Istituto dei Sistemi Complessi

VESPA: a **V**ibrational **E**xcitation **S**pectrometer with **P**yrolytic-graphite **A**nalyzers

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(2) NBI, Copenhagen, Denmark
(3) ESS, Lund, Sweden

EUROPEAN SPALLATION SOURCE

Consiglio Nazionale delle Ricerche

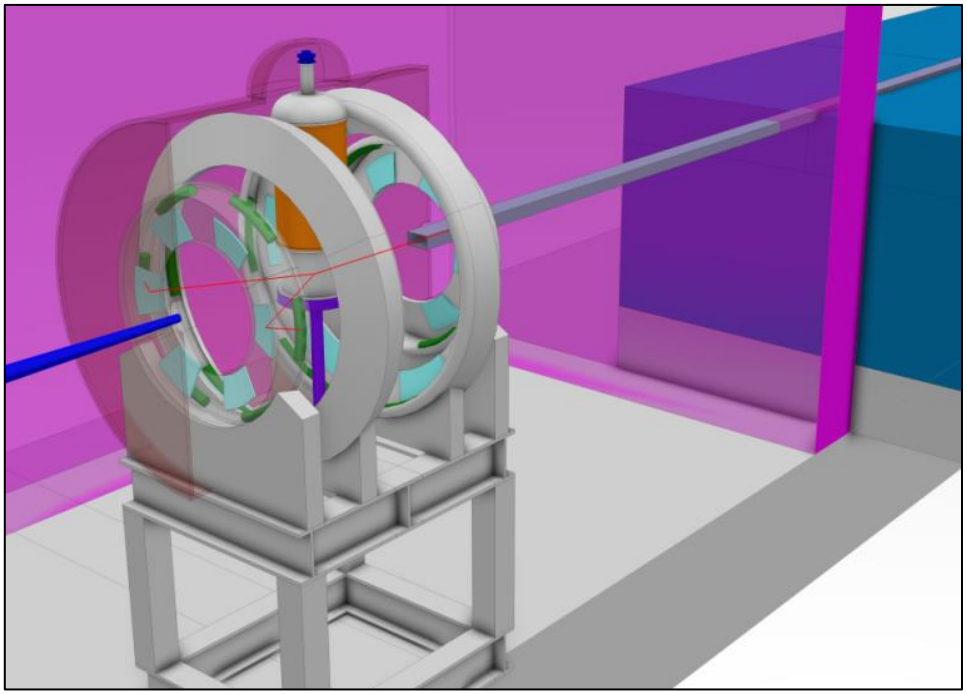
Presentation outline

1. ***VESPA*: what is it?**
2. ***VESPA*: research areas**
3. ***VESPA*: complementary & unique**
4. ***VESPA*: instrument overview**
5. ***VESPA*: choppers & energy resolution**
6. ***VESPA*: high resolution**
7. ***VESPA*: high intensity**
8. ***VESPA*: secondary spectrometer**
9. ***VESPA*: science & sample environment**
10. ***VESPA* ...**

1. VESPA: what is it?

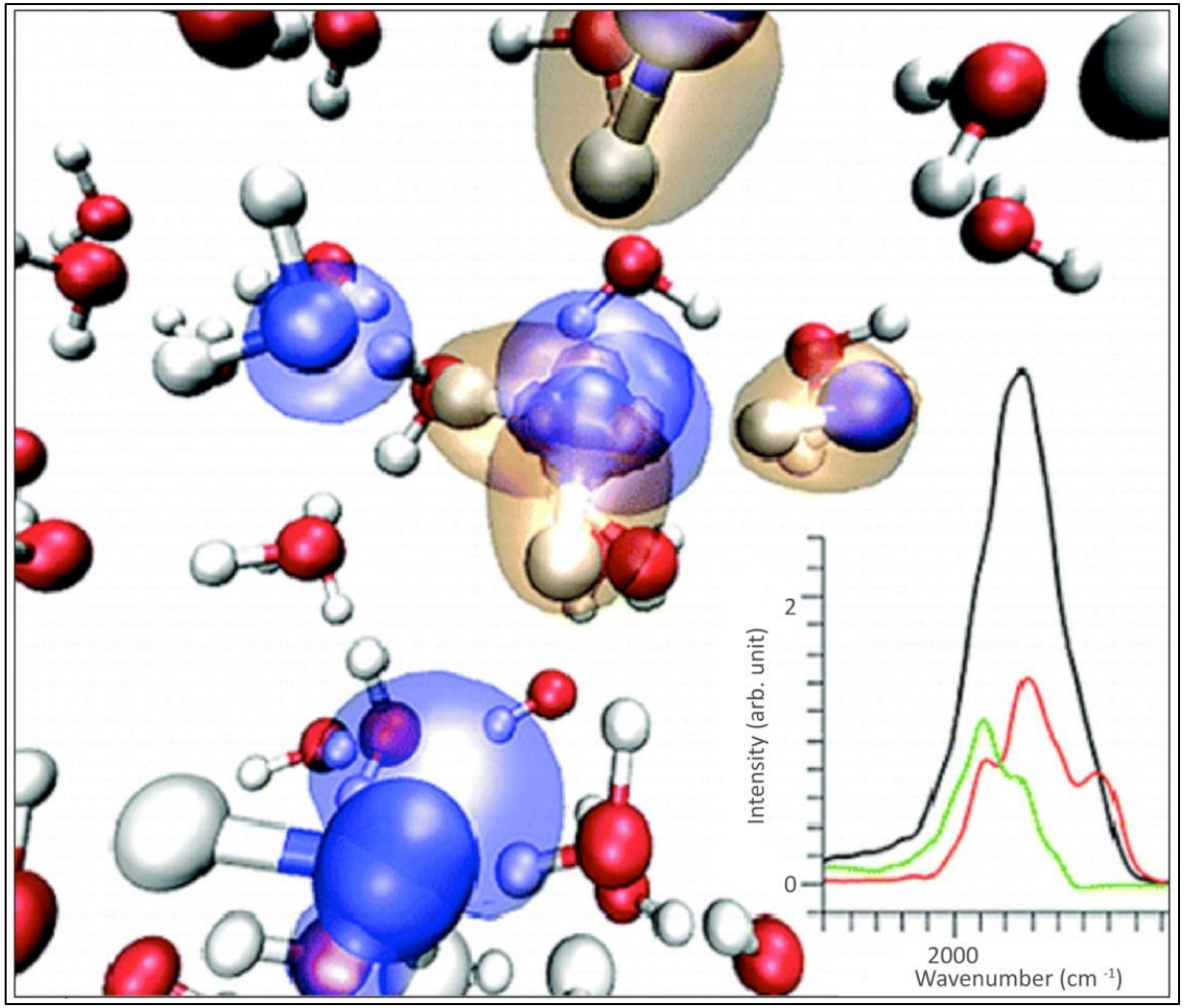
V. E. S. P. A. *(**V**ibrational **E**xcitation **S**pectrometer with **P**yrolytic-graphite **A**nalysers)*

A crystal-analyser inverse-geometry time-of-flight spectrometer fully devoted to ***Neutron Vibrational Spectroscopy (NVS)***



It'll be the ***only*** inelastic instrument at ***ESS*** focused on ***molecular vibrations*** in ***chemistry*** and ***material science!***

Why vibrational spectroscopy?



Vibrational spectroscopy is a technique widely used in scientific and technological research, fundamental as well as applied:

- probing potential **energy surfaces** and **interatomic interactions**;

- permitting the identification of **bonds** and **functional groups**, as well as their transformations;

- determining the **vibrational density of states** (related to various thermodynamic properties).

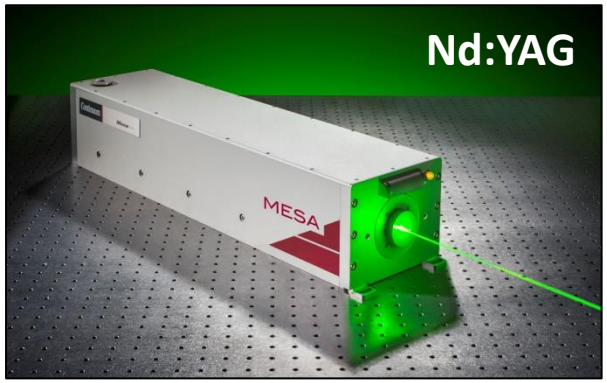
Neutrons vs. IR/Raman

Vibrational spectroscopy: cross-sections and intensities

σ(Raman)~10^{-28} cm^2/molec.; J_{ph}(Nd:YAG)~10^{20} cm^{-2}s^{-1}

σ(Neutr.)~10^{-24} cm^2/molec.; J_n(ILL)~10^{15} cm^{-2}s^{-1}

σ(IR)~10^{-18} cm^2/molec.; J_{ph}(Globar)~10^{20} cm^{-2}s^{-1}



So why neutron vibrational spectroscopy?

