THE
NMR
NEWSLETTER

No. 450

March 1996

Acorn NMR Inc.
46560 Fremont Blvd. #418
Fremont, CA 94538

(510) 683-8595
(510) 683-6784 FAX
info@acornnmr.com

http://www.acornnmr.com
ftp.acornnmr.com

New! **Introducing MacNUTS for the PowerPC**

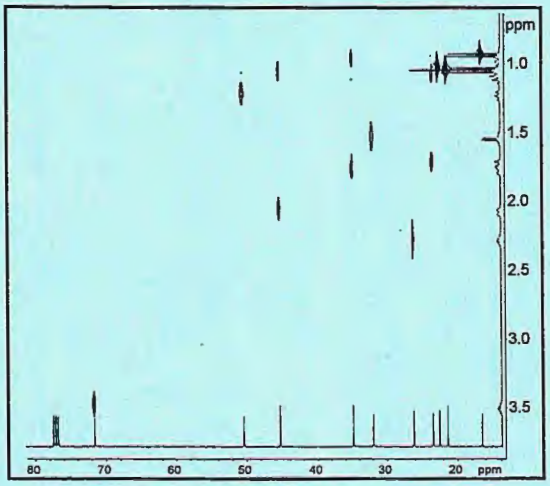
Speed comparison for a large (128K complex) FID:

	Windows NT 90 MHz Pentium	PowerPC 132 MHz 604	PowerPC 66 MHz 601
Fourier Transform	**2.5 sec**	**2.2 sec**	**4 sec**
Quick AutoPhase	**4 sec**	**7.8 sec**	**9 sec**

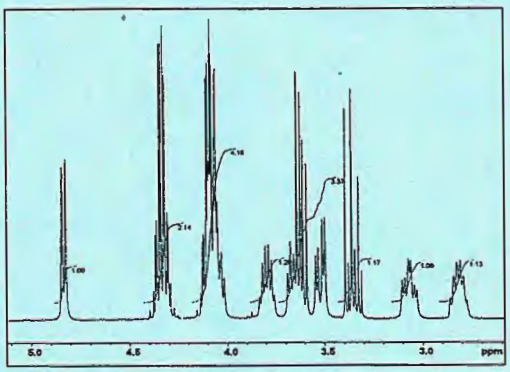
NUTS product line for Windows and Macintosh:

NUTS Lite — Basic 1D processing	$ 75
NUTS-1D — Extended processing features	$499
NUTS-2D — Complete 1D and 2D package	$750
Virtual Spectrometer option — teaching tool which simulates an NMR spectrometer (the Virtual Spectrometer can be added to NUTS-1D or NUTS-2D)	$250

Site licenses are available. Description of NUTS feature and demo copies of NUTS are available via ftp from **ftp.acornnmr.com** or via the World Wide Web at **http://www.acornnmr.com**



Visit our suite at ENC 96
Embers Living Room



Copy spectra from NUTS into reports to create high quality figures

SPONSORS OF *THE NMR NEWSLETTER*

Abbott Laboratories
Aldrich Chemical Company, Inc.
American Microwave Technology
Amgen, Inc.
Anasazi Instruments, Inc.
Bruker Instruments, Inc.
Cambridge Isotope Laboratories
Cryomag Services, Inc.
The Dow Chemical Company
Eastman Kodak Company
E. I. du Pont de Nemours & Company
Glaxo Wellcome
Hewlett-Packard Company
Isotec, Inc.
JEOL (U.S.A.) Inc., Analytical Instruments Division
The Lilly Research Laboratories, Eli Lilly & Company
Merck Research Laboratories
Nalorac Cryogenics Corporation
Otsuka Electronics USA Inc.
Oxford Instruments
Pharmacia and Upjohn, Inc.
Programmed Test Sources, Inc.
SINTEF Unimed MR Center, Trondhiem, Norway
Tecmag
Unilever Research
Union Carbide Corporation
Varian NMR Instruments

FORTHCOMING NMR MEETINGS

Advances in NMR Applications, Symposium at Pebble Beach, CA, **March 17, 1996**; Contact: Nalorac's ENC Coordinator, 841-A Arnold Drive, Martinez, CA 94553; (510) 229-3501; Fax: (510) 229-1651; e-mail: sales@nalorac.com; See Newsletter 449, 38.

37th ENC (Experimental NMR Conference) "Farewell to Asilomar", Asilomar Conference Center, Pacific Grove, CA, **March 17 - 22, 1996**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073. See Newsletter 448, 23.

Society of Magnetic Resonance, Fourth Scientific Meeting and Exhibition, New York, NY, **April 27 - May 3, 1996**; Contact: SMR Office, 2118 Milvia St., Suite 201, Berkeley, CA 94704; (510) 841-1899; Fax: (541) 841-2340. E-mail: info@smr.org . Future meetings: 1997, April 12-18, Vancouver, BC, Canada; 1998, April 18-24, Sydney, Australia; 1999, Philadelphia, PA; 2000, Denver, CO.

NMR Symposium at the 38th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, **July 22-25, 1996**; Contact: Dr. Joel R. Garbow, Monsanto Company, 700 Chesterfield Parkway North, St. Louis, MO 63198; (314) 537-6004; Fax: (314) 537-6806; e-mail: jrgarb@snc.monsanto.com; See Newsletter 445, 48.

continued on inside back cover

Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

26 Jan 1996
(received 1/29/96)

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

Dear Barry,

SPINCALC and DISPOR

In the past month or two, I have written a couple of computer programs in which Newsletter readers might possibly be interested. SPINCALC is a program for calculating the time development of spins(current maximum=2) under the combined influence of chemical shift, spin-spin coupling, magnetic dipolar relaxation, and applied rf field. If two coupled spins are treated, the relaxation behavior is calculated using the Redfield treatment, but with the inclusion of both secular and nonsecular terms, which affect the development in the presence of rf excitation. The user specifies the initial conditions(shifts, J, rotational correlation time, rf phase and power) and the evolution time. The program produces a table of density matrix vectors as the spins system evolves during this time. The rf may then be turned on or off as desired, and the evolution pursued further.

If any one would like to get this program and try it, it can be obtained using the ftp protocol at the 620 NMR Laboratory site. The net address is nmr620.chem.cmu.edu and one logs in as anon. The password is spincalc. One then 'gets' as many files as one wants.

The other program is called DISPOR, and it calculates the dipolar interactions for pairs of nuclei in a molecule partially aligned by the effect of a high magnetic field on magnetically anisotropic groups present in the molecule. The user supplies a geometry by specifying the internuclear distance, and direction relative to some reference coordinate frame for each of the internuclear vectors, and the principal magnetic susceptibilities and direction of the principal axes for each of the magnetically anisotropic groups. The spectrometer frequencies for the two nuclei(equivalent to specifying the magnetic field strength), and the temperature of the sample are also input. The program then adds all the susceptibility tensors, making the appropriate rotational similarity transformations, diagonalizes the result, to get the principal axes and susceptibilites of the whole molecule, and calculates for each internuclear vector the dipolar interaction between the nuclei.

This is also available at nmr620.chem.cmu.edu -- login in as dispor, password = dispor, and the files to get are dispor.f(the FORTRAN code for dispor), dispor.res, which is a sample copy of input and output, and dispor.doc, which explains the program.

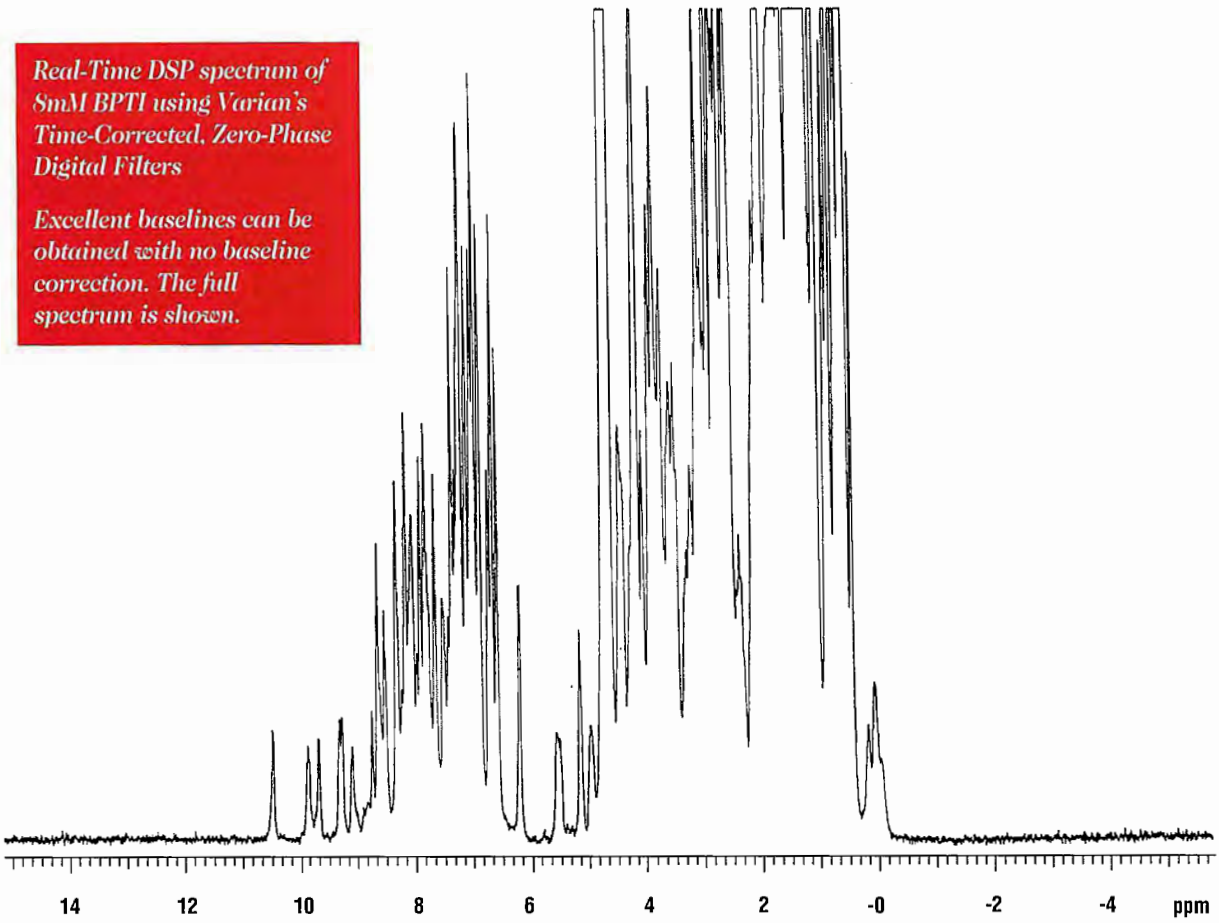
See you at the ENC?

Sincerely

Aksel

Aksel A. Bothner-By

The Last Word in DSP From the First Name in NMR



Real-Time DSP spectrum of 8mM BPTI using Varian's Time-Corrected, Zero-Phase Digital Filters

Excellent baselines can be obtained with no baseline correction. The full spectrum is shown.

At Varian, DSP Means "Designed for Superior Performance"

Digital signal processing combines over-sampling and digital filtering to improve signal/noise in spectra. But digital isn't magic. Like analog design, digital design has to be done right!

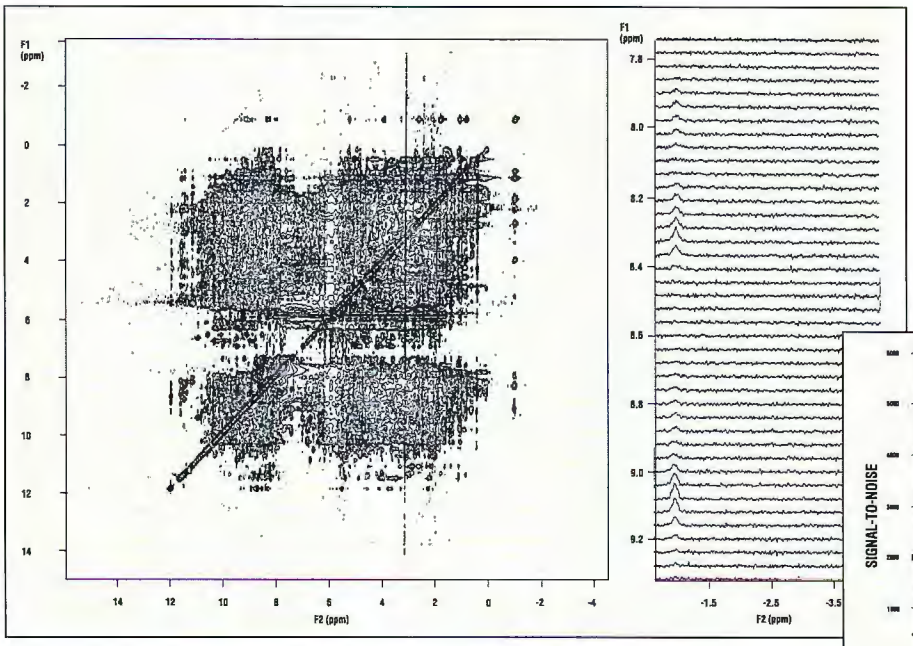
Digital filters improve signal-to-noise by reducing the amount of noise that "folds in" to the spectrum and by decreasing digitization noise. But some digital filters result in degraded baselines and produce FIDs with a "build-up curve" that you can't use with all processing software. Varian's Time-Corrected Zero-Phase Digital Filters™ give you S/N improvement, flat baselines, and "normal" FIDs — all at the same time.

When dynamic range becomes a problem and you need to reduce the gain on your spectrometer, signal-to-noise can degrade substantially. Varian's Real-time DSP, with its high sampling rate and 20-bit precision, lets you obtain full S/N at lower gains and optimum S/N at any gain.

At Varian, we sell performance, not buzzwords. To arrange a demonstration of Varian's superior DSP capabilities, contact the Varian office nearest you.

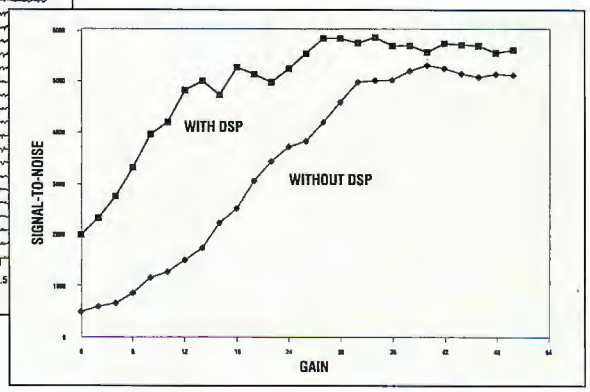
varian

DSP from Varian – Designed for Superior Performance



2D NOESY of 10mM lysozyme using DSP with absolutely no baseline correction or linear prediction. The expanded stacked plot on the right shows some of the weakest cross-peaks with no hint of "wandering baseline".

Plot of S/N vs receiver gain with and without DSP, showing the large improvements possible with Varian's DSP.



Feature	Benefit
• Real-time digital filters (available on UNITY*INOVA*™ and UNITY*plus*™)	• Minimize data storage requirements in acquisition and host computers
• Time-Corrected Zero-Phase Digital Filters™	• Superior baseline performance
• Choice of real-time digital filters	• Optimize performance based on application
• AnalogPlus™ filter	• Improves S/N up to 10% without sacrificing baseline performance
• Brickwall filter	• Quantitative accuracy across the entire spectrum
• 400 kHz sampling rate (UNITY*INOVA* only)	• Greater oversampling brings greater S/N gains
• 20-bit precision	• Obtain the full benefit of oversampling
• No "build-up curve" at front of FID	• FIDs can be processed normally using any software
• Inline digital filters, processing data after acquisition but before storage on host computer (available on all Sun-based Varian spectrometers including UNITY*INOVA* and GEMINI 2000)	• Allows full flexibility of digital filtering without the time constraints of real-time filtering; minimizes data storage requirements on host computer
• Post-acquisition digital filtering (available on all Sun-based Varian spectrometers including UNITY*INOVA* and GEMINI 2000)	• Allows repeated digital filtering on the same data to allow optimization of parameters
• User-programmable coefficients	• Any desired digital filter can be used
• Frequency shifting	• Provides bandpass as well as lowpass filters
• Low receiver noise floor	• Allows DSP to reduce digitization noise and increase S/N

Manufacturing Facilities Varian NMR Instruments, Building 4, 3120 Hansen Way, Palo Alto, California 94304-1030, Tel 415.493.4000 • **Australia** Mulgrave, Victoria, Tel 3.9.560.7133 • **Austria** Vösendorf, Tel 1.69.5445 • **Belgium** Brussels, Tel 2.721.4850 • **Brazil** São Paulo, Tel 11.820.0444 • **Canada** Mississauga, Ontario, Tel 1.800.387.2216 • **China** Beijing, Tel 1.256.4360 • **France** Les Ulis, Tel 1.6986.3838 • **Germany** Darmstadt, Tel 06151.7030 • **Italy** Milan, Tel 2.921351 • **Japan** Tokyo, Tel 3.5232.1211 • **Korea** Seoul, Tel 2.3452.2452 • **Mexico** Mexico City, Tel 5.514.9882 • **Netherlands** Houten, Tel 3063.50909 • **Russian Federation** Moscow, Tel 095.203.7925 • **Spain** Madrid, Tel 91.472.7612 • **Sweden** Solna, Tel 8.82.00.30 • **Switzerland** Zug, Tel 42.448.844 • **Taiwan** Taipei, Tel 2.705.3300 • **United Kingdom** Walton-on-Thames, Tel 01932.898.000 • **United States** California, Tel 800.356.4437 • **Other sales offices and dealers throughout the world**

varian

MAG-8488A/620

THE COLLEGE OF STATEN ISLAND
THE CITY UNIVERSITY OF NEW YORK

February 5, 1996
(received 2/8/96)

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

Ramped-Amplitude Cross Polarization with Phase-Modulated Decoupling for NMR of Biological Solids

Dear Barry:

In order to improve the resolution, signal-to-noise ratio, and quantitative reliability of the CPMAS ^{13}C NMR spectra obtained for crystalline and semisolid biological solids, we have recently evaluated ramped-amplitude cross polarization (RAMP-CP)[1] and phase-modulated decoupling (PM)[2] techniques on our widebore Varian Unity*plus* 300 spectrometer. These experiments were carried out in a 5-mm triple-tuned Supersonic HXY probe from Doty Scientific; the proton decoupling schemes were implemented using either Varian's waveform generator or a custom pulse sequence.[3] The samples highlighted here are [2-^{13}C,^{15}N]glycine and suberin, a biopolyester that grows within the cell-wall matrix of wounded potato tissue.

For a rigid solid such as glycine spun at 9 kHz, PM decoupling reduces the ^{13}C linewidth by 30% and increases the signal-to-noise ratio by 20% when compared with conventional 70-kHz CW decoupling (**Figure 1**); similar improvements are observed with the published two-pulse modulated decoupling scheme and a four-pulse version of the experiment.

Again because of glycine's rigid structure, RAMP-CP enhances the S/N significantly (30%) only if the CPMAS ^{13}C spectra are obtained under rapid-MAS conditions, for which the spin rate is comparable in magnitude to its ^{1}H-^{13}C dipolar interactions. However, RAMP-CP peaks are close to 20% broader at the base when compared with the spectra that result from standard constant-amplitude CP with CW decoupling. When RAMP-CP is combined with PM acquisition (**Figure 2**), it is possible to achieve a 40% narrowing of the lines, but the signal sensitivity suffers considerably (a loss of 24%).

Are PM decoupling and RAMP-CP techniques useful for ^{13}C NMR of semiflexible solid biopolymers such as potato suberin? **Figure 3** shows that RAMP-CP yields an impressive 55% improvement in signal-to-noise ratio, with particular enhancement of signals from the nonprotonated carbons and also modest gains in resolution. Since motional averaging may reduce the heteronuclear dipolar couplings to values similar to the MAS speed, RAMP methods are useful in overcoming the effects of Hartmann-Hahn mismatch. PM decoupling offers no additional improvements in spectral quality, possibly because the 80-kHz decoupling field strengths exceed the dipolar couplings in our spinning suberin sample. This work, along with related results for model biological membranes,[4] suggests that the RAMP-CP method should be used routinely to obtain CPMAS ^{13}C NMR spectra of semisolid polymers and biopolymers.

Sincerely yours,

Feng Qiu
Postdoctoral Research Associate

Ruth E. Stark
Professor of Chemistry

[1] G. Metz, X. Wu, & S.O. Smith; *J. Magn. Reson. A* **110**, 219 (1994); [2] A.E. Bennett, C.M. Rienstra, M. Auger, K.V. Lakshimi, & R.G. Griffin, *J. Chem. Phys.* **103**, 6951 (1995); [3] submitted to the Varian Userlib (Solidslib) as RACP; [4] C. Le Guerneve & M. Auger, *Biophys. J.* **68**, 1952 (1995).

