

NEUTRON SPECTROSCOPY

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Introduction and application to KH bistrifluoroacetate

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Spectroscopy

- Spectroscopy: Observation of radiation or particles interaction with matter in order to determine its structure and the forces between its components.
- Energies:
 - Rotational: $\sim 10^{-4}$ eV, cm^{-1} , microwaves or IR
 - Electronic states: \sim eV, 10^4 cm^{-1} , visible, rX
 - Vibrational: $0.1 \sim 10^{-1}$ eV, 10^3 cm^{-1} IR
- Magnitudes and units
 - Wave number (energy) $\bar{\nu} = 1/\lambda$ (photons), cm^{-1}
 - $E = h \nu = h c / \lambda = h c \bar{\nu}$
 - $1 \text{ eV} = 8070 \text{ cm}^{-1} \sim 10^4 \text{ cm}^{-1}$
- Neutrons
 - $E = \frac{p^2}{2m}$, $p = \frac{h}{\lambda}$ \rightarrow $E = \frac{h^2}{2m \lambda^2}$

Some characteristics of vibrational spectroscopy

| | E cm ⁻¹ | E eV | λ Å | ν=E/h THz |
|----------|-----------------------|--------------------------|-----------------------|-----------------------|
| Infrared | < 5000 | <0.6 | > 2 · 10 ⁴ | > 150 |
| Raman | ~ 2 · 10 ⁴ | ~ 2.5 | ~ 5 · 10 ³ | ~ 600 |
| rX | ~ 10 ⁸ | ~ 1.24 · 10 ⁴ | ~ 1 | ~ 3 · 10 ⁶ |
| neutrons | 5000-1 | 0.6-10 ⁻⁴ | 0.4-26 | 150-0.03 |

- Distances between atoms ~ Å
- IR or Raman: in-phase vibrations of thousands of molecules or atoms
- To study molecular structure or crystals: rX o neutrons
- rX do not allow determination of vibrational levels

Optical techniques: IR or Raman

- Interaction of electric field with matter
- Dipole moment:

$$\vec{M} = \vec{M}_0 + \sum_j \frac{\partial \vec{M}}{\partial x_j} x_j + \dots$$

- Estates and energies of a molecule or crystal:

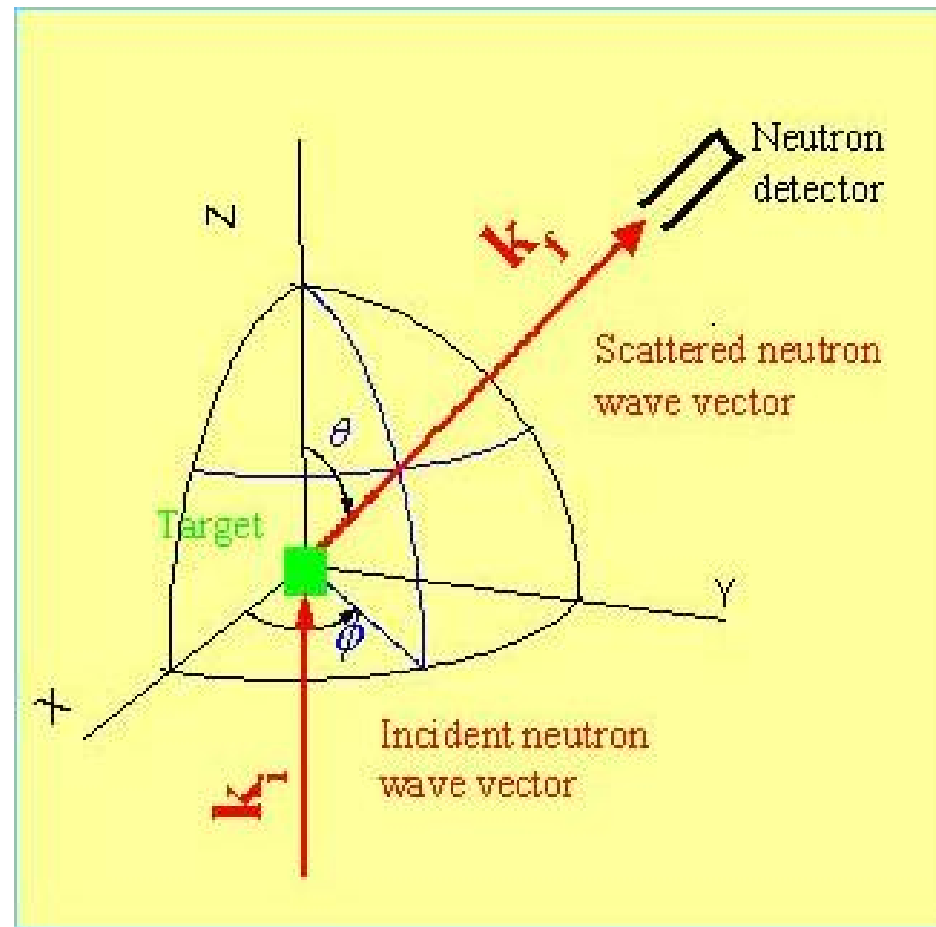
initial: $|\phi_0\rangle$ E_0 ; final: $|\phi_f\rangle$ E_f

- Intensity I of a energy band $\nu_0 = \frac{E_f - E_0}{h}$:

I proportional to $|\langle \phi_0 | M | \phi_f \rangle|^2$

- Only vibrations the produce a change in the dipole moment are infrared active
- Only vibrations that produce a change in polarizability are Raman active
Polarizability α : $\vec{M} = \alpha \vec{E}$

