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NMR NEWSLETTER

No. 425

February 1994

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FORTHCOMING NMR MEETINGS

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

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Dr. B. L. Shapiro
TAMU NMR Newsletter

January 12, 1994
(received 1/21/94)

Two spins and two rf fields

Dear Barry,

the zero quantum frame is a useful concept for a treatement of two scalar coupled spins both irradiated by an rf field. The concept, e.g., allowed to propose the refocused J cross-polarization experiment (G. C. Chingas et all. : *J. Chem. Phys.* **74**, 127 (1981)) or was behind the design of FLOPSY family of broadband homonuclear cross-polarizations (K. Kadkhodaie at all.: *J. Magn. Reson.* **91**, 437 (1991)). A closer inspection of the Hamiltonian for a such two spin system reveals that it can be divided into two mutually commuting Hamiltonians $\hat{H}^D$ and $\hat{H}^Z$:

$$\hat{H}^D = (B_S(t) + B_I(t))\ (\hat{S}_x+\hat{I}_x)/2 - J/2(\hat{S}_y\hat{I}_y-\hat{S}_z\hat{I}_z),$$
$$\hat{H}^Z = (B_S(t) - B_I(t))\ (\hat{S}_x-\hat{I}_x)/2 + J/2(\hat{S}_y\hat{I}_y+\hat{S}_z\hat{I}_z).$$

The $B_S(t)$ and $B_I(t)$ are constant-phase, amplitude-modulated rf fields acting selectively on the first and second spin S and I, respectively.

Further analysis showed that it is useful to divide the density matrix space into three subspaces: *i.* the mentioned zero quantum subspace (spanned by operators $(\hat{S}_x-\hat{I}_x)/2$, $(\hat{S}_y\hat{I}_y-\hat{S}_z\hat{I}_z)$ and $(\hat{S}_y\hat{I}_z+\hat{S}_z\hat{I}_y)$), *ii.* double quantum subspace (with the base operators $(\hat{S}_x+\hat{I}_x)/2$, $(\hat{S}_y\hat{I}_y+\hat{S}_z\hat{I}_z)$ and $(\hat{S}_y\hat{I}_z-\hat{S}_z\hat{I}_y)$) and *iii.* the single quantum subspace which includes all other coherences of the two spin system. The time evolution proceeds separately within each of the subspaces, the evolution within three dimensional zero quantum and double quantum frames being described by the well known analogy of the single spin rotation while the evolution within the single quantum subspace is more complicated, but can still be expressed in an analytical form. The detailed account will be submitted to the J. Magn. Reson.

Yours sincerely,

V. Blechta

Vratislav Blechta

Jan Schraml

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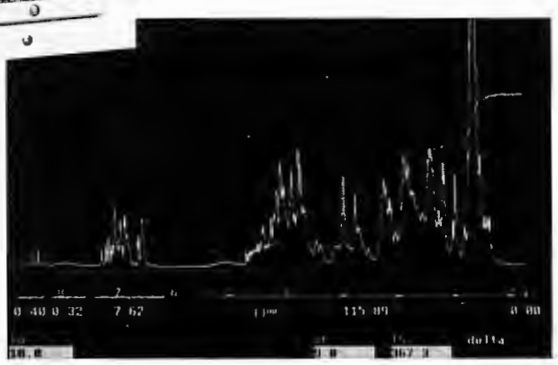

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Input VSWR	< 2:1
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Duty cycle	Up to 10%
Amplitude rise/fall time	250 ns typ.
Amplitude droop	5% to 20 ms typ.
Phase change/output power	10° to rated power, typ.
Phase error overpulse	4° to 20 ms duration, typ.
Noise figure	11 dB typ.
Output noise (blanked)	< 20 dB over thermal
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16th December 1993
(received 12/20/93)

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

Dear Barry

COUPLING OF HPLC AND NMR SPECTROSCOPY

It is probably an opportune time to let you know about some recent work we have been doing in the drug metabolism area to evaluate this technique in collaboration with Manfred Spraul at Bruker and Ian Wilson at Zeneca Pharmaceuticals.

We have been using the world's most expensive and powerful HPLC detector to characterise the metabolites of a number of drugs found in body fluids such as urine, blood plasma and bile. This HPLC detector is in fact a Bruker 600MHz NMR spectrometer and we have found that a good separation of typical drug metabolites is possible using fairly standard HPLC conditions, i.e. standard C18 columns and with water/acetonitrile gradient elution. The NMR resonance positions of both solvent components depend on their proportions in the mixture and as this changes during an elution, it is necessary to carry out a blank run to determine the frequencies of both components at all proportions used in the gradient run and then to construct appropriate frequency lists to allow double variable frequency solvent suppression throughout the HPLC run. We have carried out on-flow detection which gives a pseudo-2D contour plot and stopped-flow experiments to obtain better signal/noise or digital resolution. We have also used ^{19}F NMR HPLC detection of fluorine-containing drugs in an on-flow manner followed by ^{1}H NMR in stopped-flow mode to characterise the metabolites. In stopped-flow mode, it is possible to carry out virtually any high resolution NMR experiment. Some examples from our evaluation studies are given here. The top figure shows the ^{1}H NMR spectrum of paracetamol glucuronide, both experimental and simulated, measured after direct injection of rat bile on to the HPLC column. The middle figure is the on-flow ^{19}F NMR detection of metabolites of the fluorine containing anti-inflammatory flurbiprofen obtained after direct injection of human urine on to the column. The bottom figure is the ^{1}H spectrum in stopped-flow mode at one of the retention times characterised by a ^{19}F NMR signal and represents the proton spectrum of a pure diastereomer of flurbiprofen glucuronide (as the drug is racemic and conjugates are only formed from D-glucuronic acid).

We think that coupled HPLC-NMR has a lot to offer for the characterisation of the components from complex mixtures whether they are drug metabolites or endogenous species in biofluids or tissue extracts or chemical synthetic mixtures and will play a major role in pharmaceutical and chemical analysis in the future. HPLC-NMR saves time in analysis and in the pharmaceutical industry this is of paramount importance.

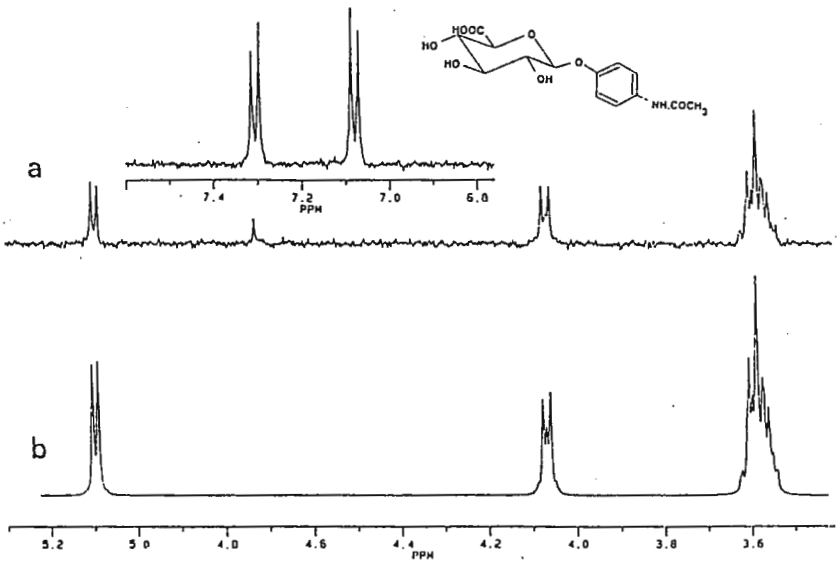
Yours sincerely

John

John C. Lindon
Department of Physical Sciences
Wellcome Research Laboratories

Jeremy

Jeremy K. Nicholson
Birkbeck College
London University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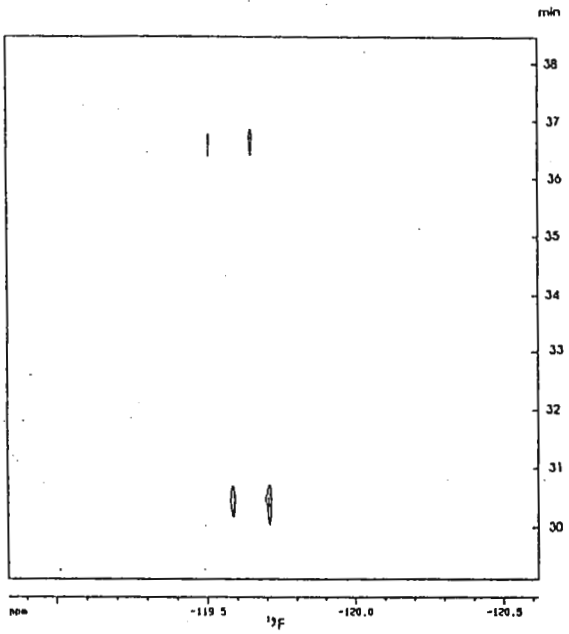
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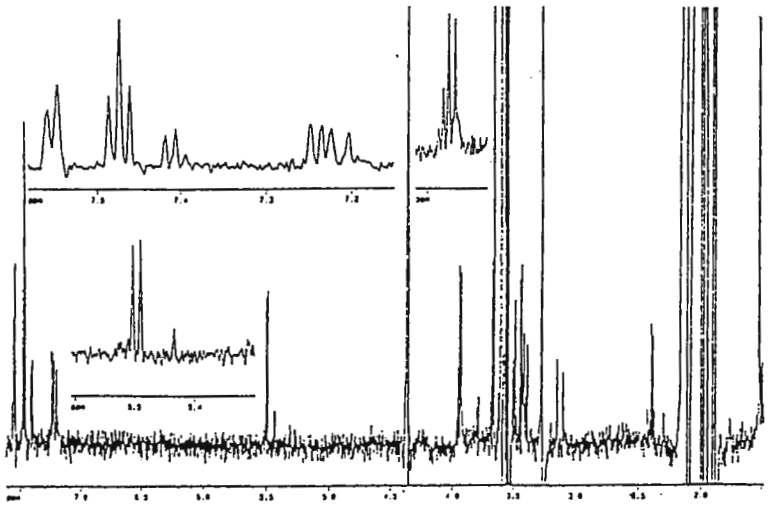

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The initial resurgence of interest in applying gradients to high resolution NMR spectroscopy focused on a single axis (z-gradient) probe design. Now, applications are being developed that require 3 gradients. GE NMR Instruments successfully pioneered three gradient high resolution probes with widely published results[1-4]. A very important application is water suppression by diffusion weighting[5]. For example, figure 1 shows results in an improved phase-sensitive HMQC experiment in which diffusion filters are employed to avoid dynamic range problems[6].

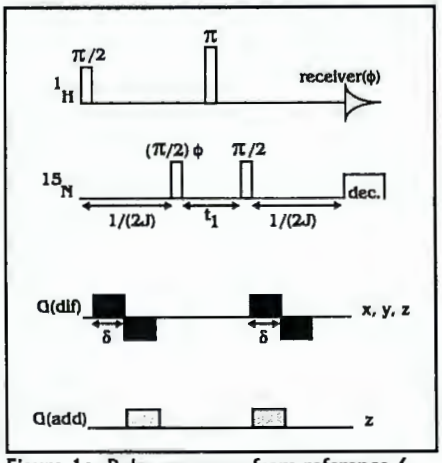


Figure 1a: Pulse sequence from reference 6

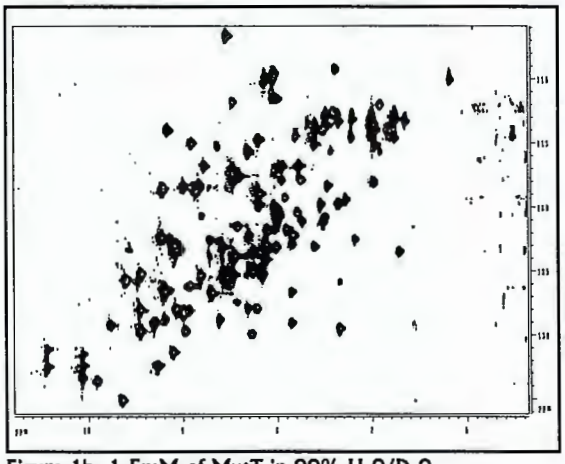
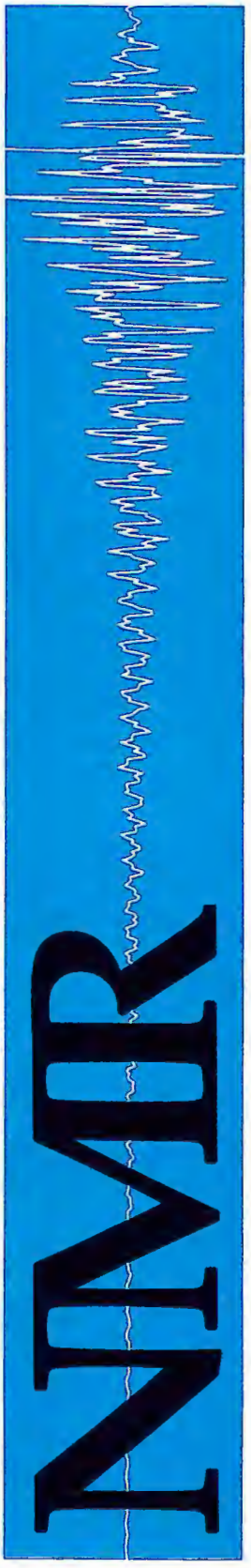


Figure 1b: 1.5mM of MutT in 90% H_2O/D_2O

With GRASP III, three gradient experiments are now available for all AVANCE users. Probes for 5mm samples are available in ^{1}H observe, inverse broadband, and triple resonance inverse configurations for 500, 600, and 750 MHz spectrometers. The compact ultra stable Acustar gradient amplifier enables z-gradient strength of up to 40 G/cm and x, & y-gradients of up to 35 G/cm! All of this packaged together with the excellent RF performance typical of Bruker probes.



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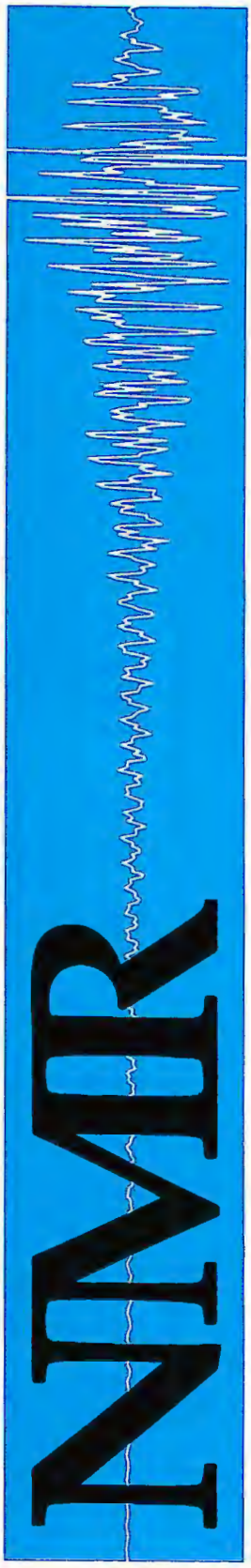

Different orthogonal gradient directions can now be chosen for different functional uses of gradients such as "crusher" gradients, diffusion gradients, coherence selection gradients, slice selection gradients or gradients at the magic angle. The availability of three gradient axes greatly improves the capability to remove inadvertent and undesirable gradient-recalled echoes. The benefits are both greater ease-of-use as well as increased flexibility for new gradient spectroscopy pulse sequences.

The AVANCE is also revolutionizing gradient generation with its new Gradient Control Unit (GCU™). The GCU is interfaced to the VME bus and driven by a modern high performance embedded Intel i960 RISC processor.

Today, with increasing emphasis placed on gradients, the GCU is the logical hardware evolution from simple square gradient generation. The power of the i960 allows, for the first time, gradients to be calculated "on the fly" as dictated by the experimental requirements. The desired gradient is generated in real time by the microprocessor without the need for traditional memory for the gradient length or shape. Best of all, it can do this simultaneously for x, y, & z-gradients.

Up to now, NMR systems had to utilize dedicated memory to pre-define the desired gradients before the execution of the NMR experiment. In complex experiments, the memory size has lead to a limitation as the number of gradient pulses incorporated into a single sequence continued to grow. The GCU's revolutionary design overcomes this restriction. *In addition, the GCU can provide gradient shaping for all three gradients, on the fly!* The gradient shapes can be linear (to give trapezoidal shape), sinusoidal (for sine shape) or arbitrary functions.

GRASP III provides for traditional single gradient applications as well as for three gradient spectroscopy experiments. Together with the GCU, extreme versatility in creating novel experiments with shaped x, y, & z-gradients becomes reality!

reference:
1. R.E. Hurd, B.K. John, P. Webb, D. Plant. *J.Magn.Reson.* **99**, 632 (1992).
2. B.K. John, D. Plant, P. Webb, R.E. Hurd. *J.Magn.Reson.* **98**, 200 (1992).
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4. R.E. Hurd, D. Freeman. *Proc.Natl.Acad.Sci. USA.* **86**, 4402 (1989).
5. P.C.M. van Zijl, C.T.W. Moonen. *J.Magn.Reson.* **87**, 18-25 (1990).
6. P.C.M. van Zijl, M. O'Neil-Johnson, C. Abeygunawardana. *J.Magn.Reson.* (submitted).

KEH/MAC-BII 9/93

Glaxo
Glaxo Inc. Research Institute

December 22, 1993
(received 12/27/93)

FELIX Processing of Bruker States-TPPI Data

Dear Barry,

Recently I was asked to help process some 2D-NOESY data obtained on a Bruker AMX-600 in France. The pulse sequence was not available, and the method by which quadrature in t_1 was obtained was not known. We do all of our data processing off-line using FELIX, and after some trial and error I discovered that the data was obtained in the States-TPPI mode. Since mostly all of the pulse experiments we do at Glaxo are written by ourselves, I hadn't realized that the States-TPPI pulse programs supplied by Bruker are not acquired with the phase cycling typically used(1). We usually use the following steps in our pulse programs to obtain States-TPPI quadrature:

```
2   d11
3   d11
    d11
4   p1 ph1
    .....,
    .....,
go=2    ph31
d11   wr#0   if#0   ip1   zd
loop to 3 times 2
d11 ip31
d11 ip31   id0
loop to 4 times l3     ;where l3= 0.5*td1
```

whereas the standard programs supplied by Bruker use a special post-acquisition processing step to "increment" the receiver phase. I wrote the attached FELIX macro to process data obtained with the States-TPPI programs supplied by Bruker. The second transform is then done in the same fashion as data acquired in the States method.

