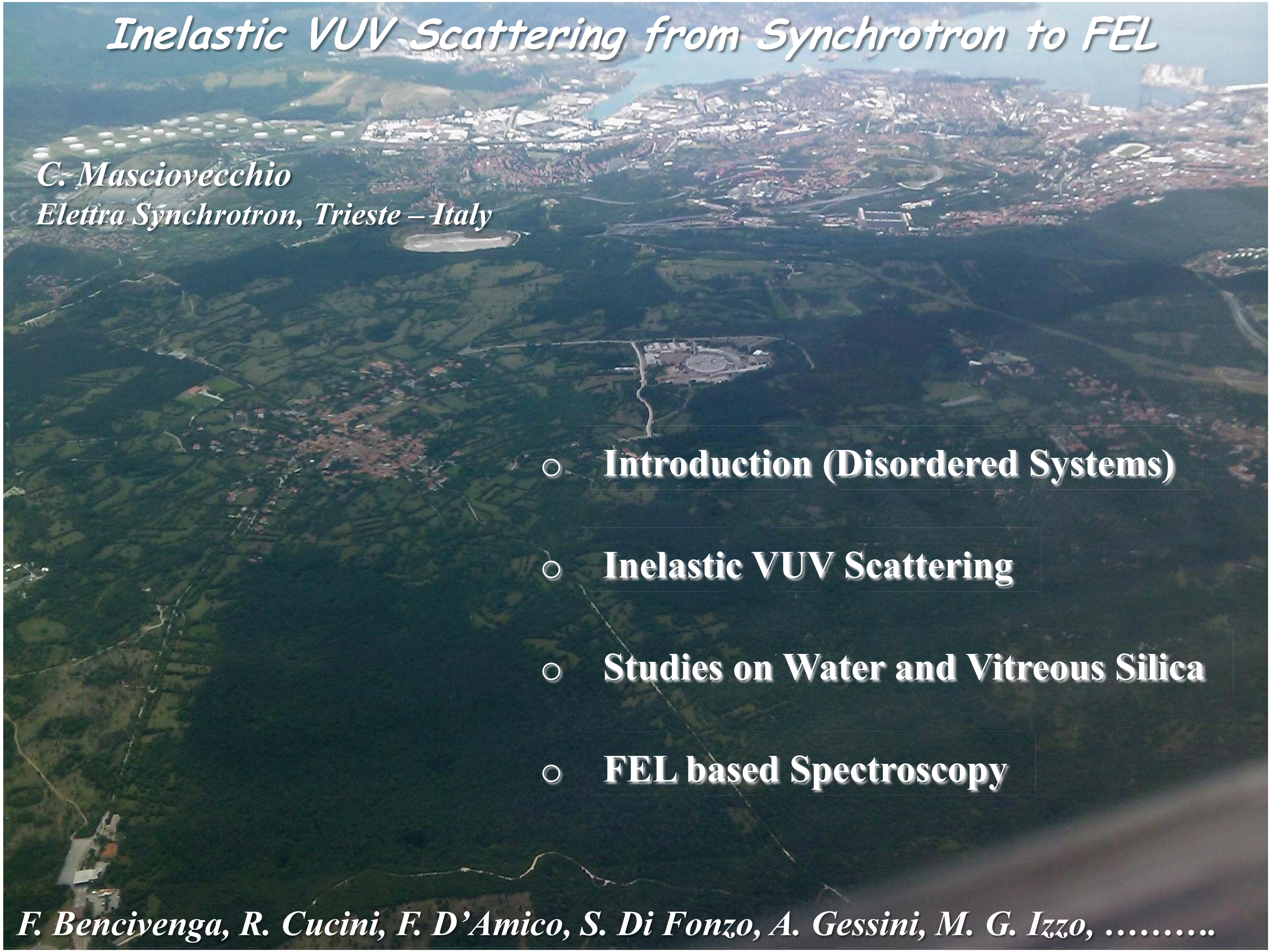
2139-28

School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

26 April - 7 May, 2010

Inelastic VUV Scattering from Synchrotron to FEL

C. Masciovecchio
Elettra Synchrotron
Tireste
Italy



Inelastic VUV Scattering from Synchrotron to FEL

C. Masciovecchio
Elettra Synchrotron, Trieste – Italy

○ **Introduction (Disordered Systems)**

○ **Inelastic VUV Scattering**

○ **Studies on Water and Vitreous Silica**

○ **FEL based Spectroscopy**

F. Bencivenga, R. Cucini, F. D'Amico, S. Di Fonzo, A. Gessini, M. G. Izzo, ……….

Why Disordered Systems ?

UNSOLVED PROBLEMS IN PHYSICS

WIKIPEDIA
The Free Encyclopedia

Condensed matter physics

Amorphous solids

What is the nature of the transition between a fluid or regular solid and a glassy phase? What are the physical processes giving rise to the general properties of glasses?

High-temperature superconductors

What is the responsible mechanism that causes certain materials to exhibit superconductivity at temperatures much higher than around 50 Kelvin?

Sonoluminescence

What causes the emission of short bursts of light from imploding bubbles in a liquid when excited by sound?

Turbulence

Is it possible to make a theoretical model to describe the statistics of a turbulent flow (in particular, its internal structures)? Also, under what conditions do smooth solution to the Navier-Stokes equations exist?

Glass is a **very general state** of condensed matter → a large variety of systems can be transformed from liquid to glass

The liquid-glass transition cannot be described in the framework of classical phase transitions since T_g depends on the **quenching rate** → one cannot define an **order parameter** showing a critical behaviour at T_g

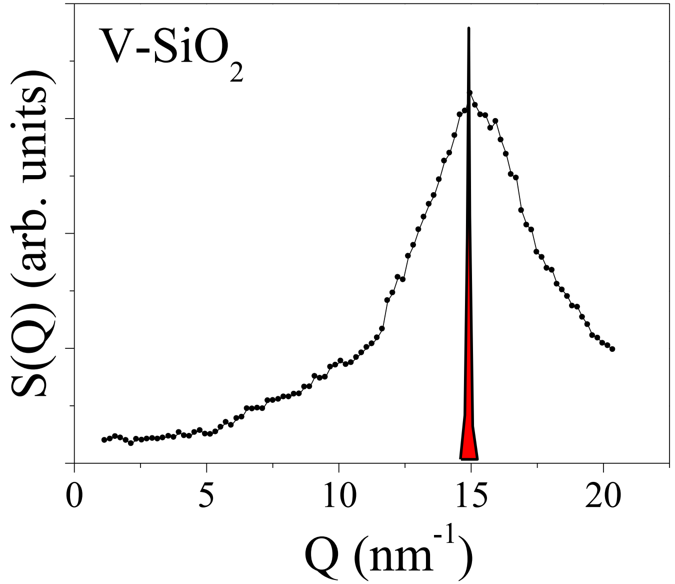
Density Fluctuation Measurements

The study of Atomic and Molecular **Density Fluctuations** (Vibrational Spectrum, Sound Modes, etc.) is of great importance to understand many physical properties of gases, liquids and solids

Crystals: Heat Capacity, Thermal Conductivity, Superconductivity

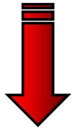
In **Disordered Systems** the lack of translational invariance has delayed experimental studies in the **Mesoscopic** region

The presence of **Diffusional** and **Relaxational** processes strongly affects the collective dynamics making experiments even more difficult



$$n(\mathbf{r}) \xrightarrow{\text{FT}} S(\mathbf{Q})$$

Topological **Disorder**



Ill definition of Brillouin Zones

The Dynamic Structure Factor S(Q,ω)

The dynamical properties associated to density fluctuations can be studied by means of scattering experiments which allow the determination of the **Dynamic Structure Factor** (Density Fluctuation Spectrum)

$$S(\mathbf{Q},\omega) = \int_{-\infty}^{\infty} dt \int d\mathbf{r} \langle (n(\mathbf{r},t) - n)(n(0,0) - n) \rangle e^{i(\omega t - \mathbf{Q}\cdot\mathbf{r})}$$

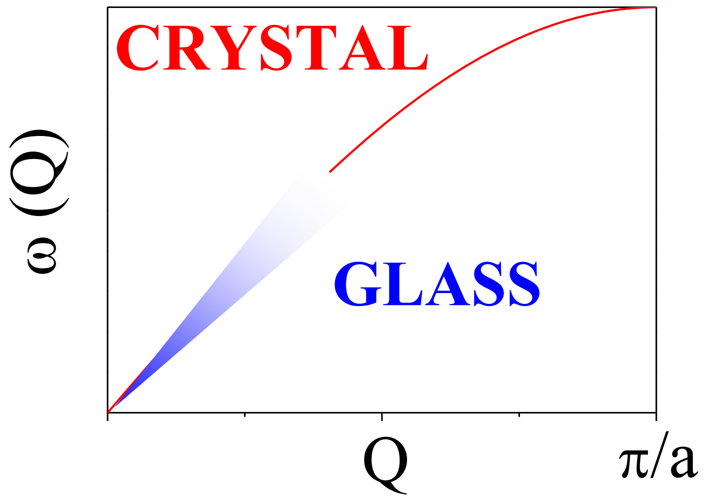
$n(\mathbf{r},t)$ Particle Density Operator

$\langle (n(\mathbf{r},t)) \rangle$ Thermodynamical average of the Density

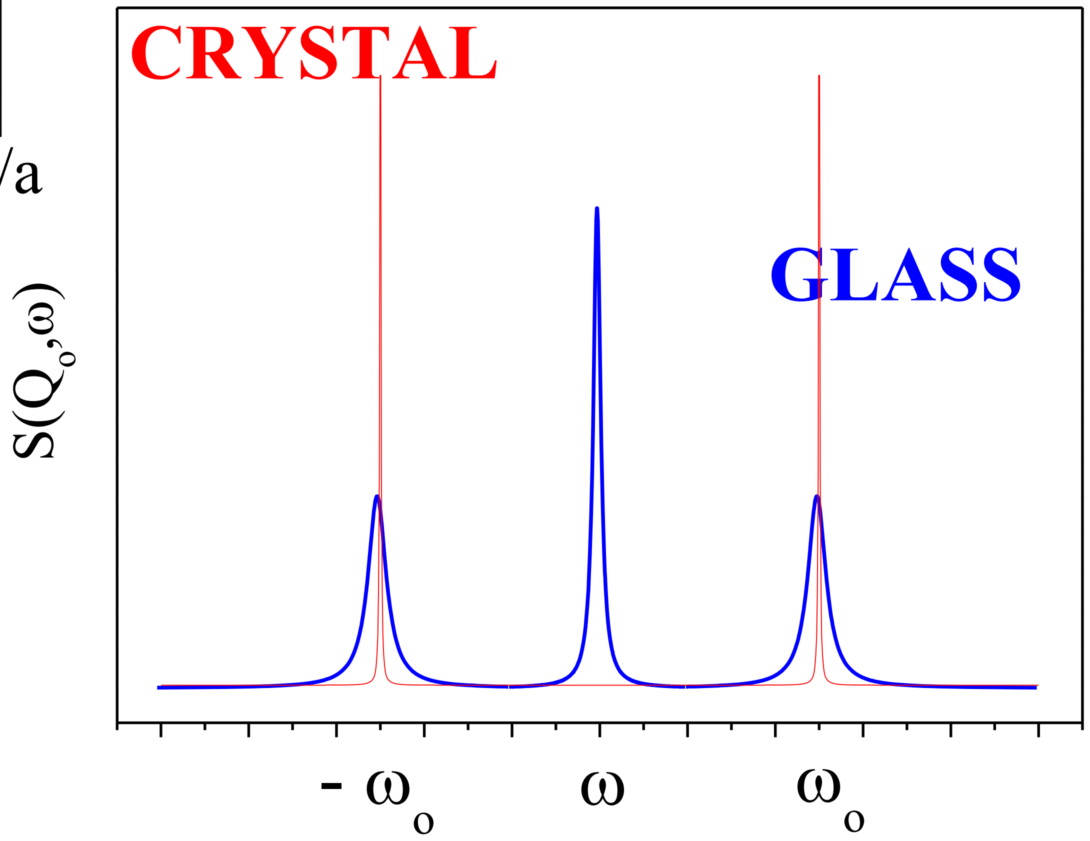
In Crystals one can measure S(**Q**,ω) in any **Brillouin Zone** (no kinematic limitations)

This is not the case for disordered systems were the **ill definition** of **BZ** makes impossible detecting phonon-like excitations out from the first **pseudo** **BZ**

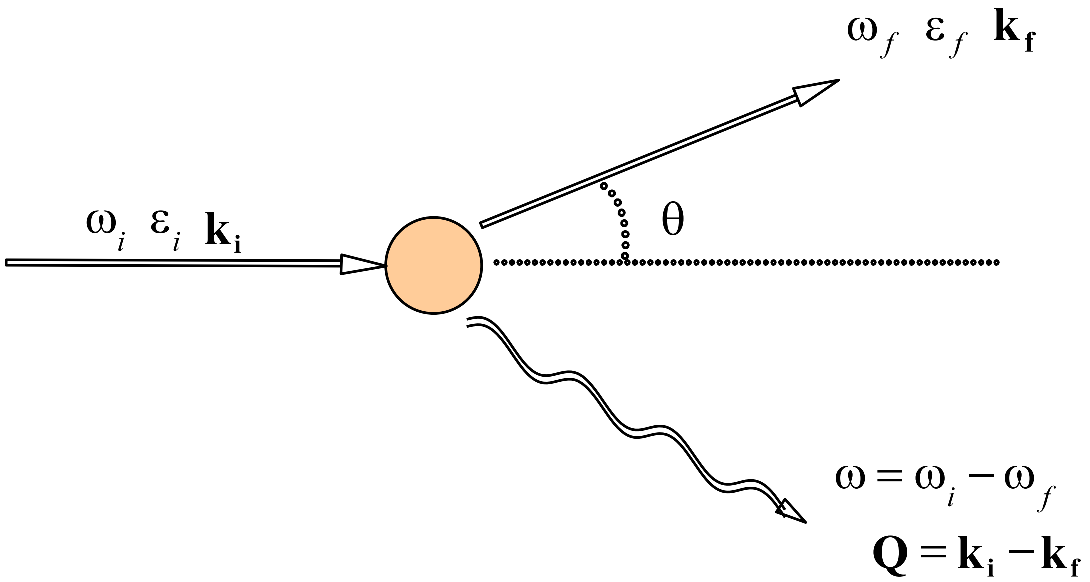
S(Q,ω) Crystal vs Glass



Dispersion Relation for an
Acoustic Vibrational Mode



Inelastic Scattering to measure S(Q,ω)



$$I_{if}(\mathbf{Q},\omega) \propto \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \delta\alpha_{if}(\mathbf{Q},0)\delta\alpha_{if}(\mathbf{Q},t) \rangle$$

Visible → UV

$$I_{VV}(\mathbf{Q},\omega) \propto \boxed{S(\mathbf{Q},\omega)}$$

Density Fluctuation Spectrum

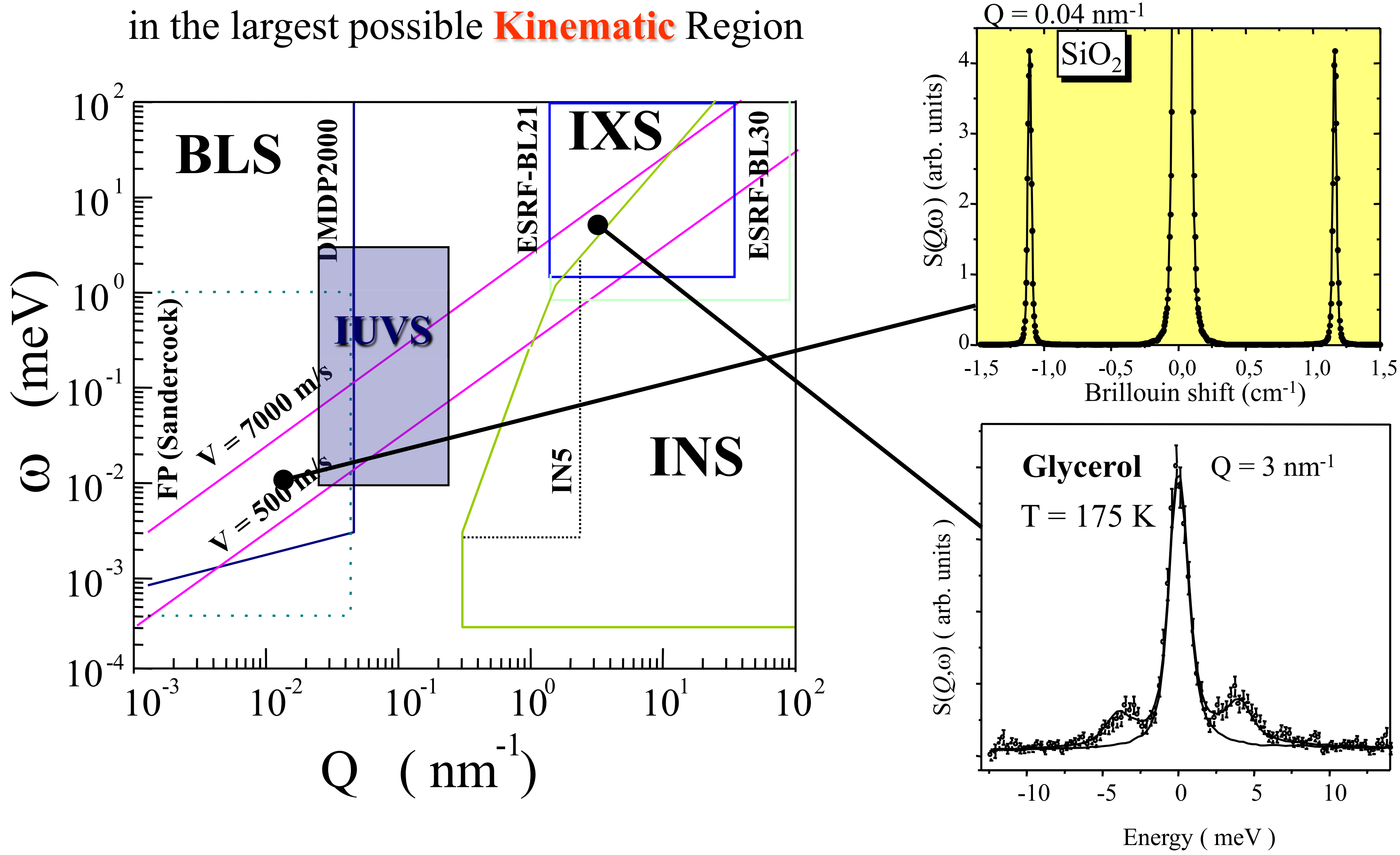
$$I_{if}(\mathbf{Q},\omega) \propto \frac{\omega_f}{\omega_i} (\varepsilon_o \times \varepsilon_1) |f(Q)|^2 \boxed{S(\mathbf{Q},\omega)}$$

X

Available probes to measure the S(Q,ω)

Interest in measuring **S(Q,ω)** in Disordered Systems

in the largest possible **Kinematic** Region



Investigations at the nanoscale

Liquids - Fluids

- **Transition from the Hydrodynamic to the Kinetic regime in Simple liquids and fluids.**
- **Effect of the Local Structure on the Collective Dynamics in Molecular liquids and H-bonded liquids.**
- **Water-mixtures (peptides, ionic liquids, etc.,..) to study i.e. effect of H-bonds in protein functionality.**

Glasses

- **Nature of the Vibrational Modes in the Mesoscopic space-time region.**
- **Relaxation Processes in Super-Cooled liquids and their relation to the Glass Transition.**
- **Vibrational and Relaxational Low Temperature Properties of Fragile and Strong glasses.**

