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D-13	Acetone- d_6	CD_3COCD_3	99.8%	0.8	24	57	0.460 (20)
D-121	Acetone- d_6 + 1% TMS	CD_3COCD_3	99.8%	0.8	24	57	0.460 (20)
D-129	Chloroform- d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-14	Chloroform- d + 1% TMS	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-21	Chloroform- d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-122	Chloroform- d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-130	Chloroform- d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-28	Chloroform- d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform- d + 1% TMS	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)

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FORTHCOMING NMR MEETINGS

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

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

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

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

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

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

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence
Should Be Addressed To:

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303, U.S.A.
(415) 493-5971

DEADLINE DATES

No. 373 (October) --- 22 September 1989
No. 374 (November) --- 20 October 1989
No. 375 (December) --- 17 November 1989
No. 376 (January) --- 15 December 1989



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ORGANIC CHEMISTRY DEPARTMENT
G.M. BADGER LABORATORIES

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

11 July, 1989
(received 7/17/89)

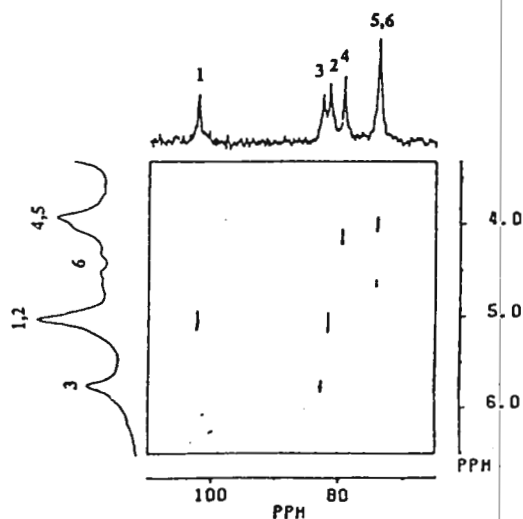
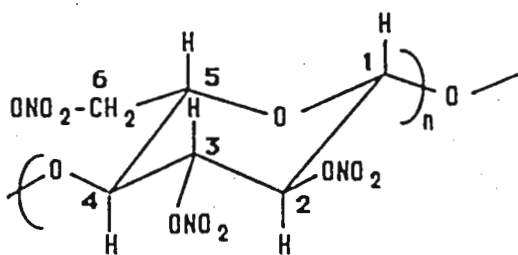
TITLE : Assignments for nitrocellulose

Dear Dr. Shapiro,

As the starting point for a study on the substituent distribution of partially and completely nitrated cellulose products, we have investigated the ^1H and ^{13}C nmr assignments for the fully substituted (2,3,6 - trinitrocellulose) product. Using the method of Buchanan et al¹, a ^1H COSY experiment revealed the assignments for the ^1H spectrum as in the Figure, in disagreement with previously published results².

^{13}C assignments have been in some disarray for years with four^{2,3,4,5} different assignments of the six ^{13}C resonances observed for trinitrocellulose. A $^1\text{H}/^{13}\text{C}$ COSY experiment revealed the ^{13}C assignments shown in the Figure, in full agreement with Panov et al⁴.

We think this represents the first *unambiguous* assignment for the polymer backbone of trinitrocellulose.



Regards,

A. Hounslow

A. M. Hounslow

I. A. van Altena

I. A. van Altena

N. J. Curtis

N. J. Curtis

1. C. M. Buchanan, J.A. Hyatt & D. W. Lowman, *Macromolecules*, **20**, 2750 (1987)
2. T. K. Wu, *Macromolecules*, **13**, 74 (1980)
3. D. T. Clark, P.J. Stephenson & F. Heatley, *Polymer*, **22**, 1112 (1981)
4. V. P. Panov, V. D. Spichak & V.P. Dubina, *Polymer Science U.S.S.R.*, **23**, 460 (1981)
5. G. L. Ryzhova & N. V. Novikova, *Polymer Science U.S.S.R.*, **27**, 1749 (1985)

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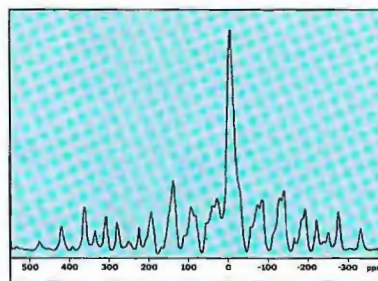
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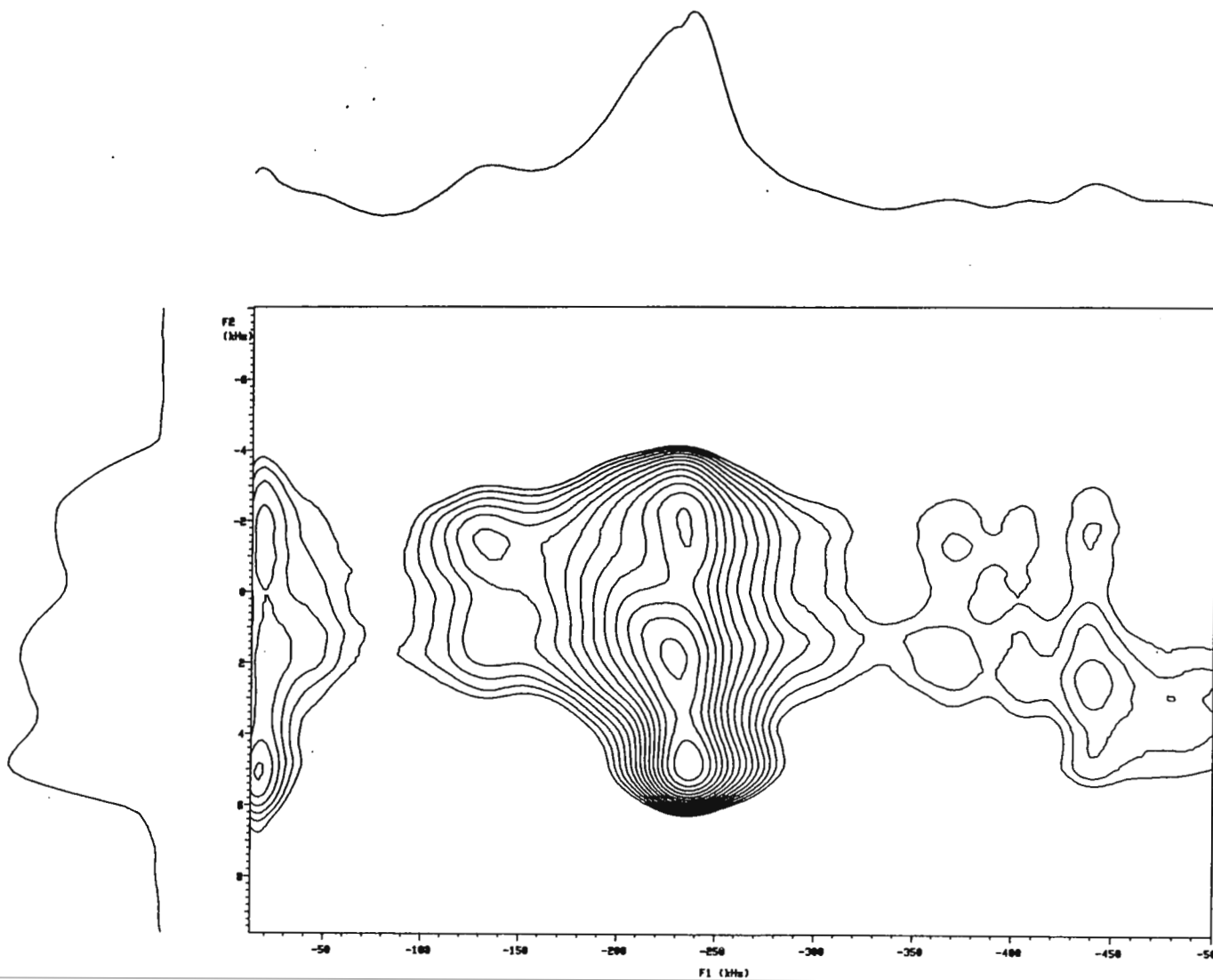
SODIUM MOLYBDATE Na_2MoO_4

Run on a Varian UNITY spectrometer, the solid 2D nutation experiment graphically illustrates the effect of pulse width on the spectra obtained. The 2D spectrum places chemical shift along F2, and gamma B_1 along F1. Signal response may be seen out as far as $3 \times$ gamma B_1 , but is usually centered about B_1 . The results obtained

vary with gamma B_1 . This ^{23}Na spectrum of Na_2MoO_4 shows that there are two ^{23}Na sites in the sample. The vertical spectrum is the projection, showing the static powder pattern. The horizontal spectrum is a trace at -1 KHz showing intensity along F1. In this spectrum, gamma B_1 is approximately 100 KHz.

Na2MoO4
Nutation experiment
23Na
exp3 pulse sequence: nutale

SAMPLE		DEC. & VT	
solvent	none	dn	H1
ACQUISITION		del	0
sfreq	105.800	dm	n
ln	Na23	dmm	n
al	0.005	dml	200
np	1024	dhp	64
sw	100000.0	homo	n
fb	49500	PROCESSING	
bs	128	gf	0.001
pw	0	gfs	not used
d1	1.000	fn	not used
tof	0	math	i
nt	4		
ct	4	werr	
alock	n	wexp	dpoen20
gain	5	wbs	
FLAGS		wnt	
il	n	DISPLAY	
in	n	gf1	0.000
dp	y	gfs1	not used
hs	nn	fn1	1024
2D ACQUISITION		DISPLAY	
sw1	1e+06	sp	-8022.2
ni	128	wp	17612.5
2D DISPLAY		vs	750
sp1	-500000.0	sc	6
wp1	487279.8	wc	180
sc2	0	hzmm	625.00
wc2	116	is	16168.13
rl1	500000.0	rl	42268.8
rlp1	0	rp	0
		th	2
		ins	1.000
		aiadcph	





Department of Chemistry
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29 June, 1989
 (received 7/3/89)

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

NON-FT SPECTRA: BAYESIAN ANALYSIS OF TIME-DOMAIN FID SIGNALS

Dear Barry,

The spectrum obtained by FT of a time-domain signal is accurate only for a continuous noiseless time-domain signal of infinite duration. For discrete noisy truncated time-domain signals, non-FT methods may provide a more accurate spectral estimate.¹ In particular, Bayesian analysis² offers the useful advantage that it automatically estimates the *precision* of its iteratively determined spectral parameters. The main disadvantage of Bayesian analysis is its lengthy computation time compared to FFT (1-6 hours vs. a few seconds for 4K time-domain data points for a 6-peak spectrum computed on the same hardware). Bayesian analysis can be useful for applications involving relatively few data points and/or requiring high precision.

Our implementation of Bayesian analysis estimates spectral parameters computed from three increasingly complex models for the time-domain signal:

$$f_1(t_i) = A_1 \cos(\omega t_i) + A_2 \sin(\omega t_i) \quad (1)$$

$$f_2(t_i) = (A_1 \cos(\omega t_i) + A_2 \sin(\omega t_i)) e^{-(t/\tau)} \quad (2)$$

$$f_3(t_i) = \sum_{j=1}^m [(A_{1j} \cos \omega_j t_i + A_{2j} \sin \omega_j t_i) e^{-(t/\tau)}] \quad (3)$$

The Bayesian "spectrum" is the probability that the signal contains a component at a given frequency. The algorithm begins by computing that probability from the undamped single-frequency time-domain signal model of Eq. 1. Armed with those initial estimates of signal frequencies as input, the algorithm then re-evaluates a probability spectrum based on the damped single-sinusoid time-domain signal model of Eq. 2. The signal frequencies and damping constant estimated from Eq. 2 are then used as input for a final probability spectrum based on the damped multiple-sinusoid time-domain signal model of Eq. 3. (Although one could attempt to compute a spectrum directly from the model of Eq. 3, the Bayesian computation time becomes excessively long unless the initial estimates for the spectral parameters are relatively close to the final values: hence, the successive estimation procedure.) Spectra are computed from the model of Eq. 3 by adding more signal frequencies until the addition of more signal frequencies fails to improve the precision of the final spectral parameter estimates.

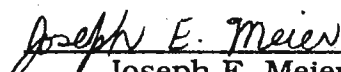
Some care is needed in comparing Bayesian and FT spectra. First, the Bayesian spectrum is inherently a *power* spectrum, rather than the *magnitude-* or *absorption-mode* spectrum typical of FT spectroscopy. Second, the spectral line *width* of an FT spectrum is approximately $(1/\tau)$ Hz, in which τ is the time-domain signal exponential damping time-constant in seconds, whereas the *width* of a Bayesian spectrum is the variance (i.e., a measure of the imprecision in our knowledge) of the ICR signal frequency. In other words, the Bayesian spectrum effectively removes the "natural" line width from the displayed spectrum, and reports it separately. Third, the Bayesian algorithm "knows" that noise is present in the time-domain signal. As a result, the presence of noise is manifested, not as random vertical displacements in the spectrum (as in the FT case), but as the *width* of the Bayesian spectral peak.

Table 1 compares the accuracy of ion cyclotron resonance (ICR) signal frequencies determined from Bayesian or FT unapodized magnitude-mode (three-point parabolic or Lorentzian³ interpolation) spectra. The Bayesian frequency estimates are more accurate than those from FT spectra (even the "exact" Lorentzian interpolation)^{3,4}, even though the Bayesian analysis was based on only 1/8 as many time-domain data points.


Figure 1 shows a Bayesian power spectrum (top) plotted as a Gaussian probability distribution from a damped multiple-sinusoid model, computed from the first 2048 data points of a time-domain ICR signal produced by seven Xe⁺ isotopes. Bayesian computation time was ~6 hours (or ~4.5 hours with closer initial estimates for the ICR frequencies). The FFT magnitude-mode spectra obtained from the full 16K time-domain data zero-filled to 32K without (middle) or with (bottom) Gaussian apodization are shown for comparison. Because of its limited number of input data points, the Bayesian analysis failed to find the lowest-abundance Xe⁺ isotope; use of more time-domain data points would presumably reveal that signal.

From our experience, Bayesian analysis is highly accurate in estimating ICR frequencies, but is much less precise in estimating relative ion abundances or time-domain damping constants. A detailed report will be published elsewhere.⁵

The authors thank Dr. L. Bretthorst, Washington University, St. Louis, MO for sharing his computer algorithm from which the present Bayesian analysis of ICR time-domain data was adapted. The authors also wish to thank Zhenmin Liang for his assistance in acquisition of experimental ICR time-domain data used to test the Bayesian analysis programs. This work was supported by N. I. H. GM-31683 and The Ohio State University.


Joseph E. Meier

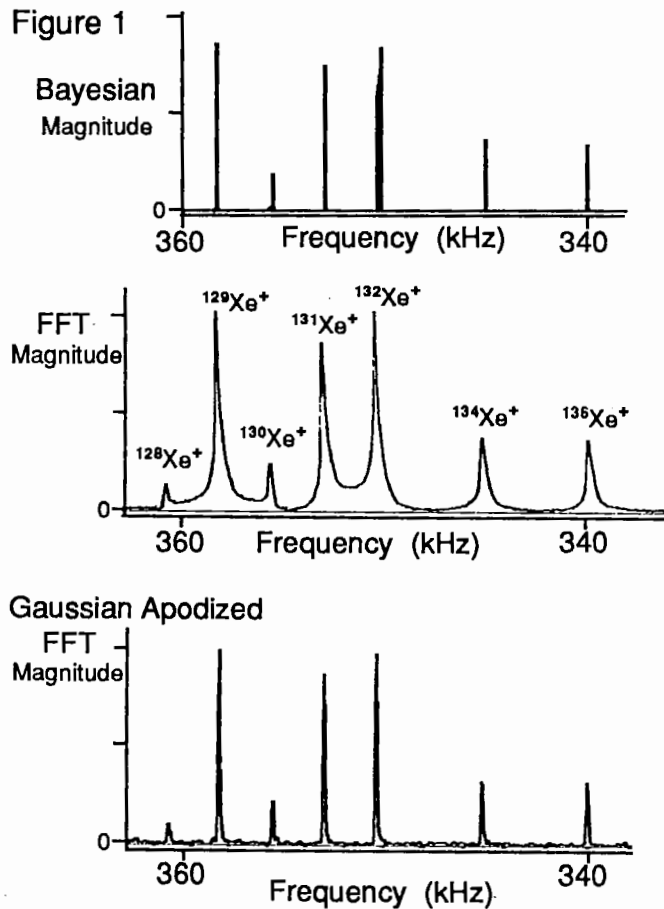
and


Alan G. Marshall

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2. Bretthorst, G. L. *Bayesian Spectrum Analysis and Parameter Estimation*, in *Lecture Notes in Statistics*, Vol. 48 (Springer-Verlag, New York, 1988).
3. Giancaspro, C.; Comisarow, M. B. *Appl. Spectrosc.* **1983**, 37, 153-165.
4. Verdun, F. R.; Giancaspro, C.; Marshall, A. G. *Appl. Spectrosc.* **1988**, 42, 715-721.
5. Meier, J. E.; Marshall, A. G.; manuscript in preparation.

Table 1. ICR frequencies for various Xe^+ isotopes (relative to $^{131}\text{Xe}^+$), computed from the known masses (left column), from FT magnitude-mode spectra (3-point parabolic or Lorentzian interpolation), and from Bayesian analysis (rightmost column).