Best Regards,

Stephen C. Brown Donald G. Davis Robert T. Gampe Robert Xu J. Michael Word

(1) D. Marion, M Ikura, R. Tschudin, & A. Bax, *J. Magn. Reson.* **85**, 393 (1989)

Glaxo
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```
ty brukstt2.mac
ty To transform BRUKER TPPI-STATES data
def infile "yourdata"
bld &infile 2 2048 2048 0                    ;build a real 2K by 2K matrix
ty matrix &infile created
mat &infile write
def phase0  "pc0"
def phase1  "pc1"
cl
def fact 1
def cnt 0
        for row 1 &nrows
        eva cnt (&cnt + 1)
        re &infile
        def datype 1
        def datsiz "TD"        ;data size acquired, Bruker parameter "TD÷2"
        bc 0.05
        em 2
        zf 2048
        ft
        ph
        zi
        def datsiz 2048
        red
        mul &fact
        if &cnt eq 2 then
                def fact -1
        else
                if &cnt eq 4 then
                        def cnt 0
                        def fact 1
                eif
        eif
        sto 0 &row
        ty row=&row $
        next
end
```

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6th January 1994
(received 1/20/94)

Dear Barry,

Separation of chemical exchange and cross relaxation effects

In general magnetization transfer spectra (selective or non-selective perturbation) depend upon cross relaxation rates and slow exchange rate coefficients. These can be separated only in special cases, i.e. cross relaxation rates may be determined quantitatively only in the absence of exchange and exchange rates only in the absence of cross relaxation. The problem lies in the difficulty of separating κ and σ, the exchange rate coefficient and the cross relaxation rate, respectively.[1] The 2-dimensional NOESY experiment is often used to estimate κ or σ by measuring the intensities (volumes) of the peaks as a function of mixing time (τ_m). Analysis of the data proceeds by eq. [1], where I is the n x n square matrix of experimental peak intensities at mixing time τ_m. I_0 is the matrix for $\tau_m = 0$ and n is the number of distinct sites. I is measured for a range of values of τ_m and these data are used to calculate the n x n matrix L. L, the magnetization transfer matrix, is the sum of kinetic (K) and relaxation (R) matrices.

$$I = \exp[L.\tau_m] \cdot I_0 \qquad [1]$$

In the trialkylaluminium-diethylamine complex $R_3Al{\leftarrow}NHEt_2$ (where R = Bu^i) the two ethyl groups of the amine moiety are equivalent but the methylene protons are bonded to a prochiral center, constituting a diasterotopic pair, giving resolved resonances at 300 K. These resonances coalesce at high temperature through exchange *via* a dissociative mechanism, where the Al-N bond is broken, followed by inversion at nitrogen and subsequent recombination. The equilibrium concentrations of free amine and free alkylaluminium are too small to be detected by NMR. The mechanism may be likened either to S_N1 whereby the complex spontaneously dissociates or to S_N2 involving displacement of the amine group at aluminium by a second amine molecule. For both cases the L matrix is 2 x 2 and may be written as:

$$\text{and} \quad L = \begin{bmatrix} -\kappa-\rho & \kappa-\sigma \\ \kappa-\sigma & -\kappa-\rho \end{bmatrix}$$

where ρ is the spin lattice relaxation rate and σ is the cross relaxation rate constant. Thus the parameters which are determined from the experiment are the *sum* ($\kappa + \rho$) and the *difference* ($\kappa - \sigma$). In some cases,[2] the value for σ is very small, and therefore, the value for ($\kappa - \sigma$) may be approximated to κ. However, the general situation is that κ, σ and ρ are of comparable magnitude, and the problem is to separate them.

The 600 MHz ^{1}H 2D NOESY spectrum showed both positive and negative cross peaks; the negative peaks are due to pure n.O.e. effects (cross relaxation) and the positive, correlating the slowly exchanging methylene protons are due to a combination of exchange and cross relaxation, with exchange being dominant. The intensities of the intra-methylene cross peaks were measured as a function of τ_m, and analysis of this volume data was made *via* an iterative procedure described by Beringhelli *at al.*[3] This gave values for $(\kappa - \sigma) = 0.85\ s^{-1}$ and $(\rho + \sigma) = 0.52\ s^{-1}$. In order to obtain a value for κ, an independent estimate for σ (H-H) is needed. We obtained this by Eq. 2, where r is the H-H internuclear distance within the methylene group (1.5 Å) and τ_c is the correlation time.

$$\sigma(\text{H-H}) = K\,\tau_c\,r^{-6} \qquad [2]$$

However, to calculate σ a value for τ_c (the correlation time) is required. This is obtained from separate experiments to measure the ^{13}C-^{1}H dipole-dipole spin lattice relaxation time T_1(dd), which is calculated from the inversion-recovery experiment to give T_1(total) and the size of the ^{13}C-{^{1}H} n.O.e. The results were: T_1(total) = 1.84 s; n.O.e. = 3.05 ± 0.1. The n.O.e. is effectively the theoretical maximum and therefore the ^{13}C relaxation is dominated by the dipole-dipole mechanism and T_1(total) ≈ T_1(dd). τ_c for the C-H interaction is then be calculated to be 1.15×10^{-11} s and this value is reasonably taken to be the same for the H-H interaction. The τ_c value is then substituted in equation [2] to give σ(H-H) = $0.29\ s^{-1}$ and the rate coefficient $\kappa = 1.13\ s^{-1}$.

This procedure is simple and effective but only valid when the correlation times for the H-H and C-H interactions are the same, i.e., when they are part of the same molecular fragment and do not have different degrees of mobility.

Happy New Year!

Yours sincerely,

G.E. Hawkes E.S. Bento K.D. Sales

REFERENCES

[1] G. Wagner, G. Bodenhausen, N. Muller, M. Rance, O.W. Sorensen, R.R. Ernst, and K. Wuthrich. *J. Am. Chem. Soc.* 1985, **107**, 6440-6446.

[2] G. E. Hawkes, E.W. Randall, S. Aime, D. Osella, and J.E. Elliot. *J. Chem. Soc. Dalton Trans.* 1984, 279-284.

[3] T. Beringhelli, G. D'Alfonso, H.Molinari, G.E. Hawkes, and K.D.Sales. *J. Magn. Reson.* 1988, **80**, 45-59.

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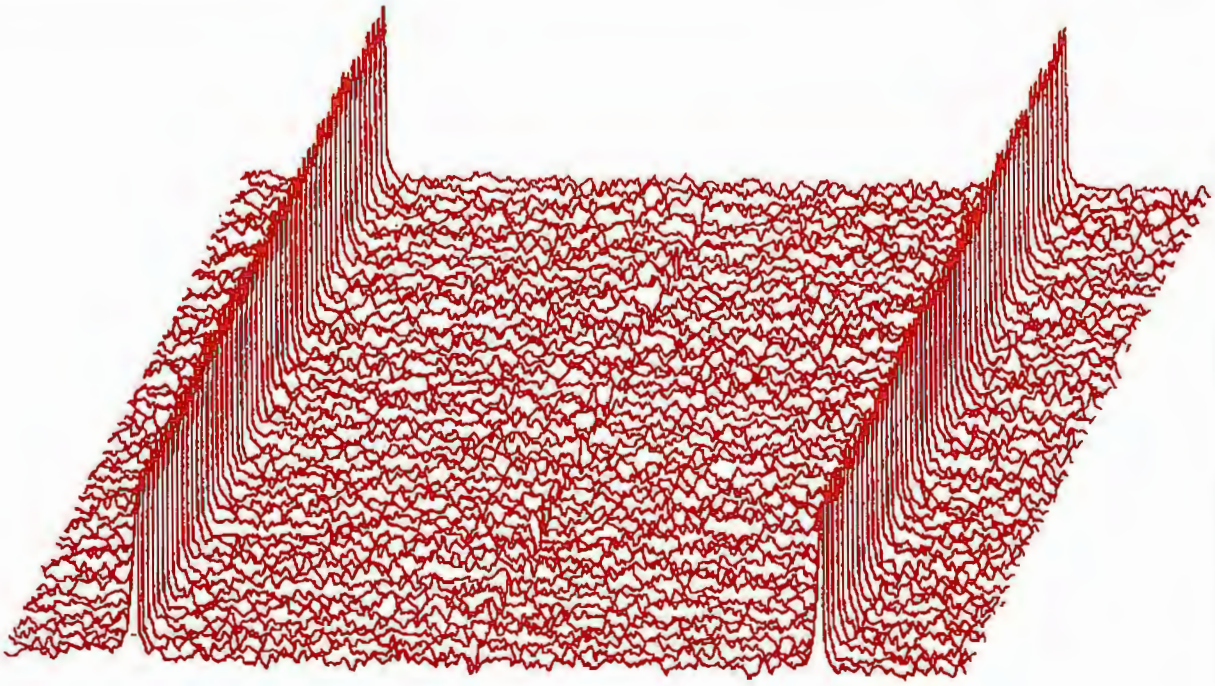

The series of heteronuclear spin-echo difference experiments shown above were obtained utilizing a UNITYplus 600 MHz system, a Triple•nmr Pulsed Field Gradient probe, and a 1% $CHCl_3$ sample, locked on deuteroacetone. The data were collected with two 1 msec, 30 gauss/cm gradient pulses applied during the spin echo, one on either side of the proton refocussing pulse. The gradients were applied without the use of B_0 compensation, eddy-current compensation, or gradient-amplifier blanking.

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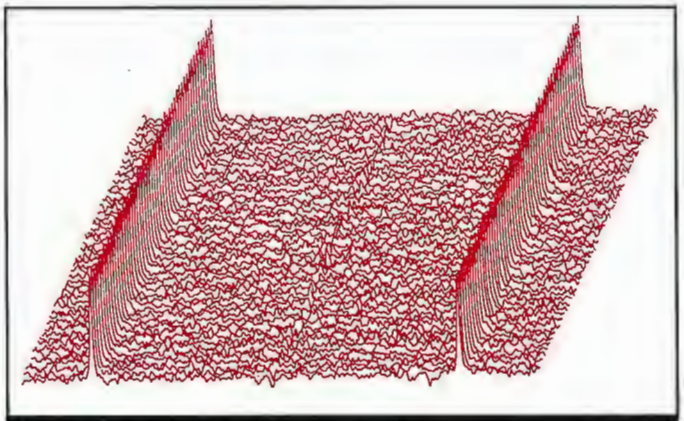

Figure 1 Heteronuclear spin-echo difference spectra of $CHCl_3$ without gradients.

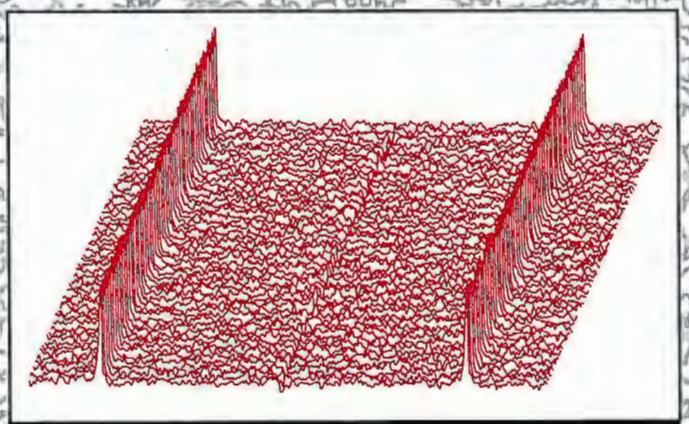

Figure 2 Heteronuclear spin-echo difference spectra of $CHCl_3$ with a single 1 msec, 30 gauss/cm gradient before the ^1H first pulse.

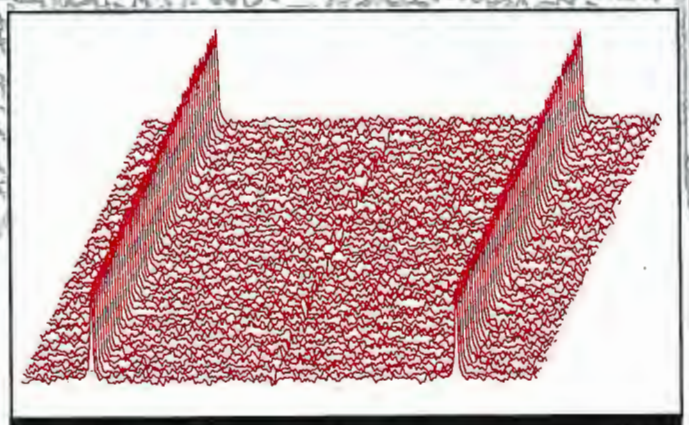

Figure 3 1 Heteronuclear spin-echo difference spectra of $CHCl_3$ with two 1 msec, 30 gauss/cm gradients during the spin echo.

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January 20, 1994
(received 1/21/94)

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

Gas Exchange on Polystyrene Beads

Dear Barry:

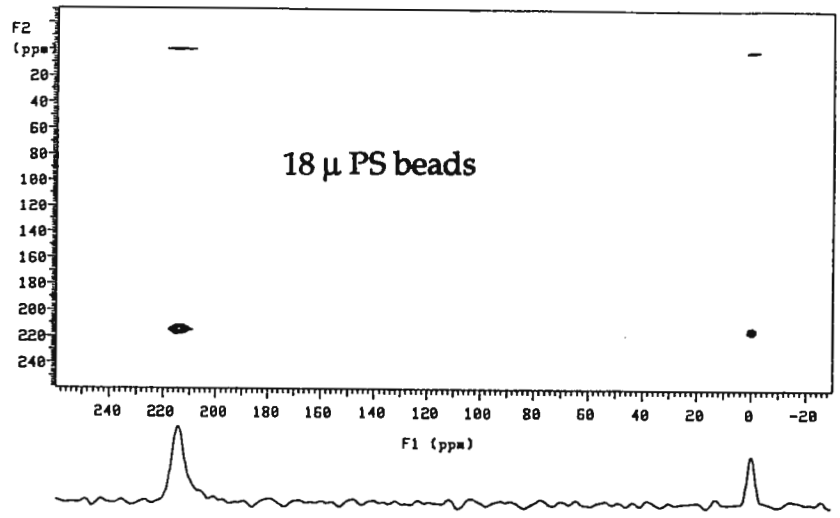
During our work on the nature and mobility of gases dissolved in polymers we noticed that there is a fairly dramatic effect on the exchange between free gas and polymer sorbed gas due to surface area. This was initially observed in the in the ^{13}C spectrum of $^{13}CO_2$ sorbed in polycarbonate: in a film sample one could clearly distinquish the free gas peak at 124 ppm (TMS) and the sorbed peak at 120 ppm whereas in a powdered polymer sample a single exchange averaged peak is observed at ~ 122 ppm. We decided recently to further study this dependence on surface area using polymer beads of different sizes and Xe gas to give us a large chemical shift between polymer sorbed and free gas. Polystyrene, where a large selection of bead sizes in readily available commercially was chosen for the polymer.

The figure shows a ^{129}Xe 2D NOESY experiment with a mix time of 5 seconds for (a) 18 μ and (b) 64 μ beads. The exchange rate is clearly enhanced for the smaller bead (larger surface area). We have made similar observations with $^{13}CO_2$ though the chemical shift dispersion is much less and the effect not so clear as with Xe. We are presently developing a theory for the exchange across the polymer surface interface to account for the observations.

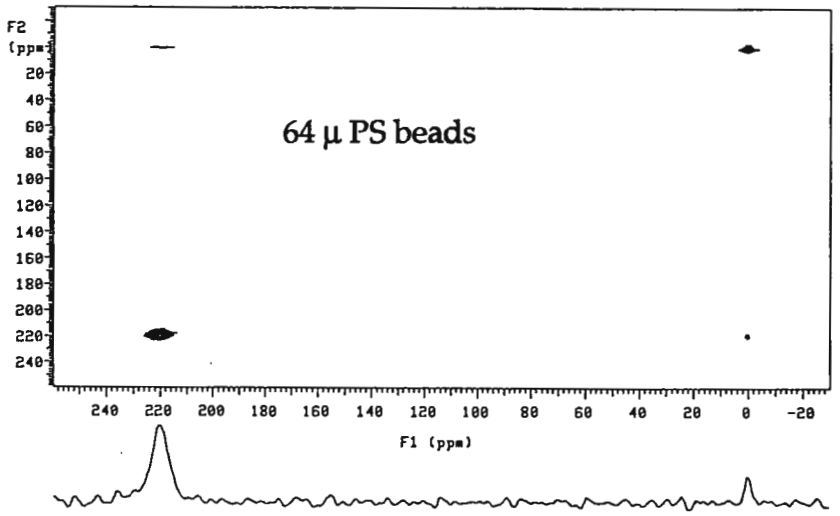
Regards,

Paul T. Inglefield Jeffrey Simpson

(a)



(b)



