Address to the Nation by the President Of India on the Science Day 2005

(New Delhi; February 28, 2005)

Can Indian science inspire youth?

Dear Citizens,

My greetings to all of you. I am indeed very happy to talk to you on this Science Day, which is celebrated on the 28th of February every year, the day one of our great scientists and Nobel Laureate Sir CV Raman made a landmark discovery. On this day, the nation pays tribute and expresses its gratitude to all the scientists who have made our dream of using the science and scientific discoveries as vehicles for economic development, a reality. If the nation's science is celebrated, it will also attract many young children to take up science as a career. In addition, the Scientists of the nation may like to rededicate themselves to create high quality scientific research output from India and make the nation proud. Science day is a day to remind us that the important ingredient for societal transformation would mainly come from science. I would like to share with you particularly the youth, the scientific progress made in our country towards enriching the society and signifying our national spirit that "Can Indian science inspire youth".

International year of Physics - 2005

One of the major breakthroughs in science in the 20th century that had an everlasting impact on the human kind is the most celebrated work of Einstein. Einstein explained, for the first time in 1905, the principle of the inertia of energy as a universal law. The famous energy equation E=MC2 was given to the world. This equation has become the basis for converting matter into energy giving birth to a new avenue called the nuclear energy for producing electricity to light up our cities and villages. Science at times is a double-edged sword. While the E=MC2 of Einstein, changed the way the humanity looked at the energy problem, it also paved the way for the design of Atom bomb. The latter application even today threatens to disturb the world peace. In spite of this, Einstein's work is most profound and opened up many areas of research and development in physics. The scientific community of the world has decided to pay tribute to Einstein by declaring the year 2005 as the International year of Physics. As announced by me

Chandrashekhara Venkata Raman was born in Tiruchirappally (Tamil-Nadu, INDIA) on November 7th 1888. The second of eight childrens of R. Chandra Shekhar Iyer and Parvathi Ammal.

He was a brilliant student at the Presidency College in Madras. In 1905 published his two first papers in the Philosophical Magazine.

He combined an efficient work in business with the scientific activity.

Summary of the discovery

1921- Travel to UK (International Universities Congress). The impact from the sky blue color in the Mediterranean Sea "*The scattering question*"

1922- Publish the first paper on the scattering of light assuming the phenomena associated with a weak fluorescence induced by the light.

1923- Study the difraccition of XR by the liquids. Alt the same time Compton discover the "secondary radiation" in the scattering process of XR by electrons. Raman extrapolated the same idea to the light scattering.

1923- Arnold Smekal predicts theoretically the "secondary radiation".

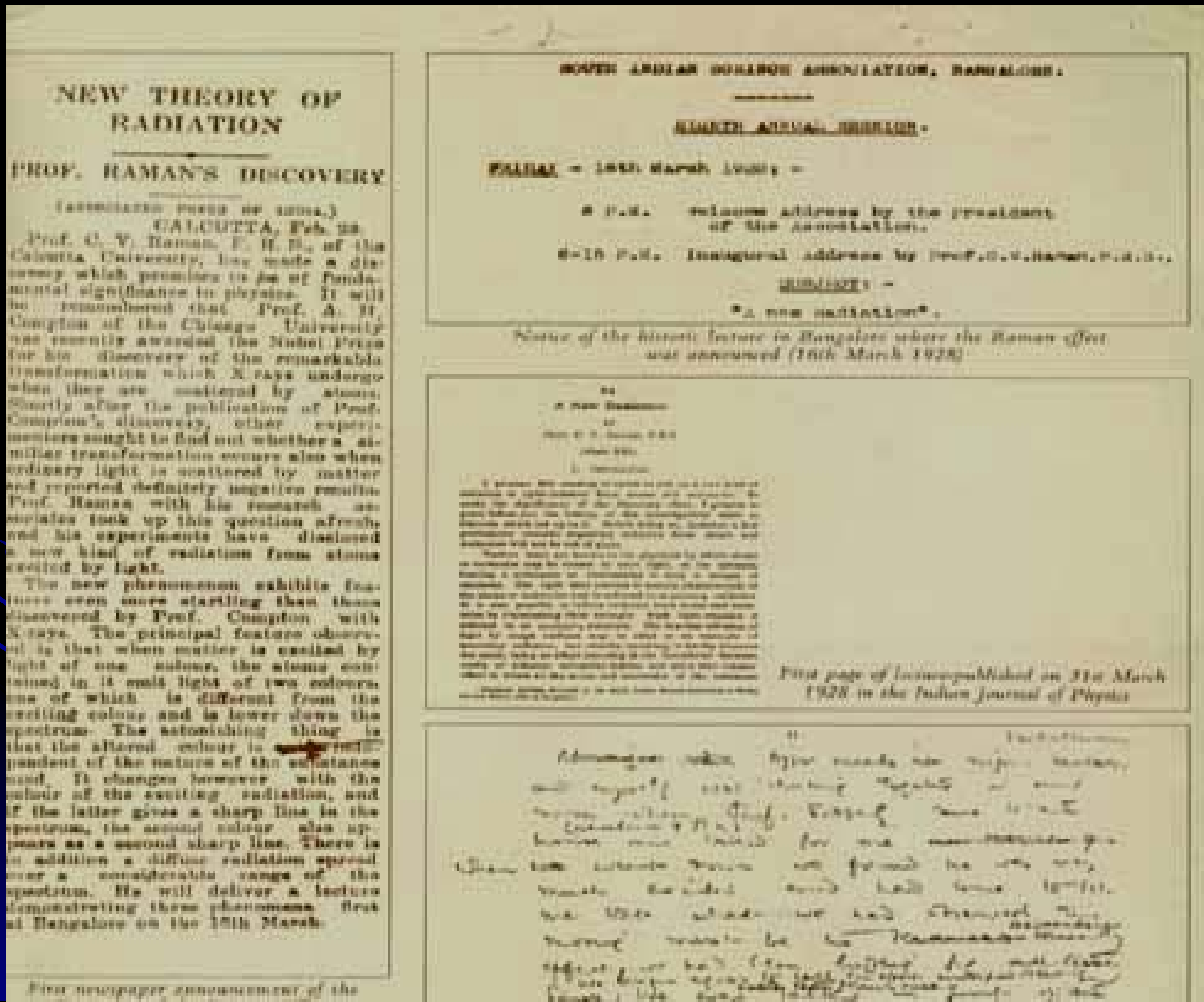
1925- Kramers&Heisenberg developed the first quantum model of the interaction between the radiation and the matter including the inelastic factor.

1927- A Raman's student discover experimentally that the "weak fluorescence" is strongly polarised.

27-28/Feb./1928- After a great experimental effort they observed a small signal in the scattering of glycerin by the sunlight with different wavelength than the incident light.

Raman called this effect “secondary radiation induced by the light”

(publication of the discovery in the Calcuta’s newspapers on February 28th)



NEW THEORY OF RADIATION

PROF. RAMAN'S DISCOVERY

(ASSOCIATED PRESS OF INDIA.)

CALCUTTA, Feb. 28

Prof. C. V. Raman, F. R. S., of the Calcutta University, has made a discovery which promises to be of fundamental significance to physics. It will be remembered that Prof. A. H. Compton of the Chicago University was recently awarded the Nobel Prize for his discovery of the remarkable transformation which X-rays undergo when they are scattered by atoms. Shortly after the publication of Prof. Compton's discovery, other experimenters sought to find out whether a similar transformation occurs also when ordinary light is scattered by matter and reported definitely negative results. Prof. Raman with his research associates took up this question afresh, and his experiments have disclosed a new kind of radiation from atoms excited by light.

The new phenomenon exhibits features even more startling than those discovered by Prof. Compton with X-rays. The principal feature observed is that when matter is excited by light of one colour, the atoms contained in it emit light of two colours, one of which is different from the exciting colour and is lower down the spectrum. The astonishing thing is that the altered colour is independent of the nature of the substance used. It changes however with the colour of the exciting radiation, and if the latter gives a sharp line in the spectrum, the second colour also appears as a second sharp line. There is in addition a diffuse radiation spread over a considerable range of the spectrum. He will deliver a lecture demonstrating these phenomena first at Bangalore on the 16th March.

First newspaper announcement of the

[illegible]

Notice of the historic lecture in Bangalore where the Raman effect was announced (16th March 1928)

[illegible]

First page of lecture published on 31st March 1928 in the Indian Journal of Physics

A New Type of Secondary Radiation

C. V. Raman and K. S. Krishnan, Nature, *121(3048)*, 501, March 31, 1928

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 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 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.

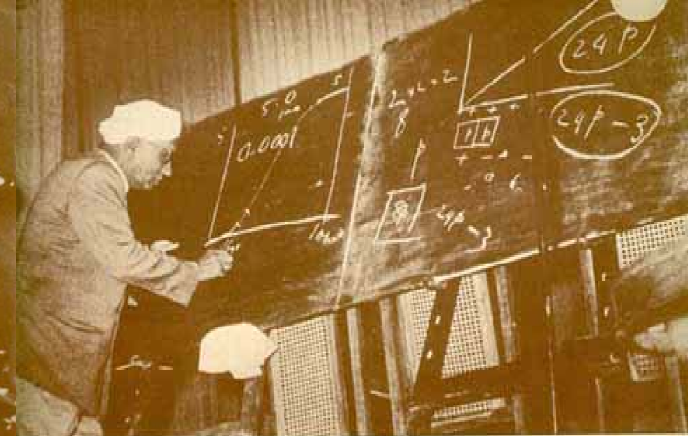
Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering, and secondly by its polarisation, which is in many cases quire strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

Table 1. Names of the persons who recommended Raman alone or Raman with others for the Nobel prize for the year 1930 (ref. 10)

Nominator	Candidate/s
E. Bloch (Paris)	W. R. Wood* and C. V. Raman
N. Bohr (Copenhagen)	Wood or Wood and Raman
O. Chwolson (Leningrad)	Half for Raman and the rest for Landsberg and Mandelstam
J. Perrin (Paris)	Raman or Raman and Heisenberg
F. L. de Broglie (Paris)	Raman
H. M. de Broglie (Paris)	Raman
R. Pfeiffer (Breslau)	Raman
J. Stark (Grosshesselohe)	Raman
E. Rutherford (Cambridge)	Raman
C. T. R. Wilson (Cambridge)	Raman

*W. R. Wood (1868–1955) was famous for his work on fluorescence ... ce radiation.