	(Computed)	$ v_{^{132}\text{Xe}} - v_{\text{Isotope}} $		(Bayesian)
		(Discrete FT) Parabolic Interpol'n	(Discrete FT) Lorentzian Interpol'n	
^{129}Xe	8,170 Hz	8,162 Hz (-0.0024 u)	8,174 Hz (+0.0012 u)	8,169 Hz (-0.0003 u)
^{130}Xe	5,408	5,327 (-0.024 u)	5,344 (-0.019 u)	5,384 (-0.0072 u)
^{131}Xe	2,680	2,678 (-0.0006 u)	2681 (+0.0003 u)	2,682 (+0.0006 u)
^{132}Xe	0	0	0	0
^{134}Xe	5,248	5,308 (+0.018 u)	5,307 (+0.018 u)	5,293 (+0.013 u)
^{136}Xe	10,342	10,390 (+0.0143 u)	10,380 (+0.011 u)	10,368 (+0.008 u)





THE UNIVERSITY OF SOUTHERN MISSISSIPPI

DEPARTMENT OF POLYMER SCIENCE

July 3, 1989

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

RE: ^{15}N CP/MAS T_1 Measurements on Nylon 6

Dear Dr. Shapiro:

We have become increasingly interested in ^{15}N CP/MAS NMR as a tool for exploring nitrogen containing polymers, principally commercially available polyamides such as nylon 6. Natural abundance measurements showed different chemical shifts for different crystal structures of the same polymer. We extended this method by preparing an isotopically enriched sample of nylon 6. The CP/MAS NMR of the labeled sample was nearly identical to the stable α crystalline sample we identified previously at natural abundance level. This resonance was at 84.2 ppm (downfield of solid glycine). A broader resonance was seen at 86.6 ppm.

We conducted T_1 relaxation experiments on the labeled sample using the method of Torchia¹. Figure 1 shows the intensity vs. tau for the crystalline peak at 84.2 ppm. The solid line is the exponential fit of the data giving a T_{1N} of 416s. Figure 2 shows the data for the peak at 86.6 ppm. The data fit a biexponential decay consistent with a two-component decay process: a fast relaxing component with T_{1N} of 1.9s and a slower component with T_{1N} of 29.6s. Based on the T_1 data, we believe this downfield resonance is that of the amorphous region of nylon 6. In addition, the two-component decay indicates that, along with the bulk amorphous component, there is a non-crystalline "interphase" region with restricted mobility. We are continuing our experiments on these and other labeled samples to gain better insight into the phase separation and mobility of these semi-crystalline materials.

¹Torchia, D. A. J. Magn. Reson., 1978, 30, 613.

Please credit this letter to Dr. Lon J. Mathias' account.

Sincerely,

Douglas G. Powell

Lon J. Mathias

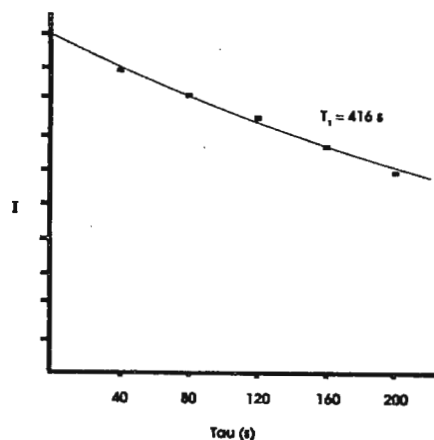


Figure 1

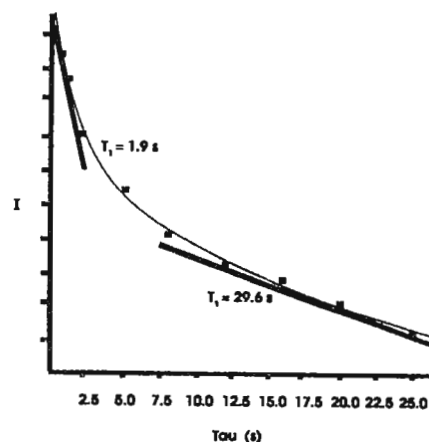


Figure 2

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82-00733	Acetone-d ₆ "100%"	99.96	(10 x 0.75mL)	55.
82-05014	Acetonitrile-d ₃ + 0.05% TMS (v/v)	99.8	10g (5 x 10 g) 25 g	25. 115. 60.
82-04097	Benzene-d ₆ + 0.05% TMS (v/v)	99.6	25 g (5 x 25 g) 100 g	45. 185. 145.
82-84078	Benzene-d ₆ "100%"	99.96	(10 x 0.75 mL)	65.
82-80554	Bromobenzene-d ₅	99.5	10 g (5 x 10 g)	50. 210.
82-80555	Bromoform-d	99.5	10 g (5 x 10 g)	30. 125.
82-00540	Chloroform-d + 0.05% TMS (v/v)	99.8	100g (5 x 100g) (10 x 100 g)	20. 85. 165.
82-70003	Deuterium Oxide EXTRA	99.996	(10 x 0.75 mL) 10 g	50. 45.
82-00813	Dimethyl-d ₆ Sulfoxide + 0.05% TMS (v/v)	99.9	25 g (5 x 25 g) 100 g	33. 155. 115.
82-00059	Methanol-d ₄ + 0.05% TMS (v/v) (~0.7 atom % ¹³ C)	99.8	10 g (5 x 10 g) (10 x 10 g) 25 g	45. 180. 345. 110.
82-02510	Trifluoroacetic Acid-d	99.5	10 g (5 x 10 g) (10 x 10 g) 25 g	19. 80. 115. 40.

***PACKAGING:** Organic solvents and deuterium oxide EXTRA are sealed in glass ampoules.
All solvents containing TMS are packaged in glass screw-cap bottles.

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85-12241	L-Alanine- ¹⁵ N, N-t-BOC derivative	99	0.5 g 1 g	125. 235.
81-12221	L-Aspartic-2- ¹³ C, ¹⁵ N Acid	99, 99	0.1 g 0.25 g	375. 875.
83-12322	Glycine-1- ¹³ C, N-t-BOC derivative	99	0.5 g 1 g	230. 425.
83-12326	Glycine-2- ¹³ C, N-t-BOC derivative	99	0.5 g 1 g	260. 475.
83-12339	Glycine-1,2- ¹³ C ₂ , N-t-BOC derivative	99	0.25 g 0.5 g	250. 465.
85-12242	Glycine- ¹⁵ N, N-t-BOC derivative	99	0.5 g 1 g	140. 240.
83-12247	L-Leucine-1- ¹³ C	99	1 g	150.
85-12245	L-Leucine- ¹⁵ N, N-t-BOC derivative	99	0.5 g 1 g	225. 400.
85-12243	L-Phenylalanine- ¹⁵ N, N-t-BOC derivative	99	0.5 g 1 g	300. 550.
83-12247	DL-Valine-1- ¹³ C	99	1 g	115.

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83-61007	Algal Biomass-(ul)- ¹³ C	99	0.5 g 1 g	150. 250.
85-61002	Algal Biomass-(ul)- ¹⁵ N	99	0.5 g 1 g	175. 300.

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June 13, 1989
(received 6/22/89)

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

Dear Dr. Shapiro:

The quantification of phosphorus-containing metabolites observed by in vivo NMR can be influenced by the broad resonance of the lipid membranes. The phosphorus resonance of the lipid membrane has a long T_1 -short T_2 and therefore can be removed by a selective saturation pulse, such as that used for a saturation transfer experiment. Indeed there are at least five examples in the literature of either partial or complete removal of the "hump" from brain and liver by various groups using a saturation channel.

I have found "hump" removal to be beneficial for my perfused liver work, and the wide bore 300 MHz machine I currently use does not have a saturation transfer channel. A method was needed that required only the observation channel (we also did not have the ability to switch from high to low power rapidly, which we now have. With the help of Gerald Pearson, and John Snyder of our high field NMR core facility, a sequence was implemented that utilizes a DANTE pulse train centered at the arrow on the figures. The pulse train consisted of 1000 pulses with 50 μ s delay between each pulse before the observation pulse. Each pulse was 1 μ s (1°).

The critical set up parameter of the technique was the delay period between the end of the DANTE train and the observation pulse. Figure 1 shows the results when a 4 ms delay was used. Figure 2 shows the results when a 2.5 ms delay was used. Figure 1 is essentially identical to spectra I obtained when a saturation channel was used (J. Magn. Reson. (1985) 61:141-144). This technique could also be used to, in effect, allow multiple saturation transfer experiments on machines that only have a single saturation transfer channel.

Sincerely,

A handwritten signature in cursive script that reads "Bill Thoma".

William J. Thoma, PhD
Department of Radiology

WJT:ks

Figure 1

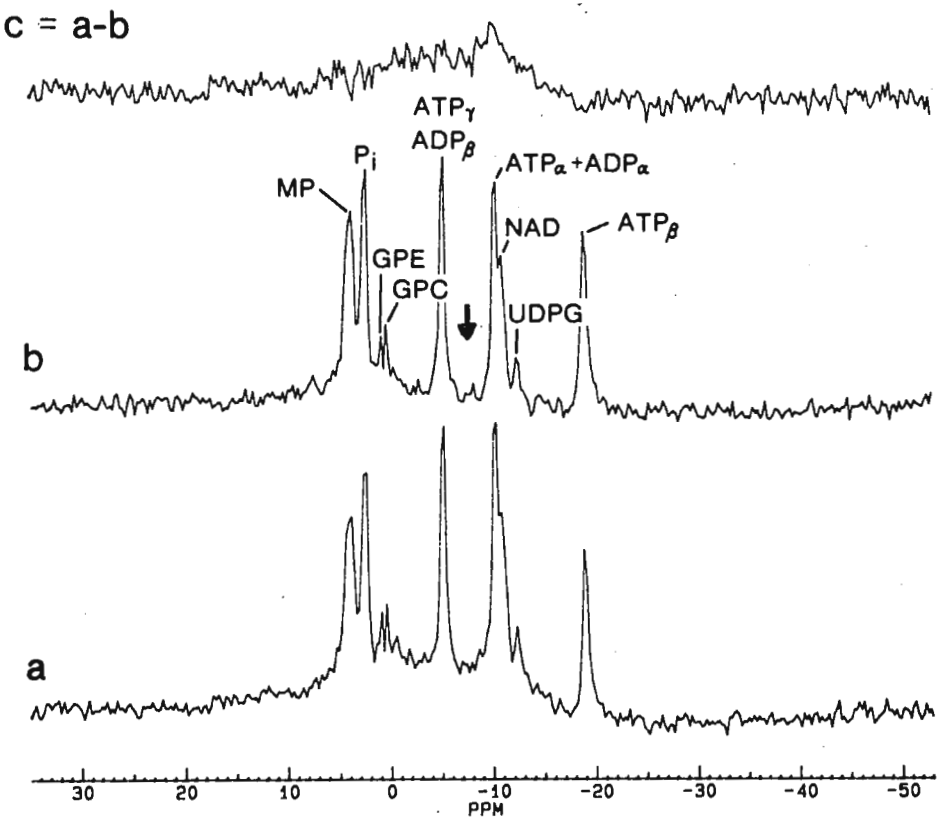
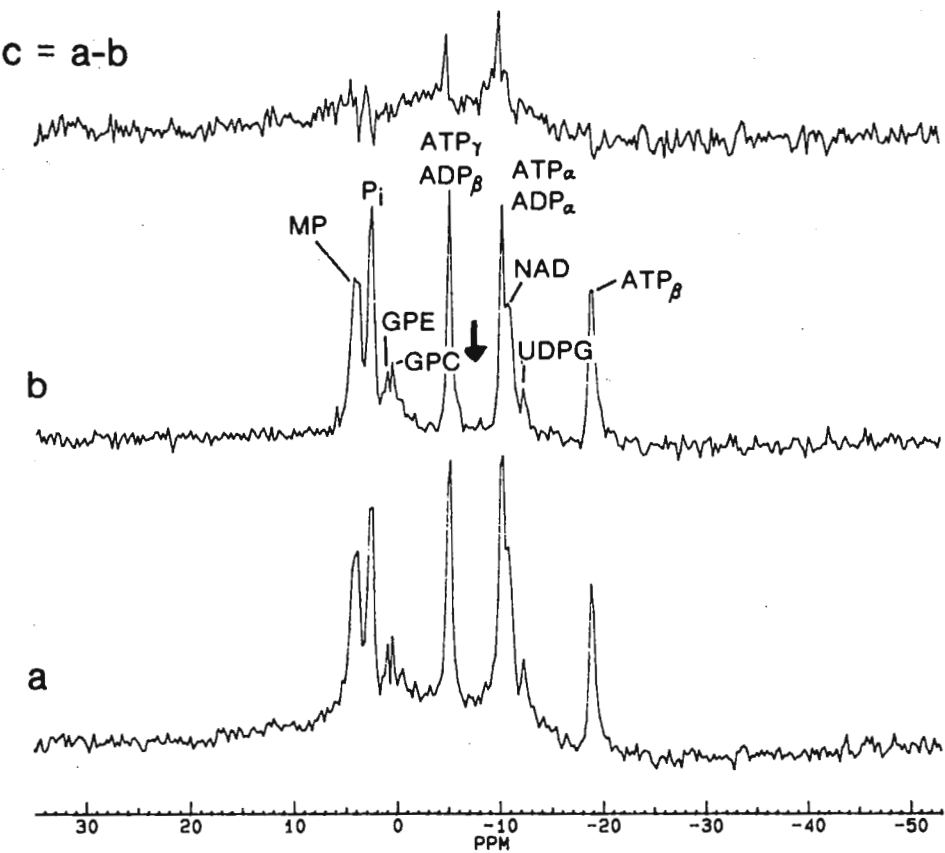


Figure 2



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SANTA BARBARA • SANTA CRUZ

(received 7/18/89)

Dear Sir:

DEPARTMENT OF CHEMICAL ENGINEERING
BERKELEY, CALIFORNIA 94720-9989

This letter is to inform you of recent development of a quadrupolar lineshape calculation program written in the *Mathematica* programming language in our laboratory. *Mathematica* is a computational package marketed by Wolfram Research, Inc., which acts both as a traditional programming language and as an interactive environment for doing mathematics. *Mathematica* is capable of processing commands both symbolically and numerically, and, when implemented on a graphics-based system such as Apple's Macintosh or NeXT, can generate high quality PostScript graphics files for laserprinter output. Its considerable flexibility, matrix processing ability, and advanced architecture, make *Mathematica* a suitable language in which to construct an NMR data processing package. Our group here at Berkeley is constructing such a package, including fitting and spectral simulations routines, such as the one discussed below.

A *Mathematica* program was written to calculate the expected ^2H -NMR powder pattern of quinoline- d_7 ($\text{C}_9\text{D}_7\text{N}$) rotating rapidly about an axis through the heterocyclic nitrogen. The program accepts a list of seven (reduced) quadrupolar coupling constants corresponding to the seven deuterons (spin-1), calculates the seven powder patterns, sums them, performs the desired broadening, and displays the final spectrum (see Figs. 1 and 2). No asymmetry is assumed. In approximating the spectrum by 200 points on the frequency scale, the program requires 3 minutes on a Macintosh II computer. If a powder pattern from a single spin-1 nucleus is desired (rather than the seven of quinoline- d_7), a separate *Mathematica* program requires 1 min. 30 sec. to calculate the broadened spectrum with 200 points on the frequency scale. The NeXT machine, utilizing the 0.8 Version of the *Mathematica* program, is able to run the above programs in 1 min. 40 sec. and 55 sec., respectively. These timing values for the single spectrum calculation (1 min. 30 sec. and 55 sec.) compare favorably with those reported in another study in which asymmetry effects were accounted for and calculation required 2 min. 30 sec. on a VAX 11/750 machine (using FORTRAN code) with an identical number of points.¹ Further development of the *Mathematica* code will address all known nuclei of spin $> 1/2$, and include asymmetry effects. A fitting routine will then be written from the core of this spectra simulations program.

1. R. Goc and D. Fiat, *Phys. Stat. Sol.(b)*, **140** (1987) 243.

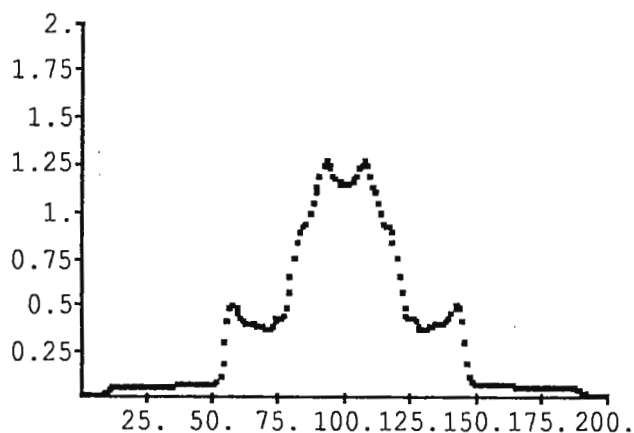


Figure 1. Motionally narrowed quinoline- d_7 powder pattern generated with *Mathematica* program on Mac II.

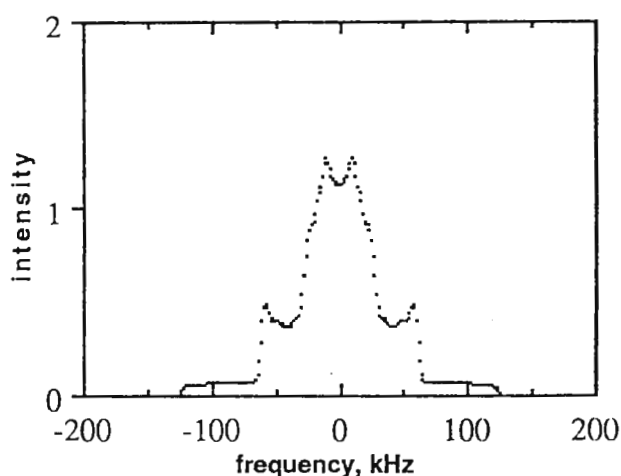


Figure 2. Same data as Fig. 1, after its work-up in Cricket Graph software package for presentation.

Sincerely,

Phil Armstrong
Research Associate
Chemical Engineering

Jeffrey A. Reimer
Associate Professor
Chemical Engineering

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

"A Handbook of Nuclear Magnetic Resonance"

by

Ray Freeman

John Wiley and Sons, 605 3rd Avenue New York, NY 101
312 pages; 1988, \$51.95; ISBN0-0470-20812-0; also
Longman Scientific and Technical, Longman House, Burnt Mill, Harlow
Essex CM20 2JE, England

As an organic chemist who sometimes does NMR, I've been increasingly pleased with the recent crop of texts on modern NMR techniques. Still they all suffer in one way or another because it is hard to describe the niceties of many 2-D experiments without getting in over my technical depth. I can pretty well follow those vector diagrams, but when it goes beyond that I'm frequently forced to punt. This valuable addition to the NMR literature could well have been subtitled "Answers to all those questions you were too embarrassed to ask."

