

THE
NMR
NEWSLETTER

No. 464
May 1997

TOCSY plus WATERGATE	Sengtschmid, H., and Sterk, H.	2
Relative Stereochemistry for Flexible Molecules	Termin, A., Gröger, S., and Poppe, L.	5
Phosphorus Speciation in Na/Ca/Phosphate Ceramics	Hawkes, G. E.	7
Heteronuclear PFG Experiments on an AM Spectrometer	Kaehlig, H.	11
NMR of Hydroxyhalides	Dybowski, C.	13
Triflate in the First Coordination Sphere of Dy ³⁺ in Isopropanol Solution	van Loon, A. M., and Peters, J. A.	14
¹ H NMR Spin-Diffusion Experiments on Composite Latex Particles	Landfester, K., Kirsch, S. P., and Roberts, J. E.	17
<i>In Vivo</i> Relaxivity at 6.3 T	Rozijn, T., and Bovee, W. M. M. J.	21
Xe-129 as a Probe of Polymer Sorption Sites	Inglefield, P. T., Jones, A. A., and Koons, J.	25
RAMOSE: Remote, Automated and Multitask Operation of NMR SpEctrometer	Gröger, S., and Poppe, L.	29
Computerized Database for Fluorine NMR Data	Pradhan, J., and Dolbier, W. R.	31
⁹³ Nb Spectra in Aqueous Solution	Clarke, A., Cox, D. J., and Howarth, O.	36
News of Old Spectrometers and Spectroscopists	Bladon, P.	37
Position Available	Marshall, A. G.	38
Position Available	Ackerman, J. L.	38

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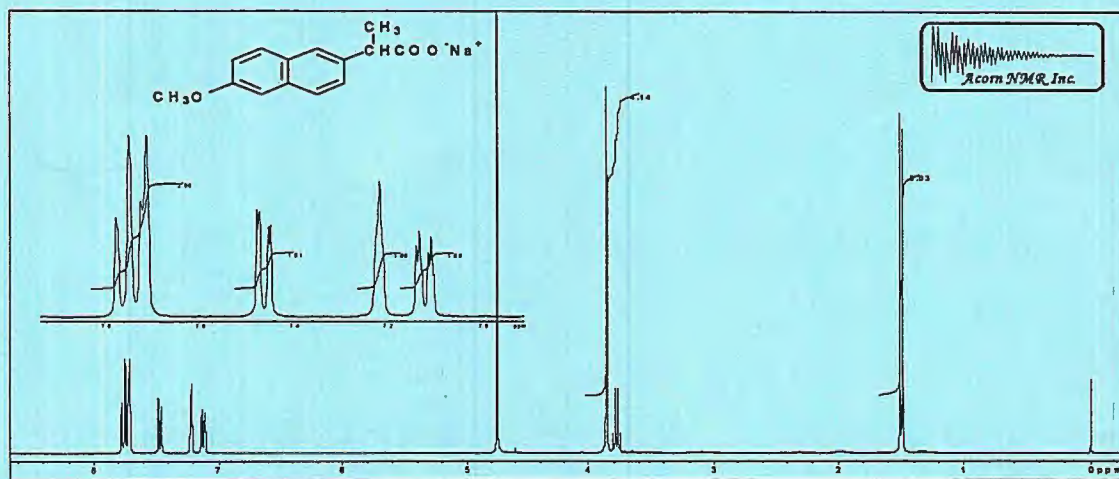


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THE NMR NEWSLETTER**NO. 464, MAY 1997****AUTHOR INDEX**

Ackerman, J. L. . . . 38	Gröger, S. . . . 5,29	Koons, J. . . . 25	Pradhan, J. . . . 31
Bladon, P. . . . 37	Hawkes, G. E. . . 7	Landfester, K. . . 17	Roberts, J. E. . . 17
Bovee, W. M. M. J. . 21	Howarth, O. . . . 36	van Loon, A. M. . . 14	Rozijn, T. . . . 21
Clarke, A. . . . 36	Inglefield, P. T. . 25	Marshall, A. G. . . 38	Sengstschnid, H. . 2
Cox, D. J. . . . 36	Jones, A. A. . . . 25	Peters, J. A. . . . 14	Sterk, H. . . . 2
Dolbier, W. R. . . . 31	Kaehlig, H. . . . 11	Poppe, L. . . . 5, 29	Termin, A. . . . 5
Dybowski, C. . . . 13	Kirsch, S. P. . . . 17		

THE NMR NEWSLETTER**NO. 464, MAY 1997****ADVERTISER INDEX**

Acorn NMR, Inc. inside front cover	Otsuka Electronics 15
AMT 23	Varian NMR Instruments 3
Bruker Instruments, Inc. 9, 27	Wilma Glass Company, Inc. 19
JEOL outside back cover	

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FORTHCOMING NMR MEETINGS

6th Meeting of AUREMN (NMR Users Association of Brazil), Rio de Janeiro, Brazil, **May 12-16, 1997**; Contact: Snia Maria C. de Menezes, Petrobas/Cenpes/Diquim/Radial 2, Quadra 07 - Ilha do Fundão, 21949-900 Rio de Janeiro, Brazil; Tel: +55 21 598-6171 and 598-6914; Fax: +55 21 598-6296; Email: sonia@cenpes.petrobas.com.br.

39th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado; NMR Symposium, **August 4-7, 1997**; Contact: J. P. Yesinowski, Code 6120, Naval Research Laboratory, Washington, DC 20375-5342; 202-767-0415; fax 202-767-0594; email yesinowski@nrl.navy.mil. See Newsletter 458, 8.

Fourth International Meeting on Recent Advances in Magnetic Resonance Applications to Porous Media, Trondheim, Norway, **Aug. 31 - Sep. 3, 1997**; Contact: John J. Attard, SINTEF Unimed MR-Center, N-7034 Trondheim, Norway. Tel: +47 73 59 89 25; Fax: +47 73 99 77 08; Email: john.attard@unimed.sintef.no.

4th International Conference on Magnetic Resonance Microscopy "Heidelberg Conference in Albuquerque", **Sept. 21-25, 1997**; Contact: E. Fukushima, The Lovelace Institutes, 2425 Ridgecrest Drive SE, Albuquerque, NM 87108-5127; (505) 262-7155; Fax: (505) 262-7043. See Newsletter 449, 37.

Missouri Magnetic Resonance Symposium (MMRS-VIII), Tan-Tar-A Lodge, Lake of the Ozarks, Osage Beach, MO, **October 31, 1997**. Contact: Frank D. Blum, Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409-0010; 573-341-4451, fblum@umr.edu, <http://www.chem.umn.edu/midwest32.html>

39th ENC (Experimental NMR Conference), Asilomar [sic] Conference Center, Pacific Grove, CA, **March 22 - 27, 1998**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87505; (505) 989-4573; Fax: (505) 989-1073. See Newsletter 460, 41.

Additional listings of meetings, etc., are invited.

KARL-FRANZENS-UNIVERSITÄT GRAZ
Institut für Organische Chemie

Dr. Heinz Sterk

A-8010 Graz, 10.3.97
 Heinrichstraße 28
 Tel. (0316) 380 DW, 5321 bzw. 5320

Unser Zeichen:

(received 3/29/97)

Dr. Bernhard Shapiro
 The NMR Newsletter
 966 Elsinore Court
 Palo Alto, CA 94303

TOCSY plus Watergate

Dear Dr. Shapiro :

Last year a brand new VARIAN UNITY 600 MHz NMR spectrometer was installed at the Institute of Pharmaceutical Chemistry at our University. As we are allowed to use this machine a few days each month, we started measuring small proteins. Unfortunately it turned out that no TOCSY pulse sequence with a Watergate step - to suppress the water signal - was supplied from the factory. If you focus the same problem, and would like to use a TOCSY with WATERGATE, add the following lines to your TOCSY program and you will easily overcome this problem.

Take tocsy.c! Type after "double ...cycles" : double gzlvl1, gt1, phincr2, phincr3, p2lvl, p180, gstab, tau, p2; /*WATERGATE*/

A few lines later where the variables are initialized type after getstr("sspul",sspul) the lines listed below. The lines at the right hand side are to be added at the end of the program. After "xmtroff(); and delay(rof2)"; add /* solvent suppression ...*/ and so on.

/* solvent suppression by WATERGATE */

/* WATERGATE parameters: */

```
gzlvl1 = getval("gzlvl1");
gt1 = getval("gt1");
phincr2 = getval("phincr2");
phincr3 = getval("phincr3");
p2lvl = getval("p2lvl");
p180 = getval("p180");
gstab = getval("gstab");
tau = getval("tau");
p2 = getval("p2");
```

```
obsstepsize(0.25); /* init small angle shifts for WATERGATE */
if (phincr2 < 0.0)
  phincr2 = 1440 + phincr2;
initval(phincr2, v6);
if (phincr3 < 0.0)
  phincr3 = 1440 + phincr3;
initval(phincr3, v8);
```

Yours sincerely



H. Sengstschmid

```
status(D);
add(oph, two, v7);
delay(tau); /* first half of echo */
zgradpulse(gzlvl1, gt1); /* dephase */
delay(gstab);
obspower(p2lvl); /* soft 90 on water - flip */
obsstepsize(0.25);
xmtphase(v6);
rgpulse(p2, v7, rof1, rof2);
obspower(p1lvl); /* hard 180 */
xmtphase(zero);
rgpulse(p180, oph, rof1, rof2);
obspower(p2lvl); /* soft 90 on water - back flip */
xmtphase(v8);
delay(SAPS_DELAY);
rgpulse(p2, v7, rof1, rof2);
obspower(tpwr);
xmtphase(zero);
delay(SAPS_DELAY);
zgradpulse(gzlvl1, gt1); /* rephase signals / dephase water */
delay(tau + gstab); /* second half of echo */
rcvtron();

/* acquire */
```

status(E);

}

H. Sterk



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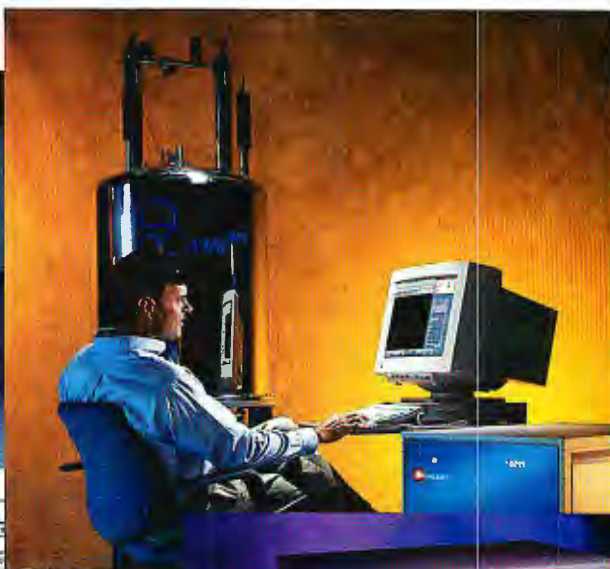
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Dr. Bernard L. Shapiro

The NMR Newsletter
966 Elsinore Court
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2.7.97 (received 4/3/97)

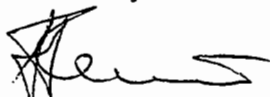
RE: Relative stereochemistry for flexible molecules

Dear Barry:

One frequent problem during synthesis is determination of the relative stereochemistry. For rigid molecules this task can be solved, in most of the cases, by one or two-dimensional NOE experiments. When the molecule is flexible, solving this problem may require measurement of heteronuclear three-bond coupling constants. For molecules with a natural isotope abundance (1% ^{13}C and 0.37% ^{15}N) these experiments require high spectrometer stability. The figure on the next page demonstrates selective measurement of such couplings as well as advantages of post-acquisition signal enhancement by the special symmetrization protocol.¹ It is important that this protocol automatically phases the antiphase signals, and by doing so, discriminates the real signal from the noise.

The answer as to what stereoisomer(s) we have in the nmr tube, immediately follows from the data in the table. Somewhat closer examination of the coupling constants reveals ca. 70% of the $^{SR(RS)}\text{I}$ and 30% of $^{SR(RS)}\text{II}$ rotamers in enantiomeric mixture.

