TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 433

October 1994

Continued on inside back cover

PTS
FREQUENCY SYNTHESIZERS

NMR-MRI HIGH PERFORMANCE DIRECT SYNTHESIZERS

The accuracy, stability and low noise you need for any experiment. Most widely accepted line of high-reliability frequency synthesizers. Thousands in use worldwide.

PTS 040

Range: 0.1–40 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 1–20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –75dBc
Phase Noise: –75dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $5,125.00*

PTS 120

Range: 90–120 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 1–20μs

Output: +3 to +10dBm; 50ohm
Spurious Outputs: –75dBc
Phase Noise: –75dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $5,125.00*

PTS 160

Range: 0.1–160 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 1–20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –75dBc
Phase Noise: –63dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $6.245.00*

PTS 250

Range: 1–250 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 1–20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –70dBc
Phase Noise: –63dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $7,155.00*

PTS 310

Range: 0.1–310 MHz
Resolution: 1Hz
Switching: 1–20μs
Phase Continuous: 1Hz–100KHz steps

Output: +3 to +13dBm; 50ohm
Spurious Outputs: Type 1 –70/65 (typ/spec); Type 2 –65/60dBc
Phase Noise: –68dBc (0.5Hz–15KHz); –63dBc

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: Type 1 $6,175.00*; Type 2 $5,625.00*

PTS 500

Range: 1–500 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 1–20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –70dBc
Phase Noise: –63dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $8,385.00*

PTS 620

Range: 1–620 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 1–20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –70dBc
Phase Noise: –63dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $9,255.00*

PTS 1000

Range: 0.1–1000 MHz
Resolution: 0.1Hz–100KHz (opt)
Switching: 5–10μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –70dBc (0.1–500 MHz), –65dBc (500–1000 MHz)
Phase Noise: –60dBc (0.5Hz – 15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $11,375.00*

PTS x10

Range: 10 MHz band, selected decade 0.1–100 MHz
Resolution: 1Hz
Switching: 1–5μs
Phase Continuous: 2 MHz band, even or odd steps

Output: +3 to +13dBm; 50ohm
Spurious Outputs: –65/–60dBc (typ/spec)
Phase Noise: –70dBc (0.5Hz–15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $2,575.00*

OTHER OPTIONS

Programmable Attenuator 0–90dB (or 0–99dB with GPIB)
n x 10 MHz output (20–140 MHz) or any 10 MHz line

*Prices are US only, and include manual & remote (BCD) control, 1 Hz resolution, OCXO std.

DDS & PHASE ROTATION AVAILABLE ON ALL OF OUR MODELS

PROGRAMMED TEST SOURCES, INC.

P.O. Box 517, 9 Beaver Brook Rd., Littleton, MA 01460 Tel: 508-486-3008 FAX: 508-486-4495

TEXAS A&M NMR NEWSLETTER NO. 433, OCTOBER 1994 AUTHOR INDEX

TEXAS A&M NMR NEWSLETTER NO. 433, OCTOBER 1994 ADVERTISER INDEX

SPONSORS OF THE TAMU NMR NEWSLETTER

Abbott Laboratories
American Microwave Technology
Bruker Instruments, Inc.
Burroughs Wellcome Co.
Chemagnetics
Cryomagnet Systems, Inc.
The Dow Chemical Company
Eastman Kodak Company
E. I. du Pont de Nemours & Company
Elbit-ATI Ltd.
Isotec, Inc.
JEOL (U.S.A.) Inc., Analytical Instruments Division
The Lilly Research Laboratories, Eli Lilly & Company
Merck Research Laboratories
The Monsanto Company
Norell, Inc.
Oxford Instruments
The Procter & Gamble Company, Miami Valley Labs
Programmed Test Sources, Inc.
Tecmag
Unilever Research
Union Carbide Corporation
The Upjohn Company
Varian, Analytical Instrument Division

FORTHCOMING NMR MEETINGS

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505)989-1073.

Keystone Symposia on Molecular and Cellular Biology, Frontiers of NMR in Molecular Biology - IV, Keystone, Colorado, **April 3 - 9, 1995**; Organizers: S. W. Fesik, T. L. James, and G. Wagner; Contact: Keystone Symposia, Drawer 1630, Silverthorne, CO 80498; Phone: (303) 262-1230; Fax.: (303) 262-1525..

International School of Biological Magnetic Resonance, 2nd Course: Dynamics and the Problem of Recognition in Biological Macromolecules, Erice, Trapani, Sicily, Italy , **May 22 - 30, 1995**; Contact: Prof. O. Jardetzky, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94305-5055; Phone: (415)723-6270; Fax: (415) 723-2253; or, Prof. J.-L. Lefèvre, ESBS, CNRS-UPR9003, Univ. Louis Pasteur, Blvd. Sébastien Brant, F67400 Illkirch Graffenstaden, France; Phone: (+33) 88-655269; Fax.: (+33) 88-655343- See TAMU NMR Newsletter 432, 38.

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995**; Contact: Dr. J. F. Gibson or Ms. G. B. Howlett - See TAMU NMR Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. Les. Field, Dept. of Organic Chemistry, Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-692-2060; Fax: +61-2-692-3329; Email: ismar-95@biochem.su.oz.au Also, see TAMU NMR Newsletter 419, 26.

NMR Symposium at the 37th Rocky Mountain Conference on Analytical Chemistry, Denver Colorado, **July 24-27, 1995**; Contact: Dr. Alexander J. Vega, DuPont Central Research and Development, P.O. Box 80356, Wilmington, DE 19880-0356; Tel. (302) 695-2404; Fax: (302) 695-1664; e-mail: vego@esvax.dnet.dupont.com. See TAMU NMR Newsletter 432, 34.

37th ENC (Experimental NMR Conference), Asilomar Cnference Center, Pacific Grove, California, **March 17 - 22, 1996*[sic]***; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505)989-1073.

38th ENC (Experimental NMR Conference), Orlando, FL, **March 23 - 27, 1997*[sic]***; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505)989-1073.

Additional listings of meetings, etc., are invited.

ISIS PHARMACEUTICALS

15 September 1994
(received 9/17/94)

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

60 Hz Sidebands due to 110V AC Fan Noise

After a one year break, we recently returned to our 4-year old Unity 400 to conduct experiments in H_2O, using time-domain post-processing to remove the solvent signal. To our surprise and chagrin, we found our spectrometer was producing 34, 60 & 120Hz sidebands which were exceeding 0.5% signal intensity and did not always phase cycle away. These had not been critical or obvious when the machine was being used primarily for service with concentrated solutions of small organic molecules, but became a problem when these signals were difficult to distinguish from 3' and 4' protons in our RNA and DNA samples.

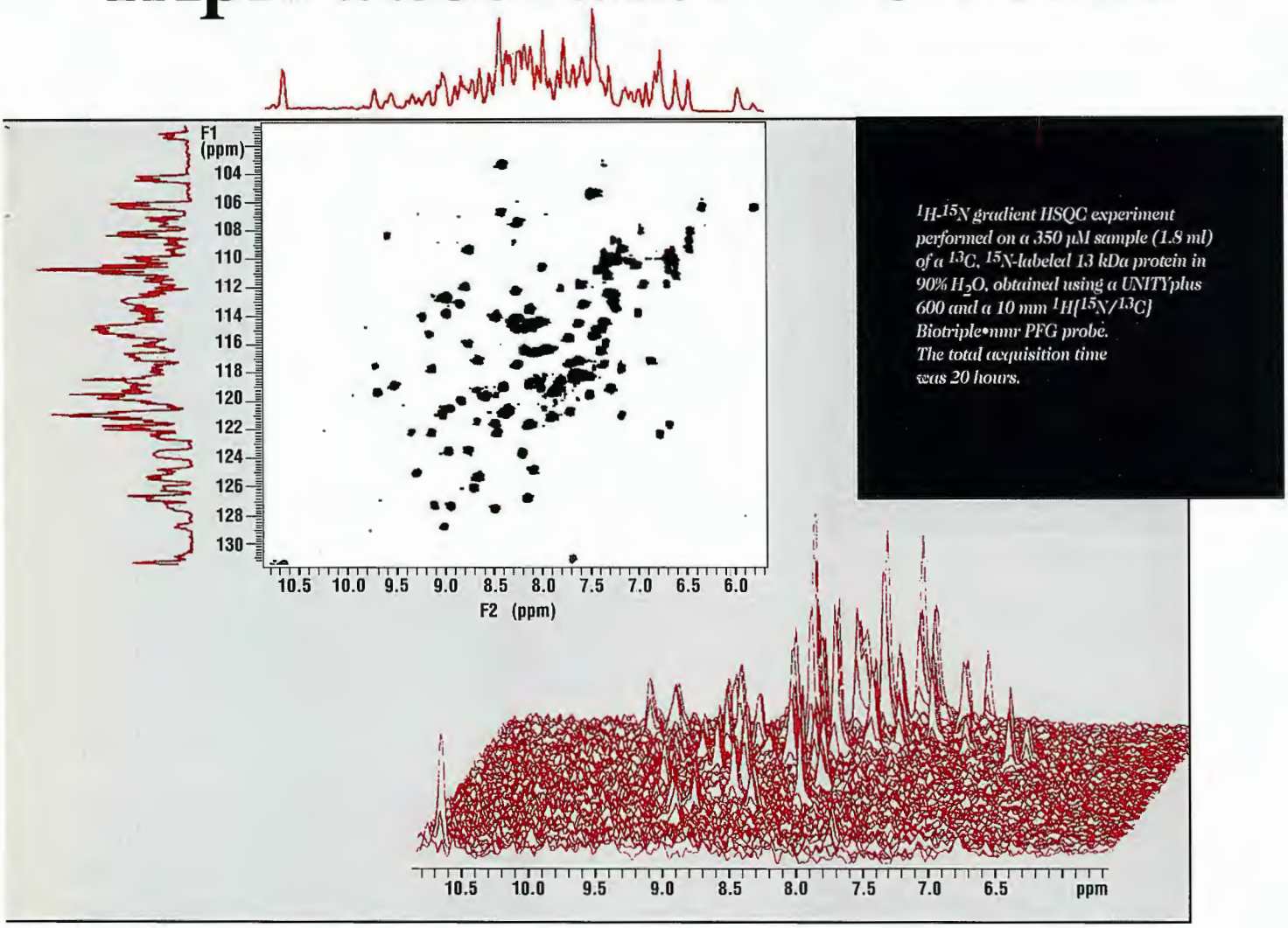
The search for ground loops connecting to local 60Hz sources outside the spectrometer yielded no suspects, so we called in the expertise of John Sandoval and Bill Long from Varian. After a rather arduous search, the source of the noise was found to be the 110V AC muffin fans which provide cooling in all Unity systems (as well as Gemini, VXR and XL models). Fans which had failed, or were in the process of failing, contributed the most noise. Whether through intuition or reasoning, Varian is no longer building spectrometers with these fans; they are instead using 12V DC fans. The fans in our system (~8 of them) have now been replaced by such units. As an interim measure we used an external low-noise 12V DC power supply, but a permanent 12V supply has now been installed inside the console. With these modest modifications, our sidebands have returned below 0.03%, near UnityPlus specifications and to a point where they no longer interfere with spectroscopy.

Yours sincerely,

Patrick Wheeler
NMR Lab Manager

Carlsbad Research Center 2292 Faraday Avenue Carlsbad, CA 92008 619 ▲ 931 ▲ 9200 FAX 619 ▲ 931 ▲ 9639

The World's First 10mm Triple Resonance PFG Probe



^{1}H-^{15}N gradient HSQC experiment performed on a 350 µM sample (1.8 ml) of a ^{13}C, ^{15}N-labeled 13 kDa protein in 90% H_2O, obtained using a UNITYplus 600 and a 10 mm $^{1}H\{^{15}N/^{13}C\}$ Biotriple•nmr PFG probe. The total acquisition time was 20 hours.

Providing the highest triple resonance sensitivity *and* high performance pulsed field gradients

ISO 9001 REGISTERED

Obtain the highest sensitivity in triple resonance PFG experiments with Varian's new 10 mm $^{1}H\{^{15}N/^{13}C\}$ Biotriple•nmr PFG probe. This probe, designed for samples which have limited solubility or are susceptible to aggregation, provides:

- **2.2-fold increase in sensitivity relative to a 5 mm probe**
- **5-fold reduction in data acquisition time relative to a 5 mm probe**
- **25% more sensitivity than an 8 mm probe**
- **Actively shielded Z-gradient for unsurpassed 10 mm water suppression performance**
- **Unmatched 10 mm ^{1}H lineshape when used with Varian's unique Ultra•nmr shims**

Look to Varian, the technology leader in biomolecular applications.

For details, contact the Varian office nearest you.

Varian Associates 3120 Hansen Way, Bldg. 4, Palo Alto, CA 94304-1030, U.S.A. Tel: 1-800-356-4437 • **Varian International AG** Kollerstrasse 38, CH-6303, Zug, Switzerland Tel: (42) 44 88 44 • **Varian GmbH** Alsfelderstrasse 6, D-6100 Darmstadt, Germany Tel: (0 61 51) 70 30 • **Varian Instruments Ltd.** 3rd Matsuda Bldg., 2-2-6 Ohkubo-Shinjuku, Tokyo, Japan Tel: (3) 3204-1211

varian

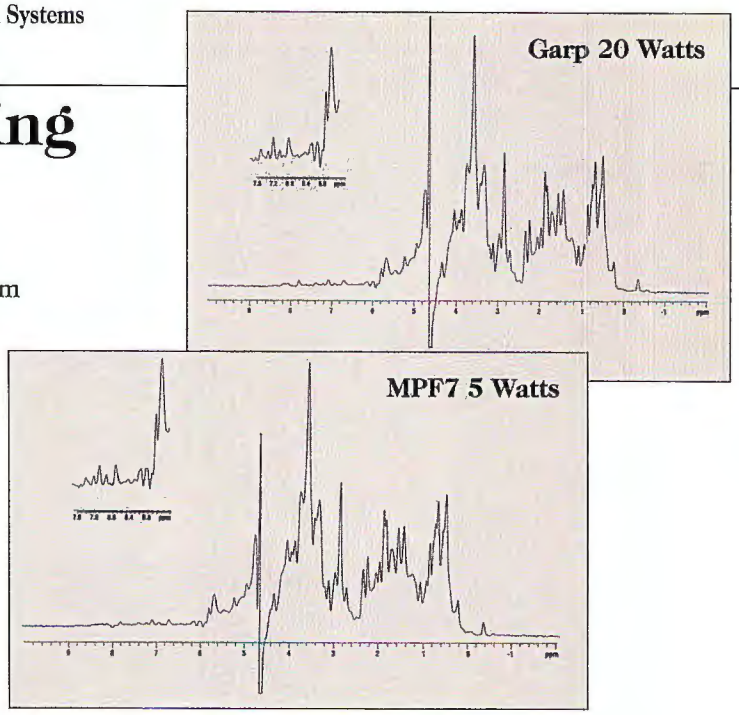
Featured at This Year's ICMRBS*

*International Conference on Magnetic Resonance in Biological Systems

Ultrabroadband Decoupling

^{1}H-^{13}C Gradient HSQC

Obtain the maximum decoupling field strength with the minimum power using the powerful Unity*plus* waveform generator. Triple resonance spectra obtained utilizing (A) a GARP broadband decoupling sequence[1] and (B) a MPF7 broadband decoupling sequence[2] at a decoupler power 6dB less than that used in spectrum (A). Both spectra were acquired using a Unity*plus* 600 spectrometer equipped with a waveform generator and a Triple•nmr PFG probe.



[1] Shaka, A.J., Barker, P.B., Freeman, R., *J Magn. Reson.*, 64, 547 (1985).
[2] Fujiwara, T., Nagayama, K., *J Magn. Reson.*, 77, 53 (1988).

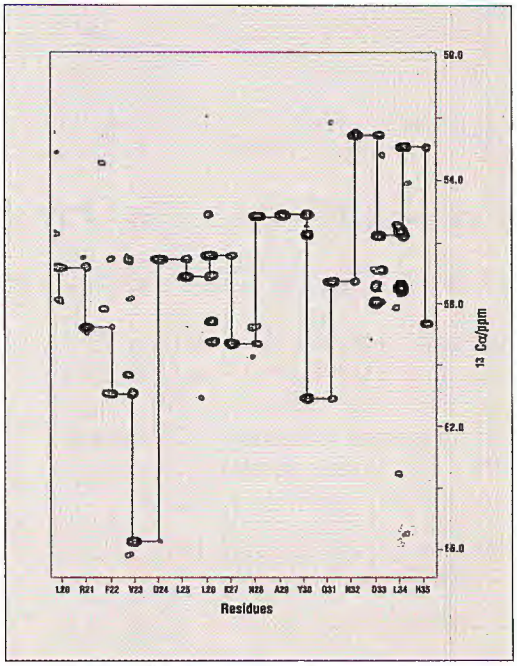
Deuterium Decoupling with Deuterium Lock

Perform deuterium-locked quadruple resonance experiments such as $^{1}H\{^{13}C, ^{15}N, ^{2}H\}$ with ease with Varian's Triple•nmr probe, a four channel UNITY*plus* system, and the UNITY*plus* Adaptive Lock.

This plot displays the resultant sequential connectivities for helices A and B of the *Trp*-Repressor/DNA Complex. Utilizing the experiment above, L. Kay and co-workers* have obtained 100% of the intra-residue and 94% of the inter-residue correlations for the 37 kDa complex.

Spectrum provided by Toshio Yamazaki, Weon Tae Lee, Matt Revington, Cheryl Arrowsmith and Lewis Kay from the University of Toronto and the Ontario Cancer Institute, Toronto, Canada.

*Yamazaki, T., Lee, W.T., Mattiello, D.L., Dahlquist, F., Revington, M., Arrowsmith, C., and Kay, L.E., "An HNCA Pulse Scheme for the Backbone Assignment of ^{2}H, ^{13}C, ^{15}N-Labeled Proteins: Applications to a 37 kDa *Trp*-Repressor Complex," *J. Amer. Chem. Soc.* (submitted).



^{2}H, ^{13}C, ^{15}N - labeled *Trp*-Repressor/DNA Complex (37 kDa) HNCA with constant time carbon evolution combined with ^{2}H decoupling

Swinburne University of Technology

Department of Applied Chemistry,
September 9 1994
(received 9/13/94)

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

OBSERVATION OF AQUEOUS FOAM DRAINAGE BY NMR

Dear Dr. Shapiro,

As the last surviving member of the Swinburne University NMR Centre, I have taken this opportunity to briefly describe the work undertaken during my PhD studies over the last few years. As part of a department-wide investigation into the waste-removal process of adsorbing colloid flotation, under the auspices of the Centre for Applied Colloid Science, my studies have concentrated on the changes in molecular structure of the surfactant molecules stabilizing the flotation foam, throughout the foam drainage process. Aqueous foams have traditionally been studied via macroscopic, physical properties, and I believe this work is novel in focussing at the molecular level of the foam.

The surfactant initially studied was SDS (Sodium Dodecyl Sulphate: $C_{12}H_{25}SO_4^-Na^+$). Foam is generated within the NMR tube by passing N_2 gas down a thin glass bubbler, through a glass frit, and then bubbling the SDS - D_2O solution. Observation has been principally via ^1H and ^{13}C relaxation (enabled by the use of SDS ^{13}C enriched at the C-1 position). The foam causes problems in the spectrometer, due to the inhomogeneous and dynamic nature of the system, which results in broad peaks (Fig 1), pulse width imperfections, and the need to complete measurements quickly. Such requirements have made it necessary to alter standard T_1 and T_2 methods. Diffusion measurements using the PFG-SE technique were also attempted with limited success due the magnetic susceptibility variations caused by the bubbles.

Multifield ^{13}C relaxation data is shown in Fig 3. This was combined with ^{13}C-{^1H} NOE measurements and interpreted using the classical equations for dipole-dominated ^{13}C relaxation. Optimized motional correlation times were determined according to the spectral density function for the Two-Step Model for surfactant motion in spherical micelles. This model gives a slow correlation time for overall molecular motion and a fast correlation time for intra-molecular rotation, along with an arbitrary Order Parameter which indicates alkyl chain flexibility. The optimized motional data was then reapplied to the dipolar relaxation equations to provide calculated NMR relaxation values. These values matched the experimental data within the expected error range, indicating that the micelle model was appropriate to describe surfactant motion in the foams.

The key to this work has been the appearance of bi-exponential ^{13}C T_2 data. This has enabled the optimization of the above motional parameters for the averaged, overall motion, as well as for SDS molecules free within the continuous solution of the foam and those bound at bubble interfaces. Only the slow correlation time (τ_s) for SDS at the bottom of a 0.1M SDS foam is shown here. (Fig 4) It can be seen that the overall value is dominated by the free SDS component, however a correlation time for SDS bound at the bubble surface is obtainable. Slow total motion of bound molecules is much slower, and decreases (τ_s increases) as foam drains. However, total motion increases for free molecules until it reaches the value calculated for micelles (4 ns). This indicates free solution gains order as the foam drains, allowing more freedom of movement within, and the formation of micelles in the ordered solution within the foam, from the excess free surfactant remaining after the bubbling process.

The differences in motion between SDS in different positions in the foam, at different times, at different concentrations and in the presence or absence of a co-surfactant, will be the subject of my thesis, and papers currently under preparation for the scientific literature.

Yours Sincerely,

Ross W. Mair

Email: rmair@stan.xx.swin.oz.au

Please credit this contribution to the account of Dr Jo Weigold.

