RAL-TR-2006-028

Vibrational Spectroscopy at Central Facilities

Stewart F. Parker, Gianfelice Cinque, Paul Dumas, Peter Gardner, Anthony W. Parker, Keith Refson, Elaine Seddon, Kevin Smith, John V. Wood

31st October 2006

Vibrational Spectroscopy at Central Facilities

On the 31st August 2006, a joint meeting of the Royal Society of Chemistry Molecular Spectroscopy Group and the Infrared and Raman Discussion Group (IRDG) was held at the Rutherford Appleton Laboratory with the theme 'Vibrational Spectroscopy at Central Facilities'. The meeting attracted around 35 people from a diverse range of backgrounds, both academic and industrial. The event provided a snapshot of the many activities in vibrational spectroscopy that are carried out at central facilities, particularly those of CCLRC. In addition, the meeting provided a forward look at the next generation infrared beamline at Diamond and an update on the progress and possibilities of 4GLS, a free-electron laser facility that will span the infrared to the X-ray regions.

This report contains the presentations of all the speakers and provides an overview of a field that is undoubtedly one of CCLRC's strengths and emphasises the world-leading capabilities in both experimental and computational science.

Stewart F. Parker

Vibrational Spectroscopy at Central Facilities:

A joint meeting of the Royal Society of Chemistry Molecular Spectroscopy Group and the Infrared and Raman Discussion Group

Thursday 31st August 2006
Venue: Conference Rooms 12 & 13, Rutherford Appleton Laboratory

10:00	Coffee and Registration
10:30	Introduction to CCLRC *Professor John Wood, CEO CCLRC*
10:45	High-Resolution Infrared Studies at the RAL Molecular Spectroscopy Facility. *Dr Kevin Smith, Atmospheric Science, CCLRC*
11:20	Time Resolved Vibrational Spectroscopy of DNA. *Professor Tony Parker, Central Laser Facility, CCLRC*
11:55	DFT Analysis of Vibrational Spectra *Dr Keith Refson, Computational Materials Science Group, CCLRC*
12:25	Vibrational Spectroscopy with Neutrons: Catalysts, Hydrides and Polyethylene *Dr Stewart Parker, ISIS Facility, CCLRC*
13:00	Lunch and photograph
14:00	Synchrotron Infrared Microspectroscopy *Dr Paul Dumas, Soleil Synchrotron, Paris*
14:50	Synchrotron Reflection Absorption Infrared Spectroscopy *Dr Peter Gardner, School of Chemical Engineering and Analytical Science, The University of Manchester*
15:25	The Infrared Beamline at the New Diamond Facility. *Dr Gianfelice Cinque, Diamond Light Source*
15:35	Update on 4GLS *Dr Elaine Seddon, Synchrotron Radiation Source, CCLRC*
16:00	Closing Remarks *Tours of facilities (ISIS, CLF, MSF) available by prior appointment*

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Professor John Wood
CCLRC
August 2006

[illegible]

- Enabling research
- Building partnerships
- Getting it right for science
- Engaging with society
- Exploiting own potential
- Developing strategy

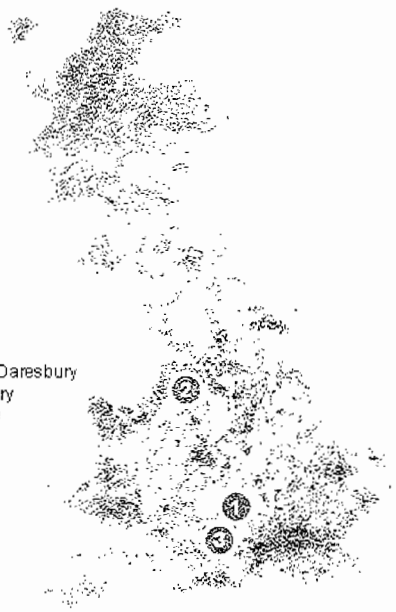
- One of eight UK research councils
- Formed by Royal Charter on 1 April 1995
- Funded by Department of Trade and Industry (Office of Science and Technology)
- 7,000 users annually
- Operating turnover £240m (2004-5)

three world class research laboratories...

CCLRC Rutherford Appleton Laboratory Oxfordshire

CCLRC Daresbury Laboratory Cheshire

CCLRC Chilbolton Observatory Hampshire



Wholly owned facilities:

- **Laser – Vulcan, Astra**
- **Neutron - ISIS**
- **Synchrotron - SRS**
- **Computing – HPCx**

Shareholder in:

- **Diamond (majority shareholder on behalf of the UK government)**
- **ILL/ESRF**

- Particle Physics
- Space Science and Technology
- Instrumentation and sensors
- E-science and grid technology
- Micro and nano-fabrication
- Energy
- Radio Communications
- Engineering design
- Knowledge transfer

Increased capacity

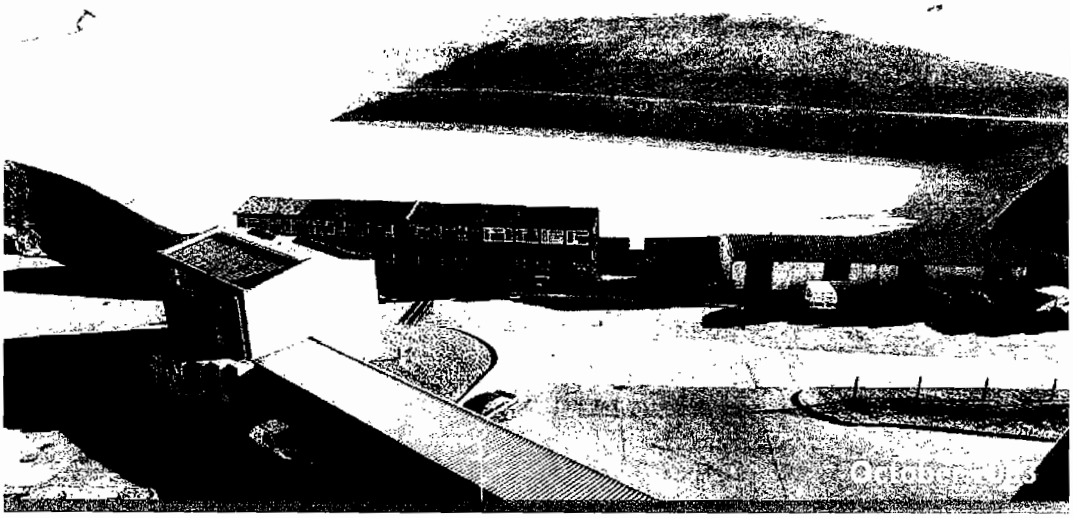
Increased capability

New opportunities for:

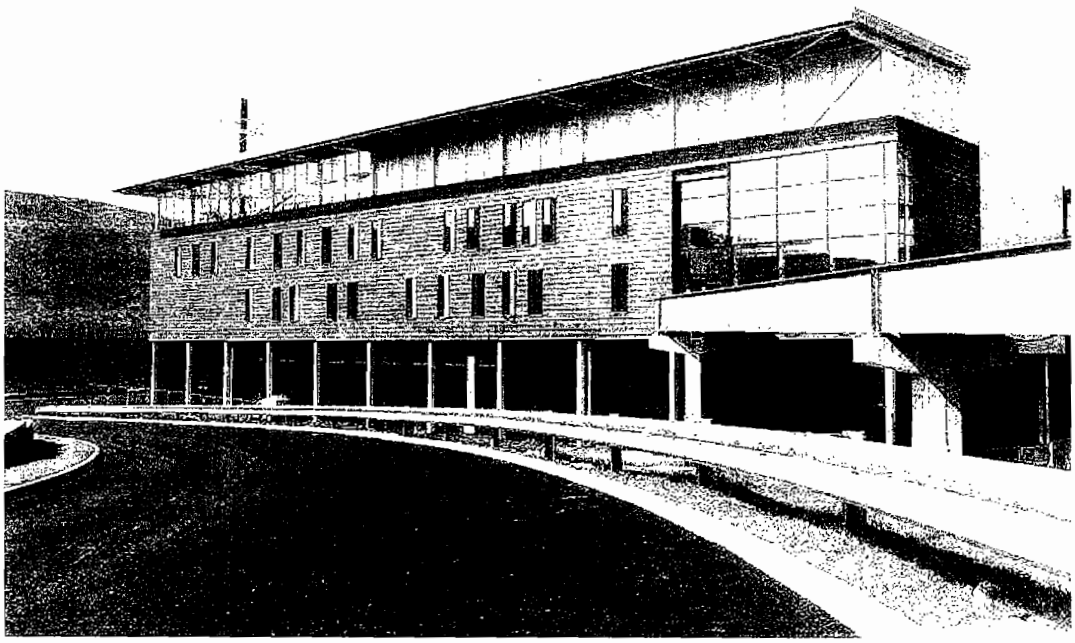
- Soft Matter
- Advanced Materials
- Biomolecular Systems

Nanoscience

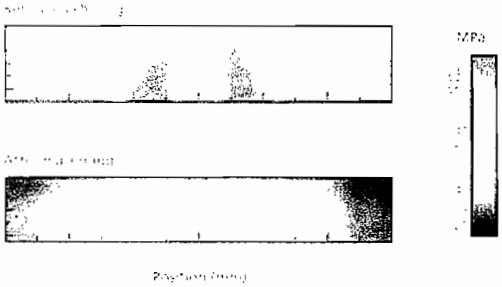
ISIS TS2



TS2 ISIS



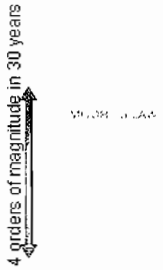
- **Neutron Strain Measurements**

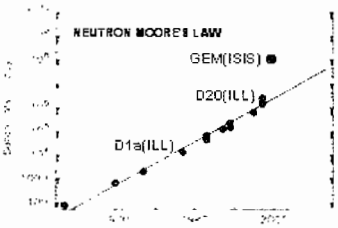


A380 wing section

Data curation

- **Volume of data increasing dramatically**
- **Issues of filtering, mining, storage and management**





Neutron powder diffraction data rates (1950-2010) (4 orders of magnitude gain with ILL/ISIS alone)

- **Conserving experimental data for future research**
- **the next big challenge**

[illegible]

Sources of mixed mode, high intensity X-rays and synchrotron light

- SRS
- ESRF
- Diamond
- 4GLS

4

[illegible]

High power, state-of-the-art laser facilities

Vulcan

- the world's highest intensity focused laser
- Recreating conditions on the sun in the lab

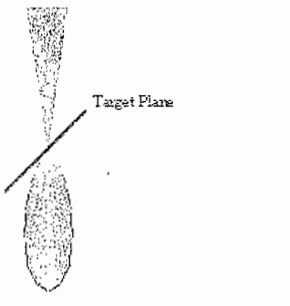
Astra

- high power, ultra short pulse titanium-sapphire laser
- Following chemical and biological reactions

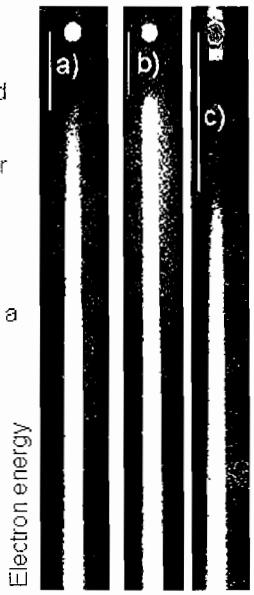
Lasers for Science

- optical tweezers

- Electron acceleration studies in gas jets
- EMP (electromagnetic pulse measurements) + buried layer heating studies
- Solid target interaction studies
- Studies of advanced fast ignitor concept for iCF (Inertial Confinement Fusion)
- Electron transport measurements in solids
- Ultra high density plasma investigations



- Highest energy accelerating field in plasma
- Brightest Gamma ray beam ever produced
- Largest laser induced nuclear conversion
- Highest flux ever delivered from a laser plasma interaction
- Capable of producing a beam with an intensity of 10^{21} w/cm^2.



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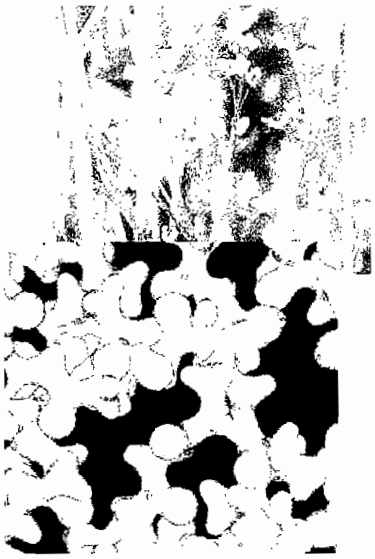
HPCx

- Europe's most powerful academic computer
- Quantum mechanics of proteins – calculations of unprecedented scale
- Electronic structure of Crambin (extracted from Abyssinian Cabbage)
- Calculation was 10 times more challenging than any published before
- Similar techniques will be used to study proteins of greater scientific value e.g. the redox potentials of Rusticyanin, a blue copper protein involved in electron transport in plants and bacteria



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Experiments at

CERN: **ATLAS, CMS, LHCb**

DESY: **H1, ZEUS**

FNAL: **MINOS**

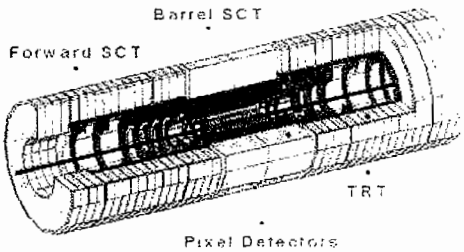
SLAC: **BaBar**

ILL: **Neutron edm**

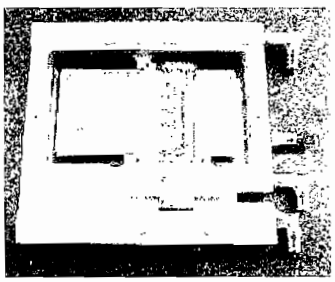
Boulby: **Dark matter**

R&D: **Linear Collider, Neutrino Factory**

ATLAS Semiconductor Tracker

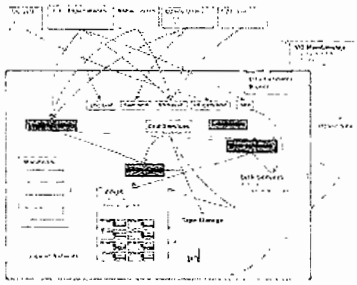


ATLAS Tracker Modules



Grid enabling CCLRC facilities

- Portals
- Data storage architecture
- Computing resources
- Visualisation



Europe's largest space science and technology department

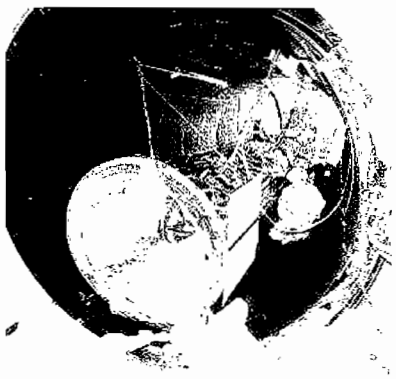
167 instruments in space

Collaborations with:

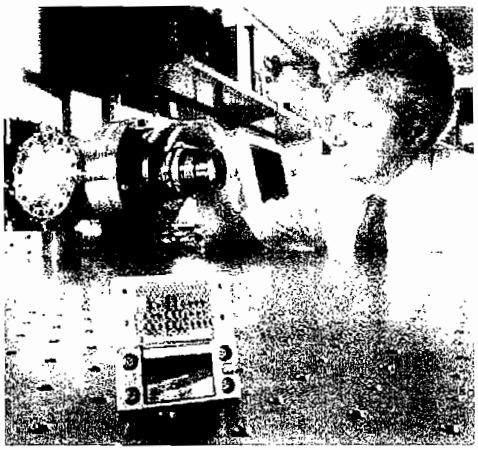
- NASA
- ESA
- PPARC, NERC

Quality assured:

- ISO 9001
- TickIT




- CCDs and cameras
- Space Coolers
- Optical/Electronics design
- Thermal structural design
- Sensors and Detectors
- Millimetre wave components
- Orbit dynamics/mission analysis
- Smart technology
- Payload operations systems

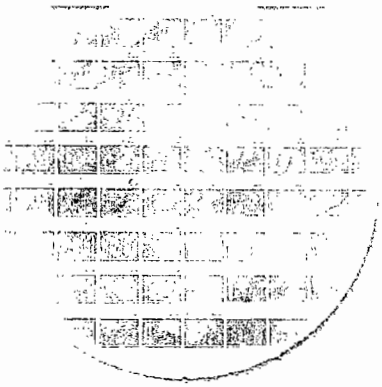


SMART-1 - Europe's first mission to the Moon

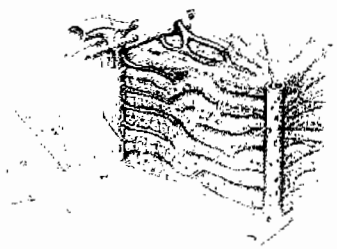
- **testing innovative technologies for future deep space missions (low mass, low volume, low power)**
- **D-CIXS - Demonstration Compact Imaging X-ray Spectrometer, designed and built at RAL**
- **Producing the first X-ray map of the Moon**

Underpinning CCLRC science

- **Microelectronics design**
- **Detector design**
- **Data acquisition electronics**
- **Control systems design**



Nature's design

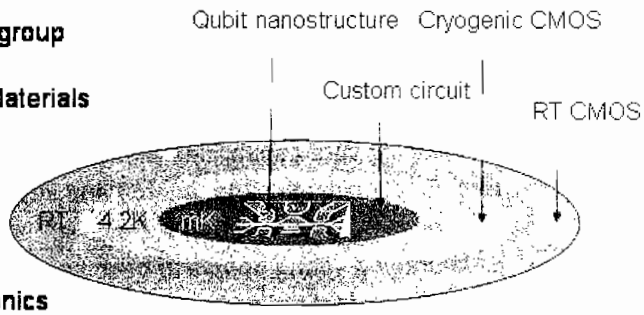


Powder blasted tissue scaffold to form sinusoid

- **Project aims to simulate complex tubes which carry blood around the liver**
- **Constructing nanometre scaffolding in which to grow liver cells**
- **Artificial liver will be used for testing drugs in the laboratory**

School of Pharmaceutical Sciences, University of Nottingham
Central Microstructure Facility, CCLRC & Mechanical Engineering, University of Leeds

- **CCLRC Microelectronics group**
- **Oxford – Department of Materials**
- **Hitachi Cambridge**
- **Oxford instruments**
- **Cambridge – Microelectronics Research Centre, Cavendish Lab**



CLIK Ltd

- formed in March 2002
- to stimulate and nurture start up and licensing opportunities for CCLRC
- Rainbow Seed Corn Fund

4 spin-out companies formed in the last 12 months:

- L3T – near patient cholesterol testing
- Microvisk – diagnostics for blood viscosity and clotting measurements
- Oxsensis – sensors for hellish environments such as jet engines
- Thruvision – terahertz imaging for security screening

- Promoting the added value of bringing together core teams to deliver world class science and to exploit innovations for the UK
- Developing core capabilities with national and international partners (e.g. focal points in nano, energy and space)
- Encouraging young people to become actively involved in vibrant science and technology

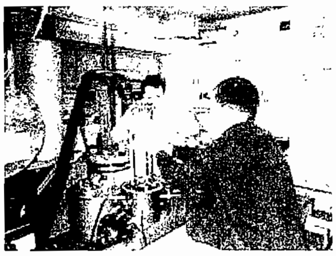
High-Resolution [illegible]
[illegible] Molecular [illegible]

Dr Kevin Smith [illegible]

CCLRC Rutherford Appleton Laboratory
Space Science & Technology Department

1

Background



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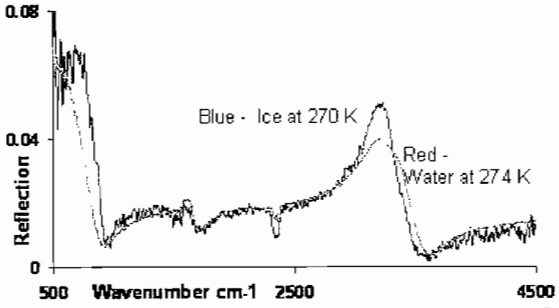
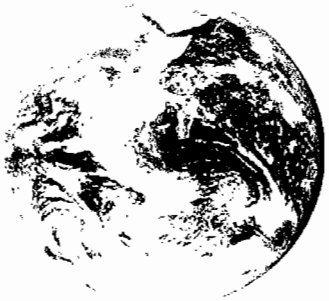

0.08
0.04
0
Reflection
Blue - Ice at 270 K
Red -
Water at 274 K
500
Wavenumber cm-1
2500
4500

3



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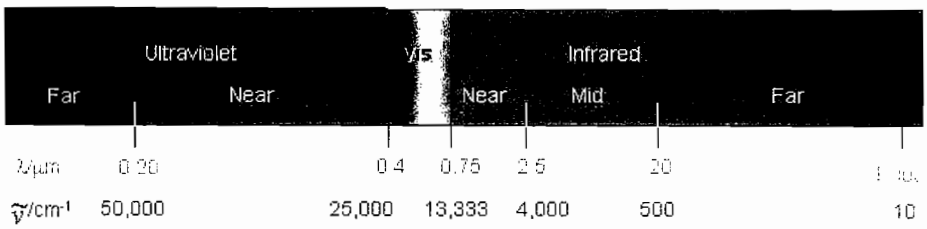
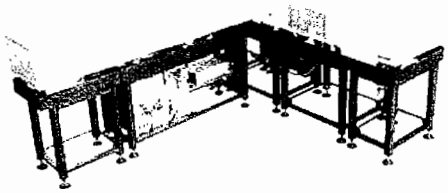
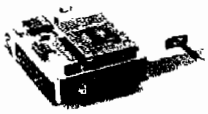
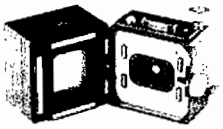

Ultraviolet
Vis
Infrared
Far
Near
Near
Mid
Far
λ/μm
0.20
0.4
0.75
2.5
20
1000
ν̃/cm⁻¹
50,000
25,000
13,333
4,000
500
10







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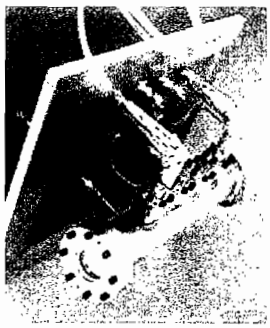

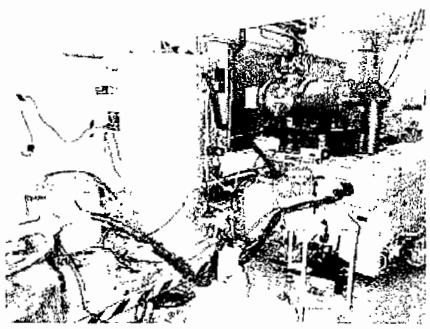

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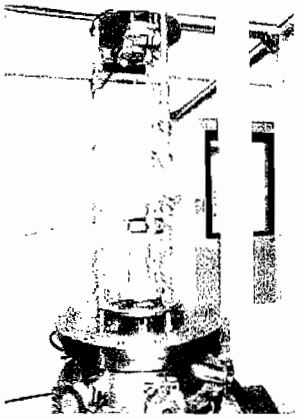
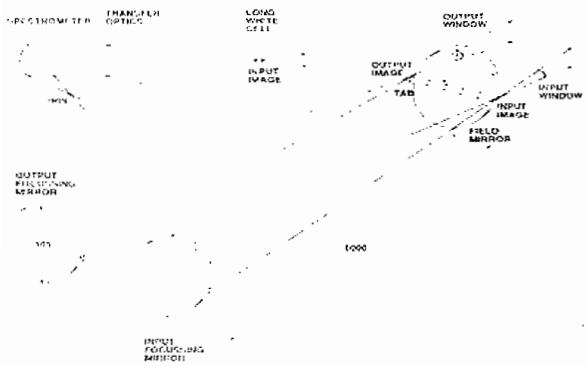


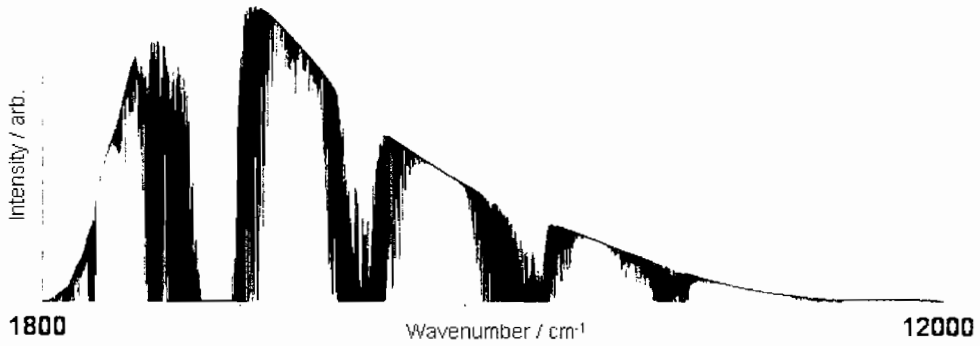


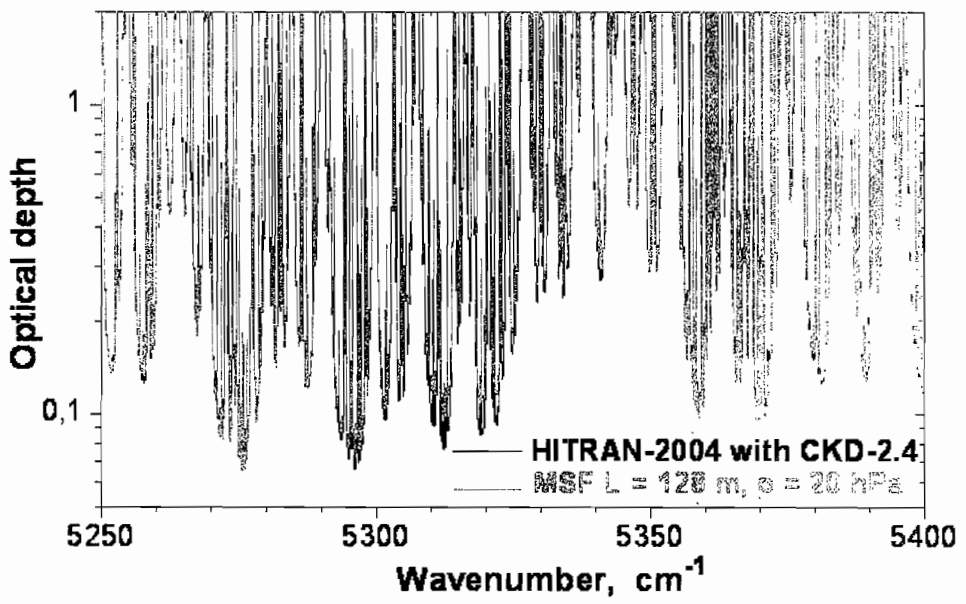
Water vapour (University of Reading)

Methane (University of Oxford)

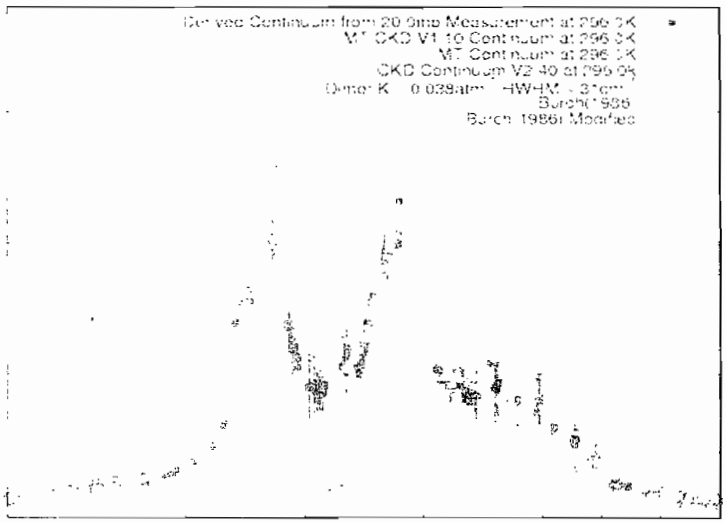
PSCs, mineral dust (University of Oxford, The Open University)

PAN (University of Leicester)

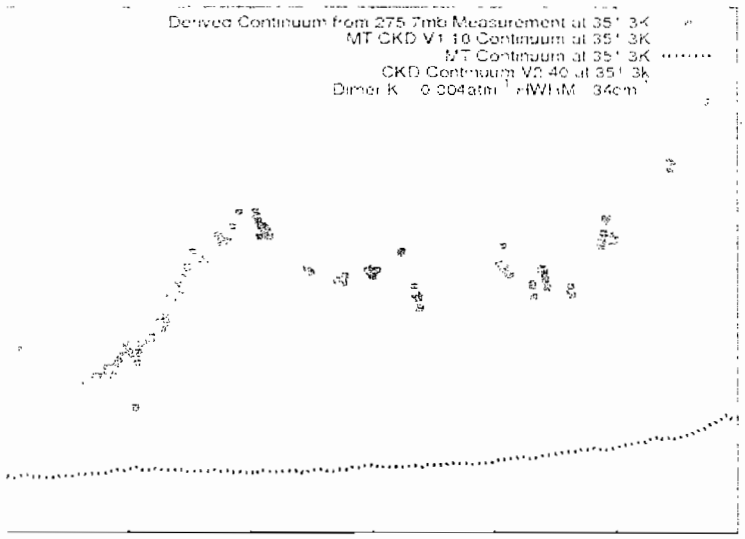

Intensity / arb.
1800
Wavenumber / cm-1
12000

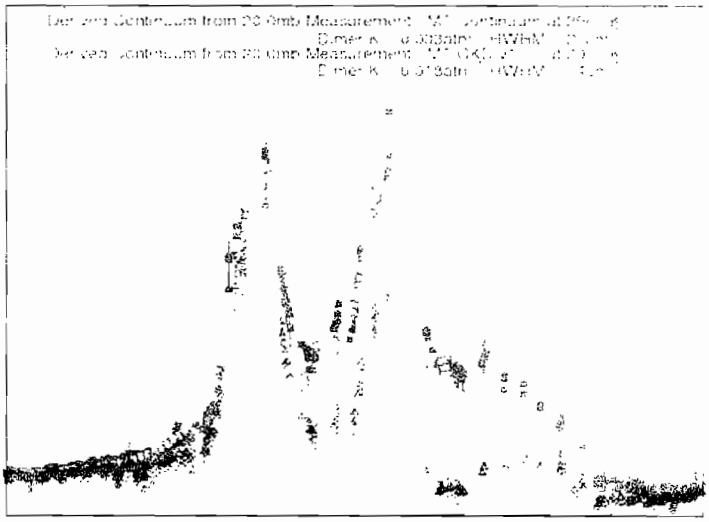

Optical depth
1
0,1
HITRAN-2004 with CKD-2.4
MSF L = 126 m, p = 20 hPa
5250
5300
5350
5400
Wavenumber, cm-1

10

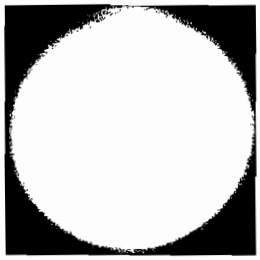

Derived Continuum from 20.0mb Measurement at 296.2K
MT CKD V1.10 Continuum at 296.2K
MT Continuum at 296.2K
CKD Continuum V2.40 at 296.0K
Burch 1986 Modified

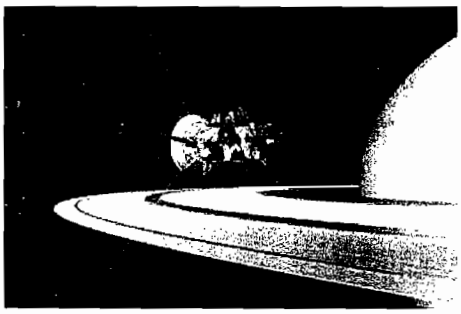
11

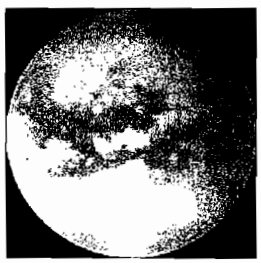

Derived Continuum from 275.7mb Measurement at 351.3K
MT CKD V1.10 Continuum at 351.3K
MT Continuum at 351.3K
CKD Continuum V2.40 at 351.3K



13

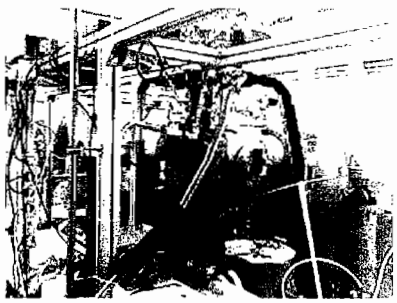


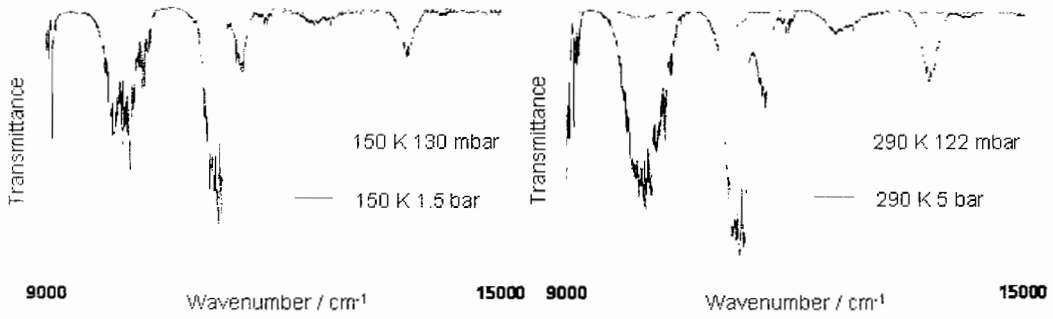




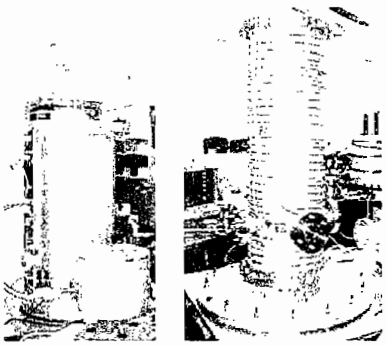
14

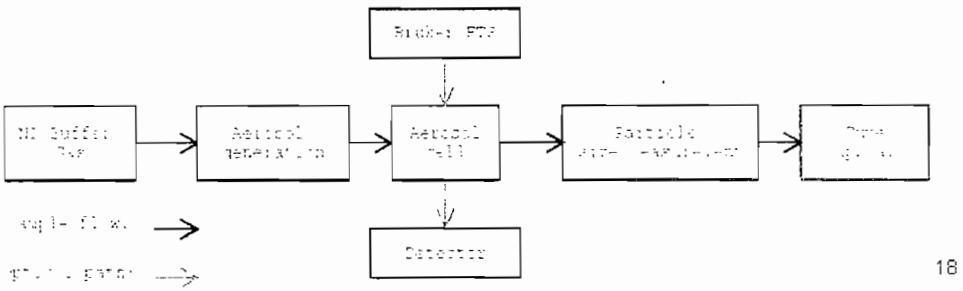
15




Transmittance
150 K 130 mbar
150 K 1.5 bar
9000
Wavenumber / cm-1
15000
Transmittance
290 K 122 mbar
290 K 5 bar
9000
Wavenumber / cm-1
15000

17





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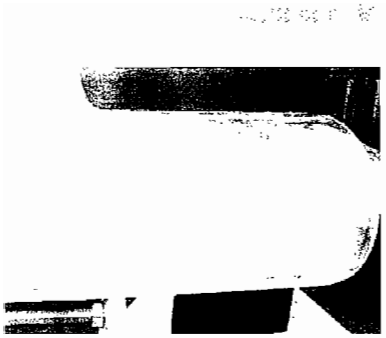

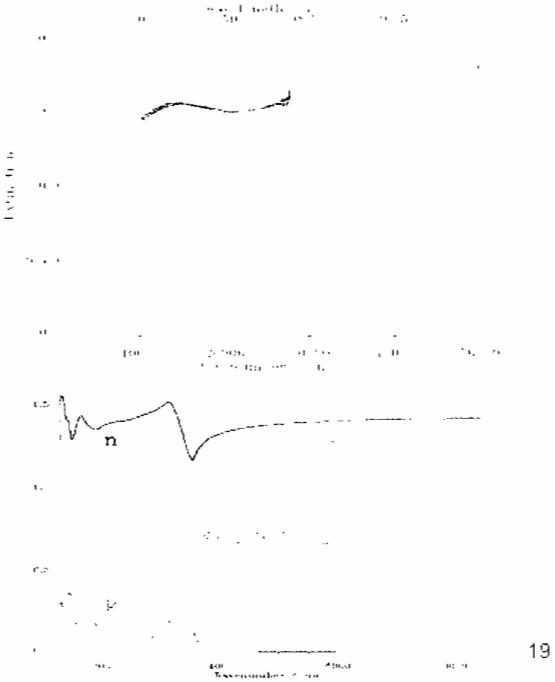

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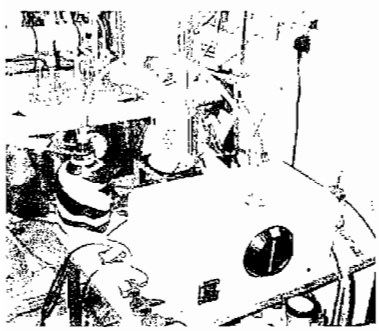
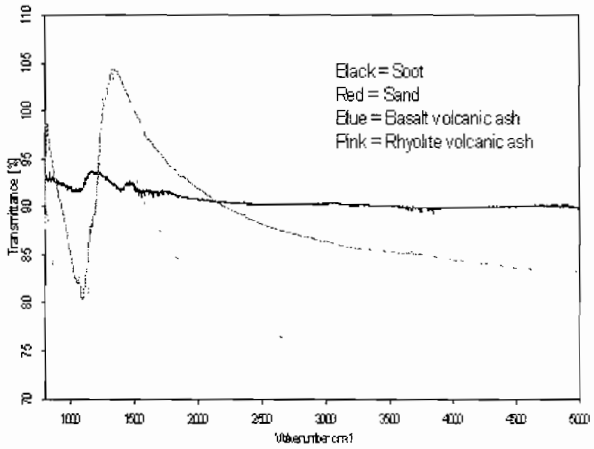
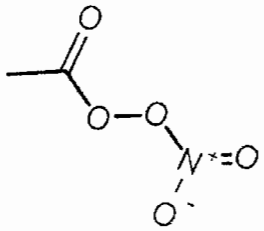



