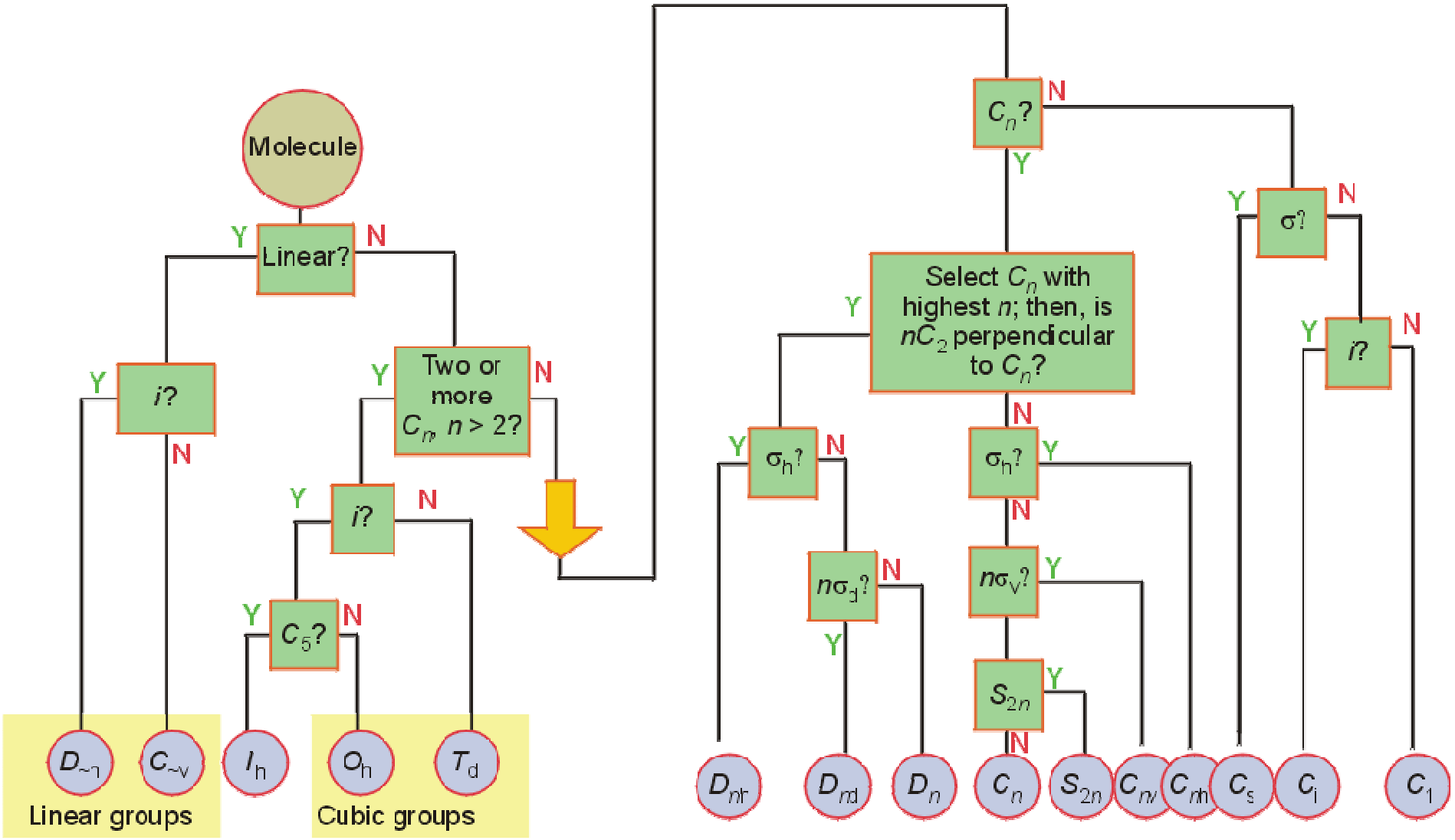
INTERNATIONAL SCHOOL
14th to 16th JUNE, NANCY (FRANCE)
RAMAN SPECTROSCOPY APPLIED TO EARTH SCIENCES AND CULTURAL HERITAGE

Theory of Raman Spectroscopy

Fernando Rull & Valentín García Baonza

MOLECULAR SYMMETRY CLASSIFICATION (POINT GROUP)



CHARACTER TABLES

Point Group

Symmetry Operations

Order C_{2v} $(h) = 4$ (1 E, 1 C_2, 1 σ_v, 1 σ'_v)

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Classes

Character: χ

Irreducible Representation for B_2

Irreducible Representation (Γ_i)

In vibrational spectroscopy we are very concerned with the symmetry of each normal mode of vibration in a molecule.

Each normal mode of vibration will (behaves like) form a basis for an irreducible representation of the point group of the molecule.

The transformation of all the atomic displacements (coordinates) will result in what we shall call a **Reducible Representation**, which should be expressed as a sum of Irreducible Representations (**Symmetry Modes**)

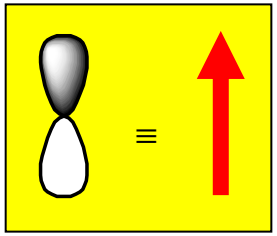
CHARACTER TABLES

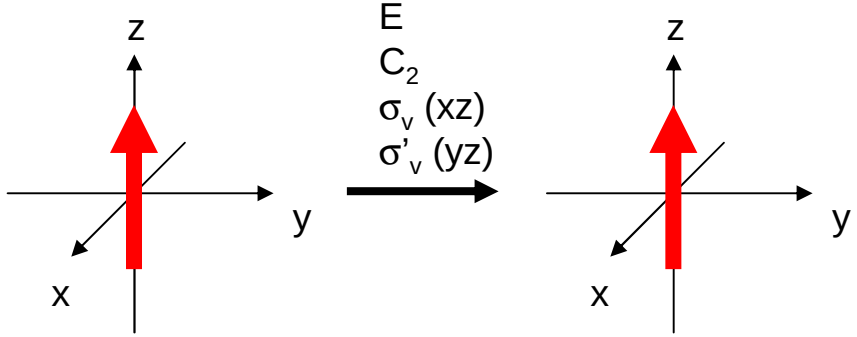
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Simmetry of Functions

C_{2v}

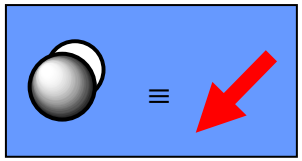
orbital p_z

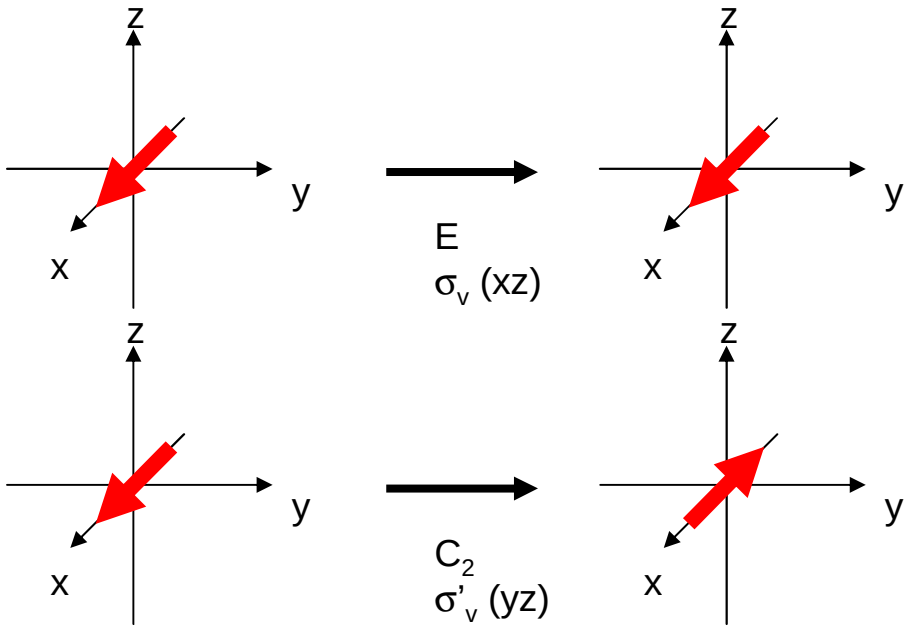




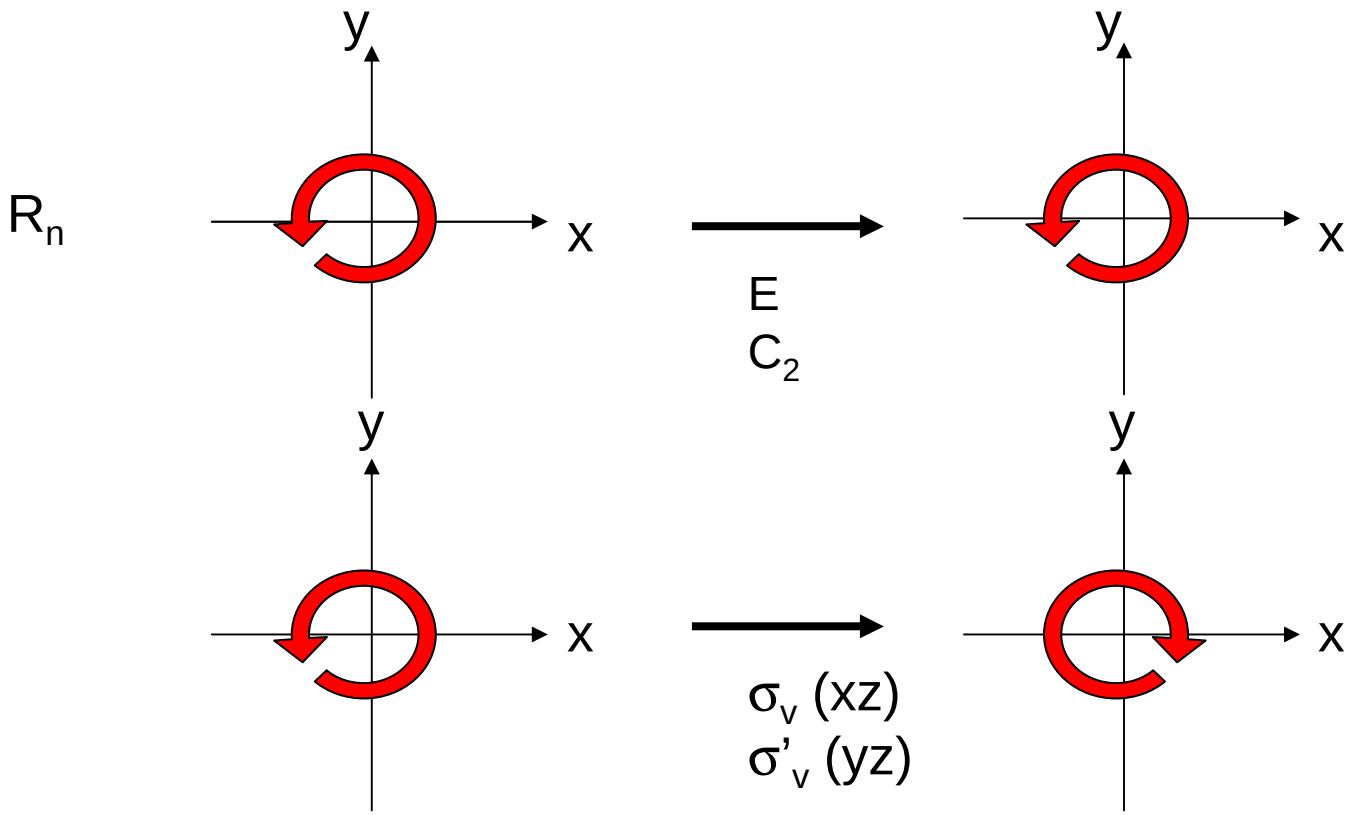
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

