Inelastic Scattering II

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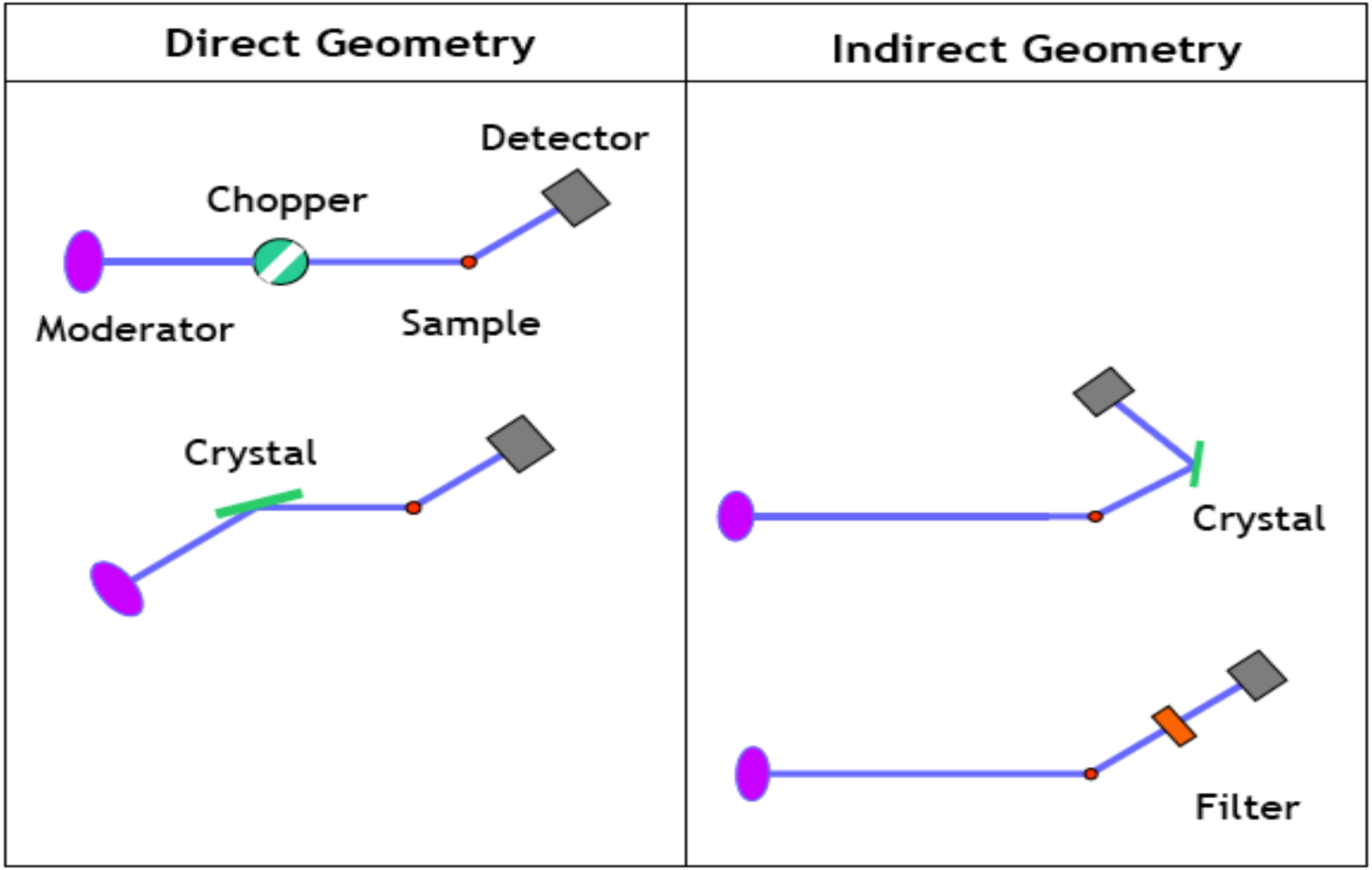
XII School of Neutron Scattering F. P. Ricci at Ettore Majorana Fundation and Centre for Scientific Culture (2014)

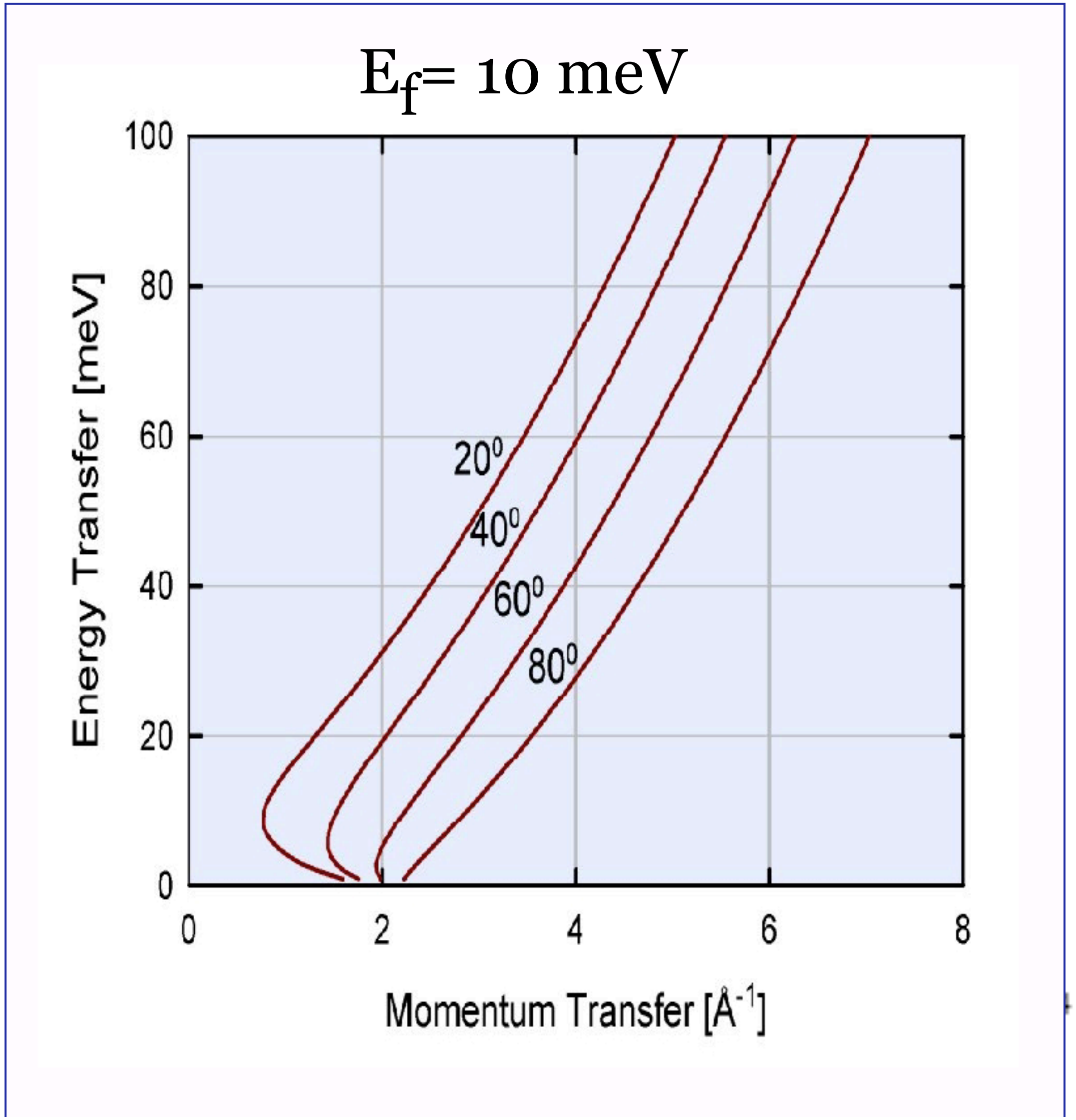
INDIRECT GEOMETRY SPECTROMETERS



TRAJECTORIES IN (Q, ω) SPACE → INDIRECT GEOMETRY

- Similarly for indirect geometry we eliminate E_i.

$$\frac{\hbar^2 \mathbf{Q}^2}{2m} = 2E_f + \hbar\omega - 2\cos\phi\left[E_f\left(E_f + \hbar\omega\right)\right]^{1/2}$$



RESOLUTION OF INDIRECT GEOMETRY SPECTROMETERS

Energy Resolution

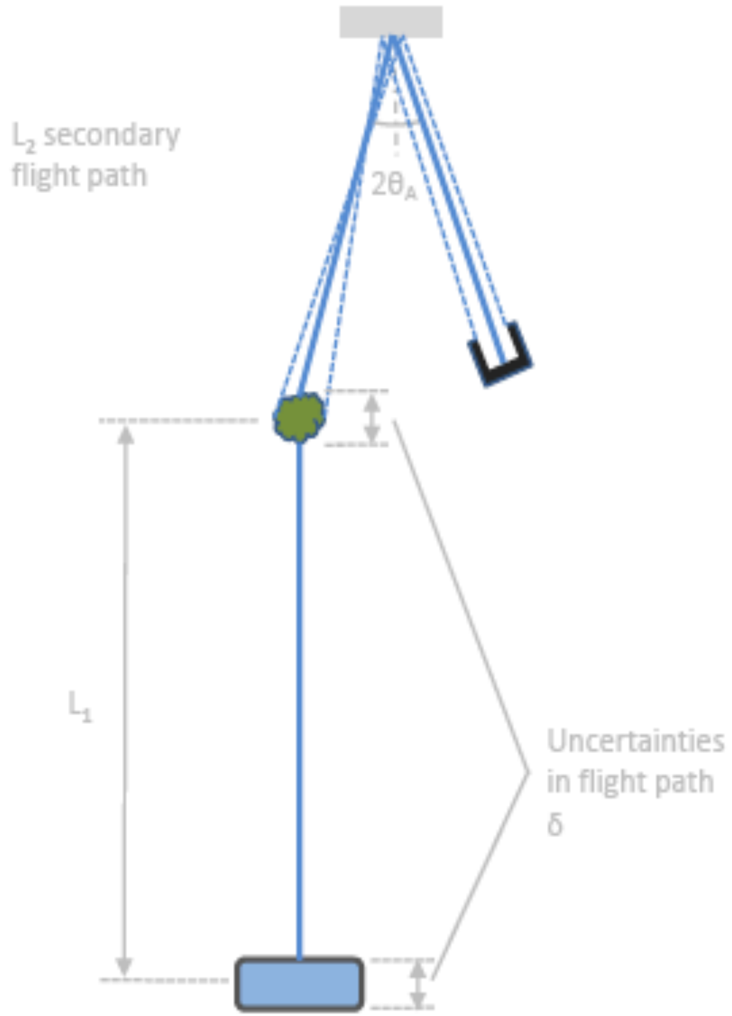
Uncertainty in the angular spread at the analyser

Timing errors due to flight path uncertainties

$$\frac{\Delta\hbar\omega}{E_i} = 2\left[\left(\frac{\delta}{L_1}\right)^2 + \left\{\frac{E_f}{E_i}\cot\theta_A \Delta\theta_A\left(1+\frac{L_2}{L_1}\left(\frac{E_i}{E_f}\right)^{3/2}\right)\right\}^2\right]^{1/2}$$

increasing θ_A or L_1 or decreasing L_2 improves resolution

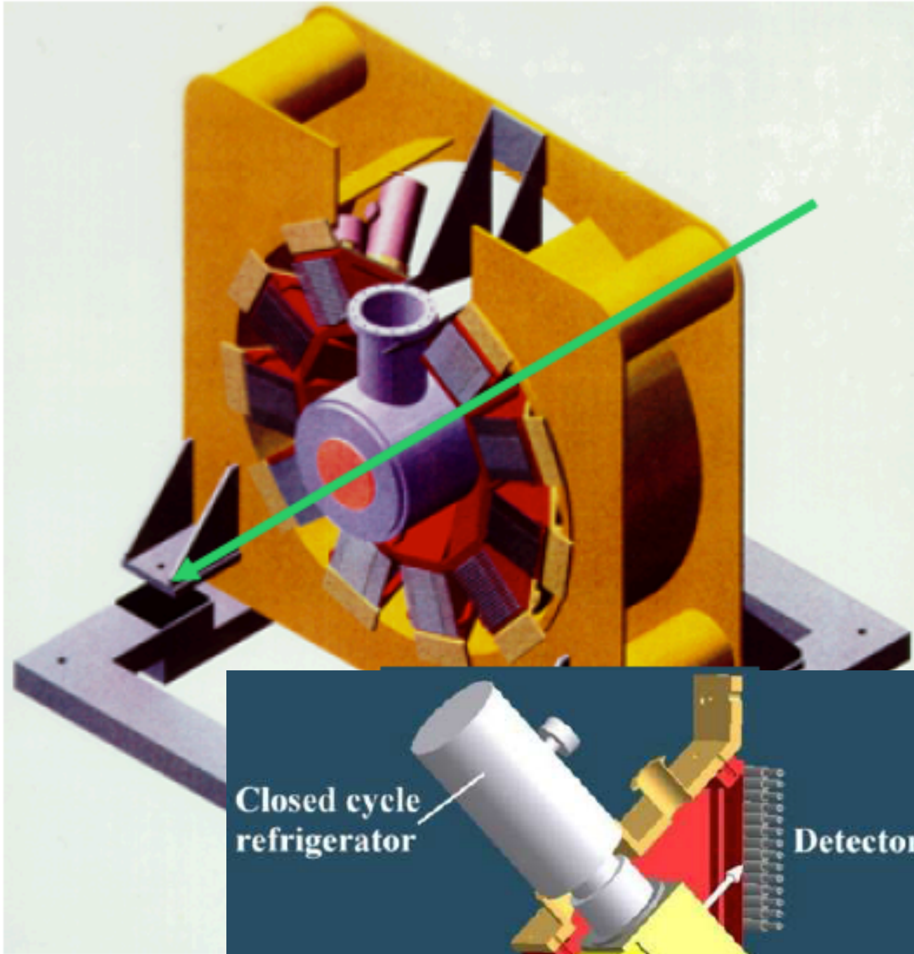
fractional energy resolution becomes worse with energy transfer, the opposite of the case for direct energy instruments.

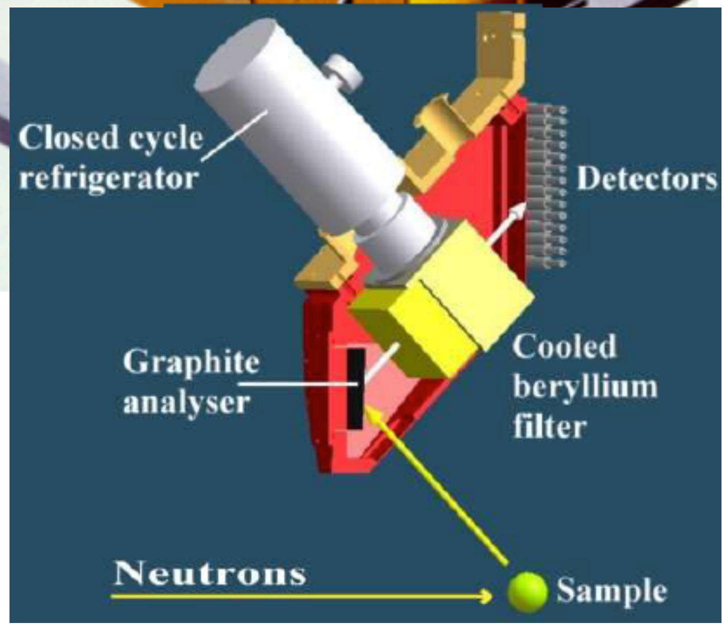


CRYSTAL ANALYZER SPECTROMETER 1 → TOSCA AT ISIS

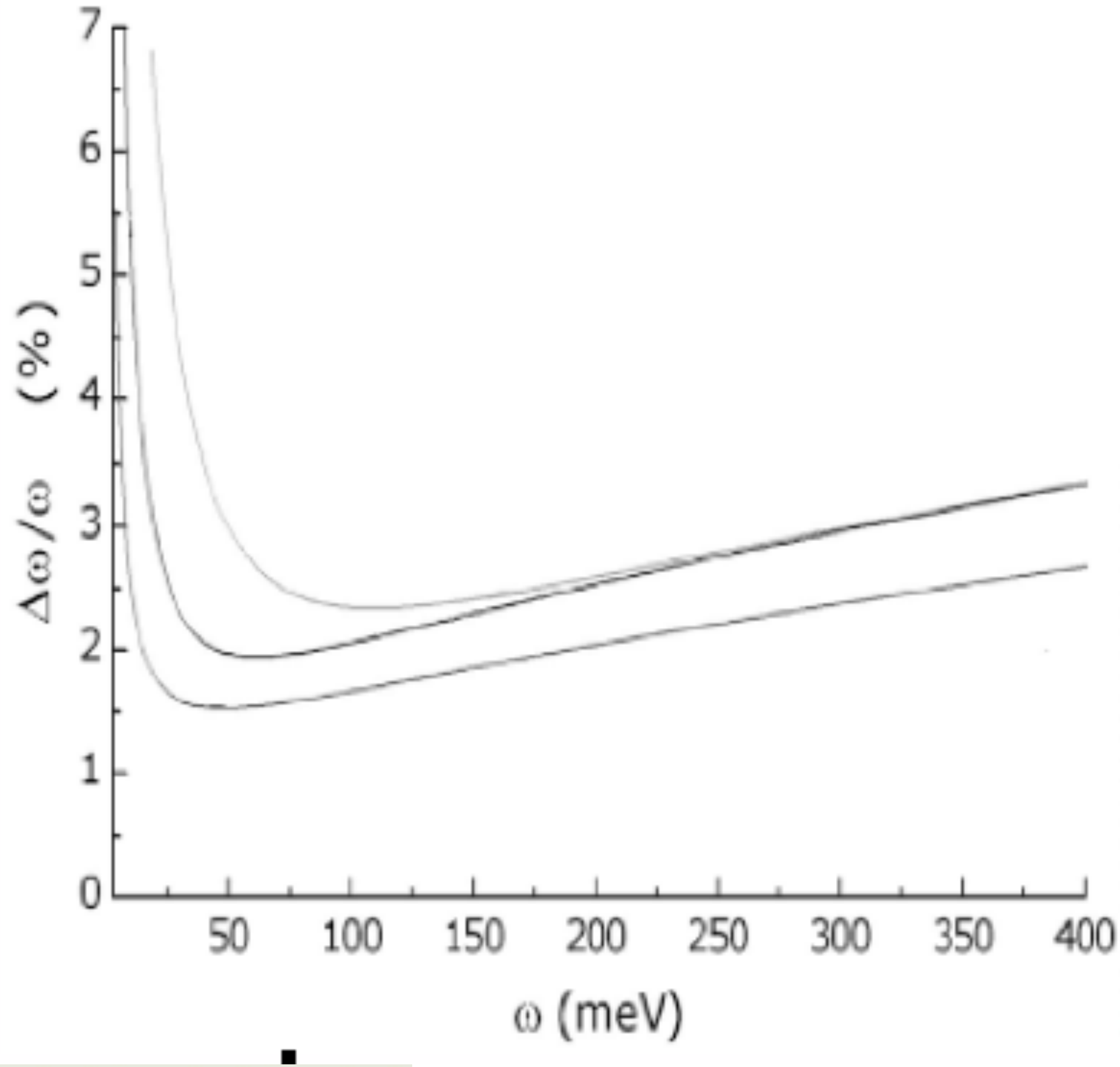
- For Molecular spectroscopy, energy information if often much more important then Q information

- Graphite analysers, E_f~3 meV
- Be filter removes higher order reflections. Cooled to reduce TDS
- The fact that sample, analyser and detectors are parallel reduces uncertainty in the scattered neutron flight time by time focussing.