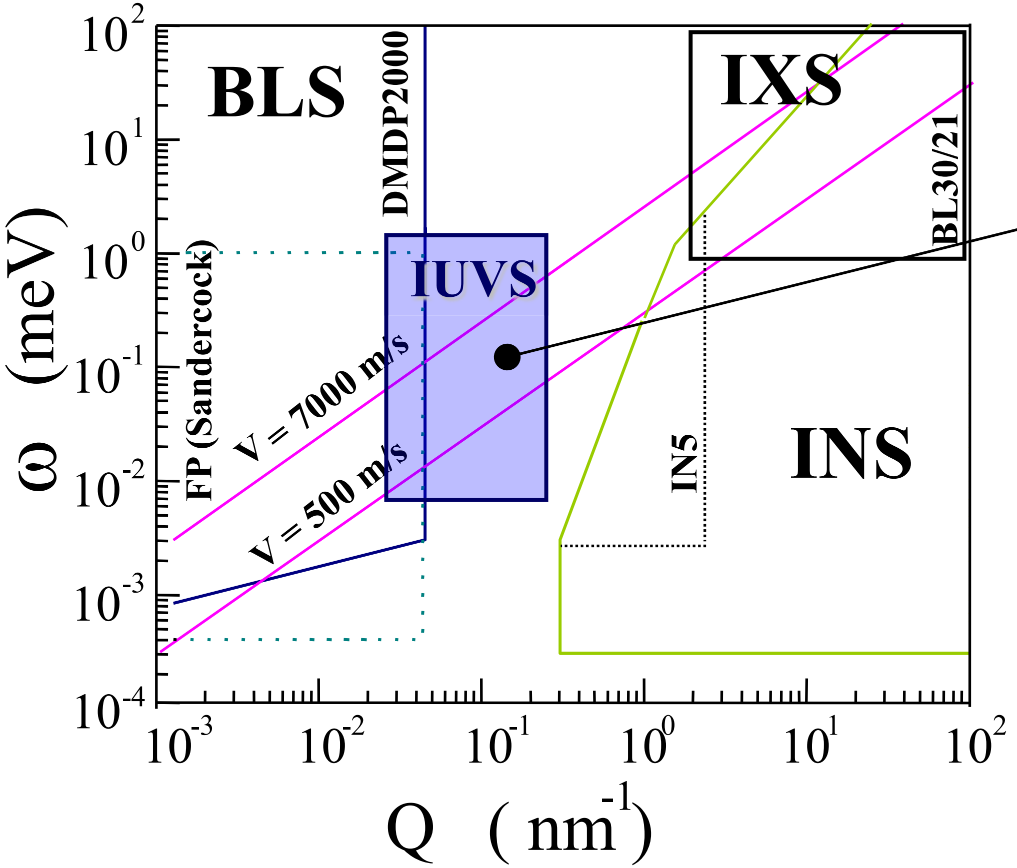
Resonant Scattering (Tunability)

- **Low count-rate experiments.**
- **Determination of Partial Dynamic Structure Factor in gas and fluid mixtures.**
- **Resonant Raman on Nanostructures.**

Inelastic VUV Scattering

- Incident **Energy** in the 5 – 11(30) *eV* range (λ ≈ **240 – 110(40)*nm***)
- High incident photon **Flux** on the Sample (> 10^{12} *photon/s*)
- High **Resolving Power** (≈ $10^5 - 10^6$)

→ ~1 *count/s*



ω ≈ 10 - 10^3 *μeV*

Q ≈ 0.02 - 0.3 *nm*$^{-1}$

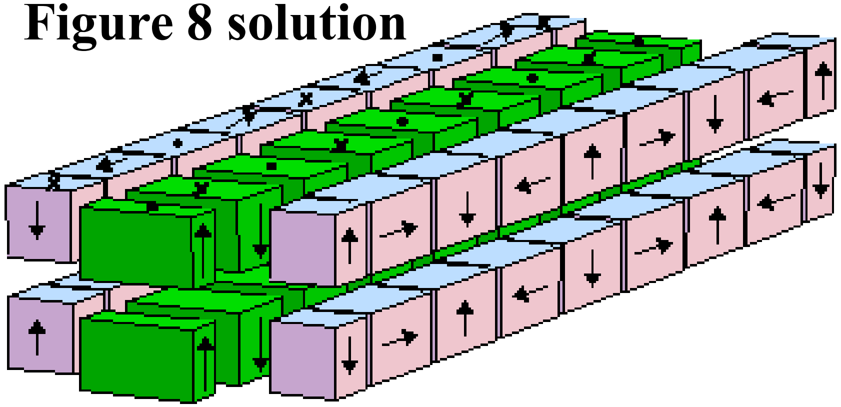
Linear Undulator ?

4.5 *m* length, **125** *mm* period, **400** *mA*

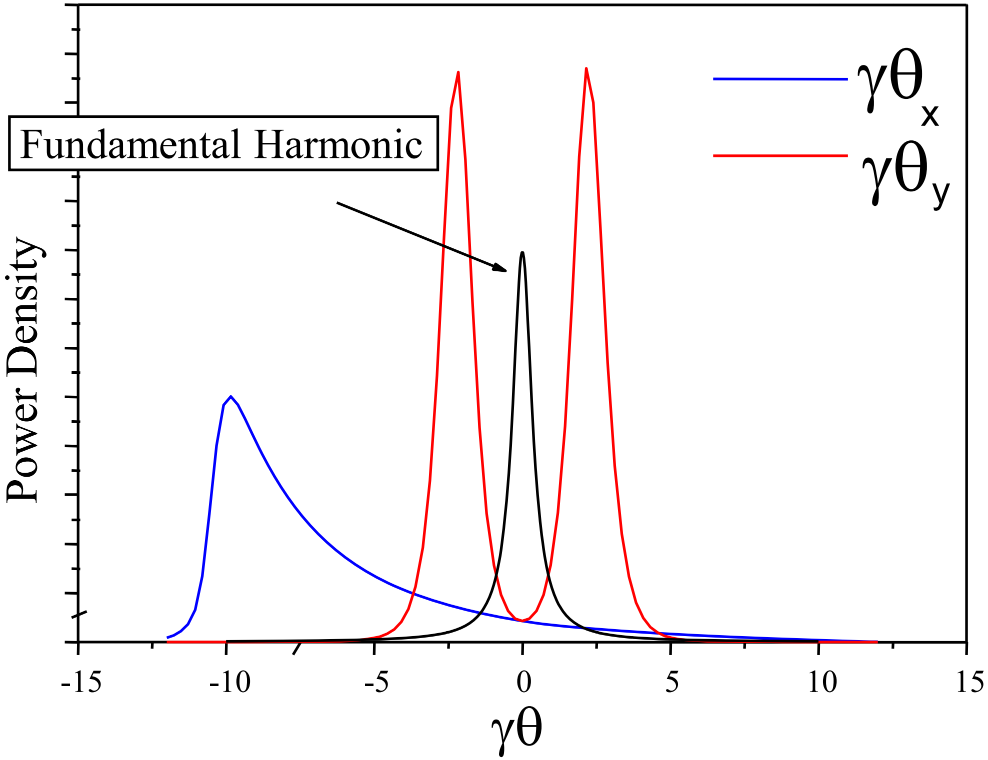
$2 \bullet 10^{15}$ *photons/s/0.1% bandwidth*

1.5 *kW* on the first mirror

Figure 8 solution



$N_p = 32$
$\lambda = 140\ mm$
$K_x = 3.4$
$K_y = 9.4$

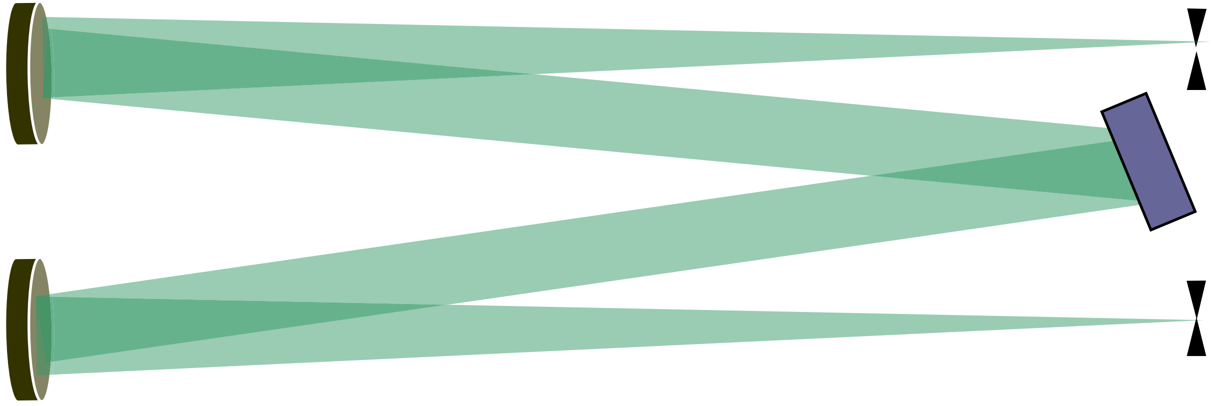


22 W on first mirror !!

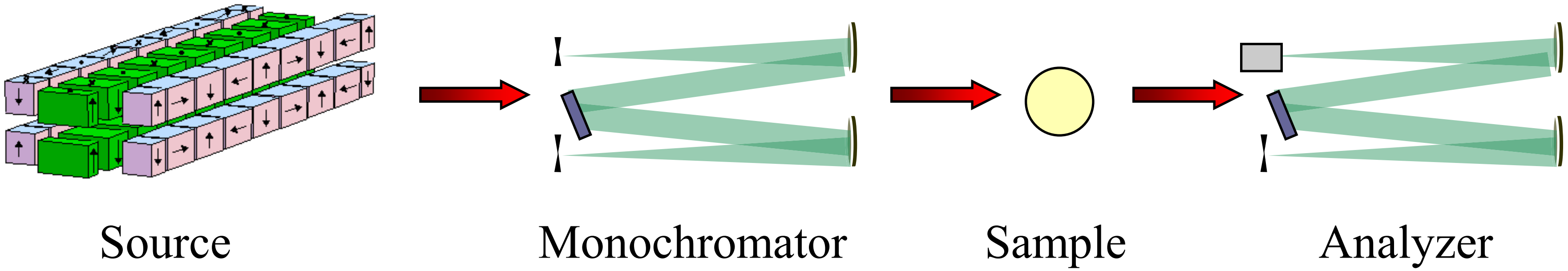
$2 \cdot 10^{15}$ *photons/s/0.1% BW* ($2 \cdot 10^{12}$ *photons/s*)

The NIM Monochromator

Normal Incidence Monochromator (**Czerny-Turner** design)



$$\frac{\Delta E}{E} = \frac{\delta\, ctg\theta}{2F} = \frac{50\mu m\; ctg(70^{\circ})}{16m} \approx 1\,10^{-6}$$



The Beamline

Scanning Resolution: 80 *nrad*

Autocollimator Control: 50 *nrad*

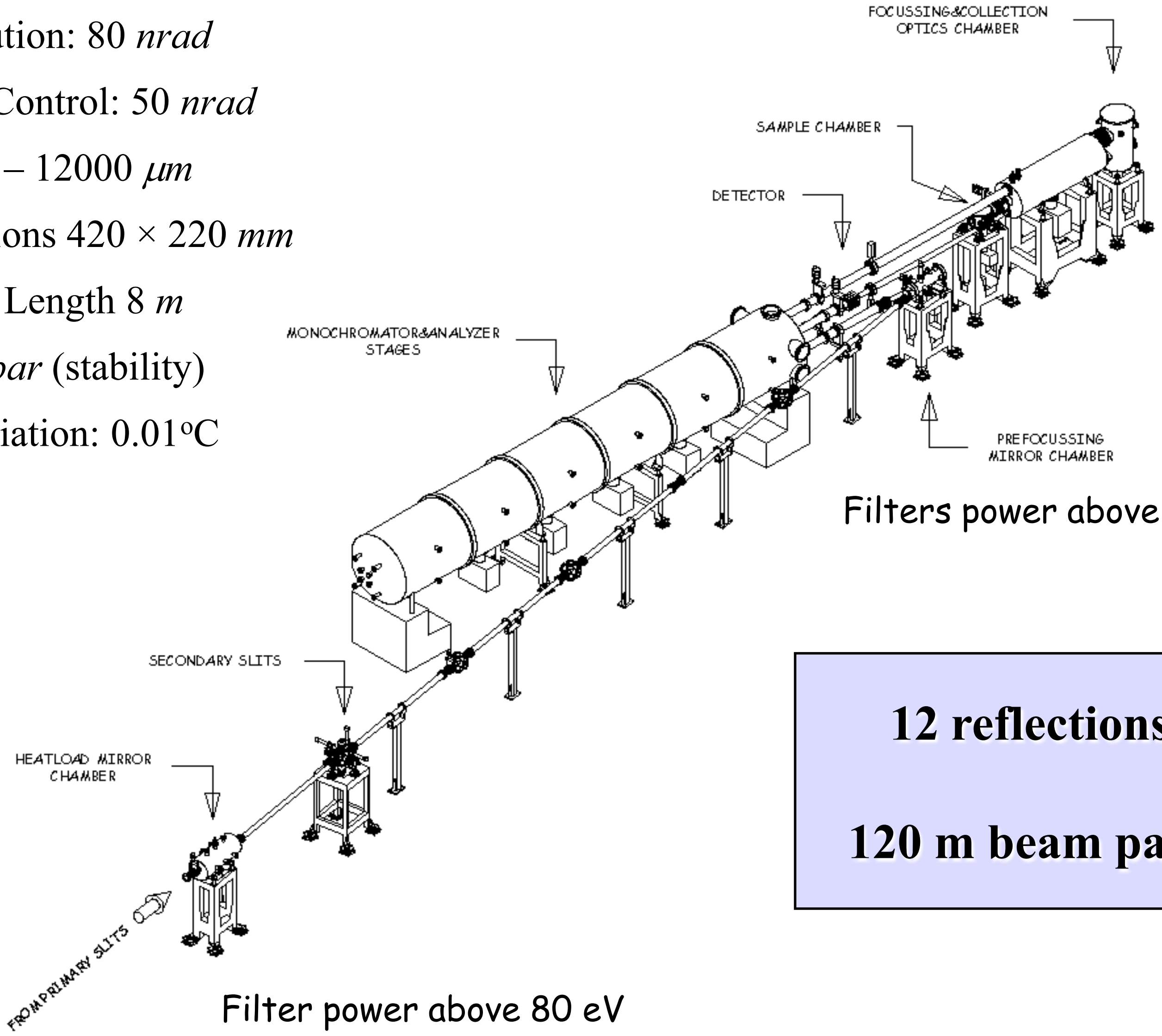
Slits Opening: 5 – 12000 μm

Grating Dimensions 420 × 220 *mm*

Monochromator Length 8 *m*

Vacuum: 10^{-8} *mbar* (stability)

Temperature Variation: 0.01^{o}C



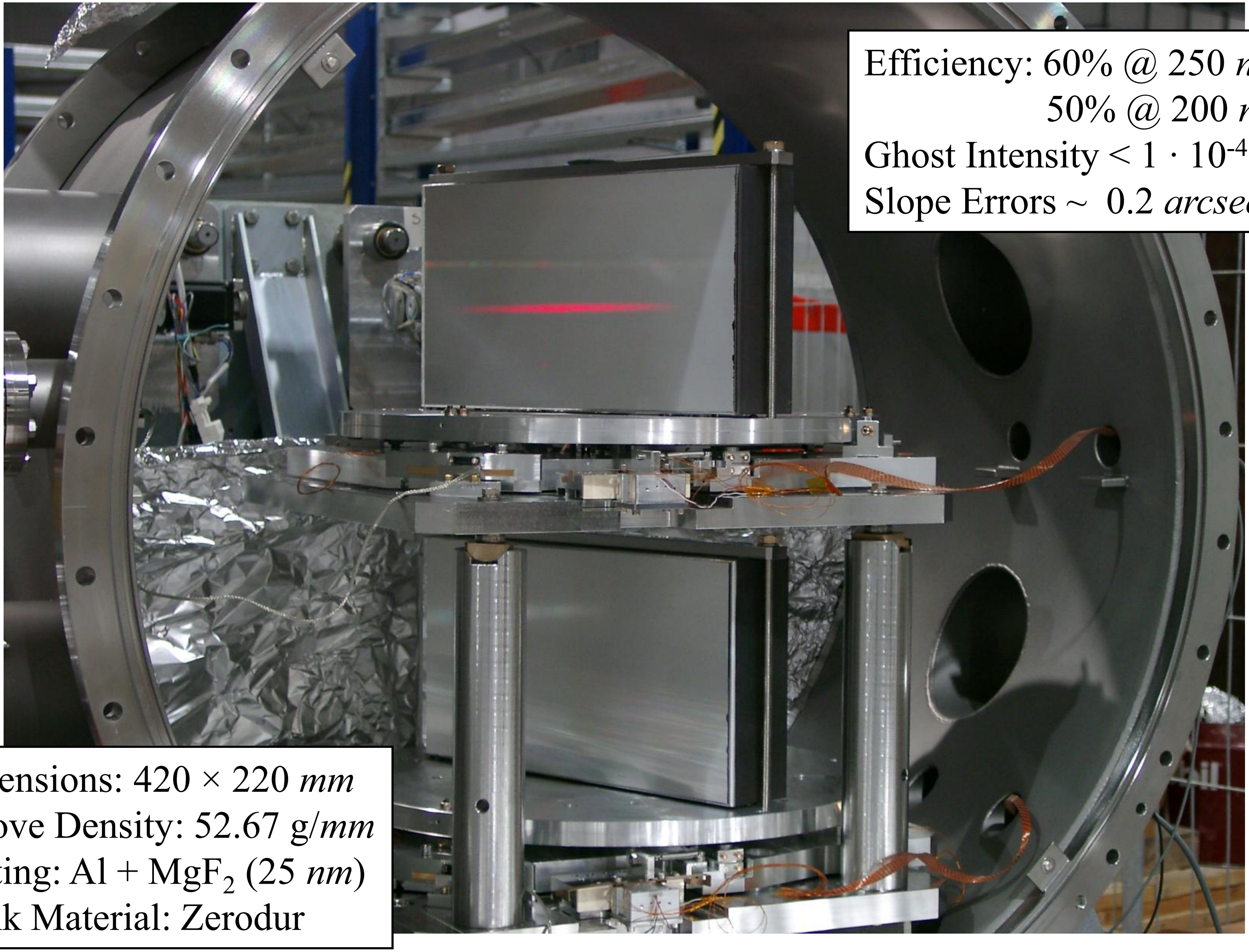
Filters power above 15 eV

Filter power above 80 eV

12 reflections

120 m beam path

The Gratings



Efficiency: 60% @ 250 *nm*

50% @ 200 *nm*

Ghost Intensity < $1 \cdot 10^{-4}$ PL

Slope Errors ~ 0.2 *arcsec*

Dimensions: 420 × 220 *mm*

Groove Density: 52.67 g/*mm*

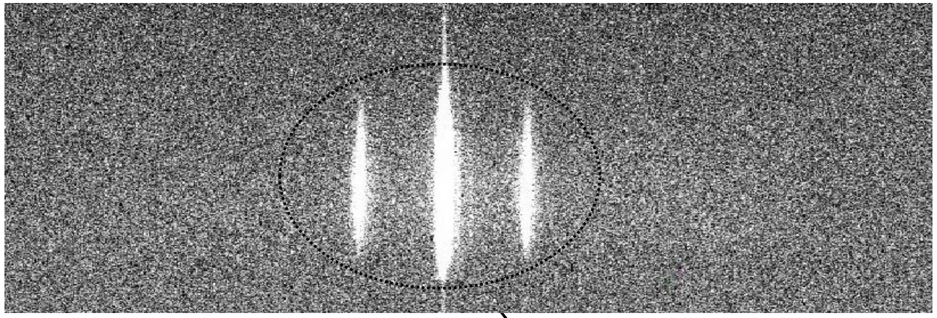
Coating: Al + MgF_2 (25 *nm*)

