TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 370

July 1989

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Isotopic Purity (D)	Density (g/cc)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetic Acid-d_4	CD_3COOD	99.5%	1.1	17	118	0.551 (32)
D-120	Acetic Acid-d_4 + TMS						
D-13	Acetone-d_6	CD_3COCD_3	99.8%	0.87	-94	57	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129							
D-14							543 (20)
D-21							0.611
D-122							
D-130							
D-28	Choloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

VARIAN

BOX/500 SHEETS

Cat. No.	Paper Size	Instrument Model	Type
WCV-100 (S-100A)	11" X 26"	HA-100, HA-100D	Gridded-Two Color
WCV-60 (A-60C)	11" X 26"	A-60, A-60A	Gridded-Two Color
WCV-XL (XL-100)	11" X 26"	XL-100 (CW and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (FT and FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
WCV-20 (CFT-20)	11" X 16 3/4"	CFT-20, FT-80, FT-80A	Gridded-Two Color
WC-11[illegible]	X 17"	All Models [illegible] 16 1/2" or 16	Blank

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FORTHCOMING NMR MEETINGS

Fifth International Symposium on Magnetic Resonance in Colloid and Interface Science, August 7-11, 1989; Newark, Delaware; Contact: Prof. Cecil R. Dybowski; See Newsletter 367, 57.

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.

Eastern Analytical Symposium, September 24 - 29, 1989; New York City; Contact: EAS, P. O. Box 633, Monchanin, DE 19710-0633; (302) 453-0785.

International Symposium NMR Spectroscopy: Structure and Dynamics of Polymeric Materials in the Solid State, Sponsored by the ACS Division of Polymer Chemistry, December 5-8, 1989; Keystone, Colorado; Contact: Mrs. Betty J. Schreiner, E.I. Du Pont de Nemours & Co., Experimental Station, Wilmington, DE 19880-0356; (302) 695-4817.

Spatially Determined NMR, Sponsored by the British Radiofrequency Spectroscopy Group; December 17-20, 1989; Cambridge University, U.K.; Contact: Prof. L. D. Hall, Level 4 RTC, Addenbrookes Hospital, Hills Road, Cambridge CB2 2QQ, England: (44) (223) 336805.

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. 372 (September) -----18 August 1989
No. 373 (October) --- 22 September 1989
No. 374 (November)---- 20 October 1989
No. 375 (December)--17 November 1989

LOVELACE MEDICAL FOUNDATION

9 June 1989
(received 6/13/89)

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

Dear Professor Shapiro,

Please enter the following announcement in TAMU NMR Newsletter.

Lovelace Medical Foundation is holding its annual symposium NONINVASIVE TECHNIQUES IN BIOLOGY AND MEDICINE in Albuquerque on September 14-15, 1989. The major areas to be covered are magnetoencephalography, video imaging, ultrasound, and NMR. The NMR related talks with the speakers are

Overview II, S. B. W. Roeder, San Diego State U.
Introduction to NMR in Biology and Medicine, E. R. Andrew, U. of Florida.
NMR Flow Studies, A. Caprihan, Lovelace Medical Foundation.
NMR of Human Heart and Other Organs, R. J. Herfkens, Cedars Sinai MRI.
In-vivo Proton Spectroscopy in Humans, R. H. Griffey, U. of New Mexico.
NMRS and Muscle Biochemistry, M. W. Weiner, VAMC, San Francisco.

Please call this meeting to the attention of your colleagues, especially in medicine and biology. For more information, please contact

Ms. Cathy Barboa
Lovelace Medical Foundation
2425 Ridgecrest Dr., S.E.
Albuquerque, NM 87108
505-262-7155.

Thank you,

Eiichi Fukushima

Bioengineering Research
2425 Ridgecrest S.E., Albuquerque, New Mexico 87108 505/262-7155

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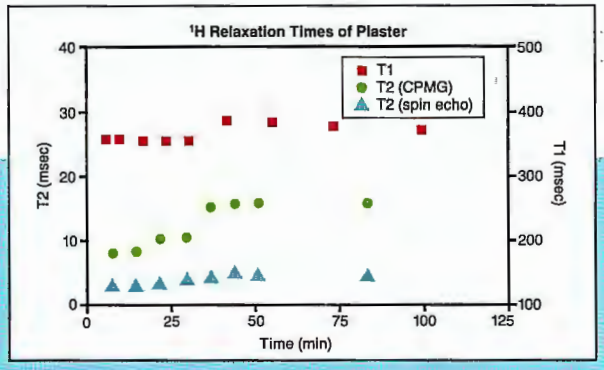

Non-destructive monitoring of the solidification of plaster at 4.7 Tesla. H-1 images obtained at (A): 18 minutes, (B): 28 minutes and (C): 38 minutes after a mixture of plaster and water (2:1 ratio) was prepared. The centers of the images are an intensity reference made of water doped with copper sulfate.

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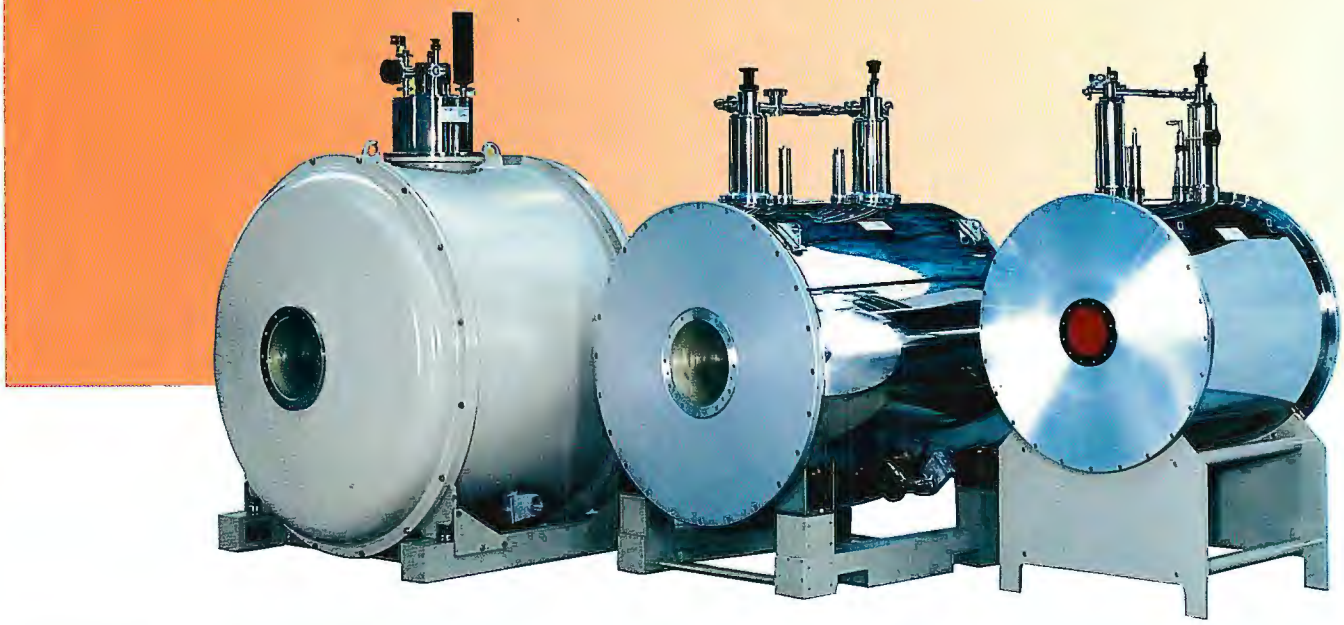
Magnet	Center Field	Magnet Bore	Clear Bore	Maximum Gradient	Plotted Homogeneity	HHLW Resolution	5 Gauss On-Axis	5 Gauss On-Radius
300/180	7.05T	183 mm	125 mm	4.0 G/cm	80 mm DSV ±6 ppm	35 mm DSV 0.1 ppm	5.60 m	4.45 m
200/330	4.7T	330 mm	254 mm	2.3 G/cm	140 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	6.95 m	5.60 m
200/400	4.7T	400 mm	324 mm	1.8 G/cm	140 mm DSV ±4 ppm	80 mm DSV 0.1 ppm	8.50 m	6.75 m
85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

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



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

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

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May 8, 1989
(received 5/24/89)

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

Reminders, Relocation
and Zero Quantum 2D-NMR with
Relayed Coherence Transfer

Dear Barry,

As you've been aware for some time, and as the rest of the world has begun to learn, judging from the number of telephone calls that I'm beginning to receive, I've left the University of Houston and am now calling Burroughs Wellcome Co. and the Research Triangle Park/Raleigh, NC area home. Thus far, I'm thoroughly enjoying the change from academia and have found the environment here quite stimulating.

In response to your reminder notice, I guess we also have to talk a little about science too. Since zero quantum NMR is generally plagued by F_1=0 Hz axial artifacts arising due to longitudinal relaxation during the evolution period (for a discussion, see: P.H. Bolton, *J. Magn. Reson.*, **60**, 342 (1984); B.T. Farmer, II, R. Ramachandran and L.R. Brown, *J. Magn. Reson.*, **73**, 534 (1987)) we have been interested in exploring approaches to this problem which may allow expanded applications for zero quantum experiments. Recently (L.R. Soltero, M.D. Johnston, Jr., R.N. Castle and G.E. Martin, *J. Magn. Reson.*, **81**, 406-410 (1989)) we have been exploring the combination of broadband homonuclear F_1 decoupling with double quantum filtration of zero quantum experiments. To date, there has been only one report of a relayed zero quantum pulse sequence, that of Müller and Pardi (*J. Am. Chem. Soc.*, **107**, 3484 (1985)). An alternative sequence which affords relayed coherence transfer using the approach of Eich, Bodenhausen and Ernst (*J. Magn. Reson.*, **104**, 3731 (1982)) in combination with broadband homonuclear F_1 decoupling and double quantum filtration to remove axial artifacts is offered by the pulse sequence shown in Figure 1.

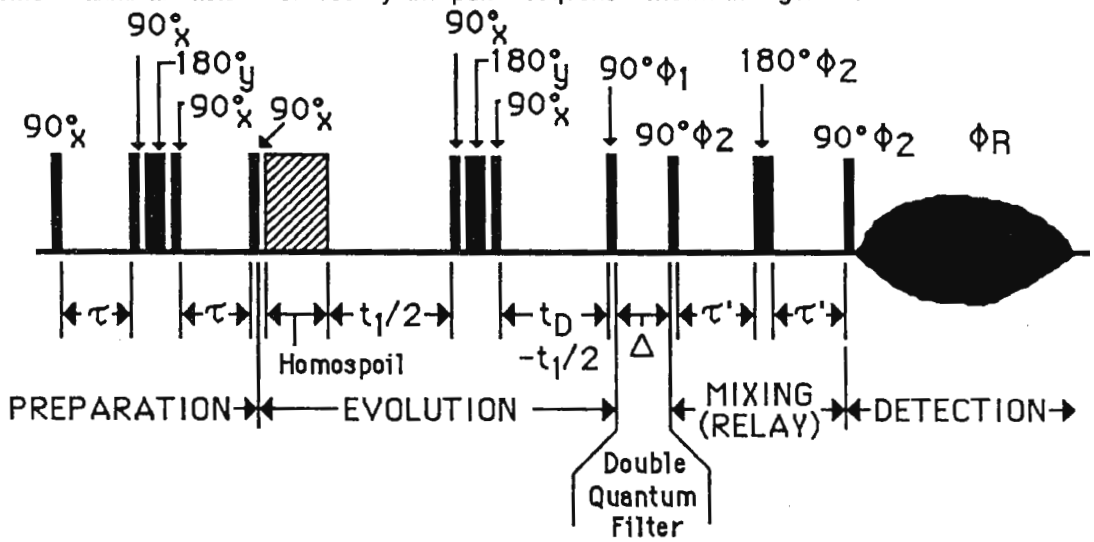
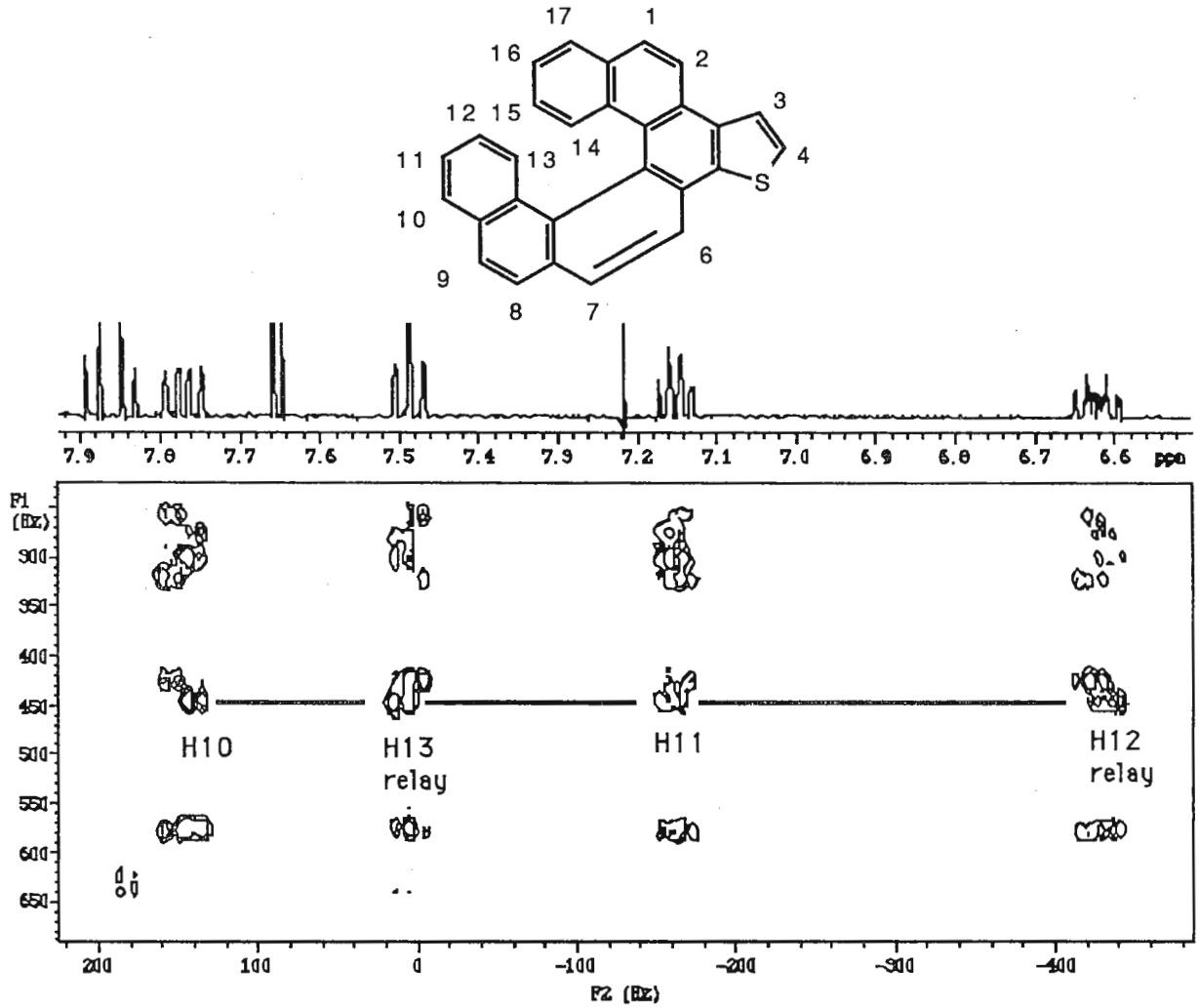


Figure 1. Zero quantum relayed coherence transfer pulse sequence with broadband homonuclear F_1 decoupling and double quantum filtration. Phase are cycled as follows:ϕ_1 0000 1111 2222 3333; ϕ_2 0123 0123 0123 0123; ϕ_R 0321 2103 0321 2103.

Data acquired using the pulse sequence shown in Figure 1 run on a Varian VXR-500 using phenanthro[3',4':3,4]-phenanthro[2,1-*b*]thiophene as a model compound is shown in Figure 2. As the experiment in its present form doesn't provide quadrature detection in F_1, the spectrum is symmetric about $F_1 = 0$ Hz and hence only one half of the final data matrix is shown. Zero quantum response frequencies in F_1 may be readily calculated by taking the algebraic difference of the offsets of the resonances in F_2 relative to the transmitter thus making the differentiation of the direct and relayed zero quantum responses a relatively facile process.



This data was acquired with an excitation tau of 142 msec and a relay period of 50 msec. The F2 spectral width was 1036 Hz with an acquisition time of 401 msec for each of 160 fids. The F1 spectral width was 1450 Hz. The data was symmetrically sinebell filtered and zero filled to a total size of 1024 X 512. This figure was plotted directly into the Macintosh using MacHP software which is available from Stevens Creek Software Ca. Ten seconds with Super Paint produced the labels.

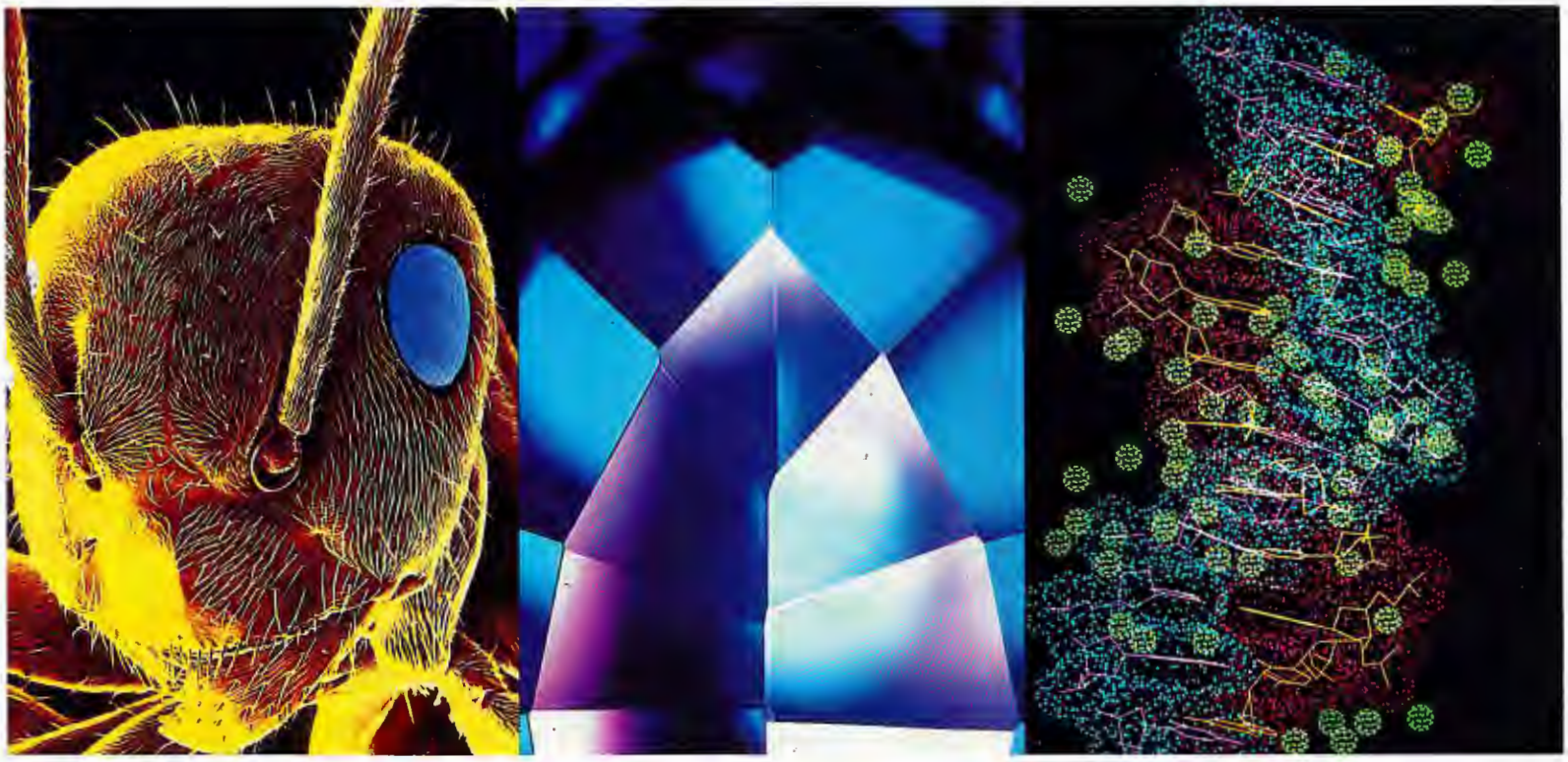
Sincerely,

Gary Martin

Ron Crouch

John Shockcor

VARIAN NMR FLEXIBILITY NOW RESOLVES PROBLEM DIVERSITY



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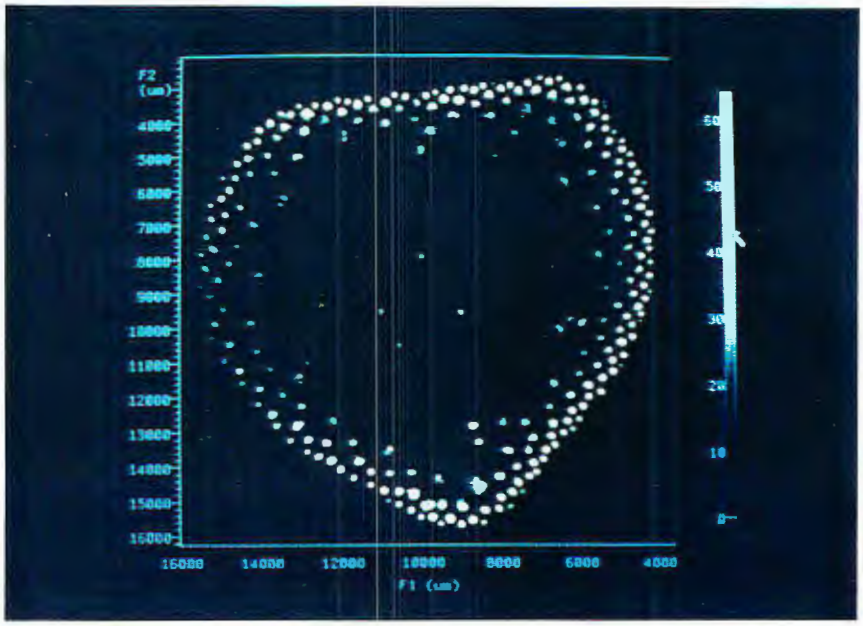
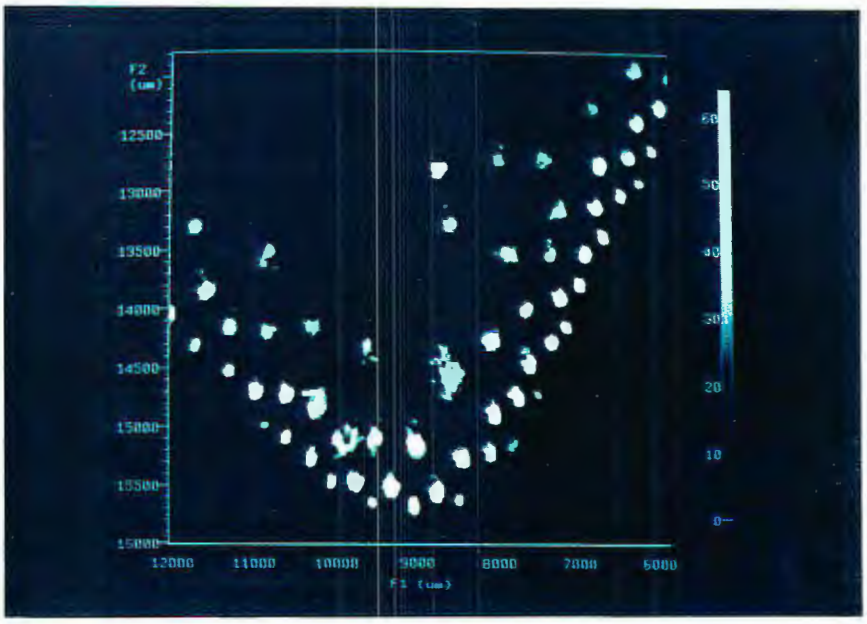
Varian's ability to extend NMR imaging techniques to small samples at high magnetic field strength provides users with the ability to do state-of-the-art experiments. Below are two examples of microimaging with a UNITY spectrometer.



