TEXAS A&M UNIVERSITY

# NMR NEWSLETTER

No. 362

November 1988

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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is *not* permitted, except by direct arrangement with the author of the letter, and the material quoted *must* be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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## FORTHCOMING NMR MEETINGS

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

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

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

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

San Francisco Symposium - *In Vivo* Magnetic Resonance Spectroscopy II, March 31 - April 2, 1989; San Francisco, California; Contact: Veterans Adm. Medical Center, Magnetic Resonance Unit, 4150 Clement Street (11D), San Francisco, CA 94121. See Newsletter 362, 69.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence Should Be Addressed To:

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

(415) 493-5971

DEADLINE DATES

No. 364 (January) — 16 December 1988
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No. 366 (March) — 17 February 1989
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September 24, 1988

Dr. Barry Shapiro
TAMU NMR Newsletter

Dear Dr. Shapiro:

**BIG PLOTS FROM LITTLE LASERWRITERS**

Several contributors have commented on using a laser writer as an output device(i.e. plotter) for NMR spectra. We have been doing this for some time, using a little set of programs developed from Hare's FTNMR. Of possible use to others is a program which will rescale the plot, and also produce 4,9,16,25... sheets of standard paper output expanding a plot to a very large scale for ease of examination. Producing such large plots using our Bruning plotter driven from the spectrometer had been a ticklish proposition, with many runs failing because of dry pens, or more technologically advanced failures, of the kind well known to all readers.

It still takes quite a time to produce these plots, and the program is currently limited to about one million drawn vectors. You also have to trim the pages ( there are cut marks), and tape them together. I am also unsure that it uses exactly the same format as Dennis Hare's current '.plt' files, but that should be easy for users to change. I am happy to send a listing of the fortran source and a UNIX shell to anyone interested, who requests it via electronic mail (addresses above). The 'manual' page for the program is reproduced below.

Sincerely,
David Cowburn David Cowburn

**NAME**
plotfx1 - expanded and multisheet plots from RUNMR output using the pm=3 option
**SYNOPSIS**
**plotfx1** *filename* {# *sheets* { *scale factor* } }
**DESCRIPTION**
*plotfx1* controls filters to produce and reformat the output from runmr to files and into the laserwriter. THIS OPTION SHOULD BE USED FOR LARGE SCALE VERY HIGH RESOLUTION PLOTTING. USE the 4014 emulators and screen dumps on the SUN and NDS terminals for general low resolution work.
*Multisheeting* can be done by entering a small integer as the second argument after the single filename, usefully in the range 2-4; each axis will be divided by this number ( min 1) to give 4,9,16,25... sheets per plot. Higher numbers than 4 are possible but not recommended. If there is no second argument, then one sheet is produced.
*Scaling* can be accomplished by entering a single number to act as both x and y scales other than 1.0 Useful ranges are 0.5 - 1.5. This is the third argument. The default value is 1.5.
Examples
plotfx1 test.plt - produces a single sheet plot of 1.5x1.5 scale.
plotfx1 test.plt 3 - produces nine sheets with the 1.5x1.5 scale
plotfx1 test.plt 2 1.2 - produces 4 sheets with a 1.2x1.2 scale.
**FILES**

/usr/local/bin/plotfx1 The shell for plotfx1.
/usr/local/bin/plotfx.outThe active fortran program for plotfx1.
/usr/spool/lwThe spool area for the laserwriter
/usr/local/src/plotfx.fSource for the program.

**AUTHOR**
David Cowburn
**BUGS**
There is a limited buffer, about 1M data entries. A message will be produced and the program continues with the full buffer if the limit is exceeded ( unlikely).
There is a builtin overlap of parts of the multisheets, to permit pasting together.
Because the toner tends to fade first at the edges, there may be difficulty making multisheet copies that are highly aesthetic. Probably one sheet can ALWAYS be used for illustration purposes.
The algorithm that windows the graphs uses a test for whether a vector enters the displayed space, excluding the overlapped region. The overlapped regions may therefore have SOME missing vectors. The 'true' display area will be correct.
The plotting at the laserw is slow, and there is the possibility that multiple runs will overflow the spool space. The output files of the form tmp{num} are in the current directory, and should not be deleted before the plot is produced. These files can be previewed with the 'tek' filter.
BE PATIENT. A large multiple contour plot may take a considerable time to process and to plot.
Unlike previous 'plotf' commands, this leaves your filename alone. Disposing of the '*plt' files is your business.

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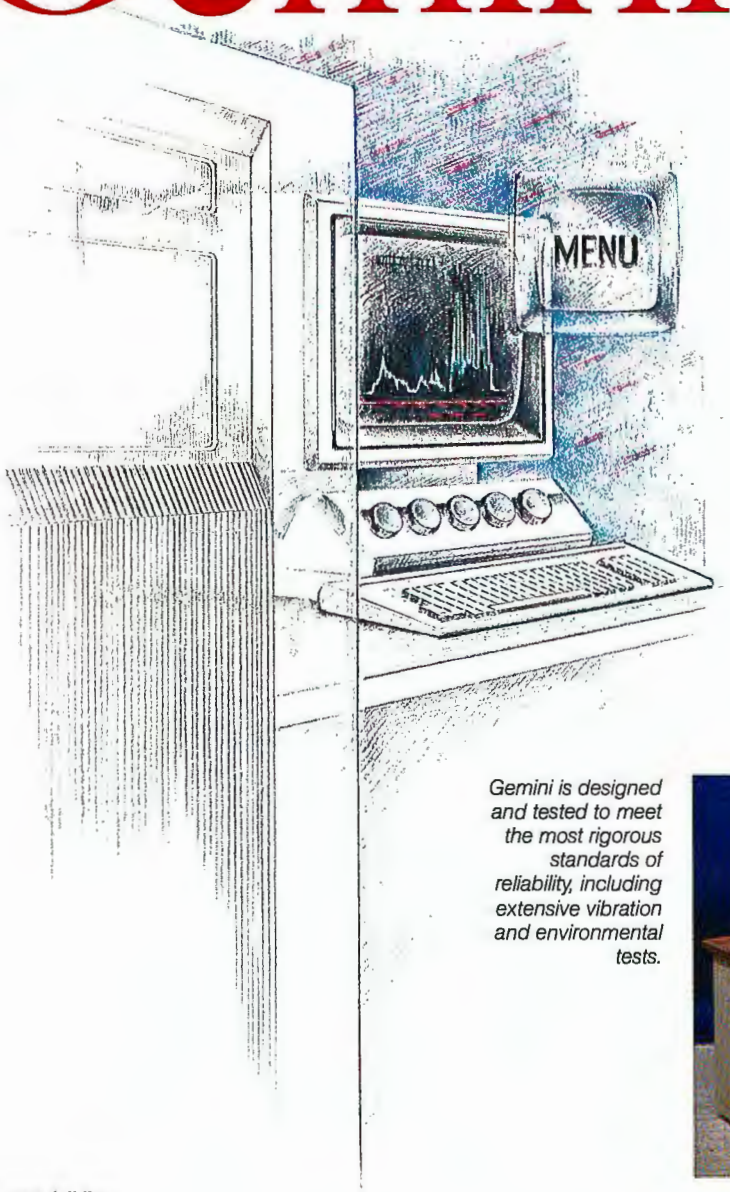


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Subject
**High field $^{17}O$ NMR on aqueous solutions of Al(III), Ga(III) and In(III) salts**

Sub-division
Department of Organic Chemistry

Dear Dr. Shapiro,

Recently, a Varian VXR-400 NMR was installed in our laboratory and so we did some experiments to get an idea of the possibilities and non possibilities at this high field. Because of our interest in metal ion coordination in aqueous solution, we performed some $^{17}O$ NMR experiments on an aqueous solution of $Al(NO_3)_3$. Surprisingly, we observed a shoulder to the bulk water signal at 25 °C. Raising the temperature to 75 °C caused narrowing of the signals, and two separated peaks could be observed (Fig. 1). Integration of the signals relative to the $NO_3^-$ $^{17}O$ signal, showed that the peak at 24 ppm corresponds to six oxygens. Therefore, this peak can be assigned to the slow exchanging water ligands of the hexa-aquaaluminum-ion: $Al(H_2O)_6^{3+}$.
The same experiment was performed on an aqueous solution of $Ga(NO_3)_3$ and once again a shoulder to the bulk water signal could be observed (Fig. 2). However, raising the temperature caused coalescense of the signals, presumably due to enhanced ligand exchange rate of the $Ga(H_2O)_6^{3+}$ ion.
An $^{17}O$ NMR experiment on an aqueous solution of $In(NO_3)_3$ revealed only one water signal, probably because of fast ligand exchange between the complex and the bulk.
Until recently, the only way to observe the bound water molecules was by adding a shift (Co(II) <1>) or relaxation (Mn(II) <2>) reagent to the solution. Obviously, the introduction of a second metal ion to the solution is a serious disadvantage in coordination chemistry research.
Meanwhile, Oldfield et al <3> and Akitt et al <4> reported $^{17}O$ NMR experiments on base hydrolyzed Al(III) solutions . The peak at 24 ppm was assigned to both bound water and hydroxy oxygens of the Al-dimer.
Currently, we are using $^{17}O$ NMR of AL(III) bound waters in a study of the coordination of Al(III) by (poly)hydroxycarboxylates.

Sincerely,

F.R. Venema J.A. Peters H. van Bekkum

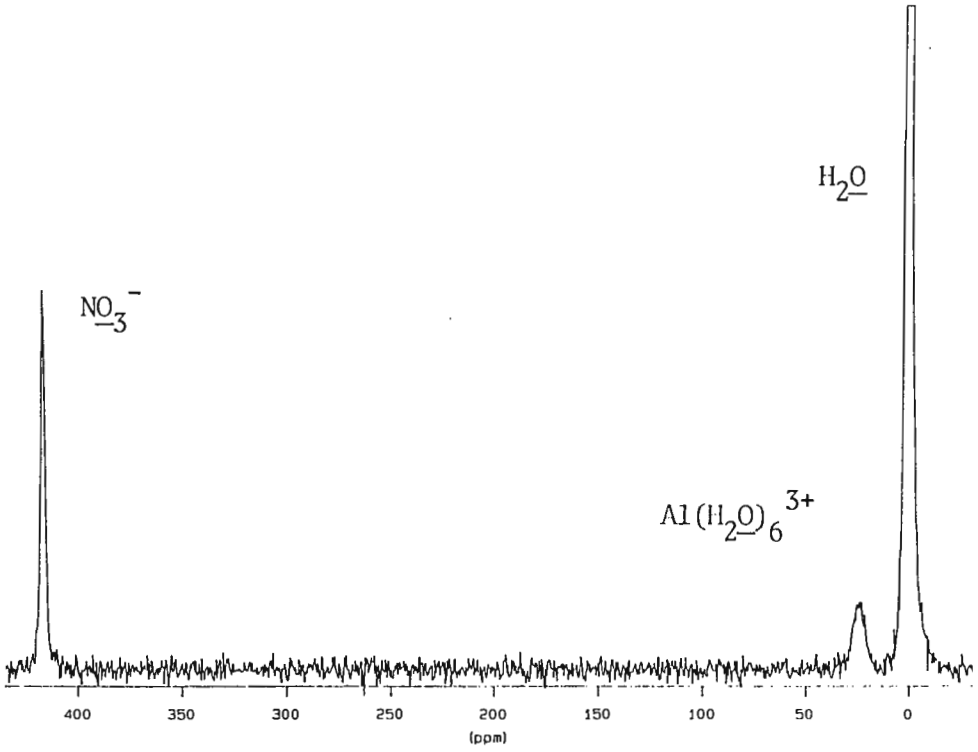


Fig. 1; 54.2 MHz $^{17}O$ NMR spectrum of 0.5 M $Al(NO_3)_3$ solution in $D_2O$ (pH = 0.5) at 75 $^{o}C$.

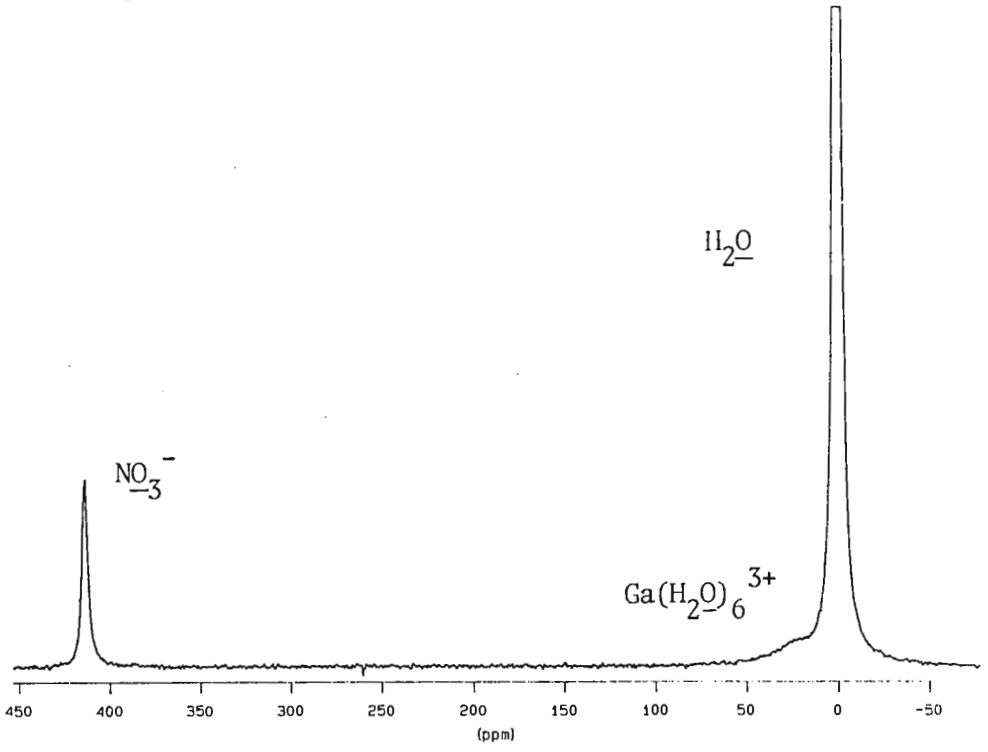


Fig. 2; 54.2 MHz $^{17}O$ NMR spectrum of 0.5 M $Ga(NO_3)_3$ solution in $D_2O$ (pH = 1.2) at 25 $^{o}C$.

<1> Jackson, J.A.; Lemons, J.F.; Taube, H.; J. Chem. Phys. **1960**, 32, 553.
<2> Hugi-Cleary, D.; Helm, L.; Merbach, A.E.; Helv. Chim. Acta, **1985**, 68, 545.
<3> Thompson, A.R.; Kunwar, A.C.; Gutowsky, H.S.; Oldfield, E.; J. Chem. Soc. Dalton Trans. **1987**, 2317.
<4> Akitt, J.W.; Elders, J.M.; J. Chem. Soc. Dalton Trans. **1988**, 1347.

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(received 9/28/88)

Dear Sir:

Analysis of Nuclear Magnetic Resonance (NMR) Spectroscopy data requires interpretation of data in the time and frequency domains. Our research group in the Chemical Engineering Department at the University of California at Berkeley has developed computer programs for NMR data manipulation and analysis based upon the **ASYST** software package. **ASYST** is a popular high level software package for the IBM PC environment available from Macmillan Software Company. The high level matrix manipulation subroutines provided by **ASYST** simplify the task of processing large data arrays.

One program, *NMRASYST*, apodizes, left shifts, smooths, Fourier transforms complex time domain data, and interactively phase corrects resultant frequency domain data. This program also autobaseline corrects the data upon loading. The data fitting programs developed, *FIT* and *TSFIT* use the newton-raphson convergence method to fit data to model functions. The programs return a plot of the data and best fit, optimized parameters, and parameter uncertainty based upon the goodness of fit. In *TSFIT* (or "time space" fit), the user must enter amplitude-time data pairs. For time domain fitting, some model functions are linear combinations of exponential decays. Variations of this program can use the general solution to the first order decay equation as it's model function as well as fit the logarithm of the data. Figure 1 shows an example of *TSFIT* applied to the rotating frame relaxation of protons in p-hydroxybenzoic acid/polyethylene terephthalate 80/20 copolymer. There is also a routine called *FIDASYST* which integrates the norm of the free induction decay. The systematic error caused by noise is corrected for and the uncertainty of the integration is calculated using a determination of the baseline noise amplitude. The free induction decay (FID) can also be fit with a polynomial using the *G0* routine. This program treats the FID as a complex array, phases both the x and y data sets, and given the dead time will extrapolate to time=0 before fitting a polynomial (using an F test) to the free induction decay from a data file.

The *FIT* programs used for the frequency domain fitting take Fourier transform data directly from data files on floppy or hard disks. For frequency domain fitting, the model functions available include: simple lineshapes (gaussian or lorentzian); compound lineshapes made up of linear combinations of gaussian and lorentzian lineshapes (specifically two and three gaussian lineshapes, and a gaussian lineshape with either one or two lorentzian lineshapes); and some specialized convoluted "heterogeneous" lineshapes found in solid state NMR spectroscopy (in particular a gaussian-convoluted Pake doublet with possible addition of a gaussian and/or lorentzian lineshape). An example of the latter two lineshapes can be found in figures 2 and 3 below. Figure 2 shows a proton magnetic resonance spectrum of amorphous hydrogenated silicon with a gaussian lineshape (dark line) of about 25 kHz FWHM, combined with a lorentzian lineshape to yield a good theoretical fit to the data (outer curve). In Figure 3, a proton spectrum from the polymer p-hydroxybenzoic acid/polyethylene terephthalate 80/20, a Pake doublet is convoluted with a gaussian lineshape (not shown) to yield the dark curve through the data. A built-in subroutine in the *FIT* programs calculates the zeroth, first, second, and fourth moments of the data. Another version, which uses an asymmetric chemical shift powder pattern as it's model function is under development (but will probably first be implemented in *Mathematica*, see below). Other frequency domain programs include integration routines which both baseline correct and integrates FFT data directly from data files.

Data and fitted lineshapes can be ported from the ASYST environment on the IBM PC's to many useful graphics programs on the Apple Macintosh for POSTSCRIPT display and laserwriter output. In addition to standard Mac programs like MacDraw II and Cricket Graph, more advanced software is beginning to be utilized to perform everything from data acquisition and analysis, to technical presentations on a Mac II. Specifically, *Mathematica* (a system for both numerical and symbolic calculations from Wolfram Research, Inc.) is being used to replicate and expand the functionality of the ASYST programing mentioned above. Hopefully, this environment will prove useful as powerful graphics implementations of *Mathematica* become widely available on UNIX platforms, Sun workstations, IBM's OS/2 PC's, and even as the standard computing environment to be bundled with the new NeXT workstation (scheduled for release on October 13,1988 as of this writing). *Mathematica* is an interpreted language itself and can output expressions in C or Fortran as well as TEX for typeset papers or presentations. *Mathematica* also produces two and three-dimensional color graphics in POSTSCRIPT. The faster coprocessor and larger RAM available (8 Megabytes) in the Mac II allow for more complex data analysis techniques within a single platform. The goal is to implement the aforementioned functionality of the ASYST programs above within the standard

computing environment of the *Mathematica* kernel on the graphical interface of the Mac II front end. The *Mathematica* kernel can also be run on another machine (like a microVAX) and accessed over a network by the Mac front end. *Mathematica* "notebooks" on all aspects of NMR data analysis are being worked on to form a user library with which various lineshape fitting algorithms can be applied to spectra within the Mac environment.

Figure 1: Rotating frame relaxation in HBA/PET 80/20

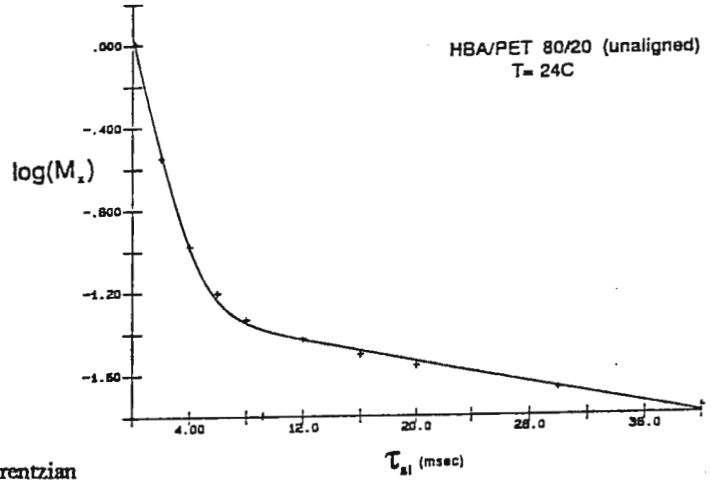
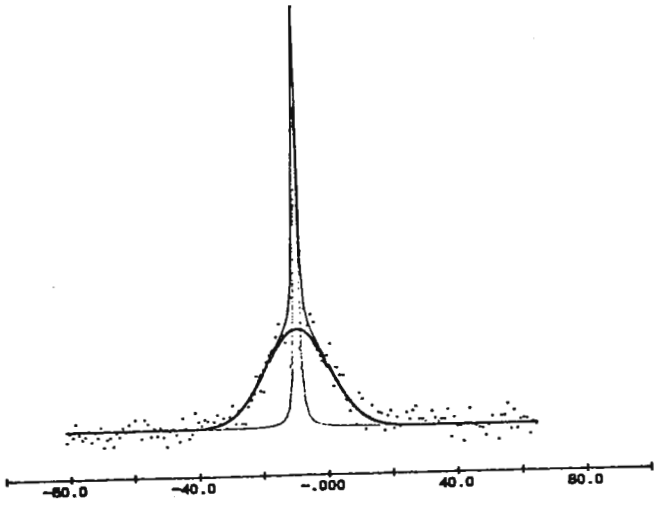



Figure 2: Gaussian and Lorentzian



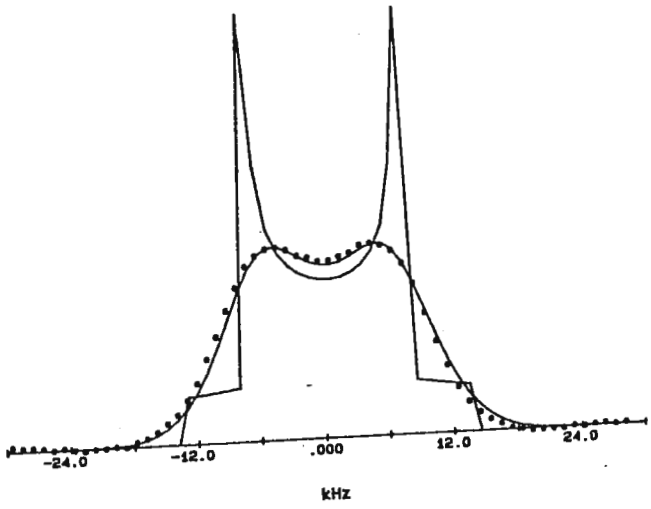




Figure 3: Gaussian Convoluted Pake Doublet

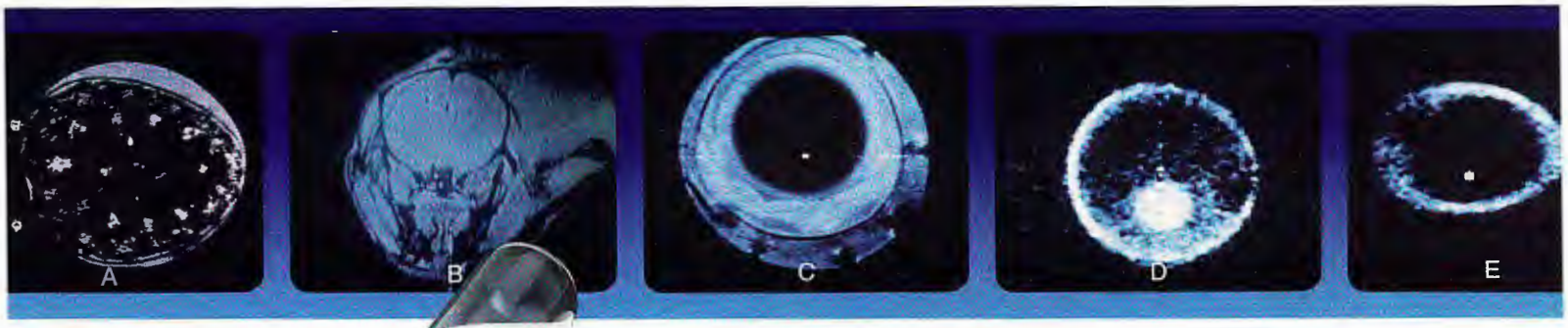
Sincerely,

Karl Amundson
Research Associate
Chemical Engineering

Bruce Berkoff
Research Associate
Biophysics

Jeffrey A. Reimer
Associate Professor
Chemical Engineering

# The NMR evolution continues:



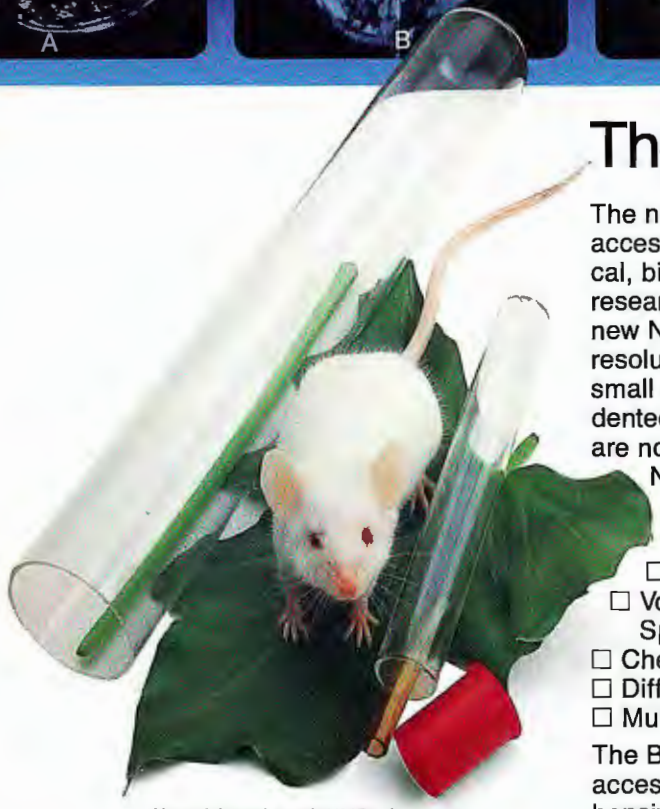



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*Fig. A: Cross sectional image of a philodendron stem. Resolution 19μ x 19μ x 300μ.*
*Fig. B: Cross sectional image of a mouse brain tumor. Resolution 100μ x 100μ x 500μ.*
*Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution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

