TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 372

September 1989

Continued on page 74

TABLE 1 DEUTERATED SOLVENTS

Need Deuterated Solvents?
WILMAD HAS YOUR SOLUTION!

Cat. No.	Description	Formula	Min. Iso. [illegible]	Density [illegible]	MP [illegible]	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.551 (32)
D-120	[illegible]	[illegible]	[illegible]				
D-13	Acetone-d_6	CD_3COCD_3	[illegible]	[illegible]	[illegible]	[illegible]	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129	[illegible]	[illegible]	[illegible]				
D-14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]43 (20)
D-21	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]0.611
D-122	[illegible]	[illegible]	[illegible]				
D-130	[illegible]	[illegible]	[illegible]				
D-28	Cholorotorm-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

Cost-conscious quality NMR solvents offered by Wilmad, such as $CDCl_3$, are frequently priced lower than more traditional sources. Included in this offering are the most common solvents, like Acetone-d_6, Benzene-d_6, D_2O, and DMSO-d_6, as well as some of the most unusual solvents for specialty applications, like 1,1,2,2-Tetrachloroethane-d_2, Octane-d_8, and Trifluroacetic Acid-d.

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

We provide the largest variety of paper and pens for NMR recorders or plotters available anywhere. Included in these listing are the newest spectrometers from Varian, Bruker, (and IBM), General Electric and JEOL, as well as the latest models, such as the Hewlett Packard 7475A, 7550A, and Thinkjet 2225A, Zeta 8 or 8A, and Western Graphtec 4730 plotters and printers.

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FORTHCOMING NMR MEETINGS

Third Missouri Magnetic Resonance Symposium, **October 24, 1989**, Columbia, Missouri; See Newsletter 371, 37.

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.

Chemical Frontiers in Magnetic Resonance of Living Systems, Workshop in the Pacific Basin Congress/American Chemical Society, **December 17-22, 1989**, Honolulu, Hawaii; See Newsletter 372, 52.

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.

Workshop on In Vivo Magnetic Resonance Spectroscopy III, **March 29 - April 1, 1990**, San Francisco, California; San Francisco, California; Contact: Dr. M. W. Weiner or Dr. G. B. Matson, Magnetic Resonance Unit, Veterans Administration Medical Center, 4150 Clement Street (11D), San Francisco, CA 94121; (415) 750-2146.

31st ENC (Experimental NMR Conference), **April 1-5, 1990**; Asilomar Conference Center, Pacific Grove, California; Contact: ENC, 750 Audubon, East Lansing, MI 48823; (517) 332-3667; Attendance: 1,200.

Frontiers of Polymer Characterization by NMR Spectroscopy, Symposium at the American Chemical Society National Meeting, **April 22-27, 1990**, Boston, Mass.; See Newsletter 372, 54.

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. 374 (November)---- 20 October 1989
No. 375 (December)--17 November 1989
No. 376 (January) -----15 December 1989
No. 377 (February) ------ 19 January 1990

CLARK UNIVERSITY
950 Main Street Worcester Massachusetts 01610-1477

Department of Chemistry
Telephone (508) 793-7116

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

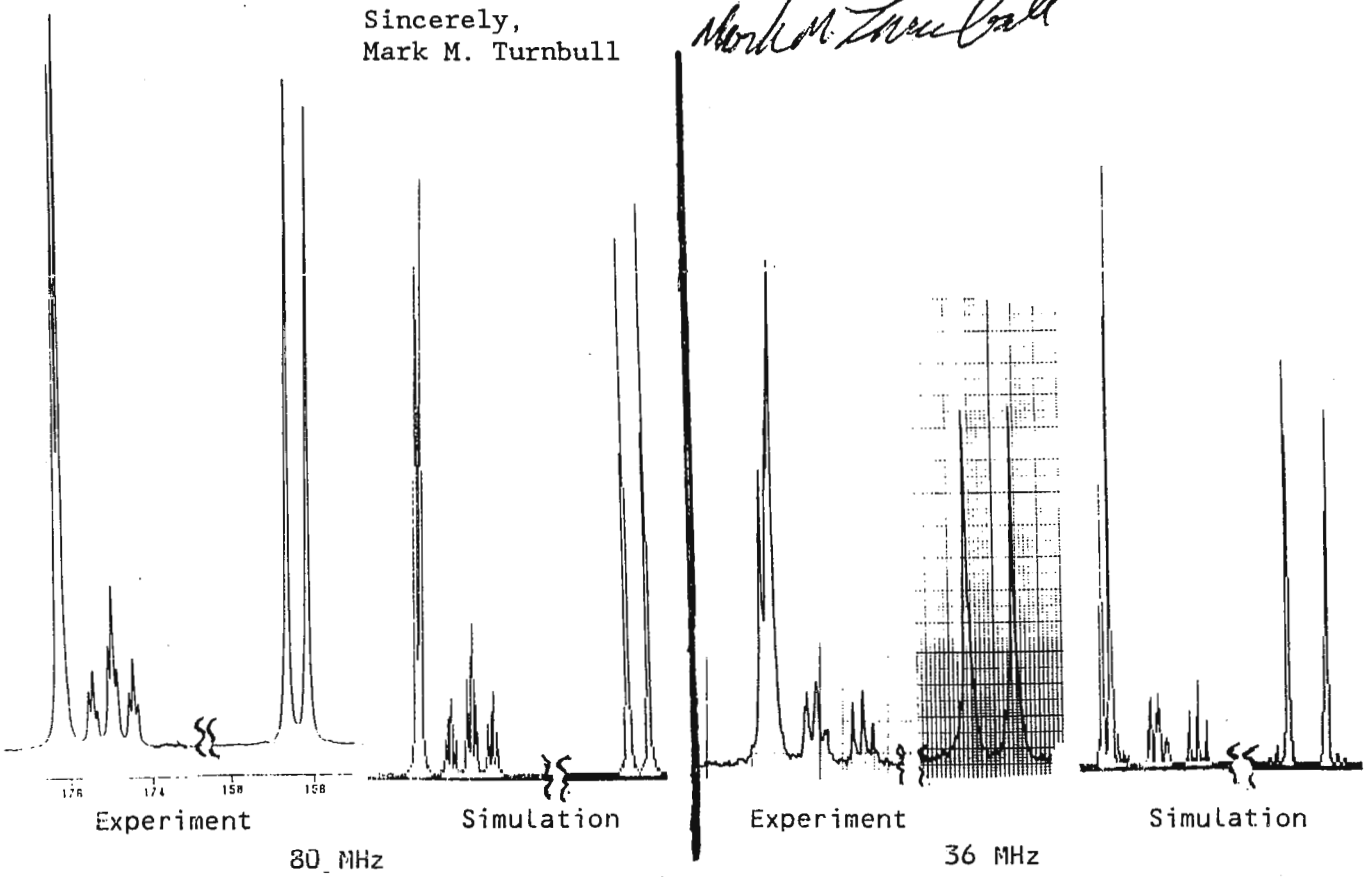
(received 8/18/89)

Classic Second-Order Effects In ^{31}P-NMR Spectroscopy

Dear Barry:

We recently encountered a classic example of second order effects in 31P-NMR spectroscopy. We prepared a $P_5O_5Cr_2$ cage molecule which exhibited the expected A_2MX_2 ^{31}P-NMR spectrum, based on its structure (Bruker AC-200 spectrometer, 80.02 MHz). We were able to simulate the spectrum quite adaquately using a standard proton simulation program (Serena Software). When subsequently speaking with colleagues at the University of New Hampshire, they described the results of a similar synthesis and its confusing ^{31}P-NMR spectrum (JEOL FX-90Q, 36.46 MHz), an apparent A_2MX system; inconsistent with the crystal structure which showed 5 P-stoms. On a whim we attempted to simulate this spectrum using their lower field strength and our chemical shifts and coupling constants; the compounds were the same. The spectra and simulations are shown.
Please credit this contribution to Paul Inglefield's account.

Sincerely,
Mark M. Turnbull



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			10 g	16.
			(50 x 1 g)	75.
			(5 x 10 g)	75.
			(100 x 1 g)	145.
			(10 x 10 g)	145.
82-00731	Acetone-d_6 + 0.05% TMS (v/v)	99.9	25 g	37.
			(5 x 25 g)	180.
			(10 x 25 g)	345.
82-00733	Acetone-d_6 "100%"	99.96	(10 x 0.75 mL)	55.
82-05012	Acetonitrile-d_3	99.8	(10 x 1 g)	25.
			10 g	25.
			(50 x 1 g)	115.
			(5 x 10 g)	115.
82-05014	Acetonitrile-d_3 + 0.05% TMS (v/v)	99.8	10 g	25.
			(5 x 10 g)	115.
			25 g	60.
82-84077	Benzene-d_6	99.6	(10 x 1 g)	20.
			10 g	20.
			(50 x 1 g)	80.
			(5 x 10 g)	80.
			(100 x 1 g)	150.
			(10 x 10 g)	150.
82-04097	Benzene-d_6 + 0.05% TMS (v/v)	99.6	25 g	45.
			(5 x 25 g)	185.
			100 g	145.
82-84078	Benzene-d_6 "100%"	99.96	(10 x 0.75 mL)	65.
82-80554	Bromobenzene-d_5	99.5	10 g	50.
			(5 x 10 g)	210.
82-80555	Bromoform-d	99.5	10 g	30.
			(5 x 10 g)	125.

Please request prices for quantites larger than are listed.
Please allow us to bid on your annual NMR solvent requirements.

82-80556	Chloroform-d	99.8	(50 x 1 mL)	50.
			100 g	20.
			(5 x 100 g)	85.
			(10 x 100 g)	165.
			1 kg	155.
82-00540	Chloroform-d + 0.05% TMS (v/v)	99.8	100 g	20.
			(5 x 100 g)	85.
			(10 x 100 g)	165.
82-70001	Deuterium Oxide	99.9	100 g	45.
			(5 x 100 g)	210.
			(10 x 100 g)	400.
			1 kg	385.
82-70901	Deuterium Oxide	99.8	**min.** 10 kg	3500.
			25 kg	8500.
82-70002	Deuterium Oxide "100%"	99.96	10 g	15.
			(5 x 10 g)	50.
			1 kg	550.
82-70003	Deuterium Oxide EXTRA	99.996	(10 x 0.75 mL)	50.
			10 g	45.
84-70001	Deuterium-depleted Water	$<5 \times 10^{-5}$	25 g	25.
			(4 x 25 g)	85.
			(10 x 25 g)	200.
			(20 x 25 g)	300.
			1 kg	500.
82-00807	Dimethyl-d_6 Sulfoxide	99.9	(10 x 1 g)	14.
			10 g	14.
			(50 x 1 g)	65.
			(5 x 10 g)	65.
			(100 x 1 g)	125.
			(10 x 10 g)	125.
82-00809	Dimethyl-d_6 Sulfoxide (multi-dose septum vials)	99.9	10 g	14.
			(5 x 10 g)	65.
			(10 x 10 g)	125.
82-00813	Dimethyl-d_6 Sulfoxide + 0.05% TMS (v/v)	99.9	25 g	33.
			(5 x 25 g)	155.
			100 g	115.
82-00061	Methanol-d_4 (~0.7 atom % ^{13}C)	99.8	(10 x 1 g)	45.
			10 g	45.
			(50 x 1 g)	180.
			(5 x 10 g)	180.
			(100 x 1 g)	345.
			(10 x 10 g)	345.
82-00059	Methanol-d_4 + 0.05% TMS (v/v) (~0.7 atom % ^{13}C)	99.8	10 g	45.
			(5 x 10 g)	180.
			(10 x 10 g)	345.
			25 g	110.
82-86007	Nitrobenzene-d_5	99.5	10 g	35.
			(5 x 10 g)	150.
82-84081	Toluene-d_8	99.6	(10 x 1 g)	45.
			10 g	45.
			(50 x 1 g)	180.
			(5 x 10 g)	180.
82-02510	Trifluoroacetic Acid-d	99.5	10 g	19.
			(5 x 10 g)	80.
			(10 x 10 g)	115.
			25 g	40.

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Dr. B.L. Shapiro
966 Elsinore Court
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U.S.A.

Your reference and date	Our reference	Office telephone	Date
	JAP/mk/453	(015) 78 5892	07-08-1989 (received 8/14/89)

Subject
Comparison of solid with liquid state NMR spectra

Sub-division
Department of Organic Chemistry

Dear Dr. Shapiro,

It is often tempting to compare solid and liquid state NMR spectra for the assignment of either of these. Recently, we came across a case, where this approach gave rise to some confusion.
5-Ketogluconic acid occurs as an equilibrium of three forms in aqueous solution (Fig. 1).
It has been shown by X-ray crystallography that the calcium salt of 5-ketogluconic acid in the solid state is the β-furanose form. Comparison of its CP-MAS ^{13}C NMR spectrum with the sodium salt liquid state spectrum shows (Fig. 2A, 2B, respectively) that the anomeric carbon of the solid has about the same chemical shift as the minor furanose form in solution. A 1:1 mixture of the sodium and the calcium salt of 5-ketogluconic acid gave a similar spectrum, but then, in addition, a small peak at δ = 104 ppm was observed. It should be noted that the concerning sample was melted in its crystal water during the measurement, probably due to the high pressure as a result of the high spinning rate.
The minor furanose form in solution, however, is not the β-anomer as is shown unambiguously by the NOESY spectrum (Fig. 3). That spectrum shows a cross peak between the protons (6) and (4) of the major compound but no cross peak could be observed between those protons in the minor component. Therefore, it can be concluded that the major compound is the β-furanose form. Great care should be taken when solid and liquid state NMR spectra are compared.

Yours sincerely,

JPeters

Joop A. Peters

MCaldeira

M. Madalena Caldeira

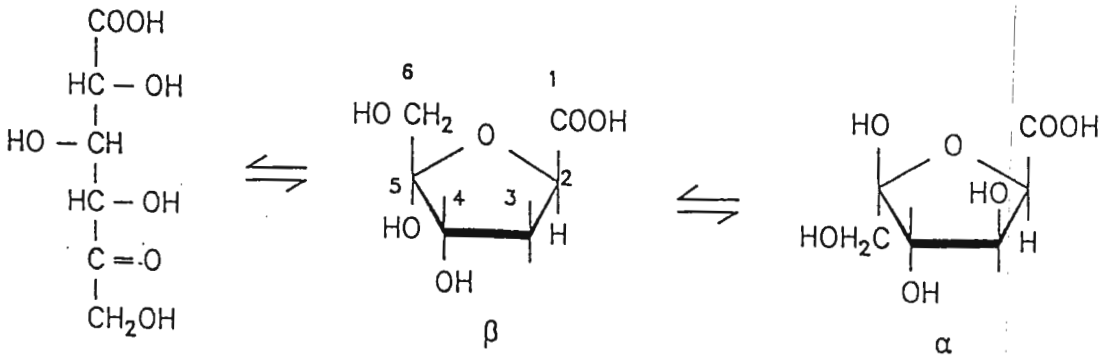

Fig. 1

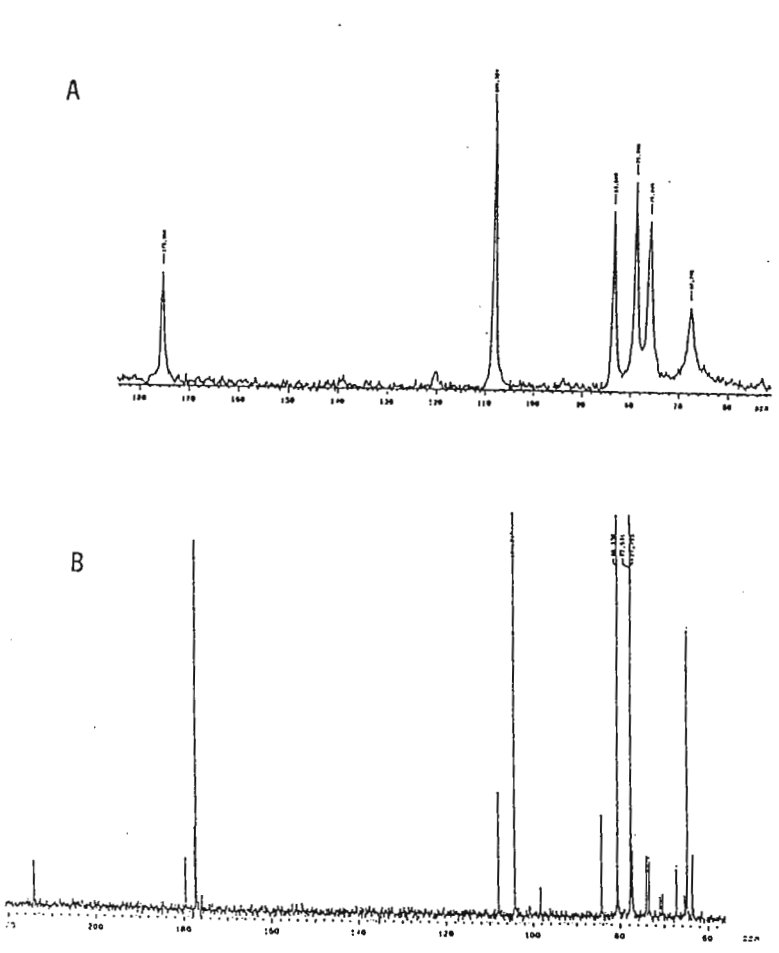

Fig. 2

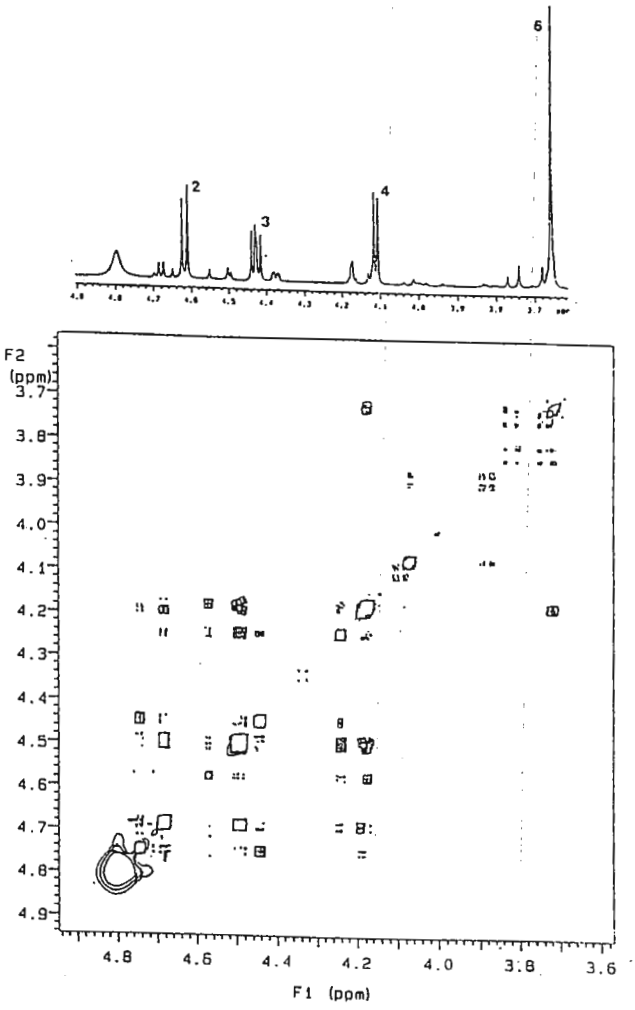

Fig. 3

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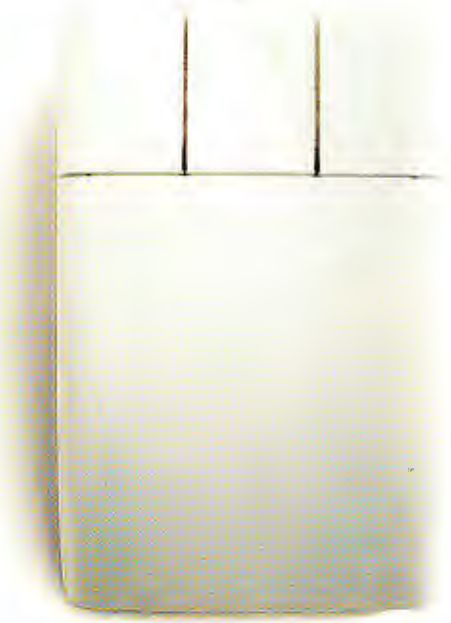

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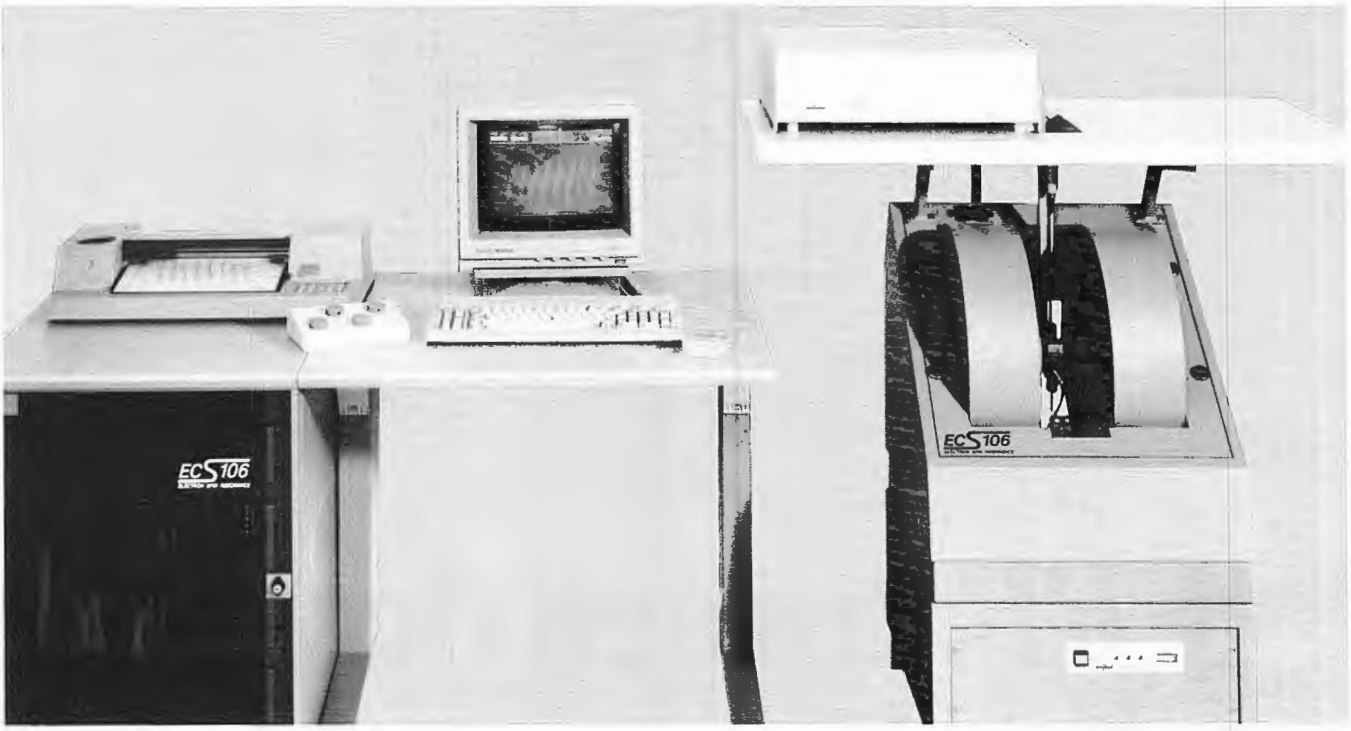

