TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 402

March 1992

Continued on page 2

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Isotopic Purity (%D)	Density (g/ml)	MP (°C)	BP (°C)	$-X_v \times 10^6$ @ (°C)
D-11	Acetic Acid-d_4	CD_3COOD	99.5%	1.11	17	118	0.551 (32)
D-120	Acetic Anhydride-d_6	$(CD_3CO)_2O$	98%				
D-13	Acetone-d_6	CD_3COCD_3	99.9%	0.84	-94	57	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129							
D-14							543 (20)
D-21							0.611
D-122							
D-130							
D-28	Choloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

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VARIAN

BOX/500 SHEETS

Cat. No.	Paper Size	Instrument Model	Type
WCV-100 (S-100/4)	11" X 26"	HA-100, HA-100D	Gridded-Two Color
WCV-60 (A-60C)	11" X 26"	A-60, A-60A	Gridded-Two Color
WCV-XL (XL-100)	11" X 26"	XL-100 (FC and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (FC 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
	X 17"	All Models	16 1/2" or 16 Blank

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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

Third Annual Workshop on Magnetic Resonance Microscopy and Materials Imaging, Charlestown (Boston), Mass., **May 11-12, 1992**; Contact: NMR Center at (617) 726-5811; fax (617) 726-5819; or email J. L. Ackerman at jerry@nmr-r.mgh.harvard.edu, or L. Garrido at garrido@nmr-r.mgh.harvard.edu. See Newsletter 402, 24.

Sixth Washington University-ENI/Emerson Electric Co. Symposium on NMR, St. Louis, Missouri, **May 18, 1992**; Contact: Karen Klein, Wash. Univ.; (314) 935-6405. See Newsletter 402, 46.

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.

Science Innovation '92, New Techniques and Instruments in Biomedical Research (sponsored by the AAAS), San Francisco, **July 21-25, 1992**; Workshops on biomedical imaging. chemical and structural NMR; Plenary session on NMR on Fri., July 24. Contact: Science Innovation '92, P.O. Box 630285, Baltimore, MD 21263; fax (202) 289-4021.

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.

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* * * * *

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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.

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DEADLINE DATES

No. 404 (May) ----------24 April 1992
No. 405 (June)----------22 May 1992
No. 406 (July)---------- 19 June 1992
No. 407 (August)---------- 24 July 1992

* * * * *

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February 3, 1992
(received 2/10/92)

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

BEWARE OF SELF-REFOCUSING GAUSSIANS

Dear Barry,

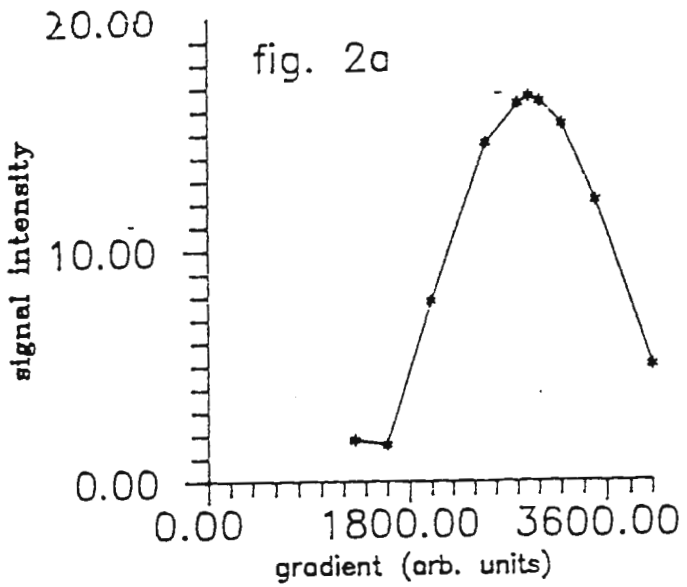
The virtues and benefits of self-refocusing 270° gaussian pulses have been extensively and eloquently described by Emsley and Bodenhausen (J. Magn. Reson. 87, 1, 1990; J. Magn. Reson. 82, 211, 1989; Magn. Reson. Med. 10, 273, 1989). Here, I would like to warn unsuspecting experimentalists of a potential pitfall when trying to implement a gradient-echo imaging sequence with gaussian excitation pulse, and trim it "from scratch". By "trimming" I refer to the adjustment of the refocusing lobe of the slice-select gradient to produce a maximal signal, and calibration of the transmitter power to obtain an empirical flip-angle vs. pulse amplitude calibration curve. For example, one may set the pulse amplitude to some value that produces a detectable signal, then adjust the refocusing gradient to maximize this signal, and then go back to a more careful transmitter power calibration, using this "trimmed" gradient. This produced the plots shown in Figure 1. It looks like the gradient is properly trimmed, and the excitation power calibrated (with a 90° pulse corresponding to A=29), right? Wrong! The pulse amplitude used in the gradient calibration accidently happened to be in the vicinity of a 270° pulse. Therefore the gradient amplitude which produced maximal refocusing was much smaller than appropriate for a 90° excitation. Once the refocusing gradient is set to this false value, however, the signal intensity vs. transmitter power curve will produce its first maximum not at 90°, but towards 270°, the exact value depending upon the gradient, the truncation level of the pulse, etc.

The obvious way not to get caught in these false maxima is of course to adjust the refocusing gradient using a true 90° (or slightly smaller) flip angle, which can be found from a simple non-selective "pulse-acquire" series using no gradients. The results of this search, and the subsequent pulse power calibration with selective excitation are shown in Figure 2. As expected, the true maxima are at much lower pulse power, and much higher gradient amplitude than those in Figure 1.

Sincerely yours,

Peter Bendel

P.S. Please credit this letter to Raffy Poupko's account.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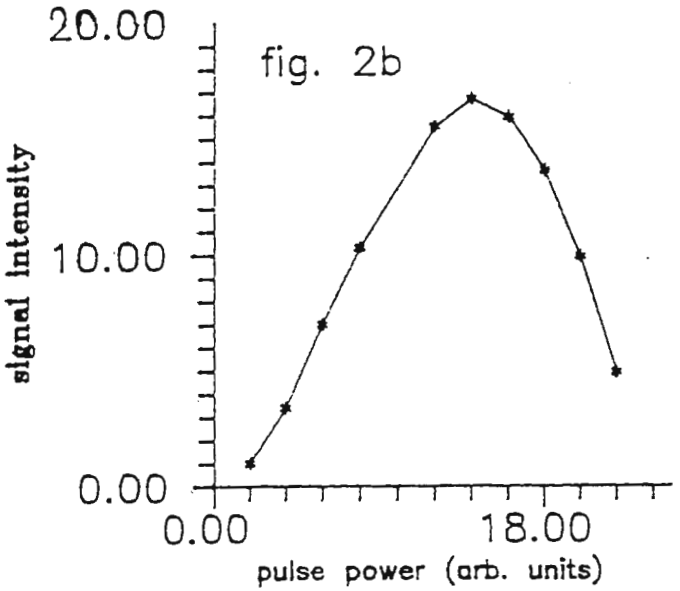
10.00
0.00
signal intensity
0.00
1800.00
3600.00
gradient (arb. units)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signal intensity
0.00
18.00
pulse power (arb. units)

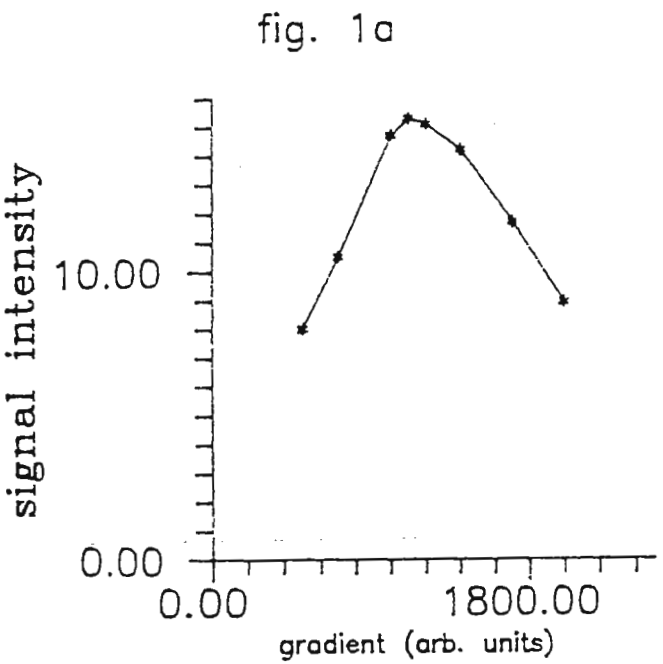
fig. 1a
signal intensity
10.00
0.00
0.00
1800.00
gradient (arb. units)

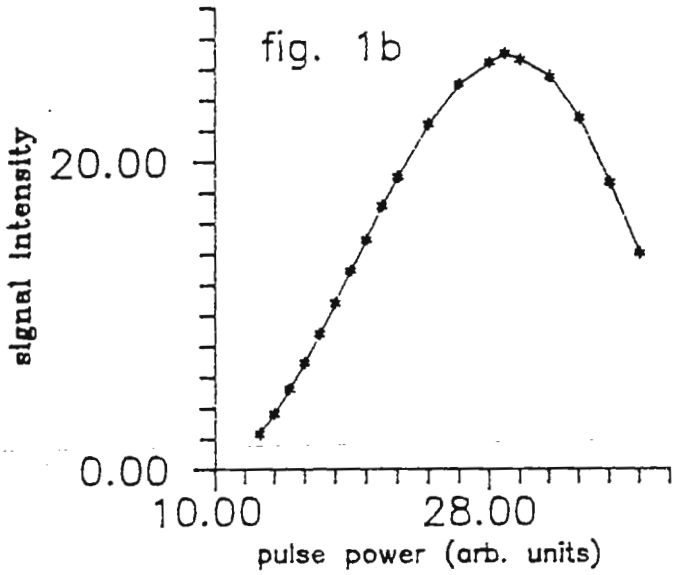
fig. 1b
signal intensity
20.00
0.00
10.00
28.00
pulse power (arb. units)

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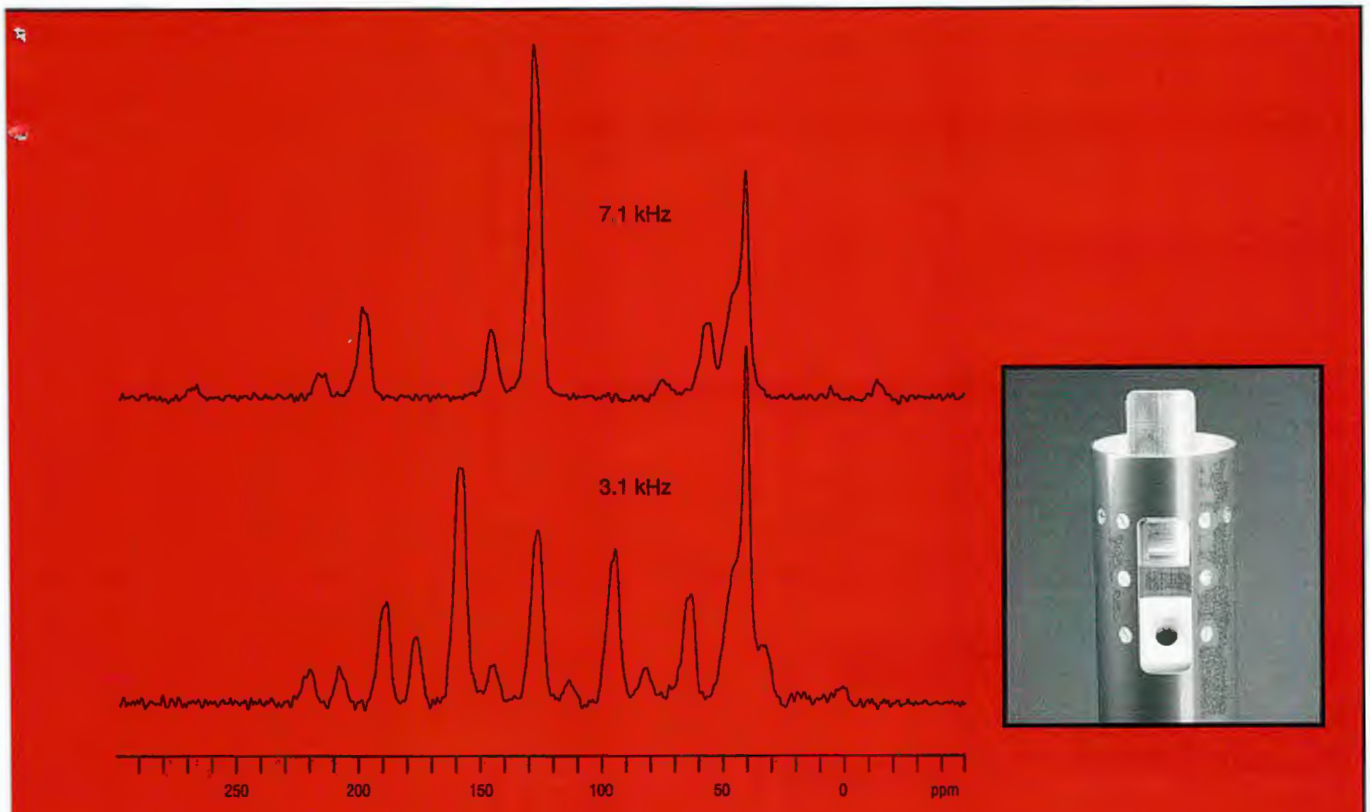

The above ^{13}C CP/MAS spectra of non-uniform cylindrical polystyrene beads (approximately 3mm length and 2mm diameter) were run on a UNITY®-400 MHz NMR spectrometer. These spectra were easily obtained over a range of spinning speeds, up to 9 kHz. These kinds of materials can only spin up to these fast spinning speeds with a MagicAngle•nmr probe.

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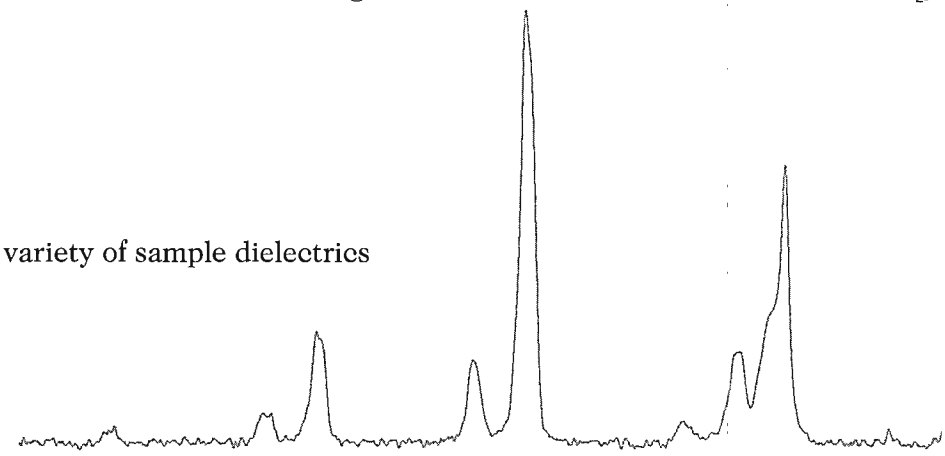

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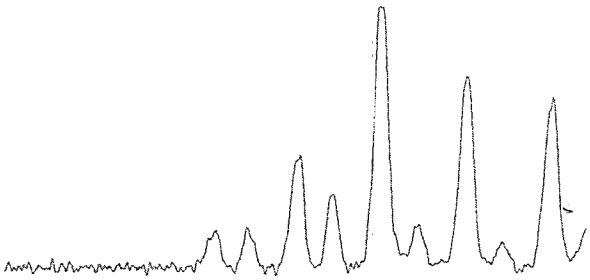

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January 10, 1992
(received 2/5/92)

Prof. B. L. Shapiro
968 Elsinore Court
Palo Alto, CA 94303

UNOCAL 76

TSP - A Convenient NMR Standard For Quantitation

Dear Prof. Shapiro,

Absolute quantitation of detectable organic solute is often desirable. A convenient way of accomplishing this is to use an internal or even external standard. TSP (3-trimethylsilyl-propionic-2,2,3,3-d^4 acid) is a readily available (e.g Aldrich, Merck) NMR reference compound that we find quite useful for this purpose. Its favorable properties include good solubility in water, unobtrusive chemical shift (0 ppm), and relatively short T1 (3.5 secs measured at ambient conditions in a neutral aqueous solution). A standard solution in either H_2O or D_2O is easily prepared and stored. The sample is prepared by carefully measuring suitable amounts of the test sample and the standard TSP solution into an NMR tube. Concentration of a given solute can then be determined from the observed relative NMR signal intensities using the following simple relationship.

$$\text{Solute concentration(ppm)} = [I_s/N_s] \times [9/I_{tsp}] \times [M_s/M_{tsp}] \times [W_{tsp}/W_{sol}] \times 10^6$$

where

I_s	=	integral area for a given solute resonance
N_s	=	nominal number of equivalent protons
I_{tsp}	=	integral area for the TSP resonance
M_s	=	Molecular weight of solute
M_{tsp}	=	Molecular weight of TSP
W_{sol}	=	Weight of solution used for analysis (gms)
W_{tsp}	=	Weight of TSP used for analysis (gms)

An example of this is shown in *Figure 1* where a series of four standard solutions containing varying amounts of iso-propylalcohol (IPA) were analyzed as such. Please note that "ppm" has been redefined to represent solute concentrations in this context! The excellent correlation (R^2= 1.00) obtained testifies to the viability of such an analysis. Unlike other techniques, water samples can be analyzed "as such" without the need for any solvent extraction procedures. Good solvent suppression is, of course, important when analyzing dilute aqueous solutions.