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*Bruker Instruments, Inc.*
*Manning Park, Billerica, MA 01821*
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4. Selective Excitation Unit consisting of:
   a. RF wave form memory
   b. RF pulse amplitude modulator
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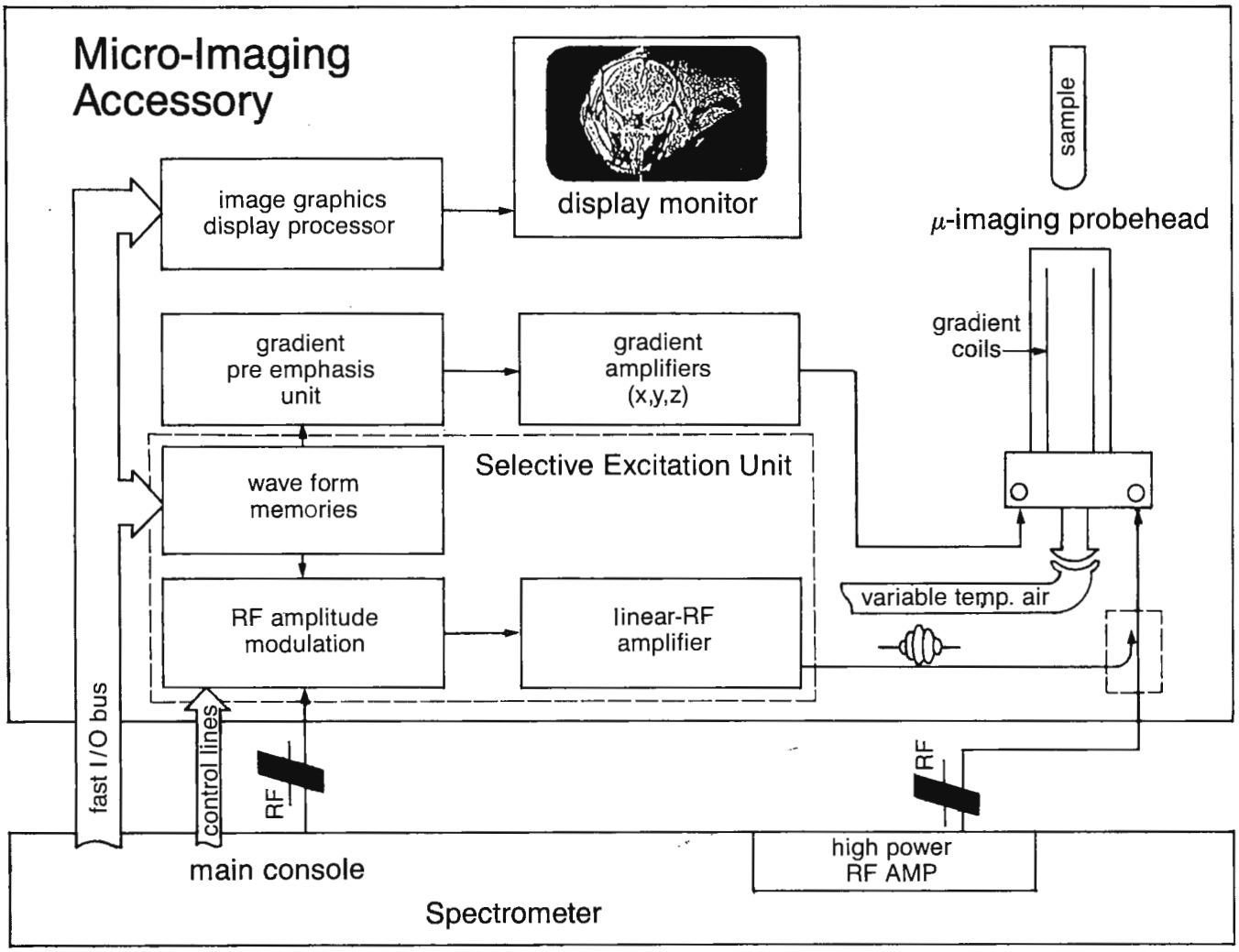
6. Imaging software

*Other nuclei available upon request



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(403)462-2798 FAX (403) 428-5376

*David Axelson*
*President*

Solid State NMR of Heavy Oil-Derived Clay-Organic Complexes

Dear Barry,

Sept. 27, 1988 (received 10/7/88)

As the letterhead indicates, I have left Energy, Mines & Resources to start my own private company. We will be offering multinuclear (solution and solid state) nmr services near the end of the year - when our Bruker spectrometer arrives. Anyone wishing additional information should write to me at the above address.

In order to initiate my subscription to the newsletter, I would like to briefly discuss some recent results obtained (during my final EMR days) concerning the characterization of clay - organic complexes derived from oil sands. Previous (non-nmr) work has indicated that the amount of insoluble organic matter present correlates with the relative efficiency of recovery of bitumen (through the formation of very stable water - in - oil and oil - in - water emulsions). Therefore the nature of the organic component of the insoluble clay - organic complexes extracted from various streams in an oil sands recovery process was examined. In particular, we were interested in determining whether the exact carbon functional group distribution was a better measure of processability than the total amount of insoluble organic matter present. Although I will dwell on the nmr results, we also employed interfacial tension measurements, thermogravimetric analysis, photoacoustic infrared, and scanning electron microscopy / image analysis in this project.

The general observations to be made actually represent a distillation of a long, on-going, study of samples taken from various points in the extraction process, including feed samples. Both 'good' (ie, low water (<5%) content emulsions) and 'bad' (high water (>5%) content emulsions) were collected over a period of 18 months. The solids (insoluble organic matter - clay mineral complexes) were extracted from these samples by both the Dean -Stark and ultracentrifugation methods. All data were obtained on a Bruker CXP200 at 50.3 MHz with 4 kHz magic angle spinning in boron nitride rotors, 4K data points, 5 μs ($90^0$) pulse width, 1 ms contact time, quadrature detection, and 5 s recycle delay. The low carbon content of some complexes (<10% by weight, corresponding to <300 μg carbon) necessitated data acquisition times of 12 to 150 hours/sample.

The most dramatic differences found are illustrated by the final centrifuge feed samples shown in Figure 1. The low water content sample (bottom spectrum) contained no detectable carboxylic acid group peaks, whereas the high water sample (upper spectrum) contained a significant intensity in this region. The remaining carbon functional group distribution was similar in all respects in these samples.

These constant differences between such sample pairs indicate that the high water content emulsions arise from the presence of very hydrophilic organic materials attached to the clay mineral surfaces. Correlations were found with processability, emulsion stability, amount and nature of bound organic matter, amount and nature of bound heavy metal minerals, and interfacial tension measurements.

Best regards,
Dave
Dr. David Axelson

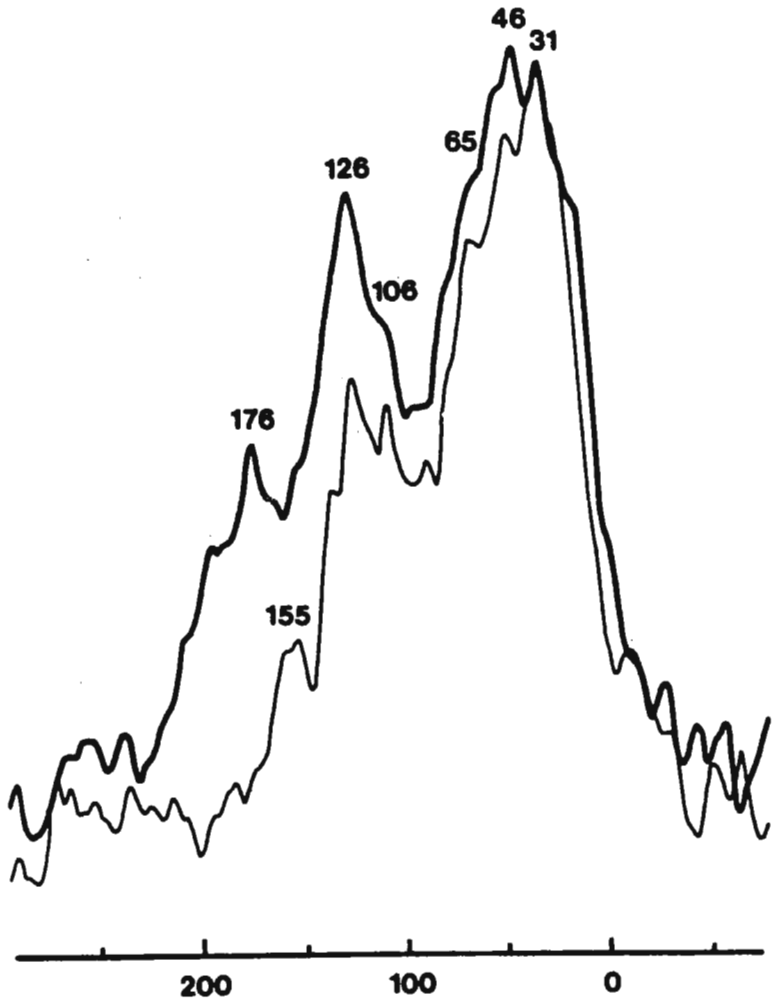


Figure 1. C-13 solid state CPMAS spectra of clay-organic complexes.

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October 3, 1988

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

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

RE: Position available for Assistant Professor of Radiology in Residence

Dear Dr. Shapiro:

A position is available for an Assistant Professor of Radiology in Residence in the Magnetic Resonance Unit at the Veterans Administration Medical Center, Department of Radiology, University of California, San Francisco. This individual should possess a Ph.D. and postdoctoral training in in vivo localization techniques, proton water suppressed spectroscopy, and brain metabolism.

Sincerely,

MICHAEL W. WEINER, M.D.
Associate Professor of Medicine and Radiology

College of Arts and Science

Department of Chemistry

UNIVERSITY OF MISSOURI-COLUMBIA
123 Chemistry Building
Columbia, Missouri 65211
Telephone (314) 882-2439

September 28, 1988
(received 9/30/88)

Professor Bernard Shapiro
966 Elsinore Court
Palo Alto, CA 94303

2-D Quadrupolar Echo of I > 1 Nuclei

Dear Dr. Shapiro:

Recently we have made the spin dynamics calculation of the response, in the frequency domain, of half integer I > 1 nuclei in anisotropic systems to the quadrupolar echo (QE) pulse sequence $\{ (\pi/2)_x\text{-}\tau\text{-}(\pi/2)_y\text{-}\tau\}$, including the effects of relaxation[1]. Contrary to the I = 1 case, the response as a function of $\tau$ is modulated by the quadrupolar precession (Fig. 1). When the QE experiment is carried out in the 2-D fashion, interesting spectroscopic and relaxation information can be extracted from the F1 spectra.

The salient features of the 2D QE spectra in the F1 dimension are as follows. The number of satellite peaks depends on whether the F1 cross-section is taken at a satellite ($\omega_2 = n\omega_Q$) or at the central line ($\omega_2 = 0$) position in F2. The splitting/linewidth ratio is reduced by an integral factor. The most important feature, however, is that the F1 spectra derived from satellite positions in F2 have a central line whose width contains a contribution from the zero-frequency spectral density, $j_0$. This linewidth is free from the effects of inhomogeneous broadening due to orientational distribution. This is in sharp contrast to the conventional 1-D spectra in which the satellite linewidth which contains the contribution from $j_0$ is usually severely broadened by such effects. Since $j_0$ can be determined accurately, the width of the orientational distribution can also be measured from the satellite linewidths in the F1 dimension.

Experiments have been performed for $^{23}Na$ (counterions) and $^{17}O$ (water) nuclei in lyotropic liquid crystals for both oriented and powder samples. The purpose of these experiments is to measure the spectral densities, particularly, $j_0$, to study the "slow" motion arising from diffusion of these species. Two systems have so far been studied, a reversed hexagonal liquid crystal (F) phase of AOT/water/ isooctane and a lyotropic nematic phase of sodium dodecylsulfate/water/decanol/sodium sulfate. Two examples can be given here from the preliminary results to illustrate the usefulness of this technique. First, the $j_0$ of $^{23}Na$ in the powder samples of the F phase is considerably larger than that of the partially oriented samples. The difference can be attributed to the presence of an additional slow motion, most likely diffusion of the counterions between domains of different orientations in the powder samples. Second, the $^{17}O$ spectral densities measured for the nematic and the oriented F phase samples showed significant difference from the $^{2}H$ relaxation results which are affected by deuteron exchange.

Sincerely yours

Tuck

Bertil Halle
Univ. of Lund

Istvan Furo
Univ. of Lund

Tuck C. Wong
Univ. of Missouri

[1] I. Furo, B. Halle, and T. C. Wong, J. Chem. Phys. (in press).

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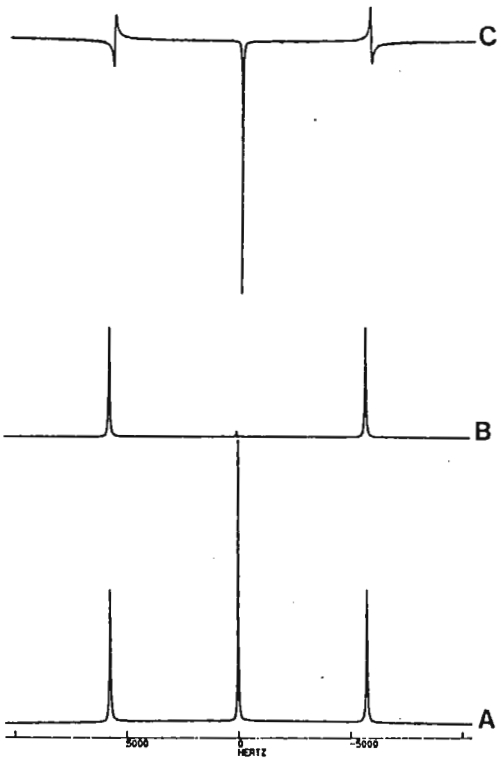



Figure 1. Experimental 1-D QE spectra for I=3/2 nuclei ($^{23}$Na) in a uniformly oriented sample. The delay $\tau$ between the two $\pi/2$ pulses is A. $\tau = 2\pi/\omega_Q$. B. $\tau = 2.3\pi/\omega_Q$. C. $\tau = 3\pi/\omega_Q$, where $\omega_Q$ is the quadrupolar splitting. The small residual satellite signals in C are due to pulse imperfections and to a small distribution of orientations in the "uniformly" oriented sample.

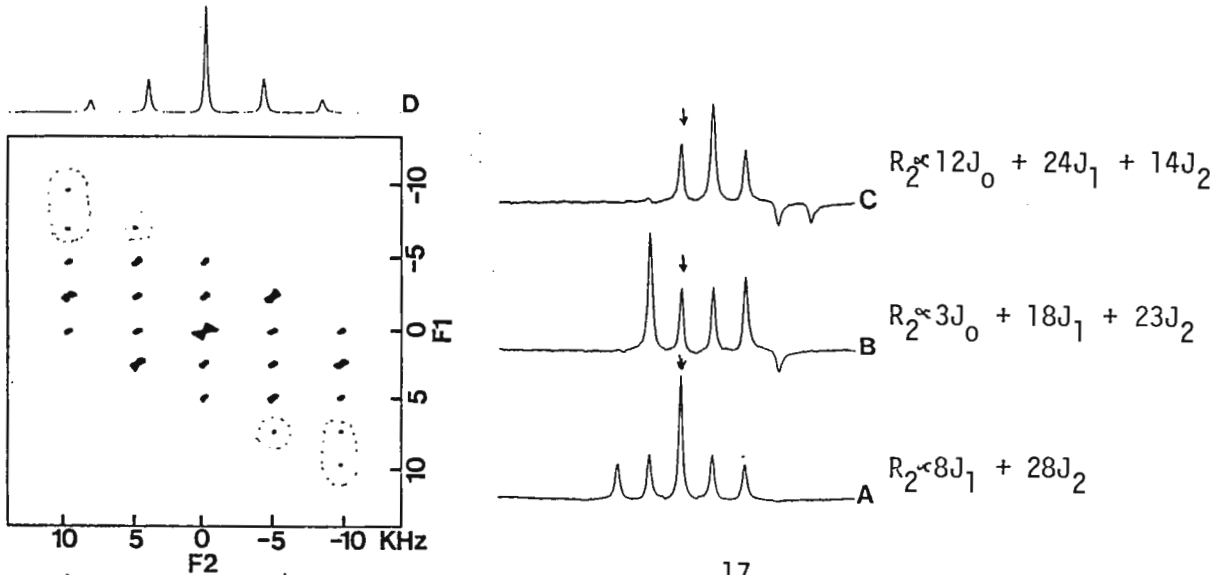



Figure 2. (left) Contour plot for a 2-D QE experiment for $^{17}$O in a partially oriented system. The negative contours are circled. (right) F1 cross-sections at A. F2 = 0; B. F2 = $\omega_Q$ ; C. F2 = $2\omega_Q$. The central lines in these F1 spectra are marked by arrows, and their linewidth in terms of spectral densities indicated. In actual linewidth measurements, the imaginary signal in $t_1$ is zeroed and a real FT is used to produce spectra in the F1 dimension.[1]

*Fremont Magnetic Resonance*
*47647 Hoyt, Fremont, CA 94539*
*415/656-2398*

# Sample Changer

Samples. They're your lifeblood. But they're also a pain in the neck. And that's why you've been pricing automatic sample changers. But how will you fit one into the budget?

At Fremont Magnetic Resonance we think that you shouldn't have to abandon your current instrument, or write a major equipment proposal simply to get an instrument accessory. So we offer an alternative to the expensive, overpowered changers offered by the major vendors- a simple, 20-sample carosel system that can be added to many modern and not-so-modern instruments.

Naturally, our changer package includes easy integration with your system, both hardware and software (the degree of integration depends on the instrument). You have complete flexibility to specify all the aquisition parameters for each sample, including v/t. The queueing order can be adjusted at any time, so when a rush job arrives, it can simply be moved to the top of the queue.

There are some applications where the sophisticated capabilities of a robot changer, or the large capacity of the other vendors' changers are essential. But if your needs are more modest, we can meet them at a more modest price.

# V/T Accessory

Accurate and steady control of temperature is increasingly being recognized as important to obtaining high quality spectra. But you couldn't tell that from the obsolete or temperamental v/t controllers on some instruments.

Good v/t control cannot be done as an afterthought, or with yesterday's hardware. That's why at FMR we've taken another look at temperature regulation. Our new design consists of three components: a digital proportional controller with dynamically sensed airflow, that fits in an IBM PC or compatible, a separate power controller unit, and a state-of-the-art heater/sensor. The heater provides better than 0.1 degree stability, and the dynamic control algorithm sensing permits accurate regulation even during slow changes in the flow rate. Because of our novel design, the regulated temperature can be as little as 15 degrees above the input temperature.

Our heater/sensors can be fitted to most commercial probes; the control software can integrate smoothly with many NMR systems. This product can be purchased with or without the host PC; call for prices and details on the degree of user transparency with your particular spectrometer.

# Off-line Plotting

Plotting takes a lot of time. Even if your spectrometer is capable of multi-tasking and plotting in background, you've probably found that fiddling around with the details of a plot has taken time that could better be used in setting up the next experiment. You may even have had to schedule additional time simply to plot some data!

PLOT is a tool that allows you to plot off-line. It requires an IBM PC or compatible computer, and supports all common graphics devices, mice, plotters and printers. After you have transferred the data file, either by serial transfer (in background on NT,QE, and GN spectrometers), Ethernet, or by emulating the spectrometer's plotter port, you may format your plot exactly as you wish, without tying up valuable instrument time.

Fremont Magnetic Resonance
47647 Hoyt Street
Fremont CA 94539
(415)656-2398

***Instrumentation Note 4***

From time to time, we all have the need to measure RF voltages on an oscilloscope and determine how much power is present. The tables below make a handy reference.

**Voltage to Watts**

| $V_{P-P}$ | $V_{RMS}$ | dBm | Watts |
|---|---|---|---|
| 0.01 | 0.0035 | -36.0 | 0.25 $\mu$Watts |
| 0.03 | 0.01 | -26.5 | 2.25 $\mu$Watts |
| 0.05 | 0.02 | -22.0 | 6.25 $\mu$Watts |
| 0.08 | 0.03 | -18.0 | 16 $\mu$Watts |
| 0.1 | 0.04 | -16.0 | 25 $\mu$Watts |
| 0.3 | 0.1 | -6.5 | 225 $\mu$Watts |
| 0.5 | 0.2 | -2.0 | 625 $\mu$Watts |
| 0.8 | 0.3 | 2.0 | 1.6 *m*Watts |
| 1 | 0.4 | 4.0 | 2.5 *m*Watts |
| 3 | 1.1 | 13.5 | 22.5 *m*Watts |
| 5 | 1.8 | 18.0 | 62.5 *m*Watts |
| 8 | 2.8 | 22.0 | 0.2 Watts |
| 10 | 3.5 | 24.0 | 0.3 Watts |
| 30 | 10.6 | 33.5 | 2.3 Watts |
| 50 | 17.7 | 38.0 | 6.3 Watts |
| 80 | 28.3 | 42.0 | 16 Watts |
| 100 | 35.4 | 44.0 | 25 Watts |
| 300 | 106.1 | 53.5 | 225 Watts |
| 500 | 176.8 | 58.0 | 625 Watts |
| 800 | 282.8 | 62.0 | 1600 Watts |

**Watts to Voltage**

| Watts | dBm | $V_{RMS}$ | $V_{P-P}$ |
|---|---|---|---|
| 0.001 | 0.0 | 0.2 | 0.6 |
| 0.003 | 4.8 | 0.4 | 1.1 |
| 0.005 | 7.0 | 0.5 | 1.4 |
| 0.008 | 9.0 | 0.6 | 1.8 |
| 0.01 | 10.0 | 0.7 | 2.0 |
| 0.03 | 14.8 | 1.2 | 3.5 |
| 0.05 | 17.0 | 1.6 | 4.5 |
| 0.08 | 19.0 | 2.0 | 5.7 |
| 0.1 | 20.0 | 2.2 | 6.3 |
| 0.3 | 24.8 | 3.9 | 11.0 |
| 0.5 | 27.0 | 5.0 | 14.1 |
| 0.8 | 29.0 | 6.3 | 17.9 |
| 1 | 30.0 | 7.1 | 20.0 |
| 3 | 34.8 | 12.2 | 34.6 |
| 5 | 37.0 | 15.8 | 44.7 |
| 8 | 39.0 | 20.0 | 56.6 |
| 10 | 40.0 | 22.4 | 63.2 |
| 30 | 44.8 | 38.7 | 109.5 |
| 50 | 47.0 | 50.0 | 141.4 |
| 80 | 49.0 | 63.2 | 178.9 |
| 100 | 50.0 | 70.7 | 200.0 |
| 300 | 54.8 | 122.5 | 346.4 |
| 500 | 57.0 | 158.1 | 447.2 |
| 800 | 59.0 | 200.0 | 565.7 |
| 1000 | 60.0 | 223.6 | 632.5 |

**20dB Attenuator**

| $V_{P-P}$ | Watts |
|---|---|
| 0.01 | 25 $\mu$Watts |
| 0.03 | 225 $\mu$Watts |
| 0.05 | 625 $\mu$Watts |
| 0.08 | 1.6 *m*Watts |
| 0.1 | 2.5 *m*Watts |
| 0.3 | 22.5 *m*Watts |
| 0.5 | 62.5 *m*Watts |
| 0.8 | 160 *m*Watts |
| 1 | 0.25 Watts |
| 3 | 2.25 Watts |
| 5 | 6.25 Watts |
| 8 | 16 Watts |
| 10 | 25 Watts |
| 30 | 225 Watts |
| 50 | 625 Watts |
| 80 | 1600 Watts |
| 100 | 2500 Watts |

$$V_{P-P} = V_{RMS} \times 2 \times \sqrt{2}$$

$$P_{Watts} = \frac{(V_{RMS})^2}{50\Omega}$$

$$P_{dBm} = 10 \times \text{Log}_{10} \left[ \frac{P_{Watts}}{0.001\ W} \right]$$

**30dB Attenuator**

| $V_{P-P}$ | Watts |
|---|---|
| 0.01 | 0.25 *m*Watts |
| 0.03 | 2.25 *m*Watts |
| 0.05 | 6.25 *m*Watts |
| 0.08 | 16 *m*Watts |
| 0.1 | 25 *m*Watts |
| 0.3 | 0.225 Watts |
| 0.5 | 0.625 Watts |
| 0.8 | 1.6 Watts |
| 1 | 2.5 Watts |
| 3 | 22.5 Watts |
| 5 | 62.5 Watts |
| 8 | 160 Watts |
| 10 | 250 Watts |
| 30 | 2250 Watts |

Columbia University in the City of New York
Department of Chemistry

New York NY10027
Havemeyer Hall

27 Sept 1988
(received 9/30/88)

Dear Barry:

The COSY Spectra of Singlets: Not As Stupid As You Might Think!

During the seemingly interminable struggle to come to grips with two-dimensional NMR spectroscopy, the arcane topic of *N*-type and *P*-type peaks sometimes rears its ugly head. Phase cycles often contain comments such as do "this" for *N*-type or do "that" for *P*-type detection. It is easy to gain the impression that the *N*- and *P*-type peaks have roughly equal intensity and although no one doubts that there *is* an advantage to detecting *N*-type peaks, it is easy to believe that the advantage is small. The diagrams sometimes used to explain the differing phase properties of the components of COSY spectra tend to perpetuate this myth.

In reality, *P*-type peaks decrease in intensity with respect to the *N*-type peaks quite rapidly as the acquisition time in either dimension increases. The major reason for this is that the *N*-type peaks are "real" echo peaks and are essentially insensitive to the inhomogeneity of the magnetic field, whereas there is no such refocussing available for the *P*-type peaks. This has important consequences for phase-sensitive COSY spectra.

Unfortunately we live in a world of inhomogeneous magnetic fields, where people seem to believe that sample spinning is undesirable in 2-D NMR. They say "It's an echo experiment". "You don't need to spin the sample during an echo experiment". "In fact, its a bad idea", they say. Well, it is undoubtably a bad idea to allow the *P*-type signals to decay away if you wish to obtain phased COSY spectra, because the *P*-type peaks are used to cancel the phase-twist component of the *N*-type peaks. If there is a large difference in intensity between the *N*- and *P*-type peaks, the resulting pure phase spectra will have low intensity.

The figure shows the result of increasing the acquisition time in the second dimension on the $F_1$ response from a unspun sample of lightly doped water ($T_1 = T_2 = 1.2$ s) using a COSY sequence without phase-cycling (i.e. 90°x-90°x-Acq. The signals are (left to right) *P*-type, axial and *N*-type in each of the three separate experiments. The only parameter which was changed was the acquisition time in the second dimension which increased (left to right) from 80 to 160 to 320 ms. Even with acquisition time in the second dimension of less than 100 ms the *P*- type peaks are still less intense than those of the *N*-type.

