

**28 January 2009**

## **The Early NMRDG: a personal Memoir**

The inaugural meeting of the Nuclear Magnetic Resonance Group (NMRDG) was held on 22 May 1964 at the Northern Polytechnic, now The London Metropolitan University. The meeting was called by Eric F. Mooney, a lecturer in Chemistry there. He served as Hon. Secretary until 1972.

There had been a preliminary meeting in late 1963 at which about 25 people attended at which it was decided to form the NMRDG. Ernie G. Cummins of Perkin Elmer had I believe suggested the formation of the Group after his involvement with the Infrared Discussion Group, which had been founded as early as 1950. He served firstly as Treasurer of the NMRDG, and then in 1972 as Secretary /Treasurer. The Chairman for the first formal meeting was David H. Whiffen from the National Physical Laboratory (NPL). The meeting attracted about 150 participants, including myself and two members of my research group (who later became Chairmen): Duncan Gillies (Royal Holloway College, University of London) and Derek Shaw (Varian Associates), who also served as Secretary from 1973. The meeting elected Norman Sheppard (East Anglia) as the first Group Chairman. He gave the very first talk 'Coupling constants and stereochemistry of hydrocarbon groupings'.

The afternoon programme consisted of a 'Brains Trust Session' and the panel consisted of Norman Sheppard, Sid A. Knight (British Petroleum Co., Ltd), and Keith McLauchlan (NPL).

A second meeting was arranged that year on 14th September at the NPL, where there was a flourishing NMR Group, including John Pople, Ray Freeman, Keith McLauchlan and Ray Abraham. The attendance was about 100 people. Even a third meeting at the end of that year was held. The venue was The School of Pharmacy, University of London, and the date was 17<sup>th</sup> December. Christmas meetings have been held ever since, usually in London.

The success of the NMRDG in the first year continued and it flourishes still.

### **Earlier UK NMR Meetings.**

There had of course been NMR meetings in the UK before 1964. There was a flourishing British Radiofrequency Spectroscopy Group (BRSG) which had been founded as early as 1956 (September). The members were mainly physicists with a few physical chemists, such as Rex E. Richards (Physical Chemistry Laboratory, Oxford

University). I attended some of its meetings having been introduced to it by Jack Powles (a founder member) and his group in Physics at Queen Mary College, which, when I arrived from Harvard in 1961, included John Strange and Peter Mansfield. There were few chemists in the group. Chairmen have included D. J. E. Ingram (1961 – 1967), Jack Powles (1967 – 70), David Whiffen (1976 –79). Ingram was also secretary (1957 –59) as was Powles (1959 – 62), and Ken Packer (1976 – 79).

There were also meetings of a chemical bent, including a meeting in Oxford in 1956 on 25<sup>th</sup> May, entitled Nuclear and Paramagnetic Resonance, which covered both Electron Spin Resonance (ESR) and NMR. This may have been the first joint NMR and ESR meeting in the UK. The meeting was arranged by the Physical Methods Group of the Society for Analytical Chemistry (chairman, J. E. Page of Boots and later Glaxo) and the Photoelectric Spectrometry Group. Rex Richards spoke on analytical uses of NMR, and ESR was covered by D. J. E. Ingram (University of Southampton), each of whom had built their own instruments, with E. E. Schneider (Physics, University of Newcastle) giving a talk entitled 'Techniques of magnetic resonance spectroscopy'.

### **The second and subsequent years**

In 1965, there were again three NMRDG meetings: the 4<sup>th</sup> at Nottingham, the 5<sup>th</sup> at Sussex, and the 6<sup>th</sup> at Queen Mary College, London University (QMC). As host at QMC I gave the first talk 'Current

NMR work at QMC'. This included Duncan Gillies'  $^1\text{H}$  ( $^{15}\text{N}$ ) 'double resonance tickling', low power DR, to map the whole  $^{15}\text{N}$  spectrum. Thereafter the number of meetings per year varied, but three was the norm: three in 1966, two in 1967, three again in 1968, two and an International Meeting in 1969, and only one in 1970, a meeting at Christmas having been cancelled.

### **Industrial participation.**

Industrial membership has always been high. In 1966 for example it was more than one third and slightly less than a half of the total, amounting to about 44%. There is always at least one committee member from industry, and industrial venues are sometimes used. Talks from industrial members began with a paper from Sid. A. Knight (BP Ltd) on 'High Field NMR' given at the first meeting. Many industrial scientists attended the inaugural meeting and all subsequent meetings, such as J. E. Page (Glaxo Ltd). Fortunately Dr. Page kept an archive of NMRDG material, which he gave me in 1978 after a conversation we had at the NMRDG International Meeting in York. At the third

meeting H. A. Willis (ICI, Plastics Ltd) talked on 'The problem of NMR documentation', and Perkin Elmer's L. K. Parker talked about 'The search for an optimum field strength' at the fourth meeting.

