TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 363

December 1988

Continued on page 64

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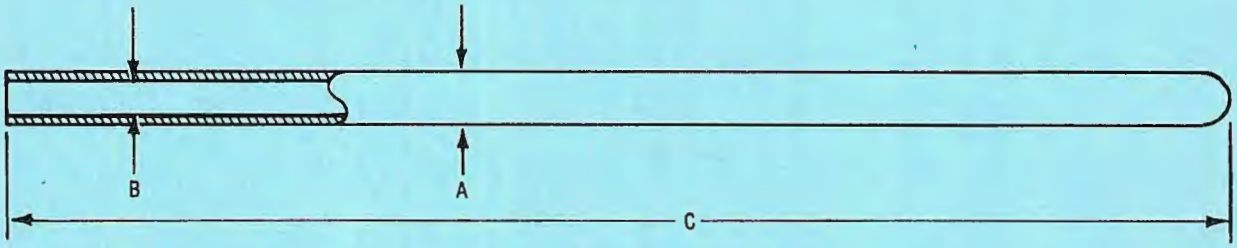

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FORTHCOMING NMR MEETINGS

San Francisco Symposium - "*In Vivo* Magnetic Resonance Spectroscopy II", March 31 - April 2, 1989; San Francisco, California; See Newsletter 363, 17.

30th ENC (Experimental NMR Conference), April 2-6, 1989; Asilomar Conference Center, Pacific Grove, California; Conference Chair: A. N. Garroway; Contact Ms. Judith A. Watson, ENC Conference Center, 750 Audubon, East Lansing, MI 48823; (517) 332-3667. See Newsletter 362, 69.

The Society of Magnetic Resonance in Medicine - Eighth Annual Scientific Meeting and Exhibition, August 12-19, 1989; Amsterdam, The Netherlands; Contact: The S.M.R.M. Business Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415)841-1899, FAX (415)841-2340.

9th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, July 10-14, 1989; University of Warwick, Coventry, England; Contact: Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, Piccadilly, London W1B 0BN, England; (01) 437-8656.

3rd Chianti Workshop on Magnetic Resonance Relaxation, May 28 - June 2, 1989; San Miniato (Pisa), Italy; Contact: L. Banci, Dipartimento di Chimica Bioinorganica, Universita degli Studi di Firenze, Via Gino Capponi 7, 50121 Firenze, Italy. See Newsletter 362, 68.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence
Should Be Addressed To:

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303, U.S.A.

(415) 493-5971

DEADLINE DATES

No. 365 (February) —— 20 January 1989
No. 366 (March)——17 February 1989
No. 367 (April) ——— 17 March 1989
No. 368 (May)———21 April 1989

University of Alberta
Edmonton
Canada T6G 2G2

Department of Chemistry
Faculty of Science
E3-43 Chemistry Building East, Telephone (403) 432-3254

October 25, 1988

Professor Bernard Shapiro
966 Elsinore Court
Palo Alto, California
U. S. A. 94303

AStoPC: A Data Transfer and WORM Archive System for Bruker Aspect 2000/3000 Data Systems

Dear Barry:

As an efficient and low cost alternative to a magnetic tape system for data archiving, we have developed an economical optical disk data archiving system for Bruker Aspect 2000/3000 data system users. This system uses an IBM PC or compatible as the "smart" device connected between the Aspect computer and the optical disk unit. We have used a Storage Dimensions 800 MByte optical disk with Corel Systems software driver, and have connected the PC to the Aspect via a parallel interface which employs a MetraByte PDMA-16 high speed interface card in the PC and a simple buffer box which connects to the reader/punch port on the Aspect.

The speed of the AStoPC transfer system is limited by the access time of the optical disk, not by the parallel transfer rate. This system transfers a 1Mword data file (including that infamous "minus 1 sector") between the hard disk on the Aspect computer and the optical disk on the PC in 12–14 minutes. Although the transfer rate for the optical disk system is slightly slower than that obtainable with a magnetic tape, there are several advantages to the optical disk system: the search time is negligible (mag. tape searches take forever!); the storage capacity of the optical disk is phenomenal; the cost (about $7000 Canadian including cost of PC clone) is much less than that of a magnetic tape system; the optical diskettes are unaffected by magnetic fields and very cost effective ($250 Canadian for an 800 MByte disk); and the AStoPC menu-driven software forces the user to store data in an organized and easily retrievable manner using tree- structured DOS directories and subdirectories.

The AstoPC archiving/transfer software is copyright protected, but copies will be distributed at low cost to university research personnel. Researchers with Bruker Aspect data systems should contact T. T. Nakashima at the above address in order to obtain copies of the AStoPC software, documentation and detailed instructions for construction of the interface box and cabling.

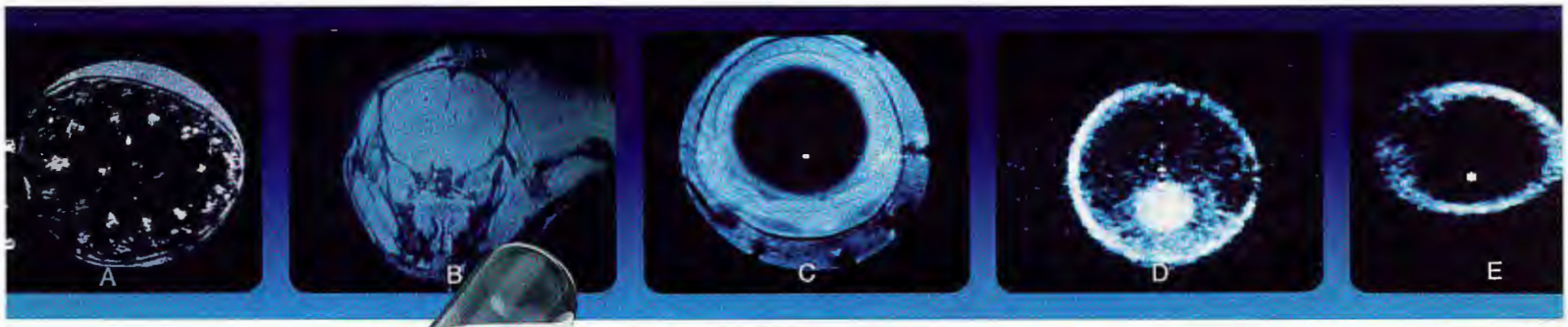
Please credit this contribution to the account of T. T. Nakashima.

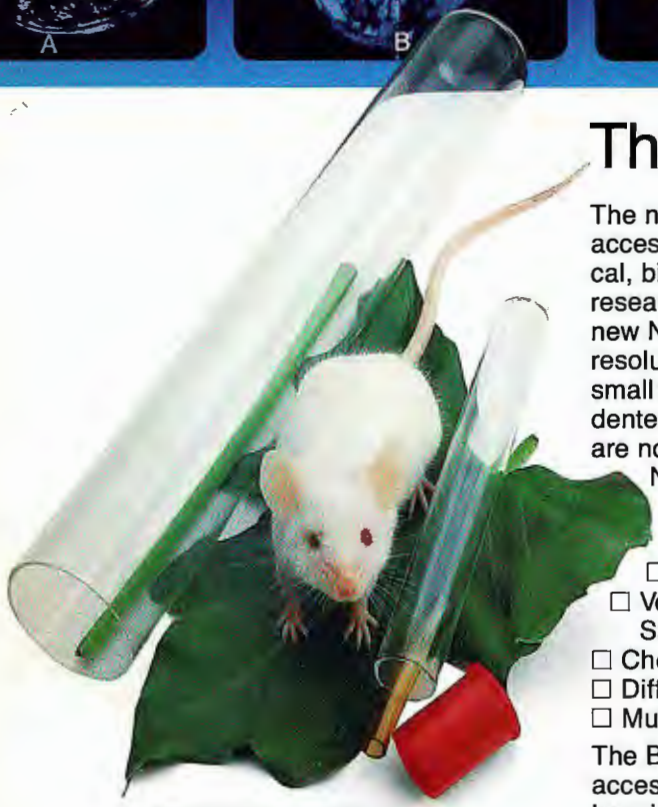
Sincerely

G. Bigam

R. E. D. McClung

The NMR evolution continues:





New visions through NMR microscopy.

The NMR microscope, at last.

The new Bruker microscopy accessory provides the medical, biological and materials researcher with an exciting new NMR capability: very high resolution NMR imaging on small samples. An unprecedented variety of experiments are now possible using the NMR microscope.

- ☐ T_1/T_2 Imaging
- ☐ Multi-Echo
- ☐ Multi-Slice
- ☐ Volume Selective Spectroscopy
- ☐ Chemical Shift Imaging
- ☐ Diffusion Imaging
- ☐ Multi-Nuclear Imaging

The Bruker NMR microscope accessory comes as a comprehensive package, requires virtually no modification of the standard spectrometer, and includes software and image processor.

Designed to work on both Bruker wide-bore AM and MSL systems, this versatile new accessory redefines the limits of spatial resolution.

The power of this technique is illustrated by the images shown above, which were obtained using an AM-400WB spectrometer with 9.4 Tesla operating field strength.

Fig. A: Cross sectional image of a philodendron stem. Resolution 19μ x 19μ x 300μ.
Fig. B: Cross sectional image of a mouse brain tumor. Resolution 100μ x 100μ x 500μ.
Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution 20μ x 20μ x 250μ.
Fig. D: Image of an ovum from laevis (frog egg). Resolution 10μ x 10μ x 250μ.
Fig. E: Diffusion of water through a piece of nylon. Resolution 50μ x 50μ x 1000μ.

Explore the potential of this technology. Ask your nearest Bruker representative for more details on the new microscope or other NMR products.

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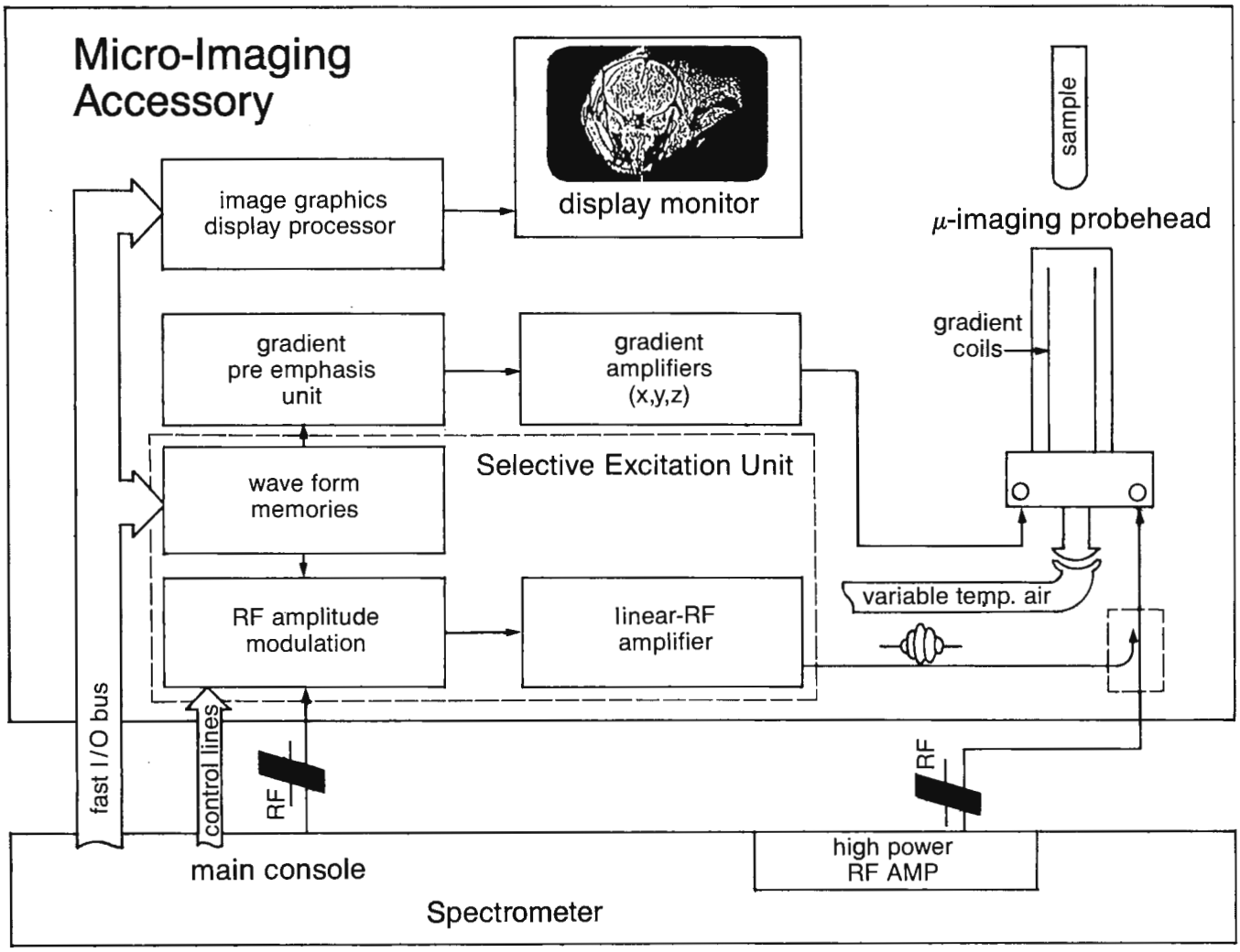
   b. RF pulse amplitude modulator
   c. Linear RF amplifier
5. Probehead with integral gradient assembly
6. Imaging software

*Other nuclei available upon request



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Dr Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
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10th November, 1988
(received 11/14/88)

Dear Barry,

Bruker-Macintosh File transfer.

Late in 1988 we took delivery of a Bruker AM-400 WB spectrometer and have spent a busy time since in learning how to operate this system. During that time we have come to appreciate the speed and reliability of the Graphtec Drum plotter. However publication quality plots are not easy to achieve using the standard ball point pens. We have therefore sought to use the lab Macintosh with its attached Hewlett-Packard 7470A plotter to produce output from the spectrometer.

In addition we hoped that this system would provide solutions to a couple of other problems. One is the need to incorporate labelled spectra into the standard word processors used in the Department, and secondly since we do not have tape backup as part of our Aspect 3000 on the Bruker we hoped to be able to archive data via the Macintosh.

Dr. John Christie of this Department wrote the appropriate software to solve the first part of our needs. His software allows transfer from the Aspect via one of the serial line outputs using Kermit running on both the Aspect and the Macintosh. The spectral file can be stored, phased, expanded, amplified, integrated, and scaled. The desired file may then be plotted on the Hewlett-Packard plotter, or transferred via the clipboard to other Macintosh applications. In particular the spectrum may be labelled expanded or otherwise manipulated in Macdraw before transferring to a word processor for incorporation into a manuscript. Just to prove it works a spectrum is included.

The transfer rate using the serial line from the Aspect to the Macintosh using Kermit is relatively slow taking several minutes for a 16K spectral file. We would like to make use of the parallel output port from the Bruker to speed up this process, but have not investigated yet the software required for the Bruker nor the parallel/serial conversion required for input into the Macintosh. With faster transfer rates we beleive that effective use could be made of the Macintosh for file backup.

Please credit this contribution to Dr. Ian Rae's account at Monash University who is kind enough to share the Newsletter with us.

Bob

Yours sincerely,
Robert T. C Brownlee.

SCHERING CORPORATION

60 ORANGE STREET BLOOMFIELD, N. J. 07003

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Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303

September 26, 1988
(received 11/7/88)

THINGS ARE ALWAYS ROESYer WHEN YOU DO THE RIGHT EXPERIMENT

Dear Barry:

We are in receipt of your notice of termination of our subscription. We hope that this contribution will reinstate us in your good graces.

Lately we have been asking ourselves more and more often, why it is that the compounds that are of greatest interest will always have some property that makes them the most difficult to study by NMR? The latest problem that we have faced has been that of intermediate size molecules, $1000 < MW < 2000$. In many molecules such as this, conformational studies are crucial aids to drug design. Unfortunately, the standard approach, application of 2D NOE techniques, fails to give answers because of the weak NOE's for systems having this "crossover" molecular weight. Fortunately, however, new techniques have been developed which make studies of these mid-range molecular systems a considerably ROESYer prospect.

Consider thiostrepton, a sulfur-containing antibiotic of molecular weight 1664, whose 400 MHz ^1H NMR spectrum is shown in Figure 1. This spectrum would at first glance appear to be quite amenable to quantitative NOE studies given the clean spectrum and essentially complete assignments[1]. However, Figure 2a shows the disappointing result. Note that, although a number of cross-peaks due to backbone interactions appear, those due to sidechain-backbone interactions are absent, the effect of sidechain mobility

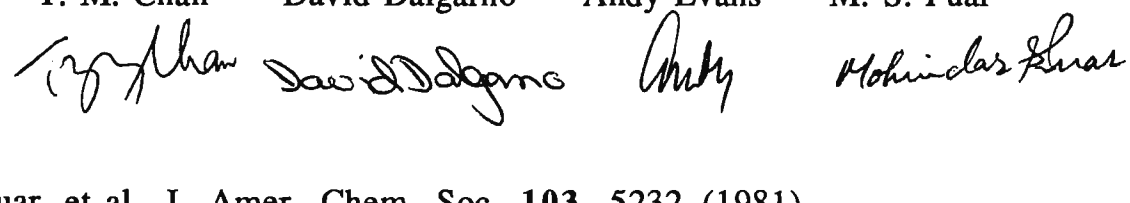
being to push the effective correlation time towards the NOE null point. This is most clearly seen in the region expanded in Figure 2b.

Rotating frame Overhauser experiments (ROESY) have been proposed[2] as a solution to this problem, since ROESY intensities do not pass through a null as a function of correlation time. We have recently implemented Ernst's offset compensated ROESY experiment[3] (using the time-shared mixing technique of Kessler[4]) on our XL-400 and decided that thiostrepton would be a good system on which to test our implementation. Figure 3 shows the ROESY spectrum of thiostrepton which reveals a wealth of crosspeaks absent in the corresponding NOESY experiment. In particular, note the large number of cross-peaks appearing in the expansion of the region corresponding to sidechain-backbone interactions. Since the offset compensated ROESY experiment lends itself to quantitative analysis, we plan to use crosspeak volumes to generate distance constraints which will allow us to determine the conformation of thiostrepton and compare it with the previously determined X-ray structure.

Since our last communication, there have been some changes in NMR at Schering. Andy Evans has come on board as Group Leader and David Dalgarno has been hired to develop a program in NMR studies of peptides and proteins. On the new equipment side of things, we have just taken delivery of a General Electric GN-500 Omega, a Varian Gemini 300, and are anxiously awaiting the arrival of a Sun 4/280 workstation.

We hope that this satisfies our technical contribution requirement. We look forward once again to receiving our copies of the Newsletter.

