

**The AONSA Prize Lecture**  
**Neutrons for Chemistry - Challenge and Opportunity**  
**22 July 2015**

At the outset I would like to thank AONSA as well as the organisers and sponsors of this lecture and the AONSA prize - which I am honoured to receive.

I show this first slide of the dawn at Manly on 22 July 2015 as this underlines what I really want to say in this lecture. Although the lecture is historical in my search for the use of neutrons in chemistry, I hope to show that we are really at the dawn of that usefulness through the marvelous and massive improvements in neutron scattering methods over the last 50 years.



**Dawn at Manly, NSW, 22-7-15**

I have subtitled the lecture “Challenge = Opportunity (in soft matter 1963-2015)” to focus on the challenge and opportunity that neutron scattering offers to chemistry. What are some key challenges for chemistry using the remarkable properties of neutron scattering as a method of understanding phenomena in solids and liquids?

I speak first of all about chemistry and the slide below shows a complex chemical synthesis of giberrellin – a natural product that promotes plant growth. My colleague Professor Lew Mander is famous for this work. He is an excellent chemist and each step in the 23 stage synthesis from 1gram of starting material, ending up with 0.1gm of giberrellin, has been carefully planned and choosing the many different reagents used to go from one step to the next with maximum efficiency is underpinned by a great knowledge and understanding of chemical reactions.



On the left hand side a free radical initiation of the polymerization is indicated for styrene, to make polystyrene, one of the world's most important plastics. At each step a new radical is formed, one molecule longer than the previous. The reaction may proceed with great speed, transforming  $10^{20}$  monomer molecules in a period of minutes or hours, depending on the conditions – the reaction could be explosive if it went too quickly. Three possible products are shown also in the figure. The wonderful thing for a chemist is that the outcome of isotactic syndiotactic and atactic forms of the polymer (which have different physical properties and uses) can be controlled by the choice of solvent, temperature and catalyst.

The process again occurs at very short times and over short distances and it is the clustering and the electrostatic properties of the solvent around the reacting molecules at the instant of reaction that determines the outcome as shown at the bottom of the slide. From the number of molecules transformed the short timescales of these processes can be inferred.

## Explorers of the Usefulness of Physical Chemistry

### Sir Cyril Hinshelwood



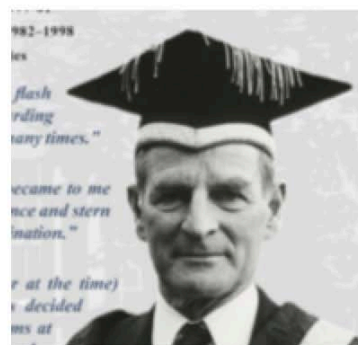
**Dr Lees Professor**  
**Nobel**  
**Chemical Kinetics**

### Sir Harold Thompson



**Fellow & Tutor**  
**St Johns College**  
**Infra-Red Spectra**

### Sir Rex Richards



**Fellow, Lincoln College**  
**Vice Chancellor**  
**NMR Chemistry**

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### A Tradition in Physical Chemistry at Oxford

How did I come to be focusing my attention on exploring the possibilities of neutron scattering for chemistry at the age of 25 and when I had just become a permanent member of the staff at Oxford University? I was fortunate to be given a scholarship to come to Oxford to do my DPhil under the supervision of Dr Rex Richards, at that time a Fellow of Lincoln College and who subsequently became Vice Chancellor of Oxford University. Rex had been the pioneering chemist of nuclear



magnetic resonance in England for determining chemical structure. He had wound his own electromagnet in the Physical Chemical Laboratory at Oxford and faced the challenge of seeing what could be done in chemistry – while most of the work in magnetic resonance was going on in physics laboratories.

His supervisor was Sir Harold Thompson, also shown in the slide who, in his turn, had been the pioneer of the use of infrared spectroscopy for chemistry since the 1930s. The slide also shows Sir Cyril Hinshelwood who at the time of my going to Oxford was Dr Lee's Professor Physical Chemistry and a Nobel laureate for his work on physical methods of following the rates of physical reactions. He was the supervisor of Sir Harold Thomson and told me that his supervisor, Sir Harold Hartley – in the old Balliol-Trinity laboratories – when doing work on electrochemistry had been accused of doing physics. Hartley had replied “what you call physics, we call chemistry”. My doctoral work with Rex Richards and a subsequent short post-doctoral period had resurrected Rex's old magnet and been aimed at finding the usefulness of the Overhauser effect for chemistry – a very open-ended project but which worked extremely well. On my appointment as a Fellow of St John's College and laboratory demonstrator at Oxford, Sir Cyril Hinshelwood had the policy that - as there was one magnetic resonance expert in the laboratory (Rex Richards) I had to find a new area. It was a very good policy.

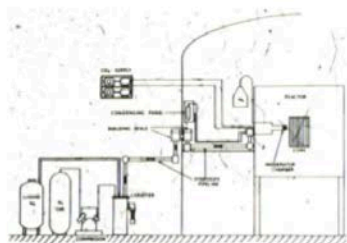
My good fortune was to meet Dr Peter Egelstaff from the Atomic Energy Research Establishment at Harwell at dinner in St John's College in 1962 as the guest of Sir Roger Elliott. Peter was interested in the dynamics of liquids using neutron scattering and, in particular in ortho and para hydrogen – of which I knew something as a chemist. It was Peter who introduced me to neutron scattering which became my focus subsequently and the “opportunity” was his having just installed at the DIDO reactor at Harwell a first high efficiency liquid hydrogen cold source as shown below.

## Chemical Neutron Scattering 1963- 4

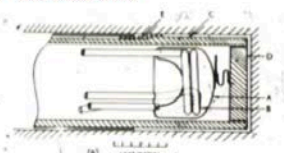
### Experimental Opportunity



- Cold Neutron Source 1962 – energy resolution
- No optical selection rules spectroscopy
- $Q, \omega$  Space
- + Peter Egelstaff



Liquid Hydrogen Cold Source DIDO 1963



The Cold Source



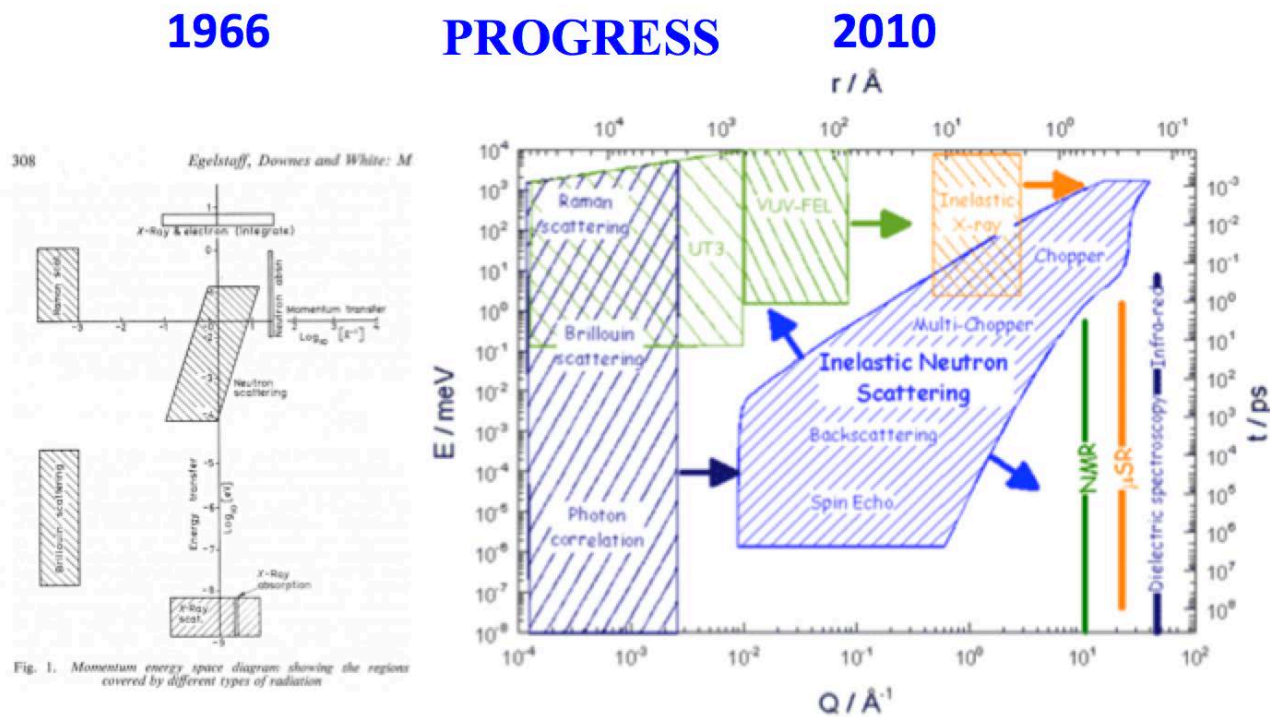
Counter bank 4H5 ToF 1963

Peter Egelstaff and the 4H5 cold neutron scattering Instrument

This was one of the best instruments of its time and I was attracted, as a spectroscopist, by the fact of no optical selection rules and by applying the spectroscopic angular dependence of the neutron spectrum. Using the  $Q, \omega$  space of neutron scattering was and is the method's principal challenge – this space contains the signatures in time and distance on the picosecond timescale – the “heart” of understanding diffusion limited chemical reactions.

The possibility of a direct link between the scattering spectrum and models for the molecular motions through space/time correlation functions was highly attractive and relevant to the sorts of things I had been teaching as fundamental ideas for the reactivity of molecules in solution. As an example of the “cage effect” which chemists talk about for polymerization, the “itinerant oscillator liquid model” of Varley Sears (Proc Phys Soc 1965, 86, p953) was very close to the notions which chemists had for fast inter-molecular reactions.

## The Egelstaff “Neutro-centric” Diagram



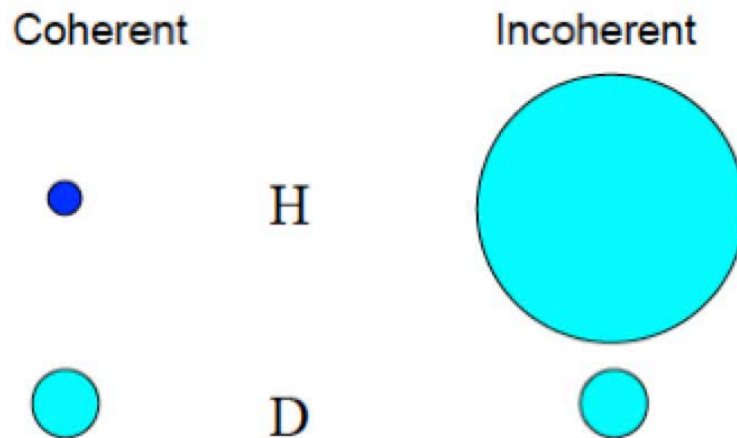
### The Egelstaff Neutro-Centric Diagram

Peter Egelstaff at that time was just publishing his book of chapters by neutron practitioners and theorists. In it and in the second paper of the work that Julia Higgins did with him (on zeolites) is the first example of what we and Peter called the “Egelstaff Neutro-centric” diagram. It showed (left hand side) how neutrons then embraced the region of  $0.1 < Q/ \text{Å}^{-1} < 10$  in momentum transfer and  $10^{11}$  to  $10^{13} \text{ sec}^{-1}$  in frequency – space and time domains around  $1 \text{ Å}$  and  $1 \text{ picosecond}$ . The complementarity of neutron scattering to other methods was clear. It was and remains a most

exciting challenge to use this space to characterize structure and dynamics. By 2010 (RHS) the space had greatly increased in its dimensions illustrating the wide scope that we now have and some of which I will illustrate in this lecture.