Neutron scattering I



Neutron scattering

Neutron scattering II

- Neutron: plane wave

wave vector: \vec{k} $k = |\vec{k}| = \frac{2\pi}{\lambda}$, energy $E = \frac{\hbar^2 k^2}{2m}$, momentum $\vec{p} = \hbar\vec{k}$

- Neutron initial and final states: \vec{k}_i , \vec{k}_f

- Momentum and energy transfer: $\vec{Q} = \vec{k}_i - \vec{k}_f$; $\hbar\omega = E_i - E_f$

- Crystal or molecule states, energies and momenta:

initial $|\phi_i\rangle$, ϵ_i , $\hbar\vec{q}_i$; final $|\phi_f\rangle$, ϵ_f , $\hbar\vec{q}_f$

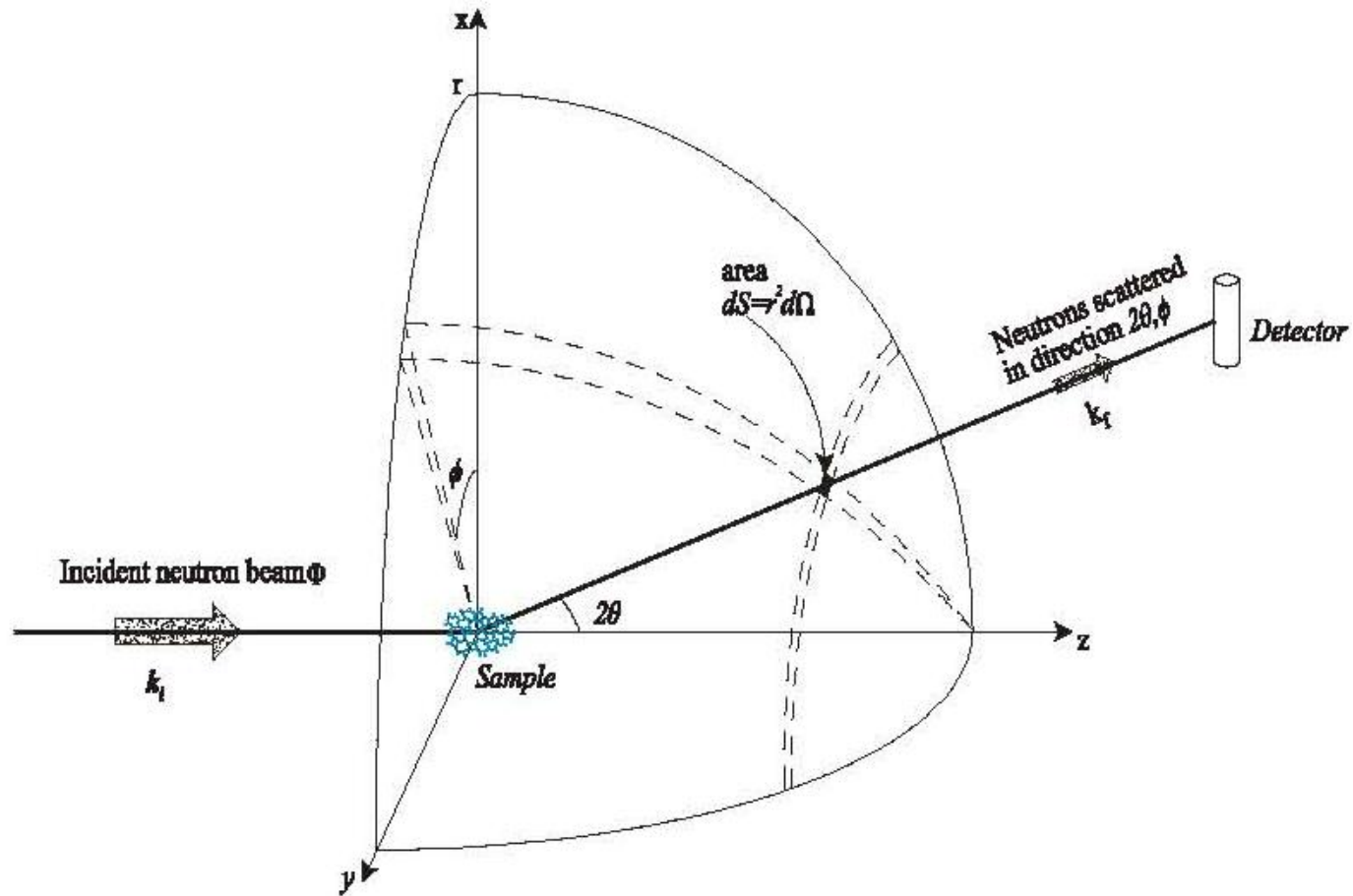
- Energy conservation. Observed frequency band:

$$\epsilon_i + \frac{\hbar^2 k_i^2}{2m} = \epsilon_f + \frac{\hbar^2 k_f^2}{2m} \quad ; \quad \omega = \frac{E_i - E_f}{\hbar}$$

- Crystal momentum conservation:

$$\vec{k}_i + \vec{q}_i = \vec{k}_f + \vec{q}_f + \vec{G} \quad ; \quad G \text{ Crystal reciprocal lattice vector}$$

Scattering cross section I



Scattering cross section II

- dn : number of neutrons per time unit scattered within a solid angle $d\Omega$
- F_i : Incident neutron flux (number of neutrons per unit of time and surface)
- Differential cross section: $dn = F_i \sigma(\theta, \phi) d\Omega$
- Total cross section: $\sigma = \int \sigma(\theta, \phi) d\Omega$, $\sigma = \frac{n}{F_i}$
- Unit: barn= 10^{-24} cm²
- Some neutron cross sections:

