TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 401

February 1992

Continued on page 2

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Isotopic Purity (%D)	Density (g/cm³)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetic Acid-d_4	CD_3COOD	99.5%	1.1	17	118	0.551 (32)
D-120	Acetic Acid-d_4 + TFA						
D-13	Acetone-d_6	CD_3COCD_3	99.8%	0.84	-94	57	0.460 (20)
D-121	Acetone-d_6 + 1% TMS		99.8%				
D-129							
D-14							543 (20)
D-21							0.611
D-122							
D-130							
D-28	Chloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

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WCV-XL (XL-100)	11" X 26"	XL-100 (and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (and FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
WCV-20 (CFT-20)	11" X 16 3/4"	CFT-20, FT-80, FT-80A	Gridded-Two Color
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FORTHCOMING NMR MEETINGS

33rd ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **March 29 - April 2, 1992**; Contact: ENC, 750 Audubon, East Lansing, MI 48823; (517) 332-3667

Sixth Washington University-ENI/Emerson Electric Co. Symposium on NMR, St. Louis, Missouri, **May 18, 1992**; Contact: Karen Klein, Wash. Univ.; (314) 935-6405.

ISMAR 92 (The XIth Meeting of the International Society for Magnetic Resonance), Vancouver, B.C., Canada, **July 19 - 24, 1992**; Chairman: C. Fyfe. Contact: ISMAR 92, Dept. of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. Tel: (604) 822-2293; FAX: (604) 822-2847; EMAIL: ismar@unixg.ubc.ca; BITNET: ismar@ubcmtsg.bitnet.

Eleventh Annual Scientific Meeting and Exhibition, Society of Magnetic Resonance in Medicine, Berlin, Germany, **August 8-14, 1992**; Contact: S.M.R.M., 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415) 841-1899, FAX: (415) 841-2340.

XV International Conference on Magnetic Resonance in Biological Systems, Jerusalem, Israel, **August 16 - 21, 1992**; Contact: Prof. Gil Navon, XV ICMRBS, P. O. Box 3190, Tel Aviv 61031, Israel.; Tel. (972-3) 5271111, Fax: (972-3) 5239099.

High Resolution NMR Spectroscopy (a residential school), University of Sheffield, England, **April 1993[*sic*]**; Organizer: Dr. B. E. Mann (Sheffield); For information, contact Ms. L. Hart, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England; Tel.: 071-437-8656.

Additional listings of meetings, etc., are invited.

Table of Contents, cont'd.

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Page Length ~~Request~~ Instruction

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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. 403 (April) ---------- 20 March 1992
No. 404 (May) ---------- 24 April 1992
No. 405 (June) ---------- 22 May 1992
No. 406 (July) ---------- 19 June 1992

* * * * *

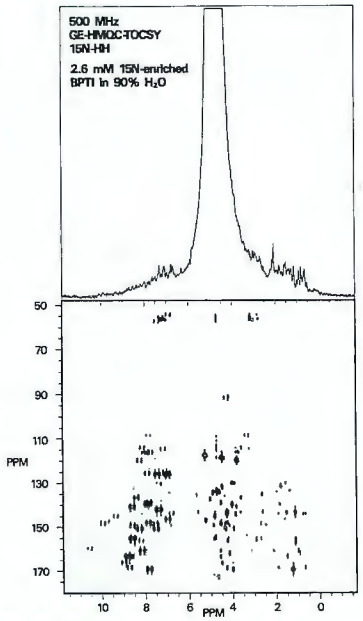
NMR UPDATE

Gradient Enhanced Spectroscopy: a new, practical answer

By Frank Huang, PhD, Paul Calderon, MS, and Boban John, PhD

Making Gradient Enhanced Spectroscopy (GES) a viable method for high resolution spectroscopy has long been of interest to researchers. The obvious benefits in speed and information content were too often overshadowed by the drawbacks of signal loss and distortion.

Technology developed at GE NMR Instruments has overcome these challenges. The S-17 Gradient Enhanced Spectroscopy Accessory with integrated inverse probehead makes GES practical for a broad range of applications in 1D, 2D, 3D and 4D experiments.



Gradient Enhanced Spectroscopy technique applied to an HMQC-TOCSY experiment demonstrates excellent water suppression without the need for presaturation or selective excitation.

Research Implications

- Speed without phase distortion or signal loss.
- Practical for 1D, 2D, 3D and 4D experiments.
- Accommodates proton and heteronuclear GES techniques.

A better design

The use of a three-axis, actively-shielded gradient set allows GE to overcome the inherent drawbacks of previous GES technology —most notably, phase distortion and signal loss:

Active shielding. Eddy current effects are the major source of phase distortion in GES spectra. Active shielding prevents interaction of strong gradients with magnet and shim components—the source of eddy current effects.

Fast, strong gradients. Short gradient pulses in excess of 20 G/cm minimize signal loss during pulse sequences.

Applications advantages

With its integral inverse probehead, the S-17 Accessory can accommodate proton as well as heteronuclear GES techniques.

Gradient fields in excess of 20 G/cm are able to suppress water in aqueous samples and to improve performance in heteronuclear experiments. Other applications advantages:

- Eliminates phase cycle requirements and subtraction error.
- Reduces T1 noise.
- Reduces collection times for 2D, 3D and 4D data sets.
- Provides lineshape independent water suppression in multiple quantum coherence selection experiments.
- Provides lineshape independent water suppression via diffusion differences for large molecular weight samples.
- Improves water suppression in experiments using selective time reversal RF pulses.
- Separates cross-correlation and exchange phenomena in NOESY experiments.
- Distinguishes chemicals inside the cell from those outside in whole cell applications.

For additional information on the S-17 GES Accessory, write to GE NMR Instruments, 255 Fourier Ave., Fremont, CA 94539.
Or call toll free:

1-800-543-5934

GE NMR Instruments

Gradient-Enhanced ^{15}N HMQC

The pulse sequence and the coherence pathway diagram for a ^{15}N GE-HMQC are shown in Fig. 1. The pulse sequence was a standard ^{13}C GE-HMQC experiment (1) with different gradient amplitudes to account for the difference between the gyromagnetic ratios of ^{13}C and ^{15}N. The 90° proton pulse creates transverse magnetization which evolves into an anti-phase state with respect to J(NH) coupling at the end of the period Δ (where Δ = ½J (NH)). The antiphase components are converted into heteronuclear zero- and double-quantum coherence by the ^{15}N 90° pulse and the multiple quantum coherences are allowed to evolve during t_1. The 180° ^1H pulse in the center of the evolution period serves to eliminate the ^1H chemical shift evolution, yielding pure ^{15}N chemical shifts along that axis. The zero- and double-quantum signals are then *coherence-order labeled* by the gradient pulses G1 and G2. After conversion into antiphase proton magnetization by the last ^{15}N 90° pulse, the desired components are refocused by the gradient G3 and detected. The application of a gradient pulse results in a phase factor being applied to the magnetization which is dependent upon gradient strength, duration, the distance from the gradient isocenter, the gyromagnetic ratios of the coupled nuclei, and the desired coherence order. The relative amplitudes of the labeling and refocusing gradient pulses will determine the selection of a specific coherence pathway and are calculated to suppress magnetization components arising from the solvent and other protons not coupled to ^{15}N spins.

The fundamental principle of coherence selection using gradients is that for a pathway to be detected, the cumulative phase factor during the acquisition must be zero:

$$G_1p'1 + G_2p'_2 + G_3p'_3 = 0. \quad [1]$$

The subscripts denote steps in the pulse sequence where p′ defines a composite coherence order for the heteronuclear case which includes the gyromagnetic ratios of the coupled nuclei:

$$p' = p^1H + (\gamma^{15}N/\gamma^1H)p^{15}N \quad [2$$

and p^1H and $p^{15}N$ are the coherence orders for the ^1H and ^{15}N spins respectively.

In the coherence pathway diagram, the relevant values of p' are given to the left and the relative gradient areas (gradient strength x duration) are given next to each gradient pulse. The following pathway (shown in *Fig. 1*):

$$H(+1) \rightarrow H(+1)N(0) \rightarrow H(+1)N(+1) \rightarrow H(-1)N(+1) \rightarrow H(-1)N(0)$$

is detected using a 5:5:1 ratio of gradient areas, since according to Equation 2:

$$5(1.1) + 5(-0.9) + 1(-1.0) = 0 \quad [3]$$

where the numbers in the parentheses refer to the composite coherence orders. Using these relative gradient areas, protons not coupled with ^{15}N spins may pass through an alternate pathway:

$$H(+1) \rightarrow H(+1) \rightarrow H(+1) \rightarrow H(-1) \rightarrow H(-1)$$

which results in a net phase factor:

$$5(1.0) - 5(-1.0) + 1(-1.0) = -1 \quad [4]$$

Thus, signals from this pathway remain defocused during the acquisition.

A 2D ^{15}N GE-HMQC spectrum of ^{15}N enriched BPTI is shown in *Fig. 2*. The spectrum was collected using a 5 mm inverse probe on an Omega™ PSG 500 spectrometer equipped with an S-17 gradient accessory. Half-sinusoid shaped gradient pulses were applied simultaneously along the X, Y, and Z axes with a maximum gradient strength of ≈20 Gauss/cm and a duration of 3.5 ms. A matrix size of 2048 × 128 resulted in 3.5 Hz resolution in the ω_2 dimension and 10 Hz in the ω_1 dimension. No decoupling was applied.

Gradient-enhanced experiments provide a viable alternative to traditional phase-cycling methods for the selection of coherence pathways. In cases where the sensitivity is adequate, gradient selection can substantially reduce the collection time in multi-dimensional experiments. The ^{15}N GE-HMQC data presented here has none of the t_1-noise from cancellation artifacts usually present in phase-cycled versions of the HMQC experiment. In addition, since the suppression of the single-quantum signals is done prior to acquisition, the receiver gain may be increased, which results in a substantial increase in signal-to-noise. For these reasons, gradient pulses should be the method of choice for coherence selection in HMQC experiments.

Reference

1. R.E. Hurd and B. K. John, *J. Magn. Reson.* **91,** 648 (1991).

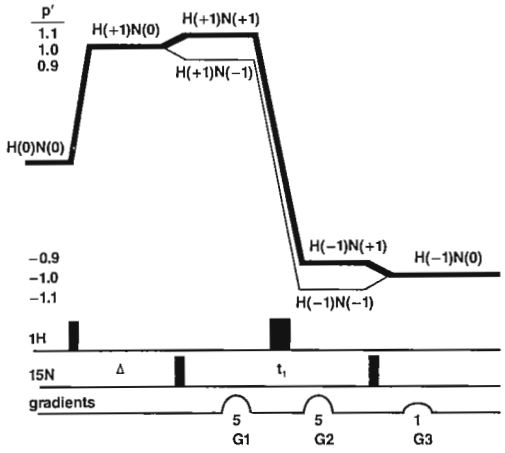


Fig. 1

Pulse Sequence and the coherence pathway diagram for a 15N GE-HMQC experiment.

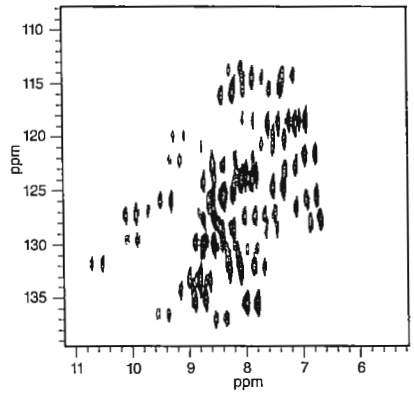


Fig. 2

A 2P Ge-HMQC spectrum of 15N enriched BPTI. The sample was 2.6mM in 90% H2). The data collection time was 2.6 hours.

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December 19, 1991
(received 12/23/91)

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

^{13}C LINESHAPES OF [2 - ^{13}C] ATP FREE AND ENZYME-BOUND

Dear Barry,

In one of our previous letters to TAMU, (Vol. 352, p. 64, Jan. 1988) we communicated the differential line broadening of proton-coupled ^{13}C doublet of [2 - ^{13}C] ATP bound to the enzyme 3-phosphoglycerate kinase. The differential broadening is readily explained on the basis of interference between two second-rank tensor interactions *viz* ^{13}C - ^{1}H dipolar interaction and ^{13}C - chemical shift anisotropy (CSA) which simultaneously contribute to ^{13}C relaxation. The effect was predicted by Hiroshi Shimizu a long time ago, (J. Chem. Phys. *40*, 3357 (1964)) and has also been the subject of some recent papers by a number of research groups. We measured this differential broadening using a number of ATP-utilizing enzymes. Some of these spectra are shown in the left-half of the figure below (ADK: adenylate kinase, PGAK: 3-phosphoglycerate kinase, CREK: creatine kinase, and MTRS: methionyl tRNA synthetase; adenylate kinase was studied with [2 - ^{13}C] AMP as well as [2 - ^{13}C] ATP). In order to analyze the lineshapes quantitatively, we determined the CSA tensor in the laboratory of Dr. U. Haeberlen at the Max Planck Institüt, Heidelberg, Germany. The tensor has no particular symmetry; the asymmetry parameter (η) is 0.72. By means of formulae derived for $\eta \neq 0$, and for isotropic molecular reorientation (single τ_c) the observed linewidths were used to determine a τ_c for each enzyme. These values were approximately proportional to the molecular masses of the enzymes indicating that it is reasonable to consider the reorientation of enzyme-bound ATP to be isotropic. There were no big surprises in any of this.

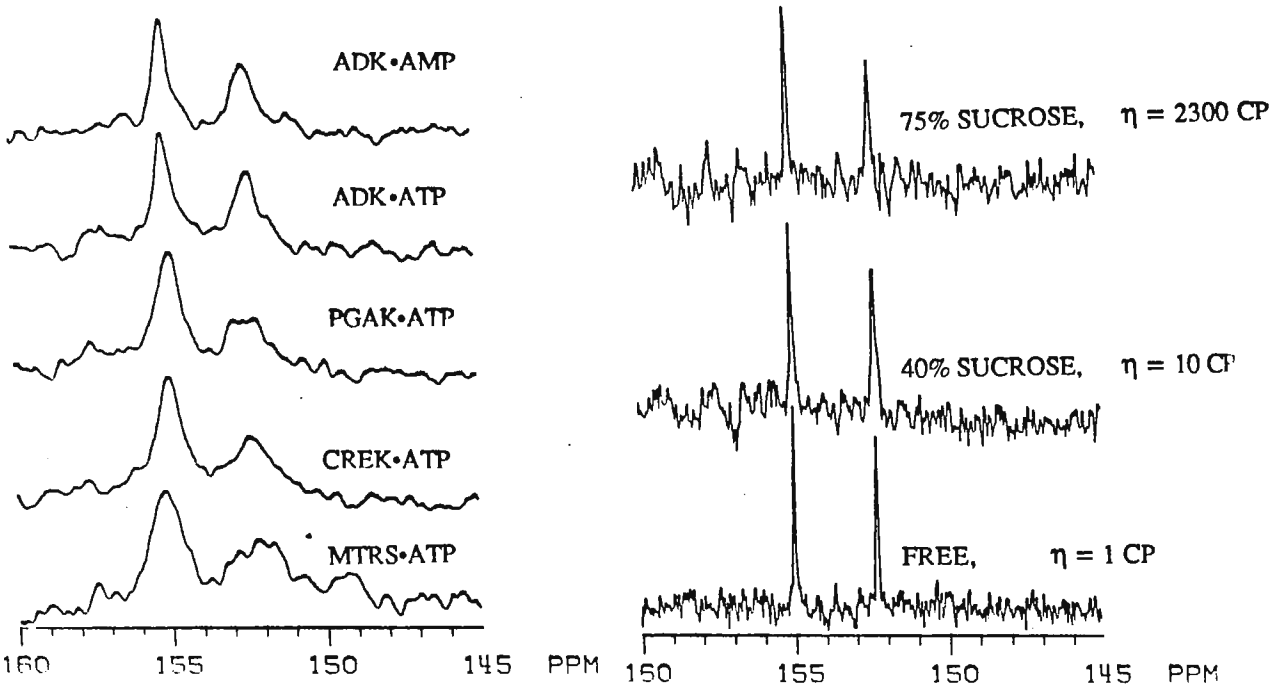
In sharp contrast to the above ^{13}C lineshapes of [2 - ^{13}C] ATP dissolved in highly viscous solutions of sucrose and glycerol show no significant broadening even at viscosities a factor of 2000 over that of water. At these viscosities the τ_c for overall tumbling of ATP should be similar to the enzymes considered (see the right-half of the figure below). A similar insensitivity to solvent viscosity obtains for ^{31}P linewidths of ATP as well. We believe that these results suggest that glycosidic rotation as well as the phosphate chain mobility in ATP with characteristic times of about a nanosecond (and rather low activation energies) are not particularly attenuated by high solvent viscosities. A corollary to this interpretation is that these motions *are* arrested in the enzyme complexes. All this will appear in a paper in J. Am. Chem. Soc. sometime during 1992.

