TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 424

January 1994

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D-129							
D-14							543 (20)
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FORTHCOMING NMR MEETINGS

Symposium (Mon., a.m., 2/21/94) *Minding the Human Brain via Functional Magnetic Resonance Imaging*, AAAS Annual Meeting, San Francisco, California, **February 18 - 23, 1994**; Contact: AAAS, Meetings Dept., 1333H St., NW, Washington, DC 20005; Phone: (202) 326-6450; Fax: (202) 289-4021.

Advanced Clinical MRI/MRS and C-13 MR Spectroscopy, Dallas, TX **March 10, 1994**; Contact: D. Christensen (214) 648-8013 or N. Bansal at (214) 648-5887. See TAMU NMR Newsletter 424, 48.

International Symposium on Biological NMR, On the Occasion of Professor Oleg Jardetzky's 65th Birthday, Stanford California, **March 24 - 26, 1994**; Contact: Ms. Robin Holbrook, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, California 94305-5055; Fax: (415) 723-2253; See TAMU NMR Newsletter 422, 47.

Symposium on *In Vivo* Magnetic Resonance Spectroscopy VII, Monterey, California, **April 9 - 10, 1994**; Contact: Radiology Postgraduate Education; Room C-324, University of California School of Medicine, San Francisco, CA 94143-0628; Phone: (415) 476-5731; Fax: (415) 476-9213; For registration, call (415) 476-5808; Fax: (415) 476-0318 See TAMU NMR Newsletter 422, 47.

35th ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **April 10 - 15, 1994**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073 See TAMU NMR Newsletter 422, 9.

Gordon Conference on Magnetic Resonance in Biology and Medicine, New England College, Henniker, NH, **July 17 - 22, 1994**; Contact: Dr. Carlyle B. Storm, Director, Gordon Research Conferences, Gordon Research Center; Univ. of Rhode Island, Kingston, RI 02881-0801; Tel. (401) 783-4011 or -3372; Fax: (401) 783-7644.

8th International Symposium on Molecular Recognition and Inclusion, Ottawa, Ontario, Canada, **July 31 - August 5, 1994**; Contact: H. Morin-Dumais, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, ON K1A 0R6, Canada; (613) 993-1212; Fax: (613) 954-5242 See TAMU NMR Newsletter 419 34

Solid-State NMR Symposium, 36th Rocky Mountain Conference on Analytical Spectroscopy, Denver, CO, **July 31 - August 5, 1994**; Contact: R. E. Botto, Chemistry Divn., Argonne Natl. Lab., Argonne, IL 60439; (708) 522-3524; Fax: (708) 252-92882 See TAMU NMR Newsletter 424, 46.

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NORTHWESTERN UNIVERSITY

Joseph B. Lambert
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December 13, 1993
(received 12/17/93)

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

Dear Barry:

We have continued our study of dynamic effects in the spectra of five-membered rings in the solid state. Previously (*J. Am. Chem. Soc.*, **113**, 8958-8960 (1991)) we reported that the ^{13}C spectrum of solid cyclopentanol decoalesces into at least four sets of resonances per carbon and that of sulfolane into two sets per carbon. We have now examined most of the simple five-membered rings and a few of the analogous six-membered rings. Some of these spectra, including those of cyclopentanone and possibly tetrahydrothiophene 1-oxide, decoalesce at or near the freezing point. Other examples, including cyclopentanol, sulfolane, cyclohexanol, cyclohexanone, and possibly *trans*-1,2-cyclopentanediol, are globular molecules that freeze into a plastic phase that retains some rotational motion. These latter spectra in the solid state closely resemble those in the liquid state, and cross polarization is not needed to obtain the spectra. Below the plastic-to-nonplastic transition, however, these molecules lose their rotational freedom and the spectra exhibit decoalescence. Cross polarization is required, and carbonyl resonances show spinning sidebands.

The slow-exchange spectra of cyclopentanone, 1-methylcyclopentanol, cyclohexanol, and *trans*-1,2-cyclohexanediol contain two peaks of equal intensity for certain carbons. Such an observation may arise either from the presence of equally populated species (conformers, positional isomers, or crystallographic sites, or from a single form with two sites that can exchange to a single averaged site upon the onset of molecular rotation. For the case of cyclopentanone, the latter explanation is excluded, because the carbonyl carbon splits into two, which is possible only when two forms are present.

X-ray structures for these five-membered rings have not been reported, presumably because of the complex phase behavior or the presence of multiple forms in the crystal. Thus it devolves upon NMR to unravel the complex structural situation for these common molecules in the solid state.

Sincerely

Joseph B. Lambert

Suzanne C. Johnson

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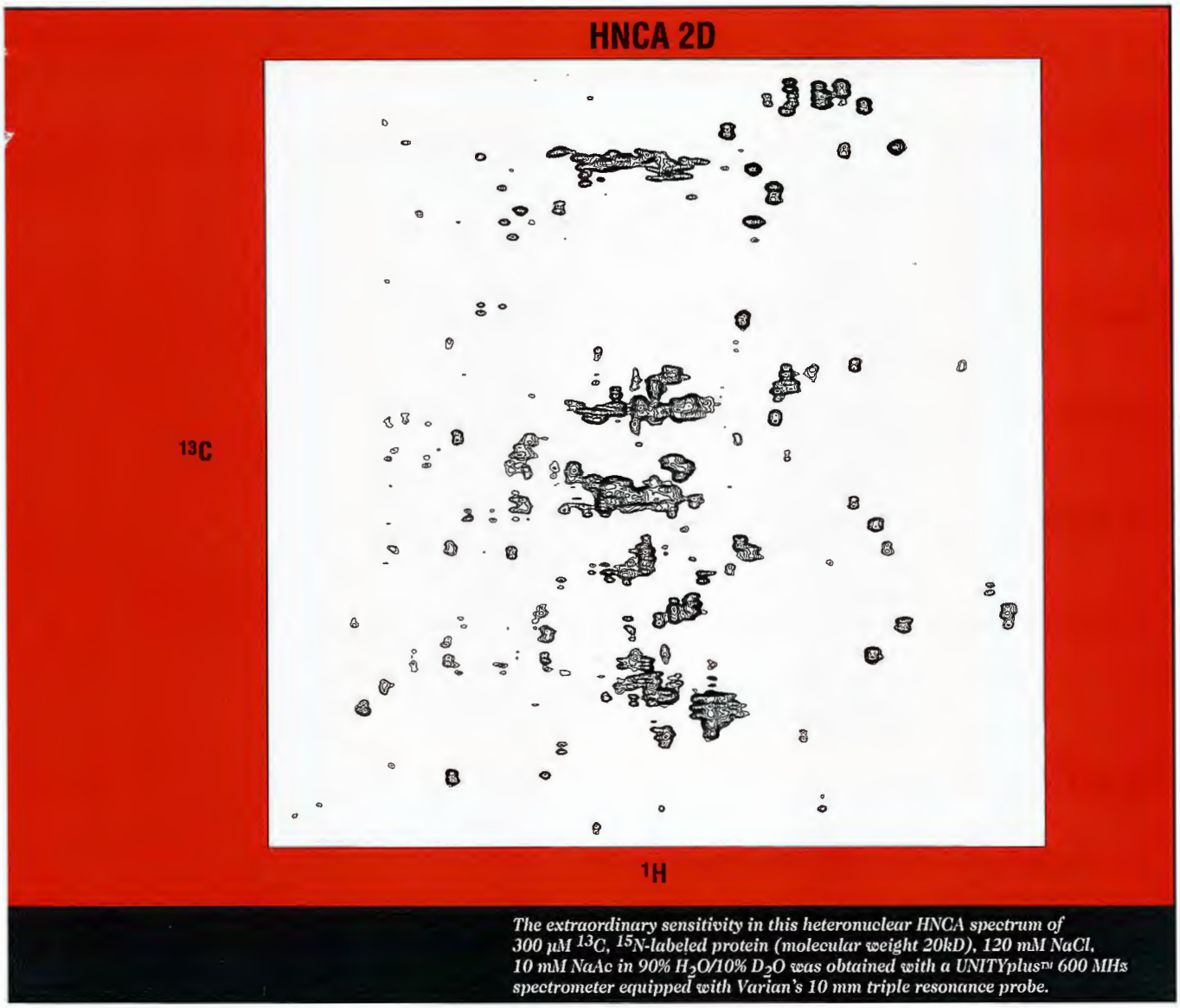

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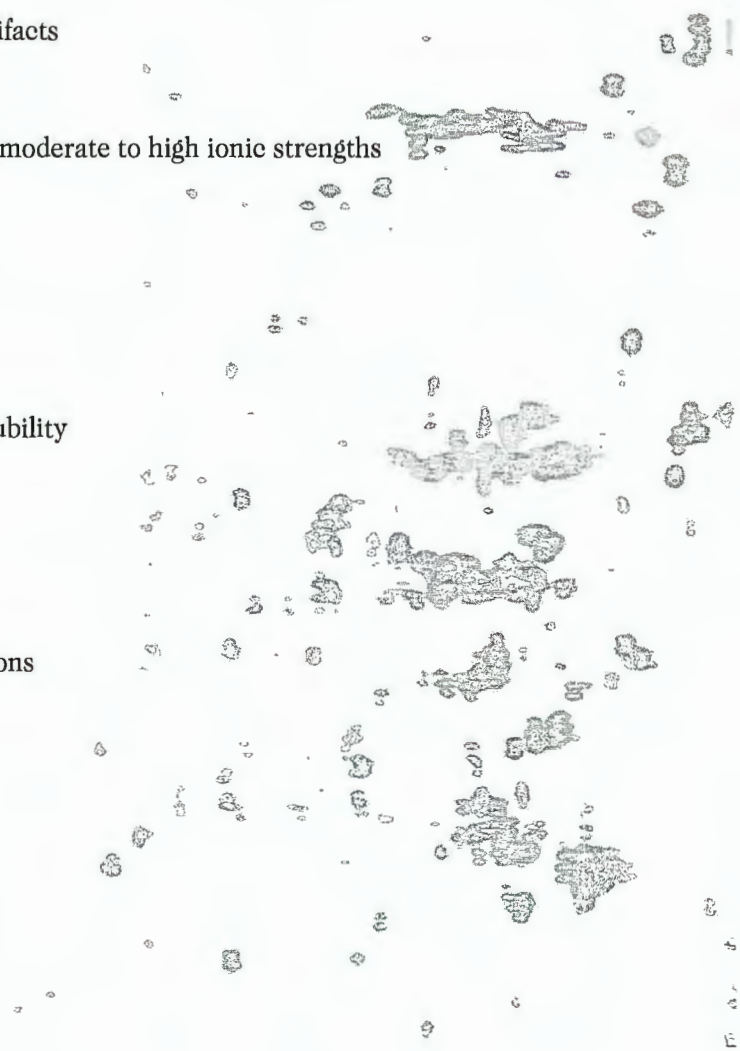

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CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

Division of Chemistry and Chemical Engineering
Gates and Crellin Laboratories of Chemistry

John D. Roberts
Institute Professor of Chemistry, Emeritus and Lecturer

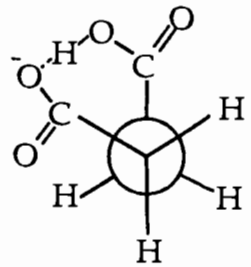
December 15, 1993
(received 12/17/93)

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

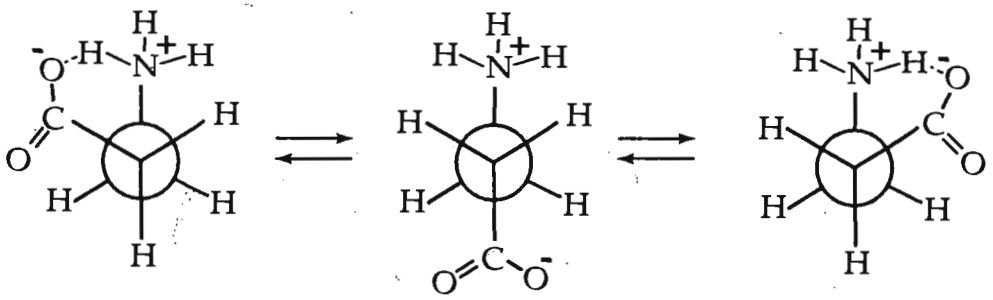
Dear Barry:

For some time now, I have been interested in the presumably worn-out field of application of NMR to conformational analysis of ethane derivatives. It turns out that, not only are there a gaggle of unsolved or unresolved problems, but the field is especially useful for me because of my interest in helping undergraduates get started with research. It works well for undergraduate research because it can be started early on without much knowledge of organic chemistry and the needed NMR can be picked up fairly easily.

Among the interesting paradoxes in this area of research has to do with conformational preferences in water solution. We have just published (Lit, E.S.; Mallon, F.K.; Tsai, H.Y.; Roberts, J.D. *J. Am. Chem. Soc.* **1993**, *115*, 9563-9567, an account of our studies of the changes of conformation of succinic acid with pH (a problem that we pointed out had some interest in a prior TAMU NMR submission, November 1986, #338, p. 12). The gist of the pH effects is that they are not large and not quite what one would expect from conventional wisdom about hydrogen bonds and electrostatic effects. Of course there are nagging uncertainties, because of the necessity to predict what the coupling constants should be for the individual conformations, for example using procedures like those of Haasnoot-Altona, and how close the rotational angles will be to the perfect staggered values. The best we could do indicated that the diacid, the monoanion and the dianion were about 80%, 70% and 43% *gauche*, respectively. As I said, the preferences are not large and one might be surprised that there is not more *gauche* for the monoanion, which conformation could be stabilized by hydrogen bonding.



More disturbing (if you believe in conventional wisdom) even than these results are those reported by Abraham and Hudson, *J. Chem. Soc, Perkin Trans. II 1986*, 1635-



1640, almost without comment, that the vicinal proton--proton couplings of β-alanine indicate that all three of the possible conformations exist in essentially the distribution expected by statistics of two *gauche* to one *trans*, **independent** of pH! This is especially troublesome for the dipolar ion for which one would expect both a favorable electrostatic, and perhaps hydrogen-bond stabilization as well, for the *gauche* conformation. Because we have measured rather different couplings with succinic acid at high pH than Abraham and Hudson reported, Diana Fort, an excellent summer undergraduate research student from Toronto repeated their experiments with pH on β-alanine and found good agreement.

Because of the rather surprising results with the dipolar ion, Diana also measured the vicinal couplings at 5° and 85° to see if there was a sizable effect that could be ascribed to entropy. However, over an 80° difference in temperature, the change in J_{13} was only about 0.2 Hz and in J_{14} only 0.4 Hz, so the effect at best is small. In addition to the examples supplied by Abraham and Hudson, we have looked at several other cases where electrostatic influences and/or hydrogen bonding might be expected to be important. We can only conclude that, while the conventional wisdom may often predict the proper direction that conformational equilibria will take in water solution, the predicted effects will usually be too small by an order of magnitude. The only exceptions are when truly bulky groups are involved, so that steric hindrance is clearly evident.

It would seem that either there must be some compensating balance between steric hindrance arising from solvation, electrostatic attractions and repulsions, entropic influences, solvent structures, hydrogen bondings, and so on, or else these effects must all be small. I wish I knew which.

Best wishes,

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Jack

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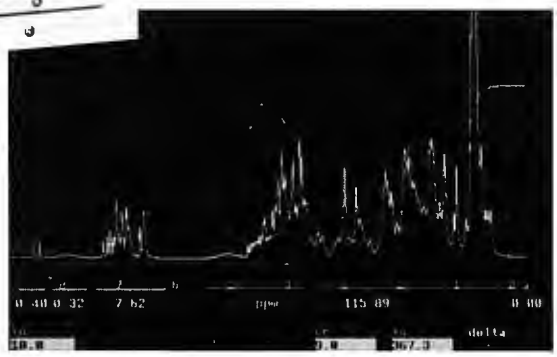

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NMR LABORATORY
381 Royal Parade, Parkville 3052, AUSTRALIA

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

November 29, 1993
(received 12/4/93)

Dear Dr. Shapiro,

Multiple Conformations of Anthopleurin-A in Solution

Anthopleurin-A (AP-A) is a member of a class of sea anemone-derived polypeptides which interact with the voltage-gated sodium channel. In the mammalian heart this results in delayed inactivation of the channel, producing a positive inotropic effect without affecting blood pressure or heart rate.

