TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 365
February 1989

Continued on page 72

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Isotopic Purity (%D)	Density (g/cc)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetic-d[illegible]	[illegible]$_3$CO[illegible]D	[illegible]	1.1[illegible]	17[illegible]	[illegible]8	0.551 (32)
D-120	Acetic Acid-d[illegible]	[illegible]	[illegible]				
D-13	Acetone-d_6	CD_3COCD_3	99.8%	0.87	-94	57	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129							
D-14							[illegible]543 (20)
D-21							[illegible]0.611
D-122							
D-130							
D-28	Choloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

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VARIAN

BOX/500 SHEETS

Cat. No.	Chart Size	Instrument Model	Type
WCV-100 (S-[illegible])	11" X 26"	HA-100, HA-[illegible], HA-[illegible]D	Gridded-Two Color
WCV-60 [illegible]	[illegible]	A-60, [illegible]-60, A-60	Gridded-Two Color
WCV-XL ([illegible])	[illegible]	[illegible]	[illegible]
WCV-XLFT-[illegible]	[illegible]	XL-[illegible] (CW 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
WC-11[illegible]	[illegible] X 17"	All Models [illegible] 16 1/2" or 16	Blank

Use Plotter Paper and Pens?
WILMAD HAS YOUR CHART!

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.

Searching for the Unusual Requirement?
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FORTHCOMING NMR MEETINGS

San Francisco Symposium - "In Vivo Magnetic Resonance Spectroscopy II", March 31 - April 2, 1989; San Francisco, California; See Newsletter 363, 17.

30th ENC (Experimental NMR Conference), April 2-6, 1989; Asilomar Conference Center, Pacific Grove, California; Conference Chair: A. N. Garroway; Contact Ms. Judith A. Watson, ENC Conference Center, 750 Audubon, East Lansing, MI 48823; (517) 332-3667. See Newsletter 362, 69.

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

9th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, July 10-14, 1989; University of Warwick, Coventry, England; Contact: Dr. John F. Gibson; (01) 437-8656; See Newsletter 364, 72.

NMR Spectroscopy In Vivo (Clinical Applications), July 10-12, 1989; Lyon France; Contact Prof. M. Amiel - see Newsletter 364, 73.

10th ISMAR Conference, July 16-21, 1989; Morzine (Haute-Savoie), France. (Note the newly announced location.); Contact: P. Servoz-Gavin, Departement de Recherche Fondamentale, Centre d'Etudes Nucleaires de Grenoble, B.P. 85X, 38041 Grenoble Cedex, France.

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

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

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. 367 (April) ——— 17 March 1989
No. 368 (May) ——— 21 April 1989
No. 369 (June) ——— 19 May 1989
No. 370 (July) ——— 16 June 1989

UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den 23.12.1988
Morgenstelle
Telefon (0 70 71) 29 67 14
(received 12/30/88)

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

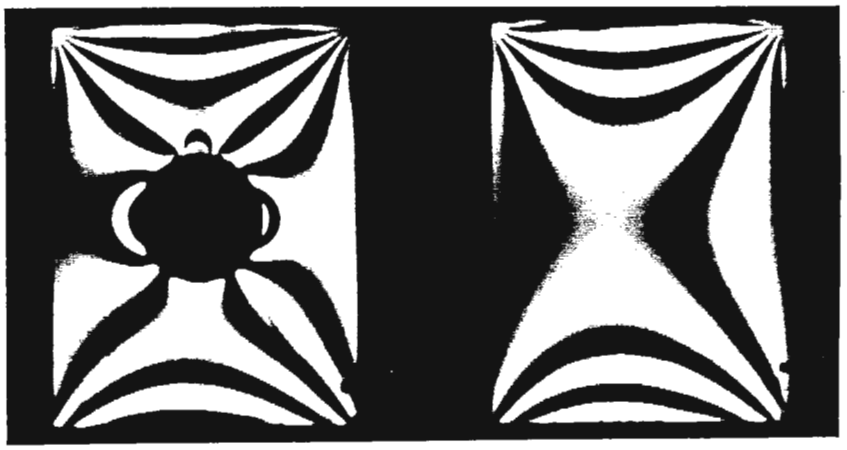
Magnetic field imaging with a 1.5 Tesla whole body imager

Dear Barry,

continueing in our efforts on quality control of magnetic resonance imagers we have built up an imaging sequence called MAGNEX, which allows to obtain an image of the magnetic field distribution within the sample. It consists of a frequency selective excitation pulse followed by a standard spin echo imaging sequence.
In the figures the dark lines correspond to equal frequency, the frequencies of adjacent lines differ by 32 Hz, that means the B - field changes by 0.5 ppm. The typical behaviour of the B - field whithin a cylindrical sample and the field changes due to a sphere containing Cu^{2+} doped water can be seen.
Whith this method we can easily observe field changes of different origin also in the human body.

Sincerely

Otto Lutz Wulf-Ingo Jung Karin Müller Markus Pfeffer



MAGNEX images of cylindrical samples (Ø: 90 mm, height: 120 mm) containing slightly Cu^{2+} doped water; on the left, the sphere (Ø: 35 mm) contains 0.1 molal aqueous $CuSO_4$ solution. Slice thickness: 5 mm, measuring time: 2 min.

INTRODUCING.....
NMR SOLVENTS

from

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			10 g	14.
			5 x 10 g	69.
			10 x 10 g	135.
82-05012	Acetonitrile-d_3	99.8	10 x 1 g	22.
			10 g	22.
			5 x 10 g	100.
82-84077	Benzene-d_6	99.6	10 x 1 g	18.
			10 g	18.
			5 x 10 g	75.
			10 x 10 g	145.
82-80556	Chloroform-d	99.8	100 g	18.
			5 x 100 g	80.
			10 x 100 g	142.
			1 kg	135.

CAT. NO.	PRODUCT	ENRICHMENT MIN. ATOM % D	QUANTITY*	PRICE† U. S. $
82-70001	Deuterium Oxide	99.9	100 g	45.
			5 x 100 g	215.
			10 x 100 g	390.
			1 kg	375.
82-70901	Deuterium Oxide	99.8	**min.** 10 kg	3500.
			25 kg	8500.
			50 kg	16250.
82-70002	Deuterium Oxide "100%"	99.96	10 g	15.
			5 x 10 g	50.
84-70001	Deuterium-depleted Water	$<5 \times 10^{-5}$	25 g	25.
			4 x 25 g	90.
			10 x 25 g	200.
			20 x 25 g	300.
			30 x 25 g	400.
			1 kg	500.
82-00807	Dimethyl-d_6 Sulfoxide	99.9	10 x 1 g	12.
			10 g	12.
			5 x 10 g	56.
			10 x 10 g	115.
82-00809	Dimethyl-d_6 Sulfoxide (multi-dose septum vials)	99.9	10 g	12.
			5 x 10 g	56.
			10 x 10 g	115.
82-00061	Methanol-d_4	99.8	10 x 1 g	43.
			10 g	43.
			5 x 10 g	171.
			10 x 10 g	325.

***PACKAGING:** Organic solvents are sealed in glass ampoules to maintain the high quality of the solvents. Dimethyl-d_6 sulfoxide is also available in multi-dose septum vials. The waters are packaged in glass screw-cap bottles, except for the "100%" deuterium oxide, which is packaged in multi-dose septum vials.

†Prices are FOB Miamisburg, Ohio for delivery in North America; please request prices for delivery to the other continents. Minimum order, $50.

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

The other NMR solvents will soon be available; we will keep you informed. In the meantime, please ask us for any compounds in which you are interested. We have many more compounds than are listed in the Interim Price List 3/88 and we are now in a position to carry out many custom syntheses. **Please call us with your requests.**

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University of Illinois
at Urbana-Champaign

School of Chemical Sciences
505 South Mathews Avenue
Urbana, IL 61801

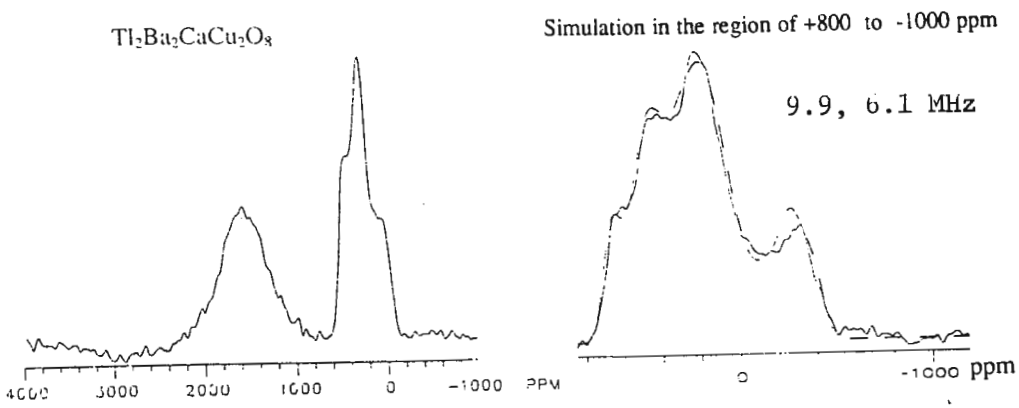
December 12, 1988
(received 12/23/88)

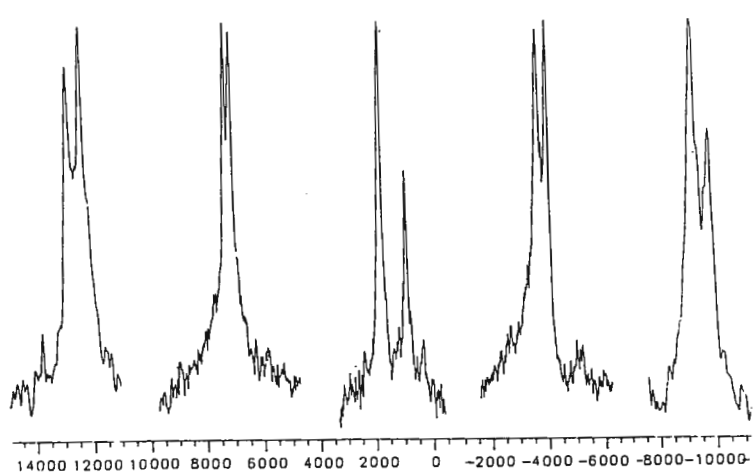
Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Barry:

^{17}O NMR of High-T_c Superconductors

We have been continuing with our recent fascination for O-17 NMR, and high temperature superconductors, and find that O-17 is a generally applicable probe of the electronic environment of all the superconductors we have tried to date. Systems currently under investigation include: $(Ba,K)BiO_3$, $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_8$, and $Tl_2Ba_2CaCu_2O_8$. We have obtained ^{17}O-labelled forms of each material, and recorded ^{17}O NMR spectra at 8.45 and 11.7 Tesla. For $YBa_2Cu_3O_{7-x}$, we have also obtained results on magnetically oriented materials. The following Figure shows a typical result on the Tl-material, together with a computer simulation, plus a composite view of some of the peaks seen with $YBa_2Cu_3O_{7-x}$.





Frequency shift (ppm from H_2O)

Our results can be summarized as follows:

1) For each of the Cu-containing systems, there is a feature which we attribute to the CuO_2 (superconducting) planar site, at about 2000 ppm downfield from H_2O.

2) For each of these systems, a second feature, or set of features, is found in a "diamagnetic" region, at around 200-800 ppm from H_2O, typically, at ~400 ppm. This is close to the isotropic chemical shifts of Y_2O_3, Bi_2O_3 and Tl_2O_3. We attribute all these features to sites other than the CuO_2 planes.

3) Normal state relaxation for each of the CuO_2 planes is much more rapid than for the non CuO_2-plane site(s).

4) Magnetic ordering of the $YBa_2Cu_3O_{7-x}$ system, in epoxy, permits determination of the e.f.g. parameters for O1, 2 and 3. For the planar oxygens (O2,3) in $YBa_2Cu_3O_{7-x}$, our results indicate the following e.f.g. parameters, in MHz:

χ_{xx}	χ_{yy}	χ_{zz}
4.1	6.5	2.4
3.9	6.5	2.6

Yours sincerely,

Eric Oldfield S. Yang C. Coretsopoulos L. Reven H. C. Lee

NMR Spectroscopist/Director of Analytical Services. The University of Illinois at Chicago is seeking an NMR Spectroscopist whose principle responsibility will be the operation and maintenance of the departmental NMR spectroscopy laboratory, including a 400 MHz Bruker, 200 MHz IBM and soon-to-be-purchased additional 300 MHz NMR Spectrometer. In addition, he/she will have oversight responsibility for the departmental mass spectroscopy facility. Collaborative research with faculty is strongly encouraged. Applicants should send a resume and three letters of reference to Jan Rocek, Head, Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680. For full consideration, applications and supportive materials should be received by January 15, 1989.* The University of Illinois is an Equal Opportunity/Affirmative Action Employer.

11/23/88 (received 12/22/88)

*Prof. Rocek has indicated that applications will be accepted after 1/15/89 until the position has been filled.

The University of New Mexico

CENTER FOR NON-INVASIVE DIAGNOSIS
1201 Yale Blvd., N.E.
Albuquerque, NM 87131
Telephone: (505) 277-8512

December 12, 1988
(received 12/21/88)

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

Subject: COSY of Brain Lipids

Dear Barry:

In the never-ending search for useful in vivo applications of proton NMR spectroscopy, our group has been studying the NMR profiles of ceramides found in the brain. Over a dozen disorders are characterized by abnormal catabolism of lipids, and changes in lipid mobility may be an early indicator of hypoxic damage. Brain grey matter is composed of 14% lipid, and white matter 34% lipid. The common lipid carriers include sulfatides, cerebrosides, and sphingomyelin. Sphingomyelin contains a ceramide unit bound to phosphoryl choline, and the ceramide generates atypical proton NMR signals from the hydroxyl and amide moieties near the head group.

The one dimensional spectrum of sphingomyelin (10 mg/mL) dissolved in deuterochloroform is shown in Figure 1. Resonances are generated by the lipid methylene, methyl, allylic, and vinyl protons, as well as the amide proton (6.9 ppm). Additional peaks can be assigned to the choline methyl and the glycerol head group protons. We have performed two-dimensional COSY experiments on this sample to assign the lipid signals between 1.5 and 2.0 ppm, and identify the chemical shifts of the beta and gamma protons. A typical spectrum is presented in Figure 1. Cross peaks are detected among a number of resonances, including methyl, methylene, vinyl, and allylic protons. Of interest, the protons at C2 and C3 of the sphingomyelin resonate at 3.8 and 3.9 ppm, but are only weakly scalar coupled. In addition, the chemical shift of the protons alpha to the amide group resonate at 2.0 ppm rather than 2.3 ppm, which is common for the alpha protons on carboxylic acids. These differences in chemical shift may be useful in monitoring lipid biochemistry in the brain non-invasively.

Sincerely,

Richard H. Griffey

Mark S. Brown

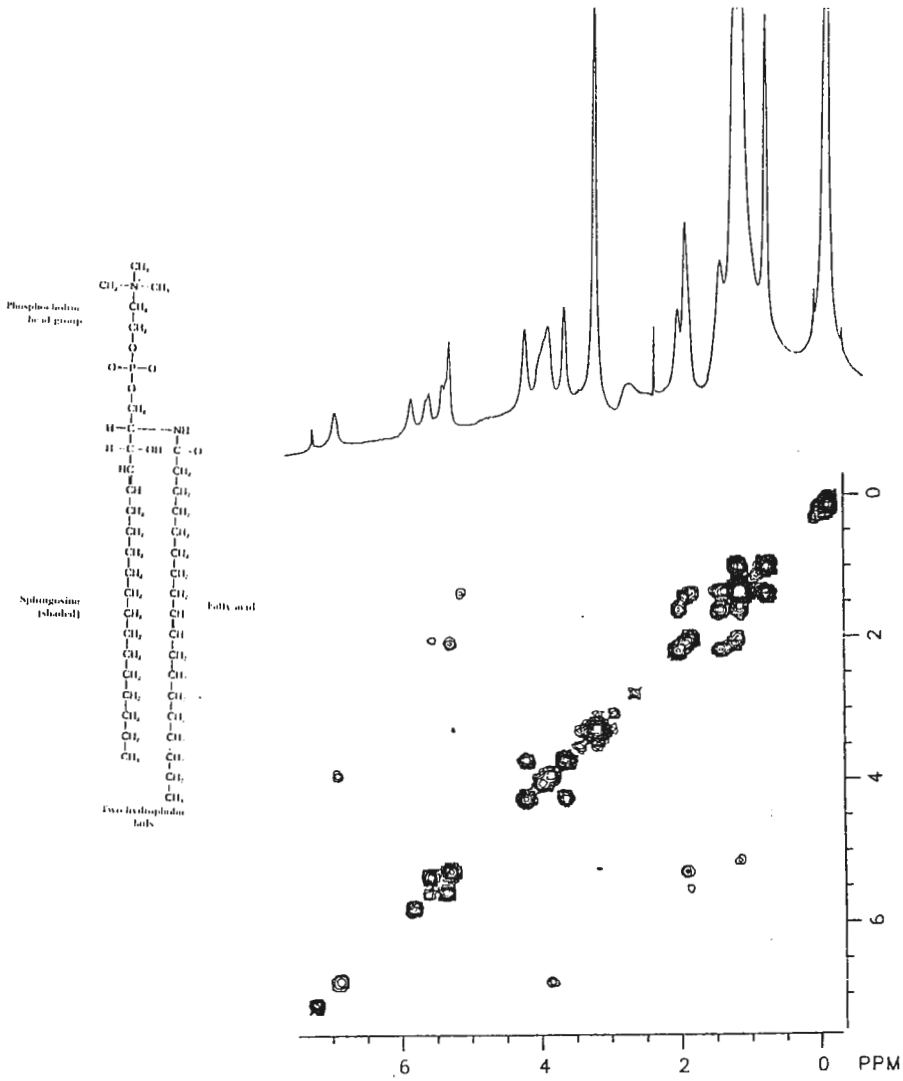


Figure 1. A COSY of a 50 mg/mL solution of sphingomyelin in $CDCl_3$. A total of 4 scans were summed into a 512x256 matrix. Data was multiplied by a sine bell in each dimension. Only a few contours are shown.

POSTDOCTORAL POSITION--NMR AND PROTEIN ENGINEERING

California Institute of Technology

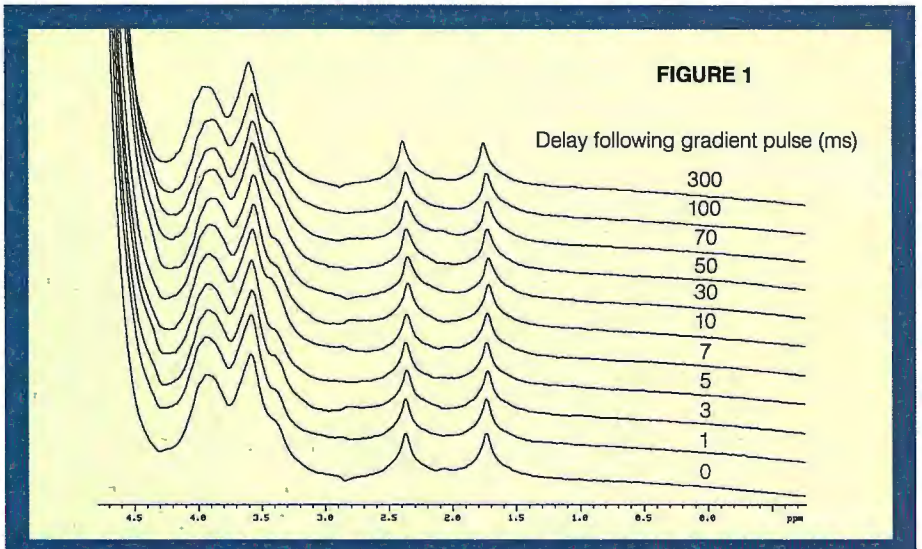
Immediate and future openings for postdoctoral research in protein engineering and NMR applications in protein structure and dynamics. We are designing, constructing, and characterizing synthetic metal-binding proteins and proteins in nonaqueous solvents. Candidates should have a PhD in chemistry or biochemistry and experience with 2D NMR techniques. Instrumentation includes two Bruker AM-500 MHz spectrometers.

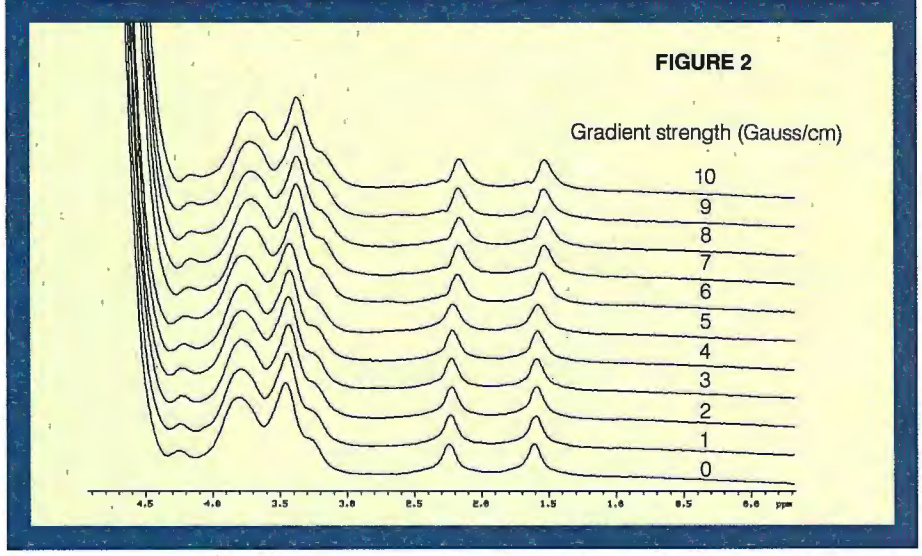
Interested parties should send a resume and names of three references to Prof. Frances Arnold, Division of Chemistry and Chemical Engineering 206-41, Caltech, Pasadena, CA 91125.

