F Fillaux, Nonlinear Double Day, Sevilla 2004

Vibrational Dynamics in Crystals

Harmonic:	Normal Modes Phonons
Nonlinear Dynamics:	Local Modes Localized Modes (Breathers, ILMs)

Are Localized Modes Eigenstates?
Are Localized Modes Observable?

I. Intrinsic Localized Modes or DQB
- The D_2 crystal
- *CO* absorbed on Ru(001)
- Acetanilide
- $Pt(en)_2Cl_2Pt(en)_2(ClO_4)_4$
- $KHCO_3$

II. Sine-Gordon Quantum Breather

Localization in Crystal Lattices

$$H = \sum_j \left[\frac{p_j^2}{2m} + V(x_j) + \frac{k_2}{2}(x_j - x_{j+1})^2 + \frac{k_4}{4}(x_j - x_{j+1})^4 + \mathrm{L} \right]$$

Harmonic: phonons
Anharmonic: localization

A. J.Sievers and S. Takeno, PRL, 61 (1988) 970

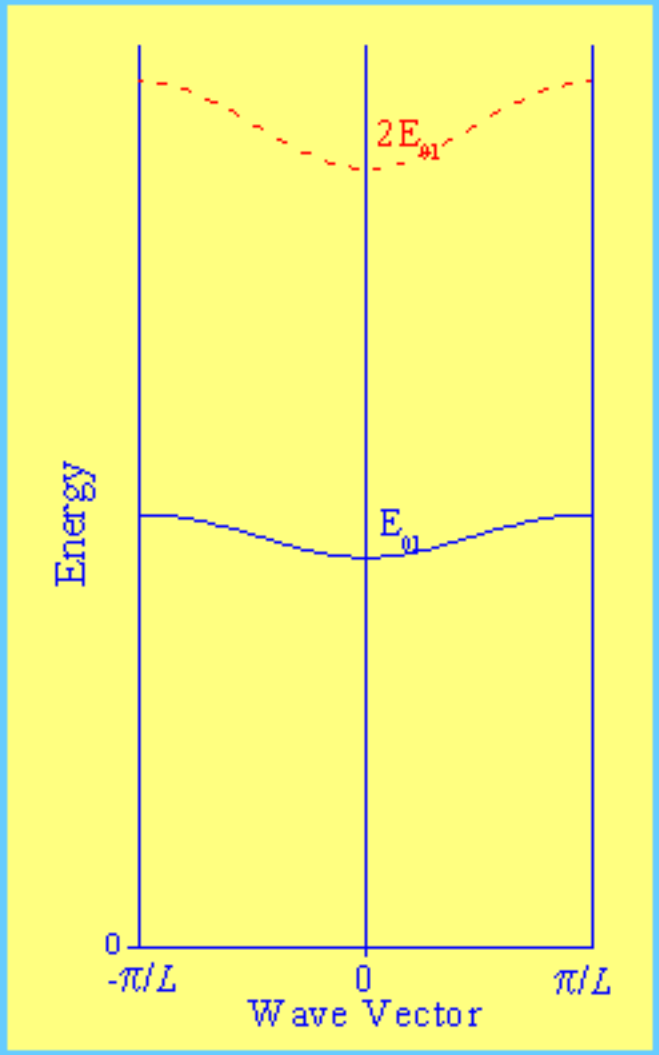
R. S. MacKay and S. Aubry, Nonlinearity, 7 (1994) 1623

Phonons in Crystal Lattices (I)

Harmonic: phonons

$$H = \sum_j \left[\frac{p_j^2}{2m} + \frac{1}{2} m\omega_0^2 x_j^2 + \frac{k_2}{2}\left(x_j - x_{j+1}\right)^2 \right]$$

$$x_j(k,t) \propto \exp\left\{ i\left[nkL - \omega(k)t \right] \right\}$$



Probing Phonons with Infrared and Raman (I)

$\Delta x \Delta p_x \approx h$ $\quad \Delta p < h/\lambda$ $\quad \Delta x > \lambda/(8\pi)$

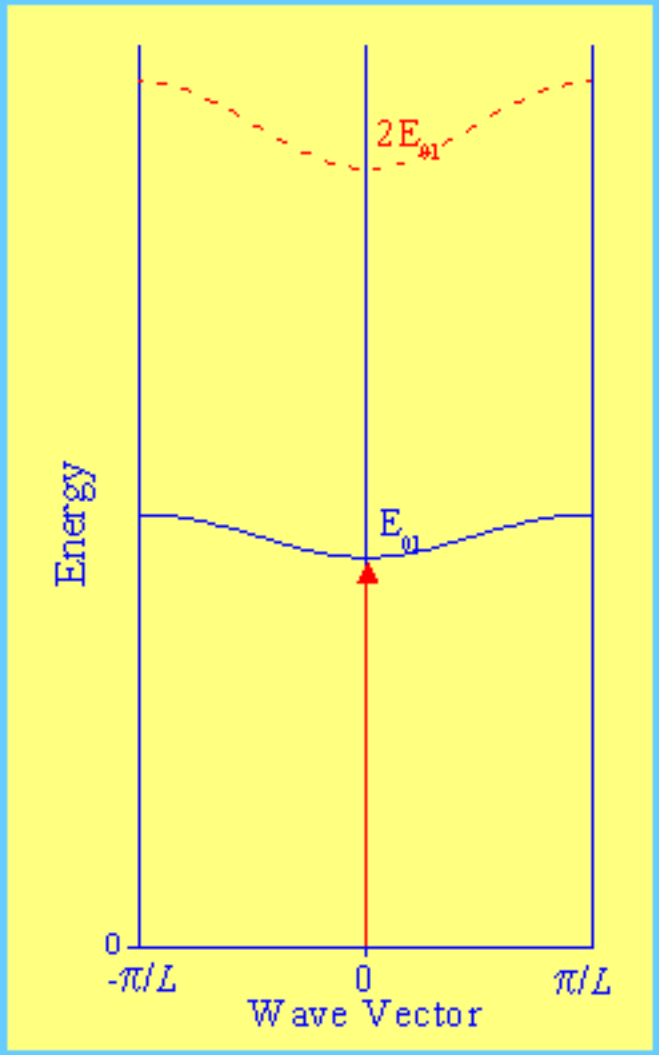
Infrared	$\lambda > 2\mu$	$\Delta x > 800\,\text{Å}$	$\mathbf{k} = 2\pi/\lambda < 3\ 10^{-4}$ Å^{-1}
Raman	$\lambda :\ 0.5\mu$	$\Delta x > 200\,\text{Å}$	$\mathbf{k} = 2\pi/\lambda < 10^{-3}$ Å^{-1}

All equivalent sites are indistinguishable.
They are all excited with phases entirely determined by the symmetry of the crystal

Probing Phonons with Infrared and Raman (II)

$$H = \sum_j \left[\frac{p_j^2}{2m} + \frac{1}{2} m\omega_0^2 x_j^2 + \frac{k_2}{2}\left(x_j - x_{j+1}\right)^2 \right]$$

$$x_j(k,t) \propto \mathbf{exp}\left\{ i\left[nkL - \omega(k)t \right] \right\}$$



Probing Phonons with Infrared and Raman (IV)

Anharmonicity (mechanical or electrical)

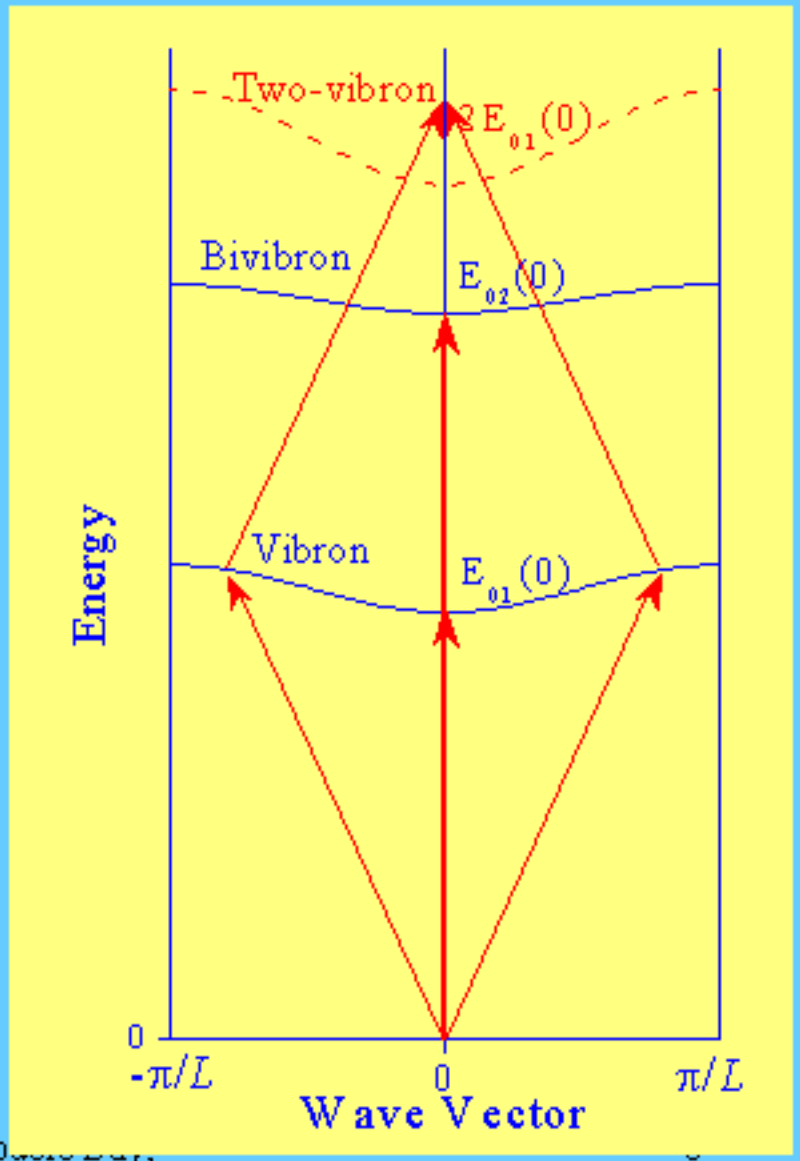
$$H = \sum_j \left[\frac{p_j^2}{2m} + V(x_j) + \frac{k_2}{2}(x_j - x_{j+1})^2 \right]$$

$$k = 0 \rightarrow E_{01}(0), E_{02}(0)\mathrm{L}$$

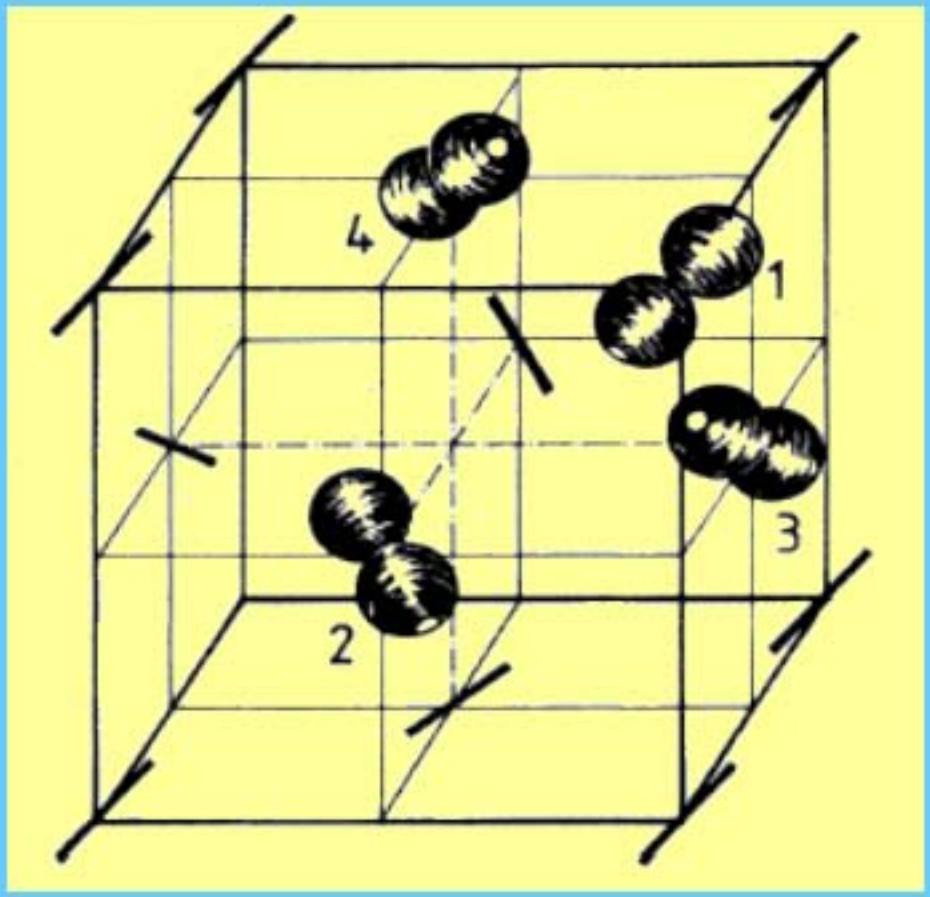
$$x_j(k,t) \propto \exp\{ i[nkL - \omega(k)t] \}$$

$$x_j(k_1,t)x_j(k_2,t) \propto \exp\{ i[nk_1L - \omega(k_1)t] + i[nk_2L - \omega(k_2)t] \}$$