Black = Soot
Red = Sand
Blue = Basalt volcanic ash
Pink = Rhyolite volcanic ash
Transmittance [%]
Wavenumber cm-1



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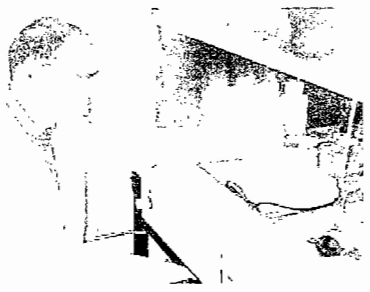

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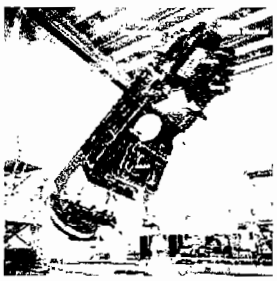
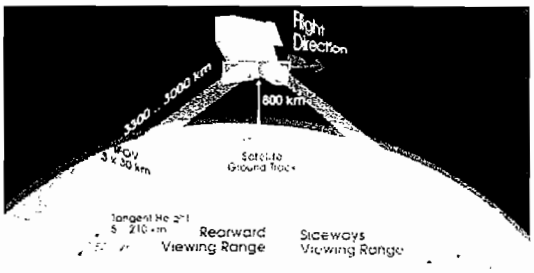
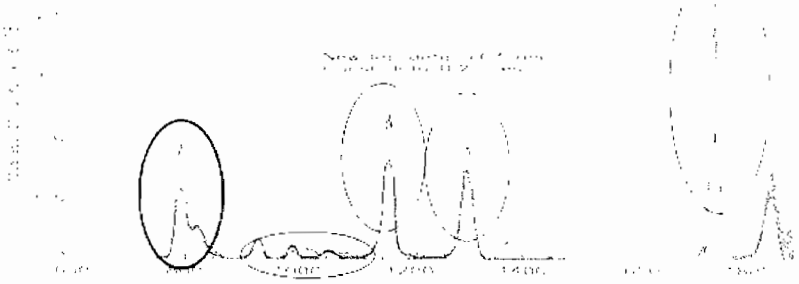



Flight Direction
3500 ... 5000 km
800 km
Satellite Ground Track
Rearward Viewing Range
Sideways Viewing Range

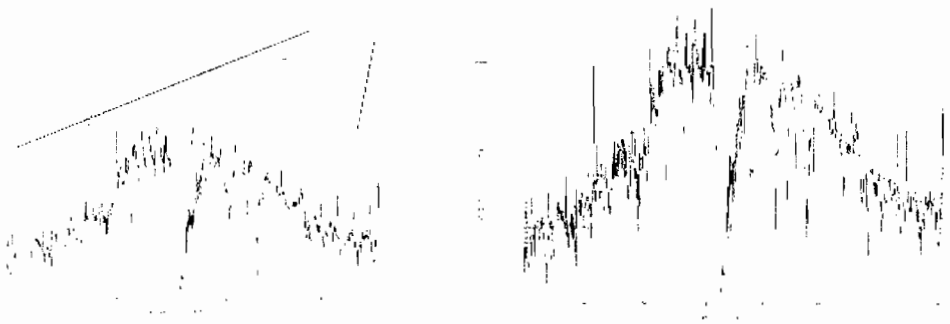

thick cloud
cloud free



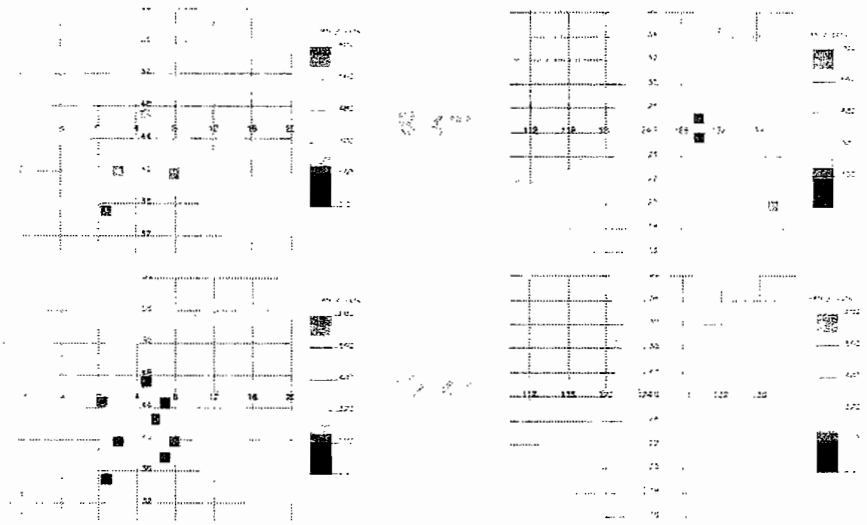
[illegible]

[illegible] based on MSF cross sections

BLACK = MIPAS atmospheric radiance spectra



[illegible]



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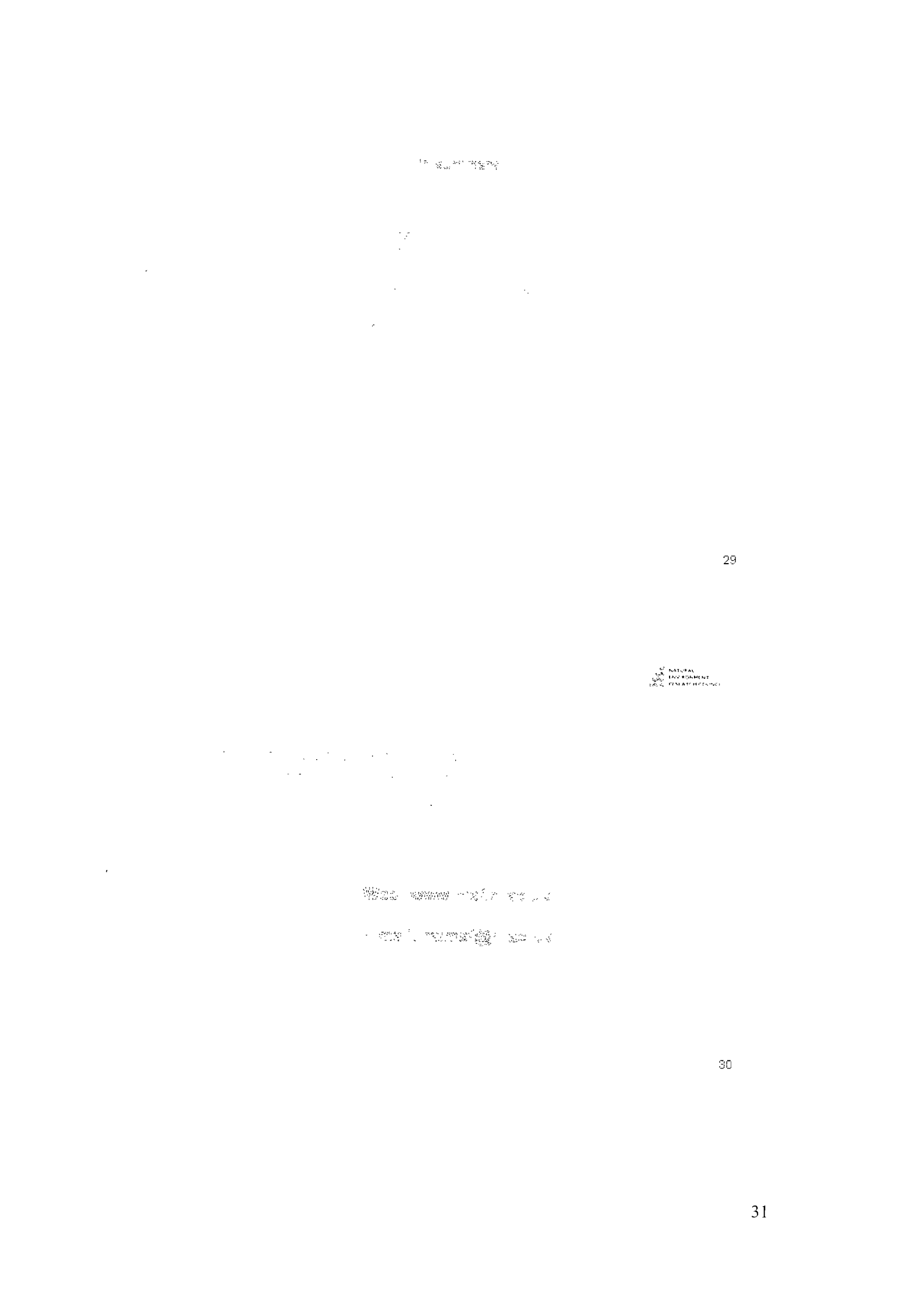


Time Resolved Vibrational Spectroscopy of DNA

Anthony W. Parker (a.w.parker@rl.ac.uk)

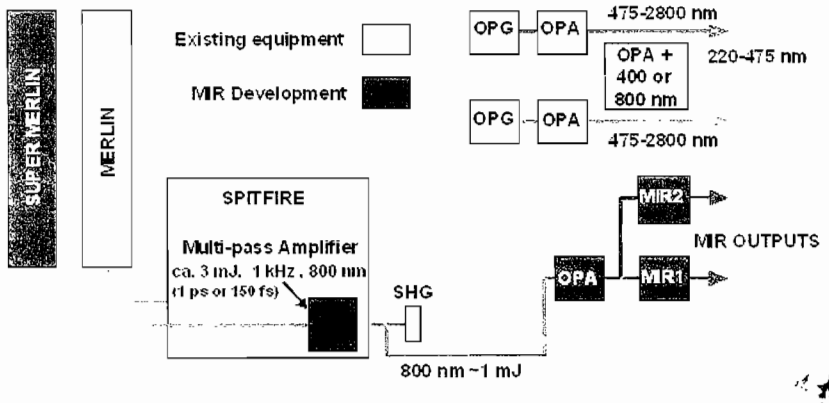
- PIRATE
- Molecular Structure of Transient Intermediates

  Nucleic Acid Bases

  UV Excitation

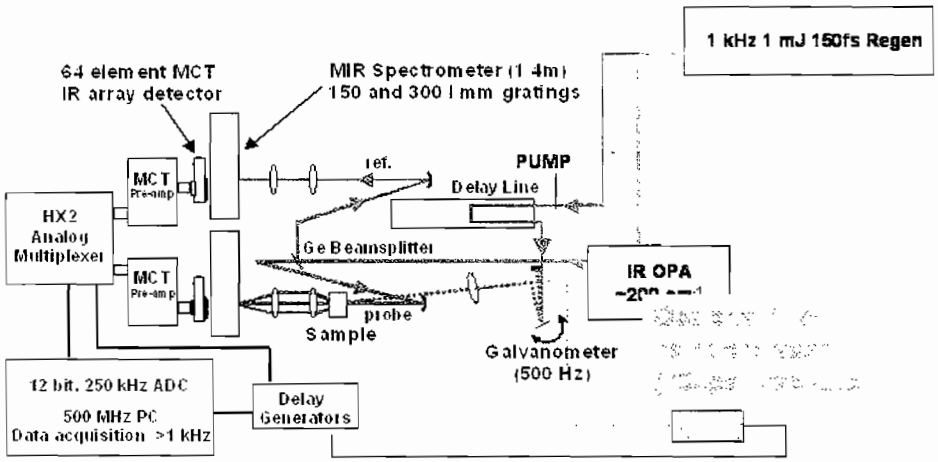
  Photoionisation

Schematic layout of the laser system and OPAs



Picosecond Infra Red Absorption Transient Excitation

The Broadband Pump-Probe TRIR Spectrometer



A High-Sensitivity Femtosecond to Microsecond Time-Resolved Infrared Vibrational Spectrometer
M. Towrie,* A. Gabrielsson, P. Matousek, A. W. Parker, A. M. Blanco Rodriguez, and A. Vlc̆ek, JR.

Levels of "potential" DNA Damage & measurement

- ***Solar Radiation - Sunny Day***
  – 200 W/m^2 gives potentially 8 x 10^{18} potentially harmful events per cell/day.

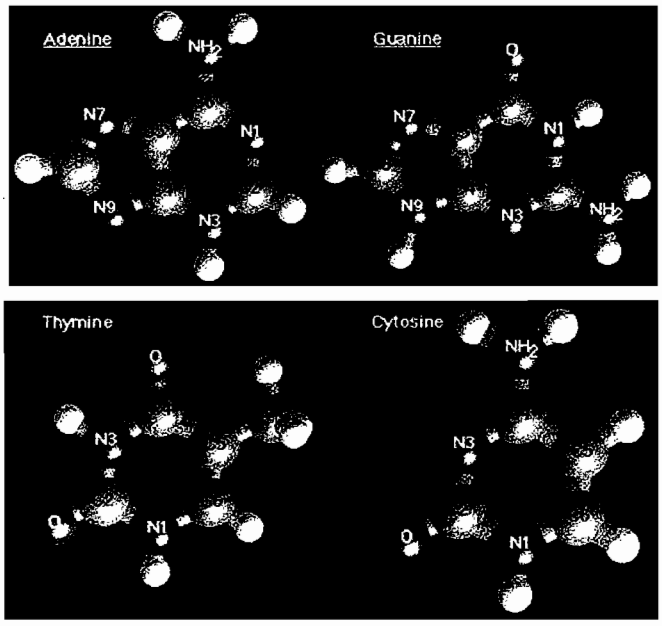
- ***Background Radiation -***
  – 100 mrem/year inflicting c. 2 harmful events per cell/day

- ***Physical carcinogens (chemical pollution)***
  say 1 ppm, air exchanged between average lung per day – 7000 l, equivalent to 0.01g toxin per day, assuming 0.1% activity, studies show pollutants generate 10^{18} radicals per gram. With finite probability of these generating deleterious effects estimated c. 3 x 10^4 potentially harmful effects per cell/day

- ***Detectivity – DNA damage detection using immuno assay (apurine /apyrimidine) utilising anti-AP and fluorescence 100 units per DNA***

Effects of electronic excitation on DNA bases, polynucleotides and DNA

Nucleic Acid Bases & DNA



http://www.blc.arizona.edu/Molecular_Graphics/DNA_Structure/DNA_Tutorial.HTML#helixaxis

UV Excitation of DNA & Components

- **UV radiation gives**

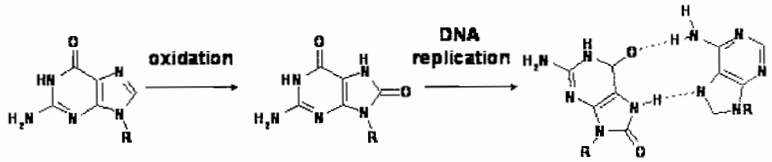
singlet	triplets
lifetimes < 1ps	$\Phi_T \leq 0.01$
$\Phi_f \leq 10^{-4}$	E_T ~300 kJ mol^{-1}

- **Chemical reactions**
  cyclobutane pyrimidine dimers

- **Photoionisation**
  Base + hν → Base$^{+\bullet}$ + electron

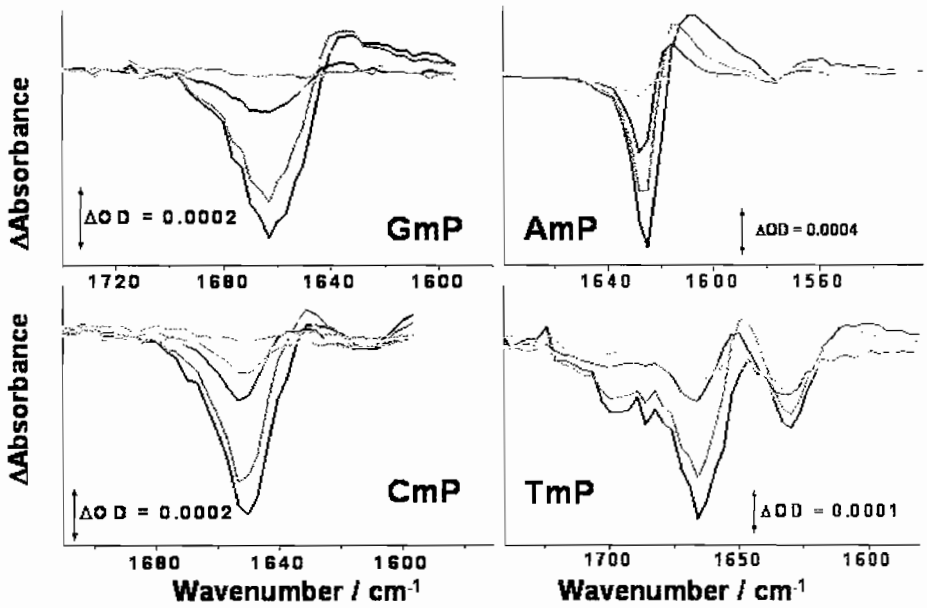
  Base$^{+\bullet}$ + H_2O → 8-oxo-G

GG/C-C can give AA/C-C on replication

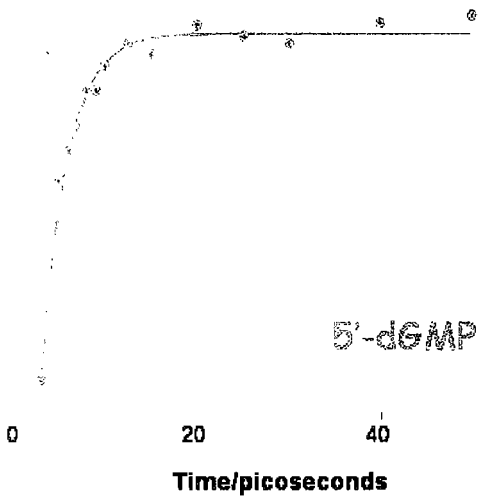


Orlov et al.-Tetra Lett 1976, vol 48, p4377; Fernando (LeBreton) PNAS 1998 vol 95 p5550; IP in solution:- 4.47/4.9 eV to 5.57/5.5 eV

267 nm pump IR probe (1-50 ps)



267 nm excitation: Kinetics

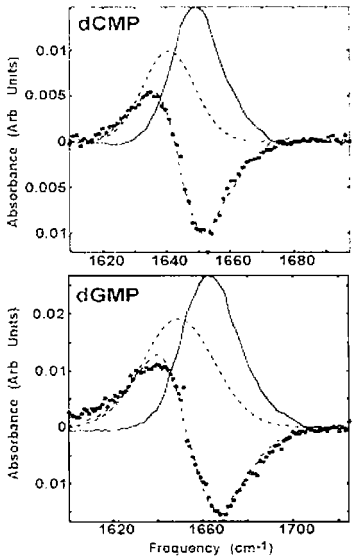


Base	lifetime
5'-dGMP	2.9 (±0.2) ps
5'-dCMP	4.7 (±0. 3) ps
5'-dAMP	4.3 (±0.2) ps
5'-TMP	2.2 (±0.1) ps

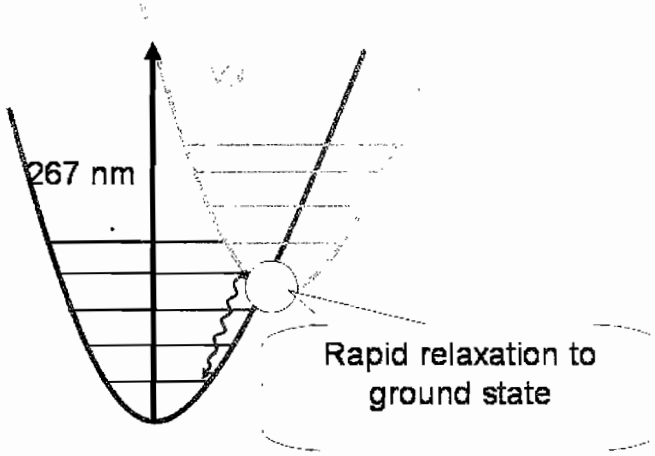
The cross-peak (T = 400 fs) of v = 1 → 2 transition

A. T. Krummel, P. Mukherjee and M. Zanni, J. Phys. Chem. B., 2003, 107, 9165.

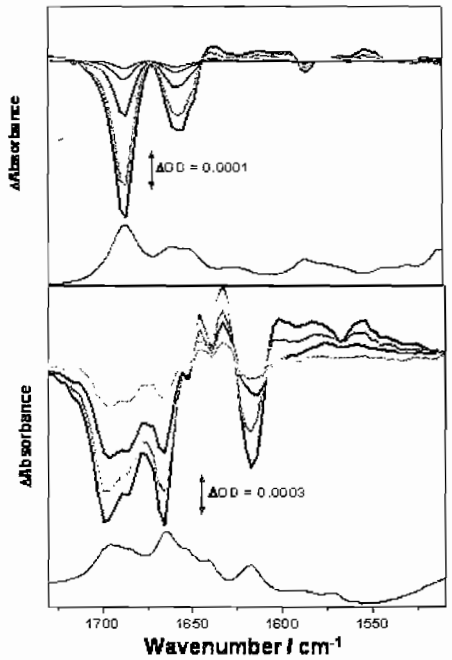
A comparable shift is identical to the 267 nm ps-TRIR study of dGMP and dCMP



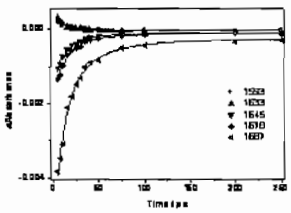
267 nm excitation: Mechanism



UV pump IR probe of poly-strands (1-1000 ps)



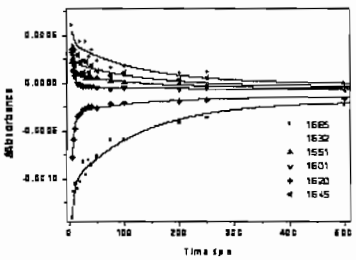
polydG-dC• polydG-dC



biexponential

τ =12 & 50 ps

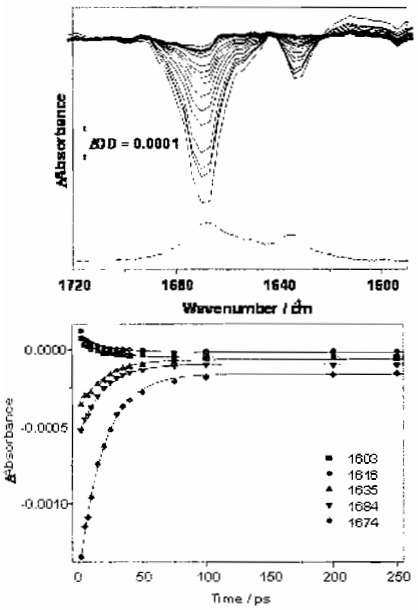
polydA-dT• polydA-dT



τ =4 &140 ps

UV pump IR probe of poly-strands (1-1000 ps)

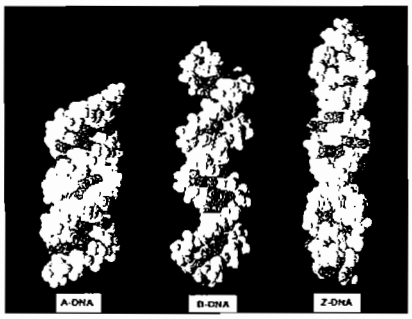
Z- polydG-dC• polydG-dC



monoexponential

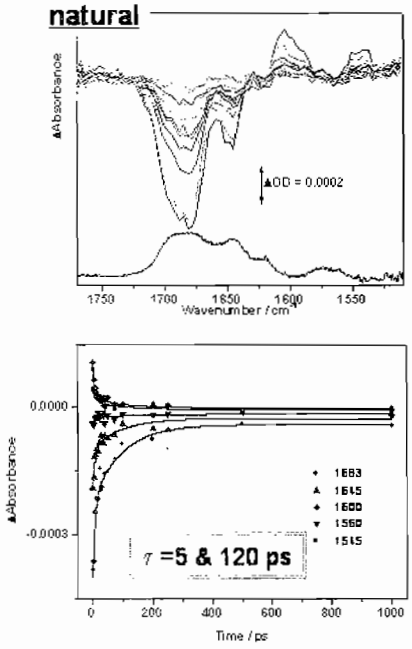
τ =19 ± 3 ps

- Solvation ?
- H-bonding?

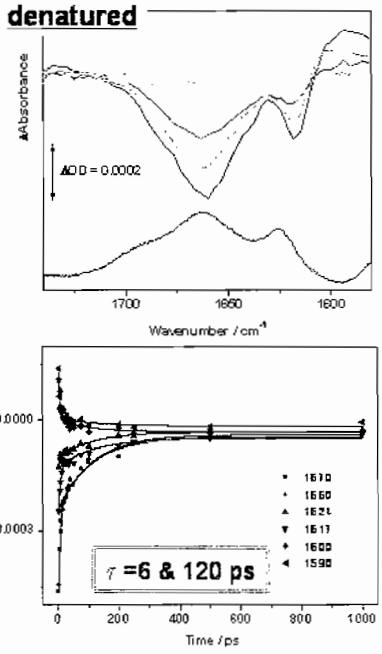


UV pump IR probe CT DNA

natural



denatured



267 nm excitation of DNA - Conclusions

•Electronic excitation leads to rapid S_1 to S_0
(in agreement with others)

•ps-TRIR used to directly observe vibrationally hot (S_0, $\nu \geq 1$) ground state nucleobases following electronic excited state relaxation.

•Polynucleotide strands give complex spectra with longer-lived transients. Assignment is less clear

M. K. Kuimova, J. Dyer, M. W. George, D. C. Grills, J. M. Kelly, P. Matousek, A. W. Parker, X. Z. Sun, M. Towrie and A. M. Whelan
Chem. Commun., 2005, (9), 1182 - 1184

Direct photoionisation of DNA bases as a step towards DNA photodamage

DNA Damage Through Radical Ion Formation

➢*S*tudy the study the primary chemical processes leading to mutations (cancer) of DNA caused by strand breakages.

Key question does DNA act as molecular wire?

➢2 processes of inflicting DNA damage

[illegible] via radicals indiscriminate

H_2O ⟶ ·OH,·H, electron + (ionising radiation) —DNA→ Reactions produce DNA products and lead to damage

[illegible] damage using 193 nm laser more precise - directly ionizes DNA

$$DNA \xrightarrow{193\ nm\ (6.4\ eV)} DNA^{+\cdot} + electron$$

+ 3.3 eV hydration energy

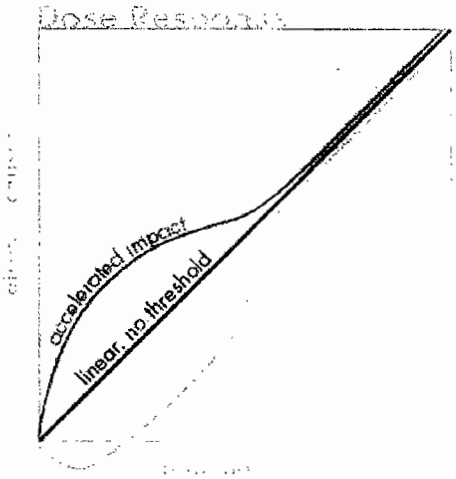
Consequence of Free Radical Damage

S. S. Wallace Free Rad Biol & Med (2002)

Lesion	Block to DNA polymerases	Lethal	Base inserted opposite in vitro	Mutagenic
Dihydrothymine	No	No	A	No
5-Formyluracil	No	No	A> G > C	T→C T→A
5-hydroxycytosine	No	No	G > A	C→T C→G
5-hydoxyuracil	No	No	A	C→T
8-Oxoguanine	No	No	C>A	G→T
Fapy-G	Yes	Yes	n.d.	No
8-oxoadenine	No	No	T>> G	Poor
α-Adenine	Yes	Yes	deletion	-1 deletion

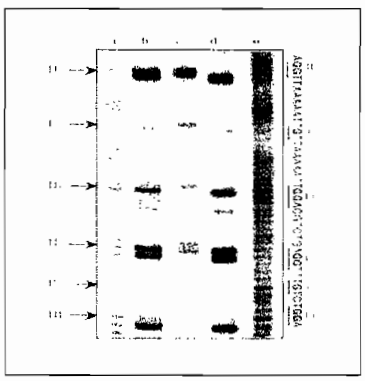
Linear no-threshold model

- The linear no-threshold model, LNT model, or LNTM is a model of the damage caused by ionizing radiation, and particularly the increased risk of cancer. It assumes that the response is linear and that this linear relationship continues to very small doses



http://whyfiles.org/020radiation/index.php?g=4.txt

DNA Damage - Base specific Sequence



Base sequence specificity of frank ssb (lane c, energy 5 mJ), Fpg excised damage (lane d, energy 2.5 mJ) and hot piperdine labile sites (lane b, 2.5 mJ) of the DNA 154 bp fragment ($A_5T_2GT_2A_5$) irradiated under aerobic conditions with 193nm light. Lanes a and e show Maxam Gilbert G+C sequence markers and hydroxyl radical cleavage sites respectively.

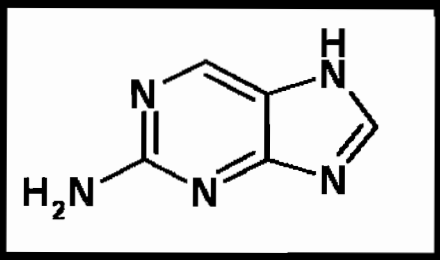
T. Melvin, S. Cunniffe, P.O'Neill, A. W. Parker & T. Roldan-Arjona Nuc. Acicds Res (1998) **21 4935**

- Study fundamental chemical events leading to DNA modification.
- 193 nm induces direct damage by monophotonic photionisation of bases.
- Strategic base sequence characterises where DNA breaks occur.
- Damage is enhanced at G sites indicating hole migration occurs (ease of oxidation G > A > C > T)
- Work shows that photoionisation results in a sequence dependent intra- ***not*** inter-strand charge migration of the radical cation of the nucleobases to G located with a few base pairs of the initial site of ionisation.

Direct DNA / bases ionisation

$$\text{Base} \xrightarrow{h\nu} \text{Base}^{+\bullet} + e$$

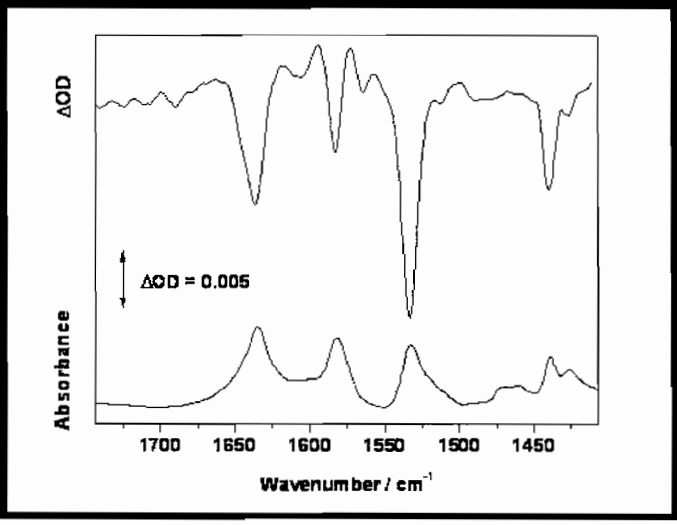
- 2-Aminopurine is Adenine analogue



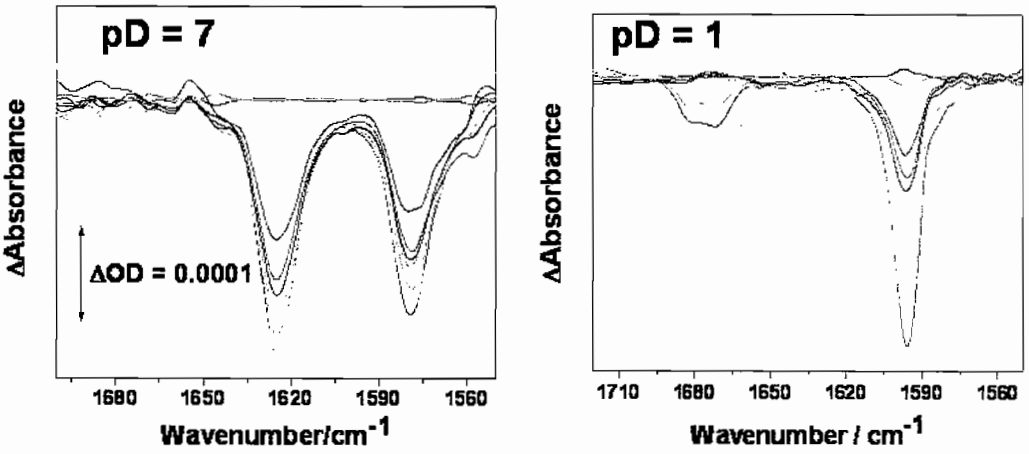
- 10 ns lifetime
- ionises at 308 nm
- participates in Watson-Crick base pairing

2-Aminopurine ionisation: 77K glass

- use of 77K H_2O glass is established method for stabilising $Base^{+\bullet}$ (EPR)

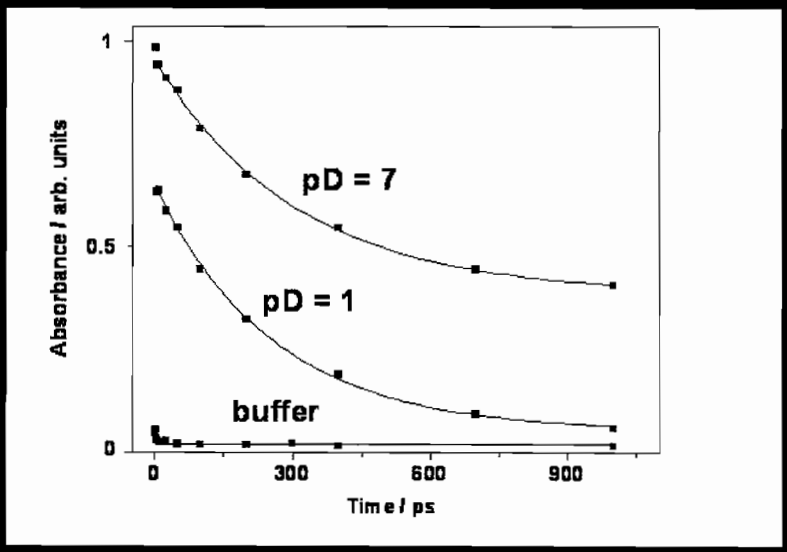


2-Aminopurine ionisation: solution



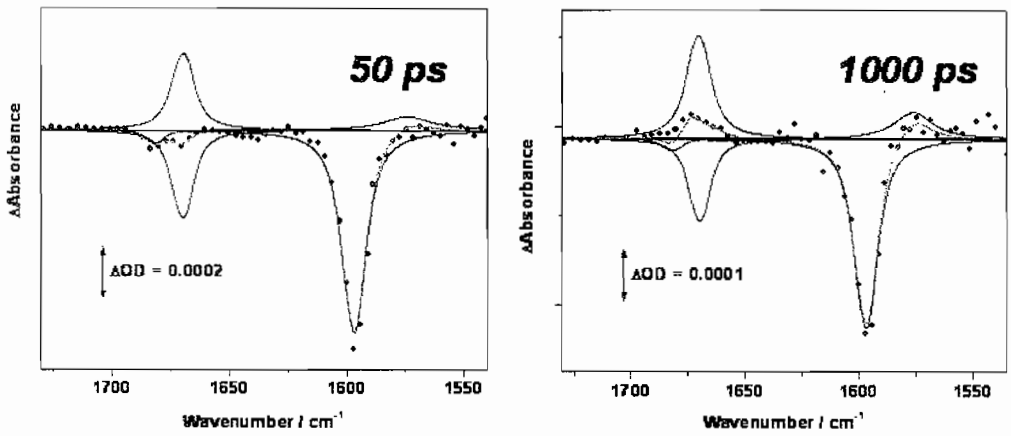
$2AP^{+\bullet}(-H^{+})$ ⇌ (pKa) $2AP^{+\bullet}$

2-AP ionisation: monitoring e_{aq} @ 800 nm



- 2AP is ionised in biphotonic process at pD=7 and pD = 1

2-Aminopurine ionisation: pD = 1



- In neutral solution 2AP+• deprotonates in < 2 *ps*
- Assignment supported by DFT calculations