High Performance Auxiliary Gradient Coils

Dedicated RF coils, optimized for a specific application or a particular sample or both, have long been a tradition in NMR imaging as well as NMR spectroscopy. Similarly, dedicated gradient coils yield dramatic performance improvements in terms of rise and fall times, maximum gradient strength, duty cycle and eddy currents. Sophisticated eddy current compensation techniques reduce any residual spatial or temporal field variations due to eddy currents to a few hundredths of a percent, thus yielding distortion free spectra and images.

At Spectroscopy Imaging Systems we are able to obtain in-plane resolution of $20\mu \times 20\mu$ in an axial cut through an okra of 1.3 cm diameter. (See image shown on front side.) An enlargement of a portion of a seed capsule within the okra displays a wall thickness of 50μ (inset on front side). The gradient coil used to obtain this excellent performance has a diameter of 125 mm and was mounted in an Oxford Instruments 4.7 Tesla, 330 mm bore magnet without removing the standard set of gradient coils. The auxiliary gradient set is capable of generating greater than 10 Gauss/cm in all orientations using the same gradient power supply as the primary gradient coil.





The excellent control of eddy currents using the smaller gradient insert is demonstrated in Figures 1 and 2. Figure 1 shows a series of spectra of the high field region of a sample containing [2^{-13}C] acetate and [1^{-13}C] glucose in H_2O/D_2O. With the sample in the center of the gradient coil, a 1 second gradient pulse of 1 Gauss/cm was applied. The gradient pulse was followed by a variable delay, a 90° RF pulse and acquisition of the resultant free induction decay. All spectra are essentially undisturbed even at delay times below 10 ms.

Figure 2 shows a typical series of spectra of the same sample at an off-center location in the magnet. A gradient pulse of 5 ms duration with an amplitude range of 0 to 10 Gauss/cm was applied, and the FID recorded at a fixed delay time of 3 ms. The sample was positioned at 22.3 mm off the center, corresponding to local gradient field of 95 kHz. All spectra are virtually undisturbed, even at 10 Gauss/cm.

The University of Alabama at Birmingham
Comprehensive Cancer Center
NMR Core Facility / CHSB B-31
205/934-5696

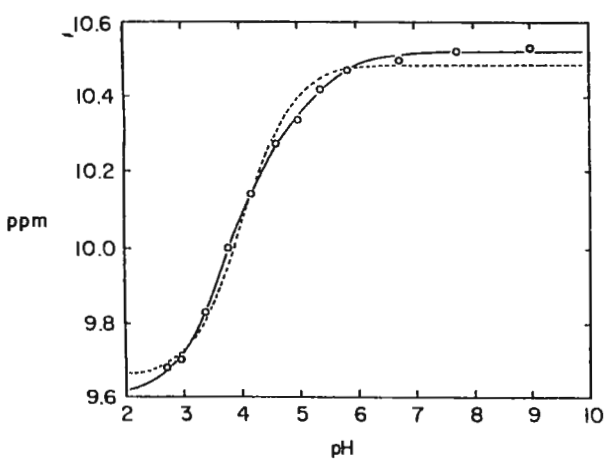
December 29, 1988
(received 1/3/89)

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

pH dependence of indole NH chemical shift in a protein

Dear Dr. Shapiro:

While investigating the pH dependence of proton chemical shifts in the variant-3 neurotoxin from the scorpion Centruroides sculpturatus Ewing, we came across an interesting situation that seemed to merit further examination. This involves the pH dependence of the indole NH proton from the lone tryptophan residue in the protein, viz., Trp-47. In the following figure, the dashed curve indicates the least squares fitting of the experimental data points (open circles) obtained for the ionization of a single acidic group, and it results in a pK_a of 4.04.



Also shown in this figure is the least squares fitting of the same data points (solid curve) corresponding to the ionization of two acidic groups with pK_a values of 3.7 and 5.25. It is clear that the solid curve gives a much better fit than dashed curve. A statistical analysis of the data using Hamilton's R-factor ratio criterion showed that the fitting with a single pK_a could be rejected at better than 99.5% confidence level compared to the fitting with two pK_a values.

The crystal structure shows that the indole NH is indeed in close proximity to the carboxylate groups of Glu-2 and Glu-49. In the 2D-NOESY spectrum of this protein obtained at 500 MHz, we do see a very weak cross peak between the indole NH and one of the β-hydrogens of Glu-2. It is interesting that both the Glu residues exhibit substantial deviations in their pK_a values from the corresponding random coil value of 4.3. The lower pK_a of 3.7 for one of the glutamic acids might be the result of a hydrogen-bonding interaction between its carboxylate group and a proton from a donor group (e.g., Trp-47 indole NH or the hydroxyl proton of a proximal tyrosine). The elevated pK_a of 5.25 for the second Glu might be the result of its spatial proximity to the first acidic group.

Yours sincerely,

N. R. Krishna

N. Rama Krishna, Ph.D.

Weyerhaeuser

Tacoma, Washington 98477
Tel (206) 924 2345

January 10, 1989
(received 1/13/89)

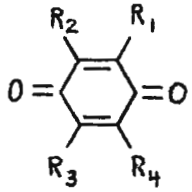
Dr. Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

UNUSUAL DESHIELDING OF METHOXYL CARBONS

Dear Dr. Shapiro:

We have been investigating, of late, reactions between lignin and diazomethane, the initial object being to measure phenolic hydroxyl and carboxylic acid groups in isolated lignins, chlorine-treated lignins, partially delignified wood pulps, and chlorine-bleached pulps. Owing to the low lignin contents of the last two sample types, ^{13}C-enriched diazomethane is used to amplify the analysis. Besides the expected $ArO{*}CH_3$ and $-CO_2{*}CH_3$ peaks at 57δ and 53δ in the ^{13}C NMR spectrum after $*CH_2N_2$ treatment, other new signals appear, such as methyl resonances at about 30δ from methylene insertion at aldehydes to give methyl ketones, and mysterious signals from 61 to 64δ with proton multiplicities corresponding to methyl groups.

Methoxyl carbons with such low shielding are not found in the Sadtler collection and apparently are rare in the literature. We were steered in the right direction by noting that some alkyl methyl ethers have methoxyl signals at 59-60δ. Since we suspected that our samples might contain enols, which methylate with CH_2N_2, we studied some compounds having alkenyl methyl ether moieties. From the benzoquinone data below, it seems that methoxyl substituents on olefinic carbons appear at δ>60 only if another electronegative substituent (e.g., methoxyl or chloro) occurs at the other olefinic carbon. We have not yet looked at open-chain analogs.



R_1	R_2	R_3	R_4	δ_C, $-OCH_3$ Solid	Soln.
OCH_3	H	H	OCH_3	59	--
OCH_3	OCH_3	CH_3	H	61, 64	--
OCH_3	Cl	OCH_3	Cl	64	62

Sincerely,

Larry Amos

Larry W. Amos
Weyerhaeuser Analytical Services

EMORY UNIVERSITY
Department of Chemistry

1515 Pierce Drive
Atlanta, Georgia 30322
404/727-6585

December 30, 1988
(received 1/7/89)

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

GN-600 Installation

Dear Barry:

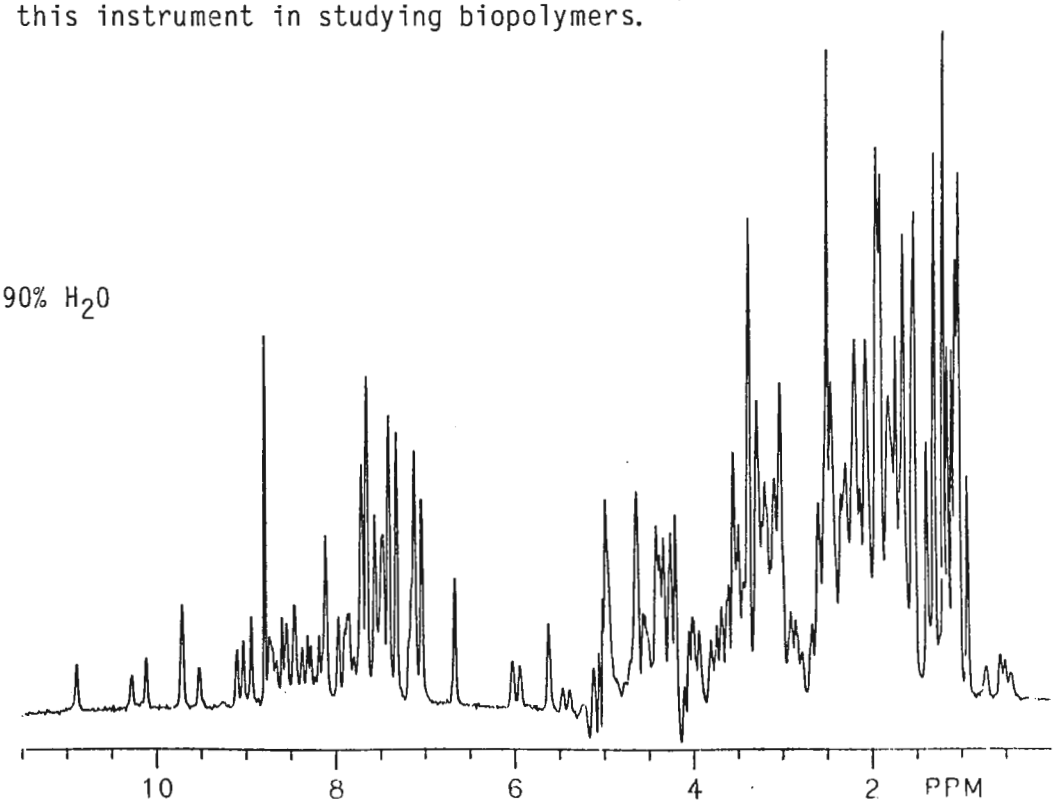
I am pleased to report that the first GN-600 has been successfully installed at Emory. I believe this makes GE the second manufacturer to install a 600 in the field and consequently further raises the level of competition in 600's, hopefully for the benefit of users. The installation went quite smoothly, notwithstanding the elaborate measures for assembling and cooling down such a massive magnet (it weighs over a ton). We have been quite pleased with the performance of the instrument for sensitivity, lineshape and resolution for our proton and broad band probes.

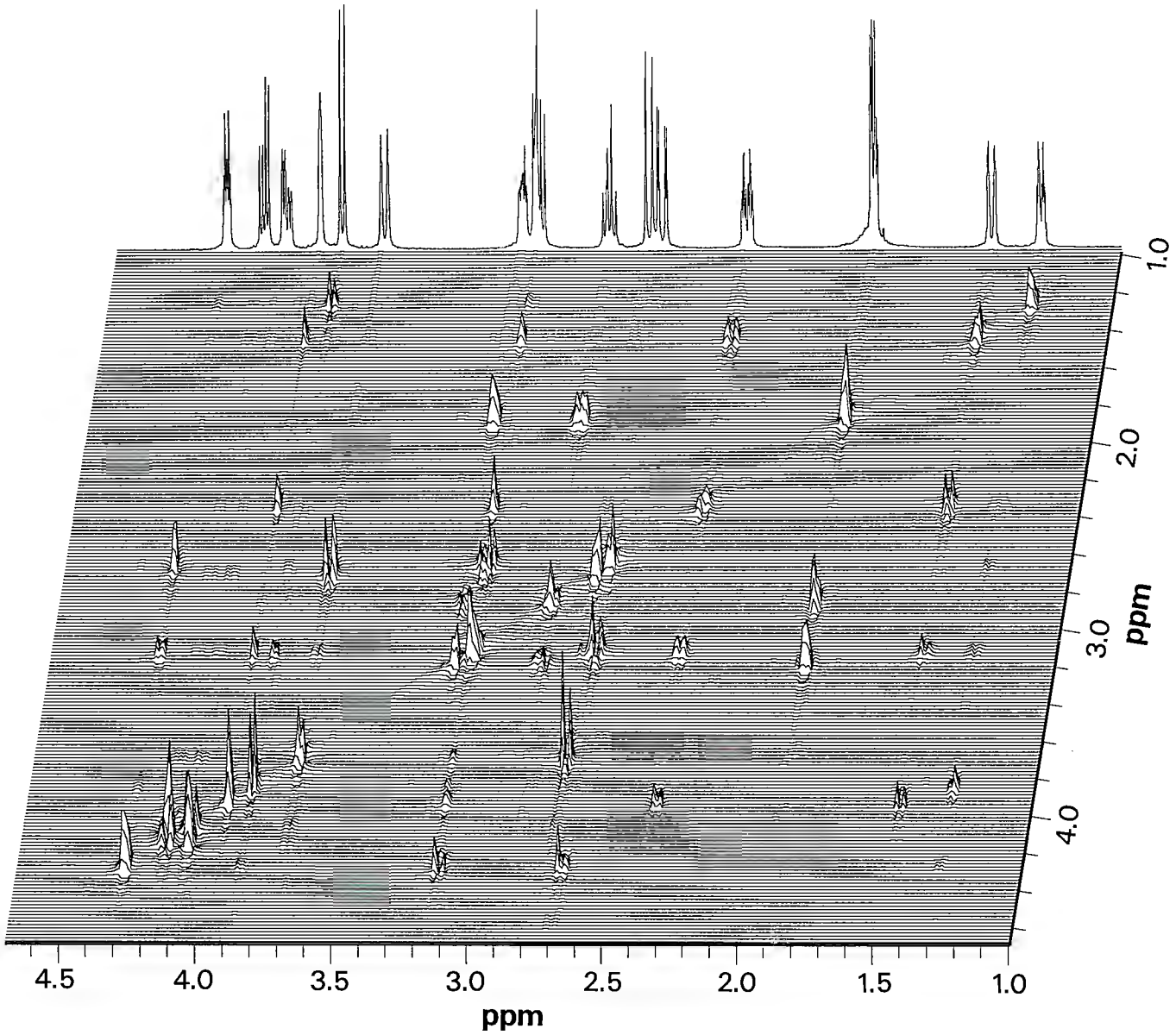
Before the system was shipped from Fremont, GE ran a sample of 2mM BPTI in 90% H_2O to test water suppression. The results were excellent, and readers of the newsletter may have seen this earlier spectrum as part of the GE ad in the December issue. We thought we would try our hand at repeating the result on site to see if it was reproduceable. In December, shortly after the magnet had been run up, we made up our own sample here, and read in the file with the original spectrum taken in Fremont (still on the disk) as a starting point. With only a very modest amount of shimming and parameter adjustment and with less experience with the instrument, we were gratified to observe the enclosed spectrum, which is comparable to the result in Fremont. We feel this augurs well for future prospects of this instrument in studying biopolymers.

Yours,

David Live

2mM BPTI in 90% H_2O





HOHAHA of Strychnine on an Omega 600

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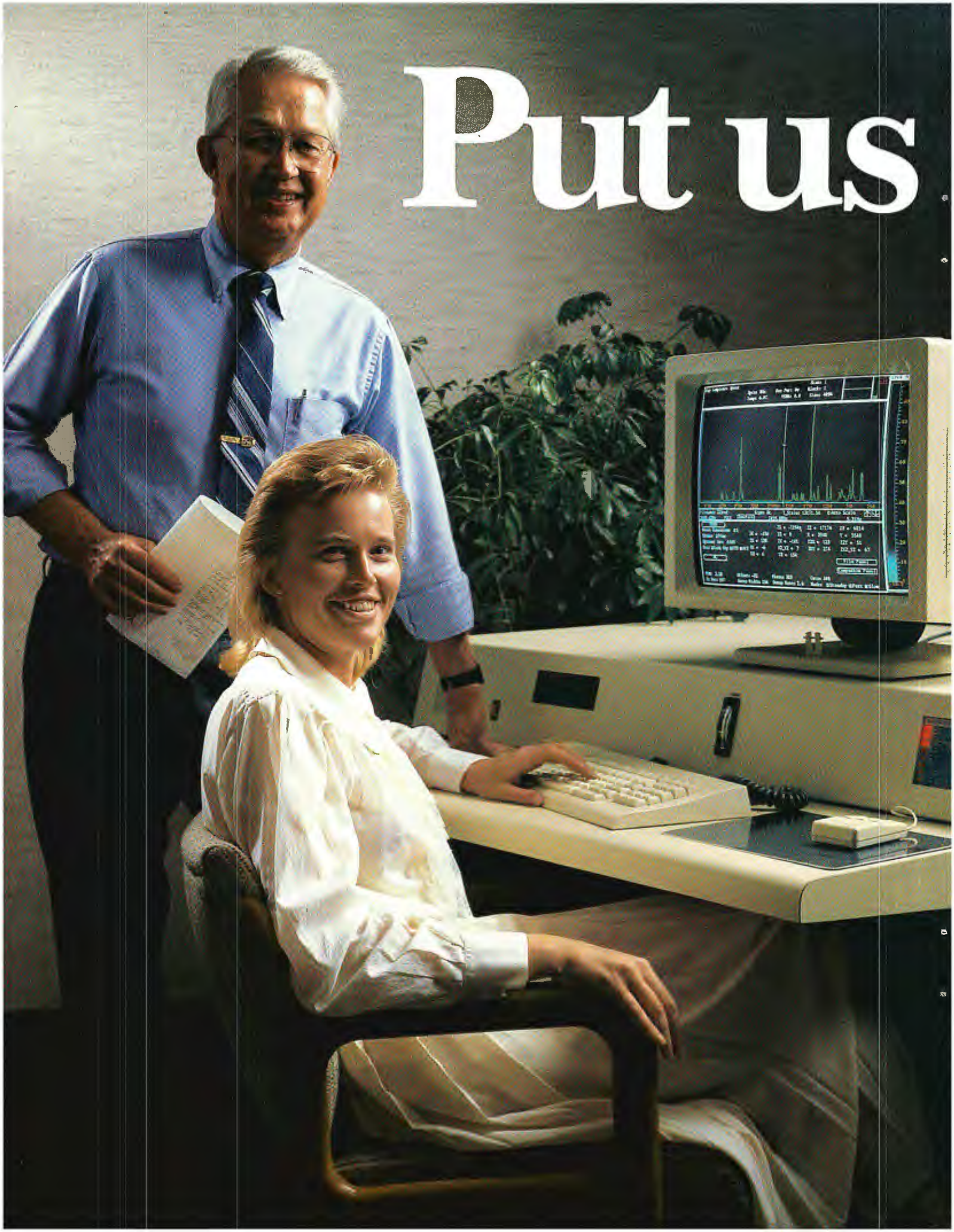
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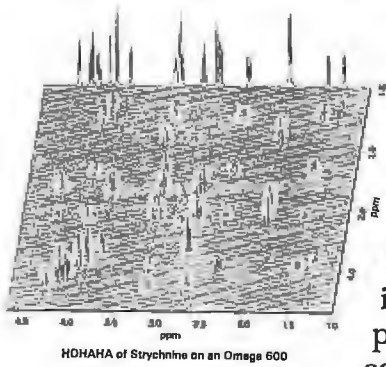

HOHAHA of Strychnine on an Omega 600

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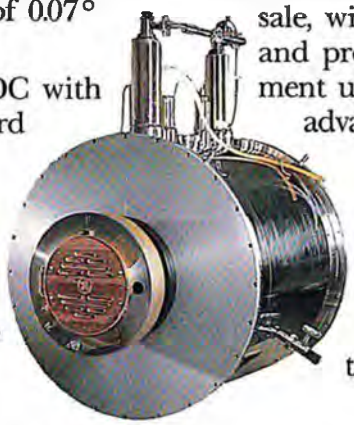

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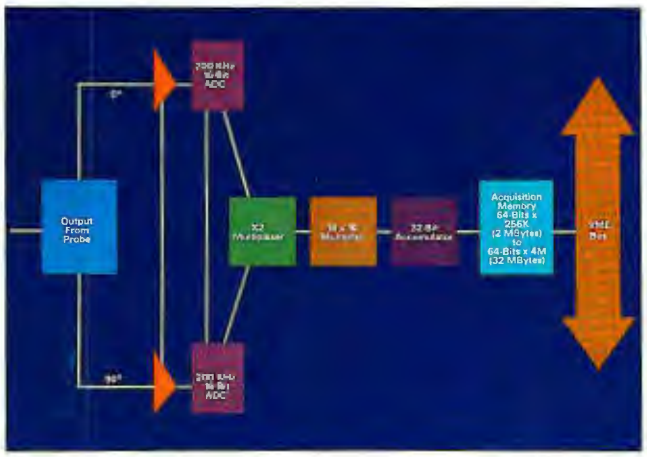

Fig. 1

The Alpha HDR digitizer.

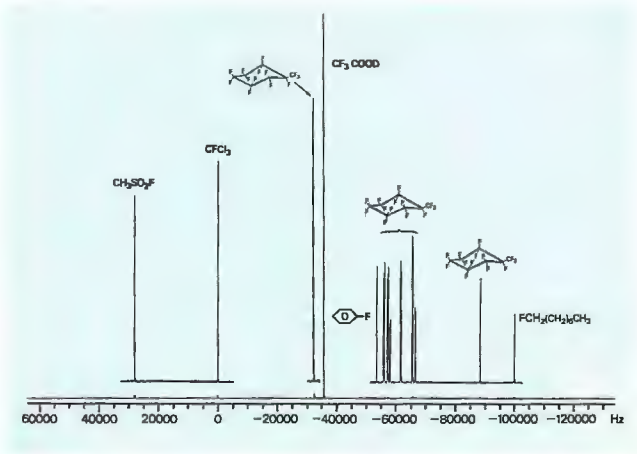

Fig. 2

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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CALIFORNIA INSTITUTE OF TECHNOLOGY

CHEMICAL ENGINEERING 206-41

December 28, 1988
(received 12/31/88)

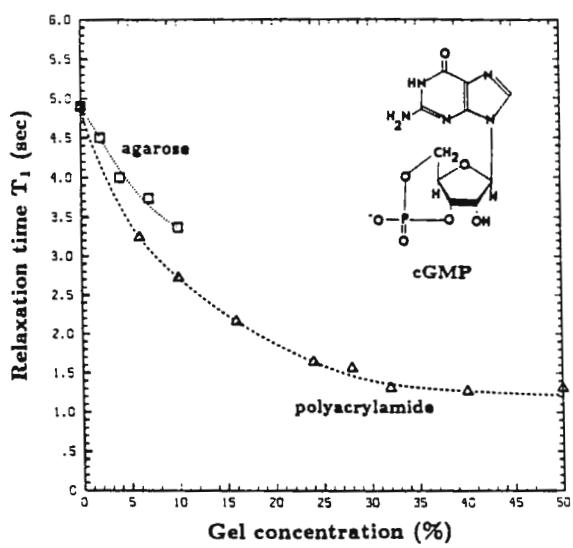
Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

Dear Dr. Shapiro:

Gels are widely used in bioengineering, and the number and importance of applications involving these materials is still increasing. The effort aimed at mapping the human genome, for example, relies heavily on the development of new electrophoretic techniques. Yet our understanding of mass transport in polymeric gels is still incomplete and the effects of the fibrous network or molecular diffusion have not been well characterized.