T. M. Chan David Dalgarno Andy Evans M. S. Puar



1 Puar, et al., J. Amer. Chem. Soc., **103**, 5232 (1981)
2 Bax, et al., J. Mag. Res., 63, **207** (1985)
3 Griesinger et al., J. Mag. Res., **75**, 261 (1987)
4 Kessler et al., J. Amer. Chem. Soc., **109**, 607 (1987)

Figure 1

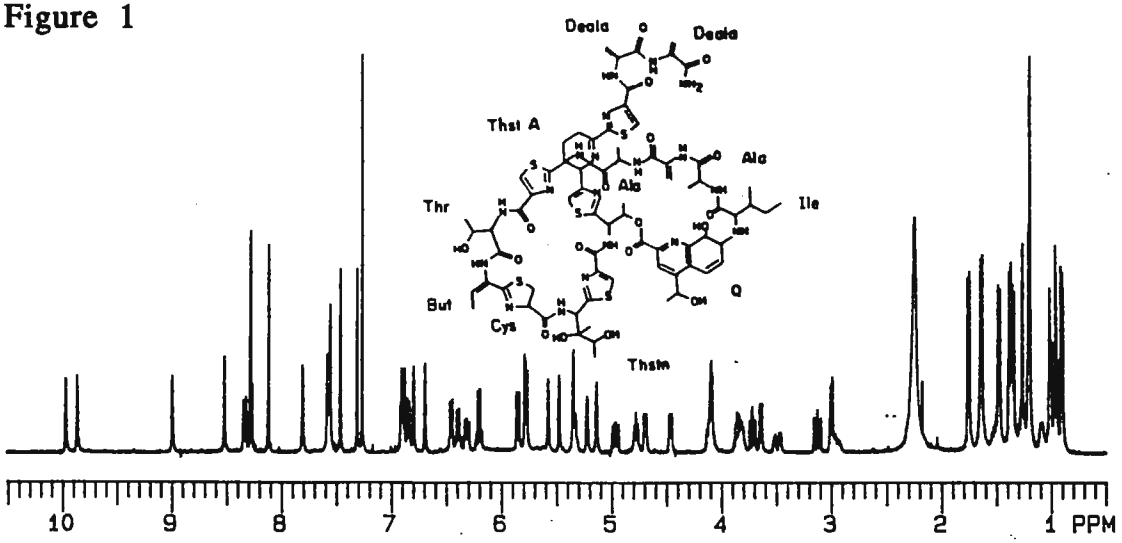


Figure 2a

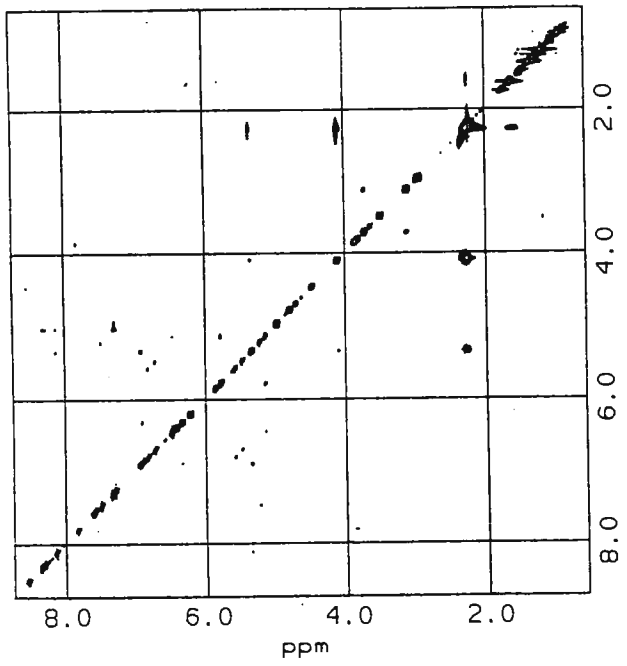


Figure 2b

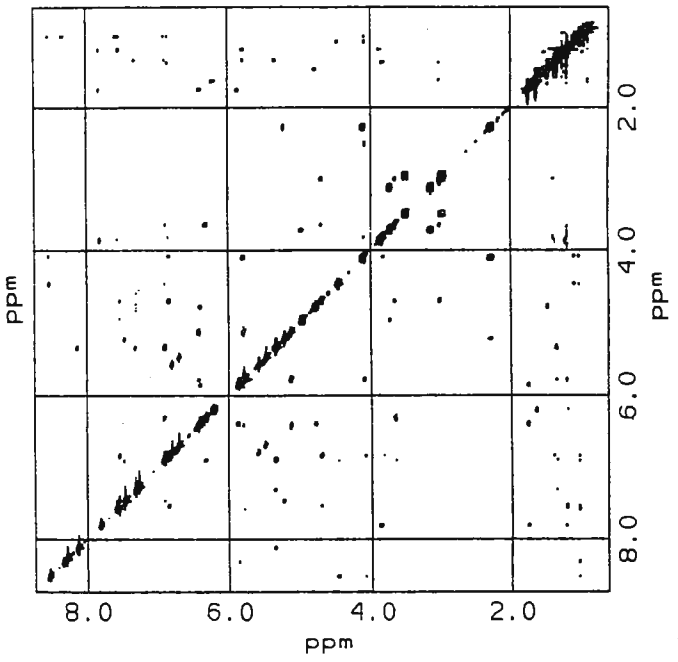


Figure 3a

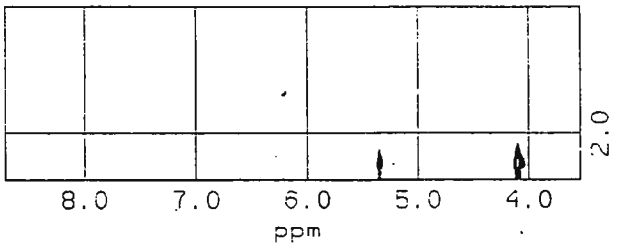
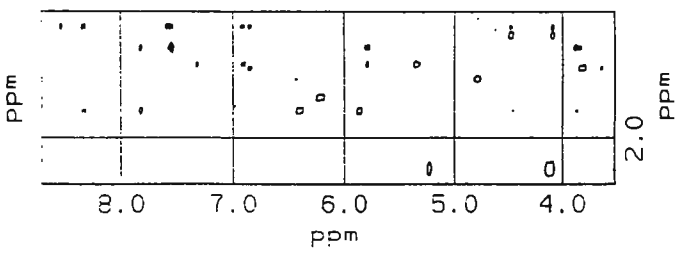


Figure 3b



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Water Suppression

RF pre-irradiation of a specific NMR resonance by the NMR instrument's decoupler has many uses. These include two of the most used biological experiments: NOE and water suppression. The most common utilization is water suppression. Since water is 110 M in ^1H and most of the interesting samples are less than 1 mM in concentration, the water resonance needs to be suppressed by a very large amount (10^5 to 10^6). Doing water suppression well is a challenging task. The degree to which artifacts in 2DFT experiments can be avoided or useful data can be extracted from experiments utilizing water suppression techniques is often dependent on how well it is done. One of the corollaries to Murphy's Law applies to this aspect of an NMR instrument's performance: regardless of how well your NMR instrument does water suppression, your experiment requires a higher level of performance. With the goal of improving water saturation performance, some important instrumental considerations are discussed below.

The observe frequency needs to be set to the exact frequency of water. It is indeed fortunate that in water saturation experiments that the water line falls in the middle of the desired spectral window and that today's NMR systems use quadrature detection. This coincidence allows the water line to be put exactly in the middle of the spectral window. If the resonance to be saturated (water) and the observe transmitter frequency are not identical the degree of saturation obtainable with today NMR spectrometers is reduced.

The decoupler and observe frequencies must be identical. For best results, the NMR instrument must be capable of generating (or be modified to generate) a decoupler signal with the identical frequency and phase of the observe transmitter. If the observe and decoupler cannot be made to be identical in frequency and phase, the degree of water saturation is significantly reduced. One way to test this condition is to write a new pulse experiment where the decoupler is used in place of the observe transmitter to excite the spectrum. Take a single scan with this new experiment, process and phase the spectrum. Each time this process is repeated the spectrum will have the same phase after processing if the decoupler and observe transmitters are identical in frequency and phase. A random phase result after each processing indicates a different frequency and/or phase for the two transmitters.

The water lineshape needs to be as lorentizian and as narrow as possible. Lineshape distortions of the water resonance at a very low level (far below the 0.11% level usually specified) can leave a large residual signal after water saturation. Poor water lineshape often produces a residual peak with a "burned out" center and/or baseline distortions. Typical problem areas are:

Poor shimming. Even with samples having broad lines, water saturation performance will benefit from good shimming.

Sample length too short. The magnetic susceptibility end effects of a restricted length sample are very large and can distort the lineshape. The sample should be 3 times the probe coil window in length and centered about the window.

Probe coil lead pickup. Signal arising from the leads of the observe probe coil can be from a different magnetic field (therefore frequency) and not be saturated. This problem often produces a residual water signal on one side of the saturated main water resonance.

To detect lead pickup, place the smallest drop of water possible in the bottom of an NMR tube. Place the tube in the instrument such that the water drop is in the center of the receiver coil. Set the instrument to do a wide sweep width (± 20,000 Hz) with a large data table (16 K). Take one scan, process with 20 Hz linebroadening and do a magnitude calculation. Integrate the entire spectrum and set the integral to 100. Now move the water drop as far down into the probe as possible. Take a single scan, process and integrate with the **same normalization constants**. Record the position of the sample and the integral value. Move the water drop up in steps of 2 millimeters, repeating the process at each step until the probe coil response area has been completely mapped. *Be careful to move far enough in both directions*, since the response will often go to zero and then return as the leads start picking up signal. This plot is also useful in telling the NMR user the depth and length of the probe coil.

Probe coil too long. As the length of the probe pickup coil increases, the sensitivity increases. Therefore in the pursuit of the holy Grail of NMR (*sensitivity*), probe manufacturers try

(Over)

to make the receiver coils as long as the magnetic field homogeneity will allow. This length is dependent on the instrinsic correction order of the magnet, purity and adjustment of the superconducting and room temperature shims, as well as the magnetic susceptibility of the probe materials and sample. As the probe coil length increases, the probes lineshape performance decreases, the sample becomes harder to shim and has a tendency to split as the resolution improves. The reduced lineshape and resolution performance reduces the water saturation performance. Probe coil lengths for today's commercial 5mm ^1H probes range from 10 to 30 mm.

The magnetic susceptibilities of the probe materials can distort the lineshapes thereby making water saturation more difficult.

Poor B_1 homogeneity of the observe or decoupler transmitter coils. Composite pulses can often help here.

Particulate matter suspended in the sample. This area is often overlooked but extremely important. Get all foreign objects out of the sample for best performance.

High protein and/or buffer *concentration*. A more dilute sample or buffer can sometimes give better results.

Decoupler Phase Rotation. After the frequency and phase of the decoupler and observe transmitters has been made identical, the decoupler phase can be phase cycled (relative to the observe phase) between scans with a custom pulse sequence. A good phase rotation is 0° on scan 1, 180° on scan 2, 90° on scan 3, 270° on scan 4 and then repeat the cycle for the duration of the accumulation. This forces any residual magnetization of the water resonance (some of which will be phase locked to the decoupler pre-irradiation pulse) to cancel during the accumulation.

RF Phase Stability. With the degree of water saturation depending heavily on the decoupler and transmitter frequencies and their relative phases, it is vital to good performance that these transmitters also have excellent pulse to pulse phase and amplitude stabilities. A symptom of phase jitter is often seen as residual signals of random phases at slightly different frequencies at the site of the presaturation. Phase and/or amplitude instabilities can also arise from disturbing the magnetic field during the pulse sequence. This can happen in a variety of ways:

Lock pull coming from either transmitter pulse interfering with the lock. Filters in the transmitter lines and the lock receiver line often help remove this interference.

Shim stability. The shim power supply can produce noise a low levels which randomizes the NMR signal's phases to a small extent. A good lock system compensates for this to some degree.

Magnet Environment. Any magnetic field variations in the environment can cause instabilities which might lead to reduced saturation.

Room Temperature. Any room temperature variation during the experiment can lead to instrumental changes leading to reduced saturation.

Power level. Adjust the decoupler power level to provide the best comprise between saturation of the water resonance and the effect on the nearby resonances. The higher the power level the better for water saturation. The water saturation time interval should be 3 to 5 times the water T_1.

Commercial

FMR provides both telephone and on site consulting services to help the NMR spectroscopist isolate and understand the instrumental influences on his experiments. Often an understanding of instrumental limitations leads directly to techniques to eliminate or reduce them. FMR also provides new hardware modules and modifications to existing modules to help reduce instrumental limitations.

FMR provides specialized probes for many applications including water suppression as well as upgrades to existing probes for improvement of sensitivity or other performance characteristics such as water saturation. For example, if you are having problems with lead pickup as described above, most probes can be modified to substantially reduce or eliminate the lead pickup.

UNIVERSITY OF MINNESOTA
TWIN CITIES

Department of Chemical Engineering and Materials Science
151 Amundson Hall
421 Washington Avenue S.E.
Minneapolis, Minnesota 55455
(612) 625-1313

25 October 1988
(received 11/10/88)

Dear Dr. Shapiro,

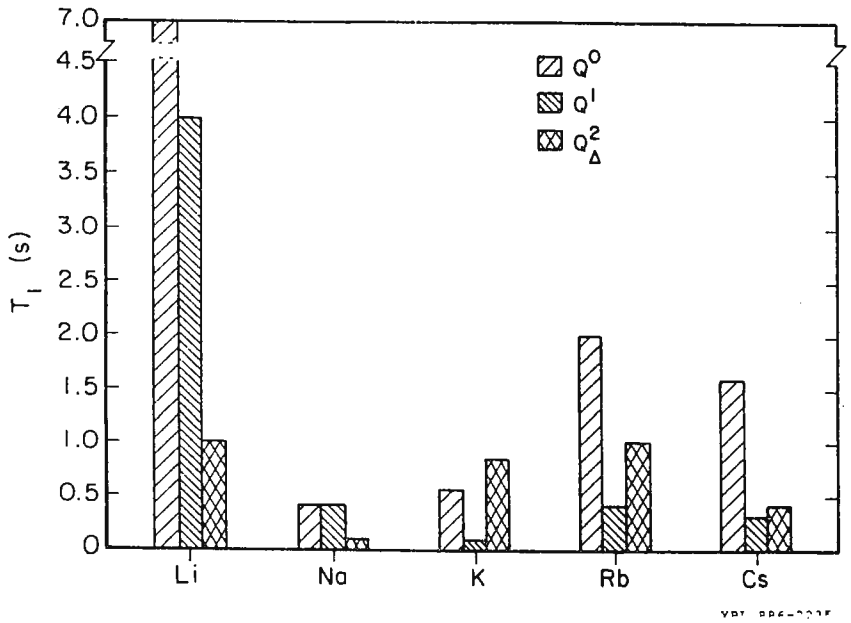
It has been established in the literature [1,2] that some alkali metal silicate solutions, unlike solid silicates, can be easily studied with ^{29}Si NMR since they exhibit conveniently short relaxation times. It is not clear, though, that this is true in all chemical conditions. I am writing to report the observation of an anomalously long Si spin lattice relaxation time in an alkali metal silicate solution.

Solutions were made with each alkali metal (except Fr) using reagent hydroxides, silica gel, and deionized water. The compositions were selected to provide the same distribution of silicate anions in each solution: monomers (Q^0), dimers (Q^1) and cyclic trimers (Q^2). The total SiO_2 concentration did not exceed 3 mol%, and the pH was constant at about 14. Spin-lattice relaxation times were measured using the CPMG sequence; they are plotted in Figure 1. Note that T_1 is significantly longer in the Li silicate solution than in any of the other solutions. Previous authors have ascribed ^{29}Si relaxation in such solutions to the influence of paramagnetic impurities such as iron [1]. The only source of iron contamination in these samples was the silica gel itself, so it is not possible that the vast variation seen in Figure 1 is due to a variation in Fe concentration. Therefore I would like to point out in this letter that in the case of Li-silicate other relaxation mechanisms that had been ruled out might be considered. One such mechanism is that proposed by Engelhardt et al [2], wherein in exchange of cations and protons on and off a charged silicate might provide a mechanism for relaxation. Another, previously ruled out [1], is the chemical shift anisotropy mechanism.

Yours sincerely,

Alon McCormick

1. Harris, R. K., and Newman, R. H., J. Chem. Soc., Farad. 2, 73, 1204, 1977.
2. Engelhardt, G., Z. Chem. 15(12), 495, 1975.



363-12

GORLAEUS LABORATORIES
LEIDEN UNIVERSITY
DEPARTMENT OF CHEMISTRY
Department of Animal Physiology

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO; CA 94303
U.S.A.

Your reference	Your letter	Our reference	Date	5, Einsteinweg
		AvW/AC	10-13-88	Phone (31) 71 - 272727
			(received 10/26/88)	direct dialling (31) 71 - 27 4262

From Dr. A. van Waarde, Prof.dr. J. Lugtenburg

Subject

IN VIVO ^{31}P-NMR OF FISH IN A VERTICAL BORE MAGNET AT 9.4 TESLA

Dear Dr. Shapiro,

For some time we have been interested in monitoring the influence of oxygen availability on the energy metabolism of fish by in vivo ^{31}P-NMR. A Bruker MSL-400 spectrometer (equipped with a vertical-bore 9.4 T magnet) and a Bruker bioprobe were available for this purpose. It was our intention to develop a flow-through system, which would fit in the bioprobe and would enable repeated measurements of the levels of sugar phosphates, inorganic phosphate, phosphocreatine and ATP besides the intracellular pH of the myotomal muscle.

The magnet is provided with shim coils and a device for sample spinning. The tube containing the shim coils is normally fixed by four bolts, which connect it to the spinning device. During in vivo experiments on fish, spinning is impossible and the space occupied by the spinning device is required for the head of the animal and the water inlet. The spinning device should therefore be removed, but for obvious reasons the shim coils should remain in their original position.

We clamped two semicircular pieces of metal (height 5 cm) around the lowest part of the shim tube, and fixed them to the bottom of the magnet with bolts. The shim tube is thus secured on its bottom end, and the spinning device can be removed without affecting the position of the shim coils.

For in vivo NMR on fish, the air lift and spinning device are raised over a distance of 10 cm. They are returned to their normal position for high-resolution NMR. This operation has been performed at least 50 times, without impairment on the field homogeneity.

The experimental fish is enclosed in a plexiglass flow-cell and immobilized by an inflatable plastic bag. The signal of the myotome is picked up with an 18 mm surface coil. The tuning range of the original LC networks in the Bruker bioprobe proved to be wide enough to enable tuning of the new coil to the phosphorus and proton frequencies, besides matching to a 50 Ohm transmission line at the phosphorus frequency of 162 MHz. A microsphere filled with a solution of methylenediphosphonate in D_2O, is mounted in the center of the coil and serves as an external intensity standard.

Some results are presented below. Figure 1A is the in vivo ^{31}P-NMR spectrum of the myotomal muscle of the Cichlid fish Oreochromis mossambicus. The spectrum was acquired after the animal had been in the magnet for a period of 2 hours in a well-oxygenated condition. Immediately after the animal is put in the magnet, the inorganic phosphate level is raised and phosphocreatine is low due to handling stress, The NMR-measurable effects of stress generally disappear within two hours. Figure 1B shows a spectrum of the same animal after 3 hours of environmental anoxia. Anoxia was introduced by bubbling of the perfusion medium with nitrogen. The labeled resonances are:

1. External standard (methylene diphosphonate);
2. Sugar phosphates;
3. Inorganic phosphate;
4. Phosphocreatine;
5. γ- phosphate of ATP;
6. α- phosphate of ATP;
7. β- phosphate of ATP.

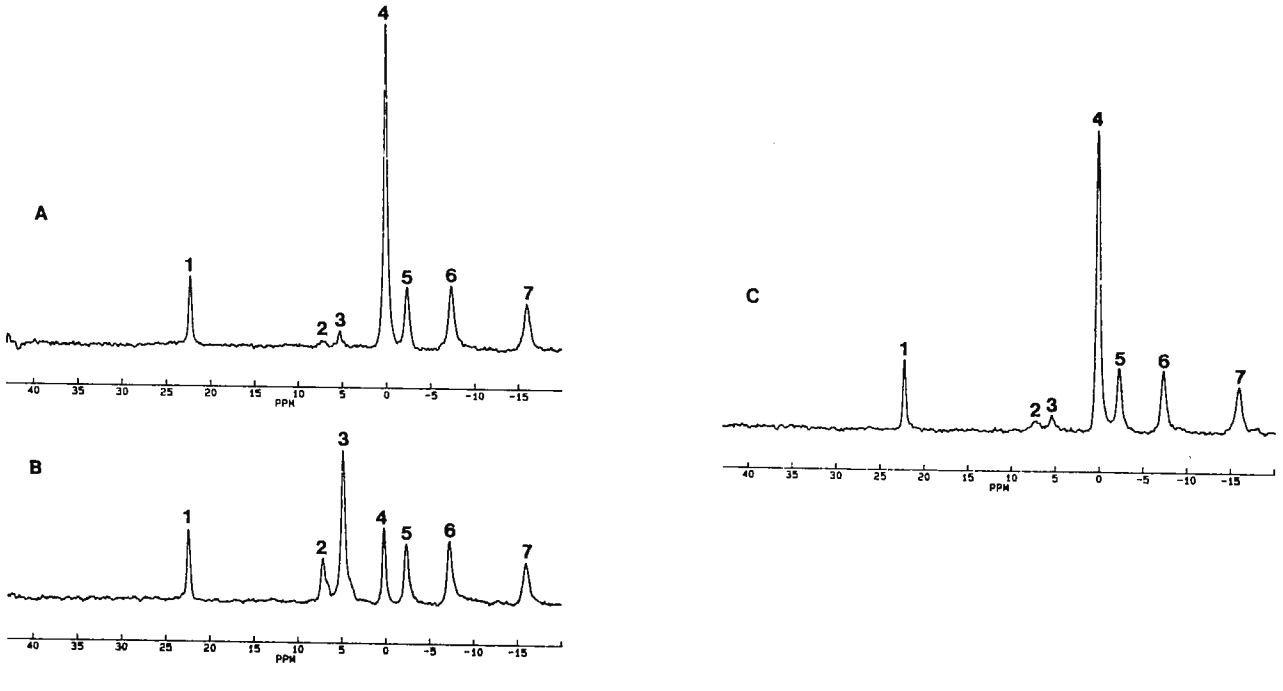
Finally, Figure 1C is a spectrum of the same animal acquired after 3 h of anoxia and 3 h of subsequent normoxic recovery.

