THE NMR NEWSLETTER

No. 491

August 1999

PTS FREQUENCY SYNTHESIZERS

FREQUENCY GENERATORS, AGILE, QUIET, FAST

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PTS FREQUENCY SYNTHESIZERS

	Frequency Range	Resolution	Switching Time	Phase-Continuous Switching	Rack-Mount Cabinet Dim.[1]	Remote-Control Interface	Price Example[2]
PTS 040	.1-40 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$5,330.00 (1 Hz resol., OCXO freq. std.)
PTS 120	90-120 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$5,330.00 (1 Hz resol., OCXO freq. std.)
PTS 160	.1-160 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$6,495.00 (1 Hz resol., OCXO freq. std.)
PTS 250	1-250 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$7,440.00 (1 Hz resol., OCXO freq. std.)
Type 1 **PTS 310** Type 2	.1-310 MHz	1 Hz	1-20μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	1 Hz resol., OCXO: $6,425.00 1 Hz resol., OCXO: $5,850.00
PTS 500	1-500 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,720.00 (1 Hz resol., OCXO freq. std.)
PTS 620	1-620 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$9,625.00 (1 Hz resol., OCXO freq. std.)
PTS 1000	0.1-1000 MHz	optional .1 Hz to 100 KHz	5-10μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$11,830.00 (1 Hz resol., OCXO freq. std.)
PTS 3200	1-3200 MHz	1 Hz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$14,850.00 (1 Hz resol., OCXO freq. std.)
PTS x10	user specified 10 MHz decade	1 Hz	1-5μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	$3,000.00 (1 Hz resol., OCXO freq. std.)
PTS D310	two channels .1-310 MHz	.1 Hz	1-20μs	standard	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,560.00 (.1 Hz resol., OCXO freq. std.)
PTS D620	two channels 1-620 MHz	.1 Hz/.2 Hz	1-20 μs	standard	5¼"H×19"W	BCD (std) or GPIB (opt)	$13,240.00 (.1 Hz/.2 Hz resol., OCXO freq. std.)

1 Bench cabinets are 17" wide.
2 Prices are U.S. only and include Manual and Remote (BCD) Control; PTS 3200 Digital Front Panel.

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FORTHCOMING NMR MEETINGS

SMASH No. 1 (*S*mall *M*olecules *A*re *S*till *H*ot), Argonne, IL, **August 15-18, 1999**; Contact: Ms. Karen McCune , (mccune_karen_a@ lilly.com, 317-276-9783) or S. R. Maple (maple_steven_r@lilly.com) or G.E.Martin (gary.e.martin@am.pnu.com) or A. G. Swanson (alistair_swanson@sandwich.pfizer.com. See Newsletter 487, 17.

Applications of NMR to Complex Systems, symposium at the American Chemical Society Meeting, New Orleans, LA, **August 22-26, 1999**; Contact: R. E. Botto, Symposium Chair, Chemistry Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439; 630-252-3524; Fax: 630-252-9288; E-mail: robert_botto@qmgate.anl.gov

NMR Technologies: Development and Applications for Drug Discovery, Baltimore, MD, **November 4-5, 1999**; Contact: Cambridge Healthtech Institute, 1037 Chestnut St., Newton Upper Falls, MA 02464; el. 617-630-1300 or (in U.S.) 888-999-6288; Fax. 617-630-1325; e-mail: chi@healthtech.com; www.healthtech.com; See Newsletter 491, 35.

Medical Imaging: NMR and Nuclear Tracers, colloquium at the 12th Entretiens Jacques Cartier, Lyon, France, **December 5-8, 1999**; See http://jade.univ-lyon1.fr/JacquesCartier/ and Newsletter 488, 38.

PITTCON 2000, New Orleans, LA, **March 12-17, 2000**; Contact: The Pittsburgh Conference, 300 Penn Cemter Blvd., Suite 332, Pittsburgh, PA 15235-5503; Phone: 412-825-3220; Fax: 412-825-3224; Email: expo@pittcon.org.

8th Scientific Meeting and Exhibition, International Society for Magnetic Resonance in Medicine, Denver, CO, **April 1-7, 2000**; Contact: ISMRM, 2118 Milvia Street, Suite 201, Berkeley, CA 94704. Tel. 510-841-1899; Fax. 510-841-2340; E-mail: info@ismrm.org; http://www.ismrm.org.

41st ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, CA, **April 9-14, 2000**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87505; (505) 989-4573; Fax: (505) 989-1073; E-mail: enc@enc-conference.org.

XIX International Conference on Mag. Res. in Biological Systems, Florence, Italy, **August 20-25, 2000**. Contact: Profs. Ivano Bentini or Lucia Banci, Chem. Dept., Univ. of Florence, Via G. Capponi 7, I-50121, Florence, Italy; Phone: +39-055-2757600; Email: icmrbs@lrm.fi.cnr.it; Fax: +39-055-2757555; http://www.lrm.fi.cnr.it//icmrbs.html.

Royal Society of Chemistry: 15th International Meeting on NMR Spectroscpy, Durham, England, **week of July 8-13, 2001**; Contact: Mrs. Paula Whelan, The Royal Society of Chemistry, Burlington House, London W1V 0BN, England; +44 0171 440 3316; Email: conferences@rsc.org\

Additional listings of meetings, etc., are invited.

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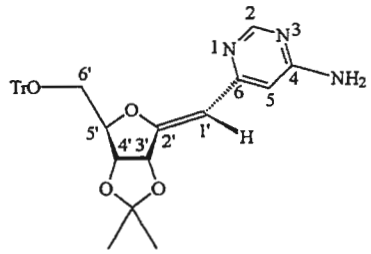
B-9000 Gent BELGIUM
Phone: ...32 9264 4475
Fax: ...32 9264 4998
e-mail: andre.debruyn@rug.ac.be

Gent, June 8th 1999
(received 7/3/99)

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

Killing illusions by QUIET-NOESY

Dear Barry,
In the course of synthesis of a split 8-azapurine we prepared compound **1** as a 50/50 mixture of the *E* and *Z* configurations. In order to obtain the compound with the correct configuration, the derivative with the Z-configuration of compound **1** had to be identified with certainty.



compound **1**: *Z*-isomer

The observed ^{1}H and ^{13}C NMR chemical shifts of both isomers of **1** did not allow to derive the configuration about the double bond, neither did the allylic long-range coupling constant between H-1' and H-3', since for both compounds the same value is found. A NOESY experiment could be very helpful, but may also be deluding if spin diffusion cross peaks occur. These are suppressed in QUIET-NOESY (1,2) by insertion of a doubly selective inversion pulse, which inverts the region around two suspected protons (quiet regions) and thus avoids unwanted cross peaks caused by spin diffusion. In the NOESY experiment of **1**-*Z*, the resonance of the aromatic proton H-5 shows cross peaks with NH2 of the base as well as with H-1' and H-3' of the ribose ring. The NOE connectitivity between H-1' and H-3'has an important structural consequence, since it points to the Z– modification. Evidently,such a cross peak is missing in the NOESY experiment of the other isomer. When the connectivity between H-5 and H-3' were true,what a proof would that be for the Z-configuration! After performing a QUIET-NOESYexperiment, with selective inversion pulses at δ 6.43 (H-5) and δ 4.69 (NH2) (H-1' being the proton that mediates diffusion) it seems that the H-5/H-3' connectivity is a diffusion peak. Independent other methods (consideration of the polarity) confirmed the conclusion from the NMR experiment We did not use a Gaussian cascade inversion pulse Q^3 as suggested in reference (2), but an i-SNOB-3 inversion pulse (3).

Sincerely Yours

André De Bruyn Serge Van Calenbergh Jan Schraml* Roger Busson** Piet Herdewijn**

*Academy of Sciences of the Czech Republic, Institute of Chemical Process Fundamentals, Rozvojova, 135, Prague 6, CS -165 02, Czech Republic. ** Lab Medicinal Chemistry, Rega Institute, KULeuven, Minderbroedersstraat, 10, B-3000 Leuven.

References: (1) Vincent S. J. F., Zwahlen C, Bodenhausen G, J. Biomolec. NMR 1996, 7, 169 - 172; (2) Zwahlen C, Vincent S J F, Di Bari L, Levitt M. H. and Bodenhausen G, J. Am Chem Soc. 1994 116, 362-368; (3) Kupce E, Boyd J and Campbell I. D. J. Magn Reson. 1995, 196B, 300-303

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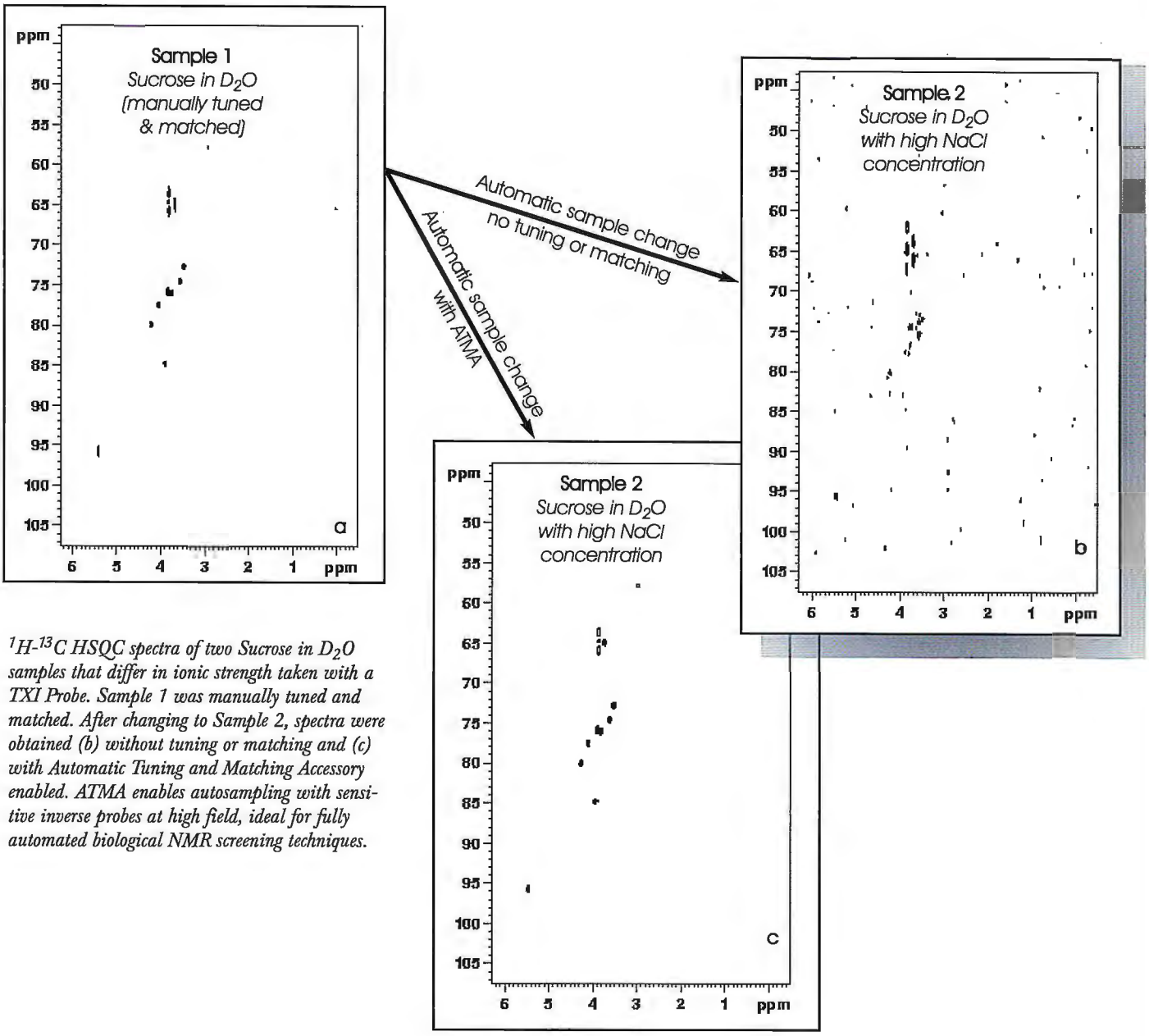
Probes incorporating an **ATM** accessory provide the maximum sensitivity, the shortest pulse widths and the largest excitation bandwith possible, all under computer control. The **ATM** accessory maximizes energy transfer from transmitter to probe to receiver and minimizes reflected power.

▲ *This new TXI Probe from Bruker incorporates an **AUTOMATIC TUNING AND MATCHING (ATM) ACCESSORY** into the probe base. **ATM** allows the spectrometer to perform tuning and matching under computer control, letting you and your colleagues concentrate on analysing results, not monitoring acquisition of spectra.*

ATM probes can be used with any AVANCE™ NMR Spectrometer with a Standard Bore magnet running NMR Suite™ 2.6 or later.



^1H-^{13}C HSQC spectra of two Sucrose in D_2O samples that differ in ionic strength taken with a TXI Probe. Sample 1 was manually tuned and matched. After changing to Sample 2, spectra were obtained (b) without tuning or matching and (c) with Automatic Tuning and Matching Accessory enabled. ATMA enables autosampling with sensitive inverse probes at high field, ideal for fully automated biological NMR screening techniques.