Blank Material: Zerodur

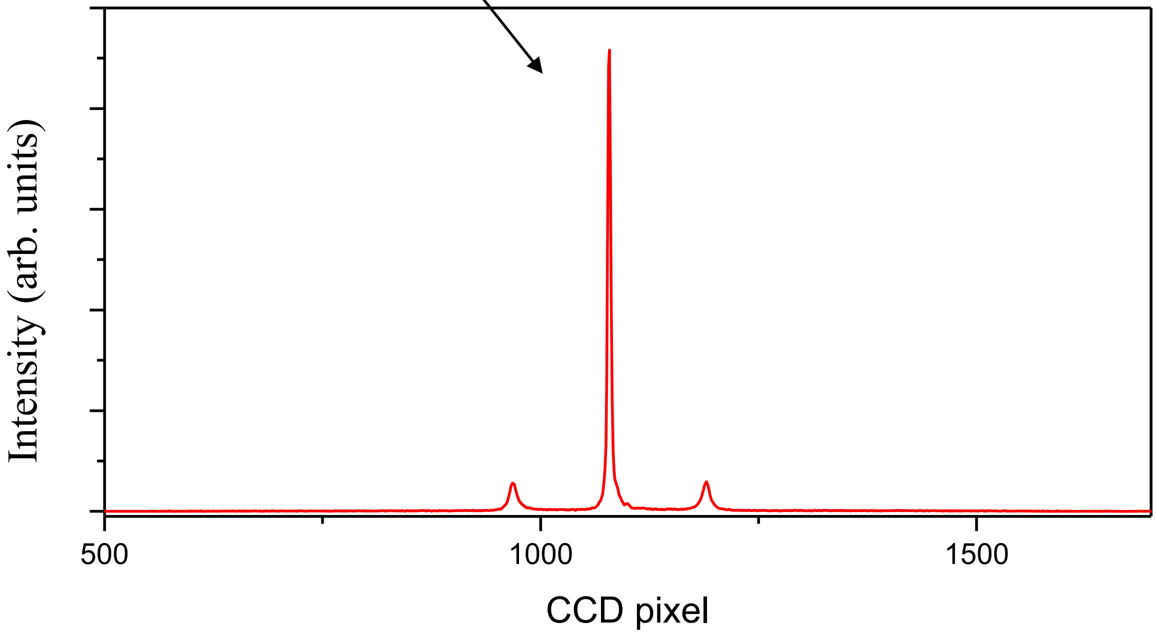
The Monochromator/Analyzer

The Spectrum

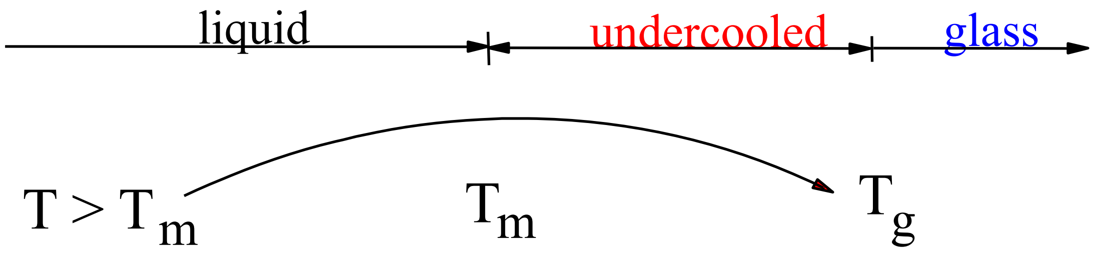
Image on CCD detector – Spectra can be collected in one single shot



Glycerol @ 260 K



Studies on Water and Vitreous Silica



Glass is a **very general state** of condensed matter

Elements (*Sulfur*, ...)
Oxides (SiO_2, ...)
Chalcogenides (As-S, ...)
Halides ($ZnCl_2$, ...)
Molten Salts ($KNO_3Ca(NO_3)_2$, ...)
Aqueous solutions (LiCl + RH_2O, ...)
Organic compounds (*Glycerol*, ...)

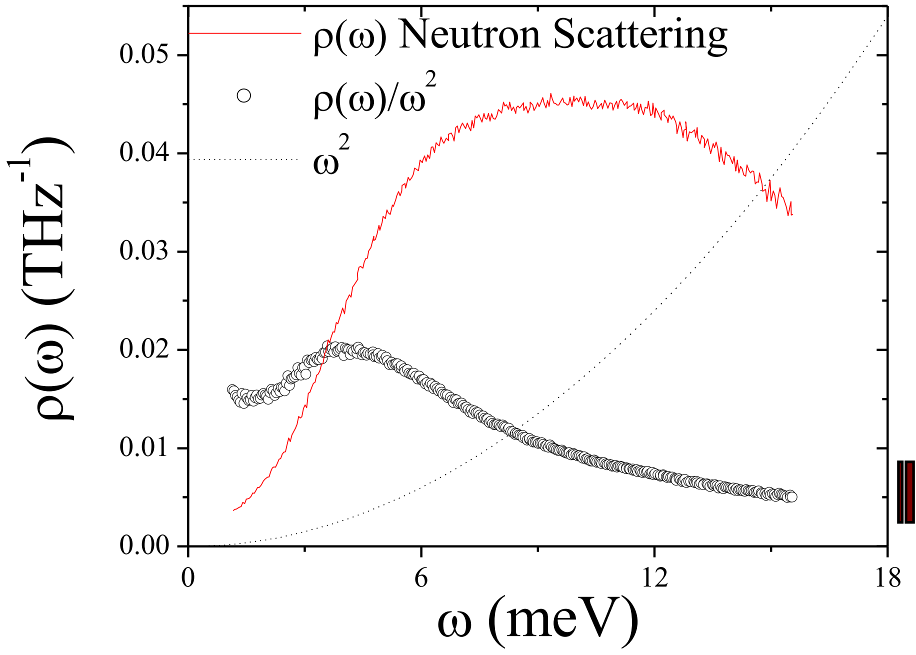
Quenching Rates
10^5 K/s *real*
10^{12} K/s *simulations*

The **viscosity** η increases by lowering T and presents one of the **largest** changes of a physical measurable quantity of a material (14 orders of magnitude)

Glass-Forming Systems

Puzzling properties

- Glass-transition mechanism
- Relaxation processes
- Thermal anomalies
- **Excess in the vibrational DOS**



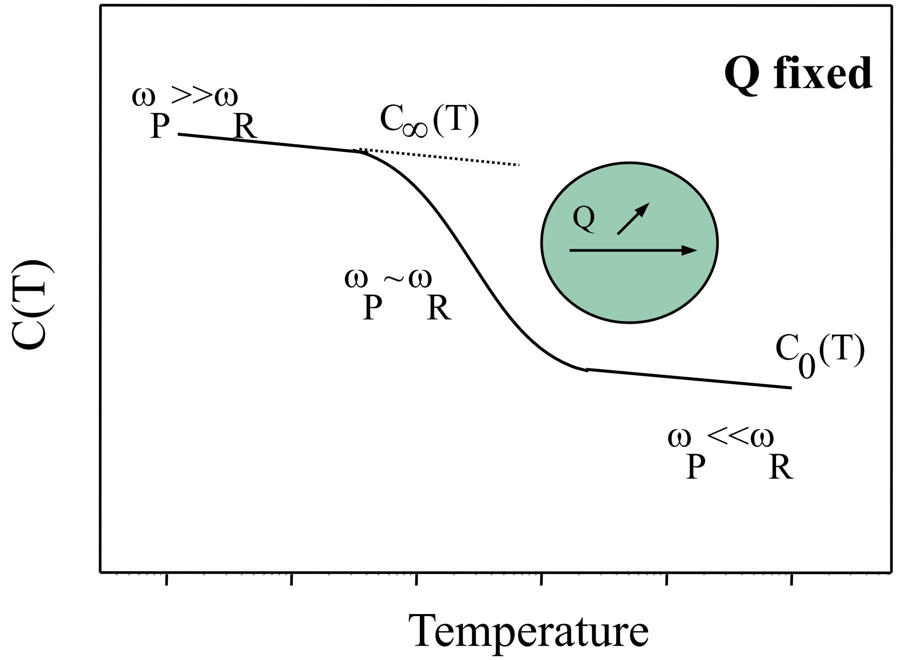
The **excess in** the vibrational density of states justifies the observed thermal anomalies (like the excess in the specific heat at low T) in glass-forming systems. Nevertheless the origin of this peak (usually called the **Boson peak**) in the V-DOS is still unclear.

The Structural Relaxation

Puzzling properties

- Glass-transition mechanism
- **Relaxation processes**
- Thermal anomalies
- Excess in the vibrational DOS

Structural Relaxation → cooperative processes by which the local structure, after being perturbed by an external disturbance or by a spontaneous fluctuation, rearranges towards a new equilibrium position

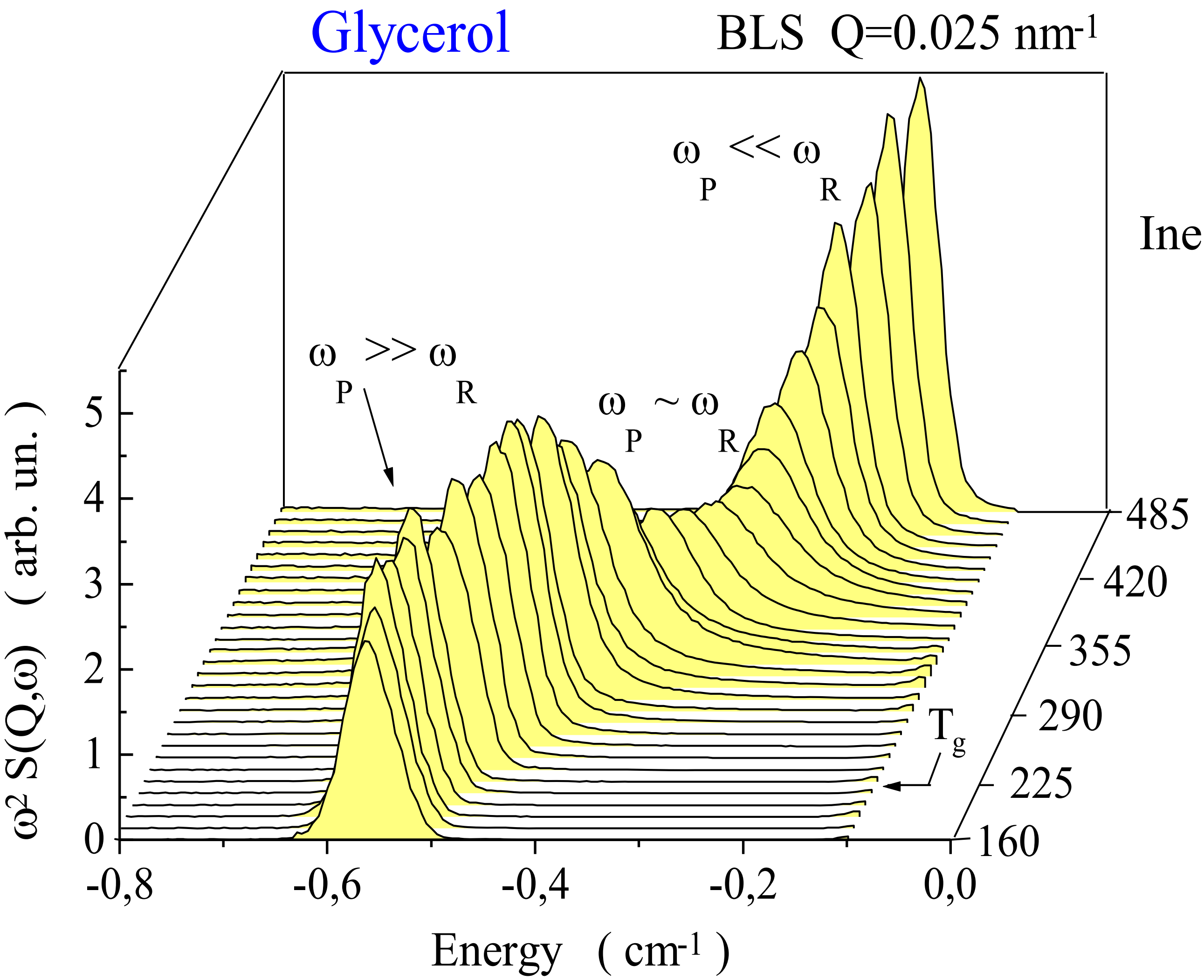


Knowledge of $C_0(T)$, $C_\infty(T)$, $\tau_R(Q)$, $C(Q,T)$

↓

Formulation of Models describing the Glass Transition

The Structural Relaxation



Inelastic peak temperature dependence

Water

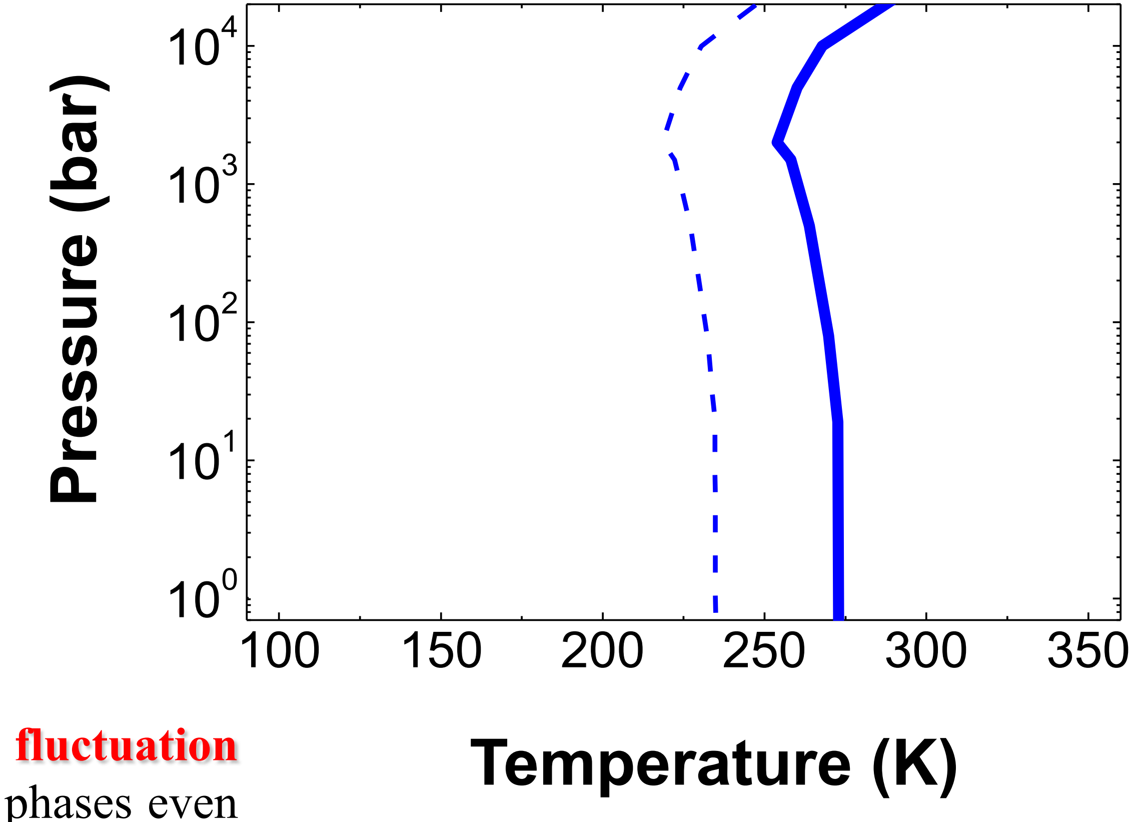
Water exhibits very **unusual** properties:

- Negative volume of melting
- Density maximum in the normal liquid range
- Isothermal compressibility minimum in the liquid
- Increasing liquid fluidity with increasing pressure

Liquid–Liquid Phase Transition

220 K – 100 MPa

P. H. Poole et al., Nature (1992)



The liquid will experience **spatial fluctuation** characteristic of the LDL and HDL phases even though the liquid has not yet **phase-separated**

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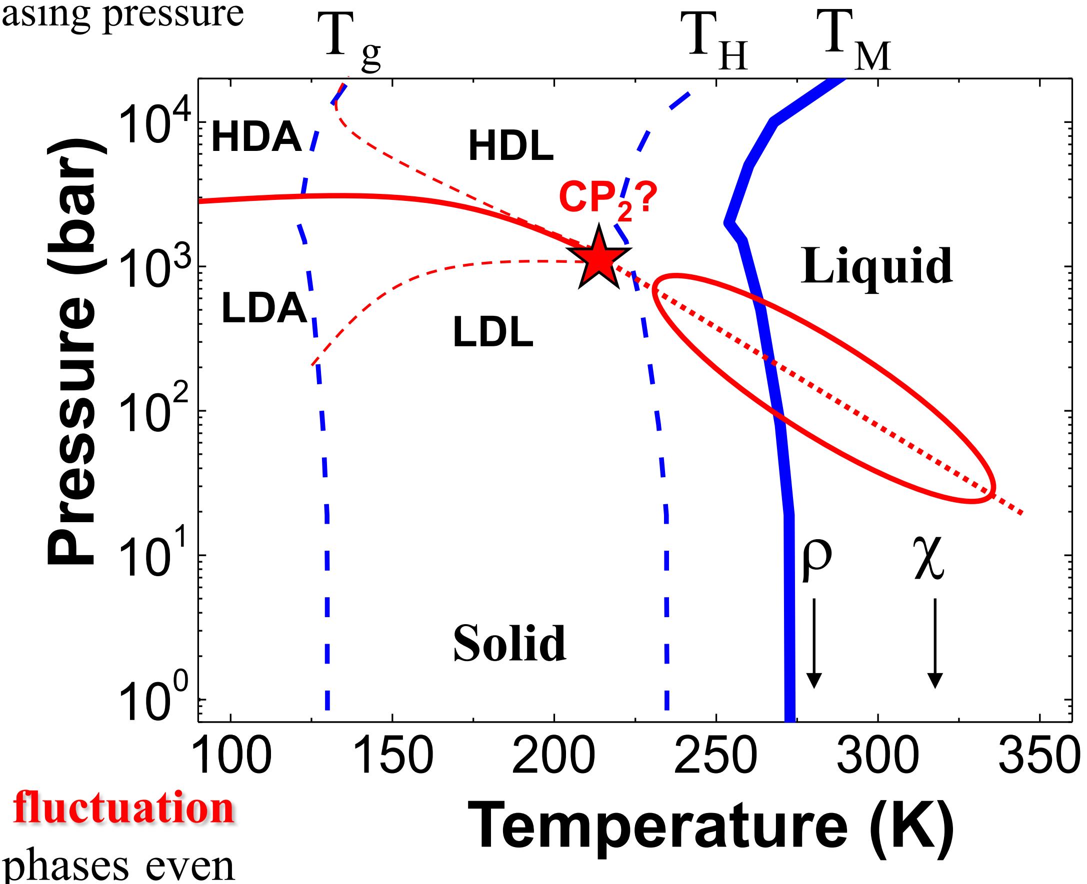

