

Nuclear Magnetic Resonance in Australia 1952-1986

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Summary

The first NMR experiment in Australia was performed by a physicist at the NSW University of Technology in 1952. While at first the physicists built their own instruments, they later began to use commercial spectrometers which had been modified to meet particular needs. Work of this type has been concentrated at relatively few centres in south-eastern Australia and the personal connections between them are explored in this account.

Australian chemists entered the field in 1962 when 10 commercial spectrometers were purchased from the Varian company in California. Since then the use of NMR techniques has expanded steadily so that most tertiary institutions, many CSIRO Divisions, and a few companies possess modern NMR spectrometers. The operations of the National NMR Centre between 1975 and 1982 are covered in detail, and the recent applications of magnetic resonance imaging to medicine are described.

Through this account, attention is paid to the ways in which Australian scientists entered the field and the special contributions they have made to it.

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1. Introduction

In 1924, Pauli postulated the existence of nuclear magnetic moments in order to explain certain hyperfine structure in atomic optical spectra.¹ Pauli's idea was that the nucleus of an atom might be regarded as behaving like a tiny bar magnet: when other details of the energy state of that atom were defined, there would still remain the question of the disposition of this nuclear magnetism. Pauli spoke of the nuclear magnetism as resulting from nuclear spin — a term which he introduced into Physics. It was not until 1939, however, that the existence of these moments were experimentally verified in the molecular beam experiments of Rabi *et al.*² The nuclear magnetic moments possessed by most nuclei — the most notable exceptions are the common isotopes of carbon (^{12}C) and oxygen (^{16}O) — interact with external magnetic fields so that new nuclear energy levels are produced. These energy levels are responsible for the extra fine structure of atomic spectra (Zeeman splitting), and transitions between the energy levels constitute nuclear magnetic resonance spectroscopy. In 1936, well before the molecular beam experiments which were the first example of nuclear resonance, Gorter had suggested that, in the presence of a large external magnetic field, the populations of the nuclear Zeeman energy levels should be perturbed by the application of the appropriate resonant radiation — that is, that magnetic resonance experiments should be possible.³

Nuclear magnetic resonance (NMR) in bulk samples — as opposed to the dilute gases used in molecular beam experiments — was first observed in 1945, and in 1946 three papers were published by two groups in the USA: Bloch, Hansen and Packard at Stanford University and Purcell, Torrey, Pound and Bloembergen at Harvard University.⁴ The two groups took quite different approaches to experiments in which the frequency of applied radiation and the magnetic field to which the nuclei were subjected were varied in search of the resonant condition. Bloch's group used the 'adiabatic' fast passage technique, which required high radio frequency (rf) powers and large superimposed field modulation with separate receiver and transmitter coils in a 'cross-coil' arrangement. Purcell's group opted for the slow passage technique and used a bridge arrangement for the sample coil, low level modulation, narrow band amplification and phase sensitive detection. The first generation of continuous wave (CW) NMR spectrometers owes more to the latter than the former group, while subsequent pulse methods derive from the former. Subsequently, Bloch described the NMR phe-

nomenon in essentially classical terms,⁵ while the Harvard group produced a quantum mechanical description, which has been dubbed 'the BPP theory'.⁶

The energy levels produced by the interaction between nuclear spins and an applied magnetic field have, at equilibrium, slightly different populations. The existence of the energy gap between energy levels, together with the unequal populations, permits a form of spectroscopy known as nuclear magnetic resonance. The NMR experiment is a non-destructive one, in which a small sample of material — on the order of a gram — is placed (usually in a glass tube) in a strong magnetic field. Wire coils placed near or around the sample are then used to deliver to it a radio-frequency signal, and absorption of this signal by the sample is detected by the instrument. The results, possibly obtained over time, are displayed on an oscilloscope or chart recorder as a series of peaks, and from them and their variation the following types of information may be derived:

- (1) the particular combination of magnetic field strength and radiation frequency which are required to produce resonance (transitions between nuclear energy levels). Such values are characteristic of nuclei and the way they are combined, by means of chemical bonds or lattice arrangements, into compounds. The effect is thus termed the 'chemical shift' of a resonance position.
- (2) the rate at which equilibrium is regained after perturbation of the system; generally a first order process which is dependent on the environments of the nuclei and may be characterised by a relaxation time.
- (3) relative intensities of resonance signals arising from nuclei of one type but found in different environments in the sample. Thus isomeric pairs such as CH_3CHCl_2 and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (both $\text{C}_2\text{H}_4\text{Cl}_2$) are readily distinguished by the dispositions of the hydrogen nuclei in the two molecules.
- (4) fine structure of the resonance signals caused by internuclear interactions and thus betraying near-neighbour relationships of atoms within a molecule. The first demonstration involved hydrogen nuclei, ^1H , which have nuclear spin $\frac{1}{2}$ and which give rise to two energy levels. Later work has made use of nuclear resonance in ^{31}P , ^{19}F , ^{13}C , ^2H , ^{15}N and almost one hundred other isotopic species which possess nuclear spin.

Until quite recently chemists were mainly interested in liquids or solutions in which the molecules tumbled freely — 10^8 – 10^{12} times a second — and which thus gave well-dispersed

spectra, the line positions being dependent on the inter- and intra-molecular environments of the nuclei under observation. Thus the position and fine detail of the observed resonances become the basis of deductions about molecular structure. While adequate theory has been developed, most work still relies on empirical structure-spectra correlations.

For physicists, mainly interested in solids, NMR was much less revealing, but the information they obtained was quite unique, and the field developed first with physicists in the 1950s. There were no commercial spectrometers, and control of the stability and homogeneity of the magnetic field applied to the sample were crude. It was mainly the improvement in these instrumental factors which revealed the dependence on molecular structure — the chemical shift — and brought chemists into the field.

Commercial, high-resolution NMR spectrometers first appeared on the world scene in the late 1950s. At that time there were several low-resolution (broad line) instruments in the hands of Australian physicists, but chemists were only able to read about possible applications in overseas journals or join in the experiments when study leaves took them to the Northern Hemisphere. When the first commercial spectrometers arrived in 1962 they came in a flood — ten of them — and the new field of activity was quickly taken up by Australian chemists, who have continued, for twenty five years, to make notable contributions.

Young chemists found it easier to take up NMR work than did those in mid-career, but the best practitioners of all ages quickly adopted NMR methods. Robert Woodward (Nobel Prize in Chemistry, 1966) writing about the organic chemists' use of physical methods in 1956 — when he was 39 years of age — noted that 'Nuclear magnetic resonance is even now on the horizon, and we shall be surprised if it does not permit another great step forward'.⁷ By 1961, the physicist H.R. Hoff, pseudonymously as novelist William Cooper, was clearly of the opinion that 'nuclear magnetic resonance has been taken over by the Chemists'.⁸ When the U.S. National Academy of Sciences surveyed the reported use of instruments by chemists, it noted that chemistry papers reporting nuclear magnetic resonance had advanced to 16% of the total by 1964, almost overtaking ultraviolet spectroscopy but still well behind infrared (36%).⁹

NMR spectrometers have always been expensive.¹⁰ A state-of-the art instrument sold for a little over US\$100,000 in the early 1960s (100 MHz), US\$400,000 in 1975 (400 MHz) and US\$900,000 in 1985 (600 MHz). Aus-

tralian prices for 60 MHz high resolution spectrometers in 1962 are shown in Table 1: for comparison, we note that a professorial salary in June that year was £4250 (\$8500) or somewhat less than one tenth the cost of a top-of-the-line spectrometer. This equation has persisted for over two decades, with professorial salary reaching \$23,596 in June 1975 and \$57,036 in June 1986. Chemistry department budgets suffered the first of the large expenses, which seem to recur with each new phase of instrumentation. For example, at Melbourne University, the expenditure for new instruments in the early 1960s was outside the normal budgetary allocation for the School of Chemistry and notionally tied to the appointment of new professors.

As sophistication and price continue to rise, the sales of spectrometers have tended to split between two extremes. On the one hand are large, expensive superconducting systems, typically 400 or 500 MHz for ¹H resonance and operating in pulse mode with large computers; on the other, smaller, less versatile and less expensive systems operating at 60 or 90 MHz — continuous wave single-scan systems with electromagnets or permanent magnets.¹¹ In Australia, spectrometers operating at 200 or 300 MHz — last decade's state-of-the art — are still common. The pattern described by Sternhell is clearly appearing here, but it is joined by a middle tier in which 200 MHz systems are purchased as 'workhorse' pulse spectrometers.

2. The Physicists

There can be no doubt that the first NMR signal seen in Australia (or indeed in the Southern Hemisphere) was that obtained by Leonard O. Bowen at the NSW University of Technology towards the end of 1952. There were, however, three separate loci from which NMR methods have diffused. Other early workers in the field were G.W. West, of the CSIRO Division of Tribophysics (1956), and G.V.H. Wilson and others at Monash University (1960). It is instructive to follow the historical development of NMR by physicists originating from these three sources.

2.1 Early days at the NSW University of Technology

Early in 1951, L.O. Bowen joined the staff of the recently-established New South Wales University of Technology, which was temporarily housed in and around the Sydney Technical College, Ultimo. He was appointed as lecturer in the School of Applied Physics, the foundation chair of which was occupied by Professor N.S.F. Astbury, whose main field of interest

was magnetism. This interest he communicated to Bowen and suggested that the recently-discovered phenomenon of NMR might prove a fruitful topic of research.

The great flowering of research in Australian universities was yet to come, and Bowen faced a number of problems which were fairly typical of the shoe-string approach then normal in Australia. The School had no magnet facilities, so the first task was to borrow from the Electrical Engineering Department, Sydney University, a small electro-magnet (Fig. 1), which, after some modification, just managed to serve his purpose. This magnet has yet to be returned to Sydney University: it is now being used in the laboratories of the School of Physics at the University of NSW!

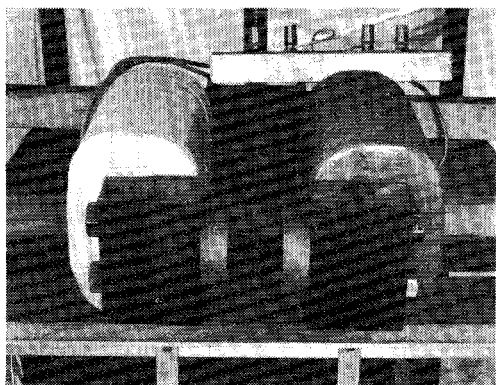


Figure 1 The primitive electromagnet used by L.O. Bowen to perform the first NMR experiment in Australia (1952). The magnet had a rectangular cross-section horse-shoe yoke and cylindrical pole pieces of $3\frac{1}{2}$ inch diameter.

At the same time, Bowen set about designing a large general-purpose, water-cooled electromagnet, with a pole diameter of 0.30m, a weight of about 2.5 tonne and a maximum power consumption of 40 kW.¹² Through the generosity of an external benefactor (J.F. Carroll), the magnet was subsequently built by the Sydney engineering firm of Jones and Rickard (Fig. 2). Concurrently, he had the School's workshops construct radio-frequency equipment necessary for the NMR experiment. He had decided to use the fast passage method of Bloch, partly because the electronic equipment was simpler than that required by the Purcell technique, but mainly because it enabled spin-lattice relaxation times (T_1) to be measured directly with comparative ease.

In common with most experimentalists, Bowen had the usual setbacks and frustrations in getting his apparatus in working order. He recalls a number of weeks spent in a futile search for resonance in a wrong region of magnetic field, due to an incorrectly calibrated

fluxmeter. Fortunately, the day did arise when that magical little blip appeared on the oscilloscope screen, and he observed, for the first time in Australia, a hydrogen NMR signal arising from molecules of water in a ferric nitrate solution.

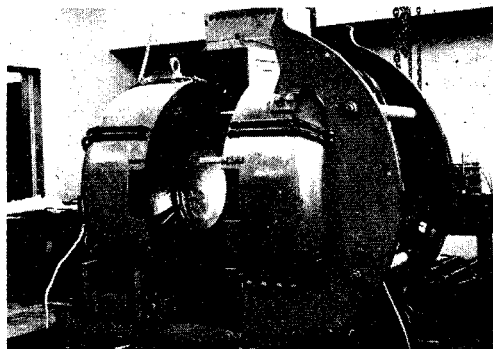


Figure 2 The general purpose laboratory electro-magnet designed by L.O. Bowen and built in 1954. The magnet poles were 12 inches in diameter and the designed maximum power consumption was 50 kW. Except for four access ports, the cylindrical yoke entirely enclosed the magnet gap, leading to high magnetic efficiency. Under operating conditions the two half yokes (here shown retracted) are closed up.