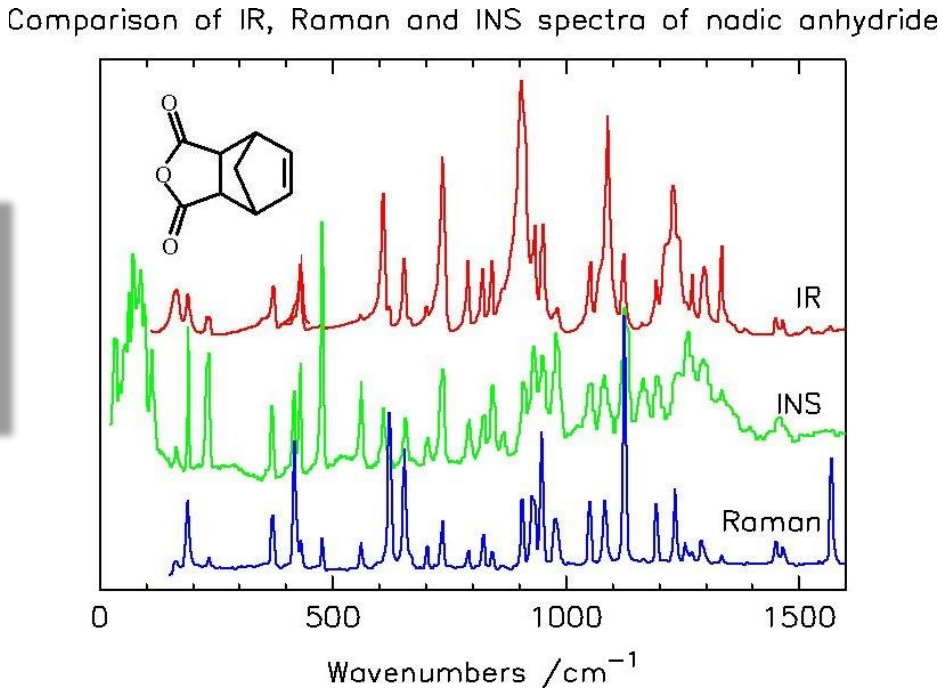
1. In Raman, **polarizability** normally grows with ***Z***: possible problems to detect protons.
2. In IR (sensitive to **electric dipole**), H-bond provides a strong signal, but can be distorted by the so-called **electric anharmonicity** (not vibrational).
3. Molecules with a **high symmetry:** many modes are **optically inactive** (*e.g.* in C_{60} more than 70%!).

4. Direct relationship between neutron spectra and **vibrational eigenvectors**.

Conclusions

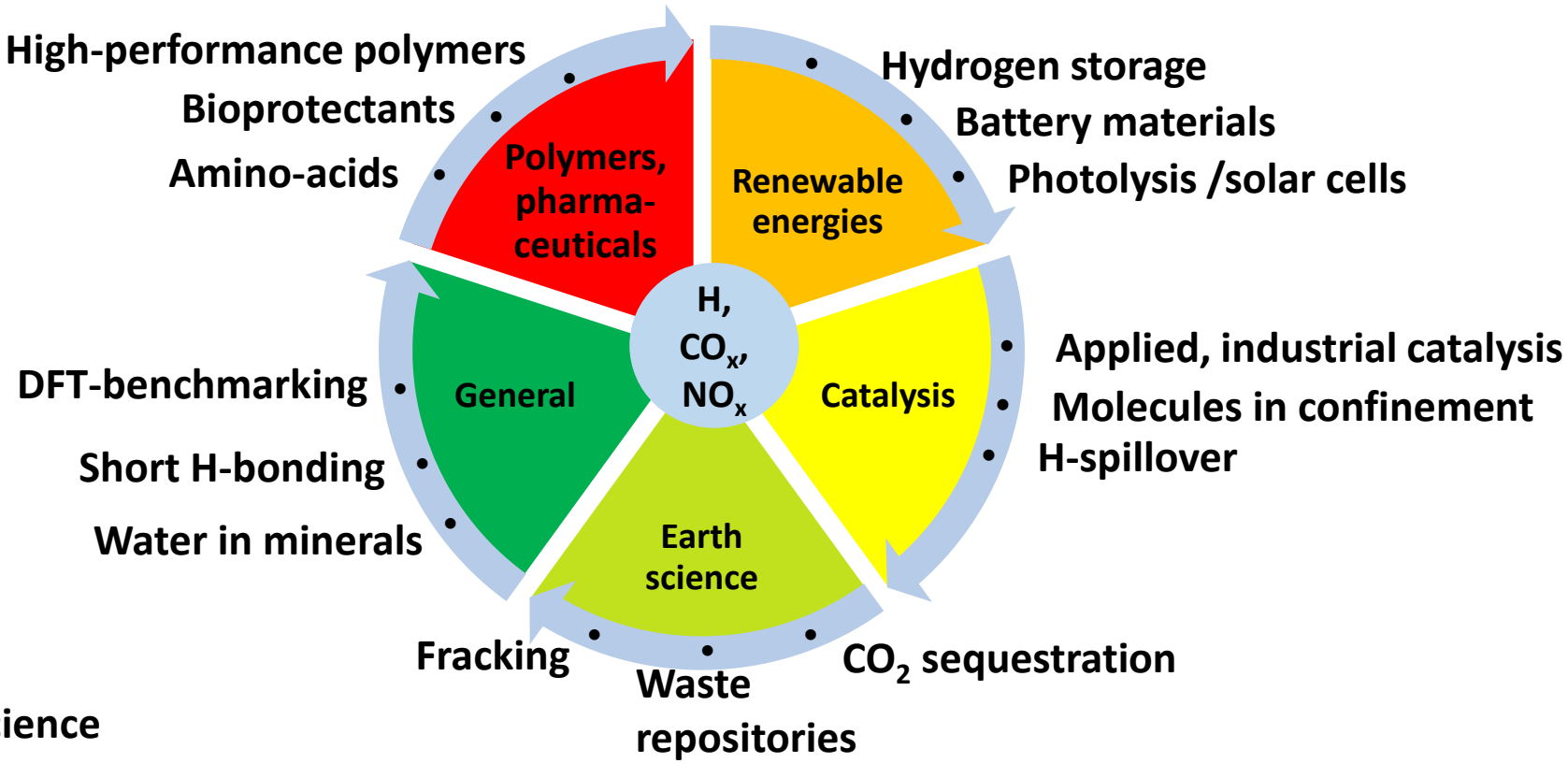
NVS is complementary to optical spectroscopies and is often crucial for studying proton dynamics!

Example: nadic anhydride ($C_9H_8O_3$) on TOSCA *(courtesy of S. F. Parker)*



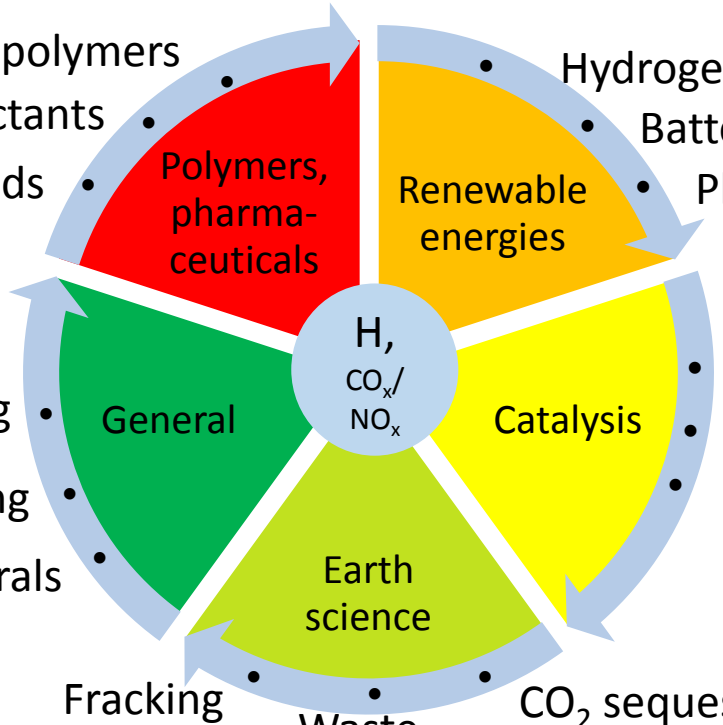
2. VESPA: research areas

*** Neutron Vibrational Spectroscopy (+ Diffraction/PDF)**



- Science

* Neutron Vibrational Spectroscopy (+ Diffraction/PDF)



High-performance polymers
Bioprotectants
Amino-acids
*high-pressure
*photocatalysis

Hydrogen storage
Battery materials
Photolysis /solar cells
*high-pressure
*gas loading
*gas analysis
*photocatalysis
*electrical cell

Applied, industrial catalysis
Molecules in confinement
H-spillover
*gas loading, reactor
*gas analysis
*photocatalysis
*electrical cell

DFT-benchmarking
Short H-bonding
Water in minerals

Fracking
Waste repositories
CO_2 sequestration
*high-pressure
*gas analysis
*gas loading

- **science**

* **Techniques**

* Neutron Vibrational Spectroscopy (+ Diffraction/PDF)