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220 K – 100 MPa

P. H. Poole et al., Nature (1992)

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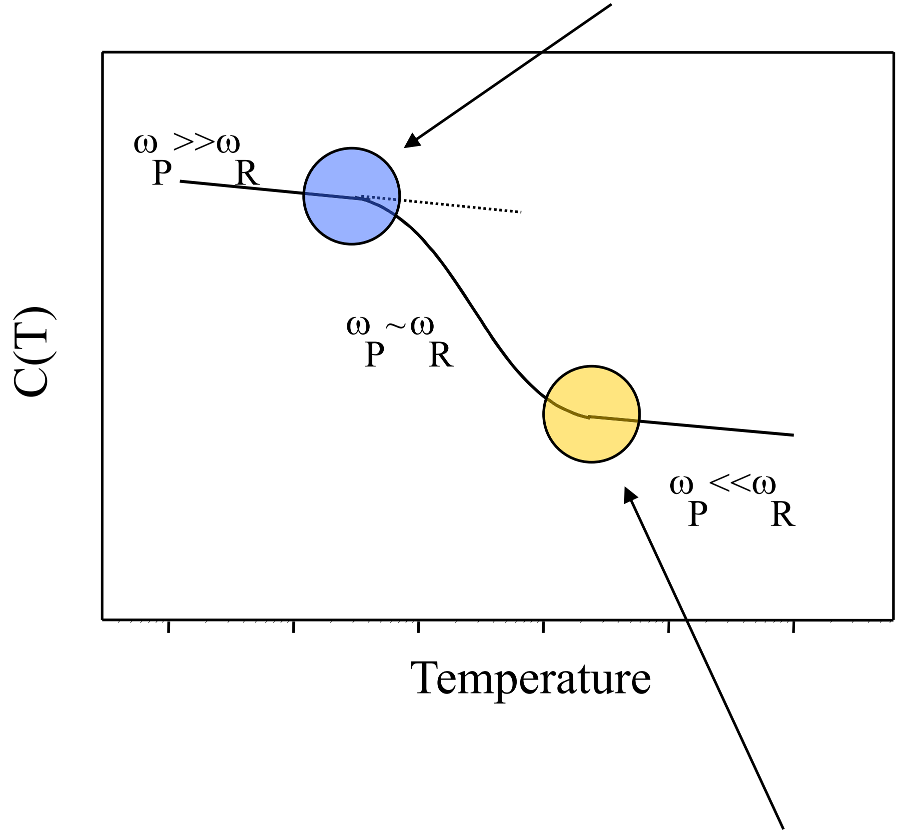
Inelastic Scattering applied to Water

high frequency investigations: **IXS** *F. Sette et al., PRL (1996)*



Best Sensitivity Condition $\omega_P \tau_R \sim 1$

For IUVS T ~ 250 K

$T_{NML} \sim 230$ K

low frequency investigations: **Ultrasonic** and **BLS** *A. Cunsolo et al., JCP (1996)*

Relaxation process in Water is strongly linked to **Hydrogen Bonds**

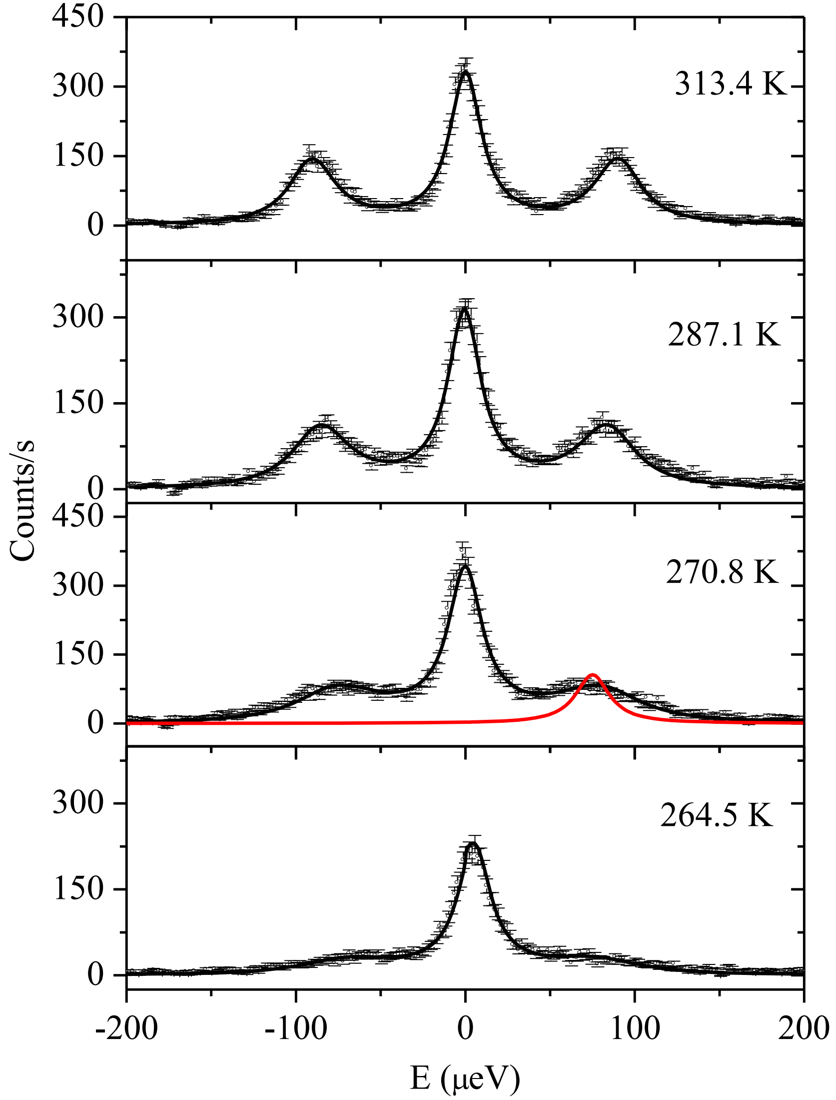
IUVS experiment

Water from liquid to undercooled state

Cell: Fused Silica Fluorescence standard Cell

Momentum Transfer: 0.1 *nm*$^{-1}$

Temperature range: 343 → 248 K



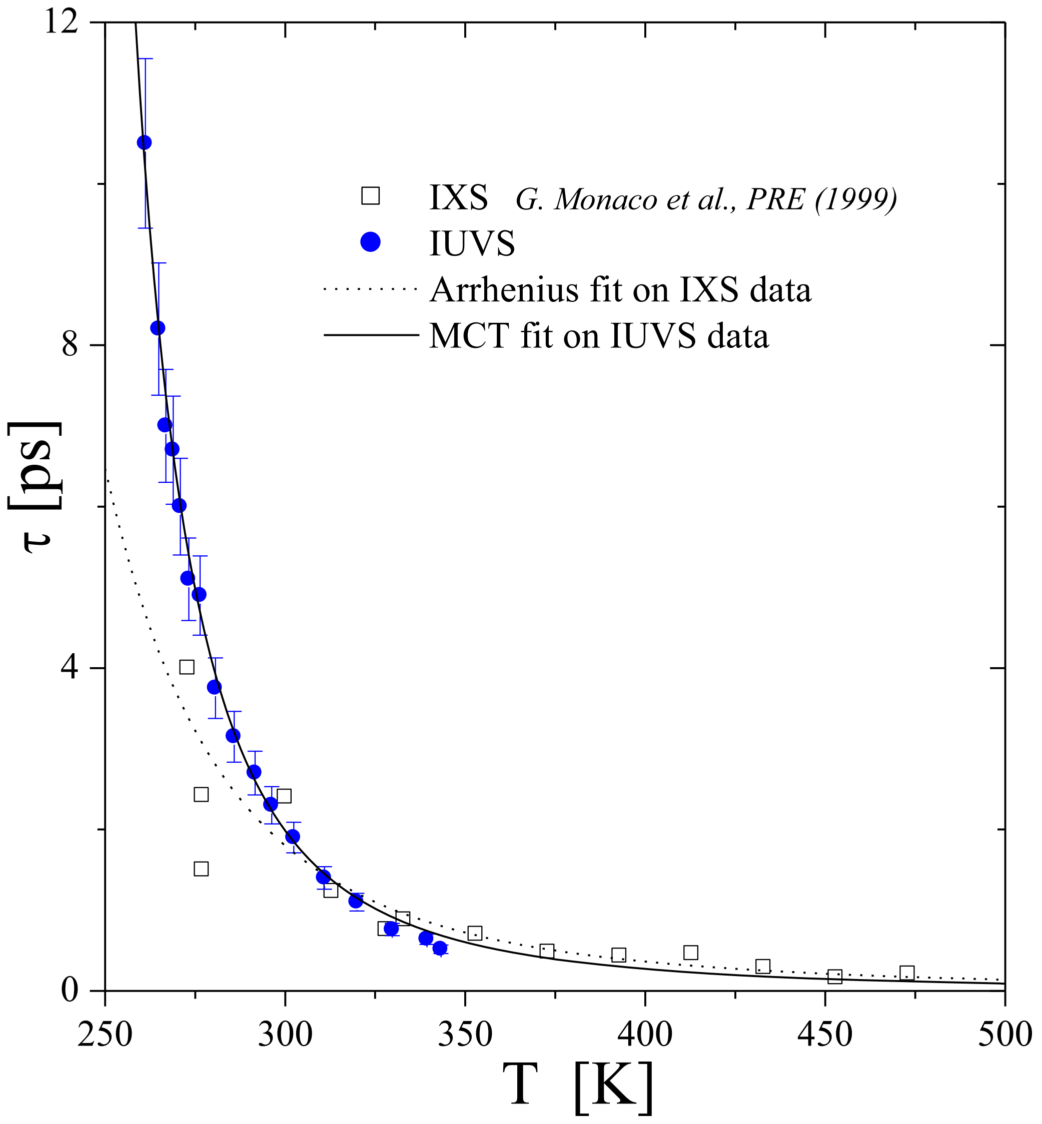
$$S(Q,\omega) = (2C_o^2Q^2/\omega)\mathrm{Im}[\omega^2 - \omega_o^2 - i\omega m_Q(\omega)]^{-1}$$

$$m_Q(t) = \omega_o^2(\gamma-1)\exp(-D_TQ^2t) + 2\,\gamma_o\,\delta(t) + \\ + (Q^2\Delta^2/\rho)\exp(-t/\tau)^\beta$$

$$\Delta^2 = \rho[C_\infty^2 - C_o^2]$$

C. Masciovecchio et al., PRL (2004)

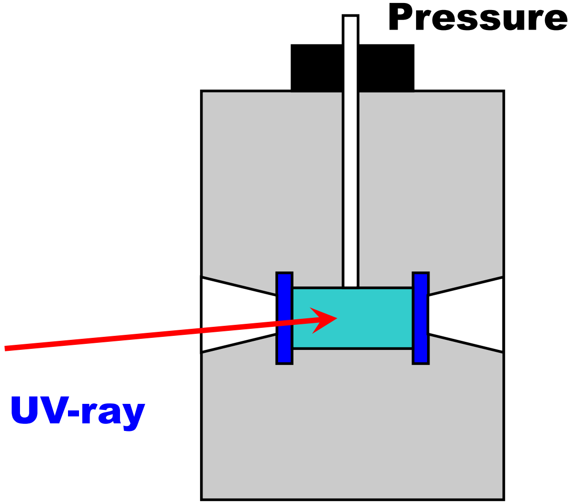
The Relaxation Time T-dependence



C. Masciovecchio et al., PRL (2004)

Let's apply Pressure to Water

High **Pressure** Set-up (Up to 4 kbar)



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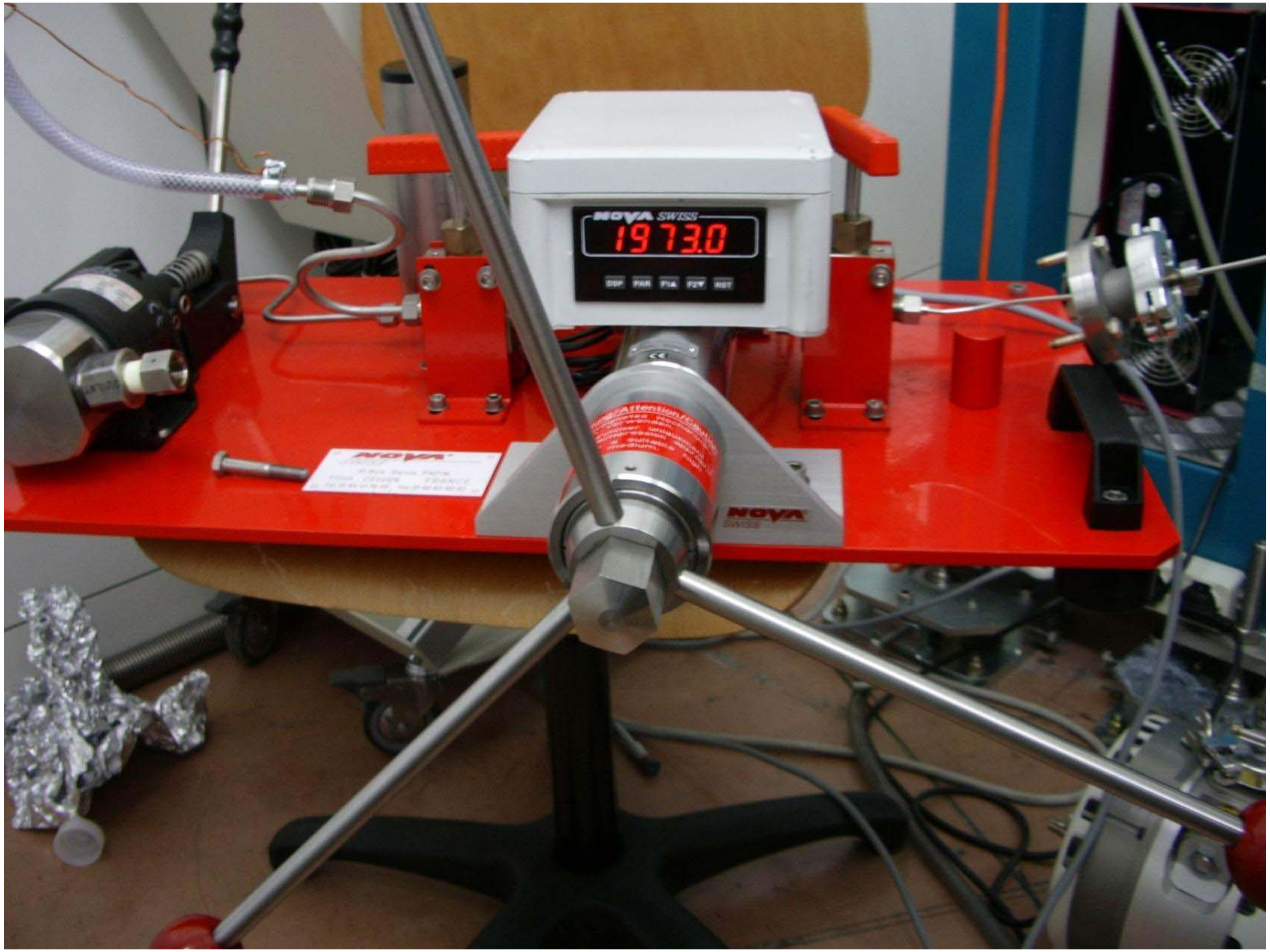
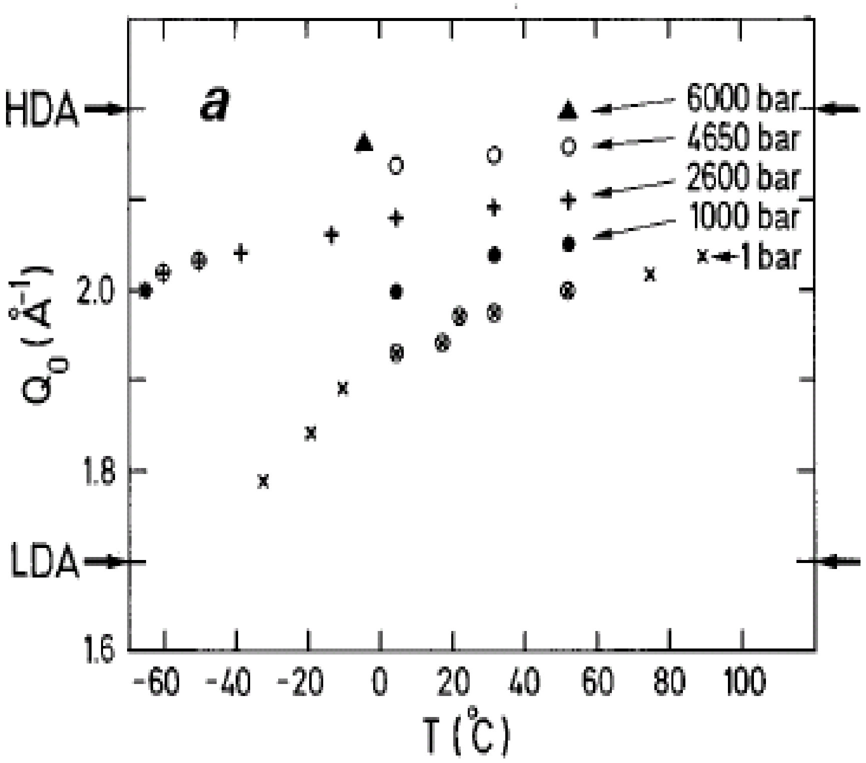
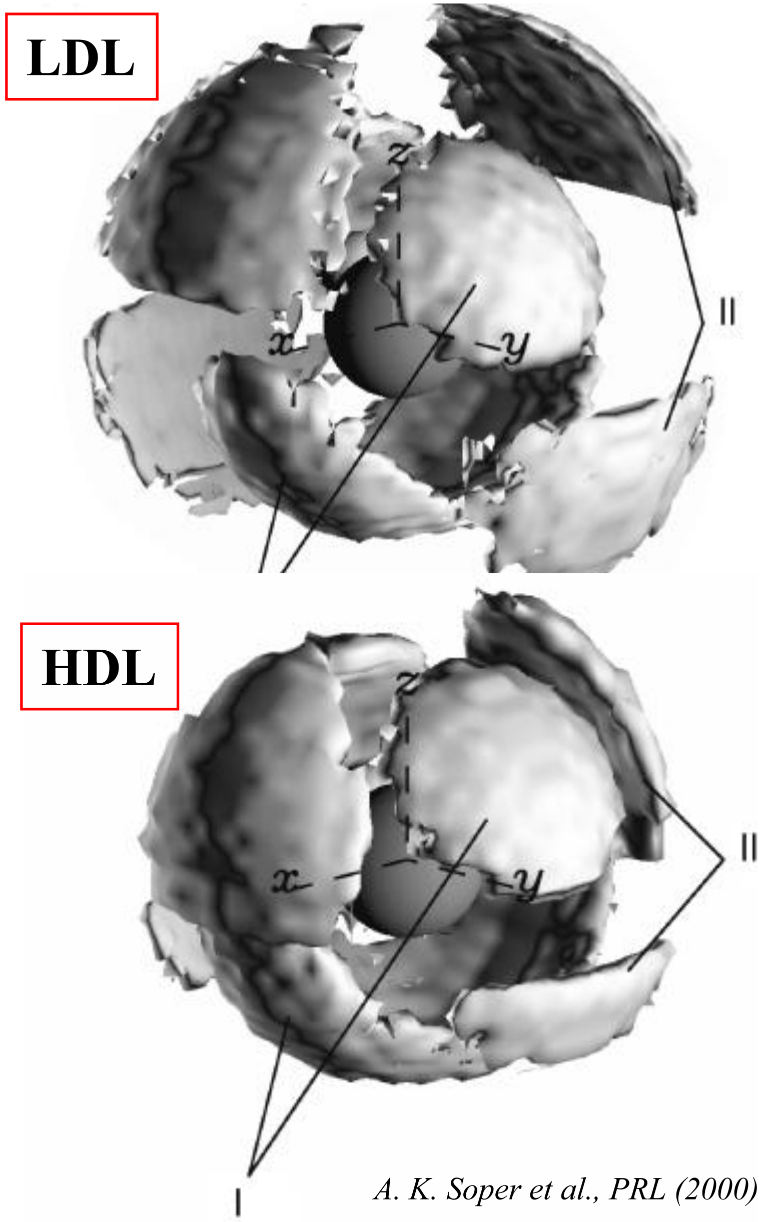


