

# Raman spektroszkópia

Történet

Két leírás: Eldines, kvantum

Kiválasztási szabályok

Szimmetriák

Raman Intenzitás

Rezonáns Raman

Speciális Raman esetek

elektronikus

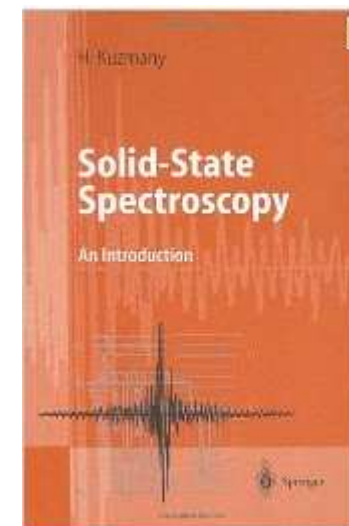
SERS, tip. enh.

ROA

near-field

Kísérleti megvalósítás

Források: Wikipedia, Hans Kuzmany: Solid-State Spectroscopy: An Introduction



**A New Type of Secondary Radiation.**

IF we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and

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Feb. 16.

Raman: legalacsonyabb rendű, jelentős energiaátadással járó inelasztikus fényszórás

Egyéb folyamatok: Rayleigh, Brillouin, Compton, lumineszcencia

# Inelasztikus fényszórás

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 R^2} (1 + \cos^2 \theta)$$

Rayleigh:

Brillouin: kis momentum transzfer, akusztikus fononokon

Compton: röntgenre erős, jelentős impulzusátadás

Lumineszcencia: fény abszorpció, emisszió. Gerjesztésben rezonáns, erős

Raman: szórt fény „emlékezik” elődjére, polarizációt részlegesen megtartja, gyenge folyamat

oszálldó elektromos tér  
+  
rezgés (frekvencia) anyagban

$$\underline{E} = \underline{E}_0 (e^{i\omega t} + e^{-i\omega t}) \quad (\text{dipól közt. helyfűggést elanyagoljuk})$$

$$H = H_0 + H'(t) \text{ ahol } H(t) = -e \underline{E} \cdot \underline{r}$$

dipól matrix elem  $\langle f | \underline{u} \cdot \underline{r} | i \rangle$  IR átmenet ha

$\underline{u} \parallel \underline{E}$  egyező vektor  $\uparrow \hbar\omega = \hbar\nu$

fény energiája éppen a rezgési állapot energiájával egyező.

Közelem: adott molekulán indukált dipól momentum

$$\underline{p}_D(\omega) = \alpha_0 \underline{E}(\omega)$$

polarizálhatóság

$$\left( \text{megvan } \underline{P} = \epsilon_0 \chi \underline{E} \right)$$

kezőtt

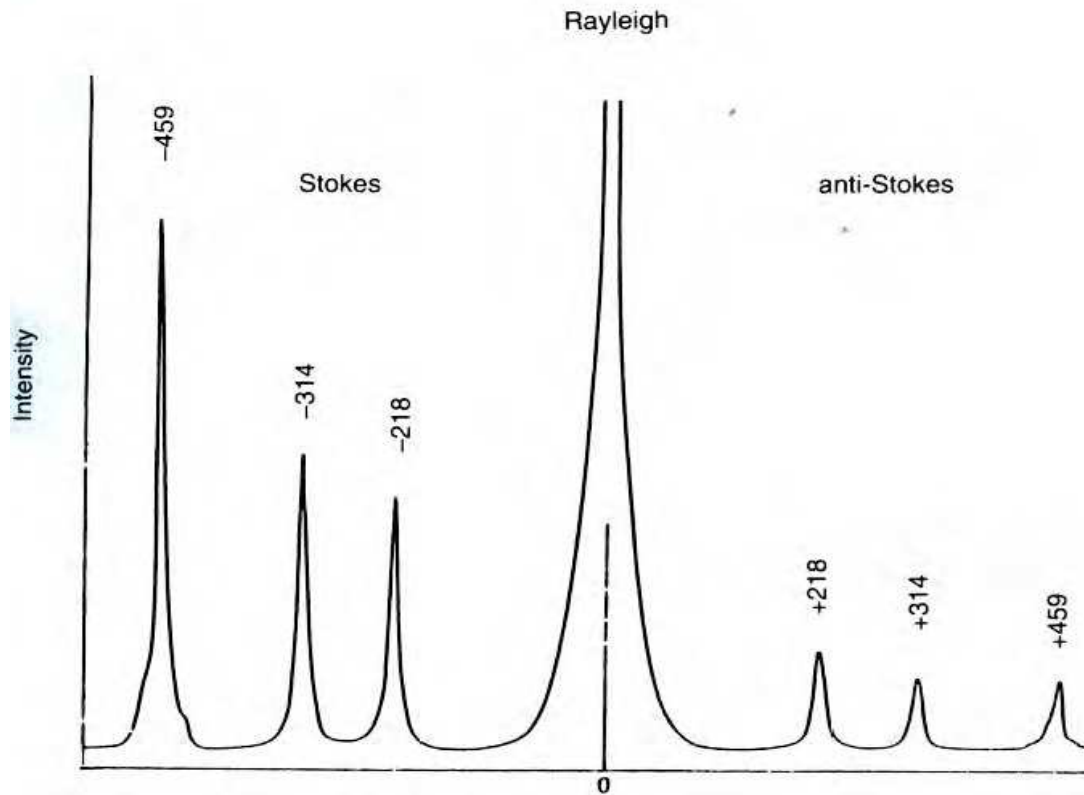
ha  $\alpha$  függ molekulán rezgéseitől:  $\alpha = \alpha_0 + \alpha_1 \cos \nu t$ ;  $\nu$ : rezgés frekvencia

$$\rightarrow \underline{p}_D(\omega) = (\alpha_0 + \alpha_1 \cos \nu t) \underline{E}_0 \cos \omega t$$

$$\underline{p}_D(\omega) = \alpha_0 \underline{E}_0 \cos \omega t + \alpha_1 \frac{\underline{E}_0}{2} \left[ \cos(\omega + \nu)t + \cos(\omega - \nu)t \right]$$

Anti-Stokes Stokes

Kristályok:  $\alpha$  polarizálhatóság helyett,  $\chi$  susceptibilitás.



Raman shift:  
 Pozitív Stokes-ra

$$\Delta\nu = \frac{1}{\lambda_{scattered}} - \frac{1}{\lambda_{excitation}}$$

Rezgések jellemzése:

Azonos atomokra:  
 Raman erős! (CNT)

molecule					
vibration					
change of $\alpha$ with Q					
$\frac{d\alpha}{dQ}$	$\neq 0$	$\neq 0$	$\neq 0$	$= 0$	$= 0$
Raman active	yes	yes	yes	no	no
change of $\vec{P}_D$ with Q					
$\frac{d\vec{P}_D}{dQ}$	$= 0$	$\neq 0$	$= 0$	$\neq 0$	$\neq 0$
infrared active	no	yes	no	yes	yes

# Általános klasszikus leírás: a Raman tenzor

Molekulára: polarizálhatóság

$$\alpha_{ij} = (\alpha_{ij})_0 + \frac{\partial \alpha_{ij}}{\partial Q_k} Q_k + \frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_k} Q_k^2 + \dots$$

Szilárd testre: szuszceptibilitás

$$\chi_{jl} = (\chi_{jl})_0 + \sum_k \left( \frac{\partial \chi_{jl}}{\partial Q_k} \right)_0 Q_k + \sum_{k,m} \left( \frac{\partial^2 \chi_{jl}}{\partial Q_k \partial Q_m} \right)_0 Q_k Q_m + \dots$$