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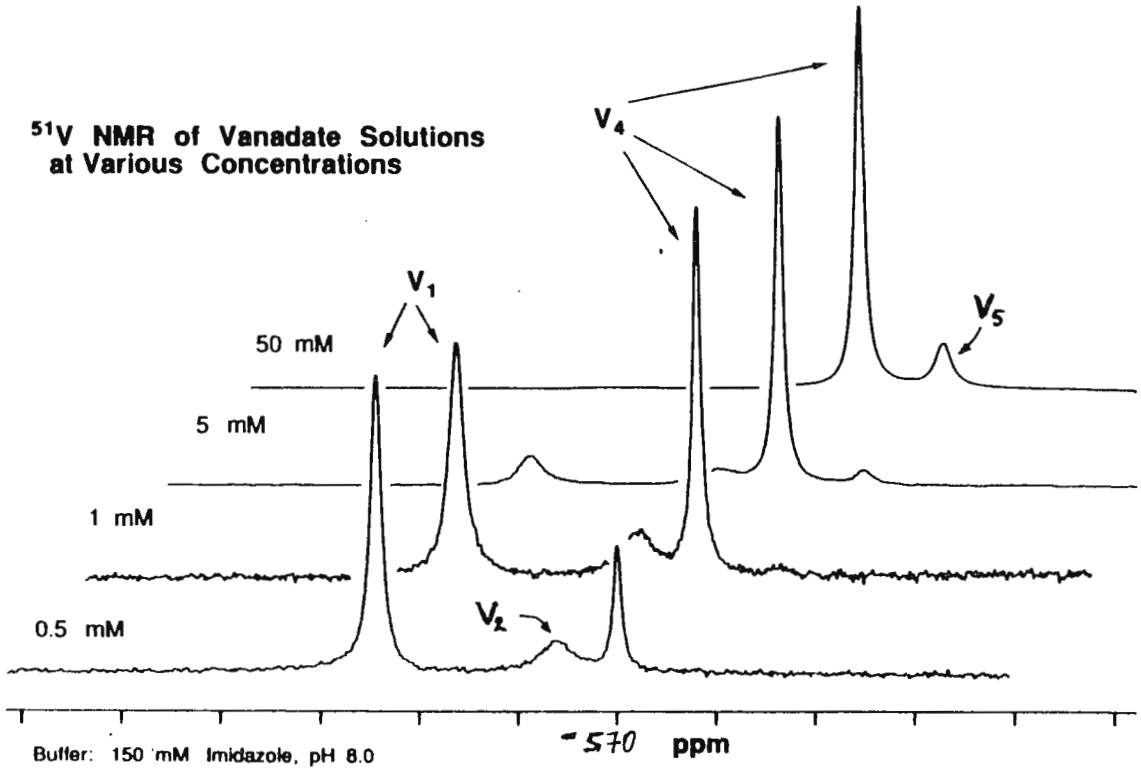
August 8, 1989
(received 8/17/89)

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

Dear Dr. Shapiro:

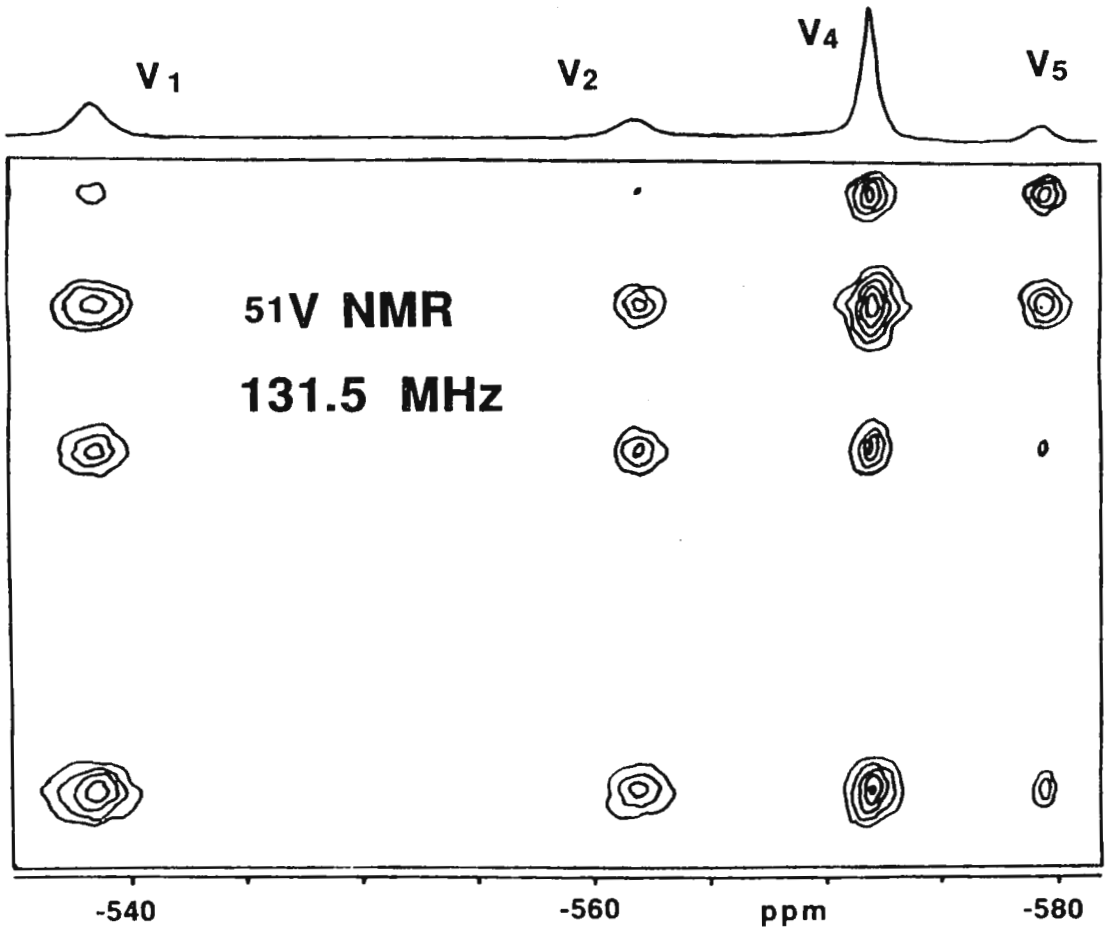
Please accept this contribution to initiate our subscription to the TAMU newsletter. We are studying the exchange of the vanadium(V) oxyanions in aqueous solution both alone and in the presence of a variety of organic ligands by using NMR spectroscopy. There are a variety of NMR active nuclei available in our systems to chose from including ^{51}V, ^{17}O, ^{13}C, ^{1}H, and ^{15}N. Vanadium-51 proves to be an especially valuable nucleus for these studies. For example, the 52 MHz vanadium-51 NMR of vanadate in aqueous solution shows the presence of four or more different vanadate species; the number actually observed is dependent on pH, ionic strength, etc.. (Figure 1). The currently accepted assignments (relating to the number of vanadium atoms) for each signal in the spectra are indicated below.



Previous studies have suggested that the oxyanion species undergo intermolecular exchange reactions.(1) There are hints of exchange broadened signals in the NMR spectra above, e.g., the signal labeled "dimer" in the 0.5mM spectrum in Figure 1. This is further evidenced by examining the T_1 relaxation times for the oxyanions at 131.5 MHz (11.7 Tesla). We find T_1 times of about 12 ms for the various species which, assuming $T_1 = T_2$ for the ^{51}V quadrupole, provides a predicted linewidth of 23 Hz or so. This is much narrower than any of the measured linewidths, e.g., 170 Hz for "dimer". Thus, we have undertaken to study the exchange dynamics of vanadate in aqueous solution.

There are, of course, a variety of NMR methods to be used for this task including variable temperature dynamic NMR (DNMR), selective magnetization transfer, and two-dimensional magnetization transfer (exchange) spectroscopy (EXSY).(2) We have chosen to use the EXSY method first since it can provide a rather complete dynamical picture in a straightforward way when numerical methods are available to treat the resulting exchange

matrix.(3) A portion of our effort has been spent refining the EXSY experiment for our purposes and developing appropriate tools for processing the data. A 2D ^{51}V contour plot of data from one EXSY experiment (mixing time 10 ms) is shown in Figure 2.



The exchange dynamics are quite complex as evidenced by the cross peak intensities. We are systematically doing rate studies of the vanadate exchange processes in aqueous solution and will report on our findings at a later date.

Sincerely yours,

CHRIS

Christopher D. Rithner
Director, Central Instrument Facility
Chemistry Department
Colorado State University
Fort Collins, CO 80523

Debbie C. Crans
Assistant Professor
Chemistry Department
Colorado State University
Fort Collins, CO 80523

(1) Heath, E.; Howarth, O.W. *J. Chem. Soc. Dalton* **1981**, 1105-10, b) Howarth, O. Chapter 5 in "Multinuclear NMR" Mason J. (Ed.), Plenum; New York, 1988, c) Whittaker, M.P.; Asay, J.; Eyring, E.M. *J. Phys. Chem.* **1966**, *70*, 1005-8.

(2) Macura, S.; Ernst, R.R., *Mol. Phys.*, 1980, **41**, 95-117.

(3) Abel, E.W.; Coston, T.P.J.; Orrell, K.; Sik, V.; Stephenson, D. *J. Magn. Reson.*, 1986, **70**, 34-53.

(received 7/27/89)

SPEED AND LIMITATIONS OF AN IBM-AT CLONE DATA STATION

Biochemistry Department, Brandeis University, Waltham MA 02254 USA

Dear Barry,

This is hopefully the last in a series of letters on the IBM AT clone computers (and their predecessors dating back 17 years) that serve as the instrument controller and data station for our home made 500 MHz. The instrument controller AT is a routine EGA version with only an added 80287 and a 3 port 8 bit parallel I/O card. Someday when I get rich I may add some of the features that the data staion (below) has, such as an ethernet port and a coprocessor card (each costing about $1000), but for the time being it serves us pretty well. The timing/control system and A/D are external to the computer, as they should be, as is a 16 bit data buffer which could be replaced by the coprocessor card. I cannot understand why people put more than the simplest computers on NMR machines; better to concentrate on a good data station and on ways to set up 2D runs with one-D spectra that easily allow the operator to preset the phase parameters to be used later for 2D FT. This is easy except for homo-COSY type 2D.

The data station is in another building, and accepts floppy discs from the NMR computer, requiring 1 1/2 to 2 floppies for a 1k*1k*32 bit data set (one million 32 bit words) after compression to reduce 32 bit words to 8 or 16 bit words when possible. The data station can then be used to transmit this immediately via ethernet to our Vax systems for processing, or data can be processed locally and plotted on a Houston 11*17 inch plotter ($1000) buffered by a 1000kB Ditron card ($700). The performance is very much enhanced by a Symmetric Research coprocessor card (not to be confused with the usual 80287 coprocessor which is also used). It contains a TI tms320c25 processor that performs 10 16 bit instructions per microsec, 256 KB of on-board bank-switchable memory, and excellent parallel I/O capability which we do not yet use. Useful, but less crucial, is a 800 by 600 super EGA display (based on a Genoa card and Nanao monitor. This monitor has excellent resolution but the color seems poor. A 16 bit VGA 800 by 600 is probably a better choice). We do not use extended memory because, where it would really make a difference (2d runs 1k*1k or larger), it would add significantly to the cost and a better computer should be considered instead. Control is via a panel, and the cursors are controlled by a joystick. A version of the program that uses the keyboard only can also be compiled, for use by people away from Brandeis with EGA and a coprocessor.

I am not sure why anyone would be interested in an AT computer for NMR if they did not already have one, but note that there are several other versions of AT programs out there. The problem is, as usual, getting data to or from such a system. Kermit is too slow for 2D, but ethernet is practical if available. We now have a floppy drive that supposedly could read quad density floppies, but as expected it can't decipher the ones emited by our XL300; if anyone knows how to convert XL300 data to AT-readable format, other than by slow serial transmission, please let me know. It would probably be feasible to locate a low cost AT computer in our NMR room to accept parallel data from the XL300 via a homemade interface, but I do not expect to be able to do the required work.

My program is available unsupported with eratic documentation to anyone who is seriously interested. The 2D display now can generate a raster map in several colors, with horizontal and vertical slices at the cursor lines. Such a display is most useful for finding peaks with low S/N.

Other features of such a program are too numerous to describe here, and I will conclude by just listing the speed of the important parts (let me know if you can do better for the same amount of money!). A one-D 8k real output point FT with two-fold zerofilling (from a 1K by 32 bit array of 512 complex points), preweighting by an arbitrary real function, and post-multiplication by an arbitrary complex function, takes 8 sec. on a 10 MHz 80286/80287 computer. It takes 2.5 sec on a 20 MHz '386/387 machine, and 1 sec on the 10 MHz data station with the coprocessor board. This is a 32 bit integer calculation, and I find that some individuals think that such a calculation is inferior to a 32 bit floating point FT. Briefly, the noise level is predictable and the only real issue is how to handle overflow of data without truncating data at the low end. We avoid this by right-shifting all the data 3 bits, after the first eight butterfly groups, which throws away only accumulated roundoff error, and by right-shifting the input data up to three bits on long runs, to throw out accumulated digitization error. We still do lots of 1D NOE runs in water, which is where overflow would most likely occur, and see none.

A 2D FT 1k*1k*32bit takes about 7 minutes, starting from a compressed file on the hard disc (40 ms 1:1 MFM) and ending with a compressed output file on this disc. This includes massaging,

zerofilling, and phasing in both dimmensions, and is hypercomplex. About half this time is calculation, and the rest is disc swapping. A 2k*1K FT takes about 18 minutes but the only 2K*2K FT we have done took about 90 minutes because the operating system (DOS 3.2) slowed the disc way down. Except for the latter, this performance seems satisfactory; truncated FT's can be performed for fast phasing but this is seldom needed (see the first paragraph). A faster disc, extended memory, a '387 computer, or more concurrency in the program would all increse speed but not dramatically for each, and by less than a factor of two in toto. Without the coprocessor board these times would be about 4 times larger.

More important is the display speed. The coprocessor is used to format one line of data for gain correction, clipping, and color-coding of one line of data, concurrent with the display of the previously formatted line by the 10 MHz 80287. It takes about 5 sec to draw 160,000 points on the screen either in a simple stack plot or a fully filled color raster display, starting from 16 bit integer data in RAM. About the same time is required to read this much data into the RAM from the hard disc. These times would decrease at least two-fold in a '386 computer with the same coprocessor board and a better disc. Without the coprocessor board, display is 5 to 10 times slower.

Thus, a relatively ordinary AT system costing around $2700 gives acceptable performance for home or student use, and with an extra $4500 investment for a plotter-buffer, coprocessor board, and high-resolution EGA/VGA, and ehernet card we have a reasonably fast workstation for our lab. Better performance is certainly possible, but would cost so much that you might as well consider a low cost Sun or Vax workstation.

The main limitation of the AT computer for 2D is that it will hold only about 200,000 16 bit words in its lower 640K of memory which is too small a fraction of a 2k*2k data set. You want to have the data in RAM so that you can get slices of the displayed map instantly. Extended memory might alleviate this limitation but might be slow on an AT. This limitation could also be removed by compressing the 2D data set with all points removed below some threshold, as already demonstrated by Zolnai et al (JMR vol. 80, P. 60, 1988). The same compression could then be used in a simple scheme for performing the 3rd dimension in 3D FT in minutes, having performed the first two dimensions as the data is collected. It remains to be seen whether this is worth the effort for us.

Alfred Redfield *al R.* 7/20/89

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Example 1

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     (sub 90° phase shifts optional)
   - MLEV and Waltz Modulation.
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   - Low cost / high performance.
2. *Upgrade <u>any</u> existing probe* to a $^{1}H\{^{31}P\text{-}^{15}N\}$ probe, or buy a new $^{1}H\{^{31}P\text{-}^{15}N\}$ probe.

Reverse Polarization Transfer Probe $^{1}H\ \{^{31}P\text{-}^{15}N\}$ 5mm Probe

	5mm	10mm
90° Pulse @ 50 Watts	15us	25us
Resolution (ODCB)	0.25	0.4
Lineshape ($CDCl_3$)	10/25	18/40
Gamma H2 (10W)		
^{15}N	2KHz	1KHz
^{13}C	3KHz	2KHz
Sensitivity (0.1%EB)		
200 MHz	60	100
300 MHz	120	200
360 MHz	170	280
400 MHz	200	330
500 MHz	300	500

Example 2

Upgrade an existing unused 20mm probe (or any other probe) to a 10mm Broadband (or any other size). Or to a 5mm ^{1}H Probe. Or rework an existing probe for improved sensitivity. Each possibility could be done for less than half the cost of a new probe:

5mm ^{1}H Probe

90° Pulse	10 us @ 50 Watts
Resolution	0.2 Hz (ODCB)
Lineshape	10/20 ($CDCl_3$)
Sensitivity (0.1% EB)	
200 MHz	80:1
300 MHz	160:1
360 MHz	220:1
400 MHz	300:1
500 MHz	400:1

Broadband Probes

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5mm		200	300	360	400	500
^{31}P		30	60	85	100	150
^{13}C		30	60	85	100	150
^{2}H	NA=4	5	10	14	16	25
^{17}O	NA=100	20	40	55	65	80
^{15}N		4	8	10	12	16
10mm						
^{31}P		130	260	340	375	450
^{13}C		150	300	360	400	500
^{2}H	NA=4	15	30	40	50	60
^{17}O	NA=100	110	220	270	300	400
^{15}N		15	30	35	40	50
12mm						
^{31}P		150	300	400	500	550
^{13}C		180	360	500	600	700
^{2}H	NA=4	20	40	50	60	75
^{17}O	NA=100	125	250	300	350	500
^{15}N		15	30	40	50	60
20mm						
^{31}P		250	500	600	750	
^{13}C		300	600	700	800	
^{2}H	NA=4	30	60	70	90	
^{17}O	NA=100	180	350	450	550	
^{15}N		25	50	70	80	

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The Shimming Process

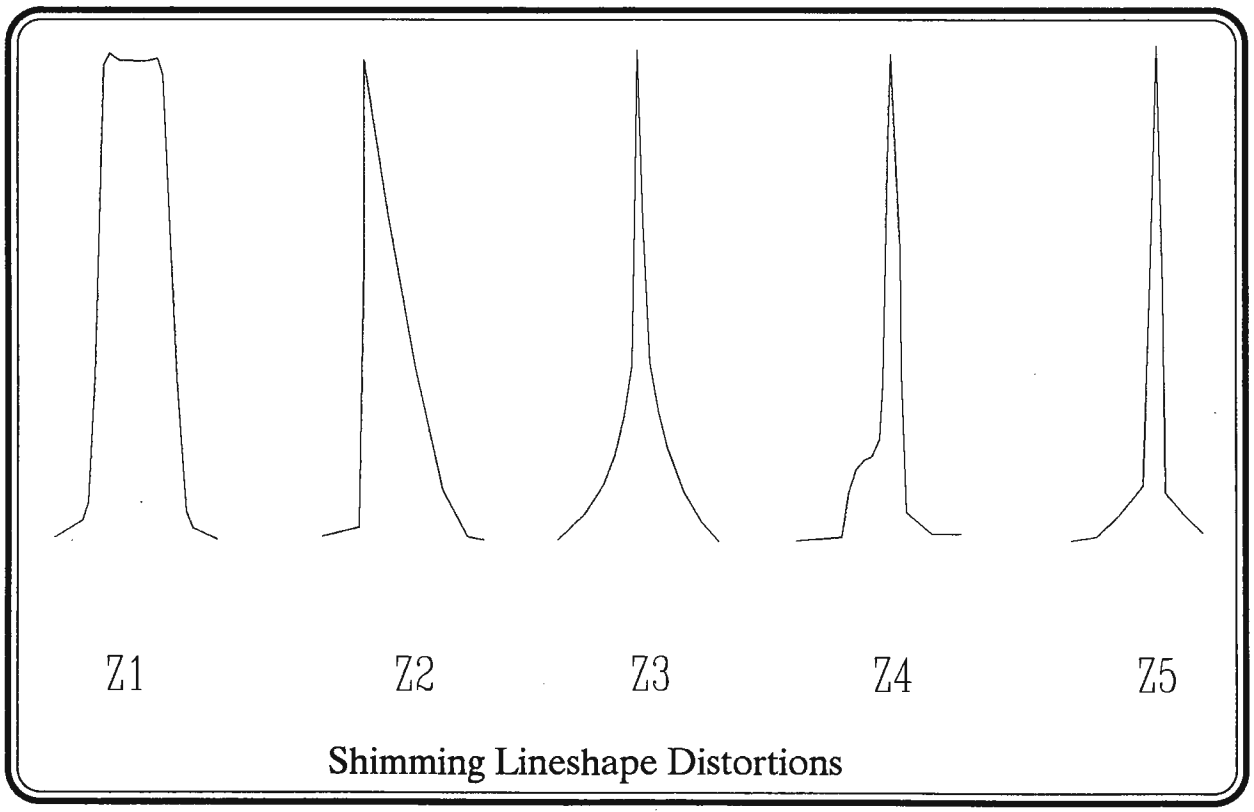
Instrumentation Note 11

It didn't Work

The previous Instrumention Note discussed the process for adjusting the spinning shims. It is not unusual for the operator to complete the shimming process and still have bad resolution and/or poor lineshape. If this happens there are some systematic things the operator can do rather than continually repeating the process with no improvement.