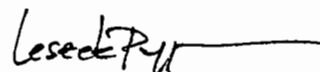
Sincerely,



Andreas Termin,

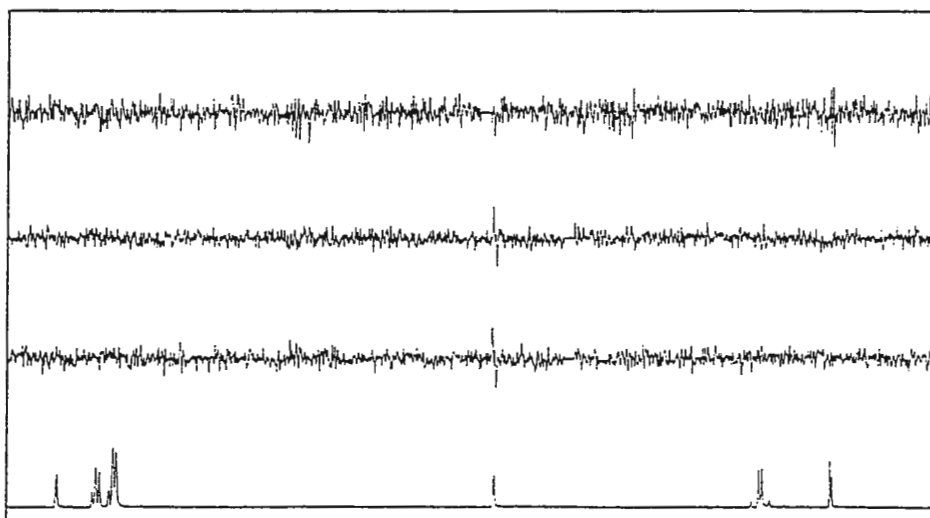


Stefan Gröger,

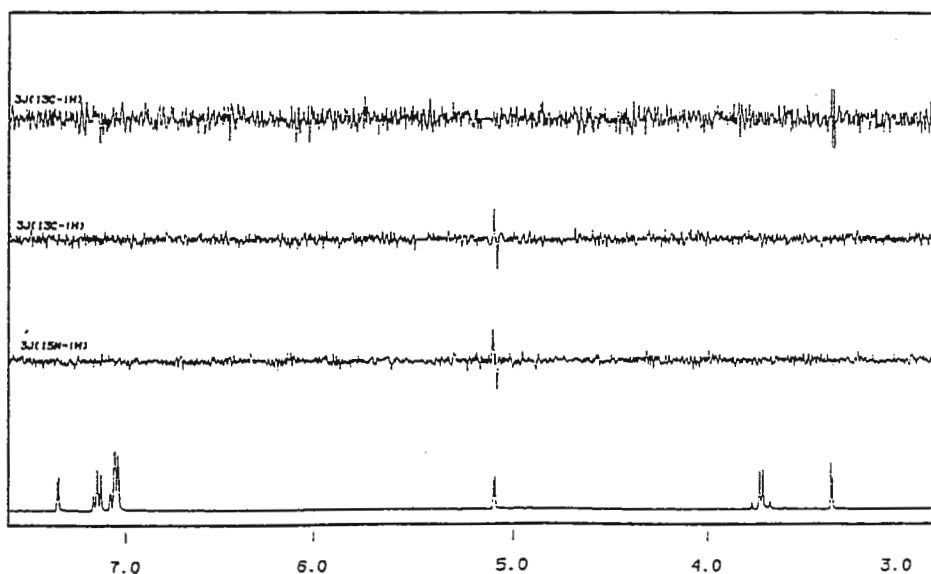


Leszek Poppe

[1] L. Poppe, S. Sheng and H. van Halbeek J. Magn. Reson. A 111, 104-107 (1994).



*phased
manually*

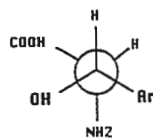


*phased
automatically*

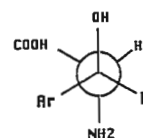
Predicted and measured heteronuclear coupling constants for the molecule of interest. L - means large (> 5 Hz for $^{13}\text{C}-^1\text{H}$, >3 Hz for $^{15}\text{N}-^1\text{H}$) and s - means small (< 3 Hz for $^{13}\text{C}-^1\text{H}$ and < 2 Hz for $^{15}\text{N}-^1\text{H}$)

$^3J_{\text{N-H}}$ $^3J_{\text{C}_{\text{COOH}}-\text{H}}$ $^3J_{\text{C}_{\alpha}-\text{H}}$ $^3J_{\text{H-H}}$

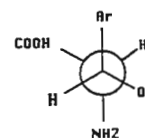
SR_I	L	S	S	S
SR_II	S	L	L	S
SR_III	S	S	S	L
RR_I	L	S	L	S
RR_II	S	L	S	S
RR_III	S	S	S	L
EXPERIMENT	L	S	S	S



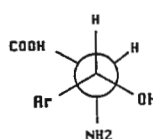
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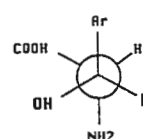
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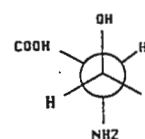
III



RR I



II



III

Structural Chemistry Group
Department of Chemistry

Queen Mary & Westfield College
Mile End Road, London E1 4NS

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QUEEN MARY

AND WESTFIELD COLLEGE
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19th March 1997

(received 3/26/97)

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

Dear Barry,

Phosphorus Speciation in Na/Ca/phosphate Ceramics

We have recently been using the combined techniques of thermal analysis, X-ray powder diffraction and solid state MAS NMR to study structure in Na/Ca/Al/phosphate¹ and Na/Ca/phosphate² glasses and their derived ceramics. These materials are potentially bioactive, and we report some of our data on the aluminium-free systems of general formula $(P_2O_5)_{0.45}(CaO)_{0.20+x}(Na_2O)_{0.35-x}$ ($x = 0.0 - 0.12$). The centre-band regions of the ^{31}P MAS spectra are shown in Figure 1, and the high frequency regions (0 to -10δ) are due to Q^1 phosphorus (chain terminating), and the low frequency regions (-18 to -25δ) are due to Q^2 (in-chain) phosphorus. The major Q^1 ^{31}P resonances occur in pairs and we assign the pair of resonances from the $x = 0.0$ sample to $Na_4P_2O_7$, for the lower sodium-content sample with $x = 0.08$ the signals at -7.7 and -10.2δ are very similar in position to those reported³ for α - $Ca_2P_2O_7$. There were four ^{31}P signals reported³ for β - $Ca_2P_2O_7$ in the range -7 to -9δ and the spectrum for the $x = 0.12$ sample shows four resolved signals attributable to the β -form, however the improved spectral dispersion of a 242.8 MHz ^{31}P MAS NMR spectrum showed four resonances at -7.0 , -7.9 , -8.6 , and -10.1δ with approximately equal intensity (β - $Ca_2P_2O_7$), and two lesser, equal intensity resonances -6.6 and -9.6δ (α - $Ca_2P_2O_7$). The total α : β ratio was *ca.* 1:10. The pairs of signals at -0.7 and -4.9δ for the samples with $x = 0.04$ and 0.08 are reasonably assigned to $Na_2CaP_2O_7$, with the higher frequency resonances due to phosphorus in the vicinity of sodium in the structure.

The Q^2 regions of the spectra in Figure 1 are very similar to those from the aluminium containing ceramics¹, and for those ceramics the principal Q^2 containing species was assigned as the cyclic trimetaphosphate phase $Na_4Ca(PO_3)_6$. Our preliminary assignment was made¹ on the basis of X-ray powder diffraction data on the ceramic. Subsequently we have determined the structure of this trimetaphosphate by Rietveld analysis of the powder diffraction data. The structure has been confirmed to contain cyclic trimetaphosphate units bridged by sodium and calcium ions, rather than a hexametaphosphate.

Hartmann *et al.*⁴ used ^{31}P dipolar recoupled 2-D NMR to show connectivity between the Q^1 and Q^2 regions of the spectra of some Na/Ca/Al/phosphate glasses, which points to the

presence of open chain metaphosphate species. In addition they observed connectivities between resolved resonances within the Q^1 region of a corresponding ceramic, indicating the presence of pyrophosphates. We have employed the same experiment on our ceramic with $x = 0.08$ (Figure 2). Like Hartmann *et al.*⁴ we see pairwise correlations within the Q^1 region, and equally important no correlation between the Q^1 and Q^2 regions. This is exactly what we would expect for the principal Q^2 species being cyclic metaphosphates.

Best wishes.

Geoff Hawkes

Geoff Hawkes

¹ I. Abrahams, K. Franks, G.E. Hawkes, G. Philippou, J. Knowles, P. Bodart and T. Nunes, *J. Mater. Chem.*, in press.

² I. Abrahams, G.E. Hawkes and J. Knowles, *J. Chem. Soc. Dalton Trans.*, in press.

³ A.K. Cheetham, N.J. Clayden, C.M. Dobson and R.J.B. Jakeman, *J. Chem. Soc. Chem. Commun.*, 1986, 195.

⁴ P. Hartmann, J. Vogel and C. Jäger, *Ber Bunsen-Ges. Phys. Chem.*, 1996, 100, 1658.

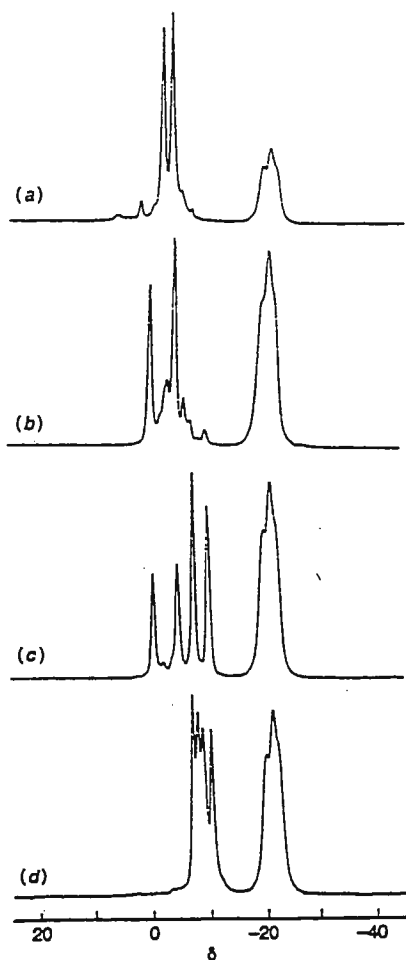


Fig. 1 Centre band regions of the 121.4 MHz ^{31}P MAS NMR spectra (Bruker MSL-300) of the ceramic samples $(\text{P}_2\text{O}_5)_{0.45}(\text{CaO})_{0.45-x}(\text{Na}_2\text{O})_{0.10-x}$: (a) $x = 0.0$, (b) 0.04, (c) 0.08 and (d) 0.12. The ^{31}P chemical shifts are referenced to external H_3PO_4 , and typical measurement conditions were 16 scans with a 100 s relaxation delay, and MAS rates ca. 7 kHz with the samples contained in a 4 mm outer diameter rotor

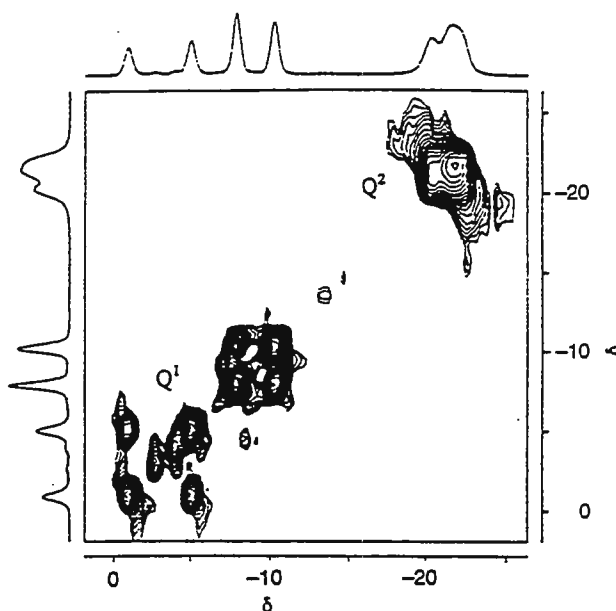
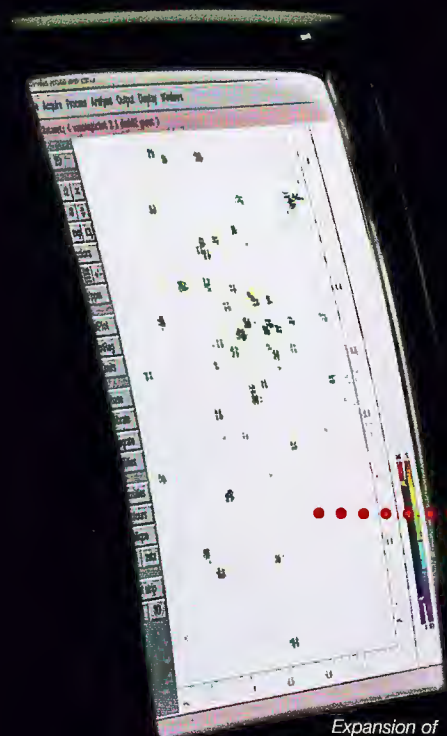