The succes of this experimental approach is shown by the excellent resolution and signal-to-noise ratio of the in vivo spectra, whereas the high phosphocreatine/inorganic phosphate ratio in the control condition indicates a situation of low stress.

Sincerely yours,

Dr. A. van Waarde Dr. G.E.E.J.M. van de Thillart Prof.dr. A.D.F. Addink

Drs. C. Erkelens Prof.dr. J. Lugtenburg



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(606) 233-5546

(606) 257-4790

October 27, 1988
(received 11/10/88)

Professor Bernard L. Shapiro
~~Department of Chemistry~~
~~Texas A&M University~~
~~College Station, Texas 77843~~ !

NMR/Molecular Modeling at the University of Kentucky - Postdoctoral Position Available.

Dear Dr. Shapiro:

I hope this letter can serve as an introduction to the new NMR/Molecular modeling facility at the University of Kentucky, and will suffice to initiate a TAMU NMR Newsletter subscription for us. The facility consists of a 500MHz NMR spectrometer (5mm $^{1}H/^{19}F$, 5mm ID, 5&10mm BB probes), an NMR data station, and a high resolution graphics workstation; we anticipate all of the instrumentation will be operational by 01/01/89. Our current research focus is the study of structure-function relationships in biopolymers, but the facility is available to outside users for other applications.

Several NMR studies are currently being initiated at the center:

1. Structure/conformation studies on glycoprotein oligosaccharides using ^{13}C and ^{1}H NMR,

2. Structure/function studies of wild type and site-specifically mutated calcium binding proteins,

3. Structure/conformation studies on lipid head groups containing inositol and carbohydrate moieties, and

4. NMR studies on the binding of ^{13}C labeled substrates to enzymes.

We anticipate several other new projects will be starting up in the new year, including studies of metal ion binding to proteins and nucleotides, and look forward to making more substantive contributions to the newsletter as all of these projects evolve.

Sincerely yours,

Judith G. Shelling
Assistant Professor

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			10 g	18.
			5 x 10 g	75.
			10 x 10 g	145.
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82-70002	Deuterium Oxide "100%"	99.96	10 g	15.
			5 x 10 g	50.
84-70001	Deuterium-depleted Water	$< 5 \times 10^{-5}$	25 g	25.
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			20 x 25 g	300.
			30 x 25 g	400.
			1 kg	500.
82-00807	Dimethyl-d_6 Sulfoxide	99.9	10 x 1 g	12.
			10 g	12.
			5 x 10 g	56.
			10 x 10 g	115.
82-00809	Dimethyl-d_6 Sulfoxide (multi-dose septum vials)	99.9	10 g	12.
			5 x 10 g	56.
			10 x 10 g	115.
82-00061	Methanol-d_4	99.8	10 x 1 g	43.
			10 g	43.
			5 x 10 g	171.
			10 x 10 g	325.

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November 15, 1988

MAGNETIC RESONANCE UNIT
University of California Service
Veterans Administration Medical Center
4150 Clement Street (11D)
San Francisco, California 94121
(415) 750-2146

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

IN VIVO MAGNETIC RESONANCE SPECTROSCOPY II
(Weekend before the ENC)

Dear Dr. Shapiro:

Dr. Michael Weiner and I are again chairing a San Francisco Symposium entitled, "In Vivo Magnetic Resonance Spectroscopy II", which consists of:

Tutorial on In Vivo Magnetic Resonance Spectroscopy
Friday, March 31, 1989 (for physicians and scientists new to the field), and

Workshop on In Vivo Magnetic Resonance Spectroscopy
Saturday and Sunday, April 1 and 2, 1989 (an advanced participation workshop).

The symposium is being held under the auspices of the University of California, San Francisco, CA, and is being held at the main auditorium at the San Francisco Veterans Administration Medical Center. The workshop ends early Sunday afternoon to enable participants to also attend the ENC conference.

The Tutorial is aimed at Radiologists and other physicians, as well as chemists, physicists, biologists, and other scientists who desire an introduction to In Vivo magnetic resonance spectroscopy. The principles of MRS will be reviewed, followed by illustrations of applications to various organs, and to clinical medicine.

The Workshop is designed to be a participatory forum in which many of the attendees will make a brief presentation concerning their recent experimental work in the area. The Workshop will emphasize developments and applications of In Vivo MRS techniques. Additional details may be obtained by calling (415) 476-5731 for program information, or (415) 476-5808 for registration information.

Sincerely,

Gerald B. Matson
Adjunct Assoc. Prof., Pharm. Chem., UCSF
Facilities Manager, MR Unit, VAMC.

Michael W. Weiner
Assoc. Prof. Med. and Radiology, UCSF
Scientific Director, MR Unit, VAMC.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California 91125

Division of Chemistry and Chemical Engineering
Gates and Crellin Laboratories of Chemistry

John D. Roberts
Institute Professor of Chemistry, Emeritus

October 20, 1988
(received 10/28/88)

Dr. Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

Measurement of the affinity of glutamate dehydrogenase for NH_4^+ by ^{15}N NMR.

Glutamate dehydrogenase (GDH) which catalyzes the reaction:

$$NH_4^+ + \alpha\text{-ketoglutarate} + NAD(P)H + H^+ \underset{}{\overset{GDH}{\rightleftharpoons}} \text{L-glutamate} + NAD(P)^+ + H_2O$$

is one of two alternative pathways of ammonia assimilation in microorganisms. To estimate the actual contribution of the GDH pathway to ammonia assimilation in the cell, it is necessary to measure not only its activity in the cell extracts but also the affinity (K_m) of the enzyme for $NH_4^{\oplus}$. In the obligate anaerobe *Clostridium kluyverii*, such studies have been hampered by the presence in cell extracts of NADH oxidase and NAD(P)H-ferredoxin reductases which cause very rapid oxidation of NAD(P)H; as a result, the specific activity and K_m for $NH_4^{\oplus}$ of NAD(P)H-GDH cannot be measured by the standard spectrophotometric method of observing the rate of oxidation of NAD(P)H.

The GDH activity can be measured through observation of the time-dependent formation of [^{15}N]glutamic acid when cell extracts are added to an assay solution containing 25 mM $^{15}NH_4Cl$, 5 mM α-ketoglutarate and 15 mM NAD(P)H. Figure 1 shows representative ^{15}N NMR spectra of such reaction mixtures obtained with a Bruker AM-500 spectrometer operating at 50.68 MHz. Significant formation of [^{15}N]glutamic acid was observed in the presence of NADPH (Fig. 1A and B) but not in the presence of NADH (Fig. 1C) or in the absence of coenzyme (Fig. 1D). Therefore, the GDH of *C. kluyverii* is NADPH-specific. The number of nanomoles of [^{15}N]glutamic acid formed in the reaction mixture was calculated from its peak intensity in the NMR spectra by comparison with the peak intensity of a known amount of [^{15}N]glutamic acid. The activity (v) of NADPH-GDH was found to be 91 mU (nanomoles of [^{15}N]glutamic acid formed per min) per mg of protein when assayed with a $^{15}NH_4^{\oplus}$ concentration of 25 mM. To estimate the affinity of the enzyme for $NH_4^{\oplus}$, the activity was measured at various concentration of $NH_4^{\oplus}$.

At $^{15}NH_4^{\oplus}$ concentration of 5 mM and 2 mM, the activity decreased to 47 and 21 mU/mg of protein, respectively. The double reciprocal plots of $1/v$ vs. $1/[NH_4^{\oplus}]$ are shown in Fig. 2.

From the Lineweaver-Burk equation,

$$\frac{1}{v} = \frac{K_m}{v_{max}} \frac{1}{[NH_4^{\oplus}]} + \frac{1}{v_{max}}$$

$$\therefore \quad -1/K_m = 1/[NH_4^{\oplus}] \text{ at } 1/v = 0$$

the K_m of GDH for $NH_4^{\oplus}$ was calculated as 12.4 mM. These results suggest that the affinity of GDH for $NH_4^{\oplus}$ in *C. kluyverii* is considerably lower than that of glutamine synthetase which, coupled with glutamate synthase, constitutes an alternative pathway of ammonia assimilation.

Very truly yours,

Keiko Kanamori John D. Roberts

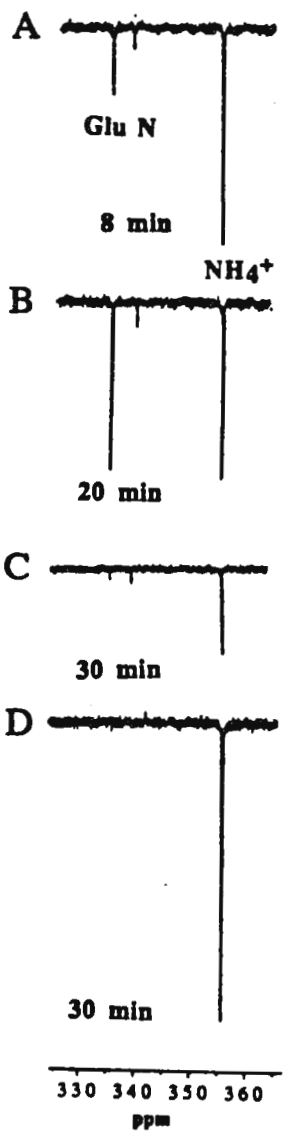

Figure 1

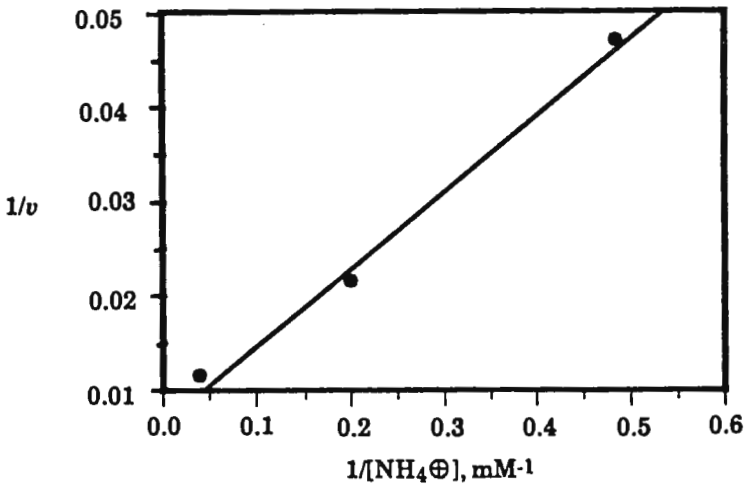

Figure 2

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SCRIPPS CLINIC
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November 5th, 1988 (received 11/9/88)

Dr. Bernard L. Shapiro
966 Elsinore Court
Palo Alto, CA. 94303

Application of Isotope-Edited NMR Techniques to Study Fab'-Peptide Complexes

Dear Dr. Shapiro:

Using isotope-edited NMR techniques, the peptide component of an Fab'-peptide complex of overall molecular weight 56kDa has been selectively monitored. The complexes consist of Fab' bound to several peptides which are identical in sequence but labelled with ^{15}N at different amide positions. The spectra were acquired using a heteronuclear multiple quantum coherence sequence, with either a pre-saturation delay or jump-return sequence to reduce the intensity of the water resonance.

The bound and free resonances of the peptide in these complexes have been observed during NMR titrations of the Fab' with peptide. The peptide is in slow exchange (relative to the chemical shift timescale), with off rates slower than approximately 15Hz. Each of the two complexes studied so far (which differ only in the peptide used to form the complex), has yielded a characteristic pattern of resonances which is unique to the particular labelled peptide examined. More specifically, one of the peptides is ^{15}N-labelled at sites which are believed to be within the epitope region of this peptide while the second peptide is labelled outside it. An example of the differences which have been detected by these NMR techniques is shown below in Figure 1. Spectrum A was recorded from a complex containing peptide labelled at residues which have been determined immunologically to be non-essential to the binding of the peptide to antibody. Similarly, spectrum B was obtained from the bound peptide component of a complex which contains ^{15}N labels at two of the four residues believed to be directly involved in binding (and are therefore within the epitope). The most notable differences to be observed from these spectra are the relative shifts of the amide protons upon binding as well as the overall linewidths of the two sets of bound resonances. The peptide labelled outside the epitope gives rise to bound resonances occurring upfield (relative to their corresponding unbound resonances) with overall linewidths which are considerably narrower than those of the second peptide shown in spectrum A. Also apparent from B which directly contrasts with the result shown in A, is the downfield shift of the bound resonances of this second peptide relative to their unbound counterparts.

The details from our studies of the two complexes which we have studied so far are given in a forthcoming paper on this subject *(Peptide Research,* in press). Further work to better characterize the NMR differences observed among the various labelled residues of the bound peptide in these complexes is underway in this lab.

Sincerely,

Pearl Tsang

Peter E. Wright

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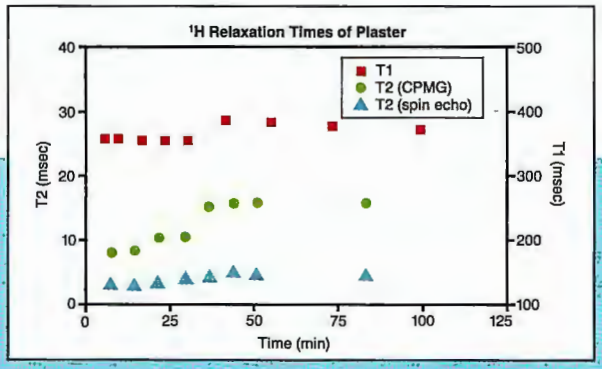

Non-destructive monitoring of the solidification of plaster at 4.7 Tesla. H-1 images obtained at (A): 18 minutes, (B): 28 minutes and (C): 38 minutes after a mixture of plaster and water (2:1 ratio) was prepared. The centers of the images are an intensity reference made of water doped with copper sulfate.

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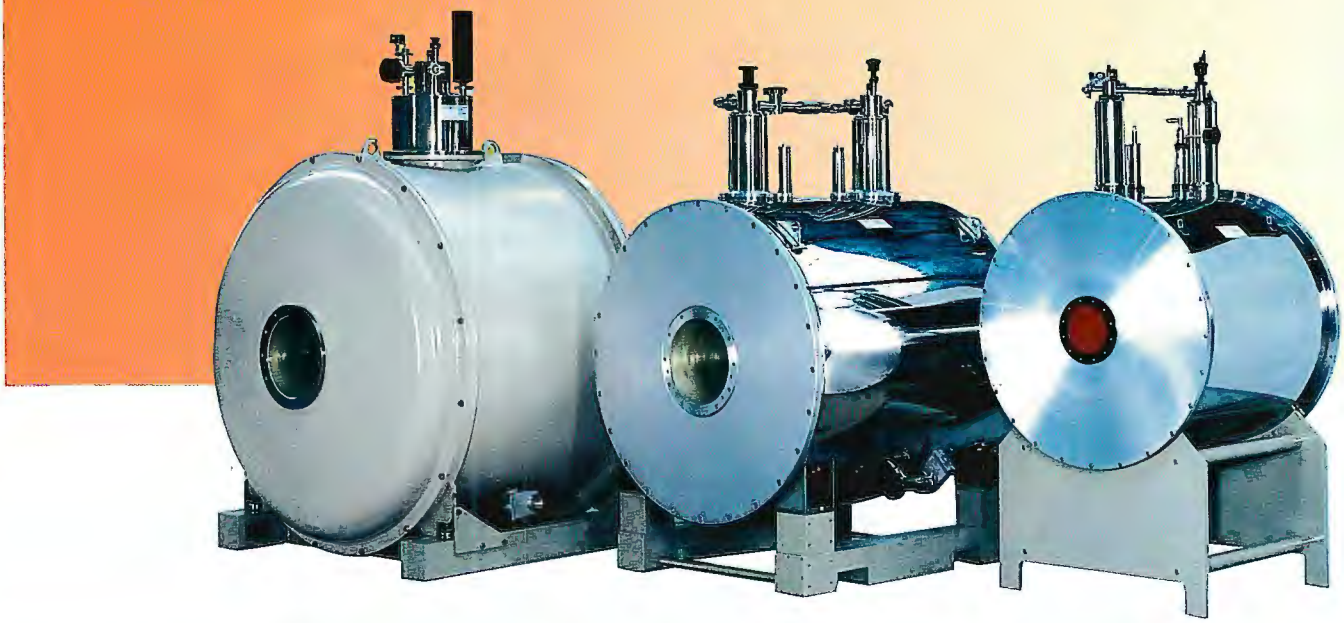
200/330	4.7T	330 mm	254 mm	2.3 G/cm	140 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	6.95 m	5.60 m
200/400	4.7T	400 mm	324 mm	1.8 G/cm	140 mm DSV ±4 ppm	80 mm DSV 0.1 ppm	8.50 m	6.75 m
85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

DSV = Diameter Spherical Volume
HHLW = Half-Height Line Width
PPM = Parts Per Million



200/400, 200/330, and 300/180 magnets for the NMR Imaging Spectrometer System.
(Photos courtesy Oxford Instruments.)

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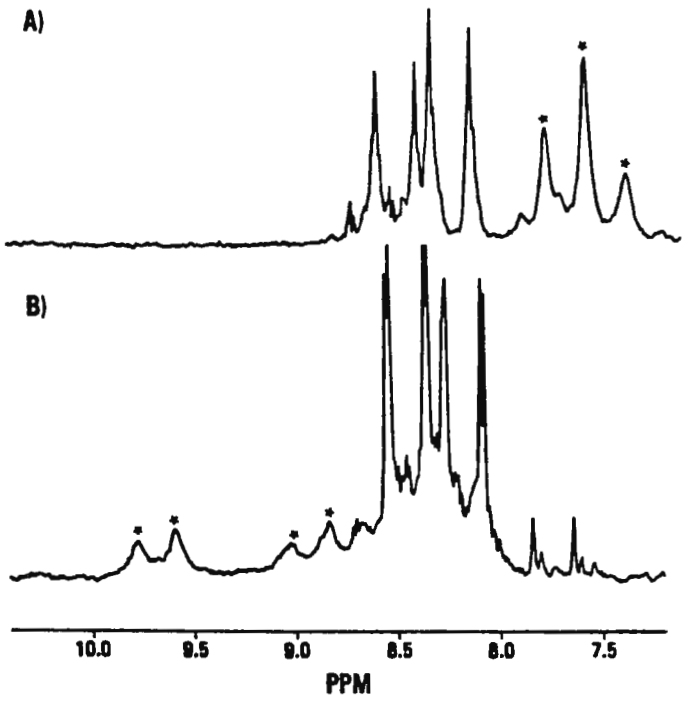

Figure 1: ^{15}N-edited NMR spectra obtained at 499.87MHz and 298°K from solutions of Fab' bound to a peptide labelled at residues outside (A) and within the binding region (B). The solutions contained excess peptide with approximate concentrations of 2:1 peptide:Fab' and maximum Fab' concentrations of 1 mM. The bound resonances are indicated by asterisks; the majority of the other resonances are due to the unbound or free peptide form also present in solution. Spectra were obtained without ^{15}N decoupling so each of the amide protons gives rise to a pair of resonances.