1. Make sure the sample is "clean" of particles and long enough to keep the end effects of the sample from being the over-riding effect on shimming. (See the previous Note on the sample).
2. Make sure all shims are working. A quick check of this can be done by observing the lock level while turning a shim control (Spinning shims while spinning and non-spinning shims while non-spinning). If you can turn the shim and not produce a change in the lock level, something is wrong. Either the instrument is not locked, the lock signal is *extremely* broad, the shim is broken or something else is very wrong. The operator needs to find it before continuing.
3. Examine the lineshape. It can give valuable clues as to which shim or shims are mis-adjusted. Compare the lineshape to the figures below. Remember the pictures are exaggerated to bring out distinctive characteristics. If the lineshape resembles any of the figures, or combination of the figures, adjust the corresponding shim or shims in LARGE steps in one direction (or the other if the first direction did not work) and reshim.

It is not usually useful to continue to struggle with the shimming process. If the operator cannot shim without excessive effort to acceptable shims, then he should look for the problem area. Instrument performance in many areas is directly dependent of proper adjustment of the shims. Resolution, lineshape and water saturation performance are examples of critical areas dependent on proper shim settings. With this in mind, if the shimming process takes too long, then look for problem areas before continuing to struggle. On average, the operator, will save more time looking at the "total picture" of shimming than he will waste looking for problems affecting shimming. In other words, make sure any problems adjusting the shims can be solved by shim adjustment. When in doubt, use the plotting process described before. It is tedious, but reasonably fail-safe.



Shimming Lineshape Distortions

THE UNIVERSITY OF SYDNEY

DEPARTMENT OF BIOCHEMISTRY

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31 July 1989
(received 8/4/89)

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

A device for keeping cells suspended during NMR experiments

Dear Barry,

The problem of the settling of cells in dilute suspensions whilst attempting to obtain NMR spectra of them is an old one in biological NMR. There are several procedures for avoiding it:

(1) For cells, such as erythrocytes, which are anaerobic metabolisers the cell density can be maintained at a high level without impairing cell function. Ever since our early red cell experiments in Oxford it has been known that using an haemocrit greater than ~70% avoids the "settling artifact" in spectra of these samples. However, in studying other cell types continuous perfusion is often required and this leads to another method of maintaining the cells in suspension.

(2) Under certain circumstances it is possible to pass a fine stream of bubbles (usually oxygen) through the suspension, from a tube which is introduced to the base of the NMR tube. Some problems are associated with field/frequency locking the spectrometer with this procedure, but nevertheless spectra of reasonable quality can be obtained.

(3) Dr Jack Cohen and his colleagues [1] have developed a procedure whereby cells can be perfused whilst they are supported in 0.5 mM threads of low melting point agarose.

(4) Dr Richard Labtoka and colleagues have introduced arabinogalactan as a means of eliminating the settling artifact. This compound has a density higher than that of normal buffers so it is possible to compose a solution of the same density as, for example, red cells and thus prevent their sedimentation [2].

(5) There have been various allusions in the literature to devices for maintaining cells in suspension, such as specially designed glass propellors which extend in from the top of the NMR tube etc. We in fact have experimented with such a device which involves a long rod extending down into the NMR tube on the end of which is a flat paddle. At the end outside the NMR tube is a 4 x 2 cm celluloid paddle which we thought would offer sufficient air resistance to ensure that the stirrer shaft rotated slower than the NMR tube which rotated in the conventional sample spinner. The device did not work.

Our lastest device works! It is simple and I hope that the diagram is self evident. Basically it is a plunger system. The nylon monofilament is sufficiently rigid, that providing one avoids kinking of the hard polythene tube, the plunger can be moved up and down easily by remote control. The monofilament in fact was "whipper snipper" cord. A conventional NMR vortex plug was drilled out to give a hole with a diameter just greater than that of the cord. The plunger was made of Tygon

tubing. One important thing to remember during the experiment is that plunging should be done between pulses, and the plunger should be left in the "up" position while acquiring spectra. Naturally, the sample is not spun with this device.

We thank Dennis Leonard, Ross Taylor and Andrew Townsend - members of the 'think tank'.

References

1. Lyons, R.C., Faustino, P.J. and Cohen, J.S. (1986) Magn. Res. Med., **3**, 663-672.

2. Labtoka, R.J., Warth, J.A., Winecki, V. and Omachi, A. (1985) Anal. Biochem., **147**, 75-79.

Yours sincerely,

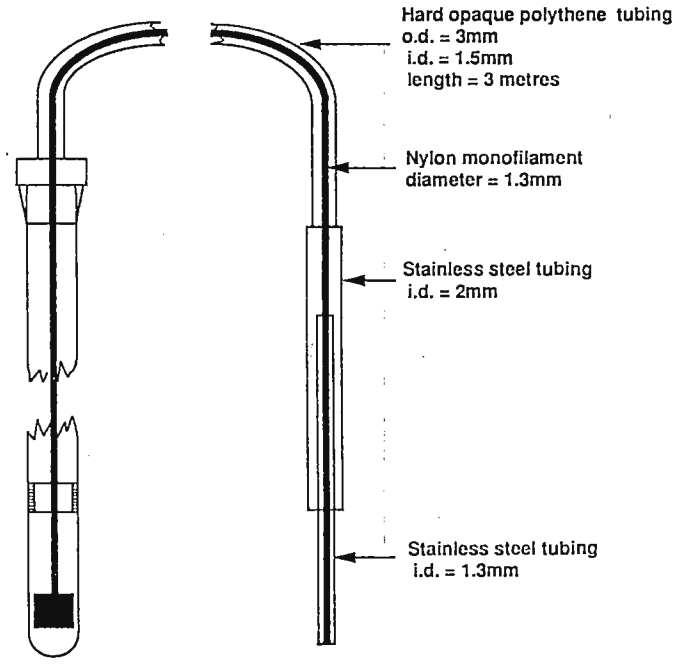
PHILIP KUCHEL
Professor of Biochemistry
Head of Department

JENNY POTTS
PhD Student

:CD/K18/20

Figure Caption

A plunger device for maintaining cells in suspension in NMR tubes. The plunger is activated via nylon monofilament in hard polythene tubing, which in our apparatus is 3 m long. The device has been used by us with both 5 mm and 10 mm NMR tubes. In spite of the fact that the sample is not spun, very good signal-to-noise is evident in the spectra of the samples.



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August 13, 1989

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

Time-of-Flight Flow Imaging

Dear Dr. Shapiro,

The time-of-flight, spin-echo imaging method is being employed in our laboratory to characterize flow dynamics in porous tube modules. Examination of flow characteristics in small structures requires the use of a non-invasive imaging technique as the presence of measurement probes will disturb the flow to an extent sufficient to invalidate the results. Use of radio-opaque dyes is also ruled out in this experiment due to the perm-selectivity of the porous tube wall. These factors will be of increased importance when more complex bioreactor systems are analyzed.

Signal intensity vs flow velocity (perpendicular to the slice plane) exhibits a biphasic response dominated at low velocities by saturation effects, and at high velocities by washout from the image slice. Peak signal intensity occurs at $\Delta Z/TR$. Data were acquired using a G.E. 2.0T/45cm imaging spectrometer.

Proper quantitative flow imaging requires that calibration images be obtained. This was accomplished by imaging laminar flow through a tube of known diameter for different flow rates. Mean velocity is calculated from diameter and fluid volume delivery rate. Peak velocity (at the center of the tube) is twice the mean velocity.

Three modifications to the spin echo sequence have been made to improve quantitative measurements. First, the number of lobes in the slice selective sinc pulses has been increased to reduce truncation artifacts in the image which can be mistaken for flow velocity variations. Second, the slice excited by the 180° pulse must be identical in thickness and position to that excited by the 90° pulse. Third, acquisitions in which $TR<<T_1$ frequently result in stimulated echo artifacts which can be confused with flow velocity variations. These can be reduced by adding spoiler gradients (half-sine) immediately following the acquisition window, and shortening the pre-delay by the corresponding duration.

Figures 1 and 2 show calibration curves for the spin-echo sequence before and following the modifications respectively. Note that the velocity for peak pixel intensity has shifted downward primarily as the result of equalizing the slice thickness determined by the 90° and 180° pulses. Figures 2 and 3 illustrate the effects of reducing truncation and stimulated echo artifacts. Prior to modification, the image shows dark streaking (particularly the upper left quadrant) which could be interpreted as flow variations, particularly if analyzing flow which is approaching turbulence. Figure 5 is a flow image of a single porous tube phantom in which flow both inside the tube, and in the region between the outer wall of the tube and the outer shell has been resolved. Figure 6 shows the velocity profile across the center of the phantom compared with a finite element prediction of the profile. Figure 7 is a mesh plot of the image in Figure 5 showing the profile across the entire structure.

Please credit this contribution to the account of Dr. Chris Sotak

Edward G. Walsh Brian J. Pangrle

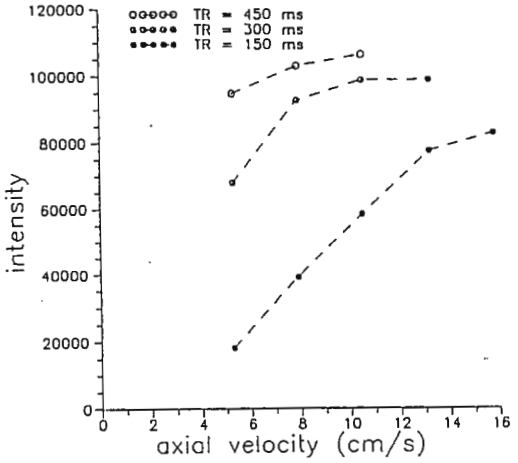


Figure 1. Calibration before modifications.

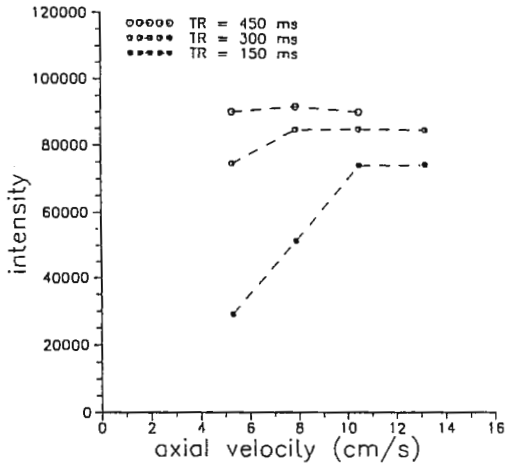


Figure 2. Calibration after modifications.

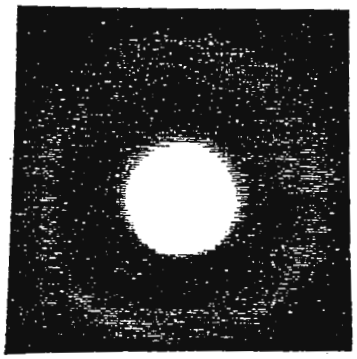


Figure 3. Flow image before modifications.

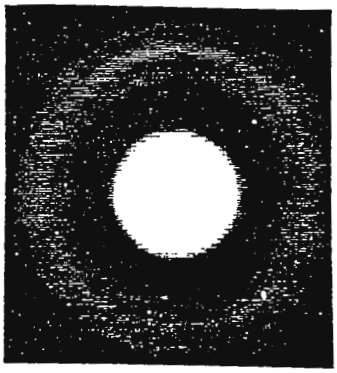


Figure 4. Flow image after modifications.

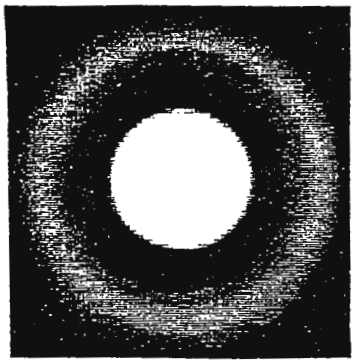


Figure 5. Flow image.

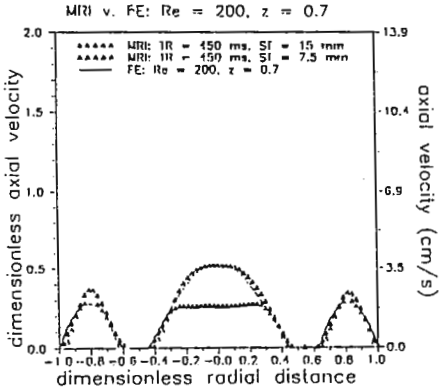


Figure 6. Velocity profile at center slice

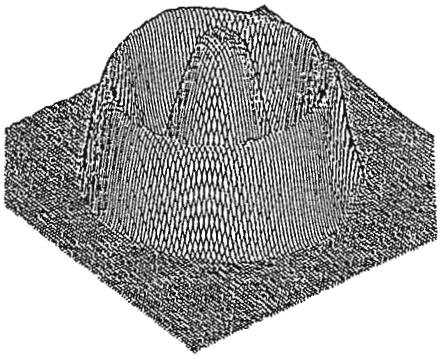
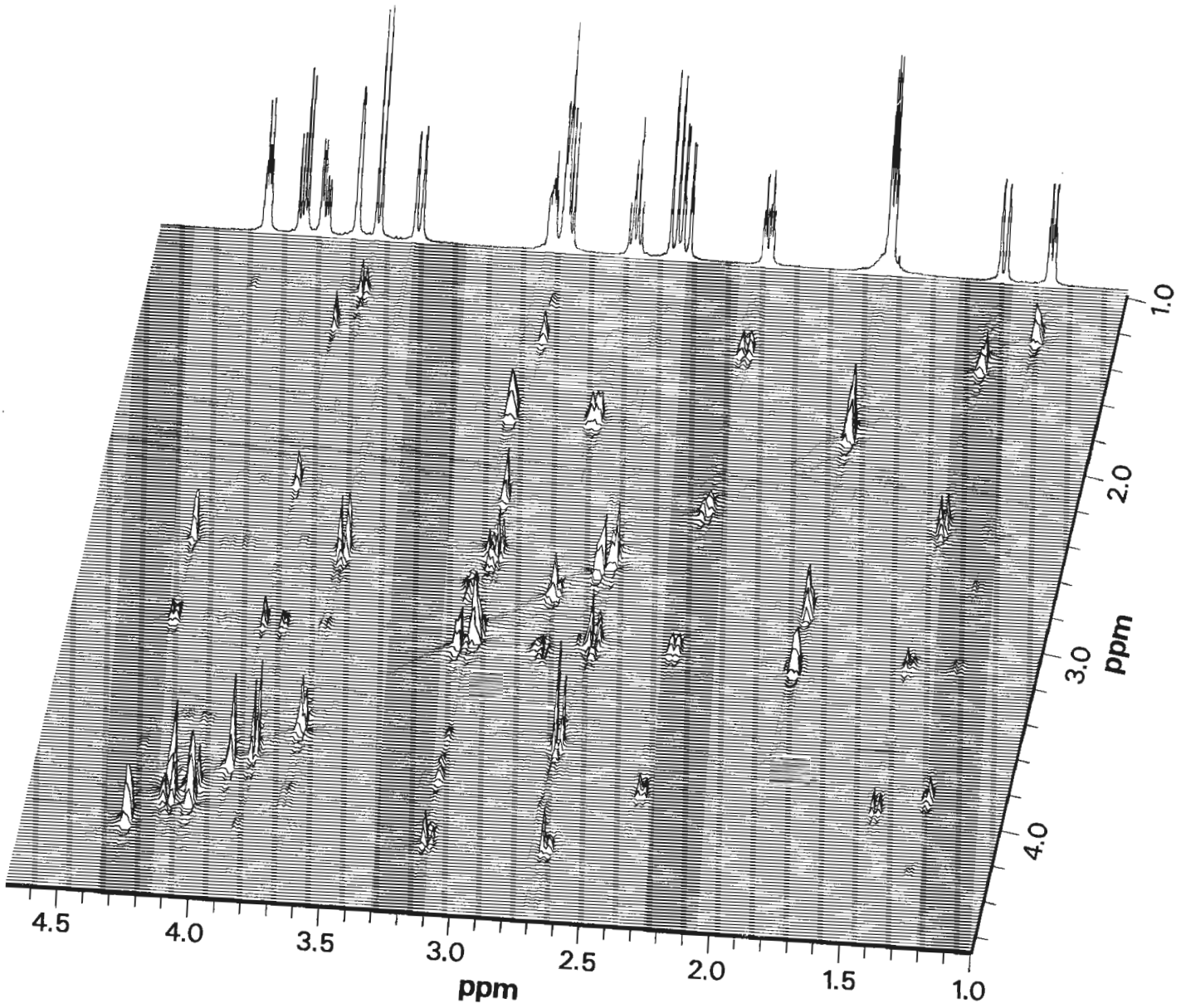


Figure 7. Mesh plot.

1. F. Stahlberg et al, J Comp Asst Tomo, 10,6:1006, 1986.



HOHAHA of Strychnine on an Omega 600

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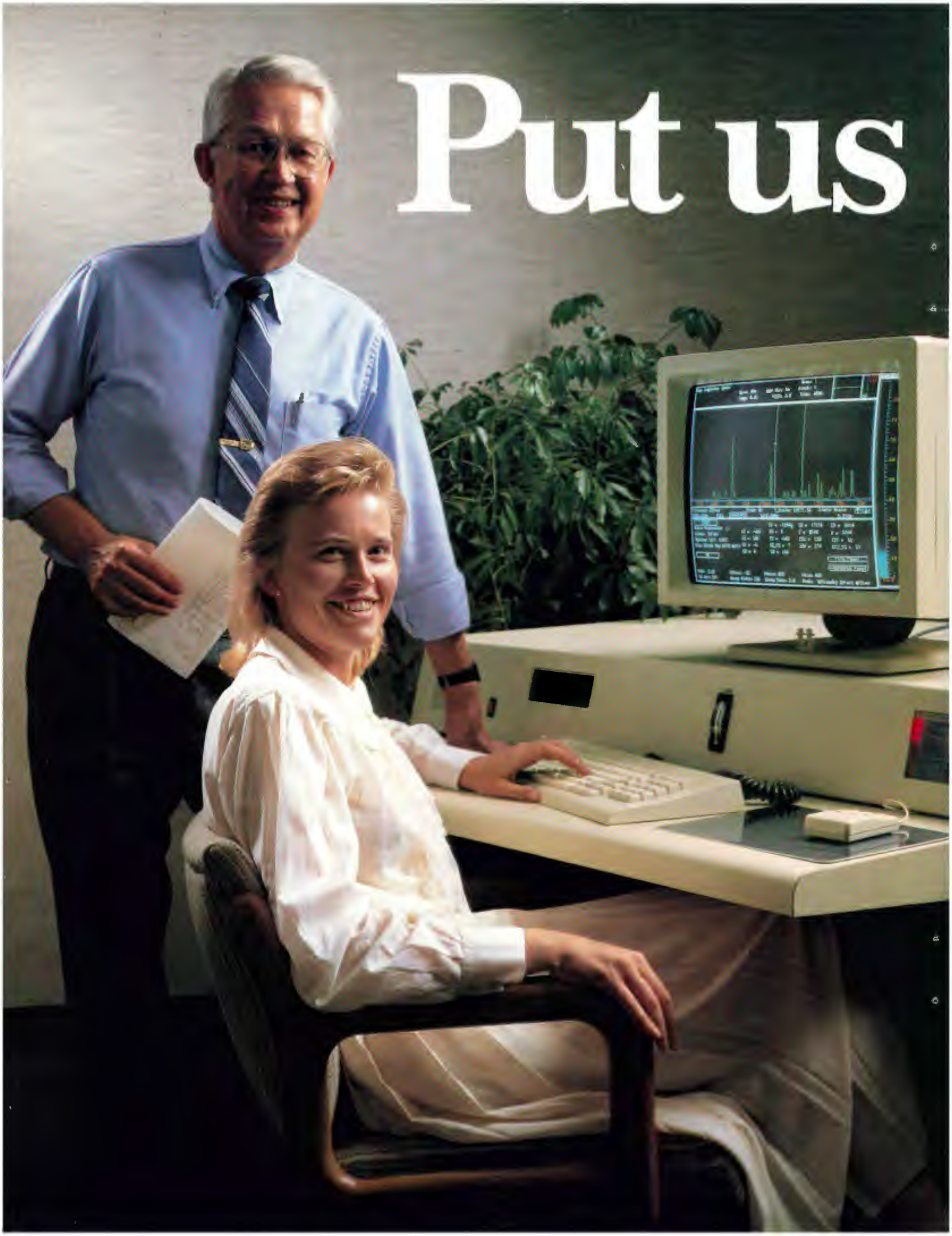
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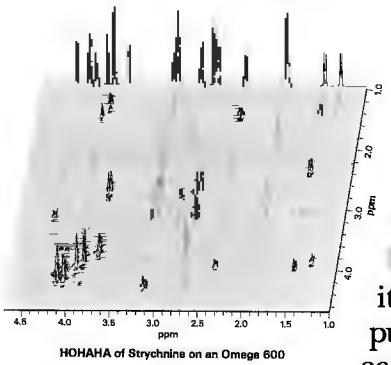

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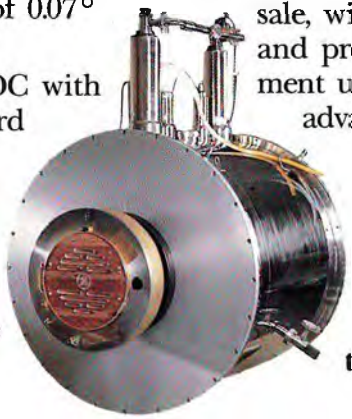

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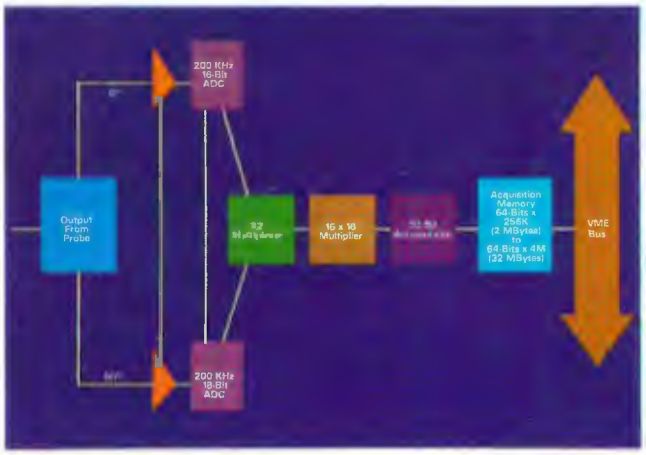

Fig. 1

The Alpha HDR digitizer.

