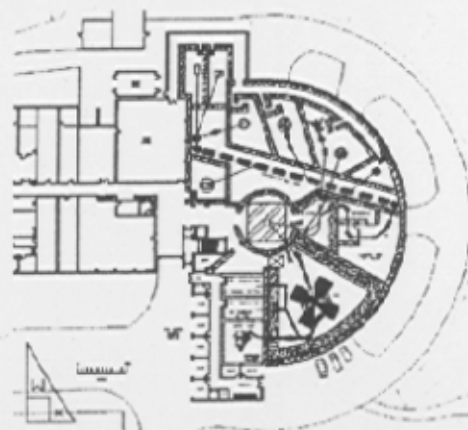
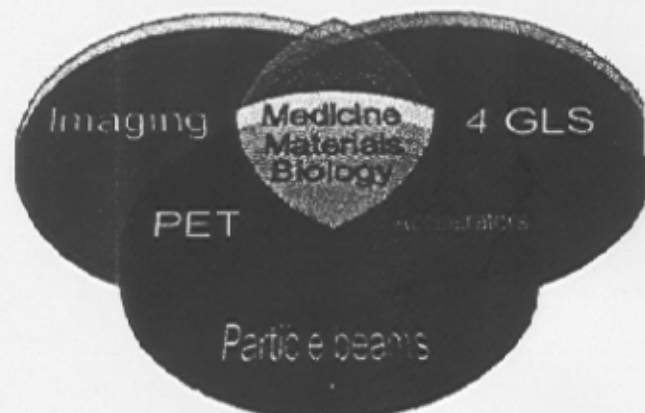
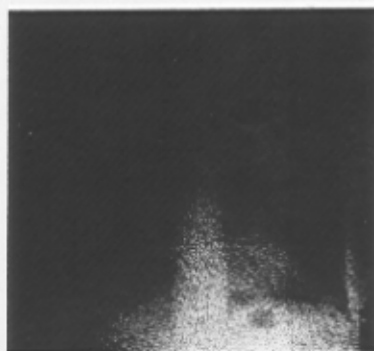
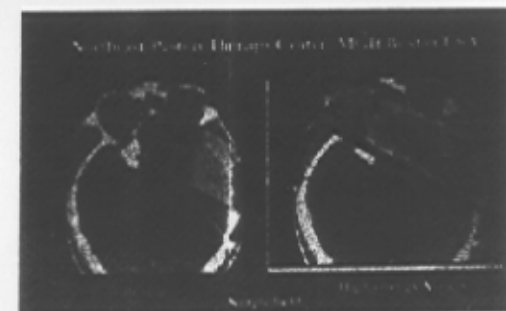
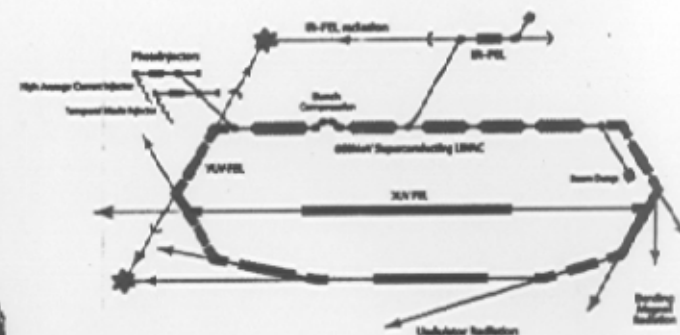


CASIM

Centre for Accelerator Science Imaging and Medicine **CASIM**



Liverpool University
Manchester University
UMIST
Lancaster University
Salford University
Clatterbridge Centre for Oncology
Christie Hospital
The Walton Centre for Neurology and Neurosurgery
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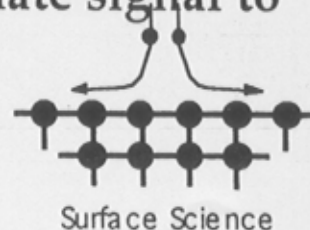
4GLS is ...

The logo for CASIM, featuring the word "CASIM" in a stylized, rounded font. The letters are black and have a slightly irregular, hand-drawn appearance. The "A" and "I" have dots above them.

-
- *A turbo-charged Low Energy Source:*
 - **Optimised high brightness radiation from ERL ring, 4-100 eV**
 - **A cavity-based VUV-FEL, 3-10 eV**
 - **An IR-FEL, tuneable over ca. 3 - 50 μm**
 - **An XUV-FEL (10 to 100 eV)**
 - **all capable of producing few 100 fs pulses**
 - **all capable of use in combination**
 - *Unique world-leading source*

Advances in RAS and RAM instrumentation using VUV FEL

- 1 Laboratory RAS and RAM instruments cover the range 1.5 eV to 5.5 eV and are limited by signal to noise. Need to extend range further into UV. Requires an intense wide band source of linearly polarised radiation.
- 2 Current Rapid RAS instrument (Meas. Sci. Technol. 12 1 2001)
Can collect RAS spectrum 1.4 eV to 3.2 eV in 0.1 sec
- 3 Laboratory RAS uses PEM which is modulated at 50 kHz giving an ultimate speed of response of 20 μ sec.
- 4 Intensity of VUV FEL will enable experiments at 20 μ sec.
Exploiting pulse structure of VUV FEL to omit PEM will allow faster measurements.
- 5 RAM instruments currently operate at a single λ and are limited by signal to noise and the read out speed of CCD.
- 6 VUV FEL will allow tunability and eliminate signal to noise limitation on RAM.



Surface Science

Further Information



WWW

<http://www.casim.ac.uk>
<http://www.4gls.ac.uk>

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4GLS

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Radioactive Ion Beams

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Medical imaging

Dr Rob Lewis
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Email. R.A.Lewis@dl.ac.uk

Potential of VUV FEL for RAS and RAM

New Science

Study of surfaces in a wide range of environments

MBE, CVD growth processes and growth transients

Electrochemistry

Molecular assembly at metal/liquid interfaces

DNA-DNA and DNA-Protein interactions

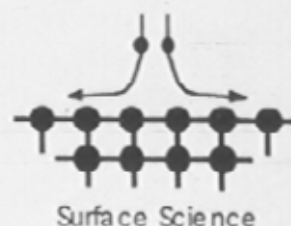
RAS Spectroscopy Fast Kinetics

Monitor Semiconductor growth at real growth rates

Phase transitions and molecular interactions on
 μ sec timescale

RAM Imaging Slow Kinetics

Tuned to λ of particular molecular species involved in
molecular interactions



RAM of CO + O/Pt(110)

Under certain conditions of Temperature and Pressure

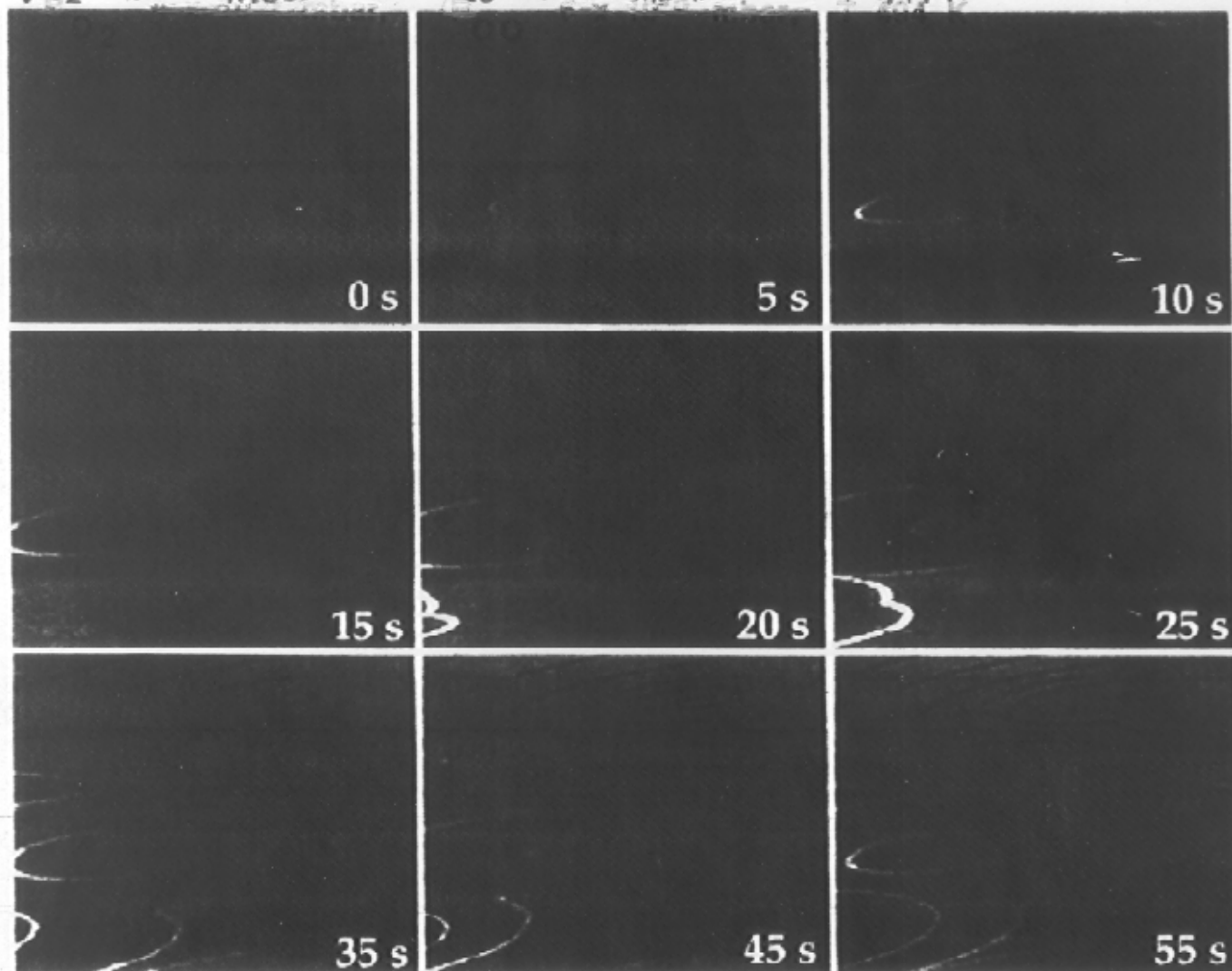
CO $\rightarrow$ CO₂ reaction oscillates $\left\{ \begin{array}{l} \text{CO/Pt(110) poisoned, no activity} \\ \text{O/Pt(110) highly active, CO} \rightarrow \text{CO}_2 \end{array} \right.$

RAM can follow dynamics of reaction front

P_{O₂} 4×10^{-4} mbar

P_{CO} 6×10^{-5} mbar

T 494 K



Low pressure - heat of reaction $< 10^{-2}$ external heating

Reaction Isothermal

Ambient pressure - heat of reaction dominates.