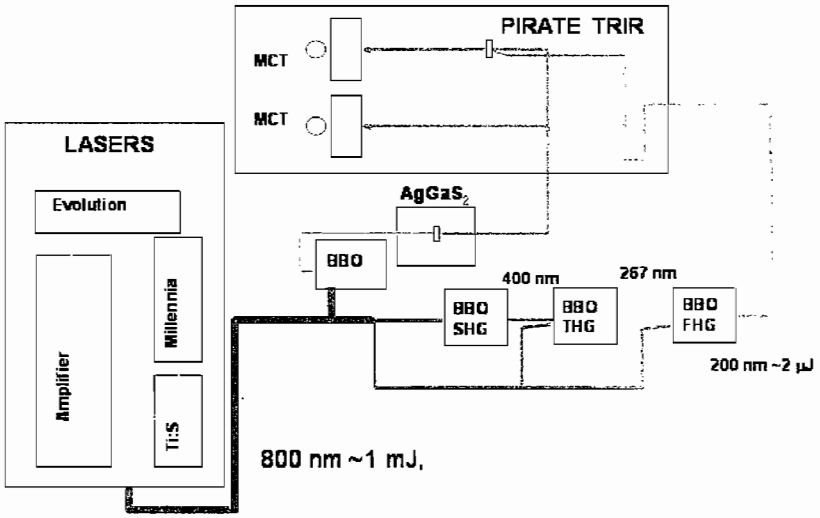
Natural DNA bases: ionisation

- **G, A, C, T are ionised in one-photon process at 193 nm**

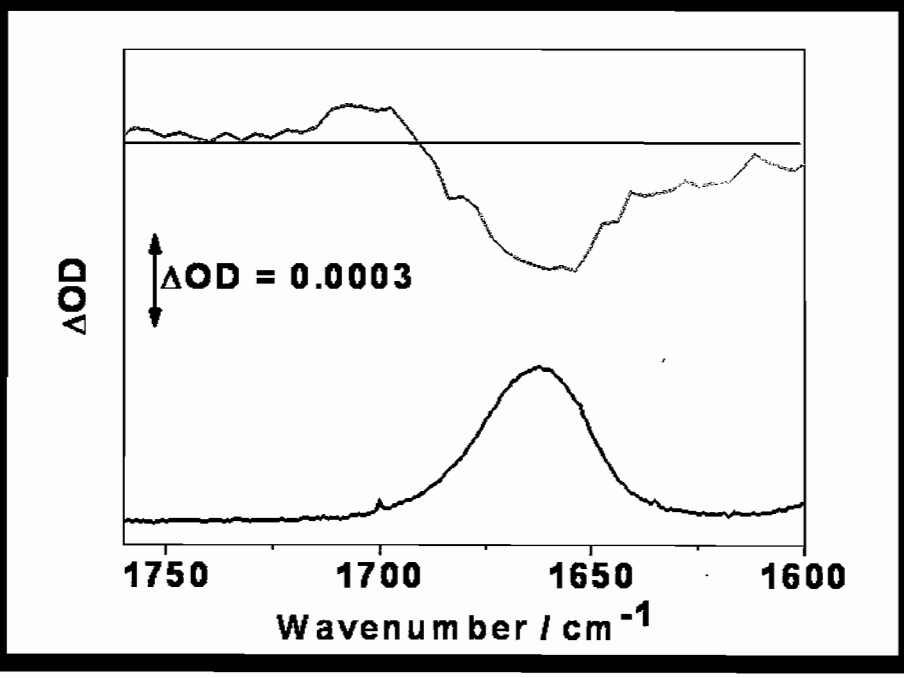
$$\text{Base} \xrightarrow{h\nu} \text{Base}^{+\bullet} + e$$

ps 200 nm excitation source was developed in RAL

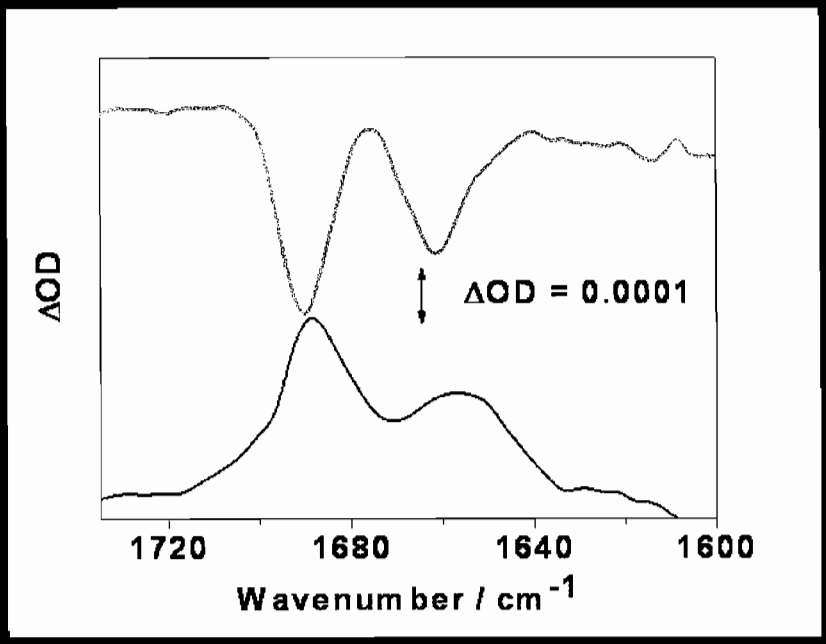
200 nm PUMP IR PROBE



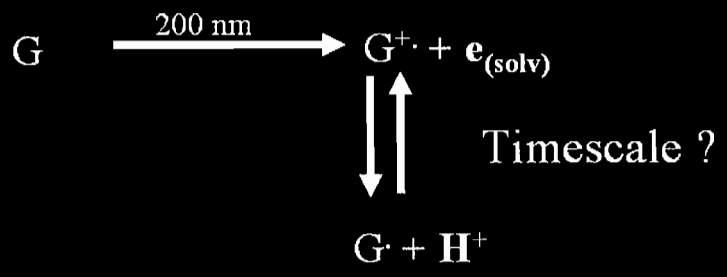
Guanine 200 nm ionisation: solution



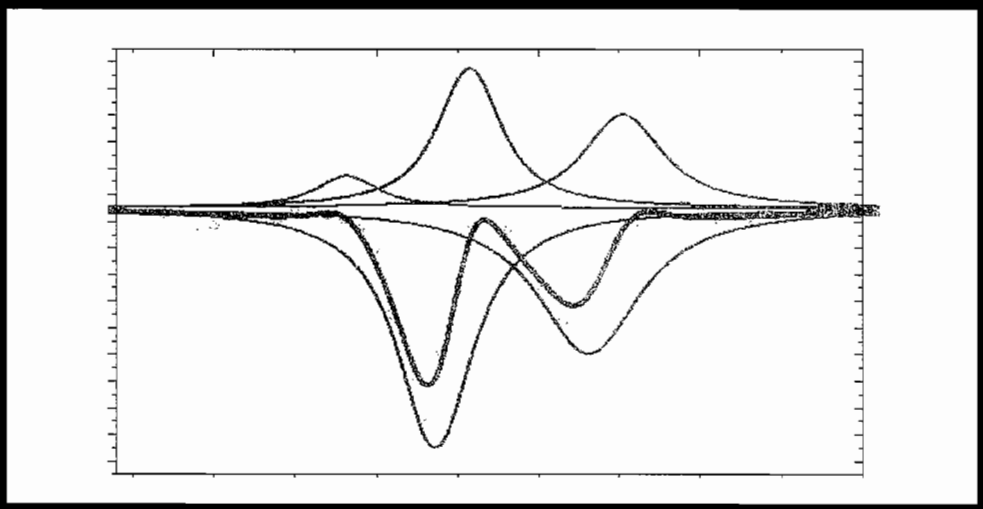
Poly(dGdC) ionisation: solution



Consequences of G Ionisation

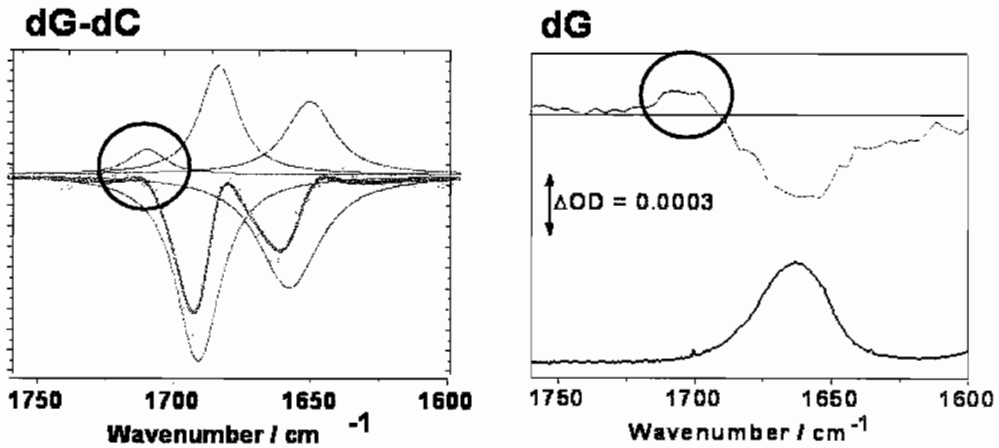


Poly(dGdC) ionisation: solution



Several transient bands are observed

DNA ionisation: solution



IR marker band of DNA damage

Ionisation yield monitoring e_{aq}

Substrate	Initial yield	Escape yield
NaCl	1	0.47
5'-GMP, pD = 7	0.03	0.03
5'-GMP, pD = 2	0.02	0.005
5'-GMP, pD = 13	0.04	0.03
5'-CMP	0.007	0.004
5'-AMP	0.005	0.003
5'-TMP	0.003	0.001
poly(dGdC)	0.05	0.03
CT DNA	0.05	0.03
50mM PO_4^{2-} buffer [a]	0.01	0.005

Photoionisation Conclusions

- 200 nm irradiation produces both excited states and photoionised species for G
- Excited states decay rapidly to vibrationally hot ground states analogous to 267 nm excitation
- C, A, T are not sufficiently photoionised
- Vibrational signature of $G^{+\bullet}$ is believed to be observed - characteristic of DNA damage
- Also, performed indirect studies using $[Co(NH_3)_4CO_3]NO_3$

MK Kuimova, AJ. Cowan, P. Matousek, AW. Parker, XZ. Sun, M. Towrie, MW. George. PNAS 2006 103: 2150-2153

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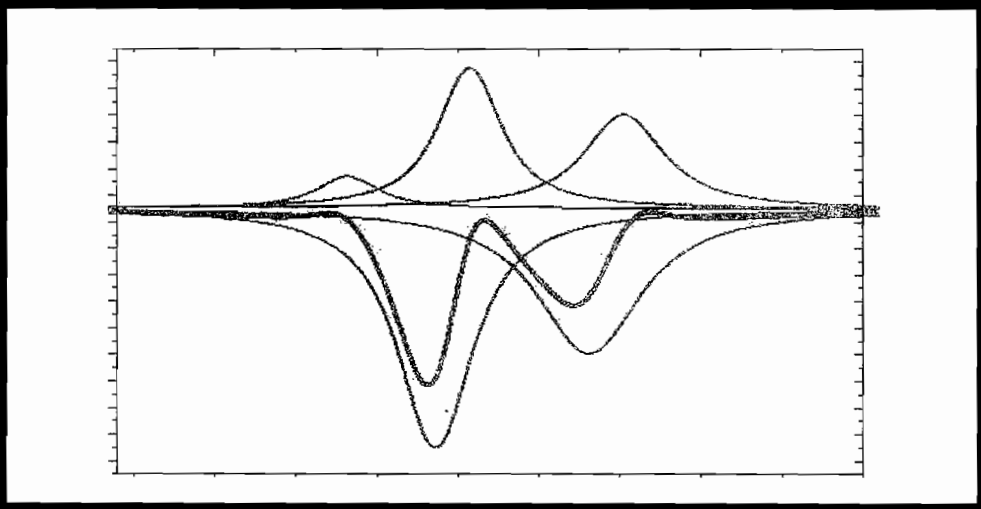
Poly(dGdC) ionisation: solution



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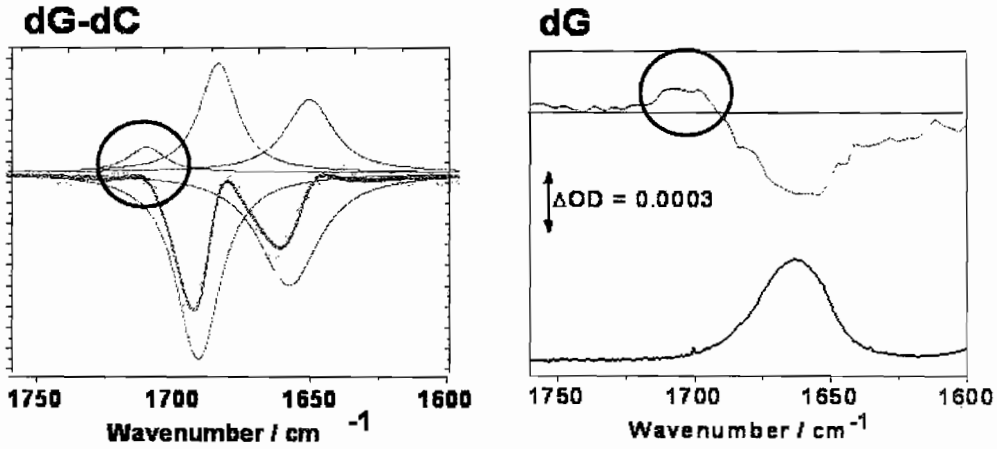
DNA ionisation: solution



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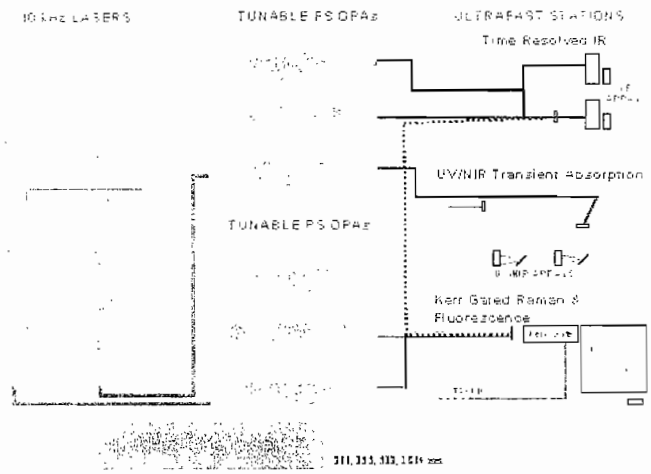
ULTRA - details

A New Generation of High Repetition Rate Spectrometer



Time resolution
50 fs – 100 μs

Spectral coverage
200 – 16000 nm

Techniques
- Infrared Absorption
- Raman
- 2D-IR
- TR - Absorption
  UV-NIR (50 fs)
- TR-Fluorescence
  < 1 ps

>60 fold faster acquisition than current state of the art - unsurpassed sensitivity.

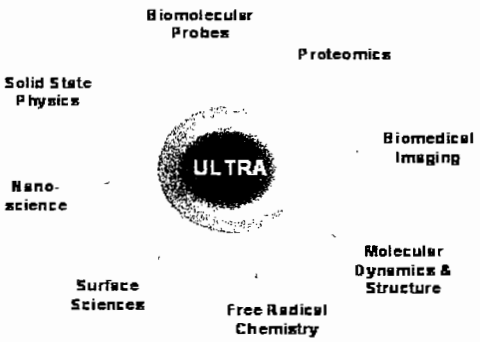
New LSF facility : ULTRA

Next Generation Laser Facility for Biological & Physical Sciences

World's most sensitive time-resolved vibrational spectrometer

Cross-disciplinary & Cross-departmental development
Leading edge technology (lasers, detectors)
Complementary to SRS, Diamond & 4GLS

Joint CCLRC/EPSRC funding (£1.78M/3yrs)



Examples of scientific applications

- **DNA Damage-**
  What are the initial steps in cell mutation and repair mechanisms?
- **Protein function-**
  Protein folding via time-resolved vibrational circular dichroism
- **Disease recognition-**
  Novel non-invasive approaches to cancer and osteoporosis diagnosis

CCLRC, Nottingham, Cambridge, MRC, Leicester, Cranfield

BIG Thanks to.....

P Matousek, M. Towrie, Kate Ronayne, S. Botchway (CCLRC, RAL)

M. W. George, J. Dyer, D C. Grills, X. Z. Sun, M. K. Kuimova (Nottingham)

M. Kelly A. M. Whelan (Trinity, Dublin)

J.O'Neil, N. Melvin, S. Cunniffe, T. Roldan-Arjona (MRC, Harwell)

£

EPSRC

DFT analysis of Vibrational Spectra

Keith Refson
CCLRC Rutherford Appleton Laboratory

22 August 2006

Contents

Experimental spectroscopies

Spectroscopic probes

IR and Raman

- Laboratory scale equipment
- Sensitive to probe dynamics, many modes active
- Instrumental limitations on frequency range
- Usually 2nd order phonons, e.g. DOS probed
- Anharmonicity contaminates spectra with multi-phonon processes

INS

- Requires intense spallation source
- Requires large single crystal or powder samples
- Probes long wavelength lattice dynamics
- Can sample entire Brillouin Zone
- No selection rules to obey

IXS

- Can probe optical modes throughout entire BZ
- Requires intense x-ray source, high resolution, e.g. ESRF Spring-8
- Can use high pressure cells
- Can be quite powder like, i.e. long counting time
- Insensitive to H

Often best: Ignore for lattice dynamics, mode assignment can be found

Ab-initio lattice dynamics

Ab initio spectroscopic calculations

- has no adjustable parameters
- can model the entire vibrational spectrum
- can perform mode assignments for vibrational and electronic
- can fill in the missing step of *structure-property relationships*
- can help to understand *structure-process* relationships
- can provide *insight* into bonding

but

- accuracy of frequencies is usually a few percent
- usually limited to *harmonic* approximation (anharmonic
  but not yet routinely)
- calculations can be computationally expensive for large
  unit cells
- Prediction of IR intensities is easy, but peak shape hard
- Prediction of Raman intensities harder (but coming)
- Prediction of INS spectra already straightforward

Ab-initio lattice dynamics

Ab-initio lattice dynamics

Ab-initio modelling

- A complete description of materials chemistry and physics given in principle by quantum mechanics of electrons and nuclei
- No adjustable or empirical parameters
- **All ab-initio methods are approximate**
- *Born-Oppenheimer Approximation* - Treat nuclei classically and assume electrons are in adiabatically in field of fixed ions.
- *Density Functional Theory* with local density or generalised gradient approximations (LDA, GGA) is method of choice for many atomic scale problems
- Can use periodic (for crystalline) or *cluster* (molecular, boundary conditions)
- Many observables related to *change* in E when system perturbed

  Phase stability - phase with lowest E is most stable at $T=0$
  Crystal Structure - given by ion positions which minimise E
  Elastic Constants - e.g. $\lambda = V \frac{\partial^2 E}{\partial \varepsilon^2}$
  Forces - ions given by ∇E
  Frequencies - of vibrational modes given by $\frac{\partial^2 E}{\partial x^2}$

- Also have electronic properties e.g. band-structures, densities of states

The CASTEP code

CASTEP (Cambridge Serial Total Energy Package) code. Authors: M. Segall, P. Lindan, M. Probert, C. Pickard, P.J. Hasnip, S. Clark, K. Refson, J. Yates

- Plane wave basis set and pseudopotential method
- Fully parallelised over FFT grid and k-points using MPI
- Proven to be massively parallel scaling on HPC resources

- Many different exchange-correlation pseudopotentials
  XC functionals: LDA, PW91, PBE, RPBE, PBESOL, WC, hybrid
- Geometry optimisation
- Built-in pseudopotential generation
- Full molecular dynamics: NVE, NVT and NPH ensembles
- MPMD ensembles
- Transition State Searching
- DFT and applied extensions
- Quasi-harmonic thermodynamics
- IR intensities, Raman activity
- Dielectric properties
- Born Effective Charges
- PAW for core-dependent properties
- NMR Chemical Shift
- Electric Field Gradient Tensors
- Mulliken population analysis
- Wannier functions
- Berry phase and E-field

Availability: Can be obtained from Accelrys Inc. or the Materials Studio GUI, or under the academic licence to any UK academic institution with HPC facilities (with DFT expertise).

Phonons from density-functional theory

The *dynamical matrix* of lattice dynamics is given by

$$D_{\alpha\beta}(q) = \frac{1}{\sqrt{M_\alpha M_\beta}} \sum_{\ell'} \Phi_{\alpha\beta}(0,\ell') e^{iq\cdot(R_{\ell'}-R_0)}$$

$\Phi_{\alpha\beta}(0,\ell')$ is the matrix of *force constants* between

Several approaches to lattice dynamics

- **Frozen phonon** method: Create a structure perturbed [illegible] and evaluate energy as function of amplitude. Need [illegible] with q
- **Finite Displacement** method: Perturb single [illegible] gives row of dynamical matrix at q
- **Supercell/Finite Displacement** Use fact that $D(q)$ [illegible] periodic replication of force constant matrix [illegible] large enough supercell, $\Phi_{\alpha\beta}(0,\ell')$ can be extracted [illegible] above
- **Density Functional Perturbation Theory**

Advantages of Density-Functional Perturbation Theory

DFPT formalism gives $D_{\alpha\beta}(q)$ directly from primitive [illegible] linear response
DFPT computes *first-order* KS orbitals [illegible] the linear response [illegible] displacement of atoms with wavevector q [illegible]
DFPT can calculate

- Born Effective Charges (a.k.a. atomic polar tensors)
- polarisability, dielectric permittivity
- LO–TO splitting
- infra-red reflectivity, absorption coefficients
- Raman tensor

LO-TO splitting and Born effective charges

- In the system LO and TO mode displacements indistinguishable
- For ionic crystals LO mode freq higher than TO mode
- Due to additional restoring force due to macroscopic polarisation
- Lyddane-Sachs-Teller relation for cubic case

- Normal using DFPT with representing electric field
- Linear response formalism also needs Born effective charges defined by

$$Z_{\alpha,ij} = V\frac{\partial P_i}{\partial u_{\alpha j}} = \frac{\partial F_{\alpha j}}{\partial \mathcal{E}_i}$$

- Polarisation per unit cell caused by displacement of atom in direction
- Force exerted on atom by macroscopic electric field

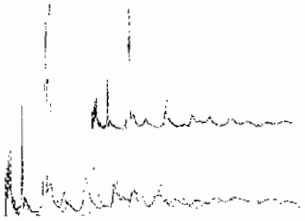
Lattice dynamics in CASTEP

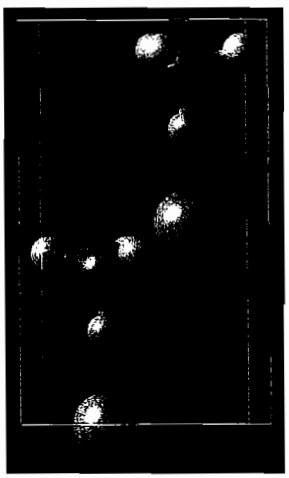
- CASTEP uses Gonze's variational formulation of DFPT
- Implemented S. J. Clark and R. D. Tulip, University of Durham (see Phys. Rev. B73, 155114 (2006))
- Full use made of space-group symmetry of crystal cell
  - Only independent elements of $\partial^2 E/\partial q^2$ calculated using LR minimiser and propagated to dependent elements
  - Brillouin-zone sampling performed using k-point set that is visible under symmetry operations of perturbation
- Almost identical approach yields ε^{∞}, Z^* and ε^0
- Currently restricted to insulators and norm-conserving pseudopotentials
- LO-TO splitting calculated
- Raman intensities
- IR spectroscopy (thermal ellipsoid plots for visualisation)
- Dielectric properties under development
- Future: interface directly to effective dispersion for LCAO
- Also: finite difference supercell method for metals

Modelling of Neutron Inelastic Spectra

Ammonium Fluoride

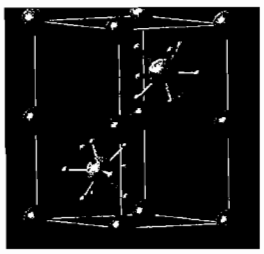
- NH_4F is one of a series of ammonium halides studied in the TOSCA spectrometer Collab Mark Adams (ISIS)
- Structurally isomorphic with ice ih
- INS spectrum modelled using A-CLIMAX software (A J. Ramirez Cuesta ISIS
- Predicted INS spectrum in mostly excellent agreement with experiment
- NH libration modes in error by ~ 5%
- Complete mode assignment achieved

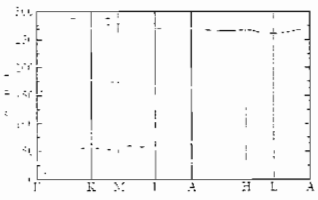


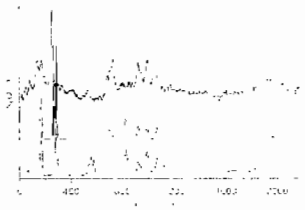


Barium Rhenium Hydride

- Scott S. F. Parker, ISIS facility, RAL
- $BaReH_9$ with unusual ReH_4^- ion has very high gravimetric hydrogen content
- INS spectrum modelled using A-CLIMAX software (A. J. Ramirez-Cuesta, ISIS)
- Predicted INS spectrum in mostly excellent agreement with experiment
- LO / TO splitting essential to model INS
- Librational modes (torsion of NH_4F)
- Complete mode assignment achieved

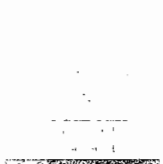


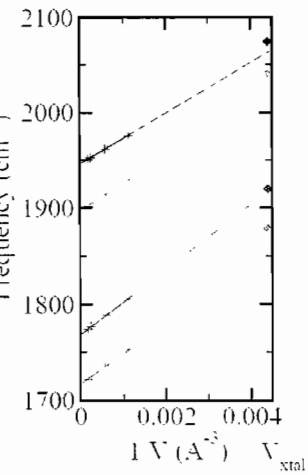




Isolated ReH_4^- ion

- Previous CASTEP calculations on isolated ReH_4^- ion gave poor match to INS
- Repeat isolated ion using CASTEP
- CASTEP model: periodic array of ions in charged cell. Explore scaling and take limit
- Mode sequences in agreement with isolated ion calc.
- Large (~150 cm^{-1}) crystal field shift
- Can also extrapolate *down* to V_{xtal}
- Extrapolated ion freqs are very close to A-point crystal freqs
- Crystal field shift is almost entirely a volume effect
- Anion modes completely insensitive to presence of cation

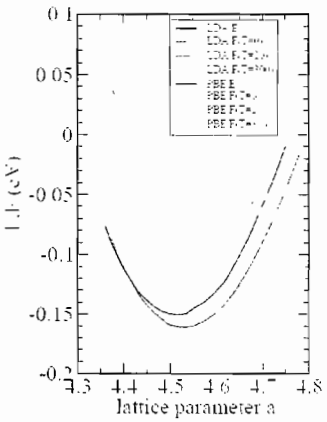




H-Storage materials MgH_2

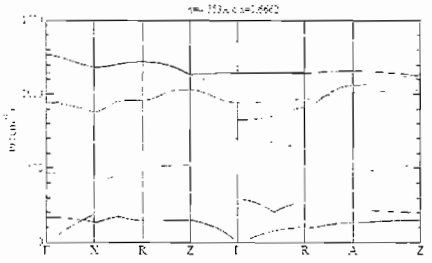
- MgH_2 is one of highest wt. % candidate hydrogen storage materials
- H_2 desorption reaction only at high T in bulk MgH_2, but ball milled and other nanostructured material promising
- Spectroscopy will be key tool investigating microstructured material.
- INS spectra measured on TOSCA by A J. Ramirez Cuesta.
- Light materials have large thermal expansivity and athermal limit inaccurate – need *quasi-harmonic free energy* minimum
- F evaluated using phonon DOS calculation at range of volumes
- LDA lattice parameter in better agreement with expt than GGA
  LDA 4.55Å, GGA= 4.60Å
  Expt=4.517Å.

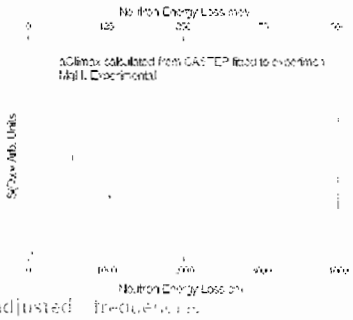
MgH2 Energy and QH Free energy



MgH_2 INS and lattice dynamics

MgH2: LDA

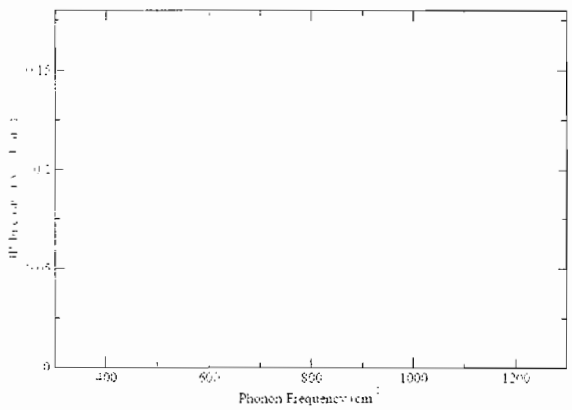




N.B. Predicted spectrum computed from adjusted frequencies.

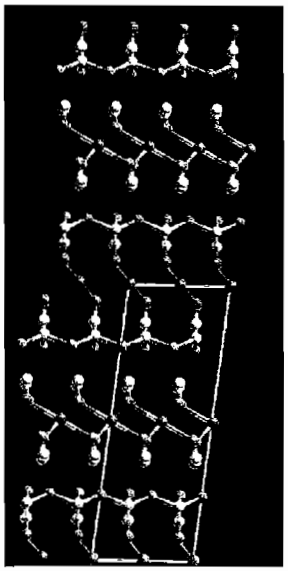
Modelling of IR and Raman Spectra

IR spectrum of α-quartz



- Straightforward to compute peak areas
- Peak shape modelling depends on sample and experimental variables
- Multiphonon and overtone terms less straightforward

High-pressure phase transition in clinochlore

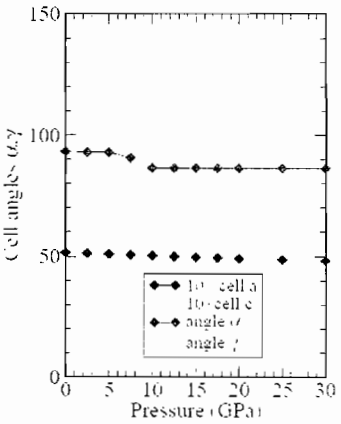


- Collaborators Dr Andrew Jephcoat (DLS) and Dr Annette Kleppe (Oxford)
- Clinochlore is H-rich chlorite which may be water-bearer in subduction zones
- Structure is mixed-layers of mica-like phyllosilicate and (Mg, Al) brucite
- Crystal structure of synthetic clinochlore is monoclinic C2/m
- X-ray powder diffraction and Raman spectroscopy show a phase transition at 10GPa
- X-ray powder data for high-pressure phase cannot be indexed for structure determination.

Ab-initio DFT results for Clinochlore

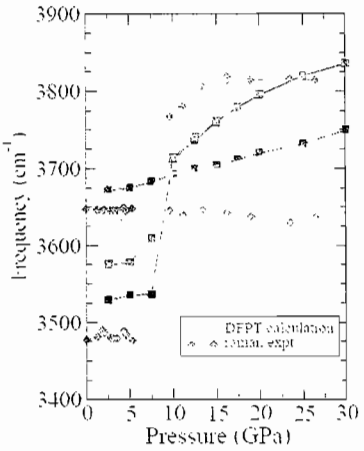
- Model Al-Si disorder using either fully ordered or all-Si approximations
- Optimize co-ordinates and simulation cell under applied pressure
- Both models show a phase transition at ~10GPa.
- Characterised by shear and compression along c-axis, change in inter-layer registration from Type IIb stacking.
- new phase is still monoclinic
- *ab-initio* prediction of new high pressure crystal structure

DFT lattice parameters of clinochlore



Vibrational Spectroscopy

- Experimental and calculated OH stretch frequencies show spread of ~200 cm^{-1} at 50 GPa
- Need resolution better than 1% for meaningful comparison
- Both calculations and expt show upward trend (rate of ~9 cm^{-1} and compression at same
- Same pattern of frequency shifts across transition observed in calculation as experiment
  - support for hope that high-P phase predicted in calculation is true structure
- Analysis of eigenvectors shows that highest freq in low-P phase becomes lowest in high-P. Mode is silicate layer OH stretch
- Modes with a gap are hydroxide layer OH stretch



Summary

- Ab initio lattice dynamics is a powerful tool for modelling experimental vibrational spectra of all kinds
- Accuracy usually a few percent except where Harmonic approximation breaks down
- Applicable to simple metals, insulators and semiconductors
- Crystal symmetry is essential for modelling INS spectra. Mode character comes for free
- Eigenvector information adds vital *structure–property* link
- Combined DFT modelling and experiment gives better *understanding*

Rutherford Appleton Laboratory

ISIS

Vibrational Spectroscopy with Neutrons: Catalysts, Hydrides and Polyethylene

Stewart F. Parker

ISIS Facility

Joint IRDG and RSC Molecular Spectroscopy meeting, 31st August 2006

Menu

Introduction: neutrons
vibrational spectroscopy with neutrons

Catalysis: adsorbed states of hydrogen on platinum fuel cell catalysts

Hydrides and hydrogen storage: $Rb_2[PtH_6]$ and $Ba[N_2]$

Polyethylene

Conclusions

ISIS

Neutrons: the subtle probe

Neutrons are NEUTRAL particles. They
- are highly penetrating
- can be used as non-destructive probes
- can be used to study sample in severe environments
- they cause little damage to the sample.

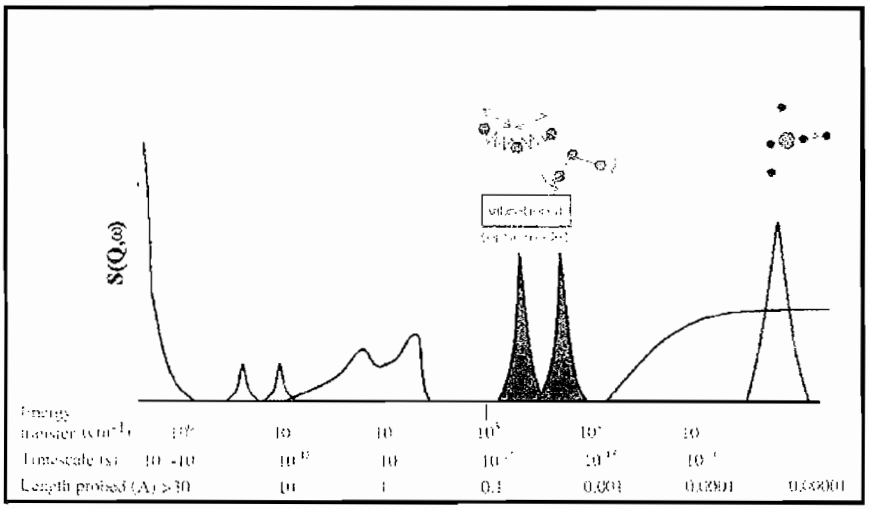
Neutrons have a MAGNETIC moment and a SPIN. They can be
- used to study microscopic magnetic structures and fluctuations
- polarised, thereby enhancing their selective power to magnetic features
- used to develop magnetic materials

The ENERGIES and WAVELENGTHS of thermal neutron are "just right"
- molecular vibrations and lattice modes.
- magnetic fluctuations.
- dynamic of atomic motion (e.g., diffusion)

Neutrons "see" NUCLEI, so they
- are sensitive to light atoms.
- can be exploited for ISOTOPIC SUBSTITUTIONS. In particular
- the neutron contrast can be varied selectively for important species such as HYDROGEN).

Neutrons tell you where atoms are and how they are moving!

Inelastic neutron scattering



Vibrational spectrum

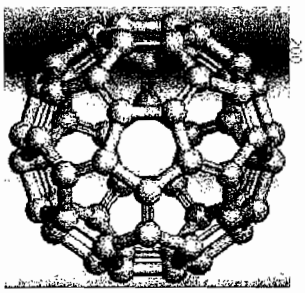
Complementary to infrared and Raman.

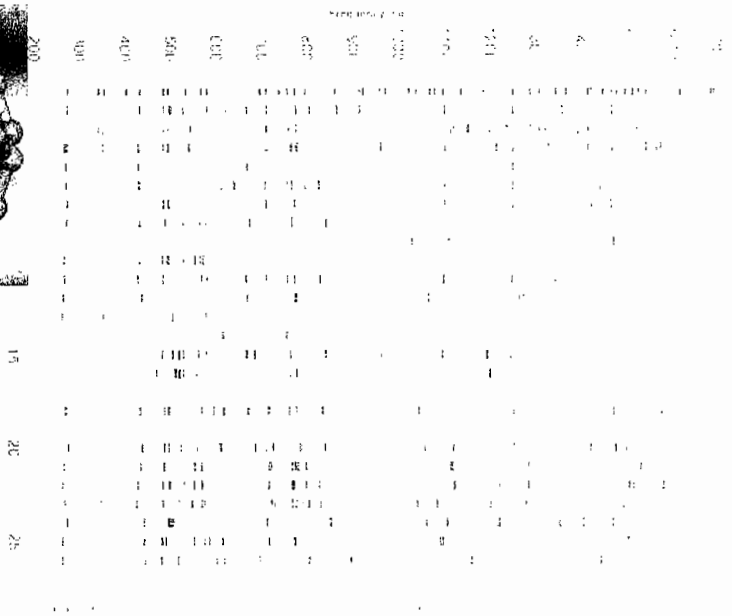
No selection rules:- interaction is with nucleus *not* electrons.

Intensities straightforward to calculate:-

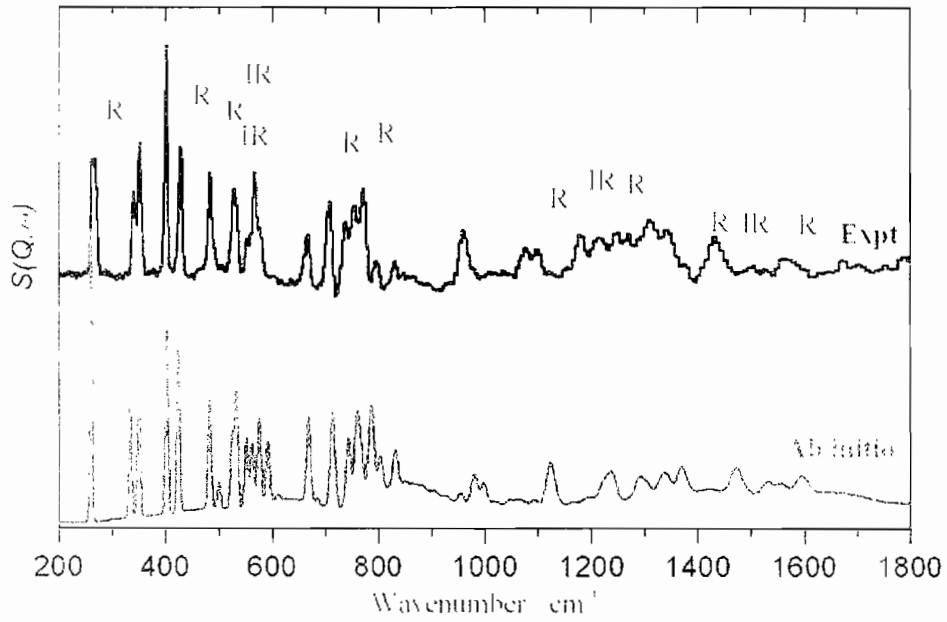
$$S(Q,\omega) = \sigma Q^2 U_\omega^2 \exp(-Q^2 U_T^2)$$

C_{60} Assignments –all wrong!