A single slice microimage of a banana. Slice selection was achieved using a selective sinc RF pulse in conjunction with slice selection gradient. The pixel resolution is 10 microns; the slice thickness is 167 microns.



This is an expansion of the single slice microimage of a banana above. Note that the water transport vessels range from 50 microns to 200 microns. Use of advanced eddy current compensation techniques to reduce residual field variations due to eddy currents yield distortion-free results.

THE UPJOHN COMPANY
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PHYSICAL CHEMISTRY NMR LAB
TELEPHONE (616)385-7431
FAX (616)385-7522
June 8,1989
(received 6/12/89)

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

MORE INFORMATION ON PLOTS

Dear Barry:

In this NMR service laboratory we generate a lot of NMR spectra that tend to get shuffled around. We routinely include some additional information on the top and bottom of all plots to help identify them. Often one needs to know how long it would take to make another copy, when old spectra were replotted, when an overnight experiment finished, which plot is the latest one, how it was referenced, etc.

Commands for this are easily included in the macros and need only a few extra parameters which are easily added to the standard experiment file. An example of a contour plot and a few simple macros are included in this communication.

The following changes are necessary:

1. Create some new parameters in each standard experiment in STDPAR. Type CRTINT(HRS) CRTINT(MINS) CRTNAM(REF) and then set REF=NONE.

2. Rename GO and GA in comlib to avoid them. RENAME(COMLIB.GO,OLD$GO) etc.

3. Create a new GO and GA in maclib that will note the time at starting, arrange for another reading at completion, and then start pulsing with AU.

4. Insert the statement CLOCK:HRS,MINS into H1, C13, GA2D and other macros that create and start experiments.

5. Insert a CLOCK:R1,R2 near the top of H1P, C13P, DO2D, and any other automatic processing routines.

6. TMSREF is called by H1P to attempt referencing to TMS. Add the statement REF=&TMS after the RL(0) command in TMSREF to note if TMS was found. If the spectrum is manually referenced type REF=TMS, or type REF=CD3OD etc. if solvent-referenced. The RFP parameter will record where you found the solvent signal.

7. Insert a call to IDENT in all automated plotting routines or type IDENT if plotting manually.

Yours,

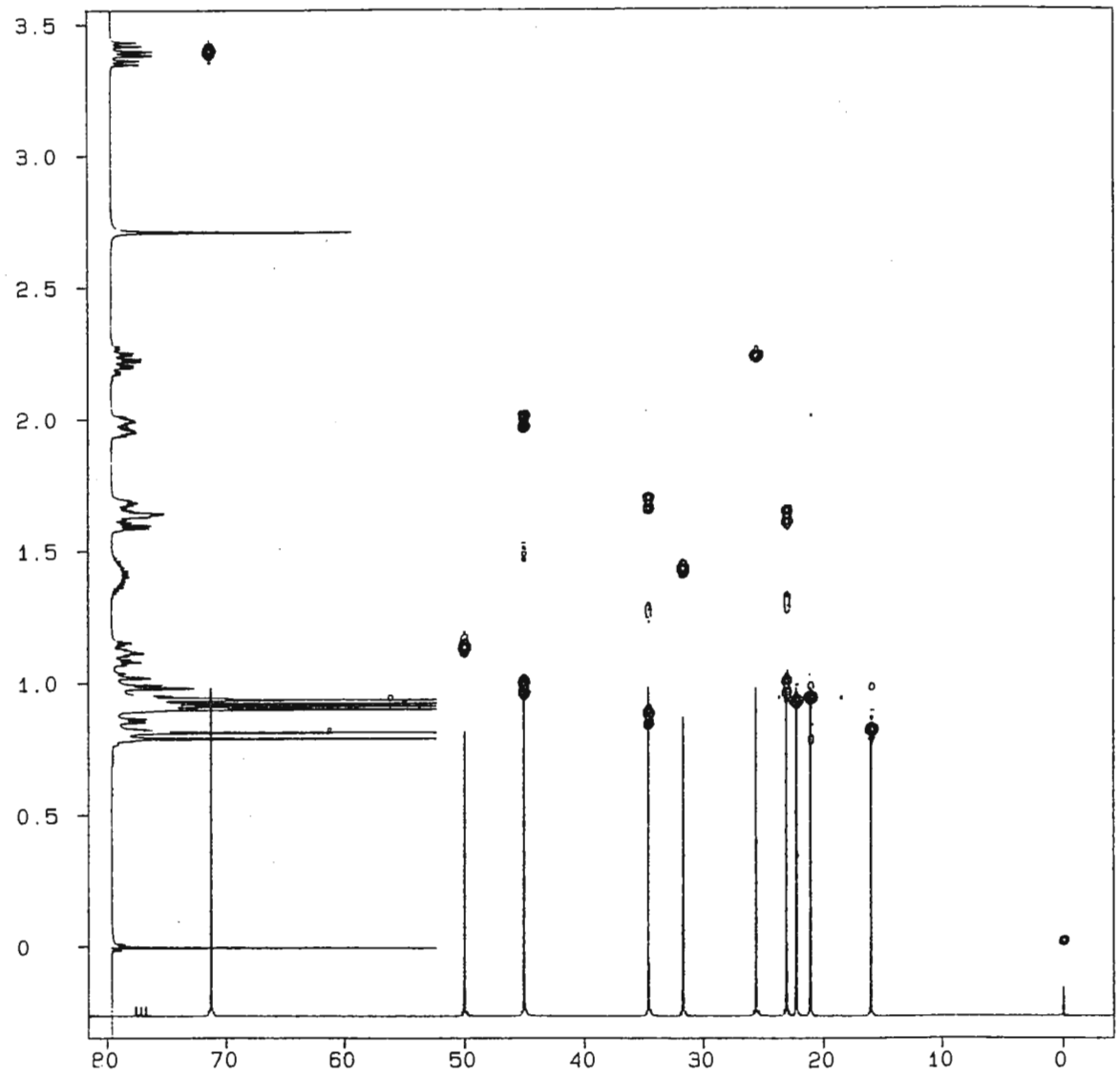
George Slomp

WORDPROCESSED ON AN XL-300 USING IDSTXT

0 REAL PEAKS HAVE BEEN BLOWN OFF SCALE

PL2DW (6, 2.5, 9, 8, 90, 90)
PLOT STARTED =11. 5 FINISHED =11: 13

F1 (PPM)



1-D

MENTHOL, 20% IN CDCL3
VARIAN XL-300 6.1E PROGRAM
STANDARD 13C OBSERVE

EXP6 PULSE SEQUENCE. AUTOC
DATE 06-05-89
SOLVENT CDCL3
FILE C

ACQUISITION		DEC. & VT	
TN	13.750	DN	1.750
SW	16501.7	DO	350.3
AT	0.993	DM	YYY
NP	32768	DMM	S
PW	15.0	DMF	9300
P1	0	DHP	N
D1	1.000	DLP	3
D2	0	PP	15.5
TO	200		
NT	512	PROCESSING	
CT	512	SE	0.318
PW90	15.0	LB	1.000
BS	512	FN	32768
SS	0	SN	40.0000
IL	N	MATH	F
IN	Y		
DP	Y	DISPLAY	
HS	NN	SP	-316.5
		WP	6468.3
		VS	15.6
		SC	90
		WC	220
		IS	500
		RFL	837.0
		RFP	0
		TH	92
		INS	1.000
		AI	

2-D

MENTHOL, 20% IN CDCL3
HETCOR
1024X1024 22 HRS.
XL-300 1H OBSERVE

EXP7 PULSE SEQUENCE. HETCOR
DATE 06-05-89
SOLVENT CDCL3
FILE HETCOR

ACQUISITION		DEC. & VT	
TN	13.750	DN	1.750
SW	6468.3	DO	-700.0
AT	0.079	DM	NNY
NP	1024	DMM	CCS
PW	15.0	DMF	9300
P1	0	DHP	Y
D1	1.000	DLP	3
D2	0	PP	15.5
TO	-4300		
NT	96	PROCESSING	
CT	96	RE	0.005
PW90	15.0	FN	1024
SW2	1168.6	SN	40.0000
NI	512	AF	0.020
BS	512	MATH	F
SS	1	FN2	1024
IL	N	RE2	0.027
IN	Y	AF2	0.110
DP	Y		
HS	NN	DISPLAY	
J1XH	140.0	SP	-316.5
JNXH	0	WP	6468.3
PRESAT	N	VS	25
HMULT	N	SP2	-102.9
SPIN	16.0	WP2	1168.6
GAIN	0	SC	90
		WC	220
		IS	500
		RFL	320.3
		RFP	0
		TH	6
		SC2	10
		WC2	220
		INS	1.000
		RFL2	101.8
		RFP2	0
		AI AV	

CURRENT DATE IS 6/7/89 EXP STARTED =16 : 10 PROCESSED =11 . 45 PLOTTED =11 : 5 REFERENCED TO TMS

```
:GA will read the clock at start of the experement
CLOCK:HRS,MINS     "save current time: HRS & MINS"
WNT=WFTA
AU


:GO will read the clock at start of the experement
CLOCK:HRS,MINS     "save current time: HRS & MINS"
WNT=N
AU


:WFTA will read the clock at start of processing
CLOCK:R1,R2
WFT


:IDENT(ARG1)  writes identification on spectrum
:ARG1=1 for printer, 2 for plotter, 3 for both
:called by all plotting macros to identify plot
IF NOT($1) THEN $1=2 ENDIF "default to plotter"
IF PLOT=&ZETA
 THEN SC=0 WC=500 NPLOT
 ELSE SC=0 WC=400 NPLOT
ENDIF
CLOCK:$8,$9 "read clock for plot starting time"

IF PLOT=&ZETA                                  "plotter = Zeta"
  MOVE(520,10)                                 "write time on plot"
  WRITE(PLOT,0,0,'DATA =',@HRS:0)
  WRITE(PLOT,22,0,' : ',@MINS:0)
  MOVE(50,0)
  WRITE(PLOT,0,0,' PLOT =',$8:0)
  WRITE(PLOT,25,0,' : ',$9:0)
  MOVE(78,-10)
  PAGE(1)

ELSE                                           "plotter = HP 7550 "
SYSINF(CONPAR.DATE):$2,$3,$4,$5
Y0=-50                          "allow access to bottom of sheet"
WRITE(PLOT,0,-50,'CURRENT DATE IS    ',$3:0,'/',$4:0,'/',$5:0)
WRITE(PLOT,93,-50,'EXP STARTED =',@HRS:0,' : ',@MINS:0)
WRITE(PLOT,164,-50,' PROCESSED =',@R1:0,' : ',@R2:0,
'      PLOTTED =',$8:0,' : ',$9:0)
 IF REF=&NONE                                  "record how referenced"
 THEN WRITE(PLOT,290,-50,'DEFAULT REFERENCING')
 ELSE
  IF REF=&TMS
  THEN WRITE(PLOT,290,-50,'REFERENCED TO TMS')
  ELSE WRITE(PLOT,290,-50,'REFERENCED TO',' ',@SOLVNT,
' AT',(@RFP/SFRQ):6:2,' PPM')
  ENDIF
 ENDIF
Y0=0                              "restore standard plotter field"
ENDIF
```

370-12

PROFESSOR DAVID M. DODDRELL

DEPARTMENT OF CHEMISTRY

Address: Queensland Medical Magnetic Resonance Research Centre
c/- Mater Hospital
South Brisbane
Queensland 4101

Telephone: (07) 846 2277
Telex: UNIVQLD AA40315
Fax: (07) 844 8010

UNIVERSITY OF QUEENSLAND

6th June 1989 (received 6/12/89)

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

Dear Barry,

The NMR-90 Conference will be held in Brisbane in July of 1990. This is a gathering of approximately 150 people who will meet in sunny Queensland to hear lectures on multipulse NMR, *in vivo* NMR spectroscopy, solid state NMR, aspects of pulsed ESR and various other goodies.

I would hope that you might advertise this forthcoming conference in your newsletter, as it may attract people from your part of the world to come and see what we have to offer "down under". Is it true that in the USA people can write off visitations to conferences against their taxation? I would be happy (for a small fee of course) to provide gilt-edged invitations to anyone who might want to use that facility.

Best wishes.

Yours sincerely,

David

David M. Doddrell

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5/89

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Avenue du Champ de Mars, 24
7000 MONS (Belgique)
Departement of Organic Chemistry
and NMR Laboratory.
Tel. 32 - 65 - 37 35 20

May 18, 1989
(received 6/12/89)

Quantitative dosage of paramagnetic nitroxides by Relaxometric titration.

Dear Professor Shapiro,

Nitroxide stable free radicals (NSFR) have received a great deal of attention since their paramagnetism and their chemical versatility make them good candidates as MRI contrast agents (1). To compare the relative efficacy of nitroxides, it is mandatory to measure their *relaxivity* which is the increment of solvent proton relaxation rate induced per mM of added paramagnetic species. The measurement of nitroxide concentration is thus essential in this evaluation. Usually the stock solutions are calibrated by weighing (if possible) and/or by double integration of the first derivative ESR spectrum using standard nitroxides solutions of known concentration as reference. This last kind of measurement can be performed with a precision of ± 5% .

We propose a new method to determine the concentration of nitroxide solutions which combines chemistry and physics. It has been show (2) that phenylhydrazine reduce nitroxides to the corresponding N-hydroxylamines through the following reaction.

$$2\ \text{>N—Ȯ} + C_6H_5NHNH_2 \longrightarrow 2\ \text{>N—OH} + N_2 + C_6H_6$$

Since N-hydroxylamines are diamagnetic compounds, the value of the solvent proton relaxation rate R_1 is proportional to the quantity of nitroxides still present in solution. In the course of a "titration" of a nitroxide solution with phenylhydrazine, it is thus

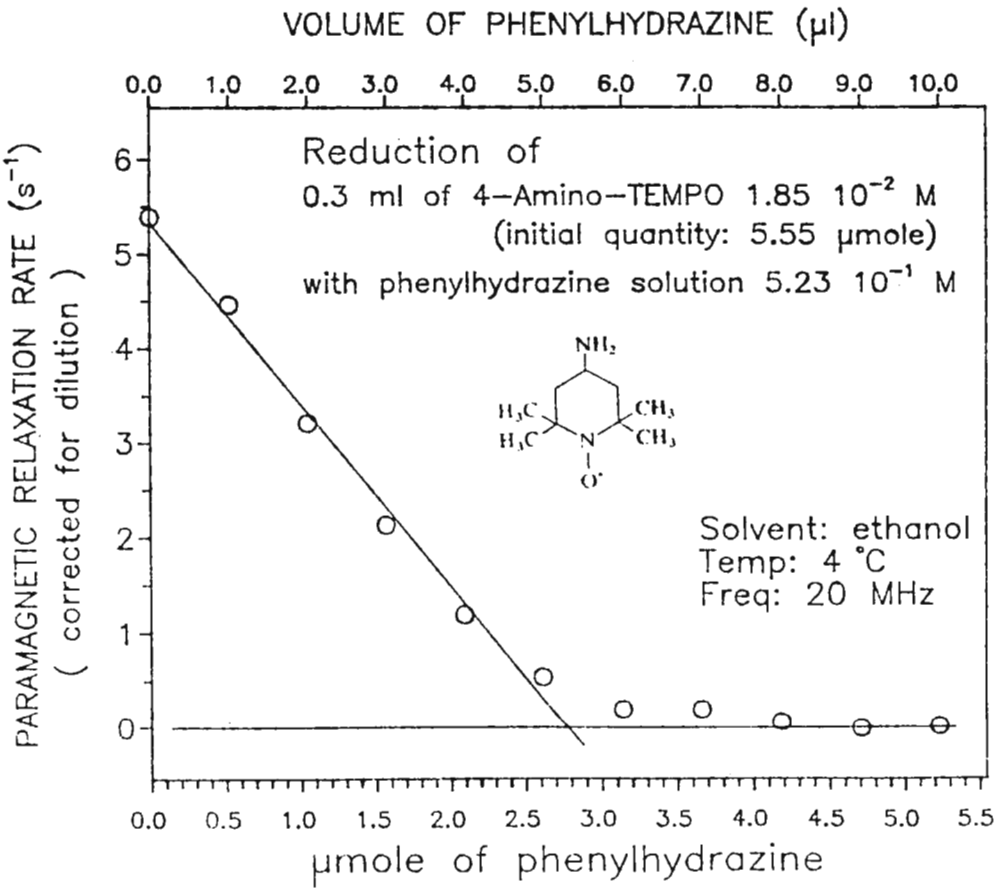
possible to correlate the evolution of the relaxation rate to the disappearance of the paramagnetic species. Provided the concentration of phenylhydrazine and the volume of the nitroxide solution are known, the titration curve allows a precise measurement of nitroxide concentration. It is important to work in oxygen-free conditions in order to avoid the reoxydation of the N-hydroxylamine in nitroxide.

The method, successfully applied on a large serie of nitroxides, is illustrated by the figure.

Sincerely,

P. VALLET Prof. Y. VAN HAVERBEKE Dr. R.N. MULLER

1. Brasch R.C., Nitecki D.E., London D., Tozer T.N., Doemeny J., Tuck L.D., Wolff S., Proceeding of the first Annual Meeting of the Society of Mag. Reson. Med. 25, 1982.
2. Lee T.D. and Keana F.W., J. Org. Chem., vol. 40, 21, 1975.



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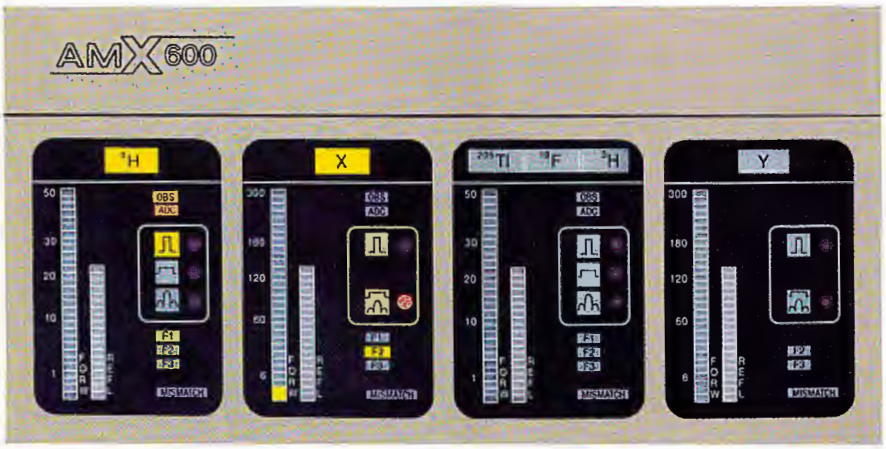

* The new AMX full routing system with PIN diodes allows micro-second switching of the frequency paths and RF transmitters on the fly. Ask your nearest Bruker representative for more details on the new AMX Series.

