“El efecto Raman y sus aplicaciones”

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

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 recommit 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

(publication of the discovery in the Calcuta’s newspapers on February 28th 1928)

A New Type of Secondary Radiation
C. V. Raman and K. S. Krishnan, Nature, 121(3048), 501, March 31, 1928
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.

Died on November 11th 1970.

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... ."
El efecto Raman:

Un descubrimiento “coordinado” ??
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....
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.
Espectro Raman CCl4

Primer espeetrógrafo usado por Raman
All these characteristics led to the idea that Raman spectroscopy could be a powerful technique for planetary exploration and in particular for detailed surface analysis on Mars.

Precedent developments

Instrument for MER
1998 Larry Haskin A. Wang
Raman en ExoMars y su evolución

2003: se presentaron 3 instrumentos
- Espectrómetro Raman-LIBS combinado: Fernando Rull (España/Francia/Inglaterra)
- Espectrómetro Raman J. Popp (Alemania)
- Espectrómetro LIBS E. Jessberger (Alemania)

La ESA propuso aunar a los tres equipos: Se formó el consorcio Raman-LIBS; Investigador Principal Fernando Rull, Co-IP Sylvestre Maurice

El principal reto tecnológico era ser capaz de desarrollar un espectrómetro combinado para ambas técnicas.

ESA convocó una ITT que ganó un consorcio industrial liderado por TNO (Holanda) con el apoyo científico del IP.
Kirchhoff_Bunsen_1823
Raman first spectrograph 1928
Larry Haskin et al. 1998
Raman Spectrum CCl4
Rull-UVA-BB 2003
S. Sharma 2008
Rull-UVA-BB/NTE 2005
Rull-UVA-Lidax 2011
PM#7 2009
RLS-2011

Raman Transmission Spectrometer Heritage
El instrumento RLS (estado actual)

<table>
<thead>
<tr>
<th>Masa</th>
<th>Basic Estimated (g)</th>
<th>Total including 10% contingency (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Spectrometer Unit (SPU)</td>
<td>853,00</td>
<td>938,30</td>
</tr>
<tr>
<td>13 Internal Optical Head (IOH)</td>
<td>209,15</td>
<td>230,00</td>
</tr>
<tr>
<td>14 ICEU</td>
<td>1076</td>
<td>1183</td>
</tr>
<tr>
<td>15 Instrument Optical Harness</td>
<td>7,50</td>
<td>9,00</td>
</tr>
<tr>
<td>16 Electrical Interconnect</td>
<td>175,86</td>
<td>193,45</td>
</tr>
<tr>
<td>4 Calibration Target</td>
<td>4,00</td>
<td>4,40</td>
</tr>
<tr>
<td>Total mass</td>
<td>2.325,01</td>
<td>2.558,20</td>
</tr>
</tbody>
</table>
Interesting feature detected (MicrOmega)

- Simulator General Description
  - XYZ positioners. 2.5µm resolution
  - Two cameras and objectives with a beamsplitter
  - Illumination system
  - Transmission Spectrometer and 532 nm laser
  - Raman iOH

- 1D sampling: along one line
- 2D mapping:
- Smart Collaborative science in coordination with other instruments
Mars environmental chamber & Simulator at UVA

- Liquid refrigeration down to -40°C
- Prepared for LN₂ refrigeration down to 77K (-196°C)
- Martian pressure and CO₂ atmosphere
- 12x30x1 mm³ viewport
- ExoMars-like sample container in copper integrated with refrigeration subsystem
- Flattener tool with angle selection
The Raman effect ?
The general process

\[ h\omega_0 = h\omega \text{ (Elastic)} \]

\[ |K_0| = |K| \]

\[ \lambda / \text{cm} \]

\[ \omega / \text{s}^{-1} \]

\[ |K| = \frac{2\pi}{\lambda} \text{ (cm}^{-1}) \]

\[ \omega = \frac{1}{T} = c/\lambda \]

\[ v = |K| = \frac{2\pi}{\lambda} = \frac{2\pi\omega}{c} \]
**ABSORCION EN EL INFRARROJO**

- Transmitancia: % $T = 100 \frac{I}{I_0}$
- Absorbancia: $A = -\log \left(\frac{\%T}{100}\right)$
- Ley de Lamber-Beer: $A = a \cdot b \cdot c$
- Ab. molar
- Espesor
- Concentración
- Rot. + Vib.
RAMAN Scattering

\[ I(v) = K \alpha^2 \]
Los fenómenos observados y por tanto la información obtenida no depende de la materia, solo de la radiación.