^{129}Xe 2D NOESY patterns for Xe sorbed in PS beads (a) 18 μ and (b) 64 μ. Free Xe gas peak is at 0 ppm, Xe sorbed in PS is at 218 ppm. Spectrum below shows a horizontal slice at 218 ppm. The relative intensity of the off diagonal (exchange) peak (right) is clearly enhanced for the 18 μ size beads.

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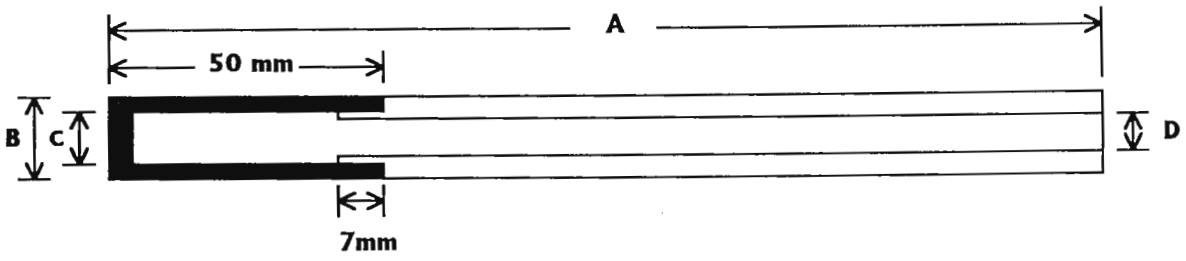

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Si-005	180	4.965 + 0 − 0.005	4.0 ± 0.1	3	± 0.02
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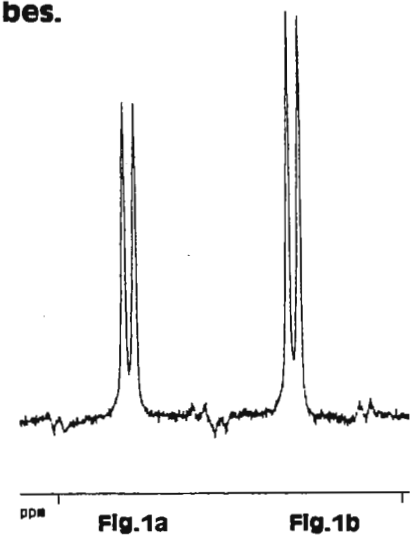
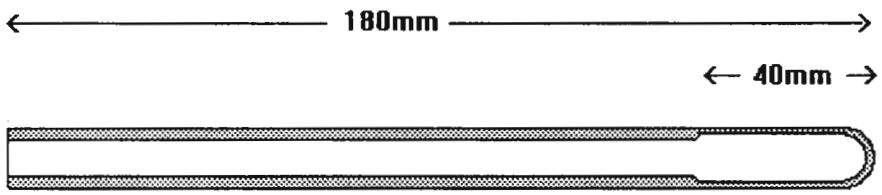


Fig.1a Fig.1b

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%.



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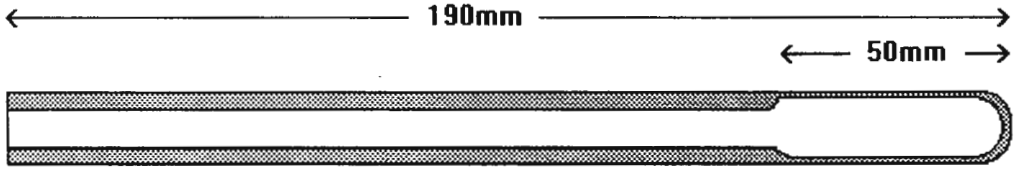

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8	ST8-001	0.25	40/ 8	8.00 + 0.00 - 0.01	7.52 ± 0.01	$31.00	$28.00
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Stanley J. Opella
Bernard E. and Ida L. Grossman Professor

December 14, 1993
(received 12/20/93)

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

re: Solid-State $^{1}H/^{15}N$ Heteronuclear Correlation Spectroscopy

Dear Barry,

All improvements in resolution of NMR spectra are valuable. Experimental methods that enhance resolution among resonances from amide nitrogen sites in peptide bonds are especially important because of the uniform chemical nature of the polypeptide backbone of proteins. Previously, we have relied primarily on a variety of isotopic labeling schemes to resolve ^{15}N resonances in solid-state NMR spectra of single crystal and uniaxially oriented samples of peptides and proteins. In general, multi-dimensional experiments offer the promise of reducing the effort needed for isotopic labeling through the use of uniformly labeled samples. In this letter, we present a two-dimensional $^{1}H/^{15}N$ heteronuclear correlation spectrum that demonstrates resolution among amide nitrogen resonances in both ^{1}H *and* ^{15}N dimensions, suggesting considerable potential for this class of experiments in solid-state NMR studies of proteins.

In order to utilize the chemical shift anisotropy of the ^{1}H directly bonded to the nitrogen in the peptide bond as a mechanism for increasing resolution, it is essential to efficiently decouple the strong homonuclear $^{1}H/^{1}H$ dipole-dipole interactions and to use a high-field spectrometer, since the amide ^{1}H chemical shift anisotropy is approximately 13 ppm (R. Gerald, T. Bernhard, U. Haeberlen, J. Rendell, and S. J. Opella (1993) *J. Amer. Chem. Soc.* 115, 777). We have found the frequency-switched Lee-Goldburg pulse sequence (A. Bielecki, A.C. Kolbert, H.J.M. DeGroot, R.G. Griffin, and M.H. Levitt (1990) *Adv. Magn. Reson.* 14, 111), as applied during t_1 of the pulse sequence outlined in Figure 1, to be highly effective at narrowing ^{1}H resonances.

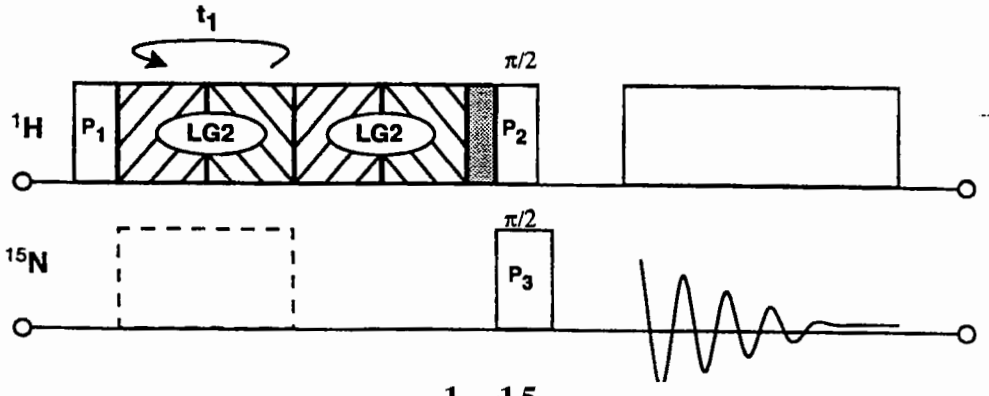

Figure 1: Pulse sequence for $^{1}H/^{15}N$ heteronuclear correlation

The spectrum in Figure 2 was obtained at a ^{1}H resonance frequency of 550 MHz and a ^{15}N resonance frequency of 55.7 MHz on a home-built quadruple-resonance spectrometer with a wide-bore 12.9T magnet (Magnex 550/89). The spectrometer has two symmetrical ^{1}H rf channels and two symmetrical X nucleus rf channels. The two ^{1}H channels enable separate optimization of the homonuclear and heteronuclear portions of the pulse sequence. The combination of frequency-switched Lee-Goldburg $^{1}H/^{1}H$ homonuclear decoupling and ^{15}N continuous on-resonance irradiation during t_1 yields single correlation peaks with ^{1}H linewidths of 300 - 400 Hz (corresponding to unscaled 1 - 1.5 ppm) and ^{15}N linewidths of 4 - 5 ppm. The pulse sequence shown in Figure 1 was applied to a 15 mg single crystal sample of N-acetyl-valyl-leucine labeled with ^{15}N in both amide sites (provided by Dr. Lila Gierasch, University of Texas). Quadrature detection was obtained through phase cycling of the P_2 and P_3 pulses. The spectrum in Figure 2, obtained with 32 scans for each of 64 t_1 values incremented by 45.6 μsec, has its frequency axes corrected for the experimental scaling factor. There are four amide resonances, two from each molecule in the asymmetric unit cell. The spectrum is notable because each correlation peak has unique ^{1}H *and* ^{15}N resonance frequencies.

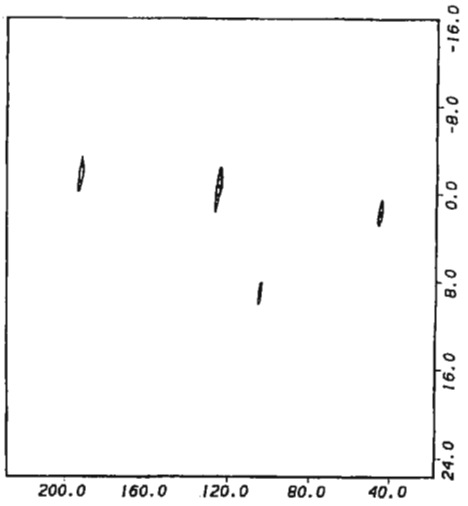

Figure 2:
Two-dimensional $^{1}H/^{15}N$ NMR spectrum of a single crystal of N-acetyl-valyl-leu. The correlation peak with a ^{15}N resonance frequency near 40 ppm was plotted at a lower contour level than the others for clarity.

Sincerely,

Stanley J. Opella

C. H. Wu

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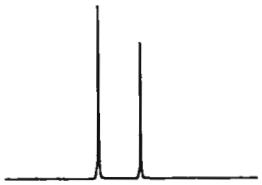
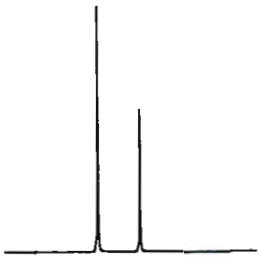
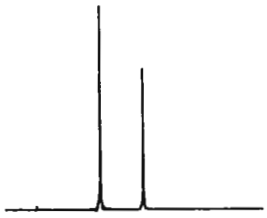


Variable amplitude cross polarization (VACP) *under* –2.6 KHz *mismatch condition*

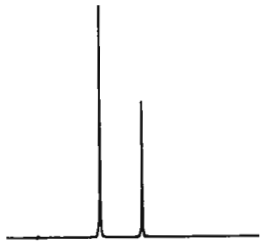
Deliberate "mismatch" of –1.9 KHz



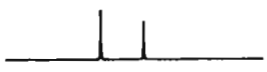
VACP *under normal match condition*



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.

KTH
(The Royal Institute of Technology)

Stockholm, December 28, 1993
(received 1/6/94)

Dept. of Inorganic Chemistry
Julius Glaser, associate professor

NMR Spectra on a Personal Computer

Dear Prof. Shapiro,

We have had our Bruker AM, AC and MSL series NMR spectrometers for some years now. Some of the hardware is eight years old, but is still alive and very intensively used. We cannot do all the fancy experiments on these machines, but for the "normal" ones there are no major problems. Though, there are some parts that would fit better into the collection of the Technical Museum of our city. Among these are certainly the data storage and transfer media, such as the 8" diskette drive (about 130 kbyte per diskette!) and the 10" magnetic tape station (8 Mbyte per tape). The tape station is very slow by today's standards and one tape cannot accommodate even a single 2D TI-NMR spectrum (of the type shown in this Newsletter **414,** 1993, 6) recorded with a decent resolution.

On the other hand, we suffer a lot from the Bruker DISNMR software. It is much younger than the hardware, but seems to be unable to keep up with the passing time. In particular, the 2D data treatment lacks several of the necessary tools.

We have solved both the data storage and the software problems by transferring the spectra to a PC using the Bruknet software. The PC had to be equipped with a suitable communication software* and an Ethernet card, but the latter is not very expensive (≈200 $). In this way, we can transfer any reasonable size FID or spectrum within seconds.

For the treatment of the data we don't need to sit in the noisy NMR room any more. Instead, all the data manipulations can be done on a PC, in the office or at home, using the MS-WINDOWS based program WINNMR. We have tested the preliminary versions of WINNMR-1D and WINNMR-2D* and found that even if there are some things that could be added or improved, these programs are superior to the old DISNMR. One can do most of the operations possible with DISNMR, but in a more elegant and pleasant way. In addition, several new features have been added which facilitate the data treatment. For example, there is a lot of freedom to change the 2D plot levels. We also like the possibility of calculating 2D volume integrals, necessary for quantitative evaluation of our EXSY spectra. The calculation times on a PC (486 type, 66 MHz clock frequency) are usually shorter than those on the ASPECT station (equipped with an array processor).

For an example of a 2D plot using a HP550C printer (originally in colors, which makes a big difference), see Figure 1 below.

* From Bruker-Franzén Analytik GmbH, Bremen, Germany.

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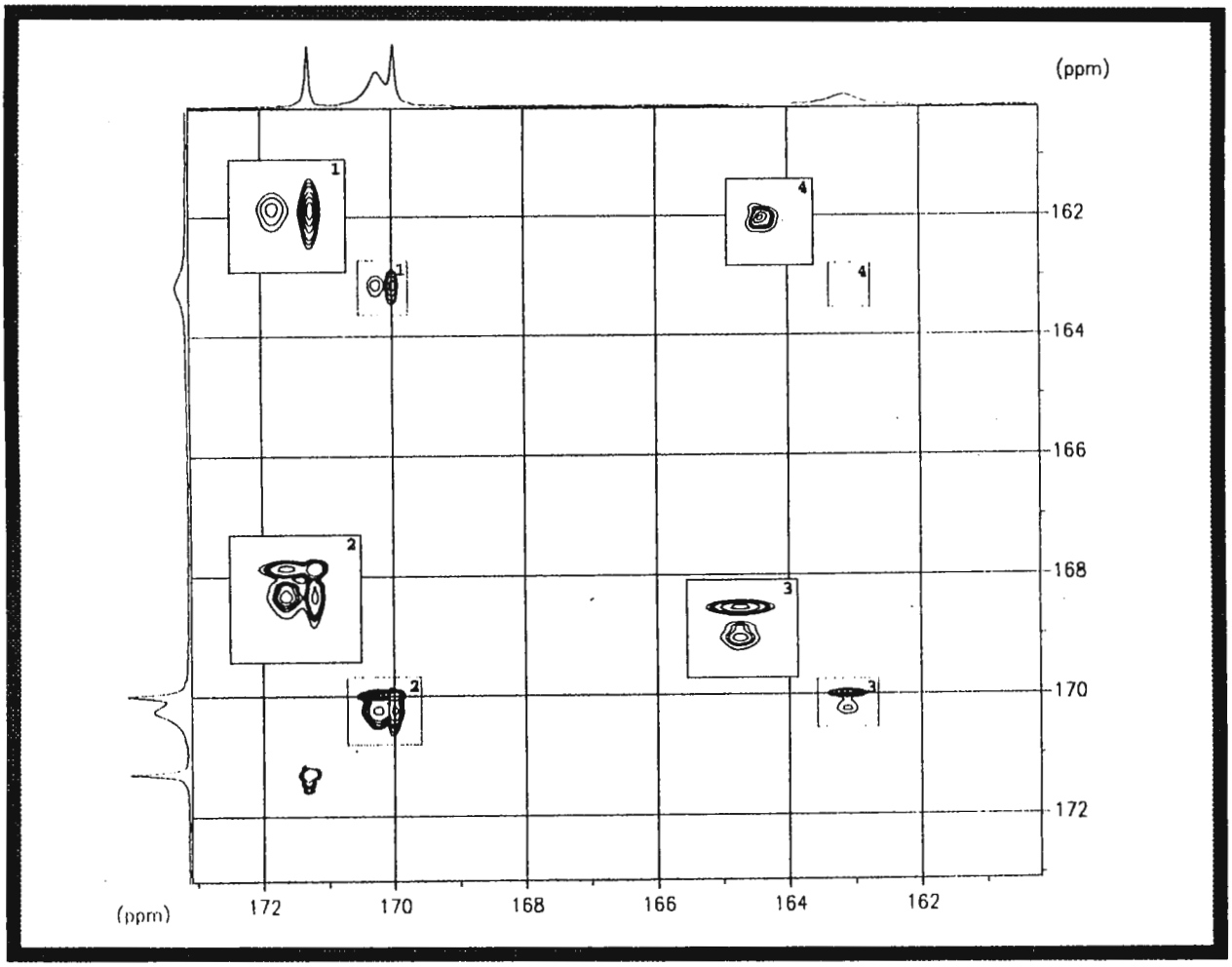


Figure 1. *C-13 NMR 2D EXSY for a 50 mM aqueous solution containing uranyl(2+) and carbonate ions. Mixing time, τ_m = 1 s.*

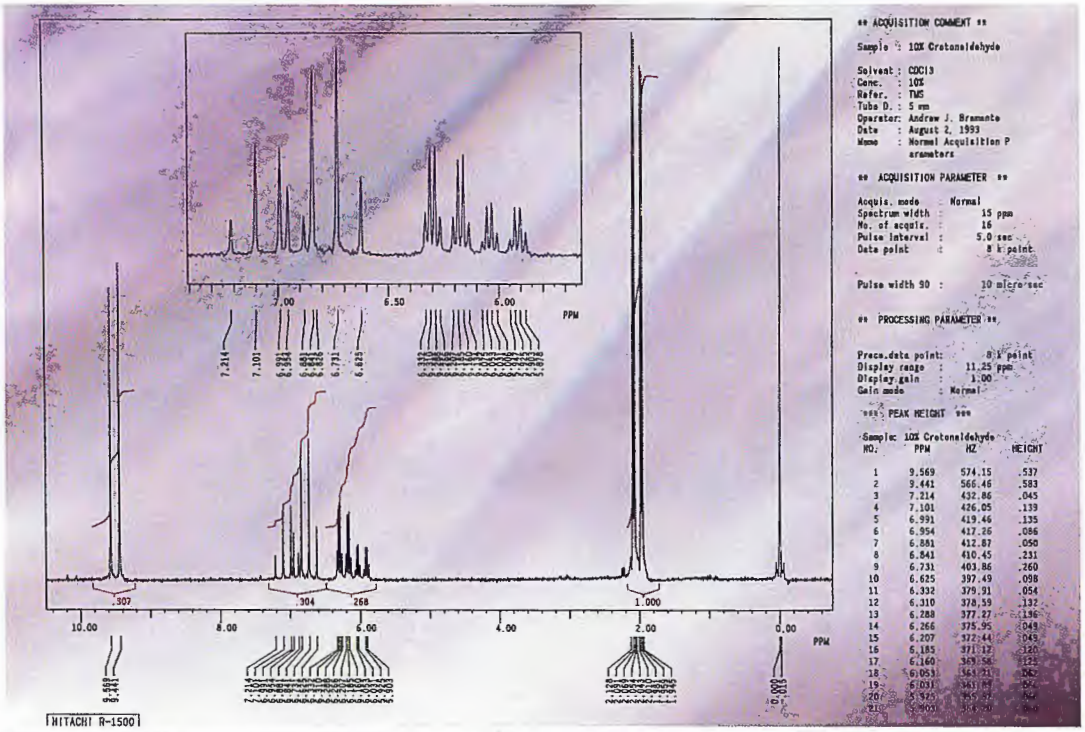
The other very important benefit of this arrangement is the possibility of storing large amounts of NMR data in a practical and inexpensive way, namely using a PC tape drive. There are nowadays several types on the market: the one we use is built-in into the computer, relatively fast and costed about 500 $. One tape can store 525 Mb (8-bit words; ≈10$/tape). What a relief!

We are now in the process of buying a new high-field NMR spectrometer, so our data storage and software problems will certainly be solved with the new equipment. Still, the PC-based arrangement will keep the advantage of being a practical way of distributing the treatment of the NMR data to the users' own offices and homes. Moreover, it is possible to import spectra into a WORD for Windows manuscript, for example.

