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New Zealand Developments in Earth's Field NMR

P. T. Callaghan[1], **A. Coy**[2], **R. Dykstra**[3], **C. D. Eccles**[2], **M. E. Halse**[1], **M. W. Hunter**[1], **O. R. Mercier**[1], and **J. N. Robinson**[1]

[1] MacDiarmid Institute, Victoria University of Wellington, Wellington, New Zealand
[2] Magritek, Wellington, New Zealand
[3] Institute of Fundamental Sciences, Massey University, Palmerston North, New Zealand

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Abstract. We review here two decades of development of Earth's field nuclear magnetic resonance (NMR), starting with the first demonstration of resonant refocusing and the generation of spin echoes, the first measurement of diffusion using Earth's field NMR, and its application to Antarctic research, the adaptation of the apparatus to allow its use indoors, in a conventional laboratory setting, and finally, the construction of a flexible laboratory-based Earth's field NMR system capable of not only a range of relaxation and spectroscopy applications but also the straightforward demonstration of NMR Imaging.

1 Introduction

The first suggestion that the Earth's magnetic field could be used to detect nuclear precession was by Packard and Varian [1] in 1954. Earth's field nuclear magnetic resonance (EFNMR) is therefore almost as old as NMR itself. Since that time, the main application of the method has been to the measurement of geomagnetism, and EFNMR magnetometry has become a well-established technique. The use of a frequency measurement is always preferred in physics, given its great potential for precision and accuracy.

In the Earth magnetic field, which has a magnitude on the order of 60 μT, the Larmor precession frequency of protons is around 2.6 kHz (i.e., ultralow frequencies or ULF). Given the usual B_0^2 dependence of signal-to-noise ratios in NMR, one might reasonably expect that the sensitivity would be too low for NMR to be observed in the Earth's field. This objection is overcome in two ways. First, because the Earth's field is exceedingly homogeneous, large samples can be used. Second, the B_0^2 problem can be partly obviated by using a large prepolarizing magnetic field, in which the spins are allowed to come to a prior thermal equilibrium at much higher levels of magnetization than would prevail in the Earth's field alone. Provided this prepolarizing field (which need not be particularly homogeneous) is switched off over a time shorter than T_1, the large magnetization persists for use in the subsequent EFNMR observation. The rate at which the magnetization is observed to grow in the presence of the prepolarizing pulse is able to be used to measure the spin–lattice relaxation time, T_1.

Of course, the great power of NMR is associated with the many terms in the nuclear spin Hamiltonian that provide insight regarding the interaction of the nucleus with its molecular environment. The chemical shift and scalar spin–spin couplings give valuable information about molecular structure, while the quadrupole and internuclear dipolar interactions can be used to reveal molecular ordering and molecular dynamics, the latter especially through the interpretation of nuclear spin relaxation processes. And of course, it was shown in the 1970s that by appropriately tailoring the magnetic field [2, 3], NMR could be used for the precise measurement of molecular diffusion, and then, through the work of Lauterbur and Mansfield in the 1970s, that it could be used for nondestructive imaging. Despite these many advances in high-field NMR, EFNMR remained largely undeveloped until the 1980s. Indeed, it is only in recent years that it has become apparent that EFNMR is, in principle, capable of a much wider range of measurements. This review traces some of the history of these recent EFNMR method developments, with reference to various international groups, though with some emphasis on research work carried out in New Zealand and Antarctica.

2 Pulsed ULF EFNMR and Spin Echoes

If the prepolarizing field is applied normal to the Earth's field and switched off sufficiently rapidly (nonadiabatically), i.e., at a rate faster than the Larmor precession rate of the nuclei, then it has the effect of generating transverse magnetization which can be subsequently observed in free precession. This static-reorientation free precession approach was the mode of operation of the original Packard and Varian experiment. In a further development, in 1971, G. Béné [4, 5] demonstrated a spin echo, using a switched static field to reverse the sense of spin polarization.