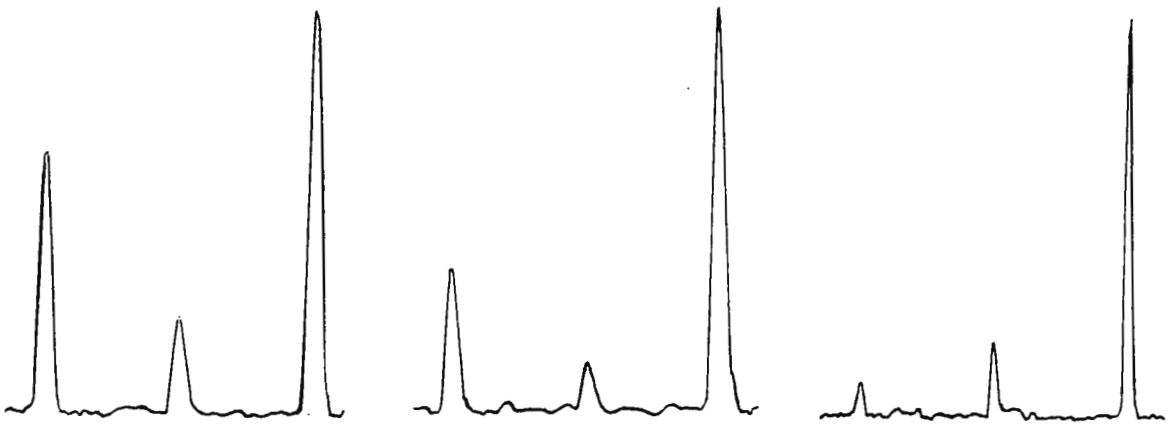
The whole purpose of phase-sensitive 2-D spectroscopy is to provide an increase in resolution over the older method of echo selection. However if the acquisition time in either dimension is increased to make full use of the improvements in resolution that phased data offers, then the intensity of the *P*-type peaks will fall off, leading to lower overall sensitivity despite the fact that the intensity of the *N*-type peaks might even improve.

This seems to suggest a strange twisted, almost recursive, loop in logic, whereby the pursuit of resolution in 2-D spectra seems initially to lead away from the principal of echo selection but leads back there since echo selection itself is inevitable.

Best Wishes

Chris

C. J. Turner



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October 3, 1988
(received 10/8/88)

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

Dear Professor Shapiro:

Re: Comparison of HOGWASH with GM.
ASPECT 3000 HOGWASH software.

There are times when, despite careful sample preparation and instrument adjustment, one needs to improve the resolution of an NMR spectrum. One of the newer resolution enhancement techniques is the unfortunately named 'HOGWASH' procedure developed by Professor Ray Freeman's group (1-3). HOGWASH has to be one of the more honest enhancement techniques in that it can subtract an experimentally determined instrument lineshape function from the spectrum.

HOGWASH has already been compared with, and generally found superior to, the Maximum Entropy Method (3). What we have done is to compare HOGWASH with the more commonly used Lorentz to Gauss transformation (GM in Brukerese). We have found that, while GM is more convenient for routine enhancement, HOGWASH can have advantages in certain situations.

Spectrum 1a shows a simulated 1 Hz doublet with a 50:1 signal to noise ratio, a $T_2$ of 0.2 s and a 4.1 s acquisition time. The splitting is lost in the linewidth. Spectrum 1b shows the effect of GM while spectrum 1c has been HOGWASHed. HOGWASH provides the same degree of resolution enhancement with less amplification of the noise.

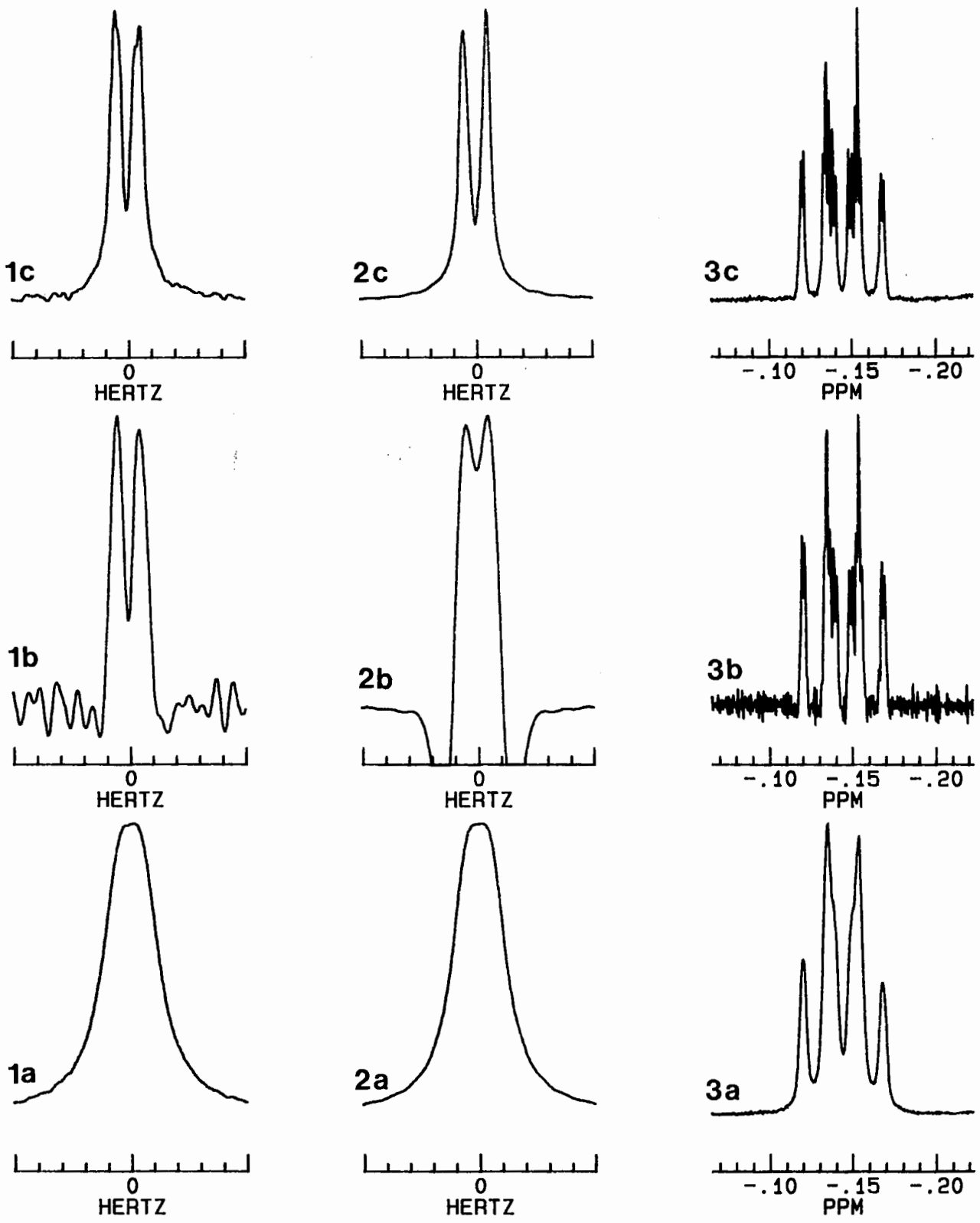
Spectrum 2a shows a simulated 1 Hz doublet with no added noise and a $T_2$ of 0.2 s. The acquisition time has been restricted to 1.0 s. In this case HOGWASH (spectrum 2c) is clearly superior to GM (spectrum 2b). This situation sometimes occurs when trying to observe very small couplings (the acquisition times become very long). The distortions in the GM spectrum are a truncation artifact. The removal of such artifacts in the F1 dimension of 2D spectra was one of the first applications of HOGWASH to NMR (2).

Spectrum 3a is the endo cyclopropyl proton of 17β-acetoxy-3α,4α-cyclopropano-5α-androstane (4). Both GM (spectrum 3b) and HOGWASH (spectrum 3c) show additional fine structure from long-range coupling to H-2β, but the signal to noise ratio of 3c is clearly better.

We have also noted that the lineshape distortions caused by severe application of GM can falsify the positions of lines in multiplets. HOGWASH is much better in this regard in that the lineshape is more natural.

All computations were performed on an ASPECT 3000 computer in PASCOM Pascal. FIDs for the simulated doublets were generated with Alex Bain's SIMPLTN program. All HOGWASH computations used a loop gain ($\gamma$) of 0.04 and a termination threshold of 0.05 times the highest peak in the spectrum. The reconstruction linewidth was 0.2 Hz.

As a final caveat we should point out that any resolution enchancement technique (GM included!) can produce false splittings and spurious peaks if abused. Even when


1c
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HERTZ
-.10 -.15 -.20
PPM
1a
2a
3a
0
HERTZ
0
HERTZ
-.10 -.15 -.20
PPM

applying GM it is prudent to have a known singlet in the spectrum to assess the effects of the enhancement.

Interested readers can obtain a copy of the program from me provided they supply a formatted 8" floppy disk.

Please credit this letter to Ted Schaefer's account.

Sincerely,

Kirk Marat.

Kirk Marat.


1. A.J. Shaka, J. Keeler, and R. Freeman, J. Magn. Reson. 56, 294 (1984).
2. J. Keeler, J. Magn. Reson. 56, 463 (1984).
3. S. J. Davies, C. Bauer, P. J. Hore, and R. Freeman, J. Magn. Reson. 76, 476 (1988).
4. A complete account of this and other ring-A cyclopropyl steroids is being prepared for submission to Magn. Reson. Chem.


---

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Person to Contact: Dr. Lee M. Middleman, Corporate Technology, Raychem Corporation
300 Constitution Drive, Menlo Park, CA 94025

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| CAT. NO. | ISOTOPE [COMPOUND] | NATURAL ABUNDANCE % | ISOTOPIC ENRICHMENT ATOM % | NUCLEAR SPIN | FREQUENCY at 11.75T MHz | QUANTITY† | PRICE U.S. $ |
|---|---|---|---|---|---|---|---|
| 84-70001 | $^{1}H_2O$ | 99.985 | 99.99995 | 1/2 | 500.133 | 25g | 25. |
| | [Deuterium-depleted Water] | | | | | 4 x 25g | 90. |
| | | | | | | 10 x 25g | 200. |
| | | | | | | 20 x 25g | 300. |
| | | | | | | 30 x 25g | 400. |
| | | | | | | 1kg | 500. |
| 82-70001 | $D_2O$ ($^{2}H_2O$) | 0.015 | 99.9 | 1 | 76.778 | 100g | 40. |
| | [Deuterium Oxide] | | | | | 5 x 100g | 190. |
| | | | | | | 10 x 100g | 375. |
| | | | | | | 1kg | 360. |
| | | | | | | 5 x 1kg | 1775. |
| | | | | | | 10 x 1kg | 3500. |
| 82-70901 | $D_2O$ ($^{2}H_2O$) | 0.015 | 99.8 | 1 | 76.778 | **min.** 10kg | 3350. |
| | [Deuterium Oxide] | | | | | 25kg | 8275. |
| | | | | | | 50kg | 16250.† |
| 82-70002 | $D_2O$ ($^{2}H_2O$) | 0.015 | 99.96 | 1 | 76.778 | 10g | 15. |
| | [Deuterium Oxide "100%"] | | | | | 5 x 10g | 50. |
| 84-70000 | $H_2{}^{16}O$ | 99.759 | 99.98 | | | 10g | 100. |
| | [$^{17}O$- and $^{18}O$-depleted Water] | | | | | 25g | 125. |
| | | | | | | 50g | 150. |
| 87-70003 | $H_2{}^{17}O$ | 0.037 | 20 | 5/2 | 67.805 | 1g | 155. |
| | [Water-$^{17}O$, normalized] | | | | | 5g | 575. |
| | | | | | | 10g | 1100. |
| 87-70004 | $H_2{}^{17}O$ | 0.037 | 40 | 5/2 | 67.805 | 0.5g | 300. |
| | [Water-$^{17}O$, normalized] | | | | | 1g | 450. |
| 88-70023 | $H_2{}^{18}O$ | 0.204 | 10 | | | 50g | 190. |
| | [Water-$^{18}O$, normalized] | | | | | 100g | 365. |
| | | | | | | 500g | 1775. |
| | | | | | | 1kg | 3500.† |
| 88-70005 | $H_2{}^{18}O$ | 0.204 | 95 | | | 1g | 85. |
| | [Water-$^{18}O$, normalized] | | | | | 5g | 410. |
| | | | | | | 10g | 800. |
| | | | | | | 25g | 1950. |
| | | | | | | 50g | 3800.† |
| 81-70002 | $D_2{}^{18}O$ ($^{2}H_2{}^{18}O$) | 0.204 ($^{18}O$) | 97 ($^{18}O$) | | | 1g | 140. |
| | [Water-$^{18}O$, not normalized] | 0.015($^{2}H$) | 70 ($^{2}H$) | 1 | 76.778 | 5g | 550. |

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September 27, 1988 (received 10/4/88)

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

Homebuilt Broadline NMR Spectrometer

Dear Dr. Shapiro:

We have recently completed construction of a homebuilt broadline NMR spectrometer. A Nicolet 1080 computer with 293 I/O controller and Diablo disk drive, Biomation 805 fast transient recorder, Rockland 5600 frequency synthesizer, and Nalorac 4.2T superconducting magnet were inherited from earlier projects at IUPUI and form the starting point of the machine. The transceiver was constructed from connectorized components, with the exception of an Amplifier Research 200L high power amplifier, a Cryomagnet's probe, and a little digital electronic circuitry. Minimal experience in rf engineering was consequently required and, hopefully, ease of repair should be insured. I shall be pleased to provide circuit diagrams, which will be included in a manuscript I intend to submit to J. Mag. Reson.

At present the spectrometer is configured for $^{2}H$ NMR only and an example of a spectrum is shown below. Construction of a $^{1}H$ decoupler to enable $^{31}P$ and $^{13}C$ NMR is currently underway.

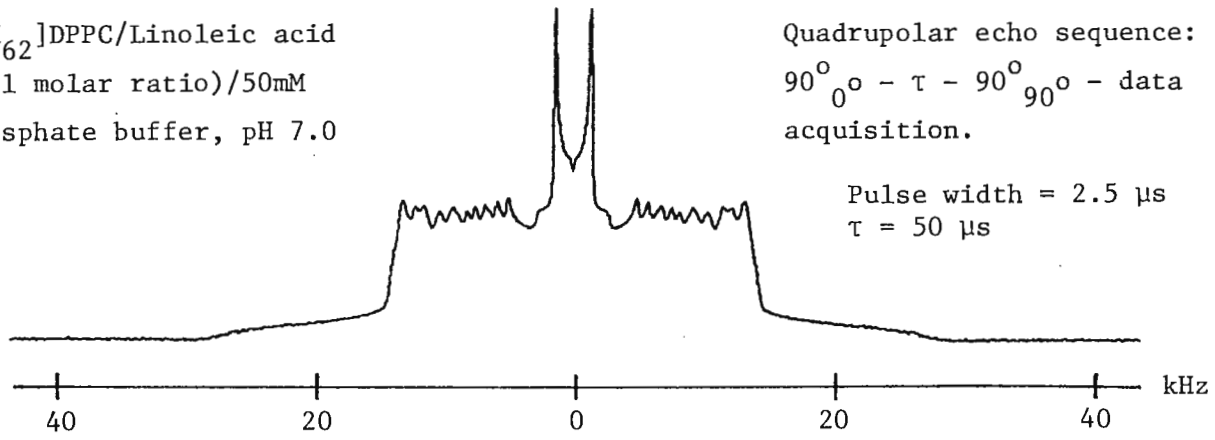
Please credit this contribution to B. D. Nageswara Rao's account.

Yours truly,

Stephen R. Wassall
Assistant Professor of Physics

Bruce D. Ray
Assistant Scientist

SRW:ml



THE ROYAL INSTITUTE OF TECHNOLOGY
*Inorganic Chemistry*
*Dr. Julius Glaser*

*Stockholm, September 26, 1988*
(received 10/8/88)

Prof. B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
California 94303, USA

# "Things are seldom what they seem .....",

# or What is the NMR time-scale ?

*Dear Prof. Shapiro,*

Thank you for your colorful remainders. Recently, we investigated kinetics of ligand exchange between the different thallium(III) chloride complexes by means of $^{205}$Tl–NMR at 9.4 Tesla.[1] We found it amusing to compare different computer–simulated Tl–NMR spectra for this chemical system and would like to share this experience with your readers.

In absence of chemical exchange between the complexes a spectrum of a solution containing 50% $TlCl^{2+}$ and 50% $TlCl_2^+$ may look like the one in Fig. 1a. However, such solutions normally contain small amounts of other species, such as $Tl^{3+}$ or $TlCl_3$ . Especially, the presence of the latter complex may introduce some undesirable effects because of the very fast reactions:

$$TlCl_2^+ + {}^*TlCl_3 \rightleftharpoons {}^*TlCl_2^+ + TlCl_3 \qquad (1)$$

and

$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3 \qquad (2)$$

The chemical shift of the species $TlCl_3$ is about 2412 ppm and only slightly more than 1% of $TlCl_3$ may move the signal of $TlCl_2^+$ to the other side of that of $TlCl^{2+}$ (cf. Fig. 1b). At lower rate constants for the reactions (1) and (2) another fortuitous effect may appear, namely that shown in Fig. 1c., where the signal of $TlCl_2^+$ is not visible any more since it is so broad that it disappears in the baseline. A different case giving nearly the same spectrum occurs when the concentration of $TlCl_3$ is about 0.8% of the total thallium(III) and the reactions (1) and (2) are very fast: the peaks of $TlCl^{2+}$ and $TlCl_2^+$ happen to be at the same frequency (Fig. 1d.). Under such circumstances it is easy to misassign these peaks and this is also what happened to us in our previous contribution to your Newsletter (no. 352).

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The Royal Institute of Technology
S-100 44 STOCKHOLM, Sweden

Telephone
Nat 08-790 60 00
Int + 46 8-790 60 00

Cable address
Technology

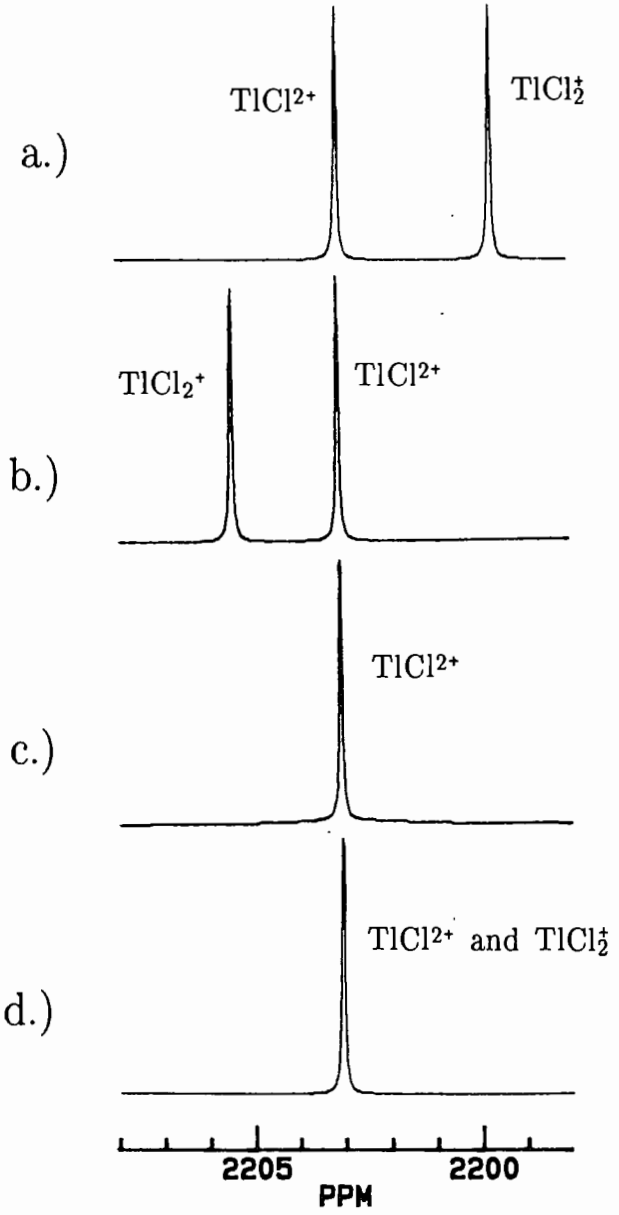
Telex
103 89 Kth stockholm

In this system also other exchange reactions take place, e.g.

$$TlCl^{2+} + {}^{*}TlCl_2^{+} \rightleftharpoons {}^{*}TlCl^{2+} + TlCl_2^{+} \quad (3)$$

and

$$TlCl^{2+} + Cl^{-} \rightleftharpoons TlCl_2^{+} \quad (4)$$




The NMR time–scale for this exchange, determined by the chemical shift difference in Hz between the exchanging sites, illustrates nicely the meaning of the (sometimes misunderstood) concept of the NMR time–scale. The chemical shift difference between the signals of $TlCl^{2+}$ and $TlCl_2^{+}$ decreases from about 1000 Hz (Fig.1a) to 0 Hz (Fig.1d) and increases again to about 500 Hz (Fig.1b). This difference varies not only with the composition of the solution but will also depend, for example, on the temperature, because of the temperature dependence of the reactions (1) and (2).

Fig.1. Simulated $^{205}Tl$–NMR spectra for aqueous solutions of thallium(III) and chloride (*see text*).

*Sincerely,*

***Istvan Banyai*** ***Julius Glaser***

[1] *Abstracts of XIX International Conference on Solution Chemistry, Lund, August, 1988.*

Université de Lausanne - Faculté des Sciences

**INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE**

Place du Château 3, CH - 1005 LAUSANNE (Switzerland)

tel. (021) 44 32 50 fax. (021) 44 32 48

Prof. Bernard L.Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U S A

28.9.1988
(received 10/11/88)

**Simultaneous observation of exchange reactions by $^{1}H$ and $^{17}O$ NMR**

Dear Prof. Shapiro,

In the course of our investigations of exchange reactions on Rhenium compounds we measured the exchange of pyridine and oxygen atoms on $ReO_2(py)_4^+$ in $D_2O$. Both exchange rates are very slow (half-life several hours). Therefore we used isotopic substitution techniques to follow the reactions. In this kind of experiment one site is prepared enriched (or depleted) in one isotope and isotopic equilibration is followed by NMR. To study the pyridine exchange we mixed the complex, dissolved in $D_2O$, with deuterated pyridine and recorded $^{1}H$-NMR spectra. To monitor the oxygen exchange we enriched the complex in oxygen-17 and dissolved it in $D_2O$. The reaction was followed by $^{17}O$-NMR. At low temperature the half-lifes exceed 10 h and we had to use the spectrometer for a week-end to obtain only one exchange rate. To save time we studied therefore the two reactions simultaneously. We mixed the complex, enriched in $^{17}O$ with $D_2O$ and deuterated pyridine (final concentrations: 6.6 $10^{-3}$ m in $ReO_2(py)_4^+$, 13 $10^{-3}$ m in pyridine-$d_5$ in $D_2O$) and put them into the NMR probe.

The spectrometer (Bruker AM 400 with 10 mm broad-band probe) was set up to measure $^{1}H$ (via the decoupling coil) and $^{17}O$ spectra. We recorded alternatively $^{17}O$- and $^{1}H$-NMR FIDs and stored them on disc. 60 FIDs of each series were measured in a fully automatic way. The spectral data used were for $^{1}H$-NMR ($^{17}O$-NMR): frequency = 400 (54.24) MHz, spectral width =6'024 (50'000) Hz , data points = 8k (2k) , number of scans = 32 (100'000) , pulse-length = 20 (14) $\mu$s . An example of the data obtained after Fourier transformation is shown in Fig. 1. The exchange rates calculated are 6.8 $10^{-6}$ $s^{-1}$ for the pyridine exchange and 1.2 $10^{-5}$ $s^{-1}$ for the oxygen exchange.

L. Helm

Dr. Lothar Helm

This work was done in collaboration with E. and K. Deutsch, University of Cincinnati.
Please credit this contribution to the account of Prof. A.E. Merbach.

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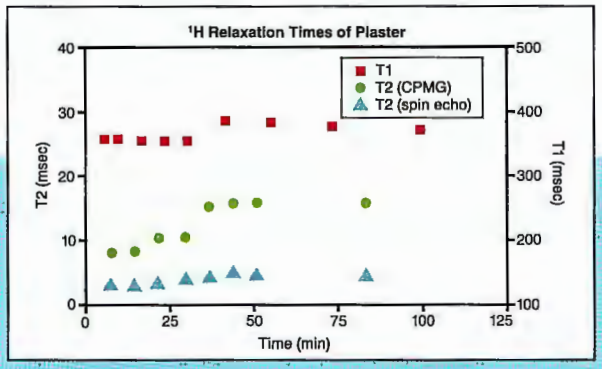


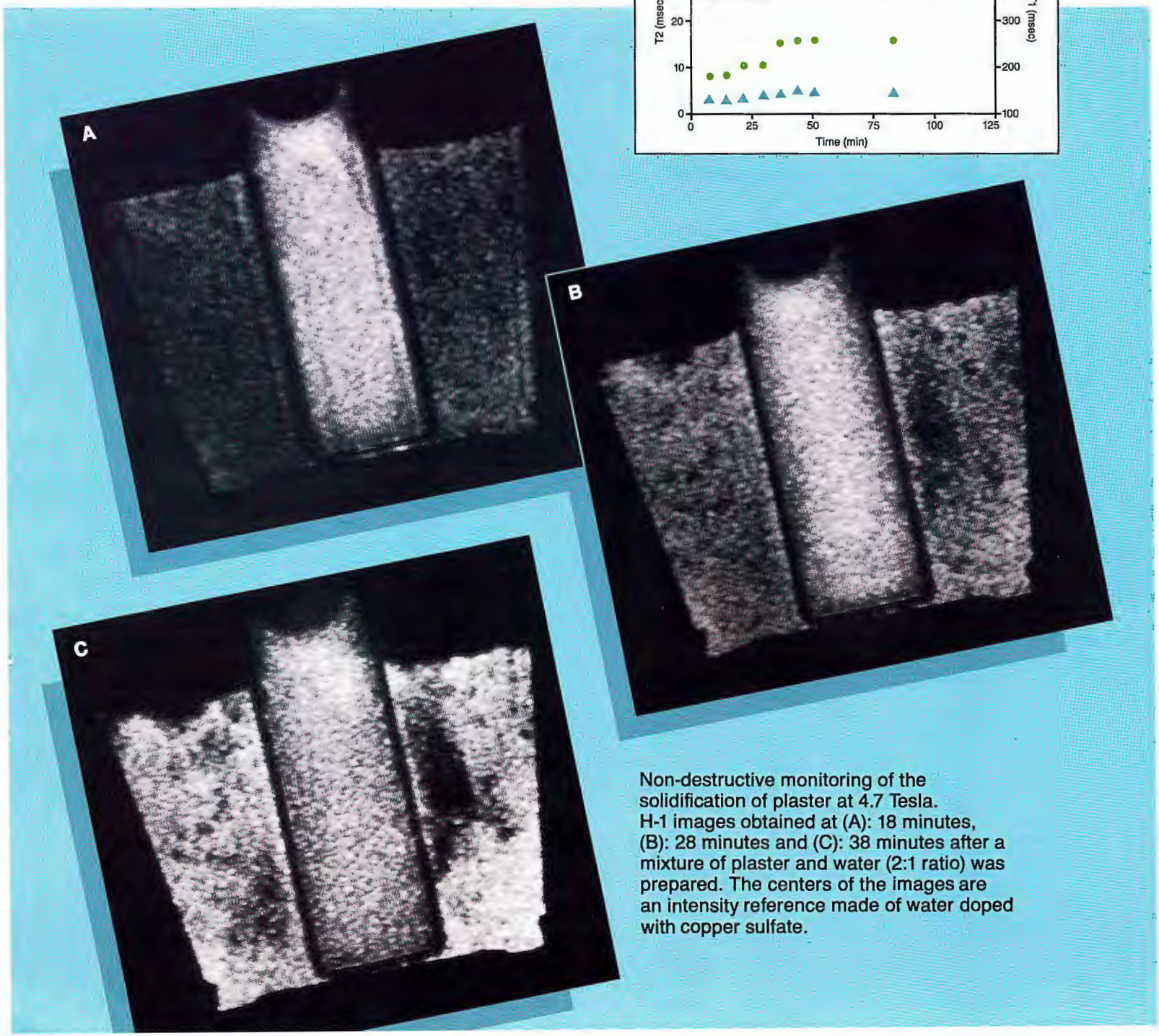


Non-destructive monitoring of the solidification of plaster at 4.7 Tesla. H-1 images obtained at (A): 18 minutes, (B): 28 minutes and (C): 38 minutes after a mixture of plaster and water (2:1 ratio) was prepared. The centers of the images are an intensity reference made of water doped with copper sulfate.