$$k = k_1 + k_2 = 0 \rightarrow E_{01}(k_1) + E_{01}(-k_1) = 2E_{01}(k_1)$$

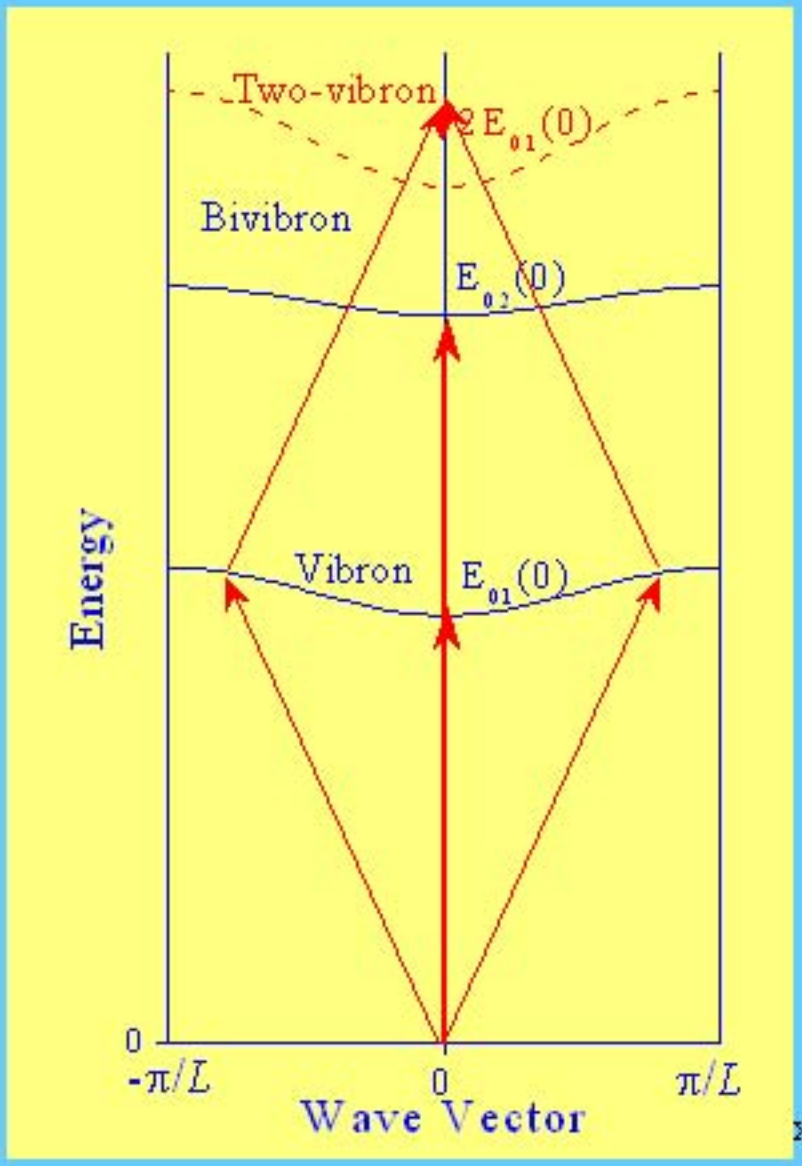


The Deuterium Crystal



I. F. Silvera, RMP, 52 (1980) 393

The Deuterium Crystal



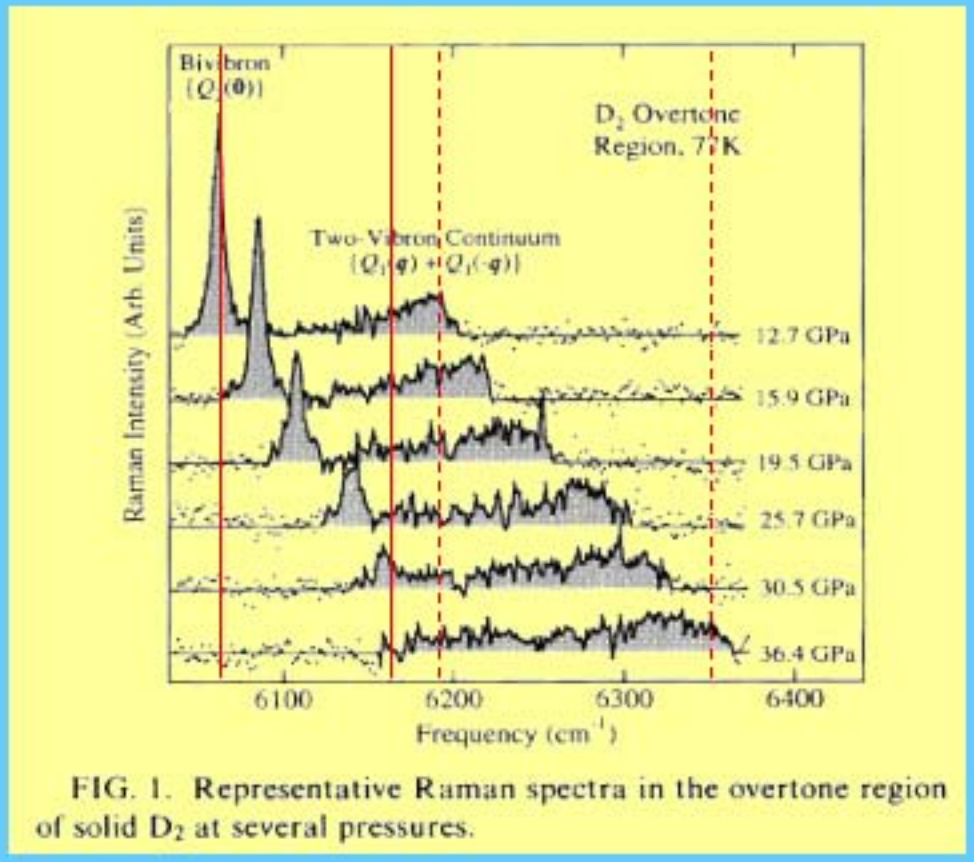


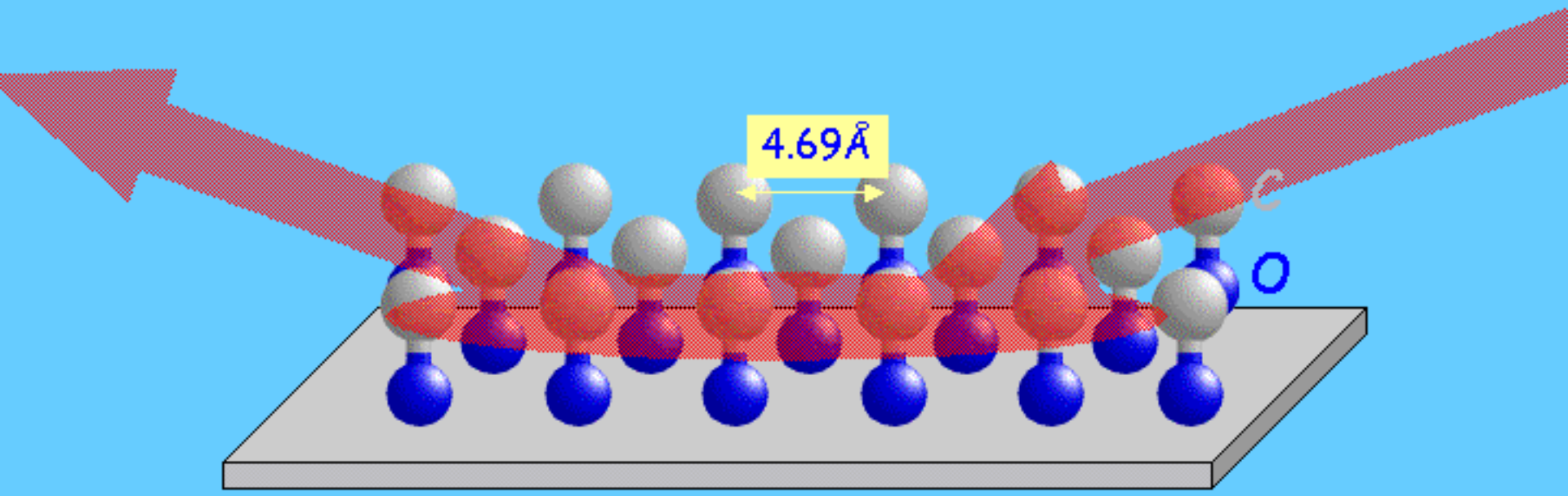
FIG. 1. Representative Raman spectra in the overtone region of solid D_2 at several pressures.

J. H. Eggert et al., PRL 70 (1993) 2301

x, Noni… Sevilla 2004.

CO Adsorbed on Ru(001)

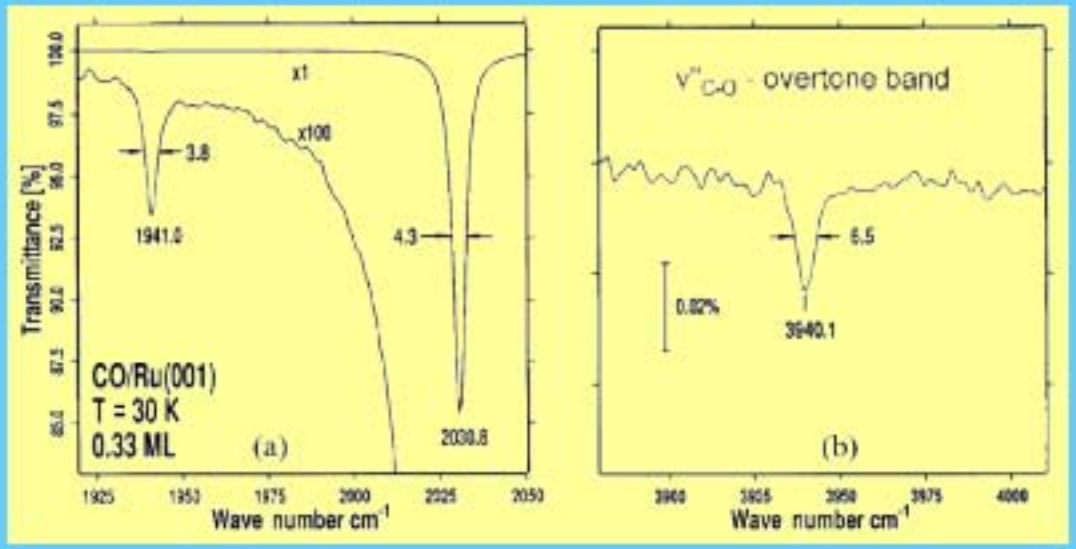
P. Jakob, PRL, 77 (1996) 4429



Infrared-Reflection-Absorption Spectroscopy (IRAS)

CO Adsorbed on Ru(001)

P. Jakob, PRL, 77 (1996) 4429



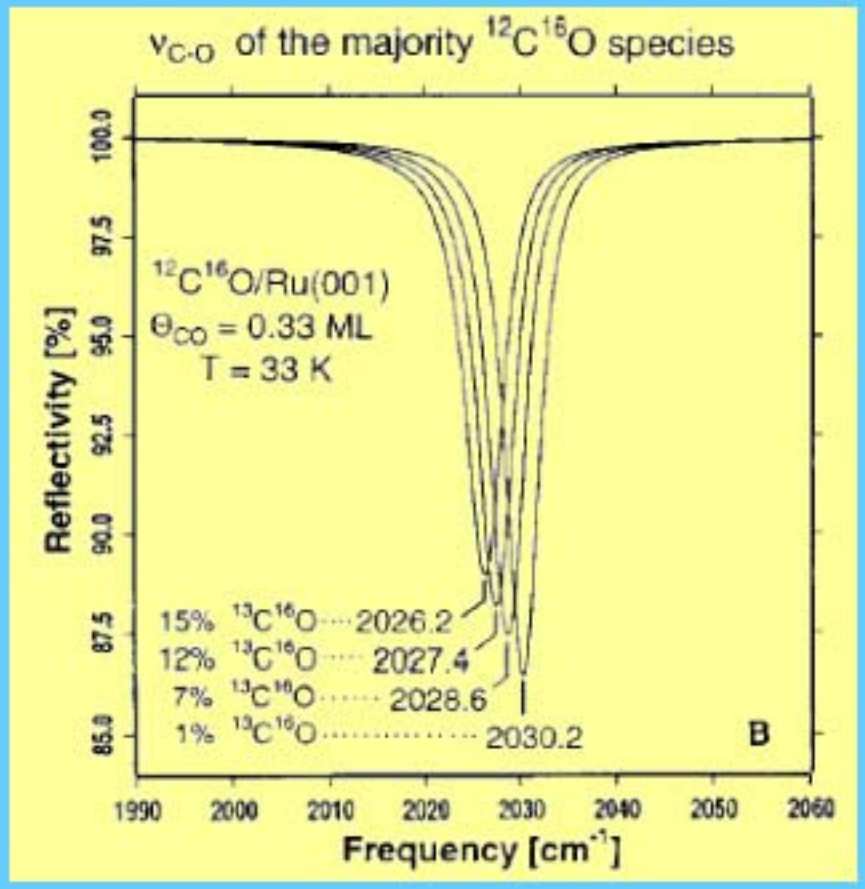
	Vibrational Frequencies [cm^{-1}]		
	$^{12}C\,^{16}O$	$^{13}C\,^{16}O$	$^{12}C\,^{18}O$
ν'_{C-O}	1988.6	1943.5	1943.3
ν''_{C-O}	3940.1	3851.4	3851.3
$\hbar\omega_e x_e$	18.5	17.8	17.6