orbital p_x



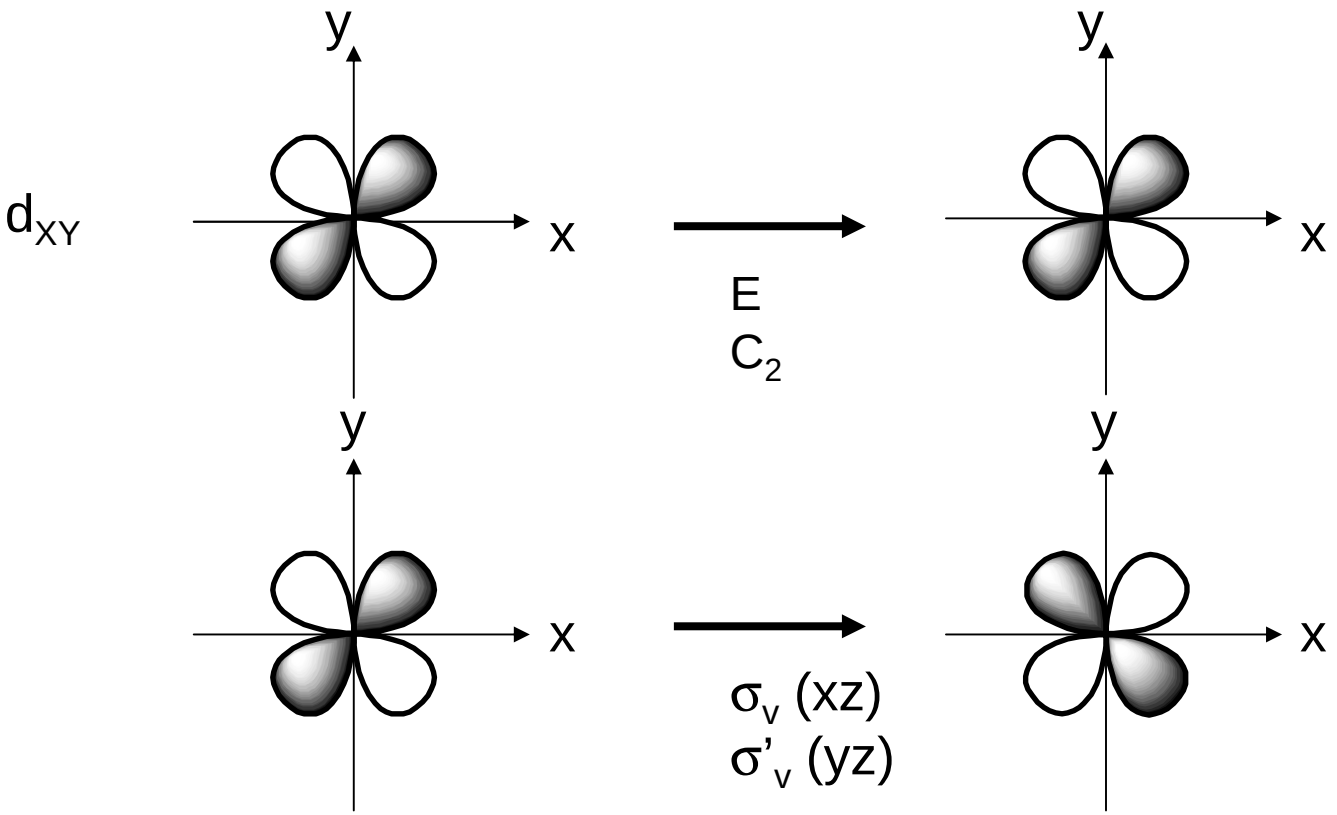


C_{2v}



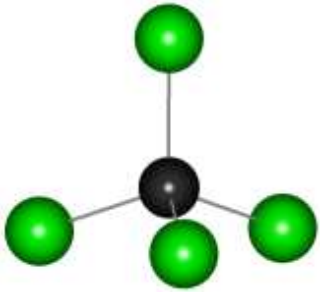
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{2v}



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

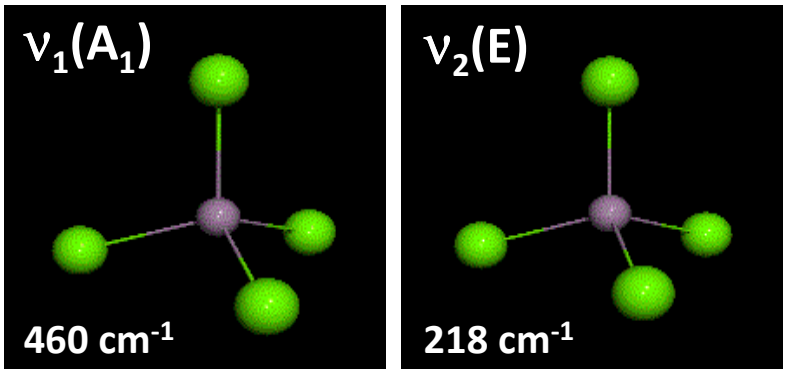
MOLECULAR VIBRATIONS

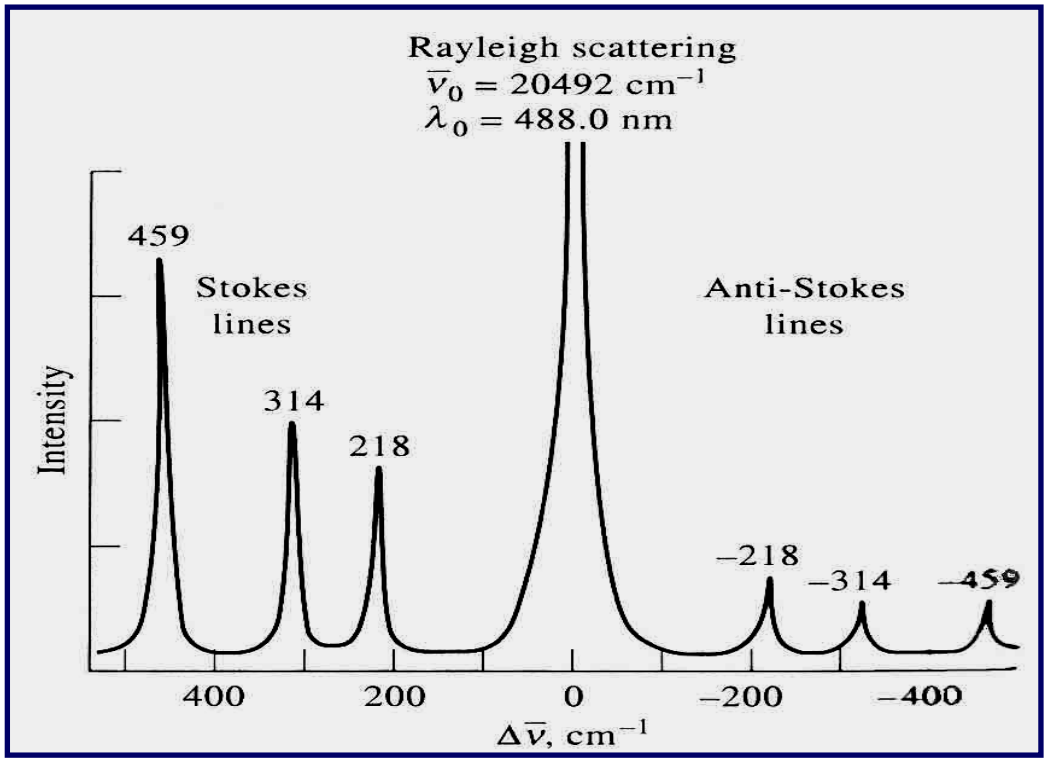


$\Gamma = A_1+E+T_1+3T_2$

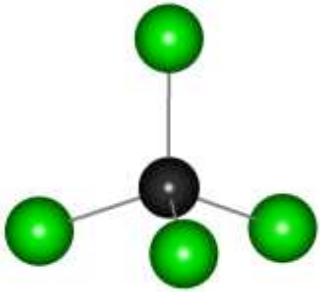
$\Gamma_{VIB} = A_1+E+2T_2$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	xyz
A_2	+1	+1	+1	-1	-1	-	-	-
E	+2	-1	+2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$
T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)	(x^3, y^3, z^3) $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$