<table>
<thead>
<tr>
<th>Tipo</th>
<th>( \lambda )</th>
<th>( E )</th>
<th>Mecanismo</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-X</td>
<td>1 A</td>
<td>10E4 eV</td>
<td>Difracción, no espectroscopía</td>
</tr>
<tr>
<td>Neutrones</td>
<td>1 A</td>
<td>0.1 eV</td>
<td>Difracción, espectroscopía</td>
</tr>
<tr>
<td>Electrones</td>
<td>0.05 A</td>
<td>10E5 eV</td>
<td>Difracción, no espectroscopía</td>
</tr>
<tr>
<td>Fotón Optico</td>
<td>10E4A</td>
<td>0.1 eV</td>
<td>No difracc., espectroscopía</td>
</tr>
<tr>
<td>Fotón IR</td>
<td>10E5 A</td>
<td>0.1 eV</td>
<td>No difracc., espectroscopía</td>
</tr>
</tbody>
</table>

La distancia interatómica es del orden de 1 A y el valor de las excitaciones vibracionales del orden de 0.1 eV
Vibracional Spectroscopy

\[ \frac{N_{as}}{N_s} = \left( \frac{g_{as}}{g_s} \right) \exp \left( -\frac{\Delta E}{KT} \right) \]
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 $q_n(t) = q_{n0} \cos(\omega_n t)$,

\[
\begin{align*}
p &= \mu_0 + \alpha(0) E_0 \cos(\omega t) + \sum_{n=1}^{Q} \left( \frac{\partial \mu}{\partial q_n} \right)_0 q_{n0} \cos(\omega_n t) \\
&+ \frac{1}{2} E_0 \sum_{n=1}^{Q} \left( \frac{\partial \alpha}{\partial q_n} \right)_0 q_{n0} \left[ \cos(\omega + \omega_n) t + \cos(\omega - \omega_n) t \right]
\end{align*}
\]
Fig. 3.3 Time dependence of the linear induced dipoles $P^{(1)}$ produced by electromagnetic radiation of frequency $\omega_0$: (a) scattering molecule not vibrating $\omega_k = 0$: $P^{(1)} = P^{(1)}(\omega_0)$; and (b) scattering molecule vibrating with frequency $\omega_k$: $P^{(1)} = P^{(1)}(\omega_0) + P^{(1)}(\omega_0 - \omega_k) + P^{(1)}(\omega_0 + \omega_k)$
The matter is intrinsically DYNAMICS

\[ V(r) = -A/r^m + B/r^n \]

\[ V(r) = k \frac{r^2}{2} \]

\[ \omega = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \]

\[ T = E + V \]
Basic question: **description of vibrations**

Displacement coordinates $\Delta r = r - r_o$
\[ \Delta r_i = r_i - r_{oi} \]

\[ i = 1,2,3 \]

Total = 3N Coordinates of motion

3N-6 are vibrations
6 are whole motions

Normal coordinates \( Q_i \)
Descripción del Movimiento

A - Cada átomo se mueve con diferente $\omega_i$

B - Para cada frecuencia el conjunto se mueve sincrónicamente pero con diferentes amplitudes

( B ) Concepto de coordenada normal Q

Frecuencia propia $\omega$

N° de $Q_i = 3N-6$
**Coordenadas Cartesianas** \( (x_i) \) (3N)

**Coordenadas internas** \( (\Delta r, \delta \phi, \delta \tau) \)
- Significado físico
- Relación con potenciales
- Eliminan 6 movimientos (3N-6)

**Coordenadas de simetría** \( (S_i) \)
- Reducen la ecuación secular
- Describen la simetría del movimiento
- Permiten establecer las reglas de selección (IR, Raman)
- Se corresponden biunivocamente con las normales
- Se puede usar el formalismo de la teoría de grupos
The cartesian coordinates description

\[ \Delta r_i = r_i - r_{oi} \]

\[ \Delta x_i \quad \Delta y_i \quad \Delta z_i \]

The internal coordinates description

3N

3N-6
The symmetry properties

\[
\begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
A_1 \\
A_2 \\
A_3
\end{pmatrix}
= \begin{pmatrix}
A_1 \\
A_2 \\
A_3
\end{pmatrix} \rightarrow \chi(C_2) = 1
\]

\[
\begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\Delta r_1 \\
\Delta r_2 \\
\Delta \phi
\end{pmatrix}
= \begin{pmatrix}
\Delta r_1 \\
\Delta r_2 \\
\Delta \phi
\end{pmatrix} \rightarrow \chi(C_2) = 1
\]

<table>
<thead>
<tr>
<th></th>
<th>(C_{2v})</th>
<th>E</th>
<th>(C_2)</th>
<th>(\sigma_v)</th>
<th>(\sigma_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>A_1</td>
<td>A_1</td>
<td>A_2</td>
<td>A_2</td>
<td>A_1</td>
</tr>
<tr>
<td>Atom</td>
<td>A_2</td>
<td>A_2</td>
<td>A_1</td>
<td>A_1</td>
<td>A_2</td>
</tr>
<tr>
<td>Atom</td>
<td>A_3</td>
<td>A_3</td>
<td>A_3</td>
<td>A_3</td>
<td>A_3</td>
</tr>
<tr>
<td>Coord.</td>
<td>(\Delta r_1)</td>
<td>(\Delta r_1)</td>
<td>(\Delta r_2)</td>
<td>(\Delta r_2)</td>
<td>(\Delta r_1)</td>
</tr>
<tr>
<td>Coord.</td>
<td>(\Delta r_2)</td>
<td>(\Delta r_2)</td>
<td>(\Delta r_1)</td>
<td>(\Delta r_1)</td>
<td>(\Delta r_2)</td>
</tr>
<tr>
<td>Coord.</td>
<td>(\Delta \phi)</td>
<td>(\Delta \phi)</td>
<td>(\Delta \phi)</td>
<td>(\Delta \phi)</td>
<td>(\Delta \phi)</td>
</tr>
</tbody>
</table>
In the description of the molecular vibrations by the symmetry coordinates, the first step is the knowledge of the point group of symmetry of the molecule. The symmetry operations of this group are supposed to act not only on the positions but also on the displacement coordinates and their velocities. Consequently, \( T \) and \( V \) are invariant by the group.