A major shift in the way EFNMR was performed came in 1982, when it was shown [6] that the Earth's field method was amenable to the same RF (radio-frequency) pulse techniques as its high-field counterpart. Because a 2.6 kHz resonant ULF pulse is used to excite the spin system from equilibrium, it was no longer necessary to satisfy the difficult nonadiabatic requirement in switching off the prepolarizing magnetic field pulse, and the enhanced nuclear magnetization could then be permitted to evolve back to be oriented along the Earth's magnetic field prior to ULF excitation. This adiabatic field reduction can be ensured by tailoring the trailing edge of the current pulse so that it falls gradually to zero (over a period of about 10 ms). The pulse sequence used is shown in Fig. 1, while sample FID and spin echo data are shown in Fig. 2.

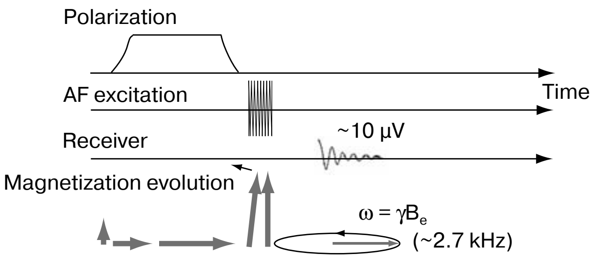

Fig. 1. Polarization, resonant excitation and signal detection sequence for a simple FID (free induction decay) collect sequence.

In that 1982 study, spin echoes were demonstrated, using ULF resonant RF pulses, with multiple resonant ULF pulses being used to demonstrate a Carr–Purcell train [7] of echoes, while in the same paper, the suggestion was made that the method could be amenable to the measurement of molecular diffusion. That first spin echo and Carr–Purcell–Meiboom–Gill (CPMG) echo train is shown in Fig. 3.

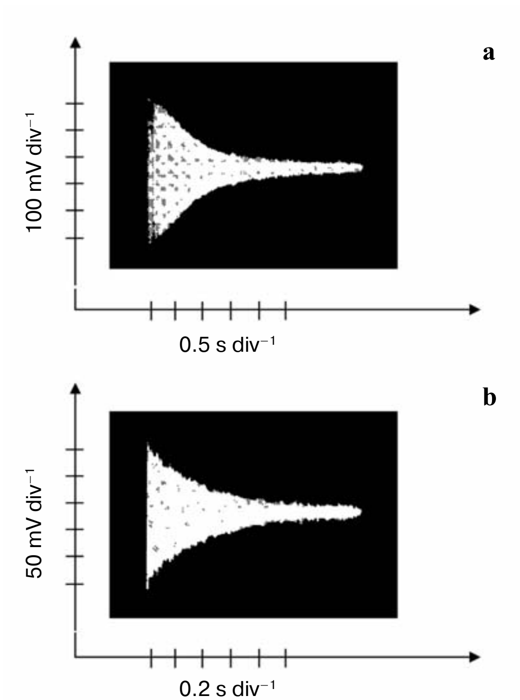

Fig. 2. Oscilloscope traces of proton NMR signal obtained from 200 ml of tap water (**a**) and ^{19}F NMR signals from 200 ml of perfluorodecalin (**b**). Adapted from ref. 6.

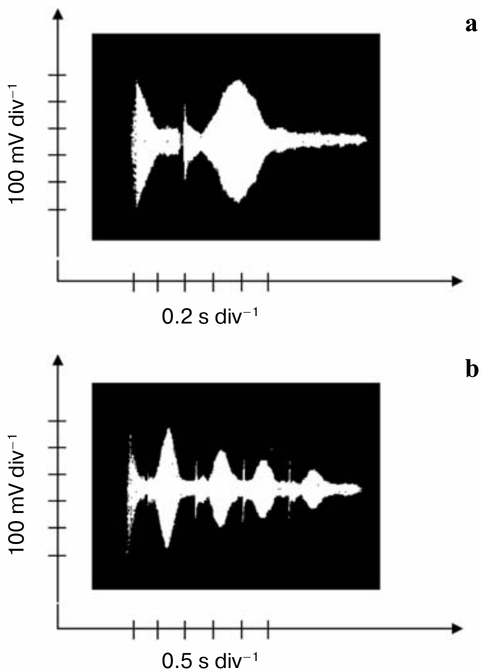

Fig. 3. Oscilloscope traces of signals obtained for Hahn echo (**a**) and CPMG train (**b**) of ULF RF pulses. Note that the homogeneity of the field has been deliberately spoiled in order to produce narrower and better defined echoes in the time domain. Adapted from ref. 6.