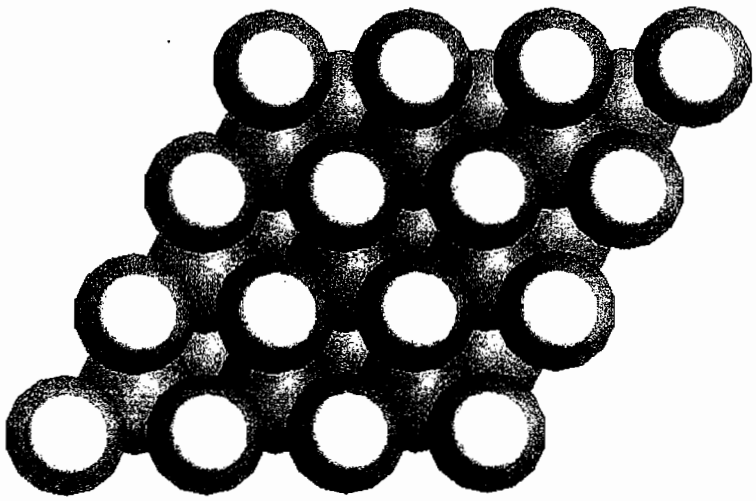




C_{60}

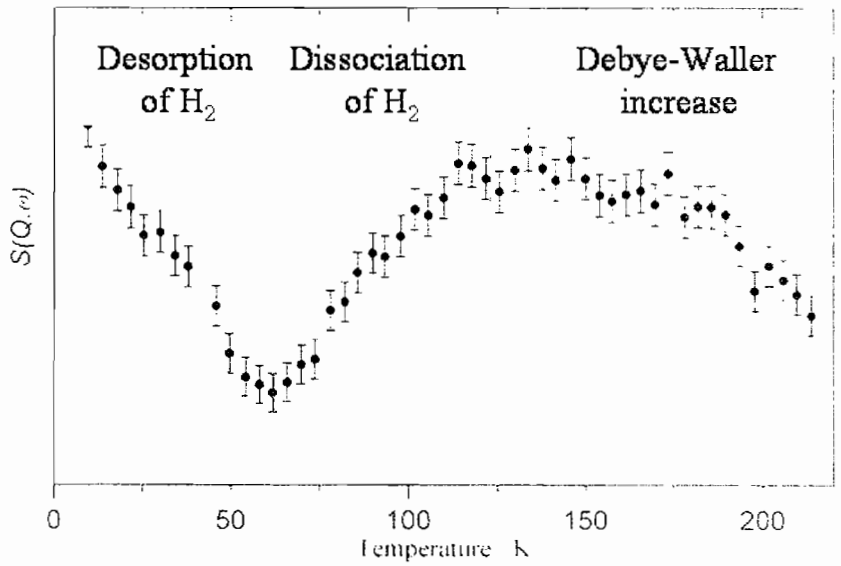


Adsorbed states of hydrogen



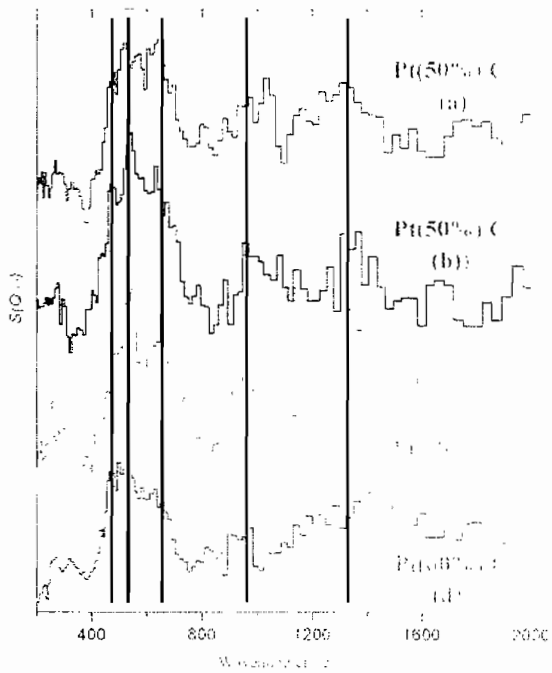
S.F. Parker, C.D. Frost, M. Telling, P. Albers, M. Lopez and K. Seitz
Characterisation of the adsorption sites of hydrogen on Pt/C fuel cell catalysts
Catalysis Today, 114 (2006) 418-421.

Dissociation of H_2 on a Pt(50%)/C fuel cell catalyst by QENS



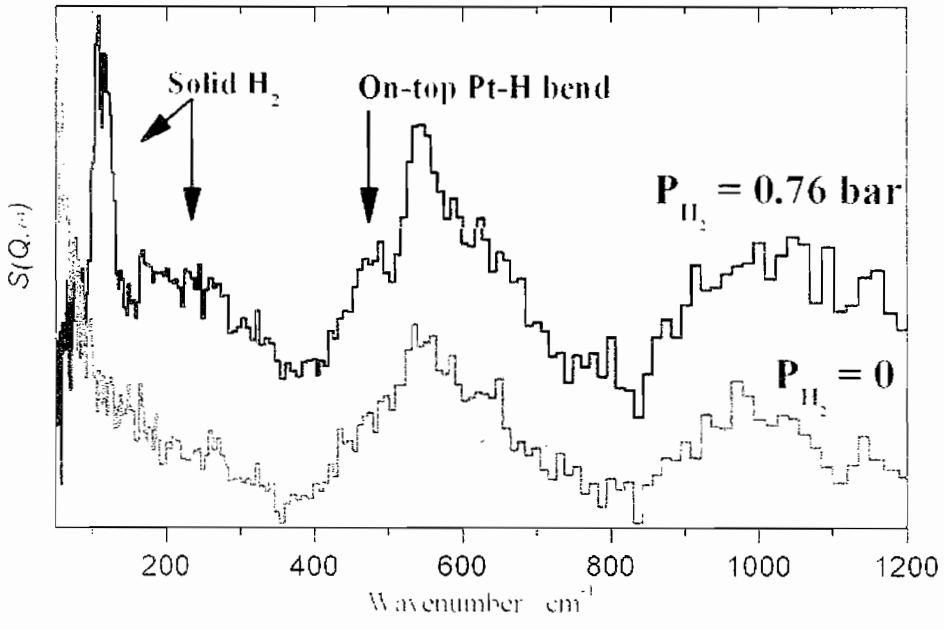
ISIS

Adsorbed hydrogen on Pt/C fuel cell catalysts

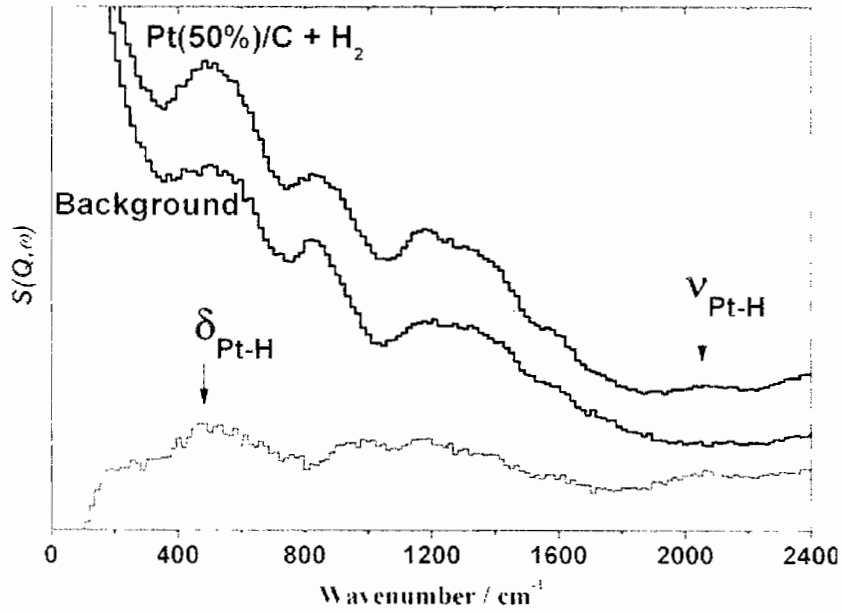


ISIS

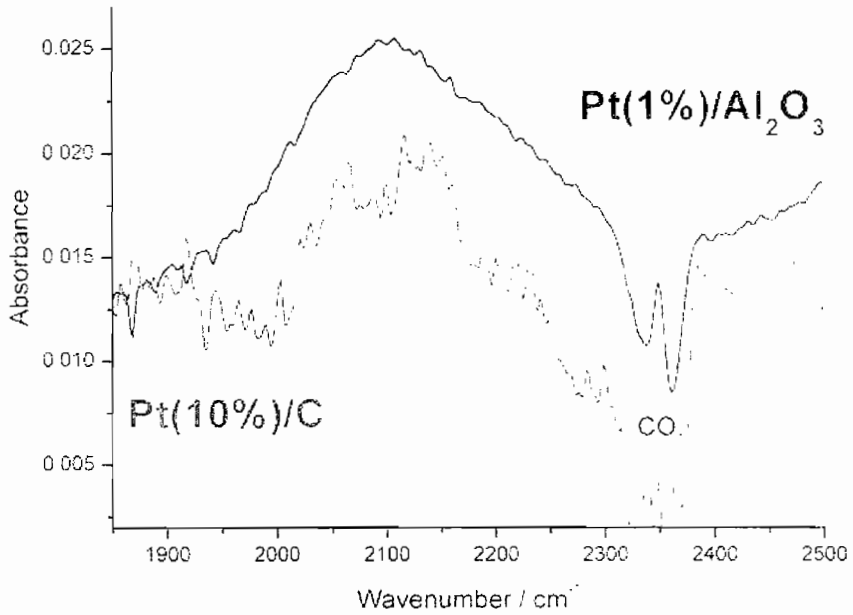
Fuel cell catalyst: Pt(58%)/C



The on-top hydrogen

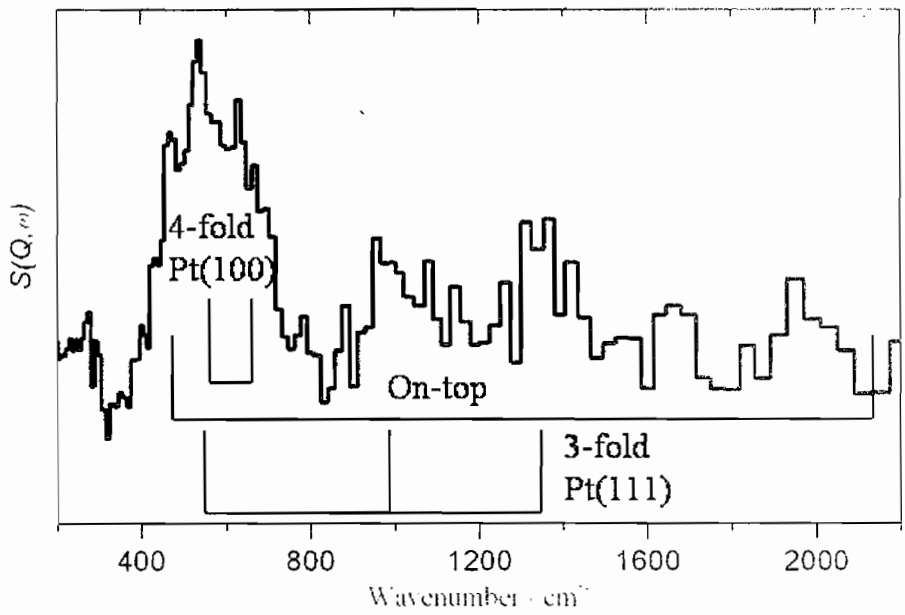


IR of Pt-H stretch of on-top



ISIS

Summary of assignments



ISIS

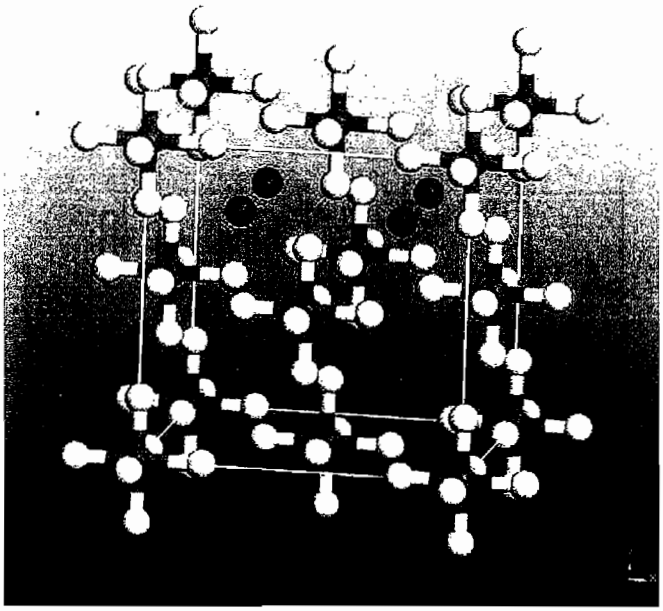
Hydrides and hydrogen storage

S. F. Parker, S. M. Bennington, A. J. Ramirez-Cuesta, G. Auffermann, W. Bronger, H. Herman, K. P. J. Williams and T. Smith
Inelastic neutron scattering, Raman spectroscopy and periodic-DFT studies of Rb_2PtH_6 and Rb_2PtD_6
J. Am. Chem. Soc.; 125 (2003) 11656-11661.

Stewart F. Parker, Jon W. Taylor, Keith Refson and Gudrun Auffermann
Spectroscopic and ab initio characterisation of alkaline earth nitrides and diazenides: detection of the N=N stretch

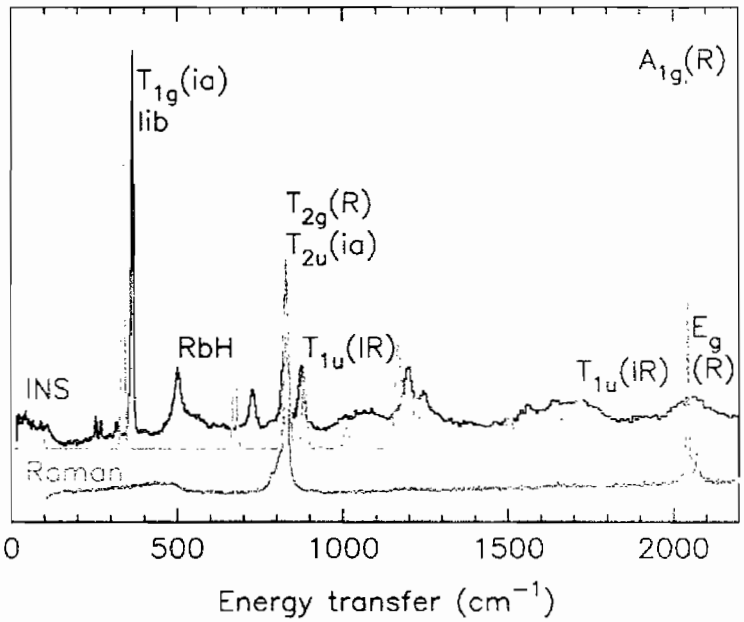
ISIS

$Rb_2[PtH_6]$



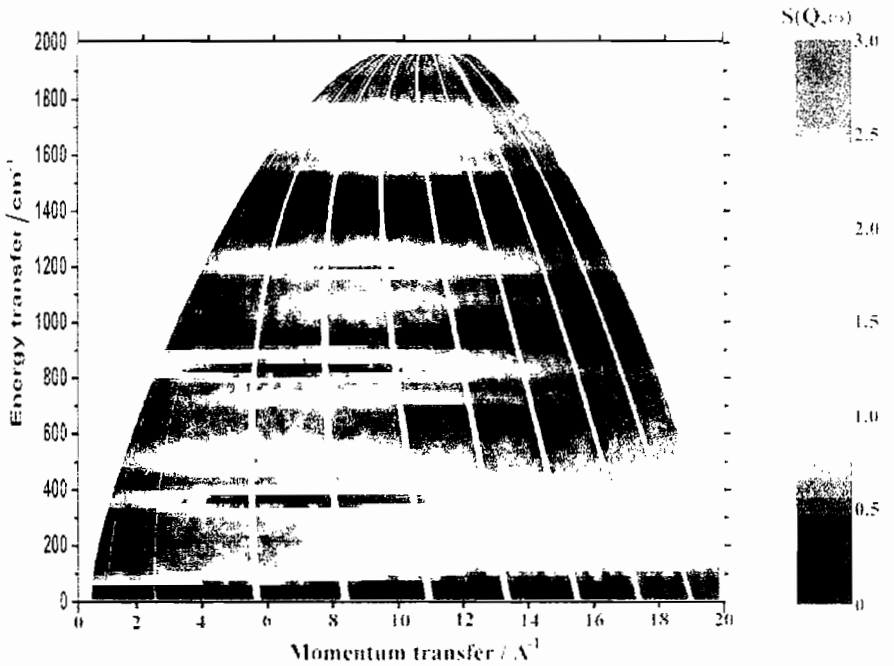
ISIS

INS and Raman spectra of O_h $[PtH_6]^{2-}$



ISIS

$Rb_2[PtH_6]$ on MARI

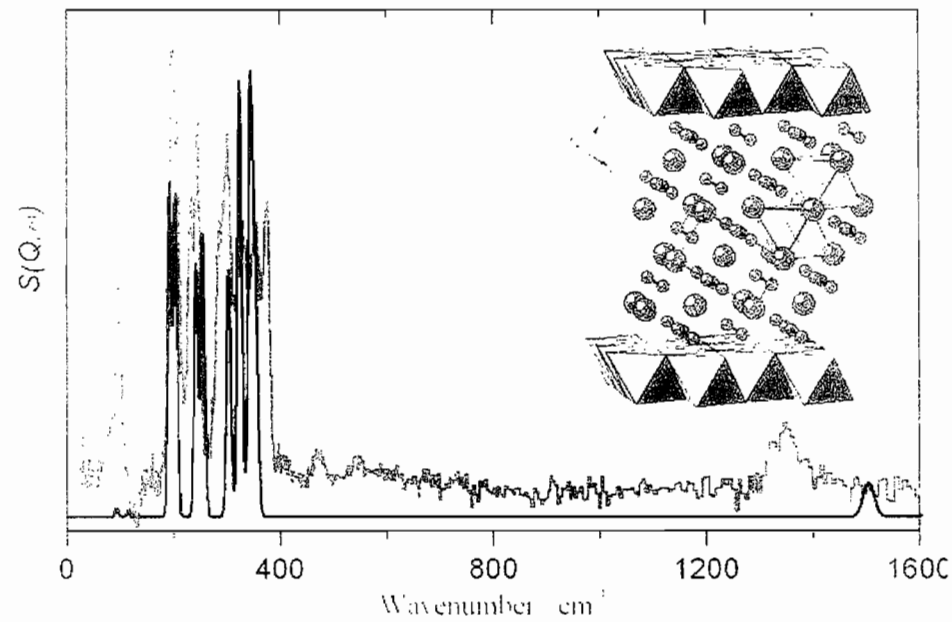


ISIS

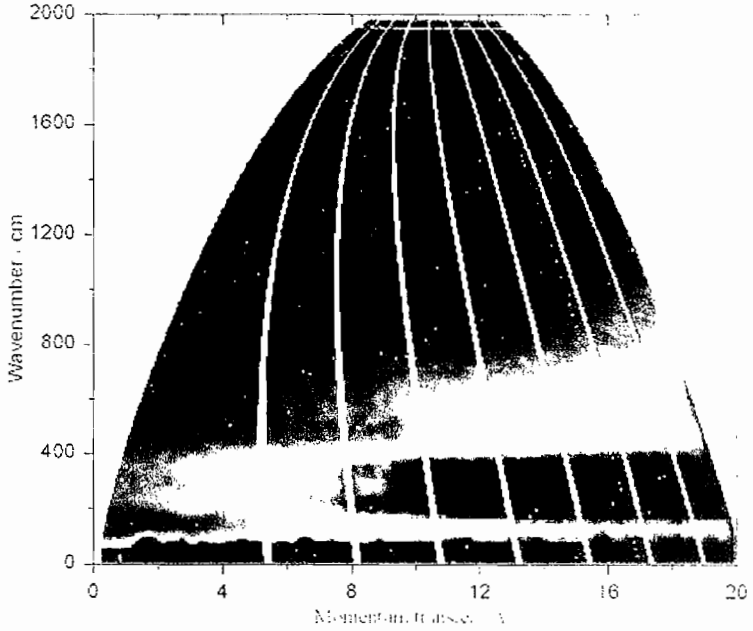
Comparison of properties of M_2PtH_6. (M = Li, Na, K, Rb, Cs). Experimental values in parentheses.

Property	Li	Na	K	Rb	Cs	Gas phase
Lattice parameter (Å)	6.564 (6.55)‡	7.1716 (7.3410)	8.2002 (8.1399)	8.6222 (8.5369)	8.9503 (8.9681)	
Pauling ionic radius M (Å)	(0.60)	(0.95)	(1.33)	(1.48)	(1.69)	
Lattice energy (kJ mol^{-1})	2223	1966	1755	1665	1577	
Pt-H / (Å)	1.639	1.641 (1.615)	1.644 (1.640)	1.646 (1.629)	1.647 (1.641)	1.678
M-H / (Å)	2.354	2.540 (2.74)	2.927 (3.12)	3.091 (3.06)	3.219 (3.52)	
ν_1Pt-D stretch A_{1g} (cm-1)	1673	1651 (1491)	1604 (1471)	1588 (1466)	1577	1387
Charge on Pt	-1.718	-1.777	-1.601	-1.511	-1.422	-1.860
Charge on M	+0.370	+0.598	+0.698	+0.703	+0.536	
Charge on H	+0.163	+0.097	+0.034	+0.018	+0.058	-0.232

$Ba[N_2]$ - metallic



Ba[N_2] on MARI



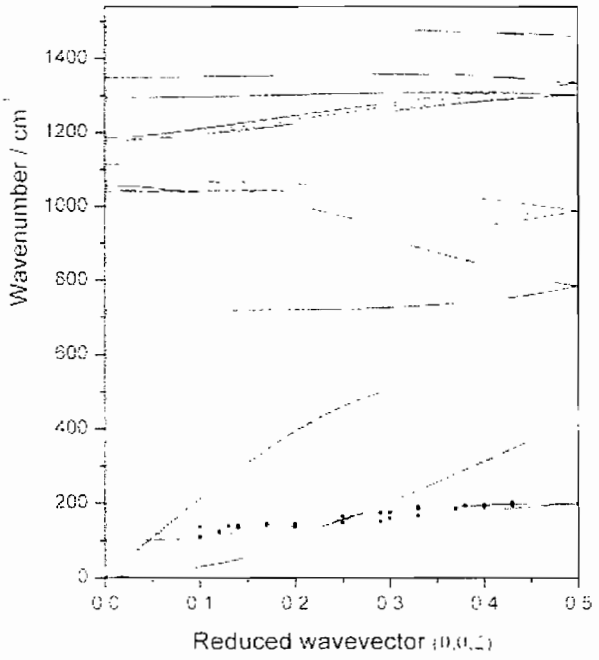
ISIS

Polyethylene

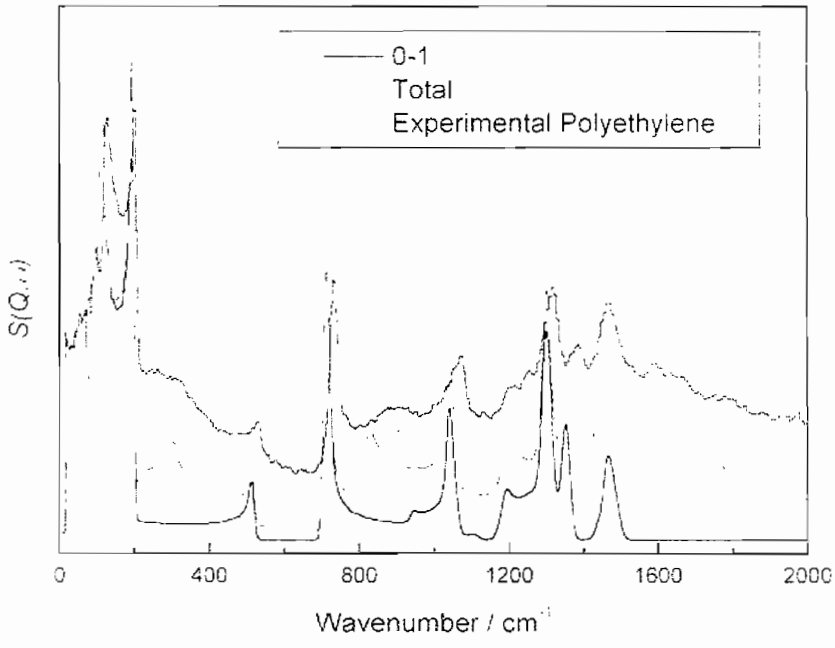
G.D. Barrera, S.F. Parker, A.J. Ramirez-Cuesta, and P.C.H. Mitchell
The vibrational spectrum and ultimate modulus of polyethylene
Macromolecules, 39 (2006) 2683-2690.

ISIS

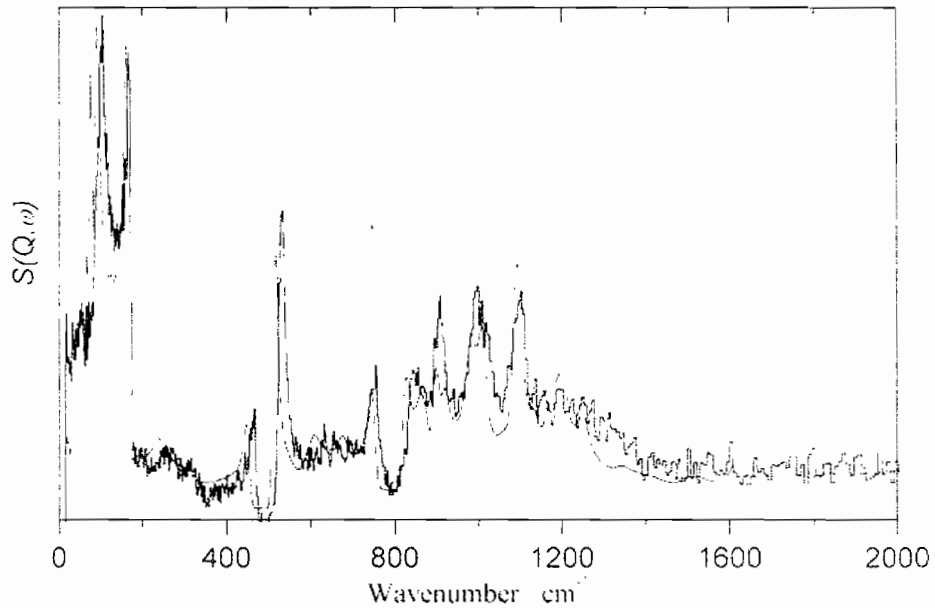
Polyethylene dispersion along chain (*c*) axis



INS spectrum of polyethylene



INS spectrum of polyethylene –D_4



ISIS

Observed and Calculated Young's Moduli (GPa) of Polyethylene

Modulus	Experimental				Theoretical			
/ GPa	Mechanical	X-ray	Raman	Coherent INS	*Ab initio*	Molecular dynamics	Force field	This work
Y_{cc}	288	235-255	280-358	329	350-400	334	286-386	360.20
Y_{bb}		2.5-5.0					9.4	12.92
Y_{aa}		1.9-3.9					9.0	13.34

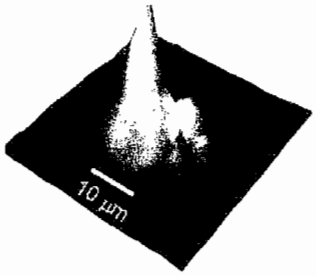
ISIS

Conclusions

Vibrational spectroscopy with neutrons provides a different view of materials
- **it allows access to forbidden modes**
- **metallic systems and catalyst supports are transparent**

Combination with *ab initio* results is mutually beneficial
- **enables unambiguous assignments of vibrational spectra**
- **provides stringent test of *ab initio* results**

Photons and neutrons are complementary
- **best science results from use of both**
- **co-location of sources (ILL/ESRF, ISIS/Diamond) promising**



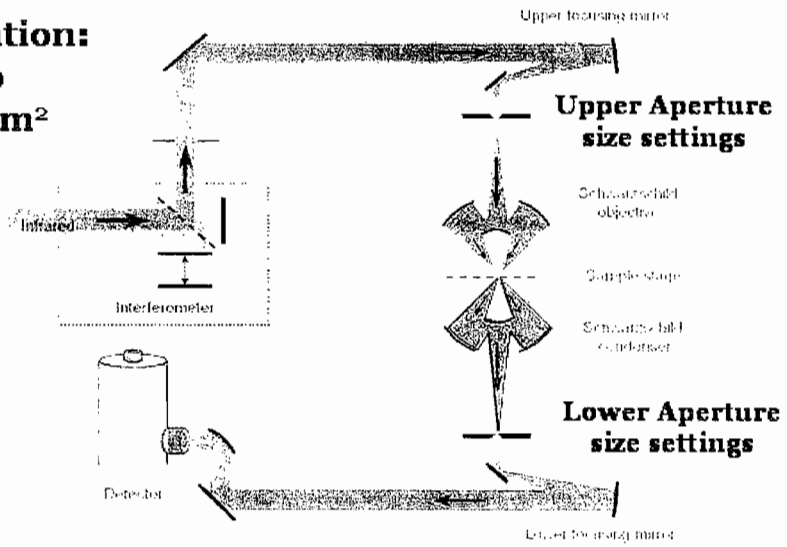
Synchrotron Infrared Microspectroscopy

Paul Dumas
Synchrotron SOLEIL
paul.dumas@synchrotron-soleil.fr

Infrared microspectroscopy with a blackbody source

Infrared microscope with blackbody : limitations

Confocal configuration: limited to ~20x20 μm² aperture

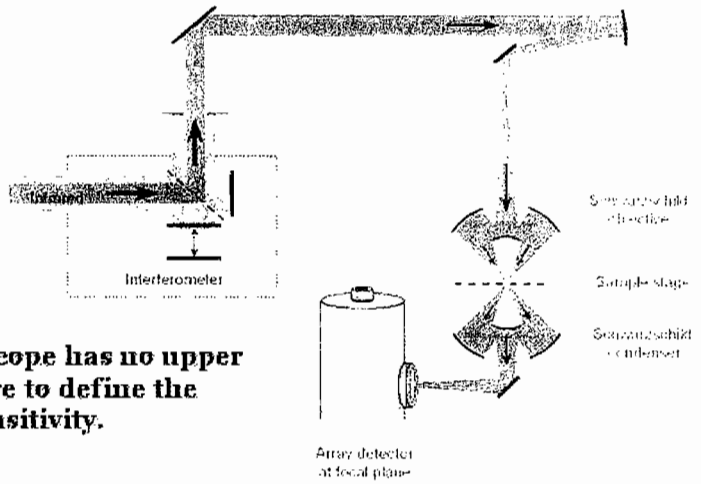


The limitation arises from the low brightness of the source

Infrared microscope with blackbody : limitations

Non-confocal configuration: Focal Plane Array Detector

Optical arrangment for detector array , or FPA



The FPA microscope has no upper or lower aperture to define the instrument's sensitivity.

Instead, each detector pixel serves as an aperture for this purpose

The need of a brighter source

In order to achieve:

-Diffraction limited domain size analysis ($\lambda/2$)

-High spectral quality (High S/N)

-Confocal configuration (contrast fidelity)

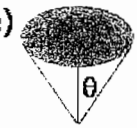
There is a need for a different infrared photon source, much brighter than the blackbody.

Confocal versus non-confocal

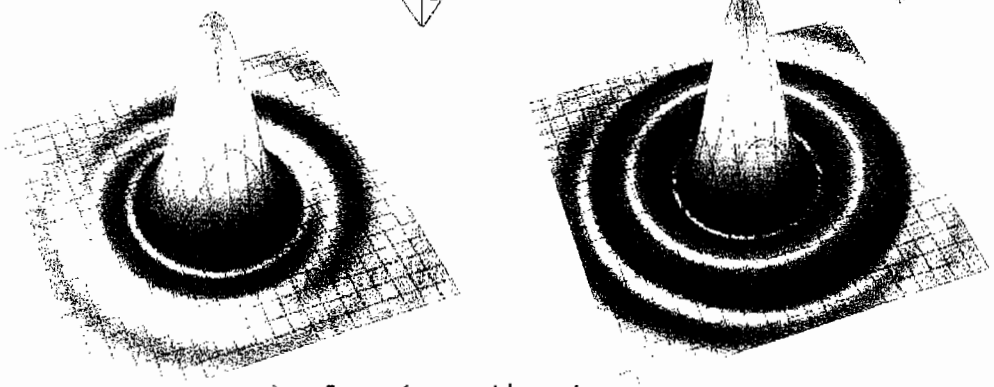
Preserving the contrast fidelity

Diffraction-limited Point Spread Functions

"Normal" (circular aperture)
$d = 1.22\lambda/(n \sin\theta)$



Schwarzschild
$d \approx \lambda/(n \sin\theta)$



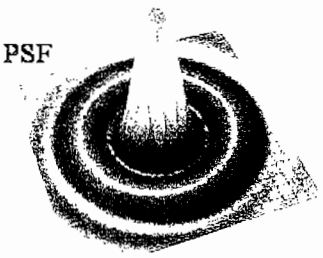
λ = 6 μm, 1 μm grid spacing

"fat" 1st order diffraction ring for Schwarzschild

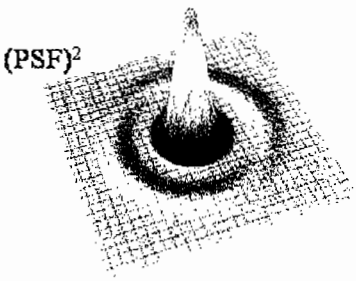
Confocal versus non-confocal

G.L. Carr

PSF



$(PSF)^2$

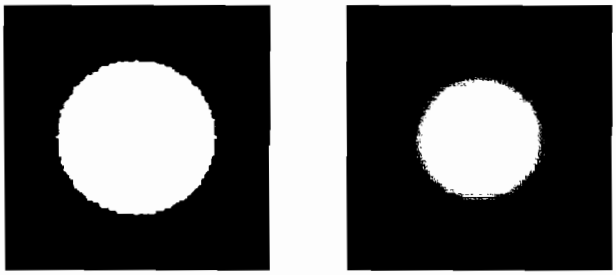


Confocal results in narrower central peaks, and also reduces effect of 1st order diffraction ring.

Example of an imaging artifact

S LEIL SYNCHROTRON

G.L.Carr, O. Chubar and P. Dumas
Spectrochemical Analysis using multichannel infrared detectors, Analytical Chemistry Series, Blackwell Publishing (2005)



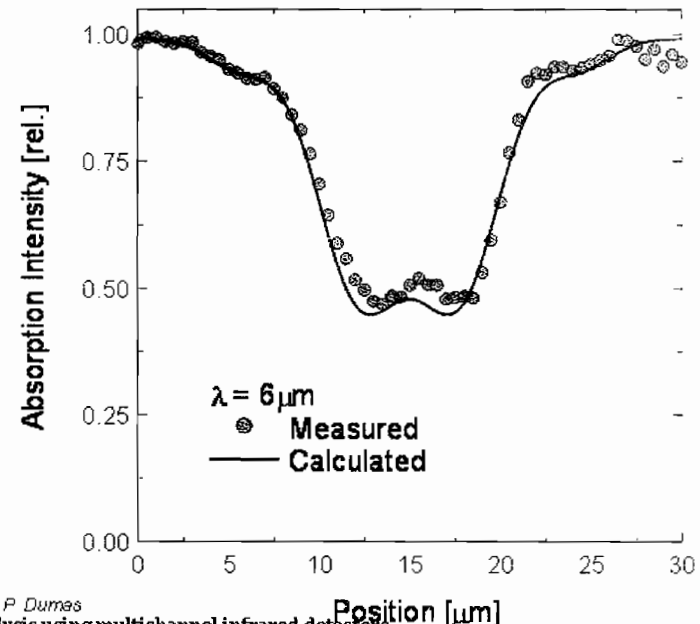
Left: object consisting of an opaque specimen except for a 12 μm diameter circular aperture
Right: calculated transmission image for a single (non-confocal) Schwarzschild objective with NA=0.65 and for λ=6 μm.

1-Note the dark patch in the center, suggesting the presence of absorbing material inside the hole

2-Note that the dimension of the hole is not preserved!

Artifact verified experimentally

S LEIL SYNCHROTRON



G.L.Carr, O. Chubar and P. Dumas
Spectrochemical Analysis using multichannel infrared detectors, Analytical Chemistry Series (2005)

Chemical imaging: FPA versus Synchrotron

Lipids profile across and hair cut

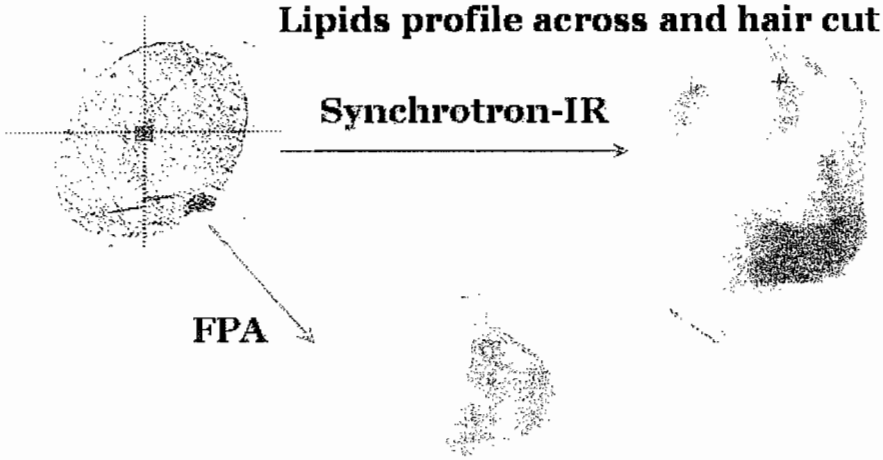


Image contrast fidelity with synchrotron!!