Using nuclear magnetic relaxation to probe molecular dynamics, we have investigated the effect of gel concentration on the rotational diffusion of cyclic guanosine monophosphate (cGMP) trapped in both polyacrylamide and agarose. The figure reproduces our measurements of the ^{31}P spin lattice relaxation times. Assuming extreme narrowing over the entire concentration range, T_1 is proportional to the effective rotational diffusion coefficient D_r at all gel densities. The results then indicate that the mobility of cGMP in a 25% w/v polyacrylamide gel is only a third of its value in free solution. The smaller decrease in D_r noted in agarose (as compared to polyacrylamide at the same weight fraction) agrees with pore size measurements on these two types of gels. Agarose is known to have a much more open structure with larger voids due to the formation of "suprafibers". In fact, the magnitude of the retardation of a molecule as small as cGMP in such a spacious network is quite remarkable.

Figure 1. ^{31}P spin lattice relaxation time T_1 of cGMP trapped in agarose and polyacrylamide at various gel concentrations. Measurements were performed at 25°C and a Larmor frequency of 81 MHz. Polyacrylamide was crosslinked using 4% bisacrylamide.



Sincerely,

Frances Arnold
Assistant Professor

Ivan Claeys
Research Associate

PASADENA, CALIFORNIA 91125

December 12, 1988
(received 12/24/88)

Professor Bernard Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Dear Professor Shapiro:

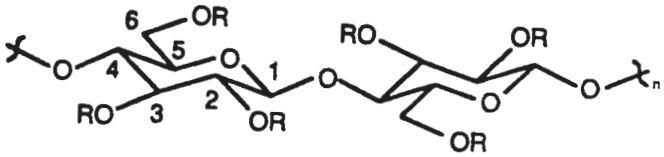
Reference: Solution Conformations of Cellulose Esters

In this contribution, we comment on our approach for determining interproton distances for cellulose esters. The approach we have adopted is similar to that of Mirau et al.[1] Pure-phase 2D NOESY spectra[2] have been acquired at various mixing times on a JEOL Model GX-400 NMR spectrometer. These mixing times are in the intermediate portion of the NOE buildup curve. Peak volumes were determined by two methods: a peak symmetry filter based on low-point symmetrization in the FTNMR software package[3] (henceforth referred to as the Hare method) and the 2-dimensional linear least squares approach of Denk, Baumann and Wagner[4] (henceforth referred to as the DBW method). Diagonal peak volumes at zero mixing time were estimated by extrapolating diagonal peak volumes from the individual mixing time experiments to zero mixing time. The peak volumes were normalized by using the method of Eaton and Anderson.[5] The NOE rate matrices for each mixing time, calculated from the individual volume matrices, were used to calculate the interproton distances. The reference proton distance (1.70 Angstroms) was the distance between geminal methylene protons, H6R and H6S.

A stacked plot of the NOESY spectrum (mixing time = 100 msec) of cellulose triacetate (CTA) is presented in the Figure with peak assignments shown. In the Table are listed fourteen interproton distances determined by using the two peak volume techniques. The average, range and standard deviation for these four determinations of each distance are also shown.

At the 95% confidence limit and based on a Student's t-test, the two methods of calculating peak volumes gave interproton distances that were statistically significantly different for the CTA sample presented here. (For cellulose tributyrate, no statistical difference was found between the Hare and DBW methods.) An F-ratio

Structures for Cellulose Triacetate (R=Ac) and Cellulose Tributyrate (R=Bu)



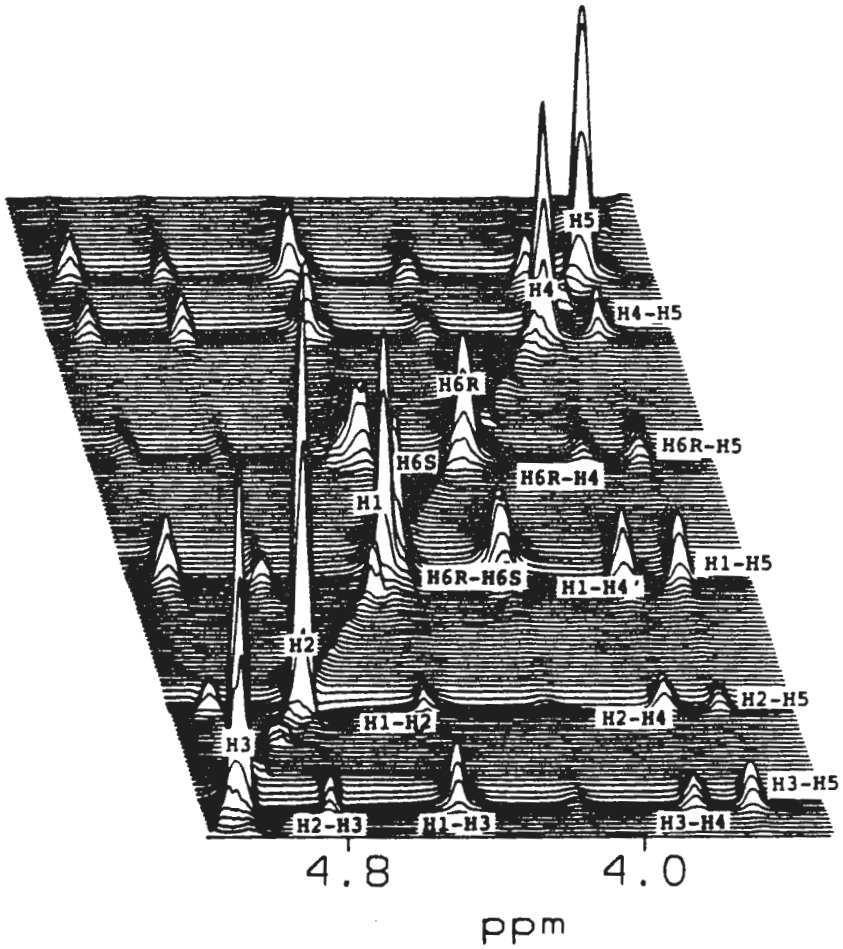


Figure. Stacked plot of the NOESY spectrum of CTA with a mixing time of 100 msec.

Table. Interproton Distances for CTA (0.35 M in Chloroform-d, 25°C)

Protons	Distances (Angstroms) 60[a]	70[a]	80[a]	100[a]	Mean	Range	StDev[b]
Based on DBW method --							
H3-H2	3.56	3.16	2.93	2.74	3.10	0.82	0.35
H3-H1	2.01	2.03	2.04	1.99	2.02	0.05	0.02
H3-H4	2.84	2.70	2.78	2.67	2.75	0.17	0.08
H3-H5	2.37	2.36	2.36	2.32	2.35	0.05	0.02
H2-H1	3.46	2.86	3.06	2.85	3.06	0.61	0.28
H2-H4	2.46	2.47	2.46	2.41	2.45	0.06	0.03
H2-H5	3.49	3.24	3.21	3.09	3.26	0.40	0.17
H1-H4'	1.98	2.02	2.03	1.94	1.99	0.09	0.04
H1-H5	2.07	2.10	2.11	2.02	2.08	0.09	0.04
H6S-H4	2.35	2.31	2.32	2.47	2.36	0.16	0.07
H6S-H5	2.26	2.24	2.25	2.32	2.27	0.08	0.04
H6R-H4	3.36	3.42	3.34	3.03	3.29	0.39	0.18
H6R-H5	2.81	2.82	3.05	2.78	2.86	0.27	0.12
H4-H5	2.34	2.35	2.35	2.34	2.34	0.01	0.01
Based on Hare method --							
H3-H2	3.49	3.35	3.22	3.05	3.28	0.44	0.19
H3-H1	2.25	2.24	2.25	2.20	2.24	0.05	0.02
H3-H4	3.22	3.03	2.91	2.94	3.02	0.31	0.14
H3-H5	2.62	2.57	2.58	2.49	2.56	0.13	0.05
H2-H1	3.73	3.36	3.66	3.23	3.50	0.50	0.24
H2-H4	2.66	2.65	2.60	2.60	2.63	0.06	0.03
H2-H5	3.88	3.65	3.64	3.37	3.64	0.51	0.21
H1-H4'	2.09	2.08	2.09	2.05	2.08	0.04	0.02
H1-H5	2.10	2.07	2.08	2.10	2.09	0.03	0.02
H6S-H4	3.64	3.49	3.39	3.15	3.42	0.49	0.21
H6S-H5	3.18	3.07	2.97	2.83	3.01	0.35	0.15
H6R-H4	3.67	3.52	3.44	3.22	3.46	0.45	0.19
H6R-H5	3.21	3.09	3.01	2.89	3.05	0.32	0.13
H4-H5	2.72	2.66	2.63	2.65	2.66	0.09	0.04

[a]Mixing time in msec

[b]Standard Deviation

Professor Bernard Shapiro

December 12, 1988

analysis of the variances (again at the 95% confidence limit) for the averages of the four determinations for each distance measured indicates that the precisions of both methods are comparable. Based on a pooled variance from the average distance determination for the two methods, the pooled standard deviation for both methods was 0.14 Angstroms. The differences in distances determined by the two methods most likely result from the sensitivity of the DBW method to choice of reference lineshape.

For this set of data, the time required to obtain the volume matrices was reduced by more than 50% by using the DBW method relative to the Hare method.

References:

1. Mirau, P. A., Bovey, F. A. , Macromolecules, 19, 210 (1986)
2. States, D. J., Haberkorn, R. A., Ruben, D. J., J. Magn. Reson., 48, 286 (1982)
3. Hare Research Inc., 14810 216th Ave. NE, Woodinville, WA 98072
4. Denk, W., Baumann, R., Wagner, G., J. Magn. Reson., 67, 386 (1986)
5. Eaton, H. L., Anderson, N. H., J. Magn. Reson., 74, 212 (1987)

Sincerely yours,

Douglas W. Lowman
Senior Research Chemist
ECD Research Laboratories
P. O. Box 1972

Charles M. Buchanan
Senior Research Chemist
ECD Research Laboratories
P. O. Box 1972

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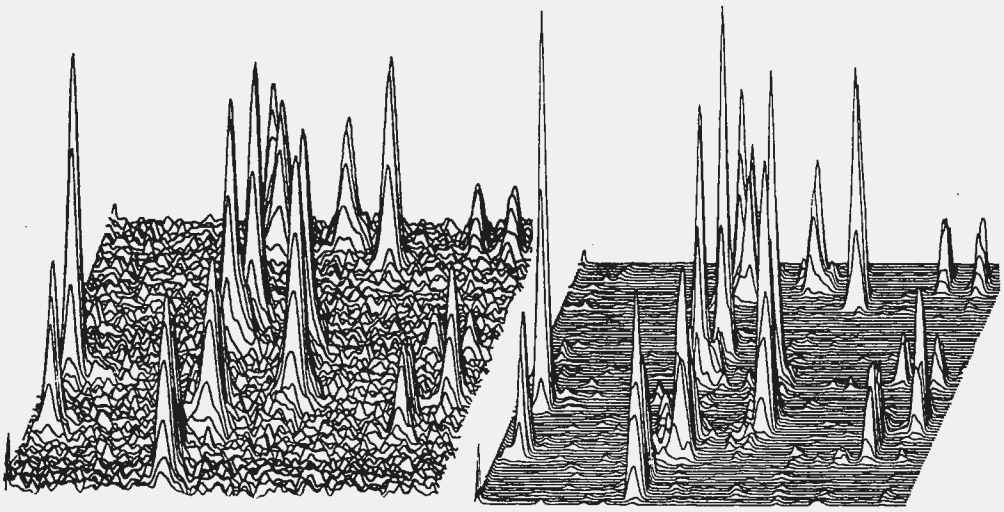
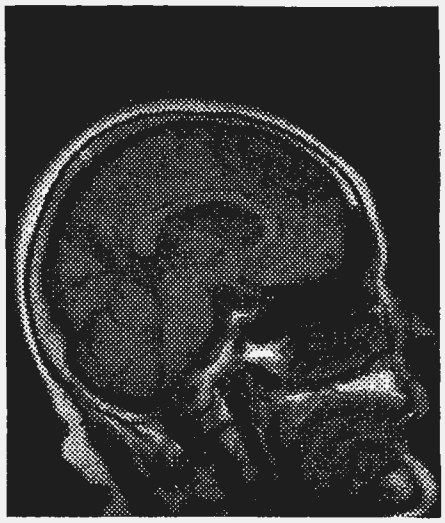


Conventional FFT and MLM processing of a NOESY spectrum of a DNA octamer–duplex (H1' to H2' and H2" sub–region)



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

January 11, 1989
(received 1/14/89)

Title: **"Solid State NMR and Metalloproteins"**

Dear Barry;

I hope you are finding your new location to your satisfaction. I would like to share with you and your readers some work that a graduate student of mine, Mr. Edwin Rivera, being doing with the solid state NMR of Cd^{2+}-substituted carboxypeptidase. This work has been accepted in the **J. Biol. Chem.** and should appear in a couple of months.

The liquid state ^{113}Cd NMR data of Carboxypeptidase A in the presence and absence of inhibitors obtained by Gettins (Gettins, P., **J. Biol. Chem.**(1986) 261, 15513-15518) have been analyzed in terms of whether the inhibitors displace water from the Cd^{2+} upon binding to the protein. This question is addressed by applying the single crystal data and the methods introduced by Honkonen and Ellis (Honkonen, R.S. and Ellis, P.D. **J. Amer. Chem. Soc.** (1984),106, 5488-5497). Calculations based upon these data demonstrate that displacement of water by a carboxyl group should lead to significant shielding of a ^{113}Cd resonance by approximately 100 ppm. Since the observed ^{113}Cd chemical shifts for carboxypeptidase A are modest and deshielding (12 to 17 ppm), it is argued that the chemical shifts imply that water is **not** displaced from the Cd^{2+} center upon binding of inhibitors to carboxypeptidase A. Rather, the Cd^{2+} ion increases its coordination number from five to six upon binding of the inhibitor.

Currently, we are following up this work by examining the crystal structure (in collaboration with Professor Rick Adams of our Department) and ^{113}Cd shielding tensor of $Cd(Im)_2(OAc)_2$. Here Im and OAc denote imidazole and acetate, respectively. Hopefully, these results will presented at the Waugh symposium during the month of January.

Sincerely,

Paul

Paul D. Ellis
George H. Bunch, Sr.
Professor of Chemistry

365-26

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DIRECTEUR : PR BERNARD P. ROQUES

Paris, January 9th 1989
(received 1/17/89)

Doctor SHAPIRO
Department of Chemistry
Texas A & M University
College Station
TEXAS 77843 - 3255

Spurious cross peaks, in HOHAHA

Dear Doctor Shapiro,

Experiments in the rotating frame through incoherent process via cross relaxation (ROESY, CAMELSPIN) or through coherent process via scalar spin-spin couplings (TOCSY, HOHAHA) have proven very useful for the identification of resonances in a drug nucleotide complex (1,2).

The two major advantages of the HOHAHA experiment are first a complete transfer of coherence, increasing therefore the sensitivity and secondly the obtention of direct or relayed informations depending on τm. However, we have noticed that running this experiment in a sample in which chemical exchange is taking placewith a relatively slow rate might lead to spurious cross-peaks corresponding either to exchange phenomena or relayed cross relaxation effects. All these spurious peaks are known to have the same phase as J cross-peaks.

Figure 1A shows the 2D contour plot of the HOHAHA spectrum obtained on a $d(GCGC)_2$: Ditercalinium complex in a 1:3 drug to helix ratio. Only the H_1' sugar proton region is represented. In this region all the H_1' sugar protons of the free and bound helices overlap with the two aromatic drug protons designated by D_9 and the two cytosine H_5 protons from the free helix. Thus, due to the very short mixing time chosen (18 msec) connectivities are expected only between H_1' sugar protons and their corresponding $H_2'H_2''$ sugar protons. However it can be seen that at 6.24 and 6.04 ppm, where only one H_1' sugar proton resonates, three cross peaks are observed. Similarly, for the resonances at 6.11 ppm assigned to the $^4C_1'$ in the free helix and to one of the drug protons D_9, two cross-peaks are observed at 2.22 ppm and 2.57 ppm, while the corresponding $H_2'H_2''$ resonate both at 2.2 ppm.

Contrastingly, in the 2D COSY experiment run in the phase sensitive mode with the same experimental conditions no such extra cross peaks are observed, and for each H_1' sugar proton there are one or two cross-peaks (see fig. 1B).

Analysis of the spectrum and the 2D maps are in favour of relayed cross relaxation phenomena for these spurious cross peaks, although the full assignment procedure is still in progress.

(1) Delepierre M, Maroun R, Garbay C, Igolen J, Roques B.P (1989) J.Mol Biol (submitted)
(2) Laugaa P, Delepierre M, Dupraz B, Igolen J, Roques B.P (1988) J. Biomol Struct. Dyn 6, 421-441

Please, credit this contribution to the subscription of Professor B.P Roques

Muriel DELEPIERRE

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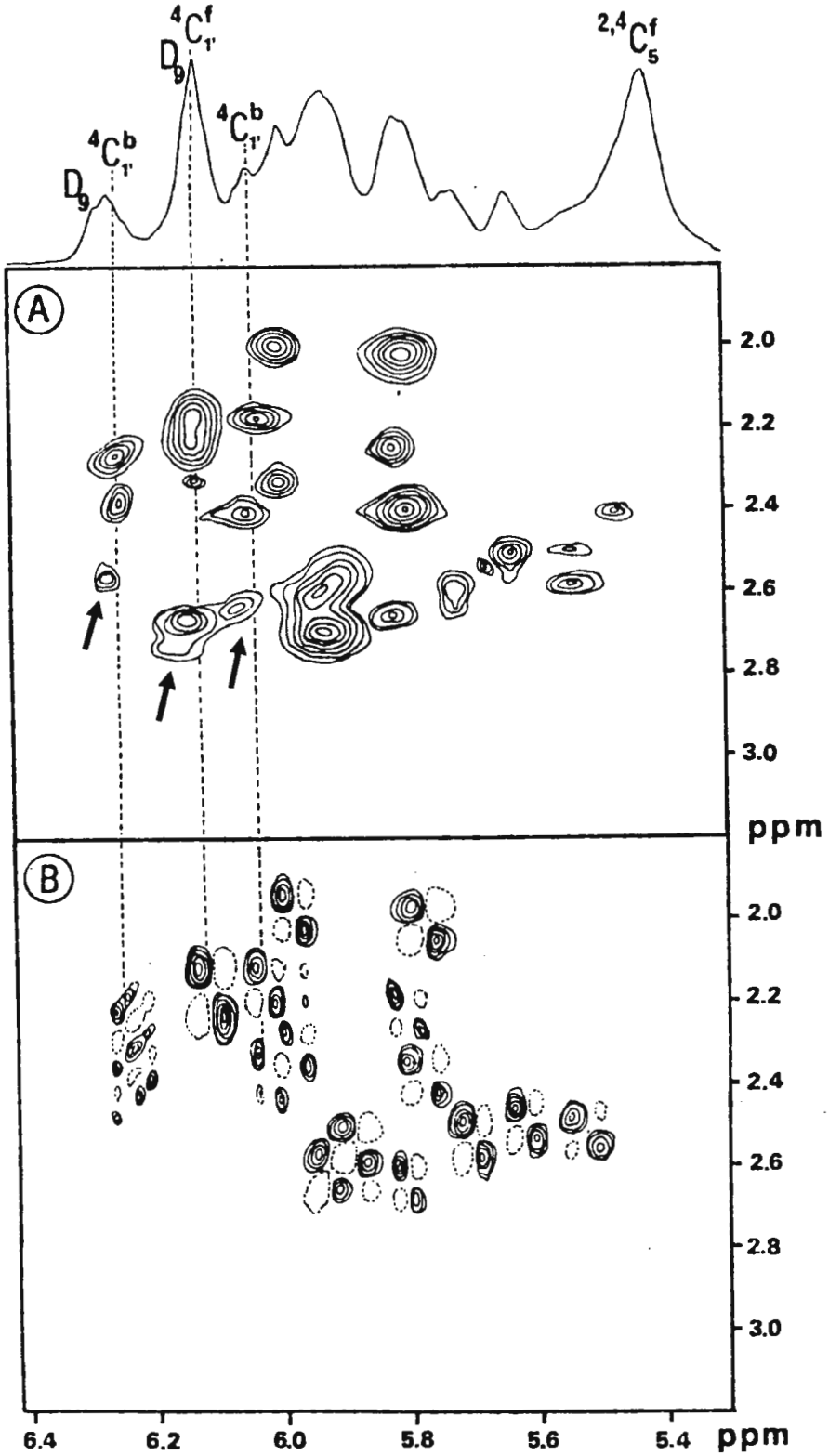

Figure 1 :
H_1' sugar proton region of the $d(^1G^2C^3G^4C)_2$: ditercalinium complex in the 3:1 drug-helix ratio at pH 58 and 27°C. Subscript f and b are relative to free and bound nucleotide PH 5.8. (A) HOHAHA experiment recorded in the phase sensitive mode, with a mixing time of 18 ms Gaussian window were applied (LB=3Hz) prior Fourier transformation (B) phase sensitive COSY experiment shifted sine bell window (SSB=4) were applied prior Fourier transformation the broken lines represent the negative components while the positive components are represented with solid lines.

DEPARTMENT OF PURE AND APPLIED CHEMISTRY
The University of Strathclyde
295 Cathedral Street
Glasgow G1 1XL SCOTLAND

3rd January 1989
(received 1/12/89)

^{13}C-Spectra of Some Cyclopentadienyl Metal Derivatives

Dear Barry,

As part of a general study of ferrocene derivatives, the spectra of the under-noted compounds were obtained. The results are of some interest in that some of the carbons which had no attached hydrogens were extremely weak. Proton decoupled spectra were obtained in the usual way, and the fully-coupled spectra were run with a simple gated-decoupling technique.