Swinburne
University of Technology

Hawthorn Campus
John Street Hawthorn
Victoria Australia

Telephone +61 3 214 8911
Fax +61 3 819 5454

Address all correspondence to
PO Box 218 Hawthorn
Victoria 3122 Australia

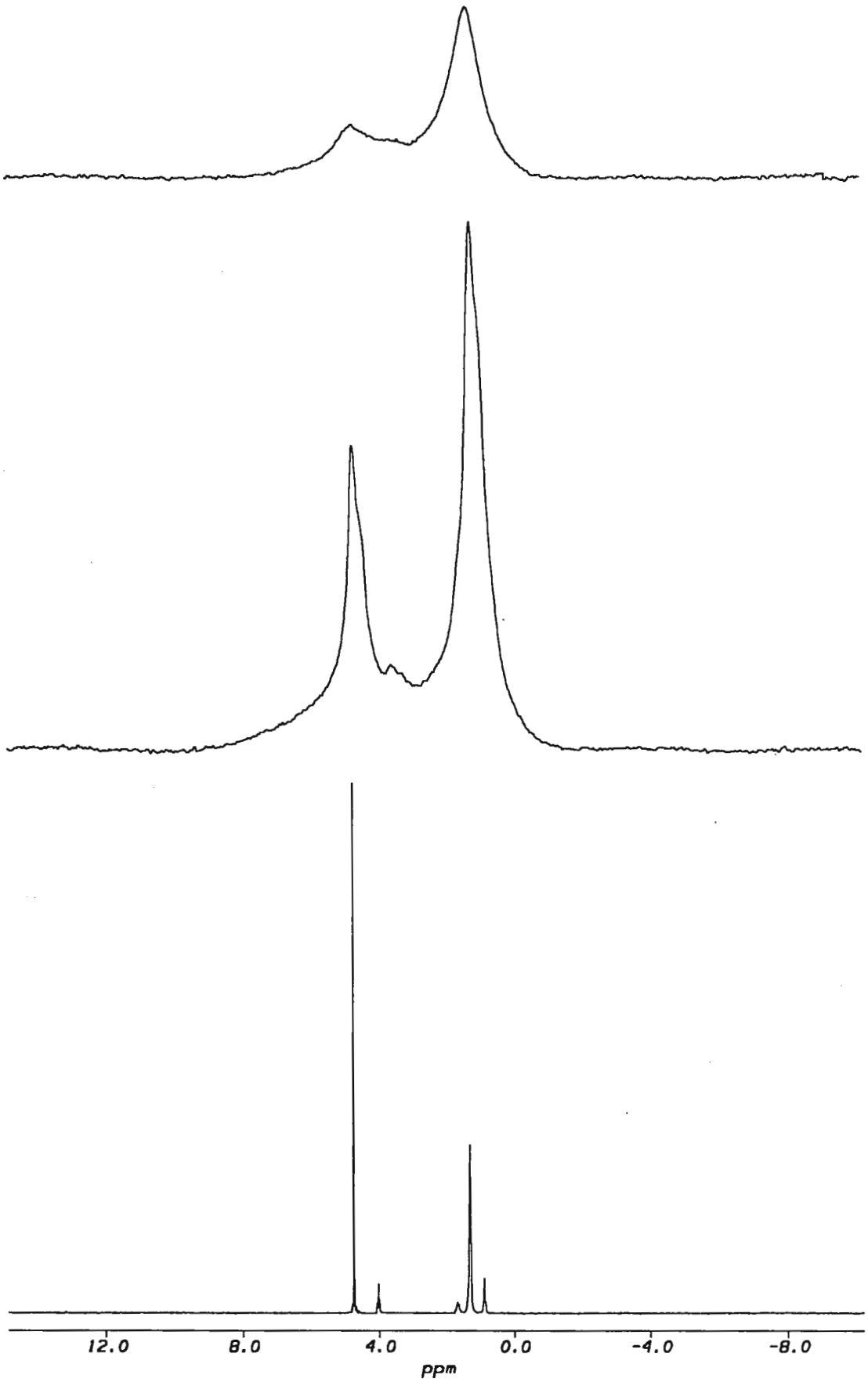


Figure 1: Comparison between standard ^1H solution spectrum of SDS in D_2O (bottom) and spectra of the foam recorded at the bottom of the foam column (middle) and at the top (top). The two foam spectra are shown at the same vertical scale, which is in turn approximately a factor of 30 greater than the vertical scale of the solution spectrum.

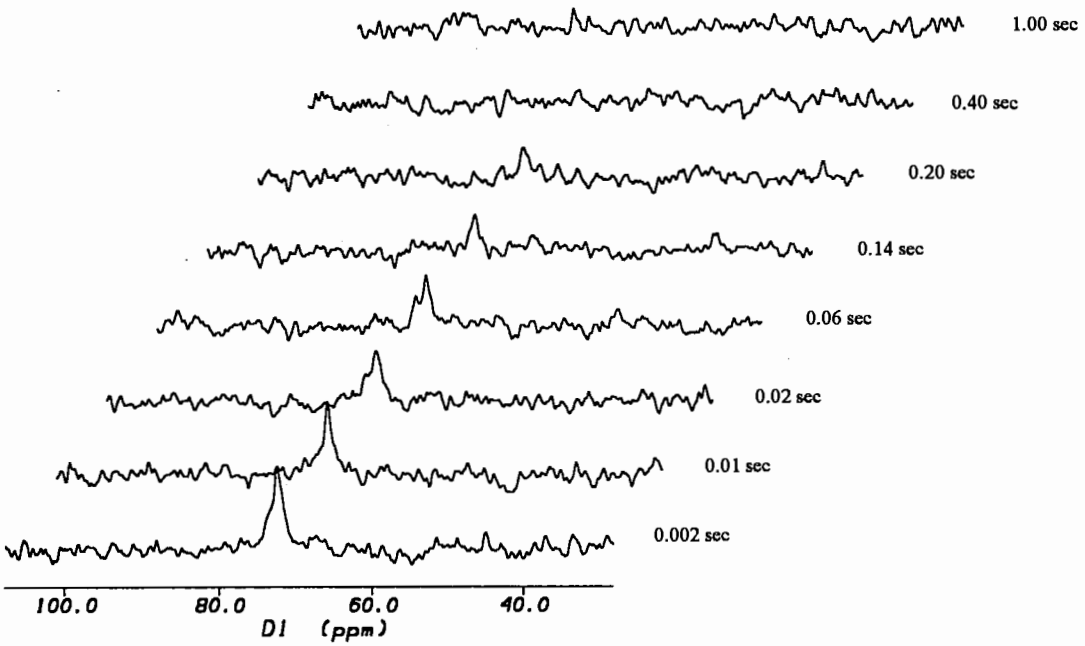


Figure 2: ^{13}C spectra of enriched SDS foam used to determine T_2, with delay times noted.

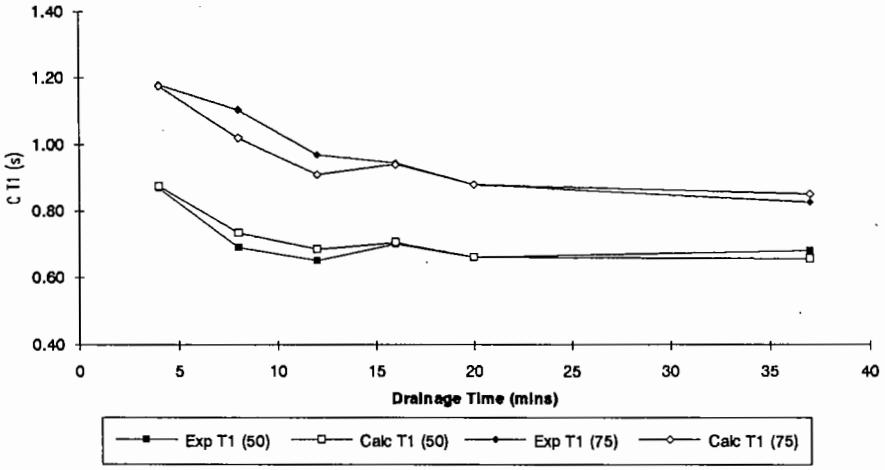


Figure 3: Comparison of experimental and recalculated T_1 data in 0.1 M SDS foams, at the bottom of the foam column. Larmor frequency is in parenthesis.

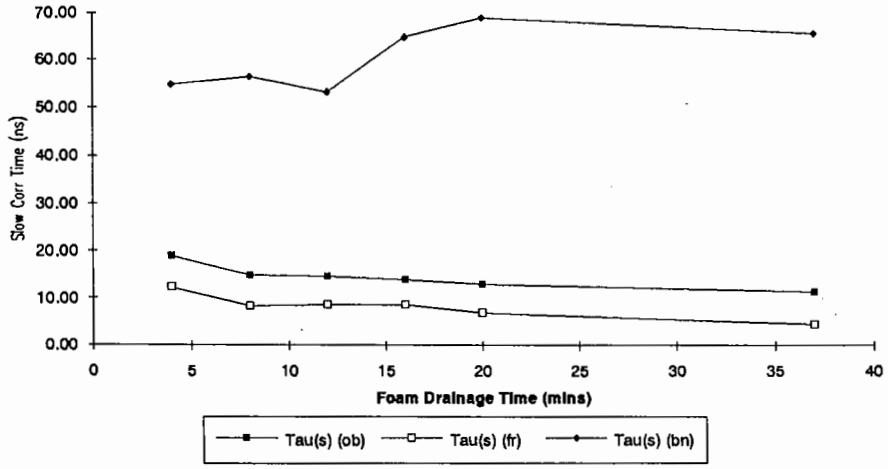


Figure 4: Optimized slow correlation time for SDS at the bottom of a 0.1 M foam column. 'ob', 'fr' and 'bn' refer to τ_s for the overall averaged SDS motion, and for free and bound SDS components respectively.

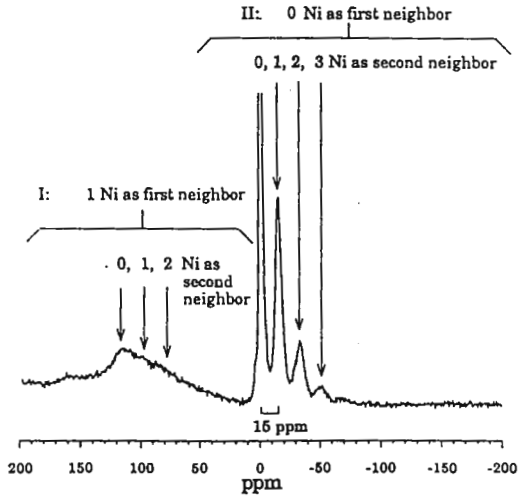
Laboratoire de RMN et Modélisation Moléculaire - UMR 50 CNRS/Bruker/Université Louis Pasteur
Institut de Chimie, BP296/R8, 67008 Strasbourg Cedex, France *Strasbourg, september 6 1994*

MAS NMR of Quadrupolar Nuclei in Paramagnetic Materials

Dear Barry,

During the last decade, "high-resolution solid-state NMR" spectroscopy has become a standard technique for studying molecular order and dynamics. Indeed, in a strong magnetic field, most of the line broadenings due to chemical shift anisotropy, dipole-dipole and quadrupolar interactions can often be suppressed by high-speed magic-angle-spinning (MAS). However, although NMR in paramagnetic materials originated in the middle 1950's with the study of bonding in transition metal fluoride single crystals [1], only a few applications of the MAS technique to paramagnetic powders have appeared. These results nevertheless demonstrate that under appropriate conditions, the paramagnetic ions provide a means for the determination of structural information [2]. In particular, ^{6}Li and ^{7}Li MAS NMR was recently shown to be very useful for studying the local environment of the lithium atoms inserted in vanadium oxide bronzes [3].

More recently, we have used ^{6}Li and ^{7}Li static and high-speed MAS NMR in order to characterize the structure of the $LiNi_{1-y}Co_yO_2$ phases ($0 < y < 1$) that are also used as cathode material in secondary batteries. As demonstrated by the Figure below, the ^{6}Li and ^{7}Li high-speed MAS spectra are found to be sensitive to hyperfine couplings with both the nearest and next nearest nickel neighbors. These short distance interactions are used to yield information on the distribution of the transition metal atoms in the $(Ni,Co)O_2$ slabs. While deviations from a random Ni/Co distribution cannot be quantified by NMR experiments on static samples, the MAS spectra clearly demonstrate that the $LiNi_{1-y}Co_yO_2$ phases have a tendency to form cobalt clusters. These results show that in favorable circumstances, MAS NMR of paramagnetic materials permits the accurate detection of short scale heterogeneities that cannot be observed by X-ray diffraction.



1. R. G. Shulman, V. Jaccarino *Phys. Rev.* **108**, 1219 (1957)
2. A. R. Brough, C. P. Grey, C. M. Dobson *J. Am. Chem. Soc.* **328**, 706 (1993)
3. J. Hirschinger, T. Mongrelet, C. Marichal, P. Granger, J. M. Savariault, E. Déramond, J. Galy *J. Phys. Chem.* **97**, 10301 (1993)

C. Marichal J. Hirschinger P. Granger

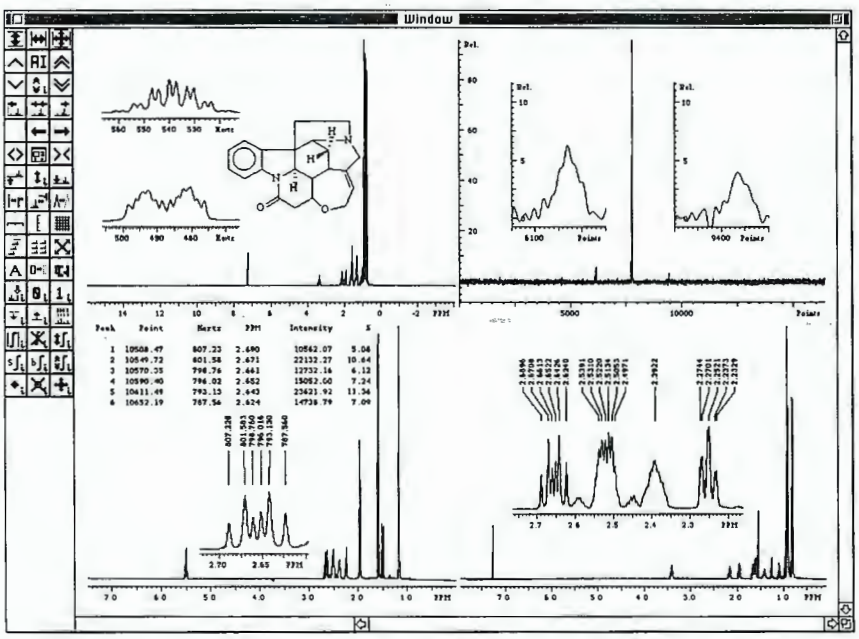
WIN-NMR FOR THE APPLE MACINTOSH

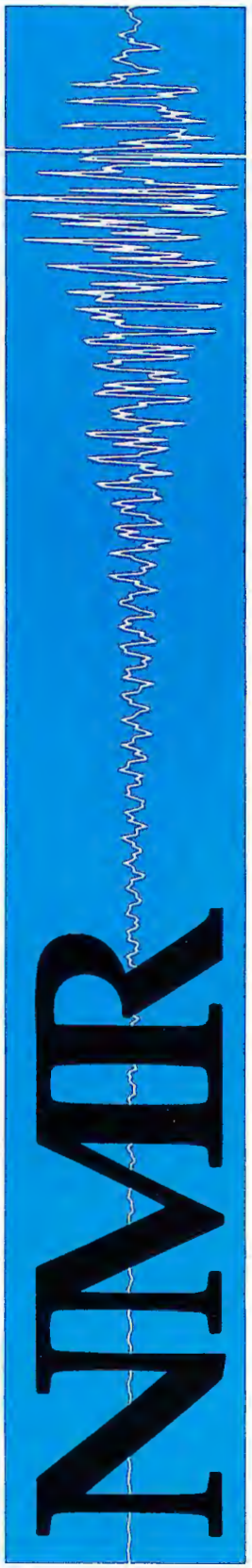
One of the most tedious tasks performed by a spectroscopist is preparing data for reports or publication. Today's word processing packages for personal computers make preparing text documents relatively straight forward. However the inclusion of chemical structures and spectral plots until recently was literally a "cut and paste" operation with scissors and glue.

Announcing WIN-NMR 3.0 for the Macintosh, the newest member of the WIN-NMR software family from Bruker. Throw away your scissors and glue. It is now possible to quickly process your 1D NMR data and prepare high quality NMR graphics to your needs. The graphics can then be exported into any word processing package that can handle encapsolated postscript (EPSF) format files.

The redesigned WYSIWYG user interface in WIN-NMR 3.0 incorporates many features found in popular drawing packages including:

- A tool palette for frequently used commands
- Undo and Redo
- Handles for the movement and resizing of objects
- Interactive data manipulation directly via the mouse, no scroll bars or dialogs
- Multiple views of single or multiple data sets on a page
- A snap grid and utilities for alignment of objects
- EPSF file export
- PICT and text paste support for structures and annotation

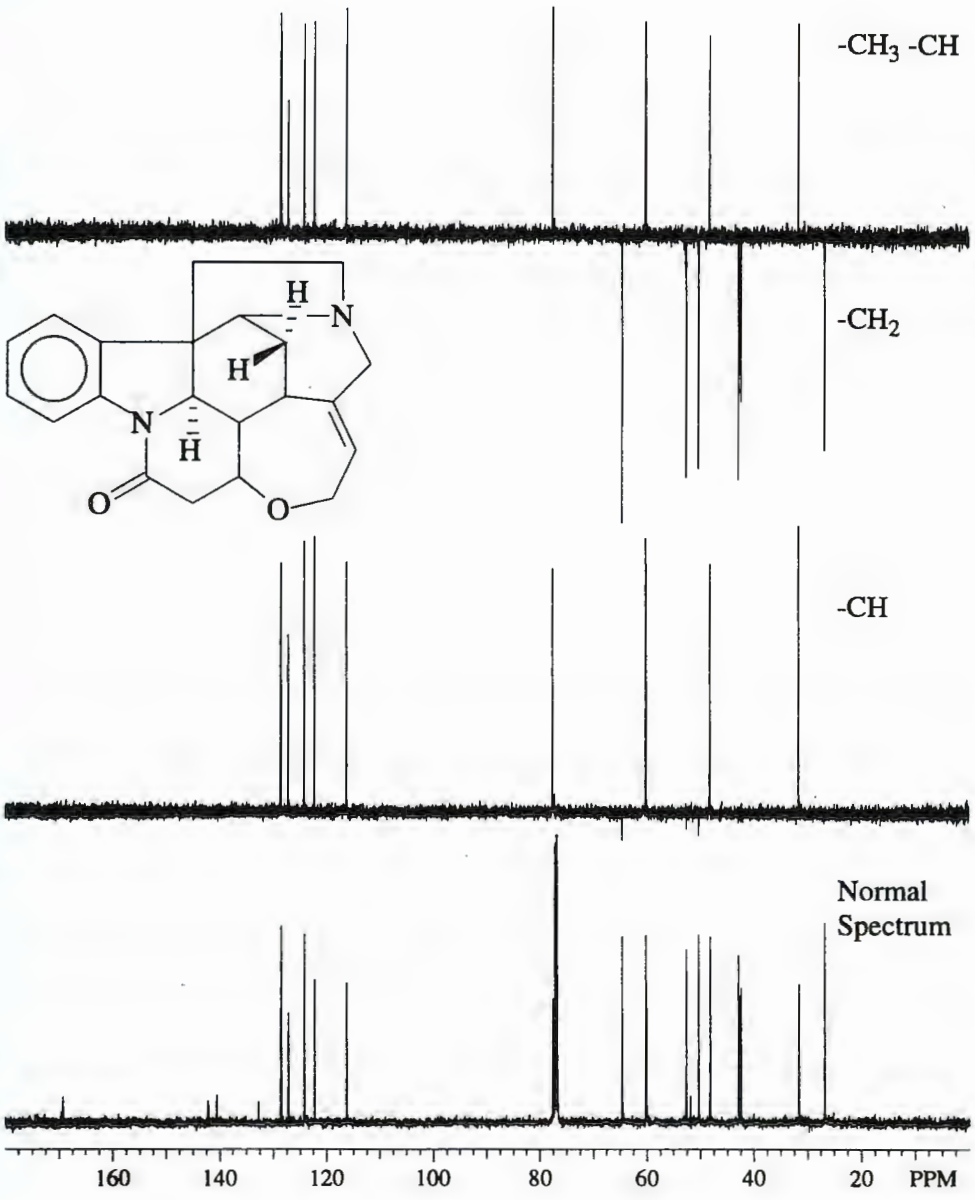




BRUKER

NMR

Below is an example of the quality of the WIN-NMR graphics that can be exported to word processors and drawing packages. The strychnine structure was drawn with Chemitosh 3.3.2 from SoftShell International.



WIN-NMR 3.0 includes additional processing commands and commands for spectral comparison. An import command has been added to simplify handling of Aspect 2000/ 3000 data.

Macintosh is a trademark of Apple Computer, Inc.

WIN-NMR is a trademark of Bruker Franzen Analytic GmbH.

ECOLE POLYTECHNIQUE
DEPARTEMENT DE CHIMIE
LABORATOIRE DE SYNTHESE ORGANIQUE
91128 PALAISEAU (FRANCE)
Fax : 1 69 33 30 10 .

Palaiseau le 1 Septembre 1994

Dr. B.L. Shapiro
TAMU NMR newletter
966 Elsinore Court
Palo Alto, California 94303, USA.

Automatic shim procedure for high resolution NMR spectrometer

Dear sir,

In NMR of protein, a high homogeneity of the field is crucial to get high resolution spectra. We are used to practicing the so-called "shim" technique in order to correct the inhomogeneity of the field's gradients. That must be done all over the useful volume of the sample and it is time consuming. An organized shim strategy may help us to find the best shims' area. Numerous gradients (about twenty) have to be adjusted in different ways and the procedure may turn out to be unsuccessful if you are in a bad shim region or if you are not used to practicing the shim technique. That is the reason why we have developed an automatic shim strategy. The interactions between the varied gradients are classified in three groups as follow:

Order 0 group, (Z, Z_0, X, Y, ...).	There is no interaction between the gradients of this group. A simple action on one gradient does not affect the other.
Order 1 group, (Z^5,Z^4,Z^3,Z^2,Z,X^3...).	A gradient adjustment of n order needs a correction of the lower n-1 order.
Order 2 group, (ZX, ZY, Z^2X, Z^2Y, Z(X^2-Y^2)).	We cannot directly observe an optimum by acting on this gradient. We need to shift one gradient far from a starting value and act on the other gradients in order to find an optimum of the lock level. This step is quite complicated and time consuming. A simplex algorithm may be used.