Consisting of a series of three to five page articles arranged in alphabetical order (some fifty nine subjects) from Adiabatic Fast Passage through Multiple-Quantum Coherence to Zero Filling, I've yet to find one subject that didn't tell me more about itself than I knew before I started. They are written like Ray talks, *i.e.* in a comprehensive and comprehensible fashion. If you have a tape of Ray lecturing, as I happen to have, you can put it on quietly in the background, and you'll think he's in the room as you read. Of course, it wouldn't be a Ray Freeman lecture without the appropriate cartoons. They are there in their rampant glory for our continued enjoyment. I expect to learn and enjoy from this book for a long time.

Originally put out by Longman's in the U.K., the volume is copublished by John Wiley & Sons in the U.S. Text, index and figures are of excellent quality.

W.B.S.

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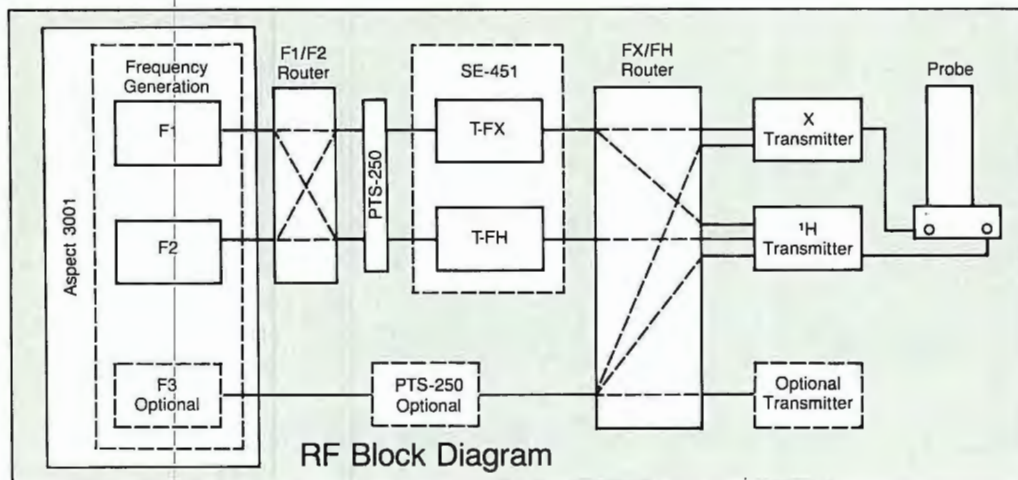
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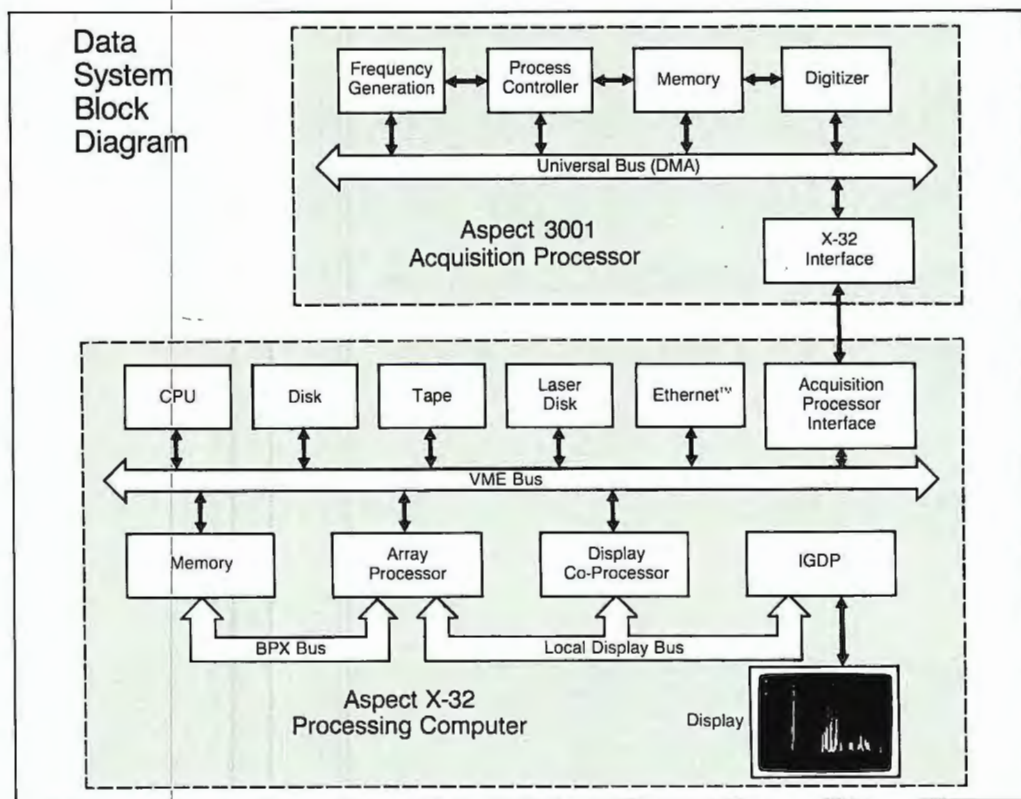


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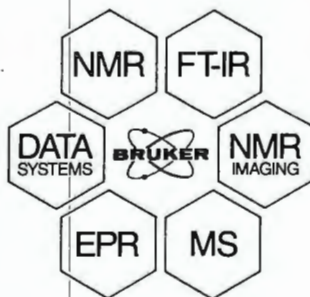


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Science Laboratories,
South Road,
Durham,
Great Britain, DH1 3LE.

Professor of Chemistry: Robin K. Harris

29th June, 1989.
(received 7/14/89)

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

Inhomogeneous (H,H) Interactions for a Template in Zeolite Theta-1

Dear Barry,

In view of recent publications by J. Forbes et al.^{1,2} and A.J. Vega³ concerning inhomogeneous proton dipolar broadening mechanisms for systems of more than two proton spins, we thought it of general interest to report a similar observation for the high-silica form of zeolite theta-1 containing the diethylamine template (Figure 1). Studies have shown that the diethylamine molecules fit closely into the main unidimensional channel and that they are closely packed with approximately one template per unit cell (the repeat distance along the channel is $\sim 5\text{\AA}$). Thus, the most feasible mode of motion is rotation about the long axis of the molecule for which it may be shown that the reduced proton-proton dipolar coupling is unlikely to be less than 24 kHz. It was therefore initially somewhat surprising to us to observe dipolar spinning sidebands at the rather modest spin rate of 2.2 kHz! It is not possible to explain the observation in terms of the equivalence of hydrogen nuclei which would allow the static proton dipolar Hamiltonian to commute with itself at different rotor orientations and thus render the interaction inhomogeneous as shown by A.J. Vega.³ However, the unidimensionality of theta-1 ensures a parallel arrangement of diethylamine molecules exists in each crystallite of theta-1. The channel direction may be considered as the director axis while the conditions of negligible intermolecular dipole-dipole interactions and fast axial rotation of the diethylamine molecules render the interaction inhomogeneous as in the case of the liquid crystalline phases studied by J. Forbes et al.^{1,2} Incidentally, the above conditions would also result in a super-Lorentzian lineshape in the static proton spectrum, which is observed (Figure 2). We hope that this snippet is enough to keep us on your mailing list! We are grateful to the B.P. Research Centre, Sunbury-on-Thames, for use of their spectrometers and for their interest in the project.

Best wishes,

Yours sincerely,



R.K. Harris



R. Challoner

1. J. Forbes, C. Husted and E. Oldfield, J. Am. Chem. Soc., 1988, 110, 1059-65.
2. J. Forbes, J. Bowers, X. Shan, L. Moran, E. Oldfield and M. Moscarello, J.C.S. Faraday Trans. 1, 1988, 84, 3821-3848.
3. A.J. Vega, J. Am. Chem. Soc., 1988, 110, 1049-1054.

Figure 1

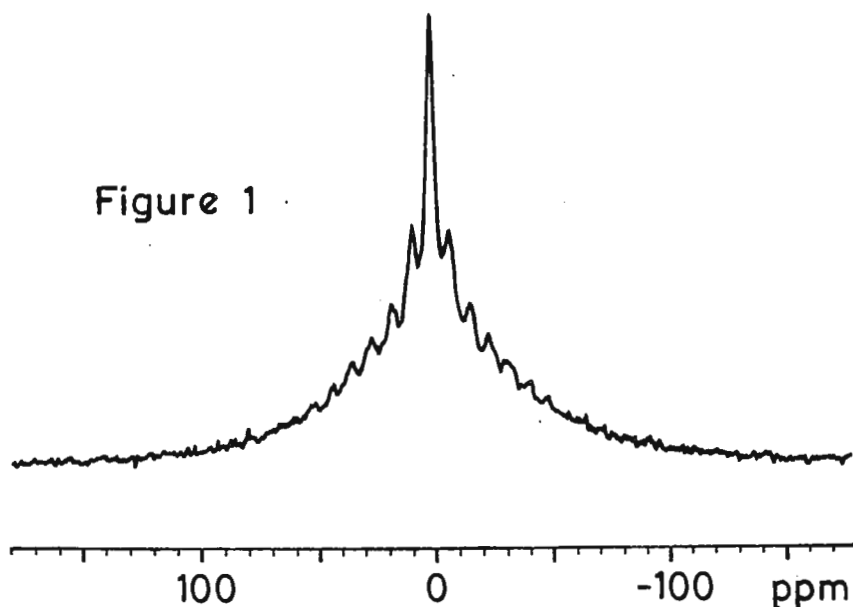
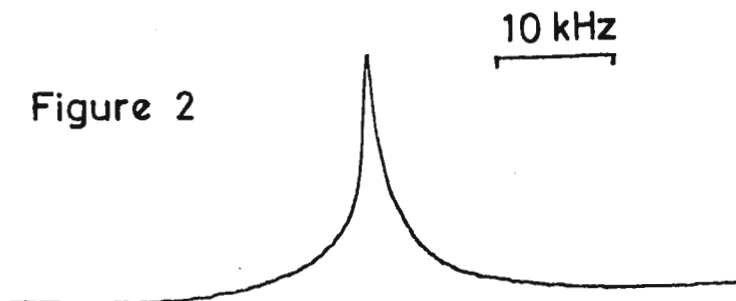


Figure 2



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Dr. David E. Axelson, Ph. D.
President

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Ravi Philar, P. Eng., MBA
Vice-President

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301-120 Holland Ave.,
Ottawa, Ontario
Canada K1Y 0X6
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SOLID STATE NMR OF RUBBER BLENDS

Dear Barry,

(received 7/18/89)

In a joint effort with the Polymer Research Group of the Department of National Defence, we have been conducting a preliminary survey of the relaxation properties of a variety of carbon black filled rubber blends.

In particular, we have been engaged in a program to : (i) determine the conditions for quantitative analysis, (ii) assess the limits of detection and resolution of individual components, (iii) determine the most appropriate experiments to correlate NMR properties with physical and mechanical behaviour, (iv) determine the minimum structural / morphological changes that are manifested as changes in these NMR parameters and (v) introduce more sophisticated methods of data analysis through the use of such procedures as factor analysis.

Solid state NMR is necessary for many blends since various treatments lead to various crosslinking and degradation processes that effectively prevent the use of solvents for NMR characterization. In any case, solution NMR will not tell us anything about solid state properties.

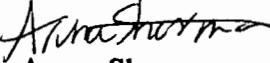
The one aspect of this work that forms the basis of this communication is the effect of ozone on rubber blends. Under relatively mild conditions (50 pphm ozone for 144 hours at 40 °C), several pairs of samples (control & exposed) were obtained for NMR study. Other parameters obtained included measures of aging (hours to first crack), hardness, tensile strength and tear strength. Both Bloch decay and cross polarization - derived pulse sequences were investigated.

For the purposes of obtaining quantitative structural information, the Bloch decay experiment is necessary. Regardless of the degree of crosslinking in this series, the substantial mobility of the major fraction of the samples severely hindered the cross polarization efficiency. This situation has been noted in previous literature on rubbers.

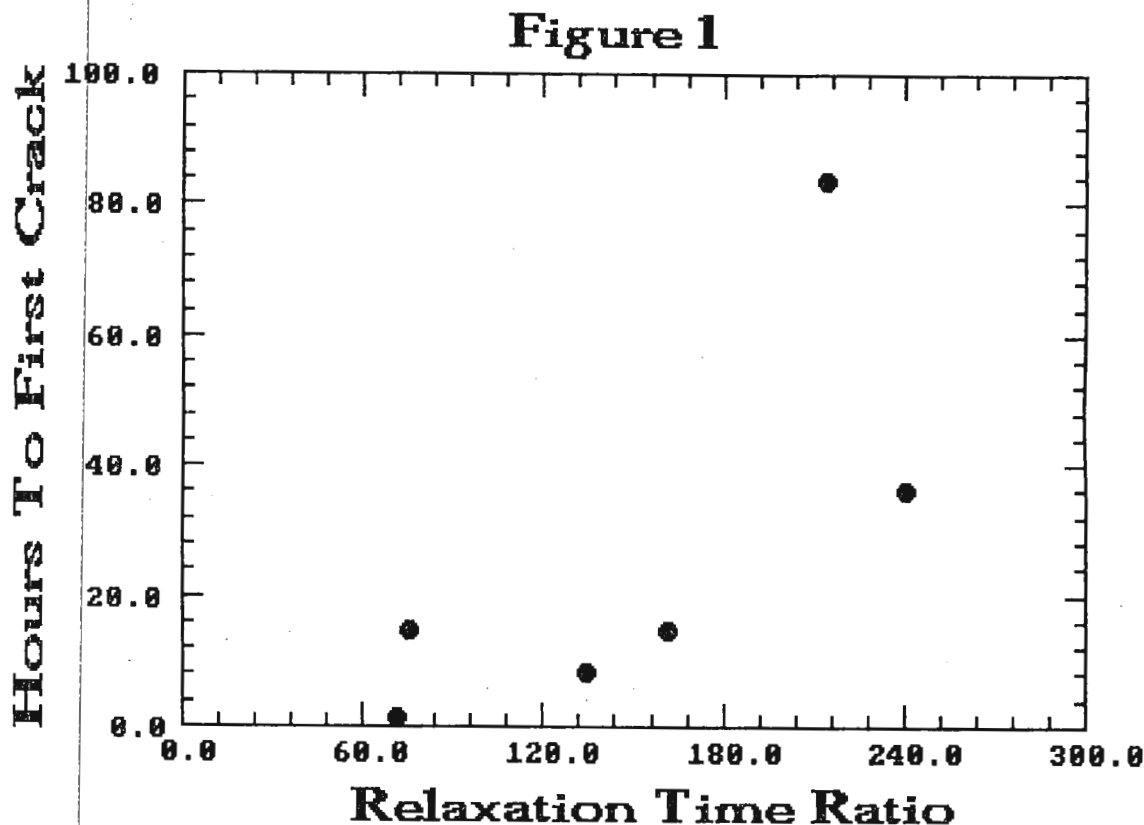
However, for those interested in correlations with the physical and mechanical properties of such materials, the use of various cross polarization-based relaxation time experiments may be fruitful. In particular, the cross polarization relaxation time, T_{CH} , and the proton rotating frame spin-lattice relaxation time, $T_{1\rho}^H$, were measured. The ratio of these numbers was plotted against one of the aging measurements, hours to first crack, with the results shown in Figure 1 for a series of butyl rubber-based blends. The relaxation times were those measured for the methylene carbon of the butyl rubber component.

Although only relatively minor differences in the compositions of the blends were deliberately introduced into the series, for the same ozone treatment, there are measurable, and significant, changes in the properties of the samples that correlate with the NMR data. A complete account of this work will be submitted later in the year for publication.


Dr. David E. Axelson

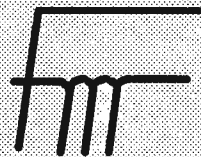

Aruna Sharma

Dr. Maryanne Scammell-Bullock



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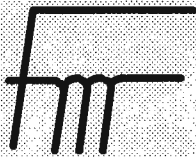
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The Shimming Process

Instrumentation Note 10

The Spinning Shims

The previous notes discussed sample preparation and the probe and shim set configuration. With this done, the user is ready to start adjusting the shims. This process is often a difficult one. At its worst the shimming process describes a multi-dimensional surface with many peaks and valleys. A three dimensional analogy to this surface would be described by walking in the mountains. The X and Y dimensions are the directions the user can walk and the altitude is the lock level. The user's goal is to walk to the top of the highest mountain. The user walks uphill and finally gets to a peak. In any direction he proceeds it is downhill. Is he on the highest peak? To complete the analogy, the user is in a heavy fog. Since he can't see beyond his arm, he can't tell if there is a higher peak in any direction. Does he continue to walk? In what direction?

With a perfect shim set, all shims are orthogonal and each gradient has no interaction with other gradients. Using our walk in the mountains analogy, it would be like walking with only one peak in the mountain range. It becomes a simple process to walk uphill to a point where its downhill in any direction. At that point you are on the one and only peak. No shim set is perfect but some are better than others. A good set of shims has only small valleys on slope or, even better, only inflexions on the mountain side. Unfortunately, this is not the case for many shim sets.

The analogy used above is three dimensional. Most NMR spectrometers have 13 or 18 shim controls making the problem a 14 or 19 dimensional one. This is an extremely difficult problem. The user needs a procedure which reduces the number of shims to be manipulated at any one time, thereby reducing the number of dimensions in the response "surface". To do this, the shims which have interactions are grouped together. This reduces the number of dimensions in the problem and eases the problem for the user. Not all shim sets have interactions to the same degree, but using the described procedure will work with all shim sets. The described procedure uses sample spinning as an additional tool to help sort out shim interactions. This helps to reduce the number of dimensions on the response surface and simplify the process.

In the described procedure, maximize means to adjust the shims for the maximum response. The response can be the height of a sweep NMR signal, the total area of a FID or the height of the lock level. In general, when starting from scratch it is best to start with a swept NMR signal and adjust just for height, not ringdown. Maximize Z^1 and Z^2 while spinning and X and

Y while not spinning. After rough adjustments, it is best to use the lock level as the response and follow the shimming procedure described. After obtaining the best response, the ultimate in resolution is best obtained by maximizing the FID area using the Z^1 , Z^2 and Z^3 spinning procedures.