Nobel Price
1930



Raman expounding his crystal dynamics

Gandhi Memorial Lecture

He studied the crystal dynamics, the mineralogy (fascinated by the diamonds), the combined analysis of XR and light interaction with crystals, the theory of music, etc….

Founder and first director of the Indian Institute of Sciences in Bangalore . India declared the national science day the 28th of February .
He publish 5 books and 475 papers.

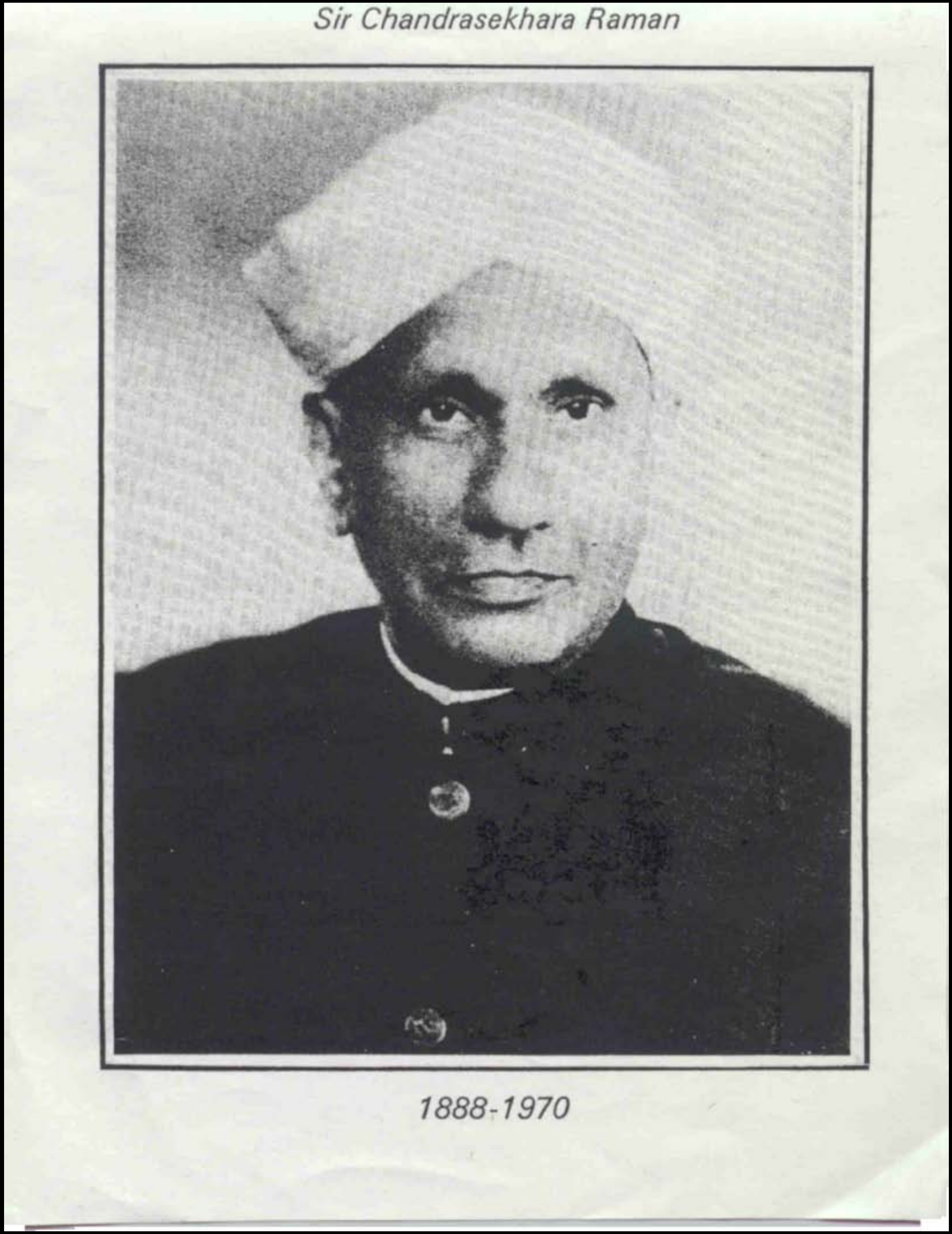
Personality: Kamala Sohonie affair

Raman in Paris, 1948 when he received the degree of D ès Sc *Honoris Causa*. With him are (from left to right) Prince L. de Broglie, R. S. Mulliken and L. Pauling.

Einstein wrote:

"C.V. Raman was the first to recognise and demonstrate that the energy of photon can undergo partial transformation within matter. I still recall vividly the deep impression that this discovery made on all of us... ."

Died on November 11th 1970.



The Raman effect:

A “coordinated”discovery ??

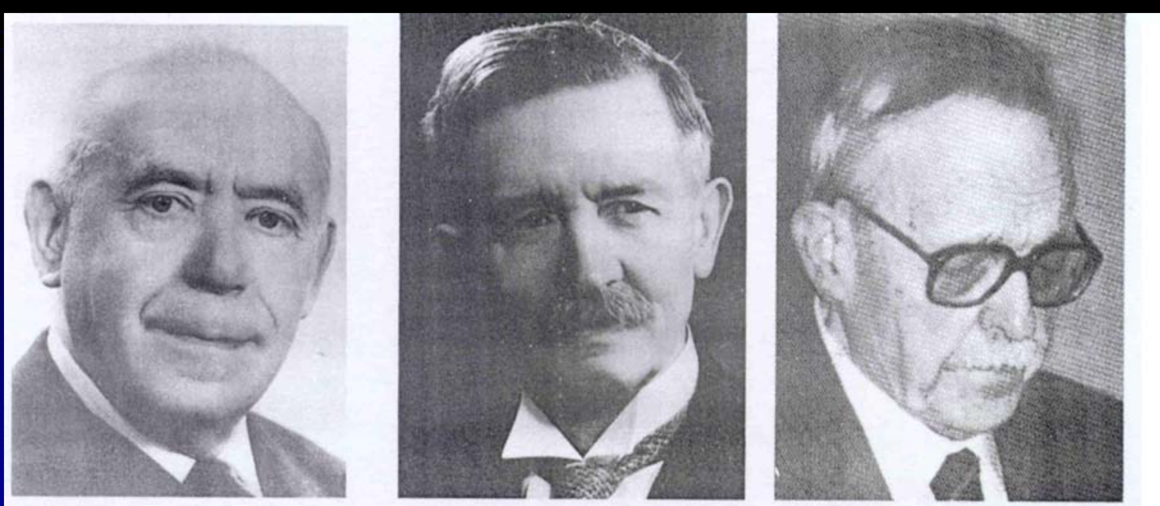
From 1913 Mandelstam and Landsgber in Russia performed similar studies using crystals, mainly quartz.

On 21 of February 1928 at the Moscow State University they observed for the first time the “secondary radiation”. But the first publication appears several months later (Naturwissenschaften, on 13 of July).

By that time Raman had performed a worldwide diffusion of the discovery. This was not well accepted by the Soviet system. Mandelstam in particular was punished….

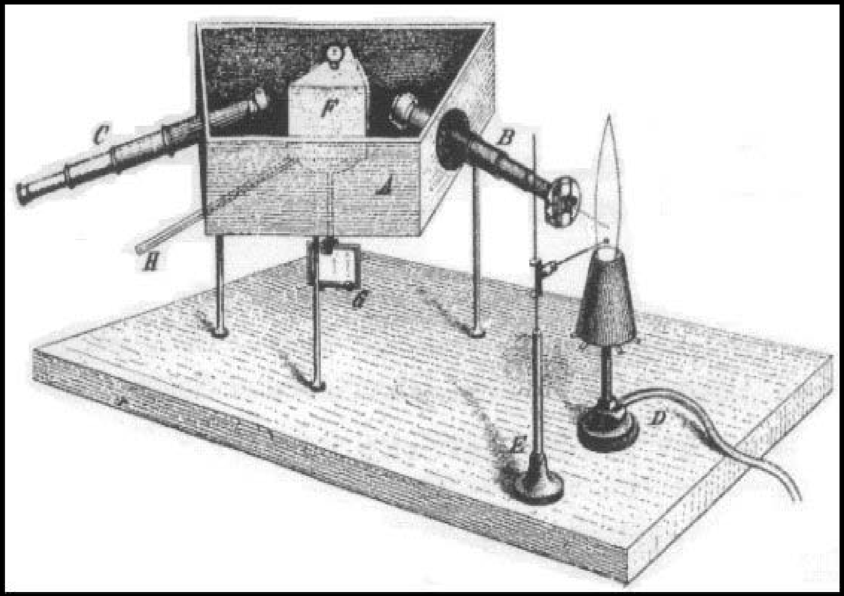
L. I. Mandelstam. G. D. Landsberg.

Also at that time, several French physicists also studied the scattering of light in gaseous phases. Mainly: Alfred Kastler, Pierre Daure, Jean Cabannes and Yves Rocard. These three last physicists discover the Cabannes - Daure effect and publish the results in March-April 1928.



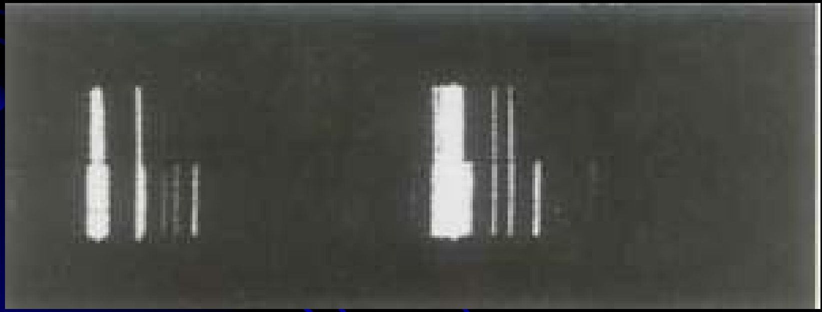
Jean Cabannes. Aimé Cotton. Yves Rocard.