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Kevin H. Gardner, Ph.D.
Assistant Professor
W.W. Caruth, Jr. Scholar in Biomedical Research

Department of Biochemistry

July 20, 1999
(received 7/21/99)

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

An update on NMRView:
New version, new scripts for 2D overlays and comparisons

Dear Barry:

In my last contribution[1], I reviewed the NMRView software package[2] that has been an extremely useful tool for my NMR research. Here I'd like to tie up some loose ends from that review:

Version 4.0.3: soon after my review was submitted, an upgrade of NMRView from version 3 to version 4 was released. This has subsequently been upgraded to the current version 4.0.3 with some minor enhancements (available at http://www.nmrview.com). Most of my previous comments are valid for the current version, although one major improvement should be noted: NMRView has switched from using a binary format database over to using the text-based NMRStar format. This provides several benefits to users, facilitating the easy reading/editing/extraction of data from NMRView databases and the deposition of chemical shift data to the BioMagResBank. As well, this move allows users to more easily transfer databases among platforms with different operating systems and architectures.

Scripts for 2D overlays, comparisons: as noted in my review and demonstrated nicely by an article in the same issue of the NMR Newsletter[3], one of the great strengths of NMRView is its flexibility. The incorporation of Tcl/Tk into the heart of NMRView allows one to easily add or modify various spectral display and analysis functions. Here I'd like to briefly mention two scripts that I've recently worked up that provide new/improved functions to NMRView and can hopefully serve as a useful example to those looking to write their own scripts for NMRView or other Tcl/Tk-driven packages. All of these scripts and others are available from my lab's homepage (http://freedom7.swmed.edu), where one can also find links to other collections of NMRView scripts on the WWW.

- *overlay:* as part of the upgrade to NMRView 4.0, the useful capability to generate displays of overlaid 2D spectra was added. I've extended these somewhat, most notably by providing a simple window interface to independently change the display/plot parameters of each spectra independently of the others in the overlay (Figure 1).
- *mcsdisplay:* as shown by many groups for a wide variety of applications, the ability to identify chemical shift changes in 2D NMR spectra can be used to quickly map out sites of ligand binding or protein/protein interfaces. These analyses can be straightforwardly achieved using the Tcl/Tk interface to NMRView's peaklist and chemical shift databases and displayed using graphical or text-based outputs.

Sincerely,
Kevin
Kevin Gardner

---

[1] NMR Newsletter #481, p.19
[2] Johnson, B.A. and Blevins, R.A. (1994) "NMRView: A computer program for the visualization and analysis of NMR data" *J. Biomol. NMR* **4**: 603-614.
[3] NMR Newsletter #481, p. 5.

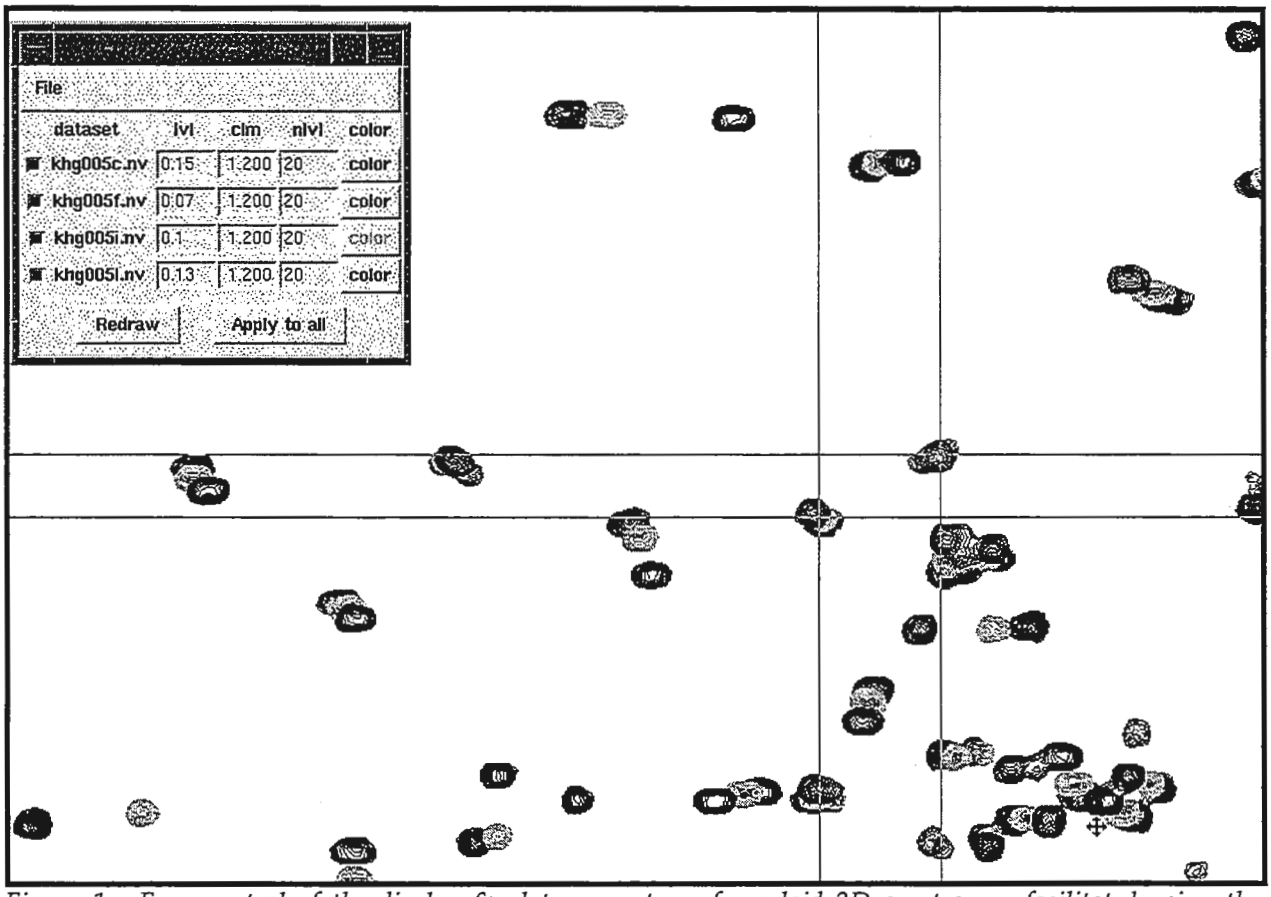


Figure 1: Easy control of the display & plot parameters of overlaid 2D spectra are facilitated using the overlay modules.

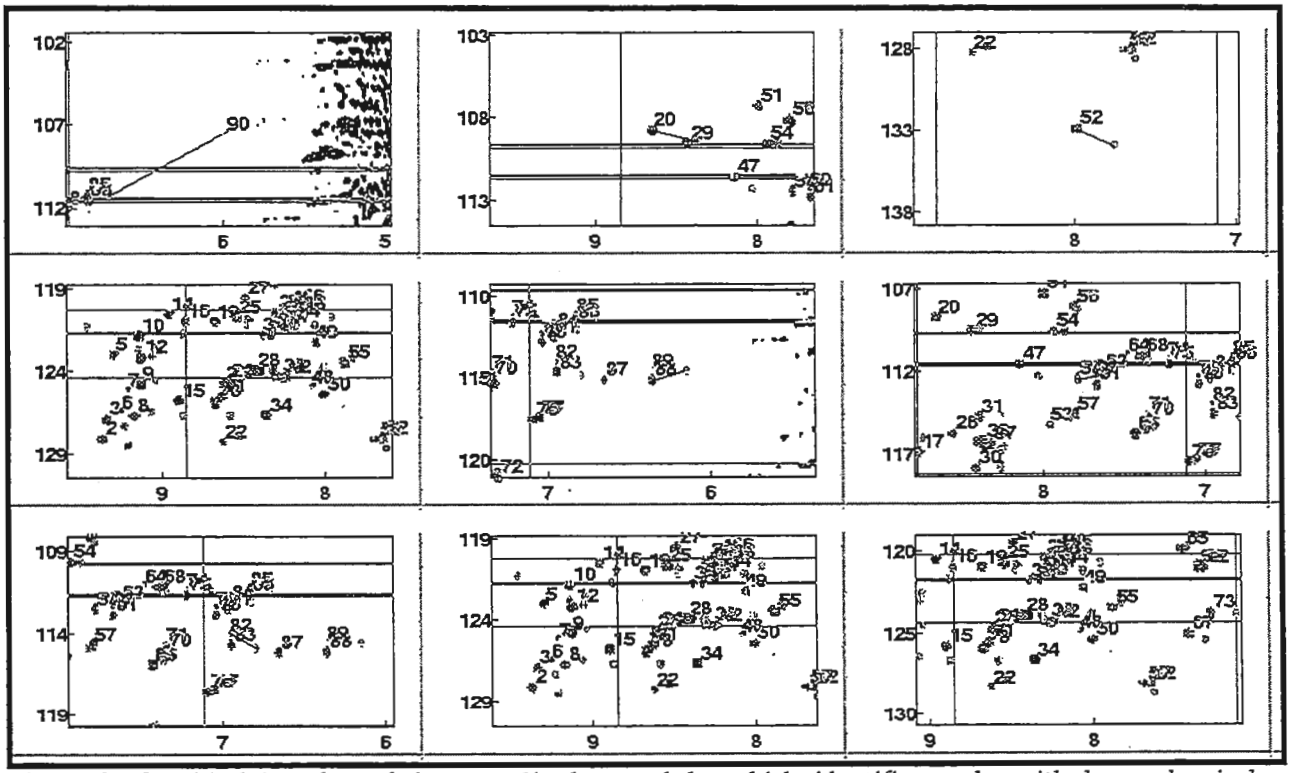


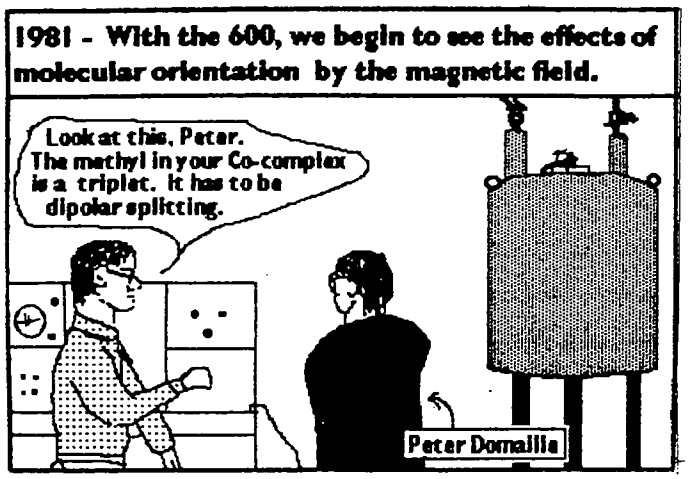
Figure 2: Graphical interface of the mcs display module, which identifies peaks with large chemical shift differences between two ^{15}N-^{1}H HSQC experiments.