This occurred late in 1952, and Bowen continued for some months familiarizing himself with the adiabatic fast-passage technique. During this period, he discovered a new method of measuring the spin-lattice relaxation time which was especially useful when T_1 was long (order of seconds).¹³ In 1953, he began a series of experiments to measure T_1 of pure water as a function of temperature. A friend and colleague, F. Gutmann of the School of Applied Chemistry, had drawn his attention to a report in the literature which alleged that there existed a discontinuity in the density of water at approximately 50°C. If such an effect did occur, it should show as a corresponding discontinuity in T_1 . Bowen found no such effect, a result which he confirmed some years later using pulsed techniques.¹⁴ Having regard to the difficulties which he faced in having no person with knowledge of NMR to talk to and in having to rely solely on what was published in the literature, it must be acknowledged that his efforts were truly pioneering in the Australian context.¹⁵ In 1954, Bowen was awarded a Fulbright Scholarship tenable at Washington University, St Louis, for the (northern) academic year 1954–55.

In 1955, the School of Applied Physics, along with two others, was transferred to the campus being developed at Kensington. Although the change of name did not occur until a few years,

it will be convenient to refer to the Kensington site as the University of New South Wales. It may also be appropriate here to mention two other issues. First and foremost was the problem of finance. Direct funding of research by the Federal Government did not occur until the establishment of the Australian Research Grants Commission in 1965. Each research group had to importune for some crumbs from that slice of the research cake allocated to the School by the University. On the technical side, it was still the era of vacuum-tube electronics. Transistors were shortly to appear in commercial quantities overseas, but only with properties of frequency response, thermal stability and reliability that left much to be desired. More significantly, there was a considerable time lag before they were released in Australia.

During his stay at St Louis, Bowen under the direction of R.E. Norberg had become acquainted with the spin-echo experiments of E.L. Hahn.¹⁶ He returned in late 1955 to the University of NSW imbued with the desire to work in this exciting new technique of Pulsed NMR. He had brought back with him detailed circuit diagrams of a 30 MHz Carr-Purcell radiofrequency pulse unit, and eventually, when the necessary finance was at last forthcoming, the pulser was contracted to be built locally by R.A. Ratcliffe of Eastwood.

In early 1956, the Carroll Magnet was installed at Kensington, together with a DC motor-generator set with which to energise the magnet. The motor was a conventional 25 h.p. 3-phase motor, but the DC generator had a history of its own. It served in the WW1 warship *HMAS Australia* and was rescued from a watery grave (*HMAS Australia* was scuttled off Sydney Heads) to serve the purposes of an impecunious research group.

In these early instruments it was the quality of the magnet field which most influenced the spectral resolution which could be achieved. The twin, stringent criteria for the magnetic field for NMR purposes are temporal stability and spatial homogeneity, and K.H. Marsden, who had joined the staff in mid-1955 as a teaching fellow, was assigned to tackle the former. Improved resolution was expected to bring with it the ability to study more complex samples than the water which had been the main target of early studies. It was proposed to stabilize the magnetic field using a proton magnetometer, the error signal from which was applied in a negative feedback sense to a power amplifier driving the field windings of the motor generator. Because of the long time-constants involved, ripple on the DC output of the generator, associated with asymmetry of the field windings, had to be removed by active filters. After trying a number of circuits for the

magnetometer, one employing a negative resistance 'transitron' (pentode) oscillator was finally chosen. The system was operational in late 1957, but the magnetic field stability was limited largely because the 'transitron' was a free-running oscillator.¹⁷ Some time later the stability was considerably improved by locking the 'transitron' to a master crystal oscillator, but this was unfortunately too late to assist E. Laisk, whose work we will describe shortly.¹⁸

In early 1957 there were very few people working on NMR in Australia.¹⁹ E. Laisk, who was in charge of the School's electronic workshop, joined the NMR research group and was given the task of designing and constructing a general-purpose spectrometer. He decided to have a choice of two input circuits — a simple tuned circuit followed by a 'Q-multiplier', and a twin-T bridge circuit. This was followed by a

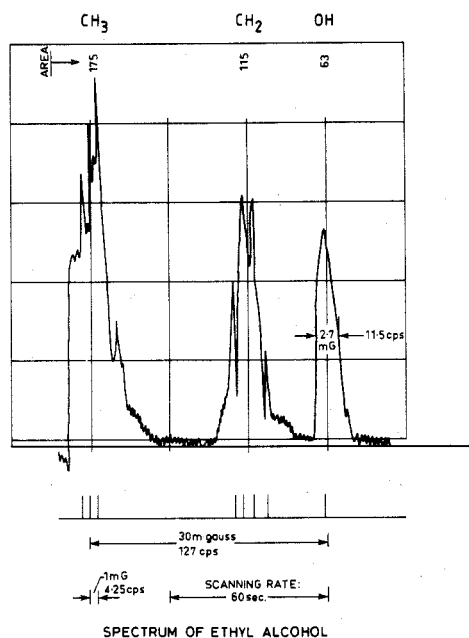


Figure 3 Proton NMR spectrum of ethyl alcohol obtained by E. Laisk in 1960 using a general purpose spectrometer designed and built by himself.

heterodyne stage with variable gain amplifier. The output stage also provided a choice, either immediate detection, or lock-in amplification and integration. By an appropriate combination of input and output circuits, modulation level and magnetic field sweep, the operational mode of the spectrometer could be varied from wide-line to medium high resolution. This is illustrated by the spectra of ethanol and gypsum shown in figures 3 and 4 respectively.²⁰

For the higher resolution work, the magnetic field homogeneity had to be increased by

mechanically paralleling the pole faces. This was a time-consuming process and had to be repeated every time the magnet was re-energised. Also the field stability obtained using the motor generator was inadequate for this work. A current-stabilised power supply was constructed using a 4 x 4 bank of large 12V accumulator batteries. These gave about 6 hours operation before recharging was necessary.

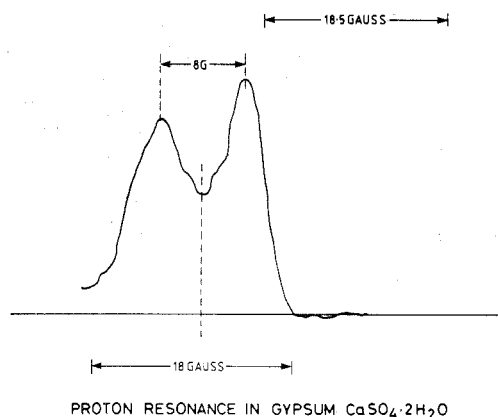


Figure 4 Spectrum of gypsum using the same spectrometer.

In view of these difficulties, it was realised that it was not possible to compete with commercially built CW high-resolution spectrometers which were then (1960) becoming available, and it was reluctantly decided to discontinue this line of work to concentrate on pulsed techniques.

The Ratcliffe rf pulser unit was delivered at the end of 1956, and shortly thereafter the first spin-echo experiment was performed in Australia by Bowen. Some initial difficulty due to saturation of the receiver, which was designed for low-level CW operation, was largely overcome by building a pre-amplifier which was gated off for the duration of the intense 90° rf pulse. The 'dead-time' was reduced to 40 μs , and over the years progressively further reduced to about 10 μs .

In the early sixties, Bowen was interested in possible ultrasonic-NMR relaxation effects in liquids, and he spent much effort in constructing the ultrasonic part of the equipment. He did not compete this work until he was able to take two years special leave at Queen Mary College, London. At this time, Marsden was interested in confirming the temperature dependence of quadrupolar relaxation in solids, specifically the sodium resonance in NaF, but he was forestalled by researchers overseas. Attempts to detect any influence on the quadrupolar relaxation by the application of an

external electric field were negated by the onset of dielectric breakdown. This period was unproductive as far as published work was concerned, but the experience of modifying the rf pulser to operate at other frequencies (10 MHz) and the building of the corresponding receiver was to prove valuable at a later date.

The science of the solid state had been an area of Australian science since the 1920s, and for physicists NMR was one of a number of techniques which found increasing application in the 1950s. The others were X-ray crystal lography (the oldest of the techniques, dating back to the Braggs' work in the second decade of the century), electron spin resonance and Mössbauer spectroscopy. Some physicists constructed their own NMR spectrometers, others purchased commercial instruments from the Varian company and modified them to suit the particular samples to be studied. Many of the early studies involved composite materials containing water, and NMR was used to characterise the environment and mobility of water molecules in such things as animal horn and wool. A major indicator of water condition was the spin-lattice relaxation time for hydrogen nuclei in the water molecules. The spin-lattice time is a measure of the time taken to achieve or return to equilibrium of the nuclear spin systems, and is directly affected by the tumbling time for mobile water molecules and the nature of the physical lattice in which the molecules are contained. Similar studies were performed on metal atoms in alloys and for ions in crystalline or ceramic materials; details are given in the next few sections.

2.2 Interactions between University of NSW and CSIRO divisions in Sydney

Following an invited lecture given by Bowen in the early sixties at the CSIRO Division of Textile Physics in Ryde, Max Feughelman expressed interest in the pulsed NMR techniques and suggested that quantitative measurements could be made on the proton signal from water adsorbed in wool. Feughelman and his colleague A.R. Haly were then collaborating with G.W. West at CSIRO, Melbourne, in such a study using CW techniques (see Section 2.3).

The suggestion was taken up in earnest in 1963, when it formed the major research topic for a Ph.D. student at the University of New South Wales, L.J. Lynch. Measurements of the relaxation times T_1 and T_2 were made on wool-water systems of various hydrations over a wide temperature range. Lynch showed that the various theories of the keratin-water interaction then in existence were incompatible with the NMR results.²¹ He was able to rec-

concile his data using a theory based on a continuous distribution of nuclear correlation times of the absorbed water molecules. The analysis was extended to experiments on other hydrated and other heterogeneous sorbed systems.²² As a result of this work, a grant was obtained from the Australian Wool Board to purchase a high power, single frequency, pulse spectrometer from Polaron Ltd., U.K. Only a few of these machines were ever built; they were comparable with the early versions of the Bruker spectrometers then being built in Germany.

In 1967, R. Outhred, a Ph.D. student in Biophysics, continued the studies of the nature of water in biological substances. As part of his experimental work, he made T_1 measurements at three different frequencies (3, 10 and 30 MHz) on hydrated systems (keratin, gelatin, agar and agarose). The variation of T_1 with resonant frequency was interpreted in terms of the complexity of the hydrated states.²³ In collaboration with T. Conlon, studies were made of the water diffusion permeability of erythrocytes. Spin-echo measurements were made of the proton spin-spin relaxation in samples of blood, the plasma of which had been doped with paramagnetic ions. From the two-component nature of the spin-echo decay, they were able to infer the exchange time for water diffusing across the blood cell membrane.²⁴

The year 1968 saw the beginning of cooperation with W.J. O'Sullivan, at that time a research fellow in the Department of Medicine, Sydney University. O'Sullivan was studying the interaction of metal ions with proteins, with particular emphasis on the association of manganese-ADP and ATP complexes with the kinase group of enzymes. The spin-lattice relaxation time T_1 of the protons in $MnCl_2$ -enzyme solutions was measured as a function of the concentration of titrated ADP or ATP. Measurements were normally carried out at 15°C and at a single frequency, although in some cases variable temperature and variable frequency measurements were made in order to elucidate the relaxation mechanisms.²⁵ The latter part of this work was carried out on a Bruker SPX 100 pulsed spectrometer, which was installed in 1973.