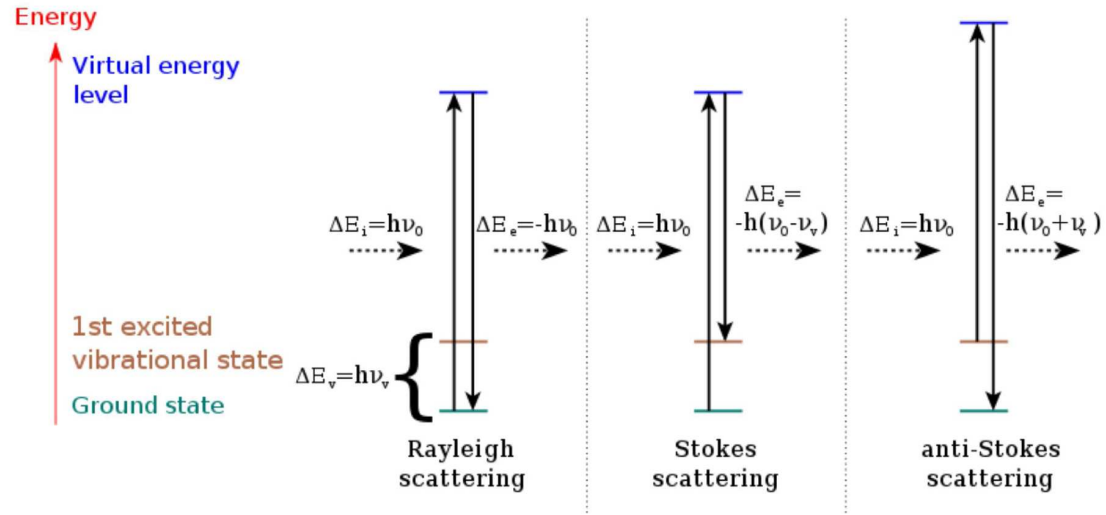
Harmonikus közelítésben csak lineáris tagig kell.

Neve: Raman tenzor, polarizáció és kristály (molekula függő)

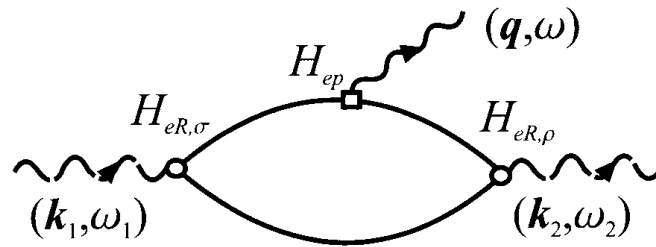
Rezgési módusok száma: normál koordináták szerinti kifejtésből, csoportelmélettel

Raman intenzitás:  $I(\omega) \sim \omega^4$        $I(\alpha) \sim \alpha^2$        $I(n) \sim n$        $I(\vec{E}) \sim \vec{E}^2$

# Kvantumos leírás:



# Feynman diagram: (1 ph. Stokes)



$$\sum_{i,f} \frac{\langle \omega_2, f | H_{er} | 0, f \rangle \langle 0, f' | H_{ep} | 0, i \rangle \langle 0, i | H_{er} | \omega_1, 0 \rangle}{(E_1 - E_i - i\gamma\hbar)(E_2 - E_f - i\gamma\hbar)}$$

# A Raman intenzitás:

$$\sigma(\omega_1) \propto \left| \int \frac{M_f M_{ph} M_0 g_{jds}(\epsilon) d\epsilon}{(\hbar\omega_1 - \epsilon - i\hbar\gamma)(\hbar\omega_2 - \epsilon - i\hbar\gamma)} \right|^2 \approx$$

$$|M|^2 \left| \int \frac{g_{jds}(\epsilon) d\epsilon}{(\hbar\omega_1 - \epsilon - i\hbar\alpha)(\hbar\omega_2 - \epsilon - i\hbar\alpha)} \right|^2$$

vibrational part is evaluated explicitly. The optical transitions are treated phenomenologically in a way similar to Sect. 7.4 for optical absorption.

To discuss the inelastic scattering processes shown in Fig. 9.11 we must evaluate the matrix element for the transition between state  $i$  and  $f$ . For the scattering process the transitions are driven by the polarization induced by the light  $\mathbf{P} = \chi \epsilon_0 \mathbf{E}$ . The matrix element has therefore the form

$$\mathbf{P}_{fi} = \langle f | \mathbf{P} | i \rangle = \langle f | \epsilon_0 \chi \mathbf{E} | i \rangle. \quad (9.22)$$

Since  $|f\rangle$  and  $|i\rangle$  are generalized wave functions the integration runs over all electronic and nuclear coordinates. If the wavelength of the light is much larger than the interatomic distances the electric field can be considered to be constant in (9.22) so that we can extract from the equation a generalised form of the susceptibility known as the *transition susceptibility*

$$[\chi_{mn}]_k = \langle f | \chi_{mn} | i \rangle. \quad (9.23)$$

$[\chi_{mn}]_k$  is a material-specific quantity determined by the electronic orbitals in the crystal. If the final and initial states are both the ground state, it turns into the susceptibility as we have discussed it so far. The situation for Raman scattering is different. We proceed similarly as in Sect. 7.4 by applying the adiabatic approximation (7.23):

$$[\chi_{mn}]_k = \int \psi_f^*(X) \varphi_f^*(x, X) \chi_{mn} \varphi_i(x, X) \psi_i(X) dx dX. \quad (9.24)$$

First we consider the integration over the electron coordinates  $x$ . Assuming that the final and the initial electronic states are the same renders for this integral the electronic part  $\chi_{mn}(X)$  of the transition susceptibility. In contrast to Sect. 7.4 we did not apply the Condon approximation. This means the susceptibility still depends on the nuclear coordinates  $X$ . If we introduce normal coordinates  $Q_k$ , we can expand the electronic part of the susceptibility with respect to the normal coordinates. Considering only the linear term of the expansion and extracting the expansion coefficient from the integral we obtain

$$[\chi_{mn}]_k = \langle \chi_{mn} \rangle_0 \langle \dots v_{ik} \dots \dots v_{fk} \dots \rangle + \sum_k \left( \frac{\partial \chi_{mn}}{\partial Q_k} \right)_0 \langle \dots v_{ik} \dots | Q_k | \dots v_{fk} \dots \rangle. \quad (9.25)$$

The bra and ket symbols represent total vibrational wave functions from the integral in (9.24). They are expressed as the product of harmonic-oscillator wave functions with the occupation numbers  $v_{ik}$  or  $v_{fk}$ .

$$\begin{aligned} \langle v_{i1}, \dots, v_{ik}, \dots, v_{in} | &= \prod_k \langle v_{ik} | \\ \langle v_{f1}, \dots, v_{fk}, \dots, v_{fn} | &= \prod_k \langle v_{fk} |, \end{aligned} \quad (9.26)$$

where  $\langle v_{ik} |$  and  $\langle v_{fk} |$  are the harmonic-oscillator wave function for occupation numbers  $v_{ik}$  and  $v_{fk}$ , respectively, as given in Appendix F.4. Since we do not use the Franck-Condon principle the oscillators are unshifted and the expectation values in (9.24) are

$$\langle v_{ik} | v_{fk} \rangle = \begin{cases} 0 & \text{for } v_{ik} \neq v_{fk} \\ 1 & \text{for } v_{ik} = v_{fk} \end{cases} \quad (9.27)$$

and

$$\langle v_{fk} | Q_k | v_{ik} \rangle = \begin{cases} 0 & \text{for } v_{fk} = v_{ik} \\ (v_{ik} + 1)^{1/2} \sqrt{\hbar/2\Omega_k} & \text{for } v_{fk} = v_{ik} + 1 \\ (v_{ik})^{1/2} \sqrt{\hbar/2\Omega_k} & \text{for } v_{fk} = v_{ik} - 1. \end{cases} \quad (9.28)$$

Because of the orthogonality of the wave functions all expectation values from (9.25) can be factorized into relationships like (9.27) and (9.28). Then, the first term in (9.25) is only different from zero if  $v_{fk} = v_{ik}$  for all  $k$ . This means, the quantum state of the system has not changed. If  $\langle \chi_{mn} \rangle_0$  is properly calculated it describes the process of absorption or Rayleigh scattering. The second term is responsible for the Raman process which is evident from the appearance of the derived susceptibility. According to (9.27) and (9.28) it is only nonzero if for all  $k' \neq k$   $v_{fk'} = v_{ik'}$  and for the mode  $k$   $v_{fk} = v_{ik} \pm 1$  holds. In this case the transition susceptibility (9.25) has the form

$$[\chi_{mn}]_{v_{ik}+1, v_{fk}} = (v_{ik} + 1)^{1/2} \sqrt{\hbar/2\Omega_k} \left( \frac{\partial \chi_{mn}}{\partial Q_k} \right)_0 \quad (9.29)$$

and

$$[\chi_{mn}]_{v_{ik}-1, v_{fk}} = (v_{ik})^{1/2} \sqrt{\hbar/2\Omega_k} \left( \frac{\partial \chi_{mn}}{\partial Q_k} \right)_0. \quad (9.30)$$

Equation (9.29) and (9.30) obviously describe the Stokes and the antiStokes Raman processes. From a comparison with (9.8) for the classical evaluation of the Raman intensity the equivalence between the tensor for the transition susceptibility and the derived susceptibility multiplied with the amplitude of the normal coordinate is evident. In the quantum-mechanical calculation the amplitude of the latter is replaced by its quantum-mechanical equivalent  $\sqrt{\hbar v_k/2\Omega_k}$ . We have dropped here the index  $i$ , for simplicity, and will do this also in the following equations.