We have been interested for some time in the elucidating the 3D structure and structure-function relationships of AP-A, and have published a low-resolution structure of AP-A (1) and a higher-resolution structure of the related polypeptide ShI (2). Even in our early studies at 300 MHz, it was clear that AP-A had far too many NMR resonances for a protein of 49 residues. We suggested then that this reflected conformational heterogeneity and that the origin of this was *cis-trans* isomerism of the Gly40-Pro41 peptide bond (3). Although we were subsequently able to confirm that conformational heterogeneity was indeed the cause of the observed peak splitting (4), it proved frustratingly difficult to confirm the role of Pro41 because of peak overlap, even at 500MHz.

With access to an AMX-600 spectrometer, we have now recorded new data on AP-A, which are being used to refine its structure in solution. The new spectra have had two spin-offs, which are the subject of this (much overdue) contribution:

i) We now have complete assignments for resonances from the major conformer of AP-A and a nearly complete set for the minor. As a result, we are able to confirm that *cis-trans* isomerism of the Gly40-Pro41 peptide bond is indeed the cause of the major peak splitting noted previously. Interestingly, however, the major conformer adopts the *cis* configuration, as indicated by the observation of Gly40 $C^{\alpha}H$ to Pro41 $C^{\alpha}H$ sequential connectivities for the major form and $C^{\alpha}H$-$C^{\delta}H$ connectivities for the minor, as shown in Figure 1A. A 2D HMQC spectrum of AP-A at natural abundance (Figure 1B) provides further support for this, with the chemical shifts of the Pro41 C^{β} resonances in the major and minor conformations being 33.5 and 30.2 ppm, respectively, in close agreement with the values of 33.1 and 30.6 ppm observed in the *cis* and *trans* forms, respectively, of model peptides. The two conformations are in slow exchange at ambient temperatures, but in a NOESY spectrum at 315 K, a chemical exchange cross peak is observed between the major and minor resonances of the well resolved Cys46NH proton.

ii) In addition to the peak splitting due to Gly40-Pro41 peptide bond isomerism, another form of conformational heterogeneity is also present in the molecule, as reflected in the observation of as many as four distinct resonances for several protons. This is illustrated in Figure 2. The relative intensities of the peaks are approximately 18:9:1:1. As these peaks are present in spectra of both AP-A purified from *Anthopleura xanthogrammica* and synthetic AP-A (5), it is unlikely that they are chemical contaminants. Rather, they appear to reflect additional conformational heterogeneity in the molecule. So having sorted out one source of heterogeneity in AP-A, we now have to identify another! In a wider context, it is likely that the presence of minor conformers of proteins in solution is more common than previously thought, and that high field NMR will identify many other examples.

(1) Torda, A.E., Mabbutt, B.C., van Gunsteren, W.F. & Norton, R.S. (1988)*FEBS Lett. 239,* 266-270.
(2) Fogh, R.H., Kem,W.R. & Norton, R.S. (1990) *J. Biol. Chem. 265,* 13016-13028; Wilcox, G.R., Fogh, R.H. & Norton, R.S. (1993) *J. Biol. Chem.,* in press.
(3) Gooley, P.R., Blunt, J.W. & Norton, R.S. (1984)*FEBS Lett. 174,* 15-19.
(4) Gooley, P.R., Blunt, J.W., Beress, L. & Norton, R.S. (1988)*Biopolymers 27,* 1143-1157.
(5) Pennington, M.W., Zadenberg, I., Byrnes, M.E., Norton, R.S. & Kem, W.R. *Int. J. Pept. Protein Res.*, in press.

Multiple Conformations of Anthopleurin-A in Solution

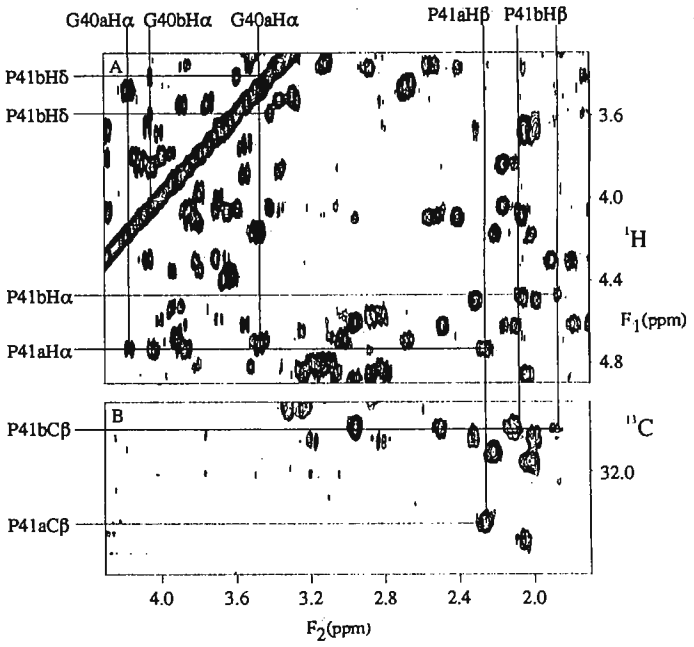


Figure 1. (A) Part of the aliphatic region of a 200ms mixing time NOESY spectrum of AP-A in D_2O at 600MHz, pH 4.8 and 300K. Sequential connectivities between proton resonances of Gly40 and Pro41 in both major (a) and minor (b) conformations are highlighted. (B) ^1H-^{13}C HMQC spectrum of AP-A (3.5mM) in 90%H_2O/10%D_2O at 500MHz, pH 4.8 and 298K.

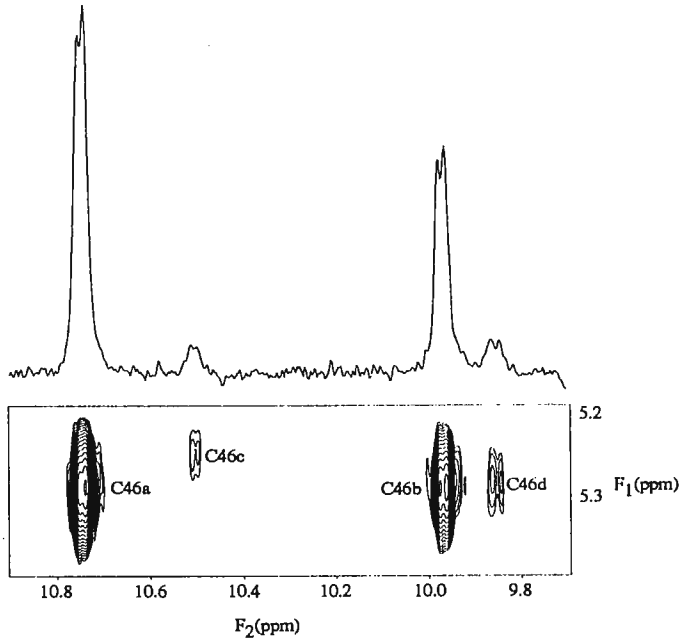


Figure 2. Part of the amide to aliphatic region of a 70ms TOCSY spectrum of AP-A in 90%H_2O/10%D_2O at pH 4.8 and 300K. Cross peaks arising from the four distinct conformations of Cys46NH are shown. The projection was calculated by summing all rows of the displayed region.

Sincerely,

Martin J. Scanlon

Raymond S. Norton

BRUKER

INTRODUCING THE QXI™ PROBE SERIES

QUADRUPLE RESONANCE X-NUCLEUS DECOUPLING INVERSE PROBES

Bruker introduces a new series of 5 mm quadruple-resonance inverse probes for 4-channel high-field AMX or AVANCE DMX spectrometers. These new high performance water suppression probes are aimed specifically at the special requirements of our NMR customers who work with labeled oligonucleotides or with nucleic acids forming complexes with fully-labeled proteins and peptides. This new probe series is called QXI™ and offers proton observation, and simultaneous decoupling of phosphorus, carbon, and nitrogen and of course still provides for a deuterium lock.

Some possible applications include (i) ^{31}P - ^{13}C - ^{15}N magnetization transfers in labeled oligonucleotides, (ii) decoupling of ^{31}P to avoid sensitivity losses during ^{13}C - ^{15}N magnetization transfers in labeled oligonucleotides, or (iii) just a convenient way of measuring both $^{1}H/^{13}C/^{15}N$ and $^{1}H/^{13}C/^{31}P$ triple-resonance experiments with the same probe.

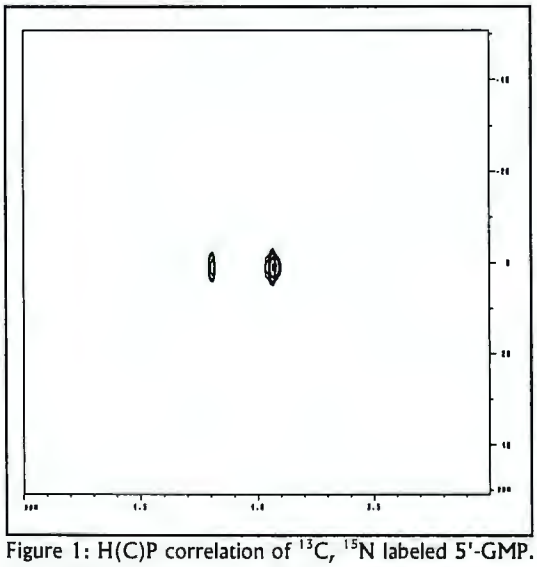


Figure 1: H(C)P correlation of ^{13}C, ^{15}N labeled 5'-GMP. The H(5',5")-P and H(4')-(C(4'))-P cross peaks are shown.

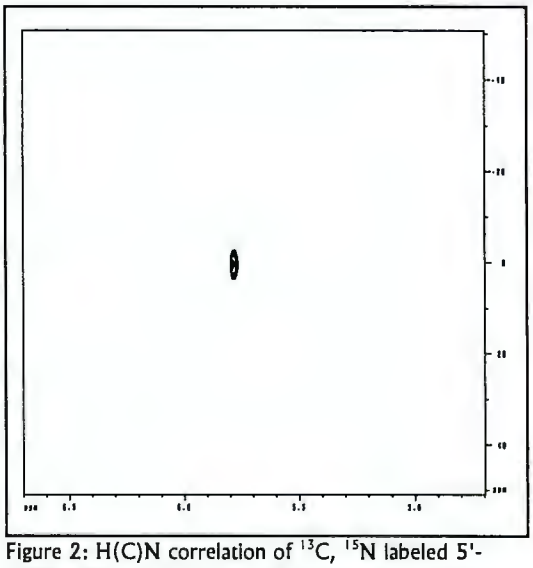
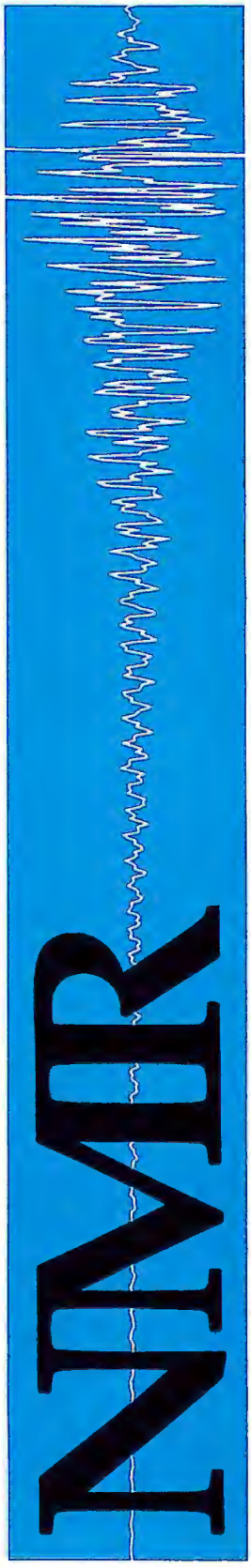


Figure 2: H(C)N correlation of ^{13}C, ^{15}N labeled 5'-GMP. The H(1')-(C(1'))-N(9) cross peak is shown.



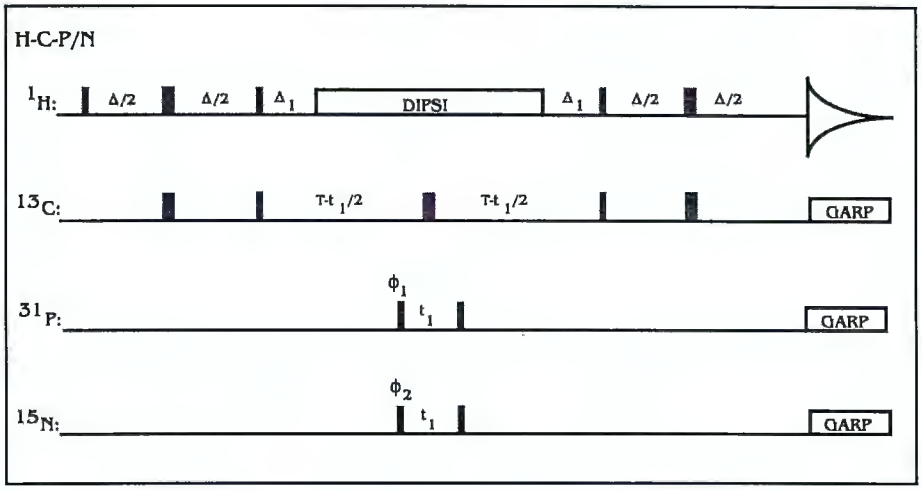


Figure 3: Pulse sequence of a simultaneous H(C)P and H(C)N experiment of ^{13}C, ^{15}N labeled 5'-GMP provided by Prof. G. King, University of New South Wales. The sets of experiments are acquired one with $\phi_1=0,2$; $\phi_2=0,2$; $\phi_{rec}=0,2$ and the other with $\phi_1=0,2$; $\phi_2=2,0$; $\phi_{rec}=0,2$. Summation of the two experiments yields the H(C)P correlation, subtraction the H(C)N correlation. Parameters: $\Delta=3.24$ ms, $\Delta_1=2.2$ ms, T=24 ms, 256 complex points in t_1 were recorded with 4 scans per increment; 1024 complex points in t_2. The spectra were recorded with a ^1H, ^{13}C, ^{15}N, ^{31}P probe on an AMX600 by H.Schwalbe, J.W. Goethe University, Frankfurt.

For a 600 MHz QXI probe we can specify proton sensitivity at S/N > 550:1 for 0.1% EB. The following 90° pulse widths are specified for an AVANCE™ DMX600:

^1H	< 10 microsec
^{31}P	< 20 microsec
^{13}C	< 15 microsec
^{15}N	< 45 microsec

This extremely good proton and inverse sensitivity and excellent phosphorus, carbon and nitrogen bandwidths should allow very demanding biological NMR experiments. The resolution, non-spinning and spinning lineshape of the QXI probes are identical in performance to Bruker's 5 mm TXI triple resonance inverse probes, which are in wide use among our customers.

In conclusion, the excellent sensitivity, short pulse widths and good resolution and lineshape of the QXI-series are ideally suited for demanding nucleic acid and other NMR experiments in water. We anticipate that the experiment shown here, will be the first in an entirely new family of NMR experiments geared towards nucleic acids research, which are technically feasible for the first time with the innovative QXI design. For more details please contact your nearest Bruker representative or applications laboratory.

Acknowledgements: We thank Prof. C. Griesinger for insightful discussions.

THE UPJOHN COMPANY

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Chemical Division

November 15, 1993 (received 12/6/93)

Dear Dr. Shapiro:

Most of our work involves supporting the process development efforts of the pharmaceutical chemists in the Chemical Division. This means rapidly identifying the exact structure of an impurity as well as providing routine 1D NMR service work. In order to devote more time to identification activities we long ago automated the acquisition and processing of 1D NMR data so that the chemists could acquire spectral data directly. The most labor intensive aspect of acquiring these data is plotting the resulting spectra and, as such, we would like to share with you some of the microprograms written over the years to lessen the burden.