Currently not enough…

A: *constant & high resolution*

B: *intensity*

C: *bandwidth (i.e.'one shot')*

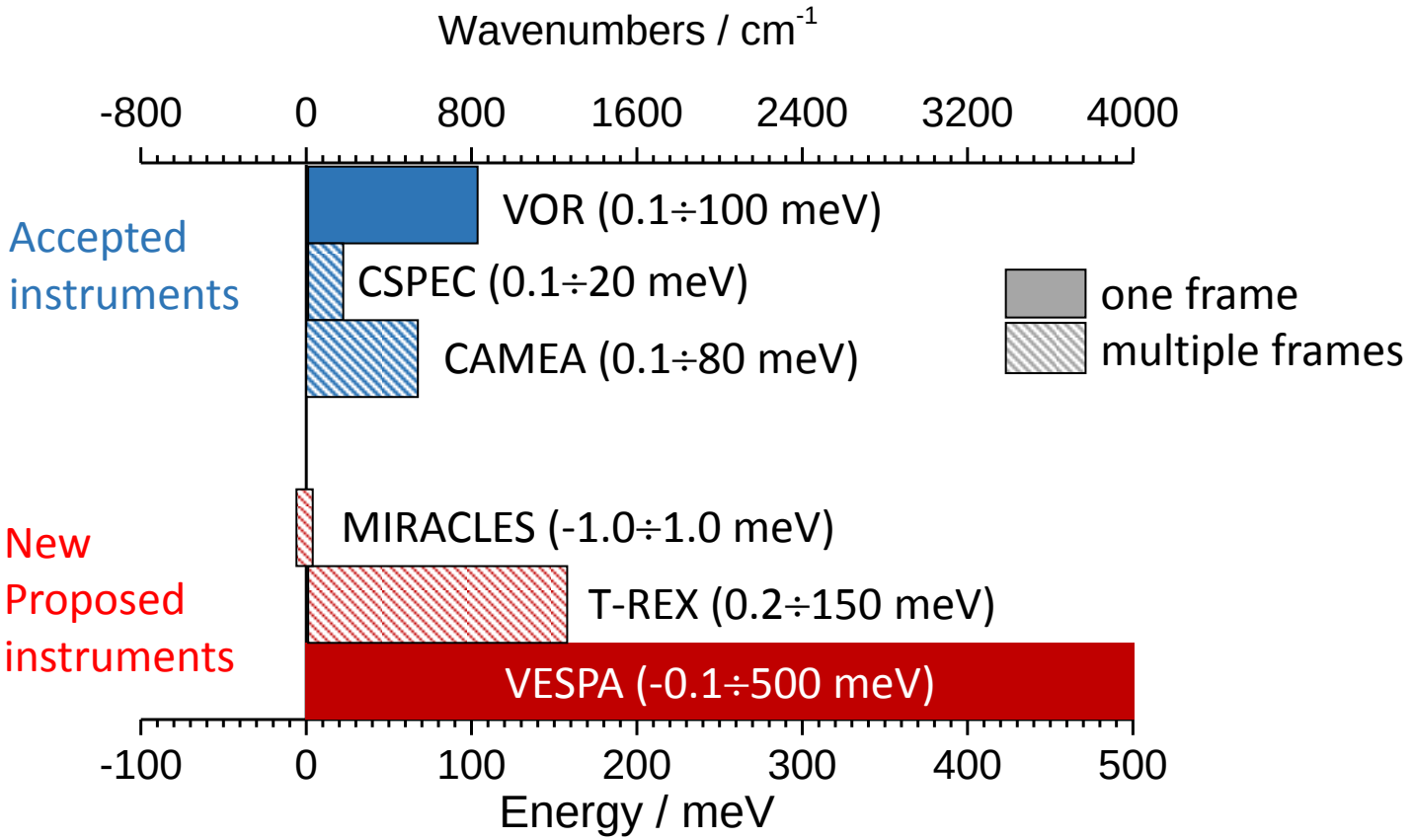
A+B+C simultaneously *is not available worldwide!*

- **science**
- *** techniques**

3. VESPA: complementary & unique

Existing **NVS** instruments at spallation sources:

- ***VISION* (US): about 3x oversubscribed;**
- ***TOSCA* (UK): about 2x oversubscribed.**



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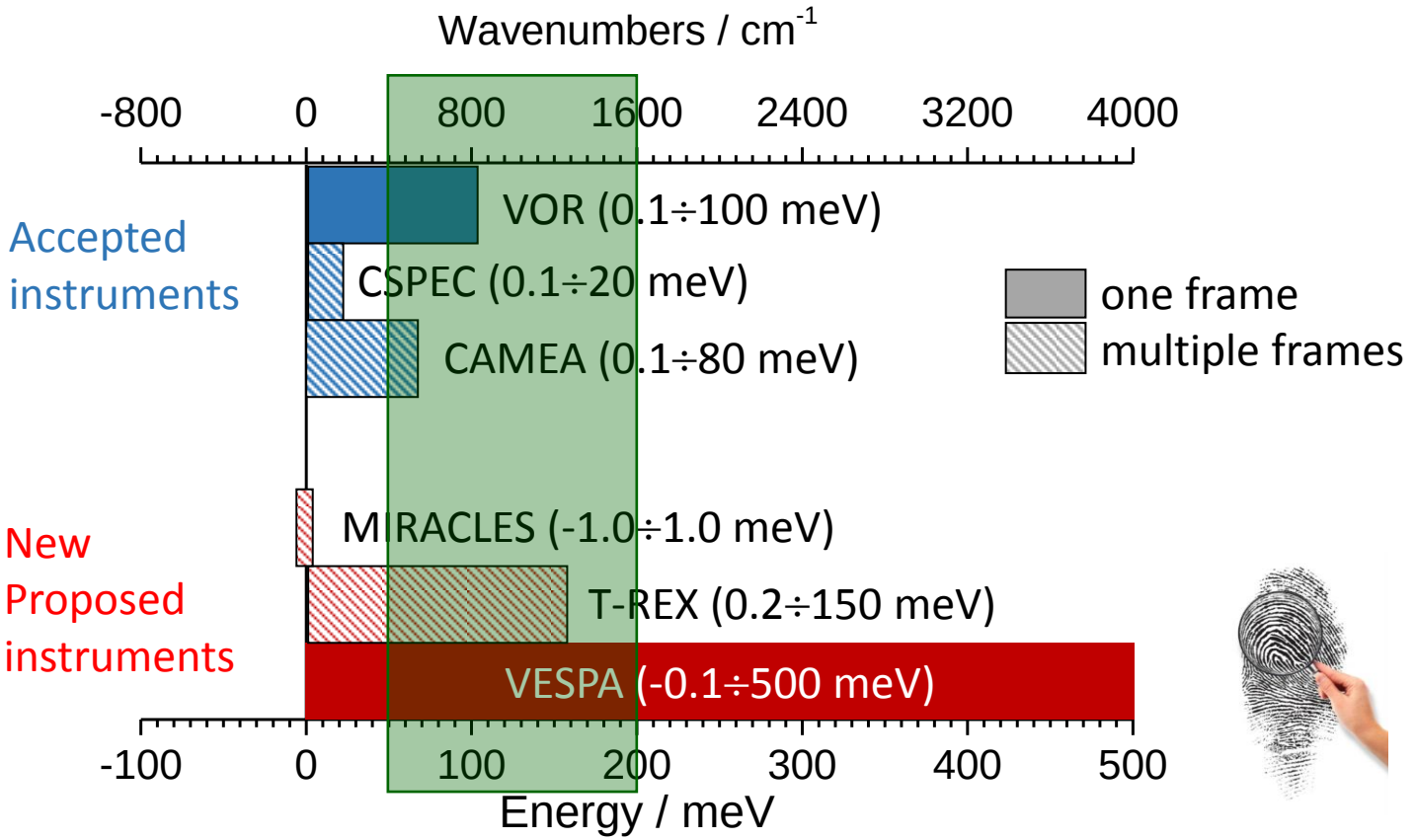
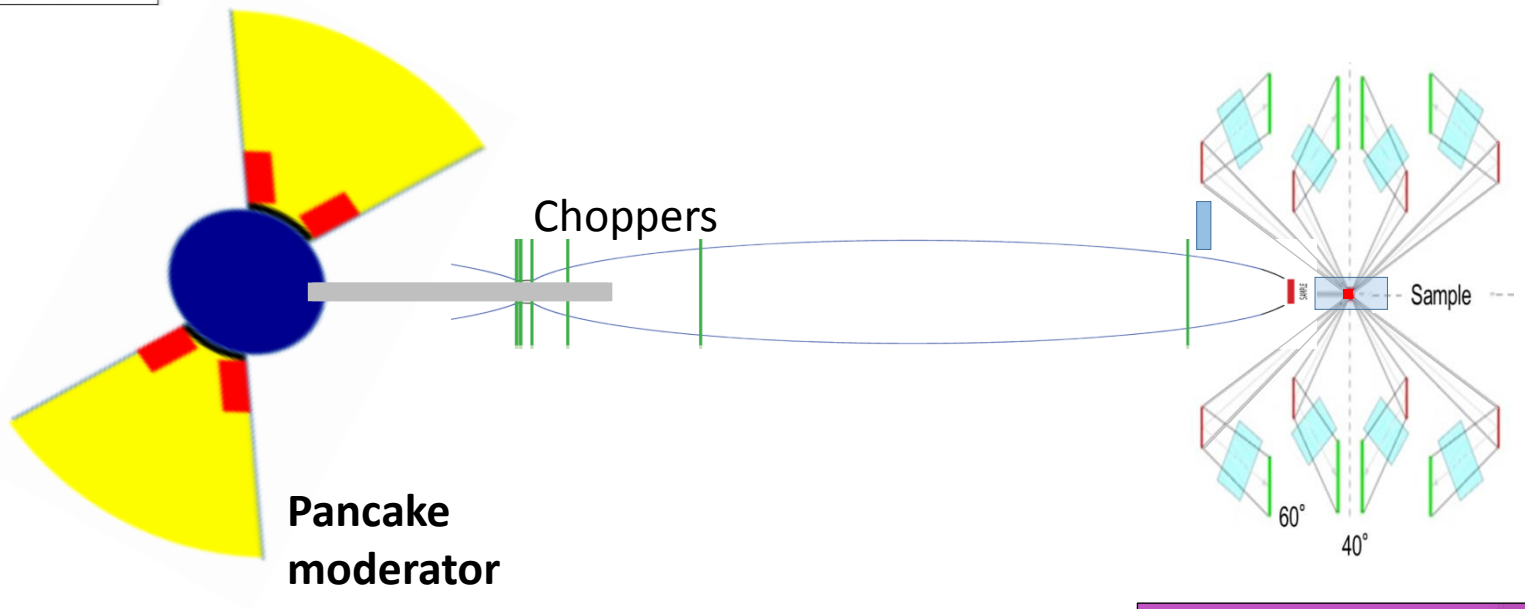
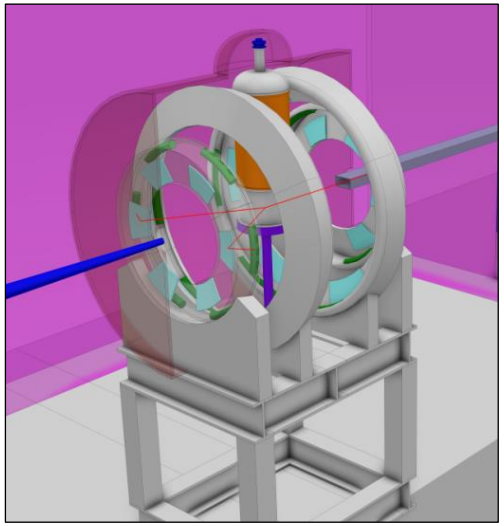


