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No. 429

June 1994

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FORTHCOMING NMR MEETINGS

Gordon Conference on Magnetic Resonance in Biology and Medicine, New England College, Henniker, NH, **July 17 - 22, 1994**; Contact: Dr. Carlyle B. Storm, Director, Gordon Research Conferences, Gordon Research Center, Univ. of Rhode Island, Kingston, RI 02881-0801; Tel. (401) 783-4011 or -3372; Fax: (401) 783-7644.

8th International Symposium on Molecular Recognition and Inclusion, Ottawa, Ontario, Canada, **July 31 - August 5, 1994**; Contact: H. Morin-Dumais, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, ON K1A 0R6, Canada; (613) 993-1212; Fax: (613) 954-5242 See TAMU NMR Newsletter 427, 38

Solid-State NMR Symposium, 36th Rocky Mountain Conference on Analytical Spectroscopy, Denver, CO, **July 31 - August 5, 1994**; Contact: R. E. Botto, Chemistry Divn., Argonne Natl. Lab., Argonne, IL 60439; (708) 522-3524; Fax: (708) 252-92882 See TAMU NMR Newsletter 424, 46.

2nd Meeting, Society of Magnetic Resonance, San Francisco, California, **August 6 - 12, 1994**; Contact: SMR Berkeley Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Tel. (510) 841-1899; Fax: (510) 841-2340.

Gordon Conference on Order/Disorder in Solids, New London, New Hampshire, **August 7 - 12, 1994**; Contact: Prof. M. A. White, Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3; Tel. (902) 484-3894; Fax: (902) 494-1310. See TAMU NMR Newsletter 421, 44.

XVIth International Conference on Magnetic Resonance in Biological Systems, Veldhoven, The Netherlands, **August 14 - 19, 1994**; Organizing Committee: M. J. A. de Bie, C. W. Hilbers, R. Kaptein; Contact: Secretariat XVIth ICMRBS, Bijvoet Center for Biolmolecular Research, Padualaan 8, NL-3584 CH Utrecht, The Netherlands; Tel. +31 30 53 2652/2184/3801; Fax: +31 30 53 7623/54 0980.

Ampere Summer School on Magnetic Resonance with Spatial Resolution, Eichstätt, Bavaria, Germany, **September 2 - 8, 1994**; Contact: L. D. Hall or B. Blümich - See TAMU NMR Newsletter 426, 56.

FACSS XXI (21st Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, Missouri, **October 2 - 7, 1994**; Held jointly with the MMRS-5 meeting *(v.i.)*. Contact: FACSS National Office, 198 Thomas Johnson Drive, Suite S-2, Frederick, MD 21702-4317; Phone: (301) 846-4797. See TAMU NMR Newsletter 428, 28.

5th Missouri Magnetic Resonance Symposium, St. Louis, Missouri, **October 5 - 6, 1994**; Held jointly with the FACSS meeting *(v.s.)*. Contact: FACSS Natl. Office, 198 Thomas Johnson Dr., Suite S-2, Frederick, MD 21702-4317; Phone: (301) 846-4797. See TAMU NMR Newsletter 428, 28.

Continued on page 30

KARL-FRANZENS-UNIVERSITÄT GRAZ
Institut für Organische Chemie

Dr.Heinz Sterk

A-8010 Graz, ...28.4.94.....
Heinrichstraße 28
Tel. (0316) 380 DW. 5322, 5320

Unser Zeichen:

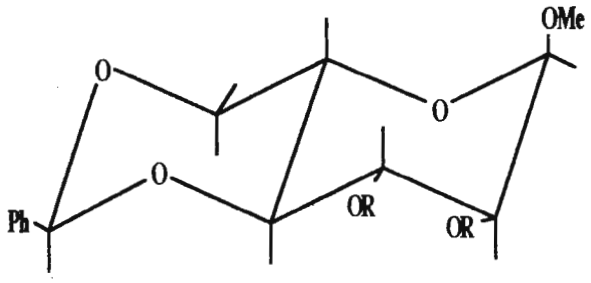
(received 5/11/94)

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

A sample for a "textbook case" NOE.

Dear Dr. Shapiro :

Sometimes one has to show NOE experiments to graduate or undergraduate students which may turn out to be not very instructive, with respect to the topic under investigation. Very often the lack of instructiveness depends solely on the lack of the right material. As a material which shows positive and negative enhancements due to it's structure I would like to recommend the following carbohydrate which can be either easily prepared, following the given literature, or if someone needs the stuff and doesn't want to prepare it, he or she could get it from our lab. Methyl-4,6-O-benzylidene-2,3-di-O-p-toluolsulfonyl-α-D-glucopyranoside shows the following structure and e.g. the following steady state NOE-difference spectrum. The weak decoupler field was applied to proton 5 which is located between the two oxygens in the benzylidene moiety resulting in a positive NOE for H4 and H6a(the stronger NOE ≈ 35%) a really tiny one for H5, whereas H2 and H6e show negative effects.

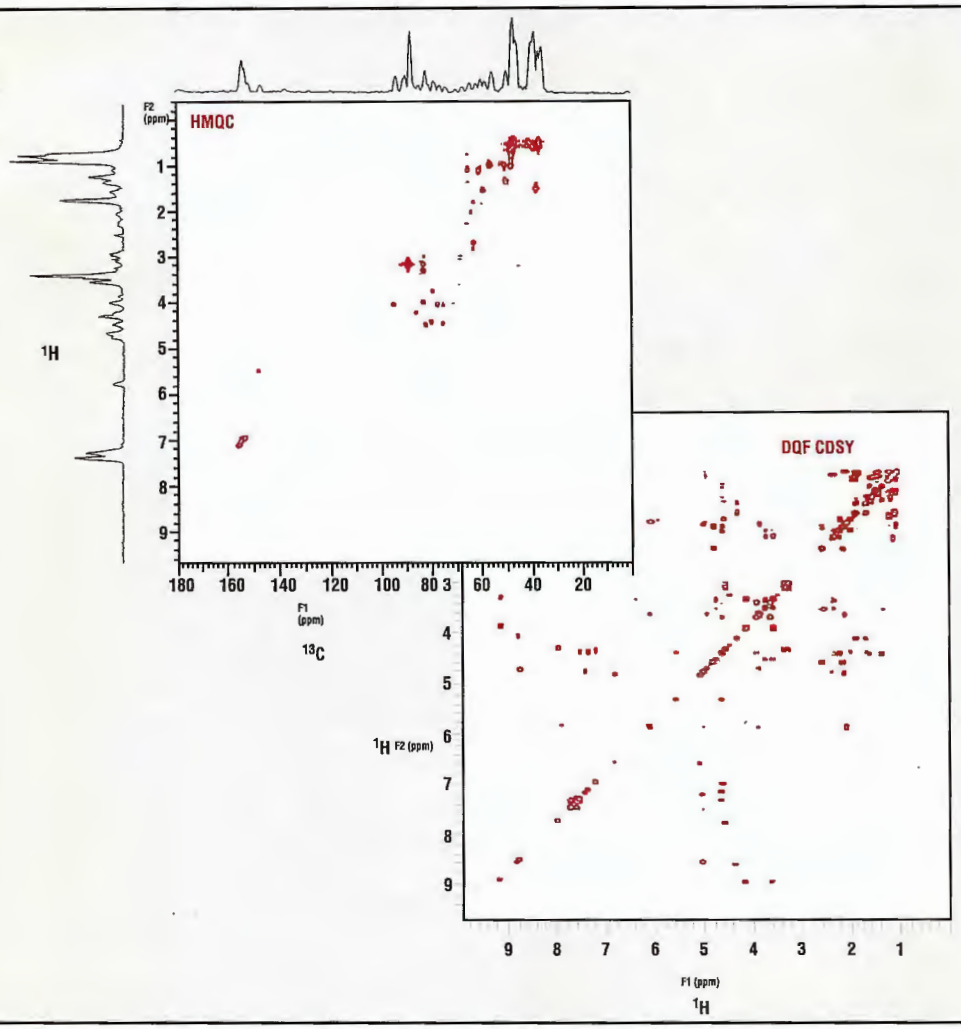


Methods of carbohydrate chemistry, N.K.Richtmyer, Bd.1 1962, 107.

Yours sincerely

H.Sterk K.Dax

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.

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April 22, 1994
(received 4/28/94)

Bernard L. Shapiro, Ph.D.
Editor, Texas A&M NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94503

Nanograms & Nano-Probes™

Dear Barry,

We've been doing some preliminary work with Varian Nano-probes™ which we feel is worth sharing with the readership of TAMUNN. As most readers of the Newsletter are probably aware, Varian introduced the Nano-probe™ a number of months ago in a homonuclear ($^{1}H/^{19}F$) format. More recently, the staff at Varian have made available to us a heteronuclear (^{13}C) version of the probe. Basically, the Nano-probes are magic-angle sideways-spinning probes for the analysis of small samples, e.g. natural products, metabolites, drug degradants, etc. With the specter of health care reform and the myriad of potential problems facing the pharmaceutical industry, any technology capable of cutting the costs and time to identify a metabolite or degradant will probably be well examined by my NMR colleagues in the pharmaceutical industry. Hence, we would like to share some of our first impressions of Varian's new probe format. In this contribution, we will present results obtained with the homonuclear Nano-probe™.

The sample cell used with the Nano-probes™ has a nominal volume of 40 μl. We've found it useful to transfer about 35μl of solution into the cell via a Hamilton syringe. After the insertion of the Teflon plunger used to seal the cell, the air bearing is glued to the glass wall of the cell using cyanoacrylate. While the gluing operation was frustrating the first few times, the process quickly became trivial. Although we've not yet tried, the Varian App Lab folks have said that you can load the cell with volumes as small as 5 μl and still get usable data.

Since we did our initial development work using the simple indoloquinoline alkaloid cryptolepine in the Nalorac Z•SPEC microprobes, it seemed only appropriate to use cryptolepine as a model compound for our maiden voyages with the Nano-probes™. As a starting point, we began with a dilution which gave us 8 μg of cryptolepine (MW 232 Da) in 40 μl of d_6-DMSO (this was before we learned it was somewhat more convenient to transfer only 35 μl into the cell!). The resulting proton spectrum obtained with this sample, less than 2 hrs after the probe was first put in the magnet, is shown in Figure 1. As will be noted from the caption with the spectrum, the spectrum shown required only 8 transients. The data are shown with the water resonance plotted on scale to give a feel for the magnitude of the water suppression needed. One other point which we've all probably largely forgotten about are spinning sidebands. We were initially perplexed by the large signals down near the upfield end of the aromatic region until it dawned on us that we were spinning the sample upwards of 2 KHz and that these were indeed spinning sidebands of the water and DMSO peaks! The important point: it is quite reasonable to record 2D spectra at this level. A COSY spectrum recorded as 1024 x 128 points with 4 transients/t_1 increment required about 5 minutes.

Moving on, we cut the sample quantity to 1 μg. Simple math dictates that every time you halve the sample concentration you must quadruple the number of transients required to attain comparable signal-to-noise. At the 1 μg level this still holds quite true; probe response was quite linear. Figure 2 shows a series of spectra plotted at 32, 128 and 512 transients for a 1 μg sample of cryptolepine in 40 μl of d_6-DMSO. The spectrum shown in the final trace is comparable to the 8 μg/8 transient spectrum shown in Figure 1. Examining the linearity of probe response still further, we ran a series of serial dilutions down to 75 ng (yes, Barry, that's an "ng" for nanograms!) and were still obtaining linear probe response at that level, albeit with numbers of

transients which were becoming quite large. In addition, at very low levels there is a considerable baseline roll to the spectrum.

During the course of our examination of probe response, we made up a sample containing 200 ng (0.85 nanomole) of cryptolepine. The full spectrum without any cosmetic "baseline enhancement" is shown in Figure 3; the expansion of the aromatic region shown has been baseline flattened. The water was suppressed with a soft 200 msec pulse; the residual protio-DMSO was irradiated during acquisition with a status flag. It is interesting to note the intensity of the ^{13}C satellites of the DMSO relative to the 200 ng resonances of the cryptolepine. Finally, a COSY spectrum of the 200 ng sample of cryptolepine recorded overnight is shown in Figure 4. The data were recorded as 1024 x 96 points with 1200 transients/t_1 increment.

In summary, our first impressions with the Nano-probe were quite favorable. The probe performed well albeit with a baseline that needed a lot of help at times. Nevertheless, the probe does provide the means of getting data for very small samples. In the contribution which follows, we will present some of the results we've obtained with the heteronuclear Nano-probe™.

Gary Martin
Organic Chemistry

John Shockcor
Pharmacokinetics &
Drug Metabolism

Ron Crouch
Organic Chemistry

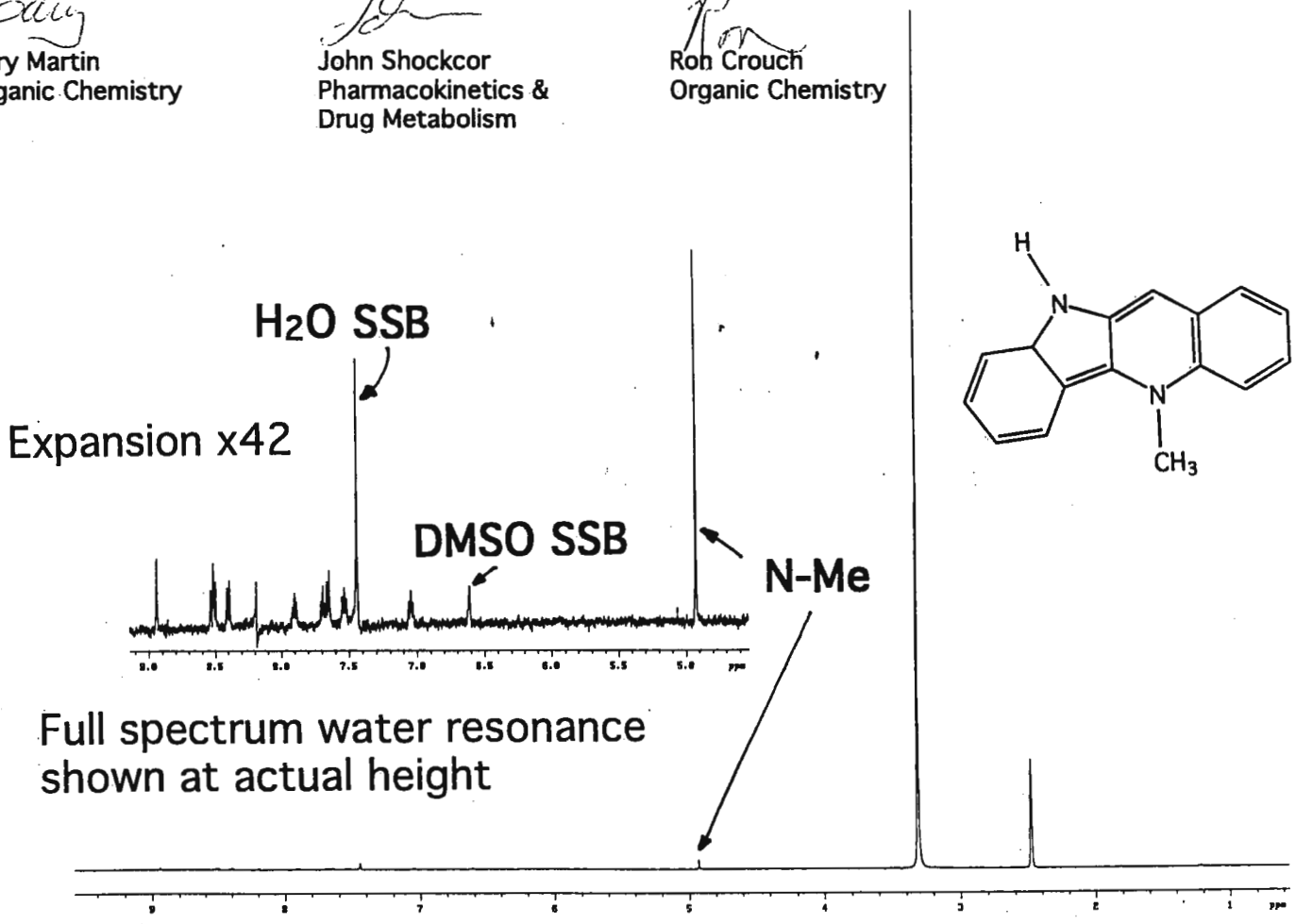

Figure 1. Proton nmr spectrum of 8 μg of cryptolepine dissolved in 40 μl of 99.96% d_6-DMSO (Cambridge) using the Varian homonuclear Nano-probe™. The residual water resonance was not suppressed and is shown full scale. The inset showing the aromatic region is a 42x vertical expansion. The resonances denoted H_2O SSB and DMSO SSB were the spinning sidebands of the residual water and DMSO resonances approximately 2 KHz downfield from their respective resonances reflecting the spinning speed of the sample cell.

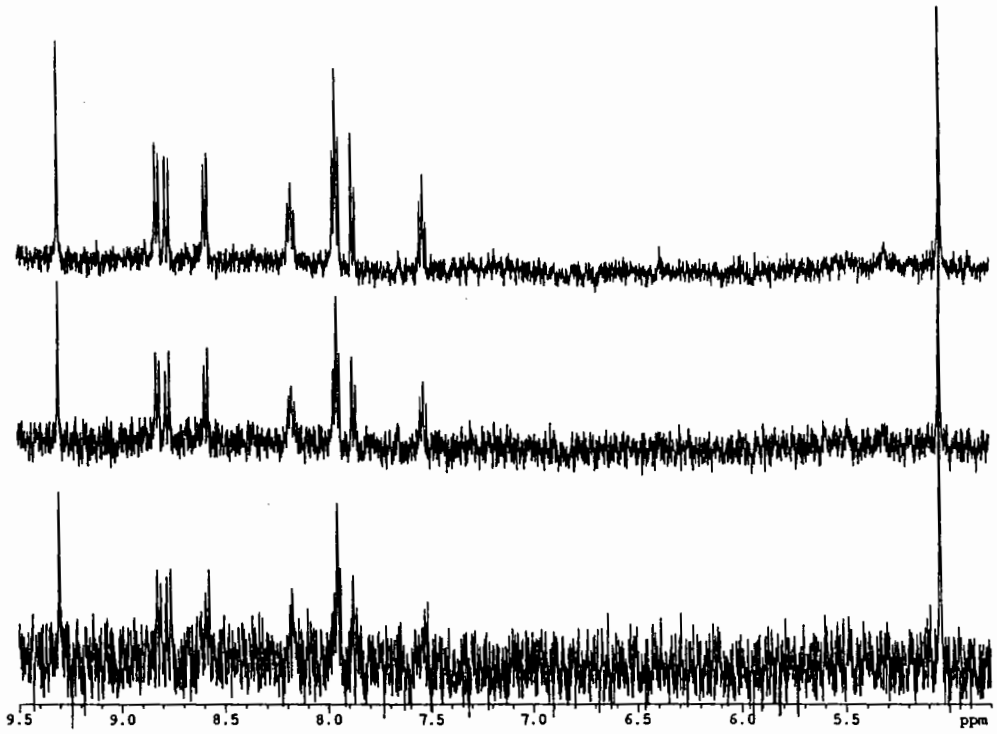

Figure 2. Spectra of a 1 μg sample of cryptolepine in 40 μl of d_6-DMSO. Spectra are plotted at 32 transients (bottom trace), 128 transients (middle trace), and 512 transients (top trace).