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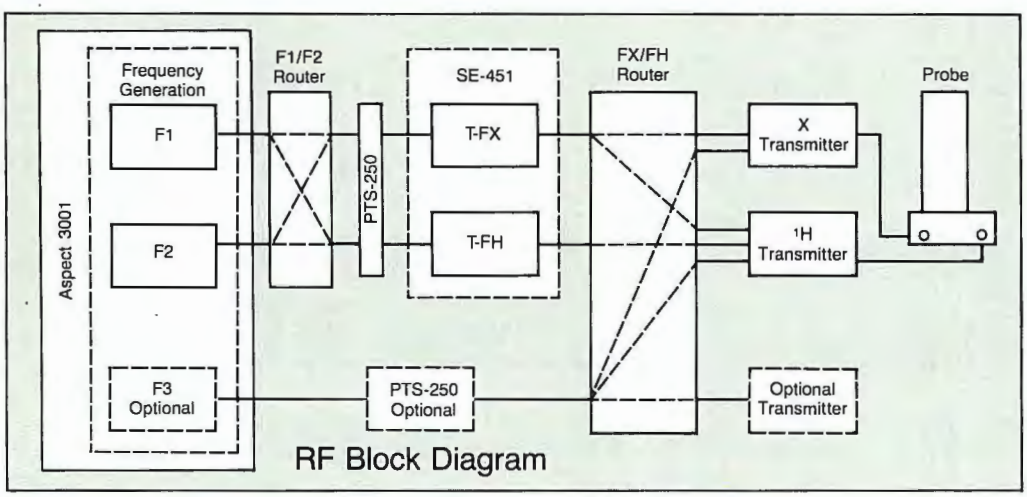
AMX Series Block Diagrams



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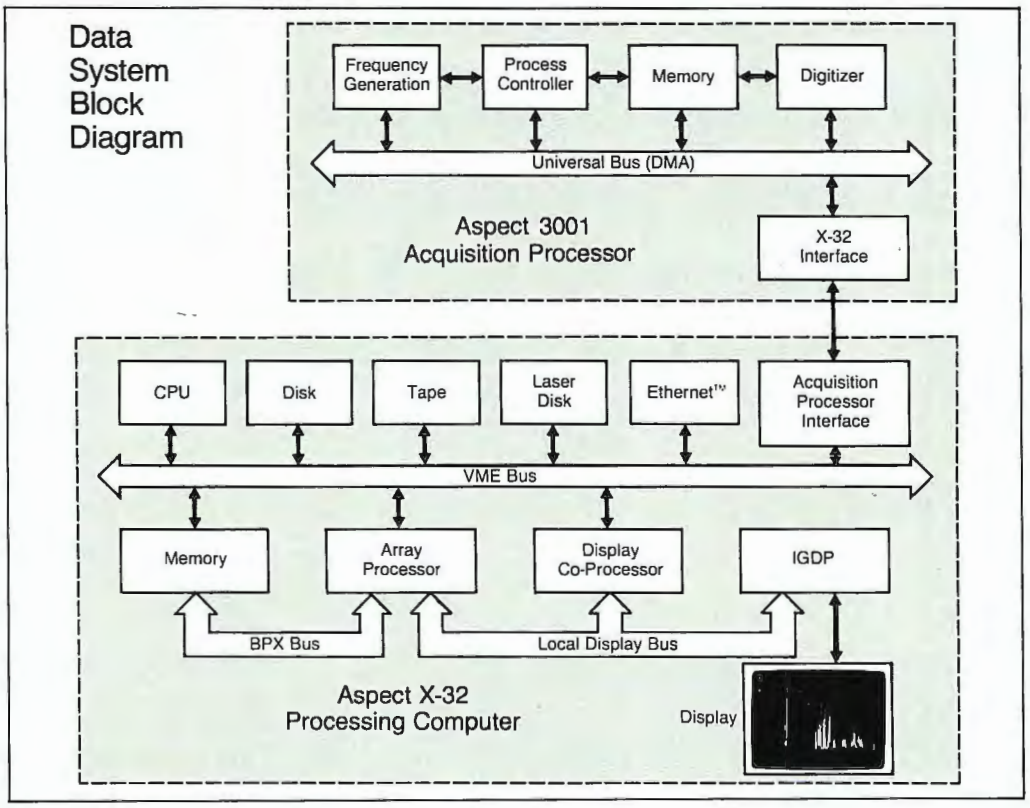

Digital Section. Integration of 32-Bit Aspect X-32 UNIX computer into console together with proven Aspect 3001 acquisition processor. The X-32 is equipped with unique 3-bus structure for optimum NMR data transfer, processing and display.

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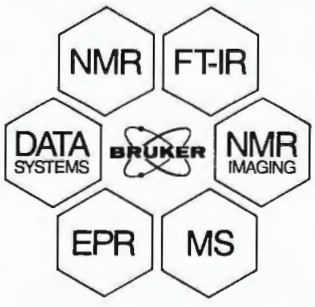

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Prof. B. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
USA

Your reference and date	Our reference	Office telephone	Date

Dear Prof. Shapiro,

Subject: Sub-division

2 June , 1989.
(received 6/12/89)

"QUALITY, improved quantitation of NMR spectra.

In our in-vivo ^1H NMR spectra considerable line overlap occurs, forcing us to quantify our spectra by fitting the NMR data in the time or frequency domain to some model function. The model decay or lineshape function in general deviates from the experimental one, resulting in an imperfect fit. This fit can be improved much by correcting the NMR time domain signal, using the experimental decay function of some reference line, in our case the in-vivo water signal.
The experimental NMR signal is given by

$$S(t) = \sum A_j e^{(i\omega_j - 1/T_{2j})t} \cdot f(\Delta\omega_0)$$

The water signal by

$$S_w(t) = A_w e^{(i\omega_w - 1/T_{2w})t} \cdot f(\Delta\omega_0)$$

$f(\Delta\omega_0)$ describes the resonance frequency distribution resulting from the B_0 inhomogeneity over the sample. S(t) is corrected $S_c(t)$ by dividing it by $S_{wn}(t)$:

$$S_{wn}(t) = S_w(t) \cdot e^{(-i\omega_w + 1/\tau)t} / A_w$$

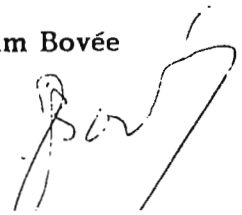
$$S_c(t) = S(t) / S_{wn}(t) = \sum A_j e^{(i\omega_j - 1/\tau_{2j})t}$$

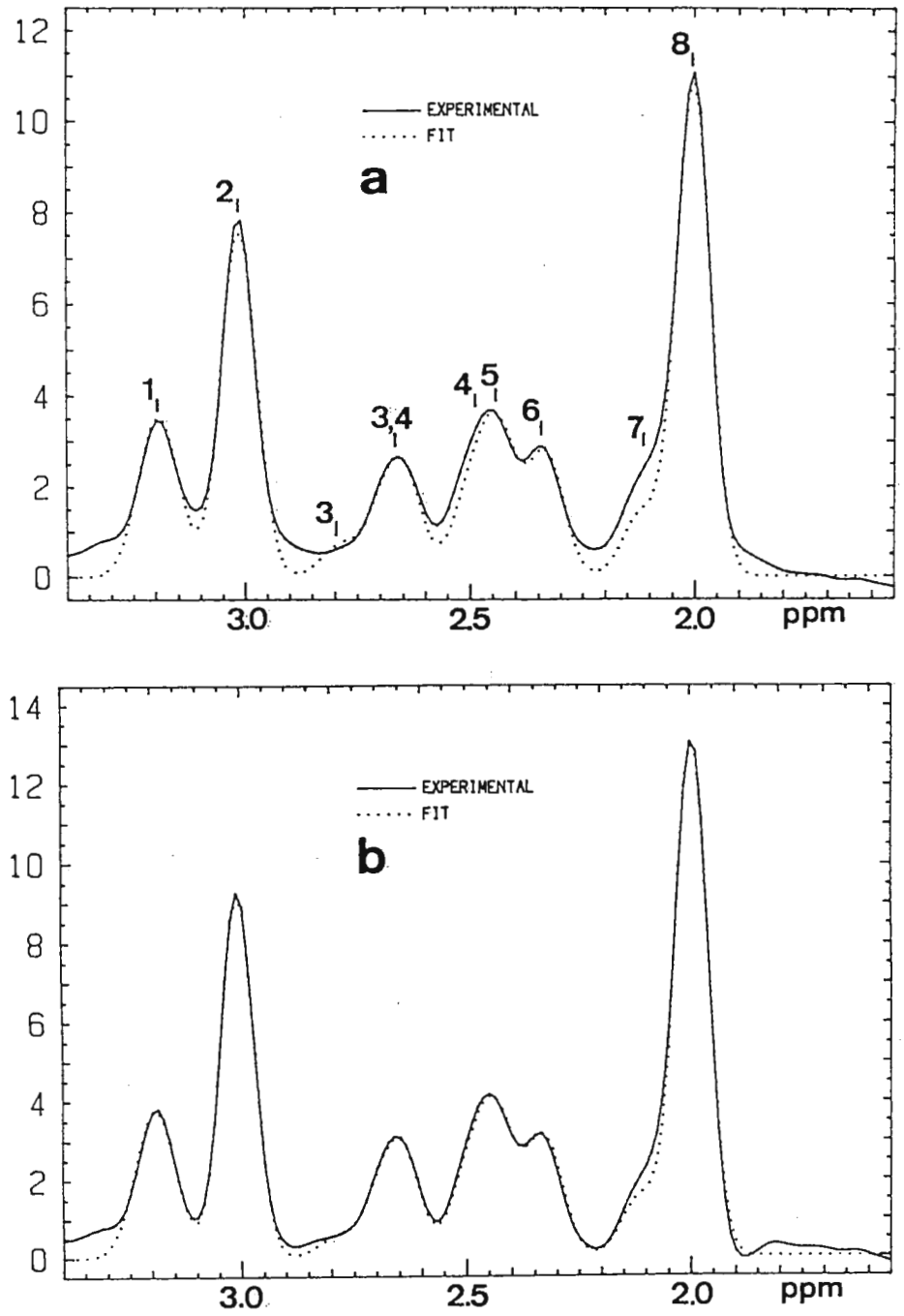
$$1/\tau_{2j} = (1/T_{2j} - 1/T_{2w} + 1/\tau)$$

$S_c(t)$ consists of a sum of pure Lorentzians, and the signal amplitudes, or peak areas are unchanged by this manipulation. τ can be chosen for optimal signal to noise time domain windowing, or equal to T_{2w}, in which case the natural linewidths can in principle be determined. The figure shows an in-vivo ^1H NMR spectrum of the brain of a conscious rat without (a) and with the correction (b). The fit is much improved, but not yet perfect. The main reasons for this are motional artefacts and not taking into account in the fit the presence of some unknown signals in the in-vivo spectrum.

Albert de Graaf

Wim Bovée





In-vivo experimental and fitted ^{1}H spectra of the brain of a rat before (a) and after (b) application of QUALITY. After a Lorentz to Gauss transformation the dataset was fitted to a superposition of Gaussian's, using a Marquardt-Levenberg non-linear least squares fit. 1:Choline, 2:(phospho)creatine, 3:β-CH_2 of aspartate, 4:β-CH_2 of N-acetylaspartate, 5:γ-CH_2 of glutamine, 6:γ-CH_2 of glutamate, 7:β-CH_2 of glutamate and glutamine, 8:CH_3 of N-acetylaspartate.

Fremont Magnetic Resonance
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Fremont CA 94539
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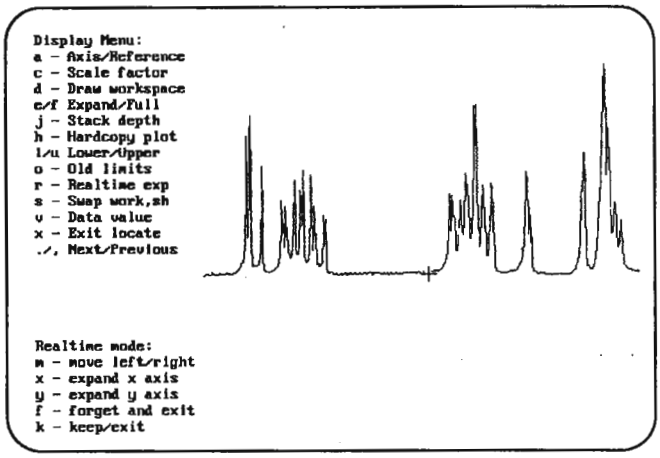
(415)623-0851 FAX

NMR Data Processing Stations

FMR and Hare Research are developing and marketing an economical alternative for off-line NMR data processing using IBM-compatible PCs. Software modules for processing and plotting NMR data can be implemented on existing PCs, printers and plotters for as little as $1000.00.

Hare Research's Felix/PC(tm) software is supplemented with a mouse-oriented, menu-based, user interface and expanded plotting capabilities supplied by FMR. Menu software greatly increases the user friendliness of the processing software for both new and occasional users. A command line interface remains in place at all times for the experienced user.

FMR can also provide a complete turnkey PC system starting at $5000.00. These turnkey data stations come configured ready to process NMR data.



1D Processing Software.

Multi-D Processing Software.

Ethernet communications systems.

Printers (dot matrix, Postscript or PCL lasers).

HPGL Compatible Plotters.

Software Support

Expanded user manuals.
User newsletter.
Telephone assistance.
Software and manual revisions while under contract.
Organized Bug report collection and feedback.
New feature request incorporation process.

Data transfer and translation programs.

Getting data from the NMR instrument or other data stations to and from the PC at a nonpainful rate and in a form useable by the PC is a critical step in making the PC a useful NMR workstation. FMR and Hare research are developing hardware and software tools for making this process as easy as possible. Software programs retaining as much parameter information as possible with the coorperation of the instrument vendors and the marketplace are being developed. Hardware solutions for the data transfers are also being developed, including:

RS-232 transfers
Kermit
Parallel transfers
Ethernet

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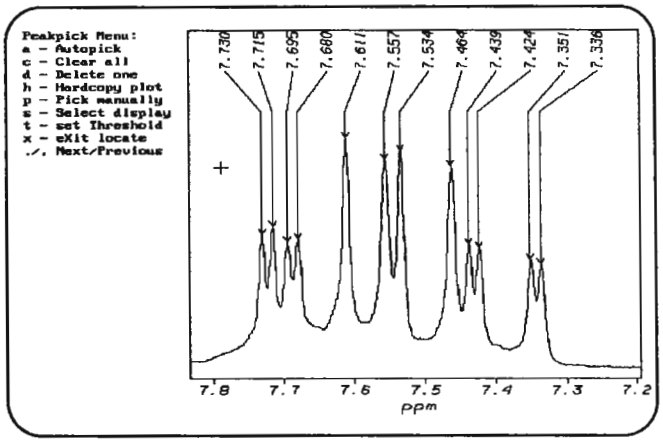

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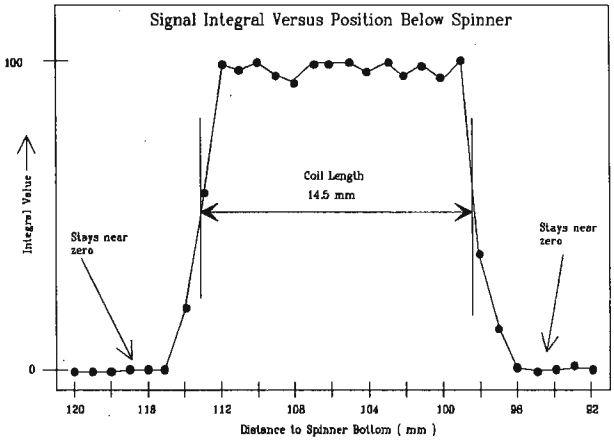
Shimming, The shims

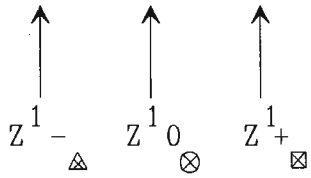
In the previous discussion of the receiver coil, the coil length and its position below the spinner were identified and plotted. One other item which is important to know before undertaking the shimming operation is the position of the coil relative to the center of the room temperature shims. The best way to determine this uses the same sample as was used for plotting the coil. The sample should be as small as possible to have useable signal intensity.

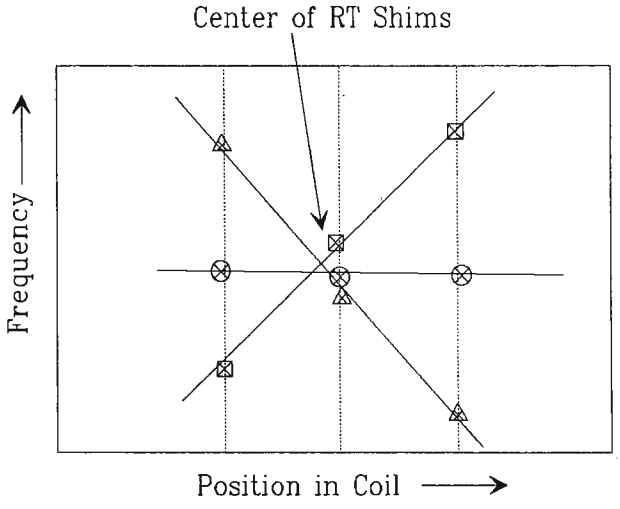
1. Start with a reasonably good set of room temperature shim values.
2. Place the sample at the 10% position through the receiver coil.
3. Take and process a 16K Word +/-10,000 Hz sweep width spectrum using magnitude calculation.
4. Adjust the ends of the processed spectrum to remove DC and tilt.
5. Take an integral of the entire spectrum and set it to a value of 100.
6. Set the frequency position of the center of the signal (i.e., the frequency position of the integral value 50) to 0 Hertz.
7. Set up a MACRO or LINK to repeat this process with the same processing and integration normalization constants.
8. Record the frequency value of the line in the spectrum at three settings of the Z^1 shim (Z^1+, $Z^1$0 and Z^1-). Use a value of Z^1 such that there is a frequency shift of 100 to 500 Hz between $Z^1$0 and Z^1+.
9. Repeat step 8 with the sample at 50% through the coil and again with the sample 90% through the coil.
10. Plot the data and connect the three points for each position in the coil. You should get a graph with three crossing lines. The position where they cross is the center of the room temperature shims. Ideally all three lines would cross at one point. This seldom occurs perfectly, so take the center of the triangle formed by the three crossing lines as the shim center.

At this point the size and position of the coil and its position relative to the center of the room temperature shims are known. The center of the shims should be at the center of the coil for minimum shim interaction and easiest shimming. An error of 2mm or more could be important. An error of 5mm or more needs to be corrected.

Receiver Coil Size







Center of Room Temperature Shims

ABBOTT

Abbott Laboratories
Abbott Park, Illinois 60064

April 27, 1989
(received 5/27/89)

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

Fully Automated Sample Preparation and Data Acquisition

Dear Dr. Shapiro:

In our ongoing effort to computerize and automate NMR spectroscopy, we have removed the single most inefficient component in the NMR laboratory: the spectroscopist.

The routine NMR spectra required in a large industrial or academic chemical research institution can number in the tens of thousands annually. In order to minimize the investment of time and manpower required for this task, the major spectrometer manufacturers provide automatic sample changers to permit the unattended acquisition of data for a large number of samples on a 24-hours a day, seven days a week basis. However, it has remained the responsibility of the individual user to prepare the sample and to give the spectrometer the necessary instructions. In a facility with restricted access to the spectrometers, this becomes a tedious and burdensome task. We describe here a system capable of the preparation of NMR samples, changing samples, automated data acquisition and automated data processing and plotting.

A Zymark Corporation Zymate II robotic workstation was chosen to integrate sample preparation with the function of a sample changer. The robotic workstation is equipped with disposable pipette tips, four solvent dispensers and accessories capable of manipulating sample vials, spinners and NMR tubes. The robot is located on a platform next to the spectrometer magnet, allowing it to insert and remove samples from the magnet stack.

A microVAX II computer functions as an intelligent interface between the robotic workstation, the NMR spectrometer and an external computer network. The microVAX is also equipped with a barcode printer and a barcode reader. The barcode reader is located on the platform with the robot. The microVAX is connected to a General Electric QE-300 via the ports for the spectrometer keyboard (spectrometer input) and printer (spectrometer output), allowing the computer to issue commands to the spectrometer and to monitor the spectrometer's response.

The details of the software developed to run this system are beyond the scope of this note; however, the system works like this:

(1) The sample submitter logs into a dedicated account on our computer network. Responding to questions from the computer, he identifies his sample, specifies the solvent desired and the experiment to be executed. The computer prints out a barcode label which he affixes to the sample vial. He then leaves the sample in a designated rack in the NMR laboratory.

(2) Periodically a member of the NMR lab will take the samples out of that rack and put them in a rack by the robot.

(3) The robot picks up a vial from this rack and puts it in the barcode reader. The microVAX reads the barcode, identifies the sample, and instructs the robot which solvent to add. The robot adds the specified solvent, vortexes the sample, filters it and pipettes it into a waiting NMR tube which it has previously inserted into a spinner.

(4) When the sample is ready, the microVAX instructs the spectrometer to eject the last sample, assuming data acquisition is finished. The robot removes the old sample from the magnet stack and inserts the new one.

(5) The robot removes the NMR tube from the spinner and replaces it in the rack. It then gets a clean tube, inserts it into the empty spinner and goes to step #3.

(6) Meanwhile, in response to commands from the microVAX, the spectrometer locks and shims. The microVAX then tells the spectrometer what experiment to run, sets the appropriate parameters and initiates data acquisition.