In the shimming procedure, it is often best to create a *shim response plot*. The plot is created by recording the response level at a series of shim values with complete shim optimization for all lower order shims at each shim setting. The resulting data can be used to construct a plot of shim setting versus response level. This is a good method because you can make sure the plot has data beyond the maxima and describes a continuous curve with no unexpected discontinuities. The presence of a discontinuity indicates an error in the shimming process.

Spinning Shims (Z^1 , Z^2 , Z^3 , Z^4 , Z^5)

Do this procedure with the sample spinning at 10-20 Hz.

1. Maximize Z^1 .
2. Maximize Z^2 . If the response increases loop to step 1. Continue until the best response is obtained.
3. Note the response level. Adjust Z^3 to decrease the lock level by 30%. Loop to step 1 and repeat the procedure until a maxima is found. It is best to make a *shim plot* as described above. The shim plot is straight forward for Z^3 and can often be done "in your head", but it forces the user to adjust the shim too far. Going too far makes sure the user has completely described a maximum.
4. Note the response level. Adjust Z^4 to decrease the lock level by 30%. Loop to Step 1 and repeat procedures in step 1, 2, and 3 to obtain one point for a *shim plot* as described above. The shim plot is not straight forward for Z^4 and the user should not do it "in his head".
5. Z^5 is a difficult shim to adjust. A procedure similar to that described in step 4 is the best procedure to follow; however it often produces a flat plot. The reason for this result is that the field gradient created by Z^5 contains a considerable amount of the lower order Z gradients. Therefore after changing Z^5 and readjusting Z^1 through Z^4 the resulting response level is often the same. Take large steps in Z^5 repeating Steps 1 through 4 for each setting. Be sure to make large enough steps to have the plot reveal a complete curve. If the plot is completely flat, put the Z^5 shim control at its mid-range and ignore it for that probe. The result could be different for other probes.

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July 17, 1989

(received 7/19/89)

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

re: Protein Surfaces by NMR

Dear Barry:

We have developed a simple and effective method for exploring protein surfaces which combines two-dimensional spectroscopy with the use of paramagnetic reagents. The method takes advantage of the antiphase nature of the crosspeaks in a phase-sensitive COSY experiment whereby a small amount of resonance broadening can produce large changes in crosspeak intensity. As a model system we have used the protein ubiquitin whose proton NMR spectrum has been almost completely assigned and for which the 1.8 Å crystal structure has been determined.^{1,2,3} We found that the organic free radical, 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl, produces differential line-broadening effects on the DQF-COSY spectrum of ubiquitin. The largest effects are observed for the exposed hydrophobic sidechains.

In Figure 1 is shown the effect of the free radical on the Ile 3, Ile 13, Ile 36 and Ile 44, $C^{\gamma}H-C^{\delta}H_3$ crosspeaks. Spectra were recorded at 500 MHz on a 5 mM ubiquitin sample in D_2O . Upon addition of 20 mM free radical, panel (b), crosspeaks for Ile 36 and Ile 44 are

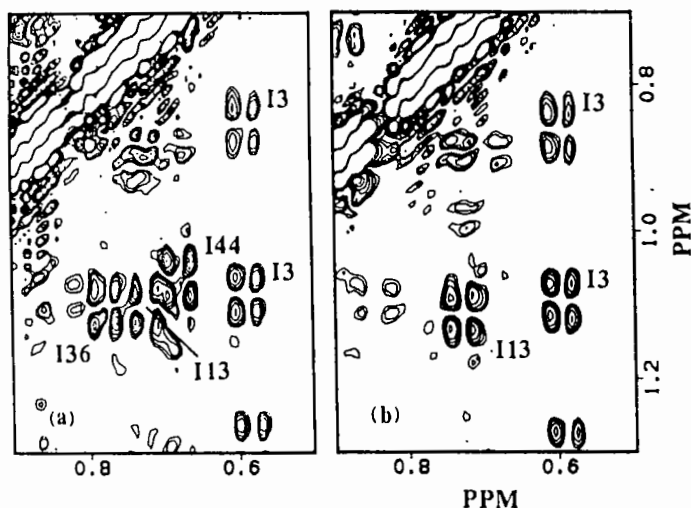


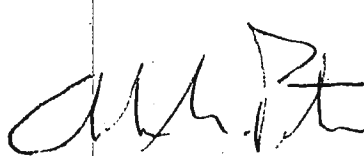
Figure 1

completely eliminated by broadening while those from Ile 3 and Ile 13 are essentially unchanged. An examination of the crystal structure shows that of the seven isoleucines

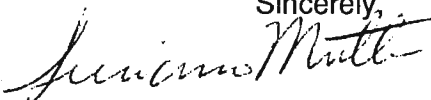
SK&F

in ubiquitin, Ile 36 and Ile 44 are the only two isoleucines with any solvent accessible surface. Similar correlations could be made for the leucine and valine sidechains. We have also examined the effect of gadolinium(III) diethylenetriaminepentaacetate complex ion on ubiquitin. This paramagnetic ion was found to interact strongly with aspartic acid and asparagine sidechains. $C^{\alpha}H-C^{\beta}H$ crosspeaks from five of the seven Asx residues of ubiquitin are eliminated at very low concentrations of the ion, ~ 0.25 mM. This is most likely due to direct coordination of the Asx carboxyl or carboxamide functions with the gadolinium. At higher concentrations the ion also effects the solvent accessible hydrophobic sidechains. A publication of the details of this work is in preparation.

Sincerely,



Andrew M. Petros



Luciano Mueller



Kenneth D. Kopple

- 1) Weber, P.L., Brown, S.C. and Mueller, L. (1987) Biochemistry 26, 7282-7290.
 - 2) DiStefano, D.L. and Wand, A.J. (1987) Biochemistry 26, 7272-7281.
 - 3) Vijay-Kumar, S., Bugg, C.E., and Cook, W.J. (1987) J. Mol. Biol. 194, 531-544.
-

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Post-Doctoral Research Associate positions are immediately available for working on an NIH research project on "Active-Site Structures of ATP-Utilizing Enzymes" by NMR Studies of ^{31}P , ^{13}C , ^{15}N , and 1H nuclei. Ph.D.'s with training either in protein biochemistry or in modern NMR spectroscopy and with interest in applications of modern NMR methodologies to macromolecular systems are encouraged to apply. The positions will be initially for one year, but can be extended for several years by mutual agreement. Please send C.V. with full particulars to Professor B. D. Nageswara Rao, Department of Physics, Indiana University-Purdue University at Indianapolis (IUPUI), 1125 E. 38th St., Indpls., IN 46205-2810. Telephone: (317)274-6897.

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

1989-07-06

**Prediction of C-13 NMR SCS in Disubstituted Aromatics;
SELINAQUATE Inadequate?**

Dear Barry,

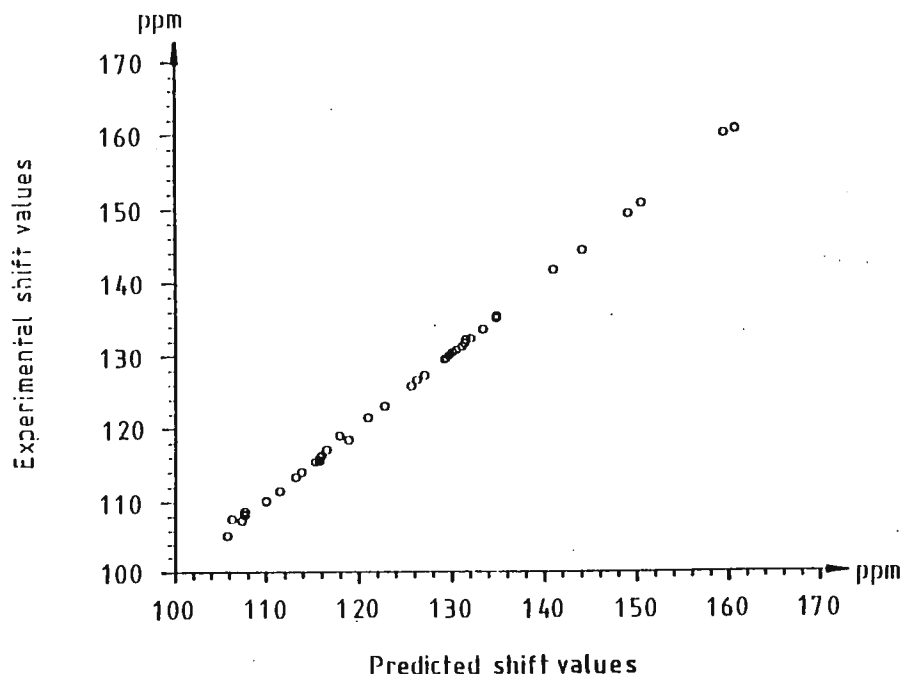
We have extended our multivariate studies of aromatics to include disubstituted systems. It is of outmost importance for those active in molecular design/ QSAR etc. to understand the non-additive behaviour in such systems. In disubstituted benzenes we found to our limited surprise that the non-additive behaviour could be predicted from the C-13 SCS of monosubstituted benzenes using a two-block PLS analysis (see figure). This means that the additional third parameter, the electron demand (ϵ) parameter, in the commonly used substituent parameter equation is superfluous.

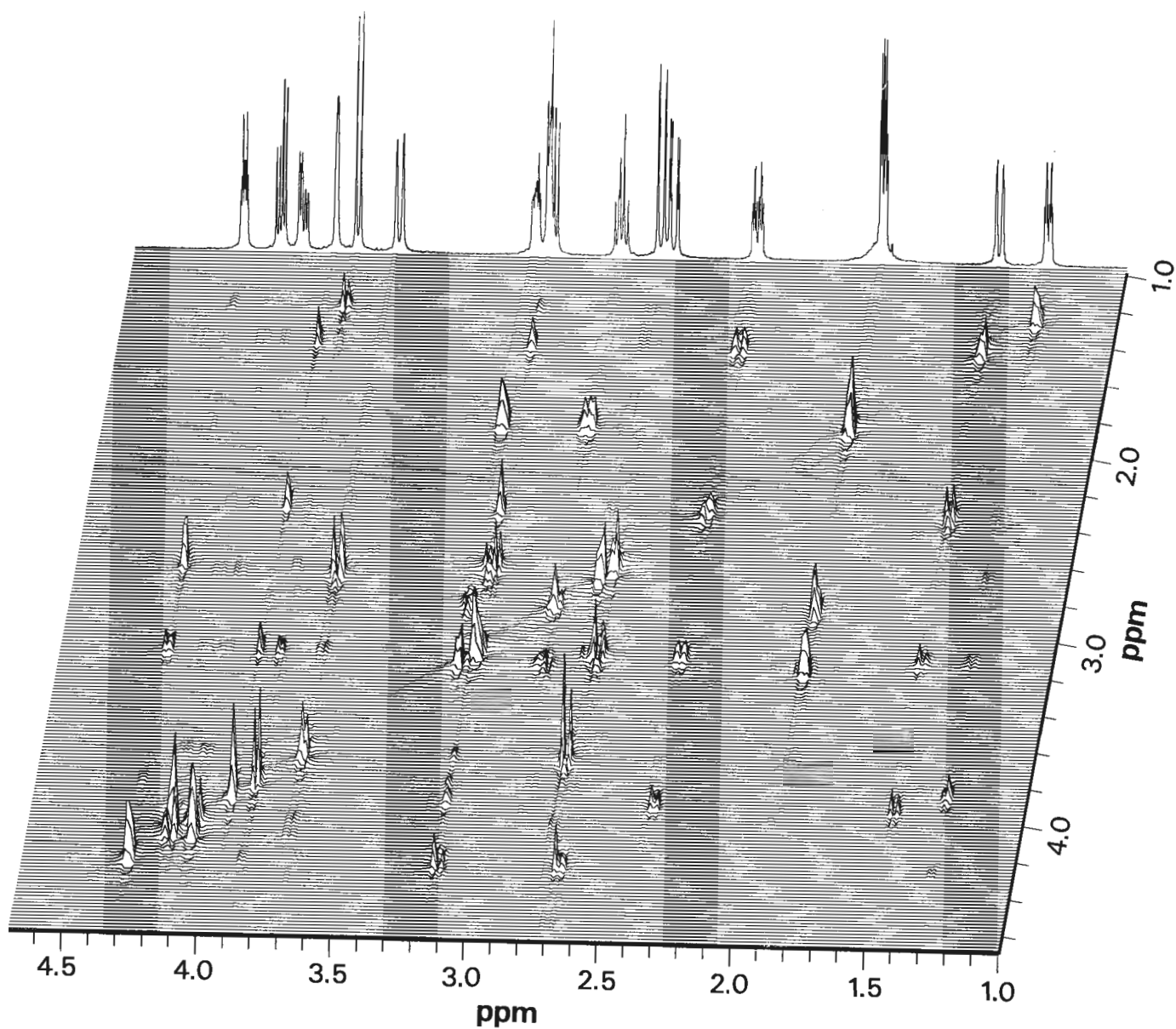
A totally different topic but related to structure determination is the use of the 1D INADEQUATE technique using selective pulses (SELINAQUATE). We have used it a little lately but I doubt that it will be of much use practically. If only two or three carbons are in doubt it might be worthwhile, but otherwise there is no gain in time (sensitivity, setup etc) relative to the normal 2D experiment.

Best regards

Ulf Edlund, prof

Fig 1



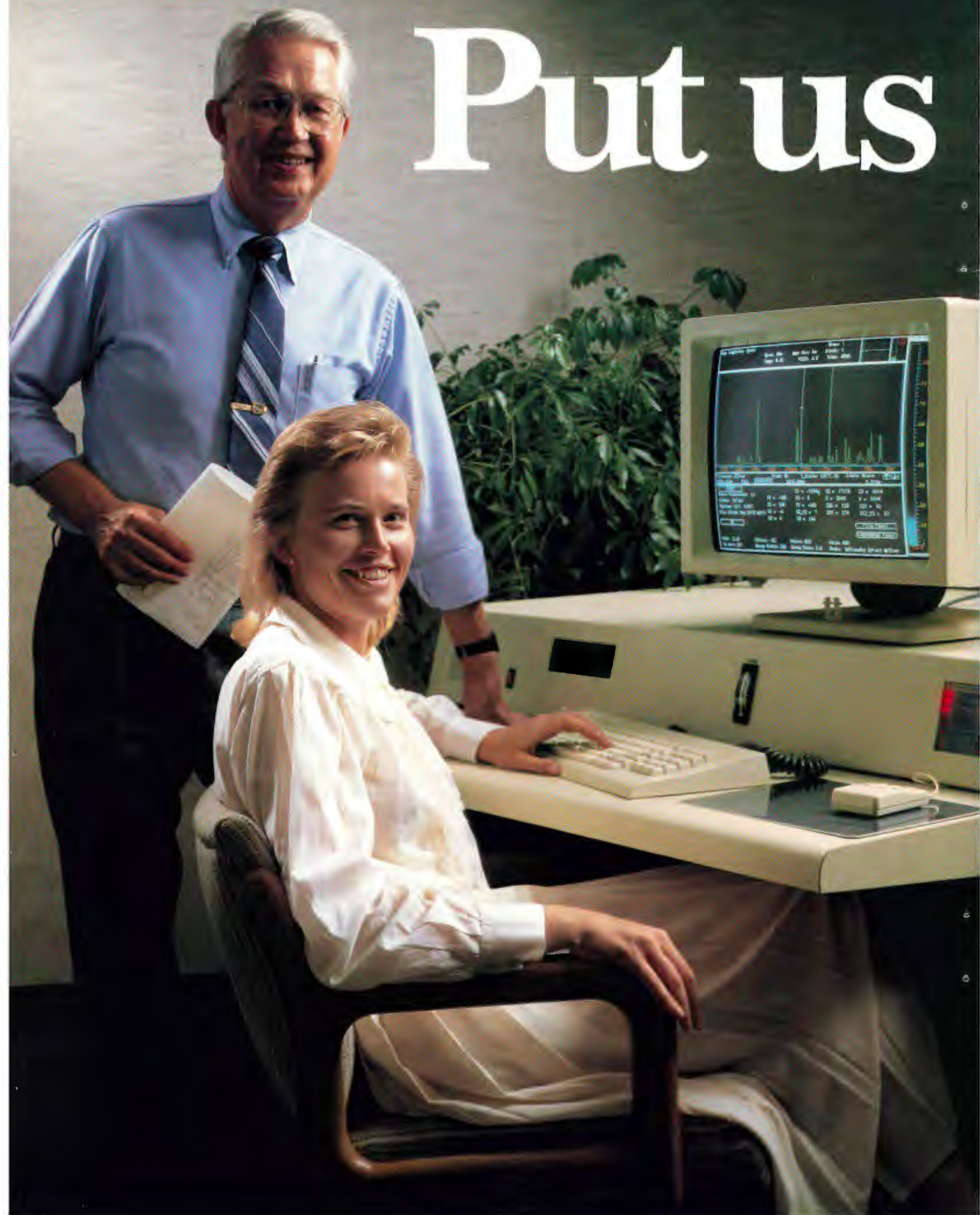


HOHAHA of Strychnine on an Omega 600



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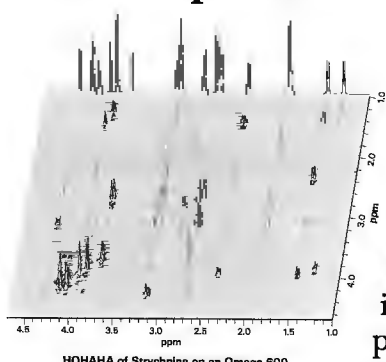


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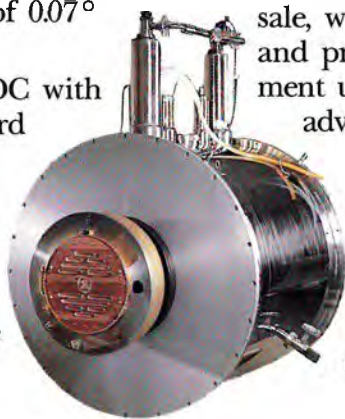
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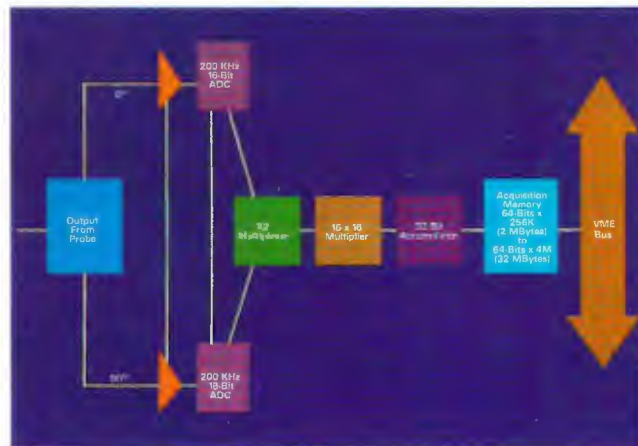


Fig. 1
The Alpha HDR digitizer.