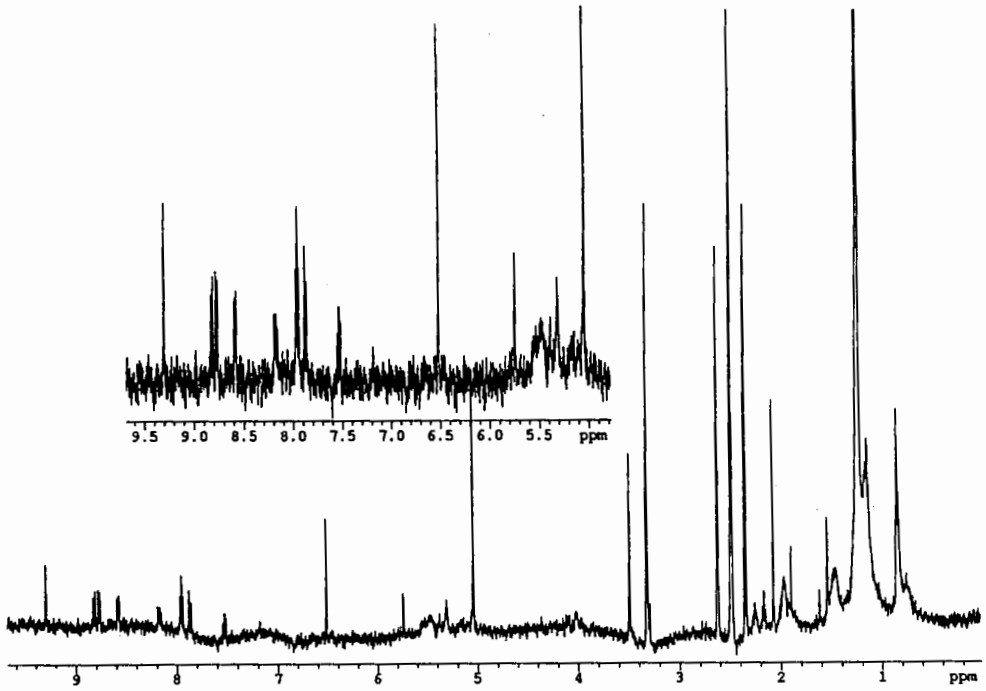

Figure 3. Spectrum of a 200 ng (0.85 nanomole) sample of cryptolepine in 40 μl d_6-DMSO. The spectrum was recorded in 1440 transients. The water resonance was suppressed with a soft pulse; the residual DMSO resonance was suppressed by on-resonance decoupling during acquisition and is plotted full scale. The ^{13}C satellites of the DMSO resonance were not attenuated by the on-resonance decoupling applied to the central multiplet. To cosmetic enhancement has been applied to the baseline of the full spectrum. The baseline in the expansion of the aromatic region has been corrected.

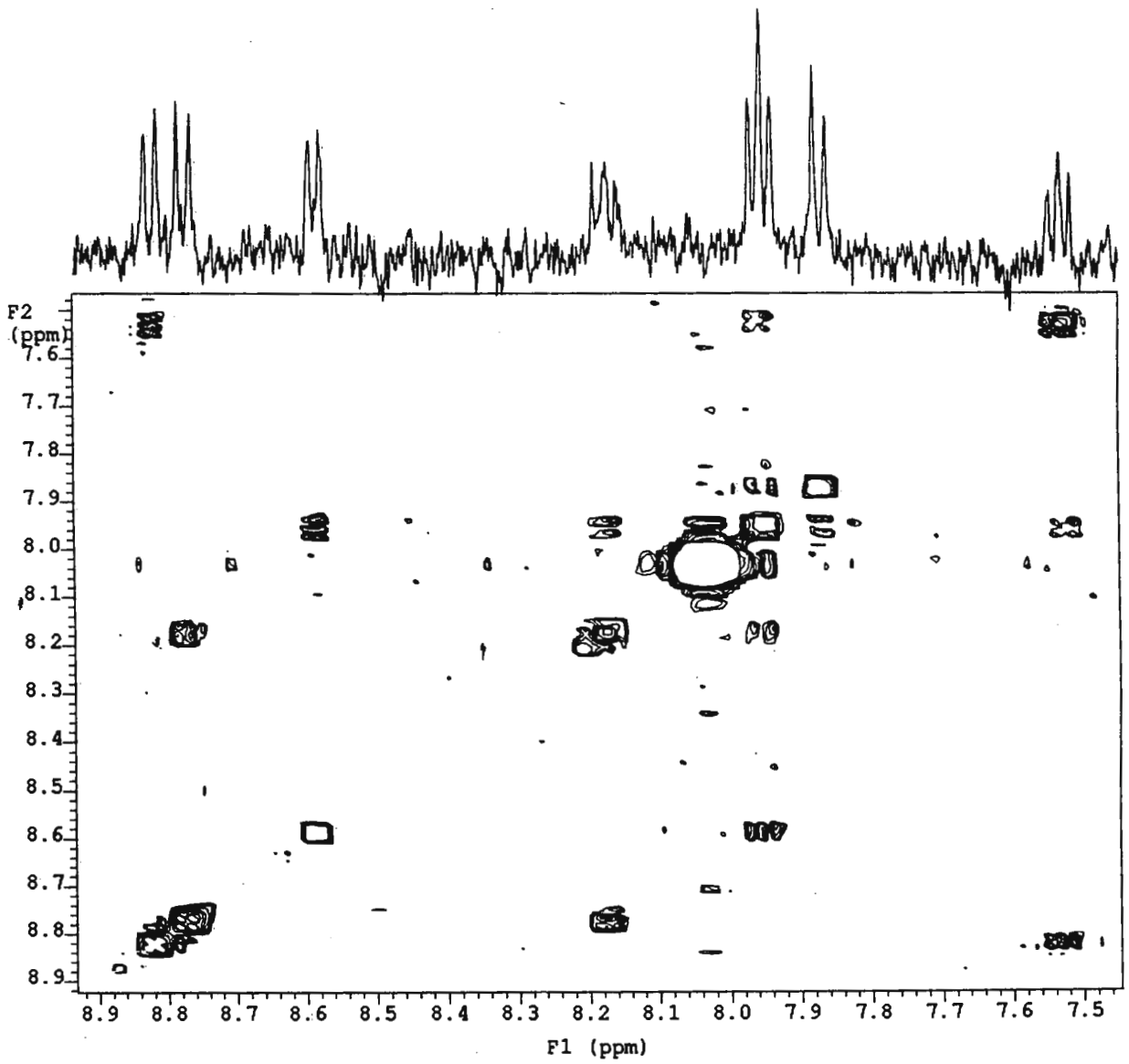

Figure 4. COSY spectrum of a 200 ng (0.85 nanomole) sample of cryptolepine in 40 μl d_6-DMSO. The spectrum was recorded as 1024 x 96 files to digitize a spectral width of 2354 Hz; 1280 transients were recorded/t_1 increment in an overnight acquisition. The water resonance was suppressed using a soft pulse; the DMSO resonance was irradiated on-resonance during acquisition as in Figure 3. The data were zero-filled to 1024 x 1024 points during processing. The reference spectrum plotted above the contour plot was taken from the spectrum shown in Figure 3. The intense response on the diagonal at 8.04 ppm arose from the folding of the residual water resonance which was outside the spectral window. The N-methyl resonance and the singlet from the H11 resonance were contained in the spectral window acquired but are excluded from this plot.

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

MERCK FROSST
Centre for Therapeutic Research

April 26, 1994
(received 5/7/94)

Dear Barry,

^{19}F NMR Studies of Ligands bound to Large Proteins

One cannot help but be impressed by the steady flow of publications detailing the 3D structures of proteins, protein complexes, and small molecules bound to macromolecules. Working within the confines of a milieu where our business and science mandates are very focused there is less room to pick and choose our proteins. The proteins we come up against place us head on with significant problems like high M_r, membrane association/aggregation, presence of paramagnetic ions, and heme cofactors. Although all these subjects have been touched on in the literature, I think it is fair to say that the available tools are less well developed.

One approach is to "divide and conquer". That is, one tries to recognize functional motifs within a large protein and concentrate on the expression and NMR characterization of these in the hope that the results are representative of the entire protein. Another popular approach is to incorporate fluorinated aromatic residues into the protein itself and measure the relatively simple ^{19}F NMR spectra.[1] Methodology which has been useful to us involves ^{19}F NMR of labeled molecules bound tightly with the protein of interest. This follows on many classical studies, but we contend there is ample room for carefully designed experiments which probe very specific structural questions using ^{19}F NMR. We have revisited the basic scheme in our studies of a fluorinated ligand tightly bound to cytosolic phospholipase A_2 (cPLA$_2$).[2] This newly-described enzyme (M_r 82,000) may be of considerable importance in inflammation. Our study closely follows that of Abeles[3], who worked on α-chymotrypsin, although we were able to study the drug-enzyme complex at a much lower concentration than possible then (0.67 mM *vs*. 2.0 mM).

Fluorine probehead technology has evolved considerably over the last few years. Our *ca.* 1986 5 mm dual ^{1}H/^{19}F probehead used for these first studies suffered from lower S/N than we needed, and an interfering broad signal. The latter was very troublesome when it came to looking at signals from bound species which have quite broad lines (*ca.* 250 Hz). We resorted to extensive post-acquisition processing (linear back prediction), but one still faces the poor usage of the digitizer word length. Bruker has since placed good effort in their ^{19}F probes, and we were very pleased with the new dual ^{1}H/^{19}F probehead we purchased for our AMX 300. The probe has the advantage that either the inner or outer coil can be easily tuned to either nucleus, and the sensitivity thereby optimized for ^{19}F or ^{1}H detection. In addition, there is no serious interfering broad ^{19}F signal derived from the probe. The S/N for ^{19}F is significantly improved on older figures, especially when the inner coil is used for this nuclide (Table 1). The absence of interfering broad peaks is shown in Fig. 1.

With carefully designed experiments, a good deal can be learnt about enzyme-inhibitor complexes using ^{19}F NMR. New hardware now makes it possible to record the spectra of bound species with line-widths of hundreds of Hz at sub-mM concentrations in less than an hour. Further S/N gains may result from digital filters.

Table 1. A comparison of pulse lengths and ^{19}F S/N sensitivity measurements (0.05% $C_6H_5CF_3$ in C_6D_6) for 5 mm dual $^1H/^{19}F$ probeheads at 282.4 MHz.

	Old	New (^{19}F Inner Coil)	New (^{19}F Outer Coil)
π/2 pulse length (μs)	9.8	5.1	9.5
S/N	114:1	428:1	227:1

Michael A. Bernstein
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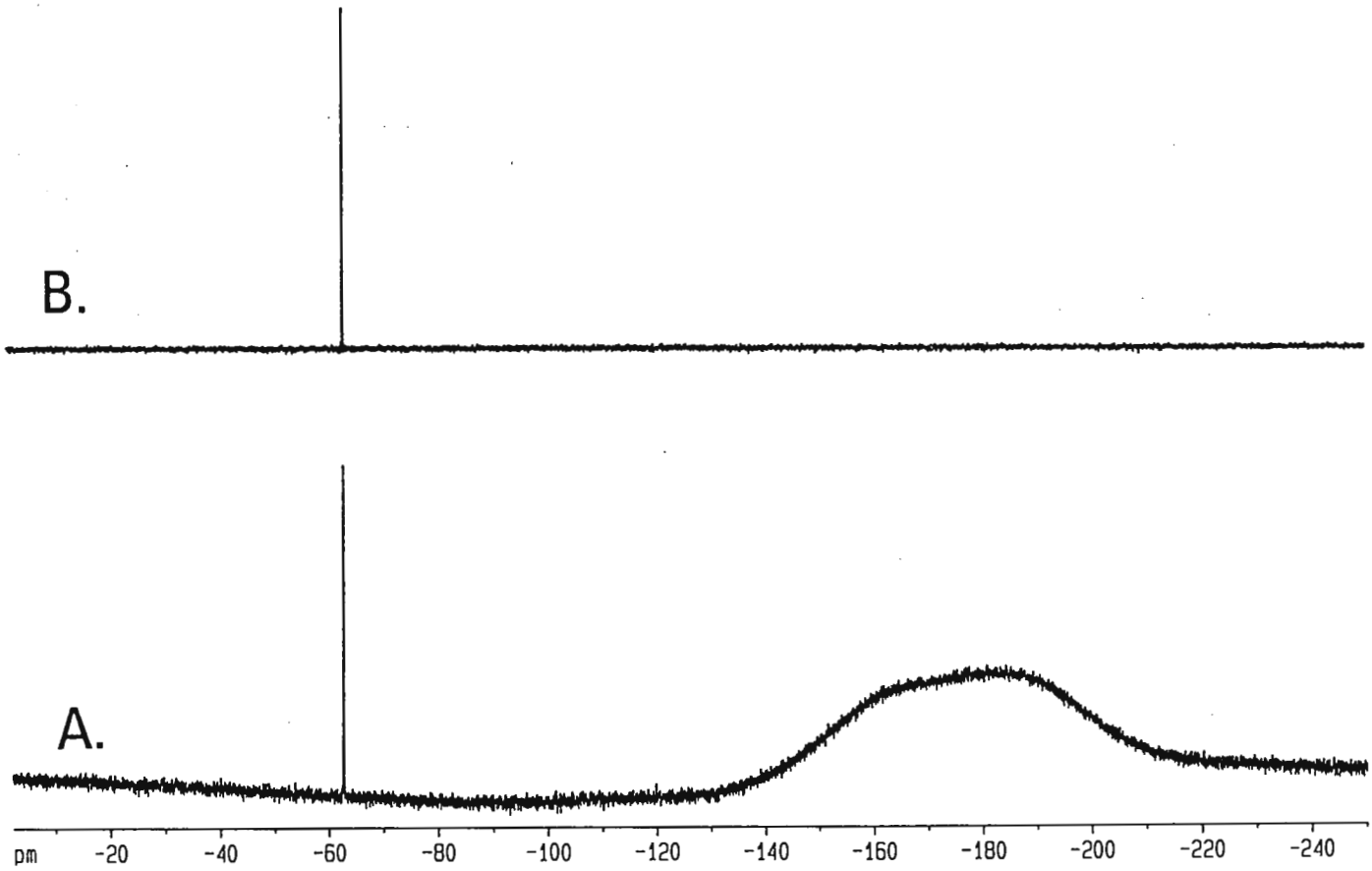
Laird A. Trimble
trimble@merck.com

1 J. N. S. Evans, D. N. Arvidson, R. P. Gunsalis and M. F. Roberts, *Biochim. Biophys. Acta*, **1160** (1992) 156, for example.
2 L. A. Trimble, I. P. Street, H. Perrier, N. M. Tremblay, P. K. Weech, and M. A. Bernstein, *Biochem.*, **32** (1993) 12560.
3 T.-C. Liang & R. H. Abeles, *Biochem.*, **26** (1987) 7603.

Fig. 1. ^{19}F NMR spectra of 0.05% $C_6H_5CF_3$ in C_6D_6 (a) using a 1986-vintage probe, and (b) using a newer generation probe. Spectra were acquired with a 90° pulse, and 1 scan. The final digital resolution was 3.7 Hz/pt, and 4.0 Hz line broadening was used.



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.

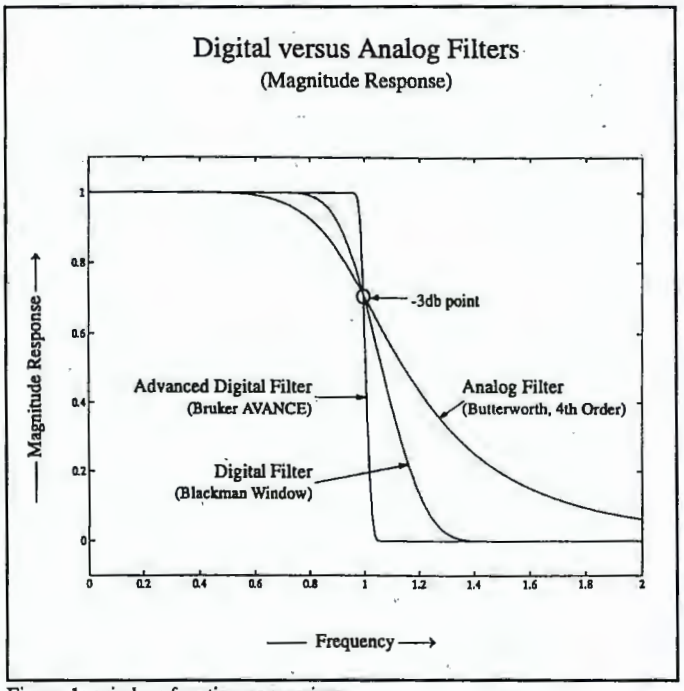
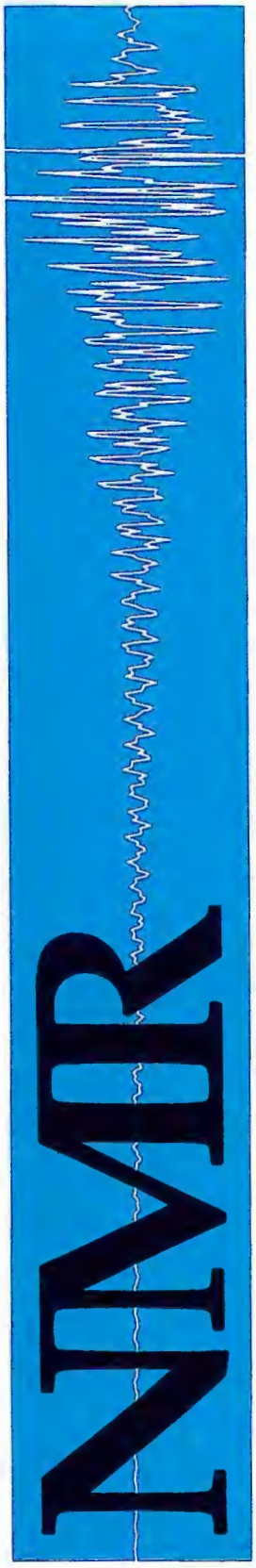


Figure 1: window function comparison



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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 to improve the dynamic range within a spectrum.