Fig. 2 Centre band region of the 242.9 MHz ^{31}P dipolar recoupled two-dimensional spectrum (Bruker AMX-600) of the ceramic with $x = 0.08$. The MAS rate was 12.0 kHz using a 4 mm outer diameter rotor, and the mixing time was 2.7 ms. Eight scans were acquired, with a relaxation delay of 12 s, for each of 512 experiments

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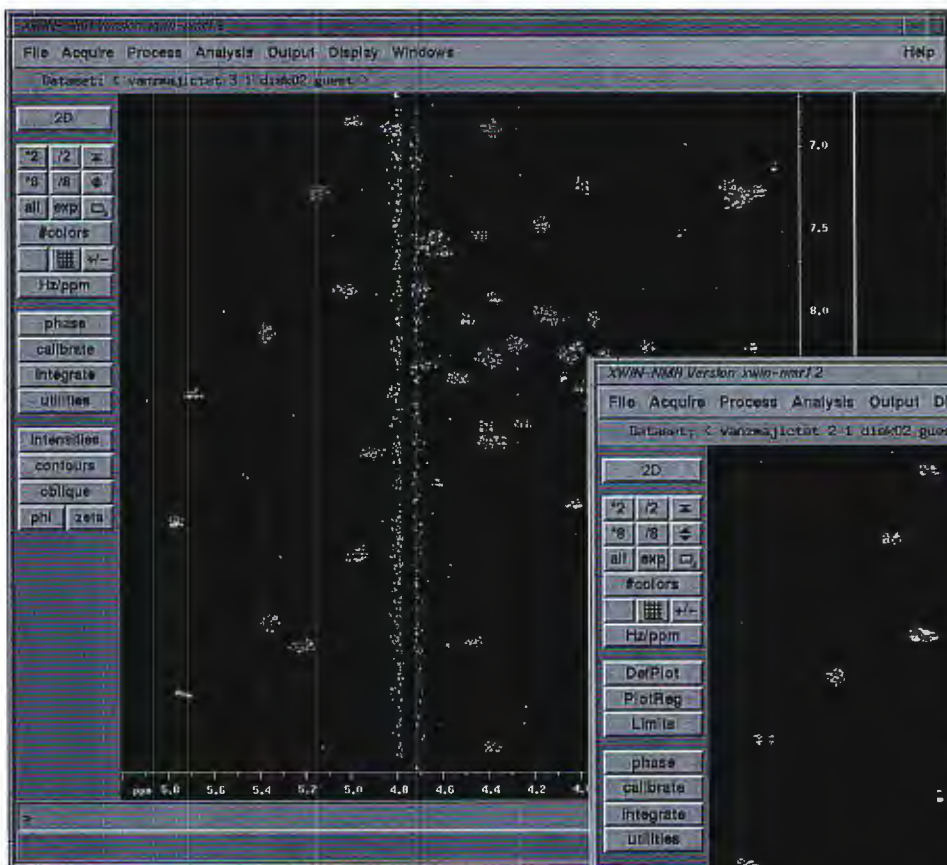
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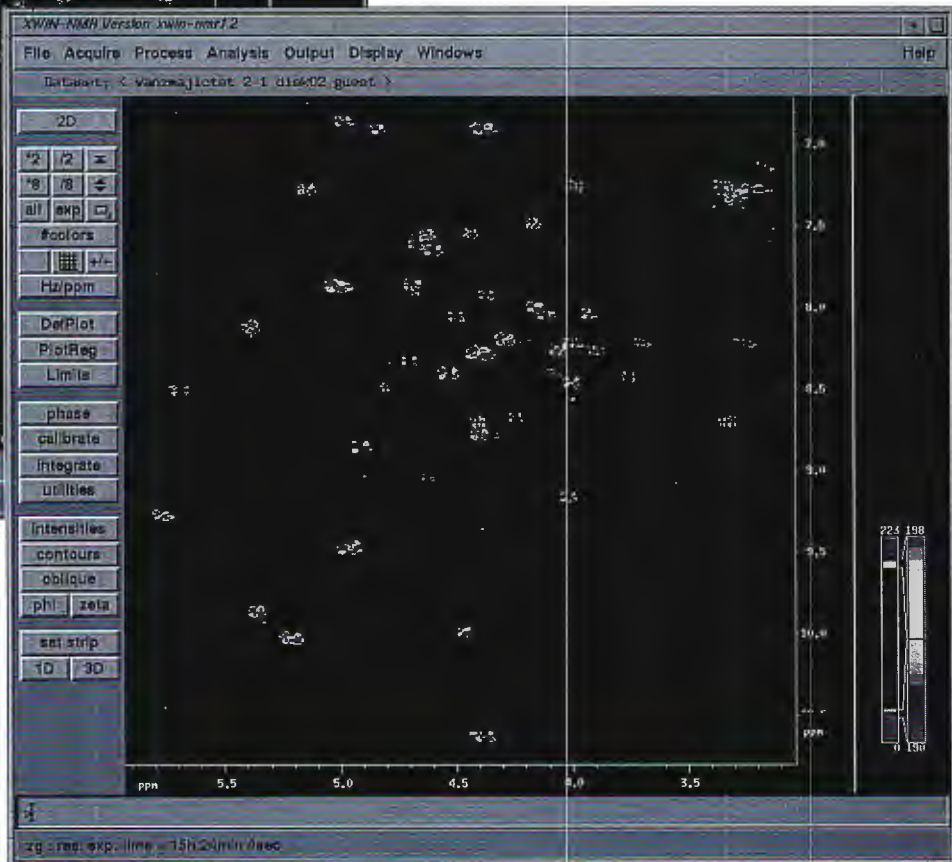
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Both experiments were acquired on the Bruker AVANCE 500 equipped with a 5 mm inverse triple resonance (TXI) probe with GRASPTM-III. The sample is 1.5 mM BPTI in 90% H₂O/10% D₂O. The experiment is DQF-COSY.

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To
Dr. Bernhard L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303
USA

(received 4/28/97)
Vienna, 20.4.1997

Heteronuclear PFG experiments on an AM spectrometer

Dear Dr. Shapiro,

Pulsed field gradient assisted techniques already belong to the standard repertoire of experiments in high resolution NMR of solutions, especially if the available spectrometer is fairly new and therefore equipped with the necessary hardware from the very beginning. Nevertheless it is highly recommendable to upgrade older instruments with such a gradient accessory. For example, in a contribution last year Prof. Sterk reported about z-gradient assisted experiments on an AM 360. We also purchased a z-gradient waveform memory, the 10 Amp BGU gradient amplifier and an actively shielded z-gradient inverse probe for an AM 400 WB.

In this contribution I want to present the pulse sequence of one of our favorite heteronuclear experiments using gradient selection to achieve a perfect suppression of unwanted signals and, in addition, to gain sensitivity, namely the sensitivity enhanced ge-HSQC with echo-antiecho selection as published by L.E. Kay, P. Keifer, T. Saarinen, J. Am. Chem. Soc., 1992, 114, 10663. The simultaneous acquisition mode has to be used, and for polarity switching of the refocussing gradient in the anti-echo part an additional RCP pulse has to be connected to the BGU gradient unit. One limitation of the DISNMR software when using gradients is that pulses cannot be calculated within the pulse sequence. So for the GARP decoupling all the necessary pulses were calculated after the determination of the low power 90° X pulse and then written into an EXE file for an easy setup. All other parameters are given below. Of course the processing of the derived data has to be done off-line; we use Xwin-nmr 1.3 or Felix 95.0 on SGI workstations.

Sincerely yours,

Dr. Kählig Hanspeter

```
;INVIEAGS.AU
;2D PFG assisted H-1/X correlation via heteronuclear single
;quantum coherence using inverse mode, echo-antiecho selection
;CPD decoupling during acquisition using GARP
;L.E.Kay et. al. J.Am.Chem.Soc., 1992, 114, 10663-10665
;
;RCP 4 has to be connected to BGU for polarity switch
;Define GARP pulses in an EXE-program for easy setup
```

```
1 ZE ;start of echo
2 D1 S1 DO
P1:D PH1
D4
(P2 PH1):D (P4 PH1)
D4
(P1 PH2):D (P3 PH3)
D0
P2:D PH1
D0
P31:Z2:C10
D20
P31:Z0:C10
D16
P4 PH4
D21
(P1 PH1):D (P3 PH4)
D24
(P2 PH1):D (P4 PH1)
D24
(P1 PH2):D (P3 PH5)
D4
(P2 PH1):D (P4 PH1)
D4
(P1 PH1):D
D22
(P2 PH1):D
D13
P31:Z1:C10
D20
P31:Z0:C10
D16
D5
3 D5:D PH9
4 D6 ADC
5 (P7 PH10 P10 PH12 P28 PH10 P30 PH12 P15 PH10 P11 PH12):C7:T:C3
(P19 PH10 P20 PH12 P24 PH10 P27 PH12 P14 PH10 P8 PH12):C7:T:C3
(P6 PH10 P17 PH12 P22 PH10 P25 PH12 P29 PH10 P12 PH12):C7:T:C3
(P16 PH10 P18 PH12 P21 PH10 P23 PH12 P26 PH10 P13 PH12):C7:T:C3
(P9 PH10):C7:T:C3
L0 TO 5 TIMES 2
6 (P7 PH12 P10 PH10 P28 PH12 P30 PH10 P15 PH12 P11 PH10):C7:T:C3
(P19 PH12 P20 PH10 P24 PH12 P27 PH10 P14 PH12 P8 PH10):C7:T:C3
(P6 PH12 P17 PH10 P22 PH12 P25 PH10 P29 PH12 P12 PH10):C7:T:C3
(P16 PH12 P18 PH10 P21 PH12 P23 PH10 P26 PH12 P13 PH10):C7:T:C3
(P9 PH12):C7:T:C3
L1 TO 6 TIMES 2
7 L2 TO 5 TIMES UPR
8 RCYC=2 PH6
WR #1
IF #1
IP5
IP5
10 ZE ;start of anti-echo
20 D1 S1 DO
P1:D PH1
D4
(P2 PH1):D (P4 PH1)
D4
(P1 PH2):D (P3 PH3)
D0
P2:D PH1
D0
P31:Z2:C10
D20
P31:Z0:C10
D16
P4 PH4
D21
(P1 PH1):D (P3 PH5)
D24
(P2 PH1):D (P4 PH1)
D24
(P1 PH2):D (P3 PH5)
D4
(P2 PH1):D (P4 PH1)
D4
(P1 PH1):D
D22
(P2 PH1):D
```

```
D13 ;RCP4 for polarity switch
P31:Z1:C10:C4
P0:C4
P31:Z0:C10:C4
D16
D5
30 D5:D PH9
40 D6 ADC
50 (P7 PH10 P10 PH12 P28 PH10 P30 PH12 P15 PH10 P11 PH12):C7:T:C3
(P19 PH10 P20 PH12 P24 PH10 P27 PH12 P14 PH10 P8 PH12):C7:T:C3
(P6 PH10 P17 PH12 P22 PH10 P25 PH12 P29 PH10 P12 PH12):C7:T:C3
(P16 PH10 P18 PH12 P21 PH10 P23 PH12 P26 PH10 P13 PH12):C7:T:C3
(P9 PH10):C7:T:C3
L0 TO 50 TIMES 2
60 (P7 PH12 P10 PH10 P28 PH12 P30 PH10 P15 PH12 P11 PH10):C7:T:C3
(P19 PH12 P20 PH10 P24 PH12 P27 PH10 P14 PH12 P8 PH10):C7:T:C3
(P6 PH12 P17 PH10 P22 PH12 P25 PH10 P29 PH12 P12 PH10):C7:T:C3
(P16 PH12 P18 PH10 P21 PH12 P23 PH10 P26 PH12 P13 PH10):C7:T:C3
(P9 PH12):C7:T:C3
L1 TO 60 TIMES 2
70 L2 TO 50 TIMES UPR
80 RCYC=20 PH6
WR #1
IF #1
IP5
IP5
IN=1
EXIT
PH1=0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3
PH2=1 1 1 1 2 2 2 2 3 3 3 3 0 0 0 0
PH3=0 2 0 2 1 3 1 3 2 0 2 0 3 1 3 1
PH4=0 0 2 2 1 1 3 3 2 2 0 0 3 3 1 1
PH5=1 1 3 3 2 2 0 0 3 3 1 1 0 0 2 2
PH6=R0 R2 R2 R0 R1 R3 R3 R1 R2 R0 R0 R2 R3 R1 R1 R3
PH9=0
PH10=0
PH12=2
;P6 = 25.5 degree pulse at low power output
;P7 = 30.5
;P8 = 45.9
;P9 = 53.4
;P10= 55.2
;P11= 62.2
;P12= 64.9
;P13= 65.6
;P14= 66.4
;P15= 69.3
;P16= 70.9
;P17= 72.7
;P18= 77.2
;P19= 85.0
;P20= 91.8
;P21= 98.2
;P22=119.5
;P23=133.6
;P24=134.5
;P25=138.2
;P26=255.9
;P27=256.1
;P28=257.8
;P29=258.4
;P30=268.3
;L2= 31.75 * 4 * (90 degree low power pulse length) => AQ
;D1 : 1-5 T1
;S1 : 1H
;P1,P2 : 90, 180 deg H-1 pulse
;D4 : 1/(4J)XH
;P3,P4 : 90,180 deg X pulse
;D0 : 3 usec
;P31 : 2 usec
;D20, P0 : gradient duration
;D16 : gradient recovery delay
;D21 : D20+D16+2*P31+P2+D0*2
;D24 : 1/4J for XH or 1/6J for all multiplicities
;D22 : D20+D16
;D13 : 2 us
;D5 : DE/2
;D6 : 2 usec
;gradient ratio according to gamma of involved nuclei
;for 1H,13C Z1 : Z2 = 1 : 4
;DS : 0 or anything else
;NS : 1 * n
;IN : 1 / 2SW(X) = DW(X)
;ND0 : 2
;NF : 2*NE
;Note : simultaneous acquisition mode required, enter 'SIM'
```