To ensure accurate quantitation, it is important to (1) employ adequate recycle delays;(2) use careful phasing and baseline correction procedures; &(3) compensate for "offset dependance" effects of solvent suppression pulse sequences(when applicable) by using a calibration curve.

The 200.057 MHZ ^{1}H NMR spectra shown in *Figure 2* were obtained using a Varian Unity-200 FTNMR spectrometer employing the WS11ECHO water suppression pulse sequence. A 4.7 X 10 $^{-3}$ M D_2O solution containing TSP was prepared for this study.

Yours Sincerely,

Victor Perrin
Research Asst.

Pradeep Iyer
Sr. Res. Scientist

Figure 1

Iso-propyl alcohol(IPA) Calibration Using TSP

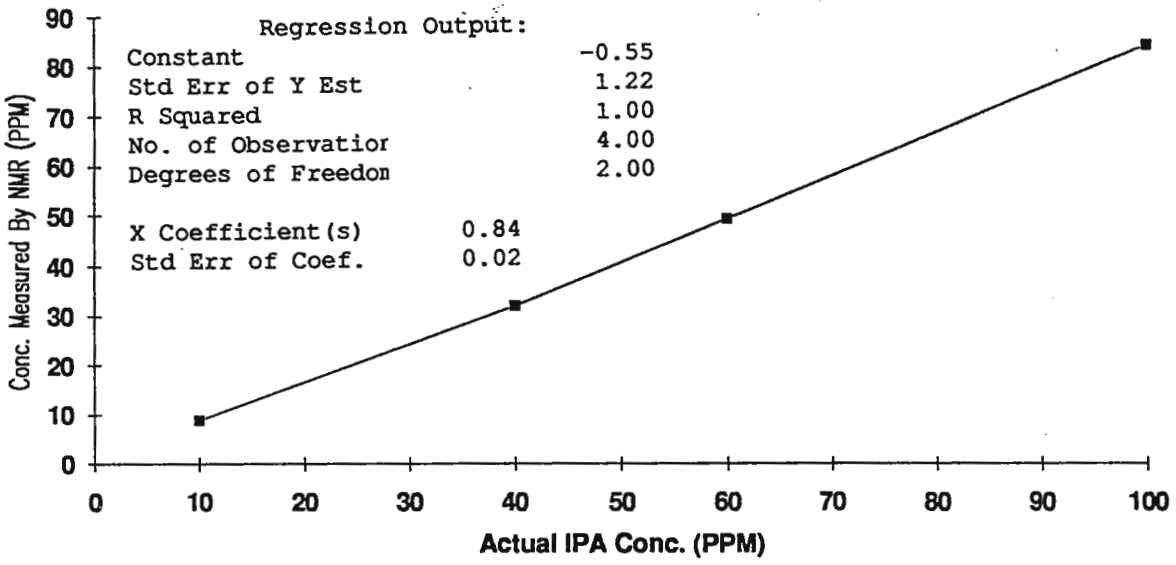
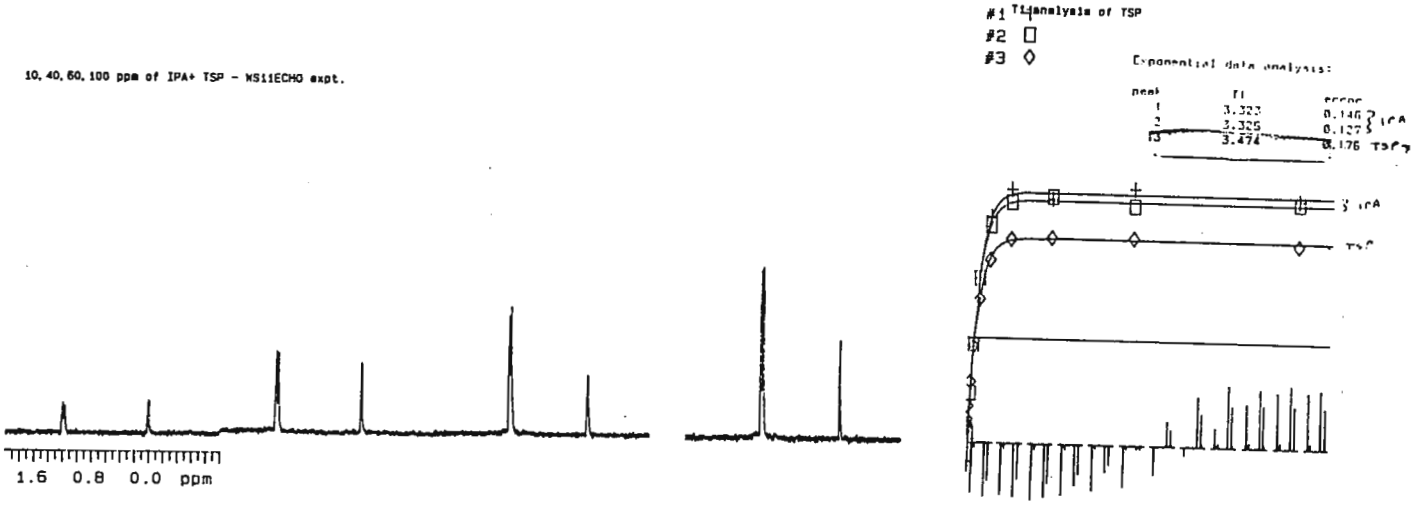


Figure 2



Faculté
des sciences

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DE SHERBROOKE

Sherbrooke (Québec) Canada J1K 2R1

Dear Dr. Shapiro:

Peak Picking

February 5, 1992
(received 2/10/92)

On commercial spectrometers, the measurements of lineshape positions and maxima are often determined with a peak picking routine. Our need to understand how such a routine worked came about in our studies of domain growth during phase separation processes (1). Cryptic explanations in spectrometer user manuals, and our experience that many people use such routines as black boxes lead us to believe that the basis of these routines should be disseminated to a larger audience.

Essentially, close to the maximum intensity, a Lorentzian lineshape

$$I(\omega) = (\pi\Delta)^{-1}\left\{1 + \left[(\omega-\omega_o)/\Delta\right]^2\right\}^{-1}$$

where Δ in the half width at half intensity, and ω_o in the resonance frequency, can be approximated by a parabola. In the vicinity of ω_o, the term in the square bracket is always small, allowing a first order binomial expansion, yielding after rearrangement

$$I(\omega) \simeq (\pi\Delta^3)^{-1}\left\{-\omega^2 + 2\omega_o\omega + (\Delta^2 - \omega_o^2)\right\}$$

This last equation has the form of a parabola (2), y(x) with its vertex at (h,k) and focus at (h, k-p), i.e.,

$$y = (4p)^{-1}\left\{-x^2 + 2hx + (4pk-h^2)\right\}$$

Three parameters h, k, and p define the parabola. Typically, the peak picking interpolation finds three experimental data points with the largest intensities for a resonance. The resulting set of three equations is then solved to uniquely determine the above parameters, which in turn give the maximum intensity of the lineshape, and its position in the spectral region of interest.

Sincerely,

Franco Cau

Serge Lacelle

1) F. Cau, S. Lacelle, submitted
2) Standard Mathematical Tables, 19th ed. Chemical Rubber Co., (1971), p.355.

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January 20, 1992
(received 1/27/92)

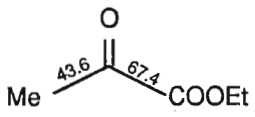
Prof. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

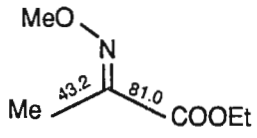
Dear Dr. Shapiro,

The Stereochemistry of α-Ketoester Methoximes Determined by $^1J_{CC}$

We became interested in the stereochemistry of methoximes of some α-ketoesters, e.g., ethyl pyruvate, as we found that several compounds which we synthesized existed as single syn–anti isomers. Although it is known that in oximes (and related derivatives), the syn carbon is shielded by *ca* 4–9 ppm compared with the anti carbon [Hawkes *et al., J. Org. Chem.* **39,** 1017 (1974)], it was not possible to conclusively determine the stereochemistry on the basis of ^{13}C chemical shifts *with only one isomer at hand.* We also tried some NOE experiments but they were inconclusive.

Unambiguous assignment of stereochemistry could however be made on the basis of $^1J_{CC}$ as follows. It has been reported [Krivdin *et al., Tetrahedron Lett.* **25,** 4817(1984)] that $^1J_{CC}$ between the oxime carbon and the anti carbon is larger than that of the corresponding ketone by *ca* 8–11 Hz. The $^1J_{CC}$ values in both ethyl pyruvate and its methoxime were determined by means of the 1D INADEQUATE pulse sequence, and the stereochemistry of the methoxime was consequently concluded to be *E* as shown below.





Sincerely,

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3200	6–220MHz	1000W
3137	200–500MHz	50W
3135	200–500MHz	150W
3134	200–500MHz	300W

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Linearity (±1dB to 200Mhz)		0-800 W	0-250 W
(to 220MHz)		0-600 W	0-200 W
Gain (typ.)		65 dB	60 dB
Gain flatness		±4 dB	±3 dB
Input/Output impedance		50 ohms	
Input VSWR		< 2:1	
Pulse width		20 ms	
Duty cycle		Up to 10%	
Amplitude rise/fall time		200 ns typ.	150 ns typ.
Amplitude droop		5% to 10 ms typ; 7% max	
Phase change/power output		10° to rated power, typ.	
Phase error overpulse		4° to 10 ms duration, typ.	
Noise figure		11 dB typ.	8 dB typ.
Output noise (blanked)		< 20 dB over thermal	
Blanking delay		< 2 μs on/off, TTL signal	
Protection		1. VSWR: infinite VSWR at rated power 2. Input overdrive: up to +10 dBm 3. Over duty cycle/pulse width 4. Over temperature	

Supplemental characteristics:

Connectors, rear panel	1. RF input: BNC (F) 2. RF output: Type N (F) 3. Noise blanking: BNC (F) 4. Interface: 25 pin D(F), EMI filtered
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System monitors	1. Thermal fault 2. DC power supply fault 3. Over duty cycle/pulse width 4. Forward/Reflected RF power
Front panel controls	1. AC power 2. Pulse width 3. Duty cycle
Cooling	Internal forced air
Operating temperature	+10 to 40°C
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February 19, 1992
(received 2/20/92)

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

"The Magic Cylinder"

Dear Barry:

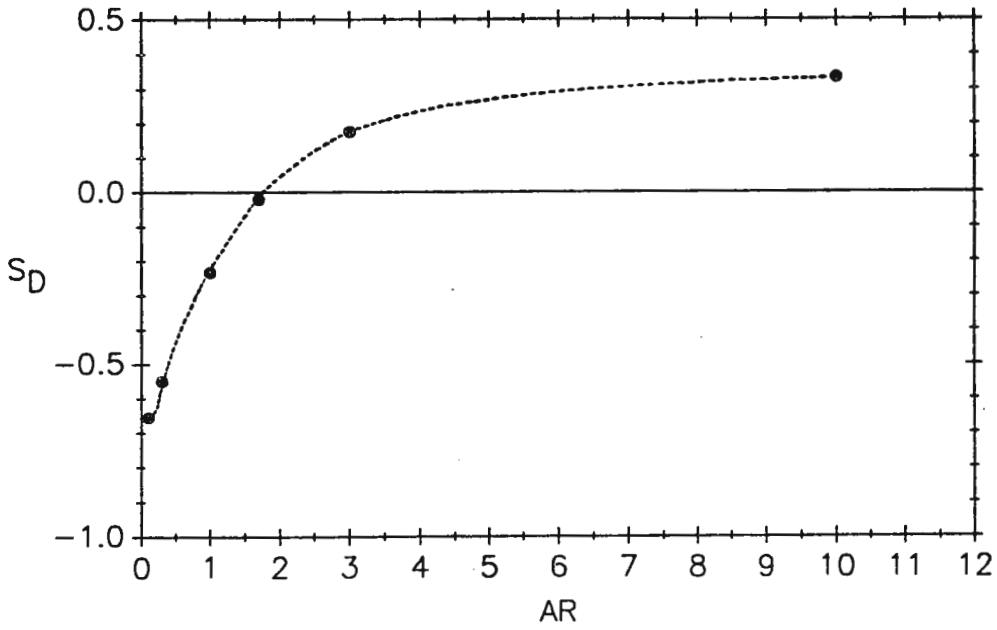
Mozart dreamed of a magic flute that could overcome any difficulty, no matter how severe. Wishing this were true, we have, however, been restrained to the natural realm of magnetostatics.

We can write the homogeneous bulk magnetic susceptibility (BMS) contribution (D_i) for spins inside a right cylinder of any dimension, oriented parallel to $\mathbf{B}_0$, as in the equation, where χ_i and χ_e are the volume BMS values for the media internal and external to the cylinder,

$$D_i = s_D(\chi_i - \chi_e) + \frac{\chi_e}{3}$$

respectively.[1,2] In this equation, s_D is a shape function of the aspect ratio, AR ($AR = V_v(\pi r^3)^{-1}$), of the sample cylinder (V_v is the volume of the inside medium); the ratio of its height to its radius, r ($r = (ID)/2$). It has been shown that $s_D = 1/3$ when AR is infinity.[2] This leads to the interesting result that the χ_e-dependence of D_i vanishes for an infinitely long cylinder.[1,2] It is also true that $s_D = -2/3$ when AR = 0, the case of an infinitely short cylinder (an infinite disk or plane).[2] Also, the inhomogeneous contribution ($\mathbf{I}_i$) is zero at these two limits.[2] However, for real cylinders, of finite lengths, not only does s_D vary between these values, but also $\mathbf{I}_i$ is nonzero: therefore, any resonance of spins inside the cylinder is, in principle, inhomogeneous. Nonetheless, if the sensitive volume of the transceiver coil is sufficiently smaller than V_v and is reasonably centered therein, only the D_i term contributes to the observed peak.[2,3]

Mozurkewich and co-workers have made numerical calculations of the inhomogeneous lineshapes of resonances from spins inside several finite right cylinders, oriented parallel to $\mathbf{B}_0$, with ARs ranging from 10 to 0.1.[4] They have tabulated the relative shifts of the positions of maximum peak intensity of the inhomogeneous resonances. We have multiplicatively scaled these so that the largest is equal to 1/3, and present them as circles in a plot of s_D vs. AR in the figure. The highest values asymptote at 1/3 when AR > 10 (ref. 5) and the lowest values sharply asymptote



at -2/3 when AR < 0.1. It is interesting to note that $s_D = 0$ when AR = *ca.* 1.8. For a parallel right cylinder of this shape, D_i is independent of χ_i! This is, of course, another consequence of the miraculous sphere of Lorentz, which we venerated in our last contribution (392-13/May, 1991). Such a "magic" cylinder (height/diameter = 0.9) has the same value of D_i as does a sphere; however, I_i is nonzero.[1,2] This is the same value of AR at which the average (magnetometric) demagnetization factor of a circular cylinder equals that of a sphere.[6] In any case, the curve in the figure can be used to evaluate the value of s_D for any shaped right cylinder oriented parallel to $\mathbf{B}_0$. This figure is taken from a manuscript we have submitted.[7]

Thus, in addition to the *magic shape* of a sphere[1,2], the *magic angle* for an effectively infinitely long cylinder[2], and the *magic concentration* of a non-diamagnetic solute in a diamagnetic solvent[1,7,8], we now have the *magic cylinder*. These are all situations where at least the D_i dependence on χ_i vanishes. If a sample enjoying such a condition is suspended in air, BMS effects are almost nonexistent since the volume BMS of air is so small, χ_e = 0.4 ppm at 293 K.[3] This might be quite helpful for a number of NMR experiments.

We acknowledge particularly stimulating discussions on this subject with Professor David Kramer and Dr. Yan Xu.