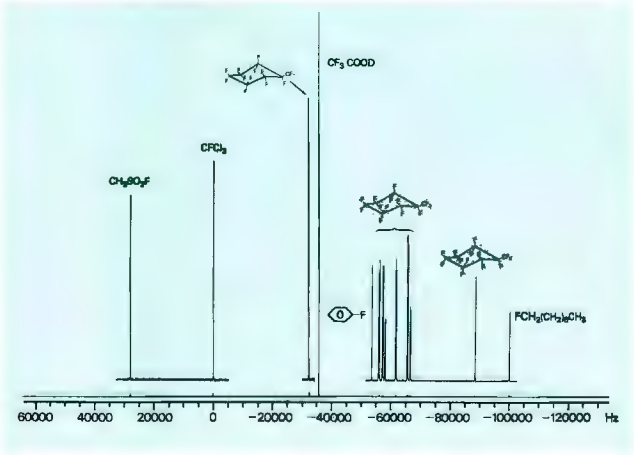

Fig. 2

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

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TAMU NMR Newsletter
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Aug. 4, 1989
(received 8/17/89)

^{15}N CHEMICAL SHIFTS IN APAMIN

Dear Professor Shapiro,

The introduction of proton detected heteronuclear NMR pulse sequences[1] , and ^{15}N isotope labeling in proteins[2] has generated chemical shift data for backbone and side chain amides. However, ^{15}N shifts are not well understood[3] and most of the new data have not been examined for correlation to elements of molecular structure. We have used indirect detection methods at natural abundance to examine ^{15}N shifts in apamin, a neurotoxin found in venom of the honey bee, *Apis mellifera*.[4] The experiment used was a 1-1 refocussed sequence from Bax and Sklenar[5] , excecuted on a GN500 spectrometer with a 5 mm probe from Cryomagnetics, Inc.[6] ^{15}N decoupling was applied during the acquisition period and data was processed with FTNMR software[7] to give pure absorption peaks with direct proton and nitrogen frequencies (Figure 1). Typically, the data matrix was 1024 × 64 × 2, with 480 scans per t_1 block to give a total acquisition time of 8 hrs.

A series of spectra over the pH range of 2 to 4 revealed some changes in amide nitrogen chemical shifts (Figure 2). The most significant are seen for residues Asn 2 and Glu 7, which move downfield by 2.2 ppm and 1.8 ppm, respectively. The proton signals also shift downfield by greater than 1 ppm, an observation originally explained by salt bridge formation between the Glu 7 side chain carboxyl and both the Asn 2 and Glu 7 α amides.[8] Addition of 2 M NaCl to the pH 4 sample shifts the Asn 2 and Glu 7 nitrogen signals, as well as the proton resonances back upfield. It is clear that titration of the carboxylate through pH 3.6 affects both nuclei in a similar fashion. There is disagreement over the status of the amide of Thr 8, which showed a significant upfield shift for the nitrogen, but a smaller upfield shift for the proton signal. A proton exchange rate that increased over the pH range suggested hydrogen bonding[8] , but NOE derived structures did not establish this.[9] Whatever the origin of the variation in exchange rates, the upfield shift of the nitrogen parallels the change to a more tightly bound proton at the higher pH.

The ability to easily obtain nitrogen chemical shift data from molecules amenable to NMR solution structure calculations may lead to useful correlations. This is particularly important for the full exploitation of ^{15}N isotope labeling in NMR studies of protein-DNA and enzyme-substrate interactions, for example.

Please credit this letter to the account of David Cowburn.

Sincerely Yours,

John Glushka

Footnotes and References

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FIGURE 1

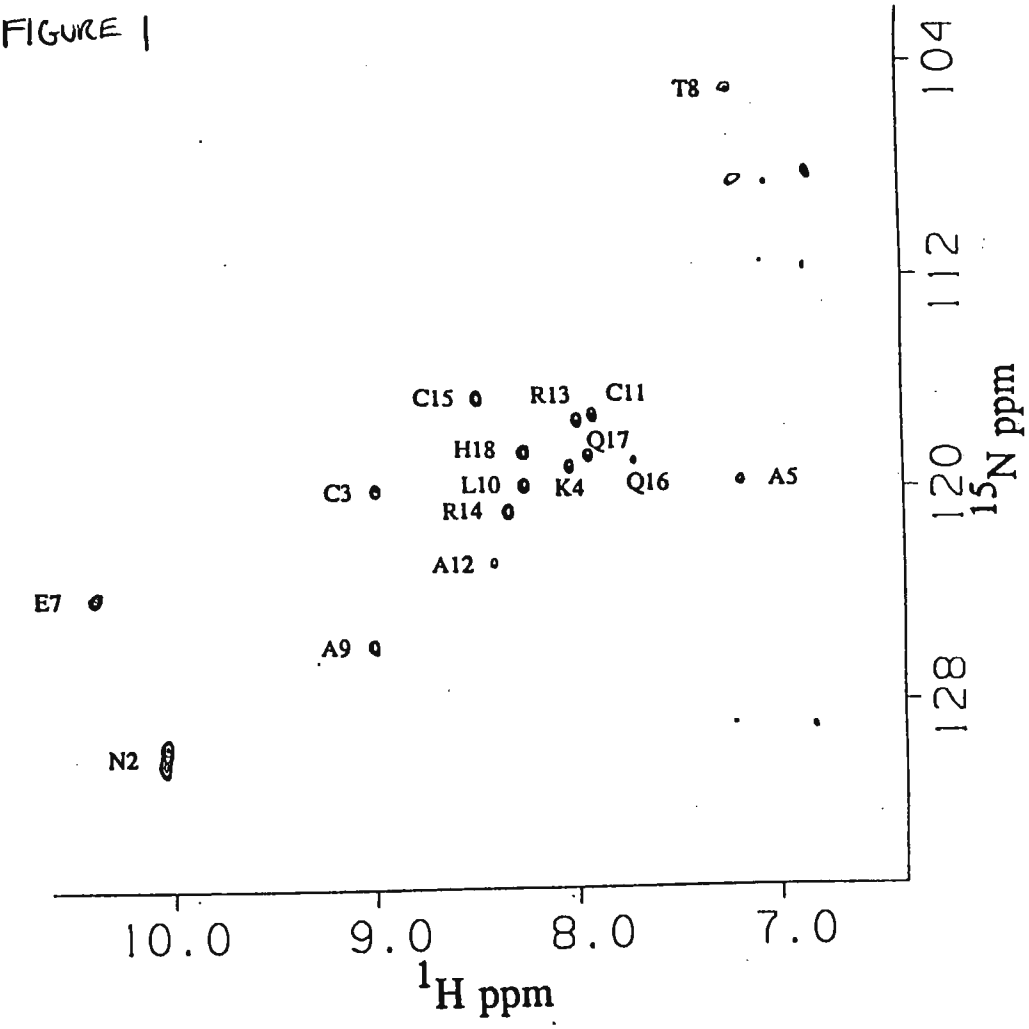

FIGURE 2

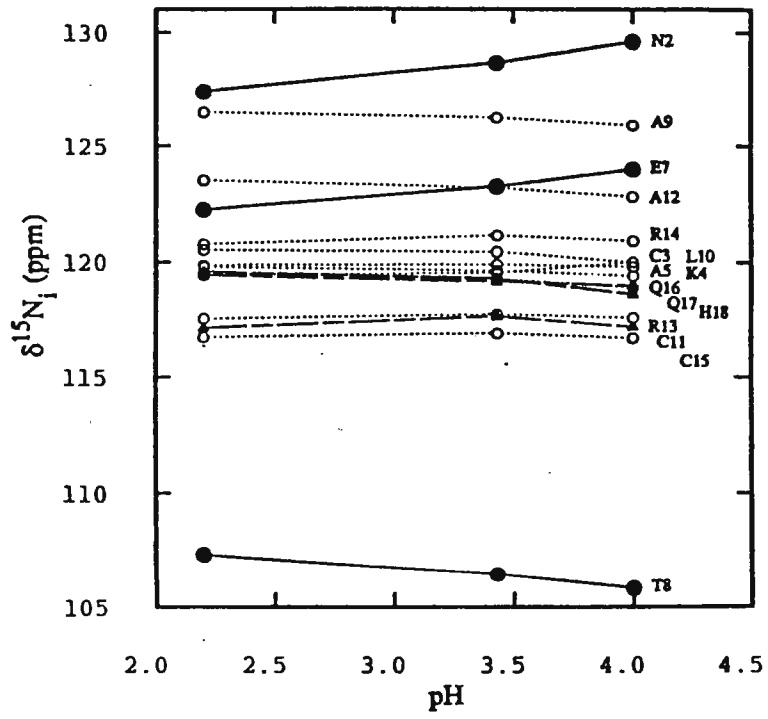

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IMAGE ENHANCEMENT USING THE MACINTOSH II

20 July 89
(received 7/26/89)

Professor Shapiro,

Since our last communication (vol #361, 1 Sept. 88), we have been using the Macintosh II (color) to enhance 2D image files generated from our GE 2T/CSI. In that communication, we wrote about the ease of transfer of image files from the Nicolet 1280 to IBM PCs. From the PC, transfer to the Macintosh II is accomplished through the TOPS Network (Sun Micro Systems). It's also easy to by-pass the PC and go straight to the Macintosh II if that's desirable. Within a matter of minutes, image files can be transferred from the MRI to the Macintosh II for processing.

Our image processing involves spatial-domain methods, or pixel manipulations. This is in contrast to frequency-domain methods which deal with the Fourier transforms. The spatial-domain methods consist of the construction of gray-level maps that correspond to specific applications (i.e. contrast stretching and noise reduction). This construction is accomplished through histogram modification techniques, like histogram equalization and histogram thresholding.

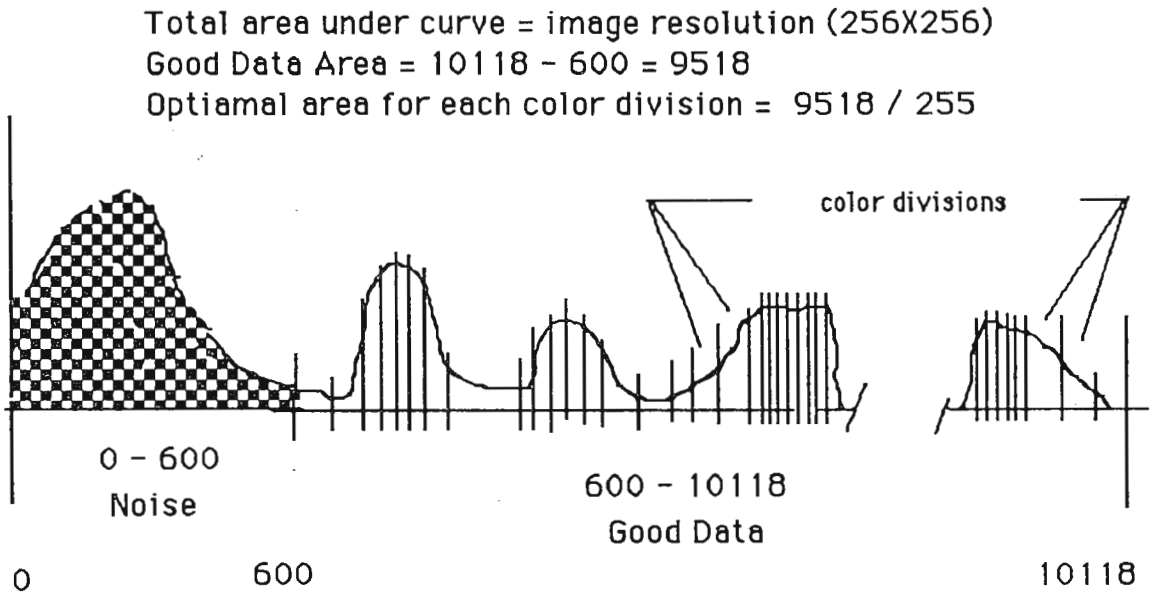
We chose the Macintosh II because of it's availability but more importantly because of it's ability. It is able to use all available installed memory for the modification techniques and able to obtain excellent graphics of 256 colors from a pallet of 2^{48} colors. The gray-levels are obtained by setting the RGB values, of the 256 color table entries, to equal values graduating from 0 to 65,535 (refer to Inside Macintosh, Volume V, Addison-Wesley).

Our first step was transporting the image file to the Macintosh II. This was accomplished through the TOPS Network and resulted in an image file (text). This text file was then rewritten to a binary format to speed-up subsequent processing of the data. The next step was reading in the binary file into our histogram modification program.

The histogram modification techniques mentioned above, equalization and thresholding, are the backbone of our program. A histogram of the data is generated on intervals of 1. The thresholding portion of the program simply evaluates the entire 2D image array and allows the user to enter a cut-off value for the noise. Not only will this clean up the presentation of the image but it will distribute gray-levels over good data (Figure 1.). The equalization portion takes the good data, after thresholding, and assigns colors based on the area under the curve. The current processing algorithms on our existing equipment simply divides the max pixel value by the number of gray-levels and assigns gray-levels to the corresponding histogram interval. In our program a variable gray-

level gradient is generated by assigning equal areas under the curve for each gray-level. This has the effect of assigning more gray-levels to regions of the histogram with large numbers of data and few gray-levels to regions with less data. Translated, the intervals are variable lengths instead of fixed lengths (Figure 1). This results in better utilization of gray-levels and increased resolution. The product of this process is written to a binary file of 256X256 pixels which range from 0 - 255. The image is then displayed on the screen.

The combination of a histogram manipulation program, faster processing times, and more gray-levels (256), has provided us with a way of presenting and interpreting our data in a better way. All code was written in Think's Lightspeed C (Think Technologies Division; 135 South Road; Bedford, MA 01730, USA; (617) 275-4800) and The Macintosh Tool Box (Inside Macintosh, Volumel I-V; Apple Computer, Inc., 1988; Addison Wesley). Also, for similar type processing contact the National Center for Superconducting Applications; Univ. of Illinois-Urbana. For more information on how you can use the Macintosh II for image processing, and a copy of our program, call us at (409) 845-4292.



MRI DATA HISTOGRAM

Figure 1

Kay Capps John W. Robinson Kevin Sherry Carl M.Edwards

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The University of Melbourne

Department of Inorganic Chemistry

Professor B. Shapiro,
Editor, TAMU NMR Newsletter,
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Palo Alto, CA 94303

July 10th 1989
(received 8/3/89)

Evidence for the Tetrafluoroaluminate Anion in Dichloromethane Solution

In the solid state all known aluminium fluoro complexes contain octahedrally coordinated aluminium with the $[AlF_6]^{3-}$ ion being the best known species. However, at high temperatures in melts $[AlF_6]^{3-}$ is known to dissociate into $[AlF_4]^-$ and F^- [1,2]. In contrast, the other halo anions are tetrahedral and aluminium-27 n.m.r. spectroscopy has demonstrated the existence of all the mixed halo complexes $[AlX_nY_{4-n}]^-$ (X and Y = Cl,Br,I) in dichloromethane solution [3,4].

No n.m.r. studies have been reported on aluminium fluoro complexes in non-aqueous media, presumably because of solubility problems. We have prepared $[Ph_3CH_2PhP][H_2F_3]$ as a stable non-hygroscopic solid by the interaction of $[Ph_3CH_2PhP]Cl$ and anhydrous HF. It is very soluble in polar organic solvents and presents an opportunity to study metal fluoro complexes in non-aqueous solvents.

The aluminium-27 n.m.r. spectrum at 25°C of a dichloromethane solution containing $[H_2F_3]^-$:$AlCl_3$ = 1:1 (i.e. F:Al = 3:1) is shown in Fig. 1a. The sharp signal at δ 102.9 is due to the $[AlCl_4]^-$ ion [3] and the other signals at δ 88.5(d), 75 and 61 ppm are due to mixed chloro/fluoro species. The spectral quality is not good because precipitation of (presumed) AlF_3 occurs a few minutes after mixing and spectra recorded after this time give no signal. Solutions containing less fluoride ion (e.g. F:Al = 2:1) show similar spectra (appropriately weighted) but precipitation still occurs. Conversely, solutions containing rather more fluoride (e.g. F:Al = 4:1) give such rapid and complete precipitation that no aluminium-27 n.m.r. signal is observed.

Solutions derived from $AlCl_3$ and a large excess of fluoride ion (F:Al > 8:1) are almost clear and are stable for several hours. Fig. 1b shows the aluminium-27 n.m.r. spectrum of such a solution. The signal at δ 47.4 ppm is sharp and shows no fluorine coupling, indicating rapid exchange between the aluminium complex and free fluoride ion. Increasing the fluoride ion concentration has no effect upon the position of the aluminium-27 resonance.

The aluminium-27 chemical shifts of all octahedral aluminium complexes so far examined fall within the narrow range of δ +3 to δ -21 ppm while tetrahedral complexes cover a wider range [5]. However, all tetrahedral mixed chloro and bromo complexes give signals which fall in the range δ 110 to δ 80. Thus the resonances shown in Fig. 1a may all be assigned to tetrahedral complexes. Experiments with varying F:Al mole ratios (but less than 3:1) demonstrate that the fluoride content is larger for those species giving signals at lower frequencies. The resonances are assigned to $[AlCl_4]^-$, $[AlCl_3F]^-$, $[AlCl_2F_2]^-$ and $[AlClF_3]^-$ respectively. The signal assigned to $[AlCl_3F]^-$ is clearly a doublet ($J_{Al,F}$ = 75 Hz) and this is the first report of an aluminium-fluorine coupling constant. There is

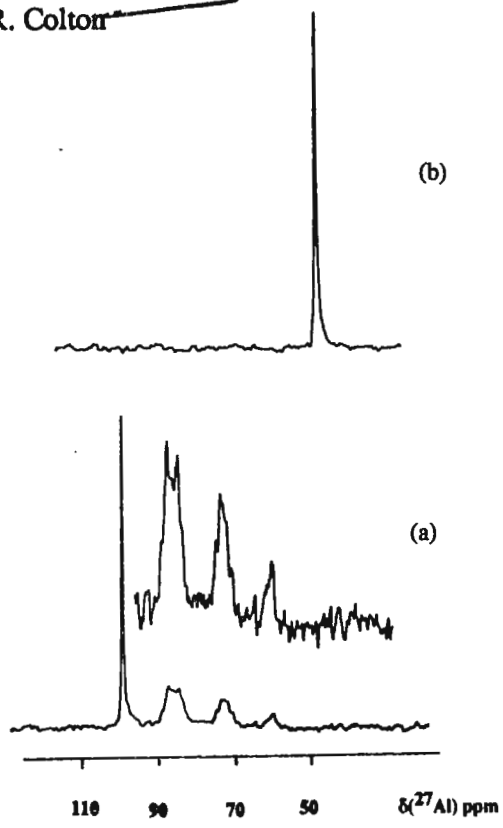
a regular decrease in chemical shift as the proportion of fluoride in the aluminate ion increases so it can readily be estimated that the chemical shift of $[AlF_4]^-$ would be about 47 ppm, so the resonance at 47.4 ppm for fluoride-rich solutions (Fig. 1b) is assigned to $[AlF_4]^-$ on this basis. Notably, this chemical shift is well outside the range observed previously for octahedral aluminium species. Thus the somewhat surprising result of these studies is that with the triphenylbenzylphosphonium cation, $[AlF_4]^-$ rather than $[AlF_6]^{3-}$ is the stable fluoroaluminate in dichloromethane solution, even in the presence of a substantial excess of fluoride ion. Since octahedral aluminium(III) complexes are dominant in aquo and aquo/fluoro media and water is a larger ligand than fluoride, the stabilization of tetrahedral $[AlF_4]^-$ in dichloromethane cannot derive from steric influeneces alone. Charge repulsions within the complexes and the low dielectric nature of dichloromethane are two factors which could destabilize the more highly charged anions such as $[AlF_5]^{2-}$ and $[AlF_6]^{3-}$.

This work was done in collaboration with Dr. P. Gary Eller of the Los Alamos National Laboratory during his tenure of a University of Melbourne Visiting Fellowship.

Please credit this contribution to the account of Dr. D.P. Kelly.

Yours sincerely,

R. Colton



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August 9, 1989
(received 8/14/89)

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

Dear Dr. Shapiro:

It has been a busy time getting all the new facility instrumentation installed and tested, but we finally made it! Unfortunately, for the last several months blasting during construction of the new MRI research facility next door has severely limited the type of studies which can be carried out during the day.