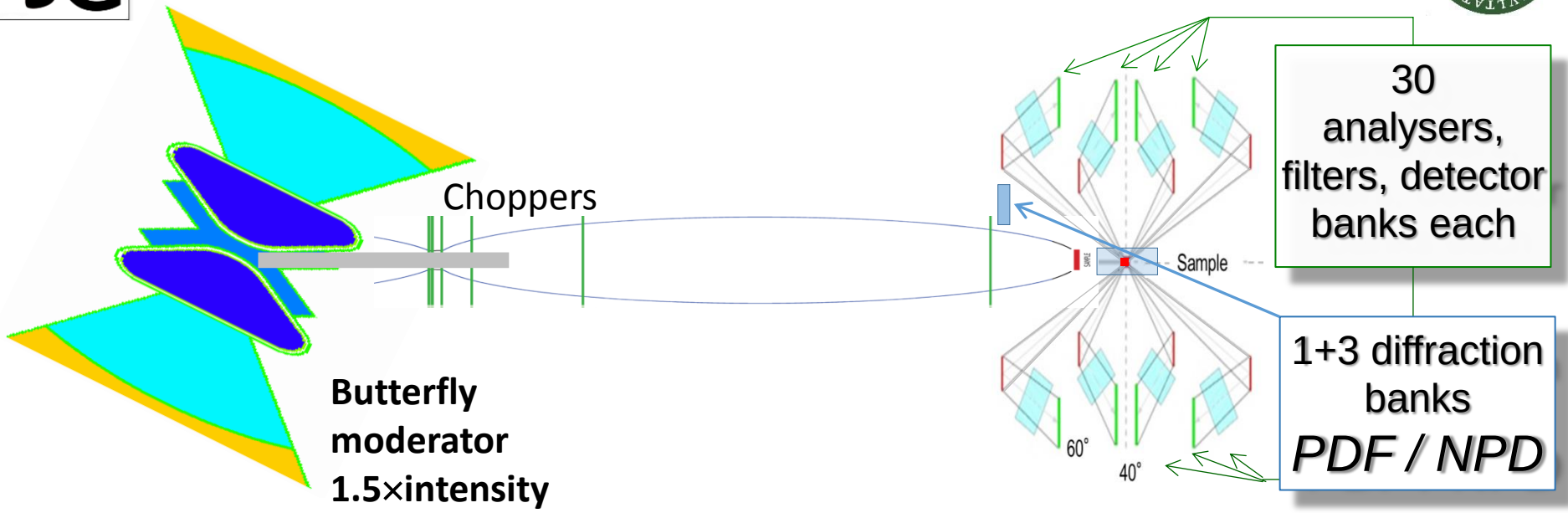
Fingerprint region!

4. VESPA: instrument overview



- Chopper system for choosing desired resolution ($\Delta E/E_0$).
- Not unconventional, but increased coverage (Ω=1.196 sr), increased flux and resolution (*ESS* source / instrument length).
- Constant resolution $\Delta E/E_0$ possible because of long pulse.





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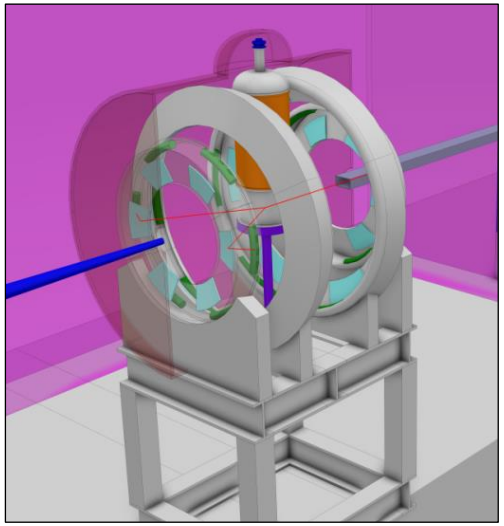
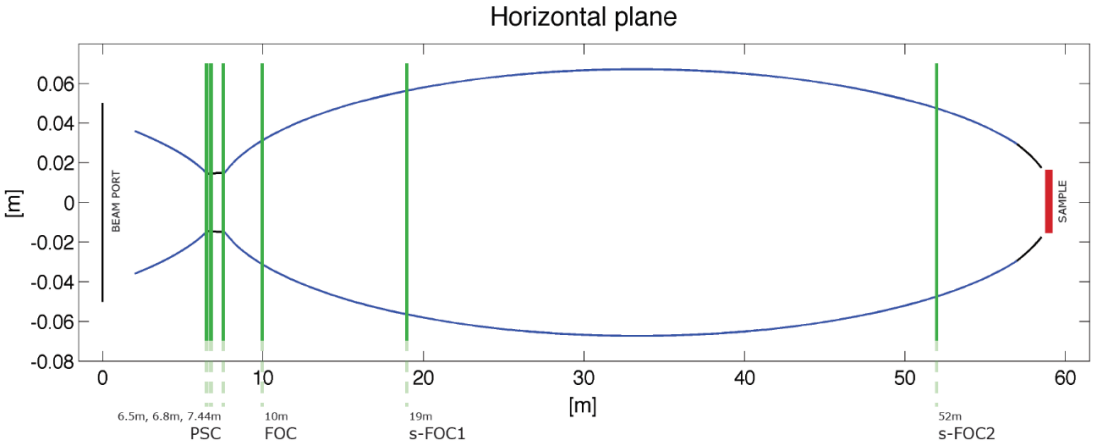
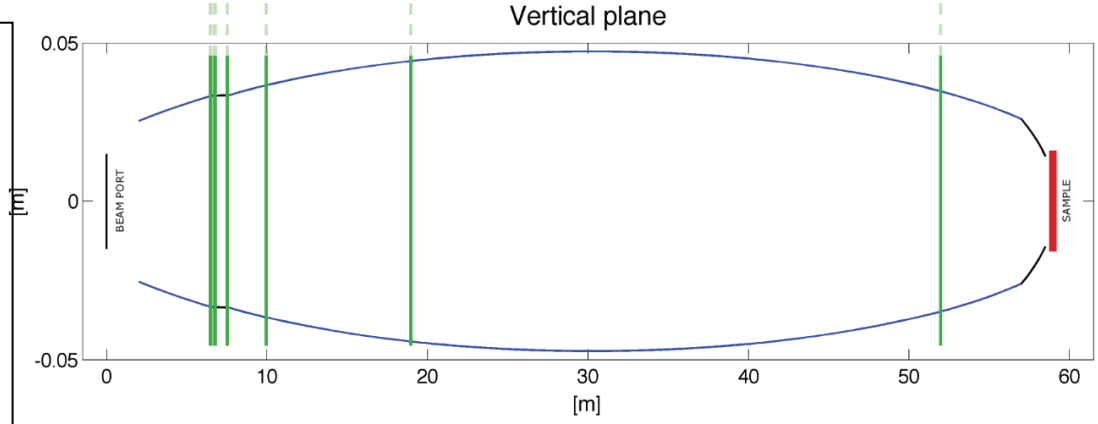


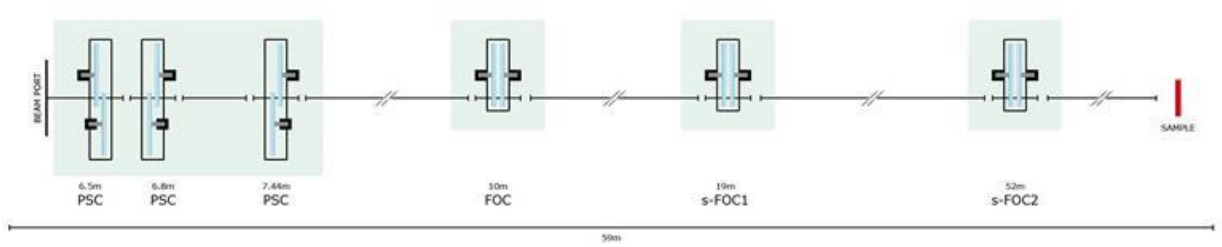
Neutron guides & choppers

- *m*=4 elliptical guide (56 m), *m*=4 linear guide (1.1 m);
- guide starts from 2 m after the moderator.