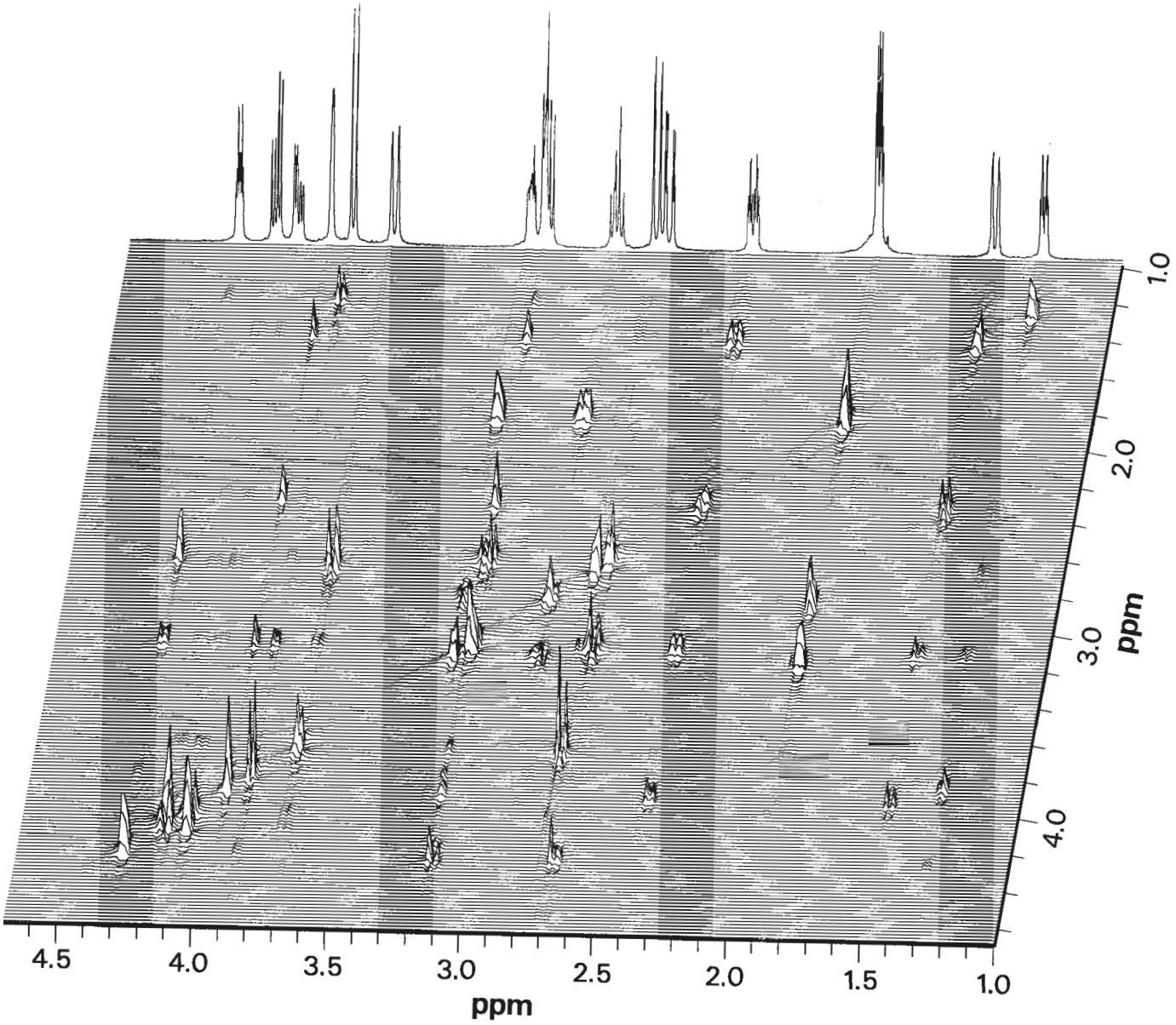
(7) When data acquisition is complete, the microVAX initiates the transfer of the data file to our main computer network where it is automatically given an identifying number, entered into a laboratory database, archived onto magnetic tape, Fourier transformed, phased, etc. Finally, the spectrum is sent to whichever of a number of plotters is nearest the individual who submitted the sample. These plotters are located in the chemistry laboratories in several buildings and are accessable to the computer via Ethernet. As often as not the spectrum will be plotted in the submitting chemist's own laboratory.

This system is currently handling about two thirds of our routine ^{1}H spectra, and the only human overhead is to put the sample vials and clean NMR tubes in the racks and remove them when they're done, and to fill the solvent reservoirs and pipette racks once a day. Sample throughput is generally limited by the spectrometer rather than the robot and is typically five to six samples per hour.

Beware! You, too, can be replaced.

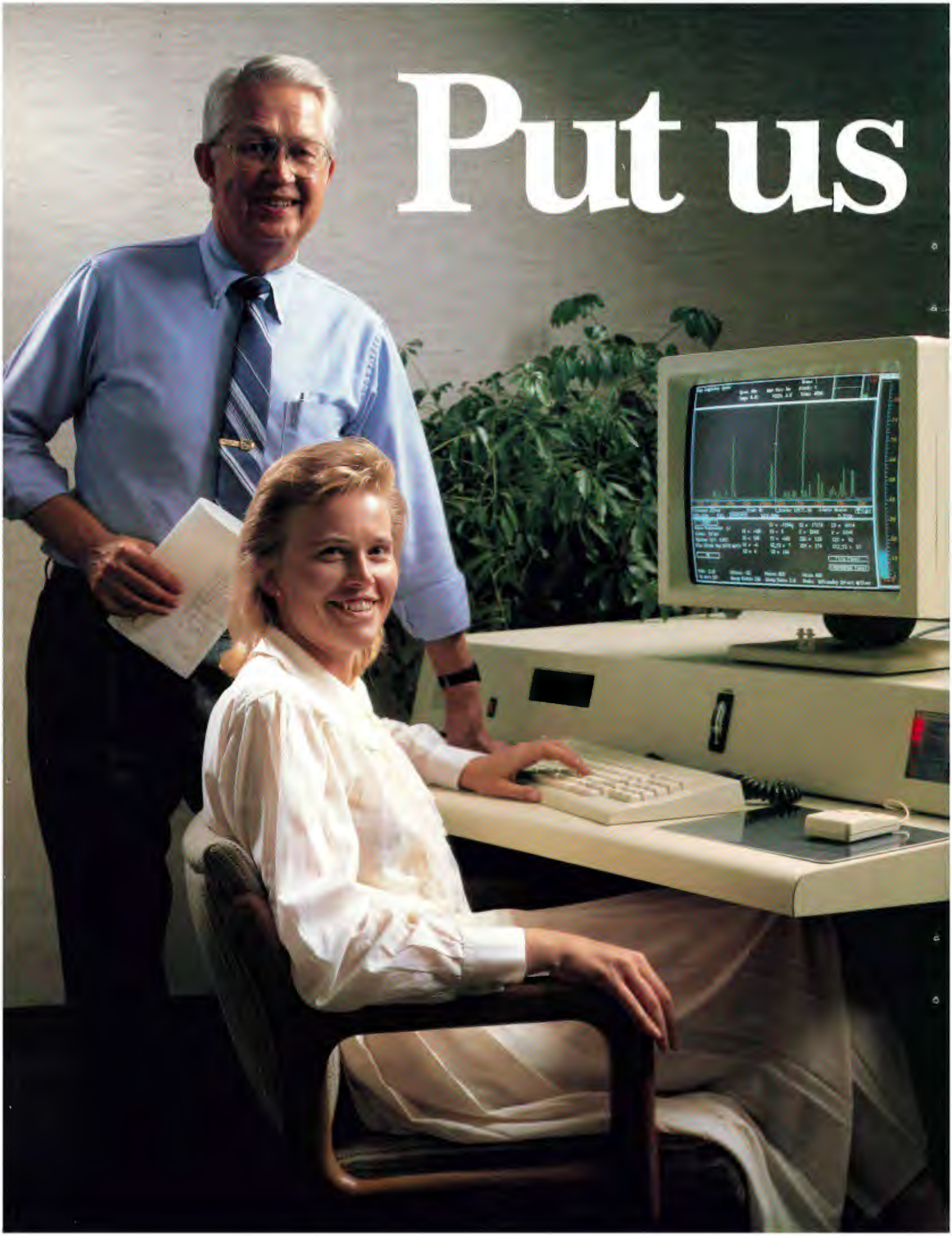
Please credit this contribution to the subscription of Ruth Stanaszek.

Steve Spanton Rich Stephens Peter Fruehan Andy Zektzer



HOHAHA of Strychnine on an Omega 600

GE NMR Instruments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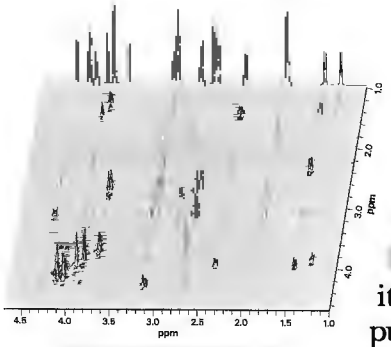

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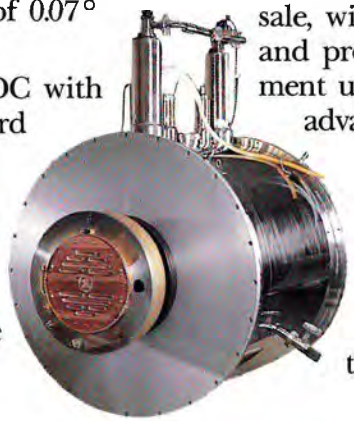

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Or call 800-543-5934. You'll be pleased with the results.

GE NMR Instruments

Alpha HDR

The New Standard in Digitizer Performance

Dynamic range vs. spectral width; spectral width vs. digital resolution. Trade-offs have been required due to NMR system hardware limitations. With the Omega™ Data system's Alpha HDR digitizer, no trade-offs are necessary. As shown in Figure 2 with a 16-bit dynamic range, 200 KHz spectral width, 64-bit complex acquisition word size, and up to 32 MBytes (4 MWords complex) of on-board acquisition memory available, the spectrometer is no longer the limiting factor when designing the most demanding experiments. Other outstanding features of the Alpha HDR include variable dwell periods, phase shifts of each sampled data point as small as 0.05 degrees, and segmentation of the digitizer memory into as many as 64K blocks. These features further distinguish the GN-series spectrometer equipped with the Omega Data System as the leader in NMR technology.

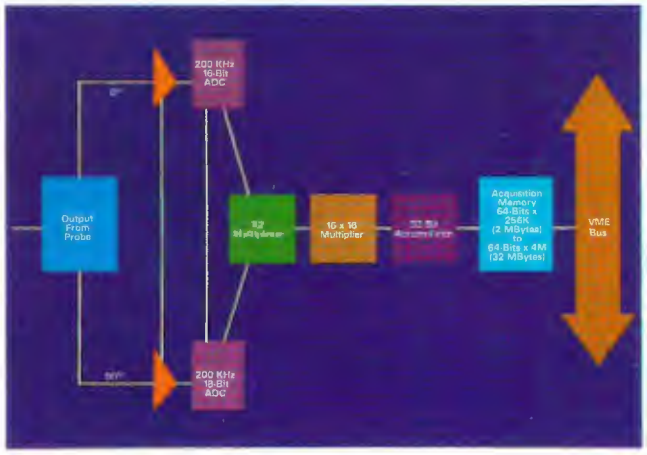

Fig. 1

The Alpha HDR digitizer.

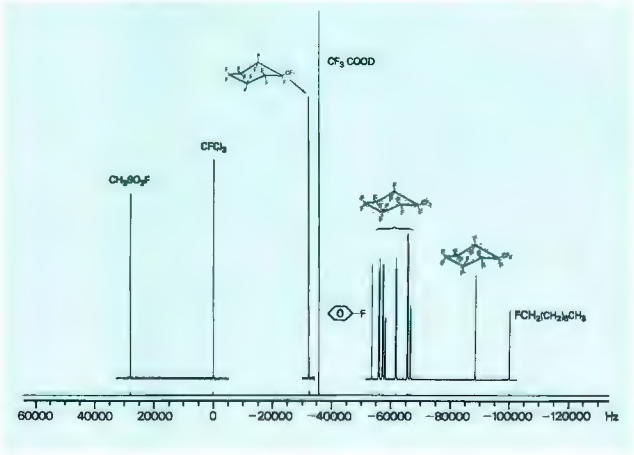

Fig. 2

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

GE NMR Instruments

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

May 19, 1989
(received 5/27/89)

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

Omega 500 Installation

Dear Dr. Shapiro:

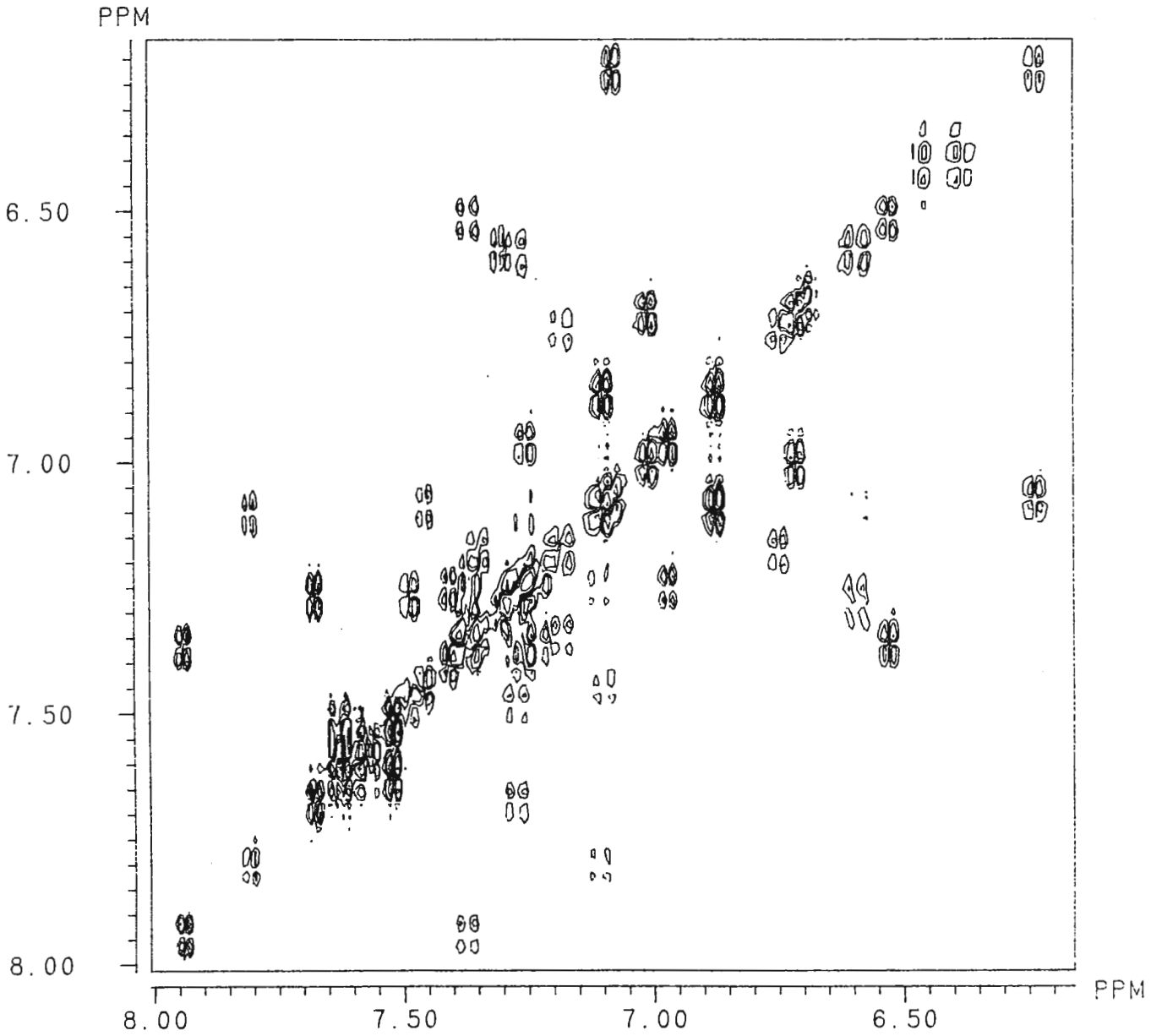
Our recent experience with the purchase and installation of a 500 MHZ spectrometer has been good. When trying to decide which spectrometer to obtain, we spoke to a number of 500 users who had experience with large molecule structure determination and we appreciate their helpful comments. A full discussion of how we chose GE would be too lengthy for this letter, but we would be glad to talk to anyone who is interested (804-924-3163). We were pleased about the fact that our Omega 500 was ordered in October, 1988 and the installation was essentially complete in January. The spectrometer has performed quite well and support from GE has been excellent. A major area of concern for us when deciding on the purchase was the integration of the Sun3 computer into the spectrometer because this is a relatively recent development by GE. We are happy to report that we have successfully used the spectrometer for both routine and more complicated experiments and have not had crash problems during acquisitions. We should note that we have not tried to do extensive processing during long acquisitions.

The figure contains the aromatic region of a phase sensitive double quantum filtered COSY spectrum of phospholipase A_2 (MW$\sim$14,000) obtained at 40°C with the Omega 500. The hypercomplex technique (States, Haberkorn & Ruben) was used and 256 t1 values were collected, each consisting of 2K complex points. Phase shifted (30°) sine apodization was used in each dimension and t1 was zero-filled once. We will soon receive a Sun4-based data station from New Methods Research, Inc. and look forward to utilizing the spectrometer and data station for a number of projects.

Sincerely,

Jeff Ellena
Department of Chemistry

Gordon Rule
Department of Biochemistry



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Anyone interested is urged to contact Prof. G.C.K. Roberts, Biological NMR Centre, P.O. Box 138, Medical Sciences Building, University Road, Leicester. U.K. (tel: +44-533-523054; Fax: +44-533-523013).

Lehigh University

Department of Chemistry
telephone (215) 758-3470

Seeley G. Mudd Building 6
Bethlehem, Pennsylvania 18015

(received 6/12/89)
June 6, 1989

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

GN-300 Modifications for CRAMPS

Dear Dr. Shapiro,

We've been interested in several experiments requiring reasonable proton multiple-pulse performance on both the observe and decouple channels of our General Electric NMR Instruments GN-300. The present instrument configuration bypasses the GN-300 power amplifiers and uses an ENI LPI-10 on the X nucleus channel, and an ENI 5100L driving a single tube tuned amplifier (285 MHz to 515 MHz) developed by Dick Braley of Amtron (Boston) with an ORAM plate supply. Each channel is capable of well over 1 kW output for times up to 20 msec. An upgrade equivalent to the "high resolution decoupler" has been implemented allowing phase coherence between the decouple and observe channels. Variable attenuators limit amplifier input to 1 mW, and pulse length protection circuitry has been added to protect the probes from overzealous graduate students (and forgetful faculty members!).

The routine observe channel multiple-pulse performance is quite acceptable; phase switching time betters the manufacturer's specifications of 1 microsecond. The decouple channel performs better than the 2 microsecond specification, but overall multiple-pulse performance does not equal the observe channel performance. The necessity to wait for the phase switching leads to longer cycle times when using the decouple channel.

We have overcome this limitation by adding an external Daico RF switch (model 100C1041) which is driven by an extra pulse programmer line. The pulse program is written such that the decoupler radiofrequency generation hardware is always on, with phase switching preceding the actual time a particular pulse is needed at the probe. The timing diagram for the decoupler and the Daico switch is shown in Figure 1. The output of the switch goes directly to the proton amplifier train.

Figure 2 illustrates actual multiple-pulse performance with this modification. The decoupler channel generates the RF pulse train, although phase coherence with the observe channel is necessary to permit signal averaging. The adamantane linewidth corresponds to .18 ppm scaled, and is virtually identical to the observe channel performance. The spectrum is scaled up by a factor of 10 to illustrate the additional artifacts that probably arise from switching and/or timing problems. We are continuing to develop this system for routine use.

More detailed information is available for those that might be interested. Please credit this contribution to the joint Air Products/Lehigh account under Bill Anderson.