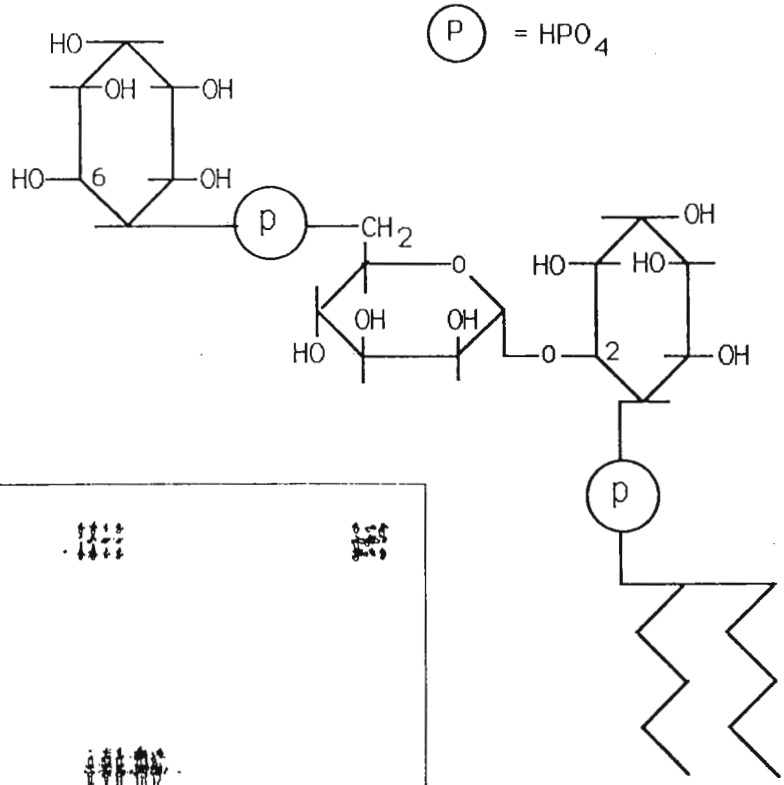
Fortunately, there is no blasting nights or weekends and we have used this time to carry out ^{1}H NMR structural studies on the head group moiety of the major sphingolipid from Saccharomyces Cerevisiae. We have determined its structure as both the isolated head group and in the intact ceramide using ^{1}H-^{1}H COSY/NOESY and ^{1}H-^{31}P correlations. This work is part of a fruitful collaboration with another member of this department, Professor Robert L. Lester.

We are currently elucidating the three dimensional structure of the mannosyl-(α1,2)inositol moiety of the head group in D_2O using one and two dimensional NOE values as distance constraints. The structure of the intact head group, and representative COSY and 1D difference NOE spectra for mannosyl-(α1,2)inositol, are attached.

Sincerely yours,

Judith G. Shelling
Assistant Professor of Biochemistry
Director, D.E. Combs NMR/MM Facility

JS:jg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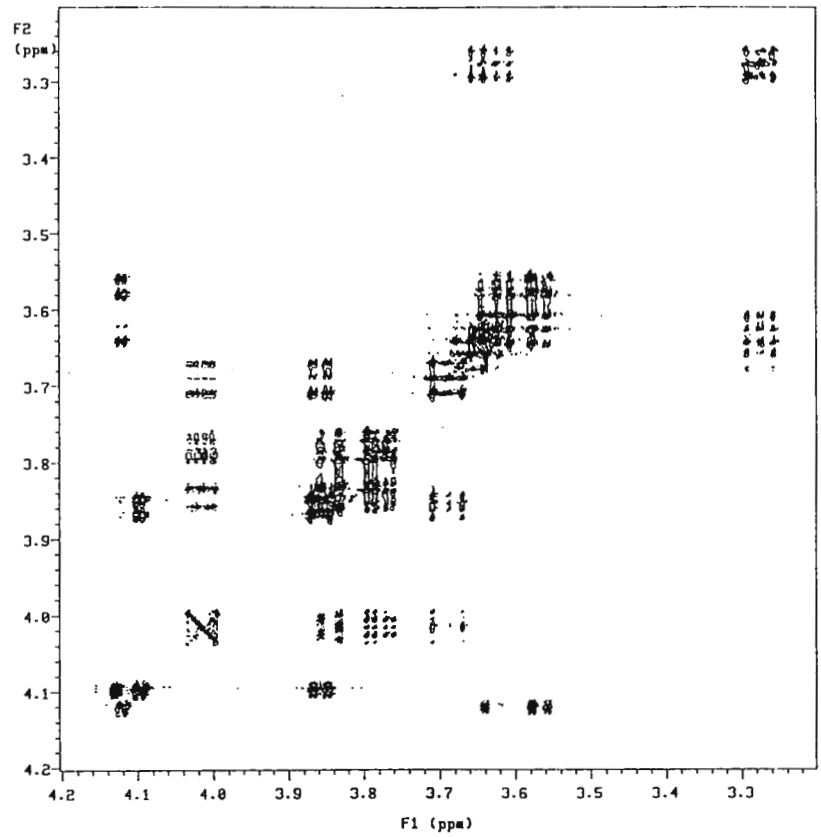
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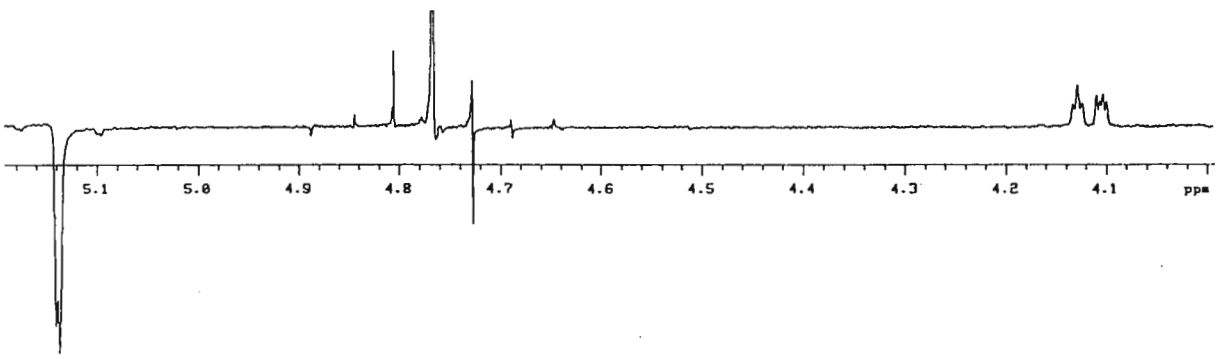
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Frank D. Blum
Department of Chemistry
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(received 8/19/89)

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

Dear Barry,

We have recently modified an ESR slow motional lineshape simulation program written by D.J. Schneider[1] for use with deuterium NMR. A similar program has been used by us before[2], but the new program uses the more efficient Lanczos algorithm for tridiagonalization of the matrix Hamiltonian and is consequently faster.

The program uses the slow-motional theory developed by Freed to calculate the theoretical lineshapes. The Hamiltonian matrix is constructed, made tridiagonal by the Lanczos algorithm, then used to calculate the spectrum. These calculated spectra can then be compared to experimental spectra to help obtain more information about the molecular motion of the material.

Figure 1 is a simulation of a spectrum with slow, isotropic diffusion ($R_{xy}=R_{zz}=10^3$ Hz) for a deuteron with an asymmetry value of 0.6. This is typical of the slow motion practical limit of the program.

Figure 2 shows a simulation of the same deuteron undergoing a two-site jump, i.e. ring flips.

Figure 3 shows a simulation of continuous, anisotropic diffusion ($R_{xy}=10^3$ Hz, $R_{zz}=10^8$ Hz).

Figure 4 shows the experimental spectrum of sodium 1-(4-hepylnonyl)benzenesulfonate-d_4 (SHBS), obtained on a Varian VXR-200 spectrometer at 30.7 MHz for deuterons using a quadrupole echo pulse sequence. 700 transients were collected. The temperature of the surfactant was 23°C.

Figure 3 is the best match to the experimental spectrum. This indicates that at this temperature, the motion of SHBS-d_4 can be described as a rapid spinning about the long axis of the molecule, with much slower reorientation about the axes perpendicular to the long axis.

The program was originally supplied for the IBM PC/AT, where execution times often approach an hour. We have very recently ported the program to a Silicon Graphics Personal Iris, which typically runs simulations in under two minutes. We hope soon to be able to fit experimental spectra using an iterative method, something that was not feasible on the PC due to the time required.

Frank D. Blum
Associate Professor

Robert B. Funchess

Joseph R. Duke

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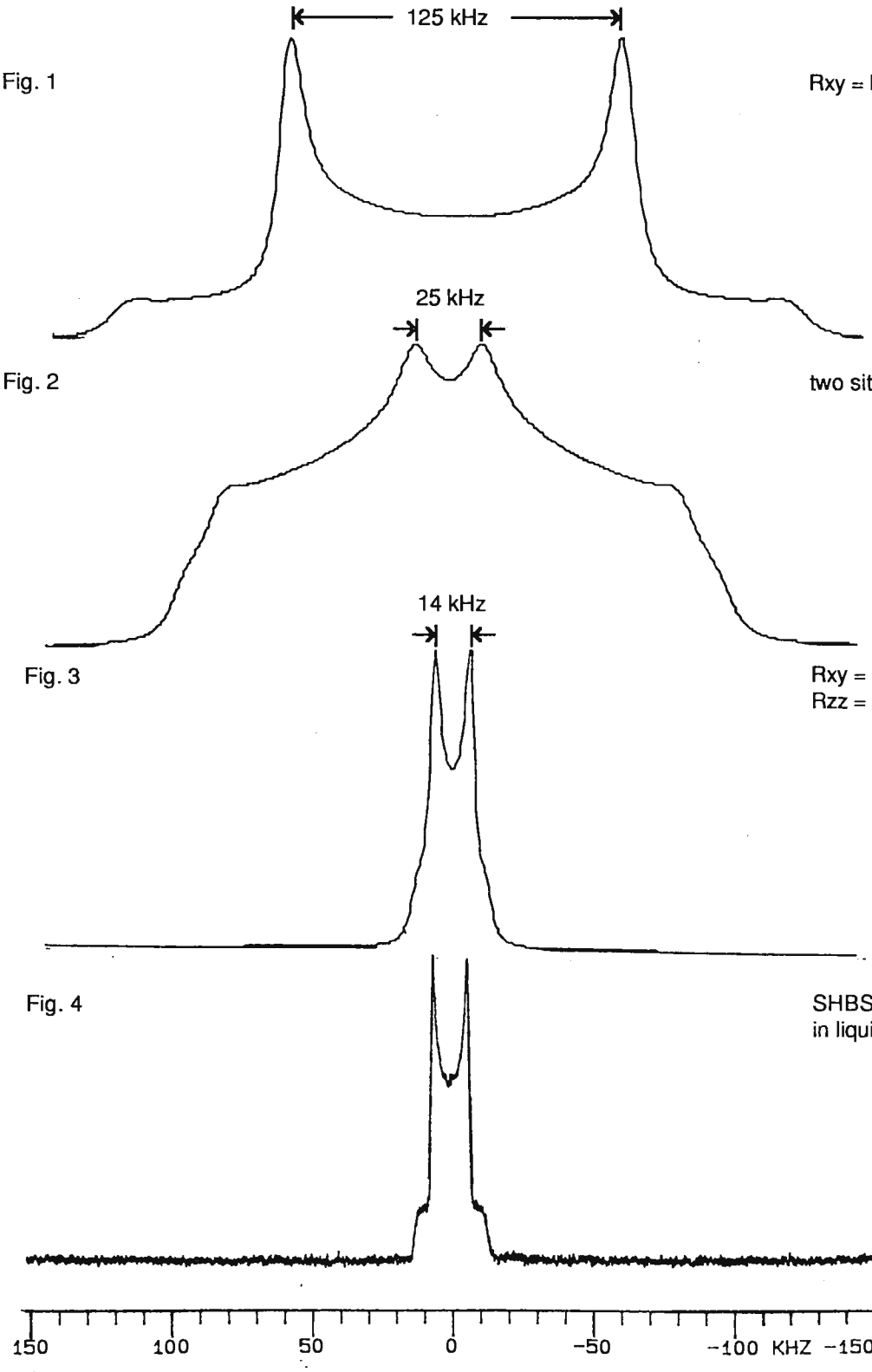

Fig. 1

$R_{xy} = R_{zz} = 10^3$ Hz

Fig. 2

two site jumps

Fig. 3

$R_{xy} = 10^3$ Hz
$R_{zz} = 10^8$ Hz

Fig. 4

SHBS-d_4
in liquid crystal

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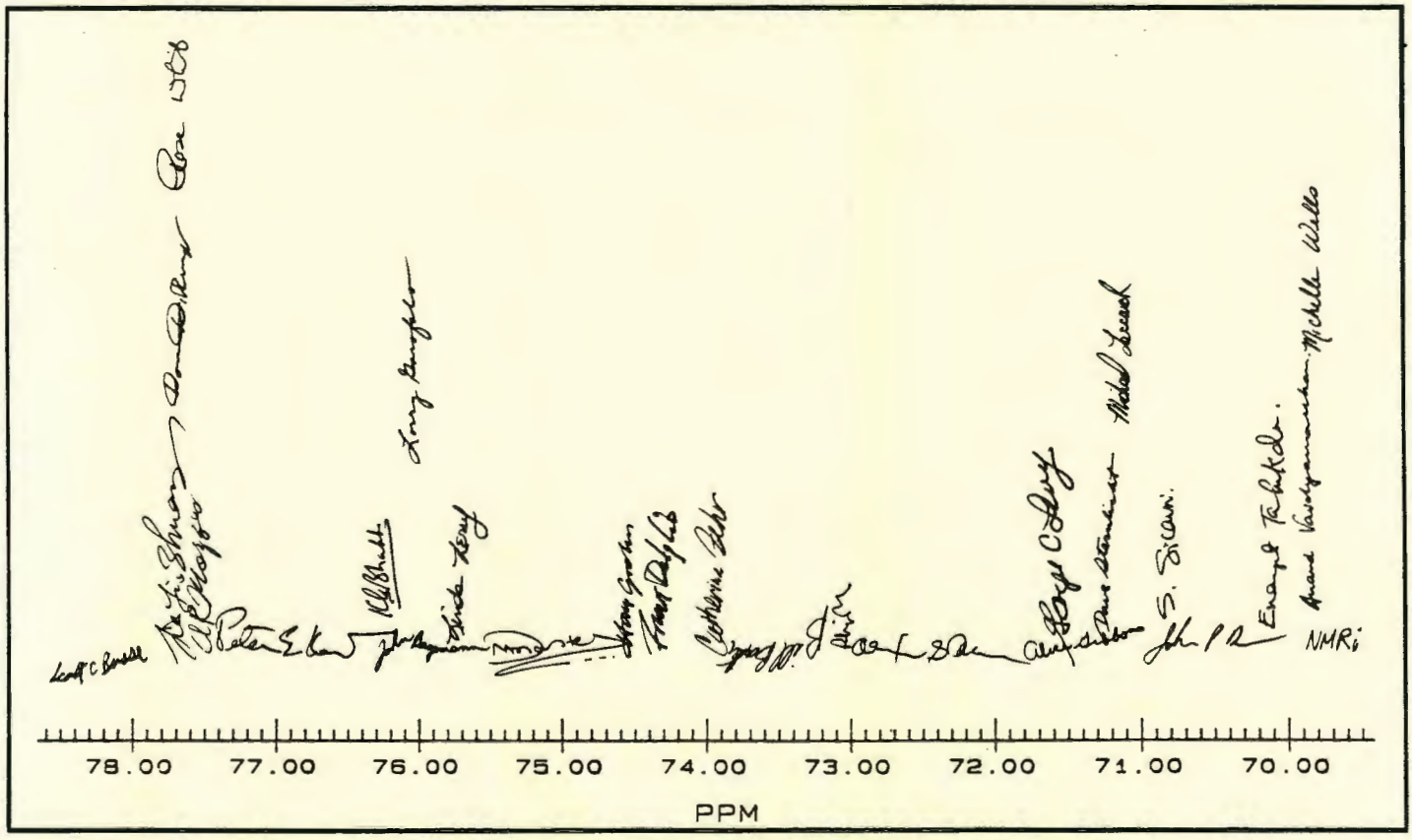

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August 16, 1989
(received 8/21/89)

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

Distribution Coefficients of Solubilizates in Micellar Systems

Dear Barry:

The conventional nmr technique for measuring distribution coefficients of solubilizates in aqueous micellar systems is the FT pulsed gradient spin echo (FT-PGSE) technique (see ref. 1 for an excellent review). Recently we have described a simple alternative to the FT-PGSE method which we thought readers of the newsletter may find of interest.

The technique we have used involves measuring the T_1 of one or more sets of chemically equivalent protons of the solubilizate in the presence and absence of a low concentration of some salt where either the cation or anion is paramagnetic. The paramagnetic species should reside exclusively in the aqueous phase of the micellar solution and the charge of the paramagnetic ion should be the same as that as the head-group of the surfactant. For example, if the surfactant is sodium dodecylsulfate (SDS) the paramagnetic species should be negative; we have used both $Mn(EDTA)^{2-}$ and the sodium salt of 3-carboxyl-PROXYL. Qualitatively, the basis of the technique is simple. If the solubilizate resides predominately in the micellar phase, solubilizate proton T_1 values will not be influenced by the addition of the paramagnetic species however if the solubilizate spends the bulk of its time in the aqueous phase, the solubilizate T_1 values will decrease upon addition of the paramagnetic salt. One can show that if the solubilizate exchanges rapidly between the micellar phase and the aqueous phase the mole fraction of solubilizate in the micellar phase, p, is given by eq.[n] 1.

$$[1] \quad p = 1 - (R_{1,obs}^{P} - R_{1,obs}) / (R_1^{P}(aq.) - R_1(aq.))$$

where $R_{1,obs}^{P}$ and $R_{1,obs}$ are the rates of solubilizate spin-lattice relaxation in the presence and absence of the paramagnetic species, respectively. Measurements of $R_1^{P}(aq.)$ and $R_1(aq.)$ are carried out on the solubilizate in aqueous solution (no surfactant present) in the presence and absence of paramagnetic species, respectively.

In applying the paramagnetic relaxation technique one must decide on the optimum concentration of the paramagnetic species. In table 1 the measured value of p for 1-butanol (0.044 m) in DTAB(0.16 m) as a function of Mn(II) concentration is examined. The apparent values of T_1 for the α-CH_2 protons of butanol in the micellar solution and in aqueous solution are 3.72 s and 4.77 s respectively. The data in table 1 indicate that the value of p is independent of Mn(II) concentration and that the error in p decreases as the concentration of Mn(II) increases. We are in the process of determining how high one can increase $[Mn(D_2O)_6^{2+}]$ before severe line-broadening precludes the accurate measurement of T_1 and or before the added paramagnetic salt influences the T_1 of surfactant protons. However on the basis of our preliminary results it is apparent that the measured

distribution coefficients are insensitive to the concentration of the paramagnetic salt over a wide range of concentrations as one would intuitively expect.

In principle, the paramagnetic relaxation method can be used in other microheterogeneous systems, including microemulsions, reverse micelles, liposomes and polymer-surfactant solutions. Finally the relaxation of NMR-active nuclei other than protons can in principle be used.

Yours sincerely,

Roderick E. Wasylishen Zhisheng Gao Jan C.T. Kwak

References:
1. P. Stilbs, Prog. Nucl. Magn. Reson. Spectrosc., 19 (1987) 1.
2. Z. Gao, R.E. Wasylishen and J.C.T. Kwak, J. Phys. Chem., 93 (1989) 2190.

Table I. ^1H T_1 values (α-CH_2 protons) of 1-Butanol in micellar and aqueous solution as a function of $[Mn(D_2O)_6^{2+}]$. The distribution coefficients are calculated using equation 1.

$[Mn(D_2O)_6^{2+}]$	$T_1^P{}_{,obsd}$	$T_1^P(aq)$	p
0.0002 m	2.17 s	2.12 s	0.27±0.11
0.0004	1.51	1.16	0.39±0.06
0.0006	1.17	0.933	0.32±0.06
0.0008	0.962	0.759	0.30±0.05
0.0010	0.789	0.626	0.28±0.05
0.0020	0.451	0.323	0.32±0.04

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Texas A&M University NMR Newsletter - Book Reviews
Book Review Editor:
Wiliam B. Smith, Texas Christian University, Fort Worth, Texas

"Interpretation of Carbon-13 NMR Spectra."

by
F.W. Wehrli, A.P. Marchand and S. Wehrli
John Wiley and Sons, 605 3td Avenue New York, NY 10158
484 pages;1988, $89.95; ISBN0-471-91742-7.

The first edition of this volume appeared in 1976 and quickly established itself as an extremely useful book for organic and biological chemists who wished to exploit carbon-13 NMR in their research. The problem set also was considered as a valuable asset when the volume was used as a classroom text. That first edition went through three reprintings as a result. However, the rapid growth of technology in the field has relegated portions of that first edition to the realm of history. An introduction to 2-D techniques, solid state NMR and *in vivo* applications are part of the overhaul of the newly published Second Edition which retains the useful portions and the five chapter format of the original.

Some sixty six pages of Chapter Two are devoted to considerations of chemical shift parameters and coupling constants with regard to molecular structure relationships. Much of this material is not available in other texts in this price range. Chapter Three on experimental methods explores the most important 2-D methods as well as the more sophisticated 1-D experiments that have appeared since the first edition. Consideration is also given to shift reagents, isotope effects and solids NMR. Nuclear spin relaxation is again covered in Chapter Four.

For many, the applications covered in Chapter Five will be the most valuable part of the book. The accompanying problem set has been expanded from twenty nine to forty one with replacement of several of the old problems by their current counterparts. Answers to all are given in the appendix. While not meant to be a thorough review, many useful references to the primary literature are given at the end of each chapter. An adequate index is included.

W.B.S.

Schering-Plough
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Bloomfield, New Jersey 07003
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Dr. Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303

August 4, 1989
(received 8/10/89)

COMPARISON OF INTERPROTON DISTANCE DETERMINATION IN SMALL MOLECULES BY TRANSIENT AND STEADY STATE NOE METHODS

Dear Barry:

Steady state difference NOE (SSNOE) is an important part of our efforts to provide support to synthetic and natural products chemists. In general, we use the technique in a qualitative way to determine the disposition of two protons (or groups of protons) with respect to some reference plane. The literature warns against the quantitative use of SSNOE in distance determinations and strongly advocates the use of transient methods (NOESY, truncated driven NOE, transient NOE) for this purpose. [1,2] We wondered, however, just how bad are interproton distance estimates obtained from SSNOE measurements on small molecules? Since we had available an X-ray crystal structure for a very rigid tricyclic organic molecule, Sch33342, we decided to carry out the necessary NMR experiments to make the comparison indicated in the title. If the readers will keep in mind the nonquotability clause of TAMU contributions, we would like to share the results of our limited analysis.