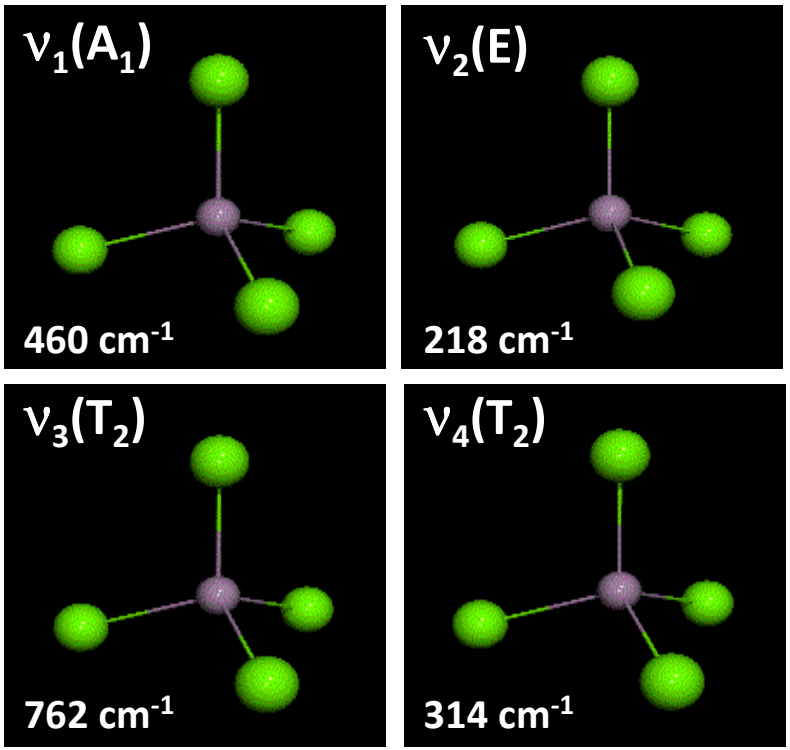


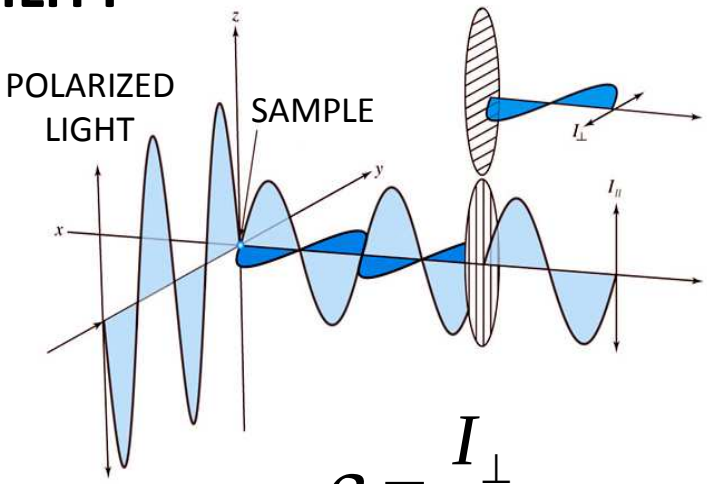
MOLECULAR VIBRATIONS AND POLARIZABILITY



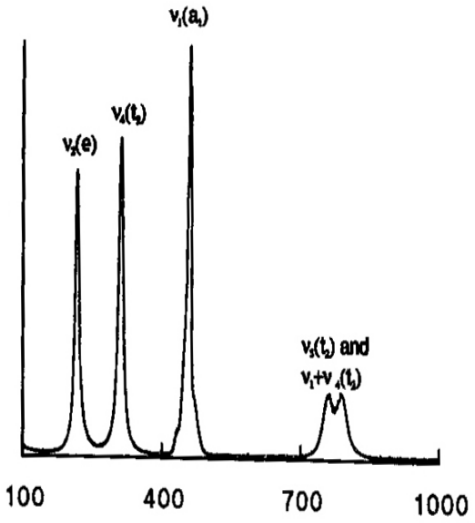
$$\Gamma = A_1+E+T_1+3T_2$$

$$\Gamma_{VIB} = A_1+E+2T_2$$

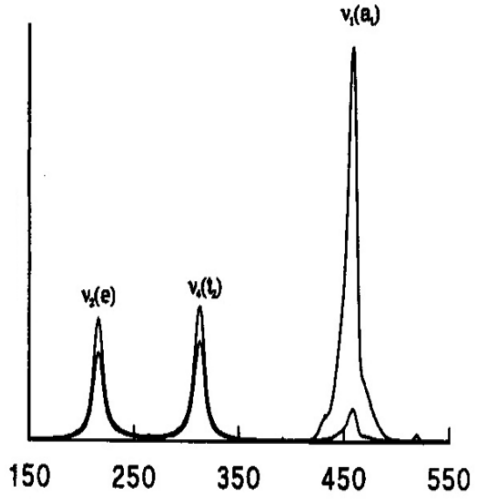




$$\rho = \frac{I_\perp}{I_{II}}$$

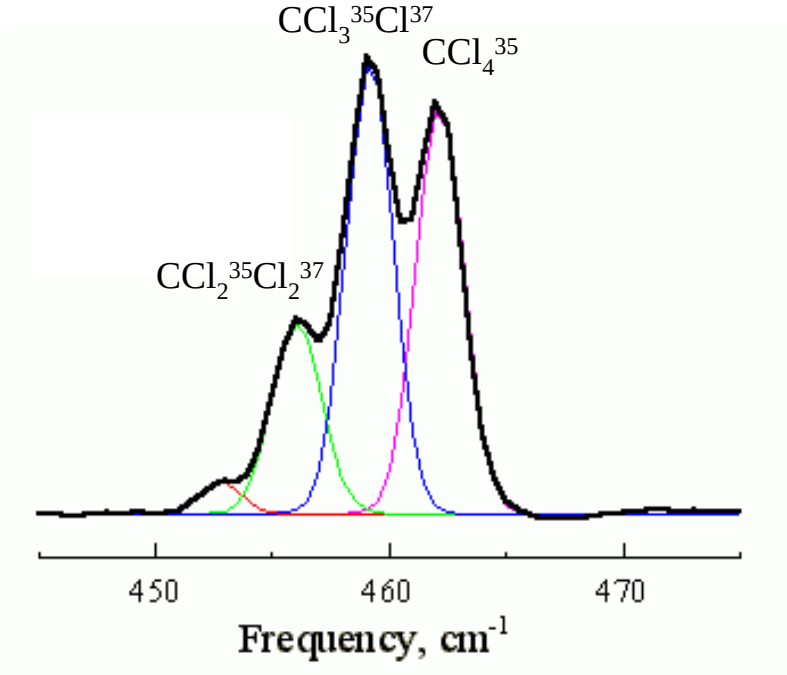


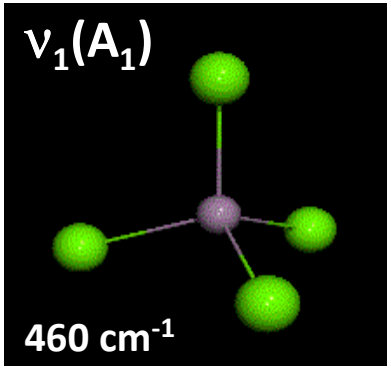
Wavenumber (cm^{-1})

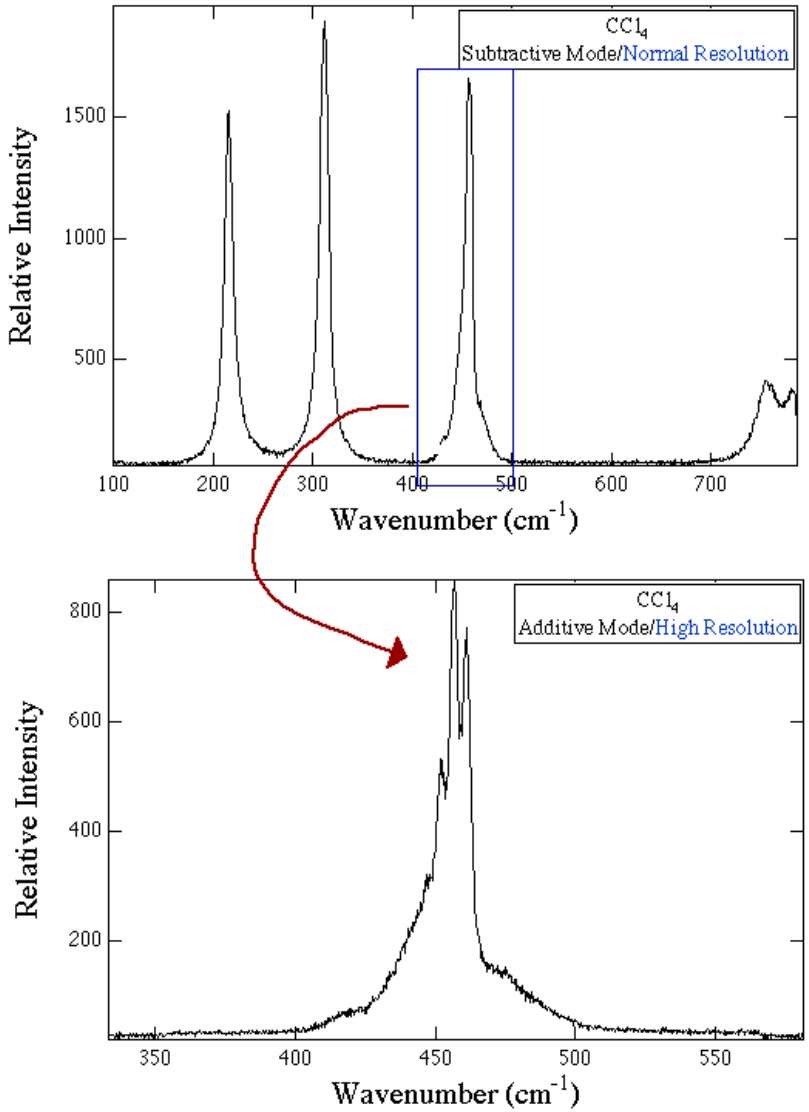


Wavenumber (cm^{-1})