The Structure Behavior



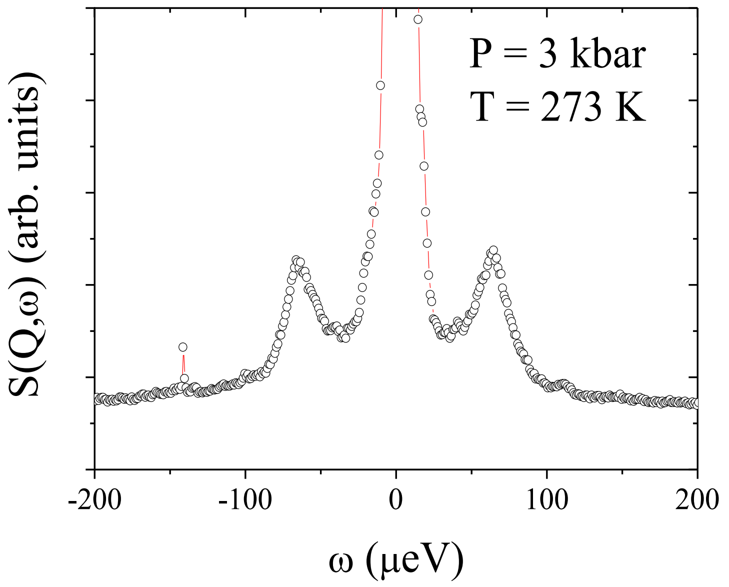
Water **Emulsions** with INS

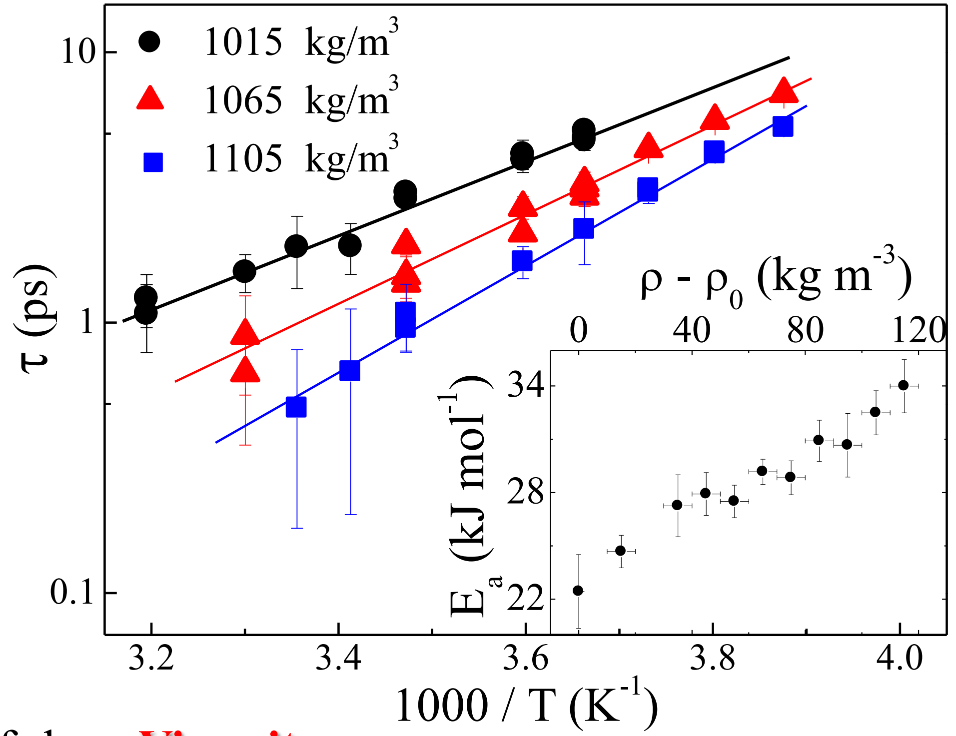
M.-C. Bellissent-Funel et al., J. Chem. Phys. (1995)



A. K. Soper et al., PRL (2000)

Relaxation Time vs. Pressure





At fixed T τ does not follow the trend of shear **Viscosity**

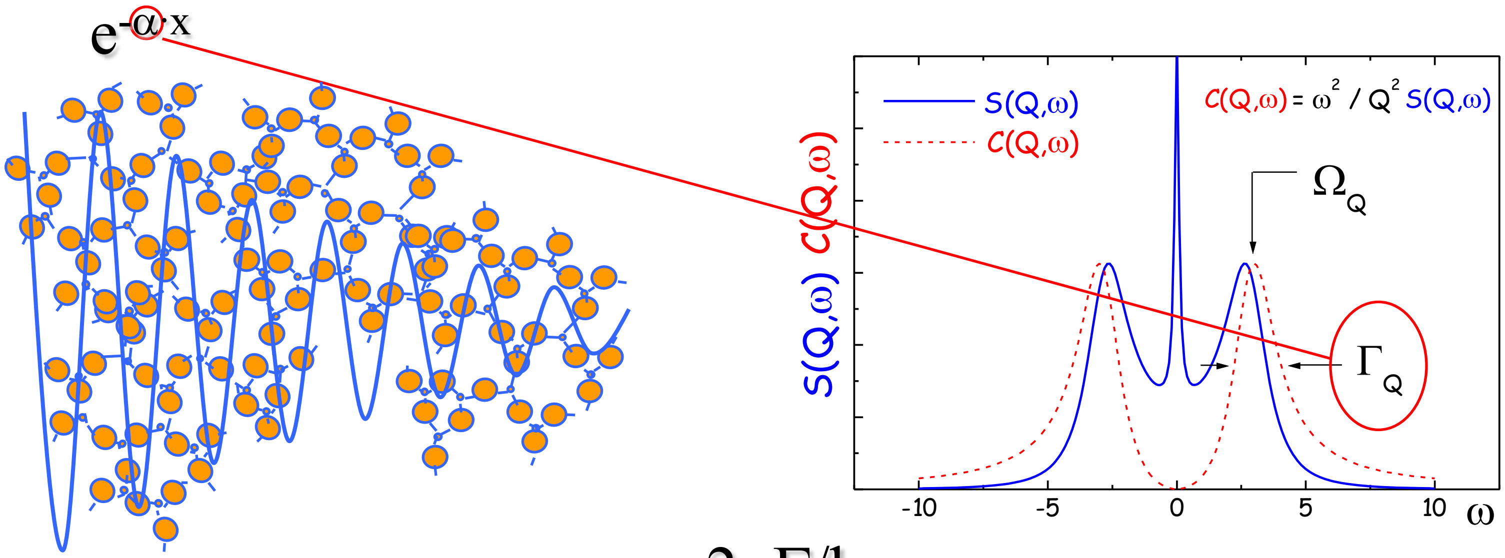
At fixed T τ **decreases** with $\rho \neq$ with respect what is commonly observed in liquids

Change of structure (change in **Entropy**) to account for the observed behaviour

Qualitative agreement with LDL-HDL phase transition hypothesis

F. Bencivenga et al. JCP (2009)

Acoustic Attenuation in Glasses



$$\alpha = 2\pi\Gamma/hc_s$$

Sound Attenuation in Glasses is very different from their Crystalline Counterpart

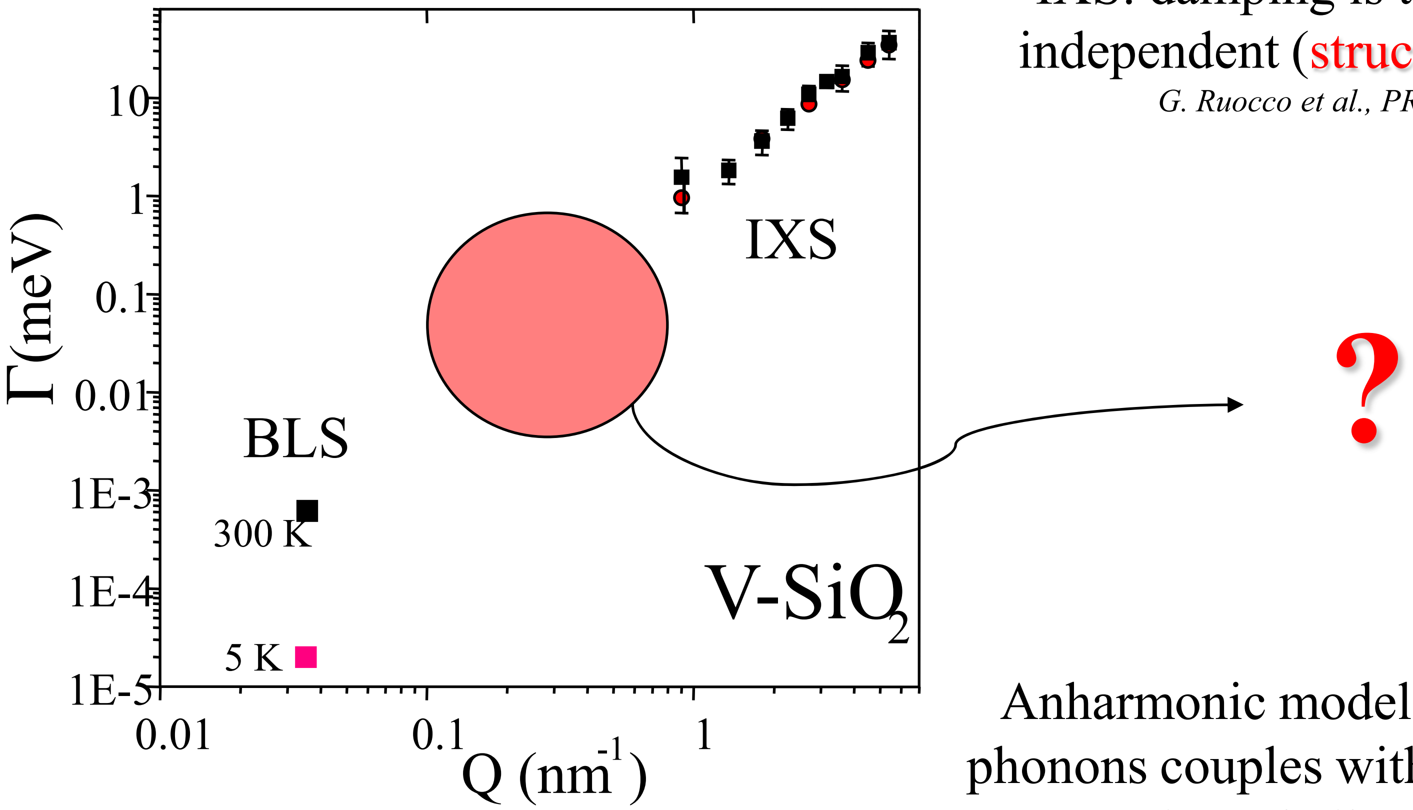
⬇

Understanding of **Thermal Anomalies** (Specific Heat and Thermal Conductivity)

At low Q's **Γ** exhibit a Q^2 dependence at (and above) room temperature which **does not extrapolate** to the Q^2 measured by IXS

Vitreous Silica

Study of the Q – T dependence of the attenuation mechanism in V- SiO_2



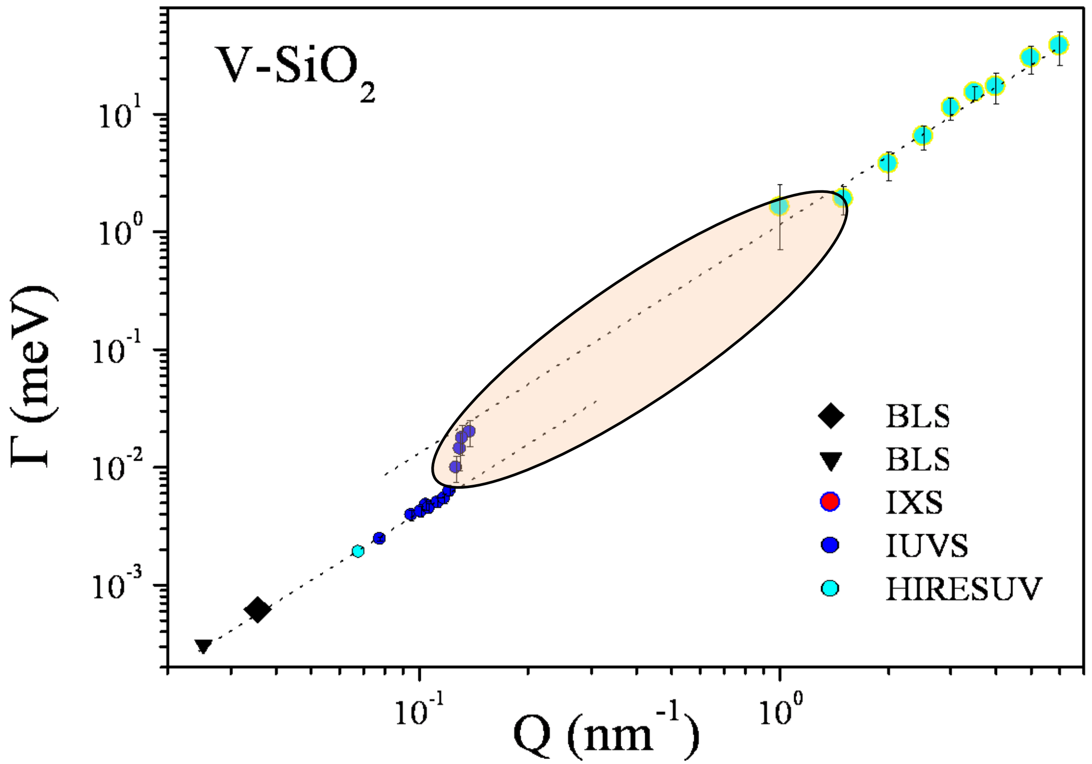
IXS: damping is temperature independent (structural origin)

G. Ruocco et al., PRL (1999)

Anharmonic model: acoustic phonons couples with thermally activated vibrations

J. Fabian et al., PRL (1999)

IUVS picture



C. Masciovecchio et al., PRL 2006

IUVS measurements demonstrate the existence of a ξ′ of about 40 nm

S(Q) maximum ~ 15 nm^{-1} → ξ′ is in the range of 100 particle size

Discriminate among models describing thermal properties

What could be the origin ?

Simulation of two-dimensional amorphous nanometric Lennard Jones systems

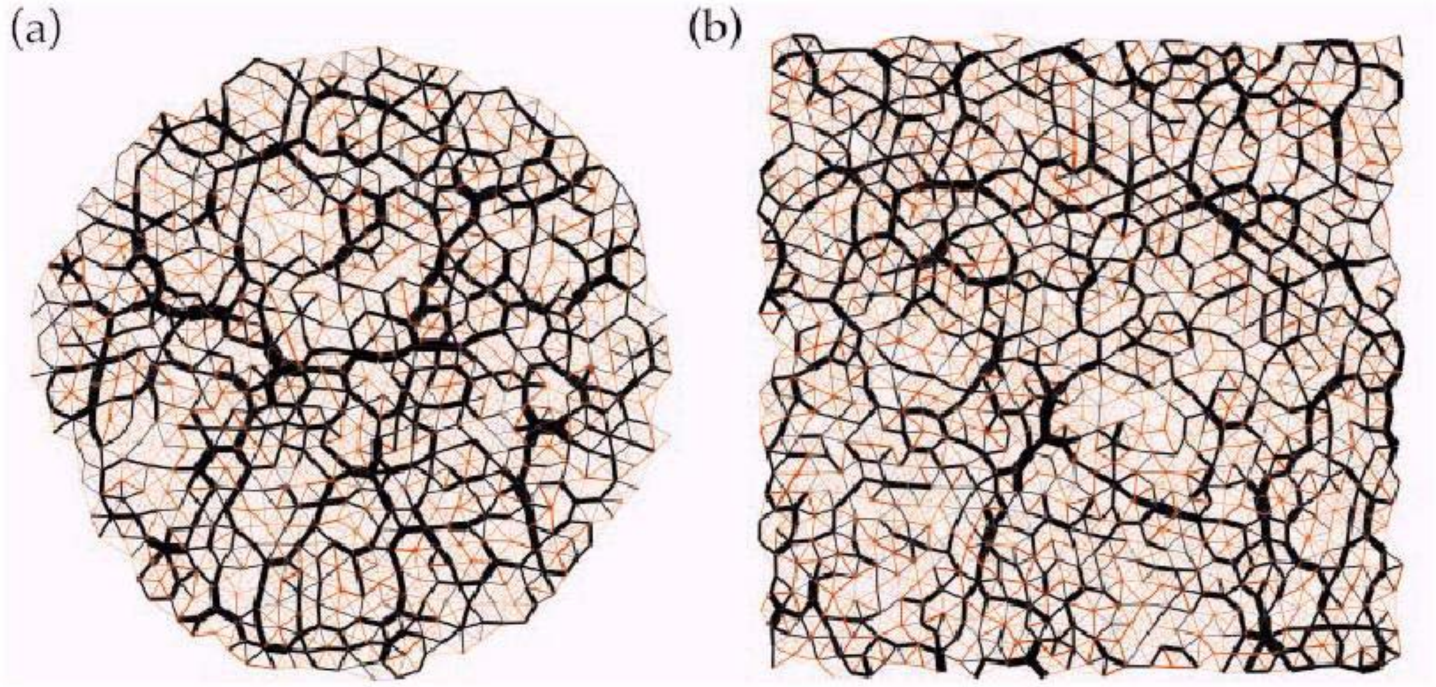
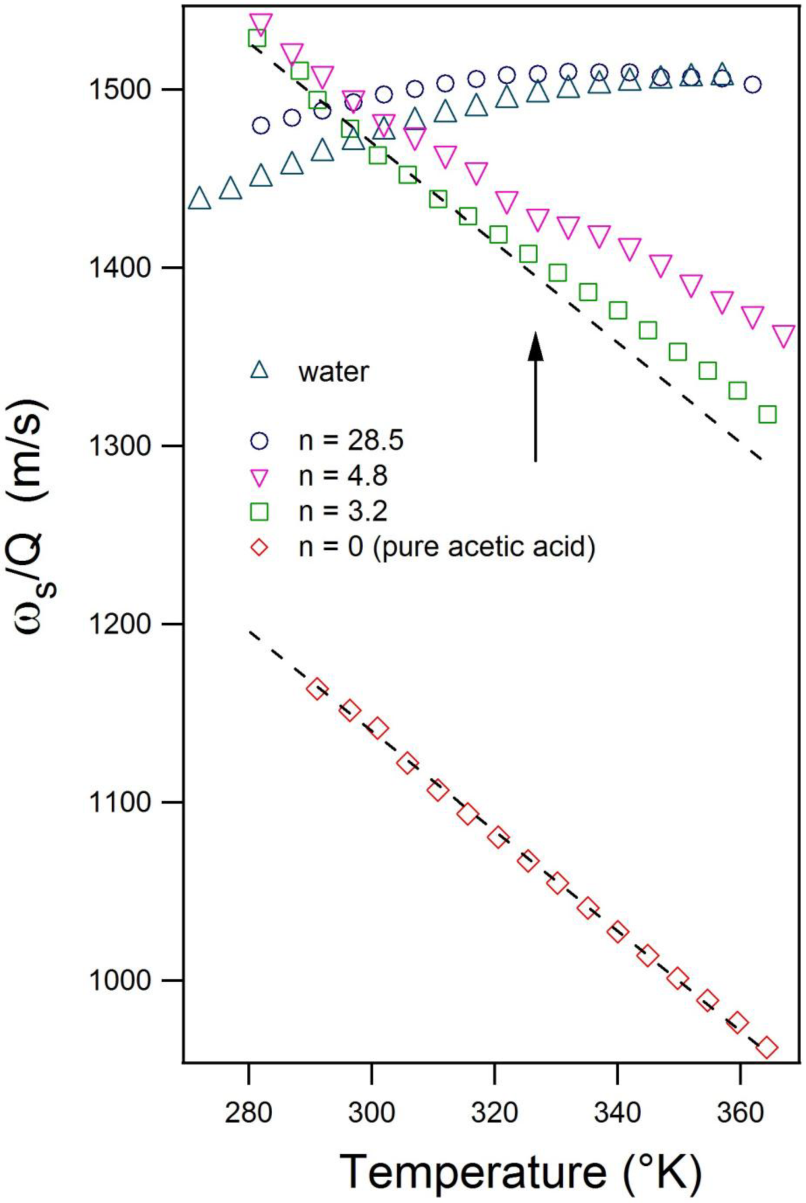


FIG. 1. (Color) Representation of the network of quenched stresses in two small quenched Lennard-Jones particle systems in two dimensions: (a) a disk-shaped aggregate of diameter $2R \approx 32a$ containing $N = 732$ particles (protocol I) on the left and (b) a periodic bulk system with $L = 32.9a$ and $N = 1000$ (protocol III) on the right-hand side. The line scale is proportional to the tension transmitted along the links between beads. The black lines indicate repulsive forces (negative tensions), while the red links represent tensile forces between the verticies. Both shown networks are very similar despite different symmetries and quench protocols. They are strongly inhomogeneous and resemble the pattern seen in granular materials. Zones of weak attractive links appear to be embedded within the strong skeleton of repulsive forces.