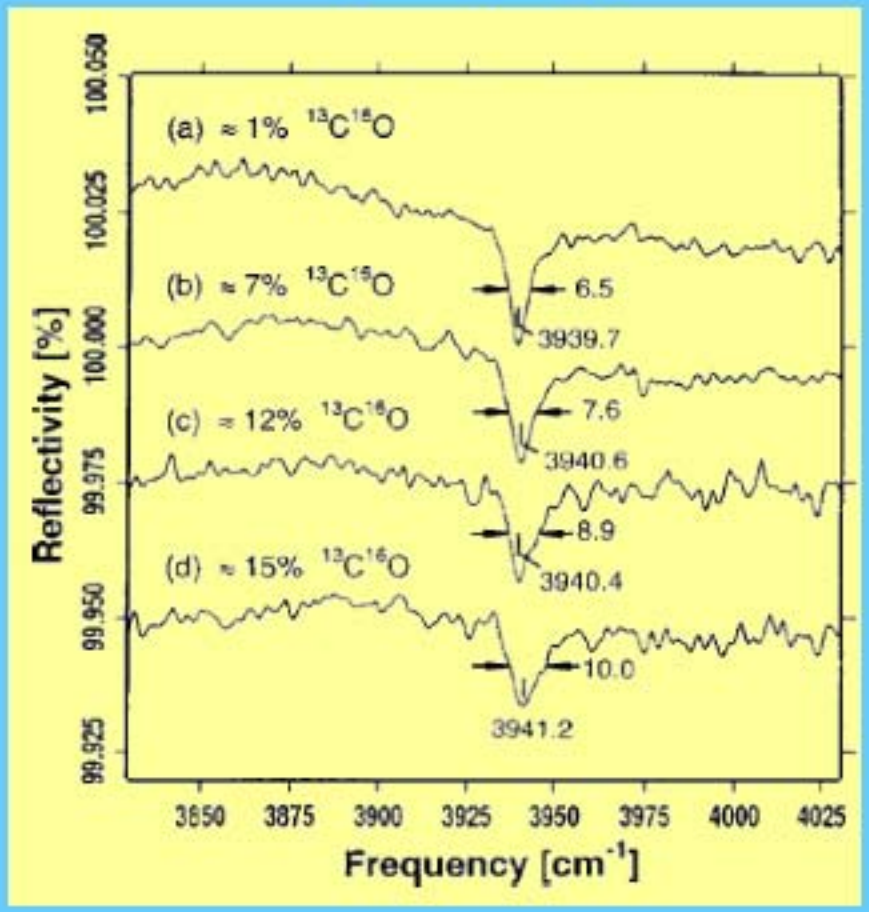
CO Adsorbed on Ru(001)

$$\Delta = \frac{W}{E_{01} - E_{01}^{*}}$$

P. Jakob, JCP, 109 (1998) 8641

$$\Delta = \frac{W}{E_{02} - E_{02}^{*}}$$





Probing Phonons with Infrared and Raman (V)

The bivibron is not a localized excitation of one molecule.

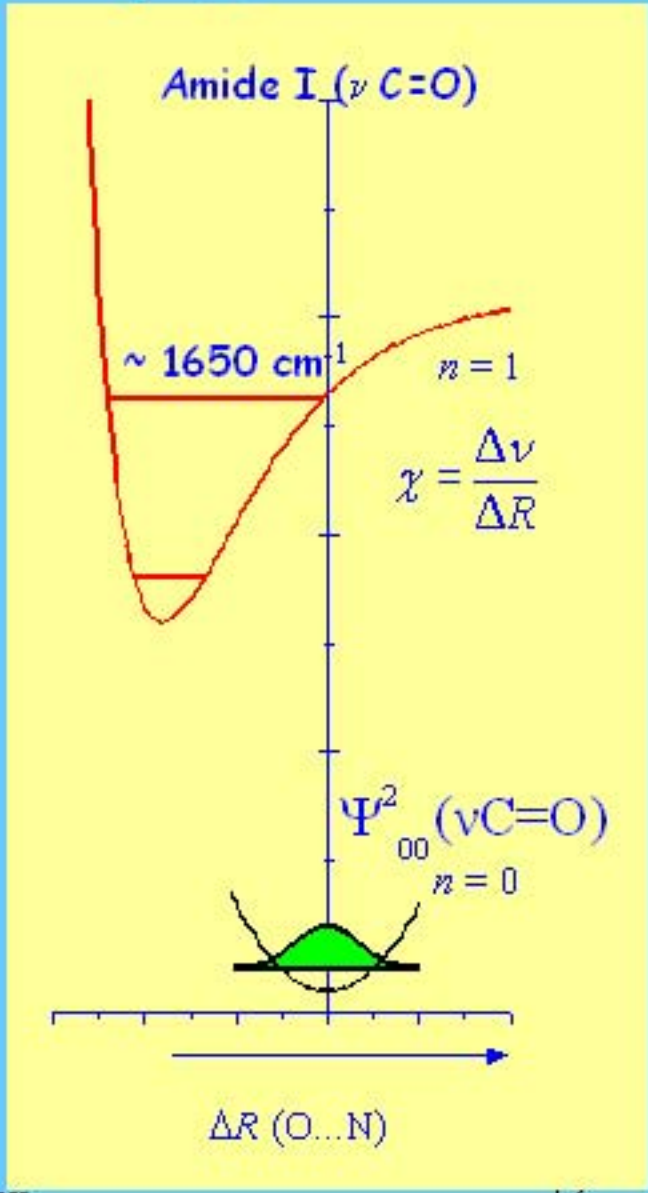
The two-vibron continuum is not a pair of excited molecules that propagate in opposite directions.

ILMs or DQBs cannot be observed with optical techniques

Acetanilide: A Long History (I)

A. S. Davydov, Stud. Biophys., **62** (1977) 1; Phys. Scr. **20** (1979) 387; Biology and Quantum Mechanics (1982)...

1. ATP $\rightarrow$ ADP + ~ 0.49eV
2. Energy storage in the Amide I vibration at ~ 1650 cm^{-1} (0.205 eV)
3. Longitudinal sound waves in α-helices prevent energy dispersion
4. Numerical simulations



Acetanilide: A Long History (II)

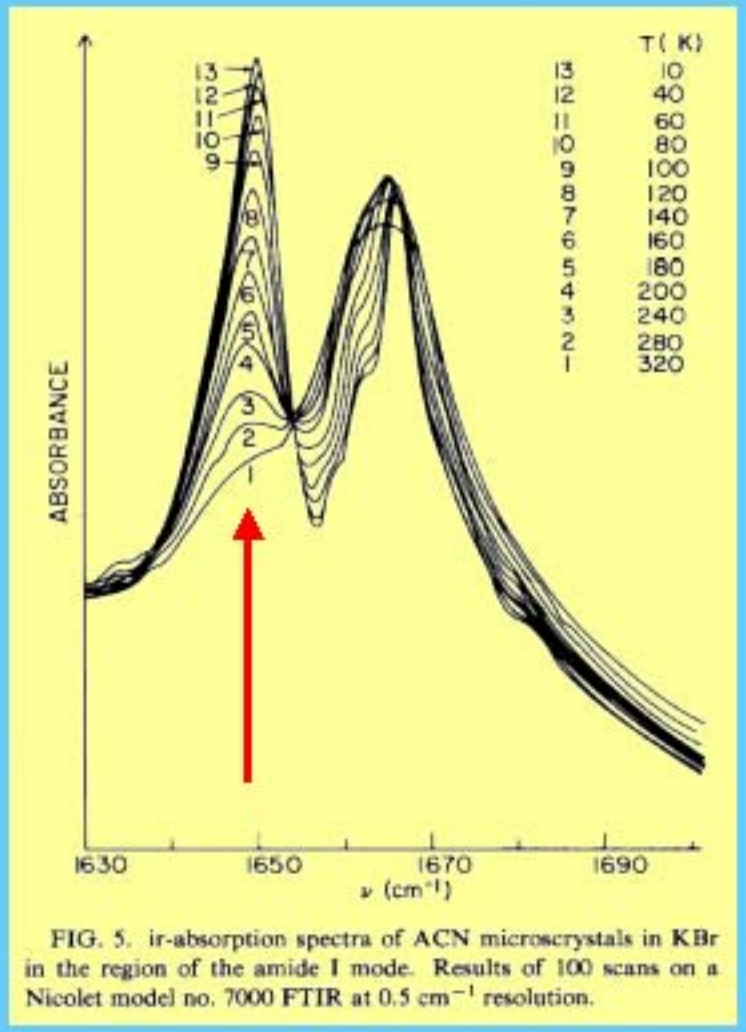
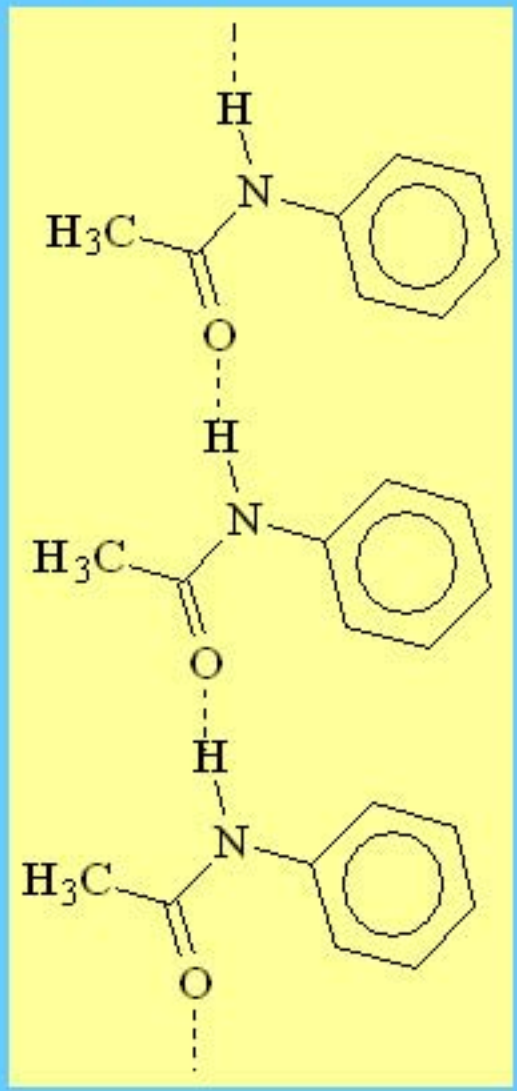


FIG. 5. ir-absorption spectra of ACN microcrystals in KBr in the region of the amide I mode. Results of 100 scans on a Nicolet model no. 7000 FTIR at 0.5 cm^{-1} resolution.

Careri *et al.*, Phys. Rev. B**30** (1984) 4689



Acetanilide: A Long History (III)

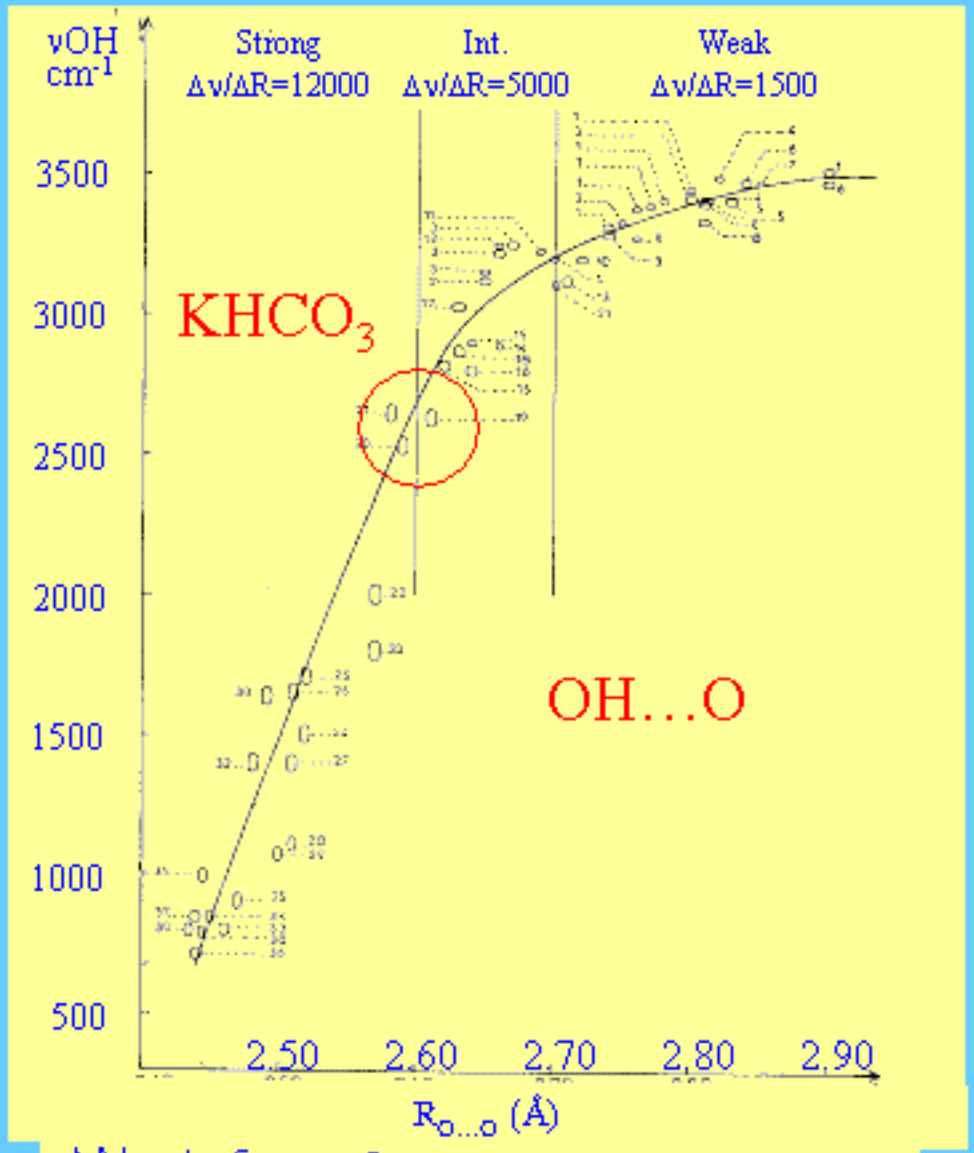
Pros

1. No other interpretation
2. Observation of the predicted overtone $\nu(n) = 1674n - 24.7n^2$
3. Calculated Temperature effect (phonon at ~ 75 cm^{-1})
4. No phase transition
5. No double well