The set of 1D NMR experiments provided to the chemists is one ^{1}H spectrum and three ^{13}C spectra (a fully decoupled (CPD), a DEPT90, and a DEPT135). The ^{13}C data is most easily interpreted when presented on a single sheet of paper as a stacked plot, as in figure 1. These experiments were acquired on a Bruker AMX instrument using the standard set of automation routines. To plot in this manner go into EDP and set the AUNMP parameter to 'proc_no' for the first two ^{13}C experiments (i.e. CPD and D135). Set the third experiment to 'PLOTCPDEPTS', which is a program written in-house to plot the spectra on a single sheet of 11x17 paper. Figure 2 lists the program with the appropriate documentation. 'PLOTCPDEPTS' requires three parameter files, 'HP75CPD', 'HP75D135', and 'HP75D90', which contain only 'plot' and 'outd' information. The contents of the 'plot' files are accessible through EDG and presented in figure 3.

Those of you using the automation routines on Bruker AM systems should use the program listed in figure 4 ('post.au'). This routine differs from Bruker's 'pr4d.au' program in that the acquisition files can be prepared as 'combined standard experiments' instead of as pseudo 2D experiments. Please note that in each of the three ^{13}C acquisition programs the line 'wr CPD' (or DEPT90 or DEPT135) must be added after the 'wr @' in the appropriate 'X0_.AU' files. These temporary data files are required by the processing routine 'post.au'. (The reason for this escapes us for the moment. It has been two years since we retired our AM systems and our memories are rusty.) As in the above case the first two ^{13}C's should not be immediately processed and should use the 'prno.au' processing program modified as in figure 5.

Sincerely yours,

Stephen Grode Mark Mowery Russ Gillis

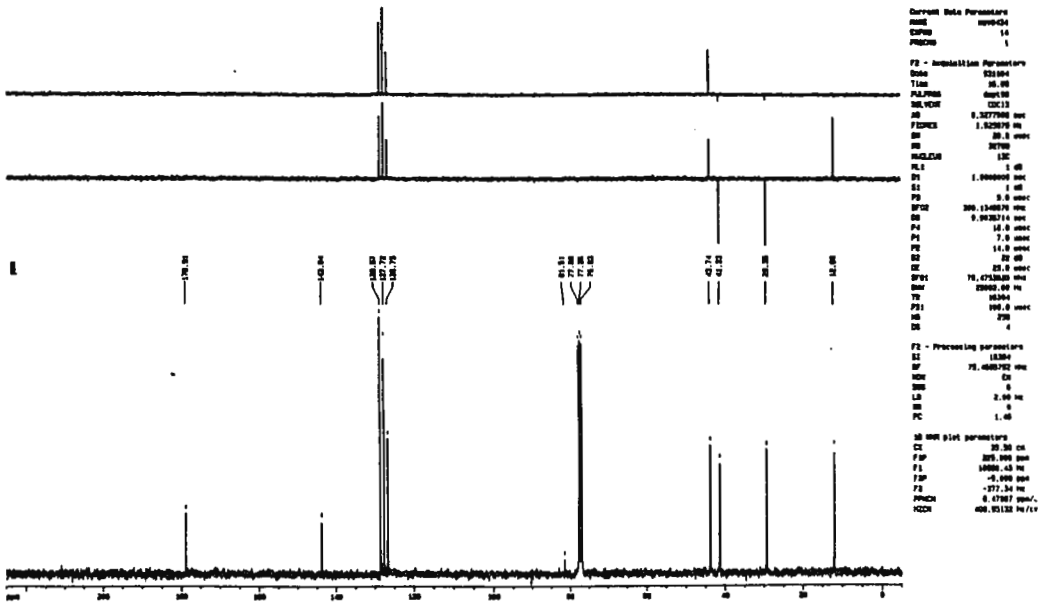


Figure 1. ^{13}C-NMR spectral data: Lower CPD, middle DEPT135, and upper DEPT90.

```
/* PLOTCPDEPTS*/

/* The data is acquired in the order CPD, D135, D90 so the current
data file is decremented two experiment numbers.*/
GETCURDATA
DEXPNO
DEXPNO

/* The data is transformed and referenced.*/
EM
FT
APK
ABS
SREF

/* Parameter files to plot the CPD are retrieved and the plot suspended. */
RPAR("HP75CPD", "all")
PLOTS

/* The D135 experiment is retrieved, transformed, and referenced (to the CPD). */
IEXPNO
EM
FT
APK
ABS
SREF

/* Parameter files to plot the D135 are retrieved and the plot suspended. */
RPAR("HP75D135", "all")
PLOTS

/* The D90 experiment is retrieved, transformed, and referenced (to the CPD). */
IEXPNO
EM
FT
APK
SREF

/* Parameter files to plot the D90 are retrieved and the plot suspended. */
RPAR("HP75D90", "all")
PLOTS

/* The suspended plots are 'flushed' and the macro ends. */
FLPLOT
QUIT
```

Figure 2. A listing of the program PLOTCPDEPTS (see text).

	HP75CPD	HP75D135	HP75D90
EDSPEC			
SXLEFT	0	0	0
SYLEFT	0	12	18
CX	35	35	35
SHEI	12	6	6
F1P	225	225	225
F2P	-5	-5	-5
DHEI	8	6	6
SZERO	.8	3	.7
X-AXIS	YES	NO	NO
TITLE	NO	NO	YES
EDTITLE			
TXLEFT			0
TYLEFT			24
TPOS			TOP
TOFFSET			0
TWIDTH			36
TMARGIN			0
TCHAR			2
PARAM	NO	NO	YES
EDPARAM			
PXULEFT			36
PYULEFT			24
PWIDTH			7
PCHAR			2
PLABELS	YES	NO	NO
EDPLABL			
PLHEI	2		
PLCHAR	2		
PLMARK	YES		
PLUNIT	PPM		
PLMUL	NO		

Figure 3. The contents to the 'plot' subroutine in the HP75* files.

```
;POST.AU

;Wait for last experiment to finish, read in temporary data file and processing file.
1       WAIT
2       RE @
3       RE CPD
4       PJ CPDP

;Process and reference CPD.
5       EM1
6       GM1
7       FT
8       APK
9       SRE1
10      WJ CPDP

;Reference DEPT experiments.
11      PJ DEPTA
12      SRE1
13      WJ DEPTA
14      PJ DEPTB
15      SRE1
16      WJ DEPTB

;Plot CPD, DEPT90, and DEPT135.
17      PJ CPDP
18      PX1
19      PP1
20      DEL CPD
21      RE DEPT90
22      EM1
23      GM1
24      FT
25      PJ DEPTA
26      APK
27      PX1
28      DEL DEPT90
29      RE DEPT135
30      EM1
31      GM1
32      FT
33      PJ DEPTB
34      APK
35      PX1
36      DEL DEPT135
37      NP
38      EXIT

;Parameter recommendations for CPDP.001, DEPTA.001, and DEPTB.001 are:
;       CPDP.001:  CY=MAXY=9, DPO offset=-.5, TITLES=NO, PARAMETERS=NO,
;       PEAK PICK=P
;       DEPTA.001:  CY=MAXY=3.8, DPO offset=19, TITLES=YES, PARAMETERS=YES
;       DEPTB.001:  CY=MAXY=3.8, DPO offset=15.2
```

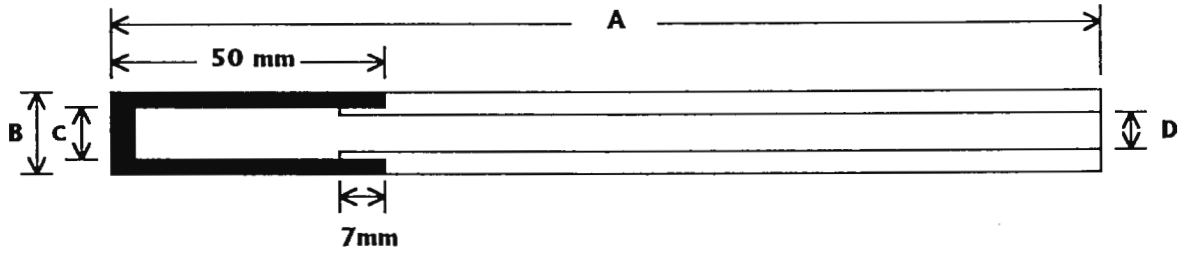
Figure 4. A listing of the program 'post.au' (see text).

```
;PRNO.AU

;Does not process experiment.

1       WAIT
2       RE @
3       EXIT
```

Figure 5. A listing of the program 'prno.au'.

ALUMINA TUBE FOR ^{29}Si AND ^{11}B NMR

Shigemi CO. has recently developed an unique alumina tube for ^{29}Si and ^{11}B NMR. The construction of the tube consists of a standard glass NMR tube connected to a highly densified alumina bottom which holds your sample. By using our alumina tube, the ^{29}Si spectrum is free from a broad ^{29}Si signal and the spinning sidebands are suppressed to a minimum owning to its precision and quality. As of now, only Shigemi can offer you this very specialized and high quality tube for a reasonable price.



Type	A Length (mm)	B OD (mm)	C ID (mm)	D ID (mm)	Camber (μ)
Si-005	180	4.965 + 0 − 0.005	4.0 ± 0.1	3	± 0.02
Si-010	190	10.0 + 0 − 0.01	9.0 ± 0.1	7.8	± 0.02

Type	Diameter	Price for 5 tubes
Si-005	5mm	$300.00
Si-010	10mm	$400.00

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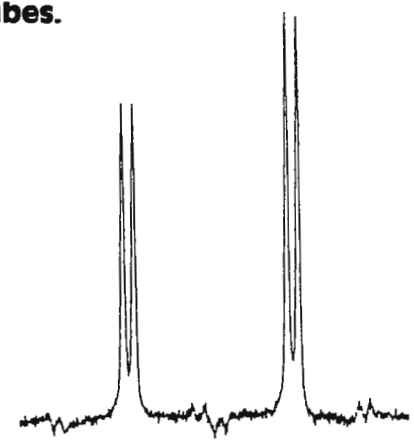
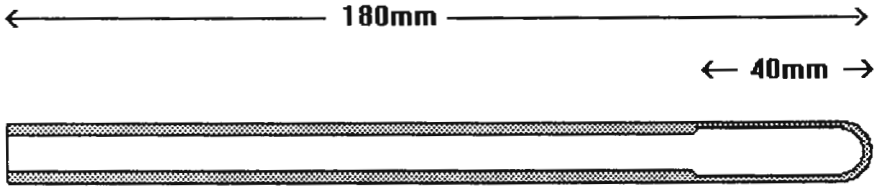
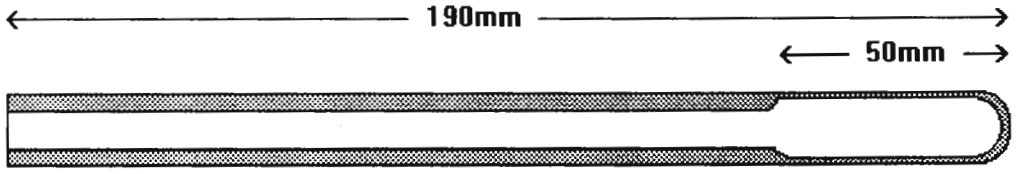


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



PST-001 and PST-002



ST8-001,ST8-002, ST10-001, and ST10-002

O.D. (mm)	Product Number	Wall (mm)	Concen-tricity/Camber (μ)	OD (mm)	ID (mm)	Price Each 1-99	Price Each 100+
5	PST-001	0.21	20/ 8	4.96 + 0.00 - 0.01	4.54 ± 0.01	$15.00	$13.50
	PST-002	0.21	40/15	4.96 + 0.00 - 0.01	4.54 ± 0.01	$13.00	$12.00
8	ST8-001	0.25	40/ 8	8.00 + 0.00 - 0.01	7.52 ± 0.01	$31.00	$28.00
	ST8-002	0.25	50/15	8.00 + 0.00 - 0.01	7.52 ± 0.01	$27.00	$25.00
10	ST10-001	0.25	40/ 8	9.98 + 0.00 - 0.01	9.52 ± 0.01	$36.00	$32.00
	ST10-002	0.25	50/15	9.98 + 0.00 - 0.01	9.52 ± 0.01	$32.00	$28.00

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Department of Physics

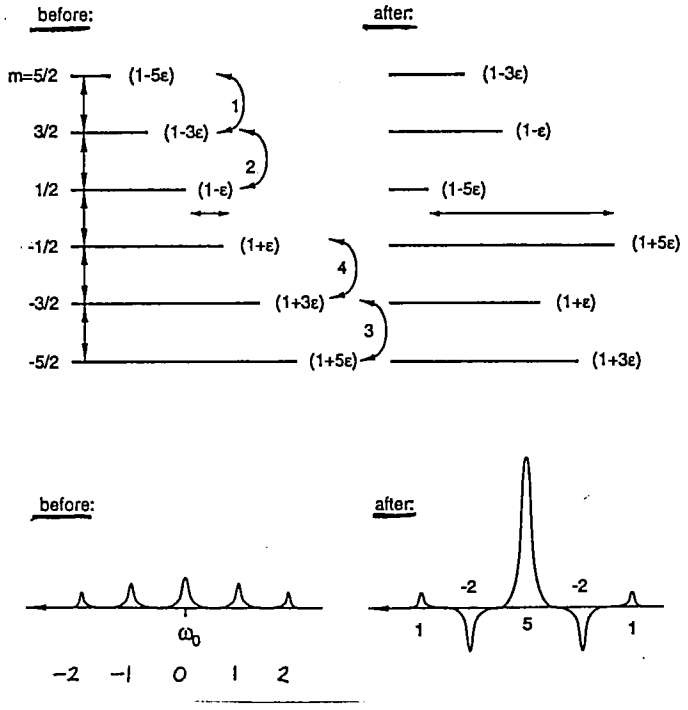
November 29, 1993
(received 12/6/93)

Dear Dr. Shapiro:

We recently reported a simple scheme for enhancing the sensitivity of central transition NMR of half-integer quadrupolar nuclei (Chem. Phys. Lett. **209**, 287, (1993)). In the present letter we discuss some of the practical aspects of the technique (probe, rf level, and frequency sources).

The basic technique is really pretty simple. The energy levels and NMR spectrum of a spin–5/2 is shown in Fig. 1 below, for the case of $\omega_Q << \omega_0$. There are five resonance transitions (2, 1, 0, -1, -2). The Boltzmann equilibrium populations are shown in Fig. 1, with $\varepsilon = \hbar\omega_0/2kT << 1$. At equilibrium, the population difference of the m = ± ½ levels is 2ε. By *selectively inverting* the satellite transitions *in the order* 2, 1, -2, -1 (or -2, -1, 2, 1), the population of m = 5/2 is transferred to the m = ½ level (and -5/2 to -½). The resulting poulations are shown in Fig. 1. The population difference of the m = ± ½ levels has been increased to 10ε, a ×5 increase in sensitivity for any subsequent experiment on the central transition.

Figure 1



In powders and glasses the satellite transitions are inhomogeneously broadened and are unresolvable. Thus, inversion by selective π pulses is not possible. But it is easy to invert the satellite transitions by *adiabatic passages*. The frequency of the rf carrier is started above the highest expected satellite and swept down in frequency, ending just above the central transition (~ 50 kHz above). As shown in Fig. 2, the process is repeated for the low frequency satellites. This procedure automatically inverts the satellites in the order 2, 1, -2, -1. In practice, a sensitivity enhancement of 4.0-4.5 is obtained for spins–5/2 (^{27}Al, ^{17}O). In general, the ideal enhancement is a factor of 2I. We note that no fussy adjustments are required: the technique simply works.

Experimental requirements: relatively low **rf powers** are adequate for the sweep. Typically, the sweep may last 5 - 20 ms with $\gamma H_1/2\pi$ = 5 kHz (as measured in solution). We commonly use a 25 watt transmitter with 5 mm samples.

For **frequency sources**, we employ an FM generator. The HP 8640 B is particularly nice, but has a narrow FM range (± 3%). The FM range can be increased by running the FM generator at a high frequency (e.g. 400 MHz) and heterodyning it down against a stable source (e.g., a synthesizer). We drive the FM input with a DAC mounted in our spectrometer's control computer. RC filtering makes the frequency vary smoothly, and not step-like. We sometimes use the FM source for the rf sweeping and a synthesizer for inspecting the central transition; this is a nearly ideal arrangement. We switch between the rf sources with a PIN-diode switch (as in Mini-Circuits' catalog).