ENERGY RESOLUTION FOR TOSCA



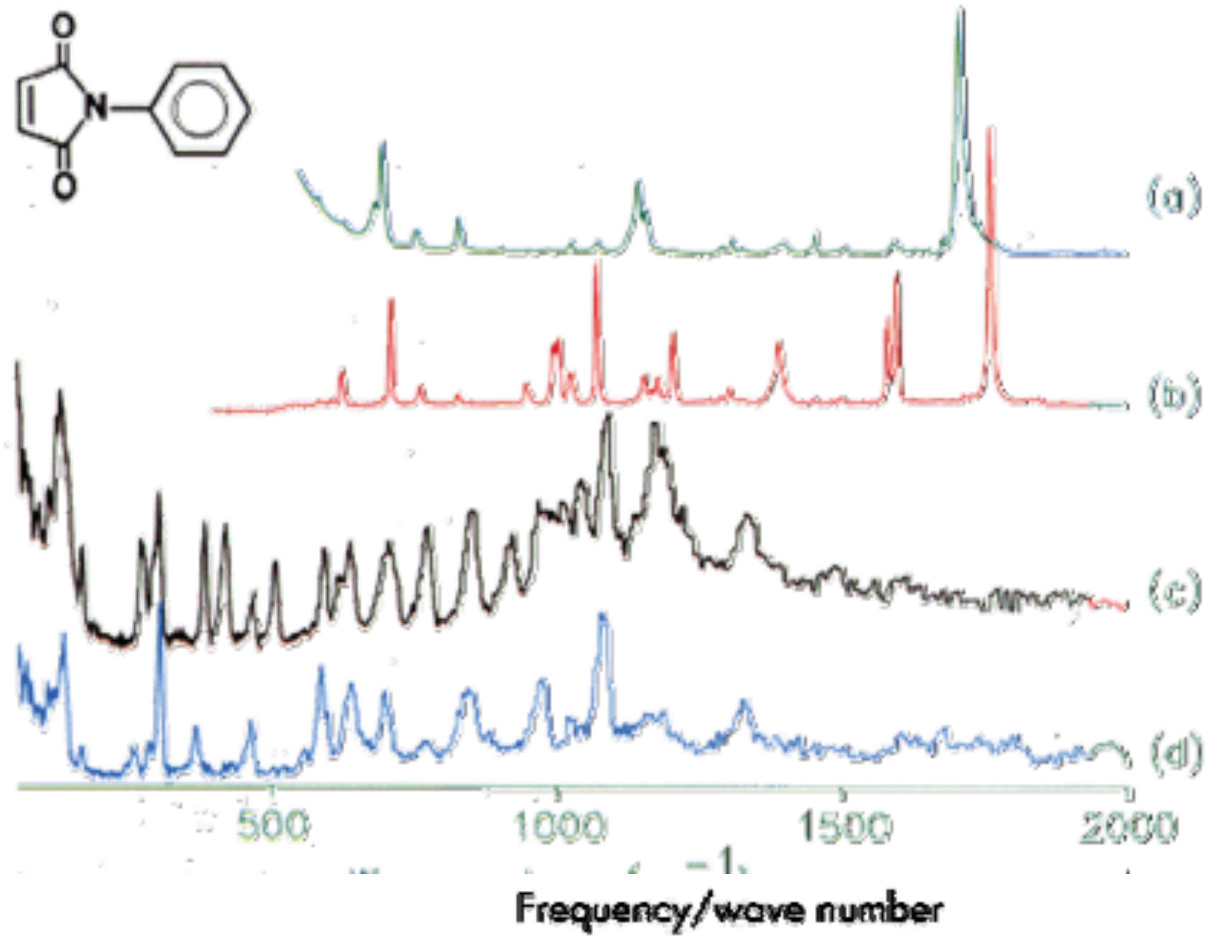
TOSCA→ EXAMPLE OF EXPERIMENT

TOSCA Data

Gives similar information to Raman and Infra-Red

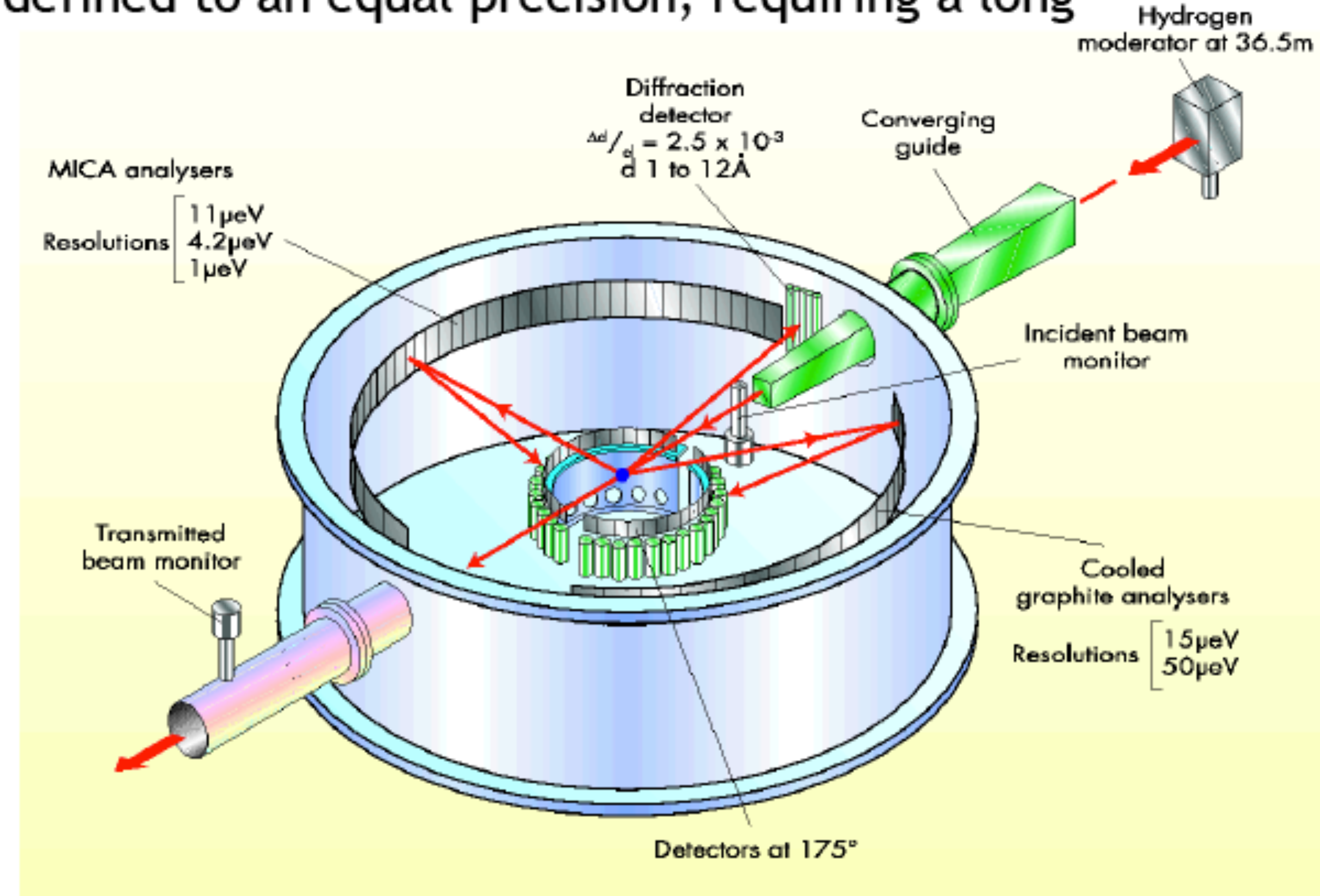
- No selection rules
- Intensity is proportional to mean square displacement
- Cross section is element dependent..
- and isotope dependent

a) Infrared
b) (b) Raman
c) (c) INS spectra of N-phenylmaleimide
d) (d) INS spectrum of N-(perdeuterophenyl)maleimide



CRYSTAL ANALYZER SPECTROMETER 2→ IRIS @ ISIS

- For a crystal analyser spectrometer, the resolution contains a cotθ_A term which can be reduced to almost zero by using a backscattering geometry.
- E_i should be defined to an equal precision, requiring a long flight path.



CRYSTAL ANALYZER SPECTROMETER 2

For a crystal analyser spectrometer, the cot θ_A term can be reduced to almost zero by using backscattering

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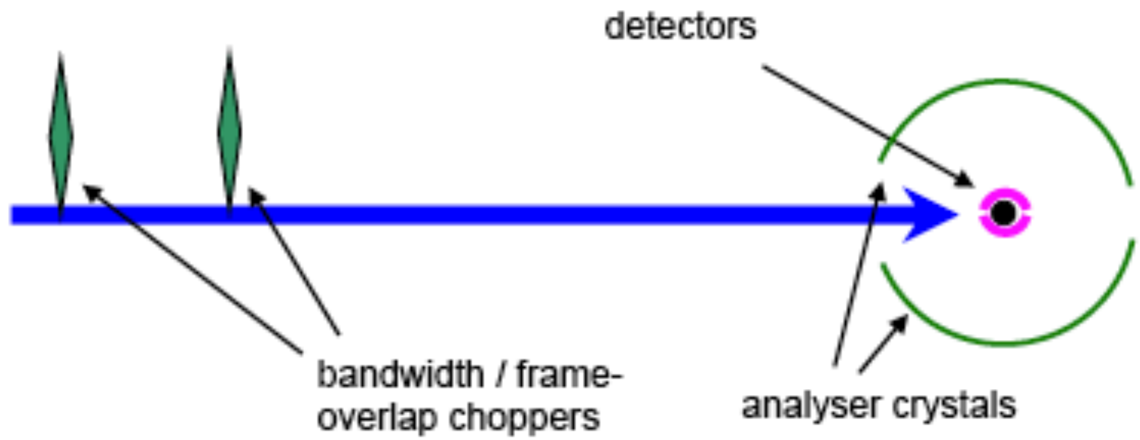
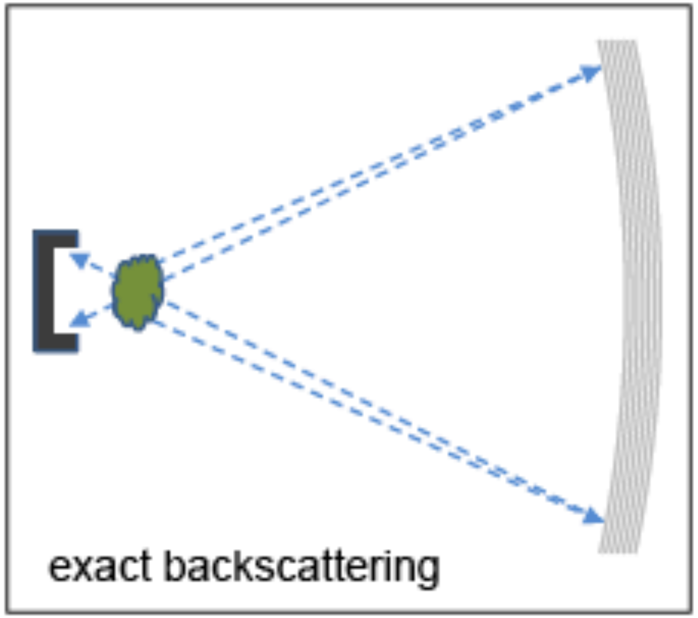
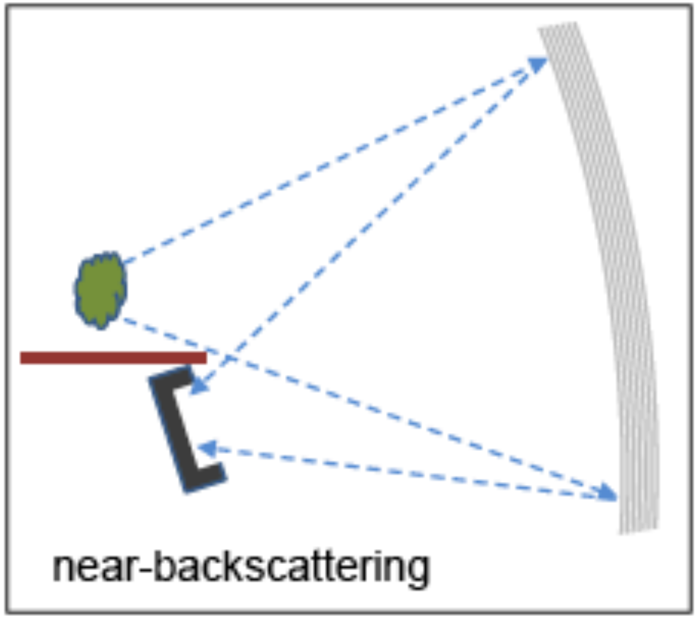




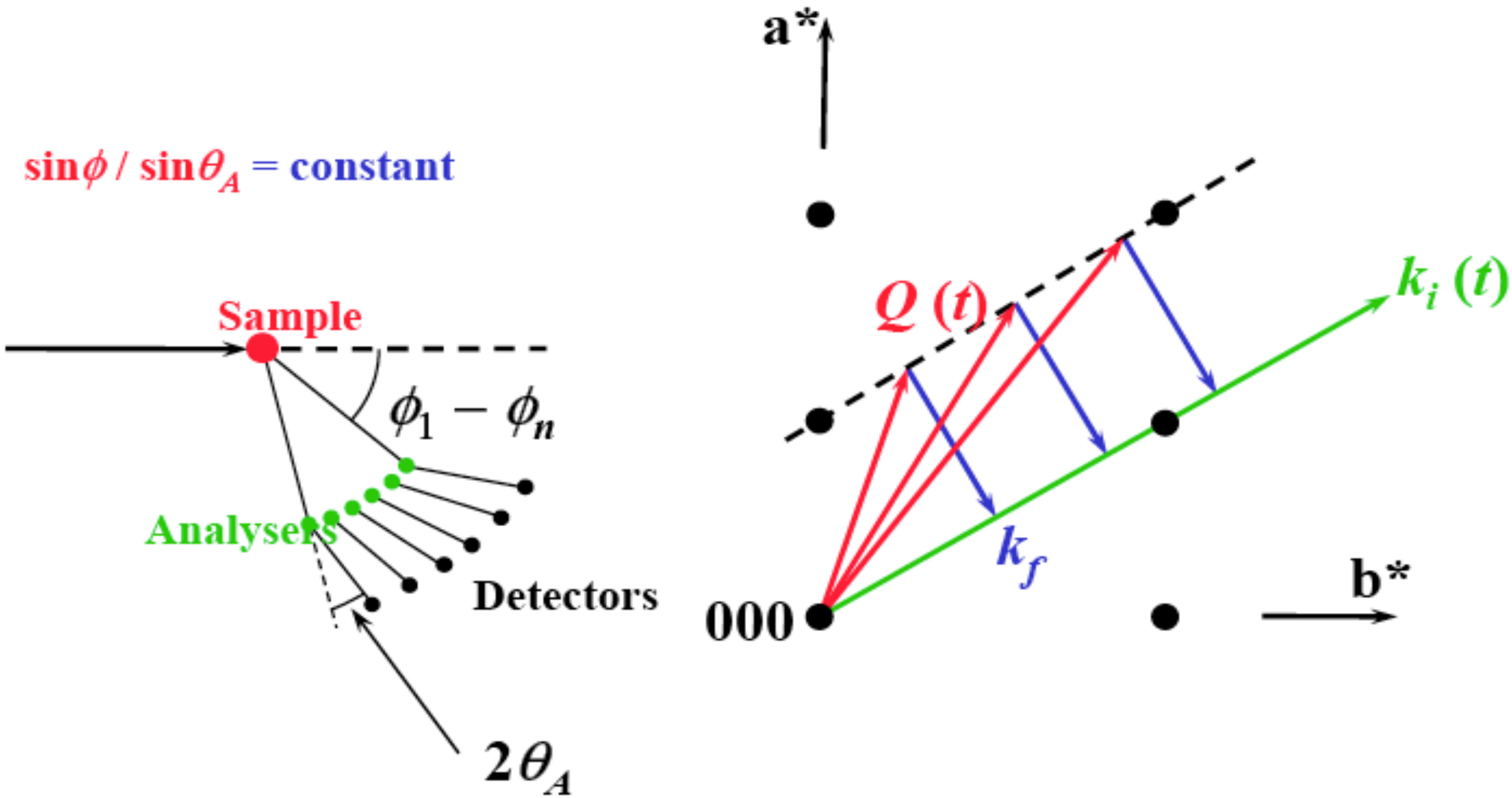
IN10, IN16



IRIS, IN13

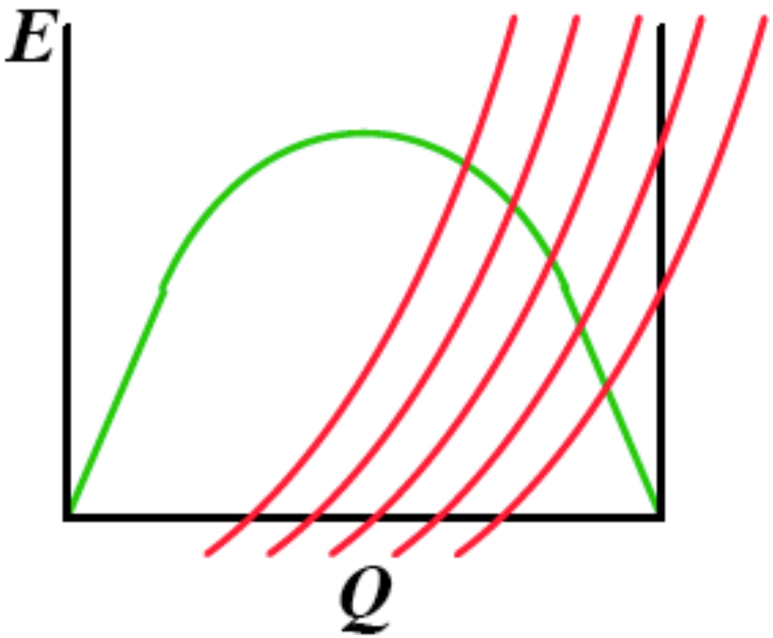
CRYSTAL ANALYZER SPECTROMETER 3
COHERENT EXCITATIONS - PRISMA

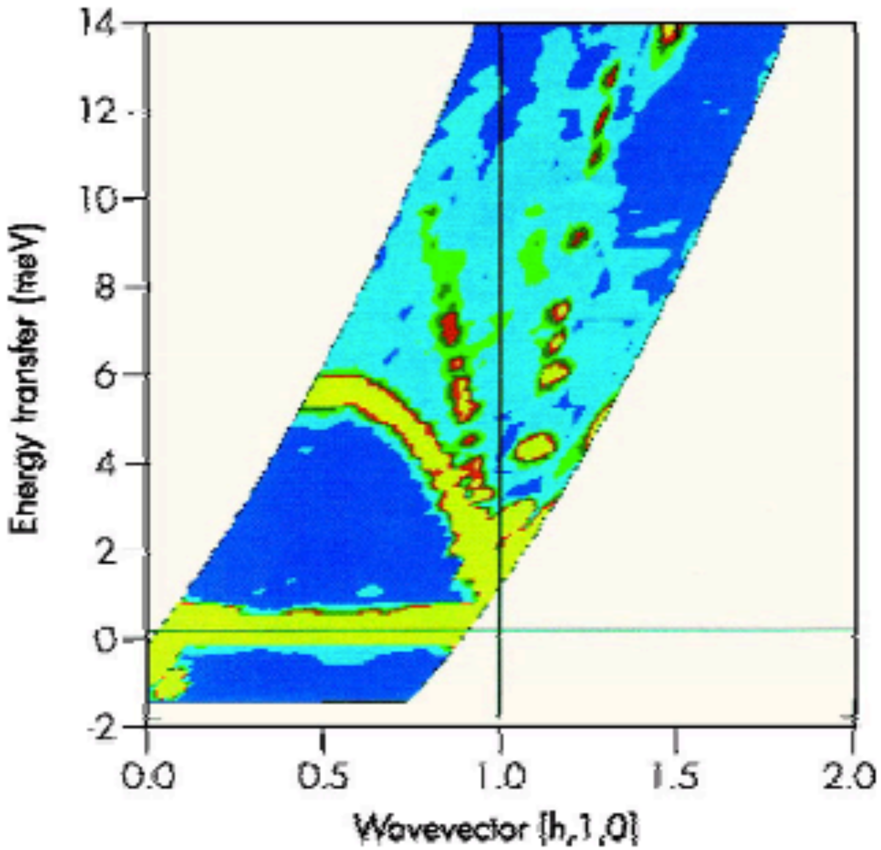
- Chopper spectrometers can be used to study coherent excitations in single crystals, **but** they are not able to directly perform scans along high symmetry directions.



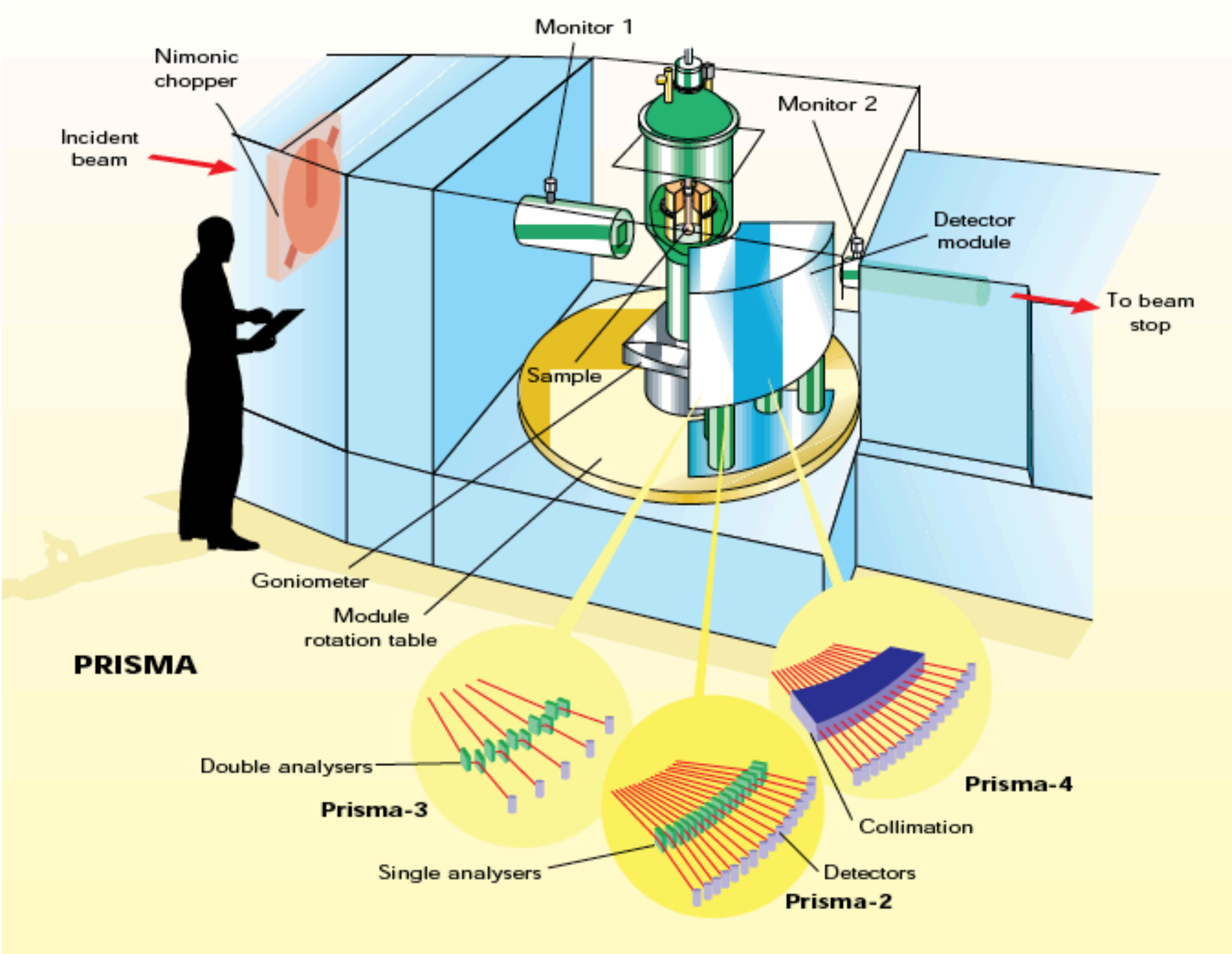
PRISMA EXPERIMENT

Phonons in ice 1h (Li, Bennington)