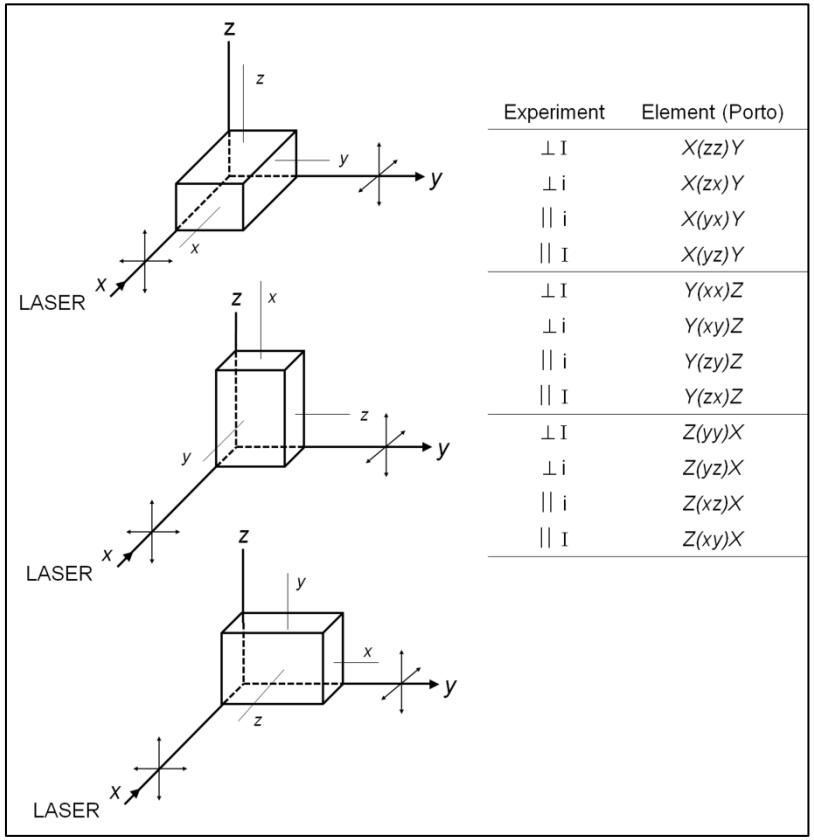
ISOTOPIC CONTRIBUTIONS



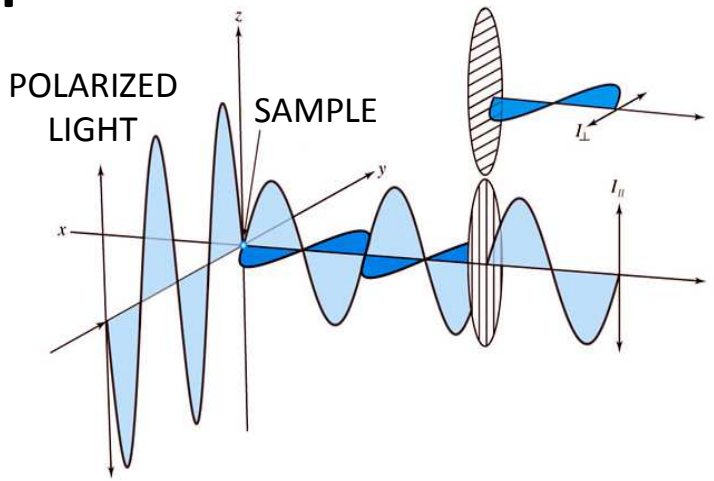


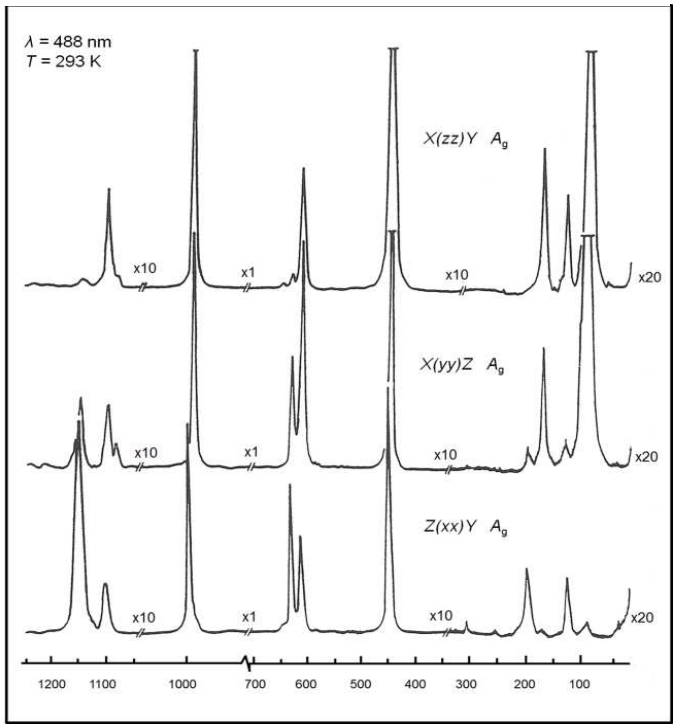


CRYSTAL VIBRATIONS AND POLARIZABILITY



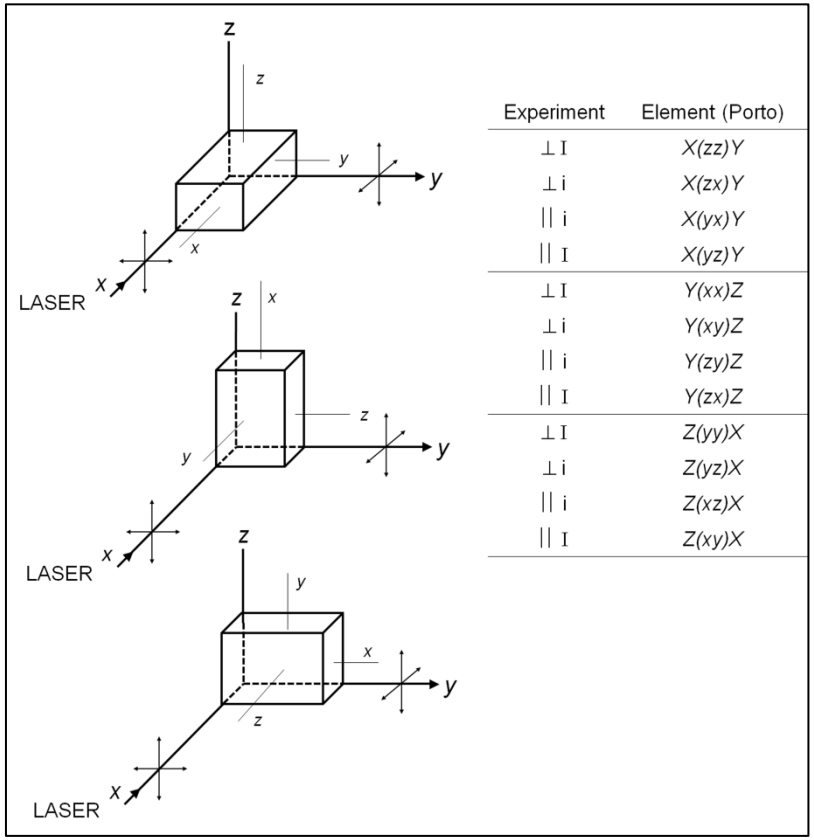
Experiment	Element (Porto)
⊥ I	*X(zz)Y*
⊥ i	*X(zx)Y*
∥ i	*X(yx)Y*
∥ I	*X(yz)Y*
⊥ I	*Y(xx)Z*
⊥ i	*Y(xy)Z*
∥ i	*Y(zy)Z*
∥ I	*Y(zx)Z*
⊥ I	*Z(yy)X*
⊥ i	*Z(yz)X*
∥ i	*Z(xz)X*
∥ I	*Z(xy)X*



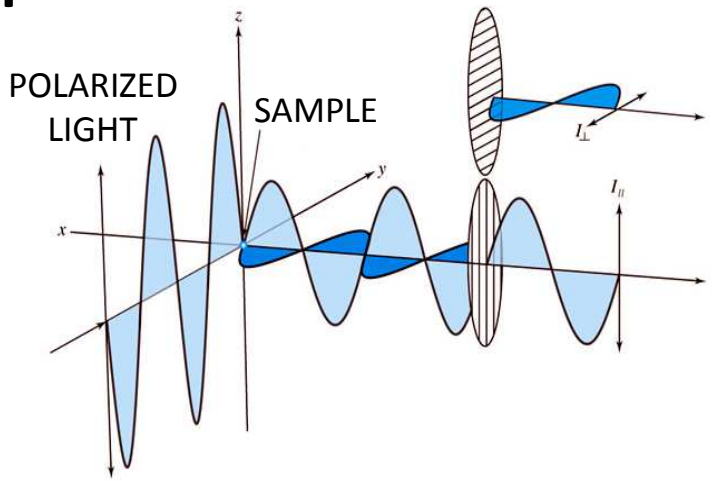


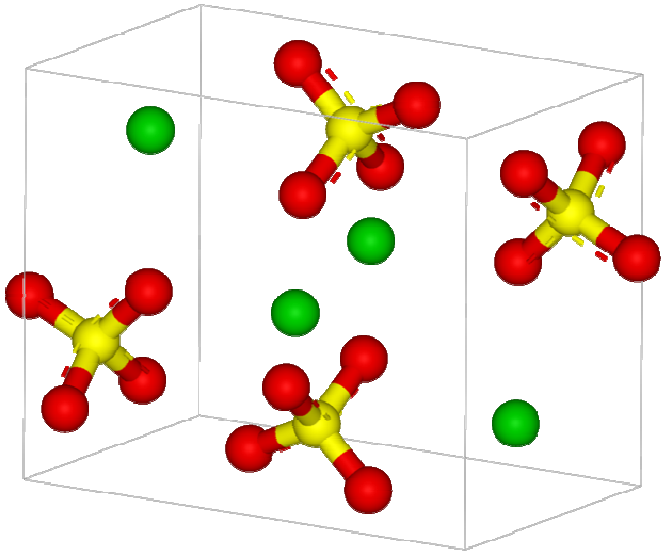
Celestine ($SrSO_4$)
Vibrations of SO_4^{2-} group
-Symmetry group in the free state T_d (43*m*)
-Symmetry domain group C_s (*m*)
-Crystallographic factor group D_{2h} (*mmm*)

CRYSTAL VIBRATIONS AND POLARIZABILITY



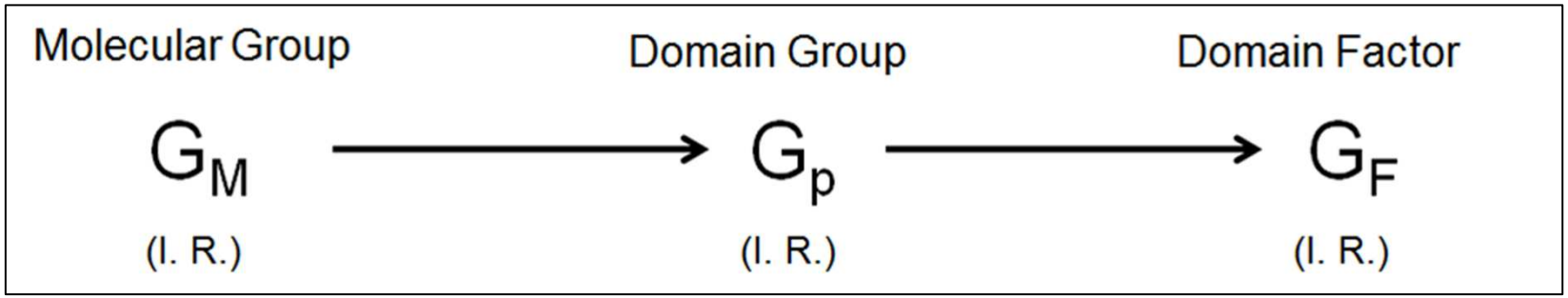
Experiment	Element (Porto)
⊥ I	*X(zz)Y*
⊥ i	*X(zx)Y*
|| i	*X(yx)Y*
|| I	*X(yz)Y*
⊥ I	*Y(xx)Z*
⊥ i	*Y(xy)Z*
|| i	*Y(zy)Z*
|| I	*Y(zx)Z*
⊥ I	*Z(yy)X*
⊥ i	*Z(yz)X*
|| i	*Z(xz)X*
|| I	*Z(xy)X*



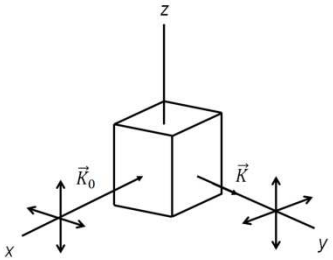


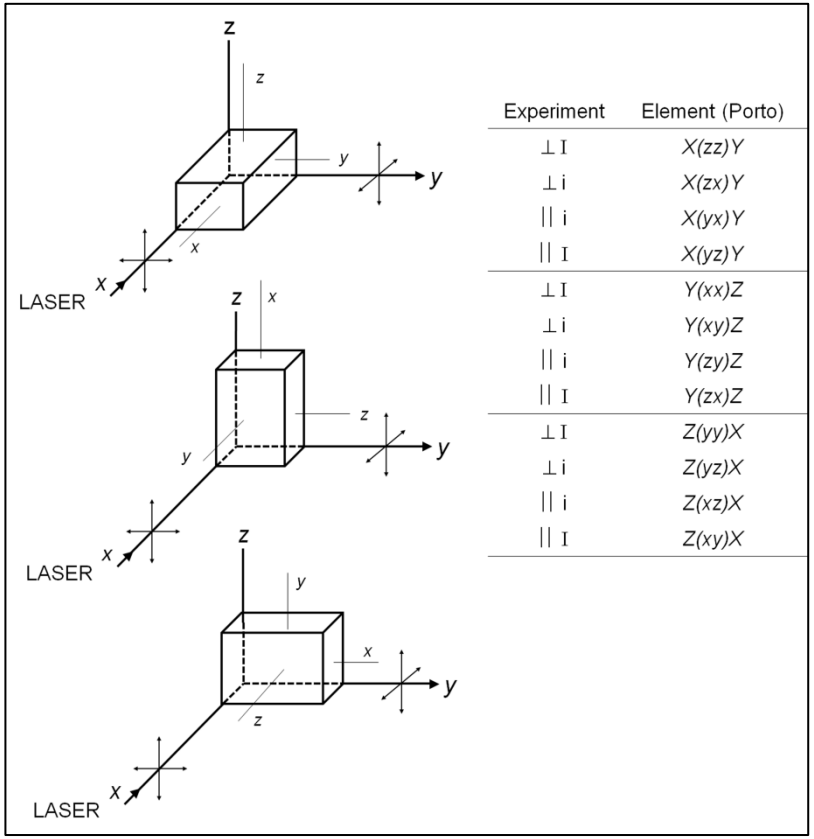
Celestine ($SrSO_4$)
Vibrations of SO_4^{2-} group
-Symmetry group in the free state T_d (43*m*)
-Symmetry domain group C_s (*m*)
-Crystallographic factor group D_{2h} (*mmm*)