The **probe** must be broadband (low Q) for the rf sweeps. But detection with a low Q probe would kill the sensitivity! So we use a probe that has both high Q and low Q ports (Fig. 3). The high-Q port is coupled to a tap on L; the tap position is adjusted to give 50 Ω resistive. The low Q tap, up higher on the coil, is *overcoupled*; thus the transmitter's output impedance broadens the resonance. Moving the tap up (away from ground) further decreases Q. To switch between the low Q and high Q ports we have used a coax relay (~ 50 ms operating time). The sweep uses low Q; the inspection pulses and detection use high Q. We have also used crossed diodes for switching (Fig. 3), with rf sweep and inspection pulses using low Q and detection using high Q. Both schemes work well. Since the low Q port is never 50 Ω resistive, it is tuned with an rf sweeper and a pick-up coil.

Though we have not tried it, a crossed-coil circuit should work too. The transmitting coil would be low Q; the inner receiving coil high Q. As shown in Fig. 3, crossed diodes across the receiving coil would help avoid coupling between the circuits. Diodes in the transmitting circuit would shift its frequency during detection, again avoiding coupling. Most glass-package diodes are magnetic; one might try using the junctions of epoxy-cased rf transistors (non-magnetic).

Sincerely,

Jurgen Haase and Mark Conradi

Jurgen Haase and Mark Conradi

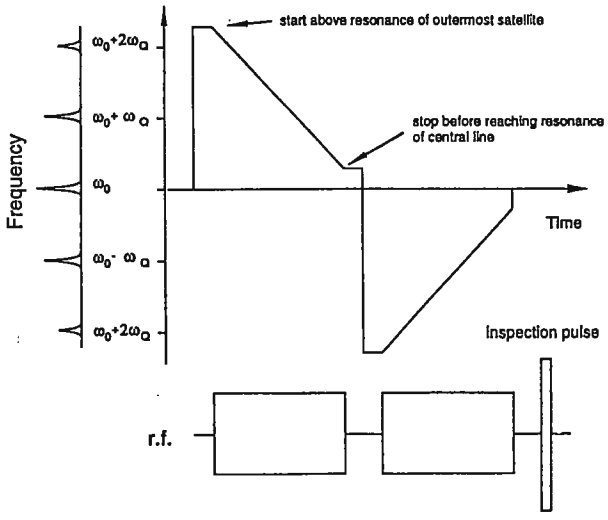


Figure 2

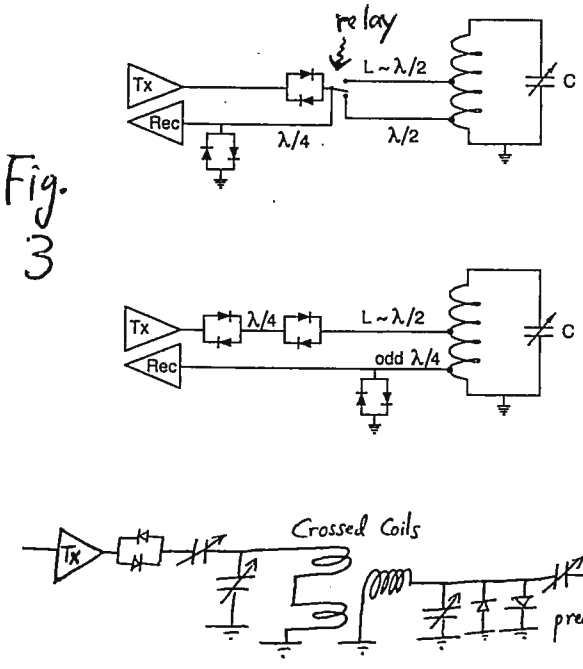


Fig. 3

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▪ DOR	▪ TOCSY
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Imaging	Solids	Liquids	Liquids+Imaging
	▪ Rotational Resonance ▪ CP/MAS ▪ HETCOR	▪ HCCH-TOCSY ▪ Reverse Detection ▪ HETCOR ▪ X-Decoupled	▪ ^{1}H, ^{19}F, Gradient Field Spectroscopy

Three Channels

Solids	Liquids	Liquids+Imaging
▪ REDOR	▪ Triple Resonance ▪ ^{1}H, ^{13}C, ^{15}N, HMQC-TOCSY	▪ H/X Gradient Field Spectroscopy

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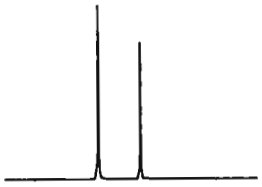
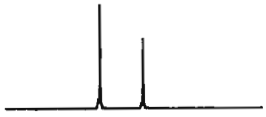
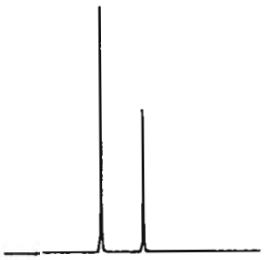


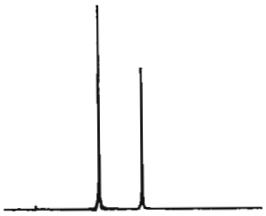
Variable amplitude cross polarization (VACP) *under* –2.6 KHz *mismatch condition*



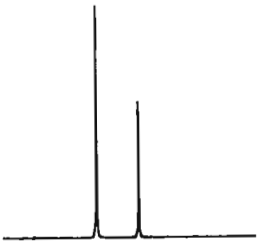
Deliberate "mismatch" of –1.9 KHz



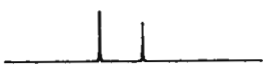
VACP *under normal match condition*



Normal "ideal" matched conditions



VACP *under* +2.0 KHz *mismatch condition*



Deliberate "mismatch" of +1.4 KHz

Chemagnetics would like to thank Professor Steve Smith for suggestion of this work and useful discussions during its implementation.

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

December 10, 1993
(received 12/13/93)

Solid State NMR of the Equine Hoof Wall

Dr. Shapiro:

The equine hoof wall has been characterized by ^{13}C solid state nuclear magnetic resonance. The structure and dynamics of the predominant protein component of the equine hoof wall, the intermediate filament keratin α-helix, were probed. Assessment of these parameters is preliminary to the determination of diffusion rates of solutions and fluorocarbon emulsions containing oxygen directly through the hoof wall to the underlying tissue.

Magic-angle sample spinning with high power proton decoupling and cross-polarization techniques provided spectra from which component carbon resonances of amino acids could be discerned. The hoof is composed of primarily four anatomical regions easily resolved by visual inspection. CPMAS ^{13}C NMR spectra of ground and dried (~10-50% water loss) material from three regions of different horses (A-C) show nearly identical chemical shifts suggesting the component keratin α-helices between regions and between horses are structurally similar. Resonances (D) of an unground and undried (native) sample from a different region of the hoof are broadened by ~150 Hz over the dried and ground samples from that same region. Another native sample analyzed with the same spectroscopic parameters revealed an aliphatic region (E) more clearly resolved than in other spectra of ground and dried samples. Major resonances in the native samples (D,E) also show a hydration-induced downfield shift of ~3 ppm.

The equine hoof wall has a definite macroscopic and microscopic orientation. This orientation is due to the horn tubules which run longitudinally from the top to the bottom of the hoof wall. The presence of any preferential molecular-level ordering of the abundant composite keratin filaments with the horn tubules was assessed with static ^{13}C solid state NMR. The carbonyl powder patterns from ~80-250 ppm of the static spectra (F,G) of samples with tubule preferential order axis parallel (F) and perpendicular (G) to the magnetic field exhibit features of a general chemical shift tensor with no observable orientation effects. A preferential orientation of the keratin fibers to the longitudinal axis of the horn tubules would reveal two different patterns, resulting from carbonyl chemical shift tensors oriented colinearly and at 90° to the applied magnetic field. The similarity in the static spectra do not suggest a bulk

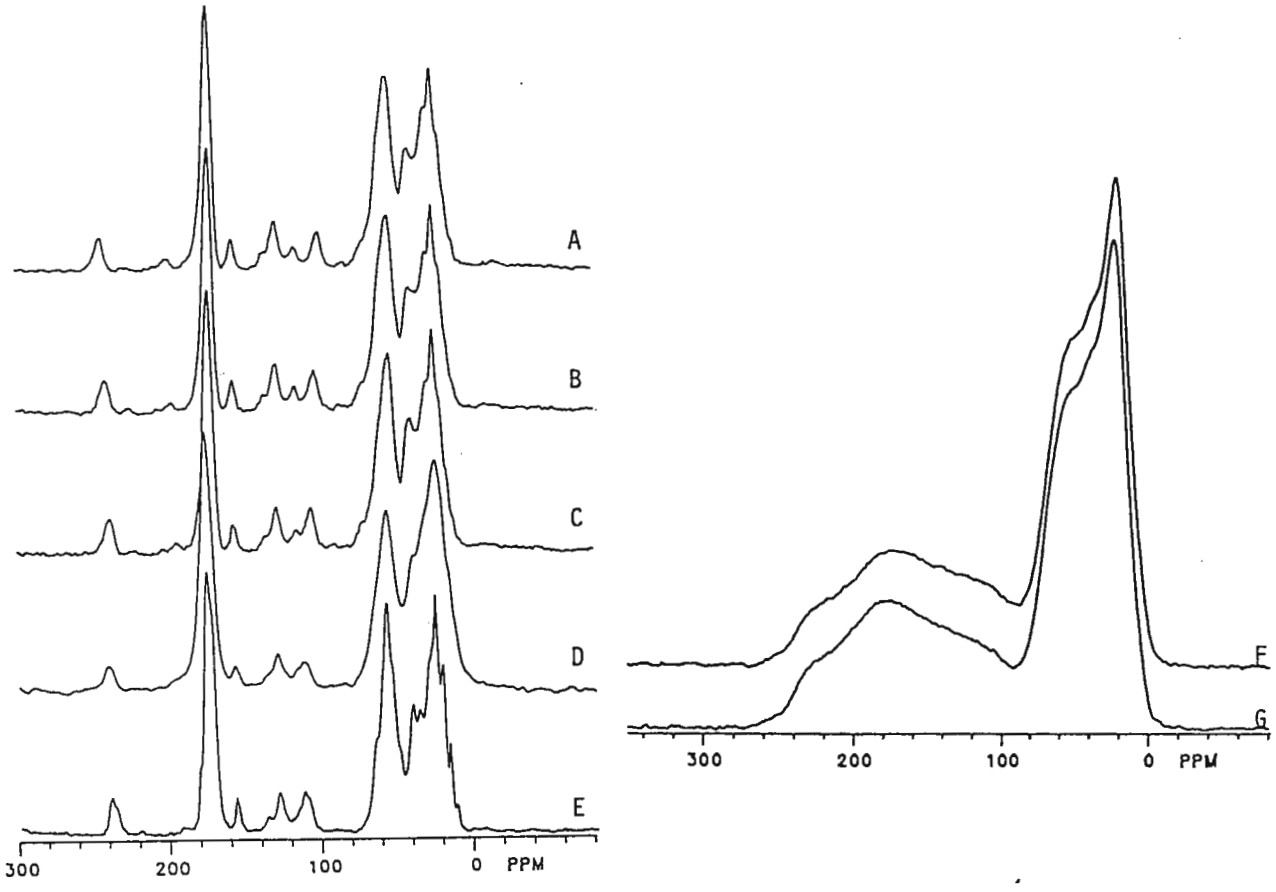
preferential orientation but support the view that the hoof is an interpenetrating fibrous polymer network with keratin arranged co- and abaxially to the horn tubules.

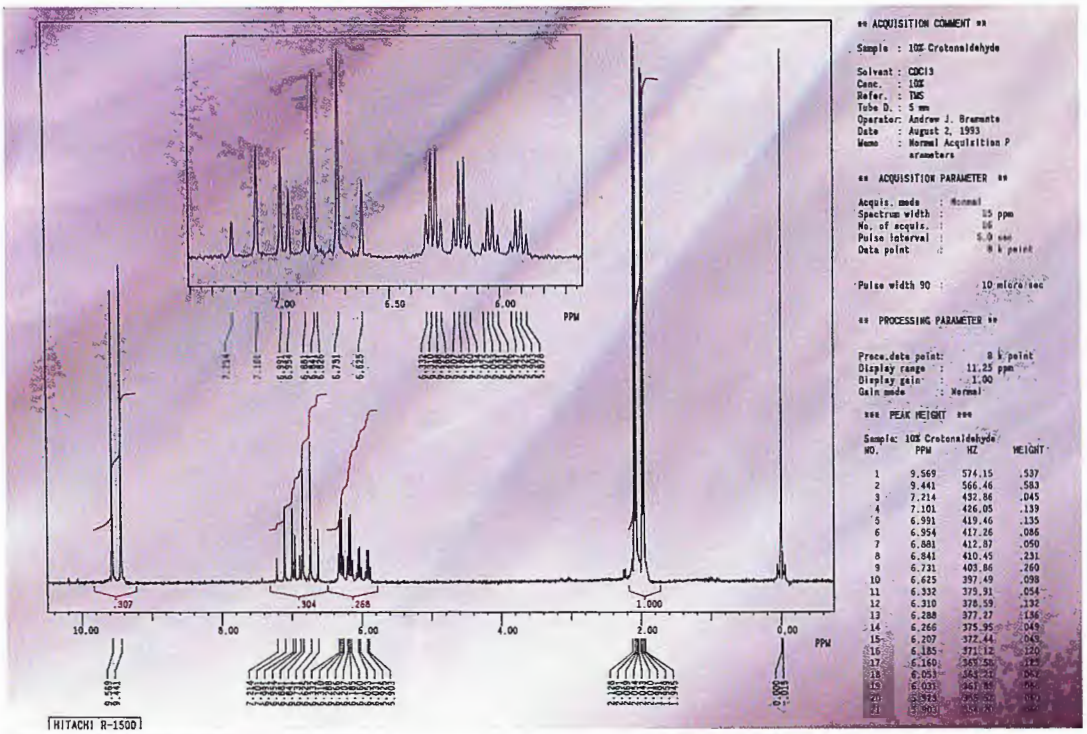
Spin-lattice relaxation times of predominant carbonyl and aliphatic carbons were evaluated. The aliphatic resonances show an order of magnitude increase in relaxation rate over the carbonyl resonances which is not unexpected since the carbonyls residing in the helices have less conformational mobility than aliphatic side chains extending into the interhelical space.

Ultimately, we wish to demonstrate the feasibility of delivering oxygenated emulsions through the hoof wall to supporting tissue rendered ischemic, or oxygen-starved by the disease laminitis. We have shown that solid state NMR is a useful technique for the characterization of the structure and dynamics of component polymeric proteins of the equine hoof wall.

Sincerely,

Matthew C. Szap Natalie Foster James E. Roberts William R. Anderson, Jr.





This R-1500 FT-NMR spectrum of crotonaldehyde represents a 16 pulse acquisition; each pulse was 10 μsec with a pulse interval of 5 seconds.

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

December 2, 1993
(received 12/6/93)

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

Re: **NMR Imaging of Solvent Transport in Macromolecular Systems**

Dear Barry:

The phenomenon of solvent transport into polymers has fascinated researchers for decades. Early on, optical microscopy revealed that systems in which a change in state accompanies solvent transport exhibit a sharp solvent front that penetrates the sample like a shock wave; such behavior has been referred to as case II transport to distinguish it from Fickian transport. The search for a theoretical basis for this type of non-Fickian behavior has been irresistible for both experimentalists and theorists; to date numerous theories abound.

Recently, we have gained considerable insight into the character of solvent transport in polymers and coal through time-resolved NMR imaging of concentration gradients during solvent uptake. Spin-echo 2-D images were obtained on 2 x 2 x 1 mm specimens in reasonable times. In order to ensure that the transport process was also two-dimensional, the upper and lower sample surfaces were protected from solvent infiltration by glass coverslip which restricted the flow of solvent to cross only the exposed faces of the sample. The experimental protocol involved immersing the sample in the solvent for a period of time, removing it from solvent, acquiring an image, and re-immersing it.

The Figure presents transient images together with one-dimensional projections for each of the three macromolecular systems. The first (a) illustrates the swelling behavior of isobutyl rubber in toluene. In the case of a rubbery material, the transport behavior is anticipated to be Fickian. Analysis of the dynamic behavior of the isobutyl rubber confirms this: during the swelling interval a steep solvent gradient observed in the frame rapidly evolves into a smooth and shallower gradient indicative of a transport mechanism which is essentially Fickian.