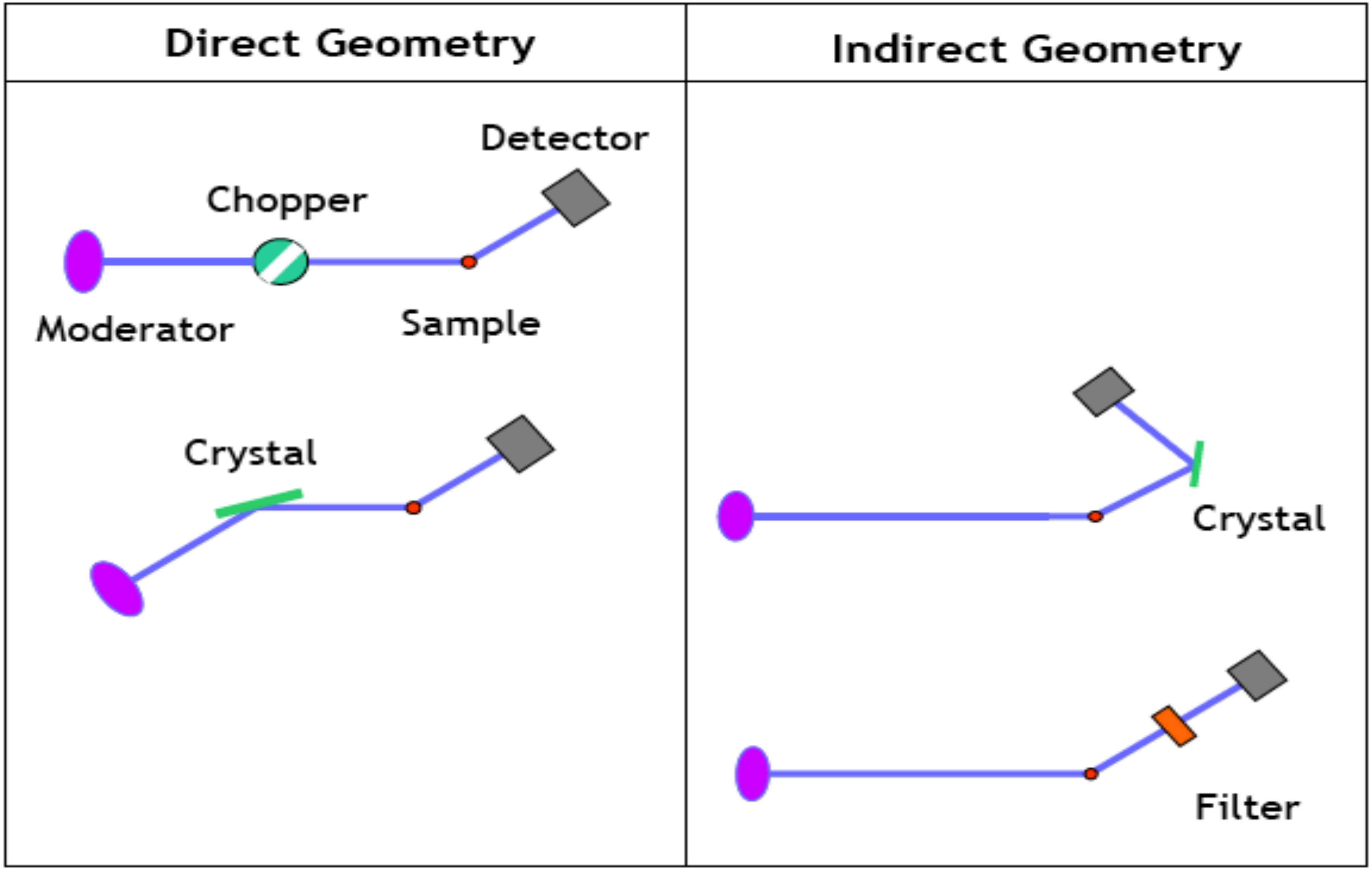




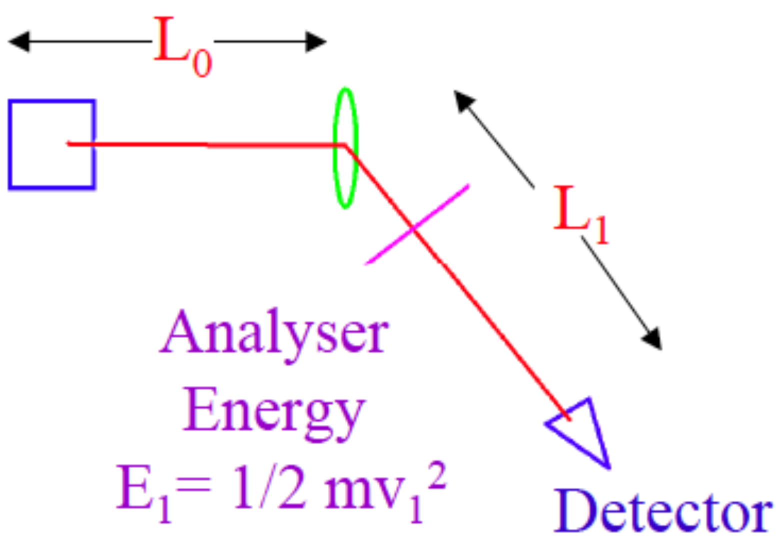
PRISMA


Monitor 1
Nimonic chopper
Incident beam
Monitor 2
Detector module
To beam stop
Sample
Goniometer
Module rotation table
PRISMA
Double analysers
Prisma-3
Single analysers
Prisma-2
Detectors
Collimation
Prisma-4

INDIRECT GEOMETRY SPECTROMETERS



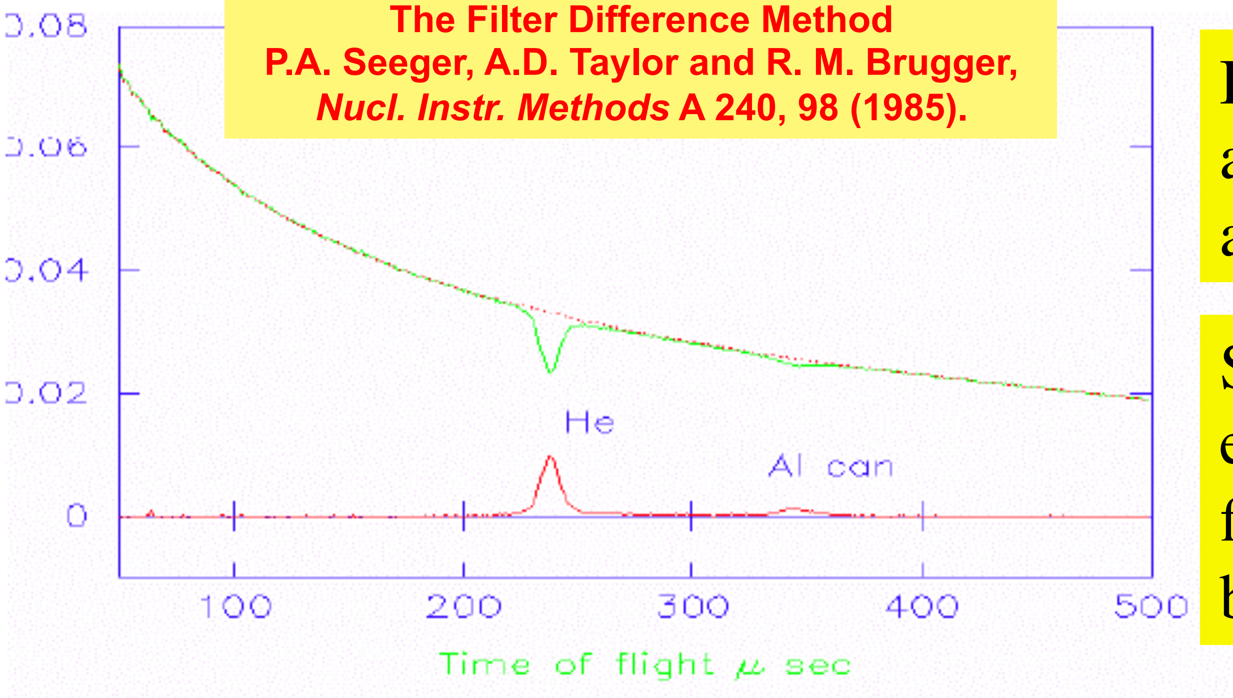
RFS mode



$$t = \frac{L_1}{v_1} + \frac{L_0}{v_0}$$

$$\hbar\omega = \tfrac{1}{2} m\left(v_0^{\,2} - v_1^{\,2}\right)$$

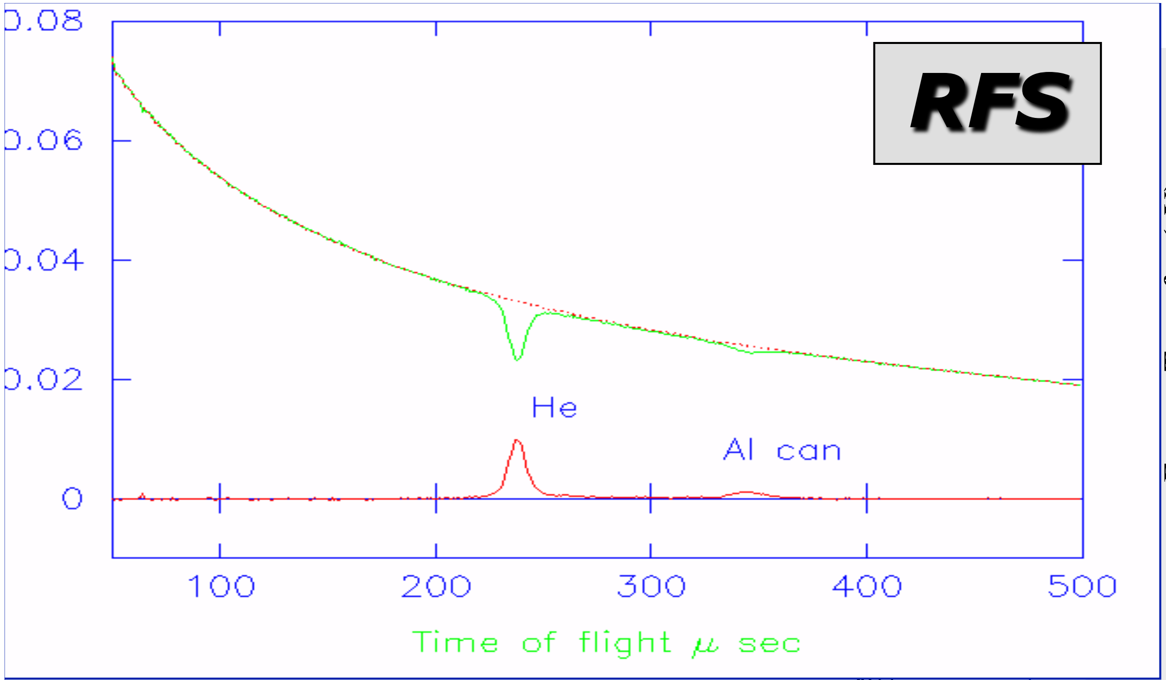
$$q^2 = m^2\left(v_0^{\,2} + v_1^{\,2} - 2v_0 v_1 \cos\theta\right)$$

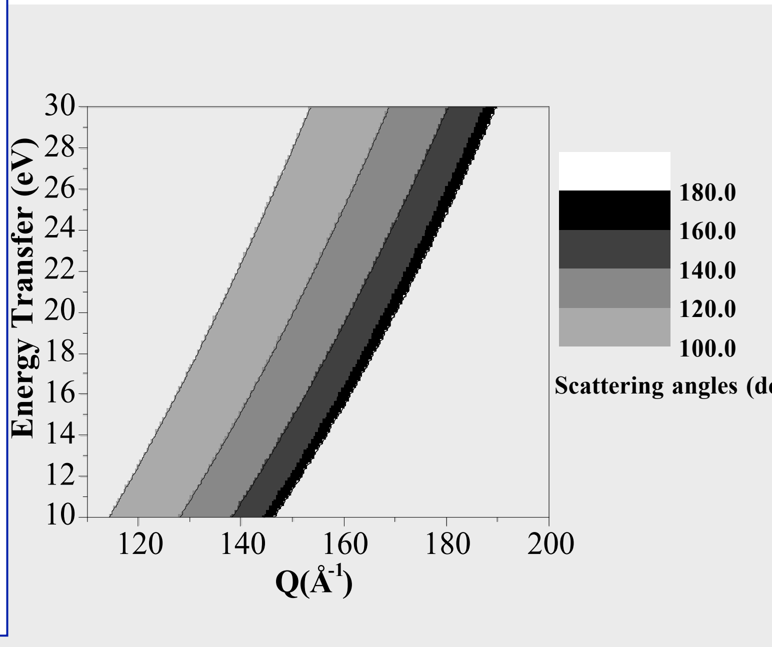


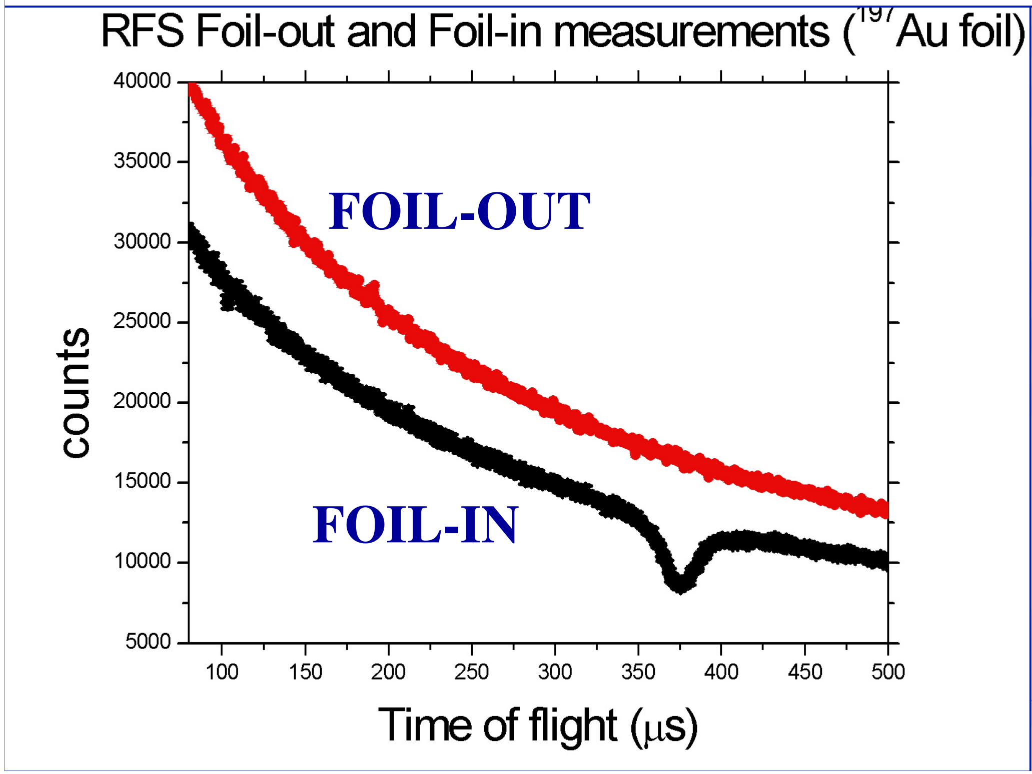
The Filter Difference Method
P.A. Seeger, A.D. Taylor and R. M. Brugger,
***Nucl. Instr. Methods* A 240, 98 (1985).**

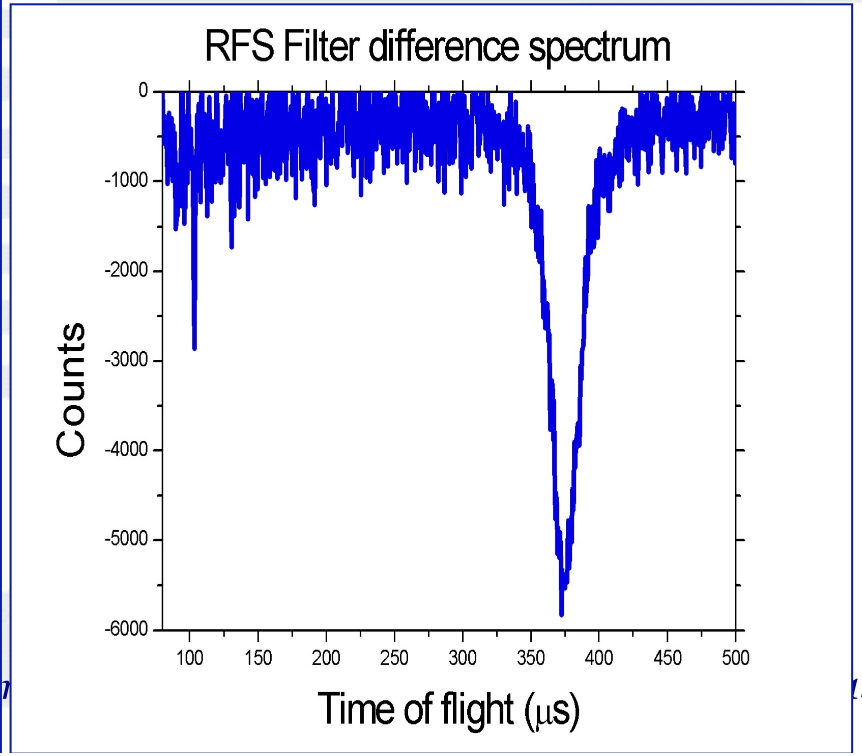
Incident neutrons of all available energies are generated at t=0

Scattered neutrons are energy selected by the filters and recorded by scintillators


RFS
0.08
0.06
0.04
0.02
0
He
Al can
100
200
300
400
500
Time of flight μ sec

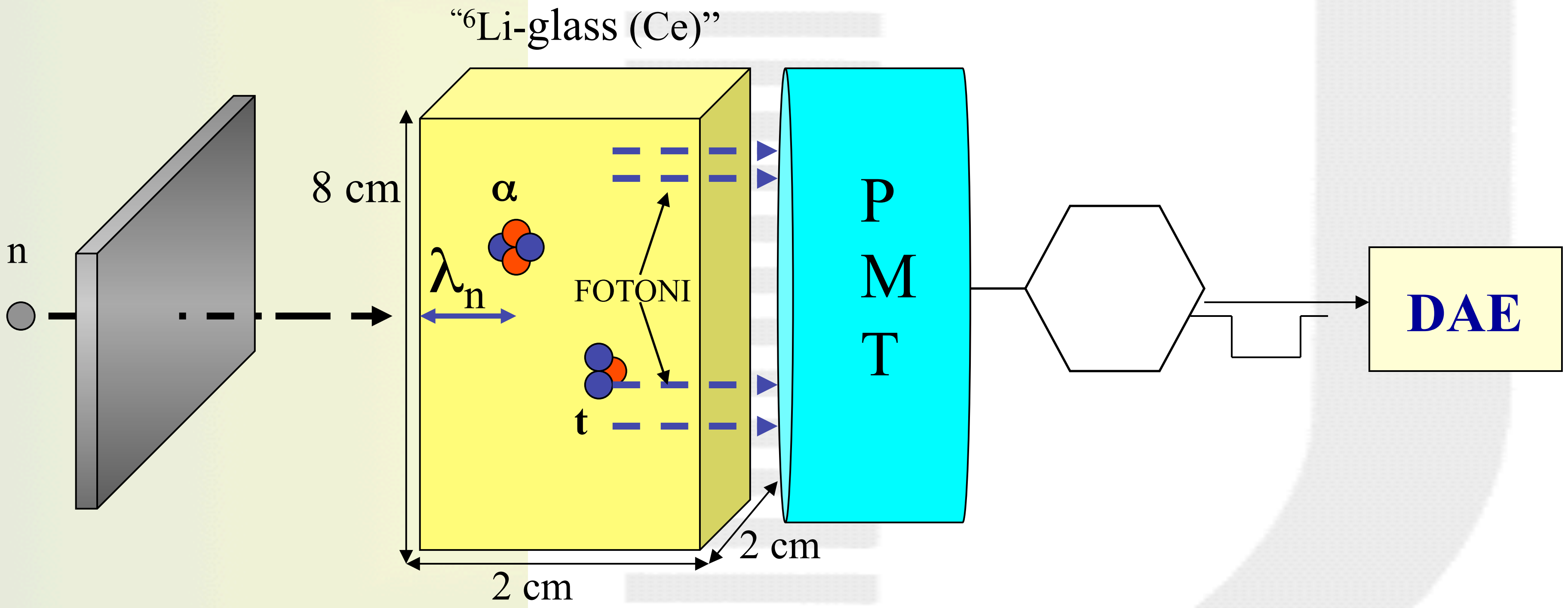

Energy Transfer (eV)
30
28
26
24
22
20
18
16
14
12
10
120
140
160
180
200
Q(Å^{-1})
180.0
160.0
140.0
120.0
100.0
Scattering angles (d


RFS Foil-out and Foil-in measurements (^{197}Au foil)
FOIL-OUT
FOIL-IN
counts
40000
35000
30000
25000
20000
15000
10000
5000
100
150
200
250
300
350
400
450
500
Time of flight (μs)


RFS Filter difference spectrum
Counts
0
-1000
-2000
-3000
-4000
-5000
-6000
100
150
200
250
300
350
400
450
500
Time of flight (μs)

RFS mode

"Filter Difference" (FD)



$\eta_{Li\text{-}glass} \approx 1/v$ - low efficency for E > 20 eV

RFS & RDS ON VESUVIO

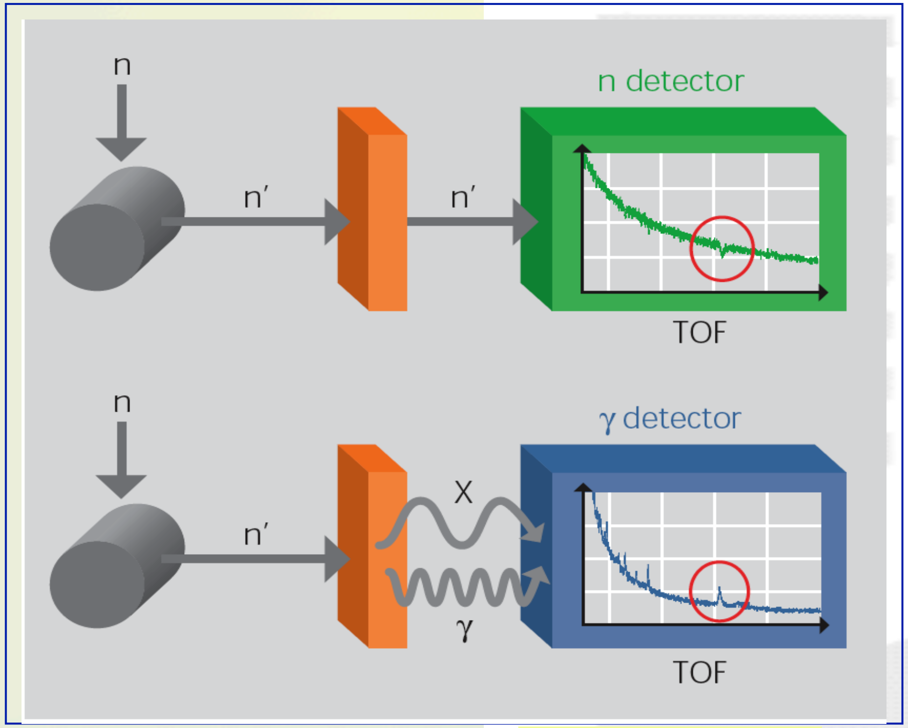
Principles of:
Resonance Filter Spectrometer (RFS)
Resonance Detector Spectrometer (RDS)