The second step is the knowledge of the irreducible representations (I.R.) of the group. These are tabulated for all point groups and are represented by tables known as the group character tables (Wilson et al., 1955; Ferraro & Ziomek, 1969; Nakamoto, 1986; Cotton, 1983; Poulet & Mathieu, 1970).

In the third step we state that the set of \( k \) normal coordinates \( Q_{ik} \) associated with a natural frequency \( \omega_i \) form a basis for a R.I. of the \( G \) symmetry group of the molecule i.e. there is a bi-univocal correspondence between:

- normal coordinates,
- I.R. of the group \( G \),
- the species of symmetry,
- the coordinates of symmetry.
\[ S_1 (A_1) = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2) \]

\[ S_2 (A_1) = \Delta \phi \]

\[ S_3 (B_2) = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2) \]

The matrix \( U \) associated with this transformation \( S = UR \) is an orthogonal transformation (\( UU^t = E \)).
Now, knowing the U matrix that relates the internal coordinates with those of symmetry, the dynamic problem resolution can be addressed according to the GF method. The matrices of the reduced masses and force constants become:

\[
U \ G \ U^{-1} = G_s \quad \quad U \ F \ U^{-1} = F_s
\]

And the secular equation of the system is then written:

\[
\begin{vmatrix}
G_s & F_s - \lambda E \\
\end{vmatrix} = 0
\]
NORMAL MODES IN WATER MOLECULE

$S_1 = Q_1$

Symmetric Stretch
$3657 \text{ cm}^{-1}$

$S_2 = Q_2$

Bend $1595 \text{ cm}^{-1}$

$S_3 = Q_3$

Asymmetric Stretch
$3756 \text{ cm}^{-1}$
RAMAN

Configuración a 90°

Espectrómetro

Láser

Configuración a 180°

Láser
\[
\begin{pmatrix}
    E_x \\
    E_y \\
    E_z
\end{pmatrix}
\begin{pmatrix}
    \alpha'_{xx} & \alpha'_{xy} & \alpha'_{xz} \\
    \alpha'_{yx} & \alpha'_{yy} & \alpha'_{yz} \\
    \alpha'_{zx} & \alpha'_{zy} & \alpha'_{zz}
\end{pmatrix}
= \begin{pmatrix}
    P_x \\
    P_y \\
    P_z
\end{pmatrix}
\]

Direction of propagation of the incident light

Direction of propagation of the scattered light

Polarization of the incident light

Polarization of the scattered light

ESQUEMA GENERAL

ESPECTROMETRO RAMAN

Instrumentación

Láser

Cabezal Raman

Muestra

Análisis e interpretación de espectros

Transmisión de datos

CCD

Espectrómetro
I(v) = Distribución espectral de Intensidad

Información
- Número de bandas
- Parámetros de banda

APLICACIONES
- Analíticas
- Estructurales

Posición / Nº de onda (v)
Intensidad (I)
Anchura (A)
Intensidad integrada S(v)
Anchura Integrada (β)
Perfil de banda (G/L)
Factor de forma del perfil
APLICACIONES ANALITICAS

Identificación de sustancias
Cuantificación

APLICACIONES ESTRUCTURALES

Análisis de los modos de vibración
Asignación de modos
(Geometría, GE, GP)
Perturbaciones al espectro
(Dinámicas, Estructurales)
Aplicaciones
Ciencia y tecnología de materiales

ATR (puntos verdes), Raman (puntos rojos)

ECCS

COL-93

MCR2

Raman

Espectros comparativos

Intensidad (unidades arbitrarias)

Wavenumber / cm⁻¹

250 500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3250

-0.0032 0.0030 0.0027 0.0024 0.0021 0.0018 0.0015 0.0012 0.0009 0.0006 0.0003 0.0000
El Hombre de los Alpes

Iglesia de Basconcillos del Tozo, Burgos, Siglo XIV

Cinabrio – Jesús
Lazurita – La Virgen
Cinabrio/minio-Sta. Ana
Minio/ocres-Apóstoles
Ocres+ carbón-
Otras figuras

ICEMAN

HOMBRE ACTUAL
El Beato de Valcavado, Saldaña (Palencia) fue escrito por el monje OBECO bajo el mandato del abad SEMPRONIO en el verano de 970 (Entre el 8 de Junio y el 8 de Septiembre). Consta de 230 folios y faltan 14 folios.

- Cinabrio (HgS)
- Minio (Pb₃O₄)
- Oropimente (As₂S₃)
- Verdigris (cardenillo)
Muchas gracias