Significant T and P variation

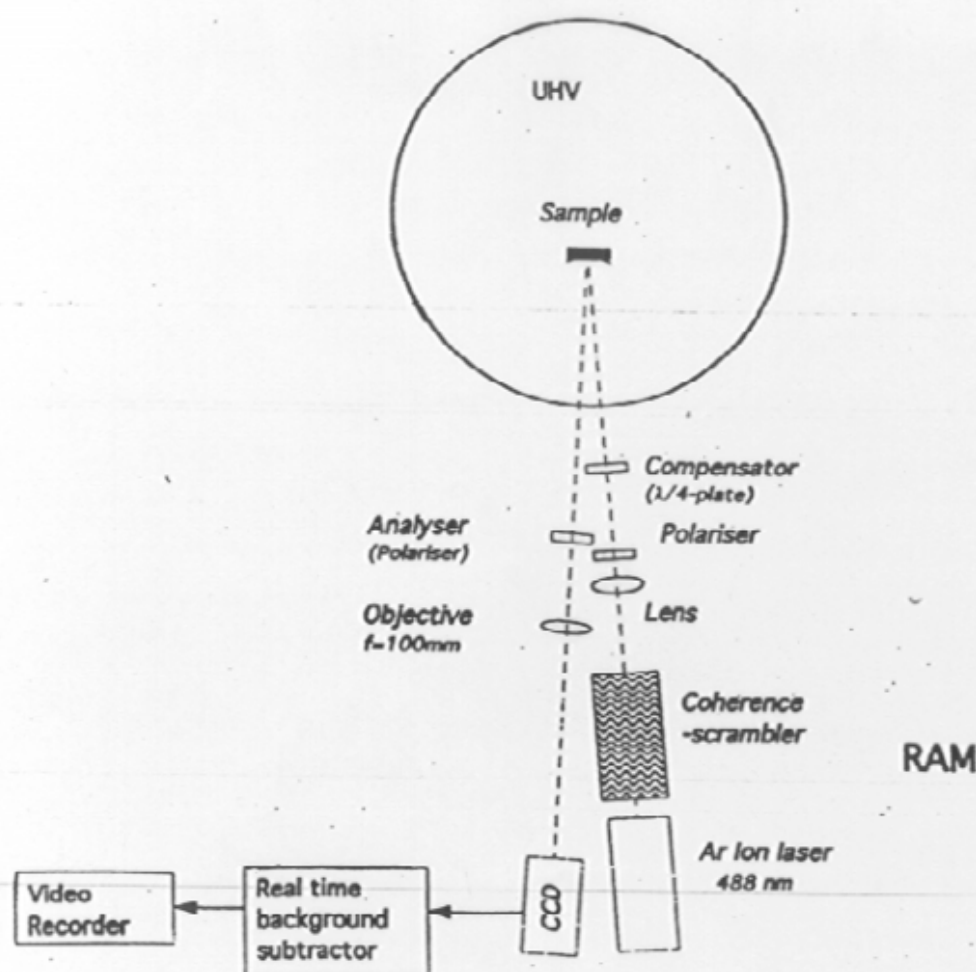
Pattern changes to "undulating raindrops"

Reflection Anisotropy Microscopy (RAM)

RAM is an optical probe of surfaces that was developed by Ertle and co-workers (Sur. Sci. 352-4 1003 1996) and is based on the sensitivity of the plane of polarisation of reflected light to the electronic and hence the chemical structure of a surface.

RAM achieves surface sensitivity in a similar way to reflection anisotropy spectroscopy (RAS) by using near normal incidence and reflection of light from the surface of a cubic crystal so that the response of the bulk cancels by symmetry.

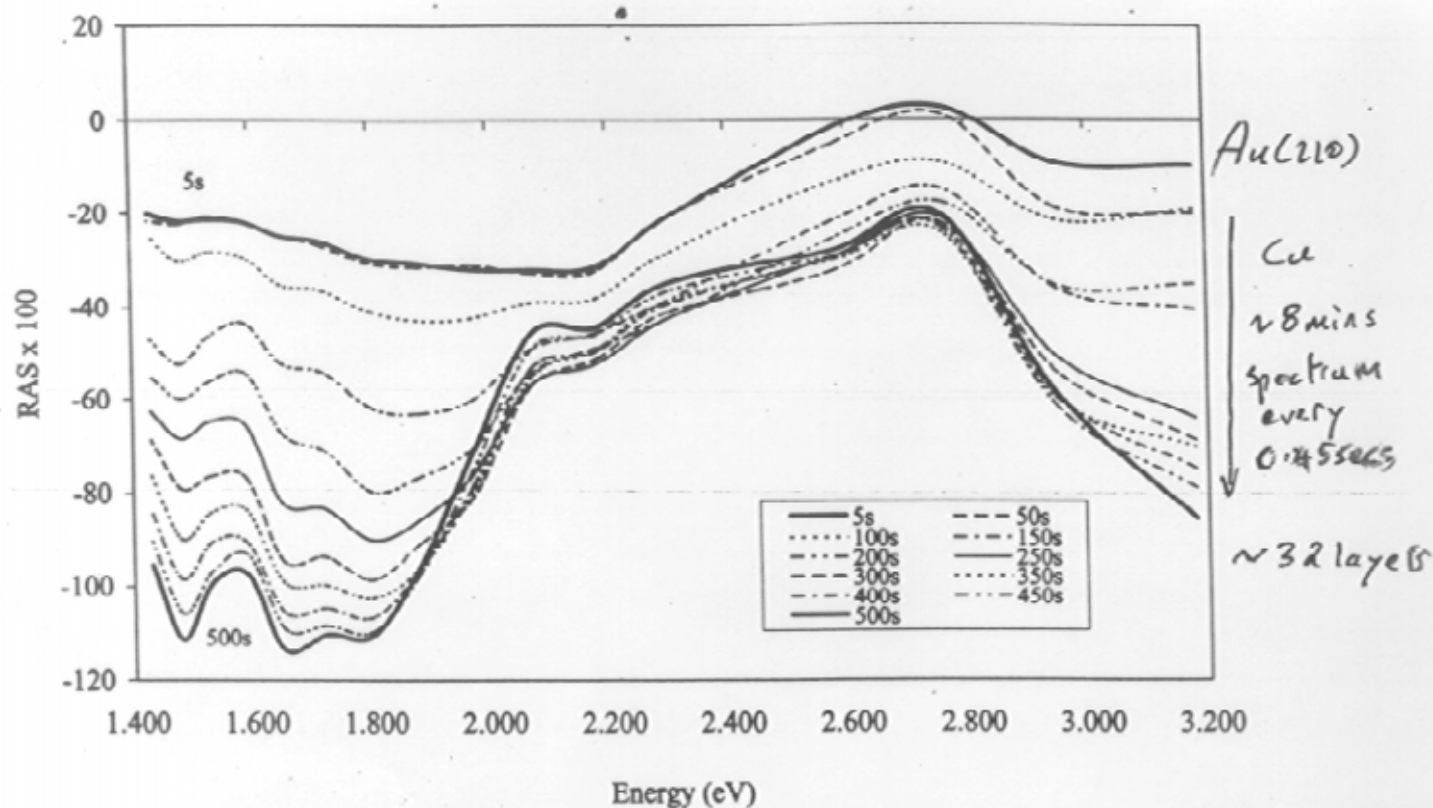
As originally developed RAM uses a Laser so it is a single frequency probe. This is a disadvantage since it cannot be used to probe specific molecules by being tuned to a particular molecular transition. As a microscope it cannot give spatial resolution better than the wavelength, λ , of light that is used. However it can be used to follow dynamic processes on surfaces and study surface processes in high pressure and liquid environments.



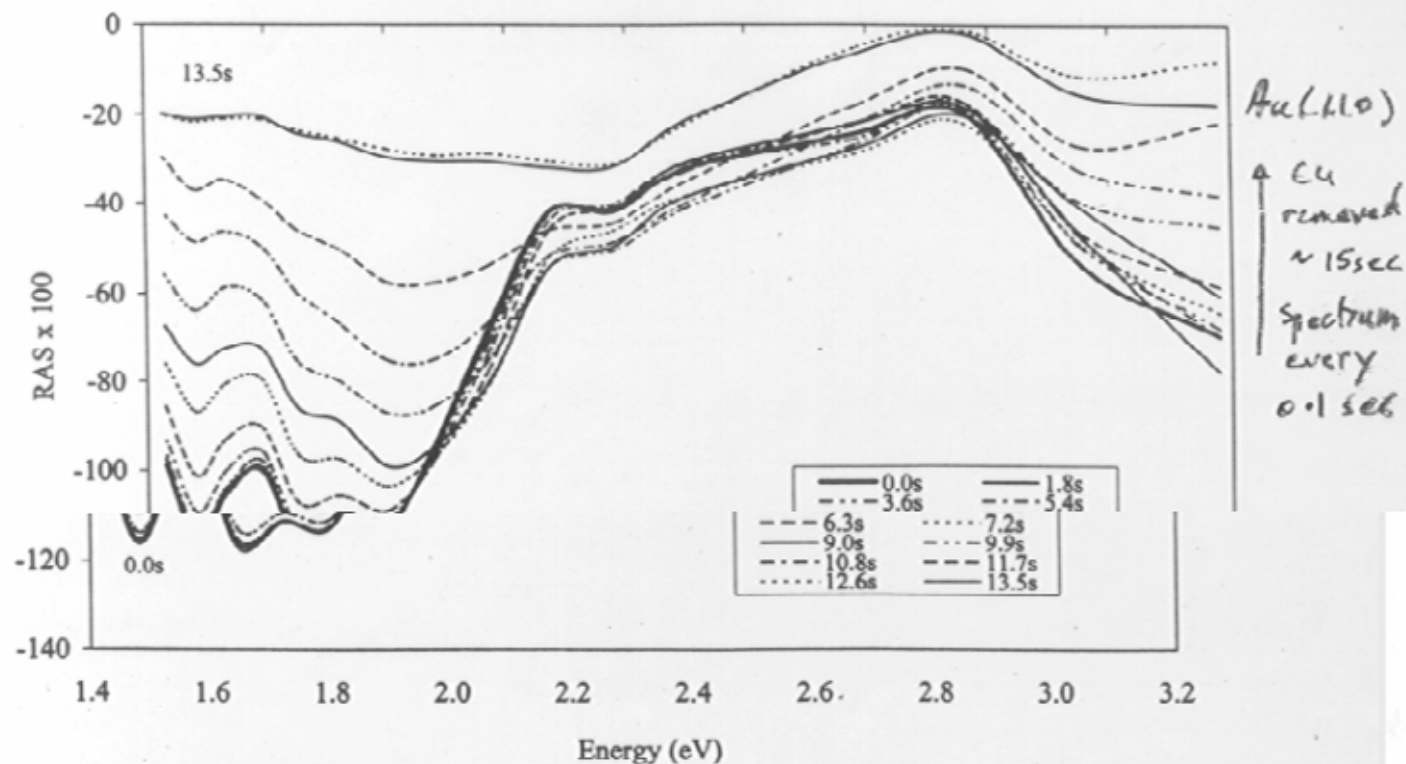
Electrochemical growth Cu on Au(110)