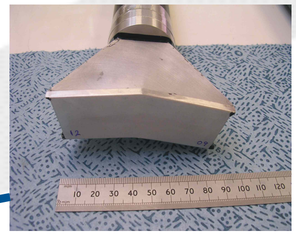
^{6}Li-glass Neutron Detectors

γ detectors

RFS

RDS



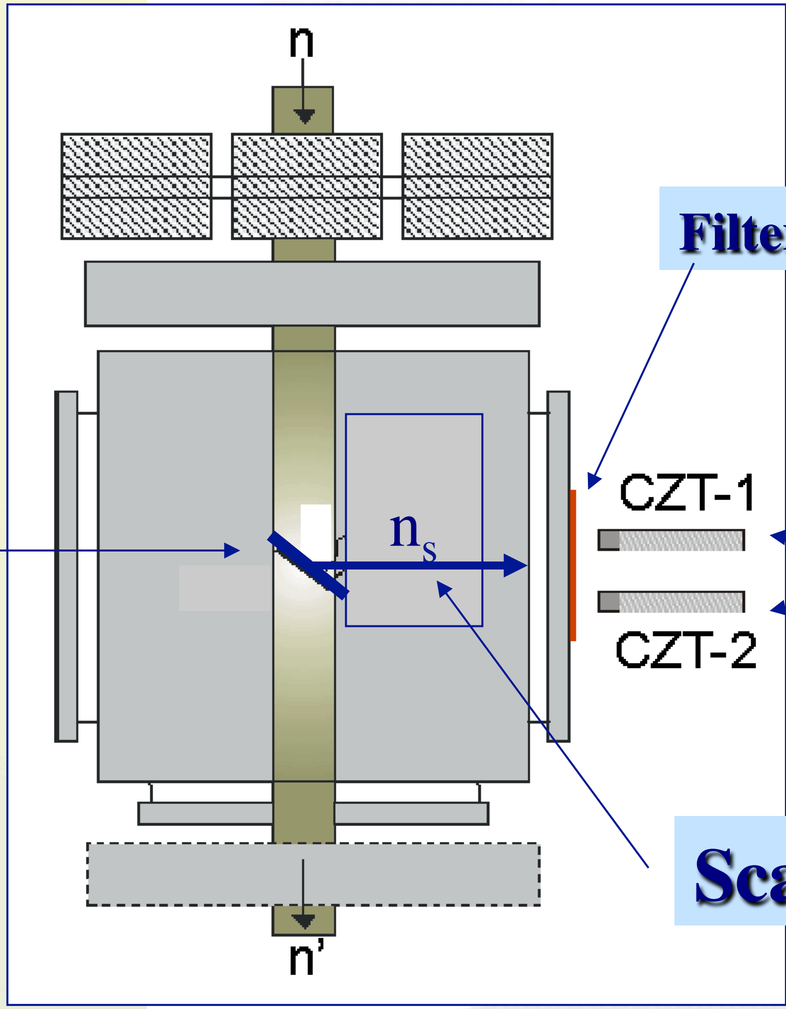


YAP scintillator

RDS mode

DINS

Sample

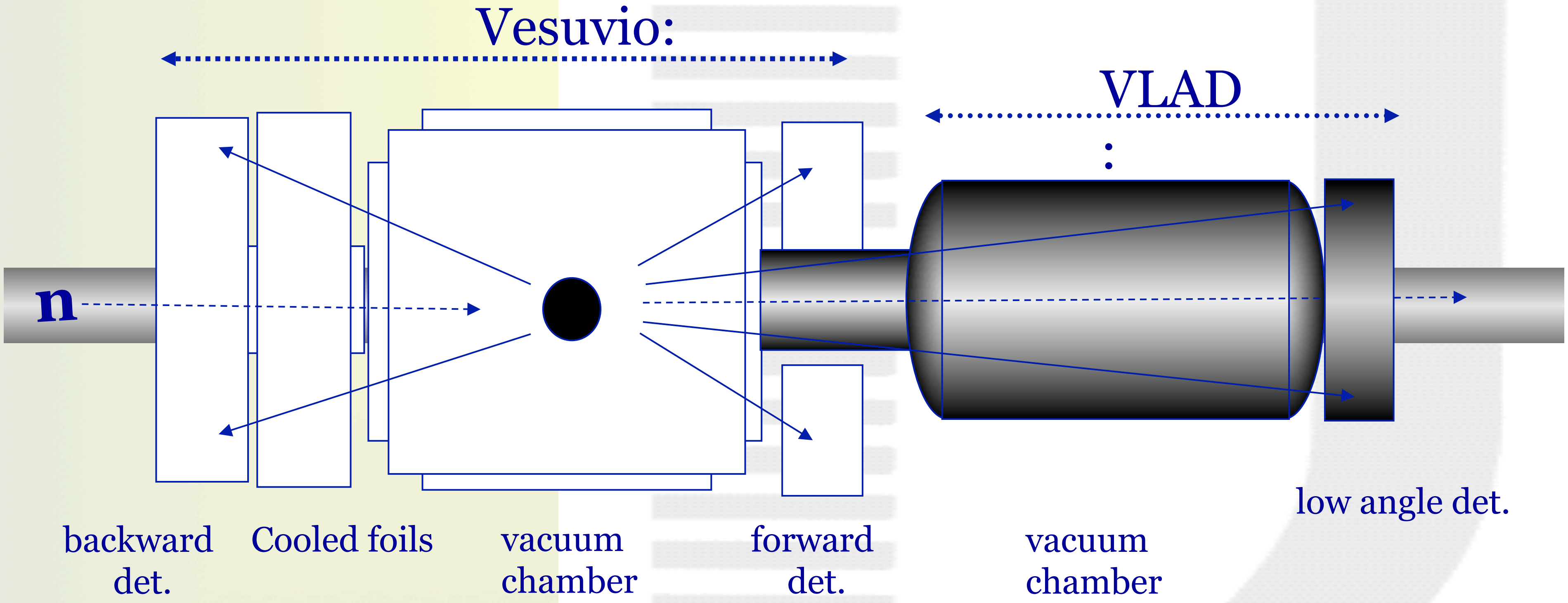


Filter ^{238}U

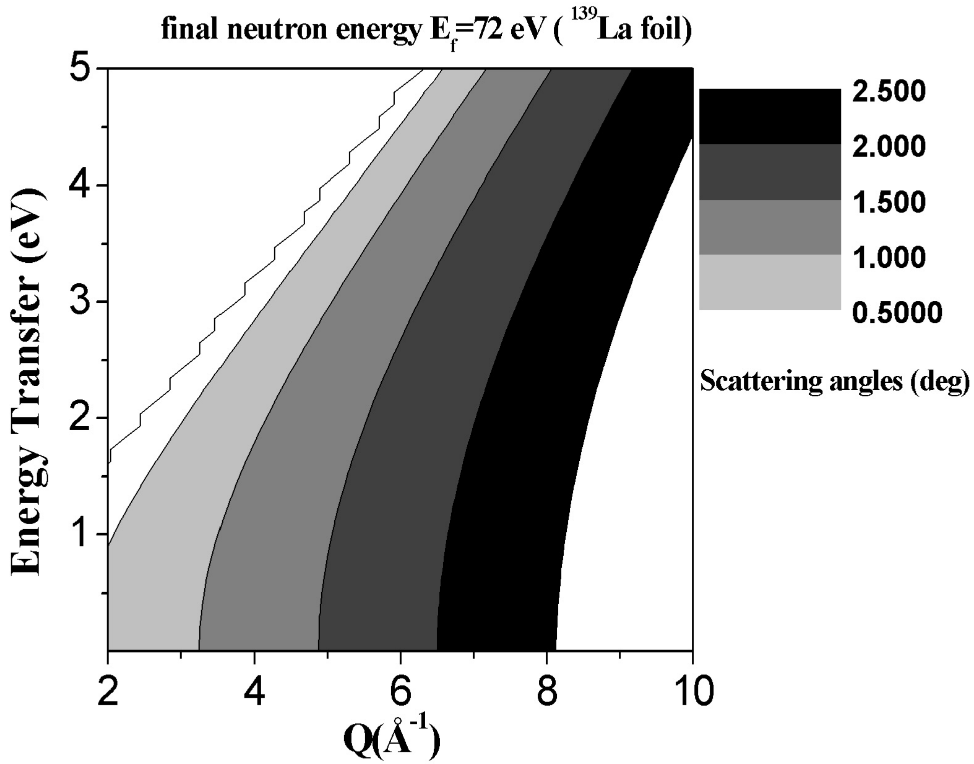
γ detectors

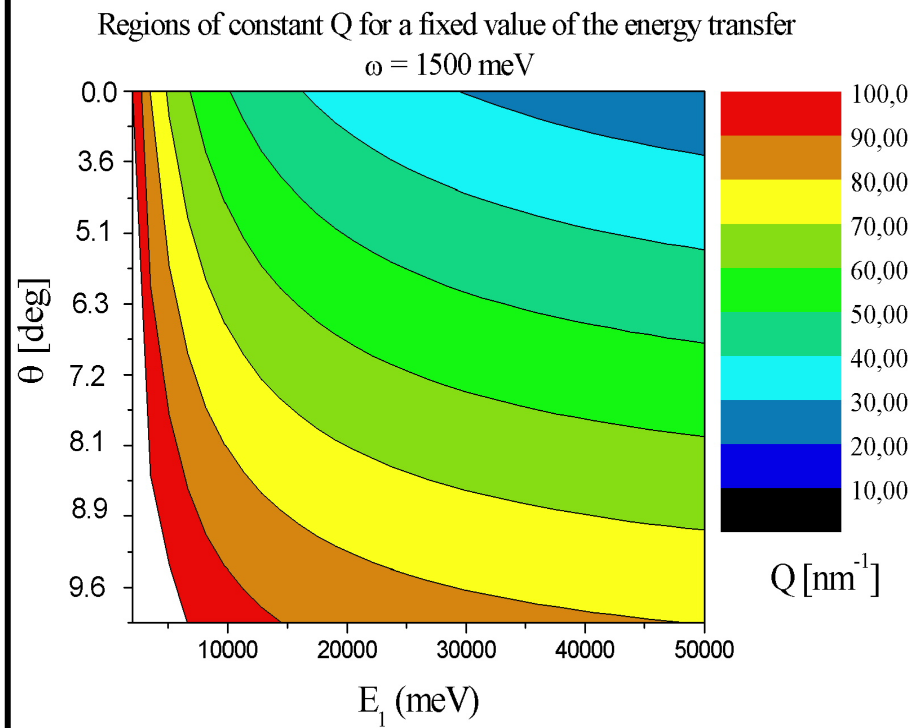
Scattered neutrons

VLAD

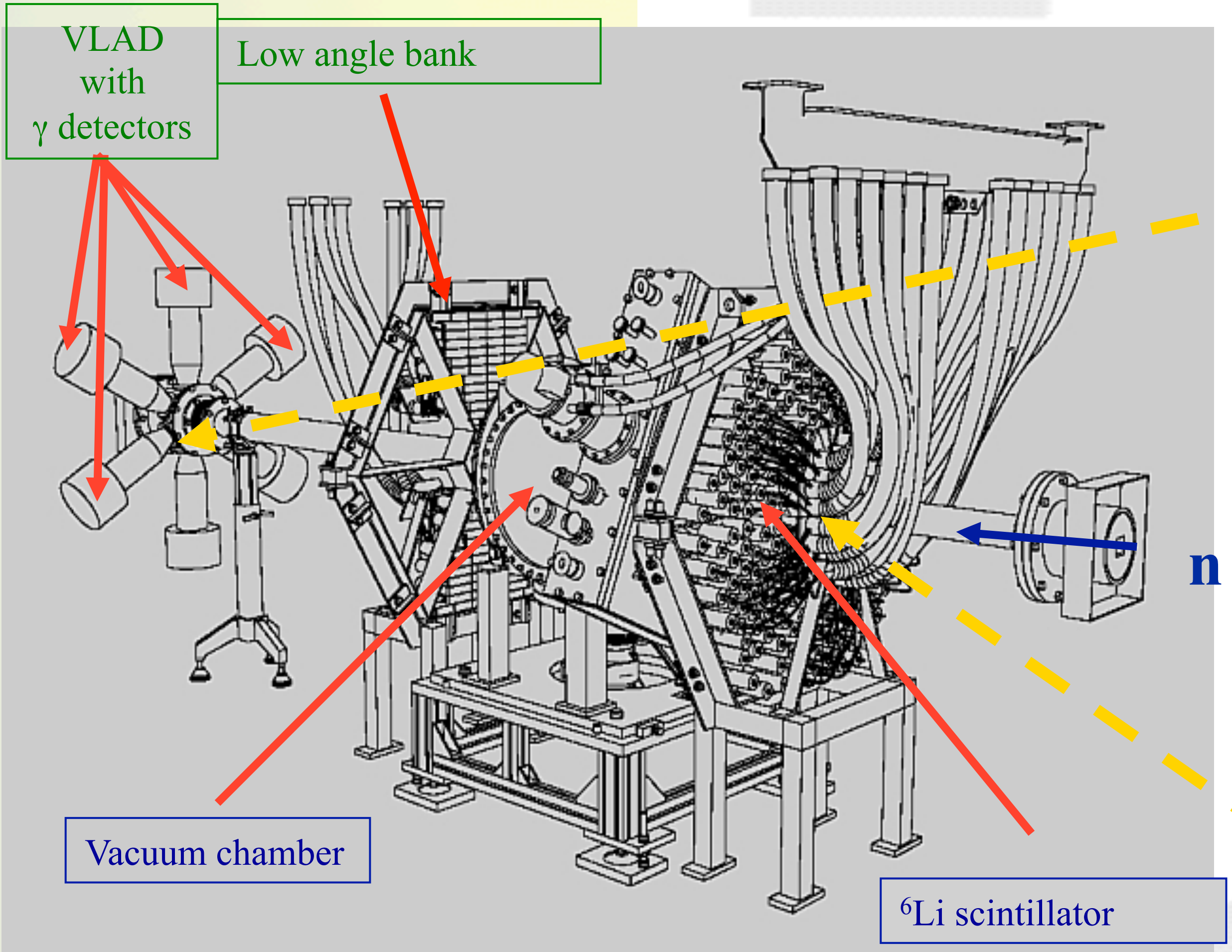

Vesuvio:
VLAD
:
n
backward
det.
Cooled foils
vacuum
chamber
forward
det.
vacuum
chamber
low angle det.

Kinematic conditions for measurements of high energy excitation



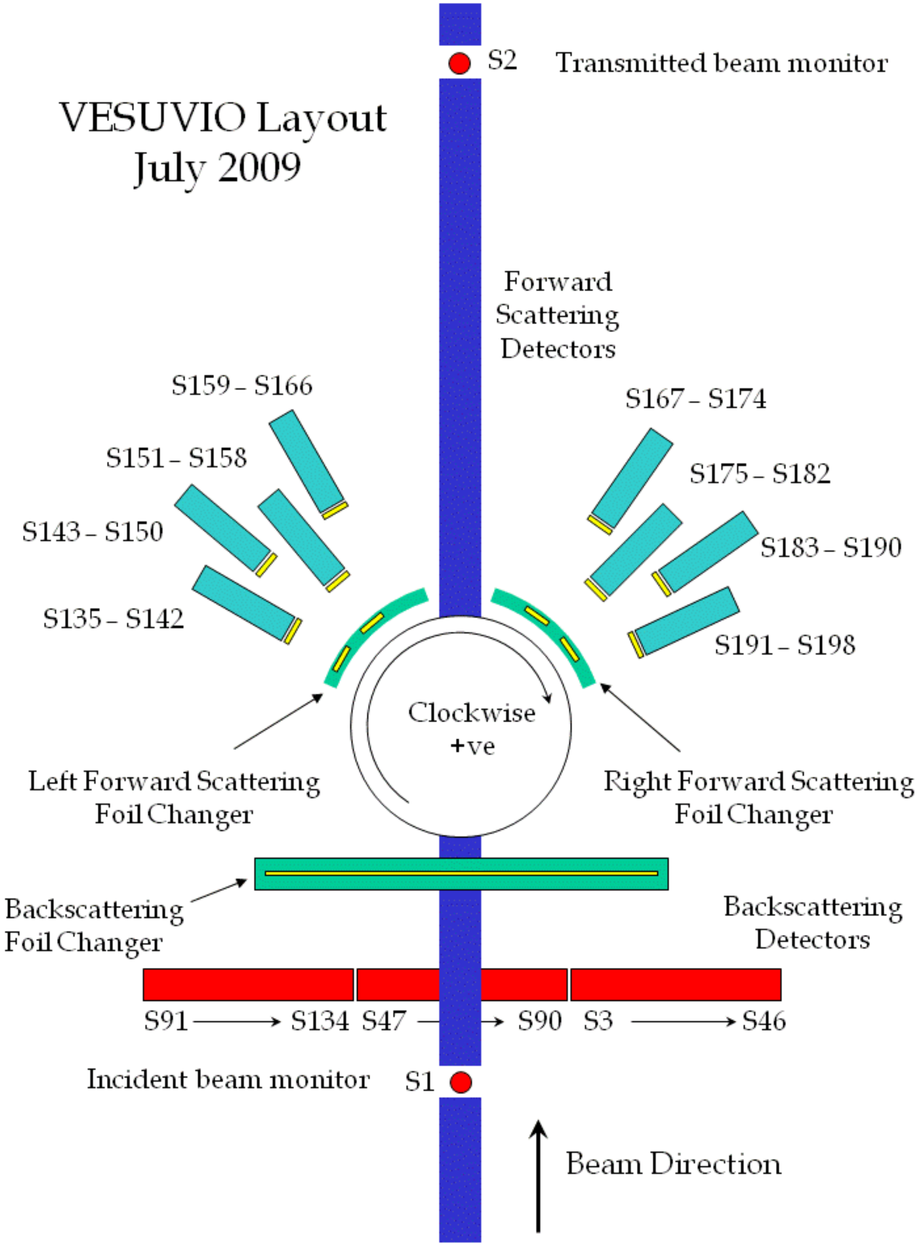


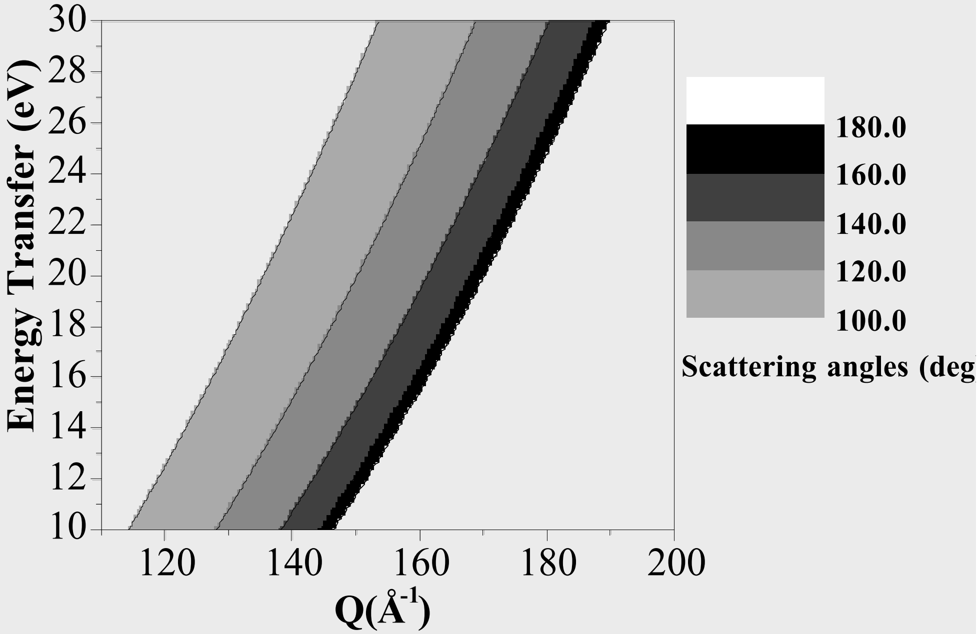
VESUVIO (DINS) & e.VERDI (HINS) RFS and RDS spectrometer



- RDS at very small scattering angles ($1° < 2\theta < 5°$)
- RDS at scattering angles ($20° < 2\theta < 80°$)
- RFS at backscattering angles

VESUVIO: Kinematic conditions





ıjorana Fundation and Centre for Scientific Culture (2014)

RESOLUTION COMPONENTS

Geometrical ↦ Gaussian

Energy ↦ Gaussian&Lorentzian

- single difference (SD)

example U foil

U resonances:

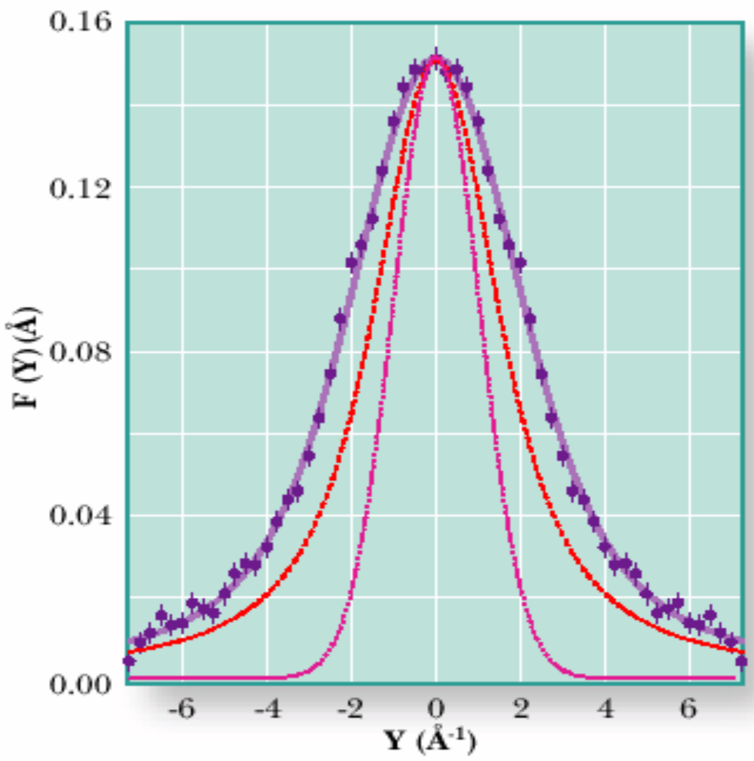
↦6.7eV,20.7eV,37eV..