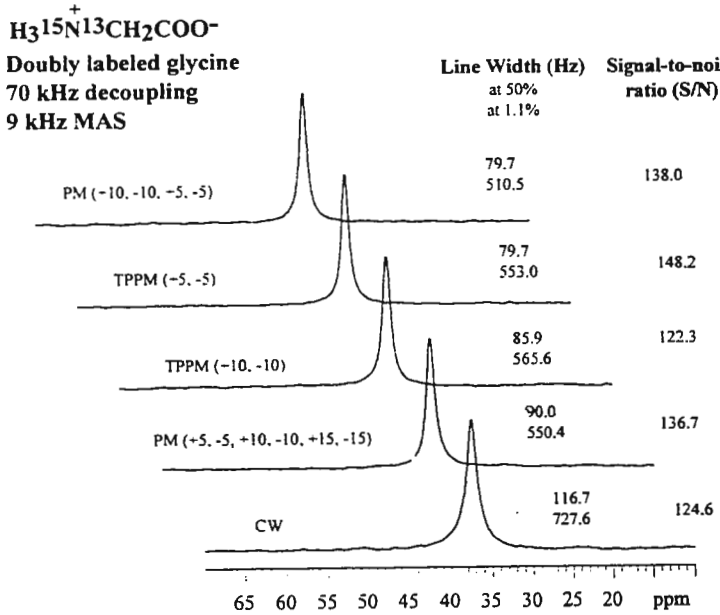


Figure 1

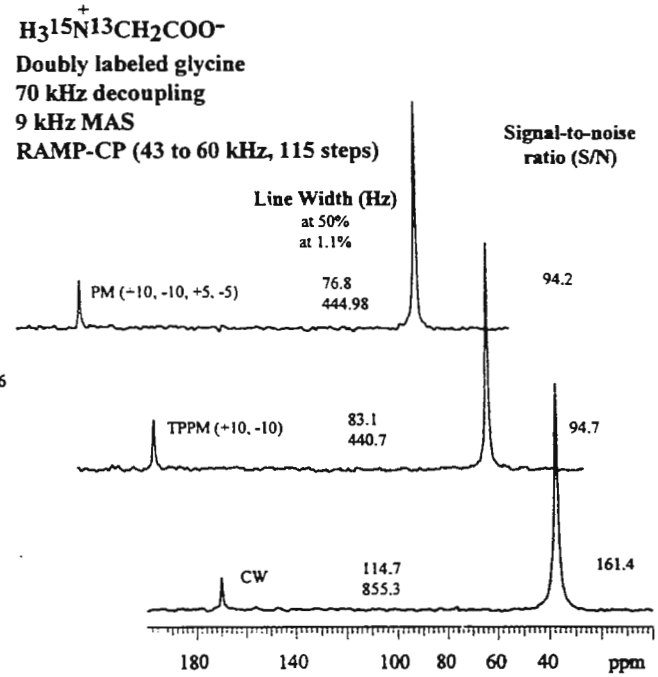


Figure 2

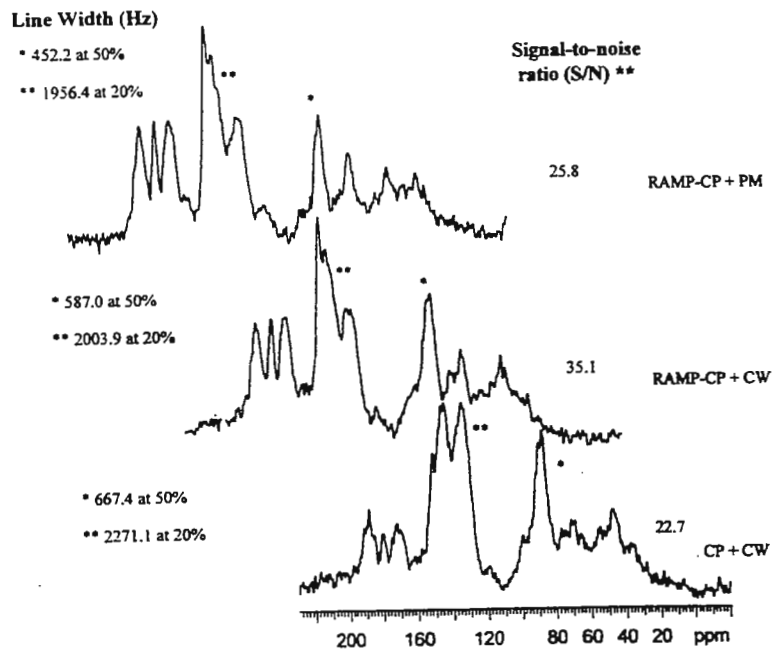


Figure 3

Washington
WASHINGTON·UNIVERSITY·IN·ST·LOUIS

Department of Physics

5 February 1996
(received 2/9/96)

Dear Barry,

We are using NMR to study supercritical water (SCW) and SCW-solutions ($T_c = 375°C$, $P = 220$ atm, $\rho = 0.33$ g/cm^3). SCW is an unique medium for chemical reactions. For example, hazardous and toxic organics can be oxidized by O_2, all dissolved in SCW, yielding benign products (CO_2, HCl, *etc.*).[1] It is also believed by geochemists that organic compounds may be formed in deep-sea hydrothermal vents.[2] Unfortunately, there is little known about aqueous chemistry under these harsh conditions.

We have now built a high-resolution NMR probe capable of handling SCW conditions, as sketched in the figure. The design builds on those of Jonas and co-workers and has the following features.[3]

1. Pressure is applied by Ar gas from a commercially available 6000 psi cylinder.
2. The heater is internal to the pressure vessel, for safety. The ratio of currents in the top and bottom sections can be adjusted, to minimize the temperature gradient. Although the heaters are non-inductive, there is some stray field. We turn the heaters off during each FID. Soon we will heat with 10 kHz AC.
3. The cylindrical, 20″ long pressure vessel is made from Ti-6Al-4V alloy (about $300 worth). The vessel is 1.5″ OD and the end nuts are 3″ diameter. This fits nicely into our new (to us) 186 MHz, 98 mm Oxford solenoid.
4. The water is held in an alumina ceramic tube (Omega Engineering). This is crucial, as SCW dissolves fused quartz. The pressure of the water and Ar gas are equalized by an O-ring sealed floating piston (at the cooled end of the vessel).
5. For protons we have reasonable resolution: 0.04 ppm, FWHM; no doubt this is limited by the materials closest to the sample.

We intend to follow chemical reactions in real-time in SCW; we also plan to do some physical measurements.

References

[1]R. W. Shaw, Th.B. Brill, A. A. Clifford, C. A. Eckert, E. U. Franck, Chem. Eng.News **69**(51), 26 (1991).
[2]E. L. Shock, Geotimes, March 13, 1994.
[3]T. H. DeFries, J. Jonas, Jour. Mag. Res. **35**, 111 (1979).

We would be happy to tell more details by phone or email.

Sincerely,

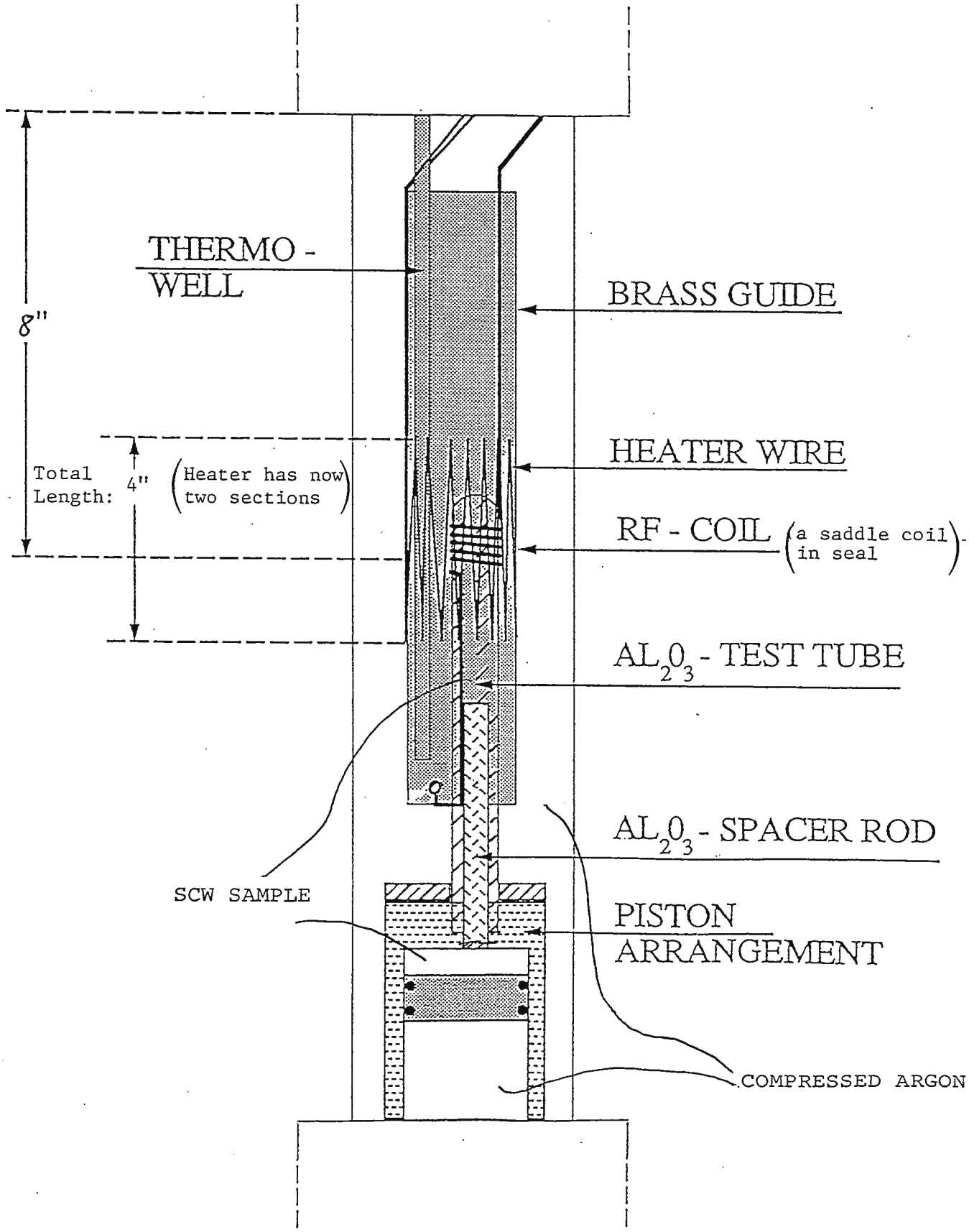
Markus Hoffmann Mark S. Conradi

Markus Hoffmann & Mark S. Conradi
Telephone: (314) 935-6292
email: mh@howdy.wustl.edu

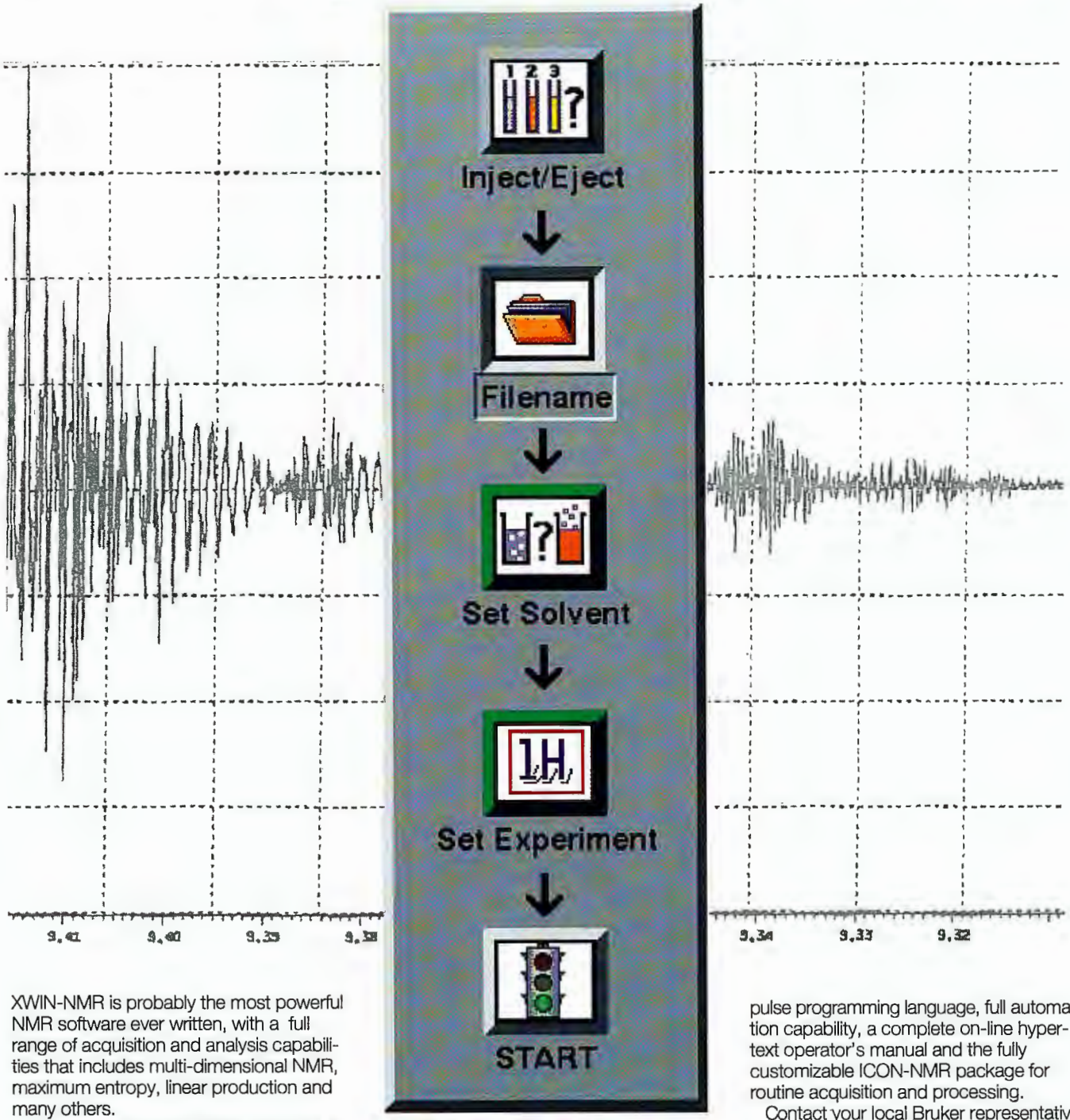
P.S. Please credit to R. E. Norberg's account

Washington University
Campus Box 1105
One Brookings Drive
St. Louis, Missouri 63130-4899
(314) 935-6276
FAX (314) 935-6219

ARRANGEMENT INSIDE THE PRESSURE VESSEL



It doesn't get any easier than this:



XWIN-NMR is probably the most powerful NMR software ever written, with a full range of acquisition and analysis capabilities that includes multi-dimensional NMR, maximum entropy, linear production and many others.

But the real power of XWIN-NMR lies in the ease with which all of these advanced features can be accessed and put to use.

Not only does it provide a fully menu-driven user interface with an industry standard layout, it also includes an intuitive pulse programming language, full automation capability, a complete on-line hypertext operator's manual and the fully customizable ICON-NMR package for routine acquisition and processing.

Contact your local Bruker representative and find out how easy NMR can be.

ICON-NMR

We're pushing NMR way past easy!

Bruker Instruments, Inc., Manning Park, Billerica, MA 01821, www.bruker.com

In Europe: Bruker Analytische Messtechnik GmbH Silberstreifen, D-76287 Rheinstetten 4, Germany www.bruker.de

BRUKER

Comprehensive Support for Innovative Systems

AVANCE™ – The easy to use Digital NMR Spectrometer

- Digital Lock
- Digital Filtering with Oversampling
- Digital Signal Processing
- Digital Signal Routing
- Surface Mounted Devices
- UNIX Workstation Computer
- X-11 Windows and MOTIF
- Quick-NMR™ Interface
- Broadest Choice of Probes
- Extensive Pre-tested Experiment Library
- Comprehensive Applications Support

Digital, modular and flexible.

Now, the fundamentally superior precision and stability of digital signal processing is available from a precedent-setting series of NMR spectrometers. With its digital advantage, the Bruker AVANCE™ series sets revolutionary standards for performance, long-term reliability and ease of use, whether for routine applications or the most demanding research. The modular architecture of the Bruker AVANCE design makes extensive use of digital signal processing technology, incorporating high performance RISC-based processors into the lock, filters, timing control unit, gradient generation, and many other key areas of the system. The result is increased sensitivity, higher dynamic range, cleaner spectra, flat baselines and unprecedented stability.

The AVANCE Series of high performance spectrometers.

The comprehensive AVANCE family of NMR spectrometers was developed in direct response to the increasing demands of the NMR community for greater performance and stability in a highly automated, easy to use instrument. Within the AVANCE series of DPX, DRX, DMX and DSX systems there is a virtual continuum of configuration options from 200 to 750 MHz, including solids, liquids and imaging. Whatever the environment or application, there is an appropriate AVANCE model to choose from. Your Bruker representative will be happy to recommend a configuration that is optimum for your needs - today and tomorrow.

For complete details or to arrange a demonstration please contact your nearest Bruker representative.

BRUKER

Comprehensive Support for Innovative Systems

Australia: BRUKER (Australia) PTY. LTD., Alexandria, New South Wales, Tel. (02) 550 64 22
Belgium: N.V. BRUKER SPECTROSPIN S.A, Brussels, Tel. (02) 6 48 53 99
Canada: BRUKER SPECTROSPIN LTD., Milton, Ontario, Tel. (604) 656-1622
P.R. China: BRUKER INSTRUMENTS, LTD., Beijing, P.R. China, Tel. (00861) 255 75 30
England: BRUKER SPECTROSPIN, LTD., Coventry, Tel. (0 12 03) 85 52 00
France: BRUKER SPECTROSPIN SA, Wissembourg/Cedex, Tel. (88) 73 68 00
Germany: BRUKER ANALYTISCHE MESSTECHNIK GMBH, Rheinstetten/Karlsruhe, Tel. (07 21) 51 61-0
BRUKER ANALYTISCHE MESSTECHNIK GMBH, Karlsruhe, Tel. (07 21) 95 28 0
BRUKER-FRANZEN ANALYTIK GMBH, Bremen, Tel. (04 21) 22 05 0
BRUKER-SAXONIA, ANALYTIK GMBH, Leipzig, Tel. (03 41) 2 35 36 05
India: BRUKER INDIA, SCIENTIFIC PVT. LTD., Bombay, Tel. (22) 626 2232
Israel: BRUKER SCIENTIFIC ISRAEL LTD., Rehovot, Tel. (972) 8 409660
Italy: BRUKER SPECTROSPIN SRL, Milano, Tel. (02) 70 63 63 70
Japan: BRUKER JAPAN CO. LTD., Ibaraki, Tel. (0298) 52 12 34
Netherlands: BRUKER SPECTROSPIN NV, AB Wormer, Tel. (75) 28 52 51
Scandinavia: BRUKER SPECTROSPIN AB, TNby, Sweden, Tel. (08) 7 58 03 35
Spain: BRUKER ESPAÑOLA S.A., Madrid, Tel. (1) 504 62 54
Switzerland: SPECTROSPIN AG, Fällanden, Tel. (01) 8 25 91 11
USA: BRUKER INSTRUMENTS, INC., Billerica, MA, (508) 667-9580,
Regional Offices in Lisle, IL, (708) 971-4300/Wilmington, DE, (302) 478 8110
The Woodlands, TX (713) 292-2447/Fremont, CA (510) 683-4300

Duke University

Duke Nuclear Magnetic Resonance Spectroscopy Center

Leonard D. Spicer, Director 919 684 4327
Anthony A. Ribeiro, Manager 919 613 8887

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

February 19, 1996
(received 2/23/96)

Re: NMR Spectral Simplification of a Highly Fluorinated Alkyl Chain

Dear Barry,

With exceptional abilities to dissolve gases such as oxygen, highly fluorinated compounds currently find application as blood substitutes, breathing media in lungs, and monitors of oxygen tension in tissues. The assignment of the fluorine-coupled 13C resonances of linear fluoro-alkyl chains is particularly not straightforward as the chemical shifts of the various carbon atoms are close to one another, and are complicated by multi-bond couplings. This is shown in the 1H-decoupled 13C NMR spectrum of the highly fluorinated alcohol, CF3-(CF2)4-CF2-CH2-CH2OH, (Fig. 1A). The six fluorinated carbon nuclei (C3 to C8) exhibit a complex pattern of >47 lines between 107 and 122 ppm with splittings due to one and multibond fluorine couplings. The two protonated carbon nuclei respectively resonate at 54.8 and 34.1 ppm (C1 - singlet and C2 - fluorine coupled triplet). The triplet at 128 ppm arises from C6D6.

The partial hydrocarbon nature of the chain is exploited to obtain a spectral simplification of the fluorinated portion in two ways. The first method uses single and multibond 2D correlations in tandem to delineate relevant cross peaks. In the single bond correlation (Fig. 2), two cross peaks from two protonated carbons (C1 and C2) are seen, and the fluorinated region is silent in the 2D map. The C1 correlation is a single cross peak, but the C2 correlation is a set of three cross peaks due to heteronuclear coupling from the C3 CF2. The splittings allow measurement of 3JHF (~18.7 Hz) and 2JCF (~21.4 Hz). The finding that the highest frequency 1H cross peak (~ 2.4 ppm) has the highest 13C frequency (~ 34.2 ppm) implies that the relative signs of 3JHF and 2JCF are alike.

In the analogous multibond correlation experiment (Fig. 3), new correlations are detected in both protonated and fluorinated carbon regions. Correlations in the protonated region are single cross peaks corresponding to 2JHC responses from H1 to C2 and vice versa. Correlations in the fluorinated region in contrast are multiple cross peaks corresponding to 2JHC and 3JHC responses from H2 and H1 to C3. Expansion of the 2JHC correlation reveals it to consist of a set of three cross peaks, *each of which is further split into three distinct cross peaks*. Thus, in this multibond correlation, 9 of the >47 lines between 107 and 122 ppm are spectrally selected. The separation between the centers of the three main peaks is ~255 Hz (1JFC) and the spacing within each main cross peak is ~18.7 Hz (2JFC). This multibond correlation is further split along the 1H axis by ~18.7 Hz (3JHF). The highest frequency 1H cross peak nearest 2.4 ppm is seen to have the lowest 13C frequency nearest 117.3 ppm, implying that 3JHF and 1JCF have opposite relative signs.

The second method uses selective INEPT. In the regular INEPT spectrum (Fig. 1B), the proton -bearing carbon signals (C1 and C2) are retained, but the fluorinated carbon and C6D6 solvent resonances are eliminated. Note that C1 appears as the expected singlet as 1JCH and the 13C shift effects are refocussed by the 180 degree pulses of the INEPT sequence, while the C2 peak appears as a triplet as the 2JFC coupling is not refocussed. In selective INEPT, soft decoupler pulses are used to excite a specific proton signal, and Fig. 1C shows the result when the C1 CH2 protons are excited with an 11.5 msec soft decoupler pulse. Small residual responses are seen in the protonated carbon region, but a larger response is obtained in the fluorinated carbon region centered near 118.7 ppm. This response is a unique nine line pattern - three triplets with intensity 1:2:1. The selective INEPT results are consistent with the 2D observations; i.e.the 118.7 ppm multiplet arises

from the C3 carbon in the presence of heteronuclear coupling from both the C3 and C4 fluorine atoms. The 2D method yields additional information on the relative signs of the hetero- nuclear coupling constants.