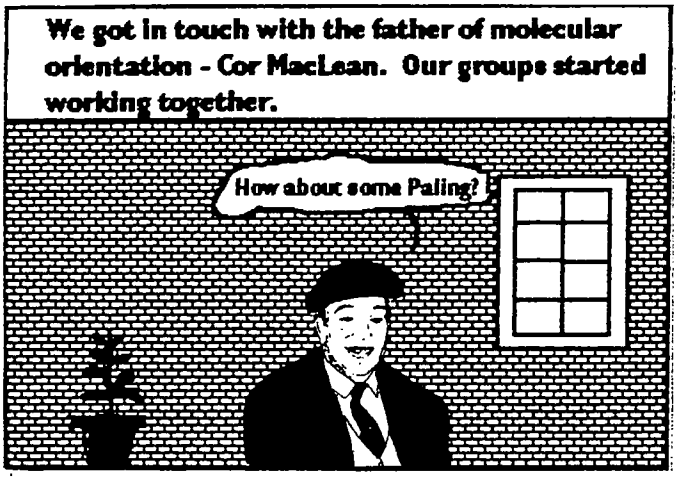
40 YEARS IN SHOW BUSINESS

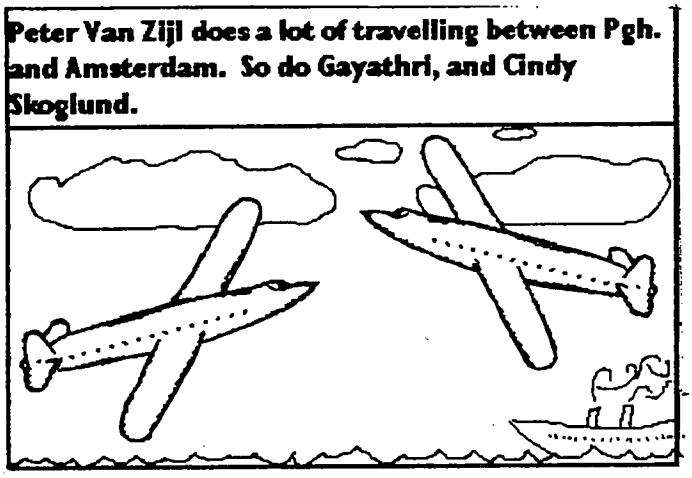
Episode 4

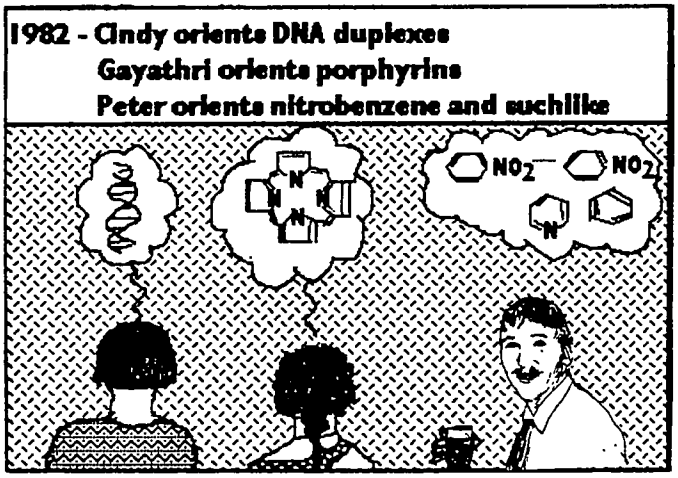
12 June 99

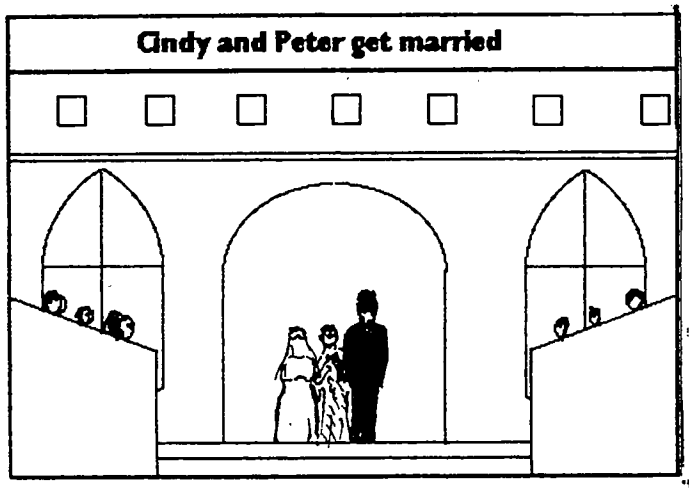
(received 7/19/99)

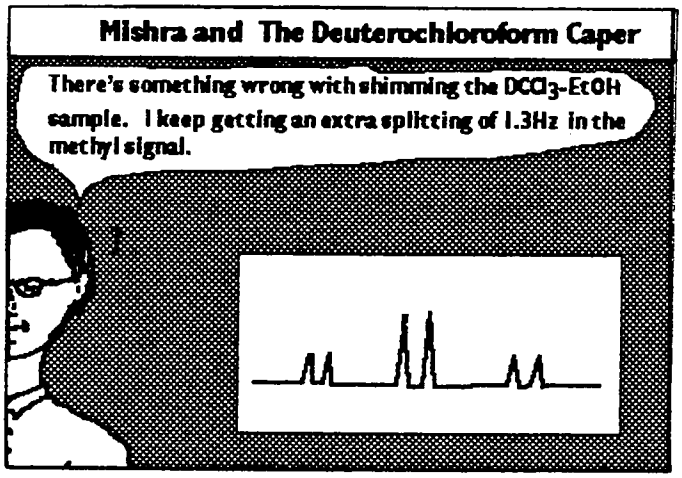






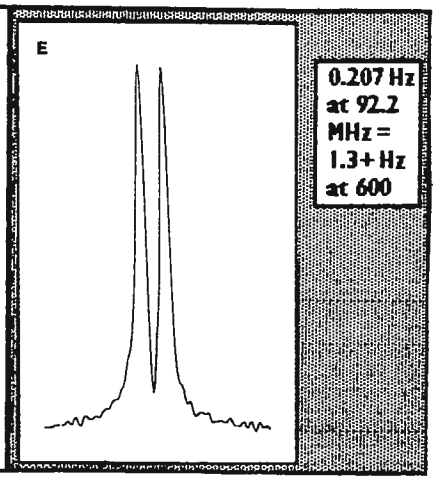




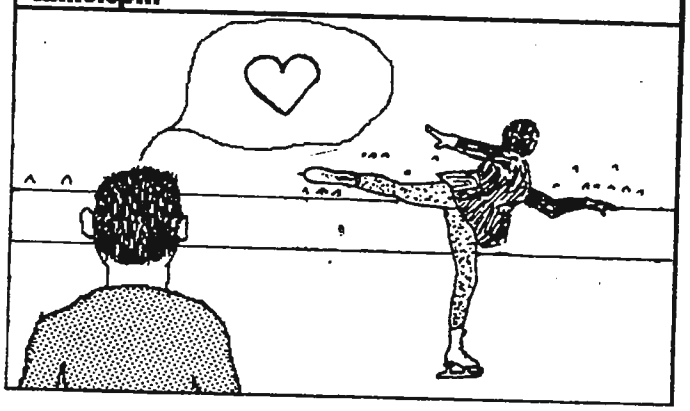


40 YEARS IN SHOW BUSINESS

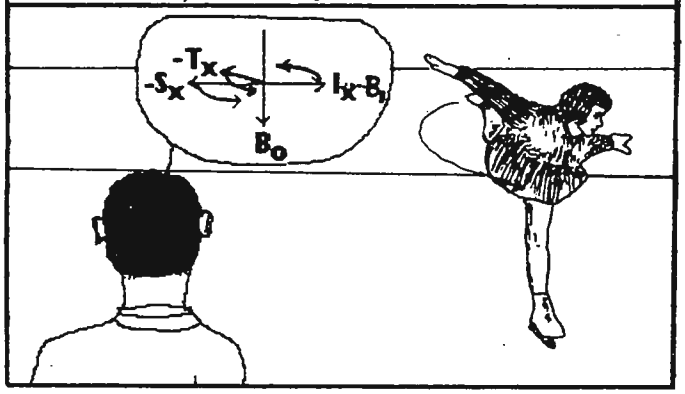
We finally looked at the deuterium lock signal from the $CDCl_3$ - It turned out to be a doublet from the quadrupole splitting, and the lock was jumping back and forth.



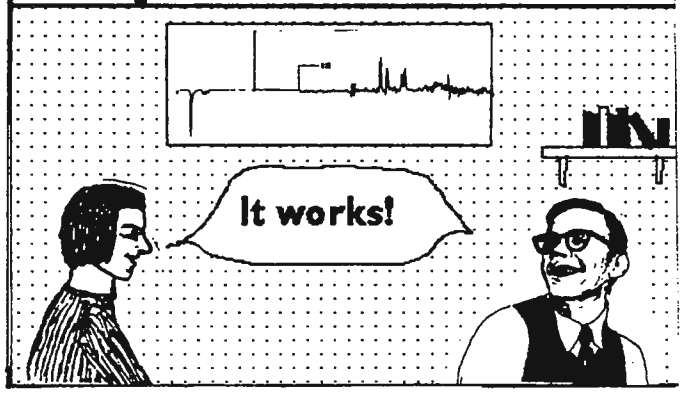
Flashback - 1952- Aksel watches Chris do a Camelspin



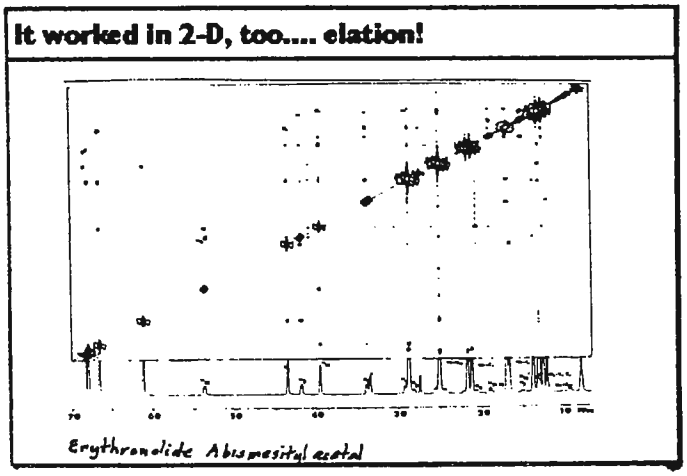
1982 - Aksel watches again, while worrying about the zero NOE, when $\omega\tau_C=\sqrt{5}/2$



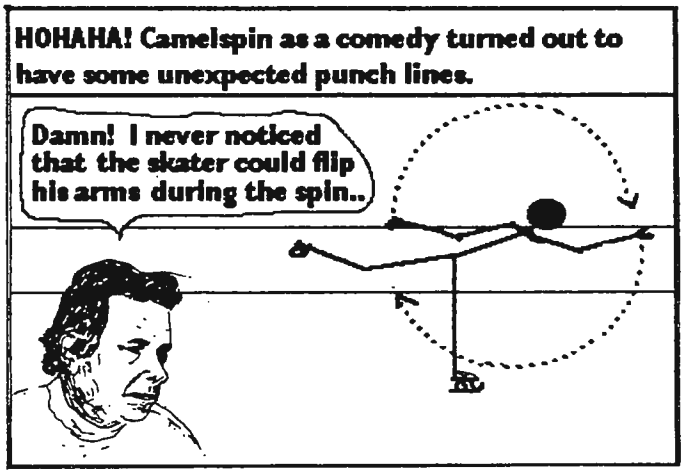
Could we get a sideways NOE? Ju-mee Lee tries it on an oligosaccharide -



It worked in 2-D, too.... elation!



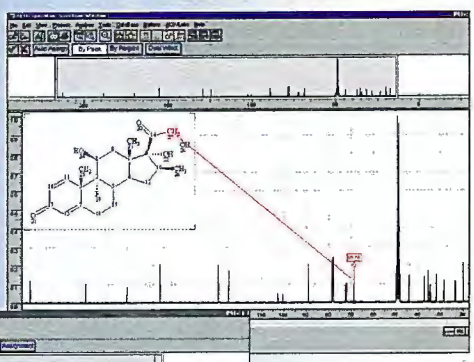
HOHAHA! Camelspin as a comedy turned out to have some unexpected punch lines.

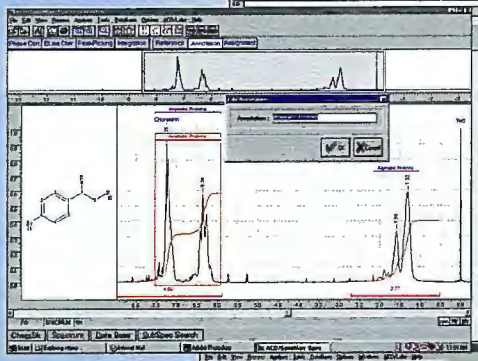


Aksel Bothner-By
ab6d@andrew.cmu.edu

ACD/NMR Processor

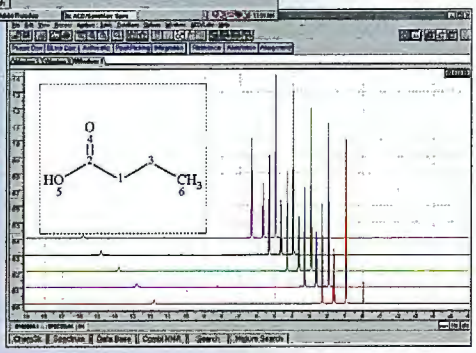
Assign a spectrum by selecting either peak or region–simply select the nucleus and drag towards the peak





On-screen annotations: ideal for identifying solvents, impurities, and polymer details including sequencing and tacticity

Overlay multiple spectra



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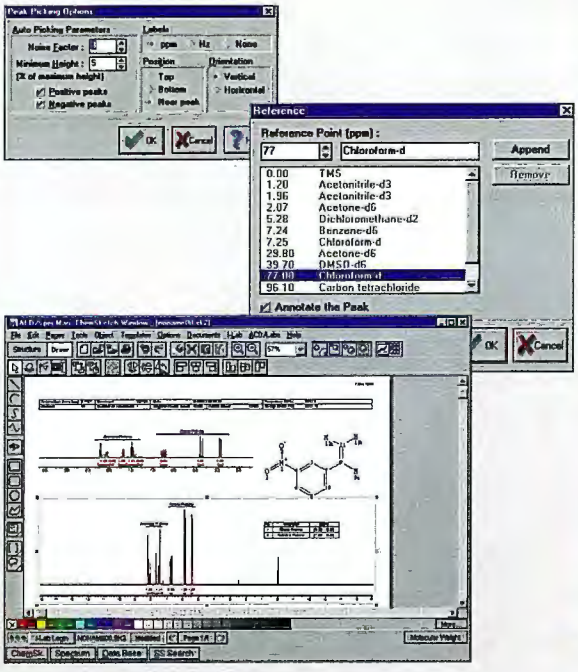

Create professional reports

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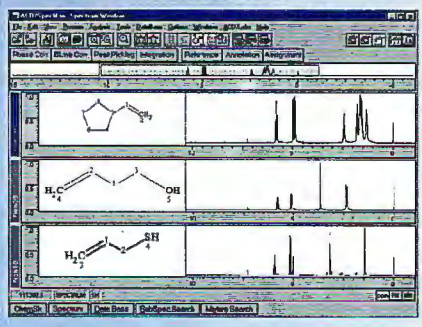