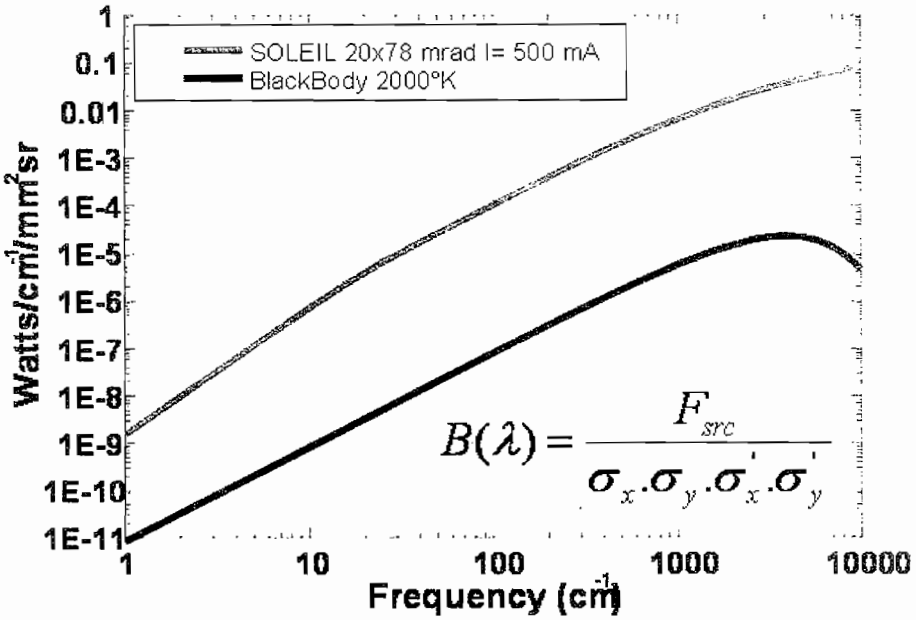
Brightness, or brilliance, or spectral radiance

Low brightness source

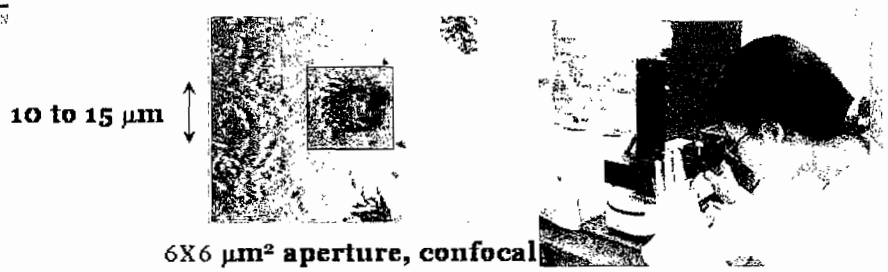
Synchrotron source is a broadband and bright source.

High brightness source

Synchrotron source: advantages

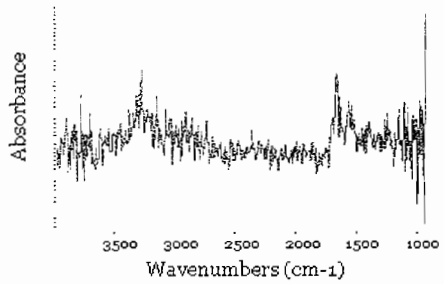


Exploiting the source brightness



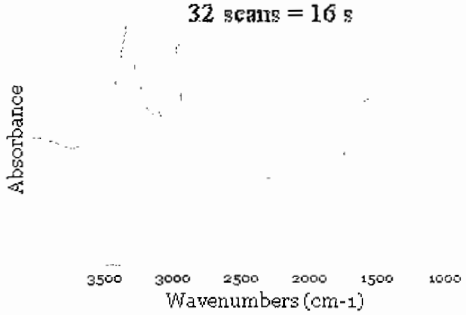
With the globar source

1000 scans = 500s



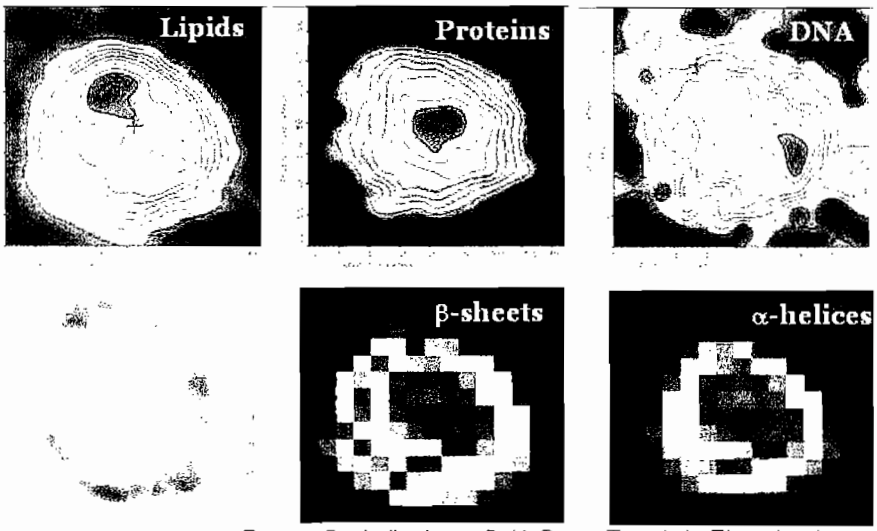
With the synchrotron source

32 scans = 16 s



Imaging at sub-cellular spatial resolution

HL60 cell, after 24 hours induction of differentiation (PMA)



Dumas,Sockalinghum, Sulé-Suso Trends in Biotechnology

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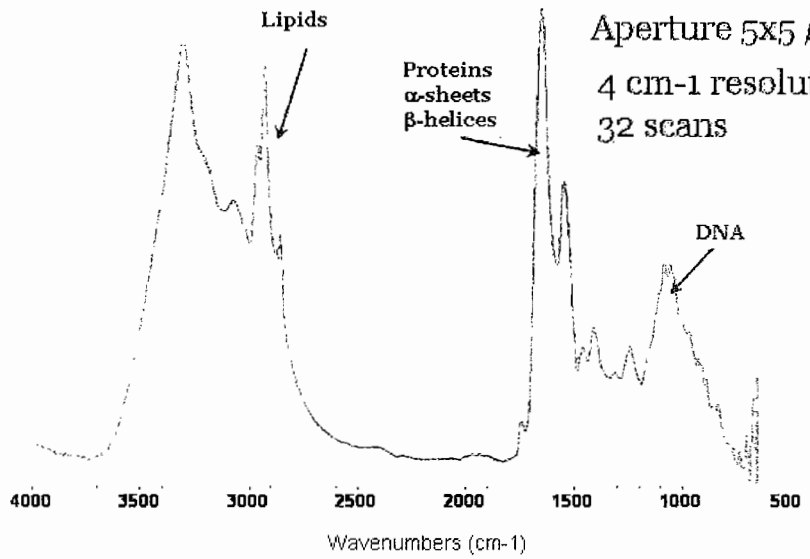
Infrared spectrum



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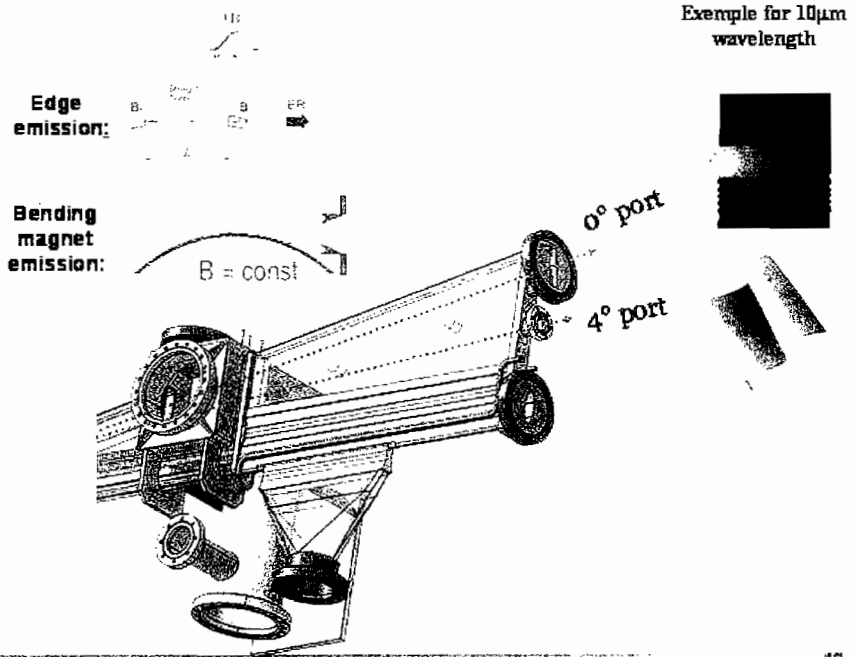
S LEIL SYNCHROTRON **Synchrotron Infrared Microscopy Beamline**

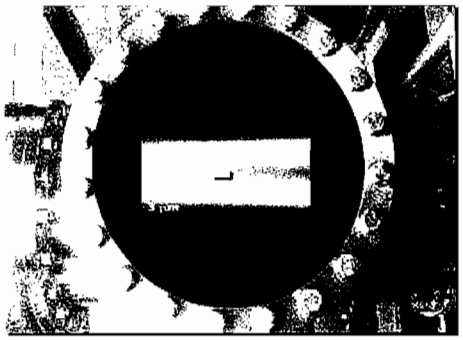
Design and Challenges

S LEIL SYNCHROTRON **Synchrotron radiation and infrared emission**

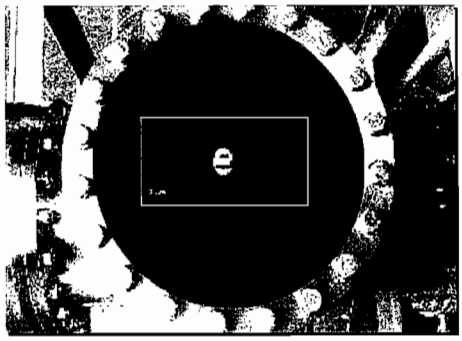


History of synchrotron IR ?

It takes much longer before being recognized as a potential source for spectroscopy



Bending magnet radiation



Edge radiation

*: calculated using the SRW code for E=2.75 GeV, 1.56 T, 7 meters straight section

Formulas for calculating infrared flux

(Non-coherent) Synchrotron Radiation from Constant Field of Bending Magnet

$$\left(\frac{dW}{d(1/\lambda)}\right)_{SR}\left[\frac{W}{cm^{-1}}\right] \approx 4.88\cdot 10^{-7}\, E[GeV]\, I[A]\, \theta_x[mrad]\, G(\lambda_c/\lambda)$$

$$G(x) \equiv x\int_x^{+\infty} K_{5/3}(x')dx'$$

$\gamma = E/m_0c^2$ = electron relativistic mass enhancement factor

θ_y = aperture

$\lambda_c = 4\pi\rho/(3\gamma^3)$ = critical synchrotron radiation wavelength for the bending magnet

$K_{5/3}$ = modified Bessel function

For a storage ring with parameters E = 2.75 GeV, I = 0.5 A, λ_c = 1.43 Å,

horizontal angular aperture θ_x = 40 mrad, at the wavelength λ = 10 μm

$$\frac{dW}{d(1/\lambda)}\left[\frac{W}{cm^{-1}}\right] \approx 2\cdot 10^{-20}\,\frac{dN}{dt\,(d\lambda/\lambda)}\left[\frac{Photons}{s\ (0.1\%bw)}\right]\left(\frac{dW}{d(1/\lambda)}\right)_{SR} \approx 1.40\cdot 10^{-6}\,\frac{W}{cm^{-1}}$$

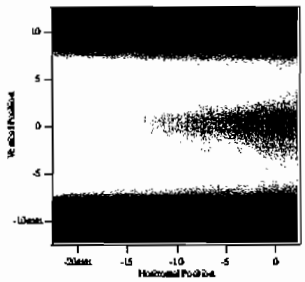
Multichannel Detection with a Synchrotron Light Source G.L. Carr, O. Chubar and P. Dumas

Infrared Synchrotron Radiation from Bending Magnet

S LEIL SYNCHROTRON

Australian Light Source

Intensity Distribution in transverse plane close to the source



Natural Opening Angle:

$\psi \sim (\lambda/\rho)^{1/3}$

$(\lambda >> \lambda_c)$

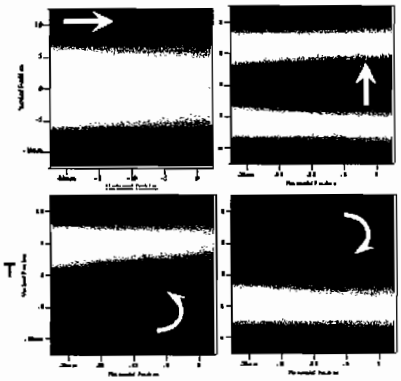
$E = 3.0$ GeV; $B = 1.30$ T

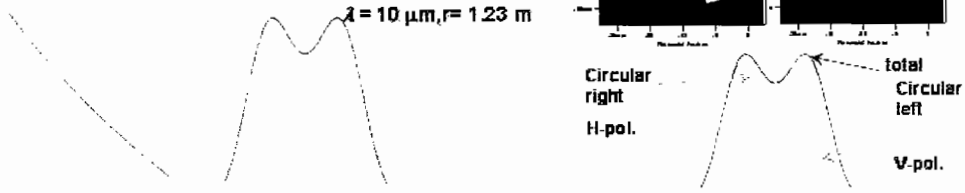
$\rho = 7.89$ m

$I = 200$ mA

$\lambda = 10$ μm, $r = 1.23$ m

Intensity Distributions at Various Polarizations





Practical Formulas for calculating infrared flux

S LEIL SYNCHROTRON

(Non-coherent) Edge Radiation from Extremities of Bending Magnet

$$\left(\frac{dW}{d(1/\lambda)}\right)_{ER}\left[\frac{W}{cm^{-1}}\right] \approx 5.76\cdot 10^{-7}\, I[A]\, H\left[\frac{\pi\cdot\theta_y^{\,2}[mrad]}{\lambda[\mu m]}\,\frac{zL}{z+L}[m]\right]$$

where $H(x) \equiv \ln(x) - \mathrm{ci}(x) + C$,

$\mathrm{ci}(x) \equiv -\int_{+\infty}^{x} \cos(t)t^{-1}dt$ is the cosine integral function

$C \approx 0.577216$ is the Euler constant

L is the distance between bending magnet edges

z is distance from downstream bending magnet edge to observation plane

Taking the following realistic parameters: I = 0.5 A, L = 10 m, z = 5 m, $\theta_y = 10$ mrad

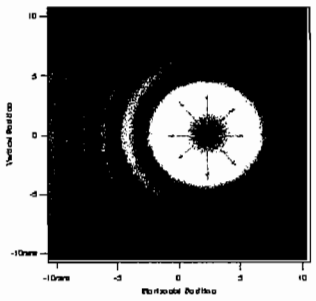
$\lambda = 10$ μm

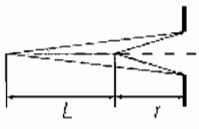
$$\left(\frac{dW}{d(1/\lambda)}\right)_{ER} \approx 1.5\cdot 10^{-6}\,\frac{W}{cm^{-1}}$$

Multichannel Detection with a Synchrotron Light Source G.L. Carr, O. Chubar and P. Dumas

Infrared Synchrotron Radiation from Edge of bending magnet

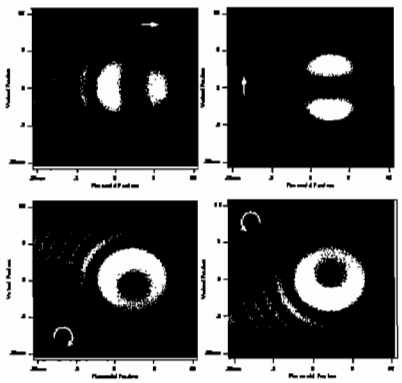
"Pure ER" is polarized "Radially"





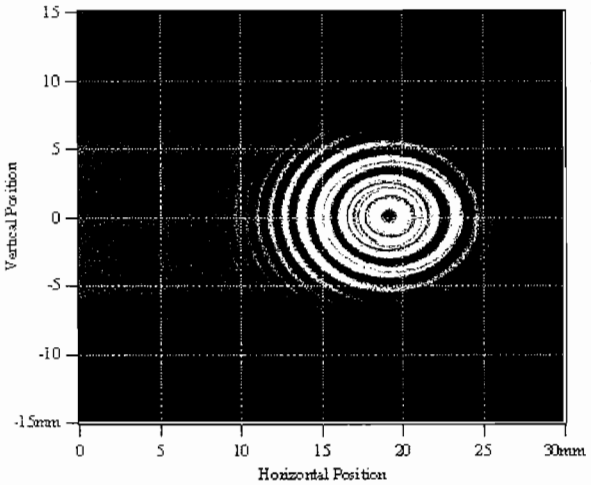
E = 3.0 GeV L = 5 m
B_{max} = 1.30 T r = 1.23 m
I = 200 mA λ = 10 μm

Intensity Distributions at Various Polarizations



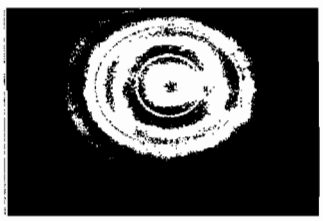
Are we confident with the simulations?

Calculated intensity profile at 6.2 meters from source
λ=0.52 microns



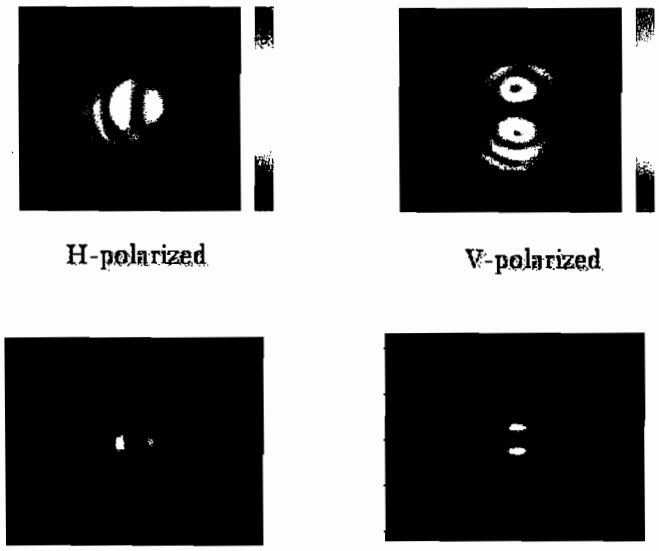
Measured at the ESRF beamline

Recorded with a CCD camera at 6.2 meters from source
λ= 0.52 microns



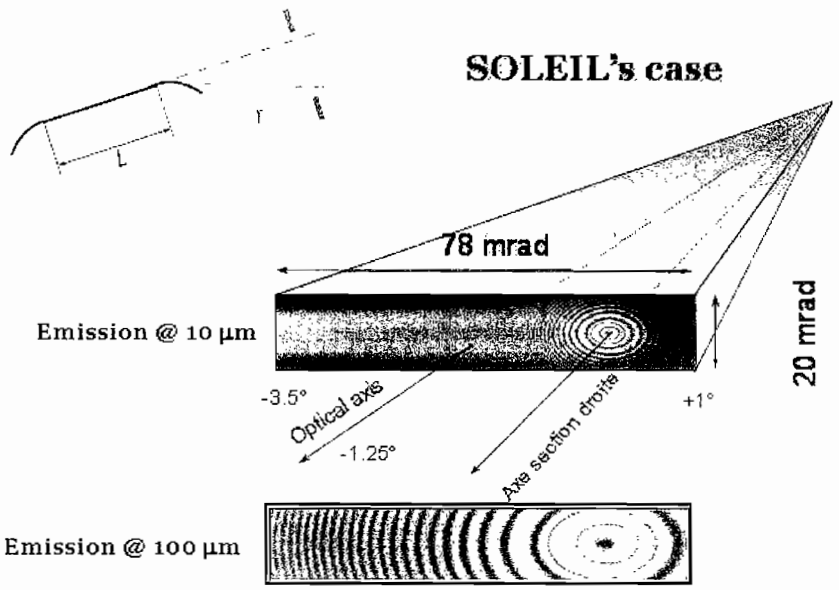
Edge radiation observed at IR beamline ESRF

Measurements done with a CCD camera, 10m from source, filter=700nm



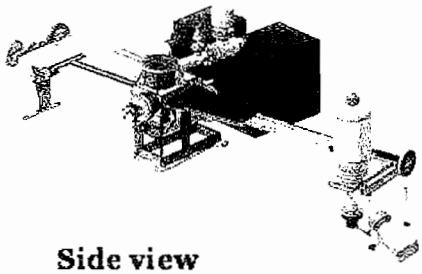
H-polarized V-polarized

Collecting the two sources



Extraction optics

Allows to collect 20 mrad vertical and 78 mrad horizontal

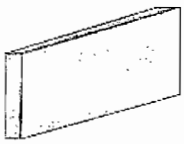


Side view

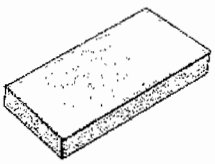
crotch

Top view

Extracting the beam



Horizontal deflection

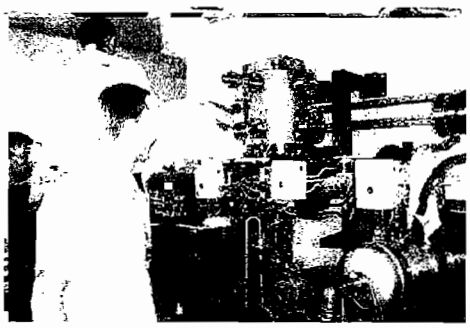


Vertical (upward) deflection

High power density on the mirror!

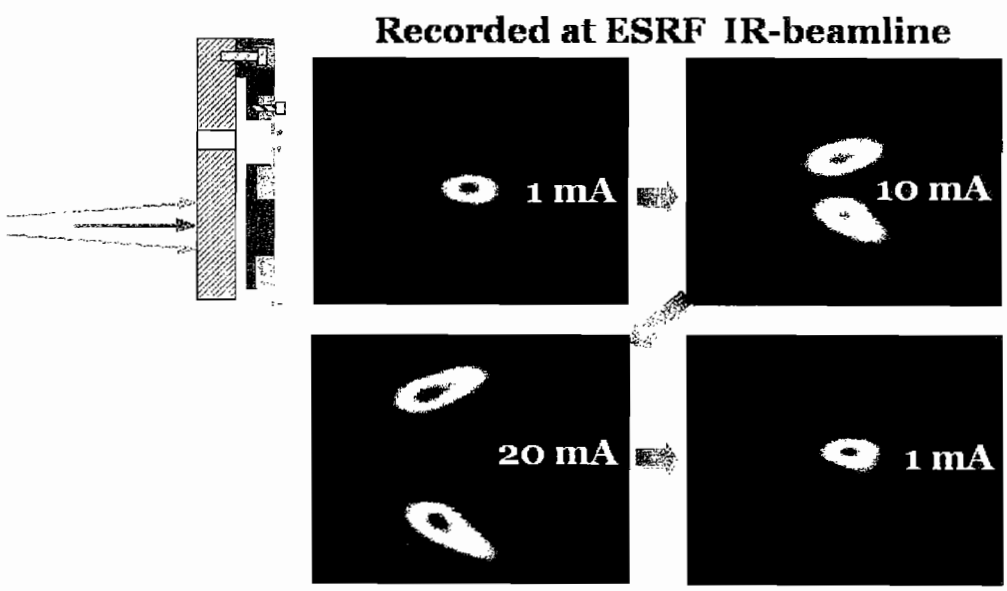
SOLEIL SYNCHROTRON

Extraction optics



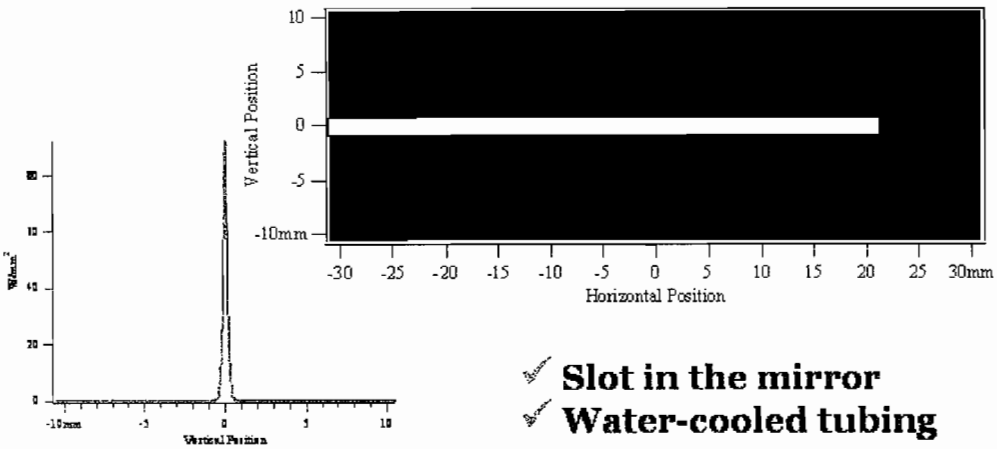
SOLEIL SYNCHROTRON

Dealing with high incident power



Calculating power on the first mirror

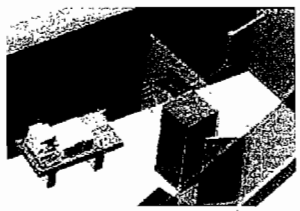
SRW- O. Chubar



- ✓ **Slot in the mirror**
- ✓ **Water-cooled tubing**

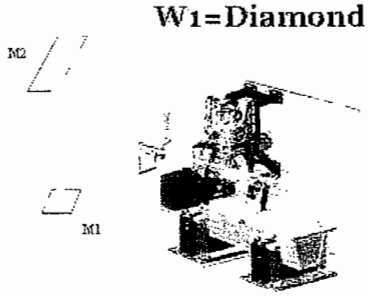
Beamline schematic

Tunnel wall



Experimental hall

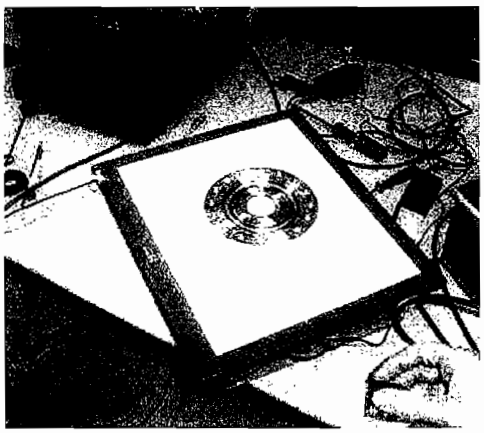
M1=extracting mirror
M2= Ellipsoid
W1=Diamond Window

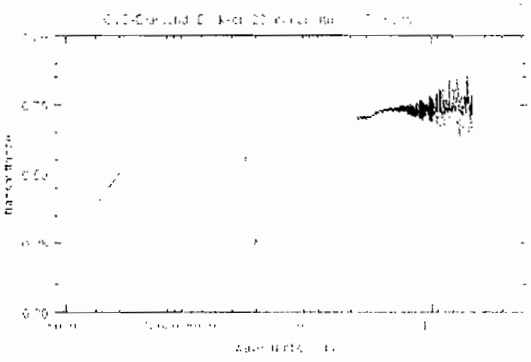


To spectrometer

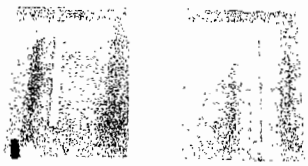
SOLEIL SYNCHROTRON

CVD diamond window@ ESRF



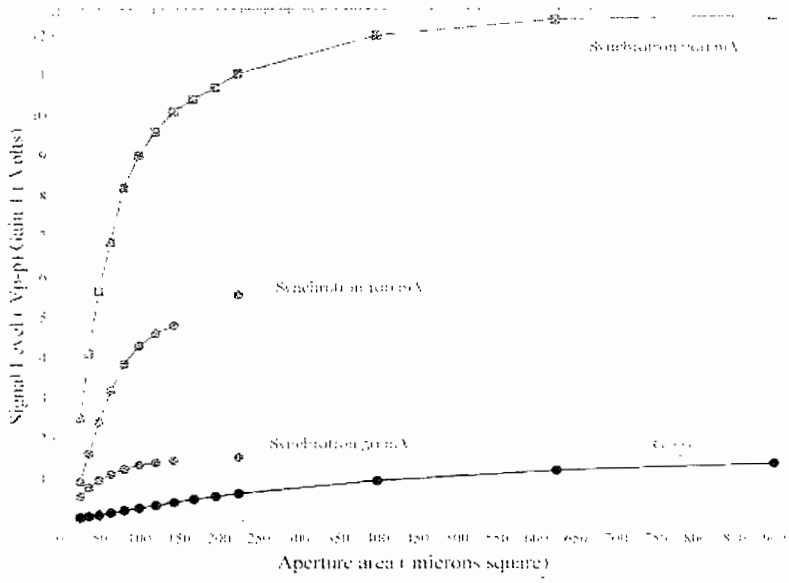


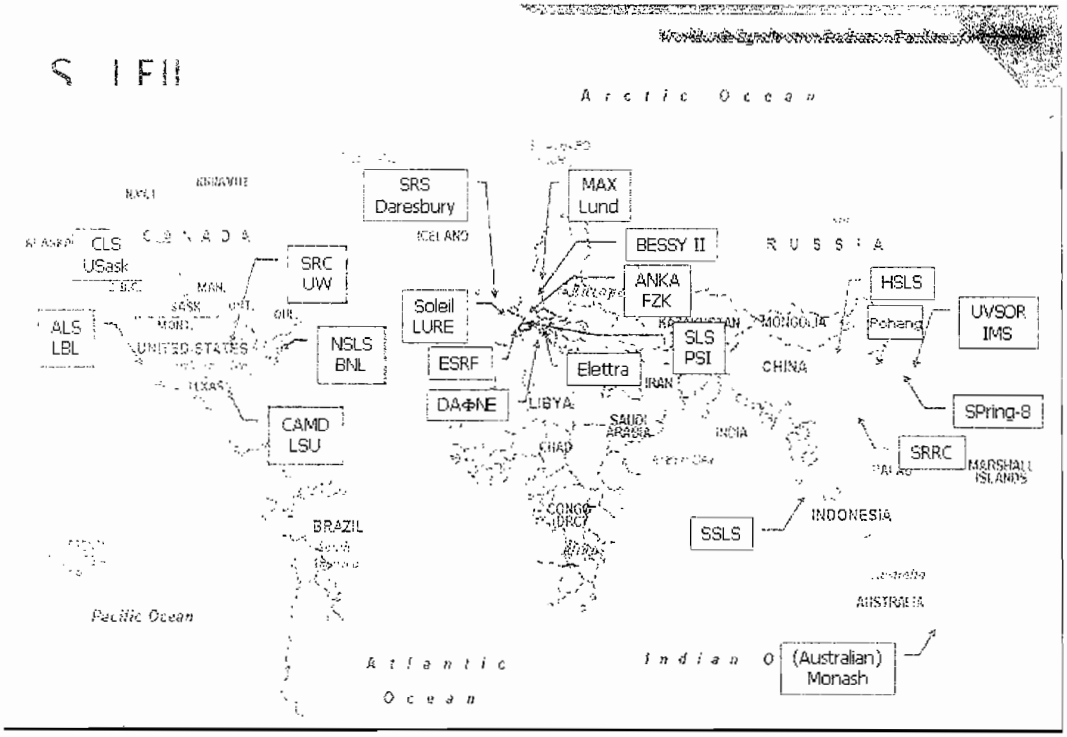
First mirror - slotted



SOLEIL SYNCHROTRON

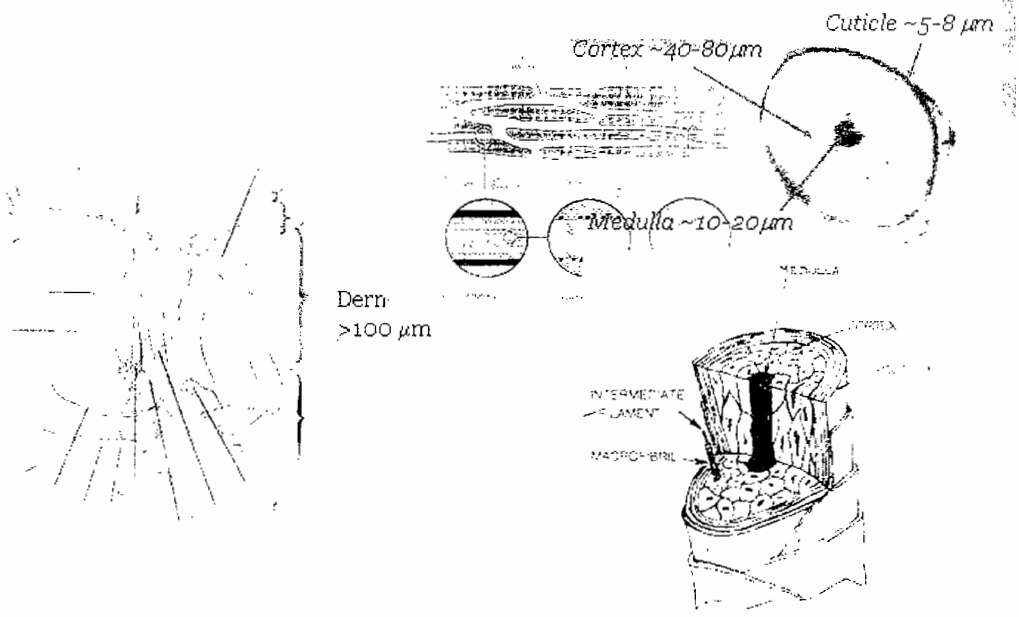
Performances achieved at ESRF





35

Biological applications: human tissues



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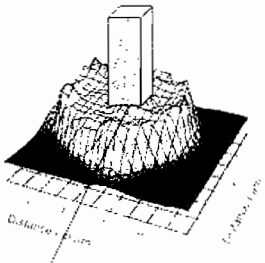
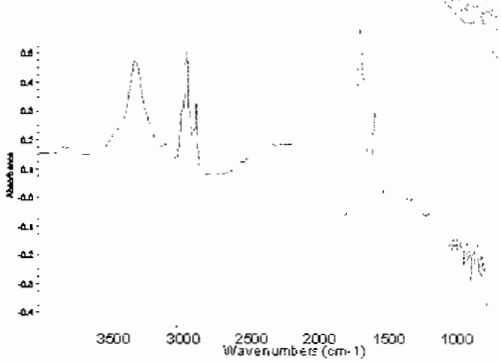
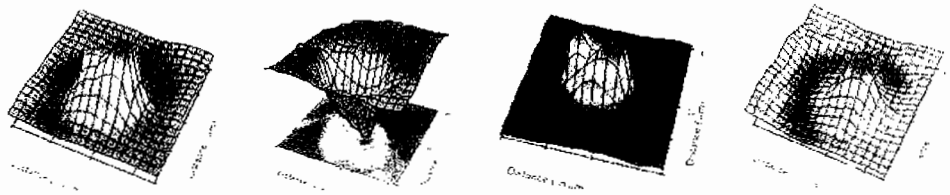
S LEIL SYNCHROTRON

Lipid profile





3x3 μm^2 aperture
1 μm step

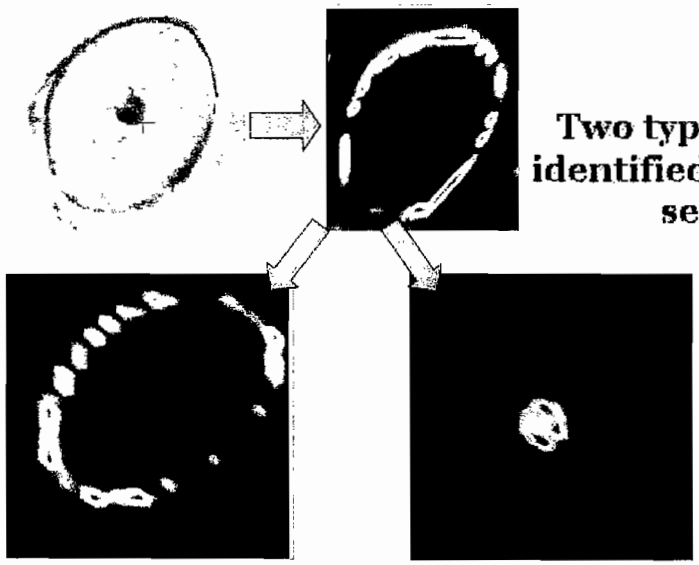


CH_2 | Amide I | C=0 | carboxylate

Intern.J. of Cosmetics Science. **23** *1-6* (2001) 369-374

S LEIL SYNCHROTRON

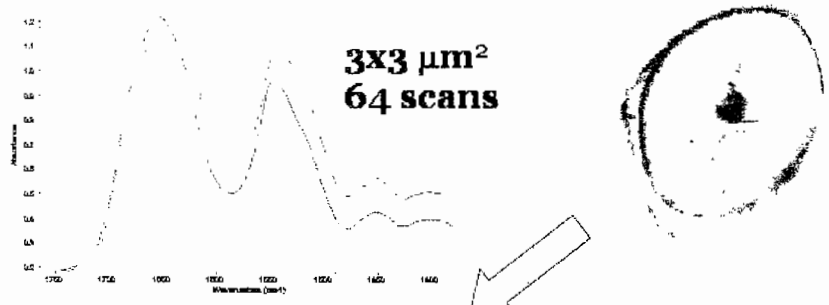
Beside chemical imaging: multivariate...



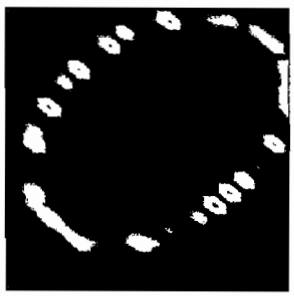
Two types of lipids identified across hair section

Two types of lipids identified by HCA (Hierarchical Cluster Analysis)

Secondary structure of proteins



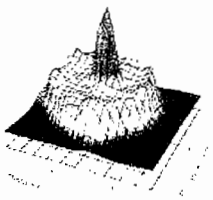
3x3 μm²
64 scans



Higher concentration in β Sheets in the cuticle.