Sincerely yours,

Durga

B.D. Nageswara Rao

^{13}C NMR (75 MHz) of [2 - ^{13}C] ATP



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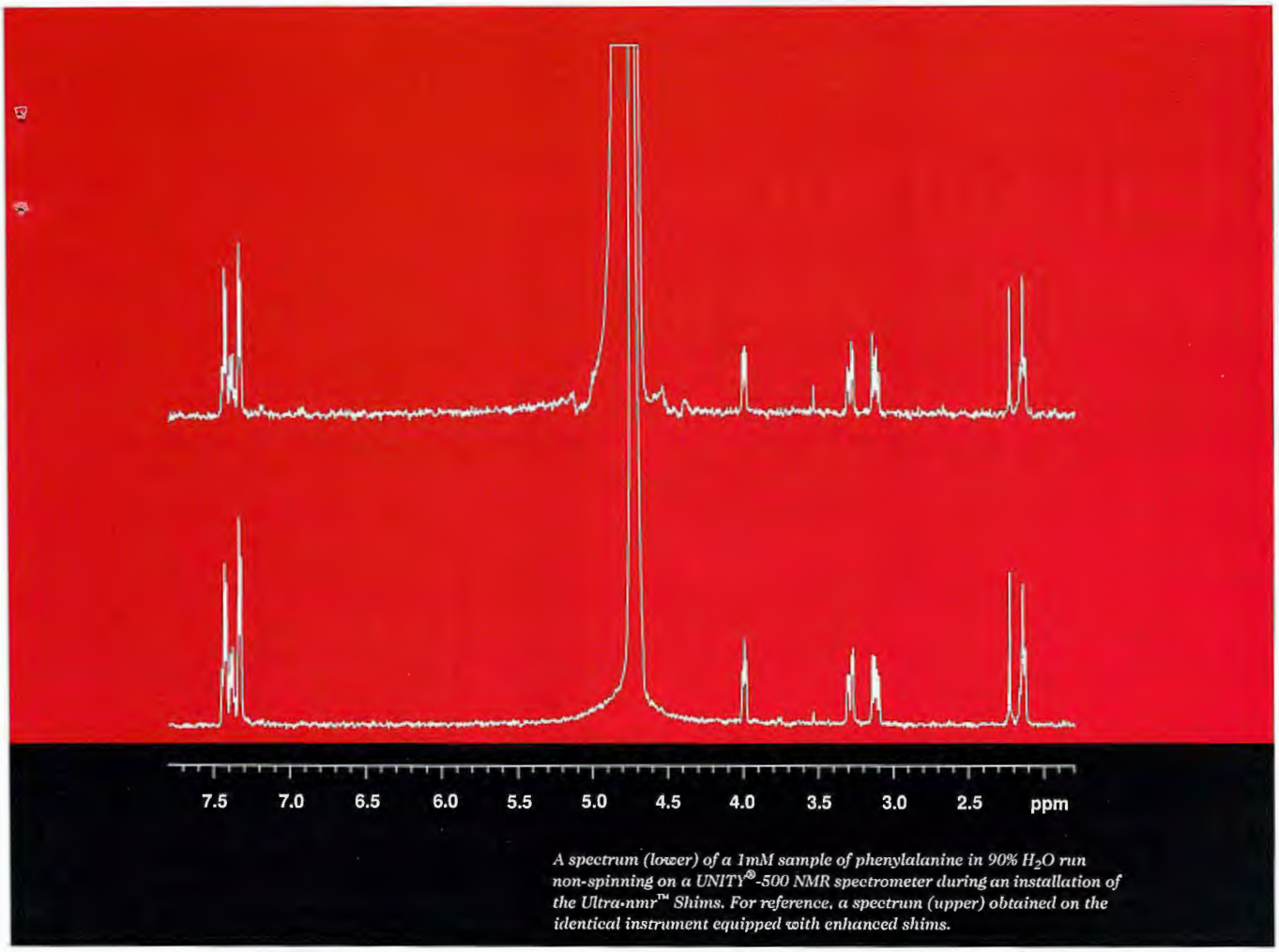

A spectrum (lower) of a 1mM sample of phenylalanine in 90% H_2O run non-spinning on a UNITY®-500 NMR spectrometer during an installation of the Ultra•nmr™ Shims. For reference, a spectrum (upper) obtained on the identical instrument equipped with enhanced shims.

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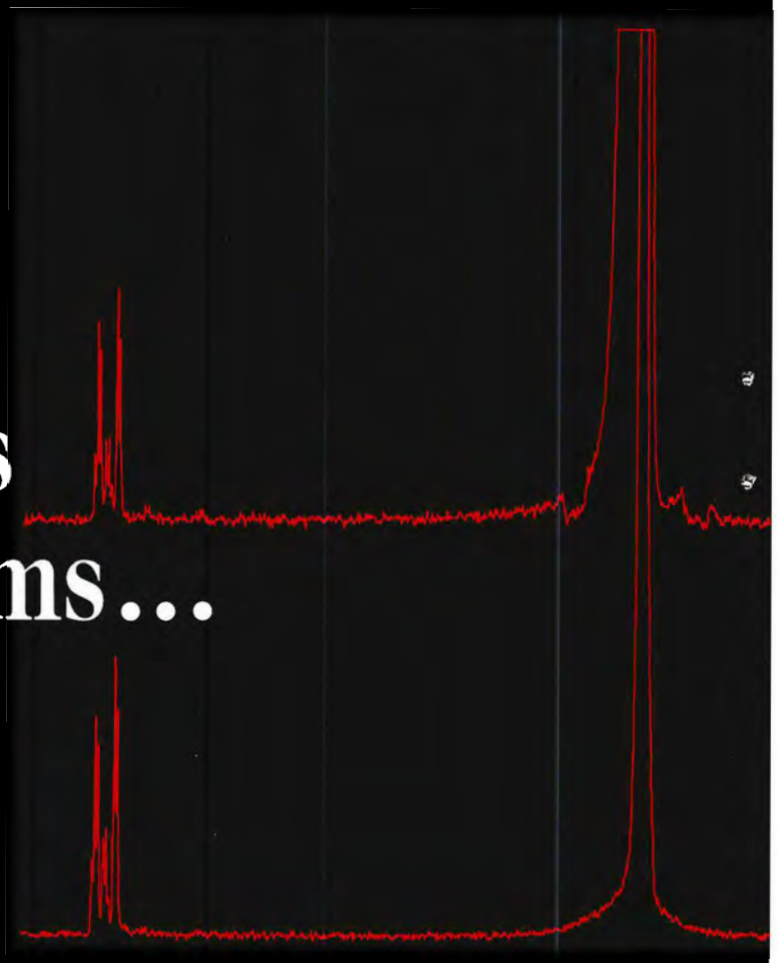

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January 8, 1992
(received 1/17/92)

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

Recollect whole 3D experiment or just corrupt fid(s)?

Dear Dr. Shapiro,

Recently, we have completed the first of our heteronuclear 3D experiments using triple resonance techniques on our Varian Unity 600 spectrometer using a fully $^{13}C/^{15}N$ labeled protein. For the HNCO experiment, we collected 48 x 32 x 512 complex points (in the ^{13}C - ^{15}N - ^{1}H dimensions) for a total of 6144 fids collected over four days. Although our acquisition time was fairly short (0.057 seconds), we managed to acquire one corrupt fid (Figure 1) possibly due to pulse breakthrough. This leads to certain disaster upon transformation in two dimensions (Figure 2A).

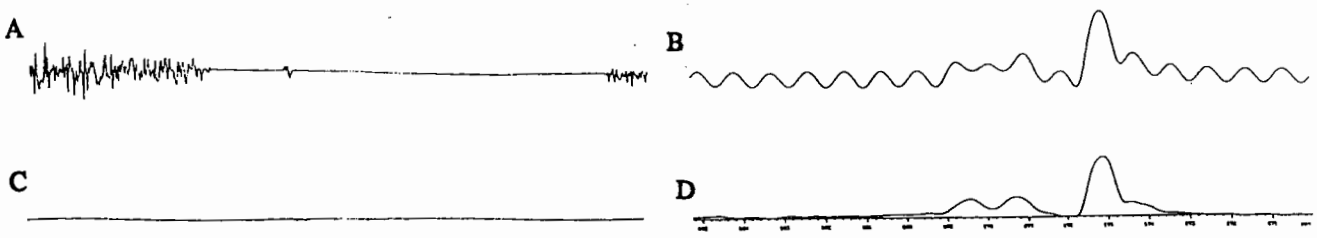

Figure 1. A comparison of (A) the corrupt fid 69 and (B) an f3 trace through the first F1F3 (^{1}H-^{13}C) plane of an HNCO experiment containing the corrupt fid, versus (C) the reacquired fid 69 and (D) the same f3 trace as (B) with the corrupt fid replaced in the data set (see below).

Rather than recollecting a whole data set, which is frustrating as well as time consuming, it would be convenient to simply recollect the bad fid. Recently, Steve Patt (of Varian Associates) has sent us a program to merge two data sets together and one of us (T.J.) has modified this program to suit our needs. To use the program, one simply needs to find the corrupt fid, calculate the proper t1 and t2 delays and the proper phase for that fid, and reacquire that fid (before leaving the spectrometer). The merge program then replaces the corrupt fid with the good fid. If one

inadvertently leaves the spectrometer before checking for corrupt fid's, the bad fid can be replaced with zeros.

Figure 2B shows an F1F3 plane (at t2=0) of our HNCO experiment after having retaken fid 69 and merging it. We are looking forward to analyzing our data and achieving a full spectral assignment in the near future.

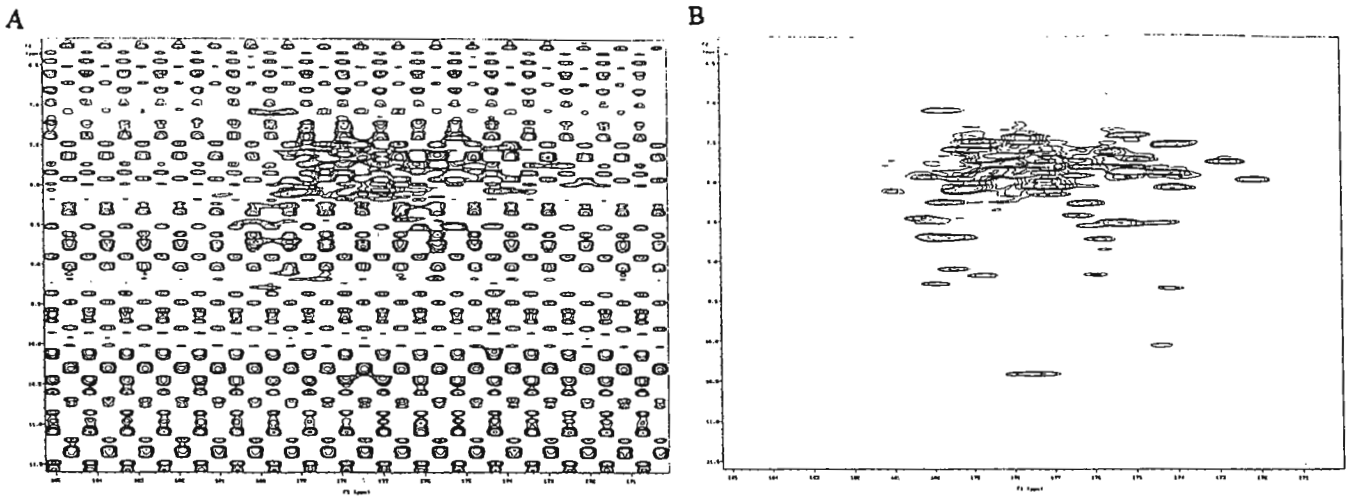

Figure 2. (A) An F1F3 plane (at t2=0) of an HNCO experiment with one corrupt fid and (B) The same plane with the reacquired fid replaced in the data set.

Sincerely yours,

Carolyn Slupsky

Tim Jellard

Brian Sykes

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IN REPLY REFER TO:

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

6120-10:JBM
10 January 1992
(received 1/18/92)

Re: Filtered Back Projection on a Personal Computer

Dear Barry,

Thank you for your colorful reminder. I hope this note will get us back in TAMU newsletter's good graces.

We have been working in the area of solid state NMR imaging for a number of years now. During this time we upgraded our old NMR computer and pulse programmer system to allow us to perform more sophisticated imaging experiments. Unfortunately, the new system is not up to processing the NMR data or constructing images so we have resorted to doing all of our data and image processing on personal computers.

For our solids imaging we continue to use filtered back projection for reasons of sensitivity and simplicity of (homebuilt) hardware. The algorithm is simple[1] and easy to implement in higher level programming environments. We are left however, with the aggravation of long image reconstruction times. As an example, Fig. 1 shows three 'images' of a delta function at zero frequency. To create the 32x32 pixel image from 32 projections (Fig. 1B) takes over 130 s on our 486 PC, while the 32x32 2-D FFT (complex floating point) (Fig. 1A) takes just 0.11 s. The additional time for filtered back projection appears to accrue from the linear interpolation of the projection data onto the 2-D Cartesian grid, and the 3 deep nested loops that this entails. Fig. 1C is also a filtered back projection image. Instead of linear interpolation, Fourier interpolation was used by zero-filling the data set 16 times, and the appropriate points for back projection were selected from the enlarged data set. This reduces the number of nested loops by one, and no additional Fourier transforms are required since filtering of the projections is performed in the time domain[2]. The image in Fig. 1C took 5 s to construct.

Furthermore, Fig. 1B is not a delta function because of the errors introduced by linear interpolation near a singularity. The errors in Fourier interpolation near a singularity occur in the form of 'sinc wiggles' which nearly average to zero on back projection (Fig. 1C). Fig. 2 shows images corresponding to those of Fig. 1 for the more realistic situation (for NMR imaging) of a non-delta function spectrum. The time domain signal is gaussian and is sampled to 2 T_2's. Now the filtered back projection images closely resemble the 2-D FFT image and the errors due to interpolation have disappeared.

All of this is probably of limited utility for your readers in NMR imaging, however we have found it to be an enlightening exercise, and the experience will cause us to look more closely at our data processing techniques in the future.

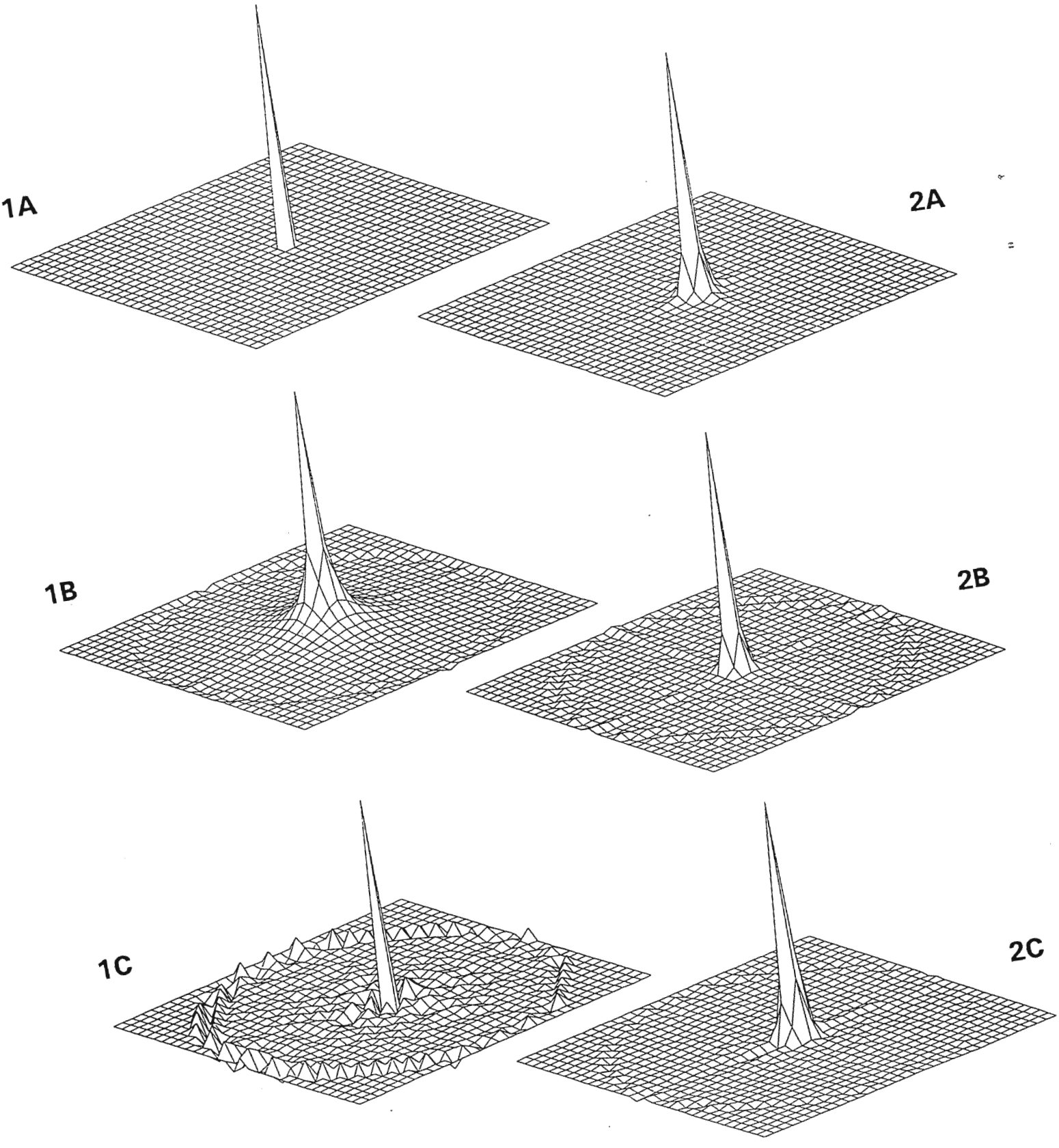
1. R. A. Brooks and G. Di Chiro, Radiology 117, 561 (1975).
2. P. Mansfield and P. C. Morris, "Advances in Magnetic Resonance," Supp. 2, NMR Imaging in Biomedicine, (Academic Press, New York, 1982).