For a comparison with the experimental results attention must be paid to the dependence of the intensities on the vibronic occupation number  $v_k$ . Since the latter is determined by a Boltzmann factor

$$W(\epsilon_k) = \frac{\exp(-\epsilon_k/k_B T)}{Z} = \frac{\exp[-\hbar\Omega_k(v_k + 1/2)/k_B T]}{\sum_{v_k} \exp[-\hbar\Omega_k(v_k + 1/2)/k_B T]}, \quad (9.31)$$

a thermal averaging of the form

$$\sum_{v_k} (v_k + 1) W(\epsilon_k)$$

is required to obtain the effective square of the Raman tensor from (9.29) and (9.30). This is similar to the thermal averaging used for the evaluation of the optical absorption from localized wave functions (7.34).

In the case of Stokes scattering the average is  $n_k + 1$  where  $n_k$  is given by the Bose-Einstein distribution for the mode  $k$

$$n_k = f_E(\Omega_k) = \frac{1}{\exp(\hbar\Omega_k/k_B T) - 1}. \quad (9.32)$$

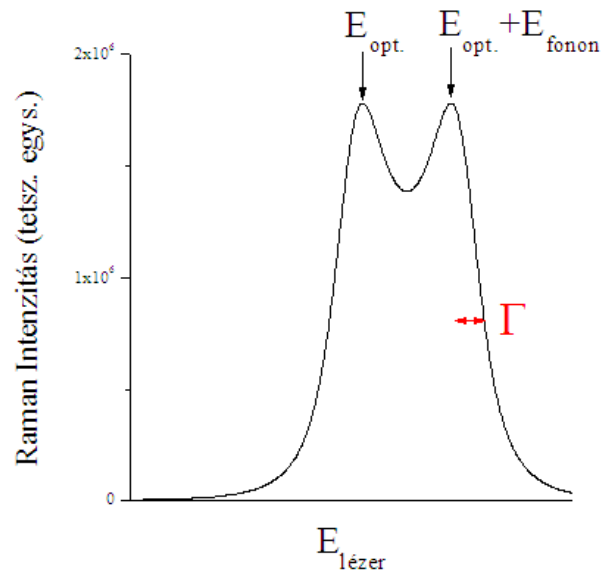
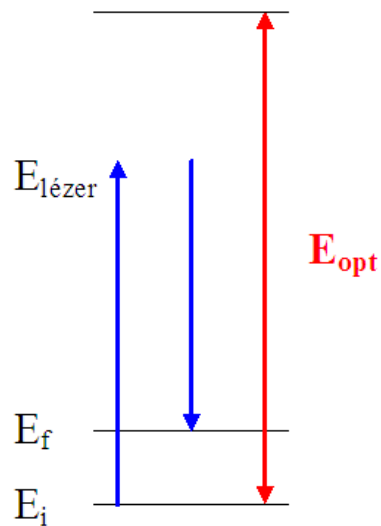
For antiStokes scattering the average yields  $n_k$ . Thus, the scattering intensity per steradian is derived from (9.13) for the incident intensity  $I_i$  by replacing  $Q_{k0}^2$  with the square of the quantum-mechanical amplitude  $\hbar v_k/2\Omega_k$  and the factor for thermal averaging  $(n_k + 1)$ .

$$\frac{d^{||} \Phi_{\perp}}{d\Omega} = \frac{\hbar(\omega - \Omega_k)^4 \mathcal{V}_0 \chi_{yz, k}^2 (n_k + 1) I_i \mathcal{V}}{32\pi^2 \epsilon_0^4 \Omega_k}. \quad (9.33)$$

A corresponding relation is obtained for antiStokes scattering.

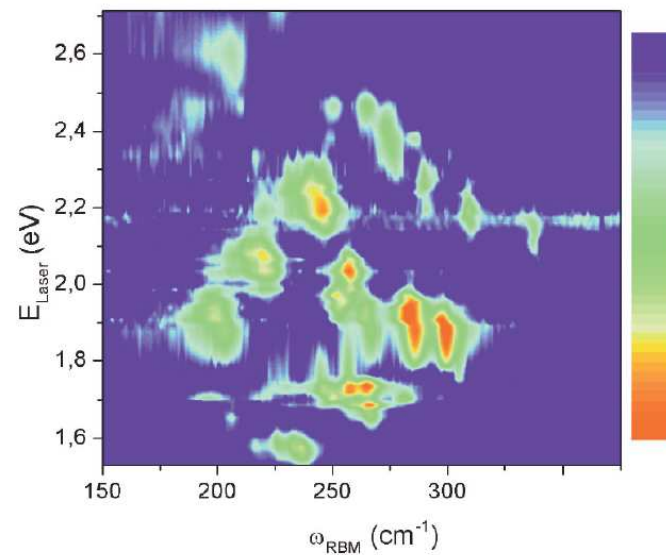


# Rezonáns Raman



$$I(E_{\text{lézer}}) \propto M_{\text{eff}}^4 \left| \frac{(E_{\text{lézer}} - E_{\text{fonon}})^2}{(E_{\text{lézer}} - E_{\text{ii}} - i\Gamma)(E_{\text{lézer}} - E_{\text{fonon}} - E_{\text{ii}} - i\Gamma)} \right|^2 \propto \frac{1}{\Gamma^4}$$

„Raman térkép”  
*Fantini et al. PRL 2004*



Speciális Raman esetek I.:  
Elektronikus

Pl. plazmon, magnon, Cooper pár

$$\omega_{pl} = \sqrt{ne^2 / \epsilon\epsilon_0 m^*}$$

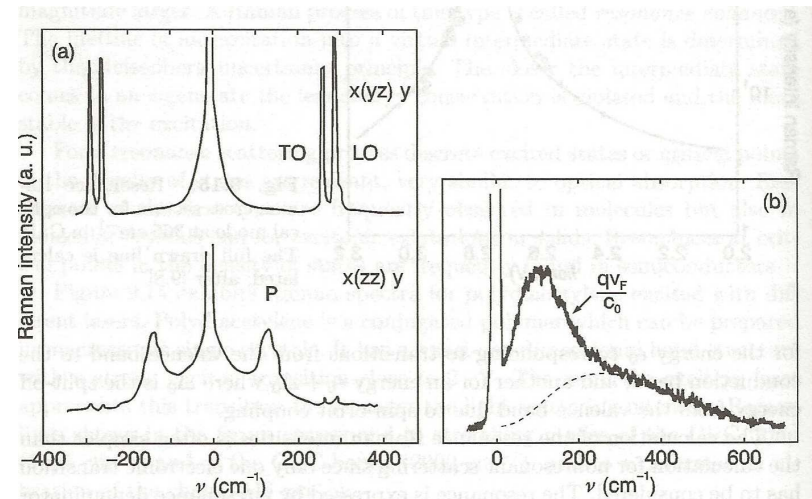
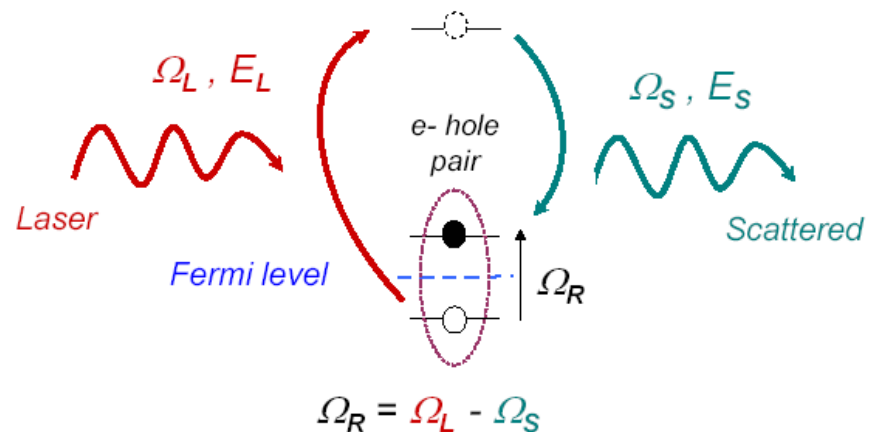


Fig. 9.16. Raman spectrum for GaAs with a carrier concentration  $n = 1.75 \times 10^{17} \text{ cm}^{-3}$  for two different scattering geometries; after [9.9] (a), and single-particle scattering continuum for  $n = 1.3 \times 10^{18} \text{ cm}^{-3}$  (b). The dashed line in (b) is an estimated contribution from a luminescence emission; after [9.10].