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Department of Physical Sciences

BMNC/88/19

Dr. Bernard L. Shapiro,
966, Elsinore Court,
PALO ALTO, CA 94303,
USA

12th October 1988
(received 10/29/88)

Dear Dr. Shapiro,

NMR, PATTERN RECOGNITION AND TOXICOLOGY

At the risk of taking a "fosselised" approach to science, we would like to describe some recent work arising from a collaboration with Jeremy Nicholson and Kevin Gartland from Birkbeck College, University of London. For several years, this group have been exploring the toxicological information available from ^{1}H NMR of body fluids and as part of a joint effort we are investigating the possibilities of computerised analysis of their data, in particular so called pattern recognition methods of displaying the data and classifying toxins based on their overall metabolic effects.

An initial approach has been to use techniques for reducing the multivariate data (in this case 15 endogenous metabolites from NMR of urine from animals given one of 10 different toxins) to two dimensions for display purposes. As well as principal components analysis we have used non-linear mapping (NLM). In essence each toxin in this case can be represented as a point in 15 dimensional space - each coordinate being the intensity ascribed to one metabolite. Hence points (toxins) which come close in 15 dimensional space will do so because of the similarity of their overall metabolic profile. NLM allows one to reduce this 15 dimensions to 2 by retaining as closely as possible, using mathematical minimisation methods, the relative inter-toxin distances. An early example is given in the figure which shows an NLM of 10 toxins using 15 metabolite intensities to define them. The points 1-4 are kidney toxins affecting the proximal tubule, 5 and 6 are kidney papillary toxins, 7-9 are hepatotoxins affecting the centrilobular region and 10 is a hepatotoxin affecting the periportal region.

Yours sincerely,

J.C. LINDON C.R. BEDDELL B.C. SWEATMAN

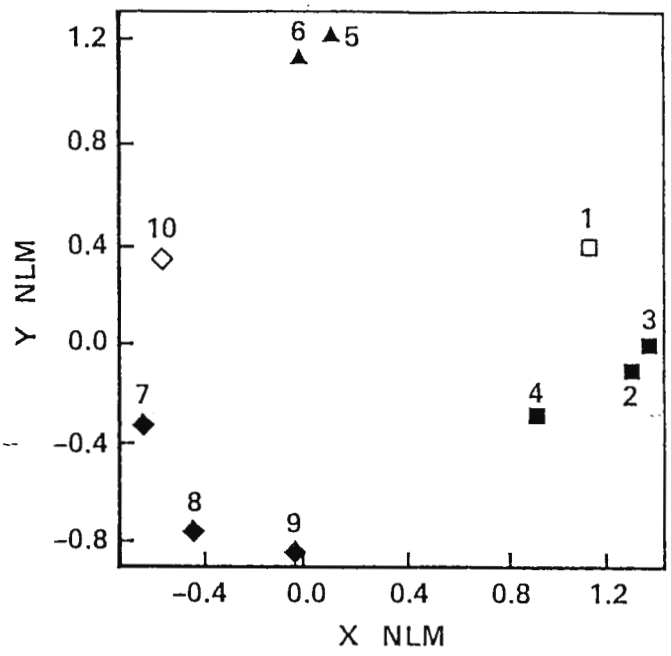

FIGURE CAPTION:

NLM of the NMR derived dataset, with equal weighting of all parameters.

The toxins are: chromate(1); p-aminophenol(2); hexachlorobutadiene(3); Hg(II)(4); propyleneimine(5); 2-Br-ethanamine.HBr(6); $NH_2.NH_2$(7); CCl_4(8); thioacetamide(9); α-naphthylisocyanate(10).

The metabolites measured are: acetate, alanine, citrate, creatinine, dimethylamine, glucose, glutamine, hippurate, lactate, lysine, 2-oxoglutarate, succinate, taurine, trimethylamine-N-oxide, valine.

NMR Spectroscopy Position at the University of Minnesota

The Department of Chemistry at the University of Minnesota will be adding two new spectrometers (500 MHz and 300 MHz) to its NMR facility (for a total of 6 instruments) and is seeking an NMR spectroscopist to augment the facility staff. Duties include the maintenance and operation of the facility instruments and applications support in the use of modern NMR techniques to solve current problems in chemical research. Candidates should also have the ability and desire to develop cooperative research projects with faculty in chemistry. This is a full time, annual renewable Research Associate position.

Minimum requirements include a Ph.D. in chemistry or related area. Experience in modern NMR techniques is desirable. Applicants should send a resume along with names and addresses of three references to: Professor Lawrence Que, Jr., Department of Chemistry, University of Minnesota, 207 Pleasant St. S.E., Minneapolis, MN 55455. Application deadline: January 31, 1989. Starting date is negotiable but should be no later than Fall, 1989. The University of Minnesota is an Equal Opportunity educator and employer and specifically invites and encourages applications from women and minorities.

The 30th ENC

(Experimental NMR Conference)

April 2-6, 1989

The Asilomar Conference Center, Pacific Grove, CA

The 30th ENC will emphasize the experimental aspects of magnetic resonance and will feature invited lectures, contributed posters, and short talks selected from the submitted posters. Time will also be allocated for informal meetings of special interest groups.

Program Highlights

SUN

Evening (7:30 p.m.): Solid-State NMR Methods: Structure, Order and Dynamics; *B. D. Bluemich, Chair.*

MON

Morning: New Directions in Sample Rotation; *F. D. Doty, Chair.*
Morning: NMR of Atomic Clusters; *J. A. Reimer, Chair.*
Afternoon: Poster Session A.
Evening: EPR by Echoes and FIDs; *H. Thomann, Chair.*

TUES

Morning: 2D and 3D NMR in Liquids; *G. Bodenhausen, Chair.*
Morning: NMR for Analysis: Large Fields and Small Molecules; *M. W. Baum, Chair.*
Afternoon: Open. Special Interest Group Meetings.
Evening: Spectral Calculations and Spectral Databases; *C. G. Wade, Chair.*
Evening: Extremes (Miscellany); *A. N. Garroway, Chair.*

WED

Morning: Novel Physical Phenomena in NMR; *R. Tycko, Chair.*
Morning: Protein NMR Spectroscopy; *S. J. Opella, Chair.*
Afternoon: Poster Session B.
Evening: Banquet.

THURS

Morning: Advances in Biological Imaging and Gradient Techniques; *J. J. H. Ackerman, Chair.*
Morning: Stress and Relaxation; *R. G. Bryant, Chair.*

Asilomar, "the refuge by the sea", occupies 105 secluded acres at the tip of the Monterey Peninsula overlooking the Pacific Ocean. The beautiful, natural setting offers a relaxed environment for scientific exchange and for recreation.

The deadline for registration and poster abstracts is January 13, 1989. To obtain registration information, contact the ENC Office, 750 Audubon, East Lansing, MI 48823, (517) 332-3667.

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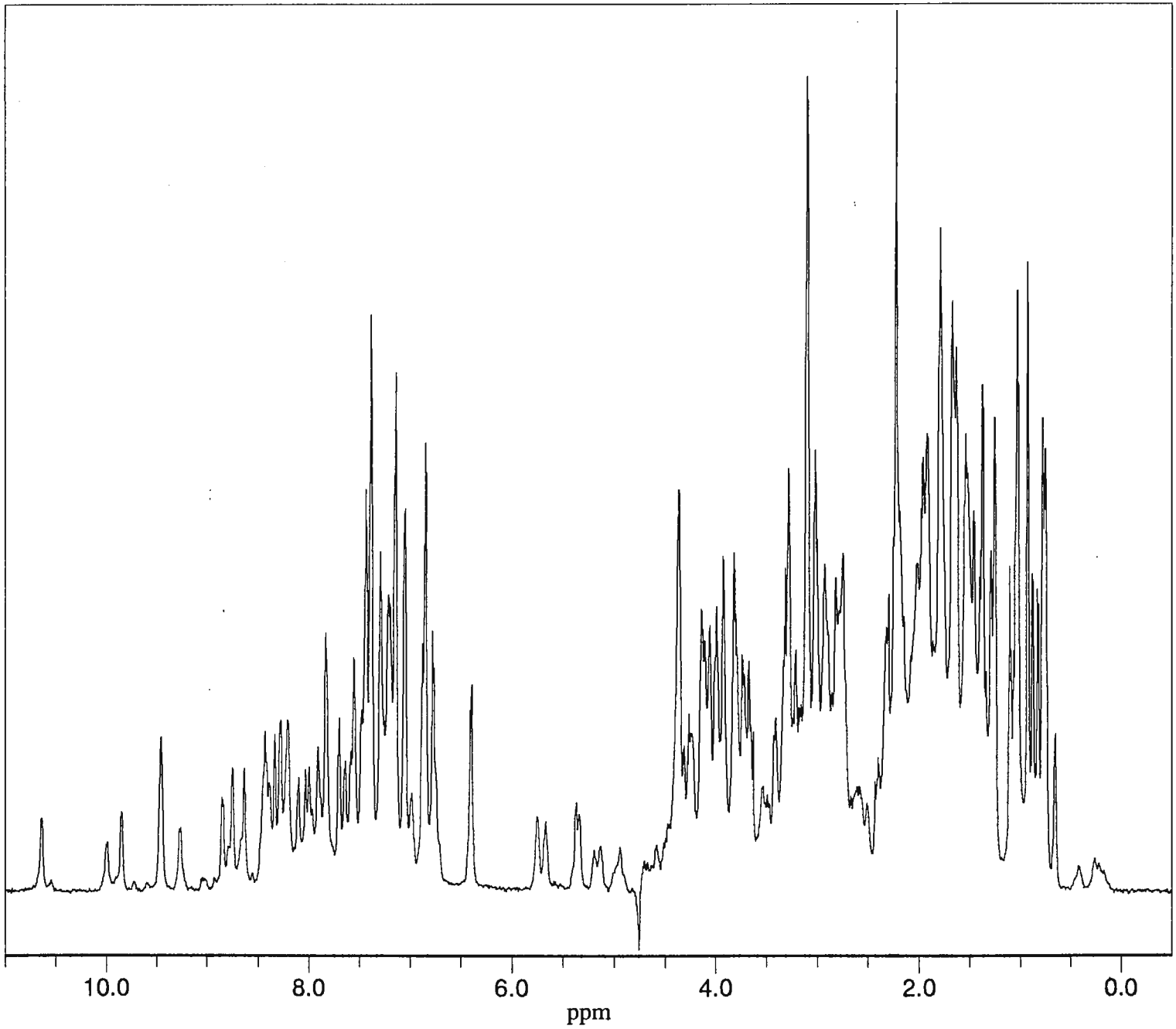

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Plot created by applab on
Thu Nov 3 19:22:47 EST 1988
Data stored by GE NMR on
Oct 20 17:52:00 1988
Comment:
2 milliMolar BPTI 37C 90% H2O

APPL Experiment
/usr/omega/pplib/noephy
t1dw = 125us
t1de = 1us
dlev = 62
d1 = 200ms
pw = 15us
dpw = 3s
pd = .1

Observe RF
FREQUENCY = 599.5928560 *MHz*
HI POWER = 63 *dB*
OFFSET = 2855.67 *Hz*

Decoupler RF
MODE = HETERO
FREQUENCY = 599.5928560 *MHz*
POWER OFF = 40 *dB*
MODULATION = CW

Receiver
GAIN = 120
BESSEL FILTER = 8100 *Hz*
PREAMP FILTER = OFF
LOCK TRAP = ON

Alpha HR Digitizer
DWELL TIME = 125 *usec*
SPECTRAL WIDTH = 16000 *Hz*
ACQ. TIME = 512 *msec*
BLOCK SIZE = 4096 *pts*
ACQUISITIONS = 32 *scans*

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

Dr. Bernard L. Shapiro
TAMU NMR News Letter
966 Elsinore Ct.
Palo Alto, CA 9430

National Institutes of Health
Bethesda, Maryland 20892
Building : 10
Room : 6N105
(301) 496-3390

November 8,1988
(received 11/12/88)

Dear Dr. Shapiro:

Very High Resolution in Vivo Localized Spectroscopy in Small Animals at High Magnetic Fields.

Investigators are generally concerned about the feasibility of high resolution localized NMR spectroscopy in small animals at high magnetic field strengths. The basis of concern is the size of the homogeneous volume of interest (VOI), which is generally smaller than 1-2 cm^3. In large homogeneous volumes, e.g. the human brain, and at low field (1.5 T) localized spectroscopy has already been demonstrated [1,2]. For small volumes and high fields (we have a 4.7 T GE horizontal bore) neighbouring tissues of different magnetic susceptibility complicate accurate localization and shimming of the VOI. We are now convinced that these problems can be solved when shielded strong gradients are available for localization procedures involving B_0 gradients.

Recently General Electric Fremont kindly provided a prototype set of shielded gradients (built by Peter Roemer) for our 4.7 T spectrometer. The available gradient strength is 200 mT/m with a bore of 15 cm. After modification of the stimulated echo (STEAM [3]) sequence excellent localized in vivo spectra were obtained (figure). The basic STEAM sequence is:

90_x - TE/2 - 90_x - TM - 90_x - TE/2 - acquire on top echo

Addition of dephasing gradient pulses greatly improved the performance of this sequence:
a) In the TM period three crushers of 80 mT/m for 2 ms assured formation of a stimulated echo free from secondary echoes;
b) In the TE/2 periods primer/crusher pairs of 110-150 mT/m for 3ms removed additional transverse magnetization generated by the third 90_x pulse. These gradients also facilitate quick dephasing of the signal in the first TE/2 period.
Strong slice selection gradients reduce the effects of susceptibility, resonance offset and shimming on the accuracy of the localization. A disadvantage of the use of strong gradients is found in signal attenuation as a consequence of diffusion effects. All of these factors are discussed in a paper that has been submitted to Magnetic Resonance in Medicine.

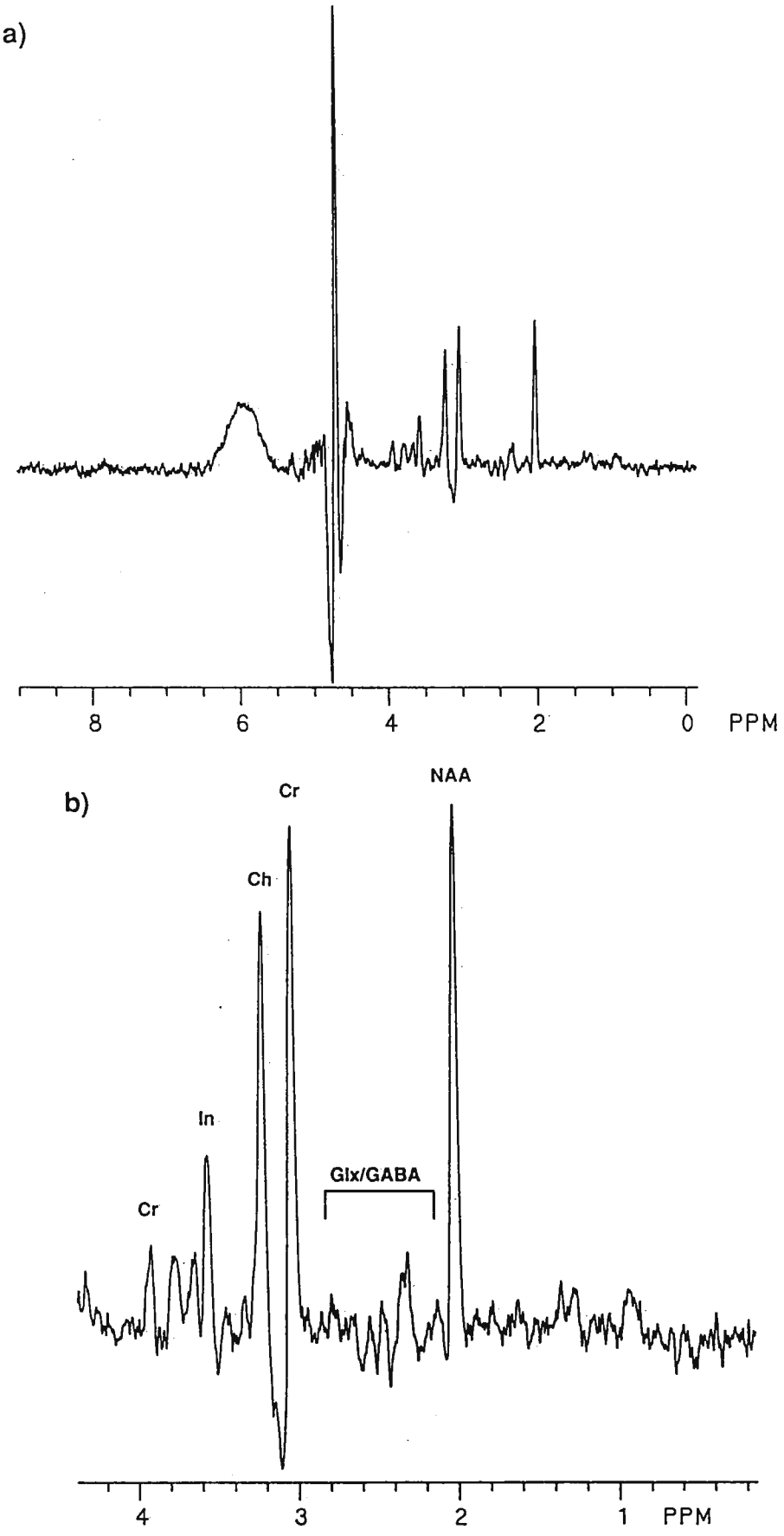
The spectrum was obtained by just placing a surface coil on the head of a cat, without any surgical procedures. Water suppresion was performed using a series of CHESS pulses [4] before the sequence and in the TM period. The nominal volume localized was 1 cm^3.

[1] J. Frahm, M.L. Gyngell, H. Bruhn, K.-D Merboldt, W. Hanicke and R. Sauter, SMRM, 7th annual meeting, 1988, p. 613. [2] P.R. Luyten, A.J.H. Marien and J.A. den Hollander, SMRM, 7th annual meeting, 1988, p.327. [3] J. Frahm, K.-D Merboldt, W. Hanicke, J. Magn. Res. 72, 502 (1987). [4] A. Haase, J. Frahm, W. Hanicke and D. Matthaei, Phys. Med. Biol. 30, 341 (1985).

Yours Sincerely,

Peter van Zijl* Chrit Moonen@ Jeffry Alger$ Jack Cohen* Scott Chesnick*

* NCI @BEIB $NINCDS



Proton spectrum of cat brain at 4.7 T. Nominal volume 1 cm^3; Slice profiles show that 93 % of the signal is within a 1.4x1.4x1.4 cm^3 cube. TE = 67 ms; TE = 50 ms; a) complete spectrum; b) expanded high field region. Linewidth of N-acetyl aspartate (NAA) is 7 Hz when using a 2 Hz line broadening. Assignments are Cr = Creatine/phosphocreatine; In = Inositol; Ch = Choline/phosphorylcholine; Glx = glutamate and glutamine.

CLARK UNIVERSITY
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Department of Chemistry

Telephone (508) 793-7116

October 26, 1988

Dr. Barry L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

RE: "Overcoming non-linear response problems immediately following the rf pulse"

Dear Barry:

In response to the deadly pink slip, my apologies for tardiness. The problem of correcting for non-linear response in the FID immediately following the pulse has been an ongoing problem in the observation of broad lines. The arbitary use of the left shift (LS) command and refocussing (echo) experiments have been employed. The echo experiments yield intensities dependent on inherent relaxation processes and motion on the timescale of the experiment. This is often informative but it is also desirable to have a method of obtaining reasonable accurate intensities and lineshapes directly from the FID.