SYMMETRY IN CRYSTALS



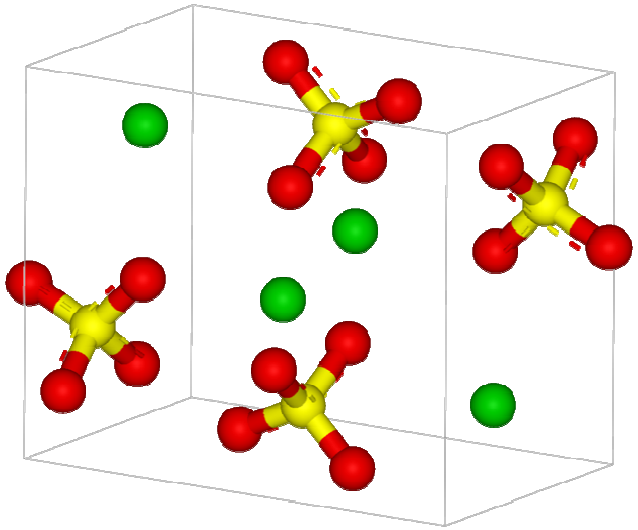
$$\begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \begin{pmatrix} \alpha'_{xx} & \alpha'_{xy} & \alpha'_{xz} \\ \alpha'_{yx} & \alpha'_{yy} & \alpha'_{yz} \\ \alpha'_{zx} & \alpha'_{zy} & \alpha'_{zz} \end{pmatrix} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix}$$





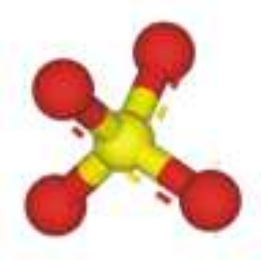
Experiment	Element (Porto)
⊥ I	*X(zz)Y*
⊥ i	*X(zx)Y*
|| i	*X(yx)Y*
|| I	*X(yz)Y*
⊥ I	*Y(xx)Z*
⊥ i	*Y(xy)Z*
|| i	*Y(zy)Z*
|| I	*Y(zx)Z*
⊥ I	*Z(yy)X*
⊥ i	*Z(yz)X*
|| i	*Z(xz)X*
|| I	*Z(xy)X*

CRYSTAL VIBRATIONS AND RAMAN ACTIVITY



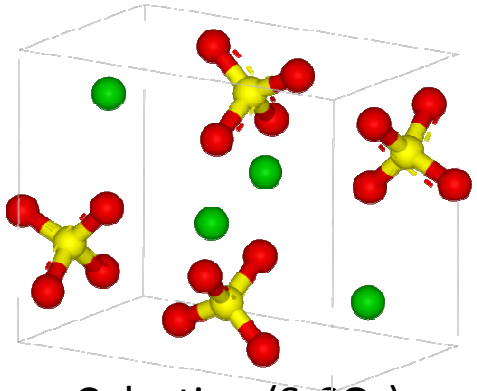
Celestine ($SrSO_4$)

Vibrations of SO_4^{2-} group



Molecular Group	Domain Group	Domain Factor
G_M	G_p	G_F
(I. R.)	(I. R.)	(I. R.)
T_d (43m)	C_s (m)	D_{2h} (mmm)

CRYSTAL VIBRATIONS AND RAMAN ACTIVITY

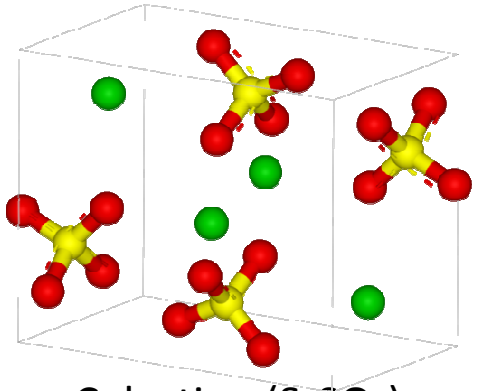


Celestine ($SrSO_4$)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Free SO_4^{2-} Symmetry Group (T_d)		Domain Symmetry Group ($C_s(xz)$)		Symmetry Factor Group of crystal (D_{2h})
$\nu_1(A_1)$	---------	4x A'	---------	$A_g+B_{2g}+B_{1u}+B_{3u}$
$\nu_2(E)$	---------	4x $A'+A''$	---------	$A_g+B_{2g}+B_{1u}+B_{3u}+$ $A_u+B_{1g}+B_{3g}+B_{2u}$
$\nu_3,\nu_4(F_2)$	---------	4x $2(2A'+A'')$	---------	$2(2A_g+2B_{2g}+2B_{1u}+2B_{3u}+$ $A_u+B_{1g}+B_{3g}+B_{2u})$
9		36		36

CRYSTAL VIBRATIONS AND RAMAN ACTIVITY

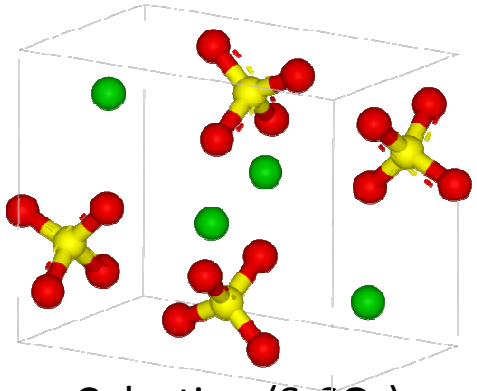


Celestine ($SrSO_4$)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Free SO_4^{2-} Symmetry Group T_d (43m)		Domain Symmetry Group (C_s(xz))		Symmetry Factor Group of crystal (D_{2h})
Translation SO_4^{2-} 4x T_x T_y T_z (F_2)	---------	4x 2A'+A''	---------	2(A_g+B_{2g}+B_{1u}+B_{3u})+ A_u+B_{1g}+B_{3g}+B_{2u}
Translation Sr^{2+} 4x T_x T_y T_z	---------	4x 2A' 4x A''	---------	2(A_g+B_{2g}+B_{1u}+B_{3u})+ A_u+B_{1g}+B_{3g}+B_{2u}
Librations SO_4^{2-} 4x R_x R_y R_z (F_1)	---------	4x A'+2A''	---------	A_g+B_{2g}+B_{1u}+B_{3u}+ 2(A_u+B_{1g}+B_{3g}+B_{2u})
		36		36

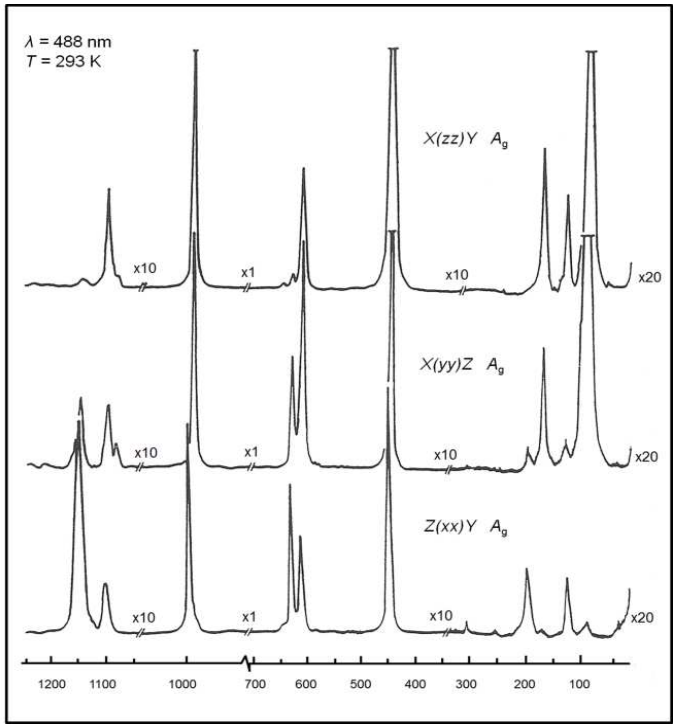
CRYSTAL VIBRATIONS AND RAMAN ACTIVITY



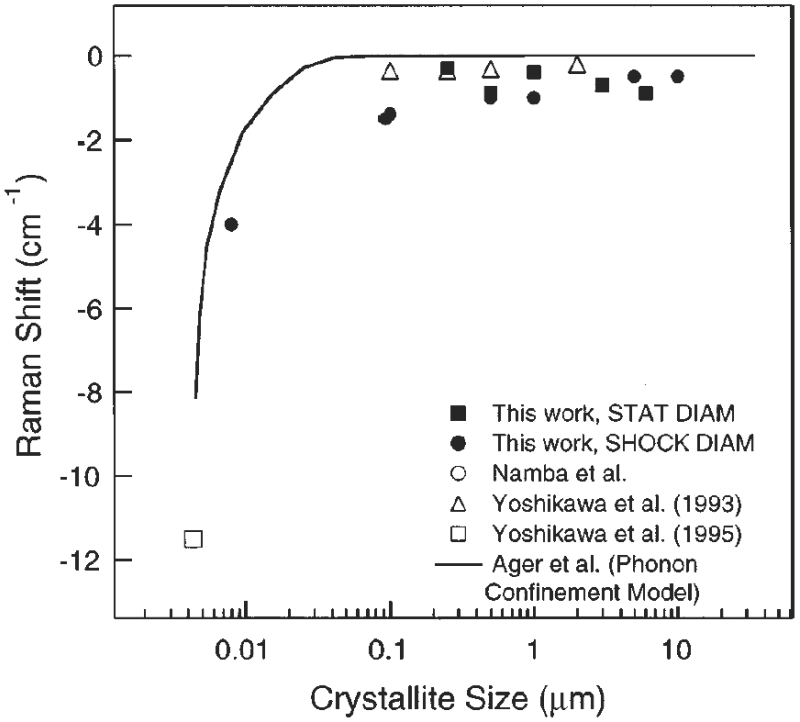
Celestine ($SrSO_4$)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{2h} Symmetry Type	Raman	IR
A_g	Active	-
A_u	-	-
B_{1g}	Active	Active
B_{2g}	Active	Active
B_{3g}	Active	Active
B_{1u}	-	Active
B_{2u}	-	Active
B_{3u}	-	Active