Regards,

Tony

Anthony A. Ribeiro (A^2R)

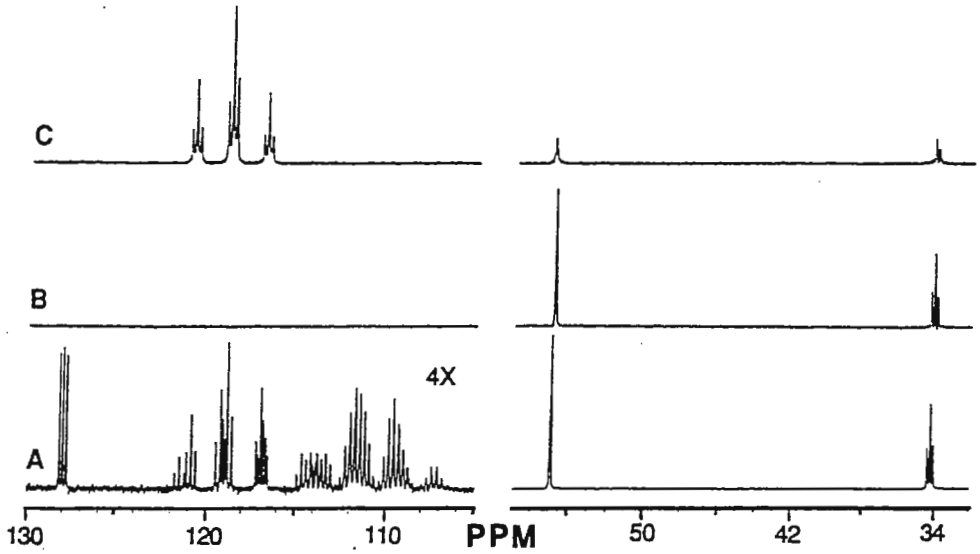


Figure 1

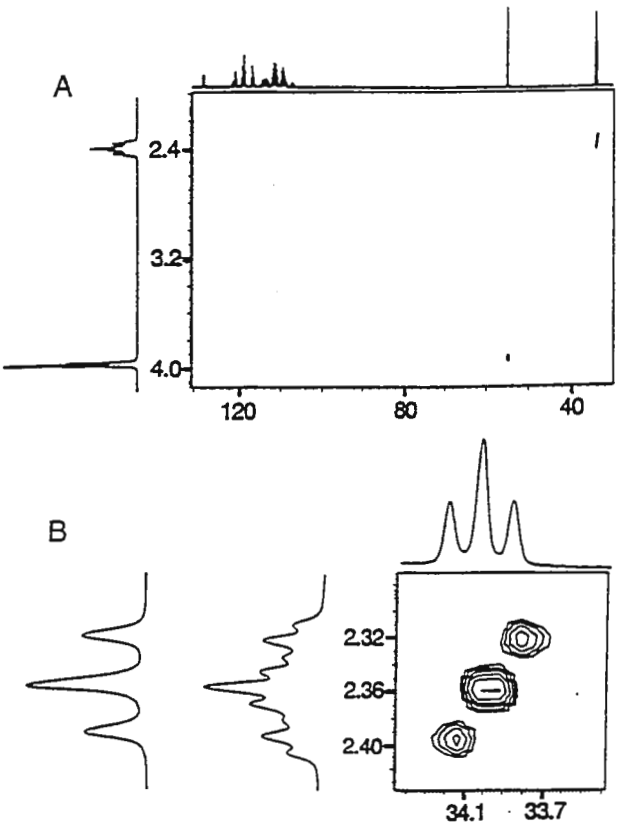


Figure 2

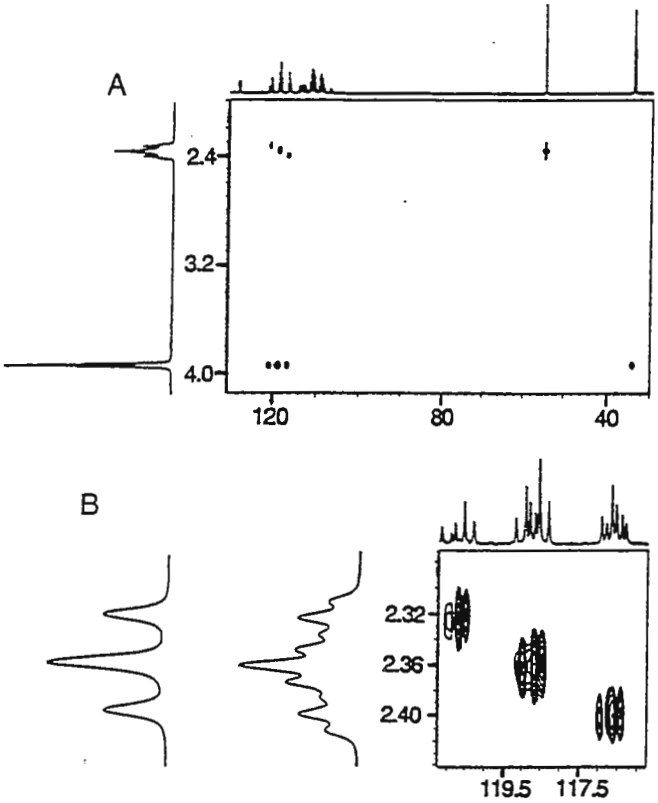


Figure 3

Model 3445/3446 Amplifiers from AMT

10-130 MHz Bandwidth

1000 and 2000 watt Models available

For High Performance NMR/NMRI Applications

Your NMR/NMRI requirements are pushing the leading edge of science and you need AMT RF power technology! The 3446 and 3445 operate from 10-130 MHz and are rated at 1000 watts for low field NMR and up to 2000 watts for NMRI applications up to 3 Tesla. AMT has brought together the highest possible RF performance at a most cost effective price. Nobody builds a better NMR/NMRI amplifier than AMT...

Additional Features Include:

- 10-130 MHz bandwidth for use in systems up to 3T
- Up to 2000 watts of power for imaging
- CW power capability for decoupling
- Blanking delay time >1 μs for multi-pulse

AMT

3080 Enterprise Street ▪ Brea, CA 925621 ▪ (714) 993-0802 ▪ Fax (714) 993-1619

Models 3445/3446

10-130 MHz, pulsed, solid-state, RF power amplifier systems

Key Specifications:

Models:	3445	3446
Frequency range	10-130 MHz	10-130 MHz
Pulse power (min.) into 50 ohms	2000 W	1000 W
CW power (max.) into 50 ohms	200 W	100 W
Linearity (±1 dB to 30 dB down from rated power)	1500 W	800 W
Pulse width	20 ms	20 ms
Duty cycle	Up to 10%	Up to 10%
Amplitude droop	5% to 20 ms typ.	5% to 20 ms typ.
Harmonics	Second: -25 dBc max. Third: -24 dBc max.	
Phase change/output power	10° to rated power, typ.	
Phase error overpulse	4° to 20 ms duration, typ.	
Output noise (blanked)	< 10 dB over thermal	
Blanking delay	< 1 μ s on/off, TTL signal	
Blanking duty cycle	Up to 100%	
Protection	1. Infinite VSWR at rated power 2. Input overdrive 3. Over duty cycle/pulse width 4. Over temperature	

Other members of AMT's NMR/NMRI Family:

3205/3200
6-220 MHz, 300/1000 W

3304/3303
30-310 MHz, 400/700 W

PowerMaxx™ series
25-175 MHz, 4kW/7 kW

3137/3135/3134
200-500 MHz, 50/150/300 W

Supplemental Characteristics:

Indicators, front panel	1. AC power on 2. CW mode	4. Overdrive 5. Over pulse width	6. Over duty cycle 7. LCD peak power meter
System monitors	1. Forward/Reflected RF power 2. Over pulse width/duty cycle	3. DC power supply fault	4. Thermal fault
Front panel controls	1. AC power	2. Forward/Reflected power	
AC line voltage	208/230 VAC, 10%, 1Ø, 47-63 Hz		

	3445	3446
AC power requirements	1400 VA	700 VA
Size (HWL, inches)	8.75 x 19 x 24	8.75 x 19 x 24
Net weight	110 lbs.	75 lbs.

AMT

FOR ADDITIONAL INFORMATION, PLEASE CALL:

AMT United States	Gigatron Associates Canada	Dressler Germany, Switzerland	JEOL Trading Co. Japan	Goss Scientific Instruments United Kingdom, France, Benelux
Ph: (714) 993-0802 Fx: (714) 993-1619	Ph: (613) 225-4090 Fx: (613) 225-4592	Ph: 49 2402 71091 Fx: 49 2402 71095	Ph: 81 3 3342 1921 Fx: 81 3 3342 1944	Ph: 44 1245 478441 Fx: 44 1245 473272

3080 Enterprise Street ■ Brea, CA 925621 ■ (714) 993-0802 ■ Fax (714) 993-1619

DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVE SW
WASHINGTON DC 20375-5320

IN REPLY REFER TO:

^{14}N in Slow Motion

Dear Barry:

14 February 1996
(received 2/17/96)

There have been relatively few solid-state NMR studies of nitrogen-14, a 100% abundant low-gamma spin-1 nucleus having typical nuclear quadrupole coupling constants (NQCC) of several MHZ. We have recently found that stepped-frequency methods and selective excitation of the fundamental transitions ($0 \rightleftharpoons +1$ or $0 \rightleftharpoons -1$) by 90°-180° spin echoes can be used to obtain ^{14}N NMR spectra from polycrystalline powders having large NQCC values, even at the relatively modest field strength of 7 T. We'd like to show an example, where we have used hole-burning experiments to measure slow motions in the well-studied spherical molecule hexamethylene-tetramine (HMT, see Figure).

The high-frequency horn of the axially symmetric HMT ^{14}N powder pattern (see Figure), which occurs 1.718 MHZ above the center reference frequency of 21.7 MHZ, yields a NQCC of 4.414 MHZ when second-order quadrupolar effects are taken into account, in agreement with previous determinations. The width of the spectrum observed is limited by the rf power. The (non-selective) 90° pulse width was measured on NH_4Cl; for the selective excitation in HMT, it was multiplied by a factor of $1/\sqrt{2}$ (from the fictitious spin-1/2 formalism).

The HMT molecule exhibits slow reorientations or tetrahedral jumps, and a variety of magnetic resonance methods have yielded correlation times of about 100 ms at room temperature. Thus it makes a good test case for developing selective ^{14}N NMR approaches to investigating dynamics. Each axially symmetric nitrogen efg tensor has its principal axis directed along one of the four 3-fold axes of a regular tetrahedron (dashed lines in Figure). Therefore, in a single crystallite, a ^{14}N efg tensor with a specific orientation with respect to the magnetic field (and hence resonance frequency) can jump to three other orientations having, in general, different resonant frequencies.

We can monitor such jumps using variants of hole-burning experiments, with one difference being that only a very limited portion of the spectrum is actually observed. Results for a DANTE train hole-burning experiment repeated only once (n=1, see pulse sequence) show that the hole (width = 4 kHz) quickly recovers to roughly 25% of its initial depth and then continues to fill in at a much slower rate (see graph). The DANTE train takes place on a short timescale, and only one-fourth (1 out of 4 orientations) of the ^{14}N nuclei in the crystallites excited are saturated. Subsequently, the tetrahedral jumps evenly distribute this saturated magnetization among all four orientations, corresponding to the rapid recovery portion of the curve. Spin-lattice relaxation takes over at longer times, in the slow recovery portion. A kinetic analysis of this 4-site exchange process provides the function used to fit the n=1 data (solid line), yielding a correlation time of 103 ms for HMT reorientation at 295 K.

Repeating the DANTE trains (i.e. setting n=16 in the pulse sequence) markedly changes the recovery behavior. In this experiment, the hole is burned, and a 100 ms delay (Δ) permits spreading of the saturated magnetization to the other three (unobserved) sites before another DANTE train is applied. Fresh magnetization is carried in by molecular reorientation and destroyed by repetitive hole-burning during the 16 cycles. This repetition creates a condition of "remote saturation" at frequencies far removed from the irradiation frequency. The recovery of the hole due to dynamics is effectively diminished in this situation, and the recovery due to spin-lattice relaxation dominates. The single-exponential fit (dashed line) of the n=16 data has a time constant of 990 ms, corresponding to a single-exponential T_1. In general, the possible presence of biexponential relaxation in selective experiments must always be carefully considered.

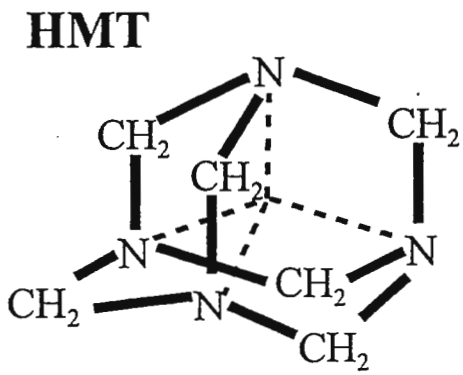
It should be pointed out that only <u>two</u> data points (for example, n=1 and n=16 with a recovery time of 100

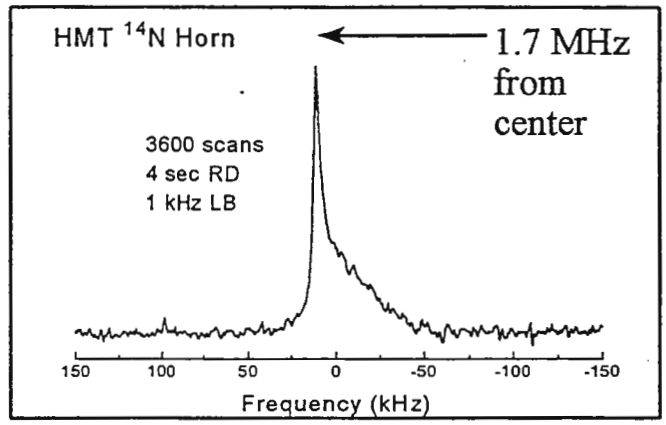
ms) are needed to provide an indication of the presence of molecular motion. We have also improved the sensitivity of the experiment by saturating the entire observed HMT peak (which represents just a small portion of the total powder pattern), which should help extend the applicability of this method to studying motions in polymers and polypeptides. This work is being written up for publication in JACS.

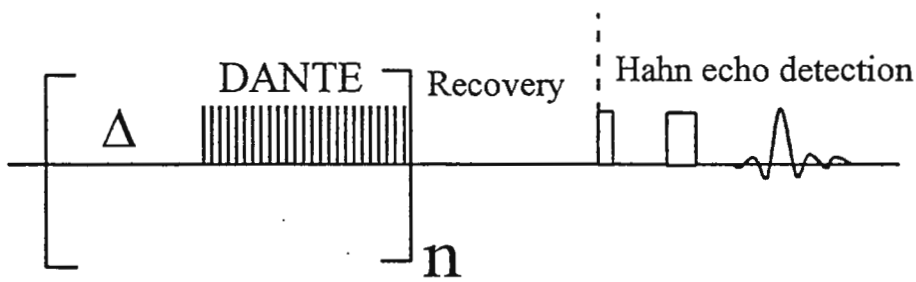
Sincerely yours,

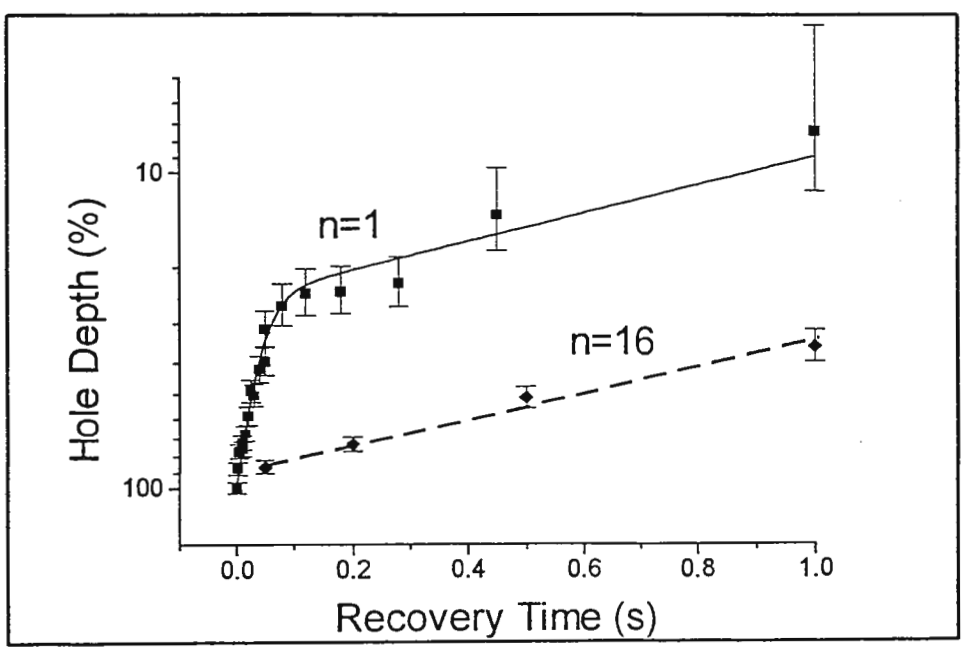
Edward A. Hill
NRC Postdoctoral Fellow

James P. Yesinowski









Otsuka Electronics USA Inc.

GOOD CONVERSATION, GREAT PRODUCTS

CRAB GRAB

WINE

NMR SPECTRA

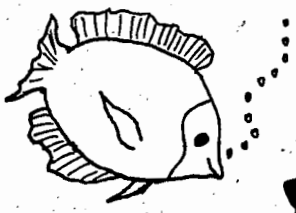
SPINSIGHT™ SOFTWARE

CMX INFINITY

SOLUTION STATE NMR

BEACH

ENC 1996



Asilomar

See us in Scripps

SOLID STATE NMR

BEER

FAREWELL TO ASILOMAR

HARDWARE

SAND AND SEA

GIFTS

PROBES

CHEMAGNETICS™

HERCULES

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599
(302) 995-3000

February 9, 1996
(received 2/21/96)

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

re: Artifact Suppression in Dilute Proton Systems

Dear Barry:

One of the recurrent themes in our laboratory has been to use solid-state ^1H NMR techniques to characterize heterogeneous materials. The systems of current interest contain associative thickeners in which we are attempting to determine the amount of undissolved solids.

These are difficult measurements to make on a 5mm high power proton probe where the total thickener concentrations are typically less than 1%. The signals are weak and samples must be prepared in D_2O to eliminate the water background. Control experiments designed to test the detection limits of the NMR experiment using dilute H_2O in D_2O revealed a broad component in addition to the water signal (Figure 1, top). This type of artifact which is negligible in solid samples with abundant protons could not be tolerated in our dilute proton system. Surprisingly, no suppression of this solid-like signal, which was initially attributed to probe background, was observed with the application of composite pulse or *depth* pulse (1) sequences. Convinced then that the source must be a noise artifact, the checklist of suggestions outlined by Fukushima and Roeder (2) was followed to systematically address the problem. Neither simple background subtraction with a blank or alternate subtraction of the signal from the sample after saturation were effective in removing the artifact. The ultimate solution was to employ a sequence that they cite (3) in which the 90^0 observe pulse is preceded with a 180^0 pulse on alternate scans such that the phase of the final observe pulse remains fixed and coherent noise is suppressed by subtraction in memory. Complete removal of the broad hump in the spectrum of dilute H_2O in D_2O using this sequence is shown in Figure 1(bottom). This sequence has also been adopted for use in ^1H T_1 saturation recovery experiments to suppress artifacts that occur at short tau values even in abundant proton samples.

References:

(1) D.G. Cory and W.M. Ritchey J. Magn. Reson.,*80*,128(1988).

(2) "Experimental Pulse NMR A Nuts and Bolts Approach", E. Fukushima and S.B.W. Roeder, Addison-Wesley, 1981, pp 468-474.

(3) T.M. Duncan, J.T. Yates and R.W. Vaughan, J. Chem Phys.,*71*, 3129-3130(1979).

Please credit this contribution to Tom Neiss' subscription.

Regards,

Mark

Mark J. Sullivan
Analytical Science Division

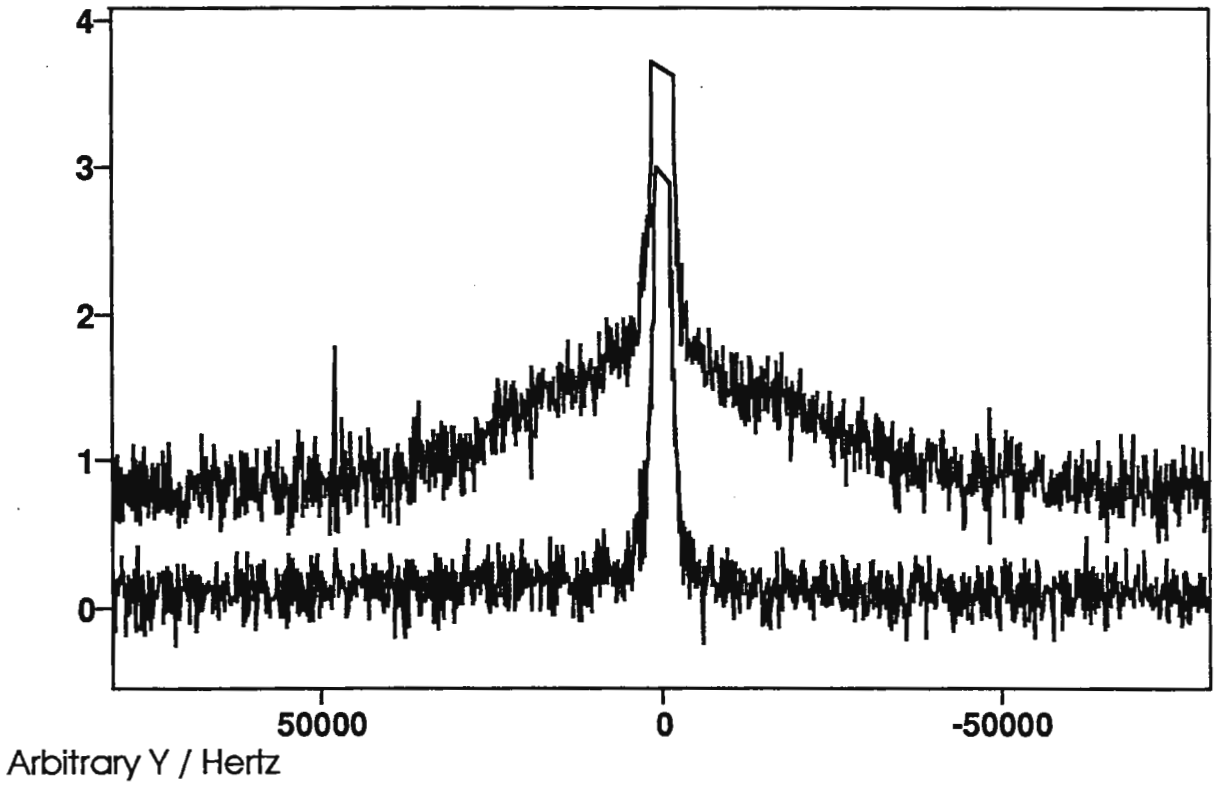


Figure 1 Top: 90(±X)-BS(±X) with transmitter phase alternation; Bottom 90(+X)-OBS(+) 180(+X)-tau-90(+X)-OBS(-) with constant transmitter phase

Set your site on Oxford Instruments at ENC 96

Oxford Instruments continues to lead the field with innovative technology that has become the benchmark of NMR magnet excellence. With over 30 years design and manufacturing experience and over 4000 successful installations world-wide, the companies products remain at the fore front of technical achievement.

The success of Oxford Instruments' products lies in the detailed appreciation of customer's applications and the constraints of their operational environment. As usual, Oxford Instruments will be attending ENC 96 and our skilled engineers will be on hand during this conference to discuss any requirements you may have. Whether you need a custom approach, or a specific application from one of our standard vertical or horizontal bore magnet systems, Oxford Instruments have the skills and expertise to give you the right solutions, along with a global support service designed to respond to your needs.

Oxford Instruments is recognised as the world leader in the design and manufacture of NMR magnet systems and our products continue to be the preferred choice for NMR specialists.

Whether you need a custom approach or a specific application, talk to the specialists at ENC 96 and specify...

Oxford Instruments

Certificate No. FM30231

ISO 9001 CERTIFIED

OXFORD

Oxford Instruments
NMR Instruments

The Oxford Instruments Heritage

Oxford Instruments are the pioneers of NMR magnet systems and associated cryogenic technology. After more than 30 years, we are still leading the way maintaining our worldwide reputation for transforming scientific ideas into usable, practical technology:

- Oxford Instruments were the first company to introduce NMR quality super-conducting magnets at 400, 500, 600 and 750 MHz.
- We designed and built the world's first compact superconducting storage ring for X-ray lithography.
- 20 Tesla magnets are routinely produced for physics research.