A. Tanguy et al., PRB (2002)

Existence of a **characteristic** length ξ below which the classical mechanical approach becomes **inappropriate**. ξ is about 30 particle sizes.

Dynamics of Water and the Hydration Shell



Change of Dynamics from pure **Acetic Acid** to water content >> than the hydration shell.

There is a **characteristic** T around 325 K which marks a crossover:

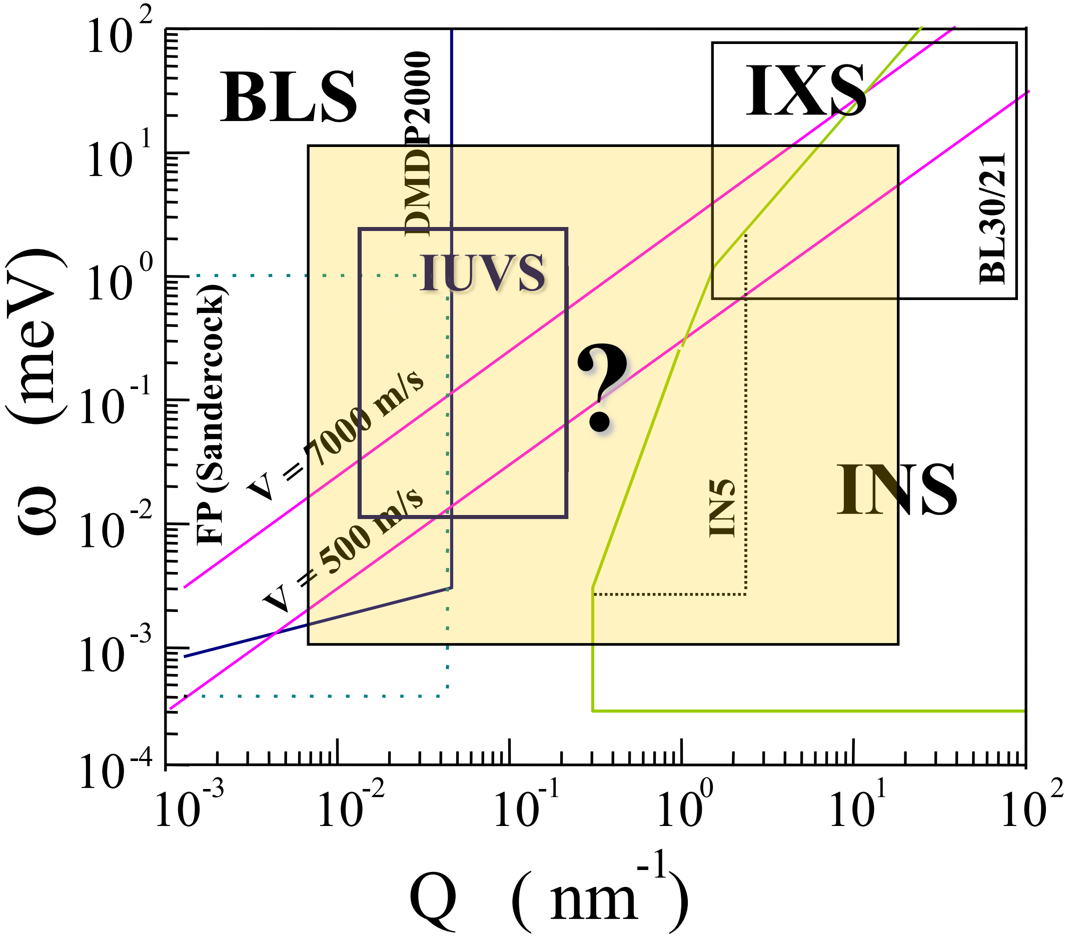
- At low temperatures hydration shell HB are stronger than bulk water ones.
- At higher temperatures hydration shell HB start to be weaker.

Loss of protein physiological functions

Needs to go to **higher Q** values in order to determine the HB activation energy.

F. D'Amico et al., submitted

Can we fill the Gap in the Kinematic Region?

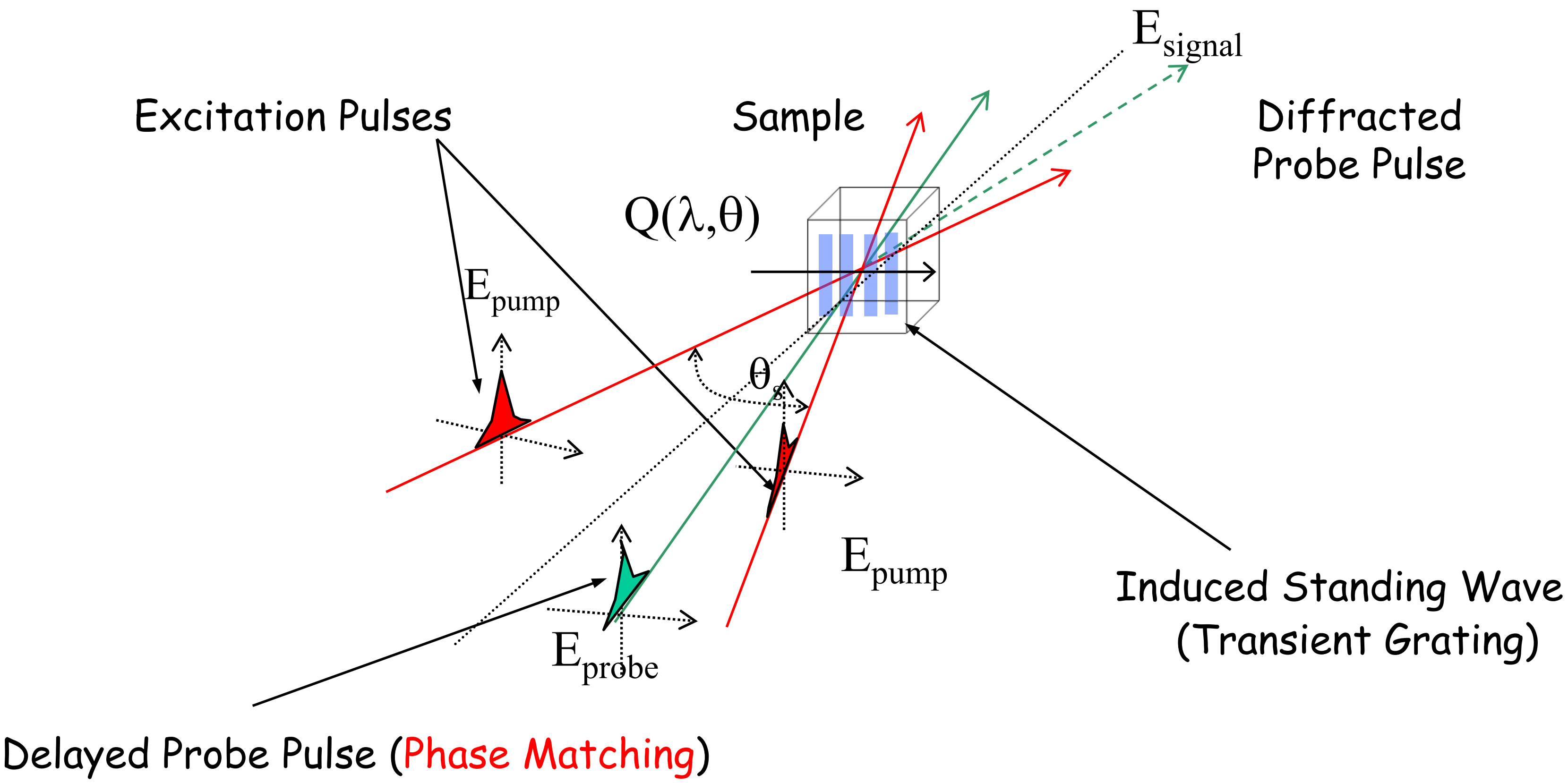


YES ! with FEL based Transient Grating Spectroscopy

TIMER

TIME-Resolved spectroscopy of mesoscopic dynamics in condensed matter

The Technique in Detail



Excitation Pulses

Sample

Diffracted Probe Pulse

Induced Standing Wave (Transient Grating)

Delayed Probe Pulse (Phase Matching)

Standing Wave Periodicity ⟹ $\xi = 2\pi/Q$ $Q = 2k_o \sin\theta_s/2$

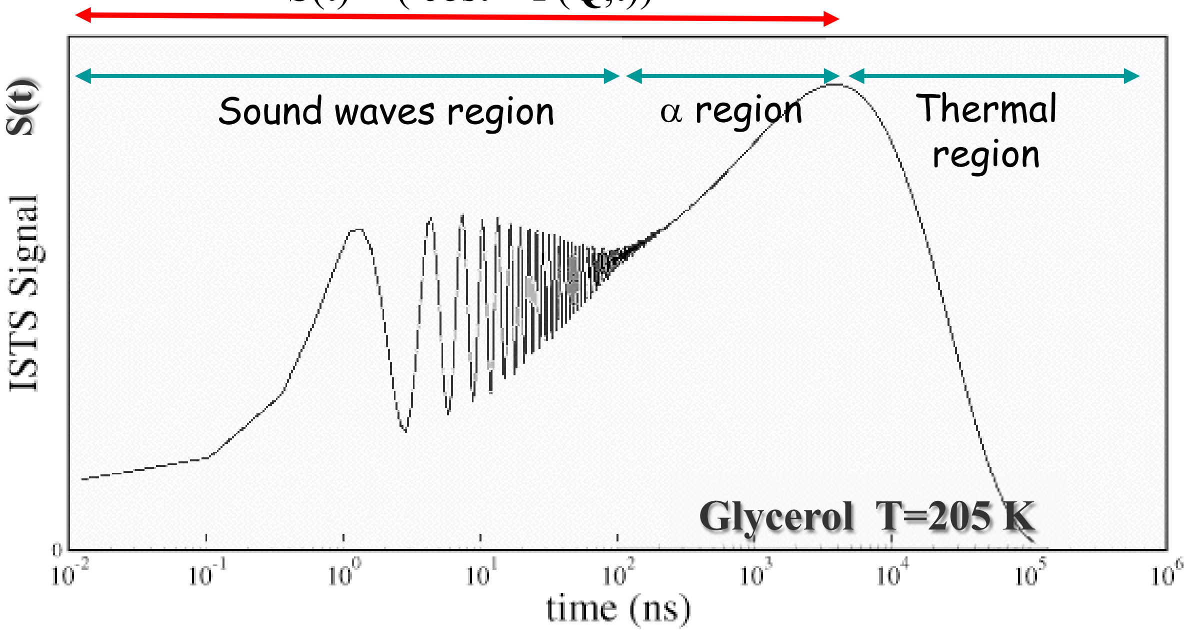
Density Modulation Amplitude Monitored in Time by the Probe Pulse ⟹ **$F(Q,t)$**

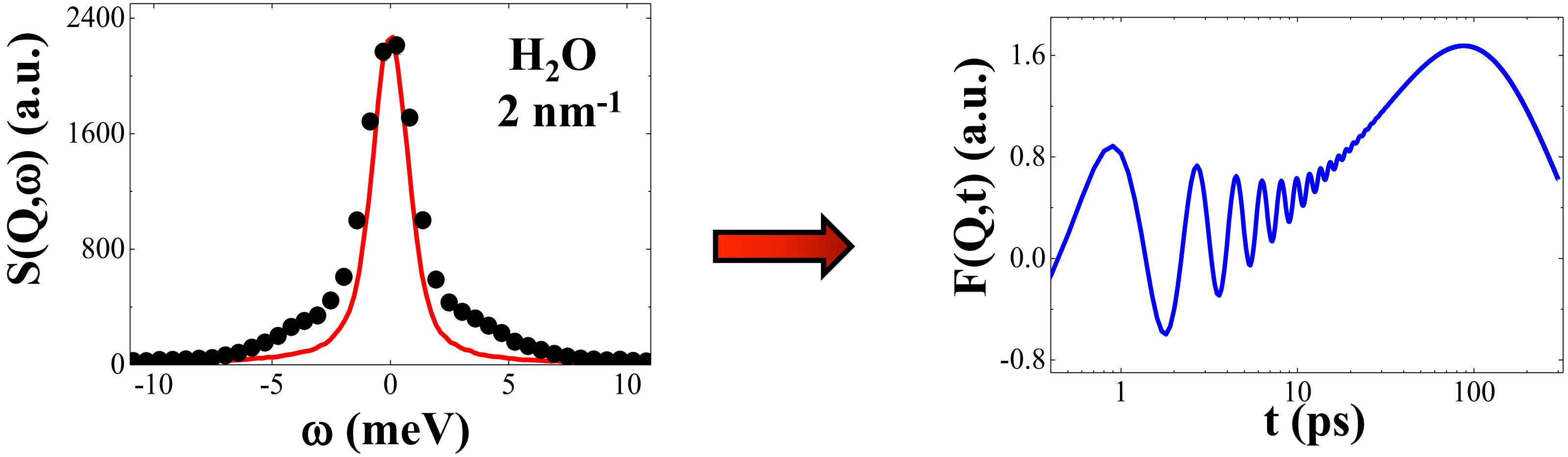
The Spectrum

Optical absorption → Temperature Grating →Time-dependent Density Response

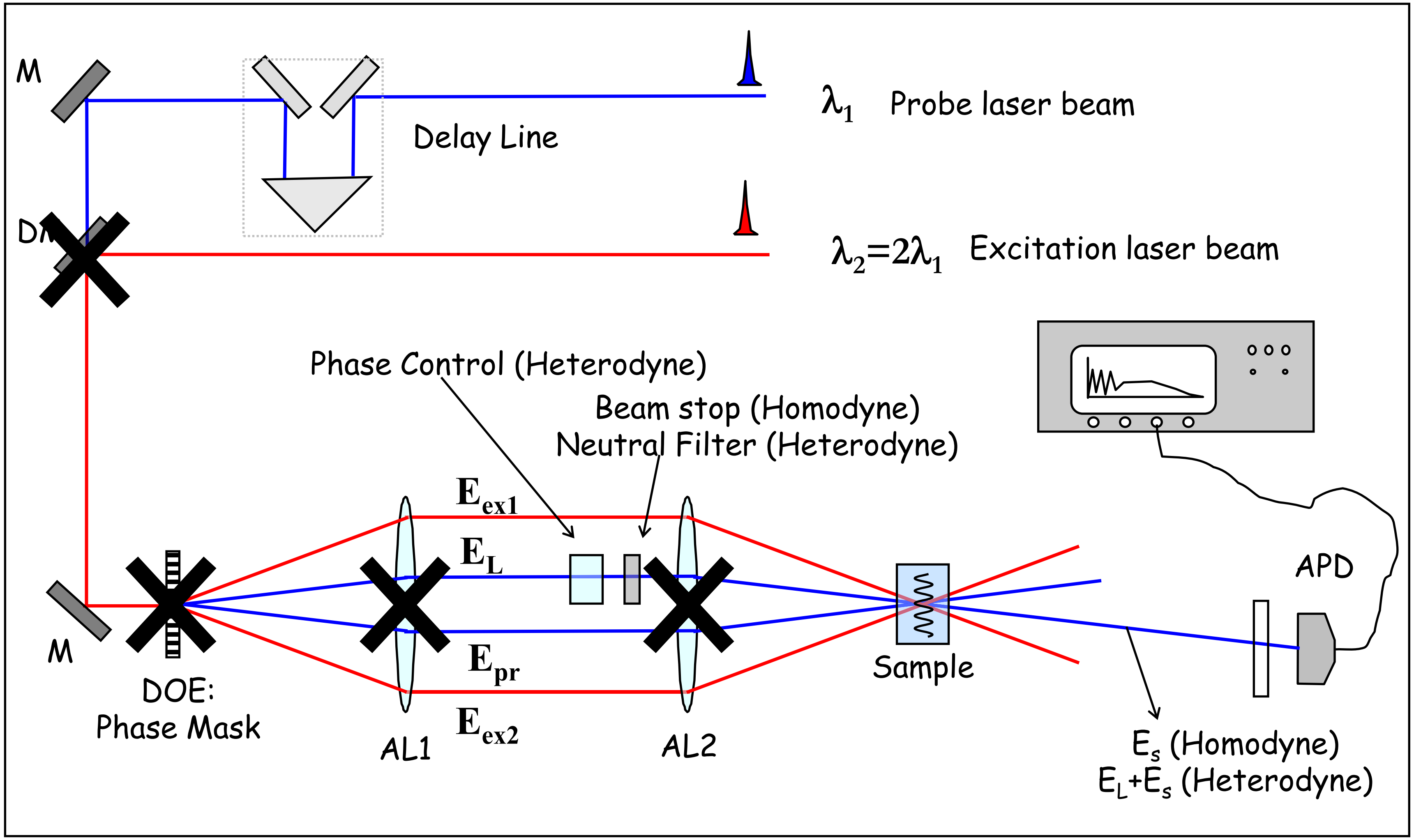
(**driven by thermal expansion**)