A global shim strategy is outlined in figure 1. After a rapid adjustment of the zero and first order groups, you get the lock of your spectrometer. An "approach strategy" is then used to raise the lock level. All the groups are involved in this step. In order to divide the XY plane shims from the axial shims we use the rotation of the sample. Then we have two steps of adjustment called 'spinning on' and 'spinning off '. It is worth noting that sometimes you need to adjust the lock phase before going on.

Finally we have to look at the FID (or at the FT datas) to obtain the best lineshape of our spectrum. This is what we consider to be the best shim region. The steps from 2 to 6 may be automated since they have only used the lock level. On our 600 MHz Bruker NMR spectrometer, we have implemented a complete program of shim tuning that we have called 'SHIMTOTAL'. The program is included in this letter and speaks for itself. You only have to lock the spectrometer and send the program by the command "Tune shimtotal".

The increment value of the shim gradients and the number of loops in the program have been set up by observing different users shims. The procedure uses the simplex method of optimisation starting with a set of gradients and slowly varies each of them in order to find the best response. We have tested our 'shimtotal' on the best shim region considered as a starting region. We expected that this best region would not be severely degraded. We have obtained a second region of shim gradients that we have characterized by three standart deviations ΔZ, ΔXY, ΔXYZ, from the best one. Again an automatic shim procedure on the second region gives us a third region

characterized by its standart deviations from the best region. We have degraded some gradients of the regions 3 and 1, and started an automatic shim procedure giving the regions 5 and 7 of shim. Figure 2 retraces the behaviour of the automatic shim in each region. All the tests have shown the efficiency of the procedure. If we send an automatic shim technique on the best region (n° 1), this latter will be a little bit degraded (n° 2). It is quite normal as our shim procedure only uses the lock level and thus, cannot take into account the general shape of the NMR signal. On the other hand, if you degrade the best region or if you start from any unknown shim region (n° 4 or n° 6), provided that you can still lock your spectrometer in this last case, the automatic shim tends to find a better shim region (n° 5 and 7). The simple 1D spectra, from each shim region, show the efficiency of the procedure (see figure 3). This program is 'soft' because we have chosen small increments with a large number of loops in order to slowly explore a shim region. An automatic shim procedure takes about twenty minutes. A strong procedure may be done by increasing the step increments but to the detriment of accuracy.

Our 'shimtotal' program has always given us a good set of gradients from which a manual procedure with the FID has been performed easily. We want to point out that the algorithm is efficient and robust as it works well from any set of shim gradients. Of course a complete automatic shim using the FID would be welcome and we really think about it.

We thank Miss Danaé Vidal for the reading and the typing of this note and Mrs Véronique Stoven for the comments of this technical note. We are grateful to Carlos Garcia, who provided us the If3 sample and got the best shim region n°1.

Alain LOUIS-JOSEPH.*

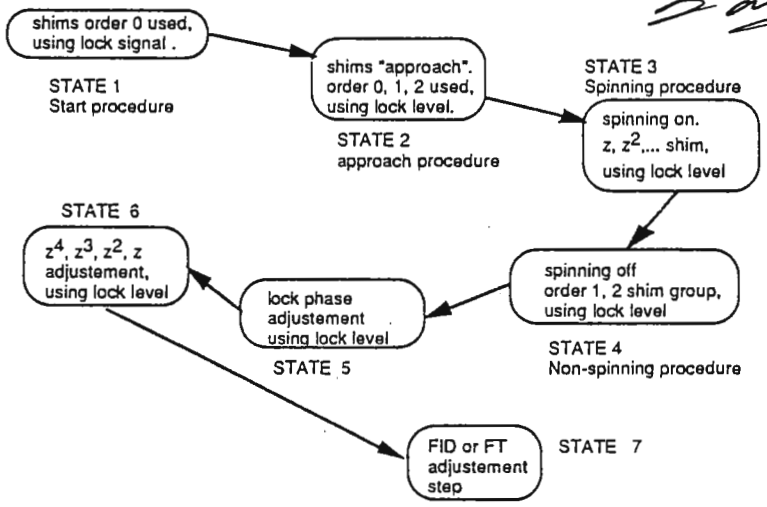


Figure 1 : General purpose shim strategy

```
LOCKPWELL 4
MAXLOCK 3500
#ASPROCHE
ROTATION OFF
LOCKPHASE 10 10
Z1 50 10
Z2 50 10
Z1 50 10
X 50 10
Y 50 10
Z1 50 10
Z3 50 10
Z2 50 10
Z1 50 10
ZX 50 10
ZY 50 10
XY 50 10
X2-Y2 50 10
Z1 50 10
Z3 50 10
Z2 50 10
Z1 50 10
Z2X 50 10
Z2Y 50 10
ZX 50 10
ZY 50 10
X2-Y2 50 10
Z1 50 10
Z4 50 10
Z3 50 10
Z2 50 10
Z1 50 10
Z2X 50 10
Z2Y 50 10
ZX 50 10
ZY 50 10
Z2 50 10
Z1 50 10
LOCKPHASE 10 10
ROTATION ON
TIME 3
Z2 20 10
Z1 20 10
END
SET Z3 100 5
SIMPLEX Z3 Z2 Z1
SET Z4 100 5
SIMPLEX Z4 Z3 Z2 Z1
SET Z5 100 5
SIMPLEX Z5 Z4 Z3
TIME 3
Z2 20 10
Z1 20 10
END
ROTATION OFF
LOCKPHASE 10 10
TIME 3
X 20 10
Y 20 10
END
SET ZX 100 5
SIMPLEX ZX X
SET ZY 100 5
SIMPLEX ZY Y
TIME 3
X2-Y2 20 10
END
SIMPLEX ZX X
SIMPLEX ZY Y
SET Z2X 100 5
SIMPLEX Z2X ZX X
SET Z2Y 100 5
SIMPLEX Z2X ZY Y
SET ZXY 100 5
SIMPLEX ZXY XY
TIME 5
XY 10 10
X 10 10
END
TIME 5
Z3 10 10
Y 10 10
END -
TIME 5
Z3 10 10
Z2 10 10
Z1 10 10
END
SET Z4 500 10
SIMPLEX Z4 Z3 Z2
AUTOSAVE ON Z4 Z2
```

Shim procedure program implemented on the 600 MHz Bruker NMR spectrometer.

* Please, credit this contribution to the account of professor J.Y. LALLEMAND.

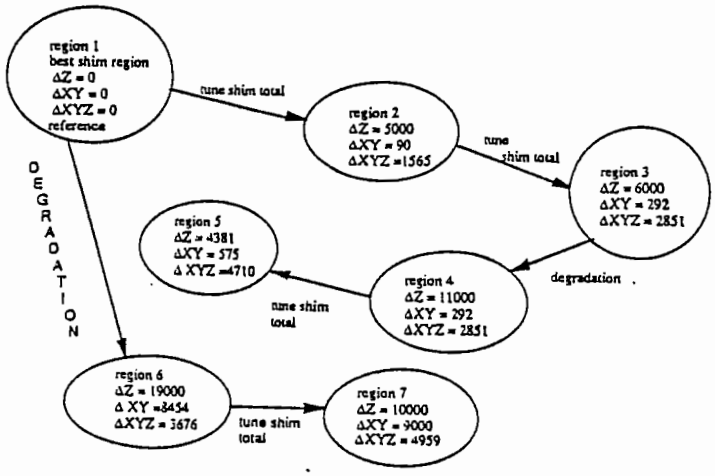
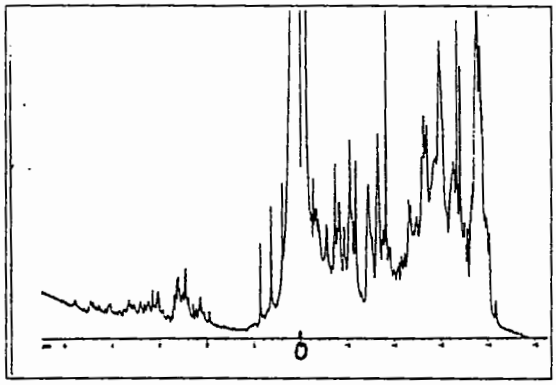
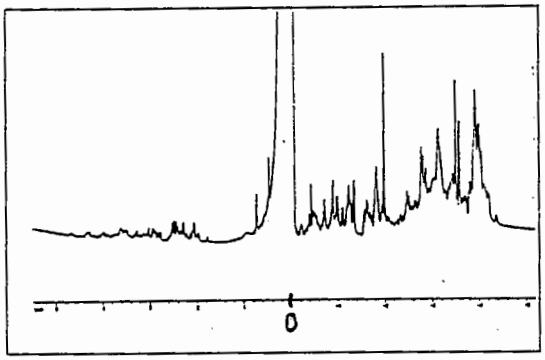


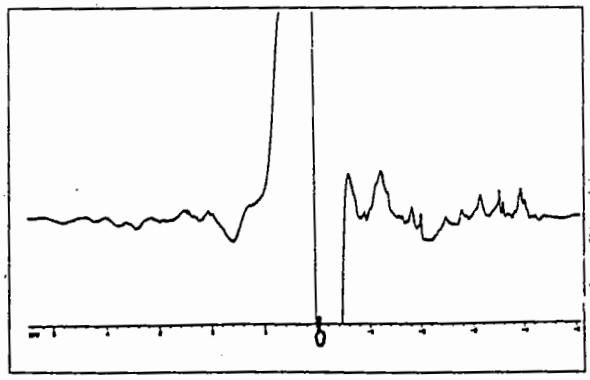
Figure 2 : State diagramm of the shim region obtained by automatic shim procedure upon the best region (number 1) of shim or manually degraded one.
ΔZ involve the Z^5, Z^4, Z^3, Z^2, Z gradient units.
ΔXY involve the X, Y, XY, X^3, X^2, X^2-Y^2 gradient units.
ΔXYZ involve the crossed term XZ^2, YZ^2, XYZ.



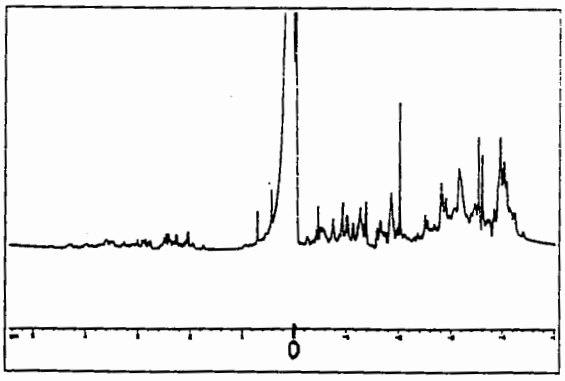
3-A : Spectrum of IF3 (Initiation Factor 3 of E. coli), 0.2 mM sample on 600 MHz NMR. The shim set (region number 1), which is the best one, is manually obtained from the lock level and the FT lineshape.



3-B : Spectrum of the IF3 sample from shim set region 2 after automatic shiming on shim set region 1.



3-C : Spectrum of the IF3 sample from the shim set region 6 from the degradation of region 1.



3-D : Spectrum of the IF3 sample from shim set region 7. An automatic shim has been performed on shim set region 6.

Figure 3 : Spectra obtained from different sets of shim gradients.

TAMU NMR Newsletter - Book Reviews

Book Review Editor: **William B. Smith**, Texas Christian University, Fort Worth, TX 76129

" TWO-DIMENSIONAL NMR SPECTROSCOPY "

Applications for Chemists and Biochemists; Second Edition

by

William R. Croasmun and Robert M. K. Carlson

VCH Publishers, 220 East 23rd Street, New York, NY 10010;
ISBN 1-56081-664-3; 1994; 950 pages; Hardcover, $125.00.

This volume is a second edition, and is a valuable follow-up to an original version now seven years old. The changes in NMR spectroscopy are reflected in the fact that the new volume is almost twice as long as the first edition. A multiple-author effort edited by Croasmun and Carlson, who also contributed chapters here as in the first edition, the new volume follows the same format as the original. While the title words "Two-Dimensional NMR" still remain in a number of the chapter headings, several of the chapters have rather extensive coverage of higher dimensional NMR techniques, and we may reasonably expect a third edition to contain the words "Multi-dimensional NMR" in the title.

Expanded from the original's nine chapters, the eleven chapters have been considerably reshuffled. As with the first edition, George Gray begins with an extensive introductory chapter aimed at newcomers to multi-dimensional methods. This is followed by by William Hull's more detailed chapter on experimental aspects. Chapter 3, Proton-Detected Heteronuclear and Multidimensional NMR, by Christian Griesinger and colleagues is new, as is Chapter 4 by Hans Robert Kalbitzer on Computer-Aided Analysis of Multi-dimensional NMR Spectra. Other new contributions are Protein Structure Calculation Using NMR Constraints, by H. Jane Dyson and Peter Wright, and Studies of Nucleic Acid Structures Based on NMR Results, by Igor Goljer and Philip Bolton. Other chapters by authors contributing to the original edition have been extensively revised to reflect changes in the field.

The cost of this volume means that many of us will rely on its acquisition by the local library. However, this is the current best volume reflecting the state of the art, and I was quite astonished by how much new material it contained. I think you might well have the same experience, particularly if your school or laboratory budgets have not allowed you to experience the latest techniques in reverse detection, pulsed field gradients and multi-dimensional NMR spectroscopy.

WBS

Introducing the NEW 3445/3446 Amplifiers from AMT

10-130 MHz Bandwidth

1000 and 2000 watt Models available

For High Performance NMR/NMRI Applications

Your NMR/NMRI requirements are pushing the leading edge of science and you need AMT RF power technology! Our NEW Models 3446 and/or 3445 operate from 10-130 MHz and are conservatively rated at 1000 watts for low field NMR and currently up to 2000 watts for NMRI applications up to 3 Tesla. AMT has brought together the highest possible RF performance at a most cost effective price. Nobody builds a better NMR/NMRI amplifier than AMT...

Call AMT today for a price that will really flip your spins!

Additional Features Include:

- 10-130 MHz bandwidth for use in systems up to 3T
- Up to 2000 watts of power for imaging
- CW power capability for decoupling
- Blanking delay time less than 1 µs for multi-pulse

AMT

a Spectrian company

3080 Enterprise Street ▪ Brea, CA 92621 ▪ (714) 993-0802 ▪ Fax (714) 993-1619

Models 3445/3446

10-130 MHz, pulsed, solid-state, RF power amplifier systems

Key Specifications:

Models:	3445	3446
Frequency range	10-130 MHz	10-130 MHz
Pulse power (min.) into 50 ohms	2000 W	1000 W
CW power (max.) into 50 ohms	200 W	100 W
Linearity (±1 dB to 30 dB down from rated power)	1800 W	900 W
Pulse width	10 ms	20 ms
Duty cycle	Up to 10%	Up to 10%
Amplitude droop	5% to 10 ms typ.	5% to 20 ms typ.
Harmonics	Second: – 25 dBc max. Third: – 12 dBc max. to 30 MHz – 25 dBc max. above 30 MHz	
Phase change/output power	10° to rated power, typ.	
Phase error overpulse	4° to 20 ms duration, typ.	
Output noise (blanked)	< 10 dB over thermal	
Blanking delay	< 1 μ s on/off, TTL signal	
Blanking duty cycle	100% max.	
Protection	1. Infinite VSWR at rated power 2. Input overdrive, up to +10 dBm 3. Over duty cycle/pulse width 4. Over temperature	

Other members of AMT's NMR/NMRI Family:

3205/3200
6-220 MHz, 300/1000 W

3415/3414
20-200 MHz, 4 kW/7 kW

3304
30-310 MHz, 400 W

3137/3135/3134
200-500 MHz, 50/150/300 W

Supplemental Characteristics:

Indicators, front panel	1. AC power on 2. CW mode 3. Overheat	4. Overdrive 5. Over pulse width	6. Over duty cycle 7. LCD peak power meter
System monitors	1. Forward/Reflected RF power 2. Over pulse width/duty cycle	3. DC power supply fault	4. Thermal fault
Front panel controls	1. AC power	2. Forward/Reflected power	
AC line voltage	208/230 VAC, 10%, 1Ø, 47-63 Hz		

	3445	3446
AC power requirements	1400 VA	700 VA
Size (HWL, inches)	8.75 x 19 x 24	8.75 x 19 x 24
Net weight	110 lbs.	75 lbs.

AMT
a Spectrian company

3080 Enterprise Street ▪ Brea, CA 92621 ▪ (714) 993-0802 ▪ Fax (714) 993-1619

(AMPX00HV) 02/94

CENTRE FOR MAGNETIC RESONANCE

PROFESSOR DAVID M. DODDRELL
DIRECTOR

9 September, 1994
(received 9/16/94)

THE UNIVERSITY OF QUEENSLAND
Brisbane Qld 4072 Australia
Telephone (07) 365 4100
International +61 7 365 4100
Facsimile (07) 365 3833
Telex UNIVQLD AA 40315

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

Dear Barry,

FIRST MRI OBSERVATION OF HIPPOCAMPUS LESIONS IN THIAMIN DEFICIENT RAT BRAIN

Over the last two years, we have used MRI and MRS to investigate biological and anatomical changes in the brain of thiamin deficient rats. The purpose of these investigations is to use them as a model for the study of the Wernicke Korsakoff (WK) Syndrome [1], a condition which is caused by acute thiamin deficiency. The disease affects alcoholics in 95 % of cases. Due to the intrinsic role of thiamin in glucose metabolism, symptoms can also be precipitated by glucose administration to thiamin deficient patients in hospitals. Following a glucose load of 1 g i.p. in the rat, abnormal levels of glucose and glutamate/glutamine/GABA have been detected using localised MRS [2]. By using an i.v. injection of Gd-DTPA, we have also been able to observe clear signs of blood brain barrier dysfunction [3].

In our most recent study, we used a surface coil to image the brain of a thiamin deficient rat, for a period of two hours after glucose administration. T_2 weighted 2DFT imaging protocols were employed to identify lesions in the brain in an entirely non-invasive fashion. We used an echo time of 18 ms, slice thickness 2 mm, summing two echoes for every image. Figure 1 shows two such images obtained before and after a glucose load. They arise from the fourth echo image, by adding echoes at 126 and 144 ms. The hyperintensity of the crown shaped region inside the brain corresponds to the hippocampus. Such marked hyperintensity at relatively long echo times, would indicate that after the administration of glucose to a thiamin deficient animal, this area may suffer either oedema or severe swelling of the tissue. In humans, the amnesia known as Korsakoff's psychosis follows one or more episodes of acute Wernicke's encephalopathy. While non-Korsakoff amnesic syndromes have been shown to be associated with a shrunken hippocampus, in long term Korsakoff patients the hippocampus appears normal [4]. Our rat model demonstrates that Wernicke's encephalopathy is followed by some alteration of function of the hippocampus. Thus, some hippocampal damage could be a component of the pathogenesis of Korsakoff's amnesia, as well as of other amnesic syndromes.

To our knowledge, this is the first non-invasive observation of lesions in the hippocampus in thiamin deficient animals, in vivo.

Yours,

Fernando Zelaya — Fernando Zelaya
Therese Wholohan — Therese Wholohan
p.p. F. Zelaya — Stephen Rose
Peter Nixon
Adrian Bower
David Doddrell

REFERENCES

1. Harper, C G. Wernicke's Encephalopathy : A More Common Disease than Realised. J. Neurol. Neurosurg. Psychiatry, 47, 426-441 (1979).

2. Rose S E, Nixon P, Zelaya F O, Wholohan B T, Zimitat C, Moxon L N, Crozier S, Brereton I M and Doddrell D M. Application of High Field Localised In Vivo ^{1}H MRS to Study Biochemical Changes in the Thiamin Deficient

Rat Brain under Glucose Load. NMR in Biomedicine, 6, 324-328 (1993).

3. Zelaya F O, Rose S E, Nixon P, Wholohan B T, Bower, A J and Doddrell, D M. MRI Demonstration of Impairment of the Blood-CSF Barrier by Glucose Administration to the Thiamin Deficient Rat Brain. NMR in Biomedicine, submitted.

4. Squire, L R, Amaral, D G and Press, G A. Magnetic Resonance Imaging of the Hippocampal Formation and Mamillary Nuclei Distinguish Medial Temporal Lobe and Diencephalic Amnesia. J. Neuroscience, 10, 3106-3117 (1990).

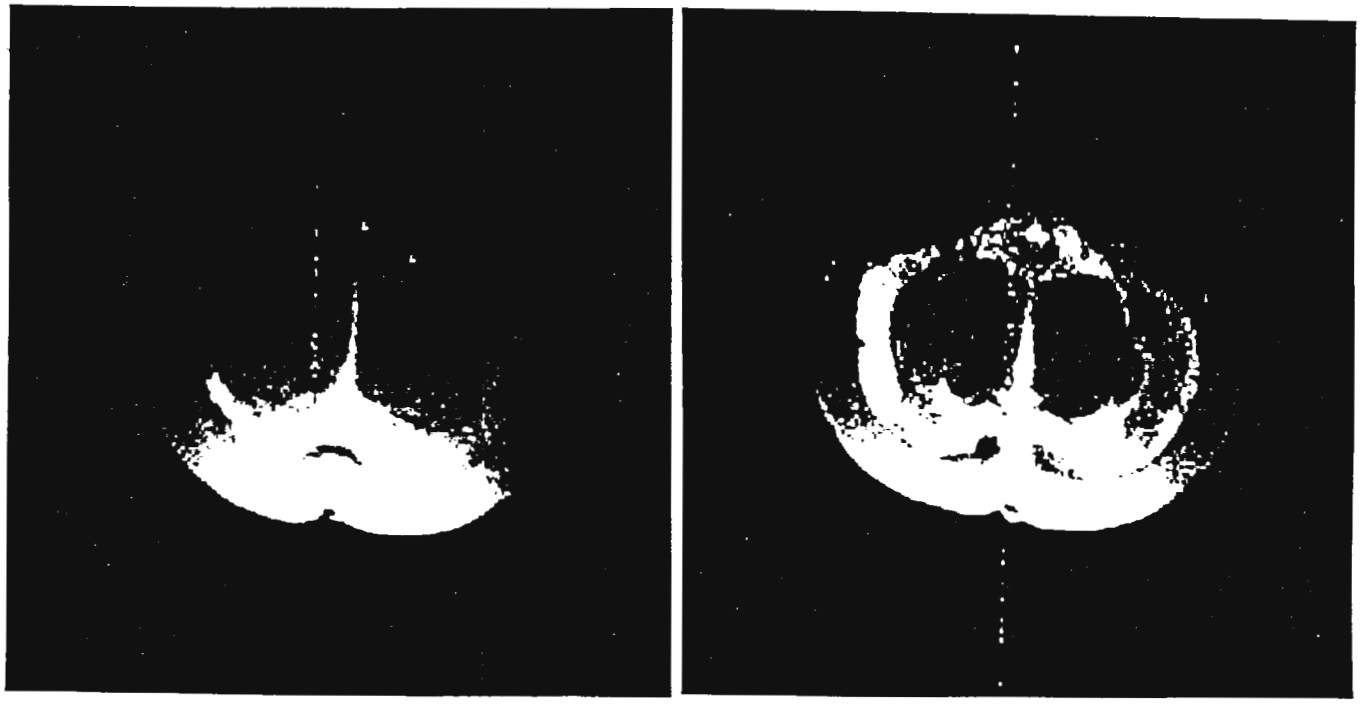


FIGURE 1

Transverse 2 mm slices at the level of the hippocampus, from the brain of a thiamin deficient rat. The image on the left is a control image taken by adding echoes at 126 and 144 ms. The image on the right was obtained using the same MRI protocol, 2 hrs after i.p. administration of 1 g of glucose. The blood glucose concentration achieved by this method is small enough not to cause hyperosmotic shock. Note the increased hyperintensity on the left hand side of the hippocampus. The asymmetry of the feature may arise from improper alignment of the animal in the magnet.