The second (b) illustrates the swelling behavior of PEMA in methanol. Clearly evident is a sharply defined solvent front which separates a swollen region from the glassy core. Swelling is essentially complete when the solvent fronts meet at the object center. In general, this behavior is typical of all polymers which pass through a glass to rubber transition during solvent uptake. The term case II has been used to describe such transport phenomena. Analysis of the transport of pyridine during the swelling of a sample of high volatile bituminous coal (c) clearly reveals a sharp concentration profile during the uptake process which is indicative of case II type transport behavior.

Data obtained from the imaging experiments has been used to construct a rigorous model governing case II transport. For solvent transport in a system undergoing a glass transition, we can define the uptake behavior using three parameters: a characteristic co-operative diffusion coefficient, governing dilation of the network; a molecular relaxation rate constant; and a critical solvent concentration above which there is a transformation of the network from a glass to a rubber.

Sincerely,

George D. Cody
Chemistry Division

Robert E. Botto
Chemistry Division

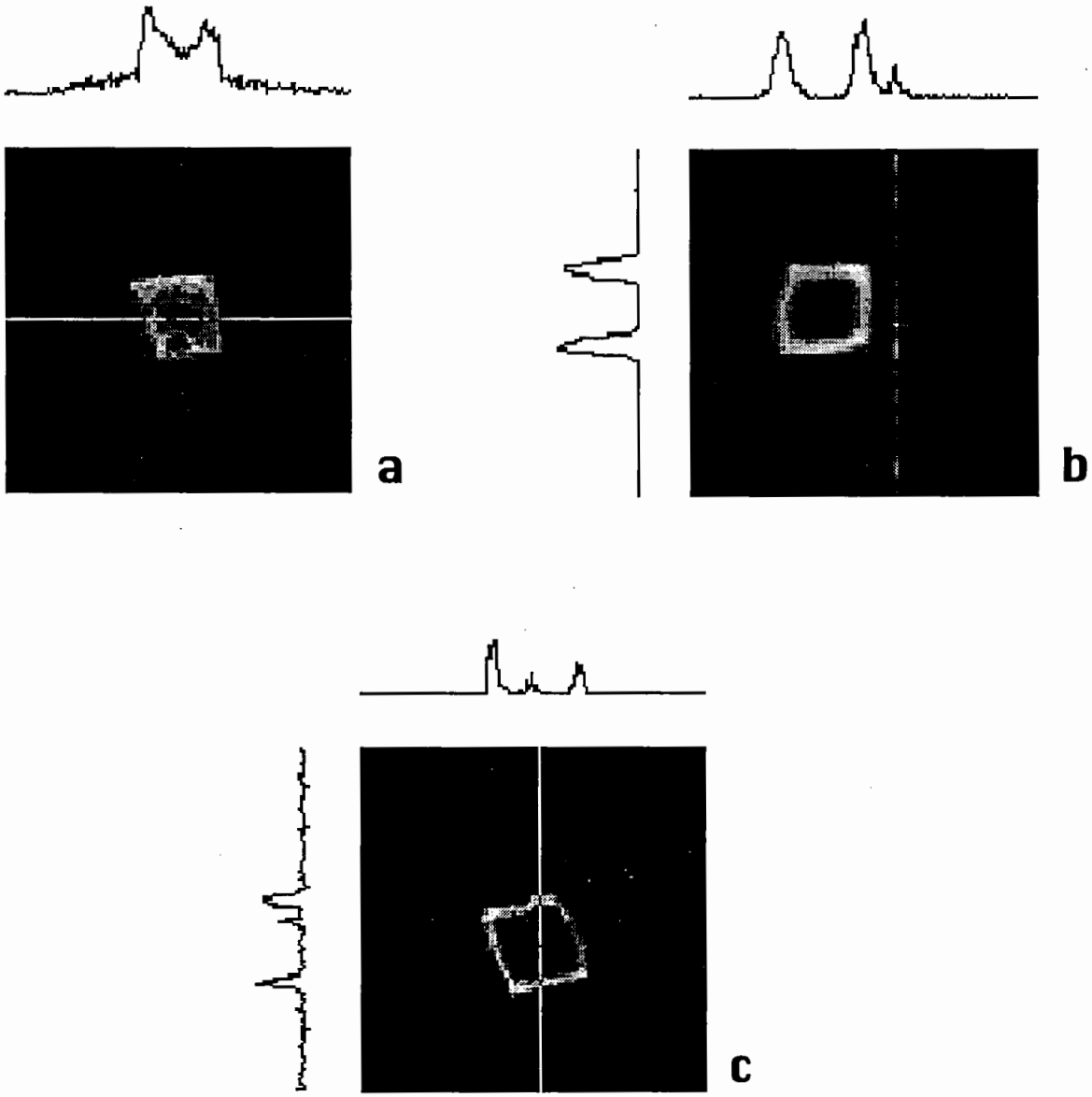

Figure. 2-D transient proton NMR images and 1-D projections of solvent transport in three macromolecular networks: (a) toluene in isobutyl rubber, (b) methanol in polyethylmethacrylate, and (c) pyridine in hv bituminous A vitrain.

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

11/23/93
(received 12/10/93)

Subject: ^{31}P-^{19}F Rotational-Echo, Double-Resonance (REDOR) NMR

Dear Dr. Shapiro,

Rotational-Echo, Double-Resonance (REDOR) NMR has been a very useful technique for retrieving information on weak heteronuclear dipolar coupling in the presence of large chemical-shift anisotropies (1). ^{13}C-^{15}N, ^{13}C-^{31}P, and ^{13}C-^{19}F REDOR NMR techniques have been developed and applied to the study of various biological systems and polymeric materials (2). Recently, we extended REDOR to ^{31}P-^{19}F spin pairs for proton-absent or proton-dilute inorganic systems. The advantages of ^{31}P-^{19}F REDOR are that 1) both ^{19}F and ^{31}P have almost 100% natural abundance, so that specific isotopic labeling may not be needed, 2) ^{19}F and ^{31}P also have large gyromagnetic ratios, allowing a greater range of measurable distances, 3) the high natural abundance and large gyromagnetic ratios result in high NMR sensitivity, and 4) for proton-absent or proton-dilute inorganic systems, ^{31}P-^{19}F REDOR can be performed on a routine two-channel NMR spectrometer.

We performed the ^{31}P-^{19}F REDOR NMR experiments on a Bruker MSL-300 spectrometer with a ^{1}H/^{19}F and multinuclear double-tuned probe made by Doty Scientific, Inc. Fluorapatite ($Ca_5(PO_4)_3F$, FAP) was used as a model sample for the experiments.

The ^{19}F-observed ^{31}P-^{19}F REDOR NMR spectra of FAP are shown in Figure 1a. After eight-rotor-cycle dephasing, the fluorine signal is almost completely dephased out. A strong difference signal is observed (Figure 1a, top). This result is expected since each ^{19}F in FAP has three nearest ^{31}P neighbors at a distance of 3.60 Å (3). The ^{19}F-observed REDOR NMR spectra of CaF_2 are shown in Figure 1b for comparison. Under the same experimental conditions, no F signal is dephased and the difference signal is null. The noise level in the difference spectrum

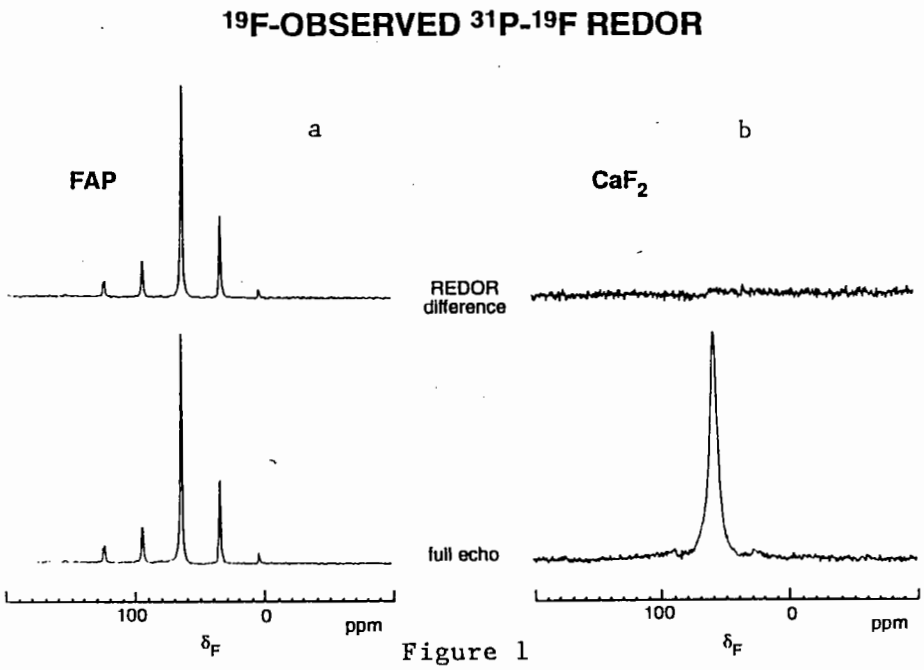

Figure 1

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shows that REDOR could detect a difference signal as small as 0.3% relative to the full-echo signal.

It is not straightforward to determine the P-F distance by ^{19}F-observed REDOR due to multiple-^{31}P dephasing in this system. The P-F distance can be determined by ^{31}P-observed ^{31}P-^{19}F REDOR. Figure 2 shows the spectra of ^{31}P-observed REDOR of FAP. The amount of dephasing is small after two- and four-rotor-cycle dephasing, and it is dominated by the nearest ^{19}F neighbor. The experimental ratios of the REDOR difference signal to full echo signal, $\Delta S/S$, after two and four rotor-cycle dephasing, can be translated to a P-F distance of 3.65 Å and 3.50 Å (2) compared to 3.60 Å from X-ray data (3). This minor disparity is due to the additional dephasing by the three next nearest ^{19}F neighbors, which are 4.9 Å away.

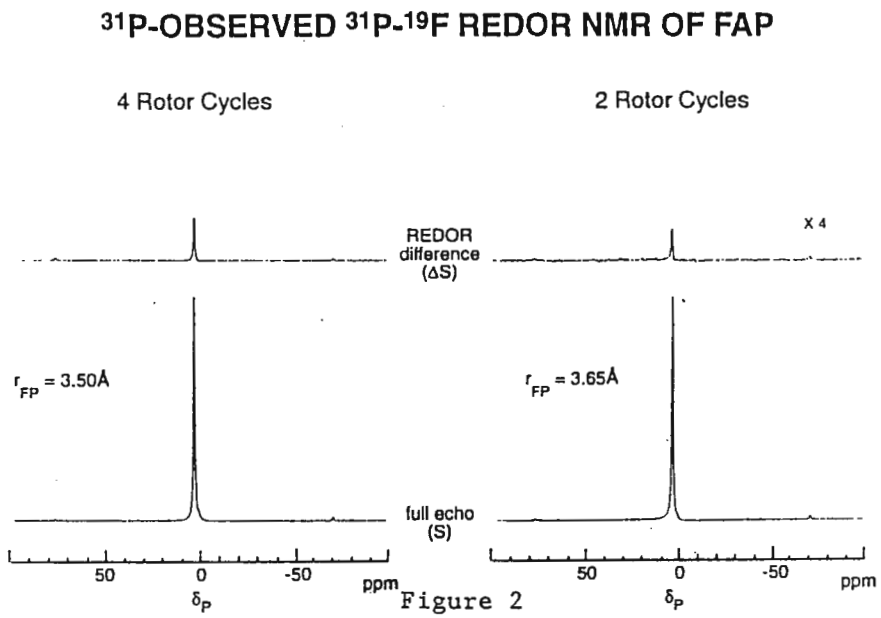

Figure 2

We have applied ^{31}P-^{19}F REDOR to studies of the interaction of ionic fluoride and hydroxyapatite, a primary inorganic constituent of dental enamel and dentine. The results are being submitted for publication.

Sincerely,

Pan Yong

Yong Pan, Ph.D

Corporate Research Division
Procter & Gamble

1. T. Gullion and J. Schaefer, *in* "Advances in Magnetic Resonance" (W. S. Warren, Ed.), Vol 13, p. 57, Academic Press, San Diego, 1989.
2. Y. Pan, T. Gullion, and J. Schaefer, *J. Magn. Reson.* **90,** 330 (1990).
3. H. G. McCann, *Arch. Oral Biol.* **13**, 987 (1968).

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NMR

DYNAMIC RANGE ENHANCEMENT

It is well known in fundamental signal processing theory that the ultimate dynamic range of an oversampled signal after digitization and data reduction by a modern Digital Signal Processor (DSP), is not only a function of the nominal dynamic range of the digitizer. At sampling rates greater than the Nyquist rate, the increase in dynamic range is equal to the square-root of the ratio of the sampling bandwidth (BW_{samp}) divided by the effective spectral width (BW_{eff}) after decimation.

$$dynamic\ \ range\ \ increase\ = \sqrt{BW_{samp}/BW_{eff}}$$

Figure 1 illustrates this point for the 16 bit 400 kHz digitizer of the AVANCE DMX in comparison to typical proton acquisition bandwidths. For instance, at its maximum sampling rate BW_{samp} = 200 kHz, and for a typical 10 kHz proton spectral width, i.e. BW_{eff} = 10 kHz, the increase in dynamic range is $\sqrt{20}$ = 4.47 > 2 bit. The total dynamic range of the oversampled and digitized signal after decimation and digital filtering by DSPs, is **greater than 18 bits**.

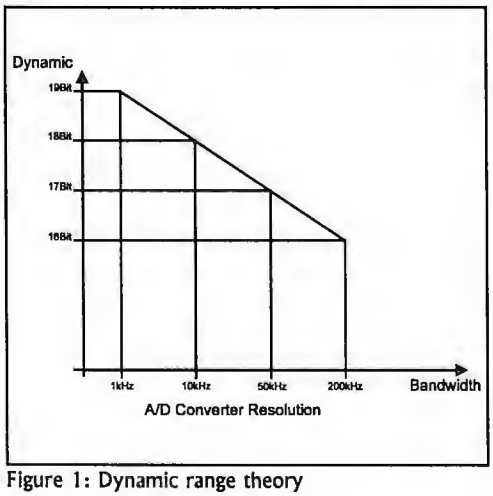

Figure 1: Dynamic range theory

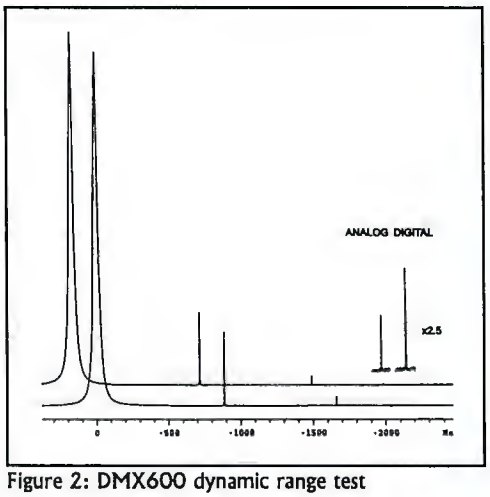

Figure 2: DMX600 dynamic range test

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NMR

Ultimately, NMR spectroscopists wish to see the "proof in the pudding", i.e. a high-dynamic range NMR experiment. For several years, Bruker has used a dynamic range sample with proton ratios of 10,000 : 100 : 10 : 1 to demonstrate the high dynamic range of the SE451™ receiver system, even without oversampling. Figure 2 shows this sample measured with a single scan with analog filtering, and with oversampling and digital filtering on an AVANCE DMX600. The smallest proton signal has been measured with the following signal-to-noise ratios:

Table 1:	Analog Filters	Oversampling & Digital Filters
S/N ratio:	80 : 1	200 : 1

The crucial point of this NMR test is that **under conditions of high dynamic range,** but otherwise identical experimental conditions, **oversampling and digital filtering on a DMX600 increase the dynamic range experimentally by a factor of 2.5.**

SIGNAL-TO-NOISE IMPROVEMENT

Analog filters are characterized by relatively gradual filter cutoffs outside the passband. This causes both signals and noise outside the analog filter passband to be folded back into the spectral region. As a result, the signal-to-noise is highest near the center frequency and is lower near the edges due to noise which is folded back from outside the passband.