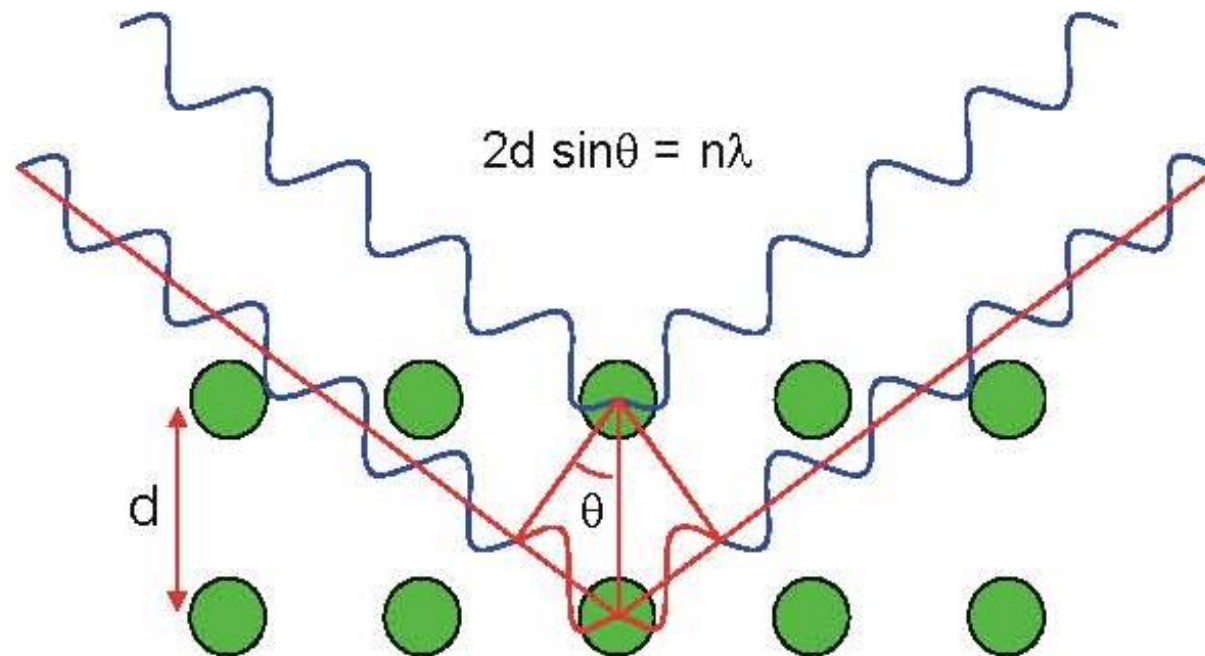
| | H | O | Al | Si | K |
|-----------------|----|---|-----|-----|----|
| Z | 1 | 8 | 13 | 14 | 19 |
| σ (barn) | 82 | 4 | 1.5 | 2.2 | 2 |

Interaction of neutrons with matter

- Neutron spin – nuclear spin
- Not affected by the electronic structure
- Hydrogen σ is at least 10 times larger than any other nucleus
- Wave lengths of $\sim \text{\AA}$
- Energies range similar to vibrational energies $\neq rX$
- Large penetration depth
- Drawbacks: larger samples, not possible with gases

Coherent elastic scattering

$$E_i = E_f \quad ; \quad \vec{k}_f = \vec{k}_i + \vec{G} \quad \text{Bragg scattering}$$



Neutron scattering types

Coherent elastic : Bragg's law

Coherent inelastic : $\hbar \omega = E_i - E_f$, $\vec{k}_i - \vec{k}_f = \vec{q} + \vec{G}$

Probes the phonon frequency dispersion $\omega_s = \omega_s(\vec{q})$ ($s \rightarrow$ band)

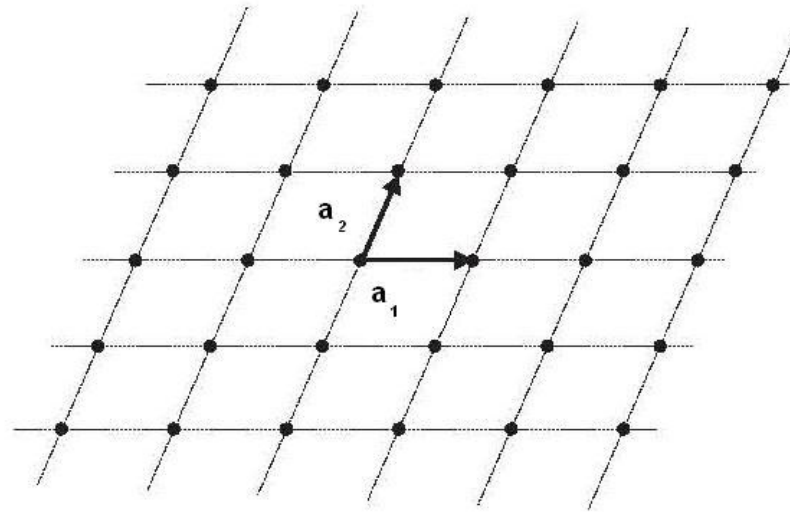
Incoherent inelastic (INS) : Probes the phonon density of states $g(\omega)$

$$g(\omega) = \sum_s \int \frac{d^3 \vec{q}}{(2\pi)^3} \delta(\omega - \omega_s(\vec{q}))$$

Incoherent elastic (IENS)

Quantum harmonic Crystal I

Direct lattice $T = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$; n_i integer ; $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$



Reciprocal lattice basis :

$$\vec{b}_1 = \frac{2\pi}{v}(\vec{a}_2 \times \vec{a}_3) \quad ; \quad \vec{b}_2 = \frac{2\pi}{v}(\vec{a}_3 \times \vec{a}_1) \quad ; \quad \vec{b}_3 = \frac{2\pi}{v}(\vec{a}_1 \times \vec{a}_2)$$