FWHM (at 6.7 eV) ↦ 0.04 eV

Doppler broadning

at RT ↦ 0.11 eV

at 70 K ↦ 0.06 eV



Scattering function F(y) for the ^3He bcc solid sample. Data (full circles); best fit (purple line); resolution function SD (red line)

From Pb sample: VESUVIO resolution determined by fitting Lorentzian $\otimes$ Gaussian convolution to the data and subtracting the Gaussian component, due to intrinsic width of the Pb sample.

HINS on VLAD $\Delta\hbar\omega / \hbar\omega$ resolution

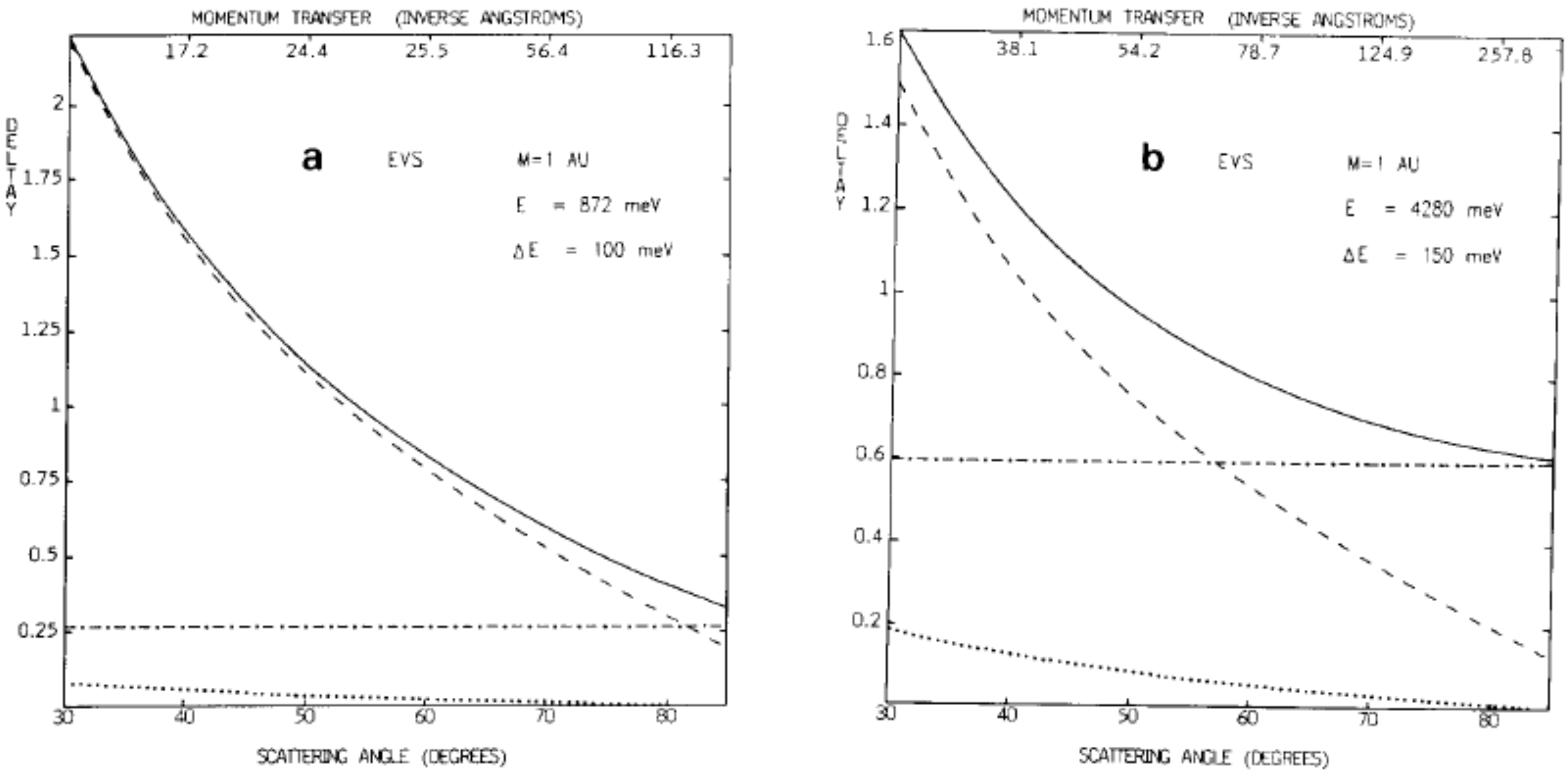


Fig. 2. The total resolution (———) and the energy (— — —), angular (·–·–·) and timing (· · · · · ·) contributions to the resolution in hydrogen ($M = 1$ amu) shown as a function of scattering angle and momentum transfer for eVS at (a) $E_1 = 872$ meV and (b) $E_1 = 4280$ meV.

C. Andreani *et al* NIM A (1989)

HINS on VLAD $\Delta\hbar\omega / \hbar\omega$ resolution

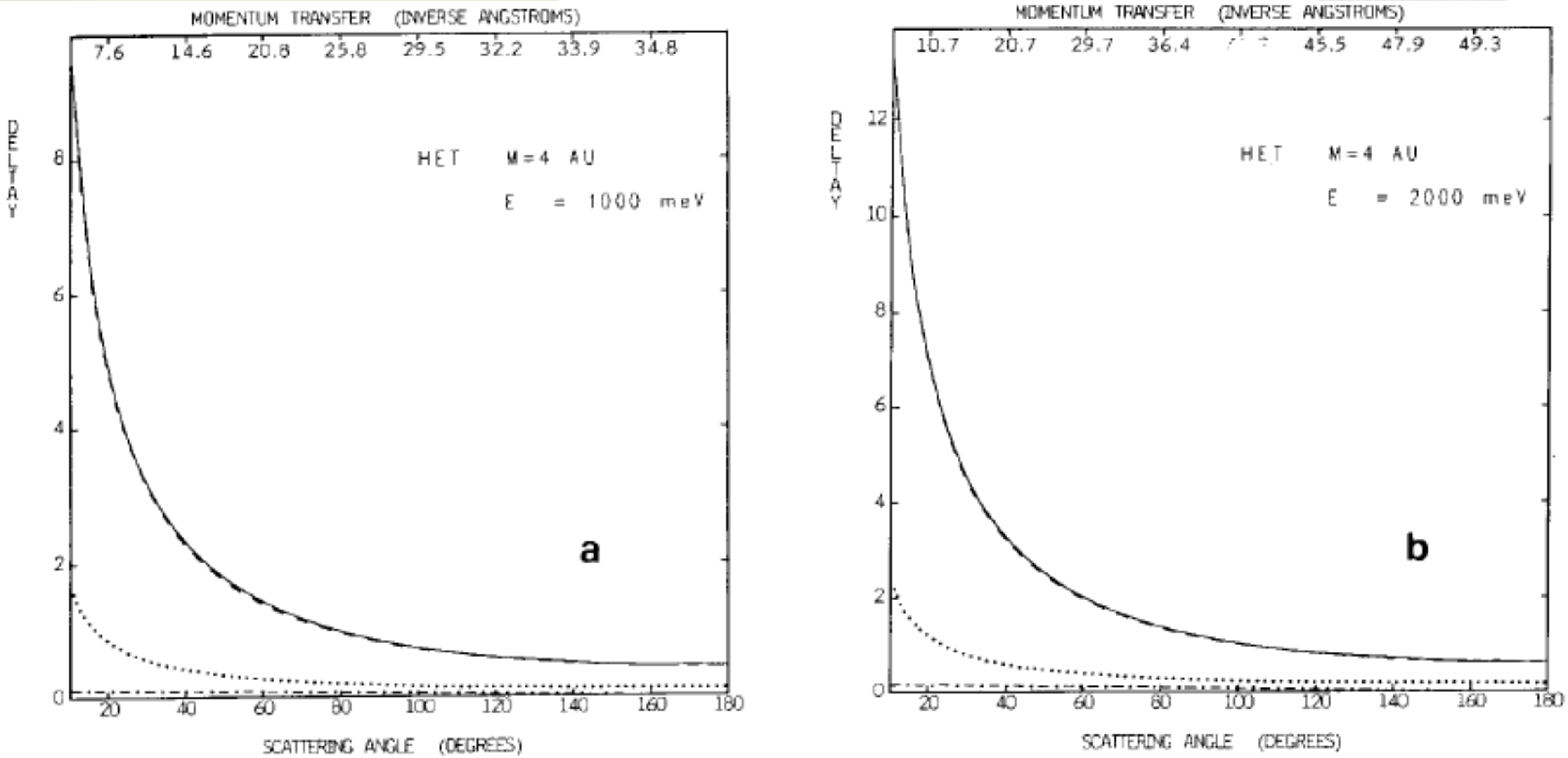
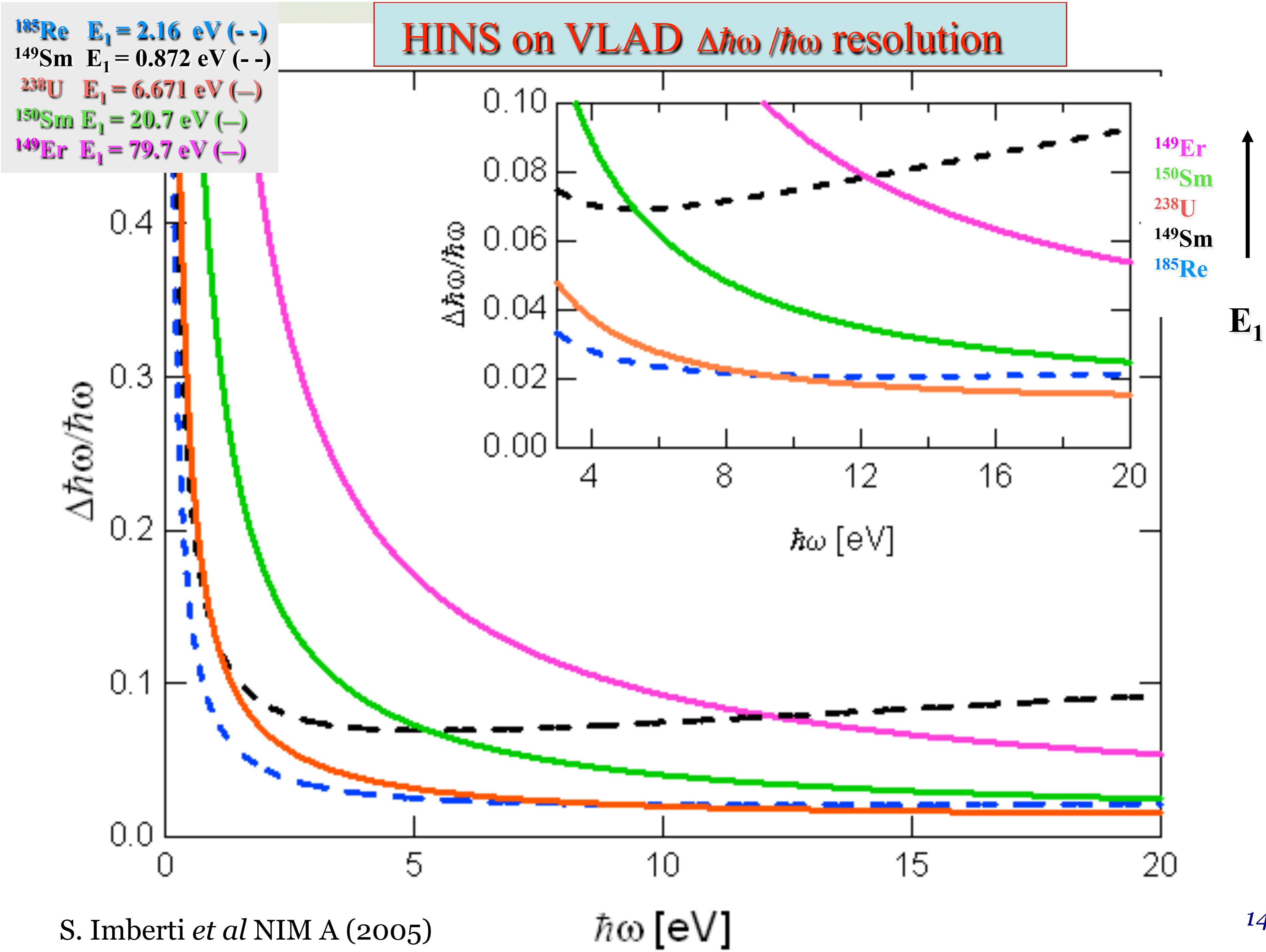


Fig. 3. The HET results for helium ($M = 4$ amu).

HINS on VLAD $\Delta\hbar\omega / \hbar\omega$ resolution



S. Imberti *et al* NIM A (2005)

Deep Inelastic Neutron Scattering

1.High *q* implies, because of Heisenberg indetermination principle, **scattered neutron explores regions of the sample of small dimension**, thus suited probe to study single particle properties, (no coherent effects from collective dynamics inside the system) (*Incoherent Approximation*); the distance over which the neutron phase change appreciably is much lower than the typical interparticle distance *d*:

$$\frac{2\pi}{q} << \bar{d}$$

2. High ω implies, because of the time-energy indetermination principle, that the **scattering process occurs in a very short time** (*Impulse Approximation, IA*).

Deep Inelastic Neutron Scattering, DINS

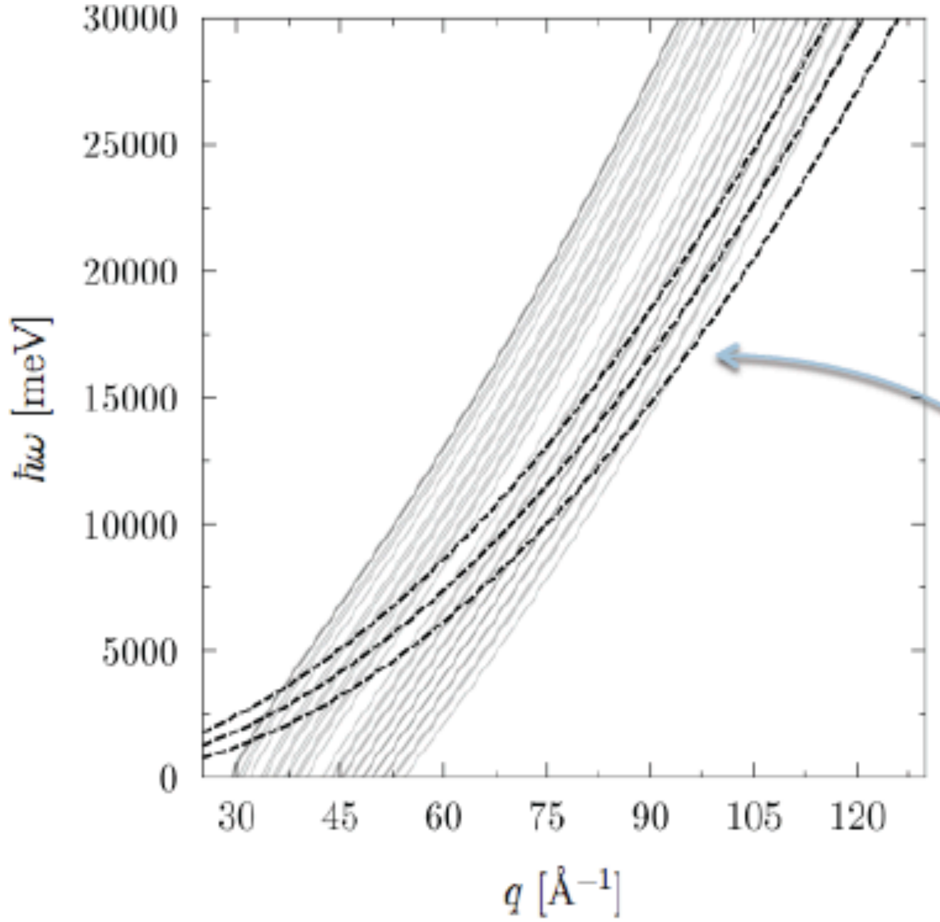
For a monoatomic system:

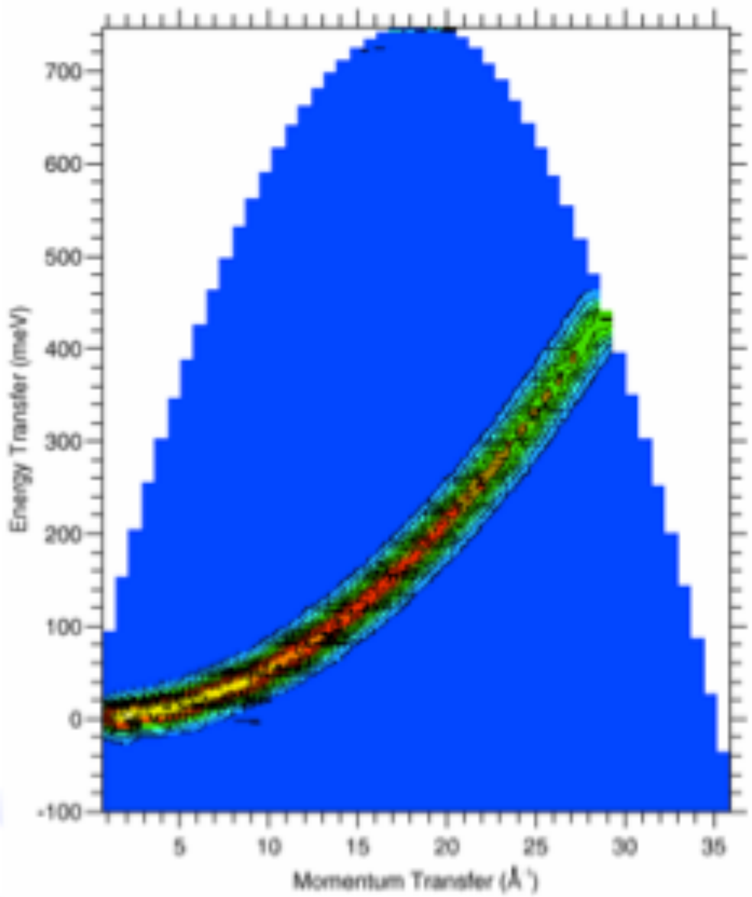
$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{\hbar}\frac{k_f}{k_i}\left[\frac{\sigma_c}{4\pi}S(\mathbf{q},\omega) + \frac{\sigma_i}{4\pi}S_i(\mathbf{q},\omega)\right]$$

Impulse Approximation: high *q* and ω

$$S_{IA}(\mathbf{q},\omega) = \int \underline{n(\mathbf{p})}\,\delta\left(\hbar\omega - \frac{\hbar^2 q^2}{2M} - \frac{\hbar \mathbf{q}\cdot\mathbf{p}}{M}\right) d\mathbf{p}$$

