TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 417

June 1993

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Phase Noise: –63dBc (0.5Hz–15KHz)

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Switching: 5–10μs

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FORTHCOMING NMR MEETINGS

11th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Swansea, Wales, U.K., **July 4 - 9, 1993**; Contact: Dr. J. F. Gibson or Ms. G. B. Howlett - See TAMU NMR Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

Gordon Research Conference: Magnetic Resonance, Wolfeboro, NH, **July 11 - 16, 1993**; Contact: Dr. A. M. Cruickshank, Gordon Research Center. University of Rhode Island, Kingston, RI, 02881-0801; (401) 783-4011 or -3372; Fax: (401) 783-7644.

35th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado: **July 25-29, 1993**; Contact: Patricia L. Sulik, RML, Inc., 456 S. Link Ln., Ft. Collins, CO 80524; Phone: (303) 530-1169.

Science Innovation '93, Boston, Mass., **August 6 - 10, 1993**; "NMR Determination of Protein Structure", Discussion Leader - Ad Bax, *NIH*; : For information contact AAAS Meetings, 1333 H Street, NW, Washington, DC 20005; Phone: (202) 326-6450; Fax: (202) 289-4021; See *Science*, 260, 557-565 (23 April 1993).

12th Annual Scientific Meeting and Exhibition of the Society of Magnetic Resonance in Medicine, New York, NY, **August 14-20, 1993**; Contact: SMRM, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Phone: (510) 841-1899; Fax: (510) 841-2340.

NMR of Biological Macromolecules, Orthodox Academy of Crete, Kolympari, Crete, Greece, **August 23 - September 2, 1993**; Contact: Ph. Dais, Chemistry Dept., Univ. of Crete, Heraklion 71409, Greece; Phone: (30) 81-238400, ex. 292; Fax: (30) 81-233669.

Second International Conference on Magnetic Resonance Spectroscopy, Heidelberg, Germany, **September 6-10, 1993**; Contact: Dr. Winifried Kuhn, Fraunhofer Inst., Ensheimer Str. 48, DW-6670 St. Ingbert, Germany; Phone: (49) 6894-89738; Fax: (49) 6894-89750, or Dr. Bernhard Bluemich, Max-Planck-Inst. for Polymer Research, Postfach 3148, D-6500 Mainz, Germany; Phone: (49) 6131-379125; Fax: (49) 6131-379100.

1993 FACSS Meeting, Detroit, Michigan, **October 17-22, 1993**; Contact: H. N. Cheng, Hercules, Inc., Research Center, 500 Hercules Road, Wilmington, DE 19808; Phone: (302) 995-3505; Fax:. (302) 995-4117. See TAMU NMR Newsletter 411, 10.

Pacific Conference, Pasadena, California, **October 19-23, 1993**; Contact: Ms. B. Belmont, Pacific Conference, 14934 S. Figueroa St., Gardena, CA 90248;Phone: (310) 538-9709.

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

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995** [sic]; Contact: Dr. Wm. A. Bubb, Secretary, Univ. of Sydney, Dept. of Biochemistry, Sydney, NSW 2006, Australia. See TAMU NMR Newsletter 414, 8.

Additional listings of meetings, etc., are invited.

TAMU NMR Newsletter

Editor/Publisher: Bernard L. Shapiro

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2nd Notice re 1993-94 Invoices and Subscription Rates

Subscription renewal invoices for the October 1993 - September 1994 year will be mailed out at the beginning of July. If you ought to receive such an invoice, and do not have it in your hands by July 15, please call or write me promptly. ***Payment* of these invoices *must be received* by me *no later than September 10, 1993* to ensure uninterrupted mailing of the Newsletter issues**. Please do not delay execution of any necessary paperwork!

Also, please be sure that the instructions on the invoice are followed precisely. In particular, *overseas subscribers* should be careful to see that their name and invoice number appear on the payment (or, better, that the extra invoice copy which is provided is returned to me with the payment check or money order). Anonymous checks, while otherwise useful, cannot always be credited to the correct account.

The subscription rate for the October 1993 - September 1994 year will remain as it is for the present year, *viz.*, US$170.00 for the twelve monthly issues, postpaid. Personal or academic subscriptions will continue to be offered at a 50% discount, at US$85.00.

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The new invoices contain an entry for an *optional* surcharge as follows: (1) for First Class mailing, available for US and Canadian addresses *only*, or (2) for Air Mail Printed Matter (AMPM) mailing *to all other countries*. (There will no longer be the possibility of sending overseas mailings by First Class *surface* mail, which turns out to be more costly and slower than AMPM.) Please adjust the amount you pay accordingly.

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B. L. Shapiro
1 May 1993,
2 June 1993.