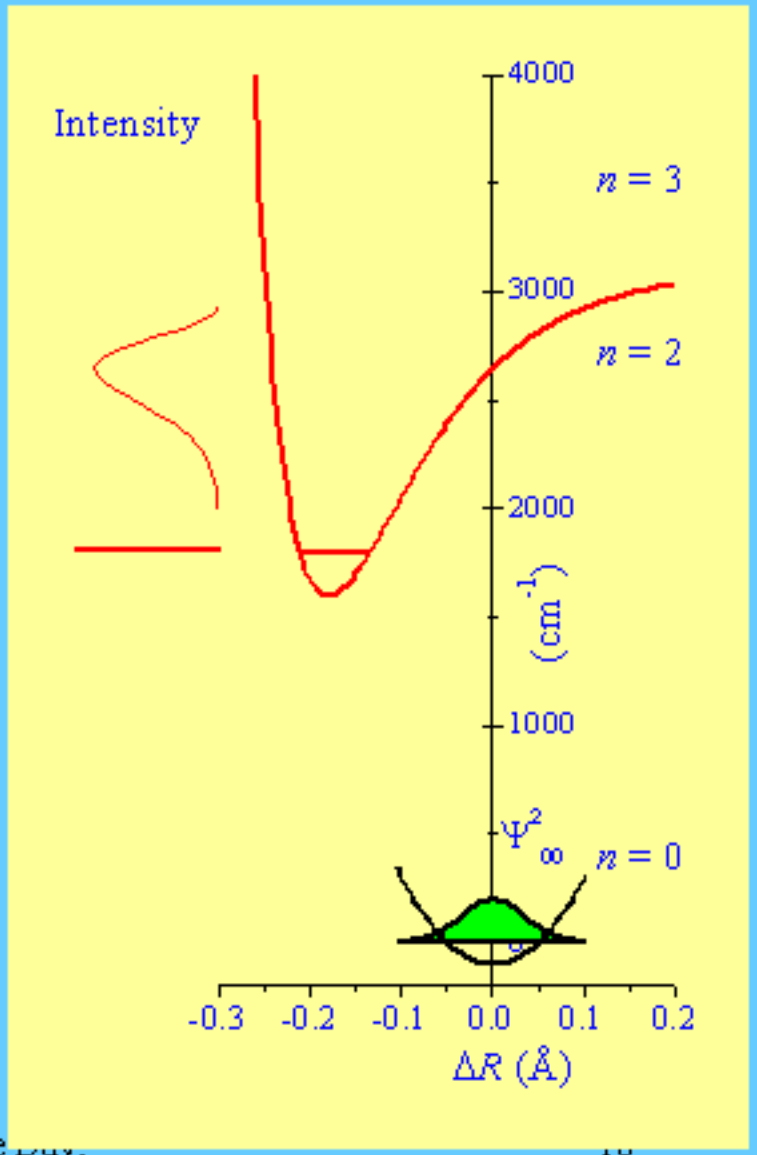
Cons

1. Picosecond experiments: nondegenerate H configurations
2. No QENS broadening at low temperature (no topological or nontopological soliton)
3. No evidence for H tunnelling
4. No evidence for coupling with acoustic phonons
5. Carreri'S band disappears in $C_6D_5CONHCD_3$
6. Polaronic defects ?

Hydrogen Bonding

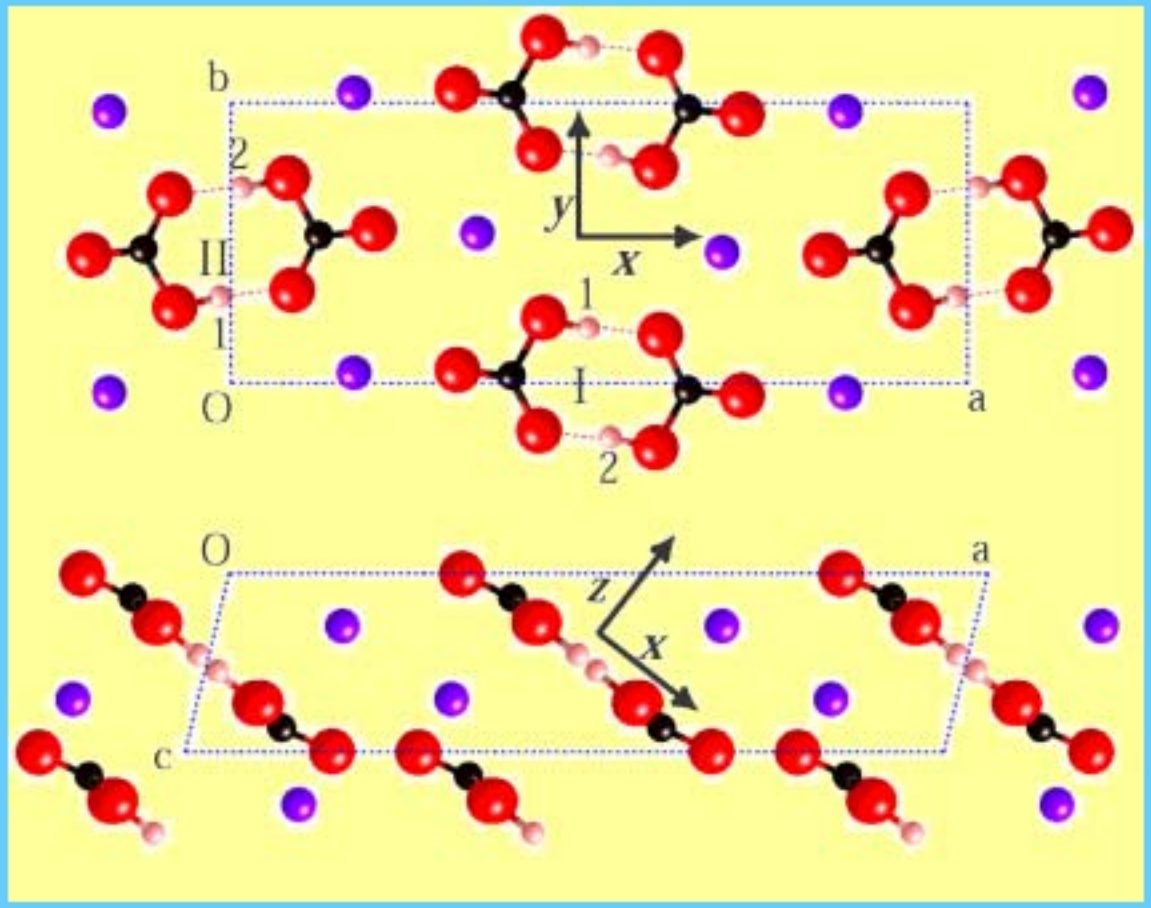


A Novak, Struct. Bonding (Berlin) **18** (1974) 177



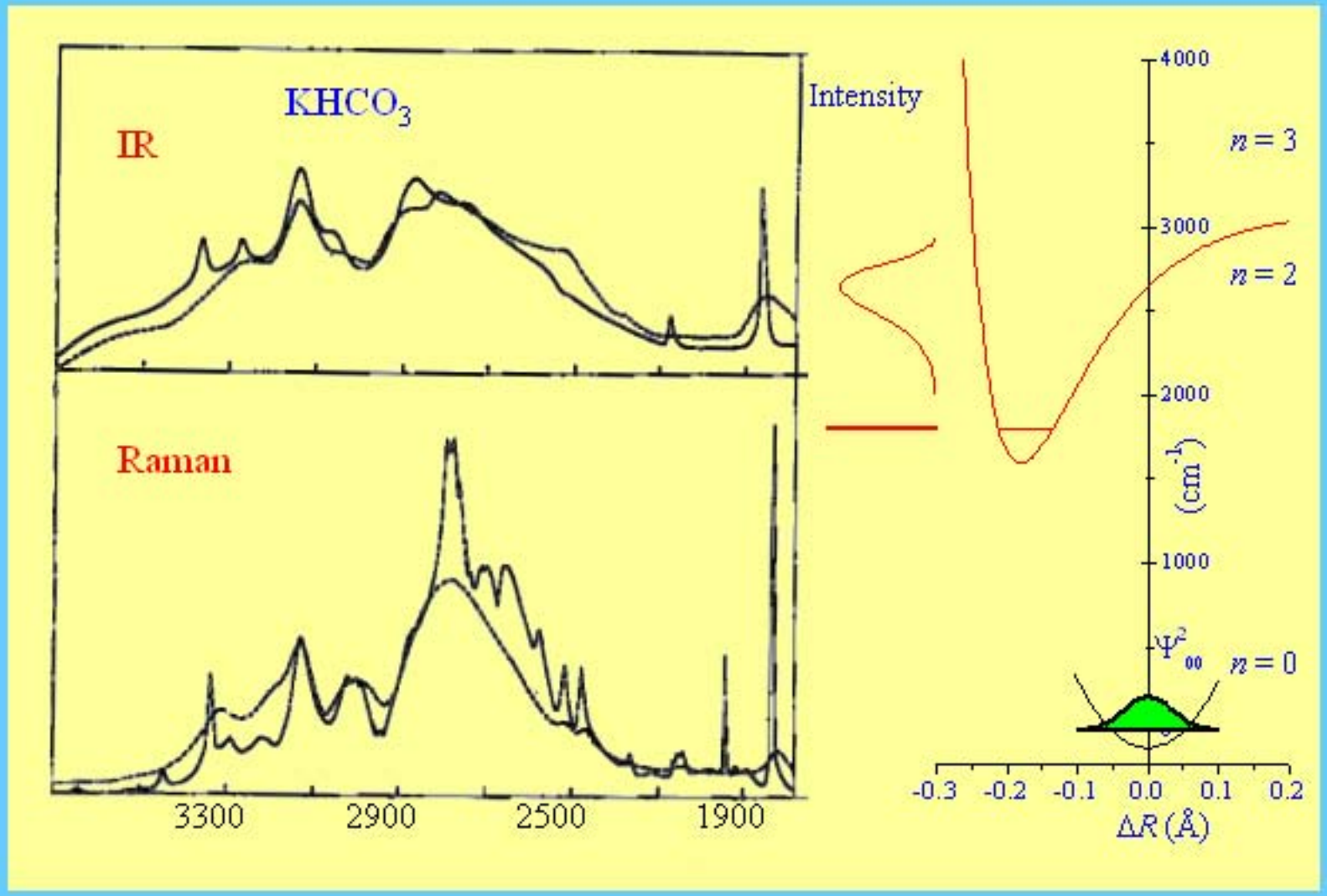
Double Day,
Sevilla 2004.

Potasium Hydrogen Carbonate $KHCO_3$



F. Fillaux *et al.*, Phys. Rev. B, in press

Potasium Hydrogen Carbonate $KHCO_3$



G Lucazeau, A Novak, J. Raman Spectroscopy **1** (1973) 573

$[Pt(en)_2]\,[Pt(en)_2Cl_2](ClO_4)_4$ Resonance Raman

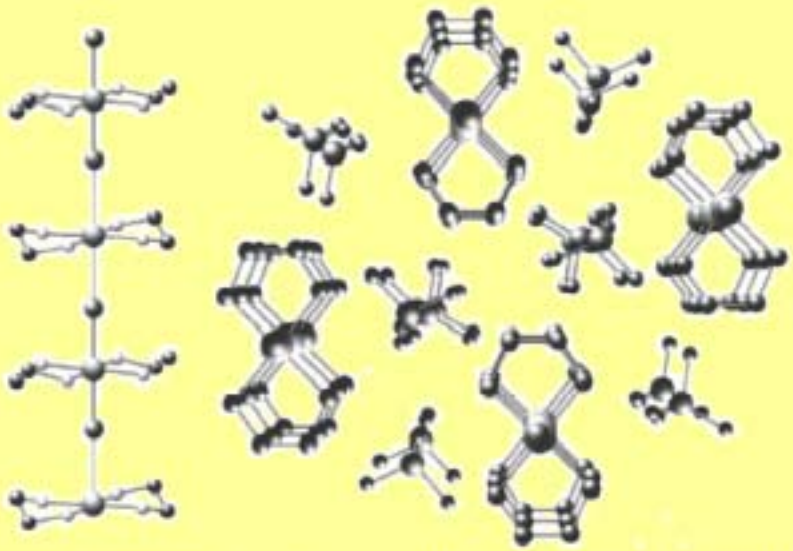


FIG. 1. Structure of $\{[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4\}$ (en = ethylenediamine; H atoms are omitted) [11]. One PtCl chain is shown on the left. Each Pt atom is coordinated by two ethylenediamine units in a near square planar geometry, while Cl ions connect the Pt sites along the chain. The packing arrangement of the 1D chains and their ClO_4^- counterions is shown on the right.

$$I_{fi}\left(\tfrac{\pi}{2}\right) = \frac{\pi^2}{\varepsilon_0^2}\left(\vartheta_0 \pm \vartheta_{fi}\right)^4 \mathfrak{S}_0 \sum_{\rho\sigma} \left[\alpha_{\rho\sigma}\right]_{fi} \left[\alpha_{\rho\sigma}\right]^*_{fi}$$

$$\left[\alpha_{\rho\sigma}\right]_{fi} = \frac{1}{hc} \sum_r \left[\frac{\left[\mu_\rho\right]_{fr}\left[\mu_\sigma\right]_{ri}}{\vartheta_{ri} - \vartheta_0 + i\gamma_r} + \frac{\left[\mu_\rho\right]_{fr}\left[\mu_\sigma\right]_{ri}}{\vartheta_{ri} + \vartheta_0 + i\gamma_r} \right]$$

$$|i\rangle = |gm\rangle = |g\rangle|m\rangle$$
$$|f\rangle = |gn\rangle = |g\rangle|n\rangle$$
$$|r\rangle = |ev\rangle = |e\rangle|v\rangle$$

$$\left[\alpha_{\rho\sigma}\right]_{gn,gm} = \frac{1}{hc} \sum_{ev} \left(\frac{\langle n|\left[\mu_\rho\right]_{ge}|v\rangle\langle v|\left[\mu_\sigma\right]_{eg}|m\rangle}{\vartheta_{ev,gm} - \vartheta_0 + i\gamma_{ev}} + \frac{\langle n|\left[\mu_\sigma\right]_{ge}|v\rangle\langle v|\left[\mu\rho\right]_{eg}|m\rangle}{\vartheta_{ev,gn} + \vartheta_0 + i\gamma_{ev}} \right)$$

B. I. Swanson *et al.*, PRL 82 (1999) 3288

$[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$
Resonance Raman

A simple interpretation is that the lowest-energy dominant peaks in the overtone spectra correspond to all quanta of vibrational energy localized in approximately one $PtCl_2$ unit, while the higher energy peak corresponds to having all quanta but one in a localized $PtCl_2$ unit combined with one quanta in the more extended fund

coupling, which is weak compared to th ated attractive interaction between ph at high energies, allows the bound multipho anta to tunnel quantum mechanically to different $PtCl_2$ units as an entity. This weak tunneling process restores translational symmetry and can be treated perturbatively.