Regards,

AN

A. N. Garroway

Joel B. Miller
Chemistry Division
Code 6120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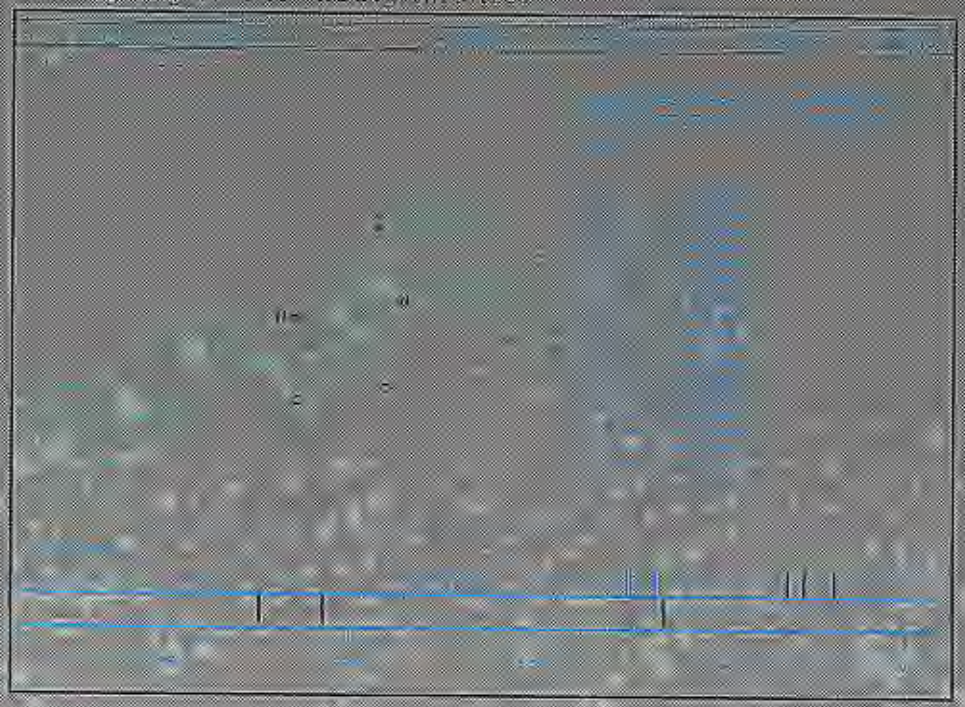

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Dr. F.J.J. de Kanter
Department of Chemistry

De Boelelaan 1083
1081 HV Amsterdam
The Netherlands

November 7, 1991
(received 1/6/92)

vrije Universiteit *amsterdam*

Chemical Shielding Anisotropy determined by NMR Spectroscopy of Dielectrically Oriented Molecules.

Dear Dr. Shapiro,

For more than twenty years one of the main topics of research of Prof. MacLean at the Vrije Universiteit at Amsterdam has been the study by NMR of molecules oriented in electric fields. The electric field NMR technique is a useful method for studying anisotropic molecular properties and spin interactions of polar and anisotropically polarizable molecules in liquid solutions. The technique has been used to investigate the nuclear quadrupole coupling which can give information about dipole moments and polarizability tensors as well as unknown quadrupole coupling constants. Other applications are the study of nuclear dipolar couplings between protons or protons and ^{13}C. Recently for the first time the chemical shift anisotropy of nuclei in liquids has been determined by electric field NMR. Two nuclei have been studied: the nitrile ^{13}C in acetonitrile and the ^{15}N in nitrobenzene.

From ^{13}C frequency changes and ^{14}N quadrupolar splitting in the NMR spectra of acetonitrile upon dielectric alignment the chemical shift anisotropy of the nitrile ^{13}C is found to be $\Delta\sigma$=+378 ppm (1). In the literature a number of values is given: 204 ppm from solid state NMR (2), 328 ppm from liquid crystal NMR (3), and 460 ppm from temperature dependent spin-lattice relaxation (4). The first and third value are obviously in disagreement with our liquid state value. Our result for acetronile is comparable to the chemical shielding anisotropy of the nitrile ^{13}C of benzonitrile, $\Delta\sigma$=354 ppm, determined by the magnetic field dependence of the spin-lattice relaxation (5). The magnetic field dependent spin-lattice relaxation of the nitrile ^{13}C of acetonitrile gives some puzzling results. From the ^{13}C spin-lattice relaxation times at 50.31 MHz, T_1=51.0 s and at 62.89 MHz, T_1=46.5 s and the field independent quadrupolar spin-lattice relaxation time of the nitrile ^{14}N, T_1=3.9, ms we find $\Delta\sigma$=419 ppm which is within experimental error equal to the electric field NMR result. However at 100.63 MHz the experimental nitrile ^{13}C spin-lattice relaxation time T_1=45.3 s. If the chemical shift anisotropy is the only field dependent ralaxation mechanism the expected spin-lattice relaxation time is 36.0 s. We are now trying to figure out what is causing the large difference between experimental and expected T_1 values at 100.63 MHz.

For the ^{15}N nucleus of nitrobenzene-d_5 there is an excellent agreement between the chemical shift anisotropy as determined by electric field NMR and by field dependent spin-lattice relaxation (6).

The first method gives $\Delta\sigma$=+271 ppm; determined from the ^{15}N frequency changes and the para-^{2}H quadrupolar splitting in the NMR spectra. From the field dependence of the ^{15}N spin-lattice relaxation (T_1=175 s at 25.35 MHz, T_1=108 s at 40.54 MHz and T_1=78.5 s at 50.70 MHz) and using the effective correlation time obtained from the quadrupolar spin-lattice relaxation of ^{14}N in nitrobenzene one obtains $\Delta\sigma$=270 ppm. Thus the chemical shift anisotropy of ^{15}N in liquid nitrobenzene, determined by the electric field NMR method, is not only smaller but also of opposite sign compared to the value reported for the solid state: $\Delta\sigma$=-398 ppm (7).
Please credit this contribution to the subscription of Dr. J. Bulthuis.
References:

1. L. Huis, F.J.J. de Kanter and C. Maclean, Molec. Phys. **73**, 1077 (1991).
2. S. Kaplan, A. Pines, R.G. Griffin and J.S. Waugh, Chem. Phys. Letters **25**, 78 (1973).
3. P. Diehl, J. Jokisaari and F. Moia, J. Magn. Reson. **49**, 498 (1982).
4. E. von Goldammer, H.D. Lüdemann and A. Müller, J. Chem. Phys. **60**, 78 (1974).
5. F.W. Wehrli, J. Magn. Reson. **32**, 451 (1978).
6. L. Huis and C. MacLean, to be published.
7. D. Schweitzer and H.W. Spies, J. Magn. Reson. **16**, 243 (1974).

Yours sincerely,

Frans de Kanter Dolf Huis

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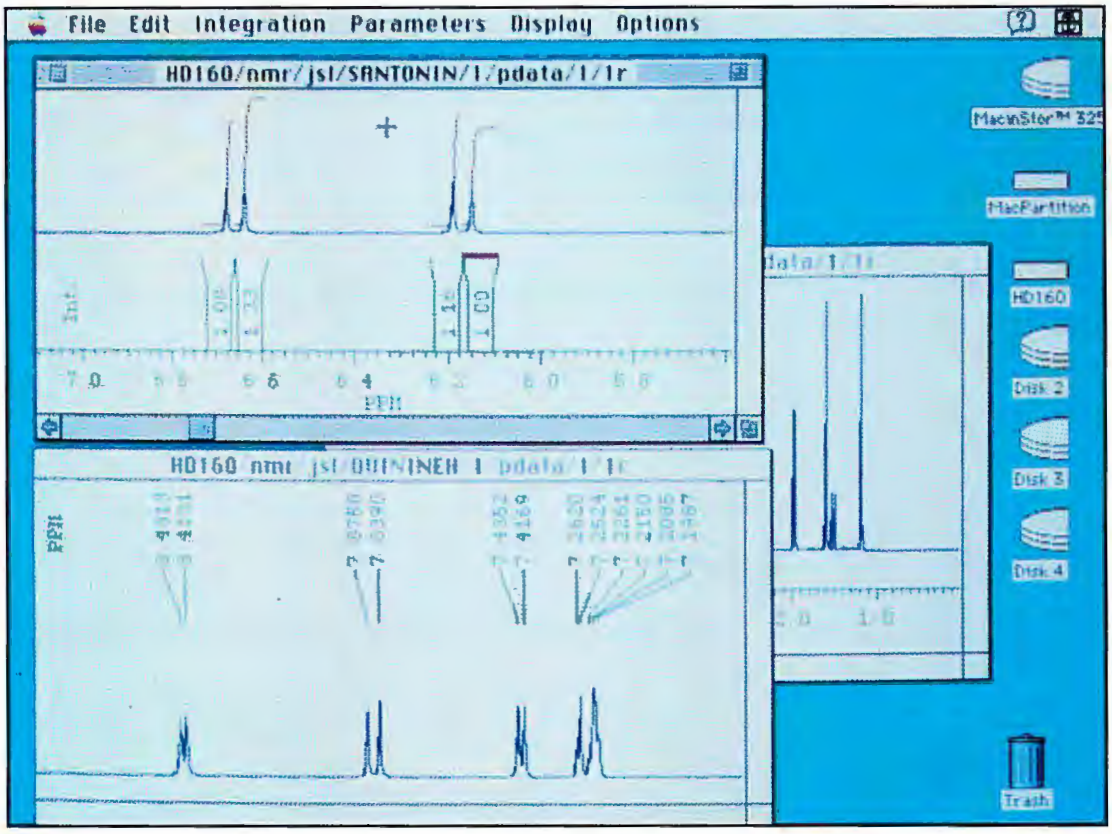

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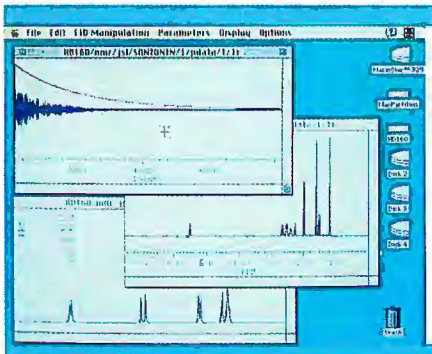

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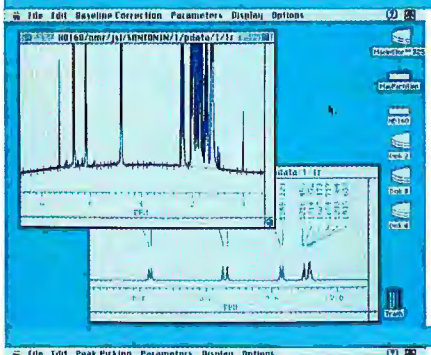

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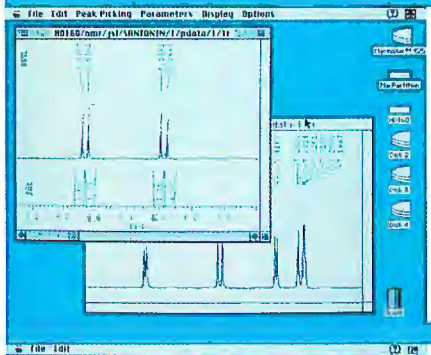

Automatic or interactive peak integration. In automatic integration the user has control over the integration threshold and grouping of multiplets. The automatically determined integrals can be individually manipulated once the automatic selection process is complete. The integration parameters can be stored for future use.

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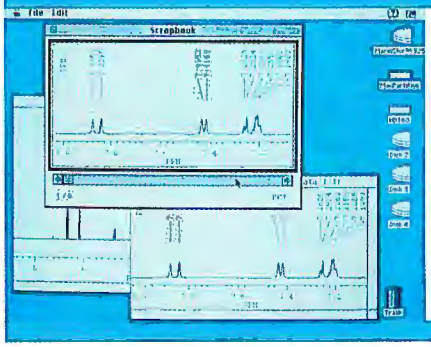

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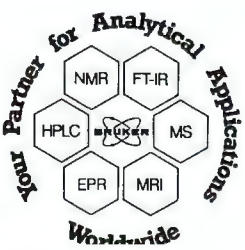

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January 20, 1992
(received 1/21/92)

Dr. B. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 943030
U.S.A.

Dear Dr. Shapiro,

The Bruker Canada Application Group recently had occasion to examine the Dante sequence and have subsequently started to convert pulse sequences which use a Dante pulse train for selective excitation to pulse sequences which use a shaped selective pulse. The advantages of the latter will be clear to anyone who has struggled with the fine tuning required for optimisation of the Dante pulse train!

The enclosed set of spectra illustrate the selectivity of the modified Dante experiment; the ease of implementation will be obvious to all AMX users!

The sample used was 300 mM camphor in benzene-d6 and the intent was to probe the utility of shaped pulse selective excitation by looking at the methylene and methine carbons at ~43 ppm which are separated (peak to peak) by 5 Hz. Selective excitation of the methyl carbon at ~20 ppm was undertaken only to reproduce the literature study. As you can see, a 900 ms (!) shaped pulse picks out the individual carbons and in the proton coupled experiment allows unambiguous assignment of the coupling constants.

Yours sincerely,

BRUKER SPECTROSPIN (CANADA) LTD.