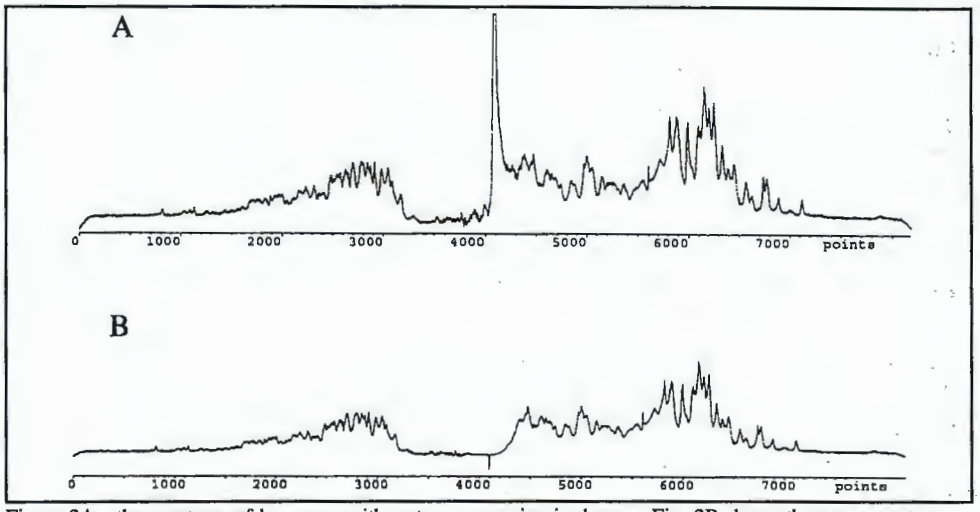


Figure 2A: the spectrum of lysozyme with water suppression is shown. Fig. 2B shows the same spectrum, after digital notch filter (200 Hz band stop), centered on the water resonance, was applied.

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

Many customers have inquired about the ability to utilize digital filtering off-line, as a research tool to develop new types of 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.

Acorn NMR

46560 Fremont Blvd., #418
Fremont CA 94538-6491
Telephone: (510) 683-8595
FAX: (510) 683-6784

Re: Lineshape Magic

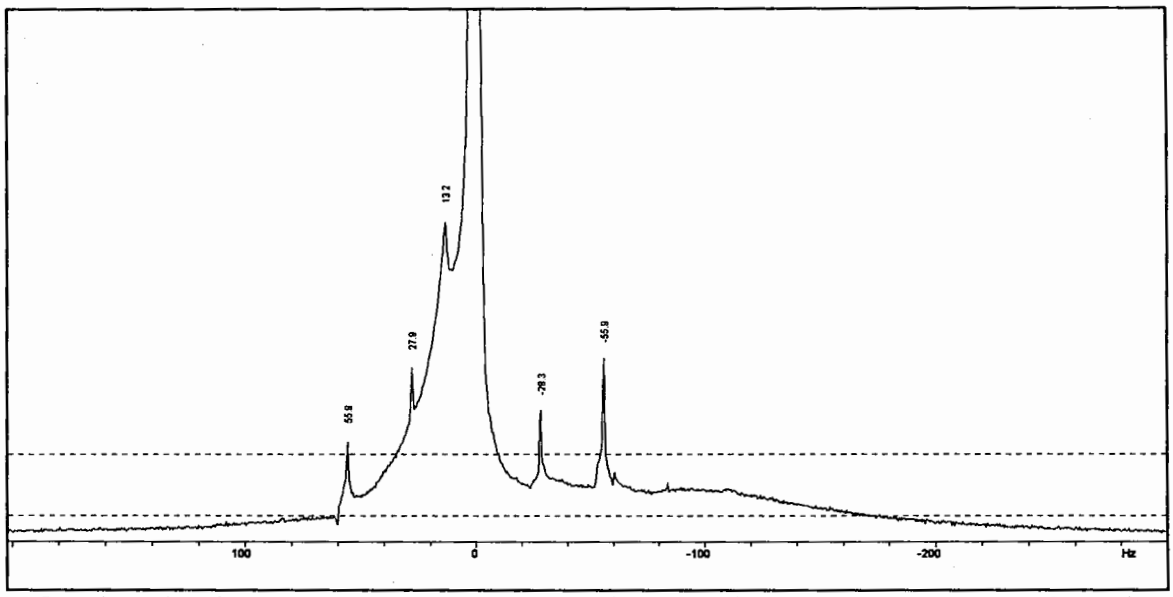
May 16, 1994

Dear Barry,

We were intrigued by a poster presented at last month's ENC by Ken Metz (Poster # WP111) entitled "Simple Technique for Improving Resolution in Heteronuclear NMR Spectra by Deconvolution with the Measured B_0 Field Distribution". The poster demonstrated a processing technique for removing lineshape distortions, based on an earlier paper by Morris (**J.Magn.Reson.**, **80**, 547, 1988) and showed some impressive improvements in lineshape.

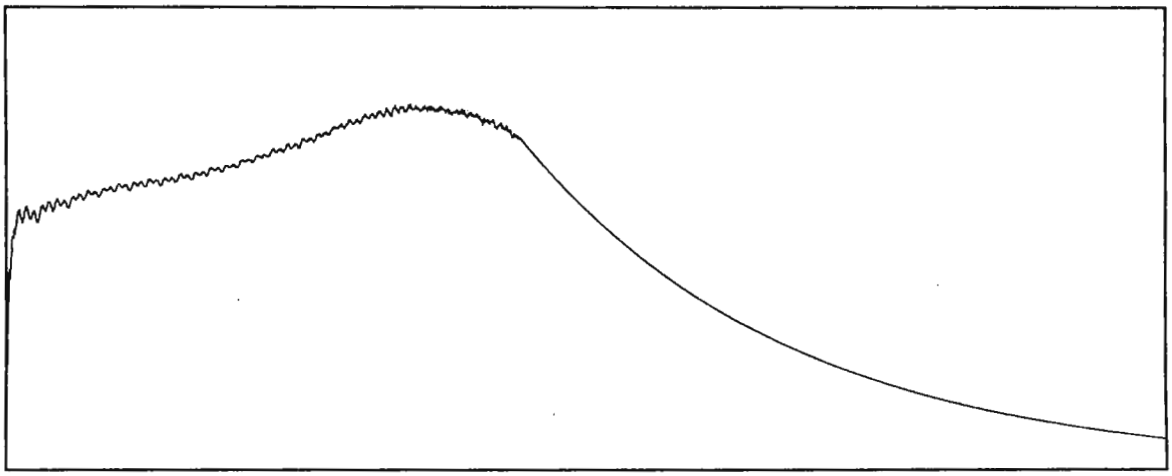
The basic idea is that if you know the shape of the distortion, you should be able to correct for it. To measure the distortion, you need a "reference" spectrum of a single, isolated peak whose ideal lineshape is known, eg., chloroform or water. A comparison of the reference spectrum and the ideal lineshape characterizes the shape of the distortion. Both ideal and reference peaks are mathematically adjusted to be at zero frequency and inverse FTed. An apodization function is created by dividing the ideal time-domain function by the reference FID. This apodization function is then applied to a real FID. The resulting lineshapes are substantially improved. The whole approach, of course, relies on the assumption that all peaks have the same distortion.

Ken kindly sent us a copy of his poster, and we programmed our in-house processing software to generate the apodization function and set out to try it. Among the probes we have for our NT360 is a 5mm ^{13}C probe which was never intended for proton observation. A quick look at the lineshape below shows why.

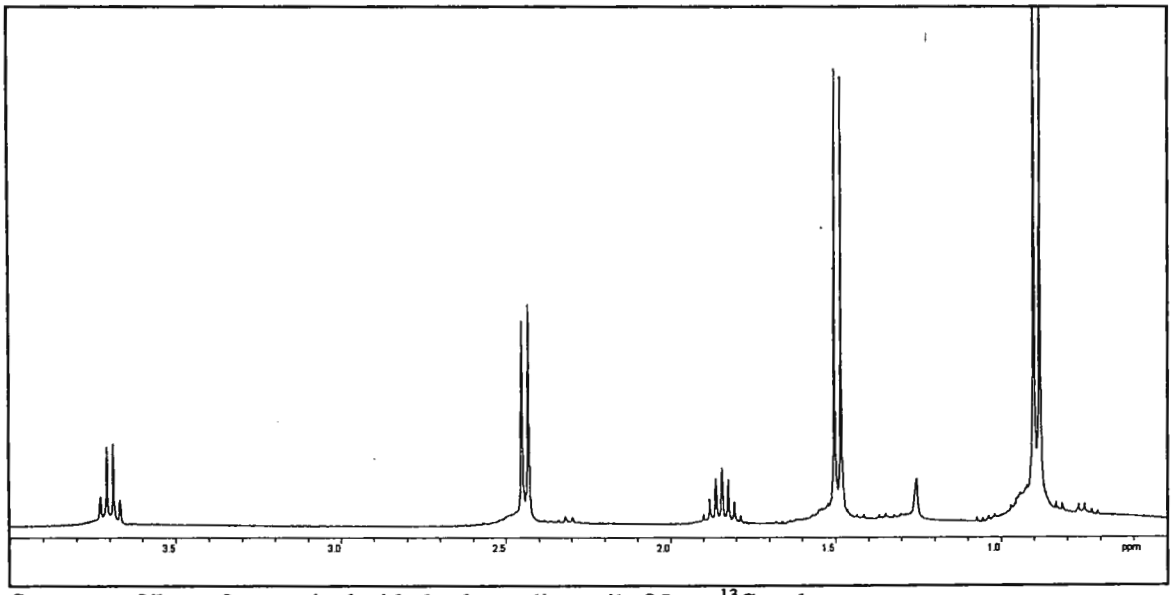


H_2O peak used as the reference for "referrence deconvolution". Spinning rate was 28 Hz. Width at half height was 0.7 Hz. Dotted lines are drawn at 0.55% and 0.11% .

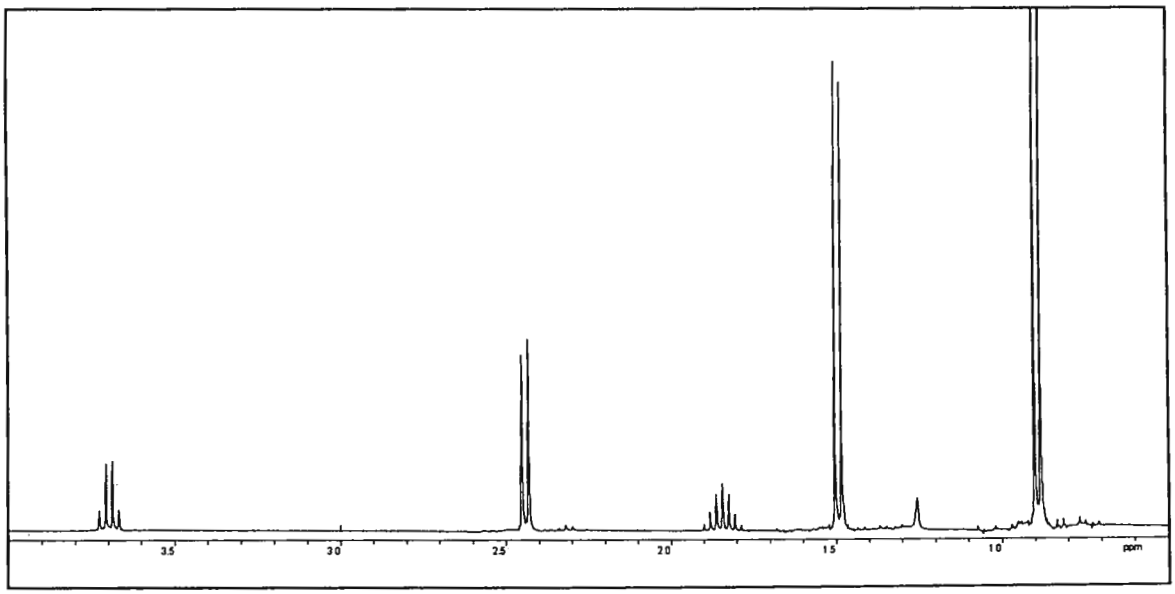
The goal was to see if reference deconvolution would yield acceptable proton spectra from data acquired with this probe. The sample is ibuprofen in $CDCl_3$. The above H_2O spectrum was used as the reference and the ideal lineshape used was a 0.5 Hz Lorentzian.



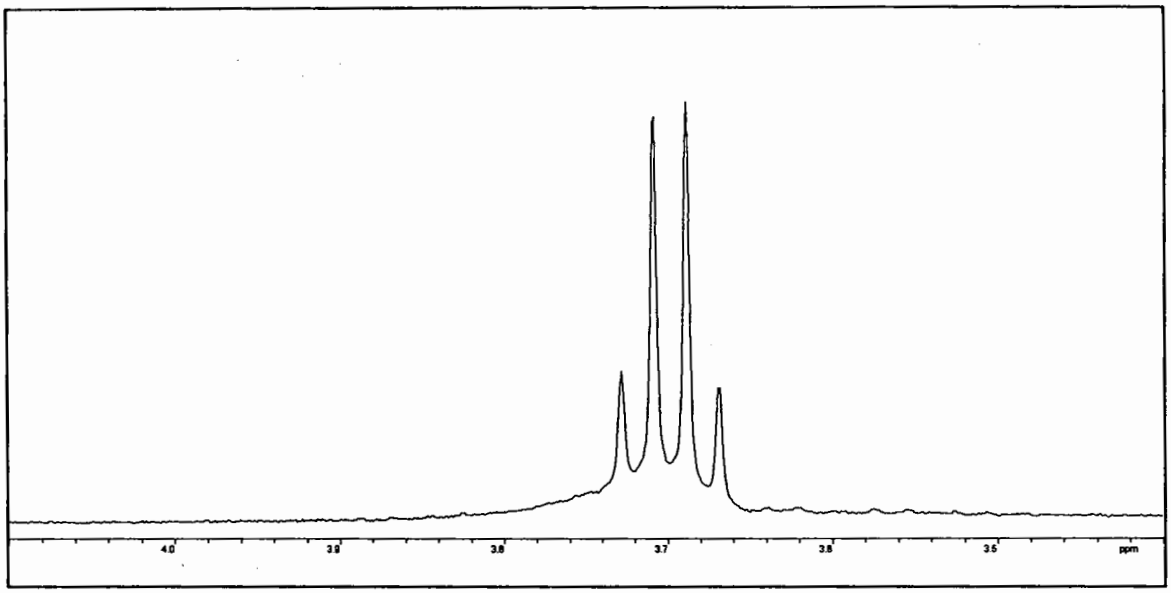
Reference deconvolution function created from the H_2O peak and a 0.5 Hz Lorentzian



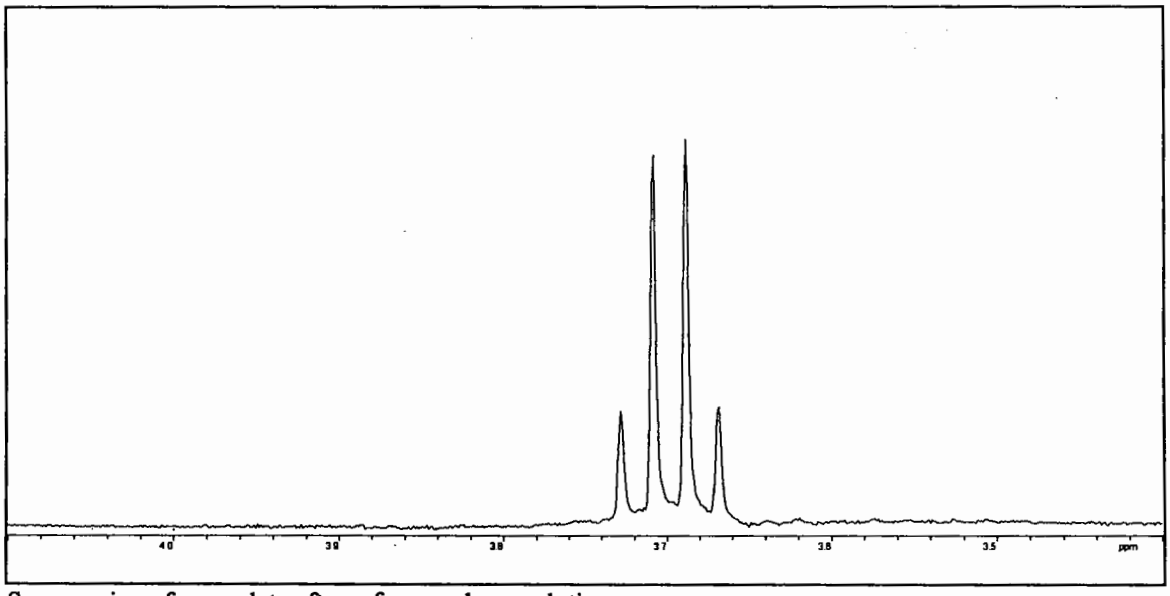
Spectrum of ibuprofen acquired with the decoupling coil of 5mm ^{13}C probe



Same data after reference deconvolution



Expansion of normal spectrum



Same region of same data after reference deconvolution

While the corrected lineshapes aren't perfect, they are substantially improved. The integral had to be corrected for a small amount of distortion at the base of the peaks, but yielded the expected ratios. The results are encouraging, even for this extreme case. We are still exploring the effects of various parameters and continue to work on improvements in implementing this as a processing technique.

Gina Miner

Woody Conover

The University of New Mexico

Department of Chemistry
Clark Hall 103
Albuquerque, NM 87131-1096
Telephone (505) 277-6655
FAX (505) 277-2609

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

April 30, 1994
(received 5/3/94)

Kinetics of Alcohol-Alkoxide Exchange

Professor Shapiro,

In our continued investigations of metal alkoxide chemistry we have begun studies using ^{17}O-enriched alcohols. These studies have revealed that alcohol interchange between the sterically encumbered metal alkoxide, $Sn(O\text{-}t\text{-}Bu)_4$, and *t*-butanol (its parent alcohol), is relatively rapid. Variable temperature ^1H NMR data do not reveal any evidence for the exchange process; however, addition of ^{17}O-enriched *t*-butanol results in incorporation of the^{17}O label into the alkoxide. To obtain the kinetic parameters for this exchange process, which is slow relative to the NMR line shape time scale, we have utilized ^1H magnetization transfer experiments were the *t*-butanol peak was selectively inverted. Figure 1 shows the time dependence of the resonances at four different temperatures. Solution of the Bloch equations were obtained using the Laplace-Carson operator method[1], allowing the exchange rates to be evaluated (for example $k_{A\text{-}B} = 0.22\ s^{-1}$ at 297 K). From an Eyring plot of the forward and reverse rate constants the activation parameters were evaluated, giving $\Delta G^{\ddagger}_{298} = 18.8 \pm 0.7$ Kcal mol^{-1}, $\Delta H^{\ddagger} = 10.9 \pm 0.4$ Kcal mol^{-1}, and $\Delta S^{\ddagger} = -27 \pm 3$ eu for the exchange process. These observations provide qualitative insight into the role of alcohol solvents during reactions of metal alkoxide compounds.