Yours sincerely,

Julius Glaser

Zoltan Szabo



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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(received 1/18/94)

DSP Data Input; Double RF Filter; Probe Burnout Inhibitor

Dear Barry:

1. In a TAMU private communication dated 11/89, we described our use of DSP's for 2DFT and display, and also the possibility of using a DSP for data input/oversampling/digital filtering. We have finally gotten around to doing the latter (J. Magn. Reson., May '94. Preprint available on request). The 1989 communication ended with the question "I wonder how many years it will be before we see the (hardware) filters disappear on new machines?". We can now report that the answer appears to be "about four years", judging by recent announcements from instrument makers. Of course, there is no guarantee that, now that digital filtering is available, hardware filters will be removed from commercial NMR's and that the cost of instruments will reflect this economy, in a way commensurate with the extra cost charged for similarly complicated items like field gradient drivers.

The key strategy in our implementation was to localize the DSP in front of the rest of our software, to avoid software headaches; and to operate with our observation carrier always off resonance to eliminate some possible artifacts. This assumes you can switch from on- to off-resonance within microsecs after the last proton pulse; an unexpected phase loss of coherence in our commercial synthesizer for jumps > 10KHz forced us to limit ourselves to a 5 KHz jump.

2. In our custom built-LDB 500 instrument, 13C and 13N pulsing and decoupling RF signals are generated separately at low level and then combined and fed to a single power amplifier, to avoid buying two power amplifiers. (Of course this is embarrassing when people ask how many het channels we have, and we have to say "1 1/2".) For triple resonance we then have the problem of passing both of the het frequencies through a filter that removes both deuteron and proton noise generated by the het system. We tried just putting 13C and 15N filters (125 and 50 MHz band filters, both K&L Microwaves) in parallel, but the 13C efficiency dropped too much. We ascertained that the 13C filter had negligibly high input impedance at 50 MHz but the 15N filter had considerable capacitative input impedance at 125 Mhz. We then constructed a composite filter with Tees directly at the input and output of the 13C filter, and empircally picked cables connected from each Tee to the ports of the 15N filter. These cables are close to 1/4 wavelength for 13C. This filter is essentially as efficient as the two filters individually. This trick would only work for two frequencies at a time, but is much simpler than alternatives such as relays or pin diodes.

3. It is distressing that probes on commercial instruments can be burned out by operator error. Below we show an obvious circuit in a box for inhibiting this (we do not say "preventing", because nothing is fail-safe). The circuit could be put into the RF lines to the probe of any commercial system; it senses power input averaged over a few seconds time and cuts the amplifier power (in our case at the 60 Hz power level) if the average power is too high, and it makes a noise. If you can't figure out how to kill the power amplifiers in your system, or don't want to, you could use a coax relay in the RF lines. It is designed so that if its power fails the power amplifiers are off. It could be made more fail-safe by having the system computer learn in some way what the box is sensing, and sounding an alarm if it did not behave as expected. If we didn't have

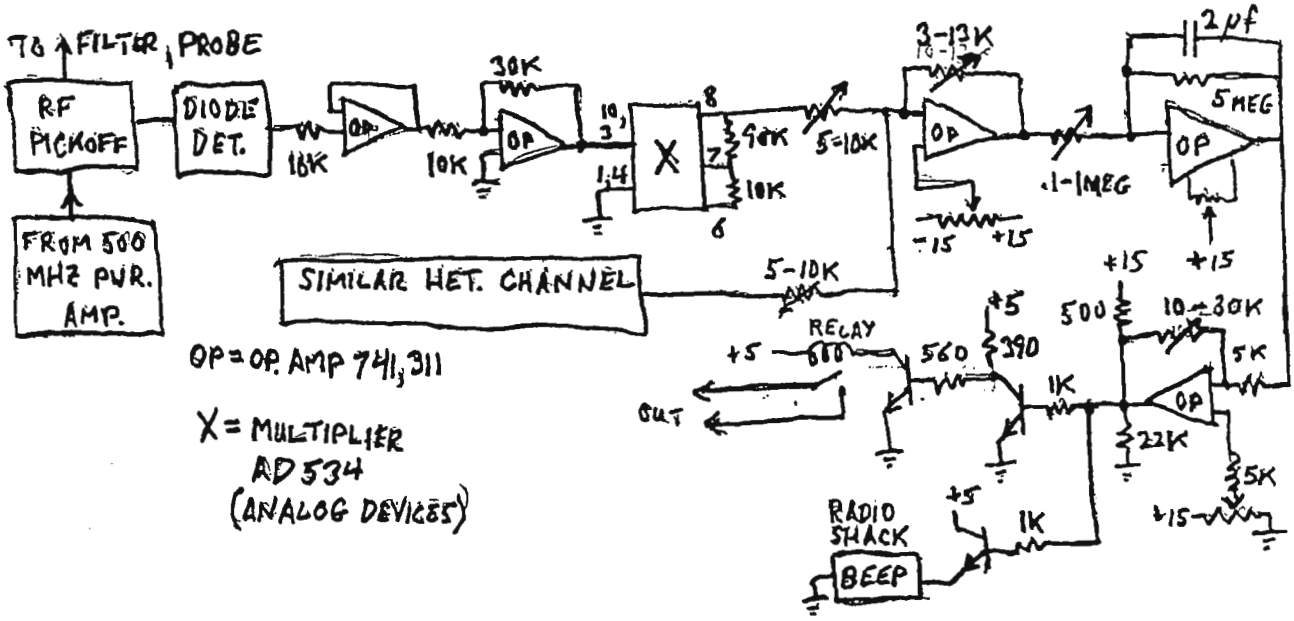
anything better to do we would arrange this and have the computer test whether the box is working, every so often. A third channel could be added to this circuit to sense gradient overpower.

Below, the pickoff circuits are: a surplus 30 db directional coupler and rf detector for the proton port, and a simple diode detector connected to the line by a very small capacitor for the het channel. The latter circuit generates harmonics and should go between the power amplifier outputs and the filters (mentioned above). The diode detectors should be designed to rise and fall in less than a microsec. These detected signals are amplified in wide-band op amps and fed to squaring circuits to produce voltages proportional to the power going to the probe. These voltages are summed and then fed to a leaky integrator with a 5 second time constant. Five seconds was picked as being longer than the period of pulsing of most experiments. The output of this integrator is sensed by a comparator and when it exceeds an average power of a few watts the power goes off. The power spontaneously comes on again in a few seconds, and this repeats until the operator does something, such as increase the recyle time. We won't say what the average power level is, that kicks it off, mostly because we haven't measured it accurately, but also because we don't want to be blamed if you burn out your probe anyway. Note that if this level is x, and the time constant of the integrator is y sec, a single strong pulse, as in a Tocsy, will turn the system off after a time such that xy joules will have been delivered to the probe. Ask your friendly probe supplier what average power and peak energy your probe can take (don't expect a very precise answer!).

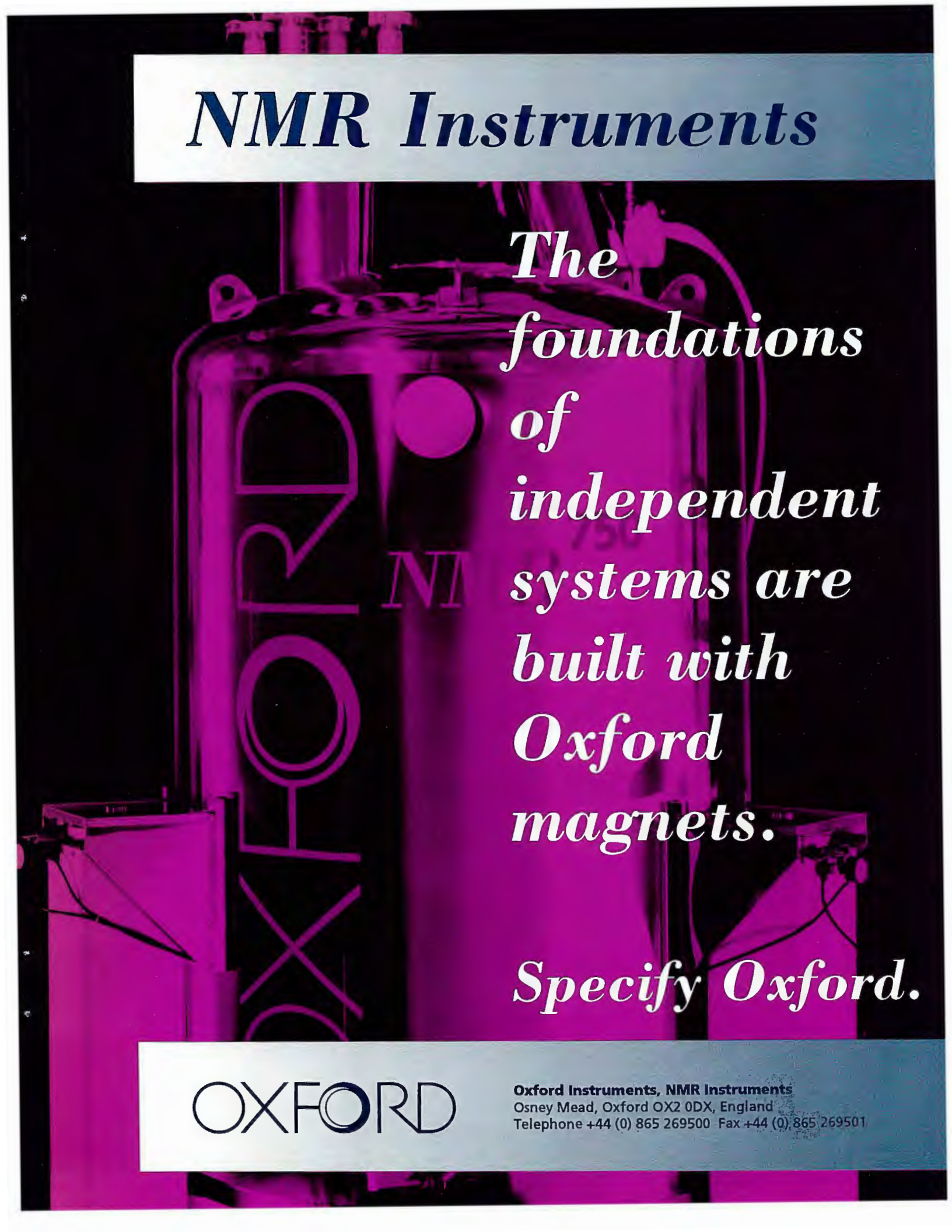
Sara Kunz
Department of Physics
Brandeis University, Waltham MA 02254, USA

Alfred Redfield
Deparment of Biochemistry

Al & Sara



NMR Instruments



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January 5, 1994
(received 1/18/94)

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IUPUI

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

Symposium on "NMR as a structural Tool for Macromolecules: Current Status and Future Directions"

Dear Barry:

I wish to utilize the TAMU Newsletter to publicize a Symposium with the above title that will be held on the campus of Indiana University-Purdue University Indianapolis (IUPUI) for three full days, October 30 through November 1, 1994, at IUPUI's University Place Conference Center and Hotel.

The lectures and discussions at the symposium will evaluate the NMR method along the line, "Where do we stand, and where do we go from here?" The lectures (about 20-24), given exclusively by invited speakers, are expected to stress the present limitations of the techniques and discuss future possibilities and strategies from both technological and methodological points of view. Participation in the Symposium will be open but limited to 250 people. There will be poster sessions on two of the three evenings of the Symposium.

The following NMR spectroscopists have thus far agreed to speak at the Symposium:

Richard R. Ernst (Keynote Speaker)	Thomas L. James	Paul Rösch
Ad Bax	Robert Kaptein	Alfred G. Redfield
Walter J. Chazin	Horst Kessler	Brian D. Sykes
G. Marius Clore	Anil Kumar	Gerhard Wagner
Stephen W. Fesik	David M. Lemaster	A. Joshua Wand
Maurice Gueron	John L. Markley	Peter E. Wright

For more information, please contact Ms. Padmini Nallana, Coordinator, NMR Symposium, Department of Physics, Indiana University Purdue University Indianapolis, 402 N. Blackford Street, Indianapolis, IN 46202-3273, USA; Tel: (317) 278-1263; E-Mail: PADMINI@INDYVAX.IUPUI.EDU; FAX: (317) 274-2393.

We will greatly appreciate if you would list this meeting for the next several months on page 1 of future issues of the TAMU Newsletter.

Sincerely yours,

B. D. Nageswara Rao
Professor and Chairman

NMR CENTER

DEPARTMENT OF PHYSICS

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January 14, 1994
(received 1/21/94)

Dr. B. Shapiro, Editor
TAMU NEWSLETTER
966 Elsinore Court
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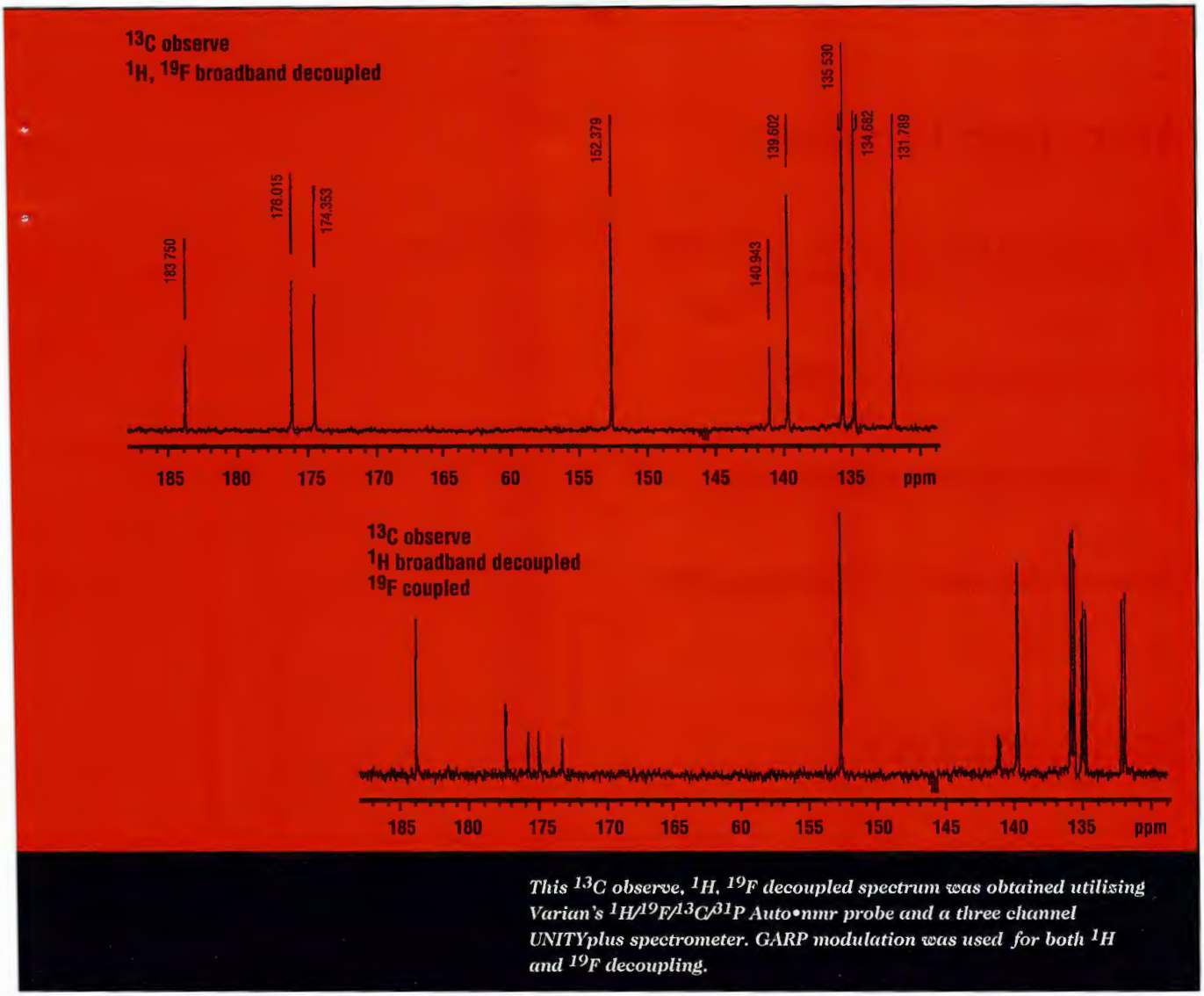

*This ^{13}C observe, ^{1}H, ^{19}F decoupled spectrum was obtained utilizing Varian's ^{1}H/^{19}F/^{13}C/^{31}P Auto•nmr probe and a three channel UNITY*plus *spectrometer. GARP modulation was used for both ^{1}H and ^{19}F decoupling.*

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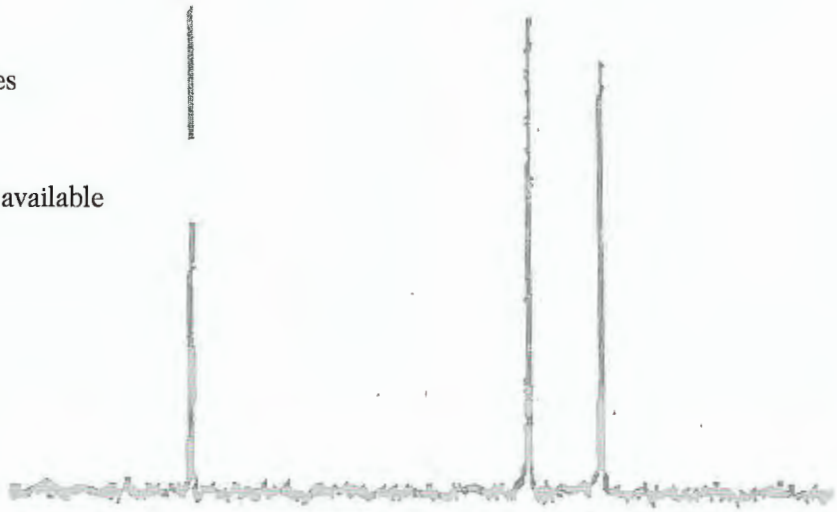

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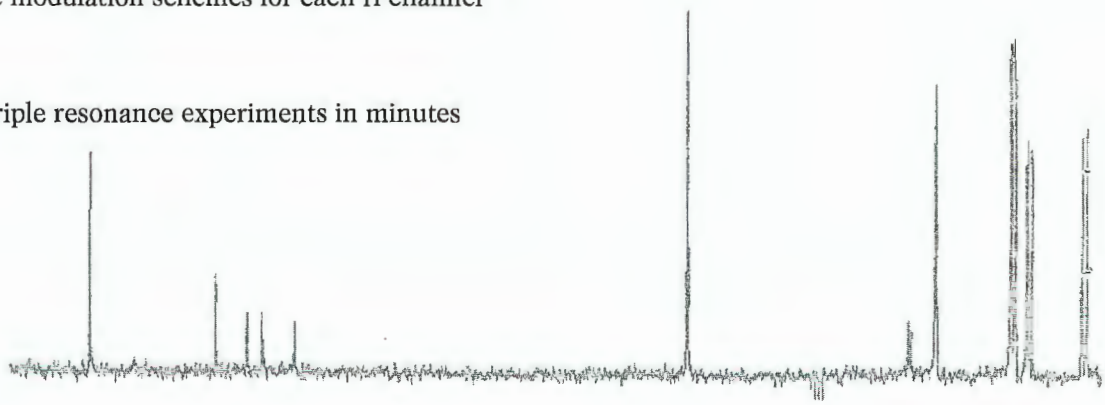

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UNOCAL 76

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

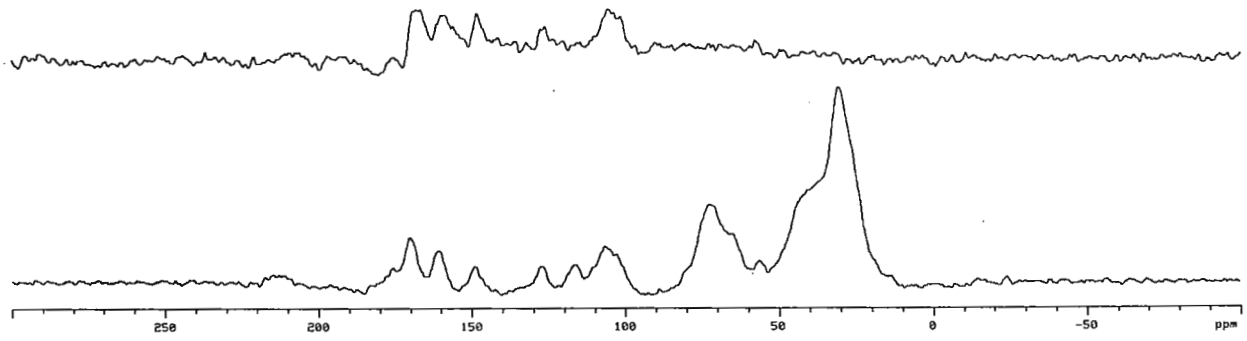
December 1, 1993
(received 1/7/94)

Dear Prof. Shapiro,

^{13}C CPMAS NMR Analysis of Lily Pollen Exine