Caroline Smith
Trevor Farrell

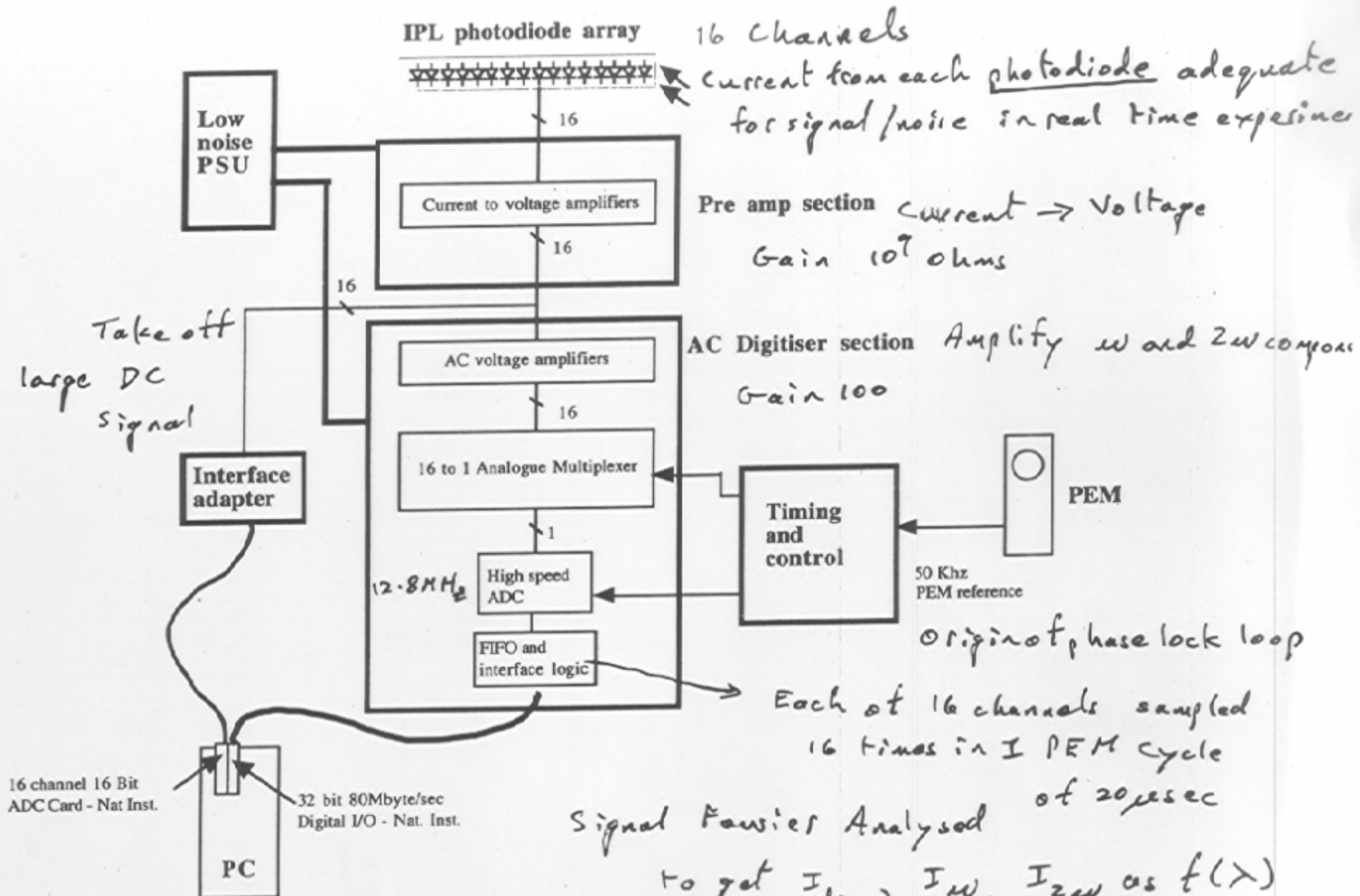
Cu on Au First Growth



Removal of Cu after 1st Growth



2nd growth ~35 } layers in 500 sec $\Rightarrow$ Nucleation of sites on
3rd growth ~49 } Au(110).

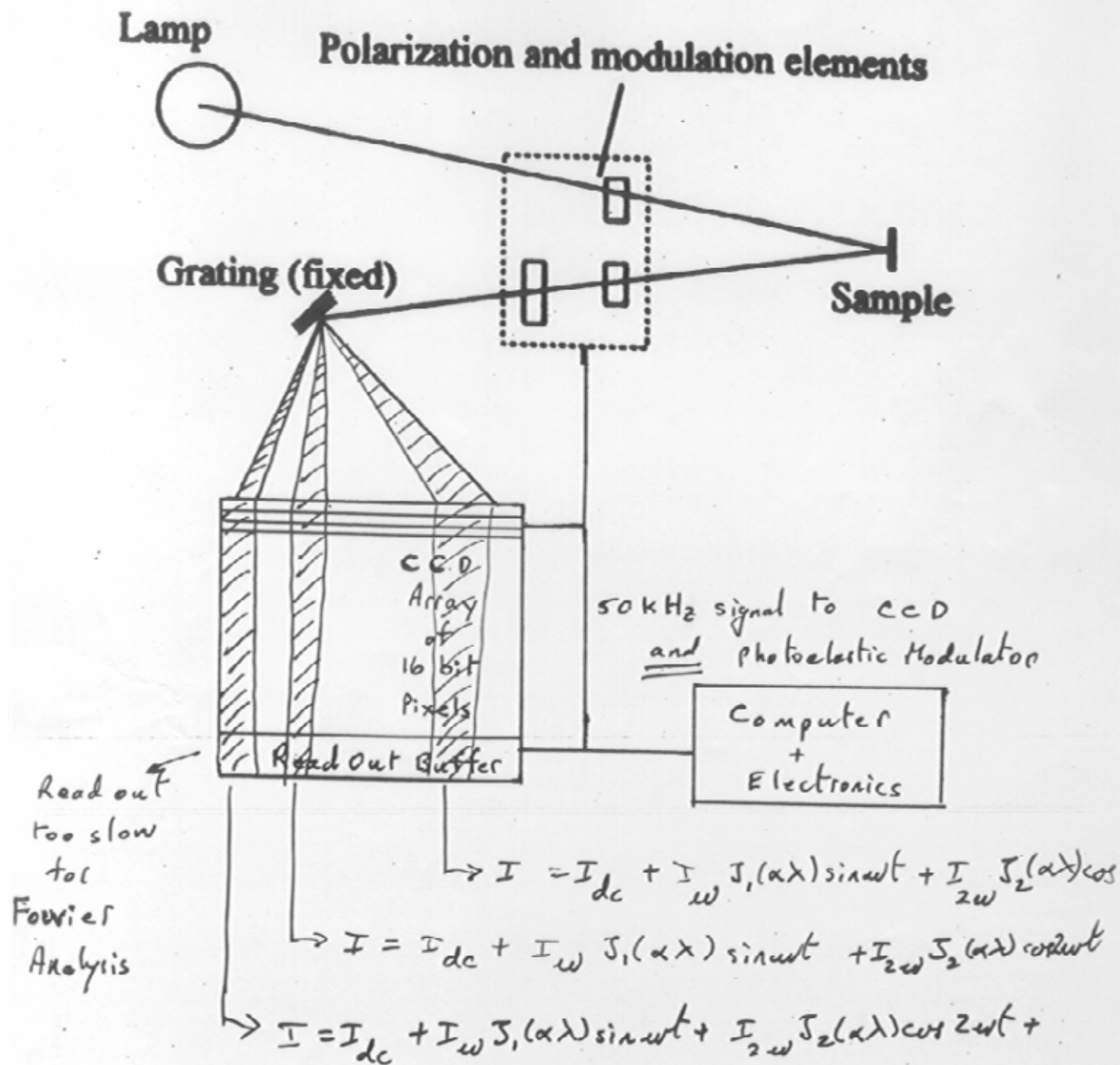


Signal Fourier Analysed
to get I_{dc} , I_w , I_{zw} as $f(\lambda)$

Standard RAS 20 sec full spectrum (1.5 - 5.5 eV)
20 msec one λ

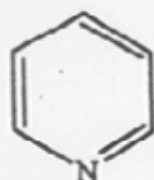
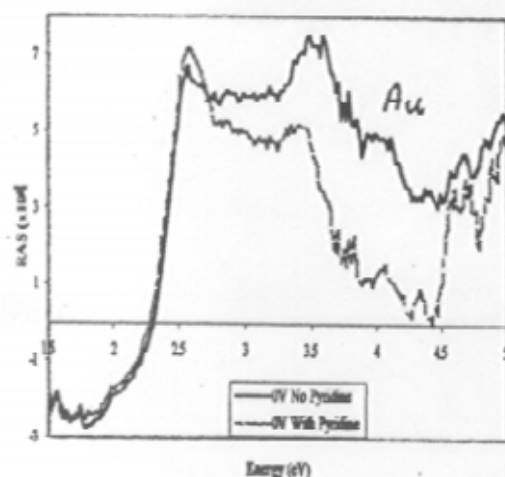
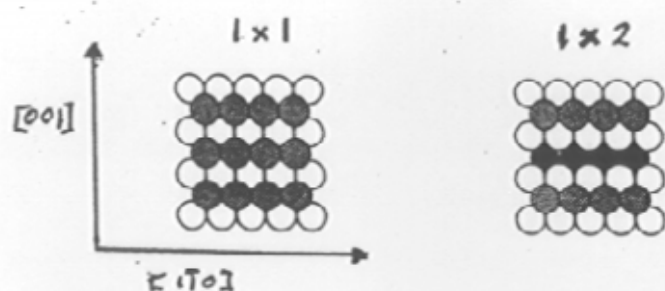
Rapid RAS 0.1 sec Full spectrum (1.4 - 3.2 eV)
2 μ sec one λ