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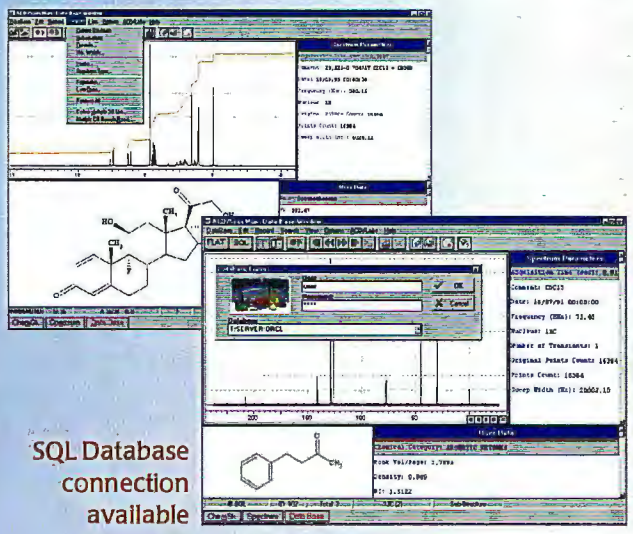

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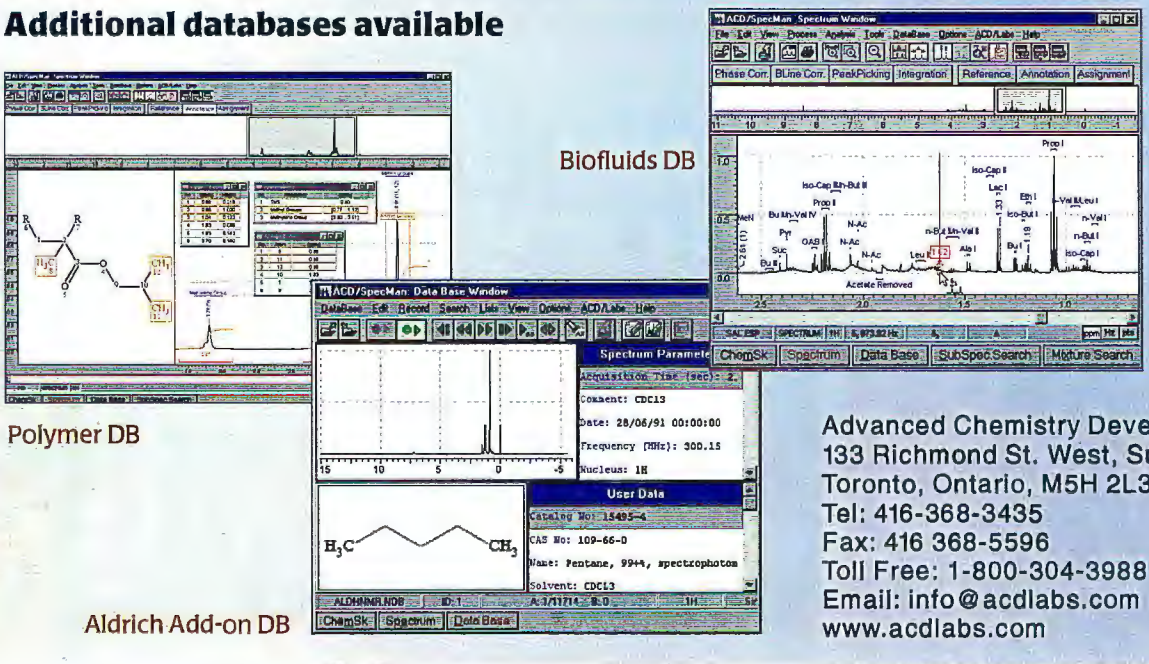

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July 9, 1999
(received 7/15/99)

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

Dear Barry:

High-temperature Pulsed Field Gradient (PFG) Probe

For the past few years, we have had a great deal of success studying polymer structure using nD PFG experiments. The PFG's are essential for obtaining interpretable spectra, as they minimize dynamic range problems. Unfortunately, until recently, PFG probes have been built to operate over a relatively narrow temperature range (near room temperature). A large fraction of the polymers we study must be heated to increase molecular mobility and/or to get them into solution. Polyethylene is an excellent example of such a polymer.

We recently accepted delivery of a Nalorac, H/C/X triple resonance probe for our 750 MHz spectrometer. This probe contains PFG coils and is designed to operate up to 130° C. We have made extensive use of this probe over the past several months (mostly for nD NMR studies of polymers). Attached are two representative spectra. The top is the PFG-HMBC spectrum of polyethylene (Figure 1a) and a selected slice at δ_H=0.91 (Figure 1c). The bottom is the phase-cycled HMBC spectrum of polyethylene (Figure 1b) and a selected slice at δ_H=0.91 (Figure 1d). The poorer signal-to-noise and numerous artifacts in the phase-cycled HMBC spectrum are from incomplete cancellation and signal distortions from improper digitization of the FID (limited by the need to digitize the large signal from ^{1}H-^{12}C of the backbone methylene carbons).

When PFG's are used for coherence selection, the receiver gain can be increased 100-fold, since the signal components from ^{1}H bound to ^{12}C never pass through the receiver system. Coherence selection is also more effective than difference methods used with phase-cycling. When phase cycling is combined with PFG coherence selection, excellent quality spectra can be obtained.

Best regards,

Peter L. Rinaldi
Professor of Chemistry &
Director of the Molecular Spectroscopy Lab

Weixia Liu
Research Assistant

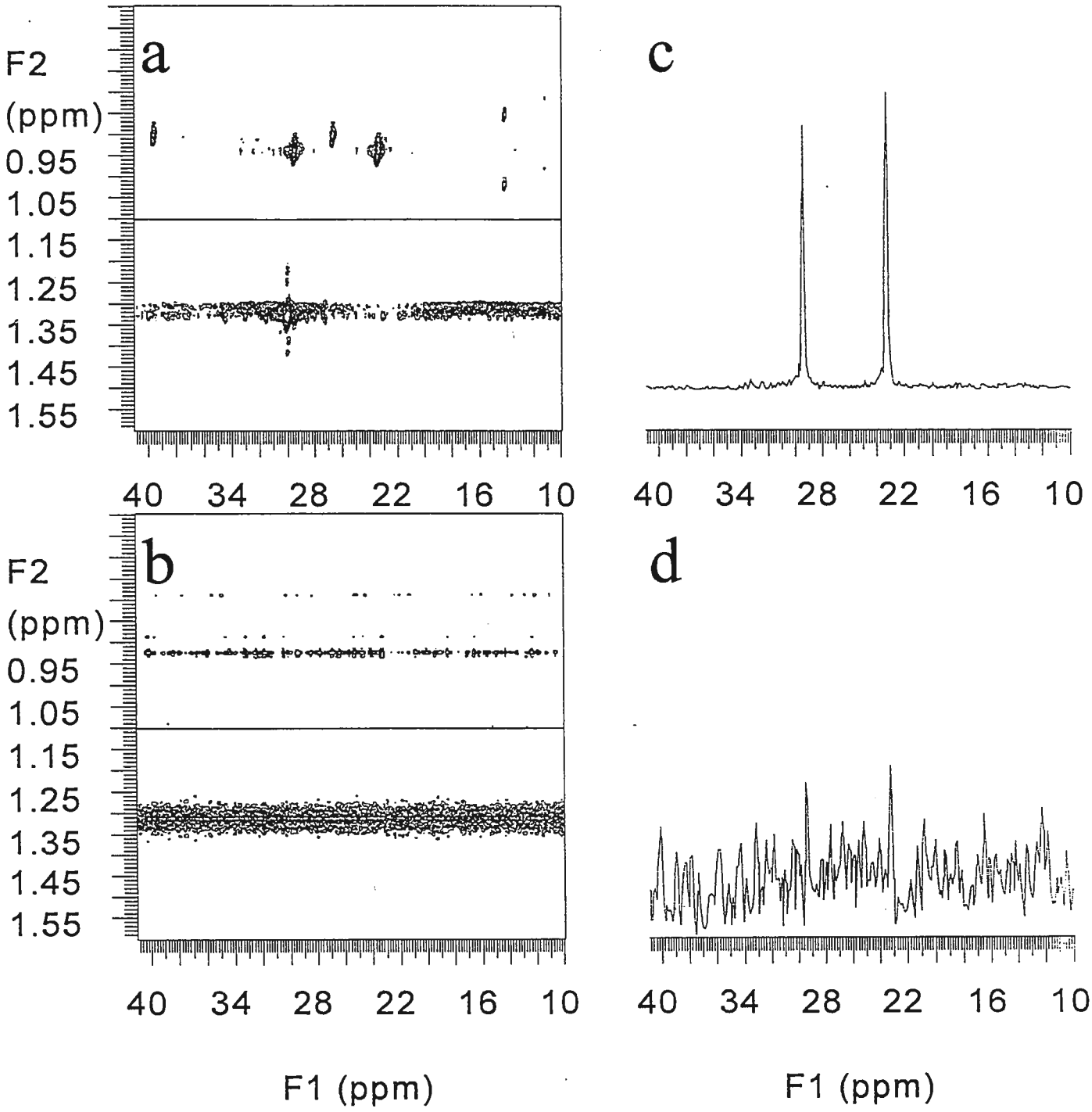

Figure 1. HMBC spectra of polyethylene (ca. 100mg) in 40% benzene-d_6 and 1, 2, 4-trichlorobenzene. a) PFG-HMBC; b) standard phase cycled HMBC; c) slice from (a) at δ_H = 0.91; and d) slice from (b) at δ_H = 0.91. The 2D-NMR spectra were obtained at 120°C with a relaxation delay of 4.0 s, Δ=1.79 ms (based on $^1J_{CH}$ = 140 Hz), and an acquisition time 0.345, eight transients were averaged for each of 1024 increments during t_1. The evolution time was incremented to provide the equivalent of a 13.9 kHz spectral window in the f_1 dimensions; and a 1kHz spectral window was used in the f_2 dimension. The gradient pulses were 2.0 ms in the duration and were 0.100 and 0.075 T/m (for the first and second PFG pulses) The total experiment time was ca. 10 hours. Data were zero filled to 4096x2048 and weighted with a shifted sinebell function before Fourier transformation. The top half of each spectrum was plotted with 6x vertical amplification to reveal the weak signals from low occurrence structures.

Novartis Pharmaceuticals Corporation
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Tel 201 503 8300

NOVARTIS

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

July 2, 1999
(received 7/6/99)

$^{1}H,^{15}N$ HSQC Spectra of the Catalytic Domain of Stromelysin (MMP-3) in Presence of DTT

Dear Dr. Shapiro,

Studies with the catalytic domain of matrix metalloproteinases (MMPs) have revealed that certain members of the MMP family require the presence of ~ 5-10 mM dithiothreitol (DTT) in buffer to prevent aggregation of the protein in solution. For example, human fibroblast collagenase (MMP-1) has been reported to show aggregation in solution without DTT present in buffer (F.J. Moy *et al.*, ***J. of Biomol. NMR***, 10, 9-19, **1997**). Moy *et al.* also noted that the $^{1}H,^{15}N$ HSQC spectrum of apo-MMP-1 in the presence of DTT shows a doubling of some resonances which disappear when a potent inhibitor is added. The proposed explanation for this phenomenon was a slow conformational change in the active site that is eliminated upon inhibitor binding. Interaction of DTT with MMP-1 was rejected as a possible cause of resonance doubling since it did not seem plausible that the inhibitor could displace DTT from all the residues exhibiting an HSQC doublet.

Because human stromelysin-1 (MMP-3) does not require DTT to prevent aggregation and since the catalytic domains of both MMP-3 and MMP-1 are structurally similar (possessing > 50% sequence identity), MMP-3 was used to examine the effects of DTT on the apo-enzyme. The $^{1}H,^{15}N$ HSQC spectrum of apo-stromelysin without DTT was obtained which revealed no doubling of resonances for this enzyme in the unbound state. We then added 5 mM DTT to the enzyme to determine if DTT interacts with apo-MMP-3. Our results showed not only a doubling of some MMP-3 amide resonances but some dramatic resonance shifts as well (Figure 1). Empirical analysis of the data suggest that residues close to the active site as well as those distant from the active site are affected (based on MMP-3-inhibitor chemical shift assignment comparison; Y-C. Li *et al.* ***Biochemistry***, 37, 14048-14056, **1998**).

These results indicate that DTT does interact with the enzyme. A possible explanation may be that the thiol of DTT weakly chelates the catalytic zinc of MMP-3 inducing a conformational equilibrium in the bound state. Upon addition of a tight binding inhibitor, DTT is displaced from the active site and a rigid enzyme-inhibitor complex is formed, yielding once again a single set of $^{1}H,^{15}N$ HSQC resonances. In view of the chemical and structural similarities that exist among the catalytic domains of MMP family members, these results strongly suggest that DTT is indeed a contributing factor to the doubling of $^{1}H,^{15}N$ HSQC resonances observed for apo-MMP-1.

Sincerely,

Xiaolu Zhang, Ph.D. Nina C. Gonnella, Ph.D.