PHONONS IN DIAMOND: SIZE EFFECTS



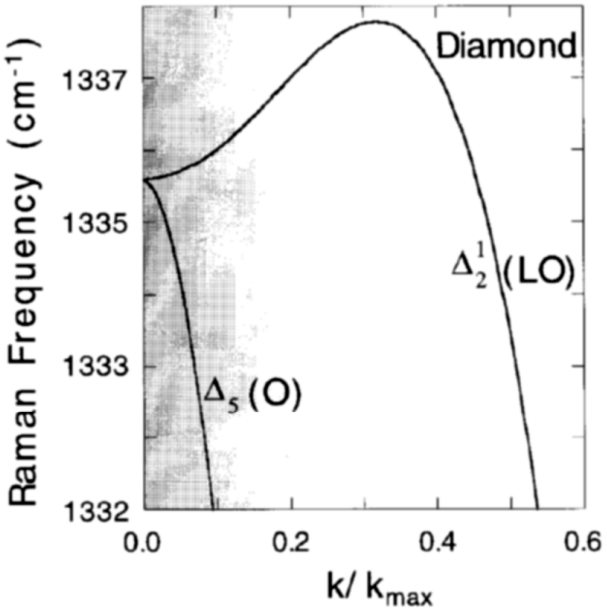


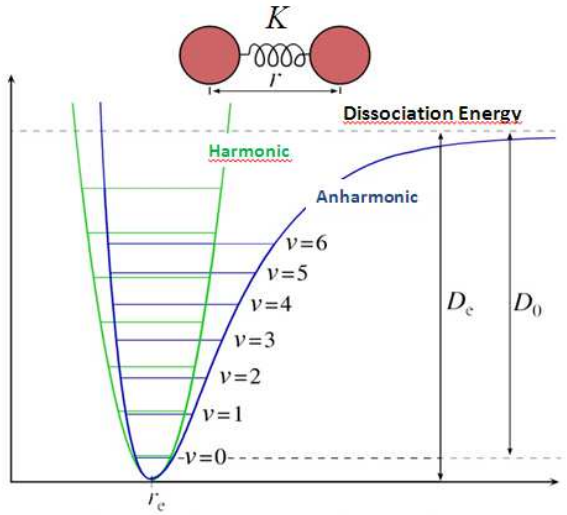
FIG. 6. Phonon dispersion curves for diamond along the $\Gamma \overset{\Delta}{-} X$ direction near the Γ point, from Ref. 45. The modes near the Γ point will contribute more strongly to the observed Raman signal, as conceptualized by the gradient-shaded region. The actual observed Raman signal is a complicated weighted average of all the modes in $\vec{k}$ space within the Brillouin zone.

Phonon confinement

$$\Psi(\vec{k},\vec{r}) = u(\vec{k},\vec{r})e^{i\vec{k}\cdot\vec{r}}$$

$$\Phi(\vec{k},\vec{r}) = \frac{1}{(2\pi)^3}\int d^3k_0 C(\vec{k},\vec{k}_0)e^{i\vec{k}_0\cdot\vec{r}} \longrightarrow I(\omega) \cong \int \frac{\exp(-k^2L^2/4)4\pi k^2}{[\omega-\omega(k)]^2+(\Gamma_0/2)^2}dk$$

PHONONS IN DIAMOND: PRESSURE AND TEMPERATURE EFFECTS

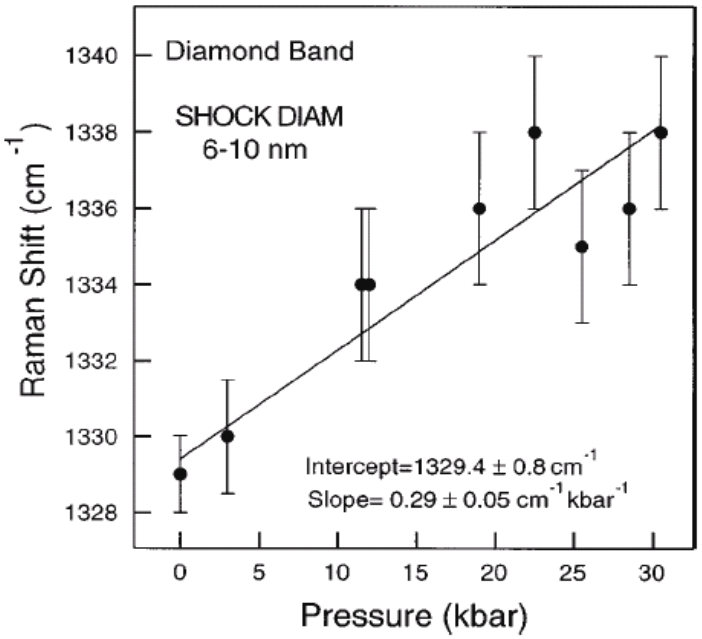


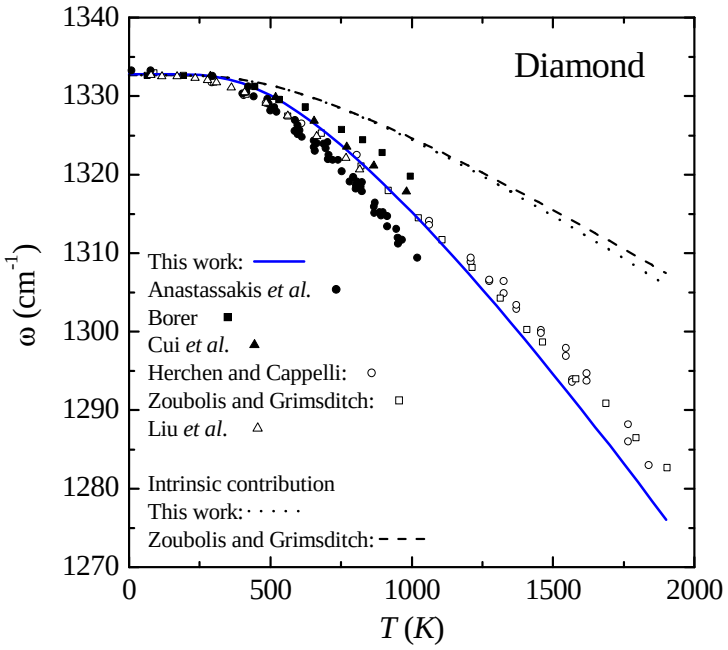
$$\text{Harmonic Energy} = \frac{1}{2} K r^2$$

K : force constant

$$\omega = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

μ : reduced mass

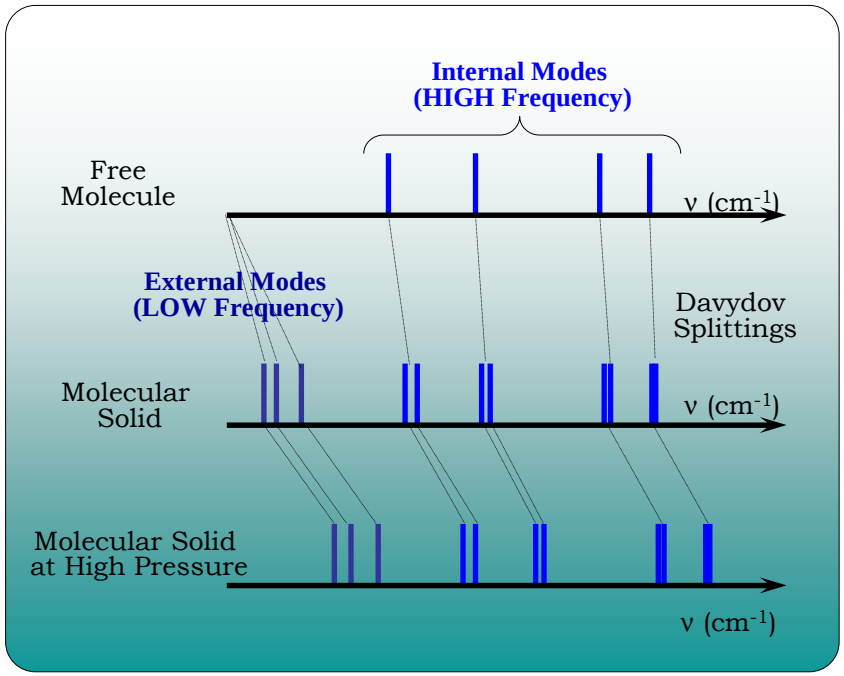


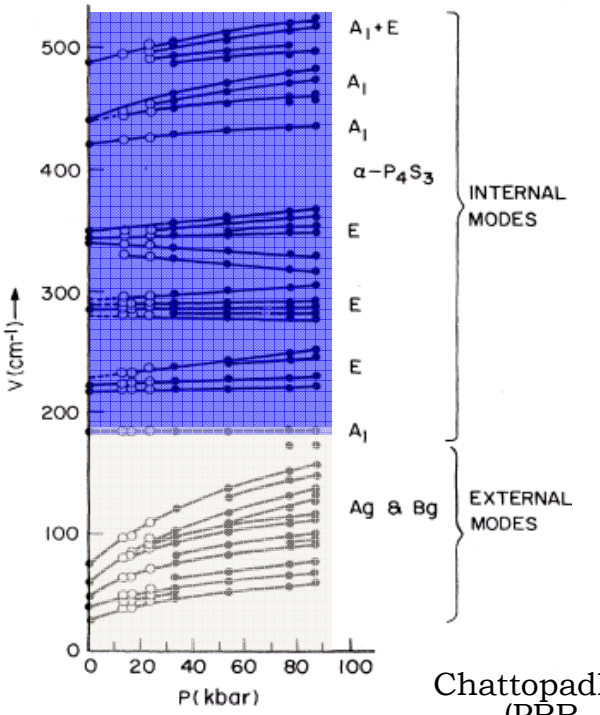


GRÜNEISEN PARAMETERS AND DAVIDOV SPLITTINGS

$$\gamma_j = -\frac{V}{\nu_j}\left(\frac{\partial \nu_j}{\partial V}\right)_T = -\left(\frac{\partial \ln \nu_j}{\partial \ln V}\right)_T \qquad \gamma_j = \frac{B_T}{\nu_j}\left(\frac{\partial \nu_j}{\partial p}\right)_T = B_T\left(\frac{\partial \ln \nu_j}{\partial p}\right)_T \qquad B_T = -V\left(\frac{\partial p}{\partial V}\right)_T$$

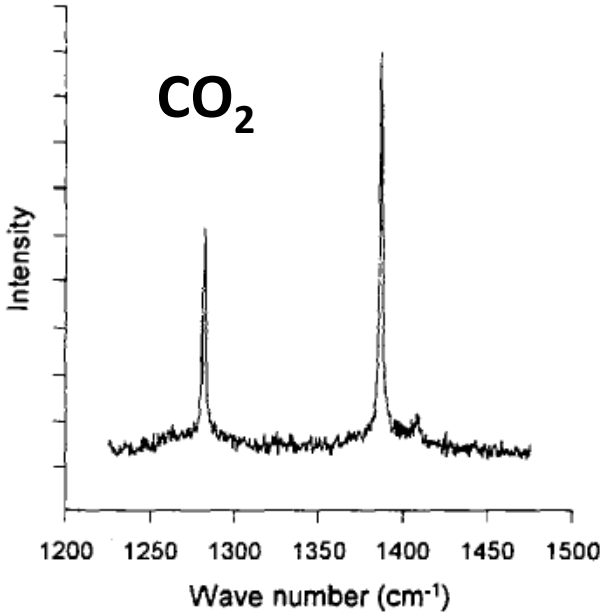
Elementary vibrational model for Molecular Crystals





Chattopadhyay et al.
(PRB, 1981)

FERMI RESONANCE



Two level Perturbation Model

$\delta = \nu_+ - \nu_-$

$R = I_+ / I_-$

W: Fermi Coupling Parameter

$$W = \delta (R)^{1/2} / (R+1)$$

$$\delta_0 = [\delta^2 - 4W^2]^{1/2}$$

$$\nu_+^{\,0} = \nu_+ - 1/2[\delta - \delta_0]$$

$$\nu_-^{\,0} = \nu_- + 1/2[\delta - \delta_0]$$

Exact Degeneration:

δ_0 is zero
δ is minimum
R =1

$$R = \left[\frac{(\delta+\delta_0)^{1/2} R_0^{\,1/2} + (\delta-\delta_0)^{1/2}}{(\delta-\delta_0)^{1/2} R_0^{\,1/2} - (\delta+\delta_0)^{1/2}} \right]^2$$

FERMI RESONANCE

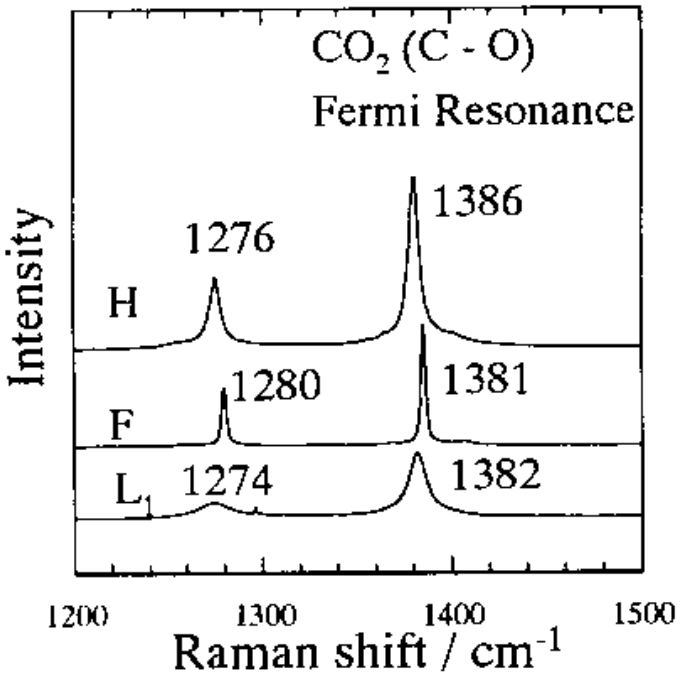
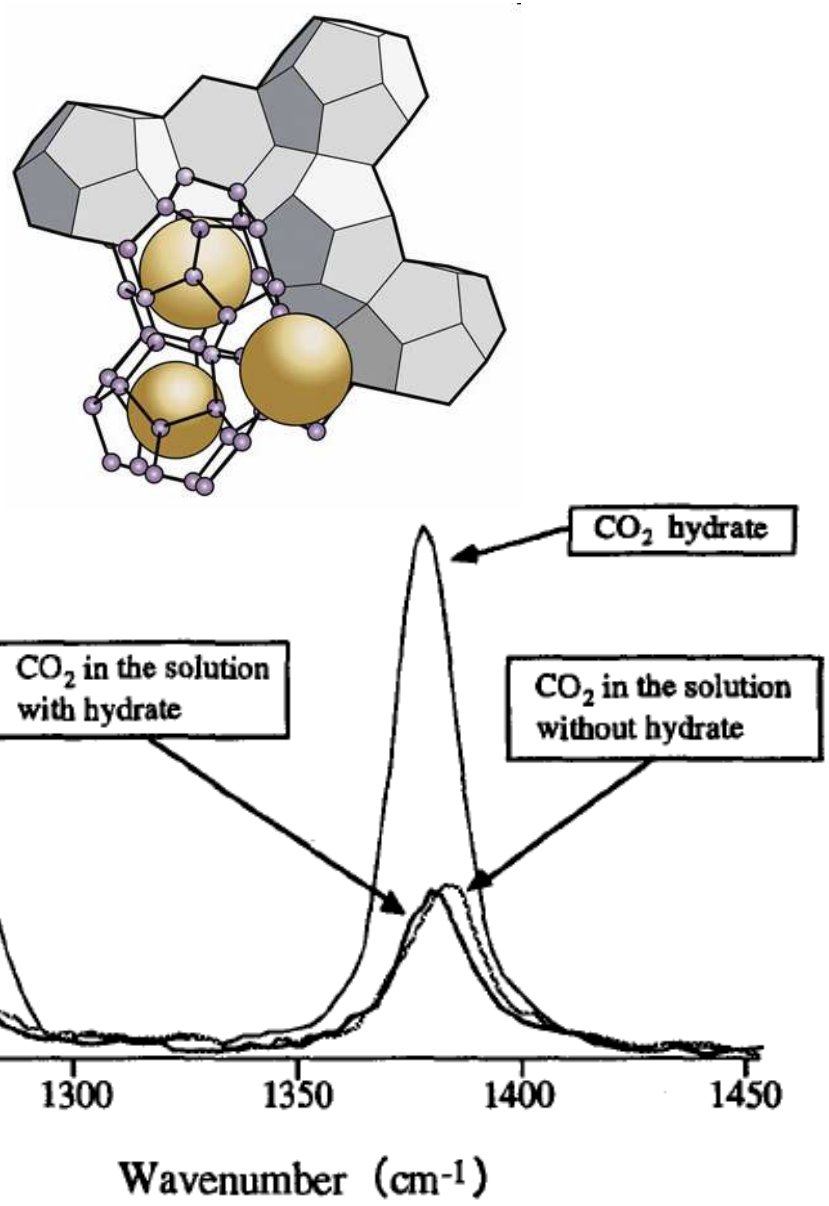
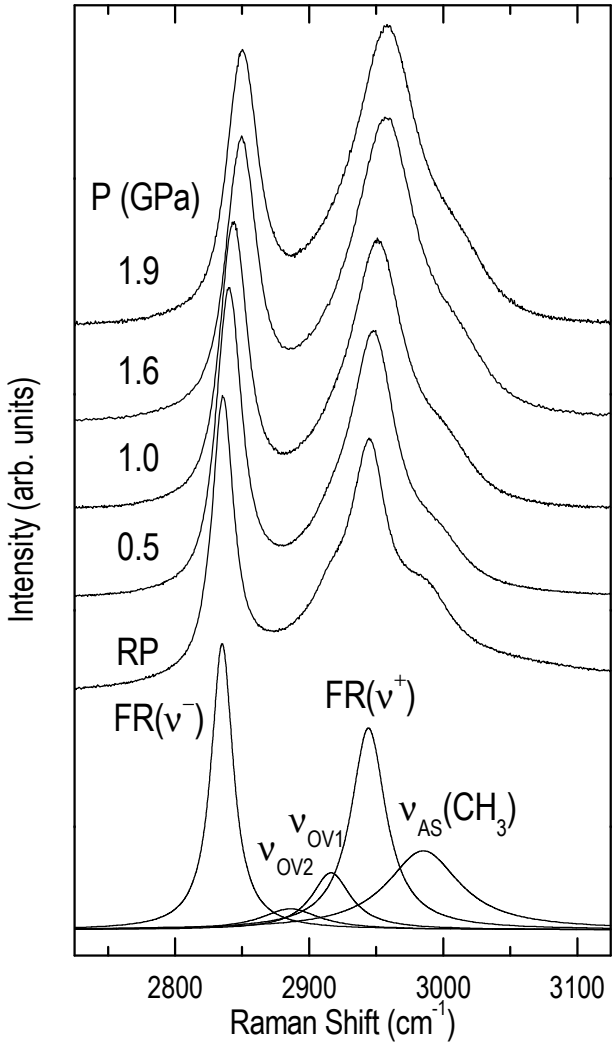


Fig. 8 Raman spectra of the CO_2 molecules in the hydrate, aqueous solution, and CO_2 fluid phases at 100 MPa; Raman peaks detected correspond to $\nu+$ and $\nu-$ of Fermi resonance



FERMI RESONANCE



$$\Phi_1 = c_{1F}\phi_F{}^0 + c_{1A}\phi_A{}^0 + c_{1B}\phi_B{}^0 + c_{1C}\phi_C{}^0$$
$$\Phi_2 = c_{2F}\phi_F{}^0 + c_{2A}\phi_A{}^0 + c_{2B}\phi_B{}^0 + c_{2C}\phi_C{}^0$$
$$\Phi_3 = c_{3F}\phi_F{}^0 + c_{3A}\phi_A{}^0 + c_{3B}\phi_B{}^0 + c_{3C}\phi_C{}^0$$
$$\Phi_4 = c_{4F}\phi_F{}^0 + c_{4A}\phi_A{}^0 + c_{4B}\phi_B{}^0 + c_{4C}\phi_C{}^0$$

$$\begin{vmatrix} (E_F{}^0 - E) & W_{FA} & W_{FB} & W_{FC} \\ W_{FA} & (E_A{}^0 - E) & W_{AB} & W_{AC} \\ W_{FB} & W_{AB} & (E_B{}^0 - E) & W_{BC} \\ W_{FC} & W_{AC} & W_{BC} & (E_C{}^0 - E) \end{vmatrix} = 0$$

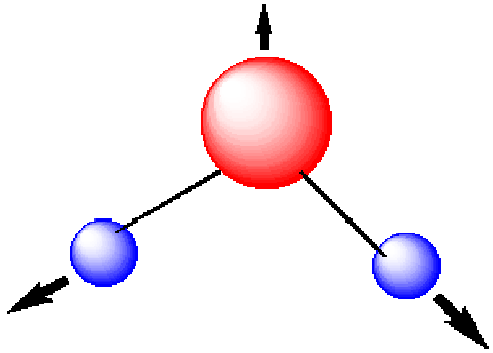
INTERNATIONAL SCHOOL
14th to 16th JUNE, NANCY (FRANCE)
RAMAN SPECTROSCOPY APPLIED TO EARTH SCIENCES AND CULTURAL HERITAGE

Theory of Raman Spectroscopy

Fernando Rull & Valentín García Baonza

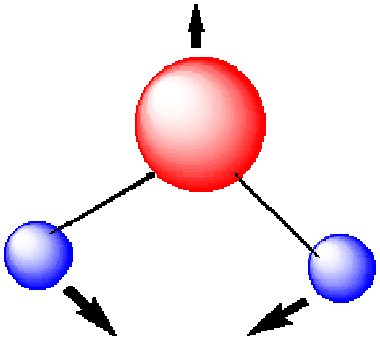
NORMAL MODES IN WATER MOLECULE

Q_3



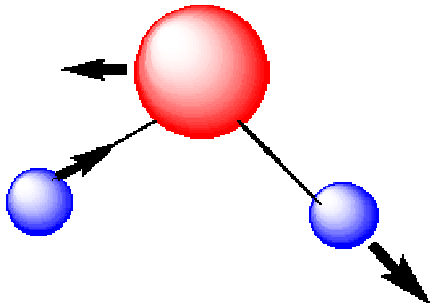
Symmetric Stretch
3657 cm^{-1}

Q_2

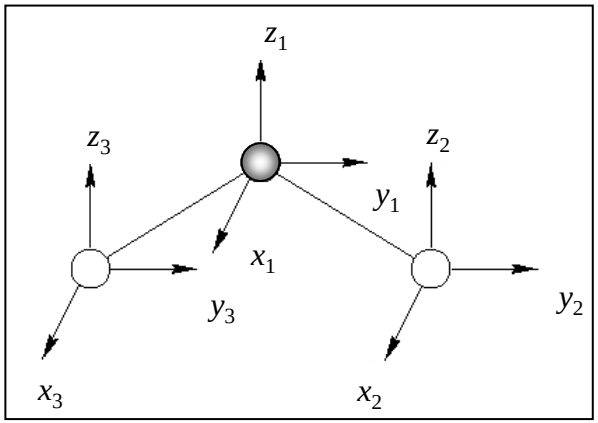


Bend 1595 cm^{-1}

Q_1



Asymmetric Stretch
3756 cm^{-1}



$$\begin{bmatrix} 1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{bmatrix} \cdot \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix}$$