The structural composition of plant pollen grain exines (the outermost coat) is scientifically of interest since they are known to be composed of very resistant polymers known as sporopollenin. Their resilient nature permits the preservation of exines in sediments where with increased burial they may eventually participate in fossil fuel formation. Earlier studies concluded that exines from a variety of plants were composed largely of carotenoids and carotenoid esters. This was not, however, supported by later studies on the biosynthesis of sporopollenin whose formation was observed to be unaffected when carotenoid biosynthesis process was inhibited.

Since sporopollenins are extremely insoluble, palynological studies used harsh conditions such as high temperatures and strong reagents like KOH, H_2SO_4, acetic anhydride, etc. This called into question if its structural integrity was maintained. An elegant solution to this problem was recently reported (Tarlyn, N.M; Franceschi, V. R; Everard J. D; Loewus, F. A, *Plant Science, 90, 219, (1993)*). Their procedure is significantly milder allowing the isolation of gram quantities of exine at room temperature. Naturally, some of this found its way quickly into our Doty CPMAS probe. Shown below are the conventional 200 MHz ^{13}C CPMAS (lower trace) along with the corresponding "dipolar dephased" spectrum (upper trace) obtained using a Varian Unity-200 spectrometer.



These spectra confirm that the exine is primarily composed of an aliphatic polymer (accounting for approximately 59% of the observed carbons) rather than carotenoid derivatives. The rest of the spectrum can be assigned to carbohydrate (~24%), olefin/aromatic (~9) and carbonyl (~8%) carbons. This finding is supportive of the similar conclusions drawn earlier (Espelie, K.E; Loewus, F.A; Pugmire, R.J; Woolfenden, W.R; Baldi, B. G; Given, P. H, *Phytochemistry, 28, 751, (1989)*).

Yours Sincerely,

Scott Stout
Sr. Res. Geochemist.

Pradeep Iyer
Sr. Res. Scientist

ROSKILDE UNIVERSITY

Associate professor Poul Erik Hansen, Institute of Life Sciences and Chemistry

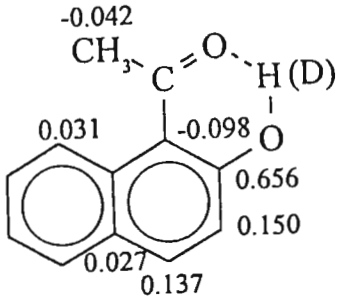
Professor B.L.Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

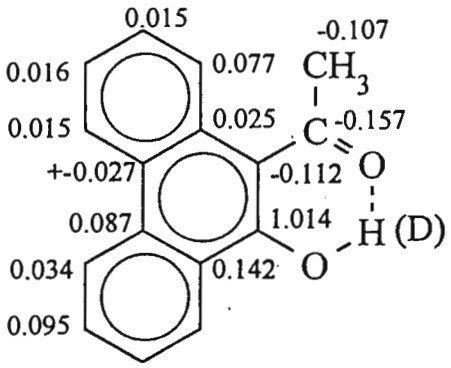
January 4 1994
(received 1/13/94)

New Type of Deuterium Isotope Effects

Dear Professor Shapiro

The study of deuterium isotope effects on chemical shifts continue to provide new and surprising results. We have found rather large two-bond isotope effects in sterically hindered intra-molecularly hydrogen-bonded compounds as shown in Fig.1.





For naphthalenes, the large effects are not seen in 1-hydroxy-2-acenaphthone nor in the corresponding aldehydes, all without steric hindrance. In sterically hindered compounds the unusual effects are seen at carbons in the proximity of the carbonyl group or at positions in conjugation with this group.

We term the effects "steric strain" effects, but they could also be called steric relaxation isotope effects. In these compounds the twist caused by the steric hindrance and the aim for planarity of the carbonyl group in order to maximize the strength of the hydrogen bond balance each other. This balance is perturbed as the hydrogen bond is weakened by deuteriation. This weakening cause a larger twist of the sterically hindered carbonyl group. The increased twist leads to chemical shift changes and hence to isotope effects.

The large effects of e.g. the phenanthrene can be distiguished from tautomeric equilibrium effects as the former are rather temperature insensitive.

With the best wishes for a Happy New Year

Simon Bolvig
Simon Bolvig

Poul Erik Hansen
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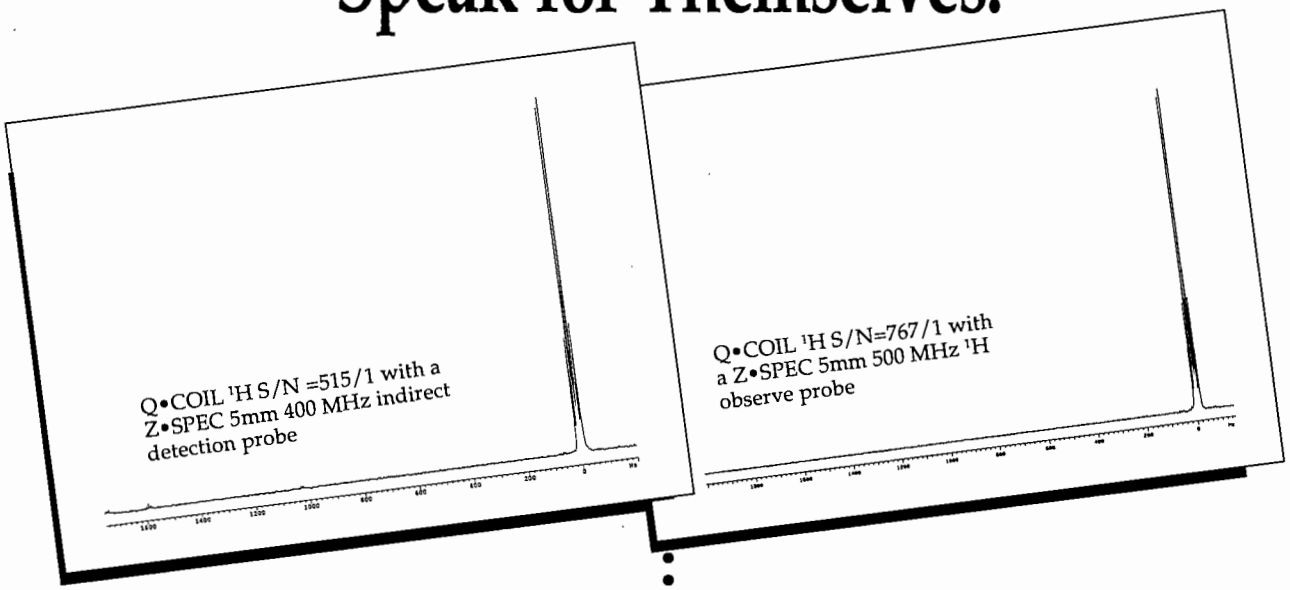

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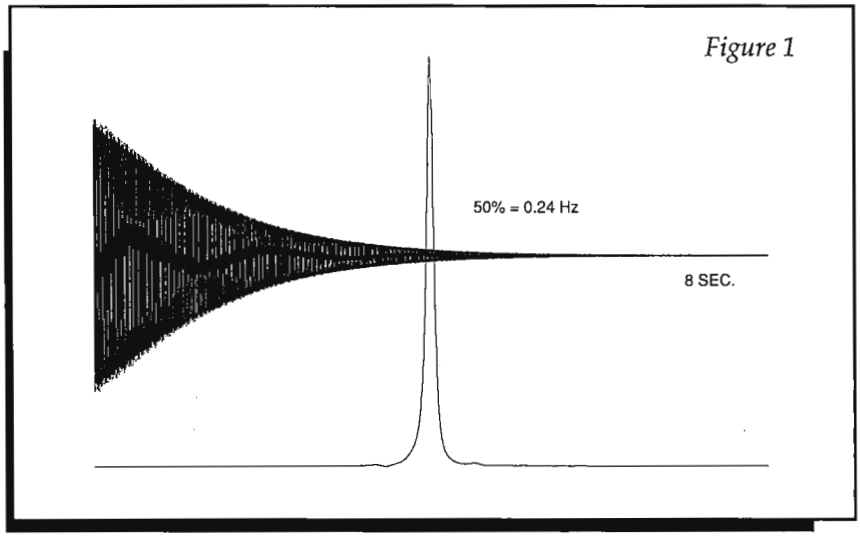

Figure 1: ^{1}H line shape determination on 1% $CHCl_3$ for Z•SPEC H 500-5 probe at 500 MHz. Resolution = 0.24 Hz.

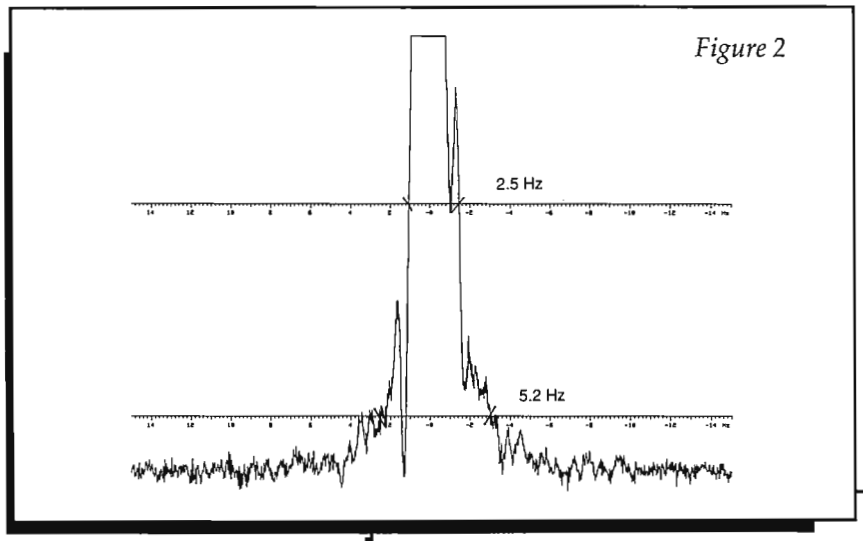

Figure 2: ^{1}H line shape determination on 1% $CHCl_3$ for Z•SPEC H 500-5 probe at 500 MHz, 2.5 Hz at 0.55% and 5.2 Hz at 0.11%.

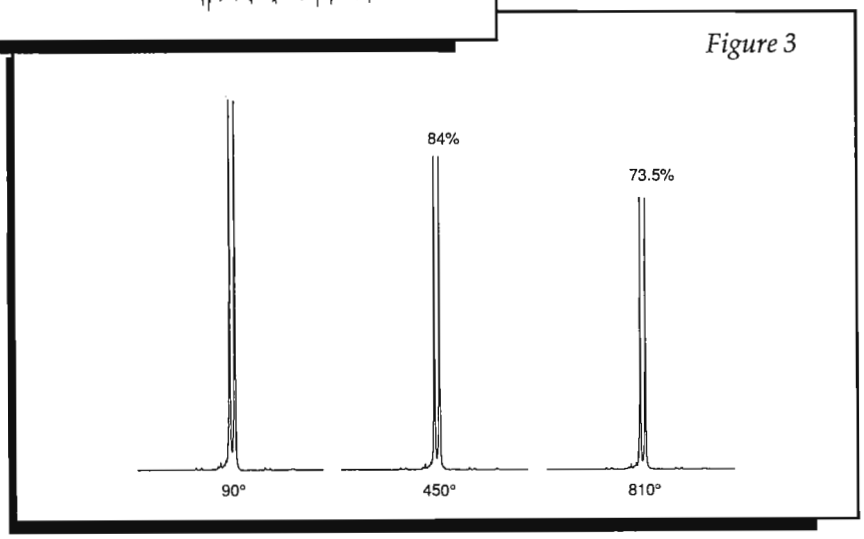

Figure 3: ^{1}H RF homogeneity determination for Z•SPEC ID 500-5 probe at 500 MHz, 84% at 450° and 73.5% at 810°.

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November 18, 1993
(received 1/7/94)

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

Dear Barry:

Silicon-29 NMR spectra on a glass-free probe.

Silicon tetroalkoxides react via the sol-gel reaction to give polymers that gel and, with relatively low temperatures, give glass-like materials. Silicon-29 NMR has been used to obtain information on the reaction kinetics and polymer precursors in these systems. When the silicon atom forms four condensation bonds Si-(O-Si)$_4$, the silicon species resembles glass and the resonance occurs at -107 to -115 ppm (TMS = 0). This species is designated Q^4 in the figure.

The top spectrum is obtained on a normal 10 mm broadband probe at 59.7 MHz. The bottom spectrum, of the same material (at 99.3 MHz), was obtained on a 10 mm broadband probe built by Nalorac Cryogenics Corporation. All the silicon glass has been replaced with other materials. The tubes used were Wilmad's Teflon-FEP 10 mm sample tube liners (no. 6010) which were extended below a 10 mm glass sleeve into the coil region. The glass sleeve was a cut-off 10 mm sample tube that served to hold the Teflon liner in the spinner.

The spectra are of tetramethoxysilane reacted in ethyl alcohol with water and a small amount of acid (a typical sol-gel reaction). A plethora of reaction products are shown in the spectra. The regions labelled Q^0-Q^4 designate the number of condensation bonds, out of the four possible, on each silicon species. The individual resonances within each region represent various numbers of alkoxides (ethoxide and methoxide) and hydroxide substitutents as well as different ring and oligomer sizes. As is easily seen in the figure, several of the resonances in the top spectrum (with the normal probe) are masked by the interfering glass signals. Q^3 and Q^4 resonances are impossible to quantify using the normal experimental setup.

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Best Wishes,

Larry W. Kelts . A J Williams

Larry W. Kelts and Antony J. Williams
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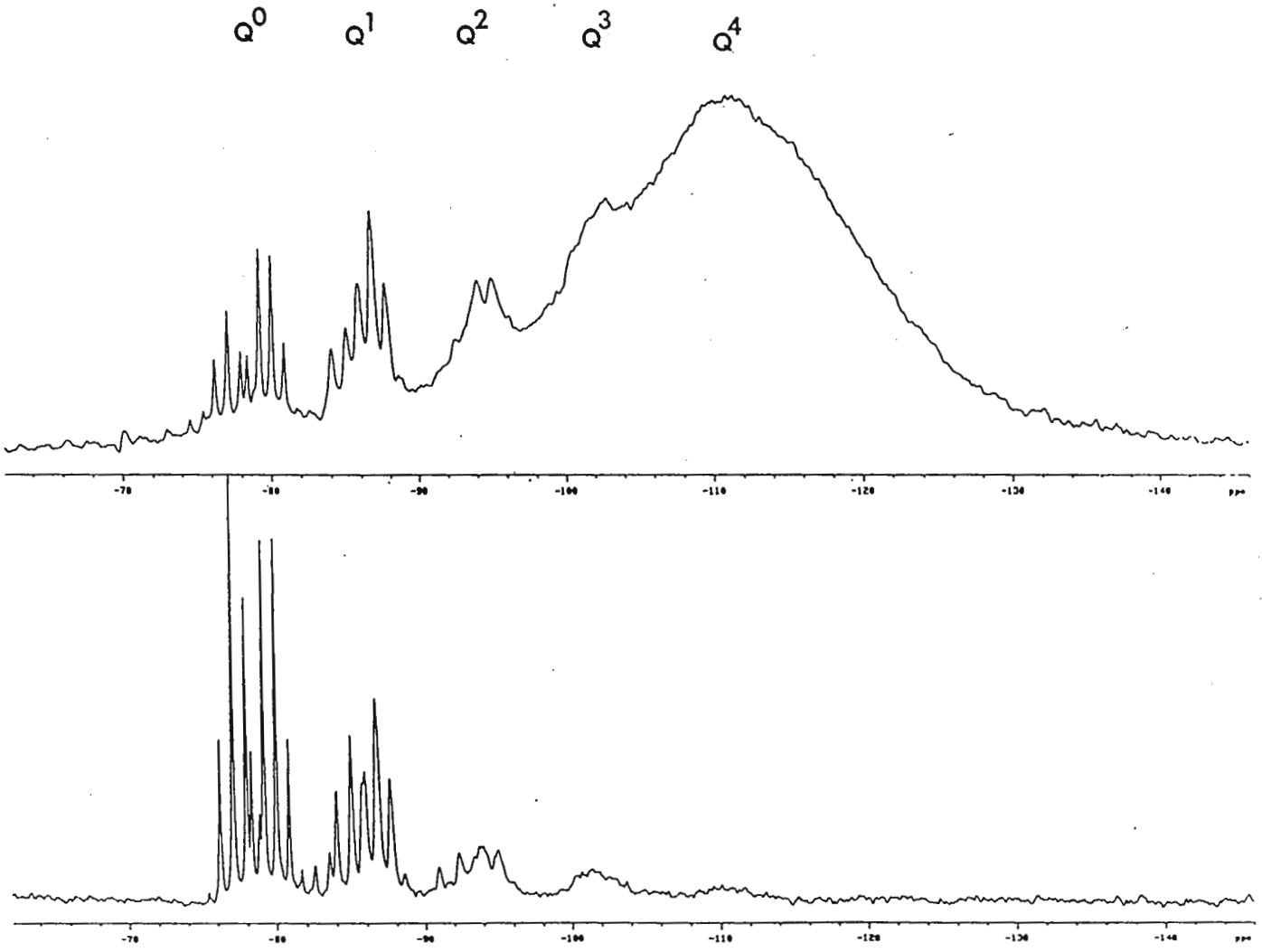
PS: Please credit this contribution to Nick Zumbulyadis' account.



UNIVERSITY OF MISSOURI-ROLLA
Missouri's Technological University

Frank D. Blum
Department of Chemistry
142 Schrenk Hall
Rolla, Missouri 65401-0249
(314)-341-4451 (or 4420)
Bitnet - FBLUM @ UMRVMB
Internet - FBLUM @ UMRVMB.UMR.EDU

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

January 4, 1994
(received 1/7/94)

Dear Barry:

Pulsed-Gradient Spin-Echo Experiments on a JEOL FX-100/Tecmag Unit

At the University of Missouri-Rolla, a JEOL FX-100 upgraded with a Tecmag Leo/J™ data acquisition system was modified to control the homospoil pulses. With the existing power supply, gradient strengths greater than 5 G/cm can be achieved from these homospoil pulses. By using the Pulsed-gradient Spin-Echo technique (1-3) diffusion data can be obtained. Diffusion experiments are important in studies of heterogeneous systems. We have used these measurements for the determination of the phase behavior of surfactant systems and studying diffusion of solvents in polymer solutions which is important in kinetics of polymerization and drying of paints.

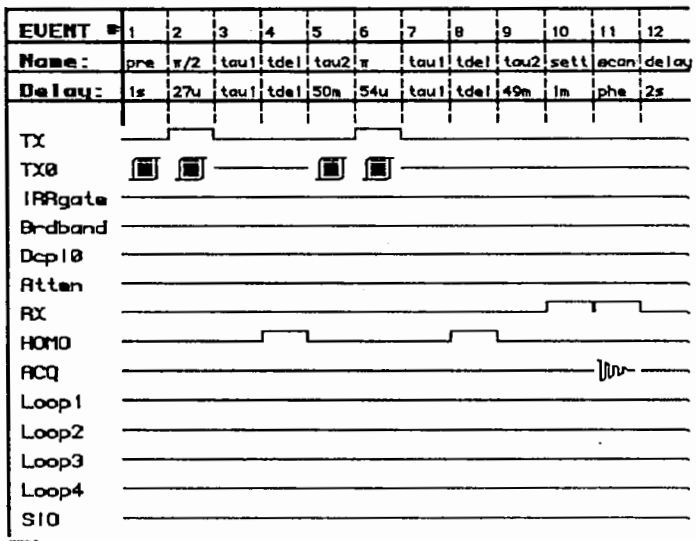


Figure 1. Pulsed-Gradient Spin-Echo pulse sequence for diffusion experiments. The RF pulses and receiver are phase cycled 0°/90°/270°/180°/180°/270°/90°/0°. RF phase tables are preloaded.

The Pulsed-Gradient Spin-Echo sequence program for the Tecmag unit is shown in Figure 1. It is a normal spin-echo experiment with the addition of a gradient pulse during each of the delays, *tdel*. A diffusion experiment requires an array of spectra where the length of the gradient pulse is being varied. However, the total echo time needs to be constant in all the spectra in order to remove T_2 effects (3). This requires that the sum of the delays *tau1* and *tdel* be constant throughout the array.

Figure 2 shows a set of spectra obtained from a sample that was a 50:50 molar mixture of H_2O and D_2O at 25°C. The values of *tdel* vary from 0 to 12 ms in 1.5 ms increments, with, *tau1* + *tdel* = 20 ms. This sample was used to calibrate the gradient strength. The equation governing the effect of the gradient pulse on the spectrum is

$$A = A_o \exp\left(\frac{-2(\text{tau1}+\text{tdel}+\text{tau2})}{T_2}\right)\exp\left(-\gamma^2 G^2 D\beta\right)$$