Best regards,

Charlie

Charles S. Springer, Jr.
Professor of Chemistry and Radiology

Wei Huang
Research Assistant

CSS:mcd

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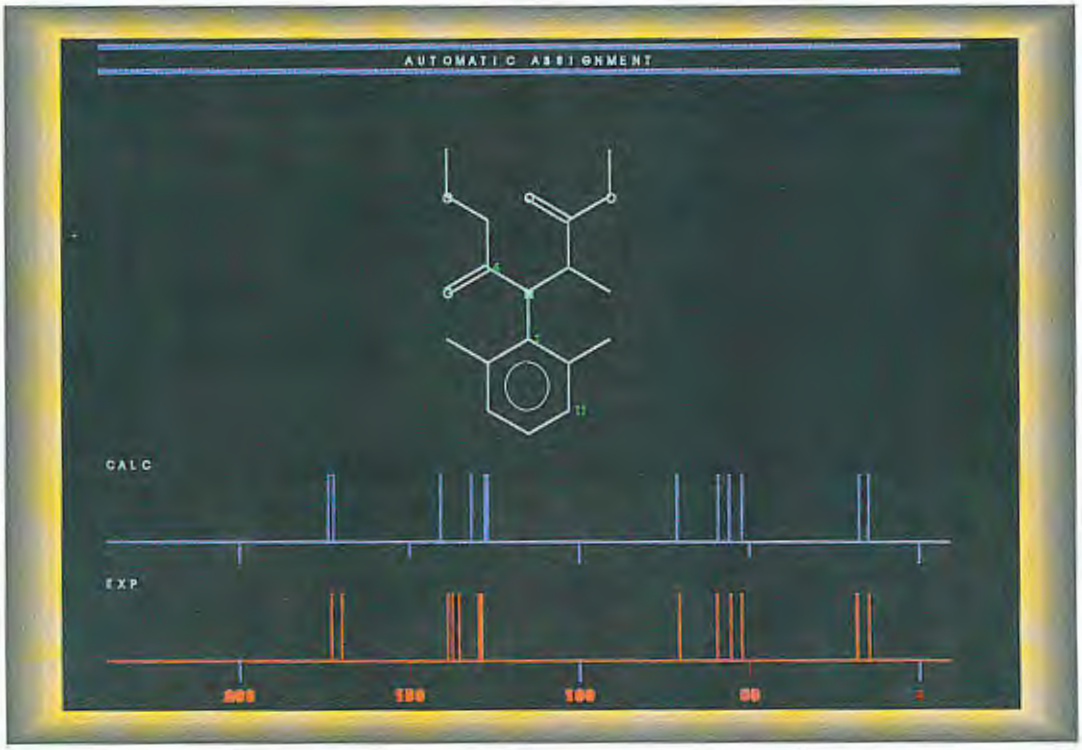

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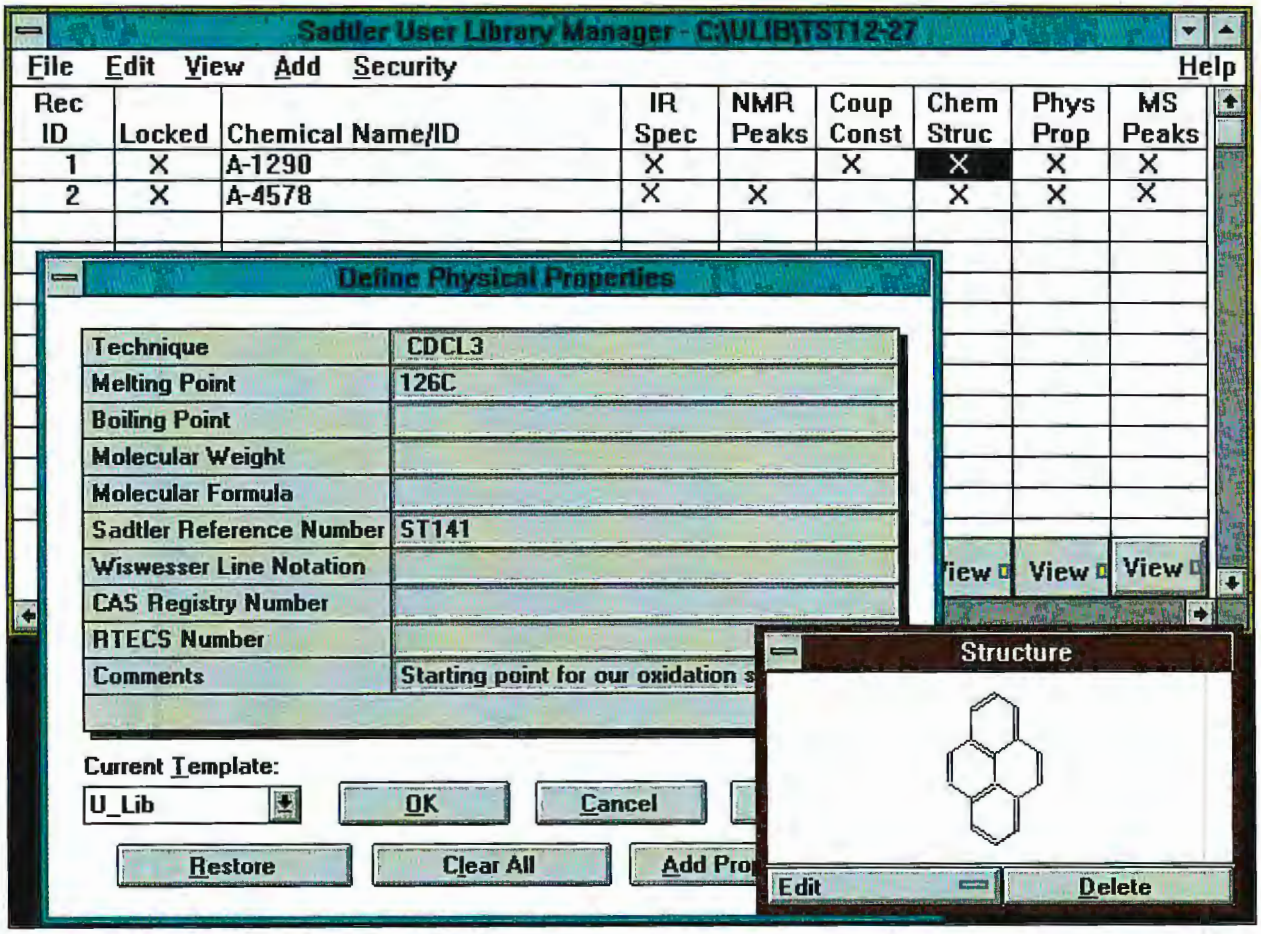

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Dr. B. L. Shapiro
TAMU NMR Newsletter
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February 17, 1992
(received 2/21/92)

Respirable Silica and NMR

Dear Barry,

Crystalline silica is classified as a possible human carcinogen by IARC Monograph 42 Supplement 7. Of particular interest to several manufacturers is the determination of the "respirable silica" content of products for spray application. The currently accepted method for analysis of crystalline silica is X-ray diffraction. The main difficulties with the X-ray protocol are interferences from other minerals at trace silica levels, and the problem with small particle size minerals less than a few microns (respirable dust $\leq$ 6 micron particle sizes). Solid-state silicon-29 NMR can successfully address both issues, provided sensitivity is sufficient. The first phase of our investigation included determination of appropriate parameters for quantitative analysis. Samples of crystalline silica (α-quartz), cristobalite, and amorphous silica were obtained, as were X-ray profiles of each material. All three silica polymorphs share the chemical composition of SiO_2, but with varying degrees of crystallinity. The crystalline quartz sample exhibited an ambient temperature silicon-29 T_1 of longer than an hour at 59.6 MHz (protons at 300.1 MHz). A protocol using a 10 degree tip angle (pulse = 1μ sec) with a relaxation delay of 20 minutes between acquisitions yields quantitative silicon NMR spectra for these materials.

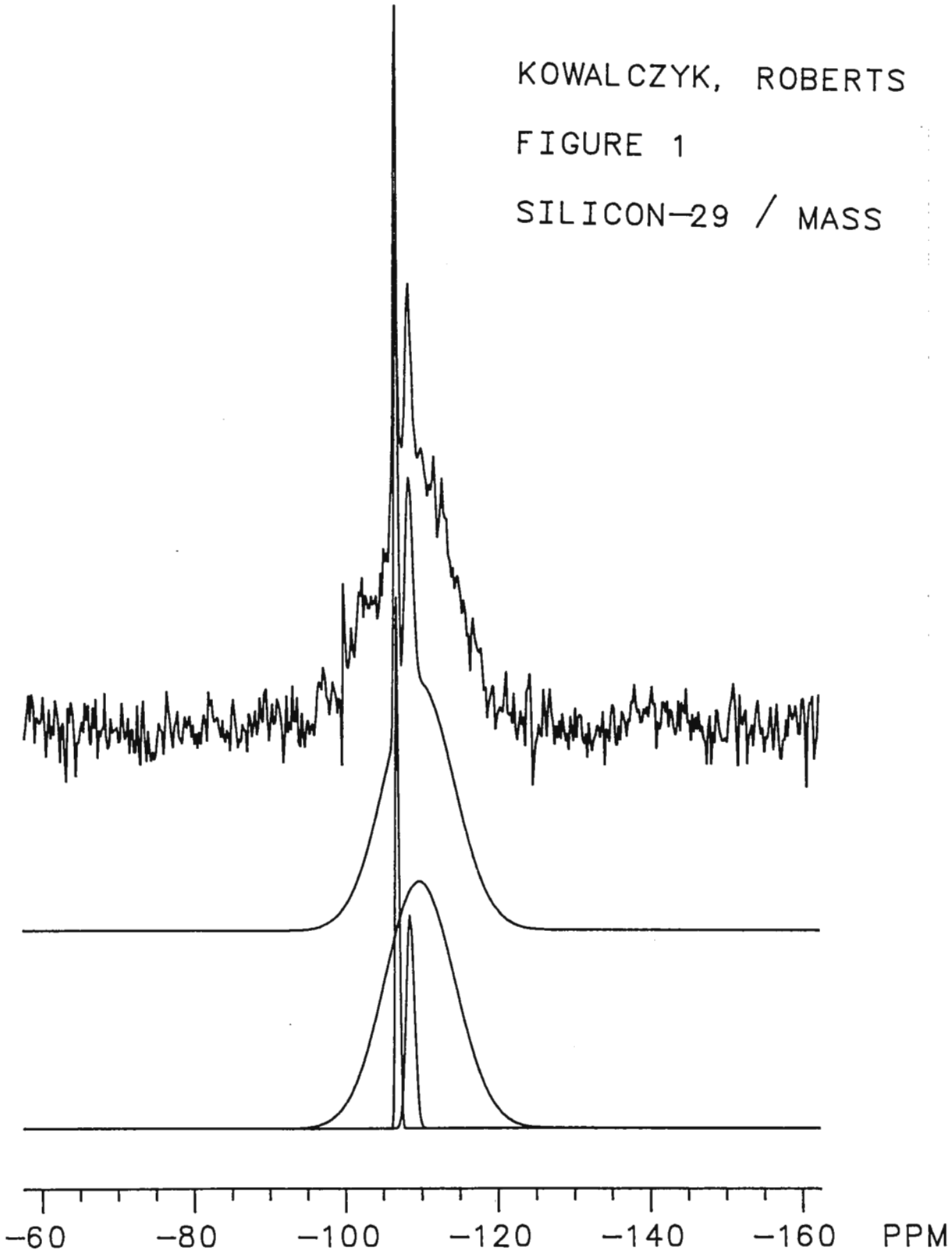
Six blends of known composition were prepared by Gary Tomaino of Pfizer as unknowns to test the NMR procedure. Non-proton-decoupled silicon-29 NMR spectra were obtained using magic angle sample spinning with speeds of 4 to 5 kHz. A typical sample required one day of signal averaging. The data acquistion time was 81 msec; processing included zero-filling and exponential line broadening equivalent to 10 Hz. Figure 1 presents a spectrum from one of the blends with all three components. The three peaks represent the α-quartz (-106.7 ppm), cristobalite (-108.3 ppm), and the broad underlying resonance from the amorphous silica (approximately -111 ppm). The curve fitting routine of the GE NMR Instruments GN-300 gives 10 % α-quartz, 11 % cristobalite, and 79 % amorphous silica. The composition based on X-ray data is 10 % α-quartz, 10 % cristobalite, and 80 % amorphous silica. This correlation between the NMR data and the X-ray analysis is considered excellent.

As is often the case, the main problem with the NMR analysis is sensitivity. For real samples, a mineral concentration step must be employed. The NMR procedure is quite time-consuming. Nevertheless, for materials containing known interferences, solid-state NMR represents a possible alternative to the X-ray protocol. Further work with production line samples is in progress.

Greg Kowalczyk

James E. Roberts

Please credit to Bill Anderson's account. The financial support of Binney & Smith (Easton, PA) and the X-ray diffraction analyses provided by Gary Tomaino of Pfizer Inc. (Easton, PA) are gratefully acknowledged.


KOWALCZYK, ROBERTS
FIGURE 1
SILICON—29 / MASS
−60
−80
−100
−120
−140
−160
PPM

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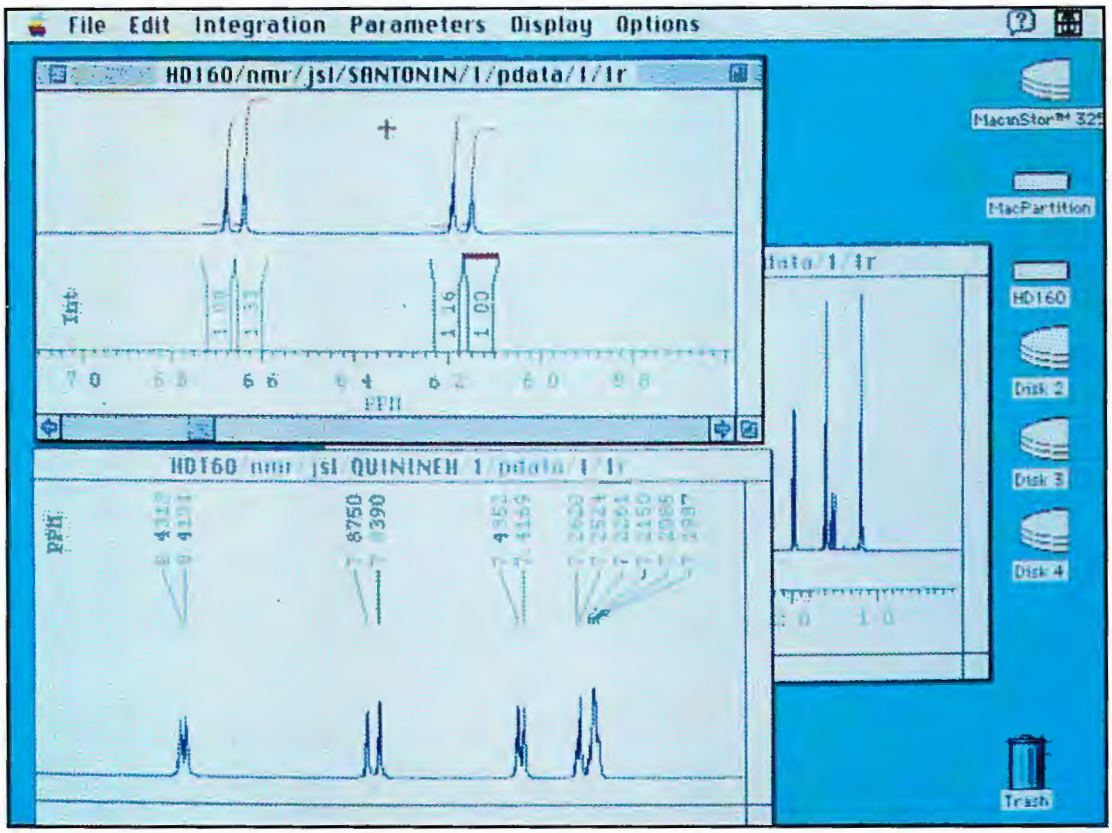

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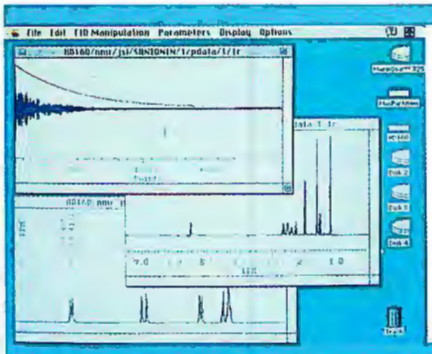

WIN-NMR can process FID and spectral data from all Bruker NMR spectrometers. The WIN-NMR data format used is identical to that of the UXNMR and UXNMR/P software. Data conversion routines are provided for all Aspect 2000/3000 based NMR spectrometers.

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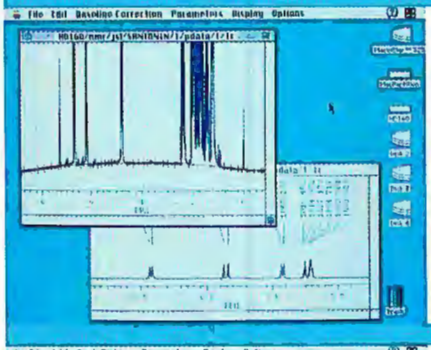

Automatic or interactive baseline correction with user control over the type and order of the function used in the correction. The entire spectrum, or only a user selected region can be corrected.

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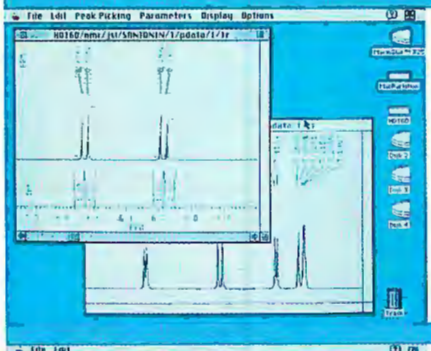

Automatic or interactive peak integration. In automatic integration the user has control over the integration threshold and grouping of multiplets. The automatically determined integrals can be individually manipulated once the automatic selection process is complete. The integration parameters can be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

In interactive integration the user has complete control over each individual integral including integration limits, slope and bias. Integral areas can be calibrated to reference peaks or to determine percent composition for the sample.

Data can be plotted on your favorite plotter or laser printer through the use of the standard Apple printer drivers or through third party plotter drivers such as MacPlot® or Plottergeist®.

The use of the cut and paste facility can be used for transferring graphics between Macintosh applications. Facilities are provided to export peak picking and integration reports, as well as ASCII data to your favorite word processor or mathematics package for further manipulation.

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Grenoble, le January 23rd 1992.
(received 1/29/92)

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

USE OF THE INDIRECT ^{199}Hg DETECTION IN MERCURY AROMATIC COMPOUND.

Dear Dr Shapiro,

We have been interested lately in selective labelling of aromatic rings with ^{199}Hg, via electrophilic substitution. We would like to use this isotope as an NMR probe to investigate lignin structure; lignins are three dimensional natural polymers, main components of wood, with a phenol-propane network, without regular and well defined repeating unit. In a preliminary step we studied the mercuriphenyle acetate.

The aromatic part of the proton spectrum (fig.1) is the superposition of an AA'BB'C and of an AA'BB'CX spectra, where the ortho coupled proton appears as weak satellites signals. From the direct NMR obsvervation of the ^{199}Hg isotope, three values are obtained for the $J^1H^{199}Hg$ couplings : ^3J= 204Hz, ^4J= 50Hz and ^5J= 19Hz. These values are introduced as refocusing delay, 1/2J, in the sequence using the indirect detection method for measurement of ^{199}Hg spectra. By suppression, with heteronuclear double quantum filtering, of signals from molecules containing no NMR active spin, ^{1}H spectra are edited for each value of J. One can read on them the chemical shift of Ha, Hb(fig.2a,2b) and Hc and observe the enhancement of the signals, on Ha spectrum (fig.2a).