[1] Kuchel, P. W. and Chapman, B. E. *J Theor. Biol.* **1983**, *46*, 1512.

Sincerely,

Todd M. Alam, James Caruso and Mark J. Hampden-Smith

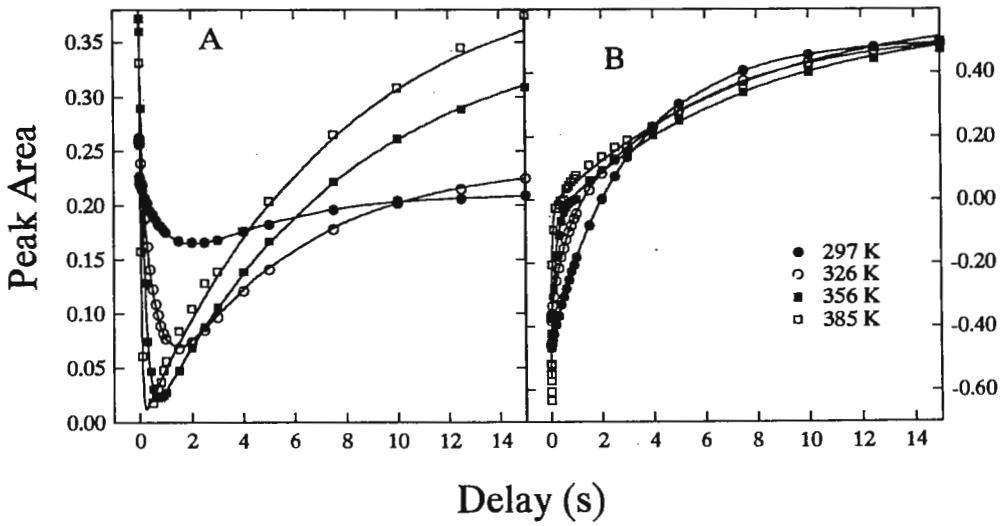


Figure 1. Time dependence of magnetization for the metal alkoxide $Sn(O\text{-}t\text{-}Bu)_4$ (A) and the selectively inverted alcohol HO-*t*-Bu (B).

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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		

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(AMPX00HV) 02/94

FINAL PROGRAM

36th Rocky Mountain Conference

July 31 - August 5, 1994

Denver Colorado

SYMPOSIUM ON NMR

(Robert E. Botto, Chair)

POLYMERS, Monday Morning, August 1, 1994

8:30 *Xenon NMR in Polymers*, J. B. Miller, Navel Research Laboratory
9:00 *Characterizing Surface Polymers with NMR*, E. O. Stejskal, N. C. State University
9:30 *Spatially Resolved Determination of Materials Properties by NMR-Imaging*, W. Kuhn, Fraunhofer Institute for Biomedical Engineering
10:30 *NMR Studies of Structure and Dynamics in Macromolecular Solids*, Ali Firouzi, University of California, Santa Barbara
11:00 *Strategies for the Studies of Non-Crystalline Synthetic and Bio-Polymers by Solid-State NMR and Atomic Force Microscopy*, Tomasz Kowalewski, Washington University
11:30 *Rotating Frame NMR Microscopy*, Klaus Woelk, Argonne National Laboratory

BIOSYSTEMS, Monday Afternoon, August 1, 1994

1:30 *Decrypting the Chemical Shift Code in Proteins: A Quantum Chemical Approach to Structure in Solids and Liquids*, Eric Oldfield, University of Illinois at Urbana-Champaign
2:00 *Recent Progress in ^{113}Cd NMR of Biological Systems...Model Compounds, Hemoglobin, and Fun & Games with Bones*, Paul D. Ellis, Pacific Northwest Laboratory
2:30 *Photochemically Induced Dynamic Nuclear Polarization in Solid State NMR Spectra of Reaction Centers from Photosynthetic Bacteria*, Ann McDermott, Columbia University
3:30 *Solid State NMR Studies of Nucleic Acids*, G. Drobny, University of Washington
4:00 *Proton NMR Study of Seeds*, Gary E. Maciel, Colorado State University
4:30 *Exchange Processes in Organic Crystals: Can the Solid-State NMR and Diffraction Results be Reconciled?*, Lucio Frydman, University of Illinois at Chicago
5:00 *Dipolar Recoupling in Solids under Magic Angle Spinning in the Spin-Locking Frame (DRAMSL)*, B.-Q. Sun, MIT

R. W. VAUGHAN LECTURE SYMPOSIUM, Tuesday, Morning, August 2, 1994

8:25 R. W. Vaughan Lecture - *Population Transfer Applied to the Indirect Observation of Nuclear Spins with Large Quadrupole Coupling Constants*, Alexander J. Vega, DuPont Central Research and Development
9:30 *Surfaces, Solids and Gases: The Phases of NMR Spectroscopy*, Cecil Dybowski, University of Delaware
10:45 *Intermediate Range Order in Glasses: A New Frontier for Solid-State NMR Spectroscopy*, Hellmut Eckert, University of California, Santa Barbara
11:30 *Spins, Light, Molecules, and Cats*, Alexander Pines, University of California, Berkeley

POSTER SESSION, Tuesday, Afternoon, August 2, 1994

2:00 - 4:00 p.m.

GENERAL, Tuesday Evening, August 2, 1994

6:30 *Solid-State NMR Studies of Isolated Two-Spin Systems Involving Nitrogen: Diazo Compounds*, Robin K. Harris, University of Durham
7:00 *Nuclear Quadrupole Resonance (NQR) Studies of Glass Structure*, Philip J. Bray, Brown University

7:30 *Field Swept NMR Spectroscopy: Applications to Zeolites*, Les G. Butler, Louisiana State University

NMR/EPR, Wednesday Morning, August 3, 1994

8:30 *Dynamic Nuclear Polarization and Electron Paramagnetic Resonance at 140 GHz*, R. G. Griffin, MIT,
9:00 *Pulsed ENDOR Spectroscopy of ^{57}Fe Containing Zeolites*, D. Goldfarb, Weizmann Institute of Science
9:30 *Dynamic Nuclear Polarization of Solvent Nuclei in Solutions Containing Free Radicals*, R. D. Bates, Jr., Georgetown University
10:30 *A ^{29}Si Dynamic Nuclear Polarization/Magic Angle Spinning Study of the Silica Surface*, Junji Kobayashi, Mitsubishi Electric Corp.
11:00 *Advances and New Application in High-Frequency Pulsed EPR and Pulsed ENDOR Spectroscopy*, J. Schmidt, University of Leiden
11:30 *Solid-State NMR and Pulsed Electron Nuclear Multiple Quantum Spectroscopic Studies of Fullerene Polymer Interfaces*, H. Thomann, Exxon Research and Engineering Company

SURFACES/INTERFACES, Wednesday Afternoon, August 3, 1994

1:30 *Structure and Dynamics in some Low-Dimensional Composite Phases*, David B. Zax, Cornell University
2:00 *Multi-Nuclear NMR Studies of Zeolite Ferrierite*, Lucy M. Bull, University of California
2:30 *Proton and ^{19}F NMR of Solid Then Films and Interfaces*, Karen K. Gleason, MIT
3:30 *Connectivities from NMR Spectrometry of Solids. Applications to Materials Research*, Karl T. Mueller, Pennsylvania State University
4:00 *Dynamics of Surface Adsorbed Polymers*, Frank D. Blum, University of Missouri-Rolla
4:30 *New Developments in NMR Studies of Solids and Surfaces*, Eric J. Munson, University of California, Berkeley
5:00 *Intermediate-Range Structural Inhomogeneities in Glasses: A Nuclear Spin-Lattice Relaxation Approach*, S. Sen, Stanford University

SPIN DYNAMICS/NEW TECHNIQUES, Thursday Morning, August 4, 1994

8:30 *^{14}N-^{1}H Level Crossing in Immobilized Proteins*, Scott D. Swanson, The University of Michigan
9:00 *Cross Polarization Double Rotation NMR*, Y. Wu, University of North Carolina,
9:30 *^{31}P-^{19}F Rotational-Echo, Double-Resonance (REDOR) NMR*, Yong Pan, The Procter & Gamble Company
10:30 *Multiple Quantum Filtration and Transfer to Heteronuclei Assigns Rare-Spin Signals*, Gerard S. Harbison, University of Nebraska at Lincoln
11:00 *High-Resolution NMR of Single Epitaxial Structures by Optical Detection*, John A. Marohn, California Institute of Technology
11:30 *VADOR: A New High-Resolution Technique for Quadrupolar Nuclei*, P. Bodart, Universite des Sciences et Techniques de Lille

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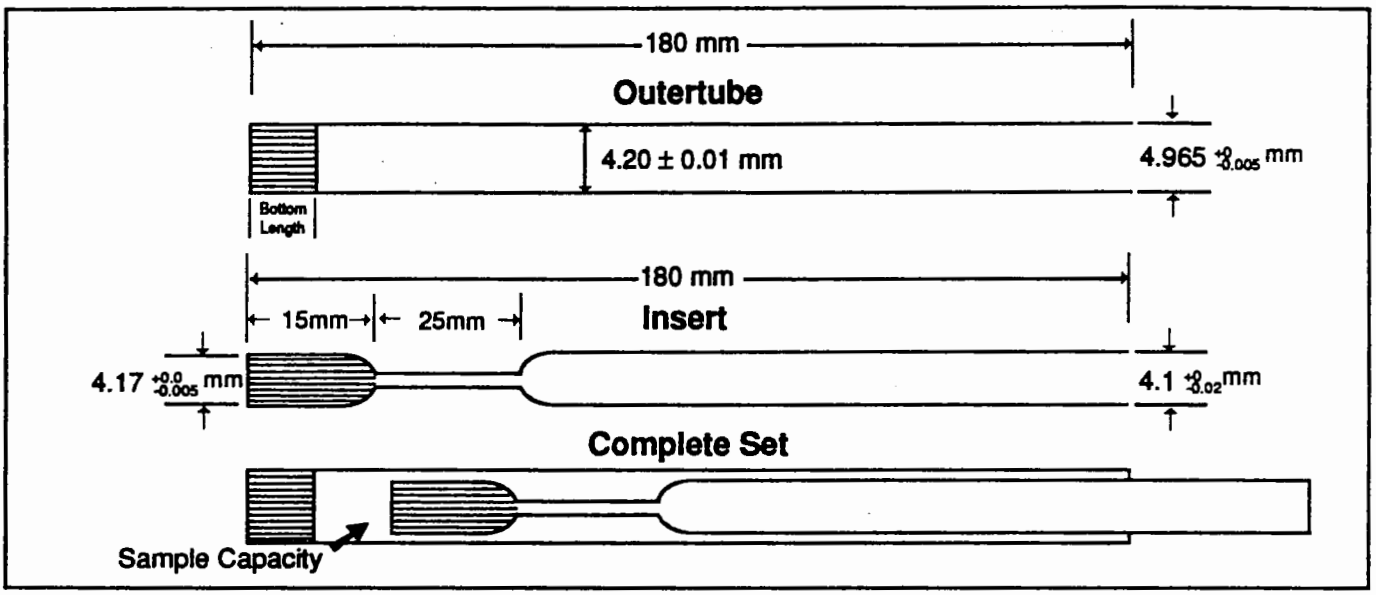

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Complete Set	Insert length (mm)	Insert ID (mm)	Insert OD (mm)	Outertube length (mm)	Outertube ID (mm)	Outertube OD (mm)	Bottom* length (mm)
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BMS-005V	180	2.6	4.1	180	4.2	4.965	15

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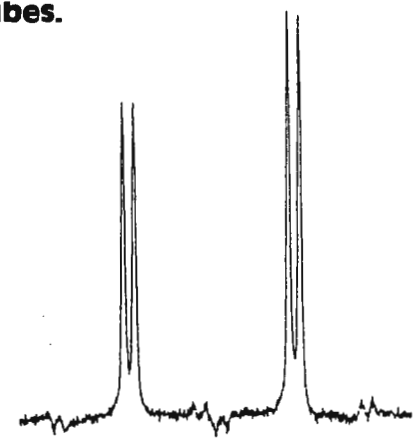
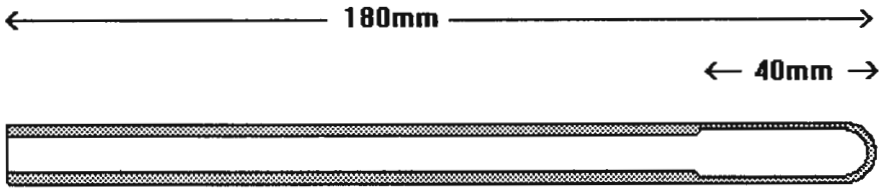
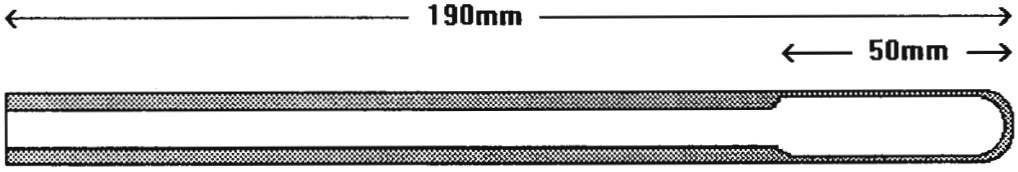


Fig.1a Fig.1b

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)	Concen-tricity/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
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SANTA BARBARA • SANTA CRUZ

May 9, 1994
(received 5/12/94)

Amplitude-Modulated RF Pulse Generation and Re-Mapping with Modulated Gradients

MAGNETIC RESONANCE UNIT
University of California Service
Veterans Affairs Medical Center
4150 Clement Street (11M)
San Francisco, California 94121
Tel: (415) 750-2146
Fax: (415) 668-2864
e-mail: mweiner@itsa.ucsf.edu

Dear Barry:

Shaped RF pulses are used extensively in MR imaging and localized spectroscopy for frequency selective excitation. Recently, computationally efficient methods have been presented for amplitude modulated RF pulse design, including the Shinnar-Le Roux (SLR) algorithm (1) which utilizes digital filter design methods (1,2). The advantage of the SLR algorithm is that the digital filter parameters can be interpreted to apply to RF pulses, so the results are known (approximately) before the design is attempted (1).

Another important class of spatially selective pulses consists of RF applied in the presence of modulated gradients (3). Such pulses may be created by refabricating a conventional frequency selective pulse to take advantage of the available gradient strength, so that the largest possible gradient strength (and larger RF amplitude) is used where the original pulse amplitude was small.

An integrated set of algorithms has been developed using the MATLAB programming language (The Math Works, Inc.) which implements the SLR algorithm for efficient RF pulse design, and includes re-mapping for refabricating pulses as discussed above. Other algorithms including the Bloch equations for a rigorous examination of pulse performance, scaling and filtering functions, a gradient refocusing tool, a pulse import/export tool, and an algorithm for examination of slice profiles in the presence of nuclear relaxation, are included (4). Both PC and Unix versions of the program, named MATPULSE, are available.

The user interface for MATPULSE consists of a series of figure menus created with MATLAB "widgets". Figure 1 depicts part of the Pulse Generation menu. Pull-down menu selections in Fig. 1 (Single Band / Dual Band, etc.) are depicted horizontally for convenience. Boxed parameters such as **Angle**, pulse length (**T (ms)**), and width (**W(kHz)**) require written entry, while the ripple parameters are set with sliders. The time*bandwidth product (**T*W**) is continuously updated, while the transition band requires selection of **TransB** for updating. Pulse calculation is initiated by selection of the **B1 Calc** button. Other figure menus are similarly constructed. The output menu selections (not shown) provide for various graphical outputs.

The MATPULSE program refabricates an RF pulse by re-mapping it directly onto a different dwell time; the original slice profile is accurately preserved, while the gradient waveform is made to adher to the specified gradient slew rate. The primary advantage of the re-mapping formulation is its simplicity. A re-mapped version of a MATPULSE-generated spin echo pulse is shown in Fig. 2, along with the associated gradient waveform. The extra gradient dip just beyond 1.5 ms is to provide re-synchronization (4).

Sincerely,

Gerald B. Matson
Facilities Manager, MR Unit, DVAMC, and
Adjunct Professor, Pharm. Chem., UCSF

Michael W. Weiner
Director, MR Unit, DVAMC, and Professor of
Medicine and Radiology, UCSF

References:

1. Pauly, J., Le Roux, P., Nishimura, D., Macovski, A., *IEEE Trans. Med. Imaging* 10, 53, 1991.
2. Shinnar, M., Bolinger, L., Leigh, J.S., *Magn. Reson. Med.*, 12, 88, 1989, and references therein.
3. Conolly, S., Nishimura, D., Macovski, A., Glover, G., *J. Magn. Reson.*, 78, 440, 1988.
4. Matson, G.B., *Magn. Reson. Imaging* (Submitted).

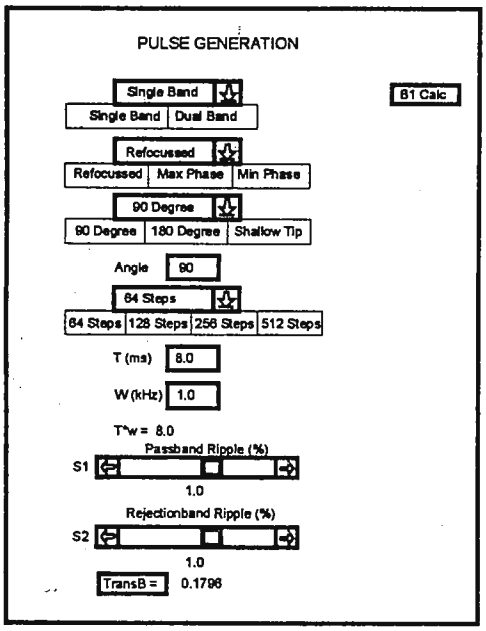


Fig. 1. The Pulse Generation Menu.