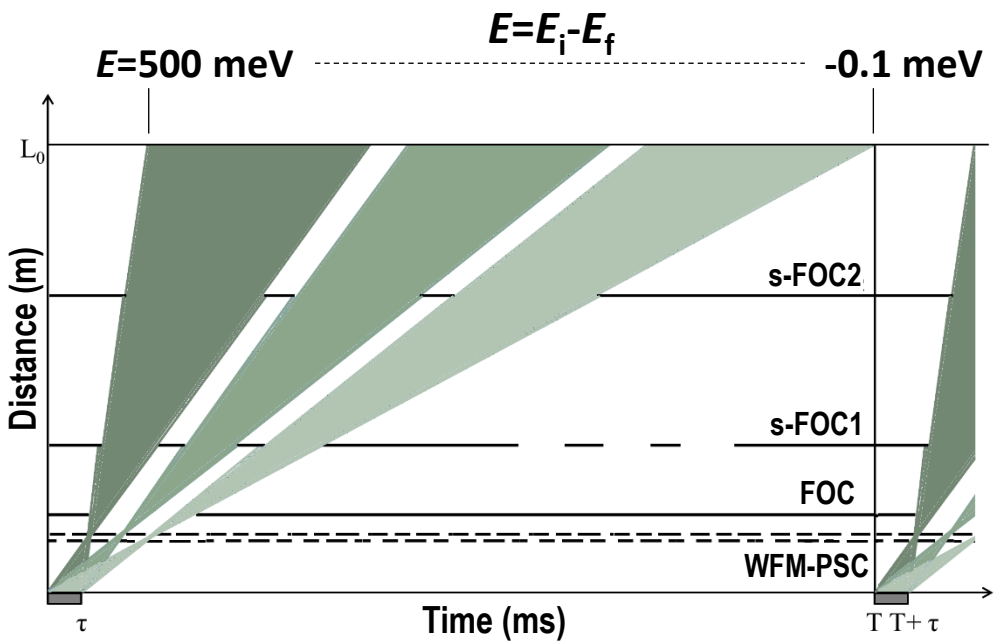
- 1st chopper position: 6.5 m;
- 3 PSC pairs (H, M, L; optical blind chop.) + FOC + 2×sFOC (1, 2);
- all choppers are counter-rotating double disks: trapezoidal transmission;
- T_0-chopper still undecided.



5. VESPA: choppers & resolution

- 3 subframes in one “shot” - use of the complete ***ESS*** pulse (**wavelength frame multiplication**);
- equivalent rel. resolution for the fingerprint region (**optical blind choppers**);
- **energy resolution** can be selected (**3 configurations**).

Chopper parameters	Low-Res.	Mid-Res.	High-Res.
WFM-PSC1 (m)	6.50	6.80	6.50
WFM-PSC2 (m)	7.44	7.44	6.80
z_0 (m)	0.94	0.64	0.30
Final Energy Resolution:	**1.1%**	**0.7%**	**0.4%**



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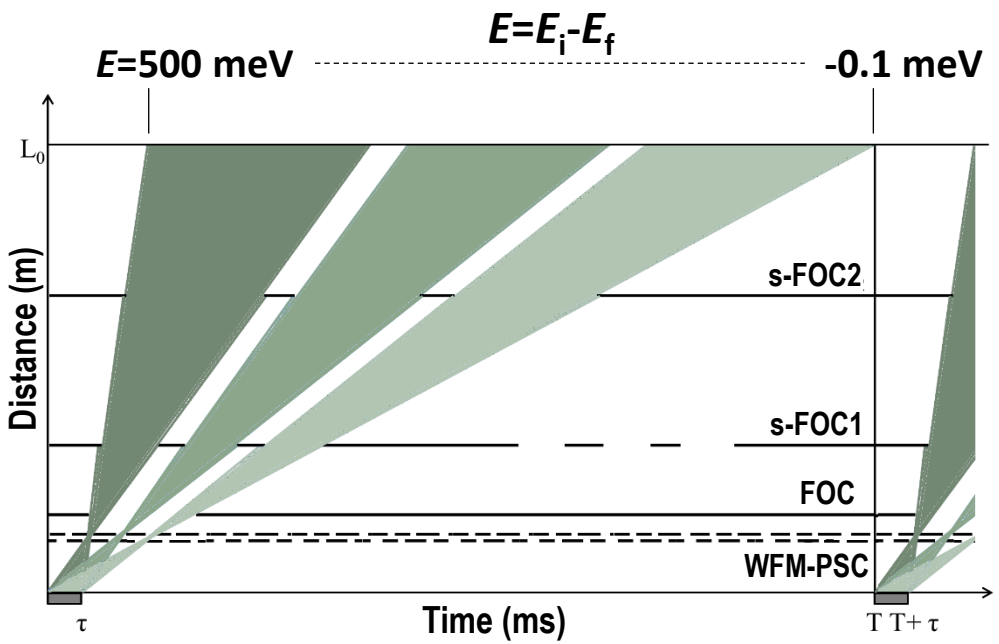
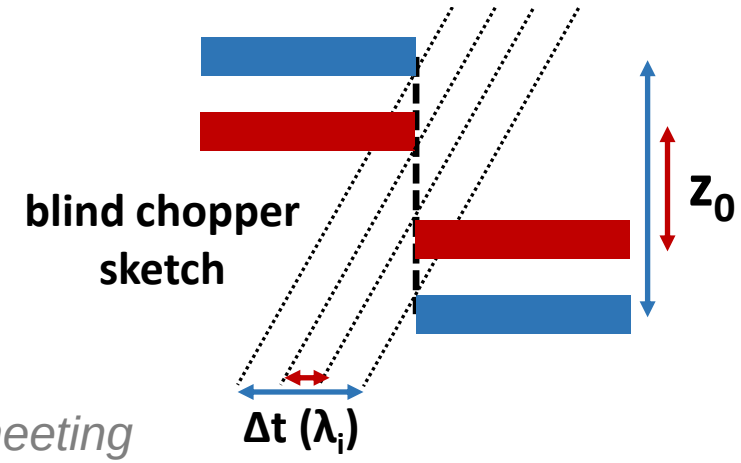
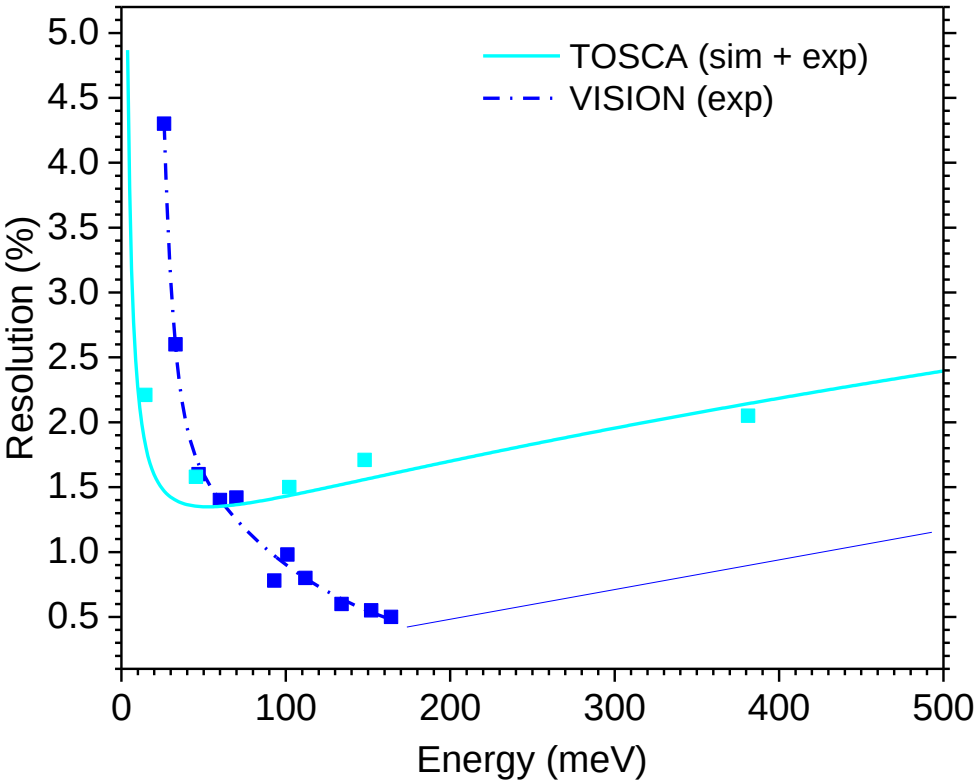
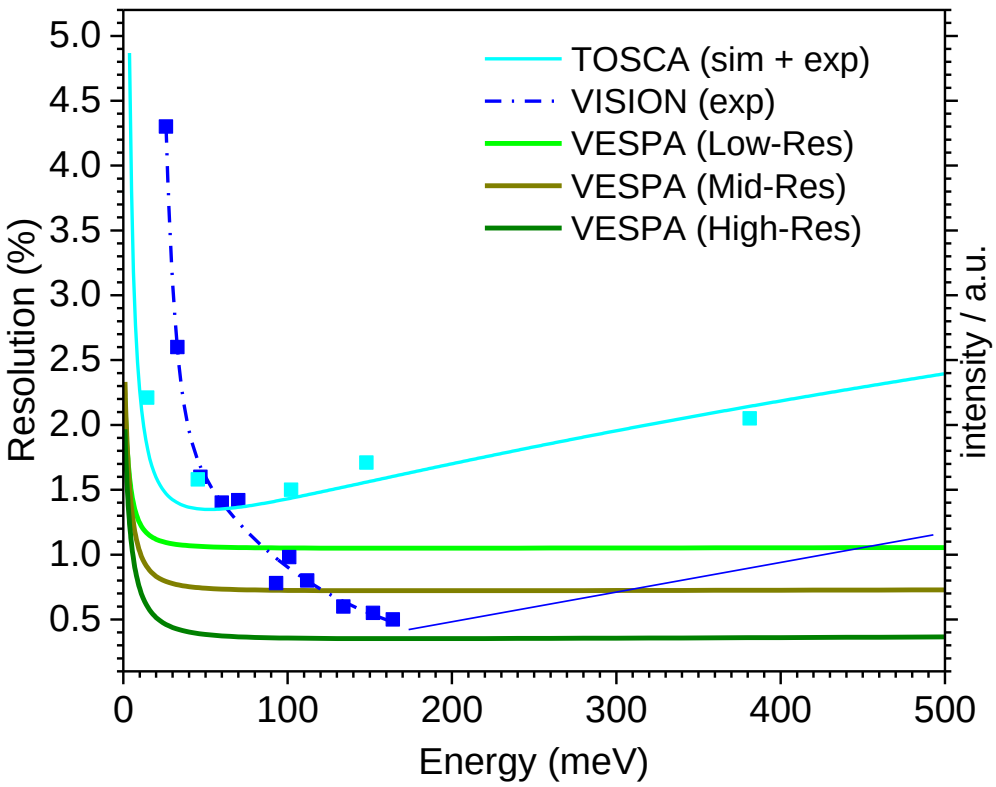