Specifying the wrong magnet could take some explaining.

The Oxford Instruments' pedigree is internationally renowned. For over 30 years we have been leading the way, creating the benchmarks for NMR magnet systems and transforming scientific ideas into usable, practical technology.

Our complete range of 100-750MHz magnets are designed, built in Oxford, the home of NMR technology, and are installed and serviced around the world, by our specialist engineers.

Working in partnership with our customers we are developing new products that will catapult NMR technology into the next millennium.

Innovation, and a commitment to create the very best, has made us the number one choice for so many. Our ability to deliver to the highest quality, time after time puts Oxford Instruments in a class of its own.

Talk to Oxford first - then decide!

Specify Oxford.

The Hulton Deutsch Collection

OXFORD

Oxford Instruments
NMR Instruments

The Oxford Instruments Pedigree

Oxford Instruments are the pioneers of NMR magnet systems and associated cryogenic technology. After more than 30 years, we are still leading the way maintaining our worldwide reputation for transforming scientific ideas into usable, practical technology:

- Oxford was the first company to introduce NMR quality super-conducting magnets at 400, 500 and 600 MHz.
- We designed and built the world's first compact superconducting storage ring for X-ray lithography.
- 20 Tesla magnets are routinely produced for physics research.

Making this happen are the people of Oxford Instruments, their expertise and dedication makes them our greatest asset and a unique resource for our customers.

Our accumulated knowledge and experience is unparalleled and some of the best minds in research technology are consistently working in partnership with our customers, exploring new techniques and setting new standards in the design and manufacture of specialist research products.

But it does not stop there; supporting our customers day to day, and around the world, is a team of engineers and technical specialists. Always on hand, they keep Oxford products fully functional and equipped with the latest refinements to keep our customers at the leading edge.

New products such as the Oxford NMR^{750} are practical examples of our innovation so you can be sure of Oxford's commitment to providing the very best in people and products for many years to come.

Standard specifications

Magnetic field Strength (^{1}H-MHz)	Room Temperature Bore Diameter (mm)	Field Stability (^{1}H-Hz/Hour)	Maximum Helium Refill Interval (Days)	Minimum Operational Ceiling Height (m)
750	51	15	60	3.8
600	51	10	120	3.4
500	51	10	150	3.2
400	54	8	365	2.8
360	54	8	365	2.8
300	54	3	365	2.8
270	54	2.7	365	2.8
200	54	2	365	2.8
100	54	1	365	2.8
500	89	15	120	3.4
400	89	10	180	2.8
360	89	10	365	2.8
300	89	3	365	2.8
270	89	2.7	365	2.8
200	89	2	365	2.8
100	110	1	119	2.8

We would be delighted to discuss your custom specification requirements for any specialist systems. For more information please contact your local Oxford Instruments sales and service organisation.

UK
Oxford Instruments
NMR Instruments,
Osney Mead, Oxford OX2 0DX,
England
Tel: +44 (0) 1865 269500
Fax: +44 (0) 1865 269501

Germany
Oxford Instruments GmbH
Kreuzberger Ring 38,
Postfach 4509, D-6200 Wiesbaden,
Germany
Tel: (611) 76471
Fax: (611) 764100

USA
Oxford Instruments Inc.
130A Baker Avenue, Concord,
MA 01742, USA
Tel: (508) 369 9933
Fax: (508) 369 6616

France
Oxford Instruments SA
Parc Club-Orsay Universite,
27, rue Jean Rostand,
91893 - Orsay Cedex,
France
Tel: (1) 6941 8990
Fax: (1) 6941 8680

Japan
Oxford Instruments K.K.
8F, Second Funato Building,
1-11-11, Kudankita,
Chiyoda-ku, Tokyo 102
Japan
Tel: (3) 3264-0551
Fax: (3) 3264-0393 · 0626

Oxford Instruments Inc.
West Regional Office,
331c Lakeside Drive,
Foster City, California 94404
USA
Tel: (415) 578 0202
Fax: (415) 578 9018

OXFORD

Oxford Instruments, NMR Instruments
Osney Mead
Oxford OX2 0DX, England
Telephone +44 (0) 1865 269500 Fax +44 (0) 1865 269501

Annotation of 2-D NMR Plots on a PC

C. Allen Bush,
Department of Chemistry and Biochemistry
University of Maryland Baltimore County
Baltimore. MD 21228

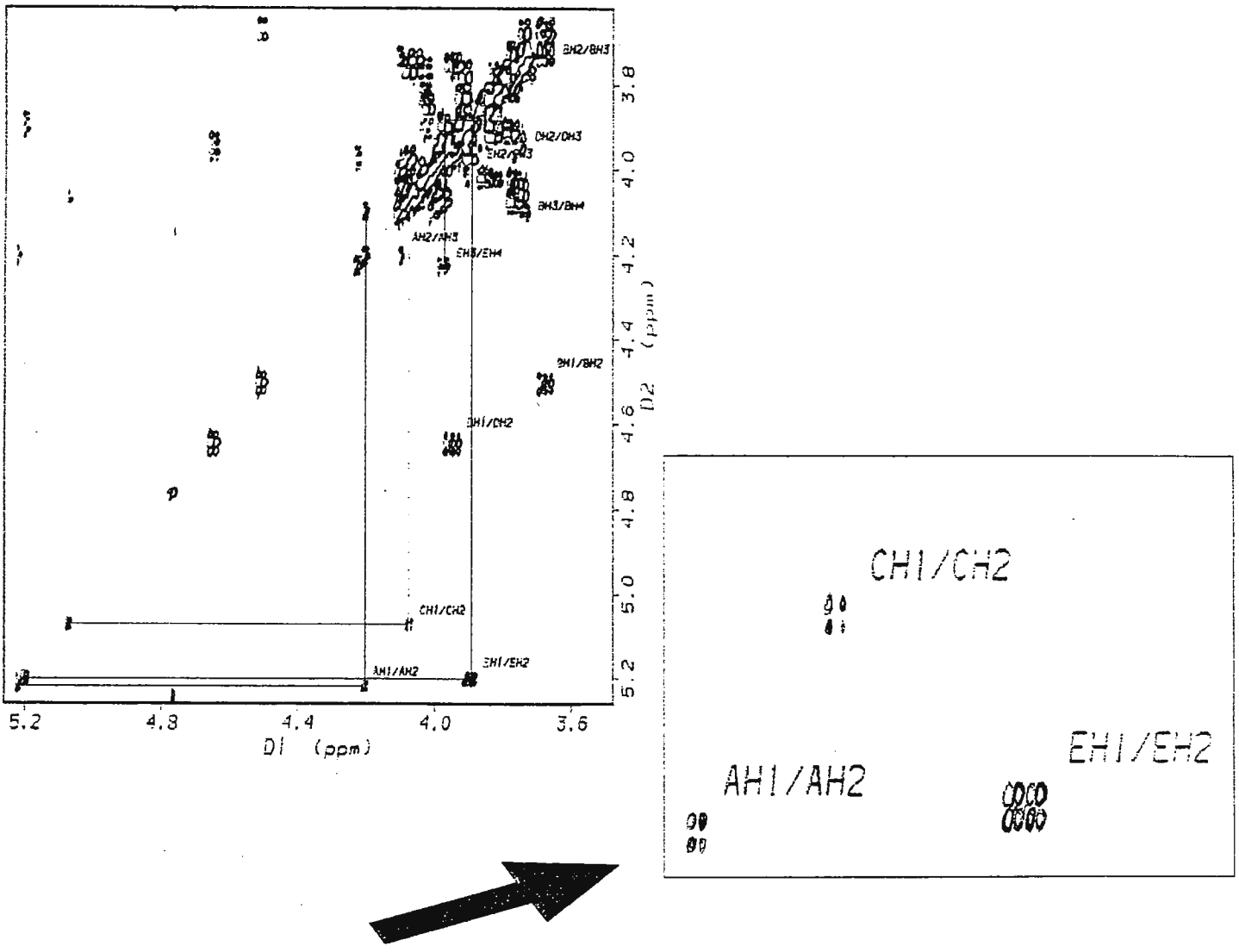
(received 9/17/94)

Several notes and comments have appeared in these pages on the conversion of plotted output from NMR programs (eg. FELIX) to popular PC and Apple graphics programs. The most recent was by Phil Bolton in the July issue regarding the incorporation of FELIX plots into Adobe Illustrator format. The interest in these conversion schemes results from the superior tools in these PC and Apple graphics programs for plot annotation, editing, expansion and incorporation into figures, slides, overheads and larger documents.

We describe a scheme for CorelDraw on the PC which has a similar capability for importing plot files in HPGL format. It is important to import in a vector format which allows for expansions without loss of resolution. Although bitmaps can be easily imported and manipulated in many graphics programs, the lines in the resulting plots look jagged on high resolution printers, especially if expansions are attempted.

In our recipe a plot file in HPGL format is made by FELIX and transferred via FTP to the PC. Since this is an ascii file, any file transfer scheme will serve. CorelDraw can 'import' this file using specified colors for the 'pens' which were used by FELIX to draw lines. The plot can then be annotated with text, lines and boxes and portions can be expanded. The file can then be printed on a color laser printer or inexpensive color ink jet printer. The example below is rendered only in black and white due to technical limitations of the TAMU Newsletter.

Although several graphics programs claim to be able to import Postscript files, we have not been able to successfully import and properly render on the screen files using this more sophisticated syntax. The simple HPGL format seems to be adequate for NMR contour plots.



Polysaccharide of *S. oralis* SK144

Specially designed

Thin Wall NMR Sample Tube

Shigemi's high precision thin wall NMR sample tube has a unique construction. The wall thickness of this particular tube is reduced only around the position of the detection coil. The result of this new invention allows an increase in the sample volume and higher sensitivity without sacrificing its mechanical strength. Therefore, there is no need for special handling during routine usage of our Shigemi NMR tubes.

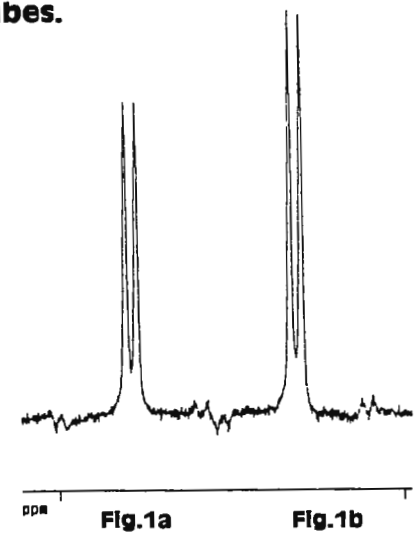
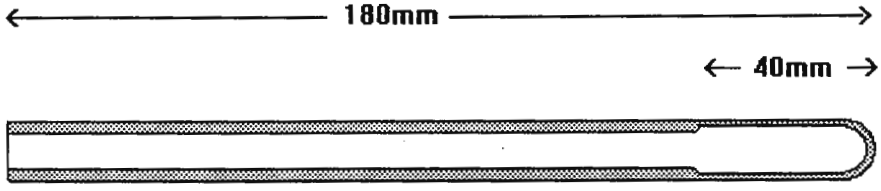
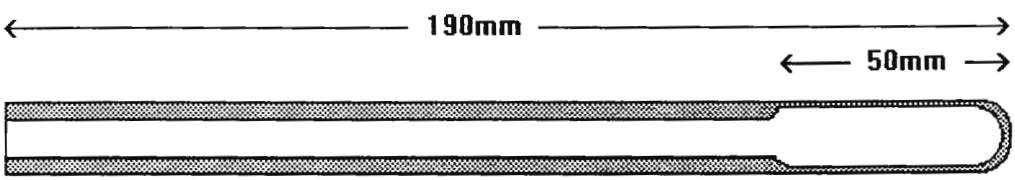


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



PST-001 and PST-002



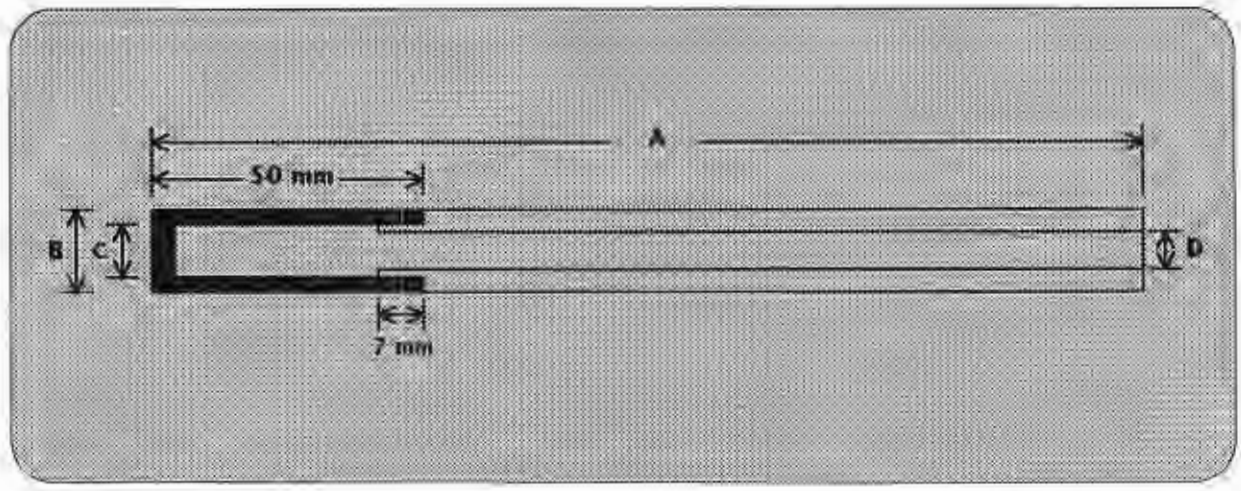
ST8-001,ST8-002, ST10-001, and ST10-002

O.D. (mm)	Product Number	Wall (mm)	Concentricity/Camber (μ)	OD (mm)	ID (mm)	Price Each 1-99	Price Each 100+
5	PST-001	0.21	20/ 8	4.96 + 0.00 - 0.01	4.54 ± 0.01	$15.00	$13.50
	PST-002	0.21	40/15	4.96 + 0.00 - 0.01	4.54 ± 0.01	$13.00	$12.00
8	ST8-001	0.25	40/ 8	8.00 + 0.00 - 0.01	7.52 ± 0.01	$31.00	$28.00
	ST8-002	0.25	50/15	8.00 + 0.00 - 0.01	7.52 ± 0.01	$27.00	$25.00
10	ST10-001	0.25	40/ 8	9.98 + 0.00 - 0.01	9.52 ± 0.01	$36.00	$32.00
	ST10-002	0.25	50/15	9.98 + 0.00 - 0.01	9.52 ± 0.01	$32.00	$28.00

SHIGEMI, INC.
Suite 21, 4790 Route 8 • Allison Park, PA 15101 • USA
Tel:(412)444-3011 • Fax:(412)444-3020

ALUMINA TUBE FOR ^{29}Si AND ^{11}B NMR

Shigemi has recently developed a unique alumina tube for ^{29}Si and ^{11}B NMR. The tube consists of a standard glass NMR tube connected to a highly densified alumina bottom which holds your sample. By using our alumina tube, the ^{29}Si spectrum is free from a broad ^{29}Si signal, and the spinning sidebands are suppressed to a minimum because of the tube's precision and quality. As of now, only Shigemi can offer you this very specialized and high quality tube for a reasonable price.



Type	A Length (mm)	B OD (mm)	C ID (mm)	D OD (mm)	Camber (μ)
Si-005	180	4.965 + 0 − 0.005	4.0 ± 0.1	2.5	± 0.02
Si-010	190	10.0 + 0 − 0.01	9.0 ± 0.1	6.5	± 0.02

Type	Diameter	Price for 5 tubes
Si-005	5 mm	$300.00
Si-010	10 mm	$400.00

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

National Institutes of Health
National Institute on Aging
Gerontology Research Center
4940 Eastern Avenue
Baltimore, MD 21224

September 13, 1994

(received 9/19/94)

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

Dear Dr. Shapiro,

HARTMANN-HAHN MISMATCH IN LONGITUDINAL EXCHANGE EXPERIMENTS

In the course of developing a longitudinal exchange experiment corresponding to lineshape studies of scaled rotational resonance (SRR) reported earlier[1], we have found that enhanced magnetization exchange does indeed occur when a SRR condition is satisifed, but also that this effect is typically masked by an additional process which results in strong exponential damping of the exchange profiles. It has been suggested that this damping phenomenon could be the consequence of proximity to a Hartmann-Hahn match condition:

$$\omega_{1I} = \omega_{1S} \pm n\omega_r \qquad (1)$$

where $\omega_1/2\pi$ is the nutation frequency for decoupling rf irradiation applied to the proton spins, $\omega_{1S}/2\pi$ is the nutation frequency for the scaling pulses applied during the longitudinal mixing period, $\omega_r/2\pi$ is the sample spinning rate, and n is a small integer. By this interpretation, the nearly exponential loss of longitudinal magnetization with increasing time is attributable to accidental leakage of carbon magnetization back to the proton spin bath via cross polarization.

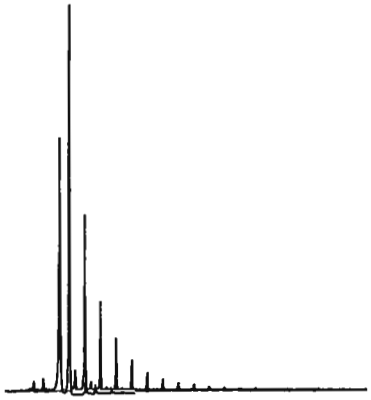
To test this hypothesis, we performed a series of off-rotational resonance exchange experiments using a Bruker AMX 400 on a sample of 2,3-di-^{13}C sodium propionate as a function of the ratio ω_{1I}/ω_{1S}. After cross-polarization of ^{13}C from ^{1}H and storage of the ^{13}C magnetization along the Z axis, N*M scaling cycles were applied to the carbon spins, where N=0,1,2...15 and M was chosen so that the mixing time increment was approximately 0.936 to 0.96 ms. Thus, the exchange profiles show a time course from 0 to about 14 ms. A β_y-$2\beta_{-y}$-β_y sequence was used with the pulses centered in each scaling cycle. For all the experiments shown here β=90° was used, and ω_{1S} and the pulse length were varied together to maintain this flip angle. During the scaling cycles, CW decoupling was applied to the proton spins with an RF field of amplitude $\omega_1/2\pi$=62.5 KHz. While the carbon power level for scaling was varied, the proton power level was kept constant. The blank time during scaling (the sum of delays before and after pulses in each cycle) was 16 μs for all experiments. All experiments were performed with the same ^{13}C resonance offset, chosen to avoid any scaled rotational resonance conditions. In the "No Scaling" control experiment, the timings were exactly the same as for the ω_1/ω_{1S}=3.5 experiments, but no carbon power was applied during the mixing period. In all experiments, the MAS spin rate was 5000 Hz.

Examining the results of these experiments, we find that signal loss with increasing mixing time becomes steadily less pronounced as the ratio ω_1/ω_{1S} increases away from 1.0. This behavior seems consistent with the accidental Hartmann-Hahn match hypothesis, but it is surprising that there is still significant signal loss for values of ω_1/ω_{1S} which should be far away from any of the conditions defined in Eq. 1. It has been suggested that carbon signal loss due to interference between the scaling pulses and the sample rotation could account for some of this residual damping, particularly for higher values of ω_1/ω_{1S} where the scaling cycle time τ_c is greater than about one-third the sample rotation period, $\tau_r = 2\pi/\omega_r$. However, a second set of experiments (not shown) in which the spin rate was varied so as to maintain τ_r/τ_c approximately equal to 4 yielded essentially the same exchange profiles as the constant spin rate experiments. Accordingly, we are exploring other mechanisms of longitudinal signal loss as well as experimental techniques to minimize these effects so as to permit the measurement of uncorrupted SRR exchange profiles.

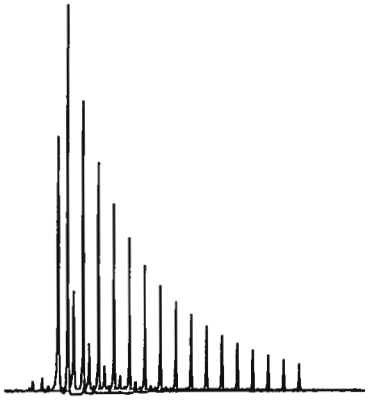
Sincerely,

Ken Fishbein Richard G. S. Spencer

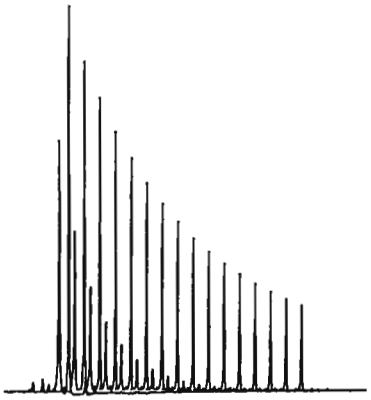
Reference: 1) R.G.S. Spencer, K.W. Fishbein, M.H. Levitt, and R.G. Griffin, J. Chem. Phys. **100**, 5533 (1994).