Reciprocal lattice : $G = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$ n_i integer $v_r = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^2}{v}$

Quantum harmonic Crystal II

Classical vibrational modes :

- Wave vector $\vec{q} = q_1 \vec{b}_1 + q_2 \vec{b}_2 + q_3 \vec{b}_3$ with $q_i = n_i/N_i$ $n_i = 0 \dots (N_i - 1)$
- band: $s = 1 \dots \gamma$ γ =bands number = number of atoms in unit cell
- Polarization vector: $\vec{\epsilon}_{s,i}(\vec{q})$ $i = 1 \dots 3$
- Classical phonon: $\vec{u}_{\mathbf{q},s,i}(\vec{r}, t) = \vec{\epsilon}_{s,i} e^{i(\vec{q} \cdot \vec{r} - \omega_{s,i} t)}$
- Dispersion relation: $\omega_{s,i}(\vec{q})$

Quantum description $3 \gamma N_1 N_2 N_3$ independent oscillators with occupation numbers: $n_{s,i}$

energy ;

$$H = \sum_{s,i,q} \left(n_{s,i}(\vec{q}) + \frac{1}{2} \right) \hbar \omega_{s,i}(\vec{q})$$

Periodicity Invariant with respect to the reciprocal lattice:

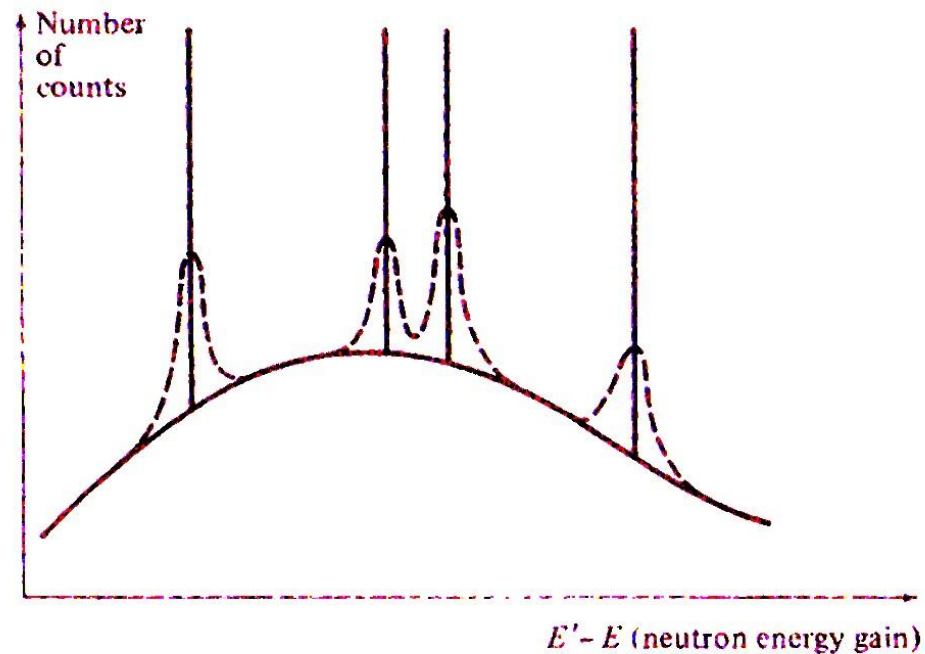
$$u_{\mathbf{q}} = u_{\mathbf{q}+\mathbf{G}} \quad ; \quad \omega(\mathbf{q}) = \omega(\vec{q} + \vec{G})$$