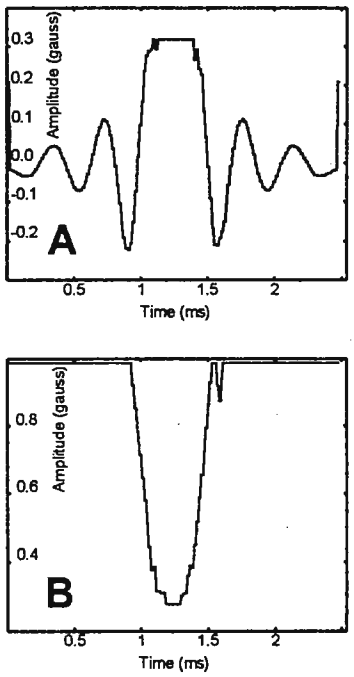
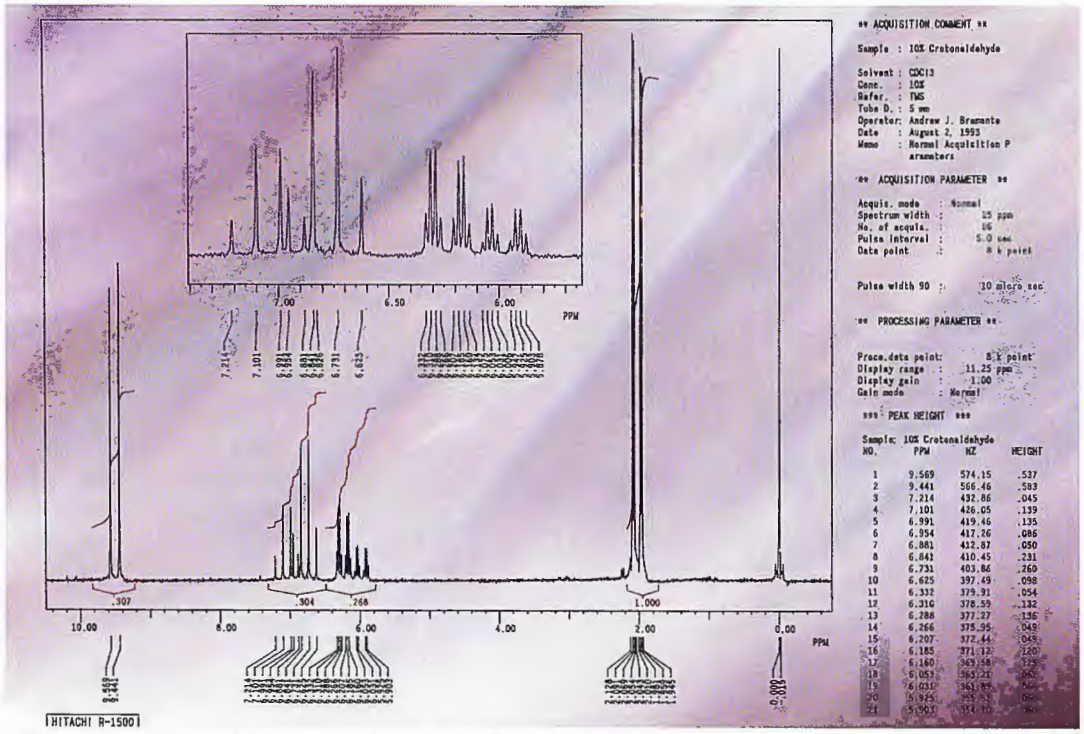


Fig. 2. Re-mapped SLR designed 180^0 pulse (A) and associated modulated gradients (B).



This R-1500 FT-NMR spectrum of crotonaldehyde represents a 16 pulse acquisition; each pulse was 10 µsec with a pulse interval of 5 seconds.

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(received 5/16/94)

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

Methionines and 750 MHz advantages at 600

Dear Barry:

The quest for higher and higher magnetic fields is to a large extent fueled by our desperate desire for increased sensitivity. The spectacular increases in S/N we have seen over the past two decades are frequently attributed to the increase in magnetic field strength we have witnessed in this time span. Indeed, whenever a higher field spectrometer was announced, the sensitivity specs appeared to jump significantly. Ascribing this gain solely to the field strength is not quite fair, however. I believe that whenever a higher field strength is announced, the manufacturers are under extra pressure to make the new instrument work better than their previous highest field spectrometer, and more detail is paid to optimizing other aspects of the spectrometer system too. One example of the latter is a new preamp developed by Bruker for their 750 MHz spectrometer which has a significantly lower noise figure than its predecessor. Considering that our last preamp upgrade of the AMX600, associated with a conversion to a digital lock system, had given us a S/N increase of nearly 10% (starting from a preamp which supposedly had a better than 2 dB noise figure), I honestly did not expect any significant gain of their newest "750-MHz-style" preamp, creatively named Sig-Max. Nevertheless, it boosted the S/N by yet another 7%, averaging over 20 measurements with the old and with the new preamp, leaving all other settings (and shimmings) unchanged. At this stage, it appears, however, that any useful further improvement in preamp technology would require the personal assistance of Maxwell's demon.

S/N is virtually always a limiting factor when studying biological macromolecules. For example, a method developed by two of my distant cousins for measuring ^{13}C-^{13}C long range J couplings[1] relies on quantitative measurement of the fraction of magnetization that can be transferred from carbon *A* to carbon *B*. When line widths are large and J couplings are small, these fractions invariably are tiny, and accurate measurement of J relies on precise quantitation of the *A* - *B* cross peak intensity. Nevertheless, this approach is feasible in proteins as large as 20 kD at concentrations as low as 1 mM and couplings smaller than 1 Hz, provided the protein is uniformly enriched with ^{13}C. An example of the 3D long-range carbon-carbon (LRCC) J coupling experiment is shown in Figure 1. This figure displays strips taken from the 3D spectrum at the $^{13}C^{\varepsilon}$ (F_2) and $^{1}H^{\varepsilon}$ (F_3) frequencies of the methionine residues in the complex between the isotopically labeled protein calmodulin and a 26-residue peptide. Not only does this spectrum provide interesting information on the values of $^{3}J_{C\varepsilon C\beta}$, it also yields valuable connectivity information permitting unambiguous assignment of the methionine methyls. From a biochemical perspective, it is interesting to note that only two of the 8 methionines that contact the peptide are in a *trans* χ_3 conformation, with $^{3}J_{C\varepsilon C\beta}$ couplings of about 2 Hz, and small (3-4 Hz) $J_{C\varepsilon H\gamma}$ values. Of the remaining six, four show clear evidence of extensive χ_3 rotamer averaging, with intermediate $^{3}J_{C\varepsilon C\beta}$ (0.6 - 1.1 Hz) and $J_{C\varepsilon H\gamma}$ couplings (~6 Hz). Methionine 76, which does not

contact the peptide and which is known to be highly mobile, gives $J_{C\varepsilon H\gamma}$=5.8/6.6 Hz and $^3J_{C\varepsilon C\beta}$=0.8 Hz. More details will hopefully appear in the Journal of Biomolecular NMR.

Kindest regards,

Ad

Ad Bax

(1) A. Bax, D. Max and D. Zax *J. Am. Chem. Soc.* **114**, 6923-6925 (1992).

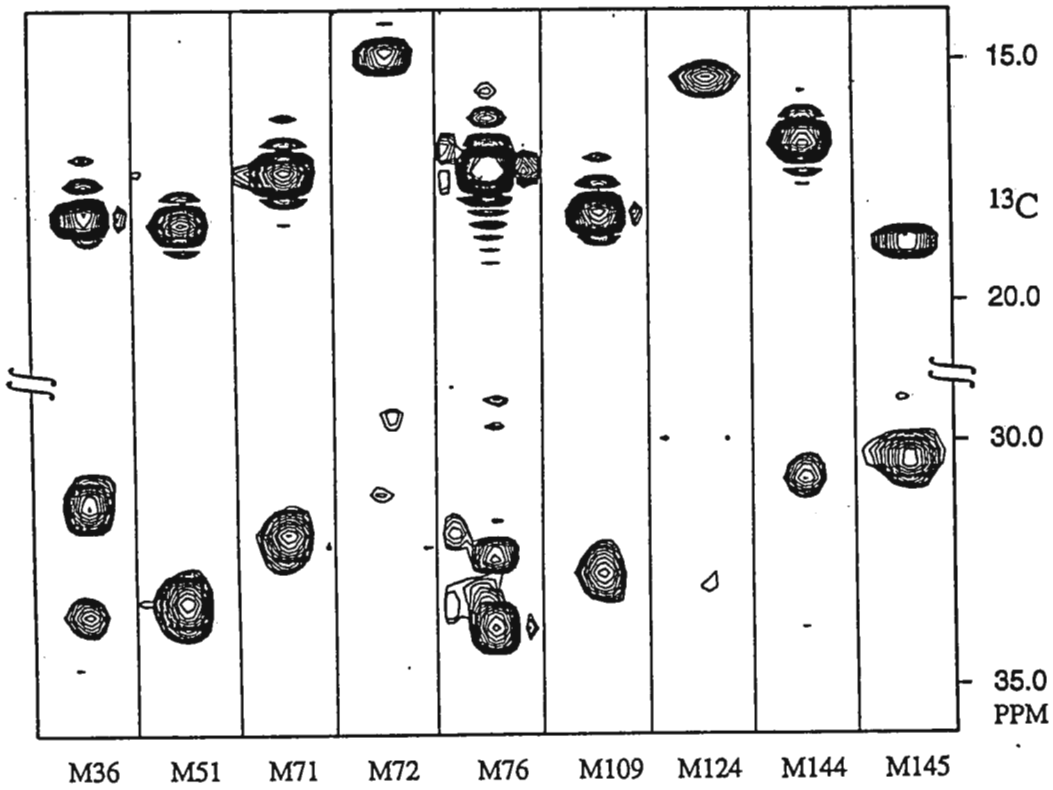

Figure 1. F_1 Strip plot of the 3D LRCC spectrum of the calmodulin/M13 complex, showing the correlations between $C^\varepsilon/H^\varepsilon$ and C^β and C^γ resonances for the methionine residues. The lowest contour level for the "diagonal" (F_1=F_2) peaks is 10 times higher than for the cross peaks (in the 29-34 ppm region). Diagonal and cross peaks have opposite phase. Contours are spaced exponentially by $2^{1/3}$.

FORTHCOMING NMR MEETINGS, *Continued from page 1.*

Symposium on "NMR as a Structural Tool for Macromolecules: Current Status and Future Directions, Indianapolis, IN, **October 30 - November 1, 1994**; Contact: Ms. Padmini Nallana, Coordinator, NMR Symposium, Dept. of Physics, Indiana University Purdue University Indianapolis, 402 N. Blackford St., Indianapolis, IN 46202-3273; Tel. (317) 278-1263; E-mail: PADMINI@INDYVAX.IUPUI.EDU; Fax: (3172) 274-2393. See TAMU NMR Newsletter 425, 31.

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505)989-1073

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995** [sic]; 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.

Additional listings of meetings, etc., are invited.

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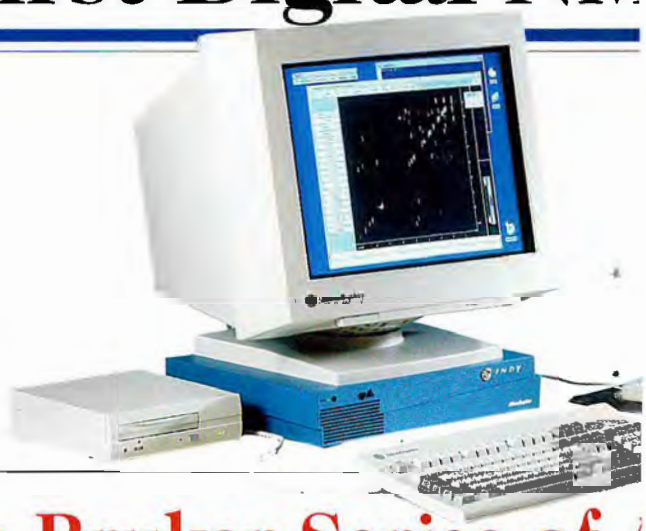

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May 18, 1994
(received 5/20/94)

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

Dear Dr. Shapiro:

NMR Analysis of Multicomponent Polymers

Many commercially important polymers contain two or more components that differ from one another in composition (for copolymers) or tacticity (for homopolymers). This multicomponent characteristic may be the result of deliberate polymer blending, specific synthetic processes (e.g., varying the comonomer feed ratio during copolymerization), or the presence of different types of initiators or catalytic sites. The NMR data for a multicomponent polymer would have contributions from each of its components, and as such would require care to analyze properly.

For two components, the classic work is that of Coleman and Fox[1] whose model assumes the coexistence of two interconverting Bernoullian propagating sites. A two-component model involving enantiomorphic-site and Bernoullian propagation has been employed for Ziegler-Natta homopolymers[2,3]. A similar two-component Bernoullian model has been used for copolymers[4-7]. Some time ago, a generalized multicomponent model has been proposed for these polymers[7,8], and a computer-assisted methodology developed for the treatment of NMR data[7,8]. Whereas the methodology can be used on the NMR data of the polymer *as is*, it has been found that best results are obtained when the NMR data of a *series* of polymer samples are available. Four approaches can be taken:

(1) The polymer is fractionated through a suitable means[7-10,13-15].
(2) During polymerization, the polymerization reaction mixture is sampled at various conversions.
(3) For copolymers, different copolymer compositions are made under similar reaction conditions but with different feed comonomer concentrations[16].
(4) A related series of polymers is obtained, prepared with essentially the same reaction conditions except that one experimental variable is systematically varied[17]. This experimental variable should change the proportions of the components making up the polymer, but does not significantly change the polymer microstructure (e.g., stereospecificity, regiospecificity, and reactivity ratios).

In each approach, the NMR data for the series of polymer samples or fractions are obtained and analyzed in a systematic manner. The methodology has been applied to copolymer sequence analysis of ethylene/propylene copolymer[7-9,16,17], propylene/1-butene copolymer[7], ethylene/1-butene copolymer[10,11], ethylene/1-hexene copolymer[12,16], and ethylene oxide/epichlorohydrin copolymer[14], and the tacticity determination of polypropylene[7,13,17], poly(1-butene)[7,8], and polyepichlorohydrin[15].

An example is shown for the analysis of the NMR data of ethylene/1-hexene copolymer through *Approach 1*. Kakugo et al[18] recently prepared this copolymer, fractionated it using temperature rising elution fractionation (TREF) and analyzed the fractions with ^{13}C NMR. The TREF elution temperature, the weights of the fractions (wt %), and the NMR triad data are given in Table 1.

Through computer-assisted analysis, the polymer can be shown[16] to consist of at least four components with the following Bernoullian probabilities for 1-hexene (P_H):

component 1: $P_H = 0.89$,
component 2: $P_H = 0.70$,
component 3: $P_H = 0.20-0.30$,
component 4: $P_H = 0.025-0.095$.

For comparison, the calculated approximate triad intensities are also given in Table 1. The component weight factors derived from this analysis are shown in Table 2. For better visualization, the component weights are also plotted as a function of copolymer composition in Figure 1. Thus, for this catalytic system there are at least four catalytic sites corresponding to these four components.

The polymer yield for each component can be calculated by multiplying the weight of the fractions (wt %) with the component weight factors (w_i). The calculation is given in Table 2. The products for each component can be summed together to give the polymer yield for that component. It appears that the catalytic site corresponding to component 1 is the most active (56% yield), followed by sites 3 and 4. The details of this analysis can be found in ref. 16.

Yours sincerely,

H. N. Cheng

Table 1. ^{13}C NMR and TREF data on ethylene/1-hexene copolymers made with δ-$TiCl_3/Al(C_2H_5)_2Cl$. Observed data taken from ref. 18; values in parentheses obtained with global analysis (program MINSQ)[a].

Fr.	Elution temp (°C)	Ethylene content	wt %	HHH	HHE	EHE	HEH	EEH	EEE
1	- 30	0.28	79.8	50.0	16.0	6.0	8.0	11.0	9.0
				(51.4)	(15,7)	(4.6)	(7.8)	(9,2)	(11.3)
2	0	0.60	1.5	16.0	13.0	11.0	7.0	20.0	33.0
				(16.9)	(13.8)	(9.9)	(6.9)	(19.8)	(32.7)
3	30	0.73	1.4	8.0	8.0	11.0	6.0	19.0	48.0
				(8.2)	(10.1)	(9.2)	(5.0)	(18.4)	(49.0)
4	50	0.78	1.1	6.4	6.4	10.6	4.3	18.1	54.3
				(5.8)	(8.2)	(8.5)	(4.1)	(17.1)	(56.4)
5	60	0.82	1.4	5.0	5.0	8.0	3.0	15.0	64.0
				(4.1)	(6.5)	(7.8)	(3.2)	(15.6)	(62.8)
6	70	0.84	2.0	4.0	4.0	7.1	2.0	13.1	69.7
				(3.4)	(5.5)	(7.4)	(2.8)	(14.7)	(66.2)
7	80	0.92	1.8	2.0	2.0	5.9	1.0	11.8	77.5
				(1.3)	(1.4)	(5.3)	(0.7)	(10.6)	(80.7)
8	90	0.95	1.9	1.0	1.0	3.0	0.0	6.0	89.0
				(0.8)	(0)	(4.4)	(0)	(8.7)	(86.5)

[a] The program MINSQ was obtained through MicroMath, Salt Lake City, Utah 84121.

Table 2. Results of the pairwise analysis of TREF/NMR data on ethylene/1-hexene copolymer. Component weight factors and polymer yields

Fr.	wt %	component weights				w_i * wt %			
		w_1	w_2	w_3	w_4	1	2	3	4
1	79.8	0.700	0.052	0.247	0	55.9	4.2	19.7	0
2	1.5	0.078	0.294	0.628	0	0.1	0.4	0.9	0
3	1.4	0	0.220	0.464	0.317	0	0.3	0.7	0.4
4	1.1	0	0.154	0.434	0.414	0	0.2	0.5	0.5
5	1.4	0	0.112	0.259	0.631	0	0.2	0.4	0.9
6	2.0	0	0.069	0.197	0.735	0	0.1	0.4	1.5
7	1.8	0	0.055	0.124	0.822	0	0.1	0.2	1.5
8	1.9	0	0.011	0.046	0.943	0	0.0	0.1	1.8
9	5.8	0	0	0	1.000	0	0	0	5.8
10	2.9	0	0	0	1.000	0	0	0	2.9
sum	99.6					56.0	5.5	22.8	15.2

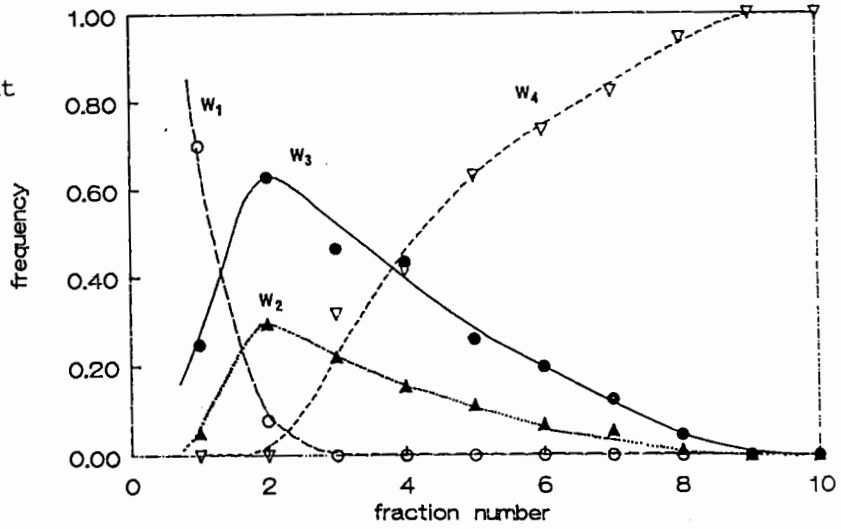

Figure 1. Dependence of the component weights (w_i) as a function of ethylene content for the ethylene/1-hexene copolymer.