Kuzmany Book

Szupravezetőkben:

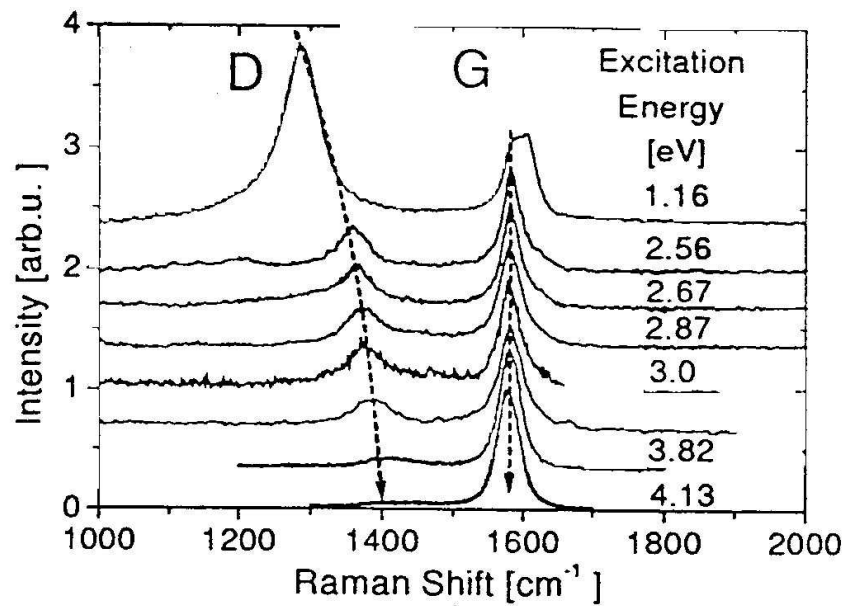


# Speciális Raman esetek II.: Nem $\Gamma$ pontbeli fonon (Kürti Jenő)

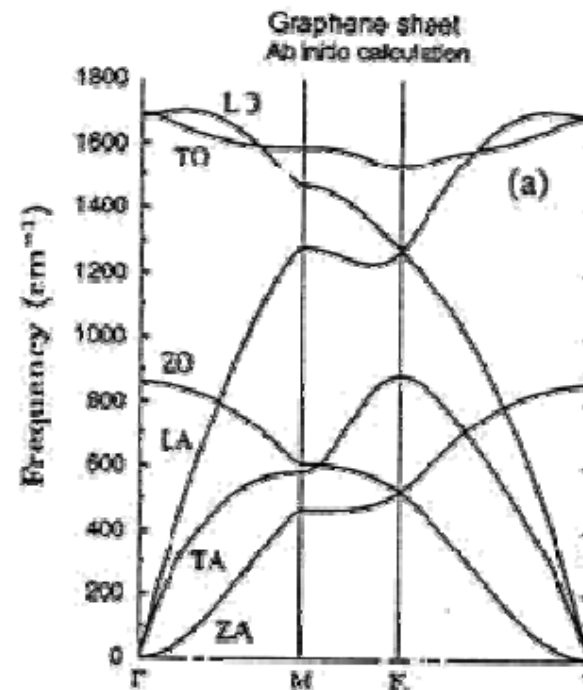
Grafít Raman spektruma, diszperzió!

D: defekt indukált módus

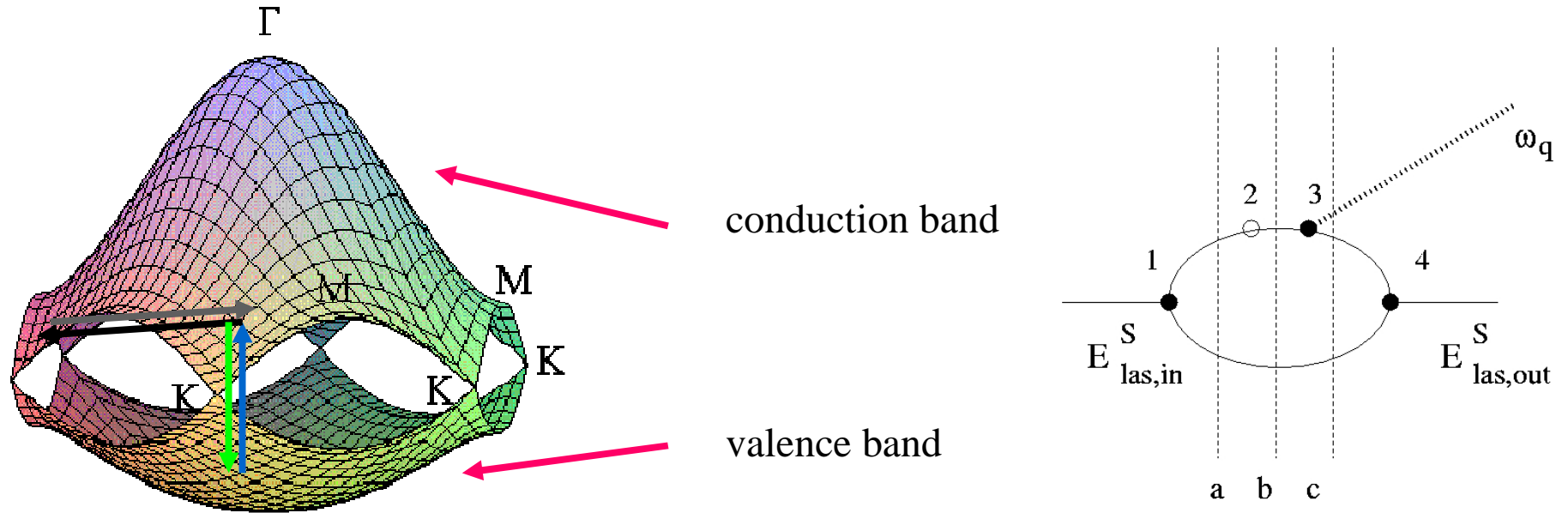
*Pócsik et al. (1998)*



# Fonon-diszperzió:



# Magyarázat: ún. kettős rezonancia



$$\sum_{a,b,c} \frac{M}{(E_{las,in}^{S,AS} - E_{el}^a - i\gamma)(E_{las,in}^{S,AS} - E_{el}^b - i\gamma)(E_{las,in}^{S,AS} - E_{el}^c \mp \hbar\omega_q - i\gamma)}$$

Egyszerre két nevező is lehet 0.