Interaction neutron – cristal

0 phonon processes : Bragg diffraction

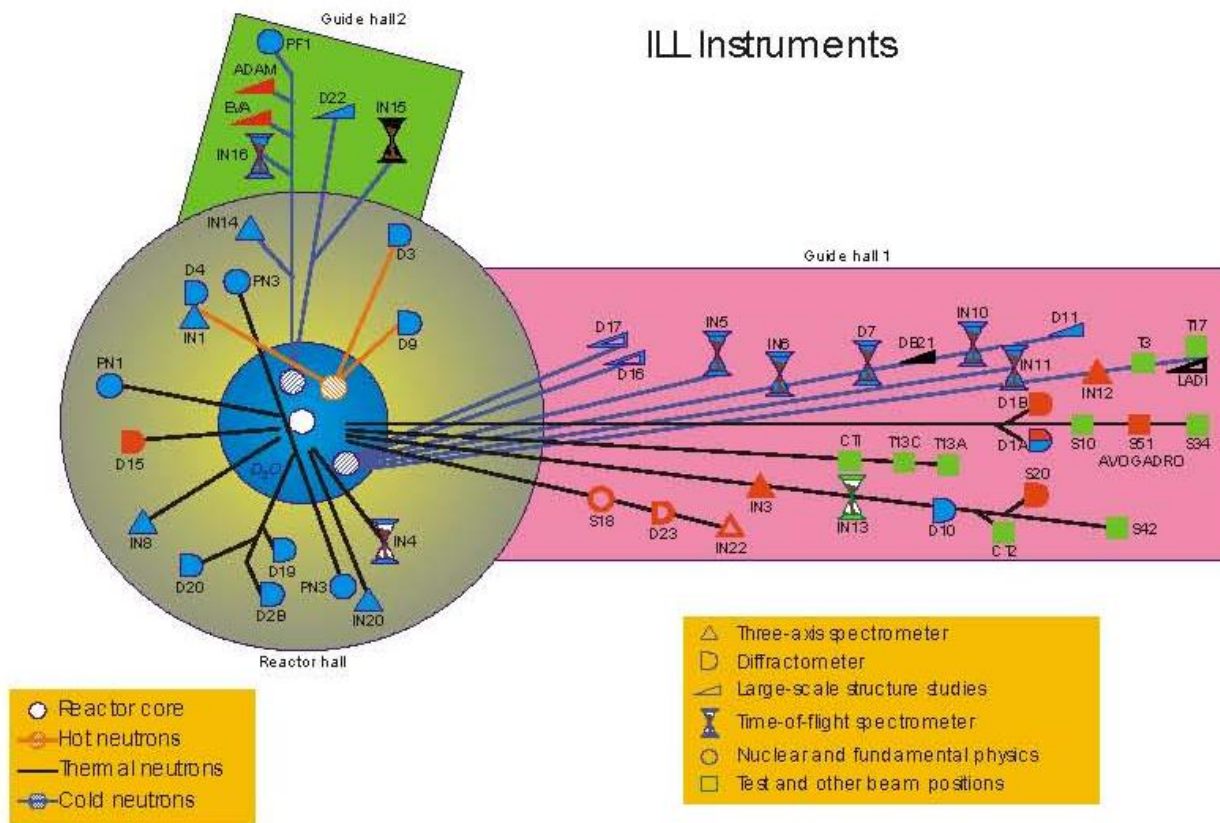
1 phonon processes : INS, sharp bands

Multiphonon processes : broad bands, consequence of unharmonicity.