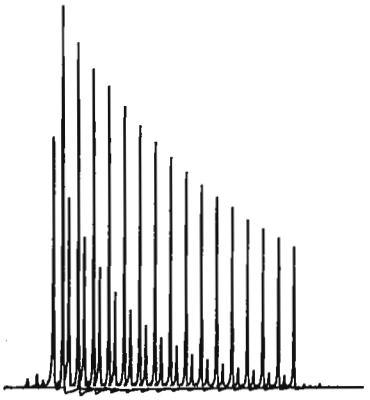
$\omega_{1I}/\omega_{1S} = 1.0$



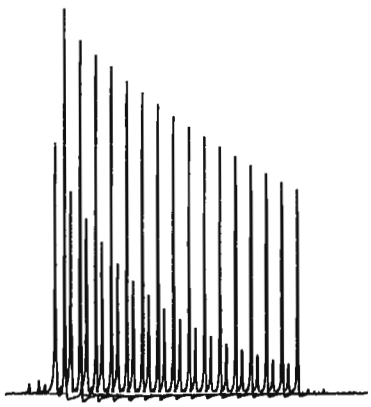
$\omega_{1I}/\omega_{1S} = 2.0$



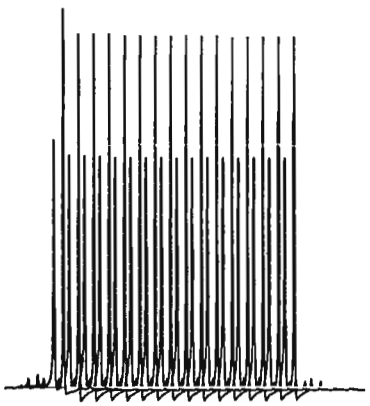
$\omega_{1I}/\omega_{1S} = 2.5$



$\omega_{1I}/\omega_{1S} = 3.0$



$\omega_{1I}/\omega_{1S} = 3.5$



No Scaling

Chemagnetics™

5.0 mm Broadband Triple Resonance Probe

The latest 5.0 mm Broadband Triple Resonance, Magic Angle Spinning PENCIL™ probe from Chemagnetics builds on the features that have become synonymous with the high performance design of the original (H, C, N) triple resonance probe. The patented PENCIL™ spinning module system incorporates such features as self-starting and trouble free spinning, and routine variable temperature operation. This is combined with a unique frequency optimized RF design to offer decoupling powers in excess of 80 kHz.

Chemagnetics

Features — Benefits

Full Multinuclear Range: ..... The X (75As-31P)and Y (25Mg-81Br) channels provide a complete range of nuclei combinations for the most demanding of experiments.

Double Resonance Mode: ..... The plug-in design allows no compromise performance for double resonance experiments.

PENCIL™ Rotor Design: ..... Large sample volume results in decreased experiment time and increased sensitivity.

PENCIL™ Double Bearing Design: ..... Smooth, stable spinning, eliminates asymmetric axial oscillation, and allows spinning of the most inhomogenous samples.

Separation of VT and Spinning gas: ..... Trouble-free constant spinning speed over complete VT Range (-150°C to 250°C).

Unique APEX™ II RF Design: ..... Allows unprecedented RF performance for reliable reproducible experiments requiring increased decoupler field strengths.

Exclusive VT Stack Design: ..... Permits full temperature range to be exploited without compromise of the probe performance.

Typical Specifications

Probe Outer Diameter	70 mm
Rotor Diameter	5.0 mm
Spinning Speed (ZrO_2 rotors)	1-12 kHz
"Y" Channel Frequency Range	^{25}Mg-^{81}Br
"X" Channel Frequency Range	^{75}As-^{31}P
"H" Channel Frequency Range	^{19}F-^{1}H
Temperature Range	−150°C to +250°C
Sample Volume	160 µL
^{1}H 90° Pulse Width	≤3.0 µs
^{13}C 90° Pulse Width (X)	≤4.0 µs
^{15}N 90° Pulse Width(Y)	≤7.0 µs

Chemagnetics™

For more information on Chemagnetics NMR Products, contact:

Corporate Headquarters
Chemagnetics
2555 Midpoint Drive
Fort Collins, Colorado 80525
USA
Phone 1 800 4 OTSUKA
or 303 484 0428
FAX 303 484 0487

United Kingdom
Otsuka Electronics Europe, Ltd.
Claro Court Business Centre
Claro Road
Harrogate, HG1 4BA
United Kingdom
Phone 0423 531 645
FAX 0423 531 647

Japan
Otsuka Electronics Co., Ltd.
2F Hashikan-LK Building
1-6, Azuma-Cho
Hachioji, Tokyo 192
Japan
Phone 0426 44 4951
FAX 0426 44 4961

The University of Texas Medical Branch at Galveston

School of Medicine
Graduate School of Biomedical Sciences
School of Allied Health Sciences
School of Nursing

Marine Biomedical Institute
Institute for the Medical Humanities
UTMB Hospitals

Department of Human Biological Chemistry & Genetics

September 6, 1994
(received 9/15/94)

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

Hey Barry, "Road Warrior NMR"

It was good to see you well and happy at this year's ENC.

Here at UTMB we have recently become instrument rich but space poor! Our Varian Unity+ 400 has found a good home in an adjoining lab to Mike Quast's SISCO 200/330, but alas our Varian Unity+ 600 is in exile in The Woodlands, Texas (88 miles away and on the other side of Houston). I'm sure there are some real good reasons for this, but when you're in Friday rush hour traffic none seem good enough. Thank goodness I only go on scheduled visits every two weeks. No allowance was made for remote operations (X-windows) at purchase and with the amazing amount of priming necessary to restart the cash pump, it's not an option right now. At least, we finally got a thinnet line into the back of the warehouse now so I can Telnet in and see how the experiment queue is progressing.

Purportedly, our dedicated building will be ready in November '94 and the 600 will move down here then. I just hope it doesn't get delayed and push us further back in Varian's queue for our 750 Unity+ installation. The moral of this story is buy the house before they deliver the new furniture.

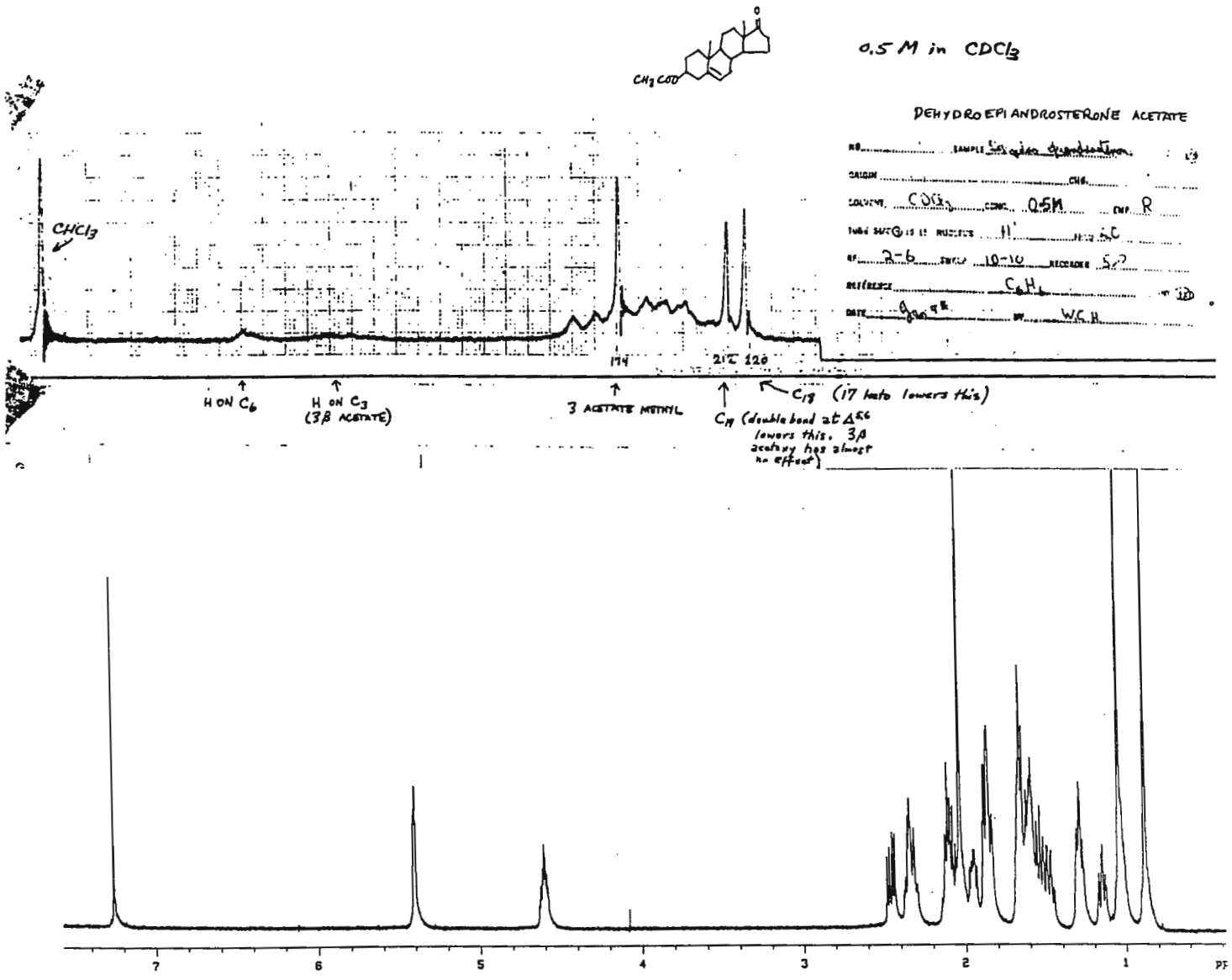
The now/then spectra shown are for a steroid (Dehydroepiandrosterone acetate) from Leland Smith's vault. The spectrum on the top is from his files (run date Jan. 1959; 40 cps - no MHz then) and the one on the bottom is our virgin data off the 600. There's no substitute for spectral dispersion. Just say "no" to magnetic degeneracy.

Yours in the double bond,

Ed Ezell

EE/gd

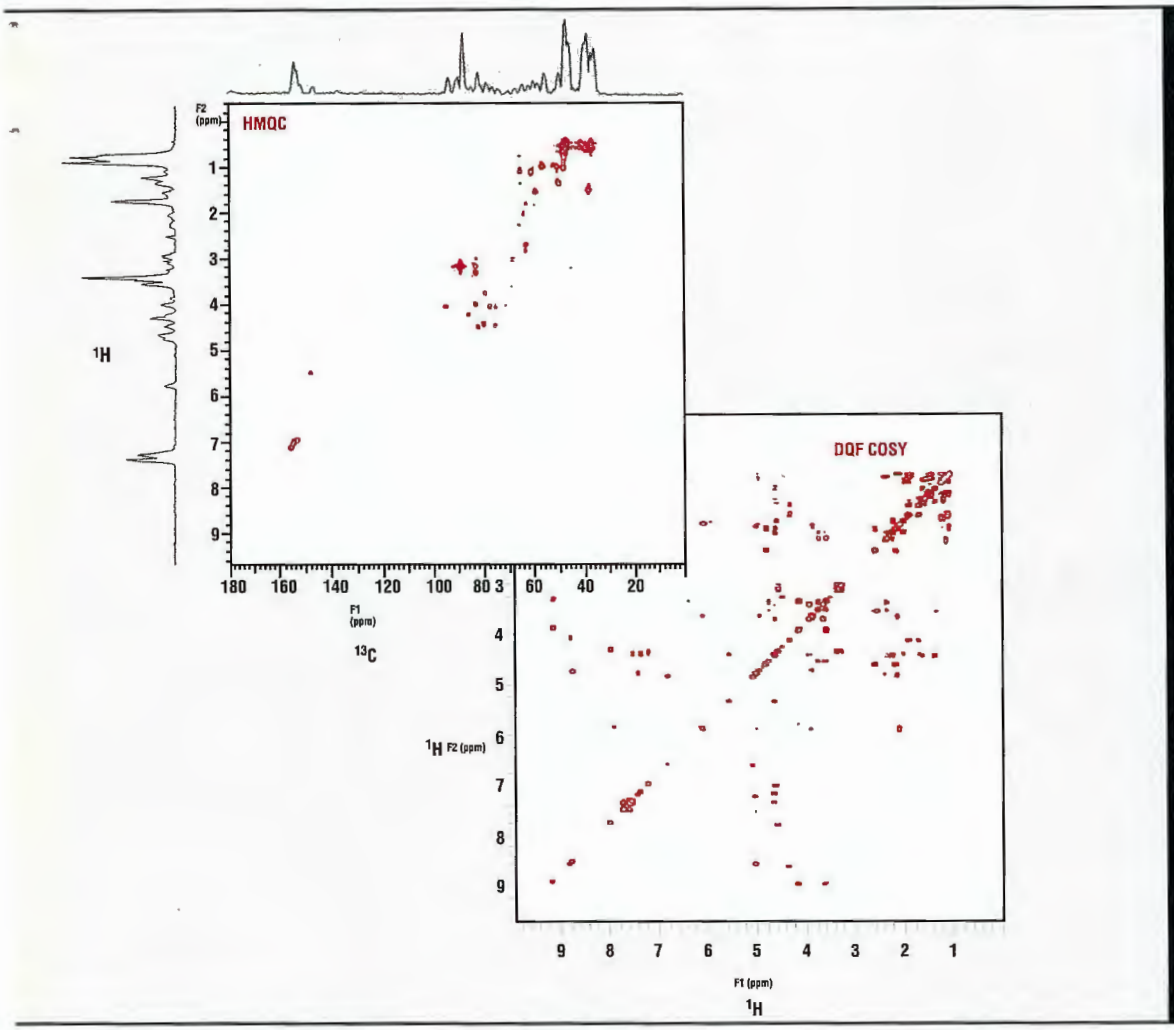
P.S. Leland Smith sends his regards, and please credit this to his account.



TOP: 40 cps File spectrum
circa 1959

BOTTOM: New improved 600 MHz
circa 1994

High-performance Pulsed Field Gradients



a) HMQC spectrum of peptide in DMSO-d_6, 2 transients per increment.

b) DQF COSY spectrum of peptide in DMSO-d_6, 1 transient per increment.

Both spectra were acquired using a UNITYplus-400 spectrometer, an Indirect-nmr Pulsed Field Gradient probe, and the Performa I Pulsed Field Gradient module.

Introducing Performa I Pulsed Field Gradients

ISO 9001 REGISTERED

Now everyone can expand their experimental capability to include pulsed field gradients with the economical Performa I PFG module.

This new addition to Varian's PFG product line provides exceptional performance at one third the price of most pulsed field gradient modules on the market.

Combined with Varian's high-performance pulsed field gradient probe, Performa I delivers enhanced sample throughput by eliminating phase cycling in experiments such as COSY. It also offers superior coherence pathway selection for indirect detection experiments including HMQC and HMBC.

This remarkable product now joins the family of Performa high-performance PFG modules, all of which are recognized for ultra-stable, reproducible, and linear gradient pulses with the fastest recovery times.

Varian Associates 3120 Hansen Way, Bldg. 4, Palo Alto, CA 94304-1030, U.S.A. Tel: 1-800-356-4437 • **Varian International AG** Kollerstrasse 38, CH-6303, Zug, Switzerland Tel: (42) 44 88 44 • **Varian GmbH** Alsfelderstrasse 6, D-6100 Darmstadt, Germany Tel: (0 61 51) 70 30 • **Varian Instruments Ltd.** 3rd Matsuda Bldg., 2-2-6 Ohkubo-Shinjuku, Tokyo, Japan Tel: (3) 3204-1211

varian

Probes

- Excellent specifications for uncompromised high-resolution liquids performance
- High rf homogeneity
- Fast gradient recovery
- Compatibility with all Performa pulsed field gradient products

Performa Pulsed Field Gradients

- Ultra-stable, low-noise gradient amplifiers for uncompromised stability and gradient pulse recovery
- High-performance transconductance amplifier technology for reproducible and linear gradient pulses
- True constant-current, transconductance amplifier technology eliminates the need for amplifier tuning or matching
- Choice of Performa modules for optimal pulsed field gradient performance in any application

Call your sales representative. Australia (3) 543 8022. Austria (1) 69 55 450. Belgium (2) 721 4850. Brazil (11) 829 5444. Canada (416) 457 4130. Denmark (42) 84 6166. France (1) 69 86 38 38. Germany (6151) 70 30. Italy (2) 753 1651. Japan (3) 3204 2111. Korea (2) 561 1626. Mexico (5) 533 5985. Netherlands (3403) 50909. Norway (9) 86 74 70. Spain (01) 430 0414. Sweden (8) 82 00 30. Switzerland (42) 44 88 44. UK (932) 24 37 41. US 800-356-4437. Other International (415)424-5424.

MAG-8130/624

varian

Schering-Plough
Research Institute

2015 Galloping Hill Road
Kenilworth, New Jersey 07033-0539
Telephone (908) 298-4000
Telex 6853298 SP KEN

August 18, 1994
(received 9/16/94)

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

Calibration of the Shifted Effects of Selective Pulses

Dear Barry:

Selective and shifted pulses are extensively used for selective decoupling or selective excitation in triple resonance experiments. The quality of these pulses is essential for the success of these experiments. For example, in an optimized refocused HNCA experiment (*J. Biomol. NMR*, 2, 195-202, 1992), a selective laminar pulse is shifted to excite the Cα carbons, while the selective decoupling is applied on the carbonyl resonances. A computer program called Pulsetool in the Varian software can be used to simulate the selective pulses based on the Bloch equations. However, we find it desirable to test the shifted effects experimentally on the actual NMR instrument. We have used a very simple method to calibrate the pulse width (pwx) of the selective pulses at a decoupler power level (pwxlvl) and to test the shifted effect. This method would also benefit those who do not have access to the Pulsetool program.

The pulse sequence we used for this purpose is similar to that for calibration of decoupler pulse widths in reverse detected experiments: 90(^{1}H) -delay($1/2J_{CH}$) - pwx(^{13}C) - Acq, where pwx is the selective pulse from a decoupler. The decoupler offset (dof) is changed stepwise at a certain pwxlvl. With a ^{13}C-labeled methanol sample only one scan is needed for each experiment and the entire experiment takes only a few minutes. The following example is used for illustration. Figure 1 shows the proton spectra of the methanol as a function of dof taken in 2 kHz steps for a selective pulse of 54 μs. A null intensity is detected at on-resonance (dof=0), indicating a 90° pulse is applied at this frequency. Maximum intensity is observed on both sides at dof= ±18519 Hz where zero power is expected in the excitation profile for a 54 μs pulse. The spectra also display the sidebands of the pulse. Figure 2 depicts the similar spectra for a selective pulse of 54 μs but shifted upfield by 18519 Hz. A maximum intensity is seen at dof=0, indicating a null in the excitation profile. A minimum intensity is presented at dof=18519 Hz (exactly where we want the pulse to be shifted), resulting from the maximum excitation by the selective pulse. The data presented here demonstrates that this simple experiment may be used to determine the excitation profile of selective pulses. An additional advantage is that the selective pulse is generated and calibrated on the actual decoupler being used in the triple resonance experiment.

Please credit this contribution to Andy Evans' account.

Best regards.