1-Cyanoferrocene (1)
δ_{CN} 120.03, δ_{C1} 51.87, δ_{C2} 71.65, δ_{C3} 70.66, $\delta_{C'}$ 70.53 ppm.

1-Isocyanoferrocene (2)
δ_{NC} 163.80, δ_{C1} 26.69, δ_{C2} and δ_{C3} 66.77, $\delta_{C'}$ 70.63 ppm.

1-Methylazoferrocene (3)
δ_{C1} 105.93, δ_{C2} 64.20, δ_{C3} 69.12, $\delta_{C'}$ 69.55, δ_{Me} 56.93 ppm.

1,1'-Bis-(methylazo)-ferrocene. (4)
δ_{C1} 107.01, δ_{C2} 65.36, δ_{C3} 70.39, δ_{Me} 57.14 ppm.

Phenylazocyclopentadienyl-methyl-tricarbonyl-molybdenum. (5)
δ_{C1} 129.0, δ_{C2} 90.91, δ_{C3} 88.11, $\delta_{C1'}$ 152.42, $\delta_{C2'}$ 122.66, $\delta_{C3'}$ 129.14, $\delta_{C4'}$ 131.36, δ_{Me} 0.25, δ_{CO} 225.31 (intensity 2) and 226.50 ppm (intensity 1).
(Carbons in the benzene ring are indicated by primes).

Assignments were made on the basis of the known effects of similar substituents in benzenoid compounds. The carbon signal for the isocyanide group in (2) was a 1:1:1 triplet due to coupling to the nitrogen atom (J = 6.4 Hz).

The reasons for the low intensity of the carbons bearing the substituents in the cyclopentadienyl rings is not immediately apparent, but it causes some trouble. In compound (5), for example, the C1 carbon signal is buried under that of C3', and was only revealed in the fully coupled spectrum. In contrast the C1' signal is reasonably intense.

Yours sincerely

Peter Bladon

Peter Bladon

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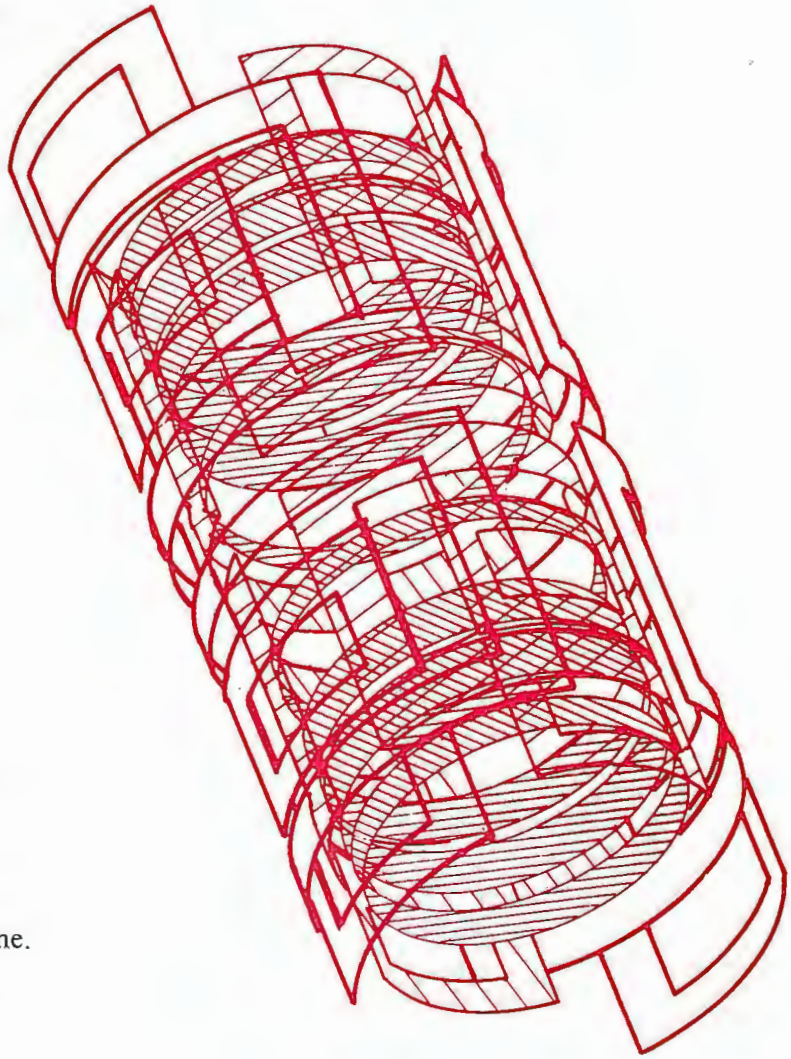

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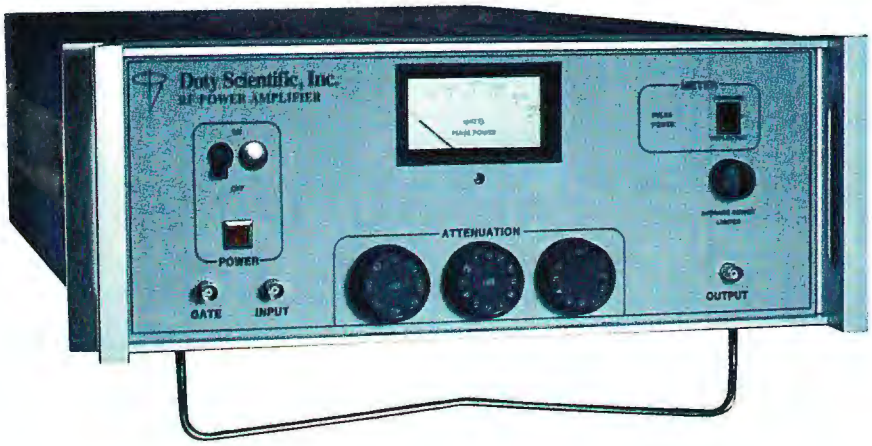

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MODEL	POWER BANDPASS (MHz)	GAIN (dB)	PULSE POWER (W)	WEIGHT (lb.)	DOMESTIC PRICE
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500A	8-130	56	500	57	9.800
1000A	8-125	58	1000	62	14,400

Rise Time: less than 50ns to 90%.
Fall Time: less than 50ns to -70dB.
80dB minimum signal blanking.

Total output noise:
Unblanked: 45dB above thermal noise.
Blanked: 25dB above thermal noise.

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THD is below 6% at any power level, any frequency.
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Phase shift change (10% to 80% of rated power): 8° max.

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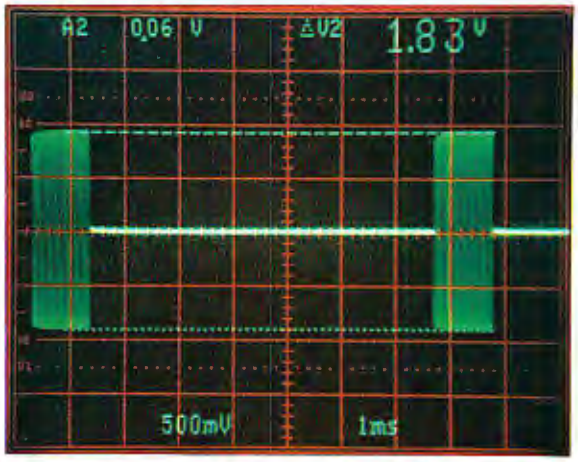
Control panel includes three rotory decade attenuators, directional pulse power meter with 300ns response time, and adjustable average power limiter.

Model 1000A operates off of 220 VAC, 50 or 60 Hz. Model 250A and 500A available in 120 VAC and 220 VAC, 50 or 60 Hz. Quiescent AC power demand is 8% of rated rf pulse power. Total efficiency at full power is 30%.



Typical 500 Watt pulse envelope.

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USA
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PROFESSOR DAVID M. DODDRELL

365-31

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF QUEENSLAND

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c/- Mater Hospital
South Brisbane
Queensland 4101

Telephone: (07) 846 2277
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Fax: (07) 844 8010

9 January 1988/9 (received 1/14/89)

Professor B. L. Shapiro,
TAMU Newsletter.

Having trouble with your 5 Gauss line?

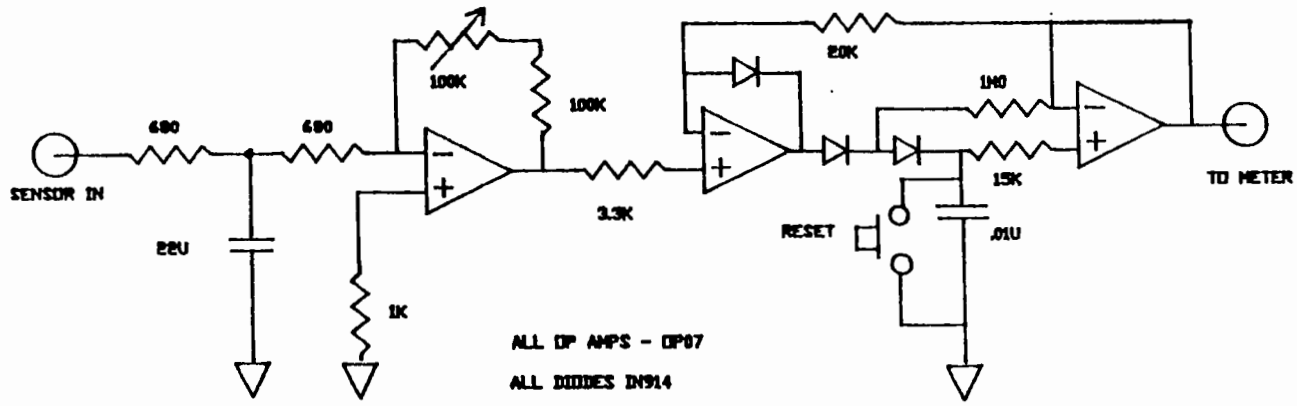
Dear Professor Shapiro,

Magnetic flux density (B) meters are generally based on the Hall Effect and are quite expensive. They also can suffer from a loss of sensitivity at low B values. Most countries seem to have adopted 5 Gauss (0.5mT) as an upper limit for public exposure (and hence limited access above this value is mandatory). When installing, moving or shielding a magnet the 5G contour must be located. We have developed a device based on Faraday Induction for location of low B contours and estimate its component cost to be about A$100.

A small (30mm Ø) coil (actually a 240V clock motor winding) was mounted on a 1m perspex tube. This sensor can be hand-held and 'flipped' repeatedly at the desired location or driven by a slip-ring motor (not included in the above costing). The induced voltage then passes to a low pass filter amplifier and peak detection circuit (see figure). The induced voltage is proportional to B (and the angular velocity). The device may be roughly calibrated using a Helmholz coil pair where

$$B = (0.8)^{3/2}\mu_0 NI/a \quad \text{and } a = \text{radius of coil.}$$

We designed the coils to give 10G/A at the mid-point and calibrated the meter for 10G full scale. It takes a few minutes of practice before hand held results are repeatable. Comparison with manufacturers' installation plots result in only about 5% error for the practiced operator.



Yours sincerely,

David M. Doddrell Stuart Crozier James Field

J. F.

Department of Chemistry
LOUISIANA STATE UNIVERSITY AND AGRICULTURAL AND MECHANICAL COLLEGE
BATON ROUGE · LOUISIANA · 70803-1804
504/388-3361

December 30, 1988
(received 1/6/89)

Dr. B. L. Shapiro, Editor
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94393

RE: MATLAB: A Programming Language for NMR Spectral Simulations

Dear Dr. Shapiro:

For the past five months, we have been using the Matlab programming language in which to write spectral simulation programs. Briefly, I would describe Matlab as FORTRAN without the hassles. Matlab is easy to learn; graduate students in an NMR class, starting with sample programs, advanced to calculating 2D nutation and Jeener echo results in a semester.

An example used in class is the calculation of the powder pattern for a pair of dipolar coupled spins at very low temperatures where a 5_x pulse is used to excite the spin system. The experimental spectrum is given in "NMR Lineshape Thermometry at Low Temperatures" P. Kuhns, O. Gonen, and J. Waugh, *J. Magn. Reson.*, **72**, 548 (1987).

The basic elements of the density matrix theory are summarized below (see "Transient Techniques in NMR of Solids", B. C. Gerstein and C. R. Dybowski, Academic, 1985). As one examines the program listing, note the relatively close correspondence between the appearence of the code and the equations, especially for equations 3 and 4.

$$H_{total} = \begin{bmatrix} -\omega_L + \omega_D\frac{(1-3\cos^2\theta)}{4} & 0 & 0 & 0 \\ 0 & -\omega_D\frac{(1-3\cos^2\theta)}{4} & -\omega_D\frac{(1-3\cos^2\theta)}{4} & 0 \\ 0 & -\omega_D\frac{(1-3\cos^2\theta)}{4} & -\omega_D\frac{(1-3\cos^2\theta)}{4} & 0 \\ 0 & 0 & 0 & \omega_L + \omega_D\frac{(1-3\cos^2\theta)}{4} \end{bmatrix} \quad (1)$$

$$\rho_{eq} = \frac{\exp(-E_k/kT)}{\sum_k \exp(-E_k/kT)} \quad (2)$$

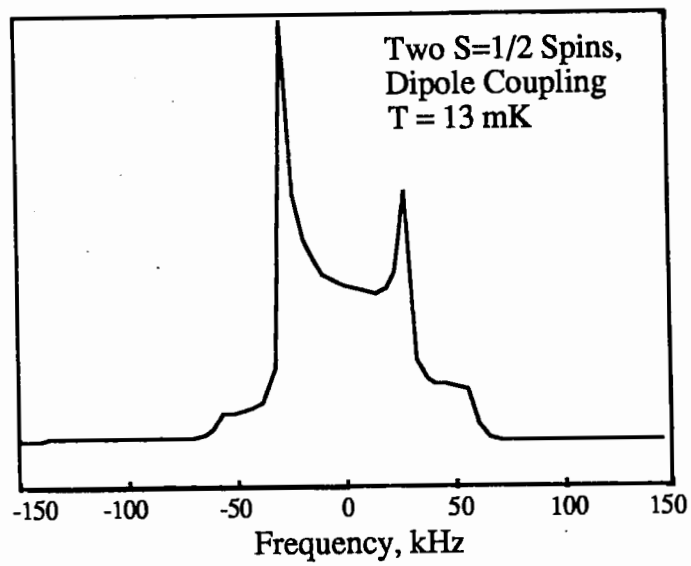
$$\rho(t) = \exp(-iH_{evol}t)\,\rho_{eq}\,\exp(iH_{evol}t) \quad (3)$$

$$FID(t) = \mathrm{trace}[I_y\,\rho(t)] - i\,\mathrm{trace}[I_x\,\rho(t)] \quad (4)$$

The complete program listing is given here, together with the spectrum calculated for T = 13 mK.

```
% Two Spins, S=1/2, at frequency vL, Dipolar coupled (A and B terms only)
clc; clear; echo on; i = sqrt(-1);  vL = 200.000e6;  w_D = 40e3;
FID_size =  64;  LB = 2e3;  inc = 60;  Temp_K = 0.013;
Left_Spectrum  = -1.5e5;  Right_Spectrum =  1.5e5; Carrier = 200.00e6;
k_Boltz = 1.380662e-16; h_bar = 1.054587e-27;  h_plain = h_bar*2*pi; gamma = 2*pi*1e8/23488;
HzPt = (Right_Spectrum - Left_Spectrum)/FID_size;  Dwell_time = 1/(Right_Spectrum - Left_Spectrum);
FID_sum = zeros(1,FID_size);
```

```
 for j = 1:FID_size
  Freq_axis(j) = Left_Spectrum + HzPt*(j-1);  Time_axis(j) = (j-1)*Dwell_time;
  Damped_exp(j) = exp(-j*Dwell_time*pi*LB);
 end
I_x = 0.5*[0 1 1 0; 1 0 0 1; 1 0 0 1; 0 1 1 0];  I_y = 0.5*[0 -i -i 0; i 0 0 -i; i 0 0 -i; 0 i i 0];
I_z =     [1 0 0 0; 0 0 0 0; 0 0 0 0; 0 0 0 -1];  H_total = zeros(4,4);

for theta = pi/inc: pi/inc: pi/2
 A = w_D*(1-3*(cos(theta))^2)/4;  B = -w_D*(1-3*(cos(theta))^2)/4;
 H_total(1,1) = -vL+ A;     H_total(4,4) = vL + A;
 H_total(2,2) = -A;                    H_total(2,3) = B;
 H_total(3,2) = B;                     H_total(3,3) = -A;

[U,E] = eig(H_total);  [E,k] = sort(real(diag(E)));  U = U(:,k); U_adj = conj(U.');

%Calculate Density Matrix in Laboratory Frame
denom = 0;
 for j=1:4   denom = denom + exp(-E(j)*h_plain/(k_Boltz*Temp_K));  end
 for j=1:4  Density(j,j) = exp(-E(j)*h_plain/(k_Boltz*Temp_K))/denom;  end
rho_eq = U*Density*U_adj;

%Start 5x pulse on Spin System
H_5x = (-5/90)*(pi/2)*I_x;
rho_5x = expm(-i*H_5x)*rho_eq*expm(i*H_5x);

%Start of time evolution
H_evol = H_total + Carrier*I_z;
for j = 1:FID_size
 tau = 2*pi*(j-1)*Dwell_time;
 U_evol = expm(-i*tau*H_evol);  U_evol_adj = conj(U_evol.');
 rho_evol = U_evol*rho_5x*U_evol_adj;
 FID(j) = trace(I_y*rho_evol) - i*trace(I_x*rho_evol);
end %end of j-loop for making FID

FID_sum = FID_sum + sin(theta)*FID;
end %end of theta-loop for powder pattern average

FID_sum_Damped = FID_sum.*Damped_exp;
Spectrum = fftshift(ifft(FID_sum_Damped));
plot(Freq_axis,Spectrum);
```



Note: One difference between this spectrum and that reported by Waugh and coworkers is the direction of the frequency axis. I suspect the experimental spectrum has the more traditional orientation with increasing frequency to the left.

Typical programs are 2-3 pages long (2D nutation of an S=5/2, Jeener echo for static system). No rigorous test of execution speed has been done but it seems roughly comparable to FORTRAN. On a VAXStation 3200, the powder pattern calculation took 2 minutes of CPU time. The assistance of Bernie Gerstein and Tom Barbara with the density matrix theory is gratefully acknowledged.

Sincerely,

Les Butler
Associate Professor of Inorganic Chemistry

University of Alberta
Edmonton

Department of Biochemistry

Canada T6G 2H7

474 Medical Sciences Building, Telephone (403) 432-5460

January 4th, 1989
(received 1/9/89)

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

Dear Barry:

Title: Measuring Sample Temperature Gradients/Using Lock Intensity for Shimming

Most NMR on biological samples is done with water as the solvent and the lock (using D_2O). The problem with water as a lock is that it's chemical shift is very temperature sensitive ($\Delta\omega/\Delta T \cong 5.1$ Hz/°C @ 500 MHz; see Figure 1). We have used this fact to measure temperature gradients in samples on our VXR-500 during VT experiments.

The experimental observation is as follows. Shimming for maximum lock intensity at ambient temperature (20°C) on a sample of 1 mM DSS in D_2O yields optimum resolution ($\Delta\nu \cong 1.10$ Hz for the CH_3 protons with LB = 0.5 Hz and AT = 2s). However, within a half hour or so of going to an elevated temperature (say +40°C), tuning for maximum lock yields $\Delta\nu \cong 1.4$ Hz. Changing only the Z (always in the same direction and by the same amounts) shim reduces $\Delta\nu$ to 1.1 Hz. An explanation is that there exists a slight linear temperature gradient along the length of the sample which "spreads out" the H_2O signal at optimum resolution but which can be compensated for using the Z shim.

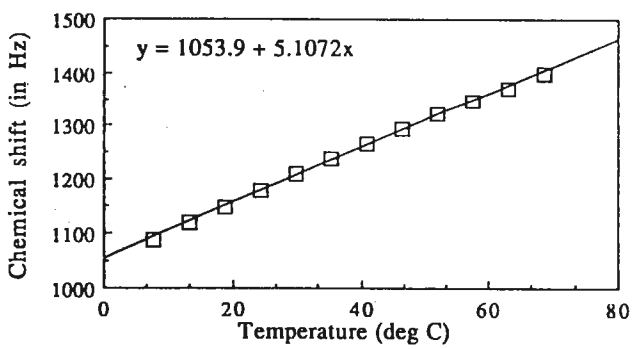
The effect can be simulated theoretically by a change in resonance frequency of approximately 0.8 Hz over the length of the coil (~ 14 mm). This corresponds to a temperature gradient of approximately 0.01°C/mm along the sample. On our instrument these small gradients can persist for quite a while after resetting of the temperature.

Elimination of gradients is important both for long term 2D NMR experiments in H_2O solutions, as well as things like "ultra high resolution" NMR [Maple & Cullerhand, J. Mag. Res. 80:394 (1988)].

Yours sincerely,

Brian

Brian D. Sykes, Ph.D.
Professor of Biochemistry



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

1989 January 09
(received 1/17/89)

SOLID-STATE NMR OF NYLON 6.6

Dear Dr. Shapiro

CP/MAS ^{13}C NMR is a powerful technique for probing the structure and conformation of polymers in the solid-state. Recently we have been attempting to employ solid-state NMR methods to characterize Nylon 6,6. The ^{13}C NMR spectra appear to be sensitive to the morphology and conformation of the polymer chains.