Rapid RAS



P. Harrison, T. Farrell, A. Maunders, C.I. Smith and P. Weightman

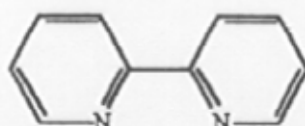
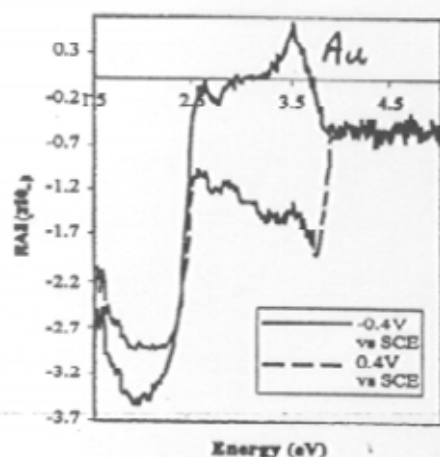
Adsorption of Pyridines on Au(110) in Electrochemical Cell



Binds through N atom

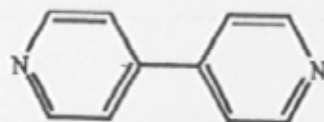
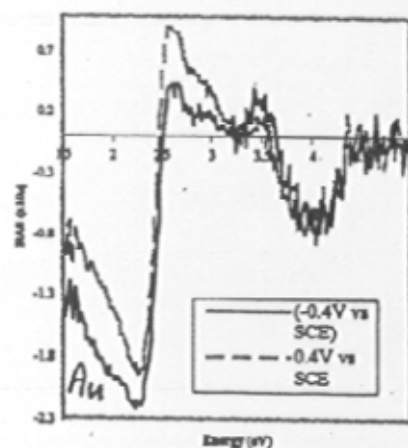
$\lambda_{\text{max}} \sim 4 \text{ eV}$

Similar changes to pyrimidine
which is a DNA base pair



2,2'-Bipyridine

Binds through N atoms at an angle 60° to surface



4,4'-Bipyridine

Binds through 1 N atom, perpendicular to surface
Can be used to attach cytochrome c to electrode

Reflection Anisotropy Spectroscopy: A New Probe for the Solid-Liquid Interface

J. Sheridan,¹ D. S. Martin,¹ J. R. Power,^{1,*} S. D. Barrett,¹ C. I. Smith,¹ C. A. Lucas,² R. J. Nichols,³ and P. Weightman^{1,†}

¹Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, United Kingdom

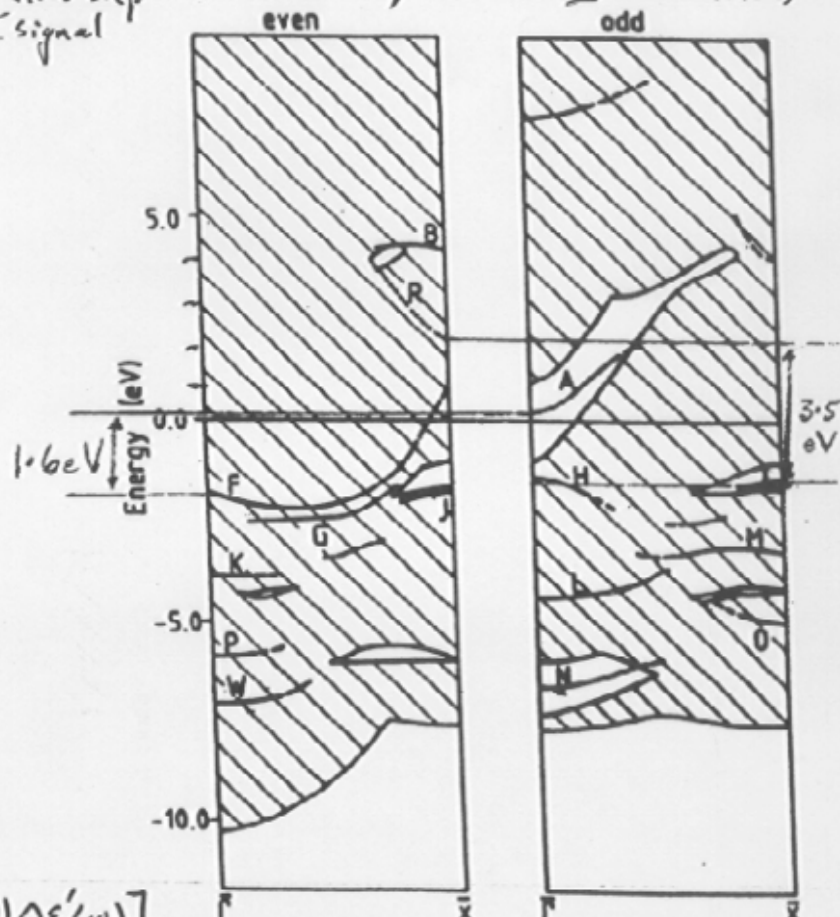
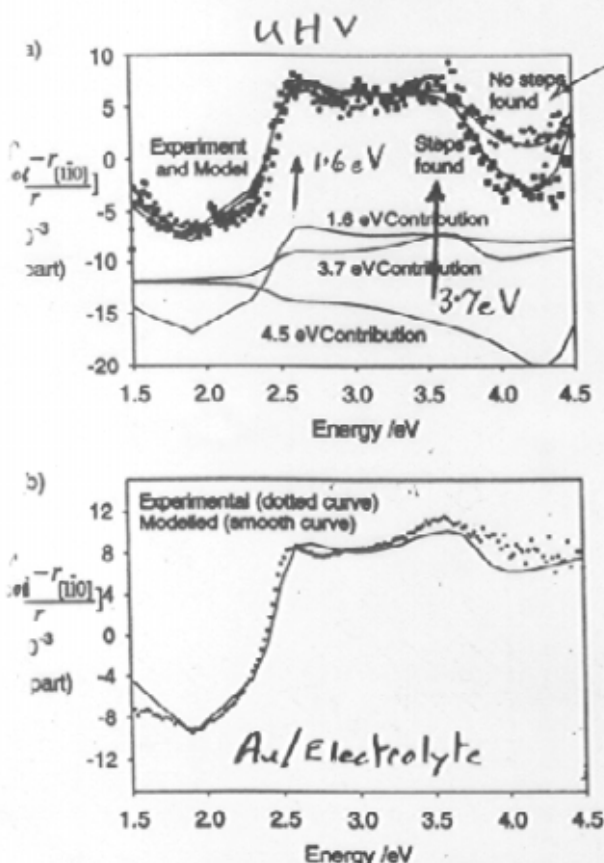
²Department of Physics, University of Liverpool, Liverpool L69 3BX, United Kingdom

³Department of Chemistry, University of Liverpool, Liverpool L69 72D, United Kingdom

(Received 22 May 2000)

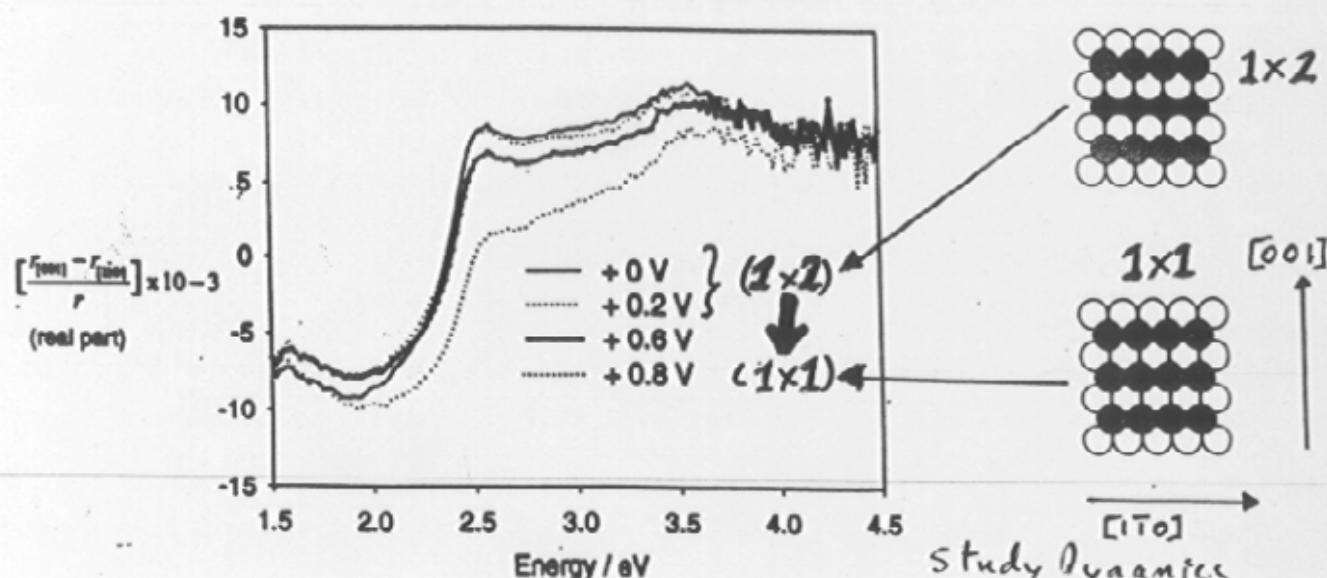
Introducing reflection anisotropy spectroscopy (RAS) as a new probe for solid-liquid interfaces, we present results for the Au(110)/electrolyte interface which serves as a model system. We demonstrate that RAS is sensitive to surface phase transitions, step morphology, and electronic surface states. Using an empirical approach, the RA spectra are reproduced and features are identified which reflect the known character of the bias voltage driven (2 × 1) to (1 × 1) phase transition. RAS is established as an experimental technique to probe the electronic structure of solid-liquid interfaces in real time to study a wide range of interface properties.