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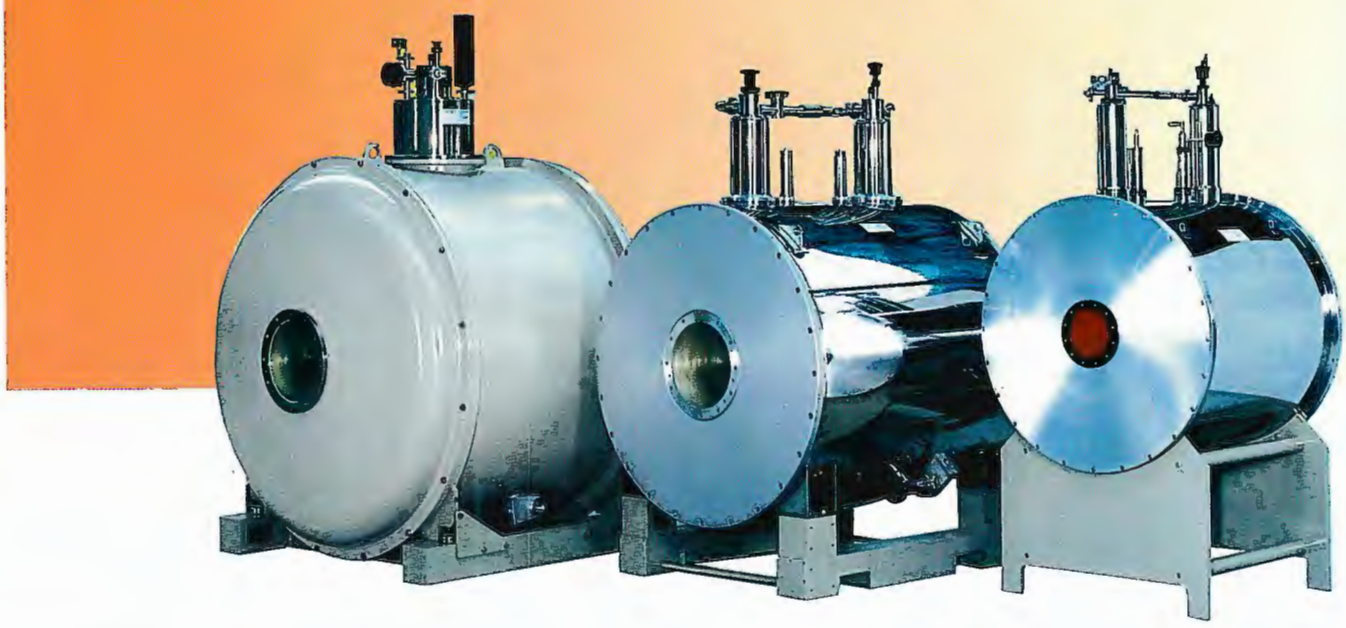
| **200/400** | 4.7T | 400 mm | 324 mm | 1.8 G/cm | 140 mm DSV ±4 ppm | 80 mm DSV 0.1 ppm | 8.50 m | 6.75 m |
| **85/310** | 2.0T | 310 mm | 225 mm | 3.0 G/cm | 100 mm DSV ±5 ppm | 70 mm DSV 0.1 ppm | 4.50 m | 3.63 m |

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



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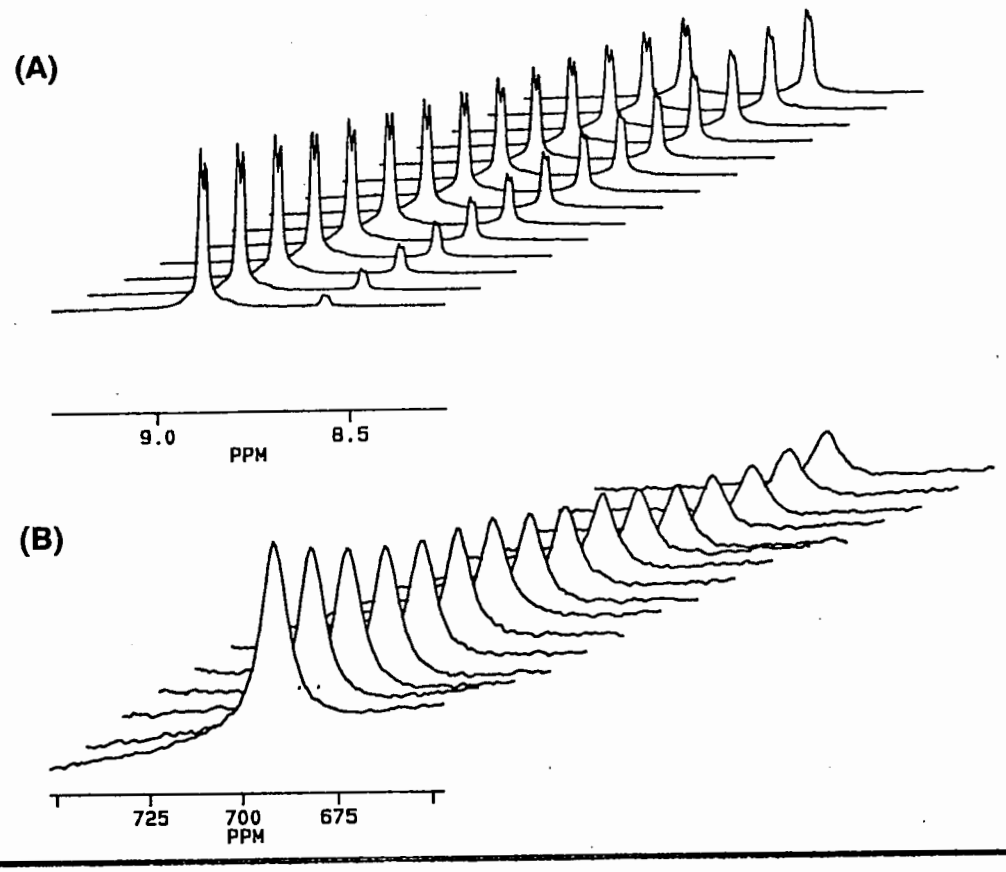
*200/400, 200/330, and 300/180 magnets for the NMR Imaging Spectrometer System.*
*(Photos courtesy Oxford Instruments.)*

Note: Equipment described is intended for investigational purposes, and is not approved by the FDA for clinical use.

Fig. 1 : Pyridine and oxygen exchange on $ReO_2(py)_4^+$ in $D_2O$. (A) Decrease of the $^1H$-NMR signal of bound pyridine (protons in 2,6 positions) and increase of the signal of the corresponding protons on free pyridine due to pyridine exchange. (B) Decrease of the $^{17}O$-NMR signal with time due to exchange between the bound $^{17}O$-enriched site with non enriched $D_2O$. The time interval is 147 min. The temperature was 296.6 K.




POSTDOCTORAL POSITION AVAILABLE

A postdoctoral position is available in my laboratory, involving the use of modern NMR techniques to study the three-dimensional structures and ligand-binding attributes of HIV proteins. Facilities include a VXR-500-S spectrometer which is dedicated to biomolecular studies; off-line processing on a VAX-8800 running FTNMR, DISGEO, and CHARMM; access to an E&S graphics system; and close interactions with our molecular modeling and X-ray crystallography groups. Applicants should be familiar with two-dimensional NMR experiments and methods of assigning resonances in protein spectra. Experience in purifying and maintaining protein samples is desirable.

Interested applicants should send me a c.v. and the names of three references.

Dr. David C. Fry
Department of Physical Chemistry
Hoffmann-La Roche, Inc.
Nutley, NJ 07110

362-30

# 500 MHz NMR AND DATA STATION USING AT-CLONE COMPUTERS

(received 10/11/88)

Dear Barry:

For the past two years our home-brew 500 MHz system has run on an IBM-AT clone (Kaypro) computer, aided by a data-station based on an identical computer. Some aspects of this setup may be of interest to your readers, even though I described it in a previous newsletter two years ago, because the data station has been revised considerably. The data station is a standard 6 MHz AT clone with a 30 MB hard disc, 80287, and EGA graphics. It uses a reliable and inexpensive 11 x 17" Houston DMP 40 plotter (~$1200) which is buffered by a 1 meg buffer ($600, Ditron Corp., 4026 W. St. John, Glendale, AZ 85308) that plugs into a slot of the AT, and a new coprocessor board ($1250 with utility software, Symmetric Research, 15 Central Way, Kirkland, WA 98033) based on a 10 mips TI TMS320c25 chip and carrying 128 K of 32 bit memory. It is controlled by, in addition to the usual keyboard, a front panel containing wheel switches for gain, expansion, and other numerical entry. The NMR instrument uses an identical computer minus the plot buffer and coprocessor board but with an added input processor/buffer and a timing system. It is "networked" to the data station via floppy discs carried down the hall. A 2D data set containing one million 32 bit words is automatically compressed (by eliminating leading zero bytes and words) to about two 5" floppies, and it takes about 7 minutes to do such a transfer (assuming one minute for walking) which also automatically provides a convenient archive. The NMR's capabilities are intentionally limited to that which is needed to set up runs.

I have written a true 32 bit integer FT program for the TMS320x25 coprocessor which will handle up to an 8k FT (8k real output, from 4k complex input points zerofilled two-fold). Larger data sets would require more programming which would be straightforward. A 1k FT takes 85 msec including preweighting by an arbitrary real function. Post-multiplication by an arbitrary (phase correcting) function, and moving data into, and later out of, the on-board memory take another 20 msec, for this size FT. This is more than 10 times faster than a highly efficient program I wrote for the 80287/86 (6mHz). Times for 2D are harder to describe: the actual hypercomplex processing time for the 2D run I mentioned above, zerofilled 2X in both dimensions to provide a 1K by 1k 32 bit data set, is theoretically 1.5 x 1024 times the one-D time, or about 3 minutes, but lots of time is spent in disc swapping (see J. Magn. Res. 52, 310 [1983]). Without the new coprocessor it now takes 40 minutes. This is cut to about 15 minutes by the coprocessor board, and may be cut to about eight or ten minutes if I install a newer fast-access hard disc, and maybe 5 minutes if I install the required extended memory and spend some time setting up efficient timesharing of FT's with other operations. The largest FT we have done is a 1K x 2K x 32bit, in 35 minutes, but I think we can do 2K x 2K with a little more programming, on 640 kB RAM.

The data station unfortunately does not now have contour plotting and for that we send the data to a central VAX via Kermit (very slow, but sometime we will spend the required $1500 to couple the AT to our ethernet). We use Dennis Hare's software, for which we are very grateful, to have the VAX plot on a laserjet whose output has to be hand-pasted to get a big 2D map. Often, instead, for simpler 2D maps we use the plotting capability of our own data station. It produces rather primitive stack-plots, and also has a new threshold plotting mode that has some of the virtues of both contours and stacks: Points above a certain positive threshold are plotted, and also points below a negative threshold, as well as points within two horizontal data points of these points. See J. Mag. Res. 78, 150 (1988) for a sample. A stacked plot takes up to 40 min., which is where the plot buffer is useful: it can be loaded with a plot in about 1/5 the time required for the plot, and the computer can then be used for data processing or analysis during the plot. A threshold plot generally takes much less time; it is not as good as a contour map for analyzing low-noise well-resolved data but is useful for finding and evaluating peaks that are shoulders of other peaks, and for displaying the quality of data (S/N ratio). We would certainly like to have a large-bed plotter and/or a plotter with paper feed but these cost over $2000 (has anyone had experience with a Zericon plotter?).

The EGA graphics has only 400 lines vertically, yet we routinely use it to display and analyze up to 200-line 2D stack plots. Peaks are generally visible as dark blobs on such a plot, but are easily picked out by our cursor which can be moved about on the screen with, currently, pushbuttons (soon a joystick). The horizontal cursor is the usual vertical line but the vertical cursor is an intensified horizontal slice though the spectrum at the cursor position (in other words, the horizontal plot at the cursor position is intensified). It is this feature which makes

the low-resolution graphics useful at high resolution, but only because the cursor can be moved by the touch of a button. I will soon provide a similar vertical slice at the position of the vertical cursor, to aid in connectivity searches. Such a display mode is useful when looking for low S/N peaks in the presence of baseline curvature due to other peaks. Currently it takes about 40 ms to draw a 256-point horizontal line, or 8 sec to draw 200 lines, starting from raw FT'd data in RAM and including gain, clipping, and threshholding routines. I expect to reduce this by at least fivefold with the aid of the new coprocessor board. In comparing this performance to that of other systems remember that a 32 bit FT has much more dynamic range than a floating point routine (which really has only 24 bit dynamic range) or, of course, a 16 bit FT which is much faster with this class of coprocessor.

I don't know if it would be hard to write a contouring program for the AT and I would like to hear from anyone who has done so, or has used an available routine.

The NMR timing system was upgraded a year ago by Sara Kunz, and is based on PALS and EPROMS. It is a state machine of hierarchical architecture. A master card based on an EPROM and a few PALS can call routines (like 214 or 1331 or soft pulses, or HOHAHA or heteropulses, or t1 intervals) that are stored on, and controlled by, several slave cards. This allows for unlimited incremental hardware expansion. The system is separate from the computer, which only provides t1 and t3 information and specifies phases via fast homemade serial output. The timer runs continuously (thereby avoiding delays due to computer-loading and also facilitating development and debugging). To try a new pulse sequence you have to burn a new EPROM, which is a pain. However, this step is generally the easy part of developing a new 2D sequence. The EPROM could be replaced by a RAM loaded from the computer, or both systems could exist side by side. If we did not already have this system in place I would seriously consider using the new coprocessor board to control a simplified timer, since it runs at 10 MHz and has 14 8-bit I/O ports available.

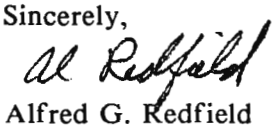
The NMR's computer does almost nothing because we have an input processor front-end that can buffer and cyclops four FIDS of 14 bit precision (see Rev. Sci. Instrum. 54, 503 [1983]). Again, if we did not already have this reliable system in place, I would seriously consider using the new coprocessor board as an input buffer. It can hold up to nearly 64K 16 bit words and I think it could handle most kinds of NMR applications.

The disadvantages of this setup are obvious: You have to write all the routines yourself and the result inevitably is inferior in looks, and much less so in function, to the commercial product.

The advantages are that the Intel-based AT computers and their successors are likely to continue to evolve compatibly in the future with inexpensive enhancements and they already provide great power for the money. There are several other coprocessors similar to the TI chip I used, or faster ones, but this one is fast enough for my purposes and is well supported and continues to evolve. The data station cost about $6000 and requires construction of a front panel, but I have written a keyboard-only version which is not quite as convenient but requires only a base computer costing about $2500 (without plotting or fast coprocessor board) so that collaborators can look at data anywhere. The NMR computer system cost around $4000 (the instrument overall cost less than $250,000 for hardware, based on an Oxford microbore). The data station was supposed to be a spare for the NMR computer but both have operated without failure for two years (downtime is always a result of some half-assimilated upgrade of the systems). This instrument has often operated without failure when the room temperature has exceeded 80 C, long after the commercial instrument in the same room has kicked off.

I expect to have the TMS320c25 software available unsupported but with good documentation fairly soon (if anyone is interested). Integrating it into a system would require some simple programming. The main software for our computer is written in C and assembly using an obsolete compiler/assembler. It is sporadically documented and the useful parts are constantly being modified. However, parts of it would be useful to someone seriously developing an AT system, and it is available unsupported to individuals.

Sincerely,



Alfred G. Redfield
Biochemistry, Brandeis University, Waltham MA 02254 USA

ICI **Agricultural Products**

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Western Research Ctr.
1200 S. 47th Street
Box 4023
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Telephone (415) 231-1000
Fax (415) 231-1368
Telex 172197

September 21, 1988
(received 10/13/88)

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

"Tautomerization of Z-D-Ribose Oxime"

Dear Barry:

It is possible to monitor the rate of isomerization of Z-D-ribose oxime by $^1$H-NMR in $D_2O$ as it is transformed into an equilibrium mixture of both E and Z isomers. D-Ribose oxime crystallizes in aqueous ethanol in the Z-form. This Z-form is less favored thermodynamically than is the E-form, as the equilibrium percentages are 80% E and 20% Z. By dissolving pure crystalline Z-D-ribose oxime in $D_2O$ the demise of the Z-form and the increase of the E-form is measured as a function of time.

Tautomerization of Z-D-ribose oxime is observed to be kinetically simple as shown in Figure A. This is a reversible first-order process and very similar to that shown previously for Z-arabinose oxime[1]. The rate of tautomerization, which is determined by the sum of the rate constants of the forward and reverse reactions is equal to $1.0 \times 10^{-3}$ $min^{-1}$ (Fig. B). This rate constant is approximately 50 times smaller than D-ribose mutarotation ($4.92 \times 10^{-2}$ $min^{-1}$)[2].

CKTseng

C. K. Tseng

JR Snyder

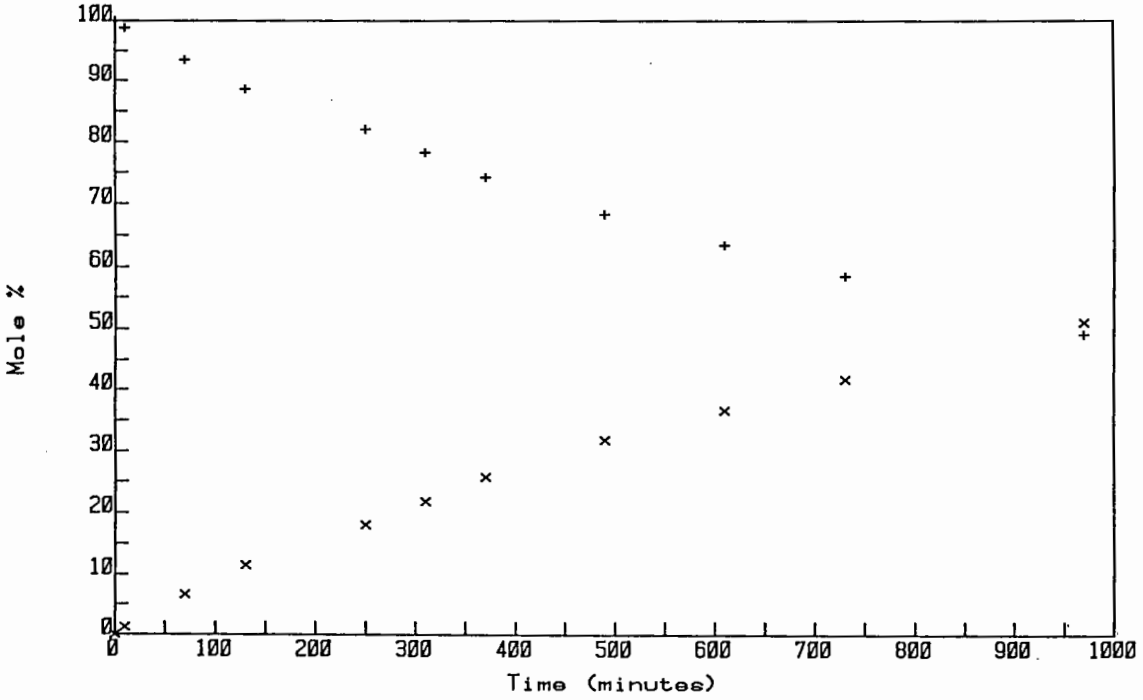
J. R. Snyder

References:

1) P. Finch and Z. Merchant, JCS Perkin I, (1975) 1682-1686.

2) W. Pigman and H. S. Isbell, Adv. Carbohyd. Chem. Biochem. (1968) 23, 11-57.

**A**


Isomerization of Z-Ribose Oxime in Deuterated Water at 20 C
Mole %
Time (minutes)
0
10
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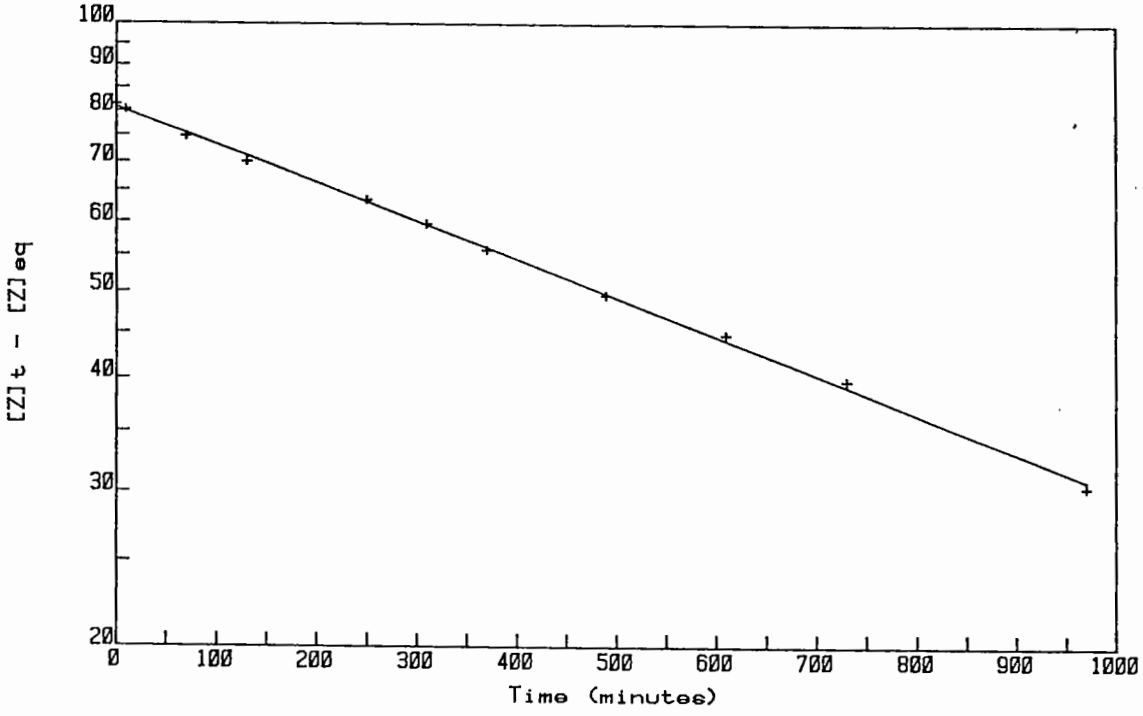
800
900
1000

**B**


Isomerization of Z-Ribose Oxime in Deuterated Water at 20 C
[Z]t - [Z]eq
Time (minutes)
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

INDIANA UNIVERSITY

DEPARTMENT OF CHEMISTRY
Chemistry Building
Bloomington, Indiana 47405
(812) 855-5513

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

October 17, 1988
(received 10/20/88)

# A Platform for Vibration Damping, Leveling, and Height Control of High Resolution Superconducting Magnets

Dear Barry:

Three years ago, we designed and constructed a platform that provides good vibration isolation, level control, and height control for a high-resolution superconducting magnet. This platform was installed under the magnet of a 200 MHz ($^1$H frequency) spectrometer, as part of our efforts to develop ultrahigh resolution. Recently, we have observed that a perfectly vertical magnet significantly improves the resolution for a spinning sample in a 500 MHz spectrometer. Also, we have received several inquiries from users of 500 MHz spectrometers who are encountering problems caused by mechanical instabilities. Therefore, we have decided to share the design of our platform. A paper will appear in the Journal of Magnetic Resonance about April, 1989. The platform requires a constant source of compressed air, at a pressure dependent on the load (see below). It provides (i) a high degree of vibration isolation, (ii) the ability to adjust the level of the platform, and (iii) an invariant vertical position independent of load. The last feature may be important for maintaining homogeneity of magnets located above concrete floors which contain embedded steel rods. The "rubber tire" vibration isolators provided as extra-cost accessories by some instrument manufacturers obviously yield a gradual change in vertical position as the weight of liquid nitrogen (1.76 lb/L) changes.

Figure 1 shows the components of the system and how they are connected together with air hoses. Figure 2 is a top view of the aluminum platform; the dashed lines show the location of the components of Fig. 1, sandwiched between the aluminum platform (which holds the magnet) and two rectangular aluminum slabs on the floor. The platform is 1 inch thick and 40×40 inches in size. For a Bruker AM-500 system, it is probably necessary to increase the length to about 50 inches, and to drill holes for attaching an adapter for an automatic sample changer. The floor slabs are 3/4-inch thick and 11×44 inches. Figure 3 shows a frontal view, and Fig. 4 gives a cross-section of one of the four vibration-isolation components (labeled *S* in Figs. 1-3). Details are presented below.