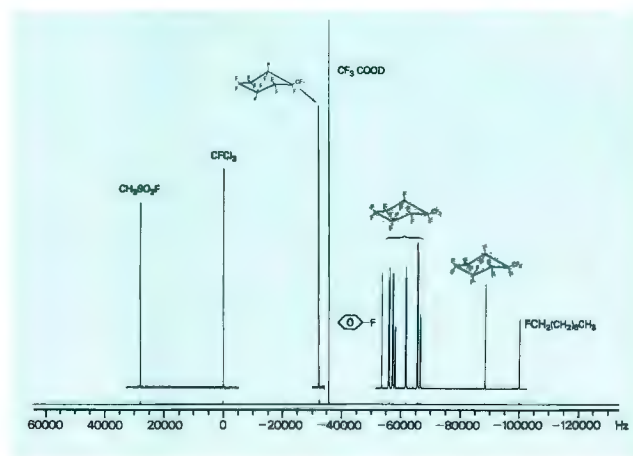


Fig. 2
200 KHz spectral width ¹⁹F spectrum acquired on a GN-500 Omega System. Note the extremely flat baseline obtained with the Alpha HDR.



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Dr. Bernard L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

26 June 1989
(received 7/6/89)

Dear Dr. Shapiro,

Yet another solvent suppression sequence. The horror! The horror!

Joseph Conrad once referred to colonial exploitation as "the vilest scramble for loot ever to disfigure the history of human conscience". If he were alive today, Conrad would no doubt feel similarly about the invention of pulse sequences for solvent peak suppression in high-resolution NMR spectroscopy.

Regrettably, here in the whited sepulchre of Cambridge, we have recently discovered that we too lack the necessary restraint to resist joining this scramble for loot.

A good selective excitation technique for solvent suppression should possess the following properties: (a) the null in the excitation profile at the transmitter frequency should be broad enough to allow for the inhomogeneous linewidth of the solvent peak; (b) the excitation bandwidth should be broad and uniform enough to excite the desired spectral region with undistorted intensity; and (c) the variation in signal phase should be very small across this excitation bandwidth. We have designed the following pulse sequence that attempts to fulfill all these criteria:

$$90_{262.8} - 4\tau - 90_{82.8} 90_{97.2} - 4\tau - 90_{277.2} 90_0 - \tau - 90_{180}$$

where the signal amplitude at an offset $\Delta\nu$ can be optimized by selecting $\tau = (4\Delta\nu)^{-1}$. This pulse sequence was derived using an intelligent admixture of hand-waving, necromancy, and various other unspeakable rites. Figure 1 shows the simulated absorptive and dispersive excitation profiles for this sequence. The rectangular absorptive excitation profile, and near absence of dispersive profile, can clearly be seen. Figure 2 shows the 400 MHz proton spectrum of 7 mM lysozyme in 90% H₂O/10% D₂O recorded using this pulse sequence. This spectrum was phased using only a very small frequency-dependent correction, whilst no baseline correction was performed. The result looks quite nice.

Please credit this contribution to the account of Jeremy Sanders.

Yours sincerely,



Steve Wimperis



Ad Davis

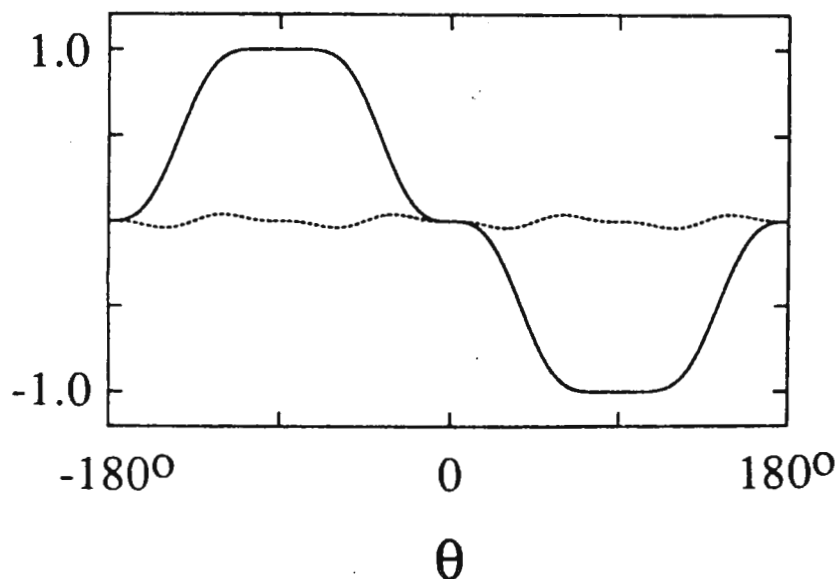


Fig.1. Computer simulations of the absorptive (solid line) and dispersive (dotted line) excitation profiles for our solvent suppression sequence as a function of the offset-dependent angle $\theta = 2\pi\Delta\nu\tau$.

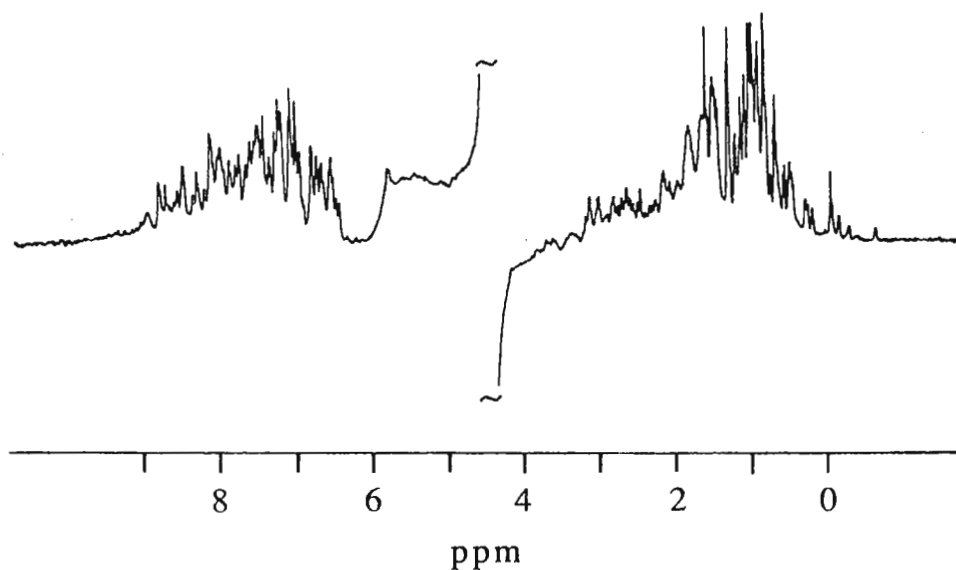


Fig.2. Spectrum of 7 mM lysozyme in 90% H₂O/10% D₂O recorded at 400 MHz using our solvent suppression sequence. The value of τ was 200 μ s, the 90° pulse length was 12 μ s and thirty-two free induction decays were acquired using CYCLOPS phase-cycling. The spectrum was phased using a frequency-independent correction and a very small frequency-dependent correction. No baseline correction was performed. One half of the spectrum has been inverted to take into account the opposite excitation amplitudes on either side of the transmitter frequency, and this results in the absorptive residual water signal (which is truncated) appearing as a discontinuity. The broad resonance to the left of the discontinuity is water signal that has been excited and detected by the non-shielded leads of the proton radiofrequency coil.



State University of New York
Health Science Center
Syracuse

College of Medicine

Department of Radiology
Division of Radiological Sciences
NMR Research Laboratory
(315) 473-8470

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

July 12, 1989
(received 7/17/89)

Dear Barry:

We have been using the phase transition in an NMR imaging sample to obtain novel physical/spatial information. Here we illustrate such an application. Suppose you go to the grocery store and buy a package of frozen squash. How do you know that it is really frozen? The image on the left represents the signal arising from a section through such a package obtained from the local store. This image was made with a spin echo sequence having an echo delay of 12 ms. Dipolar interactions should have eliminated any signal. In light of such strong evidence, do you suppose the grocer would agree to adjust his freezer?

Next we wanted to thaw this package for a late evening snack. Following 2 min (on high) in a GE microwave, one obtains the image shown on the right. (The signal, however, is an order of magnitude stronger than that observed previously.) Do microwave ovens have shim adjustments for improving homogeneity?? The field of view is 150 mm which is large enough that non-linearities in the gradients make the package look very non-rectangular.

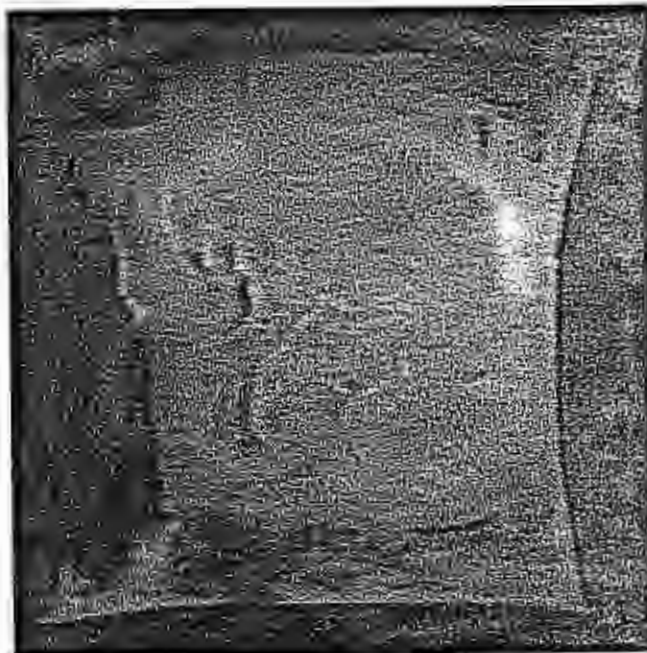
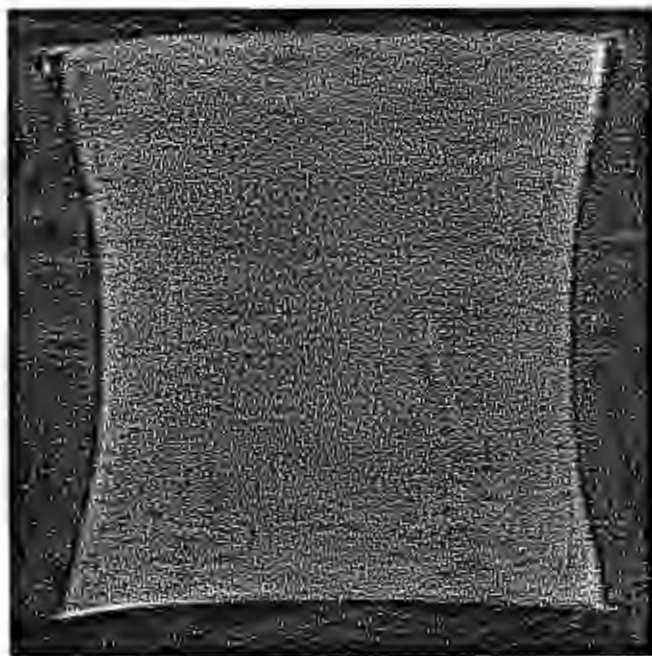
Best regards,

Nikolaus M. Szeverenyi

Steve Falen

squash.im1

squash.im2



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2145 Sheridan Road
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JOSEPH B. LAMBERT
Professor of Chemistry
(312) 491-5437

June 20, 1989
(received 6/26/89)

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

Dear Barry:

We have been looking at simple five-membered rings in the solid state by VT CP/MAS techniques. For cyclopentanol the spectrum changes from just three peaks at -75°C to at least 19 peaks at -140°C . At first we thought we were freezing out multiple conformers, but then we looked at cyclohexanol under the same conditions. It also split into a multiplicity of peaks. We now are seeing a lot of published VT work in the solid state, and we urge workers to avoid simple explanations in terms of multiple chemical forms (conformers, tautomers, etc.), without compelling reasons. More likely, different crystalline forms are present.

Sincerely,



Joseph B. Lambert

Liang Xue

Title: Cyclopentanol and Cyclohexanol in the Solid

A Rare Editorial Comment: My old friend Joe has, I feel, pushed the concept of succinctness to the maximum - at least. I hope that this contributionette will not be construed as a useful precedent. You are not usually so coy, Joe . . .

B. L. S.

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Tuck C. Wong
Department of Chemistry
University of Missouri-Columbia
College Avenue
Columbia, MO 65211
(314) 882-7725
BITNET: CHEM1060@UMCVMB

Frank D. Blum
Department of Chemistry
University of Missouri-Rolla
Rolla, MO 65401
(314) 341-4451
INTERNET: C2828@umrvmb.ums.edu
BITNET: C2828@UMRVMB

____ I (we) plan to attend the Third Missouri Magnetic Resonance Symposium.

____ I (we) plan to present a poster entitled _____

____ Please send us further information.

Also send information to the following person(s):

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Chemical Division

June 16, 1989

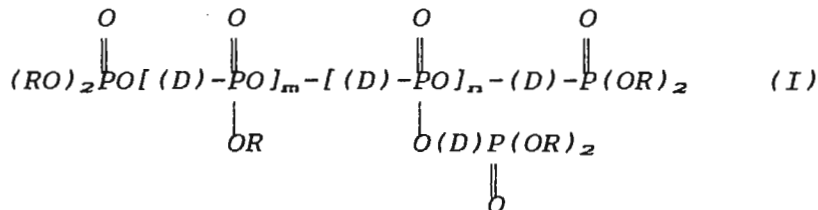
Dr. Bernard L. Shapiro
 Editor/Publisher
 TAMU NMR Newsletter
 966 Elsinore Court
 Palo Alto, CA 94303

(received 6/19/89)

Title: NMR Characterization of Phosphorus Flame Retardants

Dear Barry:

We would like to report some of the NMR techniques, we have used to characterize oligomeric phosphorus flame retardants, the general structure of which is as follows:



Where D = $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ or $-\text{CH}_2\text{CH}_2\text{O}-$ and the RO- group is either a primary and/or secondary alkoxyl.

With ^{31}P gated-decoupling (Figure 1), resolution-enhanced coupling (Figure 2) and long-range heteronuclear APT¹ NMR (Figure 3), we are able to distinguish the distribution of different alkoxyl groups around each phosphorus nucleus. The resolution-enhanced coupling spectrum, Figure 2, shows that the ^{31}P NMR splitting pattern correlates with the total number of α -protons on the alkoxyl groups surrounding the phosphorus. The APT NMR spectrum with long-range heteronuclear couplings of P-O-C-H, Figure 3, also shows the correlated multiplicity of each peak. The three peaks, in Figure 1 Region C, having the same multiplicities arise as a result of the two asymmetric centers of the two 2-chloro isopropanoxyl groups.

With the addition of ^{13}C NMR experiments to identify the possible alkoxyl groups, we are able to determine the stoichiometric numbers m and n in Structure (I) and the distribution of various alkoxyl groups around each phosphorus.

Sincerely yours,

Biing-Ming Su
 Biing-Ming Su

Dave

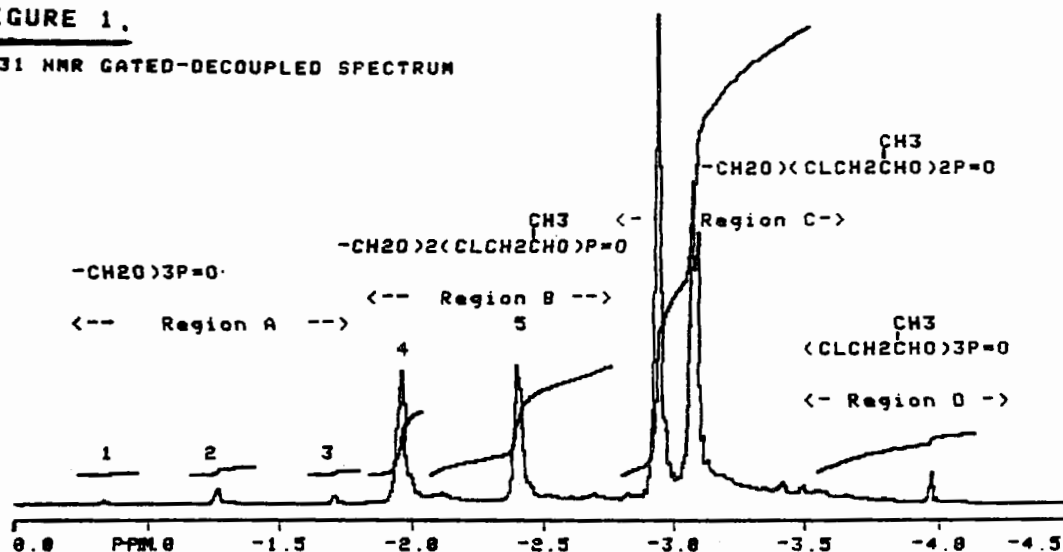
David H. Marr

¹ H Jancke, R. Radeaglia, J. Needs, and A. Porzel, *Org. Magn. Reson.* 22, 376 (1984).