3 EFNMR in Antarctica: Sea Ice Brine Diffusion Studies

With the demonstration of the Hahn echo [8] and of CPMG echo trains [7], it was clear that EFNMR could be used as a tool to measure spin–spin (T_2) relaxation as well as molecular diffusion. This idea led to a project in which an EFNMR apparatus was developed for use in Antarctic sea ice studies. The motivation for this work was the significant interest shown by New Zealand researchers concerning the role of Antarctic sea ice in global climate and ecology modeling [9, 10]. The annual sea ice that forms around the Antarctic continent each Southern Hemisphere winter exerts an important influence on the global energy, biomass and carbon dioxide balance. This ice, between 1 and 2 m thick, covers an area of about $20 \cdot 10^6$ km^2 in winter and whereas the open ocean of the summer reflects only 5% in sunlight, the sea ice reflects over 90%, a significant factor in determining the Earth's albedo.

In October 1994 (Southern Hemisphere spring), the first rudimentary EFNMR apparatus was taken to McMurdo Sound and used to obtain proton NMR signals from unfrozen brine in extracted sea-ice cores [11]. Successive measurements were made on sea ice over three further spring seasons [12–15] in the vicinity

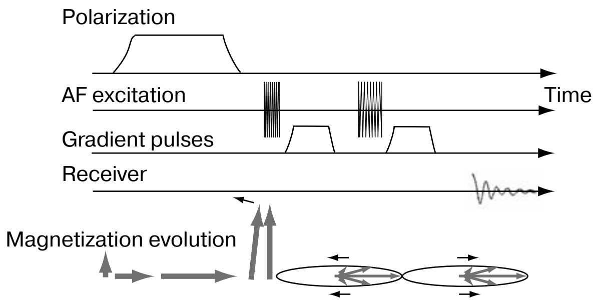

Fig. 4. Polarization, resonant excitation and signal detection sequence for a pulsed gradient spin echo sequence.

of Cape Evans, McMurdo Sound, on each occasion with successively improved apparatus. It was apparent that the NMR method provides a rapid measurement of brine volume, and that the results of those measurements were in excellent agreement with calculations based on the measured values of salinity and temperature in each sample. Later versions of the apparatus [12–15] permitted pulsed gradient spin echo NMR measurements of brine diffusivity, using the pulse sequence shown in Fig. 4.

Remarkably, the signal-to-noise ratios for experiments carried out in Antarctica were particularly favorable owing to the very low level of ULF interference in that environment. Figure 5 shows an FID obtained from a water sample at 6 °C along with the resulting spectrum. Because of the narrowness of the line width (ca. 1 Hz), band pass filtering permits a very high level of signal sensitivity.

The first version (extracted core probehead) of the Antarctic probe required the placement of cylindrically shaped samples in a horizontally aligned transceiver solenoid, as shown schematically in Fig. 6a. This was the mode in which we operated during visits to Antarctica in 1994 and 1995 [11, 12]. Sea ice cores were extracted using a specially constructed auger [16] and placed within the NMR

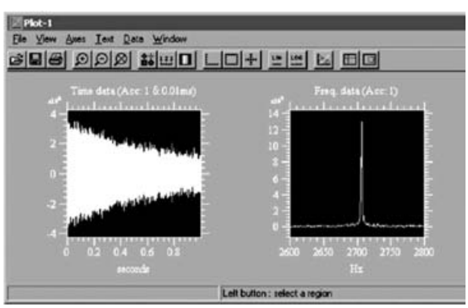

Fig. 5. FID resulting from a single scan from a water sample obtained at McMurdo Sound Antarctica, November 2002.