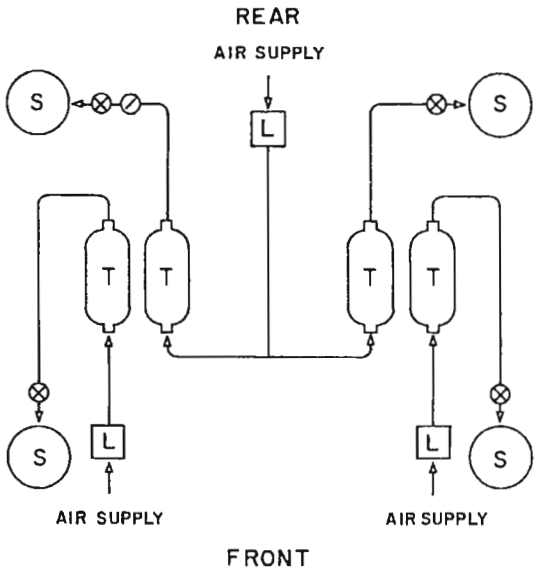



Figure 1. Components and connections. Each arrow designates air flow.

The four items labeled *S* in Figs. 1-3, are 1S3-011 Super-Cushion Air Springs from Goodyear Tire & Rubber Co., Greensburg, Ohio 44232, each designed for a load of 60-370 lb. Our magnet weighs about 500 lbs when full of liquid nitrogen. The required compressed air pressure for a 125 lb (per

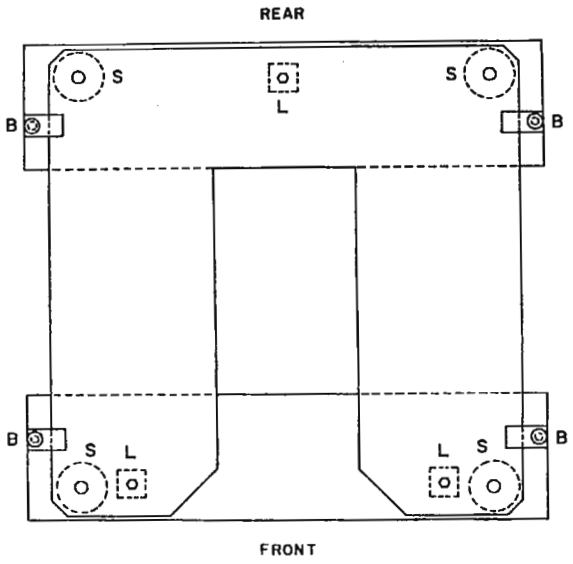



Figure 2. Top view of platform.

device) load is about 35 psi. The pressure gauge shown in Fig. 1 acts as a load monitor; it shows the effect of load change as a result of liquid nitrogen evaporation. The much larger weight of a magnet of a 500-MHz instrument (about 1200 lb fully loaded) will require a pressure of about 80 psi; we recommend a source of compressed air at 100 psi. An alternative would be to use Goodyear 1S5-005 Super-Cushion Air Springs, which are designed for loads in the range 200-1120 lb per device; then the operating pressure would be about 30 psi. We suggest the use of the "Super-Cushion Air Spring Industrial Engineering Manual", available from Goodyear, for design decisions. Please note that, unlike the convolute-bellows ("rubber tire") devices, the 1S3-011 and 1S5-005, which are sleeve-type rolling-lobe assemblies, have to be placed inside restraining metal cylinders, because they are designed to resist vertical loads only. Figure 4 is a cross section of the 1S3-011 inside its aluminum restraining cylinder, made in our machine shop. The two important dimensions of the restraining cylinder, in millimeters, are shown in Fig. 4. Other features of this cylinder are based on recommendations contained in the Super-Cushion Air Spring Industrial Engineering Manual. The top of each restraining cylinder is bolted to the platform; the bottom aluminum plate of Fig. 4 rests on one of the rectangular aluminum slabs (see Figs. 2 and 3).

Each air spring has a needle valve attached to its 1/8-inch NPTF fitting (in order to create a flow restriction), which is then connected to a 1-liter stainless steel ballast tank (304L-HDF4-1000 sample cylinder from Whitey Co., Highland Heights, Ohio 44143), labeled

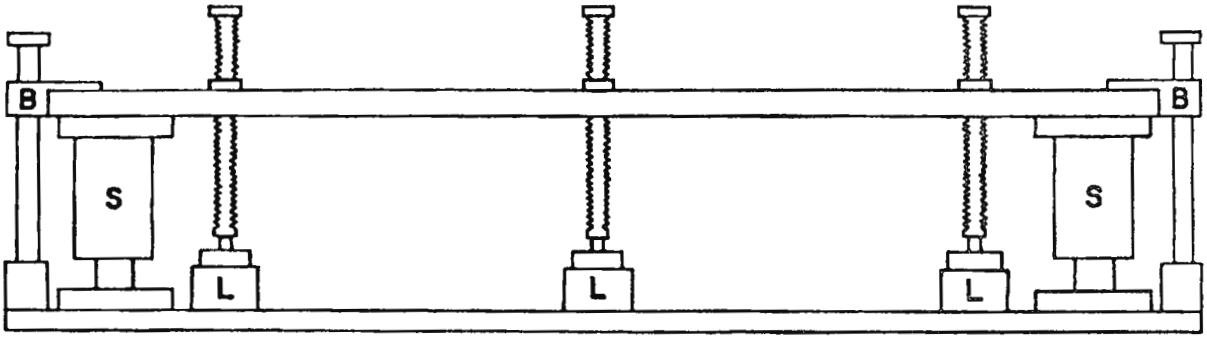



Figure 3. Front view.

*T* in Fig. 1. Each of the two front ballast tanks is then connected to an automatic servo air level control, labeled *L* in Figs. 1-3, purchased from Peabody Noise Control of Dublin, Ohio 43017; this item did not have a part number. A single level control device is connected to the two back ballast tanks (Fig. 1). Filtered, dry building air is supplied to the input of each level control device; it then flows through the ballast tanks and needle valves into the air springs. The flow rate is very low, and is a function of the intensity of floor vibration and consumption rate of liquid nitrogen (and to a lesser degree liquid helium).

Long brass bolts located above the level control devices (see Fig. 3) are in contact with the level sensing rods of these devices. They are threaded (3/4-16) through the aluminum platform and can be adjusted individually to compensate for floor irregularities.

The items labeled *B* in Figs. 2 and 3 are 3/4-inch linear bushings from Thomson Industries, Manhasset, New York 11030, attached to the platform. They enclose Thomson 3/4-inch case-hardened rods attached to the bottom aluminum slabs. This arrangement prevents lateral motion and tilting.

The compressed air lines (Fig. 1) consist of 3/8-inch O.D. and 1/16-inch wall polyvinyl chloride tubing reinforced with braid molded into the tubing, purchased from Bay Rubber Co., Oakland, CA 94621. For ease of installation and service (see below), we use Swagelok Quick-Connect type QC4 fittings from Crawford Fitting Co., Solon, Ohio 44139 at most connection points of Fig. 1.

In three years of operation, this platform has not had any component failures. However, we have suffered from failures of the building compressed air system. Even though we "protect" the air source with our own high-efficiency water and oil removal filters, after a shutdown the building compressed air source produces such copious amounts of oily water that some of it has reached the platform components. We do not know the short-term and long-term effects of water and oil on these items. Therefore, we are now setting up an automatic switch from building air to nitrogen gas (from a tank) upon building air shutdown. It will be a latching system that will require manual switching back to compressed air.

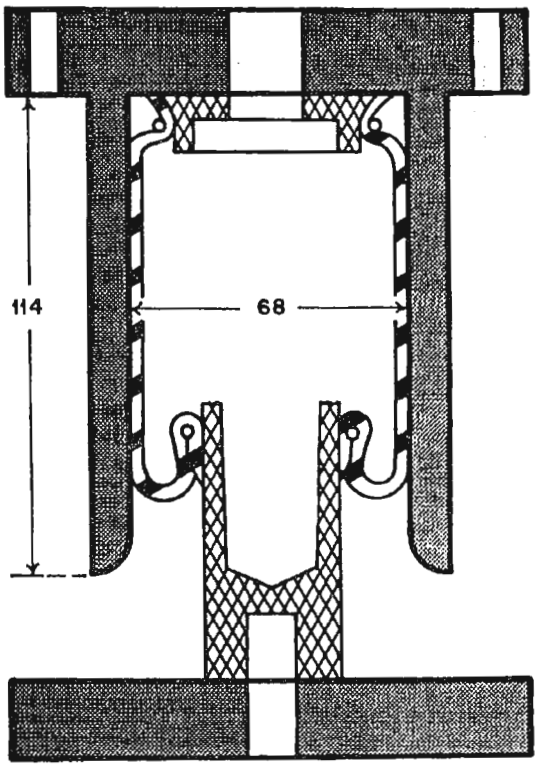



Figure 4. Goodyear 1S3-011 Super-Cushion Air Spring (thick diagonal shading) and its upper and lower retainers (cross hatching) enclosed in the restraining cylinder. Important design dimensions are given in millimeters.

Best regards,

Adam Allerhand

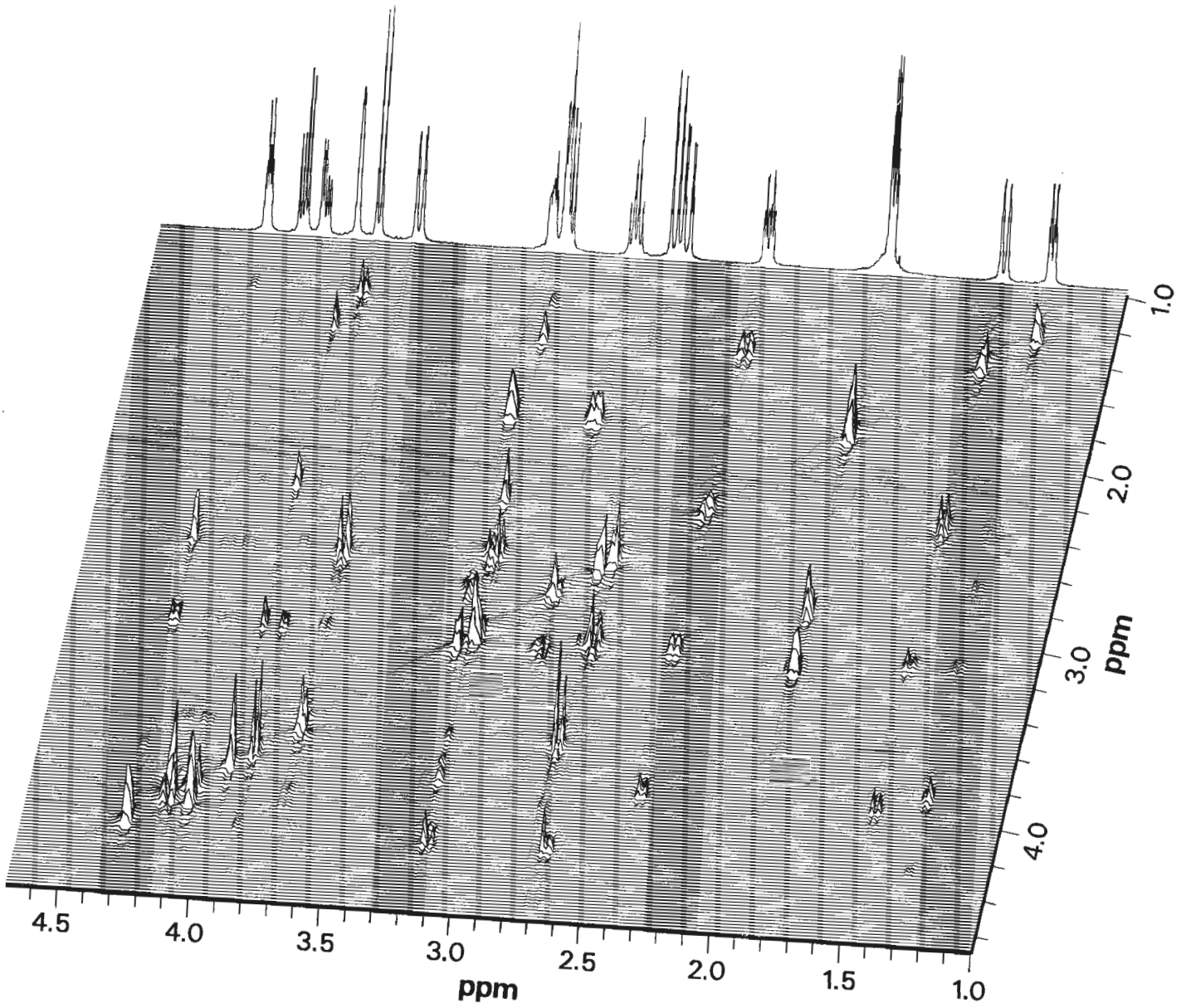
Steven R. Maple

Steven R. Maple

## Postdoctoral Position

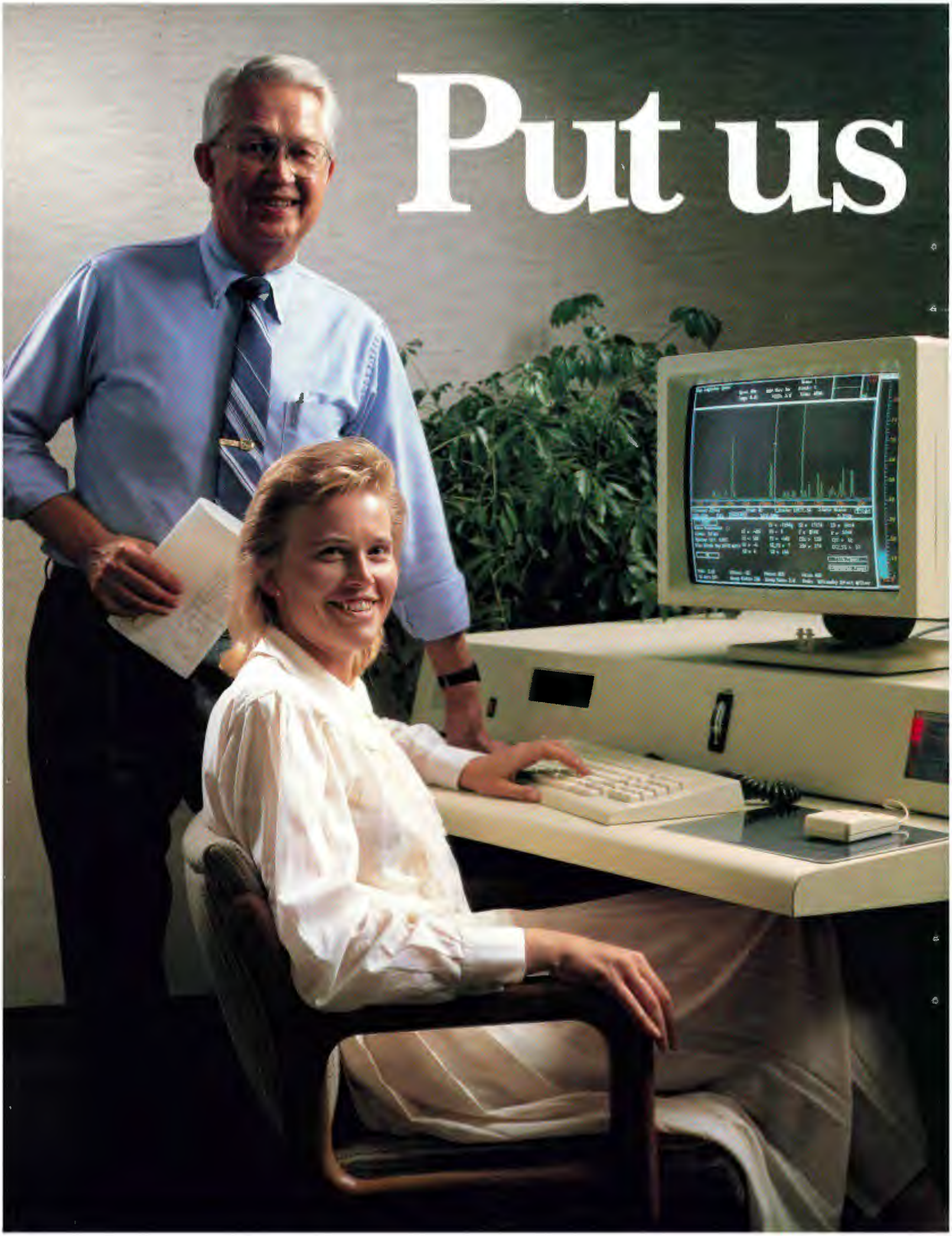
A postodoctoral position in peptide conformational studies is available at Ciba-Geigy Pharmaceuticals. The individual we are seeking should have a Ph.D. or equivalent and extensive experience in 2-dimensional NMR techniques, particularly as it relates to peptide structure determination. Knowledge of DISGEO and/or HARE software programs is also desired. Opportunities to work with an academic institution involved in solutions of peptide or protein conformations will be included.

The position could become available as early as January 1989. Interested persons should apply to Dr. Nina C. Gonnella, CIBA-GEIGY Corp., 556 Morris Ave., Summit, N.J. 07901. Tel. (201) 277-7265




**HOHAHA of Strychnine on an Omega 600**

***GE NMR Instruments***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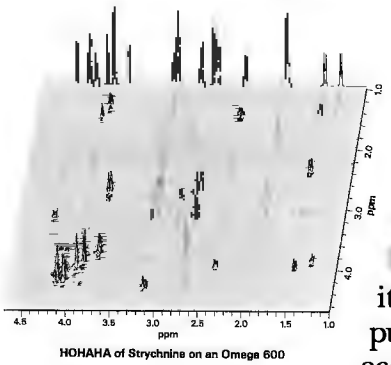

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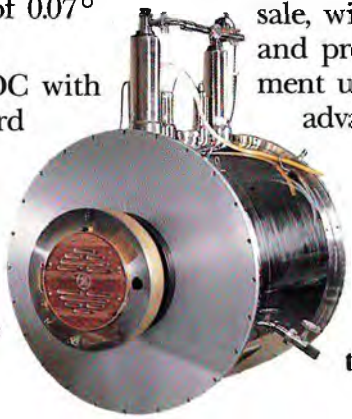

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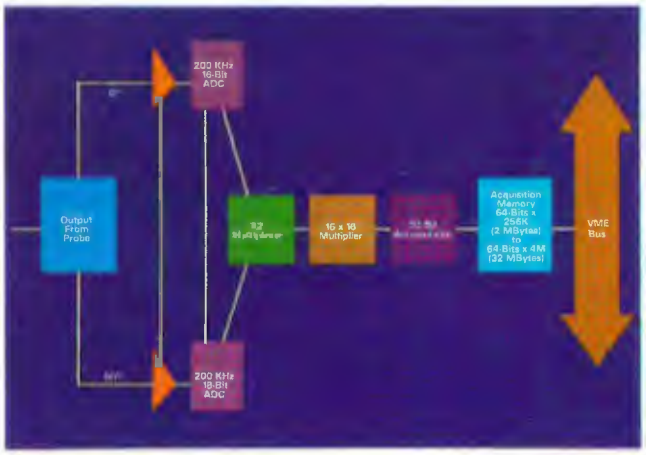


**Fig. 1**

*The Alpha HDR digitizer.*

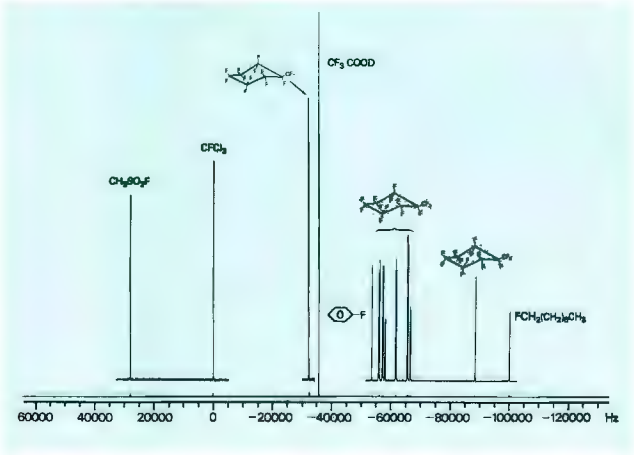


**Fig. 2**

*200 KHz spectral width $^{19}F$ spectrum acquired on a GN-500 Omega System. Note the extremely flat baseline obtained with the Alpha HDR.*


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Swiss Federal Institute of Technology Zurich

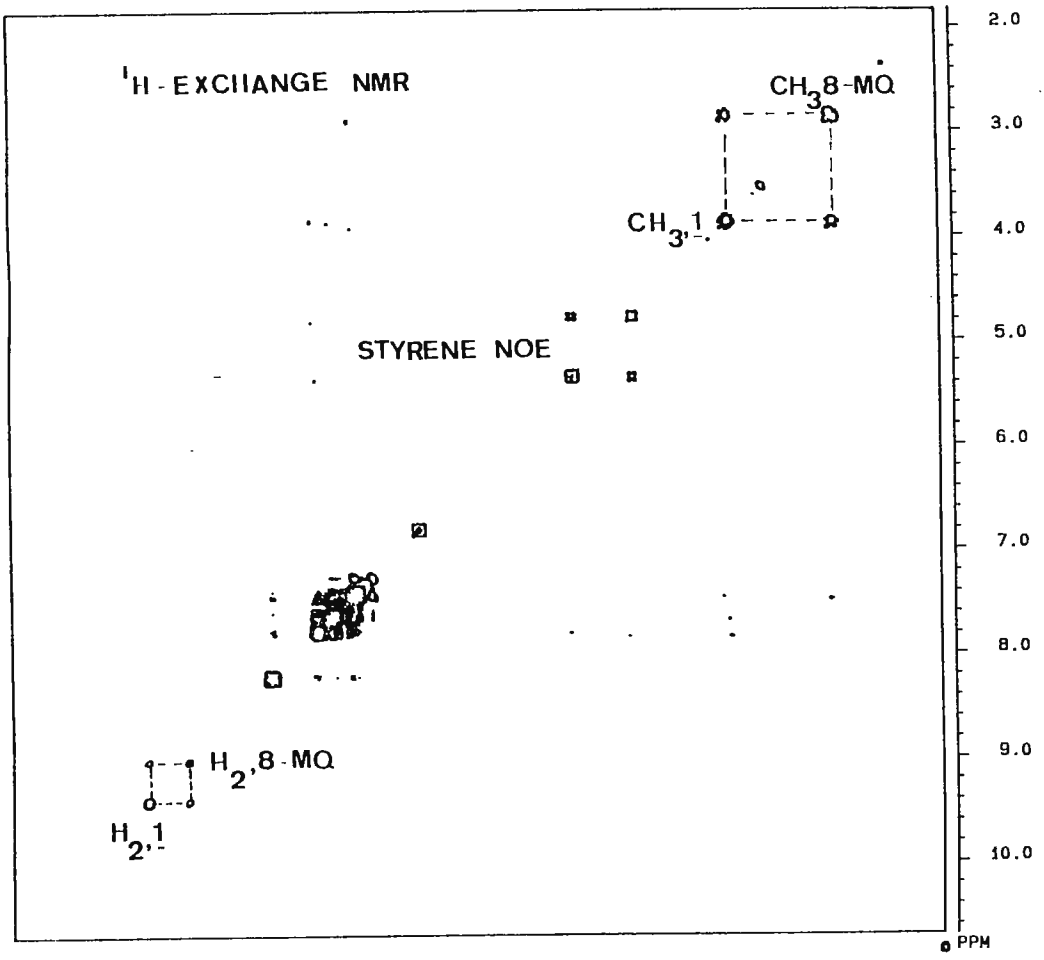
*Laboratorium für anorg. Chemie*
*Prof. Dr. P.S. Pregosin*

(received 10/14/88)

Dear Barry,

Our continuing interest in weak C-H bonds to Pt(II)[1] has prompted us to study the interaction of the methyl group of 8-methylquinoline, 8-MQ, with the metal in trans-$PtCl_2(PhCH{=}CH_2)(8\text{-MQ})$, **1**. As in previous examples[1] we observe, for **1**, a coupling from the methyl to the $^{195}Pt$, J = 12.8 Hz. The complex is dynamic on the NMR time scale at RT as shown by 2-D Exchange Spectroscopy (see figure) suggesting rather weak Pt←H-C bonding.

Best wishes




Suggested Title: Weak Pt←H-C Interactions

1. A. Albinati, C.G. Anklin, G. Ganazzoli, H. Rüegg and P.S. Pregosin, Inorg. Chem. 26 (1987) 503; A. Albinati, C. Arz and P.S. Pregosin, Inorg. Chem. 26 (1987) 508; C.G. Anklin and P.S. Pregosin, Magn. Res. Chem. 22 (1985) 671.

THE UNIVERSITY OF MELBOURNE
Department of Organic Chemistry

Professor: D. W. Cameron
Telephone:(03) 344 6492

Head: D. P. Kelly
Telephone: (03) 344 6464

5th October, 1988
(received 10/12/88)

Professor B. L. Shapiro,
966 Elsinore Court,
PALO ALTO. CALIFORNIA. 94303.
U.S.A.

Dear Barry,

Inverse detected, Long Range C-H Correlation
spectrum of a bisbenzimidazole on a JEOL GSX400

In connection with our work on the synthesis of DNA binding compounds, we have prepared a range of bisbenzimidazoles related to Hoechst 33258. One such molecule prepared by Dr Robert Hook is the 3-amino-5"-piperidino-analogue shown in the Figure, for which we have now assigned all the quaternary carbon resonances using the inverse ($^1$H) detected long range CH correlation technique.

With the assistance of the staff at the JEOL Applications Laboratory in Tokyo, we obtained the long range correlated 2D map shown in the Figure. The pulse sequence (EXMOD) VHMBC was used, together with values PI1 = 60 ms ($2\ ^nJ_{CH}$)$^{-1}$ and PI3 = 3ms ($2\ ^1J_{CH}$)$^{-1}$, PW3 = 12 $\mu$s, 128 points in $F_1$, 512 points in $F_2$ and 128 scans for a relatively concentrated solution in $C_3DOD$ at 40°C (sealed, degassed, non-spinning). The pulse sequence is that of Bax and Summers[2], although other sequences are available.[3,4]

Assignments of the protonated carbons are straight forward and based on our previous assignments for iodo-Hoechst and model compounds[5] and normal 2D homonuclear and heteronuclear correlation spectra run previously on our GX400 in Melbourne. Carbon 4" is uniquely shielded between two ortho N atoms, at 101.8 ppm, from which point H-H and C-H correlation spectra allow identification of the three aromatic spin systems; (2, 4, 5, 6), (4', 6', 7') and (4", 6", 7").