Nuclear quantum effects on proton momentum distribution

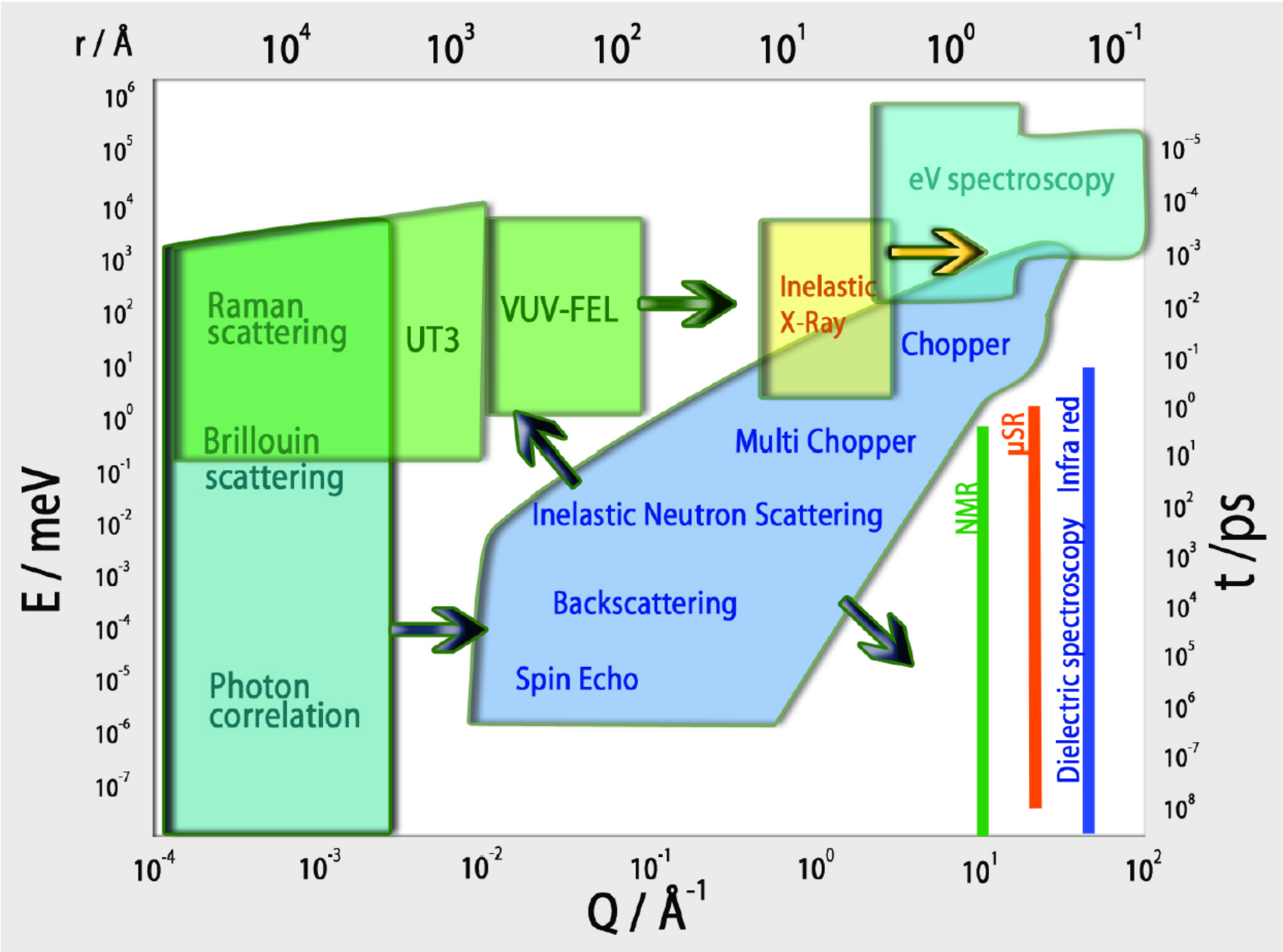




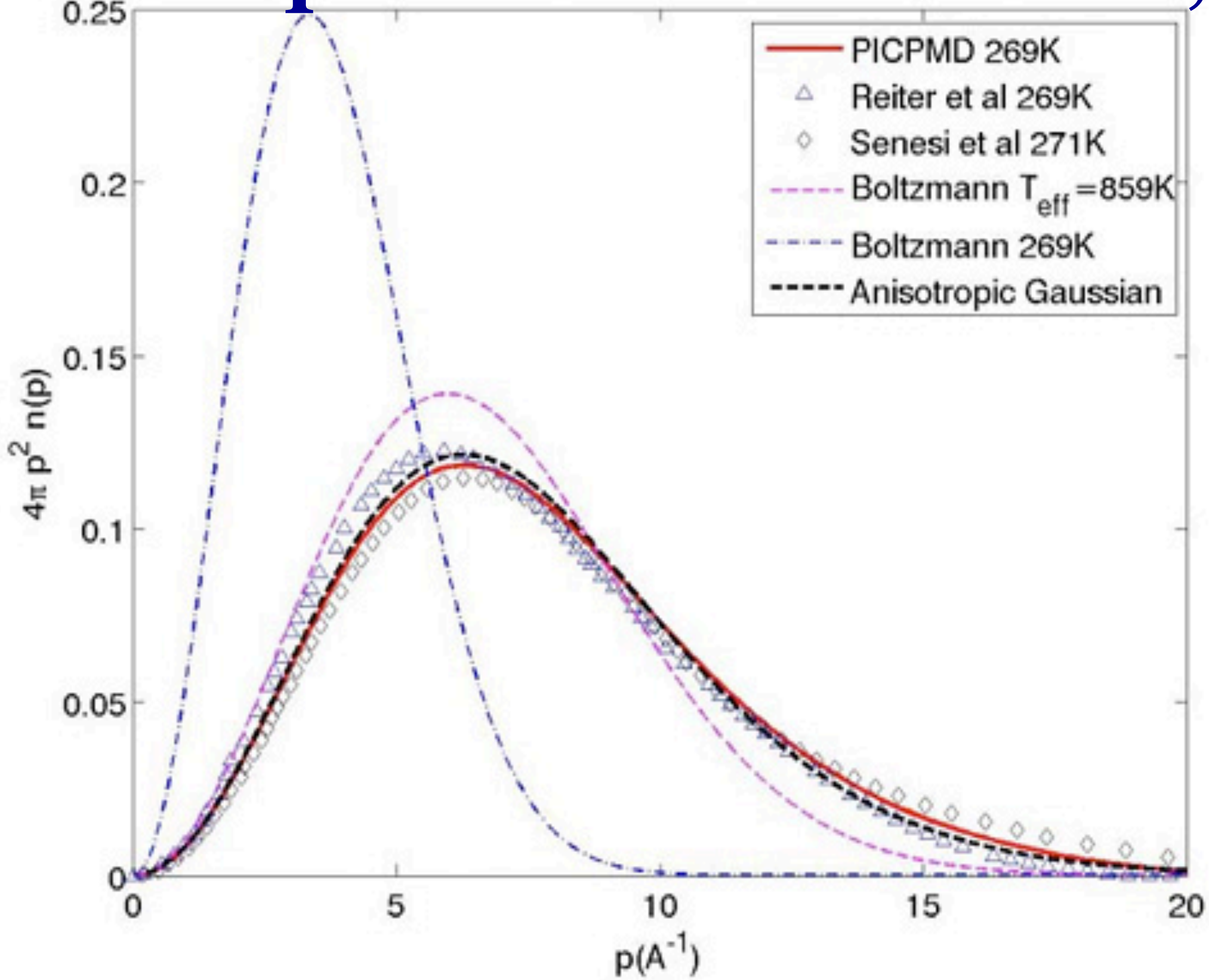
Vesuvio Beamline at the ISIS neutron source -UK

DINS

Figure 2. Schematic plot illustrating the kinematical $(q, \hbar\omega)$ range accessed by different spectroscopic techniques; on the top right of the figure the t and r ranges for DINS (10^{-5} ps $< t < 10^{-3}$ ps, 0.1 Å$< r <$ 0.2 Å) and HINS (10^{-6} ps $< t < 10^{-2}$ ps, 0.2 Å$< r <$ 2 Å) spectroscopy is shown.



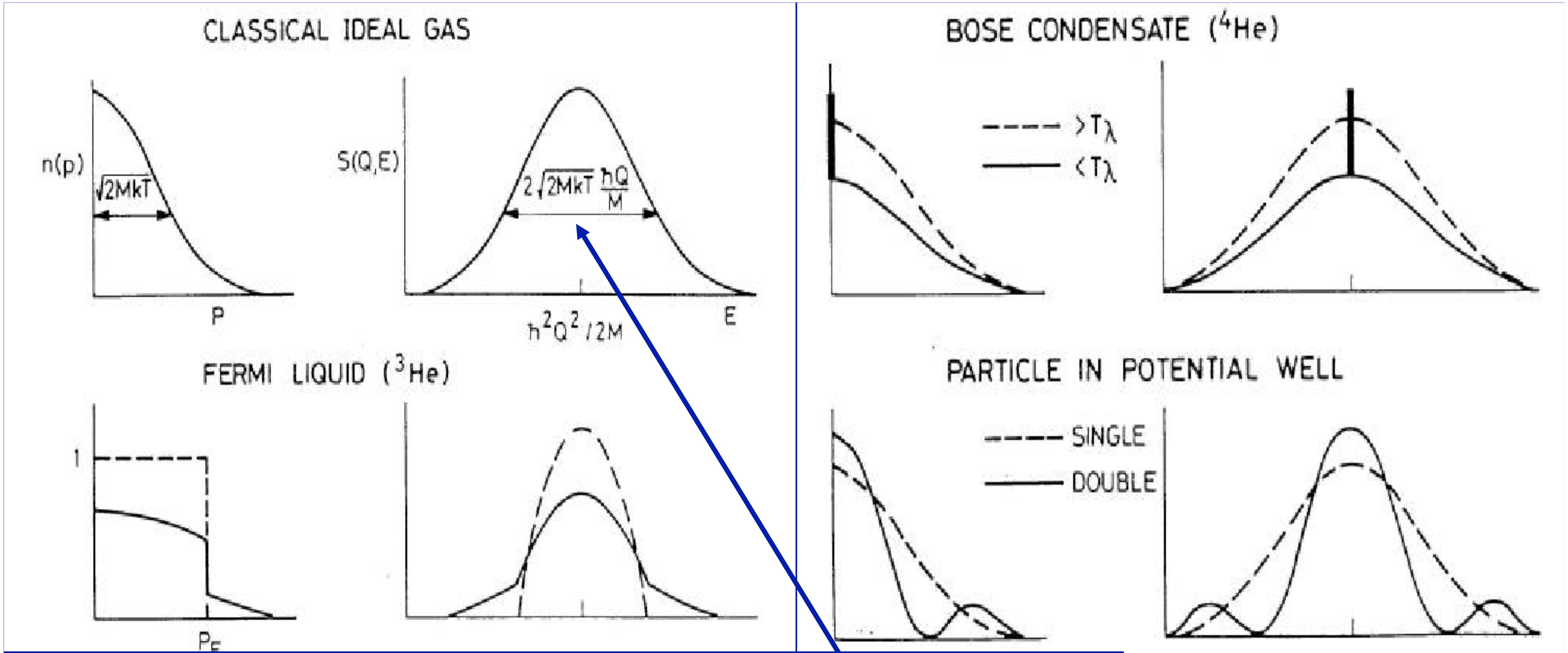
Nuclear quantum effects in Ice, T=296K



The spherically averaged momentum distribution of the protons (shown here for ice at T=296 K) is quite different from the classical Maxwell-Boltzmann distribution at the same temperature. The path integral ab-initio molecular dynamics (PICPMD) result agrees well with two experiments (Reiter and Senesi). The Maxwell-Boltzmann distribution that fits better the PICPMD data has T=859 K. An even better fit is obtained with an anisotropic (multivariate) Gaussian distribution.

ulture (2014)

Courtesy of Roberto Car (Princeton University)



$$n(\mathrm{p}) \propto \exp\left[-\mathrm{p}^2/(4Mk_BT)\right] \Rightarrow \sigma^2 = 2\mathrm{Mk_BT}$$

Classical system

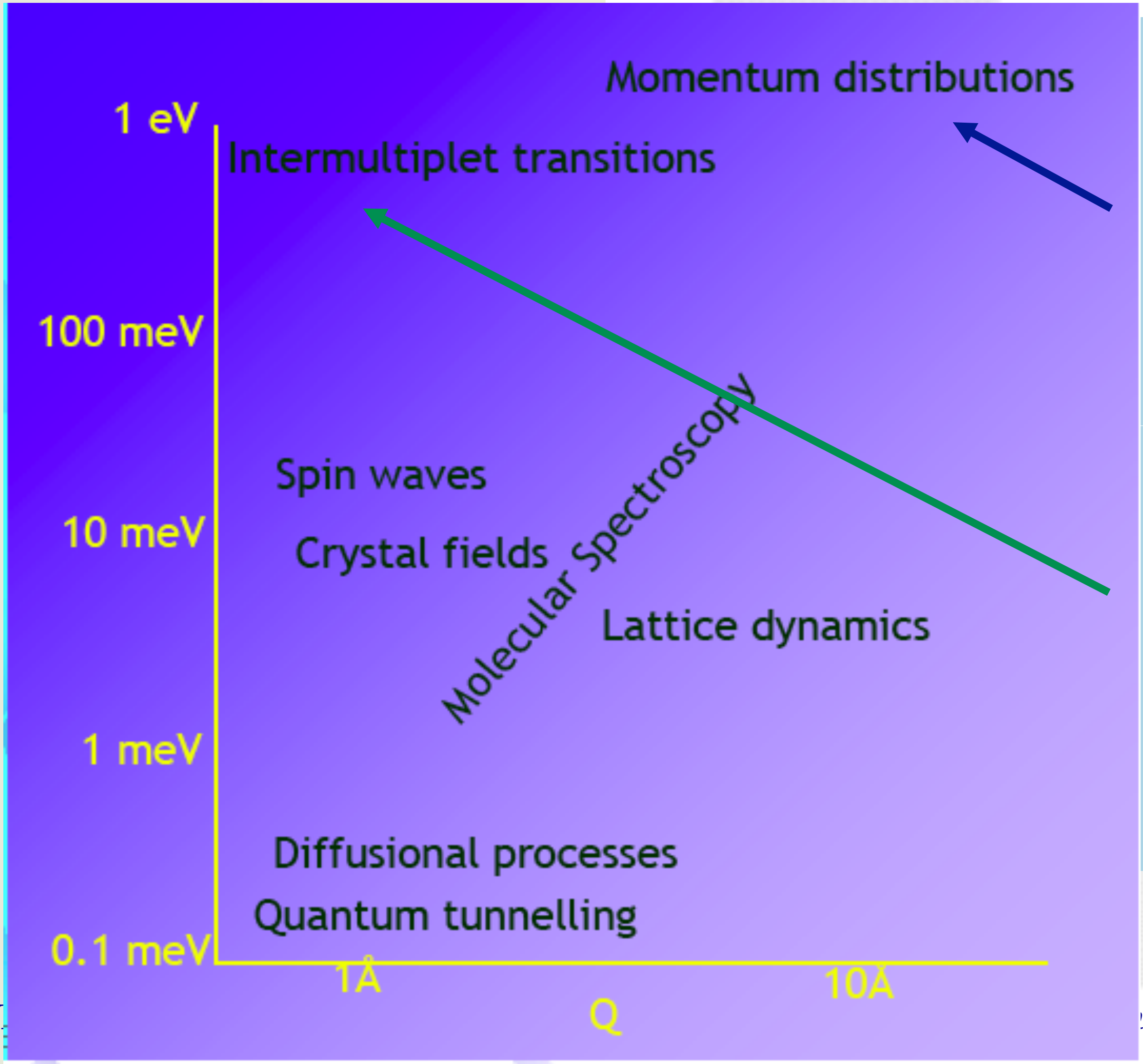
Peak width of S(Q,ω) provides a direct measure of $<E_K>$

$$<E_k> = \frac{1}{2M}\int n(\boldsymbol{p})p^2 d\boldsymbol{p}$$

$$n(\vec{p}) = \left|\int \psi(\vec{r})\exp(i\vec{p}\cdot\vec{r})d\vec{r}\right|^2$$

Momentum Distribution is "Diffraction Pattern" of Wave function

eV SPECTROSCOPY



(DINS):

- $<E_k>$
- n(p)

VESUVIO

•(HINS):

- **high energy excitations**

eVERDI

EXAMPLES

Light and heavy particles quantum dynamics

Nuclear Quantum Effects

$\Delta x \, \Delta p \geq \hbar / 2$

$< E_K > \;\&\; n(p) \rightarrow$ PES

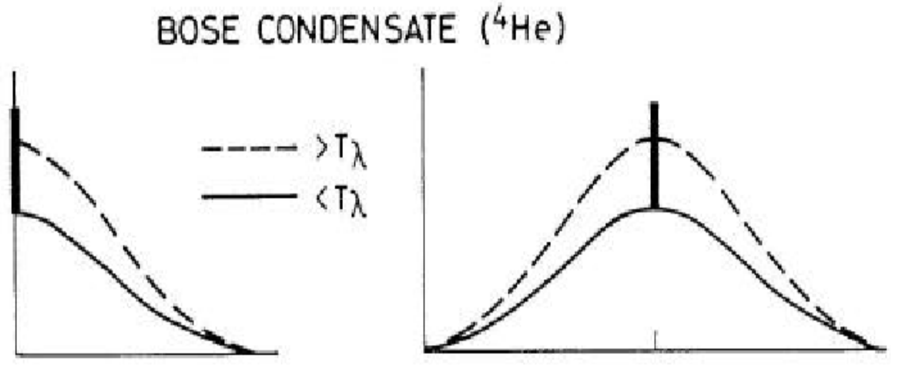
$$n(\vec{p}) = \left| \int \psi(\vec{r}) \exp(i\vec{p} \cdot \vec{r}) d\vec{r} \right|^2$$

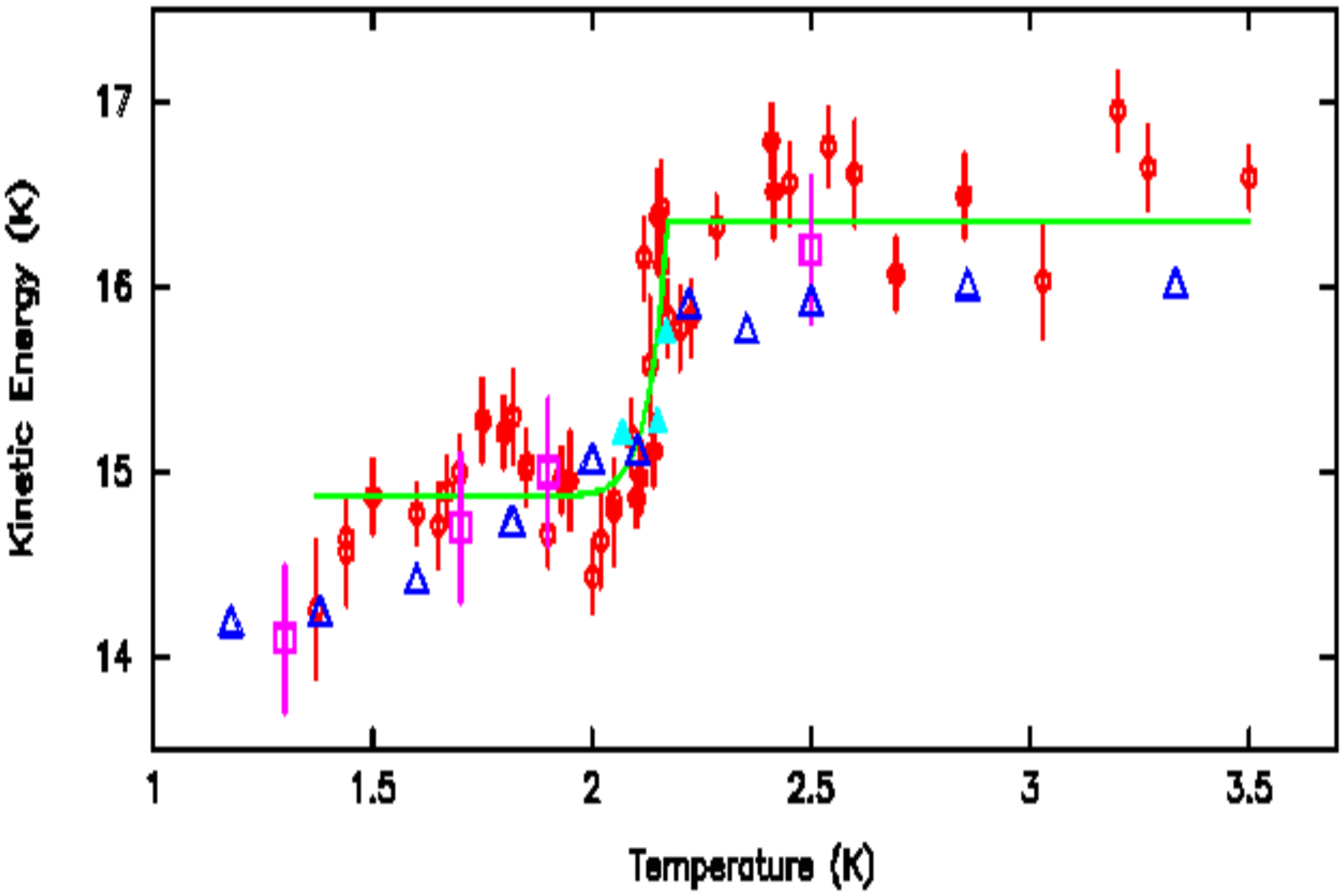
$$< E_k > = \frac{1}{2M} \int n(\boldsymbol{p}) p^2 d\boldsymbol{p}$$

$\left\{ \textbf{localization} \right\}$ → **excess of $<E_K>$**

DINS on VESUVIO

Mean Kinetic Energy of ^4He





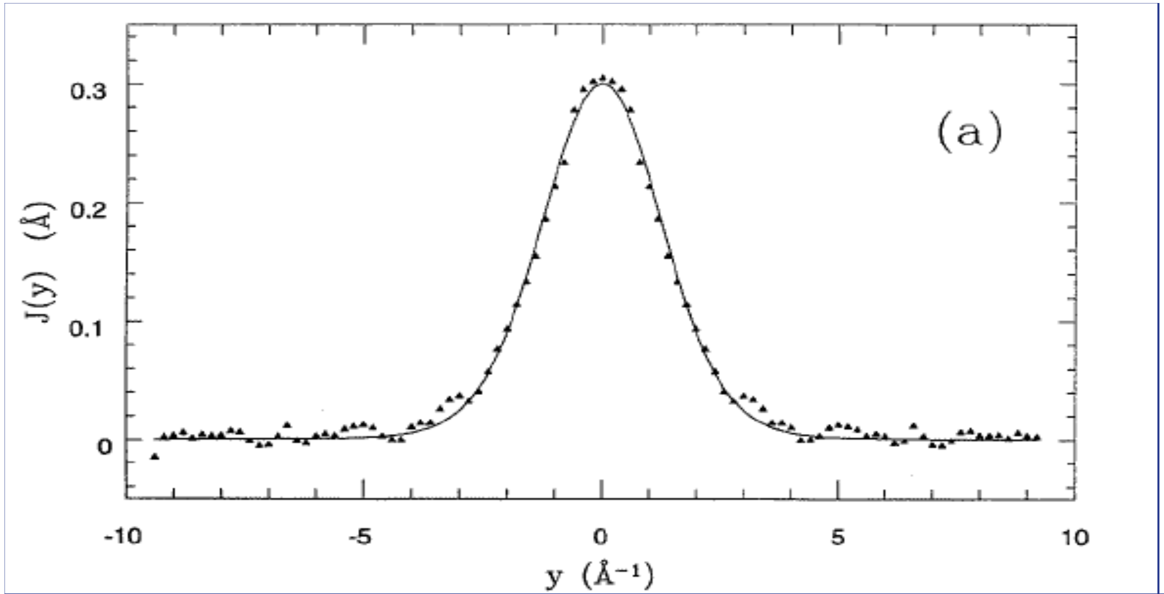
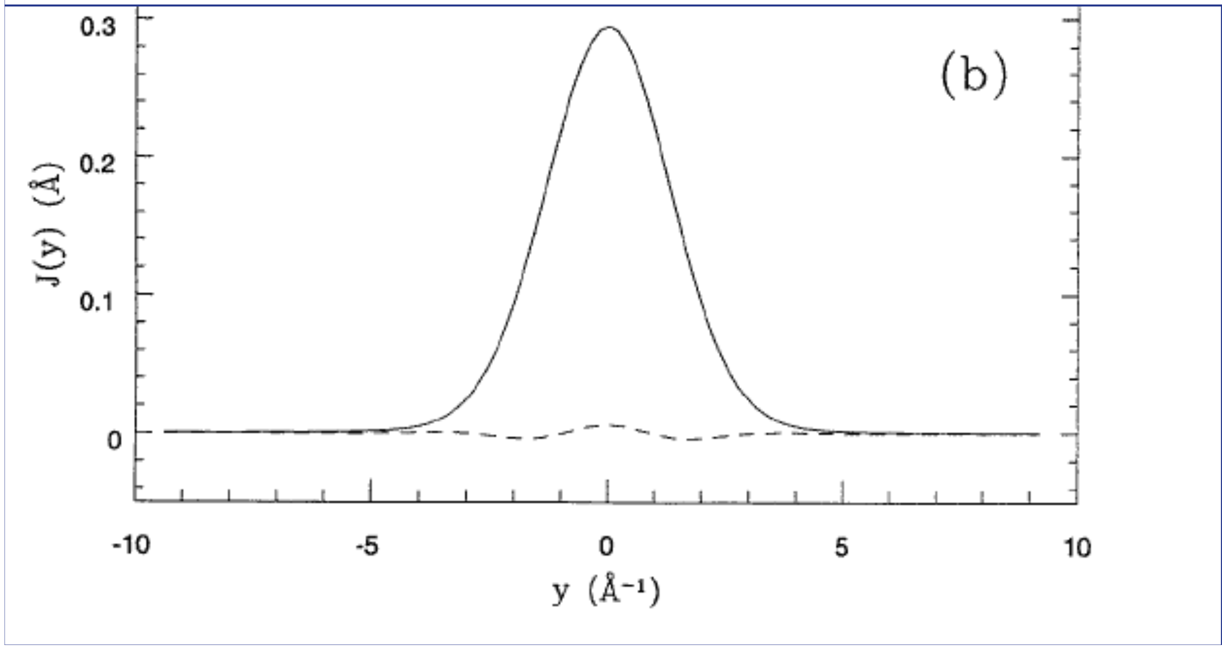