(C.Thomsen and S.Reich, PRL 85, 5214, 2000)

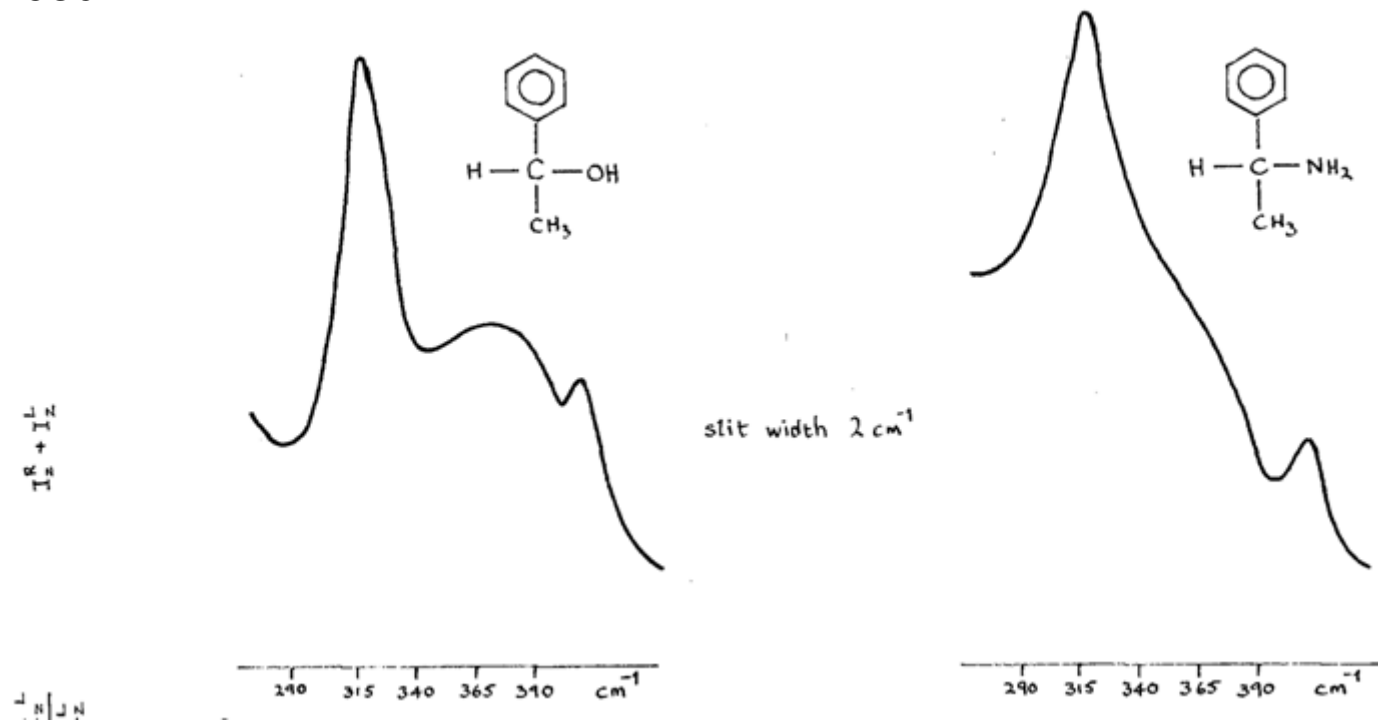
Speciális Raman esetek III.:  
SERS, Tip Enhanced, ROA

„The exact mechanism of the enhancement effect of SERS is still a matter of debate in the literature.” Wiki

Felületi plazmonok vagy lokális töltésátvitel

Hasonló a tip-enhanced

Raman optical act



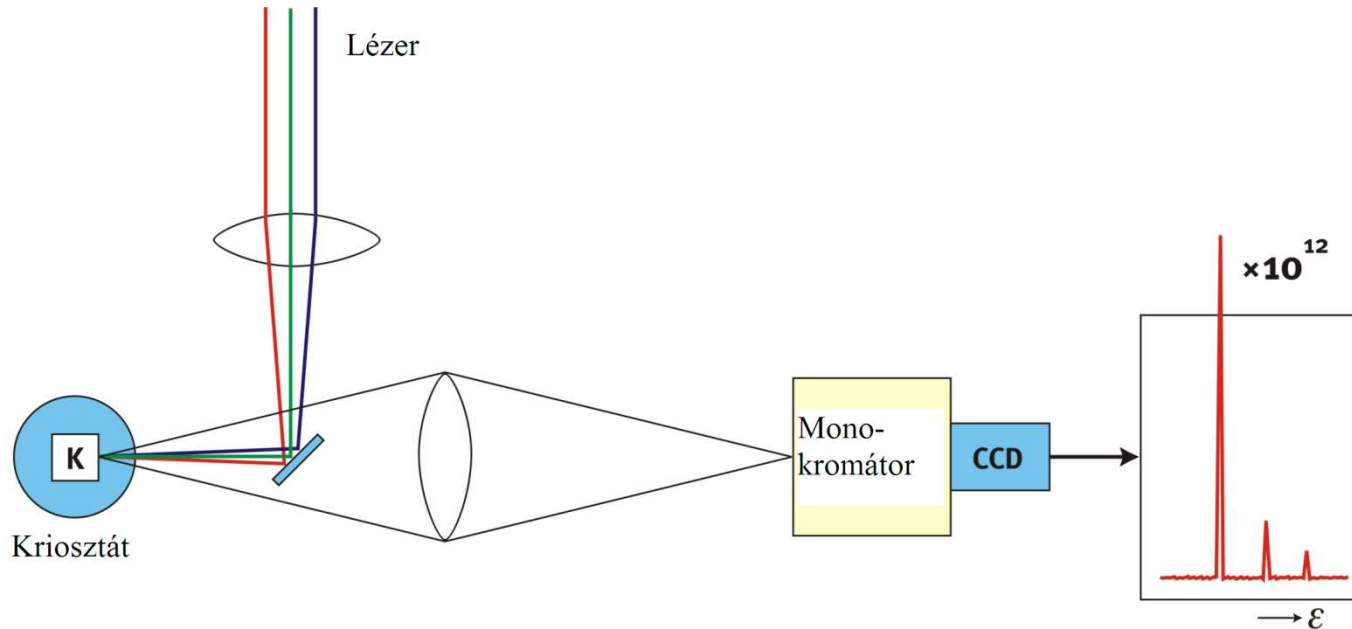
L. D. Barron, M. P. Bogaard and A. D. Buckingham. *J. Am. Chem. Soc.* **95**, 603 (1973)

# Kísérleti megvalósítás

Gerjesztés  
Fénygyűjtés  
Rayleigh elnyomás  
Spektrográf  
Detektor

napfény, Hg-arc, lézerek  
refraktív, reflektív optika  
triple spektrográf, interf. szűrők  
Czerny-Turner, FT  
single-channel, multi-channel

BW <math>1 \text{ cm}^{-1}</math>  
kis  $f/\#$ , achromatikus  
effektív, R-hez közeli  
resol. <math>1 \text{ cm}^{-1}</math>  
nagy Q.E.

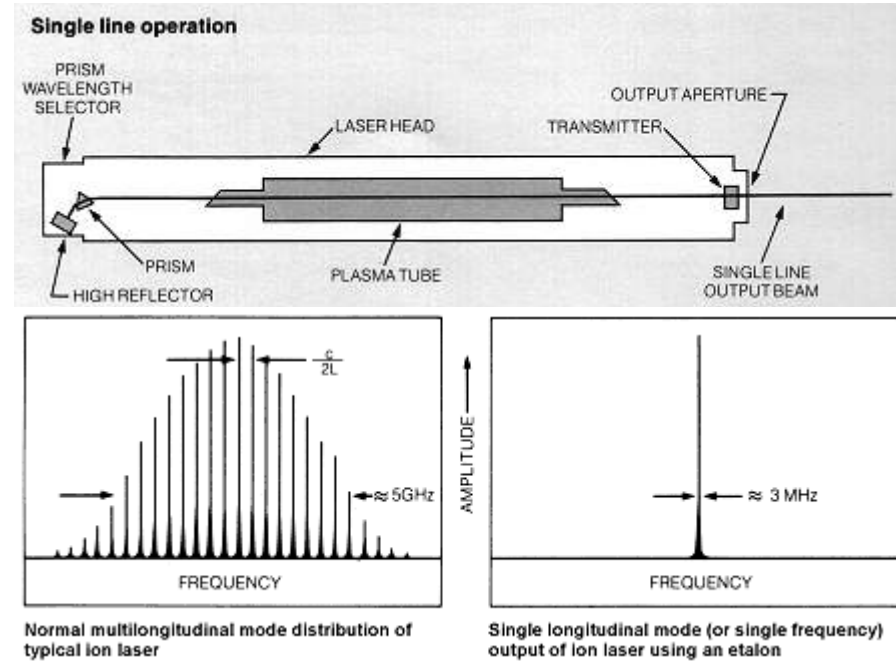


# Gerjesztés

## Gázlézerek:

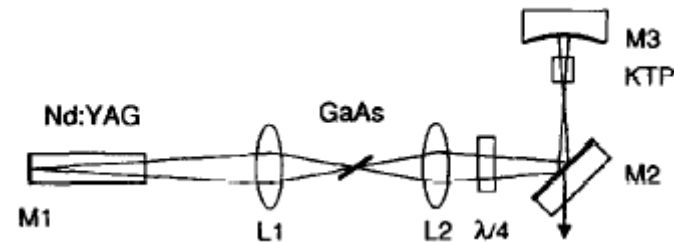
Ar-Kr lézer (>20 vonal, pl. 488, 515, 647 stb.)