On the contrary, digital filters have extremely sharp cutoffs, and provide almost 100 dB attenuation, at the point where an analog filter has its 3 dB point. Therefore, aliased peaks are not a problem, and practically no noise is folded back into the spectrum from outside the passband. Therefore, S/N is approximately constant within an NMR spectrum when digital filters are used. This point is illustrated by the plot in Figure 3.

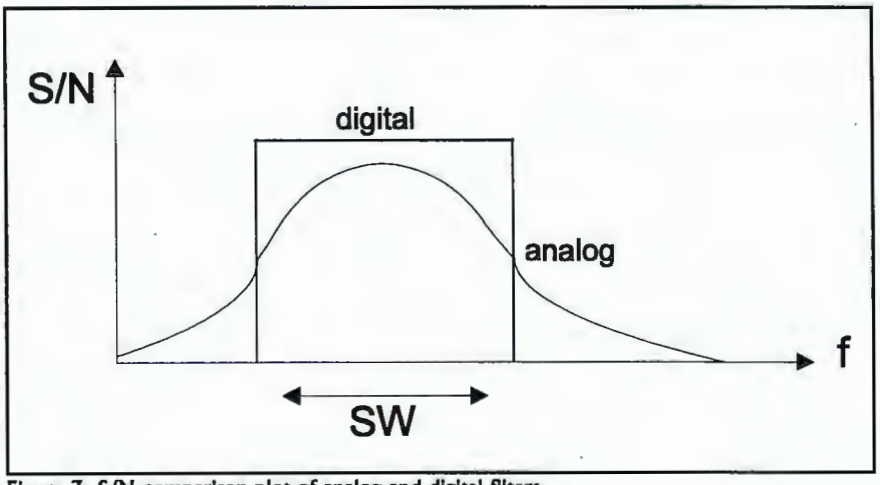


Figure 3: S/N comparison plot of analog and digital filters

It is clear that in the standard 0.1% ethylbenzene (EB) sensitivity tests used in NMR, the apparent signal-to-noise ratio increases significantly when only 200 Hz of noise are measured near the center of the EB spectrum. A more realistic test is shown in Figure 4, where the noise in EB is measured over a 2 ppm region form 4.8 to 6.8 ppm. At 600 MHz the spectral region for EB of approximately 8 ppm corresponds to a spectral width of only 5 kHz, and in an analog filtered EB test significant noise is folded in from outside the spectral region. With digital filtering on an AVANCE DMX600 no noise is folded back, and the sensitivity of the experiment is excellent: on a 5 mm proton selective probe the **measured S/N is greater than 900 : 1.**

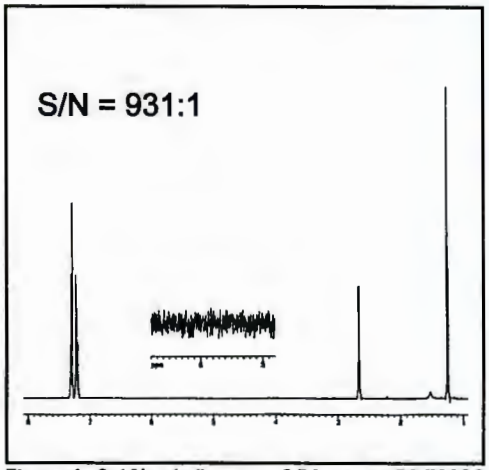


Figure 4: 0.1% ethylbenzene S/N test on DMX600 with digital filtering

Perhaps more interesting is a biological NMR experiment on lysozyme, where the signal-to-noise ratio is measured for the amide region near the edge of the spectrum. As illustrated in Figure 3, at the edge of the spectrum the sensitivity advantages of digital filtering should be even more significant. Indeed, Figure 5 demonstrates a **30% signal-to-noise improvement** specifically in the amide region when digital filtering is employed on a DMX600, compared to analog filters.

Similarly, a standard 2 mM sucrose sample exhibits a **signal-to-noise improvement of 25%** on the anomeric protons for digital filters compared to analog filters on an AVANCE DMX600 under otherwise identical conditions. This point is illustrated in Figure 6.

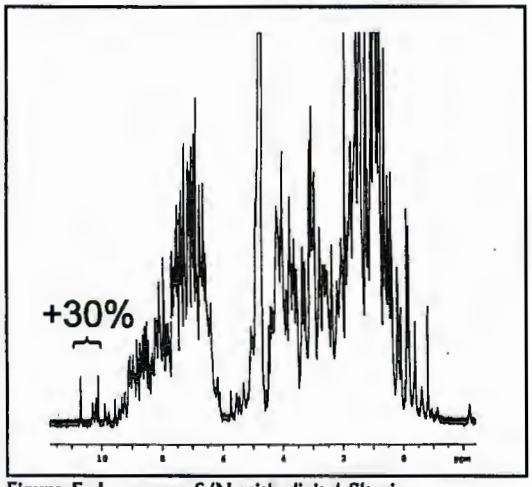


Figure 5: Lysozyme S/N with digital filtering

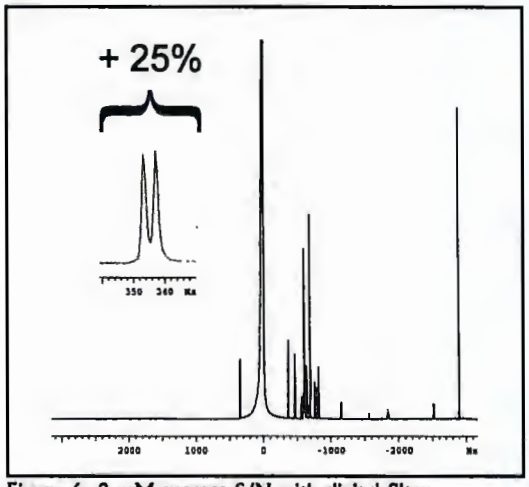
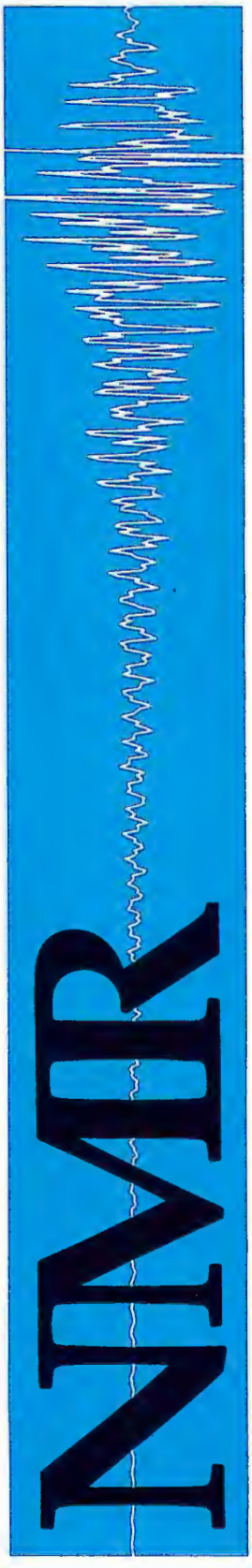


Figure 6: 2 mM sucrose S/N with digital filter



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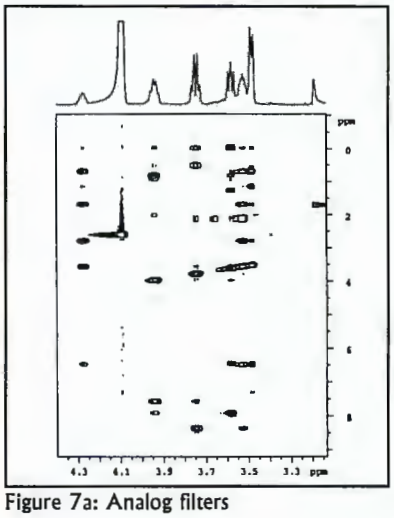

Figure 7a: Analog filters

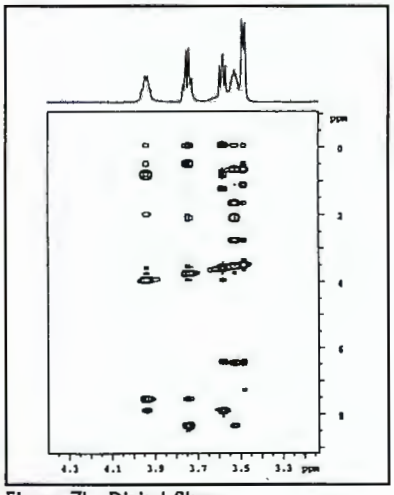

Figure 7b: Digital filters

SHARP FILTER CUTOFFS OF FINGERPRINT REGIONS

Often it is desirable to measure only selected "fingerprint" regions in multidimensional NMR spectroscopy for optimal efficiency. Oversampling and digital filtering, due to the steep filter cut-off in the acquired dimension allow the acquisition of artifact-free fingerprint regions without concern about folded sample or solvent peaks.

In the example chosen here a small spectral region is selected from the 2D NOESY spectrum of gramicidine. In Figure 7a the region from 3.1 to 4.4 ppm is selected with analog filters, but folded peaks and artifacts make this approach unpractical. On the other hand, in Figure 7b the same region is shown, but in this case selected by digital filters on a DMX600. **The "fingerprint" region is free of artifacts and folded peaks when digital filtering is employed.**

Finally, the combination of shaped selective or band-selective pulses in F1 with oversampling and digital filtering in F2 is illustrated in Figure 8. Obviously, this combination permits spectral selectivity in several dimensions. It is expected that the **combination of shaped pulses with digital filtering** will be a powerful tool for carrying out efficient selective experiments of lower dimensionality which are equivalent in information content to higher-dimensional experiments without the need to acquire for long periods of time. For example, it is attractive to carry out a series of selective 2D (3D) experiments, to obtain structural information equivalent to 3D (4D) experiments, when the higher spectral dispersion over several dimensions is required only for certain cluttered regions with overlapping spectral features (as is often the case).

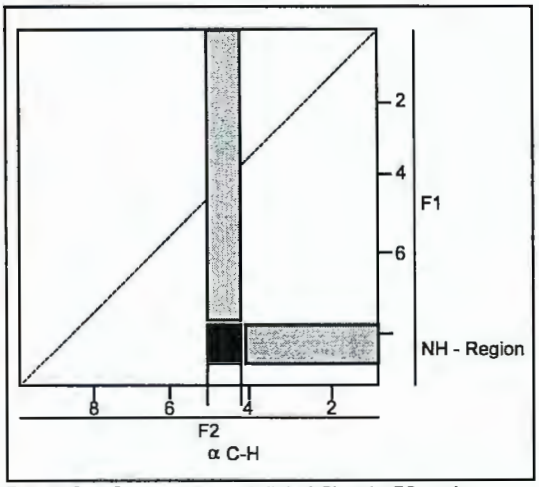

Figure 8a: Combination of digital filter in F2 and bandselective EBURP2 in F1

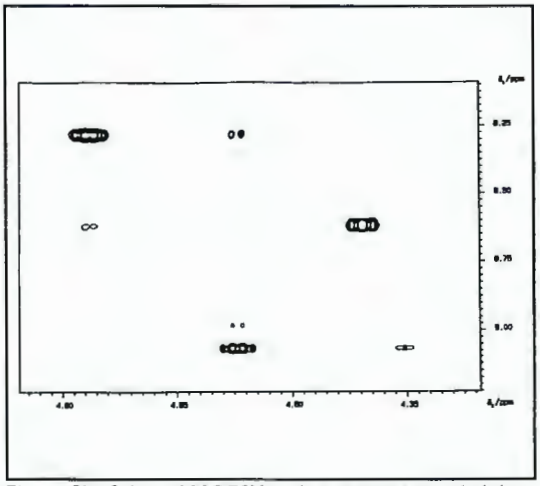

Figure 8b: Selected NOESY region of amides and alpha-carbons for gramicidine on DMX600 (as in Fig. 8a)

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December 8, 1993
(received 12/11/93)

INSTITUTE OF ANALYTICAL RESEARCH

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

Big Shakes and Big Cans

Dear Dr. Shapiro,

We recently finished installing our new Bruker AMX2-600 NMR spectrometer equipped with an Oxford magnet. During the installation of the magnet we devised a method for securing the system in case of earthquakes. In the past we secured magnets by bolting brackets to the floor which prevented the magnet stand from sliding or tipping over. The 600 MHz magnet, however, presented a couple of more problems. First, the magnet is not secured to its stand. This is especially dangerous since the vertical acceleration in an earthquake can exceed the acceleration of gravity, which would separate the magnet from its stand. Second, this magnet is substantially heavier and has a much higher center of gravity than those on our lower field instruments making the floor brackets alone ineffective. We decided the best method was to secure both the top and bottom of the magnet system. The top of the magnet was attached to the concrete walls and the steel girders above the magnet using 1/2" Dacron line obtained from our local boating store. The magnet stand was first secured to the magnet using anodized aluminum brackets made in our machine shop and then steel brackets were bolted to the floor to prevent the system from sliding during an earthquake. These brackets were carefully designed to not touch the stand so that the system remains isolated from the floor vibrations. We figure if these safety devices fail in an earthquake we will have many more things to worry about than the state of our NMR spectrometers (like the building falling down). If anyone would like details of how our magnet is secured please write to me or Mike Maddox.

Joseph Pease

Joseph H. Pease

UNIVERSITÉ LOUIS PASTEUR
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FACULTÉ DE CHIMIE

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67008 STRASBOURG CEDEX
Téléphone 88 41 68 00
Boîte Postale 296 R 8
France

Strasbourg, le November 24, 1993
(received 12/6/93)

Relaxation of quadrupolar nuclei in clusters.

Dear Bary,

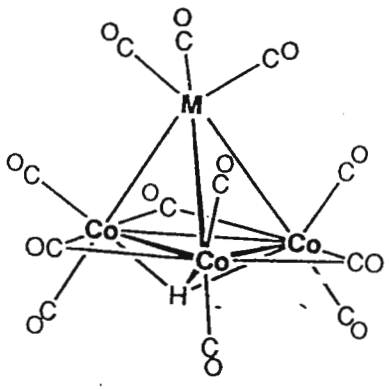
We have recently measured the relaxation time of cobalt on tetrahedral clusters (see figure below) in solution. The relaxation mechanism is largely quadrupolar and the experiments show a monoexponential behaviour which means that, according to Abragham, we are in the extreme narrowing case where the usual formulae apply.

On the other hand, we have all the electric and magnetic parameters from the solid state spectra (J. Hirschinger, P. Granger, J. Rosé, J. Phys. Chem., 1992, 96, 4815). If we accept that these parameters remain in solution, it is easy to deduce the correlation time of those species.

The table below shows that the result is surprisingly good for those molecules which have quite different relaxation times. The simple model of the sphere in a viscous liquid is a well suited model which gives a radii of gyration which agree with the molecular geometry. Other models does not fit so well. This type of rigid molecules, where the cobalt is not directly in contact with the solvent seems to be appropriate molecules for the theory of relaxation.