In 1963 it was evident to me that because of the absence of optical selection rules – and accessibility of all molecular motions – some method was needed to simplify the exploration of  $(Q, \omega)$  space. This point was driven home to me early in 1963 by my first experiment with Peter Egelstaff to look at the dynamics of liquid and the liquid crystalline phases of para-azoxyanisole on the 4H5 spectrometer. NMR had shown how different these two phases were but in neutron scattering at that time, the spectra looked very similar. Isotopic and atomic contrast looked to be the way to distinguish the motions of interest from all the rest. This was the first and remains a key feature of our use of neutron scattering. The contrast we looked to in the first instance was that provided by the great incoherent scattering of hydrogen compared to deuterium, oxygen and silicon and our first experiments were directed by this.

## Exploring Contrast Strategies



### Isotopic contrast in Neutron Scattering

Julia Stretton-Downes (my first PhD student) and I worked with Peter Egelstaff to detect the motions of trapped molecules in quinol clathrates. The quinol molecule shown in the slide below makes a cage because the hydroxyl groups at each end of the benzene ring join with those of other molecules to seal a box in which molecules as big as methyl cyanide or methanol can be incorporated. Julia produced the fully deuterated quinol using heavy water and the hydrogenation apparatus in the Dyson Perrins Laboratory and our first paper “localized vibrations of trapped molecules” appeared in Physical Review Letters 1966, 17, 533-536.

# Host-Guest Interactions

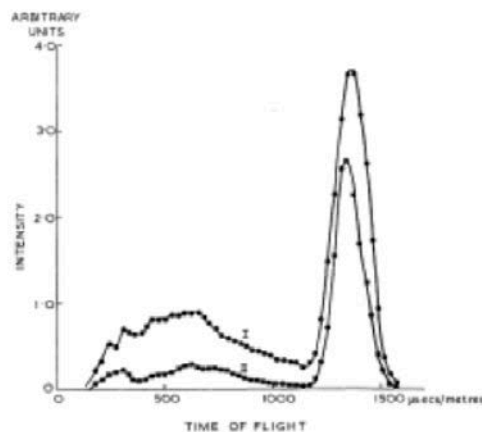
## Deuterium Contrast 1963- 7



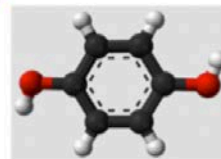
**Peter Egelstaff**



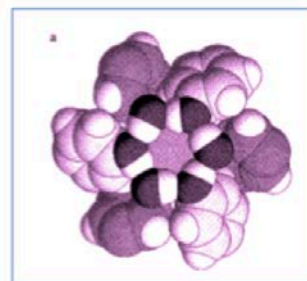
**Julia Higgins (née Downes)**



**Protonated Guest (CH<sub>3</sub>CN)**  
**Deuterated Host (Quinol Clathrate)**



**Quinol**



**Quinol Clathrate**

**“Localised Vibrations of Trapped Molecules”** J.S Downes, J.W.White, P.A. Egelstaff & V. Rainey  
*Phys. Rev. Lett.*, 17: pp. 533–536 (1966)

**Isotopic Contrast to explore host – guest dynamics**

The time of flight neutron inelastic scattering from the included methyl cyanide molecule (upper curve) is qualitatively different and clearly differentiated from that of the deuterated host lattice (lower curve). The spectra show the “rattling modes” of the included molecule and their coupling to the host lattice dynamics. With only about 60 data points in the whole time of flight spectrum the fine structure was blurred.



## “NATURAL” CONTRAST

**H<sub>2</sub>O vs SiO<sub>2</sub>**

**1966**

**“Molecular Motion in Molecular Sieves by Neutron Scattering Spectroscopy”.**

P.A. Egelstaff, J.S Downes & J.W.White.  
*Molecular Sieves, Soc. of Chem. Ind.*, pp. 306–318 (1968).

**Water, CH<sub>3</sub>OH in Al SiO<sub>4</sub> lattice**



**Peter Egelstaff**



**Julia Stretton - Downes**

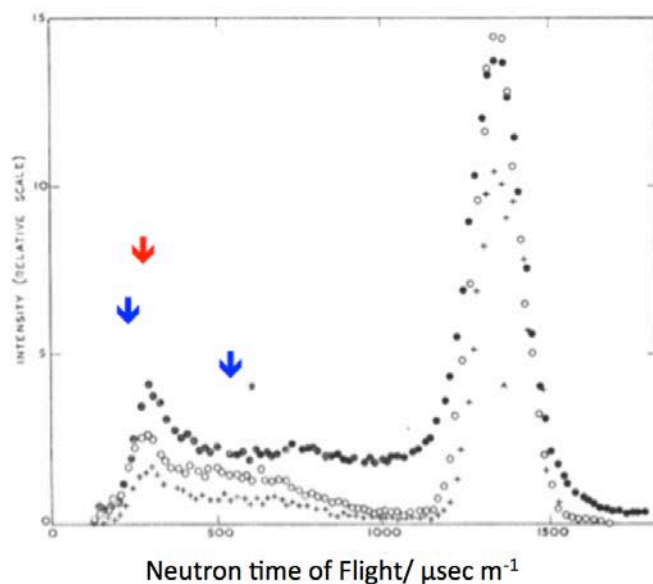
**Molecular Dynamics in Zeolites**



Use of the “natural contrast” between an included hydrogenous molecule and the aluminosilicate lattice of zeolite frameworks was also studied at that time to define the residence time and internal diffusive properties of molecules and these industrially important catalyst materials. The paper in the Society of Chemical Industry publication 1968 “Molecular Sieves” pp306-318, sets out many of the theoretical principles and interpretation of the dynamics of trapped molecules. The data show very little broadening of the quasi elastic peak, strong modification of the low frequency dynamics and (inset) the importance of rotational diffusion for the trapped molecules. As spectrometers have improved over the past 50 years, this subject continues to be of interest. It is not only because the molecular dynamics can be recorded but also because of the great changes in the low frequency liquid spectrum as well as the quasi elastic region are apparent and depend upon the molecular properties as shown below.

## Water in Molecular Sieve 1966

*Egelstaff, Downes and White: Molecular Motion in Molecular Sieves*

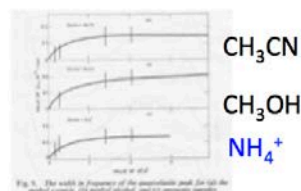


• **Quasielastic**  
changed  $g(\omega)$

• **H<sub>2</sub>O liquid**

o **Sieve + NH<sub>4</sub><sup>+</sup>**

+ **H<sub>2</sub>O Sieve**



P.A. Egelstaff, J.S Downes & J.W.White.  
*Molecular Sieves, Soc. of Chem. Ind.,*  
pp. 306–318 (1968)

### Dynamics of Ammonia, Methyl cyanide and Methyl Alcohol in Molecular Sieve 3A

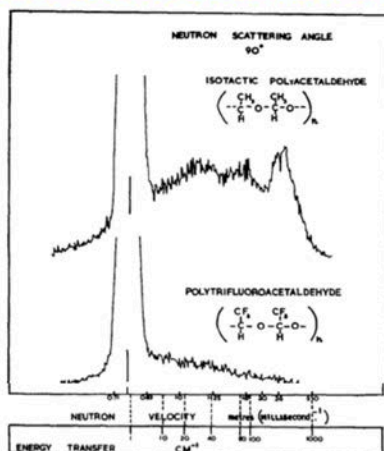
In this preliminary phase of exploring neutron possibilities for chemistry, the use of contrast to simplify the spectra of polymers and molecular liquids was also studied. In polymers, there was great interest in identifying the torsional and low frequency motions of methyl groups – thought to be important for understanding polymer relaxation phenomena and phase transitions (this interest continues to this day where the onset of methyl group rotation has been used to characterize the softening of protein dynamics (see for example the lecture by Katherine Woods in this conference). Lacking the funds and the competence to perform methyl group deuteration we did an experiment to identify the methyl groups by comparing the neutron scattering from isotactic poly acetaldehyde



and poly trifluoroacetaldehyde – where the hydrogens have been replaced by fluorine on the methyl groups. This spectrum published in 1967 shows the major changes in the density of states for the molecular motions – clearly identifying the methyl torsional region of the methyl group spectrum.

## ATOMIC SUBSTITUTION

### POLYTRIFLUORO ACETALDEHYDE

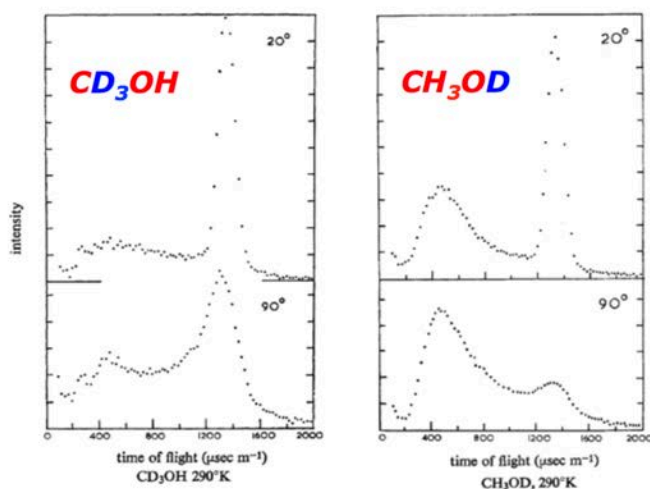


Longster, G. F. and White, J. W. – Vibrational Assignments in Polymer Neutron-scattering Spectra by Atomic Substitution. *J. Chem. Phys.*, 48: pp. 5271–5273 (1968).

### Identifying Methyl torsions in Polymers – Atomic Substitution

For molecular liquids, the aim was to see whether the dynamics of one part of the molecule were different from that of another. The objective, ultimately, was to look at molecules in which fast proton exchange was occurring and to identify the signature of such diffusion limited chemical reactions. That the two parts of a molecule give different spectra is shown by the contrast variation experiment on methanol published in the discussions of the Faraday society, 1967, 43, pp169-183.

## Liquids-Isotopic Contrast 1967



Neutron Scattering Spectroscopy of Liquids. Aldred, B. K., Eden, R. C. and White, J. W. *Discuss. Farad. Soc.*, 43: pp. 169–183 (1967).

Separating the Dynamics of different parts of the same molecule by Isotopic Contrast

This paper not only shows separately the dynamics of the methyl group and the OH group on these liquids but was also our first foray into the dynamics of strong acid solutions – subsequently followed up by George Stirling and by Andrew Taylor (in his DPhil thesis). Andrew did a remarkable job successively eliminating effects of centre of molecule diffusion and molecular rotation to try to identify (with Jean-Claude Lassegues) the possible signature of the fast proton transfer. Modern spectrometers with variable resolution in the picosecond time-range will undoubtedly add to these pioneering measurements.

## MOLECULAR SPECTROSCOPY

### **CONTRAST by HYDROGEN AMPLITUDE WEIGHTING 1968**

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_{\text{inc } j}^{\nu} = \frac{k}{k_0} \frac{1}{N} \sum_j (b_{\text{inc}}^2)_j \exp[-2W_j] \exp\left[\frac{-\hbar\omega}{2kT}\right] \frac{\hbar(\mathbf{Q}\cdot\mathbf{C}_j)^2}{4N\omega_\nu M_j} \text{csch}\left[\frac{\hbar\omega_\nu}{2kT}\right] \delta(\omega_\nu - \omega) \quad (2)$$

where the Debye-Waller exponent  $W_j$  is given by

$$W_j = \sum_{\nu} \coth\left[\frac{\hbar\omega_\nu}{2kT}\right] \frac{\hbar(\mathbf{Q}\cdot\mathbf{C}_j)^2}{4N\omega_\nu M_j}. \quad (3)$$

Here  $\mathbf{C}_j^{\nu}$  is the displacement of the  $j$ th atom in the mode  $\nu$  and  $M_j$  is the mass of the  $j$ th atom.



**Reynolds, P. A.** and White, J. W. – Inelastic Neutron Scattering from Molecular and Crystal Excitations in Aromatic Molecular Crystals. *Discuss. Farad. Soc.*, 48: pp. 131–147 (1969).