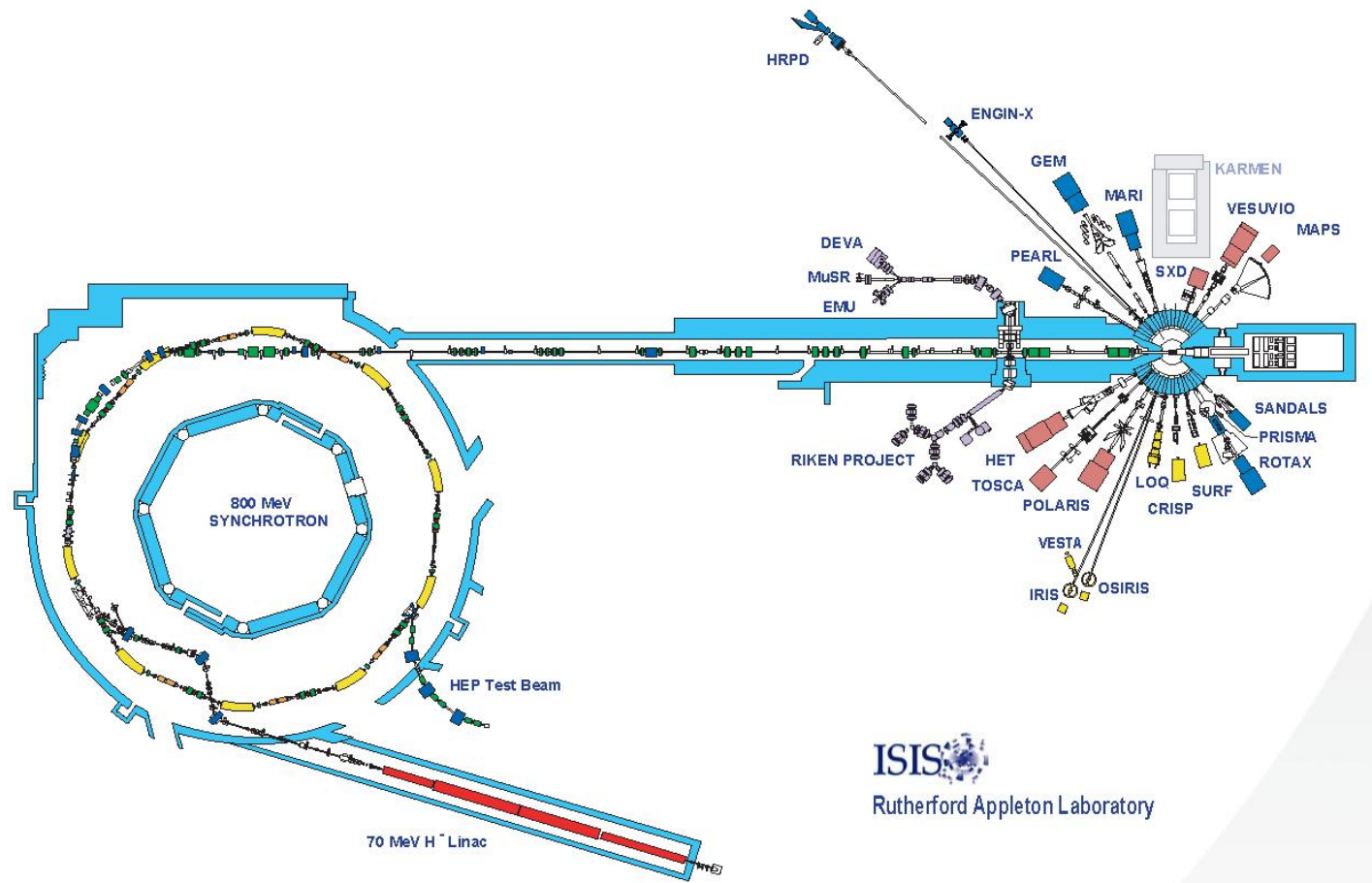
Neutron production I

Nuclear reactor



Neutron production II

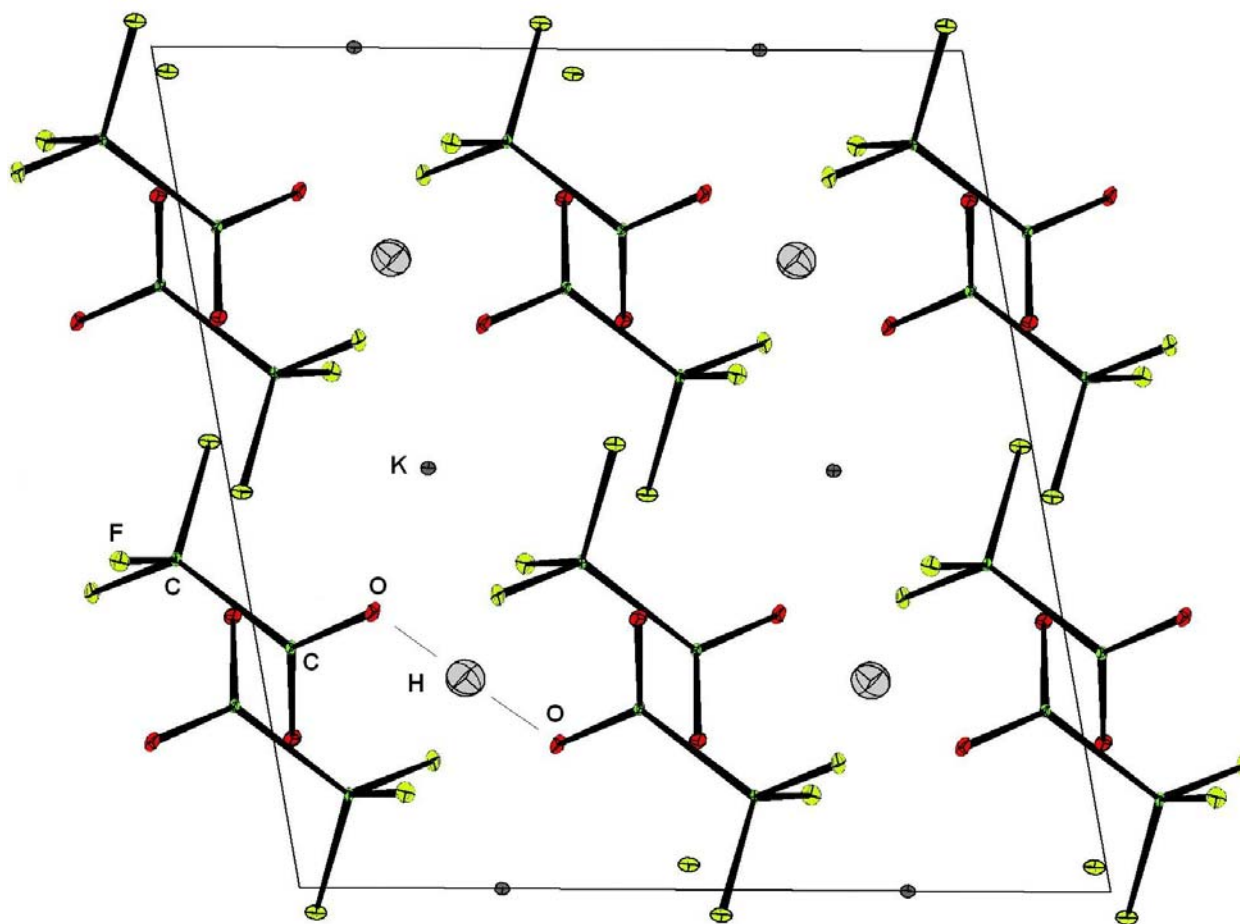
Spallation



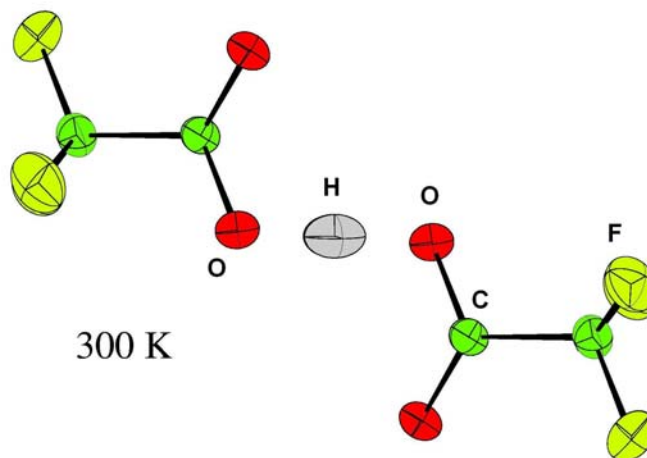
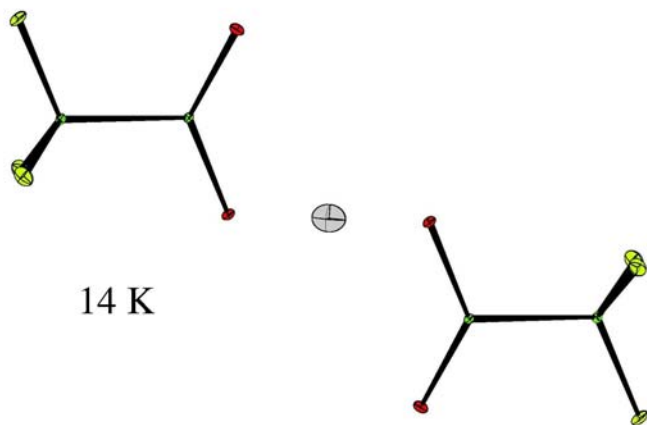
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Determination of hydrogen-bridge potential

Crystal: Potassium (or Cesium) hydrogen bistrifluoroacetate: $\text{KH}(\text{CF}_3\text{COO})_2$
 $\text{CsH}(\text{CF}_3\text{COO})_2$