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Cecil Dybowski
Professor

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

April 7, 1997
(received 4/11/97)

NMR of Lead Hydroxyhalides

Dear Barry:

Thank you for the gentle warning in the color of my alma mater. As you know, I have had an ongoing interest in the detection of ^{207}Pb NMR in solid materials, in part because it, being that isotope with the highest atomic number having spin $\frac{1}{2}$, represents the end of the "known world" of spin $\frac{1}{2}$. But NMR may be potentially useful in delineating the chemical state of lead materials in the environment, another important use for this spectroscopy.

One important reaction of lead ion is the partial hydrolysis to produce the PbOH^+ moiety, and the Hydroxy halides are well known solids. We have examined these solids with lead NMR spectroscopy and some preliminary results are given in the table, along with our data for the dihalides. Shifts are in ppm relative to external tetramethyllead (δ scale), referenced through the isotropic shift of $\text{Pb}(\text{NO}_3)_2$ and are probably accurate to better than ± 5 ppm. As one may see, the isotropic shifts of the hydroxyhalides cluster near of -600 ppm and may easily be distinguished from the corresponding dihalides whose shifts are much different.

Compound	δ_{iso}	Compound	δ_{iso}
PbI_2	-29	$\text{Pb}(\text{OH})\text{I}$	-546
PbBr_2	-981	$\text{Pb}(\text{OH})\text{Br}$	-639
PbCl_2	-1715	$\text{Pb}(\text{OH})\text{Cl}$	-706
PbF_2	-2666		

The nature of these shifts is interesting, and we are investigating them further, including evaluation of the anisotropic components. However, these data clearly show it would be relatively easy to detect the hydroxyhalides and the dihalides with solid-state NMR in a sample of environmental interest and distinguish them.

Yours,



Cecil Dybowski
Professor

(received 3/25/97)

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

Triflate in the first coordination sphere of Dy^{3+} in isopropanol solution.

Delft, March 18, 1997

Dear Dr. Shapiro,

Lanthanide ions have been shown to be catalytically active in many organic reactions. We are investigating the Meerwein-Ponndorf-Verley reduction ¹⁾ catalyzed by Ln(III) chelates. This reaction involves reduction of a ketone to an alcohol with the use of, for instance, isopropanol as hydride donor. The unique paramagnetic properties allow the determination of the structure of the complexes involved in solution.

We are interested in the number of isopropanol molecules coordinated to lanthanides in the presence of various anions. The role of non-alkoxide anions present in the MPV reaction is noted by several authors as being very influential with respect to the rate of the reaction, to such extent that some anions present will totally quench the reaction, whereas others will speed up the reaction considerably. Triflate is among those which increase the reaction rate. A very powerful technique to probe the first coordination sphere of lanthanide ions is ^{17}O NMR.

Previously, we have shown that the Dy(III) induced ^{17}O shifts of oxygen atoms coordinated to Dy(III) are predominantly of contact origin and that the bound shifts are almost independent of the nature of the oxygen atom or of the structure of the Dy(III) complex²⁾.

If the exchange between a Dy(III) bound and a free ligand is fast on the ^{17}O NMR time scale, the Dy(III) induced ^{17}O shift of the oxygen donor atom can be used to obtain information on the first coordination shell of the concerning complex. It can be derived that the slope of the curve of the Dy(III) induced ^{17}O shift vs. the molar ratio of Dy(III) /ligand is proportional to the number of oxygens in the first coordination sphere.

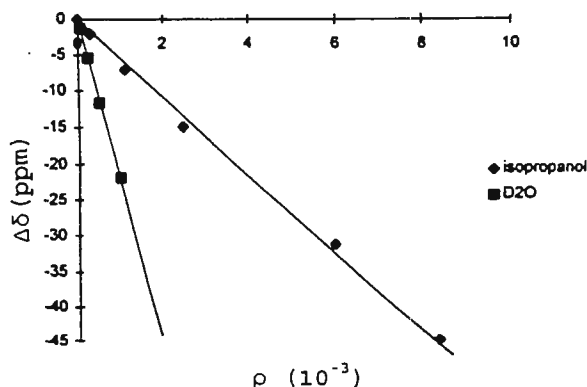
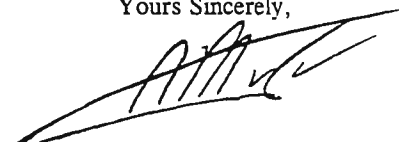


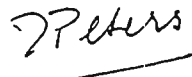
Fig. 1 ^{17}O chemical shifts for D_2O and isopropanol at various concentrations $\text{Dy}(\text{O}_3\text{SCF}_3)_3$ (in mol Dy / mol solvent). Values are corrected for bulk magnetic susceptibility.

This is illustrated in Figure 1. The ^{17}O shift of D_2O induced by $\text{Dy}(\text{O}_3\text{SCF}_3)_3$ was measured for calibration. It is known that under these conditions Dy(III) is coordinated to 8 D_2O molecules. The slope of the line is -21800 ppm and, therefore, each bound oxygen atom gives rise to an induced shift of -2725 ppm. The ^{17}O shift of isopropanol upon addition of $\text{Dy}(\text{O}_3\text{SCF}_3)_3$, however, shows a much smaller slope of -5400 ppm, which indicates that only $(-5400 / -2725 =)$ 2.0 isopropanol molecules are bound in the first coordination sphere of Dy(III) . Since the coordination number of Dy(III) is usually 8-9, this means that 6 oxygens of the 3 triflate anions are present in the first coordination sphere. CF_3SO_3^- anions must therefore be bound in a bidentate fashion. Thus, in isopropanol all triflate ligands, which are normally considered very weakly coordinated, stay firmly (bidentately) bound in the first coordination sphere of Dy^{3+} !

Yours Sincerely,



Arjen M. van Loon



Joop A. Peters

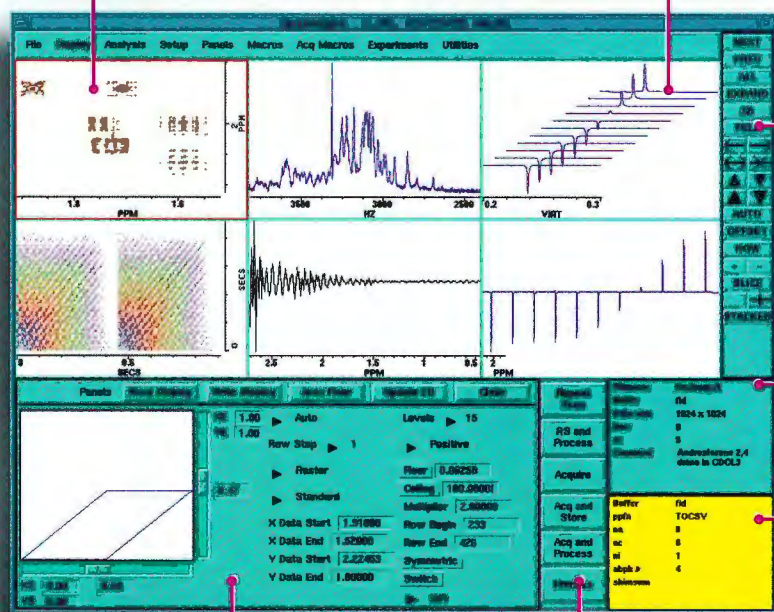
References:

1. C.F. de Graauw, J.A. Peters, H. van Bekkum, J. Huskens, *Synthesis* 1994, 1007
2. J.A. Peters, J. Huskens, D.J. Raber, *Prog. Nucl. Mag. Res. Spec.* 28, 1996, 283-350

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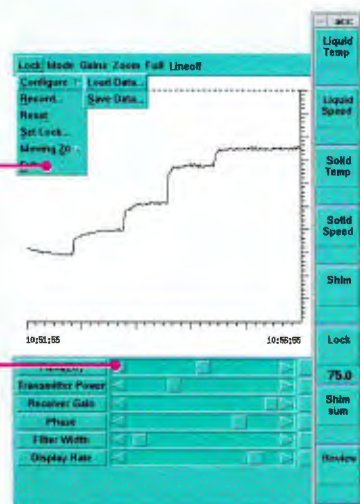
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(received 4/28/97)

Lehigh University**¹H NMR Spin-Diffusion Experiments on Composite Latex Particles**

Dear Dr. Shapiro,

Solid-state NMR methods based on ¹H spin-diffusion experiments have been developed for the characterization of heterogeneities in polymers and polymer blends /1/. They also have been used for the characterization of the interphase structure and the interphase thickness of composite colloidal polymer particles produced by two-step emulsion polymerization /2/. The dipolar filter used for the spin-diffusion experiment is sensitive to different mobilities in the system. Up to now we have only characterized particles where none of the components in the mobile and the rigid phases were the same. In recent experiments, we determined the structure of a latex prepared by a two-step emulsion polymerization where in the first step a copolymer of poly(butyl methacrylate-co-methyl methacrylate) (P(BuA-MMA) (ratio: 67/33) was synthesized and in the second step a homopolymer of poly(methyl methacrylate) (PMMA) was added. For the first NMR measurements, the latex was freeze-dried to obtain the particles with the original morphology. At room temperature, the ¹H NMR spectra at 300 Mhz show a superposition of a broad line (20 kHz) and a narrow line (800 Hz). For the selection of the soft component, the dipolar filter was used with one filter cycle consisting of 12 pulses separated by a delay time, t_d , varied from 2 μ s to 80 μ s. Depending on the filter strength represented by t_d between the pulses in the filter, the spin-diffusion curves at room temperature show different behavior (Figure 1a). At weak filter strengths ($t_d = 2 \mu$ s to 6 μ s), the curve has a low slope at short mixing times and reaches a constant final value between 0.7 to 0.8 indicating that 70 % to 80 % of the particle is detected as mobile. The curves with these weak filters are sensitive to the entire structure of the particle and indicate a core-shell morphology of the particles. The spin-diffusion takes place from the selected core + interphase to a thin pure shell (Figure 2a). With an effective phase separation of both phases the final value is expected to be 0.5. That means that a portion of the PMMA of the second polymerization step is mobilized by diffusion in the preexisting copolymer core. These curves detect the whole particle with a broad interphase between the phases. Even for core-shell polymers consisting of homopolymers, diffusion of the PMMA in the PBuA homopolymer phase was observed, but the diffusion is even more favorable in the case of a copolymer because of an increase in the compatibility of the phases. At a filter strength of 10 μ s, the curve reaches the final value of 0.5 expected of the stoichiometric ratio of the components. For stronger filters (20 μ s to 80 μ s), the decay in the spin-diffusion curve at short mixing times is very fast and the final value drops to 0.07. With these filter strengths very small heterogeneities in the core are detected. Only 7 % of the particles, probably highly PBuA-rich domains in the core, are selected by the dipolar filter. Then the spin diffusion takes place to the surrounding phase in the core and the shell (Figure 2b). The spin-diffusion is no longer sensitive to the entire structure of the particles, but to the structures in the copolymer phase. These measurements show that depending on the filter strength it is possible to be sensitive to the entire structure of composite particles or to the structure of the mobile copolymer where one component can be the same as in the rigid phase.