Adapting the treatment of Bell and Saunders[3,4] for a rapidly tumbling two spin system we can write

$$\eta_i\{j\} = \frac{\sigma_{ij}}{2\sigma_{ij} + \rho_i^*}$$

where $\eta_i\{j\}$ is the SSNOE measured for proton i when proton j is irradiated, σ_{ij} is the cross relaxation rate constant and ρ_i^* accounts for non-dipolar relaxation and for dipolar relaxation of spin i by protons other than j in the molecule. Thus,

$$\eta_i\{j\}^{-1} = 2 + \rho_i^* / \sigma_{ij}.$$

Note that if $\rho_i^* = 0$ no distance information can be obtained by SSNOE measurements. Bell and Saunders state that the "2" in the above equation can be neglected, but this is true only in the case of small NOE's where the ρ^*/σ_{ij} term is much larger than 2. In the analysis reported here we have retained the "2". Distance and dynamic information can be added by writing the isotropic expression for σ_{ij},

$$\eta_{ij}\{j\}^{-1} - 2 = \rho_i^*/\sigma_{ij} = 2\rho_i^* r_{ij}^6/(\tau_{ij}\hbar^2\gamma^4)$$

If we are using a particular interaction kl as a marker (eg., a geminal methylene having an interproton separation of 1.785 A) then the unknown distance can be obtained from the ratio

$$\frac{\eta_i\{j\}^{-1} - 2}{\eta_k\{1\}^{-1} - 2} = \frac{\rho_i^* r_{ij}^6/\tau_{ij}}{\rho_k^* r_{k1}^6/\tau_{k1}} \qquad \text{(Equation 1)}$$

Herein lies the rub: in order to get exact distance estimates from SSNOE measurements we require that $\rho_i^* / \tau_{ij} = \rho_k^* / \tau_{k1}$. However, we expect $\rho_i^* = \rho_k^*$ since there should be varying amounts of "other" dipolar contributions for different protons. In addition, we expect $\tau_{ij} = \tau_{kl}$ because of differential motional freedom for different protons and because in real world molecules isotropic averaging of all ij vectors does not occur. Thus, it is unlikely that the ρ^*/τ ratios are equal. On the other hand, there is potential saving grace in the sixth root factor: if the ratios are off by as much as a factor of two, for example, this would cause an error of only 12% in the distance determination.

Caveats notwithstanding we wanted to see what kinds of problems would be encountered in a practical situation. SSNOE measurements were carried out with and without deoxygenation on three samples of Sch33342 dissolved in varying proportions of DMSO-d_6 and CD_3CN. Assuming equality of the ρ^*/τ ratios in equation 1, we made 19 separate SSNOE distance determinations of seven different distances.

NOESY measurements were conducted on a non-deoxygenated sample of Sch33342 in 80% /20% CD_3CN/DMSO-d_6 (v/v). For three different mixing times, seven NOESY distances were obtained by diagonalizing the experimental NOESY volume matrix with our previously described program, ROENOE[5], using the same geminal protons for the marker distance as was used in the SSNOE measurements. The coordinates of the protons of Sch33342 were obtained from the X-ray structure by means of a proton spawning program which places the protons at the correct positions based on the heavy atom coordinates. We thank Dr. John Clader of Schering-Plough Research for assistance with this program.

A "standard deviation" was calculated according to

$$s = \sqrt{\sum (r_{NOE} - r_{X\text{-}ray})^2/(n-1)}$$

where r_{NOE} is the distance determined either by SSNOE or NOESY, $r_{X\text{-}ray}$ is the distance determined by X-ray, and n is the number of distance determinations.

For both SSNOE and NOESY we obtain interproton results in good agreement with X-ray distances, although we found that if we carried out the SSNOE analysis neglecting the previously mentioned "2", the distances obtained were consistently shorter than the X-ray values by some 0.2 A. The results were as follows:

Technique	No. of Distances	Standard deviation (A)	Maximum deviation (A)
Steady State NOE vs. X-ray	19	0.138	0.30
NOESY vs. X-ray	21	0.086	0.16

The interproton distances used in these measurements ranged from 2.27 to 2.62 A. Plots of NOE vs. X-ray distances are given in Figures 1 and 2.

These results imply that NOESY estimates of proton-proton distances are in tighter agreement with X-ray results than those determined by steady state techniques. However, distances determined by SSNOE appear to have an error no worse than a factor of two larger than the errors from NOESY.

We have not carried out studies to rigorously exclude potentially systematic errors (effect of recycle time, effect of amount of power used to saturate, etc.) and are offering the results given here in the hope of stimulating some discussion of the use of SSNOE for routine quantitative distance determination. We strongly suspect that some of the scatter seen here in the SSNOE data is due to the difficulty in obtaining undistorted integrals of the difference spectra. In any case, we are pleased with the general agreement between SSNOE, NOESY, and X-ray results.

Best Wishes,

T. M. Chan T.M.C. AE

David Dalgarno David

C. Anderson Evans

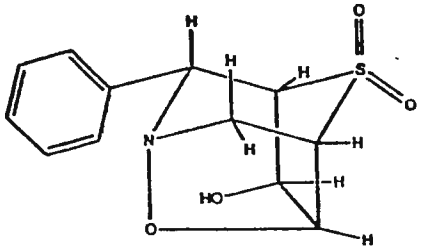
1 Wagner and Wuthrich, J. Magn. Reson., **33**, 675 (1980)

2 Sanders and Hunter, Modern NMR Spectroscopy, Oxford University Press, 1978, p. 169

3 Bell and Saunders, *Can. J. Chem.*, **48**, 1114 (1970)

4 Noggle and Schirmer, Nuclear Overhauser Effect, Academic Press, 1971, pp. 51ff

5 Chan, Evans, Al-Haj and Dalgarno, 30th ENC, Asilomar, 1989



Sch 33342

Figure 1: Steady State NOE

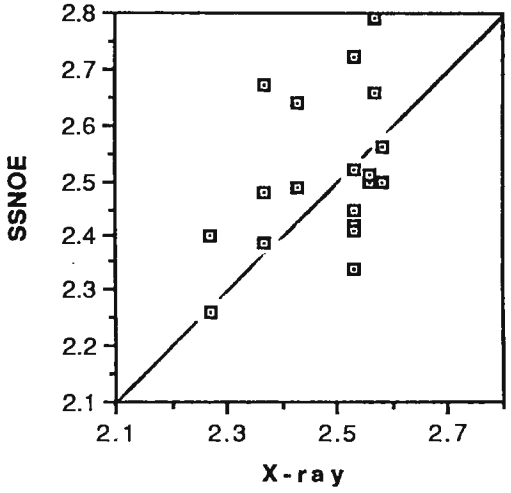
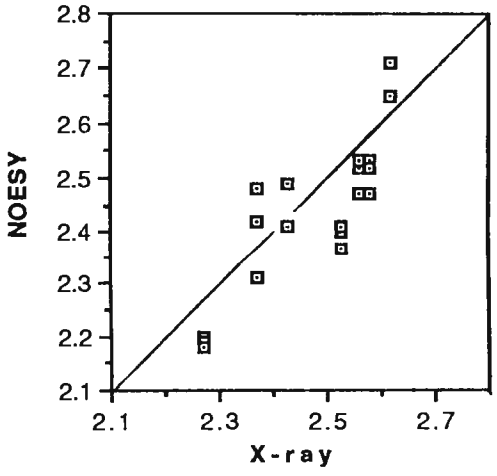


Figure 2: NOESY



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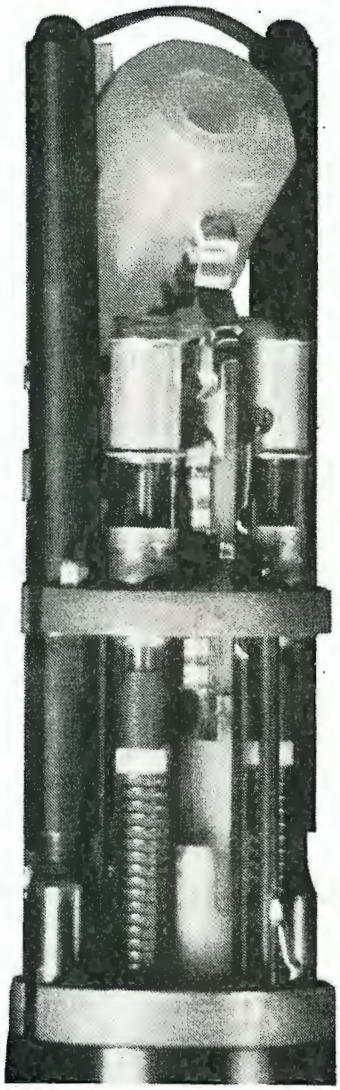

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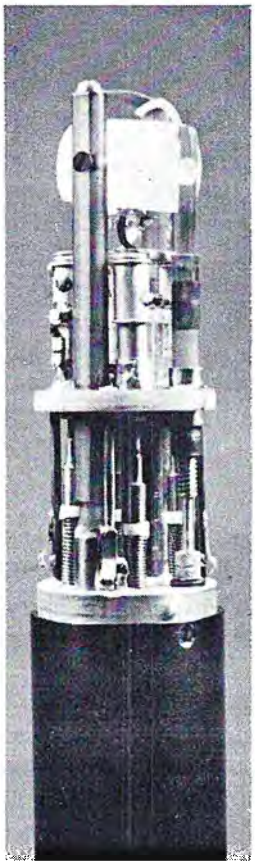

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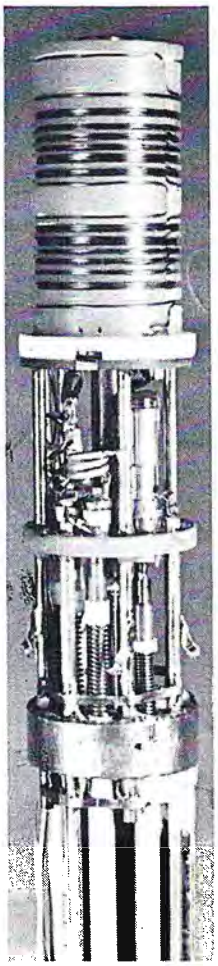

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The workshop speakers include **Dr. Charles S. Springer, Jr.** of the State University of New York, Stony Brook, who will describe uses of molecular paramagnetism for *in vivo* NMR and **Dr. Robert G. Shulman** of Yale University, who will talk about high resolution ^{1}H and ^{13}C NMR studies of brain metabolism. **Dr. Robert S. Balaban** of the National Institutes of Health will describe the molecular mechanisms underlying NMR/MRI image contrast, and **Dr. Kamil Ugurbil** of the University of Minnesota will discuss spatially localized NMR spectroscopy for the elucidation of cell energetics. Taken together, these talks serve to emphasize the important role of chemists and chemistry in delineating the molecular level interface between physics, biology, and medicine.

This symposium covers a particularly timely topic, since new NMR techniques have proliferated during the past 10 years and commercially available instrumentation has reached new levels of sophistication. With these tools in hand, we are just now experiencing the beginnings of a revolution in our understanding of the chemistry of living things.

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(received 8/18/89)

Professor Bernard Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Re: The INAPT Experiment

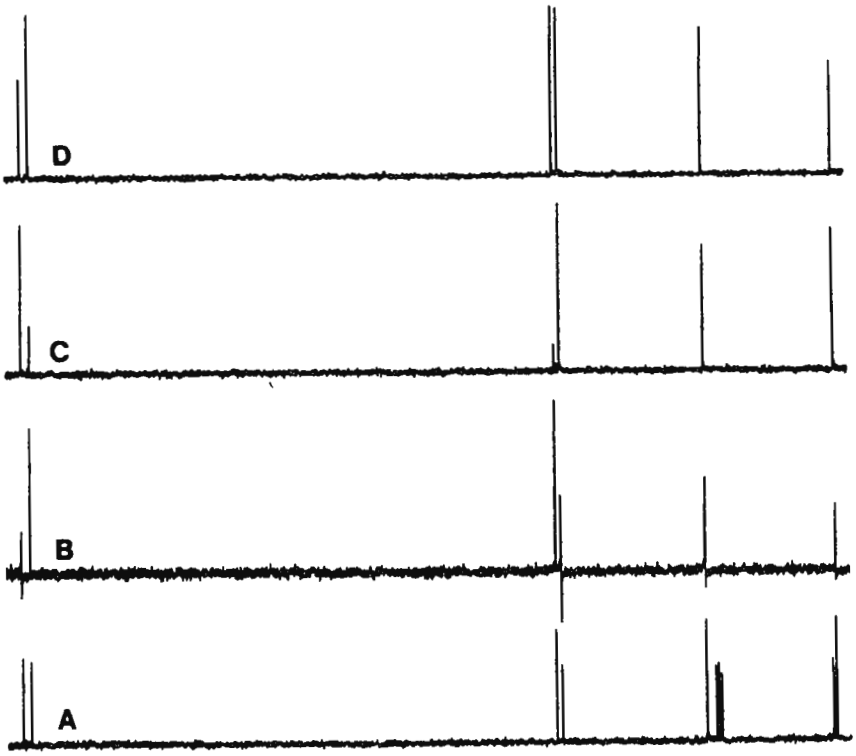
Dear Barry:

Initially when setting up Bax's INAPT experiment (J. Magn. Reson., 57, 314 (1984)), the basic Bruker INEPT microprogram was used, substituting soft (90=18ms) for hard proton pulses. For the test molecule, 3,4-dihydro-naphthalene-1-one, this modification worked fine because only one or two carbon resonances were enhanced as each proton is irradiated. However, phasing problems may develop if more than two resonances are enhanced (see Fig. B), and arises because the intervals between the carbon 90 and the 180 and between the carbon 180 and acquisition are different. With appropriately modified microprograms (see pulse sequence in above reference) results in Fig. C (delays=30ms) and Fig. D (delays=5ms) were obtained. Figure A is the normal spectrum (196-55 ppm) and all spectra obtained with 96 scans. So, when using selective pulse sequences, the length of the pulses must be taken into account. One note of caution: do not replace only the first proton 90 with a selective pulse, otherwise unwanted proton couplings are activated.

Sincerely,

Tom Nakashima

Tom Nakashima



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Department of Chemistry
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New York

Christopher J. Turner
(212) 280-4601 Voice
(212) 932-1289 Fax

8/15/89 (received 8/21/89)

ARTIFACTS IN COSY

Dear Barry:

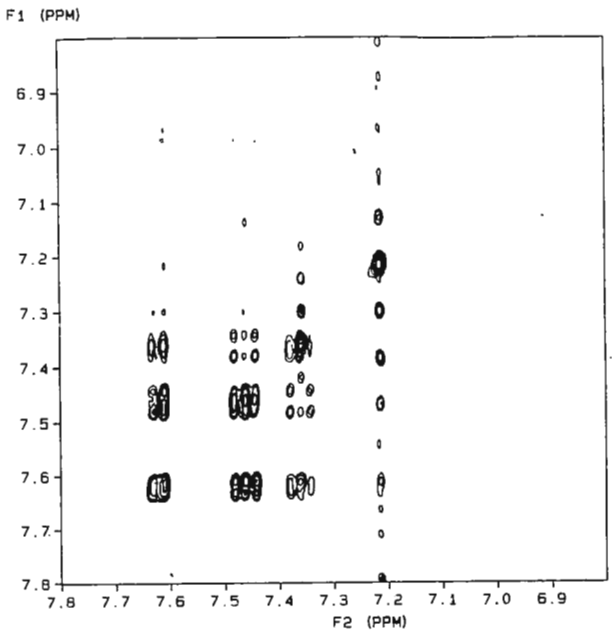
Repetition rate artifacts in COSY spectra make up a surprisingly large proportion of the stuff which is often called "T_1-noise". The spectrum below demonstrates these artifacts in a 90°-90° absolute value COSY spectrum of Trans-Stilbene, measured with a spectral width of 400 Hz in each dimension, an acquisition time equal to the recycle time equal to 0.64 seconds, 4 transients and 128 increments. The average proton relaxation time was 3 seconds in this air-saturated chloroform solution.

These artifacts can be thought of as echoes. Thus, all the usual remedies are applicable. Some people like homospoil pulses, others advocate strong RF pulses, while random delays are also popular. The problem with all of these techniques is that they take time. The first two methods seek to destroy all the magnetization remaining from the last transient before starting on the next, thus it is necessary to insert a delay to allow the Z-magnetization to build up. Random delays can be a little tricky to implement sometimes. Are they really random? Equally well, do we actually want them random, or does systematic incrementation of a short delay make more sense? In any case, random delays take time.

An alternative strategy suggests itself; one which requires the minimum delay and that is to cancel these artifacts by phase cycling. The magnitude of these artifacts is very sensitive to the exact order in which the steps of the phase cycle are taken. More about this subject later.

Best Wishes

Chris



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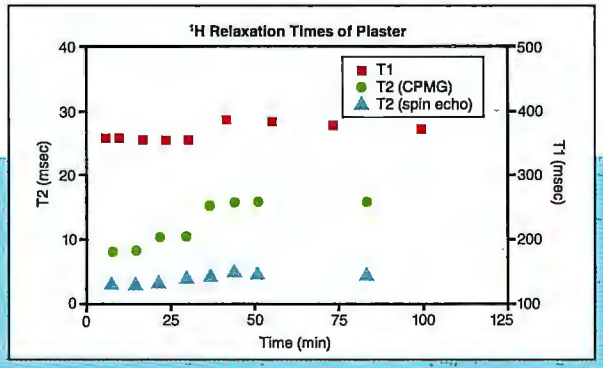

Non-destructive monitoring of the solidification of plaster at 4.7 Tesla. H-1 images obtained at (A): 18 minutes, (B): 28 minutes and (C): 38 minutes after a mixture of plaster and water (2:1 ratio) was prepared. The centers of the images are an intensity reference made of water doped with copper sulfate.

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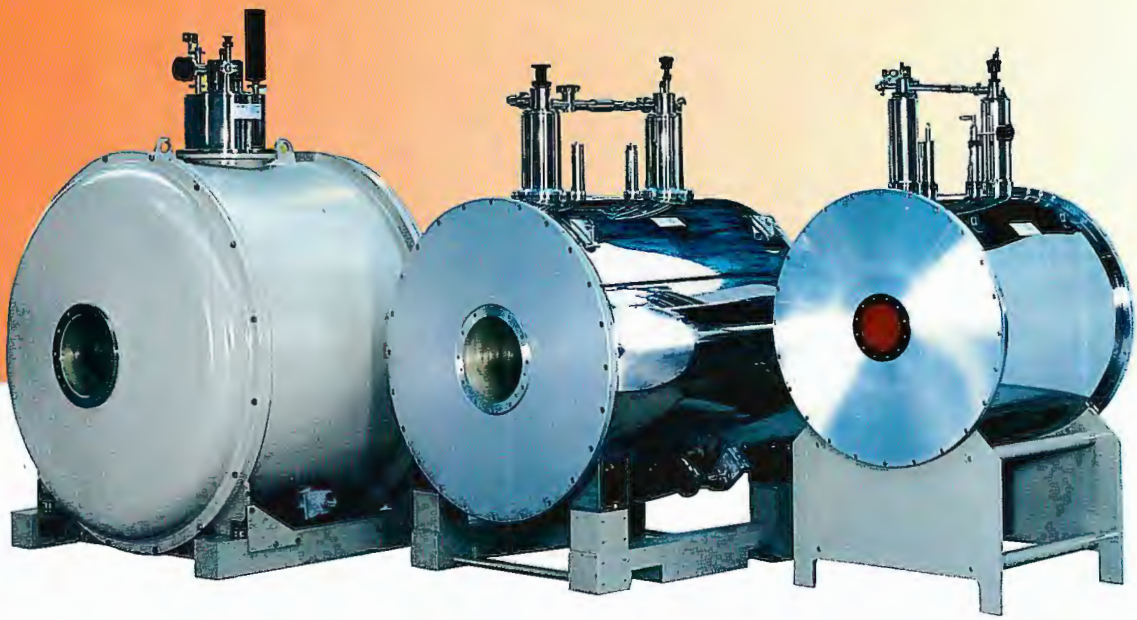
200/330	4.7T	330 mm	254 mm	2.3 G/cm	140 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	6.95 m	5.60 m
200/400	4.7T	400 mm	324 mm	1.8 G/cm	140 mm DSV ±4 ppm	80 mm DSV 0.1 ppm	8.50 m	6.75 m
85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

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



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

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University of Illinois
at Urbana-Champaign

School of Chemical Sciences
142B Roger Adams Lab, Box 34-1
1209 W. California
Urbana, IL 61801

August 4, 1989
(received 8/14/89)

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

TITLE: Relative Sensitivites vs. Coil Q

Dear Dr. Shapiro:

I. From Hill & Richards (Abragam)[1,2], the NMR system signal-to-noise performance of an experiment after a 90° pulse is given by:

$$\frac{Vs}{Vn} = \kappa \frac{\eta(Q\omega_o V_c \frac{\mu_o}{4\pi})^{1/2}}{(F4kT\Delta t)^{1/2}} M$$

II. The nuclear magnetization: $M = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT} Bo$

III. For the relative signal response from two nuclear experiments a ratio using the above can be made:

$$\frac{\frac{Vs_1}{Vn_1}}{\frac{Vs_2}{Vn_2}} = \frac{(Q_1\omega_{o1})^{1/2}\gamma_1^2 N_1 I_1(I_1+1)}{(Q_2\omega_{o2})^{1/2}\gamma_2^2 N_2 I_2(I_2+1)}$$

IV. In the above ratio it is assumed that with respect to the sample material, only the values shown may change. Otherwise, if coil Q can be considered to vary directly with frequency, i.e. $\frac{Q_1}{Q_2} = \frac{W_{o1}}{W_{o2}}$, and noting that $\frac{W_{o1}}{W_{o2}} = \frac{\gamma_1}{\gamma_2}$, the ratio in III reduces to:

$$\frac{Vs1/Vn1}{Vs2/Vn2} = \left(\frac{\gamma_1\gamma_1}{\gamma_2\gamma_2}\right)^{1/2} \left(\frac{\gamma_1}{\gamma_2}\right)^2 \frac{N_1 I_1(I_1+1)}{N_2 I_2(I_2+1)}$$

$$= \left(\frac{\gamma_1}{\gamma_2}\right)^3 \frac{N_1 I_1(I_1+1)}{N_2 I_2(I_2+1)}$$

However, if coil Q can be considered to vary as the square root of frequency, i.e. $\frac{Q1}{Q2} = \sqrt{\frac{\omega_{o1}}{\omega_{o2}}}$, then the ratio in III reduces to:

$$\frac{Vs1/Vn1}{Vs2/Vn2} = \left(\frac{\gamma_1}{\gamma_2}\right)^{11/4} \frac{N_1 I_1(I_1+1)}{N_2 I_2(I_2+1)}$$

In SI units:

η = probe coil filling factor
κ = Numerical factor ~1, coil geometry related
$\omega_o = 2\pi f$
f = Larmour frequency = $\gamma Bo/2\pi$
V_c = probe coil volume
μ_o = permeability of free space: $4\pi 10^{-7}$ m/kg/s^{2}A^2
F = Receiver noise factor
k = Boltzman's constant = 1.38×10^{-3} m^2/kg/s^{2}k
T = Sample temperature °K
Δt = effective bandwidth in Hz
N = spins/unit volume
γ = gyromagnetic ratio
$\hbar = \frac{h}{2\pi} = 1.0546\times10^{-34}$m^{2}kg/s
I = Spin
B_o = Magnetizing field in Tesla
Q = Coil quality factor

V. The ratio of the sensitivities given in IV above gives a ratio of relative sensitivity with respect to the choice of Coil Q variation:

$$S_{rel} = \frac{\left(\frac{\gamma_1}{\gamma_2}\right)^3}{\left(\frac{\gamma_1}{\gamma_2}\right)^{11/4}} = \left(\frac{\gamma_1}{\gamma_2}\right)^{1/4}$$

VI. The published values of "relative sensitivites", e.g. Bruker Almanac '86 appear to be based on the receptivity relation given by Harris and Mann[3] and is similar to the equation in IV where coil Q varies directly with Larmour frequency. For example, ^1H vs ^2H:

$$D_xP = \left|\frac{9.21}{60.00}\right|^3 \quad \frac{1(1+1)}{1/2(1/2+1)} = 9.645\text{x}10^{-3}$$

or for ^{23}Na vs ^1H:

$$D_xP = \left|\frac{15.87}{60.00}\right|^3 \quad \frac{3/2(3/2+1)}{1/2(1/2+1)} = 9.252\text{x}10^{-2}$$

VII. The foregoing suggests that the relative sensitivities given in the Bruker Almanac '86 are somewhat pessimistic by a factor of $\left(\frac{\gamma_1}{\gamma_2}\right)^{-1/4}$ when coil Q is considered to vary as the square-root of Larmour frequency. However, in practice, all the factors bearing on sensitivity, including the way coil Q varies with frequency, may not be known exactly. In which case, the Bruker tables would be valid, if only a crude estimate of relative sensitivity is desired.