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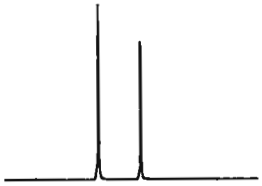
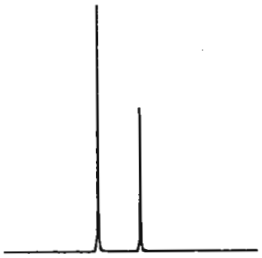
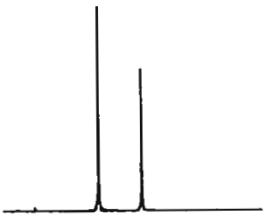


Variable amplitude cross polarization (VACP) *under* –2.6 KHz *mismatch condition*

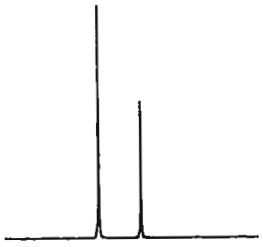
Deliberate "mismatch" of –1.9 KHz



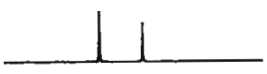
VACP *under normal match condition*



Normal "ideal" matched conditions



VACP *under* +2.0 KHz *mismatch condition*



Deliberate "mismatch" of +1.4 KHz

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

JEOL

Biometrology Laboratory
1-2 Musashino, 3-Chome,
Akishima, Tokyo 196, Japan

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

April 23, 1993
(received 5/10/93)

USEME

Dear Prof. Shapiro,

We have developed a new pulse sequence (*vide* Figure 1; ϕ=75° or 105°) for the recovery of homonuclear dipole-dipole interactions under Magic Angle Spinning (MAS) conditions. It consists of Spin Echo (SE) and Magic Echo (ME) pulse sequences respectively in the first and second halves of the MAS rotor period. This **U**nified **SE** and **ME** (**USEME**) sequence refocusses evolution under isotropic chemical shifts and recovers homonuclear interactions only; also combats the problems due to offset, chemical shift anisotropy, heteronuclear dipolar interactions and isotropic chemical shift difference.

Performance of USEME was experimentally investigated on a Chemagnetics CMX 300 MHz spectrometer at several MAS frequencies. Experimental and numerically simulated longitudinal magnetization transfer due to the ^{13}C-^{13}C dipolar interaction from CH_2 to CO in a doubly-labeled glycine as a function of USEME mixing time is shown in Figure 2. Slight mismatch between experimental and numerical results are due to rf field inhomogeneity and residual ^{13}C-^{1}H dipolar interactions.

We believe that the dipolar correlation by **dipolar-HOHAHA** with **USEME** as a mixing sequence is a most useful technique for the structural studies of biomolecules. Complete design of USEME and its applications in multi-dimensional NMR experiments will soon be published.

Reference

1. T. Fujiwara, A. Ramamoorthy, K. Nagayama, K. Hioka and Fujito, *J. Am. Chem. Soc.* (submitted for the publication, 1993).