If, during a spin-echo experiment, magnetic-field-gradient pulses are applied in an appropriate manner, the echo signal is reduced due to the diffusion of the resonant nuclei. This phenomenon formed the basis of the Ph.D. thesis of D.S. Webster, who began his research project in 1968. He designed a novel 'quadrupole' coil (surrounding the sample) for applying the field gradient pulses.²⁶ This coil was rapidly adopted by overseas groups and became the standard for commercial self-diffusion probes;

today it used to produce the intense field gradients necessary in microscopic magnetic resonance imaging.²⁷ Using this coil design and electronic circuitry employing silicon controlled rectifiers, Webster was able to obtain gradient pulses sharper and more intense than any previously published. Measurements were made at various temperatures and hydration levels in wool fibres and rhinoceros horn, in directions parallel and transverse to the axis of the keratin macromolecule. In all cases the diffusion of the absorbed water was found to be anisotropic. Measurements were also carried out on whole muscle tissue from the pit-head toad and the shellfish *Balanus*. In the latter case there was evidence that diffusion was restricted by cellular barriers.²⁸

Between 1972 and 1974, Webster was a research fellow at the Diffusion Research Unit of the Australian National University, which was engaged in the accurate determination of the diffusion properties of liquids and aqueous solutions by radio-active isotope tracer methods. Working with the director of the unit, R. Mills, Webster set about complementing this work by constructing a NMR-field gradient apparatus incorporating his recent developments. For this purpose he used one of the first Bruker Minispec spectrometers brought to Australia, and was able to obtain results whose accuracy was comparable with that of the tracer technique.²⁹

J.M. Pope joined the school in 1975 from Monash University, where he had spent the previous two years and where, in collaboration with B.A. Cornell, he had studied water-membrane systems (see Section 2.4). Pope continued the work begun at Monash, and, using the recently acquired Bruker pulsed spectrometer, extended his studies to the interaction of anaesthetics with lipid bi-layers.³⁰ Other research ventures using relaxation measurements included the study of spin diffusion in solid polymers,³¹ and investigation of the diffusion of hydrogen absorbed in metallic lattices.³² More recently, Pope has been involved in magnetic resonance imaging and (at the Royal North Shore Hospital) *in vivo* spectroscopy.

In 1975, G.J. Bowden joined the School of Physics, UNSW, from the National Standards Laboratory (NSL) of CSIRO. His major research interests lay in the field of solid state physics, both theoretical and experimental. With various research students he began experiments, extending over a number of years, on a series of rare-earth intermetallic compounds. Spin-echo measurements were made, using the Bruker instrument and a 45–65 MHz frequency range, on the internal hyperfine magnetic field of the compounds. Spin re-

orientation and domain wall studies were pursued, over the temperature range 4.2–300 K.³³

In collaboration with workers at NSL, Bowden has been investigating oriented nuclei in antiferromagnetic crystals. These NMRON experiments (NMR of Oriented Nuclei) involve the use of a radio-active isotope of the magnetic ion, CW NMR stimulation (~ 500 MHz) of the nuclear energy levels in the internal magnetic field, and the detection of nuclear orientation by gamma-ray spectroscopy, with experiments being carried out at temperatures near 20 mK.³⁴ Finally, mention must be made of Bowden's contribution to the theory of MQ (multiple quantum) NMR. Together with a research student, W.D. Hutchinson, He has developed a tensor operator formalism for the analysis of multiple transitions in spin $I > \frac{1}{2}$ systems.³⁵

After a short period at the Weapons Research Establishment, South Australia, L.J. Lynch joined the CSIRO Wool Research Laboratories, Ryde, in 1968, and there extended the work of his Ph.D. research, still using, for a few years, the facilities at UNSW. Proton exchange between the sorbed water and the labile groups of the keratin substrate was studied,³⁶ and anisotropic motions were detected in water sorbed in highly-oriented bulk keratin such as rhinoceros horn.³⁷

Lynch was joined at CSIRO by D.S. Webster in 1974, and over a period they built two high-power pulse NMR systems based around a 12-inch Varian magnet and a wide-gap Bruker magnet, the hybrid electronics being based on Bruker consoles. Earlier work of this group included investigations into the freezing and other transitions of sorbed-water phases in heterogeneous materials.³⁸ They also detected and investigated effects on the observed spin-lattice relaxation of spin-diffusion between sorbed water and substrate phases.³⁹ This has led to the development of a new general approach to the problem of diffusion-coupled spin-lattice relaxation. An analogy between phenomena which govern diffusion-coupled spin-lattice relaxation in heterogeneous materials, and those which govern the heat conduction properties of heterogeneous systems in which there are distributed heat sources and sinks, has been demonstrated. G. Simms, a Ph.D. student working with the group, has shown how this analogy allows the adaptation of much theory developed for particular heat conduction problems to the design of selective excitation NMR experiments for studies of heterogeneous systems in which coupled spin-diffusion/spin-lattice relaxation occurs.⁴⁰ A major achievement of this CSIRO group has been the development, over a number of years,

of techniques to allow *in situ* pulsed proton NMR measurements of materials during heating to high temperatures. This has developed into a thermal analysis methodology, and has been extensively applied to the study of pyrolysis of coals and other organic materials.⁴¹

2.3 CSIRO Tribophysics

Whereas L.O. Bowen, the first practitioner of NMR in Australia, had begun work in NMR without serving an overseas 'apprenticeship', G.W. West of the Division of Tribophysics, CSIRO, came to the field by a more conventional route. Following eight months study leave with Prof. N. Bloembergen at Harvard and then E.R. Andrews at Bangor, Wales, he returned to Australia in 1956 and began the construction of a CW spectrometer based on the Pound-Knight-Watkins marginal oscillator circuit and designed for solid-state measurements. West also built a twin-T bridge input, 'high resolution' instrument for proton measurements. He worked initially with a home-made permanent magnet, but in 1958 he managed to acquire a 12-inch electromagnet from Varian, who were then producing their first batch of commercial instruments. In 1965, he began the construction of a home-made pulsed spectrometer which, together with the CW instrument, was subsequently interfaced with a PDP-8 mini-computer.

In 1986, West acquired a Bruker MSL 400 spectrometer, which was installed at the Clayton site of the Division of Materials Science and Technology — constructed from the former Tribophysics and Chemical Physics divisions — and where research into solid-state NMR is pursued by West and T. Bastow. West thus has the longest association with NMR research of any Australian, stretching from the mid-1950's to the present day. Some of his early collaborative work is recorded in Section 3.1. In his own field of interest, he began with NMR studies of metallic alloys, particularly β -brass,⁴² and extended this to intermetallic compounds in a series of experiments spanning many years.⁴³ During this time, he also performed proton NMR experiments on water in layer-silicates,⁴⁴ and on calcium sulphate hemihydrate. Since 1975, he has turned his attention to NMR studies of minerals, notably zeolites,⁴⁵ and of glasses.⁴⁶

From a historical viewpoint, particular reference must be made to West's early (1960) CW NMR studies of the state of water in wool, in collaboration with M. Feughelman and A.R. Haly of CSIRO's Wool Research Laboratory, Ryde, since this work initiated extensive investigations into sorbed-water and biological systems which has developed widely in Australia over the years.⁴⁷

2.4 Monash University and its role in the establishment of other groups

In the early sixties, NMR research commenced in the Department of Physics, Monash University, when British solid state physicist and foundation chairman of the department, Bob Street, purchased a Varian wide-line NMR spectrometer. Street's Ph.D. student, G.V.H. Wilson, made a definitive analysis of the effects of modulation broadening on NMR and ESR lineshapes.⁴⁸ He also began NMR measurements in the internal hyperfine field of Fe-Co and Fe-Ni alloys, which was to become a popular technique for the study of the atomic-scale distribution of electronic magnetisation.⁴⁹ Following a post-doctoral period at Oxford University, Wilson returned to Monash in 1965 and, with Ph.D. student D.H. Chaplin, began the construction of a 10 mK cryostat necessary for experiments on oriented nuclei. Later, in 1971, both joined the staff of the Faculty of Military Studies, UNSW, at Duntroon. In 1985, this became the Australian Defence Force Academy, a University College of UNSW, with Professor G.V.H. Wilson as its first Rector.

The Duntroon experimental work involves the study of nuclei oriented in the internal hyperfine field of intermetallic compounds of the transition and rare-earth elements. After NMR stimulation of the magnetic energy levels, changes are detected in the anisotropy of the gamma-ray emission from an appropriate radio-active isotope. Such radiative detection enables an increase in the sensitivity by a factor which can be as large as 10^{10} , and makes possible for the first time the study of a variety of dilute alloys and the accurate measurement of many nuclear and quadrupole moments.⁵⁰ Professor Wilson's group has concentrated on transient techniques, since the data from such experiments are easier to interpret than those obtained from conventional NMR. Many of the experimental techniques used in NMRON were first developed at either Monash or Duntroon, including, for example, single adiabatic passage, multiple-pulse spin echoes, and frequency-modulated pulse techniques.⁵¹ Their most recent innovation is MAPON (Modulated Adiabatic Passage-Oriented Nuclei), a technique suggested by Professor P.T. Callaghan of Massey University, New Zealand. This technique, which uses a single modulated adiabatic passage, enables extremely weak quadrupole interactions to be measured.⁵²

B.A. Cornell began his NMR research as a Ph.D. student (with G.J. Troup) at Monash University in 1970. He constructed a pulsed spectrometer designed to operate at the resonant frequencies of deuterium, oxygen-17 and

sodium-23 in the field of a 12-inch Varian electromagnet, and also for proton resonances in the range 1 to 40 MHz. Cornell acknowledges the help given by G.W. West in the design of this equipment. The research work involved the study of biomolecules and, in collaboration with J.M. Pope, who was then a Senior Tutor at Monash, he investigated the binding of water to model biological membranes and showed that the bound water, which formed an integral part of the membrane structure, exhibits anisotropic motion. In the course of their experimental work, they developed a new technique for the study of slow molecular motions, which involved the measurement of spin-lattice relaxation in the off-resonance rotating frame.⁵³ It was in a discussion group organised by Cornell and Pope that the organic chemists S.R. Johns (CSIRO) and I.D. Rae (Monash) learned the basics of pulse NMR.

In 1977, Cornell returned to Australia after a post-doctoral fellowship year at London University and joined the CSIRO Division of Food Research, North Ryde. In the following year he was able to obtain, jointly with the Division of Fossil Fuels (now including Lynch and Webster) a Bruker CXP 100 FT solid state spectrometer and to begin his carbon-13 research. Studies of cross-polarization were made in biological samples and, in particular, in membrane dispersions from biological material and model membranes prepared from synthetic surfactants. Concurrent proton, deuterium and phosphorus-31 measurements were made on these systems.⁵⁴

The acquisition in 1983 of a CXP 300 spectrometer, with its accompanying increased sensitivity, has allowed studies to be extended to natural-abundance carbon-13 in organic single crystals. This has enabled the compilation of a library of carbon-13 shielding tensors for use in the interpretation of spectra from organic molecules.⁵⁵ Studies have also been made into the conformation and dynamics of molecules in both synthetic and biological membranes.⁵⁶ The group has currently a number of Ph.D. students working on research projects involving carbon-13, proton-enhanced spectroscopy in biological materials.

It is perhaps stretching a point to associate C.A. Sholl with the Monash NMR group, because his Ph.D. studies in the Department of Physics involved not NMR but a theoretical study of electric field gradients in ionic solids. He first became interested in nuclear spin relaxation in 1966, during a post-doctoral year at the University of Bristol. On his return to Australia, he joined the staff of the Department of Physics, University of New England, Armidale, where he continued to develop the theory of nuclear quadrupole relaxation in liq-

uid metals, in collaboration with overseas colleagues.⁵⁷

In about 1973, Sholl became interested in the theory of nuclear spin relaxation in solids due to the dipolar interactions of species undergoing translational diffusion.⁵⁸ Since that time he has made a number of significant theoretical advances in this area. The nuclear relaxation rates predicted by the diffusion models he has developed have been widely used in the interpretation of NMR measurements on interstitial hydrogen and deuterium in transition metals. More recently, he has contributed to the theory of nuclear spin relaxation due to paramagnetic ions in crystals.⁵⁹

2.5 NMR diffusion in the Australian physics community

The foregoing sections have described the origin of NMR work by Australian physicists, and its spread over more than thirty years. There are, after that time, only three laboratories where physicists now pursue NMR experiments, and one outpost of NMR theory in Armidale.

The work begun at the University of New South Wales in the early 1950s has continued. It has been fertilized from the smaller Monash group, and has, in its turn, trained most of the staff working on NMR in CSIRO's Sydney laboratories. Monash is the other source of personnel for the CSIRO group. NMR activity at Monash diminished after Wilson's time and well before Street left (to become Vice-Chancellor at the University of Western Australia) in 1978. The spectrometer has not been upgraded, and although used occasionally, it is no longer a research instrument. The third active group in Australia is situated in CSIRO's Melbourne laboratories, ironically adjacent to the Monash campus, where materials science (some of it in collaboration with Monash chemists) provides many opportunities for NMR experiments.