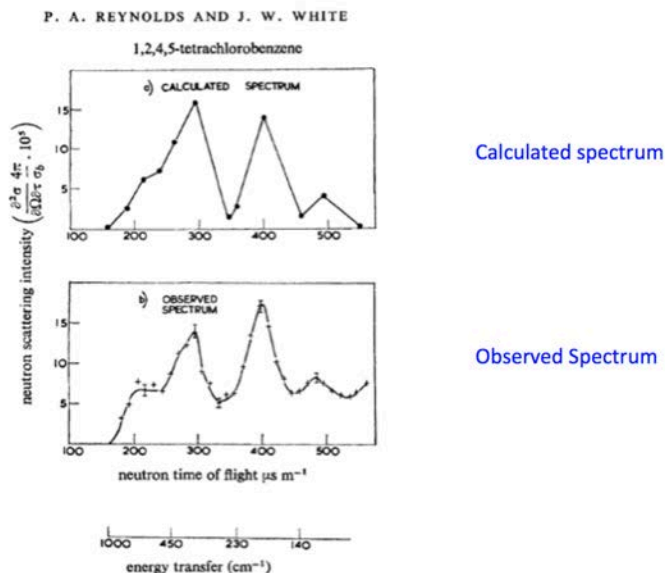
#### **Calculation of Neutron Inelastic scattering spectra.**

Molecular spectroscopy by inelastic neutron scattering was explored in parallel with the above. The dynamics of trapped molecules had left us with the impression – which Julia dubbed “the first law of neutron scattering” – that all neutron spectra looked very similar. There had been beautiful experiments done by Iyngar, Venkataraman and their colleagues on ammonium salts showing the harmonics of the torsional vibrations in solids but no attempts to demonstrate calculable neutron inelastic scattering spectra from molecular solids. Philip Reynolds, as an Honors student at Oxford, undertook this for the molecules in para dichlorobenzene and 1,2,4,5-tetrachlorobenzene crystals.

We were helped in 1967 by a new cold source in 4H5 (the supernova) and by the construction of a new spectrometer in the DIDO reactor (the 6H instrument) in which George Stirling played a very big part with Peter Egelstaff and George Haines. This instrument had carefully engineered flight paths and with Philip’s calculated the hydrogen amplitude weighted density of states for the molecular vibrations showed the potential of using both the eigen vectors and frequencies in assignment and development of molecular force fields.. Discussions of the Faraday Society 1969,

48, pp131-147, conclusively shows the correspondence between the calculated and the observed spectrum for 1,2,4,5 tetrachlorobenzene and opened up many possibilities for molecular spectroscopy. Nervousness about the validity of the 1-phonon approximation, the lack of cubic symmetry, multiple scattering effects and anharmonicity which had surrounded discussions about the observability of molecular vibrations in “soft” materials was removed.

## 1,2,4,5 TETRACHLORO BENZENE



### Calculated and Observed Hydrogen Amplitude weighted INS Spectrum

Comparison of the infrared spectrum of cobalt tetracarbonyl hydride in the vapour and the neutron inelastic scattering spectrum in the solid in the same energy region (JWW White and CJ Wright Chemical Communications, 1970 p970) illustrates the value of hydrogen eigen-vector weighting as a contrast method in molecular spectroscopy.

### Contrast from H Eigenvector Weighting $\text{Co}(\text{CO})_4\text{H}$

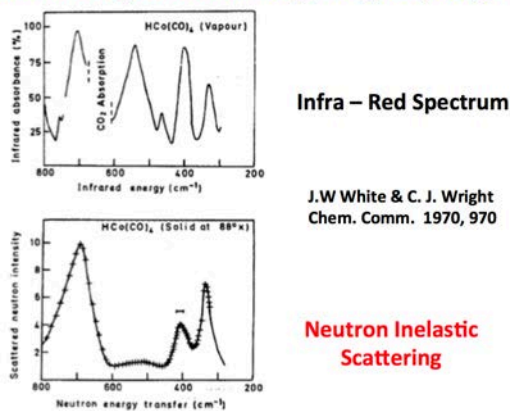


FIGURE. Neutron and I.r. spectra of  $\text{HCo}(\text{CO})_4$  compared.  
Incoherent Inelastic Neutron Spectra of Hydridocarbonyls. Mid-infrared Vibrational Frequencies for  $\text{HCo}(\text{CO})_4$

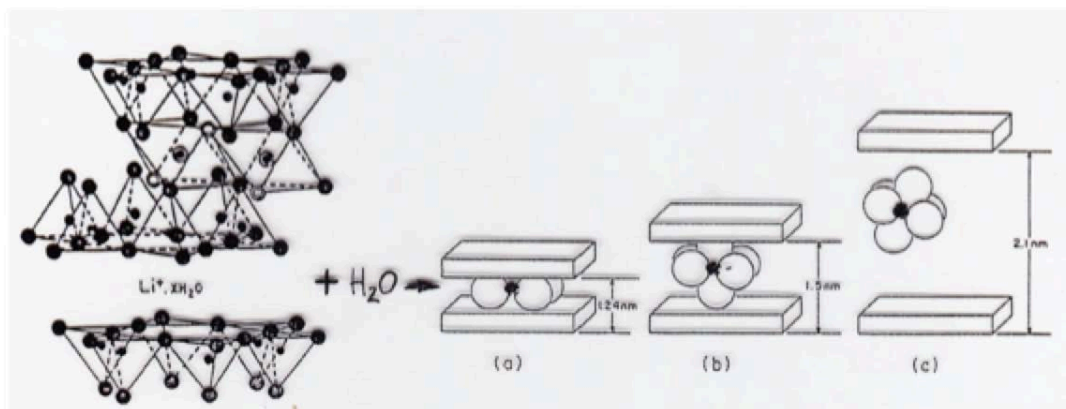
### Comparison of Infra-red and Inelastic neutron scattering spectra

The neutron spectrum is simpler and different to the infra red spectrum because the infrared strong carbonyl stretching motions are not very neutron active whilst all molecular bending modes which couple to the bending motion of the hydrogen atom in this tetrahedral complex are strongly represented. This method has now become a powerful tool in chemistry – identifying the dynamics of molecules at interfaces, in catalytic processes, and in polymers since it has been possible to bring powerful computer modeling to bear to allow coupling between intra- and inter-molecular force fields to fit the whole density of states region. (eg. J. Howard, T. C. Waddington and C. J. Wright, Chem. Phys. Lett. 56, 258 (1978), Review of the analysis of molecular vibrations using INS Nuclear Instr. and Methods in Phys. Res. G.D Kearley et al. A354, 53, 354 (1995); Vibrational Spectroscopy with Neutrons. P. C. H. Mitchell, S. F Parker, A. J. Ramirez-Cuesta and J. Tompkinson. World Scientific, 2005.

## SURFACE CHEMISTRY

In 1968, surface chemistry seemed to be a promising chemical area in which neutrons could contribute. Our experiments on zeolites had shown that with “natural contrast” good signal-to-noise for included molecules could be obtained. Thus, despite opinion “that neutron scattering would not be useful for studying adsorbed molecules: as neutrons were penetrating radiation...” we decided to look at the potential of the technique for surface chemistry. Because of the great “polywater” debate in the early 1970s (that this new form of water with remarkable properties was produced in thin capillaries of high surface area/volume) we decided to study vermiculite and montmorillonite clays whose water content could be systemically varied in the spaces between the impermeable ca 1nm thick clay platelets.

# Thin Layers of Water in Vermiculites and Montmorillonites—Modification of Water Diffusion



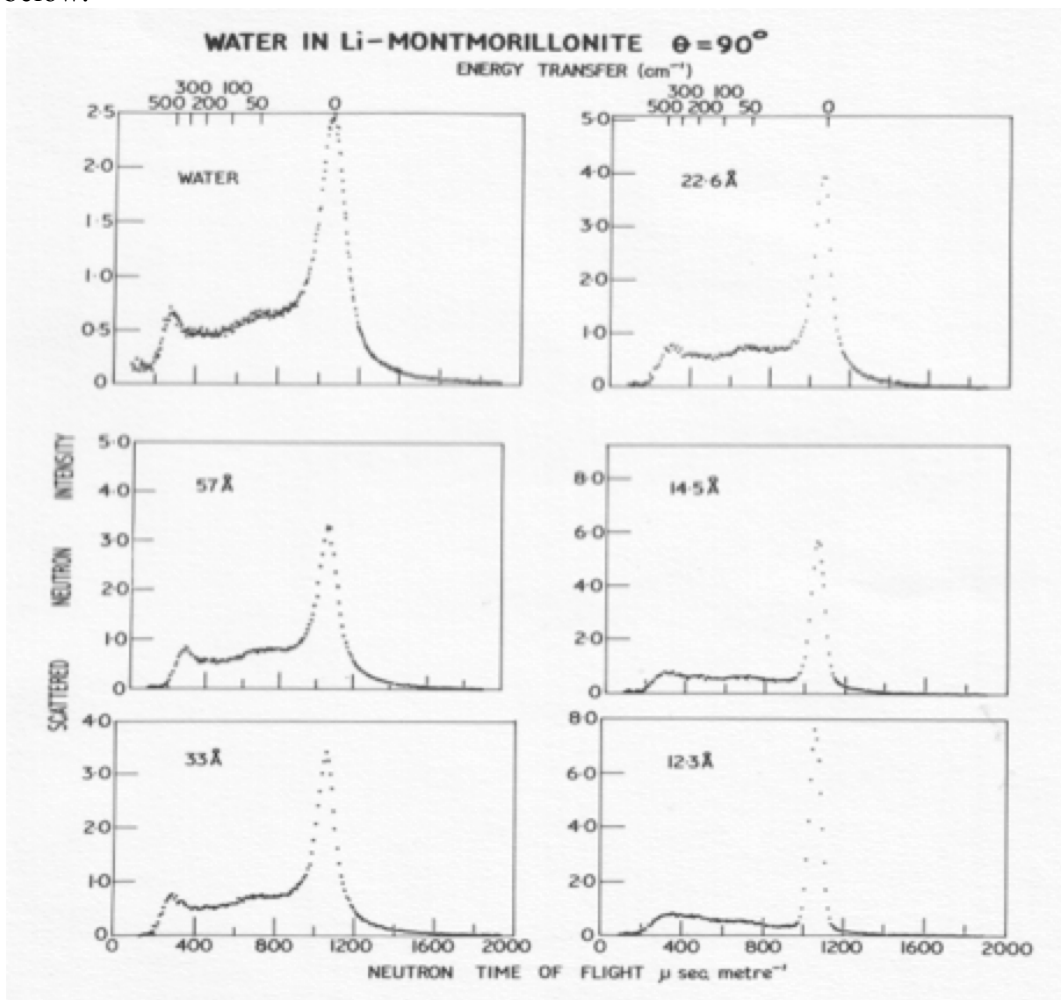
**S.Oleinik and J.W.White**

NATURE PHYSICAL SCIENCE VOL. 236 MARCH 6 1972

**p16**



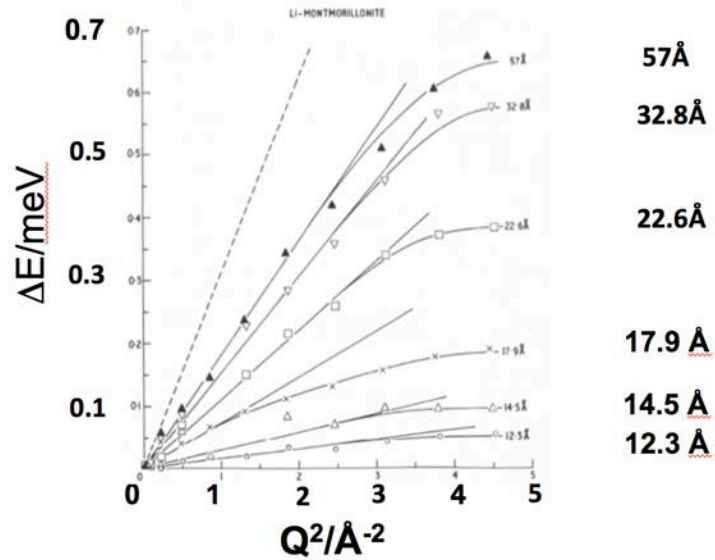
The figure above shows the way in which the clay sheets, composed of silica tetrahedral packed around octahedra containing magnesium or aluminium for example, can be swelled by added water. In preliminary experiments we discovered quickly that it was essential to have a clay expert to prepare the hydrate-able clay films and we were greatly helped by the method of Posener and Quirk who sent Stan Olejnik, one of their students, from Western Australia. Stan made the films and the data were reported in Nature Physical Science, 1972, 236, p16. The clays were swollen by equilibration with water vapour over solutions of known salt concentration up to swellings of 57Å from about 2Å between the ca 10Å clay sheets. The time of flight spectra of the included water are shown below.