For another experiment, the latex was dried at room temperature where it formed a film. The film shows only a broad line in the ¹H spectrum, the narrow line having disappeared. This indicates that the PBuA-rich domains had diffused into regions with lower mobility or that PMMA had diffused into the PBuA-rich domain. The spin-diffusion experiment could no longer be performed at room temperature because the dipolar filter could not distinguish different mobilities in the system. The sample was heated up in the probe to 60 °C where a component with a line width of 400 Hz was

detected. In Figure 1b the spin-diffusion curves of the film are shown. The slopes at short mixing times are comparable to the slopes measured on the freeze-dried sample at room temperature. This indicates that a large structure (with weak filters) and small domains (strong filters) can be detected. But at longer mixing times the curves do not reach an equilibrium indicating large phases, but also extended interphases in the system. Even with a weak filter (2 μs), the value after a mixing time of 800 ms ($30 \text{ ms}^{1/2}$) reached final values of 0.6. This means that the systems became more rigid because of the film formation process. With a strong filter strength (80 μs), the final value reaches 0.2. This allows the conclusion that after the film formation, two phases with different mobilities can still be detected where one phase represents a PBuA-rich phase and the other a PMMA-rich phase, but the mobility of the PBuA-rich phase is decreased compared to the freeze-dried sample.

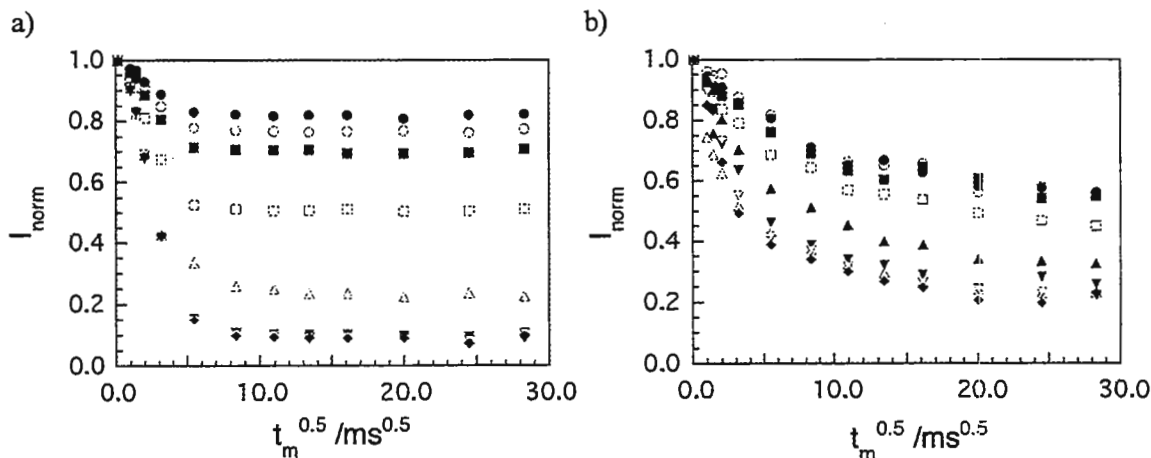


Figure 1: a) Spin-diffusion curves of the freeze-dried particles; b) spin-diffusion curves of the film. Different filter strength: ● 2 μs ; ○ 4 μs ; ■ 6 μs ; □ 10 μs ; ▲ 20 μs ; △ 30 μs ; ▼ 40 μs ; ▽ 60 μs ; ◆ 80 μs .

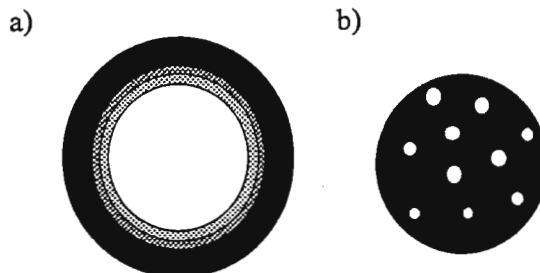


Figure 2: a) With weak filter strengths, the spin-diffusion is sensitive to the entire structure of the particle; b) with strong filter strengths the small heterogeneities in the copolymer of the core are detected.

/1/ K. Schmidt-Rohr, H.W. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press, London, 1994.

/2/ K. Landfester, C. Boeffel, M. Lambla, H.W. Spiess, *Macromolecules* 1996, 29, 5972.

Sincerely,

Katharina Landfester
Katharina Landfester

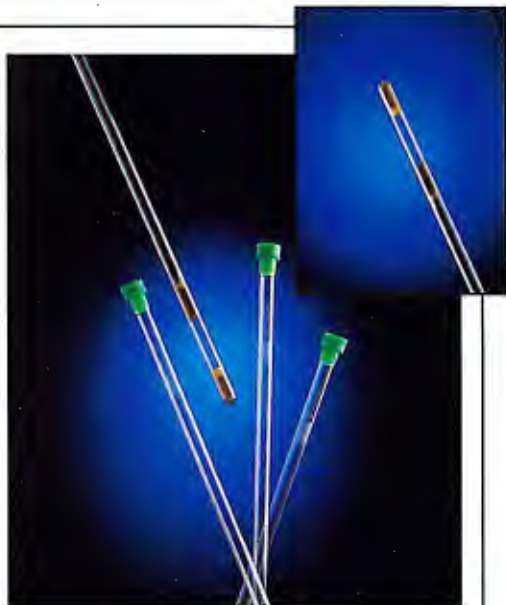
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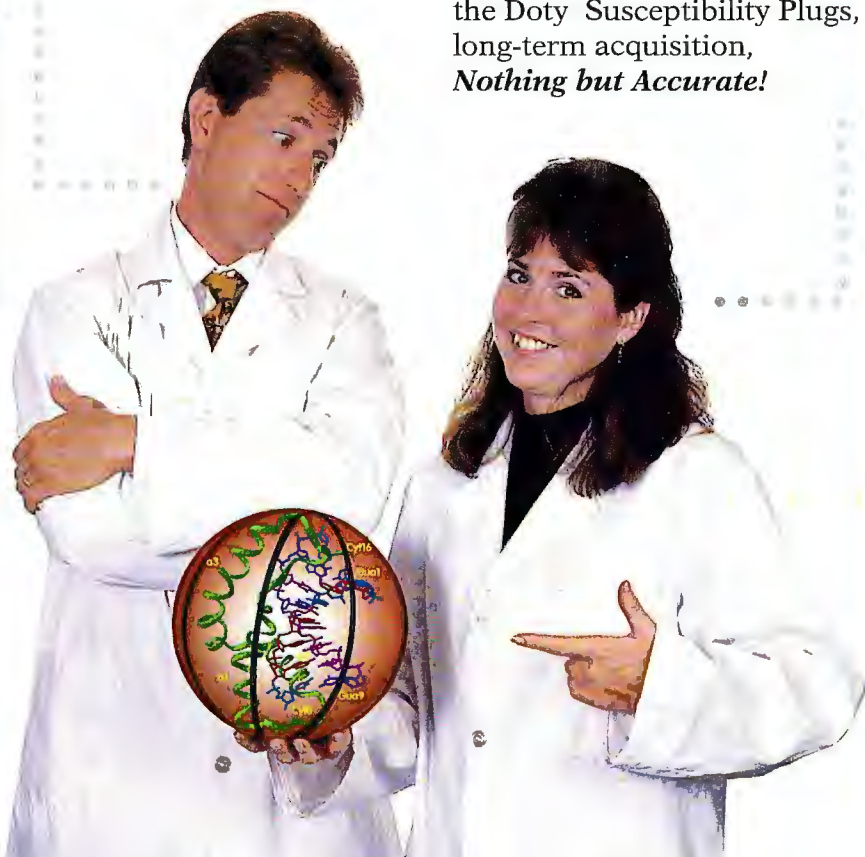
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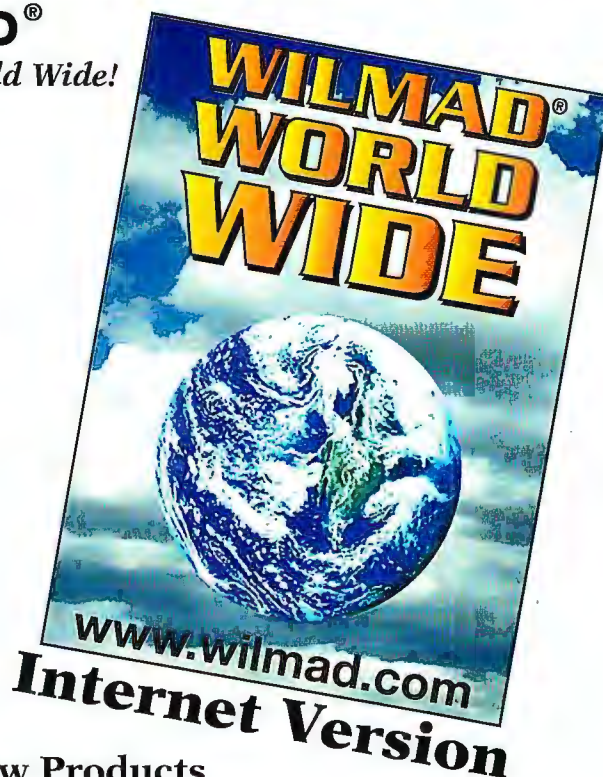
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Office telephone

Date

31 15 786041

April 3, 1997.

(received 4/12/97)

Subject

Sub-division

In vivo relaxivity at 6.3 T.

From the in-vivo relaxivity β_1 tissue GdDTPA concentrations can be determined, and from these physiological parameters like leakage space (V_i), blood flow (F) and extraction (E) in brain tumors, characterising and monitoring the influence of any therapy on them. These parameters can be assessed by dynamic MRI studies after a short bolus injection of Gd-DTPA. Using multi-compartmental models [1,2] the tracer uptake by the tissue is described with the next equation.

$$C_i(t) = \sum (Y_i \cdot e^{\lambda_i t}) + G e^{-\frac{FE}{V_i} t} \quad (1)$$

$C_i(t)$ is the tissue tracer concentration. $\sum (Y_i \cdot e^{\lambda_i t})$ and G are determined by the plasma tracer concentration and the boundary conditions for $t=t_0$, the starting point of the measurement. Using T_1 weighted image sequences or direct fast T_1 measurements $\beta_1[\text{Gd}]$ can be obtained. Direct T_1 measurements are to be preferred because they are insensitive to T_2 and T_2^* effects of Gd-DTPA; $\beta_1[\text{Gd}]$ is then found from $T_1^{-1} = T_{10}^{-1} + \beta_1[\text{Gd}]$.