Dr. Charles Rodger
Product Manager - NMR

Howard Hunter

Dr. Howard Hunter
Applications Chemist-NMR

Peter Krygsman

Dr. Peter Krygsman
Applications Chemist- NMR

CR:ag

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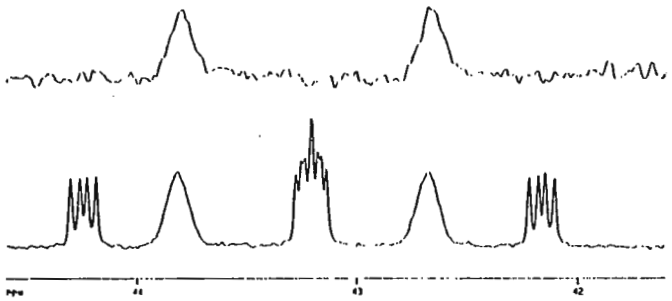
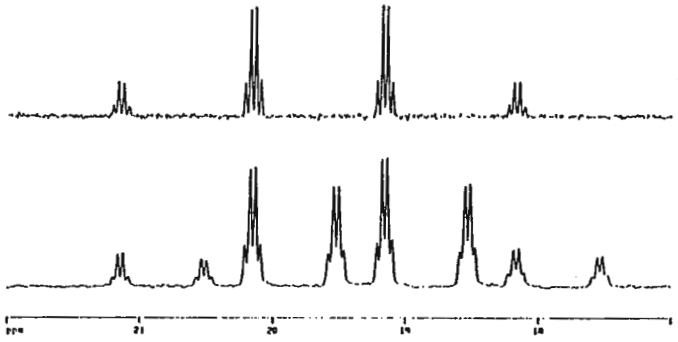
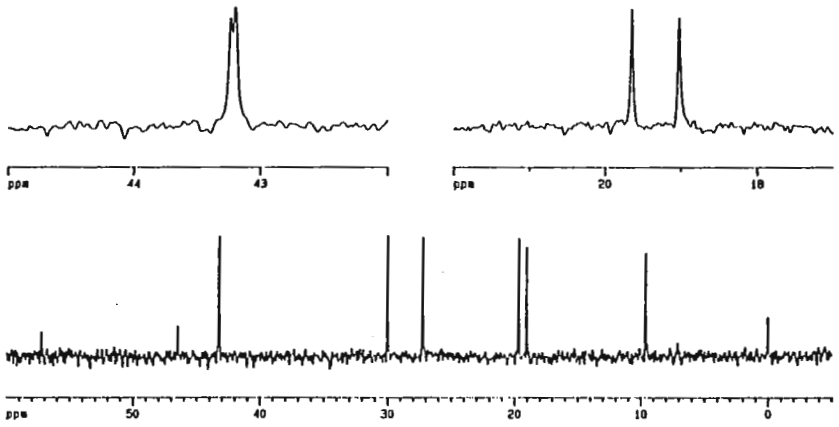
amx500, proton coupled carbon-13 reference spectrum (lower)
and selective excitation experiment (upper)



amx500, proton coupled carbon-13 reference spectrum (lower)
and selective excitation experiment (upper)



amx500, carbon-13 reference spectrum
camphor sample



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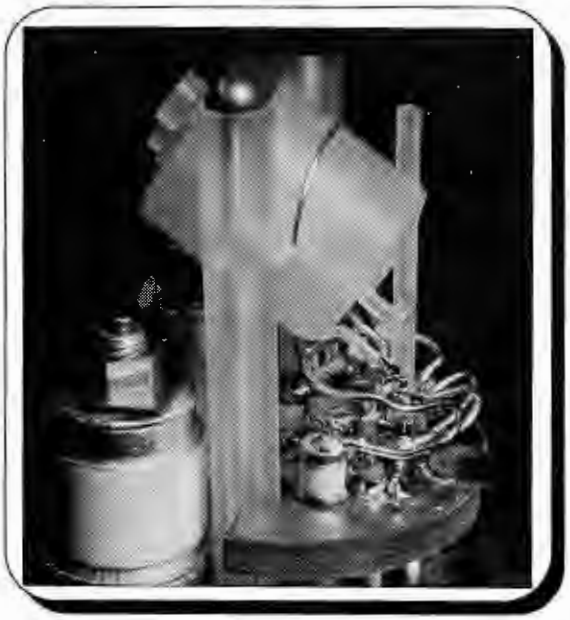

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January 7, 1992
(received 1/13/92)

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

Phenyl Ring Dynamics of Poly(L-phenylalanine)

Dear Professor Shapiro,

We are studying the side-chain dynamics of polypeptides. Here we present the solid state ^{2}H-NMR results of the fully deuterated phenyl rings of poly(L-phenylalanine). Figure 1(a) shows the temperature dependent spectra from -81°C to 45°C. Outer and inner quadrupole splittings, having 127 kHz and 29 kHz, respectively, are observed in the series of spectra. T_1 values of outer and inner components are about 1 s and 20 ms, respectively, at 22°C. The intensity of the inner component increases and its line shape changes significantly with increasing temperature. No more changes of line shape and quadrupole splitting are observed at above 45°C. These confirm that the outer component corresponds to p-deuteron and the inner one to o- and m-deuterons.

We analyzed these spectral changes by the line shape simulation program, MXQET[1)], under the assumption of the phenyl ring undergoing the flip-flop motion about the C_γ - C_ζ axis and, therefore, that of p-deuteron of the ring being static. We also assumed that the quadrupole coupling constant is 180 kHz and the asymmetric parameter is 0.05. The calculated spectra with one flipping rate are displayed in Figure 1(b), and are in good agreement with the observed in the lower and higher temperature regions. It is found in the calculated spectra that the deep concavity in the center is observed in the intermediate exchange region, and that line shapes do not change except for these flipping rates and have not the concavity. These imply that slower and faster motions also contribute to the observed spectrum. In order to fit the line shape, we had to consider the distribution of the flipping rate. We assumed the normal distribution for the flipping rate, and recalculated the spectrum, as shown in Figure 1(c). Results are in very good agreement with the observed. The flipping rate is found to distribute widely in the range of six order.

We thanks Drs. R.R. Vold and R.L. Vold for providing MXQET.

1) M.S.Greenfield, A.D.Ronemus, R.L.Vold, R.R.Vold, P.D.Ellis, and T.E.Raidy, *J.Magn.Reson.*, **72**, 89(1987).

Sincerely,

T. Hiraoki A. Kogame

Toshifumi Hiraoki Akiyoshi Kogame

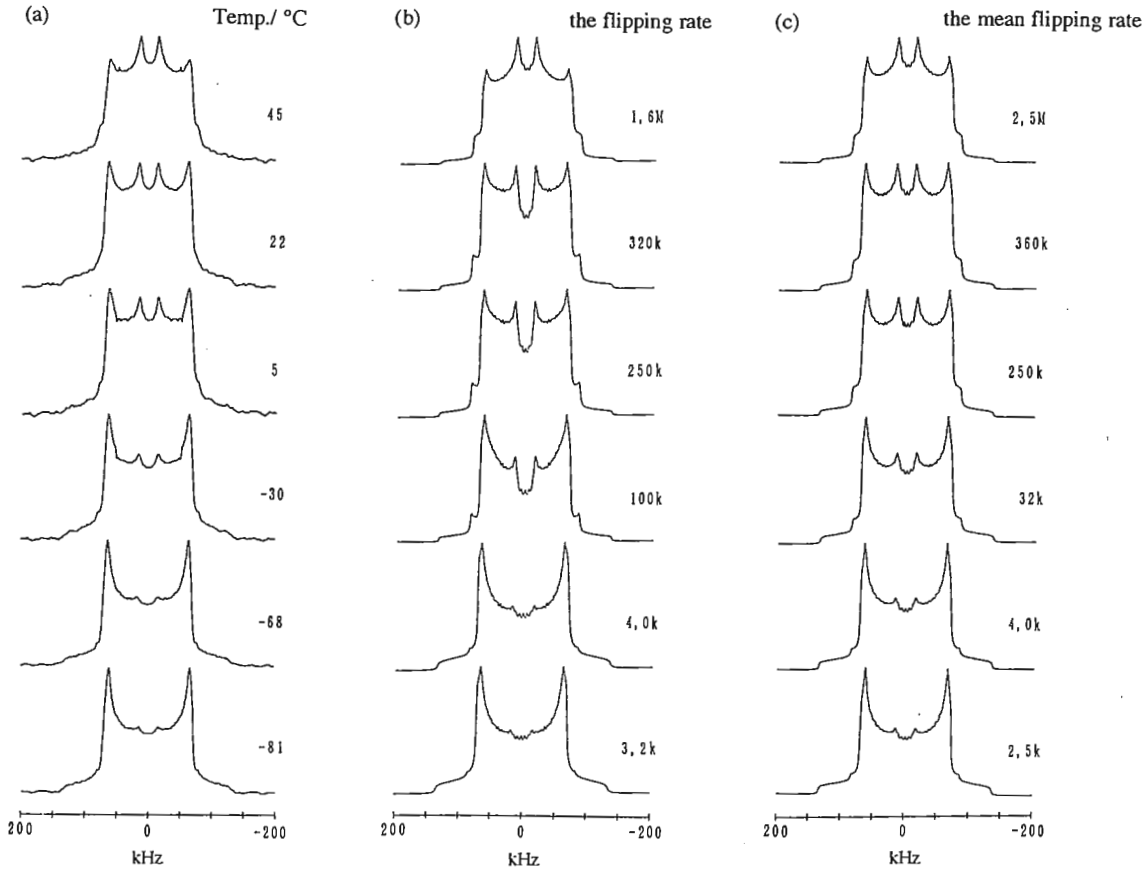

Figure 1. Temperature dependence quadrupole echo spectra of the deuterated phenyl ring of poly(L-phenylalanine): (a), observed spectra; (b), calculated spectra with one flipping rate; (c), calculated spectra with the normal distribution for the flipping rate.

CALIFORNIA INSTITUTE OF TECHNOLOGY

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
THE CHEMICAL LABORATORIES

January 21, 1992
(received 1/24/92)

Dear Barry:

Equipment Available - GN-500 to Omega Upgrade

Hardware which I originally purchased for upgrading a GN-500 with ^{1}H and broadband decouplers, at Emory University, to an Omega 500 is available for sale, It was used for a time as an auxiliary data station for another Omega system, but never installed on the 500. The upgrade parts moved with me when I moved to Caltech last year. The unit has a Sun 3/160 computer with a Sky array processor, 8 MBytes of memory and a 360 MByte disk. Presently it is not being used because of incompatibility with the hardware at Caltech. Anyone interested should contact David Live. Since I am on an extended visit to Ad Bax's lab, the appropriate address in: David Live, LCP/NIDDK, Bldg 2 Rm. B1-03, NIH, Bethesda, MD 20892; phone (301)-496-2679.

Sincerely,

David Live

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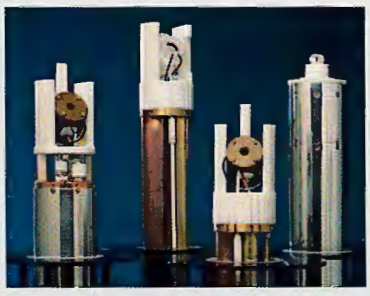

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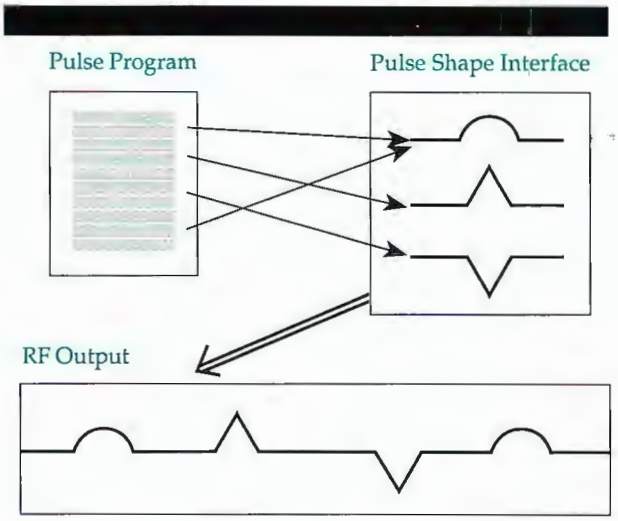

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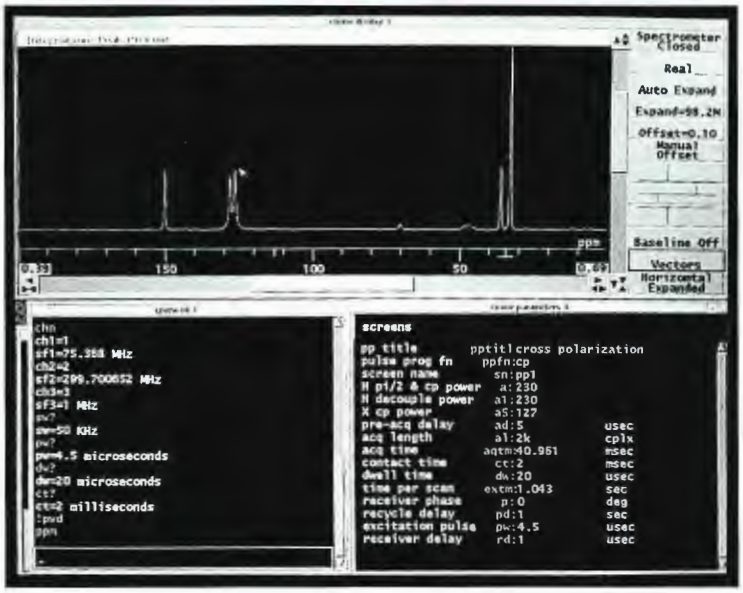

As you adjust the shims, the pulse width, spin rate, magic angle and the other parameters which affect your results, you can view the FID or spectrum in *real time* on your workstation. You can easily analyze and store the data since it's displayed in a standard data window. Then, when you have final results, you can save both the FID and the spectrum to disk for easy retrieval.

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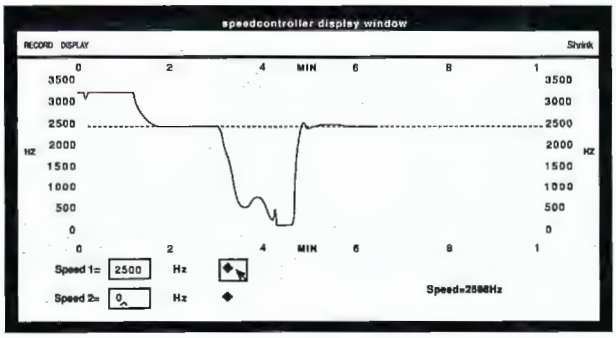

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LEONARD D. SPICER, DIRECTOR
ANTHONY A. RIBEIRO, MANAGER

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(919) 684-6287

December 13, 1991
(received 12/20/91)

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

Anisochronicity in Taurine Conjugated Bile - Back to the NMR Classroom

Dear Barry,

I describe aspects of an anisochronicity in the taurine moiety of certain bile salts. Fig. 1 shows a 500 MHz 1H NMR spectrum and structure for sodium taurocholate. The C25 and C26 methylene protons of the taurine group resonate at 3.5 and 3.0 ppm. At low concentrations (monomer), they are well resolved triplets with 7 Hz vicinal coupling. With increase in concentration (aggregation occurs), the C26 retains its well resolved triplet character, while the C25 protons become chemical shift non-equivalent with discernable geminal coupling. This behavior looked like one of the second order analyses problems in Bob Vold's NMR class. Indeed, the C25 methylene protons of taurine conjugated bile salts in aggregated form have a typical AB pattern and couple to the C26, giving a quartet of triplets (Fig. 2). More interestingly, a plot of (2C-J) vs inverse concentration shows <u>linear</u> behavior and provides a new way to estimate critical concentrations of aggregation. The anisochronicity is preserved in mixed micellar solutions of bile salts and phosphatidylcholine. A manuscript is in press (1).

Incidentally, our assignment of the C25/C26 methylene pair is based on a COSY in H2O (Fig. 3), which clearly shows the cross peak from the NH (peak W at 8 ppm) to the 3.5 ppm multiplet (peak P). The published literature has the reverse assignment.

Sincerely,

Tony

Anthony A. Ribeiro

(1) R. Stevens, A. Ribeiro, L. Lack & P. Killenberg, J. Lipid Res., in press.