**Neutron time of flight spectra of water in Lithium Montmorillonite at various swellings**

The immediate interest was the extent to which the water spectrum changes with water layer thickness,  $d$ . At low energy transfers (time of flight near  $800 \mu \text{ sec metre}^{-1}$  (the density of states is progressively reduced as the water layer thins) and the quasi elastic scattering becomes narrower. (These data again are quite relevant to the effect of hydration on the dynamics of proteins for example.) Analysis of the quasi elastic scattering (below) shows the strong variation of the low  $Q$  slope of the energy width as a function of  $Q^2$  (where  $Q$  is the momentum transfer  $= (4\pi/\lambda) \sin \theta$ , and  $\theta$  is the half scattering angle  $= 45$  degrees here, and  $\lambda$  the neutron wavelength). This slope is a measure of the self diffusion constant of the water included between the clay sheet.

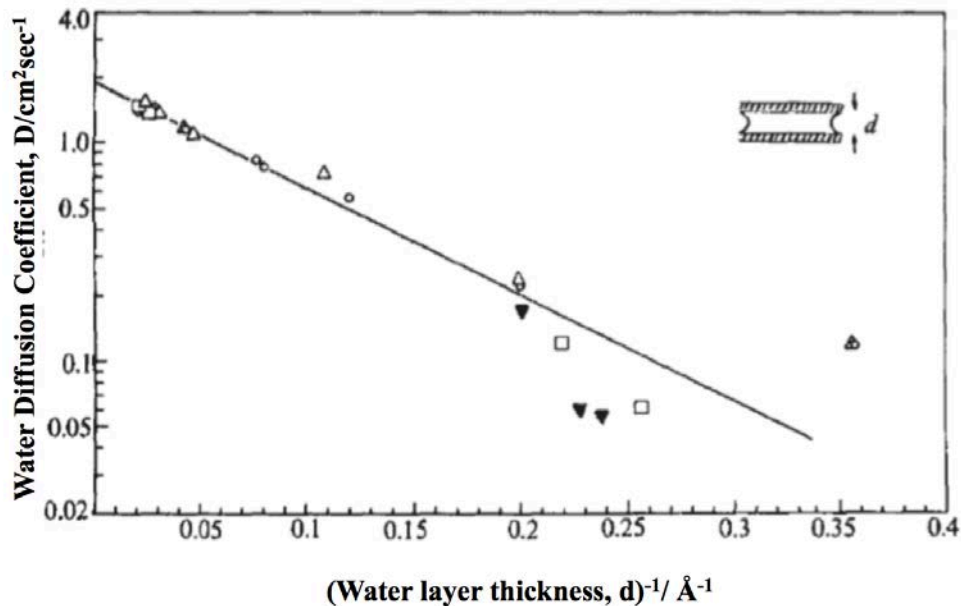
## THIN WATER Li VERMICULITE



Energy width of the Quasi-elastic scattering from water as a function of thickness/Å.

The water self diffusion coefficient,  $D$ , drops smoothly as a function of inverse thickness as shown by the beautiful scaling below.

## Scaling of the Measured Diffusion Coefficient



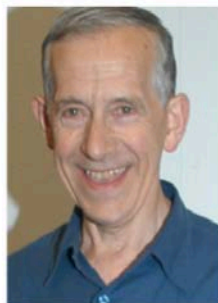
Scaling of the Log (water diffusion coefficient) with reciprocal water layer thickness

The logarithm of the diffusion coefficient scales as the reciprocal of the water layer thickness, a thickness of the order of 5 Å. This scaling can be understood in terms of the classical thermodynamics of a fluid in a capillary structure for which the radius of curvature of the meniscus

is related to the liquid surface tension and the molecular volume (Kelvin Equation). Our scaling formula assumes that the confinement confers an additional free energy barrier for diffusion to that of the normal fluid at the measured temperature. Using the Kelvin equation and accepted values for the surface tension and the molecular volume, a slope of  $10.2\text{\AA}$  is calculated for the scaling function - compared to the experimental value of  $13\text{\AA}$ . It should be noted that this thermodynamic description of the effects of confinement relates to a molecular description of the change in water free energy involving the kinetics of exchange of the included water between the surface and the contained ions and noting, that as the water thickness decreases, so also does the relative proportion of these charged species increase – as in a concentrated ionic solution.

In parallel with these water experiments, two students Robert Anderson and Philip Gamlen, studied the neutron scattering from simple molecules adsorbed on carbon and in graphite intercalation compounds. Their work, and that of others in France and the USA, showed that thermodynamic descriptions, such as those provided by adsorption isotherms for these molecules, could be explored in terms of the interfacial structures. By inelastic scattering from the isoelectronic ammonia and methane adsorbed on graphite Phil Gamlen showed the consequences of non-wetting of the carbon surface (ammonia) and registration of the methane at low coverages on the hexagonal close packed surface. A large extension by Robert Thomas and other colleagues by the discovery of quantum mechanical tunneling in the inelastic neutron scattering from methane adsorbed on graphite showed the means of testing intermolecular potentials for the adsorption process by neutron inelastic scattering.

## **STRUCTURE & DYNAMICS of ADSORBED MOLECULES 1969-**



Thomas, R. K., [Trewern](#), T. D. and White, J. W. –  
**Structure and Dynamics of Graphite  
Intercalation Compounds.** Part 3: Crystal  
and Dynamics and Binding in  $C_8K$ ,  $C_8K H_{2/3}$  and  $C_8K D_{2/3}$   
by Inelastic Neutron Scattering. *J. Chem. Soc., Faraday  
Trans. I*, 78: pp. 2399–2410 (1982).

[Hüller](#), A., Smalley, M. V., **Thomas, R. K.** and  
White, J. W. – **Rotational Tunnelling  
of Methane Adsorbed on  
Graphite:** Inelastic Neutron Scattering  
Spectra. *Mol. Phys.*, 44: pp. 533–555 (1981).



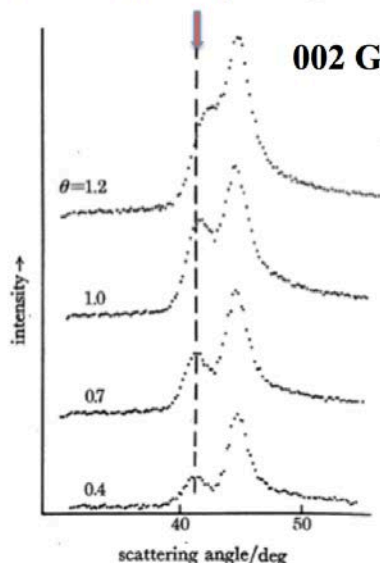
The structural signature for deuterio-methane adsorbed on graphite (to ensure that coherent scattering from the molecule contributed to the diffraction pattern) is shown below. The strong peak at scattering angle of about 44 degrees in 2 theta gives the 002 reflection of the graphite substrate. At increasing coverages, provided by increasing the dose of deuterated methane, the growth of a

second peak at 2 theta of about 41 degrees shows the formation of a registered layer of deuterated methane molecules on the graphite.

### Diffraction Pattern CD<sub>4</sub> on Vulcan Graphite $\lambda=2.4\text{\AA}$

$\sqrt{3} \times \sqrt{3}$   
commensurate peak @ 20K

BET Type II  
Adsorption Isotherm

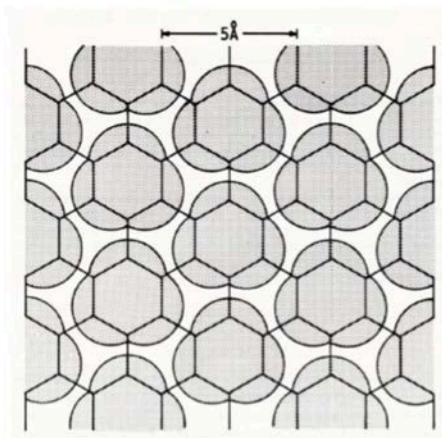


$\theta$  denotes the coverage  
in monolayers

Commensurate peak grows  
and does not shift with  
increased adsorption  $< \theta = 1.0$   
ie low Intermoleclar interactions

Growth of the  $\sqrt{3} \times \sqrt{3}$  commensurate layer of CD<sub>4</sub> on Graphite with increased dose

### Structure of CD<sub>4</sub> on Oriented Graphite



$\sqrt{3} \times \sqrt{3}$  Registered 2D layer

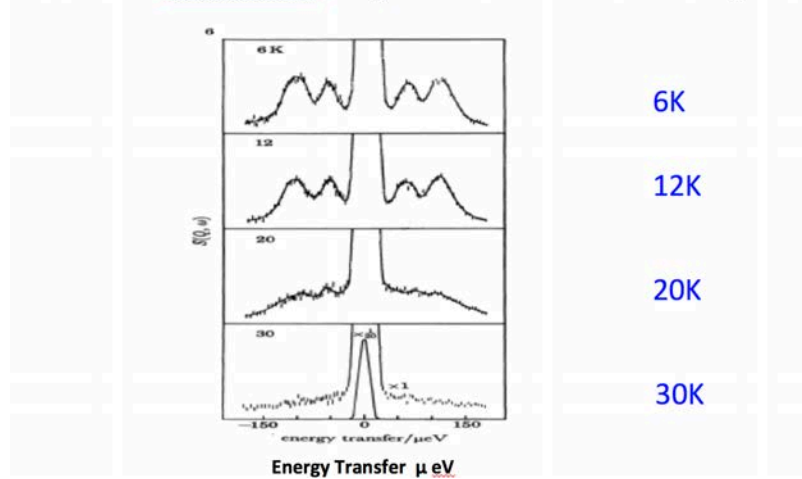
Commensurate Adsorption of CD<sub>4</sub> on hexagonal graphite

The ease of performing this measurement was greatly facilitated by the availability of the D1B multidetector powder diffractometer at the Institut Laue Langevin in Grenoble subsequent to Britain joining that Institute in 1973. Similarly the discovery of rotational tunneling for adsorbed CH<sub>4</sub> on powdered graphite and its temperature dependence shown below, was possible because of the IN5



instrument at ILL. Two broad tunneling transitions on each side of the elastic peak can be seen at 6K, fading away to a broad distribution arising from rotational tunneling by 30K - note the freezing point of methane is 91K.