The observer is led to question why the NMR methods are confined to so few of Australia's physics laboratories, when, as we shall see, they have become commonplace in chemistry. The instrumentation required for research in this area has always been expensive. When NMR experiments were new (in the 1950s), this was clearly a great disadvantage, but it fails to explain their sluggishness in the financial hothouse — relatively speaking — of the 1960s and early 1970s. There were three sites of initiation for the sub-discipline of NMR in Australia — UNSW, CSIRO Melbourne and Monash University — and it is notable that all of the present groups can trace their heritage to these beginnings. Is this per-

haps because theory and practice are so difficult, so that an NMR apprenticeship is mandatory, or because the techniques are of limited applicability?

Since no special difficulties are claimed in published work — at best none that cannot be overcome by rigorous applications of theory, technical facility and financial aid — the latter is the more likely cause. Nuclear magnetic resonance, in the hands of Australian physicists, has been a solution in search of problems. Much NMR work of the first two decades involved the study of water — often water associated with some animal, mineral or biological materials — and the actual *results* of NMR experimentation have not been important milestones in the development of Australian science. The same could be said of NMR applications to solid-state physics in other parts of the world; so the Australian situation was not unique. Writing in the late 1980s, however, we see indications that this situation could change. In contributions to NMR theory and the development of instrumentation, Australian physicists have made more lasting contributions, to which we hope we have given due recognition above.

3. The Chemists

3.1 Overture

If there was a bridge between NMR physicists and chemists, it was the spectrometer operated in the CSIRO Division of Tribophysics by Dr Geoff West and discussed in Section 2.3. A Varian 0.8 Tesla magnet was purchased in 1958 and a spectrometer constructed about it, operating at 33 MHz for ¹H resonance. There was no flux stabilizer and the instrument was used for solid-state work; for example, a study of β -brass.⁶⁰ The first chemist to cross the bridge was Bill Forbes, who was Principal Scientific Officer at the CSIRO Division of Protein Chemistry, in Parkville, from October 1959. Forbes had collaborated previously with Gib Bogle,⁶¹ and it was through Bogle that he learned of West's spectrometer. It was situated just over one kilometre away on the campus of Melbourne University, where Tribophysics had a building to the south of the Chemistry School. Forbes arranged in 1961 for the purchase of a flux stabilizer for the spectrometer, and initiated a study of solvent resonance line widths for water, methanol and ethanol sorbed by wool.⁶² The work was submitted for publication in September 1963, by which time Forbes had taken up an appointment at Waterloo, in Canada.⁶³ One of his co-authors on that paper was Howard Bradbury, whose later work also appears in this account.

Two Melbourne University graduate students in chemistry had spectra run on West's spectrometer in the early 1960's, but the results were inconclusive and so never found their way into publication, although they are mentioned in theses. George Baldwin, working with Don Stranks, obtained spectra of beryllium fluorides, which were also recorded later on the Monash instrument.⁶⁴ Valda McRae⁶⁵, who worked with Tom O'Donnell, mentions spectra of an SbF_6Br species, but no other details are available.

The major users of NMR were to become the organic chemists, and their interest was extensively aroused by a Varian spectrometer on display at the first IUPAC Congress on the Chemistry of Natural Products, scientific sessions of which were held in Sydney and Melbourne in August 1960.⁶⁶ The Varian company brought to Sydney for a few weeks their new model A60, which recorded ^1H resonance at 60 MHz in the field (1.4 Tesla) of an electromagnet. Stability was maintained by a field-frequency lock established with a capillary of water built into the probe adjacent to the 5mm sample tube. The volume of solution required was 0.5 ml, and temperatures other than ambient could be established by a stream of gas flowing past a heating coil, a thermostat and finally the sample. Spin-decoupling was available, and signal enhancement through

spectral accumulation followed within a few years.

This 1960 conference was also notable for an interview with Australian Arthur Birch, then Professor of Organic Chemistry at Manchester, which was published in the *Melbourne Herald*.⁶⁷ Birch gave his reasons for working outside Australia as better opportunities in general and, in particular, access to such facilities as NMR spectrometers. His talk on the structure elucidation of geijerine showed exactly how NMR and mass spectrometry could be used by organic chemists.⁶⁸

3.2 The first commercial spectrometers

It was nearly another year, however, before Australian chemists were able to place their first orders for Varian NMR spectrometers with the local agent, H.B. Selby, and it was 1962 before these instruments arrived in Australia (see Table 1). There is some uncertainty about the exact date, but the University of Queensland seems to have been first in the field when their A60 arrived in February 1962. The first publications resulting from its use were those of Dr Ray Carman,⁶⁹ who joined the Department of Chemistry in 1961, having already had considerable experience with applications of NMR to organic chemistry.⁷⁰ Physical organic chemist, Peter Wells, used

Table 1: Varian NMR spectrometers in Australia, 1961–62

Institution	Ordered	Delivered	Operation	Cost (£)	Model
Univ. Qld, Chemistry Dept.	16.11.61	Feb 62		11,025	A60
Monash Univ.	April 61	Jan–Feb 62	Mid Mar 62	24,289	DP60*
Univ. Adelaide Org. Chemistry Dept.	June 61	Jan 62	Later Mar 62	21,444	DP60
CSIRO Div. Coal Res.	–	–	Mar 62	–	A60
CSIRO Div. Organic Chem.	30.1.62	18.4.62	–	10,998	A60
Univ. W.A. Org. Chemistry Dept.	–	June 62	–	–	A60
Univ. of Sydney Org. Chemistry Dept.	–	Aug 62	–	13,000	§ A60
Univ. Melbourne Org. Chem. Dept.	approved 1961	Sep 62†	–	25,000	HR60
CSIRO Div. Chem. Phys.	–	April 62	–	19,150	HR60
Univ. of N.S.W. Chemistry School	–	June–July 62	–	–	A60

* upgraded to HR-100, Sep. 62 and to HA-100, 1966

† earliest record

§ budget for purchase

this instrument extensively over the next few years in his work with nitro-compounds.⁷¹ The electronics technician who looked after the Queensland instrument, Noel Harris, later became Varian's field engineer in Australia. Chemists at Monash University, just beginning their second year of teaching, were next. Writing in 1986, R.D. Brown, foundation professor at Monash, recalled:

I therefore looked for something that would look slightly special about the department and hit on the idea that we should get one major facility that might not be available in many other places. I decided on an NMR spectrometer and was able to get agreement from the Vice-Chancellor and Council for spending what was then a very large sum of money on such a machine.⁷²

The cost of the spectrometer — over £24,000 — was comparable to the annual budget for the Chemistry Department — £33,000 in 1961. The spectrometer purchased by Monash was the more expensive model, DP60. This dual purpose spectrometer did not have a field-frequency lock, but was equipped for high-resolution ^1H resonance at 60 MHz and for a wide-line NMR with a range of other nuclei, made possible by a variable-frequency rf unit and several probes. It was installed by experienced Varian field engineer 'Cappy' Joller, and research began with Michael Heffernan and Ph.D. student Peter Black.⁷³ Between his graduation from Melbourne University (Ph.D. 1959, supervisor R.D. Brown) and his appointment at Monash, Heffernan worked at University College, London, with D.P. Craig and R.F.M. White. One topic of his research was a high resolution NMR study of phosphonitrilic halides,⁷⁴ but at Monash he took up the study of nitrogen and oxygen heterocyclics. Brown and his colleagues had performed quantum-mechanical calculation on such systems,⁷⁵ and NMR studies were intended to explore the relationship between ^1H chemical shift and calculated charge density or localization energy. The spectra proved in many cases to be quite complicated, and this led to Heffernan and his students becoming expert in spectral analysis using the iterative program LAOCOON.⁷⁶

In September 1962, the Monash spectrometer was upgraded to 2.39 Tesla, becoming a model HR100 capable of ^1H resonance at 100 MHz, with line widths typically no more than 0.5 Hz. This involved a new magnetic field homogeneity control unit, new pole pieces, increased magnet current and slim (2.5 cm) probes, thus improving resolution but ruling out the use of wide-line probes in the instru-

ment. The modification was performed by Varian's Glen Engler, assisted by Gary Van Wessem from the Australian agent for Varian, H.B. Selby. Apart from ^1H resonance, the instrument (Fig. 5) was successful in recording ^{19}F (94.1 MHz) and ^{31}P (25.1 MHz) resonances; but the lack of signal-averaging meant that ^{13}C NMR was out of the question for non-enriched samples.

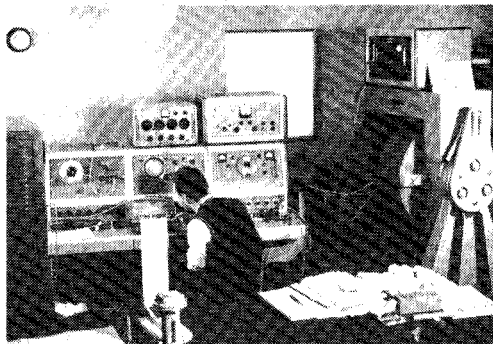


Figure 5 Michael Heffernan and the Varian HR60 at Monash.

The HR-100 was further modified to HA-100 by the addition of internal field-frequency lock based on a strong ^1H resonance; for example, that of $(\text{CH}_3)_4\text{Si}$ in the sample. This occurred in 1966, shortly after replacement of a blocked cooling coil in the magnet, and the resulting resolution was 0.28 Hz in frequency sweep and 0.22 Hz in field sweep mode. The spectrometer served the Department well until it was decommissioned in 1979, the magnet being sold to Melbourne University.

The University of Adelaide also purchased a less-than-routine spectrometer — a Varian DP60, at about twice the price of an A60 — and it went into operation in March 1962 under the supervision of J.M. Clark-Lewis and Tom Spottswood. NMR had already been a subject of great interest in the Department of Organic Chemistry for some years; the spectrometer was housed there, with Physical and Inorganic staff having some time allocated to them. Professor Geoffrey Badger had included a ^1H NMR spectrum in his book written in the late 1950s,⁷⁷ and graduate student Alan Moritz gave the first Departmental seminar on nuclear magnetic resonance, drawing examples from the then-small literature.

Lloyd Jackman was Adelaide's first Ph.D. graduate in Organic Chemistry (1951, supervisor G.M. Badger), and he subsequently became a staff member of Imperial College, London, where he took up the study of nuclear magnetic resonance. His book was one of the early texts which catered for organic chemists who wished to use this new technique in the

late 1950s and early 1960s.⁷⁹ Jackman spent three months as a visitor at Adelaide towards the end of 1959, following which Clark-Lewis spent a period of leave at Imperial College (Oct 1960–May 1961), where he applied NMR methods to the study of flavan derivatives, which formed the major part of his later work.⁸⁰ Clark Lewis was appointed to the chair at Flinders in 1963, and the arrival of their first students in 1966 was followed closely by the installation of a Varian A60 in their new department. In 1982, Flinders purchased from Adelaide University their original NMR spectrometer, which had been upgraded to DP60-IL (internal lock) not long after it was installed. T.M. Spottswood, his initials singularly apposite for a NMR spectroscopist, was an Adelaide Ph.D. graduate (1959, supervisor G.M. Badger), who was appointed to a lectureship in 1962 with the understanding that he should undertake NMR work, which duty he indeed undertook with conspicuous success.

Before his appointment at Adelaide, Spottswood was one of a group of young scientists at the CSIRO Division of Coal Research, North Ryde, who were pressing for the purchase of a nuclear magnetic resonance spectrometer. The others were Jim Shannon and Sev Sternhell, and their efforts were successful — the A60 went into operation early in 1962. Sternhell had returned to the Division in December 1961 from Imperial College, where he had completed his Ph.D. with Derek Barton and had become acquainted with applications of NMR to organic chemistry. In Sydney, he worked consistently in this field, and co-authored the second edition of Jackman's book.⁸¹ He moved in 1965 to the Department of Organic Chemistry at the University of Sydney, succeeding Ern Ritchie as Professor in 1977, while Shannon turned his attention to mass spectroscopy and went to a chair at the University of NSW, from which he retired in 1986. While at CSIRO, Sternhell worked with coal and coal-derived products, and also collaborated heavily with other organic chemists, contributing much to the development of magnetic resonance in Australia. His work was marked by close attention to line-width and resolution in ¹H NMR spectra, and among many other interests, he has continued to study long-range spin-spin couplings in allylic and benzylic systems.⁸² The spectrometer with which he began his work (serial numbers: console 218, magnet 207) arrived in March 1962, being later moved to CSIRO's Division of Applied Chemistry in Melbourne in 1971 and, after some further years of service, to the Museum of Victoria.