A direct fast T_1 measurement, a modification of the inversion recovery turbo FLASH pulse sequence [3] was used. After the inversion pulse, images are acquired continuously using an interleaved EPI sequence instead of turbo FLASH. For one T_1 measurement 32 images of 90×90 and a FOV of $30 \times 30 \text{ mm}^2$ were acquired in 9.6 s, giving an apparent $T_{1,\text{app}}$ according to $1/T_{1,\text{app}} = 1/T_1 - \ln[\cos(\alpha)]/TR$, where α is the flip angle. $\beta_1[\text{Gd}]$ is simply found from:

$$\beta_1[\text{Gd}] = \frac{1}{T_{1,\text{app}}} - \frac{1}{T_{10,\text{app}}} \quad (2)$$

Experiments were performed on skeletal muscle of 11 anaesthetised wistar rats on a home built 6.3 T animal system. Bolus injections of Gd-DTPA solutions (0.025 - 0.4 mmol/kg) were administrated via tail veins (a normally used dose is 0.1 mmol/kg). A T_{10} measurement was done and after the bolus injection the T_1 measurement was started when $[\text{Gd}]_{\text{tissue}} = [\text{Gd}]_{\text{bloodplasma}}$. During the T_1 measurement also 0.5 ml blood was sampled to determine $[\text{Gd}]$ in blood by ICP emission spectroscopy. Phantom studies showed that the results of this fast T_1 method were in good agreement with conventional Inversion Recovery T_1 results.

From in-vitro experiments on a tube of water, performed at different temperatures, a relaxivity $\beta_1=3.1 \text{ (mM.s)}^{-1}$ was found for body temperature (37°C). According to literature [4] β_1 is fairly constant for different fluids and over a wide range of field strengths. It was found to be in the order of 4 (mM.s)^{-1} for room temperature, which is in agreement with our own measurements after correction for the temperature difference. In tissue different compartments can be recognised: the intra- and extravascular space, which both can be split in an intra- and extracellular compartment. Between the intra- and extravascular space slow water exchange exists, resulting in two independent relaxation curves for both compartments. Since the intravascular compartment is only 3-5% of the whole muscle tissue, only the $T_{1,\text{bulk}}$ value from the entire extravascular compartment, in which fast water exchange between the intra- and extracellular space can be assumed, is observed. $1/T_{1,\text{bulk}} = f_e/T_{1,e} + f_i/T_{1,i}$, where f_e is the extracellular and f_i is the intracellular volume fraction. Since Gd stays extracellular for the measured T_1 can be written:

$$\frac{1}{T_{1,\text{bulk}}} = \frac{f_e}{T_{1,e,0}} + f_e \cdot \beta_1 \cdot [\text{Gd}]_e + \frac{f_i}{T_{1,i,0}} = \frac{1}{T_{1,0}} + \beta_{1,\text{bulk}} \cdot [\text{Gd}]_e \quad (3)$$

$$\beta_{1,\text{bulk}} = f_e \cdot \beta_1 \implies \beta_1 = \beta_{1,\text{bulk}}/f_e.$$

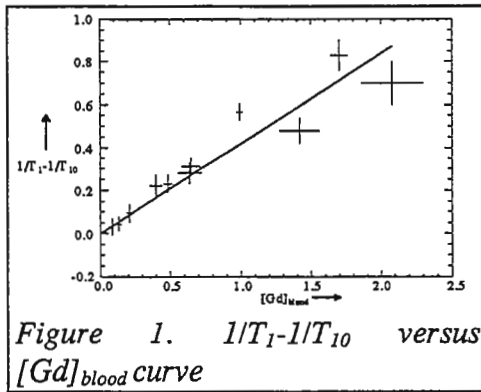


Figure 1. $1/T_1 - 1/T_{10}$ versus $[\text{Gd}]_{\text{blood}}$ curve

Figure 1 shows the $1/T_1 - 1/T_{10}$ versus $[\text{Gd}]_{\text{blood}}$ curve from which a $\beta_{1,\text{bulk}}=0.42 \text{ (mM.s)}^{-1}$ is found. Measurements were performed under the condition that $[\text{Gd}]_{\text{plasma}} = [\text{Gd}]_{\text{interstitialspace}}$. Since blood consists for only ~60% of blood plasma and since Gd remains extracellular, $[\text{Gd}]_{\text{plasma}} = [\text{Gd}]_{\text{blood}}/0.6$ resulting in a corrected value: $\beta_1 = 0.6 \cdot \beta_{1,\text{bulk}}/f_e$. For muscle tissue f_e is ~8% [4] resulting in: $\beta_1 = 7.5\beta_{1,\text{bulk}}$. From this it follows that β_1 is in the order of 3 (mM.s)^{-1} , which is in agreement with the in-vitro measurement.

Within the experimental error, the relation between $1/T_1$ and $[\text{Gd}]$ seems to be linear for the normally expected in-vivo $[\text{Gd}]$ range. When β_1 is assumed to be fairly constant, the measured bulk relaxivity $\beta_{1,\text{bulk}}$ is very sensitive to variations in the extracellular volume fraction f_e . Since f_e is generally relatively small, little variations in f_e result in large variations in $\beta_{1,\text{bulk}}$. In tumour tissue f_e is generally unknown and absolute determination of $[\text{Gd}]$ in tumour tissue by MRI is therefore very difficult. However the parameter of interest in equation (1) is the rate constant $F.E/V_t$. For the determination of this rate constant it is sufficient when the relative concentration $\beta_{1,\text{bulk}} \cdot [\text{Gd}]$ is known.

References.

- [1] Tofts P.S. et. al. [1991], *Magn. Reson. Med.* 17:357. [2] Larsson H.B.W. et. al. [1990], *Magn. Reson. Med.* 16:117. [3] R. Deichmann et. al. [1992], *Magn. Reson. Med.* 96:608. [4] Donahue K.M. et. al. [1994], *Magn. Reson. Med.* 32:66.

Tom Rozijn

Wim Bovee

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April 22, 1997
(received 4/25/97)

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

"Xe-129 as a Probe of Polymer Sorption Sites"

Dear Barry,

We have been doing a reasonable amount of Xe NMR in polymers and in certain cases it can be a very useful probe. Often low temperature spectra ($\sim -90^{\circ}\text{C}$) are necessary to freeze out exchange of Xe between different sites. The determining factor in this is the diffusion constant of Xe gas in the polymer.

In the case of poly (4-methyl -1- pentene), PMP, interesting correlations can be seen with respect to the morphological structure of this semicrystalline polymer. The figure shows the Xe^{129} spectrum of a high crystallinity sample of PMP at temperatures of -80 , -70 , -60 and -50°C from top to bottom. The resonances of 250 and 230 ppm are assigned to two distinct crystalline sites. The amorphous resonance appears at about 220 ppm as determined from a highly amorphous sample. The spectral evidence of two distinct crystalline sites is in agreement with a computer simulation of methane gas in PMP (F. Mueller-Plake, J. Chem Phys. 1995, 103, 4346) where two different sites for gas sorption in the crystalline phase were noted. Both xenon and methane are of comparable diameters.

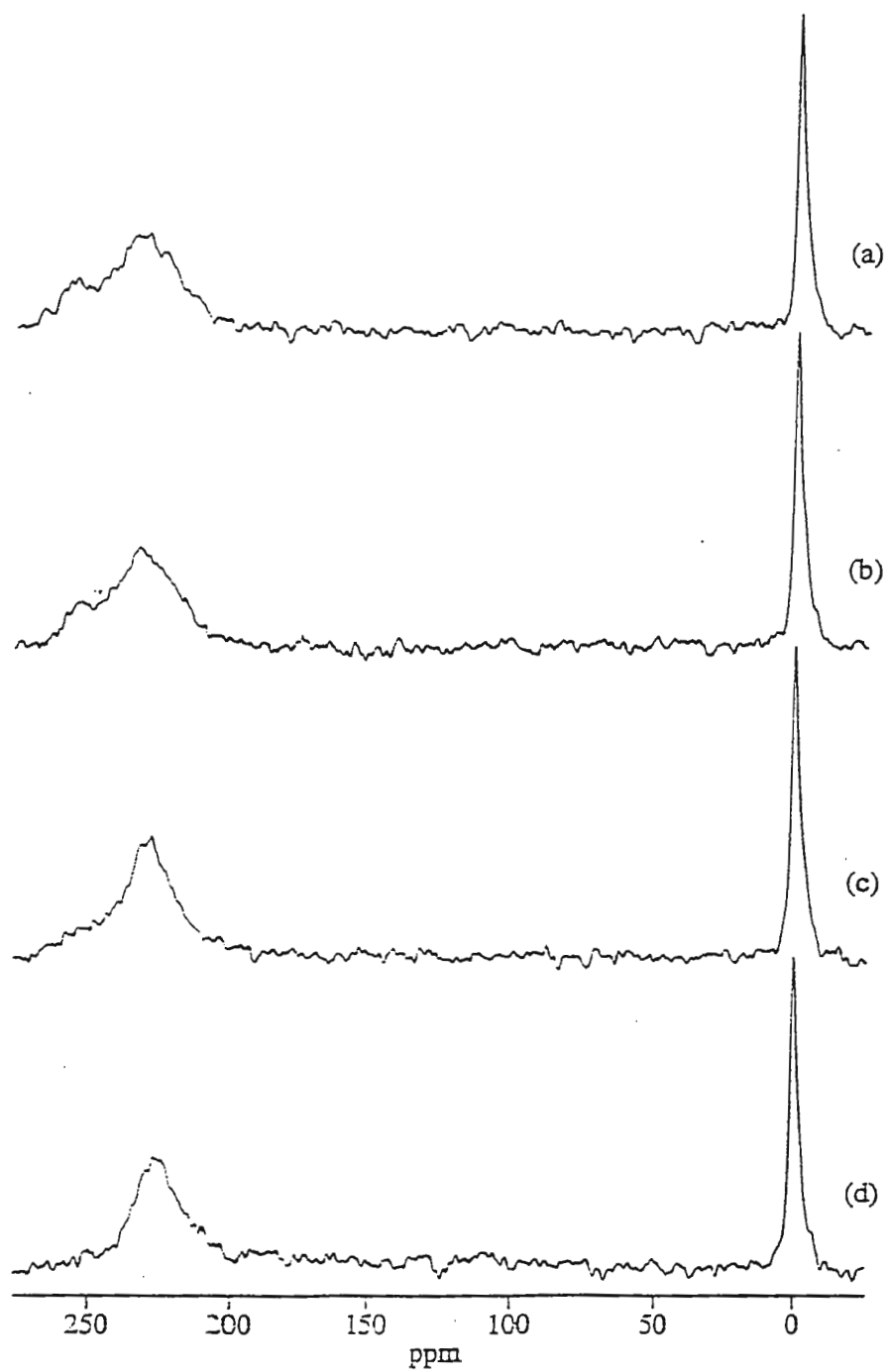
It appears that Xe^{129} NMR can be an extremely sensitive indicator of different structure environments in polymers with complex morphologies.