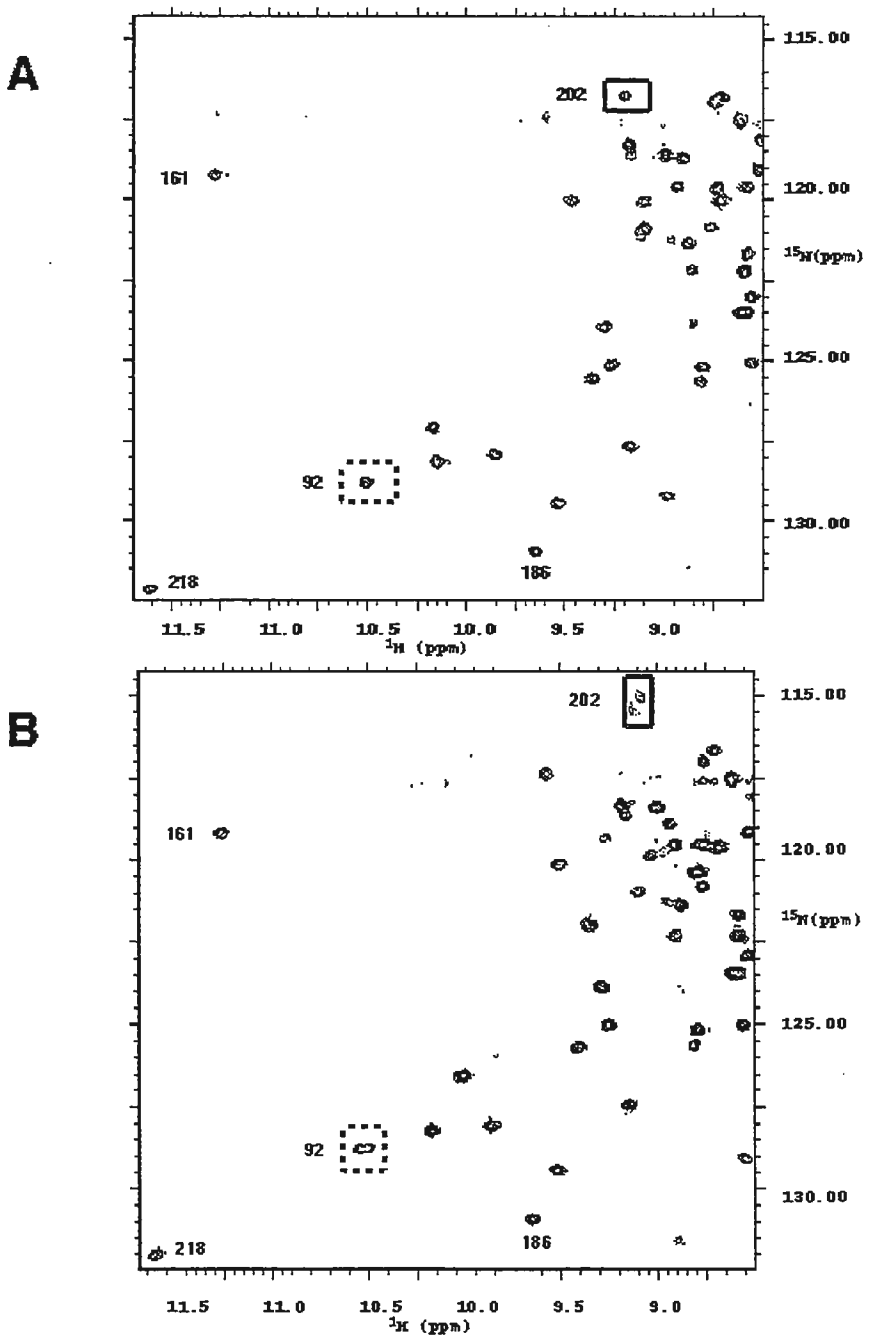

Figure 1 (**A**) Expanded region of the $^{1}H,^{15}N$ HSQC spectrum of apo-stromelysin-1 and (**B**) expanded region of the $^{1}H,^{15}N$ HSQC spectra of apo-stromelysin-1 in the presence of 5 mM DTT. Both spectra were acquired at 30 °C in buffer containing 20 mM $Tris_{d11}$, 20 mM $CaCl_2$, 0.02% NaN_3, 90% H_2O/ 10% D_2O, pH 6.8. Spectra show a doubling of Trp 92 amide ring proton and shift of Glu 202 amide resonance in the presence of DTT.

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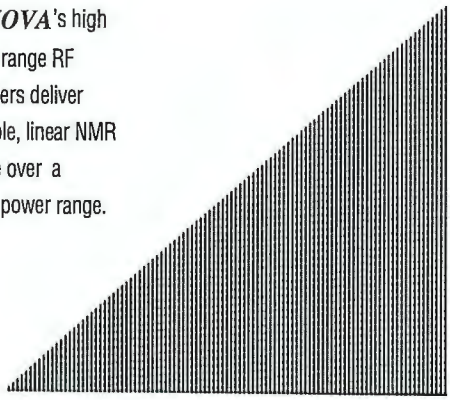

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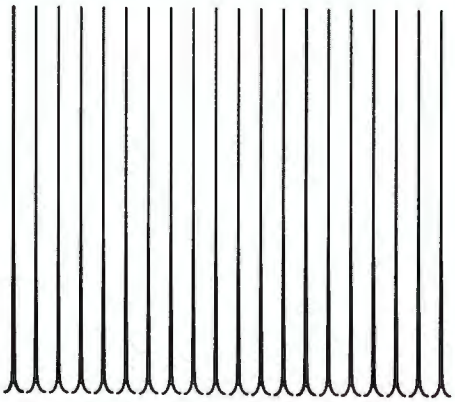

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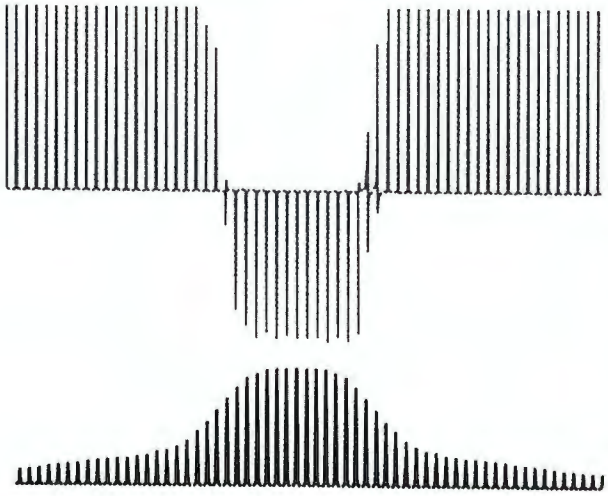

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July 27, 1999
(received 7/28/99)

Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303-3410

Early Days of NMR in the Southwest:
Fourth Installment

Dear Barry,

There are many interesting connections between the beginnings of NMR in the Southwest and the NMR pioneers in educational institutions in the East (mainly Harvard University) and in the West (Stanford University). Although not all of the early NMR efforts were great successes, they were important in the evolution of the field. As mentioned in the previous installments of this history, oil company research laboratories in Texas and California pioneered in applications of NMR to important, fundamental problems of the petroleum industry. Laboratory managers were aware of this new technology and many of them eagerly embraced it, being imbued with faith in the prospects of scientific research and having funds to pursue new ideas. I begin this installment with a laboratory that was particularly well-connected with the pioneers.

TEXACO

Gerhard Herzog, the manager of the Texaco Geophysical Laboratory in Bellaire (Houston), Texas, was responsible for starting NMR there. He and his wife were good friends of many years with Felix Bloch, a fellow Swiss. As soon as Bloch started publishing his pioneering NMR work, Herzog became convinced that NMR might be a useful tool for finding oil. Although he knew and understood few of the details of NMR, he began filing patents involving NMR to find oil, with NMR well logging being the ultimate goal.

Dr. Elmer Eisner, a theoretical physicist who was familiar with NMR, joined Texaco in March, 1951. He had taught at Rutgers in the 1940's and knew of Torrey's NMR work there. Later, he went to Argonne National Laboratory; while there, he visited with Erwin Hahn, another violinist, at the University of Illinois in Urbana and discussed NMR spin echo work. Immediately upon Eisner's arrival at Texaco, Herzog had him read and comment on his NMR well logging patent application. The patent application was filed soon thereafter (July 26, 1951). This was the first patent application for the use of NMR down a bore hole. Laboratory research to pursue the development of NMR well logging was started soon thereafter.

Charles W. Wilson, III, was hired by Herzog to work on NMR, under the supervision of B.

D. Lee, an electrical engineer. Wilson's NMR roots were from the East. George Pake received his physics Ph.D. in 1948 in Purcell's laboratory at Harvard University. In July, 1948, he went to Washington University in St. Louis and proceeded to set up his magnetic resonance laboratory in the physics department. Wilson was one of his early students and they collaborated in an early application of NMR to the study of polymers. In the spring of 1952 he received his Ph.D. and then spent the fall term at Stanford University. While there, he became friends with Felix Bloch (that was just a month before Bloch and Purcell received their Nobel Prize). Hahn had recently left Stanford to become a research physicist at the IBM Watson Computing Laboratory at Columbia and his first thesis student, Donald E. Maxwell, was writing his Ph.D. thesis under Bloch (a most painful process, according to Maxwell). Maxwell instructed Wilson in the use and maintenance of his spin-echo apparatus.

Texaco purchased a 12-inch electromagnet (serial no. approximately 9) with power supply from Varian in 1952 and Wilson built a broadline NMR machine that operated at 30 - 40 MHz, using commercial components whenever practicable. The laboratory was close to the KPRC TV tower whose signals were a constant problem, but Lee was zealous in making sure that Wilson followed proper rf shielding methods. He made NMR measurements on oil and water in sand packs with the goal of distinguishing oil from water in porous rock formations in the earth. Later, making use of Maxwell's design of spin-echo apparatus, he added spin-echo capability and was able to obtain the spin-echo from water and other simple liquids with large T_2 values. Because of insufficient rf power to obtain short pulses, he decided to stick with the broadline cw apparatus. Tests to determine whether oil-bearing rock formations could be distinguished from water-bearing formations were not encouraging. In addition, because NMR well logging was the ultimate goal, it was clear that ingenious ideas were needed to overcome the basic problem of very low signal-to-noise ratios expected from porous formations in the earth were needed. Such ingenious NMR ideas did not surface and Wilson became convinced that successful NMR well logging was not feasible. In 1956, Texaco dropped the NMR well logging project and Wilson accepted a position at Union Carbide Chemicals Co. in South Charleston, West Virginia, to perform NMR research on polymers.

Even though the laboratory project was dropped, the NMR well logging patent applications were vigorously pursued, possibly out of concern for licensing fees. In the Texaco concept, the proton NMR signal from liquids in the earth's rock formation would be observed in the magnetic field generated by a permanent magnet located in the logging sonde, whereas, the California concept involved observation of the NMR signal in the earth's magnetic field (at a much lower Larmor frequency, but with a much larger effective "sample" volume). A lawsuit was filed by Texaco Development Corporation of New York against a group of California companies, mainly Chevron, to support the Texaco ideas as expressed in their prior patent application.

At the time that the Texaco lawsuit was commenced, in the late 1960's, the California method, which made use of the Varian technique for measuring the earth's magnetic field, was being used for oil well logging by Chevron. Texaco learned about Charles P. Slichter of the University of Illinois physics department and asked his technical advice. The question was not whether the patent is the best scheme; it was about whether the patent is technically correct and then what it covers. So the question Slichter had to consider was whether or not the Texaco patent described a system which could be made to work.

Before that time, in the mid 1950's, Slichter and his student, Thomas E. Carver, had done their Overhauser effect experiment where they looked at proton NMR at the relatively low frequency

of 50 KHz where the signal-to-noise ratio is small. For the purpose of the suit, Slichter thought that Carver might be a good addition to the team and recommended that he be added. Slichter also looked carefully at how one might go about making such an apparatus and actually came up with a detailed concept of good parameters to use, including consideration of what the NMR lineshape would be.

John R. Zimmerman, then at Southern Illinois University in Carbondale, testified, on behalf of the California/Chevron group, that Texaco's ideas would not work. Of course, in the lawsuit, the Chevron group had the difficult task of proving lack of feasibility. Slichter and Carver concluded that there were no fundamental reasons why the Texaco scheme would not work; it was strictly a signal-to-noise problem. The Chevron people put together a couple of demonstrations designed to support their contention, but they never succeeded in making a clear case of infeasibility. In any event, despite the frustrations of Wilson, Texaco prevailed in the patent contest.

After the demise of the NMR well logging project, NMR at Texaco in Bellaire was dormant until 1980. Then, Robert M. Riddle left the University of Minnesota and arrived to set up the first analytical NMR effort there with the acquisition of a JEOL FX-90Q high resolution NMR spectrometer.

TEXAS CHRISTIAN UNIVERSITY AND THE UNIVERSITY OF TEXAS AT AUSTIN

The story of the importance of NMR spectroscopy to the Texas Christian University chemistry department perhaps starts with lecture by Felix Bloch in the Physics Department at Florida State University in 1954, that was attended by William B. Smith. The spectrum of liquid ethanol with the three different peaks of the three different protons convinced him of the utility of NMR spectroscopy. Then, at the American Chemical Society meeting in Saint Louis in the spring of 1961, Varian exhibited the A-60 NMR spectrometer, just a week after it was introduced. Both Smith and Bill Watson of TCU visited the exhibit. W. O. Milligan of the Welch Foundation also attended the exhibit and encouraged them to submit a proposal to acquire such a machine at TCU. They did so, and received prompt approval. That machine was operated daily for five years, when it was replaced by a new A-60. In 1967 a 100 MHz instrument (Varian HA-100) was added to their instrumentation. Their interests were, and continue to be, in the NMR spectroscopy involving organic and inorganic chemical applications.