The CSIRO Division of Organic Chemistry, located at Fisherman's Bend in Melbourne, took delivery of its A60 in April 1962

(console 210, magnet 216). This new venture received strong support from Denis Horn, who joined the Division in December 1961 from DSIR in Pretoria. Horn spent 1958 on leave in Washington D.C., working with E.C. Horning on alkaloid chemistry at the National Institutes of Health. He spent a short time also with Varian Associates in Palo Alto, California, where he worked with Jim Shoolery. Back in South Africa, the DSIR spectrometer, a Varian HR60, was in the hands of the physicists, so the NMR section of Horn's work on diterpenes was shared with LeRoy Johnson of Varian.⁸³

When Horn arrived in Melbourne, he found plans afoot to establish an NMR centre at Melbourne University under the auspices of Professor Lloyd Jackman, who had been appointed but had not yet arrived to take up the chair of Organic Chemistry. The chief of Horn's Division, J.R. Price, and his deputy, J.M. Swan, were persuaded, however, to get their own spectrometer, which was delivered in record time. Early work with it involved structure elucidation,⁸⁴ part of the search for medicinal compounds in Australian plants,⁸⁵ and significant work on the chemistry of organo-aluminium compounds.⁸⁶ Tom Batterham, already experienced in the use of NMR in flavonoid chemistry, worked in the Division for two years before moving to the Australian National University in 1965. His book on NMR spectra of heterocyclic compounds appeared in 1973 shortly after his death.⁸⁷

Another significant contributor to NMR studies with organic natural products was Stan Johns, who came to the Division in 1964. Johns had learned to use an A60 during his postdoctoral years at the National Research Council in Ottawa. Although in the same building as Schneider and Bernstein,⁸⁸ Johns had worked with Leo Marion, Ted Edwards and a fellow postdoc., New Zealand-born R.A. Bell. Johns continued to be a major contributor of ¹H and ¹³C NMR work until the time of his death in 1986.⁸⁹

In Melbourne, the CSIRO chemists provided occasional spectra for their colleagues in universities and also set up a commercial NMR service for researchers at ICI and Monsanto, the spectra being run after November 1964 by an RMIT student, John Saunders, who worked an afternoon shift ending at midnight or after.⁹⁰ Saunders left the Division in 1967 and took his Ph.D. at McMaster University in Canada, working with Johns' former NRC colleague and old friend Russell Bell, on nuclear Overhauser effects, and publishing seminal papers in this area.⁹¹ His subsequent career took him to the Universities of Sherbrooke and New South Wales (Director of NMR Service, 1981–1985), and most recently to the Division of

Biological Sciences of the National Research Council of Canada, where he occupies an office near the old A60 room where Johns and Bell won their spurs.

On the other side of the country, the University of Western Australia also had an early Varian A60 (console 235, magnet 231), which arrived in June 1962. It was mainly used by students elucidating diterpene structures in graduate work directed by White and Jefferies,⁹² although other staff members did use the instrument (Fig. 6). It was sold to Murdoch University in 1981, just ten years after UWA purchased their Bruker HX90 spectrometer.



Figure 6 M.W. Fuller at the controls of the Varian A60 in Perth. Photograph courtesy of Perth *Sunday Times*.

Sydney University's A60 spectrometer (console 295, magnet 285)⁹³ arrived in August 1962 in time to be part of the *Tools of Science* exhibition, which was mounted in the Chemistry School as an adjunct to the ANZAAS Jubilee (75 years) Congress of that year.⁹⁴ Much of the pressure for the purchase came from Alex Robertson, who joined the Organic Chemistry Department in September 1961. Robertson completed his Ph.D. at Sydney in 1957 (supervisor A.J. Birch, who moved to Manchester before Robertson had completed his studies), and his postdoctoral career was divided between the National Research Council of Canada in Ottawa (1957–1959 with Dr Leo Marion) and the U.S. National Institutes of Health in Washington D.C. (1959–1961 with Bernhard Witkop). Robertson had used NMR in his work with Witkop, had attended the NMR conference at Stanford University, which marked the opening of the Stauffer Laboratories in April 1961, and had visited Varian Associates in Palo Alto on his way back to Australia. These experiences are reflected in his published work.⁹⁵ In late 1961, he and Dr Ritchie applied to NIH for money to purchase an NMR spectrometer for Sydney. They learned early in 1962 that their application had been unsuccessful, but Vice-Chancellor Stephen Roberts

made the sum of £30,000 available to Chemistry to allow the purchase of an A60 NMR spectrometer and also an electron spin resonance spectrometer to be used by Dr Lyons, who shortly thereafter moved to the University of Queensland. The Sydney NMR instrument served mainly the organic chemists at Sydney University and at the neighbouring University of NSW.⁹⁶

In that marvellous year of 1962, a Varian NMR spectrometer also arrived at the University of Melbourne. In negotiations with their new Professor of Organic Chemistry, Lloyd Jackman, the University agreed to purchase an NMR spectrometer and a mass spectrometer. The exact date of arrival of the Varian HR60 is not known, but the earliest operating record (6 September 1962) is in Jackman's handwriting, and it is likely that it was installed by the Varian field engineer who came to Australia to install the Sydney instrument discussed above. The department was a productive one, as Jackman's research group flourished; but one of its first applications was the completion of a structure elucidation by R.G. Cooke.⁹⁷ Some earlier spectra for this project had been provided by C.S. Barnes, an Australian organic chemist (CSIRO, later CSR Chemicals) who was spending a period of leave at Stanford University.

The one instrument purchased in this period primarily for use by non-organic chemists was a Varian HR60 for the CSIRO Division of Chemical Physics, which was installed in the Fisherman's Bend laboratories in 1962 and which moved with the Division to Clayton in October 1964. Lloyd Rees, Chief of the Division, had noted in the early 1950s that NMR was likely to be useful for investigating the structures of solids, and in April 1956 he went to California to pursue the idea. He visited H.M. McConnell, C. Holm and C. Reilly at the Shell Development Laboratories in Emeryville, and also C. Kittel and C. Kip at nearby Berkeley. Rees returned to Australia convinced that his Division must have NMR facilities; but funds were so short that it was 1960/61 before an order could be placed. In 1959, however, Rees encouraged one of his staff, Clive Coogan, to take up a fellowship to work with NMR pioneer H.S. Gutowsky at the University of Illinois. Coogan returned to the Division at the end of 1961, just ahead of the HR60. It was used exclusively with solids,⁹⁸ although Coogan also made theoretical studies of complex spin systems which were more relevant to liquid-state NMR.⁹⁹

The final instrument to be discussed in this section was the A60 delivered to the University of New South Wales in June or July of 1962. It is hard to reconcile this date with the infor-

mation that some spectra were provided by the Sydney spectrometer which arrived in August of that year! Published work from the UNSW spectrometer was very slow to appear, however, despite the fact that the Organic Chemistry Department was then in its heyday, and NMR results obtained in other laboratories were included in the work of Eade and Simes.¹⁰⁰ Peter Clezy was first into print with 'local' spectra, recorded by Vic Pickles on the Varian A60.¹⁰¹ The spectrometer was 'retired' in 1978 to the School of Physics, where it continued to serve for undergraduate laboratory teaching. In the late 1960s, the department recruited J.D. Stevens, whose important paper with Lemieux had spectacular effects on the field of carbohydrate chemistry.¹⁰²

A significant event for organic chemists in Australia in these early NMR days was a one-day symposium arranged by CSIRO as part of their series of Annual Discussion meetings. It was held in Melbourne on 22 February 1963, and attended by 120 scientists from Adelaide, Melbourne and Sydney.¹⁰³ The names of speakers already mentioned in this account include Jackman, Spotswood, Sternhell, Robertson, Moritz, Coogan, Heffernan and Horn; the only other speaker was W.C. Taylor from Sydney University. These people, and a few others, also made up the NMR section of the Fourth Australian Spectroscopy Conference, held in August 1963 in Canberra.¹⁰⁴ Thirteen papers were devoted wholly or in part to NMR spectroscopy, a substantial increase over the single paper (Coogan and Gutowsky, on ^1H and ^{23}Na spectra of solid NaSH) given at the third conference which was held in Sydney in August 1961.¹⁰⁵ The ANZAAS Congress held in Sydney in August 1962 had featured only five NMR papers, one of them by L.F. Johnson, who was visiting from Varian, U.S.A.¹⁰⁶

In eight out of these ten cases, the NMR spectrometers were purchased by chemistry departments in which one or more of the staff had already become familiar with the use of NMR spectra and the operation of the spectrometer in overseas laboratories. Although they covered a range of complexity, the spectrometers were essentially 'turn-key' systems, and advances made by chemists consisted not in theory or instrumentation — in contrast to the physicists — but in the chemical significance of the results they obtained with their new instruments. Determining the structure of an organic molecule — a task which might have taken months or, in cases of classical difficulty, years of a scientist's time and many grams of material — could now often be accomplished in an hour or two, using less than one tenth of a gram which was recovered unchanged from the NMR experiment. Since

the determination of molecular structure is at the heart of organic chemistry, it is little wonder that the NMR technique was so widely adopted in Australia, as it was in many other countries. As will be seen in the next section, this led several other companies to join battle with Varian as suppliers of NMR spectrometers.

3.3 Market penetration by spectrometer manufacturers

The rush of initial purchasing was followed by a two-year lull, which was broken in 1965 when two of the newer institutions purchased instruments from a company which had just entered the NMR field (Perkin-Elmer). Varian continued to do well, however, with seven more sales before yet another competitive range of instruments appeared on the scene. This third entrant (JEOL) was to capture most of the Australian market for small (up to 90 MHz) NMR spectrometers by the end of the 1970s. The final company to appear on the Australian scene (Bruker) did not make its first sale until 1971 but, by the mid-1980s, had come to dominate the upper end of the market. Sales by these four companies, including model number and initial location, are listed in Table 2. The list is as complete a compilation of installations to the end of 1986 as could be achieved, with the possible exception of some Varian instruments purchased in the middle years, for which no company records have survived.

3.3.1 Perkin Elmer

Varian's Australian monopoly was broken by the British company Perkin-Elmer, who installed two of their R10 spectrometers at the Australian National University in January 1965. This 60 MHz ^1H NMR spectrometer used a 1.4 T permanent magnet developed by Perkin-Elmer in conjunction with Mullard (latter Swift-Levick). Like the early Varian models, it was a vacuum tube instrument. A transistorised version, the model R20, was developed a few years later by the Japanese company Hitachi, under a cross-licensing agreement. Perkin-Elmer were thus first in the field with permanent magnet instruments, being also first with a 2.1 T (90 MHz for ^1H resonance) permanent magnet in their model R32. Two of these 90 MHz instruments were sold in Australia, to chemists at Monash and La Trobe Universities.