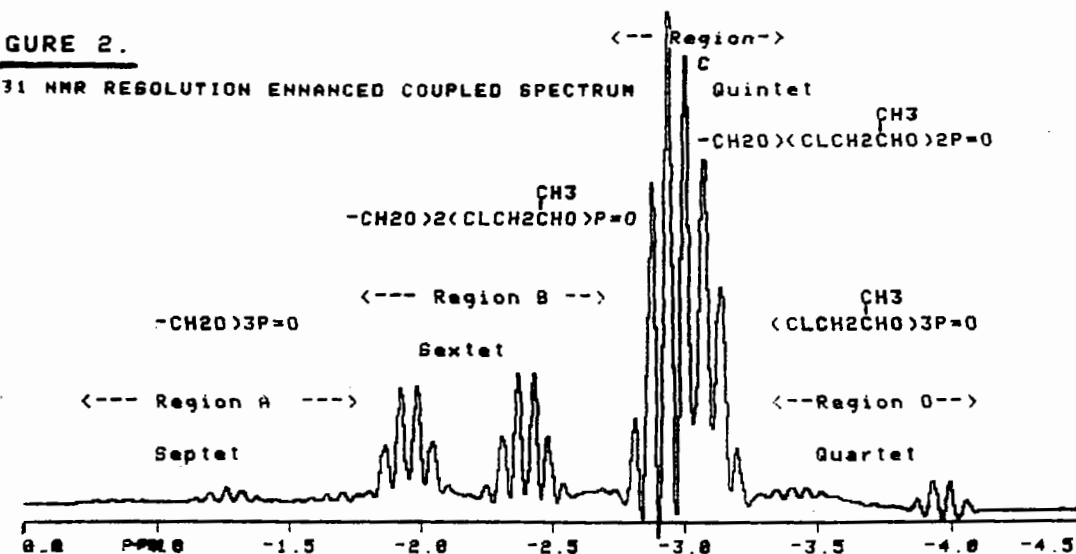
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FIGURE 1.

P-31 NMR GATED-DECOUPLED SPECTRUM

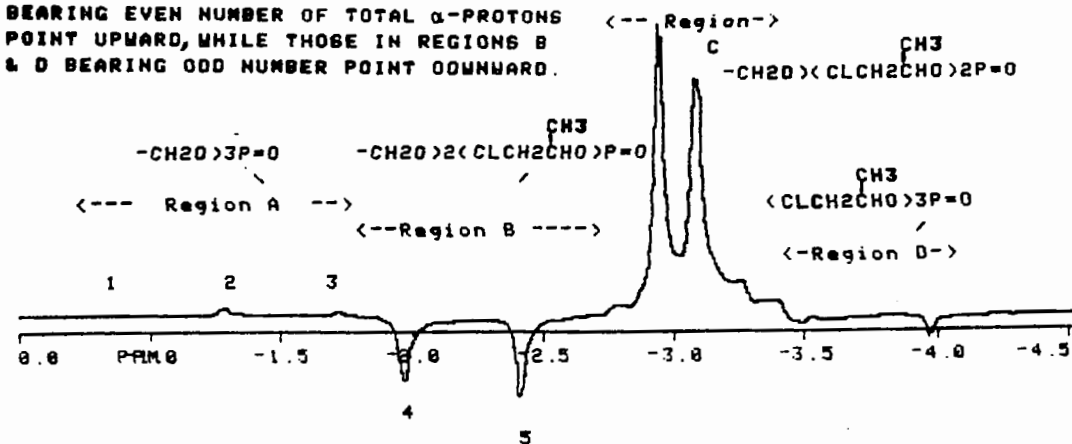
**FIGURE 2.**

P-31 NMR RESOLUTION ENHANCED COUPLED SPECTRUM

**FIGURE 3.**

P-31 APT NMR

PHOSPHATE STRUCTURES IN REGIONS A & C
BEARING EVEN NUMBER OF TOTAL α -PROTONS
POINT UPWARD, WHILE THOSE IN REGIONS B
& D BEARING ODD NUMBER POINT DOWNWARD.



nmr and polymer networks

It has been known for fifteen years, that NMR in swollen polymer gels has rather peculiar features not to be found in other systems, such as polymers in solution or in bulk, or low molecular weight compounds. These peculiarities are usually attributed to simultaneous liquid-like and solid-like behavior of swollen polymer gels, the latter due to the stability of restrictions imposed on chains by the knots of the network. The origin of this behavior is easily found in the structure of a network. A polymer network comprises linear chains connected with each other by knots. From a NMR point of view a chain between knots differs basically from a free chain or a dangling chain, because a segment of a free chain has principal possibilities for isotropic rotation under appropriate conditions (dilution, high temperature). This does not hold true for a network segment; its motion is anisotropic until the knots are broken. The major consequence of restrictions being imposed by the knots is impossibility in principle to average out tensorial interactions to zero by raising temperature or adding solvent to a swollen crosslinked polymer system. The residual interactions are shown to depend strongly on the properties of the networks. It is evident that the higher the density of the network, the less are the possibilities for averaging out tensorial interactions. This dependence gives the clue for a procedure of crosslinking density evaluation on the basis of NMR measurements of residual tensorial interactions. In an ideal network all chains have an equal size, all knots the same functionality, there are no dangling chains. That means that all chains have similar NMR behavior. But a chemist usually deals with an irregular network comprising dangling chains and chains of different length. So the resultant line in the spectrum should be a superposition of peaks produced by the different chains of the sample. The broadest signal comes from the most heavily crosslinked part of the sample, the most narrow contribution to the line from dangling chains and slightly crosslinked regions. Actually lineshapes for ^1H and ^2H NMR of swollen polymer networks are peculiar with very broad wings and relatively narrow peaks clearly indicating a possibility for superposition of the lines of different width. In spite of its power NMR is not routinely used by chemists for characterizing networks. One reason is the absence of a theory of NMR behavior of dangling chains and detailed theoretical consideration of diverse manifestations of networks irregularities.

The purpose of this letter is to try to attract the attention of theoreticians to this subject.

Mark I. Lifshets
New York University
4 Washington Pl. R#514
New York, NY 10003

(received 7/7/89)

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July 7, 1989

(received 7/13/89)

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

Peptide Dynamics from ^{13}C NMR

Dear Barry:

We have been using ^{13}C NMR relaxation measurements (T_1 , T_2 , & steady state NOE) to study side chain and backbone dynamics of peptides. A major aim of the work is to apply more than one experimental technique to the same molecules in order to assess the accuracy and reliability of the motional parameters deduced from the measurements. The approach we elected to take was to synthesize peptides containing a $^{13}\text{C}\delta_1$ -labeled tryptophan residue (^{13}C at the 2-position of the indole ring). In this manner, both NMR and fluorescence measurements of the dynamics could be performed readily on identical peptides. Among the peptides chosen for investigation were melittin and three analogs thereof. Melittin, which contains only a single trp, was originally isolated from bee venom. It is an extensively studied, 26 residue, cytolytic peptide with well characterized solvent-dependent conformations. The analogs differed from native melittin in the placement of the trp residue in the sequence. $^{13}\text{C}\alpha$ -labeled gly also was incorporated into the sequence of the peptides at the 12-position to give an additional probe of the peptide motion.

The formalism of Lipari & Szabo (*J. Am. Chem. Soc.* 104, 4546-4559 (1982)) was used to analyze the ^{13}C relaxation which was dominated by dipole-dipole interactions between the ^{13}C nucleus and the attached proton (or protons for gly) with chemical shift anisotropy making a non-negligible contribution for the $^{13}\text{C}\delta_1$ -trp. In the Lipari & Szabo approach, the relaxation is described in terms of three motional parameters, τ_m , a correlation time for the overall motion of the peptide (which we assumed to be isotropic), τ_e , an effective correlation time for the local motion of the labeled amino acid residue, and \mathcal{S} , an order parameter related to the amplitude of the local motion. A definite model for the motion is not assumed other than taking the overall and local motions to be independent. Once values are obtained for \mathcal{S} , a specific interpretation of the motion can be made. We introduced a similar method to analyze trp fluorescence lifetime and steady state anisotropy data. Excellent agreement between the motional parameters found from the two techniques was obtained.

A few additional comments regarding the NMR results are worth mentioning. If the relaxation measurements are made only at a single NMR frequency, then in principle one has three parameters (τ_e , τ_m , and \mathcal{S}) to find from the three relaxation measurements. Therefore, the parameters can be obtained from the appropriate relaxation expressions more or less directly. A problem with such analysis is that no clear idea results for the range of motional parameters that is consistent with the data. In addition, we found that T_2 values were often small and difficult to measure accurately. For those reasons, we adopted a graphical, and what we believe to be more useful, approach for obtaining values for the parameters of the local motion by calculating τ_e and \mathcal{S} .

Indiana University - Purdue University at Indianapolis

as functions of τ_m from the measured T_1 and NOE values for physically reasonable τ_m . Examples of such analyses are shown in the figures. The sensitivity of the τ_e and S values to the data is apparent from the curves thus giving one the opportunity to assess then the significance of particular values found for those parameters. The curves shown are for melittin monomer and tetramer. In the tetramer, the trp side chain was found to have a more restricted range of spatial motion accompanied by a smaller correlation time. The dynamics of the analogs, which gave no indications of forming discrete oligomers, were similar to monomeric melittin's.

Please credit this letter to the account of B. D. Nageswara Rao.

Best regards,

Marvin

Marvin D. Kemple
(IUPUI)

F.G.P.

Franklyn G. Prendergast
(Mayo)

A.J.W.

Arthur J. Weaver
(UT-Dallas)

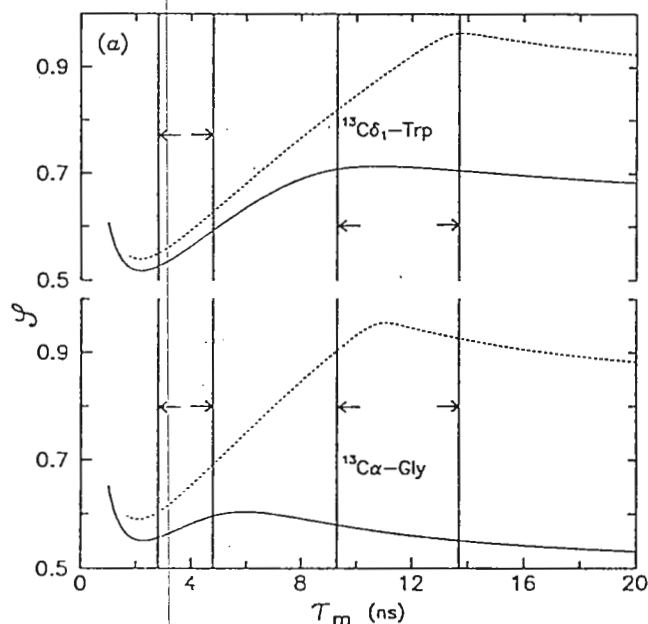


Figure 1. Curves generated from T_1 and NOE data obtained at 75.4 MHz for the $^{13}\text{C}\delta_1\text{-trp}$ and $^{13}\text{C}\alpha\text{-gly}$ labels displaying allowed values for the order parameter in melittin monomer (—) and tetramer (----) in D_2O as a function of the overall correlation time (τ_m). Regions delineated by arrows indicate the range of overall correlation times predicted (from calculations) for unstructured melittin monomer (2.8-4.8 ns) and for melittin tetramer (9.3-13.7 ns).

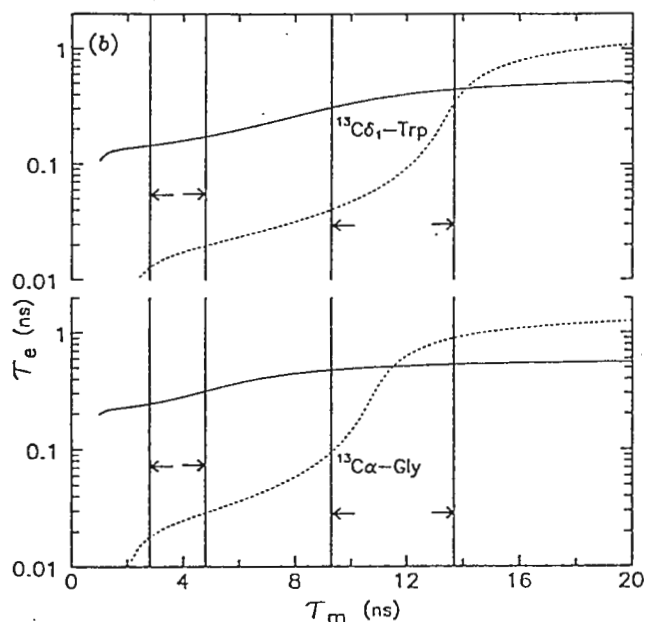
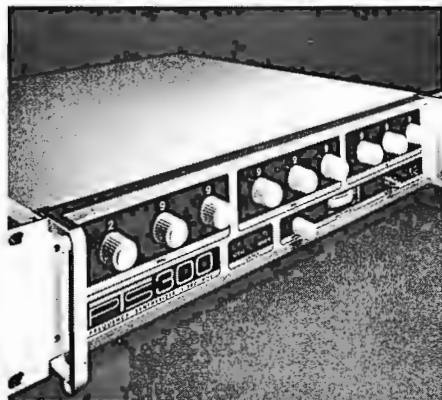


Figure 2. Curves generated as in Fig. 1 displaying allowed values for the effective correlation time (τ_e) as a function of the overall correlation time for melittin monomer (—) and tetramer (----) in D_2O . Regions appropriate for monomer and tetramer are delineated as in Fig. 1.

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FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, June 24, 1989.-
(received 7/13/89)

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

Title: A two level MASER oscillator

Dear Dr. Shapiro:

We found in this laboratory that a non-neutralized preamplifier can, under certain conditions, oscillate just like a crystal controlled oscillator, but using protons immersed in a magnetic field as frequency determining device, and following the relation: $\omega = \gamma \cdot B_0$.

We have, in fact, A TWO LEVEL MASER OSCILLATOR.

The funny thing is that the oscillations are intermittent! The device behaves somewhat like "a lighthouse", sending a burst of oscillation every 10-40 seconds, depending on the sample used.


Once we understood the phenomenon we modified Bloch's equations and integrating these numerically we found that we could account perfectly well for the lighthouse effect, that is, the pulsating nature of the oscillations and the path of the magnetization vector M_0 in space and in time.

Adding an automatic gain control to the circuit we have been able to produce stable, constant amplitude oscillations.

The device is, in fact, a very precise magnetometer. Unfortunately it only works with intense and very homogeneous fields.

Full details of all this shall be published elsewhere. I hope to be able to present them at the next ISMAR meeting.

Yours sincerely.


Valdemar J. Kowalewski

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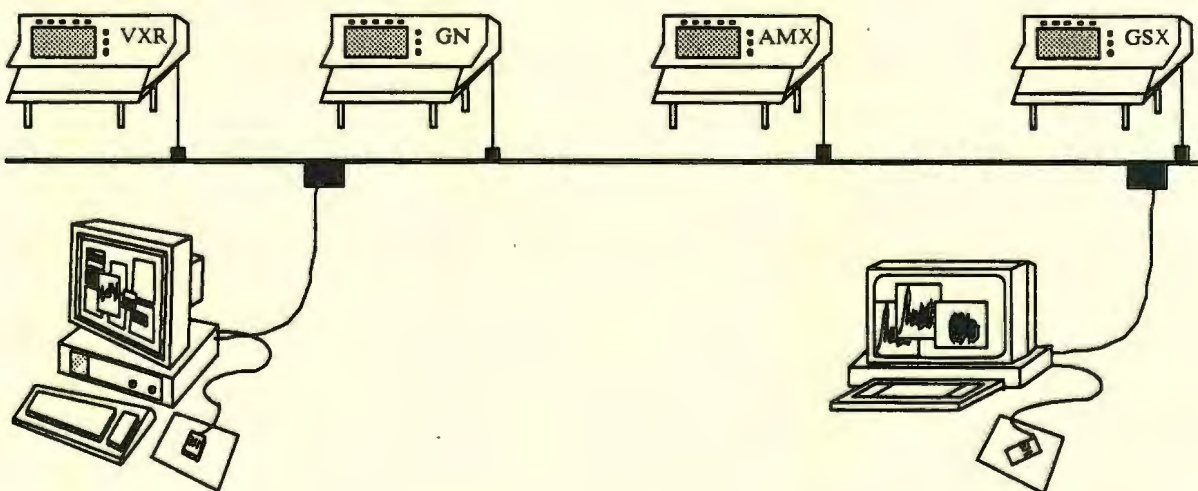
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Houghton, Michigan 49931

College of Sciences and Arts
Department of Physics
906/487-208629 June 1989
(received 7/3/89)Prof. B. L. Shapiro
Editor TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Professor Shapiro-

GPIB SEND CIRCUIT

Some time ago I sent you a schematic for a GPIB (IEEE-488) receive only circuit which we have found very useful for our homemade NMR spectrometer. In the last year we have added a send only circuit which is attached to optically encoded knobs. Through software these knobs function to change the phasing, baselines, etc., similar to knobs on commercial spectrometers.

The send only circuit is a bit more complicated than the receive only circuit since, during the addressing part of the cycle, it must receive as well. In the drawing I have included, the handshake is handled for the most part by the circuitry on the left side of the diagram while the addressing is handled by the circuitry in the center of the diagram. On the right side are the four channels (only one is shown explicitly) for the data.

The use of the GPIB interface to our computer has proven to us to be very useful. We recently changed computers in our spectrometer to a '386 based machine. No other hardware changes to our spectrometer were necessary.