### **International visitors.**

International visitors soon appeared. The first was Jim N. Shoolery from Varian Inc, California, who gave the opening talk at the 2nd meeting on 'Recent Developments in High Resolution NMR'. Len Reeves (Univ of British Columbia) spoke at the 4<sup>th</sup> meeting about 'The exact correlation of spin – spin coupling constants with atomic number'. Professor K. H. Hauser spoke at the 5<sup>th</sup> meeting.

### **Early officers and membership.**

At the inaugural meeting there were elections at a business session after lunch and Norman Sheppard was elected chairman, with Eric Mooney as Hon. Secretary and Ernie Cummins as Hon. Treasurer. The membership list of July 1966 gives Rex E. Richards as chairman, and David H. Whiffen as vice chairman. Eric Mooney had by this time moved to the University of Birmingham, and he and Ernie Cummins continued in office. The 1966 mailing list shows 236 members mostly chemists with only a few physicists. Clearly the founding of the group had been opportune.

The third chairman (1966 or 67 - 69) was John A. Elvidge (then at Battersea College of Science and Technology) who was the chairman in charge for the first International Meeting of the NMRDG in 1969 held in Birmingham.

### **International Meetings.**

The International meetings became very popular. They began on a three year cycle with the retiring chairman giving way to the incoming chair, but a two year cycle was initiated after 1981 in 1983. The list of meetings below includes the year held, the name of the retiring chairman responsible, and the venue:

**Birmingham**, 1969, J. A. Elvidge; **Surrey**, 1972, L. H. Sutcliffe; **St. Andrews**, 1975, E. W. Randall; **York**, 1978, J. Feeney; **Exeter**, R. K. Harris, 1981; **Edinburgh**, J. W. Feeney, 1983; **Cambridge**, D. Shaw, 1985; **Kent**, G. E. Hawkes, 1987; **Warwick**, D. G. Gillies, 1989; **St Andrews**, O. Howarth, 1991; **Swansea**, D. Davies, 1993; **UMIST**, J. Lindon, 1995; **Exeter**, K. J. Packer, 1997; **Edinburgh**, J. Nicholson, 1999; **Durham**, J. Everett, 2001; **Cambridge**, D. Neuhaus, 2003; **Stevenage**, Duncan Farrant (2003 – 2005); **Oxford**, Tim Claridge (2005 – 2007).

### **The Chemical Society.**

After much discussion in the NMRDG committee under Rex Richards' chairmanship, the NMRDG became a subject group of The Chemical Society. The main issue was a loss of autonomy but the logic of a large Society to underwrite international meetings held sway. Eric Mooney's letter to members in 1966 reported that an NMRDG party, consisting of Rex Richards, David Whiffen, and himself, met Mr. Ruck Keene, the General Secretary of the Chem. Soc., to discuss the issue. The change was confirmed at the 8<sup>th</sup> NMRDG meeting held in Liverpool (12/09/1966).

The NMRDG was invited to join either the Organic Division or the Inorganic Division neither of which was suitable because of the ubiquitous nature of NMR. An Interdisciplinary Division was set up to accommodate the NMRDG, and the ESR and Mossbauer Groups also joined. The Chemical

Society, the Royal Institute of Chemistry, the Faraday Society and the Society of Analytical Chemistry amalgamated in 1980 to form the Royal Society of Chemistry.

### **The formation of the European Experimental NMR Conference (EENC). 1974.**

The 21<sup>st</sup> UK NMRDG on 4<sup>th</sup> April 1973, was notable for being a joint meeting with the NMRDG of the Royal Dutch Chemical Society. It was held at the University of Essex in order to be near Harwich, the port most of the Dutch used. About 40 stalwart Dutch came and joined about 90 UK islanders. The topic was '<sup>13</sup>C NMR' and four talks were given by the guests, one of whom was from Belgium: A.D. Clague (Shell laboratories, Amsterdam) on 'The micro structure of polybutadienes'; '<sup>13</sup>C shifts and T<sub>1</sub> relaxation in allenes', M. J. A. de Bie (Utrecht University); '<sup>13</sup>C NMR of aromatic ketones - solvent effects', J. Runsink (Groningen University); and '<sup>13</sup>C studies of enamine derivatives', D. Tourwe (Free University of Brussels). Most of the work reported was with the newly available Pulse – Fourier Transform (FT) method.

