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New Methods of Research

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The 26th meeting of the Nmr Discussion Group allowed leading European spectroscopists to review experimental techniques in nmr. New experimental methods and minor experimental procedures were discussed; and decisions were made about future meetings.

The 26th meeting of the Nmr Discussion Group was held recently at Canterbury in the Rutherford College of the University of Kent. The theme was 'Experimental techniques in nmr', and the meeting had two objectives. The first was to provide a forum for discussion by practising spectroscopists of both major developments in new techniques, and minor experimental details of procedures already in use which are not normally presented in lectures at the application's level. The second longer range objective was to discover the opinion of some of the leading European nmr spectroscopists, from both physics and chemistry, about the desirability of repeating the venture. The argument here is that since the specialist nmr audience in any one European country is small, and the number of technical innovators is smaller still, a larger than national grouping is necessary. This contrasts markedly with the situation at the application's level.

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Productive complications

The first session, with Dr M. J. A. de Bie as chairman, began with a general review of the latest technical developments by Dr D. G. Gillies (a reporter on this topic for the society's specialist reports in nmr). Dr D. Hoult then showed some ^{31}P spectra at 130 MHz taken on a *supercon* spectrometer which incorporates many of the latest technical features and is located in Dr R. E. Richard's group. Dr Hoult paid particular attention to one of these—quadrature detection in the Fourier mode—and stressed the simplicity of the construction as if in answer to the earlier plea by Dr Gillies for avoidance of unproductive complications in circuitry.

Dr L. Lunazzi was chairman of a session on orienting techniques in which Dr J. W. Emsley talked of the practical difficulties of obtaining good spectra from solutes dissolved in liquid crystal solvents. The effects of temperature, sample inhomogeneity and even history were discussed, as well as methods for the removal of the broad background signal from the solvent. The consequences of sample spinning for the different configurations of field and spinning axis in electromagnets and superconducting solenoids were discussed. Separation of isotropic from anisotropic parameters is possible. Dr C. A. de Lange then spoke of the difficulties in analysis of data from POF_3. The discussion focussed on the analytical procedures, their error analysis and on whether differences in geometries derived by this and the electron diffraction method were significant. Professor C. MacLean concluded the session with an account of the procedures for the observation, with high resolution, of the nmr spectra from samples oriented by strong electric fields. The particular difficulty was the design of a cell in which sufficiently high electric fields could be produced, ionic currents

suppressed and high homogeneity of the magnetic field achieved.

On the first evening an 'open forum' was held to discuss abstracts of various submissions. The topics were: CIDNP (Dr R. Kaptein); provision of service instrumentation (Dr C. Baker); and T_1 measurements—in solid adamantane (Dr M. Imanari), by continuous wave methods (Dr F. Heatley) and by homo-spoil sequences in which new computer software is used to automate the process, calculate T_1 and the nuclear Overhauser effect (Dr M. J. A. de Bie). Also, Dr H. J. Jakobsen illustrated the Fourier equivalent of the transitory selective irradiation (TSI) method of double resonance which he named selective population transfer (SPT).

Spectra of solids

On the second day with Professor J. G. Powles as chairman, Dr P. Mansfield reviewed the techniques by which high resolution spectra from solids could be obtained: sample rotation, multiple pulse methods, and the cross polarization double resonance methods. In a consideration of laminated samples, he used the formalism of diffraction techniques to describe a new experiment which consists, in Fourier transformation, of the decay resulting after a multipulse sequence has been applied to a sample subjected to a field gradient. The result is a map of the density of the resonant nuclei across the sample. This was illustrated with the 'print' of a finger (sampled *in vivo*). The chemist's current use of the term 'fingerprint' is outdated since the metaphor has become reality. Dr A. Kumar followed with a discussion of the cross polarization technique. Improved control of power levels may be affected by variation of the duty cycle.