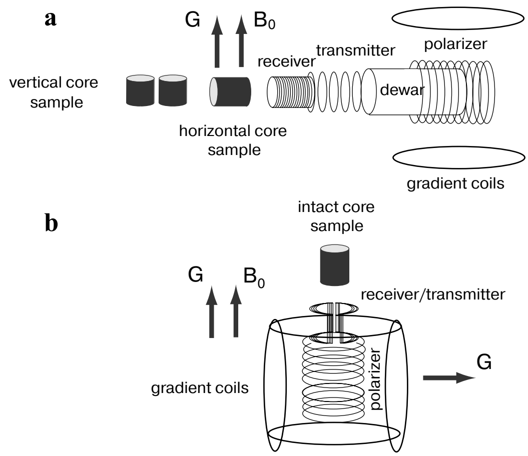

Fig. 6. Schematic configurations of polarizing, transmitter/receiver and gradient coils used for extracted core probehead in 1994, 1995 (**a**) and in situ probehead in 1997 Antarctic seasons (**b**).

probehead which was situated in a tent close to the coring site. This probehead was equipped with magnetic field gradient coils comprising a 100 turn Maxwell pair of 270 mm mean diameter and 240 mm mean spacing, fixed in a vertical orientation. The next improved probehead version (ice sheet probehead) was capable of insertion directly into the ice sheet, once a suitable annular hole is cut around the free standing core sample [13, 14]. This was used during the third visit to McMurdo Sound in 1997 and is shown schematically in Fig. 6b. It incorporated a vertically oriented solenoid polarizing coil comprising 504 turns of 1.6 mm diameter enameled copper wire, along with a saddle coil pair wound from 0.2 mm diameter enameled copper wire, used as a common receiver and transmitter coil. A pump was used to drive external air down to the polarizing coil so as to reduce any temperature rise associated with the polarizing pulses. Figure 6 shows the configuration of the coils used to make brine content and diffusion measurements in the 1994 and 1995 (Fig. 6a) and 1997 (Fig. 6b) seasons.

Over this period, the spectrometer hardware used to drive the Antarctic Earth's field apparatus evolved considerably. In 1994 and 1995, a Tecmag ARES pulse sequencer (Tecmag Inc., Houston, Texas) controlled by a Macintosh computer

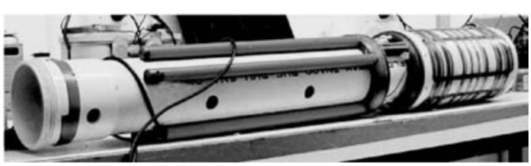

Fig. 7. The "Sleeve" probehead, lying on its side, and showing the gradient coils on the outside surface.

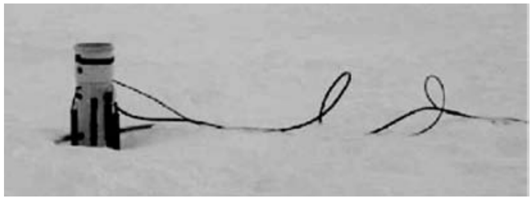

Fig. 8. Sleeve probehead inserted in McMurdo Sound sea ice.

was employed, with the magnetic field gradient coil and prepolarizing coils being driven by Kepco (Kepco Inc, Flushing, NY) OPS 25-10M current supplies. In 1999 a complete stand-alone spectrometer was developed [17] which formed the basis of the 2005 Magritek Terranova Earth Field Spectrometer (Magritek Limited, Wellington, New Zealand).