Multiple Scattering

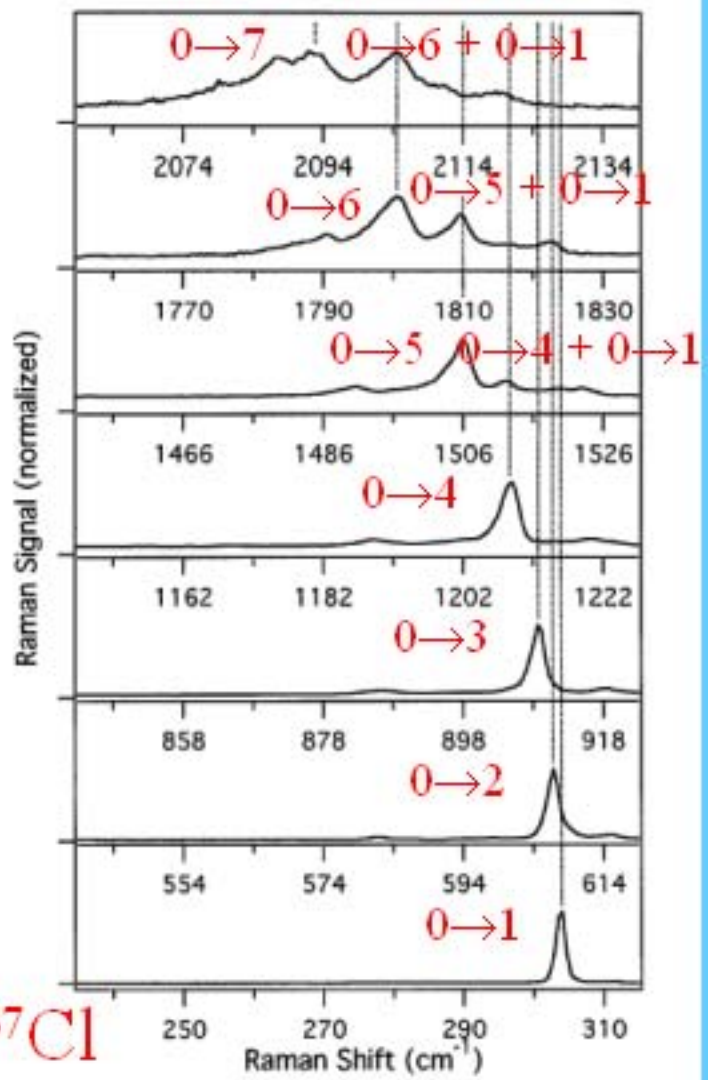
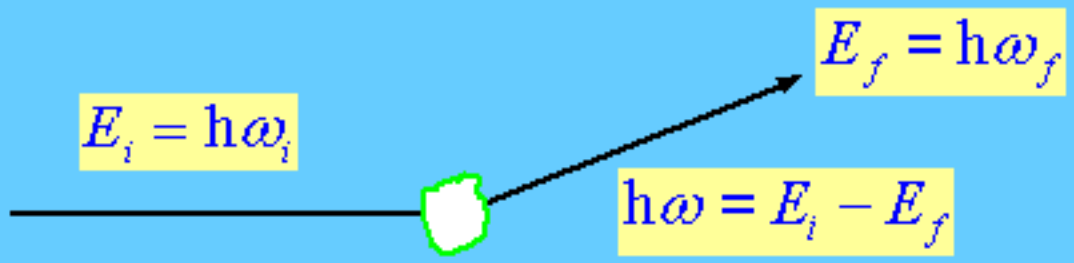
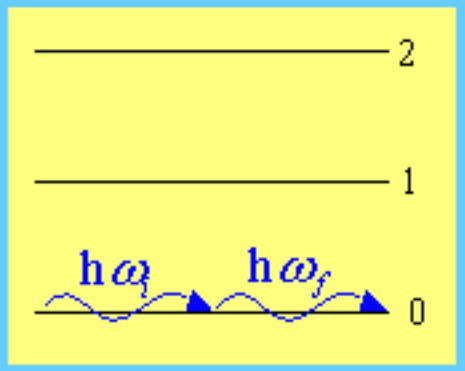


FIG. 3. Fundamental and overtone regions of the isotopically pure $Pt^{37}Cl$, presented as in Fig. 2, but with 304 cm^{-1} offsets. the appropriate integral multiple of the 312 cm^{-1} fundamental frequency. All spectra have been scaled vertically to equal peak intensities.

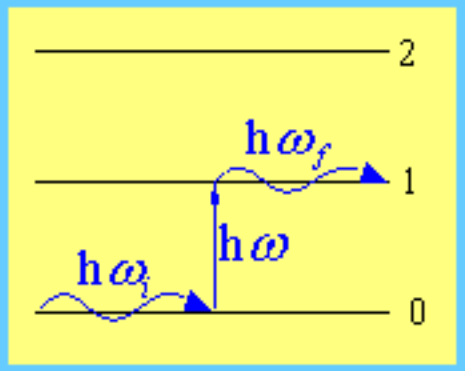
B. I. Swanson *et al.*, PRL 82 (1999) 3288

Inelastic Neutron Scattering

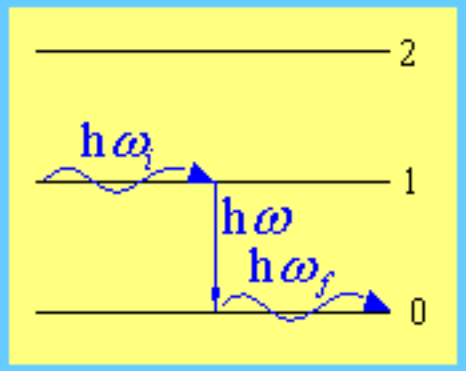




Elastic

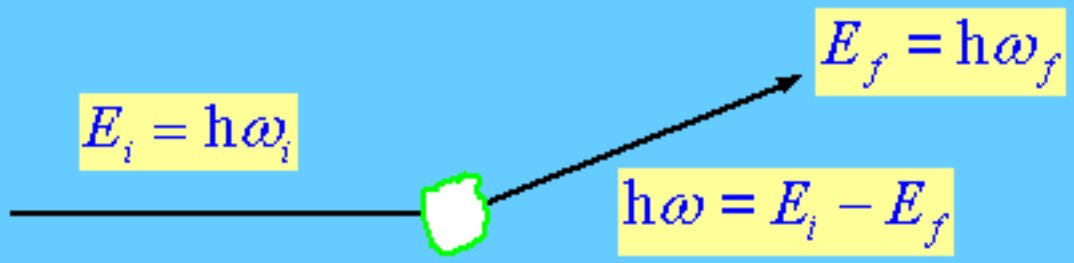


Energy-loss



Energy-gain

Inelastic Neutron Scattering

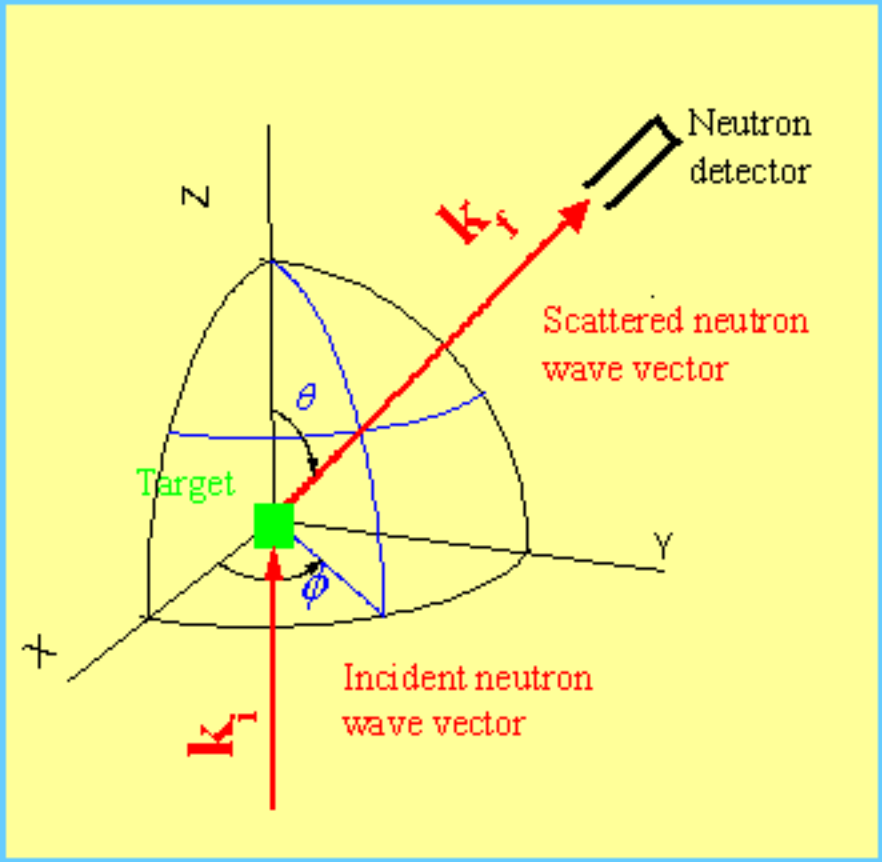


Nuclear Cross-section
Contrast
Penetration Depth
Wavelength
Scattering Function: $S(\mathbf{Q},\omega)$

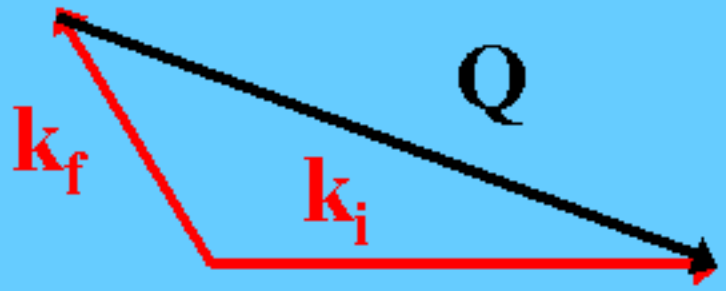
Probing Phonons with INS (I)

$\Delta x \Delta p_x \approx \mathrm{h}$	$\Delta p < h/\lambda$	$\Delta x > \lambda/(8\pi)$	$\mathbf{k} = 2\pi/\lambda$
Infrared	$\lambda > 2\mu$	$\Delta x > 800\,\mathrm{\AA}$	$\mathbf{k} < 3\ 10^{-4}$ Å^{-1}
Raman	$\lambda:\ 0.5\mu$	$\Delta x > 200\,\mathrm{\AA}$	$\mathbf{k} < 10^{-3}$ Å^{-1}
Neutrons	$\lambda:\ 10 - 0.1\,\mathrm{\AA}$	$\Delta x > 10^{-2}\,\mathrm{\AA}$	$\mathbf{k} = 0.6 - 60$ Å^{-1}