Thomas G. Neiss
Graduate Student

James E. Roberts
Assistant Professor of Chemistry

FIGURE 1

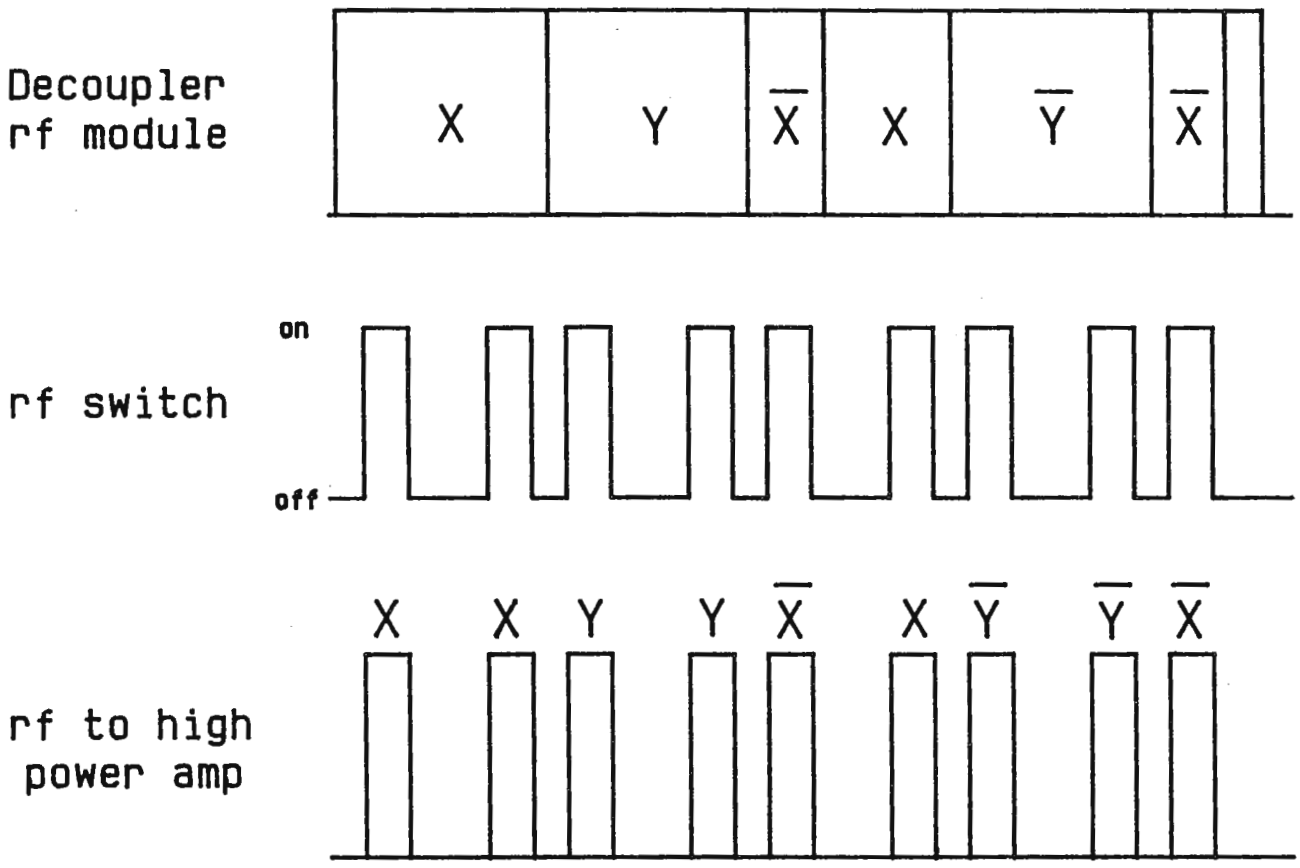
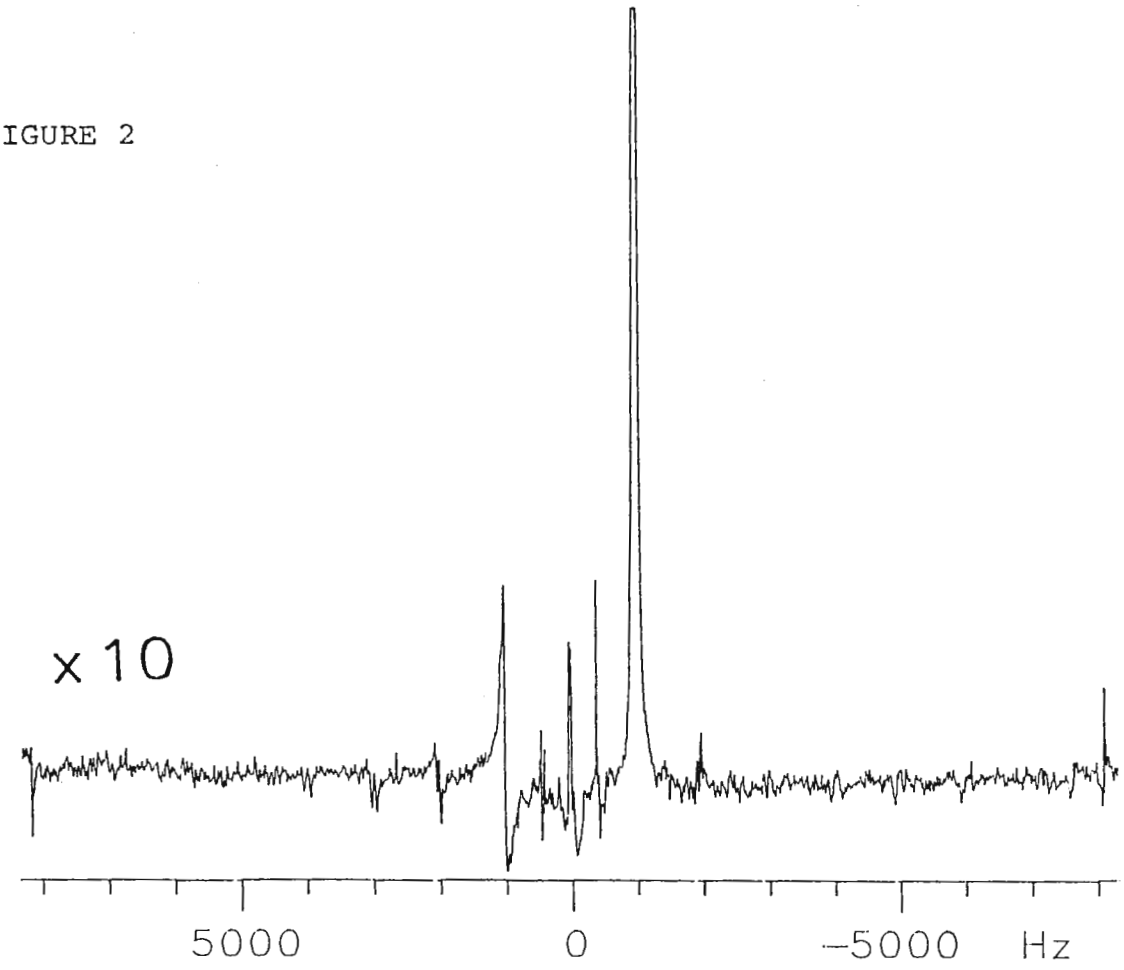


FIGURE 2



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The University of Akron

Department of Chemistry (216) 375-7372
Akron, OH 44325

May 15, 1989 (received 5/24/89)

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

A Comparison of 300 and 600 MHz Spectra

Dear Dr. Shapiro:

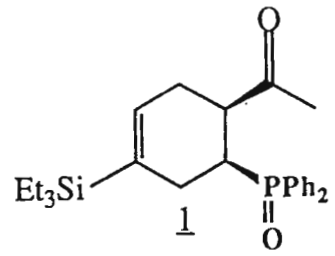
Recently we have been involved in determining the structure and relative stereochemistry of a number of cyclohexene derivatives which were synthesized via a Diels-Alder reaction. At 300 MHz, significant overlap occurred in the ^{1}H NMR spectrum between the region 2.7 - 3.0 ppm which made structural interpretation of 1 difficult. Attempts to change the solvent did not assist in distinguishing the resonances in this region. Benzene-d_6 afforded the best phase-sensitive COSY spectrum at 300 MHz, which is shown in Figure 1.

At 600 MHz, the four proton resonances were completely distinct. The connectivity via spin-spin coupling was straightforward with the high field phase-sensitive COSY spectrum, Figure 2. The relative stereochemistry was assigned with the aid of a NOESY spectrum at 600 MHz.

Sincerely yours,

Peter Rinaldi

Maritherese Tokles



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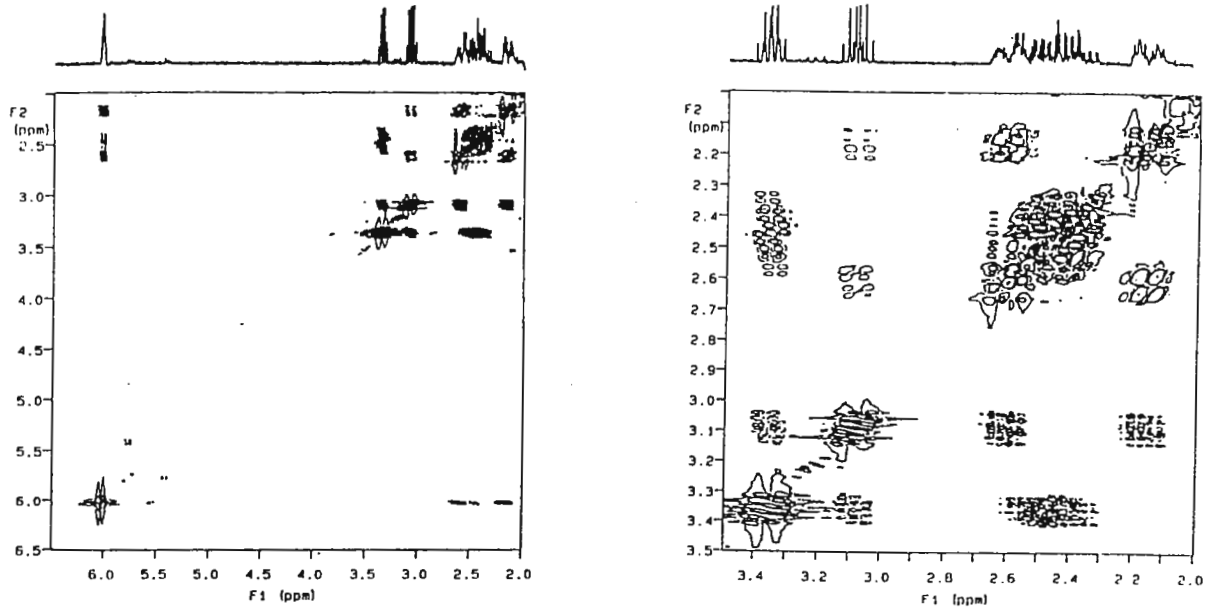

Figure 1. (a) Phase-sensitive COSY spectrum of 1 in C_6D_6 recorded at 300 MHz. (b) Expansion of the upfield region.

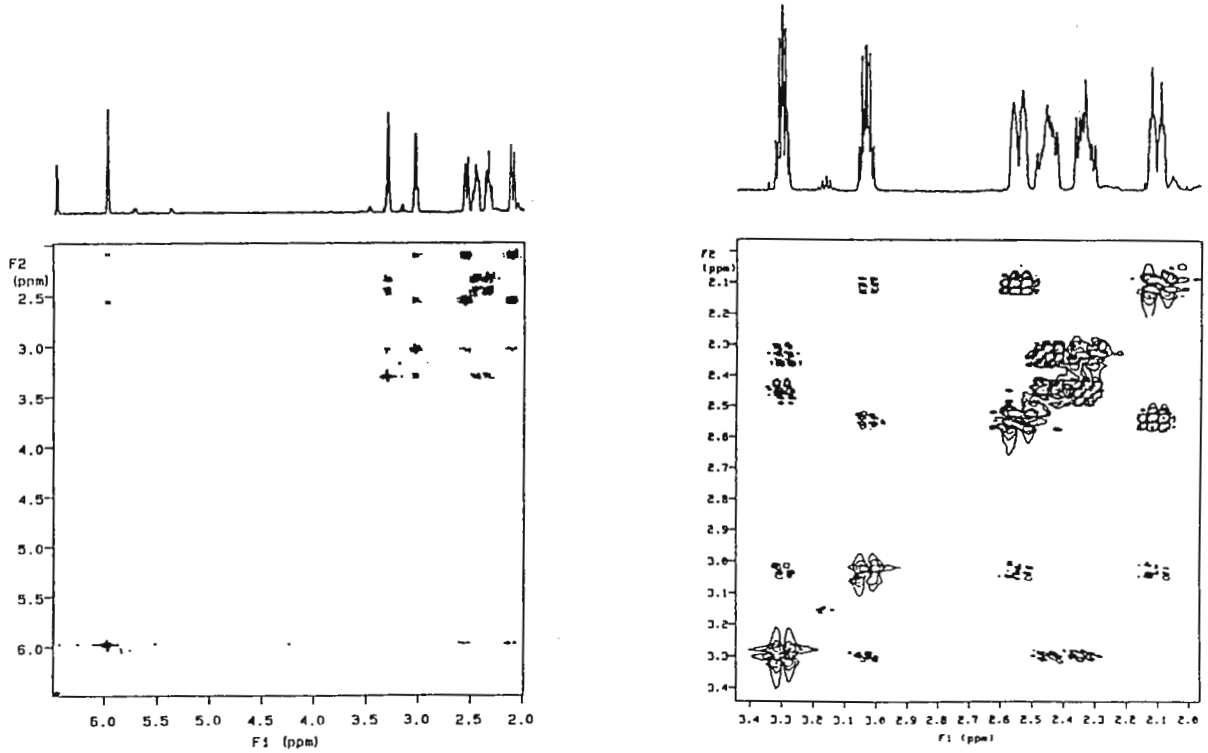

Figure 2. (a) Phase-sensitive COSY spectrum of 1 acquired under identical conditions at 600 MHz. (b) Expansion of the upfield region.

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Washington
WASHINGTON·UNIVERSITY·IN·ST·LOUIS

Department of Chemistry

June 7, 1989
(received 6/12/89)

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

Re: **Concomitant Quantification of Metabolism and Blood Flow *via* $^{2}H/^{31}P$ NMR *in Vivo***

Dear Barry:

Quantification of tissue metabolite levels *in vivo* represents one of the most promising routs toward the diagnosis of disease and monitoring of the effectiveness of therapeutic treatment. However, performing an NMR measurement that quantitatively reflects the metabolite levels *in vivo* is difficult. Thulborn and Ackerman proposed a method using a doubly tuned antenna for determining the quantitative molar concentrations of tissue metabolites *in vivo*. By comparing the metabolite signal intensities of interest with the ^{1}H signal intensity of tissue water that serves as the internal concentration (and sensitive volume) reference, one can readily obtain the molar concentration of metabolites even with the spatially inhomogeneous sensitive volume of a surface-coil type local antenna.

There have been a number of applications reported recently in the literature employing modifications of the Thulborn method. Our laboratory has been using this approach to examine the metabolic dysfunction resultant from sepsis (septic shock) in a laboratory rat model of this disorder (the number one cause of death in the surgical intensive care unit). In our adaptation of the Thulborn method, we employ a $^{2}H/^{31}P$ doubly tuned surface-coil antenna to study rat leg muscle *in vivo*. The derivation of metabolite concentrations such as phosphocreatine (PCr) and ATP was accomplished by comparing the naturally occuring ^{2}H signal intensity of tissue water with the metabolite signal intensities. For our purposes, the biggest advantage of this protocol is that we can follow also *via* ^{2}H NMR the tissue blood flow through the same region of tissue where the metabolite levels are measured. This offers a correlation between metabolic status and blood flow within a specific tissue in the same subject. This provides an important multiparameter approach to the pathophysiological analysis of sepsis. An outline of the protocol we employ is as follows:

a) Construct a doubly tuned $^{31}P/^{2}H$ surface-coil antenna or a single tuned antenna with an external tuning circuit capable of tuning the antenna readily to either ^{31}P or ^{2}H frequencies.

b) Prepare a series of aqueous tissue-like samples (salt solutions) containing different concentrations of inorganic phosphate (P_i). A ferric nitrate/EDTA solution was prepared and added as a relaxation agent to ensure that the T_1 or P_i in solution is not longer than T_1's of metabolites *in vivo*.

c) Prepare a reference "point sample" (microsphere) giving strong ^{31}P and ^{2}H signals (2 *M* K_2HPO_4 in 20% D_2O was used in our experiment) for flip angle calibrations. Pulse width *vs.* flip angle calibration should be performed for each measurement with a new sample in case of changes in sample loading.

d) Data acquisition ($^{2}H/^{31}P$) should be carried out quantitatively (TR > 3-5 T_1) with the same pulse flip angle. All acquisition parameters are identical for calibration and *in vivo* experiments.

e) Establish a plot of the ratio of ^{2}H HOD and ^{31}P P_i signal intensities *vs.* P_i molar concentration from the calibration experiments. This should result in a linear relationship (Figure 1).

Washington University
Campus Box 1134
One Brookings Drive
St. Louis, Missouri 63130-4899

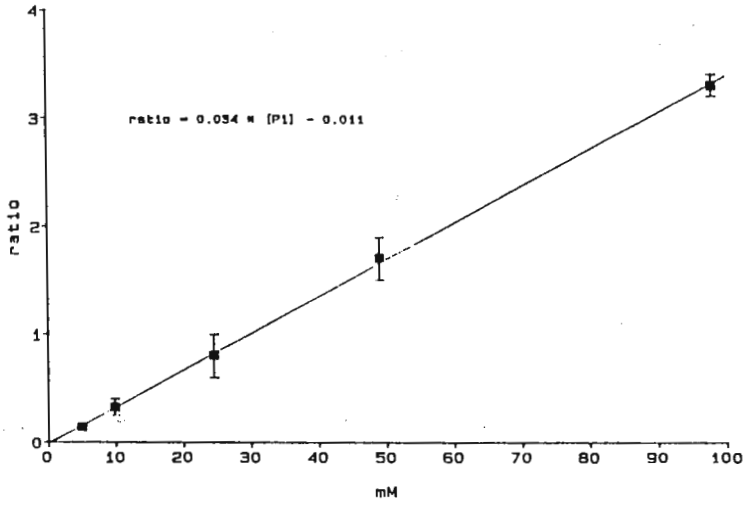

Figure 1. Calibration curve of the ratio of HOD and P_i peak areas *vs.* the concentration of P_i. Both ^2H and ^{31}P NMR experiments were acquired under the same conditions as in later *in vivo* experiments. [Pi] = 5, 10, 25, 50, 100 m*M*. Each point represents the average of five independent measurements.

f) Obtain *in vivo* the resonance intensity ratios of HOD and phosphate metabolites of interest (Figure 2). Using this number (ratio) determined *in vivo* and the calibration curve discussed in e) above, find the absolute concentration of the relevant metabolites.

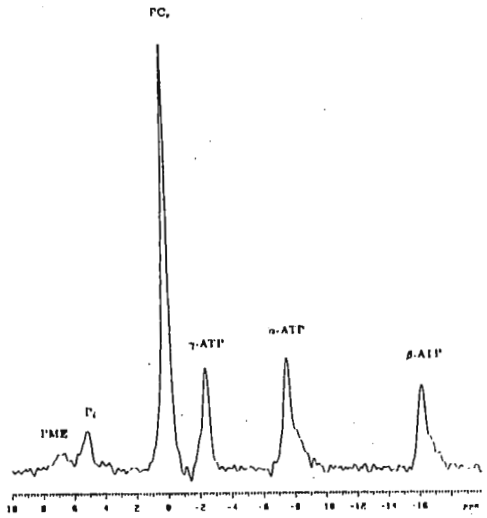

Figure 2. *In vivo* ^{31}P NMR spectrum of leg muscle from a septic rat. Data acquired quantitatively with a 135 degree pulse at the center of the surface coil. $[PCr]_{control} = 29 \pm 5$ m*M* SD (n=17); $[ATP]_{control} = 8 \pm 1$ m*M* SD (n=17); $[PCr]_{septic} = 24 \pm 6$ m*M* SD (n=13); $[ATP]_{septic} = 8 \pm 2$ m*M* SD (n=13). Reported concentrations are not corrected to the intracellular volume fraction of tissue.

g) Following this $^{31}P/^2H$ measurement of metabolite concentration, employ the ^2H NMR measurement of blood flow *via* D_2O washout analysis (Figure 3) to monitor tissue perfusion rate [ml-blood/(100 g-tissue·min)].

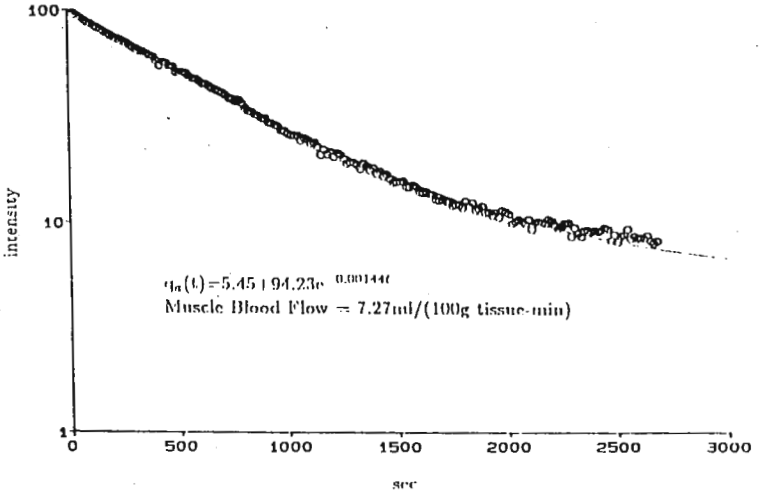

Figure 3. *In vivo* septic rat leg muscle D_2O washout time course. ^2H NMR experiments were collected quantitatively also with a 135 degree pulse at the center of the surface coil. Each point represents a 15 sec time-averaged signal acquisition. The entire curve is fitted to a 3-parameter single exponential decay function. This accounts for tracer recirculation.

Sincerely,

Sheng-Kwei Song

Richard S. Hotchkiss

Joseph J.H. Ackerman

Duke University

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May 15, 1989
(received 5/23/89)

Professor B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 947303

^{6}Li-^{1}H HOESY in the Aldol Reaction

Dear Professor Shapiro:

The two-dimensional heteronuclear NOE experiment (2-D HOESY) was first described by Peter Rinaldi (1) and Yu and Levy (2) several years ago. Compared to the wide-spread use of homonuclear NOE spectroscopy, the heteronuclear experiment has been used surprisingly only in a few cases to explore the through-space interactions of neighboring nuclei. Working together with Michael Nichols and Professor Ned Arnett (Duke Chemistry), we have been exploring the use of this effect in characterizing organolithium compounds, particularly metal-enolate ion pairs involved in the "modern" aldol condensation.

Although the aldol reaction is over 150 years old, it is only since the 1970s that it has become recognized as one of the most important classes of chemical reactions. The "modern" aldol reaction uses metal ion amide bases in hydrocarbon solvents to form the anion for the condensation reaction. When sodium or potassium are the counterions in the "modern" aldol, results consistently show evidence of a simple equilibrium between the metal ion and the metal-enolate ion pairs. However, in the lithium case, the condensation is complicated by association effects featuring dimers, tetramers, etc. in solution. Since the distances from the metal ion to the organic moieties vary in the x-ray crystal structures of lithium aldolates, it was hoped that ^{6}Li-^{1}H HOESY could yield insights into the regioselectivity about the metal ion in solution. While ^{6}Li has nuclear spin >1/2 and therefore a quadrupole moment, its quadrupole moment is small; Wehrli (3) found up to 35% dipolar relaxation through ^{6}Li-^{1}H interactions in alkyllithium compounds and was able to measure the first $^{6}Li\{^{1}H\}$ NOE effects. Figure 1 below shows the 2-D ^{6}Li-^{1}H HOESY spectrum for ^{6}Li-labeled lithiopinacolonate·THF in cyclohexane-d_{12} at 12°C obtained on a GE GN-500 spectrometer. HOESY parameters were based on those of the Schleyer group (4) and phase cycling was that of Yu and Levy (2). The only cross peaks detected were those predicted from the crystal structure for the tetrameric aggregate. Identification of the structurally interacting species is, of course, of great interest and has

BOX 3711, DUKE UNIVERSITY MEDICAL CENTER
DURHAM, NC 27710

allowed a description of the thermochemistry of a structurally defined aldol reaction (5).

Sincerely,

Anthony A. Ribeiro

1. P.L. Rinaldi, J. Amer. Chem. Soc. 105:5167 (1983).
2. C. Yu and G.C. Levy, J. Amer. Chem. Soc. 106:6533 (1984).
3. F.W. Wehrli, Org. Magn. Reson. 11:106 (1978).
4. W. Bauer, T. Clark and P. Schleyer, J. Amer. Chem. Soc. 109:970 (1987).
5. E.M. Arnett, F.J. Fisher, M.A. Nichols and A.A. Ribeiro, J. Amer. Chem. Soc. 111:748 (1989).