While the in situ probehead permitted an intact free-standing ice core to be sampled, it was necessary to cut away a basin of sea ice around the probe so that separate Maxwell pair gradient coils could be placed in position. Cutting this basin typically took 20 min, exposing the ice core to different ambient temperatures than those prevailing in the ice sheet. In 2002, this perturbative and labor-intensive step was eliminated by making the gradient coils and probe an "all-in-one" piece of apparatus (gradient sleeve probehead) [15] (Fig. 7). For this probe, a narrow annular hole is cut in the ice sheet for insertion of the probe. As a result the core sample is preserved in a state close to its natural environment and the amount of time consumed in preparing each sample is vastly re-

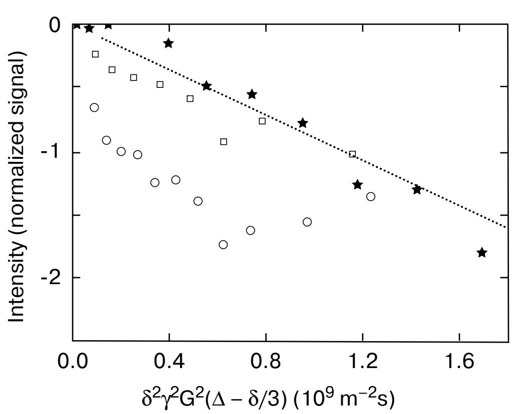

Fig. 9. Data from the 1995 and 1997 season measurements of Callaghan et al. are shown as open circles and open squares, respectively (publication date 1999). For the 1995 season data (publication date 1997), $\Delta = 108$ ms and the depth was 46.5 cm. For the 1997 season data, $\Delta = 208$ ms and the depth was 40 cm. The linear dotted line gives calculated attenuation for Antarctic sea water in equilibrium at -10 °C. 2002 season measurements at a depth of 42 cm with $\Delta = 200$ ms are given for comparison (solid stars). Taken from ref. 15.

duced. The sleeve probe allowed measurement, in situ, of the diffusion of brine in first-year sea ice not only as a function of depth but most notably probing diffusion in the transverse (horizontal) direction as well (Fig. 8).

Over the different seasons of the Antarctic work, it has become apparent that the EFNMR apparatus is very effective in measuring sea ice brine diffusion at different depths. However, the results have differed according to the season and apparatus used. In particular, in the 1995 and 1997 seasons, a rapidly diffusing component of brine was observed, an effect which has been attributed to Benard convection in large brine pockets. However, in 2002, using the improved apparatus, no such rapid convection was observed. Comparative Stejskal–Tanner plots are shown in Figure 9 for diffusion measured in the vertical direction, at a depth below the sea ice surface of 40 to 50 cm. Further measurements in the 2006 season using the identical apparatus should elucidate whether this variation was a consequence of seasonal ice sheet variation or of the different probe design.

4 EFNMR in the Laboratory: Imaging and Spectroscopy

For practical reasons, EFNMR has until recently been limited to outdoor environments, i.e., locations far from any disruptions to the local homogeneity of the Earth's magnetic field and sources of ULF noise. If this method is to gain more widespread use, it is essential to develop means by which the apparatus may be situated indoors. Recently we have considerably reduced the ULF noise problem by using the polarizing coil as a screen, shorting it during signal acquisition. Furthermore, the apparatus incorporates three axis (G_x, G_y, G_z) shims so that the resolution may be further optimized. By shimming, and by careful placement of the apparatus on a wooden stand in a suitably selected region of a laboratory, a homogeneous field region may be found in which the proton NMR resonance is less than 1 Hz in line width. The remaining requirement for sophisticated laboratory-based experiments is a powerful NMR spectrometer capable of generating multiple phase-controlled RF pulses, allowing signal averaging and phase cycling. The apparatus used is a modified Terranova Earth's field NMR system (Magritek Limited). These developments have enabled us to turn our attention to the use of EFNMR in automated experiments allowing more than one dimension. In particular, we have sought to achieve simple implementations of NMR imaging and two-dimensional (2-D) NMR spectroscopy, in the laboratory environment.

The idea of EFNMR Imaging is not new. Stepisnik et al. [18] and Mohoric et al. [19, 20] have demonstrated 2-D imaging in the Earth's magnetic field and also self-diffusion weighted imaging and velocity imaging. In that previous work, carried out with the apparatus outdoors, a reference coil, coupled with heterodyne detection, was used to compensate for any drift in the Larmor frequency due to variations in the Earth field during an imaging experiment. We have shown that a much simpler approach, in which field drifts are measured and experimental time limits set, proves highly effective and that no such signal reference method is needed [21].