Yu-Sen Wang

Barbara Lyons

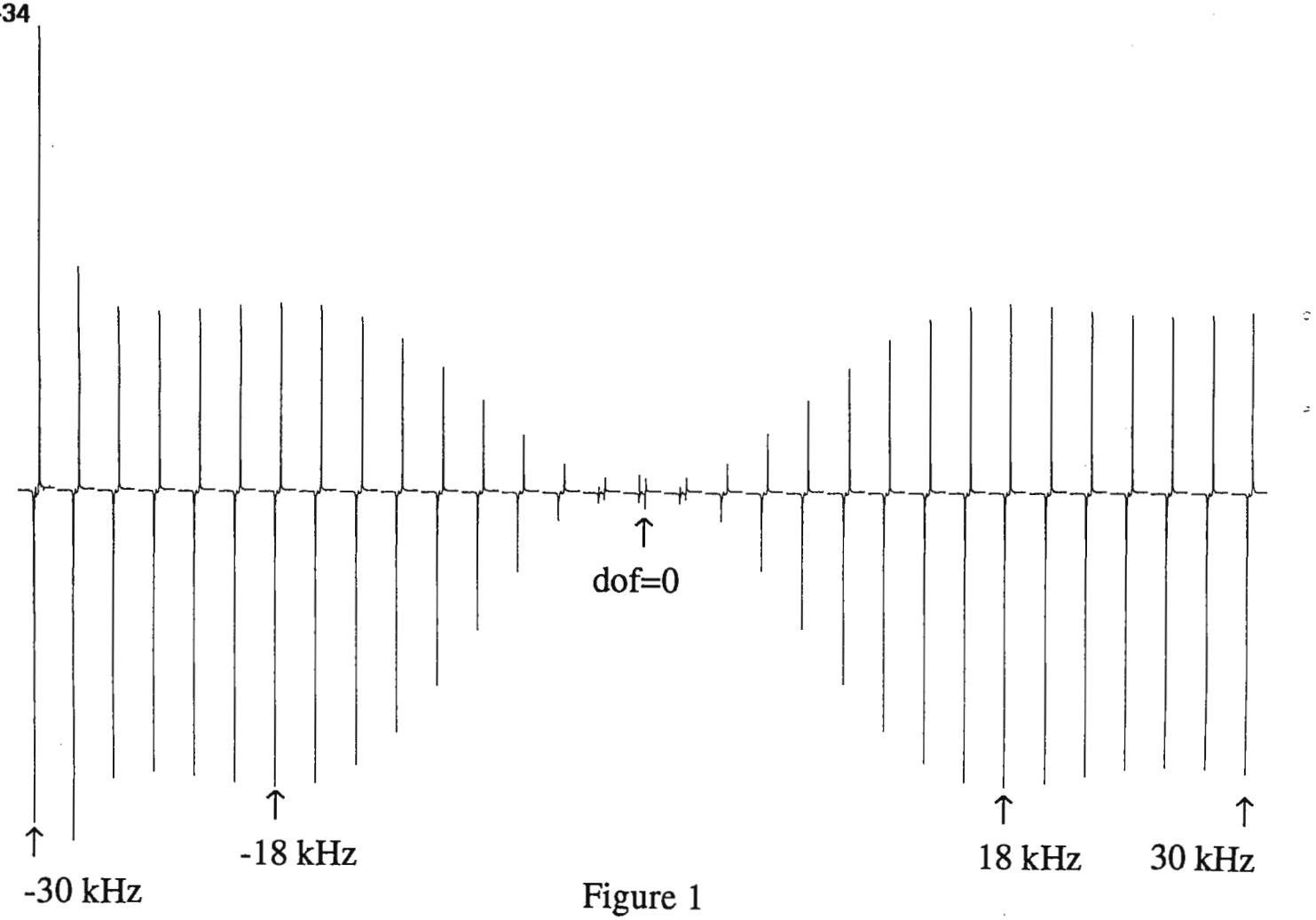


Figure 1

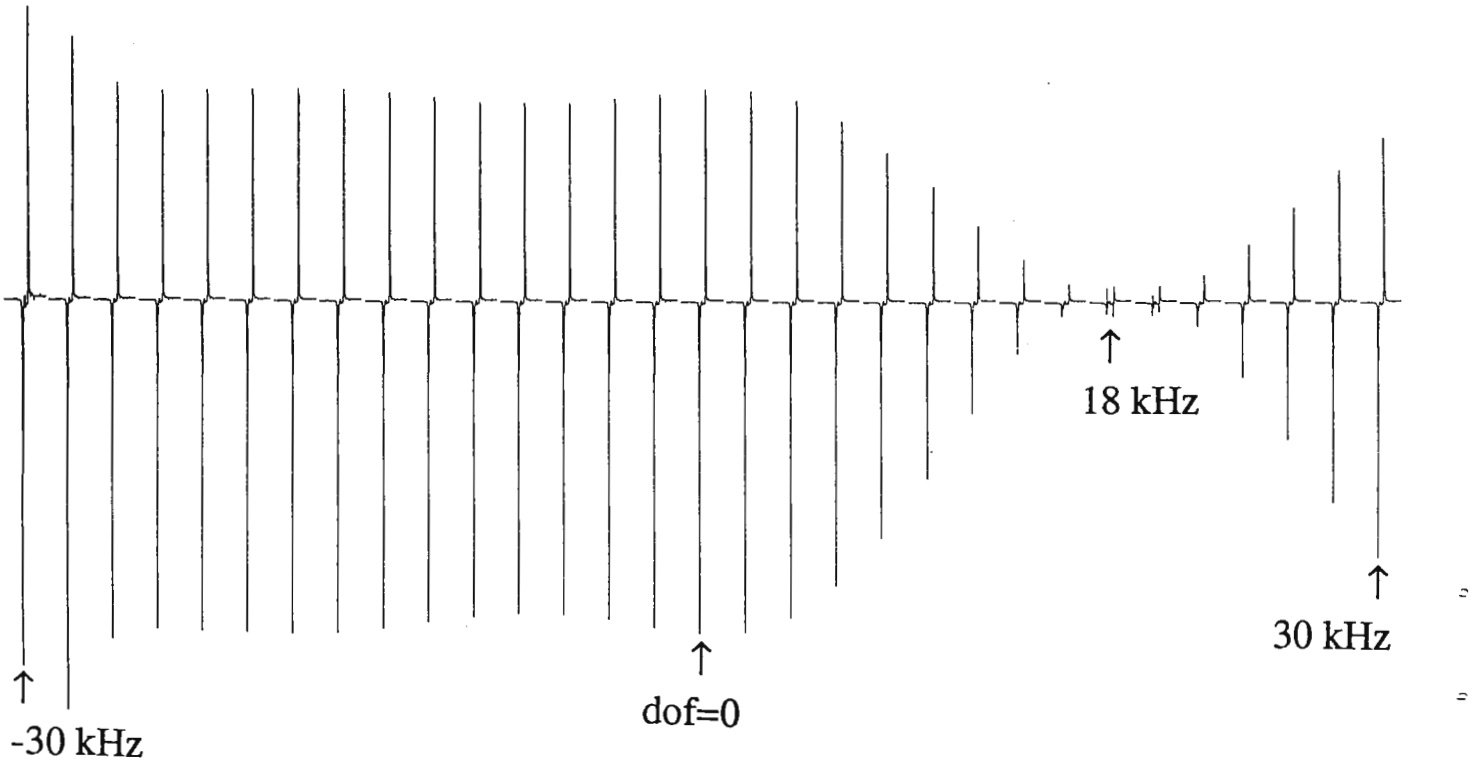


Figure 2

ROCHE RESEARCH CENTRE

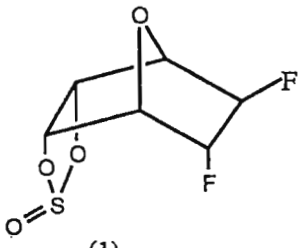
Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
California 94303
U.S.A.

19 September 1994
(received 9/23/94)

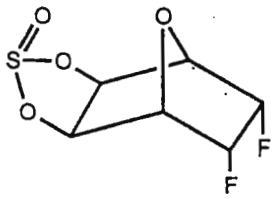
Dear Barry,

A Novel Bis-Fluoro Derivative from *chiro*-Inositol

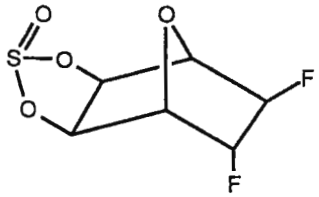
Through a collaboration with Paul Coe and Peter Maunder in Birmingham University we examined the product of the reaction of *chiro*-inositol with SF_4/HF. The suggested product was the bicyclo compound (1), based on the analogous reaction product from *myo*-inositol which has the structure (2).[1] Detailed nmr analyses of the *chiro*-inositol product (COSY, NOE difference experiments, some selective decoupling and complete analysis of the largely first-order ^{1}H, ^{13}C and ^{19}F spectra with the aid of PANIC) indicated the probable structure (3), confirmed by x-ray crystallography.



(1)



(2)



(3)

At the highest resolution on our Bruker DRX-400 spectrometer, the ^{1}H and ^{19}F spectra showed considerable multiplicity (a splitting headache!) as shown in Fig 1. Twenty one couplings were identified despite the fact that the vicinal couplings to the bridge protons from the endo protons were zero. Assignment was further complicated by the tendency for the long-range J's to have closely similar values. Signs of the latter couplings were not obtained. Full data are given in Table 1.

Finally, the ^{13}C - ^{19}F couplings were of interest since those over three bonds provide a nice test of a Karplus type $\cos^2 \Ø$ relationship. The four values in (3) vary from 2.73 Hz to 11.79 Hz in accord with this relationship.

I hope this contribution staves off expulsion for a while.

Yours sincerely,

W A Thomas I W A Whitcombe H S Simmonite

1. P L Coe, L D Proctor, J A Martin and W A Thomas, J. Fluorine Chem. 1992, 58, 87-92.

Roche Products Limited
40 Broadwater Road
Welwyn Garden City
Hertfordshire AL7 3AY
Telephone (0707) 366000
Telefax (0707) 373504
Telex 262098 ROCHEW

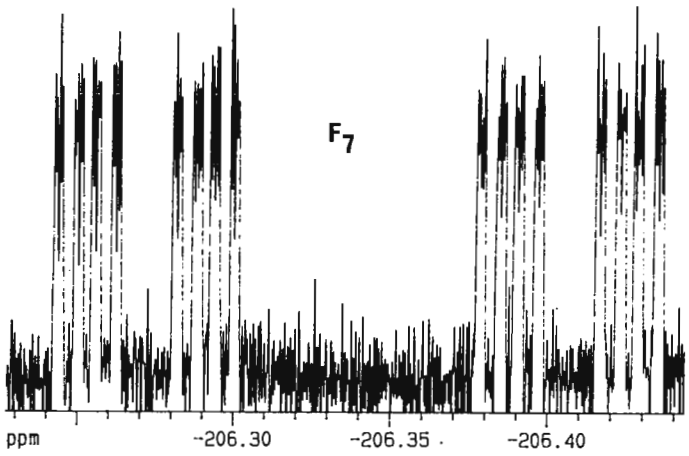
Registered Office
40 Broadwater Road
Welwyn Garden City
Hertfordshire AL7 3AY
Registered Number
100674 London

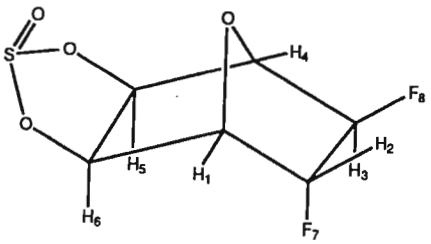
Table - Couplings and Shifts for CD_3CN Solution

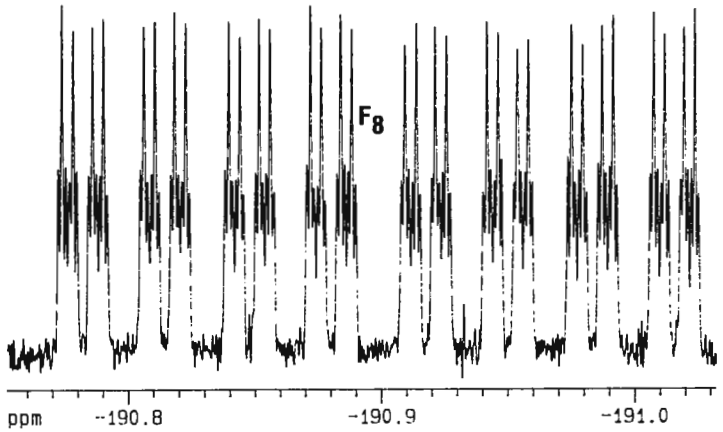
Nucleus	1	2	3	4	5	6	7	8
δ (CH_3CN)	4.85	5.12	4.90	4.74	5.12	5.26	-206.3	-190.9

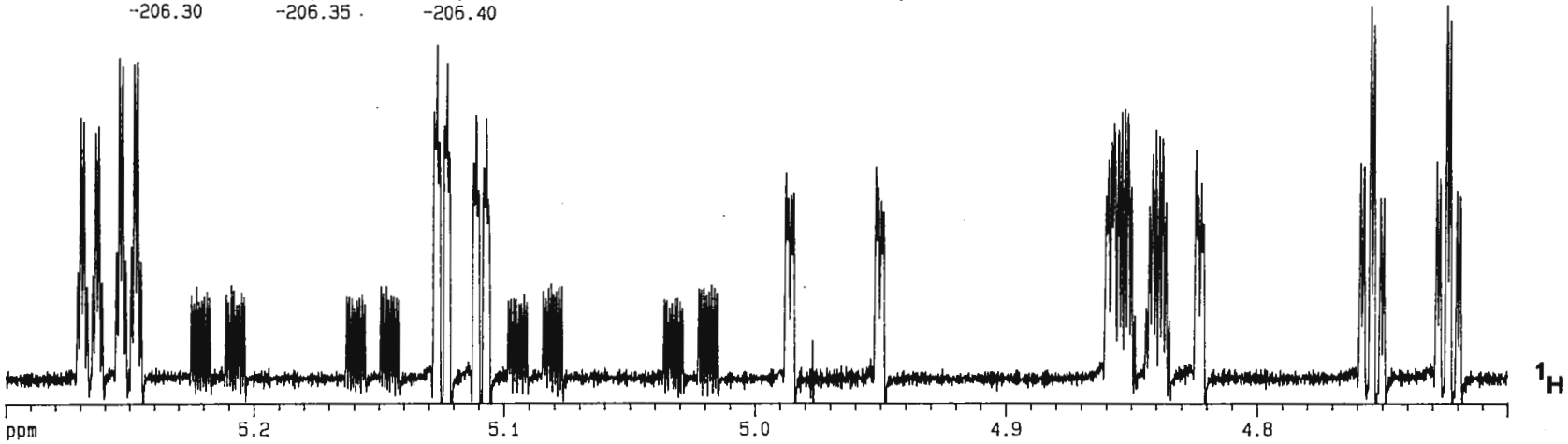
Nuclei	12	13	14	15	16	17	18	23	24	25	26	27	28	34
J	5.52	0.40	1.54	0.44	0.00	0.64	0.52	0.88	1.68	0.00	0.37	50.68	24.72	0.00

35	36	37	38	45	46	47	48	56	57	58	67	68	78
0.00	0.00	14.42	50.96	0.00	0.48	0.00	12.17	6.30	0.28	1.62	2.46	0.46	-4.50









PROGRESS IN DIGITAL FILTERING

ON-THE-FLY IN-LINE DIGITAL FILTERING ON THE AVANCE™

All spectrometers in the *AVANCE* continuum utilize real time oversampling and digital filtering for sampling rates of 400 kHz or less. Dedicated very fast digital signal processors (DSPs) are placed in-line on the Receiver Control Unit (RCU), which is located in the *AVANCE* VME acquisition bus, and receives the digitized signal from the ADC. The DSPs on the RCU are extremely fast and can execute up to 100 million mathematical operations per second (not just 100 MIPS). In this manner oversampling, digital filtering, and on-the-fly decimation can be utilized for all high resolution and CP/MAS acquisitions on the *AVANCE* series; all the benefits of oversampling and digital filtering, such as improved dynamic range, steep filter cutoffs, flat baselines, improved signal-to-noise, etc., are provided at all times, without the need for increased data storage or additional operator-intensive manipulations.

Bruker has invested heavily into fundamental digital filtering research, and has developed a unique and novel window function with extremely steep cutoffs. Figure 1 shows various window functions that have been described in the literature. As can be seen, the proprietary *AVANCE* window function provides much steeper cutoffs, and thus, suppression of unwanted signals, than traditional window functions such as the Blackman window function. This is essential for optimal data quality and absence of artifacts.

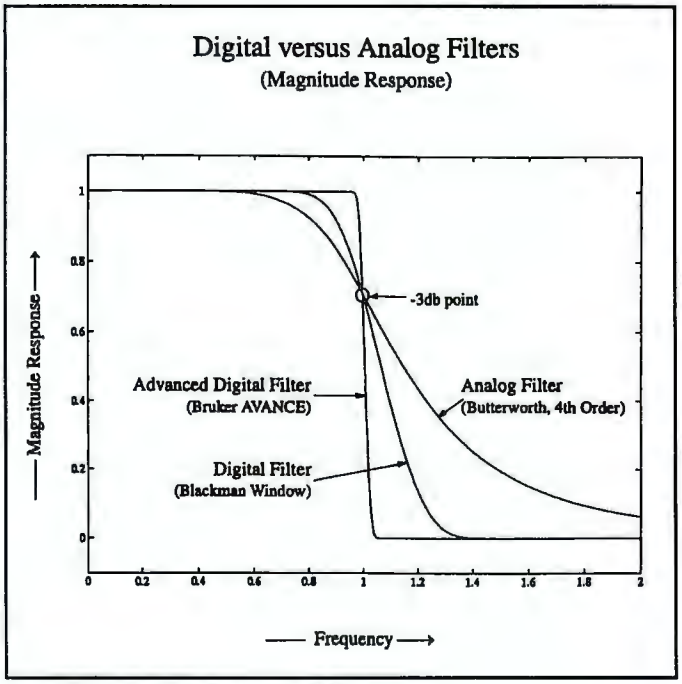
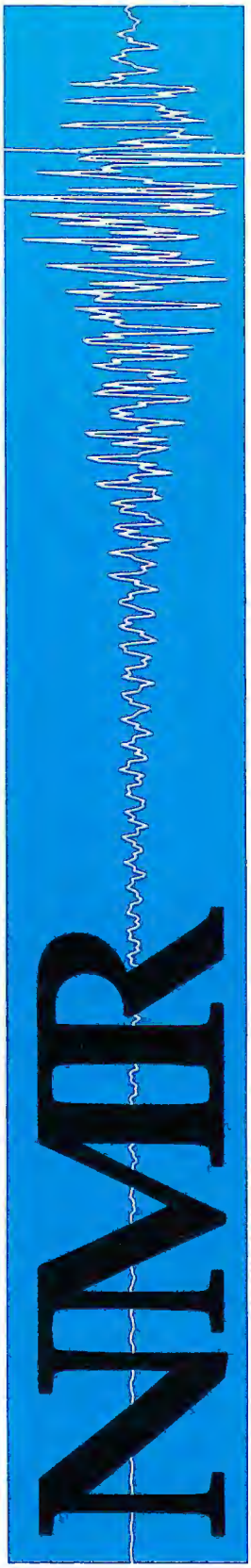


Figure 1: window function comparison



BRUKER

NMR

DIGITAL NOTCH FILTER

In response to customer demand, Bruker now provides a digital notch filter on the *AVANCE* series. Figure 2 shows the spectrum of lysozyme A) with and B) without the digital notch filter. The digital notch filter applied in the time domain can be utilized for the suppression of unwanted signals, for instance water, or other high intensity peaks.

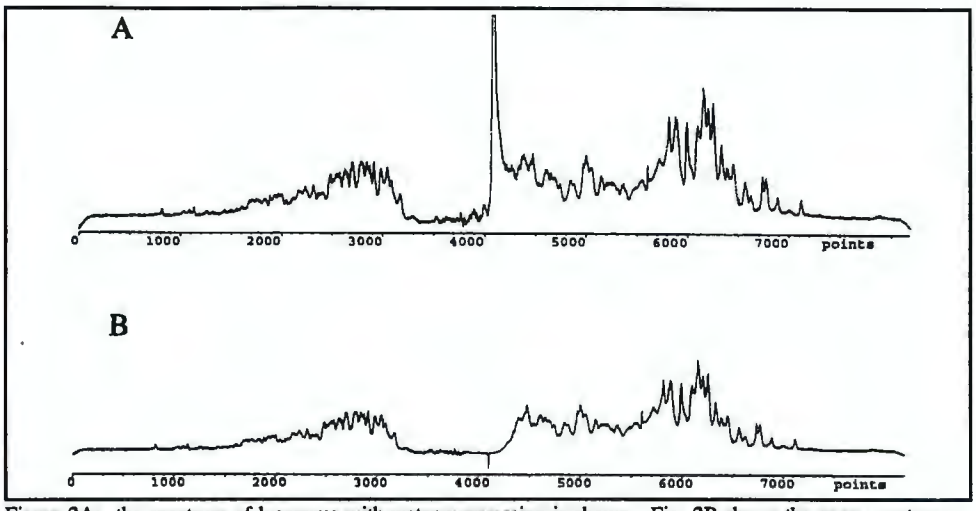


Figure 2A: the spectrum of lysozyme with water suppression is shown. Fig. 2B shows the same spectrum, after digital notch filter (200 Hz band stop), centered on the water resonance, was applied.

OFF-LINE DIGITAL FILTER SOFTWARE FOR AM, AMX AND AVANCE CUSTOMERS

Many customers have inquired about the ability to utilize digital filtering off-line, on spectrometers not yet equipped with on-line real-time digital filters, or simply to become familiar with the applications and benefits of digital filtering. Bruker suggests to utilize the Signal Processing Toolbox available within the program MATLAB (from The MathWorks, Inc. in Natick, MA, phone: (508)653-1415). The MATLAB Signal Processing Toolbox provides an easy user interface for creating various digital filters, including finite impulse response (FIR) and infinite impulse response (IIR) digital filters. The effect of the number of coefficients (tabs) on the quality of the digital filter, and on computational times can be explored. Moreover, various published window functions are available.

Bruker customers can transfer their AM or AMX data to an off-line Silicon Graphics workstation, or utilize the SGI host computer of an *AVANCE* spectrometer. MATLAB also runs on Macintosh and PC computers and can be used in conjunction with Bruker's popular WIN-NMR™ software packages on these platforms. Data transfer from WIN-NMR or UXNMR to MATLAB is easy and can be done in binary or ASCII form. After the application of digital filters, the results can easily be transferred back to UXNMR or WIN-NMR for Fourier transformation, further processing and plotting.

THE UNIVERSITY OF MICHIGAN
BIOPHYSICS RESEARCH DIVISION
930 N. UNIVERSITY
ANN ARBOR, MICHIGAN 48109-1055

September 21, 1994
(received 9/23/94)

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

Cross-polarization-driven HCCH of a protein in H_2O using pulsed field gradients

Dear Dr. Shapiro:

Solvent (water) suppression techniques using pulsed-field gradients in multi-nuclear NMR have mostly exploited either a heteronuclear gradient echo selection or a fast homospoil of unwanted magnetization during the zz- magnetization state in an Inept coherence transfer step.

Relatively little attention has gone out to manipulate the spin system such that the magnetization of interest is in z, while the solvent is kept in the xy plane and exploiting this situation for pathway selection (and thus solvent suppression) using gradients. The cross-polarization-driven HCCH experiment provides the opportunity to arrange this situation (Fig 1). The ^{13}C magnetization is placed in the z-direction after the evolution time t_2. At this time, the solvent resonance will be in the xy plane irrespective of the phase of the first excitation pulse due to the isotropic nature (homonuclear) of the multi-pulse sequence used for cross polarization. Now the solvent can be suppressed with great efficiency by a pulsed field gradient, while leaving the ^{13}C magnetization of interest unaffected. For longer t_1 and t_2 times, some solvent magnetization will relax back to z; this component is rotated into the xy plane by a 90^o proton pulse and dephased by the second gradient.

Figure 2 shows a projection on the ^1H-^1H plane of this 3D CP-HCCH experiment recorded with a 18 kDa protein in 95% H_2O, 25 ^oC. Note that virtually continuous Hα cross peak density is obtained crossing the position of the H_2O resonance (we also have some quadrature images in this very dataset). A complete account of this work will be submitted for publication soon.