### Rotational Tunnelling CH<sub>4</sub> on Vulcan Powdered Graphite

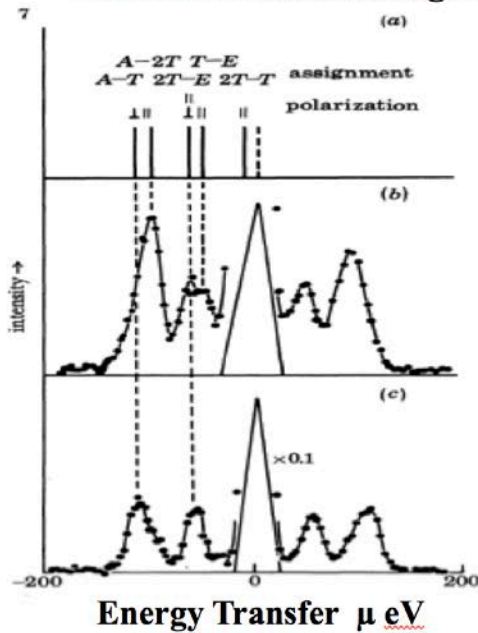


**First Observation of Rotational Tunnelling by an Adsorbed molecule**

By using oriented graphite, the orientation of the graphite C axis and the momentum transfer could be changed and at the same time the spectrum resolution improved. These data for the momentum transfer Q parallel and perpendicular to the surface are shown below.

## CH<sub>4</sub> on Oriented Graphite (IN5)

### Rotational Tunnelling Spectrum @ $\theta=0.7$ , 4K



**Assignment of Transitions**

**Q parallel to Surface**

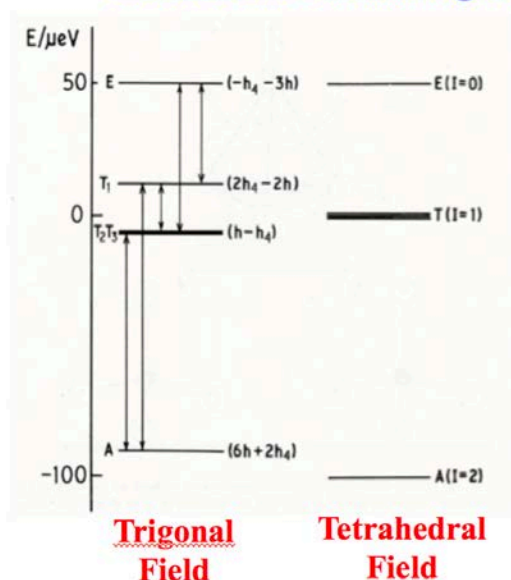
**Q perpendicular to Surface**

**Polarisation**

**Polarisation of the Tunnelling Spectrum of CH<sub>4</sub> on oriented Graphite**

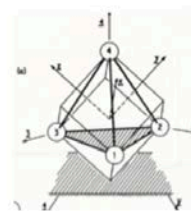
# CH<sub>4</sub> ON GRAPHITE

## Rotational Tunnelling States



Alfred Huller

**I = Total  
Nuclear Spin  
Angular Momentum**



### Splitting of the methane rotational pocket state levels and their nuclear spin angular momenta

Professor Alfred Huller contributed greatly to the understanding of these spectra and their assignment. The slide above shows his calculations of the rotational energy levels of the methane molecule in a tetrahedral field and in the trigonal field (appropriate to adsorption on the surface of graphite). For the calculation it is assumed that the molecule is held in a field of methane molecules (tetrahedral field – methane solid) or at the surface (trigonal field). The rotations of the molecules are hindered by these potentials but because of the low molecular motions of inertia about its molecular axes, tunneling between the “pocket states” of the librations occurs. A key differentiator between the tetrahedral and trigonal fields is the splitting of the T state (spin angular momentum = 1) by the trigonal field. This small splitting of 1.4  $\mu\text{eV}$  was observable on the same sample using the ILL back scattering instrument IN10 and allowed several models for the combined intermolecular and surface potentials responsible for the adsorption to be tested – slide 31. These types of measurement have since been greatly extended by John Larese and others to test adsorption potentials for metal oxide surfaces relevant to catalysis and thus provide a way to detailed and chemically useful information.

### CHEMICAL REACTIONS

The subject of chemistry is concerned with chemical reactions as well as structures and so we turn to examples in which neutron scattering can provide detailed information on reaction chemistry. Finding the mechanism of formation of zeolite catalysts and the production of highly crystalline catalyst films – chemistry in solution and at interfaces. The first example was to find out how molecular templates direct the formation of the zeolite ZSM-5, a material which can catalytically convert methanol to the aromatic molecule paraxylene. This work was undertaken subsequent to 1985 when I was an Argonne Fellow at the Argonne National laboratory in Chicago over a five year period. That opportunity allowed me (at the invitation of the Director, Walter Schriesheim) to make

contact with any division at the Argonne Laboratory and talk about their work with them. This was a happy process which resulted in several collaborations, the one here with Lennox Iton (Materials Physics and Chemistry Divisions) and others at the Intense Pulsed Neutron Source, including my very able former pupil Frans Trouw and colleague Stephen Henderson.

## Template Directed Synthesis - Zeolite ZSM-5

SMALL-ANGLE NEUTRON SCATTERING STUDIES OF THE TEMPLATE-MEDIATED  
CRYSTALLIZATION OF ZSM-5 TYPE ZEOLITE†

L. E. Iton<sup>1\*</sup>, F. Trouw<sup>2</sup>, T. O. Brun<sup>1</sup>, and J. E. Epperson<sup>1</sup>

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J. W. White<sup>3\*</sup> and S. J. Henderson

Research School of Chemistry  
The Australian National University, Canberra, Australia

Received by  
APR 09 1990



Lennox Iton

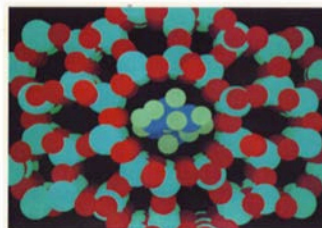
IPNS Argonne National Laboratory  
Chicago



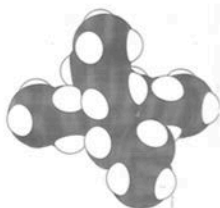
Frans Trouw

### Argonne National Laboratory 1986- 1990 Collaboration

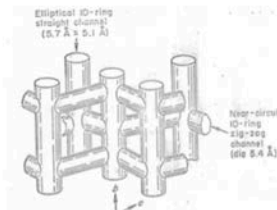
It was Lennox Iton who drew my attention to a challenge in a recent review that “zeolite crystallization is one of today’s most complex chemical problems. More than 100 different types of zeolites have been synthesized under very different conditions. This synthesis of new structures is strongly influenced by many aspects of the basic gel chemistry such as gel composition, pH, temperature, digestion time, starting materials etc and also by the cations used in the synthesis (BM Lock, TR Cannon and CA Messina 1985). This was an exciting challenge with wide scope and one where neutrons could be useful.



Para-xylene in the straight channels



Tetrapropyl ammonium cation



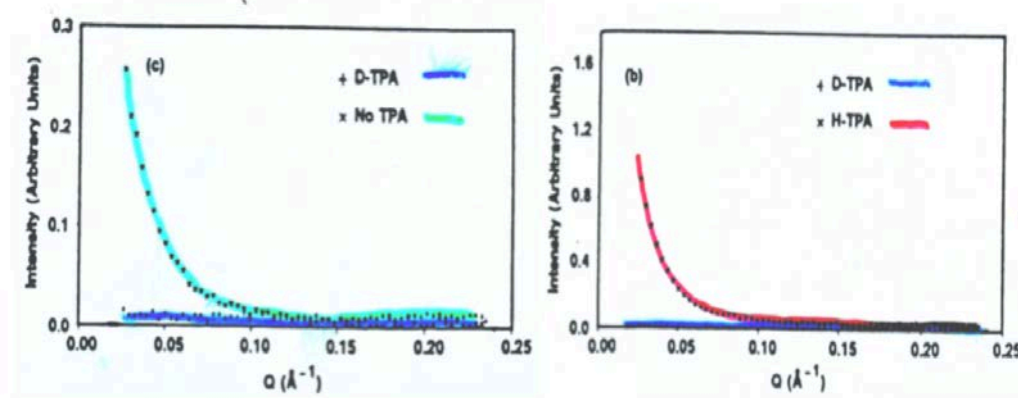
Tetrahedrally directed channel structure

**Snug fit of p-Xylene in ZSM-5, tetrahedral template molecule & the ZSM-5 channel structure**

The structure of this zeolite, ZSM-5 containing the paraxylene molecule is shown above. The "snugness" of the molecule in the crystal is the key to the discrimination of this catalyst against other substituted benzenes. Its high porosity, (above) helps its efficiency as a catalyst. The tetrapropyl ammonium ion template molecular shape and the structure it produces in hydrothermal synthesis are also illustrated.

We supposed that the directing effect of the template to assemble the silicate species in solution would result from the structuring of the gel upon addition of the tetrapropyl ammonium ion. We did not suppose that this would happen at room temperature but that we would eventually see incorporation of the ion into the gel in the hydrothermal synthesis at high temperature (the final porous zeolite catalyst has to be prepared by burning out the hydrocarbon template with oxidation at elevated temperatures.)

## Room Temperature SiO<sub>2</sub> Gel structured by Template



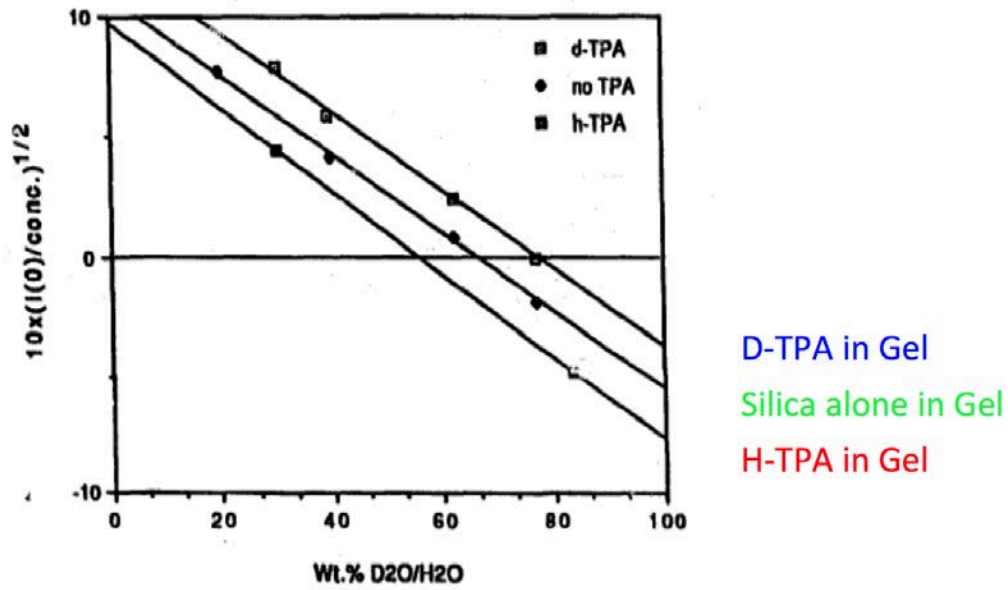
Momentum Transfer ,  $Q/\text{\AA}^{-1}$

**D-TPA Gel is contrast matched in 77% D<sub>2</sub>O + 23% H<sub>2</sub>O**  
**Silica and H-TPA Gel are not matched in 77% D<sub>2</sub>O + 23% H<sub>2</sub>O**

It was thus a surprise to find that even at room temperature, the gel was structured by the template. This is demonstrated above by the small angle scattering from the gel with no deuterated tetrapropyl ammonium salt added is strong in 77% D<sub>2</sub>O: 23% H<sub>2</sub>O but very weak if the deuterated template had been added to the room temperature solution. Neutron scattering length contrast matching of this silica+ deuterated template occurred in the mixture of 77% D<sub>2</sub>O: 23% H<sub>2</sub>O. When hydrogenous tetrapropyl ammonium ions were used, the scattering was strong in 77% D<sub>2</sub>O: 23% H<sub>2</sub>O, illustrating that the hydrogenous template/SiO<sub>2</sub> complex had a difference scattering length density to that when the deuterium template was used.

Contrast variation plots for the soluble silicate gels (square root of the intensity of scattering at zero Q as a function of the weight percent heavy water in the mixture) show this effect clearly (below).