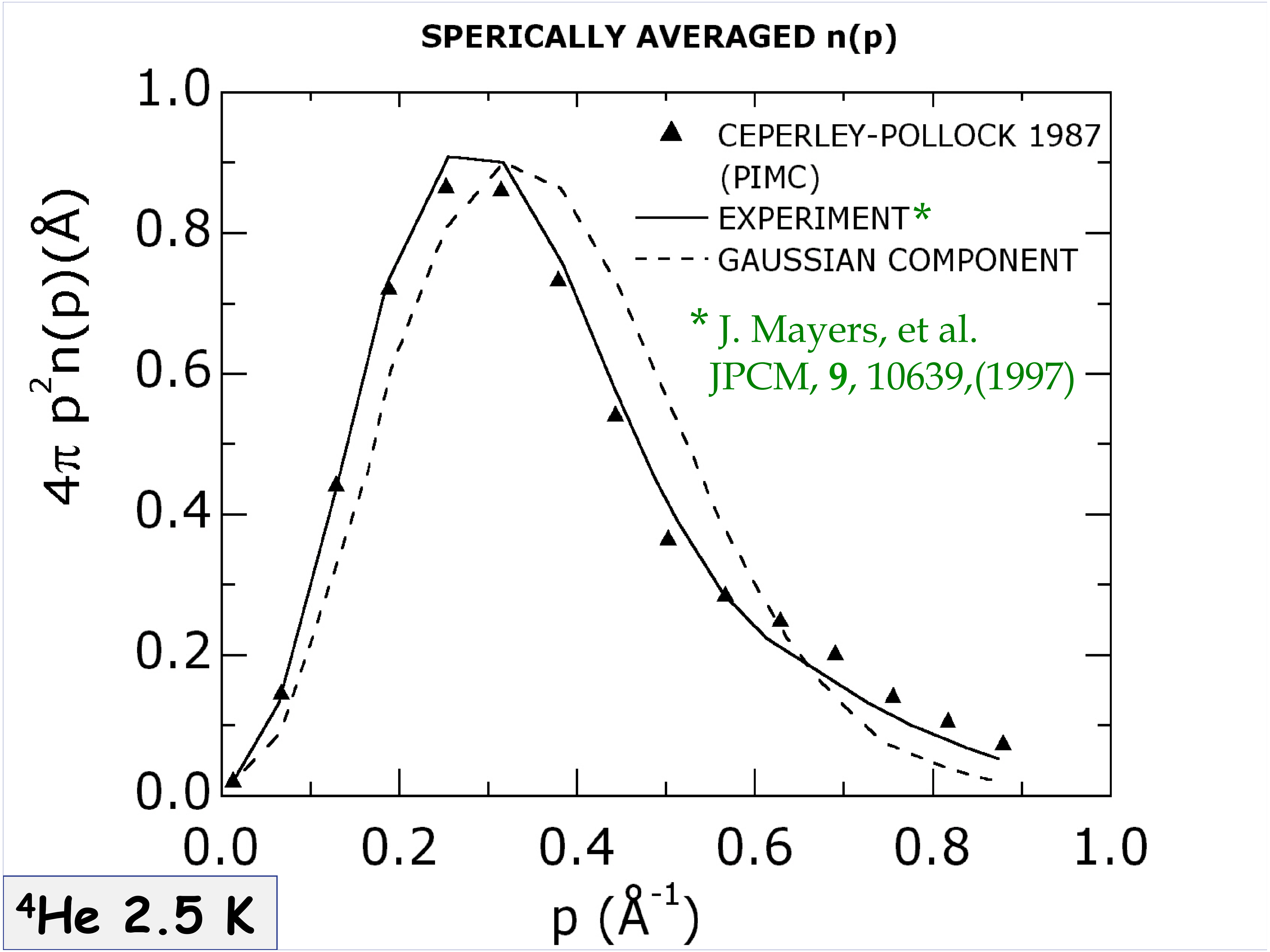
Figure 3. (a) The response function $J(y)$ for ^{4}He at 2.5 K from the cooled U filter: triangles are the experimental data; the solid line is the result of the fit. (b) The solid line is the Gaussian component of the fit; the dashed line is the non-Gaussian component, with both including a resolution contribution.



^{4}He at 2.5 K

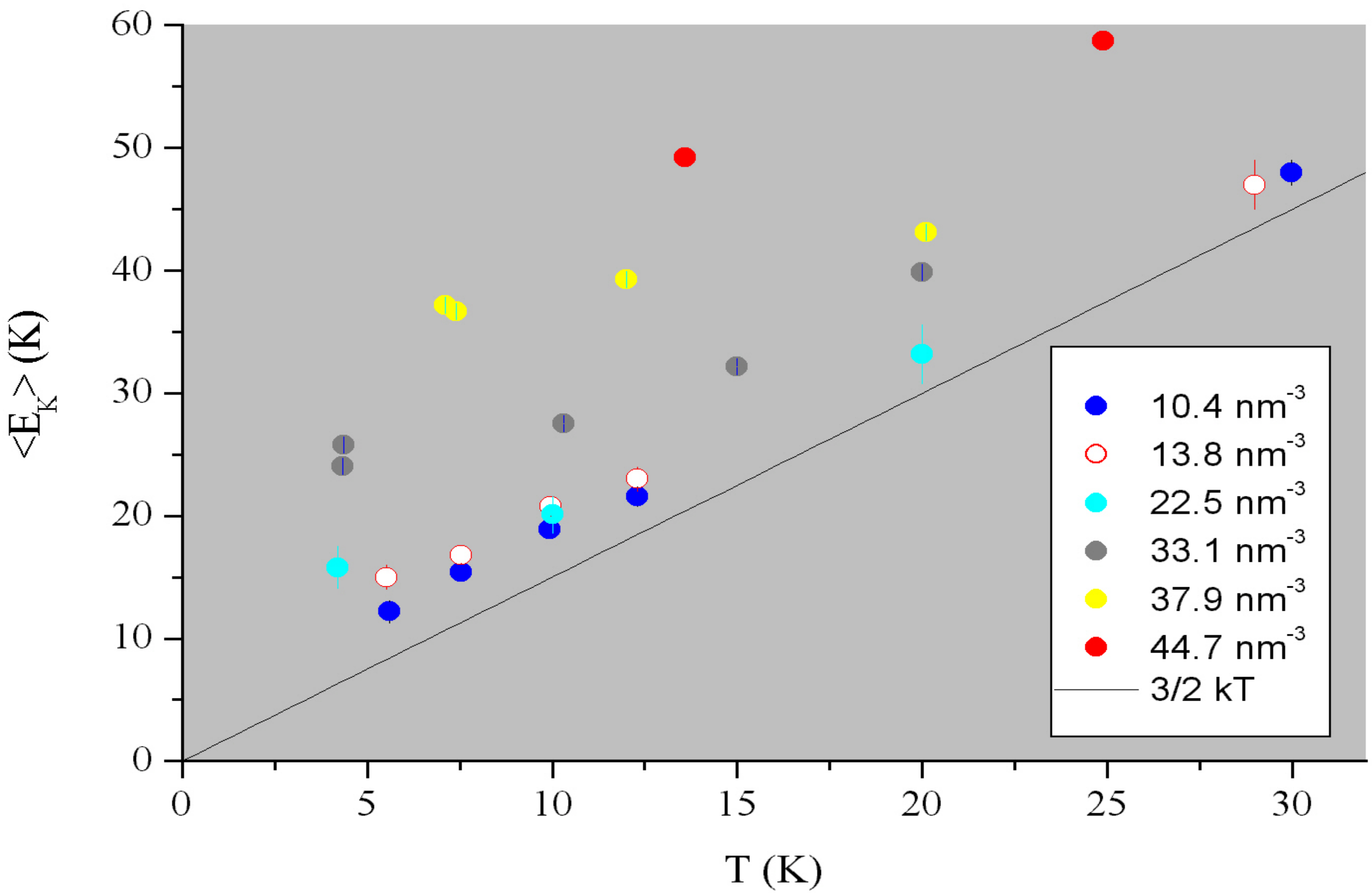
δ =0.63 ± 0.06

* J. Mayers, et al. JPCM, 9, 10639,(1997)



SPERICALLY AVERAGED n(p)
CEPERLEY-POLLOCK 1987 (PIMC)
EXPERIMENT*
GAUSSIAN COMPONENT
* J. Mayers, et al. JPCM, 9, 10639,(1997)
4π p²n(p)(Å)
p (Å⁻¹)
0.0
0.2
0.4
0.6
0.8
1.0
⁴He 2.5 K

Liquid ^{4}He $<E_K>$ > 3/2 KT!



DINS in p-H_2

N(p) Gaussiana

$\langle E_K \rangle_{TRAS}$ vs T

ρ = 22.41 nm^{-3}

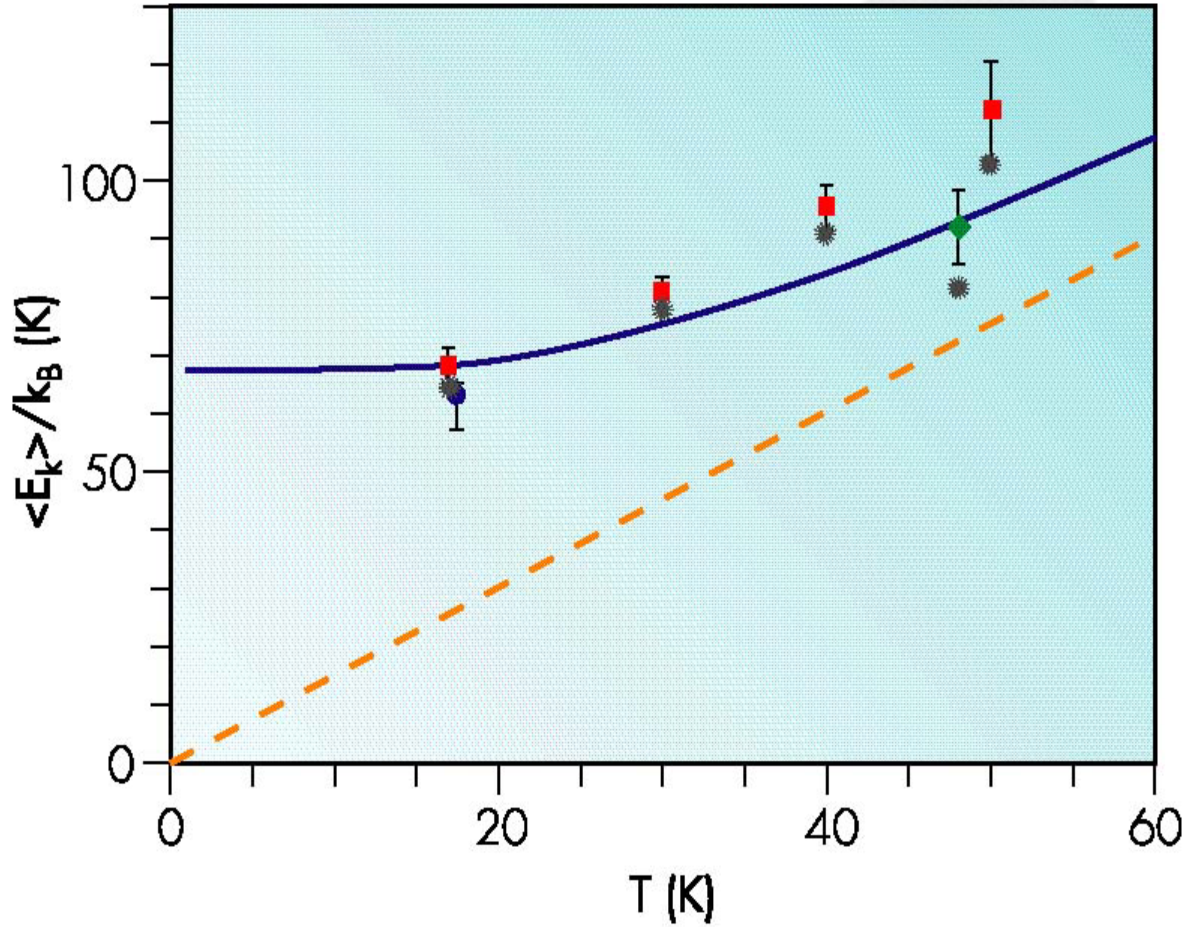
ρ = 10.45 nm^{-3}

Langel et al.

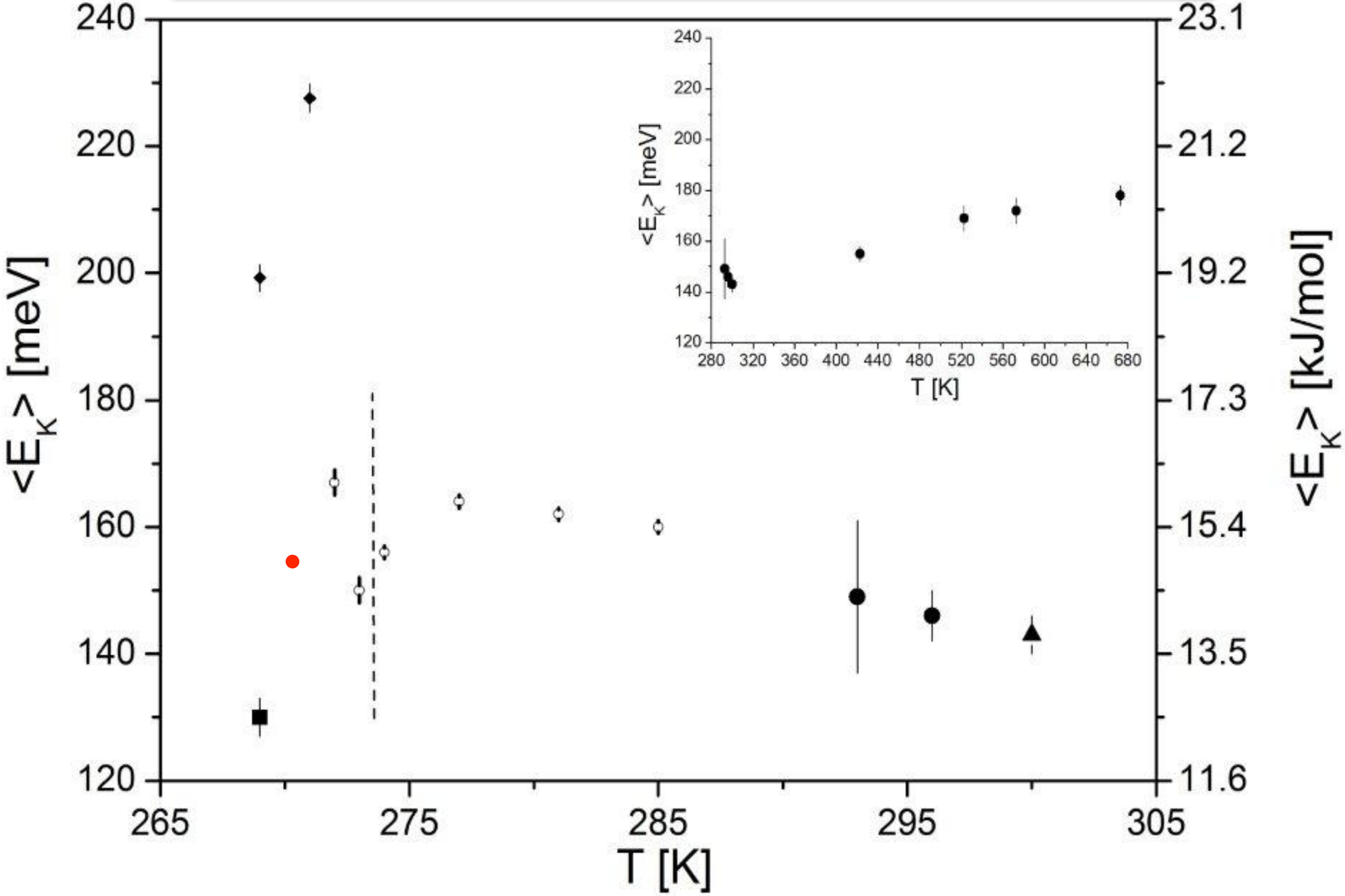
* PIMC

-- classic model

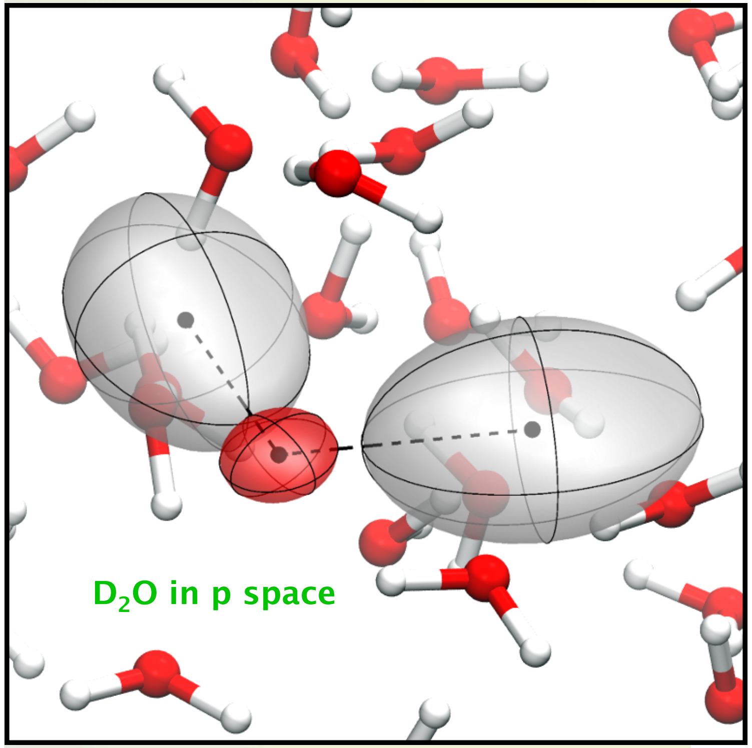
___harmonic model

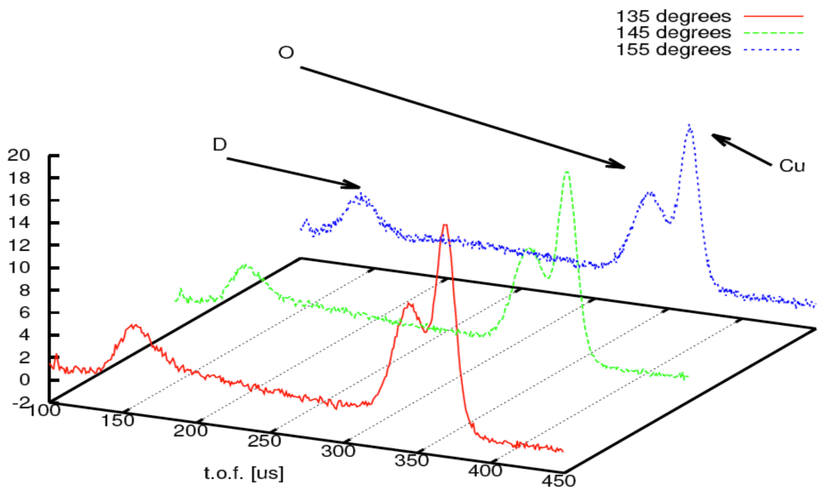


Water: Stable an Metastable Phases

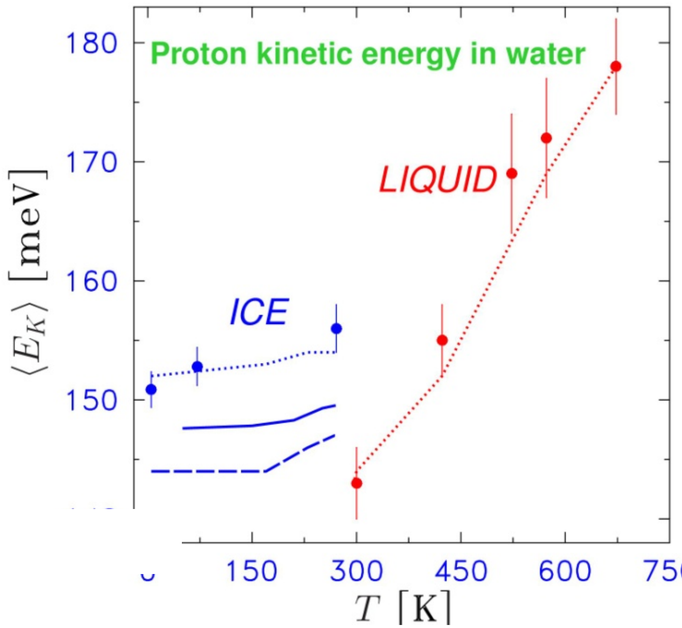


Results from H, D and O in D_2O



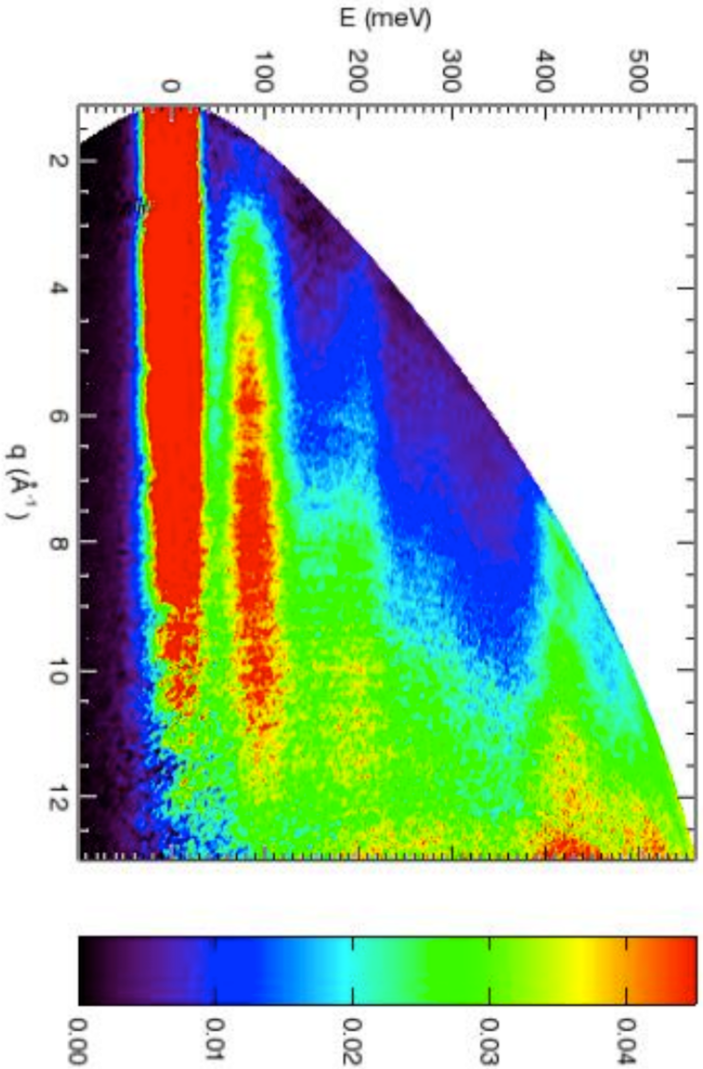


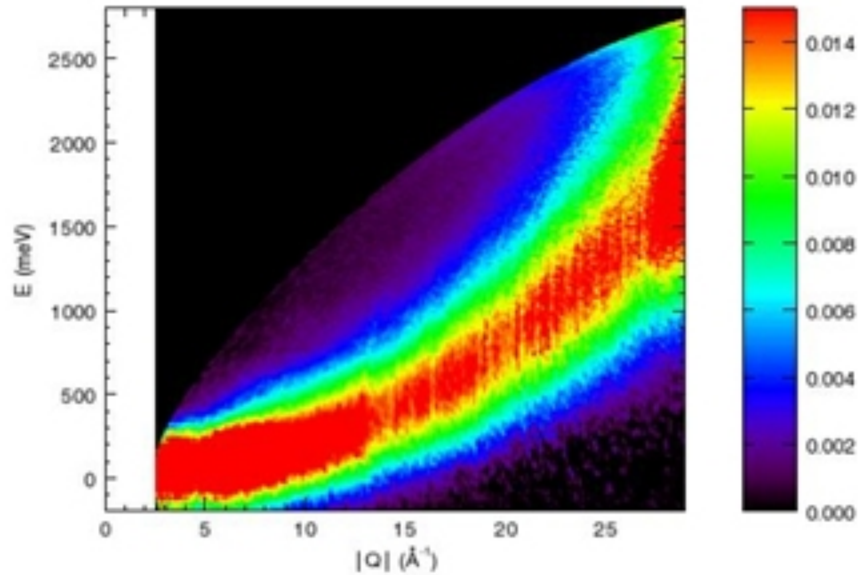
G. Romanelli, *et. al.* J.P.C.L. **4** (19), 3251 (2013).