Best Regards,

Paul T. Inglefield

Alan A. Jones

Jeff Koons



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SPECIFICATIONS

MAGNET

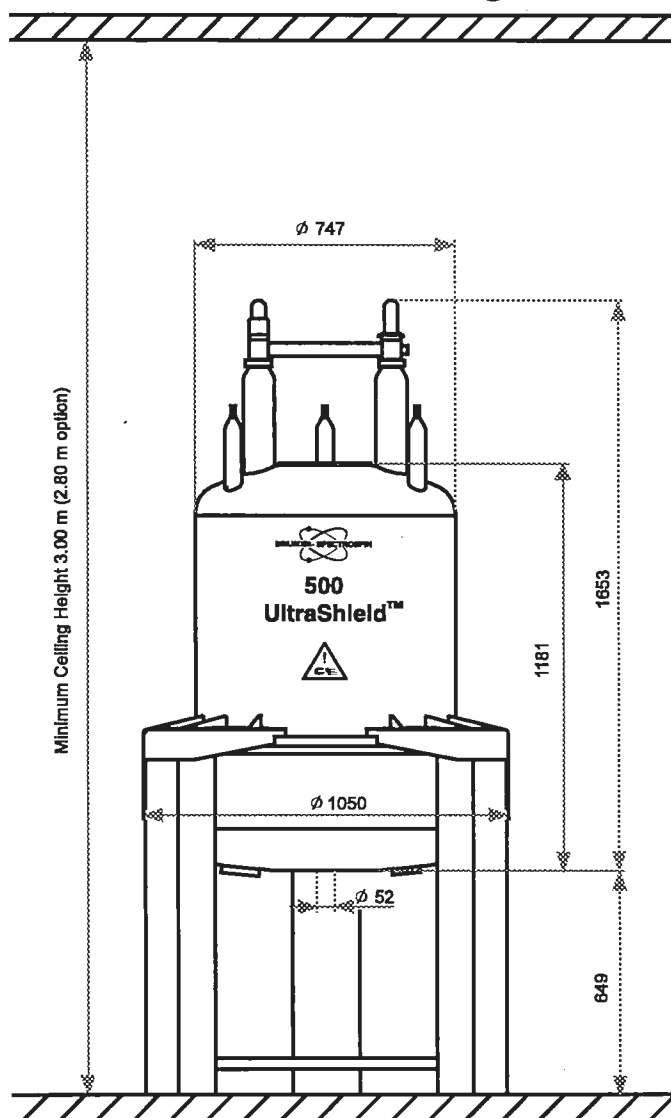
Central Field	11.7 Tesla
NMR Frequency	500 MHz
Field Drift	< 7.5 Hz/hr
Superconducting Shims	$z, z^2, z^3, x, y, xz, yz, xy, x^2-y^2$
Axial Range with Field Homogeneity better than 10 ppm (w/o RT Shimming)	~ 60 mm
5 G Line from the Magnetic Center	
-radially	< 1.3 m
-axially	< 1.9 m
Resolution at 50% 1% CHCl ₃ 5 mm spinning	< 0.45 Hz
Lineshape	
1% CHCl ₃ 5 mm non-spinning	
at 0.55%	< 6 Hz *
at 0.11%	< 12 Hz *
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* Typical values obtained with the BOSS II™ shim system.

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Dr. Bernard L. Shapiro

The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

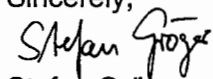
2.7.97 (received 4/3/97)

RAMOSE: Remote, Automated and Multitask Operation of NMR Spectrometer

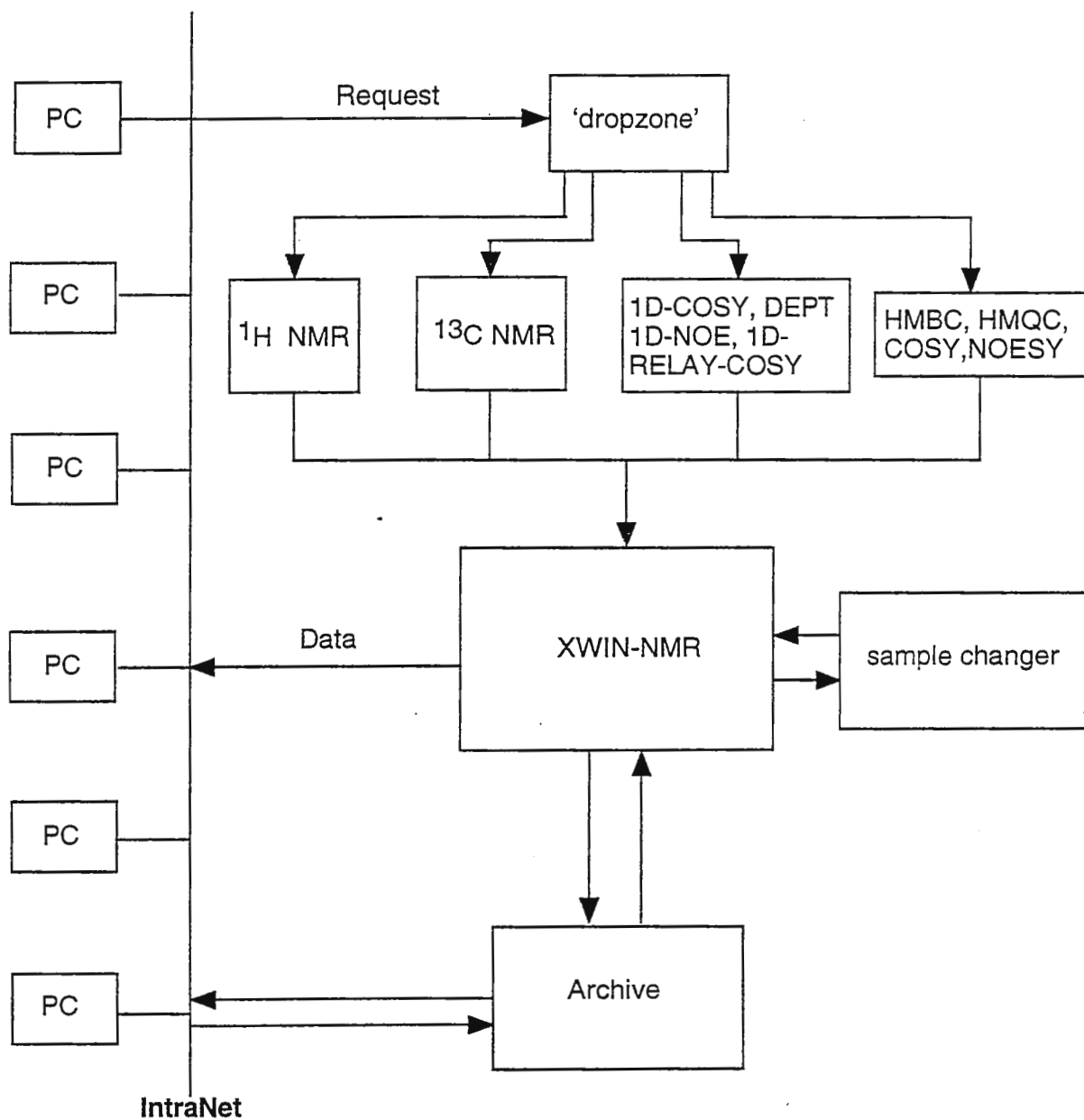
Dear Barry:

We have successfully implemented an automation procedure on our DRX-400 spectrometer, an instrument which mainly serves chemists in their synthetic efforts. The setup, which is drawn on the next page, is very simple. All jobs are first spooled in one directory from which they are transferred to different subdirectories according to the type of experiment (^1H , ^{13}C , 2D etc.) and there they wait for prioritized execution. The longest experiment allowed during the day does not exceed 20 minutes, which in many cases is sufficient for 2D-experiments. In this way, the throughput time for obtaining standard proton spectra is kept at a minimum and any dead-time is avoided. During the night, the instrument works with left-over samples from the day or serves for long-term experiments. The system consists of a set of C-shell/cron scripts which decide the priority of experiments, fix jams and send warning messages to the users such that the spectrometer works non-stop. Operator intervention is needed only to replenish the magnet with cryogenes. We have looked into the queuing theory to improve efficiency but unfortunately, sample submission by chemists does not resemble any of the known distributions. We have dubbed our setup RAMOSE which, according to Webster's Dictionary (10th Edition) means *consisting of or having branches* and corresponds to the ramose structure of the directory tree on the nmr-server computer.

Sincerely,


Stefan Gröger


Leszek Poppe





4567 St. Johns Bluff Road, South
Jacksonville, Florida 32224-2645
(904) 646-2830 FAX (904) 928-3885

COLLEGE OF ARTS AND SCIENCES
Department of Natural Sciences

March 3, 1997
(received 3/15/97)

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

Title: Computerized Database for Fluorine NMR Data.

Dear Dr. Shapiro,

I wish to inform you that we are building a computerized database for the NMR data of the fluorine-19 nucleus. In this database it is possible to access structures of molecules, other nmr parameters, and literature references. This can be achieved by entering any or a combination of the following parameters, fluorine chemical shifts, values of coupling constants, partial chemical structures, as well as the year of publication, journal title, and/or the authors. A copy of the layout is provided to illustrate the information that can be used and is accessible.

The software requirement for this database is very modest, ISIS2.02 database program from MDL Information Systems, Inc. is required along with ISIS draw program which can be downloaded from the Internet.

We will be happy to share this data with anyone who might be interested in this database if they would send us a self addressed envelop and a blank high density, three and a half inch floppy disk formatted for IBM. So far we have compiled data on fluorinated cyclopropane structures and in interests of completeness if there is such data that has not been published, we would add it to our database if permitted to do so.

Yours sincerely,

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

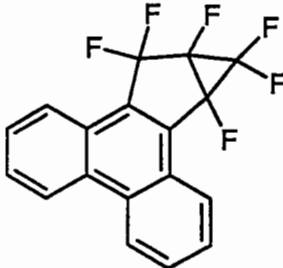
Jyotsna Pradhan
Department of Natural Sciences
University of North Florida
Jacksonville FL 32216
e-mail jpradh@osprey.unf.edu

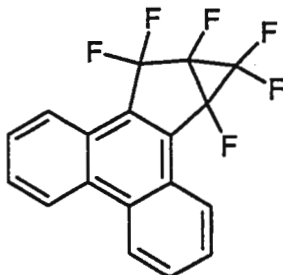
A handwritten signature in cursive script, appearing to read 'William R. Dolbier'.

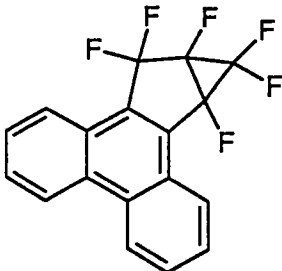
W. R. Dolbier
Department of Chemistry
University of Florida
Gainesville FL 32611
e-mail wrd@chem.ufl.edu

Explanations of the fields in the F-19 nmr data-base, unless specified below to the contrary, all these fields can be used to search the data base

Structure	Whole or partial structure in this field can be used to search the data base.
Authors	all authors for a paper are given in the database and it is possible to search using any author's name.
Notes	Information in this field cannot be used to search the database, information such as the instrument frequency, the solvent used etc. is given here.
Notes 1	Information cannot be used to search the data base, this box is used to indicate any labeling of atoms that the authors may have used.
F-shift	Chemical shift for each fluorine atom is given. If the authors have labeled the fluorine atoms in the molecule and the spectra, then the label would be shown in "Notes 1".
spltgpatrn	The splitting pattern of a particular fluorine signal and if the integration value is given then this field cannot be used for a search.
cc. FF	Coupling constants between two fluorine atoms. If a fluorine atom couples with more than one fluorine atom then the other coupling constants are shown in the next tables.
FF expln	nJFF indicates the bond distance (n) between two fluorine atoms that are coupled, i.e. 3JFF means that the two fluorine atoms, whose coupling constants is given in the previous box, are 3 bonds apart.
cc. HF	Coupling constants between fluorine and hydrogen atoms in the molecule.
HF expln	Details of the particular hydrogen and the fluorine atoms that are coupled, i.e. 2HF means that the coupling atoms are two bonds apart.