Best regards,

Molecule	T_1 (μs)	$\tau_c \times 10^{11}$ sec
$HFeCo_3(CO)_{12}$	839	2,7
$HRuCo_3(CO)_{12}$	241	2,8
$FeCo_3(CO)^-_{12}$	166	2,6
$RuCo_3(CO)^-_{12}$	293	2,8



M = Fe
M = Ru

Pierre GRANGER

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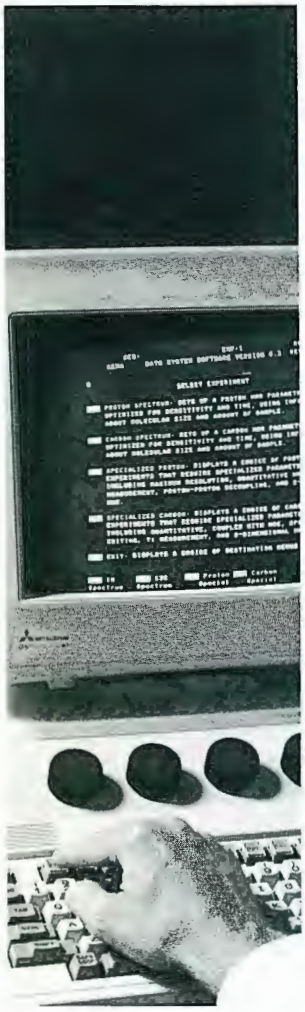

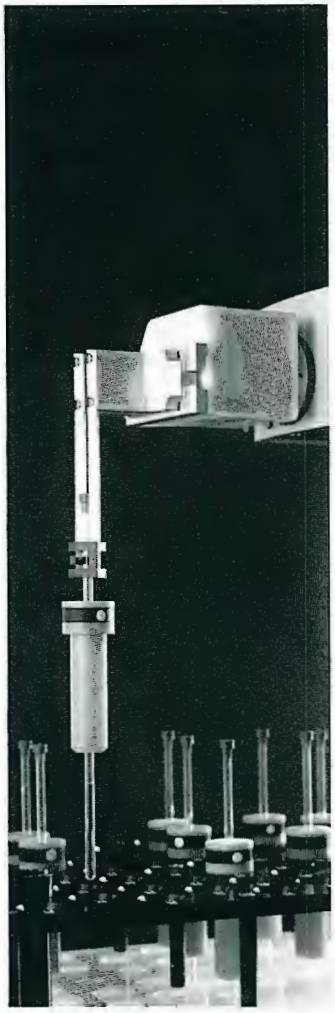

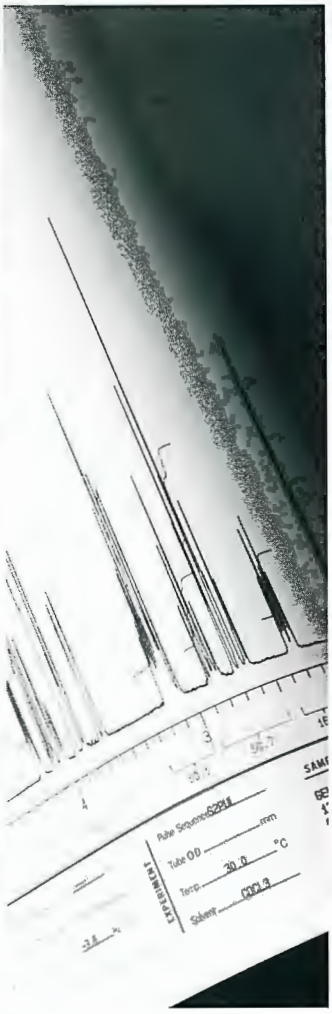

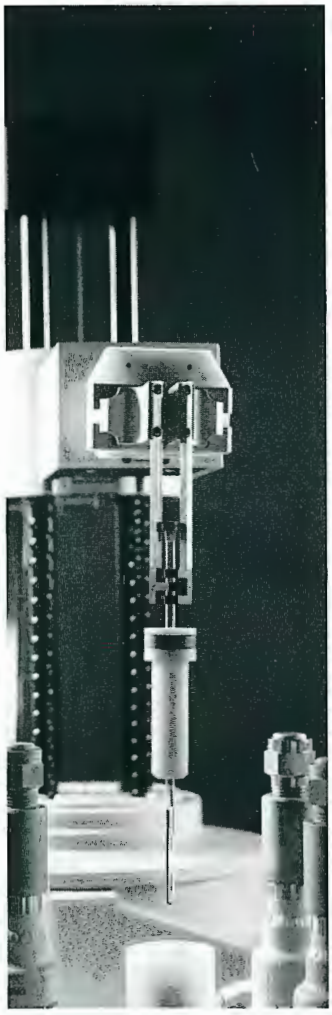

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December 13, 1993
(received 12/17/93)

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

Color Figures for Sun/SGI.

Dear Barry:

There has been a fair amount of discussion in the Newsletter about how to get publication quality figures. Black and white figures are necessary, but it would also be nice to get high resolution color figures. We have used two handy tools for this purpose. On our SGI boxes running Felix, we have used the Irix tool "snapshot." A more powerful tool is "xv" which runs on both Suns and SGIs. We use xv to capture an image of a color 2D contour plot for example. We write out the image in SGI format, even on the Sun, and then convert it to PICT format with the the "topict" tool in the SGI 4Dgifts directory, or the "imconv" tool available from the San Diego Supercomputer Center. The PICT file can then be transferred to your favorite Macintosh. We have been using MacDraw Pro to dress up the images and then make color slides using a LaserGraphics slidemaker.

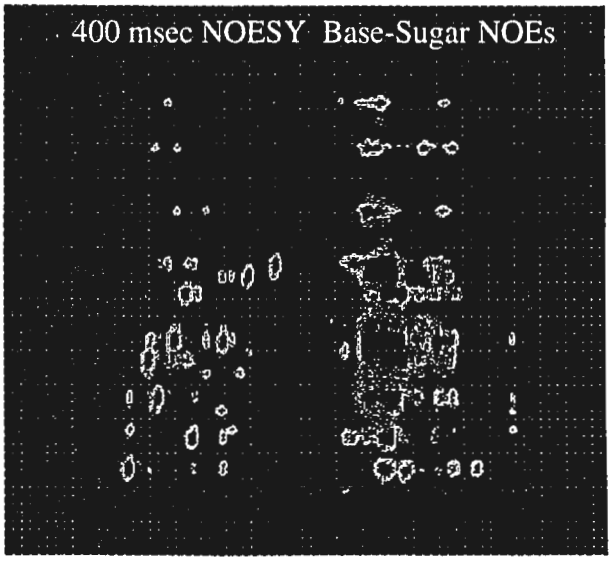
I have made the binaries for xv_sun and xv_sgi as well as the man page available for anonymous ftp from adenosine.pharm.utah.edu. Sources that go right up on the SGI can be found on jhunix.hcf.jhu.edu in the directory public_domain_software/SGI/xv. An email address for SDSC is consult@y1.sdsc.edu.

The figure has been converted to black and white, but on the slide is glorious color straight from a Sparc1 running VNMR.

Sincerely yours,

Darrell R. Davis

tRNA^{Trp} - Cm Hairpin



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Salt Lake City, Utah 84112
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Faculty of Chemical Technology and Materials Science
Delft University of Technology

1992

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

Delft, December 6, 1993
(received 12/17/93)

Title: A ^{113}Cd NMR Study on an Alkylamino Sugar

Dear Dr. Shapiro,

As part of our research program, studying the conversion of carbohydrates, a number of amino sugar compounds with potential as metal sequestering ligand properties have been synthesized. ^{113}Cd NMR is a valuable tool to study the coordination of these ligands.
We observed ^{113}Cd resonances for complexes of N-donor ligand L in aqueous solution at ambient temperature.

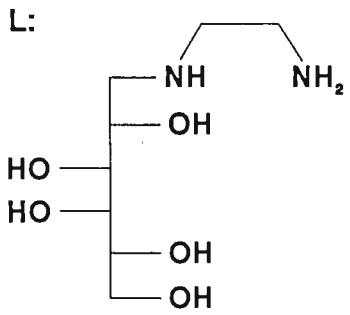
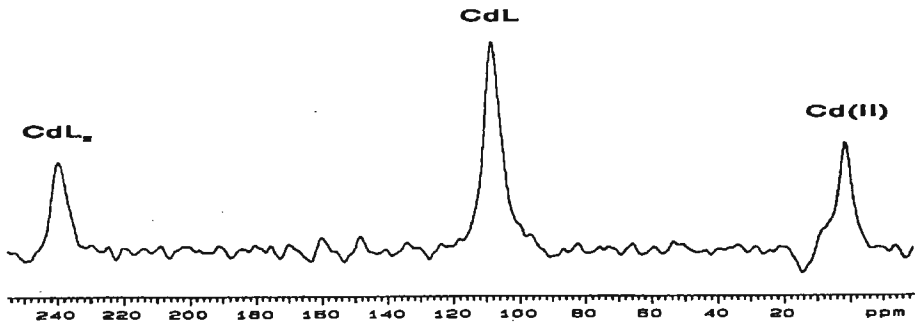


Figure 1 shows the ^{113}Cd NMR spectrum at (Cd(II)/L) molar ratio (ρ) 1 at pH 7.5. At ρ = 1 free Cd(II) (0 ppm), CdL (108 ppm), and CdL_2 (239 ppm) give distinct resonances indicating these species to be in slow exchange.
The ^{113}Cd NMR spectra carried out at pH 12 at several ρ values show the presence of CdL_2 (228 ppm) and CdL_3 (276 ppm). Comparison of these chemical shifts with literature values suggests that both N-atoms of the ligand L are coordinated with Cd(II) in these species. Current research is being carried out to investigate the existence of additional coordination between one of the OH groups in the carbohydrate chain and Cd(II).

Figure 1



Yours sincerely,

Hendrik Lammers

Joop A. Peters

Herman van Bekkum

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85-12267-9	L-Glutamine-$^{15}N_2$, α-N-t-BOC Derivative	99 atom%
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85-12245-5	L-Leucine-^{15}N, N-t-BOC Derivative Monohydrate	99 atom%
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December 16, 1993
(received 12/18/93)

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

Dear Barry:

Application of the Simultaneous Determination of Magnesium and pH from the ^{31}P Shifts of ATP

Evidence that the intracellular concentration of free magnesium ion [Mg_f] may serve a regulatory function has renewed interest in its quantitation. In our studies, we prepared model calibration solutions as a function of total [Mg]/[ATP] and pH and numerically modelled the three ^{31}P NMR chemical shift differences of ATP ($\delta(\gamma\text{-}\alpha)$, $\delta(\alpha\text{-}\beta)$ and $\delta(\gamma\text{-}\beta)$) (1). We also used these calibration surfaces to obtain improved shift limits. This is necessary for the standard [Mg_f] method of quantitation which assumes fast exchange and a single apparent K_D for MgATP.

We now present a high field (9.4 T) *in vivo* demonstration of our 2-dimensional calibration methods for determining magnesium ion concentration [Mg] under conditions of fluctuating pH. The effect of 3 h of hypoxic-ischemic (HI) insult on intracellular brain [Mg] was evaluated using a well established 7-day-old rat model of cerebral HI (2). During the final hour of HI there was a significant increase in free magnesium as well as in the ratio of total [Mg]/[ATP]. The normal, HI, and early recovery (1-2 h) values of free [Mg] were 0.336 +/- 0.015, 0.501 +/- 0.104 and 0.326 +/- 0.08 respectively. These results are consistent with the temporal decrease in [ATP] during hypoxia and its return toward the normal neonatal value of 2.8 mM during recovery. Despite numerous papers which claim changes in [Mg] with altered physiological state, little attention has been paid to the uncertainty in the final result. Figure 1 shows a graphical representation of the uncertainty in either [Mg_f] or [Mg_T]/[ATP_T] for an uncertainty in both chemical shift difference and pH. The small uncertainty in $\delta(\alpha\text{-}\beta)$ for normal brain was obtained by averaging of numerous controlled measurements. With consideration of $\delta(\gamma\text{-}\alpha)$, the error in the pH of the ATP compartment may also be calculated. This evaluation of ATP shifts is general for most *in vivo* applications and will favor lower [Mg_f] values than most prior estimates.

A software package, denoted as *MAGPAC* (*MAG*nesium and *P*H from *A*TP *C*alculation), has been written to perform all of the necessary calculations and uncertainty plots from the input ^{31}P NMR shifts. A user friendly IBM PC version of *MAGPAC* is available and can be accessed by ftp to anonymous@ psunmr.nmr.hmc.psu.edu in the pub directory.

(1) G.D. Williams, T.J. Mosher and M.B. Smith, *Anal. Biochem.* **214**, 458-467 (1993).
(2) G.D. Williams, C. Palmer, D.F. Heitjan and M.B. Smith, *Neurosci. Lett.* **144**, 103-106 (1992).

Sincerely,

Gerald D. Williams
jerry@psuhmed

Michael B. Smith
mbs@nmr.hmc.psu.edu

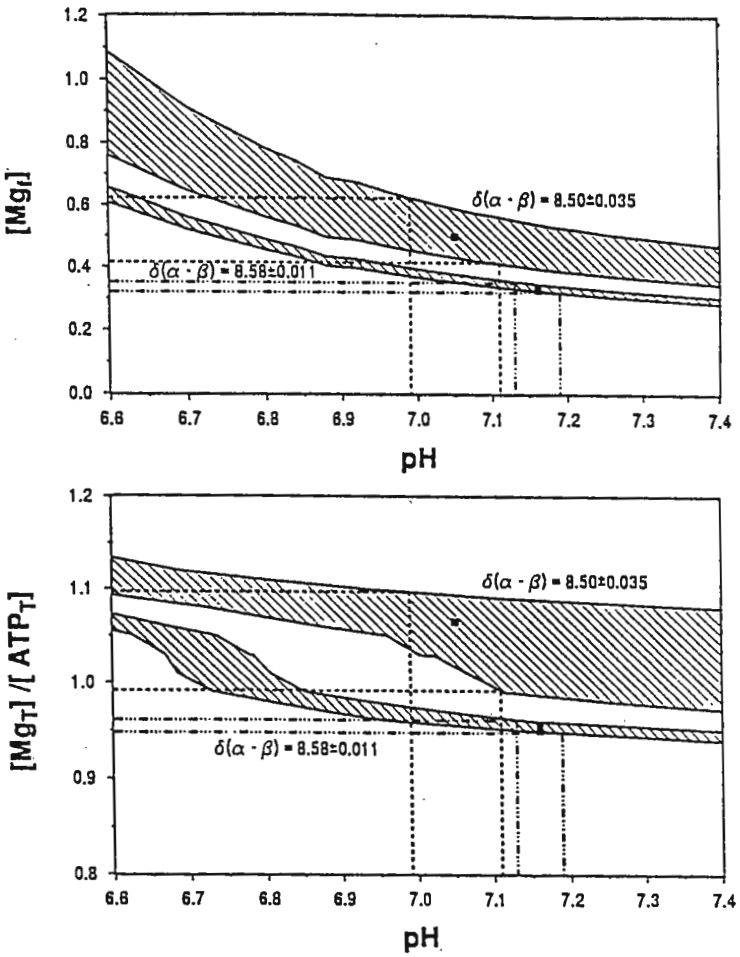

Figure 1: [Mg_f] (upper plot) and [Mg_T]/[ATP_T] (lower plot) error representation due to chemical shift and pH uncertainties. The shaded regions bracket the standard deviation in chemical shift, while the dashed lines locate the uncertainty in [Mg] for the estimate of the uncertainty in pH. Normal 7-day-old rat brain [Mg] (lower shaded region of each plot) is compared with the values at 2-3 h of hypoxic-ischemic insult (upper shaded region of each plot). A pooled t-test of the final results support a significant difference in [Mg] for the two populations ($P < 0.0001$).

THE OHIO STATE UNIVERSITY

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

December 2, 1993

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

Dear Barry:

Preliminary Announcement

Solid-State NMR Symposium
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1994 Vaughan Lecturer: Alexander J. Vega

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TAMU NMR Newsletter - Book Reviews

Book Review Editor: **William B. Smith**, Texas Christian University, Fort Worth, TX 76129

" A Dictionary of Concepts in NMR "

by

S.W. Homans

Oxford University Press, Walton Street, Oxford OX2 6DP;
revised, paperback edition; 1992; ISBN 0-19-854765-X $29.95, 373 pages.

My first reaction on inspecting this new edition of "A Dictionary of Concepts in NMR" was that this must largely duplicate "A Handbook of Nuclear Magnetic Resonance" by Ray Freeman. But I quickly discovered that this was not so. The author claims that "the aim of this work is to aid chemists and biochemists familiar with the basic principles of NMR to understand the bewildering array of acronyms and technical jargon which is to be found in the literature." I think he has succeeded admirably. While there are the inevitable overlaps with portions of the Freeman book, they actually complement each other quite nicely, and I am glad to have both of them on my bookshelf.

The single most obvious difference (other than the lack of cartoons) is the inclusion of a considerable amount of mathematical background. The point is made by citing four appendices titled as follows: Properties of cartesian product operation; Trigonometric identities; Matrix algebra; and Rotation operators. No one would pretend that these are detailed treatments, but they do get your feet wet if you willing to wade in.

Many entries are accompanied by references for further reading.