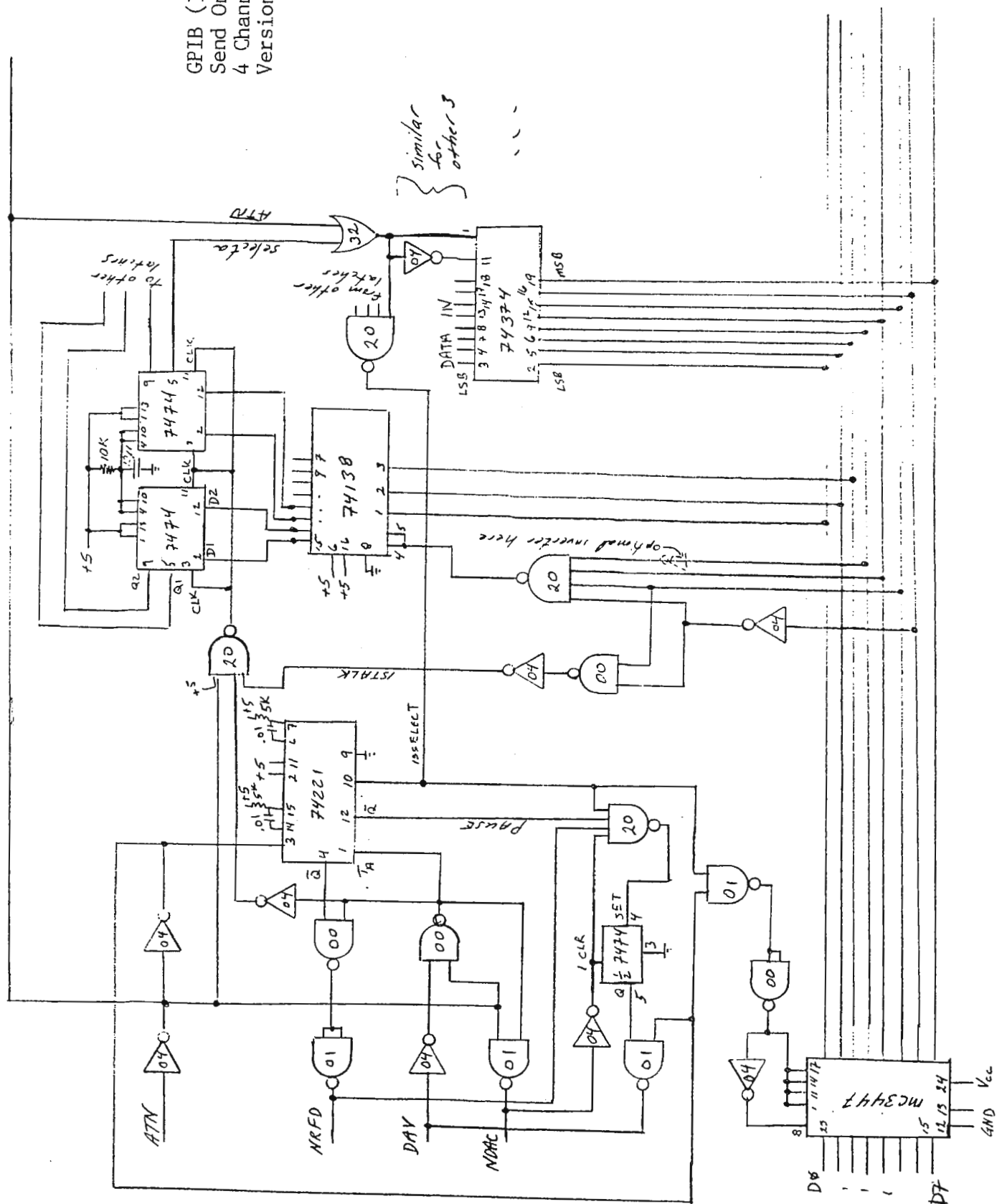
This circuit has been successfully used along with our receive only circuit as well as several commercial units with GPIB (or HP-IB) capability.

Sincerely,

Bryan H. Suits

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UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Chemistry

123 Chemistry Building
Columbia, Missouri 65211
Telephone (314) 882-2439June 25, 1989
(received 6/26/89)Professor Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo alto, CA 94303Reverse Detection on an NT spectrometer

Dear Dr. Shapiro:

Since the reverse (proton) detection of heteronuclear 2-D spectroscopy has demonstrated great sensitivity enhancement, we have recently modified our vintage NT-300 spectrometer to implement this capability. A Tecmag DecKit 2 decoupling kit and a ENI 325 LA (50W) power amplifier were used as the heteronuclear decoupling channel. So far, we have been using a normal broadband probe (rather than an "inside-out" probe). Therefore the set-up is relatively inexpensive (< \$10K). The results have been reasonably encouraging. A one-bond ^{13}C - ^1H correlation map can be routinely generated for 2-3 mg of sample (in a 5 mm tube) of moderate molecular weight in several hours. Long-range (multi-bond) correlation of the same samples in an overnight run. However, experiments with heteronuclear broadband decoupling have not been as successful.

A one-bond carbon-proton correlation map of methyl-enriched yeast tRNA^{Phe} in a phosphate-buffered saline of pH 7.2 in D₂O (~1 mM) obtained in about 12 hours is shown here. As it can be seen, virtually all 13 methyl groups are resolved and assignment can be made accordingly. A similar map of poorer quality obtained by direct ^{13}C detection took 15 times longer to accumulate.

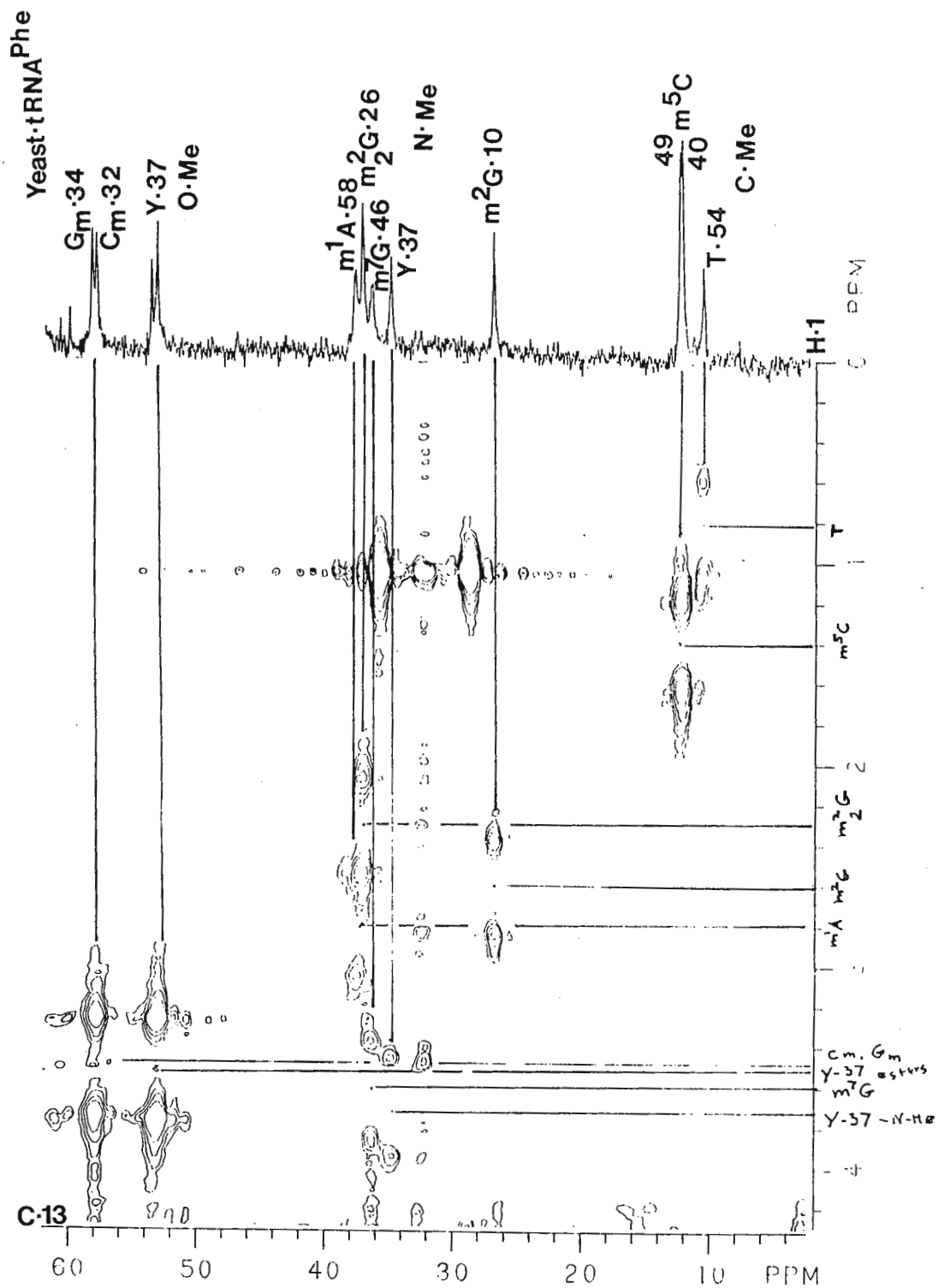
Sincerely yours,

A handwritten signature in cursive script, appearing to read 'Hanna'.

Hanna Sierzputowska-Gracz

A handwritten signature in cursive script, appearing to read 'Tuck'.

Tuck C. Wong



One-bond carbon-proton correlation map of methyl ^{13}C -enriched yeast tRNA^{Phe} from reverse detection.



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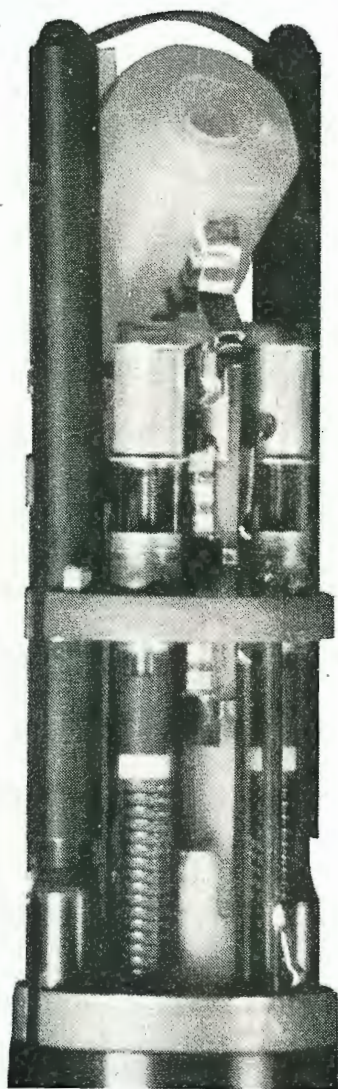
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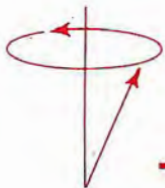
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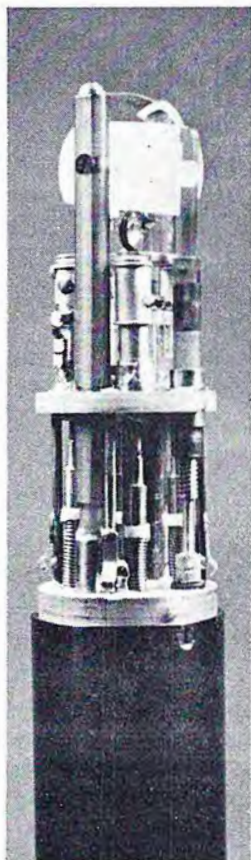




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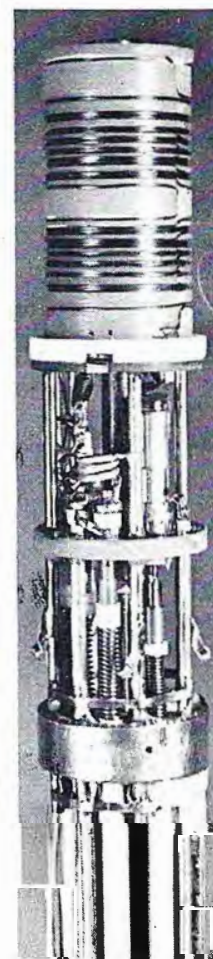
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Research & Development

July 12, 1989
(received 7/15/89)

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

RHEUMATOID ARTHRITIS AND NMR

Dear Dr. Shapiro:

Rheumatoid arthritis and NMR may seem to be the most unlikely partners. However, we have found a one-dimensional NMR imaging experiment to be an effective monitor for the course of the disease *in vivo*, using an experimental model. Rheumatoid-like arthritis was induced in rat leg joints by injecting modified Freund's adjuvant (MFA) containing *Mycobacterium butyricum* in the tail. Joint effusion, soft tissue inflammation, proliferation of synovial cells, and inflammatory cellular invasion of the joint are some of the features in this model and are characterized histologically. The NMR technique provided a simple and reliable quantification of fluid content (joint effusion and soft tissue edema) and cellular influx into the joint.

Proton spin-echo signals with 20 echo delays were obtained from a joint of the rat hind leg (± 15 mm from the center of the joint) using selective pulses. Signals were normalized with reference to an external capsule that contained a known amount of water. A single linear gradient was applied continuously during data acquisition, thereby frequency encoding the position of the capsule and of fluid and fat in the leg. The T2 relaxation data of a rat leg joint before (on day 0; normal) and after MFA injection (on day 12, 15, 19, 22 and 28; arthritic) are shown in Fig. 1. A single exponential did not fit the resulting T2 decay but rather suggested a two-component model. The fit to a double exponential yielded two components of NMR-active hydrogen contents with a short T2 (~ 21 ms for normal, ~ 30 ms for arthritic) and a long T2 (~ 79 ms for normal, ~ 110 ms for arthritic) respectively.

As seen in Fig. 2, both the long and short T2 components of hydrogen content are sensitive to the inflammatory process. In the saline-treated MFA rats, the hydrogen contents with long and short T2 increased by factors of ca. 9 and ca. 2 respectively on day 28 in comparison with values in normal control rats. The increase in the long T2 (relatively more mobile) component most likely arose from free fluid (joint effusion and soft tissue edema). Although in principle, T2-weighted MR images can be used to quantify and characterize fluid collections in arthritic joints, the entire T2 relaxation curve, as well as molar concentration of hydrogen can be measured more accurately using the 1D imaging technique. The increase of the short T2 (relatively less mobile) component may have resulted from the infiltration into the joint space of cellular lipids (from inflammatory cells and proliferative synovium) and fibrins.

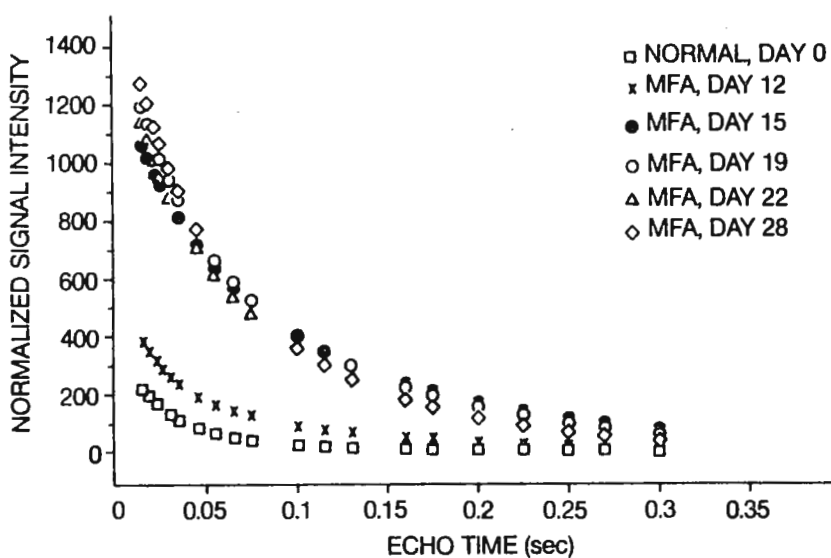


Fig. 1. Integrated and normalized signal intensity from the joint area of a rat hind leg as a function of echo delay. The rat was injected with MFA on day 0 and followed through day 28.

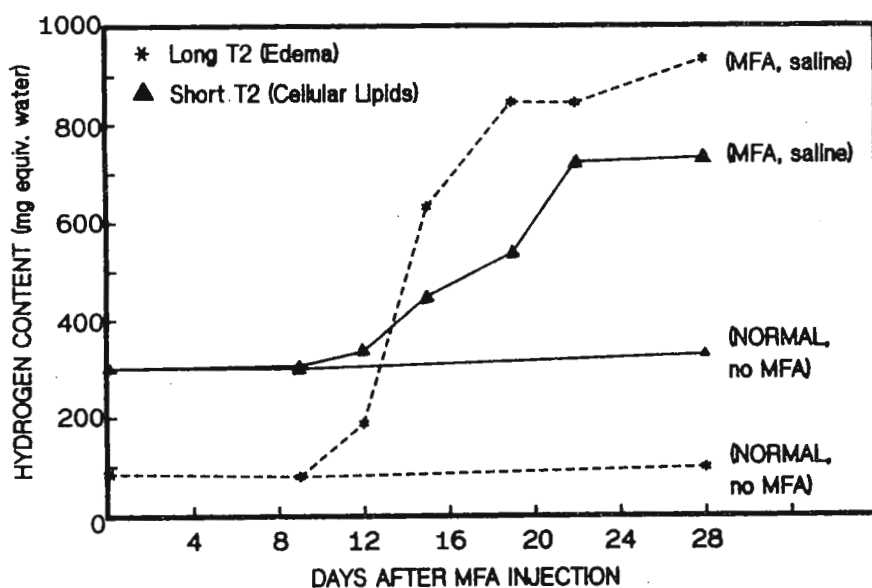


Fig. 2. Two components of hydrogen contents as a function of post-injection period. Each data point is an average of data from five rats.

The one-dimensional imaging technique provides noninvasive and reproducible quantification of selected pathological parameters for evaluating disease activity and therapeutic treatment in experimental arthritis, and may have possible utility in clinical arthritis studies.

The experiments were performed on a GE 2T CSI imaging system at the laboratory of Dr. Nick Szeverenyi (Upstate Medical Center at Syracuse) whose help is gratefully acknowledged. Please credit this contribution to the account of Dr. S. C. Lee.