ID 3	Name					
Title Thermal Rearrangement of 9,10-bis(trifluorovinyl)phenanthrene.						
journal j.org.chem.	year 1993	vol.page.notes 58, 7064-69		Author Dolbier		
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	Fshift.b -112.4	spltgpatn.b dm, 1F	cc.FF.b 268.0	FF.expln.b 2JFF	cc.HF.b	HF.expln.b
	Fshift.c -137.7	spltgpatn.c dddm, 1F	cc.FF.c 173.2	FF.expln.c 2JFF	cc.HF.c	HF.expln.c
	Fshift.d -147.7	spltgpatn.d dtd, 1F	cc.FF.d 173.2	FF.expln.d 2JFF	cc.HF.d	HF.expln.d
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ID 3	Name					
Title Thermal Rearrangement of 9,10-bis(trifluorovinyl)phenanthrene.						
journal j.org.chem.	year 1993	vol.page.notes 58, 7064-69		Author Dolbier		
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	Fshift.c -137.7	spltgpatn.c dddm, 1F	cc.FF.c 13.7	FF.expln.c 3JFF	cc.HF.c	HF.expln.c
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	Fshift.h	spltgpatn.h	cc.FF.h	FF.expln.h	cc.HF.h	HF.xpln.8

ID	3	Name																					
Title																							
Thermal Rearrangement of 9,10-bis(trifluorovinyl)phenanthrene.																							
journal		j.org.chem.		year		1993		vol.page.notes		58, 7064-69		Author		Dolbier									
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				Fshift.e		-216.3		spltgpatn.e		m, 1F		cc.FF.e				FF.expln.e				cc.HF.e		HF.expln.e	
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		Fshift.h				spltgpatn.h				cc.FF.h				FF.expln.h				cc.HF.h		HF.xpln.8			

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PROF. RAY DUPREE

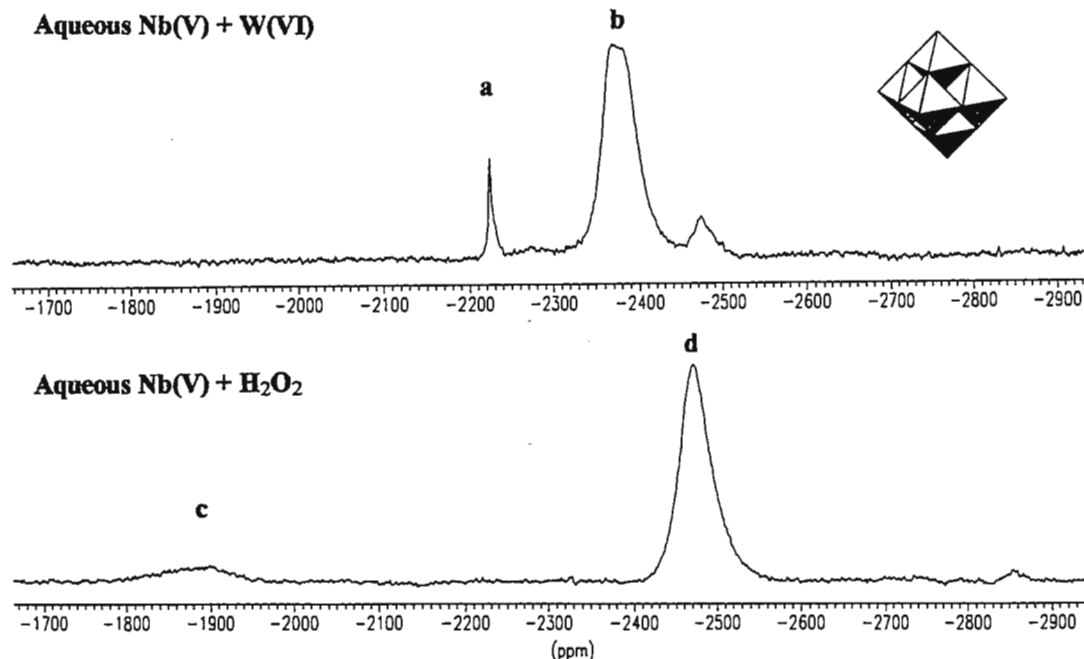
Dr. B L Shapiro, The NMR Newsletter
966 Elsinore Court, Palo Alto, CA 9430315th April, 1997

(received 4/25/97)

⁹³Nb Spectra in Aqueous Solution

Dear Barry,

⁹³Nb is a sensitive NMR nucleus, albeit with a largish electric quadrupole moment. The chemistry of Nb^V halo species has been studied by NMR, but there have been no reports of ⁹³Nb NMR spectra from aqueous niobates, or their simple derivatives. The reasons are largely chemical: aqueous niobate chemistry is dominated by almost insoluble, protonated forms of the hexaniobate anion, [Nb₆O₁₉]⁶⁻. This has the classic double-octahedron structure shown below, where the six Nb atoms lie at the centre of the six oxygen octahedra.



We have started a pilot study of aqueous niobate chemistry, to complement our extensive work on aqueous vanadate chemistry. We have tried two tricks for creating soluble species. One is to replace some of the Nb^V ions in the hexaniobate structure with *e.g.* W^{VI} ions. This can only be done by a solids fusion method, making it hard to be sure of the products. However, we are reasonably sure of the main species in the upper spectrum shown, because their relative intensities correlate with the amount of tungsten added to the fusion mixture, and also because the same mixed-metal anions can be identified by electrospray ionisation mass spectrometry of the solutions. We propose that species *a* is [W₅NbO₁₉]³⁻ and that *b* is [W₄Nb₂O₁₉]⁴⁻. The relative narrowness of the *a* resonance is also observed in the corresponding tungstovanadate species, because the Nb atom lies precisely on an axis of symmetry, and thus experiences no first-order electric field gradient.

Another trick is to add peroxide, because this normally helps to break up larger anions. By analogy with peroxovanadates, species *c*, in the lower spectrum, is probably a monoperoxoniobate and *d* a diperoxoniobate anion. Again, we have ESI-MS data to support this assignment. However, we now need a more thorough study of the shift changes with pH. I should perhaps mention that we are using one more simple trick throughout, namely to boost solubility and reduce linewidths by operating our ACP400 at 90 °C. The reference was external NbCl₅.

Best regards,

Adam Clarke

David Cox

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15th April 1997
(received 4/23/97)

Dr. Barry Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto CA 94903

News of Old Spectrometers and Spectroscopists

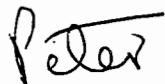
Dear Barry,

The problem arises sometimes as to what to do with the residue of old spectrometers, when all the valuable bits (like the magnets) have been sold for scrap. Some of your readers will remember the Perkin-Elmer R10 and R14 machines much loved (and cursed) by British operators many years ago. Well the frames which supported the magnet heaters and the outer casing of the magnet from one of these have proved very useful round my garden. Covered with plastic or netting they protect our young plants from the frosts and the attentions of birds. In one year the offspring of a pair of crows which fell out of the nest, and which its parents refused to look after, was kept within a cage formed from one of these frames, until it could be sent to a wild-life sanctuary!

Pensioned-off spectroscopists like myself present another sort of problem; how to keep a subscription to the excellent newsletter without much new experimental work to report. I hope that this letter will suffice.

Kind regards and best wishes

Yours sincerely,



Peter Bladon

NMR Faculty Position

The National High Magnetic Field Laboratory and the Departments of Physics and Chemistry at Florida State University invite applications for a tenure-track position at the rank of Assistant Professor to begin in August, 1997. Departmental affiliation and teaching, at the graduate and undergraduate levels, will be in Physics or Chemistry, depending on the candidate's research area. Primary consideration will be given to candidates who Ph.D. and post doctoral experience with solid state NMR techniques and applications in one or more of the following disciplines: chemistry, materials science, or condensed matter physics. Preference will be given to candidates proposed research takes maximal advantage of NHMFL's resources (25T, 10 ppm, soon to be 1 ppm resistive magnets; and 20 T, 1 ppm; 15/17 T, 1 ppm; 14 T 1 ppb, and other superconducting magnets).

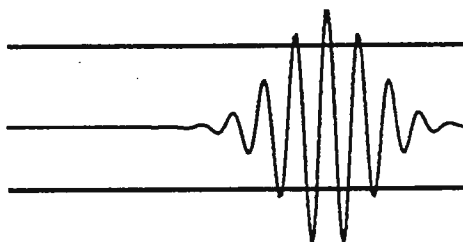
The candidate's research should complement on-site research activities, ranging from condensed matter physics (e.g. highly correlated electron systems, low dimensional electron systems, semiconductors, heavy Fermion systems, cuprates and field-induced phenomena) to materials science and chemistry (e.g. structure and dynamics in solid catalysts, zeolites, polymers, glasses, etc.). The successful applicant will be expected to develop an independent externally-funded research program, and to interact with and extend the existing external users program.

Consideration of applicants will continue until the position is filled. When applying, please reference position #55426. Please submit a curriculum vitae, statements of research accomplishments and plans, a list of three references, and arrange for coursework transcripts to be sent to: Alan G. Marshall, Chair, NMR Faculty Search Committee, National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310 or by FAX to (904) 644-1366. Florida State University is an Affirmative Action/Equal Opportunity Employer and encourages minority and women applicants.

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Please send your CV and arrange for three letters of recommendation to be addressed to Jerome L. Ackerman, Biomaterials Laboratory, NMR Center, Room 2301, Department of Radiology, Massachusetts General Hospital, 149 13th Street, Charlestown, MA 02129-2000; phone 617-726-3083, fax 617-726-7422, jerry@nmr.mgh.harvard.edu. MGH is an Affirmative Action/Equal Opportunity Employer.



MGH NMR Center

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Deadline Dates

No. 465 (June) 23 May 1997

No. 466 (July) 27 June 1997

No. 467 (Aug.) 25 July 1997

No. 468 (Sept.) 22 Aug. 1997

No. 469 (Oct.) 26 Sept. 1997

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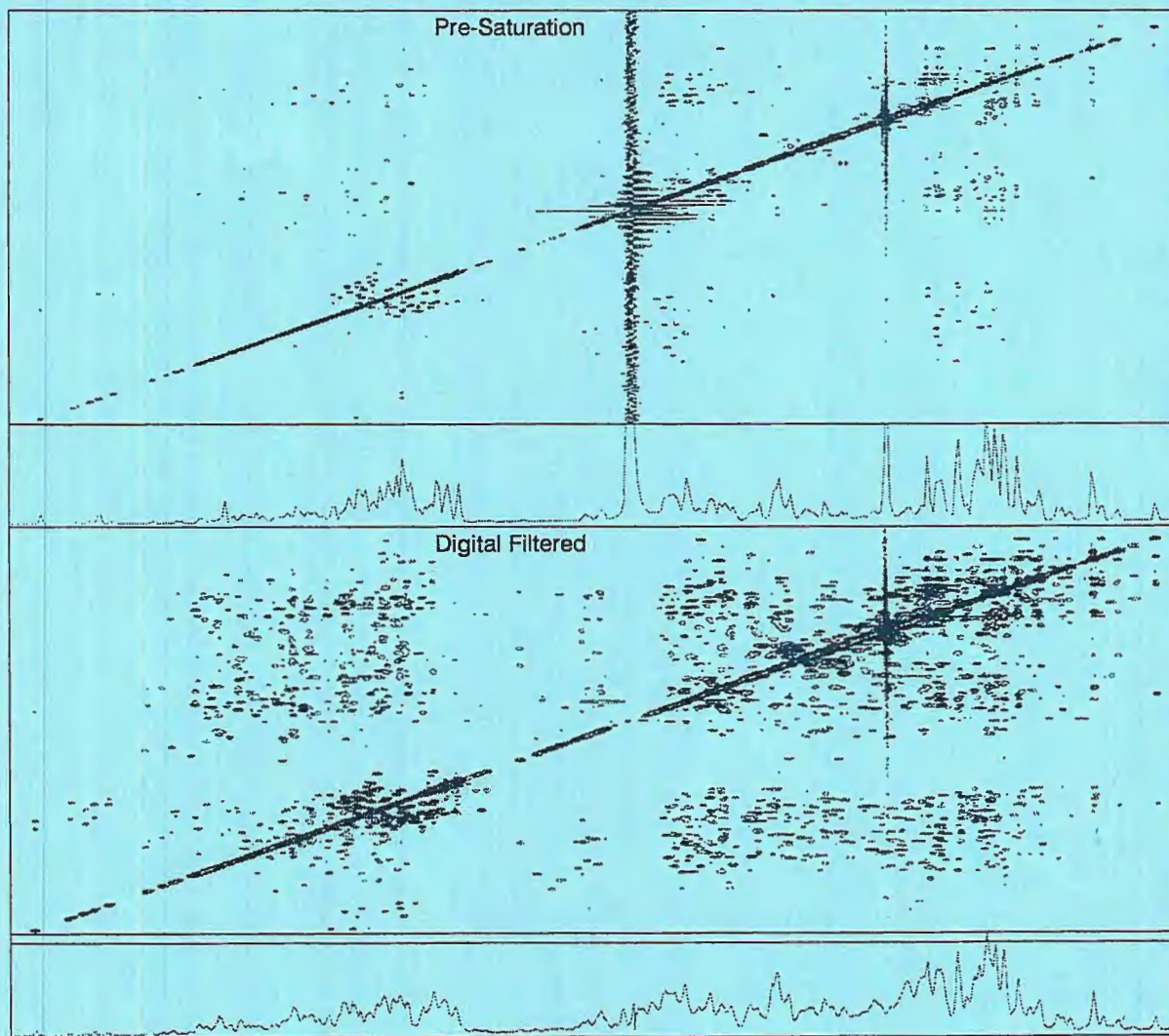


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