The instruments

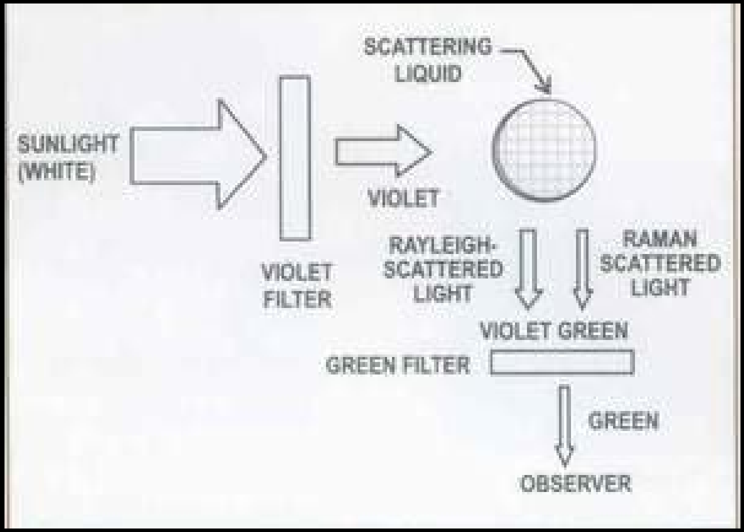


Espectrograph_Kirchhoff_Bunsen_1823

First spectrograph used by Raman



Raman spectrum CCl4



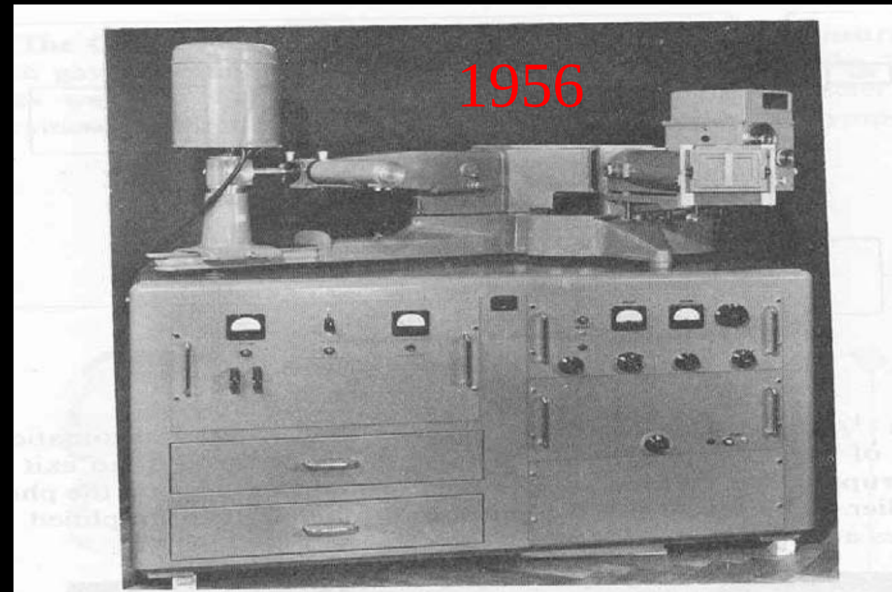


Fig. 1. Hilger E612 Raman spectrometer.

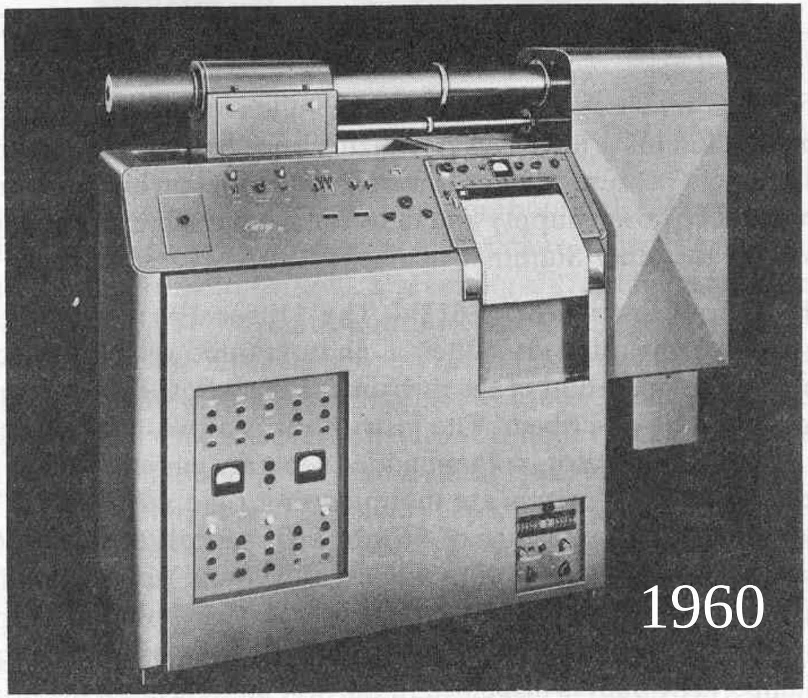


Fig. 3. The Cary Model 81 Raman spectrophotometer.

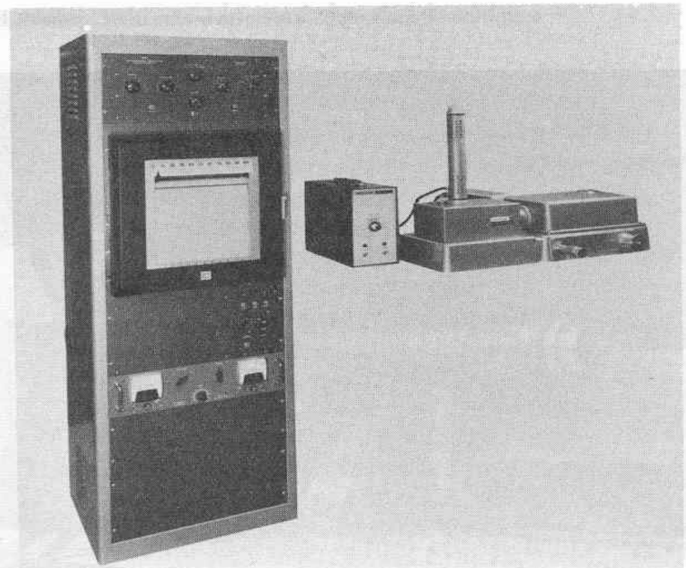


Fig. 8. Perkin-Elmer laser Raman spectrophotometer source mounted on top of instrument.

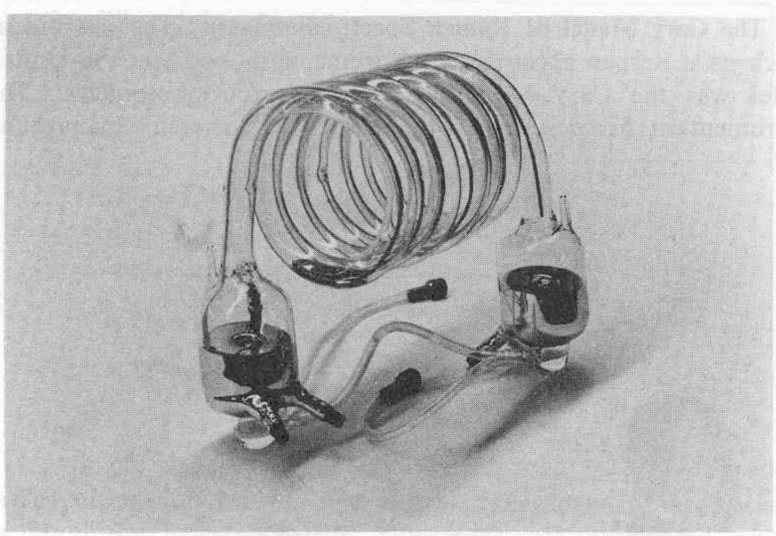


Fig. 5. The mercury arc lamp used in the Cary Model 81.