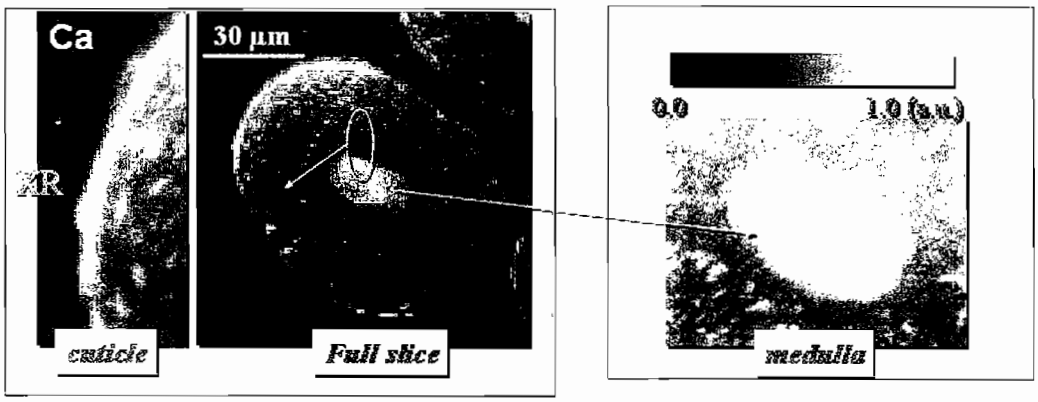
3- Combining synchrotron-based microanalysis

Hair study....



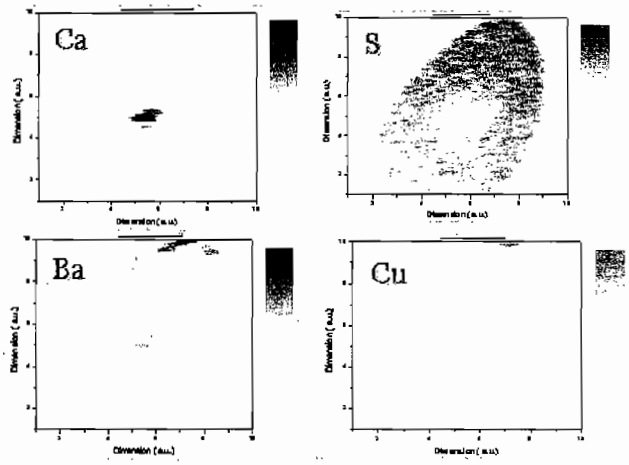
Lipid distribution
Across hair cut
(infrared)

J. Susini et al.

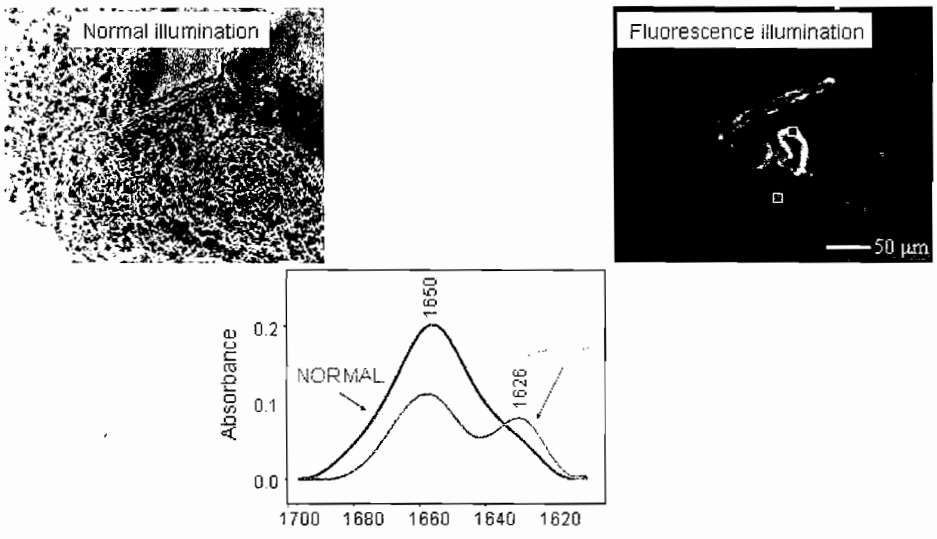


S LEIL
SYNCHROTRON

X-ray fluorescence microcopy at ID 22 (ESRF)
S. Bohic, A.Somogyi,A. Simionivici,J. Susini, P.Dumas



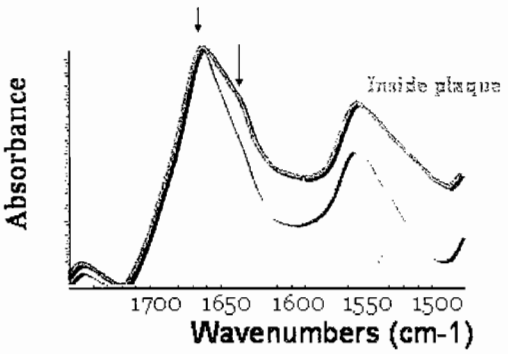
S LEIL
SYNCHROTRON

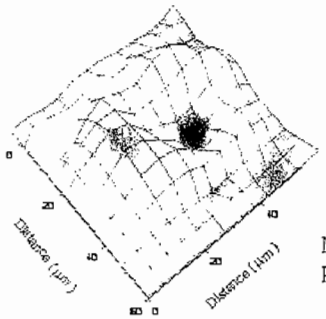


Lisa M. Miller, Paul Dumas, Nadege Jamin,[3]Jean-Luc Teillaud,Judit Miklossy, and Laszlo Forro
Rev. Sci. Instrum (2003)

Alzheimer's disease

Imaging beta misfolding



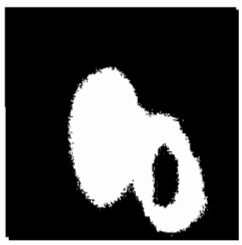


M. Lankosz, M. Boruchowska, J.Chwiez Cracow(Poland)
P. Dumas (SOLEIL/LURE)

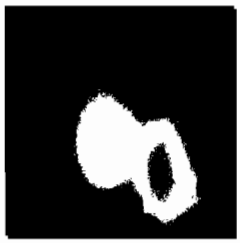
Cell differentiation

Induced by Phorbol Myristate Acetate (PMA)
(morphology and activity changes)

HL-60 few minutes after « activation »



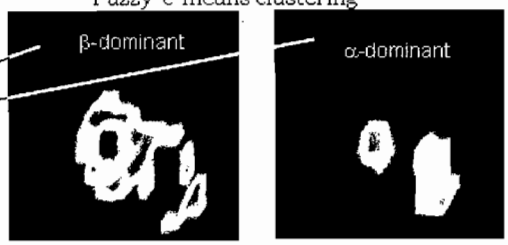
Lipids profile



Protein profile
(Amide I)

20 μm

Fuzzy-c-means clustering



J.L. Teillaud, N. Jamin, L. Miller and P.Dumas

mjw23

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S LEIL
SYNCHROTRON

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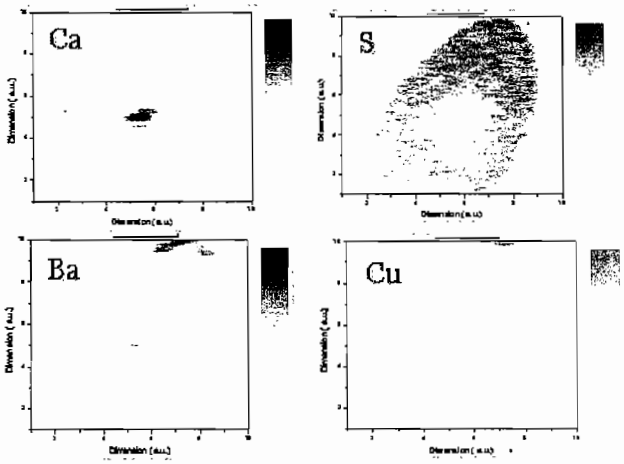

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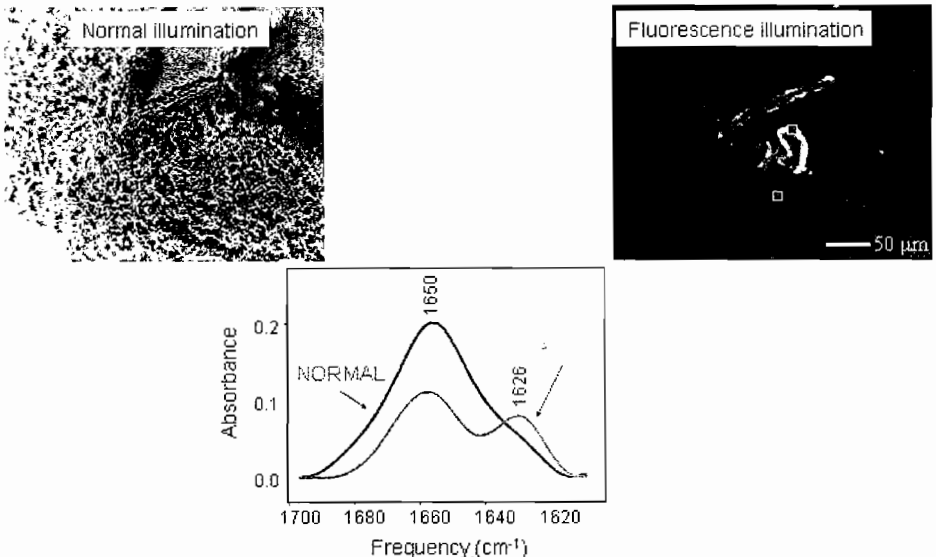

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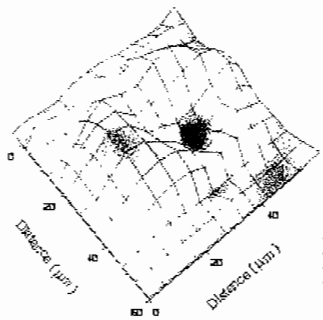

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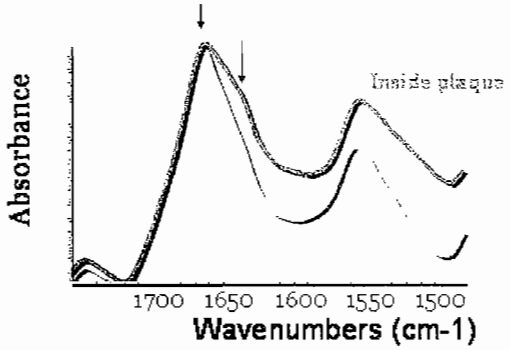

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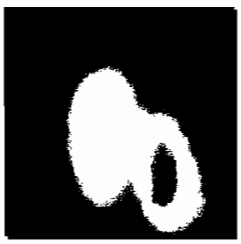
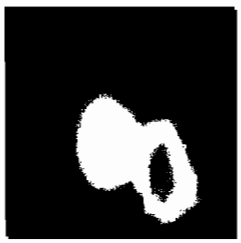


Lipids profile



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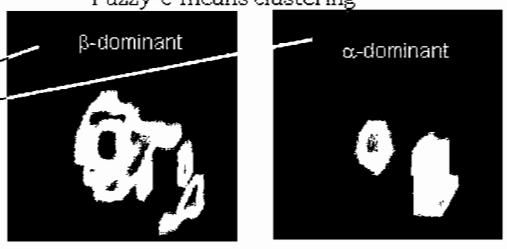
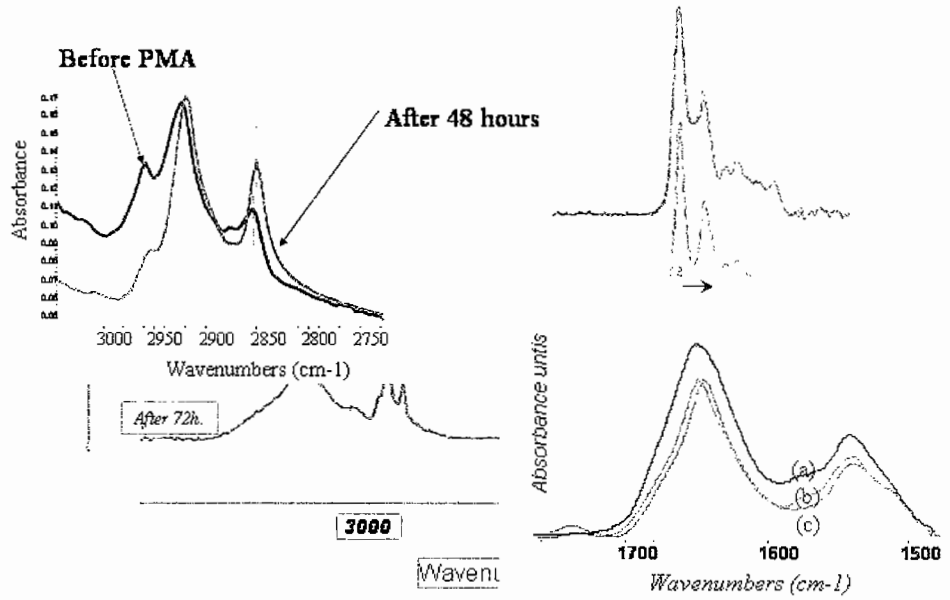


1750 1700 1650 1600 1550 1500
Wavenumbers (cm-1)

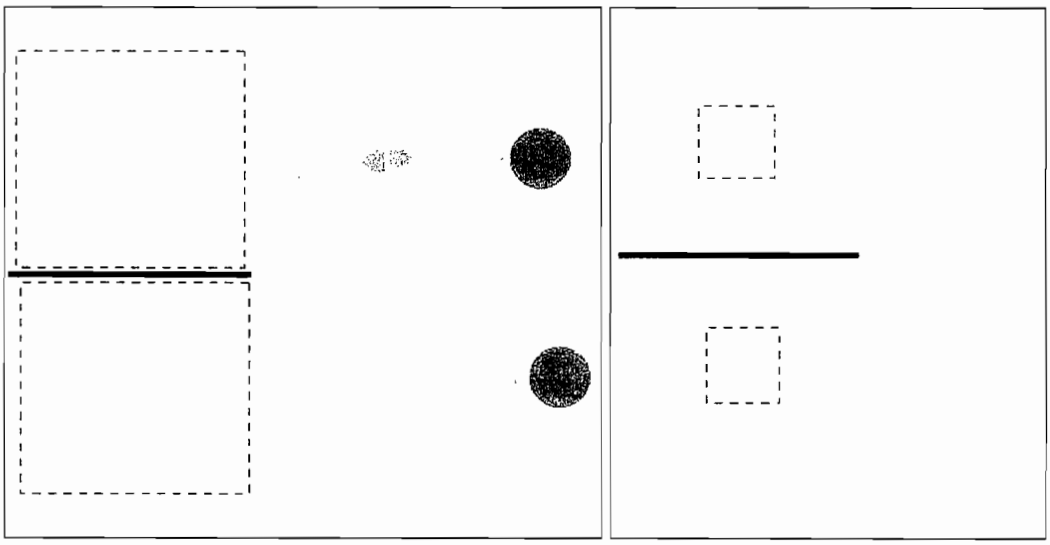
J.L. Teillaud, N. Jamin, L. Miller and P.Dumas

S LEIL SYNCHROTRON

Spectra recorded with a 3x3 μm^2 aperture in the nucleus

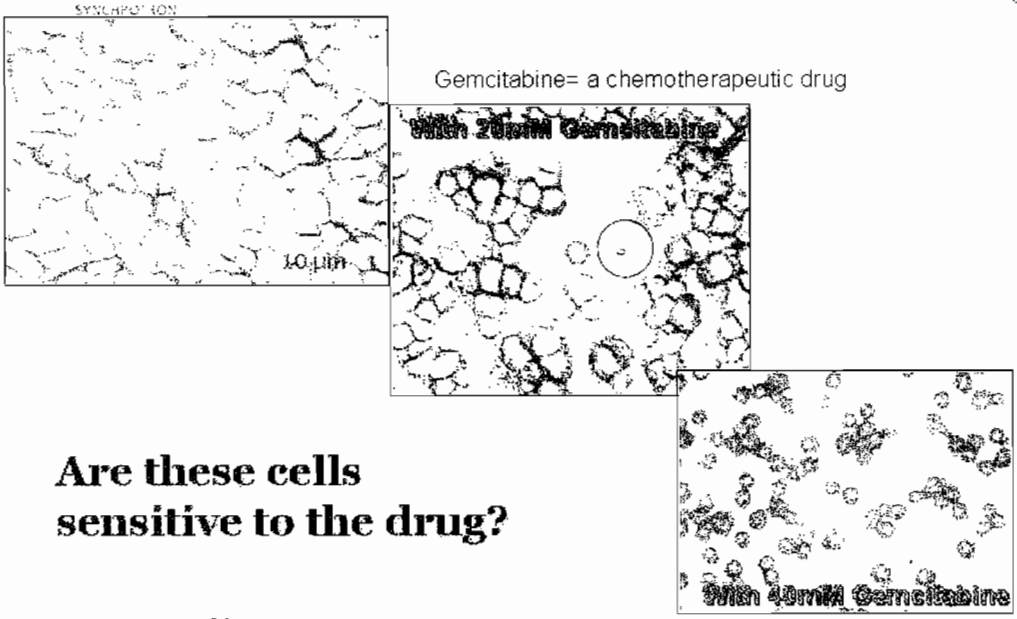


S LEIL SYNCHROTRON



SKMES lung cancel cells line

S LEIL



Gemcitabine= a chemotherapeutic drug

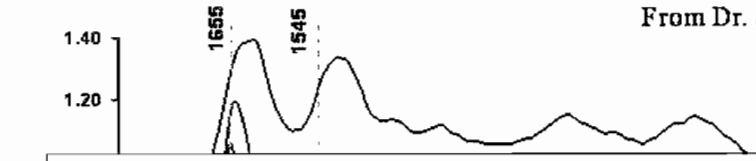
Are these cells sensitive to the drug?

From Dr. Josep Sulé-Suso

SKMES lung cancel cells line

S LEIL

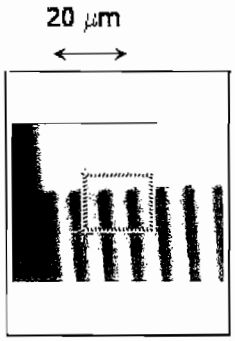
From Dr. Josep Sulé-Suso

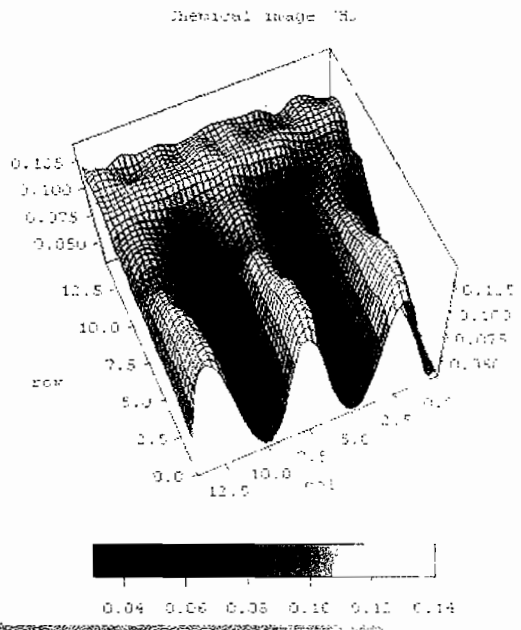


the biochemical changes in these cells measured with synchrotron IR micro-spectroscopy could help us to better clarify the state of a single cell, i. e.,

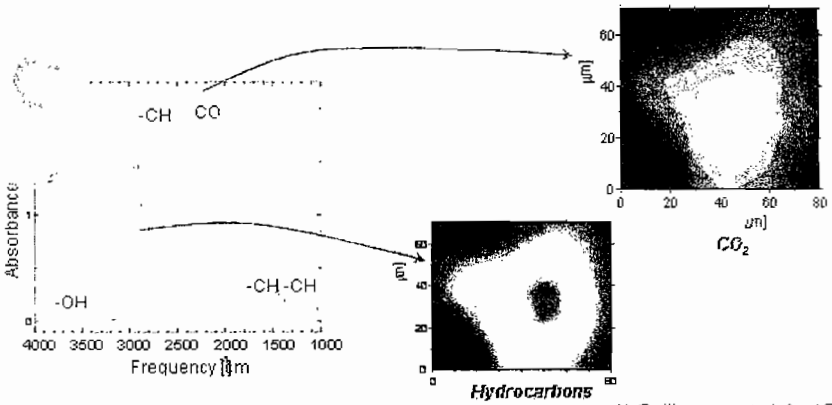
- ***alive without damage,***
- ***alive with damage but able to recover,***
- ***alive but entering a death pathway and unable to recover,*** **or**
- ***dead.***

Gold grid deposited on silicon wafer
imaging the protective layer on top of the gold grid





Inclusions in rocks



N. Guilhaumou et al. Appl.Spectrosc.

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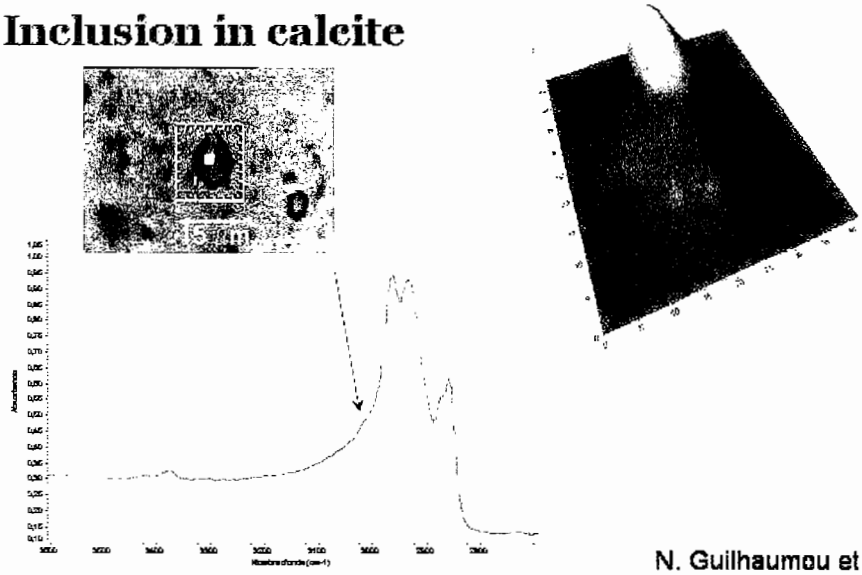
Small inclusions in rocks

Inclusion in calcite



N. Guilhaumou et coll.

Aperture= 3x3 µm²

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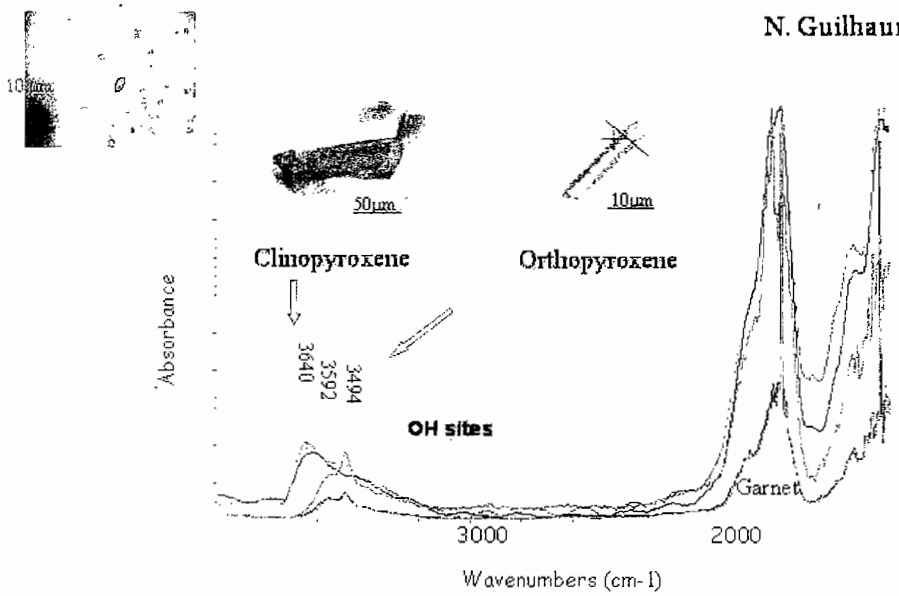
Water in deep seated minerals (200-400 kms)

N. Guilhaumou et al.



Summary

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- Synchrotron IR microscopy has became an important analytical tool in synchrotron facilities
- Such facilities are of high ratio scientific/cost
- Association with fluorescence is desirable
- Good S/N and higher spatial resolution.... Statistical treatment (unsupervised or supervised)
- Complementarities with other synchrotron based techniques are very potential especially if combined studies are performed on the same sample.

Acknowledgments

S LEIL SYNCHROTRON

Special thanks to my long term collaborators:


G.Larry Carr (NSLS)
Gwyn P. Williams (JLab)
Lisa M. Miller (NSLS)
O. Chubar (SOLEIL)
F. Polack (SOLEIL)



And

J. Susini (ESRF)
P. Elleaume (ESRF)
K. Scheidt (ESRF)

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Synchrotron Reflection Absorption Infrared Spectroscopy

Peter Gardner
The University of Manchester

RSC-IRDG Rutherford Appleton Laboratory – 31 August 2006

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Outline of Talk

Reflection absorption Infrared Spectroscopy (RAIRS)

Why do we need a synchrotron

What can we do with it

(Surface dynamics CO on metal surfaces)

CVD growth of SnO_2

Model Z-N catalysts

Outlook

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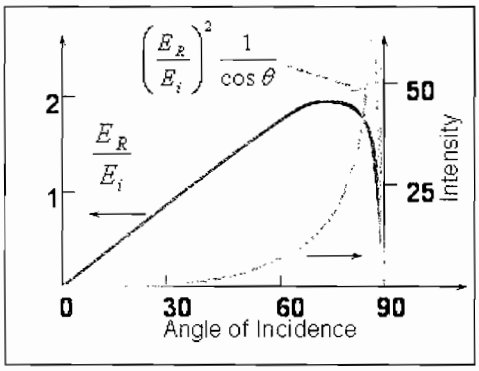
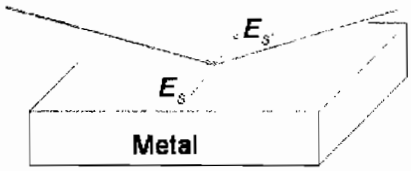
Reflection-Absorption Infrared Spectroscopy RAIRS





This is the basis of the "Metal Surface Selection Rule"

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Reflection Absorption Infrared Spectroscopy RAIRS

An experimental technique that enables IR spectra to be obtained from molecules or thin films on highly reflecting metal surface

Highly sensitive – fractions of a monolayer

Metal Surface Selection Rule – simple spectra, orientation information

Particularly relevant to adsorbates on model catalytic systems

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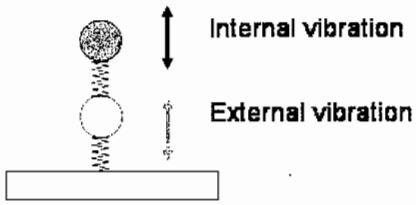
The method was used extensively in the late 1980s and early 1990s to study adsorbates on metal surfaces

In the mid 1990s there was an explosion of interest in using RAIRS for the study of SAMs on Au and Ag surfacs

However the standard RAIRS set-up using an LN2 cooled MCT detector is limited to monitoring internal vibrations of the molecules



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Why do we want to use a synchrotron?

Above 800 cm^{-1} a conventional lab based RAIRS system easily out performs the synchrotron

Below 500 cm^{-1} the synchrotron starts to have an advantage and below 300 cm^{-1} this advantage is significant

Most metal-adsorbate stretches are in this low frequency region of the spectrum

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Early days of far IR-RAIRS

Preliminary data by Bradshaw and Schweizer taken at BESSY in 1986 did not look promising

Gwyn Williams at Brookhaven pioneered the Far IR RAIRS method in 1990 with the completion of U4IR. ***Nucl. Instrum. Methods A291 (1990)***

Collaborations with P. Dumas, F. Hoffman Y. Chabal B. Persson A. Volokitin, C. Hirschmugl and others resulted in a series of seminal papers mainly on low frequency vibrations of CO on low index faces of metal surfaces.

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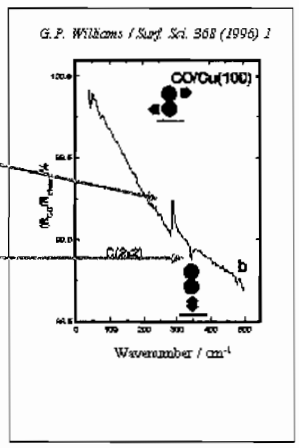
First observation of dipole forbidden modes

Parallel mode forbidden by MSSR

Perpendicular mode allowed by MSSR



At the same time M. Chester, P. Hollins M.Surman started to build station 13.3 on the SRS.

Initial source instability slowed progress

In the late 1990s we started to look at adsorbates on oxide surfaces

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Infrared Studies of CVD Precursor Molecules on Thin-film Oxide Surfaces

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CVD Growth of SnO_2 on Float Glass

$$SnCl_4 + 2H_2O = SnO_2 + 4HCl$$

$$SnCl_4 + O_2 = SnO_2 + 2Cl_2$$

We want to study the formation of SnO_2 on SiO_2

RAIRS is straight-forward on a metal surfaces but, it is difficult to do on oxide surfaces due to poor

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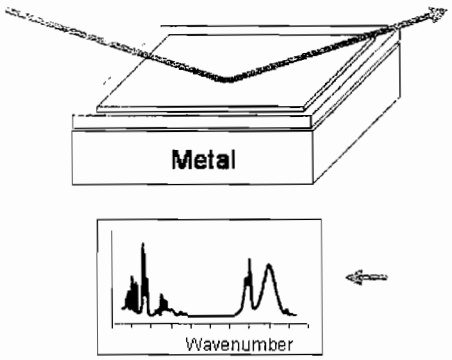
The Buried Metal Layer Method



If the thickness of the oxide is << λ then the reflection will be dominated by the metal but the surface chemistry being probed will be that of the oxide

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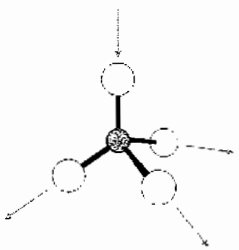
Why work at Daresbury?



ν_3 Sn-Cl (asym)
408 cm^{-1}

Sn-Cl stretching modes in the region 300 – 450 cm^{-1}

Conventional RAIRS shows poor sensitivity below 800 cm^{-1}

Low intensity of conventional source necessitates the use of synchrotron radiation

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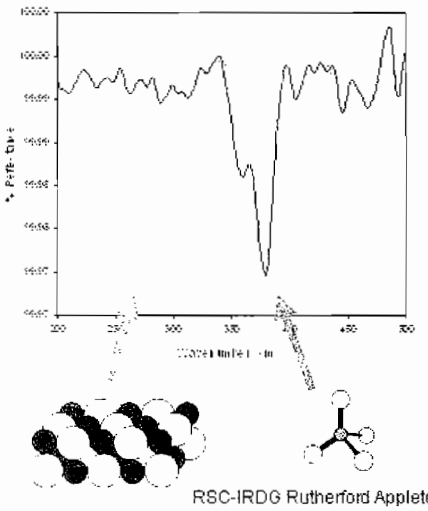
RAIRS spectrum of tin tetrachloride on thin-film (100 nm) silica / W sample at 291K



At 291 K spectra are consistent with molecular adsorption

On Na doped SiO_2 spectra are consistent with the formation of small NaCl clusters

M. J. Pilling, P. Gardner, M. E. Pemble and M. Surman,, Surface Science Letters, 418, (1998), 1-7

M. J. Pilling, P. Gardner, R. Kausar, M. E. Pemble and M. Surman, Surface Science, 433-435, (1999), 22-26,

M. J. Pilling, Nurhayti, P. Gardner, A. Awalludin, M. E. Pemble, and M. Surman, Accelerator-based Sources of Infrared and Spectroscopic Applications, Eds. G. Lawrence Carr, Paul Dumas, Proceedings of SPIE Vol 3775, page 192-200 (1999)

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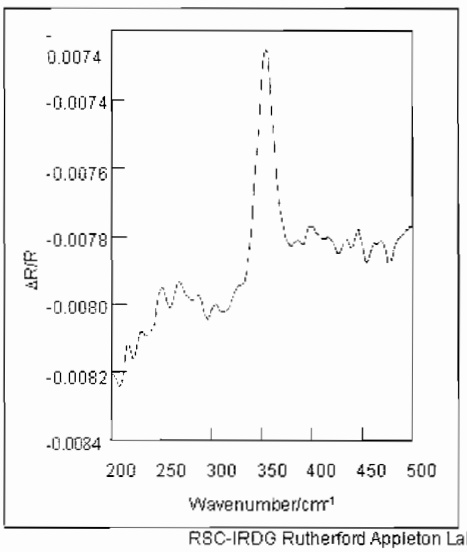
RAIRS spectrum of 25L tin tetrachloride on SnO_2 at 291K



On a thin film SnO_2 surface adsorption results in an inverse adsorption band

Is this due to the $SnCl_4$?

Need to revisit the theory of the RAIRS experiment

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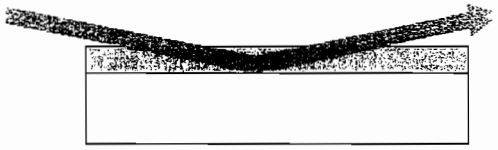
Greenler Calculations

The Greenler equations are extensions of the well know Fresnel relationships, which define the reflectivity at the interface between two isotropic materials.



n_1-ik_1 Vacuum (fixed)

n_2-ik_2 Adsorbate (fixed)

n_3-ik_3 Metal (fixed)

The reflectivity R' for a particular thickness of adsorbate layer is compared with the reflectivity R in the absence of the adsorbate

$$\Delta R / R = (R' - R) / R$$

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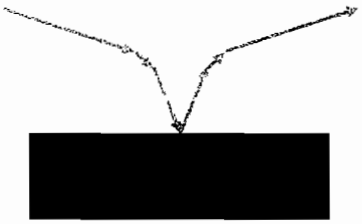
Greenler-Buried metal layer

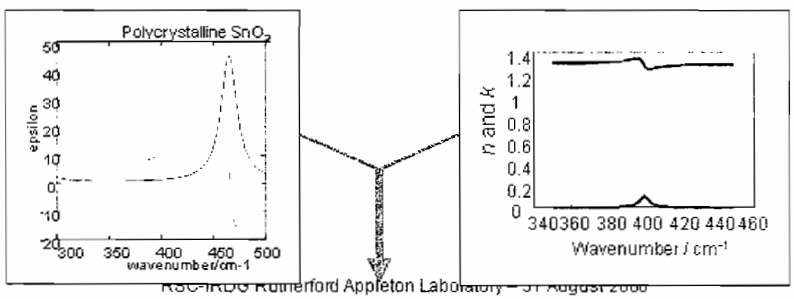


n_1-ik_1 Vacuum (fixed)

n_2-ik_2 Adsorbate (variable)

n_3-ik_3 Oxide (variable)

n_4-ik_4 Metal (fixed)



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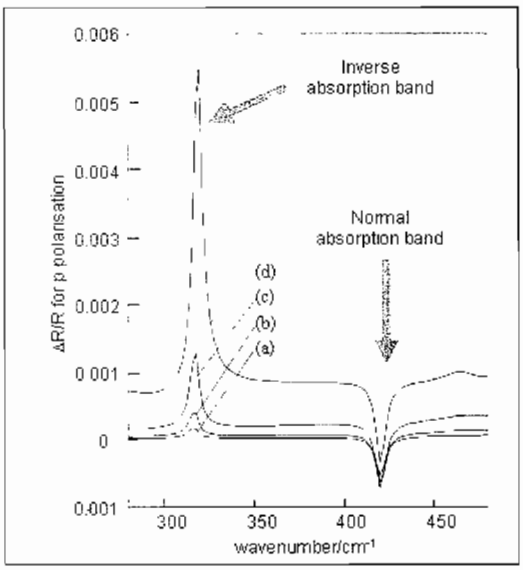
Typical wavenumber-dependent 4-layer Greenler calculation for a adsorbate with *k* maximum at 420 cm^{-1}



Calculations can qualitatively reproduce the inverse absorption band

They suggest that the inverse absorption band is induced by the adsorbate but is not related to the vibrational properties of the adsorbate

This is confirmed by experiments with $SnBr_4$

A. Awaluddin, M. J. Pilling, P. L. Wincott, S. Le Vent, M. Surman, M. E. Pemble and P. Gardner, Surface Science 505 (2002) 63-69

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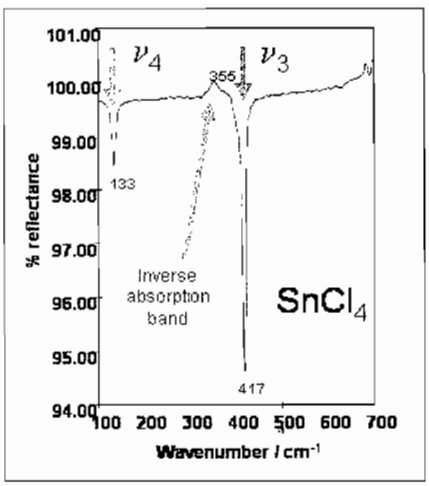
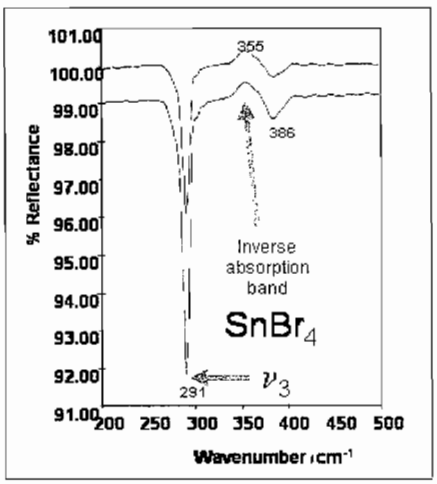
Confirmation using $SnBr_4$

	ν_1	ν_2	ν_3	ν_4
$SnCl_4$	369	95	408	126
$SnBr_4$	222	59	284	86

The $SnBr_4$ has no vibrational modes above 300 cm^{-1}





M. J. Pilling, S. Le Vent P. Gardner, A. Awaluddin, P. L. Wincott, M. E. Pemble and M. Surman, Anomalous inverse absorption features in the far infrared RAIRS spectra of $SnCl_4$ on thin-film SnO_2, J. Chem Phys 117 (2002) 6780-6788

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The calculations show that the band is related to the optical properties of the bulk oxide film

This stimulated additional theory work related to Far IR RAIRS on non-metallic surface

P. Gardner, S. LeVent, M. J. Pilling
A theoretical investigation of the far-infrared RAIRS experiment applied to a buried metal layer substrate
Surface Science 559 (2004) 186 – 200

M J Pilling, P Gardner, S Le Vent
Considerations of Optical Anisotropy in the Simulation of Reflection Absorption Infrared Spectra
Surface Science 582 (2005) 1

S. LeVent, M. J. Pilling, P.Gardner
A theoretical study of inverse features in far-infrared RAIRS spectra from non-metallic substrates
Surface Science 587 (2005) 150

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Far infrared RAIRS studies of MgClx/TiCly thin-films related to model Zieger-Natta catalysts

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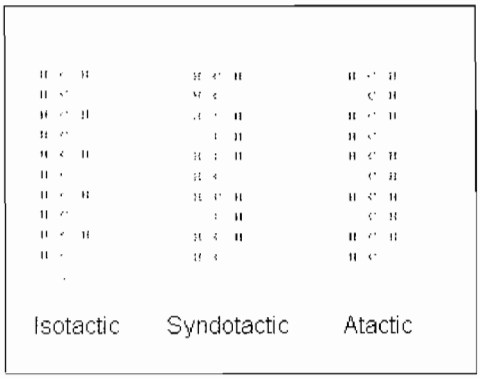
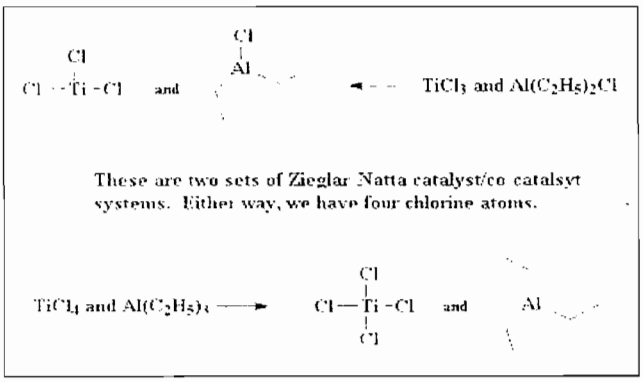
Zeigler Natta Catalysts

Zieger Natta Catalysis is an important method of vinyl polyermerisation enabling polymers of a specific tacticity to be made



The Z-N catalyst



Creation of the active site is generally achieved via the chemisorption of $TiCl_4$ on a high area $MgCl_2$ support, followed by alkylation and reduction by an aluminium alkyl. Utilisation of this type of catalyst results in both high yields and selectivity of the desired isotactic polymer.