2. T. Fujiwara, A. Ramamoorthy, K. Nagayama and K. Hioka, Abstract P158, 34th ENC, St. Louis, Missouri(March, 1993).

Sincerely,

A. RAMAMOORTHY T. FUJIWARA K. NAGAYAMA

Figure 1

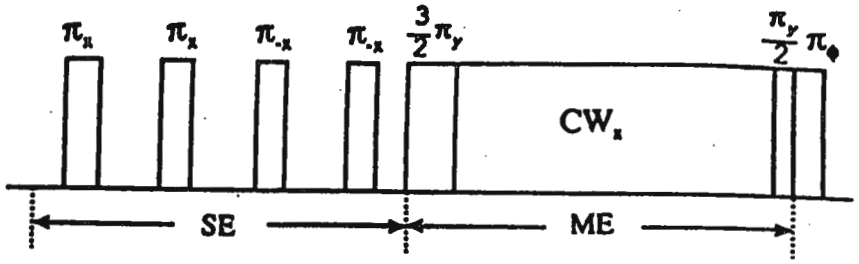
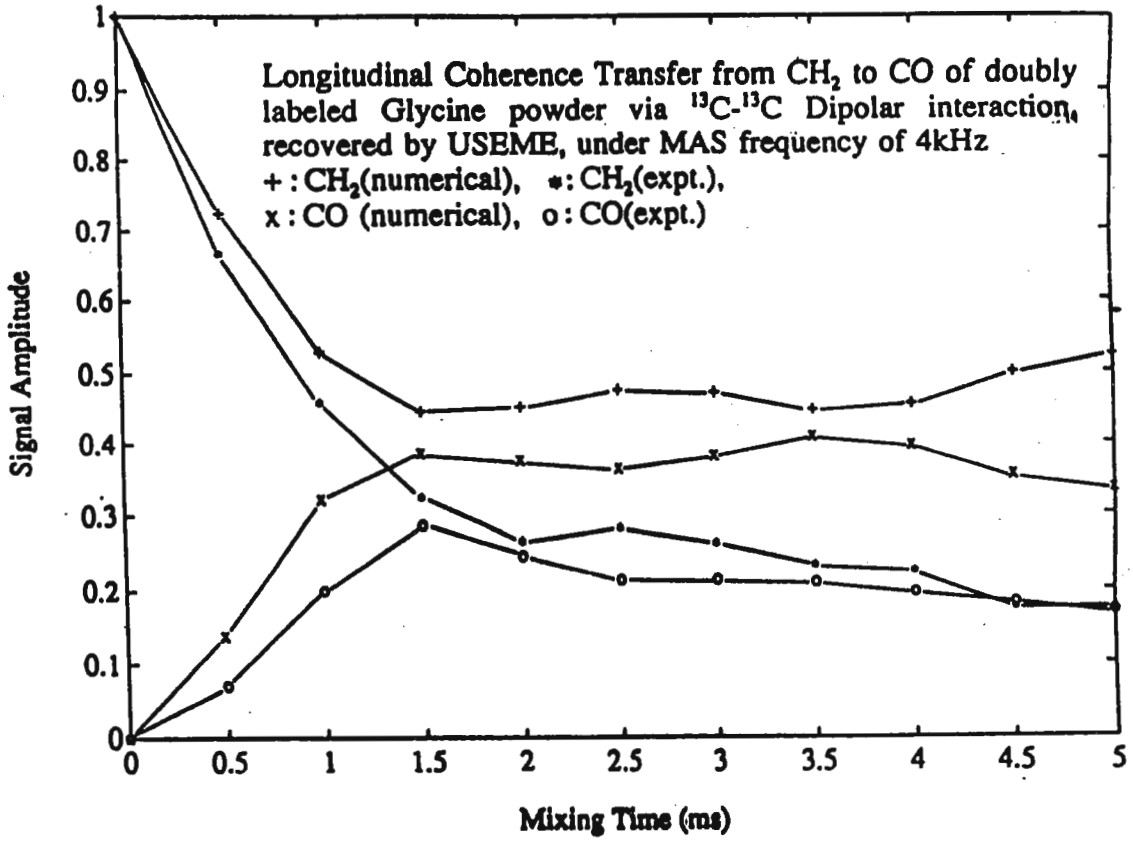


Figure 2



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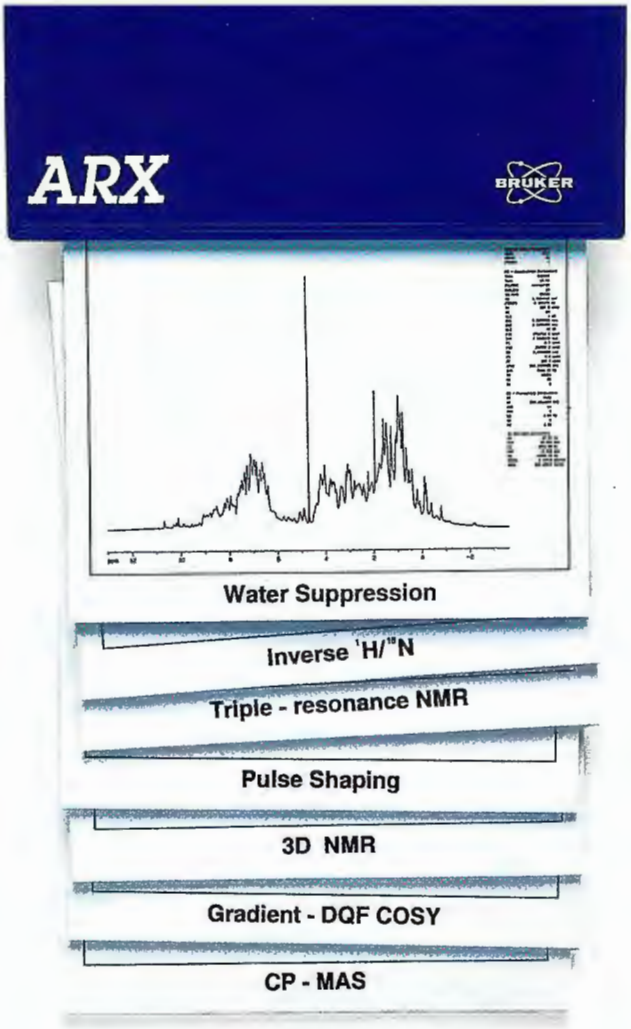