where $\beta = \text{tdel}(\Delta - \text{tdel}/3)$ and $\Delta = \text{tau1} + \text{tdel} + \text{tau2}$. If Δ is kept constant, a plot of ln A versus β yields a straight line with a slope of $-\gamma^2G^2D$. The diffusion coefficient (D) of HDO at 25°C has been previously measured to be 2.209×10^{-9} m^2/s.[3] The gradient strength measured was 5.22 G/cm.

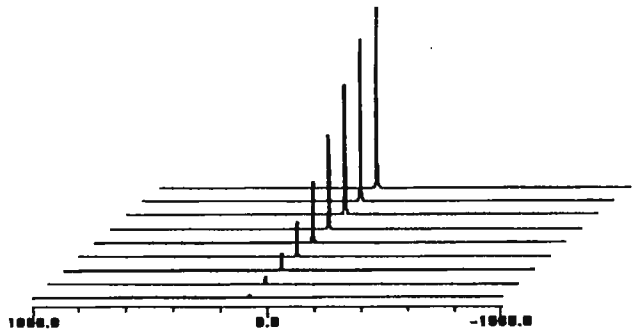


Figure 2. 50:50 molar mixture of H_2O and D_2O at 25°C. With *tdel* ranging from 0 to 12 ms in 1.5 ms increments.

Hardware Modifications

On the Leo/J unit, any of the control lines on connector J5 or J6 can be assigned to control the homospoil pulse. We choose control line 47 on connector J5. A cable was connected from J5 to the homospoil driver card. The homospoil driver card is located under the right side of the counter top by the shim potentiometers. To access this, remove the two screws on the upper corners of the front panel of the counter top. The front panel then swings down on hinges located on the bottom corners of the panel.

In the JEOL schematic manual, this circuit board is called the "Spoiling Driver" (JEOL schematic number NT03-0411). The pulse input to the board is normally high, and the gradient output is active when the input is in a low state. Since the JEOL operates on negative logic (active low state), a modification to the board is required. To invert the logic in the circuit on the homospoil board, eliminate the inverter represented by Q2 in the circuit. This modification as well as the Spoiling Driver circuit is shown in Figure 4.

After the modification, there is no detectable change in performance of the homospoil driver circuit. For pulse gradient experiments, adjust the potentiometer in the driver circuit to about 1.2 A . For normal operation, adjust the current to about 800 mA. If the FX is reconfigured back to the original configuration with the TI980B computer and the JEOL programmer, the Spoiling Driver board must NOT be connected to the spectrometer since a continuous gradient would be applied.

In the future we hope to write a C resource which will enable diffusion coefficient to be calculated within MacNMR using the SLICE window.

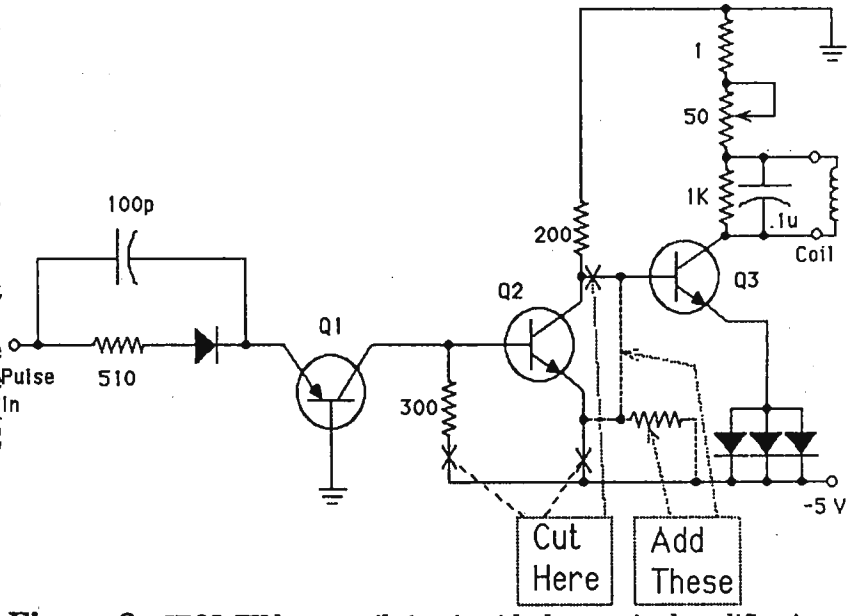


Figure 3. JEOL FX homospoil circuit with the required modifications for pulsed gradient experiments. The added resistor is 4.3 K ohms.

References

1. Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1964**, *42*, 288.
2. Blum, F.D. *Spectroscopy* **1986**, *1(5)*, 32.
3. Stilbs, P. *Prog. NMR Spectros.*, **1987**, 19, 1.
4. Mills, R. *J. Phys. Chem.* **1973**, 77, 685.

Sincerely

Frank D. Blum
Professor of Chemistry

Joseph A. Counsil
Research Engineer

R. Allen Waggoner
Post-Doctoral Fellow

P.S. Allen has moved to: The Lovelace Institutes, 2425 Ridgecrest Drive, S.E., Albuquerque, NM 87108.

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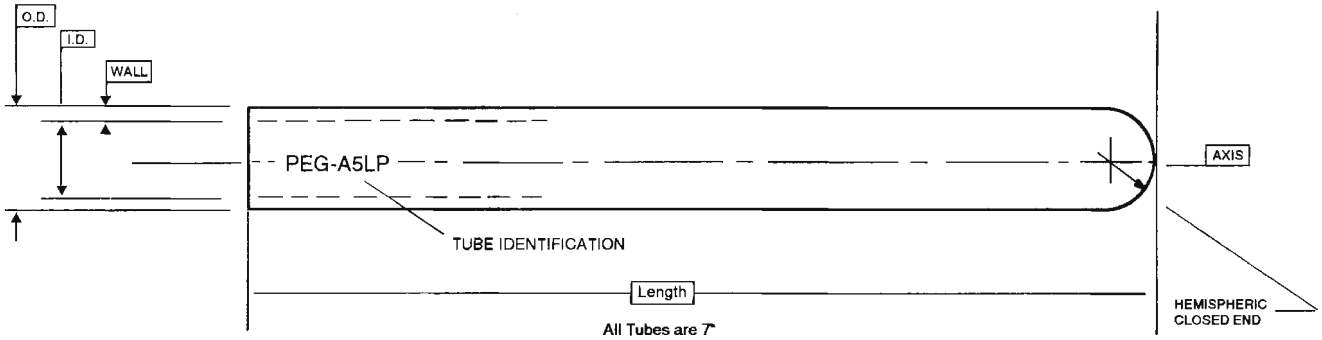

ACE Cat. No.	Megahertz (MHz) Inst. Frequency	O.D. inches	O.D. Tolerance	I.D. inches	I.D. Tolerance	Concentricity I.D.to O.D.	Camber (Over 7" Lgth.)
16XXA5LP-07	>500	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0005"	≤ .00025"
160XA5LP-07	360	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0010"	≤ .0005"
1600A5LP-07	200	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0015"	≤ .0010"
1600B5LP-07	150	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0020"	≤ .0015"
1600C5LP-07	100	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0020"	≤ .0020"
16XA10LP-07	360	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0015"	≤ .0005"
160A10LP-07	150	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0020"	≤ .0010"
160B10LP-07	80	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0030"	≤ .0015"
160C10LP-07	60	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0050"	≤ .0020"
			DISPOSABLE NMR TUBES				
1600A5LS-07	80	.1955	+.0000"/-.0005"	.165	±.005	≤ .003	≤ .002
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1600B5LP-07	5mm/7"	★27.50	★137.50
1600C5LP-07	5mm/7"	★22.50	★112.50
16XA10LP-07	10mm/7"	★93.75	★468.75
160A10LP-07	10mm/7"	★78.75	★393.75
160B10LP-07	10mm/7"	★68.00	★340.00
160C10LP-07	10mm/7"	★51.25	★256.25
1600A5LS-07	5mm/7"	★17.50	★ 87.50
1600A5RS-07	5mm/7"	★ 8.00	★ 40.00

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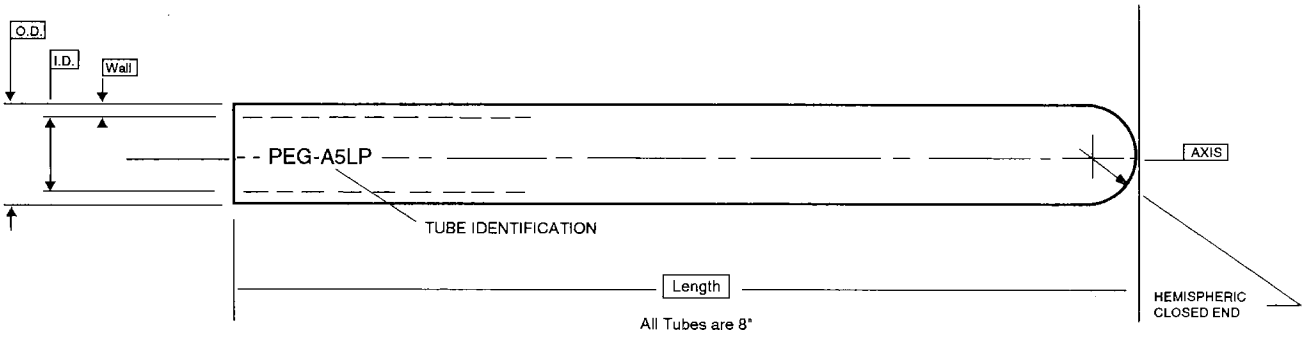
TUBE SPECIFICATIONS

5 and 10mm x 8" length



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16XXA5LP-08	>500	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0005"	≤ .00025"
160XA5LP-08	360	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0010"	≤ .0005"
1600A5LP-08	200	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0015"	≤ .0010"
1600B5LP-08	150	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0020"	≤ .0015"
1600C5LP-08	100	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0020"	≤ .0020"
16XA10LP-08	360	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0015"	≤ .0005"
160A10LP-08	150	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0020"	≤ .0010"
160B10LP-08	80	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0030"	≤ .0015"
160C10LP-08	60	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0050"	≤ .0020"
			DISPOSABLE NMR TUBES				
1600A5LS-08	80	.1955	+.0000"/-.0005"	.165	±.005	≤ .003	≤ .002
1600A5RS-08	60	.196	±.003	.165	±.005	≤ .005	≤ .002

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160XA5LP-08	5mm/8"	★47.75	★238.75
1600A5LP-08	5mm/8"	★40.75	★203.75
1600B5LP-08	5mm/8"	★30.25	★151.25
1600C5LP-08	5mm/8"	★24.75	★123.75
16XA10LP-08	10mm/8"	★97.50	★487.50
160A10LP-08	10mm/8"	★83.75	★418.75
160B10LP-08	10mm/8"	★72.25	★361.25
160C10LP-08	10mm/8"	★56.25	★281.25
1600A5LS-08	5mm/8"	★19.25	★ 96.25
1600A5RS-08	5mm/8"	★ 8.50	★ 42.50

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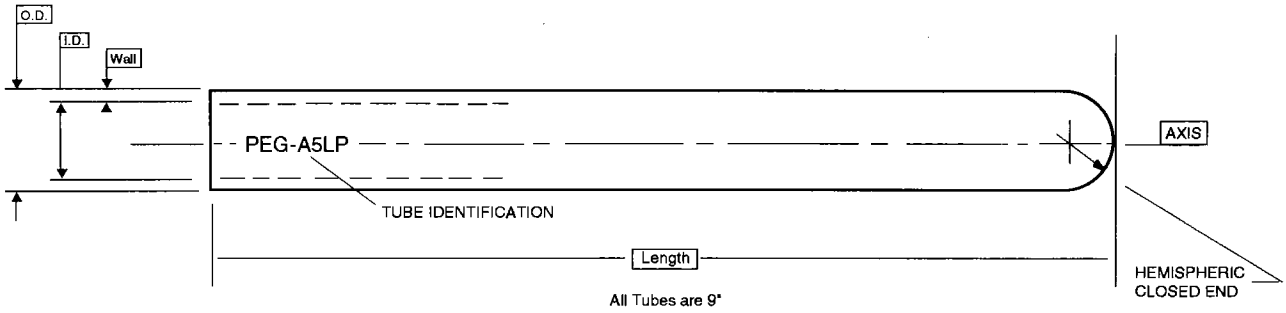
TUBE SPECIFICATIONS

5 and 10mm x 9" length



All Tubes are 9"

ACE Cat. No.	Megahertz (MHz) Inst. Frequency	O.D. inches	O.D. Tolerance	I.D. inches	I.D. Tolerance	Concentricity I.D.to O.D.	Camber (Over 9" Lgth.)
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1600A5LP-09	200	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0015"	≤ .0010"
1600B5LP-09	150	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0020"	≤ .0015"
1600C5LP-09	100	.1955	+.0000"/-.0005"	.1655	+.0005"/-.0000"	≤ .0020"	≤ .0020"
16XA10LP-09	360	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0015"	≤ .0005"
160A10LP-09	150	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0020"	≤ .0010"
160B10LP-09	80	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0030"	≤ .0015"
160C10LP-09	60	.3937	+.0000"/-.0005"	.3569	±.0005"	≤ .0050"	≤ .0020"
			DISPOSABLE NMR TUBES				
1600A5LS-09	80	.1955	+.0000"/-.0005"	.165	±.005	≤ .003	≤ .002
1600A5RS-09	60	.196	±.003	.165	±.005	≤ .005	≤ .002

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160XA5LP-09	5mm/9"	★ 52.50	★262.50
1600A5LP-09	5mm/9"	★ 45.00	★225.00
1600B5LP-09	5mm/9"	★ 33.25	★166.25
1600C5LP-09	5mm/9"	★ 27.25	★136.25
16XA10LP-09	10mm/9"	★101.75	★506.25
160A10LP-09	10mm/9"	★ 88.75	★443.75
160B10LP-09	10mm/9"	★ 76.50	★382.50
160C10LP-09	10mm/9"	★ 62.00	★310.00
1600A5LS-09	5mm/9"	★ 22.25	★111.25
1600A5RS-09	5mm/9"	★ 9.00	★ 45.00

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Fax : 1 69 33 30 10 .

Palaiseau, le 10 Janvier 1994
(received 1/18/94)

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

HEATING BLOW/PUMP STICK FOR HELIUM MAINTENANCE

Dear sir,

Following many icing problems in the auxiliary helium tank of our 600MHz Oxford magnet (1989) we have developped a strategy using a homebuilt Heating Blow/Pump device wich allows the removal, under safe conditions, of persistent solid air plug inside the auxiliary He dewar.

This procedure proved to be much more efficient than the classic one using heated copper rod and avoids violent helium boiling as well as overheating leading to a potential damage of the system.

The structure of the Heating Blow/Pump stick (HBPS*) is outlined in figure 1. It uses a controlled heater at the end of a coaxial tubes system allowing to work as an hot He gas inlet or an outlet connected to a vacuum in order to remove liquid and gas formed during the melting of the solid air plug. It is made of one external stainless steel tube and an inner copper one, the tube diameters are respectively 9 x 7 mm and 6 x 4 mm. The electric heating cartridge is crimped on the copper tube filled with silicon oil in order to provide a good thermical conductibility along the stick. We use a medium flux Vulstar cartridge with a specific load of 7 W/cm^2 for a maximum power of 100 W with a heating resistor of 90 mm length. In this device of a high accuracy the heating part is installed close to the external surface to improve the thermal exchange. The tightness of the inner tube with the cartridge is provided by a soldered joint of tin.