Making this happen are the people of Oxford Instruments, their expertise and dedication makes them our greatest asset and a unique resource for our customers.

Our accumulated knowledge and experience is unparalleled and some of the best minds in research technology are consistently working in partnership with our customers, exploring new techniques and setting new standards in the design and manufacture of specialist research products.

But it does not stop there; supporting our customers day to day, and around the world, is a team of engineers and technical specialists. Always on hand, to keep our products fully functional and equipped with the latest refinements.

New products such as the Oxford NMR[750] are practical examples of our innovation so you can be sure of Oxford Instruments commitment to providing the very best in people and products for many years to come.

Standard specifications

Magnetic field Strength (^{1}H-MHz)	Room Temperature Bore Diameter (mm)	Field Stability (^{1}H-Hz/Hour)	Maximum Helium Refill Interval (Days)	Minimum Operational Ceiling Height (m)
750	51	15	60	3.8
600	51	10	120	3.4
500	51	10	150	3.2
400	54	8	365	2.8
360	54	8	365	2.8
300	54	3	365	2.8
270	54	2.7	365	2.8
200	54	2	365	2.8
100	54	1	365	2.8
500	89	15	120	3.4
400	89	10	180	2.8
360	89	10	365	2.8
300	89	3	365	2.8
270	89	2.7	365	2.8
200	89	2	365	2.8
100	110	1	119	2.8

We would be delighted to discuss your custom specification requirements for any specialist systems. For more information please contact your local Oxford Instruments sales and service organisation.

UK
Oxford Instruments
NMR Instruments,
Osney Mead, Oxford OX2 0DX,
England
Tel: +44 (0) 1865 269500
Fax: +44 (0) 1865 269501

Germany
Oxford Instruments GmbH
Kreuzberger Ring 38,
Postfach 4509, D-6200 Wiesbaden,
Germany
Tel: (611) 76471
Fax: (611) 764100

USA
Oxford Instruments Inc.
130A Baker Avenue, Concord,
MA 01742, USA
Tel: (508) 369 9933
Fax: (508) 369 6616

France
Oxford Instruments SA
Parc Club-Orsay Universite,
27, rue Jean Rostand,
91893 - Orsay Cedex,
France
Tel: (1) 6941 8990
Fax: (1) 6941 8680

Japan
Oxford Instruments K.K.
8F, Second Funato Building,
1-11-11, Kudankita,
Chiyoda-ku, Tokyo 102
Japan
Tel: (3) 3264-0551
Fax: (3) 3264-0393 · 0626

Oxford Instruments Inc.
West Regional Office,
331c Lakeside Drive,
Foster City, California 94404
USA
Tel: (415) 578 0202
Fax: (415) 578 9018

OXFORD

Oxford Instruments, NMR Instruments
Osney Mead
Oxford OX2 0DX, England
Telephone +44 (0) 1865 269500 Fax +44 (0) 1865 269501

NATIONAL TAIWAN UNIVERSITY

DEPARTMENT OF CHEMISTRY
P.O Box, 23-34
TAIPEI, TAIWAN, REPUBLIC OF CHINA
PHONE:02-3635357 3620421
FAX:886-2-3636359 3630290

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

February 9, 1996
(received 2/16/96)

Re: **^{13}C CP MAS NMR, charge transfer and molecular dynamics in solid C_{60}(γ-Cyclodextrin)$_2$.**

Dear Dr. Shapiro:

Water-soluble complex C_{60}(γ-CyD)$_2$, where CyD is cyclodextrin, has been recently reported.[1] We have performed the ^{13}C CP/MAS NMR experiments on solid C_{60}(γ-CyD)$_2$ with variation of the contact time. The sample as prepared was compared to the complex D-C_{60}(γ-CyD)$_2$ in which protons of γ-CyD hydroxyl groups were exchanged to deuterium using D_2O. For D-C_{60}(γ-CyD)$_2$, the cross polarization rate, T_{CH}^{-1}, between protons of γ-CyD and carbons of C_{60} was measured to be 0.23 ms^{-1}, while for C_{60}(γ-CyD)$_2$ it was 0.28 ms^{-1}. A minor difference in T_{CH}^{-1} for both samples, is in agreement with previous result which showed that substitution of proton in the $C_{2,3}$-OH group of γ-CyD by deuterium is hampered due to strong intramolecular hydrogen bonding. Hence, that is impossible to differentiate either the C-H or C-OH groups the major cross polarization path is associated with. On the other hand, we found that under the same experimental conditions (the same contact time) the signal intensity of C_{60} in ^{13}C CP/MAS spectrum is greatly enhanced for the deliberately wetted C_{60}(γ-CyD)$_2$ rather than for the sample as prepared after freeze-dry procedure. Thus, the NMR data showed that the residual water associated with the complex seemed to play an important role in mediating the interaction between C_{60} and γ-CyD. Regarding the charge transfer, we found that C_{60}(γ-CyD)$_2$ in solid state exhibits characteristic ESR spectra consisting of two signals. The major asymmetrical one with isotropic g=2.0018 and typical ΔH_{pp}=3.2 G is assigned to C_{60}. Intensity of second signal with g=2.0024 and a typical linewidth of 1.4 G varied from sample to sample with different residual water associated with γ-CyD. The stochastic Liouville method for the ESR relaxation in the slow motional region due to the axially symmetrical secular g-tensor[2] was applied for the lineshape simulation for the signal of C_{60}. The temperature dependent lineshape was reliably fitted by the strong jump reorientational diffusion model.[2] The reorientational correlation time τ_R of order of 10^{-7} sec (at RT) evaluated from such a spectral simulation indicates that C_{60} in between γ-CyD cages reorientates much slower as compared to analogous reorientation in pristine or alkali-metal doped C_{60}.[3]

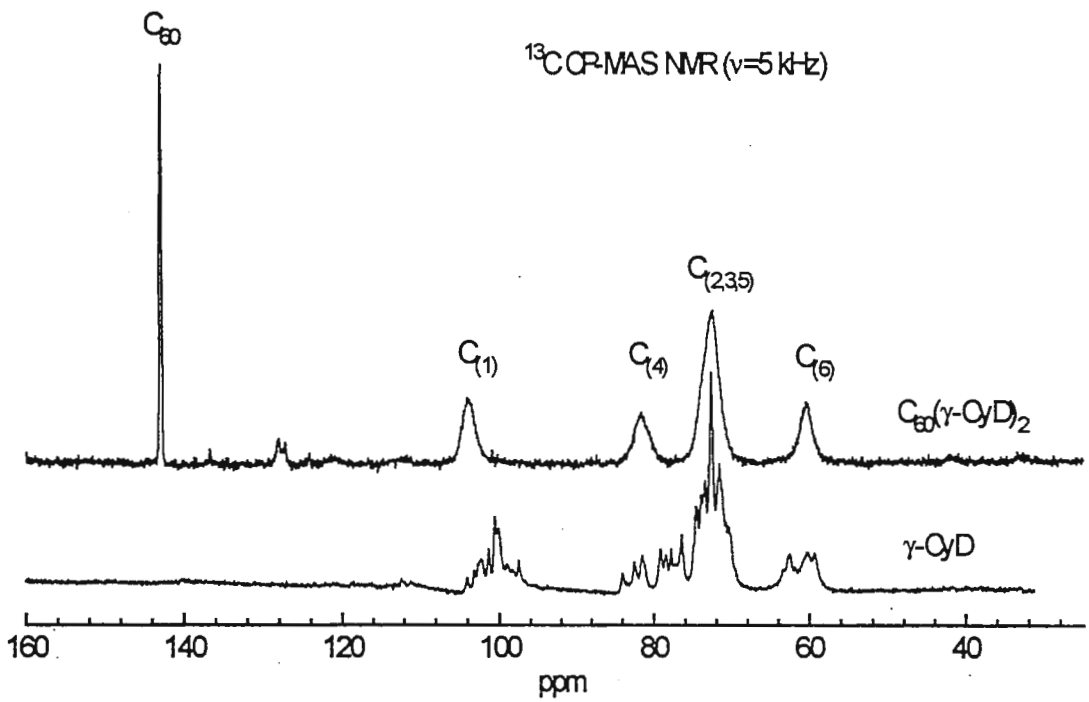


Figure 1. ^{13}C CP MAS NMR spectra taken at ambient temperature in $C_{60}(\gamma\text{-CyD})_2$ (upper) and in pristine γ-CyD (lower) in the field 11.7 T.

1. (a) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc. Chem. Commun.* **1992**, 604; (b) Yoshida, Z.; Takekuma, H.; Tekekuma, S.; Matsubara, Y. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1597.
2. (a) Freed, J. H.; Bruno, G. V.; Polnaszek, C. F. *J. Phys. Chem.* **1971**, *75*, 3385; (b) Freed, J. H. In *Spin Labeling: Theory and Applications*; Berliner, L., Ed.; AcademicPress: New York, 1976; p 53.
3. Tycko, R.; Dabbagh. G.; Fleming, R. M.; Haddon, R. C.; Makhija, A. V.; Zahurak, S. M. *Phys. Rev. Lett.* **1991**, *67*, 1886.

Sincerely,

W.-Y. Tseng Y.-H. Chen I. I. Khairullin Lian-Pin Hwang

Wen-Yi Tseng Yu-Huei Chen Ilias I. Khairullin Lian-Pin Hwang

Automatic NMR Sample Preparation

The comprehensive mobile station for automatic NMR sample preparation is designed to fully meet the requirements of high-throughput analytical laboratories. Its high modularity with up to 16 stations facilitates fast exchangeability of individual stations to easily adapt to changing needs. This includes fast teach-in for high operational accuracy. The functionality includes automatic identification of sample vials, dissolving the sample in typical NMR solvents, filtration, filling of NMR sample tubes and sealing with plastic cap, inserting the tube into a spinner and attaching a barcode collar. Samples are prepared in racks of 64, ready for loading into BRUKER's automatic sample changer.

Technical Data

Input trays:	holding 64 vials each
Output trays:	holding 64 sample tubes each
Solvent dispensers:	0.51 capacity per solvent, 4 solvents max/per dispenser station
Pipette storage station:	ca. 140 pipettes
NMR sample tube dispenser and assembly station:	available for 5 mm tubes
Sample filtration and dosage station:	ca. 128 filters, 128 caps
Barcode collar dispenser:	ca. 150 collars
Dimensions:	with stations 1800 x 970 mm
Height closed:	170 mm
Height open:	210 mm
Width without stations:	800 mm
Width when closed with stations:	970 mm

Width when both covers open:	1700 mm
Weight:	200–250 kg depending on layout
Power (dissipation):	220 V 4A
Air pressure:	5 bar
Accuracy of repetition:	± 0.05 bar
Typical sample preparation time:	ca. 6 minutes
Automatic teach-in for all stations	
Communication between stations:	RS 485
Communication to data system:	RS 232
Maximum number of stations:	16
Data system:	PC-compatible 80386/486 system using MS WINDOWS® 3.1

NMR/B951/10.94

MS WINDOWS® is a trademark of Microsoft

GERMANY BRUKER ANALYTISCHE MESSTECHNIK GMBH
Silberstreifen, D-76287 Rheinstetten
Tel. (07 21) 51 61-0, Fax (07 21) 51 71 01
Wikingerstr. 13, D-76189 Karlsruhe
Tel. (07 21) 59 67-0, Fax (07 21) 59 67-173
BRUKER-FRANZEN ANALYTIK GMBH
Fahrenheitstr. 4, D-28359 Bremen
Tel. (04 21) 22 05-0, Fax (04 21) 22 05-1 02
BRUKER SAXONIA ANALYTIK GMBH
Permoserstr. 15, D-04316 Leipzig
Tel. (03 41) 2 35 24 53, Fax (03 41) 2 35 36 05

FRANCE BRUKER SPECTROSPIN SA
34, rue de l'Industrie, F-67160 Wissembourg
Tel. (88) 73 68 00, Fax (88) 73 68 79
SWITZERLAND SPECTROSPIN AG
Industriestr. 26, CH-8117 Fällanden
Tel. (01) 8 25 91 11, Fax (01) 8 25 96 96
NETHERLANDS BRUKER SPECTROSPIN NV
Bruynvisweg 18, NL-1530 AB Wormer
Tel. (75) 28 52 51, Fax (75) 28 97 71
SCANDINAVIA BRUKER SPECTROSPIN AB
Enhagslingan 6, S-183 39 Täby
Tel. (00 46) 87 58 03 35, Fax (00 46) 67 92 51 68

SPAIN BRUKER ESPAÑOLA, S.A.
O'Donnell, 46. 7.°D, E-28009 Madrid
Tel. (1) 504 62 54, Fax (1) 504 47 86
BELGIUM N.V. BRUKER SPECTROSPIN S.A.
27, Av. des Courses/Wedrennenlaan, B-1050 Bruxelles
Tel. (02) 648.53.99, Fax (02) 648.86.34
ITALY BRUKER SPECTROSPIN SRL
Via Giovanni Pascoli, 70/3, I-20133 Milano
Tel. (02) 70 63 63 70, Fax (02) 2 36 12 94
U. K. BRUKER SPECTROSPIN LTD.
Banner Lane, Coventry CV4 9GH
Tel. (02 03) 85 52 00, Fax (02 03) 46 53 17

JAPAN BRUKER JAPAN CO, LTD.
21-5, Ninomiya 3-Chome, Tsukuba-shi, Ibaraki 305
Tel. (0298) 521 234, Fax (0298) 580 322
USA BRUKER INSTRUMENTS, INC.
Manning Park, 19, Fortune Drive, Billerica, Mass. 01821-3991
Tel. (508) 667-95 80, Fax (508) 667-39 54
CANADA BRUKER SPECTROSPIN LTD.
555 Steeles Avenue East, Milton, Ontario L9T 1Y6
Tel. (905) 876-46 41, Fax (905) 876-44 21
AUSTRALIA BRUKER (AUSTRALIA) PTY. LTD.
P.O. Box 202, Unit 7, 163 Mc. Evoy Street, Alexandria NSW 2015
Tel. (02) 550-6422, Fax (02) 550-3687

YOUR PARTNER FOR ANALYTICAL APPLICATIONS WORLDWIDE
NMR FT-IR QC BRUKER MS EPR MRI

UNIVERSITY OF ST. ANDREWS

SCHOOL OF CHEMISTRY,
THE PURDIE BUILDING,
THE UNIVERSITY,
ST. ANDREWS,
FIFE KY16 9ST
SCOTLAND

Tel: (01334) 463815 (Direct Line)
(01334) 476161 (Switchboard)
FAX (01334) 463808
E-mail fgr@st-andrews.ac.uk

From: Dr F. G. Riddell

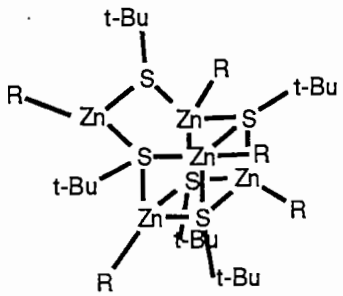
Prof B. L. Shapiro (Editor)
The NMR Newsletter,
966 Elsinore Court
Palo Alto, CA 94303

15 - 02 - 96
(received 2/20/96)

Dear Barry,

Some pretty CP/MAS spectra of ZnS clusters

I thought that the readers of the NMR Newsletter might be interested in some rather pretty CP/MAS NMR spectra to come from David Cole-Hamilton's group recently. They are of zinc sulphide alkyl clusters with the general structure below. The basic skeleton is a cube of zincs and



sulphurs with one side removed (top left as drawn) to be replaced by another Zn-S bond. It resembles a basket with a handle. All the zincs carry alkyls (methyl or ethyl) and all the sulphurs *t*-butyls. In principle there are five distinct zincs, five sulphurs five alkyls and five *t*-butyls.

In solution the methyl compound is fluxional[1] and the ^{13}C spectrum shows only one methyl resonance and one *t*-butyl group. In the solid (CP/MAS) there are clearly seen to be five distinct t-butyls and five methyl resonances in the ratio 1:2:1:1. One of the quaternary *t*-butyl carbons is clearly distinct from the others and is probably from the *t*-butyl in the "handle" section of the molecule. This is another interesting example where the dynamics of molecular change are drastically different in the solid from in solution. We wondered if we could induce fluxionality in the solid state by heating the substance but the risk of it decomposing to smell the MSL lab out deterred us.

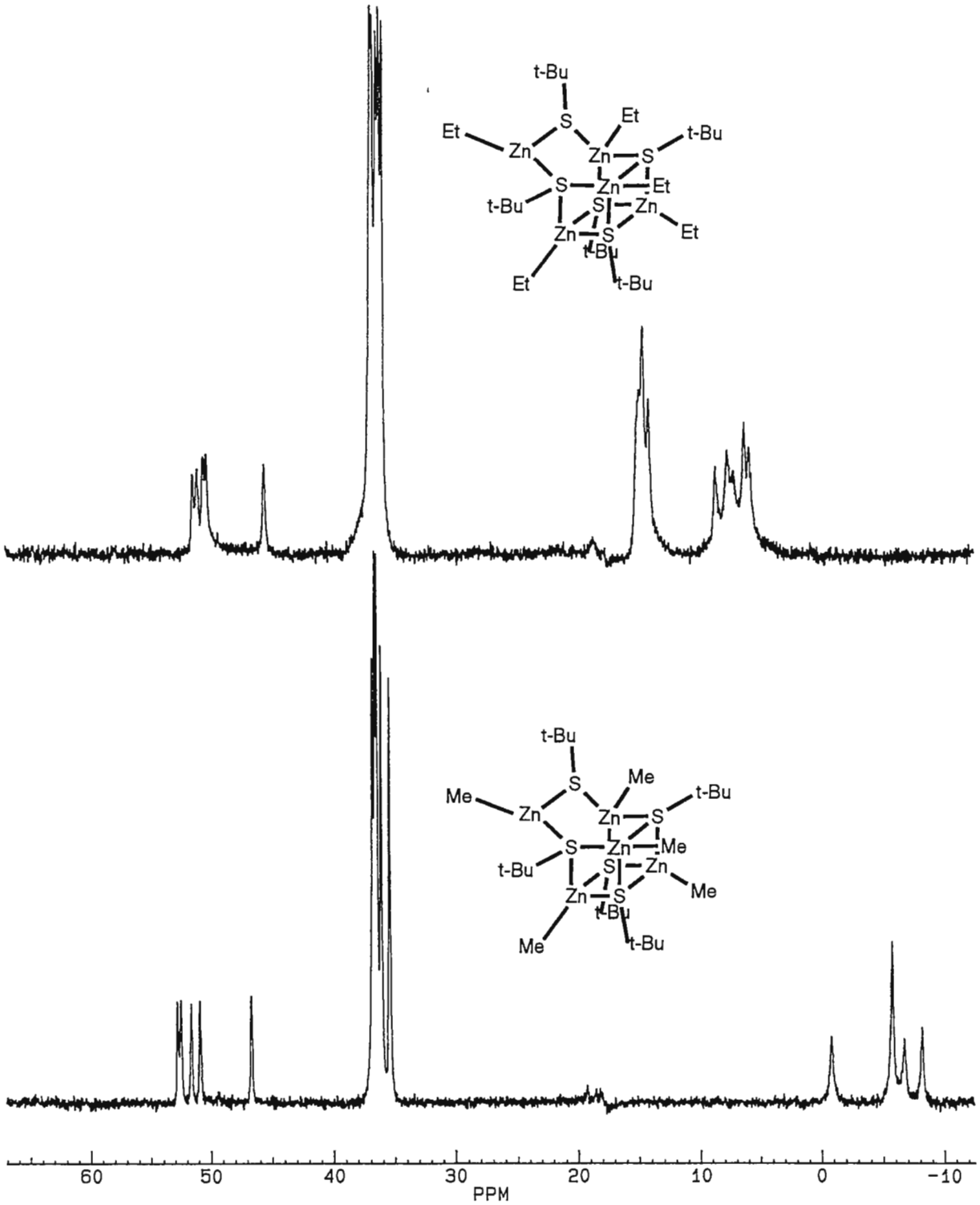
Nigel Pickett recently made the corresponding ethyl compound and it gives a remarkably similar spectrum confirming its structure.

Best wishes, Yours sincerely,

Frank

Frank Riddell **David Cole-Hamilton** **Nigel Pickett**

1, *J. Mater. Chem.*, 1995, **5**, 731 - 737.


t-Bu
S
Et
Et
t-Bu
Zn
Zn
S
S
Zn
Et
t-Bu
S
Zn
Zn
Et
Zn
S
t-Bu
Et
t-Bu
t-Bu
S
Me
Me
t-Bu
Zn
Zn
S
S
Zn
Me
t-Bu
S
Zn
Zn
Me
S
t-Bu
Me
t-Bu
60
50
40
30
20
10
0
-10
PPM

ARE YOU IN CYBERSPACE?

WILMAD ★ FAX BACK ★ WILMAD

Please take a minute to let us know if you'll be stopping by to check out Wilmad's all *new* **1996 *NMR Interactive Catalog*** at

www.wilmad.com

☐ ***Yes!*** I'll be stopping by to check out what's new with Wilmad NMR.
(Available Now!)

☐ ***No...*** I won't be seeing you on the 'net... but send me a printed version of the new Wilmad NMR catalog!
(Available mid year 1996)

Co. Name: _____

Name: _____

Address: _____

City: _____ State: _____ Zip: _____

Phone: _____

Fax: _____

E-Mail: _____

☐ I'm interested in getting the catalogs checked below:

☐ EPR ☐ IR ☐ UV/Vis/Fluor ☐ AA/ICP ☐ Precision Bore

☐ Please take my name off your list.

WILMAD

Fax to... **800-220-1081**
International Fax... **609-697-0536**

January 25, 1996
(received 2/5/96)

Hierarchical Timer/Control System

Dear Barry:

For 25 years we have been working part-time on more or less elaborate timer/control systems for NMR, starting with the one in Adv. Mag. Reson. **5**, 81 (1971). Over the past 10 years we've settled on what we call a hierarchical architecture, which I'll describe.

First some general remarks. Reflecting its almost continuous evolution over these years, our timer control retains some quaint archaic features such as some direct switch control of times, and (therefore) BCD-based counters, and a couple of EPROMs instead of computer loaded RAMs, though it uses the latter widely. Eventually we will have the switches computer-polled and all memories computer loaded, while retaining the extensive front panel switch-control which is so convenient. The system is based on roughly 40 PALs and is in a single vector cage having 10 6 by 8" cards, not all of which are used.

"Hierarchical" means that there is a single very simple central control unit, and computer-loaded master program memory which it reads. Each line on the control program "calls" a slave processor to perform a macro instruction. The latter can be a single pulse or delay, or an elaborate composite pulse or other series of events, including a FID digitization sequence. The master and slave processors have similar and fairly standard architecture, the heart of which is a PAL-encoded 6 bit program counter. It does not loop, but each macroinstruction can be repeated up to 255 times, for use in HOHAHA sequences etc. This system is so versatile that we've never approached the current limit on the length of a program, of 64 macroinstructions. The main program consists of a series of numbers, as a form of machine language, but it is not nearly as bad as it sounds because the instructions have comments attached to them, and are moved about as complete lines with a program editor to make new programs. An instruction consist of 3 8-bit hex numbers. The first specifies the macro, the second a phase sequence, and the third specifies which repetition counter is to be used, and what decoupler channels are to be used.