A simulation of the proton and Mercury spectra with the PANIC program, using the J and δ values found, give a satisfactory fit with the experimental spectra.

The spectra were recorded from DMSO-d_6 solution in 10-mm tube, on a 400 MHz Bruker spectrometer; in the REVOBS sequence the D_1 relaxation delay is 3sec. ,and the D_3 delay for phase switching is 2μsec.

We apologize for our long silence and hope to be reinstated in your list with this contribution, credited to Prof. D. Gagnaire's subscription.

Sincerely,

R. Nardin V. Neirinck D. Robert

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fig.1

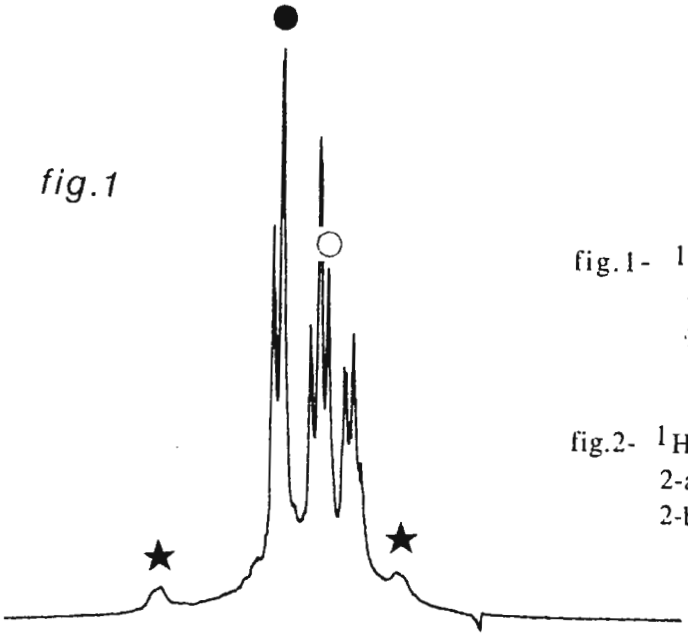
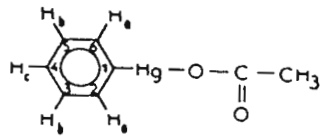
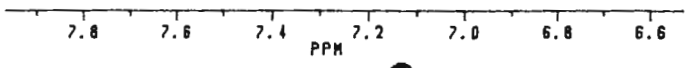


fig.1- ^{1}H spectrum of mercuriphenyle acetate (arom. part)
● δ Ha= 7.38 ppm read on spectrum 2-a)
○ δ Hb= 7.29 ppm read on spectrum 2-b)
δ Hc = 7.19 ppm ★ Ha - ^{199}Hg satellites

fig.2- ^{1}H spectra from indirect detection of ^{199}Hg :
2-a) ● Ha, with $^{3}J(^{1}H\text{-}^{199}Hg)$= 203Hz ;
2-b) ○ Hb, with $^{4}J(^{1}H\text{-}^{199}Hg)$= 50Hz





a)

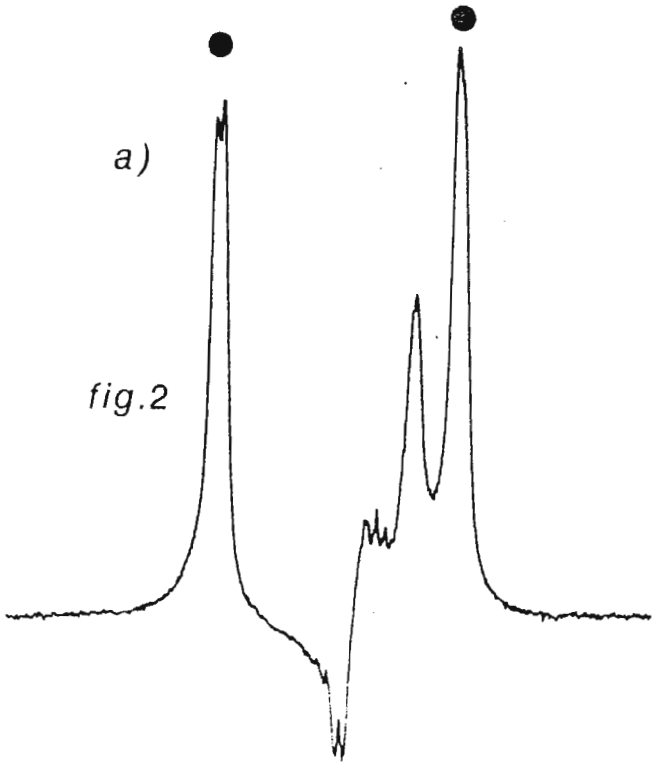
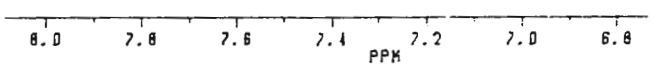


fig.2



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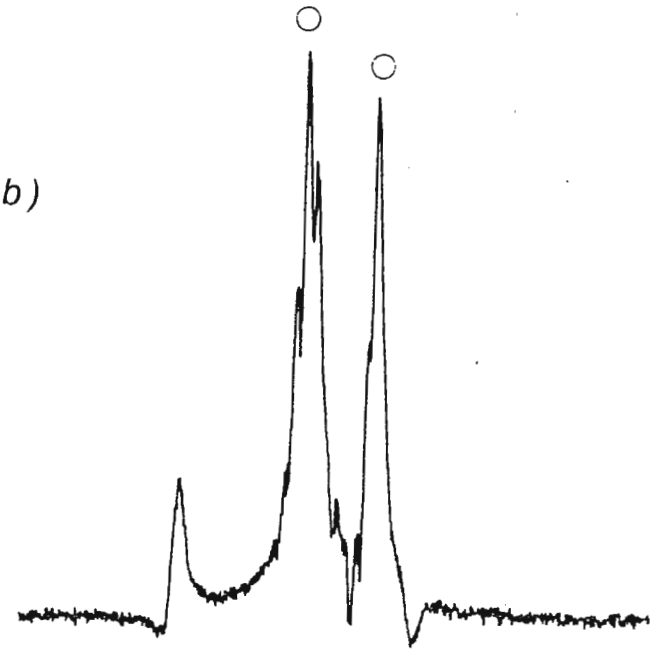

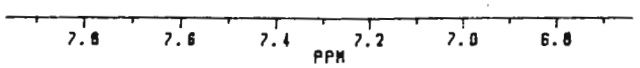

WORCESTER POLYTECHNIC INSTITUTE

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January 24, 1991 (received 1/31/92)

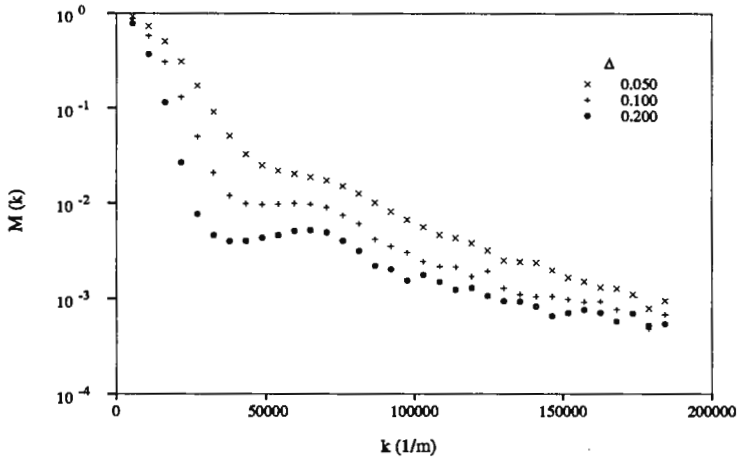
Professor Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore court
Palo Alto, CA 94303

Dear Dr. Shapiro,

The monitoring of molecular displacements by pulsed field gradient (PFG) NMR has proven to be a valuable tool for probing restricted geometries. Most previous efforts have focussed on analyzing the decay in magnetization due to diffusion in experiments where the independent variable is the time a spin is allowed to diffuse. Recently, emphasis has been placed on the Fourier relationship between acquisition space and real space. Experiments conducted on model systems have proven the utility of the technique.[1,2] For the past year we have been applying this technique to systems having complicated pore geometries and large inherent gradients due to susceptibility contrasts.

A wavevector, k, may be defined by the area under the gradient pulse in a PFG stimulated echo (STE) sequence, and used as a probe. The intensity of the NMR signal, $M(k)$, from fluid saturating a solid matrix is observed as k is varied. This provides a direct measure of the Fourier transform of the diffusion propagator. The effects of restrictions appear in k space data as deviations from a "freely diffusing" gaussian at large values of k and provide information on the characteristic length scales of the confining geometry. The observation of the propagator as the diffusion time, Δ, is varied is believed to provide information on permeability to fluid flow. Unfortunately, the internal gradients prohibit the use of a standard STE sequence and has been observed to produce erroneous results. A new sequence is under development that drastically reduces the contribution from internal gradients and may have the added advantage of increased phase stability of the echo.

Below is a plot of k space data that we collected to validate the new sequence. The data was acquired from a model system studied in Ref. 2: a disordered polystyrene sphere pack with a mean sphere diameter of 15.8 um. The "bump" occurs when k is equal to the inverse of the pore *spacing*, or simply the sphere diameter. Similar results have been observed in a ceramic system with uniform pore geometry, and in oil core samples. This feature is less prominent in these systems, and appears more as a "plateau".



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Lawrence L. Latour Limin Li Christopher H. Sotak

MASSACHUSETTS GENERAL HOSPITAL ◆ HARVARD MEDICAL SCHOOL

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February 20, 1992
(received 2/21/92)

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

Third Annual Workshop on Magnetic Resonance Microscopy and Materials Imaging

May 11–12, 1992

Massachusetts General Hospital, NMR Center, Charlestown (Boston), MA

Dear Barry:

This is to remind your esteemed readers of our Workshop coming up in May. Spring is a beautiful time of year to visit New England, tour Boston, and especially enjoy the historic Charlestown Navy Yard in which the MGH Biomedical Research Laboratory resides.

This year's featured speakers include Robin Armstrong from the University of New Brunswick *("Electric Current Imaging")*, Larry Berliner from Ohio State University *("EPR Imaging of Polymers, Solid Materials and Tumors")*, Winfried Kuhn from the Fraunhofer Institute for Biomedical Engineering in Germany *("Investigation of Aging Processes and Crosslinking in Elastomers by T_1-, T_2-, and $T_{1\rho}$-Parameter Selective NMR Microscopy")*, and Paul Lauterbur of the University of Illinois *("How Does MRμI Differ from MRI?")*. Additional talks accepted at this time cover the topics of imaging and spectroscopy of biomedical materials (silicones) *in vivo*, localized solid state cross polarization with surface coils, biodegradable drug delivery systems, gas imaging of porous solids, echo planar imaging, and noninvasive histochemistry in plants.

We are seeking additional contributed papers until the deadline of April 1. You may send an abstract to "Materials Workshop, NMR Center, Massachusetts General Hospital, 149 13th Street, Charlestown, MA 02129." We have reserved a block of rooms at the local Holiday Inn Government Center (call 617-742-7630 and specify "MRI Workshop"). Rooms fill early, and the reservation must be made by April 20 to get the discount. If you travel by United Airlines, our "official" airline, call their meeting desk at 800-521-4041, and specify Meeting ID 530BS for a discount. Registration fees will be $125, and $25 for students and postdocs. For more information, call the NMR Center at 617-726-5811, fax -5819, or email Jerry at jerry@nmr-r.mgh.harvard.edu or Leo at garrido@nmr-r.mgh.harvard.edu.

Best regards,

Jerome L. Ackerman Leoncio Garrido

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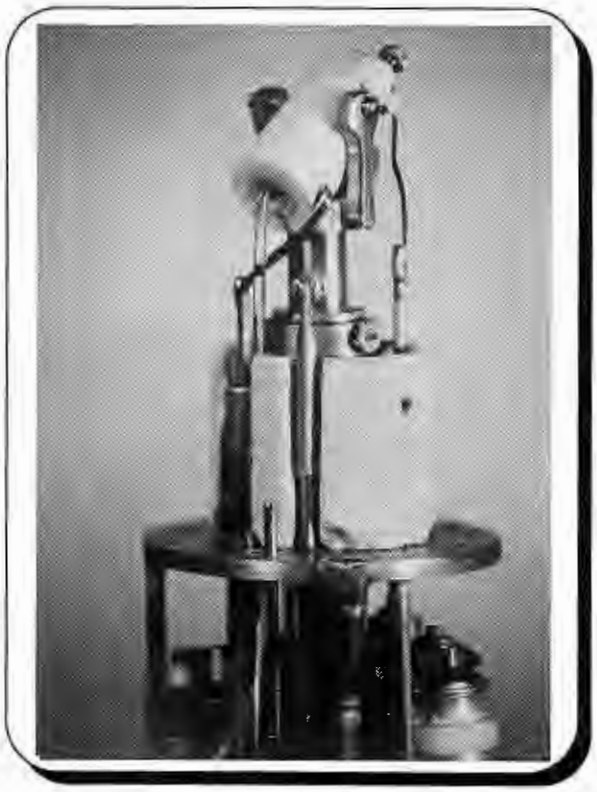

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PS/BMNC/92/3

Dr. B.L. Shapiro,
966 Elsinore Court,
PALO ALTO, CA 94303,
USA.

15 January, 1992
(received 1/31/92)

Dear Dr. Shapiro,

J-RESOLVED SPECTRA OF BIOFLUIDS

In the situation as usually found in high resolution NMR, the signal-noise ratio increases with the field strength and the dispersion also increases making the information content in the spectrum easier to interpret.

This is fine when the noise really is electronic noise, but in the case of biofluid spectra, the "noise" comes from many overlapping resonances of low intensity, "chemical noise". In this situation, increasing the field strength increases the spectral complexity. At low field strengths much of the information is hidden as broad envelopes; at intermediate fields (say 400 MHz for ^{1}H) some resonances are well separated so the information is obvious (patent) but some is still overlapped or hidden (latent). At the highest field strengths (600 MHz) some of this latent information becomes patent.

We have been exploring how to get at the latent information and have been running a series of 2D spectra at 600 MHz using the instrument at the University of Edinburgh (with a great deal of help from Ian Sadler and his team there). As well as COSY, TOCSY and HMQC which all help, we have been pleasantly surprised by the quality of information in simple ^{1}H 2D-J resolved spectroscopy.

Being a spin-echo technique, there is good suppression of broad resonances so this is a bonus for fluids such as plasma which are high in protein and in complex matrices such as bile. High digital resolution is easy to achieve in a short period of time. Many of the small molecules accessible by ^{1}H NMR of biofluids have first order NMR spectra so the artefacts introduced by second order spin systems are minimised. The figure shows an example of the ^{1}H 2D-JRES spectrum of human cerebrospinal fluid. Although many of the resonances have already been assigned, we have been able to use this method to assign others and to map metabolite variations in adults and babies and in a number of disease states such as infections such as meningitis, multiple sclerosis and other degenerative diseases.