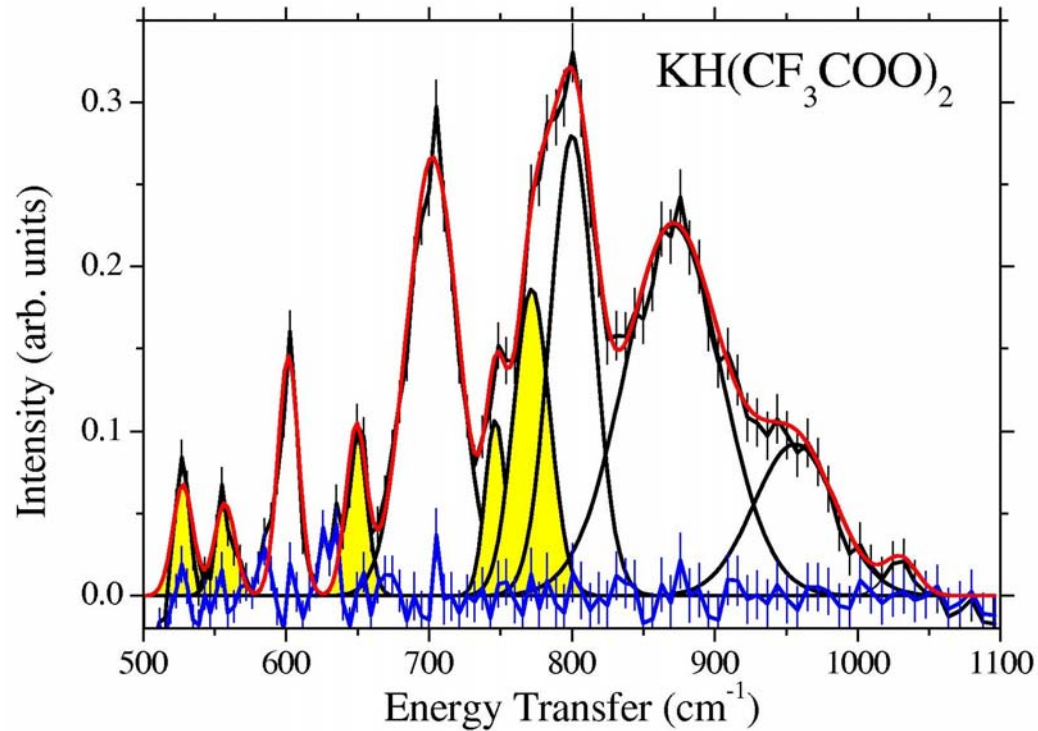


$\text{KH}(\text{CF}_3\text{COO})_2$ at different temperatures



Some data and INS spectrum

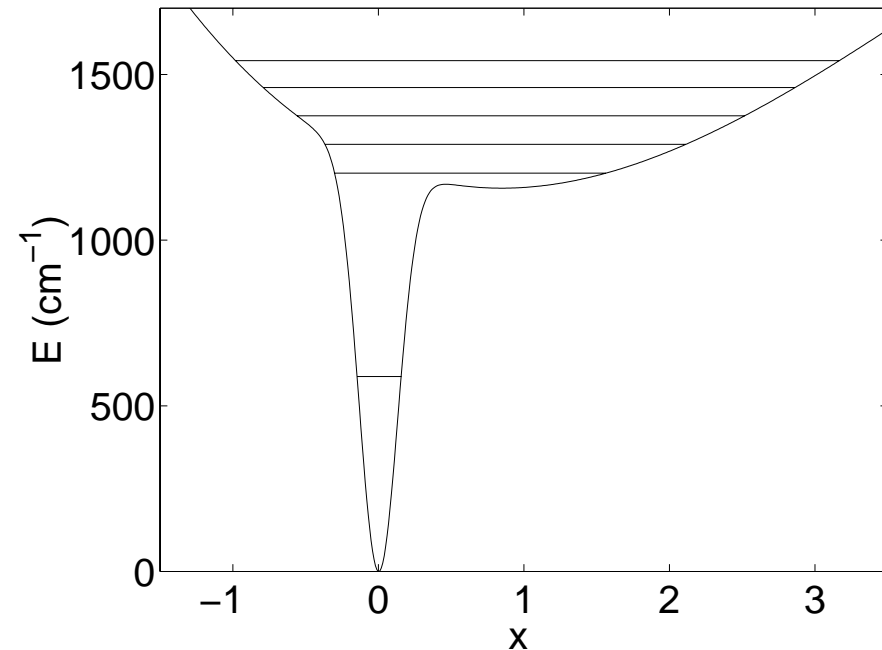
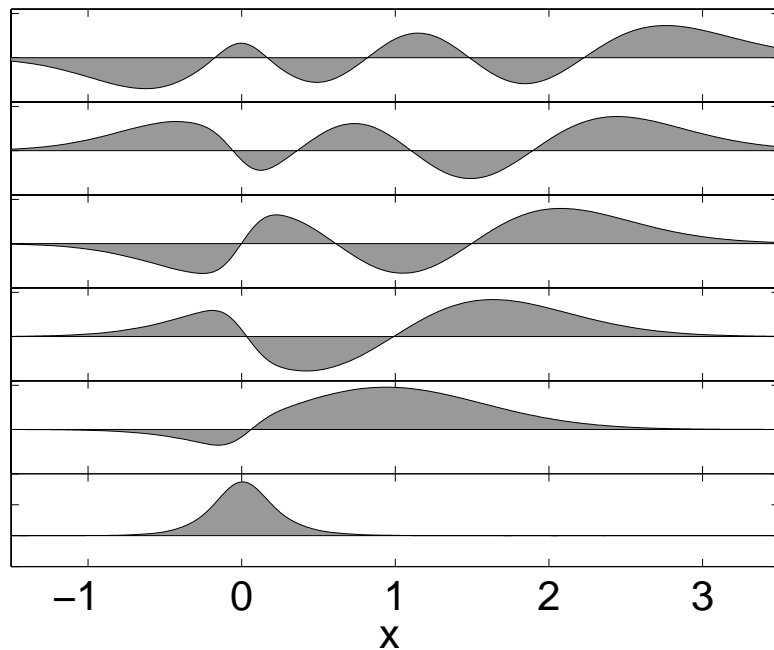
- Bond length O \cdots O : 2.436 Å
- The proton is exactly at the center