Fig. 1

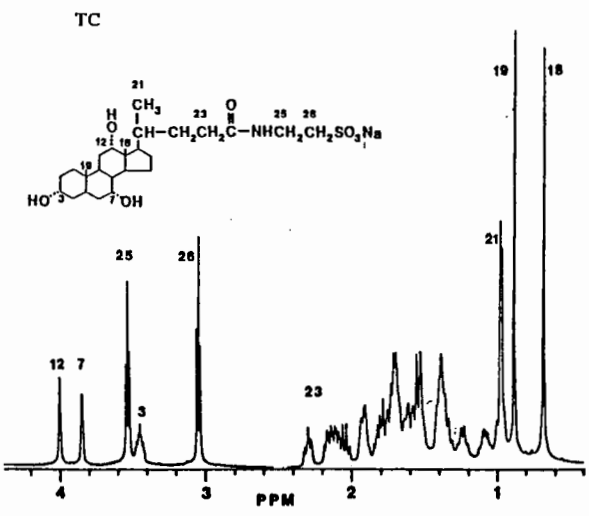


Fig. 2

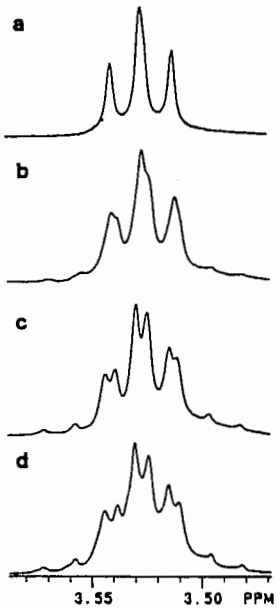
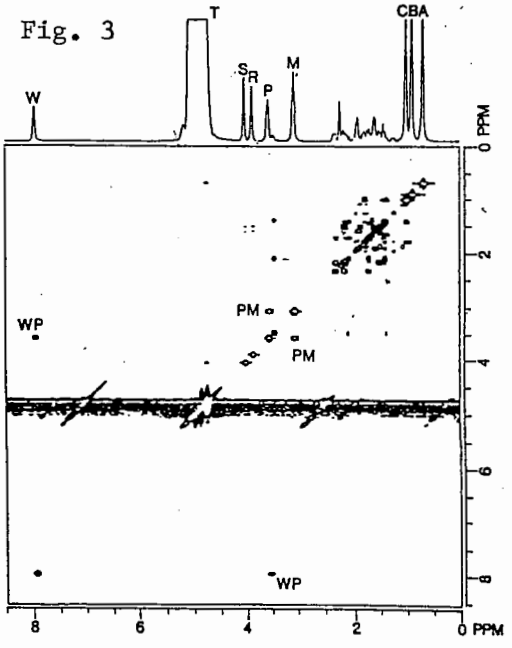


Fig. 3



BOX 3711, DUKE UNVERSITY MEDICAL CENTER
DURHAM, NC 27710

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Ottawa, Canada K1S 5B6

1942-1992

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

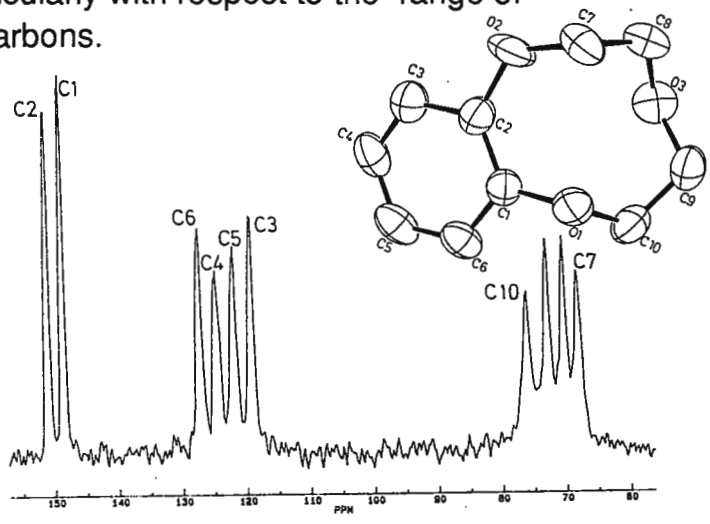
Dec. 17,1991
(received 12/26/91)

Title: Benzo-9-Crown-3, ^{13}C CPMAS NMR and Ab Initio Shift Calculations

One of the objectives of our work over the last few years has been to attempt to elucidate in detail the stereoelectronic factors contributing to ^{13}C NMR chemical shifts. In order to calculate ^{13}C shieldings, one must have a good knowledge of the experimental geometry of the molecule of interest and also a system in which conformational features are not averaged. Recently, we have determined the X-ray crystal structure of benzo-9-crown-3 ether as well as its ^{13}C CPMAS spectrum (below), in which all 10 resonances are clearly resolved at 45.3 MHz (Bruker CXP-180). The molecule is also small enough to be handled by ab initio calculations via the localized orbital local origin (LORG) approach, a project in which we are collaborating with Dr. R.A. Kirby and Prof. T.D. Bouman at Southern Illinois University. The calculated isotropic shifts and experimental results are tabulated below.

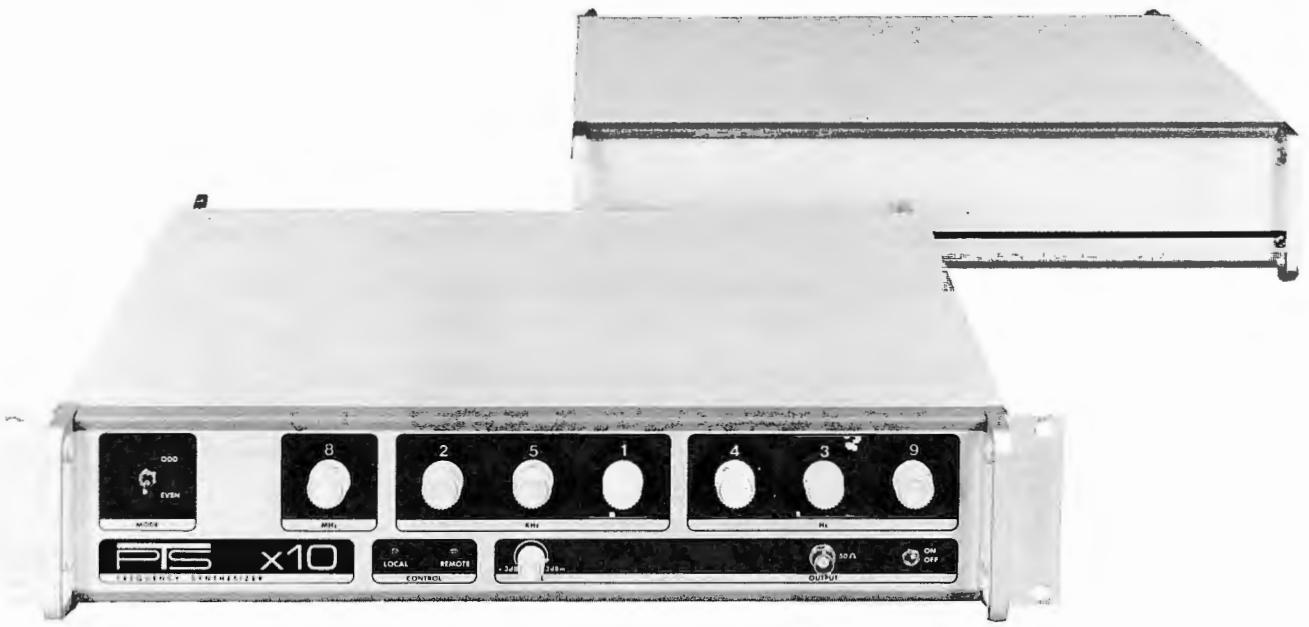
Considering that the calculations are for an isolated molecule in the gas phase and that the experimental shifts are for the solid, we feel that the agreement is quite good, particularly with respect to the range of shifts for aromatic and aliphatic carbons.

	Calculated	Observed
C1	150.0	148.7
C2	152.9	151.0
C3	126.9	119.0
C4	136.8	124.6
C5	134.4	121.8
C6	137.9	127.2
C7	61.9	68.2
C8	69.6	70.4
C9	69.7	72.9
C10	70.1	76.1



G.W. Buchanan
Professor of Chemistry

Department of Chemistry ☐ Steacie Building ☐ (613) 788-3841
Department FAX (613) 788-3749



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- fully programmable BCD or GPIB, with remote-only versions available

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With its low spurious output, fast switching capability, ultra-low phase noise and digital phase rotation, the **PTS x10** sets new standards in performance/price for low noise synthesized sources.

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> **Example:** Consider the **PTS x10** configured to cover the 40–50 MHz decade.
>
> With switch-selected ***even*** coverage, phase-continuous spans are:
> 40–41.999999, 42–43.$\bar{9}$, 44–45.$\bar{9}$, 46–47.$\bar{9}$, 48–49.$\bar{9}$
>
> With switch-selected ***odd*** coverage, phase-continuous spans are:
> 39–40.999999, 41–42.$\bar{9}$, 43–44.$\bar{9}$, 45–46.$\bar{9}$, 47–48.$\bar{9}$

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Frequency	
Range:	specified 10 MHz decade, 0.1–100 MHz (0.1–10, 10–20, . . . , 90–100 MHz)
Resolution:	1 Hz (0.1 Hz optional via remote - control only)
Control:	manual by 10-position dial; remote by TTL-level parallel BCD or GPIB (optional)
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non-phase-continuous:	5 μseconds
phase-continuous:	$<1\,\mu$s transient, 1 μs delay
100 KHz thru 1 Hz digits:	$<1\,\mu$s transient, 1 μs delay, phase-continuous
Output	
Level:	+3 to +13 dBm (1V into 50Ω)
Flatness:	±0.25 dB
Impedance:	50Ω
Control:	manual by front panel control; remote by analog voltage
Spurious Outputs	
Discrete:	−65/−60 dBc (typical/specified)
Harmonics:	−40/−35 dBc (typical/specified)
Phase Noise:	−70 dBc (0.5 Hz to 15 KHz integrated, including effects of internal standard)
£ (1 Hz):	−110dBc/10 Hz, −122dBc/100 Hz, −132dBc/1 KHz
	−133dBc/10 KHz, −134dBc/100 KHz
Noise Floor:	−135dBc/Hz
Frequency Standard	(note: internal or external standard required for operation)
Internal:	3×10^{-9}/day (OCXO) or 1×10^{-8}/day (TCXO)
External:	10.000 MHz, 0.4–2.0Vrms into 50Ω
	5.000 MHz, 0.5–2.0Vrms into 50Ω
General	
Auxiliary Output:	10.000 MHz, 0.4V into 50Ω
Operating Ambient:	0–55°C, 95%R.H.
Power:	105–125V, 50–400 Hz, 30W (100V, 220V, 240V optional)
Dimensions:	19 × 3.5 × 19 inches max. (rack or bench cabinet)
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Manual controls, BCD interface	**$2050.** —(note: excludes optional Frequency Standard)
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(received 12/27/91)

December 23, 1991

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

SUBJECT: Bruker decoupler pulses

Dear Professor Shapiro:

We are using our two older Bruker spectrometers (AM-400 and AM-500) for a variety of inverse detection experiments, both for small molecule structure elucidation and for isotope-enriched protein structure determination. We have purchased several upgrades from Bruker to improve system performance; the 451 MHz upgrade improved both systems' reliability and stability greatly.

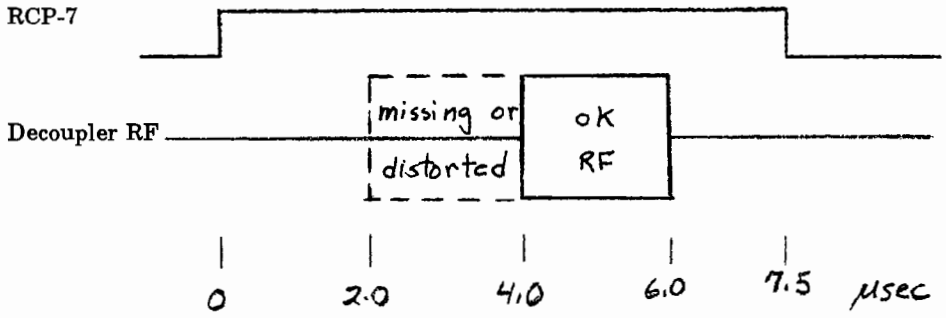
In the course of testing the reverse detection mode, we noticed some anomalies in the behavior of the proton pulses coming from the Bruker decoupler. For instance, at a decoupler power level of 20L the following pulse program line

(P1 PH1):D:E

with P1 = 4 usec would produce a 2.1 usec pulse. At different power levels, the pulse behavior was even more erratic, often turning on briefly (one usec), dropping to zero, and then turning on normally. The following pulse program line clarified the situation for us:

(P1 PH1):D:E P21:C7

with P1 = 4 usec and P21 = 7.5 usec. This line produces simultaneous pulses, one RF from the decoupler (with built in 2 usec delay) and one TTL from RCP line 7 from the process controller.



The answer has probably been determined many times before by other labs; the AGC of the decoupler amplifier chain involves feedback that can be adjusted to compromise amplitude for rise/fall times, and each system can be different -- depending on whose screwdriver was last on the scene.

Rather than fight this problem, we chose to simply bypass the decoupler modulation and amplification functions. The output of the 451 LO unit is sufficient to drive any of the commercially available external RF amplifiers, and the RCP lines can be used to switch between power levels. The RF phase shifting and frequency generation plus basic pulse generation from the Bruker console is retained, however. Because the external amplifier is used for the observed nucleus, care must be exercised to turn it off (really OFF) when not pulsing. Crossed diodes or amplifier blanking (another possible pulse length problem due to rise and fall times) is the solution here.

This basic modification works well, is somewhat clumsy in programming pulse sequences, and nicely replaces a decoupler system which is antiquated with respect to current inverse detection pulse sequences.

Sincerely,

Paul Fagerness

Paul Fagerness

Department of Chemistry

Head of Department:
Dr K.D. Sales BSc PhD

Departmental Fax 081 981 8745

Queen Mary and Westfield College
Mile End Road
London E1 4NS

Telephone 071 975 5555
Fax 071 975 5500
Telex 893750

December 17th 1991
(received 12/27/91)

Imaging Soils: Positions Available

Dear Barry,

I expect to have a postdoctoral position available in April 1992. It will be for three years for spectroscopic and imaging work mainly on soils. Topics in which we are interested are: susceptibility effects on images, imaging of liquids in soils (and other solids), nutrient flow in soils and plant roots, high field (14.1T) studies of microbes in soil and of intact soils (solid state). Associated work will involve ESR and Mössbauer spectroscopies.

The project is in collaboration with Professor D.S. Powlson, Head of the Soils Department at the Rothamsted Experimental Research Station and will be supported by the Agricultural Research Council.

Equipment we have available includes a SISCO imaging spectrometer (4.7T, 33 cm bore), a Bruker MSL 300, a Bruker WH 400, and a 14.TT spectrometer equipped for solids (of as yet unknown provenance).

The starting salary will be approximately £14,000 per year and the work will also have the support of a Technician post (salary ~£11,000) which is also being advertised.

Anyone interested should write to me directly with appropriate references and a cv.

Best wishes from all the group including Geoff Hawkes, the nominal subscriber, for the New Year.

Yours sincerely,

Ed Prof.Edward W. Randall

RESEARCH ASSOCIATE POSITION: NMR SPECTROSCOPIST

A Research Associate position is availale immediately in the in vivo NMR Laboratory at the Health Sciences Centre of The University of Manitoba in Winnipeg, Canada. The laboratory is equipped with a 7.1 T/21 cm Biospec spectrometer, together with dedicated operating and complete physiological support facilities. AMX-300 and AMX-500 spectrometers are also conveniently located in the city, and a high-field clinical spectrometer is now being installed for research purposes. The main interest of the laboratory is the use of NMR imaging and spectroscopic methods for monitoring the development and the treatment of neurological disorders. The successful applicant will have a strong NMR background, though experience in the biological area is not essential. Applicants should send a CV and 3 letters of recommendation to:

Dr. James Peeling
HSC NMR Laboratory
Department of Pharmacology
A006 Chown Building
753 McDermot Ave.
Winnipeg, MB, CANADA
R3E 0T6

PENNSTATE

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Hershey, Pennsylvania 17033
(717) 531-7178

10 January 1992 (received 1/16/92)

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

Dear Professor Shapiro:

Statistical Analysis of Serial NMR Data

We have been using NMR to evaluate the effects of treatments on cerebral energy metabolism during hypoxia-ischemia. In our model, damage is produced in a 7-day postnatal rat by ligating the right carotid artery then exposing the rat pup to 8% O_2 for 3 hours. ^{31}P NMR spectra are obtained at intervals during hypoxia, producing serial data on variables such as relative ATP levels [1] .

In the past it has been common to analyze such data by doing two-sample t-tests (or ANOVA if there are more than two treatment groups) at each time point. One asserts that the drug preserves energy metabolism during time ranges when the drug group is significantly closer to normal than controls. From a statistical perspective, there are two main problems with this approach. First, conducting repeated significance tests at the 5% level understates the probability of a type I error; that is, the chance of falsely declaring the treatment groups to be different—if the drug really has no effect—far exceeds the nominal 5%. Second, the resulting sequence of significance tests does not yield a parsimonious description of the energy metabolism curves, which in our experience are smooth and regular.

Our solution to these problems is to fit smooth curves to the data, making comparisons between groups in terms of the coefficients of the curves. The curves that we use are the cubic splines, a family of models that is as easy to use as the cubic polynomials but is richer in shapes [2]. Specifically, our model asserts that the NMR value for a given animal is a sum of three parts: (i) a mean value for animals in that group (which can be described by a cubic spline), (ii) an animal-specific random effect, and (iii) a random error. We assume that the random errors may be correlated in time within animal as in an AR(1) time series [3]. To describe differences between treatment groups, one simply plots the fitted curves on the same axes. One tests whether two curves are the same by testing equality of their coefficients. It is also easy to estimate mean NMR values across a range of times and to compare these values between treatment groups.

The figure shows a cubic spline analysis of data from a study of the effects of deoxycoformycin (DCF) on hypoxic-ischemic neuropathology [1]. Rat pups were pretreated with either saline or 50 or 500 μg/kg DCF. The plot shows the fitted ATP concentration (relative to prehypoxic baseline) for each of the three groups during three hours of hypoxia and

two hours of recovery. As the figure indicates, ATP levels decline during hypoxia and recover only incompletely after reoxygenation. Comparison of mean ATP during the second and third hours showed that the DCF-500 group had significantly greater relative ATP than the saline controls (p=.004) whereas the DCF-50 group did not differ significantly from saline controls (p=.40).