Now the recent long range CH spectrum shows only the three bond correlations ($^2J_{CH} \sim 0$) and allows the assignments of $C_{3a',3a"}$ and $C_{5',5"}$ from $H_{7',7"}$; $C_{7a',7a"}$ from $H_{6',6"}$; $C_{2',2"}$ from $H_{6,6'}$ and $C_{1,3}$ from $H_5$.

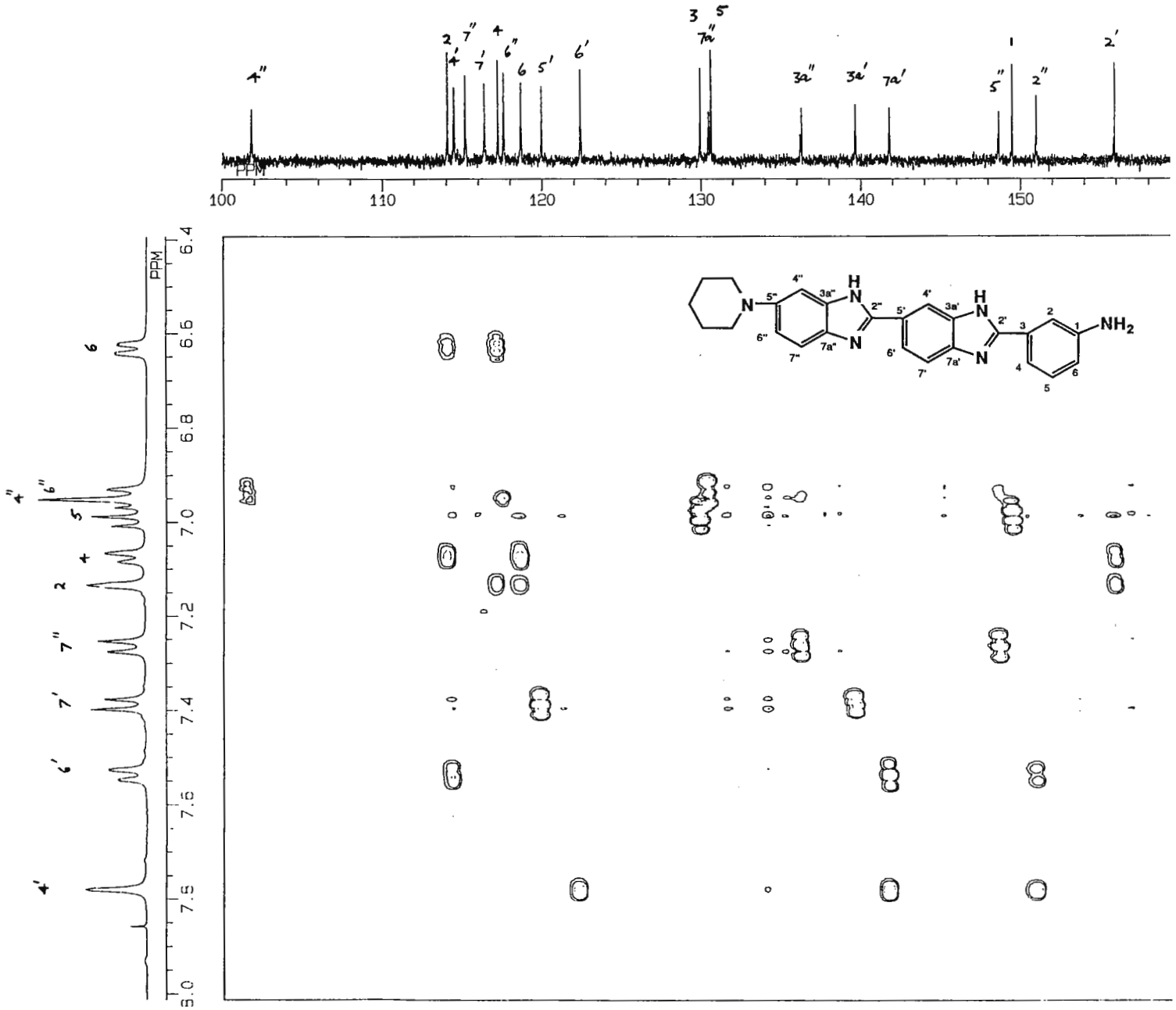
Further details are available for anyone who is interested.

Yours sincerely,

D. P. Kelly.

DPK:EC

1. Aust. J. Chem., 1987, 40, 97-105.
2. J. Am. Chem. Soc., 1986, 108, 2093-94.
3. TAMU-NMR 353-46; Magnetic Reson. in Chem., 1988, 26, 0000.
4. Magnetic Reson. in Chem., 1988, 26, 631-652.
5. Aust. J. Chem., 1986, 39, 373-381.




Micronotices:

* Timely responses to 'Reminder' notices would be appreciated, for sending 'Ultimatum' notices is an expensive nuisance. Removing someone from the mailing list and restoring his/her listing is also expensive and a burden. Thanks.

* I'll be happy to include meeting notices, etc., if such are sent to me.

* Am still hoping for some feedback, sequels, or whatever type of response to the cartoons by Wendy Goldberg . . . .

B.L.S.

362-44

***Dr. J. K. M. Sanders***
0223-336411 (Direct line)
0223-336300 (Switchboard)
0223-336362 (FAX)

University Chemical Laboratory
Lensfield Road
Cambridge
CB2 1EW

Our ref JKMS/JJ

3 October 1988 (received 10/13/88)

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

Dear Barry

**NMR of Polyhydroxybutyrate in vivo**

It's always satisfying when a simple NMR experiment solves a long-standing problem in biology or chemistry. Here is an example from Glenn Barnard, one of my graduate students.

Polyhydroxybutyrate (PHB), and its copolymer with hydryoxyvalerate, are storage polymers produced by a range of micro-organisms. They are high-melting solids with exciting potential as biotech competitors to traditional polyethlenes. So what's the problem? Well, 'everybody' in the field 'knows' the polymers are solid, so they have worried for many years how the bio-synthetic and degradative enzymes could operate effectively on lumps of plastic.

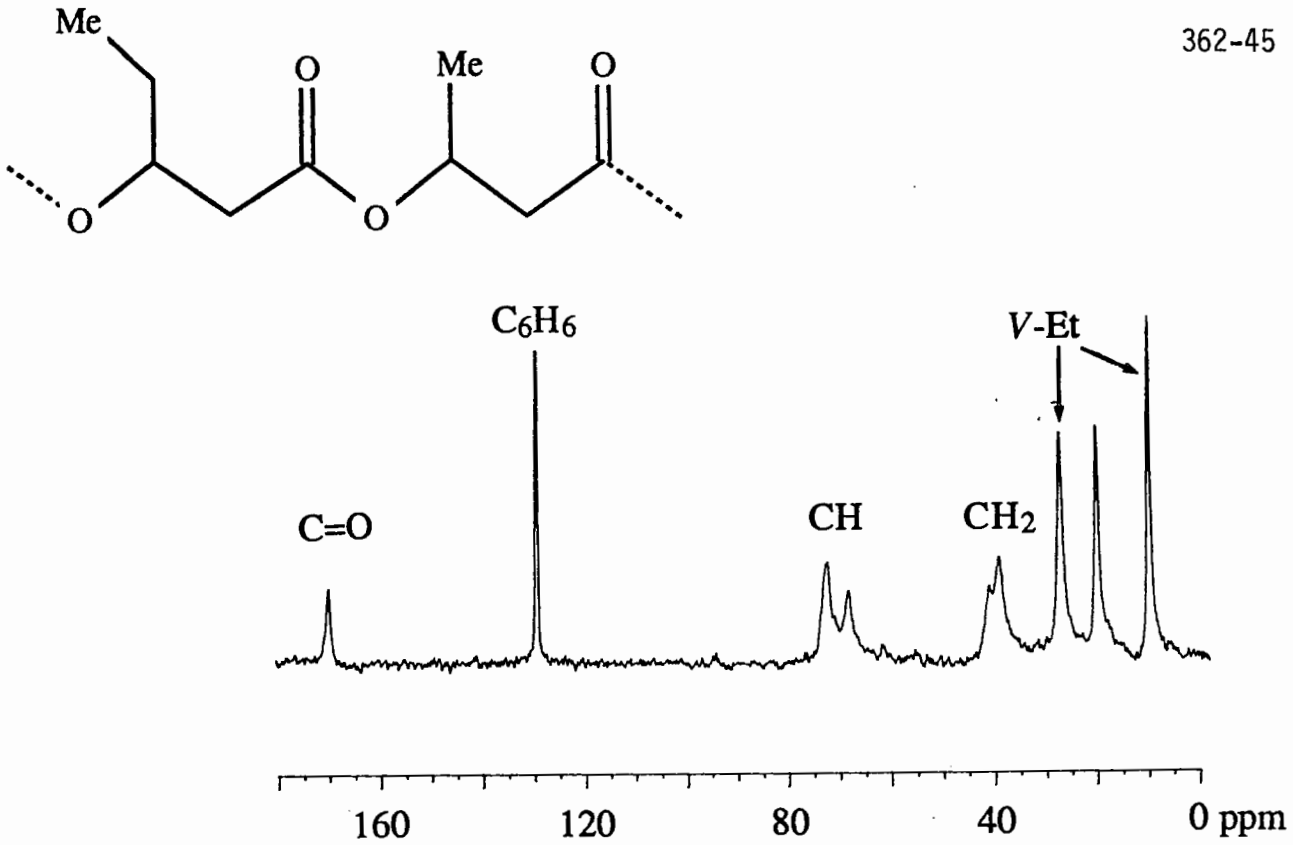
Our natural abundance $^{13}C$ spectra of the live cultures (see figures), acquired with 1000 transients or less, immediately provide an answer: the polymer is not solid in vivo! To be more precise, its physical properties (T1, T2, NOE...) are consistent with an amorphous polymer well above its glass point. Much easier for an enzyme to munch.

That solves the enzymes' problems, but why is the polymer so mobile in vivo? We have evidence that it is kept in this metastable state by hydration, that it solidifies on isolation or on being mistreated. All previous physical studies on PHB were actually on the dehydrated, solid form. We believe that ours is the first study of PHB physical chemistry in vivo.

A preliminary report of this work appeared in FEBS Letters, 1988, **231**, pp 16-18, and a full paper will be published in the Journal of Biological Chemistry in early 1989.

Best wishes

Jeremy



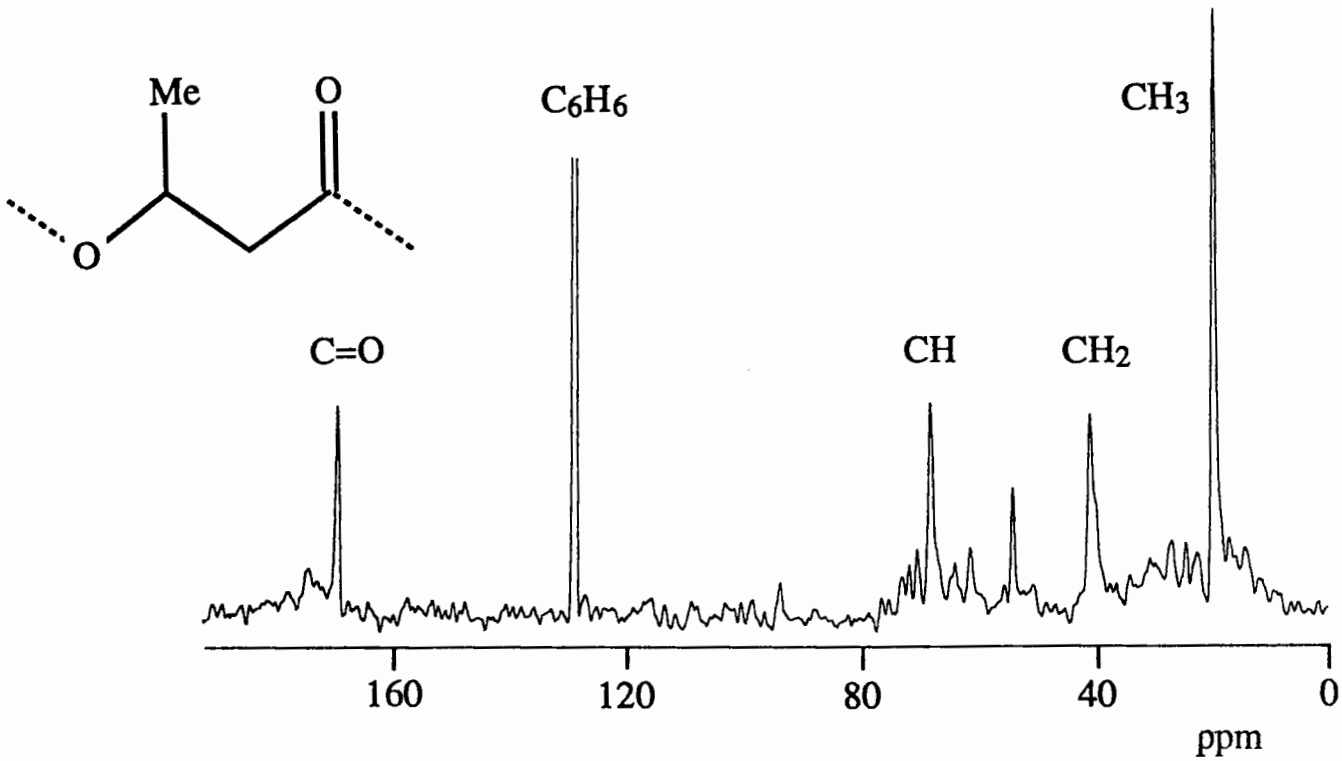




Figure : Natural abundance $^{13}C$ spectra of live suspensions of Alcaligenes eutophus. The culture producing pure PHB was grown on acetate, while the copolymer wasproduced by a propionate-fed culture. The benzene standard was in an external capilliary.

# LABORATOIRES DE CHIMIE

Département de Recherche Fondamentale de Grenoble

*Centre d'Etudes Nucléaires de Grenoble - 85 X - 38041 GRENOBLE Cédex - FRANCE*


Grenoble, le *10 Octobre 1988* (received 10/15/88)

N° référence :

*CONFORMATIONAL STUDIES OF FREE NITROXIDES RADICALS BY N M R*

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

***Dear Barry,***

*Stable nitroxides radical have been early recognised as "spin labels" and studies as such by EPR. Instead, the use of NMR has been limited to proton spectra of concentrated solutions (1). With selectively labelled $^{13}C$ compounds, a new conformational tool is proposed from $^{13}C$ spectra of dilute solutions.*

*A glucosidic example is given, compound 1 (fig.1) : tetramethylpiperidin-1-oxyl-4-yl 2,3,4,6 tetra-O-acetyl-β-D-glucoside. The main distance between the $^{13}C$ and the NO group depends principally on the Psi angle, with a new way to test the variations of this angle with external parameters. The compound 1 has been prepared according N.R. PLESSAS and I.J. GOLDSTEIN with some adaptations. Scales for concentrations, separation of contributions governing the relaxation value T1 of the $^{13}C$ enriched compound, are indicated on fig. 1.*

*The following procedure is used :*

- *a determination of the relaxation T1 values of the $^{13}C$-1 at different concentrations.*
- *an extrapolation at infinite dilution for 1/T1 values (suppression of the intermolecular paramagnetic contribution, proportional to the concentration).*
- *substraction of the intramolecular diamagnetic contribution (by use of a diamagnetic model : hydroxylamine form of compound 1).*

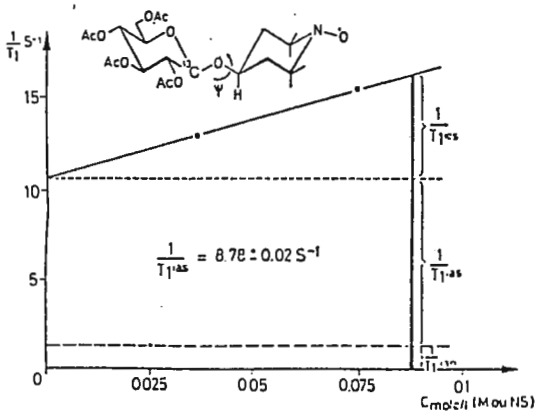



*Fig. 1*

*Legend*

*ies : intermolecular electronic spin*

*las : intra molecular electronic spin*

*ian : intra molecular nuclear contribution*

*NS : number of spin*

*Références*


*1 - R. BRIERE, H. LEMAIRE, A. RASSAT, P. REY and A. ROUSSEAU, Bull. Soc. Chim. Fr., 4770 (1967)*

*2 - N.R. PLESSAS and I.J. GOLDSTEIN, Carbohydr. Res., 89, 221 (1981)*

*3 - A. BLANCHARD, F. CINGET, P. FRIES, D. GAGNAIRE, L. ODIER and Ph. VOTTERO, Communication at the 4th Bratislava Symposium on Saccharides, 1988.*


*F. CINGET* *D. GAGNAIRE* *Ph. VOTTERO*

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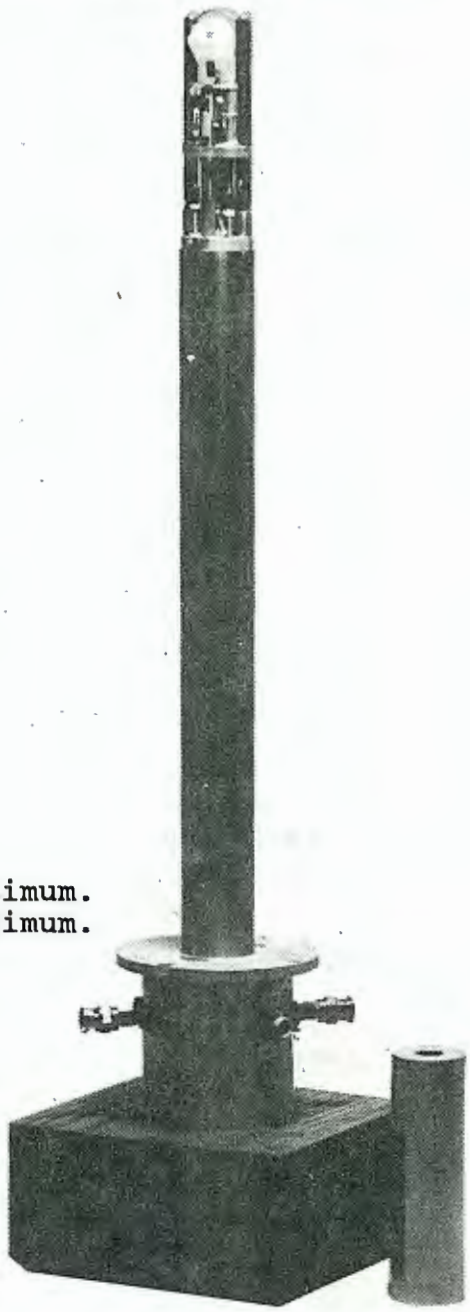

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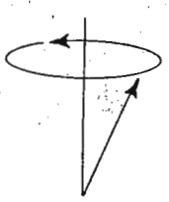

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UNIVERSITY OF MISSOURI-ROLLA

College of Arts and Sciences

Department of Chemistry

142 Schrenk Hall
Rolla, Missouri 65401-0249
Telephone (314) 341-4420

Professor B. L. Shapiro
~~Department of Chemistry~~
~~Texas A & M University~~
~~College Station, TX 77843-3255~~ !!

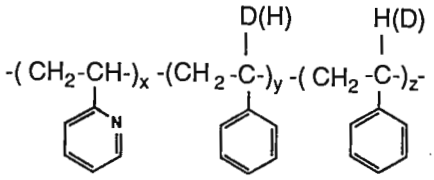
October 9, 1988
(received 10/18/88)

Deuterium NMR study of adsorbed polymers

Dear Barry:

Touché!

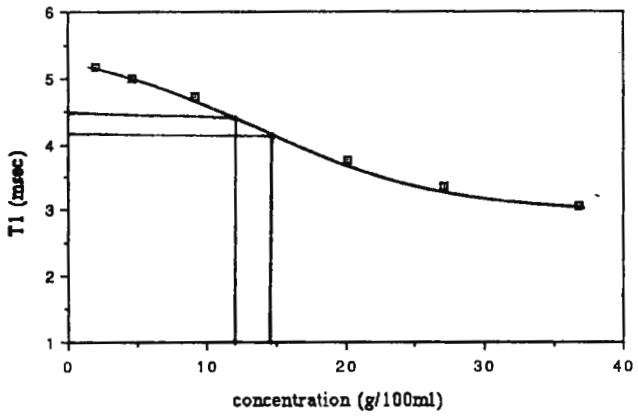
Thank you very much for your recent yellow ☒ Reminder ☐ Ultimatum.
Recently we have attempted to probe the dynamics of block terpolymers adsorbed on silica surface. The block terpolymers chosen for the study were made of two different triblocks namely, poly(vinylpyridine-styrene-deuterostyrene) (PVPSDS) and poly(vinylpyridine-deuterostyrene-styrene) (PVPDSS). These have previously been studied by Granick et. al. (JACS, **108**, 1986, 2869). The structure of these are:




These polymers were adsorbed on silica (Cab-O-Sil M-5) from toluene solutions such that a monolayer coverage of the polymers was obtained on the surface. The monolayer coverage for these polymers from toluene was experimentally determined to be about 1.9 mg/m$^2$ of silica surface. When this polymer is adsorbed on silica the vinylpyridine portion of the polymer attaches itself to the surface while the styrene portion remains in solution forming mainly tails of adsorbed polymer in solution.

The deuterium $T_1$ values for the two swollen terpolymers, PVPSDS and PVPDSS, saturated with toluene were found to be 4.18 msec and 4.47 msec respectively and the $T_2$ values were 2.20 msec and 2.51 msec, respectively. The $T_1$ and $T_2$ values are larger for PVPDSS compared to PVPSDS indicating that the segmental motion of deuterostyrene is relatively more restricted when it is closer to vinylpyridine (and hence to the surface) as in PVPDSS than in PVPSDS. The figure shows a plot of $T_1$ as a function of deutero-polystyrene in toluene at room temperature. At room temperature the concentration of PVPDSS and PVPSDS based on $T_1$ was found to be about 14.5% and 12.0%, respectively (shown in the figure).

We believe that one can determine the concentration of the polymer as a function of the position of the label, with $T_1$ providing the local concentration. $T_2$ gives a measure of longer range perturbations of the motion of the labelled moiety. We are currently appliying this technique to other polymer/surface systems.




Sincerely,

Brijnaresh Sinha

Frank D. Blum
Associate Professor

an equal opportunity institution

The University of Akron

Department of Chemistry
Akron, OH 44325

(216) 375-7372

October 12, 1988
(received 10/17/88)

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

Sequencing Peptides with HOESY Experiments

Dear Barry:

Typically it is possible to assign the proton NMR resonances to and determine the structures of individual amino acid fragments in peptides by identifying cross peaks in COSY experiments. However, it is not possible to determine the primary amino acid sequence from these sepctra since the network of vicinal J-coupling interactions needed to produce cross peaks is broken by the presence of the backbone amide carbonyl group. We have used heteronuclear 2D-NOE spectroscopy (HOESY) to sequence low molecular weight peptides. The method utilizes the fact that a carbonyl resonance receives a substantial fraction of its NOE from the alpha-proton of the amino acid fragment and the NH proton of the adjacent amino acid fragment. By correlating the carbonyl carbon resonances with the alpha- and NH-proton resonances by virtue of NOE it is possible to identify both the source of the carbonyl signal and the identity of the NH on the adjacent amino acid. Proton resonance assignments are obtained from the double quantum filtered COSY spectra.

The technique of amino acid sequencing is demonstrated using the decapeptide Gramicidin-S(1); a spectrum is shown in Figure 1. Simultaneously, the carbonyl assignments obtained from this experiment resolved the disputed assignments of the phenylalanine and proline carbonyl resonances which have been reported by other workers.

Combined application of COSY and HOESY offers an excellent method for determining the primary structure of small peptides. It also provides a means of simultaneously assigning the carbonyl $^{13}C$ resonances. We have performed $^{13}C$ HOESY experiments with a solution of 1 in DMSO at 4.7, 7.05, and 9.4 T. From these experiments we conclude that the optimum field strengths for obtaining HOESY spectra appear to be 4.7 - 7.0 T. At higher field strengths chemical shift anisotropy dominates the relaxation of carbonyl groups reducing the magnitude of the NOE and offsetting any sensitivity gain which might be expected. Therefore, in order to successfully apply this methodology at higher field where higher sensitivity and better spectral dispersion will be achieved, heteronuclear rotating frame experiments must be employed, analogous to the CAMELSPIN/ROESY experiments used for proton homonuclear NOE. The onset of slower molecular motion and higher field strength also produce broader carbon lines (linewidth at half height >3 Hz for our sample) as well as smaller NOE's. This degrades the sensitivity of experiments such as COLOC which rely on the ability to resolve

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long range couplings. We have not been able to obtain COLOC spectra correlating alpha-CH and NH protons with the carbonyl resonances using the same Gramicidin-S sample which produced the HOESY spectrum in Figure 1.