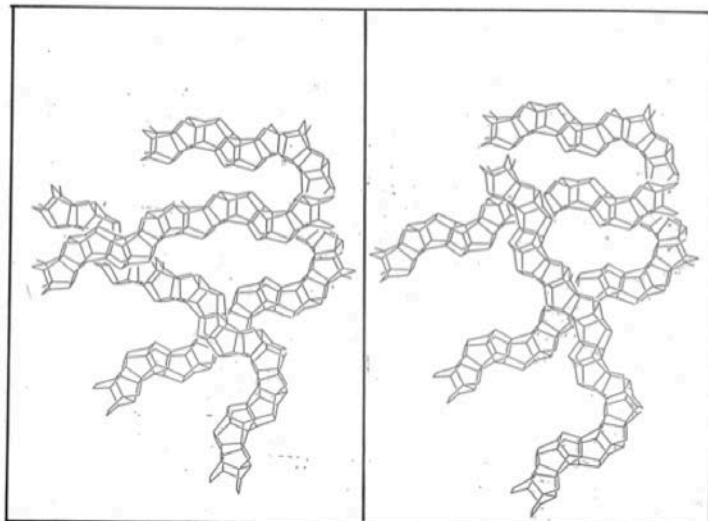




**(Neutron Scattering length)<sup>1/2</sup> vs Weight % D<sub>2</sub>O Contrast Variation plots for ZSM-5 gels.**

The contrast matching point for the silica alone is at 66% heavy water, that for the deuterated template is at 77% and for the hydrogenous template at 56%. These results show that the silica gel is organized by the template at room temperatures to structures which have the stoichiometry of the formed catalyst silicate template ratio. In parallel with experiments using a nanoparticle silicate source for the synthesis, no such structuration occurred although for both synthesis heating under hydrothermal conditions produced the same final catalyst material.

### ***Embryo – Crystals – Quickly Formed***



**Schematic of the Template hydrophobic + charge effect on soluble silicate gel structure**

We invented the idea of “embryo crystals” (above) which are quickly formed on adding the template to the gel and whose structure densifies during hydrothermal process. A number of papers were subsequently published on this system.

## IPNS Argonne

Watson, J. N., Brown, A. S., Iton, L. E., White, J. W. – Detection of TPA–silicalite precursors nucleated during the room temperature aging of a clear homogeneous synthesis solution. *J. Chem. Soc., Faraday Transactions*, 94(15): pp. 2181–2186 (1998).

Watson, J. N., Iton, L. E., Keir, R. I., Thomas, J. C., Dowling, T. L., White, J. W. – TPA–Silicalite Crystallization from Homogeneous Solution: Kinetics and Mechanism of Nucleation and Growth. *Journal of Physical Chemistry B*, 101(48): pp. 10094–10104 (1997).

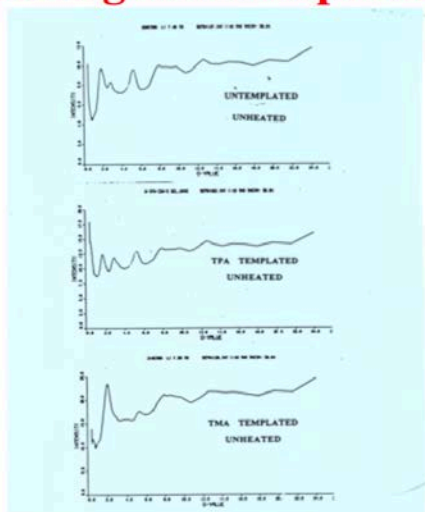
Dougherty, J., Iton, L. E. and White, J. W. – Room Temperature Aging of a ZSM–5 Preparation Detected by Small Angle X–ray and Neutron Scattering and NMR Spectroscopy. *Zeolites*, 15: pp. 640–649, (1995).

201. Edler, K. J., Dougherty, J., Durand, R., Iton, L., Kirton, G., Lockhart, G., Wang, Z., Withers, R. and White, J. W. – Small Angle X–ray Scattering from MCM41 and its Synthesis Gels – Optimisation of the Synthesis Parameters. *Colloids and Surfaces*, 102: pp. 213–230 (1995).

Brun, T. O., Epperson, J. E., Henderson, S. J., Iton, L. E., Trouw, F. and White, J. W. – Small–Angle Neutron Scattering Studies of the Template–Mediated Crystallization of ZSM–5 Type Zeolite. *Langmuir*, 8: pp. 1045–1048, (1992).

### EXPERIMENTS TO FOLLOW UP

## High Q Scattering and Template modification



**Untemplated –  
Unheated**

**TPA TEMPLATED  
unheated**

**TMA TEMPLATED  
Unheated**

2 10 16 22 28

**Momentum Transfer, Q/Å<sup>-1</sup>**

### Neutron Scattering Distribution functions from 300K soluble silicate gels

The induction of structure at room temperature may be an interesting matter to follow up. The very high Q scattering possibilities of the IPNS diffractometers allowed us to do some tests of diffraction out to about 30 Å<sup>-1</sup>. The results (below) are for room temperature gel mixtures with templates which

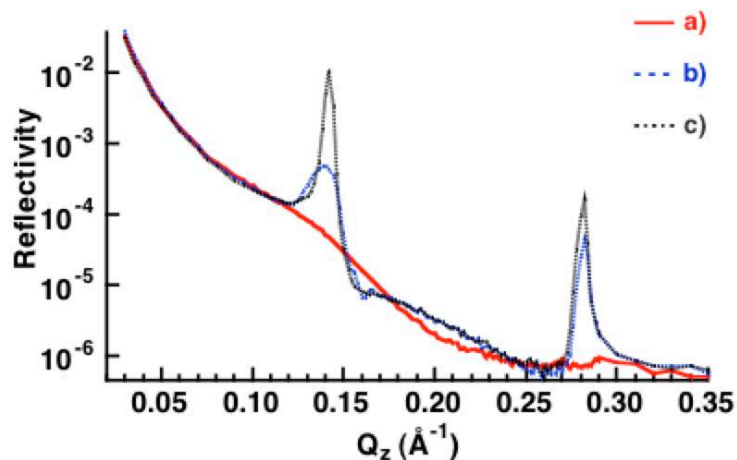
produce different zeolites from soluble silicate gels. The top image shows the diffraction from the untemplated unheated gel with strong peaks near  $2, 6\text{\AA}^{-1}$  and the lower two are the diffraction patterns for a tetrapropyl ammonium unheated gel and a tetramethyl ammonium unheated gel. Obvious differences in these distribution functions suggest that, with modern instrumentation such as SANDALS at the Rutherford Laboratory ISIS source, and the diffractometers at J-PARC which can reach  $50\text{\AA}^{-1}$ , there is much to be discovered of chemical interest in these processes.

## CATALYTIC THIN FILMS

Chemical reactions, that produce microporous and mesoporous crystalline films at the air-water interface can be followed effectively by neutron and x-ray reflectivity and the neutron contrasts are of particular value for establishing the sequence of reactions as the film grow.

For silicate and titanium dioxide films, the experimental method was simply to mix the reagents such as a hydrolysable silicon or titanium ethoxide or butoxide with the surfactant template and a little dilute hydrochloric acid to initiate hydrolysis. The aggregation of the silicate or titanate oligomers so formed in solution can be controlled by the size of the anion associated with a positively charged surfactant or by the surfactant choice. This synthetic process for soluble silica and the tetramethyl ammonium ion (as template) is illustrated below.

## X-ray reflectivity at the air - water interface, shows an “induction period”



Stephen Holt

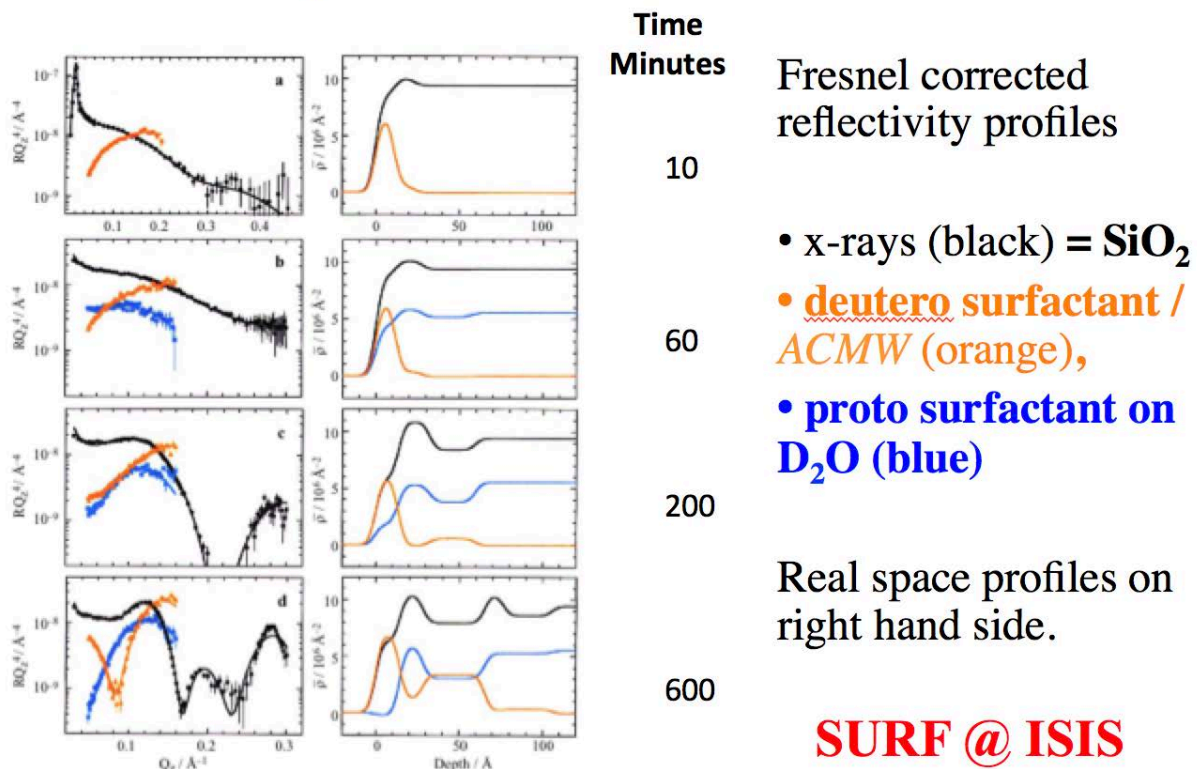
Tony Brown  
Philip Reynolds  
Jeremy Ruggles  
Jeff Penfold

**a) 530 minutes, b) 608 minutes, and c) 687 minutes.**

X-ray reflectivity from a growing template silicate film at the air-water interface

Three stages of the ‘induction period’ before a crystalline film is seen are shown in the x-ray reflectivity at the air-water interface as a function of time. Initially (red curve) only a broad reflectivity at about  $0.13\text{\AA}^{-1}$  appeared after about 530 minutes of reaction at room temperature. This long induction time is characteristic of reactions at the interface and related to the kinetics of assembly of the templated species which within another 100 or 200 minutes produces the sharp peak structure characteristic of hexagonal close packing of rod-like micelles at the interface. Combining neutron and x-ray reflectivity allows the chemical composition of the growing film to be measured in a parallel experiment- as the solution chemistry is highly reproducible.

