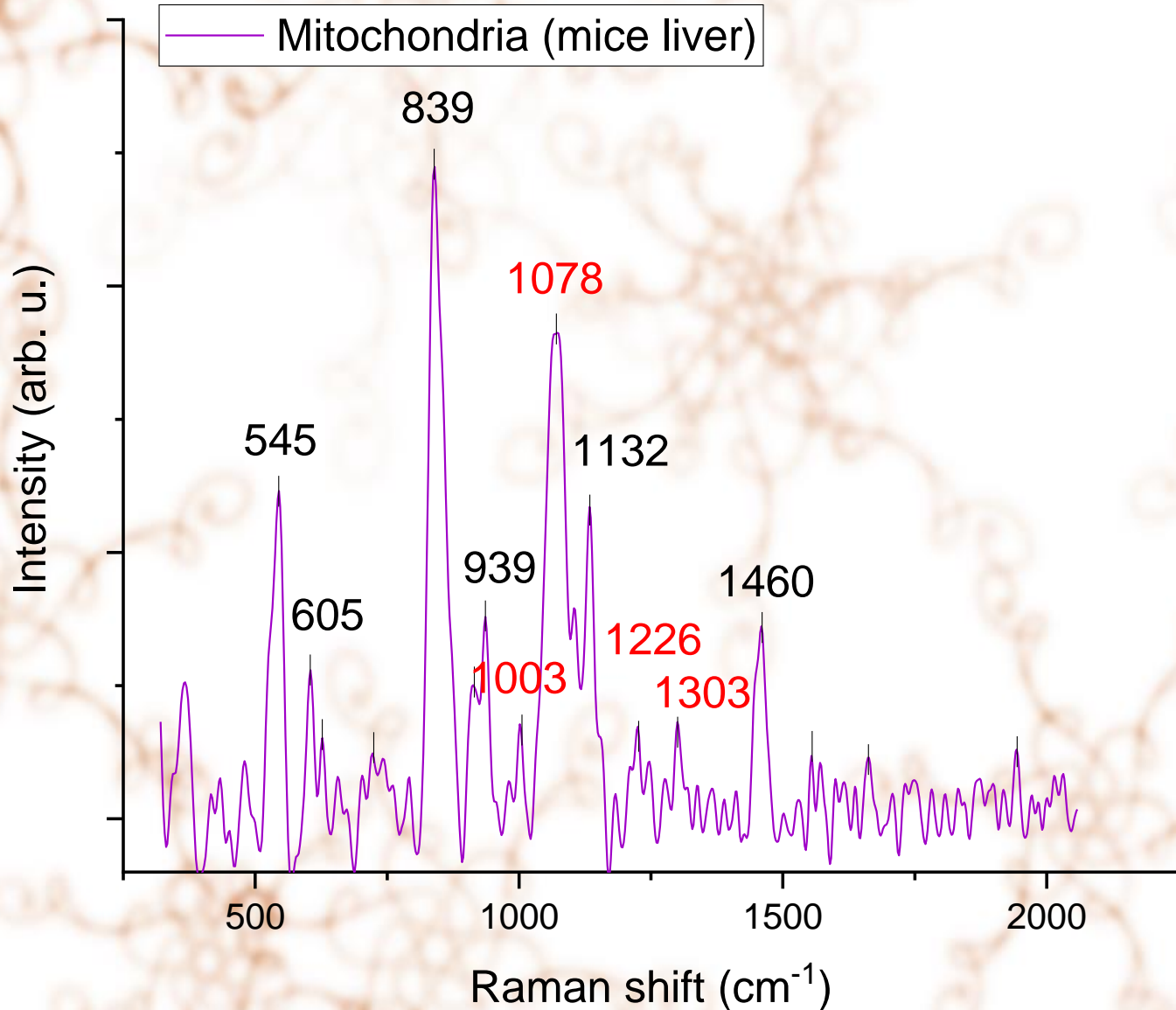
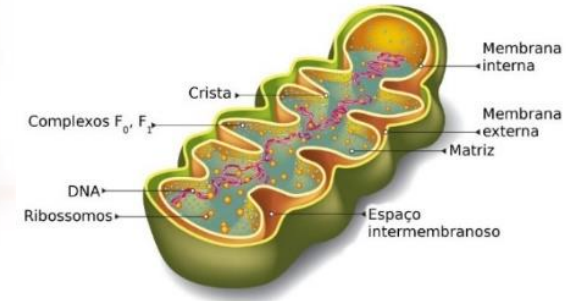
Table 1. Raman bands for mitochondrial (averaged over 30 mitochondria) and their tentative assignments.

Bands ( $\text{cm}^{-1}$ )	Assigned to
721	Adenine (C-C, ring mode)
1003	Ring breathing mode breathing mode of phenylalanine
1266	Amide III
1303	Amide/DNA:O-P-O- and CH <sub>2</sub> deformation (lipid)
1437-1443	CH <sub>2</sub> deformation (lipids and proteins)
1446	CH <sub>2</sub> bending modes and CH <sub>3</sub> deformation of lipids and proteins
1602	Tyrosine/Phe/Tryptophan
1655	Amide I





# Application: Mitochondria



# Conclusão

O ER rapidamente se tornou uma importante ferramenta para estudos de estados rotacionais-vibracionais

Importante técnica de caracterização estrutural

Caracterização de Materiais

São dados relativamente rápidos de serem obtidos, mas de difícil análise

# Referências

**Derek A. Long - The Raman Effect A Unified Treatment of the Theory of Raman Scattering by Molecules.**

Strommen, D. P. In *The Handbook of Instrumental Techniques for Analytical Chemistry*; Settle, F. A., Ed.; Prentice Hall, PTR: Upper Saddle River, NJ, 1997; p 994.

Carey, P. R. *J. Raman Spectrosc.* 1998, 29, 861–868.

Raman, Chandrasekhara Venkata, and Kariamanikkam Srinivasa Krishnan. "A new type of secondary radiation." *Nature* 121.3048 (1928): 501-502.



*Thank you!*



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