We have been using a rather simple approach which can be employed when the form of the lineshape is known and accurate intensity information is desired. The experimental FID is first corrected for receiver nonlinearity via the LS command, in our system 14μsec is an appropriated blanking time which yields a FT spectrum which does not exhibit the problem of base line distortion. Recognising that this experimental lineshape is not an accurate representation of the NMR signal a correction has to be applied. The method we use involves taking a calculated theoretical frequency spectrum, both the real and imaginary part, and performing an inverse discrete Fourier transform to yield a theoretical FID. The appropriate amount of early time response in accordance with the blanking is deleted (14μs in the case described) and the resulting time domain signal Fourier transformed to yield a frequency spectrum which can be compared to the experimental lineshape for fitting. Adjustments are made to the initial theoretical spectrum to optimise the fit and the process is complete.

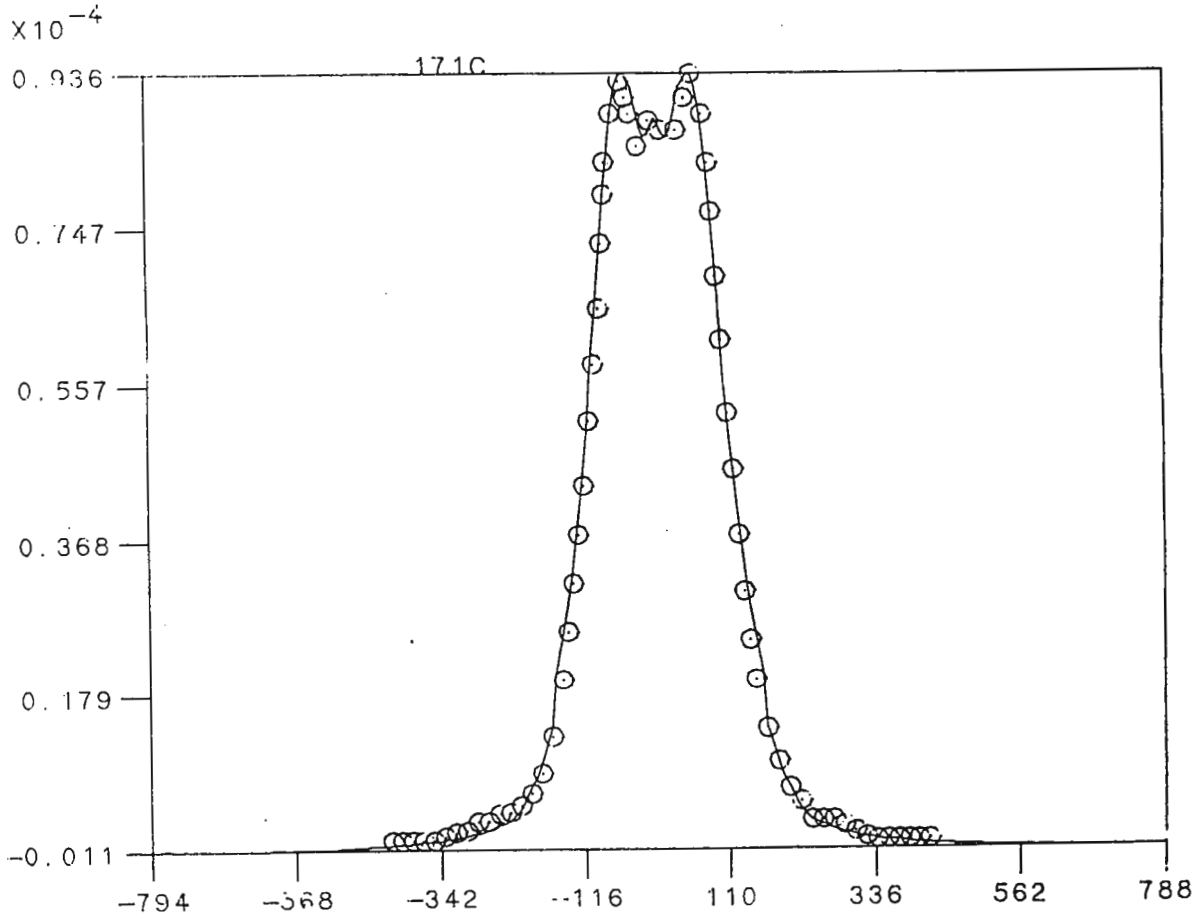
Two points have to be mentioned. After deleting the appropriate number of time domain points from the theoretical FID generated by the inverse FT, the first data point in the resulting FID must be set to the mid value of the first point and the last point of the data set. Also if we wish to calculate the intensity loss due to LS, the intensities of the theoretical and experimental LS FID'S must be normalised. In our case left shifting to the extent of 14μs produced an intensity loss of 19% for a proton Pake pattern of width approximately 25kHz. A useful discussion of the discrete Fourier transform and inverse Fourier transform appropriate to this is given in "The Fast Fourier Transform" by E. Oran Bingham (Practice Hall Inc.) A typical fit of an experimental (points) and theoretical (line) spectrum obtained after left shifting is shown. The original theoretical lineshape obtained from this proceedure has a Pake splitting of 2.515 gauss and a gaussian broadening of 5900hz. If the correction procedure is not employed, errors in the Pake splitting on the order of 22% are obtained.

Sincerely,

Ka-Loh Li Paul.

Ka-Loh Li & Paul T. Inglefield

KLL/PTI:gms



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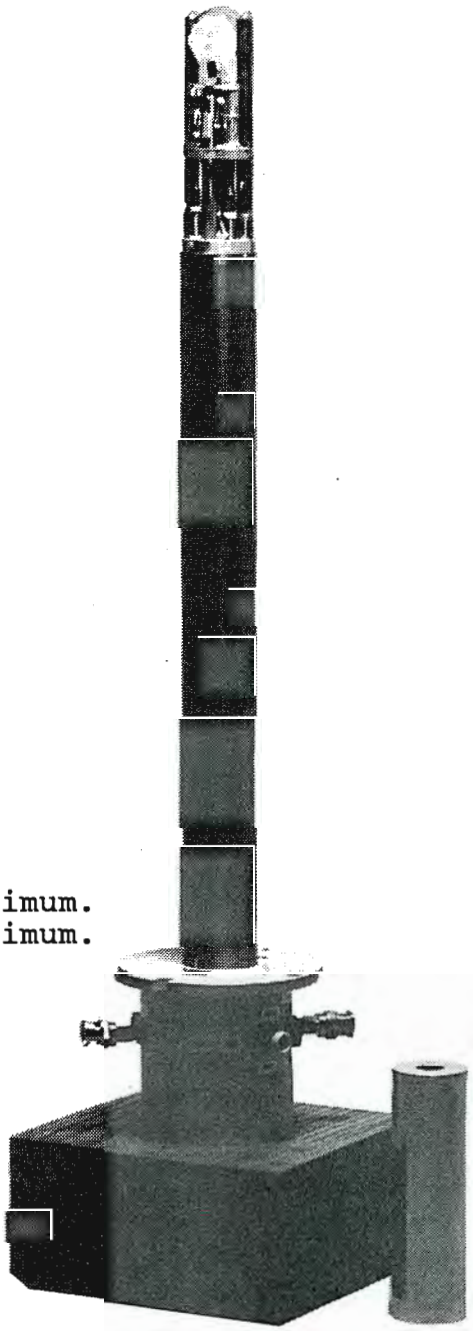

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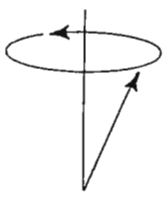

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Dr. B. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303.

October 25, 1988
(received 11/1/88)

Dear Bary,

^{2}H 2D exchange of Bullvalene in nematic solvents

We have recently applied 2D exchange spectroscopy[1] to deuterium NMR of small molecules in liquid crystalline solutions.[2] The approach is similar to that used by Spiess et al.[3] in solids and employs a combination of Zeeman- and quadrupole-order sequences. The case of the Cope rearrangement in bullvalene is particularly interesting because of the appearance of high order cross peaks. From the structural formula the rearrangement process can be expressed in terms of a simple exchange connectivity diagram[4] as shown in the enclosed figure.

The figure also depicts a low temperature 1D-spectrum of bullvalene-d_{10} dissolved in ZLI2452, and a sequence of three 2D-exchange spectra for different mixing times, τ_m. It may be seen that in the spectrum for τ_m=2ms only first order cross-peaks appear, i.e. cross-peaks between diagonal signals directly connected in the exchange diagram.

As the mixing time increases higher order cross-peaks show up. Thus in the τ_m=5ms spectrum the second order cross-peak (1,2) represents deuterons that started at site 1 in the beginning of the mixing time, transferred to site 3 and ended up in site 2 at t=τ_m. In the τ_m=10ms spectrum we observe another second order cross-peak (3,4) and in addition a third order signal (2,4) which corresponds to deuterons that started at site 2 and transferred via sites 3 and 1 to site 4. Quantitative measurements confirm the expectation that the integrated intensities of the first, second and third order cross-peaks increase respectively as τ_m, τ_m^2 and τ_m^3 (for short mixing times).

The example shows how deuterium 2D exchange in liquid crystalline solutions can provide information on the mechanism and rate of chemical processes as well as structural data and information about ordering parameters.

With best wishes,

C. Boeffel, Z. Luz, R. Poupko, H. Zimmermann

1. J. Jeener, B.H. Meier, P. Bachman and R.R. Ernst, J.Chem.Phys. 71, 4576 (1979).
2. C. Boeffel, Z. Luz, R. Poupko and A.J. Vega, Israel J.Chem. (in press).
3. C. Schmidt, S. Wefing, B. Blümich and H.W. Spiess, Chem.Phys.Lett. 130, 84 (1986).
4. Y. Huang, S. Macura and R.R. Ernst, J.Am.Chem.Soc. 103, 5327 (1981).

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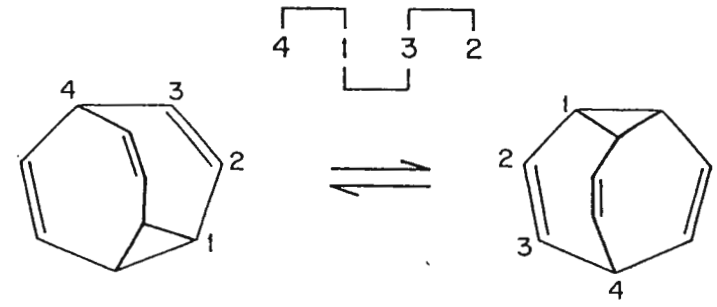

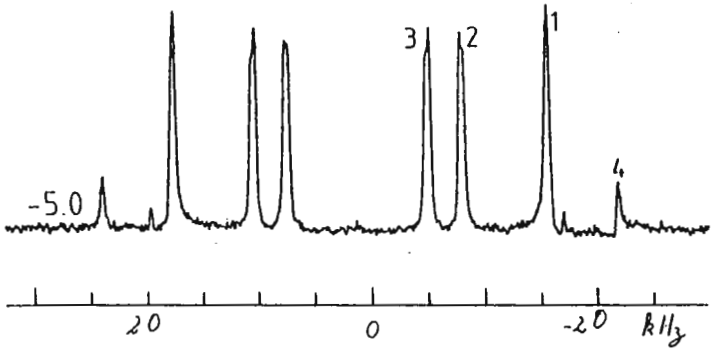

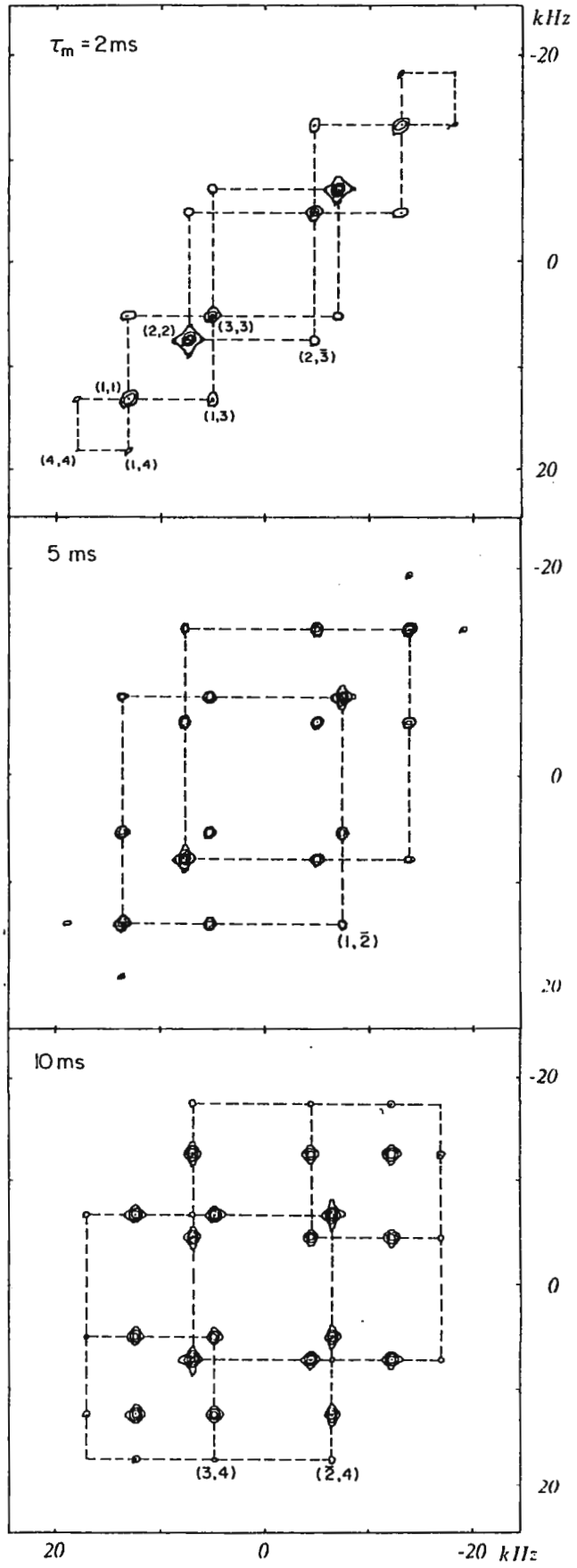

Above: 1D deuterium NMR spectrum of bullvalence-d_{10} (3.8wt%) in the nematic solvent ZLI2452 at -5°C and the exchange connectivity diagram for the Cope rearrangement process. Right: 2D exchange spectra of the same solution as above at +5°C and different mixing times, τ_m, as indicated.

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November 15, 1988
(received 11/19/88)

Dr. Bernard L. Shapiro, Editor
Texas A & M NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Title: Proton decoupling at 7T with 420 mW RF power

Dear Dr. Shapiro:

Proton decoupled carbon-13 NMR spectroscopy of biological samples at high magnetic fields critically requires efficient proton decoupling. Recent innovations which use periodic sequences of composite pulses have greatly improved the efficiency of heteronuclear decoupling. Among these improvements, the WALTZ-16 (1) decoupling sequence stands out due to its high quality of decoupling over wide bandwidths, and because it requires only a modest amount of radio frequency power. These periodic sequences have long repetition periods at low B_2 fields resulting in weak sideband responses in the observed spectrum.

The WALTZ-16 sequence implemented in the process controller of our AM-300 spectrometer failed to produce the quality of decoupling demonstrated in the literature (1). Therefore, we constructed a version of the hard-wired circuit with an ultra-fast modulator to preclude degradation of the decoupling sequence by phase transient interference (2). (Results are scheduled to appear in the January 1989 issue of J. Magn. Reson.) Figure 1 shows proton decoupled carbon-13 spectra of formic acid using different values of decoupling field strength. The plot width is 10 Hz, and each spectrum is plotted at the same amplitude to illustrate the variation in linewidth. In A, a hard-wired WALTZ-16 circuit and our ultra-fast modulator were used. In B, the composite pulse decoupling (CPD) WALTZ-16 implemented in the AM-300 was used. (Identical results were achieved using an AM-500, also.) In Figure 2, we again compared the two WALTZ-16 circuits using 1 M cholesteryl acetate in $CDCl_3$. Part A shows the spectrum obtained using our hard-wired circuits, and part B that obtained with the AM-300 modulation scheme. Part C is the difference between A and B. The decoupler frequency was placed at 4 ppm in the proton spectrum, and a $\gamma B_2/2\pi$ field of 2 kHz was used.

In other experiments using a $\gamma B_2/2k$ field of 1.4 kHz (produced by 420 mW RF power) we found that the hard-wired WALTZ-16 and our ultra-fast modulator provided a 3dB decoupling bandwidth of 3200 Hz. This bandwidth is adequate for use at 300 MHz. However, cycling sidebands were more intense at the lower decoupling field strength. We determined that the cycling sideband signals could be suppressed by varying the decoupler modulation clock frequency during the time averaging period. By limiting clock frequency changes to a few percent, the quality of decoupling remained high. In Figure 3 proton decoupled carbon-13 spectrum of formic acid (1000 scans) show cycling sidebands produced by the WALTZ-16

sequence using a hardwired circuit and our ultra-fast modulator ($\gamma B_2/2\pi$ = 1.4 kHz). In the lower spectrum of each panel a second order spinning sideband is identified with an arrow. The intensity scales are expressed as a percentage of the height of the main signal (at 0 Hz) which has been truncated. In panel A, the spectra using the WALTZ-16 modulation. In panel B, the spectra using WALTZ-16 with repetitive incrementation of the decoupler clock frequency. (A full report is scheduled to appear in the March 1989 issue of J. Magn. Reson.)

Best wishes,

Doug

George D. Markham Robert W. Dykstra

/pb

(1) A. J. Shaka, J. Keeler and R. Freeman, J. Magn. Reson. 53, 313 (1983).
(2) M. Mehring and J. S. Waugh, Rev. Sci. Instrum. 43, 649 (1972).

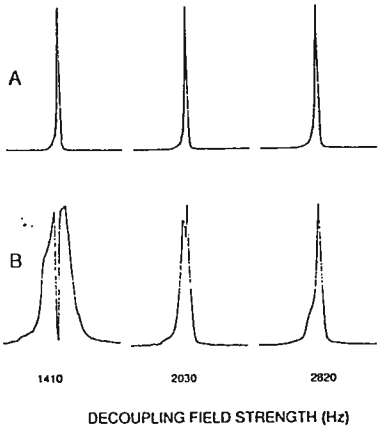

Fig. 1

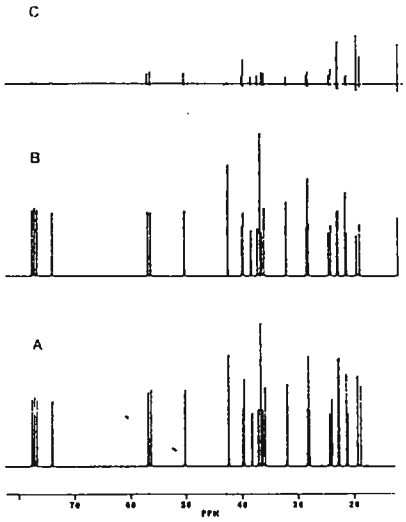

Fig. 2

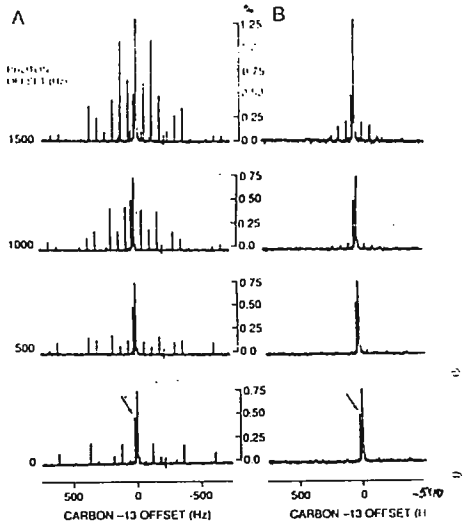

Fig. 3

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Laboratoire de Chimie Fine aux Interfaces
Institut de Chimie B6 - Université de Liège - Sart-Tilman par 4000 Liège - Belgique

(received 11/8/88)

Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto, CA.94303

Structure and Microdynamics of the Water Layer
Next to a Charged Aluminosilicate Sheet.