1. Abragam, A., The Principles of Nuclear Magnetism, Oxford University Press, London 1961, P83.

2. Hill, H. D. W., Richards, R. E., Journal of Scientific Instruments (Journal of Physics E), 1968, Series 2, Vol. 1.

3. Harris, Robin K., Mann, Brian E. NMR and the Periodic Table, Academic Press, N.Y., 1978, P4.

Sincerely yours,

Brian W. Voth

Vera V. Mainz

Brian Voth
Electrical Engineer
credit to: Molecular Spectroscopy Laboratory

Vera V. Mainz
Molecular Spectroscopy Laboratory

Agricultural Products

June 27, 1989
(received 7/24/89)

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

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Western Research Ctr.
1200 S. 47th Street
Box 4023
Richmond
California 94804-0023
Telephone (415) 231-1000
Fax (415) 231-1368
Telex 172197

Subject: ^{13}C-NMR Spectrum of a N,N-Dialkenyl Amide

Dear Barry:

It has been shown previously that the carbon chemical shifts for N,N-dialkyl amides (Structure I) behave in a predictable manner (1).

The carbon nuclei in the corresponding α, β, γ and δ positions in the two carbon chains differ in their chemical shifts. The α and β carbons resonate downfield in the *anti* chain compared to these two carbons in the *syn* chain. The γ and δ carbons resonate upfield in the *anti* chains (1).

We wished to find out if this trend held for N,N-dialkenyl amides (Structure II).

The carbon spectrum of II (Fig. 1, 100 MHz) shows eight resolved resonances. The 400 MHz ^{1}H spectrum of II shows two well resolved multiplets corresponding to the two N-methylenes (α) at 4.07 and 4.02 ppm. We reasoned that the N-methylene *cis* to the methine would show a larger ^{1}H-NOE enhancement than the N-methylene *trans* to the methine. Indeed by performing a 1-D NOE difference spectrum we measured a larger increase in the downfield multiplet (4.07) compared to the multiplet at higher field. Next we showed by a HETCOR experiment that the α-CH_2 *anti* to the carbonyl resonated downfield from the α-CH_2 *syn* to the carbonyl. By using ^{1}Jc,c from a 1-D INADEQUATE experiment we showed unequivocally that this N-N-dialkenyl amide's carbon chemical shifts behave in the same predictable manner as its saturated counterpart.

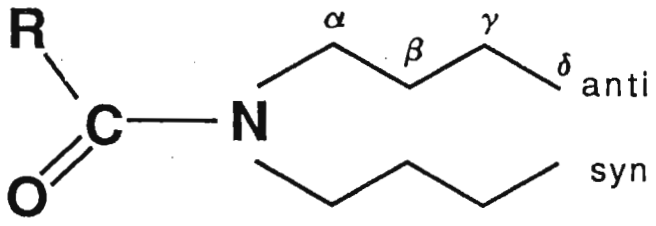
Sincerely,

Joseph R. Snyder

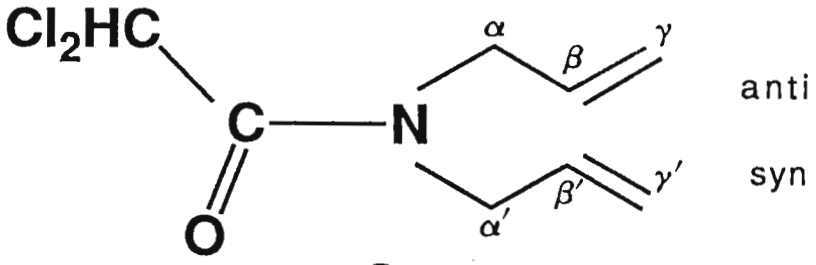
C. K. Tseng

1. Fritz, H., Hug, P., Sauter, H., Winkler, T., and Logemann, E., Org. Mag. Res., 9, 108, (1977).

encls.

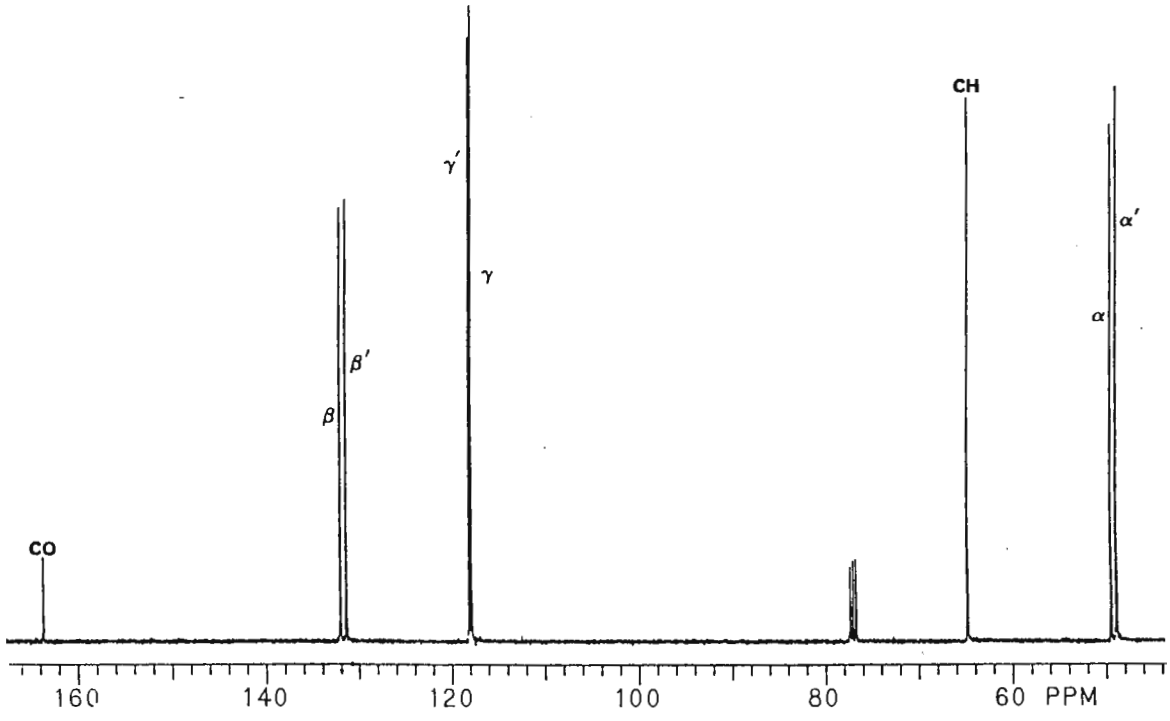


Structure I



Structure II

1



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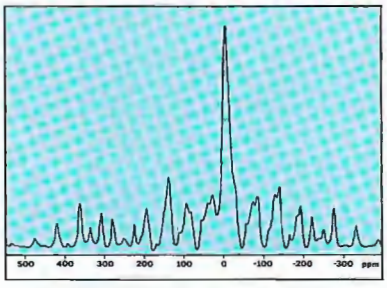

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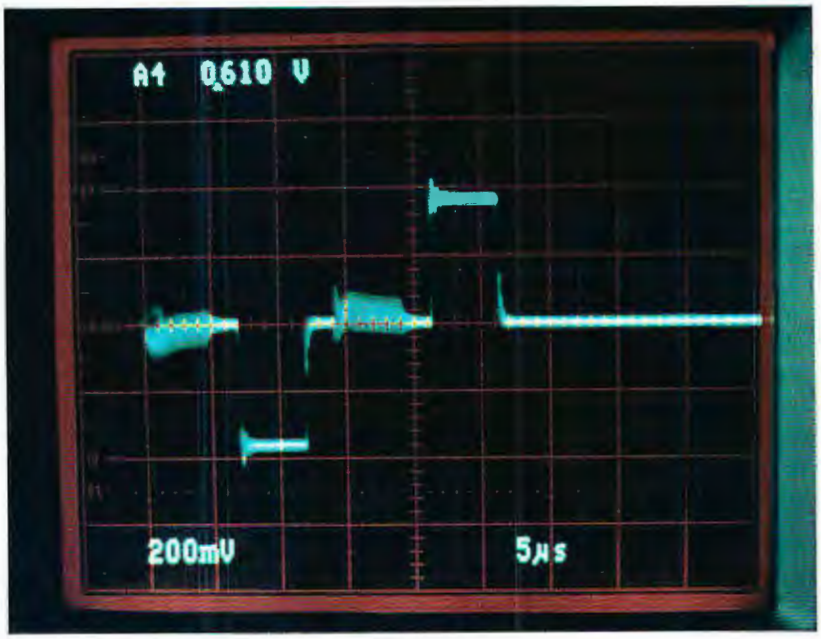
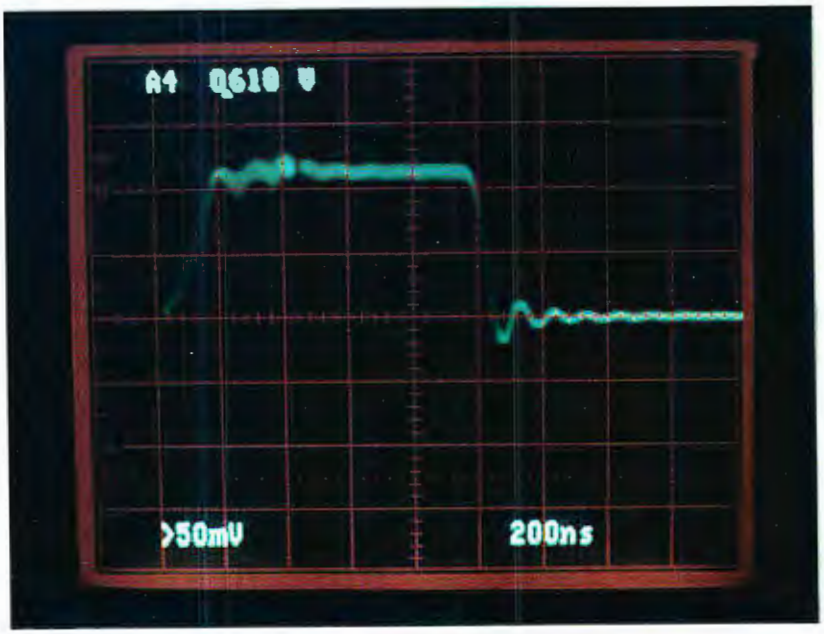


Pulse Shape, 1H 0-90-180-270 Phase Shifts Run on a Varian UNITY-300 spectrometer, this phase detected trace shows the speed of phase settling when switched from one quadrant to the next. The time axis is 5 µsec/div. and each 200W pulse is 5 µsec long followed by 1 µsec dead time during which the phase is shifted 90°. Note that the 0° and 180° phases are far more sensitive and so apparently show more "noise". This is an artifact of the measurement.



Pulse Shape, 1KW at 46MHz, 1µsec Pulse Also run on a UNITY-300 spectrometer, this is the ^{2}D frequency at 7.05T. The time axis is 200 ns and shows the excellent phase stability of the 1KW pulse. The amplitude and phase are 90% stable at 200 ns and are 100% stable by 400 ns. Fall Time is $\sim$ 50 ns.

University of Delaware

DEPARTMENT OF CHEMISTRY
NEWARK, DELAWARE 19716

August 18, 1989
(received 8/23/89)

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

Banging One's Head Against the Wall -- Relaxation in Tiny Spaces

Dear Barry,

We put spins in some difficult situations here at Delaware, so it's rather nice for them to relax once in a while. One of the interesting nuclei we have investigated is xenon-129, as is the vogue nowadays in zeolites. I am interested in the fact that xenon certainly has a much shorter spin-lattice relaxation time in these samples than does bulk xenon gas, although to my knowledge no one has reported a measurement. In the figure we show our measurements of T_1 as a function of the inverse uptake for xenon in Y zeolite at 297K. We know paramagnetic centers contribute to some degree. One can understand the data if one assumes rapid exchange between xenon in two areas where T_1 is different. When one site is saturated, the dependence of the figure is predicted. What the two areas are, we cannot be sure at the moment, but it seems likely that regions near the surface of a pore and in the middle of the pore have different environments, as has been predicted theoretically.[1] Thus, these would seem to be candidates for the two regions between which exchange is occurring.

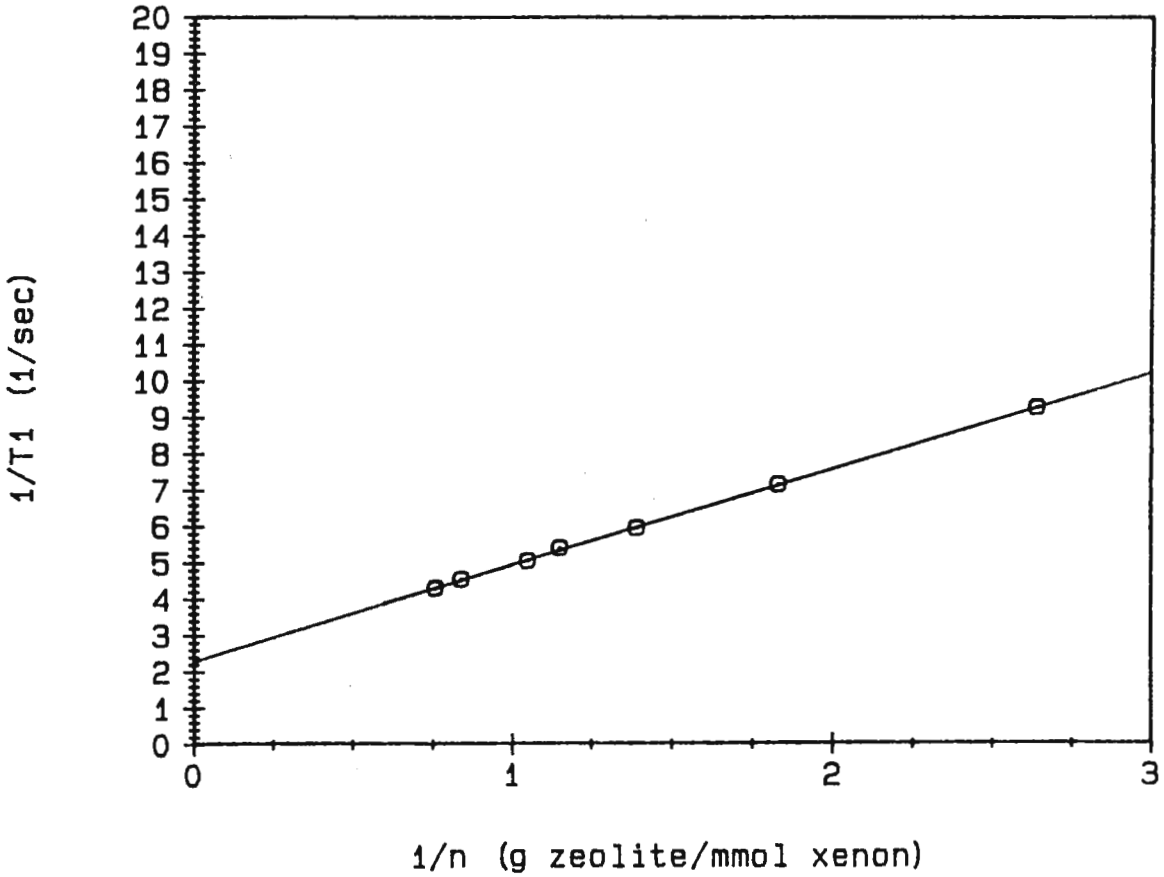
Relaxation can be fun after measuring chemical shifts of xenon. It may also give us some insight into the nature of the collisional processes that are the underlying causes of the changes we see in the xenon NMR spectra as a function of the uptake. We are continuing this project with the idea that it will complement measurement of xenon chemical shifts in these sorts of systems. Perhaps others have interest in these kinds of experiments as a way of studying interactions with walls of zeolites.

Yours truly,

Cecil

Cecil Dybowski
Professor of Chemistry

[1] Bug, A. L. R. *Internat. J. Thermophys.* **1989**, *10*, 469.



RELAXATION TIME OF XENON-129 VERSUS INVERSE UPTAKE FOR XENON IN Na-Y ZEOLITE.