Yours sincerely,

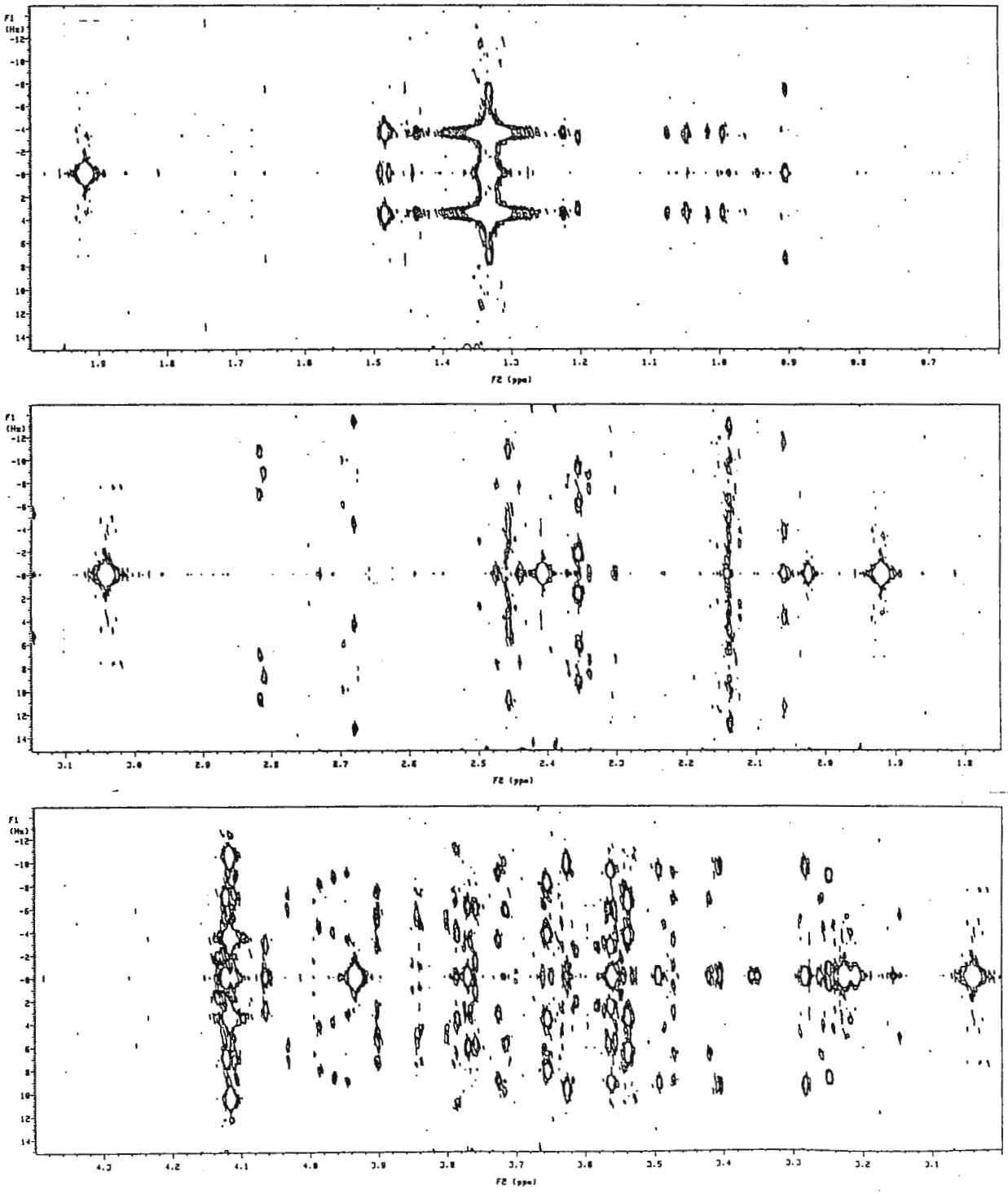
John

J.C. LINDON
Department of Physical Sciences
Wellcome Research Laboratories

Jeremy

J.K. NICHOLSON
Department of Chemistry
Birkbeck College - University of London

2D-J-resolved 600 MHz ^{1}H NMR spectrum of
human cerebrospinal fluid



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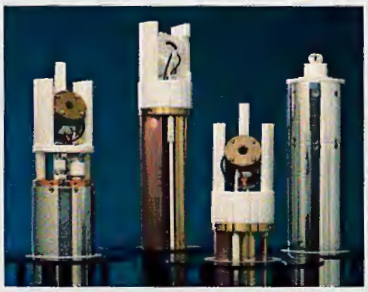

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February 7, 1992
(received 2/14/92)

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

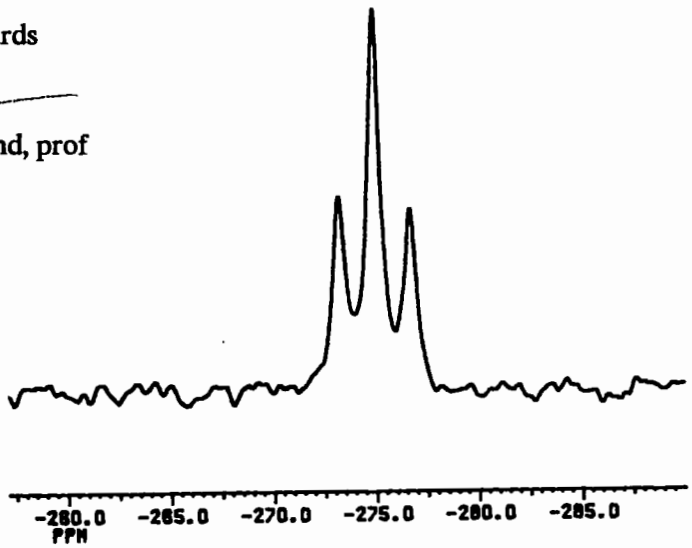
Dear Barry,

Direct NMR Spectroscopic Evidence for Solvated Triorganostannyl Cations

We have for a long time been interested in the structure of solvated organosubstituted group 4 element ions. Species like triorganostannyl salts are generally considered either as having a tetrahedral arrangement or as a trigonal bipyramidal structure where in the latter case the solvent molecule occupies the axial position. The preferred structure is to a large extent depending on the donicity of the solvent. Doubly solvated species have been suggested occasionly, but rejected due to insufficient experimental evidence. To our surprise we could reach slow exchange conditions by polar solvent titration of these species in inert solvents. At low temperature using HMPA-d_{18}, we could to our surprise also resolve the Sn - ^{31}P coupling, and a representative ^{119}Sn spectrum is shown below for triphenylstannyl perchlorate ($^{1}J_{SnP}$= 163 Hz). The observed triplet is thus consistent with a trigonal bipyramidal structure where HMPA occupies both axial positions. For stannyl chlorides or bromides, the induced Sn shifts and SnC couplings suggests a similar geometrical arrangement but the Sn signal is deshielded by approximately 25 ppm relative the signal of the doubly solvated compound and the doublet pattern ($^{1}J_{SnP}$ = 140 Hz) suggests that the preferred arrangement is a structure, where only one HMPA molecule is attached to the axial position.

Best regards

Ulf Edlund, prof



$Ph_3Sn^+ \cdot 2HMPA\ ClO_4^-$

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NORTHWESTERN UNIVERSITY

Joseph B. Lambert
Professor of Chemistry

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Facsimile (708) 491-7713

January 30, 1992
(received 2/6/92)

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

Dear Barry:

The characteristic carbon-13 chemical shift of the central carbon of carbocations (R_3C^+) generally lies in the range of δ 180-335, depending on substitution. We have recently prepared stannyl cations (R_3Sn^+) and found that their tin-119 shifts have a similar range. Tetravalent tin exhibits a large range but generally is found in δ -60 to +200. Pentavalent tin is invariably upfield of analogously substituted tetravalent tin, with a typical range of δ -90 to +30. The divalent species recently observed by Sakurai, Grützmacher, and others is in the range δ 700 to 2400. There have been few observations of trivalent tin. Birchall observed Me_3Sn^+ FSO_3^- below -30°C in highly acidic media at δ 322, but the species decomposed above this temperature.

We have now developed new methods for the preparation of trivalent tin, which enable us to study its chemical shift under ambient conditions. We prepare R_3Sn^+ by hydride removal from R_3SnH or by chloride removal from R_3SnCl. We observe stable species whose tin-119 chemical shift is solvent and anion dependent. We have thus far made observations for R = Me, Bu, and Ph. As the perchlorate and for R = Bu, the resonance is δ 245 in CD_2Cl_2, 231 in C_6D_6, and 150 in sulfolane, the most nucleophilic solvent. For the less nucleophilic and hence less interacting triarylborate anion, δ 360 was observed. We do not know if 360 represents the lower field extreme of these species. The observations at higher field for the perchlorates and for the more nucleophilic solvents indicate a range of interactions. For example, the perchlorate in sulfolane probably has some pentacoordination character even though the chemical shift is still some 200 ppm away from the pentacoordinated range.

Joseph B. Lambert

Barbara Kuhlmann

Title: Tin-119 Chemical Shifts for Trivalent Tin
JBL:cs

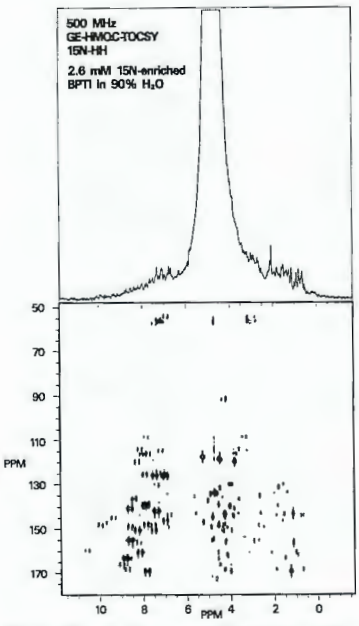
NMR UPDATE

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° ^{1}H pulse in the center of the evolution period serves to eliminate the ^{1}H 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:

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

and p^1H and p^{15}N are the coherence orders for the ^{1}H 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*):

$$\mathrm{H}(+1)\rightarrow \mathrm{H}(+1)\mathrm{N}(0)\rightarrow \mathrm{H}(+1)\mathrm{N}(+1)\rightarrow \mathrm{H}(-1)\mathrm{N}(+1)$$
$$\rightarrow \mathrm{H}(-1)\mathrm{N}(0)$$

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:

$$\mathrm{H}(+1)\rightarrow \mathrm{H}(+1)\rightarrow \mathrm{H}(+1)\rightarrow \mathrm{H}(-1)\rightarrow \mathrm{H}(-1)$$

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).

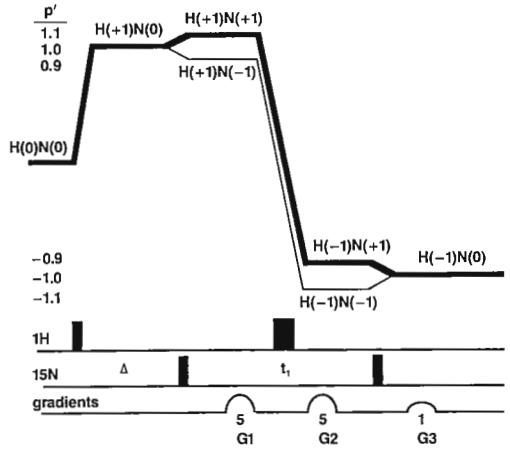


Fig. 1

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

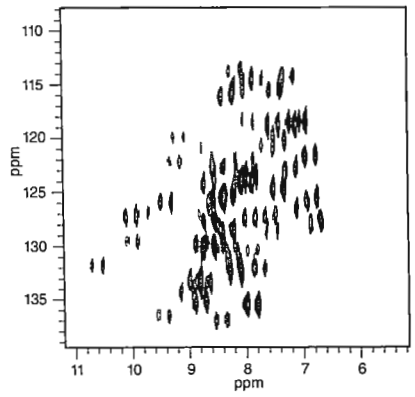


Fig. 2

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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Miami Valley Laboratories
P. O. Box 398707, Cincinnati, Ohio 45239-8707

(received 2/18/92)

BANDERSNATCH: A Strategy-independent Computer Program for Assigning Protein NMR Data

Dear Barry,

We are working on a computer program, called BANDERSNATCH, for reducing the time required to assign protein NMR data. With the ongoing development of new experimental methods, a variety of strategies are now available for carrying out the assignments. The aim of developing BANDERSNATCH is to create a useful tool for assisting any assignment strategy, involving spectra of any experimental design or number of dimensions.

All assignment strategies require systematic searches for patterns of peaks in collections of multidimensional NMR data. Strategies differ to the extent that they require identification of different patterns. To be useful for all assignment strategies, an assignment program must have the ability to search any spectrum or set of spectra for any desired pattern of peaks. BANDERSNATCH achieves this generality by implementing a simple language for specifying peak patterns, and by having the ability to output successful pattern recognition events in an operator-defined format.

A peak pattern may be defined as a set of peaks in which each member shares one or more coordinates with at least one other member of the set. For example, the set of peaks which corresponds to amide, alpha, and the two beta protons of an amino acid residue in a conventional cosy spectrum is {(amide, alpha); (alpha, beta-1); (alpha, beta-2)}. In the program, peak patterns are specified in short "script" files. These scripts specify the files the peaks must come from, and the coordinates the members of the set must have in common.

The following script would instruct the program to pick amide, alpha, and beta shifts for each spin system rooted in a list of fingerprint (amide, alpha) cross peaks. The part of the script giving the program access to the fingerprint (fgrprt) file and to two copies of the cosy file (cosy_1 and cosy_2) is omitted. The symbol "*" tells the program to match any chemical shift, and symbols such as "fgrprt[2]" tell the program to match the second coordinate of the fingerprint peak found on a previous line.

```
fgrprt (*, *)
cosy_1(fgrprt[2], *)
cosy_2(fgrprt[2], *)
(output) fgrprt[1], fgrprt[2], cosy_1[2], cosy_2[2]
```

With this script, the program would proceed as follows: For each fingerprint peak it matched (it would match them all), it would look in the cosy_1 spectrum for an alpha-beta cross peak. After finding one, it would look in the cosy_2 spectrum for another alpha-beta cross peak. The final line in the script instructs the program to output the amide, alpha, and both beta chemical shifts to the file "output". After writing this line, the program would return to recursively checking the spectra for more occurrences of the specified pattern. Scripts for any desired pattern may be similarly defined.

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We are testing this approach using artificial spectra calculated from published chemical shifts of a small protein (BPTI). Our experience so far is that the pattern searching capability works rapidly and thoroughly. There is, however, a price to pay for the generality offered by this approach. Often, the program finds "trivial" occurrences of patterns that must be removed from the output files. A routine has been added to BANDERSNATCH that specializes in finding and removing these occurrences. We have also learned that logical operators (eg., ((pattern-A or pattern-B) and pattern-C) ...) would improve greatly the performance of the program. We expect to have a fully working version with these features ready within the next few months.

Regards,

Charlie Eads

Charlie Eads

P. S. Bob Honkonen will be leaving our lab shortly. Please address future ultimata, reminders, and TAMU issues to me at the above address.

Agricultural Products

(received 2/15/92)

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

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

Subject: Carbon Chemical Shift Assignments of D-Fructose Oxime

Dear Barry:

The carbon chemical shift assignments for the E and Z isomers of D-fructose oxime (I, II) are listed below. Carbon chemical shifts have been assigned by the use of (2-^{13}C) fructose oxime, 2D ^{13}C-^{1}H correlation spectroscopy and off-resonance decoupling. The C-1 carbons were assigned by inspection of the (2-^{13}C) fructose oxime spectrum (^{1}JC1C2E = 45.1 Hz < ^{1}JC1-C2Z = 52.6 Hz)[1,2]. These values for the JC1,C2 coupling constants are similar to those previously found in the aldopentose oximes where the E isomer is smaller in magnitude by approximately 8 Hz. Assignments for C-1 were verified by chemical shift. As in the aldopentose oximes, the carbon γ-gauche to the N-hydroxyl will be shielded compared to its isomer. In fructose oxime, C-1 in the E-form is γ-gauche to the N-hydroxyl and is shielded by 5.1 ppm compared to C-1 in the Z-form. The chemical shift assignments of C-2 (the imino carbon) were determined by off-resonance decoupling. In the proton coupled carbon spectrum, C-2 of E and Z fructose oxime appear as quartets. The hydroxymethyl protons at C-1 split the C-2 carbons into triplets and the C-2s are further split into quartets by the protons at H-3. By selectively irradiating the H-3Z proton, and observing the proton-coupled carbon spectrum, the downfield quartet collapsed to a triplet. The H-3Z proton was assigned by chemical shift and coupling constant. The C-3 carbon resonances were assigned by 2D C-H correlation spectroscopy. The C-3 assignments could be verified by chemical shift. As above, the carbon γ-gauche to the N-hydroxyl will be shielded. There is a 3.2 ppm difference between C-3Z and C-3E with the former being upfield. The carbon chemical shift assignments for C-4 and C-5 for both isomers were assigned by 2D C-H correlation spectroscopy.

CHEMICAL SHIFT OF D-FRUCTOSE OXIME

	C1	C2	C3	C4	C5	C6
E	56.4	162.9	71.2	73.1	72.5	64.4*
Z	61.5	161.7	67.9	72.8	72.4	64.5*

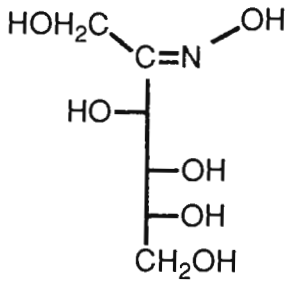
The assignments for C-6 are ambiguous and need further investigation.

1) Krivdin, L.B. and Kalabin, G.A., Tetrahedron Letts, 25, 4817, 1984.
2) Snyder, J.R., Carboh. Res., 198, 1, 1990.

Please change the subscription name from C.K. Tseng to Joseph R. Snyder. Thank you.