The topic of the 23<sup>rd</sup> NMRDG meeting in 1974 was 'Experimental techniques in NMR'. The meeting duration was extended to three days, and many invitations were extended to other European groups. This was effectively the first meeting of The European Experimental NMR Conference (EENC), although I wanted to call it the zeroth!. It was started in imitation of the very prestigious annual American meeting, the Experimental NMR Conference (the ENC) which continues very successfully to this day. The emphasis was to be on experimental techniques rather than applications, although this approximate division was not subsequently always adhered to. The suggestion to have such a meeting was made to me by Jim Emsley, who later said the idea had been suggested to him by Kjeld Schaumburg (Copenhagen). There was not enough instrumental and technical development in the UK alone for such a series of meetings so a European base seemed sensible. The meeting was held at the University of Kent at Canterbury. Kent recommended itself for a number of reasons. There were two prestigious groups there: Jack Powles had gone to Kent from QMC as the first Professor of Physics, and Charlie Brown had a good group in the Chemistry Department. Another reason was that Canterbury was close to the channel ports!

I reviewed the meeting with an article in *Chemistry in Britain*, 1974, 10, 443. There were approximately 150 participants, one third of whom were from 'overseas', as were one half of the chairmen. The chairmen on the first day were M. J. A. de Bie in a session reviewing Technical Developments, and L. Lunazzi, with a session on orienting techniques (including the use of liquid crystal solvents, and of electric fields). There was an evening 'open forum' with presentations on Chemically Induced Nuclear Polarization (CIDNIP), T<sub>1</sub> measurements both by continuous wave methods and pulse methods involving homospoil sequences, and with automated sequences for the calculation of T<sub>1</sub> and the nuclear Overhauser effect. The Fourier equivalent of the transitory selective irradiation method of double resonance was discussed by Sture Forsen (University of Lund), and became known as 'selective population transfer'. On the second day Jack Powles took the chair for a session on high resolution nmr of solids. Peter Mansfield reviewed line-narrowing by sample rotation, and also by multiple pulse sequences. He presented an NMR image of a finger *in vivo*, the NMRDG's first magnetic resonance image (MRI). Ray Freeman was chairman for a session on Fourier transformation with Richard Ernst comparing continuous wave (c.w.) spectra with pulse Fourier (FT) methods for 'dynamic' systems such as in CIDNIP, and DR experiments. Other chairs were Rex Richards, Madame Martin, and F. W. van Duersen.. Other topics were: nuclei with low abundance and sensitivity; relaxation reagents; and relaxation measurements of quadrupole nucleides. Richard Ernst and Peter Mansfield latter became Nobel laureates.

The original idea was that the EENC would circulate around national NMRDGs. The Dutch NMRDG hosted the second meeting in 1976, and Keld Schaumburg hosted the third in Copenhagen, in 1977.. A committee was soon appointed, however, but there was no constitution and no elections, and the committee remained largely unchanged for more than 25 years! Also it became cheaper to attend the ENC rather than the EENC at least for UK spectroscopists. The agreement between the NMRDG with the EENC was for each to hold interleaved annual meetings, with the NMRDG's Intenational meetings being held in the UK, and the EENC elsewhere in Europe. My suggestion to celebrate the 25<sup>th</sup> meeting by holding it in the UK failed, mainly because of opposition from John Gibson of the RSC and the English committee member. I was glad to see the EENC rolled up in 2005, along with the NMRDG's International

meetings and the Ampere meetings, into a new organization, the European Magnetic Resonance group (EUROMAR).

## **NMR TOPICS**

Not all the NMRDG meetings had single themes. It was usual for a number of topics to be discussed. Many were applications in organic chemistry such as Alan R. Katritzky's talk 'Some applications of NMR to Organic Chemistry' given at the second meeting, and Ray Abraham's 'Introduction to proton chemical shifts' at the third meeting. The fourth meeting offered talks such as the determination of configuration of reduced cyclic compounds (Harold Booth, University of Nottingham) and NMR spectra and confirmation of unsaturated ketones (C. J. Timmons, Nottingham). Sometimes the host Institution would use one of the sessions to present work going on there. Occasionally though a meeting would have a theme. Some of the topics in the early meetings are presented below. A review of these topics over a ten year period shows the growth of the technique and its applications.