The phase part of the instruction, really a peripheral output, specifies one of a library of phase cycles, contained in a memory, which in effect translate the numbers represented by a FID counter into phases. We represent these in a way that takes advantage of the modulo-4 character of 90° times n shifts that dominate NMR, to get something that I can understand better than those x, y, -x, -y or 0-1-2-3 sequences used in commercial notation. These are overall phases affecting all the pulses in a macro (het and homo can be specified independently), and are added to relative phases that are specified by the macro programs.

Each slave is programmed to do several or many macros, either by use of PAL-based firmware, or a memory. These change much less often than does the main program, but their structure is rather similar. The phase code mentioned above

can be used for other things, such as specifying which one of a set of gradient amplitudes stored in a small memory is to be turned on, and what its sign is.

It is a state machine, except that it switches between different clocks, as needed--one real-time, one for FID digitization, and one based on the lowest RF IF frequency. All slave modules can use either the central preset timer, or internal asynchronous clocks in rare cases. The preset timer's intervals are selected by nine lines.

Although this description resembles that of a series of CPUs/ microprocessors/DSP's on a commercial bus, the architecture is closer to the older wide-Fifo design common about 10 years ago, but the double layer of control makes unlimited and unpredicted expansion simple. This architecture is more suited to the needs of an NMR spectrometer, as compared to some designs which resemble a supercomputer in their ability to time share tasks, that in our case do not require the intelligence of a true peripheral CPU.

Currently we have implemented about 70 macroinstructions run by 4 slave controllers. A few of the macro instructions and at least 1 controller are either experimental or partly obsolete, and may be eliminated. The design of the controllers has evolved to an easily adapted form: a PAL-based local address counter, easily extended to many bits using TTL counters, a memory (24 bit word or less, size unlimited); a macrocode recognition circuit using PALs; and output buffers, possibly intelligent. Thus, what we can do is not inhibited by timer limitations; modifications to the timer are always easy compared to the expense of adding the capability it controls.

The dead time between macros is 1 clock periods (1 μsec) but the clock could be 0.1 μsec if we used computer-only control as mentioned. There is no dead time between microinstructions except that required for amplitudes and phases to settle, less than 0.1 μsec.

Peripherals such as output channels generally share resources such as pulse waveform generators and power amplifiers, and the slaves provide gates and routing controls for these signals, and simple address control for the address counters of memories that contain digitized waveforms.

This overall design will not seem nearly as novel as it seemed to us when we planned it about 10 years ago. Its main strength is one of scale and versatility. While there is a degree of standardization, each part can be made no more elaborately than needed, yet the architecture is completely open, and it has no limitations. Our system is not very fast, but again there's no limit other than what circuits will do.

Sincerely yours,

Sara + Al

Sara Kunz and
Alfred G. Redfield

Isotec Inc.

Cordially invites you to visit our Hospitality Suite at the 37th ENC

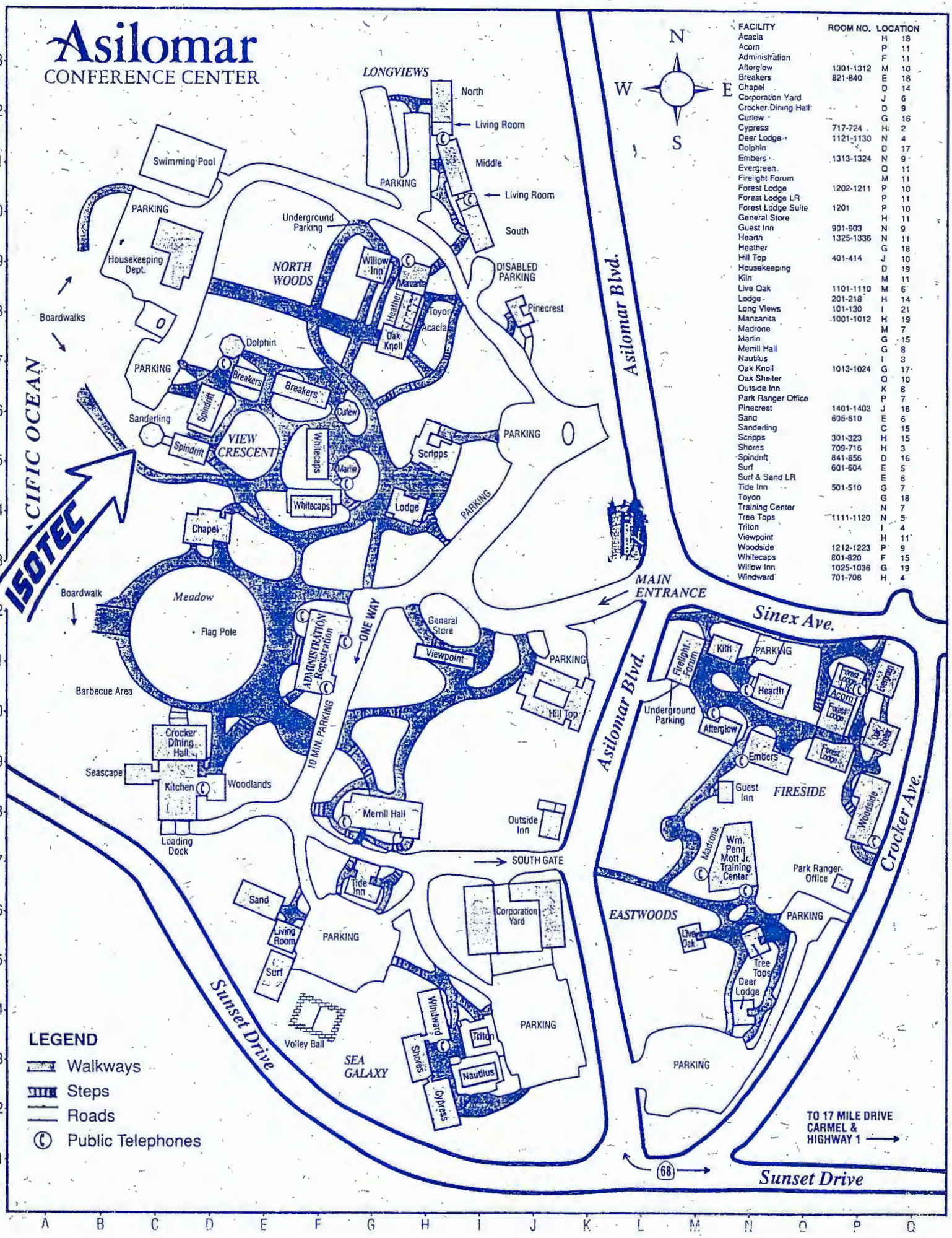
Open each evening,
Sunday through Thursday
9:00 PM

SANDERLING
(see reverse for location)

ISOTEC INC.
A Matheson; USA Company

3858 Benner Rd., Miamisburg, OH 45342
Tel: (800) 448-9760 Fax: (513) 859-4878
EMail: isosales@isotec.com

Asilomar
CONFERENCE CENTER



FACILITY	ROOM NO.	LOCATION	
Acacia		H	18
Acorn		P	11
Administration		F	11
Afterglow	1301-1312	M	10
Breakers	821-840	E	16
Chapel		D	14
Corporation Yard		J	6
Crocker Dining Hall		D	9
Curlew		G	16
Cypress	717-724	H	2
Deer Lodge	1121-1130	N	4
Dolphin		D	17
Embers	1313-1324	N	9
Evergreen		Q	11
Firelight Forum		M	11
Forest Lodge	1202-1211	P	10
Forest Lodge LR		P	11
Forest Lodge Suite	1201	P	10
General Store		H	11
Guest Inn	901-903	N	9
Hearth	1325-1336	N	11
Heather		G	18
Hill Top	401-414	J	10
Housekeeping		D	19
Kiln		M	11
Live Oak	1101-1110	M	6
Lodge	201-218	H	14
Long Views	101-130	I	21
Manzanita	1001-1012	H	19
Madrone		M	7
Marlin		G	15
Merrill Hall		G	8
Nautilus		I	3
Oak Knoll	1013-1024	G	17
Oak Shelter		Q	10
Outside Inn		K	8
Park Ranger Office		P	7
Pinecrest	1401-1403	J	18
Sand	605-610	E	6
Sanderling		C	15
Scripps	301-323	H	15
Shores	709-716	H	3
Spindrift	841-856	D	16
Surf	601-604	E	5
Surf & Sand LR		E	6
Tide Inn	501-510	G	7
Toyon		G	18
Training Center		N	7
Tree Tops	1111-1120	N	5
Triton		I	4
Viewpoint		H	11
Woodside	1212-1223	P	9
Whitecaps	801-820	F	15
Willow Inn	1025-1036	G	19
Windward	701-708	H	4

FOX CHASE
CANCER CENTER

5-Feb-96 (received 2/10/96)

Department of Nuclear Magnetic Resonance
and Medical Spectroscopy

7701 Burholme Avenue
Philadelphia, Pennsylvania 19111
215 728 3049
FAX 215 728 2822

In Vivo ^{31}P Polarization Transfer and Decoupling From ^{1}H in 3D Localized NMR Spectroscopy of Human Brain

Dear Dr. Shapiro,

In vivo ^{31}P magnetic resonance spectroscopy (MRS) facilitates direct, non-invasive observation of nucleoside triphosphates (NTP), inorganic phosphate (P_i), and phosphocreatine (PCr), related to cell energetics, and phosphomonoesters (PME's), [phosphoethanolamine (PE) and phosphocholine (PC)] and phosphodiesters, (PDE's), [glycerophosphorylcholine (GPC) and glycerophosphorylethanolamine (GPE)], primarily related to phospholipid metabolism. Unfortunately, MRS on humans is limited by the low magnetic fields (under 2 Tesla) and short 30-50 min. measurement time. The consequent low signal-to-noise-ratio (SNR) and spectral line-overlap combine to make quantitation of metabolite level difficult. Although this difficulty is partially addressed by proton decoupling (1), further improvement of the SNR, which cannot come at the expense of longer measurement or higher fields is desirable.

Additional sensitivity and resolution could be obtained by heteronuclear polarization-transfer (PT) used extensively in high-resolution NMR. SNR gain of up to $\gamma_{1H}/\gamma_{31P}\approx 2.4$ fold can theoretically be realized for ^{31}P *J*-coupled to ^{1}H's (2) and an additional $[T_1(^{31}P)/T_1(^{1}H)]^{0.5}$ is achievable by decreasing the recycle-time (TR) to the shorter T_1 of the protons (3). The problem is that PME's and PDE's have no direct ^{31}P-^{1}H bonding. Consequently, the *J*-couplings are small, 5-7 Hz, imposing long pulse delays, (τ_1, τ_2 in Fig. 1) approaching 100 ms and the ^{31}P-^{1}H and ^{1}H-^{1}H couplings are approximately the same.

Spatially localized NMR spectra can be obtained by chemical shift imaging (CSI) (4, 5) which consists of RF excitation, θ, followed by phase-encoding gradient pulses $\boldsymbol{G_x}$, $\boldsymbol{G_y}$, $\boldsymbol{G_z}$, and FID detection after the gradients are turned off (*cf.* Fig. 1). Since θ is unrestricted in nutation-angle, frequency or spatial-selectivity; any sequence resulting in net coherent transverse magnetization may be used, in particular either a hard pulse or **R**efocused **I**nsensitive **N**ucleus by **P**olarization **T**ransfer [RINEPT (2)], as shown in Fig. 1. In addition, heteronuclear-decoupling can be applied because no RF or gradients are needed during detection.

We used a Siemens Magnetom, equipped with a second rf channel, home built ^{1}H-decoupler and dual tuned, head size birdcage coils. We acquired two 8×8×8 3D ^{31}P CSI matrices, one with "hard pulse" Ernst angle excitation, θ_E, followed by RINEPT (*cf.* Fig. 1). The results from three adjacent voxels are shown in Fig. 2 together with the images of that slice. The gain, ×1, ×1.6 and ×1.8 for PE, GPE and GPC, respectively is due to T_1 differences between ^{31}P and ^{1}H. The RINEPT γ_{1H}/γ_{31P} gain is lost in part due to ^{1}H-^{1}H homonuclear *J*-coupling, the elimination of which is currently under investigation.

Sincerely,

Oded Gonen Afsaneh Mohebbi Truman R. Brown

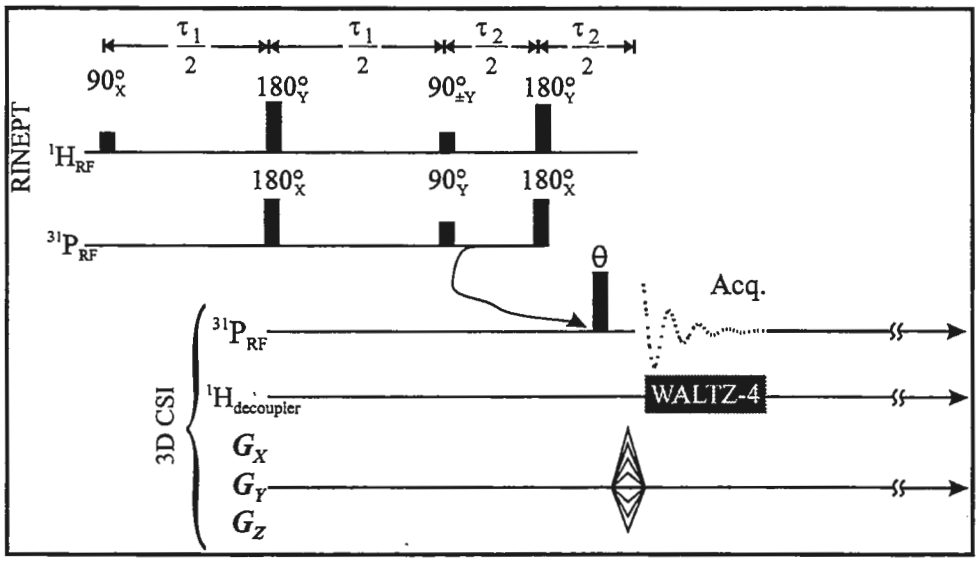


Fig. 1 Schematic representation of 3D CSI with a "hard" pulse or RINEPT and ^{1}H decoupling

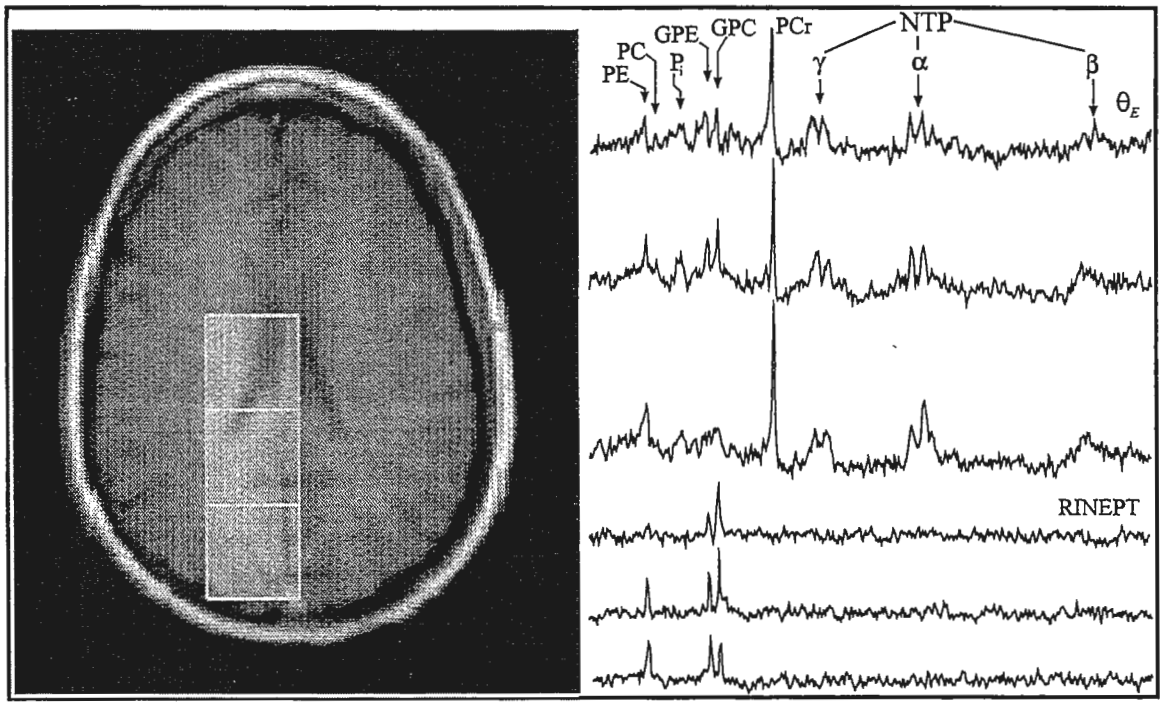


Fig. 2 Direct excitation CSI spectra from the highlighted region (27 ml voxels) of a female volunteer's brain (top, right) and RINEPT from the same region (bottom right)..

1. P. R. Luyten *et. al. NMR Biomed.* **1**, 177-183 (1989).
2. D. P. Burum and R. R. Ernst. *J. Magn. Reson.* **39**, 163-168 (1980).
3. A. Pines, *et al. J. Chem. Phys.* **59**, 569-590 (1973).
4. T. R. Brown *et al. Proc. Nat. Acad. USA* **79**, 3523-3526 (1982).
5. A. A. Maudsley *et al. J. Magn. Reson.* **51**, 147-152 (1983).

Cambridge Isotope Labs

Celebrating 15 Years of Growth and Excellence!

1981 1996

Join us at ENC '96

Hospitality Suite

Location: Marlin

Dates: March 17, 18, 19, 20, 21

Time: 7:00 pm to 12:00 midnight

Please stop by to discuss your stable isotope requirements, or fill out the information below and mail or fax it back to CIL to receive our current product literature. We can also be contacted through e-mail at *cilsales@isotope.com*

MY AREA OF INTEREST IS:

- __ Growth Media
- __ RNA/DNA Products
- __ Amino Acids/Sugars
- __ Deuterated NMR Solvents
- __ Magnetic Resonance Spectroscopy
- __ Stable Isotope Labeled Compounds, General Research
- __ Metals
- __ Other _____

Name: _____

Company: _____

Address: _____

_____

Phone #: _____ **Fax #:** _____

Stop by for some pizza, beer, wine and a free CIL T-Shirt.

***Hop aboard CIL's* Bio-Express™!**

varian associates / 3120 hansen way, box d-298 / palo alto, ca 94304-1030

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

February 16, 1996

Suppression of Radiation Damping using Pulsed Field Gradients

Dear Barry,

Vladimir Slkenar (JMR A, 114,132(1995)) has demonstrated a clever way of suppressing radiation damping by using matched bipolar Z-axis pulsed field gradients. In brief, strong coherent magnetization excited by an RF pulse is immediately dephased by a weak magnetic field gradient. Of course, all magnetizations are dephased as well, but no data is acquired during this period. Sometime later an opposite amount of dephasing is applied with another field gradient to refocus all magnetizations, including any subject to radiation damping. If this whole period were an evolution time in a 2D or 3D experiment, all chemical shift and J-coupling precession would be identical to that experienced in the case of no gradient, but no radiation damping of strong signals would have occurred. The beauty of this idea is that it may be used with any z-axis pulsed-field gradient probe without the compromise of performance expected with Q-switching or feedback circuits. It does require that the hardware be able to produce stable and reproducible very low current gradients.

In suppressing the radiation damping during t1 of a 2D experiment, this technique ensures that the natural T1 and T2 of the solvent determines that lifetime of solvent magnetization, and hence the linewidth of magnetization evolving during t1 that may get transferred to another proton during a mix time of a NOESY experiment. The NOESY crosspeak produced by this chemical exchange will have a linewidth in F1 determined by the lifetime of the solvent coherence in t1. Sklenar showed dramatic line-narrowing of water exchange peaks in NOESY spectra.

I have incorporated this idea in a WATERGATE NOESY experiment (Figure 1). I have compared data with gradient strengths of 0, 100, and 500 mG/cm (Figure 2) and have seen no need to use larger than 25-50 mG/cm (Figure 3). Note the dramatic narrowing of the exchange crosspeaks. In some cases the non-suppressed radiation damping linebroadening is so severe that the exchange crosspeak is not even visible!

The pulse sequence coding is almost trivial and I have enclosed my implementation of the gradient pulses for the relevant periods. There is no need to worry about the first increment of t1=0 since one can just eliminate the gradient pulses entirely.

Radiation damping will still occur in the mix period of a NOESY experiment. In fact, in some cases this is an advantage in that it restores the water to its equilibrium position, removing the saturating effect of the first two pulses. Use of a non-excitation element such as jump-and-return, S or SS, or watergate with a proper "flip-down" selective pulse prior to the watergate element can leave the water in a non-saturated state prior to acquisition. This preserves the magnetization "reservoir" used to populate exchangeable protons such as amides.

However, if the objective of the study is to measure chemical exchange crosspeaks, the radiation damping in the mix period will actually cause a reduction of exchange crosspeak intensities because the water magnetization is at its equilibrium value for a major part of the mix time for all values of t1. As Sklenar suggests, use of a weak (homospoil) gradient during mix prevents the action of radiation damping and the water magnetization is left to relax via normal (4-5 sec.) T1, producing full exchange crosspeak intensities. A dramatic comparison is given in Figure 4 where the same section of the NOESY spectrum is plotted in stacked form for the cases of (a) radiation damping both in t1 and mix; (b) radiation damping in t1 only; and (c) no radiation damping in either t1 or mix.

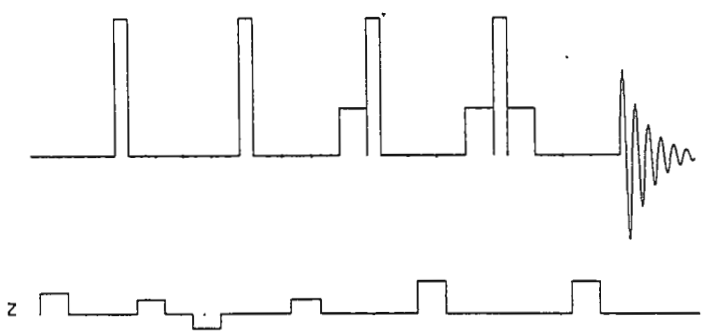
varian associates / 3120 hansen way, box d-298 / palo alto, ca 94304-1030

If exchange crosspeaks are not of interest these approaches are of less impact. The use of a gradient in the mix period will ultimately produce partially-saturated water, even if a non-excitation read pulse is used, since the water does relax slowly in the mix period. In these cases, it may be desirable to permit radiation damping in mix. It is always desirable, however, to use the gradients in t1, since there may be an accidental coincidence of chemical shifts of an aliphatic proton and water. Any NOESY crosspeak for this proton at its F1 chemical shift will be broadened just like those for water.