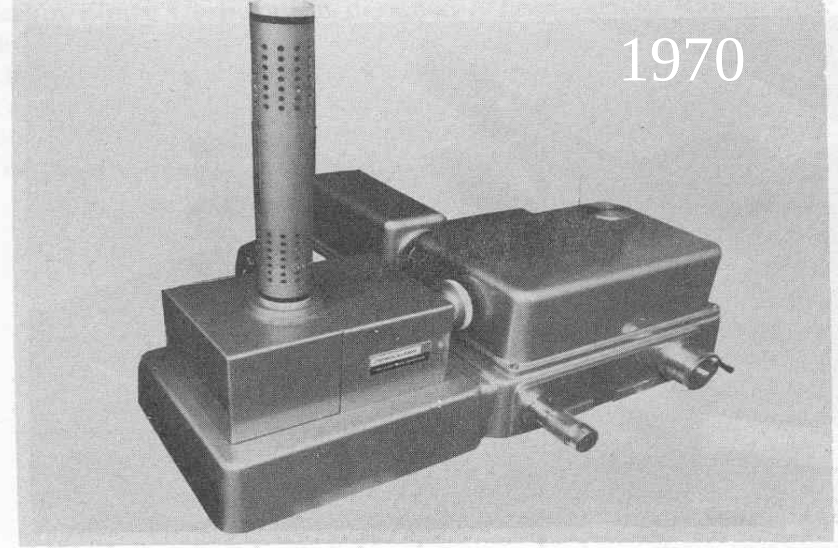
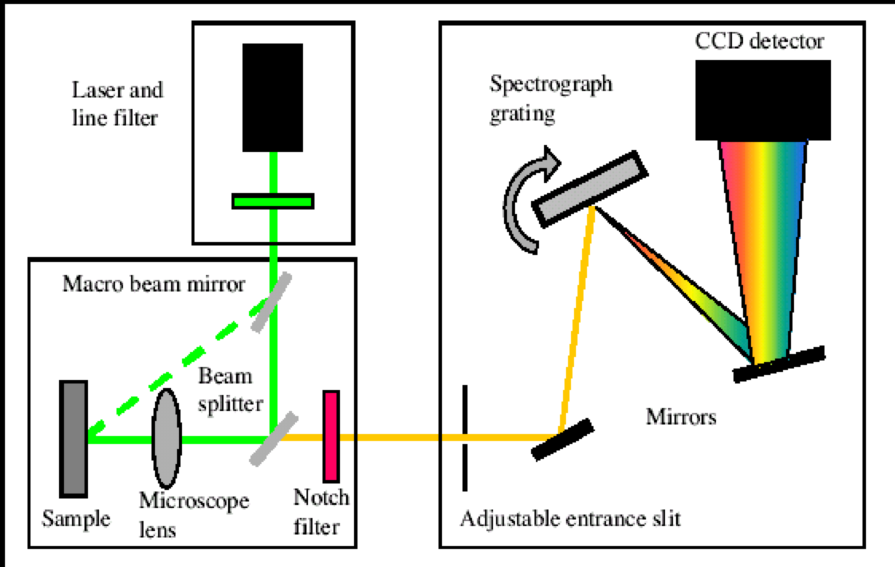
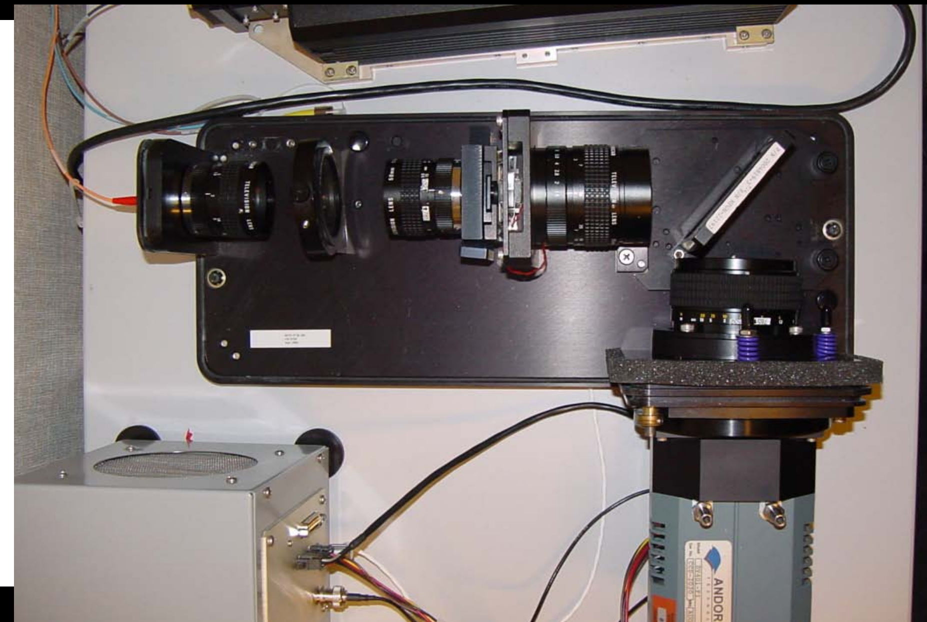
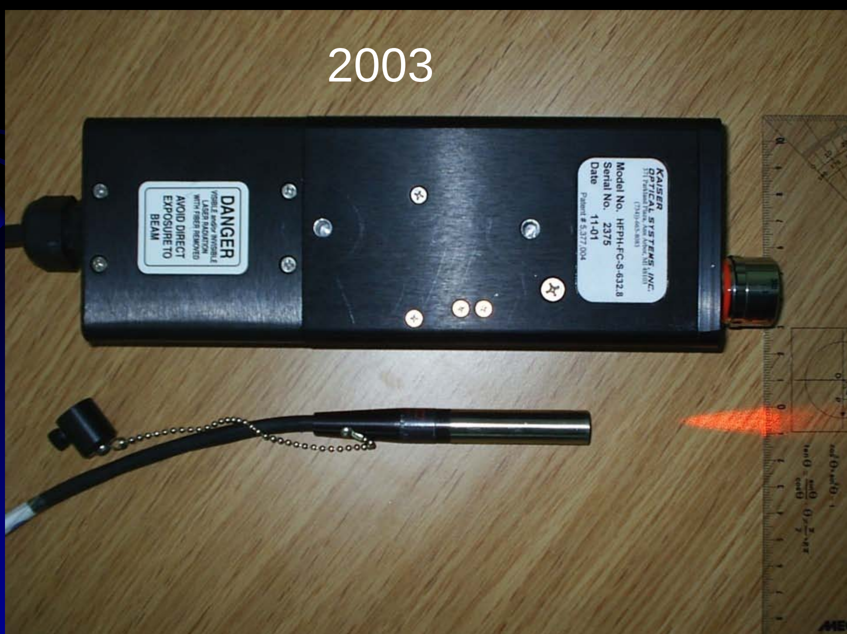
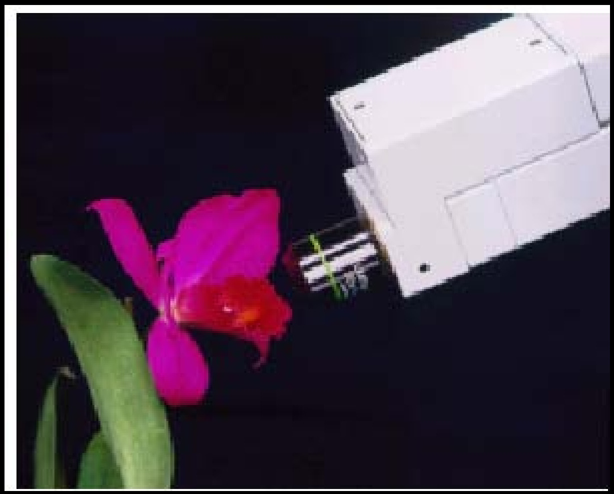


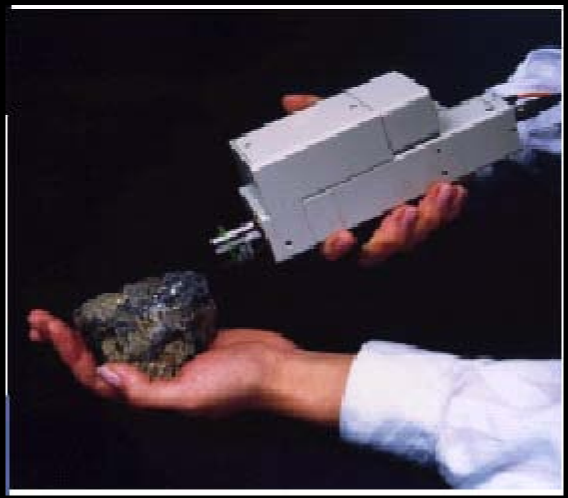
Fig. 9. Close-up of Perkin-Elmer laser Raman spectrophotometer source mounted on top of instrument.


CCD detector
Laser and
line filter
Spectrograph
grating
Macro beam mirror
Beam
splitter
Mirrors
Sample
Microscope
lens
Notch
filter
Adjustable entrance slit