### ***Nucleides.***

Most commercial spectrometers in the early 1960s were for  $^1\text{H}$  solution work employing c.w. methods, but other nuclei soon appeared in NMRDG programmes.  $^{19}\text{F}$  was the topic of I. J. Lawrenson (National Chemical Lab.) in the 2nd meeting.  $^{13}\text{C}$  came as early as the 5<sup>th</sup> meeting: K. H. Hausser (Heidelberg) talked about the 'Enhancement of  $^{13}\text{C}$  resonance signals by the Overhauser technique'. I mentioned  $^{15}\text{N}$ , albeit in enriched samples, at the 6<sup>th</sup> meeting, as well as  $^{19}\text{F}$  in polyfluoroaromatics. Then in 1966 at the 7<sup>th</sup> meeting  $^{19}\text{F}$  was the subject of four talks from four different groups: Jim Feeney (Varian Associates Ltd); Les H. Sutcliffe and S. M. Walker (Liverpool); Jim W. Emsley (University of Durham); and L. F. Thomas and A. Peake (Birmingham). Then came 'Alkali metal and halogen resonances in strong electrolytes' (Chris Deverell, PCL, Oxford),  $^{71}\text{Ga}$  (J. W. Akitt and N. Greenwood, University of Newcastle), and  $^{11}\text{B}$  (Eric Mooney – the Hon Secretary's first talk to the group – who was then at Birmingham). Ken J. Packer (East Anglia) had already in the 4<sup>th</sup> meeting spoken on 'The shapes of multiplets in the NMR spectra of nuclei with spin  $I = \frac{1}{2}$ , due to coupling with nuclei with  $I > \frac{1}{2}$ '. From memory I think he covered the amusing  $^{19}\text{F}$  10-line multiplet in the  $(\text{NbF}_6)^-$  anion. Surprisingly  $^{31}\text{P}$  made a quite late appearance in 1967. Tritium was introduced by John Elvidge (then at Surrey) in 1971. as did the first  $^{15}\text{N}$  pulse Fourier Transform (FT) at natural abundance. Deuterium spectra at natural abundance, FT work with proton noise decoupling, appeared first in 1972.

### ***Multiple Resonance.***

By 1964 double resonance (DR) was a well established technique, although not commercially available, and John Baldeschwieler and I (Harvard University) had published the first review of its Chemical Applications in Chem. Rev. in 1963. The BBSRG had held a meeting on 23<sup>rd</sup> January 1963 at the NPL on Multiple resonance techniques. Speakers were: David W. Turner (Imperial College, London University) on heteronuclear DR; Ray Freeman on homonuclear work, Keith McLauchlan (NPL) on double quantum transitions; Rex Richards on nuclear electron DR; and J.M. Baker (PCL), on electron-nuclear DR (ENDO). Most of the papers at the 5<sup>th</sup> NMRDG meeting in Sussex in 1964 were about DR. David Turner even talked about *pulsed* double resonance. Robin K. Harris (East Anglia) introduced 'Some chemical applications of DR', and as we have seen Hausser talked about the Overhauser enhancement. This meeting was arranged to come directly after a meeting of the IRDG. I mentioned  $^1\text{H}\{^{15}\text{N}\}$  'tickling' work in my talk at the 6<sup>th</sup> meeting: 'Current NMR Research at Queen Mary College'. In this work Duncan Gillies mapped out the whole  $^{15}\text{N}$  of formamide- $^{15}\text{N}$ . This constituted NMR in two frequency dimensions albeit in the c.w. mode, as did Ray Freeman's homonuclear proton work about this time.

Triple resonance in the form of double tickling was first covered by my student Roger Price in the 15<sup>th</sup> meeting held in Bristol in 1969. It was homonuclear work involving the protons in 2,3-dibromopropionic acid, and in vinyl acetate. The next meeting also contained a paper 'Some applications of triple resonance experiments' given by Bill McFarlane (Sir John Cass College, London).

### ***Solid State NMR***

This topic was introduced as early as 1965 at the 4<sup>th</sup> meeting, which was held at the University of Nottingham, by the resident physicist, E. R. Andrew: 'NMR experiments with solids'. He had been a pioneer in using rapid spinning of the solid at the 'magic angle' (54 degrees and 28 minutes) to narrow the NMR line, when he was at the University of Bangor in 1959. The topic had to wait many years for it to become commercially available to chemists. Andrew was a founder member and first chairman (1957 – 61) of the BRSG, the inaugural meeting of which was held in Bangor.