Although it may seem that these considerations only apply in homonuclear experiments, they are also true in heteronuclear indirect detection or triple-resonance experiments in which the water is explicitly made to be primarily at equilibrium, the "water-friendly" experiments. These usually involve water "flipback" pulses or special phase-cycling to always "place" the water magnetization back along +Z for any significant time during the sequence, and particularly just before acquisition. If the experiment is NOESYHSQC, for example, the above considerations apply for the NOESY portion of the sequence. Figure 5 shows the impact of properly treating radiation damping during the NOESY evolution and mixing periods.

Sincerely Yours,

George Gray
NMR Applications Lab




```
.
pulse(pw,v1);
if (d2>0.0)
{
 zgradpulse(gzlvl, 0.4*d2);
 delay(0.1*d2);
 zgradpulse(-gzlvl, 0.4*d2);
 delay(0.1*d2);
}
pulse(pw,v2);
.
.
.
```

Figure 1. Watergate NOESY sequence for suppression of radiation damping with psg code for evolution time. The weak (25 mG/cm) gradients during t1 are on for a total of 80% of the evolution time. The first point in t1 skips the gradients since t1=0. (For first-order phase correction of zero in F1, the non-gradient delays in t1 should be corrected for AP bus delays and finite pulse widths.)

Figure 2: Watergate NOESY on 2mM BPTI in 90% H2O. Expansion showing water exchange crosspeaks. Left: no gradients in t1; Middle: 100 mG/cm gradients in t1; Right: 500 mG/cm gradients in t1.

Figure 3: Same as Figure 2: Lower plot has no gradients in t1; Middle plot has 25 G/cm gradients in t1; and Upper trace is the F2 slice at the water frequency in F1.

Figure 4: Same as Figure 3: Left plot is for no gradients in t1 or mix; Middle plot is for gradients only in t1; Right plot is for gradients in both t1 and mix.

Figure 5: HH 2D planes from gradient-based NOESY-HSQC: Upper plane has no gradients in t1 or mix; Lower plane has gradients in both t1 and mix: 1D plots are F2 slices at the water frequency in F1.

Figure 2

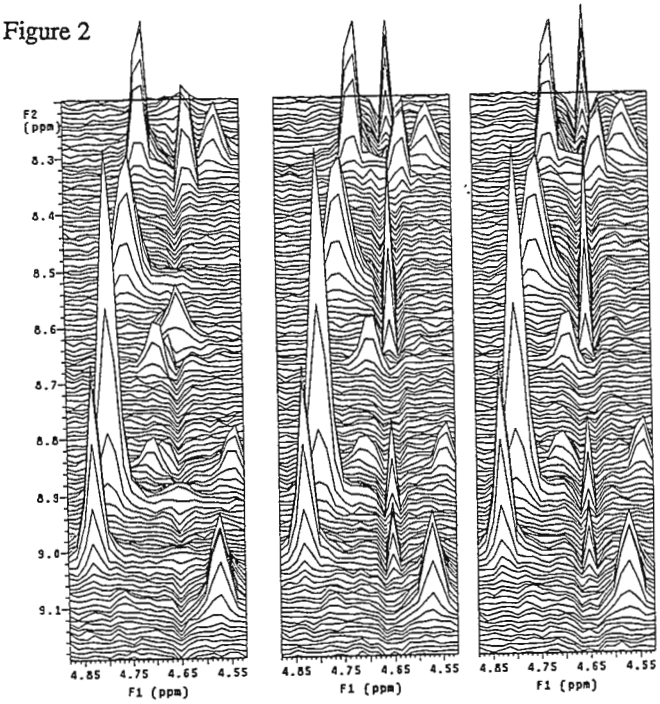


Figure 3.

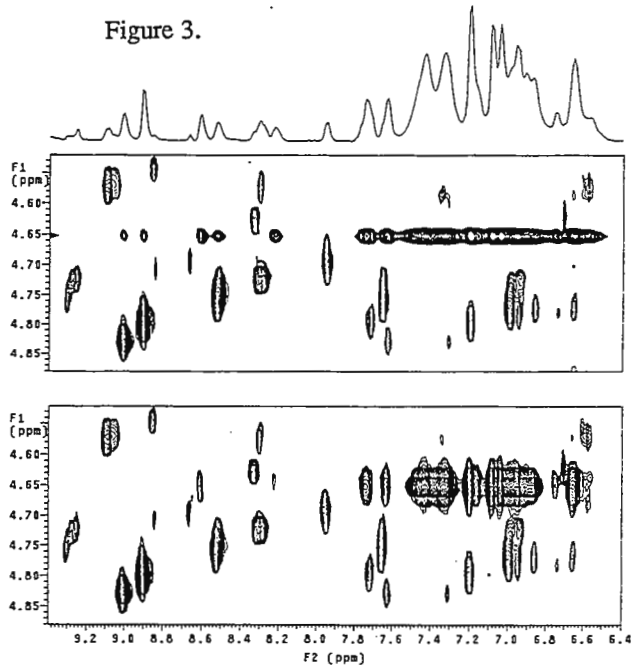
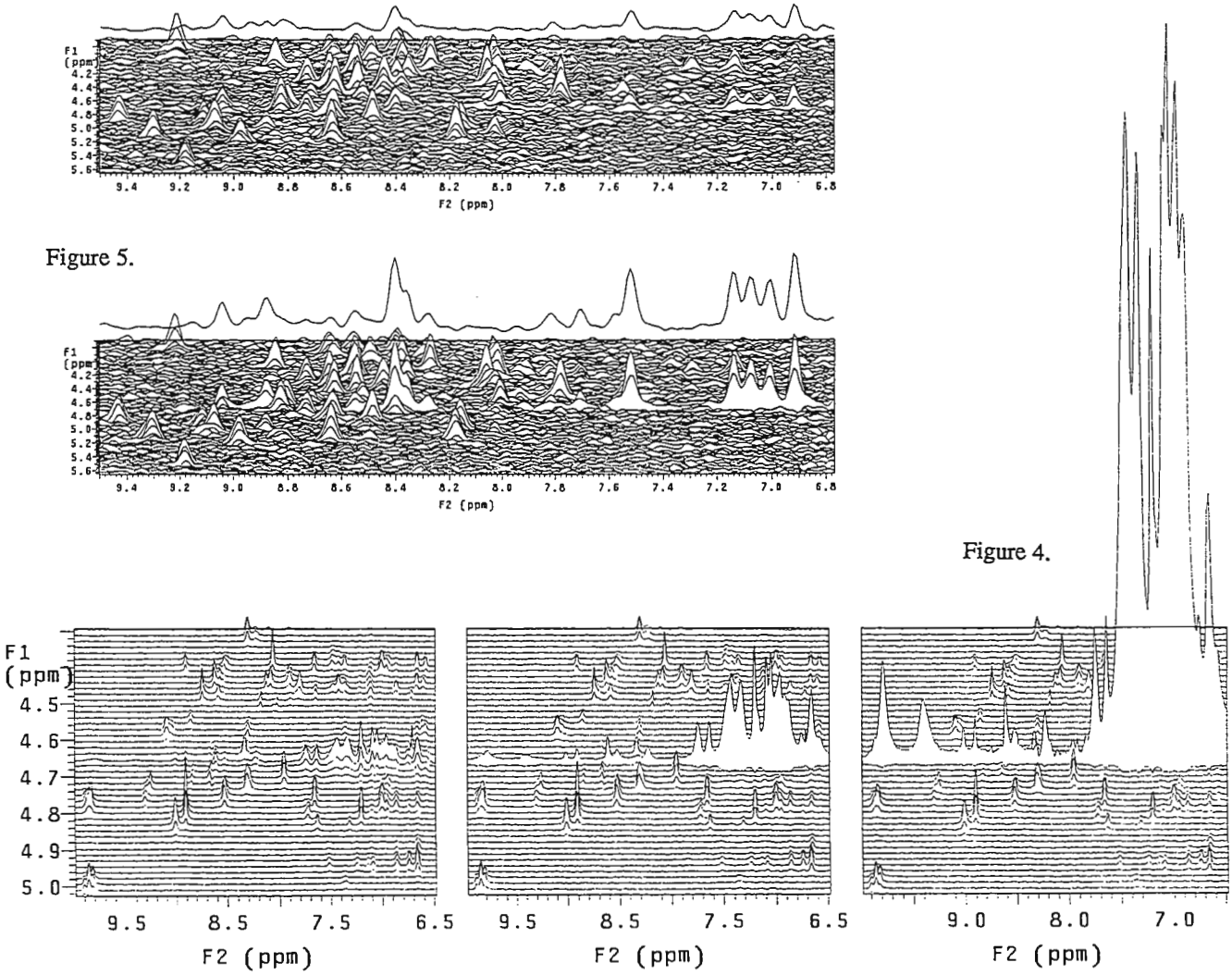


Figure 5.

Figure 4.



UNIVERSITY OF THE PACIFIC

College of the Pacific

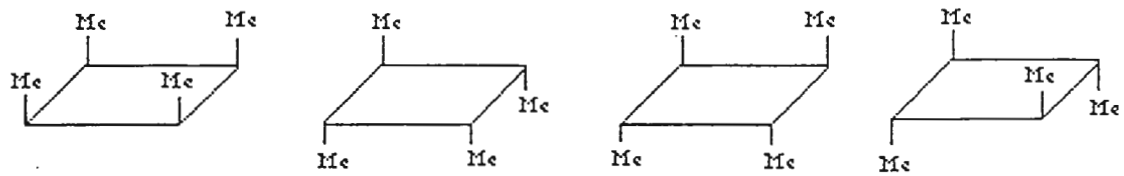
Department of Chemistry

(received 2/14/96)

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

Methyl Chemical Shift Differences in the atropoisomers of 5, 10, 15, 20-tetrakis-(2-methylphenyl)-21H, 23H-porphine

X-ray crystallographic studies of tetraphenylporphyrin show that the phenyl rings are restricted in their rotation and are roughly perpedicular to the macrocycle ring (α= 60-80°).[1] Because of steric hindrance between phenyl ring ortho-substituents and β-pyrrole protons, rotational isomerism or atropoisomerism has been detected in a number of ortho-substituted tetraarylporphyrin free bases; i.e., the free-base ortho-substituted tetraphenylporphrins exist in four different diastereomeri.c conformations that are separate species on the NMR time scale when rotation of the aryl rings is slow: C_{4v} (four ortho-groups up), C_s (one ortho group up, three groups down) C_{2h} (two *cis* groups up, two *cis* groups down) and D_{2d} (two *trans* groups up and two *trans* groups down).
The four isomers differ in symmetry hence in the number of individual methyl lines with the C_s isomer showing three lines.



C_{4v}	C_s	C_{2h}	D_{2d}
1.996	2.079, 2.041, 2.028	2.047	2.060 ppm at 20°
2.000	2.076, 2.038, 2.030	2.055	2.055 ppm at 40°

Quite some time ago we reported that the mixture of four atropoisomers of the title compound gave a six line pattern with an unusual solvent and temperature dependence[2]. We have subsequently separated the mixture into its four component atropoisomers (by HPLC methods). The four atropoisomers differ not only in the orientations (α) of the 2-methylphenyl group but in solution there may also be considerable out-of plane ruffling or bending of thse porphyrin rings so that the chemical shift behaviour of the methyl can only be rationalized in terms of the geometry and ring current effects for each porphyrin structure. All four compounds show different chemical shift changes with temperature (-30° to +60°C) suggesting that they do not share a common set of conformational deformations upon heating. The chemical shifts observed at 20° and 40° are given above. Note that this is well below the temperature in which there is phenyl ring rotation and hence interconversion of the isomers. The rate of isomer interconversion becomes rapid on the nmr time scale at elevated temperatures (> 160°) and the methyl resonances coalesce to a singlet.

1. D. C. Barber, D. S. Lawrence and D. G. Whitten, *J. Phys. Chem.*, **1992**, 96, 1204-1215.

2. M. J. Minch and C. Huang, ACS 203rd National Meeting, San Francisco, April 8, 1992.

Mike Minch, Larry Spreer and Ru Zhou

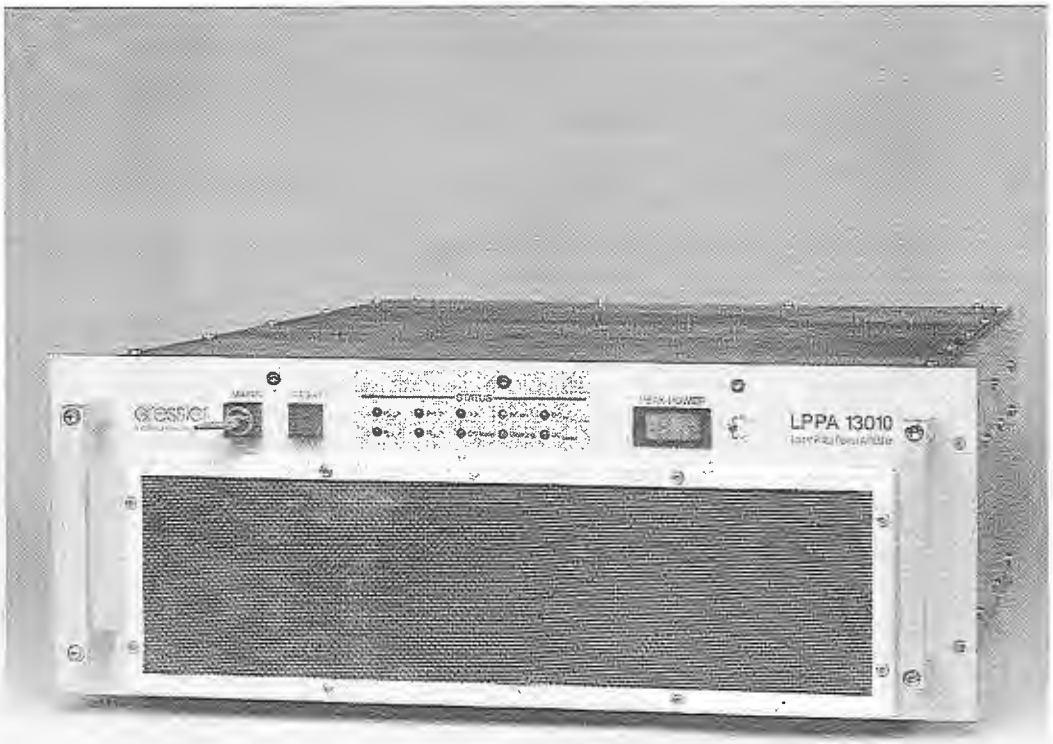
Mike

See dressler USA
in the *Lodge* at the 37th ENC

Model Line LPPA

Pulse Power 400 - 8000 W

Frequency ranges within 10 - 500 MHz



Linear RF amplifiers for NMR/MRI applications

dressler
hochfrequenztechnik gmbh

dressler USA

Lowell A. Beezley
2501 North Rose Drive
Placentia, CA 92670
Phone (714) 528-7217
Fax (714) 528-3513

Technical performance:

	LPPA 13010	LPPA 13020	LPPA 20010	LPPA 5004	LPPA 20080	
Frequency	10 – 130 MHz	10 – 130 MHz	175 – 205 MHz	200 - 500 MHz	175 – 205 MHz	
RF pulse power	1000 W	2000 W	1000 W	400 W	8000 W	into 50 Ohms
	700 W	1400 W	–	–	–	(105 - 130 MHz)
CW output power	100 W	200 W	150 W	100 W	1000 W	into 50 Ohms
Impedance	50 Ohms	50 Ohms	50 Ohms	50 Ohms	50 Ohms	N type
Gain	60 ±4 dB	63 ±4 dB	60 ±2 dB	56 ±2 dB	69 ±2 dB	at Pmax.
Linearity	±0.5 dB	±0.7 dB	±0.4 dB	±0.8 dB	±0.8 dB	1 – 80% P_{RF}
Harmonics 3xf	-14 … -25 dBc	-14 … -25 dBc	-18 … -25 dBc	-15 … -30 dBc	-18 … -25 dBc	at Pmax.
Harmonics 2xf	-25 dBc or better for all models					
Pulse width	20 ms	10 ms	20 ms	20 ms	10 ms	at Pmax.
RF pulse energy	10 Ws	10 Ws	10 Ws	10 Ws	40 Ws	max
Pulse droop	0.1 – 0.3 dB	0.2 – 0.4 dB	0.2 dB	0.1 – 0.3 dB	0.3 – 0.4 dB	at Pmax.
Pulse rise time	500 ns	500 ns	300 ns	200 ns	300 ns	
Pulse fall time	60 ns	60 ns	30 ns	30 ns	30 ns	
Noise blanked	-160 dBm/Hz	Noise floor for all models				
Noise unblanked	-120 dBm/Hz	Noise floor for all models				
Displays	● 3 1/2 digit LCD meter for forward power or reflected power					
	● RESET push button and indicator					
	● RF on	● Blanking	● P forw.	● DC RF	● CW Mode	
	● P*T	● P DC	● P reflected	● DC control	● Thermal overload	
Interface	Description see text above					
	Input levels 5 – 24 V DC. Outputs 5 V TTL					
	Analog Inputs and Outputs 0 – 10 V DC					
Cooling	Forced air cooling. Air inlet at the front panel. 0 – 40 degrees C.					
Weight	18 kp	22 kp	18 kp	18 kp	170 kp	
Dimensions	19" 4 Units = 178 mm all models				19" 40 Units = 178 cm	
Depth	550 mm all models				550 mm	
Power supply	180 – 240 V AC 50/60 Hz				380/400 V 3 phase	
Power Factor	0.95 - 0.98 PFC corrected for the latest IEC-555 regulations					
Specifications to change without notice						March 1995

dressler
hochfrequenztechnik gmbh

Werther Str. 14-16 • D-52224 Stolberg
Phone (+49)24 02/7 10 91 + 7 10 92
Fax (+49)24 02/7 10 95 • Germany

ZENECA *Pharmaceuticals*

1800 Concord Pike
PO Box 15437
Wilmington
Delaware 19850-5437 USA

February 1, 1996 (received 2/5/96)

Debra L. Banville, Ph.D.
Physical Sciences Group
EMAIL: banvilledl@zen.com

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

Natural Abundance N15-NMR on Small mM Water Soluble Proteins is Really Possible

Dear Barry,

While large proteins (>> 50 residues) are generally easier to express and isotopically label, expression and hence isotopic labeling of smaller proteins is generally more difficult. Despite this limitation, indirect detection experiments, e.g. 2D 1H{X} HMQC, HSQC, and HMBC, have allowed assignment of many carbon resonances on these smaller unlabeled proteins in the millimolar concentration range. But natural abundance 15N still remains an on-going problem. The main reasons for these difficulties includes the percent of naturally abundant material found in 15N (99.9% 1H and 1.1% 13C versus 0.36% 15N); the relative insensitivity of 15N (1000 : 16 : 1 for 1H : 13C :15N), and finally the large dynamic range problem during proton detection when trying to suppress the ~110 M water proton signal while observing the millimolar protein protons.

I recently had a demonstration of the reduced volume probe capabilities on the Bruker 2.5 mm and the Varian 3 mm gradient probes at 600 and 500 MHz, respectively. A small water soluble protein was dissolved into water (10% D2O) and pipetted into a reduced volume NMR tube. In the case of the Varian system it was placed in a reduced volume Shigemi 3 mm tube with matched magnetic susceptibility above and below the sample (requiring ~80-90 ul volume or a 16 mm sample height). The final protein concentration was ~5 mM. In the case of the Bruker, the protein was placed in a Shigemi capillary tube (requiring ~50 ul volume) giving an ~6 mM concentration.

Both samples were gradient shimmed. It should be noted that the Shigemi reduced volume tubes require careful selection, in my experience some of these tubes are better matched than others and are subsequently easier to shim. Both samples shimmed up well enough to provide excellent water suppression. For example, after gradient shimming Z1 through Z6, the Varian water peak had a 8 Hz line width near its base after presaturation! Similar results were observed with the Bruker probe. A series of experiments including a 1H{15N} HSQC with gradients were performed on these samples. The HSQC resulted in discernible 1H/15N signal within 30 minutes. The Varian experiment was run for 3 hours giving excellent signal to noise that enabled me to assign 90% of the 15N resonances based on the amide proton assignments.

For water soluble proteins these reduced volume gradient probes and reduced volume tubes allow natural abundance 15N amide assignments to be possible with a 5-10 fold increase in concentration. Other advantages include better quality 1H{13C} HMBC data which already suffers badly from a lower signal to noise ratio than the single bond experiments.

Many thanks must go to Clemens Anklin from Bruker Instruments and Boban John from Varian Instruments who performed these instrument demonstrations for me.

Sincerely,

Debra Banville

Debra Banville

***Please credit Lydia Chang's account at Zeneca Ag Products in Richmond, CA.**

Sandia National Laboratories
Operated for the U.S. Department of Energy by
Sandia Corporation
LOCKHEED MARTIN
P.O. Box 5800
Albuquerque, NM 87185-1407

Linear Prediction, Linear Vanadium Polymers, and MAS NMR[1]

Dear Dr. Shapiro,

(received 2/10/96)

The investigation of quadrupolar nuclei using high speed solid-state MAS NMR continues to be an area of interest at Sandia National Labs and the University of New Mexico. For many of these nuclei the spectra are influenced by both the quadrupolar coupling and chemical shift anisotropy. By iterative simulation of the spectra the quadrupolar and anisotropic chemical shift tensors can be obtained, and in some instances the relative orientation of the two principal axis systems. One of the more annoying instrumental artifacts encountered in these type of investigations is the baseline roll arising from the distortion of the first few acquisition data points. Prior to any attempt to simulate the experimental data, this baseline roll must be corrected. Previously, use of a polynomial baseline correction (with varying degrees of success) was the only processing option available to us. In this letter we would like to report the use of *linear prediction* for the elimination of baseline roll in MAS experiments.

Linear prediction has been used to eliminate this instrumental distortion in a variety of situations (especially during instrumental demos), and is now a common component of processing software on newer instruments. The software on our slightly older instrumentation (1993) does not have the capability for linear prediction, nor does the vintage of our instrument computer system allows us to use the newest software releases. Recently Acorn NMR has included linear prediction in their PC software, allowing us to include linear prediction in the processing of our MAS spectra. The ^{51}V MAS NMR spectra of a vanadium containing linear polymer synthesized at the University of New Mexico are shown in Figure 1. The top spectrum is an enlargement of the central and satellite transitions over an approximately 158 kHz range. Note the non-symmetric baseline roll inherent in these type of experiments following a simple transform. The lower spectrum was obtained after using linear prediction to correct the first 4 data points, with only a few seconds required for the calculation. The improvement in the baseline is clearly evident. Initial uses of the simple linear prediction processing for a variety of MAS experiments on quadrupolar nuclei (^{27}Al, ^{51}V, ^{23}Na) have proven successful and provide an alternative to the more tedious baseline fits.