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Department of Chemistry

May 6, 1994
(received 5/12/94)

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

^{27}Al and ^{13}C NMR Relaxation in Aminoalanes

Dear Barry:

We have been investigating Group 13-Group 15 reaction chemistry for some time using primarily multinuclear, variable-temperature NMR methods. Recently, two series of aminoalane dimers were reported. Their ^{27}Al chemical shifts fall in a narrow range, indicative of tetracoordinate aluminum. However, $\nu_{1/2}$ for the^{27}Al resonances varies significantly with R and R' in $[R_2AlR']_2$. Our ^{27}Al NMR studies suggest primarily quadrupolar relaxation with a simple correlation time effect. For example, for $[Me_2AlNMe_2]_2$, τ_c is calculated to be 7.3 ps at 22°C by using the Abragam quadrupolar relaxation equation (1961) and with the NQR data of Dewar (1973). This compares favorably with τ_c = 4.0 ps as determined from our ^{13}C T_1^{DD} data for the -NMe_2 group. The E_A values for molecular reorientation as calculated from the variable-temperature ^{27}Al and ^{13}C relaxation data are 10.0 and 12.2 kJ/mol, respectively. In addition, the ^{27}Al $\nu_{1/2}$ varies linearly with molar volume for the $[Me_2AlR']_2$ series (r = 0.987; ten aminoalanes). Finally, for the $[R_2AlNMe_2]_2$ series, where R = Me, Et, Pr^n, Bu^n, and Bu^i, both the ^{27}Al and ^{13}C relaxation rates increase in the order Me < Et < Pr^n < Bu^i < Bu^n. There is a linear correlation between the ^{13}C $(T_1^{DD})^{-1}$ for the -NMe_2 group and the ^{27}Al $(T_2)^{-1}$, where r = 0.997.

Best regards.

Charlie

Charles L. Watkins
Professor

Larry K. Krannich
Professor and Chairman

The University of Alabama at Birmingham
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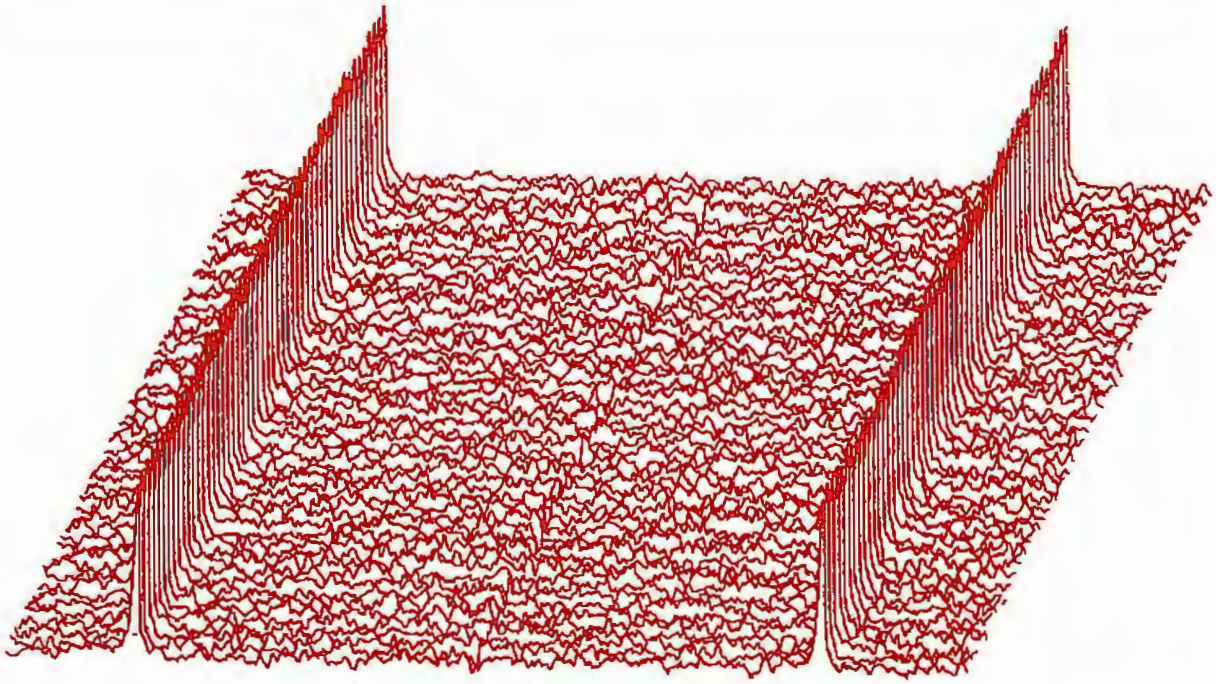

*The series of heteronuclear spin-echo difference experiments shown above were obtained utilizing a UNITY*plus *600 MHz system, a Triple•nmr Pulsed Field Gradient probe, and a 1% $CHCl_3$ sample, locked on deuteroacetone. The data were collected with two 1-msec, 30 gauss/cm gradient pulses applied during the spin echo, one on either side of the proton refocussing pulse. The gradients were applied without the use of B_0 compensation, eddy-current compensation, or gradient-amplifier blanking.*

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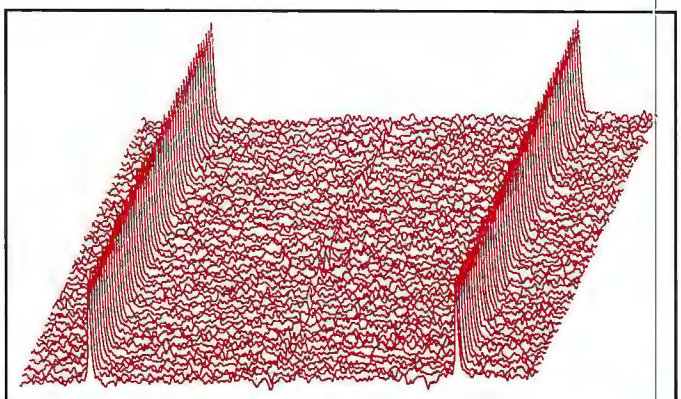

Figure 1 Heteronuclear spin-echo difference spectra of $CHCl_3$ without gradients.

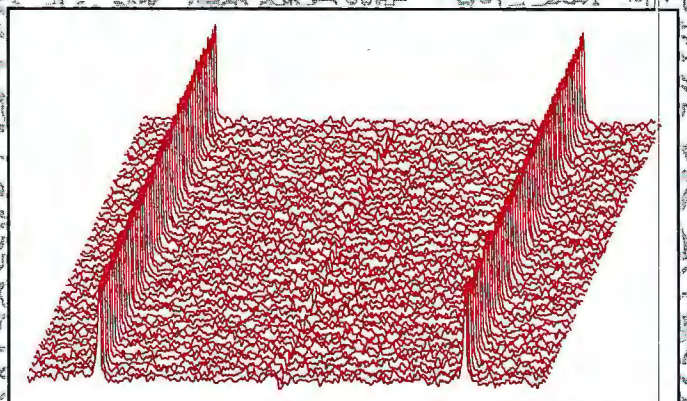

Figure 2 Heteronuclear spin-echo difference spectra of $CHCl_3$ with a single 1 msec, 30 gauss/cm gradient before the ^1H first pulse.

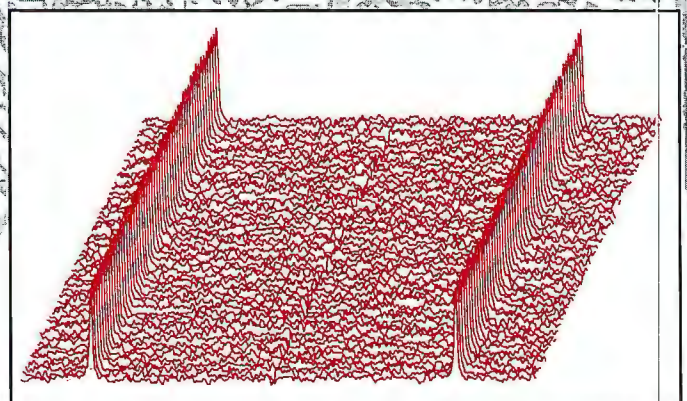

Figure 3 1 Heteronuclear spin-echo difference spectra of $CHCl_3$ with two 1 msec, 30 gauss/cm gradients during the spin echo.

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(received 5/16/94)

SILICON-29 NMR STUDIES OF CROSS-CONDENSATION REACTIONS

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

Dear Dr. Shapiro:

The chemical synthesis of glasses and ceramics provides a convenient method for producing high purity, homogenous materials. A general strategy for the design of improved materials has been the synthesis of multicomponent systems. These efforts may take the form of organic/organic copolymers, organic/inorganic hybrids and multicomponent inorganic materials. The effectiveness of the strategy often depends on the degree of mixing of the components. Mixing can be achieved on a molecular level when covalent bonds are formed between components. In this letter we describe how ^{29}Si NMR can be used to distinguish between self- and cross-condensation reaction products in an organic/inorganic hybrid.

When tetraethoxysilane (TEOS) is reacted with methyltriethoxysilane (MTEOS), three kinds of condensed species are possible, two due to self-condensation ((i) and (ii)) and one due to cross-condensation (iii):

$$T + T \quad \text{---> TT} \quad \text{(i)}$$
$$Q + Q \quad \text{---> QQ} \quad \text{(ii)}$$
$$T + Q \quad \text{---> TQ} \quad \text{(iii)}$$

where T represents the silicon in MTEOS and Q represents the silicon in TEOS. Using limited amounts of water, we are able to investigate the relative importance of self- and cross-condensation during the early stages of the reaction.

The full scale spectra of pure MTEOS, pure TEOS and the 50 MTEOS: 50 TEOS hybrid are shown in Fig 1. The spectrum of the MTEOS sol-gel exhibits signals characteristic of T^0, T^1 and T^2 where the superscript, n = 0 - 3, refers to the number of bridging oxygens. The spectrum of hydrolyzed TEOS exhibits resonances due to Q^0, Q^1 and Q^2 where the superscript, n = 0 - 4, again refers to the number of bridging oxygens and the subscript, m, is the number of hydroxyl groups. The m is omitted for species which are unhydrolyzed. The ^{29}Si NMR of the MTEOS/TEOS mixture shows resonances in both the Q and T regions.

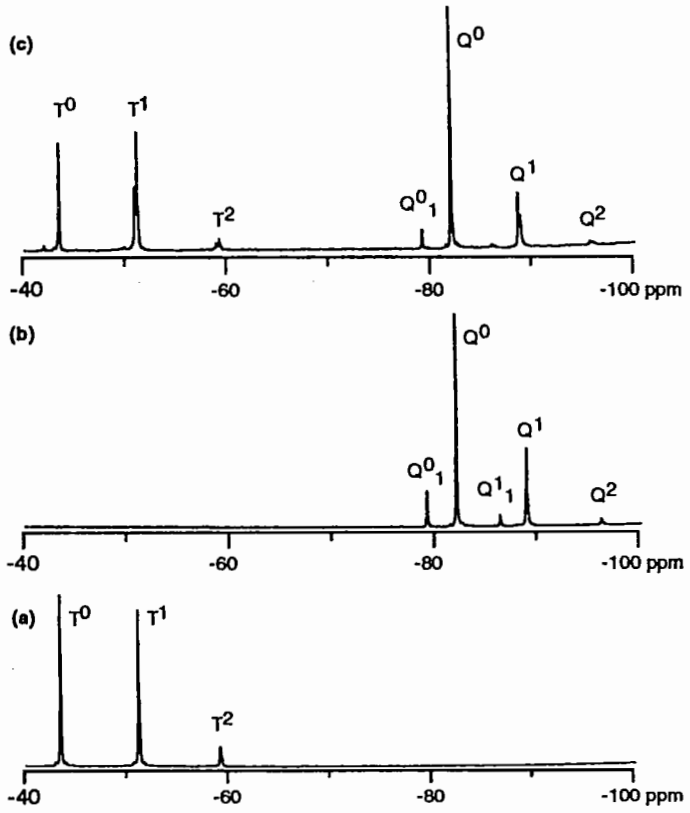

Figure 1. ^{29}Si NMR of (a) MTEOS, (b) TEOS, and (c) the hybrid 50 MTEOS : 50 TEOS sol-gels.

The primary positions of the T and Q silicons, as shown in Fig 1, are determined by the nearest functional groups. For example, all of the resonances near -51.0 and -88.8 ppm correspond to T^1 and Q^1 silicons, respectively. If we expand these regions, as shown in Fig 2(a) and (b), we find that each resonance is actually composed of several components which correspond to the various functionalities of the adjacent silicon. The assignments were made by recognizing that the intensity of resonances of symmetric silicons such as $\underline{T^1}\underline{T^1}$ and $\underline{Q^1}\underline{Q^1}$ are independent of the intensity of any other resonance in the spectrum, while the intensity of the resonance assigned to the $\underline{T^1}T^2\underline{T^1}$ silicon is always twice the intensity of a resonance in the T^2 region (the observed silicons are underlined). Figs 2(c) and (d) show the T^1 and Q^1 regions of the spectrum of the hybrid sol-gel. In addition to the resonances of self-condensed species, there are several resonances which correspond to cross-condensed species. These assignments were made in a similar fashion to those above. For example the intensity of the $\underline{T^1}\underline{Q^1}$ resonance was equal to that of the $T^1\underline{Q^1}$ resonance throughout the course of the reaction.

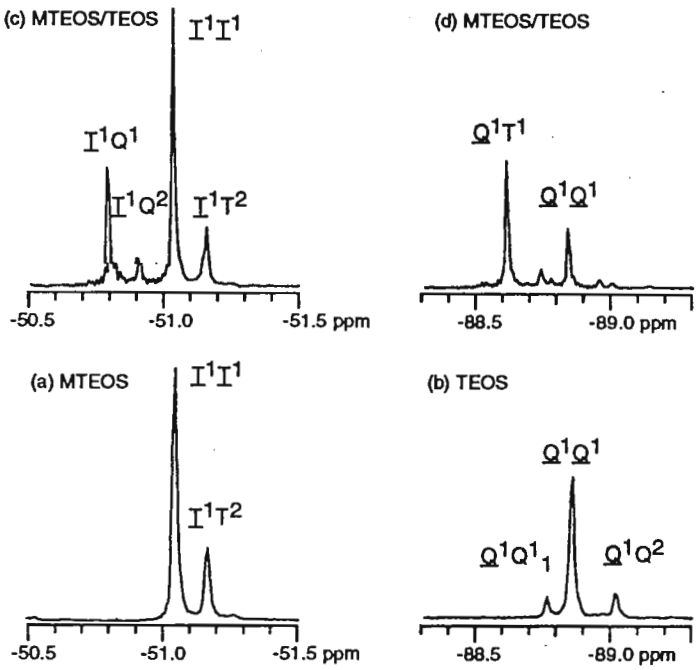

Figure 2. The ^{29}Si NMR spectra (a) the T^1 region of pure MTEOS, (b) the Q^1 region of pure TEOS, (c) the T^1 region of 50 MTEOS : 50 TEOS and (d) the Q^1 region of the 50 MTEOS : 50 TEOS sol-gels.

Careful study of hybrid sol-gels as a function of reactant ratios, water content and reaction times have allowed us to assign numerous resonances of self- and cross-condensed silicons without the difficult and tedious task of synthesizing model compounds. The silicons in intermediate products, such as silanols which cannot be easily isolated, have also been assigned. These spectra are being used to study the kinetics of self- and cross-condensation reactions in a variety of silicon based hybrid materials.

Sincerely,

S. Prabakar
UNM/NSF Center for Micro-Engineered Ceramics
University of New Mexico,
Albuquerque, NM 87106

Roger A. Assink
Sandia National Laboratories
Albuquerque, NM 87185-0367

This work was supported by the U.S. Department of Energy under Contract DE-AC04-94AL8500.
Please credit this contribution to the account of Paul Cahill.