## Induction Phase Growth of Multilayer Film of $\text{SiO}_2$ at the air-water interface



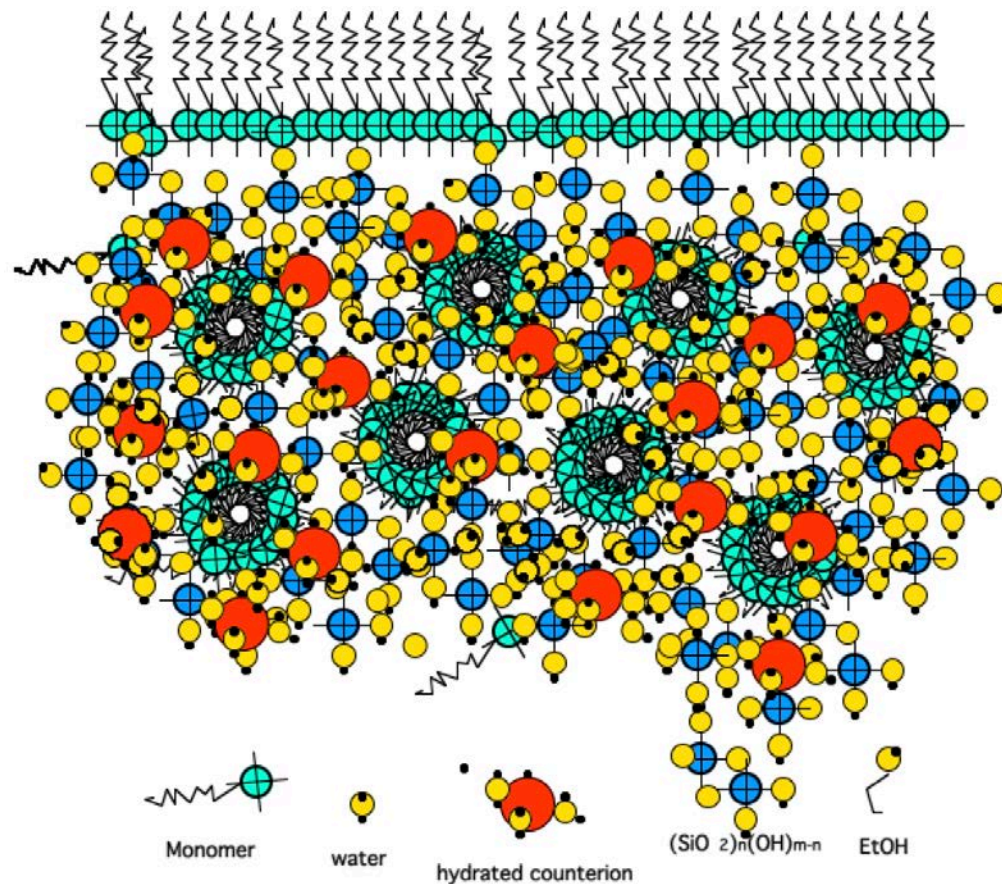
**Neutron Contrast Variation shows the changing components in growing templated silicate film with time.**

The left hand side of the above slide shows the reflectivity profiles (where the reflectivity has been divided by  $Q^4$ ), and two neutron contrasts (proto surfactant on  $D_2O$  (blue) and deuterio surfactant on air-contrast-matched-water (ACMW) (red) for times between 10 minutes after mixing and 600 minutes after mixing. The data from these reflectivity measurements (neutron and x-ray) can be co-refined as well as the profiles for the individual contrasts. These are shown on the right hand side of the figure. At short times, the deuterio-surfactant on air-contrast-matched-water (orange curve) shows the well established scattering and density distribution of surfactant adsorbed at the interface;



the x-ray profile (black) shows this also but, in addition, a small peak at about 25Å deeper into the solution showing that silica oligomers have already adsorbed to the surfactant.

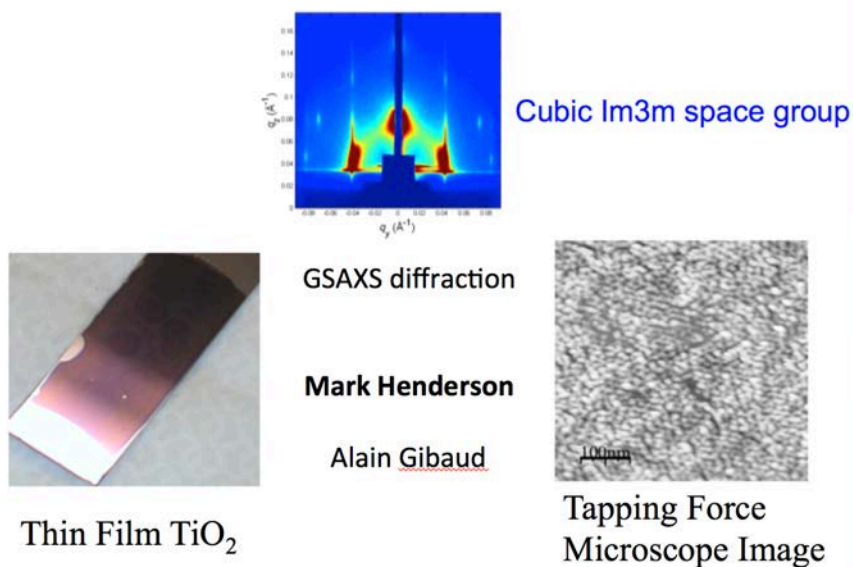
The same features are present in the 60 minute data with the proto-surfactant on heavy water experiment (blue) showing a small dip in the density profile between about 30 and 55Å. This shows us the adsorption of a second layer of surfactant beneath the monolayer structure already established at the air-water interface. This phenomenon is more pronounced at 200 minutes where the corresponding layer of deuterium surfactant is visible against air-contrast-matched water. Finally at 600 minutes, three or four silicate layers are already established and the alternating layers of surfactant (double thickness compared to the surface monolayer) are seen. The figure below shows the way in which the surfactant and silica are arranged in this growing templated film.



**Structure of a templated silicate film growing at the air-water interface**

Templated films with mesoporous structure can be grown at interfaces and a good method is to dip a substrate – such as a clean glass slide repeatedly into a surfactant- silicate or titanate solution at the correct humidity to maintain the solution phase structure on the surface as the plate is withdrawn. The chemistry of the synthesis solution can be varied so as to control the porosity and allow doping in the resultant film eg N-doping to a mesoporous TiO<sub>2</sub> film for water splitting or water clean-up applications. Such films may have high crystallinity as well as mesoporosity as shown by the slide - made by dipping.

## Mesoporous TiO<sub>2</sub> Water Splitting Films



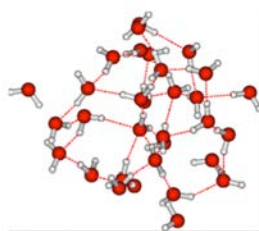
### Highly Crystalline Mesoporous N- doped TiO<sub>2</sub> film

The films are clear and the forced tapping microscope shows the mesoporous structure in them after the polymeric surfactant used to make them by dip-coating surfactant-containing titanate solution was done. X-ray reflectivity from that film shows the high degree of crystallinity in the cubic Im3m space group from grazing incidence small angle scattering perpendicular and parallel to the latter. The combination of x-ray and neutron scattering is always desirable to obtain additional contrasts to those available from isotopic substitution.

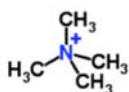
## LIQUID SOLUTIONS

To end this lecture, I want to illustrate the enormous potential of modern neutron scattering instruments for understanding liquid solutions of central interest to chemistry.

### Effect of Solute on Water Structure/Dynamics



Structure Making



N(CH<sub>3</sub>)<sub>4</sub>Cl in D<sub>2</sub>O

N(CD<sub>3</sub>)<sub>4</sub>Cl in H<sub>2</sub>O

Contrast between Ion and Solvent (Water) @ 260K

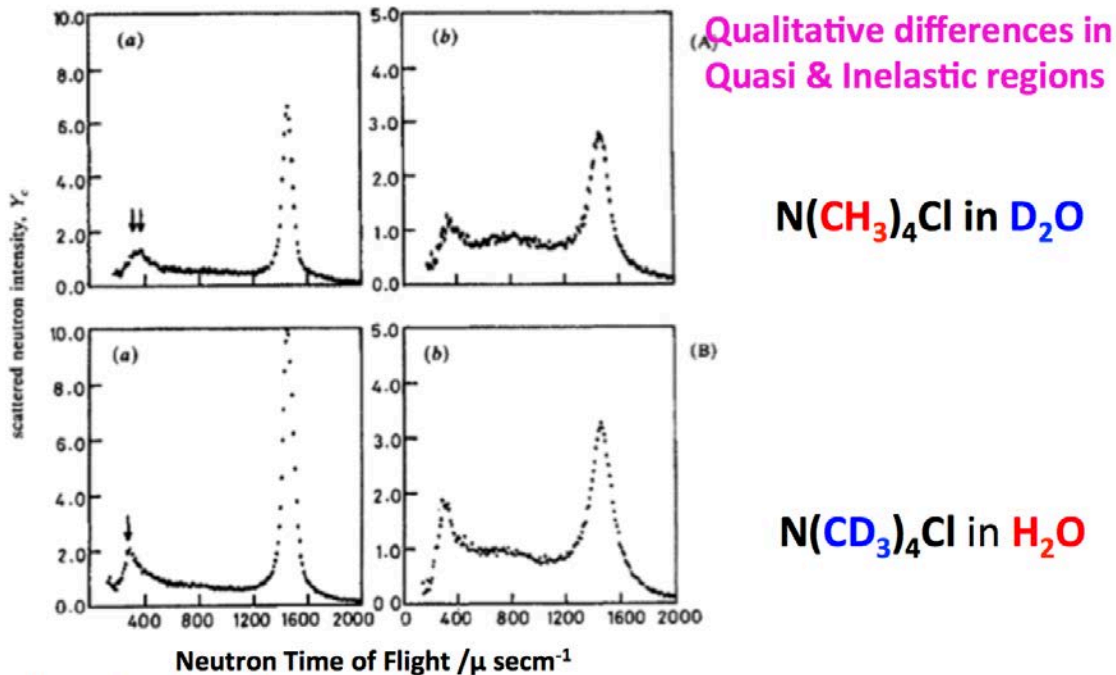
Structure of Liquid water at 25C (Wikipedia) & relative size of the tetramethyl ammonium ion.

The focus is still on finding out how liquids and solutes contained in them structure the water and move with respect to one another. The Slide above shows an image of the structure of water (from Wikipedia) with the tetramethyl ammonium cation. Dissolving that cation and its salts into water will obviously perturb the structure shown. Our experiments in the 1970s using quasi-elastic neutron scattering showed the strong effect of dissolved salts on the water self diffusion coefficient. For example, small cations such as lithium have the effect of decreasing the water diffusion coefficient and are said to be *structure-making* for that reason. By comparison, dissolving potassium iodide causes the diffusion coefficient as measured by quasi elastic scattering to increase. Such ion pairs are said to be *structure-breaking*. Understanding such effects of the solutes on water and other solvents is at the heart of chemistry and biology.

Looking a the slide again, it could be supposed that such a big ion as the tetramethyl ammonium ion would break the water structure – as iodide does. Our experiments in the early 1970s and the late 1980s used contrast variation for both the tetramethylammonium ion and the water to investigate the reciprocal effects of this ion on the water and the water on the motions of the ion. This is a sort of paradigm of what might happen (see later) in protein sensitivity to deuterium.

## Ion and Solvent **Contrasted** in Water (260K)

(a)  $2\theta=45$  and (b) 90 deg.



Brown, Newbery, Thomas and White *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**(1), 17-33

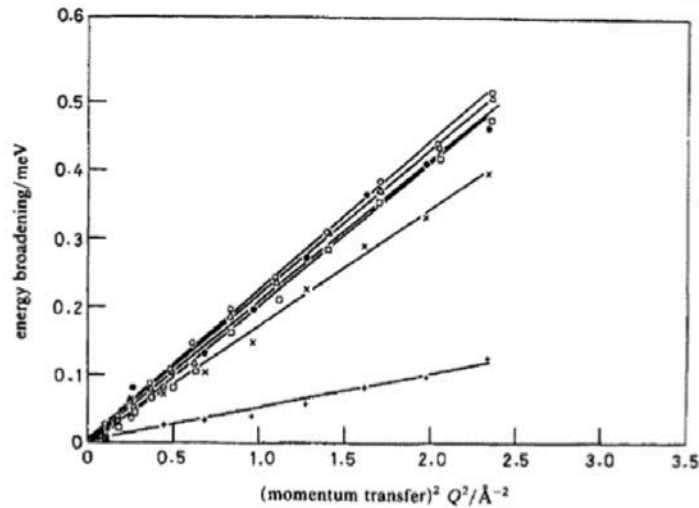
The neutron time of flight spectra for tetramethyl ammonium ions in water with contrast variation

The Slide above shows the effect of looking at either the ion (upper curves) or the water in contrast to the ion (lower curves) on the neutron time of flight spectra at two angles of scattering, 45 degrees

and 90 degrees. The obvious differences here are just as great as those seen for the differently deuterated methanol molecules in the 1960s or the effects of the water layer thickness in clays described above. With the instrumentation available in the 1970s, a quasi elastic analysis could be made for the effect on water by varying the fully deuterated tetra methyl ammonium chloride concentration. This is shown in the slide below.