$S(t) \approx (\text{cost} - F(\mathbf{Q},t))$



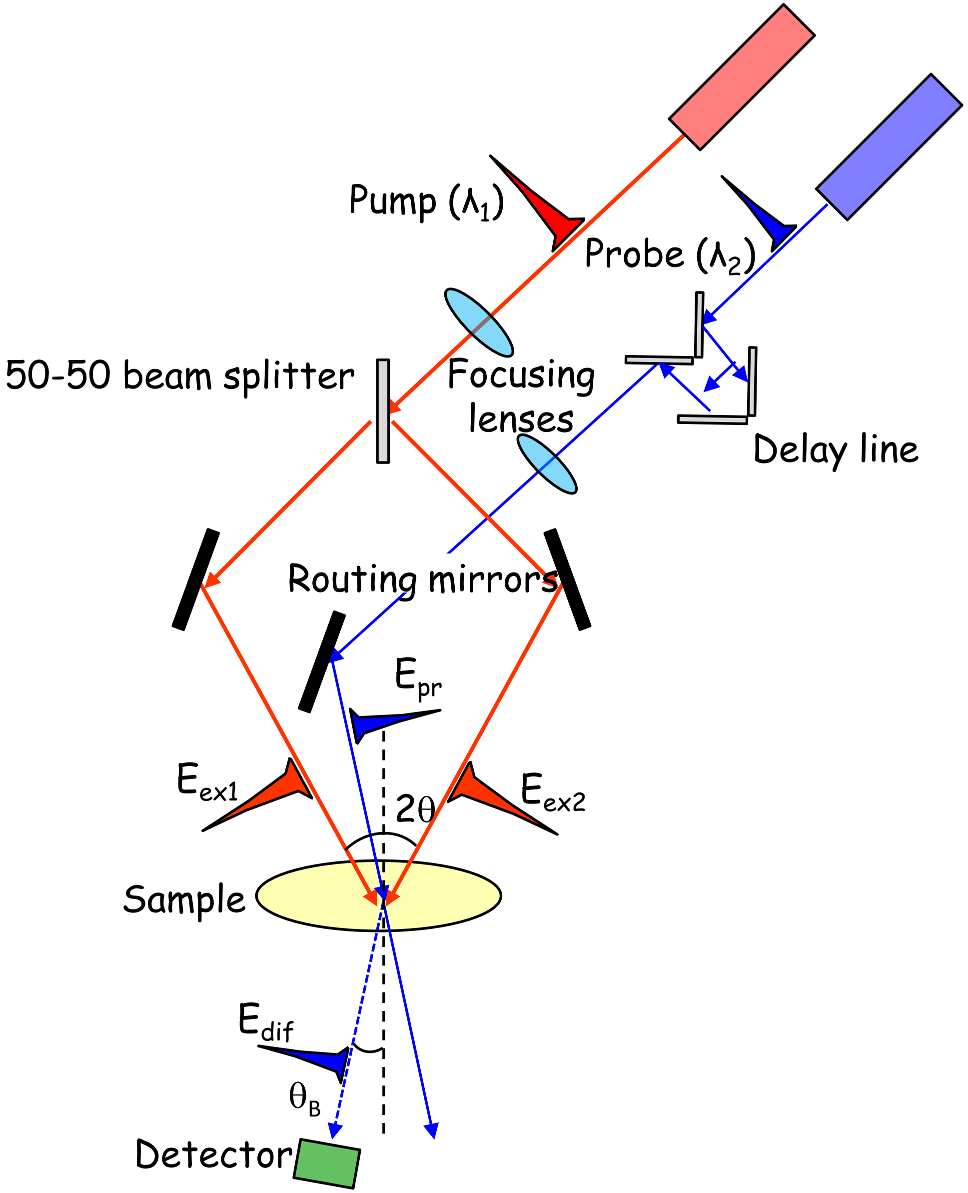


Typical Infrared/Visible Set-Up



Challenge: Extend and modify the set-up for UV Transient Grating Experiments

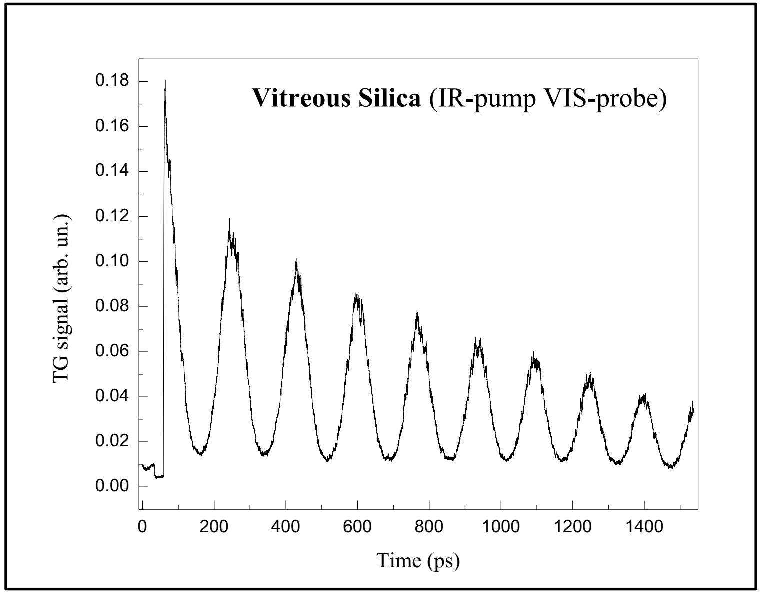
First developments



Source: table-top Ti:Sapphire

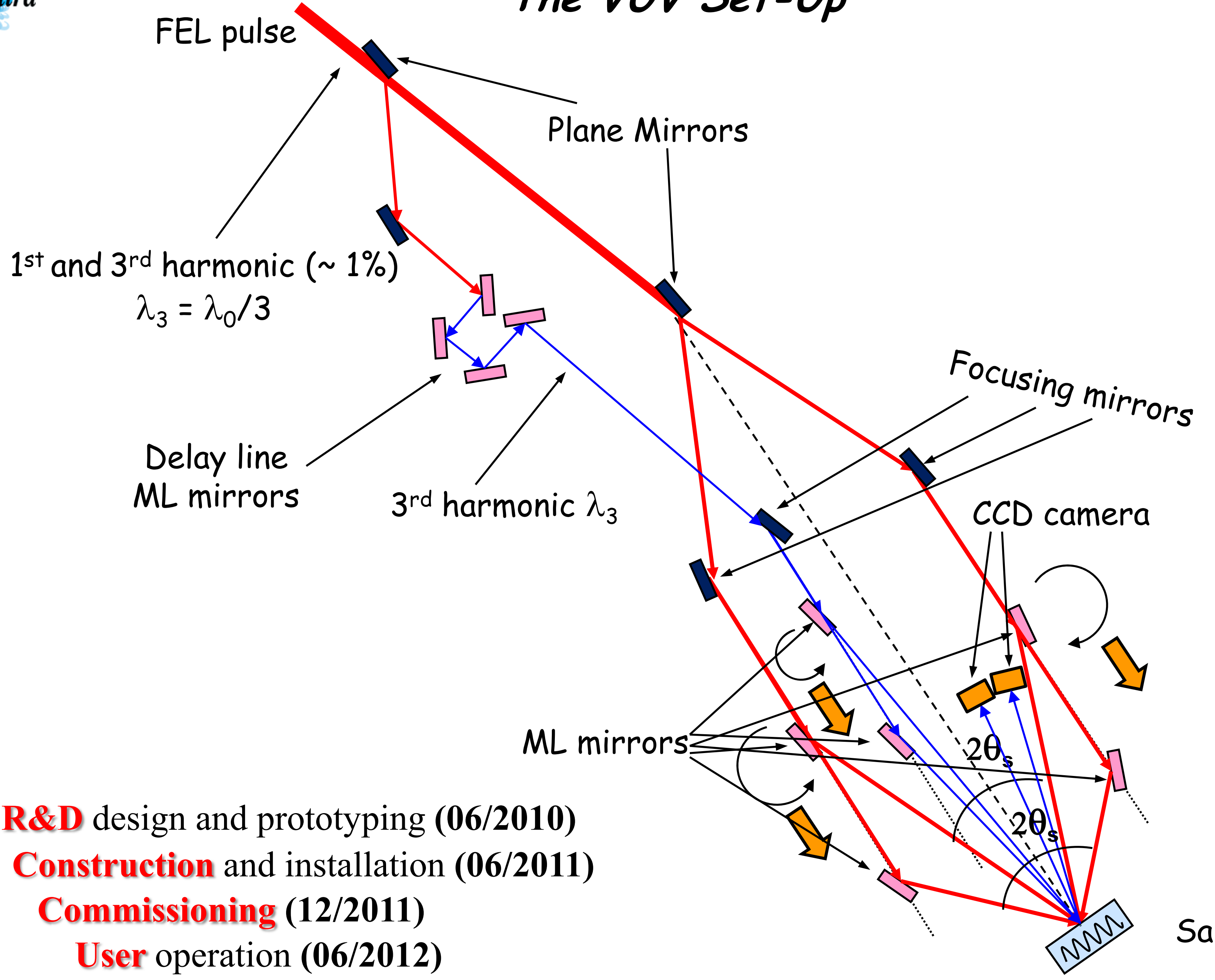
$\Delta t = 35 - 10^3$ fs
E = 3.5 mJ
rep rate = $1 - 10^3$ Hz

λ_1 (pump): 800 nm
λ_2 (probe): 400 nm
$\Delta t = 100$ fs



R. Cucini et al., in preparation

The VUV Set-Up



FEL pulse

Plane Mirrors

1st and 3rd harmonic (~ 1%)
$\lambda_3 = \lambda_0/3$

Delay line
ML mirrors

3rd harmonic λ_3

Focusing mirrors

CCD camera

ML mirrors

$2\theta_s$

$2\theta_s$

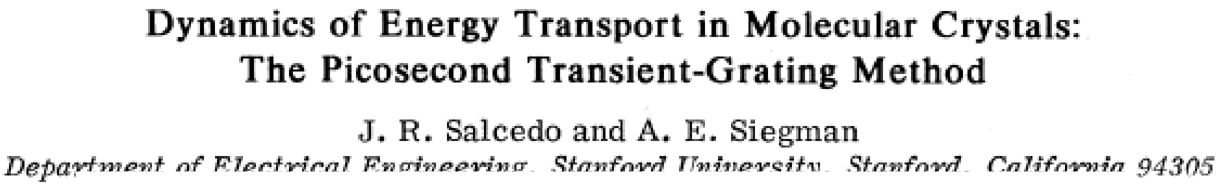
Sample

R&D design and prototyping **(06/2010)**
Construction and installation **(06/2011)**
Commissioning **(12/2011)**
User operation **(06/2012)**

Other Possible Experiments

Heat Transport, Diffusion phenomena, Flow Studies, Concentration Grating, Electronic Energy Transfer, Photochemical Reactions, Optical Damage ………………

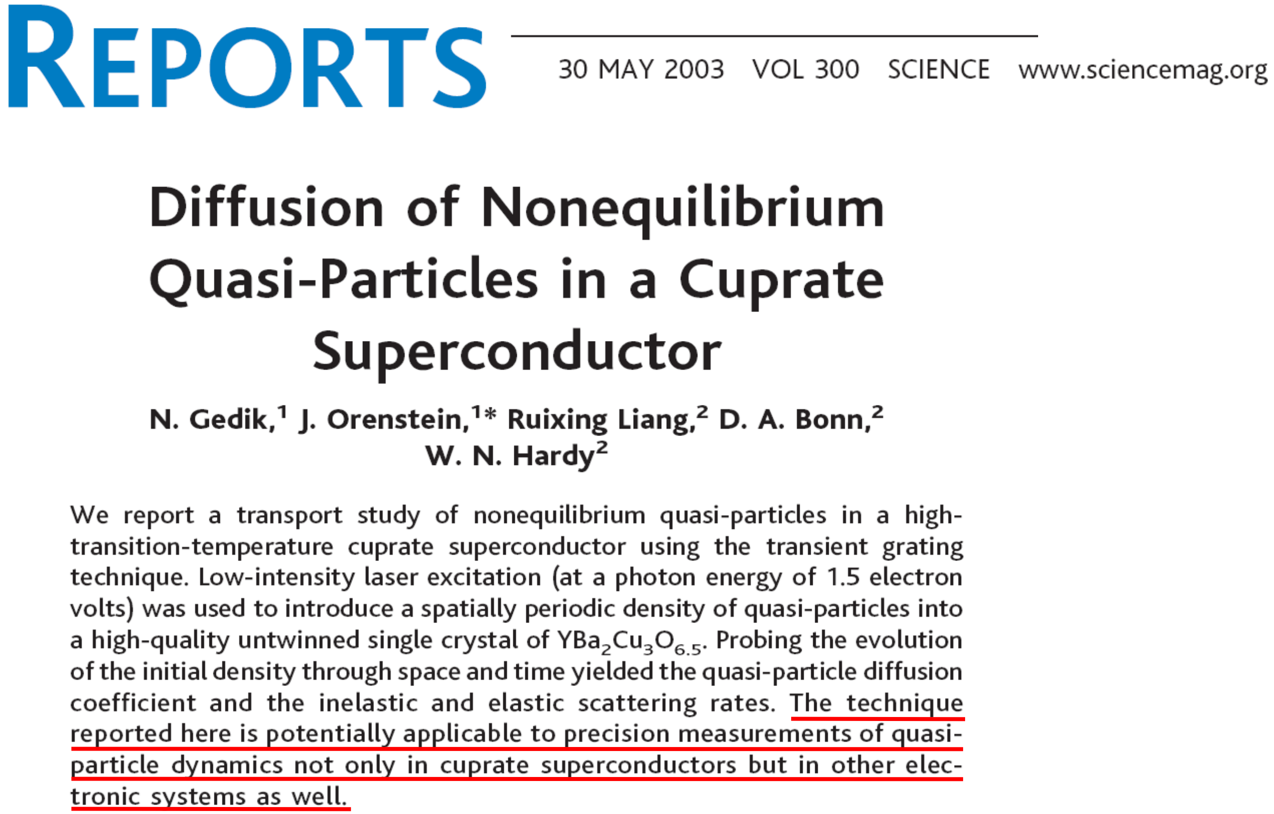
H. J. Eichler et al., J. Appl. Phys. 44, 5455 (1973)



Dynamics of Energy Transport in Molecular Crystals: The Picosecond Transient-Grating Method

J. R. Salcedo and A. E. Siegman

Department of Electrical Engineering, Stanford University, Stanford, California 94305



REPORTS

30 MAY 2003 VOL 300 SCIENCE www.sciencemag.org

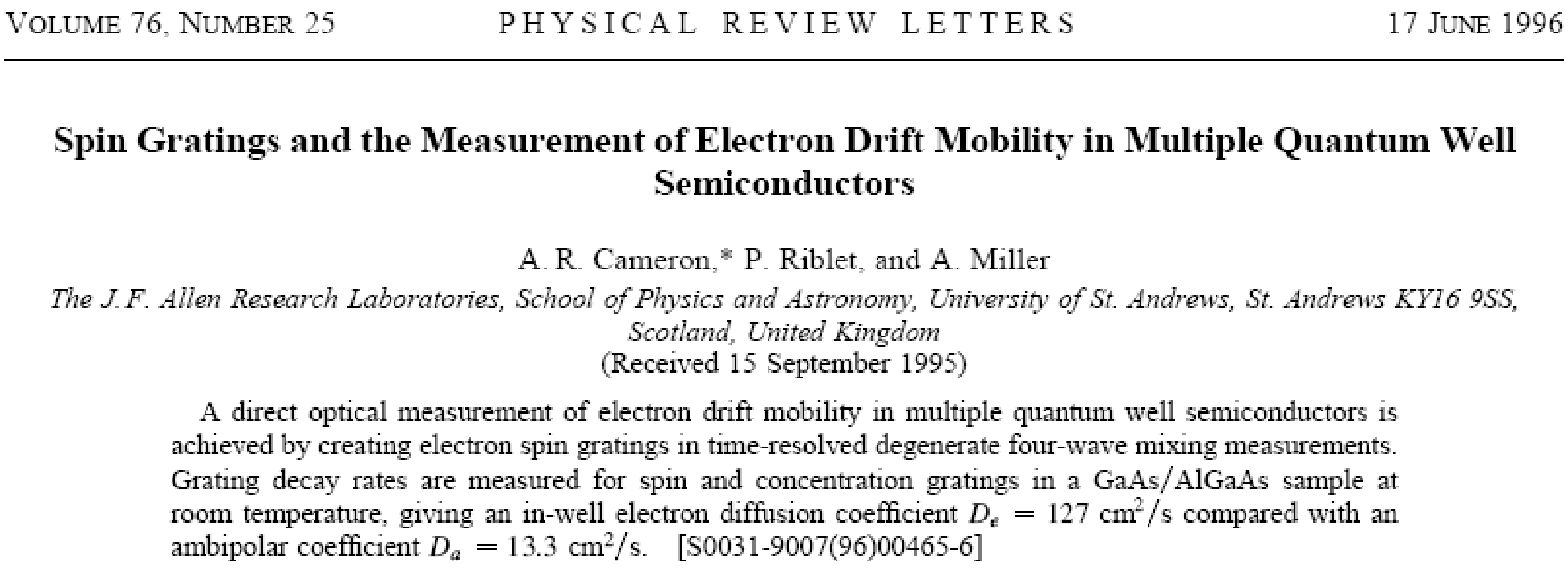
Diffusion of Nonequilibrium Quasi-Particles in a Cuprate Superconductor

N. Gedik,[1] J. Orenstein,[1]* Ruixing Liang,[2] D. A. Bonn,[2] W. N. Hardy[2]

We report a transport study of nonequilibrium quasi-particles in a high-transition-temperature cuprate superconductor using the transient grating technique. Low-intensity laser excitation (at a photon energy of 1.5 electron volts) was used to introduce a spatially periodic density of quasi-particles into a high-quality untwinned single crystal of $YBa_2Cu_3O_{6.5}$. Probing the evolution of the initial density through space and time yielded the quasi-particle diffusion coefficient and the inelastic and elastic scattering rates. The technique reported here is potentially applicable to precision measurements of quasi-particle dynamics not only in cuprate superconductors but in other electronic systems as well.