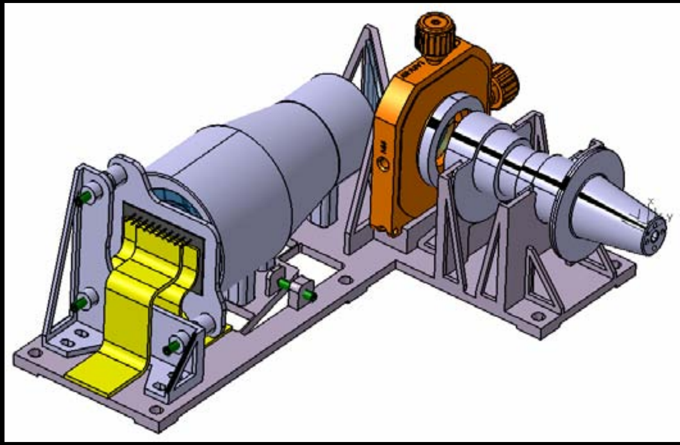

2003
DANGER

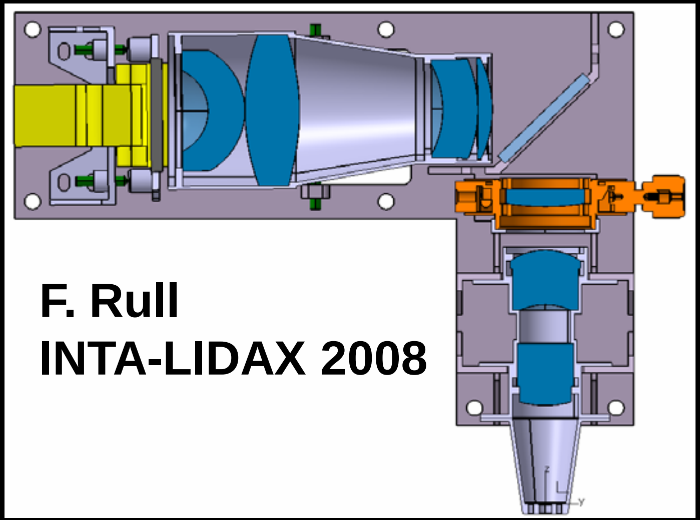


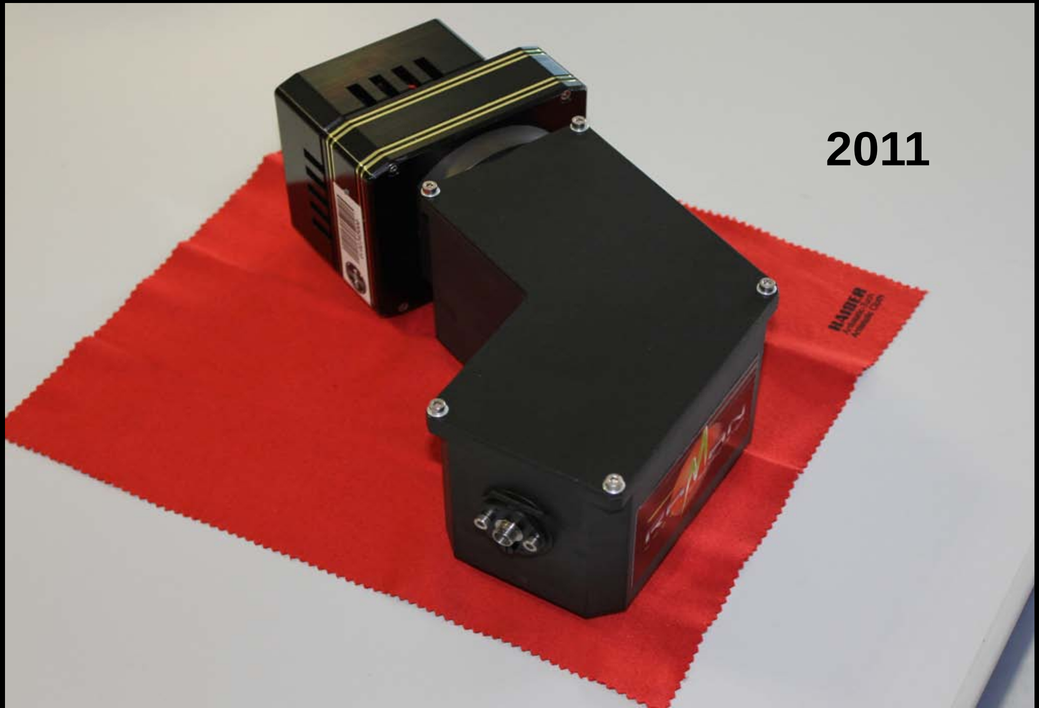


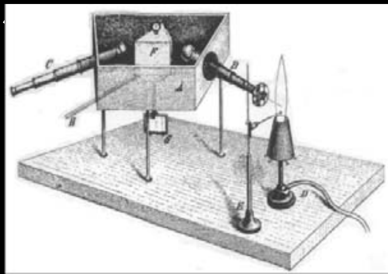
2005

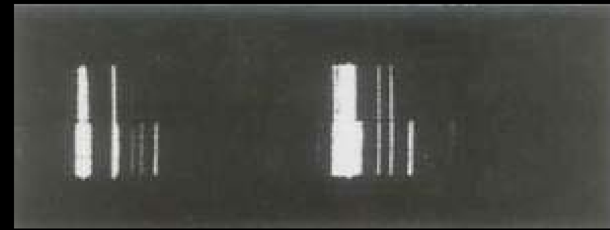
Science Simulators and Raman Operation







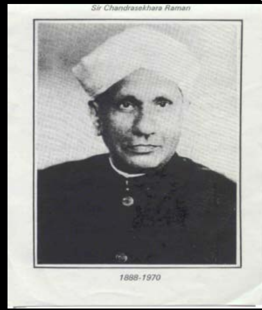




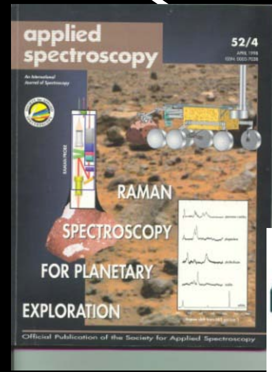
Raman Spectrum CCl4

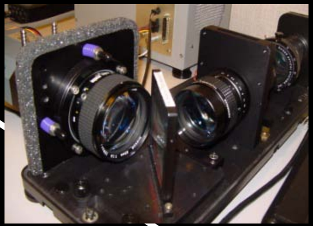
Kirchhoff_Bunsen_1823

Raman first spectrograph 1928

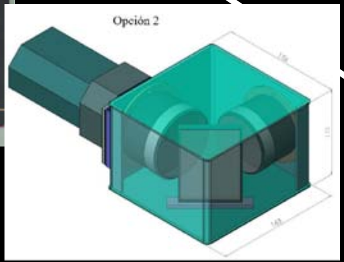


Larry Haskin et al. 1998





Rull-UVA-BB 2003



S. Sharma 2008

Rull-UVA-BB/NTE 2005

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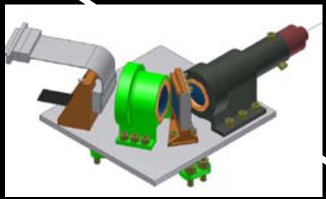
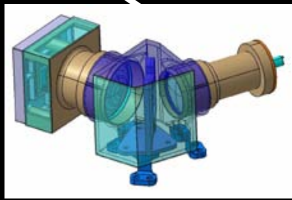


RLS-2011



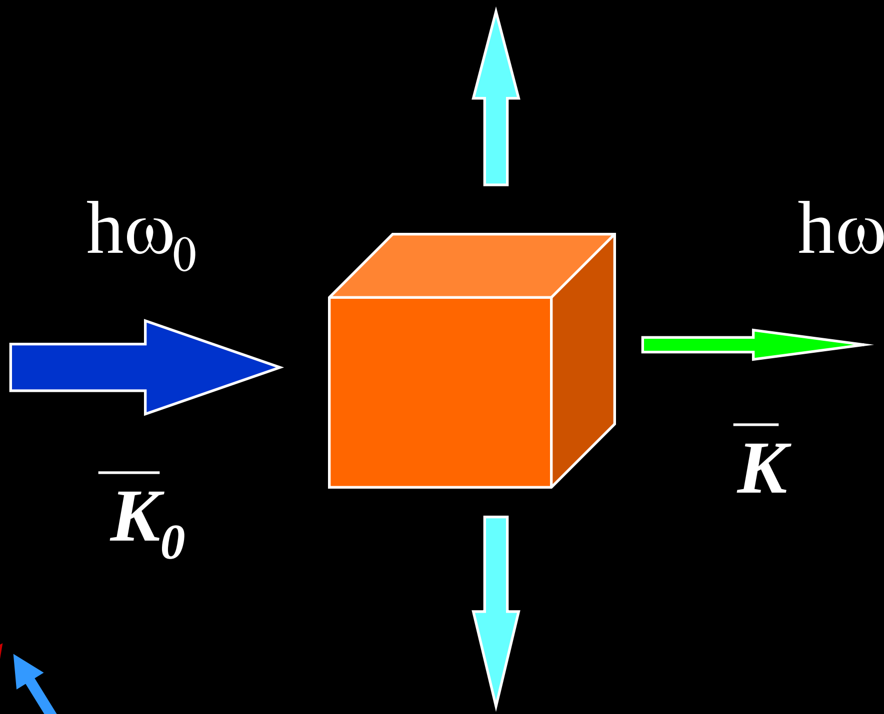
Rull-UVA-Lidax 2011

Raman Transmission Spectrometer Heritage

The Raman effect ?



The general process



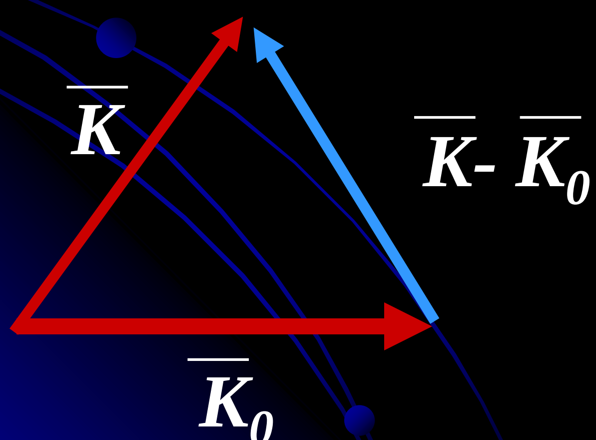
λ / cm

ω / s^{-1}

$|K| = 2\pi/\lambda$ (cm^{-1})

$\omega = 1/T = c/\lambda$

$\nu = |K| = 2\pi/\lambda = 2\pi\omega/c$



$h\omega_0 = h\omega$ (Elastic)