A space of 0.5 mm is free for the gas or liquid circulation. A bidirectional entry valve allows to connect to a pressurized helium gas source or to vacuum. It is thus possible

* We thank Marc Godfrin for the design and the construction of the equipment.

DCSO Ecole Polytechnique 91128 Palaiseau France. tél : 69334861 fax : 69333010

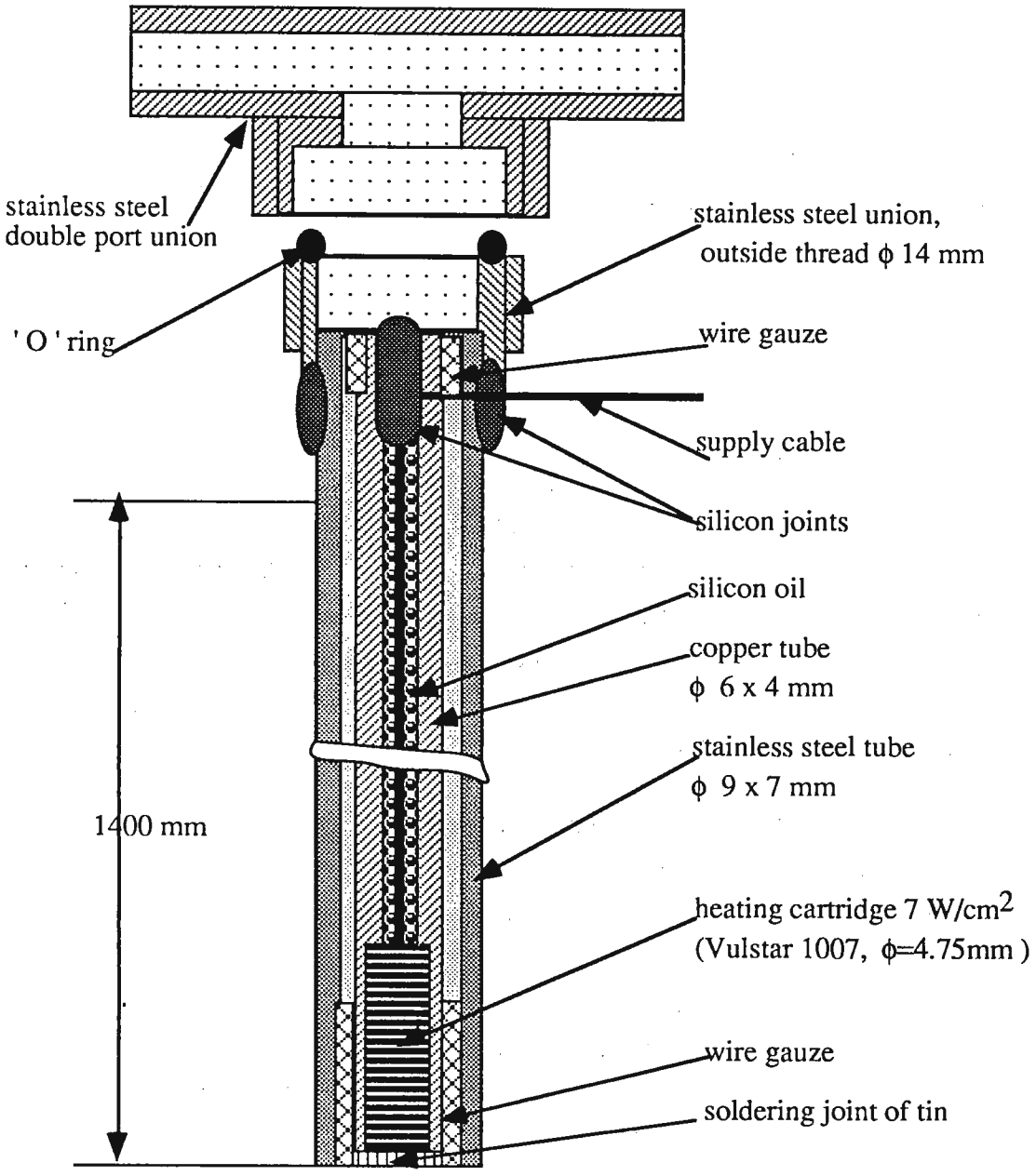

Figure 1 : Heating Blow/Pump Stick construction scheme

DCSO Ecole Polytechnique 91128 Palaiseau France. tél : 69334861 fax : 69333010

either to blow hot helium gas or to pump out any liquid or gas formed during the operation.

The implementation of the HBPS has been done on our 600 MHz on several occasions and the configuration is shown in figure 2. The stick is held at a constant, elevated temperature during the whole operation by controling the voltage (~ 85V) on the cartridge heater (~ 50W). First the HBPS is introduced in the dewar with a moderate helium gas flow. The helium injection is stopped when the system is in contact with the solid air plug and the HBTS is connected to vacuum. The descent through the ice cap then occurs gently (~ 2cm / min) and is followed by graduation on the higher part of the stick.

This simple and cheap realisation proved to be very useful to get a efficient removal of ice while risk of quenching was reduced.

Sincerely yours

Alain Louis-Joseph

Jean-Yves Lallemand

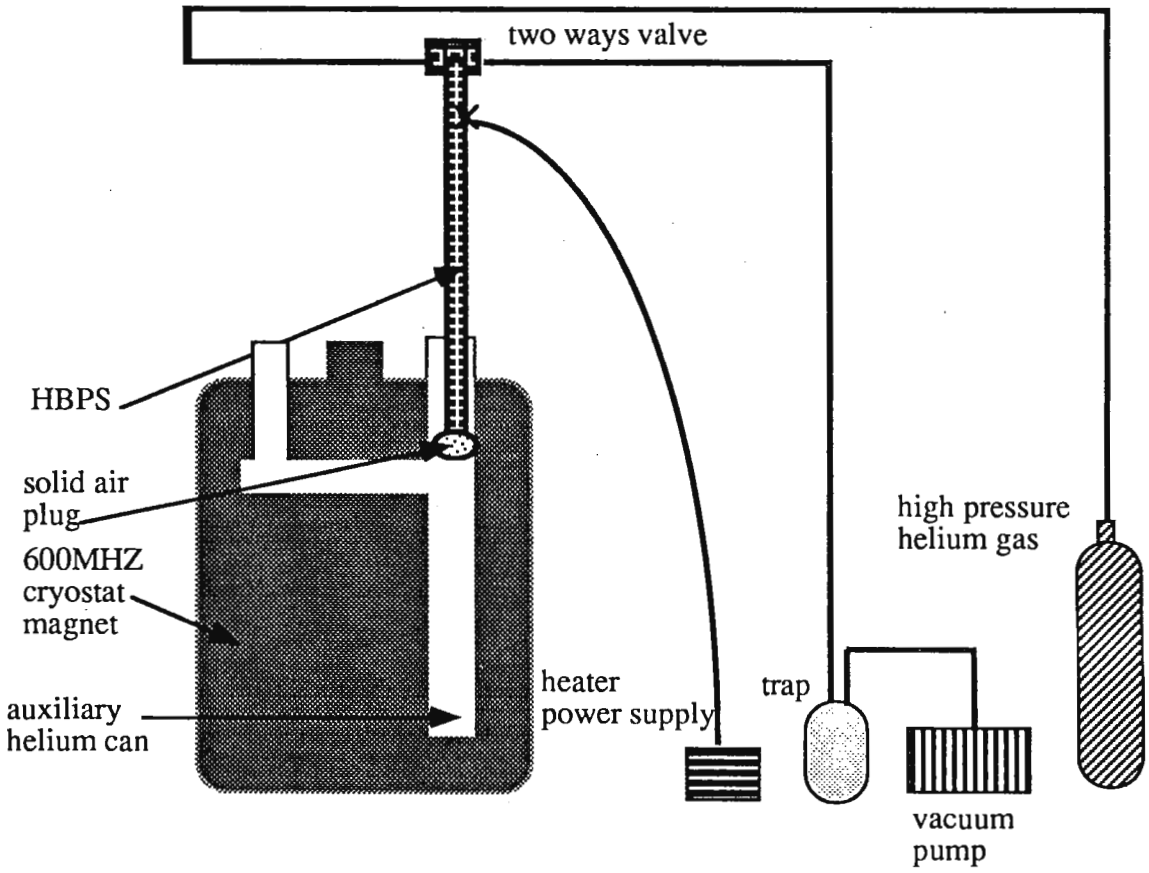

Figure 2 : Implementation of the HBPS on the auxiliary helium can corked with ice

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COLLEGE OF CHEMISTRY BERKELEY, CALIFORNIA 94720

Bruker Spectrometers: t_1- Noise, Clock Problems.

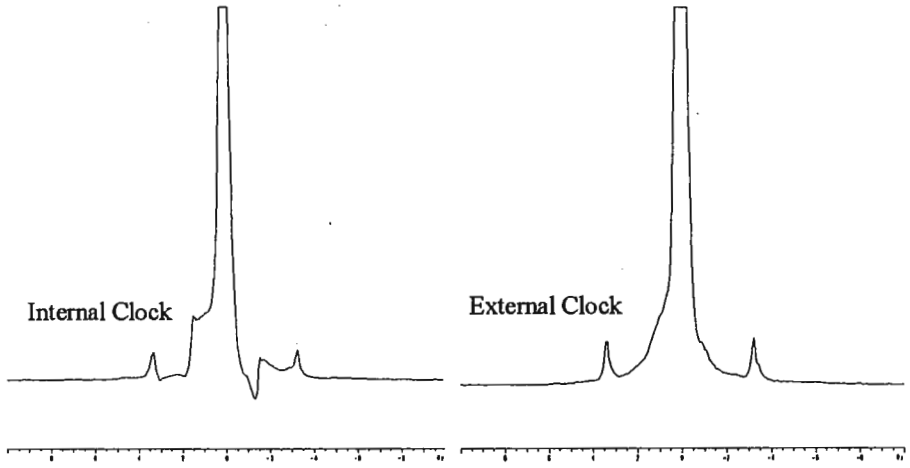
January 12, 1994
(received 1/19/94)

Dear Barry,

Last Fall we noticed that our 1984 Bruker AM-500 seemed to show excessive t_1-noise compared to our other spectrometers. The major problem was that inverse experiments showed periods of bad suppression, i.e., on several FID's the suppression of ^{12}C-bound protons was several times worse than average.

Several potential sources were looked at. To look at the RF stability, we connected a PTS-500 at the preamp housing to an unused BNC; this provides enough RF-leakage to get a strong "signal" without overloading the preamp. We set the synthesizer to about 499.99 MHz, the observe channel was set for the frequency difference to be near zero. We found that, over the course of a few tens of seconds, there would be sudden, small jumps, suggesting phase stability problems. This is consistent with the symptoms we had observed if the phase changes occur during the acquisition of one add-subtract cycle. For comparison, we ran inverse suppression difference experiments (using $CHCl_3$) with the internal and the PTS-500's 10 MHz as external clock. The latter gave much better results, comparable to what we expected to see. Since we have had previous problems with clocks, we built a "Clock Supply" unit to buffer, amplify and split up a clock signal to supply the spectrometers in the lab. This unit is driven by a recently repaired 10 MHz clock in an older PTS-160.

A few weeks later, we found side bands of 45 to 55 Hz on the AMX-300, leading to strong ridges in 2D spectra. This was traced to an oscillation of the Helium bath in the magnet Dewar. An oscillation damper supplied by Bruker cured that problem. At that time, we noticed that we also had side bands at about 1.7 Hz which we previously overlooked. Using our new external clock eliminated this problem as well. Below are single scan TMS spectra from the AMX-300:



I remembered that I saw a similar problem on a 1989 AMX-400, but never found the cause. Again, switching to the External Clock Supply cured the side bands.

Just before the Holidays, we received a clock replacement from PTS and installed it on the AMX-300 synthesizer. Much to our surprise, the side bands reappeared! I am not really sure yet if the fault is with the clock, though. The engineers at PTS had several very helpful suggestions. One possibility is that there might be some local interference affecting the internal clock only. Since the external clock is very well isolated, it would not be affected (at least, not as much). We will need to test this thoroughly by using the replacement clock to drive the External Clock Supply.

We also had a careful look at our older BVT-1000 V.T. Units. There had been earlier mention of room temperature fluctuations affecting the calibration of the Ice-Bath reference. On our units we did not find a problem. Putting the Thermocouple Amplifier into an oven, we measured a change of about 0.3 ° C between 25 ° and 45 ° ambient. We did find that the power supplies (especially the +5V) are prone to 60 Hz ripple; the AC voltage seems low. Replacing the 4700µf cap with 10,000µf in the 5V power supply and the 470µf cap with a 2200µf cap in the +15V power supply eliminates the ripple.

We also looked at the effect of the power level when using the decoupler amplifier to pulse protons with Inverse experiments. On the AM-500, a level of 4H reduces t_1-noise by about a factor 2 compared to 0H. (We did not look at other values).

Best regards,

Rudi Nunlist

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82-00808-7	Dimethyl-d_6 Sulfone	98 atom%
82-04043-7	Ethylene-1,1-d_2	98 atom%
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SAN FRANCISCO, CALIFORNIA 94143

December 30, 1993

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

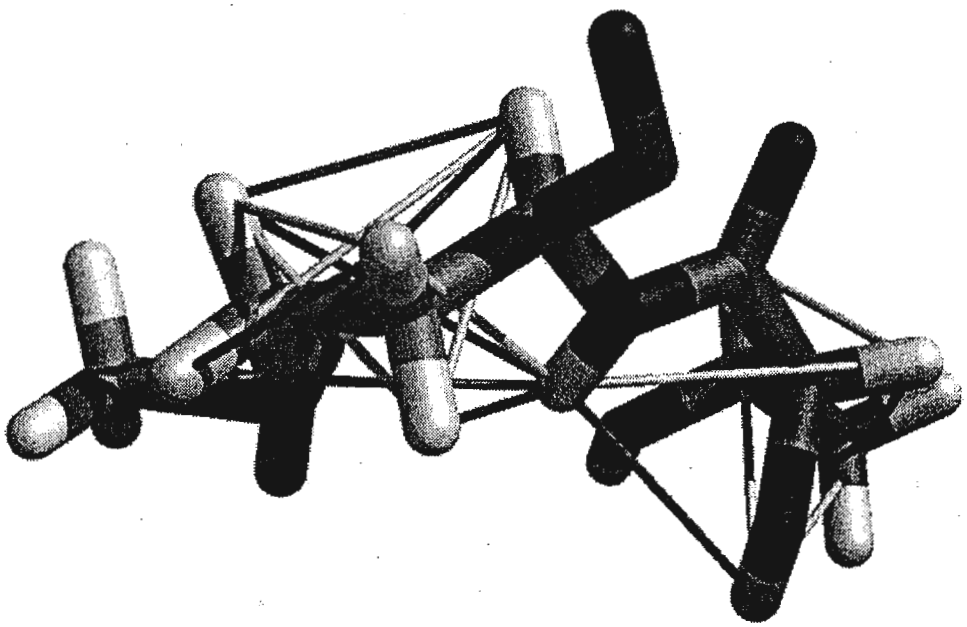
Dear Barry,

We would like to inform NMR spectroscopists who solve structure problems of a new capability of the MidasPlus molecular modeling package. The new capability permits the display of NMR restraints. During structure refinement it is very useful to be able to visualize NMR restraints. This is especially valuable in identifying misassignments or ambiguous assignments and mutually incompatible restraints. The *noeshow* delegate of MidasPlus will read a variety of file formats and display the molecule with restraints. The formats that *noeshow* currently reads include MARDIGRAS input and output, and AMBER output and AMBER/Interface input. The color of the restraints indicates whether or not the restraint is violated or satisfied. Distance and angle constraints may both be displayed. The figure shows a black and white rendering of a fragment of an ω-conotoxin with distance restraints and angle restraints, although one typically looks at the molecule with 3D color graphics. Part of a protein is shown here although *noeshow* also displays restraints on nucleic acids.

Some commercial molecular modeling packages also display constraints, however MidasPlus is a relatively inexpensive package for academic users. Those readers who already have MidasPlus can obtain *noeshow* from Eric Pettersen without charge (pett@cgl.ucsf.edu). Others interested in obtaining MidasPlus should contact Norma Belfer (norma@cgl.ucsf.edu). *noeshow* is implemented as a perl script and therefore the freely available perl scripting language must be installed on the system using *noeshow*. Perl is easy to install and can be obtained by anonymous ftp from *ftp netlabs.com* in the directory *pub/outgoing/perl4.0*. Please credit this contribution to the account of Dr. I. D. Kuntz.

Yours sincerely,

Shauna Farr-Jones Ph.D. Eric Pettersen, Vladimir J. Basus Ph.D.



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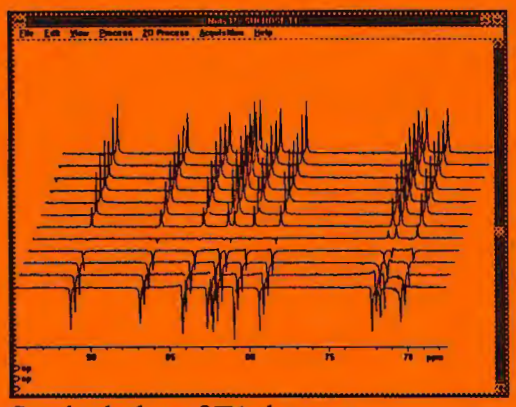
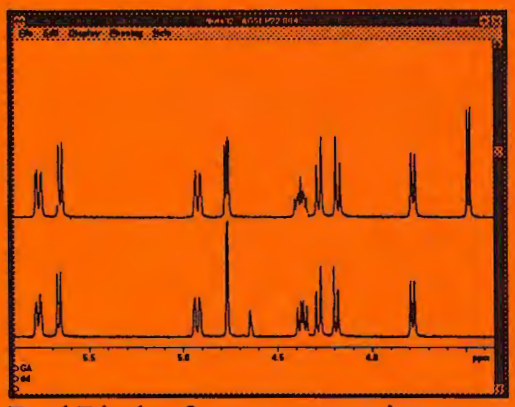
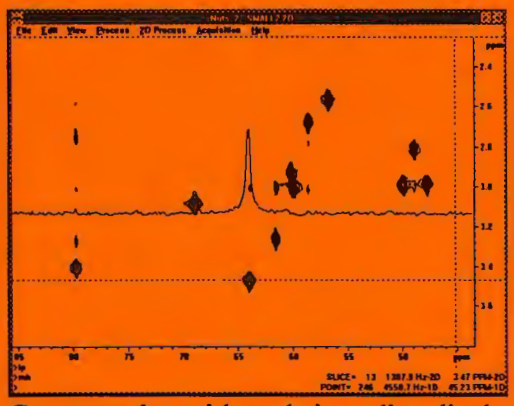


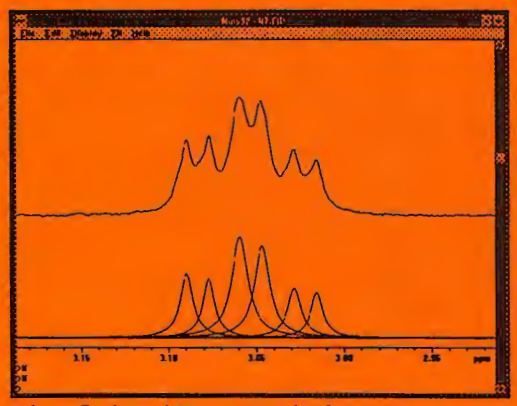
Stacked plot of T1 data set



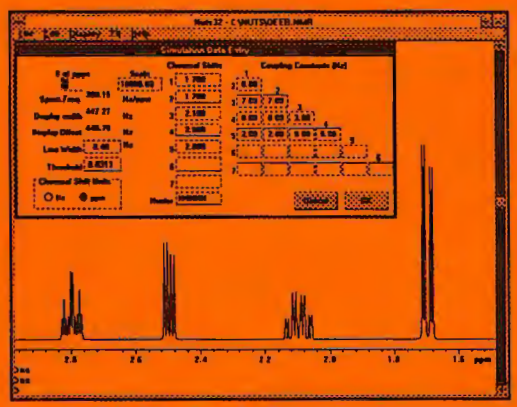
Dual Display for easy comparisons



Contour plot with real-time slice display



Line fitting / Deconvolution



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Copying Spectra into Reports

Application Note 1

One has a tendency to think that incorporating NMR spectra into reports should be done with electronic cutting and pasting instead of Xerox machines, scissors and tape. However, often this leads to unsatisfactory results and we resort to the mechanical method. The electronic process can be done at very high quality if you understand the software applications. This discussion focusses on using the Microsoft Windows for the IBM PC clipboard, but the considerations are general and apply equally well to the Macintosh or UNIX.