Spin Dynamics

TG can excite Spin Waves using orthogonal polarization



VOLUME 76, NUMBER 25 PHYSICAL REVIEW LETTERS 17 JUNE 1996

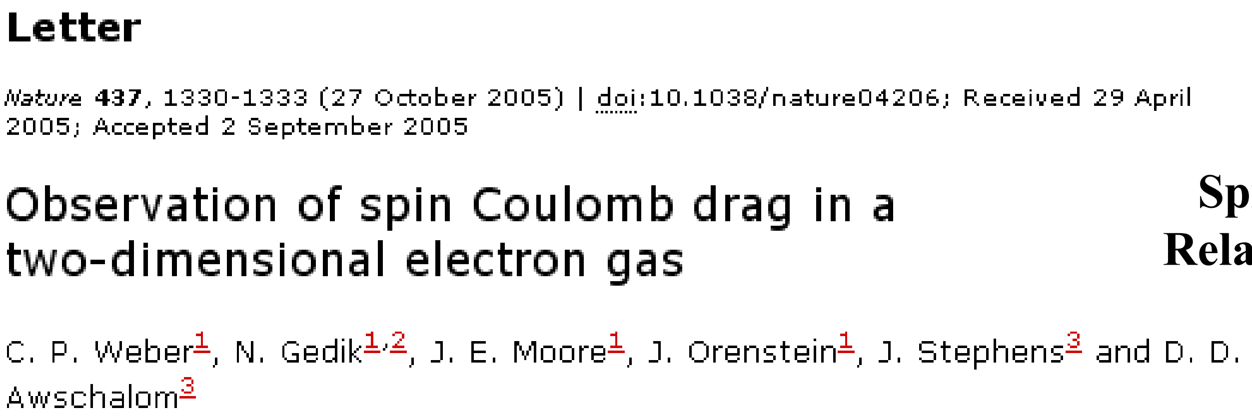
Spin Gratings and the Measurement of Electron Drift Mobility in Multiple Quantum Well Semiconductors

A. R. Cameron,* P. Riblet, and A. Miller

The J. F. Allen Research Laboratories, School of Physics and Astronomy, University of St. Andrews, St. Andrews KY16 9SS, Scotland, United Kingdom

(Received 15 September 1995)

A direct optical measurement of electron drift mobility in multiple quantum well semiconductors is achieved by creating electron spin gratings in time-resolved degenerate four-wave mixing measurements. Grating decay rates are measured for spin and concentration gratings in a GaAs/AlGaAs sample at room temperature, giving an in-well electron diffusion coefficient $D_e = 127\ \text{cm}^2/\text{s}$ compared with an ambipolar coefficient $D_a = 13.3\ \text{cm}^2/\text{s}$. [S0031-9007(96)00465-6]



Letter

Nature **437**, 1330-1333 (27 October 2005) | doi:10.1038/nature04206; Received 29 April 2005; Accepted 2 September 2005

Observation of spin Coulomb drag in a two-dimensional electron gas

C. P. Weber[1], N. Gedik[1,2], J. E. Moore[1], J. Orenstein[1], J. Stephens[3] and D. D. Awschalom[3]

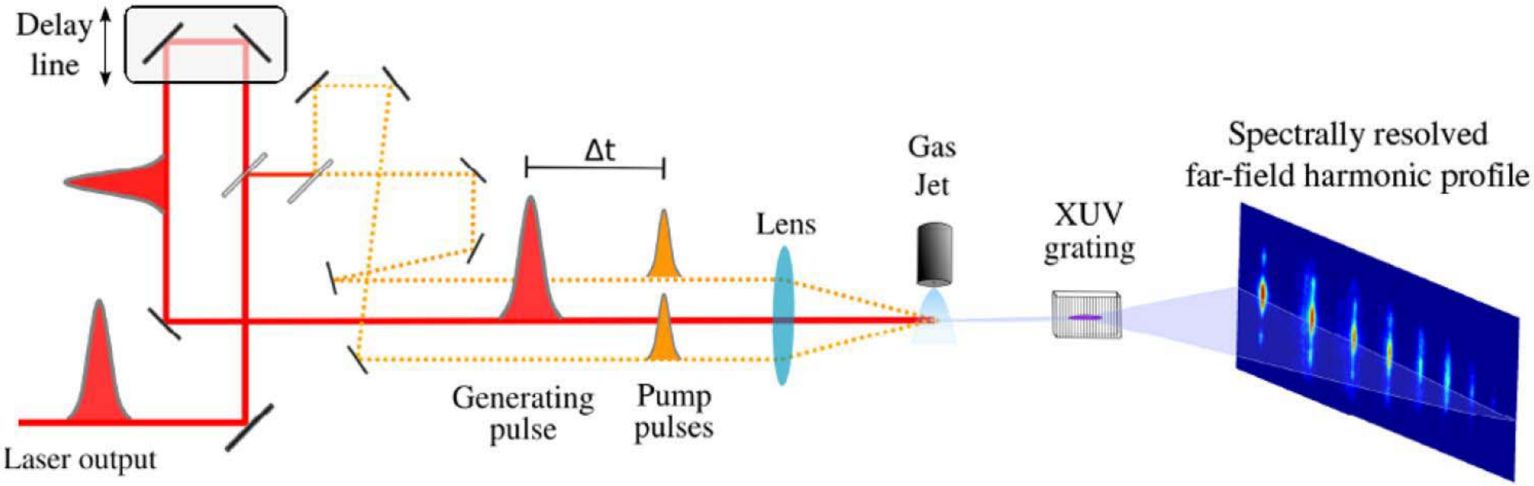
Spin Diffusion and Relaxation in a 2-dim. Electron Gas

HHG in a Gas Jet

PRL 100, 143903 (2008) PHYSICAL REVIEW LETTERS week ending 11 APRIL 2008

High-Order Harmonic Transient Grating Spectroscopy in a Molecular Jet

Y. Mairesse,[1,2] D. Zeidler,[1,3] N. Dudovich,[1,4] M. Spanner,[5] J. Levesque,[1] D. M. Villeneuve,[1] and P. B. Corkum[1]



The harmonic signal encodes structural information on the orbital → full reconstruction

"......High harmonic transient grating spectroscopy can be extended to all forms of molecular excitation and to weak resonant excitation......"

The **Sample Side**

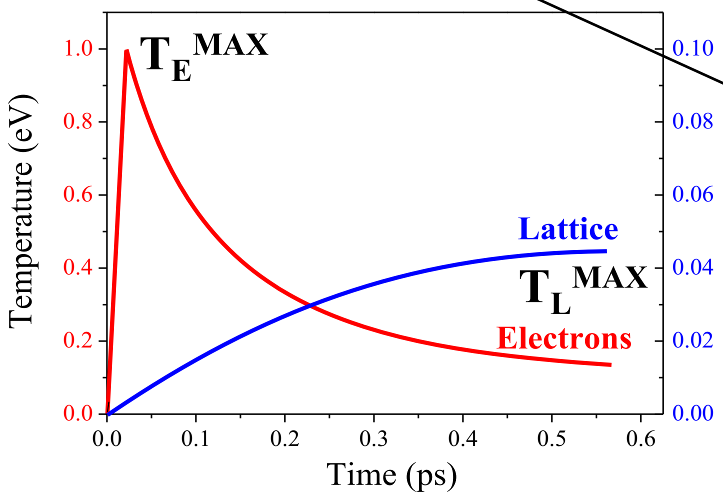
Short pulses with very high peak power **Δt ~ 100 fs ; Peak Power ~ 5 GW ; E ~ 100 eV**

What happens to the **Sample?** Non-equilibrium distribution of electrons

Converge (electron-electron & electron-phonon collisions) to equilibrium (Fermi-like)

During this complex dynamics atoms go through a relaxation process due to the dramatic changes of the potential energy surface

The intensity of the FEL pulses will determine the process to which the sample will undergo: simple heating, structural changes, ultrafast melting or ultrafast ablation



T_E^{MAX}
T_L^{MAX} } **Δt, Peak Power, E, Sample, Fluence, …..**

TIMER **TIMEX**

TIMEX

Going Extreme with TIMEX: Warm Dense Matter (WDM), ultrafast heating and melting, study of the dynamics of melting and nucleation

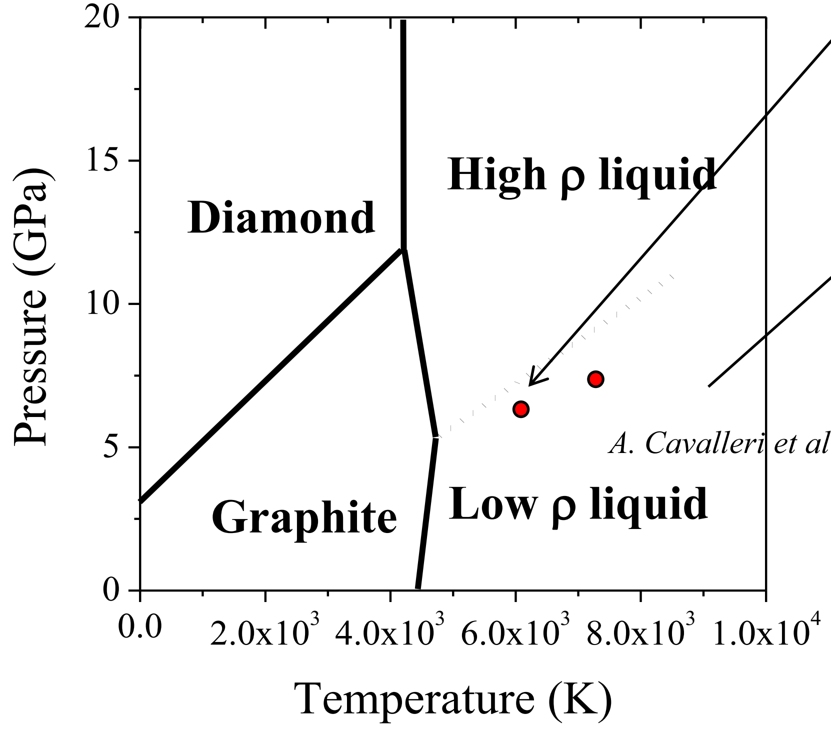
The phase diagram of carbon is poorly understood *A. Ludwig, Z. Electrochem. (1902)*

Pioneering Femtosecond Experiment

D. H. Reitze et al., PRB (1992) → *N. Bloembergen, Nature (1992)*

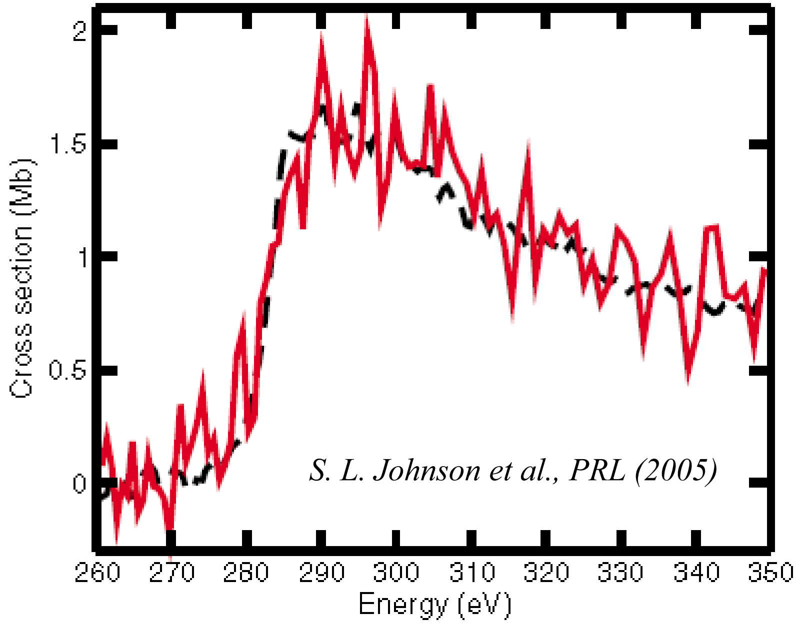
"Femtosecond Experiments can be improved by using probe pulses in the VUV ...... to determine individual Drude parameters...." → dielectric function ε

Hypothetical phase diagram of Carbon



A. Cavalleri et al., EPL (2002

Time-Resolved X-Ray Abs Spectroscopy



S. L. Johnson et al., PRL (2005)

Long Times (t > 100 ps), Tamped sample

EIS beamline - TIMEX

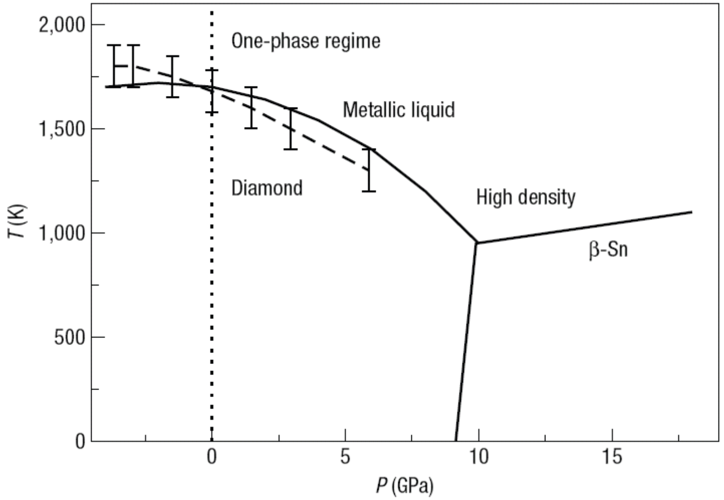
Use the FEL **Tunability** to measure a XANES spectrum

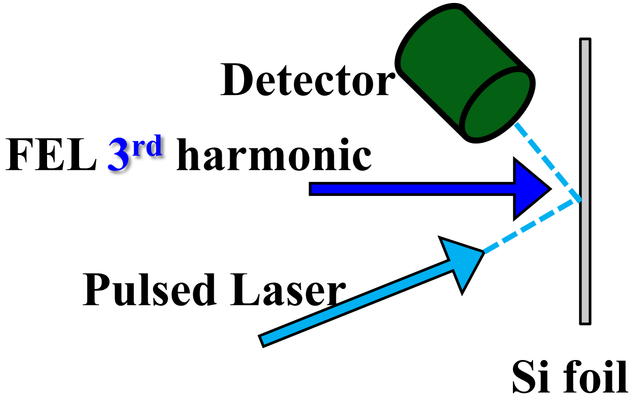
LETTERS

A density-driven phase transition between semiconducting and metallic polyamorphs of silicon

PAUL F. MCMILLAN[1,2]*, MARK WILSON[1], DOMINIK DAISENBERGER[1] AND DENIS MACHON[1]

[1] Department of Chemistry and Materials Chemistry Centre, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[2] Davy-Faraday Research Laboratory, Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK
*e-mail: p.f.mcmillan@ucl.ac.uk



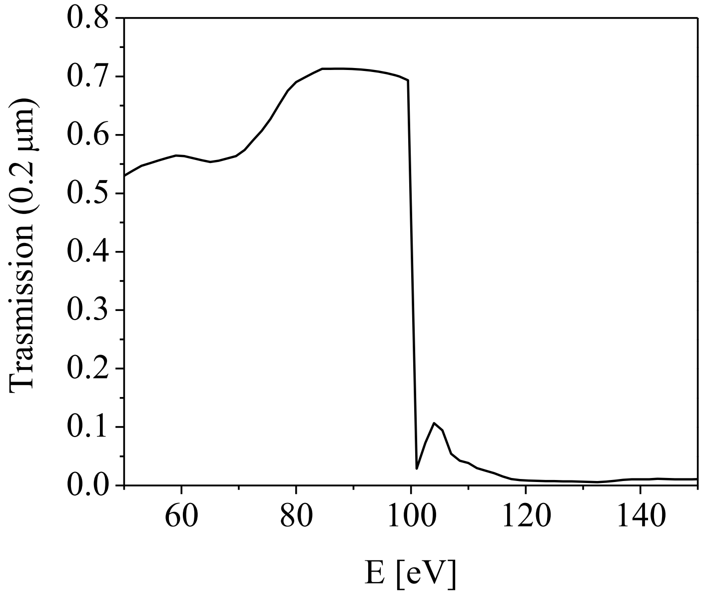


Detector

FEL 3rd harmonic

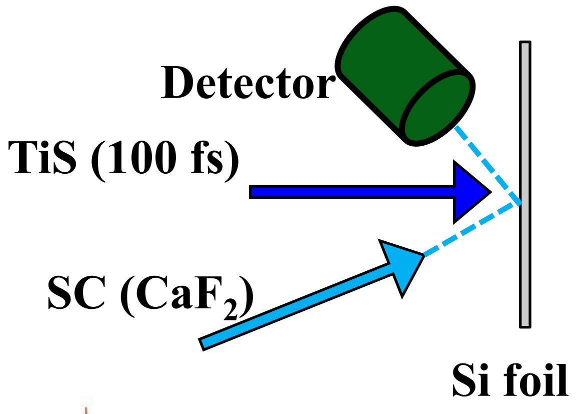
Pulsed Laser

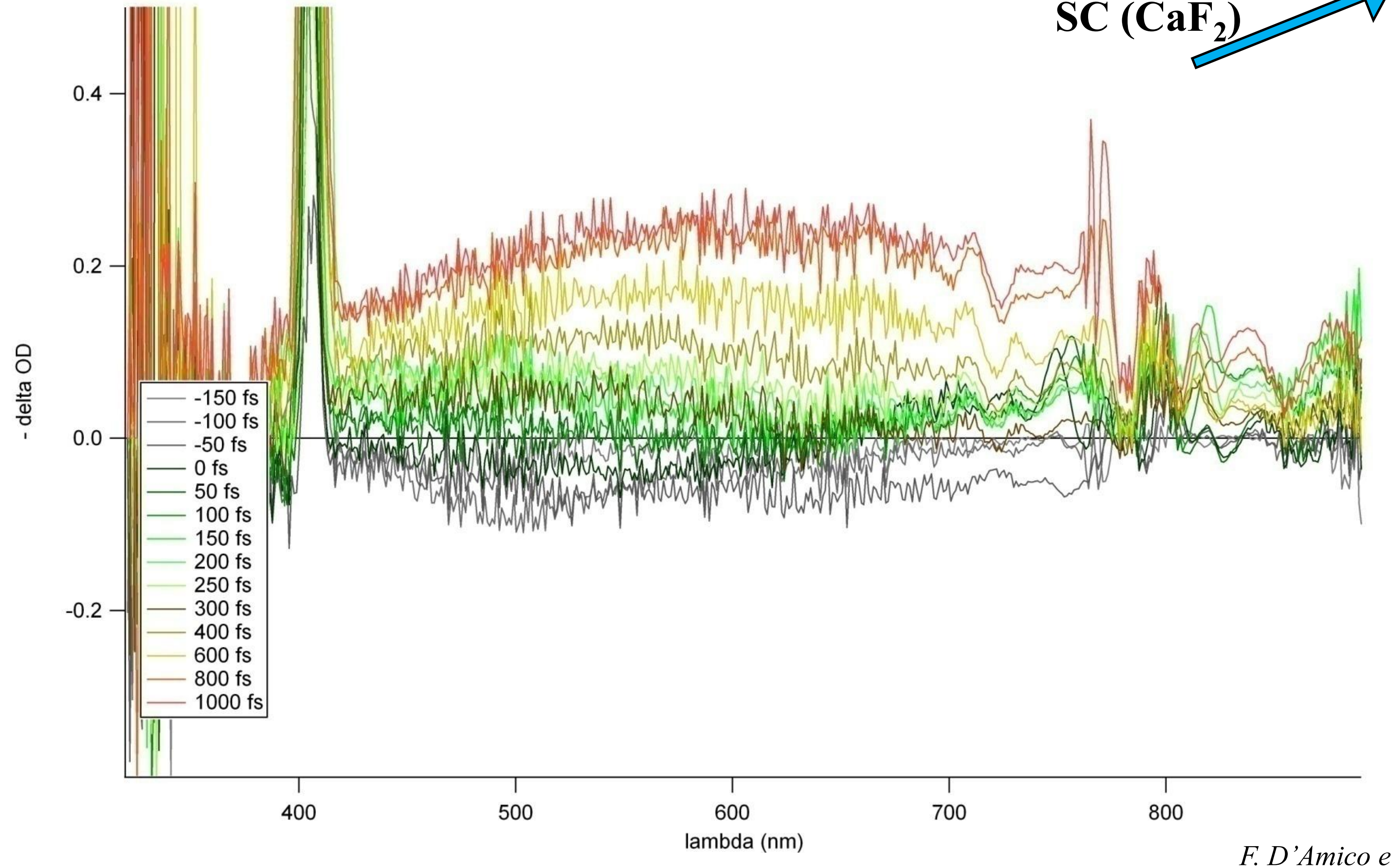
Si foil



Jitter may be kept ~ 30 fs

TIMEX first developments





F. D'Amico et al., in preparation