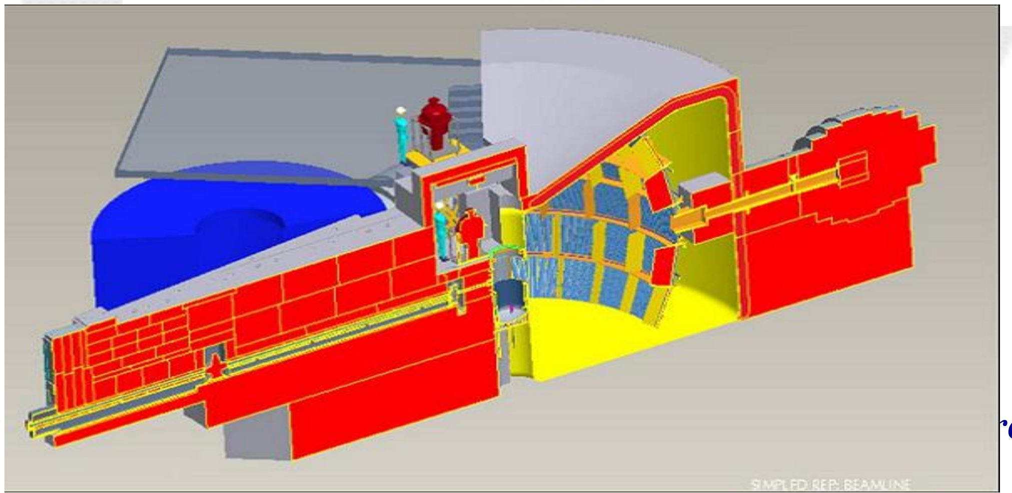


R. Senesi, *et al CP* **427**, 111 (2013)

Simultaneous INS and DINS measurements possible at SNS- SEQUOIA beamline







at … *re (2014)*

Inelastic Neutron scattering: a probe for H vibrations and Zero Point Kinetic Energy components…

$$lim_{q\to 0}\frac{S_{inc}(q,E)}{q^2}2ME\frac{e^{[2W(q)]}}{[n(E)+1]} = g_{exp}(E)_H$$

Low wave vector + high energy transfers

$$S(\vec{q},\omega) = \hbar\int d\vec{p}\, n(\vec{p})\,\delta\left(\hbar\omega - \frac{\hbar^2 q^2}{2M} - \frac{\vec{p}\cdot\hbar\vec{q}}{M}\right)$$

For the OH Stretching range

$$\langle E_K\rangle = \frac{\langle p^2\rangle}{2M}$$

$$\langle E_K\rangle_{OH} = \frac{3}{4}\int_{355}^{480} g_{exp}(E)_{OH}\, E\, dE$$

High wave vector +high energy transfers = Deep Inelastic Neutron Scattering

Harmonic+decoupling assumption

$$\langle E_K\rangle \approx \langle E_K\rangle_{OHstr} + \langle E_K\rangle_{bend} + \langle E_K\rangle_{libr}$$

$\langle E_K \rangle$ components and H-bond

$$\langle E_K \rangle_{OH} = \frac{3}{4}\int_{355}^{480} g_{exp}(E)_{OH}\, E\, dE$$

$$\langle E_K \rangle = \frac{\langle p^2 \rangle}{2M}$$

$$\frac{\langle E_K \rangle_{OH}}{\langle E_K \rangle}$$

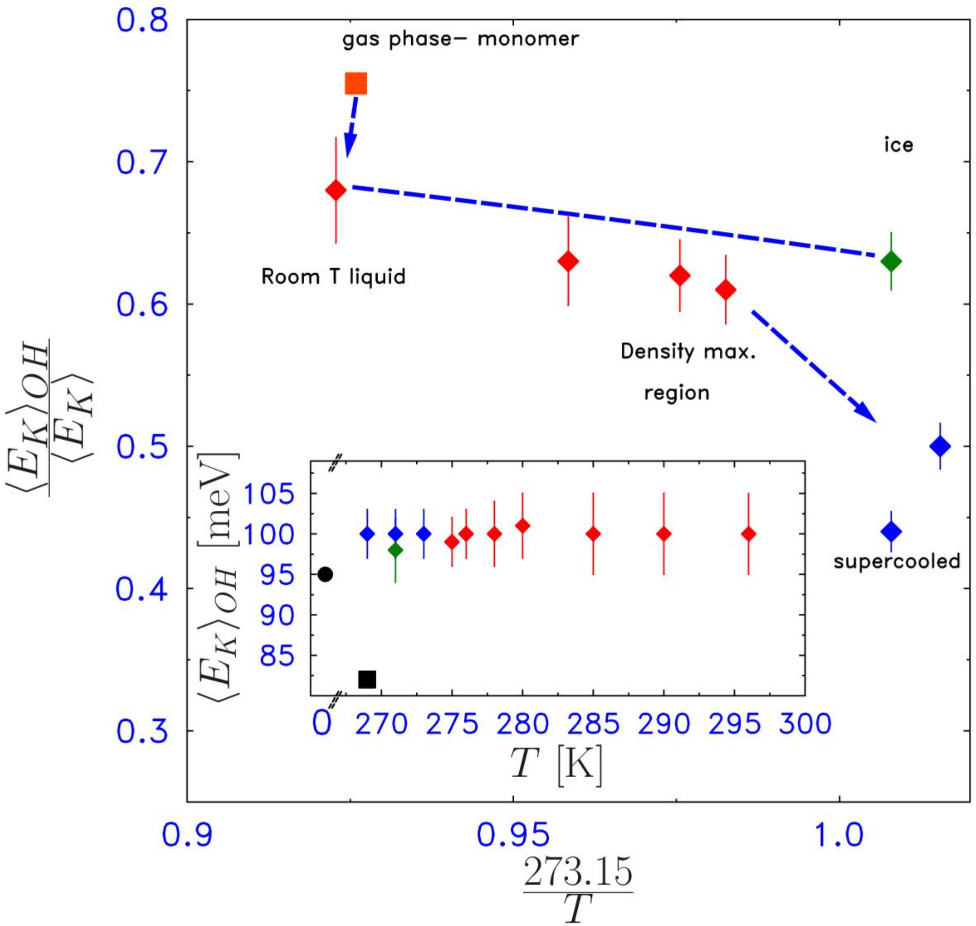
For various phases and temperatures

1- Evaluate the stretching kinetic energy from INS data (example from SEQUOIA)

2- Use total kinetic energy at same temperatures from previous DINS data (ISIS-VESUVIO)

3- Ratio of stretching to total kinetic energy is sensitive to intermolecular interactions, including H-bonding?

Mean kinetic energy components and H-bond



$$E_K\rangle_{OH} = \frac{3}{4}\int_{355}^{480} g_{exp}(E)_{OH}\, E\, dE$$

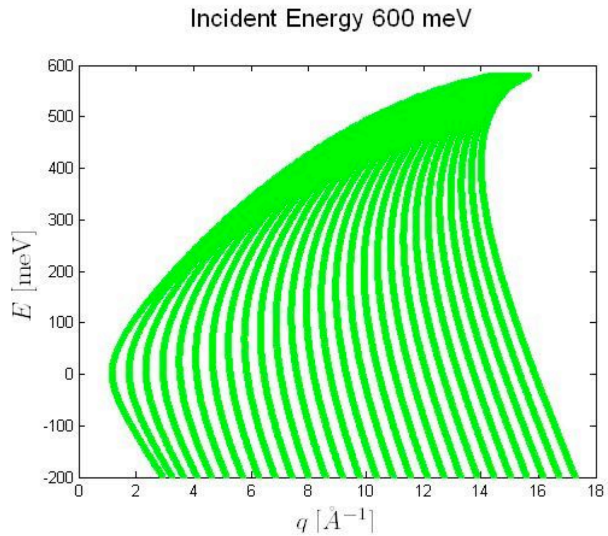
$$\langle E_K \rangle = \frac{\langle p^2 \rangle}{2M}$$

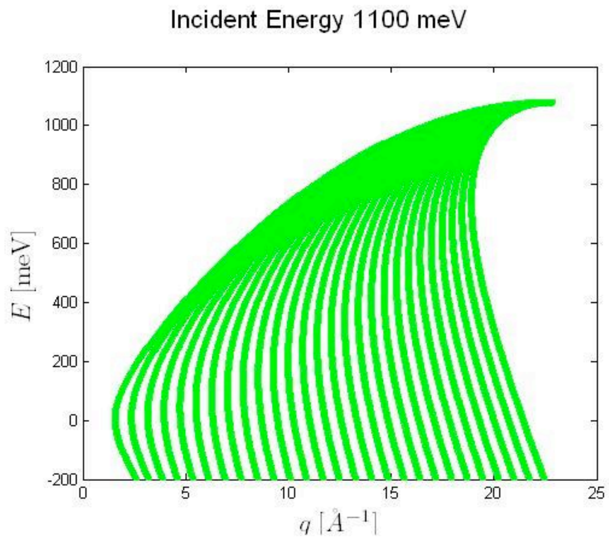
ndation and Centre for Scientific Culture (2014)

Supercooled water*

DINS + INS

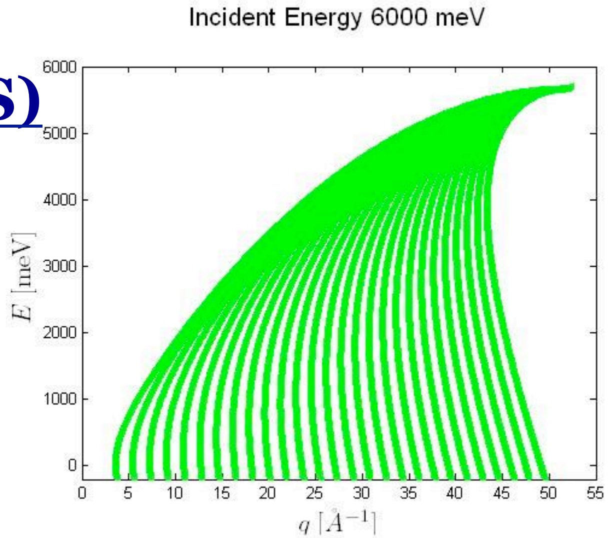
	T [K]
INS	263, 265, 268, 269, 270, 271, 274, 277, 281, 283
DINS	265, 268, 270

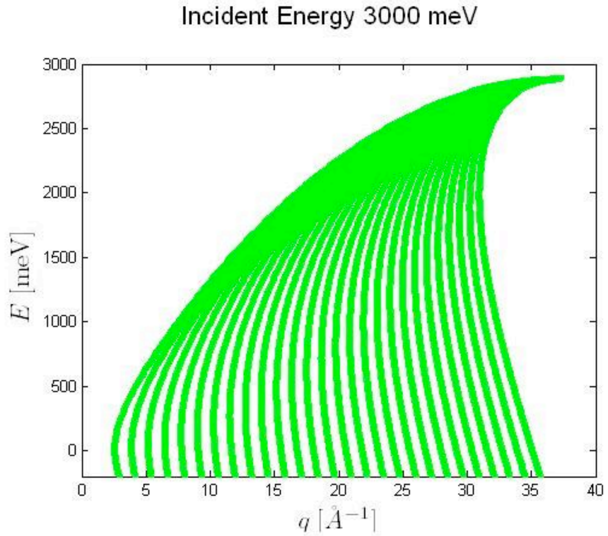


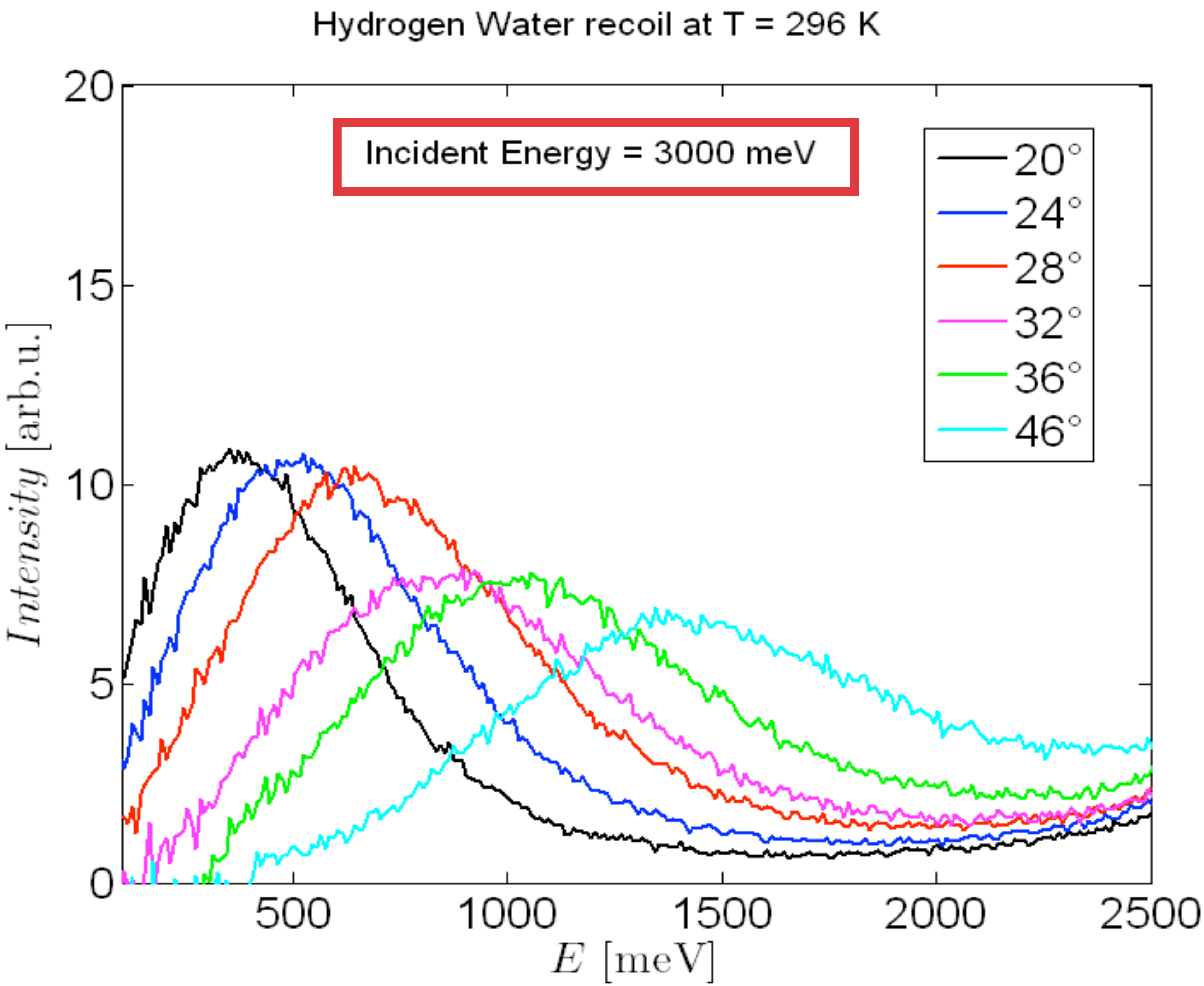


<u>DINS and INS</u>
<u>On SEQUOIA (SNS)</u>

Al CELL
THICK = 0.25 mm

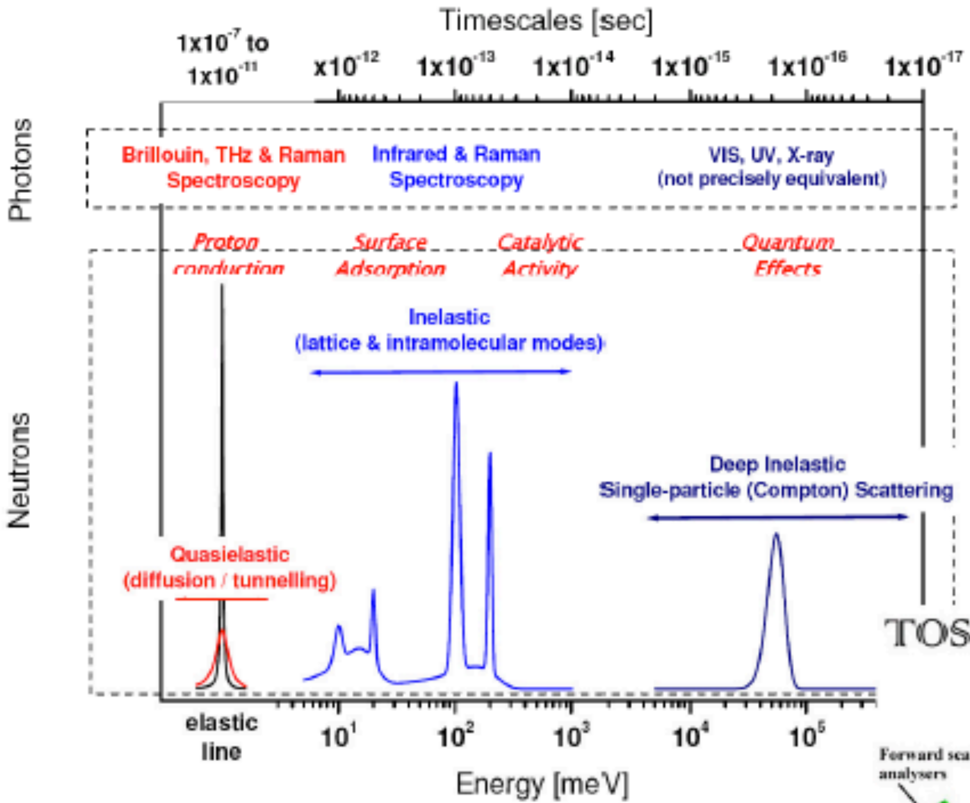


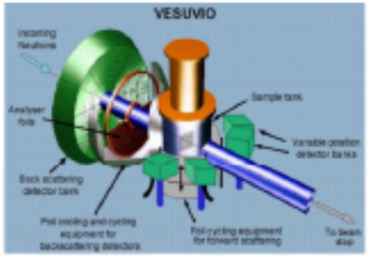



Hydrogen Water recoil at T = 296 K
Incident Energy = 3000 meV
20°
24°
28°
32°
36°
46°
Intensity [arb.u.]
E [meV]
0
5
10
15
20
500
1000
1500
2000
2500

(2014)

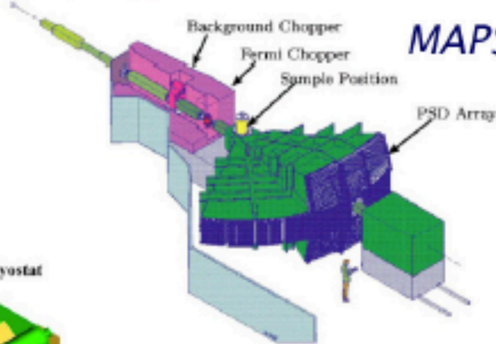
Neutron Spectroscopy at ISIS





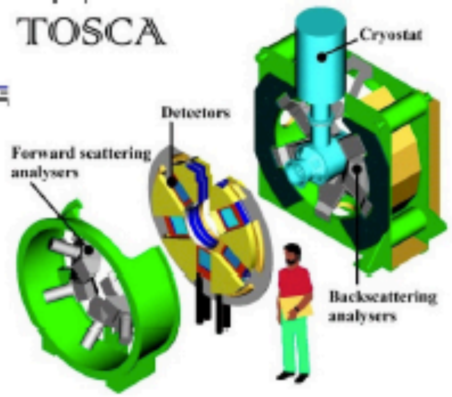
Simultaneous high-resolution diffraction

MAPS



High energies

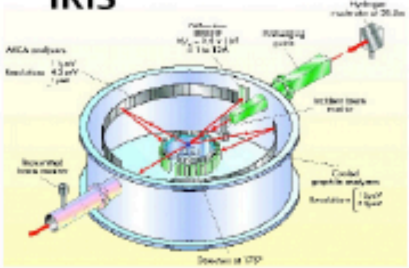
TOSCA



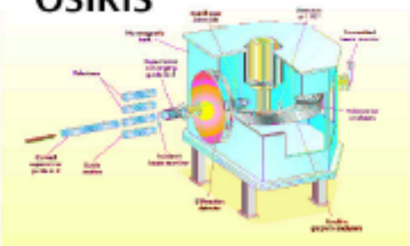
Intermediate energies (infrared, Raman)

Widest spectral range in the World

IRIS



OSIRIS



Low energy (Brillouin, THz)


THANK YOU
QUESTIONS?