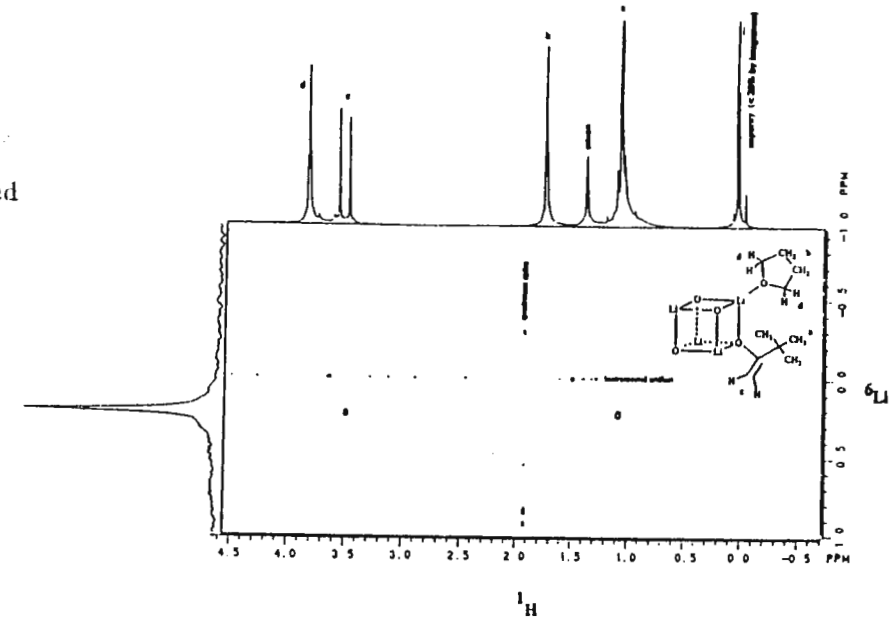

Fig. 1 ^{6}Li-^{1}H$_6$HOESY spectrum of (^{6}Li) labeled lithiopinacolonate·THF in cyclohexane-d_{12} at 12°C. Total measuring time was 11 hr. ^{1}H scale residual C_6H_{12} = 1.38 ppm. ^{6}Li scale 2M LiOH/D_2O (external) = 0.00 ppm.

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Department of Chemistry

June 2nd, 1989
(received 6/6/89)

Dr. B.L. Shapiro
966, Elsinore Court
PALO ALTO (CA) 94303
U.S.A.

Magnetic Susceptibility Effects in Coaxial NMR Tubes

Dear Dr. Shapiro:

We have been studying the effects of hydrodynamic flows on the critical properties of the binary mixture cyclohexane/aniline (1). A variety of flows are generated in the annulus of two concentric and independantly rotating NMR tubes. In the early days of NMR, coaxial tubes provided a means of measuring chemical shifts of a substance in the annulus while the reference was found in the cavity of the inner tube (or vice-versa) (2). While this arrangement was convenient to eliminate solubility and contamination problems, differences in the magnetic susceptibilities of the substance and the reference lead to slightly different magnetic field strengths in the annulus and the cavity of the inner tube. When the coaxial cells are rapidly rotated single peak resonances are found in the spectrum of the substance. In the static case, a broad doublet for each resonance would result from this bulk magnetic susceptibility effect (2). The observed splitting is proportional to the difference in the volume magnetic susceptibilities of the substance and the reference in addition to the shape of the sample. This effect is observed in figure 1A where the ^{1}H spectrum is presented for neat cyclohexane in the annulus of two concentric and static NMR tubes (r_{inner} = 2.5 mm, r_{outer} = 5.0 mm) with D_2O and TMS in the inner tube. As the magnetic susceptibility is proportional to the square of the magnetogyric ratio and the number of NMR active nuclei, a splitting reduced by a factor of 1/3200 is expected for the ^{13}C NMR spectrum of cyclohexane in this arrangement, i.e. a splitting on the order of 3 mHz. Indeed no splitting is observed in Fig. 1B for the ^{13}C spectrum. Therefore by monitoring the ^{13}C resonance of cyclohexane in the binary mixture at criticality in the annulus of coaxial NMR tubes these susceptibility effects can be neglected.

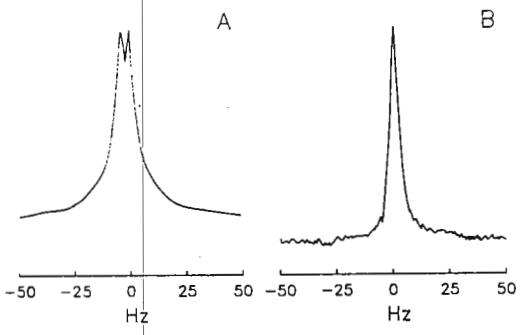

Fig. 1
T=22°C

Sincerely,

S L

Serge Lacelle

Serge Bérubé

(1) S. Lacelle, F. Cau, and L. Tremblay (submitted)
(2) J.R. Zimmerman and M.R. Foster, J. Phys. Chem. 61, 282 (1957)

Thomas L. James, Ph.D.
UCSF Magnetic Resonance Laboratory
Department of Pharmaceutical Chemistry
The University of California
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May 19, 1989
(received 5/25/89)

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

Dear Barry:

An important development in the area of *in vivo* NMR has been the advent of localized spectroscopy which enables monitoring the NMR spectrum of a defined region of interest within a larger sample. Our lab has been involved in both "high-resolution" 2D NMR and *in vivo* NMR. So perhaps it is not surprising that we would try to obtain localized 2D spectral NMR. In the few cases in which 2D NMR was applied to heterogeneous systems, spectra were obtained from the whole sample without any spatial localization. The present study explored the feasibility of performing localized 2D NMR experiment using a surface coil. In principle this could be accomplished by phase-encoding. The experiment consists of a conventional COSY sequence with a phase-encoding pulsed gradient at the beginning of the evolution time (t_1), i.e., immediately after the first 90° pulse of the COSY sequence. Thus, for each increment of the phase encoding pulse gradient, one has to step through all values of t_1. A 3D Fourier transform will generate a one-dimensional spatially localized COSY spectrum.

Experiments were performed on our Quest-4300 (Nalorac) instrument equipped with an Oxford 4.7T magnet, 22.5 cm usable bore, using the phantom shown in Fig. 1. A two-turn, 2 cm surface coil (tuned to 200.1 MHz), was used. Four scans were averaged for each of the 128 incremental delays in the COSY experiment. The acquisition time in the t_1 and t_2 dimensions were 41.28 and 81.92 ms, respectively (Fig. 2A). The resulting 128×256 matrix was transformed with zero-filling in the t_1 dimension, resulting in a 256×256 square matrix . For the localized COSY experiment, the same parameters were used. In addition, eight sine-bell-shaped pulsed gradients of 1.92 ms duration were incremented in 0.096 Gauss/cm steps, giving a slice thickness of 2.5 mm and a total field of view (FOV) of 2 cm. The resulting three-dimensional matrix (8×128×256) was processed on a Sun 3/160 computer using 3D FT software written by us. The data matrix was zero-filled once giving a matrix of 8×256×256 data points. The unlocalized COSY spectrum (Fig. 2A) clearly displays two intense cross-peaks from the CH_3 groups at 1.30 ppm to the CH_2 of the ethanol and the CH group of lactic acid at 3.78 and 4.10 ppm, respectively. Fig. 2B shows two of the eight slices resulting from 3D FT of the data set. The eight slices clearly demonstrate that even with only eight phase-encoding steps, there is no contamination; each slice shows the COSY spectrum of only one compound. Slices 1-4 which were above the surface coil manifest the COSY spectrum of lactic acid only, while slices 5-8 exhibit the spectrum of ethanol which was below the coil (see phantom in Fig. 1). The intensities of the 2D spectra in the different slices are as expected, accounting for the shape of the phantom used as well as the rf field gradient of the surface coil.

Sincerely yours,

Yoram Cohen Lee-Hong Chang Thomas L. James

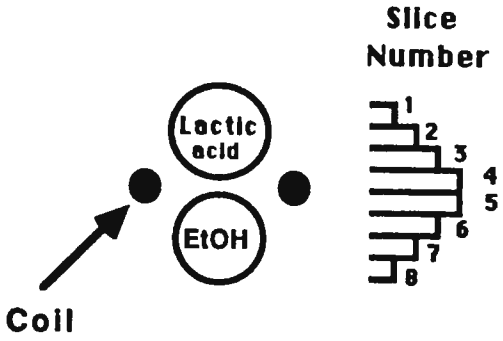
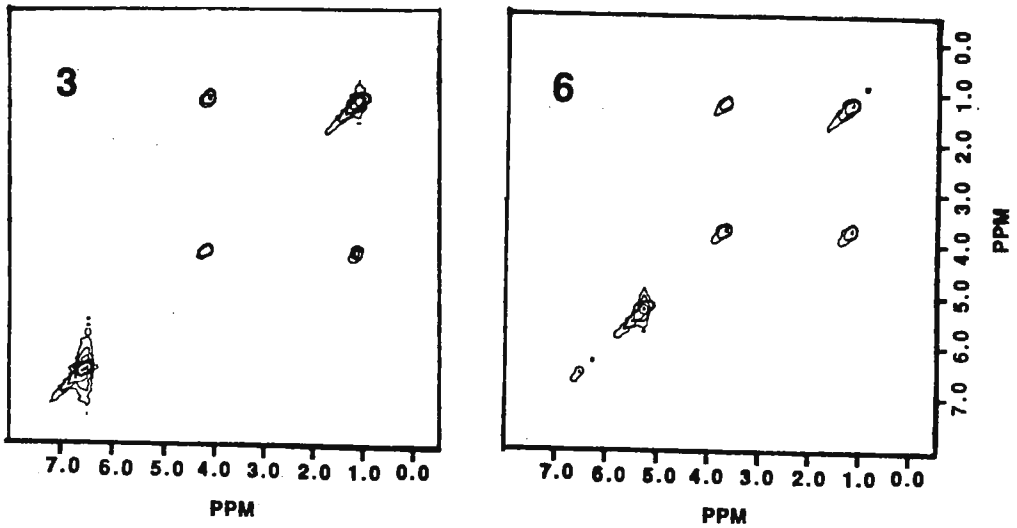


Figure 1

B



A

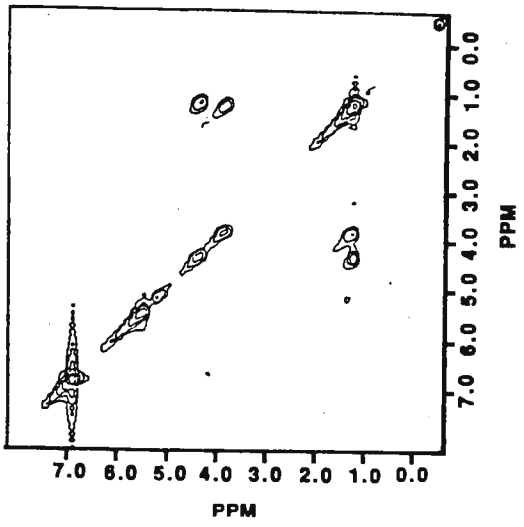


Figure 2

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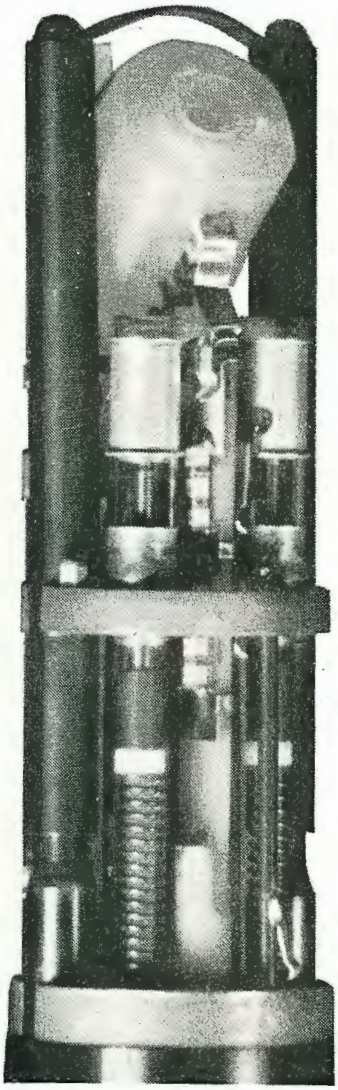

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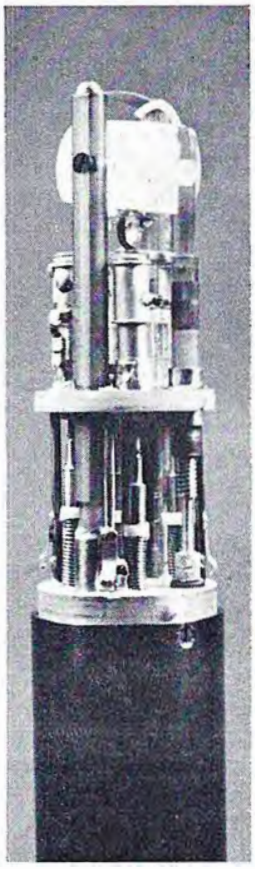

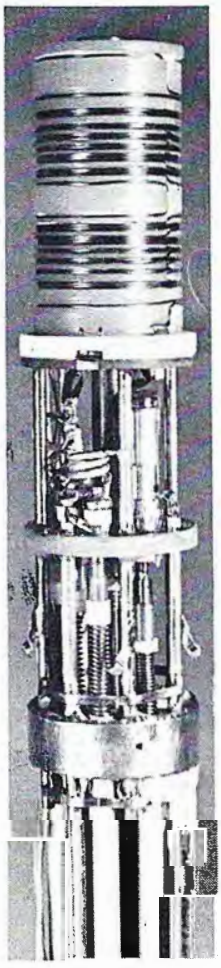

* * DAS * *

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June 7, 1989
(received 6/12/89)

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

Dear Barry,

Since a majority of our NMR work is done on biological molecules either naturally occuring or synthetic and usually of limited quanity, we are always interested in ways to increase the sensistivity of our experiments.

We have implemented the P.COSY experiment described by Bax (D. Marion and A. Bax, *J. Magn. Reson.* **80**,528-533 (1988)). This experiment eliminates the dispersive character of the usual COSY diagonal peaks yielding high-resolution spectra of a quality comparable to the DQF-COSY experiment but with twice the sensistivity. The purging of the dispersive character of the diagonals is accomplished by subtracting the result of a COSY spectrum recorded with a 0^0 mixing pulse from the usual COSY spectrum. Instead of recording a complete 2D data matrix for the 0^0-COSY experiment, the same data can be obtained from a single FID. By left shifting the data of this single FID, the time-domain data for successive t_1 increments of the 0^0-COSY experiment are obtained.

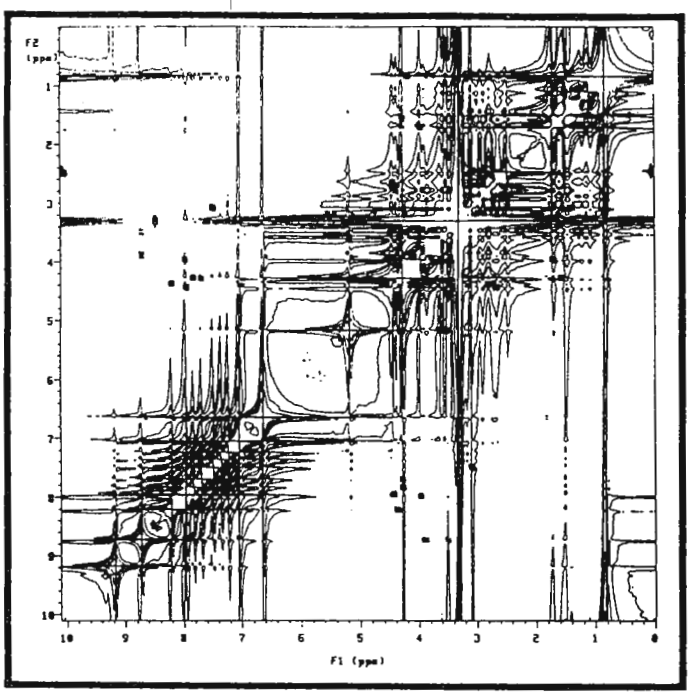
In essence, the experiment consists of obtaining the usual 2D phase-sensistive COSY data and a 1D reference spectrum. The 1D spectrum is obtained using the COSY pulse sequence and phase cycling but with the power of the second 90^0 pulse set to zero (i.e. a 0^0 pulse), with twice the number of data points, and with 16 times the number of scans per t_1 increment. Only the t_1=0 data are collected. The recycle times for the COSY and the 1D reference spectrum are adjusted such that the length of the experiments from the first 90^0 pulse to the end of the recyle delay are equal for both. Data are processed using a C-program that scales, left shifts and subtracts the reference FID from the COSY data array to generate a new, P.COSY data set.

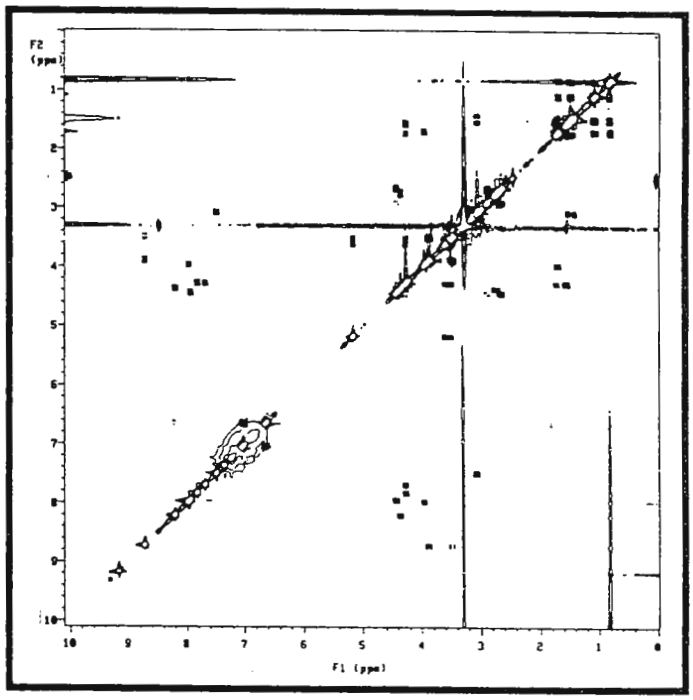
The COSY and P.COSY spectrum of a small peptide is shown in the top figure and a 60 hr. P.COSY acqusition for hen lysozyme (7 mmol., 90% H_2O) is shown in the bottom figure. It seems to us that the phase-sensitive, DQF-COSY experiment is now obsolete.

Sincerely,

John J. Likos

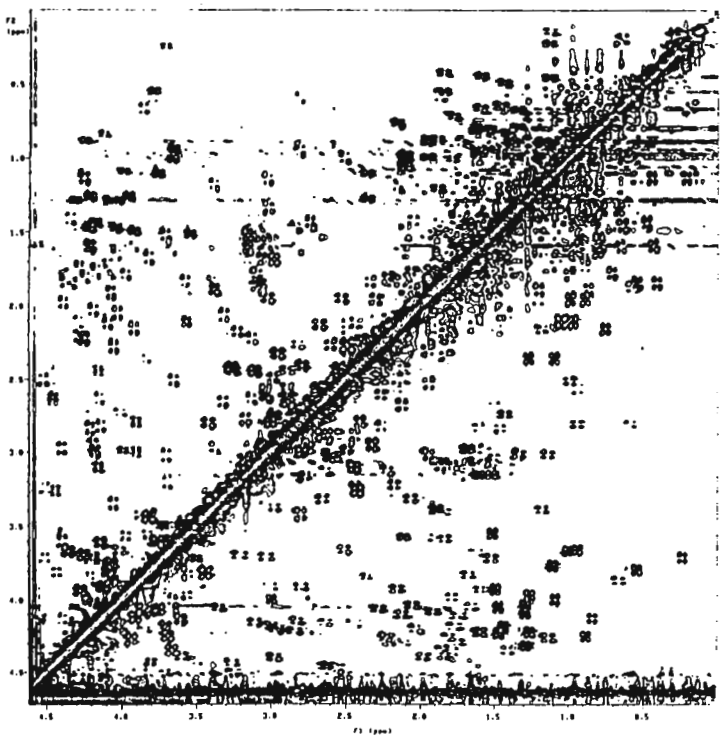
William C. Hutton

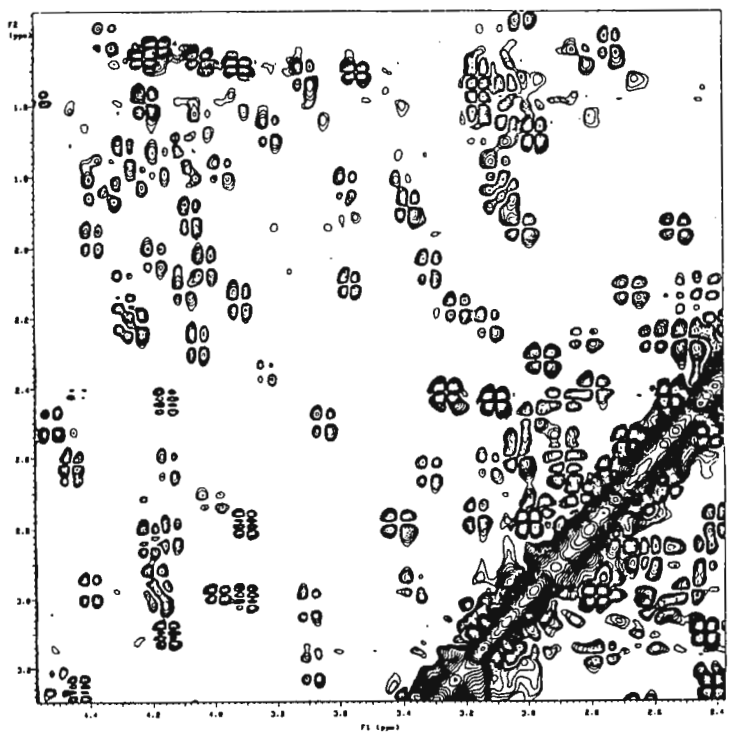




phase-sensitive COSY **P.COSY spectrum**

Conditions for data collection, processing and display were identical for both spectra . There was no baseline correction or first data point manipulation of the fid .