With Dr R. E. Richards as chairman, Dr C. Dijkema spoke of spectra from smectic systems in which sample orientation was achieved macroscopically between glass surfaces. The utility of the dipolar term was extolled by Dr N. Boden (another special reporter for the society) who showed that it could be evaluated from analysis of the amplitude of the so called 'solid' echo, and Dr K. J. Packer concluded the session with an account of the response of protons in tissues to different pulse sequences. Different sections of the tissues gave different measurements and the experiments allow distinction of tissue water and dynamically ordered water.

Fourier transformation

In a session on Fourier methods (chairman Dr R. Freeman), Professor R. R. Ernst contrasted excitation by 'white' noise or a pulsed monochromatic frequency with continuous wave (cw) excitation by a swept monochromatic frequency. The inequivalence of the cw and pulse methods was clearly described and elegantly illustrated for a number of cases, including CIDNP and double resonance experiments. Professor Ernst recommended the use of small pulse angles as a possible but only partial solution for giving Fourier spectra which approximate to conventional cw spectra. Dr D. Shaw then spoke of 'flexible excitation' in which 'coloured' radiation is used. The pulses can be shaped and tailored to exclude excitation of unwanted frequency regions. He also described other methods for reducing unwanted peaks in the spectrum.

Dr H. Bildsøe compared fast scan cw and pulse spectroscopy at a discussion chaired by Madame Martin. A complex division of the Fourier transforms of the spectrometer response and the analytical signal replaces their normal comparison in a phase sensitive detector. An alternative to the pulse shaping technique was described by Dr J. L. Delayre. This CHIRP method uses frequency sweeping of the pulses and apparently allows more efficient use of the radiofrequency power. Dr I. D. Campbell, on the subject of resolution problems with very large molecules, discussed variants of difference spectroscopy in which the differences were produced by pH, temperature, double resonance and by relaxation reagents.

Relaxation methods

Under the chairmanship of Dr R. E. Richards, Dr O. Lutz described the methods of Schwenk *et al.* for the observation of nuclei with low abundance and sensitivity including ^{43}Ca, ^{67}Zn and ^{113}Cd. Ancillary techniques—Overhauser effects, the use of paramagnetic relaxation reagents, gated decoupling experiments—were illustrated by Dr R. K. Harris for the case of ^{29}Si.

In the last session, experimental interest in Dr M. Holz's talk on relaxation measurements of some quadrupolar nuclei ($Br^{79,81}$, $Rb^{85,87}$ and Cs^{133}) focussed on the large, 50 mm, sample tube and more importantly on the extended automation of the T_1 measurements. This was also the theme of the talk by Dr M. Norris who described similar 'interactive computer control and variation' of the sample temperature and the pulse conditions to allow automatic calculation of accurate T_1 values. The formal sessions were concluded by the chairman, Dr F. W. van Duersen, after Professor M. L. Martin had spoken of the theoretical and experimental difficulties in the evaluation of energy barriers by ^{13}C and ^{1}H experiments.

European cooperation

The meeting was successful in its two objectives. The audience of approximately 150 was exposed to reviews and details of nmr techniques. In terms of European cooperation, the attendance augers well. Over one third of the participants and one half of the speakers were from overseas, so that the native audience did not dominate. There was a large consensus in favour of repeating the venture, within a period of one and two years. It is proposed that the venue should change from one European centre to another. The Dutch Nmr Discussion Group (affiliated to the Analytical Division of the Royal Dutch Chemical Society) offered to promote a second meeting probably in the autumn of 1975. The difficulties are likely to be limiting discussions to the experimental emphasis and to attracting a larger representation from physicists. Our discussion group will take the opportunity of the next meeting to return the visit our Dutch colleagues paid on the occasion of our joint meeting at Essex in 1973.

Since we believe that coordination of conference activities is important, our next international meeting at St Andrews (July 6th–11th, 1975) will not be concerned with experimental aspects of nmr but will concentrate, in a hopefully complementary fashion, on the theory of nmr and on applications in a few selected areas of chemistry.