We recommend our method as an efficient means of modeling serial NMR data.

Sincerely,

Daniel F. Heitjan (Biostatistics)
internet: dheitjan@biostats.hmc.psu.edu

Gerald D. Williams* (Radiology–NMR)
bitnet: JERRY@PSUHMED

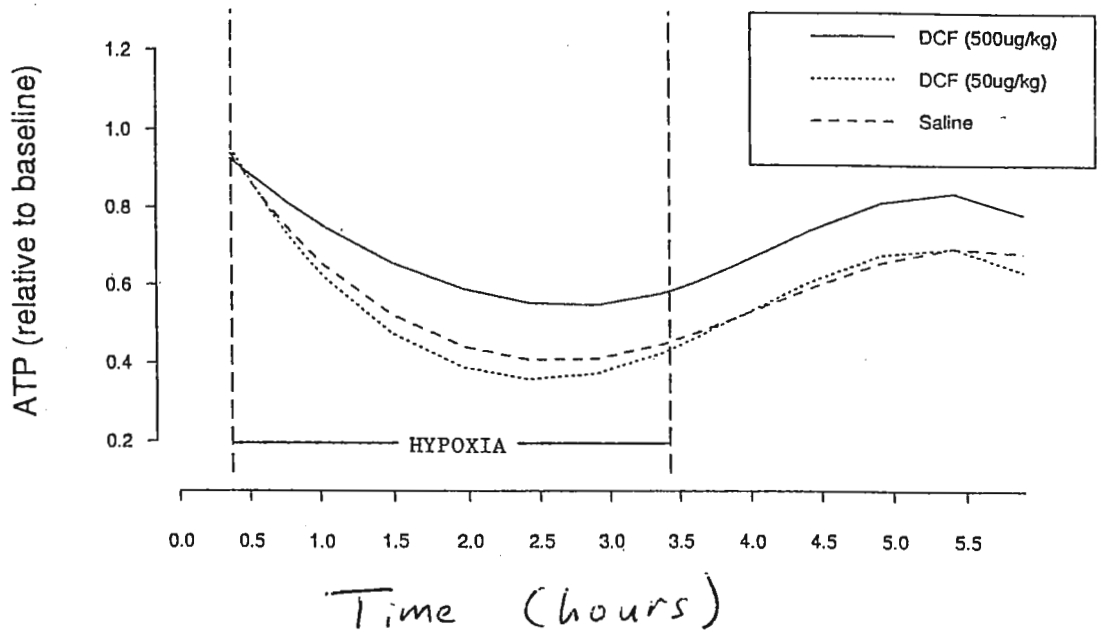
Charles Palmer (Pediatrics)

Michael B. Smith (Radiology–NMR)

[1] Williams, Palmer, Roberts, Heitjan and Smith, 1992 *NMR Biomed*, in press.

[2] Durrleman and Simon, 1989 *Stat Med* **8**:551–561.

[3] Chi and Reinsel, 1989 *J Am Stat Assoc* **84**:452–459.



*Please credit to the account of Dr. Williams.

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DEPARTMENT OF CHEMISTRY
Lensfield Road
Cambridge CB2 1EP

Professor Barry Shapiro,
TAMU Newsletter,
966 Elsinore Court,
Palo Alto,
California 94303 USA

16 December 91
(received 12/26/91)

Dear Barry,

"Getting Ping into Shape"

For some time now we have been using a selective excitation technique which we call *spin pinging* after its inventor Ping Xu. The trick is to prepare the magnetization along the +Y axis with a hard pulse and *then* apply the soft pulse. The strongest response occurs when the soft pulse is 180° but the profile is very insensitive to the flip angle. The signal is obtained in the difference mode:

hard 90°(+X) soft 180°(+X) Acquire(+)
hard 90°(+X) soft 180°(+Y) Acquire(–)

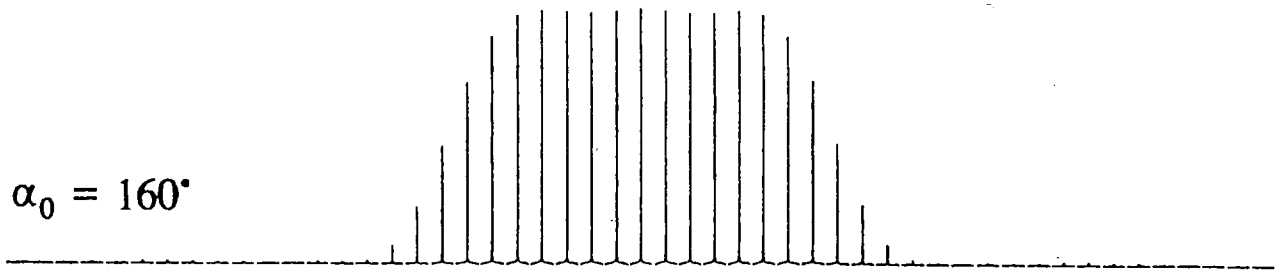
The appropriate DANTE sequence may be used instead of the soft pulse. Dispersion-mode components are everywhere negligible and the absorption-mode approximates a sinc^2 function rather than the sinc function obtained with straightforward selective excitation with a rectangular soft pulse. This means that the sidelobe responses are much less obtrusive.

Spin pinging lends itself very well to pulse shaping schemes provided that they are symmetrical in time. For example, if the soft pulse is shaped according to an isosceles triangle, the frequency-domain excitation profile approximates a sinc^4 function which has negligible sidelobe responses. In fact, triangular shaping works about as well as Gaussian shaping (and is simpler to implement in practice). If necessary, periods of free precession can be included before and after the soft pulse, but they should also satisfy this symmetry requirement.

Even better results can be achieved by specifically designing a suitable soft pulse shape. We have used an operator-guided evolutionary algorithm for this purpose. The new pulse gives uniform excitation over a prespecified band of frequencies with negligible excitation elsewhere. Spin pinging is particularly suitable for this purpose since it inherently has negligible dispersion at all offsets. The pulse shape was defined as a finite Fourier series with only cosine terms (time-symmetric pulse) and was implemented in practice either as a 32-step histogram, or a 32-pulse DANTE sequence. If anyone out there is interested, the first 16 ordinates are given in this table (normalized to a maximum of 1023):

(1)+77	(2)+67	(3)+48	(4) +23	(5) –9	(6) –50	(7) –100	(8)–152
(9)–184	(10)–167	(11)–73	(12)+109	(13)+363	(14)+643	(15) +883	(16)+1023

An experimental test (shown below) confirms that the response is essentially trapezoidal in profile with a uniform central region, narrow transition regions and negligible excitation elsewhere.



Kindest regards, Ray Ray Freeman 吳哲新 Xi-Li Wu 許平 Ping Xu

THE ROYAL INSTITUTE OF TECHNOLOGY

Department of Physical Chemistry

Professor Peter Stilbs

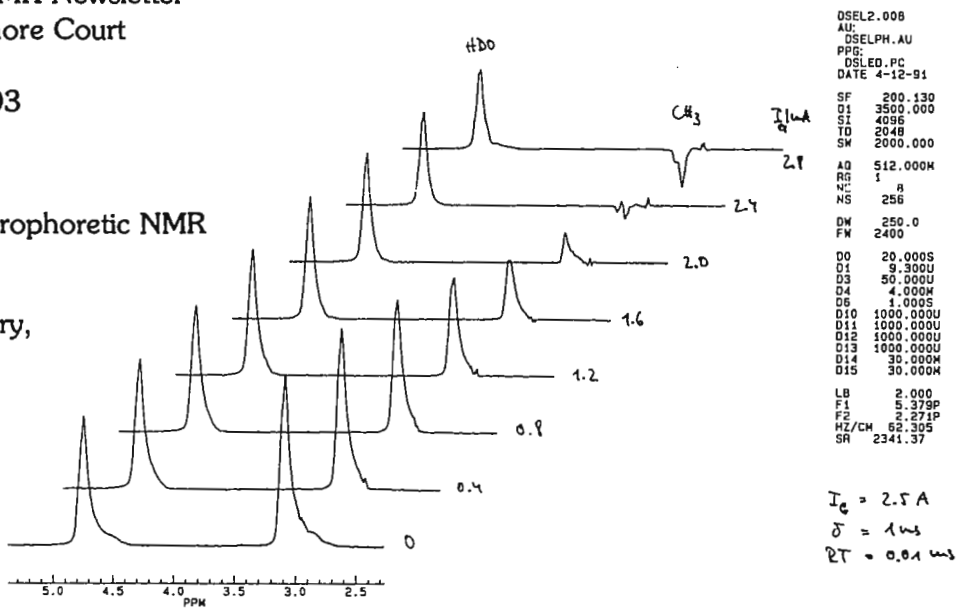
(received 1/9/92)

January 3, 1992

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

Re: Electrophoretic NMR

Dear Barry,



Thank you again for your kind "ultimatum" - time really passes fast these days...

With a lot of help from C.S. Johnson and coworkers at University of North Carolina me and my postdoc Dirk Schulze have managed to get a setup working - our first useful spectrum is shown above. It shows the beginning of the cosinusoidal amplitude oscillation of the positively charged ion in an EFG experiment on tetramethylammonium chloride in aqueous solution. (for references on EMR, see e.g. Johnson and He, Adv. Magn. Reson. 13 (1989) p. 131). The experiment was done with a temporary setup, based on Bruker micro-imaging probe. Future experiments will be based on a decicated EMR probe that has just been delivered to us.

We are quite excited about possible future applications, and hope to report these in our next TAMU newsletter contribution.

Yours Sincerely

Peter

Peter Stilbs

Address: Prof. Peter Stilbs
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RESEARCH CENTRE

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinor Court
Palo Alto
California 94303
U.S.A.

6 December 1991
(received 1/15/92)

Dear Barry,

Fluorine for Hydroxyl - a Fair Exchange?

Replacement of a hydroxyl group by fluorine in carbohydrates, nucleosides and inositols is currently used as a pharmaceutical ploy to try to modulate their biological function, often with a fair degree of success. One suggested reason for using fluorine is its supposed propensity for acting as a hydrogen bond acceptor, a view which is the subject of some controversy.

In a collaborative study with Eric Chambers and Professor Ray Abraham in Liverpool University we have been using nmr to investigate the effect of OH → F replacement in a variety of sugars and inositols. Substitution of the ring hydroxyls for fluorine in glucose has no significant effect on conformation, as expected, though mutarotation behaviour is modified somewhat. However, interesting observations were made from the spectra of 4-deoxy-4-fluoro-D-glucose (4DFG), 6-deoxy-6-fluoro-D-glucose (6DFG) and 6-deoxy-6-fluoro-D-galactose (6DFGa) in D_2O and DMSO or acetone. Some of these compounds have been looked at before by NMR[1,2] but without a full analysis of the results. With the aid of COSY and ID-TOCSY experiments at 400 MHz, both α and ß isomers due to mutarotation could be sorted out in the spectra. We particularly focused on the rotational isomerism about the C_5-C_6 bond as a test of conformational preference, with the results shown overleaf.

The following conclusions can be made:-

(i) Despite the small atomic radius of fluorine, rotamers with C-OH and C-F bonds parallel in a 1,3 relationship are disfavoured, particularly rotamer tg in 6FDG and 4FDG. Presumably the repulsion is dipolar rather than steric.

(ii) The 1,2 gauche effect favours the gt rotamer in 6FDG and 6FDGa.

(iii) There is no evidence for any OH - - - F hydrogen bonding, confirming our general disbelief in this phenomenon.

(iv) α and ß isomers at C-1 behave similarly.

In the inositol series, attempts in Birmingham University (collaboration with Lee Proctor and Dr Paul Coe) to prepare a difluoroinositol derivative led to a compound (I) to which we assigned the structure shown, after some deliberation

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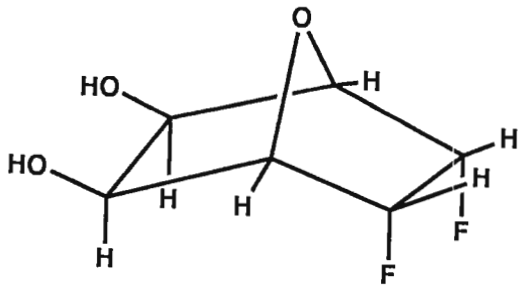
(confirmed by x-ray later). The problem with the nmr is the plane of symmetry providing an AA^1 BB^1 CC^1 DD^1 XX^1 spin system (yes, the OH's also couple) and since long range couplings abound in this structure a full and complete analysis is still not quite finished, but not far away.

With best wishes.

Yours sincerely,

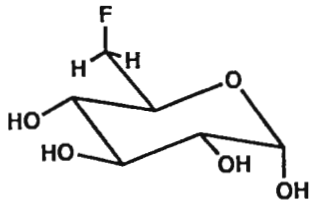
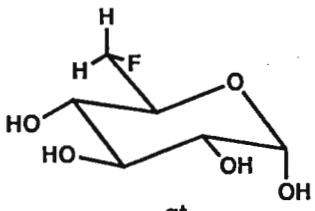
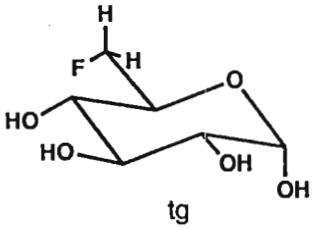
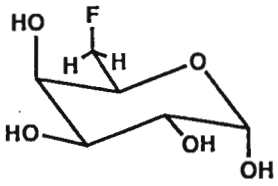
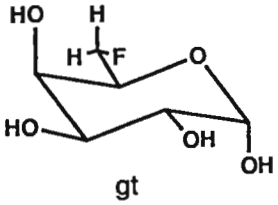
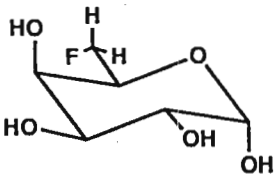
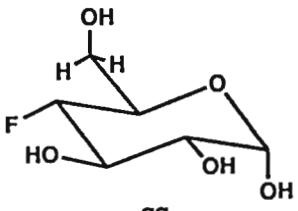
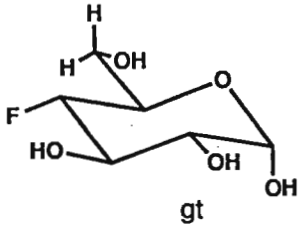
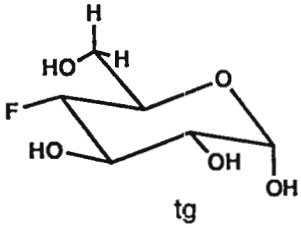
Dr W A Thomas



(I)

1. L. Evelyn and L.D. Hall, Carbohyd. Res. 1976, 47, 285.
2. A. De Bruyn et al, Acta Cienc. Ind. 1978, 4, 103.

Rotamer Populations

	gg	gt	tg
6DFG			
D_2O	60%	40%	0%
DMSO	50%	50%	0%
6DFGa			
D_2O	19%	76%	5%
DMSO	16%	74%	10%
4DFG			
D_2O	59%	41%	1%
Acetone	62%	36%	2%

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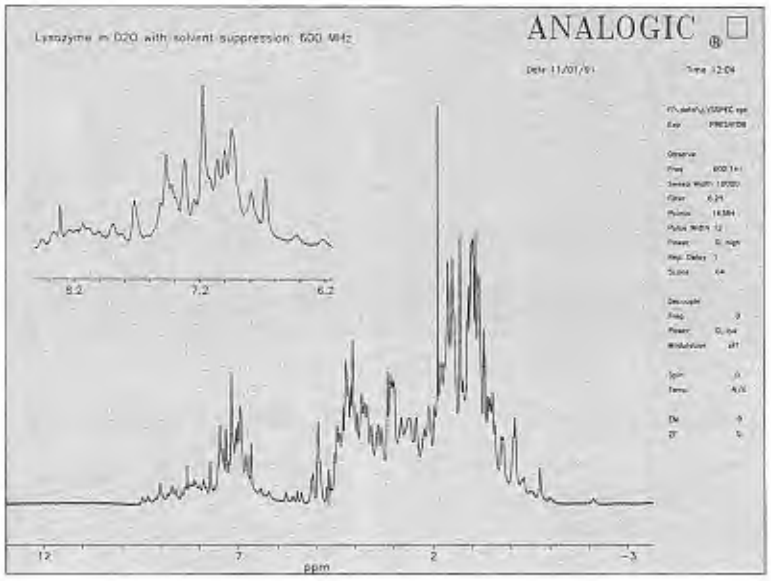

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PHYSICAL CHEMISTRY 2
CHEMICAL CENTER
UNIVERSITY OF LUND
Prof. Sture Forsén

22 January 1992
(received 1/24/92)

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

Production of large quantities of protein fragments for structural studies by 2D NMR.