Theory for Au(110) 1 × 2
Xuetal Phys. Rev. B 39 5599 (1989)



Theory: Fresnel 3 phase Model

$$\text{Re}\left(\frac{A}{r}\right) = -\frac{2\omega d}{c} [A(\omega)\Delta\epsilon_s''(\omega) + B(\omega)\Delta\epsilon_s'(\omega)]$$



Sensitivity of Reflectance Anisotropy Spectroscopy to the Orientation of Ge Dimers on Vicinal Si(001)

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IRC in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom

S. Bose

Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, German

A. I. Shkrebtii

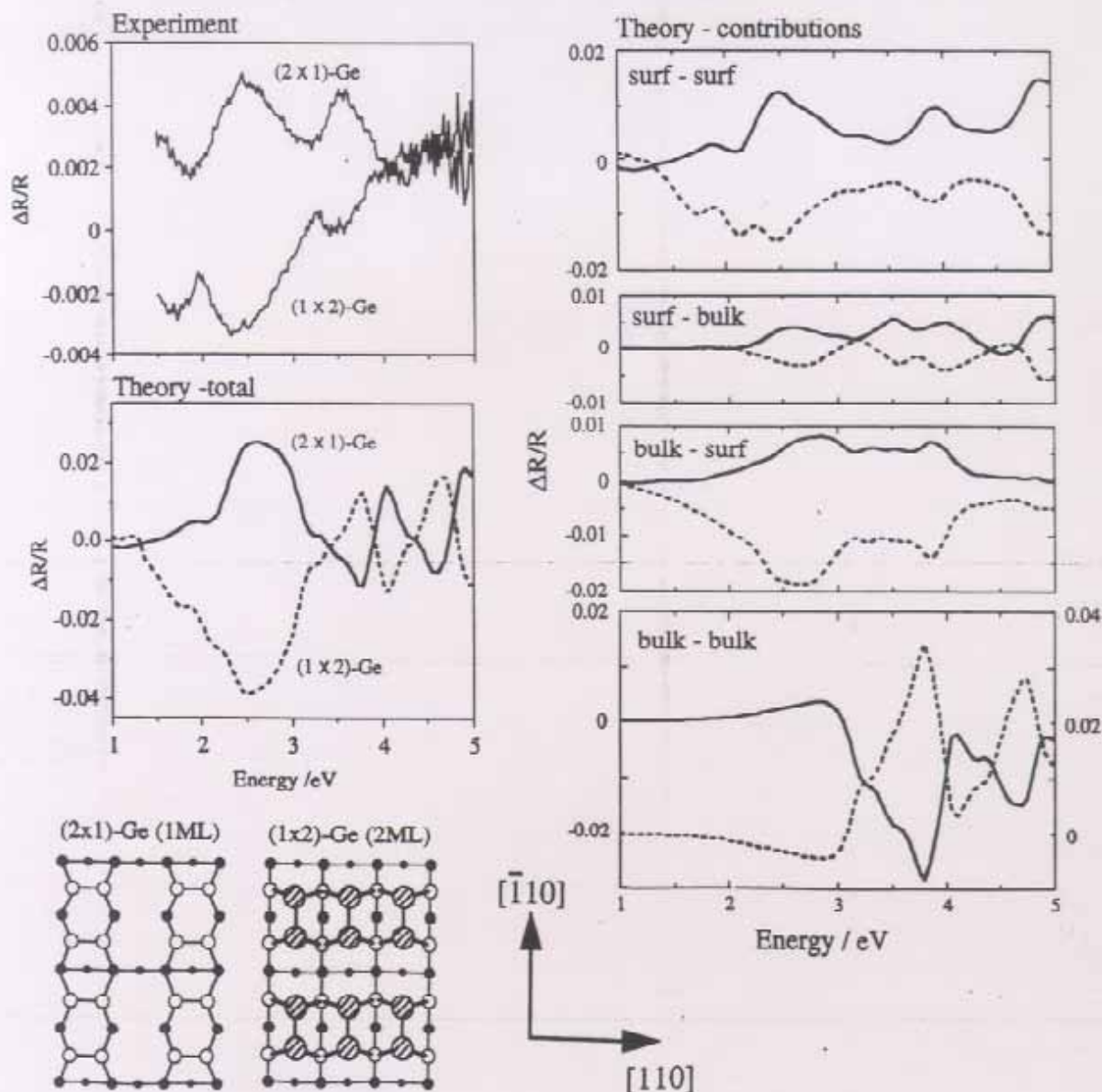
Department of Physics, University of Toronto, 60 St. George Street, Toronto, Ontario, Canada M5S 1A7

R. Del Sole

Department of Physics, University of Roma "Tor Vergata," Via della Ricerca Scientifica, 1-00133 Rome, Italy

(Received 11 September 1997)

Reflectance anisotropy spectroscopy (RAS) is employed to follow the initial room temperature growth of Ge dimer layers on clean vicinal Si(001)-(1 × 2). The experimental data show structure in the region of 2.5 eV which changes sign depending on Ge dimer orientation. Comparison with microscopic calculations for one monolayer and two monolayer Ge coverages reveals excellent agreement with experiment, demonstrating that surface states localized on Ge dimers are responsible for the RA response in the region of 2.5 eV. This provides the first clear and unambiguous proof that a dimer related transition can be responsible for the RAS sensitivity to dimer orientation.



Adsorbate Azimuthal Orientation from Reflectance Anisotropy Spectroscopy

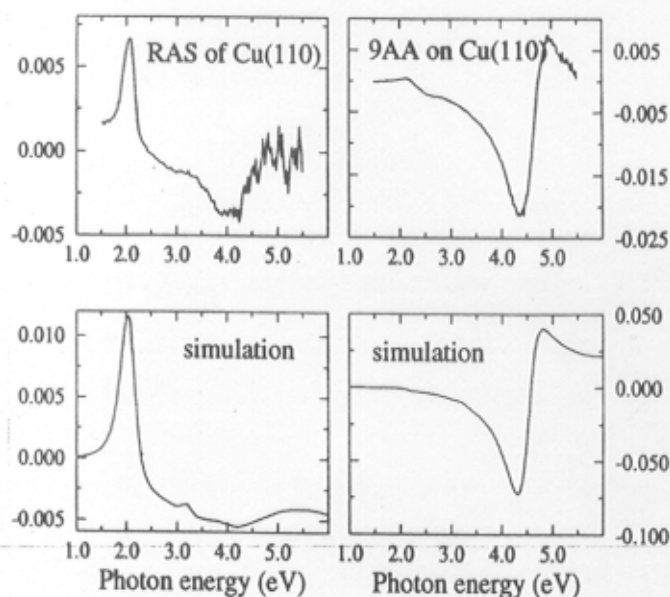
B. G. Frederick,* J. R. Power, R. J. Cole, C. C. Perry, Q. Chen, S. Haq, Th. Bertrams,
N. V. Richardson,[†] and P. Weightman

IRC in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom

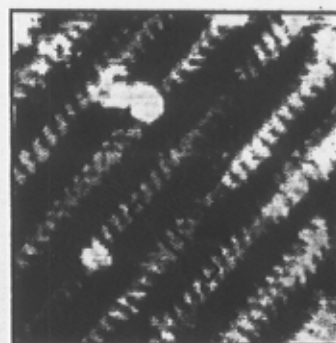
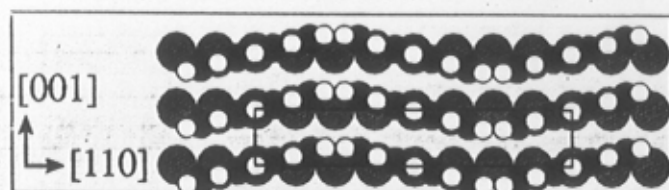
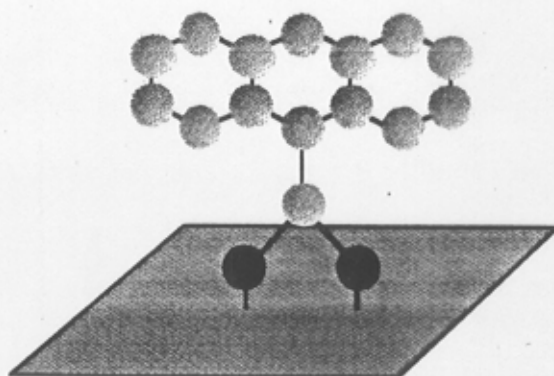
(Received 9 December 1997)

We have determined the azimuthal orientation of an adsorbate on a metal surface from an intramolecular-transition-derived feature in reflectance anisotropy spectroscopy (RAS). Adsorption of 9-anthracene carboxylic acid onto $p(2 \times 1)\text{O}/\text{Cu}(110)$ led to an ordered structure with a strong (2%), derivativelike feature at 4.5 eV. Fresnel theory predicts the measured intensity, functional behavior, and sense of the RAS signal for the molecule aligned along [110]. IR measurements confirm that the molecular plane is perpendicular to the surface and STM measurements support the azimuthal orientation. We reassign the sense of the clean $\text{Cu}(110)$ surface RA spectrum. [S0031-9007(98)06135-3]

PACS numbers: 68.45.-v, 33.20.Kf, 73.20.At, 78.40.-q



9 Anthracene carboxylic acid (9AA)



Study of Surface States on Cu(110) Using Optical Reflectance Anisotropy

Ph. Hofmann, K. C. Rose, V. Fernandez, and A. M. Bradshaw

Fritz-Haber-Institute der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

W. Richter

Institut für Festkörperphysik der TU Berlin, Sekr. PN 6-1, Hardenbergstrasse 36, 10623 Berlin, Germany

(Received 9 March 1995)

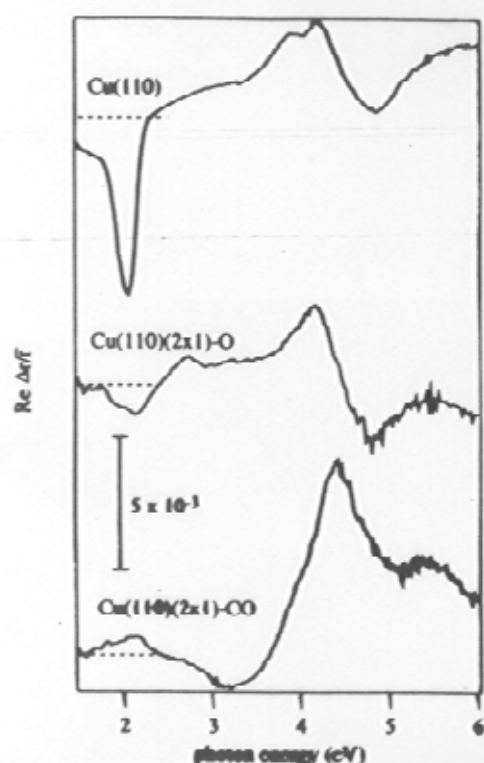


FIG. 1. Real part of the RAS spectrum for clean Cu(110), Cu(110)-(2 × 1)-O, and Cu(110)-(2 × 1)-CO. The dashed horizontal lines represent the zeros of the corresponding spectra.