Sincerely,

Peter L. Rinaldi

Fred J. Swiecinski

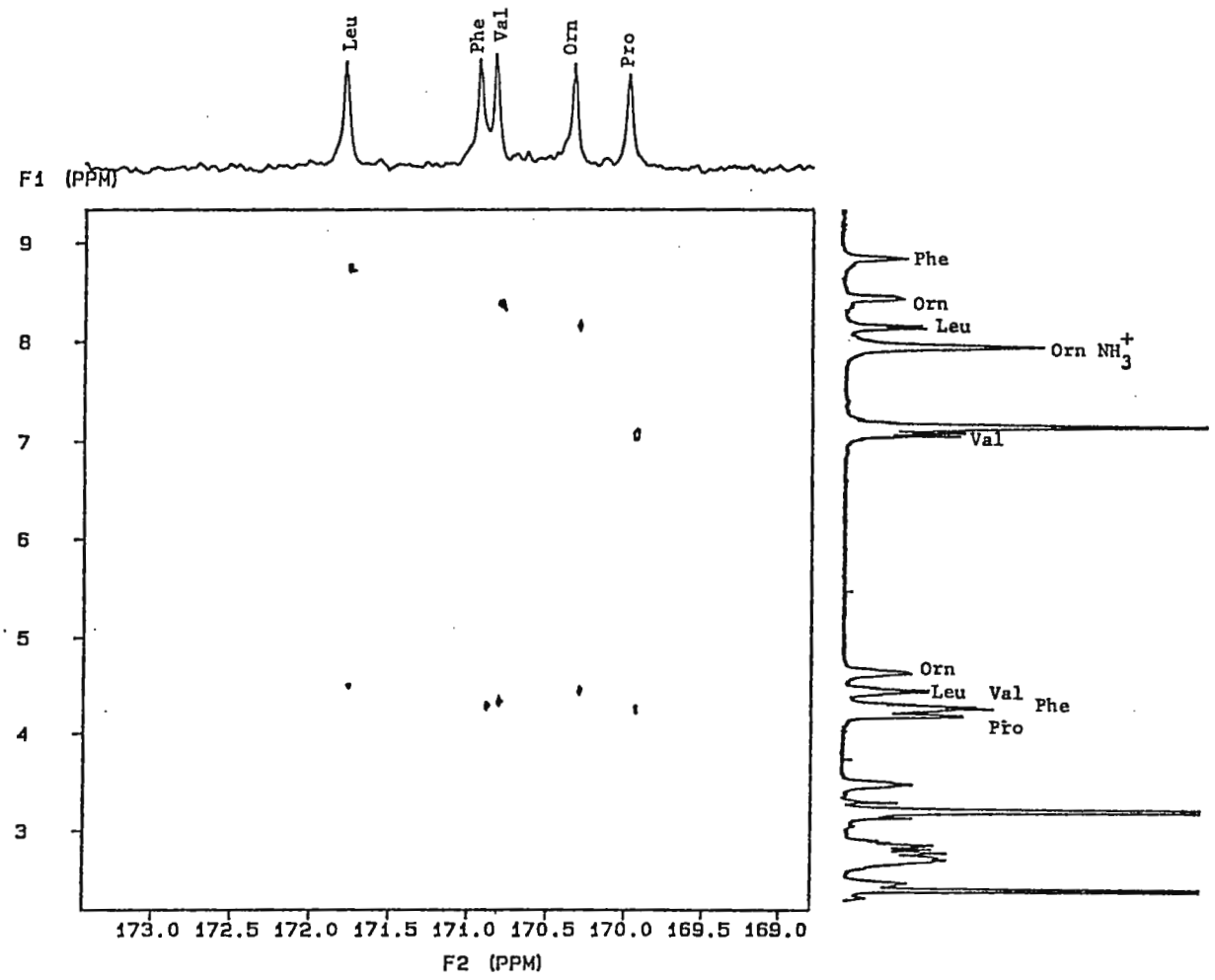


Figure 1

Phase sensitive $^{13}C(^{1}H)$ HOESY spectrum of 35 mM 1 in DMSO-$d_6$ obtained at 75 MHz and 50°. Exact experimental conditions are described in the text. Cross peaks are observed between each $^{13}C$-carbonyl resonance and a single $^{1}H$ resonance in the $CH_{alpha}$ region, permitting the assignment of the $^{13}C$ signal to a specific amino acid fragment. With the exception of Phe carbonyl (171.2 ppm) which is bond to the nitrogen of Pro, each $^{13}C$ resonance also exhibits a cross peak to an NH proton resonance, allowing identification of the adjacent amino acid fragment.

School Of Biochemistry

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

(received 10/17/88)

Dear Prof. Shapiro

**Deuterium isotope Effects on $^{14}N$ and $^{1}H$ Nuclear Shielding of Ammonium Ions**

The large variation in $^{1}\Delta N(D)$ found by various authors made me suggest in a previous contribution, that pH could play a role. We (Antonin Lycka and myself) have now looked more closely into this problem and have found that it is actually the counterions, that makes the difference: $^{1}\Delta N(D)_{tot}$ in ppm ( ~2 M solutions)

| | |
|---|---|
| $ND_4Cl$ | 1.32 |
| $ND_4Br$ | 1.43 |
| $ND_4I$ | 1.56 |
| $ND_4NO_3$ | 1.09 |

$$^{1}\Delta N(D)_{tot} = \delta NH_4 - \delta ND_4$$

$^{1}\Delta N(D)$ depends both on the nature and the concentration of the counterion. With this in mind litterature values can now be explained. A value at infintie dilution of 1.19 ppm can be estimated. $^{2}\Delta H(D)$ is negative in the isotopomers of the ammonium ion and it depends both on the nature and the concentration of the counterion according to our findings. $^{2}\Delta H(D)$ is numerically largest (most negative) in dilute solution suggesting that hydrogen-bonding may be the cause of the negative sign and that the direct isotope effect is positive as found for $^{1}\Delta N(D)$ and becoming more positive with increasing concentrations of the counterion.

One way of explaining the negative isotope effect could be non-directional hydrogen bonds.[1] Jameson and coworkers[2] have recently suggested that the unusual sign could be due to intermolecular effects such as eccentricity and hydrogen-bonding, but suggesting that the counterions contribute to these intermolecular effects. This is clearly contrary to our findings.

Yours sincerely
Poul Erik Hansen

1. P. E. Hansen, In Ionic and non-ionic Hydrates, ed. H.Kleeberg, Springer, 1987, p. 77-80.
2. J.K.M.Sanders, B.K.Hunter, C.J.Jameson and G.Romero, Chem.Phys.Lett. 143, 471 (1988).

PS! As I am spending a sabbatical year at the University of New South Wales would it be possible to redirect my copy to the above adress until the end of June next year? yes. pls

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DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, N.Y. 13244-1200

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

**UTILIZATION OF GRAPHICS SUPERCOMPUTERS IN LABORATORY COMPUTER NETWORKS FOR NMR DATA PROCESSING**

Dear Barry:

The advent of the new graphics supercomputers: Ardent Titan, Stellar GS-1000, Silicon Graphics 4D/200 series, Apollo DN-10000 -- brings extraordinary opportunities to the NMR laboratory. These new workstations combine near-Cray 1S compute power with ultra-high-speed 2D and 3D graphics. Furthermore, these systems, or less-expensive compute server versions (starting at ca. $70K for a 32 MB RAM Titan with 700 MB disk) can be configured as main nodes of NMR laboratory computer networks, supporting 5 to 8 or more users **simultaneously** with minisupercomputer NMR data processing.

All of these new computers use UNIX and X-windows graphics, Version 11. Thus, users at *very* inexpensive workstations can process on the net with local graphics, but at near-supercomputer speeds. Also, early in 1989, X-windows will become available on new **high-speed** Ethernet graphics **terminals** costing less than the lowest priced Tektronix serial terminal. Furthermore, PC's and all DEC computers will support X-windows by mid-1989.

The NMR scientist gains tremendous flexibility in this environment. Who would have thought that 4K x 4K 2D FT processing could be brought to less than 10 minutes in 1989, at practical cost. Equally important, speed on non-vector calculations is also efficient, supporting the full range of NMR processing algorithms at speeds at least comparable with the largest VAX systems - and significantly faster in most cases.

In about two months, after we have had some experience with our Stellar GS-1000 and NMRi's Ardent Titan (2-processor version, to be upgraded to 4-processors in February), we will report specific NMR processing benchmarks. We will also tell you how well our new optical fiber-based 1.5 MHz network works, between NMRi and Syracuse University. This new network link runs both TCP/IP and DECnet protocols and fully supports high speed X-windows graphics across the 1.5 mile connection. (For that matter, for more than six months, Cornell University scientists have used **NMR2** software on S.U.'s VAX 8800 and Alliant FX/80 computers. The 60 mile NYSERnet TCP/IP connection between Cornell and S.U. also runs at 1.5 MHz).

Scientists on NYSERnet or NSFnet can **now** access our software on Stellar, Alliant, Sun-4 or, soon, Silicon Graphics computers. Just call Dr. William Curtiss and ask for a user account.

Yours sincerely,

George C. Levy
Science & Technology Professor

GCL/dg

# Mobil Research and Development Corporation


October 13, 1988
(received 10/17/88)

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


RESEARCH DEPARTMENT
DALLAS RESEARCH LABORATORY
P.O. BOX 819047
DALLAS, TEXAS 75381-9047

13777 MIDWAY ROAD
DALLAS, TEXAS 75244-4312


**Al NMR and Distortions in Minerals**

Dear Barry:

As you may recall from several previous contributions to your famous NMR Newsletter, I have been using aluminum MAS NMR to characterize clay minerals. As enlightened NMR spectroscopists already know, a 2:1 clay mineral is composed of stacked alumino-silicate layers which are sandwiches of an octahedrally coordinated sheet between two tetrahedrally coordinated sheets. The octahedral sheet typically contains Al and/or Mg atoms each of which is in the center of an octahedron which has oxygen atoms at the vertices. The tetrahedral sheet contains Si atoms in the center of tetrahedrons which have oxygen atoms at the vertices; however, many clay minerals have varying amounts of Al for Si substitution in this sheet.

A forthcoming publication (American Mineralogist, sometime in 1989) describes the results of Al MAS NMR measurements on tetrahedral aluminum in 2:1 clay minerals made at magnetic fields of 6.35T and 11.74T. These measurements enable the evaluation of the isotropic chemical shift ($\delta_i$) and the second-order quadrupole effect parameter ($SOQE = QCC[1 + \eta^2/3]^{1/2}$) from the first-moment of the NMR peak. Atomic substitutions (typically, Mg for Al in the octahedral sheet and Al for Si in the tetrahedral sheet) result in changes in the $\delta_i$ and SOQE values of the aluminum in the tetrahedral sheet.

A long time ago, Ghose and Tsang (American Mineralogist, 1973) published QCC and $\eta$ values (determined from CW measurements on single crystals) for tetrahedral aluminum in framework (three-dimensional) aluminosilicates along with the tetrahedral shear strain (sum in the tetrahedron of the absolute values of the tangent of the deviation of the O-Al-O bond angles from the tetrahedral angle). Figure 1 shows that in these minerals there is a linear relationship between QCC (and SOQE) and tetrahedral shear strain.

As shown recently by Weiss et al. (American Mineralogist, 1987), the atomic substitutions in the two-dimensional clay layer cause distortions in the tetrahedral sheet which change the silicon chemical shift. Figure 2 shows that this also occurs for aluminum, in agreement with Kinsey et al. (American Mineralogist, 1985). Figure 3 shows that the atomic substitutions also increase SOQE, parallelling the increase in SOQE and QCC resulting from O-Al-O angle deviations from the tetrahedral angles in three-dimensional aluminosilicates. This congruency may indicate that the atomic substitutions in two-dimensional 2:1 clay mineral layers cause O-Al-O angle distortions. If the aluminum $\delta_i$ changes result from these same angular distortions, we might expect a correlation between $\delta_i$ and SOQE. Figure 4 shows good correlations for both dioctahedral layers (squares) and trioctahedral layers (circles). (In Figures 2-4, the unfilled symbols represent special cases and are not included in the regression calculations which yield the straight lines.) Hence, O-T-O angular distortions (T=Al or Si) correlate well with both $\delta_i$ and SOQE in $SiO_4$ and $AlO_4$ tetrahedrons.

Sincerely,

Don

D. E. Woessner
Senior Research Associate

DEW/mon
Attachment

Figure 1

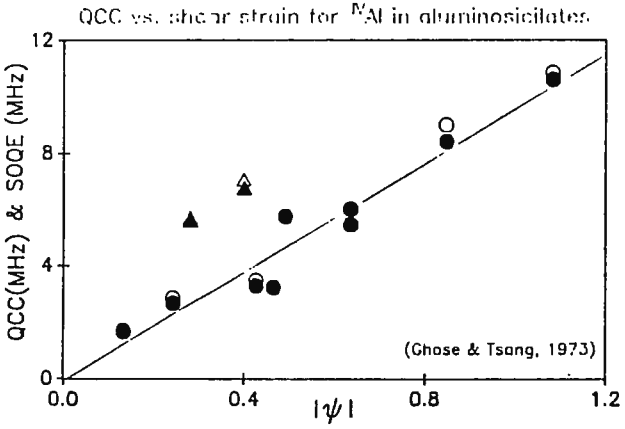



Figure 2

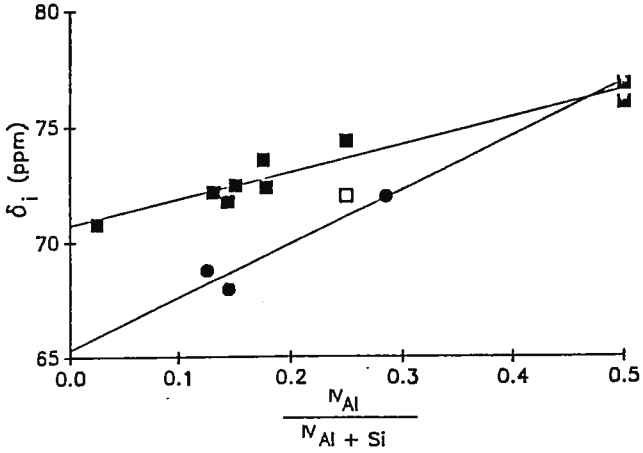



Figure 3

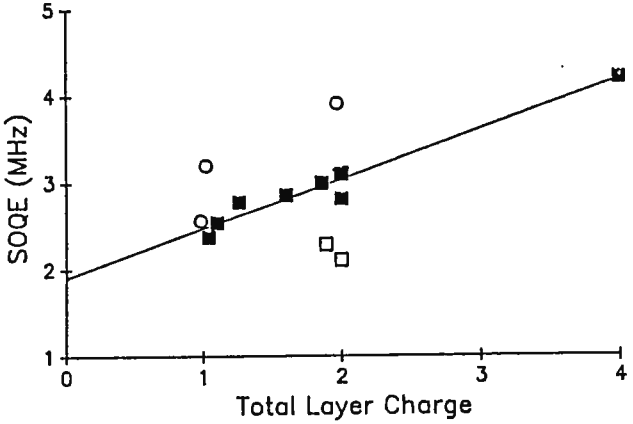
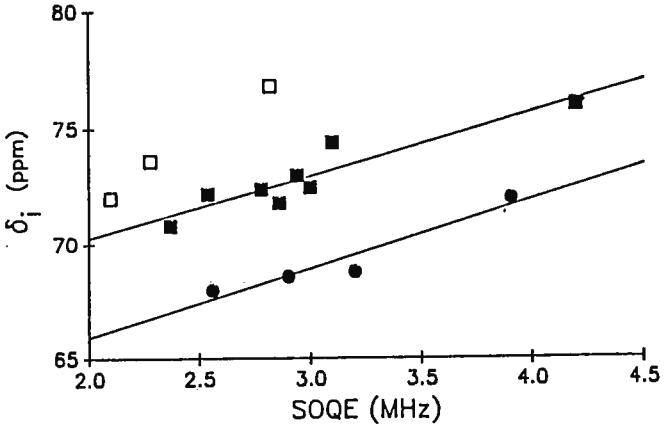



Figure 4



University of North Texas

College of Arts and Sciences
Department of Chemistry

October 14, 1988
(received 10/17/88)

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

**$^{13}C\{^{1}H\}\{^{6}Li\}$ Triple Resonance Experiments. Selective Observation of Alkyllithium Aggregates**

Dear Dr. Shapiro:

We are currently working on the devlopment of several experiments which are based on $^{13}C\{^{1}H\}\{^{6}Li\}$ triple resonance. Here we report on the selective observation of alkyllithium aggregates using $^{6}Li$ J-modulated $^{13}C$ spin-echo spectra.

Shown in the figure are $^{13}C$ spectra for the alpha carbons of $[t\text{-BuLi}\cdot 2OEt_2]_2$ at 12.8 ppm and non-fluxional $(t\text{-BuLi})_4$ at 10.8 ppm. Spectrum **A** is the normal $^{13}C\{^{1}H\}$ spectrum showing $^{13}C$-$^{6}Li$ coupling. Spectrum **B** is the $^{13}C$ spin-echo spectrum with t=0. Spectrum **C** is a spin-echo spectrum with t=0.128 sec (optimized for observation of dimers) and spectrum **D** is the spin-echo spectrum with t=0.184 sec (optimized for observation of static tetramers). As can be seen in these spectra, different alkyllithium aggregates can, in fact, be selectively observed. A complete discussion of the method will appear elsewhere.

All spectra were run on a Varian VXR-300 with a Varian triple resonance accessory. The probe was a 10 mm tunable Varian probe with the lock channel modified for $^{6}Li$ irradiation at 44.1 MHz. $^{6}Li$ decoupling was accomplished by use of the output of an external synthesizer, amplified to 10 watts. We would like to thank John Kilpatrick of Varian for his design and set-up of the triple resonance hardware.

Please credit this to Alan Marchand's account.

Sincerely,

Ruthanne D. Thomas

Donald H. Ellington

Ruthanne D. Thomas
Associate Professor of Chemistry

P.O. Box 5068 • Denton, Texas 76203-5068
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Phone: 302-772-3311

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Wilmad

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Date 3/25/83 Name L. WAYKOLE Title GRA. STUDENT

Address B.S.U. Box 200, Chem. Dept.

Emory University, Atlanta, GA 722

Phone: 329-6208

(404)

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Address BOX 40 MTSU

MURFREESBORO, TN 37132

Phone: 615 898-2954

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IRVINE, CA 92714

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Date 1-8-82 Name L. Overman Title Professor

Address Department of Chemistry

University of California

Irvine, CA 92717 Phone: 714-833-7156

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Type of NMR equipment used in the above evaluation Varian EM 360 A

Date Name Scott Vanderhart Title Asst. Prof.

Address University of California

Alameda Peak, Los Angeles 92110

Phone: 213-[illegible]

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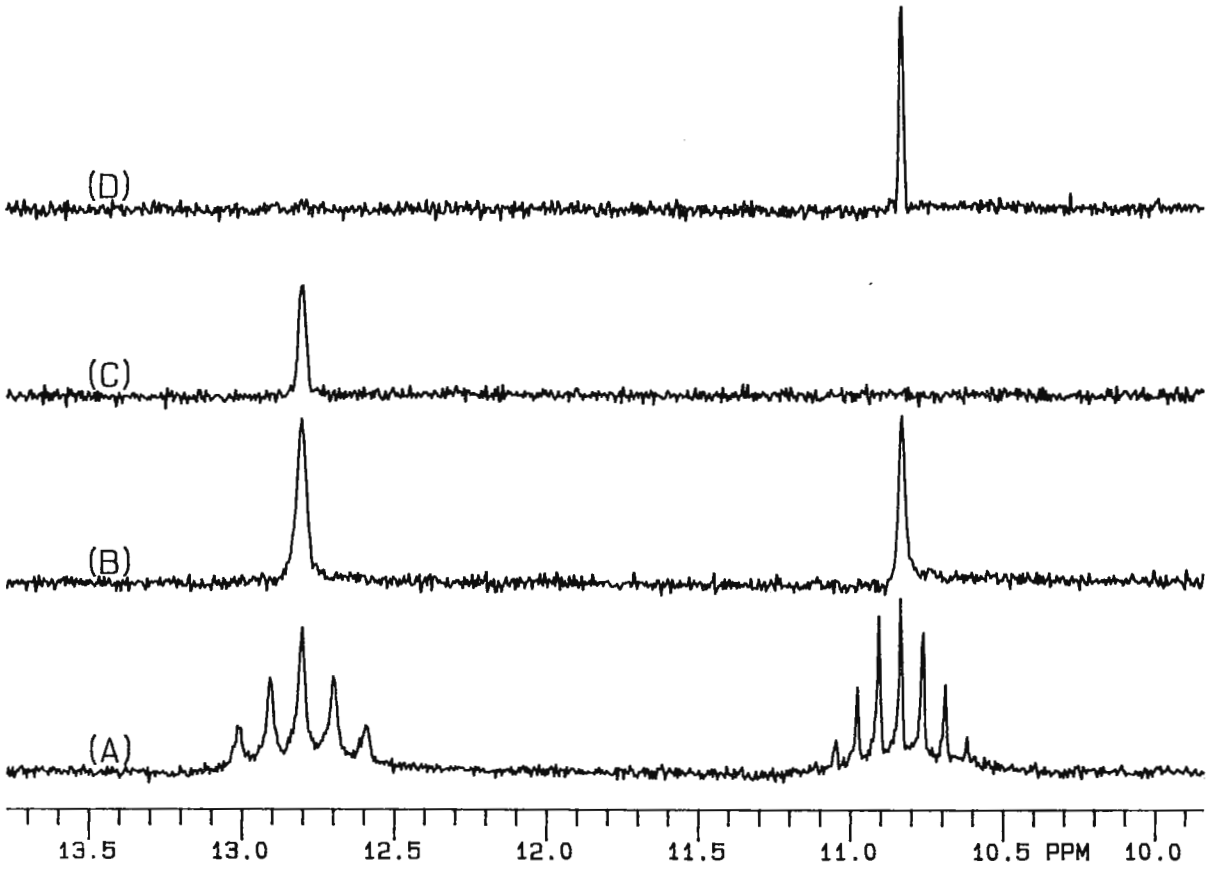


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October 6, 1988 (received 10/15/88)

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

**Model-Independent and Dependent Analysis of the Global and Internal Dynamics of Cyclosporin A**

Dear Professor Shapiro:

Recently we have used $^{13}C$ NMR relaxation studies to investigate the dynamics of a small cyclic peptide, cyclosporin A (Figure 1). By using the model-independent theory of Lipari and Szabo,[1] we have simultaneously determined both the overall correlation time for the molecule and the amplitudes and timescales for the internal motions of all resolvable proton-bonded carbons.

The model-free approach proposes a simple form for the spectral density function $J(\omega)$:

$$J(\omega) = \frac{2}{5}\left[S^2\left\{\frac{\tau_1}{1+(\omega\tau_1)^2}A + \frac{\tau_2}{1+(\omega\tau_2)^2}(1-A)\right\} + (1-S^2)\left\{\frac{\tau_1}{1+(\omega\tau_{1e})^2}A + \frac{\tau_2}{1+(\omega\tau_{2e})^2}(1-A)\right\}\right]$$

where $1/\tau_{1e} = 1/\tau_1 + 1/\tau_e$ and $1/\tau_{2e} = 1/\tau_2 + 1/\tau_e$

Here, $\tau_1$ and $\tau_2$ are two correlation times describing anisotropic overall correlation times, with A a "mixing" parameter ranging from 1 to 0. For each carbon an effective correlation time $\tau_e$ for the internal motion is measured, as well as the generalized order parameter $S^2$ between 1 and 0 describing the amplitude of that motion. When overall molecular reorientation is isotropic, the formula can be simplified, such that $\tau_1, \tau_2 = \tau_m$ and A = 1.

The generalized order parameter has a model-independent significance since no specific model for the internal motion has been assumed in the formula above. On the other hand, $\tau_e$ has no physical meaning unless interpreted within the framework of a specific motional model. We have used this form of the spectral density to fit the $^{13}C$ relaxation data obtained at 75 and 125 MHz for cyclosporin A. Calculated values for the dipolar spin-lattice relaxation time $T_1$ and steady state NOE can be least-squares fit to experimental values using the well-known expressions

$$\left(\frac{1}{T_1}\right)^{DD} = \frac{\hbar^2\gamma_H^2\gamma_C^2}{4r_{CH}^6}\left[J(\omega_H-\omega_C) + 3J(\omega_C) + 6J(\omega_H+\omega_C)\right]$$

$$NOE = 1 + \frac{\gamma_H[6J(\omega_H+\omega_C) - J(\omega_H-\omega_C)]}{\gamma_C[J(\omega_H-\omega_C) + 3J(\omega_C) + 6J(\omega_H+\omega_C)]}$$

A fitting algorithm was developed which finds the best parameters $S^2$ and $\tau_e$ for each carbon at a given constant value of the global parameters $\tau_1$, $\tau_2$, and A. The error function used was as follows:

$$Error = \sum_{\omega_1,\omega_2}\sum_{i=1}^{N}\left(\frac{T_1^{obs} - T_1^{calc}}{T_1^{obs}}\right)_i^2 + \left(\frac{\left(\frac{NOE}{T_1}\right)^{obs} - \left(\frac{NOE}{T_1}\right)^{calc}}{\frac{NOE}{T_1}^{obs}}\right)_i^2$$

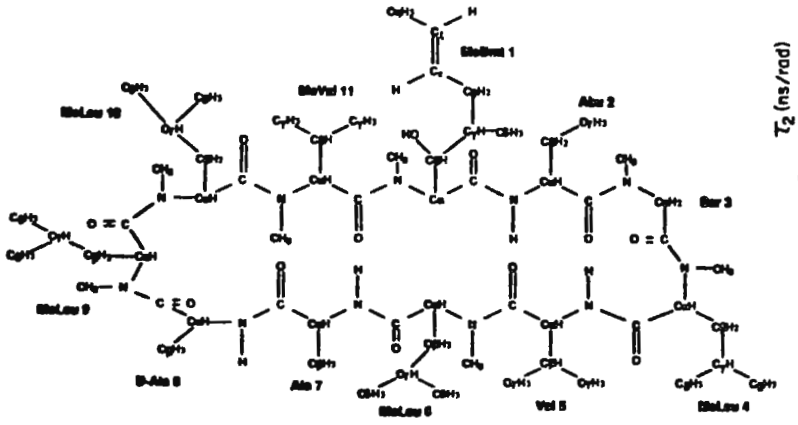

FIGURE 1: Cyclosporin A, molecular weight 1201.5. MeBMT is (4R)-4((E)-2-butenyl)-4,N-dimethylthreonine. Abu is α-aminobutyric acid. Sar (= Sarcosine) is N-methylglycine.

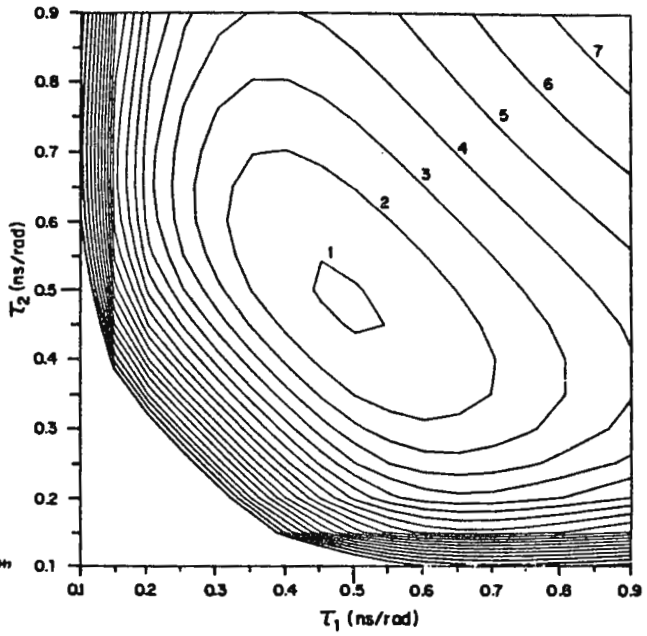


FIGURE 2: Contour plot of the error as a function of $\tau_1$ and $\tau_2$ for A = 0.5. Changes in $\tau_1$ and $\tau_2$ were made in steps of 0.05 ns/rad. The minimum occurs at $\tau_1, \tau_2 \equiv 0.475$ ns/rad. The error function is given by equation 5 for the fitting procedure described in the text and the error levels for each contour are as follows: 1 = 0.637; 2 = 0.682; 3 = 0.730; 4 = 0.781; 5 = 0.835; 6 = 0.894; 7 = 0.956. Note that when $\tau_1$ equals $\tau_2$ as was found here, A is meaningless and the error volume encloses a minimum for all values of A.