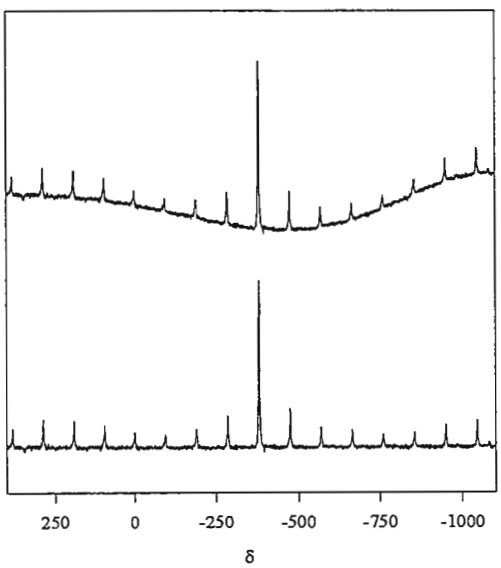


Figure 1. ^{51}V MAS NMR of a linear vanadium polymer obtained on a Bruker AMX400, using a 4 mm MAS broadband probe, at a resonant frequency of 105 MHz, a spinning speed of ν = 10 kHz, a 1 μs dwell, and a 4.5 μs dead time. In the upper spectrum no baseline correction has been applied. In the lower spectrum, the first 4 data points were modified using linear prediction. No additional baseline correction was performed.

Sincerely,

Todd M. Alam[2] Charles E.Daitch[3] Philip D. Hampton[3]

[1] This work is supported by the US Department of Energy under Contract DE-AC04-94AL85000.
[2] Properties of Organic Materials Department,Sandia National Laboratories, Albuquerque, NM 87185-1407
[3] Department of Chemistry, University of New Mexico, Albuquerque, NM 87131

Multi-Nuclear ^{1}H-X LARGE-Sample MR Microscopy

New RF Resonator

Highest B_1 homogeneity

Highest sensitivity

Double resonance

Fully multinuclear ^{1}H/^{19}F-X

Quick, simplified tuning

Force-Cancelled Gradients

for fastest recovery and lowest acoustic noise.

#24-40, for Narrow Bore:

For fields up to 750 MHz

15-mm sample for ^{1}H/^{19}F-X

25 G/cm at 100% duty cycle

#50-72, for Wide Bore:

For fields up to 600 MHz

40-mm clear rf bore for ^{1}H/^{19}F

3 to 22-mm clear-bore rf inserts for ^{1}H/^{19}F-X

12 G/cm at 100% duty cycle

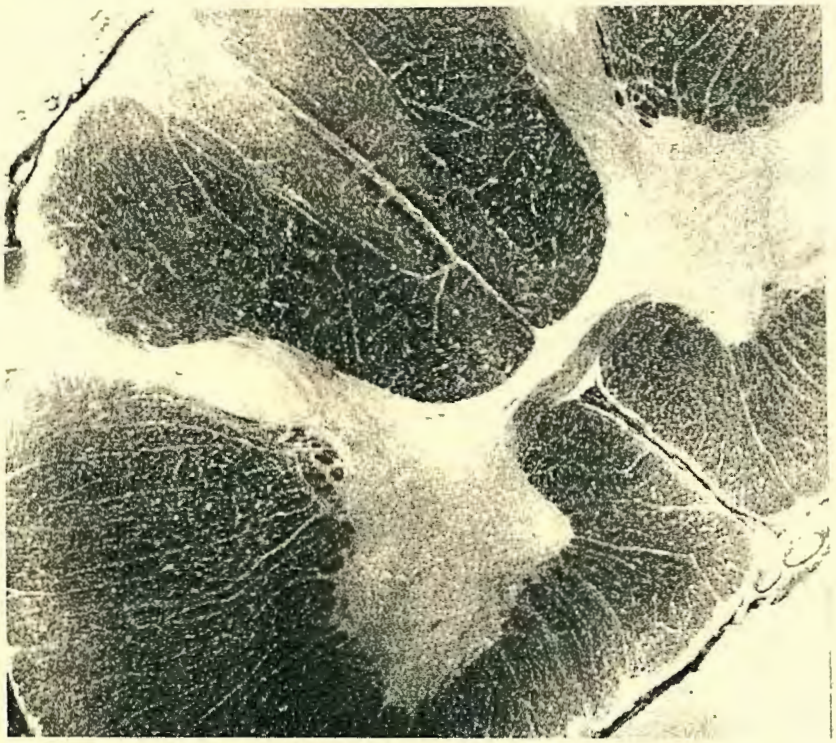
#85-120, for Super-Wide Bore:

85-mm clear gradient bore

3 to 60-mm clear-bore rf inserts for ^{1}H/^{19}F-X

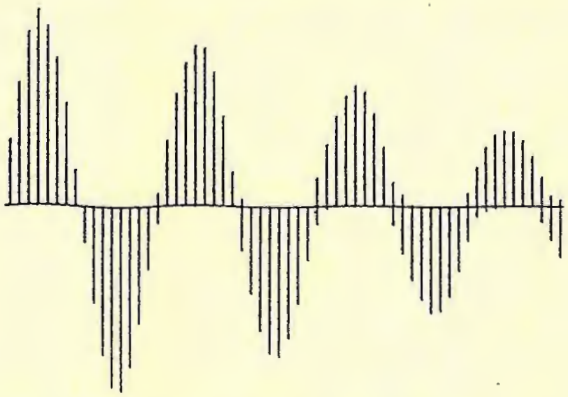
7 G/cm at 100% duty cycle

Images:
Kumquat - Univ. of Sydney, Australia
Spinal Cord- Univ. of Florida



20-Micron Resolution in a 600 MHz NB with 15-mm FOV

A diffusion-weighted image of a postmortem normal human cervical spinal cord section using a Doty 15-mm micro-imaging probe with 24-40 gradients in a Narrow Bore Varian 600 Unity+. The bright butterfly-shaped region represents gray matter which contains nerve cell bodies. The darker region encompassing the gray matter is the white matter, which consists primarily of nerve fibers. In-plane resolution is better than 20 µm with a 15-mm FOV (8 mm shown). Image provided courtesy of the Center for Structural Biology, University of Florida.



B1 homogeneity for 40-mm MRI: Pulse-width array in 300/89 with 50-mm 120 G/cm gradients, 41-mm rf coil diameter, 36-mm diameter x 25-mm length water phantom. B1 inhomogeneity (mean absolute deviation) is under 5%.

Doty Scientific, Inc.

700 Clemson Road, Columbia, SC 29223 USA

Ph. (803) 788-6497 Fax: (803) 736-5495 sales@doty.usa.com

Mayo Foundation

Rochester, Minnesota 55905 Telephone 507 284-2511

Mayo Clinic Mayo Medical School
Mayo Graduate School of Medicine

Slobodan I. Macura, Ph.D.
Biochemistry and Molecular Biology

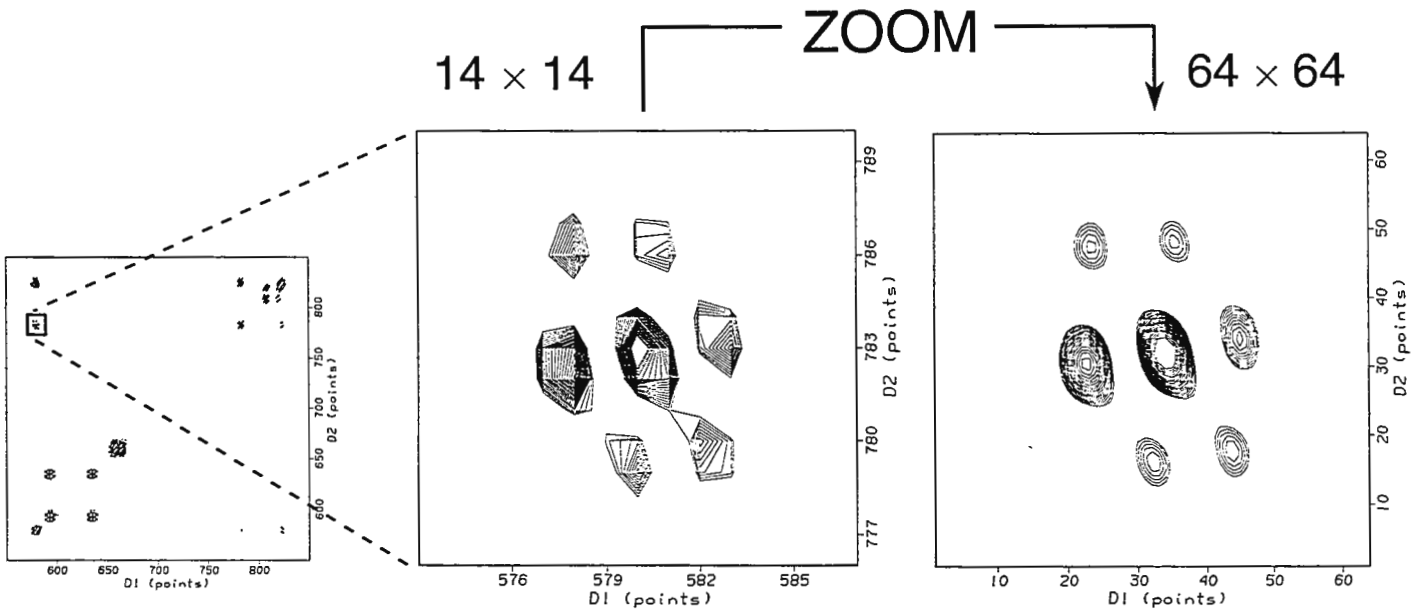
(received 1/30/96)

January 26, 1996

Zooming of Multidimensional NMR Spectra

Dear Barry:

Recently we have developed a method, which we term "zooming", that provides high digital resolution in any region selected from an n-dimensional data set. The region selected can be of arbitrary size (any number of data points). In the zooming approach as implemented in the "ZOOM" computer program the desired region of the frequency-domain spectrum is first extracted. Next, a "pseudo-FID" for the selected region is constructed by n-dimensional inverse Fourier transformation. The resulting time-domain data block is zero-filled in n-dimensions and finally Fourier transformed back to the frequency domain. As an example we present "zooming" of a crosspeak from 2D E.COSY spectrum of *cyclo*-Glycyl-Proline. The original spectrum is of 2k x 2k data points over 14 ppm. A selected region of 14 x 14 data points is zoomed to 64 x 64 data points, dramatically increasing analog representation of the cross-peaks.



We described the basic principles behind the zooming approach and demonstrated its application to the analysis of 2D and 3D NMR data from proteins in the forthcoming paper(1). The implementation described there is for spectra consisting of real or absolute-value data; at least one zero-fill must have been applied in each dimension during the initial processing of the data. ZOOM is standalone program and handles data in the Felix format. It is available at http://www.nmrfam.wisc.edu/ .

1. Zs. Zolnai, N. Juranić, J. L. Markley and S. Macura, J. Magn. Reson. A, in press

Sincerely yours,

Zsolt Zolnai, zsolt@mayo.edu
Nenad Juranić, juranic@mayo.edu
John L. Markley, markley@nmrfam.wisc.edu
Slobodan Macura, macura@mayo.edu

SYMPOSIUM

ADVANCES IN NMR APPLICATIONS

FEATURING THE LATEST DEVELOPMENTS IN EXPERIMENTAL TECHNIQUES

at the Inn at Spanish Bay, Pebble Beach, CA

Sunday, March 17, 1:30-5:00 p.m.

Agenda Includes:

Resolving Ambiguities in NOESY Data for Larger Proteins.
David P. Cistola, Michael E. Hodsdon, and Jay W. Ponder, Washington University School of Medicine

Practical Aspects of Diffusional Filters in Protein NMR.
J. Prestegard, M. Andrec, J. Lim-Weaver, and E. Sayers, Yale University

Structures of Protein-Nucleic Acid Complexes.
Angela Gronenborn, National Institute of Health

Exploring the Submicro World.
Ron Crouch and Toby Zens, Nalorac Corporation

Applications of $^{1}H/^{13}C/X$ Triple Resonance NMR In Polymer Science.
Peter Rinaldi, University of Akron

Long-Range Gradient Enhanced $^{1}H/^{15}N$ Correlation Spectroscopy at Natural Abundance.
Gary Martin, Pharmacia & Upjohn, Inc.; Ron Crouch, Nalorac Corporation

Combinatorial Chemistry - Fad or Future - A Personal Perspective.
Michael Shapiro, Sandoz Research Laboratories

Helium-3 NMR Spectroscopy - Inside and Outside of Molecules.
M. Saunders, H.A. Jimenez-Vasquez, and R.J. Cross, Yale University

---------- NALORAC ----------

841-A Arnold Drive, Martinez, CA 94553 - ☎ (510) 229-3501- Fax: (510) 229-1651
E-Mail: sales@nalorac.com

Almost Every NMR and MRI Test Depends On This Moveable Part

. . . and **Voltronics** makes most of them. By working closely with this community of researchers and engineers for 26 years, we offer you a broad line of the latest non-magnetic precision trimmer capacitors.

Features:

- Truly non-magnetic. Distortion of magnetic field below one part per 600 million.
- Long life, non-rotating piston design.
- O-ring seal.
- Linear tuning with positive stops.
- Tuning screw does not go in and out, allowing extended shaft option.
- High Q to over 5 GHz on some parts.
- Quartz, glass, sapphire, Teflon® and air dielectrics.

Standard Line:

Over 144 catalog parts including:

- Max. capacitance from 3.5 to 120 pF.
- Peak RF voltage to 15KV.
- Greatly expanded Teflon Line.
- A .48" (12.2mm) x .23" (5.8mm) diameter 9pF Teflon trimmer with 1.5KV peak RF voltage.

Custom Design

- We'll be glad to modify a standard part or design a new one for you.

Special Designs

- Dual trimmers — Differential and Split Stator.
- Antennas and coils fused to quartz or glass tubes.
- Non-magnetic slip clutch to protect capacitor stops.

New Catalog

- Our new catalog lists many non-magnetic and standard parts. It includes data on RF peak voltage ratings and high frequency Q measurements.

For further information and our new catalog, call, fax, or write Voltronics or your local representative.

Voltronics
CORPORATION

100-10 FORD ROAD • DENVILLE, NEW JERSEY 07834
PHONE: 201-586-8585 • FAX: 201-586-3404

Teflon is a registered trademark of E.I. DuPont Co.

POSTDOCTORAL FELLOW

We are looking for a Postdoctoral fellow to study structures of large proteins by NMR. The group in Roskilde, Denmark is especially interested in applying isotope effects and heteronuclear chemical shifts combined with more traditional techniques. We are waiting for the delivery of a Varian Inova 600 MHz spectrometer and have acces to a 800 MHz instrument of the same kind. Roskilde is the burial place for danish kings and queens just 20 miles west of Copenhagen. The stipend is supposed to start in the fall.

The candidate should have a good background in structure determination of proteins by NMR.

Application including CV and a list of publications plus names of two contact persons should be sent Professor Poul Erik Hansen, Department of Life Sciences and Chemistry, P.O.Box 260, DK-4000 Roskilde, Denmark. FAX (+45) 45757721. e-mail: poulerik@virgil.ruc.dk.

Nicolet NT-200 WB available

Recently we have replaced our 14 years old Nicolet NT-200 WB apparatus by a new machine. The machine has been fully operational until now. The system consists of 4.7 T. Oxford magnet (98 mm bore); Nicolet 1280 computer (256 K memory); 5 mm H-1, 5 mm C-13, 12 mm 10-30 MHz, 12 mm 30-80 MHz probes; Samsung color monitor; Mannesmann printer; Zeta 912 plotter; VT accessory and rapid scan unit. The software includes a C-13 NMR spectrum library. If interested please contact A. Sinnema or J.A. Peters via e-mail at PETERS@TUDSV1.TUDELFT.NL or via fax: +31-152781415.

The NMR Newsletter: Small Notices:

1. Our new e-mail address is : **shapiro@nmrnewsletter**. Please don't use the previous Compuserve address.

2. We have just invested in a 90's hula hoop, aka a Web site. For those trendies without anything better to do, you can find our page at **http://www.nmrnewsletter.com**.

Please try to remain calm in the face of these earth-shaking developments.

B. L. Shapiro
2/20/96

MASSACHUSETTS GENERAL HOSPITAL ✦ HARVARD MEDICAL SCHOOL

MGH-NMR CENTER
NMR RESEARCH LABORATORIES
MGH IMAGING CENTER
MR EDUCATION CENTER

Bldg. 149, 13th Street
Mailcode 1492301
Charlestown, MA 02129-2060
Phone: (617) 726-
Fax: (617) 726-7422

Room 149-2301
Phone: 617-726-3083; Fax: -7422
Internet: jerry@nmr.mgh.harvard.edu

February 21, 1996
(received 2/23/96)

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

The "Magic Angle" Effect

Dear Barry:

A rather curious observation, known for a number of years but never satisfactorily explained, in clinical MRI of bone and cartilage is often referred to as the Magic Angle Effect. Occasionally, it is seen that the lamellar cartilage on articular (joint) surfaces, when caught in the image in cross section, has a brightness that varies with the angle between the tangent to the surface and the static field direction, and is maximal for that angle being about 55°. (The value of $\cos^{-1} 3^{-1/2}$ in the medical literature is 55°, not 54.7° as has been previously believed; as this value has yet to receive ANSI or ISO certification, I shall refer to it as θ_M henceforth.)

The effect has been discussed at length, for example in [1] and [2]. The interpretation of the effect lies in the long established arrangement of the fibrils of the highly ordered collagen protein molecules which comprise a significant fraction of cartilagenous tissue. Because of the motionally restricted nature of the protein, protons on the protein or in ordered water molecules within the tissue experience significant direct dipole-dipole coupling, which is of course minimized at the magic angle. At such orientations, the lengthening of T_2 values leads to a stronger echo signal for a given echo time, and hence increased image brightness.

Other factors which have been implicated are partial volume effects and the anisotropic effects of magnetic susceptibility boundaries between tissues.

However, there are occasionally (private) observations of the Magic Angle Effect occurring at angles other than θ_M. This raises the question of whether the effect is real. Are we perhaps dealing with higher rank tensors? A cold fusion-type phenomenon? Or something else?

The presumed connection between angle dependent apparent T_2 increases and direct dipole-dipole couplings did not sit well with me for the following reason. Figure 2 of reference [1] is often cited as the physical basis for this contrast mechanism. It displays a diagram of a representative collagen fibril with hydrogen bonded waters; at a fibril angle of θ_M, the dipolar linewidth among water protons should be minimized.

Although this sketch suggests the general concepts, it is wrong in the essential details. The angular factor $(3\cos^2\theta - 1)$ in the dipole-dipole coupling refers of course to individual spin pairs, not the molecular axis. The dominant relaxation mechanism in water is intramolecular—between the two protons of the water molecule—because of their proximity and rigid geometry. The internuclear vector between these proton pairs is not generally aligned at θ_M with respect to B_0 when the fibril axis is so aligned. In reality, these spin pair orientations will be distributed uniformly about the fibers. Dipole-dipole couplings between protons which are part of the collagen fibrils themselves will likewise arise from a distribution of angles for any orientation of the fibrils. Considering that there are many thousands of coupled spins in each collagen molecule, the likelihood that there is a distinct predominance of proton near-neighbors with coupling vectors precisely aligned with the fibril axis, and which would thus exhibit the Magic Angle Effect as described in the literature, is remote indeed.

In other words, high orientation of fiber axes does not impose similar uniaxial orientation on the vectors connecting pairs of spins on or within the fibers, as is well understood in the physical chemistry literature (witness the unusual chemical shift powder patterns of highly oriented polymers, for example).

To explore the dipolar explanation, I ran a primitive numerical simulation to convince myself of the above long winded commentary. To model the protein, I used an ensemble of rotationally disordered all trans polyethylene chains, assumed that the most significant coupling is between the geminal protons, and ignored couplings between protons on different carbons. Taking the exponential rate constant for the spin echo decay as being proportional to $\mid P_2(\cos\theta) \mid$, I summed up the echo amplitude for each member of the ensemble at various multiples of the reduced echo time $\mathrm{TE}/T_2{}^{min}$. The quantity $T_2{}^{min}$ is the T_2 corresponding to $P_2(\cos\theta) = 1$.

The results are shown in the figure for various fiber tilts. The curves correspond to different reduced echo times, and are not normalized with respect to each other. It appears that there is indeed a Magic Angle Effect, although not at θ_M, but rather approximately the compliment of θ_M. At short echo times (lower curves), most spins contribute to the signal, and the angular effect is small. At longer echo times, the short T_2 components are filtered out of the signal (*i.e.*, T_2 weighting). When the fiber angle is zero (parallel to B_0) all spin pairs have the same orientation with respect to the field. As the fiber is tilted, some of the pairs come close to θ_M, and therefore contribute to the very long T_2 component of the signal. At an angle which is significantly less than θ_M, the largest population of magic angle pairs is achieved, while past that angle, the population of magic angle pairs is reduced again.

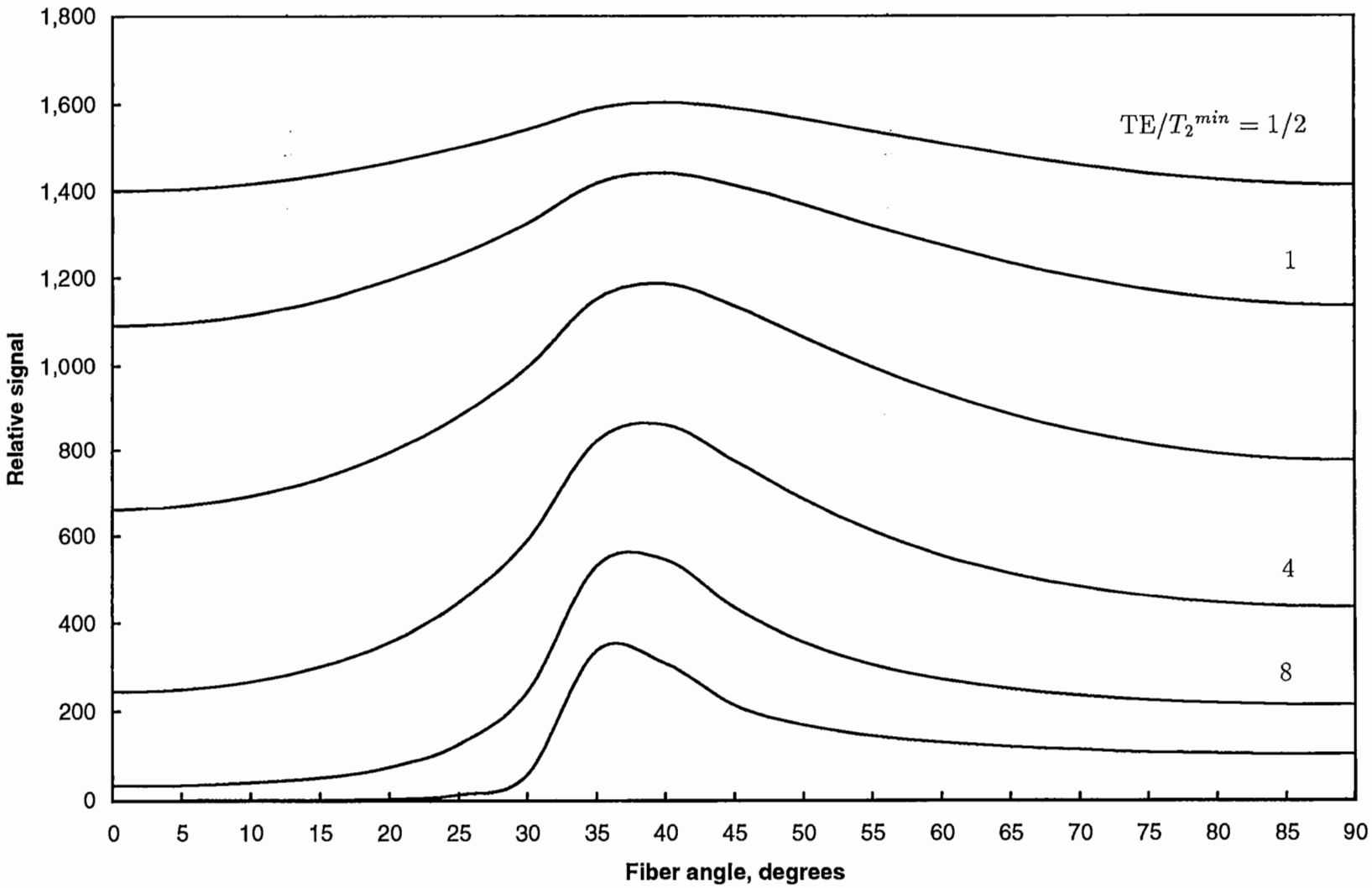
A full report is being prepared.