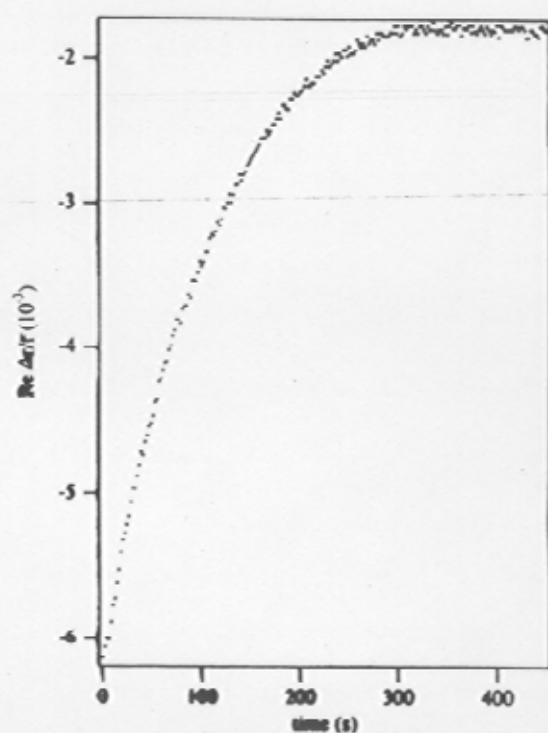
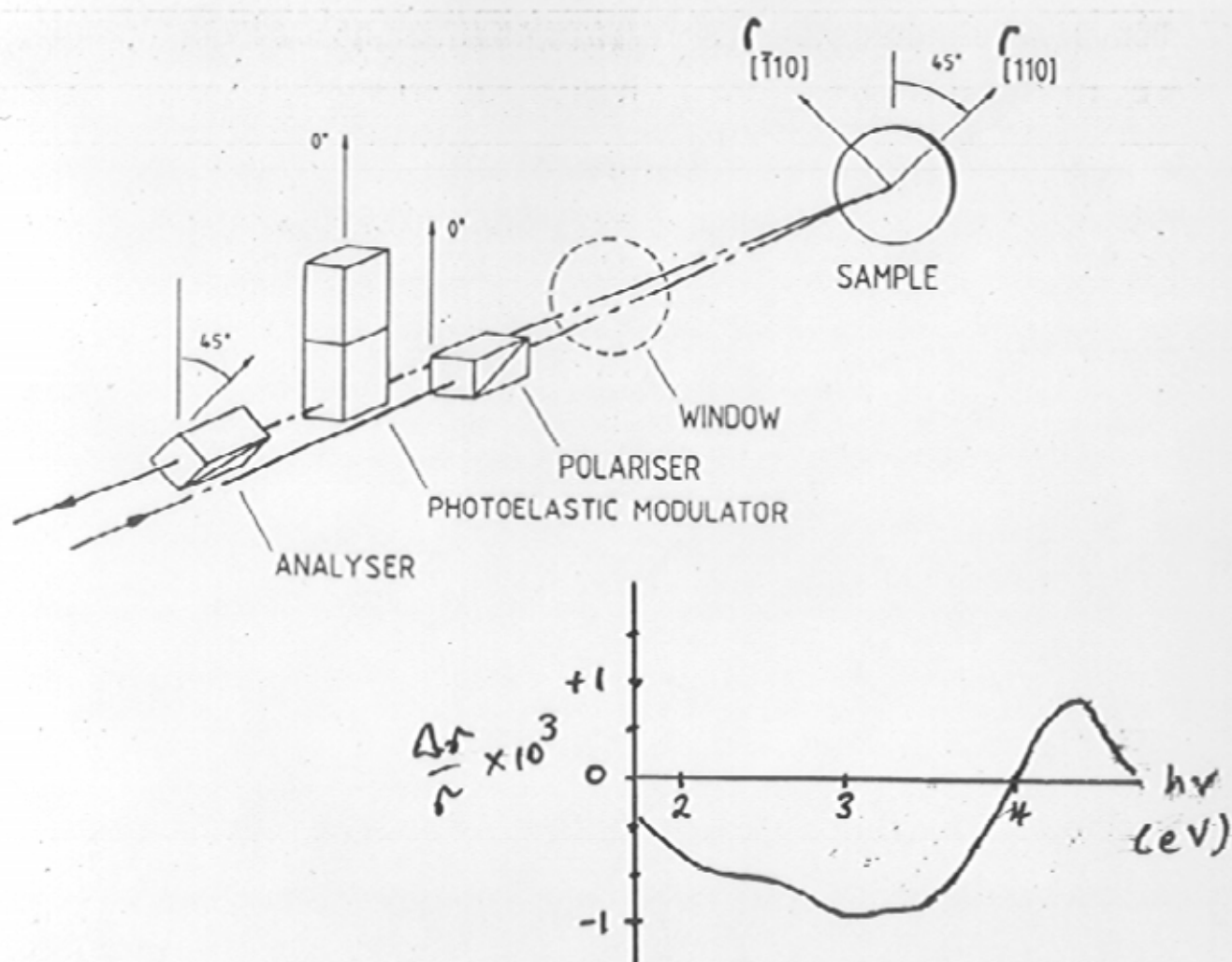


FIG. 4. Real part of the RAS complex reflectivity at 2.1 eV as a function of time during exposure of the clean surface to molecular oxygen at room temperature, beginning at $t = 0$ s.

Reflection Anisotropy Spectroscopy (RAS)



Characteristics of RAS

- 1 External to UHV environment.
- 2 Very high sensitivity, $\sim 1/100$ of a monolayer
- 3 Real time changes, single $\lambda \sim 20$ m sec
- 4 Theory is making progress
 - a) local probe on a molecular scale
 - b) characteristic of electronic structure
- 5 Potential for studies;
 - a) at high pressure
 - b) of the liquid-solid interface

A microscopic probe of macroscopic anisotropy

Reflection Anisotropy Spectroscopy: A new probe of surfaces and interfaces.

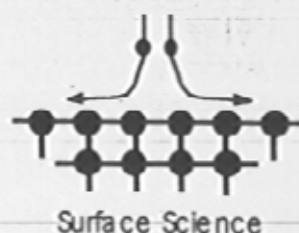
Reflection Anisotropy Spectroscopy

An optical probe of surfaces

Developed in 1980's as probe of
semiconductor surfaces and growth

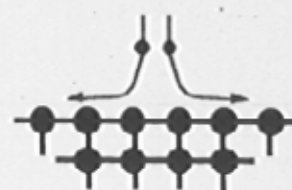
Late 1990's application to metal surfaces

2000 1st study of metal/liquid interface



Dreams of Photoemission at the Cooper Minimum on the 4GLS SASE FEL

- 1 Very testing. Requires measurements over a very wide photon energy range.
- 2 Science restricted to d or f orbitals with a radial node
- 3 High photon intensity means can study dilute systems
 - a Test of alloy theory at the dilute limit
 - b Test of ideas of electron localisation and screening for d type donors in semiconductors
 - c Study of δ doped layers in semiconductors
 - d Development of electronic structure as nanostructures are assembled from atoms



Surface Science

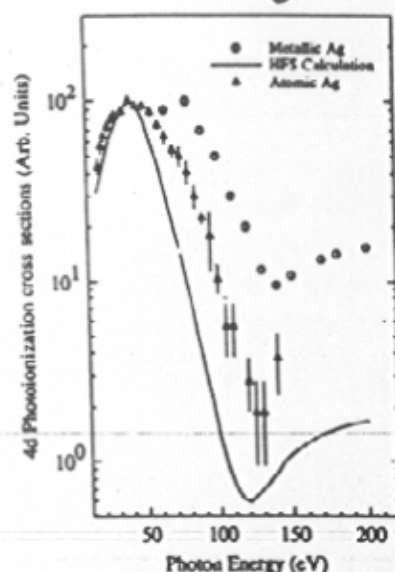
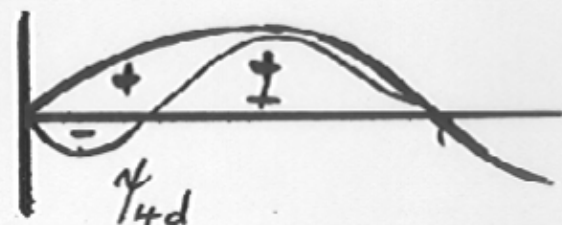
Solid State effects on valence wavefunctions: Cooper minimum photoemission

Photoelectron cross-section depends on wavefunction.
For photoelectron energies $> 10 - 20$ eV above threshold the cross-sections, σ , of core levels are $\sim$ independent of phase.
Wavefunctions with a node show a Cooper minimum (CM).
CM of 4d wavefunctions in solid is sensitive to environment.

Independent particle frozen orbital approximation

$$\sigma_{nl}(h\nu) = \text{constant} [l R_{l-1}^2(\epsilon_k) + (l+1) R_{l+1}^2(\epsilon_k)]$$

$$R_{l\pm 1}(\epsilon_k) = \int_0^\infty P_{nl}(r) r P_{\epsilon, l\pm 1}(r) dr$$

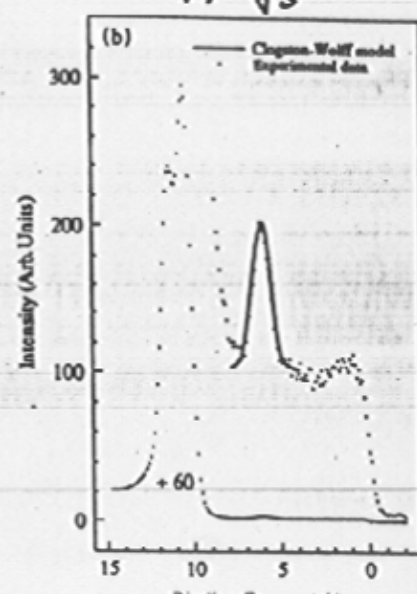
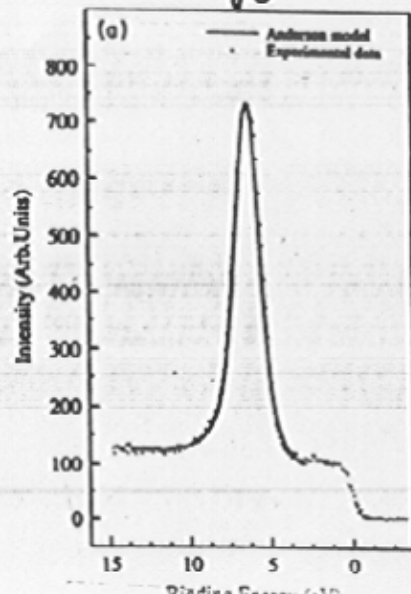
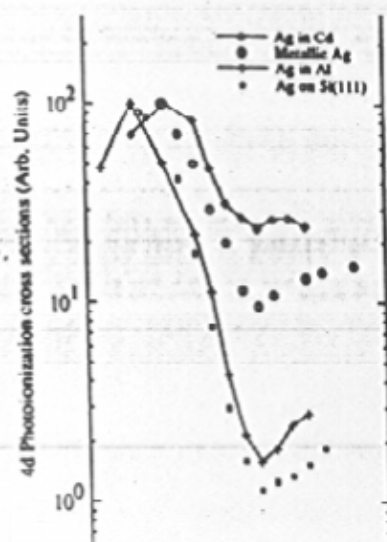