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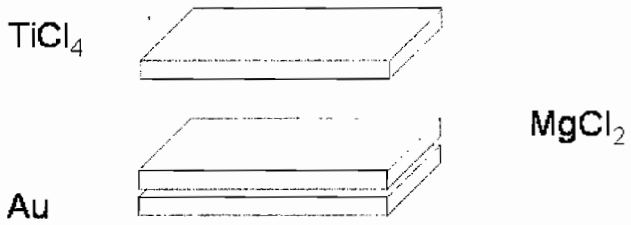
Preliminary work by Somorjai et al have shown that model Z-N catalysts can be prepared under UHV conditions but the exact nature of the surfaces produced is still open to question



The ideal method of producing the model catalyst would be to deposite $TiCl_4$ on top of the $MgCl_2$ on a suitable substrate e.g. Au

$TiCl_4$ will not stick on $MgCl_2$

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In order to get $TiCl_4$ to adsorb we need reduced Mg sites

This may be achieved in a number of ways

Adsorb on pure Mg

Electron beam irradiation of $MgCl_2$

Pre adsorption of $TiCl_4$

During adsorption of $TiCl_4$

These different methods produce different types of films that may have different surfaces.

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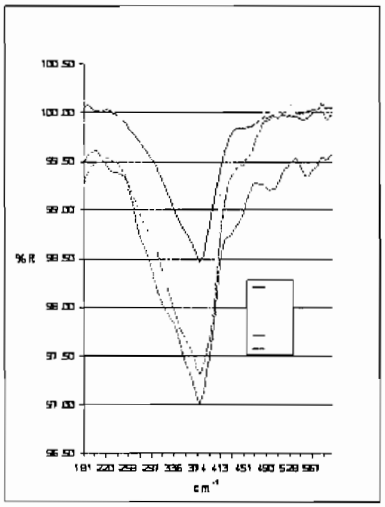
RAIRS spectra following exposure of a thin-film of Mg on Au, to varying amounts of $TiCl_4$



$TiCl_4$ does stick at 300 K to the Au/Mg surface but the resulting RAIRS spectrum is very broad ~ 200 cm^{-1}

The positions of these bands are consistent with transmission far infrared spectroscopy performed on α–$MgCl_2$ and β-$MgCl_2$ [2] where absorption bands have been observed at 407cm^{-1}, 372cm^{-1}, 329cm^{-1}, 276cm^{-1} and 248cm^{-1}.

What about the Ti?

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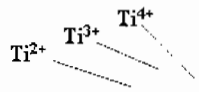
XPS of Au/Mg/$TiCl_4$



900 L

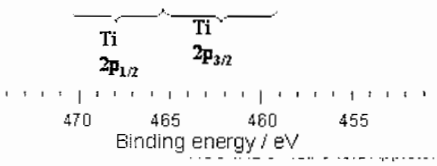
600 L

100 L

The XPS spectra clearly show three different oxidation state of Ti.

This is clearly very complex

We need to simplify the system



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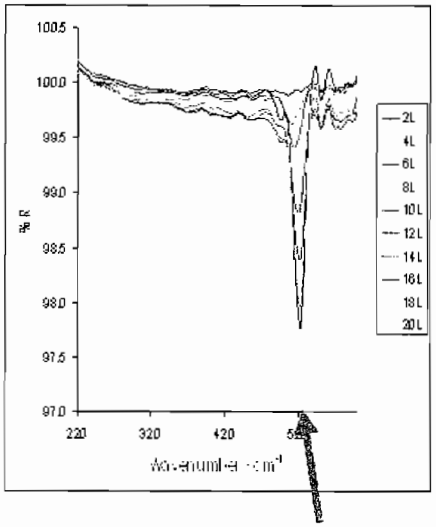
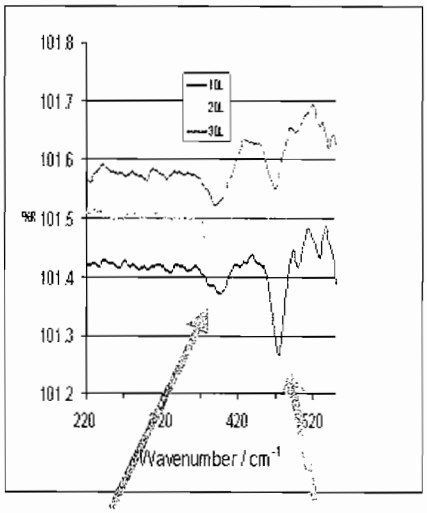
$TiCl_4$ on Au at 120 K

Without e-beam



e-beam



Multilayer $TiCl_4$

$TiCl_2$

$TiCl_4$

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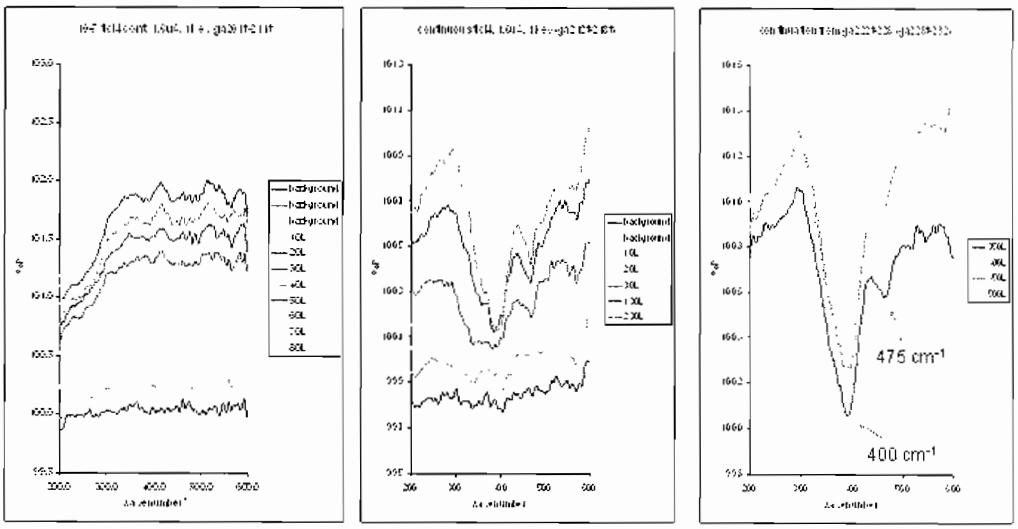
$TiCl_4$ on Au at 300 K using e-beam



Little observed at low exposure

Two broad bands at high L consistent with $TiCl_2$ and $TiCl_4$

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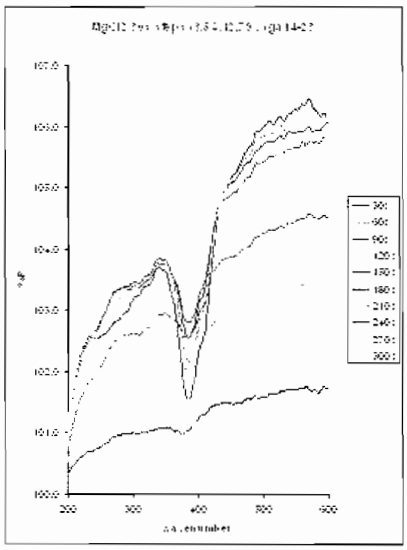
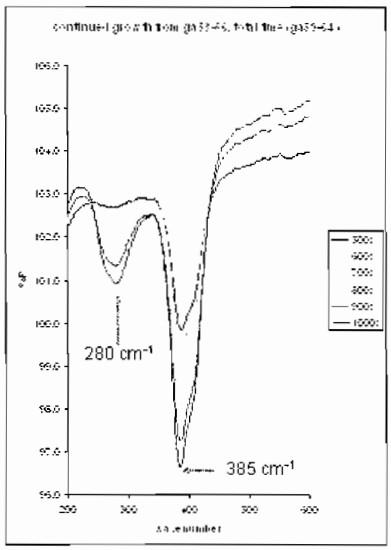
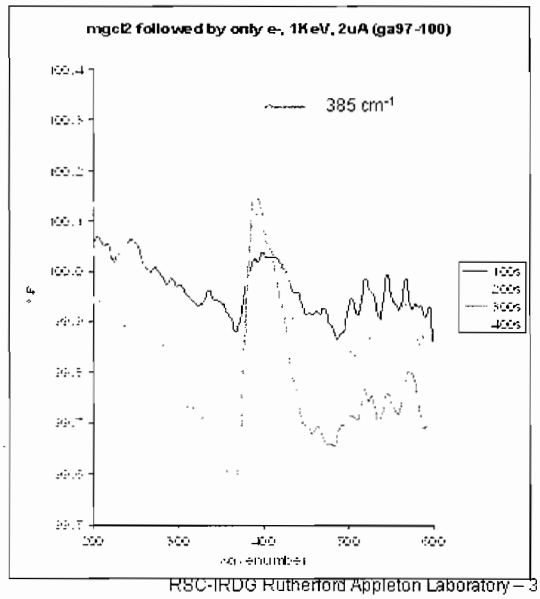
$MgCl_2$ on Au at 300 K





$Au/MgCl_2$ with e-beam only



Loss of $MgCl_2$

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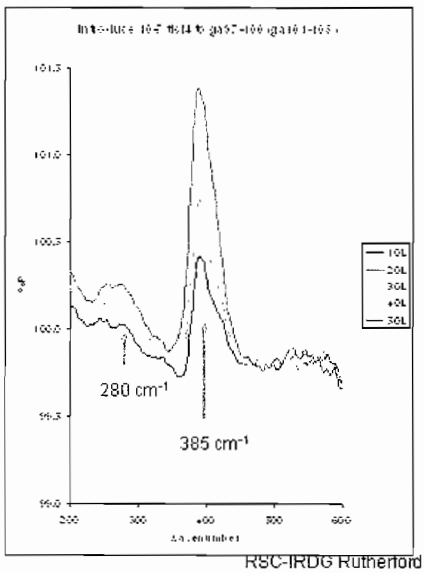
Adsorption of $TiCl_4$ on Au/$MgCl_2$ with e-beam



Under these conditions all we observe is loss of $MgCl_2$.

Where is the $TiCl_x$?

M. J Pilling, M. J. Cousins, A. Amiero Fonseca, K. C. Waugh, M. Surman, P. Gardner
Far Infrared RAIRS and XPS Studies of TiCl4 Adsorption and Reaction on Mg Films.
Surface Science 587 (2005) 78

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Conclusions

The Au/$MgCl_2$/$TiCl_x$ system is a very complex one

Production of a film that is a good model of the catalyst is not straight forward

It is not at all clear that the model of the surface produced by Somorjai is correct

Far IR RAIRS alone is not going to solve this problem on its own

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Outlook

Far-IR RAIRS using synchrotrons has been carried out successfully only at Brookhaven and Daresbury. Both these station have now closed

Why?

There was only a small user community
The technique is complicated and good results difficult to obtain.
Only a few systems worked.
Poor source stability on second generation machines

New third generation sources should have better source stability

There is need for one good far IR RAIRS station.

Call it THz-RAIRS or RATZS and it might get funded!!!!!

MANCHESTER 1824

Acknowledgements

MSc Students
Danny Bird
Sarah Bickerstaff

PhD Students
Sunil Patel
Mike Pilling
Mrs Nurhayati

Post Docs
Mike Pilling

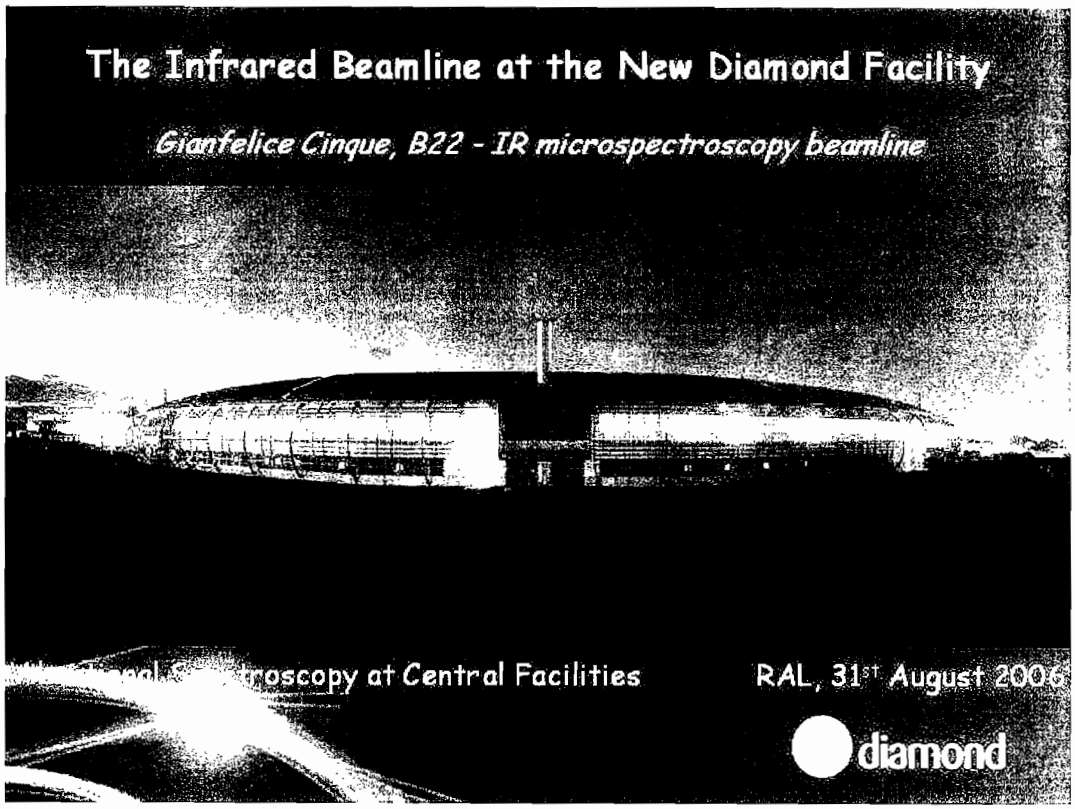
S Le Vent

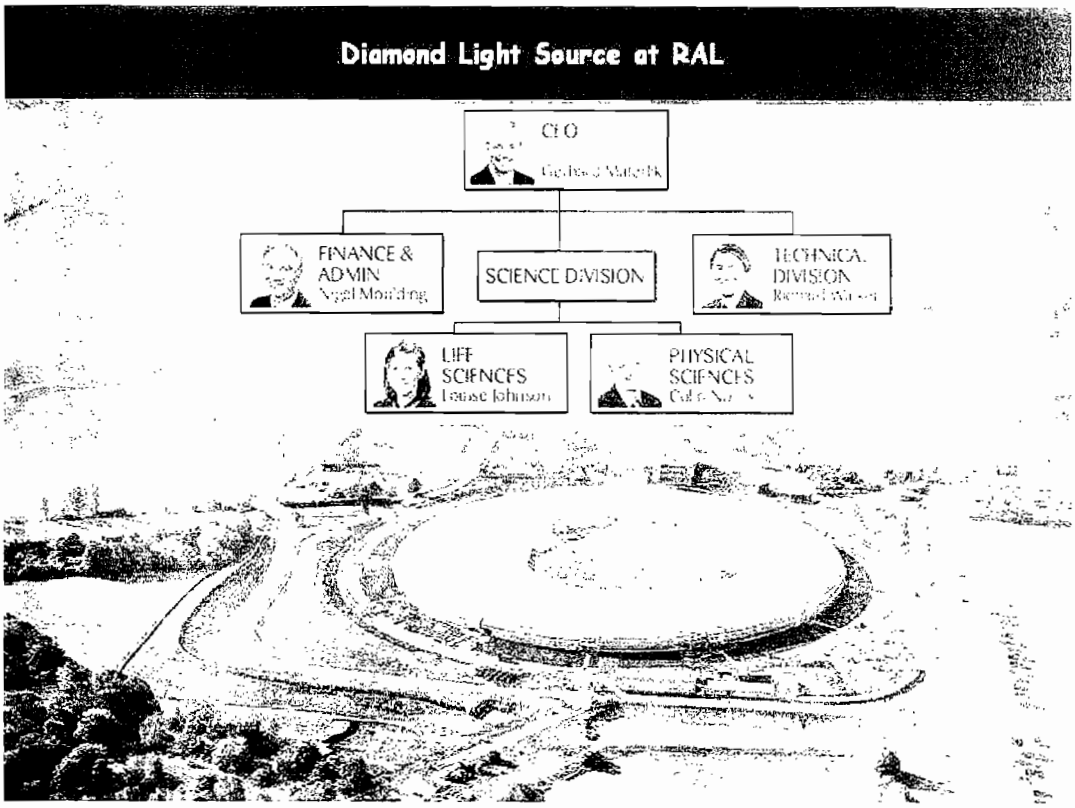
Mark Surman Daresbury

Martyn Pemble Salford
Paul Wincott
Amir Awaluddin

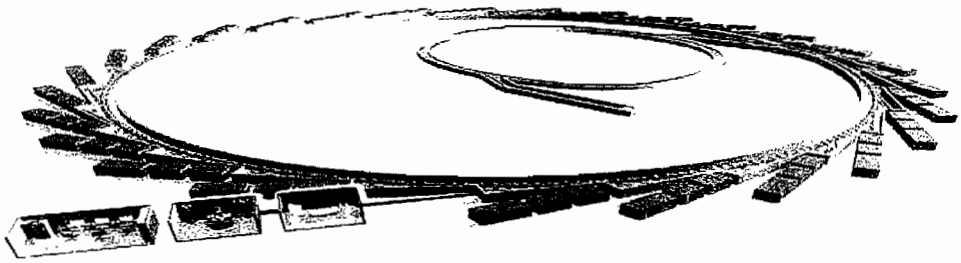
Mike Chester, Nottingham
Peter Hollins, Reading

EPSRC


The Infrared Beamline at the New Diamond Facility
Gianfelice Cinque, B22 - IR microspectroscopy beamline
roscopy at Central Facilities
RAL, 31st August 2006
diamond


Diamond Light Source at RAL
CEO
FINANCE & ADMIN
SCIENCE DIVISION
TECHNICAL DIVISION
LIFE SCIENCES
PHYSICAL SCIENCES

Key Machine Parameters

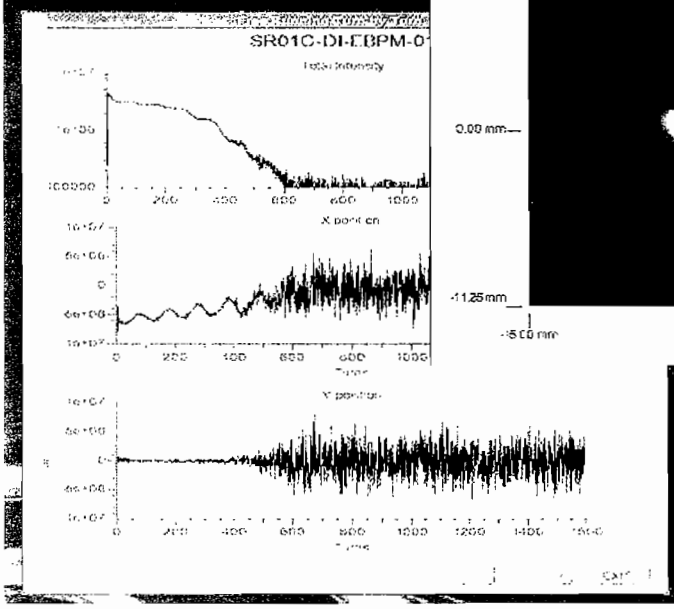


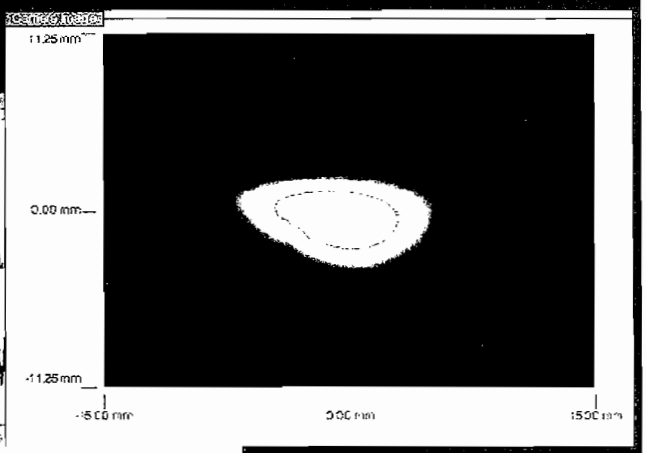
Electron Beam Energy	3 GeV
Circumference - Storage Ring	561.6 m
Number of cells	24 double-bend achromatic 6-fold symmetry
Insertion devices	4 x 8 m & 18 x 5 m
Dipole field	1.4 T
[illegible] current	300 mA (500 mA)
[illegible]ittance	2.74 nm rad (hor) 0.0274 nm rad (ver)
Beam life [illegible]	>10 h (20h)

diamond

Beam in the storage ring

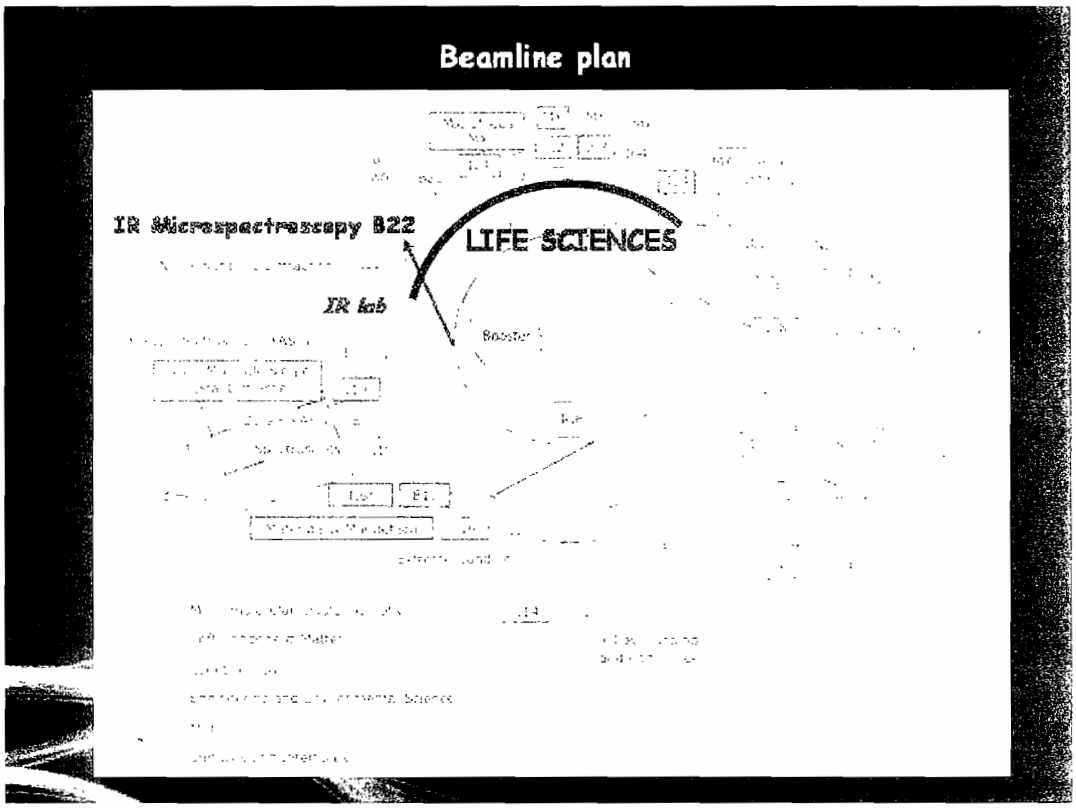
First circulating beam
4th–5th May 2006

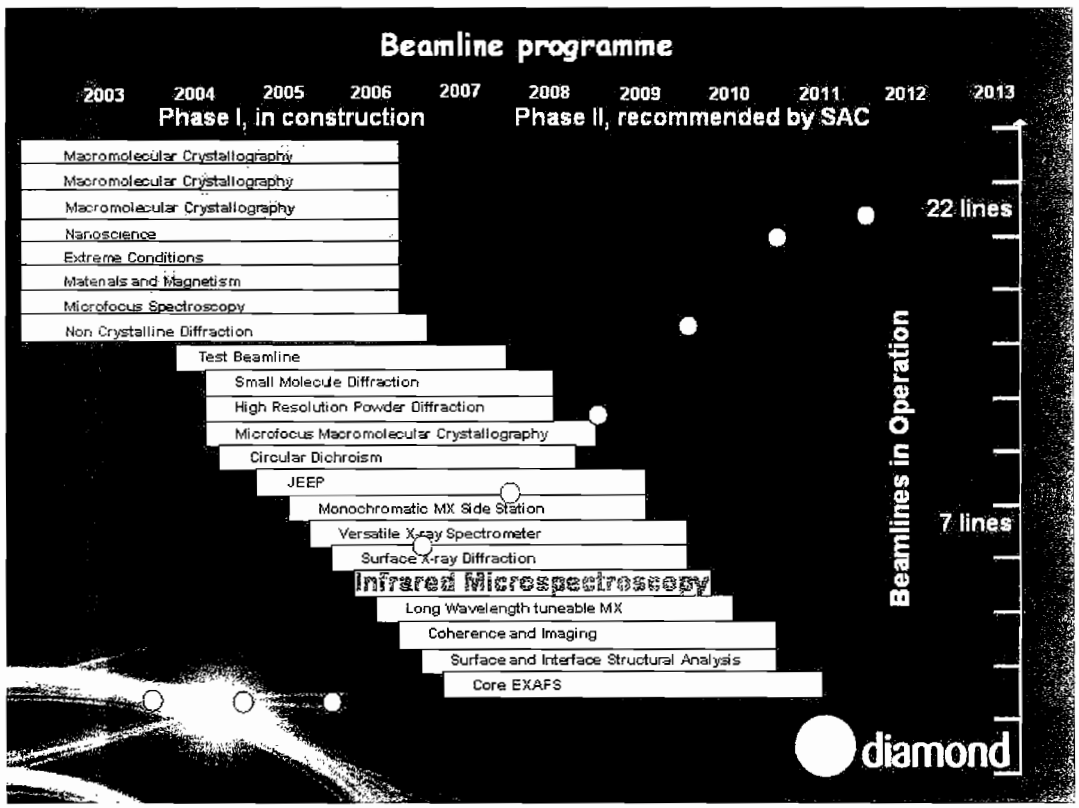




600 turns in the storage ring
6th–7th May 2006

diamond


Beamline plan
IR Microspectroscopy B22
LIFE SCIENCES
IR lab


Beamline programme
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
Phase I, in construction
Phase II, recommended by SAC
Macromolecular Crystallography
Macromolecular Crystallography
Macromolecular Crystallography
Nanoscience
Extreme Conditions
Materials and Magnetism
Microfocus Spectroscopy
Non Crystalline Diffraction
Test Beamline
Small Molecule Diffraction
High Resolution Powder Diffraction
Microfocus Macromolecular Crystallography
Circular Dichroism
JEEP
Monochromatic MX Side Station
Versatile X-ray Spectrometer
Surface X-ray Diffraction
Infrared Microspectroscopy
Long Wavelength tuneable MX
Coherence and Imaging
Surface and Interface Structural Analysis
Core EXAFS
22 lines
7 lines
Beamlines in Operation
diamond

Diamond SAC 2003: proposal of an Infrared Beamline for Microspectroscopic Analysis

Mike Chesters, University of Nottingham
Mark Tobin, Australian Synchrotron Project
Peter Hollins, University of Reading
Paul Dumas, Soleil
Liane Benning, University of Leeds
Andrea Russell, University of Southampton
Neil Everall, ICI, Wilton
Nick Terill, Diamond

Conclusions:

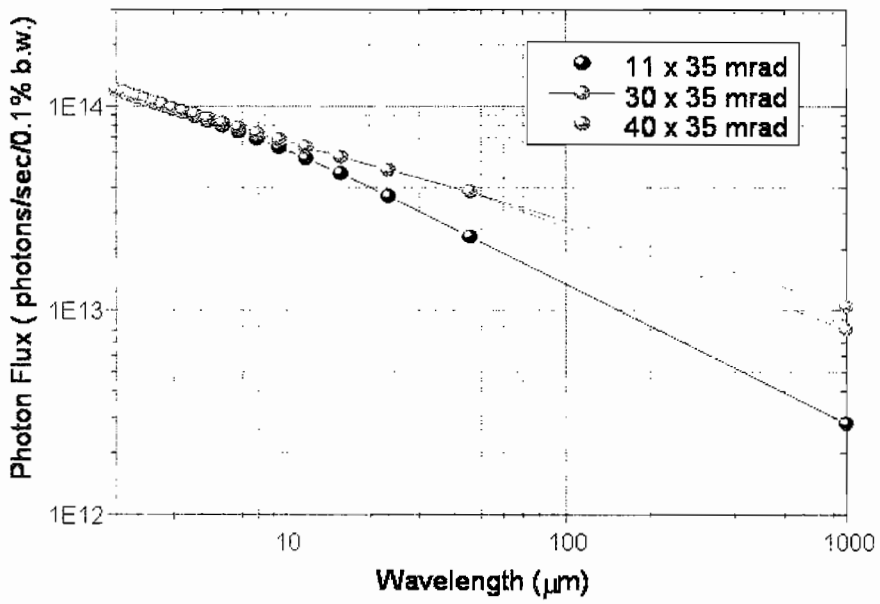
- Performance in the mid-IR (500-4000 cm^{-1}) will not be compromised by restricting the vertical acceptance angle to 11 mrad. **Provision of a 30 mrad vertical opening angle is recommended.**
- Flux in to a 4-5 μm^2 spot at 2000 cm^{-1} compared to a conventional blackbody source:

(ex) SRS 13.3	x 20
(till 2008) SRS 11.1	x 200
Diamond IMS	**> 1500**

- The use of edge radiation to provide 2 beamlines at one bending magnet should be investigated.

diamond

Diamond SAC 2003 IMS beamline proposal



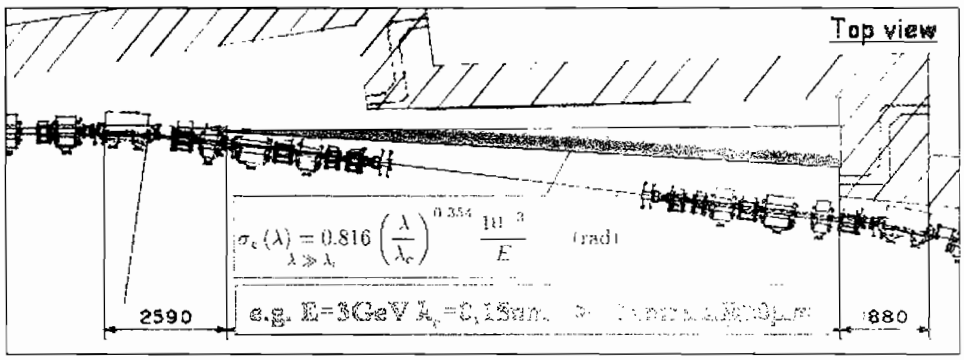
diamond

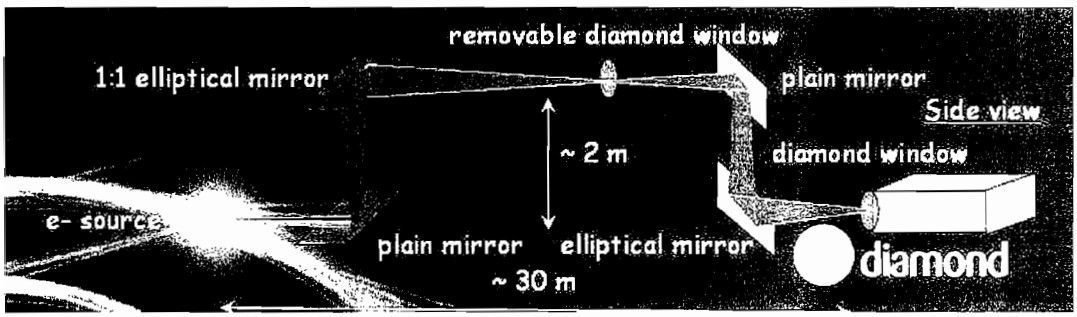
Scientific case for the IR microspectroscopy beamline at Diamond
experienced UK community working on FTIR, IR microspectroscopy and SR in fields like:

- Life Sciences and Biomedicine:
  - Single cell studies
  - Sub cellular analyses
  - Cancer diagnosis
- Solid state physical chemistry
  - Surfaces
  - Interfacial science
  - Catalysis
- *to be explored*
  - *High pressure and FTIR*
  - *Archaeology and Fine Arts*
  - *science*
  - *ic science*

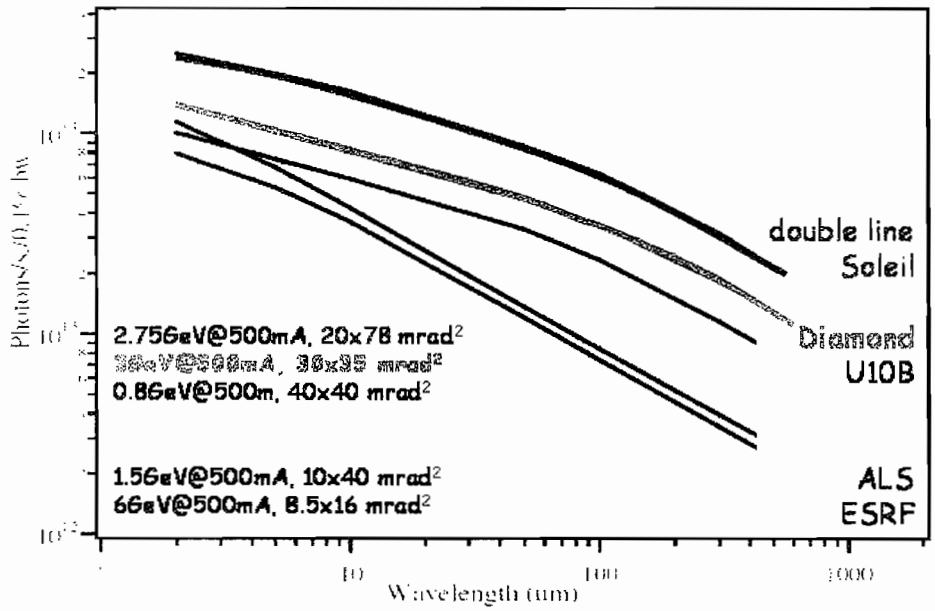
diamond

Front end and optics sketch





Diamond IR source



Pascale [illegible] ALLES Infrared Beamline on the third Generation [illegible] facility SOLEIL, WIRMS, http://www.synchrotron-soleil.fr/portail/recherche/lignes/alles/ALLESNEWS_01-06_img/WIRMS.pdf?openelement