When an application such as NUTS transfers the screen information into the clipboard, it has two methods of doing the transfer: Copy the screen **bitmap** to a section of computer memory or record the drawing **instructions** for the displayed picture to memory. In both cases, control of that memory is transferred to the clipboard. For a bitmap, the clipboard object consists of pixels stored at the density of the display device (the monitor), each pixel being assigned a color. In black and white, this reduces to the pixel being turned on or off. If you make the window full screen before capture (a good idea to get the most bits into the bitmap), the bitmap will have the resolution of 640 by 480 (VGA) or 800 by 600 (SuperVGA). The higher the resolution of the initial graphics device, the bigger the bitmap object that is created and the better its resolution.

The second method creates an object in the clipboard consisting of draw instructions for reproducing the picture from which it was created, such as NMR data-point-to-data-point line draw operations. The resulting object is at the resolution of the source data, usually much higher than that of the screen. In Microsoft Windows, this object is called a Metafile or sometimes a MetaPICT.

The object captured from the source program can be "pasted" into other applications, such as a word processing program. Each application takes the object from the clipboard and displays it on the computer screen and, perhaps more important, prints it to another graphics device (the printer). Most word processing applications allow the clipboard object to be resized to fit the desired space in the report. In the case of a bitmap, this involves two complicated processes of taking a bitmap of one resolution, stretching or shrinking it in both directions, and then displaying this bitmap at the two different resolutions of the computer screen and the printer. Early software applications just overlapped the two bitmaps, which resulted in picture distortions, missed data and blank spots. Modern applications have smarter processes which do it with fewer distortions, but some are smarter than others. Typically, Pagemaker will do a better job of displaying such a bitmap than Word for Windows.

If the word processing application supports Metafile clipboard objects, displaying and resizing the object is much easier. All the application has to do is "play back" the draw operations into the resized area for the pasted picture. To print the report to a printer, the word processing application can simply "play" the draw operations to the printer at the printer's resolution. This is much simpler than translating bitmaps from one size to another and results is much less distortion of the clipboard object. Because the Metafile can contain more information about the spectrum than a screen bitmap, the Metafile can be much larger. It has better resolution, but it can take a very long time to display the picture in a report. Many word processors can display the picture as a blank frame "placeholder" while editing. This way the frame of the picture is displayed and the word processing operator does not have to wait for the drawing of the clipboard object.

NUTS gives the operator the option of placing the processed NMR spectrum into the clipboard as a bitmap or as a Metafile. This gives the operator the maximum flexibility for using other software applications and compromising between speed of display and printing and output resolution.

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Dr. B. L. SHAPIRO
TAMU NMR Newsletter
966 Elsimore Court
Palo Alto , California 94303
USA

January 6, 1994
(received 1/18/94)

Dear Doctor SHAPIRO

Cocrystallization of sugar anomers revealed by high resolution solid state ^{13}C NMR

Crystallization from a solution containing two isomers generally yields crystals of the less soluble component. However, it has been reported that for some free sugar solutions, cocrystallization of a small amount of the β isomer in the major α isomer lattice can occur.

When the two anomeric isomers of methyl D-xylopyranoside (α isomer: axial methoxy; β isomer: equatorial methoxy) crystallize from solution, high resolution solid state CP/MAS ^{13}C NMR provides interesting information about the nature of the crystalline powder.

The solid state ^{13}C NMR spectra of the two isomers are different. The α isomer crystallizes with two inequivalent molecules per asymetric unit of a monoclinic cell, and presents two resonances for each type of carbon atom in the solid state ^{13}C NMR spectrum[1] (exept for C-3, see Fig. 1A).

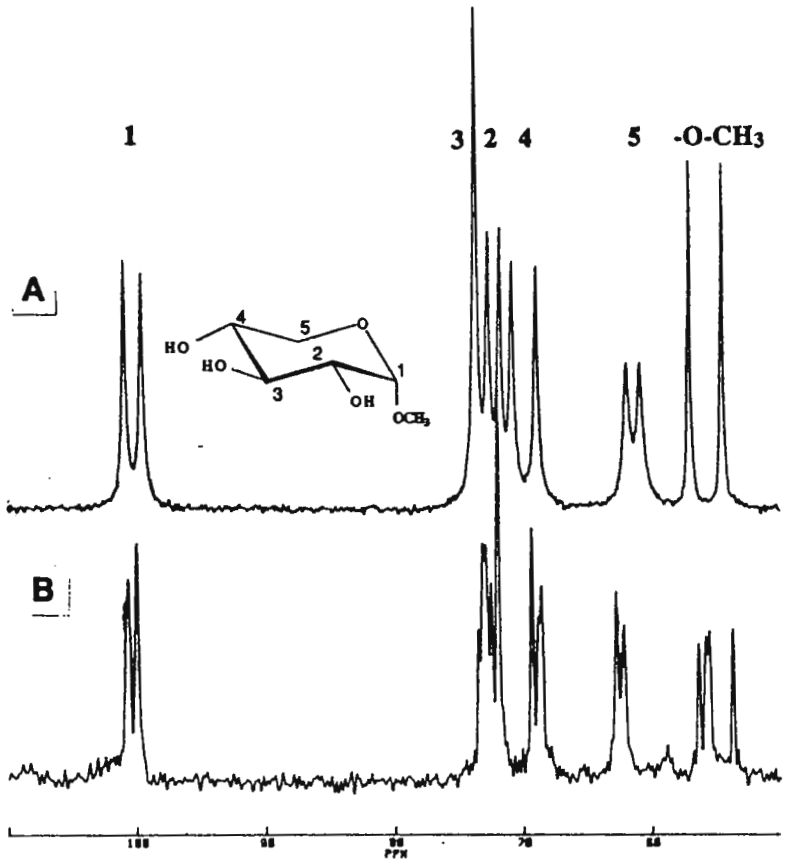
Crystallization of the methyl α- and β-D-xylopyranoside from a solution yields a crystalline powder containing 4% of the β isomer, whose spectrum is shown in Fig. 1B. In this spectrum the signals due to the β isomer are not observed because of its low concentration (4%). Nevertheless, this spectrum is more complex than that of the pure α isomer (Fig. 1A) and shows 19 different signals (instead of 11 signals for the pure α isomer). Particularly, there are 4 resonances for the methoxy carbon at 55 ppm, i.e, two doublets. Extrapolating this observation to the whole spectrum we expect to see 22 signals in the spectrum of Fig. 1B. The two doublets observed for each type of carbon atom in the α isomer in the presence of the β isomer indicates the existence of *two types of crystal*, both having two different molecules per asymetric unit, i.e, two polymorphs.

This is an example where high resolution solid state ^{13}C NMR can provide a rapid characterisation of a powder, before undertaking a more detailed X-ray-diffraction single crystal study, when possible.

Please credit this letter as a contribution by Dr P. VOTTERO.

Dr Marc VINCENDON Dr Michel BARDET Dr Lyndon EMSLEY

1- M.G. Taylor , R.H. Marchessault , S. Perez , P.J. Stephenson , and C.A. Fyfe , Can. J. Chem. , 63 , 270 , (1985).



High resolution solid state ^{13}C CP/MAS NMR spectra (50MHz) of:
A- Pure methyl α-D-xylopyranoside.
B- Methyl α–D-xylopyranoside cocrystallized with 4% of the β isomer (equatorial methoxy).

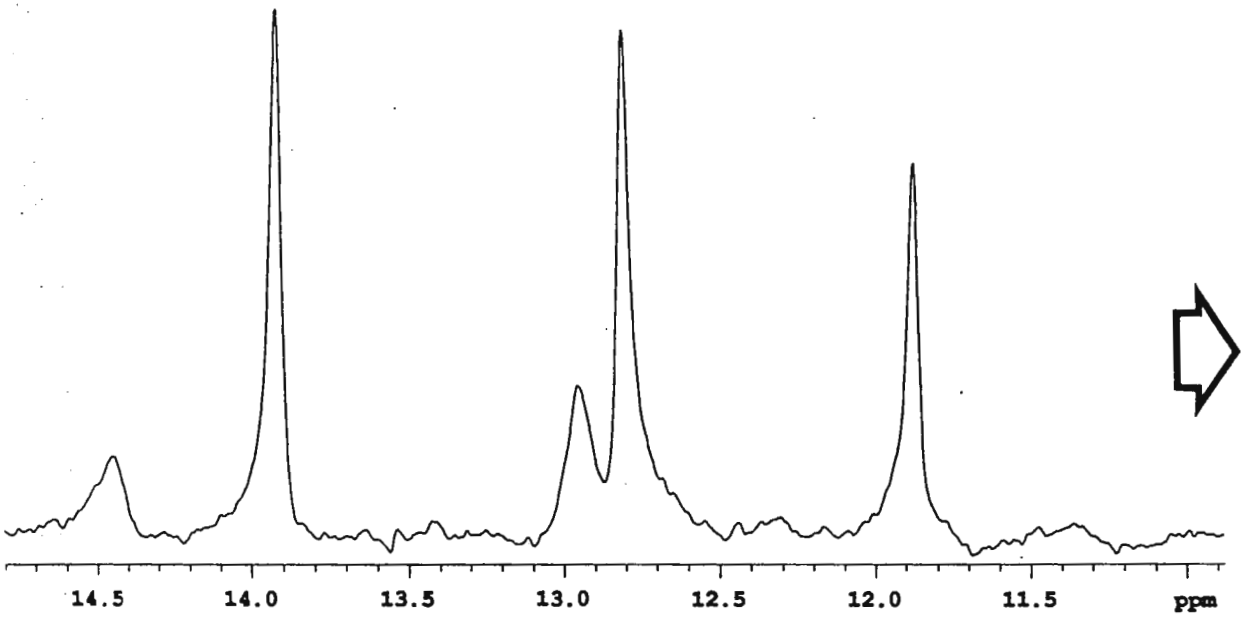


Figure 1-Spectra of imino region of duplex RNA obtained by using pulse sequence 1

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

(received 12/27/93)

December 22, 1993

Selective Inversion/Recovery Using Shaped Pulses

Dear Barry:

We have been performing studies using our UNITY 500 MHz instrument to determine the exchange rates for imino hydrogens in duplex DNA and RNA by using shaped pulses for selective excitation. The advantages are clear, an even excitation profile is generated over a defined region with little or no excitation of the large H_2O signal. While the idea is straightforward and reasonable, we worried that the millisecond time scale for the shaped pulses would cause errors in our T1 calculations and effect our exchange rate values. We have acquired some preliminary data comparing the T1 estimates for the imino hydrogen for an AU base pair in DMSO by using a variety of inversion/recovery pulse sequences that use either shaped pulses or hard pulses or a combination of the two. The T1 value for the AU imino hydrogen as determined by using three different pulse sequences are shown in Table I. Pulse sequence I uses a hyperbolic secant pulse (3 msec) and a TOPHAT pulse (2 msec) for the inversion and read pulses. Pulse sequence II uses rectangular pulses for each. Pulse sequence III uses rectangular pulses but also incorporates an extra 2 msec constant delay in addition to the variable recovery delay. Shown in the figure is a typical spectrum using pulse sequence I on a duplex RNA oligonucleotide in H_2O.

Pulse Sequence	T1	Error
I	0.955	0.008
II	0.989	0.013
III	0.982	0.012

Sincerely yours,

William H. Gmeiner

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Interested applicants should send a resume to Professor Chin Yu, Department of Chemistry, Hsinchu, Taiwan. FAX: 886-35-711082. Tel: 886-35-721524. E-mail: cyu@chem.nthu.edu.tw

FORTHCOMING NMR MEETINGS, *Continued from page 1.*

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.

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.

Symposium on "NMR as a Structural Tool for Macromolecules: Current Status and Future Directions, Indianapolis, IN, **October 30 - November 1, 1994**; Contact: Ms. Padmini Nallana, Coordinator, NMR Symposium, Dept. of Physics, Indiana University Purdue University Indianapolis, 402 N. Blackford St., Indianapolis, IN 46202-3273; Tel. (317) 278-1263; E-mail: PADMINI@INDYVAX.IUPUI.EDU; Fax: (3172) 274-2393. See TAMU NMR Newsletter 425, 31.

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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♣ ◆ ♥ ♠ ♣ ◆ ♥ ♠

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. 427 (April)	25 March 1994
No. 428 (May)	22 April 1994
No. 429 (June)	20 May 1994
No. 430 (July)	24 June 1994

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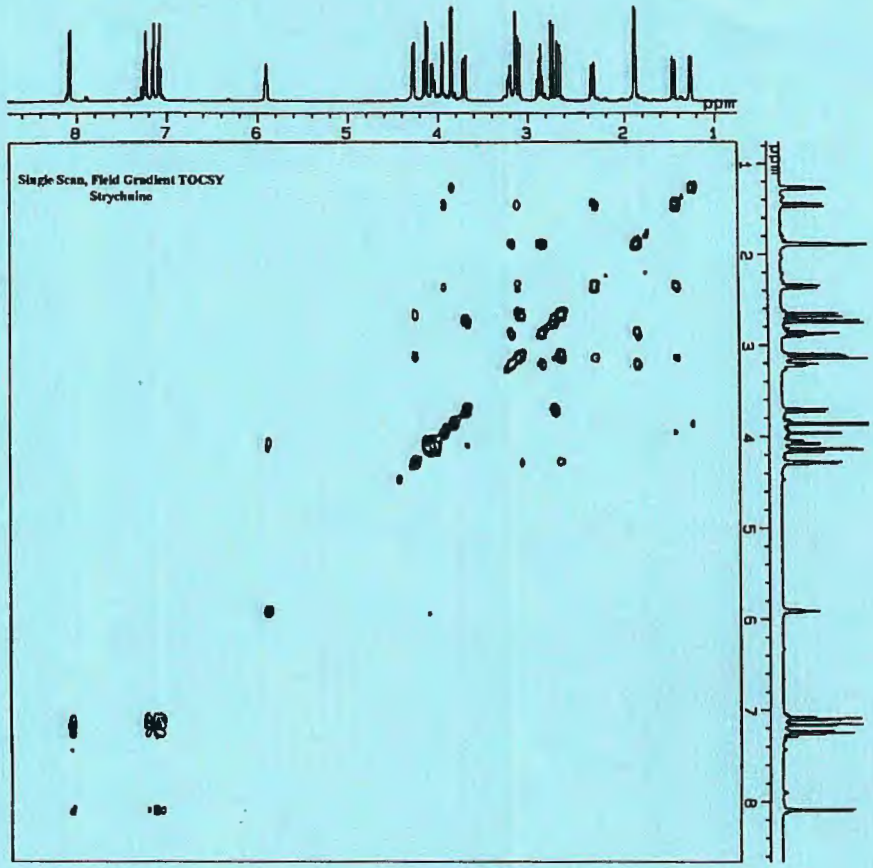
Gradient Probes



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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