He-Ne (633)



## Szilárdtestlézerek:

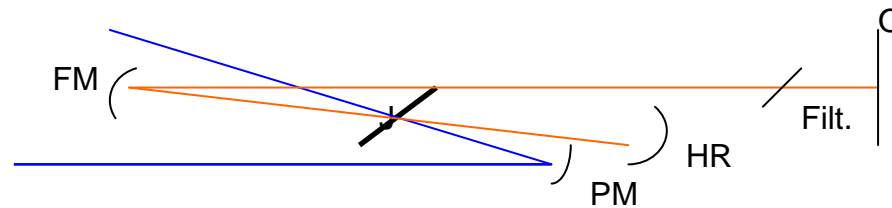
Nd-Yag (1064 nm, v. 2x= 532, 3x=355)



## Hangolható lézerek:

Festéklézer

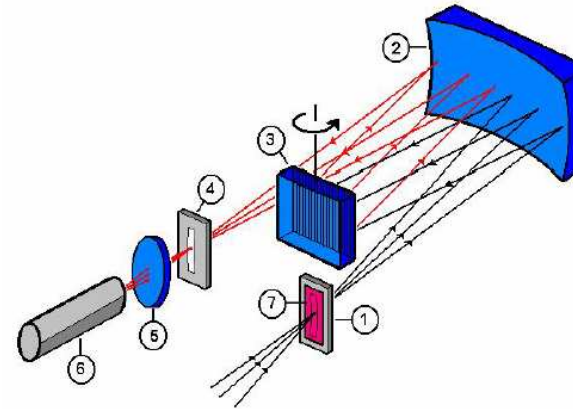
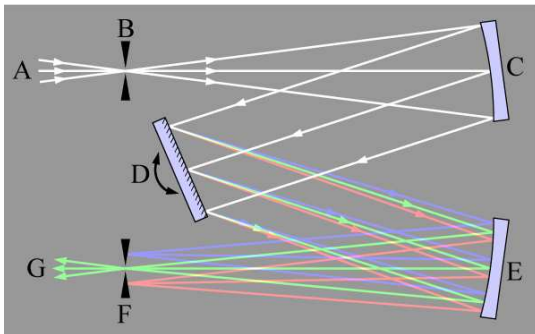
Ti:Sapphire



# Lézer szűrés

plazma vonalak, fluorescens háttér stb.

Szűrése: monokromátorral (Czerny-Turner v. Fastie-Ebert), max. 20 % TRM



Modern megoldás: interferencia szűrők (létezik: BP, LP, SP), 98 % (!) TRM.

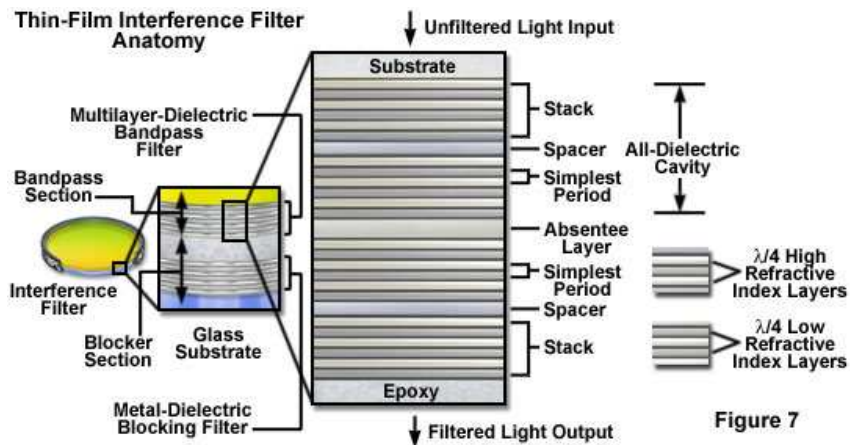
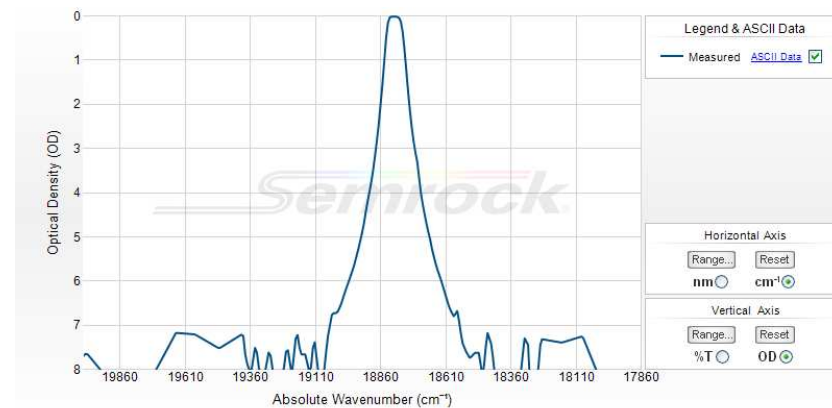


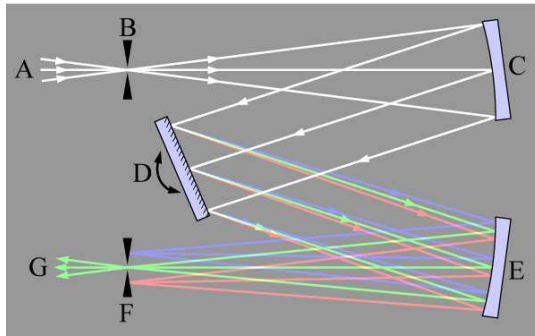
Figure 7



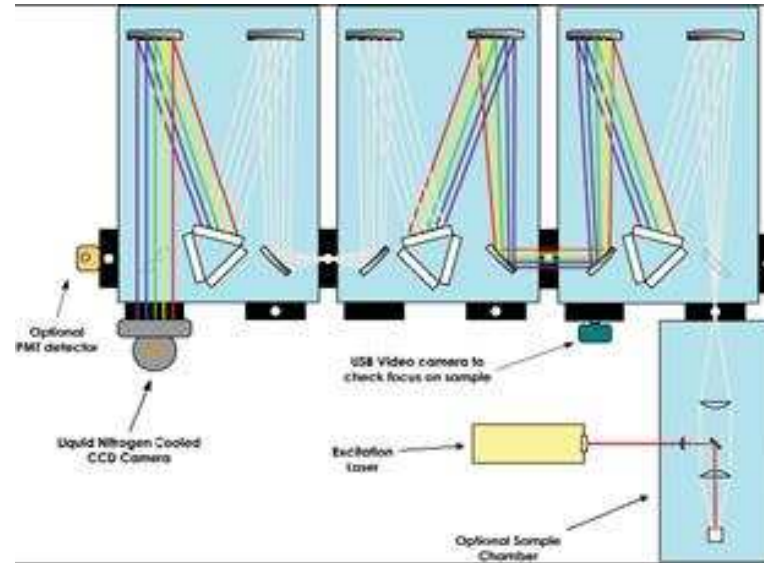


# A spektrográf

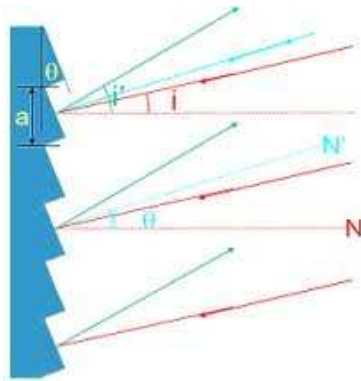
## Diszperzív spektrométer:



Triple subtractive spectrometer (15 éve volt csúcsmodell)



Blazing!