Dear Barry,

One of the key determinants of the activity of clay catalysts is their surface acidity. Expressed in H_0 (Hammett acidity function) units, it is about 0 for many clay minerals. It can go down to values between -5 and -8, i.e. in-between the acidity of concentrated nitric acid and of sulfuric acid oleums, for suitably dried montmorillonites of certain types. It becomes an important question to ascertain in detail the reasons for such high Brønsted acidities.

It appeared to us that multinuclear magnetic resonance could answer this question. The prescription calls for suspending a bentonite, Ecca Gum BP (English China Clay, St. Austell, Cornwall) in heavy water, using sufficient amounts (0-50 mg per mL) for a gel to form. The sample is then introduced in a strong magnetic field (B_0 = 7.1 T), without spinning. One waits for a while -- having a Belgian chocolate mousse or coffee, for instance -- for the sample to get oriented by the field.

The residual quadrupolar splittings of the deuterons (or of oxygen-17 at natural abundance) come from those very water molecules we meant to get a look at, in fast exchange with gallery and bulk water. The residual splitting changes sign when the intersticial cations are exchanged from the original sodium to calcium. This indicates a switch in prefered water reorientation : from around the hydrogene-bond anchoring D_2O to the negatively-charged aluminosilicate sheet, to around the electrostatic bond between a lone pair on oxygen and the cation. Deuterium relaxation rates provide the correlation time descriptive of this reorientation : 1.6 ns in the sodium case. For the same sodium case, because different spectral densities (and different mixes of these) determine the longitudinal and the transverse relaxation rates, one can also obtain the reorientational correlation time for hydrated sodium counterions stuck by atmospheric condensation at the clay interface : 8.2 ns. It is to be expected that the solvation waters should reorient, due to libration for instance, somewhat faster than the cations they are attached to.

This is, to our knowledge, the first time that the condensed counterions are thus observed in rather direct manner; and that evidence is provided that indeed there are water molecules squeezed in-between the counterions and the charged surface, in agreement with the original concepts of atmospheric condensation theory (outer sphere complexes).

The correlation time obtained here for condensed sodium cations is similar to that reported recently for sodium ions in the vicinity of a silica sample (1). We have analyzed the data according to the standard approach in the field (2). Similar observations of a sign change for the residual quadrupolar splitting have been published recently for a liquid crystalline case (3).

The clay used here is the same as we have employed to catalyze nitric acid nitration of toluene with excellent results : yields of 75% plus, a <u>para</u> preference up to 80%, and a turnover of 850 at the very least (4). Now we shall endeavor to use it to catalyze biochemical reactions, of the type needed to make Belgian chocolate fuel us with energy. In the meanwhile, enjoy Californian wines!

With warmest personal regards,

Dr. Jean Grandjean

Dr. Pierre Laszlo

(1) H.M. Jang and D.W. Fuerstenau, Langmuir, 3, 1114 (1987).
(2) B. Halle and H. Wennerström, J. Chem. Phys., 75, 1921 (1981).
(3) W. Guo and T.C. Wong, Langmuir, 3, 537 (1987).
(4) A. Cornélis, A. Gerstmans, and P. Laszlo, Chemistry Letters, in press.

Sample n°	Ca^{2+} / Na^{+}	Δδ, ±0.1Hz
Na Ecca:1	0,002	+16.3
2	0.020	+14.4
3	0.0653	-2.2
4	0.1266	-14.6
5	0.1642	-19.4
6	0.2080	-20.6
7	0.4638	-22.2

Table 1. ^{2}H quadrupolar splittings at 299 K for clay suspensions (0.0238 g/mL D_2O) as a function of the Ca^{2+} / Na^{+} ratio.

Sample n°.	Mg^{2+} / Na^{+}	Δδ, ±0.1Hz
1	0	+16.3
8	0.0206	+12.7
9	0.0422	+7.5
10	0.1464	0
11	0.1987	0
12	0.2728	0

Table 2. ^{2}H quadrupolar splittings at 299 K for clay suspensions (0.0238 g/mL D_2O) as a function of the Mg^{2+} / Na^{+} ratio.

Sample n°.	$\Delta\delta(^{17}O)/\Delta\delta(^{2}H)$
1	5.0
2	5.0
4	5.0
5	± 3
7	± 0

Table 3, Ratio of the oxygen-17 to the deuterium quadrupolar splittings for selected samples at 320 K.

University of Delaware

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
NEWARK, DELAWARE 19716

November 3, 1988
(received 11/7/88)

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

"Deuterated Organic Molecules as Probes of Zeolites"

Dear Barry:

In our continuing study of zeolites, we have decided to take advantage of the excellent solid-state deuterium capability of our Bruker MSL-300 NMR spectrometer. We have obtained samples of the pentasil ZSM-5 having different Si/Al ratios, prepared with a perdeuterated trans-stilbene probe.[1] The structure of the ZSM-5 can be described as straight and sinusoidal, intersecting channels with radii on the order of 5.5 Å. Our initial studies reveal that the deuterium line shapes, which monitor the motion of the trans-stilbene, are dependent on the Si/Al ratio of the ZSM-5. The solid-state deuterium spectra shown are those of the probe in ZSM-5 with Si/Al = 34 at a) room temperature and b) 353 K and with Si/Al = 490 at c) room temperature and d) 353 K.

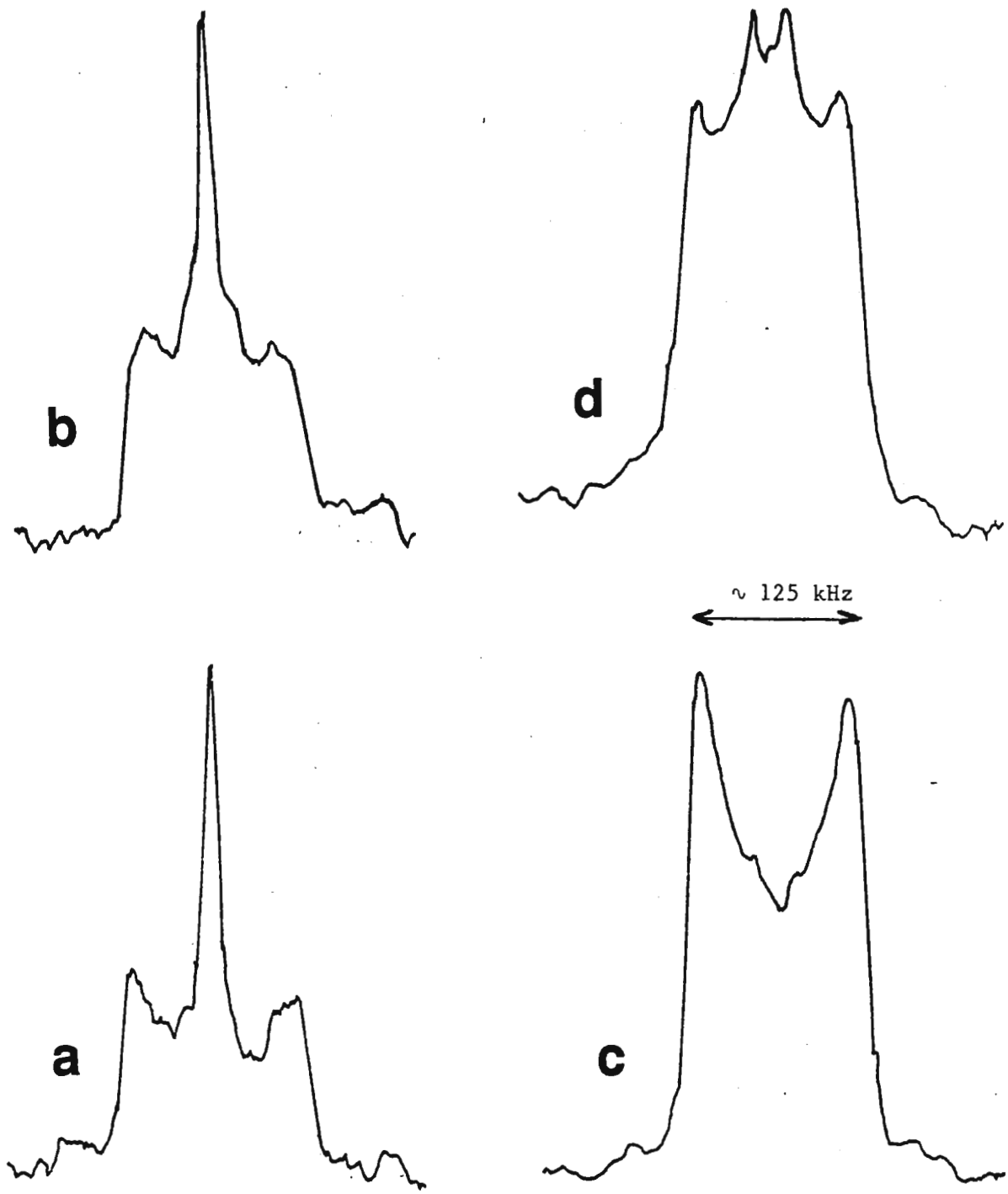
The large splitting observed in all of the spectra represent probe molecules that are rigidly held, possibly within the sinusoidal channels of the zeolite. As the temperature is increased, a small population of probe molecules exhibits increased mobility. Of interest is the fact that the probe molecule's mobility increases with decreasing Si/Al ratio. Some probe molecules incorporated in the less siliceous ZSM-5 exhibit isotropic motion, whereas those in the highly siliceous ZSM-5 undergo only restricted motion, as reflected in the line shapes. Similar effects are observed in fluorescence spectra of the trans-stilbene in these materials. A possible explanation of these results may be that the aluminum tends to incorporate around the intersections of the channels, and therefore a higher density of sodium cations associated with the aluminum would be found in this area. The trans-stilbene would tend to be drawn to these sodium rich areas, thus allowing isotropic motion in these larger free volumes.

Our initial studies on these systems show some interesting facets that are observable with NMR spectroscopy. We are investigating these deuterium spectra to better understand the materials and the interactions that affect the spectroscopy.

Best Wishes,

Cecil Dybowski Roger Crecely Jon S. Kauffman

(1) Samples were prepared and kindly contributed by V. Ramamurthy and D. Corbin at the E. I. du Pont de Nemours and Company.



^{2}H NMR spectra of deuterated trans-stilbene (3-4% w/w) sorbed in ZSM-5 of varying silicon-to-aluminum ratios. a) Si/Al=34 at 298K; b) Si/Al=34 at 353K; c) Si/Al=490 at 298K; d) Si/Al=490 at 353K. The data were acquired at 46.073 MHz with the solid-echo sequence ($t_{\pi/2}$ = 2.5 μs and τ = 20 μs). To achieve more efficient use of power a 5-mm insert was used in the usual ^{2}H probehead.

THE UNIVERSITY OF TEXAS
Southwestern Medical Center
AT DALLAS

Department of Radiology
Biomedical Magnetic Resonance Center

Southwestern Medical School
Southwestern Graduate School
of Biomedical Sciences
Southwestern Allied Health Sciences School

3-Nov-88
(received 11/7/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, Ca. 94303

Dear Dr. Shapiro,

I wish to describe an imaging gradient system which we assembled on a 1 meter diameter 1.8T Oxford magnet. Each channel (x, y & z) uses six STASIS^{R} 500 watt audio stereo amplifiers modified to provide DC response while operating in the bridging mode through current equalizing resistors. The left and right channels of each amplifier are connected to provide a differential output, balanced with respect to ground across the gradient coil so that the center of the coil is at virtual ground potential. Each gradient coil consists of two half coils connected in series at the center through a 0.02 ohm current sensing resistor.

We experimented with a current regulated servo system in which the output current is held proportional to an input demand signal. Continued problems with system instability lead us to abandon that approach in favor of an open-loop system. The open-loop system response is linearized by preemphasizing the input signal to maximize the system slew rate and minimize the overshoot. With a rectangular input signal, we obtain rise times of 0 to 90% of full signal or a drop from full signal to 10% of 1.5 mSec for the Z gradient and 700 uSec for x & y. The overshoot is a little less than one percent of the full output at 200 amps.

We also used input preemphasis to provide eddy current compensation. In principle, system linearization and eddy current compensation could have been provided in one step but it was easier conceptually to handle those tasks in stages. The eddy current preemphasis unit consists of four op-amp differentiators each with an adjustable time constant and gain. The differentiator outputs are summed with the original demand signal to provide a preemphasized demand signal. The goodness of eddy current compensation was assessed using a small solenoid coil to drive an integrator. The coil, which taken from an electromechanical relay, was positioned 5 cm from the center of the gradient being tested and on axis for the other two gradients.

The vital statistics for the system are:

Usable Volume:	0.33 meter^3, (diam. = 65 cm. len. = 100 cm)
Gradient Strength:	Z axis: 0.661 gauss/cm at 136.6 amps
	Y axis: 0.417 gauss/cm at 95.8 amps
	X axis: 0.491 gauss/cm at 104.9 amps
Maximum Current:	200 amps
Slew rates with eddy current compensation:	Z axis: 133 A/msec
	X & Y axes: 286 A/msec

Figure 1 is a simplified schematic diagram of the system and Figure 2 is a saggital one slice head image of a volunteer. The image consists of 512 real plus imaginary points * 256 phase encoding steps with tr=550 mSec and te=35mSec. It took 2.3 minutes to acquire.

This contribution should be credited to Dr. Ray L. Nunnally's account.

Sincerely yours,

George G. McDonald

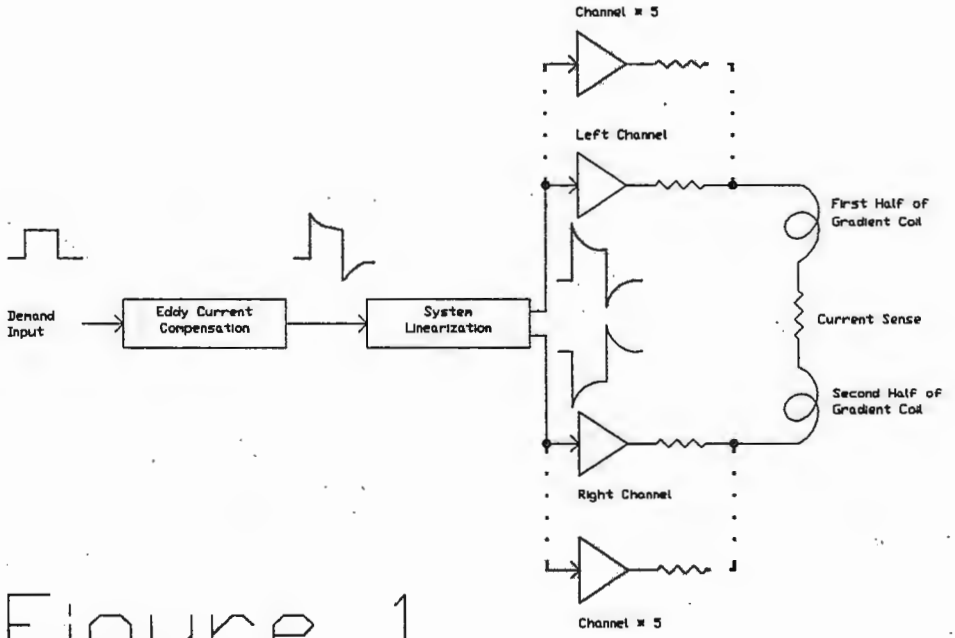


Figure 1

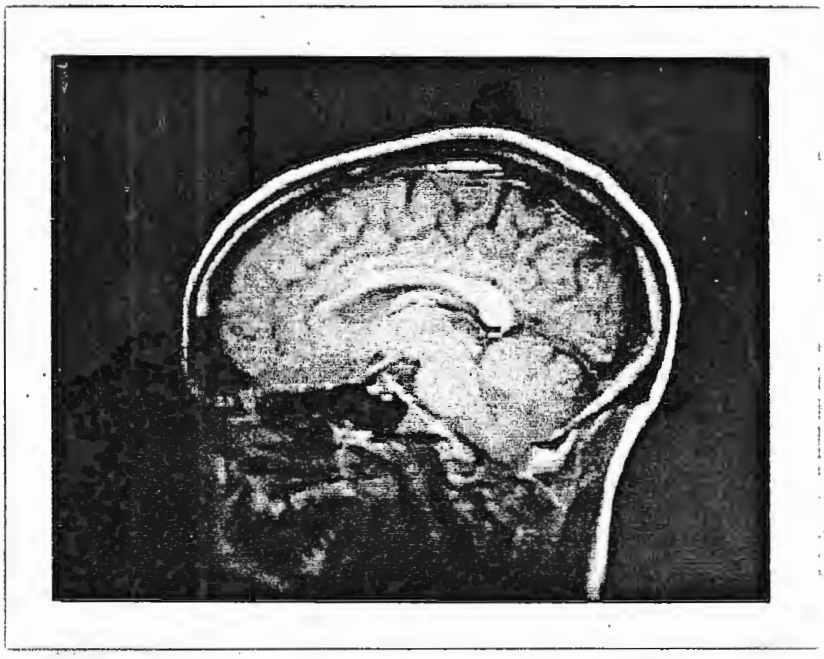


Figure 2

THE UNIVERSITY OF CONNECTICUT

The College of Liberal Arts and Sciences
Department of Chemistry
Box U-60, Room 151
215 Glenbrook Road
Storrs, Connecticut 06268

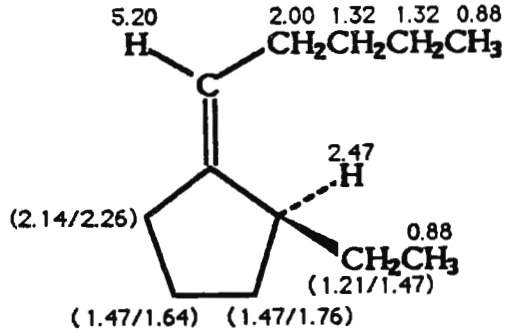
November 10, 1988
(received 11/15/88)

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

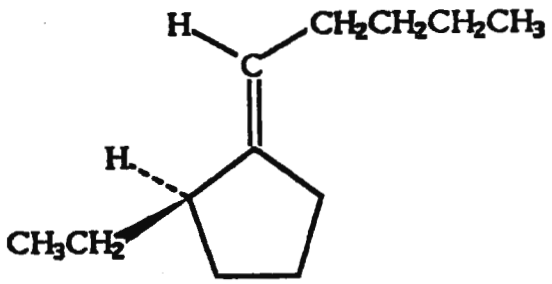
NOE-DIFFERENCE AND NOESY

Dear Barry:

As part of a continuing investigation of the cyclization of alkenyl and alkynyllithiums [J. Am. Chem. Soc. 1988, 109, 2442] we had need to distinguish between two possible structures, I and II, for a product formed via anionic cyclization.



I



II

The chemical shift assignments are based on COSY-techniques. The chemical shifts as well as long range J-couplings do not permit an unambiguous differentiation between the two isomers. Since our instrumentation is not ROESY'ied yet, we rely on NOE difference spectra, Figure 1. The results of Figure 1 combined with the chemical shift data confirm structure I as the isomer present. The pertinent NOE-values range from 1 to 5% and T1-estimates from 1 to 7 sec. Hence for a phase-sens. NOESY (TPPI) experiment the choice of a mixing time τ_m = 2 sec represents a less than optimum value. Nevertheless the results from this NOESY experiment shown in Figure 2 are in good agreement with the NOE-difference spectra. Compare outlined connectivities in Figure 2 with spectra A and B in Figure 1.