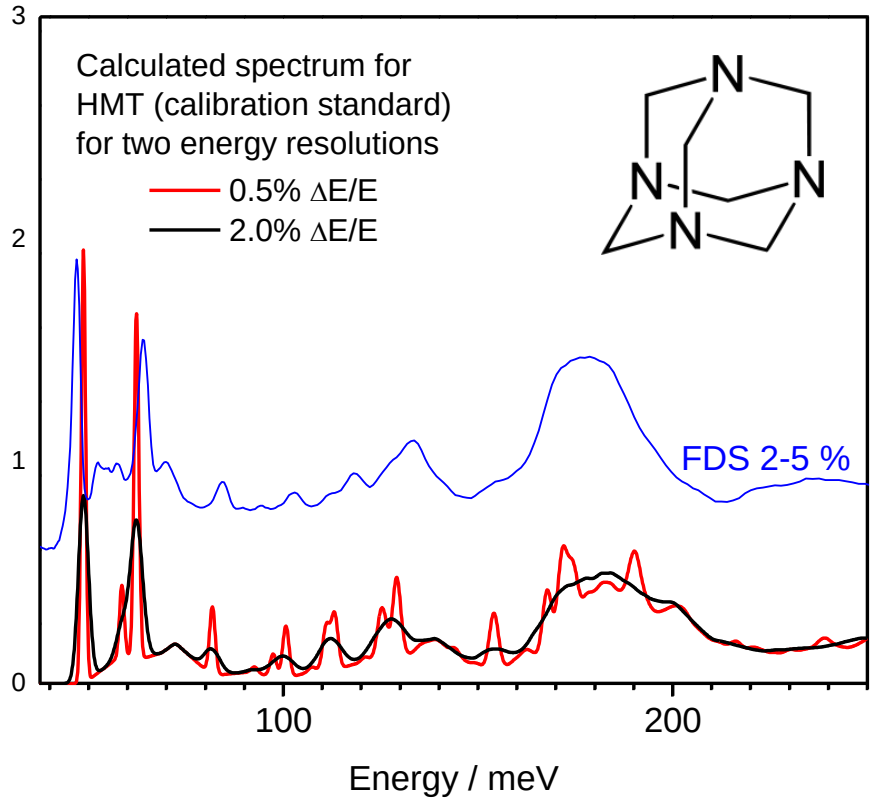


6. VESPA: high resolution



TOSCA: D. Colognesi *et. al, Appl. Phys. A* **74**, S64 (2002).
VISION: L. Daemen, private communication (2015).



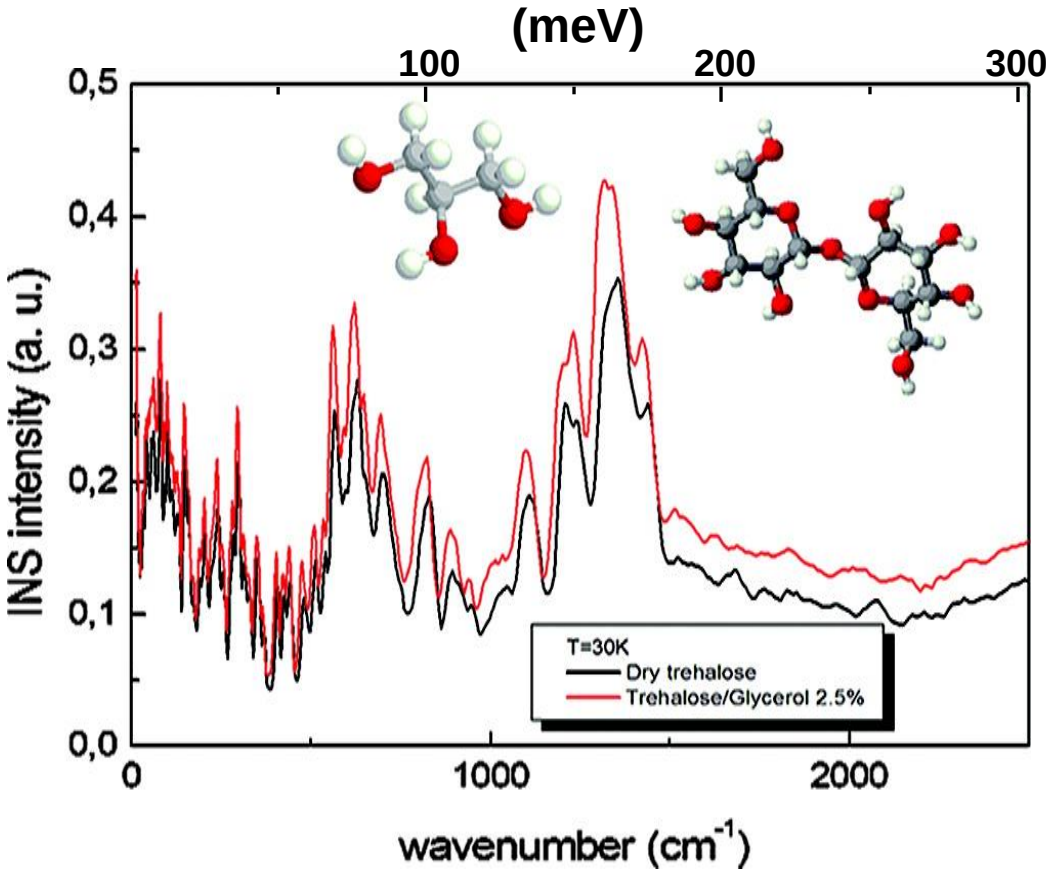


TOSCA: D. Colognesi *et. al, Appl. Phys. A* **74,** S64 (2002).

VISION: L. Daemen, private communication (2015).

Hi-resolution examples: bioprotectants

***VESPA** resolution is 2x better than TOSCA (1.5-2%)!*

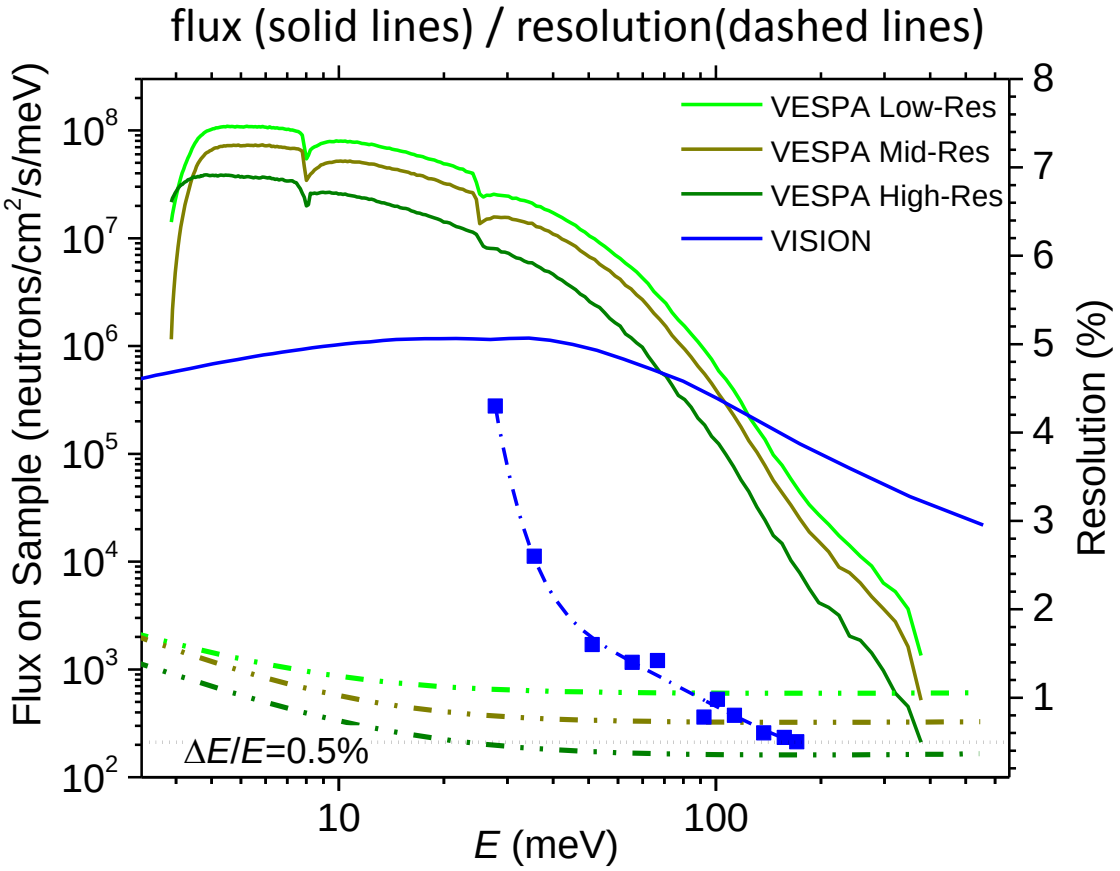


TOSCA: *spectra of dry trehalose (red line) and a mixture of trehalose plus 2.5 wt-%. glycerol (black line).*