## H<sub>2</sub>O Quasielastic Broadening (CD<sub>3</sub>)<sub>4</sub>Cl in H<sub>2</sub>O

(CD<sub>3</sub>)<sub>4</sub>Cl  
concentration  
Mole ion / Mole water



1:103  
1:48.5  
1:33.9  
1:28  
1:16

1:4.7

*J. Chem. Soc., Faraday Trans. 2, 1988, 84(1), 17-33*

### Effect of various concentrations of the tetramethyl ammonium ion of water diffusion

In the upper curve, the ratio of the ion to the water is 1/103 molar – water is in great excess and the quasi elastic broadening corresponds to only a slight decrease in the water self diffusion coefficient. Even this big ion is “*structure making*” as shown by the 1/4.7 concentrated salt solution in the lower curve.

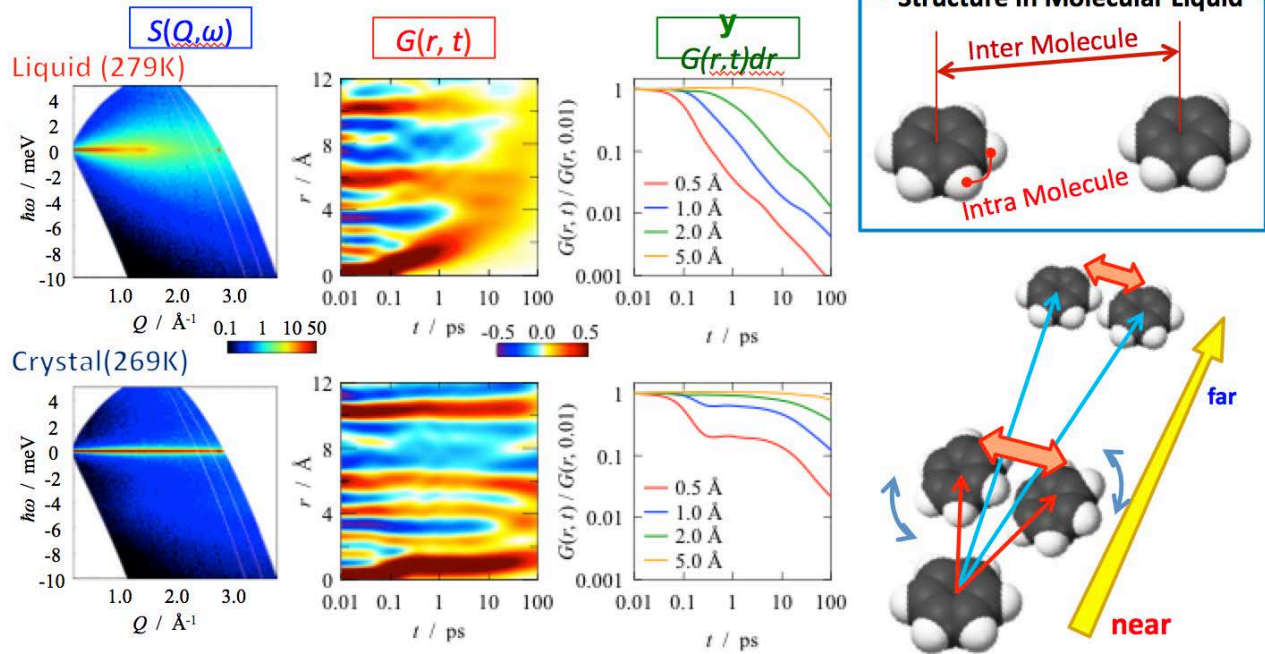
What is the effect on the ion? The D<sub>2</sub>O solutions show this. Comparisons were made with NMR and tracer diffusion measurements of the ion centre of mass diffusion agree with reasonably. More interesting though, is the effect of the tightened water structure on the rotational diffusion of this large ion – again this can be measured and is reported – illustrating the reciprocal effect of water and solvent.

I’ve chosen this example to illustrate a whole range of experiments for the future. It may be possible through experimental developments first at the ISIS spallation neutron source by Andrew Taylor and Masa Arai who built the MARI spectrometer. Andrew and Masa realized the potential of collecting as much of the (Q,ω) space as possible and MARI showed the potential of this for the crystal and spin dynamics of solids. The idea has come to full flowering – again through Masa Arai and his colleagues at J-PARC in the recent study of liquid benzene by Kikuchi et al (slide 58). With this J-PARC instrument, the chemically fascinating phenomena of separability of inter-molecular



and intra-molecular motions on the timescale of pico seconds has been realized. The data for the solid benzene (lower curves) in the real space of distance and time compare vividly with the liquid  $G(r,t)$  above.

## A Challenge in $G(r,t)$ -Analysis on $(C_6H_6)$



- $G(r,t)$  gives some detailed information in a Inhomogeneous System  
Structure and its time development
- $S(Q,\omega)$  is useful for a periodic system

Kikuchi et al.

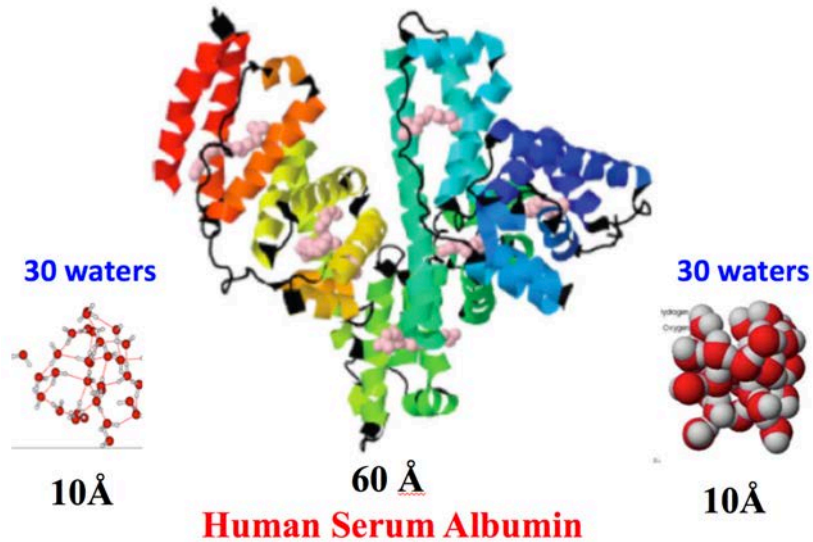
**The great challenge for neutron scattering from liquids has been taken up – with stunning results.**

One can only imagine the possibility of now separating and looking at the itinerant oscillator behavior of a solute surrounding by its caged liquid as postulated in the long held chemical belief for solution kinetics. The selective deuteration of the solvent and the solute could produce contrast-separated  $G(r,t)$  for the two species. The chemical importance of such measurements would be of great value conceptually.

I wish to end with my most recent experiments, again involving the notion of the effects of a solvent on a solute structure and dynamics. Here the solute is the prevalent blood protein human serum albumin shown in slide 60 alongside two models of clusters of about 10 water molecules. The structure of this molecule has been closely studied by x-ray diffraction to a resolution of about 2Å by Curry et al. One of the roles of HSA is to carry fatty acid molecules around the body but it is

a general transport protein because its large number of alpha helices all have both hydrophobic and hydrophilic components.

### Effect of Solvent on Molecule



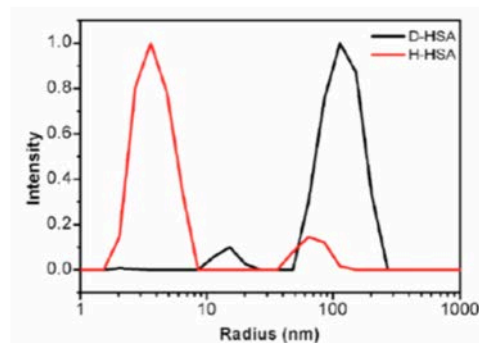
What effects would a change from H<sub>2</sub>O to D<sub>2</sub>O have on such a molecule?

In attempting to complete a study of the interaction of HSA with small silica nanoparticles, we became sensitive to a problem with the molecule itself when it had been fully deuterated in heavy water as the defatted form.

### HUMAN SERUM AGGREGATION

Sunday 26 May 2013

Light scattering at 25C in heavy water SPB from a 1mg/ml solution of "native" fatted human serum albumin and a 1mg/ml heavy water solution of overexpressed fully deuterated, defatted human serum albumin.



Radius 100nm would contain ca.  $100^3/4^3 = 150,000$  Monomers

#### Dynamic Light Scattering from native and recombinant – deuterated, defatted HSA.

The side above shows the dynamic light scattering measured from a solution fo the native protein (available commercially from Sigma (red) and the sample of recombinant protein produced by expression of the gene in heavy water by recombinant methods. While the native protein had a

radius of gyration of about 4nm, the recombinant material was highly aggregated to particles of about 100nm radius. Our current study is to discover the origin of this which may be due to the factors shown below.

## HUMAN SERUM AGGREGATION

### Proposal to ILL Science Council 8- 2013

**The proposal was to study the origin of the aggregation and discover any matters of general significance.**

Aggregation could be due to one or a combination of causes:

- the “native” forms (fatted and defatted) are stable\*
- that the recombinant molecule was defatted
- that the recombinant molecule was fully deuterated
- Heavy water – light water and pH effects.

\*J.W.White, D.Hess, J. Raynes, V.Laux, M. Haertlein, T. Forsyth, A. Jeyasingham.  
European Biophysics J. (2015) 44, 367-371

#### Possible causes of deuterated HSA aggregation

In a collaboration with the deuteration laboratory at the Institut Laue Langevin, Grenoble, eight different samples of recombinant material have been produced by expression of the gene to produce hydrogenous and deuterated protein, in fatted and defatted form, and dissolved in H<sub>2</sub>O buffer or D<sub>2</sub>O buffer. We have no significant differences in the aggregation behavior of these systems.

A clue to the phenomena is in the recent work of Egington and Becket (Biochemistry 2013, 6595-6600) who have found large solvent isotope effects on protein association thermodynamics (slide 65). Their study of the free energy of formation of the homodimer for the biotin repressor protein indicates a very modest isotope effect from the solvent of about 7 kcal per mole in the free energy. This, however, is the difference between very large” opposing enthalpic and entropic forces of  $41 \pm 3$  and  $-48 \pm 3$  kcal per mole respectively. For me this illustrates the very subtle balance upon which nature works and therefore the potentially high effects of subtle changes produced by molecular deuteration of proteins or a change in solvent, pH, degree of deuteration and salt content. I have no doubt that neutron scattering combined with light scattering, circular dichroism and careful calorimetry will allow the systematics of these phenomena to be uncovered.

#### Conclusion

This lecture has been mostly about work between 1963 and 1990 - though some things that I highly prize could not be included. I thank the many students, collaborators and post doctoral colleagues whose excellence and friendship I have appreciated for many years. I also thank colleagues in all of the neutron facilities where our work has been done. Without their contribution to the science and to instrument development neutron scattering would not be where it is today – a key method for unique understanding of Chemistry, Physics, Biology and the science of Materials.