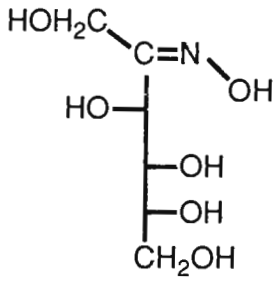
Joseph R. Snyder

JRS:djg/tamu.jrs/1-14-92



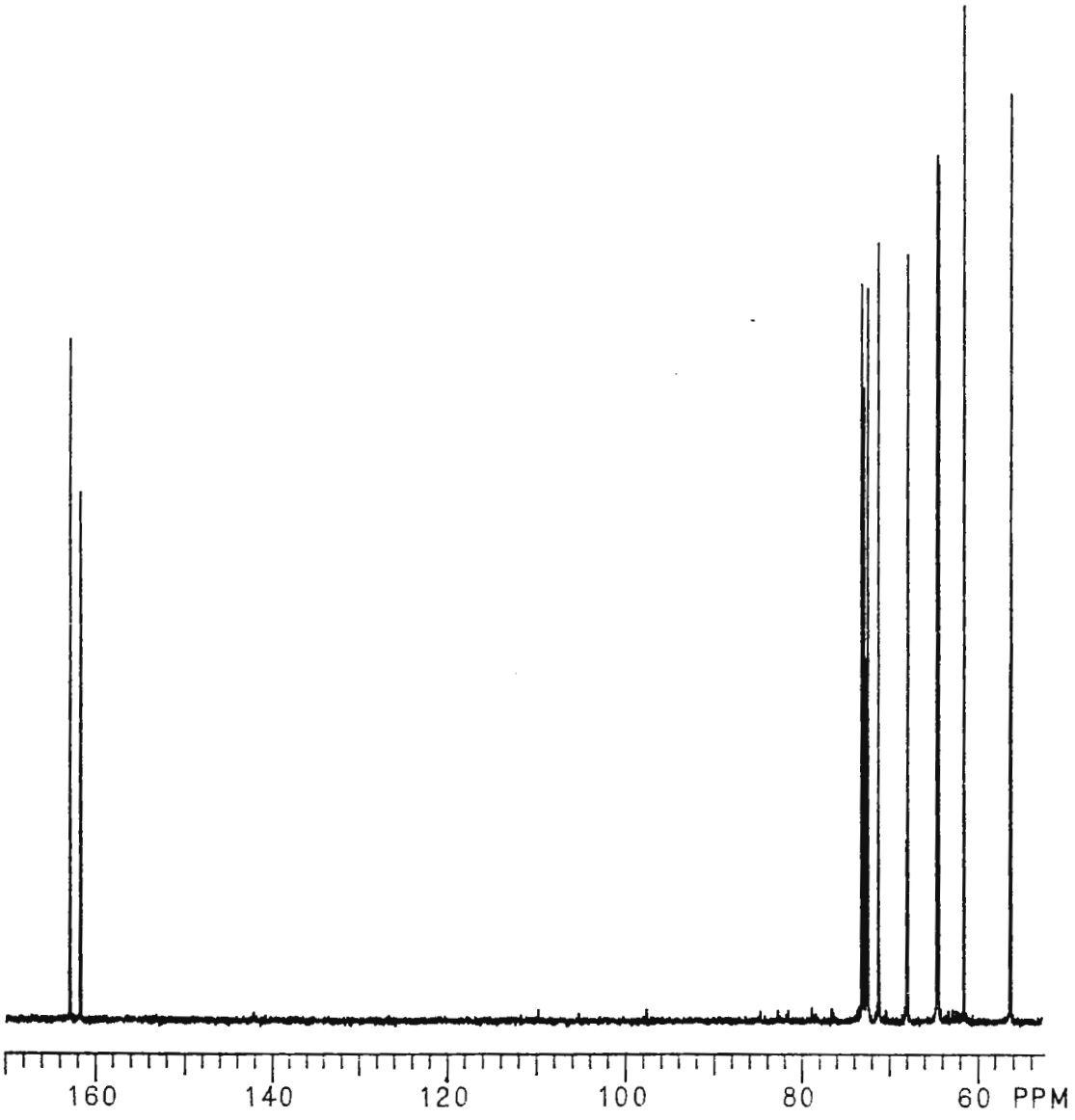
***E*- D-FRUCTOSE OXIME**

I



***Z*- D-FRUCTOSE OXIME**

II



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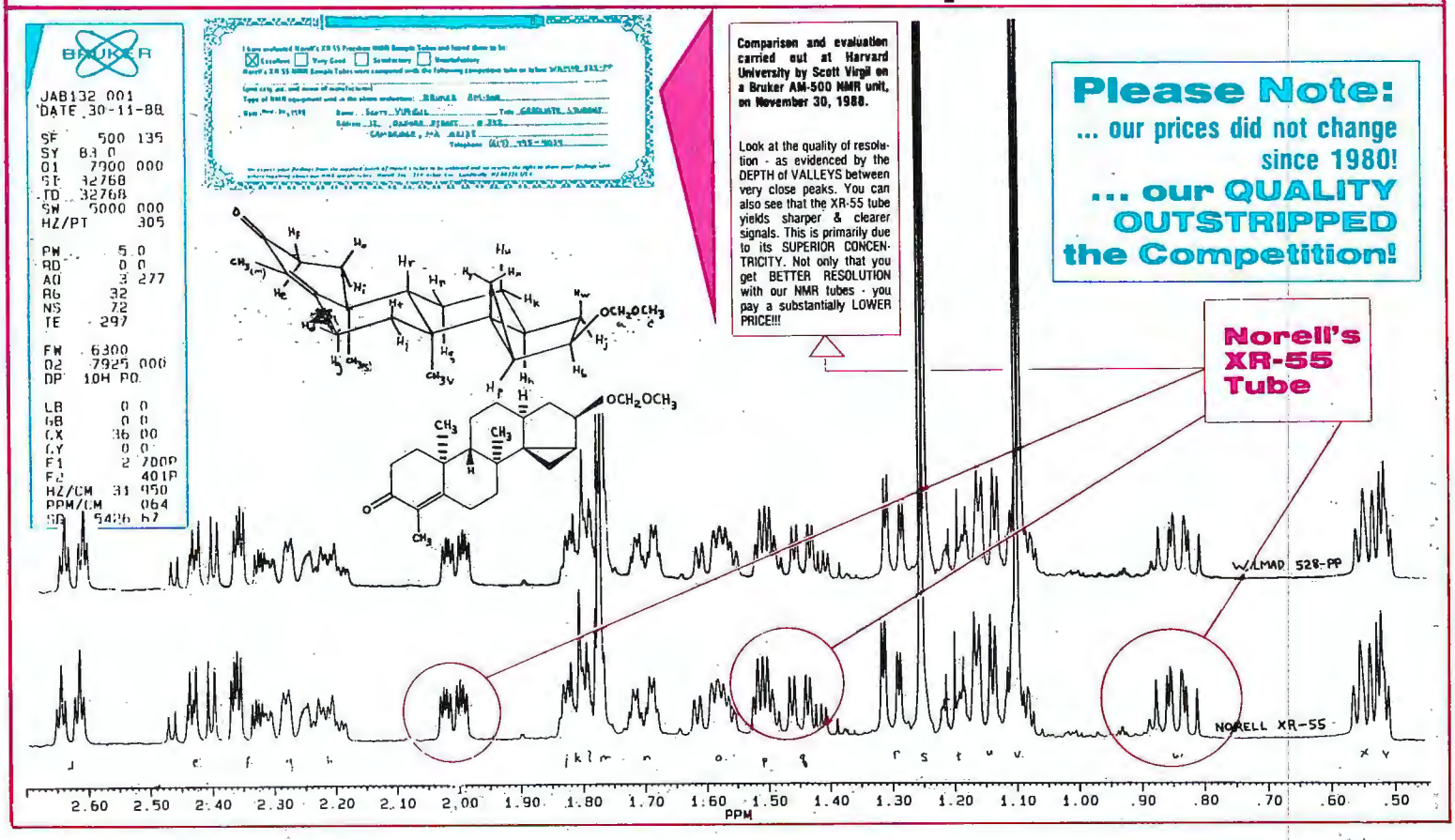

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Area Code 409
772-2811

24 January 1992
(received 1/31/92)

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

RE: ^{17}O NMR SPECTRA OF STEROIDS

Dear Barry:

Current increased interest in ^{17}O NMR spectroscopy has yet to be extended to natural products such as steroids and alkaloids and to drugs and drug metabolites.[1] Despite remarks of others that studies of (^{17}O)-steroids be ill-advised we undertook to examine ^{17}O NMR of steroids, one of our fancies. No ^{17}O signals are observed at natural abundance (0.037%), but we are pleased to note that ^{17}O signals were readily recorded for solutions of appropriately labeled cholesterol and congeners.

The considerable bulk of the sterol molecule and its assumed effect on the ^{17}O correlation time restricted our interest for some time, but the opportunity came to label cholesterol by hydrolysis of *i*-cholesterol (3α,5α-cyclocholestan-6ß-ol) with (^{17}O)-water (45% ^{17}O). Spectra of (^{17}O)-cholesterol in CD_3CN at 75° gave a concentration independent (over 3.8-35 mM) signal at δ_0 38.8 (vs. external water), $W_{1/2}$ 700 Hz (S/N 32:1), broadening to 1350 Hz at 27°. More dilute solutions also had narrower band half-widths (567 Hz for 3.8 mM). Other (^{17}O)-steroids derived from (^{17}O)-cholesterol likewise gave data (CD_3CN, 75°): cholesterol 3ß-formate δ_0 201.0, $W_{1/2}$ 525 Hz; cholesterol 3ß-acetate δ_0 198.4, $W_{1/2}$ 617 Hz; cholesterol 3ß-propionate δ_0 193.0, $W_{1/2}$ 850 Hz; 5α-cholestan-3ß-ol δ_0 38.9, $W_{1/2}$ 650 Hz; 5α-cholestane-3ß,5,6ß-triol δ_0 34.1, $W_{1/2}$ 527 Hz. Error is estimated at ±2 ppm.

In the more viscous $CDCl_3$ at 50° similar signals were obtained for (^{17}O)-cholesterol [δ_0 39.7, $W_{1/2}$ 960 Hz], cholesterol 3ß-acetate [δ_0 194.8, $W_{1/2}$ 1140 Hz], and cholesterol 3ß-propionate [δ_0 189.3, $W_{1/2}$ 1400 Hz]. (^{17}O)-Cholesterol in CCl_4 at 60° gave a signal δ_0 35.7, $W_{1/2}$ 900 Hz.

These data are entirely consistent with expectations based on ^{17}O data recorded by others for smaller organic compounds. That the band widths for cholesterol and congeners compare with $W_{1/2}$ 450-1000 Hz for isobutanol, *sec*-butanol, and *tert.*-butanol[2] evinces that correlation time for steroids may not be any greater limitation for applications than is the case for such simpler compounds.

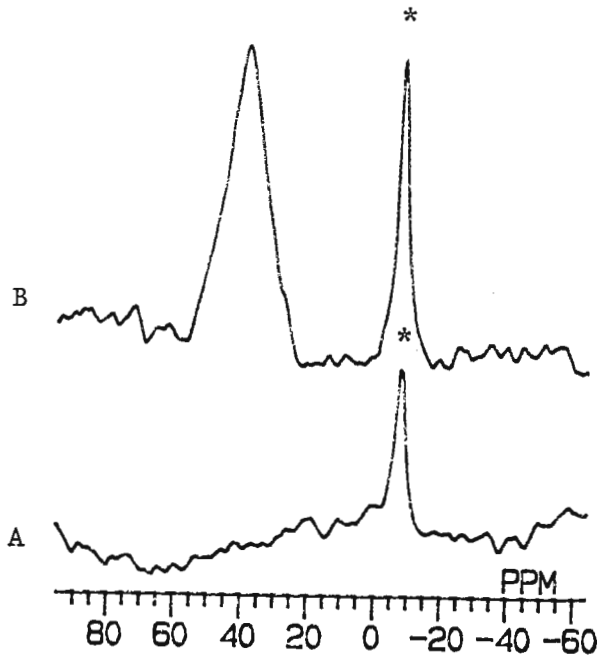
The insignificant δ_0 difference for cholesterol and 5α-cholestan-3ß-ol suggests the Δ^5-homoallylic double bond not influence the 3ß-alcohol chemical shift, but the shielded signal for the 3ß,5α,6ß-triol ($\Delta\delta_0$ -4.7 ppm) may reflect a true (though minor) shielding effect of the 5α- and/or 6ß-hydroxyls on the 3ß-hydroxyl signal. Likewise, for the 3ß-esters, increased carbon substitution appears to cause minor shielding effects.

These results suggest that ^{17}O NMR spectroscopy of the more complex natural products such as steroids not now receiving attention may find applications of interest.

Yours truly,

Leland L. Smith Josef E. Herz Edward L. Ezell

1. D. W. Boykin, ^{17}O NMR Spectroscopy in Organic Chemistry, CRC Press Inc., Boca Raton,FL, 1991.
2. H. A. Crist, P. Diehl, HR Schneider, and H. Dahn, Helv. Chim. Acta, **44**, 865-880 (1961).



^{17}O NMR SPECTRA OF CHOLESTEROL

(CD_3CN, 75°, vs. external H_2O)

A. At natural abundance

B. ^{17}O-enriched

* Internal Galveston moisture

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(received 2/1/92)

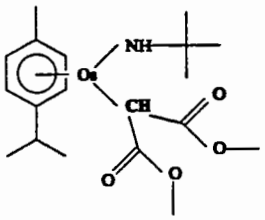
COLLEGE OF CHEMISTRY BERKELEY, CALIFORNIA 94720

Measurement of ^{187}Os - ^{13}C couplings using ^{1}H-^{13}C HMQC experiments.

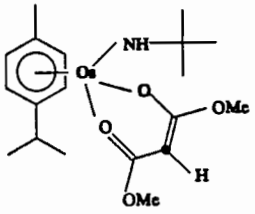
Dear Prof. Shapiro,

A question arose in our laboratory recently which involved determining whether the malonate ligand of complex 1 was carbon bound (**1a**) or oxygen bound (**1b**) to the osmium center. Arene osmium compounds usually maintain a formal 18 electron configuration, so the bis-oxygen bound structure may have been expected on these grounds.

1a - C bound

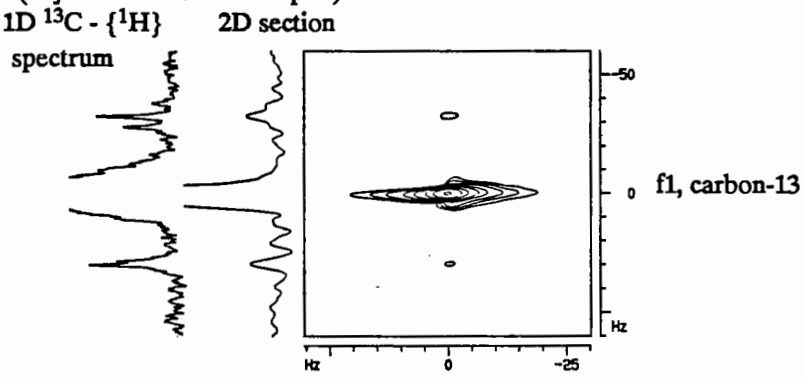


1b - O,O bound



One obvious way to go about this was to measure the ^{187}Os - ^{13}C coupling constant of the highlighted carbon, a sizeable coupling being indicative of a C - bound ligand. The ^{13}C resonance of the relevant carbon (leftmost trace in the figure below) does indeed show satellites due to a large coupling with the 1.64 % of ^{187}Os present in the natural abundance sample [$^{1}J(^{187}Os - ^{13}C)$ = 63 Hz]. However, we thought it would be both interesting and useful to get the same information from the ^{187}Os satellites present in a proton detected ^{1}H - ^{13}C HMQC experiment, for a number of reasons; first, the use of broadband ^{13}C decoupling would remove any ^{13}C - ^{13}C satellites which are present and overlapping with the ^{187}Os satellites in the normal ^{13}C - $\{^{1}H\}$ spectrum; second, we wished to compare sensitivity.

The results of our initial attempt are shown in the figure, along with a more informative carbon cross section through the satellites (adjacent to the contour plot):



The cross section through the satellites shows that only the $^{1}J(^{187}Os - ^{13}C)$ of 63 Hz is retained but also that the signal to noise ratio in the 2D experiment is only marginal. The problem in this case is that the $^{2}J(^{187}Os - ^{1}H)$ coupling constant is small and so the satellites lie upon the "t_1 noise" line, which contains artefacts from residual signal from protons bound to ^{12}C and "real" t_1 noise from protons bound to ^{13}C but without an ^{187}Os spin (only 0.018 % of the protons give rise to the satellite signals of interest).

In this case the ^{12}C bound protons were suppressed using the usual BIRD sequence, so careful optimization of the inversion-recovery delay should help. Repeating the experiment with presaturation of ^{12}C bound proton resonance did not improve matters. We are working on a selective excitation of just the ^{13}C satellites to eliminate this problem.

Yours Sincerely,

Graham Ball Rick Michelman

Graham Ball Rick Michelman

402-46

Washington
WASHINGTON·UNIVERSITY·IN·ST·LOUIS

Department of Chemistry

January 30, 1992
(received 2/4/92)

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

Dear Barry:

We now have titles for the upcoming ENI/Emerson Electric Company Symposium to be held at Washington University this May 18*th*, 1992. We would appreciate the placement of this complete announcement in the *Texas A&M University NMR Newsletter* as space limitations allow.

The Sixth Washington University-ENI/Emerson Electric Company Symposium on Nuclear Magnetic Resonance will be held Monday, May 18, 1992, in the Department of Chemistry at Washington University in St. Louis, Missouri. The symposium will feature: **Richard Ernst,** Laboratorium für Physikalische Chemie Eidgenössische Technische Hoschschule speaking on *Dynamics in NMR*; **Juli Feigon,** University of California at Los Angeles speaking on *DNA Triplexes and Quadruplexes*; **Robert Griffin,** Massachusetts Institute of Technology speaking on *Rotational Resonance in Dipolar Coupled Spin Systems*; **Harden McConnell,** Stanford University speaking on *Paramagnetic Antibodies* and **Hans Thomann,** Exxon Research and Engineering Company speaking on *Magnetic Resonance Studies of Soliton Charge and Spin Dynamics in Conducting Polymers*. The symposium, sponsored by Emerson Electric Company, is open to all interested in the development and application of new techniques in nuclear magnetic resonance. For additional information, contact symposium coordinator Karen Klein at (314) 935-6405.

Thank you for your cooperation.