Spectrometer sales were stimulated by instrument displays at International Symposium on Electron and Nuclear Magnetic Resonance (Fig. 7), sponsored by the Australian Academy of Science and held at Monash University in 1969.¹⁰⁷ Perkin-Elmer engineer, Peter Dean, came to Australia to demonstrate

Table 2: NMR instruments in Australia 1965–1986

Year		Perkin Elmer		Varian		JEOL		Bruker
1964	R10	ANU-JCSMR ANU-Chemistry						
1966		—	A-60 HA-100 HA-100 HA-100-11	Flinders Melbourne CSIRO-Organic Def. Stds. Labs (now MRL)		—		—
1967		—	HA-60-1L HA-100 A-60d	New England Sydney La Trobe		—		—
1968	R12	Vic. Coll. Pharm.	A-56/60	Monash	JNM-4H-100 JNM-4H-100 JNM-C60HL	Tasmania UNSW ANU-Res. School Chem		—
1969	R20 R12	Newcastle Syd. — Pharmacy	T-60 T-60	La Trobe Adelaide	—	—		
1970	R12	Sec. Teacher Coll. Melb. (later Melb. CAE)	T-60	CSIRO — Animal Health	JNM-PS-100 JNM-PS-100 Minimar 100	Queensland NSWIT James Cook		—
1971	R12 R12A R12A	Melbourne RMIT Toowoomba	XL-100	Sydney (upgraded to FT 1975)	JNM-MH-100 JNM-MH-100	James Cook ANU — Res. School Chem.	HX-90	W Australia
	R12A R20 R20B	SAIT	SAIT	WAIT			JNM-MH- 100	Queensland
1972	R24	Caulfield I.T. (now Chisholm)	EM-360	Sydney	JNM-MH-100	ANU-Chemistry		—
1973	R24 R12B	Wollongong Swinburne I.T.	T-60	ANU-JCSMR	JNM-PFT-100	La Trobe	WH-90 HX-90E	Monash Adelaide

Table 2: NMR instruments in Australia 1965-1986

Year	Perkin Elmer		Varian		JEOL		Bruker	
1974	R12A	Footscray I.T.	EM-360	Queensland			WP-60	UNSW
	R12A	Geelong (Gordon Inst. now Deakin)	T-60	CSIRO — Textile Physics Geelong				
	R12A	Ballarat CAE					HX-90	Sydney
	R12A	Warrnambool IAE						
	R12B	Caulfield I.T.						
	R24A	Queensland — Pharmacy						
1975	R24A	La Trobe	CFT-20	Sydney	JNM-PMX60	ANU — Res. School Chem.	HX-90	Griffith
	R24A	CSIRO — Animal Physiol	CFT-20	CSIRO — Organic	JNM-PMX60 JNM-FX60	Adelaide ANU — Res. School Chem.	HX-270	National NMR Centre
1976	R24A	W Australia	EM-360	Queensland				
	R32	Monash						
1977	R32	La Trobe			JNM-FX60Q JNM-FX100	Sydney Melbourne	WP-80/DS	W Australia
1978			FT-80A	Prince Charles Hosp. Brisbane	JNM-PMX60	Inst. Med. Vet. Sci. Adelaide	WP-80/DS	Adelaide
					JNM-FX60Q JNM-FX100 JNM-FX100	James Cook UNSW — Biochem Queensland		
1979			CFT-20	ANU			HX-90R	Monash
			XL-200	Macquarie			WP-200	BHP Melb.
							CXP-200	Res. Labs CSIRO — Food Res.

the R12 at Monash, and then at another conference in Sydney, before installing it in the Pharmacy Department of Sydney University in September 1969. Two years later, Dean emigrated to take up a position with Perkin-Elmer in Australia, where he is now Service Manager.



Figure 7 Postmark commemorating the international meeting.

Details of Perkin-Elmer NMR sales world wide are given in Table 3, which was compiled from information supplied by their Australian subsidiary. During the decade from 1967, they held about 25% of the market for which they competed, but this activity was insufficient to generate the funds which would sustain development at the rapid pace being set by other manufacturers. Perkin-Elmer sold only a few of their model R34, which had a 5.1 T superconducting magnet (they never did mar-

ket an electromagnet instrument) before quitting the field of nuclear magnetic resonance in 1979.

Their most active period in Australia was 1973–4, when they sold six instruments to the Victoria Institute of Colleges for installation at Swinburne, Caulfield, Footscray, Geelong, Ballarat and Warrnambool Colleges of Advanced Education. Victoria was their happy hunting ground, since 14 of their 27 sales were in that state, where the company had its Australian headquarters. Most of these spectrometers were still in use in the mid-1980s, some of them eighteen years old.

Although Perkin-Elmer retired from the field, their collaborators at Hitachi continued to offer spectrometers for sale in Australia through local agents.¹⁰⁸ One went by this route to the University of the South Pacific in Fiji, and others (R24B) to the Universities of Western Australia and New South Wales.

3.3.2 Varian

Despite competition from Perkin-Elmer, Varian spectrometers continued to sell well in the second half of the 1960s. By then, most of them were 100 MHz instruments which were purchased by chemists because they offered increased sensitivity and dispersion. One of the exceptions was Noel Riggs, at the University of New England in Armidale, who once commented to one of the authors that he preferred 60 MHz spectra because unravelling them was 'more fun'. He hastened to add that they also contained more information, such as signs of coupling constants, which could be extracted by careful analysis. Work of this type had been done with aromatic systems by Hefner's group at Monash,¹⁰⁹ and Riggs and his

Table 3: Perkin-Elmer NMR spectrometers

Model*	¹ H Resonance Frequency	Year of Introduction	World Sales	Australian Installations §
R10	60†	1961	100	1965 (2)
R12	60	1967	350	1968 (1), 1971 (3) 1969 (1), 1973 (1) 1970 (2), 1974 (5)
R14	100	?	?	nil
R20	60	?	?	1969 (1), 1971 (2)
R24	60	?	?	1972 (1), 1975 (2) 1973 (1), 1976 (1) 1974 (1), 1981 (1)
R32	90	1972	150	1976 (1), 1977 (1)
R34	220	1976	7	nil

Sub categories not given e.g. R12A and R12B reported as R12

† Some early R10's operated at 40 MHz

§ Reported as year (number of installations)

students produced results of high precision with cyclic aliphatic systems just a few months after their Varian HA-60-IL was commissioned.¹¹⁰

Within a few years, however, Varian lost the market for the higher field spectrometers to JEOL (100 MHz) and Bruker (90 MHz). Since most of the 60 MHz sales went to Perkin-Elmer, the seventies were lean years indeed for Varian NMR in Australia, as they were all over the world.¹¹¹ To some extent, this was true of the parent company as well, so it is pertinent to summarise Varian's NMR history here.

Varian Associates was founded in California by two brothers in 1948, their initial products being klystrons for generation of microwave power, and fluxmeters which were the forerunners of modern nuclear magnetic resonance spectrometers. As purveyors of NMR instruments, they dominated the 1950s and 1960s, introducing most of the world's structural chemists to the power of NMR methods. The company had always been cautious about introducing new products into the market place, and this ensured that the high costs of company research and development had to be passed on to customers. When buyer resistance to top-of-the-range spectrometers was encountered, Varian placed most of its effort into smaller instruments, for which there was a very much larger market. Thus the T60, a permanent-magnet instrument of the late 1960s, was followed in the early 1970s by EM360 and EM390 (60 and 90 MHz ^1H spectrometers, respectively), which are still marketed in the mid-1980s. In this field, however, there was stiff competition from Perkin-Elmer and JEOL, while the latter company and Bruker grew fat on sales of higher-field instruments. Varian's XL100 was an excellent spectrometer, but aggressive marketing by its Japanese and German competitors prevented it achieving the hegemony which the A60 had enjoyed a decade before.

Varian finally realised that there was money to be made at the upper end of the market, and internal reorganisation of the company removed some of the diversity (mass spectrometers, for example) which had grown in place of NMR interests. The result was a series of high field spectrometers with superconducting magnets, beginning with the XL200, and this has restored some of Varian's competitiveness.

To return to the 1960s, however, Varian were first to develop high resolution pulse Fourier transform instruments, and they hold the original patents in this field. Chemists were not especially interested, however, until they began to rely more on carbon magnetic resonance.¹¹² The low receptivity of this nucleus

($\gamma_{\text{C-13}}/\gamma_{\text{H-1}} = 1/4$) and its low natural abundance (1.1%) required repetitive scanning and data accumulation, to which FT methods were ideally suited.

Before the FT revolution, a number of chemists used continuous wave methods to obtain ^{13}C spectra. In 1969, the Australian Research Grants Committee provided funds for Professor Riggs to bring the New England 1.4 T spectrometer under control of a Varian 620i computer for the recording of ^{13}C spectra.¹¹³ His colleague in this work was David Doddrell, a Queensland graduate who returned to Australia as a Queen Elizabeth Fellow after extensive experience in the United States with J.D. Roberts (California) and Adam Allerhand (Indiana).¹¹⁴ From New England (1971–1974), Doddrell moved to the new Griffith University, where he established a strong NMR group and rose to the rank of Professor, before moving in 1986 to a chair at the University of Queensland.

At Fisherman's Bend in Melbourne, CSIRO chemists Stan Johns and Ian Willing also took this route, upgrading their HA100 (2.3 T) instrument to Spectrosystem 100 by the addition of a Varian 620i (later 620L) computer, and obtaining good carbon spectra. An example is that of the alkaloid shelhammerine (Fig. 8) which took a week to accumulate and covered two metres of chart paper!¹¹⁵

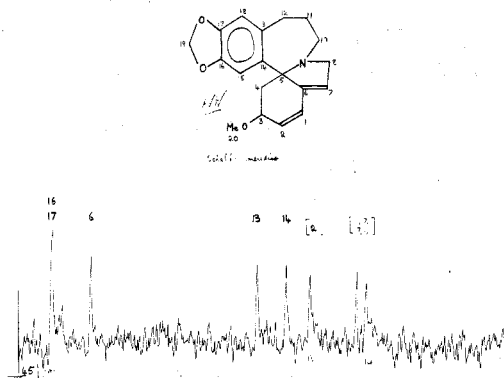


Figure 8 Carbon-13 spectrum of shelhammerine recorded by S.R. Johns and R.I. Willing at CSIRO.

By the time that Varian marketed their first dedicated ^{13}C instrument in 1972, it was clear that pulse FT provided the way forward. Two other Australian spectrometers were converted for pulse operation in the first half of the 1970s, but by that time a number of Bruker pulse FT spectrometers had been installed, beginning with the HX90 instruments at the University of Western Australia, which recorded 90 MHz ^1H spectra and 22.62 MHz ^{13}C spectra.

At Melbourne University, Dr David Kelly and Robert Craig in 1972 received ARGC fund-

ing to convert their old Varian HR60 so as to record ^{13}C resonance in the pulse FT mode, a task which took them two years.¹¹⁶ Such was their success that they got another ten years of service from this spectrometer, although during that time it received replacement magnet cooling coils, one each from defunct HA100 instruments at Melbourne and Monash Universities. Organic chemists at Sydney University took delivery of a Varian XL100 continuous wave spectrometer in 1971, and it was modified in the field by Varian engineers in 1975 to effect conversion to pulse FT spectroscopy.

Varian's permanent-magnet spectrometers, the EM-360 and EM-390 for ^1H resonance only, sold slowly in the 1970s, but sales have been brisk in the 1980s. The 60 MHz version, with 18 sold, is Australia's most popular NMR spectrometer. With larger spectrometers the company was less successful (Table 2), the XL-200 at Macquarie standing alone between the 100 MHz and 400 MHz sales to Sydney University in 1971 and 1985 respectively. Since then there have been four more Varian superconducting systems installed, with another five installed or ordered since 1986. Of particular note, and especially significant for Varian's re-emergence as an NMR power in Australia, is the trio of instruments sold to ANU, which are operated under the direction of Larry Brown in the Research School of Chemistry.

3.3.3 JEOL

The Japan Electron Optics Company began in

1949 with, as the name implies, manufacture of electron microscopes, a field in which it is still prominent. Leading from this magnet-based technology, they have developed mass spectrometers and electron spin resonance and nuclear magnetic resonance spectrometers — the first (JNM1) in 1956 — with great success.

JEOL (A/asia) Pty Ltd was established in June 1966, and their first Australian NMR sale was a 100 MHz (2.3 T) ^1H spectrometer, installed at the University of Tasmania in 1968. This was followed by a similar installation at the University of N.S.W. and a 60 MHz system at the Australian National University. These and subsequent sales are listed in Table 4, which was compiled from data supplied by the company.