Dear Dr. Shapiro,

The last several years have seen an upsurge in the study of protein fragments or modules. This is especially true for structural studies by high resolution NMR in which the examination of these fragments simplifies the task of assignment and structure determination. These studies, however, demand large quantities of polypeptides that are not normally produced from a natural source. Several strategies, including large scale peptide synthesis, chemical or proteolytic cleavage, or direct production of fragments by recombinant DNA techniques, have been used to address this need. Nevertheless, these strategies can, in some cases, fail to produce sufficient quantities of protein for NMR analysis.

With our collegue, Johan Kördel, we have recently developed a method which combines mutagenesis and chemical cleavage to obtain protein fragments of a specific size and composition. For some years we have been examining the structure of the calcium binding protein, calbindin D_{9k}, by 2D-NMR. This protein consists of two calcium binding loops of the EF-hand type. We wished to examine the structure and calcium binding properties of the individual loops but were frustrated in our attempts cleave the protein between the two loops proteolytically. We turned to recombinant DNA techniques to insert a unique methionine residue to serve as a target for cleavage by cyanogen bromide. In this way, it was possible to select the cleavage point and produce large quantities of the fragments for study. From 250 mg of purified P43M calbindin D_{9k}, we were able to produce 166 mg of purified fragments after cyanogen bromide cleavage. As shown in the figure, preliminary examination of the structure of the fragments by ^1H 1D-NMR indicates that the structure is relatively unchanged from that of the intact protein. ^1H and ^{15}N 2D-NMR experiments are in progress to more precisely determine the structural effects of the cleavage. A more complete account of this research will appear in *FEBS Letters*.

Best regards,

Bryan E. Finn Mats Wikström Eva Thulin Sture Forsén

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PHYSICAL CHEMISTRY 2 CHEMICAL CENTER P.O.B. 124 S-221 00 LUND, SWEDEN	PHYSICAL CHEMISTRY 2 CHEMICAL CENTER GETINGEVÄGEN 60 LUND C SWEDEN	University exchange INT +46 46 10 70 00 Direct INT +46 46 10 95 95	INT +46 46 10 45 43 Telex 33533 LUNIVER S	CHEMCENTER LUND SWEDEN

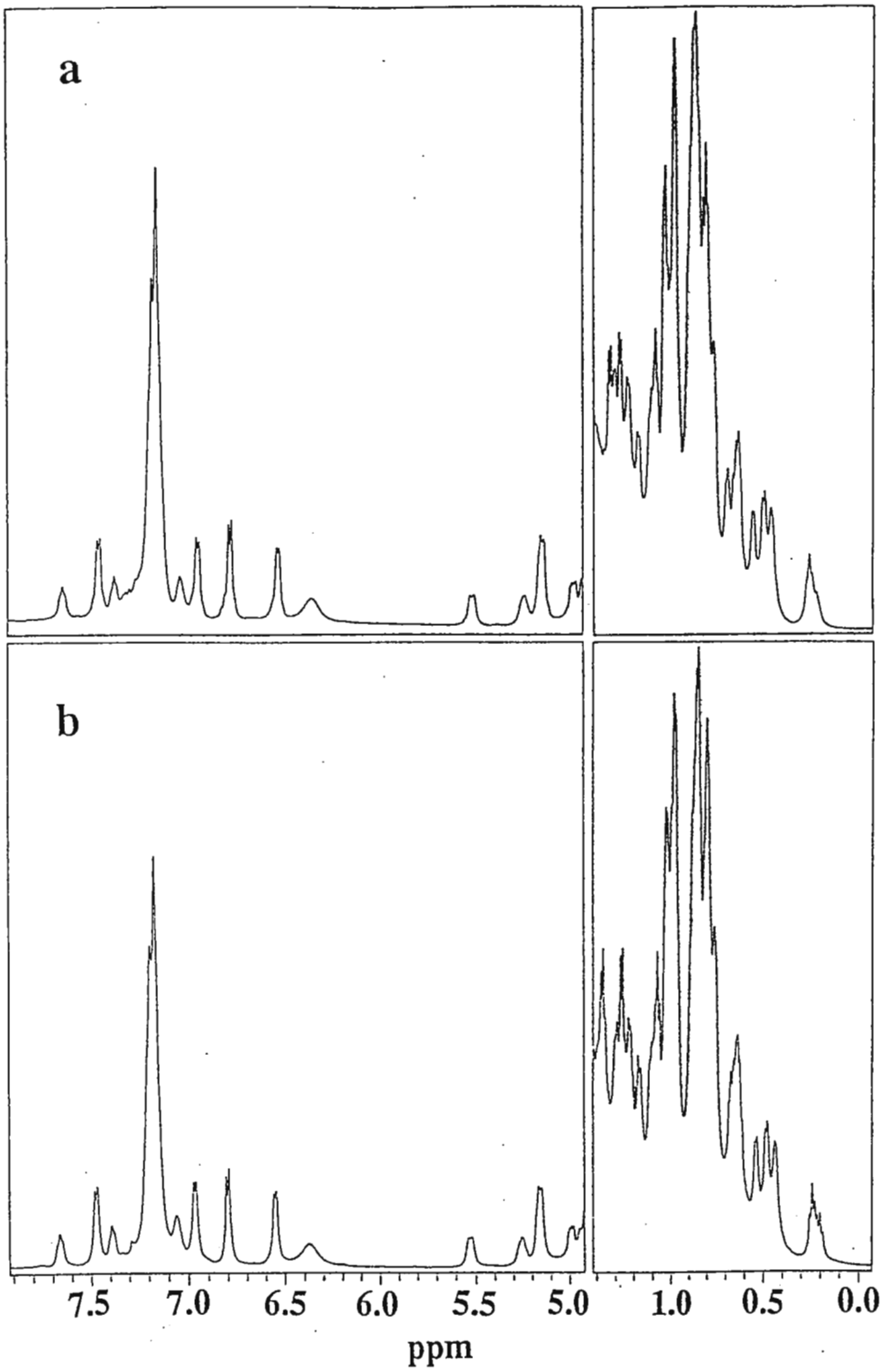

Figure 1. ^{1}H 1D-NMR spectra of: a) P43M calbindin D9k and b) a 1:1 mixture of fragments of P43M produced by cyanogen bromide cleavage.

INSTITUT KLINICKÉ A EXPERIMENTÁLNÍ MEDICINY

IK+E M

RADIODIAGNOSTICKÉ PRACOVIŠTĚ

146 22 PRAHA 4 - KRČ
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Dr.B.L.Shapiro
966 Elsinore Court
Palo Alto
CA 94303
U.S.A

(received 1/21/92)

"APPLICATION OF THE TIME DOMAIN BASELINE CORRECTION IN IN-VIVO SPECTROSCOPY"

Dear Dr.Shapiro:

Baseline roll from the point of calculation is caused by the error in several points of FID. To eliminate these distortions we applied the time domain baseline correction algorithm which uses the 1+1 evolution strategy approach [1]. The time domain correction enables additional phase correction which is impossible in the case of polynomial baseline fit.

The evolution strategy algorithm is very simple and robust and has often been used in magnet design and electrical engineering. The algorithm consists of two steps repeated in a loop:
a) from current state x generate new child configuration y:

$$y_i = x_i + \text{random}(\mu_i);\ i=1,....n$$

b) we chose the best configuration from 'parent' x and 'child' y. A criterion we use in this decision is the sum of squares of baseline value in user specified points.

The random number dispersions are systematically varied so that probability of parent 'death' (e.g. y is better than x) is about 0.2. The algorithm is very fast (no gradient evaluation is necessary) and surprisingly efficient.

The algorithm is part of a home-made program system for medical application of in in vivo NMR data processing. The system is written in C languague and runs on any PC AT equipped with VGA or EGA card and coprocessor. One example of human calf spectrum evaluation is enclosed.

Dr.Milan Hájek
Inst.Clin.Exp.Medicine
Prague

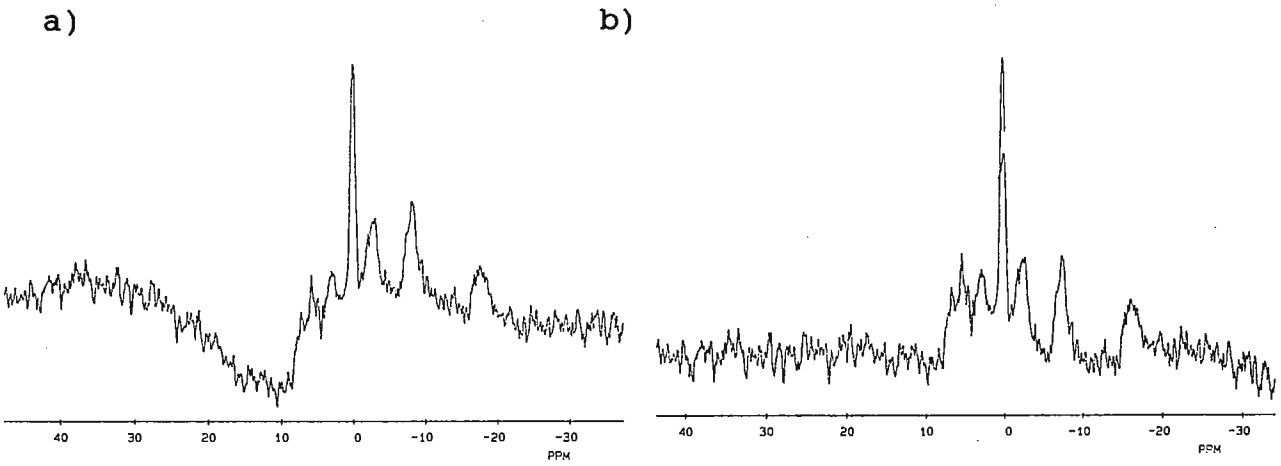
Dr.Pavel Kessler
Inst.Sci.Instruments
Brno

Czechoslovakia

References

1. A.Gottwald, Proc.IGTE Symp. Gratz 1990, pp23-28.

Figure 1.
Human calf spectrum with heavy baseline distorsion before (a) and after the time domain correction (b) (first 4 points of FID affected , fifty baseline points were defined).



Cornell University

Department of Chemistry
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Ithaca, New York 14853-1301 USA

Dr. Aidan T. Harrison
Director, NMR Facility
(607) 255-7593

20 January 1992
(received 1/24/92)

Barry Shapiro, Editor
TAMU Newsletter
966 Elsinore Court
Palo Alto, CA 94303

EQUIPMENT AVAILABLE

Dear Barry:

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Sincerely,

Aidan T. Harrison

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*U.S. Patent No. 4,998,976

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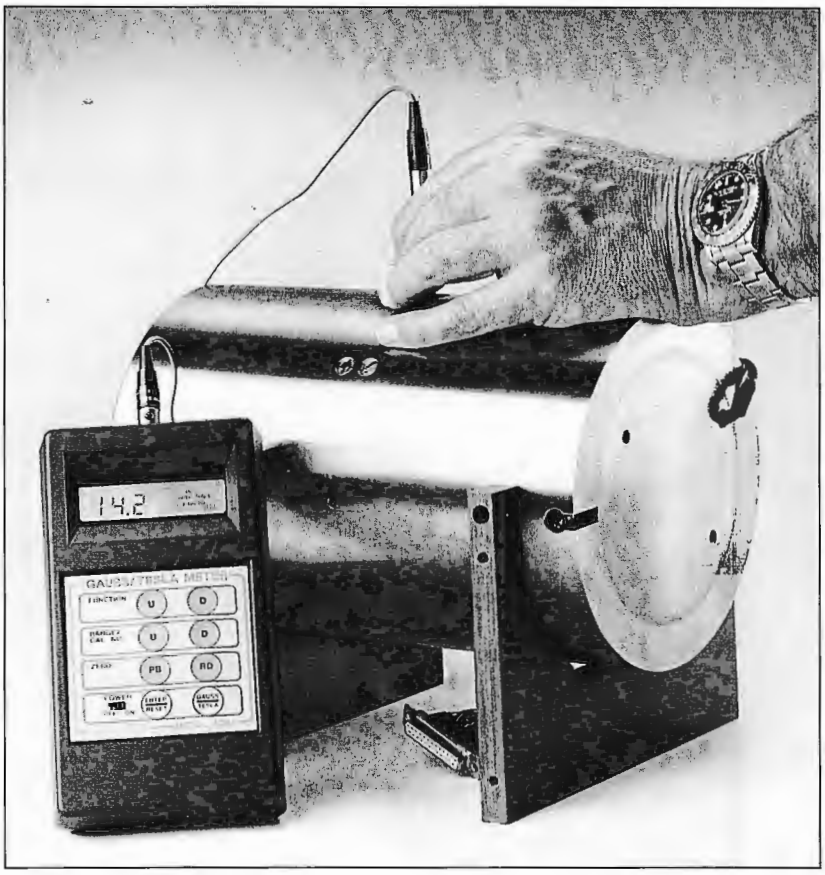

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Room Temperature Required:	0 - 50° C
Magnet Heater Power:	<10 watts
Fringe Field:	One gauss line is within magnet cylinder

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*U.S. Patent No. 4,998,976

The University of Akron

Department of Chemistry (216) 972-7372
Akron, Ohio 44325

January 15, 1992 (received 1/21/92)

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

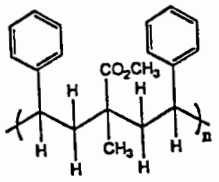
Dear Barry,

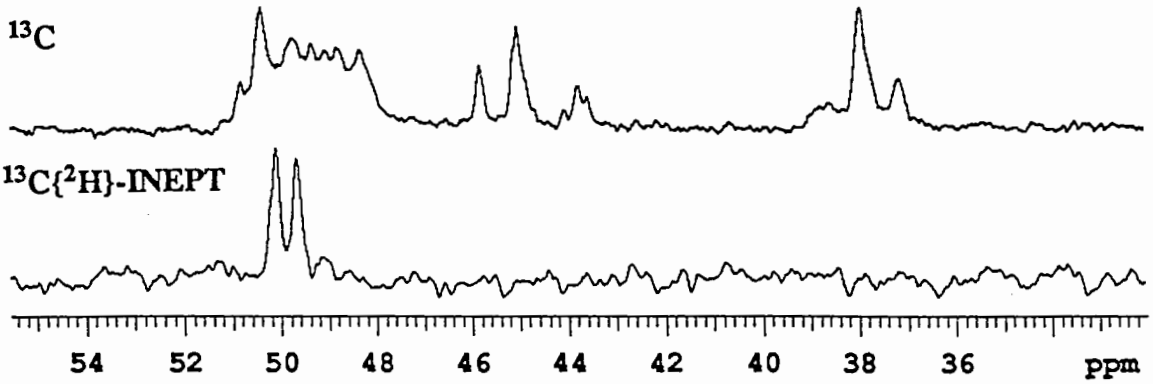
Characterizing minor structural components in a regular polymer are the most crucial for determining that polymer's properties, but the resonances from these components often are obscured by numerous signals which are much more intense. Incorporation of labels, combined with selective polarization transfer enables us to observe the resonances from minor structural components without interference from the resonances of the rest of the polymer. In this manner, we can monitor the relative rates that different monomer sites in polymers participate in chemical reactions at low conversions. For example, the methoxy proton resonances of styrene—methyl methacrylate and related copolymers are sensitive to monomer unit sequence distribution and stereosequence distribution effects. When submitting the copolymers to transesterification with CD_3ONa, it is possible to monitor the incorporation of CD_3O^- groups into the copolymers. This yields detailed information about the relative reactivities of MMA units in the copolymers which is in accord with the information obtained from kinetic and radiotracer studies.

The 1:2:1 ratio of coisotactic, coheterotactic, and cosyndiotactic methoxy carbon resonances which exits before deuteration is not present in the deuterated samples of the copolymer as illustrated in the $^{13}C\{^2H\}$-INEPT spectra. Hence, the replacement rate of OCH_3 groups with OCD_3 groups in the 3 configurations is not equal but occurs preferentially in the cosyndiotactic polymer.

Sincerely,

Maritherese Tokles, Darlene Hensley, Jerry Hatvany, H. James Harwood and Peter Rinaldi





THE UNIVERSITY OF UTAH

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January 19, 1992
(received 1/22/92)

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

NCC Triple-tuned Probe Performance.