The beginnings of NMR in the physics department had interesting antecedents. There were NMR linkages of the physics departments of Texas Christian University and The University of Texas at Austin with those on the east coast. Alfred W. Nolle received his Ph.D. in physics at MIT in 1948, specializing in acoustics. While there, he became a close friend of Herbert S. Gutowsky in the chemistry department of Harvard University, and also of Bloembergen of the Harvard physics department. Gutowsky received his Ph.D. in chemistry in 1948, under George Kistiakowsky. He went to the University of Illinois and set up NMR in the physical chemistry division of the chemistry department. Nolle moved to the physics department of The University of Texas and became interested in the applications of NMR to areas such as polymers, solid state physics, and NMR relaxation in liquids. Nolle was an excellent instrumentalist and, in the period 1954 - 1956, built a pulse NMR machine, utilizing a battery-operated electromagnet, that would be used for liquids.

In this same time frame, I was a student of Gutowsky at the University of Illinois for whom

I built the pulse NMR machine in his laboratory. The console was built from circuits designed by John C. Buchta, an electrical engineering graduate student. The system used a Varian six-inch electromagnet. Also, Gutowsky and Nolle had maintained close personal and professional contacts over the years, visiting each other every year.

In 1956, Prem Mahendroo started his Ph.D. work with Nolle. Mahendroo was an accomplished instrumentalist and proceeded to rebuild the pulse NMR machine that Nolle had built, to make it suitable for research on solids. He increased the signal-to-noise ratio, made the amplifiers more powerful to make shorter rf pulses, added phase sensitive detection, and designed and constructed a pulse programmer. Also, the battery-powered electromagnet was replaced by a Varian six-inch electromagnet.

Connections with universities in both the eastern U. S. and in India continued to be important. George B. Benedek, a Ph.D. student of Bloembergen at Harvard, carried out NMR relaxation time measurements on organic liquids as a function of pressure. Bloembergen sent Benedek's thesis to Nolle in 1956 for comments, and Nolle passed it on to Mahendroo. Mahendroo had been a student in India, carrying out research on electronic absorption spectra in organic liquids. In this work, he observed that the electronic absorption spectra changed upon degassing the liquids. Recalling these observations, Mahendroo carefully examined the experimental procedure and noted that the samples were not degassed. Because oxygen is paramagnetic, and paramagnetic ions had been observed to shorten the hydrogen relaxation times of water, he thought that Benedek's data interpretation may be affected by the presence of dissolved gasses. This suggestion was given to Bloembergen.

Then, in 1958 Mahendroo attended the seventh meeting of the AMPERE Society in Paris and met Guenther Laukien. Laukien was a German physicist who had carried out proton NMR relaxation in solutions of paramagnetic ions at the University of Stuttgart and had presented a paper at that meeting. In conversations with Mahendroo, Laukien revealed that he was considering the establishment of an NMR company. Mahendroo advised him against it, saying that setting up such a company would be too difficult and that he should continue doing physics research. Laukien did not heed this advice and, in 1960, founded Bruker Physik in Karlsruhe to make pulse NMR machines.

Around the same time, Mahendroo received his Ph.D. from The University of Texas and accepted a position in the TCU physics department. About 1960 he had one of his students construct a home made pulse NMR machine as a thesis project, using a Harvey-Wells iron electromagnet. However, Mahendroo wanted a more powerful pulse NMR machine for his research and contacted Varian to obtain one (years earlier, Varian had delivered a pulse NMR machine to Magnolia/Mobil in Dallas). However, Varian would not build him one because "there was no market to warrant building them." (This was four or five years after Varian had visited Gutowsky to assess the commercial feasibility of pulse NMR machines; the negative assessment was later reversed with the development of pulse Fourier transform NMR spectrometers.)

About this time, the first Bruker pulse NMR apparatus in the U.S. was delivered to a university in Connecticut. This machine was delivered according to a European custom in which the customer would install the machine and make it work. This machine never did work satisfactorily, because the recovery time after a pulse was too long. Laukien called Mahendroo for help, and Mahendroo became a consultant for Bruker. Mahendroo ordered a pulse NMR console

from Bruker, to be integrated with the Harvey-Wells magnet. Later, in 1965, he received the first working Bruker NMR machine in the U. S. It was installed by Bruker; Berthold Knuettel came to Fort Worth from Karlsruhe to install the machine himself. Mahendroo used this machine for many years in NMR research on solids.

SOUTHWEST RESEARCH INSTITUTE

Besides research in university and industrial laboratories, independent contract research organizations incorporated NMR in a wide range of special applications. The first work in NMR at Southwest Research Institute in San Antonio (SwRI) was for a project sponsored by Corn Industries Research Foundation (CIRF) to investigate potentially useful means for rapid measurement of protein in corn products - such as starch. The project manager was John P. O'Meara, a food scientist. William L. Rollwitz, a young electrical engineer with an M.S. from MIT, provided the electronics and instrumentation expertise. After considering, and rejecting, several measurement means from the literature, they became aware of the then recent work in NMR and recognized the possibilities offered by this new science. In 1952 Rollwitz began the design and fabrication of an NMR instrument. This was completed in late 1952 and immediately produced detectable proton signals from liquid samples. Their entire instrument was built at SwRI. It operated at a frequency of 1.0 MHz using a long, multilayer, multiturn solenoid coil (about one foot internal diameter and four feet long) with regulated direct current to provide a quite steady magnetic field of approximately 235 gauss. A second coil allowed magnetic field modulation from an audio frequency power amplifier. The sample coils were shielded and typically one to two inches in diameter and two to four inches long. The detector used a balanced bridge (very critical and not very stable) operating with a continuous wave (cw) radiofrequency excitation. It worked well for measuring hydrogen in liquids but it was inadequate for solids and proteins.

While the initial SwRI NMR work did not solve the protein measurement problem it did, however, generate a lot of interest for measuring moisture in starch and, subsequently, in many other materials. The early starch moisture work used cw detection working at higher frequencies (10-20 MHz range), with an iron core magnet and more stable instrumentation that was also developed at SwRI. The rights to this design were subsequently transferred (by CIRF) to Schlumberger-Doll Research which upgraded the instrument with the intent of marketing it as an industrial moisture meter. However, these plans did not materialize and the design and prototype were sold to Varian in 1961. Apparently the industrial process market was not ready for NMR as it then existed.

Nevertheless, at SwRI research and related efforts to develop magnetic resonance technology (both methods and instruments) to solve a wide variety of detection, inspection, measurement and control problems for industrial and governmental applications continued uninterrupted. O'Meara left SwRI in the late 50's and Rollwitz directed the NMR effort until 1972 when he became an Institute Scientist and continued in NMR R & D as a principal investigator and as an advisor and consultant until his retirement in 1991. Since 1972, Derwin King has had responsibility for the overall magnetic resonance program.

In 1955 King did the first electron spin resonance work at SwRI and developed an ESR instrument for studying radiation-induced free radicals. This was followed by many other ESR studies and instrumentation developments over the years for animal tests, free radical detection, coal quality measurements, etc. In 1960, King developed a nuclear quadrupole resonance detector and used it to study a number of nitrogen and chlorine resonances, particularly in chlorates and

hexamethylenetetramine as part of their interest in propellants and explosives. This led into a very substantial series of NMR, NQR, and ESR programs extending over many years for propellant quality control, detection of concealed explosives in airport luggage, etc.

A considerable effort at SwRI was also directed toward development of magnetic resonance instruments for on-line measurements, flowmeters, hydrocarbon gases and oils. Some interesting, unusual instruments include a tractor-driven NMR device that monitored soil moisture just below the surface (to calibrate the infrared moisture sensors in satellites), instruments that monitored drying of concrete in highway construction and the moisture content of asphalt, and mine detectors. The predominant interest of SwRI's clients continues to be the development of special sensors and associated instruments to measure moisture in products or in production processes.

There will be more history in the next installment.

Sincerely,

Don

Donald E. Woessner
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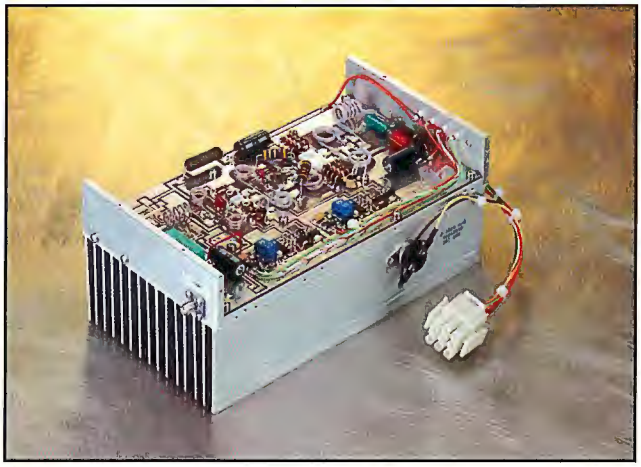

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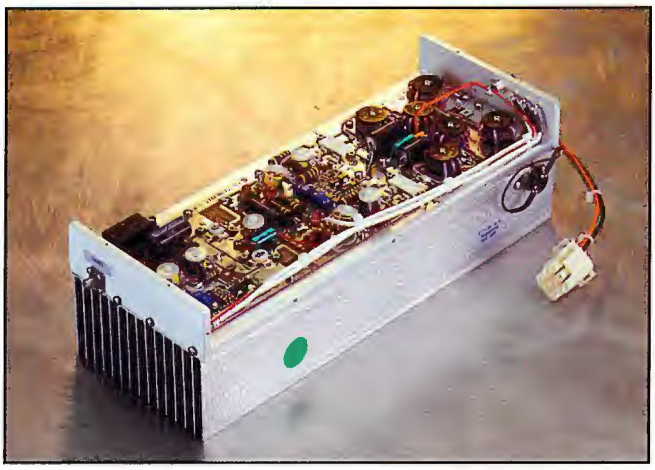

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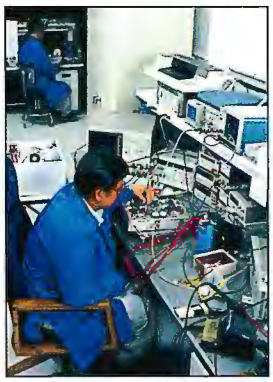

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Dr. Bernard L. Shapiro
The NMR Newsletter
966 Elsinore Court
PALO ALTO, CA 94303
USA

Vienna, July 1, 1999
(received 7/12/99)

RAY FREEMAN IN AUSTRIA

Dear Dr. Shapiro,

in answer to your call for contributions dealing with Ray Freeman I gladly present some of Ray's adventures with Austrian peculiarities which should not be concealed from the NMR community. As for the classification possibilities offered [1], I would prefer to go for "whatever"; in my experience, the "whatevers" have always been and still are among the most fascinating characteristics of Ray Freeman.

The first time that I had the pleasure to listen to Ray Freeman was at the 9th EENC in Bad Aussee in the Austrian federal state of Styria (keep this in mind, it will become important later on!) [2]. In his lecture which dealt with selective excitation [3] I was deeply impressed not only to learn that the half-Gaussian pulse which was just the rage at this time had been named after the famous mathematician Carl Friedrich Halbgauss but also to have the opportunity to admire this guy on a slide which looked rather similar to the picture at the right side.

At the same event, a reception given by local authorities was celebrated as is usually the case at congresses and symposia. The governor of Styria delegated some subordinate member of the Styrian government as his representative who delivered a boring speech, repeatedly mispronouncing the name of one of the local organizers, H. Hönig from the Technical University of Graz, as "Dr. König" (which means "Dr. King" in English). Ray Freeman, whose German is quite a lot better than he usually admits, of course got the point, and in his return address he expressed his delight of being honoured by the presence of the "King of Styria", causing amusement among the audience and total confusion of the government member.

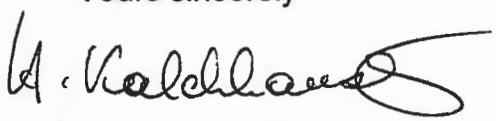
The next time I had the possibility to enjoy Ray Freeman's presence was at the Igler NMR-Tage, a two-day symposium jointly organized by the University of

Innsbruck and Varian International in Igls, a village near Innsbruck [4]. In retrospect, this event should rather be called the 1st Igler NMR-Tage, having prospered since and developped to a well-accepted biennial meeting. The title of Ray's lecture held at this opportunity already indicated his progress towards the degree "Master of Spin Choreography" awarded at the Cambridge festival [5]. On this occasion, a speakers dinner took place in a nearby restaurant. Being the time of carnival, the dinner was suddenly disturbed by some guys in (ugly) masks who for some reason tried to brush the hair of the participants with big brooms. I remember that Ray observed the incident with great amusement - however, only up to the point when the invaders decided to treat him the same way. Actually, this was the only occasion when I saw him loose his good temper.

To my knowledge, it was for a lecture given at the University of Graz when Ray Freeman visited Austria as a guest of the Austrian NMR community for the last time up to now [6]. I remember a witty and interesting presentation of the subject (J-resolved 2D NMR spectroscopy revisited), but that is nothing which has to be mentioned explicitely when talking about Ray. Alas, I had to return to Vienna immediately after the lecture and, therefore, no chance to enlarge my collections of "whatsoevers"; however, as I was informed later by colleagues from Graz, there was a lot of amusement this evening - as expected, I am inclined to add.