The data was collected on a Varian VXR-500 spectrometer using 1K x 2K hypercomplex points . The data was zero-filled to 4 K x 4K and the first point of each fid was multiplied by a constant before Fourier transformation. Baseline correction (3rd order polynomial) was applied in both dimensions. All data processing was done on SUN 4 workstations using Varian's VNMR software. The P.COSY data set was created with a C-program that was integrated into the VNMR software.

Hare Research, Inc.
14810 216th Avenue NE
Woodinville, Washington 98072
TEL: (206) 788-2374
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Statement of Company Policy

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TEL: (206) 788-2374
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Hare Research Technical Report

Subject: van der Pitfaals (??)

Barry —

I have recently noticed a problem that occurs in distance geometry calculations. The problem is most pronounced in protein structures, although the problem can occur with virtually any type of molecule. I thought I'd share this with TAMU readers and stave off a dreaded pink sheet for at least a little while.

The problem concerns the use of a van der Waals contact distance for unknown lower bounds. That is, when the lower bound between two atoms is not known, the sum of the van der Waals radii is used as the smallest distance that the atoms may approach each other. The atomic radii used may be a hard sphere radius (i.e., where the potential crosses through zero), or the equilibrium radius (i.e., where the potential is at a minimum).

Before describing the problem with this approach, consider what the lower bound is used for in distance geometry calculations. In the best of all possible distance geometry worlds, one would know every distance exactly. Since this is not the best possible world[1], most distances in a biomolecule are not experimentally known. Instead we use lower and upper distance limits *that are chemically and torsionally possible.* So what is the smallest distance that can occur between two atoms? Normally, the sum of the van der Waals hard sphere distances is the lower limit.

But not in the case of polarizable atoms! Hydrogen bonds are typically 20–25% shorter than the "closest possible distance", and salt bridges are also quite short. Most persons and DG programs (to my knowledge) either do not or cannot explicitly define all hydrogen bonds. Thus many or all lower bounds are too restrictive for hydrogen bonds to form, resulting in distorted structures (this is quite noticeable in helices).

What we have done in our DSPACE program (v3.4) is to allow less restrictive lower bounds to occur for polarizable groups. Users of DISGEO, DGEOM, DISMAN should check to see how lower bounds are handled in these programs. Of course, if the structures produced by the DG program is energy minimized using AMBER, CHARMm, etc., this problem will go away.

I would enjoy receiving comments on this problem from other DGers, especially those who are using programs other than DSPACE. Please call me at (206) 789-7559 or send me a fax at the number shown on the letterhead.

Paul

Paul L. Weber

[1] Where we are just a heartbeat away from having President Quayle!

V.V. Krishnamurthy
varian
Instrument Group

06/12/89

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

PHASE-SENSITIVE COUPLED CH CORRELATION SEQUENCE FOR LONG-RANGE J MEASUREMENT

Dear Dr. Shapiro:

My recent move from UC, Berkeley to Varian had (unforgivably?) delayed my contribution to TAMU newsletter by at least 2 months. With this contribution I hope to be reinstated in your list.

The coupled version (sequence A) of the Freeman-Morris sequence is free from any modulation of cross peak intensity due to passive couplings

H: $90°-t_1/2-\quad -t_1/2-!--\Delta_1--90°$

C: $\qquad 180° \qquad\qquad 90°\text{-Acq.}(t_2)$ (A)

and it has been argued[1] that the decrease in S/N is often not very significant compared to the danger of accidental missing of cross peaks due to wrong choice of Δ_2. Sequence A, without BB decoupling during t_2, provides a coupled spectrum along the carbon dimension but, due to the presence of the 180 pulse midway through the evolution (t_1), achieves heteronuclear BB decoupling along the proton dimension. This sequence can be visualised as an extension of the Fully coupled heteronuclear correlation sequence (B), also referred to as FUCOUP, with hetero-

H: $90°------t_1-----90°$

C: $\qquad\qquad 90°\text{-Acq.}(t_2)$ (B)

nuclear decoupling along the F_1 dimension.

The FUCOUP sequence in a phase-sensitive fashion can be used to measure long-range CH coupling constants[2]. However, FUCOUP provides a redundancy of information in that the CH coupling constant appears in both dimensions of a cross peak. Since, the resolution along F_1 is generally limited and the coupling constant can be measured more conveniently along F_2, this redundancy sacrifices some sensitivity because of splitting (or broadening) of the cross peak along F_1. On the other hand, sequence A (which, being analogous to FUCOUP, is designated PACOUP - PArtly COUPled CH correlation sequence) should give more sensitivity than FUCOUP, because of BB decoupling during evolution, and still retain the CH coupling information along F_2. We modified sequence A into a phase sensitive fashion (sequence C) and compared its sensitivity to that of a phase-sensitivite FUCOUP sequence and its use in measuring long-range CH coupling constants. The results are shown for the C_2H_6 and C_6H_2 cross peaks of nicotinamide in the Figures.

H: $90°-t_1/2-\quad -t_1/2-!--\Delta_1/2--180°--\Delta_1/2--90°$

C: $\qquad 180° \qquad\qquad 180° \qquad 90°\text{-Acq.}(t_2)$ (C)

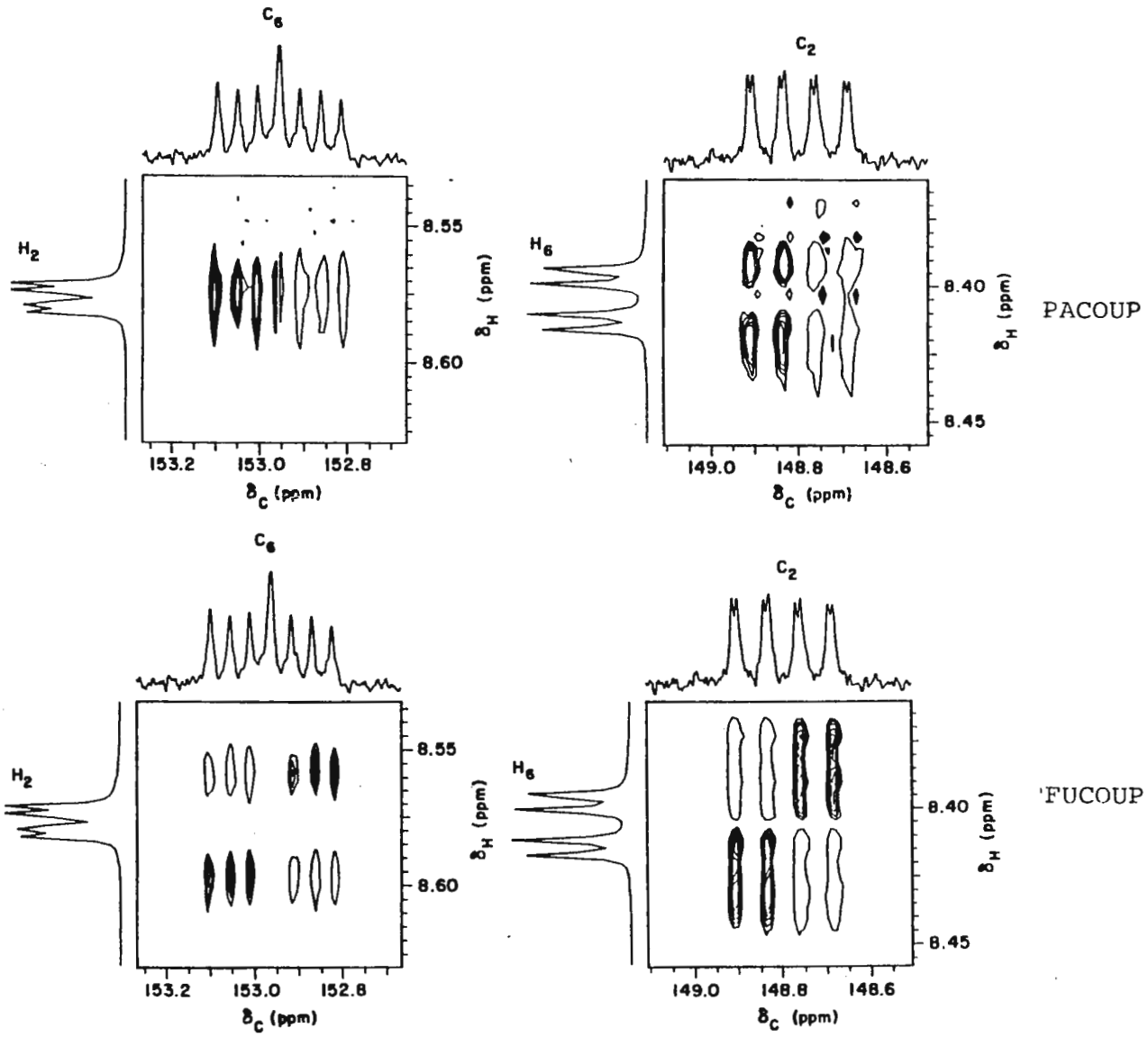

Fig. 1. C_2H_6 and C_6H_2 cross peaks (one of the two one-bond doublet components) from a phase-sensitive FUCOUP (sequence B) and PACOUP (sequence C with Δ_1 = 46.3 ms) of 1M nicotinamide in D_2O. See Fig. 2 from cross sections.

Even in simple compounds, where all CH coupling constants to a particular carbon can be measured conveniently from a high resolution proton coupled carbon spectrum, unambiguous assignment of a specific coupling to a specific CH spin pair is not possible without selective irradiation experiments. The phase-sensitive FUCOUP and PACOUP experiments, on the otherhand, provide a method to not only measure the coupling constants to a high degree of resolution (dependent on the digital resolution along F_2) but also assign them to a specific CH spin pair based on the cross peak chemical shifts and the anti-phase nature of the active couplings. The phase-sensitive PACOUP sequence (with judiciously chosen

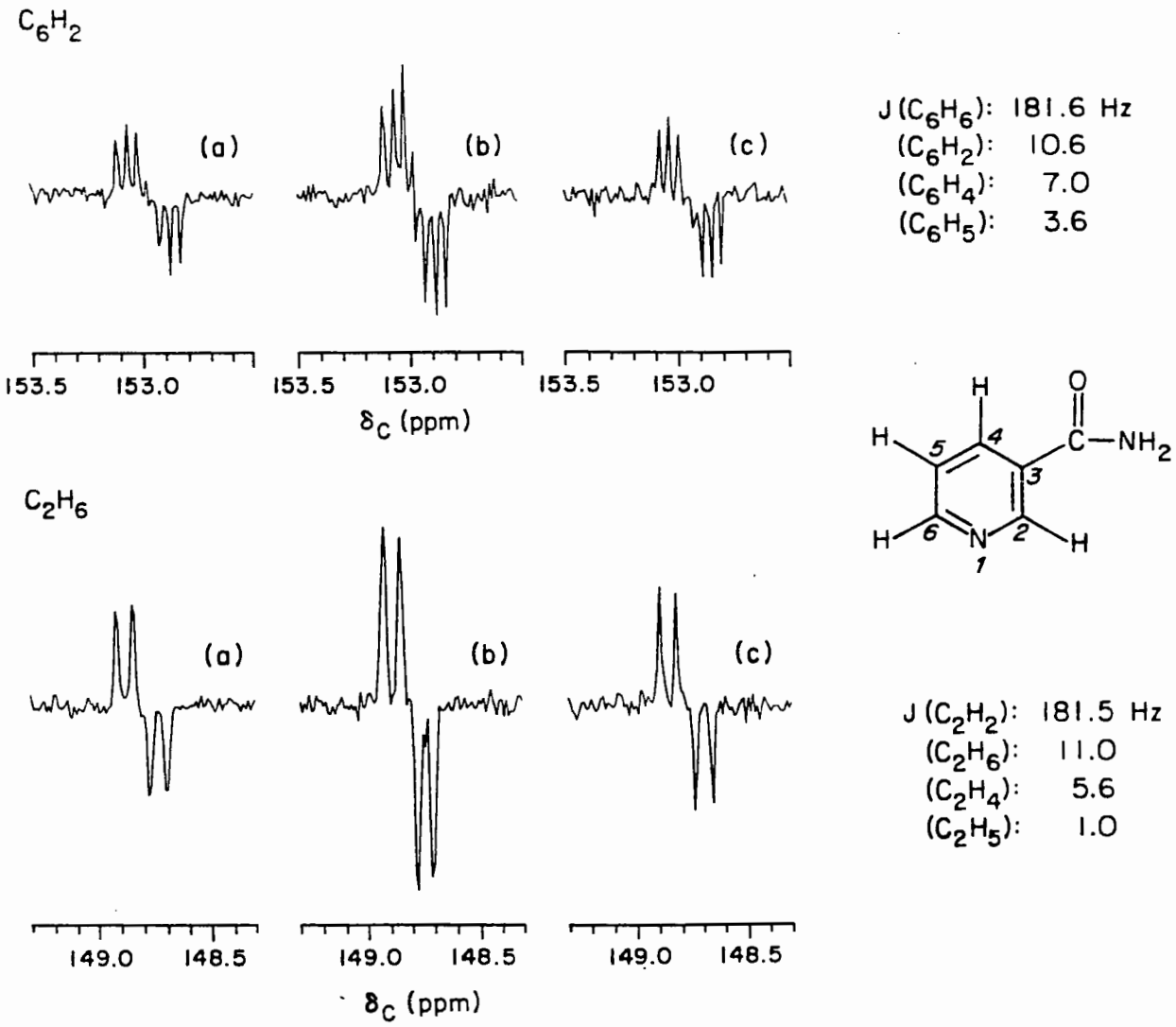

Fig. 2. F_2 (carbon) cross sections of C_2H_6 and C_6H_2 cross peaks from phase-sensitive (a) FUCOUP, (b) PACOUP (Δ_1 = 46.3 ms - optimized for 10.8 Hz) and (c) PACOUP (Δ_1 = 71.4 ms - optimized for 7.0 Hz) spectra of 1M nicotinamide in D_2O.

polarization transfer delay) is better in sensitivity than its FUCOUP counterpart, when used for measuring (or assigning) long-range CH coupling constants.

Sincerely,

V.V.Krishnamurthy
Sr. NMR Applications Chemist.

References:

1. V.V. Krishnamurthy & R. Nunlist, J. Magn. Reson., 80, 280 (1988).
2. A. Bain, J. Magn. Reson., 77, 125 (1988).

Texas A&M University NMR Newsletter - Book Reviews

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

"Introduction to Pulse NMR Spectroscopy"

by

Thomas C. Farrar

Farragut Press, P.O. Box 5102, Madison, WI 53705, U.S.A.;
xvii + 211 pp; 1989; $24.95; ISBN 0-917903-00-5, paperback.

This is the second edition of the book originally published in 1987. The new edition is divided into seven chapters, two appendices, a list of references and an index and is intended as in introduction to pulsed NMR spectroscopy for the beginning graduate student or the chemist who wants to improve their knowledge of modern pulsed NMR spectroscopy. While the book of necessity contains numerous mathematical equations, the reader is not required to derive them and the equations are presented with sufficient clarity of accompanying text such that the novice is not overwhelmed. Wide margins and two separate pages are provided for notes which will make the book especially useful in the classroom or in the laboratories where numerous chemists need to develop an understanding of the basics of pulsed NMR spectroscopy. There is an abundance of figures which enhance the explanations contained in the text. The printing is of good quality, but I would have found reading the text easier if the captions for the tables and figures had been set in a font different than the text. The text is free of serious typographical errors. References to basic papers and specialized texts giving greater coverage to each of the topics are provided througout the text.

Chapter I, *Fundamental Concepts*, (34pp) takes the reader through some of the history of NMR spectroscopy, develops formulae for line shapes, energy levels, transition frequencies and intensities, and introduces the concepts of the rotating frame and Fourier transformation.

In chapter II, *NMR Pulse Experiments*, (28pp) pulse methods are explained with many diagrams of spin vectors and the results of pulses on the various axes. Relaxation is introduced together with methods for measuring T_1, T_2, and $T_{1\rho}$. Table 2.1 does not meet the standards for diagrams established throughout the remainder of the text.

Chapter III, *Instrumentation*, is a very brief (18pp) introduction to the construction of pulsed NMR spectrometers.

Chapter IV, *Relaxation Mechanisms*, (29pp) contains a more extensive discussion of relaxation mechanisms introduced in chapter I.

Chapter V, *Fourier Transform NMR Calculations*, (13pp) expands on the calculation of the Fourier transform introduced in Chapter I and covers the advantages of pulse methods and signal processing. Exponential multiplication, zero filling and phase correction are introduced. There is a brief discussion of maximum entropy and auto-regressive methods as alternatives to Fourier transformation.

Chapter VI, *Sensitivity Enhancement Techniques*, (36pp) discusses the sensitivity problem which has plagued NMR spectroscopy since its inception and various methods developed for improving the sensitivity of the method, including INDOR, nuclear Overhauser enhancement, selective population inversion, INEPT and RINEPT.

Chapter VII, *Two-dimensional NMR Spectroscopy*, (28pp) introduces the concept of 2-dimensional experiments, covering 2-D J-resolved, COSY, HETCOR and NOESY.

Appendix A is a 2 page review of vector analysis and appendix B is a list of useful constants.

The publisher's attempt to keep the cost of the book within the budget of graduate students will be greatly appreciated in an era where $120 books are common and this book will be a welcome addition to those who need an introductory text to pulsed NMR spectroscopy.

Discounts on the list price can be obtained by contacting the publisher directly. A hardbound edition is available for a list price of $39.95

Michael L. Maddox
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6-25.....$9.25 ea.
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DEPARTMENT OF CHEMISTRY

June 7th 89
(received 6/16/89)

NMR OF MOISTURE SORPTION IN EPOXY RESINS

In response to your pink thing, please accept this as fulfillment, and credit to F.G.Herring's account.

Moisture sorption in epoxy resins can reduce their strength by 40% so the phenomena has received a fair amount of attention from NMR groups in the last few years. The current picture is rather confused, partly because of mixed experimental methods and loose terminology, and partly by a possible mis-interpretation of the results. Unfortunately we don't have the space to review all the work, but we would like to give our interpretation.

One can either soak the epoxy resin in water, or stand it in a humid atmosphere. We will restrict ourselves to the latter approach. The former approach confuses the issue with macroscopic phenomena such as bulk water being drawn into cracks by capillary action. In our case we exposed 300mg pellets of Hercules 3506 to 97% humidity for four months, resulting in the uptake of ≈10mg of water (or deuterium oxide, as the case maybe).

Terminology also causes confusion, most workers refer to bound and free water without providing any real definitions. We consider water 'free' if it retains the same no. of degrees of freedom (DF) as in the liquid and 'bound' if one or more of the translational or rotational DF are lost (on the NMR timescale). It is 'solid' if all the translational or rotational DF are lost. (again on the NMR timescale). The NMR timescale will depend on the experiment and must be defined separately.

So what did we find ? The water vapor uptake follows a simple square-root law implying a normal diffusive process into a single site. The proton NMR spectrum of epoxy/water is a single broad line (≈20kHz), no separate water peak is in evidence. Deuterium NMR (done with great difficulty on a Bruker CXP-200) gave the spectrum shown in Fig.1; two peaks of equal width (80Hz) and intensity, separated by 4.2ppm. This may be interpreted a number of ways, each of which is discussed below.

a) It is too large to be a proton-deuterium splitting implying water at two sites. b) Two sites seem unlikely as the sites must be sufficiently different to cause a 4.2ppm shift, but similar enough to be equally populated. Also the proton spectrum shows no such doublet, which would clearly show up as a spike on the 20kHz line. c) The proton (deutrons) maybe in different sites (see Fig. 2a), but this would also show up in the proton spectrum. Furthermore it's unlikely that in such a case the relaxation times of the two peaks would the same. d) The final interpretation (the one we favour) is that the water is attached as shown in Fig. 2b.That is the water is bound at the oxygen, but freely rotates about the oxygen. In this case the proton spectrum would be a broad powder pattern, (albeit with dipolar broadening much reduced) and hence swamped by the epoxy resin protons.On the other hand the deuterium spectrum will be a motionally narrowed spectrum with a

splitting determined by $1/3-\cos^2\theta$. However, in this case θ is $\approx 54°$ so that the splitting will in fact be very small so something like a doublet will be observed. This also means that the motion is highly anisotropic which may explain the multiple relaxation times observed by other workers, which is more appealing than multiple binding sites.

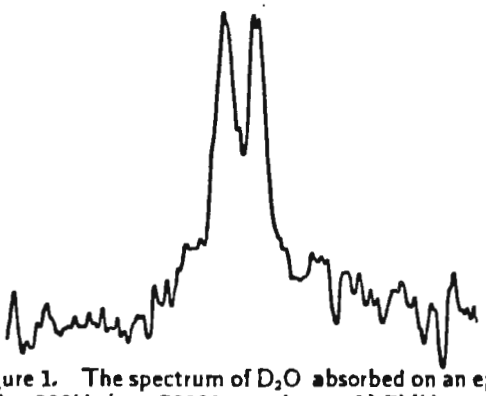

Figure 1. The spectrum of D_2O absorbed on an epoxy resin. 200Hz/cm, 50000 transients., 30.7MHz

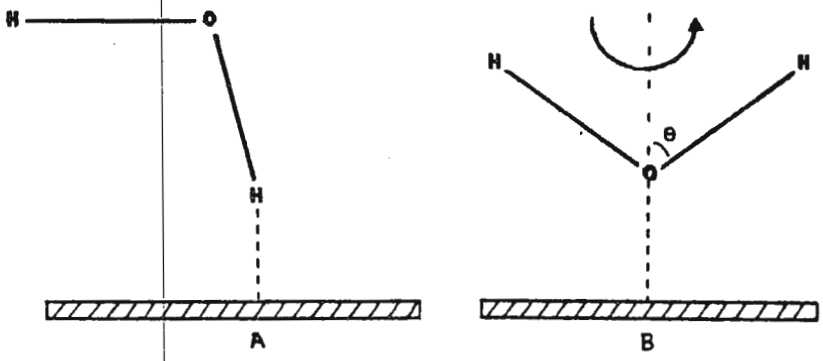

Figure 2. Possible binding confugurations for water to an epoxy substrate.