$|K_0| = |K|$

The matter is intrinsically DYNAMICS

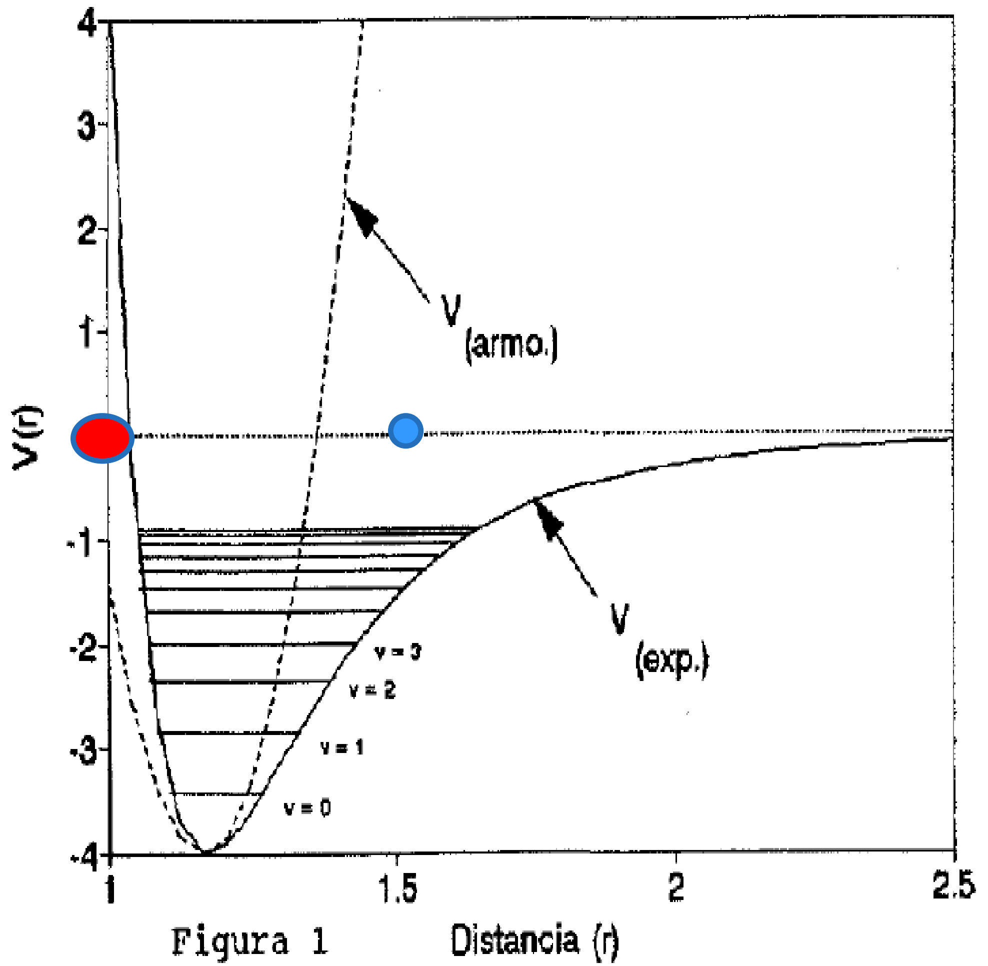


Figura 1

- $V(r) = -A/r^m + B/r^n$

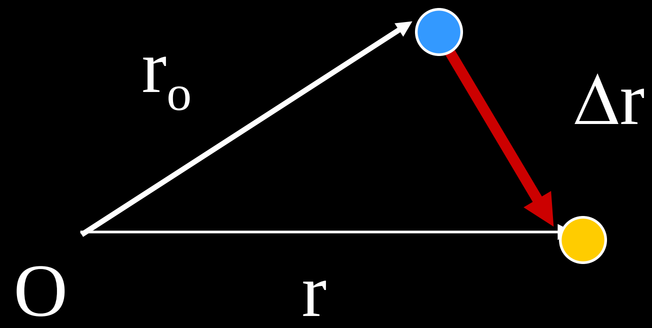
$$V(r) = k\,r^2/2$$

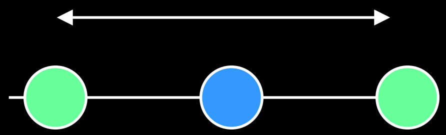
$$T = E + V$$

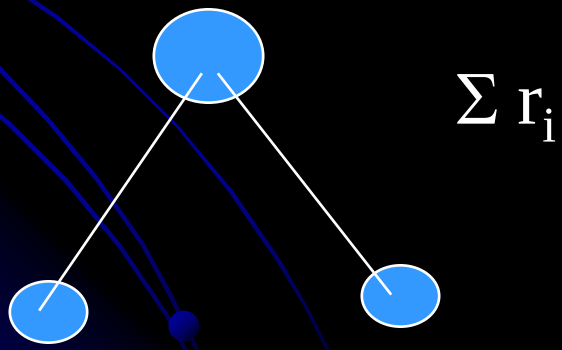
$$\omega = 1/2\pi(k/\mu)^{1/2}$$

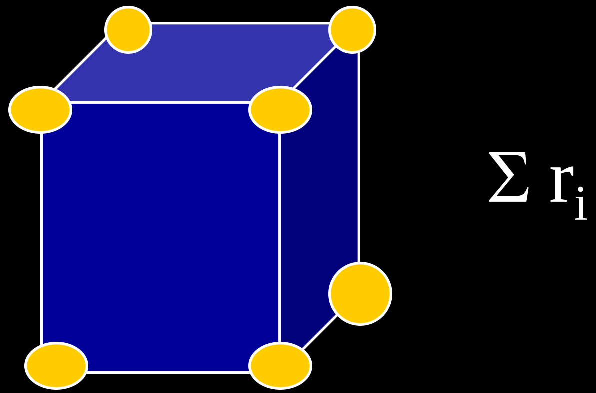
Basic question : description of vibrations

Displacement coordinates $\Delta r = r - r_o$

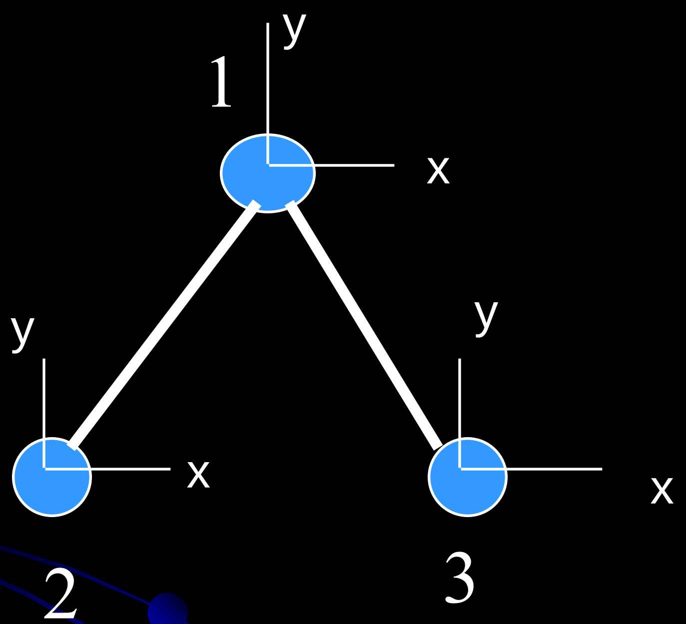








Cartesian Coordinates



$\Delta r_i = r_i - r_{oi}$

$i = 1,2,3$

Δx_i

Δy_i

Δz_i

Total = 3N Coordinates of motion

3N-6 are vibrations
6 are whole motions

Normal coordinates Q_i

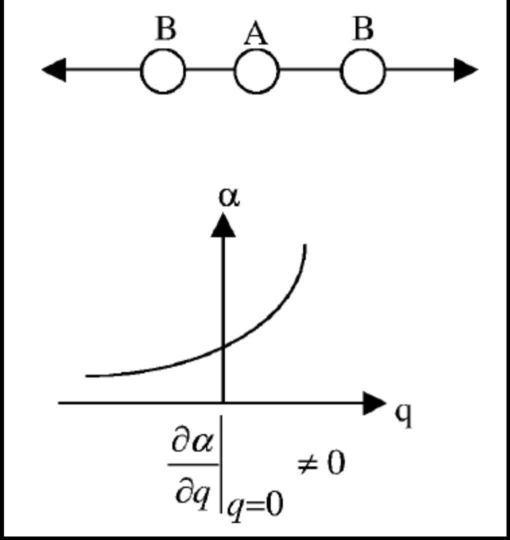
Classical Approach to the Raman effect

When a molecule is subjected to the electric field $E = E_0\cos\omega t$ of electromagnetic radiation, the dipolar moment of the molecule p is given by:

$$p = \mu_0 + [\alpha]E$$

If the movement is described by $q_n(t) = q_{n0}\cos(\omega_n t)$,

$$p = \mu_0 + \alpha(0)E_0\cos(\omega t) + \sum_{n=1}^{Q}\left(\frac{\partial\mu}{\partial q_n}\right)_0 q_{n0}\cos(\omega_n t)$$
$$+\frac{1}{2}E_0\sum_{n=1}^{Q}\left(\frac{\partial\alpha}{\partial q_n}\right)_0 q_{n0}\left[\cos(\omega+\omega_n)t + \cos(\omega-\omega_n)t\right]$$