Calculation of the potential

$$-\frac{\hbar^2}{2m^*} \frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi \quad ; \quad m^* = 1 \text{ uma?}$$

$$\text{With:} \quad V(x) = V_p(x) + V_g(x) = \sum_{l=1}^6 v_l x^l + \sum_{l=1}^3 a_l \exp(-b_l x^2),$$



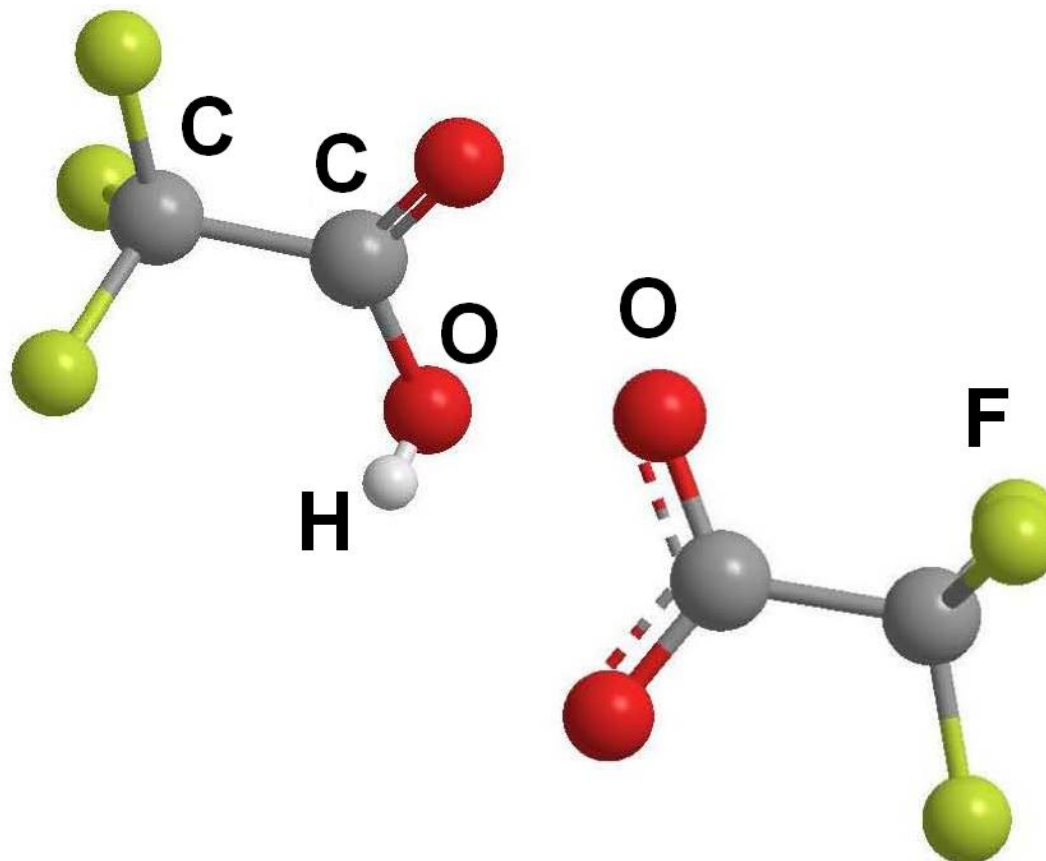
Theoretical –experimental comparison

INS OH stretching frequencies and intensities for $\text{KH}(\text{CF}_3\text{COO})_2$.

Calculated: $V = -185.074 x + 122.598 x^2 - 10.506 x^3 - 1232.04 \exp(-28.149 x^2)$, V and x in cm^{-1} and \AA , respectively.

| Transitions | Observations | | | Calculations | | |
|-------------------|-------------------------------|----------------------------|--------------|-------------------------------|----------------------------|--------------|
| | freq. (cm^{-1}) | Q (\AA^{-1}) | int. (au) | freq. (cm^{-1}) | Q (\AA^{-1}) | int. (au) |
| $0 \rightarrow 1$ | 601 | 6.0 | 0.25 | 614 | 6.1 | 0.38 |
| $0 \rightarrow 2$ | 703 | 6.5 | 0.96 | 701 | 6.5 | 0.93 |
| $0 \rightarrow 3$ | 798 | 6.9 | 1.00 | 787 | 6.9 | 1.00 |
| $0 \rightarrow 4$ | 870 | 7.2 | 0.76 | 872 | 7.2 | 0.59 |
| $0 \rightarrow 5$ | 956 | 7.6 | 0.58 | 953 | 7.5 | 0.37 |

Non-bonding states



Isis proposal

Title Determination of the effective oscillator masses for protons in strong symmetric hydrogen bonds

Applicants : Franois Fillaux (LADIR-CNRS), Alan Cousson (Saclay), JFR Archilla (GFNL, Sevilla), John Tomkinson (ISIS)

Objective : Measurement of the of scattering function $S(Q, \omega)$