Inelastic Neutron Scattering

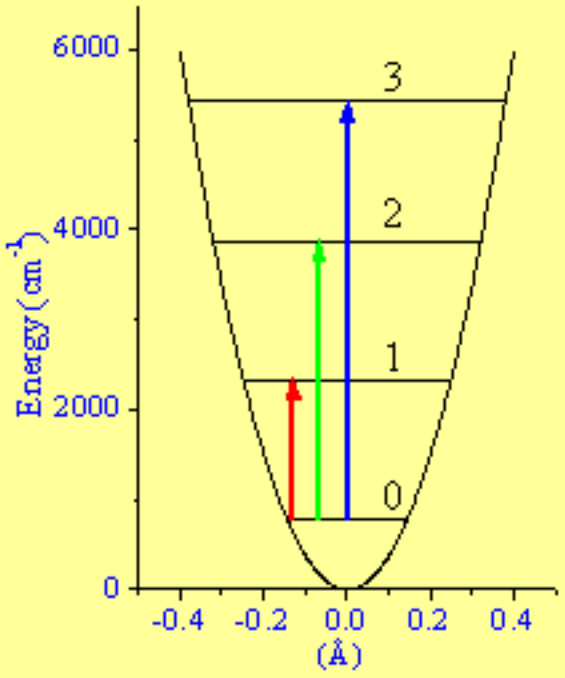


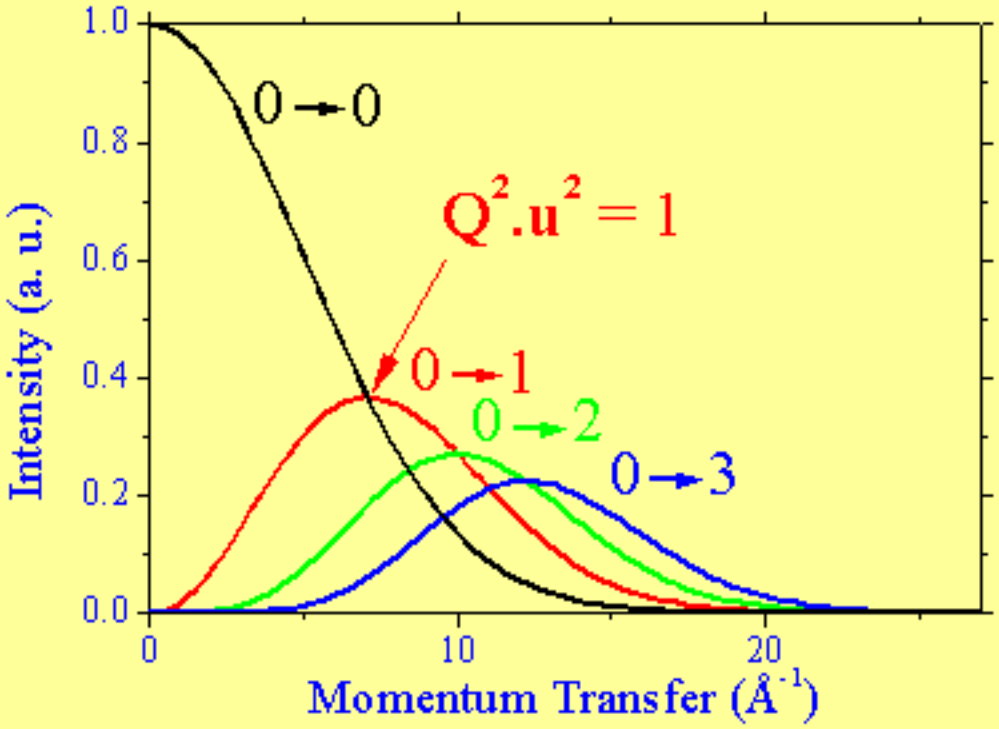
The incident and scattered neutrons are described by planar waves with wave-vectors $\mathbf{k_i}$ and $\mathbf{k_f}$, respectively.
The scattering vector is :
$\mathbf{Q} = \mathbf{k_i} - \mathbf{k_f}$



$$S(\mathbf{Q},\omega) = \left|\left\langle \Psi_i(\mathbf{r}) \middle| \exp(i\mathbf{Q}.\mathbf{r}) \middle| \Psi_f(\mathbf{r}) \right\rangle\right|^2 \delta(\omega - \omega_{if})$$

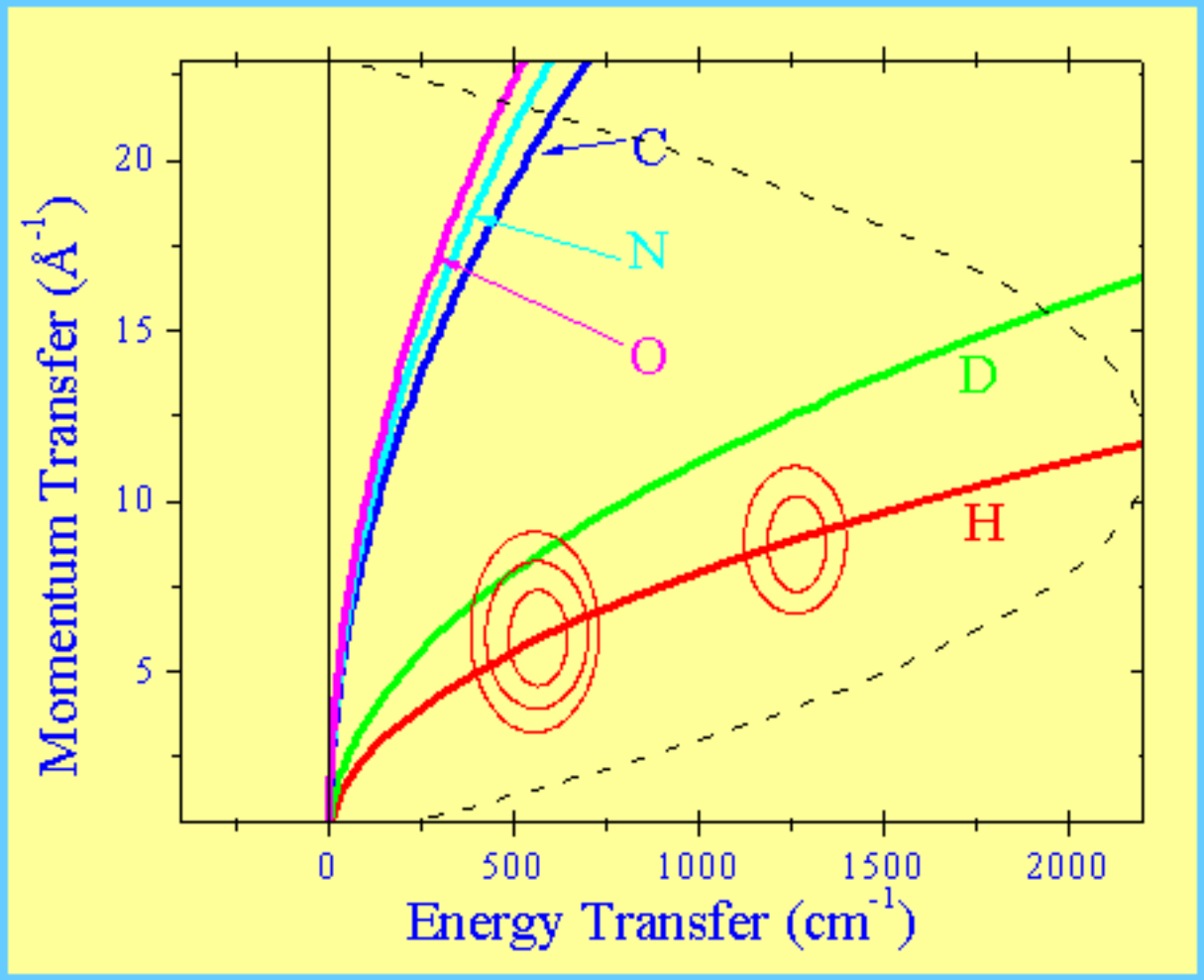
Harmonic Oscillator





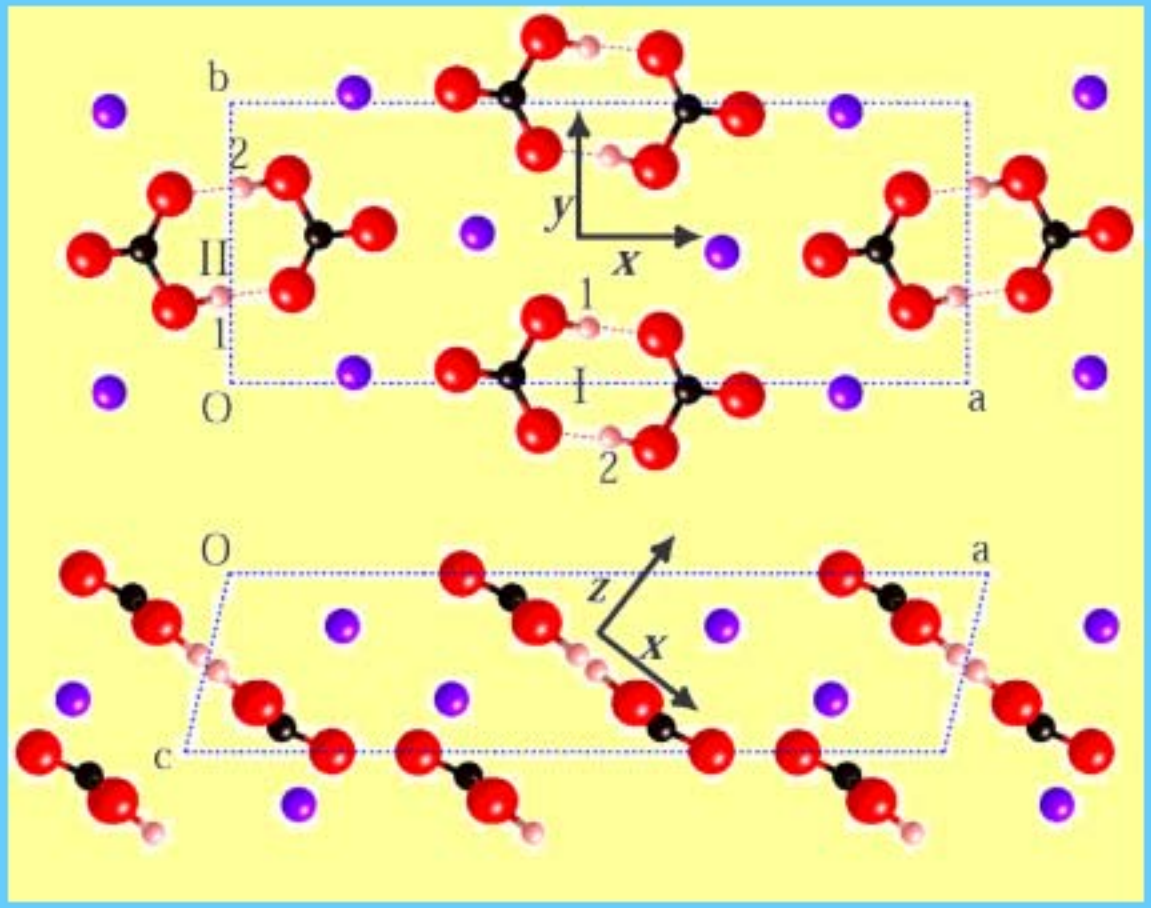
$$S_{0\to n}(\mathbf{Q},\omega) = \frac{(\mathbf{Q}.\mathbf{u})^{2n}}{n!}\exp\left(-\mathbf{Q}^2\mathbf{u}^2\right)\delta\left(n\hbar\omega_0\right)$$

Recoil lines



$$E = \frac{h^2 k^2}{2m_n} \approx 16.759 k^2 \left(\mathrm{cm}^{-1}, \mathrm{Å}^{-1}\right)$$

Potassium Hydrogen Carbonate $KHCO_3$



F. Fillaux *et al.*, Phys. Rev. B, in press

Pair of Coupled Harmonic Oscillators

$$H = \frac{1}{2m}\left(P_1^2 + P_2^2\right) + \frac{1}{2} m\omega_{0x}^2 \left[\left(x_1 - x_0\right)^2 + \left(x_2 + x_0\right)^2 + 2\lambda_x \left(x_1 - x_2\right)^2\right]$$

Normal coordinates

$$\begin{cases} x_G = \frac{1}{2}\left(x_1 + x_2\right) \\ x_R = \left(x_1 - x_2\right) \end{cases} \quad \begin{cases} P_G = \left(P_1 + P_2\right) \\ P_R = \frac{1}{2}\left(P_1 - P_2\right) \end{cases} \quad \begin{cases} \mu_G = 2m \\ \mu_R = \frac{m}{2} \end{cases}$$

$$H = \left\{\frac{P_G^2}{2\mu_G} + \frac{1}{2}\mu_G^2\omega_G^2 x_G^2\right\} + \left\{\frac{P_R^2}{2\mu_R} + \frac{1}{2}\mu_R\omega_R^2\left[x_R - \frac{2x_0}{1+4\lambda}\right]^2\right\} + m\omega_{0x}^2 x_0^2 \frac{4\lambda}{1+4\lambda}$$

Normal frequencies

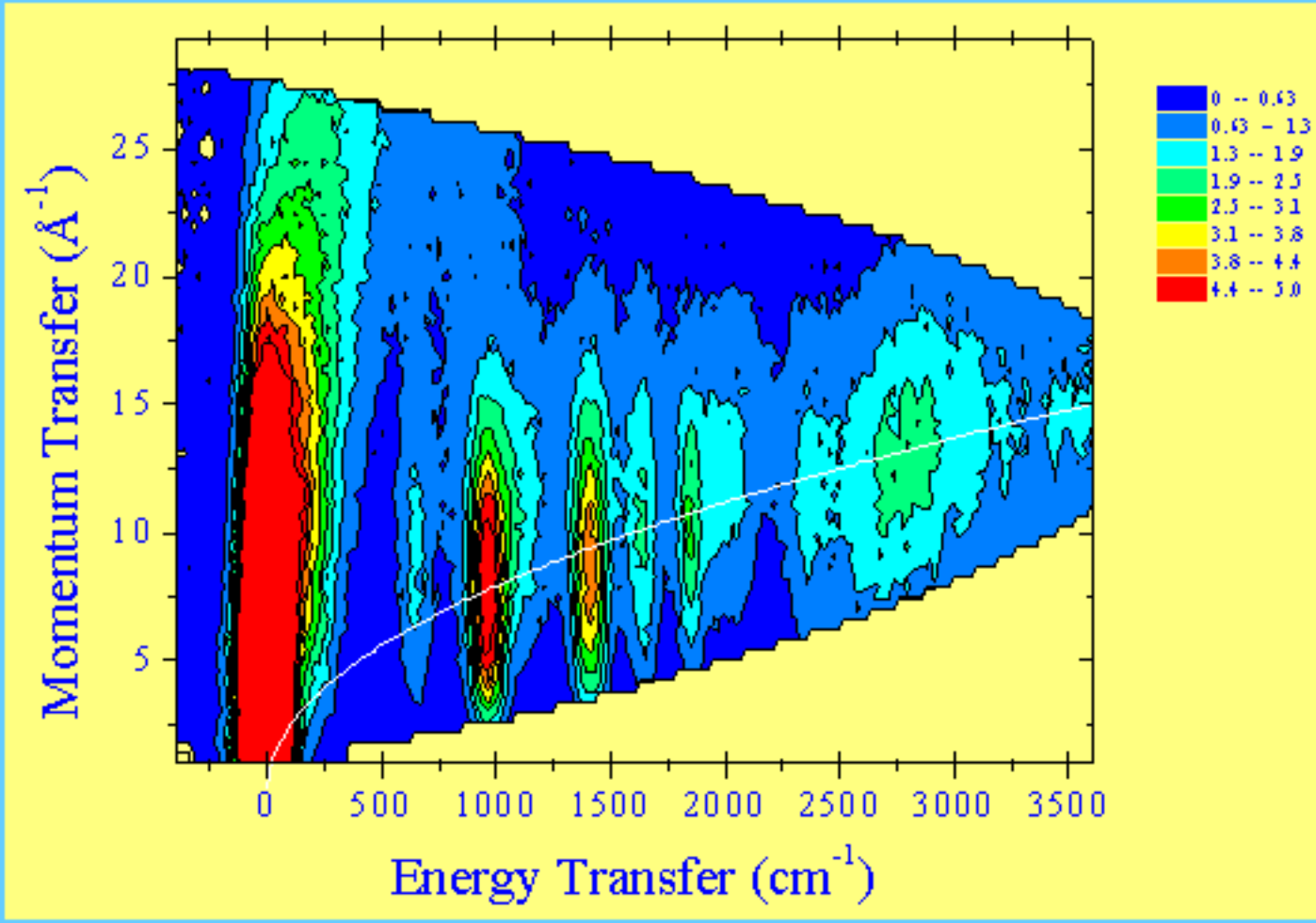
$$\omega_G = \omega_{0x} \quad \text{and} \quad \omega_R = \omega_{0x}\sqrt{1+4\lambda_x}$$