A contour plot of the relative error versus $\tau_1$ and $\tau_2$ at A = 0.5 is shown (Figure 2). Our results show that cyclosporin exhibits isotropic reorientation with a correlation time $\tau_m$ of 0.475 ns/rad (in chloroform at 298K). Using a simple hydrodynamic calculation when $\tau_m = 4\pi r^3\eta/3kT$, $\eta = 0.00542$ gm/cm•s, r is calculated to be 10Å. The estimated dimensions of cyclosporin A from the crystal structure correspond to a prolate ellipsoid with major and minor axes of 23Å and 10Å; a sphere of equivalent volume would have r = 13Å.

The generalized order parameters obtained indicate that a range of motions of varying degrees of restriction are present. These order parameters may be compared to order parameters generated by specific motional models, such as the Woessner model for rotation of methyls, or diffusion in a cone. An indepth analysis of our results is being published elsewhere. A number of interesting conclusions may be obtained from this study. For instance, the generalized order parameters for motion of the N-methyl groups correlate well with participation of the carbonyl of the same peptide bond in a hydrogen-bonding interaction. Also, the dynamic information obtained from the order parameters yielded information about the static geometry. We were able to confirm solely on the basis of the model-free parameters the presence of a *trans* rather than *cis* configuration of the double bond in the sidechain of MeBmt 1.

Our results indicate that this method of analysis is sufficient to define *both* the internal dynamics of macromolecules as well as the overall reorientational behavior. Combined with new techniques for both selective isotopic enrichment and detection of low sensitivity nuclei such as $^{13}C$ and $^{15}N$, this technique promises to expand our abilities to quantitatively study the dynamics of larger macromolecules of biological interest.

Sincerely,

Martin Dellwo

Josh Wand

P.S. Please credit this contribution to R.W. Dykstra

[1] Lipari, G., & Szabo, A. (1982) *J. Am. Chem. Soc. 104*, 4546-4559.

362-64

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October 20, 1988
(received 10/22/88)

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

Compensating for Differential $T_1$ Relaxation in the STEZQC Technique

Dear Dr. Shapiro:

The STimulated Echo Zero Quantum Coherence (STEZQC) spectral editing technique has recently been suggested for obtaining *in vivo* lactic acid spectra from a localized volume *(1)*. The STE sequence (Figure 1), in addition to localization *(2-5)*, creates ZQ (and higher order) coherences in coupled spin systems following the first two 90° pulses. The ZQC's evolve during the interval $t_1$ and manifest themselves as an amplitude modulation of the corresponding single quantum signal generated following the third 90° pulse. The ZQ modulation frequency equals the chemical shift difference (in Hz) between the coupled spins. Noncoupled spins, on the other hand, experience no modulation during the $t_1$ period since isolated spin-1/2 nuclei only undergo single quantum transitions. Subtracting two volume localized spectra with the appropriate ZQ evolution periods constructively add signal from metabolites with coupled spins and cancels signal from interfering noncoupled resonances.

The STEZQC technique is illustrated in Figure 2 using a phantom containing 100 mM N-acetylalanine in 90% $D_2O$. This compound contains an $AX_3$ spin system similar to that found in lactic acid as well as a noncoupled methyl resonance at 2.0 ppm from the N-acetyl moiety. The data were acquired from a 0.5 cc volume within the phantom using our 2.0T/45 cm GE CSI-II imaging spectrometer. Spectra A and B in Figure 2 were acquired with $t_1$ periods of 12 and 14 msec, respectively. This temporal difference is equal to a half cycle of the ZQ modulation frequency (250 Hz at 2.0T) and gives amplitude-modulated signals which are antiphase with respect to each other. The absolute value of one of the $t_1$ periods is chosen to coincide with the most negative or positive excursion of the amplitude modulated signal. The resulting difference spectrum, Figure 2C, edits the noncoupled methyl resonance from the spectrum.

It should be noted that a small residual signal is present in the difference specrum arising from the edited resonance. This results from different extents of $T_1$ relaxation (of the longitudinal STE magnetization stored along the -z axis) during the two ZQ evolution periods. For example, a $T_1$ relaxation time of 200 msec (a typical value for *in vivo* lipid -$CH_2$- protons) will give rise to an approximately 1% difference in signal amplitude for the $t_1$ periods employed. Since the *in vivo* lipid concentration can be as much as 400 mM (in muscle), a 1% residual signal would be of the same order of magnitude as the lactic acid concentration one is trying to measure.

This problem can be circumvented by acquiring the data such that the extents of $T_1$ relaxation are the same for both component spectra. Consider the component of the difference spectrum where the $AX_3$ methyl resonance is inverted, that is, at $t_1$=12 msec and 4 msec increments (or decrements) thereof. If half of the data is acquired with $t_1$=12 msec and the other half with $t_1$=16 msec, then the average $T_1$ relaxation during the $t_1$ interval will equal that which occurs during an equal number of $t_1$=14 msec acquisitions. The difference spectrum from data acquired under these conditions, Figure 3C, shows essentially no residual signal. The improvement is better appreciated in the expansion in Figure 4. This acquisition scheme should enhance the performance of the STEZQC technique, particularly when measuring lactate in environments containing large concentrations of interfering lipid signal.

Sincerely,

Chris Sotak

Chris Sotak
Assistant Professor
Department of Biomedical Engineering

1. C. H. Sotak and D. M. Freeman, *J. Magn. Reson.* **77**, 382 (1988).
2. J. Frahm, K. D. Merboldt, and W. Hanicke, *J. Magn. Reson.* **72**, 502 (1987).
3. G. McKinnon, Works in Progress, 5th Annual Meeting of the Society of Magnetic Resonance in Medicine, Montreal, August 19-22, 1986, pg. 186.
4. J. Granot, *J. Magn. Reson.* **70**, 488 (1986).
5. R. Kimmich and D. Hoepfel, *J. Magn. Reson.* **72**, 379 (1987).

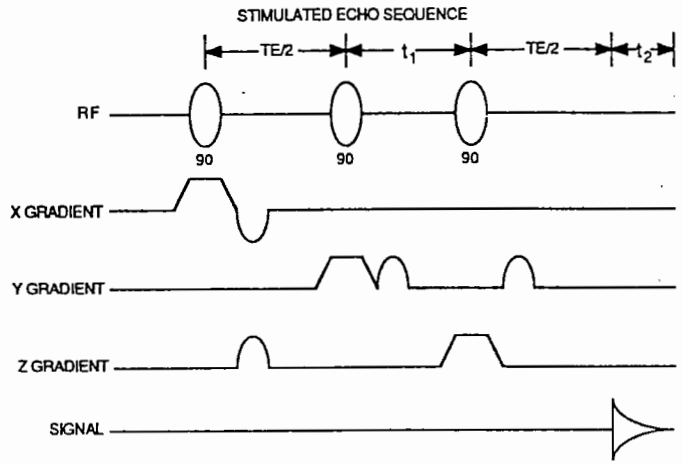


Figure 1. Stimulated echo (STE) pulse sequence for volume localized spectroscopy

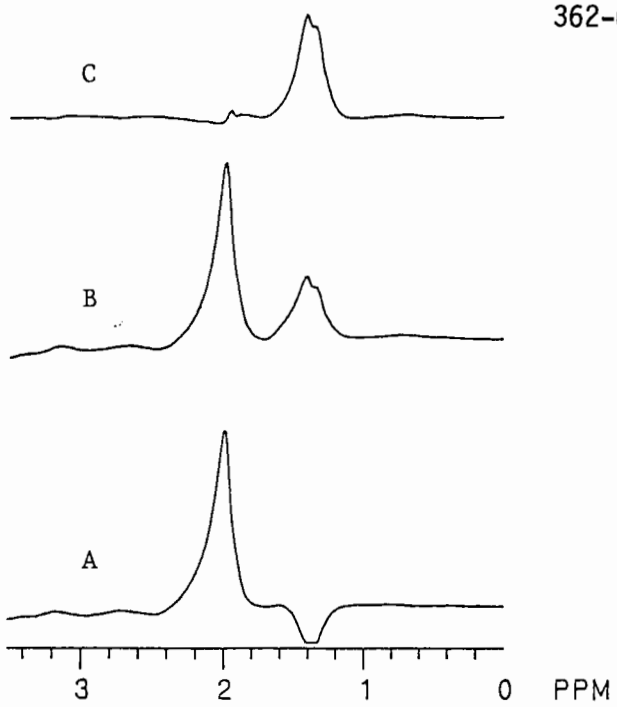


Figure 2. STE spectra from a 0.5 cc volume within a phantom containing 100 mM N-acetyl alanine in 90% $D_2O$ (only the upfield methyl resonances are shown). The TE/2 interpulse delay was 68 msec (1/2J for the coupled methyl doublet). (A) Spectrum is the sum of two blocks of 16 averages with $t_1$=12 msec. (B) Spectrum is the sum of two blocks of 16 averages with $t_1$=14 msec. (C) Spectrum B minus spectrum A.

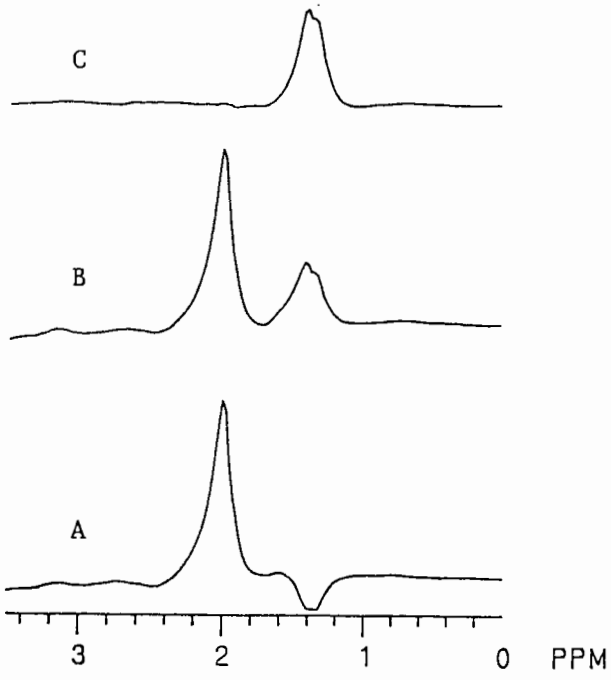


Figure 3. STE spectra from same volume as in Figure 2. The TE/2 interpulse delay was 68 msec. (A) Spectrum is the sum of a block of 16 averages with $t_1$=12 msec and a block of 16 averages with $t_1$=16 msec. (B) Spectrum is the sum of two blocks of 16 averages with $t_1$=14 msec. (C) Spectrum B minus spectrum A.

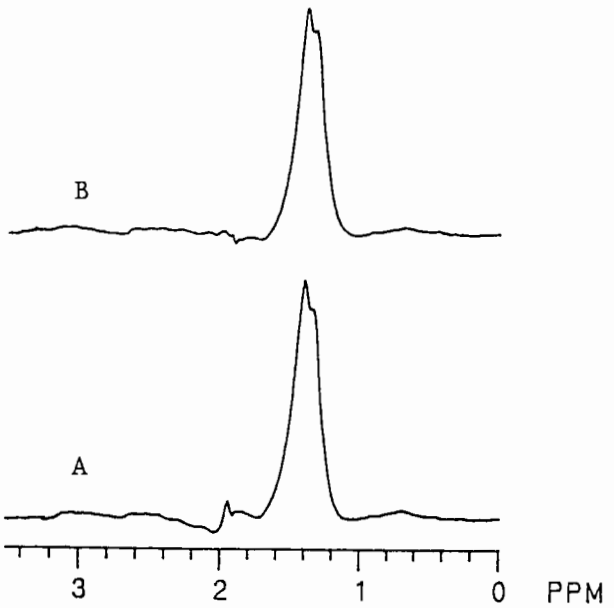


Figure 4. (A) Expansion of Figure 2C. (B) Expansion of Figure 3C.

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

20 September 1988
(received 10/22/88)

Dear Dr Shapiro,

Risk-free Sample Insertion for Hands-on NMR

We have recently installed a Bruker AC200 for open access use by chemists. This complements an overnight proton and carbon service using an AM250 with autosampler and heteronuclear and specialist NMR services on an AM360.

The operating philosophy for any hands-on machine was that it should be capable of producing a rapid throughput of good quality proton spectra for a wide range of users. Also, that the training and expertise required to achieve these objectives would not be a barrier to its initial or continuing use.

The 1988 Bruker software release allows an 'EXE' control program to be written which initiates all of the automatic functions necessary to lock, shim, acquire and plot a spectrum, simply by presenting the operator with a screen display of input instructions and options, which can be initiated on single key commands. A combination of overlapping use of different jobs for acquisition and for processing and plotting, together with plot queueing has resulted in a potential throughput of up to 10 spectra/hr. 100 people were trained to prepare samples and operate this system, in a series of group sessions lasting 45 minutes each.

For operational reasons, it was decided not to purchase an autosampler so this required manual loading of the sample into the magnet. The EXE program co-ordinates the timing of the sample inject/eject with an instruction to place the sample in the top of the magnet. However, with so many users our greatest fear was that sooner or later someone would place a sample in the magnet without the sample-lift air being on. With a hands-on machine, anything that can go wrong, will eventually.

The safety guard which we have designed is attached to the top of the probe assembly and when the sample-lift air is off, covers the inlet port thereby preventing insertion of a sample.

However, when the sample-lift air is on a piston, activated from the same compressed air supply, retracts the guard. A beryllium spring returns the guard over the inlet port when the air pressure is reduced as a sample is lowered into the magnet.

The fitting of this simple mechanical device constructed in non-magnetic materials of aluminium, acetyl and beryllium caused no noticeable changes to the shim values or the effectiveness of the sample-lift. It has worked faultlessly for 7 months and in doing so, has removed the major risk of probe damage. How many of us would wish to see the same risk removed from our own working environment?

Please credit this to David Reid's subscription (if he still has one after the ULTIMATUM).

Yours sincerely

P J Moore  D Harrison  S A O'Connor

SK&F

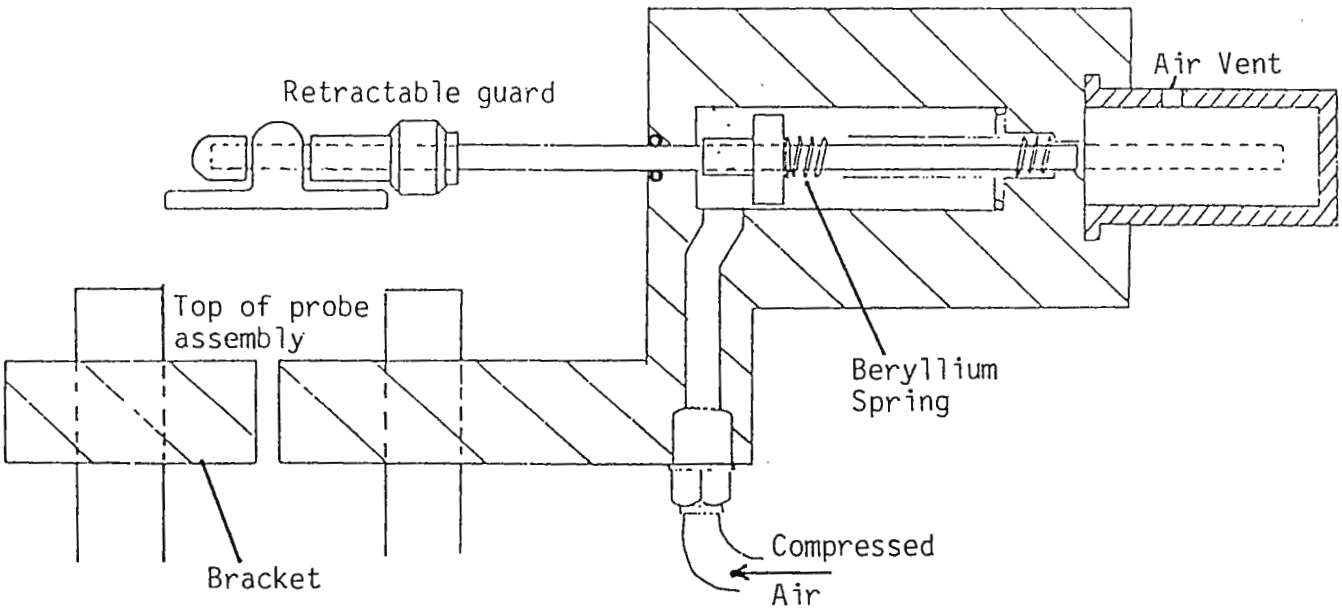


Figure: Schematic diagram for pneumatic sample-insertion guard

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POSTDOCTORAL RESEARCH ASSOCIATE

Position available 1/1/89 for in vivo NMR spectroscopic study of liver metabolism in tumor-bearing animals with CSI and Nicolet spectrometers. Ph.D. degree in biochemistry, chemistry or physiology with primary experience in NMR spectroscopy required. Prior experience in animal procedures preferred but not required. Send resume and 3 references to: Katherine Liu, M.D., Department of Surgery, University of Illinois at Chicago, Box 6998, Chicago, Il 60680. The University of Illinois is an affirmative action/equal opportunity employer.

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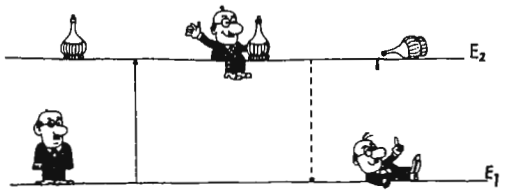


# 3rd Chianti Workshop on Magnetic Resonance NUCLEAR AND ELECTRON RELAXATION

San Miniato (Pisa), Italy, May 28 - June 2 1989

**THIRD CHIANTI WORKSHOP ON MAGNETIC RESONANCE RELAXATION**

San Miniato, Italy May 28 - June 2, 1989

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SECOND ANNOUNCEMENT

The Workshop aims to bring together those involved with the theory and application of nuclear or electron spin relaxation to the study of the structure and dynamics of molecules. The topics to be discussed will include the structure of biologically active molecules, particularly by the combination of nuclear Overhauser measurements with molecular dynamics simulations, natural and synthetic polymers, micellar and molecular liquid crystals, model membranes and motion of molecules within clathrates. The Workshop will also embrace the development of experiments, the testing of theories against data obtained on model systems, and computer simulations of molecular dynamics.

The speakers will include: G. Bodenhausen (Lausanne), V. Bystrov (Moscow),C. Chachaty (Saclay), J. H. Freed (Cornell), B. Gaffney (John Hopkins, Baltimore), G. Gayda (Marseille), P. J. Hore (Oxford), J. S. Hyde (Wisconsin), J. Huttermann (Hamburg), T. L. James (San Francisco), R. Kaptein (Utrecht), S. H. Koenig (IBM), G. Kothe (Stuttgart), J. Kowalewski (Stockholm), G. Lindblom (Umea), G. R. Luckhurst (Southampton), D. Marsh (Gottingen), K. Mobius (Berlin), G. Navon (Tel Aviv), F. Noack (Stuttgart), P. L. Nordio (Padua), K. Salikov (Kazan), A. Schweiger (Zurich), M. J. Stapleton (Illinois), Y. D. Tsvetkov (Novisibirsk), R. L. Vold (San Diego),R. R. Vold (San Diego), N. Yordanov (Sofia), C. Zannoni (Bologna).

The meeting is to be held in the Tuscan town of San Miniato, near Florence, and intending participants should write for further details to L. Banci, Dipartimento di Chimica Bioinorganica, Universita degli Studi di Firenze, Via Gino Capponi 7, 50121 Firenze, Italy.

ADDRESSES:

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E. GAGGELLI, Dept. of Chemistry, University of Siena, Pian dei Mantellini 44, 53100 Siena, Italy - Tel. 577/47054, Fax 577/280405

# The 30th ENC

## (Experimental NMR Conference)

## April 2-6, 1989

## The Asilomar Conference Center, Pacific Grove, CA

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

## Program Highlights

**SUN**

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

**MON**

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

**TUES**

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

**WED**

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

**THURS**

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

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

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

TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 362
November 1988

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B.L.S.

# CSI 2T Applications

## Shielded Gradients and Localized Spectroscopy

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

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

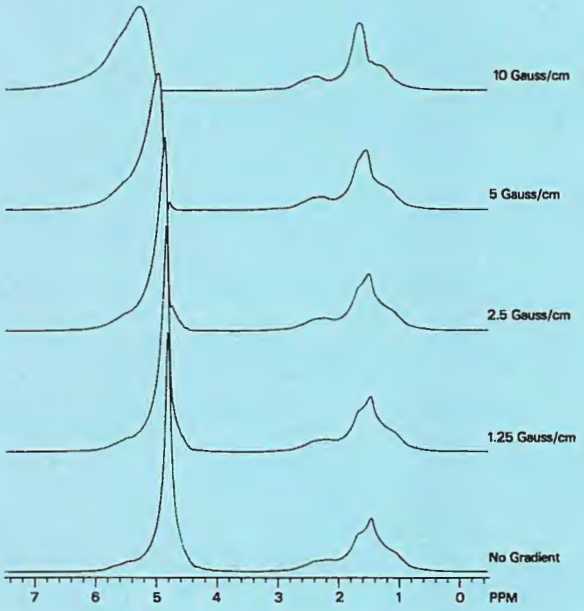


*Fig. 1—Using an oil/water phantom, a 10 G/cm gradient will create a water frequency profile extending from 156 KHz to 280 KHz away from normal water resonance. Residual gradient effects of less than 0.01% (50 Hz at 10 G/cm) are observed in a spectrum acquired beginning 1 msec after a 20 msec gradient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

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

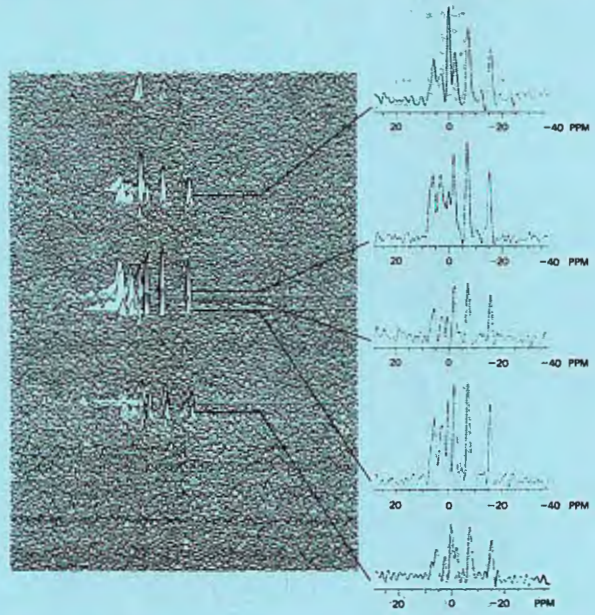


*Fig. 2—Stacked plot showing 512 phosphorous spectra from 60 mm cubed region of a live rat. Each trace corresponds to 7.5 mm cubed region (voxel) from within the region of interest. The offset traces clearly show the achievable spectra and spatial resolution of the technique, as well as demonstrating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

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# JEOL'S GSX-FT NMR Systems

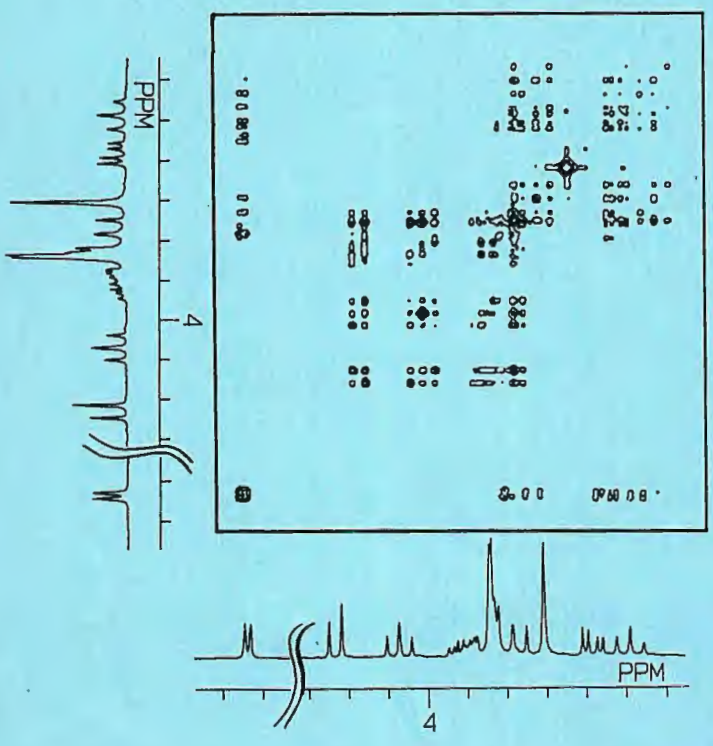
## Application: Pulse Programming

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

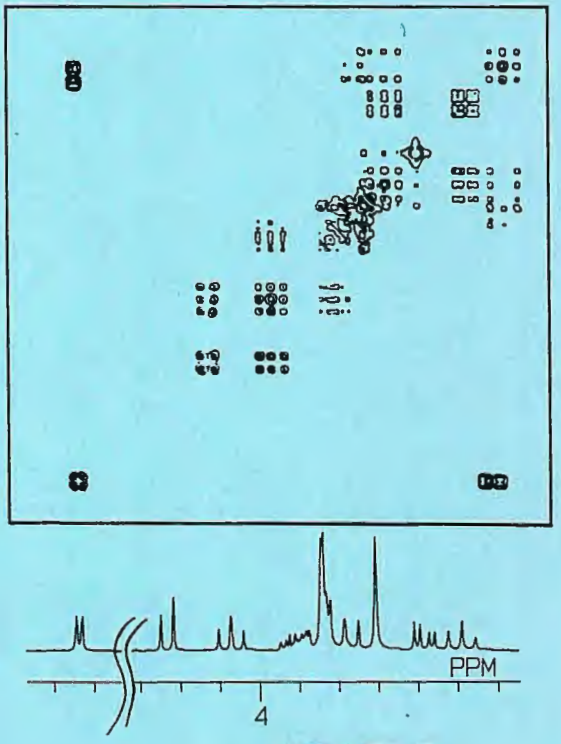
The HOHAHA experiments which use MLEV-17 for spin locking are very good for providing connectivity, especially in small molecules which produce poor RELAY experimental results. The spin locking allows coherence transfer which can be controlled by the mixing times. Directly coupled protons can be detected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

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

HOHAHA DATA




COSY DATA




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

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