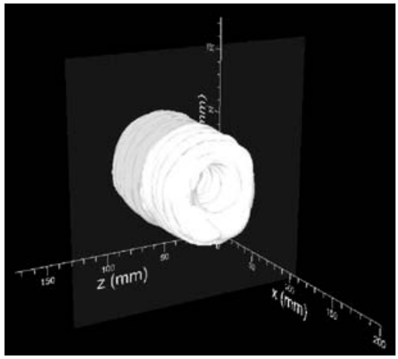

Fig. 10. 3-D MRI of a phantom, consisting of a 500 ml bottle of water with an empty tube in the center, acquired in the Earth's field using the spin-echo method. The field of view was 175 mm isotropic with a matrix size of 64×16×16 (zero-filled to 64 isotropic). Total imaging time was 1 h and 36 min. Four signal averages were employed.

The Terranova EFNMR probe consists of three concentric coils: a polarizing (B_p) coil, a gradient coil and a B_1 excitation–detection coil. The B_p and B_1 coils are coaxial solenoids and the gradient coil, used for diffusion measurements, is a collection of Maxwell and Helmholz turns on a 0.1 mm thick flexible PCB which is wrapped around the existing diffusion gradient coil within the Terranova apparatus. Thus, the probe was modified for imaging without necessitating any modifications to its original structure. The Terranova EFNMR spectrometer provided a three-axis current source with a maximum available current of ±300 mA, yielding a maximum gradient of approximately 80 mT/m. Experiments are con-

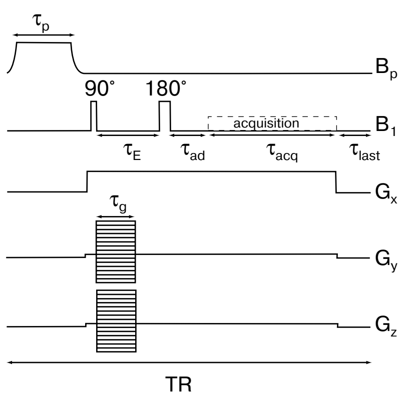

Fig. 11. Pulse sequence diagram for imaging in the Earth's magnetic field using spin echoes. The pulse sequences incorporates a prepolarizing pulse of duration τ_p prior to each line in **k**-space. Shim currents are output to the gradient coil between the polarizing pulse and the B_1 pulse and are maintained throughout the excitation and detection time periods. All gradient pulses are superimposed on top of the shims.

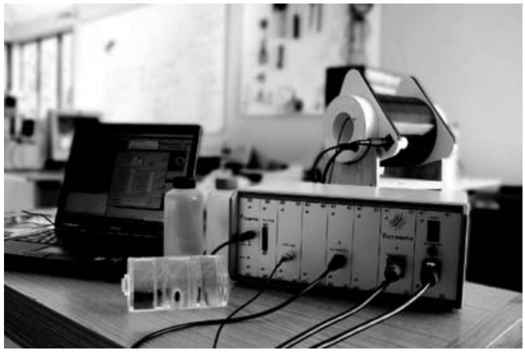

Fig. 12. Photograph of the modified Terranova EFNMR apparatus.

trolled by a PC connected to the spectrometer via a USB interface while data was processed using the software package Prospa v2.0 (Magritek Limited).

Figure 10 shows the 3-D image of a water phantom acquired using a spin-echo, spin-warp imaging sequence presented while the pulse sequence used is shown in Fig. 11. The total imaging time was 1 h and 36 min. Figure 12 shows the Terranova apparatus composed of a probe, spectrometer and laptop computer.