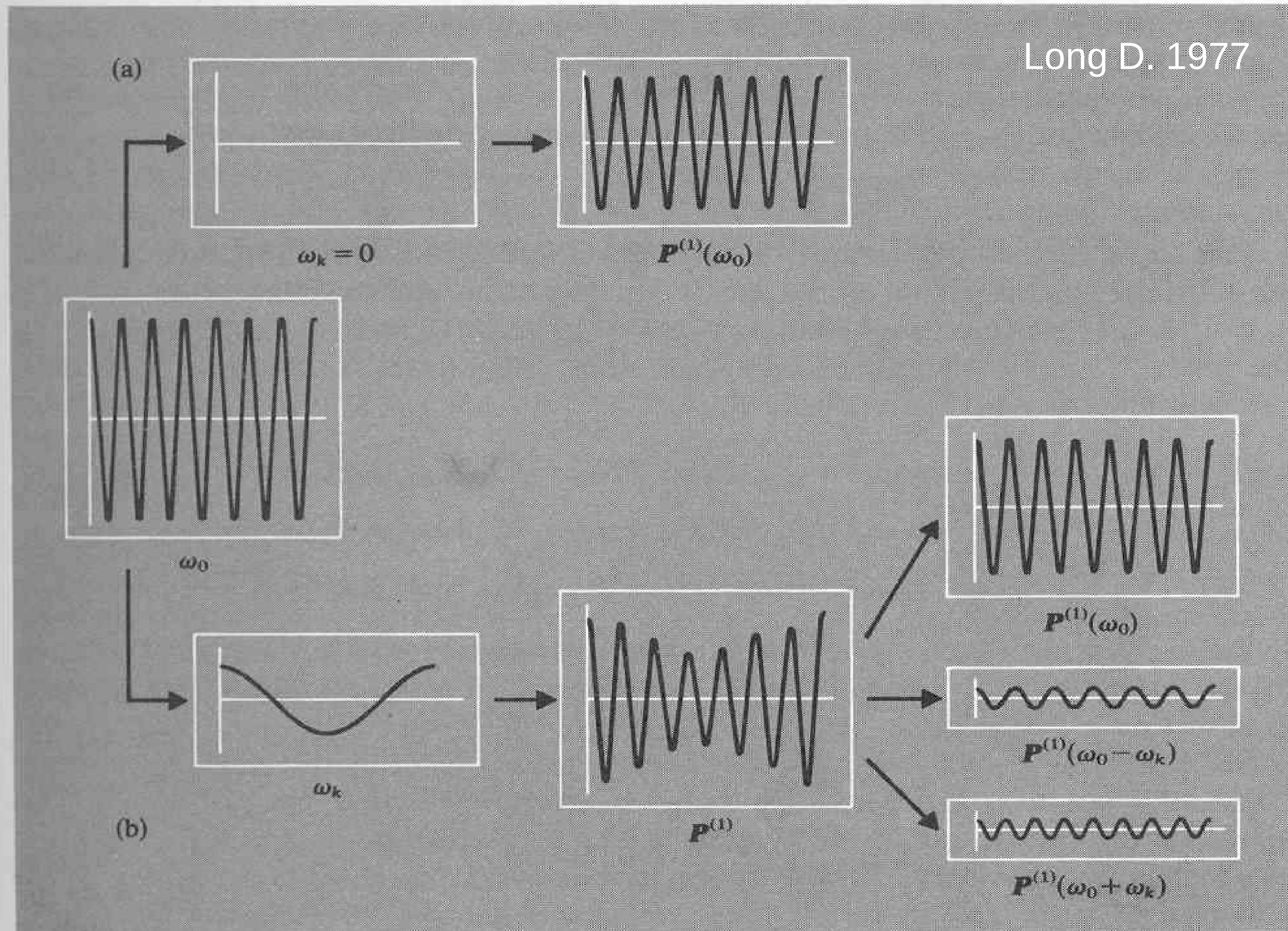
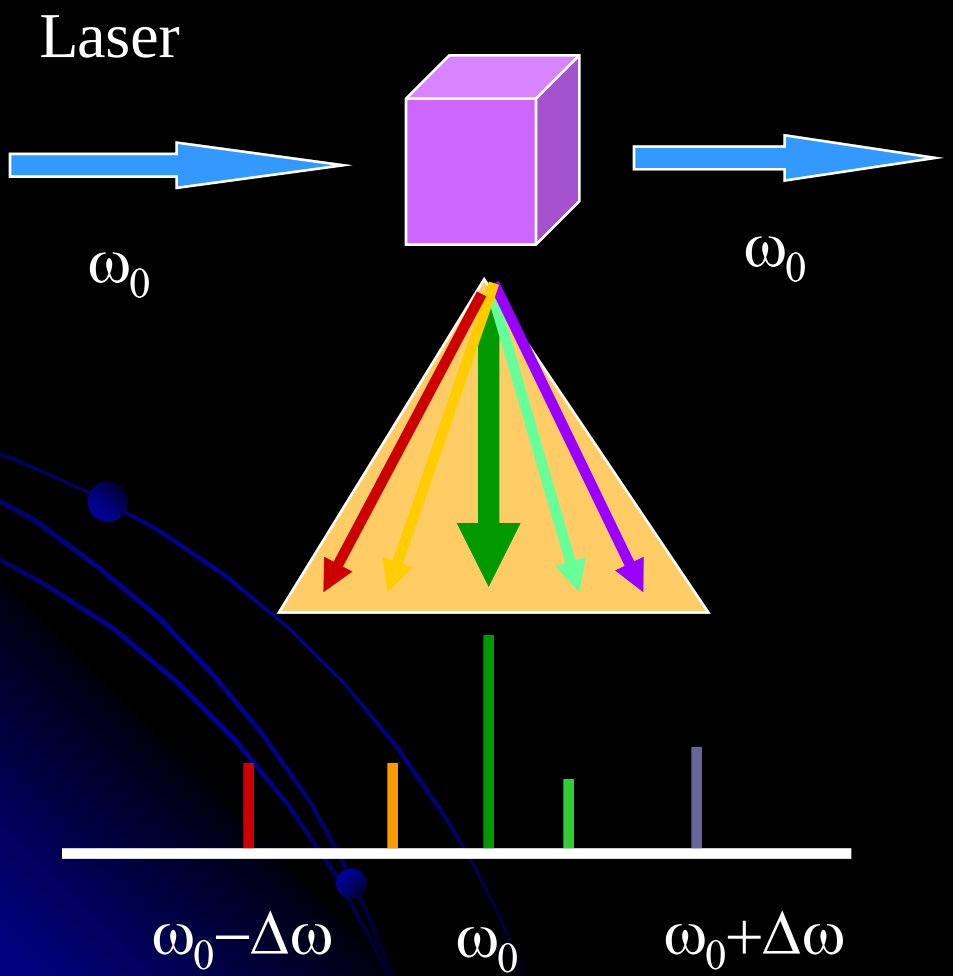
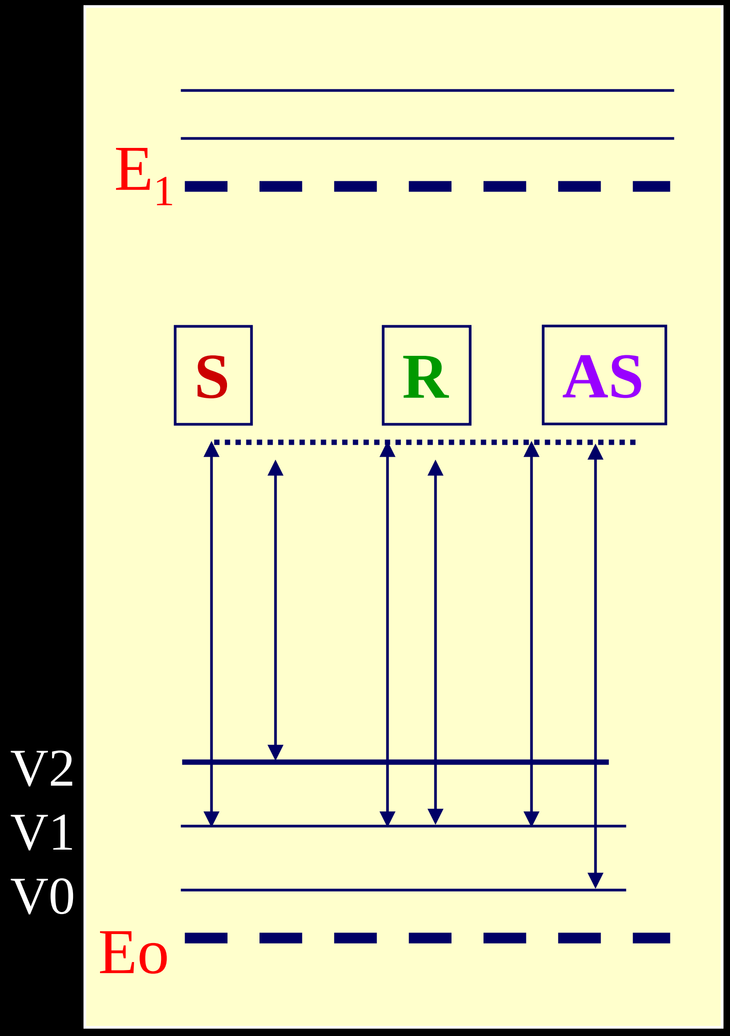


Fig. 3.3 Time dependence of the linear induced dipoles $P^{(1)}$ produced by electromagnetic radiation of frequency ω_0: (a) scattering molecule not vibrating $\omega_k = 0 : P^{(1)} = P^{(1)}(\omega_0)$; and (b) scattering molecule vibrating with frequency ω_k: $P^{(1)} = P^{(1)}(\omega_0) + P^{(1)}(\omega_0 - \omega_k) + P^{(1)}(\omega_0 + \omega_k)$