Eigen states

$$\left.\begin{aligned} \Psi_{\alpha\sigma} &= \Psi_\alpha^G\left(x_G\right) \times \Psi_\sigma^R\left(x_R - \sqrt{2}x_0'\right), \\ E_{\alpha\sigma} &= \left(\alpha + \frac{1}{2}\right)\hbar\omega_G + \left(\sigma + \frac{1}{2}\right)\hbar\omega_R \end{aligned}\right\}$$

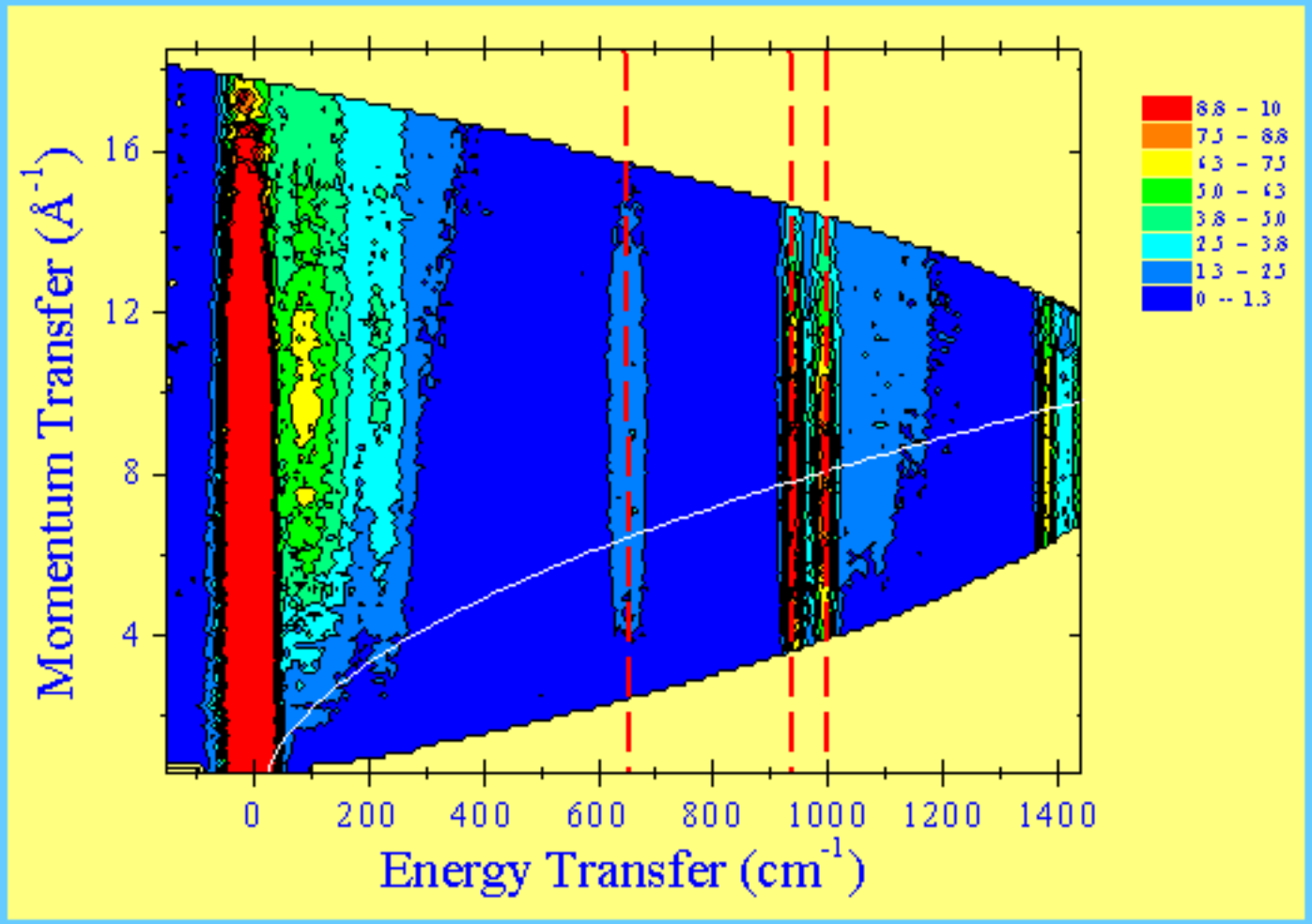
$KHCO_3$ INS

$E_i = 4000\ cm^{-1}$

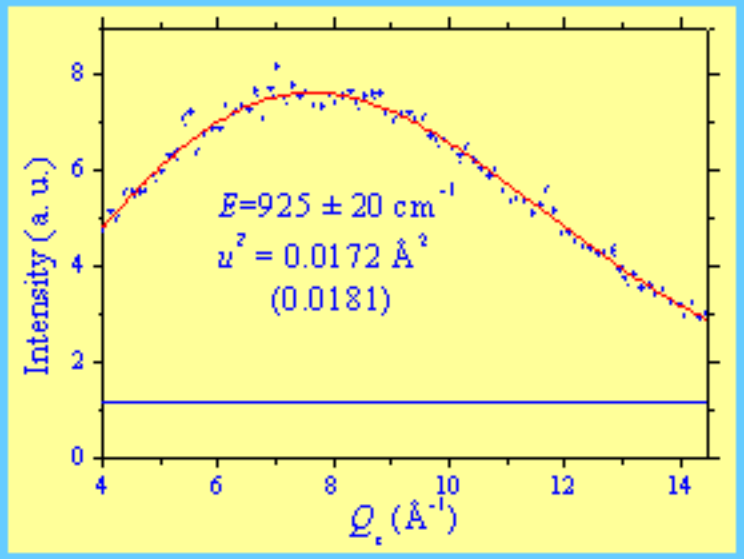


$KHCO_3$ INS

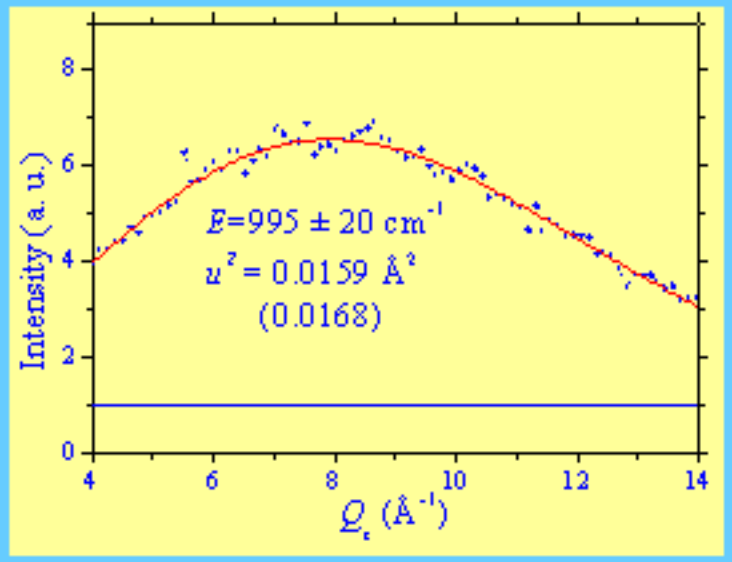
$E_i = 1600\ cm^{-1}$



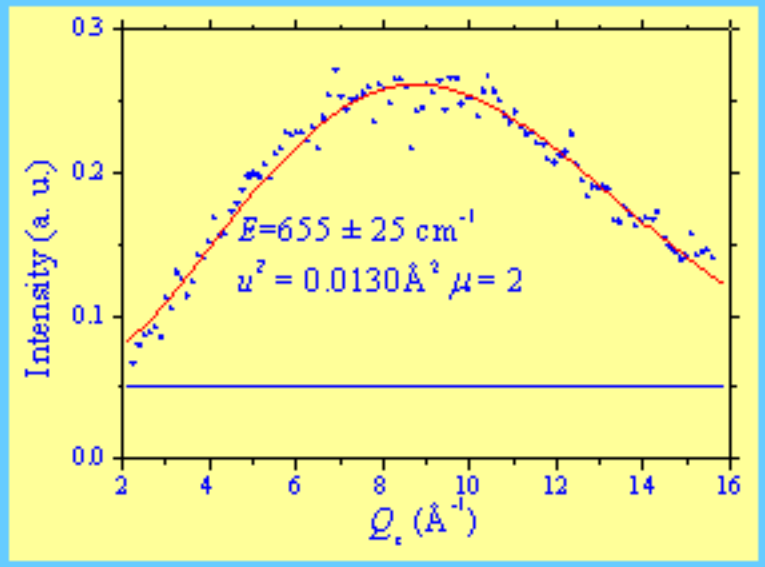
γ-OH_{ip}



γ-OH_{op}



δ-CO_3



Pair of Coupled Oscillators

$$H = \frac{1}{2m}\left(P_1^2 + P_2^2\right) + \frac{1}{2}m\omega_{0x}^2\left[\left(x_1 - x_0\right)^2 + \left(x_2 + x_0\right)^2 + 2\lambda_x\left(x_1 - x_2\right)^2\right]$$

Normal coordinates

$$\begin{cases} x_a = \dfrac{1}{\sqrt{2}}\left(x_1 + x_2\right) \\ x_s = \dfrac{1}{\sqrt{2}}\left(x_1 - x_2\right) \end{cases} \qquad \begin{cases} P_a = \dfrac{1}{\sqrt{2}}\left(P_1 + P_2\right) \\ P_s = \dfrac{1}{\sqrt{2}}\left(P_1 - P_2\right) \end{cases}$$

$$H = \left\{\frac{P_a^2}{2m} + \frac{1}{2}m\omega_{0x}^2 x_a^2\right\} + \left\{\frac{P_s^2}{2m} + \frac{1}{2}m\omega_{0x}^2\left(1 + 4\lambda_x\right)\left[x_s - \sqrt{2}x_0'\right]^2\right\} + m\omega_{0x}^2 x_0^2\frac{4\lambda_x}{1 + 4\lambda_x}$$

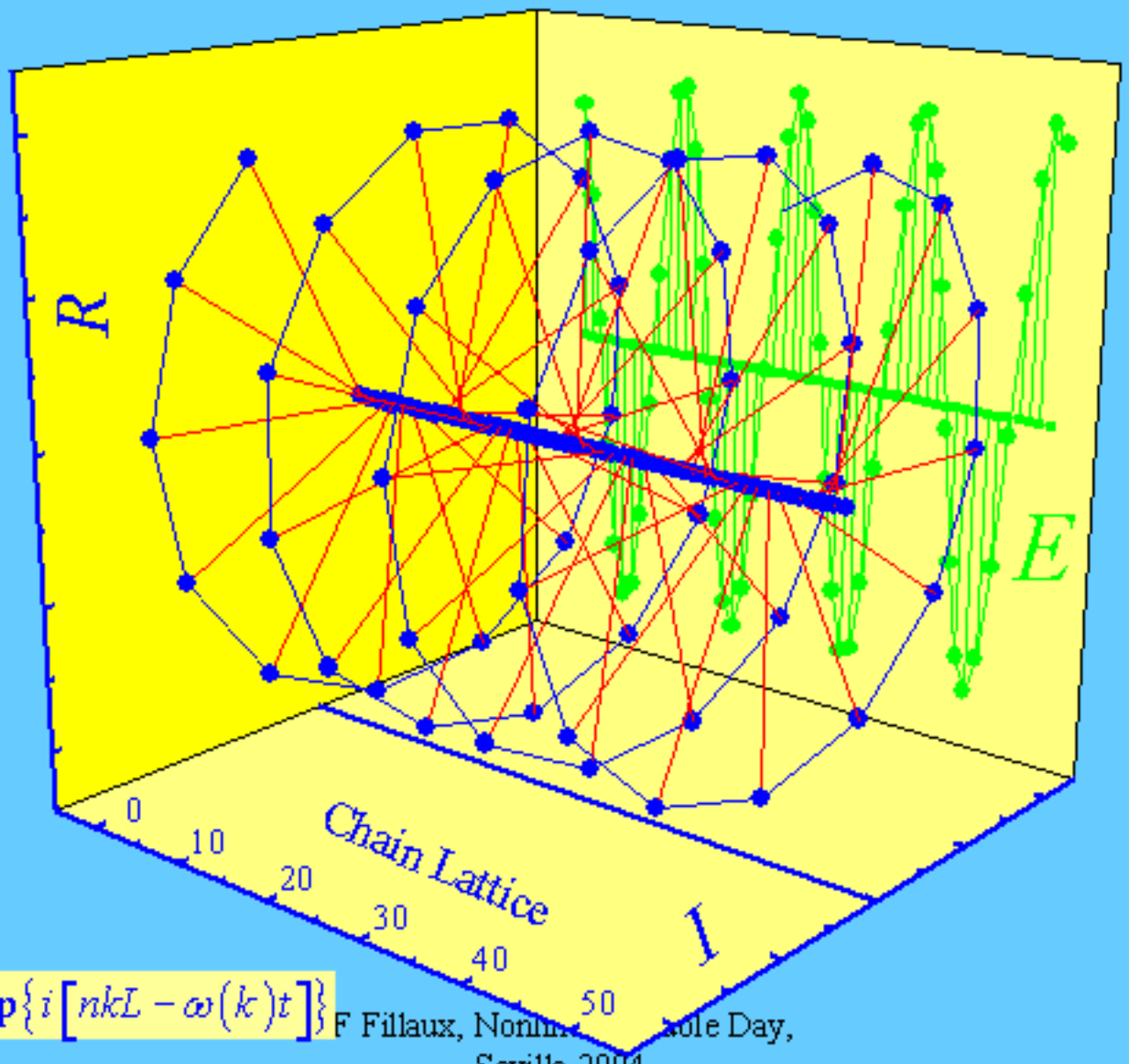
Normal frequencies

$$\omega_a = \omega_{0x} \quad \text{and} \quad \omega_s = \omega_{0x}\sqrt{1 + 4\lambda_x}$$