Sincerely,

Hong Wang

Erik Zuiderweg

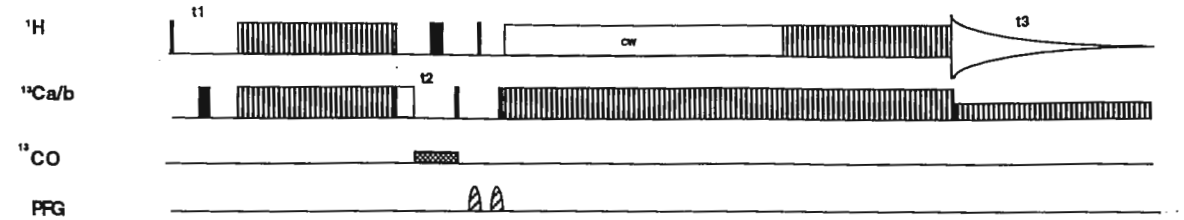


Fig. 1: Pulse scheme for the gradient-enhanced, CP-driven HCCH discussed in the text.

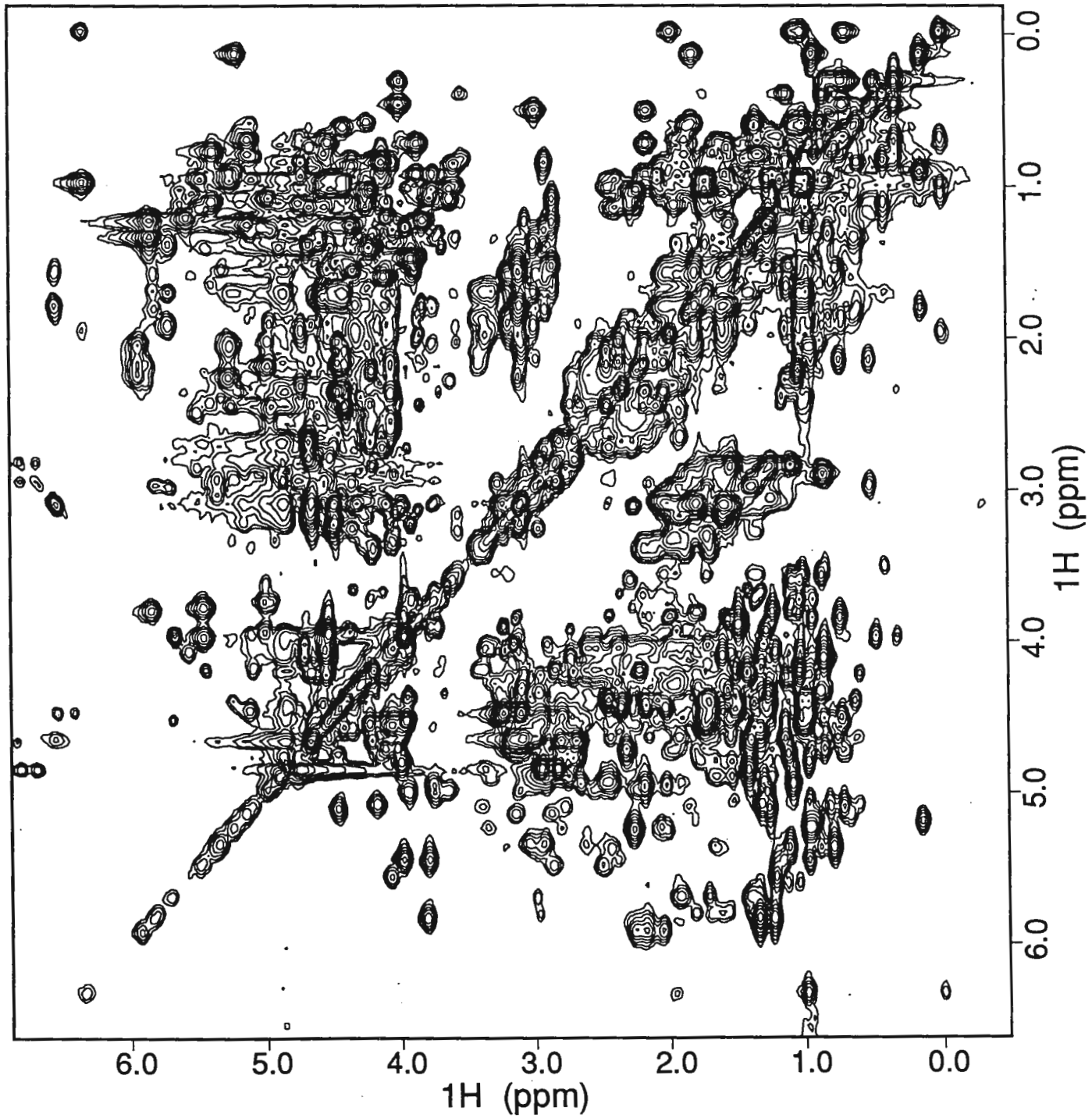


Fig. 2: Projection of the 3D gradient-enhanced CP-HCCH spectrum (a 18 kDa protein in 95% H_2O, 25 °C).

Biomolecular NMR Laboratory
Bldg. 34, Room 211
Hoffmann-La Roche Inc.
340 Kingsland Street
Nutley, New Jersey 07110-1199
Direct Dial (201) 235-7663

Hoffmann-La Roche

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

September 16, 1994
(received 9/19/94)

Shimming Characteristics of 10mm Samples in Water

Advanced heteronuclear multidimensional NMR methods have enabled detailed structural studies of larger proteins. Higher molecular weight proteins often suffer from low solubility or increased aggregation at millimolar concentrations relative to peptides and smaller proteins. It is therefore becoming important to evaluate and establish technologies which allow application of triple- and quadruple- resonance experiments to sub-millimolar samples. When planning sample preparation, it is important to know precisely how much pure, isotopically-labeled protein must be obtained from the fermentation broth. For samples of limited solubility, it is equivalent to ask the question: how much volume is required for the NMR sample? Here we describe preliminary investigations with a Varian 10mm triple-resonance ^{1}H-^{13}C-^{15}N probe related to ease of shimming and water suppression performance for samples of different volumes. A stock solution of 1mM Phenylalanine, 10mM sodium acetate, 10mM 3-trimethylsilyl-propionate (TSP), and 90:10::H_2O:D_2O has been used to compare water suppression and shimming characteristics for 3.00, 2.00, 1.50, and 1.33 ml samples. Figure 1 illustrates the specific configurations for each sample with respect to sample volume, depth, and Teflon vortex plugs which were used as crude, magnetic-susceptibility-matching plugs. Figure 2 shows expansions of 1D ^{1}H NMR spectra near the residual water frequency for each sample. The small upfield resonances come from the 1mM Phe H^{α} (4.0 ppm) and H^{β} (3.3 and 3.1 ppm) protons. These spectra were collected on our UNITY*plus* 600, without spinning, using four transients, with presaturation of water. In each case the time spent shimming was limited to approximately 10 to 15 minutes. Therefore the results presented here represent those which are "easily attainable" rather than "optimal" values (Varian triple-resonance 10mm probes have residual H_2O linewidths as low as 90 Hz in the 1mM Phe sample under optimal conditions). Table 1 contains measurements made from these presat spectra.

Examination of the spectra of Figure 2, and the first two columns of Table 1, demonstrates the general trend toward reduced water suppression performance as the sample volume is decreased. In contrast, the signal-to-noise (S/N) of the 10mM TSP resonance (not shown) shows little or no correlation with sample volume. Assuming the active volumes are filled in each case one would expect that the ideal S/N of TSP would be the same for each case. Therefore the variation in TSP S/N might be interpreted as a reflection of how difficult it is to obtain good shims for each respective sample configuration. The last column of Table 1 illustrates the calculated S/N expected under the various sample configurations assuming that the fixed amount of solute in the 3.00 ml sample had been concentrated into the lesser volumes. The improved S/N and reduced costs associated with limiting the sample volume necessary for heteronuclear NMR studies on solubility-limited proteins is a motivating factor in

Figure 1.

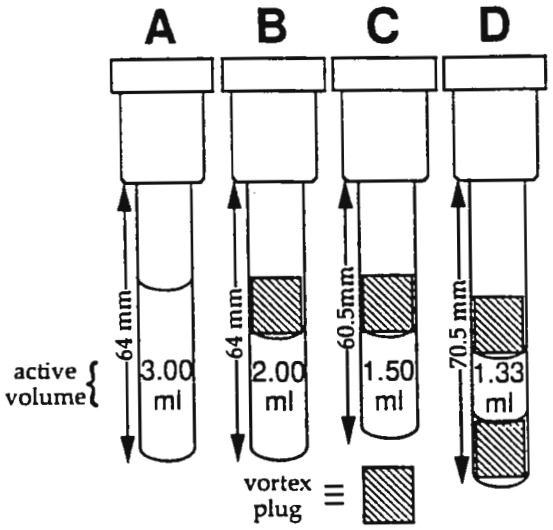


Figure 2.

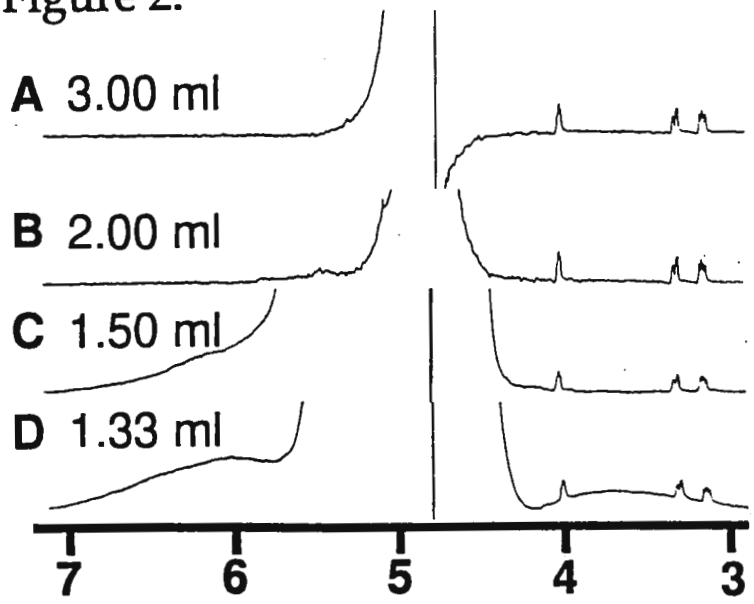


Table 1.

Volume	Residual H_2O linewidth	Measured S/N of TSP (constant concentration)	Calculated S/N of TSP (constant amount of solute)
3.00 ml	250 Hz	2500	2500
2.00 ml	370 Hz	2800	4200
1.50 ml	1200 Hz	1750	3500
1.33 ml	1530 Hz	2200	4960

the development of improved large-volume triple-resonance probe and NMR tube technologies such as: Z-gradient triple-resonance 10mm probes, matched-susceptibility 10mm NMR tubes, and matched-susceptibility 10mm plugs. These developments could allow the observation of high-sensitivity NMR signals by efficiently filling the active volume with the smallest sample possible while eliminating the water suppression problems associated with having the susceptibility junctions in close proximity to the edges of the probe coil.

Please credit this contribution to the account of David C. Fry.

Sincerely,

Steven Donald Emerson
Senior Scientist, Biomolecular NMR
Physical Chemistry Department

David C. Fry
Director, Biomolecular NMR
Physical Chemistry Department

Upgrade 300 - 500 MHz Spectrometers for Optimal Non-spinning Performance

Magnet Mapping

Field Analysis

Field Shimming

Anti-vibration System

MATRIXSHIM™

The performance of the magnet systems used with all NMR spectrometers up to 750 MHz is optimized by identifying the ideal shim center, fully characterizing the inhomogeneities, as well as appropriately adjusting the room temperature and/or the superconducting shims. The above process coupled with an adequate anti-vibration system, a MATRIXSHIM system and modern probes, provides the spectroscopist with the maximum achievable high resolution NMR performance.

FEATURES	BENEFITS
❒ Optimize shim corrections	❒ Optimum line shape and sensitivity
❒ Dampen environmental vibrations	❒ Minimum spectral artifacts
❒ Upgrade to MATRIXSHIM	❒ Non-spinnning lineshape approaches spinning lineshape
❒ Higher order shim capability	❒ Optimal lineshape for small volume, 8 or 10 mm samples
❒ RS-232 remote control capability	❒ Optional console linked control
❒ Available for 51, 54 and 89 mm bore magnets	❒ Available for most commercial magnet systems

RESONANCE RESEARCH

MAGNET MANAGEMENT OPTIMIZES MAGNET PERFORMANCE

The Resonance Research (RRI) approach to optimizing magnet performance includes four discrete components: an automated magnetic field mapping system, a precision current source, a shim system and an anti-vibration system.

AUTOMATED BROAD BAND MAGNETIC FIELD MAPPING

The Model FMU-800 mapping system is a computer-controlled unit produced by RRI which is used for the analysis of inhomogeneities and shimming of NMR magnets.

The heart of the system is a helical-path electromechanical probe with a sample volume of less than 1 mm^3.

The mapping system is capable of analyzing axial gradients from z0 to z10 and radial gradients from x/y to c8/s8 with magnets from 4.7 to 18 tesla. A full mapping and analysis is complete in approximately 30 minutes.

FIELD SHIMMING

RRI produces MATRIXSHIM™ for NMR magnets. This series includes a wide variety of shims from 20 to 39 gradients for 51, 54 or 89 mm bore magnets. A typical shim system, the MHU 423/51, is based on an array of coils and can control up to 8th order axial and 6th order radial terms without the loss of nominal bore dimensions.

Installation of MATRIXSHIM or serial shim systems can be optimized in less than 24 hours.

If the upgrade requires, the super-conducting shim system can be optimized in less than 6 hours.

PRECISION CURRENT SOURCES

RRI produces the MATRIXPOWER™ series of precision power supplies for use with all commercial high performance NMR shim systems.

An integral component of MATRIXSHIM, the precision current sources are available to upgrade older serial shim systems for increased power and to eliminate spectral artifacts. The precision current sources provide exceptional drift characteristics; as an example, the thermal drift is less than 15 ppm per ^0C and noise is less than 10 ppm from 10 Hz to 50 kHz.

VIBRATION-ISOLATION SYSTEM

The TMC high performance, pneumatic vibration isolation legs are available from RRI for magnets from 300 to 750 MHz.

TOTAL MAGNET MANAGEMENT

RRI provides the spectroscopist with an automated, iterative three-step-process of mapping/analysis and shimming that ensures an optimum homogeneous field.

The MATRIXSHIM system offers non-spinning lineshape approaching spinning lineshape for many sample volumes.

The TMC vibration-isolation system minimizes spectral artifacts.

All specifications are subject to change without notice as part of our continuing improvement program

For more information contact:

Resonance Research
778 Praderia Circle
Fremont, CA 94539
Tel (510) 651-6768
Fax (510) 651-8085

Resonance Research
43 Manning Road
Billerica, MA 01821
Tel (508) 671-0811
Fax (508) 663-4063

RESONANCE RESEARCH

Lehigh University

Department of Chemistry
telephone (215) 758-3470
fax (215) 758-3461

Seeley G. Mudd Building
Lehigh University
6 East Packer Avenue
Bethlehem, PA 18015-3172

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

September 22, 1994
(received 9/23/94)

CHARACTERIZATION OF AQUEOUS POLY(VINYL ALCOHOL) GELS BY NMR

Dear Dr. Shapiro:

We are using magnetization transfer experiments to evaluate the interaction of water with poly (vinyl alcohol) as an initial step toward defining gels in general by NMR. We will be evaluating magnetization transfer data by a curve-fitting method originally described by Eads (*Carbohydrate Polymers* **20** 1993, 51-60). This method will allow us to analyze cross-relaxation curves as a sum of a Gaussian component, characteristic of the rigid component of the gel,and a Lorentzian component,characteristic of the liquid-like component in the gel. We plan to correlate the area of the Gaussian component to the crystallinity of the gel and corroborate it with the percent crystallinity found by DSC analysis.

Thus far, we have evaluated magnetization transfer as a function of polymer concentration (Figure 1). The total area and the area of the Gaussian component should increase linearly with an increase in concentration if the only contributing factor to the magnetization transfer is simply the increase in polymer concentration. This is not the case; at concentrations above 40% PVA the curve deviates from linearity. This may be due to an increase in crystallinity or the formation of a supermolecular structure within the gel. We have also evaluated magnetization transfer as a function of storage time and temperature. The total area and the Gaussian component increases as a function of storage time. The solid-like component also increases with decreasing storage temperature as a function of time.

We have evaluated magnetization transfer as a function of aging at 23 °C on a series of PVA gels with the same M_n and the same M_w but with different degrees of hydrolysis (Figure 2). The total area and the Gaussian component of these samples increases with time and with increasing degree of hydrolysis. The magnetization transfer experiment can discriminate PVA samples based in their degree of hydrolysis.

Subsequent experiments will involve evaluating magnetization transfer as a function of PVA gel dissolution time, dissolution temperature, storage time, storage temperature and thermal history. We plan to measure the T_1 and T_2 relaxation times to quantify the amount of polymer bound water as a function of the listed conditions. Our overlying goal is to use this PVA gel system as a means of establishing the NMR measurable parameters associated with the characterization of gels and the dynamic behavior that governs their physical and mechanical properties.

Sincerely,

Lori Ellen Stephans Natalie Foster William R. Anderson, Jr

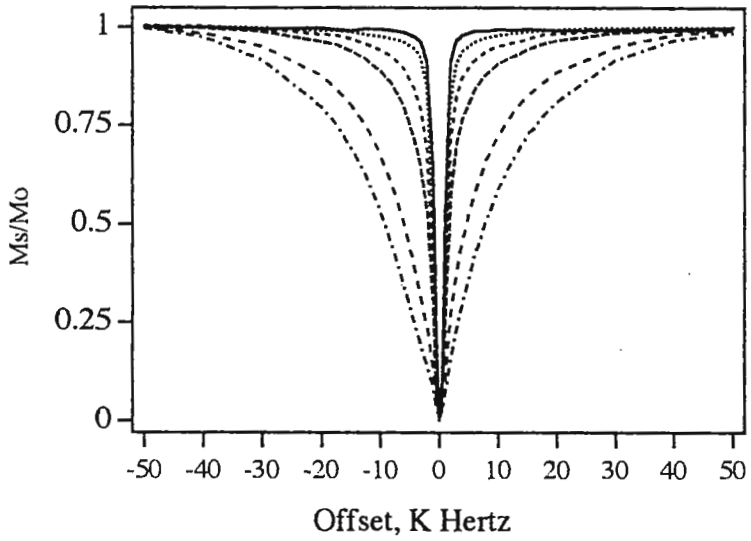


Figure 1 . Offset frequency dependence on the water magnetization as a function of polymer concentration via selective saturation . The PVA used in this analysis was 80% hydrolyzed and had a M_n of 10,000. (——) 10%, (·····) 20%, (·-·-·) 30%, (·---·) 40%, (- -) 50% and (·---·) 60% PVA/water by weight.

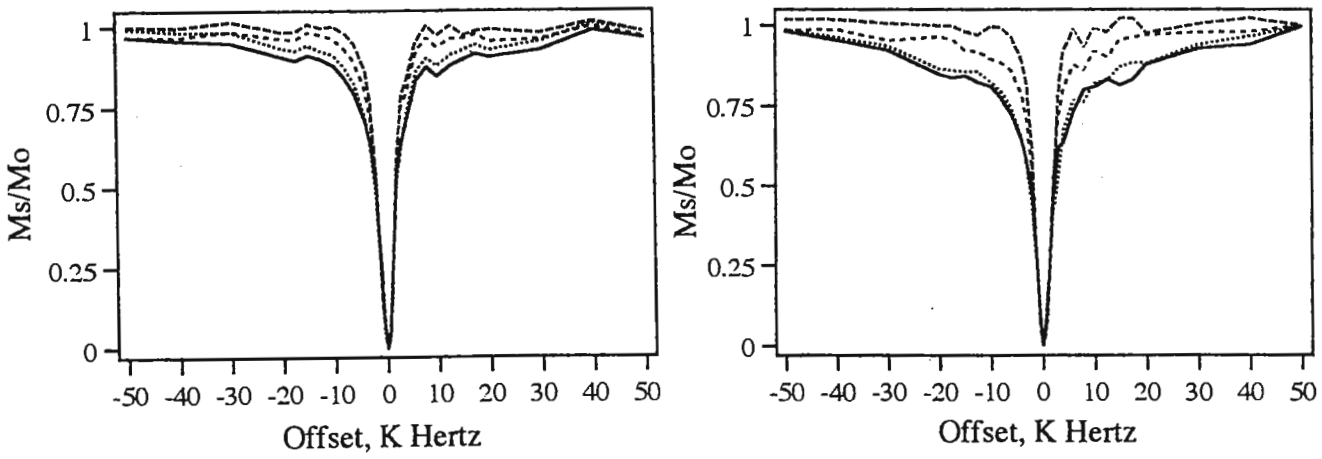


Figure 2. Offset frequency dependence on the water magnetization as a function of the degree of hydrolysis of PVA. The samples are 20% by weight PVA/ water aged at 23 °C for 1 day (left) and for 14 days (right). The samples analyzed had the following degrees of hydrolysis: (——) 99.3+, (·····) 98.0-98.8, (----) 95.5-96.5, and (·---·) 87.0-89.0.

ISOTEC INC.

A Matheson® USA Company

Stable Isotopes for Research and Industry

For more than fifteen years, **ISOTEC** continues to be the world's leading commercial producer of enriched stable isotopes and the leading manufacturer of quality stable isotope labelled compounds. **ISOTEC** separate and enriches its own stable isotopes and synthesizes isotopically labelled compounds at its facility. **ISOTEC** produces the highest isotopically enriched and chemically pure labelled compounds. **ISOTEC** is constantly adding new compounds to meet the growing demands of the scientific community.

ISOTEC continues to grow. We have just completed the installation of our fourth ^{13}C and fourth and fifth ^{15}N, ^{17}O and ^{18}O distillation columns. The recent addition of many highly qualified Ph.D. chemists from the former MERCK isotope group, enhances **ISOTEC'S** commitment to continually provide superior quality products. Future plans include the expansion of our custom synthesis laboratories and additional distillation columns. Immediate plans include the addition of several GMP laboratories and several new laboratories for providing more custom synthesis capabilities for our clients.