The most recent focus of EFNMR has been in the domain of NMR spectroscopy. Appelt et al. [22] have demonstrated astonishingly high-resolution *J*-coupling spectra for a number of organic molecules acquired in the Earth's magnetic field. However as in the Mohoric et al. [19, 20] imaging experiment, their measurements were performed outdoors. Further, Appelt et al. [22] used a single-shot polarization technique which required their sample to be mechanically transported from one magnet to another, making multiple acquisition very difficult. We have recently shown that it is possible to take advantage of the capability of our apparatus to operate indoors to observe heteronuclear *J*-couplings via the classic COSY experiment [23]. A key factor permitting this development has been the flexible

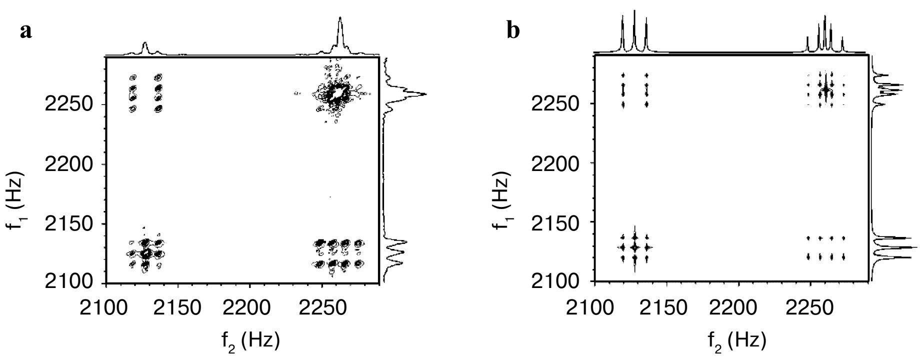

Fig. 13. Experimental (**a**) and simulated (**b**) 2-D COSY NMR spectra obtained at audiofrequencies of 2.28 kHz (^{19}F) and 2.43 kHz (^{1}H) for trifluoroethanol.

pulse programming and RF pulse phase control that the apparatus permits. Of course, as with the Appelt experiment, it is only possible to observe heteronuclear *J*-couplings [24], because the low field causes homonuclear chemical shifts to vanish below the spin–spin coupling. We have chosen to demonstrate heteronuclear COSY with a fluorine-hydrogen compound, trifluorethanol. 512 evolution steps (1.82 ms intervals) were used, along with direct digitization of about 2.4 kHz 16 kB point acquisition domain signals with 0.68 Hz resolution in the acquisition domain. Total experiment time was 14 h and a 500 ml sample volume was used. Figure 13 shows the experimental and simulated 2-D COSY spectra, the higher-frequency resonances arising from ^{1}H resonances and the lower-frequency resonances from ^{19}F. The 1-D NMR spectrum is seen in the projections.

5 Conclusions

This review has covered aspects of EFNMR work carried out by the New Zealand group, with some reference to other work. In the interests of a more complete record, one should also mention the pioneering work on ground water detection using EFNMR by Shushakov et al. [25], the chemical-shift-resolved Xe EFNMR work of Appelt et al. [26], and the low-field SQUID-detected NMR work of Burghoff et al. [27], in which *J*-couplings have also been observed.

The advent of NMR imaging and 2-D NMR spectroscopy in a laboratory setting marks a new stage in the development of EFNMR, both as an analytical tool and as a platform for the demonstration of fundamental NMR phenomena. EFNMR has the virtue of apparatus simplicity, low cost, and ease of portability. Students can quickly come to understand NMR phenomena which could normally only be observed using the most sophisticated and expensive research apparatus, bringing the power of NMR to the realm of the undergraduate. And yet the method is more than a teaching tool and its portability, while limiting for some purposes, will always cause the method to find application in the outdoors, and potentially in extreme environments, as our Antarctic work has shown.

But there is another and very interesting reason why EFNMR matters. The very existence of such remarkable magnetic resonance phenomena in Earth's field raises questions about the role of resonant molecular processes in nature. After all, every living organism is bathed in the Earth's magnetic field, and every living organism is subject to pulses of ULF fields due to "whistler-mode" waves caused by lightning, and of course to human generated ULF from electrical machinery and from power line transmission, The astonishing power of low-field NMR certainly raises new questions and the idea of "nature's magnetic resonance" should be of wide interest.

Acknowledgment

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Authors' address: Paul T. Callaghan, MacDiarmid Institute, Victoria University of Wellington, PO Box 600, Wellington, New Zealand
E-mail: paul.callaghan@vuw.ac.nz