Sincerely yours,

Timo V. Ovaska William F. Bailey Thomas K. Leipert

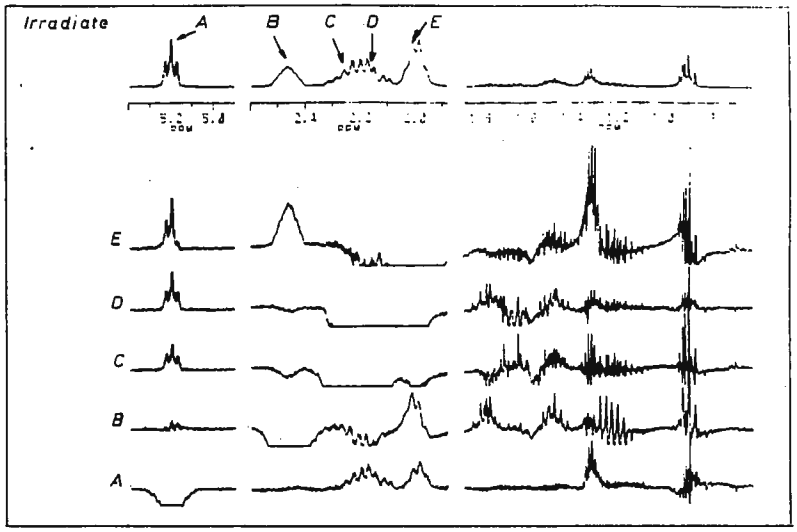


Figure 1. NOE Difference Spectra of I

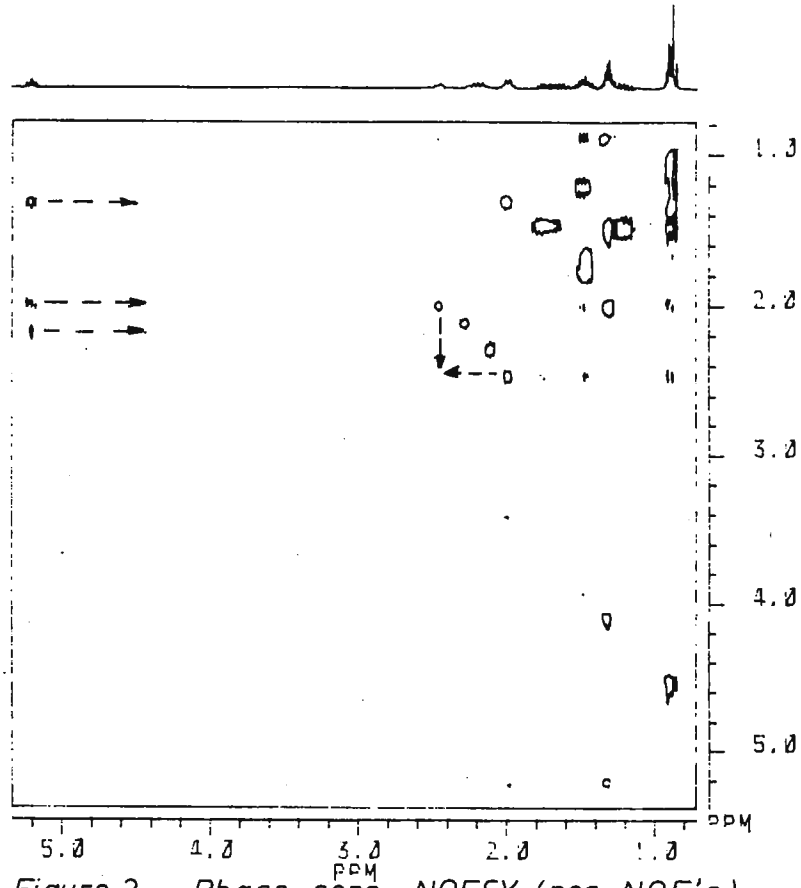


Figure 2. Phase-sens. NOESY (pos. NOE's)

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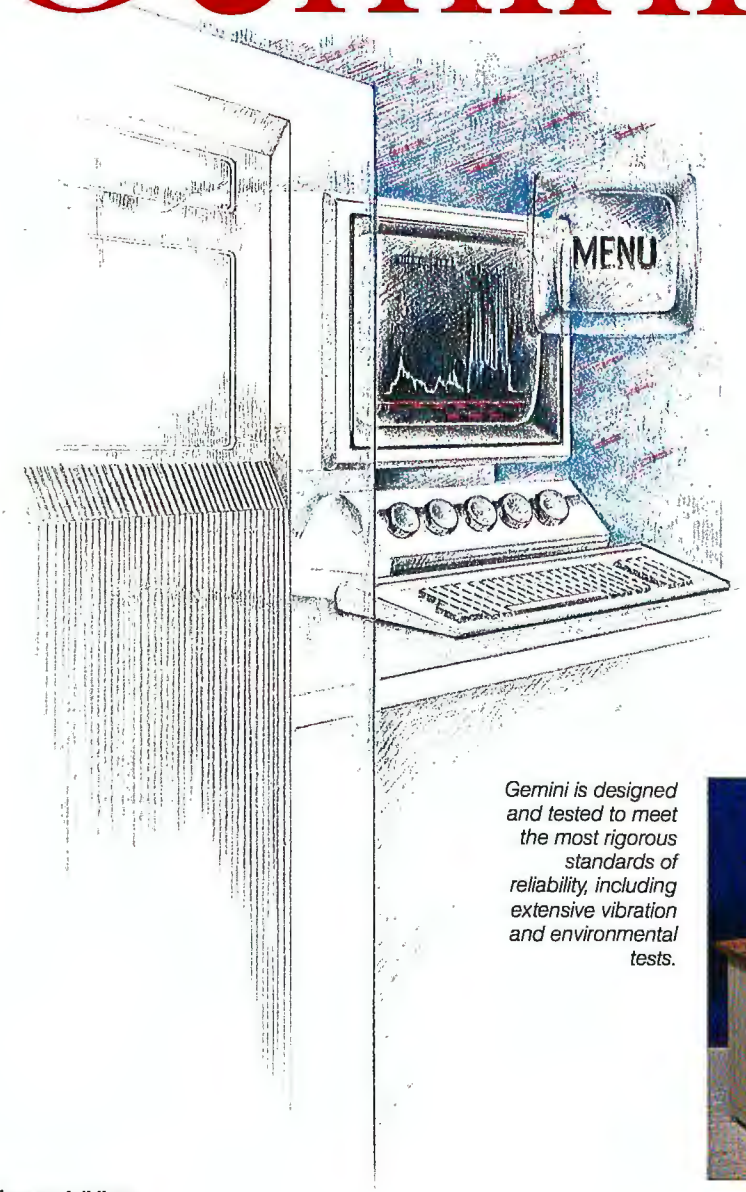

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NMR WITH A FUTURE

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Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor:
William B. Smith, Texas Christian University, Fort Worth, Texas.

" Two-Dimensional NMR Spectroscopy,

Applications for Chemists and Biochemists "

Edited by

William R. Croasmun and **Robert M. K. Carlson.**

VCH Publishers, Inc., 220 East 23rd Street, Suite 909, New York, NY 10010, U.S.A.;
511 pages; 1987; $95.00; ISBN 0-89573-308-0.

This work is volume 9 in the excellent VCH series *"Methods in Stereochemical Analysis"*. In keeping with the current trend, multiple authors introduce the subject of NMR first from the viewpoint of theory and then with a large number of applications drawn from a variety of fields of interest.

The chapters (in order of appearance) and authors are as follows: Chapter 1: *Introduction to Two-Dimensional NMR Methods* (George A. Gray); Chapter 2: *Experimental Aspects of Two-Dimensional NMR* (William E. Hull); Chapter 3: *Strategies for Applying Combinations of Two-Dimensional NMR Experiments* (Michael A. Bernstein); Chapter 4: *Two-Dimensional NMR Spectroscopy on the Immunosuppressive Peptide Cyclosporin A* (Horst Kessler, Hartmut Oschkinat and Hans-Rudolf Loosli); Chapter 5: *Internal Motion and Structure of DNA* (David R. Kearns); Chapter 6: *Application of Two-Dimensional NMR Methods in the Structural Analysis of Oligosaccharides and Other Complex Carbohydrates* (Janusz Dabrowski); Chapter 7: *Steroid Structural Anlaysis by Two-Dimensional NMR* (William R. Croasmun and Robert M. K. Carlson); Chapter 8: *Application of Two-Dimensional NMR to the Characterization of Organic Compounds: Relative Configurational Assignment of a Key Synthetic Precursor to Spatol* (Peter L. Rinaldi); Chapter 9: *Two-Dimensional NMR Experiments in Natural Products Chemistry: Biological and Geochemical Applications* (Gary E. Martin).

The text assumes some familiarity with conventional 1D FT NMR operation. Gray's introductory chapter is in the form of a series of answers to questions which might be posed by an experienced chemist lacking previous contact with 2D NMR. It is informative and well-written, a comment which applies equally well to the other chapters in this very useful book. The editing has resulted in a volume in which multiple authorship proves no disadvantage, as there is much new material in each chapter with very little repetition. This book is highly recommended, both for the experienced organic chemist or biochemist and for the student.

W. B. S.

Hercules Incorporated
Research Center
Wilmington, DE 19894
(302) 995-3000
Telex: 83-5479

October 12, 1988
(received 10/31/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 95303

Enhancements for FTNMR Software: AN NMC User Interface

Dear Dr. Shapiro:

We purchased a microVAX computer (microVMS operating system) and Dennis Hare's FTNMR software approximately a year and a half ago, in order to enhance the data processing capabilities of our aging Nicolet NT spectrometers (NMC Dexter2 software). Data files are transferred from Nicolet 1280's to the microVAX over RS-232 lines using VAXTRN software from Nicolet. Files are converted to FTNMR format using the NMRCONVERT program supplied to us by Rod Farlee from DuPont CR&D. While this data transfer process is workable for processing individual files, it is not suited for the routine processing of large amounts of data.

One of the main limitations of this scheme is that essential parameters for processing (e.g. reference) and plot annotation (sample i.d., date, comment, etc.) are not carried into the FTNMR environment. With the assistance of Rod and Dennis, we are now able to conveniently circumvent this problem through the use of FTNMR macro files. Perhaps a more elegant way to achieve the same objective would be to implement a new command in FTNMR for reading parameters. However, we have found it to be considerably easier to use the simple FTNMR macro commands than to write FORTAN subroutines. We have modified NMRCONVERT to simultaneously generate an expanded parameter list in an FTNMR macro file along with the standard data file which currently contains a minimum (but increasing) number of parameters. The parameters are read as user-defined symbols. Therefore, in FTNMR, macros using only the generic symbol names can be written for data processing. We have taken advantage of the versatile text formats available in FTNMR to generate plots that are fully annoted like those produced directly on the NT systems. We are currently writing additional macros to provide an NMC-like user interface for FTNMR for the convenience of our Nicolet users. One example of this is to create a scratch area in the symbol list where the current processing parameters are held. This will enable the user to read a series of data files and transform, phase and reference them with a uniform set of parameters, as is done in NMC.

A further enhancement that is currently being implemented is to extract the pertinent information from each file header for entry into a spectral database. We welcome any suggestions that your readers may have regarding commercial or public domain database software or file management systems. We would be pleased to provide copies of the modified NMRCONVERT program (Fortran 77) and our FTNMR macros to anyone sending either a TK-50 cassette or 9-track tape.

Yours truly

Mark

Mark J. Sullivan
Analytical Science Division

MJS:kal
5958U

Permanent Position for Biological NMR Spectroscopist
Monsanto Company - St. Louis, Missouri

There is an opening for a biological NMR spectroscopist in Monsanto's Corporate Research Laboratories. This is a permanent position that consists of developing collaborative research projects that apply NMR methods for direct structural determination of biomolecules.

The qualified candidate should posses a Ph.D. in Biophysics, Biochemistry or related field plus two years relevant post-doctoral experience in the use of 2D-NMR methods for protein or oligo-nucleotide structural determination. It should also be emphasized that the ability to complete projects and publish the results will be important for career advancement.

Joining our expanding structural biology group, the candidate will also interact extensively with the molecular modeling, protein crystallography and Life Sciences NMR groups. Facilities available in Monsanto's Life Sciences Research Center include 500 MHz (2) and 300 MHz (3) spectrometers, data workstations and extensive computational and graphics capabilities. The highly interactive and multi-disciplinary environment offers a unique opportunity to apply structural information to problems in biology, medicine and agriculture.

Interested candidates should send a *curriculum vitae* and at least two letters of reference to

Dr. Charles A. McWherter
Structural Biology Group/AA4I
Monsanto Company
700 Chesterfield Village Parkway
St. Louis, MO 63198

The Monsanto Company is a Fortune 500 company and an equal opportunity employer. (11/15/88)

THE UNIVERSITY OF UTAH

November 10, 1988
(received 11/16/88)

Dr. Bernard.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Polyethylene Crystallinity Measured by Static CP NMR

Dear Barry:

We have found that the static, cross-polarized ^1H decoupled solid state NMR spectrum of a linear polyethylene yields a powder pattern that is not of the conventional form. Computer simulation demonstrates that the experimental spectrum has contributions from each of the two phases of the sample. The ratio of the two integrated tensor patterns is in good agreement with the crystallinity of the sample.

The sample is a linear polyethylene produced by Phillips Petroleum Co., and its crystallinity has been measured with standard techniques to be 73% crystalline. Our experiment was conducted on a Bruker CXP-100 (2.35 Tesla field) spectrometer using the common cross polarization pulse sequence (using a 8.5 μs 90° ^1H pulse, a 3 ms contact time, a 40 ms acquisition time, and a 3 s delay time between acquisitions).

The computer simulation (POWDER[1]) is a simplex fitting routine that simulates experimental spectra by varying the principle values and line broadenings in each of two powder patterns until the sum of squares of deviations between the experimental data and the simulated spectrum is minimized. The ratio of the two integrated powder patterns is also a free parameter in the simulation.

Since there are no chemical differences between the two phases of polyethylene, it must be assumed that motional averaging is responsible for the differences between the simulated powder patterns representing the two phases of the sample. It is well known that fast molecular motions can average non-symmetric powder patterns into axially symmetric forms like the one shown in the Figure 1 below.

The result of the fit gives a crystallinity of 80%, which overestimates the known crystallinity by 7%. If this result is corrected for the inefficiency of cross polarization resulting from motions in the amorphous phase, the crystallinity is between 77% and 73%. The principle elements of the chemical shielding tensor for the crystalline phase are σ_{xx} = 51.1, σ_{yy}.= 33.9 and σ_{zz} = 15.5.ppm from TMS. The principle elements of the chemical shielding tensor representing the amorphous phase are σ_{xx} = 40.2, σ_{yy}.= 36.4 and.σ_{zz} = 13.7 ppm from TMS.

Sincerely,

David M. Grant

Craig Hughes

[1] D.W. Alderman, M.S. Solum and D. M. Grant, *J. Chem. Phys.* **1986**, *84*, 3717.

Department of Chemistry
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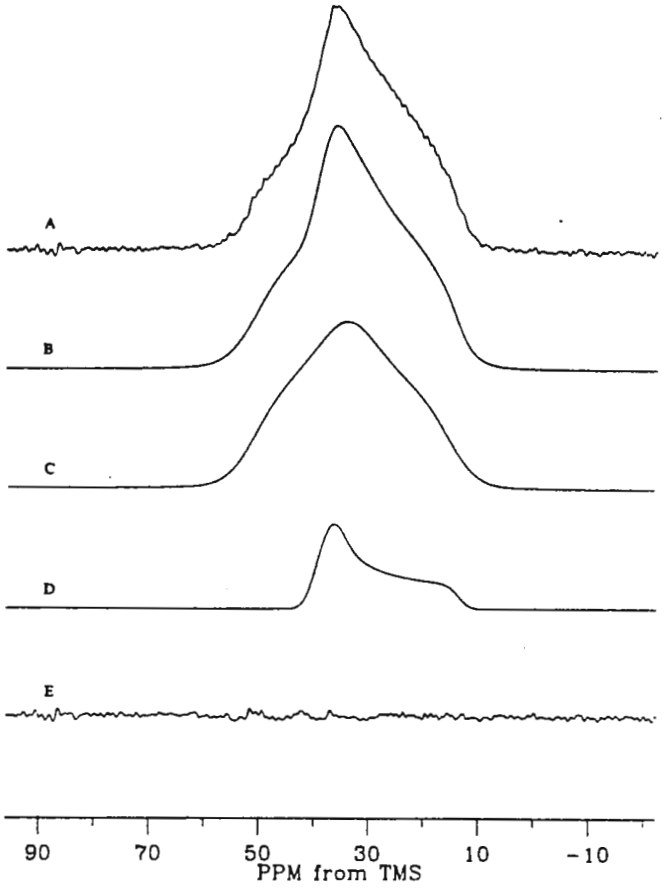


Figure. 1. (A) Cross-polarized, ^{1}H decoupled, static 25.152 MHz ^{13}C NMR spectrum of Phillips 6050 fluff polyethylene. The spectral window was 5 kHz, no line broadening, 24,150 transients. (B) Calculated "best fit" spectrum, the sum of the crystalline and the amorphous tensor components. (C) The crystalline tensor. (D) The amorphous tensor. (E) Residual spectrum (experimental spectrum - "best fit"). The chemical shifts are relative to the methyl resonance of hexamethylbenzene (17.6 ppm from TMS).

Tel: 0223 336342
Telex: 81240 CAMSPL G
Bitnet: JHK10@PHX.CAM.AC.UK
FAX: 0223 336362

Dr. James Keeler
University Chemical Laboratory
Lensfield Rd.
Cambridge CB2 1EW, U.K.

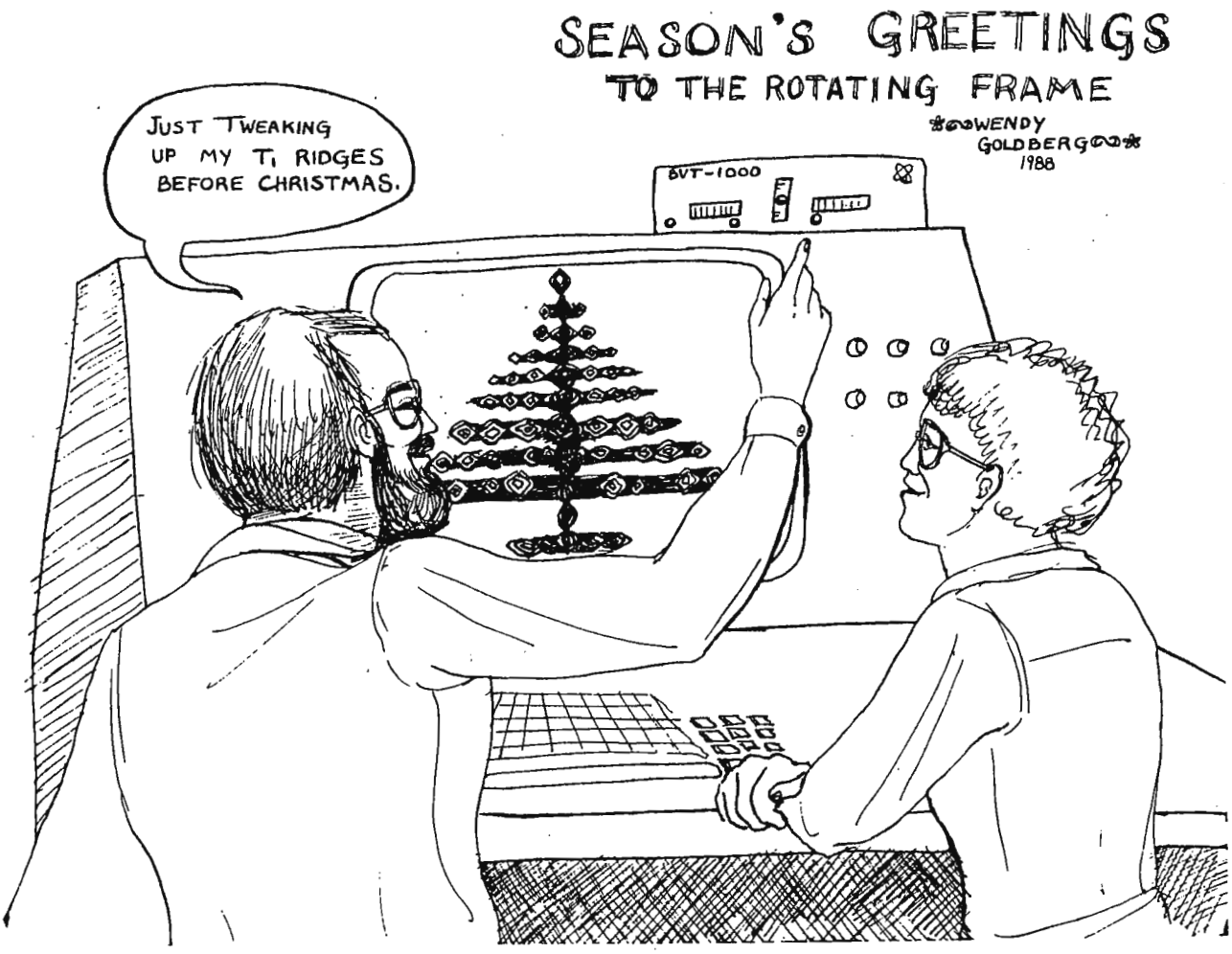
I have a position available for a postdoctoral research assistant to work on one or more of the following areas: (1) an extension of previous work on broadband decoupling to include quadrupolar nuclei in anisotropic systems, (2) investigation of the use of special relaxation processes, such as cross-correlation and related phenomena, in structural studies, (3) electric field induced NMR by mechanical modulation, (4) electric field induced multiple quantum transitions in chiral systems.