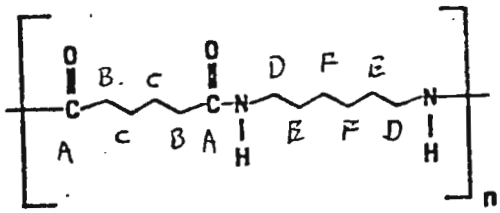
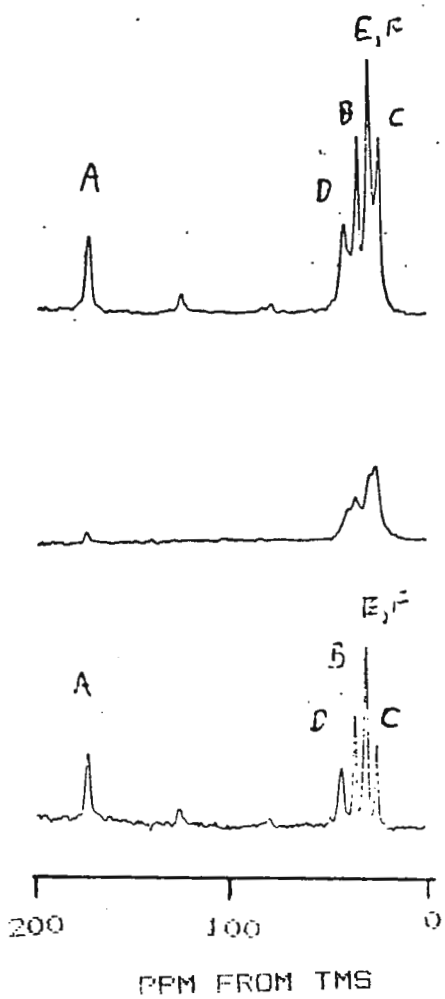


Figure 1 shows the 50 Mhz solid-state ^{13}C spectra of a typical Nylon 6,6 sample. Part A is the CP/MAS spectrum while part B is the spectrum acquired with 90 pulses and a short (1 sec) recycle delay to show only the fast relaxing component of the sample. Part C is the subtraction of part B from part A which yields the spectrum of the slower relaxing components of the sample.

The peak assignments are as indicated in the figure. The fast relaxing component (T_1's = 100-200msec) has broader linewidths (there is some broadening of the carbons directly attached to the nitrogen due to residual $^{13}C-^{14}N$ dipolar couplings). This indicates that this component is likely due to nylon chains in an amorphous environment with a distribution of conformations. The more rigid components are likely due Nylon chains in an extended zig-zag conformation. T_1 measurements show that the peaks due to the extended conformation have a slow relaxing component (40-60 secs. for CH_2 carbons) and a component with an intermediate T_1 values (7-10 secs. for CH_2 carbons). The slowest relaxing component is likely due to nylon chains in a crystalline environment while the remainder must be in some type of intermediate phase.



Sincerely

Michael McKinnon

365-38

GE NMR Instruments

General Electric Company
P. O. Box 4905, Fremont, CA 94539

OPEN-ACCESS DATAFILES FROM OMEGA SPECTROMETERS

19 December, 1988
(received 12/24/88)

Dear Barry:

GE NMR Instruments historically has maintained the philosophy that NMR datasets are most useful to the spectroscopist if he can do what he wants with them, rather than being restricted to the capabilities provided by the instrument manufacturer. Even the most complete software package will not satisfy the needs of every user. Creative researchers will always be wanting to try new analysis functions and to experiment with new mathematical methods.

GE NMR has always accommodated this need by providing users with detailed information about our file formats so their own programs and third-party software can interpret our NMR data files. In some cases, we have even provided special communications software to facilitate the data transfer to other computers.

Our implementation of an "open architecture" design in our Omega software carries this philosophy even further. Through convenient access to the c-shell and its UNIX tools, the user now has the capability to write his own routines and functions in a high level language, then easily incorporate them as new commands directly into the NMR software package.

There is still the desire, though, to access and decipher NMR files for use by external user-generated (or purchased) programs. Unfortunately, the very goal of providing maximum file flexibility to the user from within the Omega environment results in a flexible (read that "non-constant") file format which is not easily interpreted by other programs. The content and the specific order of the file's parameter section is dynamic, since it may include such information as the specific pulse program which generated the data (not just its name) and the processing history of the data. Furthermore, in order to allow Omega software to access arbitrary regions of multidimensional data most efficiently, the individual data blocks are not stored in a sequential linear manner, but rather are partitioned and interleaved according to a formula dependent on the magnitude of each dimension. (Currently up to 4-dimensional datasets are supported).

We would like to report that we just simplified the task of those who wish to access Omega data and parameter values. We took advantage of the built in flexibility of the system to compose a UNIX c-shell script which calls previously existing Omega commands to create a separate file. This new file contains the spectral parameters in an easy to interpret format followed by the data reordered in the straight-forward linear fashion. To provide maximum accessibility, the parameter portion is stored entirely in ASCII text format, and is listed in the form:

```
keyword        value
keyword        value
...
```

The keywords are mostly self-explanatory descriptors, such as `f1_freq`, `f2_freq`, `spec_width`, etc. The user may specify whether the spectral data will be appended to the same file or will be saved as a separate file. If made part of the same file, the data must also be stored as ASCII text; if stored as a separate file, the user may choose whether it be stored as ASCII text or in floating-point binary format. (The latter conversion is done by a very simple [8 line] C program which must be entered and compiled.)

The advantage of an ASCII datafile, of course, is that any high school student who knows BASIC can write a program to locate the desired parameters and read the data. The disadvantage is the large expansion factor required to represent the data in ASCII decimal format. It is for that reason that we expect the binary option will be chosen most frequently.

Omega users already have the tools to create these output files by writing a script which calls the `header -a` command (lists all the header parameter values in the above format) and the (until now undocumented) `print_data` command. Until the script and its companion C program get distributed with the Spring software release, we will be happy to send hardcopies of these files to Omega users upon request. They can be typed in and used as is, or can be customized to meet your specific file format needs. Requests may be made by calling 1-800-GE-USERS (in California, 415-683-4369).

Sincerely,

Tom Raidy

Thomas E. Raidy
Senior Software Engineer

Craig VanAntwerp

Craig L. VanAntwerp
Manager, Software Engineering

PHILIPPS-UNIVERSITÄT MARBURG

FACHBEREICH CHEMIE

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MARBURG, DEN 5.1.89 (received 1/17/89)
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Prof. Dr. B. L. Shapiro
TAMU-NMR Newsletter
966 Elsinore Court
Palo Alto, Cal. 94303
USA

Useful Hints: / Laserplotter / Home Control / Networking /

Dear Professor Shapiro,

As often discussed in this journal the weak point of nmr automation is the plotter with its problems of paper feed and pen function. Our solution to this problem has been the purchase of a RG04 controller from Nofatek-Systems, Zettachring 10, D-7000 Stuttgart, West Germany. This box converts the HPGL commands for the HP 7550 plotter to HP Laserjet Serie II language. In addition we bought the Laser Jet and a 1000 sheet feeder to replace the original paper tray of the Laser Jet. Thus with an investment of about 10,000 DM in total we have replaced the plotter by the above system on our automatic sample changer at the Bruker AC-300. No software changes are necessary, since the RG04 controller behaves for the ASPECT 3000 just like an original HP 7550 Plotter. Our customers soon adapted to the DIN-A4 spectral size; routinely they get for a proton spectrum 4 - 5 sheets of paper with an overview spectrum and automatic expansions of 20 Hz/cm. During half a year of operation we have printed with this system about 50,000 sheets of paper and have had no output problems at all.

We are running the sample changer as an open system. Graduate students are allowed to put their samples in by answering the questions of the Bruker "Easy Dialogue". For this we have designed 11 standard experiments from which to choose. Now, there are always some people who are able to stop any system. Since our instruments are linked via Ethernet to a VAX in the university computing center it is easy to recognize problems from home late at night. The recipe is as follows: Login at the university VAX with your PC via modem and telephone. Start the Bruknet interpreter (RUN BRKCMD.EXE) on the VAX and get the XXXXJOUR.NAL file from the Bruker spectrometer. Read this file and consider, whether it is worth getting out in the cold.

We have connected a PC to the Bruker spectrometer using the Wisconsin PCNMR+ software which we find a very useful asset to 1D-nmr spectroscopy. File transfer currently works by distributing diskettes in the department. It is possible, however, to transfer spectra via ETHERNET using the BRUKNET protocol to the VAX and from there with KERMIT protocol to any connected PC either in the department or at home. At the time of writing, this file transfer works physically, however we have to find out a proper file conversion, which makes these files understandable to PCNMR+. We would be grateful for any suggestions.

Sincerely yours

(Dr. S. Berger) (Dr. P. Bast)

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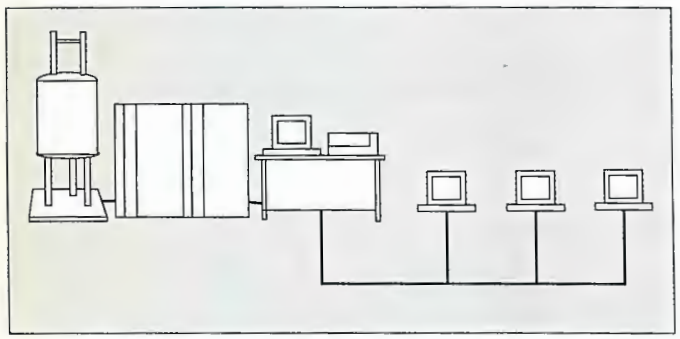

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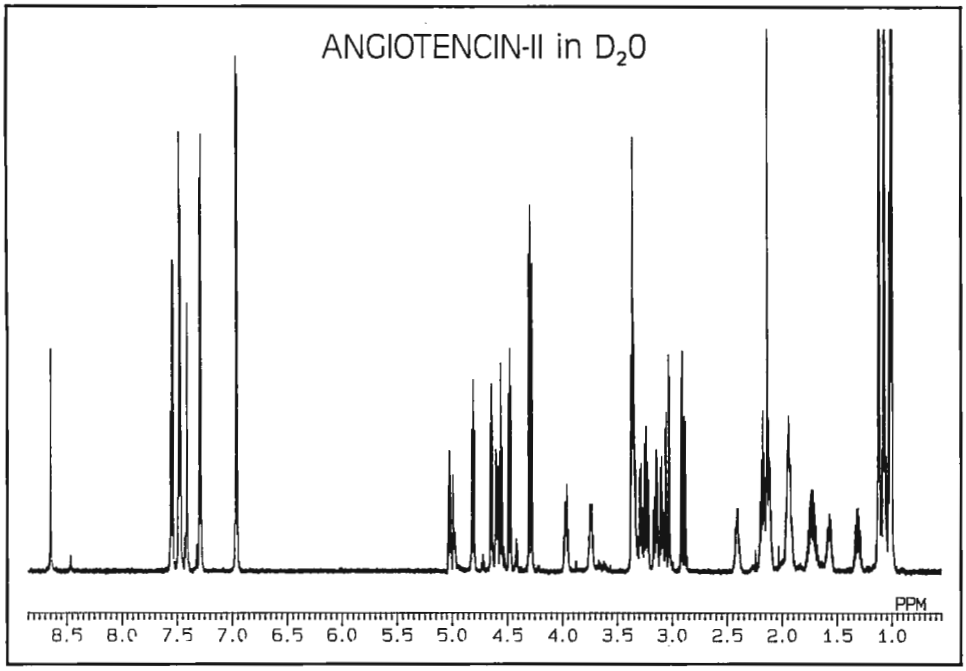
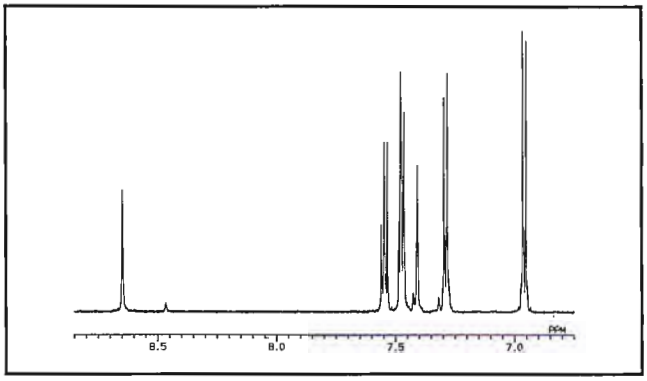
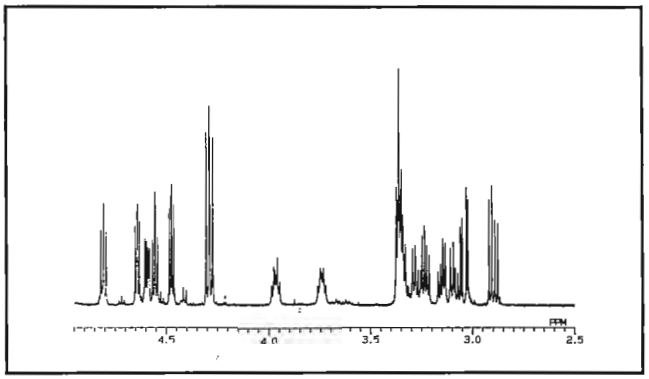
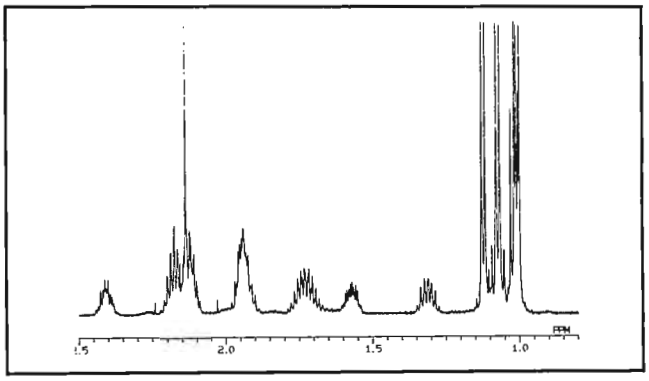


JEOL in its continuing commitment to the scientific community announces an operational 600 MHz NMR spectrometer at its Akashima applications laboratory. The Oxford Instruments 14.1 Tesla superconducting solenoid with JEOL's well proven matrix shim system, benchmark Rf technology, and excellence in probe design combine to provide the highest dispersion in 600 MHz performance. If your research and applications in macro molecules or low gamma nuclei requires 600 MHz performance, you owe it to yourself to call JEOL.

The above data is of Angiotencin-II in D_2O and was processed under normal one dimensional conditions. If you are presently evaluating 600 MHZ NMR spectrometers, we would be pleased to arrange for you to see the GSX-600.







Please Contact:

JEOL

Serving Advanced Technology

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Swiss Federal Institute of Technology Zurich

Laboratorium für Physikalische Chemie
Prof. Dr. R.R. Ernst

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Postadresse:
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8092 Zürich
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0430

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

(received 12/27/88)

HYPERFINE–SELECTIVE ENDOR:

A NEW EDITING METHOD FOR ESR–DETECTED NMR SPECTRA

Dear Barry,

When one is browsing through the past century of TAMU letters, one might obtain the impression that there is only one universal technique of observing nuclear magnetic resonance: via direct measurement of nuclear spin precession. This is certainly incorrect. Numerous other ways of observation have been proposed and developed, such as perturbed angular correlation of radioactive emission, optical detection, and detection via ESR. This last possibility has not only reached maturity but has become a technique of great practical value for the indirect high–sensitivity detection of nuclear resonance in paramagnetic compounds through electron nuclear double resonance (ENDOR) spectroscopy.

ENDOR is much related to the wellknown heteronuclear experiments used to observe low sensitivity nuclei indirectly via proton resonance, although true coherence transfer between nuclear spins and electron spins is usually impractical because of the short electron spin T_2 relaxation times. A typical pulsed version of ENDOR, the so–called Davies–ENDOR is illustrated in Fig.1 (disregarding for the moment the indicated field jump ΔB). The initial selective ESR π pulse interchanges the populations of levels 2 and 4 in the energy level scheme of a two–spin 1/2 system that is used as an example. The subsequent selective NMR π pulse leads to saturation of both ESR transitions (24) and (13) whenever either transition (34) *or* transition (12) is inverted. This can be detected via an ESR $\pi/2$–π pulse sequence that causes an unattenuated echo unless an NMR transition is hit. By measuring the echo amplitude as a function of the applied radio frequency it is possible to obtain point by point an NMR (ENDOR) spectrum of a paramagnetic molecule.

Often, ENDOR spectra are complicated and insufficiently resolved. For example, the single crystal NMR spectrum of copper picolinate, Cu(II)pic$_2$, diluted in zink picolinate, shown in Fig.2a, consists of a superposition of ^{1}H and ^{14}N resonances. This (in conventional NMR unusual) situation is here

FIG.1

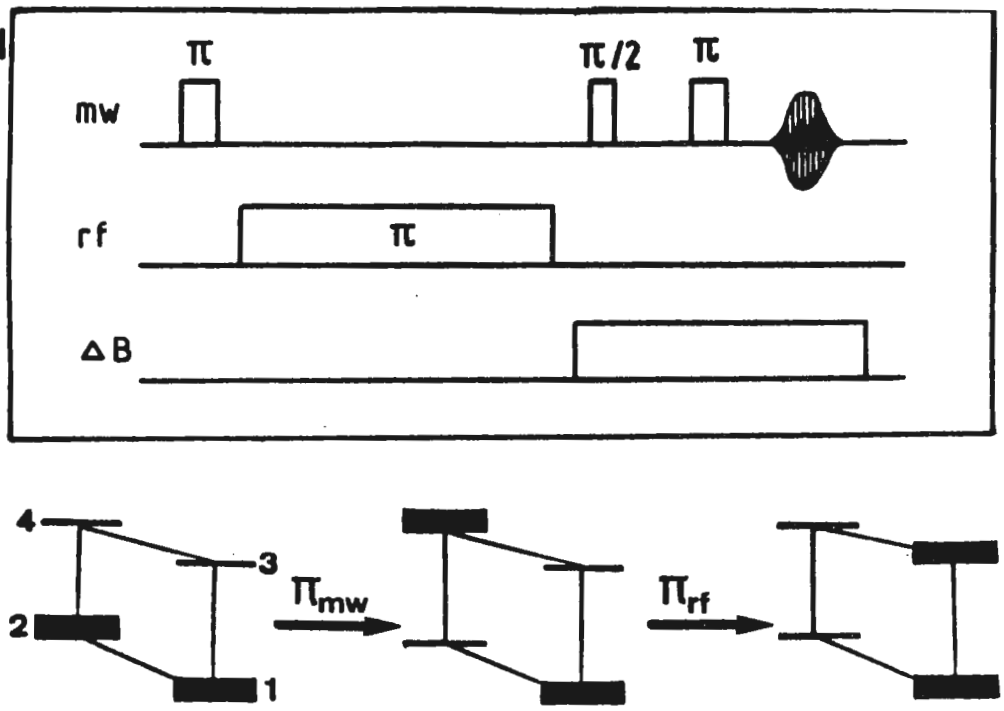
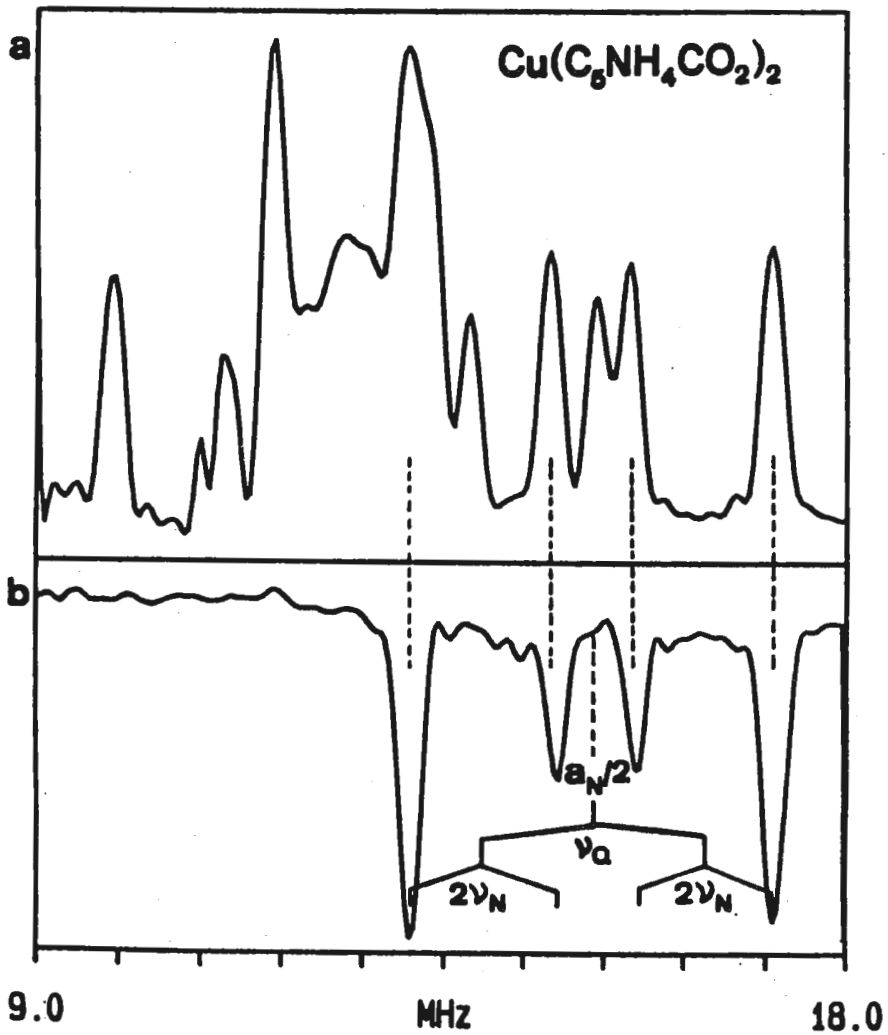

π
π/2
π
mw
rf
π
ΔB
4
3
2
1
π_{mw}
π_{rf}

FIG.2


a
$Cu(C_5NH_4CO_2)_2$
b
$a_N/2$
ν_Q
$2\nu_N$
$2\nu_N$
9.0
MHz
18.0

caused by the very large hyperfine coupling constants (for ^{14}N: 30 MHz, for ^{1}H: 0–6 MHz). For simplification of such a spectrum, it is possible to use an editing technique, called "hyperfine–selective ENDOR" that allows the selection of NMR lines with a predetermined value of the hyperfine coupling constant.

In Fig.2b, the four ^{14}N lines that involve a hyperfine coupling constant of 15 Mhz have been selected. All ^{1}H lines are suppressed, leading to a spectrum that can be interpreted in terms of electron–nuclear hyperfine interaction, ^{14}N Zeeman interaction, and ^{14}N quadrupolar interaction.