[1] Erickson SJ, Prost RW, Timins ME. The "magic angle" effect: background and clinical relevance. Radiology. 1993; 188: 23–25.

[2] Rubenstein JD, Kim JK, Morava-Protzner I, Stanchev PL, Henkelman RM. Effects of collagen orientation on MR imaging characteristics of bovine articular cartilage. Radiology. 1993; 188: 219–226.

Best regards,

"Magic Angle" Effect for All Trans Polymethylene



PENCE
Protein Engineering Network of Centres of Excellence
713 Heritage Medical Research Centre
University of Alberta
Edmonton, Alberta
T6G 2S2

Telephone (403) 492-6540
Fax (403) 492-1473

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

21 February 1996
(received 2/23/96)

Clean HOESY

Dear Dr. Shapiro,

Our group has been working with ^{19}F-^{1}H HOESY for some time now prompted by the exciting results of Cistola and Hall[1]. In the early testing of the sequence we found, in addition to the the expected NOE peaks, contributions from apparent multiple quantum coherences. These contributions diminish with increasing mixing time, completely disappearing at approximately one second(figure 1). In order to characterize the nature of these peaks we subjected the sequence to rigourous NMR testing but we did not find any satisfactory answers in the retinue of standard tests that were performed.

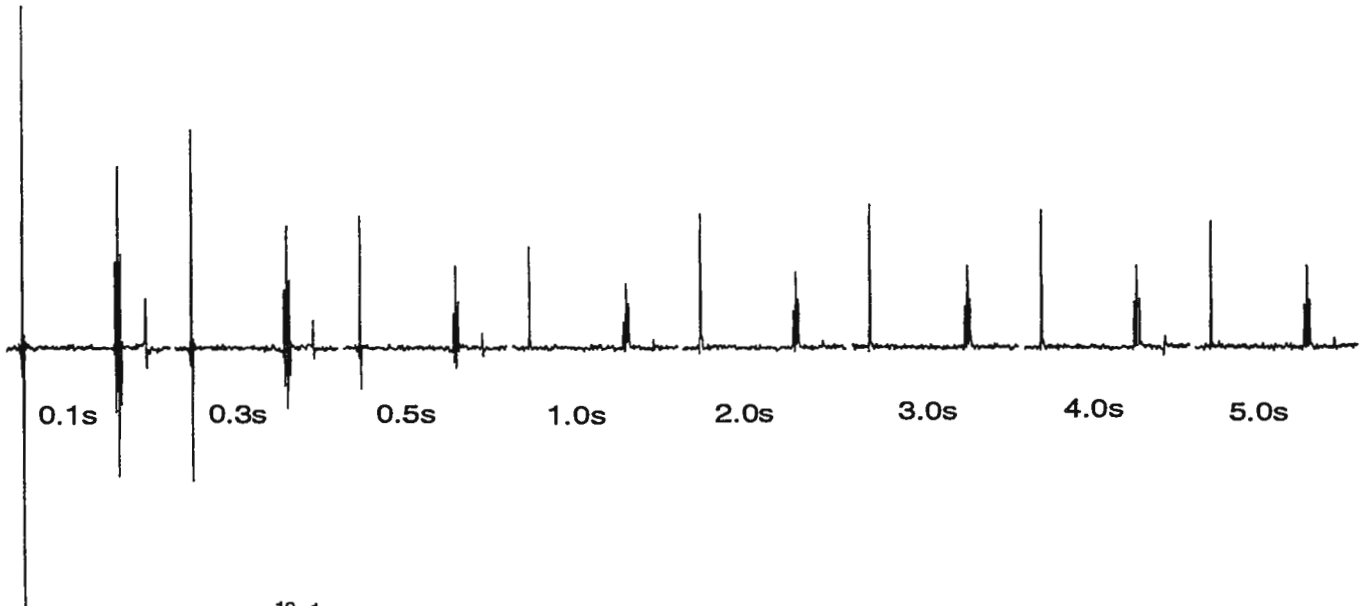


Figure 1. One dimensional ^{19}F-^{1}H HOESY NMR spectra of aqueous solutions of trifluoroacetic acid (TFA) and trifluoroethnol (TFE) acquired at various mixing times (indicated beneath each spectrum). Note that the antiphase nature of the peaks diminishes to zero at approximately one second and the NOE reaches a maximum at around three seconds. The T1 of TFA and TFE are 3.1 and 5.0 seconds respectively.

The anomolous peaks are similar in appearance to the multiple quantum crosspeaks observed in H_2O as described by various groups[2]. This observation led us to consider several explanations for the appearance of these peaks such as radiation damping, quantized radiation damping and the dipolar demagnetising field[3]. These explanations, however, did not seem appropriate due to the nature of this heteronuclear experiment, the experimental configuration (5mm sample in a 10mm probe) and the absence of gradient pulses. A viable explanation can be derived from a transient change in the nuclear susceptibility of the sample. This effect has been shown to induce phase changes and frequency shifts in high resolution NMR experiments in protonated solvents such as H_2O[4](figure 2).

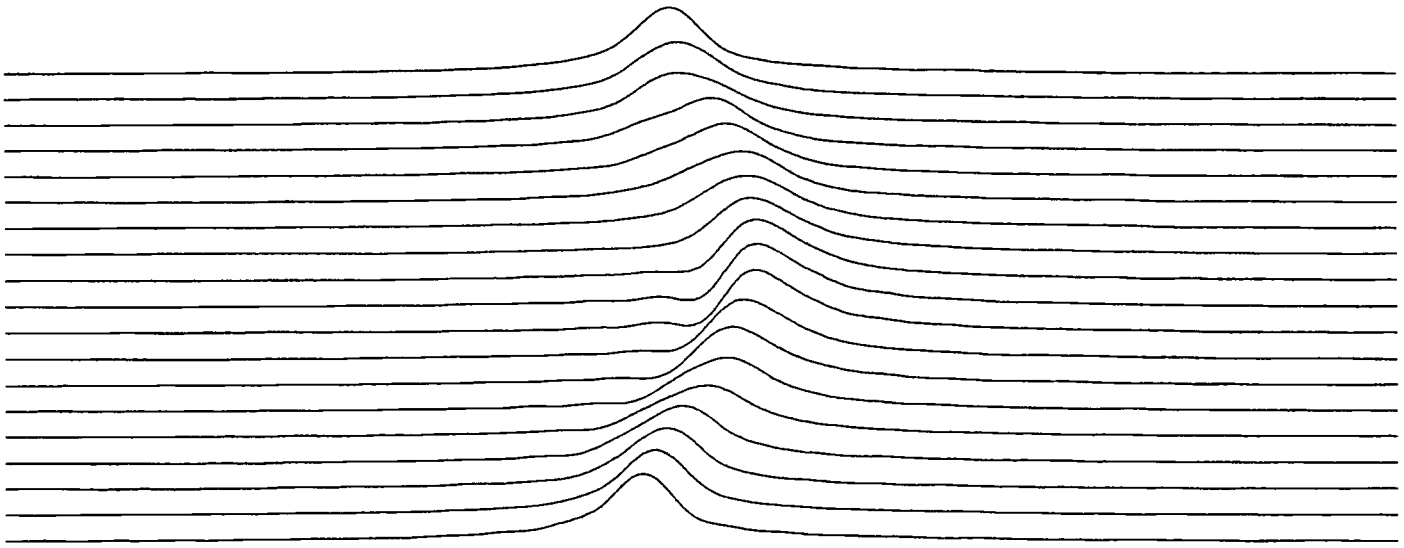


Figure 2. One dimensional ^{19}F-^{1}H HOESY NMR spectra of aqueous TFA and TFE demonstrating the effect of increasing the proton pulse angle from 20(bottom) to 340(top) degrees. The spectra were acquired without a field frequency lock and show a maximum phase change and frequency shift(0.45 Hz.) at a proton pulse angle of 180 degrees.

We have designed a number of pulse sequences and phase cycles that attempt to compensate for the phase distortions and frequency shifts induced by the proton pulses. It turns out that the insertion of an appropriately phased, composite 180 degree fluorine pulse between the final proton pulse and the beginning of the mixing time is sufficient to reduce the distortions to manageable levels even at short mixing times(figure 3).

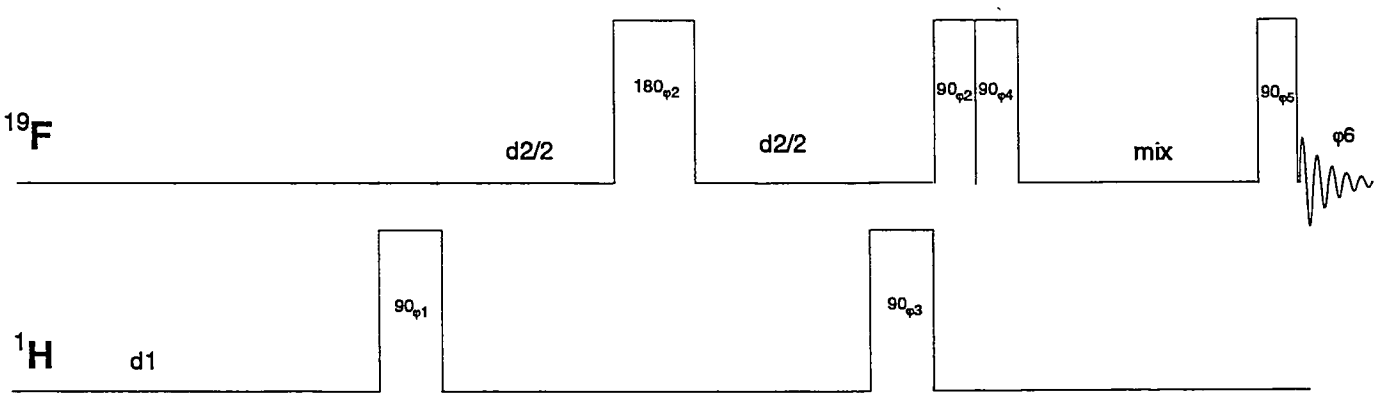


Figure 3. Pulse sequence for clean HOESY. This sequence differs from the original by the insertion of a composite 180 degree fluorine pulse following the final proton pulse and before the mixing time. The phase cycle for this sequence is: φ1=(x,-y,-x,y,y,x,-y,-x)2, φ2=y, φ3=(-x,-y,x, y,-y,x,y,-x)2, φ4=(y)8, (-y)8, φ5=(x,x,-y,-y,y,y,-x,-x)2, φ6=(x,-x,-y,y,y,-y,-x,x)2

Two dimensional ^{19}F-^{1}H clean HOESY NMR spectra (figure 4) show dramatic reductions in the unwanted contributions that arise from transient changes in the nuclear susceptibity, however the cancellation of these signals has also shown a reduction in the S/N of the experiment. We are continuing work on this problem in order to improve both the suppression and the S/N.

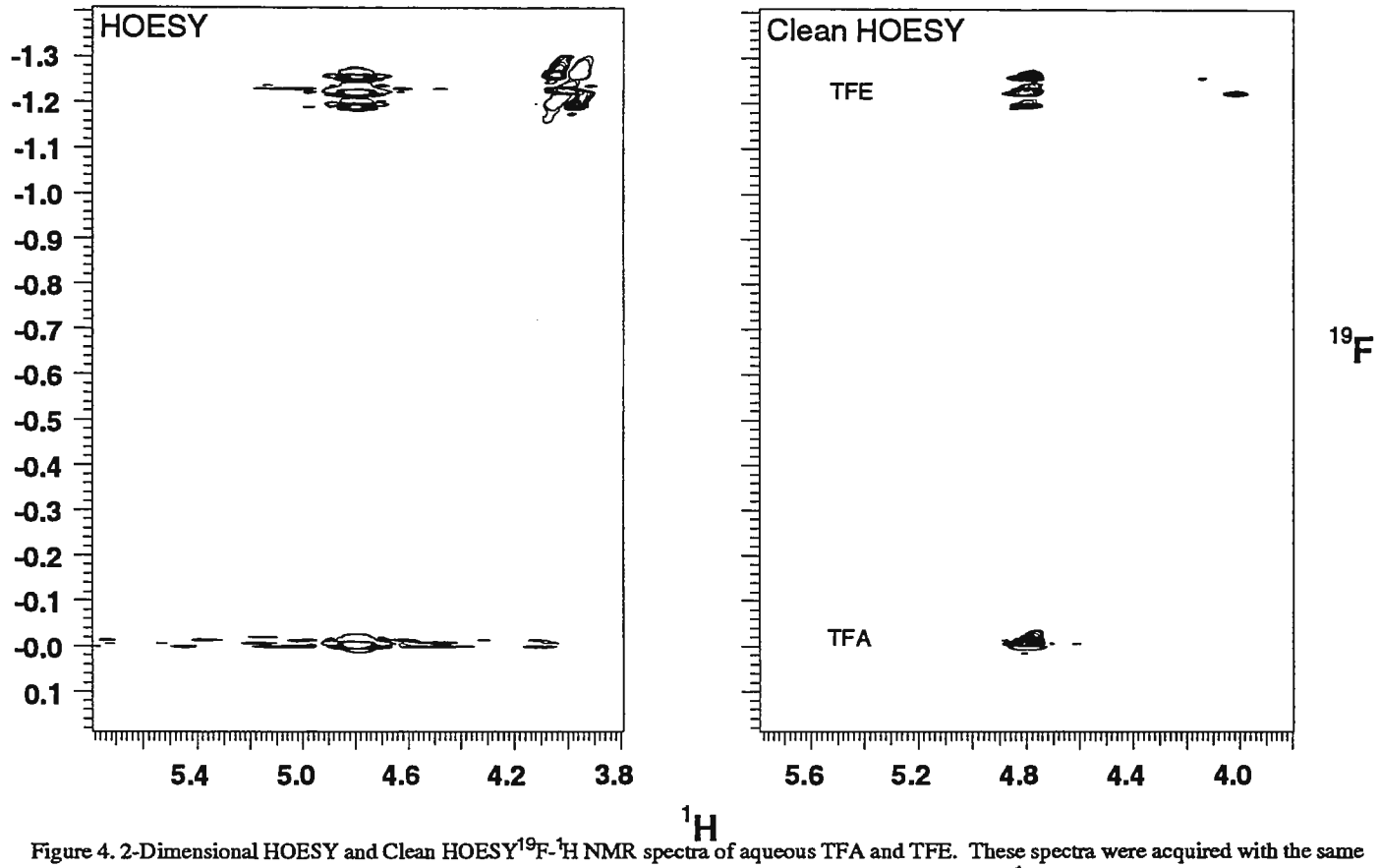


Figure 4. 2-Dimensional HOESY and Clean HOESY ^{19}F-^{1}H NMR spectra of aqueous TFA and TFE. These spectra were acquired with the same experimental parameters and are plotted at the same vertical scale. The mixing time is 0.5 seconds and no ^{1}H decoupling was employed during signal acquisition.

References:

1. D. P. Cistola and K. B. Hall, *J. Biomol NMR* **5**: 415-419 (1995)
2. W. S. Warren et. al., *Science* **262**: 2005-2009 (1993)
3. R. Bowtell, *J. Magn. Res.* **100**: 1-17 (1992)
4. H. T. Edzes, *J. Magn. Res.* **86**: 293-303 (1990)

We would like to thank Dave Cistola and Kathleen Hall of Washington University, St. Louis for providing us with the HOESY sequence and the use of their spectrometer for testing our variants of Clean HOESY.

Sincerely,

Bruce Lix Frank D. Sönnichsen Brian D. Sykes

Address all Newsletter correspondence to:

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

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

Deadline Dates

No. 452 (May)	26 April 1996
No. 453 (June)	24 May 1996
No. 454 (July)	28 June 1996
No. 455 (August)	26 July 1996
No. 456 (Sept.)	23 Aug. 1996

*Fax: (415) 493-1348, at any hour. Do not use fax for technical contributions to the Newsletter, for the received fax quality is very inadequate.

⇒⇒⇒ E-mail: shapiro@nmrnewsletter.com [Do not use the previous Compuserve number.]

http://www.nmrnewsletter.com

FORTHCOMING NMR MEETINGS, continued:

XVIIth International Conference on Magnetic Resonance in Biological Systems, Keystone, Colorado, **August 18 - 23, 1996**; Contact: ICMRBS, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073. See Newsletter 448, 36

Missouri Magnetic Resonance Symposium (MMRS) and FACSS Meeting, Kansas City, MO, **Sept. 29 - Oct. 4, 1996**; Contact: (MMRS) Frank D. Blum, Dept. of Chemistry, Univ. of Missouri-Rolla, Rolla, MO 65409-0010; 573-341-4451 fblum@umr.edu. (FACSS) 198 Thomas Johnson Dr., S-2, Frederick, MD 21702-4317.

38th ENC (Experimental NMR Conference), Orlando, FL, **March 23 - 27, 1997**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073.

4th International Conference on Magnetic Resonance Microscopy "Heidelberg Conference in Albuquerque", **Sept. 21-15, 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.

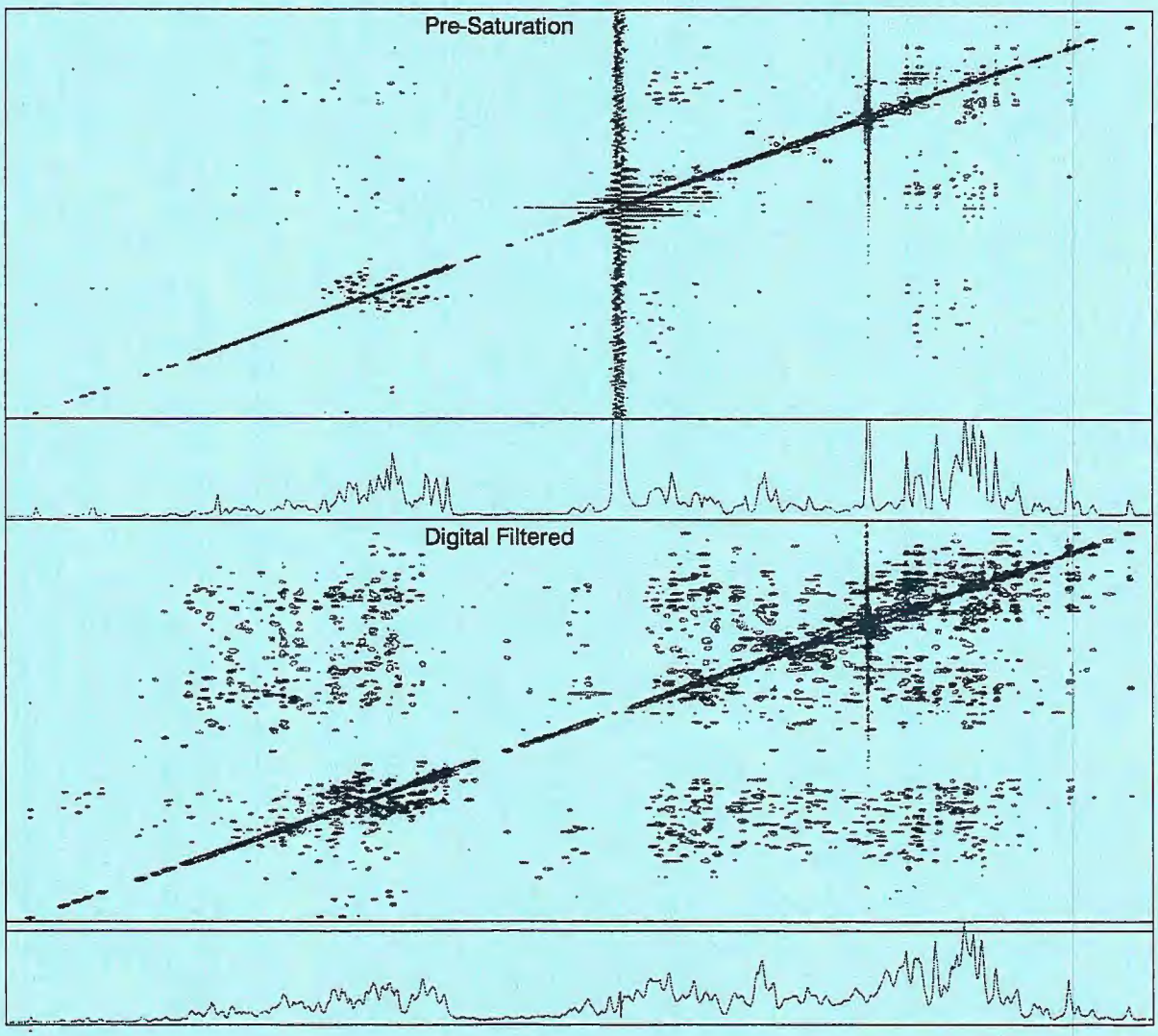
Additional listings of meetings, etc., are invited.

The Newsletter's fiscal viability depends very heavily on the funds provided by our Advertisers and Sponsors. Please do whatever you can to let them know that their support is noted and appreciated.

Mailing Label Adornment: Is Your Dot Red ?

If the mailing label on your envelope is adorned with a large **red dot**: this decoration means that you will not be mailed any more issues until a technical contribution has been received.

ECLIPSE NMR Advantage: Digital Filtering



Eclipse NMR *The Better Way!*

This data shows the digital filtering capability of JEOL USA's ECLIPSE NMR workstation. Eclipse does digital filtering via software after the data is acquired, not via hardware during acquisition. This offers a significant advantage because with software digital filtering the acquisition is completed before you filter the data.

JEOL feels spectrometer time is best spent acquiring new data rather than repeating experiments because conditions were not optimized. It takes more time to write this kind of software, but JEOL took the time. Now you can use the ECLIPSE NMR Advantage to your advantage.

JEOL USA, Inc.
11 Dearborn Road
Peabody, MA 01960
Tel: 508/535-5900
FAX: 508/536-2205
EMAIL: NMR@JEOL.COM

JEOL
Analytical Instruments Division
MS · NMR · ESR