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Resolution Test					
All 5 mm ^{1}H 5+10 mm ^{13}C	ODCB/C_6H_6	0.2	0.2	0.2	
Lineshape Test					**SSB %**
All 5 mm ^{1}H	10% $CHCl_3$	6/12	7/15	7/15	<1
All 5 (10) mm ^{13}C	80% C_6H_6	3/7 (3/7)	3/7 (3/8)	4/8 (4/8)	<0.5 (<1)
Sensitivity Test					
5 mm ^{1}H Selective	0.1% EB	175	250	450	<10
5 mm ^{1}H Inverse Detection	0.1% EB	135	190	350	<15
5 mm ^{1}H Dual, QNP, VSP	0.1% EB	100	140	200	<15
5/10 mm ^{13}C QNP, Dual	ASTM	100/320	160/450	180/600	<15/<20
5/10 mm ^{13}C QNP, Dual	10% EB	70/200	100/300	150/400	
5/10 mm ^{13}C VSP multinuc.	ASTM	100/320	160/450	180/600	<15/<20
5/10 mm ^{13}C VSP multinuc.	10% EB	70/200	100/260	150/320	
5/10 mm ^{15}N VSP multinuc.	90% Form.	10/35	15/55	20/70	<25/<30

EB = ethylbenzene (for ^{13}C with ^{1}H-dec.);
ASTM = 60% C_6D_6 in dioxane
Form. = formamide (^{1}H-dec. without NOE)
lineshape: ^{1}H = $CHCl_3$ linewidth at ht. of ^{13}C-satellites/at 2^{0} this level
^{13}C = C_6H_6 linewidth at 0.55% / 0.11 level (^{1}H-dec.)
SSB = Spinning sidebands measured with 8 transients
QNP: 5 or 10 mm ^{1}H, ^{31}P, ^{13}C, ^{15}N
VSP: 5 mm ^{15}N – ^{13}P; 10 mm ^{109}Ag – ^{31}P.

Console	Dimensions and weights are approximate; voltage +10/ – 5% max. variation; other line freq. and voltage upon request
dimensions electronics cabinet	w 130 x d 0.75 x h 1.20 m
weight	450 kg
power (dissipation)	220 V/50 Hz/16 A (ca. 4 kW)

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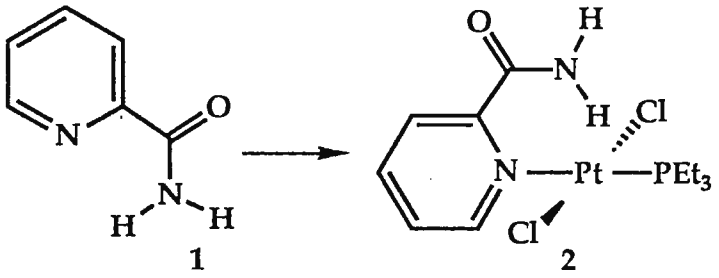
TAMU NMR Newsletter
Editor/Publisher B.L. Shapiro
966 Elsinore Court

Palo Alto, CA 94303, USA

Zurich, May 6, 1993
(received 5/10/93)

Dear Barry,

We have been searching for molecules containing molecular fragments which can function as NH donors to a transition metal, i.e., the bonding should be of the type $R^1R^2N\text{-}H\text{----}ML_n$. As part of our study we have been considering whether the "properly situated"NH in **1** would cooperate. To this end we have prepared **2** whose ^{15}N, ^1H correlation spectrum is show, below. There are clearly two different amide signals,



and both are shifted downfield relative to the uncoordinated pyridine-2-carboxamide. The coordination chemical shift of the ^{15}N is ca. 18ppm and NOE measurements suggest that the proton is indeed situated as suggested by **2**. Moreover, with only a little coaxing, **2** loses HCl to form a new complex with the deprotonated amide nitrogen acting as ligand. This is interesting in terms of how metals might interact with peptides NH bonds, but we have a way to go before we are convinced about the bonding.

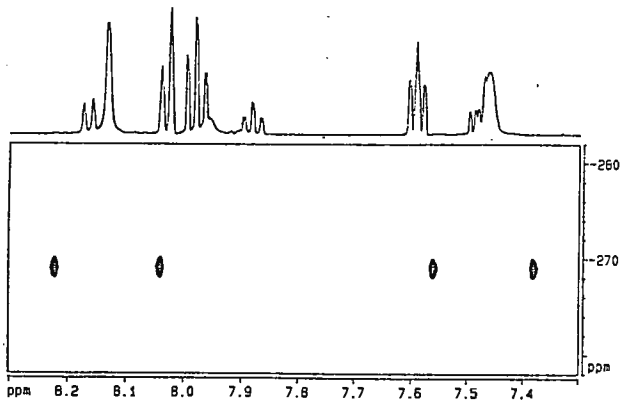


Fig. 2. $^{15}N,^1H$ correlation for **9** showing the connectivity to the two low field NH signals. The vertical axis with the ^{15}N signal is referenced to CH_3NO_2.