Taking the freedom not only to speak for myself, but for the whole Austrian NMR community, I want to express our best wishes to Ray Freeman for the future and at the same time the hope that we will soon be able to welcome him again in our country.

Yours sincerely



Hermann Kalchhauser

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[1] The NMR Newsletter, June 1999, No. 489, p 2

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[3] Ray Freeman, Jan Friedrich, Simon Davies, *Multidimensional Correlation Spectroscopy*

[4] Igler NMR-Tage, Igls/Innsbruck, Austria, February 10–11, 1994

[5] Ray Freeman, *Spin Gymnastics with Soft Pulses*

[6] *Simplification of Proton NMR Spectra by Removing Spin-Spin Splittings*, University of Graz, June 11, 1997

Prof. Dr. F. H. Köhler
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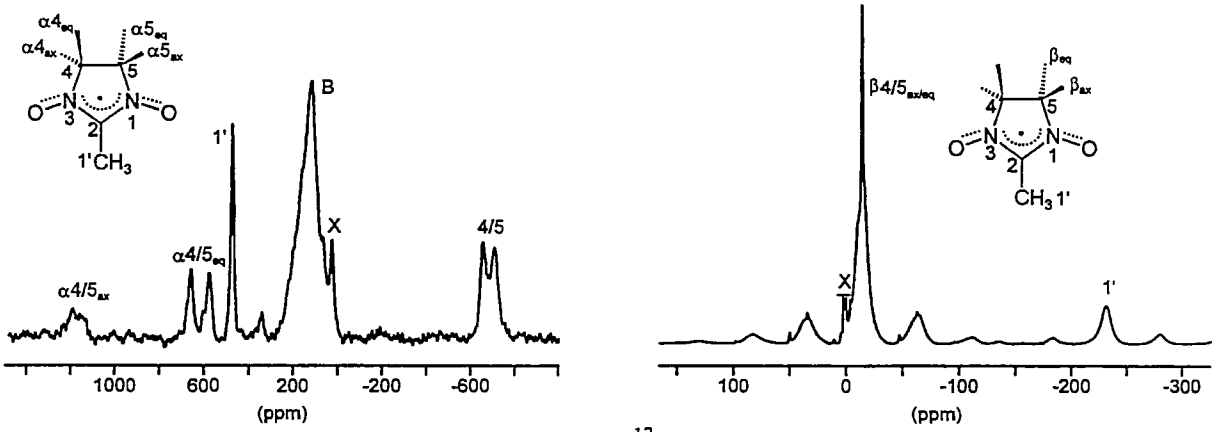
July 13, 1999 (received 7/17/99)

Solid-State MAS NMR of Nitronylnitroxide radicals

Dear Dr. Shapiro,

a rapidly increasing number of organic chemists is being attracted by materials science, and a particularly challenging topic is the assembly of organic radicals to molecule-based magnetic materials.[1] Although there are now quite some examples for which spontaneous magnetization and thus bulk-magnetic behavior has been found, the preparative chemist would be glad to have a general blue print that increases the success rate of his efforts. An important element of such a blue print is the distribution of the spin density within the paramagnetic molecule, as current theoretical approaches to magnetic interactions make use of spin densities. These can be obtained by NMR spectroscopy.

It is true that (mostly) proton NMR spectra of organic radicals in solution have been known for a long time,[2] but for comparison with magnetic measurements it is desirable to investigate solid samples. Therefore, we have started a project on nitronylnitroxides (see model in the figure) of which the *p*-nitrophenyl derivative (*β*-form) was the first to exhibit bulk magnetism.[3] It turned out that well resolved ^{13}C MAS NMR spectra can be obtained, because the signal shift/width ratio is favorable; an example is given in the figure. The signals can be assigned based on comparison of similar radicals and theoretical considerations, and the shift data can be related to spin densities. Juan Novoa's group in Barcelona has shown that the experimental results are in good agreement with DFT calculations. This is very encouraging, because it establishes MAS NMR spectroscopy as an alternative to (expensive) polarized neutron diffraction for spin mapping of radicals.



MAS NMR spectra of 2-methylnitronylnitroxide. Left: ^{13}C NMR spectrum at 30 °C, spinning rate 10 kHz; B = background signal of the probe head, X = impurity. Right: ^{1}H NMR spectrum at 41 °C, spinning rate 14,5 kHz. Unlabeled signals are spinning sidebands.

^{1}H MAS NMR spectra may be also useful. In the present example (right part of the figure) efficient hyperconjugative spin transfer to the 1'-methyl protons is evident while the distinction of the methyl groups at C4/5 is only partly possible.

Of course, the whole story is more detailed, additional topics being improvements brought about by ^{2}H MAS NMR spectroscopy, solid state dynamics and hydrogen bonding. It has been submitted for publication, and we hope you can read it soon.

Sincerely yours,

(Frank H. Köhler) (Henrike Heise)

(1) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. *Magnetic Properties of Organic Materials*, Lahti, P (Ed.), Marcel Dekker, New York, Basel, 1999.
(2) Eaton, D. R.; Phillips, W. D. *Adv. Magn. Reson.* **1965**, *1*, 103.
(3) Turek, P. et al. *Chem. Phys. Lett.* **1991**, *180*, 327.

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Professor Poul Erik Hansen
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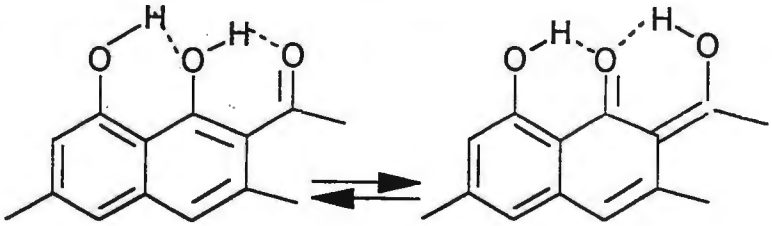
May 7 1999
(received 6/30/99)

Tautomerism of hydroxynaphthones revealed by $\Delta^{17}O(D)$ and $^{p}\Delta^{1}H(T)$ isotope effects

Dear Professor Shapiro
Recently, we have looked into use of deuterium isotope effects on ^{17}O chemical shift. Secondary isotope efffects are roughly proportional to the chemical shift range so that is promising. The drawback is clearly the very broad ^{17}O resonances. For some hydrogen bonded systems the linewidth is OK and the isotope effects are large. In addition, the measurements are done on ^{17}O enriched compounds. The chemical shift difference between a C=O and an OH oxygen is roughly 400 ppm. This kind of isotope effects should be well suited to detect tautomerism. For symmetrical systems like β-diketones the intrinsic effects were found to be close to zero as the $^{1}\Delta^{17}O(D)$ and $^{5}\Delta^{17}O(D)$ are of similar magnitude, but have opposite signs.



We certainly had some conclusive evidence for **1**, as we found an $\Delta^{17}O(D)$ of –16 ppm. $\Delta^{17}O(D) = \delta^{17}O(H) - \delta^{17}O(D)$. The intrinsic effect $^{5}\Delta^{17}O(D)$ varies considerably and is up to –8 ppm in compounds with very short O....D distances. The main cause of the large isotope effect found for **1** is an equilibrium contribution. A distinct change in the equilibrium is thus seen upon deuteriation. This is one of the first naphtalenes of β-diketone type involved in tautomerism (A is the dominant tautomer). One explanation could be that the O..O distance according to ab inition calculations is short for both tautomers.
We have also observed interesting primary tritium isotope effects for this system. Again is the equilibrium contribution considerable.

Yours sincerely
Simon Bolvig

Poul Erik Hansen

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Dr. B. Shapiro,
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June 24 1999 (received 6/25/99)

Dear Barry,

Thank you for your colorful reminder. I apologize for my tardiness, and I hope this late, colorful, epistle reaches you in time to avoid the "dreaded ultimatum".

While not studying the application of gaseous restricted diffusion to porous media characterization, we have spent time making laser-polarized liquid xenon, and considering some of the applications. We have already shown that this liquid permits extremely high sensitivity images, and the potential for very high resolution micro-images from traditional spin-warp techniques without the need to signal average [1].

Xenon liquifies at around 165 K at atmospheric pressure, and this means it is relatively easy to keep a glass cell of xenon in its liquid state for lengthy periods in an NMR spectrometer. The advent of laser polarization techniques, which enhance the polarization of xenon by 3-4 orders of magnitude compared to that at thermal equilibrium, allows the study of a gas sample with magnetization density similar to that of water. In turn, liquifying the gas once it has been laser-polarized creates a two-phase system in which both the gas and liquid have extremely high magnetization density. Xenon may be the only system that provides such a combination at reasonable temperatures that can be achieved with standard lab glassware. Therefore, laser-polarized xenon permits easy study of the gas/liquid system, with the ability to selectively pulse or observe either phase.

Our sample setup was very simple. After laser-polarization, the sealed glass cell containing 3 atm ^{129}Xe was placed in liquid nitrogen, freezing the xenon. The cell was then placed in a glass dewar containing an ice-slush bath of iso-octane, which maintained a temperature of ~ 165 K. The dewar was then placed upright in a solenoid rf coil in a horizontal 4.7T magnet with clear 20cm bore. The xenon often remained in the liquid state for 15-20 minutes, allowing lengthy NMR experiments to be performed, where the limitation was usually rf depletion of the enhanced magnetization, rather than the lifetime of the liquid droplet.

Having observed two-phase exchange between the gas and liquid [1], we hoped to quantify the evaporation and velocity of the convection in the gas above the evaporating liquid, as Seymour et al. have done previously in water [2]. The Pines group has recently demonstrated velocity profiles measured from laser-polarized xenon flowing through a pipe inside an NMR spectrometer [3]. However, the nature of convection inside a sealed system dictated that we use full spatial resolution, and so acquire 2D velocity images of the xenon gas above the liquid droplet. To enhance this effect, the xenon was preferentially frozen along one side of the glass cell, and held in the liquid nitrogen longer, to ensure one side of the glass cell was colder than the other.

Once the cell was in place in the rf coil, small flip angle pulses monitored the xenon spectrum until the broad solid peak disappeared. At this stage, full velocity encoded image data sets, using the Fourier method of Callaghan [4], were acquired in 1 cm thick slices at various positions up the tube. Typically, two complete velocity images could be obtained from each sample, each image resulting from 64 k-space rows with 8

velocity encoding gradients, for a total of 1024 low-flip angle excitations, over about 5 minutes of acquisition time. As the gas is laser-polarized, it is preferable to omit the 180° pulse, and so the base sequence was a pulsed gradient echo [5]. The sequence is illustrated in Fig. 1.

The velocity images are shown in Fig. 2. Images at three different slice locations up the tube are shown – just above the liquid droplet, in the middle of the tube, and near the top. For each slice, an image was acquired with velocity encoding parallel to the tube (y axis – images on left side of the page), and another with the velocity encoding transverse (z axis – images on the right). The intensity scale is consistent for the y or z velocity image at all slice positions, but not between the series of images. In the images with y axis gradient encoding, the peak velocities are + 40 and – 40 mm/s, while for the images with z axis encoding, velocities are + 6 to – 6 mm/s.

The largest amount of flowing gas, and the highest velocities are, as expected, observed just above the liquid droplet, when velocity encoding is parallel to the tube. Here, the liquid is evaporating and the gas beginning to move up the warmer side of the tube (left side of tube in the image). On the other, cooler, side of the tube, the cooling gas is heading back down the tube, before condensing into the liquid drop again. Observation further up the tube shows this same consistent pattern, with high positive and negative velocity at the left and right edges of the tube, respectively, and negligible upwards velocity in the middle of the tube. However, the magnitude of the velocity, and the amount of gas undergoing coherent motion decreases further up the tube, away from the liquid droplet. Velocity in the plane of the tube is less obvious. Only at the top of the tube is there coherent motion in one direction, from left to right of the tube. Otherwise, velocity is negligible incoherent across the tube, as may be likely if the gas is cooling, and changing from upward to downward motion in the tube.

We hope these images illustrate the power and speed of velocity encoded imaging of flow laser-polarized gases, and are that they reproduce satisfactorily for your readers.