ISOTEC'S reputation for chemical purity and isotopic enrichment of its stable isotope compounds is unmatched in the industry. Our high purity, deuterated NMR solvents are gaining increasing acceptance by researchers all over the world. Some deuterated NMR solvents with enrichments to 99.999 atom % are exclusively available from **ISOTEC INC.**

ISOTEC'S expanding market share confirms our leadership as the world's largest producer and supplier of stable isotopes.

To receive additional information or quotation, please contact

ISOTEC INC.

3858 Benner Road, Miamisburg, Ohio 45342 U.S.A. • Phone (513) 859-1808
Telex 288278 • Fax (513) 859-4878 • Easy Link 62014510

NEW NMR Solvents Available Exclusively From ISOTEC, INC!

☐ 82-02094-2	**Acetic Acid-d_4 "100%"** 99.96 atom%	10x0.8ml	$63.00
☐ 82-00811-1	**Dimethyl-d_6 Sulfoxide** 99.996 atom% (first batch limited quantity, 99.998)	10x0.3ml 10x0.5ml 10x0.8ml	$100.00 $163.00 $260.00
☐ 82-70041-0	**Deuterium Oxide ULTRA-D** 99.999 atom%!	10x0.8ml 1x10g amp	$65.00 $60.00
☐ 82-00062-1	**Ethyl Alcohol-d_6 "100%"** 99.96 atom% (anhydrous)	10x0.8ml	$190.00
☐ 82-00254-4	**Pyridine-d_5 "100%"** 99.96 atom%	10x0.8ml	$160.00
☐ 82-03021-4	**Tetrahydrofuran-d_8 "100%"** 99.96 atom%	please request size and price	

prices FOB Miamisburg

☞Isotec also offers 0.6ml and 0.3ml sizes for bulk orders of the following NMR solvents:

Acetone-d_6	99.9 atom%	Dimethyl-d_6 Sulfoxide	99.9 atom%
Benzene-d_6	99.6 atom%	Methyl Alcohol-d_4	99.8 atom%

To receive a copy of our new catalog, technical information, price quotations, or to place an order please call:

ISOTEC INC.
A Matheson® USA Company

3858 Benner Road
Miamisburg, Ohio 45342
(800)448-9760 FAX (513)859-4878

NORTHWESTERN UNIVERSITY

Joseph B. Lambert
Clare Hamilton Hall Professor of Chemistry

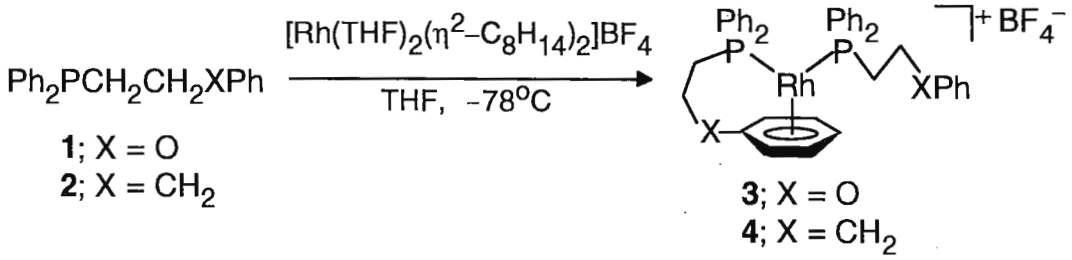
Department of Chemistry
2145 Sheridan Road
Evanston, Illinois 60208-3113
Telephone (708) 491-5437
Internet lambert@casbah.acns.nwu.edu
Facsimile (708) 491-7713

September 15, 1994
(received 9/19/94)

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

Dear Barry:

My colleague Chad Mirkin and his students Elizabeth Singewald and Allison Levy have uncovered an interesting intramolecular interchange of arene and oxygen ligands on rhodium. Molecule **1** when bound to Rh is hemilabile in the sense that it contains the strongly binding and



substitutionally inert phosphine group as well as the weakly binding and substitutionally labile arene and oxygen groups. On reaction of either **1** or its carbon analogue **2** with $[(\eta^2\text{-}C_8H_{14})_2Rh(THF)_2]BF_4$, the illustrated compounds were formed, **3** and **4** respectively. The η^6, piano-stool geometry around Rh was proved in the solid state by X-ray crystallography for both products. Data in CD_2Cl_2 are consistent with similar structures in solution. Thus the characteristic upfield resonances for a bound, η^6 arene are found for **3** at δ 6.75 (ortho to O), 6.88 (meta), and 4.63 (para), as proved by 2D COSY and HETCOR.

The bound arene group in **3** undergoes a slow, intramolecular exchange with the unbound OPh arene group. This process is slow on the NMR time scale in 1D ^1H and ^{31}P spectra but is manifested in the 2D EXSY experiment (Figure 1). The cross peak is clearly evident for exchange between the para protons of bound (δ 4.63) and unbound (δ 7.00) arene. Variable temperature EXSY experiments provided activation parameters of $\Delta G^{\ddagger}$ = 17.7 kcal mol^{-1}, $\Delta H^{\ddagger}$ = 19.6 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = 6.1 cal mol^{-1} K^{-1}. The most likely intermediate is the symmetrical cis-oxygen-coordinated compound **5** illustrated in Figure 2. Such an intermediate not only avoids a coordinatively unsaturated rhodium species but is supported by observations with the carbon analogue **4**. This latter compound under comparable conditions does not undergo the exchange reaction. Lacking the pendant oxygen atom, **4** cannot form the square planar cis-phosphine, cis-ether complex **5**. The exchange reaction of **3**

therefore resembles an intramolecular displacement rather than arene dissociation. Such a ring exchange is unprecedented for $Rh^{I}(PR_3)_2$ but is known for $Cr(CO)_3$ (T. G. Traylor and M. J. Goldberg, *J. Am. Chem. Soc.*, **1987**, *109*, 3968), which, however requires forcing conditions (170°C under pressure).

Sincerely,

Joseph B. Lambert

Title: Arene-oxygen Exchange by EXSY

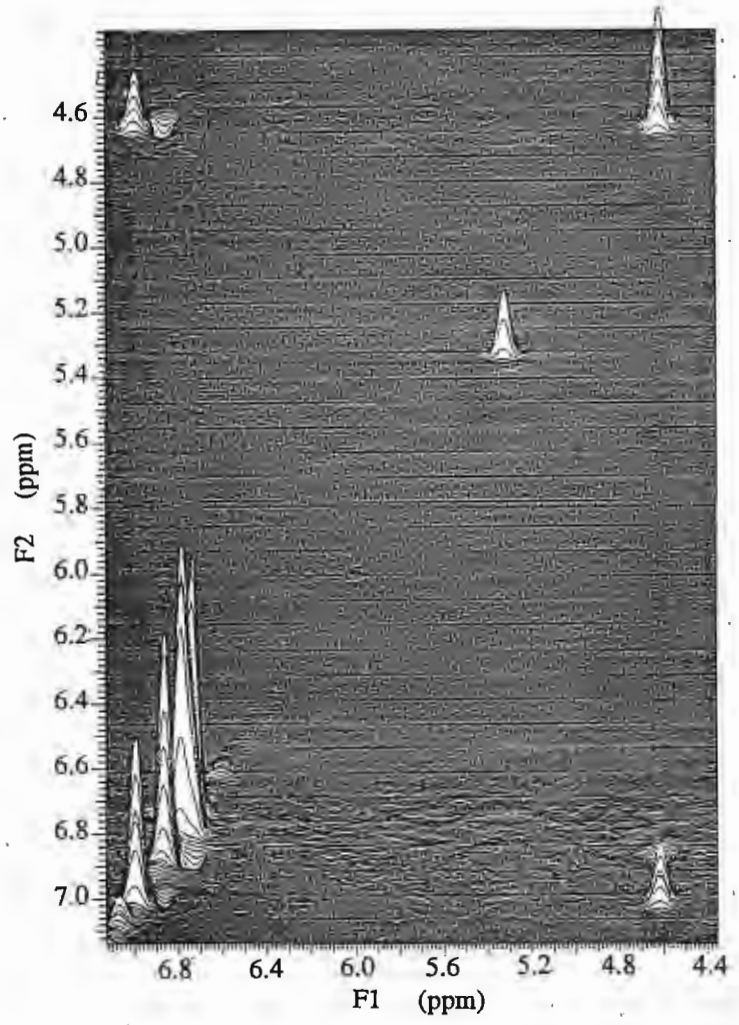


FIGURE 1

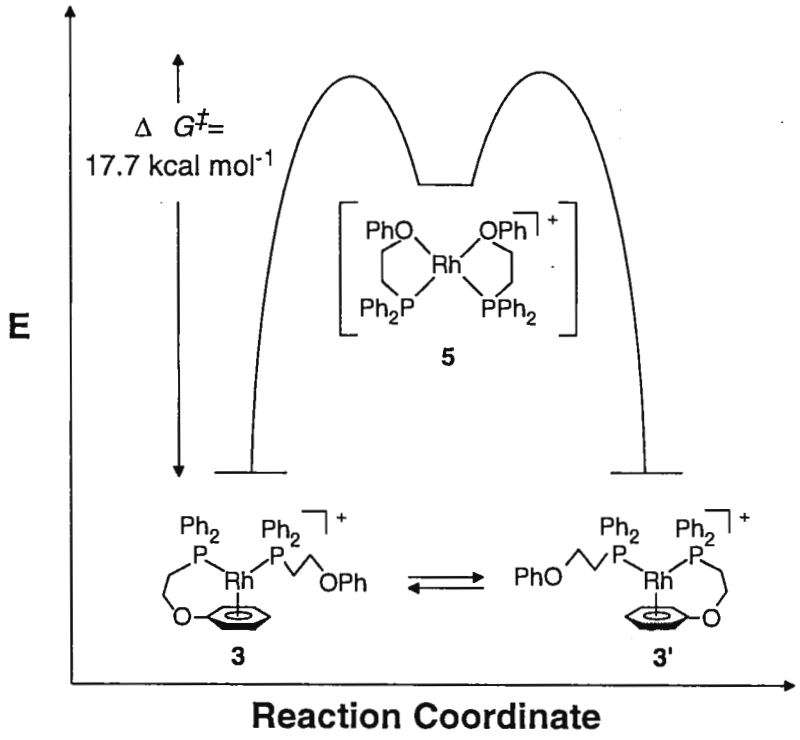


FIGURE 2

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
McCORMICK ROAD
CHARLOTTESVILLE, VIRGINIA 22901

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

September 9, 1994
(received 9/12/94)

GE Omega Disk Replacement

Dear Dr. Shapiro:

Our GE Omega 500 was originally equipped with a Sun 3/160 and two 300 MB CDC Wren4 SCSI disks. The boot disk recently died and we replaced it with a Seagate ST3390N 330 MB disk. We formatted, partitioned, labeled, and installed software on the new disk with no apparent problem. However, the Sun would not boot from the new disk. After a few frustrating hours, we decided to reconfigure the system so that the final working Wren4 was used as the boot disk and the new Seagate disk replaced the working Wren4. This configuration works without problems. We did not determine the cause of the Sun - Seagate incompatibilty but did obtain the following useful information from Rich Shoemaker, Univ. of Nebraska - Lincoln. Rich contacted Falcon Systems when he needed to replace a disk on a spectrometer that is similar to ours. Falcon determined that Rich's SCSI card was incompatible with their SCSI disks and sold him a new SCSI card and disk that worked well on his system. Falcon seems to be a good source of replacement disk hardware and technical support.

Sincerely,

Jeff Ellena

Jeff Ellena
jfe@virginia.edu
804-924-3163

International School of Biological Magnetic Resonance, 2nd Course: Dynamics and the Problem of Recognition in Biological Macromolecules

ETTORE MAJORANA CENTRE FOR SCIENTIFIC CULTURE

Erice, Trapani, Sicily, Italy
22-30 May 1995

Preliminary Program and Lecturers

Basic NMR Methods for Structure and Dynamics Studies	
Basics of Liquid State NMR Spectroscopy	Hartmut Oschkinat, EMBL Heidelberg, Germany
Basics of Solid State NMR Spectroscopy	Stanley Opella, University of Pennsylvania, USA
Heteronuclear Relaxation and Molecular Dynamics	Gerhard Wagner, Harvard Medical School, USA
Proton Exchange and Internal Dynamics	Walter Englander, University of Pennsylvania, USA
Methods for Isotopic Labeling of Biomolecules	John L. Markley, University of Wisconsin, USA
Simulated and Observed Molecular Dynamics	
Molecular Dynamics and Interaction Simulation	Martin Karplus, Harvard University, USA
Simulating Protein and Nucleic Acid Molecular Dynamics	Michael Levitt, Stanford University, USA
Dynamics Observed in the *trp* Repressor	Oleg Jardetzky, Stanford University, USA
Dynamics of Peptides Observed by NMR and Other Physical Methods	Rudolf Rigler, Karolinska Inst., Stockholm, Sweden
Dynamics of Polysaccharides	Robert G. Shulman, Yale University, USA
Protein-Small Molecule Interactions	
Enzyme-Ligand and Inhibitor Interaction	Gordon C. K. Roberts, University of Leicester, UK
Structural and Dynamical Consequences of Ion Binding on Metalloproteins	Sture Forsén, University of Lund, Sweden
Protein Motion and Folding	
Protein Structure and Dynamics Studied by Spectral Editing	John L. Markley, University of Wisconsin , USA
Pathways of Protein Folding	Christopher M. Dobson, Oxford University, UK
Nucleic Acids and Protein-Nucleic Acid Interactions	
Plasticity of DNA Structure and Mutagenesis	Jean-François Lefèvre, Louis Pasteur University, France
Structure and Dynamics of RNA	Cornelius Hilbers, University of Nijmegen, NL
Interaction between *trp* Repressor and *trp* Operator	Oleg Jardetzky, Stanford University, USA
NMR Studies of Protein-Nucleic Acid Complexes	Rolf Boelens, Utrecht University, NL
Protein-Protein Recognition	
Protein A and G Interactions with Antibodies	Gordon C. K. Roberts, University of Leicester, UK
Antigen and Superantigen Recognition by MHC Class II Receptor	Theodore Jardetzky, Northwestern University, USA
Inhibitor-Protease Interactions	Tad Holak, Max-Planck-Institut, Munich, Germany
Crystallographic Studies of Protein-Protein Interactions	Rudolf Ladenstein, Karolinska Inst., Stockholm, Sweden
Protein-Lipid Interactions	
NMR Studies of Protein Membrane Interaction	Stanley Opella, University of Pennsylvania, USA

PURPOSE OF THE SCHOOL

The School will be devoted to the analysis of the dynamic behavior of biological macromolecules by Nuclear Magnetic Resonance and the implication of dynamics on the mechanism of recognition between macromolecules or macromolecules and small substrates. The subjects listed above will be explored in detail during the course. Students are encouraged to submit abstracts and some student research will be selected for presentation in workshops.

NMR has reached the stage where both three-dimensional structure of macromolecular complexes and dynamics can be studied quite accurately. An integrated approach between these two aspects should be utilized more and more in future research. The proposed course will bring together the interesting features of such an integrated approach.

VENUE

The Ettore Majorana Centre for Scientific Culture was founded in 1963 in the pre-medieval mountain town of Erice near Palermo as a Conference Centre, taking its inspiration from the Italian Physicist, Ettore Majorana. The Centre's lecture halls are located in two restored monasteries and the ancient Palazzo Ventimiglia. School participants are housed in the Centre Institutes or local hotels and meals are taken at local restaurants.

GENERAL INFORMATION

Prospective participants should apply to either:

Prof. Oleg Jardetzky
Stanford Magnetic Resonance Laboratory
Stanford University
Stanford, CA 94305-5055
USA
fax: +415/723-2253
phone: +415/723-6270
jardetzky@camis.stanford.edu

or

Prof. Jean-François Lefèvre
ESBS, CNRS-UPR9003
Université Louis Pasteur
Blvd. Sébastien Brant
F67400 Illkirch Graffenstaden
France
fax: +33/88 65 53 43
phone: +33/88 65 52 69
lefevre@bali.u-strasbg.fr

stating: (1) date and place of birth, nationality, qualifications and present position; (2) address, fax and phone numbers and email address; and (3) list of publications.

Applicants interested in submitting unpublished results should send the title and an abstract of about 200 words. Selected papers will be presented and discussed in special sessions.

The total fee, including full board and lodging (arranged by the School) will be approximately US $1,000. Limited financial aid available. Participants should arrive by 5 p.m. on the 22nd.

THE CLOSING DATE FOR RECEIPT OF APPLICATIONS IS MARCH 20, 1995. NO APPLICATION FORM IS REQUIRED.

Attendance will be limited to ~75 students, to be selected by the Co-Directors. Further details will be mailed with the acceptance letter.

Oleg Jardetzky
Co-Director of the School

A. Zichichi
Director of the Centre

Jean-François Lefèvre
Co-Director of the School

Table of Contents, cont'd.

♣ ♦ ♥ ♠ ♣ ♦ ♥ ♠

All Newsletter correspondence should be addressed to

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

(415) 493-5971 - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

Deadline Dates

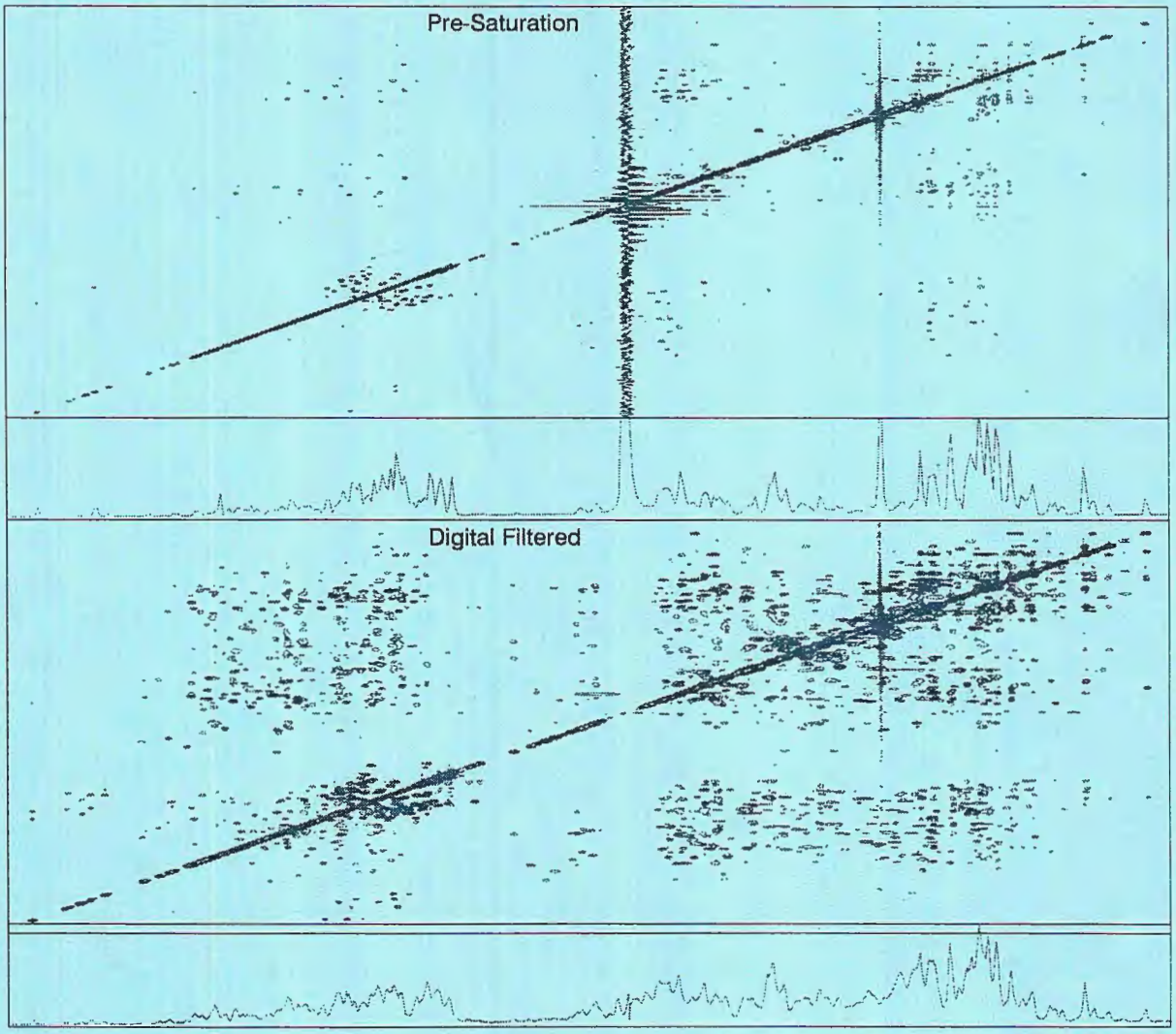
No. 435 (December)	18 Nov. 1994
No. 436 (January)	16 Dec. 1994
No. 437 (Feb.)	27 January 1995
No. 438 (March)	24 February 1995

☆ **The Newsletter's fiscal viability depends very heavily on the funds provided by our Advertisers and Sponsors. Please do whatever you can to let them know that their support is noted and appreciated.**

Mailing Label Adornment: Is Your Dot Red ?

If the mailing label on your envelope of this issue is adorned with a large red dot or circle: this decoration means that you will not be mailed any more issues until a technical contribution has been received by me.

ECLIPSE NMR Advantage: Digital Filtering



Eclipse NMR *The Better Way!*

This data shows the digital filtering capability of JEOL USA's ECLIPSE NMR workstation. Eclipse does digital filtering via software after the data is acquired, not via hardware during acquisition. This offers a significant advantage because with software digital filtering the acquisition is completed before you filter the data.

JEOL feels spectrometer time is best spent acquiring new data rather than repeating experiments because conditions were not optimized. It takes more time to write this kind of software, but JEOL took the time. Now you can use the ECLIPSE NMR Advantage to your advantage.

JEOL USA, Inc.
11 Dearborn Road
Peabody, MA 01960
Tel: 508/535-5900
FAX: 508/536-2205
EMAIL: NMR@JEOL.COM

JEOL
Analytical Instruments Division
MS · NMR · ESR