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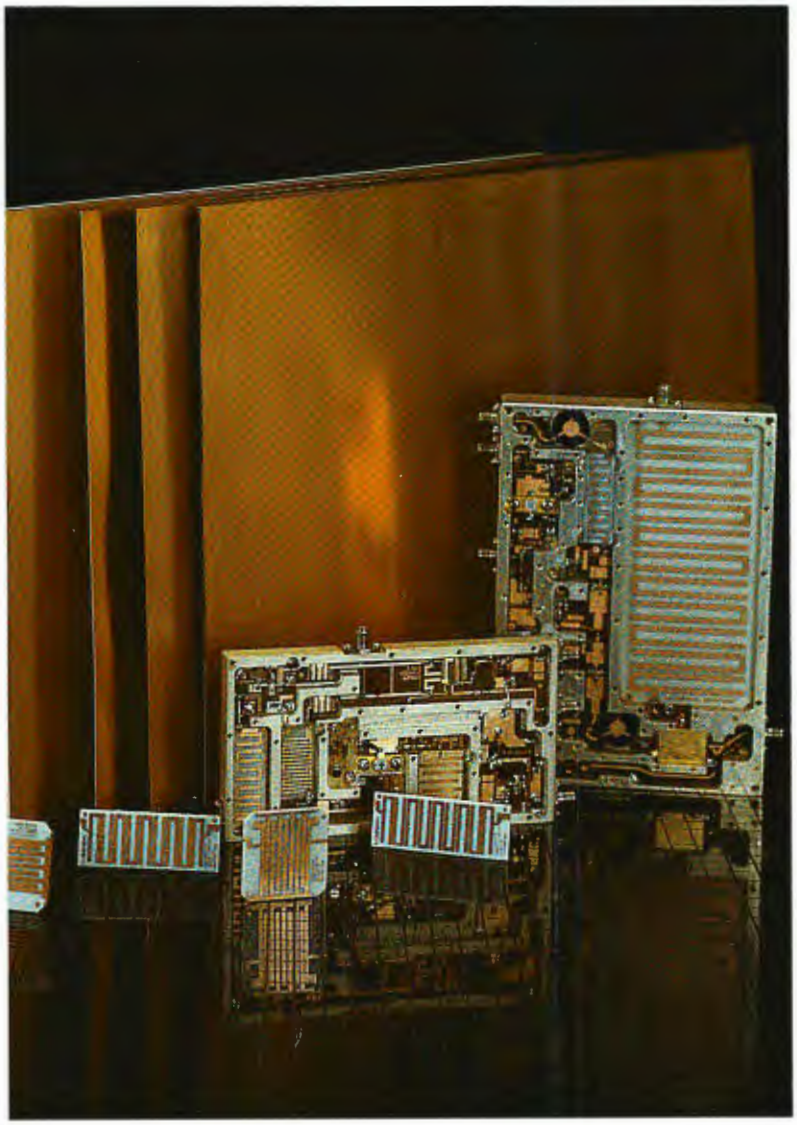

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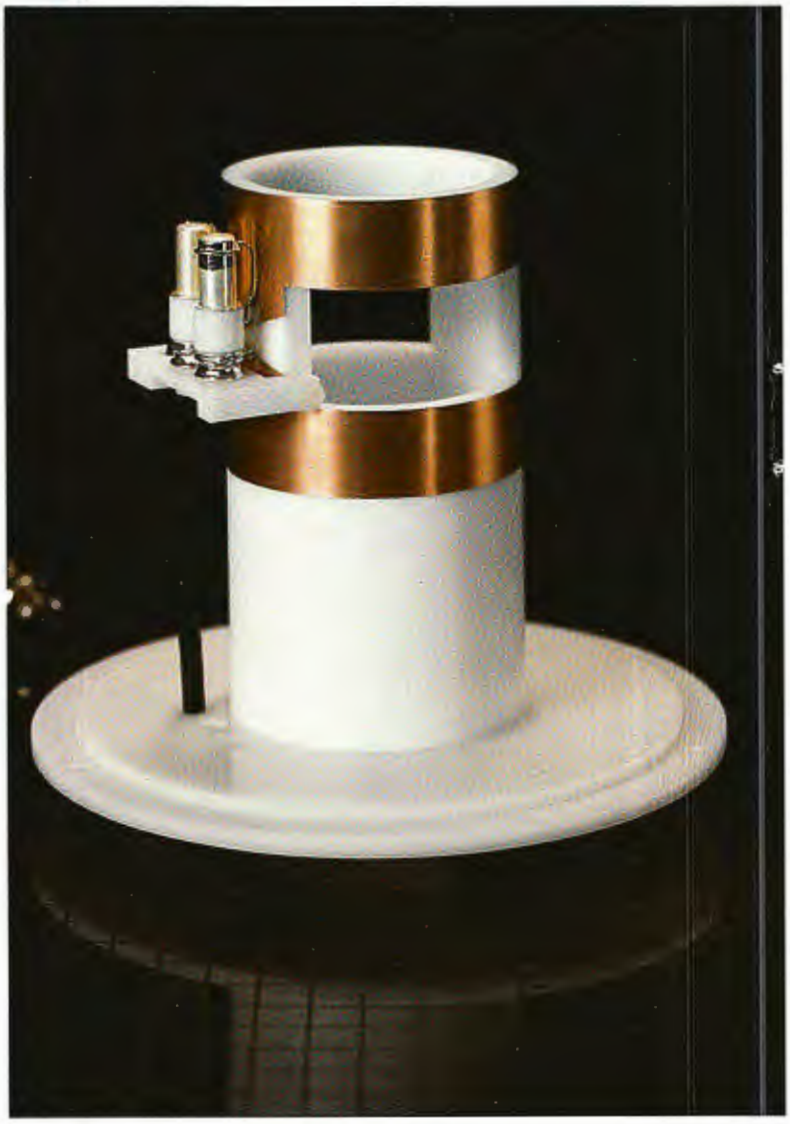

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Dr. B. L. Shapiro
TAMU Newsletter
966 Elsinore Court
Palo Alto, CA 94303

July 16, 1989
(received 7/22/89)

Semi-automatic Analysis of NMR spectra

Dear Dr. Shapiro,

As anyone who has done more than a few soon discovers, analyzing an NMR spectrum can be a bit tedious. This is especially true with so-called ultra high resolution spectra of small molecules, where one may have anywhere from several dozen to several hundred resolved peaks for a given spin system. Programs that perform automatic analysis based on the digitized spectrum relieve all tedium. However, they are often overwelmed by the data required for these spectra (30 to 80 sec. acquisition times, 32k to 512k data points after zero filling) in order to see splittings on the order of 0.025 Hz. Thus, we have modified the NUMARIT (1) program to do semi-automatic analysis.

An initial guess at the spectral parameters still has to be made, but this is usually not too difficult, especially as one is often doing a series of related molecules. You supply all the experimental peak frequencies (usually a modified peak pick listing), but need assign only enough transitions to define the spectral parameters that are to be optimized. The program ignores assignments whose differences are greater that a given number times the current rms deviation, and re-assigns experimental peaks whose differences are less (intensity is not takes into account at the moment). As usual, this is repeated until the rms deviation converges, generally within 10 iterations.

As an example, consider the analysis of t-butylbenzyl ether at 300 MHz. The initial guess was made based on parameters for benzyl alcohol. Seventy peaks were initially assigned, out of about 400 that were picked (the minimum intensity was slightly above the noise). The anaylsis converged in 7 iterations with an rms deviation of 0.0068, with 208 out of 279 ring transitions assigned. This took about 13 sec. on an Amdahl 5870, or about 5 min. on a 20 MHz pc. Since the initial guess was fairly good, the program was not confused by the impurity peaks due to benzyl bromide (starting material) in the 2205 to 2155 Hz. region. The spectral parameters are also consistent with other benzyl ethers analysed in this lab.

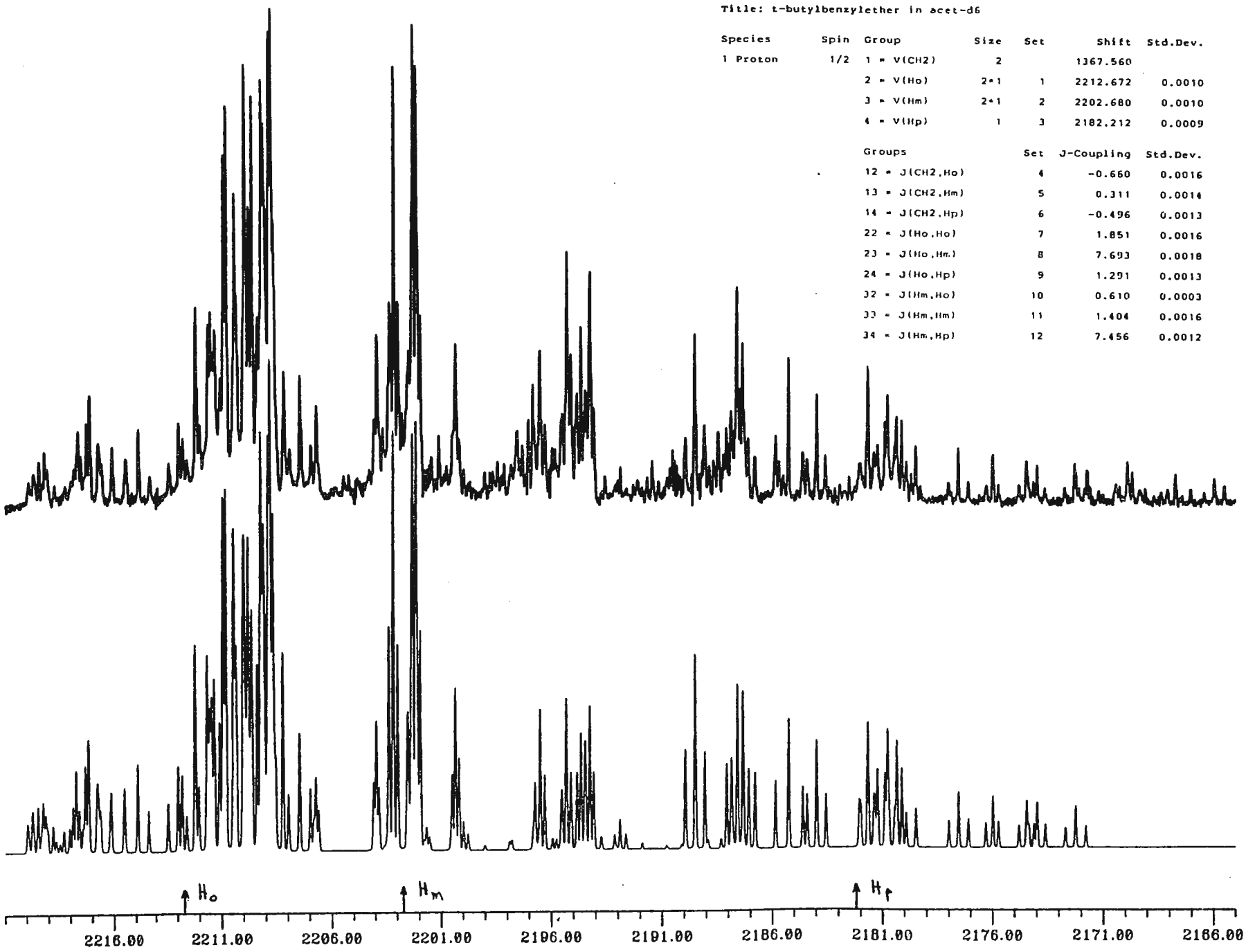
Please credit this to Ted Schaefer's account.

1) J. S. Martin and A. R. Quirt, J. Magn. Reson. 5 (1971), 318
The NMR program library. Daresbury Laboratory, Daresbury U.K.

Yours sincerely,

Rudy

Rudy Sebastian


Title: t-butylbenzylether in acet-d6
Species Spin Group Size Set Shift Std.Dev.
1 Proton 1/2 1 = V(CH2) 2 1367.560
2 = V(Ho) 2*1 1 2212.672 0.0010
3 = V(Hm) 2*1 2 2202.680 0.0010
4 = V(Hp) 1 3 2182.212 0.0009
Groups Set J-Coupling Std.Dev.
12 = J(CH2,Ho) 4 -0.660 0.0016
13 = J(CH2,Hm) 5 0.311 0.0014
14 = J(CH2,Hp) 6 -0.496 0.0013
22 = J(Ho,Ho) 7 1.851 0.0016
23 = J(Ho,Hm) 8 7.693 0.0018
24 = J(Ho,Hp) 9 1.291 0.0013
32 = J(Hm,Ho) 10 0.610 0.0003
33 = J(Hm,Hm) 11 1.404 0.0016
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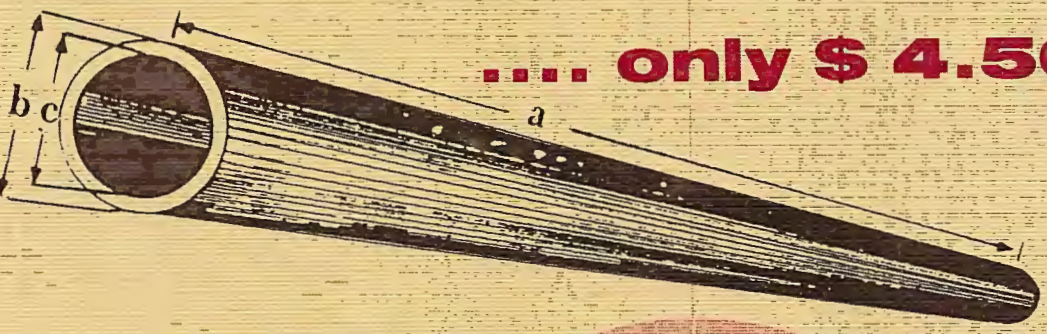

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100-299.....$2.45 ea.
300 +.....$2.40 ea.

No. XR-55 PRECISION FOR medium and high resln. NMR

Standard tube length: 178mm (7 inches);
o.d. 4.97 ± 0.025mm (0.001 in.)
i.d. 4.20 ± 0.025mm (0.001 in.);
camber ± 0.03mm (0.0015 in.);
For additional length, add $0.08 per cm ($0.20/in)

1-99 tubes...$2.20 ea.
100-299.....$2.00 ea.
300 +.....$1.90 ea.

No. 505-P PRECISION for medium and high resln. NMR

Standard tube length: 178mm (7 inches);
o.d. 4.97 ± 0.03mm (0.001 in.);
i.d. 4.20 ± 0.03mm (0.001 in.);
camber ± 0.04mm (0.002 in.);
For additional length, add $0.08 per cm ($0.20/in)

1-99 tubes...$1.80 ea.
100-299.....$1.75 ea.
300 +.....$1.70 ea.

No. 502 THROWAWAY TYPE

Standard tube length: 178mm (7 inches)
o.d. 4.97 ± 0.05mm (0.002 in);
i.d. 4.20 0.05mm (0.002 in);
camber ± 0.07mm (0.003 in);
For additional length, add $0.08 per cm ($0.20/in)

1-99 tubes...$0.80 ea.
100-299.....$0.75 ea.
300 +.....$0.70 ea.

LARGE VOLUME NMR SAMLE TUBES

10mm o.d. *THIN WALL* NMR SAMPLE TUBES

No. 1008-UP ULTRA PRECISION for ultra high resolution NMR

Standard length: 178mm (7 inches);
o.d. 10.00 ± 0.013mm (0.0005 in.);
i.d. 8.76 ± 0.025mm; (0.001 in.)
camber ± 0.007mm (0.0003 in.);
For additional lenght, add $0.20 per cm ($0.50/in.).

1-5 tubes....$14.50 ea.
6-25.....$13.75 ea.
26 +.....$12.95 ea.

No. 1005-P PRECISION for medium and high resln. NMR

Standard length: 178mm (7 inches);
o.d. 10.00 ± 0.013mm (0.0005 in.);
i.d. 8.76 ± 0.025mm (0.001 in.);
camber ± .013mm (0.0005 in.);
For additional length, add $0.20 per cm ($0.50/in.).

1-5 tubes....$9.50 ea.
6-25.....$9.25 ea.
26 +.....$9.00 ea.

20mm o.d. *THIN WALL* NMR SAMPLE TUBES

No. 2005-P PRECISION for medium and high resln. NMR

Standard length: 178mm (7 inches);
o.d. 20.00 ± 0.01mm;
i.d. 17.70 ± 0.02mm;
camber ± 0.03mm.
For additional lenght, add $1.00 per cm ($2.50/in.).

1-5 tubes....$38.00 ea.
6 +.....$37.25 ea.

NOTE: Other tube sizes available, please inquire.

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PTFE Machined Tube Caps
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Positions Available. Spectral Data Services, Inc. has two openings for NMR spectroscopists. Duties include operation and maintenance of three high field spectrometers, as well as data analysis and customer relations. B.S. or Ph.D. in physical science required. Salary negotiable. Resumes to: Dr. Gary L. Turner, Spectral Data Services, Inc. 818 Pioneer, Champaign, IL 61820; phone (217)352-7084.

OPPORTUNITIES IN NMR RESEARCH

Several NMR positions are currently available in the Biological Chemistry Department at the University of California, Davis.

Postdoctoral

in vivo: **research focuses on applying high resolution NMR/imaging techniques to study intermediary metabolism. Projects include the role of ion transport in ischemic myocardium, key metabolic events affected by photoactivated anti-tumor agents used for gliomas, regulation of metabolic fluxes in transgenic animals, and spectroscopic development to observe metabolic fluxes in a localized tissue region. Perfused cells, organs, and intact animal studies are planned.**

protein structure: **questions center on structure/function interaction and the process of folding: the projects include 1) structural determination of peptide inhibitor analogs of c-AMP dependent kinase with 2-D NMR and correlation between the biochemical function and specific amino acid perturbations. 2) mapping the structure of ribosomal protein in vitro and in the intact ribosome in order to deduce specific functional role in translation. 3) defining the interaction of structural perturbation and protein folding in the model SNase protein, both wild type and different mutant classes.**

Engineer **maintaining and developing the NMR instrumental capabilities.**

Applications should include curriculum vitae and references. Both applications and inquiries should be direct to:

Dr. T. Jue
Med: Biological Chemistry
University of California, Davis
Davis, CA 95616

INDUSTRIAL POSITIONS IN PROTEIN AND OLIGONUCLEOTIDE NMR. These are well funded start ups on both coasts studying ligand/receptor interactions and RNA tertiary structure as a basis for rational drug design. Interested parties should call or write to Marc Andelman , BIOSOURCE Inc. , 118 Washington St. , Holliston, MA 01746, telephone (508)-429-8414. BIOSOURCE is an employer paid recruiting firm that specializes in positions with the biotechnology and pharmaceutical industries.

TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 372
September 1989

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Mailing Label Adornments.

If the mailing label on your envelope of this issue is adorned with a large **red dot** or circle: this decoration means that no further issues will be sent until a technical contribution has been received.

If the mailing label on your envelope of this issue is adorned with a large **red "X"**: this decoration means that your 1989-90 subscription fee has not been received as of 11 September, and that your subscription will expire or be suspended unless payment (or some definite word about payment) is received by 23 October (for U.S. and Canadian subscribers) or 17 November (for overseas subscribers). I hope all will understand both that the Newsletter has bills to pay and that my time and patience for the collections game are limited.

Subscribers located at government agencies are asked especially for their *active* assistance in dealing with their disbursing offices, for I am increasingly reluctant to drain my time with the long back-and-forth paperwork which *some* agencies seem to enjoy. Thanks for your help.

Page Length Request.

Attention overseas subscribers: If you must use paper which is longer that 11", *please* take care that nothing appears below 10" (25.5 cm) on your pages. It is costly to make reductions. Thank you.

B.L.S.
31 August 1989

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.

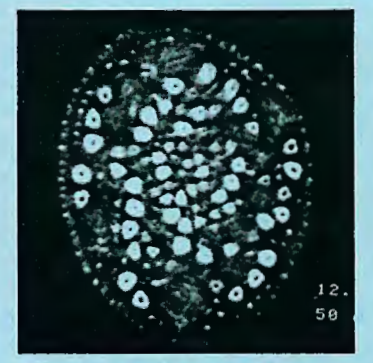

Fig. 1—Agapanthus bud
Matrix 256 × 256, TR 200
Slice 2 mm, TE 30
FOV 12.8 mm, NEX 4,
45° Tip Angle DEFT
Sequence

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.

GE NMR Instruments

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WEST GERMANY 4969 760 7431, TELEX 041 2002 GEG

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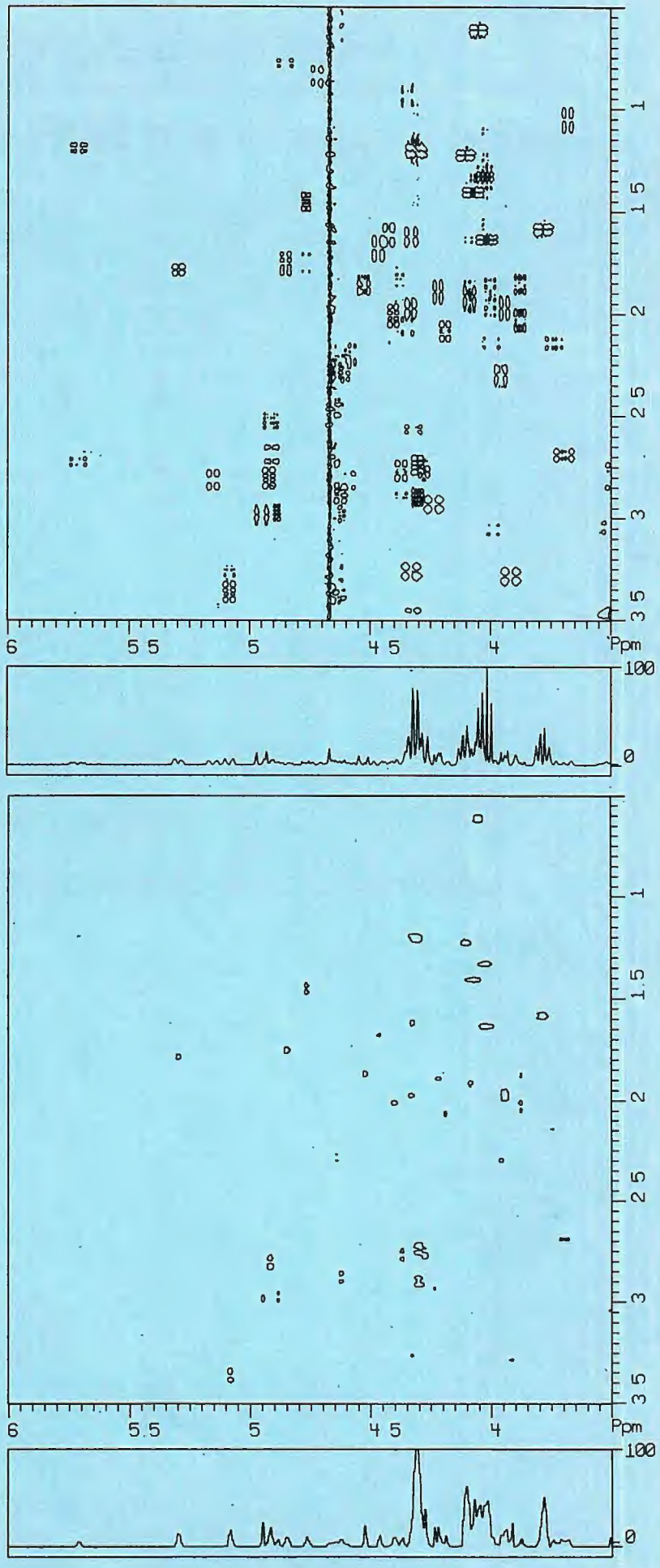
VPLX

A GSX UPGRADE

JEOL USA introduces the VPLX data processing package, our latest upgrade to the GX and GSX NMR spectrometers. When used with the latest network options of Multi-PLEXUS, VPLX provides the power and speed of a VAX™ and eliminates the need to learn a new set of software commands.

In addition to allowing for off-line processing, VPLX offers advanced functionality such as MEM/LPZ and Symmetry Filtering. The top data shows the normal NH to alpha region in a double quantum filtered COSY of BPTI in water. This matrix was produced on a GSX-400, processed on VPLX, and printed on a laser printer. The bottom data is identical to the first with the exception that a symmetry filter has been applied to the matrix. This symmetry filter discriminates on the basis of the known phase relationship of true COSY peaks. Each of the COSY peaks that passes through the filter is reduced to a centroid representation.** This filtering allows for the rapid elimination of spurious cross peaks and is the first step necessary for computer based spectral interpretation.

For more information, contact JEOL.



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**JC Hoch, S Hengyi, M Kjaer, S Ludvigsen, and FM Pousen, "Symmetry Recognition Applied to Two-Dimensional NMR Data", Carlsberg Res., Commun., Vol. 52, p.111, (1987).