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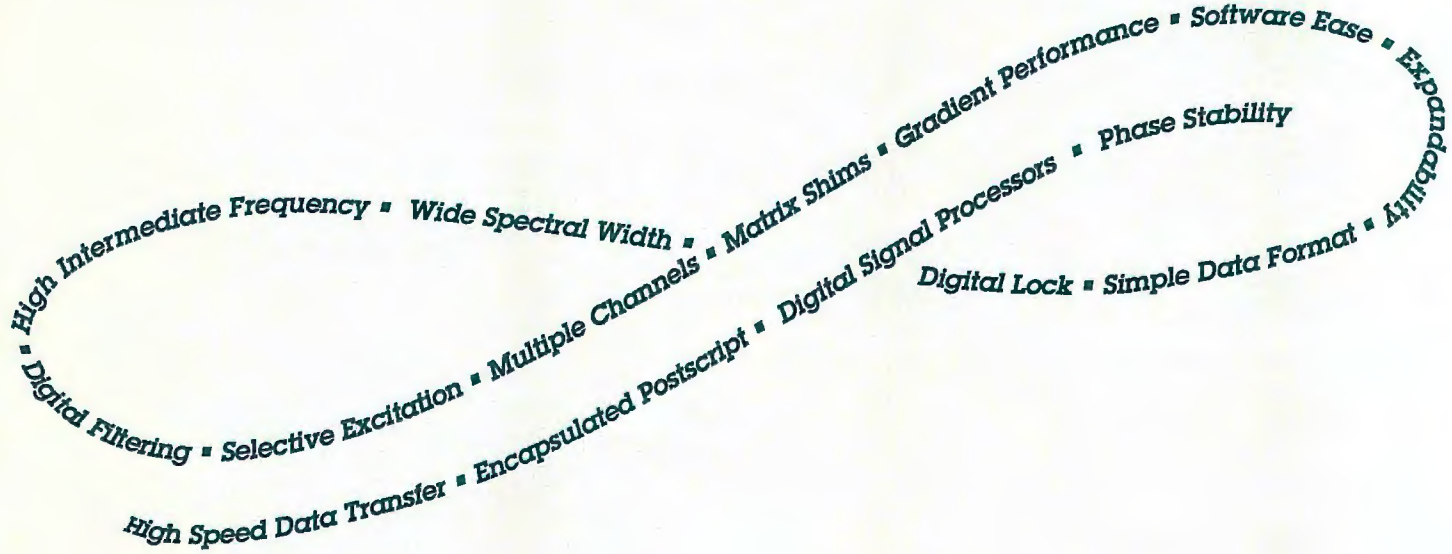

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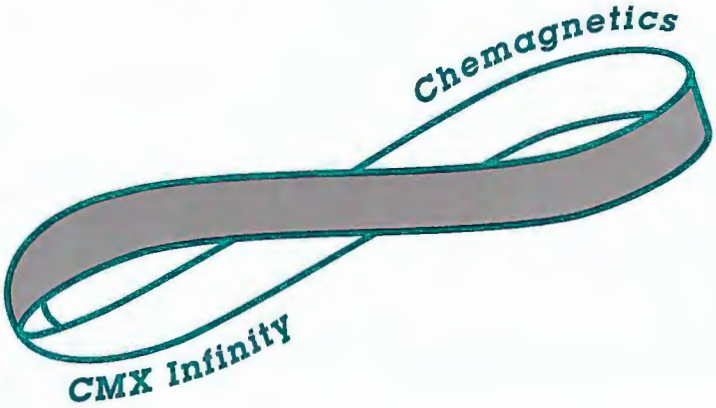

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May 6, 1994
(received 5/12/94)

Dr. Bernard L. Shapiro
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Palo Alto, CA 94303

Z1 Profile Shimming

Dear Barry:

I have recently become aware of a new shimming technique that has proven to be most useful in at least two different situations. The technique is called Z1 profile shimming and was introduced by Woody Conover in a poster (#187) at the 34th ENC in St. Louis. The essence of this technique is to apply a large Z1 gradient to the sample, broadening the linewidth to several hundred hertz. If the magnetic field is otherwise homogeneous, the lineshape should be a rectangular window. Variations from this ideal, square shape are fairly easy to associate with the various higher order axial gradients. Even order gradients (Z2, Z4, ...) will produce asymmetric distortions of the lineshape with one end being high and the other end being low. Odd order gradients (Z3, Z5, ...) produce symmetric distortions with both ends being either too high or too low. In both cases, higher order gradients affect the edges to a greater extent than the middle, and the lower order gradients have a more uniform effect on the entire lineshape. The user then adjusts the higher order gradients for a square line shape, removes the large Z1 gradient and then touches up and fine tunes the Z1/Z2 gradients. All that is required is a mechanism for shimming on lineshape. The Varian Unity console provide this capability, but a simple single pulse experiment with manual adjustment of gradient values between pulses can also be used, although it is not as convenient. The strength of this shimming tool is in being able to definitively find 'good' values for the high order gradient when the homogeneity is poor and/or the lock system does not provide a sensitive measure of magnetic field homogeneity. A major advantage is that the method does not depend on having a sharp resonance to shim on, requiring instead only a single strong line to use to map the field. In fact a relatively broad line such as water is advantageous since the sample can be pulsed rapidly enough to do real time shimming, rather than every 15 to 30 seconds as would be required with a very narrow line.

The first place this is useful is in shimming either a new probe or an existing probe after cryo-shimming a magnet. Two of our 200 Mhz systems were down after the first of the year for new magnet seals. After completing the cryo-shimming and installing the system probe, 45 minutes of Z1 profile shimming was sufficient to get the room temperature shims down to nominal lineshape specification. At this point conventional shimming got lineshape down to typical system performance. In the past, it has sometimes taken a day or more of searching to find values for room temperature Z3 and Z4 that are even close to being proper.

The other place that Z1 profile shimming has been beneficial is in shimming protein samples in 90% water on our 500 Mhz systems. The water resonance is broad enough to provide very little guidance in shimming on the lock level, but does provide a very good signal for profile shimming. By using profile shimming on peptide and protein samples in 90% water, without paying a lot of attention to sample column length, we can typically shim the field in under 20 minutes such that the narrowest features in the spectrum are in the range of 1-2 Hz full width at half height (non-spinning). Before using the profile method, we carefully adjusted the sample column height to a predetermined value and shimmed for as much as several hours only to get rather mixed results.

The single greatest advantage of the Z1 profile shimming method is that it gives the user a mechanism for making a clear decision on the value for each of the high order axial gradients, even when the sample resonances are broad. On samples with very sharp signals and a very narrow lock line, shimming based on lock level will still give superior ultimate results, but the profile shimming can still find a good set of starting values for a new probe or a re-energized magnet.

If someone wanted to explore using this profile shimming, I am aware of two possibilities. First is the shimsim program distributed by Varian in their user library. This is a shimmins simulator, and there are both Sunview and OpenLook versions of this available to run on a Sun workstation. They will permit you to introduce a large Z1 gradient and then examine the effect of misadjustment of the higher order Z gradients.

The second possibility is the SAM (Shimming Ain't Magic) program from Woody Conover at Acorn NMR. This is a shimming simulator program that runs on a PC to permit examination of a lineshape as a function of axial gradients. In addition, the manual that comes with this program provides several pages of detailed description regarding the Z1 profile method in particular as well as a discussion of shimming in general and the effects of probe material susceptibility to sample shimming. This program also includes a command to generate a random set of axial gradient errors so that the user can practice shimming an unknown field, whether by the profile method or any other technique.

Either of these programs will provide the user a chance to explore the effects of various gradients and gradient combinations on a theoretical basis. It is fairly easy to recognize a single gradient error in profile shimming, but it can take some practice to recognize a combination of two or three different gradients. Exploring these combinations with a shimming simulator can save many hours of practicing on the magnet. In practice, real magnets and shim systems are not necessarily ideal or theoretical. My experience with our two 500 Mhz systems bears this out. The older system has an Oxford 23 shim set, and after shimming with the Z1 gradient applied, it is normal to get some Z3 error back as you remove the large Z1 gradient. This is simply the Z3 component of the Z1 gradient. There does not appear to be significant amounts of Z2 or Z4 in the Z1 gradient, however. Our newer 500 has the 39 shim set from Resonance Research. This shim system makes provision for purifying the gradients, so that a Z1 gradient is 'pure' Z1. My experience with this system is that there is virtually no reshimming necessary on the Z3 or Z5 gradients as the Z1 is removed, indicating that the Ultra Shims are indeed significantly purer that those of the older Oxford shim set. I don't know that this additional purity is tremendously useful outside of profile shimming, but it certainly seems useful to know that the Z1 control really does change just the Z1 gradient.

I recommend Z1 profile shimming to your readers as another tool for their toolbox of shimming techniques. It is not a panacea for every problem, but it is a powerful tool to have available.

Sincerely,

Steven K. Silber
Senior Research
Instrumentation Specialist

Shimming Ain't Magic

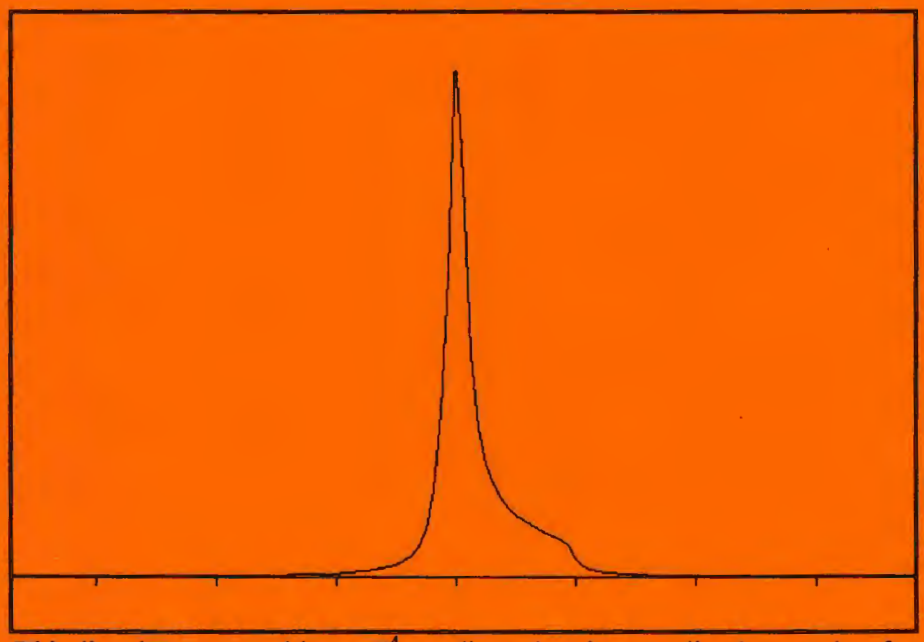
Shim Simulation and Training Software

SAM allows the user to practice on-axis shimming with gradients up to Z^8, providing a controlled environment in which to learn how different shim gradients affect lineshape. **SAM** can also generate a random magnetic field on which to practice shimming. The goal is to develop an understanding of the effects of shim gradients so that the process becomes less frustrating.

SAM comes with a Guide to Shimming which describes

- a systematic shimming procedure
- how to recognize the cause of many common shimming problems
- use of tools such as a Z1 Profile for determining correct values for high order shims
- how magnetic susceptibility affects lineshapes

The Guide to Shimming is also available separately.



This lineshape resembles a Z^4 gradient, but is actually the result of a combination of Z^2 and Z^3. Look familiar?

SAM 1.1 Software for IBM PC (math coprocessor required).....$250.00
(includes Guide to Shimming)
Guide to Shimming (without SAM program).....$100.00

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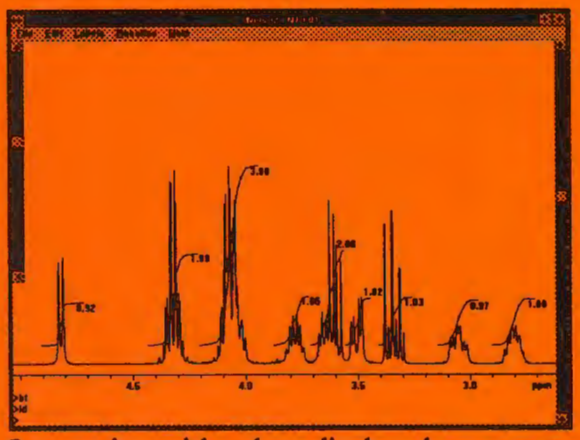

Integration with values displayed on screen

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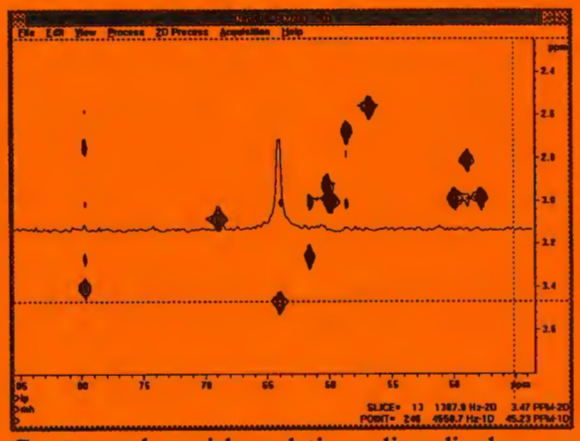
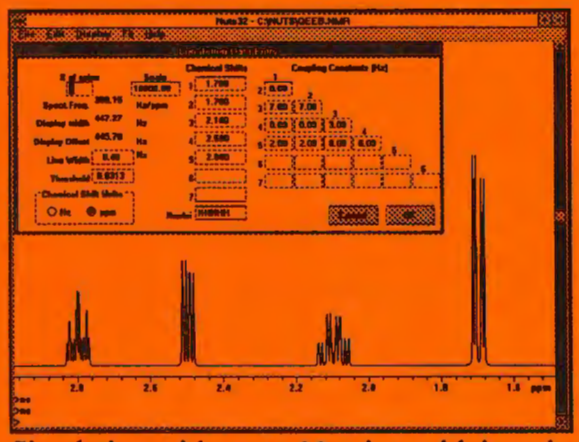


Contour plot with real-time slice display



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15 May 94
(received 5/19/94)

Dr. B.L. Shapiro
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Palo Alto, CA 94303

ACCURACY OF PROTON NMR PURITY DETERMINATIONS

Dear Dr. Shapiro

In recent years with the advent of Good Laboratory Practices and governmental regulations it has become essential to address the question of accuracy and precision in regard to purity determinations. When quantitation has been discussed in the NMR literature the focus has been on determining the optimum tip angle and relaxation delay for a single resonance. However, when high accuracies are desired it is necessary to use an internal quantitation standard of known purity. The addition of a quantitation standard changes the criteria of the optimization: the quantity of interest becomes the relative concentration of the material being assayed; i.e., the integrated intensity ratio, I(sample)/I(std.).

For simplicity, assume that the sample and quantitation standard each produce a single resonance in the NMR spectrum. If the carrier is placed midway between the two peaks then off resonance effects arising from a finite pulse length can be ignored. The use of $\pi/2$ pulses and a relaxation delay equal to 5 times the longer T_2 (= T_1) reduces the variation in intensity anomalies due to transverse interference to ≈ 0.01%. If the ratio of the spin-lattice relaxation times, T_1(std.)/T_1(sample), is approximately equal to unity, then using a relaxation delay of $5T_1$'s is appropriate. When T_1(long)/T_1(short) = 1.25 the error in the ratio of the two magnetizations becomes 0.49% and increases to 0.68% as T_1(long)/T_1(short) ⇒ ∞. Increasing the relaxation time to $7T_1$(long) reduces the error in I(sample)/I(std.) to 0.09% when T_1(long)/T_1(short) ⇒ ∞. Caution still must be used! If any of the resonances chosen for the purpose of quantitation are the product of even a *mildly* coupled spin system, then a relaxation delay of $7T_1$(long) is no longer sufficient. In this case the relaxation behavior for each individual line comprising the multiplet is not described by a single T_1 but a linear combination of "T_1's" (which are not necessarily the same linear combination for each line of the multiplet). The resulting multi-exponential relaxation behavior for lines of complex multiplets can result in *overshoots* for lines with faster initial relaxation rates and lead to gross errors if the relaxation delay is chosen injudiciously. For example, in a mixture containing known quantities of tris-(hydroxymethyl)-aminomethane (TRIS) and acid potassium phthalate (both NIST standards), with relaxation delay equal to $5T_1$ (T_1 estimated from the null tau value for the slowest relaxing line of the AA'BB' multiplet of KH phthalate), the experimentally observed error in the integrated intensity ratio, I(KH phthalate)/I(TRIS), is approximately 12.5%. At $7T_1$ the experimentally observed error is ≈ 4%. Increasing the relaxation delay to $10T_1$ reduces this error to acceptable levels; i.e. to ≈ 0.2%.

Besides the pulse length and relaxation delay a third experimental parameter must be considered if high accuracy quantitations are desired. This final experimental parameter is the number of points/line, which is

defined by the ratio of the digital resolution to the half-width at half-height for a given resonance ($DR/\Delta\omega_{1/2}$). This ratio determines how well the discrete spectrum is described by a continuous lineshape function. The accuracy of integration for the discrete lineshape is dependent on $DR/\Delta\omega_{1/2}$, the choice of integration limits and to a lesser extent the method of integration. For Lorentzian lines 99.9% of the area is obtained when the integration limits are set to $\pm 637\Delta\omega_{1/2}$. Unfortunately, for a typical spectrum consisting of many resonances the use of such wide integration windows in not practical. Although, reducing the integration limits to $\pm 64\Delta\omega_{1/2}$ might avoid contributions due to other resonances it also reduces the accuracy to 99.0%. However, the important quantity of interest is I(sample)/I(std.) and as long as the integration limits for lines are the same, $\pm n\Delta\omega_{1/2}$, no loss in integral accuracy occurs. The extent to which the ratio $DR/\Delta\omega_{1/2}$ effects the accuracy depends on the method of integration. Of the three basic integration methods (Riemann Sums, Simpson Sums and deconvolution) simple Riemann Sums seem to require higher digital resolution to yield the same level of accuracy (compared to a continuous lineshape). In the case of simple Riemann Sums as long as $DR/\Delta\omega_{1/2} \leq 1$ the variation in integration compared to a continuous Lorentzian is less than 0.2%. The word variation is used here instead of error because the difference in the area of the discrete and continuous spectrum is dependent on the fortuitous position of top of the peak relative to the nearest point of the discrete spectrum. Thus, if a proton spectrum covers a range of 10ppm (6000Hz at 600MHz) and $\Delta\omega_{1/2}$ of the resonances is 0.1Hz then 64K complex data points would be needed to describe the FID to fulfill the requirement $DR/\Delta\omega_{1/2} \leq 1$! Zero-filling the FID or using linebroadening are also ways of reducing $DR/\Delta\omega_{1/2}$.

Following these guidelines the error; i.e., difference between the true value and the observed value, of an assay can be kept to within 0.5%.

Practical Tips

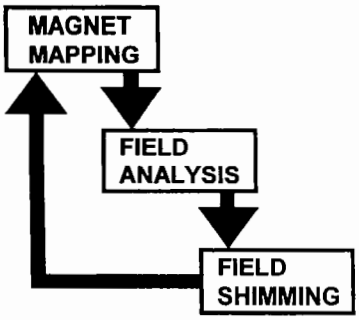
1) tune probe and measure $\pi/2$ pulse for assay sample, **2**) select resonances for quantitation and measure T_1's (remember: impurities tend to have resonances very similar to main product so select peaks carefully), **3**) choose the appropriate relaxation delay: $5T_1$, $7T_1$ or $10T_1$, **4**) select the spectral window and the size of the FID such that $DR/\Delta\omega_{1/2} \leq 1$, **5**) set the number of acquisitions to yield sufficient S/N $\approx$ 1000:1 (although S/N was not discussed here, it has a greater impact on precision than on accuracy), **6**) apodize, Fourier transform and phase the spectrum, **7**) baseline correct each resonance or group of resonances locally, **8**) choose identical integration limits, same $\pm n\Delta\omega_{1/2}$, **9**) integrate each resonance separately and adjust slope and curvature if needed.

Next time I'll answer the question of precision and whether or not the precision of the integration based on multiple experiments overshadows an accuracy of 99.5%?

Dennis L. Hasha

Dennis L. Hasha

Magnet Management for Optimal Performance



The performance of the magnet system used with most NMR spectrometers can be optimized by a three step process in which the inhomogeneties in the magnetic field are mapped, analyzed and corrected. The ideal shim center is identified, the inhomogeneties are fully characterized and appropriate adjustments of the super conducting and room temperature shims are made. This process, coupled with modern probes, provides the spectroscopist with the maximum achievable high resolution NMR performance.