The first Fourier transform NMR spectrometers to be installed for customers in Australia were JEOL models PS100, at the New South Wales Institute of Technology and at the University of Queensland, in 1970. These were hybrid instruments, also capable of operating in continuous wave mode, the first purely pulse FT JEOL instrument being the PFT-100, which arrived at La Trobe University in December 1973. La Trobe chemists also purchased an FX200, the first JEOL instrument to have a superconducting magnet, which was installed in December 1980; led by Bob Brownlee and Max O'Connor, they have made particular use of the multinuclear capabilities of this spectrometer.^{117,8} There followed six other superconducting systems of increasing sophis-

Table 4: JEOL NMR spectrometers in Australia

Frequency (MHz) for ^1H operation	Model numbers	Magnet*	Australian Installations
100	4H-100	E	1968(2)
	MH-100	E	1971(3), 1972(1)
	PS-100	E	1970(2), 1973(1)
	PFT-100	E	1973(1)
	PX-100	E	1977(1), 1978(2)
60	C60HL	P	1968(1), 1969(1), 1972(1)
	PMX60	P	1977(2), 1978(1), 1980(1)
	PMX6051	E	1982(2)
	FX60	E	1975(1)
	FX60Q	E	1977(1), 1978(1)
90	FX90Q	E	1978(1), 1983(1)
			1980(3), 1984(1)
			1981(6), 1985(2)
200	FX200	SC	1980(1), 1982(1)
270	GX270	SC	1986(2)
400	GX400	SC	1984(1), 1985(2)

* E = electromagnet, P = permanent magnet, SC = superconducting magnet

tication, half of them having 9.2 T magnets and operating at 400 MHz for ^1H resonance. The computing power of these larger JEOL spectrometers was initially limited by software development, but by the mid-1980s this awkwardness had been overcome.

From 1975 to 1979, JEOL placed six Fourier transform spectrometers with Australian customers, and then began sales of the very successful model FX90Q. Eventually, fourteen of these spectrometers were sold, making it the second most popular model ever marketed in Australia. All told, JEOL sold 45 NMR spectrometers in Australia and seven in New Zealand (two C60HL, three FX60, one FX90Q and one GX270/89) in the period 1968–1986.

3.3.4 Bruker

The 8th Australian Spectroscopy Conference held at Monash University in Melbourne in 1971 served to introduce the Bruker company to Australia, and also to encourage the growing interest of Australian chemists in ^{13}C .¹¹⁹ H.B. Selby, whose offices were located close to Monash University, had been agents for Varian until 30 June 1967, when that company set up its own organisation in Australia. Shortly afterwards, Ben Selby approached Bruker representatives at the ACHEMA meeting in Europe and secured for his company their Australia agency, from 1969. The first visible result was the demonstration of a Bruker HX90 spectrometer in the Monash first-year chemistry laboratory, where ^1H and ^{13}C spectra were recorded for eager customers.

The Bruker organisation has two foci in Europe, the one — Bruker Spectrospin AG — located in Zurich and concerning itself with high resolution instruments; the other — Bruker Analytische Messtechnik GmbH — operates at Karlsruhe and Silbersteissen in Germany, and is concerned more with high-power instruments for the study of solid samples. In this account, however, the company will be referred to as 'Bruker', because both types of instruments have been marketed through a common organisation. Selby remained the agent until October 1984, when Bruker strengthened its own organisation and opened a separate office in Sydney.

Although business was brisk for the HX90, delegates to the 1971 conference heard only three NMR lectures. The speakers were Alan Moritz, Bruce Cornell (see Section 2.4) and John Grutzner, one of Lloyd Jackman's former students from Melbourne University who had settled down at Purdue. Like David Grant in 1969,¹²⁰ Grutzner spoke about ^{13}C resonance and introduced many of his audience to the technique of off-resonance decoupling.

That same year, chemists in Western Aus-

tralia took delivery of a HX90 (not, however, a pulse/FT instrument), and the conference demonstration model was moved to Selby's demonstration area in Notting Hill, where a service was offered to interested users. The instrument was used in sales promotions, and there also grew up around it a small NMR group who held irregular meetings and went on to organise a series of national symposia. Operations at Selby's were in the hands of Max Greaves and Hans Holenweger, a Bruker engineer. So far, Bruker are the only company to have imported a spectrometer for customer service and sales. The original HX90 was sold to Griffith University when Doddrell went there in 1974. It was replaced with a HX90R, which was in turn sold to Monash in 1979.

Bruker installed their first Australian super-conducting system, the HX270, at the National NMR Centre in 1974. Although beaten to the next sale by Varian (the XL200 at Macquarie), Bruker have dominated sales of high-field spectrometers in the last decade, with installation of 19 spectrometers (to the end of 1986) compared to Varian's six and JEOL's seven.

3.4 The National NMR Centre

The dispersion afforded by the use of high magnetic fields generated by superconducting solenoids was appreciated most by polymer chemists; the first two such instruments in Britain, for example, were at ICI's Runcorn laboratories for Polymer and Petrochemical research. In Australia, no one institution could afford such an instrument, and there was support from the Polymer Division of the Royal Australian Chemical Institute, amongst others, for a national facility to be established.¹²² This was achieved in 1972 with a Commonwealth Special Grant of \$550,000, and the Centre opened in April 1975.¹²³ The selection of an instrument was in the hands of a committee, which met three times during 1973. The members were R. Street (Australian Research Grants Committee Chair), D.R. Stranks, G.W.K. Cavill and B.D.O. Anderson from ARGC, and discipline specialists S.R. Johns, D.M. Doddrell, S. Sternhell and J.R. Pilbrow (an electron-spin-resonance spectroscopist from Street's Department of Physics at Monash).

One strong proponent was Howard Bradbury of the Australian National University, who had been involved in some of the very early NMR work described above.¹²⁴ His interest had developed during a year as Visiting Professor at Cornell University, where he collaborated with Harold Scheraga on a study of the protonation of histidine residues in ribonuclease.¹²⁵ This was a heroic 60 MHz

study, which Bradbury continued upon his return to Australia, using the 60 MHz instrument with signal averaging (PDP-8) available to him at the A.N.U., and 'borrowing' time on 100 MHz instruments at Melbourne University and CSIRO's Fisherman's Bend laboratories.

For about five years, beginning in 1970, Bradbury was able to gain access to superconducting spectrometers in Britain and America, with support for travel and instrument time from the ARGC. Thus he was able to record spectra on Varian 220 MHz instruments (all CW) at Palo Alto, ICI Runcorn (access provided by the Science Research Council of Great Britain) and the Atomic Energy Research Establishment at Harwell. A period of leave working with David Phillips gave access to the pulse/FT Bruker HX270 instrument at Oxford University, which Bradbury continued to use until 1975, when Australia's National NMR Centre opened and he became its heaviest user. In this period and together with his students — Ray Norton and Larry Brown — Bradbury completed studies of ribonuclease, lysozyme, bovine α -lactalbumin and insulin.¹²⁶ Although Bradbury himself has now moved out of NMR work, his students form the largest identifiable group in Australia NMR today: Brown (ANU), Norton (UNSW), Fenn (Darwin), Galloway (Brisbane NMRC) and Carver (Wollongong).

Alan Jones, who had completed his Ph.D. at Monash with Michael Heffernan,¹²⁷ was appointed as officer in charge of the National NMR Centre, and a Bruker HX270 spectrometer was installed in February 1975. Jones had spent postdoctoral periods with Grant in Utah and Maciel in Colorado, and been a faculty member at the University of Alberta before returning to Australia. The Centre was initially equipped to run ^1H and ^{13}C spectra, with ^2H (deuterium) and ^{15}N capability added later. The facility was funded by the Commonwealth Department of Science and housed in the Department of Chemistry at the Australian National University. Samples were mostly to

be submitted by mail, for which containers and packing were supplied. At first, users were charged, but after the first full year of operation the ARGC granted time to applicants, and only non-grantees had to pay. There were remarkably few of these, industry and CSIRO users consuming only one to two percent each of the spectrometer's operating time. Little wonder: typical charges for such work were \$90/hour for industry and CSIRO and \$60/hour for non-ARGC university users.¹²⁸

At the first the Centre operated with a fixed charge for each type of spectrum; for instance (January 1977), \$15 for a routine ^1H spectrum, \$20 for a broad-band decoupled ^{13}C spectrum, and \$100 for overnight and weekend runs. The Centre soon came under government pressure to recoup a higher proportion of its operating costs (Table 5). Later a system of hourly charges was introduced: \$30 an hour for peak (attended) time and \$20 for off-peak (unattended) time in 1981, rising to \$35 and \$25 respectively in 1982. After approaches by some heavy users to the management committee, the Minister (Hon. David Thomson) approved rates of \$100 for overnight, \$175 for two nights and \$250 for a full weekend.

The workload of the Centre increased rapidly, as is shown in Table 6. Of particular note is the decline in ^{13}C usage when laboratories around Australia purchased pulse/FT spectrometers capable of such work, as described in earlier sections. At the same time, the demand for spectra of large bio-molecules increased, and ^1H spectra were required in this work. Since long runs or series of spectra were often involved, the combined result was a four-fold increase in the proportion of ^1H time in the first five years of the Centre's operation. Typical of such ^1H users were J.H. Bradbury, P.E. Wright and W. Moore, who were granted, in 1979, 900, 500 and 350 hours respectively of spectrometer time. The smallest user in this period was allocated 5 hours. It is little wonder that Jones was under extreme pressure from users who were suspicious that the 'first-come-

Table 5: Some Financial Details of Operation of National NMR Centre

Financial Year	Expenditure	Income from Service fees
1975/76	92,500	23,100*
1976/77	not available	2,200
1977/78	92,500	3,800
1978/79	118,200	15,900
1979/80	132,800	
1980/81	128,800	
1981/82	137,000	
1982 to Dec.	114,500\$	

* ARGC users were charged; after this, time was granted to successful applicants.

\$ Only \$70,000 of this was operating cost, the rest being allowed for dispersal of the staff and instrument.

Table 6: Spectrometer Usage at National NMR Centre (% of available time)

Year	Nucleus			Down Time	Free*
	¹ H	¹³ C	² H + ¹⁵ N		
1975	13	43	–	7	38
1976	12	38	5	16	29
1977	24	35	16	8	17
1978	37	39	12	2	11
1979	44	31	9	3	13
1980	45	35	8	4	7

* The initial agreement with Dr Jones was that 10% of time would be available to him for his own research which, in the event, often took the form of collaboration with other scientists whose work benefited from Jones' expertise.

first-served' policy of the Centre might not be working in their favour. Reflecting the nature of grant- and academic-years, samples were submitted at an increasing rate as each calendar year wore on, and waiting times stretched from a week to as much as eight weeks. Larger users, of course, were able to schedule work in advance, and a number of groups had operators trained by the Centre so as to allow their personal attention to the spectrometer at nights and weekends. In 1977–79, the Centre ran spectra on 240 samples for 55 users. This comparatively small number must be seen in the light that most of these were samples too difficult to be handled in local laboratories, so the Canberra work was often tedious or difficult—or both. A report by Jones in February 1980 identified 108 publications in which spectra recorded at the Centre had been reported.

From the beginning, the Centre was under the control of a management committee, as set down in a Memorandum of Agreement between the Australian National University and the

Commonwealth of Australia. The original five-year agreement of 5 February 1974 was renewed on 28 February 1979, but only until 31 December 1982 which, as we shall see, became the closing date of the Centre. The structure and membership of the management committee are shown in Table 7.

In September 1979, with superconducting spectrometers operating at 200 or more MHz (for ¹H resonance) beginning to appear in state universities, the Management Committee agreed to forward to the Minister a recommendation for upgrading of the Centre. The centrepiece of this proposal was the purchase of two new spectrometers: a Bruker WM500, only recently available, and an NMR instrument for measurements with solids, a Bruker CXP300. The total cost was estimated to be a little over \$900,000. Progress was slow, and in December 1980 Professor Swan, Chairman of the Management Committee, wrote to the Minister to press the Centre's case. He proposed the purchase of a WM-500 during 1981/82 and a CXP300 in 1982/83, concluding that unless

Table 7: Management Committee of the National NMR Centre

Category	Membership		
	Inception 1975	Jan. 1984	Jan. 80– Dec. 82
1. Two representatives of ARGC, one of whom shall be appointed chairman (listed first in columns at right).	D.R. Stranks K. Boardman	A.L.J. Beckwith E.O.P. Thompson	J.M. Swan R.G. Wake
2. One representative nominated by the Department of Science (later Science and Environment)	K. Creech	R.S. Goleby	R.S. Goleby
3. One representative nominated by ANU.	I.G. Ross	I.G. Ross	R.N. Warrener
4. One representative of another university, to be appointed by the other members.	S. Sternhell	S. Sternhell	D.M. Doddrell

something like this were done, 'the National NMR Centre will rapidly cease to be recognisable or viable as a national research facility'.