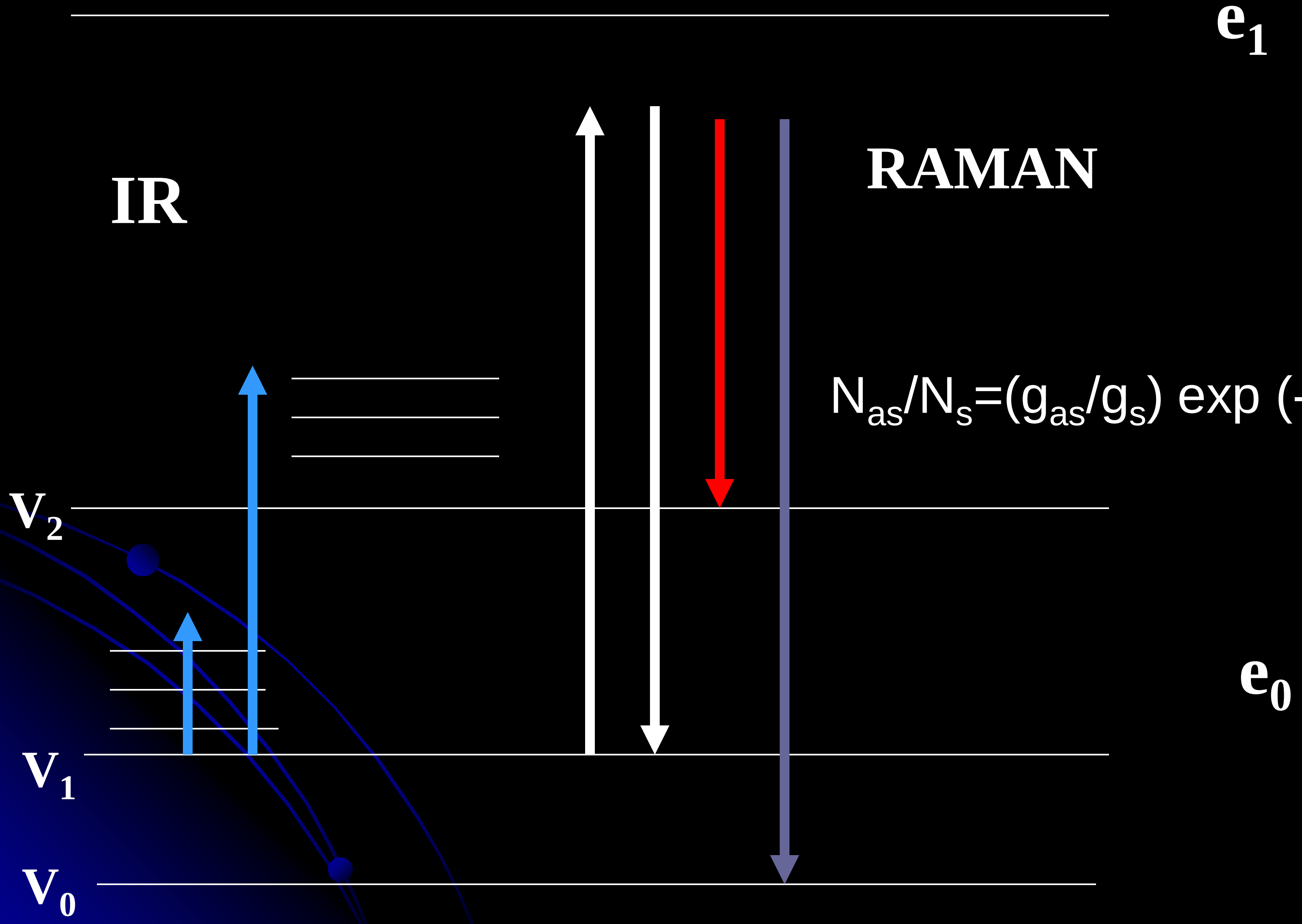
RAMAN Scattering

$$I(v) = K\,[\alpha]^2$$





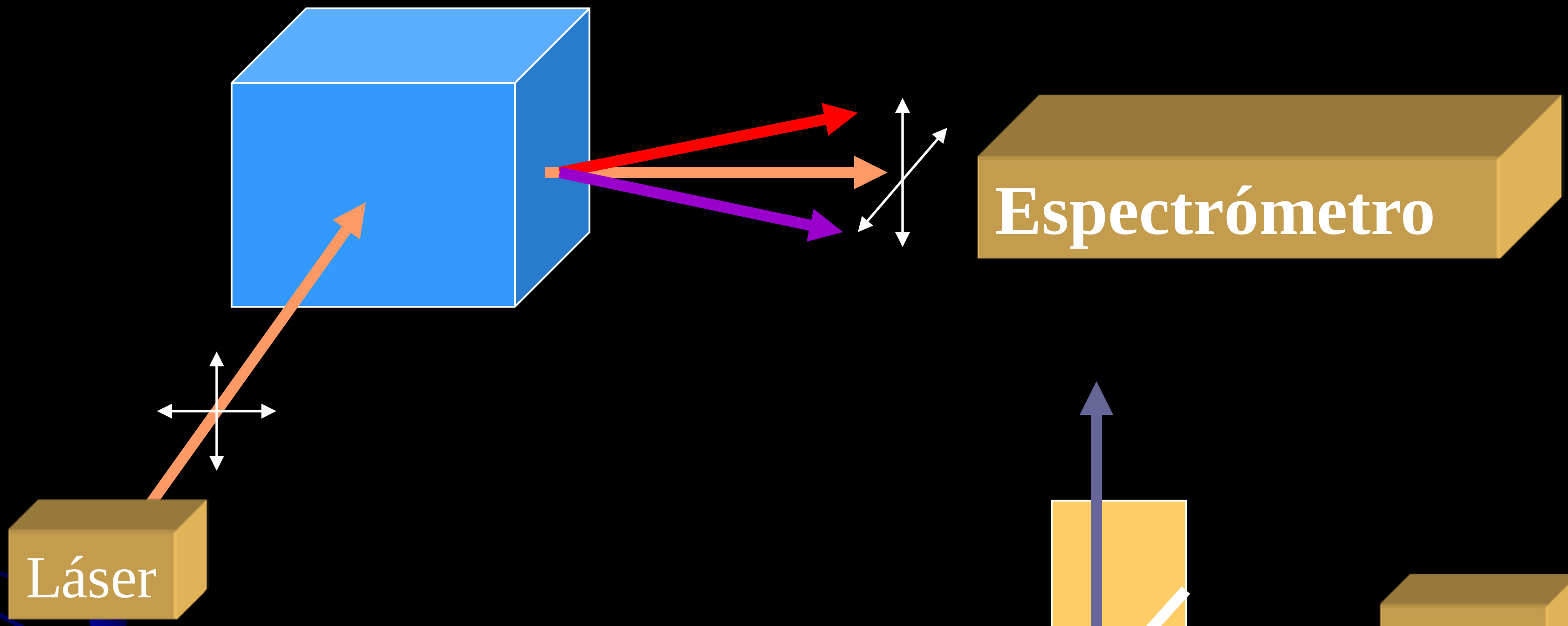
Vibracional Spectroscopy

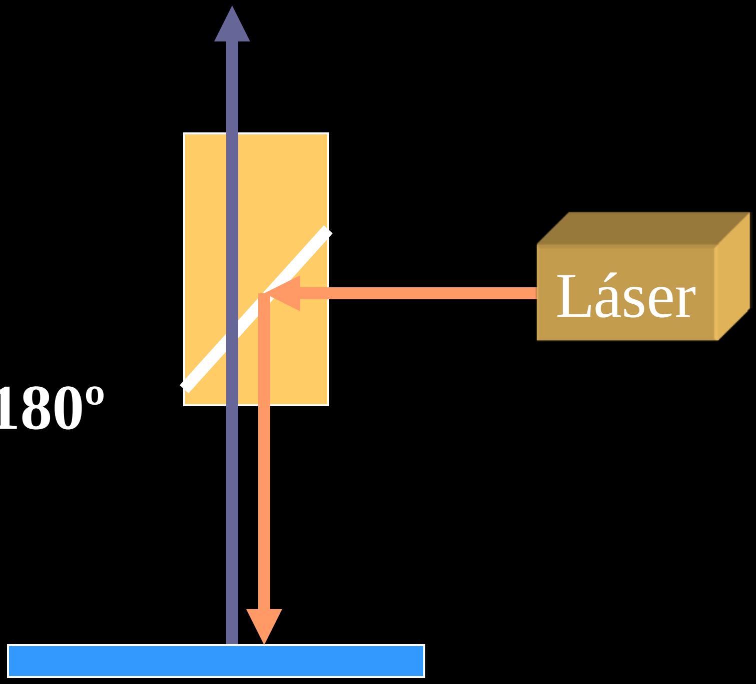


$N_{as}/N_s=(g_{as}/g_s)\ \exp\ (-\Delta E/KT)$

RAMAN

Configuración a 90º





Configuración a 180º

An interesting property of these invariants is that can be used to calculate the space average values of the individual tensor elements. In the case of a symmetric tensor we have

$$\overline{\alpha^2_{xx}} = \overline{\alpha^2_{yy}} = \overline{\alpha^2_{zz}} = \frac{45\bar{\alpha}^2 + 4\gamma^2}{45}$$

$$\overline{\alpha^2_{xy}} = \overline{\alpha^2_{yz}} = \overline{\alpha^2_{xz}} = \frac{\gamma^2}{15}$$

Thus a symmetric tensor can be expressed as the sum of two symmetric tensors using the above equations, $\alpha = \alpha_{iso} + \alpha_{aniso}$ where

$$\alpha_{iso} = \begin{pmatrix} \bar{\alpha} & 0 & 0 \\ 0 & \bar{\alpha} & 0 \\ 0 & 0 & \bar{\alpha} \end{pmatrix}$$

$$\alpha_{aniso} = \begin{pmatrix} \alpha_{xx} - \bar{\alpha} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} - \bar{\alpha} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} - \bar{\alpha} \end{pmatrix}$$

The isotropic part has no angular dependence and the anisotropic part is dependent on the orientation.

The Raman Intensity

According to the Placzek´s classical approach, the differential cross section for Raman scattering at right angles of the direction of an incident plane-polarised light for the vibration i described by the normal coordinate Q_i is given by

$$\frac{d\sigma_i}{dQ_i} = \frac{1}{45} C g_i \left[45(\bar{\alpha}_i')^2 + 7(\gamma_i')^2 \right]$$

where C is a constant, gi is the degeneracy of the i vibration and the quantity

$$A_i = \left[45(\bar{\alpha}_i')^2 + 7(\gamma_i')^2 \right]$$

is known as the Raman activity of the i vibration. This quantity is also known as the absolute differential Raman scattering cross section.

see Weber, 1979; Long, 1977; Bogaard & Haines, 1980; Hemert & Blow, 1981

The measured intensity under a monochromatic illumination of intensity I_0 is given by,

$$I_i = \frac{(2\pi)^4}{45} C g_i \frac{(\nu_0 - \nu_i)^4}{1 - \exp^{(-hc\nu_i/KT)}} A_i \cdot I_0$$

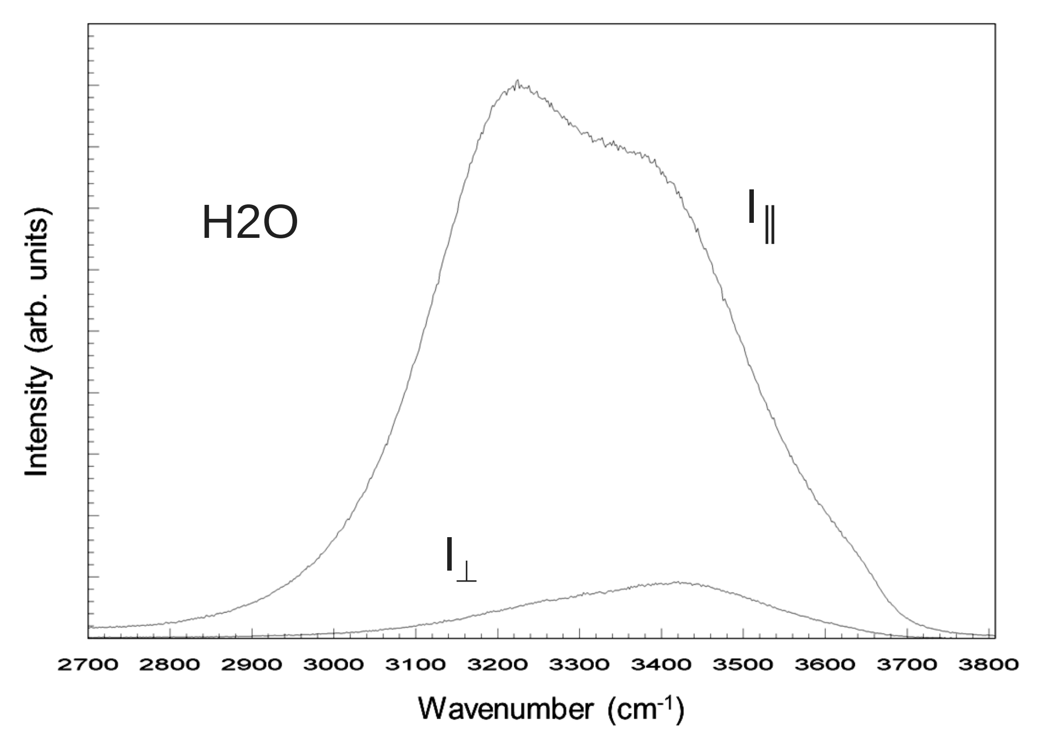
The main challenge for estimating the intensity of Raman vibrations in the condensed state is the difficulty to obtain the parameter Ai. Many work has been devoted to this task starting from isolated molecules. The problem is how to transfer Ai from the isolated molecule to the associated state.

In the case of liquids the key parameter is the internal field factor which derives in the most accepted form from Onsanger´s model of the dielectric molecular polarization. In this case the intensity measured under monochromatic illumination of intensity I_0 at 90º angle is given by

$$I_{i(liquid)} = \frac{(2\pi)^4}{45} C g_i \frac{(\nu_0 - \nu_i)^4}{1 - \exp^{(-hc\nu_i/KT)}} A_i \cdot \frac{n_i}{n_0} \frac{\left(n_i^2 + 2\right)^2 + \left(n_0^2 + 2\right)^2}{81}$$

In these cases the polarization properties can also supply important information about the symmetry properties of the molecular assemblages constituting the sample. The measure of the $I_{\parallel}$ intensity and $I_{\perp}$ intensity which are obtained analyzing the polarization parallel and perpendicular to the excitation polarization respectively allow estimating the depolarization ratio $\rho = I_{\perp} / I_{\parallel}$ for a given vibration

$$\rho = \frac{I_{\perp}}{\mathrm{I}_{\mathrm{II}}} = \frac{3(\gamma')^2}{45(\overline{\alpha'})^2 + 4(\gamma')^2}$$



Band shapes

When a molecular /atomic system is irradiated with an electromagnetic radiation the response is proportional to the correlation function of the elements that interact with the incident radiation and depending on its nature the response will be temporal, spatial or both. In the case of Raman spectroscopy the correlation is temporal and in the case of X-Ray diffraction is spatial.

Also the response is mediated by the interaction with the instrument: optics, slits, detectors, electronics…