We don't consider this the definitive interpretation of the results, but it certainly clarified the issues for us.

P.S.Phillips and F.G.Herring

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B.L.S.

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(received 6/15/89)

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

Self-Diffusion of Water in Aqueous Electrolytic Solutions

Dear Dr. Shapiro,

Our recent works on self-diffusion effects lead us to an interesting observation on the effects of electrolytes on the water diffusion. As can be seen from the figure, the self diffusion coefficient of water is strongly affected by electrolytes, both to lower and higher diffusion coefficients. There are at least two reasons for this behavior: Firstly, water molecules may be firmly attached to the dissolved ions (hydration), and hence diffuse together with the ions at a strongly decreased velocity. Since in a self-diffusion measurement according to fast exchange no distinction between "free" and "bond" water molecules can be made, this direct hydration effect tends to make the total self-diffusion coefficient in solution lower than in pure water. Secondly, the water structure is distorted by some ions. Bulk water is known to be a highly structured liquid, with local tetragonal hydrogen bonds to nearly four neighbors, for every water molecule. Ions can either increase or decrease this hydrogen-bonding ratio per water molecule. While increasing occurs only in case of hydration in the primary hydration sphere, structure breaking occurs on all water molecules. This effect tends to make the water diffuse more rapidly in solution than in pure water. The behavior of the water diffusion is very similar to what is found when measuring the water relaxation rates.

Our measurements were performed using the Pulsed-gradient Spin-echo method (PGSE). The gradient pulses were created simply using the homospoil unit of our Varian XL 200 system. Pulse sequence and simple modification of the homospoil unit (changing of two resistors) were adopted from literature. At first we had very severe problems with the stability of our system, that could be solved running the experiments in a "locked" mode (not in the "auto-lock" mode!), after appropriate adjusting the offset in an unlocked mode. Different problems occurred with the temperature controller. Thermostating the probe at 25° caused thermal gradients within the sample which terribly increased the self-diffusion coefficients, even after several hours of waiting. So we are not able to work with any temperature control. In addition self diffusion measurements are very sensitive to any macroscopic motion of the sample! Therefore it

is essential to run the experiments on nonspinning tubes. Furthermore we have even found that it is necessary to wait for some minutes after placing the sample into the magnet before one can start the measurement.

Yours sincerely,

M. Geringer H. Sterk

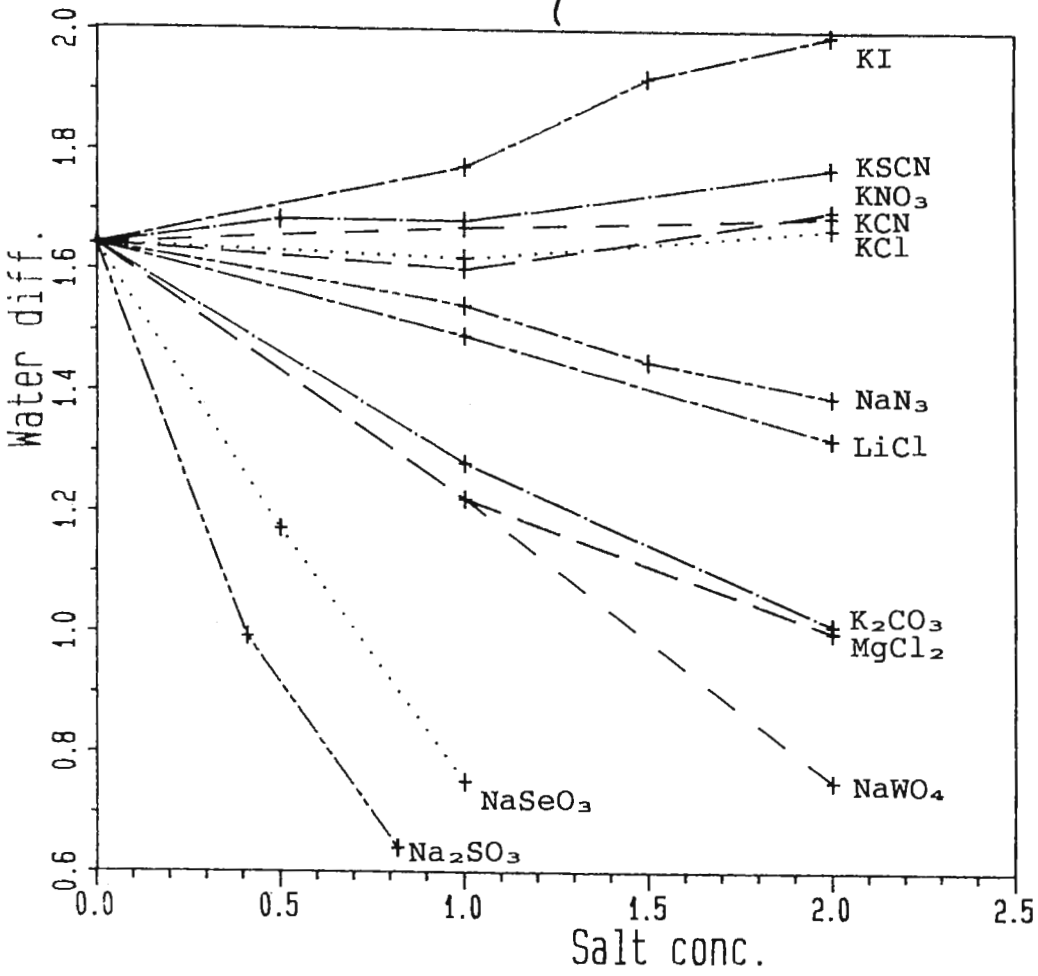

Figure. The variation of the self-diffusion coefficient ($10^{-9}m^2/sec$) of HDO in D_2O as a function of molar salt concentration.

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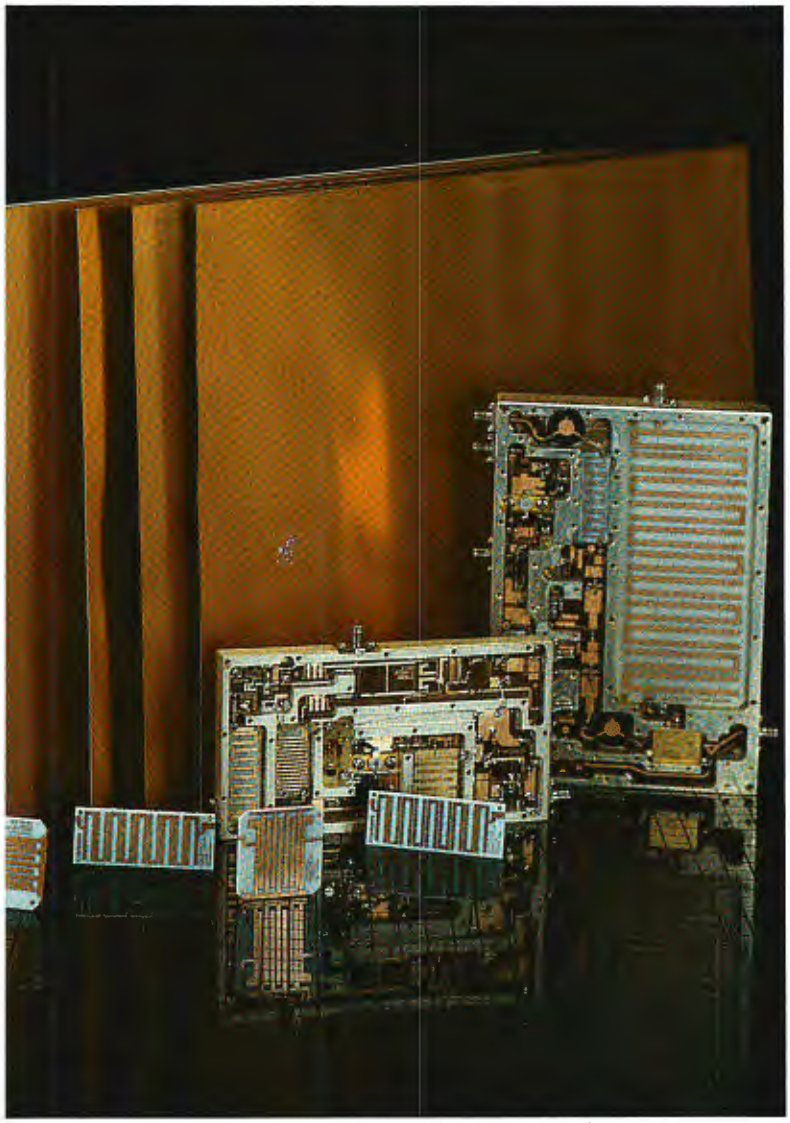

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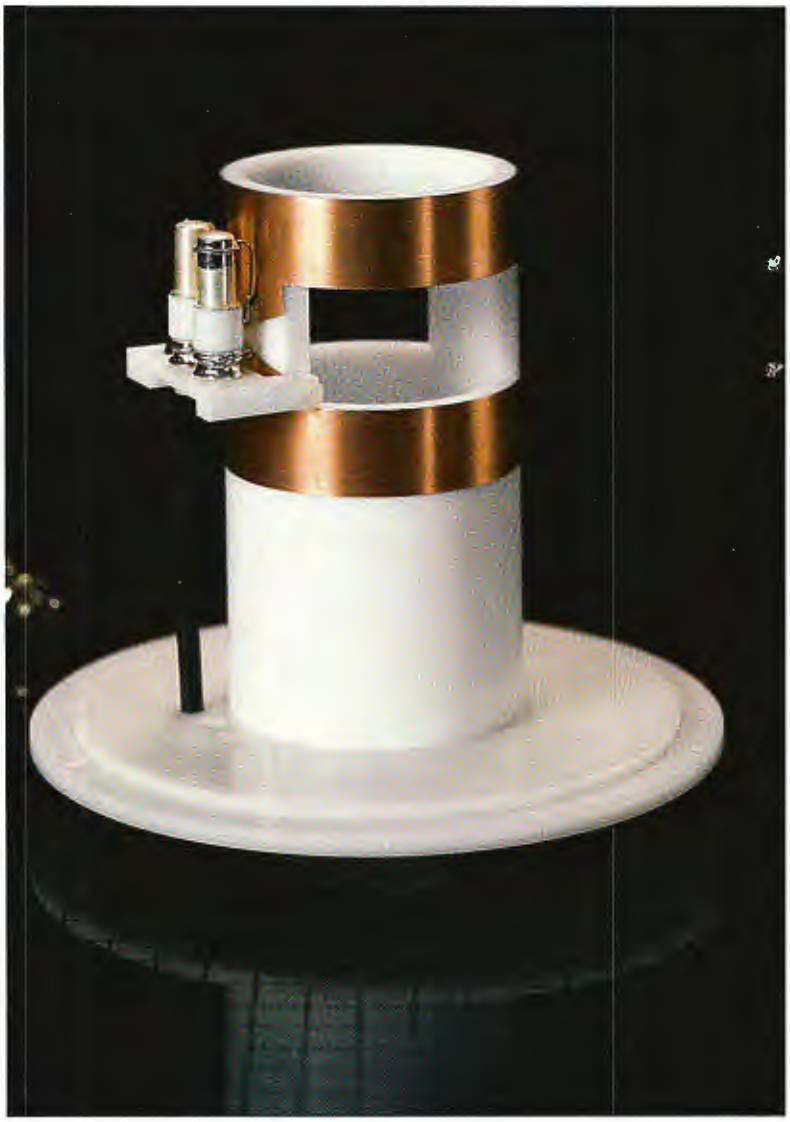

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please credit: Angelika Sebald, Lawrence H. Merwin

Bayreuth, June 8, 1989
(received 6/15/89)

^{119}Sn CP MAS with high-speed magic angle spinning

Some of our work concentrated in the area of heavy metal spin-1/2 nuclei, and in this context we became interested in the characterisation of amorphous tin(IV) oxide gels.

It is quite obvious that such heavy nuclei as ^{119}Sn are promising candidates for structural investigations, simply because of their usually large chemical shift range. It is equally obvious, therefore, that for amorphous materials the chemical shift dispersion will be much larger than for e. g. ^{29}Si in amorphous silica gels. This is where high-speed magic angle spinning could be extremely useful for future applications, especially if it is feasible to achieve satisfying cross polarisation performance at high spinning rates.

Recently, we tried to establish reliable criteria for such experiments using the amorphous tin(IV)oxide gel, $MeSn_{11}O_{21.5} \times H_2O$. From a practical point of view we found the following:

i) it is straightforward to set the ^{119}Sn Hartmann-Hahn matching condition at high spinning rates using the same procedure as for "normal" ^{119}Sn CP MAS experiments[1];

ii) as is well known from ^{13}C CP MAS studies, the Hartmann-Hahn match has to be readjusted for the different (high) spinning rates - doing this in intervals of approx. 2 kHz appeared to be a workable compromise;

iii) as is to be expected, the cross polarisation efficiency does degrade at spinning rates of 8 kHz. However, for heavy nuclei this loss is generally compensated by the reduction in the number of spinning sidebands at the higher speed and the subsequent concentration of intensity in the centre band and remaining sidebands;

---

[1] R. K. Harris and A. Sebald; Magn. Reson. Chem. 25, 1058 (1987)

iv) the use of high magnetic field strengths for such studies is not necessarily a blessing: generally because of the large shielding anisotropies involved, and for amorphous materials also because of the increased chemical shift dispersion. In the ideal world one would therefore like to perform such experiments at reasonably low magnetic field strengths and with high-speed magic angle spinning. However, it should be pointed out that it is not straightforward to build such probes for low frequencies - and so far such low-frequency probes are not commercially available.

In figure 1a the 111.9 MHz ^{119}Sn CP MAS spectrum of $MeSn_{11}O_{21.5} \times H_2O$ (spinning rate 4 kHz, run on a MSL 300) is shown, while figure 1b shows the ^{119}Sn CP MAS spectrum of the same compound at a spinning rate of 8 kHz. Several features are obvious from these two spectra:

i) there are at least 3 resonances around - 600 ppm (typical region for hexa-coordinated tin in tin(IV)oxides), a forth one at slightly higher shielding becomes visible at even higher spinning rates (not shown);

ii) the resonance of the organotin moiety can be assigned from the comparison of the two spectra (-387 ppm), which is almost impossible from "slow" spinning spectra alone, due to badly overlapping spinning sidebands;

iii) the relative intensity of the organotin-resonance in the high-speed spinning spectrum is much lower than in the conventional ^{119}Sn CP MAS spectrum (1.25 ms contact time is there the optimum contact for this resonance). Obviously, when going to high MAS rates not only the Hartmann-Hahn match, but also the contact times need to be re-adjusted.

Work in this field is being continued, and a more detailed study of various tin(IV)oxide gels will be published. We would like to thank P. Harrison, University of Nottingham, U. K., for his generous loan of samples, and H. Foerster, Bruker Analytische Messtechnik, Karlsruhe, for letting us use the MSL 400 at their facilities.

Sincerely,

Angelika Sebald

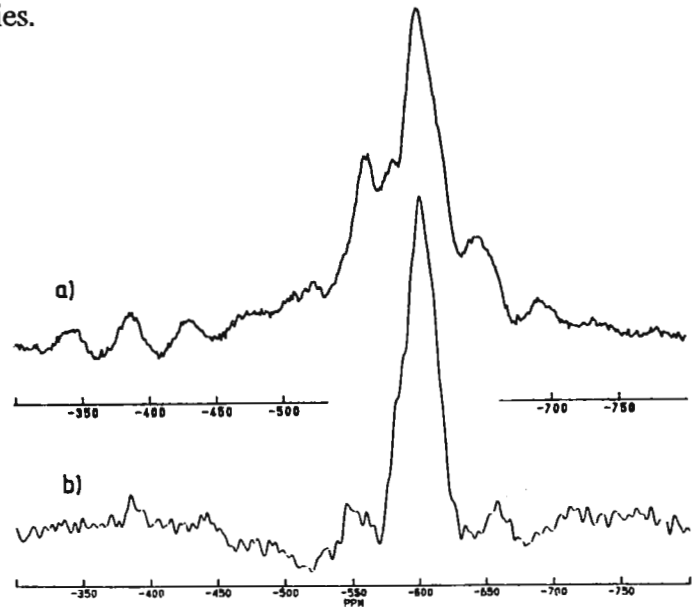

Figure 1 a) 111.9 MHz ^{119}Sn CP MAS spectrum of $MeSn_{11}O_{21.5} \times H_2O$. 1.25 ms contact time, recycle delay 10s, spinning rate 4 kHz, 6700 transients
b) 149.2 MHz ^{119}Sn CP MAS spectrum - same conditions, but spinning rate 8 kHz, 800 transients.

CSI 2T Applications

Shielded Gradients and NMR Microscopy

In spin warp imaging, there is a trade-off between minimum TE and maximum resolution. Even if rise and fall times were zero and phase encoding occured during the entire echo delay, a ±2 Gauss/cm gradient range and a TE of 2 msec would provide best case resolution of 0.32 mm. This translates to a 7 cm field of view in a 256 × 256 matrix. To improve resolution by a factor of 10, TE may be increased by a factor of 10 (which is not acceptable in a sample with short T2 values) or gradient strength may be increased by a factor of 10. The long echo times required for T2 weighted images create an undesired loss of signal in many non-T2 weighted image experiments. These effects, however, are tolerable at 2 Gauss/cm for resolution at the 100-200 micron level.

Clearly, added signal that would be available with a shorter TE would be useful. The current practical limits of high signal-to-noise NMR micro imaging are greatly reduced by high strength shielded gradients. A 50 micron resolution image of an Agapanthus bud is shown in Figure 1. Unlike very high field (>7 Tesla) micro NMR imaging, magnetic susceptibility effects at 2T do not compromise the 50 micron digital resolution obtained during these gradient strengths.

In a second example, (Figs. 2 and 3), 25 micron resolution is achieved in a small phantom by using a moderate access (5 cm) rf coil. The phantom consists of seven small capillary pipets in a 5 mm NMR tube. Data was collected as a 32 × 256 × 256 DEFT data set.

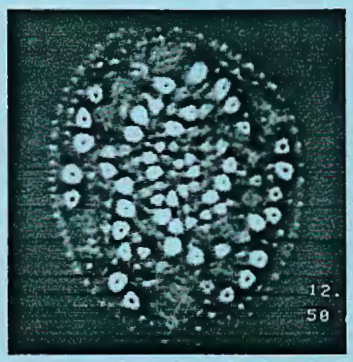

Fig. 1—Agapanthus bud
Matrix 256 × 256, TR 200
Slice 2 mm, TE 30
FOV 12.8 mm, NEX 4,
45° Tip Angle DEFT
Sequence

Fig. 2—16 contiguous 1 mm slices
FOV 6.4 mm, NEX 4.
TR 150 msec, Field Strength 2T, TE 14 msec

Fig. 3—Expanded view of four of the 16 slices shown in Fig. 2.

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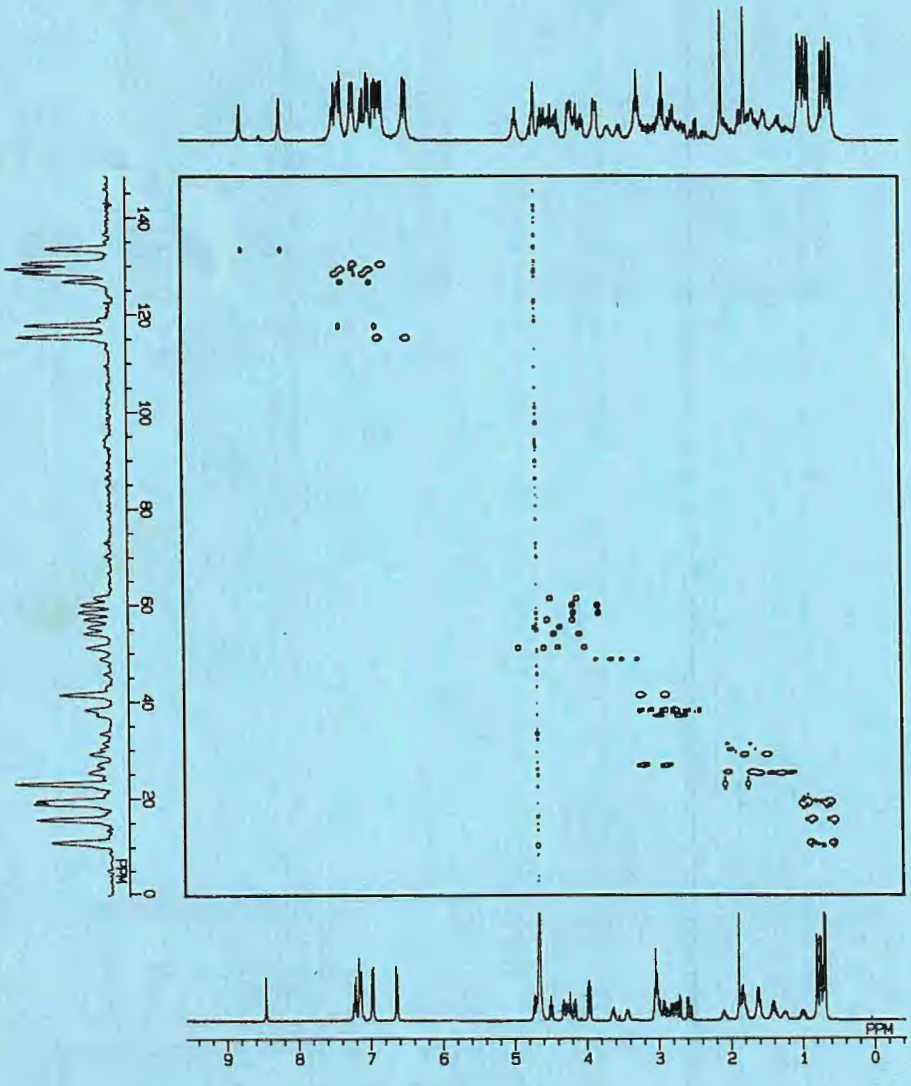

*Sample courtesy of Dr. Jeffrey Hoch (Rowland Institute For Science, Inc.)

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