Mai megoldás: 1 monokromátor+LP (long pass) szűrő

**Felbontás: rés méretétől függ. Optikai leképezés jósága: résre mennyi fény jut**

FT-Raman: (nincs rés!, szimultán mérés, stabil hullámhossz)

# Fénygyűjtés

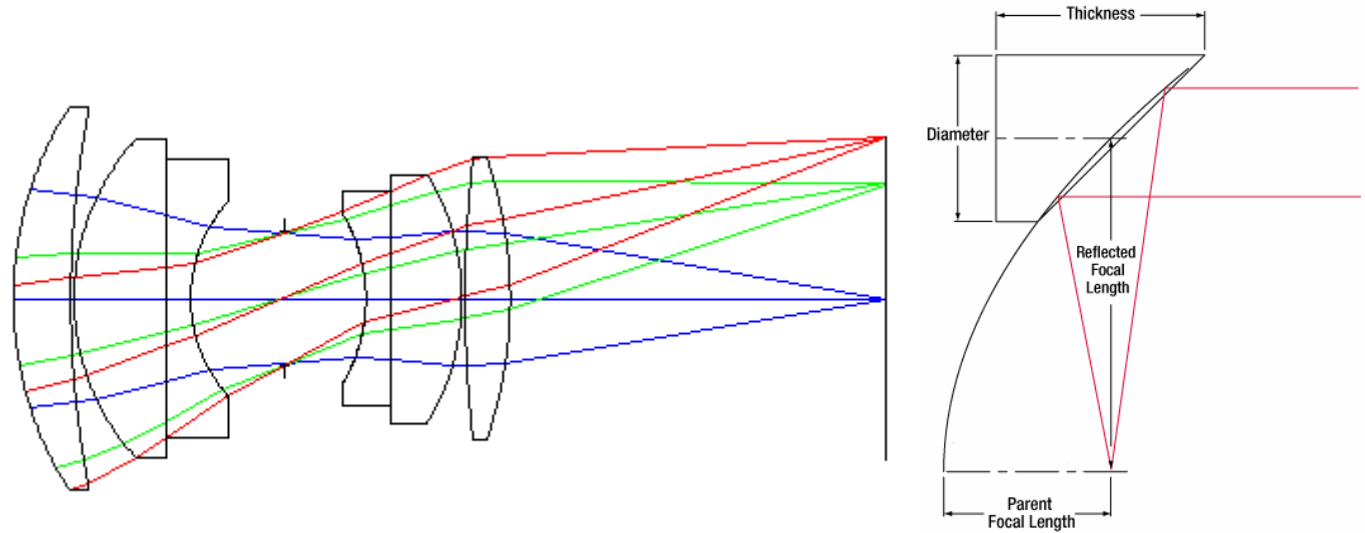
Minta leképezése egy résre (tipikusan 100 mikron), spektrométer f-szám illesztés

Nagy N.A. szám (kis f/#), akromatikus

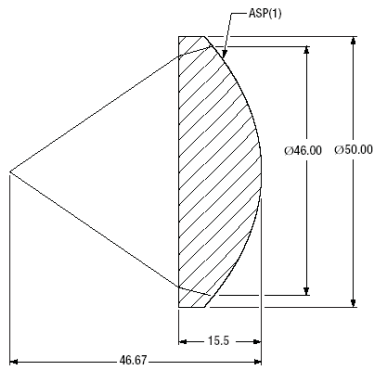
legmodernebb megoldás: mikroszkóp objektívek (túl nagy energia sűrűség)

Cassegrain (tükrös)

Jó megoldás: kamera objek megfordítva!



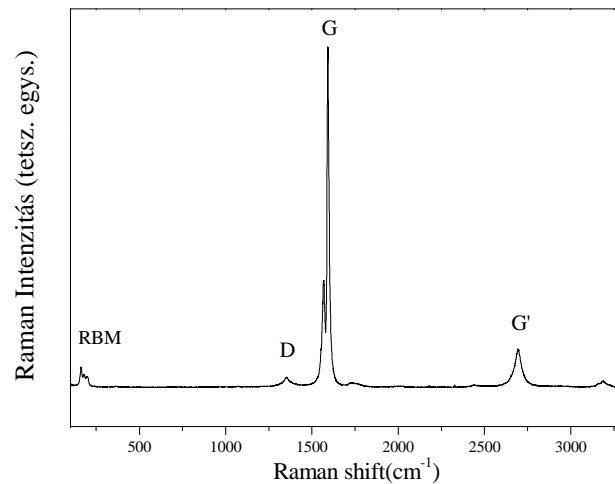
FT-Raman: aszférikus szinglet (nem akromatikus) de működik mivel nincs rés



# Detektorok

FT-Raman, NIR: LN2 hűtött Germánium  
Vagy: InGaAs CCD v. single-channel  
Látható: régen PMT (10 % Q.E.)  
Most: CCD (25 micron/pixel), LN2 hűtött

## Példák



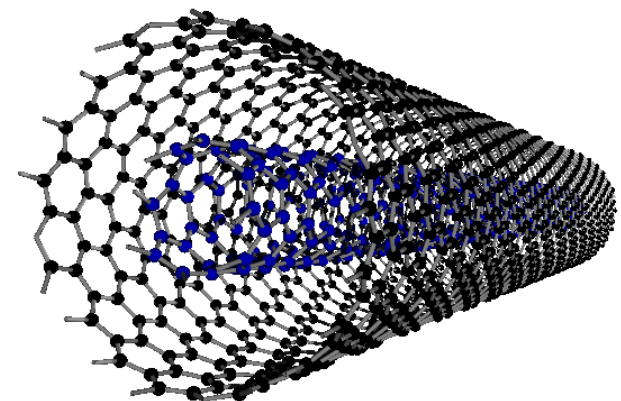
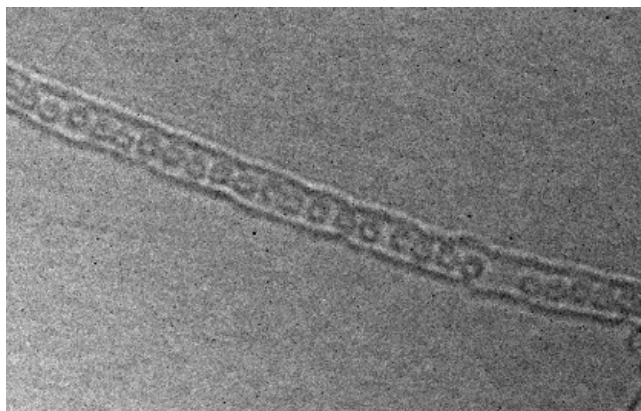
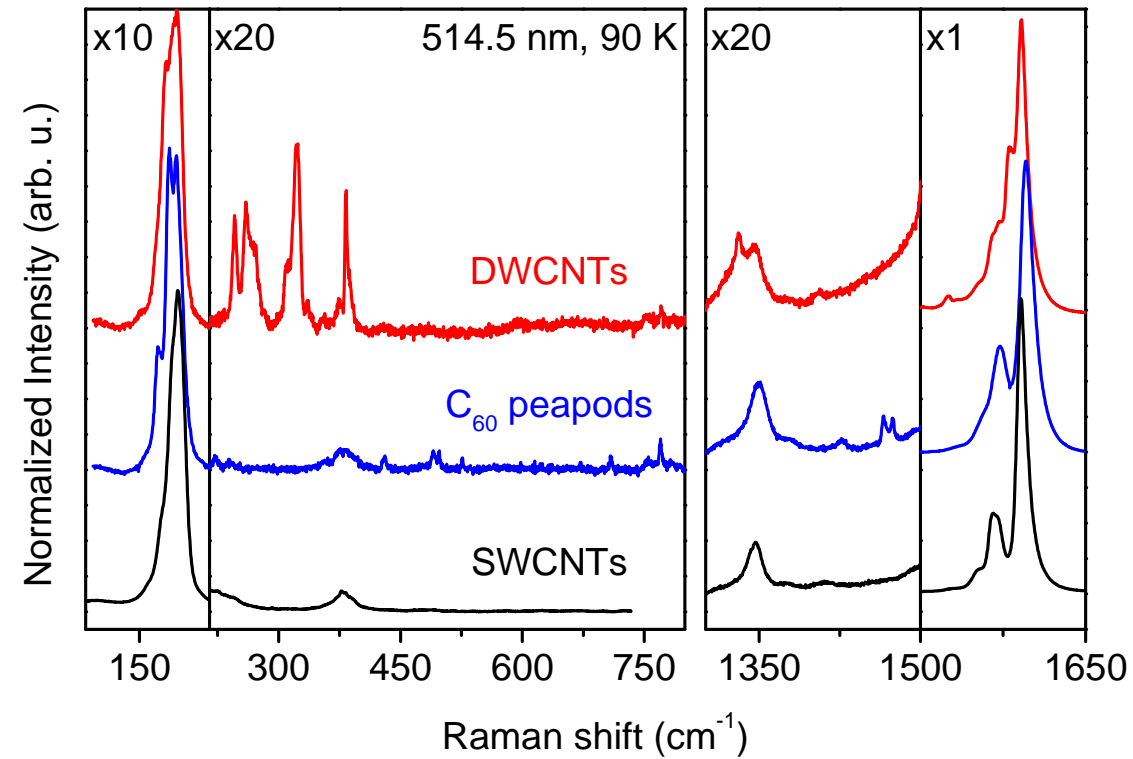
Radiális lélegző módus (RBM)