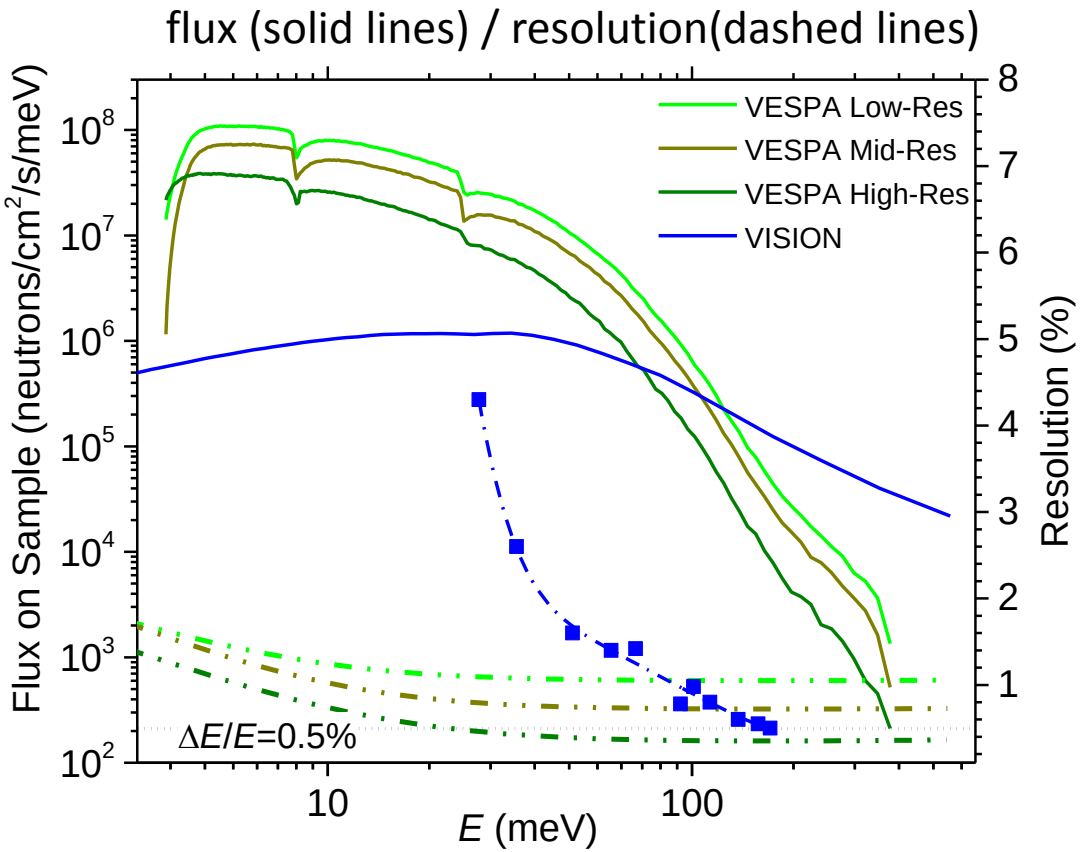
- Hydrogen bonding network greatly affected by addition of 2.5% glycerol!
- Bioprotectant system (cryo/lyo – stem cells), not present in mammals.

from S. Magazù *et al., J. Phys.Chem.* **B115**,11004 (2011).

7. VESPA: high intensity



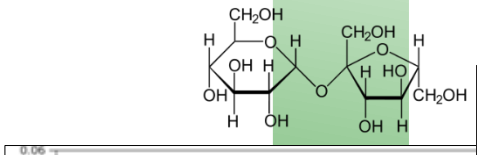
Perfectly suited for the *ESS* long pulse…
making new spectroscopy (*i.e.* high pressure, catalysis, hydrogen storage etc.) possible with neutrons!



2000:
6 mmol. 'H'

⇩

2015:
0.08 mmol 'H'



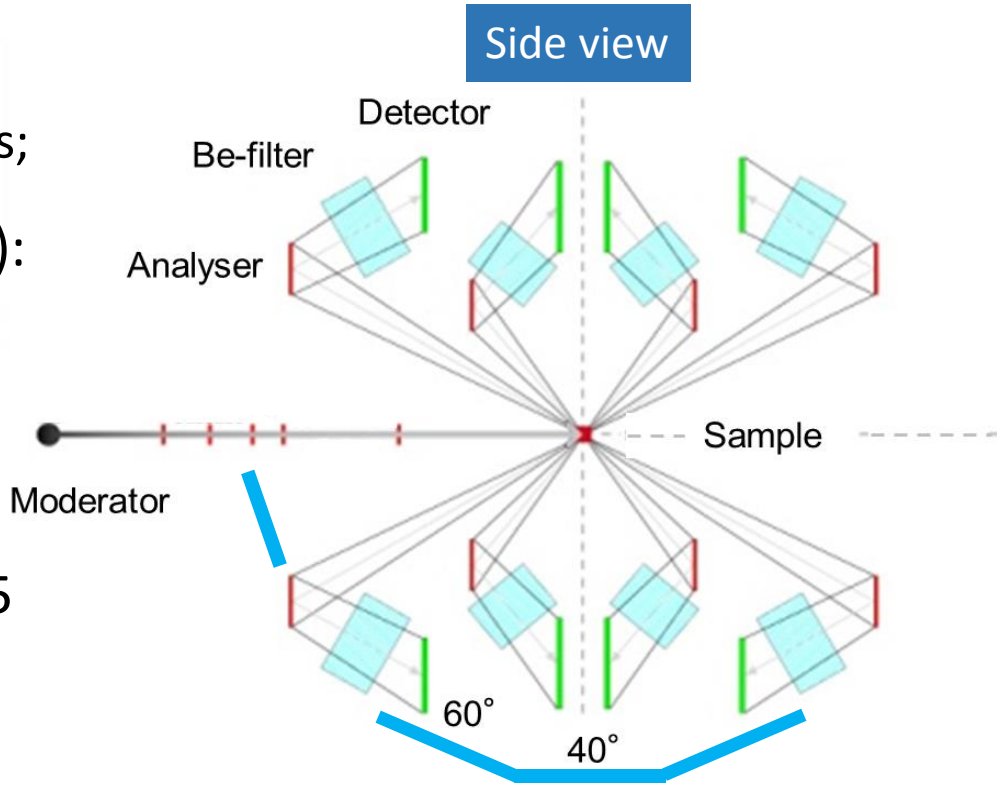
2020:
VESPA
0.01 mmol 'H' (?)

Perfectly suited for the ***ESS*** long pulse…
making new spectroscopy (*i.e.* high pressure, catalysis, hydrogen storage etc.) possible with neutrons!

8. VESPA: secondary spectrometer

- **4 arms:**
  - 2 in backsc. (130°, 150°)
  - 2 in forwardsc. (30°, 50°)

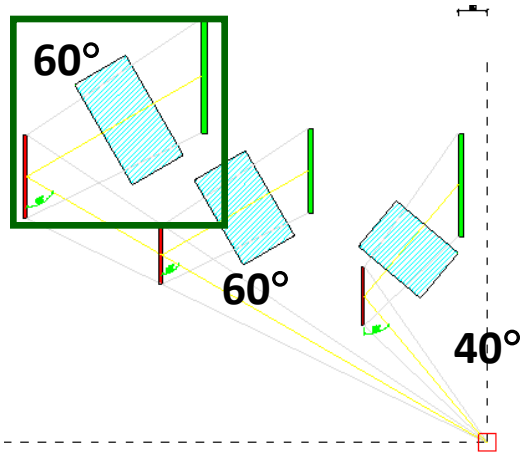
  } 30 modules;
- **4 final energies** (selected by HOPG):
  - 2.4 meV (60° Bragg angle);
  - 4.4 meV (40° Bragg angle).
- **Cold Be filters** still usable (E_{cut}=5.2 meV).
- **Squashed ^{3}He tubes** (200×12.5×2.5 mm^3, 20 bar): 20 in each module.
- **4 diffraction banks** (NPD, PDF):
  - 3 mid resolution;
  - 1 high resolution.

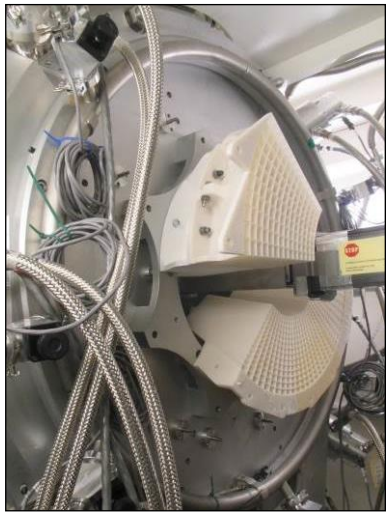


	Backscattering bank	Equatorial banks
2θ (deg.)	152-174	75-105
Q **(Å^{-1})**	31.37-2.77	24.92-1.74
d **(Å)**	0.2-2.3	0.25-3.6

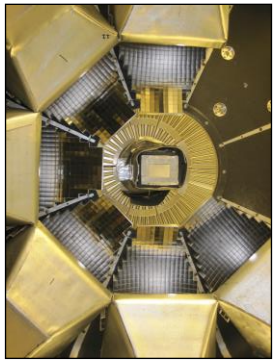
Secondary spectrometer details

- 2×2 sets of HPOG analysers (40° & 60°) in forward- and backscattering: Ω= 1.20 sr;
- 3rd proposed set of Cu (?) analysers (≈ 60°) for upgrade at a later point: Ω = 1.52 sr (28% more coverage).