The required technique is quite simple as is indicated in Fig.1. Instead of observing the echo of the ESR line that has been initially inverted by the π pulse, a rapid magnetic field jump (within 1 μs) is executed before applying the echo sequence such that another ESR line, shifted by the selected hyperfine coupling constant (in the schematic example, it is transition (13)), comes into resonance. By adjusting the amplitude of the field jump, it is possible to select a particular value of the hyperfine splitting. In effect, a polarization transfer has been achieved between two hyperfine ESR lines separated by the selected hyperfine coupling constant. The hyperfine selective ENDOR spectrum is recorded again point by point by sweeping the rf frequency. A 2D extension that produces 2D hyperfine–resolved NMR (ENDOR) spectra is rather straight forward. A detailed description of this experiment is in print in Chemical Physics Letters.

Sincerely yours,

Arthur Schweiger R.R. Ernst

Zürich, December 20, 1988

Sandia National Laboratories

Albuquerque, New Mexico 87185

Jan 16, 1989

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

Analysis of Silica-Bound Propanesulfonic Acid by ^{29}Si NMR

Dear Dr. Shapiro,

We have been preparing ion exchangers for catalytic applications by functionalizing silica gel with sulfonic acid. Colloidal silica, synthesized by the method of Stober (W. Stober, A. Fink, and E. Bohn, J. Coll. Interface Sci., 26, 62 1968) was selected as a high surface area support. Mercaptopropyltrimethoxysilane was reacted with a stable dispersion of the colloidal silica in DMF. The resulting mercaptopropyl groups were oxidized to propane sulfonic acid by a toluene solution of tert-butylhydroperoxide.

^{29}Si MAS NMR was used to characterize the support and the nature of the bonding between the propane sulfonic acid and the support. Since the support contains few hydrogens and quantitative results were required, direct polarization experiments rather than cross-polarization experiments were employed. Spin-spin relaxation times were typically between 30 and 40s so a pulse repetition of 150s was used. A typical ^{29}Si spectrum at 39.6 MHz employing 512 accumulations is shown below. The resonances at -91, -100 and -110 ppm with respect to TMS correspond to the Q^2, Q^3 and Q^4 silicons respectively of the colloidal silica. Resonances at -56 and -66 ppm correspond to the silane bonded to the substrate with 2 and 3 oxygen linkages respectively. Deconvolution of the spectra with Gaussian lineshapes yielded relative areas of 8.5, 17.4, 4.0, 29.0 and 41.2 % for the resonances from low field (-55.9ppm) to high field (-110.4ppm). The relative amount of silane bonded to the substrate with one oxygen linkage was estimated to be less than 1 %.

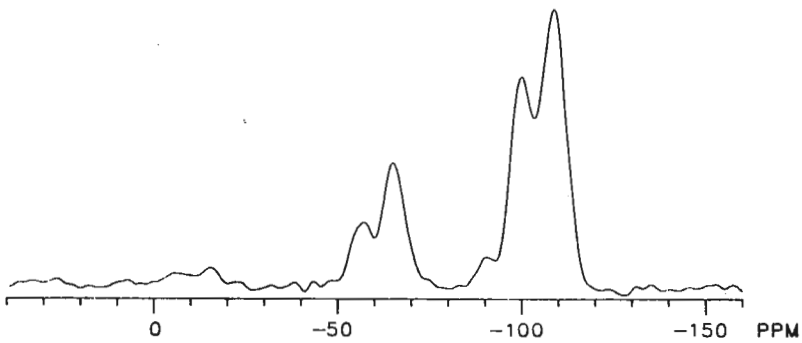
Sincerely,

Roger

Roger A. Assink
Sandia National Laboratories
Albuquerque, NM 87185

Rickey D. Badley and Warren T. Ford
Oklahoma State University
Stillwater, OK 74078

Please credit this contribution to the account of P. Cahill.



The ^{29}Si MAS NMR spectrum of propoanesulfonic acid on colloidal silica.

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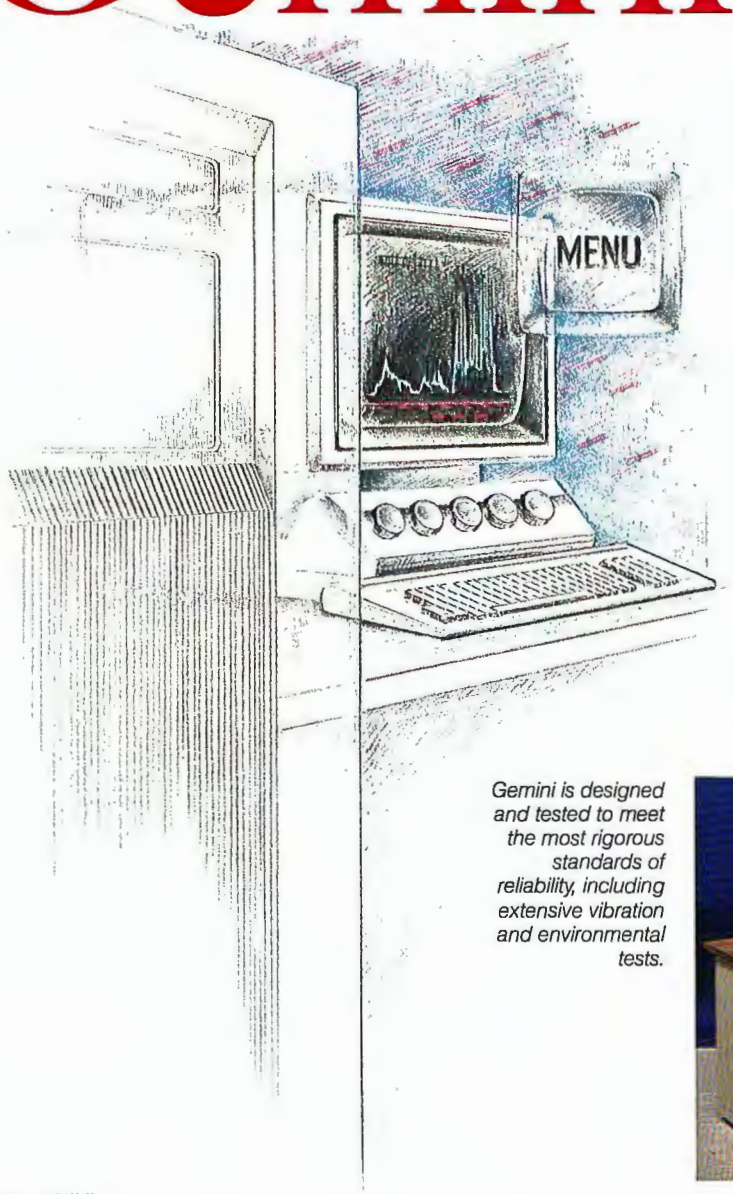

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(415) 952-1366

January 10, 1989

(received 1/11/89)

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

Dear Dr. Shapiro,

Achieving increasingly shorter scanning times in magnetic resonance imaging makes it important to be able to do the prerequisite tuning and calibration rapidly. A previous report (1) of one such method employs the first Hahn echo and stimulated echo from a 3 rf pulse sequence to determine the flip angle. We present a new algorithm which we believe is more robust and in addition can discriminate flip angles over a range of 360 degrees.

Consider a $\theta - \tau - \theta - 3\tau - \theta$ pulse train which generates the following echoes after the third pulse (2):

$$\begin{aligned}
S_1 &= \tfrac{1}{2} M_o \sin^3\theta e^{-2\tau/T_2} && \text{at } t = 5\tau \\
E_2 &= -M_o \sin\theta \sin^4(\theta/2) e^{-6\tau/T_2} && t = 6\tau \\
E_{23} &= M_z(\tau) \sin\theta \sin^2(\theta/2) e^{-6\tau/T_2} && t = 7\tau \\
E_{13} &= \tfrac{1}{4} M_o \sin^3\theta e^{-8\tau/T_2} && t = 8\tau
\end{aligned}$$

The expression for E_{23} uses the value of the residual magnetization just prior to the second rf pulse. If we assume $\tau \ll T_1$ then this expression becomes $E_{23} = M_o \cos\theta \sin\theta \sin^2(\theta/2) e^{-6\tau/T_2}$. Notice this signal passes through zero at $\theta = 90$.

Our work concentrates on using various combinations of the four echoes to provided a simple expression for the flip angle. For example

$$\mathcal{R} = E_{23}/(S_1^{(1-b)/3}(-E_2)^b E_{13}^{2(1-b)/3})$$

contains no T_2 dependence. If we assume $\tau \ll T_1$ then this reduces to

$$\mathcal{R} = 2^{(2+b)/3} \cot\theta \cot^{2b-1}\theta/2$$

However, this was not found to be sufficiently accurate for our use due to fast relaxation times in fatty tissues where E_{23} does not cross zero at the same point where S_1 and E_{13} achieve their maxima. While this would not pose a problem with longer T_1's this does pose a systematic inaccuracy in the procedure.

Instead, we have since decided to concentrate on ratios of echoes that do not use E_{23}. For example, the ratio

$$(S_1 E_{13}^2)^{1/3}/E_2 = -2^{1/3} \cot^2 \frac{\theta}{2}$$

can be used. This ratio has some attractive advantages:

1. It is independent of T_1 and T_2.
2. The estimate is robust. That is, since $\cot\theta/2$ is unbounded, there is no restriction on allowable value for the ratio.
3. We have found that this gives the most accurate results in the range $\theta \sim 180$.

We are able to distinguish $\theta < 180$ from $\theta > 180$ by keeping track of relative phases of the signals of S_1. This allows a complete determination of flip angle up to 360 degrees.

Some data were acquired using an mineral oil phantom with an rf pulse length of 10 msec and a 20 msec delay between pulse centers (τ). A graph of the calculated flip angle from the data is shown in the figure. As we can see, the algorithm provides an accurate estimate over a wide range of flip angles. For very low flip angles, the calculation is inaccurate. The calculated flip angle in the region around 180 degrees is much more accurately calculated.

The actual rf calibration consists of a trial pulse, calculation of the flip angle and readjustment. Typically, the scheme converges in 2 or 3 iterations. Since we do not require full T_1 recovery between sequences, the pulse rate is determined only by the computer's ability to acquire data and perform the calculation and allowing for a prudent level of signal to noise. Possible problems may arise if the flip angle is initially set to be greater than 270 degrees. In this case, the update increases the rf level and results in an overflip. (Notice that 270 degrees is an unstable point. The updating scheme will not normally be able to converge to this value.) We can then implement a simple check to ensure we are not flipping by 270 or 450 degrees by a final pulse at one third or one fifth the rf level.

We have found this to be a very rapid and robust method of adjusting rf amplitude. The entire process requires only a few seconds of data acquisition and consistently yields identical results with other slower techniques.

Sincerely,

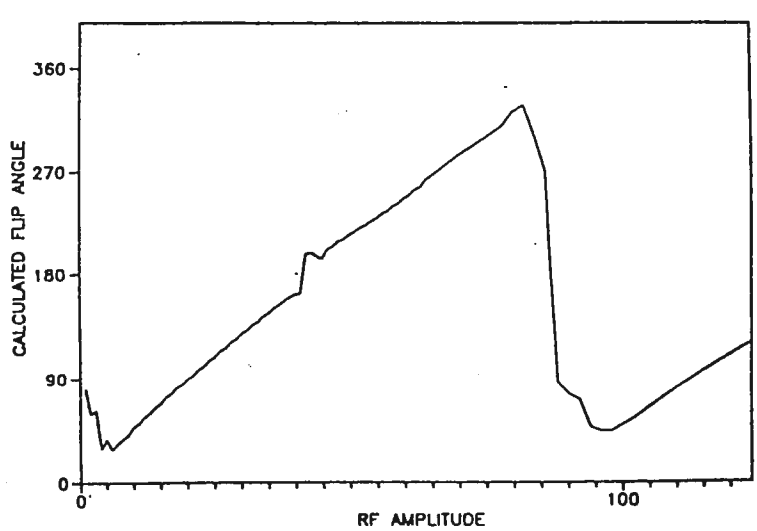
David M. Kramer

Joseph W. Carlson

(1) van der Muelen, P and van Ypern, G.H., *Proceedings, Society of Magnetic Resonance in Medicine Fourth Annual Meeting* 1129 (1985)

(2) Woesner, D.E. *J. Chem Phys.* **34** 2057 (1961)

Calculation of the flip angle based on our final algorithm.



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Dr. Bernard L. SHAPIRO
TAMU NMR Newsletter
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Wissembourg, le 15th December, 1988
(received 12/28/88)

Indirect experiments via 19F detection :

19F -183W correlation and T1(183W) determination

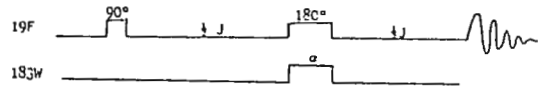
Dear Barry,

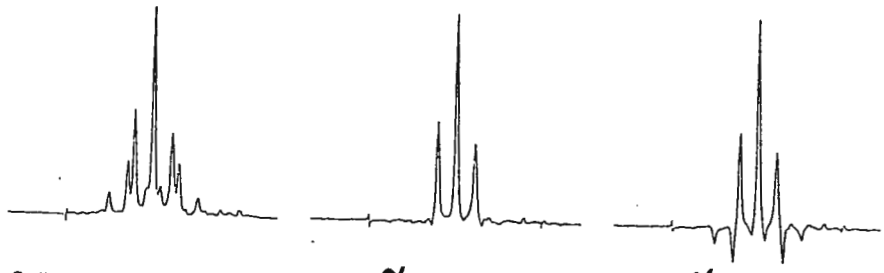
Usually, the inverse experiments are run via 1H detection. On the other hand, 19F is also a candidate of choice to start such an indirect scheme.

The experiments were run on an AM 400 equipped with a 5 mm inverse probehead. The proton channel of this probehead was retuned at the fluorine frequency. This 19F frequency was generated by the BSV7 broadband transmitter and the tungsten frequency (16.67 MHz) via a BSV3/BX accessory equipped with a 200 W pulsed amplifier (3-66 MHz). The sample is a fluorinated polytungstate (1) (H2W12F039) H5 - 0,37 M/D20, 5 mm tube.

Determination of the 90° pulse (183W)

This determination can be done by using an echo type sequence whose the 180° pulse acts as a symmetrising operator with respect to the hetero (F19-W183) J coupling.



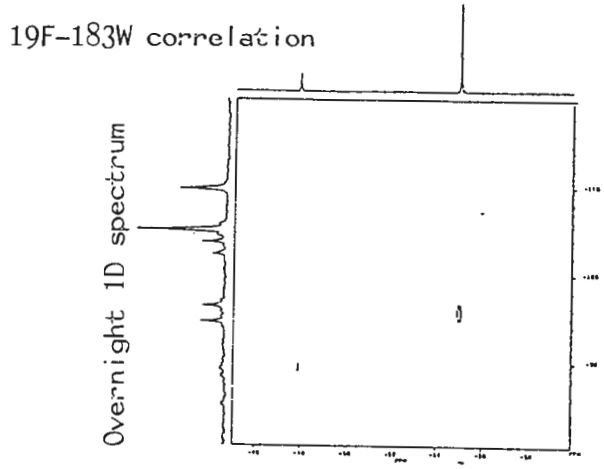


α = 0 °
W satellites/central peak in phase

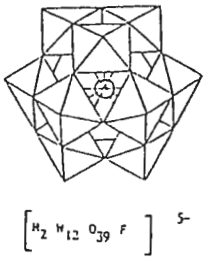
α = 90°
W satellites cancelled

α = 180 °
W satellites/central peak antiphase

Indirect correlation 19F-183W of (H2W12F039) H5



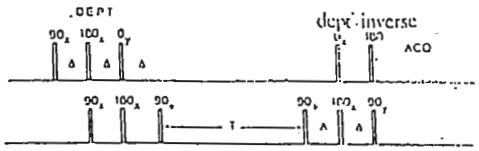
Time : about 2 hours



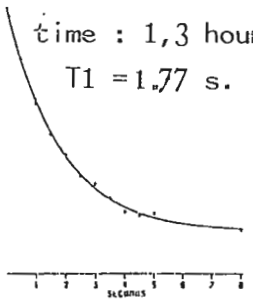
With this correlation, we can very easily detect the existence of a second species, barely detectable in the tungsten spectrum. This species is certainly the βisomer of the starting material.

Indirect determination of T1(183W) via 19F detection (2) and comparison with direct determination

This determination was done by using an inverse DEPT sequence following a DEPT sequence

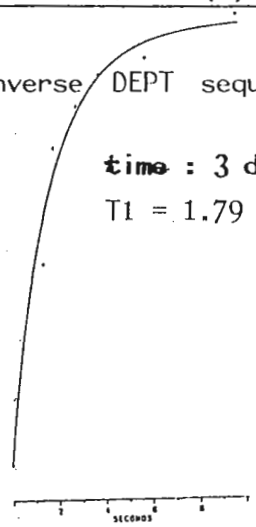


time : 1,3 hours
T1 = 1.77 s.



Indirect determination of T1 (183W)

time : 3 days
T1 = 1.79 s



Direct determination of T1 (183W)

The fit between the indirect and direct T1 measurements is excellent. On the other hand, from experimental time comparison, the indirect determination of T1 will certainly prove an excellent method for insensitive nuclei such as 57Fe, 1870s, 103Rh...

Sincerely,

M. BOURDONNEAU

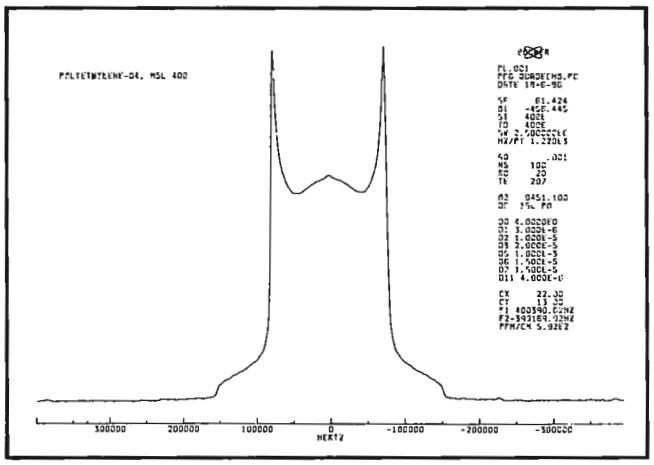
C. BREVARD

Bibliography :

1. J. LEFEBVRE, F. CHAUVEAU, P. DOPPELT and C. BREVARD, J. Am. Chem. Soc. 103, 15, 1981

2. V. SKLENAR, D. TORCHIA and A. BAX, J. Magn. Reson. 73, 375-379, 1987

MSL Performance Characteristics



The ^2H lineshape of deuterated polyethylene. This pattern is a superposition of a more or less gaussian line from the amorphous segments of polyethylene and a broad pake doublet for the crystalline $=CD_2$ fragments.

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- ☐ 1 Kw RF power
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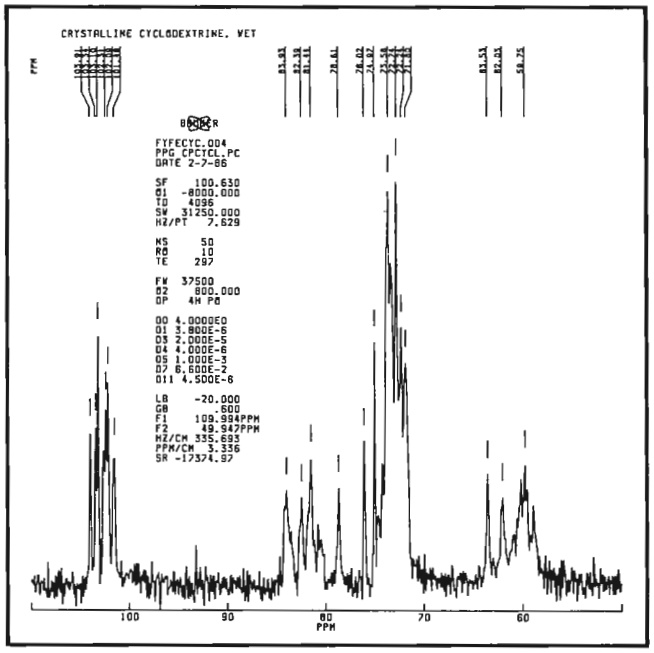
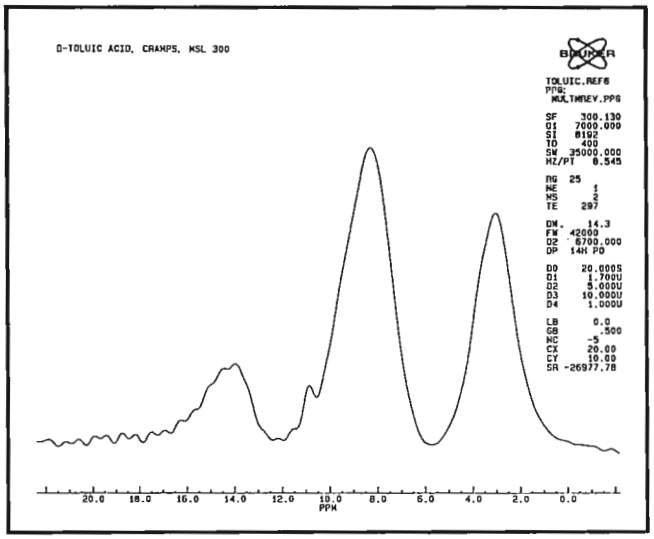


Crystalline cyclodextrine. A high level of decoupling power is needed to achieve the high resolution shown in this spectrum. This is even more true when the sample is wet, as in this case, since the dielectric losses are greater.



The CRAMPS spectrum of o-toluic acid. The peaks for methyl-, phenyl- and carboxyl protons are clearly resolved.

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Abbott Laboratories
Abbott Park, Illinois 60064

January 6, 1989 (received 1/9/89)

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

Dear Dr. Shapiro:

Re: "Utility of Heteronuclear 3D NMR"

We have recently described[1] an approach to resolve spectral overlap using heteronuclear three-dimensional NMR experiments in which a heteronuclear shift correlation and a homonuclear 2D NMR experiment (e.g., COSY, NOESY) are combined. More recently, we have been applying these 3D NMR techniques to several systems in our laboratory.