Ag atoms (theory)	2.3
Ag atoms	1.7
Ag on Si	1.9
Ag in Al-Ag	1.8
Ag metal	1.0
Ag metal	1.1
Ag metal	1.5
Ag metal	1.7
Ag metal	1.7
Ag in Cd-Ag	0.5
Cd in Cd-Ag	1.1

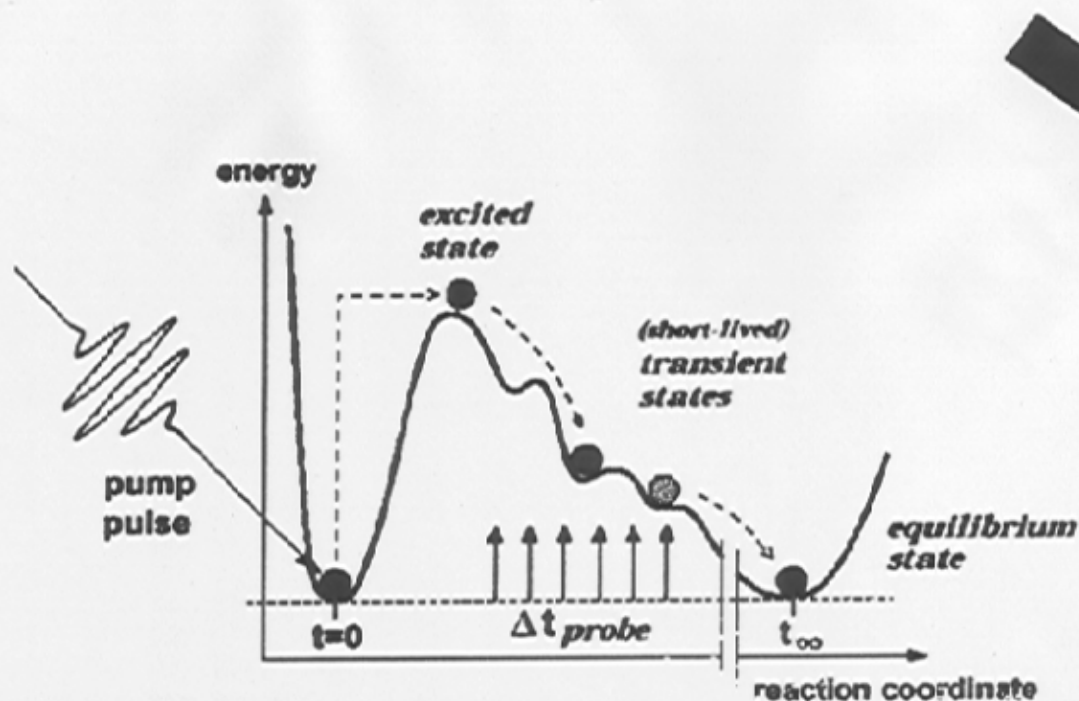
$\log_{10}(\sigma_{\max}/\sigma_{\min})$

$Al_{95}Ag_5$

$Cd_{97}Ag_3$



- short pulses with tailoring of the repetition rate
- pump-probe
- real time monitoring of reactions



ACCESS TO KEY PROCESSES

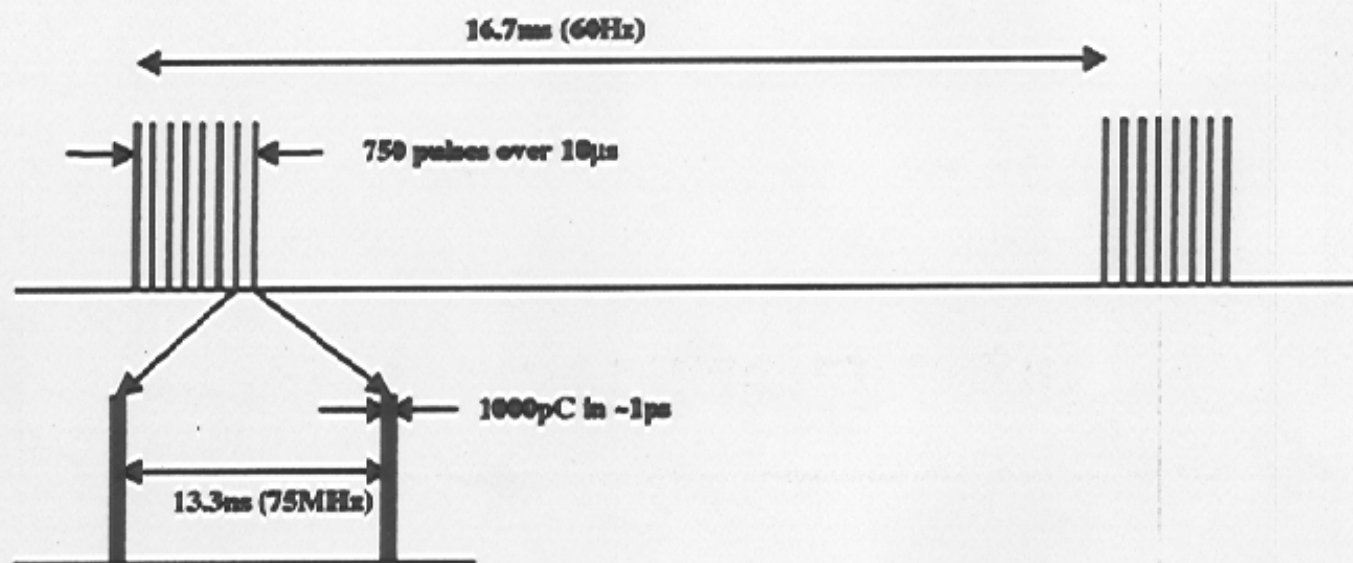
**bond breaking and
making in real systems**