FEATURES	BENEFITS
* Computer automated map-analysis-shim cycle	* Analysis and characterization of inhomogeneities in superconducting magnets
* Helical path electromechanical probe with less than 1 mm^3 sample volume	* Full mapping and analysis in ~ 30 min
* Adjustment of superconducting shim systems	* Optimized in less than 6 hours
* Instalation of serial or matrix shim systems	* Optimized in less than 24 hours
* Automated control of the shim power supply	* Unattended shim calibration and convergence
* 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 approach to optimizing magnet performance includes three discrete components: an automated magnetic field mapping system, a precision current source and a shim system.

The Model FMU- 800 Broad Band Automated Magnetic Field Mapping System

The Model FMU- 800 mapping system is a computer-controlled unit 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 includes an internal broadband RF synthesizer (200-840 MHz), a ^1H spectrometer, and a 24-channel, 16 bit DAC shim driver module. It 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. The mapping system can complete a map in less than 30 minutes.

The Shim System

Resonance Research produces MATRIXSHIM ™ shims for NMR magnets. This series includes a wide variety of shims for 51/54 and 89 mm bore magnets. A typical shim system, the MHU 463/51, 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.

Precision Current Sources

Resonance Research produces the MATRIXPOWER ™ series of precision power supplies for high performance NMR shim systems. These shims 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.

MATRIXPOWER power supplies are configured to meet the need of the specific system and may include analog control input, local or remote potentiometer control, OPTO-22 compatible control, or intelligent, local control.

Total Magnet Management

Resonance Research provides the spectroscopist with a complete system to optimize the performance of your magnet. The automated, iterative three step process of mapping/analysis and shimming ensures that the system provides an optimum homogeneous field. In routine operation, extremely homogeneous and stable fields are ensured by the precision current source.

All specifications are subject to change as part of our continuing improvement program.

For more information contact:
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43 Manning Road
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Tel (508) 671-0811
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DAVIS, CALIFORNIA 95616

May 17, 1994 (received 5/19/94)

Observation of Scalar Cross Peaks in Large Paramagnetic Proteins

Dear Dr. Shapiro:

We have been studying the application of scalar correlation methods to paramagnetic systems, especially paramagnetic proteins. Our early studies (1) showed useful results from simple magnitude COSY (MCOSY) on our test system, the cyanide-ligated form of the 44KDa heme protein horseradish peroxidase (denoted HRP-CN). However, initial attempts to use the TOCSY experiment were unsuccessful, and further careful inspection of MCOSY data showed some cross peaks between non-spin coupled protons (2). Further reflection by ourselves (2,3) and others (4) has now shown that some of the characteristics of high molecular weight paramagnetic systems, rapid relaxation in general and the Curie spin relaxation mechanism in particular, require special considerations for the set-up of scalar correlation experiments and analysis of their results. Some of our recent conclusions are detailed through Figure 1.

Trace A of Figure 1 shows a portion of the hyperfine shifted reference spectrum of HRP-CN with assignments for the heme 4-vinyl group and the proximal His-170. Trace B shows the MCOSY slice through the H170 $C_{\beta 2}H$, producing cross peaks to the geminal $C_{\beta 1}H$ and vicinal $C_{\alpha}H$. But are these cross peaks actual scalar correlation? Trace C shows the phase-sensitive COSY (PCOSY) slice through $C_{\beta 2}H$, showing that the cross peaks consist of antiphase components *in-phase* with respect to the diagonal. This phase behavior indicates (3) that the origin of the cross peaks is actually dominated by cross correlation arising from the effect of Curie spin relaxation on two spatially proximate (but not necessarily spin coupled) protons. Trace E shows the PCOSY slice for the 4_{α} vinyl; the large J and relatively large distances in the vinyl group produce antiphase cross peaks 90° *out-of-phase* to the diagonal, indicating these peaks are truly scalar in origin (3). Trace D shows the slice through H170 $C_{\beta 1}H$; the phase behavior shows its geminal partner's peak is dominated by cross correlation while the peak to $C_{\alpha}H$ (having a larger J_{HH} than $C_{\beta 2}H$-$C_{\alpha}H$) is largely scalar in origin. Hence COSY experiments in large paramagnetic proteins can give peaks due to scalar and/or cross correlation (through space) mechanisms; a careful analysis of phase behavior in PCOSY is required to distinguish between them. In some cases we have seen (2) COSY cross peaks between spatially proximate but completely non-spin coupled protons in the heme pocket.

The above suggests the TOCSY experiment to resolve these ambiguities. As mentioned, initial attempts to use TOCSY were unsuccessful; the first step in obtaining success was to recognize that the rapid T_2 relaxation required the use of very short mixing times; trace F shows the TOCSY slice of $C_{\beta 1}H$ with a mixing time of 6 msec. Due to strong cross relaxation present in a 44KDa system (ca. 50Hz for geminal protons) the opposite phase ROESY response dominates for the geminal $C_{\beta 2}H$. Using CLEAN-TOCSY to suppress cross relaxation results in trace G, showing all scalar cross peaks in phase with the diagonal and giving the clearest evidence of scalar correlation of any of the data in Figure 1. A more complete and detailed presentation of all this should appear shortly (2).

Sincerely,

Jeff de Ropp

Jeffrey S. de Ropp Zhigang Chen Gerd. N. La Mar, Director

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(4) I. Bertini, C. Luchinat, D. Tarchi *Chem. Phys. Lett.* 203, 445-449 (1993).

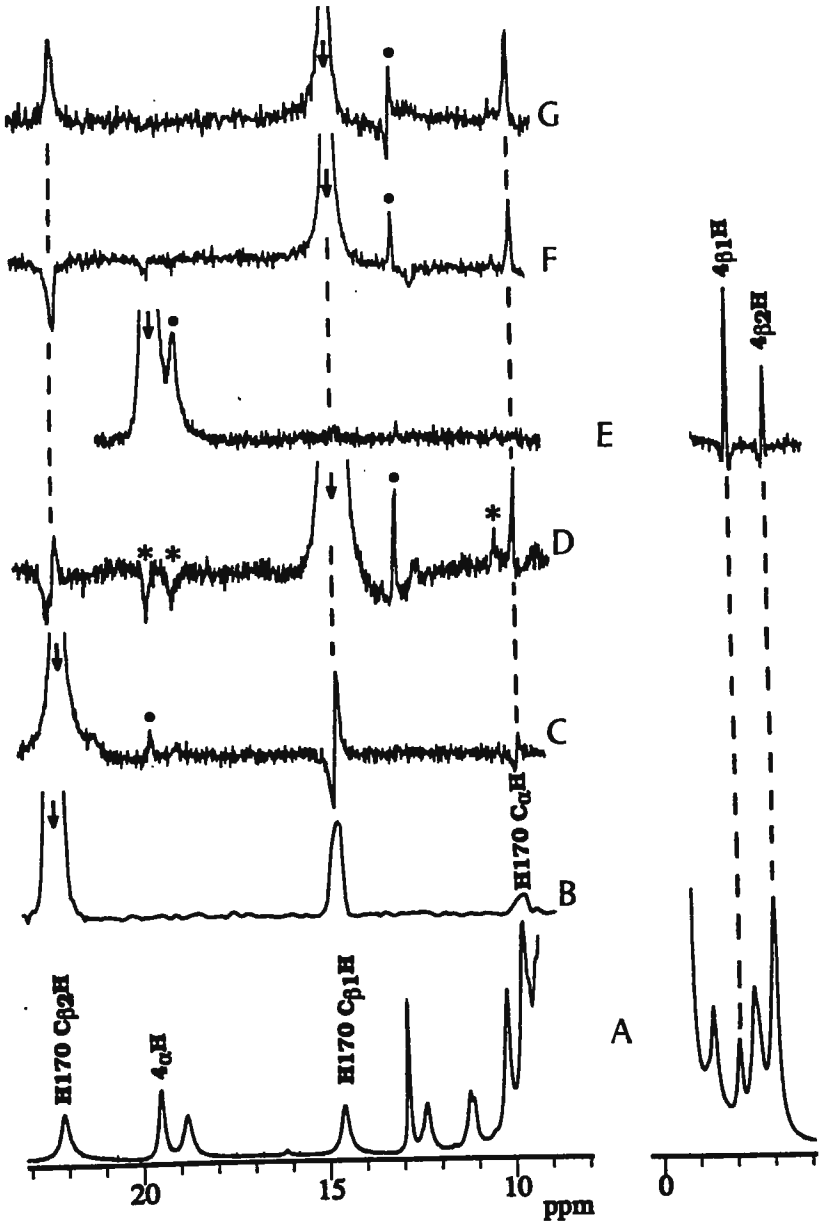

Figure 1: Traces of HRP-CN at 55°C, 500MHz, as explained in text. (*) denotes artifacts and (•) off resonance effects.

POSITION AVAILABLE

NMR Spectroscopist/Engineer position at the UC Davis NMR Facility. Principle duties: maintain/repair instruments and assist users. Must have knowledge of FT-NMR and relevant electronics; experience with field gradients and probe building preferred. Opportunities exist for collaborative or independent research. Appointment and salary commensurate with experience. Submit CV and names of three references to: G.N. La Mar, NMR Facility, UC Davis, Davis, CA 95616 by July 15. *The University of California is an equal opportunity/affirmative action employer.*

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BIOLOGICAL N M R CENTRE

4th May, 1994
(received 5/11/94)

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

Spectral Data Conversion and Baseline Correction Programs

Dear Dr. Shapiro,

Our laboratory uses a combination of commercial and academic packages, including FELIX, NMRCOMPASS, ANSIG, EASY and UXNMR, to carry out routine NMR processing, assignment and data analysis. However, each of these packages produces and/or requires spectral data of distinct format. In order to avoid the need of repeating the tedious data processing procedure for different NMR analysis package to produce the spectral data of the required format, we have developed an inter-conversion program (**MTX2MTX**) to convert processed spectral data into formats required by the various packages mentioned above as well as spectral data formats defined by the user. The generalised modules developed for **MTX2MTX** to read spectral data of different format have also been incorporated directly into utility softwares developed in-house. With this flexible spectral data format approach, the user of these utility programs can even cut out the data conversion procedure.

One such utility program is **NDBASE**, which is a fully automatic baseline correction program for NMR spectrum of any order of dimensions. In many experiments, the first few data points of the FID may be falsified due to penetration of the pulses into the receiver and to the transient response of the audio filters to the incoming signal (1). These mistakes in the first few data points will cause baseline offset and baseline roll in the NMR spectrum (2). Many methods have been proposed to correct the baseline problems although not all being satisfactory. We have hence developed a reliable and fully automatic baseline correction program.

The routine used by **NDBASE** to perform automated recognition of baseline regions in a selected 1D slice is an improved version of the algorithm proposed by Dietrich et al. (3). Briefly, the numerical first derivative of the selected 1D data is obtained in order to eliminate effects of baseline offset and baseline roll. An initial threshold, which is used to differentiate the baseline from peak areas, is calculated from the MEAN + 3* STANDARD DEVIATION of all the data points in the entire pseudo power spectrum. A new threshold is computed using points below the threshold. This procedure is repeated until a consistent final threshold is reached. Finally, baseline regions with single data point or less data points than one or both of the neighbouring peak regions are eliminated from the baseline list since they most likely correspond to peak maxima or saddle parts between two peaks in the original 1D data. Least-squares-fit polynomial up to any degree selected by the user can be used to fit the identified baseline regions, though polynomial up to fourth degree in general will be adequate. The user of **NDBASE** also has the options to select a submatrix area and one or more dimensions in which the baseline correction will be performed

The programs **MTX2MTX**and **NDBASE** have been used routinely to process 2D and 3D NMR spectra measured in our laboratory. Fig. 1a shows a raw 2D NOESY spectrum of Cloramphenicol acetyl transferase - Coenzyme A complex without baseline correction while Fig.1b shows the same spectrum after baseline corrected by **NDBASE** along $\omega 2$. At present, these programs have been implemented on Silicon Graphics workstations. Both programs have been developed in modular routines written in Fortran77 and C languages, therefore they can be readily implemented into other computers.

Yours Sincerely,

Kong Hung Sze

Kong Hung Sze

Gordon C.K. Roberts

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2. D.G. DAVIS, J. Magn. Reson. **81**, 603 (1989).
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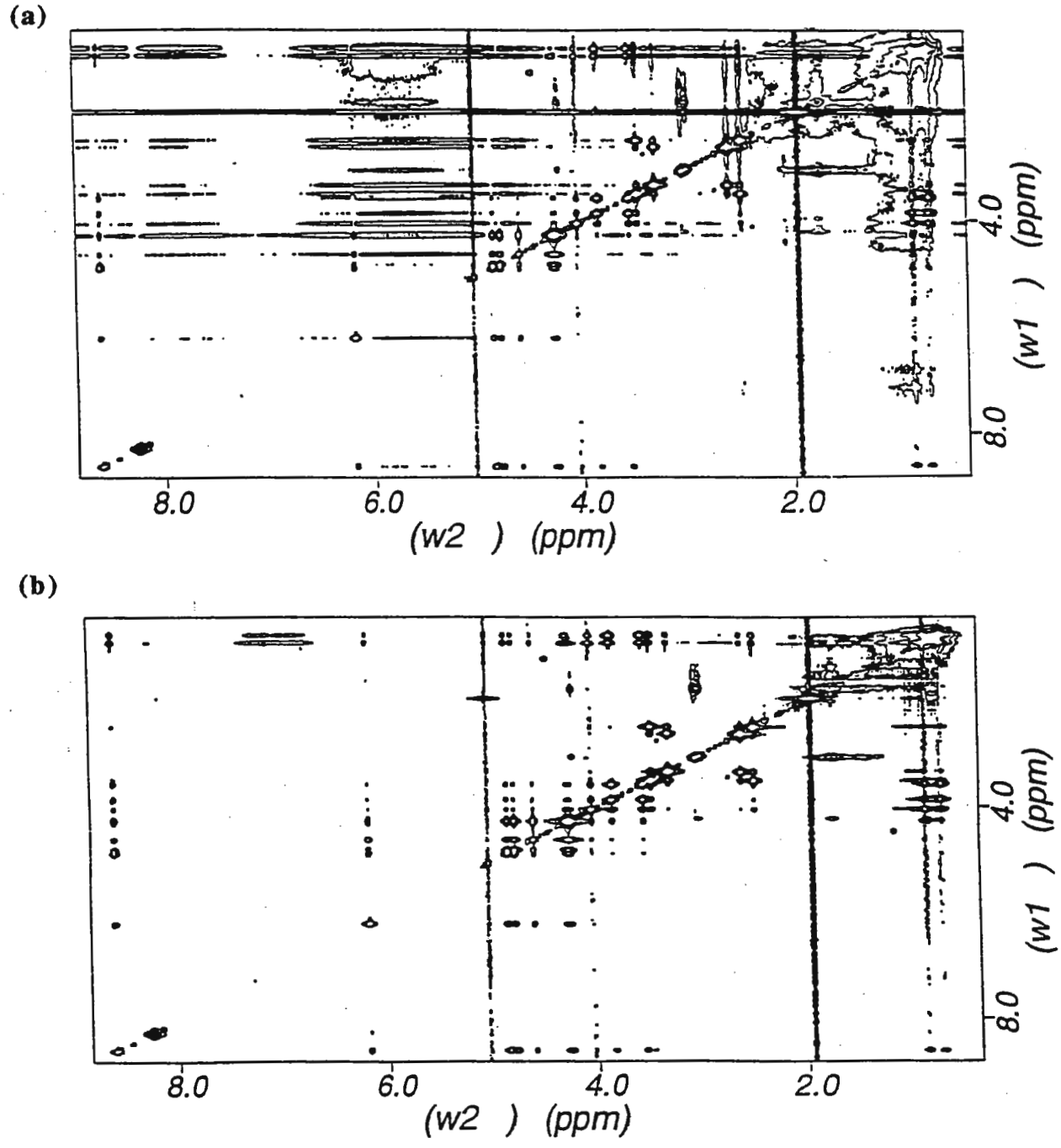

Figure 1. 2D NOESY spectrum of Cloramphenicol acetyl transferase - Coenzyme A complex: (a) raw data without baseline correction; (b) baseline corrected by **NDBASE** along ω2.

TAMU NMR Newsletter

Editor/Publisher: Bernard L. Shapiro

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Notice: In the hope that advertising revenues will hold up, the subscription rate for the October 1994 - September 1995 year will remain at the current level. Invoices will be mailed on 1 July for receipt of payment by 9 September. Please help by processing your invoice promptly. Many thanks.

BLS 1 June 1994

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

Deadline Dates

No. 431 (August)	22 July 1994
No. 432 (September)	26 August 1994
No. 433 (October)	23 Sept. 1994
No. 434 (Nov.)	21 October 1994

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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.

TAMU NMR Newsletter

Editor/Publisher: Bernard L. Shapiro
966 Elsinore Court, Palo Alto, CA 94303, U.S.A. (415) 493-5971; Fax: (415) 493-1348.

* * * Help ! Help ! Help ! **Help !** **Help !** * *

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i) For those with computers, try using a **smaller type font**. The body of this page is printed in 10 point type, which I believe is adequate for most purposes. Even 12 point is acceptable, I suppose. The computerized can also employ non-integral spacing of lines so that sub- and superscripts don't collide with lines below and above.

ii) **PLEASE** avoid *excessive* margins, but you must **leave no less than 0.5" (1.3 cm) margins on both sides and on the top and bottom of *all pages*, including figures, etc.**

Instruct your secretaries to avoid normal correspondence esthetics or practices, however time-honored or 'standard' ! This page has margins on both sides of 0.6" (*ca.* 1.55 cm), which is very adequate. Margins of the same size at the top and bottom are sufficient also, but don't worry if there is more space at the end of your document, for I can often use such spaces for notices, etc.

Also, please avoid large amounts of unused space at the top of letters. Give thought to the sizes of figures, drawings, etc., and please mount these so as to use the minimum space on the page.

***** If you have a two- or three-page contribution, please **do NOT staple the pages together**. *****

You are reminded that regardless of the standard paper length you use, *all material* - letterhead, text, figures, addresses printed at the page bottom, *everything - must end no more than 10" (ca. 25.3 cm) from the top of the paper.*

iii) 'Position Available', 'Equipment Wanted', and Similar Notices. These are always welcome, but not for subscription credit, of course. Such notices will appear, however, *only* if received with these necessarily rigid constraints: a) Single spaced; b) both side margins 0.6 - 0.7" (1.5 - 1.7 cm.)- NOT WIDER; c) the minimum total height, please, but definitely no more than 4.5" (11.5 cm.) This will let me place such notices wherever a bit of space occurs.

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Contributions which fail to meet any of these specifications may be returned for re-working.

Thank you! Your cooperation in making the Newsletter economical and tidy-looking will be appreciated, as will your efforts to keep my work to a reasonable level.

B.L.S. 5/94

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