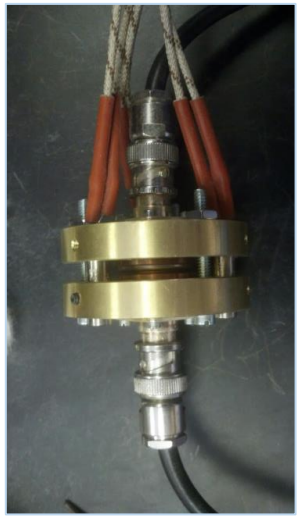


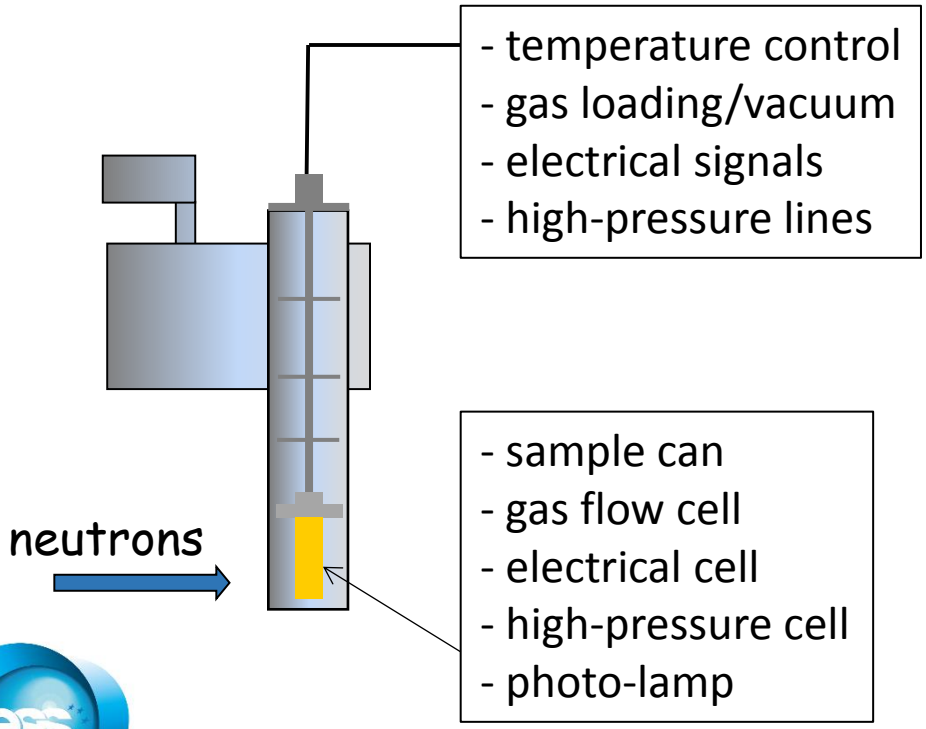
Secondary spectrometer details from *VISION* (SNS, USA).



9. VESPA: sample environment

- Sample size: 30x30 mm^2 or less;
- closed-cycle refrigerator (*in-situ* temperature studies etc.);
- sample changer (high-throughput).

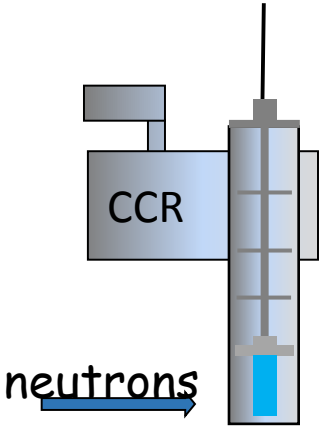




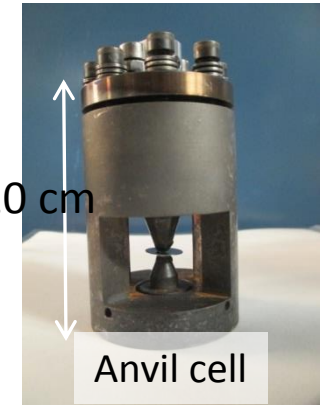
Data modeling

- ***ESS*** Data Management & Software Center (DMSC);
- DTU Copenhagen (DFT calculations – GPAW);
- other possible collaborations…

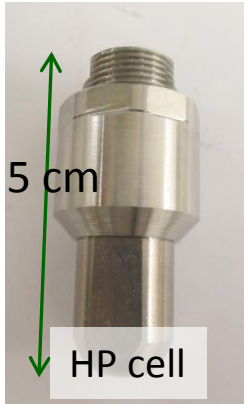
- **Sample sticks and cells:** *in-situ* measurements, high pressure cells, flow cells, gas manifold, photo-lamp/ battery cell;
- **low-temperature sample changer;**
- **hardware/software interface.**



- sample can;
- gas flow cell;
- electrical cell;
- high-pressure cell;
- photo-lamp.



Anvil cell



HP cell

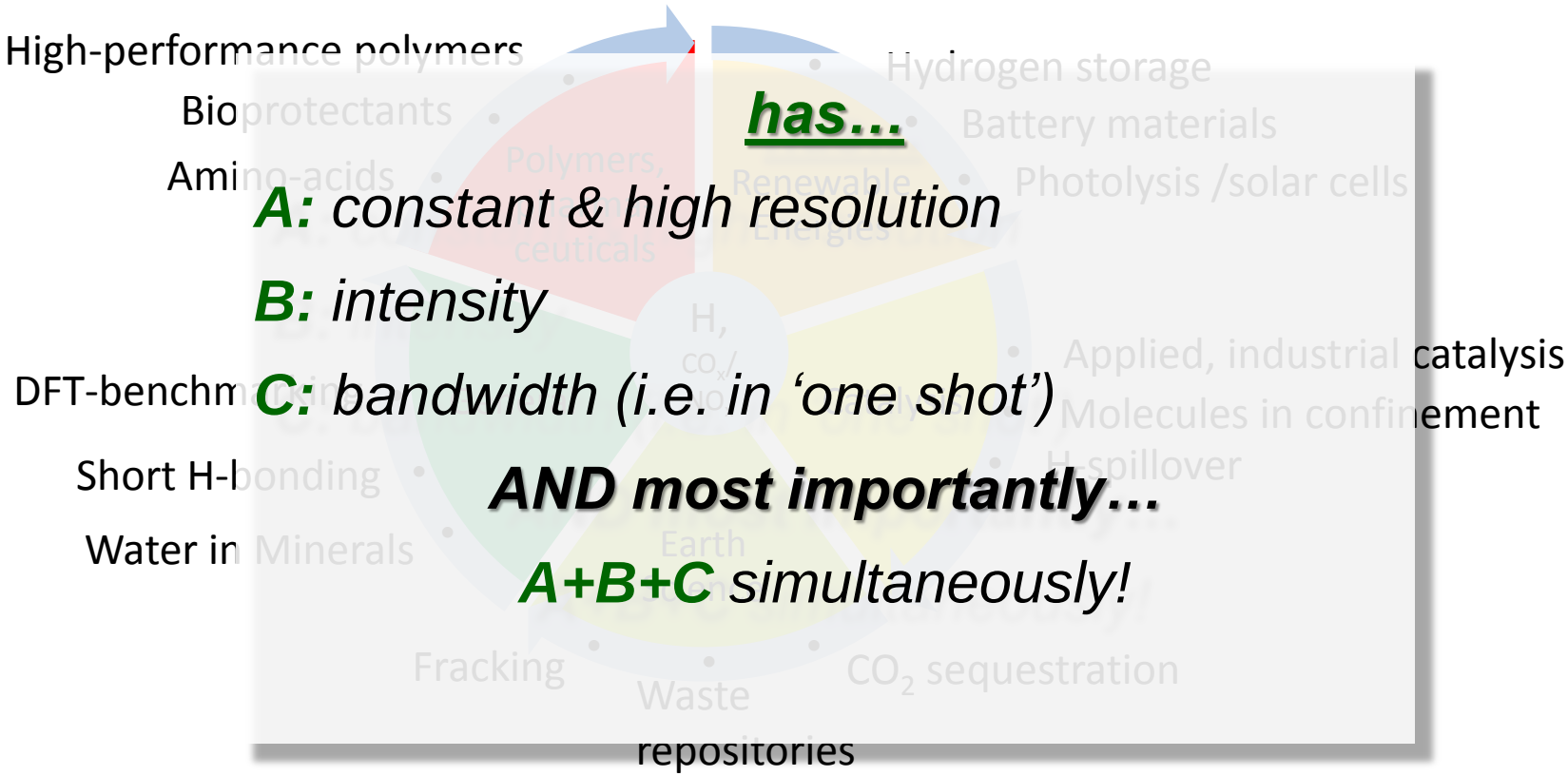

Flow cell


Battery cell


Sample stick and auxiliary equipment in hutch


Gas manifold

10.*VESPA...*


High-performance polymers
Bioprotectants
Amino-acids
DFT-benchm
Short H-bonding
Water in Minerals
Hydrogen storage
Battery materials
Photolysis /solar cells
Applied, industrial catalysis
Molecules in confinement
H-spillover
Fracking
CO_2 sequestration
Waste
repositories
has…
A: *constant & high resolution*
B: *intensity*
C: *bandwidth (i.e. in 'one shot')*
AND most importantly…
A+B+C *simultaneously!*

VESPA: a strong support from

Prof. J. Nielsen,
Prof. C. Damsgaard
Dr. P. Willendrup
DTU

Prof. B. Hudson
SYRACUSE UNIVERSITY

Prof. A. Horsewill
The University of Nottingham
UNITED KINGDOM · CHINA · MALAYSIA

Prof. P.A. Georgiev
TU - Sofia

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University of Salford MANCHESTER

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Prof. J. Larese
THE UNIVERSITY of TENNESSEE KNOXVILLE

Dr. L. Daemen
OAK RIDGE National Laboratory

Dr. D. Lennon
UNIVERSITY of GLASGOW

… and still growing!

Prof. A. Albinati
UNIVERSITÀ DEGLI STUDI DI MILANO

This talk is dedicated to the dear memory of **Dr. Marco Zoppi** (1946-2015).

VESPA (formerly called ***VSI***) is an instrumental proposal for ***ESS*** originally conceived by Marco in 2012. He passed away unexpectedly in June this year.

Many thanks to the audience members for their kind attention to the presentation of ***VESPA…***


1943
1947
1953
1976
1978
1985
1996
2010
2013
2020