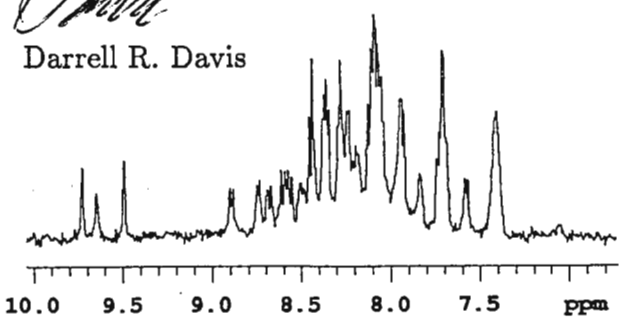
Dear Barry:

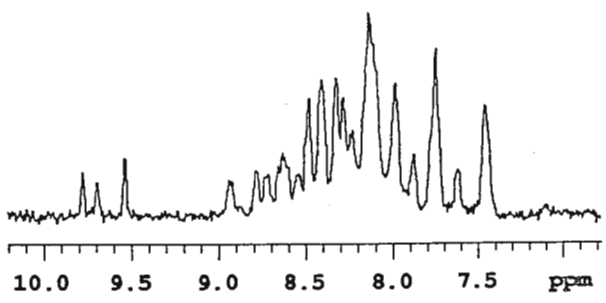
We have recently finished installing the third channel of our Unity-500 and have done some initial test experiments on our $^{1}H[^{13}C,^{15}N]$ triple tuned probe from NCC. We used a 10 mM sample of doubly-labeled glycine in D_2O to measure the proton and carbon 90's and a 5 mM sample of ^{15}N labeled uracil in DMSO to measure the nitrogen decoupler 90. The numbers are: ^{1}H - 8.5 μsec, ^{13}C - 12.0 μsec, and ^{15}N - 24.0 μsec. On our spectrometer the ^{1}H and ^{13}C 90's were at "full-power." We were satisfied with these numbers so haven't investigating delivering more power, they probably won't go much lower. On the nitrogen channel we were able to deliver enough power to arc the probe, so 24 μsec is probably the best we can do. Sensitivity is comparable to our NCC indirect detection probe and our Varian $^{1}H/^{19}F$ probe. A value of 450:1 was obtained with very little effort for a S/N measurement on ethylbenzene.

The spectra below are for ^{1}H-^{15}N HMQC experiments on the antibiotic Nisin A, approximately 1 mM in 90:10 H_2O:D_2O. This ^{15}N-^{13}C labeled sample was provided by John Vederas and Mark Zabriskie at the University of Alberta. The two spectra are transforms of the 1st increments of 2D experiments with (left) and without (right) GARP-1 ^{13}C decoupling. 32 Transients were collected for each increment and ^{15}N was decoupled in both experiments using WALTZ-16

Sincerely yours,

Darrell R. Davis





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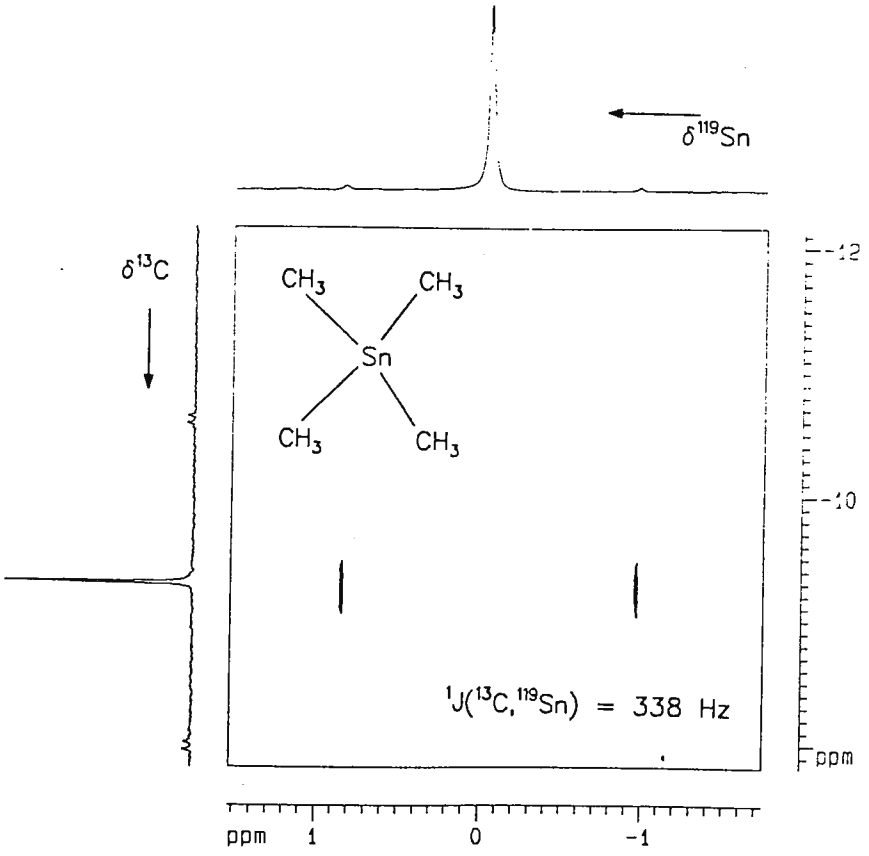
Prof. Dr. B. L. Shapiro
TAMU-NMR Newsletter
966 Elsinore Court
Palo Alto, Cal. 94303
USA

2D $^{13}C,^{119}Sn$ Correlation

Dear Barry,

We show here what we believe is the first $^{13}C,^{119}Sn$ correlation spectrum. It was obtained by ^{119}Sn detection using the HMQC-method on our AMX-500. We work with a special inverse multinuclear probe which has an extra ^{13}C channel double tuned to the ^{1}H coil. With this probe we have already obtained $^{31}P,^{13}C$ [1] and $^{13}C,^{29}Si$ [2] correlations. We feel that these heteronuclear X,Y correlations are very helpful for signal assignments.



Sincerely yours

[S.Berger] [P.Bast]

[1] P. Bast, S. Berger and H. Günther, submitted.
[2] P. Bast, S. Berger, submitted.

Texas A&M University NMR Newsletter - Book Reviews

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

"Density Matrix Theory and its Applications in NMR Spectroscopy"

by

Thomas C. Farrar and John E. Harriman

The Farragut Press, P.O. Box 5102, Madison, WI 53705, U.S.A.;
xi + 191 pp.; 1991; $24.95; ISBN 0-917903-02-1 (softcover);
$39.95; ISBN 0-917903-03-X (hardcover)

The authors intend "to provide a brief, hopefully lucid, presentation of density matrix theory which could be read and understood by first year graduate students." This is the first of a planned two-volume series emphasizing the use of density matrices in NMR. The second volume will be concerned with relaxation effects. A companion volume [T. C. Farrar, *Introduction to Pulse NMR Spectroscopy*, The Farragut Press, Madison (1989)] is also recommended by the authors.

The first chapter (62 pages) is about one-third of the material in this volume. The first few sections are a review of the pertinent background material in quantum mechanics including operator algebra, vector spaces, and several definitions of the density matrix. The last two sections of Chapter 1 emphasize angular momentum, rotation operators, and time-dependent quantum mechanics. In Chapter 2 (20 pages) the formalism of the first chapter is applied to a collection of single spin-1/2 nuclei. The spin-echo experiment is treated first in terms of matrices and then by means of the super-operators as the algebraically simpler method. Chapter 3 briefly (8 pages) presents an analogous development for spin-1 nuclei.

The heart of this text is contained in Chapter 4 (60 pages). Following an analysis of the energy levels and spectra for AB/AX spin systems, the time evolution of the density matrix is described for a spin-echo sequence and for INEPT/DEPT type experiments. The final chapter (11 pages) deals with certain topics in tensor algebra which will be important for describing relaxation effects in the planned second volume of the current series.

The bibliography cites 7 books, 3 papers, and 2 computer programs. There are four appendices (17 pages) containing angular momentum formulas, basis matrices, and spin multiplication tables.

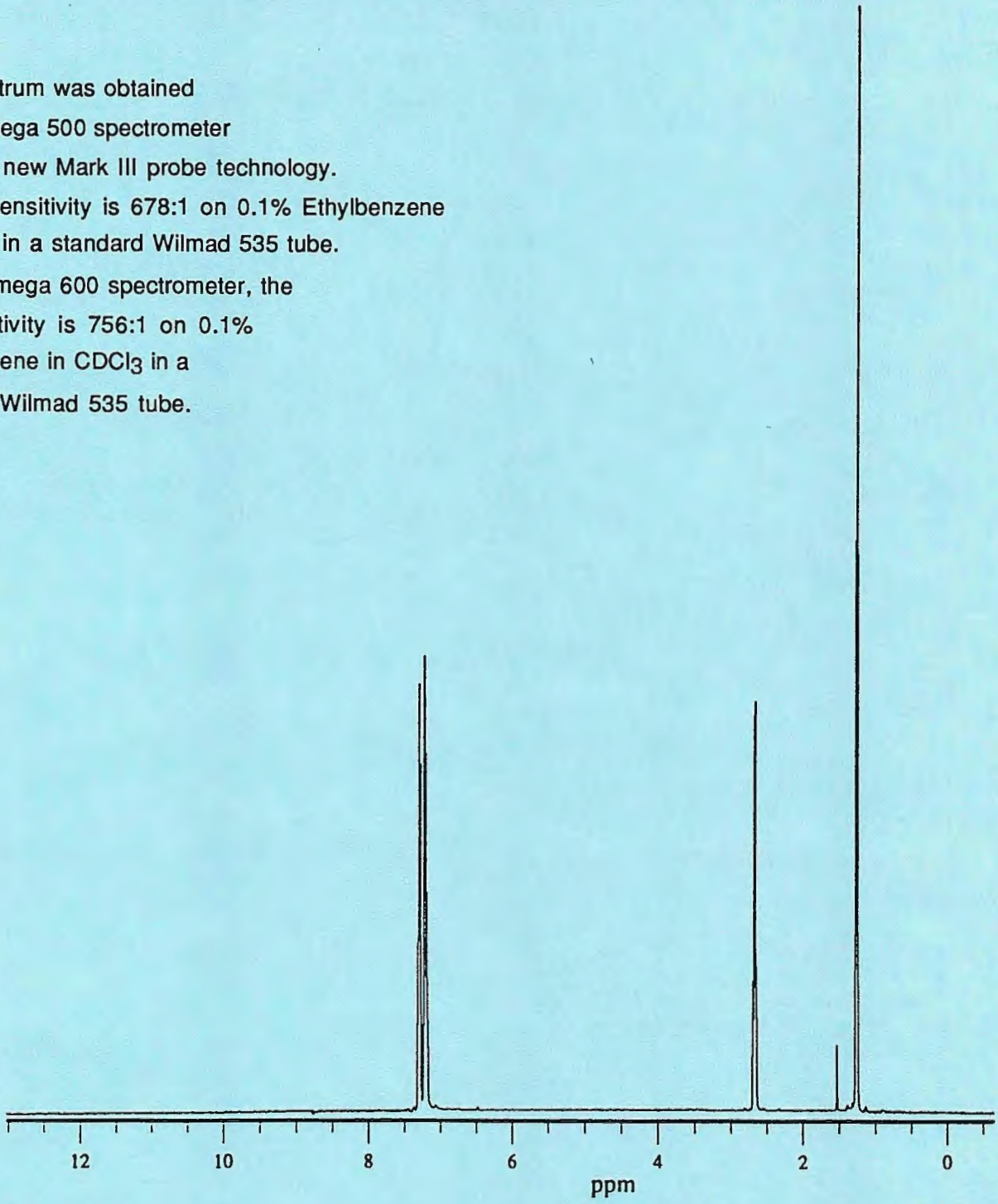
Last year we used Goldman's book for the graduate course in magnetic resonance theory. This was an alternative to using selected chapters from texts on quantum mechanics, angular momentum, and magnetic resonance. It is possible that the three books in this series by Farrar might be suitable for this purpose.

Mike Barfield
University of Arizona

Probe Performance

High Sensitivity 5 mm ^1H Probes

This spectrum was obtained
on an Omega 500 spectrometer
using the new Mark III probe technology.
The ^1H sensitivity is 678:1 on 0.1% Ethylbenzene
in $CDCl_3$ in a standard Wilmad 535 tube.
For an Omega 600 spectrometer, the
^1H sensitivity is 756:1 on 0.1%
Ethylbenzene in $CDCl_3$ in a
standard Wilmad 535 tube.



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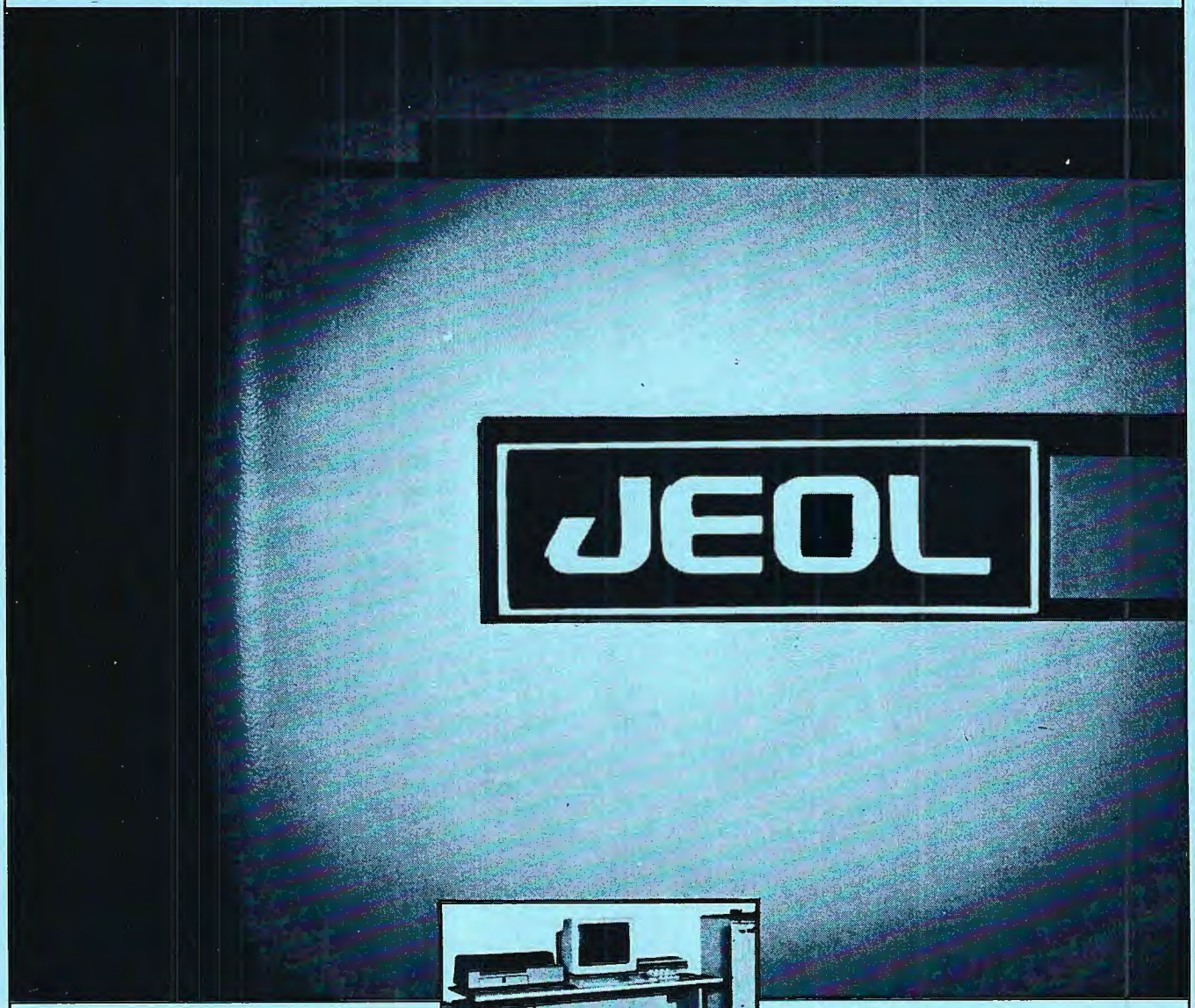
Of all the advanced technology on this research-level NMR, this may be the most important piece of hardware.



JEOL's Alpha series FT NMR system offers a research-level NMR spectrometer that sets a new standard of performance and reliability.

The Alpha combines event bus architecture, experiment definition language, dynamic RF control, pulse shaping and matrix shims into an extremely flexible, high speed precision machine with exceptional sensitivity.

One of the Alpha's most important features isn't listed on a technical data sheet, however. It's the reputation for quality and service that JEOL has earned over the years.

All of our machines are designed for reliability, flexibility and durability. And the outstanding service and applications support provided by our customer service staff makes sure that our high-performance equipment always performs to your satisfaction.

For a demonstration or more information about the JNM-A400/A500/A600 Alpha series of FT NMR systems and JEOL's customer service organization, call 508-535-5900 or write to JEOL USA, 11 Dearborn Rd., Peabody, MA 01960.

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