Eigen states

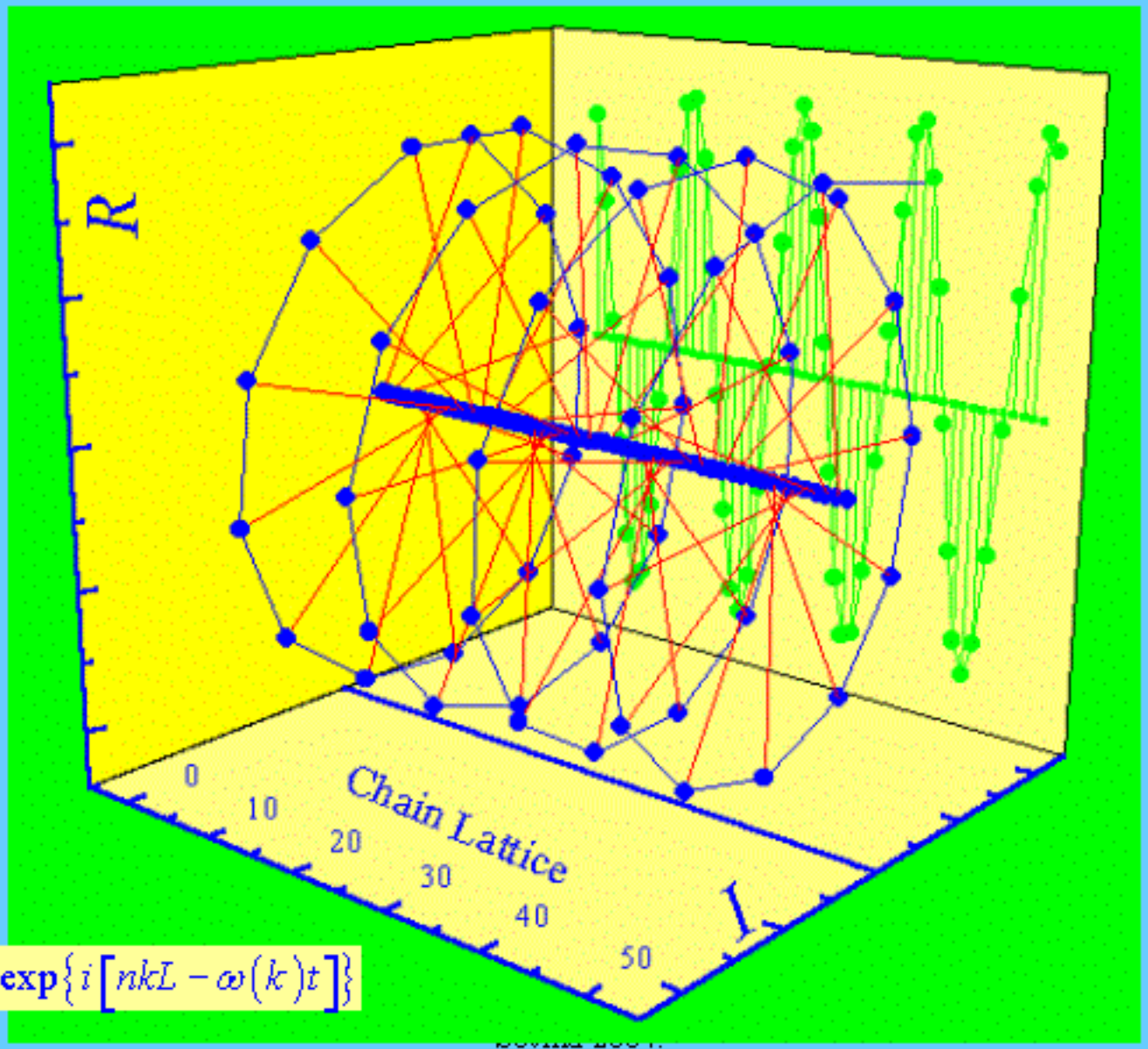
$$\left.\begin{aligned} \Psi_{a\sigma} &= \Psi_a^a\left(x_a\right) \times \Psi_\sigma^s\left(x_s - \sqrt{2}x_0'\right), \\ E_{a\sigma} &= \left(\alpha + \frac{1}{2}\right)\hbar\omega_a + \left(\sigma + \frac{1}{2}\right)\hbar\omega_s \end{aligned}\right\}$$

Phonons in Crystal Lattices (II)



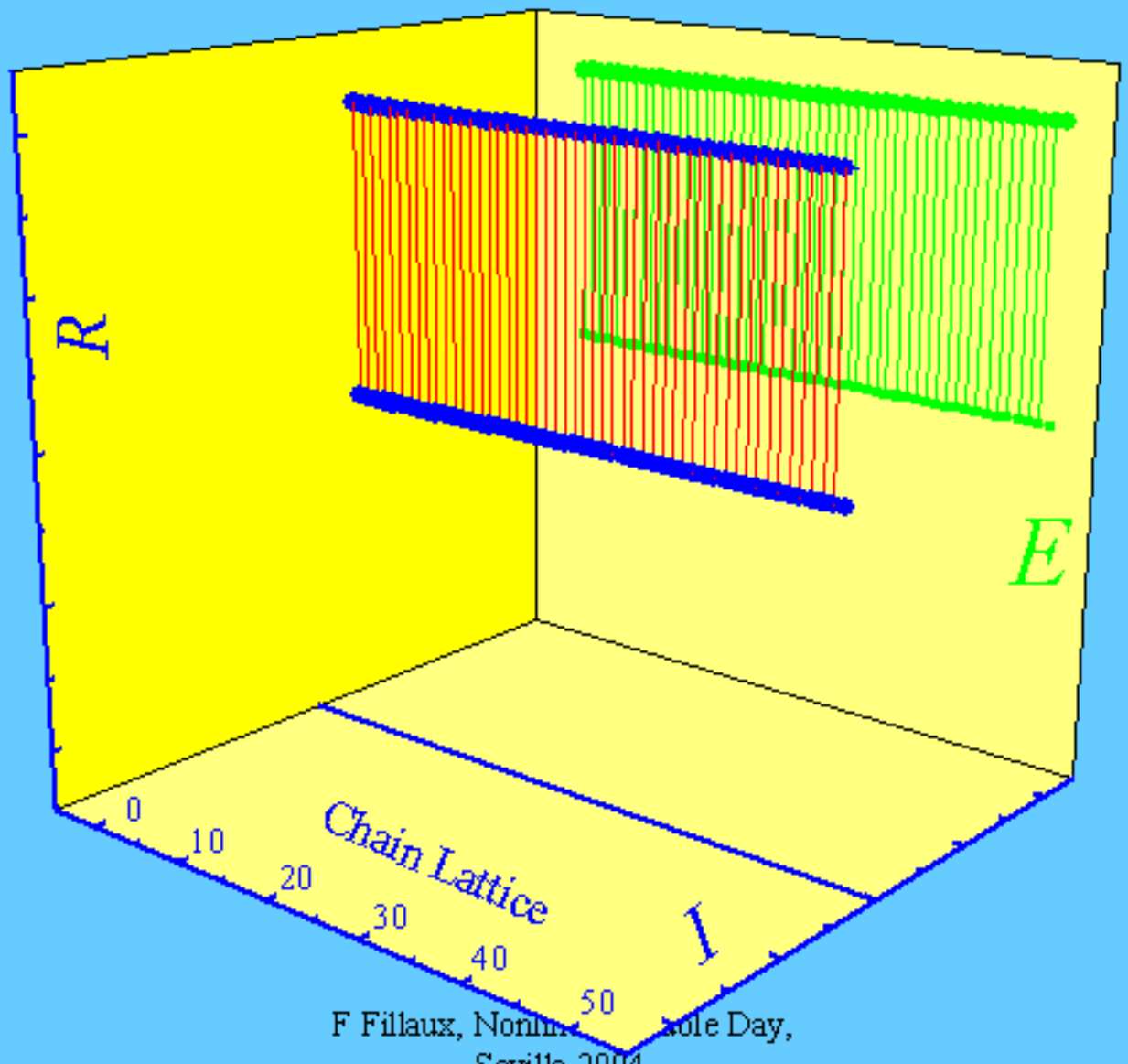
$$x_j(k,t) \propto \exp\left\{i\left[nkL - \omega(k)t\right]\right\}$$

Phonons in Crystal Lattices (III)



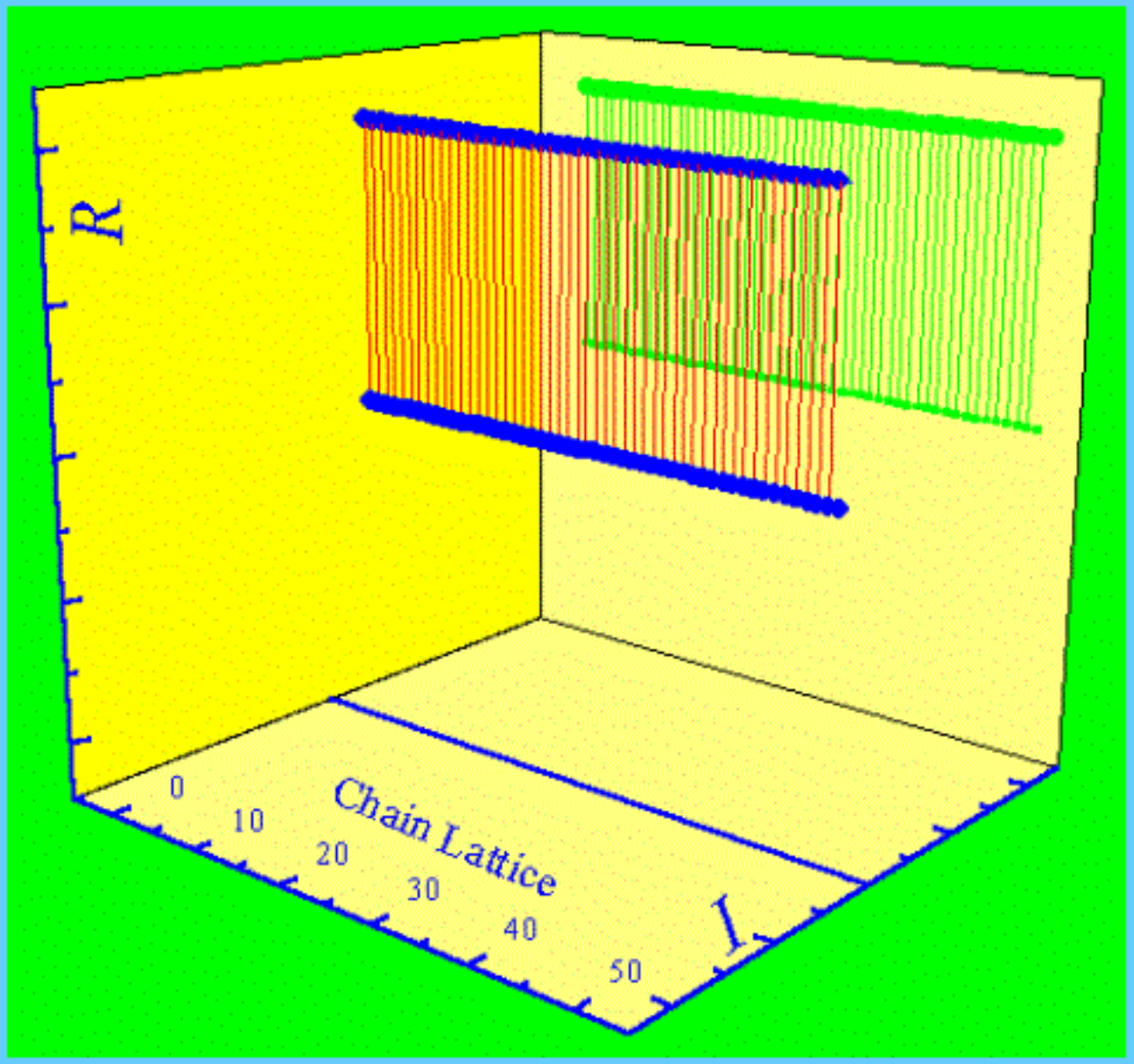
$$x_j(k,t) \propto \exp\{i[nkL - \omega(k)t]\}$$

Probing Phonons with Infrared and Raman (III)



$k = 0$

Probing Phonons with Infrared and Raman (III)



$k = 0$

Inelastic Neutron Scattering