### ***NMR of paramagnetic molecules.***

Few organic chemists had an interest initially in paramagnetic compounds, and indeed most samples gave very broad lines. Some however do not, such as some of the lanthanide complexes, and 2<sup>nd</sup> order paramagnetics, such as complexes of Re (III) and Osmium (IV) which do not have unpaired electrons like 1<sup>st</sup> order paramagnetics have. The first talk, entitled 'Contact shifts', in this area was given by Leslie Pratt (Imperial College, London) at the 3<sup>rd</sup> meeting, and Dr. Williamson (Aberdeen University) described shifts induced by cobaltous salts on the spectra of alkyl alcohols in the 12<sup>th</sup> meeting. C. L. Honeybourne and G. A. Webb presented 'Isotropic proton shifts in some paramagnetic complexes'. 'Lanthanide induced shifts in proton and <sup>13</sup>C NMR' were described by my colleague Gerry P. Moss (QMC). Soon shift reagents and relaxation reagents for modifying NMR spectra, and in some cases deriving molecular geometries, became very popular. They were 'rediscovered' in the MRI era which started about 1974, and relaxation reagents are now widely used in clinical MRI.

### ***Oriented Molecules.***

Molecular structures and intranuclear distances could also be deduced for solutes dissolved in 'liquid crystal' solvents. The 24<sup>th</sup> meeting held in Lancaster University in 1973 was devoted to this topic. There was an introductory talk by Lodovico Lunazzi (University of Bologna), and two talks from David Buckinham's group at Cambridge. John Briggs from my group (QMC) described the precise structural results obtained from the proton and <sup>15</sup>N NMR spectra of 'oriented' pyrrole – <sup>15</sup>N in a nematic solvent. This work was accurate enough to warrant vibrational corrections of the intranuclear distances which were made by Jim W. Emsley (University of Southampton).

### ***High magnetic fields.***

In 1964 the highest proton frequency was 100 MHz (2.35 Tesla) but in 1968 Malcolm McIvor (I.C.I, Petrochemical and Polymer Division) presented proton work at 220 MHz on a Varian instrument which used a superconducting solenoid. Academic groups were invited by SRC to evaluate the instrument and the increase in sensitivity and the separation of shifted peaks afforded by the higher magnetic field. Derek Shaw and I revisited some Re (III) and Os (IV) phosphine complexes, and were able to change an assignment. The instrument was however still using C.W. techniques and was overtaken by the introduction of pulse Fourier techniques.

### ***Fourier pulse methods.***

Most chemists had NMR spectrometers which functioned in the continuous wave (c.w.) mode in the early days of the NMRDG.

Pulse methods were in use for the determination of relaxation times, but few chemical groups had pulse capabilities, and initially most chemists were slow to realise the potential. Then Fourier transformation (FT) of the 'free induction decay' (FID) in the time domain to give a spectrum in the frequency domain became possible easily without resort to mainframe computers. This was owing to the advent of the small dedicated computer in the laboratory, and the invention of the fast Cooley – Tukey algorithm reported in 1965. The first two pulse FT spectrometers in the UK were delivered in 1969 to my group at QMC and then to Sid Knight's group at BP. They were Bruker HFX 90 instruments with a proton operating frequency of 90 MHz. By 1971 an NMRDG meeting devoted to pulse techniques was possible. It was the 20<sup>th</sup> meeting and was held at the Scientific Societies' Lecture theatre with a record 160 participants.

Derek Shaw (then at Varian Associates) spoke of Fourier studies of relaxation times, and Jim Feeney (MRC) talked on 'T<sub>1</sub> studies of <sup>13</sup>C and methods of assignment'. Ken Packer (East Anglia) spoke of the 'Use of pulsed magnetic resonance to study translational motion of molecules'. There were two talks from QMC given by Alasdair White and John Briggs on <sup>15</sup>N work at natural abundance. Roger Price of Bruker presented 'New developments in Fourier spectroscopy'.

A revolution in techniques had taken place. There was an immense gain in sensitivity in FT work. The sensitivity was increased further by spectral accumulation. Later came spectra in two frequency dimensions, 2D spectra, and in three. Many nucleides of low receptivity and natural abundance came into range in reasonable accumulation times. This is illustrated by the report of the first 5 years (1971 – 1975 inclusive) of the FT installation at QMC on which I ran a national service, with the aid of Les Farnell. There were 3,658  $^{13}\text{C}$  spectra, 1,697  $^{15}\text{N}$  spectra, 83  $^2\text{H}$  spectra, 47  $^1\text{H}$  spectra and 34 'others'. The average cost (total grant/number of spectra) was only £16 pound per spectrum.

Later came: spectra in two frequency dimensions, 2D spectra, and in three; FT solid state work at high resolution; work on large molecules including peptides and enzymes; work on quadrupolar nucleides and many other developments, including the use of high magnetic fields as high as 21.13 Tesla (900 MHz for protons), and of course Magnetic Resonance Imaging. All these topics were at 'the state of the art' were covered by presentations at the NMRDG meetings.

A full history of the NMRDG 1964 – 2008 is in preparation and will appear on the NMRDG website soon, in 2009.

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