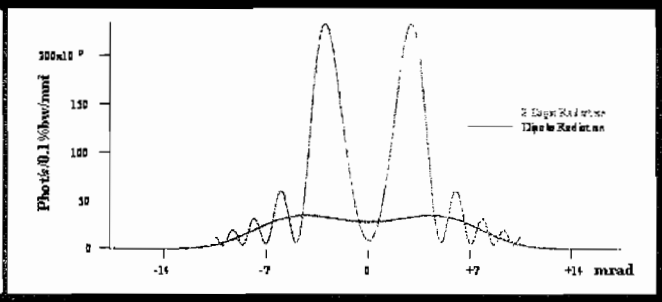
diamond

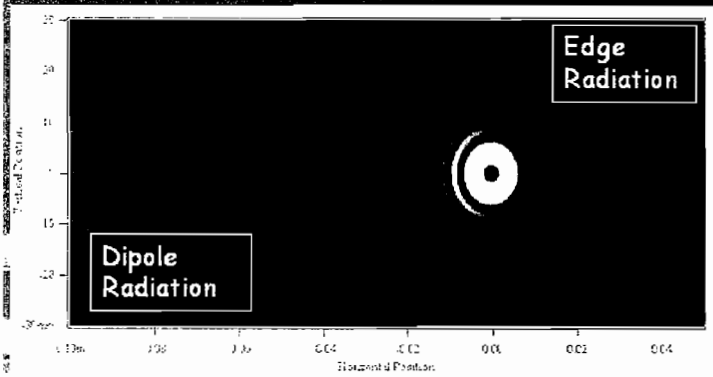
Transition Edge Radiation as Far IR source

e.m. radiation by a relativistic charge in a rapidly changing magnetic field, e.g. bending magnet ends

$$\lambda^{edge}{}_c \approx \frac{L_{edge}}{\gamma^2}\left(\approx 3nm\right)$$

$$\lambda^{BM}{}_c \approx \frac{R}{\gamma^3}\left(\approx 0.15nm\right)$$

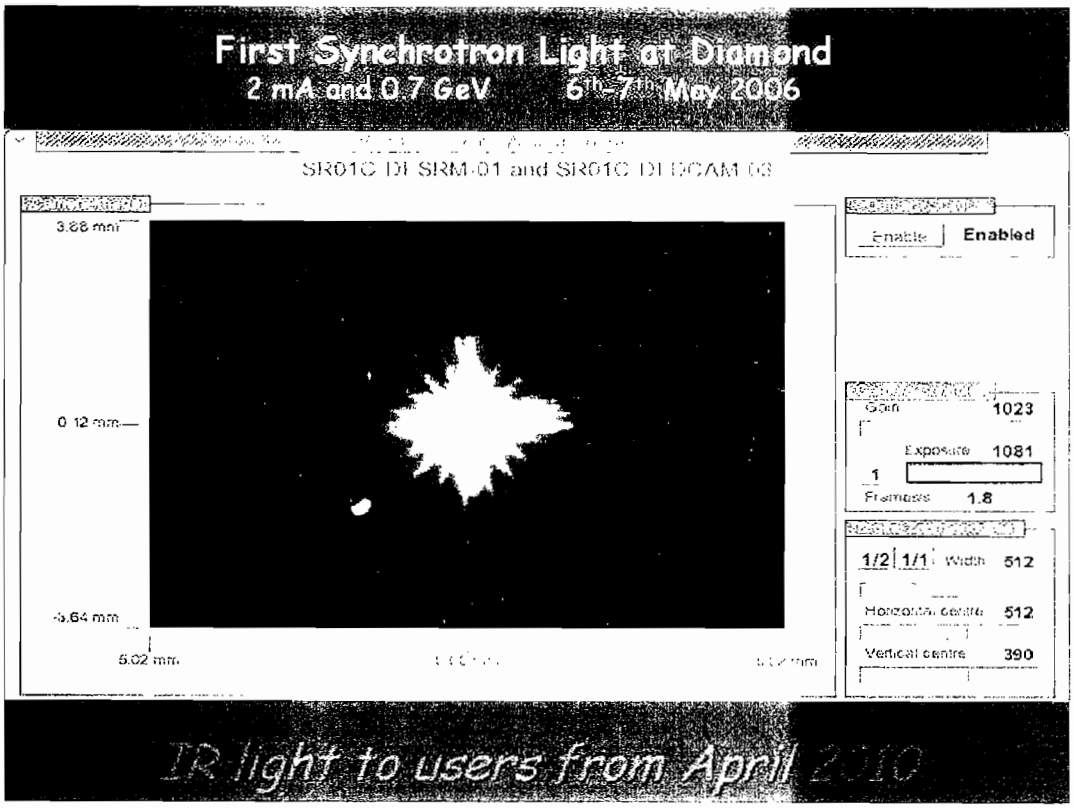


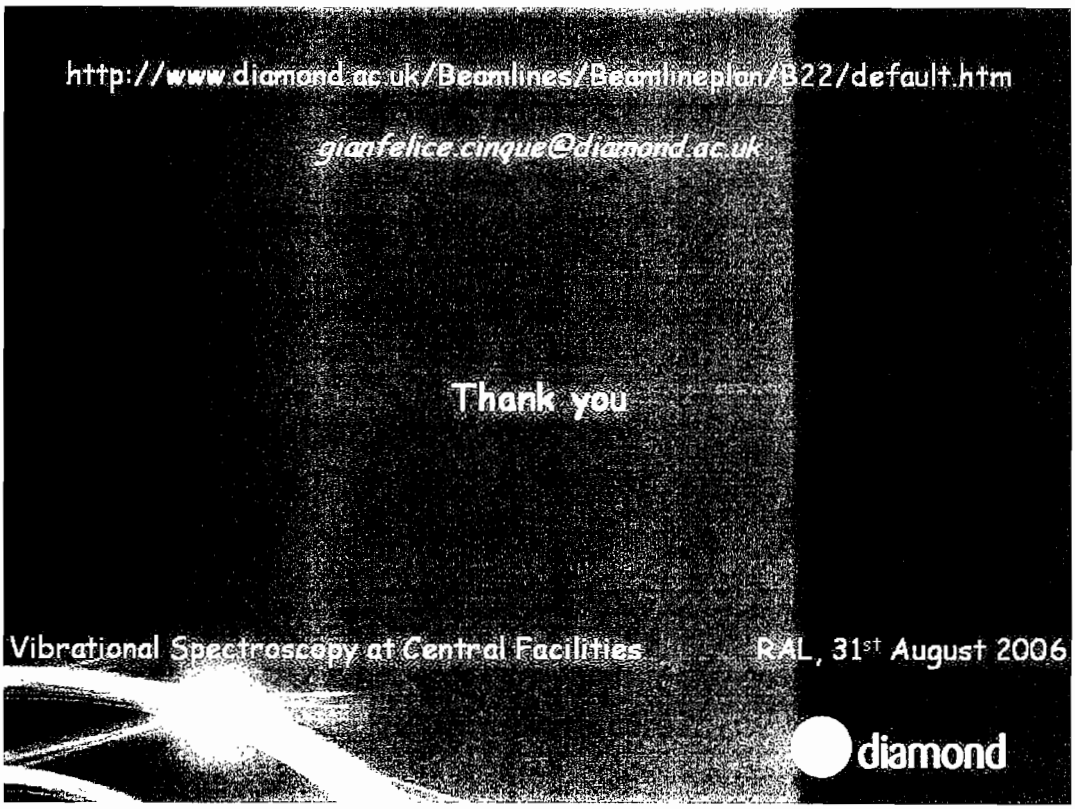


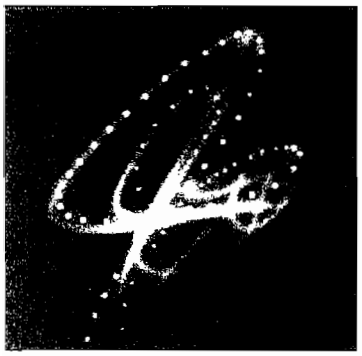
Assuming $\lambda >> \lambda_c$:

- no flux on axis
- peak flux cone at $1/\gamma$
- radially polarised

From J.A.Clarke, Edge Radiation, 4th August 2000 CLRC Accelerator Physics and New Sources Group

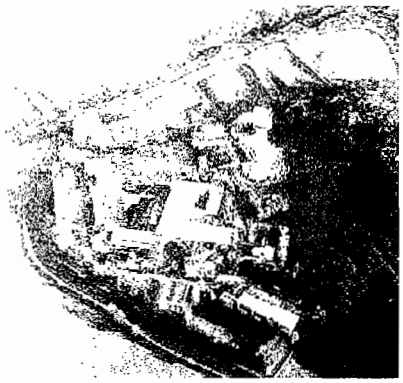

First Synchrotron Light at Diamond
2 mA and 0.7 GeV 6th-7th May 2006
SR01C DI SRM-01 and SR01C DI DCAM-03
3.88 mm
0.12 mm
5.64 mm
5.02 mm
Enable
Enabled
Gain
1023
Exposure
1081
1
Frames
1.8
1/2
1/1
Width
512
Horizontal centre
512
Vertical centre
390
IR light to users from April 2010

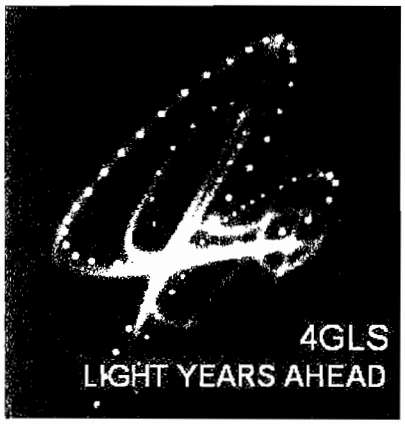

http://www.diamond.ac.uk/Beamlines/Beamlineplan/B22/default.htm
gianfelice.cinque@diamond.ac.uk
Thank you
Vibrational Spectroscopy at Central Facilities
RAL, 31st August 2006
diamond



4 The UK's energy recovery linac free electron laser facility

Vibrational Spectroscopy at Central Facilities — Elaine Seddon, August 2006





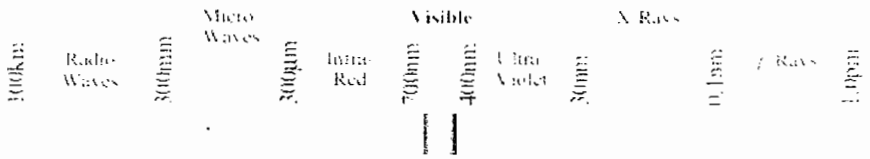
Acknowledgements

- The 4GLS Team
- The 4GLS International Advisory Committee
- The 4GLS Steering Committee
- National and international scientific community
- Funding: OST/DTI, CCLRC, NWDA and EU

4GLS information http://www.4gls.ac.uk

4GLS Update

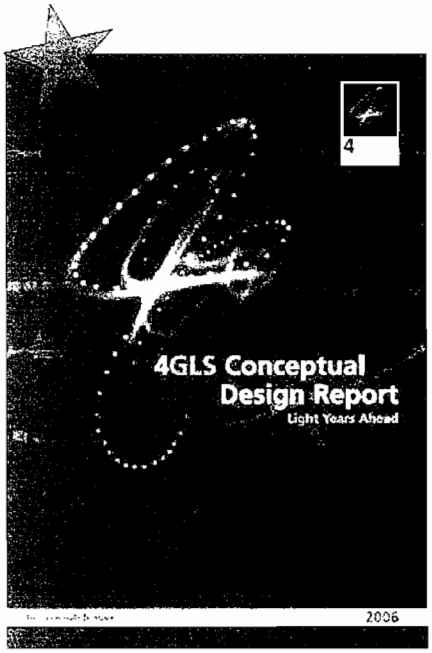
- Milestones and hurdles
- 4GLS machine update (focus on longer wavelength systems)
- Flavour of some of the science potential of 4GLS



4GLS: timescales

✓ April 02	Scientific case approved (Gateway 0)
✓ Nov 02	Business case approved (Gateway 1)
✓ April 03 & 04	£13.9 M funding for prototype accelerator (ERLP) and R&D (OST £8 M, CCLRC £5.9 M)
✓ Feb 05	EUROFEL R&D work funded (Euro 9M)
✓ March 05	Funding for 4GLS Technical Design (CCLRC £1.6 M)
✓ Nov 05	£3 M NWSF funding for ERLP science
✓ Spring 06	4GLS CDR
▫ late 06	Prototype construction complete
▫ 2007	Report on 4GLS phase I, ERLP operational, 4GLS TDR
▫ 2008/09 ??	Approval for 4GLS procure and start build
▫ 2012/13 ??	Facility starts to become available to researchers

4GLS: CDR April 2006



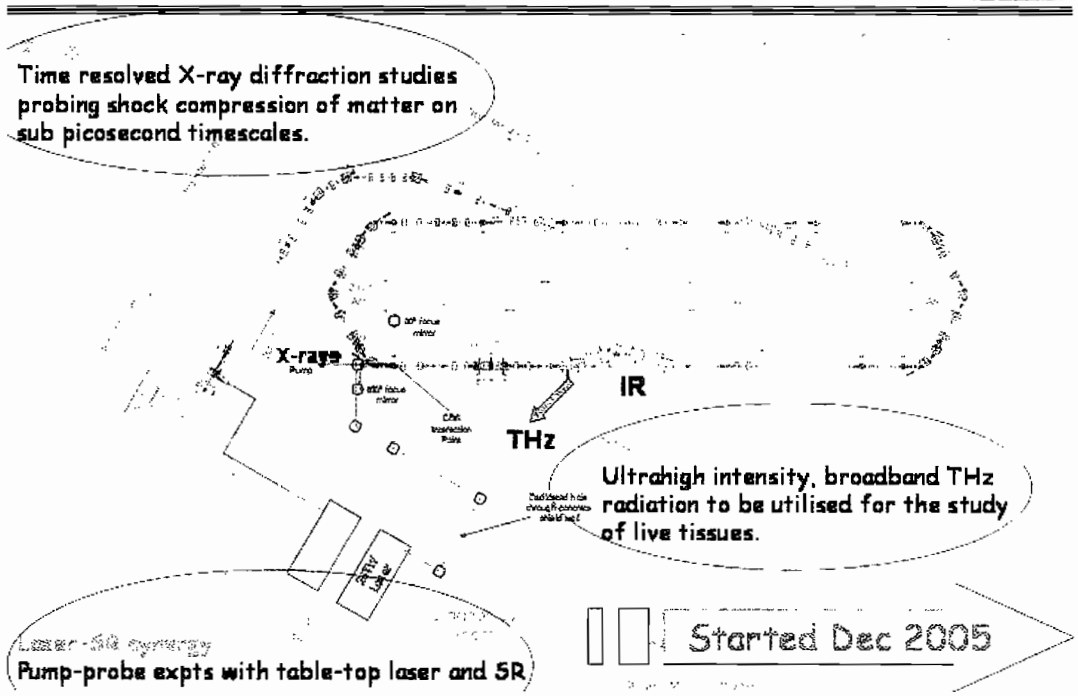
- 4GLS Conceptual Design Report launched
- Available as a CD or on the web at http://www.4gls.ac.uk

CDR launch

4GLS Phase I results:

First Beam from the ERLP Photoinjector August 2006

ERLP photon science: NWSF £3M, 3 years



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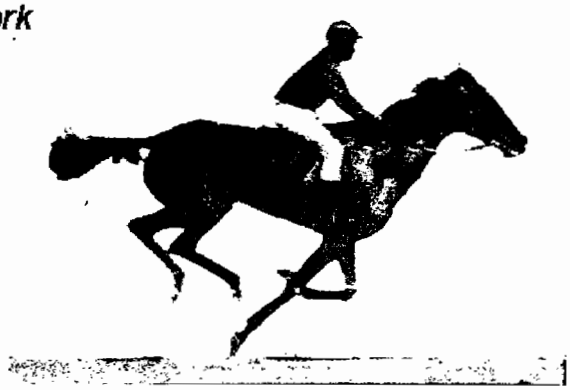
The Science Need...

Fundamental requirement to understand the *dynamic* behaviour of matter, often in very small (nm) units, on very fast (fs) timescales

Need not just to determine *structure* with high precision, but to understand *how these structures work*

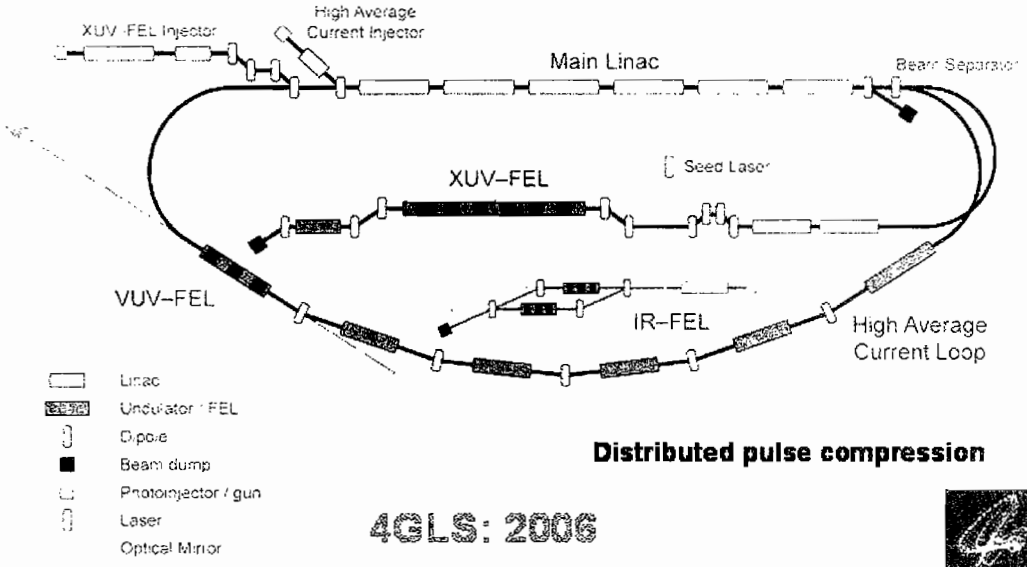


The Science Need...

Require an *ultra-high brightness* low energy facility that allows the use of *ultra-short pulsed* sources both individually and in combination

4GLS is being designed to meet this need

4GLS combines superconducting ERL, SR, laser and FEL technology in a fully integrated multi-source, multi-user facility

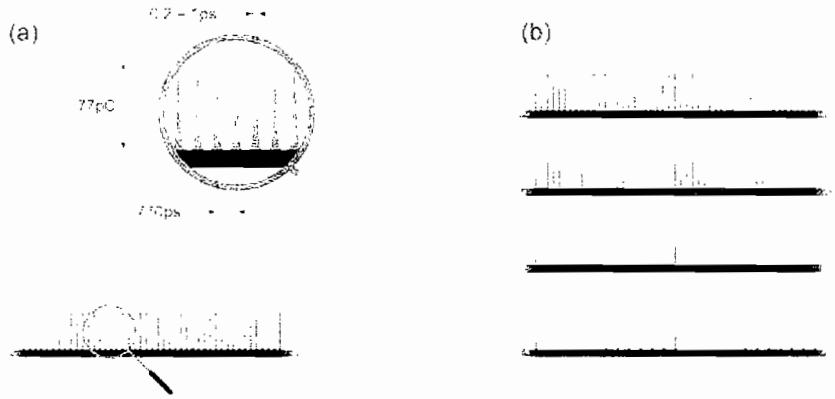


Distributed pulse compression

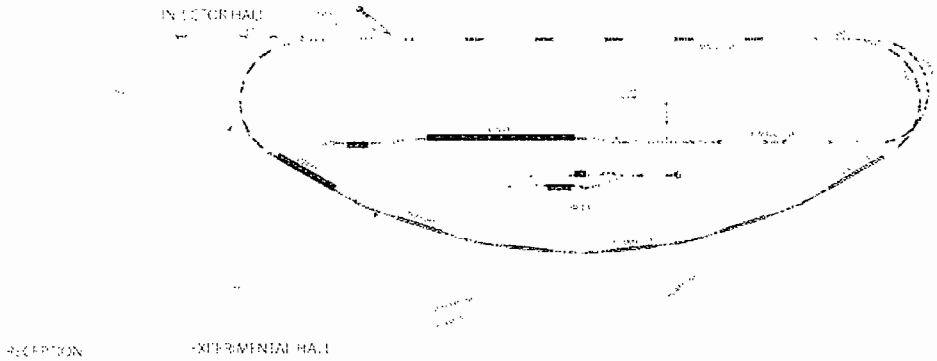
4GLS: 2006

Pulse structures: High Average Current Loop

- **Considerable flexibility in bunch patterns**



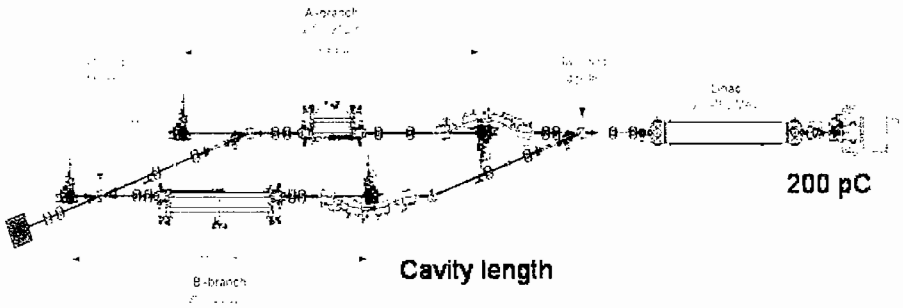
ERL Layout



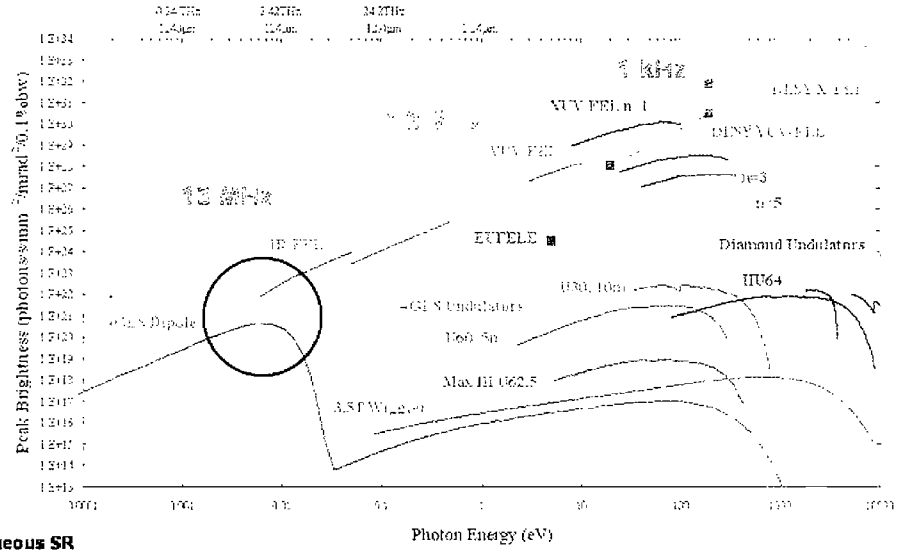
Multiuser facility

The IR-FEL

- 2.5 to 200 μm
- Bunch length 1-10ps rms
- Variable polarisation
- SC linac > stability
- CW or macropulse
- Tuning - JLAB lased at 20-100W over 0.7 to 4.8 μm in seconds
- Partial waveguiding to get to longer wavelengths?
- Max pulse energy ~50 μJ

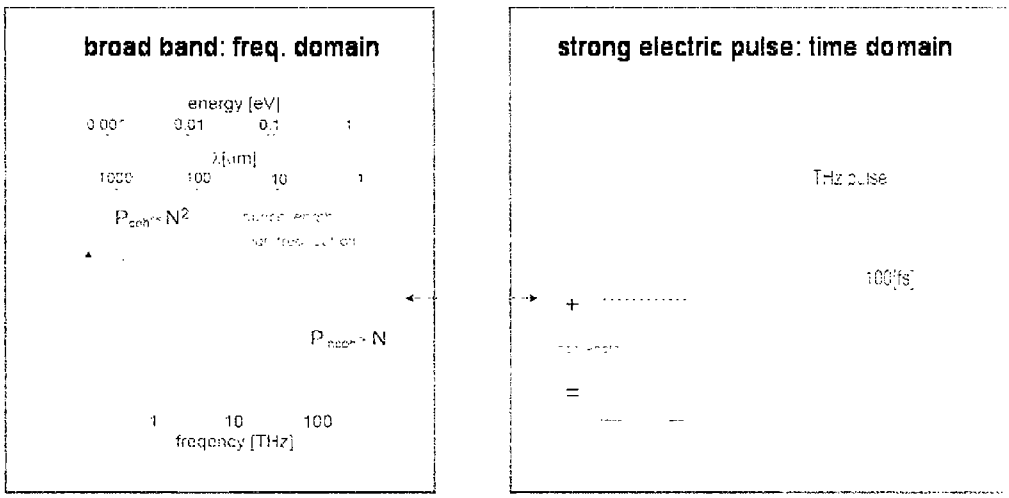


4GLS Photon Output



Spontaneous SR
Range: up to 1keV
Pulse length: few ps down to 100 fs
Repetition rate: 1.3GHz max

Broad band THz short pulse



broad band photon source in frequency domain,
strong electric field pulse in time domain

Courtesy of A. Nilsson

Coherence

Temporally coherent (transform limited) beams have:

Spectral width × pulse duration ≈ 2 eV fs

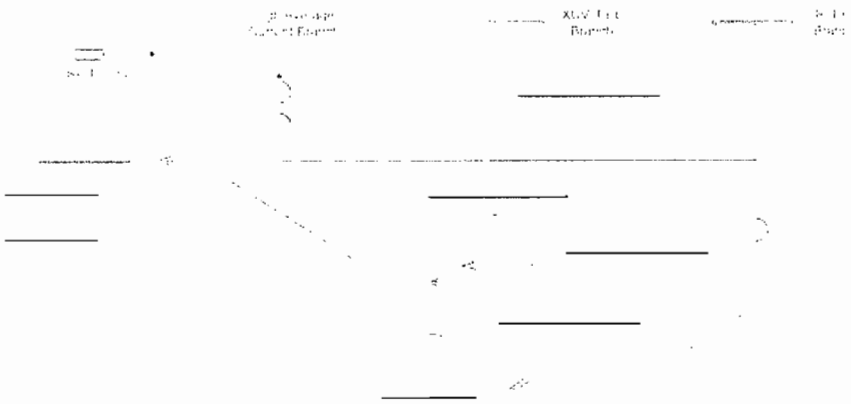
Spatially coherent (diffraction limited) beams have:

Beam area × divergence ≈ $1/(2E^2)$ mm^2 $mrad^2$

where E is the photon energy in eV

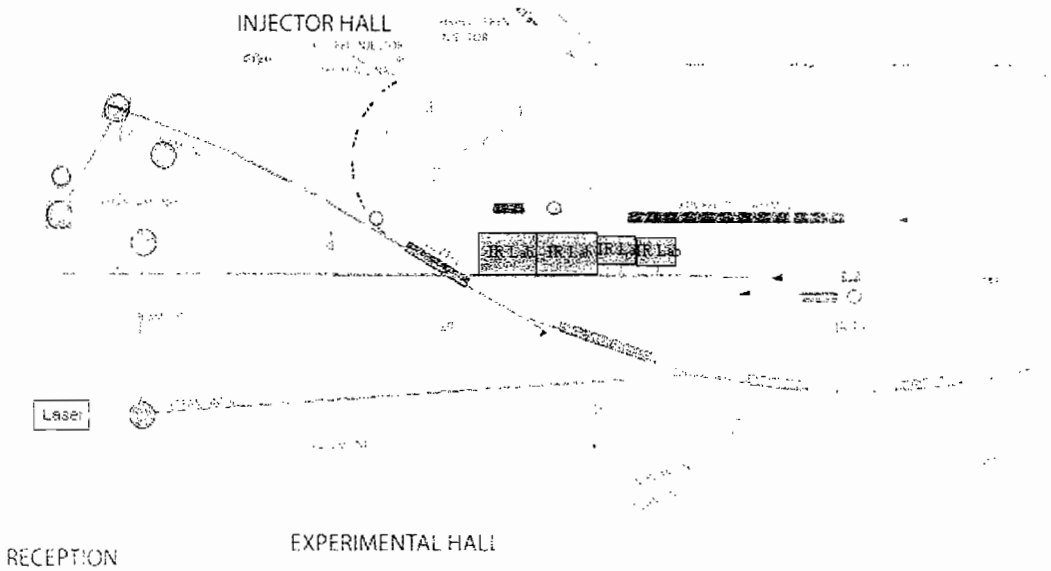
(Exact values depend on pulse and beam profiles)

Combining Sources



Ultimate Target: pairs of sources synchronised to the 10s fs level

Illustrative combinations: IR FEL and THz distribution added

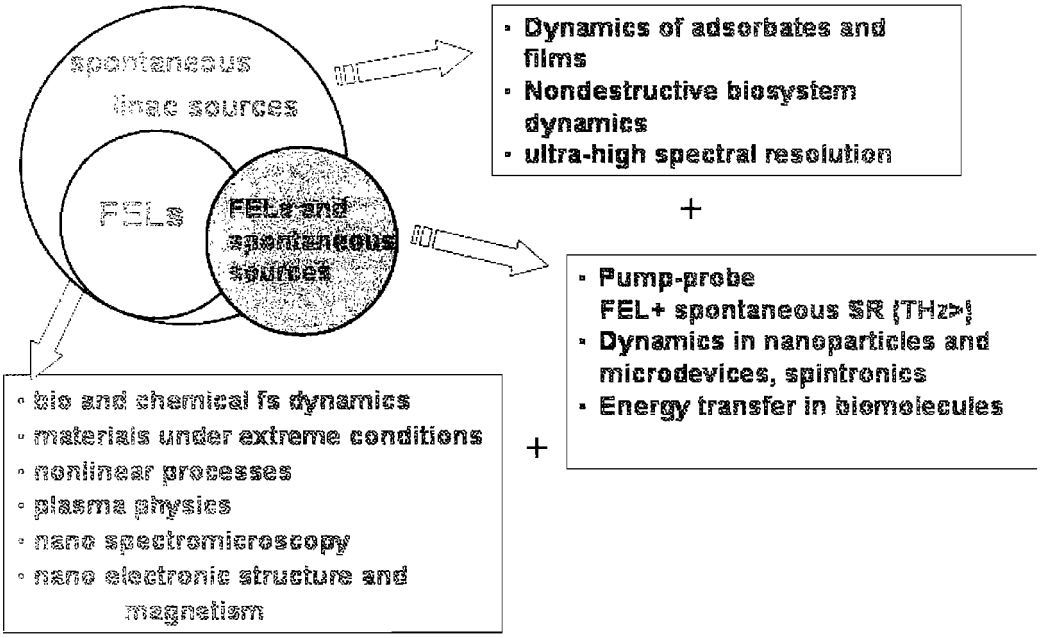


A suite of light sources optimised for THz to soft X-ray wavelengths...

- **free electron lasers**
- **undulators and bending magnets**
  THz to soft X-ray
- **combinations of sources**
  internal and/or with conventional lasers

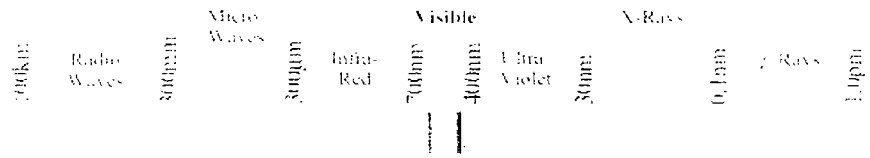
World leading combination - unique experimental flexibility and cost effective delivery

4GLS. Greater than the sum of the parts



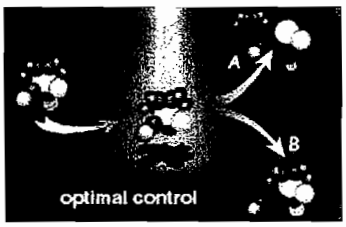
4GLS Update

- Milestones and hurdles
- 4GLS machine update (focus on longer wavelength systems)
- Flavour of some of the science potential of 4GLS



Overview

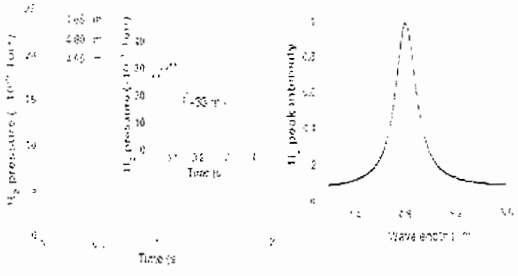
- Unprecedented probe of electron motion in atoms and molecules
- Capability to pioneer a new generation of ultra-fast time resolved experiments revealing short lived intermediates in catalytic reaction pathways



- The technology to underpin the development of the next generation of electronic devices charge and spin dynamics
- Development of innovative dynamic imaging techniques
  - on large scale for disease recognition
  - on nanoscale for biomolecular function in live cells

FEL ALONE: Mode-selective control of chemical reactions, Vanderbilt IR FEL, Liu et al.

Desorption of hydrogen by resonant excitation of the Si-H vibrational stretch



Liu, Feldman, Tolk, Zhang and Cohen, Science **312** 1024 May 2006

Irradiation of a mix of 15%H 85%D atoms on Si(111)
FEL fluence 0.8J/cm^2 per macropulse (100mJ per macropulse), 50-90cm^{-1} bandwidth
Tuned from 4.2-5.6μm, quadratic laser intensity dependence
No evidence of bulk heating

Desorption non-statistical 95 % is H_2 <5% HD or D_2
Peak in H_2 desorption at 4.8 μm (0.26 eV) ν(Si-H) terrace sites

FEL ALONE cont.: Mode-selective control of chemical reactions
Vanderbilt IR FEL, Liu et al.

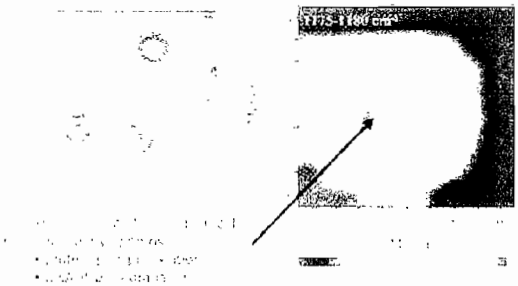
Conventional wisdom large molecules and molecules on surfaces expect many well coupled low frequency modes giving rapid energy randomisation (~ psec). Leads to thermal rather than selective results.

Power and tuneability of IR FEL enabled excitation of a particular vibrational mode and diverted reaction from thermal pathway

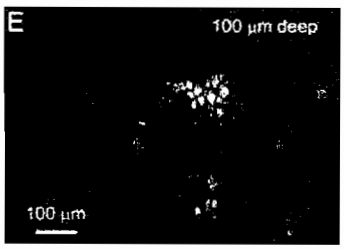
Potential impact on:

1 the storage, transport and delivery of hydrogen for the hydrogen economy
2 reactive chemistry on surfaces leading to room temperature refining

FEL ALONE cont.: Near-field Imaging:
Sub-cellular IR Spectromicroscopy



Cell changes during apoptosis (P Dumas, SR IR, SOLEIL)

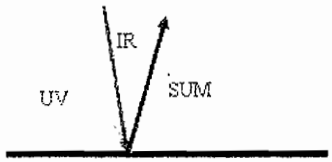


CARS image, mouse ear (lipid CH_2 symmetric stretch) Xie *et al.*, PNAS, **102**, 16807 (2005)

- Overcome diffraction limit using near-field imaging/IR FEL:
  ⇨ 30-50 nm resolution *cf.* current best (microns)

Combined sources

Double resonance Sum Frequency Spectroscopy and imaging: New Horizons



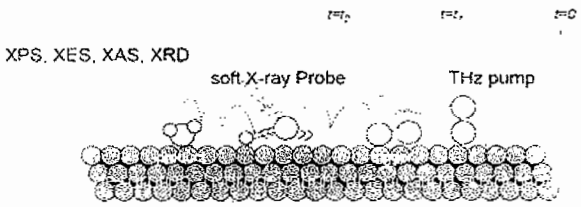
IR $\lambda > 10$ μm
UV, tune to optimise non-resonant interaction

- Exploits tuneability of both IR FEL and VUV FEL
- Conformation of large admolecules
- Adsorbate dynamics
- Membrane rafts & proteins, lipid bilayers, oxide catalysts...
- Enormously widens range of surfaces and vibrations

- Imaging applications using near-field SFG signal (SNOM probe): below diffraction limit

Combined sources

Probing elementary surface reactions, Anders Nilsson group and collaborators



4GLS

Pump: THz,

Probe: XPS, XES, XAS, IR

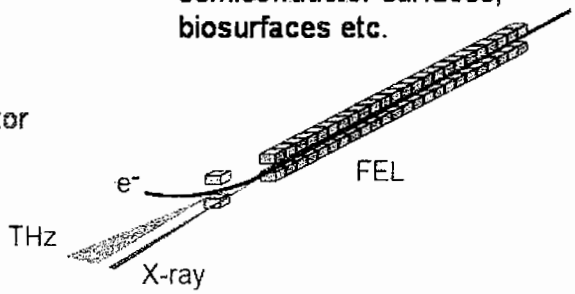
BM & XUV FEL

or far-IR FEL & undulator

Probe of reaction coordinate

Selective detection of surface species

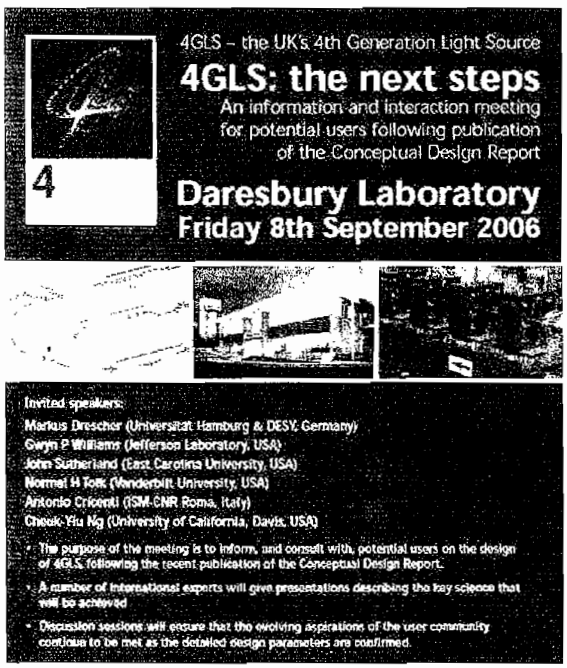
Relevance to catalysis, fuel cells, environmental science, semiconductor surfaces, biosurfaces etc.



4GLS

- multiuser facility
- state-of-the-art sources by themselves (THz to soft X-ray)
- undulators and FELs
- source combinations including table-top laser
- Bringing together laser and SR expertise and skills

- fully optimised detectors and on line diagnostics crucial for full exploitation



International Collaborations

International development programmes

- JLab
- Cornell
- Stanford
- Rossendorf
- DESY
- FERMI@Elettra
- EUROFEL collaboration

Exploring the Nature of Matter

Jefferson Lab

4GLS funding

NWDA

northwest development agency

- **Contribution to capital (ca. £4.5 M)**
- **Provision of 4GLS building thro' leaseback (*ca.* £24 M + vat)**

- ca. £~~80-200~~ M to build and commission (not including VAT)

Linac-based light sources