E, $\chi(E)=9$

$$\begin{bmatrix} -1&0&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&-1&0\\ 0&0&0&0&0&0&0&0&1\\ 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&-1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0 \end{bmatrix} \cdot \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{bmatrix} -x_1\\ -y_1\\ z_1\\ -x_3\\ -y_3\\ z_3\\ -x_2\\ -y_2\\ z_2 \end{bmatrix}$$

C_2, $\chi(C_2)=-1$

$$\begin{bmatrix} 1&0&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&-1&0\\ 0&0&0&0&0&0&0&0&1\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&-1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0 \end{bmatrix} \cdot \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{bmatrix} x_1\\ -y_1\\ z_1\\ x_3\\ -y_3\\ z_3\\ x_2\\ -y_2\\ z_2 \end{bmatrix}$$

σ_v , $\chi(\sigma_v) = 1$

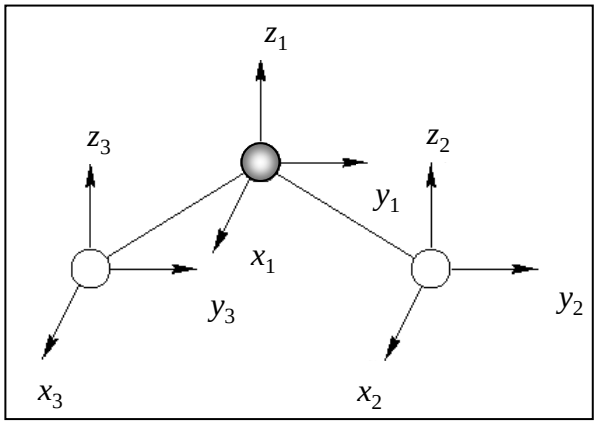
$$\begin{bmatrix} -1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{bmatrix} \cdot \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{bmatrix} -x_1\\ y_1\\ z_1\\ -x_2\\ y_2\\ z_2\\ -x_3\\ y_3\\ z_3 \end{bmatrix}$$

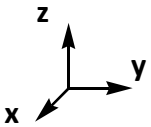
σ_{v} , $\chi(\sigma_{v}) = 3$

$$\Gamma_{red} = (9)E + (-1)C_2 + (1)\sigma_v + (3)\sigma_v'$$

$$\Gamma_{red} = 3\,A_1 + 1\,A_2 + 2\,B_1 + 3\,B_2$$

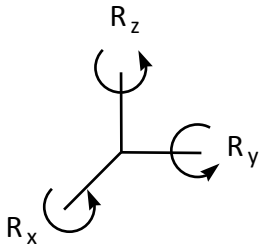
C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz





$\Gamma_{tran} = A_1 + B_1 + B_2$

$$\begin{aligned} \Gamma_{tot} &= 3A_1 + A_2 + 2B_1 + 3B_2 \\ -(\Gamma_{tran} &= A_1 + B_1 + B_2) \\ -(\Gamma_{rot} &= A_2 + B_1 + B_2) \\ \hline \Gamma_{vib} &= 2A_1 + B_2 \end{aligned}$$



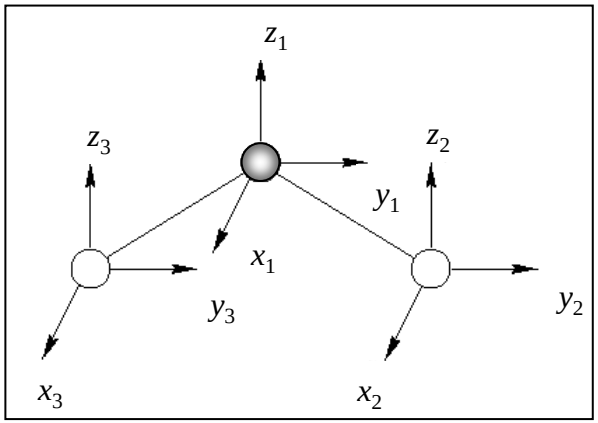
$\Gamma_{rot} = A_2 + B_1 + B_2$

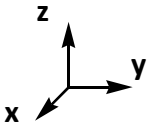
$\Gamma_{red} = (9)E + (-1)C_2 + (1)\sigma_v + (3)\sigma_v'$

$\Gamma_{red} = 3\,A_1 + 1\,A_2 + 2\,B_1 + 3\,B_2$

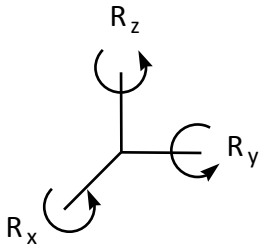
$\Gamma_{Vib} = 2\,A_1 + B_2$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz





$\Gamma_{tran} = A_1 + B_1 + B_2$

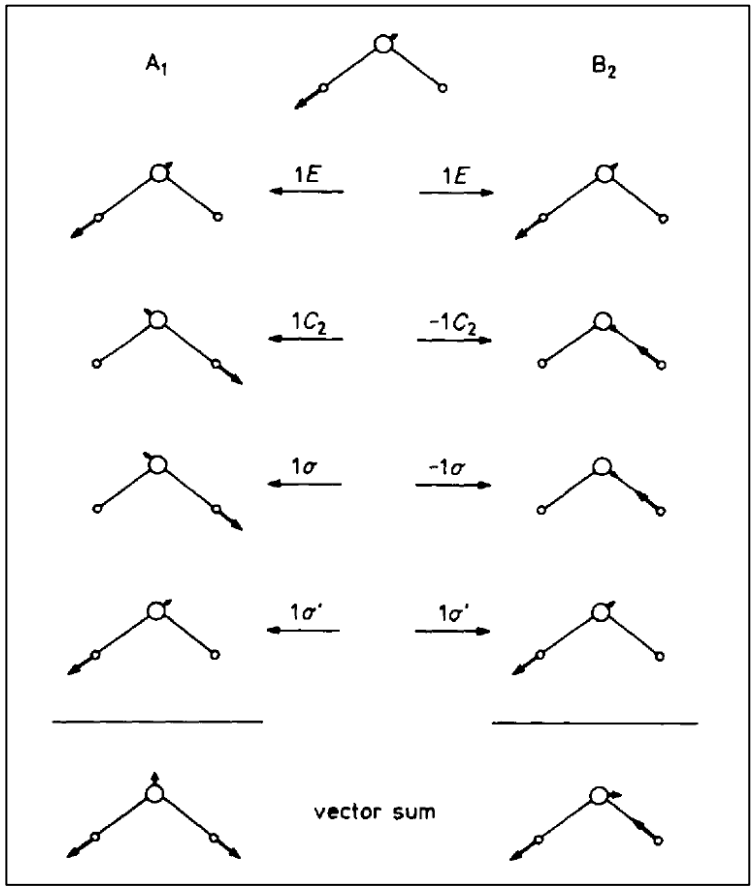


$\Gamma_{rot} = A_2 + B_1 + B_2$

$\Gamma_{red} = (9)E + (-1)C_2 + (1)\sigma_v + (3)\sigma_v'$

$\Gamma_{red} = 3\ A_1 + 1\ A_2 + 2\ B_1 + 3\ B_2$

$\Gamma_{Vib} = 2\ A_1 + B_2$



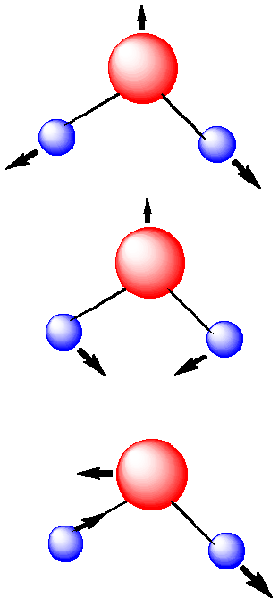
$$\hat{P}^{A_1}\Delta r_1 \approx 1\cdot E\cdot\Delta r_1 + 1\cdot C_2\cdot\Delta r_1 + 1\cdot\sigma\cdot\Delta r_1 + 1\cdot\sigma'\cdot\Delta r_1$$
$$= \Delta r_1 + \Delta r_2 + \Delta r_2 + \Delta r_1 \approx \Delta r_1 + \Delta r_2$$
$$\hat{P}^{B_2}\Delta r_1 \approx 1\cdot E\cdot\Delta r_1 + (-1)\cdot C_2\cdot\Delta r_1 + (-1)\cdot\sigma\cdot\Delta r_1 + 1\cdot\sigma'\cdot\Delta r_1$$
$$= \Delta r_1 - \Delta r_2 - \Delta r_2 + \Delta r_1 \approx \Delta r_1 - \Delta r_2$$

RAMAN ACTIVITY

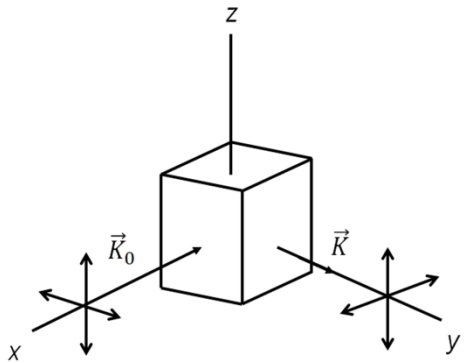
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Simmetry of Functions

$$\Gamma_{Vib} = 2\,A_1 + B_2$$



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



$$\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle \neq 0$$

RAMAN ACTIVITY IN CRISTALS

							número de vibraciones					IR	Raman
D^6_{3d}	E	$2S_6$	$2C_3$	$S_6^3(i)$	$3C_2$	$3\sigma_v$	*Tot*	*Tr*	*FT*	*FR*	*Int*		
A_{1g}	1	1	1	1	1	1	**1**	**0**	**0**	**0**	**1**		x^2+y^2,z^2
A_{1u}	1	-1	1	-1	1	-1	**2**	**0**	**1**	**0**	**1**		
A_{2g}	1	1	1	1	-1	-1	**3**	**0**	**1**	**1**	**1**		
A_{2u}	1	-1	1	-1	-1	1	**4**	**1**	**1**	**1**	**1**	z	
E_g	2	-1	-1	2	0	0	**4**	**0**	**1**	**1**	**2**		(x^2-y^2,xy), (xz,yz)
E_u	2	1	-1	-2	0	0	**6**	**1**	**2**	**1**	**2**	(x, y)	
N(p)	*10*	*2*	*4*	*2*	*4*	*0*							
N(s)	*4*	*2*	*4*	*2*	*2*	*0*							
N(s-v)	*2*	*0*	*2*	*0*	*2*	*0*							
$\chi(Tot)$	**30**	**0**	**0**	**-6**	**-4**	**0**							
$\chi(Tr)$	**3**	**0**	**0**	**-3**	**-1**	**1**							
$\chi(FT)$	**9**	**0**	**0**	**-3**	**-1**	**-1**							
$\chi(FR)$	**6**	**0**	**0**	**0**	**-2**	**0**							
$\chi(Int)$	**12**	**0**	**0**	**0**	**0**	**0**