In one application, a 3D NOESY-HMQC experiment was performed on a dilute (0.7 mM) solution of the inflammatory protein, C5a (MW 8500), uniformly labeled with ^{15}N. Using this 3D technique, the NOESY spectrum of C5a was dramatically simplified by editing with respect to the ^{15}N chemical shifts. Our results indicate that the improved resolution offered by the 3D experiment will greatly facilitate the assignment of the proton NMR signals of proteins. Furthermore, these experiments allow additional internuclear distances to be obtained from otherwise overlapping NOE cross peaks. In addition, ^{15}N resonance assignments were easily obtained from the 3D data on C5a which are useful for studies on protein dynamics.

An important characteristic of heteronuclear 3D NMR is that a large one bond J-coupling is involved in one of the coherence transfer steps. This feature makes this technique applicable for the study of even larger proteins than C5a. Indeed, we have applied the 3D NOESY-HMQC experiment to a uniformly ^{15}N-labeled enzyme, CMP-KDO synthetase (MW=27,500), complexed with an inhibitor and CTP. Using this 3D technique, the NOESY spectrum of the ternary complex, which was extremely complex due to severe spectral overlap, was markedly simplified by the 3D technique.

We have also found[2] that heteronuclear 3D NMR experiments can be applied to small molecules with ^{13}C at natural abundance. This has been demonstrated in a 3D HMQC-COSY experiment on a concentrated solution of the aminoglycoside, kanamycin A (Figure 1). Ambiguities in the assignments which arise from protons resonating at the same frequency are resolved in this 3D experiment by editing the COSY data by the ^{13}C frequencies. Analogous to a two-dimensional heteronuclear relay experiment, the 3D HMQC-COSY experiment provides relay information by correlating the chemical shifts of a carbon, the attached proton(s), and their scalar coupled partners. In contrast to the heteronuclear relay experiment, however, the 3D experiment uniquely defines the frequency of the relay spin which is important for resolving spectral overlap when ^{13}C signals resonate at identical frequencies.

Thusfar, heteronuclear 3D NMR experiments have shown considerable promise for resolving spectral overlap for isotopically labeled biomacromolecules and small molecules at ^{13}C natural abundance. At present, however, detailed analyses of 3D data are difficult due to the lack of suitable software.

Therefore, much of our recent effort has been devoted to the development of software to improve our capabilities to analyze the 3D data sets. Some of the features already included in the program are the rapid selection of 2D planes from 3D spectra and a 3D peak-picking routine which will be useful for the semi-automatic analysis of the 3D data.

Sincerely,

Stephen Fesik, Robert Gampe, Ed Olejniczak, Erik Zuiderweg

[1]Fesik, S.W. and Zuiderweg, E.R.P. (1988) J. Magn. Reson. 78, 588.
[2]Fesik, S.W., Gampe, R.T., Jr. and Zuiderweg, E.R.P. (1989) J. Am. Chem. Soc., in press.

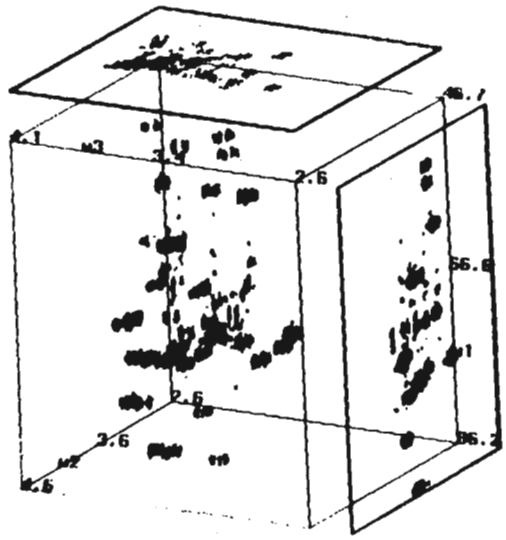


Figure 1. Three-dimensional contour map of a 3D HMQC-COSY spectrum of kanamycin A. Projections of the data set on the ω_2,ω_3 (top) and ω_1,ω_2 plane (side) are shown. The 3D data set was acquired on a Bruker AM500 NMR spectrometer, processed using a CSPI minimap array processor, and displayed on a Silicon Graphics workstation using software developed at Abbott Laboratories.

University of Arkansas for Medical Sciences

4301 W. Markham
Little Rock, Arkansas
72205-7199

January 10, 1988
(received 1/19/89)

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

Dear Barry:

Although lithium is used extensively in affective disorders, little is known about its distribution in the body or its mechanism of action. Patient monitoring and elucidation of lithium biochemistry in vivo are difficult due to the lack of suitable methods for following the distribution of lithium in various organs. Beyond NMR spectroscopy there are no known methods for following lithium concentrations in vivo. Clinically, lithium levels are usually measured in blood serum by flame photometry. Typically these levels are kept between 0.5 and 1.2 meq/L, which has been found to be a useful therapeutic range. Higher levels can induce toxic effects. Of course, the level in serum says nothing concerning the level in the brain, the presumed site of action.

In collaboration with Drs Joe Newton and E. Walker of the Little Rock Veterans Hospital, Dr. S. Ramaprasad, D. Cardwell, J. Sprigg, and I have used lithium-7 in vivo NMR spectroscopy at 24.83 MHz to follow the level of lithium in both brain and muscle in a normal volunteer and several patients. Work was performed on a slightly modified General Electric Signa magnetic resonance imaging system equipped with an in vivo spectroscopy accessory. A 15-cm, single-loop, distributed-capacitance, transmit/receive surface coil was used for excitation and detection. A small vial of 50 mM LiCl in 12.5 mM dysprosium chloride was placed near the coil as an external peak area standard. Figure 1 shows the 24.83 MHz lithium spectra acquired from the back of the head on a normal volunteer on 900 mg Li_2CO_3 per day on days 1 and 5 after starting Li therapy. The leftmost peak is the peak due to lithium in brain; the peak marked "std" is due to the dysprosium shifted LiCl vial. Each spectrum took 13 minutes to acquire. Clearly, in a short time we can quantitatively follow the progress of lithium in the brain of human patients. Figure 2 shows the results for the volunteer, who was on lithium for 5 days, and followed for 3 days after termination of therapy. The levels in serum, as measured by flame photometry, rise very rapidly and then fall off after the drug is discontinued. The levels in muscle are also quite high, comparable to those in serum. The level in brain is considerably lower, although it does track the level in serum. The actual concentration of lithium was obtained by comparing the in vivo result to that obtained on a 1 Mm LiCl solution

in 2 % agarose as a model of lithium in the brain. At this point these concentration values should be considered approximate.

Our results are similar to those reported by Renshaw and Wickland (Biol. Psychiatry 23, 465, 1988). However, their values for muscle were halfway between the values for serum and for brain.

Sincerely,

Richard A. Komoroski
Associate Professor
Radiology & Pathology

RAK/ms

FIGURE 1 Li-7 In-Vivo NMR Human Brain

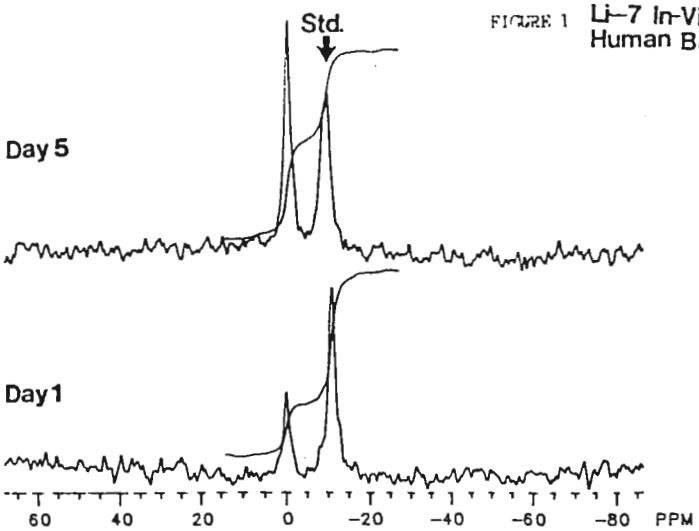
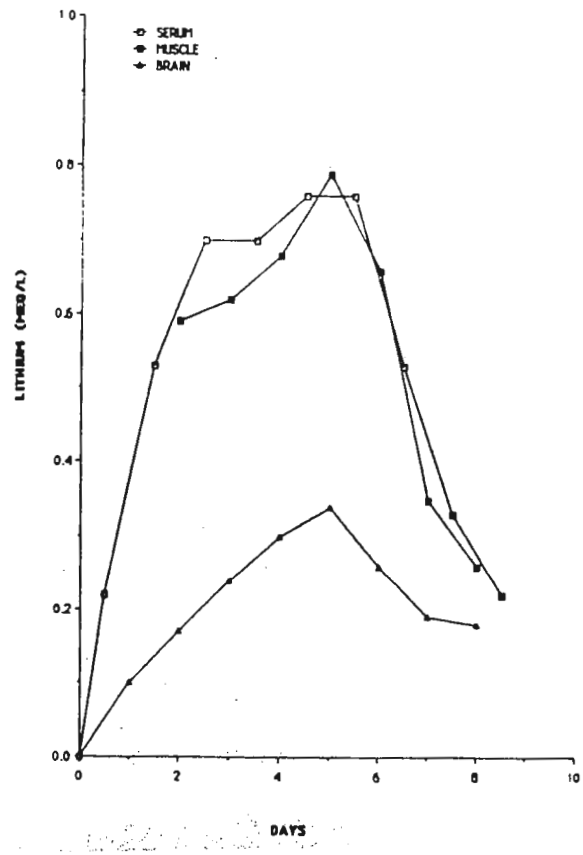


FIGURE 2

LI-7 In Vivo NMR NORMAL SUBJECT



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THE HISTORY OF NMR DATA PROCESSING

1st GENERATION	CAT, hard-wired time averaging
2nd GENERATION	Hard-wired magnitude FFTs
3rd GENERATION	Minicomputers added to spectrometers, Memory-based FFT and limited post-processing
4th GENERATION	Array processors, raster graphics, integrated cpu's and satellite stations, some advanced signal analysis methods
5th GENERATION	Intelligent Software and expert systems, networking, pattern recognition, advanced statistical methods, extensible.

UNIVERSITY OF CAMBRIDGE
DEPARTMENT OF CHEMISTRY
Lensfield Road
Cambridge CB2 1EP

Professor Barry Shapiro,
Editor, TAMU NMR Hamletter,
966 Elsinore Court,
Palo Alto,
CA 94303.

Clipping DANTE'S Wings

1 December 88
(received 1/9/89)

Dear Barry,

When someone starts a new job, they might ask the question whether it is more logical to be paid in advance or in arrears. It was Kurt Wüthrich (1) who showed us the answer in his paper on F_1 ridges in two-dimensional NMR -- pay in advance but halve the first paypacket. Alternatively pay only at the mid-point of each month.

This principle is pretty general; if we want to represent a continuous function in digital form we should be careful about the amplitudes of the first and last data points. Recently we came across this effect in DANTE sequences. If the envelope of the DANTE sequence is rectangular (all component pulses of equal amplitude) then the frequency-domain excitation pattern contains two artefacts -- the baseline has an appreciable positive offset and the wiggles in the baseline are more pronounced than they need be. These effects are stronger the fewer the number of pulses in the sequence. In fact they are quite evident in our very first calculations of the DANTE excitation spectrum (2).

The baseline offset disappears if the *last* pulse of the DANTE sequence is halved, while the excessive baseline wiggles go away if the *first* pulse is halved. We could think of this as slicing up the equivalent long-duration soft pulse into rectangular sections, each of which is represented by a single hard pulse in the DANTE sequence.
The first and last sections would have only half the area of those in the rest of the sequence.

This undesirable baseline offset effect is particularly marked if a half-Gaussian shaped DANTE sequence is used, because the last pulse has high intensity. When we used such shaped pulses for coherence transfer experiments (3) we were obliged to halve the intensity of the last pulse, otherwise off-resonance excitation was much too strong. Alternatively a delay equal to half the interpulse interval can be introduced at the end of the DANTE sequence before data acquisition.

Kindest regards,

Ray

Ray Freeman

(1) Otting, Widmer, Wagner and Wüthrich, J. Magn. Reson. **66**, 187 (1986).
(2) Bodenhausen, Freeman and Morris, J. Magn. Reson. **23**, 171 (1976).
(3) Davies, Friedrich and Freeman, J. Magn. Reson. **75**, 540 (87);**76**, 555 (88).

Université de Nancy I

Laboratoire de Méthodologie RMN

D. CANET
Professeur

Professor B.L. SHAPIRO
TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO, California 94303
U.S.A.

January 9, 1989 (received 1/19/89)

Title: *A simple pulse sequence for evaluating the efficiency of a proton inverting pulse via carbon-13 measurements.*

Dear Professor Shapiro:

The heteronuclear cross-relaxation term σ (for instance between carbon-13 and proton) can be deduced from the Nuclear Overhauser Enhancement Factor affecting the carbon-13 under investigation, in conjunction with the knowledge of the ^{13}C longitudinal relaxation time. This procedure entails however a number of difficulties associated with the decoupler gating and the alternative transient NOE method may be preferred. The latter makes use of an initial proton inverting pulse, followed by a mixing time τ and finally a carbon-13 observing pulse. σ is obtained from the initial slope of the curve representing the reduced ^{13}C magnetization $[I(\tau)/I_{eq}]$. However, this initial slope not only depends on σ but also on the initial conditions, that is $-2S_{eq}$ (S being the proton magnetization) in ideal conditions of proton inversion. In a non-ideal case, the initial conditions should write $-(1+k)S_{eq}$, where $k \leq 1$ is related to the efficiency of the inverting proton pulse. In order to accurately determine σ, it is therefore mandatory to evaluate k.

This can be simply achieved in the following way: Consider a carbon-13, J-coupled to a single proton, and whose resonance coincides with the carrier frequency. k can be derived from the comparison of the spectra resulting from the two sequences (run alternatively, the relevant fids being stored in separate memory blocks):

I : $(\pi/2)_x(^{13}C)$-1/2J-1/2J-(Acq. with proton decoupling)

II: $(\pi/2)_x(^{13}C)$-1/2J-$(\pi)(^{1}H)$-1/2J-(Acq. with proton decoupling)

At the end of sequence I, carbon-13 magnetization lies along -y whereas partial refocusing, depending on the efficiency of the proton inverting pulse, occurs along +y for sequence II and k is obtained from the ratio of the two relevant intensities.

I hope that this modest contribution will reinsert us in your mailing list.

Yours sincerely,

D. Canet K. Elbayed J. Brondeau

B.P. 239 - 54506 VANDŒUVRE-LES-NANCY Cedex (France) - Tél. ~~8 328.93.93~~ 83912049

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- The synthesizer frequency source does not have phase shifting. In this case 90° and 180° phase shifts can be generated with the 90° Phase Shifter Module.
- Second transmitter at the observation frequency. In this homonuclear case, any frequency source in the laboratory can, and usually does, produce a leakage signal in the observe spectrum regardless of the degree of gating. When the synthesizer frequency is 10 MHz removed from the observe frequency, the gating circuitry is able to completely blank the Auxiliary Transmitter frequency when it is gated off.

Configuration I uses a filter to select the desired frequency sideband for operation.

Configuration II uses the frequency directly from the synthesizer and requires that the synthesizer be capable of doing all required phase shifting. This configuration is not recommended when the auxiliary transmitter is to be used as a second homonuclear transmitter. This mode of operation requires no additional filters.

Both configurations are capable of operating with synthesizers generating sub 90° phase shifts.

The Auxiliary Transmitter is of modular construction, and can be purchased as a complete package or by the module. The modules are useful for updating existing instruments. FMR provides the modules and instructions for the do-it-your-selfer or will update your transmitter or decoupler in its facilities. The complete package is available as a stand alone transmitter when used with a synthesizer and power amplifier.

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Probe Upgrades

Existing NMR probes can be re-worked to provide improved performance at a cost much less than buying a new probe. Sometimes the increased performance level can make an older instrument more useful. This is especially true if the money for a new NMR system is not available. The degree of re-work depends on many elements which can be different with the starting probe versus a re-worked probe. Any of these factors may be a reason to re-work an existing probe.

- Sensitivity.
- Resolution.
- Lineshape.
- Insert size.
- Different nucleus.
- Addition of other nuclei.
- VT range.
- Addition of a decoupling channel.

Sensitivity

Many older probes have sensitivities considerably less (30 to 50%) than the probes being sold with new NMR instruments. The higher sensitivity performance is seldom due to better noise figure from the NMR console. As a rule of thumb, 1 dB better noise figure will improve signal to noise performance by 10%. Unless they are broken, most older spectrometers have a noise figure in the 2 to 3 dB range. New consoles are usually in the 1 to 2 dB range. Therefore, improving the console noise figure can sometimes give 10 to 20% better signal to noise. Re-working an older probe can often give 50 to 200% improvement in sensitivity.

New experiments.

- An old ^{1}H probe can have its sensitivity improved and a X nucleus decoupling channel added. This would give not only an improved ^{1}H probe, but a Reverse Polarization Transfer (RPT) probe.
- An old probe of one nucleus can be re-worked to a probe of a new nucleus.
- Broadband probes can have their tuning range expanded to allow probes to be changed less often.
- ^{1}H/X Probes can be constructed from either a ^{1}H or and X nucleus probe.

Prices

The performance level of a re-worked probe can be predicted and *specified* **if** the current sensitivity performance of that nucleus on any size insert **and** the system noise figure are known. Guidelines for expected performance level can be given in other cases. Call us to discuss you specific circumstances.

Costs for rebuilding probes vary considerably depending on the starting and ending points. Some generic price categories are shown below. Call us for a quote for your specific requirements.

Rebuilding an existing probe. (same nucleus. insert size etc.)
Converting a ^{1}H probe to an RPT probe. (same ^{1}H coil)
Converting to a different nucleus. (same insert size)
Converting to a different insert size.

New probes are also available at competitive performance and prices. Call to discuss you needs and obtain a quote.

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Westhollow Research Center
P.O. Box 1380
Houston, Texas 77001

November 22, 1988

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

SUBJECT: TARGET FACTOR ANALYSIS OF PROTON NMR SPECTRA OF AROMATIC MIXTURES

Dear Barry:

We have been investigating the use of target factor analysis (TFA) (1) as a method of identifying pure components in complex mixtures. Here we describe a simple example of principal component analysis (PCA) followed by TFA. The aim of PCA is to discover the dimensionality of complex data sets (e.g., sets of mixture spectra). TFA can then be performed using the results of the PCA. Suspected underlying factors (e.g., pure component spectra) are tested for existence within the multidimensional space described by the principal components (PC's). In this manner, existence of pure components (real factors) in mixtures can be verified.

Standard solutions of pure polycyclic aromatic compounds were made in CD_2Cl_2 . Monoaromatics were represented by toluene, diaromatics were represented by naphthalene, triaromatics were represented by phenanthrene, and tetraaromatics were represented by 1,2 benzanthracene plus pyrene. Only one standard solution was made for the tetraaromatics (benzanthracene plus pyrene), and therefore subsequent mixtures created from the standard solutions always have the same benzanthracene / pyrene ratio. From the four standard solutions, eight mixtures were made. An attempt was made to accurately maintain the monoaromatic concentration at a constant level in the mixtures, while variations were intentionally introduced in the di , tri , and tetraaromatic components. The reasoning behind creating such mixtures was as follows. By keeping the benzanthracene / pyrene ratio constant, only one degree of freedom is introduced in the spectra (total tetraaromatic concentration). Presumably, this single degree of freedom would be accounted for by PCA . Similarly, by trying to keep the absolute concentration of toluene constant, there would presumably be no change from spectrum to spectrum for the monoaromatic region resulting in no degrees of freedom introduced by the monoaromatic component. This relies on the ability to maintain a consistent toluene concentration. This mixture structure would presumably require three degrees of freedom to describe the changes between spectra.

Proton NMR spectra were recorded at 500 MHz on a Bruker AM-500. Spectra were recorded for all eight mixtures, for all pure components, and the mixture standard solution of benzanthracene and pyrene. An internal reference of CH_2Cl_2 at 5.2 ppm from TMS was used. Figure 1 shows the mixture spectra, while Figure 2 shows the pure component spectra (not including pure pyrene and pure benzanthracene). The raw data matrix was compiled by dividing the 1000 point aromatic region into 10 equally spaced regions (0.26 ppm / region) and then integrating all of the mixture spectra. The 8×10 data matrix was then multiplied by its transpose to generate an 8×8 covariance matrix on which PCA was performed. PCA results in 8 eigenvalues and eigenvectors. A large eigenvalue implies that its associated eigenvector is weighted heavily in explaining the variance and covariance within a data set. Since we are looking for variance within the data that is above the noise level, we can safely exclude some of the lightly weighted eigenvectors and still adequately retain the high signal-to-noise peaks we are interested in.

For this study, it was decided to employ the measurement of "imbedded error", as well as the "indicator function" , both developed by Malinowski (1), to help decide which eigenvalues and eigenvectors to omit. The imbedded error , and the indicator function are plotted in Figure 3. The imbedded error seems to have a break at four PC's . This is normally how the imbedded error is used; a large second derivative denotes the number of PC's. The indicator function was designed to avoid the question of "how big a second derivative is big enough" when using the imbedded error. The indicator function normally has a minimum at the real number of PC's. For the data used here, the indicator function has a minimum at five PC's.

Thus it seems clear that retention of only four or five PC's (eigenvectors) will adequately describe the variance in the data. The fact that the number of PC's is apparently four or five is encouraging since we know that there are five pure components in the mixtures. We were apparently unable to maintain

constancy of the toluene concentration (not surprising). We had expected to only see four PC's clearly emerge. The possible existence of a fifth is slightly disturbing. Perhaps the benzanthracene / pyrene ratio is not perfectly constant from mixture to mixture.

Having determined the number of PC's (five for this case), we then perform target factor testing to check whether or not variations in concentration of a pure component within the mixtures is responsible for some of the dimensionality. To do this, we employed the SPOIL function [1]. The SPOIL function is a measure of "how well a given pure component spectrum fits in the data space described by the PC's". Small values of the SPOIL function (0 to 3) imply that it is highly likely that the pure component is present and may be considered to be a real physical factor that is causing spectral variations. Large values (6 and greater) imply that it is not likely the pure component is present in the mixtures. Values between 3 and 6 fall in a grey area of indecision.