Best wishes

Suggested title:
Interactions between NH-bonds and Pt(II).

NSITC hands-on training in science

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

Email: rmair@stan.xx.swin.oz.au
May 5 1993

(received 5/14/93)

PLOTS FROM 'OLD' SPECTROMETERS

Dear Dr Shapiro

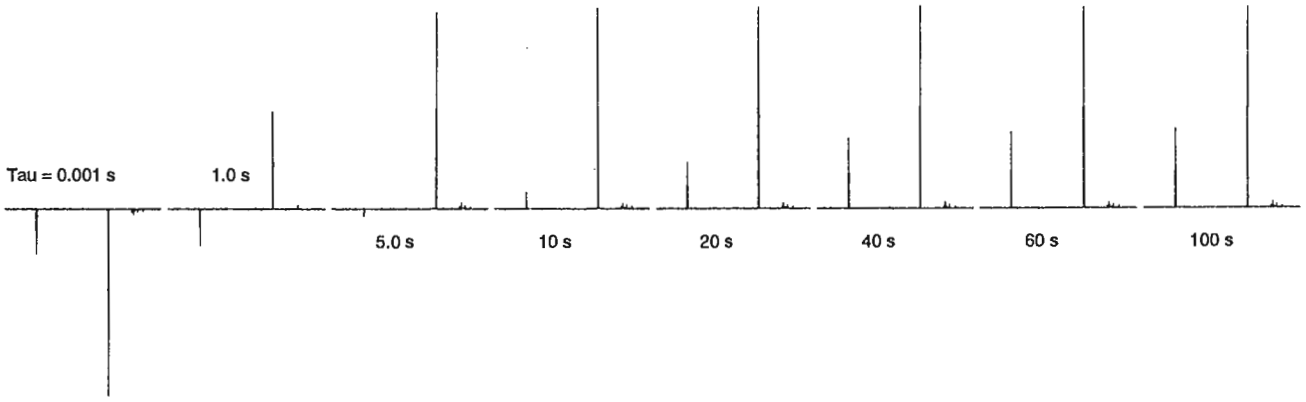
There has been some recent interest in your newsletter concerning the removal of spectra from the system that produced them, to remote computers to allow simple incorporation into reports prepared on word-processors. I would like to demonstrate the usefulness of the so-called 'neanderthal DOS machine' for this purpose, as well as describe how plots can be rescued from an 'old' pre-unix spectrometer.

Previous discussion has centered over converting HPGL files, either plotted from a unix-based spectrometer or from FELIX on a unix system, and then converting these files to a form suitable for a Macintosh. However, it should be noted that both Word for Windows 2.0 and Wordperfect for Windows, running on a PC, will allow the insertion of an HPGL file directly, with no conversion to another format. In addition, once in Word for Windows, the user can then enter the Microsoft Draw module, to allow further annotation of their plot, as would be done in any specific drawing package, before printing the result as a Word document.

Having mastered this task for plots produced from our own copy of Felix, I spied the HPGL plotter supplied with our pre-unix Gemini 200 spectrometer. Capturing the HPGL file, instead of having it plotted out, should then allow its incorporation into Word in the same way. Borrowing the method from the Plotview for Mac manual, we simply unplugged the cable that normally feeds into the plotter, and instead connected it to another 25 pin serial plug, on the other end of which was a 9 pin plug which went straight in the COM port on the PC. We used the Telix communications program, and screen captured the HPGL data files, after having typed the usual 'PL' command on the NMR. However, at this stage, we were presented with a problem. Word would only accept 'structured' HPGL files, while our plotter gave us 'unstructured' files. A Computer Science student in the department (Conrad Wong) quickly supplied us with a converting program, which now gives us HPGL files suitable for use in Word.

This allows very quick incorporation of 1-D spectra, which would otherwise require saving on streaming tape, and being taken to our Iris, for re-proccessing on FELIX, before a HPGL plot could be generated. It also allows useful Varian plot formats which are generated with a single command, such as 2-D spectra with 1-D spectra along the axes, or horizontal stacked spectra such as the relaxation experiment below, to be incorporated with far more ease than going via FELIX.