$$\nu_{\text{RBM}} = C/d(n,m)$$

$$C \sim 230 \text{ cm}^{-1} \text{ nm}$$

# Kétfalú nanocsövek Raman spektruma

*R. Pfeiffer et al. Phys. Rev. Lett. (2003)*



# Nanocsövek izotóp nyomjelzése

## Izotóp függő jelenségek a természetben

Rezgési spektrum \*

Más phonon energia:

fajhő eredete

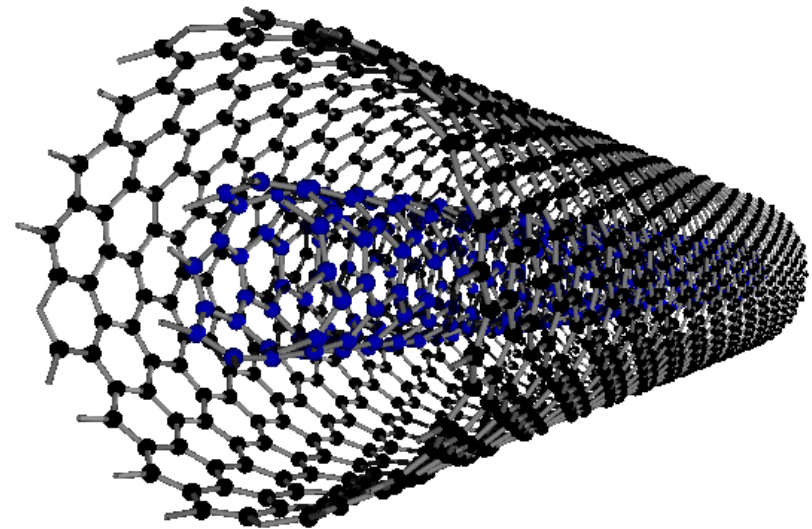
szupravezetés

Kvantum információ elmélet

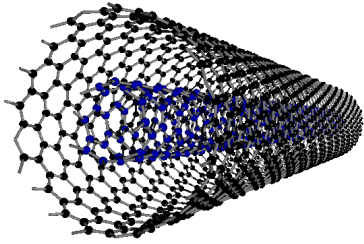
Nanocső keletkezés folyamata \*

NMR \*

● :  $^{12}\text{C}$   
● :  $^{13}\text{C}$



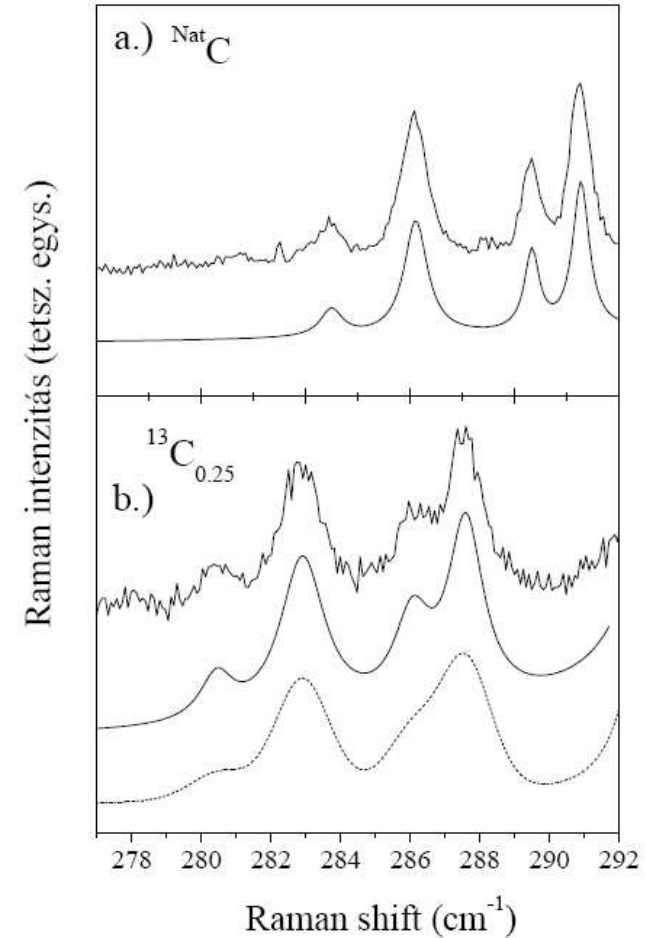
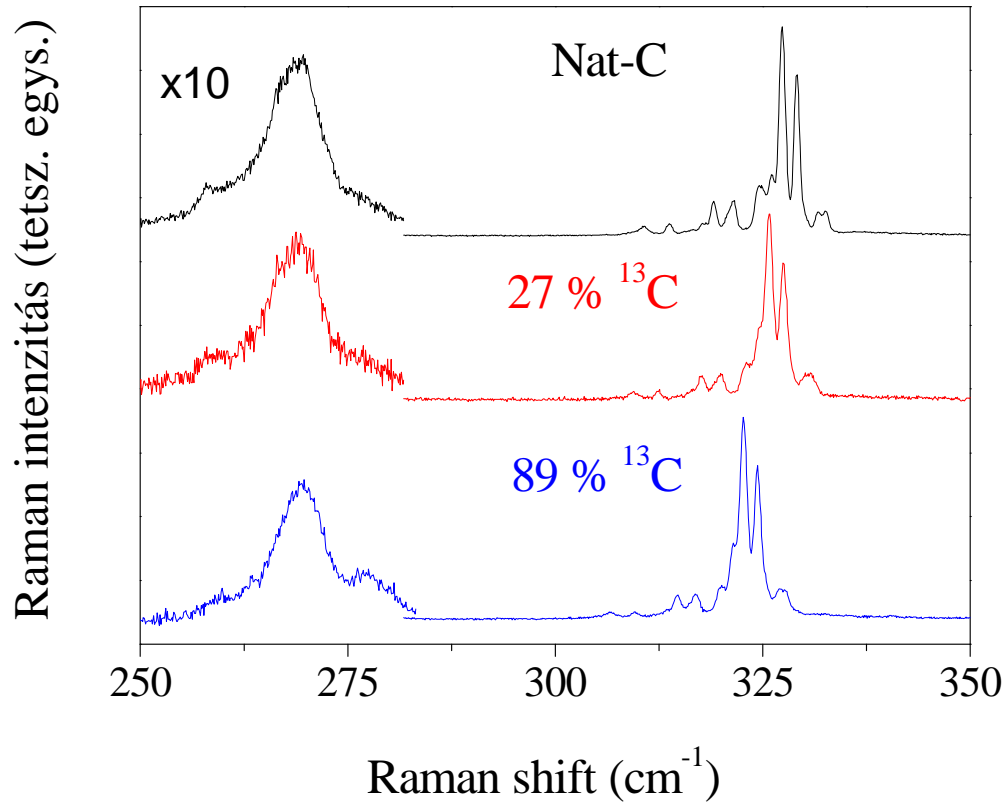
*F. Simon: "Isotope engineering of carbon nanotubes"  
könyvfejezet, Taylor & Francis, 2010*



# <sup>13</sup>C dúsított nanocsövek

*Simon et al. Phys. Rev. Lett. (2005)*

676 nm, 90 K



$$\nu = \nu_0 \sqrt{\frac{12}{12+c}}$$

Inhomogén kiszélesedés <sup>13</sup>C eloszlás miatt  
*Kürti Jenő, Zólyomi Viktor*