Sincerely yours,

Jake

Jacob Schaefer
Professor of Chemistry

JS/kk

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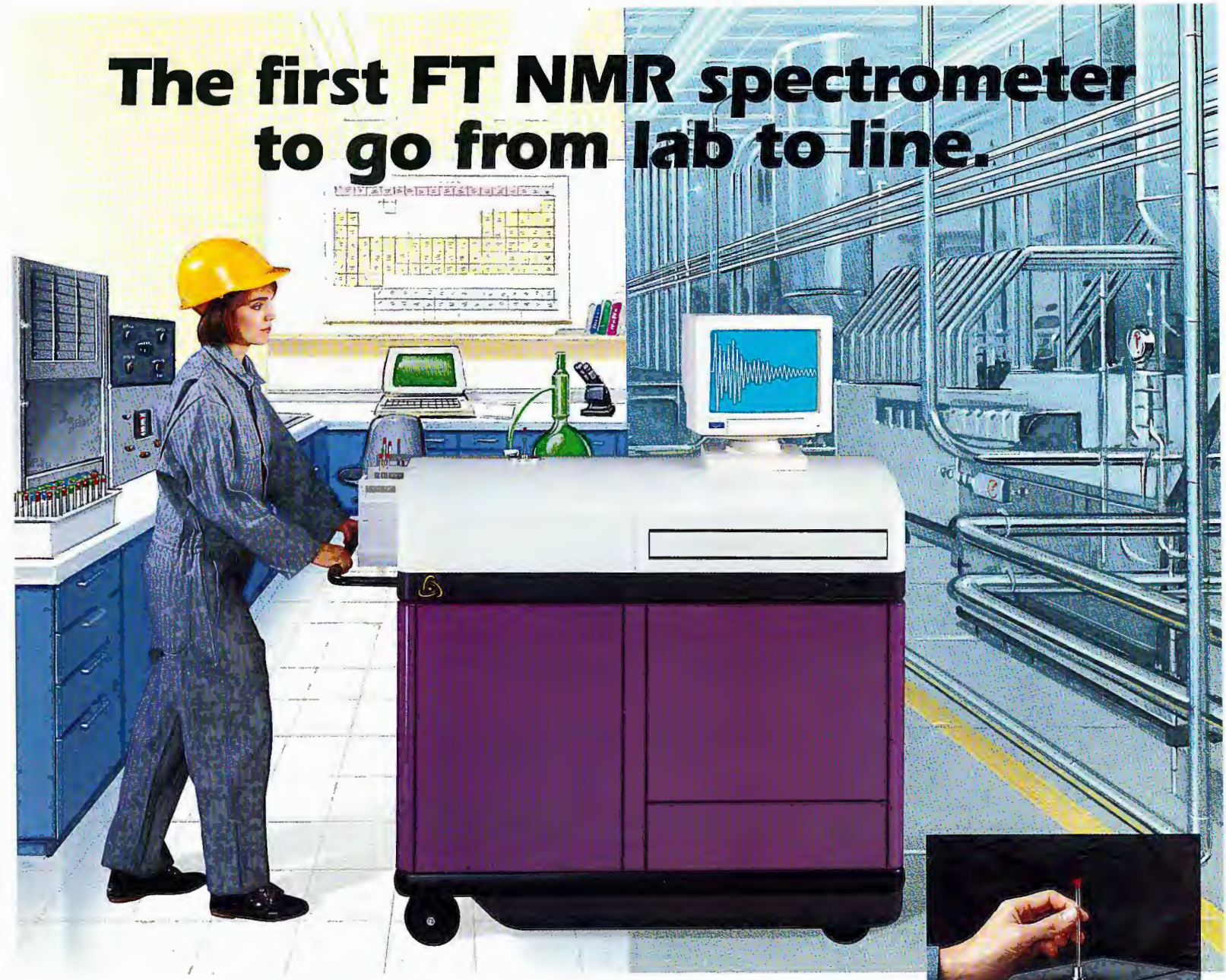

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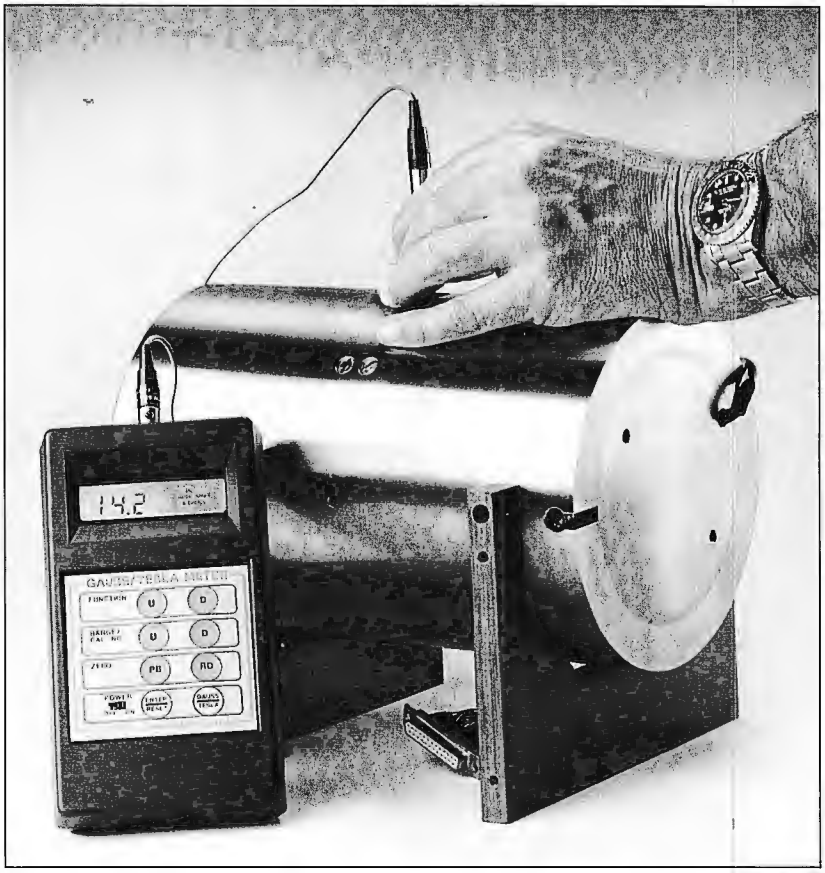

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*U.S. Patent No. 4,998,976

Dr Bernard L. Shapiro
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February 12, 1992
(received 2/14/92)

Dear Barry:

Last Spring we were fortunate to have Ernest Laue visit our laboratory from Cambridge and work with us setting up triple resonance experiments ($^{1}H, ^{15}N, ^{13}C$) on our new AMX600. As usual with new experiments on new hardware we found ourselves reinventing the wheel and playing catch-up with the published literature. Then we devised and implemented two new 4D experiments which have proven invaluable for sequentially assigning the backbone nuclei ($^{1}H_N$, ^{15}N, $^{13}C_\alpha$, $^{1}H_\alpha$, $^{13}C_{\alpha-1}$, $^{1}H_{\alpha-1}$) of larger proteins. The method is currently being published with ubiquitin as an example (1) with additional work in preparation on p21$^{Ha\text{-}ras}$ (166 residues).

The sequential assignment protocol does not require sidechain spin system identification. However in proteins > 15kD overlap does still occur in the 4D data, requiring amino-acid spin system identification to remove the ambiguity. Additionally, the sidechain contacts are required for more accurately defining structures via 4D NOESY ($^{15}N, ^{13}C$) and ($^{13}C, ^{13}C$). We have used the published 3D HCCH-COSY and HCCH-TOCSY schemes (2) to correlate the ($^{13}C_\alpha, ^{1}H_\alpha$) backbone assignments from our 4D sequential assignments with the sidechains. These latter two 3D experiments (particularly the DIPSI-3 spin-lock in the TOCSY) are quite demanding on a 600 because of the large ^{13}C dispersion.

Over the past few months we have improved the quality of our data substantially by implementing the following modifications. The first change was to concatenate the pulses in the first INEPT portion of the sequence (3) to remove a composite ^{13}C (π) pulse which resulted in a S/N improvement. Secondly, we found considerable improvement in performance and flexibility by removing the high power switching of the BSV-10 and using the lower power (linear) amplifier as a buffer to drive a final stage 300W AMT with RF filtration before and after the AMT. Slight losses in the filters are quite acceptable since we have power to burn (literally!-these experiments can put a probe at risk). The 8 power levels available on the linear amplifier allow the flexibility of stronger spin-locks, crisper (non-droopy) hard pulses and more selective π pulses which do not excite COSY transfer to ^{13}C=O. For some annoying reason we have to hard-code the GARP decoupling for it to remain synchronous. Although in H_2O solution we maintain our receiver gain at 128 we see 120 Hz line voltage artefacts. The current experiments in D2O allow higher gain (1024) which reduces the 120 Hz pickup in the signal between the receiver and the audio-filter/ADC combination. Lastly, our experience with the use of the Cambridge 2D MEM algorithm in the 4D data analysis (1) allows us to truly minimize the number of t_1 and t_2 increments in the 3D experiments to keep the sensitivity maximized.

Please credit this contribution to 'Tricia Watson's account. In the interest of a one page letter I have not included any figures. We hope to have it all together on a poster for the ENC.

Until then best wishes,

Peter

Peter Domaille

(1) E. D. Laue, W. Boucher, S. Campbell-Burk, P.J. Domaille, *J. Am. Chem. Soc.*, **114**, 0000, (1992). (2) A. Bax, G.M. Clore, P.C. Driscoll, A.M. Gronenborn, M.Ikura, L.E. Kay, *J. Magn. Reson.*, **87**, 620 (1990); A. Bax, G.M. Clore, A.M. Gronenborn, *J. Magn. Reson.* **88**, 425 (1990); (3) L.E. Kay, M. Ikura, A. Bax, *J. Magn. Reson.* **91**, 84 (1991).

BASIC RESEARCH PROGRAM

Operated for the National Cancer Institute by Advanced BioScience Laboratories, Inc.

February 4, 1992
(received 2/8/92)

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

Macromolecular NMR Section at NCI-FCRDC & Positions Available

Dear Barry;

I would like to inform my colleagues of my new address and indicate the availability of a number of new positions.

As of the first of this year, I have taken on a new position to establish the Macromolecular NMR Section within the Macromolecular Structure Laboratory at NCI-FCRDC. This group will focus on protein and protein-complex structures to complement other Sections within the Lab, which include X-ray Crystallography and Molecular Aspects of Drug Design. Instrumentation is in the procurement phase and will include state-of-the-art triple resonance capabilities at 600 MHz. Computational facilities will include Silicon Graphics workstations and network access to the Biomedical Super-Computing Center at NCI-FCRDC, which includes VAX 6000 series, Convex 220, and Cray Y/MP systems.

There are several positions available in this group:

Post-doctoral and *Scientist Levels* (total of 4 positions): (i) NMR experience/interest in isotope edited 2D/3D/4D NMR spectroscopy and structure calculations via distance geometry and restrained molecular dynamics strategies; this includes both NMR methodology and application to protein systems. (ii) Biochemist/Molecular biologist with experience and interest in over-expression and production of stable isotope-enriched proteins and nucleic acids, plus interest in structural studies.

Electronics specialist: Experience and interest in NMR instrumentation and development of new devices for maintenance and enhancement of instruments. Interest and/or experience in pulsed field gradient technology and waveform amplitude/phase modulation is desired. Interaction with the Macromolecular NMR Section staff and another NMR group at NCI-FCRDC.

Scientific Programmer/Systems Administrator: Responsibility for setup and administration of multiple workstation network (including spectrometers) and interconnection with the Biomedical Super-Computing Center. Knowledge of UNIX, C, and Fortran with interest in scientific applications (sophisticated data processing [e.g. FELIX, MEM, LP, distance geometry, etc.] and/or molecular modeling) required.

Any interested parties should contact me at the address below.

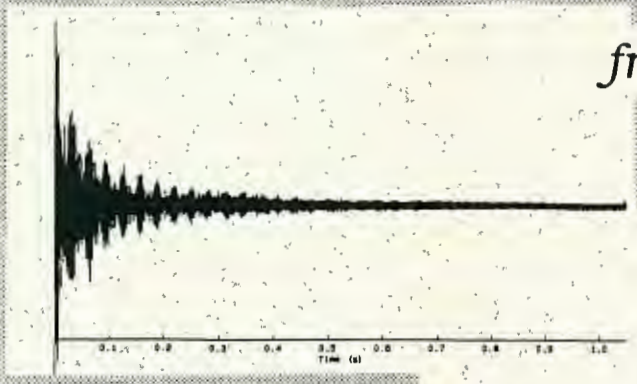
Sincerely yours;

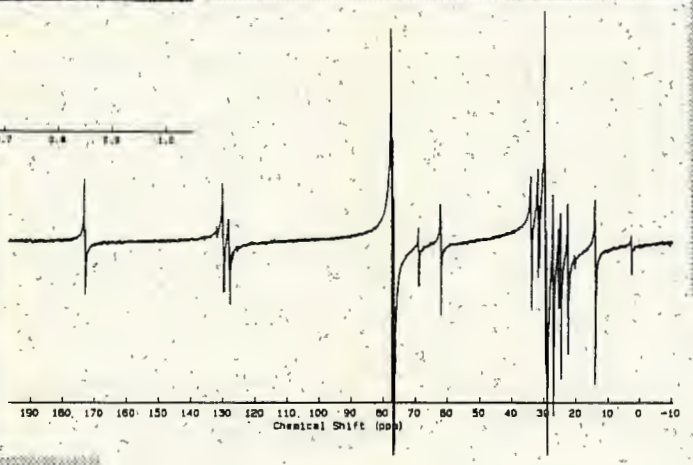
R. Andrew Byrd
Macromolecular NMR Section/MSL/ABL
NCI-FCRDC
P.O. Box B, Bldg. 538
Frederick, MD 21702-1201

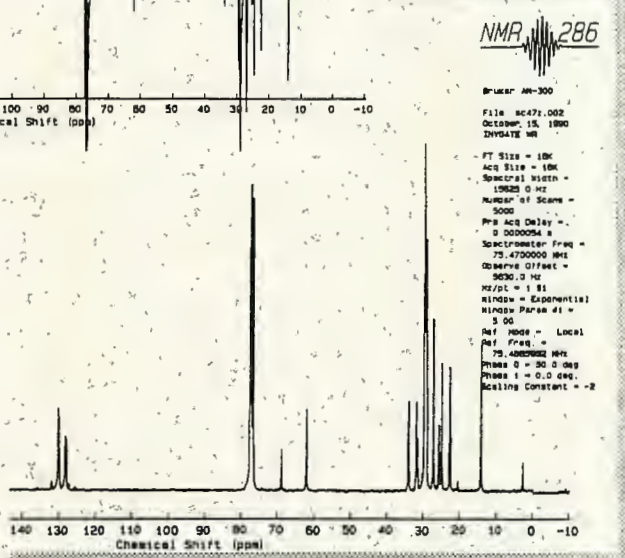
Complete NMR Processing with

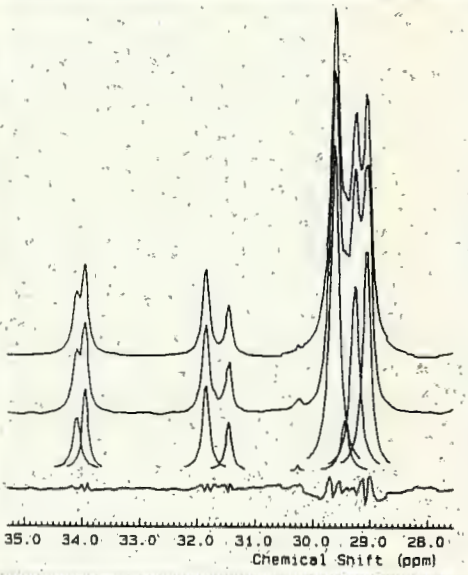
NMR-286

from FID









to final report

Fitted Peaks from file: sc47z.002

Peak	Hz	ppm	Intensity	Area	Width	Shape	Norm Area
1	2574.87	34.118	0.1555	2.7897	11.422	Loren	0.0357
;+/-	1.5E-0001	2.0E-0003	1.1%	3.0%	2.0%		
2	2563.56	33.969	0.2448	3.3528	8.719	Loren	0.0429
;+/-	7.6E-0002	1.0E-0003	7.8E-0001%	2.2%	1.4%		
3	2405.16	31.870	0.2543	4.1727	10.444	Loren	0.0534
;+/-	6.3E-0002	8.3E-0004	6.0E-0001%	1.5%	8.8E-0001%		
4	2375.48	31.476	0.1441	1.9394	8.569	Loren	0.0248
;+/-	1.0E-0001	1.3E-0003	1.2%	2.9%	1.7%		
5	2285.05	30.278	1.811E-0002	8.654E-0002	3.043	Loren	0.0011
;+/-	5.0E-0001	6.7E-0003	22.6%	53.4%	30.8%		
6	2236.44	29.634	0.9657	20.7202	13.659	Loren	0.2651
;+/-	3.0E-0002	4.0E-0004	1.9E-0001%	5.1E-0001%	3.2E-0001%		
7	2222.31	29.447	0.1518	2.8937	12.132	Loren	0.0370
;+/-	1.9E-0001	2.5E-0003	1.7%	5.7%	3.9%		
8	2209.15	29.272	0.5528	11.6649	13.434	Loren	0.1492
;+/-	5.6E-0002	7.5E-0004	4.2E-0001%	1.4%	1.0%		
9	2193.77	29.069	0.6611	12.9798	12.500	Loren	0.1660
;+/-	3.7E-0002	4.9E-0004	2.7E-0001%	7.4E-0001%	4.7E-0001%		
10	2048.89	27.149	0.5137	8.2342	10.204	Loren	0.1053
;+/-	3.1E-0002	4.1E-0004	3.0E-0001%	7.2E-0001%	4.2E-0001%		
11	1930.16	25.576	0.1894	3.0652	10.302	Loren	0.0392
;+/-	8.3E-0002	1.1E-0003	8.1E-0001%	2.0%	1.2%		
12	1872.60	24.813	0.3811	6.2706	10.475	Loren	0.0802
;+/-	4.2E-0002	5.5E-0004	4.0E-0001%	9.7E-0001%	5.7E-0001%		

;Chi Square = 10204.22
;Total peak area = 78.1698
;469 Data points
;36 Independent Parameters
;36 Variables

Quantitative NMR with **NMR-286**

NMR is inherently quantitative but our software usually leaves us guessing at the peak areas. NMR-286 uses an interactive Marquardt driven peak fitting routine to help you get the most out of your spectra. NMR-286 is a ***must*** for researchers doing serious quantification of their spectra. Look at these features:

- Parameters can be frozen, freed or linked at will to incorporate prior knowledge of the spectrum.
- The output contains the best-fit parameters as well as their standard deviations and the full variance-covariance matrix.
- You can compare the calculated and observed spectra and see the residuals in Dual Display.
- Clusters of up to 30 overlapping peaks can be pulled apart, even if the component peaks appear only as shoulders.