Sincerely,

Babul

Babul Borah

INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

Place du Château 3, CH - 1005 LAUSANNE (Switzerland)

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

(received 7/11/89) 6.7.1989

A HIGH-PRESSURE, HIGH-RESOLUTION NMR PROBE WORKING AT 400 MHz

Dear Prof. Shapiro,

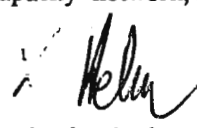
Nuclear magnetic resonance at elevated pressure has been used for studying physical and chemical phenomena since the pioneering work of Benedek and Purcell.¹ Since 1970, several research groups have been demonstrated the possibility of performing NMR measurements at relatively high resolution and pressures of a few hundreds of MPa (1 MPa=10 bar). In 1976 the first high pressure kinetic² FT-NMR experiment was performed with a probe³ having the high spectral resolution and sensitivity required to run mechanistic studies in solution. Later on, a second probe-head was built for a wide-bore superconducting magnet with a magnetic field of 4.7 Tesla.⁴


To take advantage of higher field magnets, giving better spectral resolution and improved signal to noise ratio, we built a high-pressure probe working at 9.4 Tesla. The high-pressure vessel is shown in Figure 1. The main problem was to feed an NMR coil placed inside a metallic vessel with a radio frequency of 400 MHz. This was achieved by a special design of the electrical feedthrough for the rf coil. In Figure 2 the internal components are shown. The two turned coil was made by Spectrospin (Fällanden, CH). To allow precise temperature measurement, the platinum resistor is placed close to the sample. The sample tube consists of an ordinary 5mm tube, cut to the adequate length and closed with two Macor caps.

The high-pressure vessel has a calculated bursting pressure of 450 MPa at 293 K and has been tested up to 250 MPa. We usually use the probe at pressures ranging from 0.1 to 200 MPa. The temperature gradient measured inside the bomb between -40 and 90°C was found to be less than $\pm 0.2^\circ\text{C}$ over the sample region. The temperature stability is better than $\pm 0.2^\circ\text{C}$ over the whole pressure range. A double tuned matching/tuning circuit allows field stabilization using the ^2H -lock.

The linewidth, obtained with a sample containing 0.18% C_6H_6 in CD_3NO_2 without sample spinning, is less than 0.5 Hz (Figure 3). The 90° pulse length is $47\mu\text{s}$ for this solution. The signal to noise of a 0.005 M $\text{Mn}(\text{ClO}_4)_2$ solution in 2.1% H_2O in D_2O is 46:1 compared to 370:1 obtained with a commercial probe using the same sample. The reason for the relatively long 90° pulse and the loss of sensitivity is due to the long distance between the coil and the rf-capacity-network, sitting just above the pressure vessel inside the magnet.


Urban Frey


Dr. Lothar Helm


Prof. A.E. Merbach

¹ G.B. Benedek, E.M. Purcell, *J.Chem.Phys.* **22**, 2008 (1954)

² A.E. Merbach, H. Vanni *Proc. XVIIth Intern. Conf.Coord.Chem. Hamburg*, 269 (1976);

A.E. Merbach, H.Vanni *Helv.Chim.Acta* **60**, 1124 (1977)

³ W.L. Earl, H. Vanni, A.E. Merbach, *J.Magn.Res.* **30**, 571 (1978)

⁴ D.L. Pisaniello, L. Helm, P. Meier, A.E. Merbach, *J.Am.Chem.Soc.* **105**, 4528 (1983)

Fig. 1: Schematic drawing of the high-pressure bomb fitting inside a wide-bore superconducting magnet. (\\ / \\ / \\ / Berylco; \\ / \\ / \\ / Vespel or Macor)

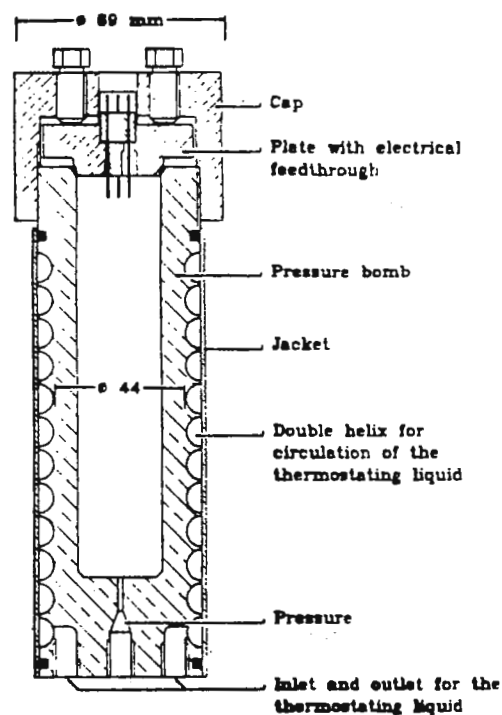
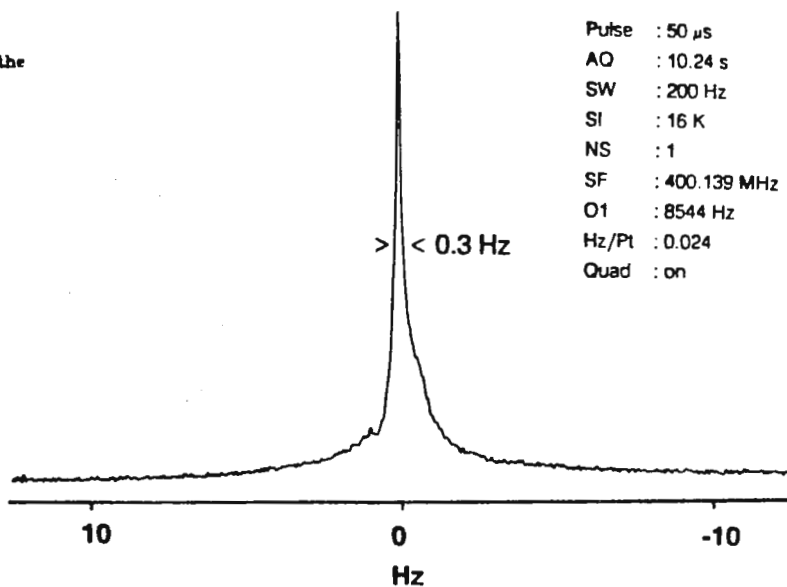
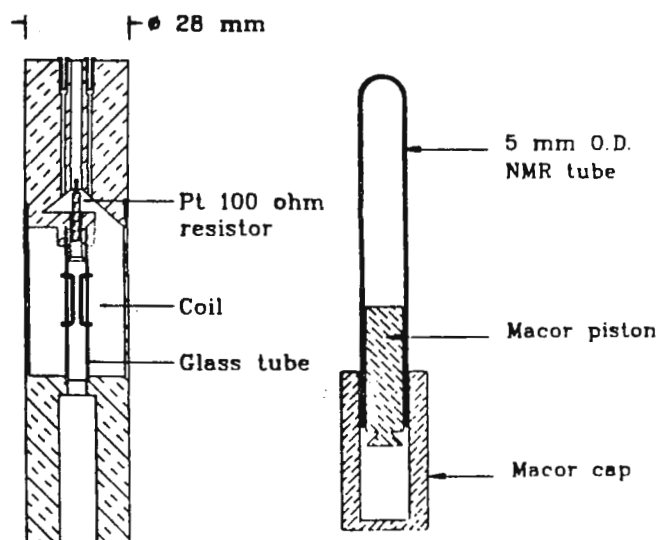


Fig. 3: 400 MHz ^1H -NMR spectrum of 0.18% C_6H_6 in CD_3NO_2 with deuterium lock at ambient temperature.

Fig. 2: Internal components of the bomb made of Vespel (left); and sample tube (right).



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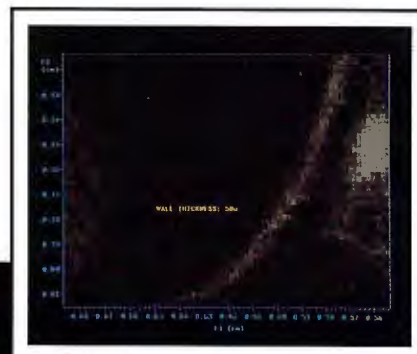
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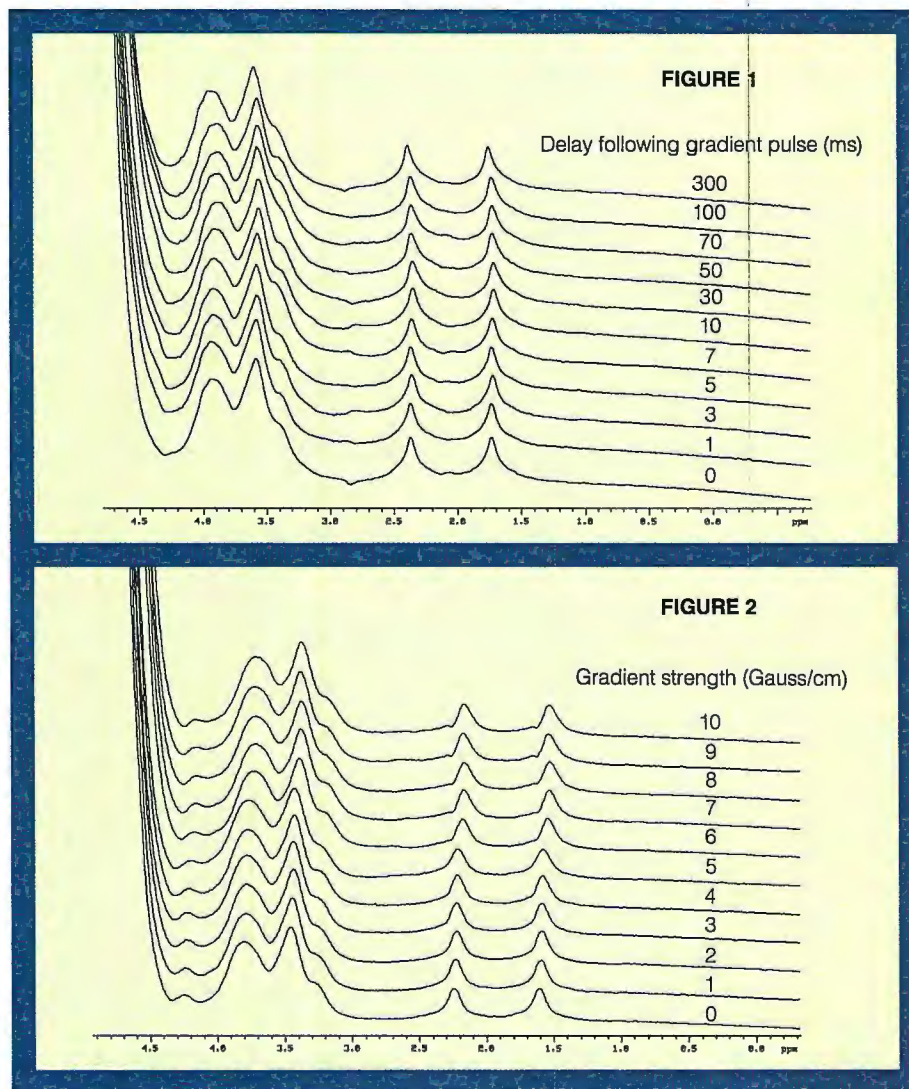


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The excellent control of eddy currents using the smaller gradient insert is demonstrated in Figures 1 and 2. Figure 1 shows a series of spectra of the high field region of a sample containing $[2-^{13}\text{C}]$ acetate and $[1-^{13}\text{C}]$ glucose in $\text{H}_2\text{O}/\text{D}_2\text{O}$. With the sample in the center of the gradient coil, a 1 second gradient pulse of 1 Gauss/cm was applied. The gradient pulse was followed by a variable delay, a 90°



RF pulse and acquisition of the resultant free induction decay. All spectra are essentially undisturbed even at delay times below 10 ms.

Figure 2 shows a typical series of spectra of the same sample at an off-center location in the magnet. A gradient pulse of 5 ms duration with an amplitude range of 0 to 10 Gauss/cm was applied, and the

FID recorded at a fixed delay time of 3 ms. The sample was positioned at 22.3 mm off the center, corresponding to local gradient field of 95 kHz. All spectra are virtually undisturbed, even at 10 Gauss/cm.

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B. L. S.

Mobil Research and Development Corporation

June 26, 1989
(received 6/29/89)

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TAMU NMR Newsletter
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NOE IN C-13 MAS

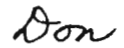
Dear Barry:

We have been interested in quantifying the NMR observable carbon in C-13 MAS measurements of solid fossil fuel materials. The ideal method would be to mix with the sample a suitable intensity standard. This reference should fall outside the chemical shift range of the sample and have suitable spin-lattice relaxation characteristics. We thought that methyl groups might be good candidates to test. We found methyl spin-lattice relaxation times of 0.62 sec in hexamethylbenzene, 1.5 sec in hexaethylbenzene, and 1.8 sec in n-octacosane. All very good. However, when measuring the C-13 methyl peak height as a function of recycle time, we found that the peak height for some samples passes through a maximum at recycle times in the 5 to 13 sec range. This effect is not trivial. For example, the methyl peak height of n-octacosane at 5 sec recycle time is 1.7 times the height at 120 sec recycle time. (Of course, we verified that this effect is not a duty cycle effect in the probe or the console.)

We postulated that this effect is due to NOE. The 20 msec proton decoupling while collecting the FID would cause a NOE enhancement to give an increased carbon signal from the following carbon pulse. When the recycle time is much longer than the spin-lattice relaxation time, the NOE enhancement decays away before the following pulse. When the recycle time is too short, the carbon resonance is partially saturated. To test this postulate, we applied a proton pulse of adjustable duration immediately before the carbon pulse (to avoid cross-polarization, the protons were not irradiated during the carbon pulse). Very long recycle times were used. The proton pre-irradiation pulse durations used were from 5 microseconds to 200 milliseconds (the maximum available on our Chemagnetics M100-S machine). The methyl peak height enhancement factors (200 msec height/5 μ sec height) we found are 1.6 for hexamethylbenzene, 1.3 for hexaethylbenzene, 1.3 for n-octacosane, and 1.9 for the protonated peak (123 ppm) of coronene. Even for a fossil fuel material, gilsonite, we obtained a 1.6 enhancement factor for the aliphatic band.

The possibility of a NOE effect on carbon counting has been mentioned in many papers. However, we do not know of any previous data on the subject. Clearly, proper precautions are in order if accurate quantitation with Bloch decays are to be obtained.

Sincerely,


D. E. Woessner
Senior Research Associate


V. A. McGeehan
Senior Staff Chemist

DEW/mon

cc: T. H. Bushaw

CSI 2T Applications

Shielded Gradients and Localized Spectroscopy

Eddy current effects are the leading cause of errors and lack of consistent results in gradient localization methods. It is not surprising, then, that actively shielded gradients, which have dramatically reduced eddy currents, represent a significant technology advance for all forms of B_0 gradient volume localization and spectroscopic imaging methods. The fast rise time and high gradient strength characteristics of the coil used in these experiments are also important.

Even without pre-emphasis, shielded gradients recover fast enough to obtain spectroscopic information at 1 msec or less after a strong gradient has been turned off (Fig. 1).

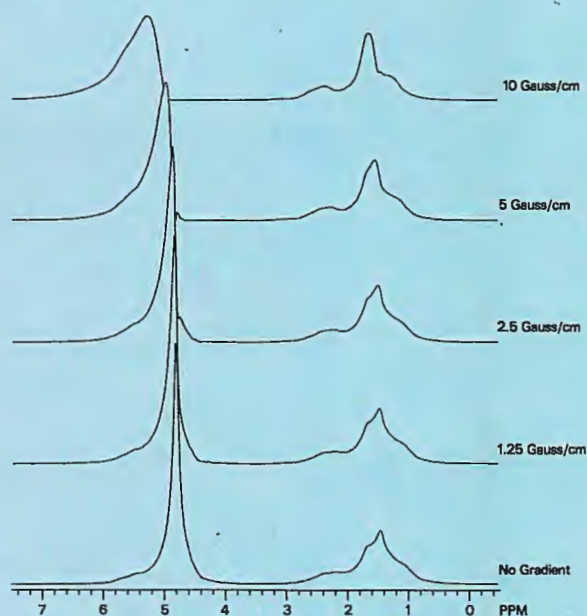


Fig. 1—Using an oil/water phantom, a 10 G/cm gradient will create a water frequency profile extending from 156 KHz to 280 KHz away from normal water resonance. Residual gradient effects of less than 0.01% (50 Hz at 10 G/cm) are observed in a spectrum acquired beginning 1 msec after a 20 msec gradient pulse.

As an example, a 4DFT spectroscopic imaging technique can resolve the four frequency domains that are associated with an NMR signal from an object: x-, y-, z-spatial coordinates and chemical shift δ . The above technique can be a practical alternative to single volume localized spectroscopy. This method allows phosphorous spectra to be obtained from well-defined regions as demonstrated in the following experiment, which was carried out on a GE CSI 2T system using high-strength, shielded gradient coils (Fig. 2). The phase-encode time is kept short (on the order of the dwell-time) to minimize phase-errors in the final spectra, as well as to avoid loss of signal due to T2 decay, which is significantly short in biological phosphates.

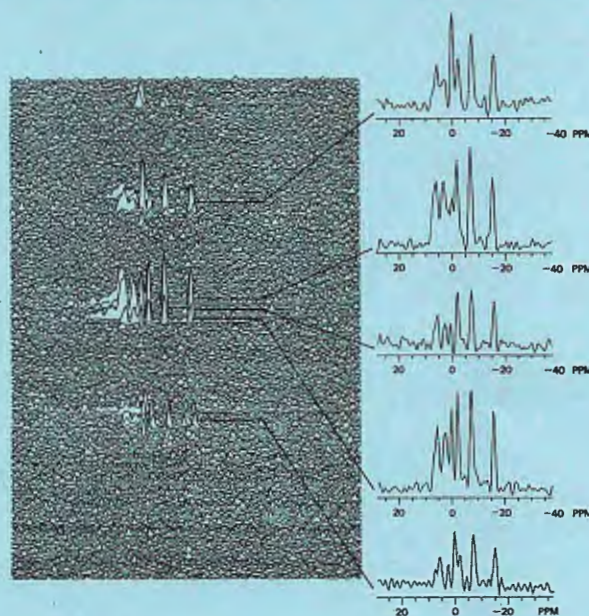


Fig. 2—Stacked plot showing 512 phosphorous spectra from 60 mm cubed region of a live rat. Each trace corresponds to 7.5 mm cubed region (voxel) from within the region of interest. The offset traces clearly show the achievable spectra and spatial resolution of the technique, as well as demonstrating localization of the liver phosphorous metabolites from that of overlying skeletal muscle. Total acquisition and processing time was two hours.



GE NMR Instruments

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A GSX UPGRADE

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

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

For more information, contact JEOL.

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