4GLS

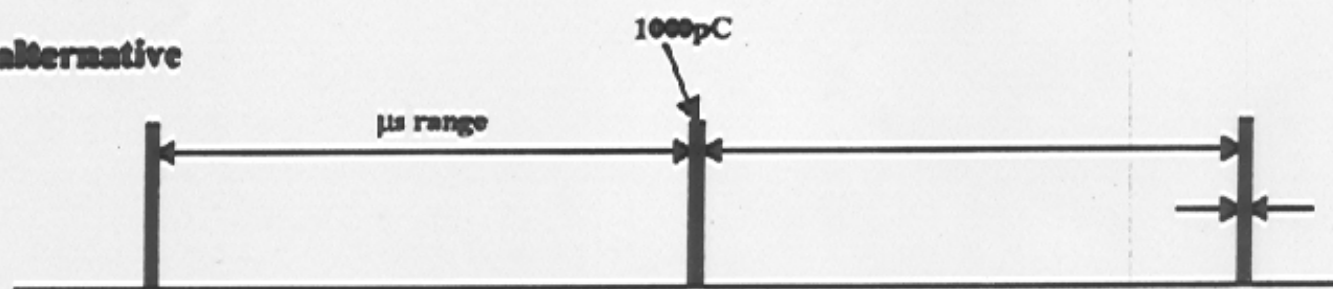
XUV-FEL pulse structure

CRISM

a) very intense short pulses - a necessity



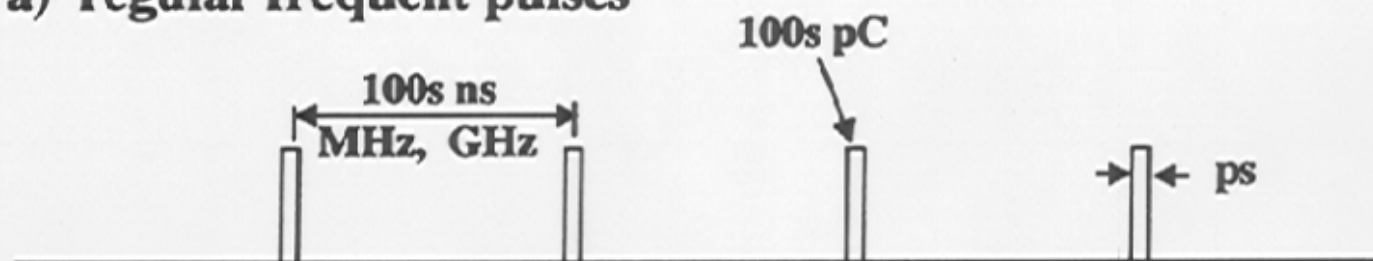
b) alternative



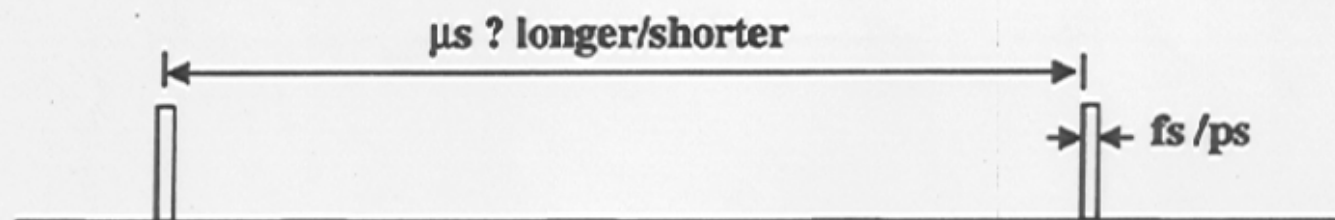
4GLS flexible pulse structure



a) regular frequent pulses



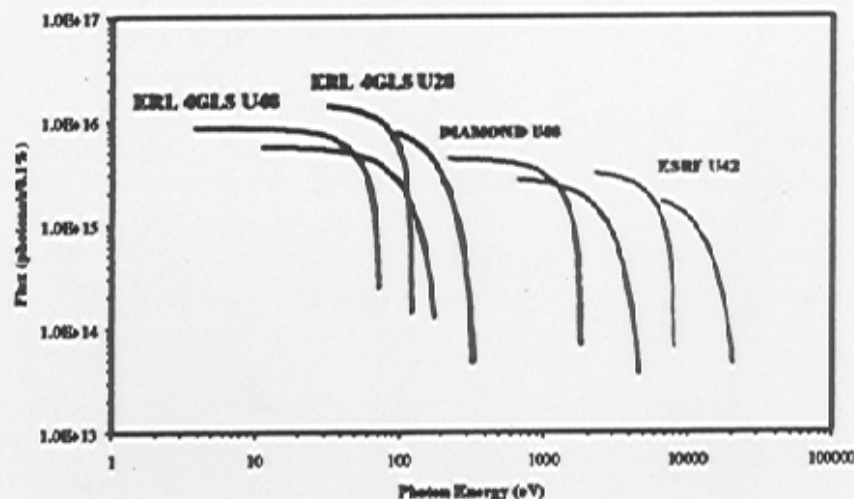
b) regular infrequent pulses



c) irregular pulses

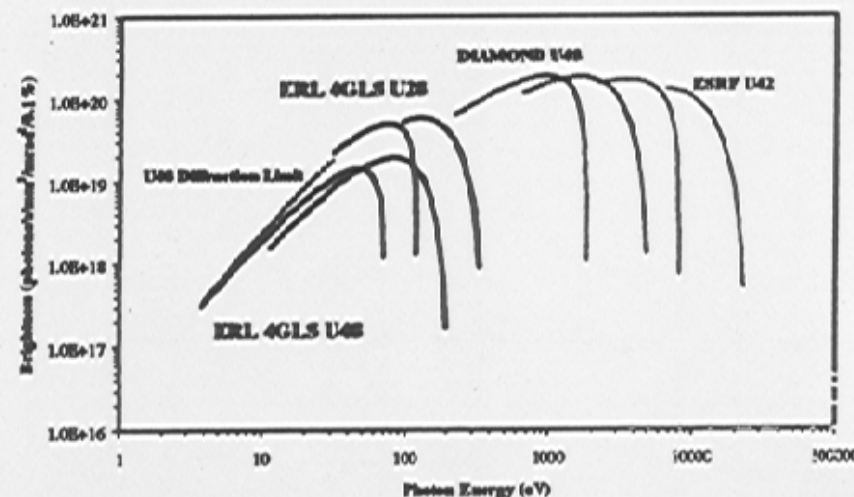
d) long pulses

4GLS undulator sources



- Optimised for high flux and brightness, in the energy range 4-100 eV.

- Up to 500-600 eV available in the higher harmonics.

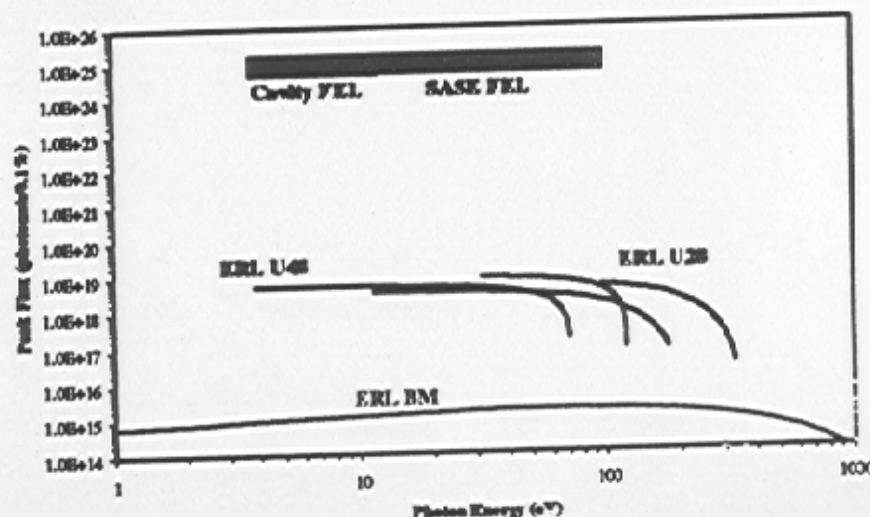
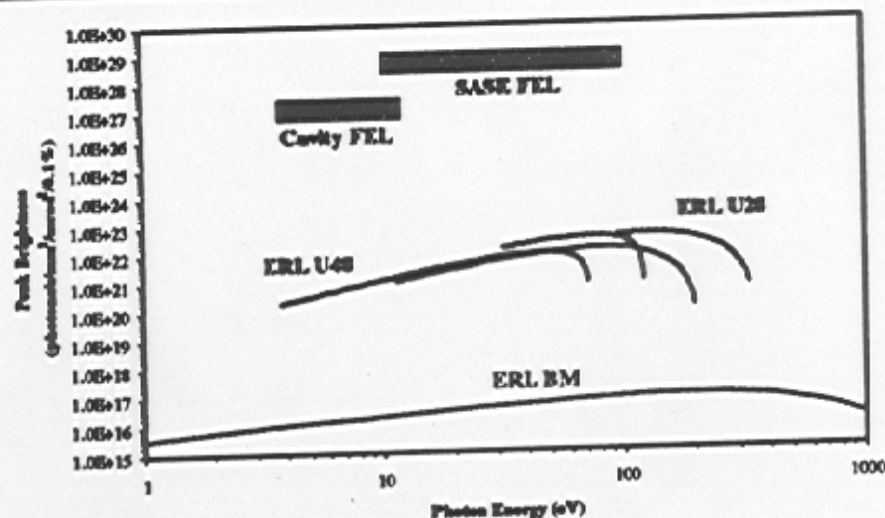


- Complements diamond by reaching to lower photon energy and delivering an order of magnitude better brightness in the sub-100 eV energy range.

4GLS

cavity VUV-FEL
and XUV-FEL sources

CASIM



- projected peak brightness 7-8 orders of magnitude greater than the spontaneous undulator output of 3rd generation storage rings.
- full transverse coherence
- 100 femtosecond time domain
- Variable polarisation
- Cavity FEL, 3-10 eV with broad tuneability, up to 25 eV possible with restricted tuneability.
- SASE FEL, up to 100 eV in the fundamental (300 eV in the 3rd harmonic).

4GLS

electron energy 600 MeV



Cavity based VUV-FEL

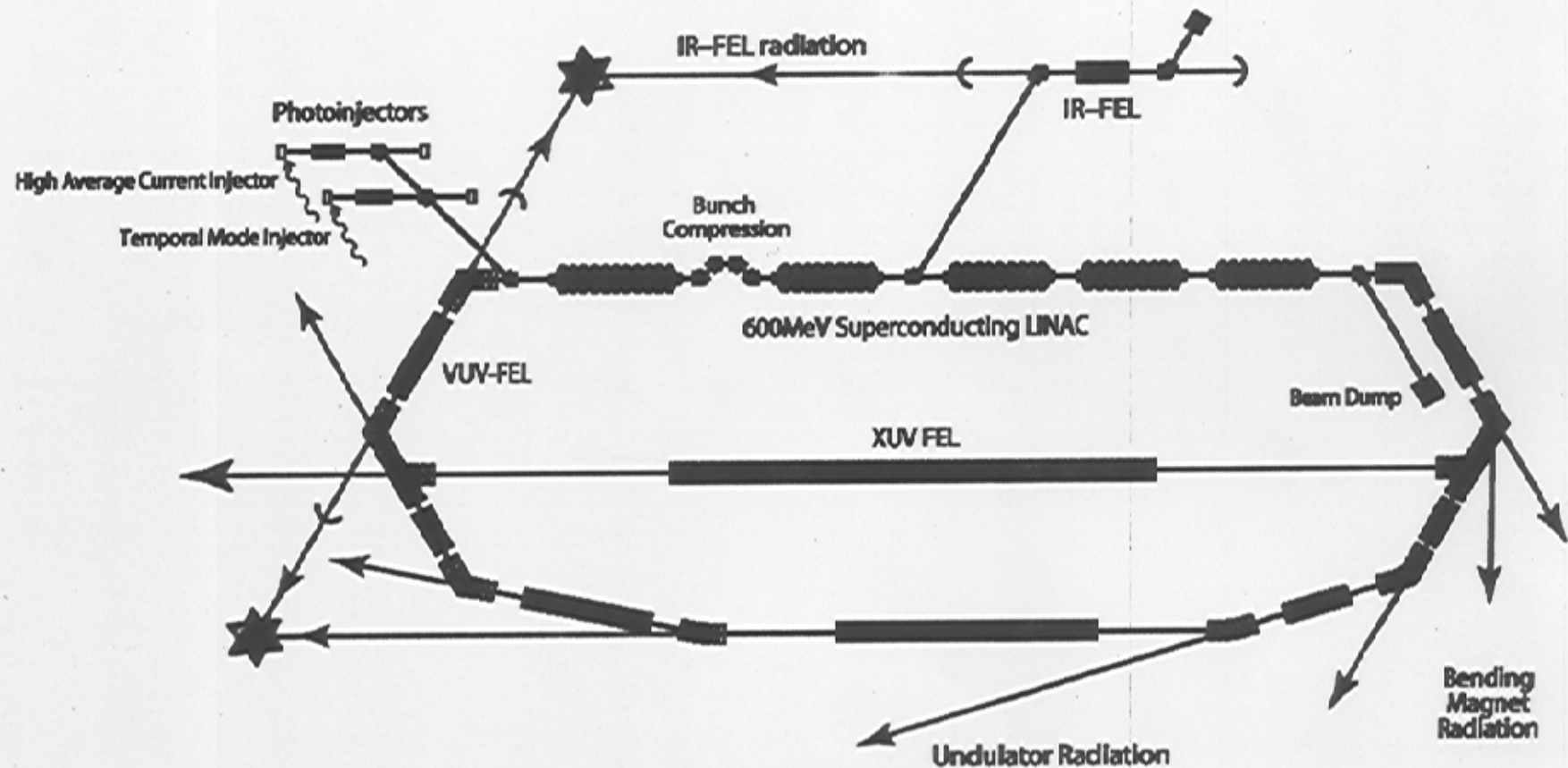
- sub ps pulses
- repetition rate, 6.25 MHz
- photons 3-10 eV broad tuneability
 - up to 25 eV possible with restricted tuneability
- peak brightness 10^{25} photons/(s mm² mr² 0.1%BP)
- photons per pulse $\sim 10^{12}$

SASE XUV-FEL

- fundamental 10-100 eV
- seeded, 10s fs long, 10s μ s separation
- peak power 1 mJ per pulse, 440 MW
- peak brightness 10^{29} photons/(s mm² mrad² laser BP)
- photons per pulse $\sim 10^{14}$

4GLS

CAESAR



Not a storage ring but an energy recovery linac, ERL

Acknowledgements



4GLS International Advisory Committee

4GLS Steering Group

4GLS Development Team

Daresbury Laboratory/Rutherford Appleton Laboratory

SRD

ASTeC

Central Laser Facility

UK Academic Community