We performed target testing for all of the pure component spectra, the benzanthracene / pyrene solution, and an intentionally adulterated naphthalene spectrum for which one of the peaks was replaced with Gaussian noise. The SPOIL function results are shown in Table 1.

Table 1, SPOIL Values for Pure Components

Component	SPOIL
toluene	1.6897
naphthalene	1.6337
phenanthrene	1.8080
tetraaromatic	0.9338
pyrene	5.2638
benzanthracene	6.1245
single naphthalene peak	14.2251

Clearly, toluene, naphthalene, phenanthrene, and the benzanthracene / pyrene solution pass the SPOIL test and, as expected, are picked as likely pure components (real factors). Pure pyrene and pure benzanthracene fall in the grey area, so it appears the method does reject to some extent pure components that vary together. The fact that the SPOIL function falls in an indecisive region for pure benzanthracene and pure pyrene is commensurate with the inability of the PC tests to determine whether there are four or five PC's. The purposefully altered naphthalene spectrum fails the SPOIL test miserably. This is encouraging, since the retained naphthalene peak does vary from spectrum to spectrum for the mixtures, but it is rejected as a pure component.

It appears that the methods of PCA and TFA may be useful for analysis of complex mixtures. The true dimensionality of data sets can be found. Moreover, TFA can be used to determine what pure components or possibly classes of pure components contribute to the variation within sets of spectral data for mixtures.

Please credit this letter to the account of Larry Sterna.

Sincerely,

Grant Haddix

Grant W. Haddix
Associate Research Engineer
Analytical Department

1) Malinowski, E.R., and D.G. Howery, *Factor Analysis in Chemistry*, Wiley-Interscience, New York 1980

Figure 1, Proton NMR Spectra of Aromatic Mixtures

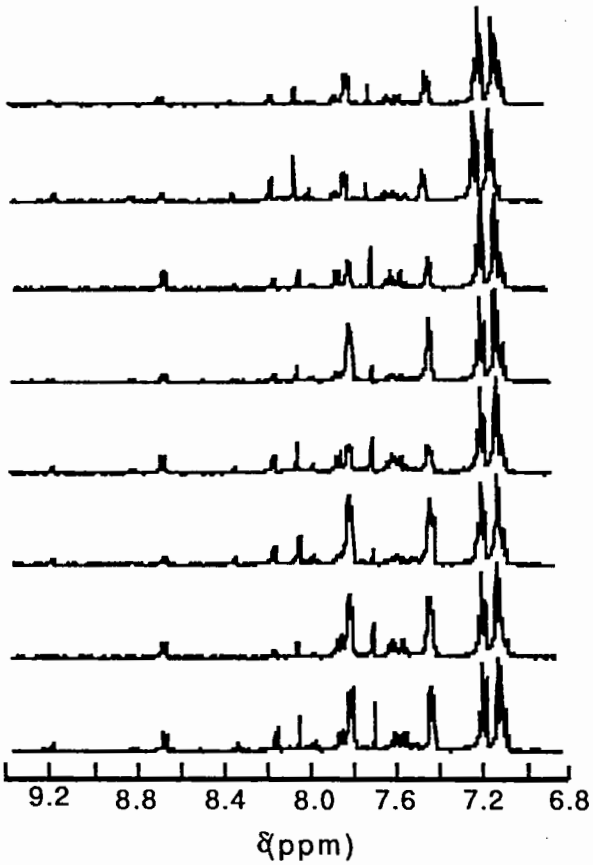


Figure 3, Determining the Number of Principal Components

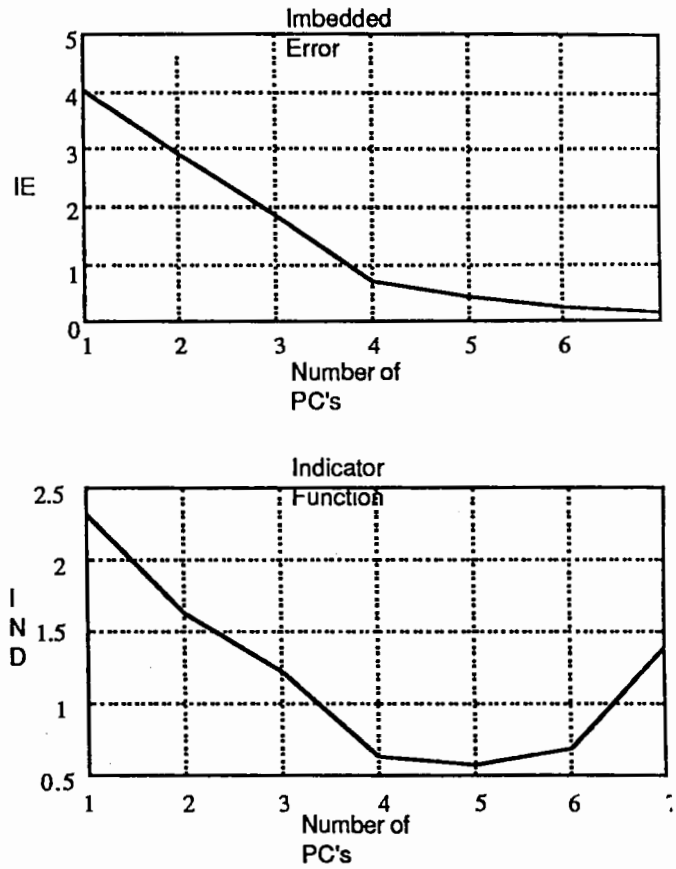
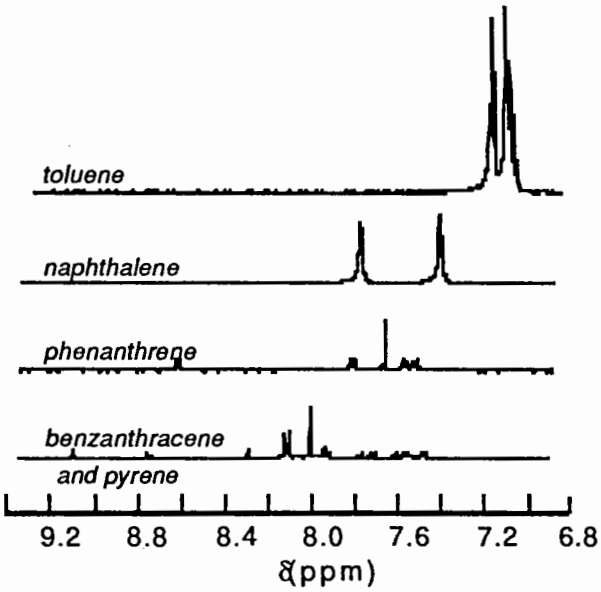


Figure 2, Proton NMR Spectra of Pure Aromatic Compounds



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PŘEDNOSTA: PROF. MUDr. ALFRED BELÁN, DrSc.
148 22 PRAHA 4 - KRČ
VÍDEŇSKÁ 800

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

(received 1/21/89)
Prague, January 4, 1989

TITLE: NEW EQUIPMENT AND TESTING OF IN VIVO METHODS

Dear Professor Shapiro:
Thank you very much for your "ultimatum" reminding me that I have been engaged in in vivo NMR spectroscopy for a couple of months now.
Eight months ago, a Magnetom 1.5 imager was installed at our institute. The system enables us, among other things, to carry out also some spectroscopic experiments. To date, our attention has been focused on study of skeletal muscle metabolism and on exploring the range of applications this system can be put to in checking organs scheduled for transplantation.
At the present time, we are completing a study designed to analyse the subjective and objective errors we make in skeletal muscle examination using the 8-cm surface coil. Just as in other quantitative measurements, S/N value is the key parameter with a bearing on the accuracy of integration. In our standard calf muscle examination (AC=512, TR=2s, flip angle = 90° or 180°, total time 17 min), S/N value for Pcr is about 128 with a standard deviation s $\cong$ 10% (for a group of ten randomized volunteers). In examinations performed during exercise when as little as 32 FID gets accumulated (measurement time is 1 min.), S/N value for Pcr is considerably lower, i.e., about 41 and s$\cong$12%. The relative error of determination of the Pcr/Pi ratio of signal intensity is in the range of 10 relative per cent in the first case, and up to 30 relative per cent in the second case. It appears these random errors may hinder inter-laboratory comparison of methods used for skeletal muscle examination, and it would be worth considering to perform inter-laboratory testing of selected methods of in vivo spectroscopy analogically to the procedure adopted in the case of ethanol analysis (1).
I hope this contribution will reach you before the deadline date set in the "ultimatum" letter.
With best regards,

Sincerely yours,

Milan Hájek

Dr. Milan Hájek
NMR Laboratory
Institute for Clinical and
Experimental Medicine
Prague

1) Guillou, C.; Trierweiler, M.; Martin, G.J.: Magn. Reson. Chem. 26, 491 (1988).

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Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
Freq. St'd: Oven, TCXO, Ext.
Interface: BCD par. or GPIB
Size: 19"W, 5¼"H, 18"D
Price: $6,400.00*

Other Options:
Progr. Attenuator, 0-90dB
(or 0-99dB with GPIB)
nx10MHz output 20-140MHz
or any 10 MHz line (20-140)

PTS 500

Range: 1-500MHz
Resolution: 0.1Hz-100KHz (opt.)
Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
Freq. St'd: Oven, TCXO, Ext.
Interface: BCD par. or GPIB
Size: 19"W, 5¼"H, 18"D
Price: $7,500.00*

Other Options:
Progr. Attenuator, 0-90dB
(or 0-99dB with GPIB)
nx10MHz output 20-140MHz
or any 10 MHz line (20-140)

PTS 300 NEW

Range: 0.1-300 MHz
Resolution: 1 Hz
Switching:
20μs (10MHz, 100MHz steps)
5μs (1 MHz steps)
1 + 2μs (transient + delay) for all steps
1 Hz-100 KHz; (phase-continuous)

Output: +3 to +13dBm; 50 ohm
Spurious Outputs: Type 1 −70/65dB (typ/spec); Type 2 −60/55dB
Phase Noise: −68dBc, (0.5Hz-15KHz) −63dBc
Freq. St'd: Oven, TCXO, Ext.
Interface: BCD par. or GPIB

Size: 19 × 3½ × 17"
(relay rack or bench cabinet)
Price: Type 1 $5,800.00*; Type 2 $5,300.00*

*Prices are US only, manual & remote, (BCD), 1 Hz res. with oven std.

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

Ihre Zeichen	Ihr Schreiben vom	Unsere Zeichen	Telefon	Telex	Datum
		Wr/ud	(05 31) 61 81 - 0 Durchwahl 353	9 526 67 gebio Telefax (05 31) 6181 515	January 12, 1989 (received 1/21/89)

Local mobility in macrolide polyethers

Dear Dr. Shapiro,

Structural elucidation of natural products by nmr continues to provide interesting snippets of information. Over a considerable period of time we have been investigating the structure of the novel antibiotic sorangicin A from the gliding bacterium Sorangium cellulosum. The X-ray crystal structure shows several unusual bond angles and bond lengths in the C15 - C20 region such that it is not possible to determine whether C17-C18 is a single or a double bond, although this is clear from the nmr data.

During an intensive investigation of the solution structure we obtained the enclosed partially relaxed C-13 spectra of the olefinic region by an inversion-recovery sequence. Spectrum b shows that four of the protonated olefinic carbons relax more slowly than the others. As the relaxation is dominated by the dipole-dipole mechanism the result indicates a local shorter correlation time in the C15 - C20 region. Increased mobility in this region explains rather nicely the problems encountered with the X-ray data.

Yours sincerely,

V. Wray

Victor Wray

R. Jansen

Rolf Jansen

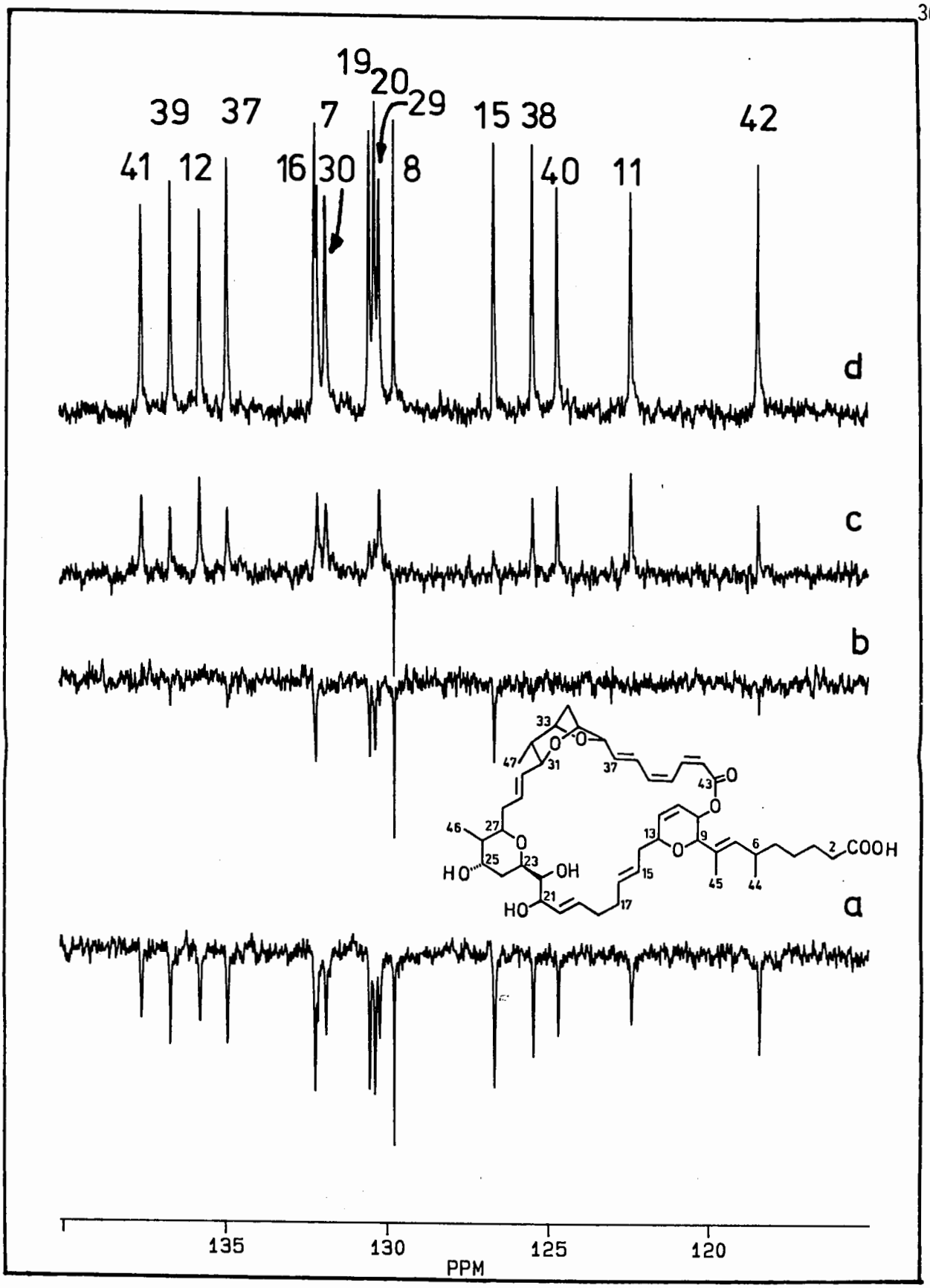

Figure. ^{13}C spectra of Sorangicin A in DMSO-d_6 taken with an inversion-recovery pulse sequence with interpulse delays of a) 0.05, b) 0.1, c) 0.2 and d) 5 s.

TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 365
February 1989

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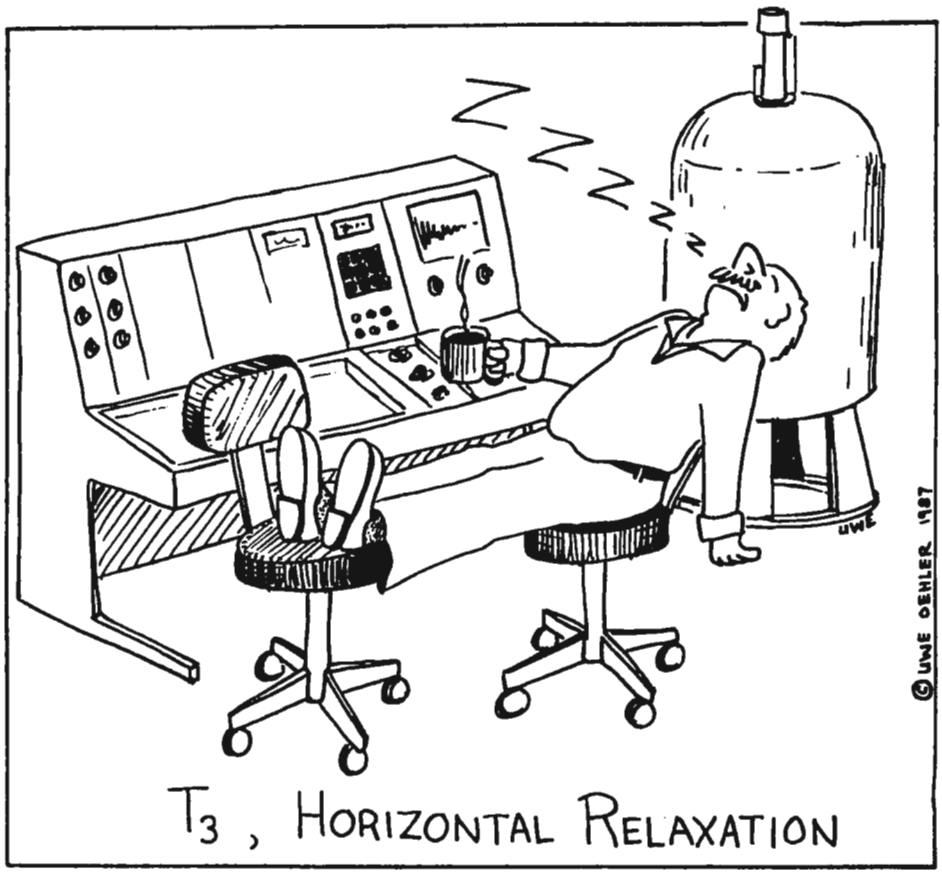

CSI 2T Applications

Shielded Gradients and NMR Microscopy

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

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

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

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

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

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

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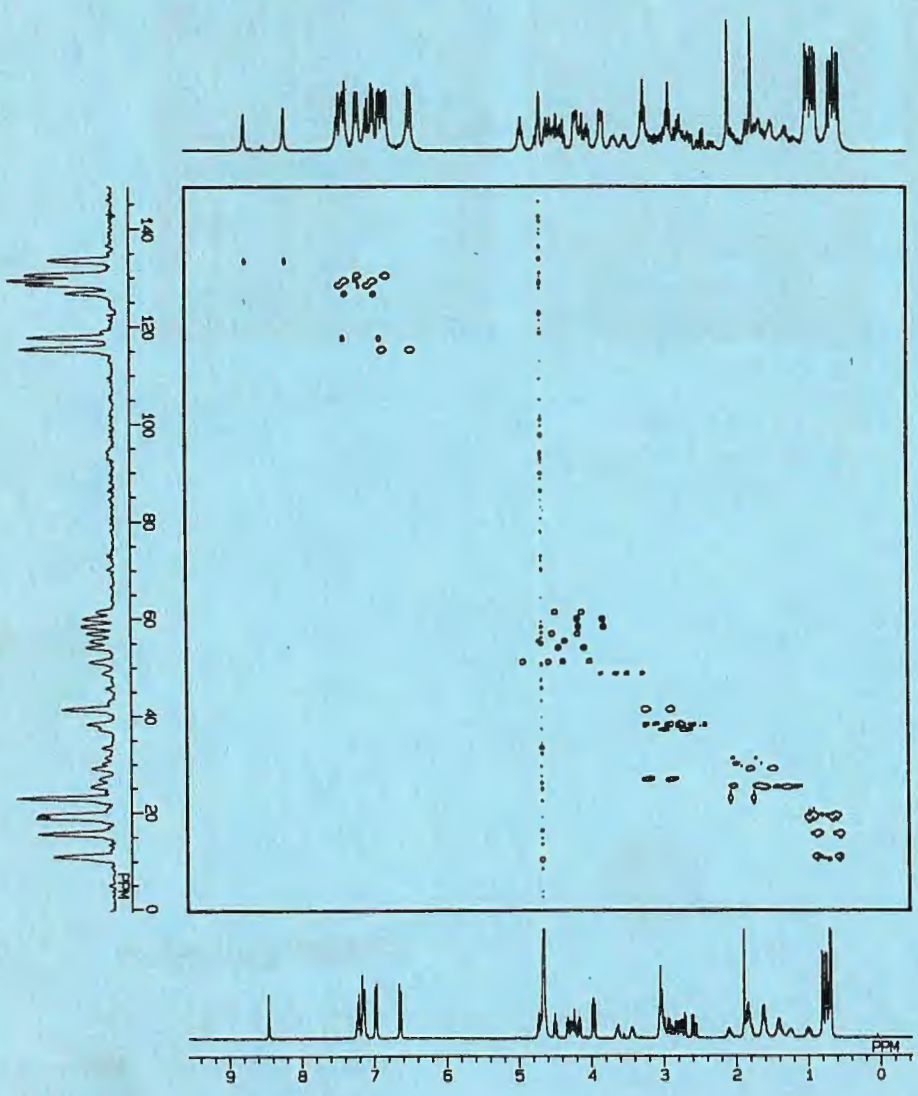
JEOL GSX-FT NMR Systems

Subject: Rf STABILITY

All of the automation, elegant experiments, and high speed computer processing will do nothing for an NMR experiment if the spectrometer is not stable. The Rf section of the spectrometer must be reproducible and clean of spurious signals over periods of days for some experiments.

One of the most demanding experiments for spectrometer stability is the reverse detection (H [C]) experiment without C decoupling. Between the relatively sharp lines and the low magnitude of the satellites, this experiment graphically demonstrates the stability of the spectrometer. As the data below shows, a standard JEOL GSX Spectrometer has the Rf stability to do these experiments.

ANGIOTENSIN-II, 3mg.in.D20



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