NMR-286 is not just a line fitting program.

It is a *powerful* and *complete* PC based NMR processing package for one dimensional NMR. Here are some of its features:

- Lightning Fast FTs — the fastest that you will find on a PC. Sizes up to 32k supported.
- Window Functions. Select from eight different window functions.
- Plotting. Plotting is extremely flexible. Send the HPGL output to a plotter, a file or a laser printer.
- Automated Processing. Almost anything that you can do from the keyboard, you can write a program to do. A powerful editor is a part of NMR-286.
- Manual. A comprehensive reference manual comes with NMR-286. It explains not only the commands used but also the ideas behind them.
- Public File Formats. NMR-286 uses file formats which are well described in the manual. You can import and export spectra as ASCII text files.
- **New!** *QUALITY* processing to make your lines Lorentzian even in the presence of bad shimming.
- **And much much more!**

Computer Requirements

A Personal Computer with CPU: 80286/287 or better. OS: MS-DOS 3.0 or greater. Memory: 640k required. Graphics: EGA, VGA or AT&T400.

Spectrometers

NMR-286 is in itself independent of the spectrometer. It requires a translation program to convert the data files to NMR-286 format. Currently we support **Bruker** (DIS, Tomikon, UXNMR), **G.E.** (GN, Omega, Signa), **Varian** (Unity, Gemini) and **Lybrics** format files. Have another type of machine? *Call!*

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NMR-286 Prices

Copies	Price per copy*
1	1500.00
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*All prices are in Canadian dollars. Canadian orders add 7% GST, Ontario orders add 8% PST. Academic institutions are eligible for a 33% discount on software. Purchase orders accepted. Shipping per order: Canada – $15.00, elsewhere $30.00. Foreign orders may be paid in the equivalent of U.S. dollars.

NMR-286 will help you use your valuable magnet time for acquiring data. You can process, examine, measure and plot your spectra when and where you want — in the lab, in your office or at home.

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THE UNIVERSITY OF UTAH

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

Feb. 14, 1992
(received 2/20/92)

An Efficient Large-Sample-Volume Rotor System for MAS Solid State NMR Experiments

Dear Barry:

The NMR spectroscopy laboratory at the University of Utah, has developed an efficient large-sample-volume rotor system for MAS solid state NMR experiments with coal samples.

^{13}C solid state NMR spectroscopy is an important method for obtaining information about coal structure; however, due to a lack of sensitivity of the ^{13}C nucleus, it is not easy to obtain the spectrum in a reasonable length of time using the traditional-size rotor system. This is especially true for the Bloch decay (BD) experiment, which is a method used to obtain quantitative data from ^{13}C spectra. Although the cross polarization (CP) method is used frequently in the solid state NMR experiments, the magnetizatiion of carbons in different environments in the CP experiment can build up at different rates, and this has raised a question regarding the quantitative accuracy of coal spectra. In our past results, we addressed this problem with the use of variable contact times (VCT), and then fit the observed spectral intensities in models in order to obtain the aromatic and aliphatic magnetization. With the large-sample-volume rotor a BD spectrum can be recorded in the same time it takes to do an entire set of CP data. Having an efficient system to do the BD experiment will allow us to compare BD and CP results.

The ^{13}C CP/MAS spectra shown in Fig. 1 indicate that the signal to noise (S/N) ratio from the large-sample-volume rotor is a factor of 4.6 better than that from the standard rotor. This improvement allows us to obtain CP/MAS spectra with the same S/N ratio with a factor of 21 savings in spectrometer time. For the case of a coal sample, the standard size rotor may require a week of spectrometer time to get a BD spectrum with acceptable S/N, whereas the new large-sample-volume rotor requires only one day.

In order to obtain reliable information from these spectra, the rotor must not have any background signal. This issue has been addressed by the use of zirconia as the rotor material. As the spectra in Fig. 2 show, there is no background peak in either the CP/MAS or BD/MAS spectra.

The large rotor system is run with 32 psi bearing gas pressure and 24 psi driving gas pressure, and reaches a spinning rate of 4 KHz. Fig. 3 shows the speed of the system as a function of the driving gas pressure. The low gas pressure feature makes this system easy to operate.

The development of this system increases the capability and efficiency of this NMR laboratory for obtaining solid state NMR data on coals.

Sincerely,

Yi Jin Jiang Mark S. Solum Ronald J. Pugmire David M. Grant

Department of Chemistry
Henry Eyring Building
Salt Lake City, Utah 84112

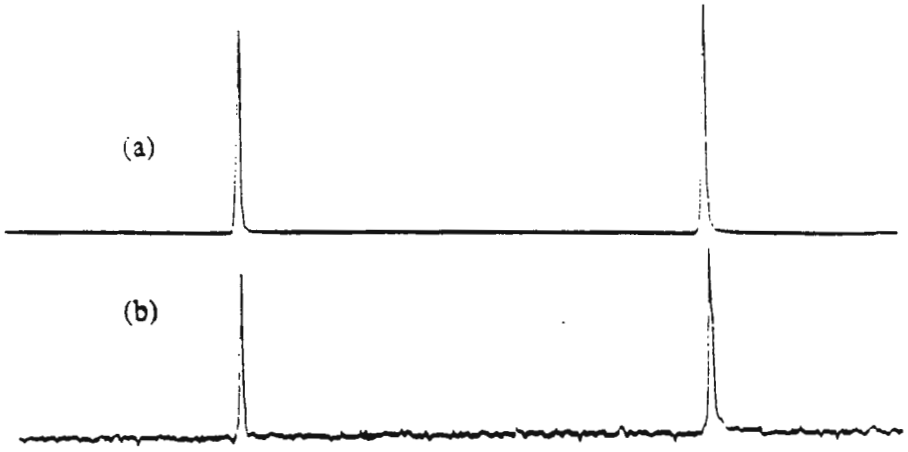


Figure 1: CP/MAS spectra of HMB taken at 25.12MHz: (a) large volume (1.8 cm^3) system, 1.10g HMB, 20 scans, 3ms contact time, 1s delay, no line broadening, S/N ratio 130; (b) small (0.63 cm^3) rotor system, 0.28g HMB, 20 scans, 3ms contact time, 1s delay, no line broadening, S/N ratio 28.

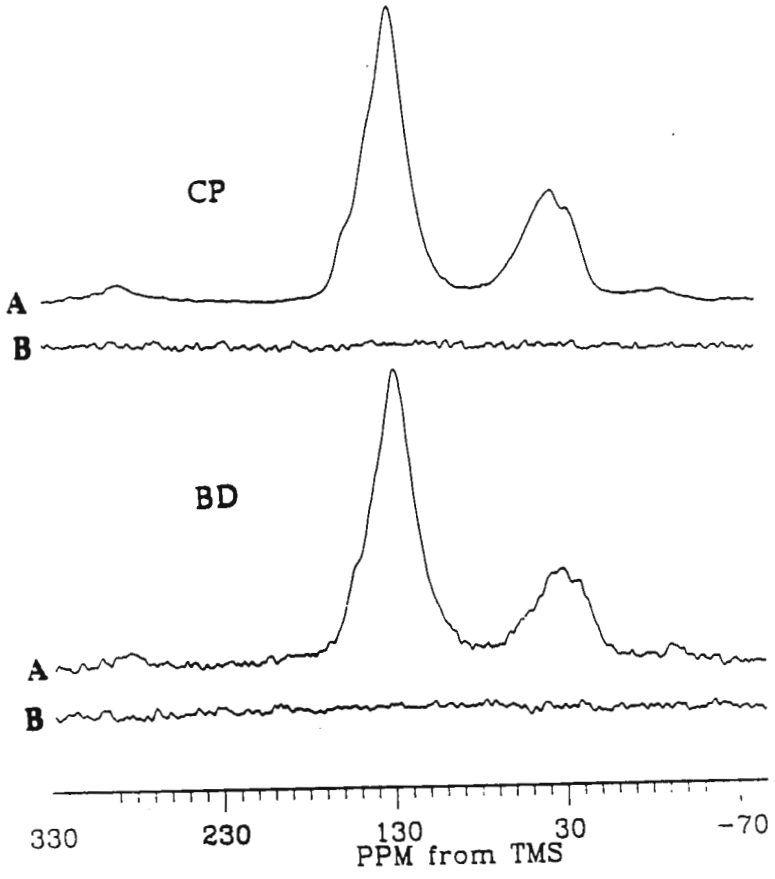


Figure 2: Comparison of the spectral lineshapes obtained for BD and CP experiments on Pittsburgh #8 Argonne Premium Coal. A is the spectrum and B is the background obtained by taking the spectrum with an empty rotor under identical conditions to A.

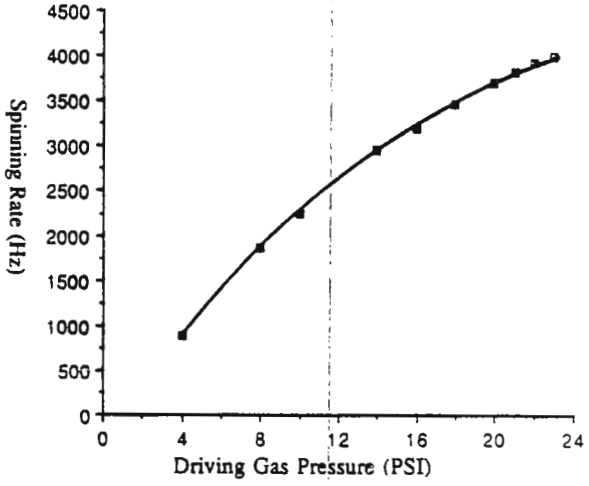


Figure 3: Plot of the spinning speed of the large volume rotor system as a function of the driving pressure used. Bearing pressure was 32 psi.

Gradient Enhanced Spectroscopy 3D

Gradient Enhanced Spectroscopy (GES) allows efficient 3D methods which require only a single acquisition per evolution time (t_1) and which generate patterns which can be used to distinguish among direct proton-carbon correlations, protons attached to an adjacent carbon, protons attached two carbon bonds away and non-identical protons attached to the same carbon. The GES 3D techniques benefit from elimination of phase cycling and avoidance of traditional water suppression and difference methods resulting in shorter experiment times and optimized receiver gain.

The sequence (Fig. 1) is a combination of a gradient enhanced HMQC experiment in which zero-quantum signal generated by ^{13}C-^{1}H coupling is selected via a 4:-3 gradient pair surrounding the final carbon $\pi/2$ pulse, and a gradient enhanced COSY experiment in which quadrature in the COSY evolution dimension is selected a 1:1 gradient pair around the final proton $\pi/2$ pulse. The resulting gradient areas are 4:-2:1. With this asymmetric pulse scheme, proton signals which are not at least indirectly coupled to ^{13}C are dephased and not observed.

3D spectra were obtained using a 256 x 128 x 128 matrix for sucrose (Fig. 2) and a 512 x 128 x 128 matrix for menthol (Fig. 3). With a predelay time of 1s, total data collection time was approximately 6 hours.

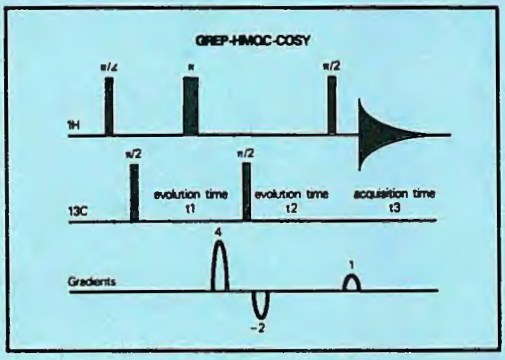


Fig. 1

Gradient-enhanced Relay Edited Proton, GREP-HMQC-COSY pulse sequence.

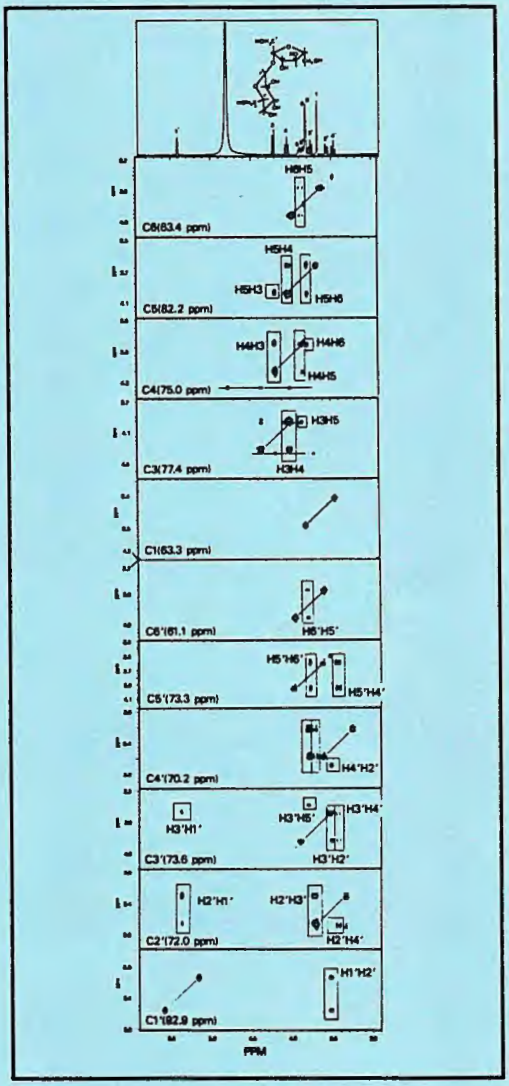
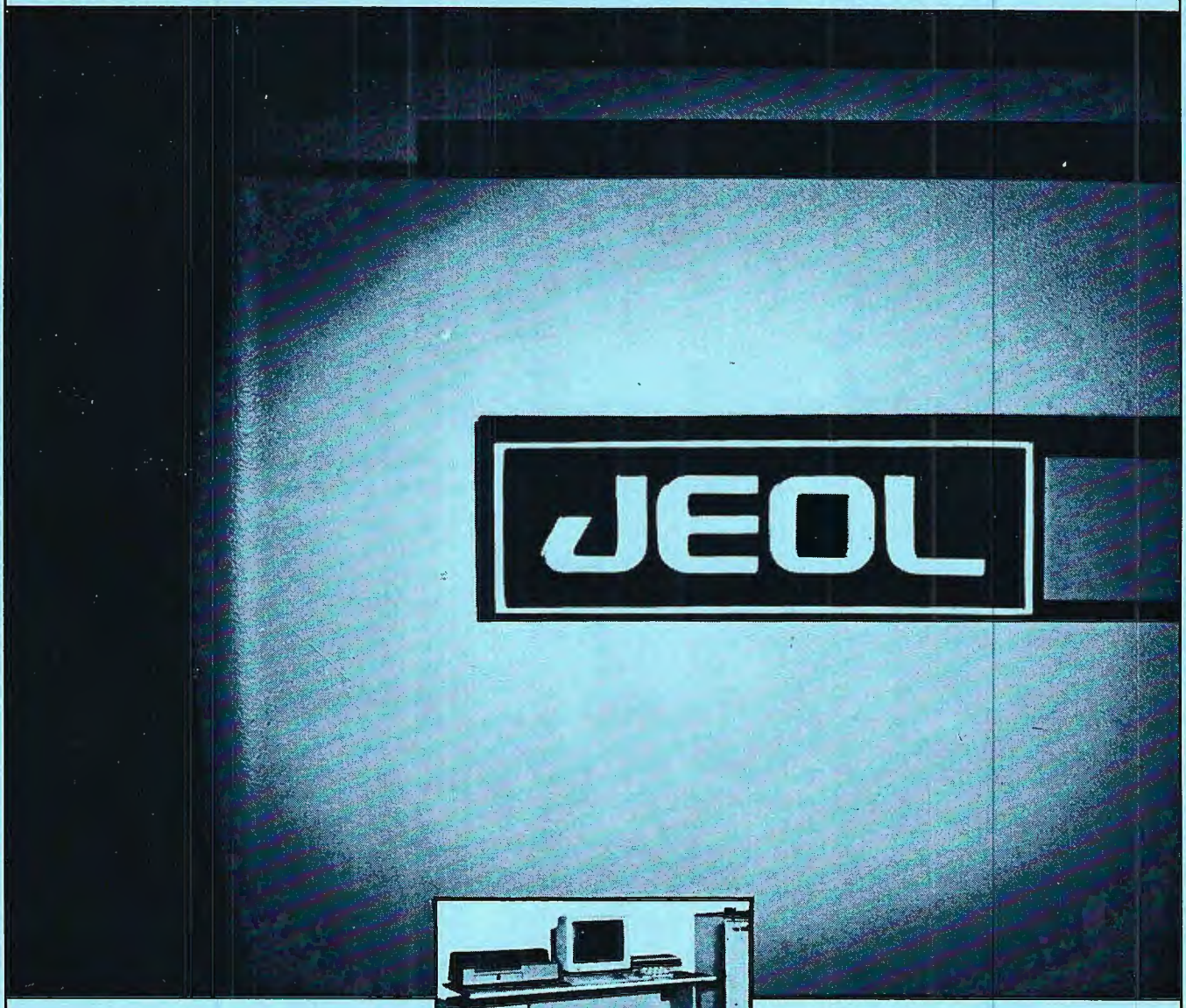


Fig. 2

Contour plots of eleven protonated carbon planes (ω_2, ω_3 planes at the appropriate ^{13}C chemical shifts in ω_1). Individual planes are identified by carbon and the chemical shift position in ω_1. The horizontal lines in C3 and C4 are at zero frequency in ω_2.

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



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