Ross Mair Margaret Wong Jon Hall Ilias (Louis) Kyratzis



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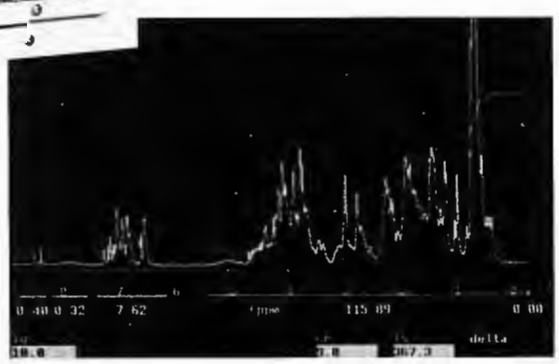

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April 26, 1993
(received 4/27/93)

Dr. Bernard L. Shapiro
Editor, Texas A&M NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

SPIN-PING HMQC/HMBC -- "SON OF SIMBA"

Dear Barry,

We very extensively utilize long-range proton-carbon heteronuclear connectivities in the process of characterizing the isolated products of synthetic reactions gone astray and in the identification of degradants of drugs subjected to stressed decomposition studies. In most instances, the HMBC experiment of Bax and Summers[1] provides quite satisfactory results. There are occasions, however, when only the connectivities associated with a single carbon are needed. Alternately, there are also times when a given carbon doesn't show a response in an HMBC spectrum. In such cases, one would normally have to resort to repeating the experiment which often represents a considerable investment in time. As an alternative, we developed the SIMBA (**S**elective **I**nverse **M**ultiple **B**ond **A**nalysis) experiment as a one dimensional analog of the HMBC experiment[2] in a fashion related to the SELINCOR experiment of Stefan Berger.[3] A similar, albeit simpler, pulse sequence was also reported just prior to ours by Keniry and Poulton.[4] Much more recently, several papers have appeared describing the implementation of selective inverse correlation experiments using chemical-shift-selective-filters (CSSF) and selective pulses.[5,6] The theme of the latter papers, parallels homonuclear experiments recently described by Xu, Wu, and Freeman.[7] Freeman and co-workers demonstrated that it is possible to select transverse components of magnetization after applying non-selective pulses for excitation. We have extended Freeman's homonuclear experiments to afford heteronuclear variants. Transverse magnetization is selected using a tailored "spin-ping" pulse after the application of non-selective 90° carbon pulses to achieve magnetization transfer.[8] Experiments can be performed either selectively or in an F_1 region-selective fashion using the spin-ping- HMQC (SP-HMQC) pulse sequence shown in Fig. 1. Alternatively, long-range experiments can be performed using the spin-ping HMBC (SP-HMBC) sequence shown in Fig. 2. Results obtained using the SP-HMQC sequence (Fig. 1) are shown for an F_1 region-selected HMQC spectrum of the complex spiro-nonacyclic alkaloid cryptospirolepine[9] in Fig. 3. A comparison of the results obtained using the SP-HMBC sequence (Fig. 2) with those obtained using our original SIMBA experiment[2] incorporating a 6 msec 90° E-BURP-2 pulse[10] are presented in Fig 4. The excited resonance is the H13 vinyl proton, coupled via three-bonds to the selectively pulsed C13b carbon resonating at 120.4 ppm. As in the SIMBA experiment shown to the right in the figure, the doublet is a function of the excited heteronuclear coupling pathway; the vinyl resonance is observed as a singlet in the conventional proton spectrum. Using the SP-HMBC experiment we note somewhat greater sensitivity and slightly better resolution.

The results shown demonstrate that Freeman's[7] spin-ping approach to transverse magnetization selection can be effectively applied to heteronuclear experiments as well as the homonuclear experiments originally described.

Best regards,

Tim Spitzer* Ron Crouch** John Shockcor# Ann Davis** Gary Martin**

*Present address: Burroughs Wellcome Co., Analytical Development Laboratories, Greenville, NC 27835
**Division of Organic Chemistry, Burroughs Wellcome Co., RTP, NC 27709
#Division of Pharmacokinetics and Drug Metabolism, Burroughs Wellcome Co., RTP, NC 27709

1.) A. Bax and M.F. Summers, J. Am. Chem. Soc., **106**, 2093 (1986). 2.) R.C. Crouch and G.E. Martin, J. Magn. Reson., **92**, 189 (1991). 3.) S. Berger, J. Magn. Reson., **81**, 561 (1989); Angew. Chem., **100**, 1198 (1988). 4.) M.A. Keniry and G.A. Poulton, Magn. Reson. Chem., **29**, 46 (1991). 5.) D. Uhrin, A. Mele, and R.A. Dwek, J. Magn. Reson., A, **101**, 98 (1993). 6.) K.E. Kover, D. Uhrin, G. Szalontal, and G. Batta, J. Magn. Reson., B, **101**, 1 (1993). 7.) P. Xu, X.L. Wu, and R. Freeman, J. Magn. Reson., **99**, 308 (1992). 8.) T.D. Spitzer, R.C. Crouch, J.P. Shockcor, and G.E. Martin, J. Magn. Reson., submitted (1993). 9.) A.N. Tackie, G.L. Boye, M.H.M. Sharaf, P.L. Schiff, Jr., R.C. Crouch, T.D. Spitzer, R.L. Johnson, J. Dunn, D. Minick, and G.E. Martin, J. Nat. Prod., **56**, in press (1993). 10.) H. Geen and R. Freeman, J. Magn. Reson., **93**, 93 (1991).