W. B. S.

Advanced Clinical MRI/MRS and ^{13}C MR Spectroscopy

Continuing Education Course at UT Southwestern Medical Center at Dallas

Thursday, March 10, 1994

PROGRAM DIRECTORS: Craig. R. Malloy, M.D., and A. Dean Sherry, Ph.D.
PROGRAM COORDINATORS: Navin Bansal, Ph.D., and Evelyn Babcock, Ph.D.

COURSE OBJECTIVE: This one day program is aimed at physicians, biomedical scientists and graduate students who are interested in the application of magnetic resonance spectroscopy and imaging to physiology. In the morning session, the role of NMR methods in the investigation of brain, heart and skeletal muscle physsiology, and breast imaging will be discussed by experts in the field. In the afternoon session, an overview of current ^{13}C NMR spectroscopy methods for analysis of intermediary metabolism will be presented.

This symposium will be held the day following the first annual meeting of the Society of Magnetic Resonance (SMR).

GUEST SPEAKERS: J. J. H. Ackerman (Washington U), Jeffry R. Alger (NIH), Steven Harms (Radiology Associates of Dallas), Douglas Rothman (Yale), Heinrich Taegtmeyer (UT, Houston), Robert G. Weiss (Johns Hopkins).

UT SOUTHWESTERN SPEAKERS: James Fleckenstein, Ronald Haller, Mark Jeffrey, Craig R. Malloy.

For more information, call: Dolly Christensen at (214) 648-8013 or Navin Bansal at (214) 648-5887.

FORTHCOMING NMR MEETINGS, *Continued from page 1.*

2nd Meeting, Society of Magnetic Resonance, San Francisco, California, **August 6 - 12, 1994**; Contact: SMR Berkeley Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Tel. (510) 841-1899; Fax: (510) 841-2340.

Gordon Conference on Order/Disorder in Solids, New London, New Hampshire, **August 7 - 12, 1994**; Contact: Prof. M. A. White, Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3; Tel. (902) 484-3894; Fax: (902) 494-1310. See TAMU NMR Newsletter 421, 44.

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995** [sic]; Contact: Dr. J. F. Gibson or Ms. G. B. Howlett - See TAMU NMR Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995** [sic]; Contact: Dr. Wm. A. Bubb, Secretary, Univ. of Sydney, Dept. of Biochemistry, Sydney, NSW 2006, Australia. See TAMU NMR Newsletter 419, 26.

Additional listings of meetings, etc., are invited.

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December 10, 1993
(received 12/14/93)

Professor B.L. Shapiro
Editor / Publisher TAMU NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303

Monitoring of Probe Heat Dissipation

Dear Barry:

Recently, we were interested in determining the heat dissipation performance of our inverse probe in the context of a heteronuclear experiment with ^{13}C decoupling. The experiment was performed by recording ^{13}C sidebands of a mixture of 20% CH_3OH (^{13}C natural abundance) / 80% $CDCl_3$ with centerband suppression by a difference experiment. As shown in Figure 1, the pulse sequence included ^{13}C off-resonance CW irradiation with a defined duty cycle and sufficient power to see the temperature rise at the start of the experiment. For our mixture, the chemical shift temperature coefficient for the OH peak was 0.016 ppm/K. Therefore, it was expected that a temperature fluctuation during the difference experiment would result into a large residual OH peak.

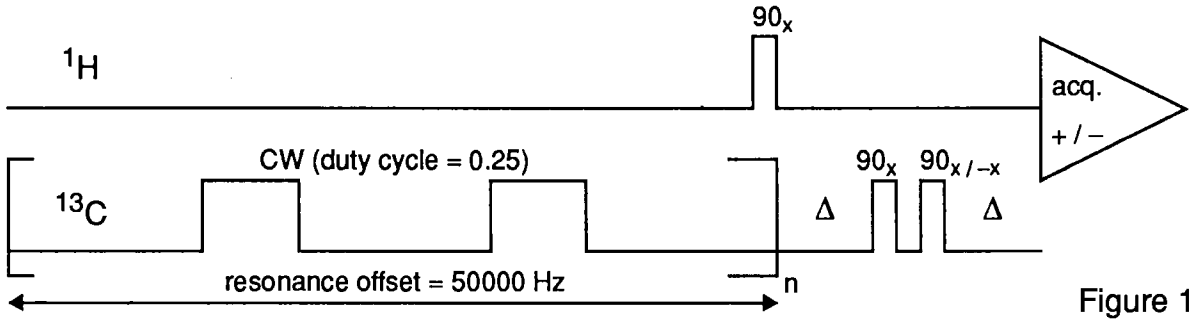


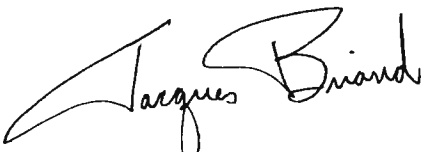
Figure 1

Two series of 64 difference experiments were performed, one for a duty cycle = 0, and the other for a duty cycle = 0.25. The former served as a reference for the steady-state intensities (magnitude mode) of the residual OH peak, the residual centerband and the two ^{13}C satellites (Figure 2). The CW pulse had a length of 16 seconds, a field strength of 3.5 KHz and a resonance offset of 50 KHz, sufficient to not disturb the ^{13}C resonance of interest. With the residual OH peak intensity, it is possible to evaluate the time it takes to reach a steady-state temperature. For a duty cycle of 0.25 it can clearly be observed that the temperature takes about 10 minutes to reach a steady-state value. The intensities were normalized with respect to the intensities of the ^{13}C satellites.

This experiment does not yield any quantitative information about the temperature inside the sample. However, it is useful for measuring the time a probe takes to reach a steady-

state temperature, assuming the experiment being performed is fairly periodic.

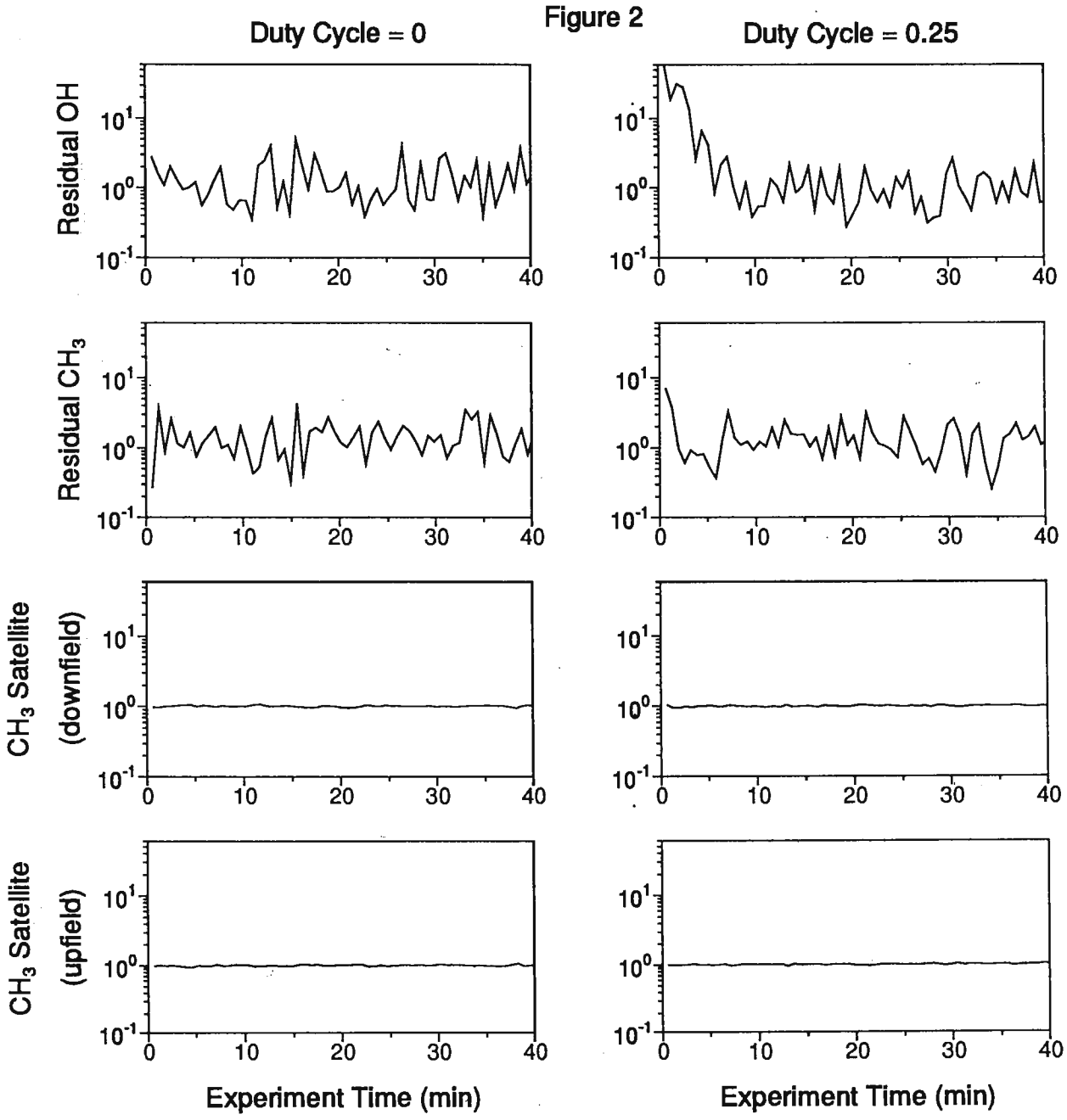
Sincerely yours,



Jacques Briand
Physical and Structural Chemistry

PS : Please credit this contribution to Susanta Sarkar's subscription.

Figure 2



Universität Bern

Institut für organische Chemie

CH-3012 Bern, Freiestrasse 3
Telefon 031 6543 11

Dr. Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 943030 USA

November 22th 1993
(received 11/29/93)

2D INVERSE LONG-RANGE C-H-SHIFT CORRELATION

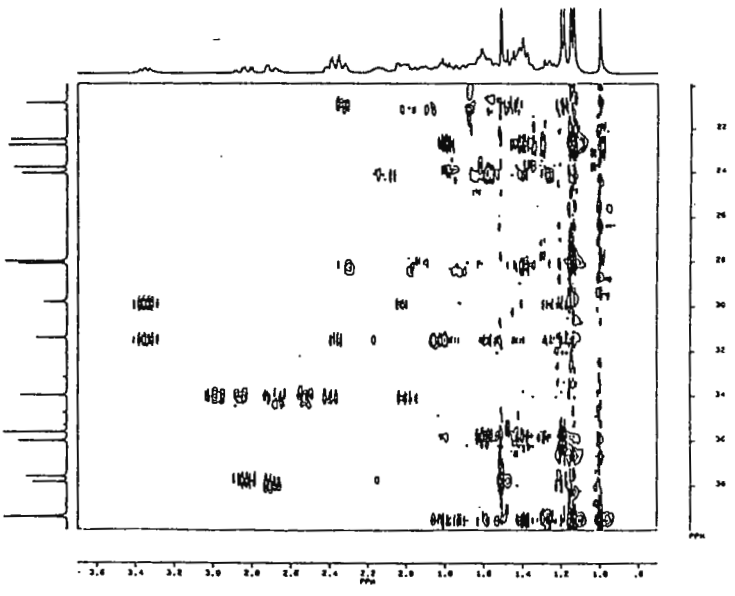
Dear Dr. Shapiro

Unsatisfied with the spectral quality achieved with the HMBC-Experiment to selectively detect and measure carbon-proton long-range coupling interactions which is probably caused by the instabilities of our BRUKER AM-400 system, we tried out the subsequent inverse experiment, which starts with (NOE enhanced) carbon z-magnetizations and which transfers the carbon-shift modulated carbon coherences to proton antiphase coherences in the final step immediately before detection. We were astonished about the high quality of the corresponding spectra, especially with respect to the suppression of unwanted C-12 proton signals. The reason for this are the three purge pulses, two of them applied as a "sandwich" with x- and y-phase respectively at the beginning and a third one immediately before acquisition. Together with the CPD decoupling at th beginning they are responsible for the highgly efficient saturation of all proton signals and the high quality even with the rather short phase cylce (see below):

```
;INCHLR2D.AU
;2D INVERSE LONG-RANGE C-H-SHIFT CORRELATION

1 ZE
3 D1 S1 CPD
  D4 S2 D0
  (P5 PH1):D    ; PURGE X
  (P5 PH3):D    ; PURGE Y
  (P3 PH5):T
  D0
  (P2 PH4):D
  D0
  D2
  (P1 PH1):D
  D3
  (P4 PH2):T (P2 PH2):D
  D3
  (P1 PH6):D
  D2
  (P3 PH7):T (P1 PH1):D
  (P5 PH3):D    ; PURGE Y
  GO=3 PH8
  WR #1
  IF #1
  IP5
  IN=1
EXIT

PH1=0
PH2=0 2 0 2
PH3=1
PH4=3
PH5=0 0 2 2
PH6=2
PH7=1 3 1 3
PH8=R0 R2 R2 R0
```



Yours sincerely

Peter Bigler

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♣ ♦ ♥ ♠ ♣ ♦ ♥ ♠

All Newsletter correspondence should be addressed to

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

(415) 493-5971 - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

Deadline Dates

No. 426 (March)	18 February 1994
No. 427 (April)	25 March 1994
No. 428 (May)	22 April 1994
No. 429 (June)	20 May 1994

♣ ♦ ♥ ♠ ♣ ♦ ♥ ♠

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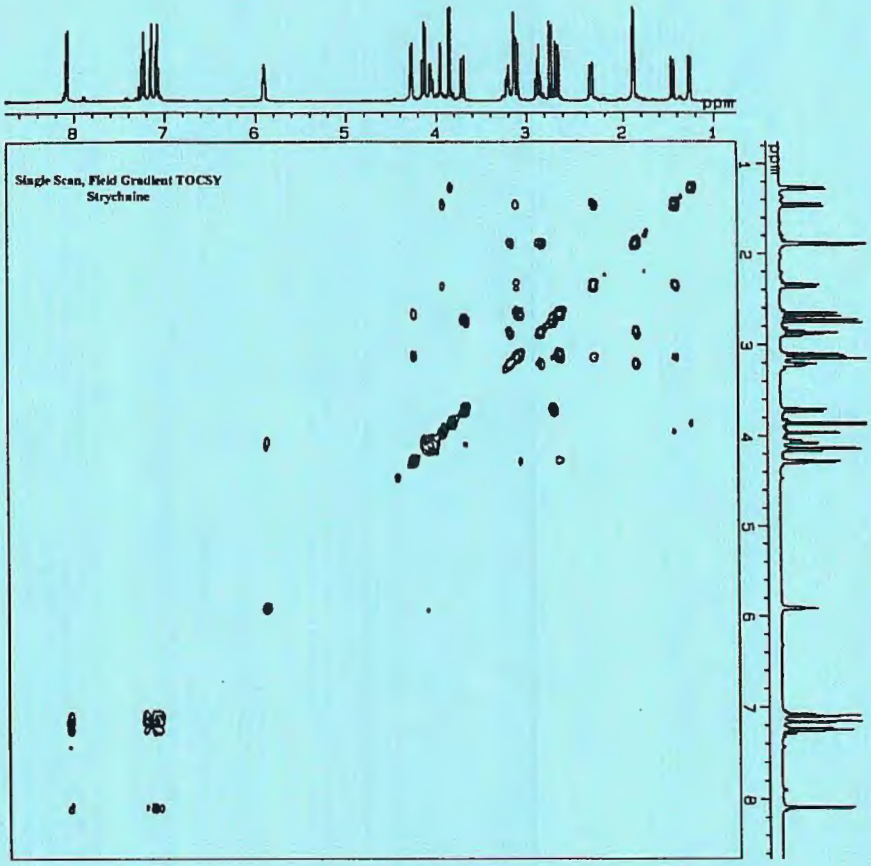
Gradient Probes



The above data is a 512 by 512 *TOCSY* spectrum and was obtained on an **Alpha**- 500 in less than 5 minutes with **JEOL**'s gradient probe. This same probe is also designed to do reverse and water suppression experiments. Pulse shaping, three channel operation, dynamic Rf control, matrix shims, as well as unsurpassed field reliability are all standard with the **Alpha**.

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