Sincerely,

Ross Mair Glenn Wong David Cory Ron Walsworth

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[2] B. Manz, J. Seymour and P. Callaghan, *J. Magn. Reson.*, **125**, 153 (1997)
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[5] R. Mair, D. Cory, S. Peled, C-H. Tseng, S. Patz and R. Walsworth, *J. Magn. Reson.*, **135**, 478 (1998)

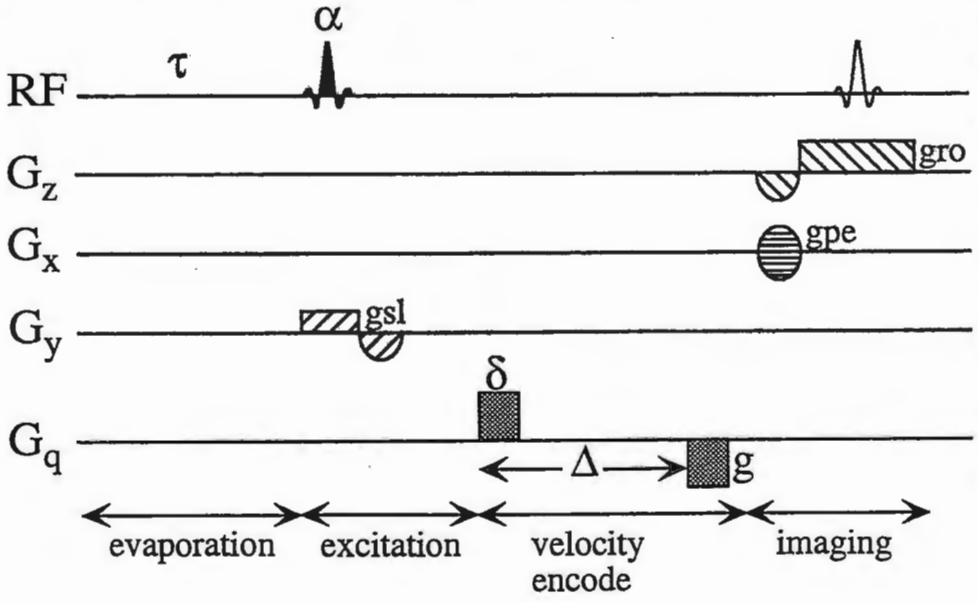

Figure 1: Pulse sequence for velocity imaging of convection in laser polarized xenon gas. The sequence is a modified PGSE technique, omitting the 180° pulse and using a gradient echo from the bipolar velocity encoding pulses to refocus spins. This method is preferable for laser-polarized samples, due to the ability of the 180° pulse to waste non-renewable enhanced magnetization. Velocity encoding gradients were applied along either the y or z axes, depending on the directionality of velocity encoding required.

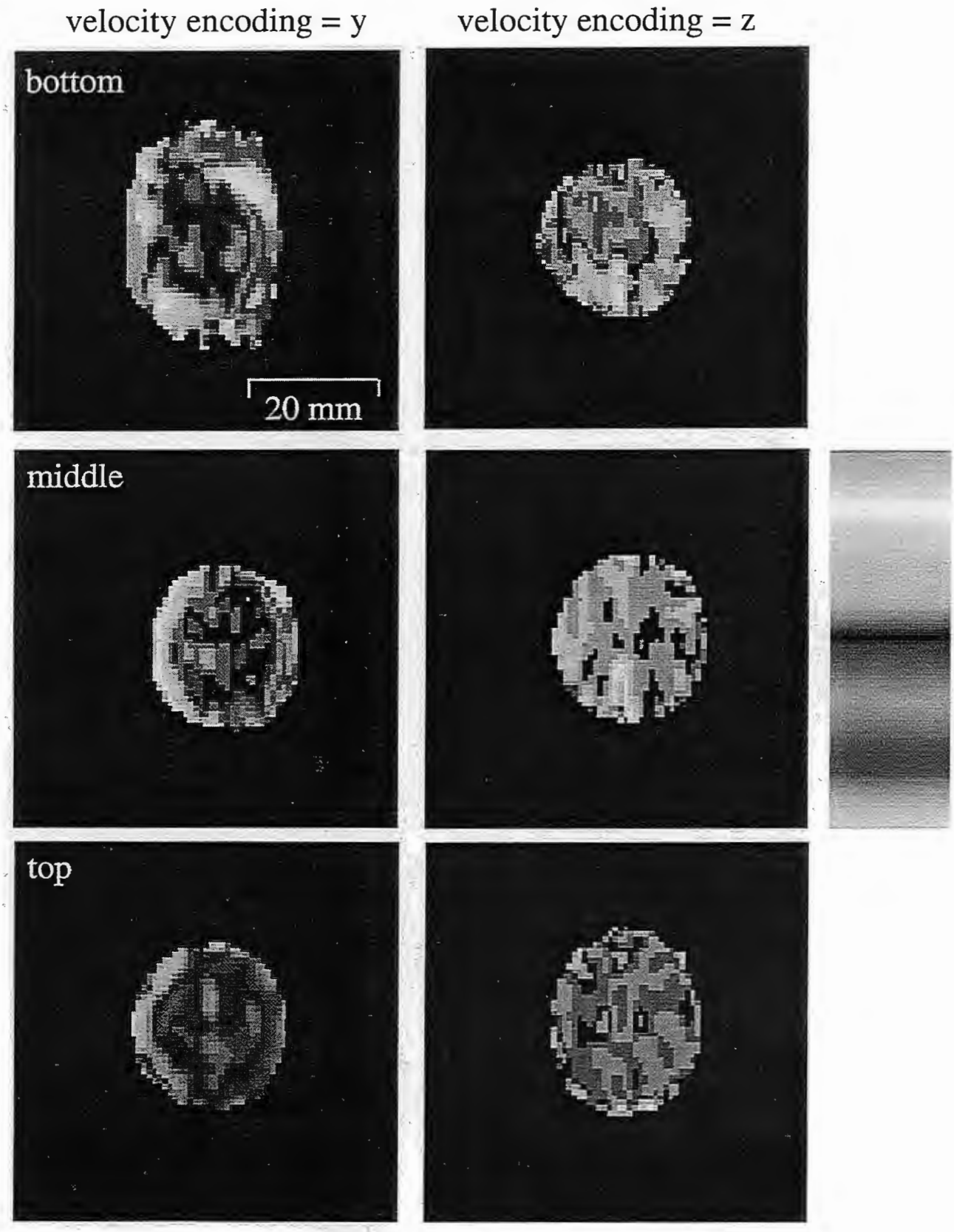

Figure 2: Velocity images of laser-polarized xenon gas undergoing convection above a liquid droplet, imaged to 3 different slice positions up the tube. Color intensity indicates velocity variation. The left column shows velocity along the length of the tube, ranging from +40 to -40 mm/s peak values. The right column shows velocity across the tube, and ranges from +6 to -6 mm/s peak values. Black denotes zero velocity.

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P.O. Box 5800
Albuquerque, NM 87185-1407

July 14, 1999
(received 7/20/99)

Bruker AMX Y Channel Heteronuclear Decoupling Using a Linear Amplifier[1]

Dear Barry,

Under both static and common MAS conditions (< 15 kHz) the question of residual X-Y heteronuclear decoupling can become a complicating factor in the analysis of various NMR results. In our lab the impact of ^{31}P-^{23}Na dipolar coupling on the observed ^{23}Na M_2 relaxation for a series of sodium phosphate glasses was recently investigated by employing continuos wave ^{31}P decoupling during the entire pulse sequence. Initially these efforts were complicate by the inability to provide a gating pulse during the data acquisition using the standard Bruker nomenclature, *go=2,* for the acquisition loop. A pulse sequence to overcome these restrictions is given below. Our AMX400 instrument is configured with a 3 channel MCI, but utilizes a linear AMT amplifier on the 3rd channel (requiring gating pulse via the c4 program call during the entire time it is on). The standard acquisition loop has been replaced by direct *adc* and *aq* commands for data acquisition. Unlike the *go=2* statement which does not allow a c4 gating command to be included, these individual acquisition commands can all include distinct c4 gating.

```
;hp_decf3
;Program for X Bloch decay with Y channel decoupling
;using linear amplifier on 3rd channel (requires c4 gate)
;for use with MCI only
; Alam 6/99 - Sandia National Laboratories

;set:
;p1 =90 degree X pulse
;d3 = suitable dead time and suppression delay
;ns=2*n or 8*n

#include <cfh>          ; make sure cfh is prepared
                        ; for your transmitter setup
1 ze
  do                    ; 1H decoupler off
  dbo                   ; Y Channel decoupler off
  tlo dlo dblo          ; First stage transmitters to low power
2 d1 dbl0 dl0           ; Set decoupling power of Y channel and 1H decouler
  2u:c4                 ; prepulse gate
3 p1:f1:c4 ph1          ; 90 degree f1 pulse
  2u:c4 cwb cw          ; Gate + cw decoupling on Y channel and 1H channel
  d3:c4 ph0:r           ;
  1u:c4 adc             ; These statements replace "go=2 ph31"
  aq:c4                 ;
  500u:c4               ;
4 rcyc=2 ph31           ;
  2u dbo                ; Y decoupler off
  2m do                 ; 1H decoupler off
5 100m wr #0
6 exit
ph0=0
ph1=0 0 1 1 2 2 3 3
ph31=0 0 1 1 2 2 3 3

; dbl0 Y channel decoupling power

; tl0 X channel power
; dl0 1H decoupling power (if used)
```

Sincerely,

Todd M. Alam

David P. Lang

[1] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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

July 9,1999
(received 7/30/99)

Title: Solid State Molecular Motion in Sucrose Octapalmitate as Studied via ^2H NMR

Sucrose Octapalmitate is a substantial component of the commercial mixture of compounds marketed by Proctor and Gamble under the brand name of "OLESTRA". It is a noncaloric fat substitute because lipase enzymes cannot recognize sucrose polyesters where 6 or more of the free OH sites have been esterified with long chain fatty acids. There is however, evidence that these compounds complex with fat soluble vitamins such as A and D, thereby depleting the availability of these vitamins to the body.

PhD student Gerald McManus is presently investigating the interactions of OLESTRA components with vitamins A and D using a combination of NMR methods. Since ^2H NMR in the solid state is a very powerful tool for determining motional types, we have begun our study with a detailed look at three deuterated sucrose octapalmitate derivatives. The first one possesses all eight palmitate chains perdeuterated, so that it contains 248 deuterium atoms. It is interesting to note that this material has a melting point of 43-44^{o}C, which is 5 degrees lower than its protio analog! We have also prepared a material with just one palmitate chain perdeuterated-ie a d-31 analog as well as a sucrose C -deuterated (d-11) analog.

Temperature dependent ^2H solid state spectra were recorded at 61MHz between 135 and 298K. Observed lineshapes were simulated using the approach of Wittebort et al (1) and the formalism of Torchia and Szabo (2). Results indicate that the sucrose moiety was static on the solid state ^2H NMR timescale, while a trans -gauche isomerisation was detected in the palmitate chains.

The activation energy for CD_2 trans-gauche isomerization was found to be 4.5 kcal/mol. For the CD_3 groups, the activation energy for this isomerization is 4.3 kcal/mol, while for CD_3 reorientation, the value is 2.7 kcal/mol.

Future experiments will deal with the influence of adsorbed vitamins A and D on these parameters.

References

1. R.J. Wittebort, E.T. Olejniczak and R.G. Griffin. J. Chem. Phys. **86**, 5411 (1987).

2. D.A. Torchia and A. Szabo. J. Mag. Res. **49**, 107-121 (1982).

With all good wishes,

G.W. Buchanan
Professor and Chairman

Address all Newsletter correspondence to:

Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303.
650-493-5971* - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

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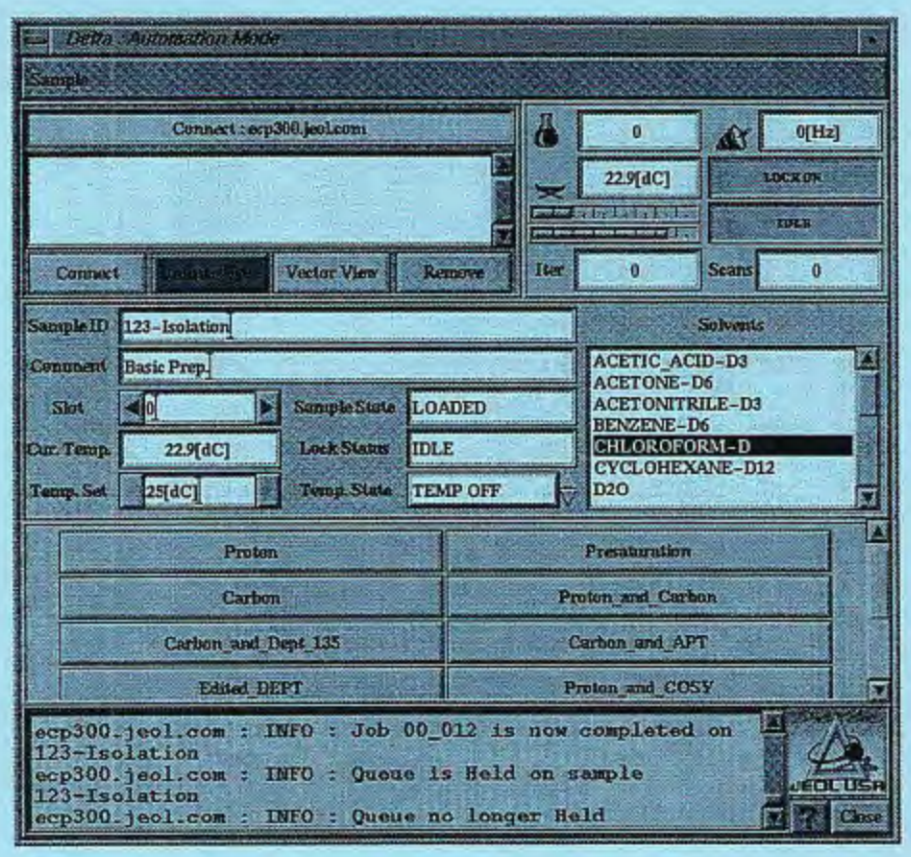

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