A meeting of the ARGC on 8 May 1980 had set up the following sub-committee to examine the NMR proposal: M. Brennan (ARGC Chairman), A. Sargeson, J. Wade, R.I. Tanner and R. Porter. This committee sought advice from a number of overseas experts — L.D. Hall, R.K. Harris, D.M. Grant, G.E. Maciel, R.E. Richards, E.D. Becker and D.H. Williams — and also received letters of support from a number of NMR practitioners in Australia. The matter dragged on, with ARGC requesting (and receiving in December 1980) a proposal to stagger spending so that \$152,000, \$96,000 and \$523,000 (for a WM-500) be spent over the next three years. On 18 August 1981, however, the Minister, Hon. David Thomson, wrote to Professor Swan with the news that the Commonwealth would not renew its agreement nor agree to fund the Centre beyond 31 December 1982. In his letter, he explained the action thus: 'Bearing in mind that there are now a number of nuclear magnetic resonance facilities around Australia with similar or superior capabilities to the National Centre, that falling demand for the facility and the Government's policy of minimising its involvement in activities which can be conducted by other organisations . . .'

The Committee of Management felt the pinch immediately, because insufficient funds were available to pay for travel of its out-of-Canberra members and the August meeting had to be minuted as 'informal', although Professor Swan and the Canberra members were present. The existing spectrometer was offered for sale to the University, who at first declined to purchase it, but at the eleventh hour agreed to buy it for joint service in the Department of Chemistry and the Research School of Chemistry. This arrangement persisted for slightly more than two years. Alan Jones returned from a short period of leave in the first few months of 1982, and in May received a letter from the A.N.U. Registrar in which he was given slightly more than his six statutory six months' notice. With nineteenth-century elegance, the letter began 'It is my melancholy duty to have to inform you . . .'.¹²⁹ Jones remained at A.N.U. for some time, teaching and compiling a report on medical NMR imaging, before moving to a position in the Department of Science.

3.5 Development of Modern Pulse Sequences

Modern NMR researchers have devoted much effort to obtaining simplified spectra from quite complex systems. Subsets of potentially massive data have resulted from the use of polar-

ization transfer and spectrum editing by means of carefully timed and oriented sequences of pulse.¹³⁰ One of the most successful sequences is DEPT — Distortionless Enhancement by Polarization Transfer — which was devised by a group at Griffith University,¹³¹ and is now supplied as part of the software package for most high-field spectrometers. The DEPT sequence involves three pulses at the ^1H frequency, and two at that of the (lower- γ) X nucleus, which has lower sensitivity and is the object of the experiment. This nucleus is commonly ^{13}C , although the technique has also found application with ^{29}Si . The inter-pulse delays are derived from the size of the H-X coupling constant, but the sequence (unlike many of its competitors) is fairly tolerant of mis-setting of this interval. The length of the final ^1H pulse is used to control the intensity of, say, the ^{13}C signal, and spectra may be produced with quaternary carbon signals nulled, with signals only for CH carbons, or with CH and CH_3 signals positive and CH_2 signals negative. Apart from the obvious value in interpretation because of selective omission of certain classes of peak from the resulting spectrum, the editing is accompanied by increased intensity because of polarization transfer from the highly polarized (more intense) ^1H nuclear spin systems.

More recent work on spectral editing by polarization transfer has come from a group at Sydney University,¹³² and other developments in multi-pulse NMR are the subject of recent research at ANU.¹³³ They represent, in the chemical arena, the combination of mathematical and instrumental skills which have been strongly characteristic of contributions by Australian physicists to the growth of NMR.

3.6 Applications of NMR to Medicine

Two types of NMR experiment are finding their way into clinical medicine. In each case the patient or the limb to be examined has to be inserted in the magnetic field generated by a large electromagnet or superconducting solenoid.

Magnet resonance imaging, formerly called zeugmatography¹³⁴ and now studiously avoiding the word 'nuclear' by adopting MRI as its acronym, is a technique with close similarities to X-ray computer-assisted tomography. Radio-frequency energy is applied to the sample by a pulse technique (the transmitter/receiver coil being wound outside the cavity), and the orientation of the secondary magnetic field thus created is varied in a systematic fashion. The result, after computer construction of an image, is a relaxation map of the tissue 'slice' being studied. The technique may be applied to ^1H ,

^{13}C , ^{31}P or ^{23}Na nuclei, but ^1H is by far the most common, and thus the image is mainly based on the presence and relaxation behaviour of water molecules in the tissue.

The MRI technique is safer than conventional tomography because X-rays are not involved. Although medical applications of the technique are only approximately ten years old, several hundred instruments have been installed around the world, and the available resolution in the image exceeds that of the X-ray technique. The first such instrument in Australia was installed in October 1985 at the Queensland Medical Magnetic Resonance Centre, part of the University of Queensland's Department of Radiology.¹³⁵

Formal consideration of MRI for Australia began with a Commonwealth report,¹³⁶ written in 1983 by Alan Jones, which recommended purchase and installation of three units for assessment; but the 1983 and 1984 Australian budgets failed to allocate funds for the purchases. Concern that adoption of the technique at private installations would force the hand of government brought pressure, which resulted in acceptance of a plan to fund the purchase of five to seven units in 1986–7. In February 1986, a private clinical MRI service did open in Sydney, followed in mid-year by government-funded centres in Sydney and Melbourne.¹³⁷

Physical scientists in at least two universities are involved in the further development of MRI. The National Health and Medical Research Council in 1981 had funded preliminary research by UNSW researchers,¹³⁸ and the leading Australian chemist in this field, David Doddrell, has recently moved from a chemistry chair at Griffith University to be Professor of Magnetic Resonance in the University of Queensland.¹³⁹ At present the technique is an extremely expensive one, with single examinations costing \$400–\$800, and concern has been expressed that installation of MRI instruments needs to be under government control in order that health expenditure may be contained.¹⁴⁰ Continued improvement can be expected in the results of MRI, but it seems likely to supplement rather than to replace X-ray tomography — itself a relatively new technique — in the near future.

The second clinical NMR technique uses a saddle coil placed on the skin of the patient, but the primary magnetic field is still provided by placing the limb, or even the whole body, inside a large magnet. The saddle coil is used, in pulse fashion, to excite spin systems from chosen volumes of tissue, which may be located well below the skin — for instance, in an organ such as the heart or a particular muscle. While ^1H studies are useful, more interest has been

shown in ^{31}P studies of such metabolites as ATP and phospho-creating, since resolution is more than adequate to separate the resonances of each molecule. The technique was pioneered by George Radda, at Oxford,¹⁴¹ and in Australia is performed only by the Queensland group headed by David Doddrell. Labelling experiments to follow the fate of particular molecules are relatively easy to perform using ^{13}C — and especially ^2H -labelled substrates.¹⁴²

4. NMR Conferences in Australia

After Selby Scientific installed the Bruker 90 MHz spectrometer at their Notting Hill showrooms in 1971, there began a series of informal meetings organized by people in the Melbourne area with interests in nuclear magnetic resonance. A degree of formality was added when the organisers — Stan Johns (CSIRO), David Kelly (Melbourne University), Bob Brownlee (La Trobe) and Ian Rae (Monash) — styled themselves the 'Melbourne NMR Committee' and opened a bank account to cater for the trickle of funds involved. The group convened at irregular intervals, often to take advantage of the visits by overseas and interstate speakers.

The committee was in close contact with Alan Jones, in Canberra, when he organised a nation conference in May 1979 and invited a number of overseas speakers including George Levy (Fig. 9) and Pierre Laszlo. This conference was a huge success, with 150 chemists and physicists in attendance, and the excess of income over expenditure was passed to the Melbourne Committee for the sponsorship of succeeding conferences.

Although the Canberra conference was advertised as the first, there had in fact been an earlier meeting, held at Selby's in October 1973 in conjunction with the Organic Group of

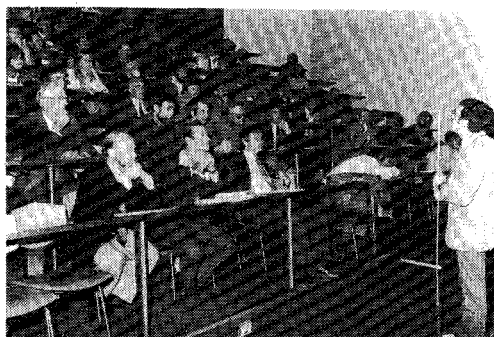


Figure 9 George Levy speaking in Canberra on the morning after the conference dinner. Photograph courtesy of the Australian National University ANU Reporter.

the Victorian Branch of the Royal Australian Chemical Institute. The speakers were Stan Johns, David Kelly and David Doddrell, and Bruker engineer Hans Holenweger.

This being the case, the conference held at the University of Queensland in August 1981 became the Third National NMR Conference, and subsequent meetings continued this sequence. In 1983, the Fourth conference was organised by a Melbourne group and held at Lorne in February — it coincided with the worst bushfires ever seen in that part of the country. The Fifth conference, organised by a Sydney group, was held in Terrigal in February 1985, and broke new ground by organising a pre-session in Sydney which dealt with medical imaging. At each of these conferences the plenary lectures were delivered by overseas and local speakers, and although most of the business was chemistry, there were sessions devoted to the work of physicists. The attendances were 130, 110 and 150 respectively, and in each case the accumulated funds were increased, so that enough money was available to help initiate the next conference and to assist the funding of visits to Australia by prominent NMR researchers in between conferences.

A further meeting was planned for Adelaide in 1987, but did not eventuate, and the next in the series was the February 1988 meeting held in Thredbo and organised by a group from Canberra. The attendance was 140, and the program showed a nice balance of physics and chemistry, which demonstrated clearly that the boundary line between the two was becoming less well-defined. This informal professional society, which has no links with organised societies such as the Australian Biochemical Society, the Australian Institute of Physics or The Royal Australian Chemical Institute, has proved most successful in bringing together biologists, physicists and chemists with mutual interests in NMR techniques. It owes its success to the energy of members of the Australian NMR community and to generous support from spectrometer companies and suppliers.

5. Concluding remarks

The development of NMR spectroscopic techniques has taken place over six decades — a period short enough to be experienced by an individual and long enough that their spread and influence can be monitored in a number of ways. The geographical position of Australian scientists makes them an ideal group in which to study this subject, and our impression is that the Australian story has much in common with those which could be compiled for other countries and regions.

The basic ideas which led to NMR experiments were adumbrated in the 1920s, and their

first experimental application was reported in 1939. The first real NMR experiments came in the 1940s, and almost another decade elapsed before the technique had diffused to Australia. Physicists who led the way were few in number, and, as pointed out in an earlier section, contemporary NMR techniques were not of wide applicability. Furthermore, their proponents had to compete with such vigorous competitors as atomic and nuclear physicists and with radio-astronomers for students and for a slice of the national or institutional cake. Consequently the field has been thinly populated and, after the early days, new centres opened only after fertilisation by staff-transfer from an existing NMR laboratory.

Applications to chemistry then followed swiftly, being evident in the northern hemisphere by the mid-1950s, at the end of the third decade of NMR development. Australian chemists first used NMR techniques in the late 1950s, while working in the northern hemisphere. From 1962, when the first 'chemical' NMR spectrometers arrived in Australia, the technique has been repeatedly reborn as high-field spectrometers, applications to many nuclei other than ^1H , the use of pulse Fourier transform techniques, and spectral editing made their successive appearances. While most chemists were content to work at the level of pattern-recognition and application to problems already in hand or conceived, two groups made more significant contributions.

The first were facilitators, who maintained NMR laboratories with a view to introducing new techniques into their sphere of operation as soon as they became available. From time to time such scientists made minor contributions to NMR through reflecting their better-than-average understanding. Their major role was to introduce their colleagues to NMR methods and to assist them in the choice and implementation of appropriate NMR experiments. Most groups involved in determination of molecular structure — university departments and CSIRO divisions — employed an NMR specialist of this type.

In just a few cases there were developments of international significance. Some of these led to great improvements in protocols for structure elucidation, and some to enhanced influence of NMR methods in such fields as protein chemistry and cell biology. At one extreme, and overlapping to a greater extent with the interests of physicists, are the extensions to body-imaging (MRI) which are rapidly becoming established.

The overall picture is one of great expenditure on equipment, avid use by most organic and some inorganic chemists and a smaller sub-set of physicists, and a few major contri-

butions to NMR theory and practice by a national group which, collectively, enjoys a fine international reputation.

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