Candidates for this post must already have, or be about to complete, a Ph. D. in some relevant area of NMR spectroscopy (either high resolution or solid state). A good working knowledge of practical NMR and a grasp of the relevant theory will be essential; some expertise in electronic construction could be useful but is not essential. Limitations imposed by the funding agency make the post unsuitable for someone who has already completed several years postdoctoral work.

The salary is age related and would be, for example, approx. £10,000 p.a. (before deductions) for a person aged 25 yrs. The post is funded for two years only.

My group currently consists of three graduate students and one postdoctoral worker. We have access to three high field NMR spectrometers and all the usual computing and workshop facilities.

Anybody interested in this post, which is available immediately, should contact me as soon as possible, preferably by telephone, FAX or electronic mail.



POSTDOCTORAL POSITION

NMR/MOLECULAR MODELING

An opening for a Postdoctoral Fellow in Physical Biochemistry is available through the Computational Sciences Center and Department of Biochemistry at the University of Kentucky. Applicants with experience in NMR or molecular modeling (molecular dynamics/mechanics) techniques are encouraged to apply, although preference will be given to those with experience in both areas.

The individual recruited to fill this position will, in conjunction with molecular modeling techniques, use NMR data to study the dynamic solution structures of oligosaccharides, polypeptides, and proteins. Two main areas of interest are the effects of carbohydrate-peptide interactions on oligosaccharide structure and structure/function relationships for wild-type vs site-specifically mutated proteins.

A 500MHz Varian NMR spectrometer (5mm $^{1}H/^{19}F$, 5mm ID, 5&10mm BB probes), a Varian NMR data station (Sun 4/280), an IBM 3090/300E/3 vectors supercomputer (CHARMM/XPLOR software), and a Silicon Graphics 4D/70GT graphics workstation (CHARMM/QUANTA software) are available for these studies. Additional NMR spectrometers (400, 300WB, 300, 200 MHz) and computing facilities are also available on campus.

Applicants should submit a current curriculum vitae and three letters of recommendation to Dr. Judith G. Shelling, Department of Biochemistry, University of Kentucky, 800 Rose Street, Lexington, KY 40536-0084; (606) 257-4790, SHELLING@UKCC.

College of Physicians & Surgeons of Columbia University | *New York, N.Y. 10032*

DEPARTMENT OF BIOCHEMISTRY &
MOLECULAR BIOPHYSICS

630 West 168th Street

November 16, 1988

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Barry:

Further Reduction of the Water "Hump" in HOHAHA or TOCSY Experiments

Most of us are probably now familiar with the HOHAHA (1) or TOCSY (2) experiments which have proven to be very useful for making amino acid assignments of proteins. The principal advantages are that, (a) relay connectivity can be observed, (b) both cross and diagonal peaks are in phase or absorptive, thereby making the experiment more sensitive than phase sensitive COSY experiments in which cross and diagonal peaks are antiphase, and (c) the spin lock composite pulse scheme seem to be more efficient in transferring magnetization between nuclei containing broad lines such as those typically present in macromolecules.

I have been engaged in NMR investigations of a relatively small (33 amino acid) polypeptide, pardaxin P-2 (3), which is a defense secretion from a species of sole found along the Japanese coast. The sample was kindly provided by Dr. Kazuo Tachibana, Suntory Institute of Bioorganic Research, Osaka, Japan. NMR spectra were recorded with a 6 mg (3.5 mmol concentration) sample in aqueous trifluoroethanol (CF3CD2OD.H2O (1:1)) solution which are conditions that ensure pardaxin adopts an ordered structure as judged by CD. For all NMR experiments, the H2O signal was suppressed by selective presaturation for 1.5 secs prior to data acquisition. The efficiency of this suppression was dramatically improved after Farraday shields were installed on the coil leads of our 5mm 1H probe (4,5). Without the shields, a broad "hump" due to H2O present in an inhomogenous region of the field was present. This hump was very troublesome, especially when it came to shimming, since the hump resembles Z4 being way off, and one can spend hours trying to shim the hump away.

Fortunately, the shields removed most of the hump, except in the HOHAHA experiment in which a small amount of residual H2O was present, possibly due to radiation damping. To remove the residual hump, I incorporated a composite 180-180^{o} pulse sequence after the MLEV-17 spin lock sequence. For the composite 180^{o} pulses, I used the GROPE-16 (6) sequence which consists of a 270^{o}-x360^{o}x90^{o}y270^{o}-y360^{o}y90^{o}x pulse train. Thus, the entire pulse sequence now becomes:

D1 90^{o}-t1-MLEV-17 180^{o}180^{o} t2

where presaturation of the H2O signal is performed during D1, the relaxation delay. The idea behind using the composite 180^{o} pulses is to refocus the phase dispersion

and remove the effects of field inhomogeneities. Since the hump presumably originates from an inhomogenous portion of the sample experiencing low rf field strength, it is not excited by the composite GROPE-16 pulses. Bax (7) used a similar idea with composite 90^{o} pulses to remove inhomogenous signals occurring in 1D spectra.

In figure 1 is shown the first real t1 increment (initial t1 is 3usecs) for the HOHAHA sequence run with and without the two 180^{o} GROPE-16 composite pulses. Both spectra were run consecutively under identical conditions. Also, a 2 msec purge pulse was inserted before and after the MLEV-17 spin lock sequence. Longer purge pulses did not cut down on the hump, but instead reduced signal to noise. The entire 2D spectrum run with the two 180^{o} GROPE-16 composite pulses is shown in figure 2.

I welcome any comments on the above modification.

Sincerely yours,

Michael G. Zagorski

Michael G. Zagorski

References:

(1) A. Bax and D. G. Davis, J. Magn. Reson. 65, 355 (1985).
(2) L. Braunschweiler and R R. Ernst, J. Magn. Reson. 53, 521 (1983).
(3) S. A. Thompson, K. Tachibana, K. Nakanishi, and I. Kubota, Science 233, 341 (1985).
(4) R. W. Dykstra, J. Magn. Reson. 72, 162 (1987).
(5) Brian Andrew, Bruker Instruments, Billerica, MA.
(6) A. J. Shaka and R. Freeman, J. Magn. Reson. 55, 487 (1983).
(7) A. Bax, J. Magn. Reson. 65, 142 (1985).

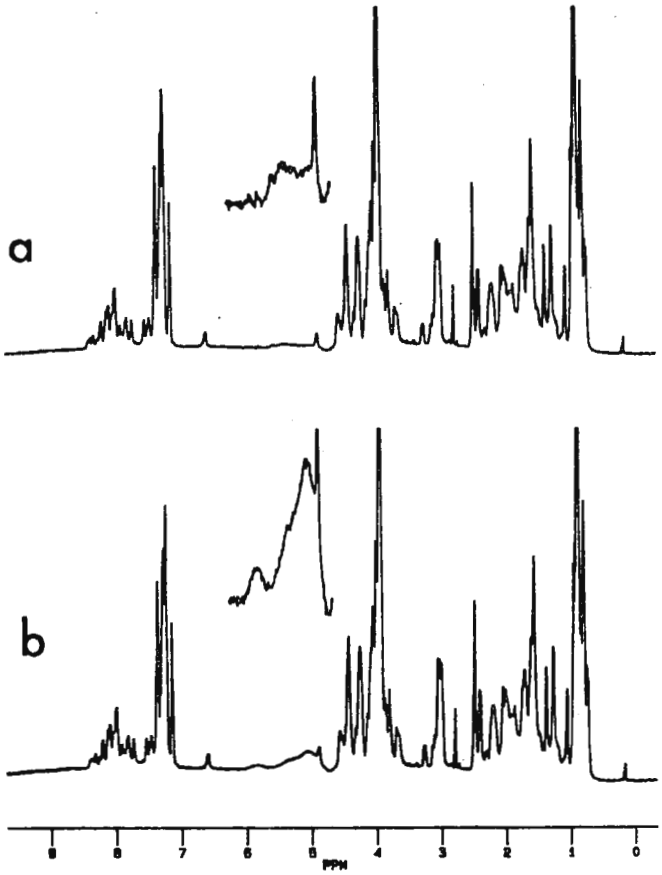


Figure 1. First real increments collected with (a) and without (b) GROPE-16 composite pulses. Total spin lock time 80 msecs.

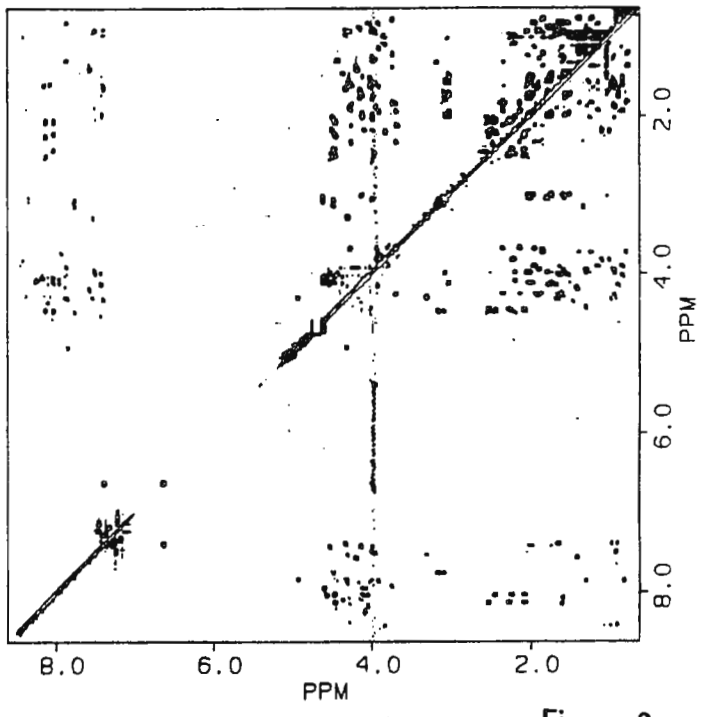


Figure 2.

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Table of Contents, cont'd.

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AFTER MONTHS OF DISAPPOINTMENT, SYDNEY ABANDONS HIS "FRIGIDAIRE" FRANCHISE IN FAVOR OF A MORE PROMISING PRODUCT.

Some Cool for Yule (nothing useful rhymes with Chanukah)

Cartoon created by Dr. **Uwe Oehler**, Dept. of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. Dr. Oehler bears no responsibility for the title. If our British and French readers fail to understand the etymological and social bases for the humor of this cartoon, they can, perhaps, at least appreciate the non-impact of some of the items in *Punch* or *Paris-Match*.

B. L. S.

CSI 2T Applications

Shielded Gradients and Localized Spectroscopy

Eddy current effects are the leading cause of errors and lack of consistent results in gradient localization methods. It is not surprising, then, that actively shielded gradients, which have dramatically reduced eddy currents, represent a significant technology advance for all forms of B_o gradient volume localization and spectroscopic imaging methods. The fast rise time and high gradient strength characteristics of the coil used in these experiments are also important.

Even without pre-emphasis, shielded gradients recover fast enough to obtain spectroscopic information at 1 msec or less after a strong gradient has been turned off (Fig. 1).

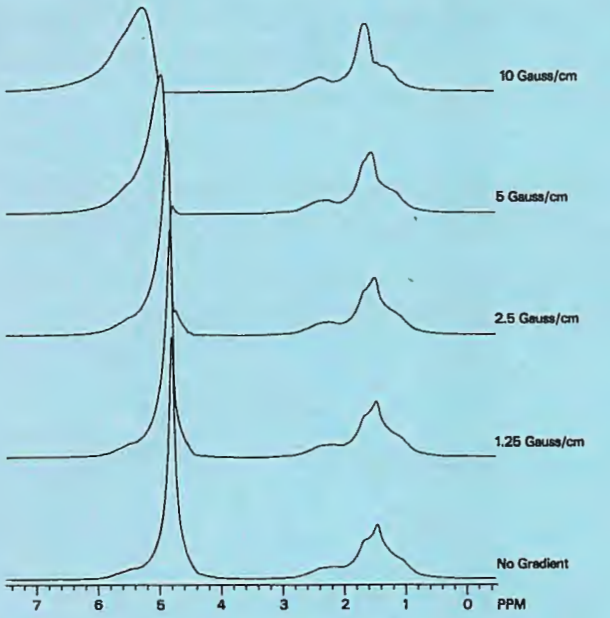

Fig. 1—Using an oil/water phantom, a 10 G/cm gradient will create a water frequency profile extending from 156 KHz to 280 KHz away from normal water resonance. Residual gradient effects of less than 0.01% (50 Hz at 10 G/cm) are observed in a spectrum acquired beginning 1 msec after a 20 msec gradient pulse.

As an example, a 4DFT spectroscopic imaging technique can resolve the four frequency domains that are associated with an NMR signal from an object: x-, y-, z-spatial coordinates and chemical shift δ. The above technique can be a practical alternative to single volume localized spectroscopy. This method allows phosphorous spectra to be obtained from well-defined regions as demonstrated in the following experiment, which was carried out on a GE CSI 2T system using high-strength, shielded gradient coils (Fig. 2). The phase-encode time is kept short (on the order of the dwell-time) to minimize phase-errors in the final spectra, as well as to avoid loss of signal due to T2 decay, which is significantly short in biological phosphates.

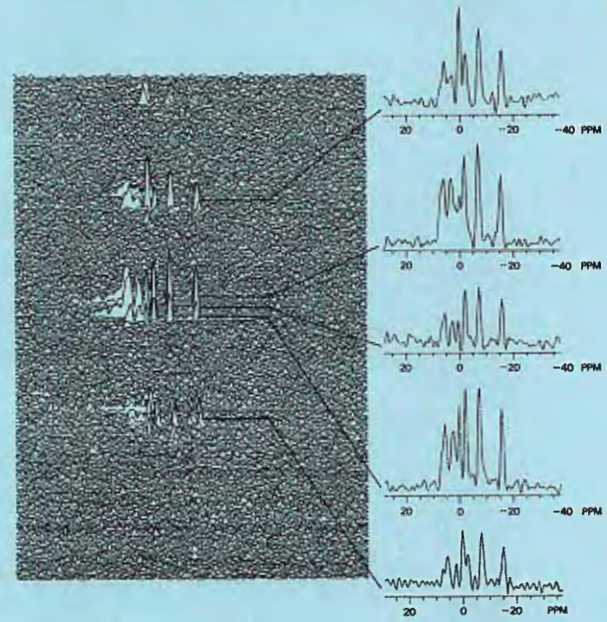

Fig. 2—Stacked plot showing 512 phosphorous spectra from 60 mm cubed region of a live rat. Each trace corresponds to 7.5 mm cubed region (voxel) from within the region of interest. The offset traces clearly show the achievable spectra and spatial resolution of the technique, as well as demonstrating localization of the liver phosphorous metabolites from that of overlying skeletal muscle. Total acquisition and processing time was two hours.

GE NMR Instruments

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JEOL'S GSX-FT NMR Systems

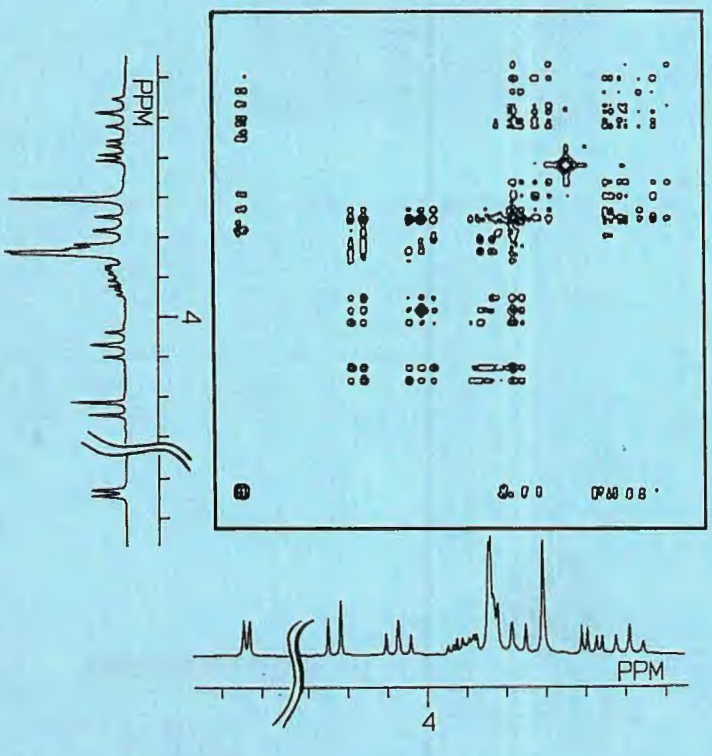
Application: Pulse Programming

The GSX pulse programmer was designed with sufficient flexibility and range to do the most sophisticated routines you see in the current literature. While these routines may be of no interest for your present NMR applications, the next issue may have just the perfect experiment. As an example of these capabilities, consider HOHAHA.*

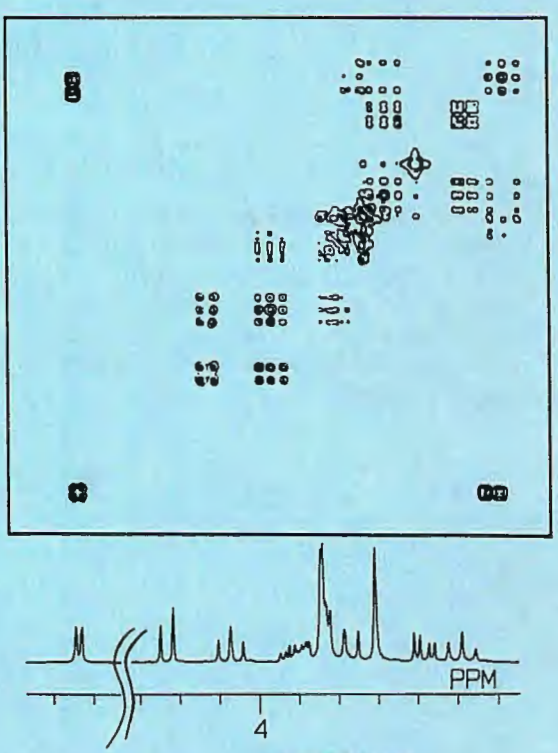
The HOHAHA experiments which use MLEV-17 for spin locking are very good for providing connectivity, especially in small molecules which produce poor RELAY experimental results. The spin locking allows coherence transfer which can be controlled by the mixing times. Directly coupled protons can be detected with short mixing times (20 ms) while longer mixing times result in relayed coherence transfers — many times with more sensitivity than RELAY experiments.

The data below are from a wide bore GSX-270 and compares the normal COSY experiment using 3 mg of sucrose in D20 with the HOHAHA experiment run on the same sample. The spin locking used for the HOHAHA produces relayed coherencies which are shown by the additional cross peaks in the contour plot.

HOHAHA DATA



COSY DATA



*Ad Bax and Donald G. Davis, *J. Mag. Res., 65, 355 (1985).*

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