Phase cycling Fig. 1: ϕ_1=00001111; ϕ_2=0000111122223333; ϕ_3=00221133; ϕ_4=01231230; $\phi_5=\phi_1$; rvcr=02201331, inverted every 16 transients; full cycle inverts ϕ_5 and rcvr every 64 transients. Fig. 2: ϕ_1=00001111; $\phi_2=\phi_1$ increment every 16 transients; ϕ_3=0000000022222222; ϕ_4=00221133; ϕ_5=01231230; $\phi_6=\phi_1$; rvcr=02201331, inverted every sixteen transients. The full phase cycle inverts ϕ_6 and the receiver phase every 64 transients.

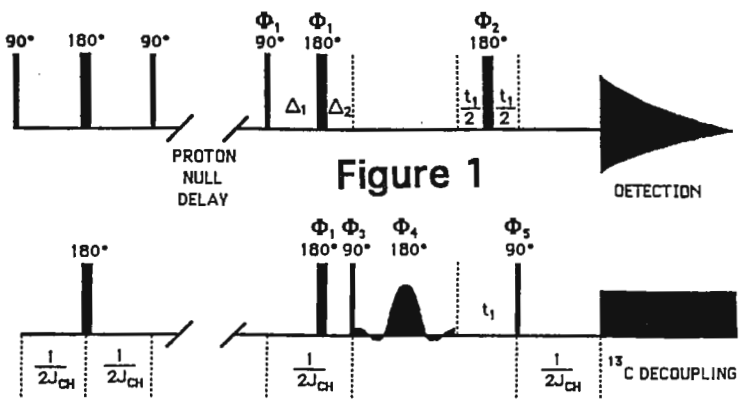

Figure 1

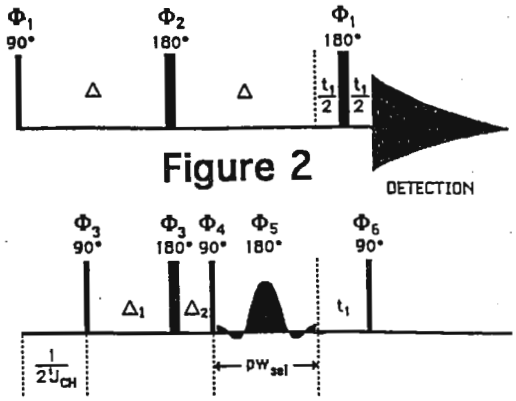

Figure 2

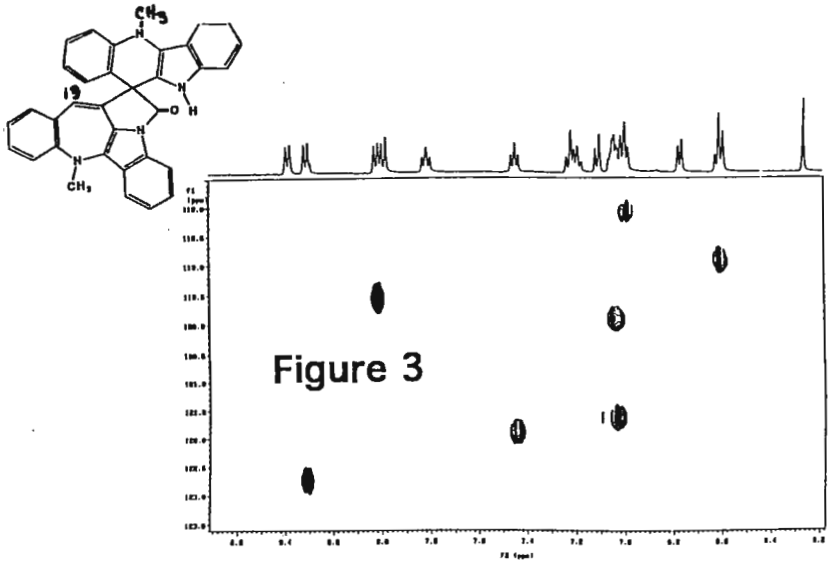

Figure 3

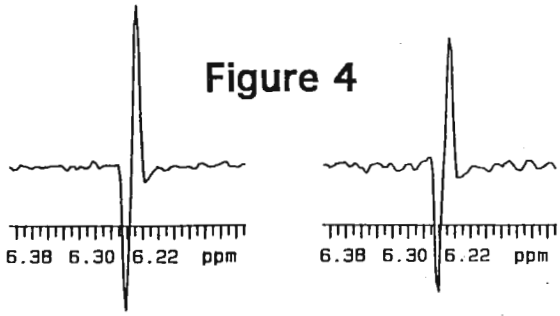

Figure 4

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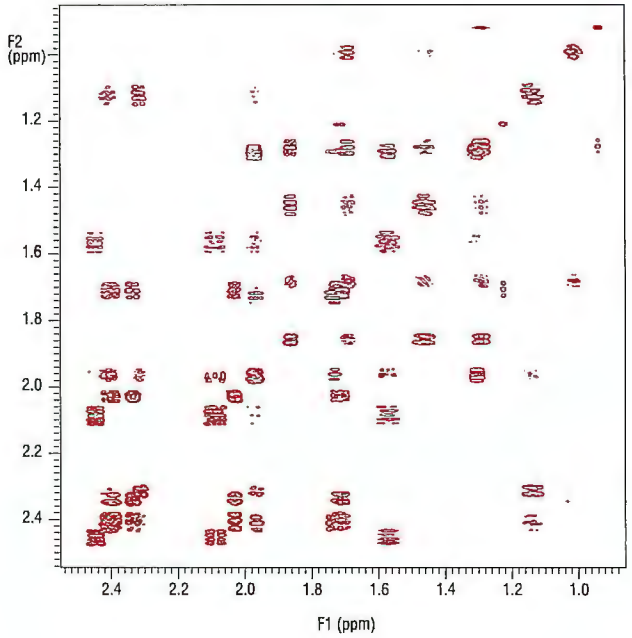

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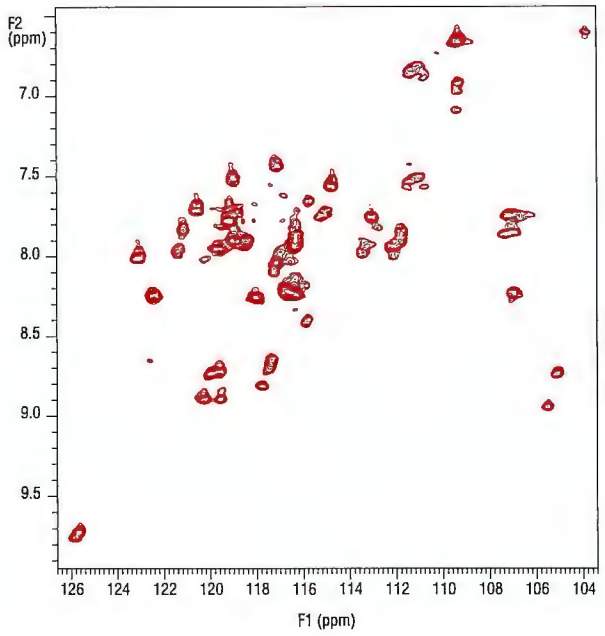

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April 22,1993 (received 4/26/93)
Professor B.L. Shapiro
966 Elsinore Court
Palo Alto, California 94303

Protection Circuit for the Variable Temperature Accessory on Varian Unity N.M.R. Instruments

Dear Professor Shapiro,

During the period while we are waiting for space to be readied for three 600, one 500, and one 400MHz. instruments in the N.M.R. facility at MSKCC, we have two 400 MHz. Unity spectrometers on loan from Varian. In our temporary space the reliability of compressed air has been less than ideal. This has raised concerns about the air supply going out during a run where either VT of decoupling is in use, and we wished to avoid any resulting damage. To this end I have constructed a simple protection circuit that might be of interest to others. A flow switch (Cole Palmer catalog #G-01362-11) is connected to the variable temperature gas flow line, and set to open at a flow of 5 LPM or less. The switch controls a 120 volt relay on a 6 outlet surge protector with remote switch made by Acco (New Jersey Office Supply #k7-50676) into which the AMT RF amplifier and the VT line plugs are connected. Thus when air flow decreases below 5 LPM these loose AC power. When the VT looses power the default gas flow bypasses the low temperature heat exchanger and the heater is turned off. When the VT comes on again, room temperature air passes over the sample, since the heater will not turn on nor will air be diverted through the heat exchanger until the parameters are reset with a manual computer command. The sample is thus protected from drastic changes in temperature due to RF heating or lack of VT control.

Sincerely Yours,

David Zuckerman

Please credit this contribution to David Live's account.

McMASTER UNIVERSITY
Department of Chemistry
1280 Main Street West, Hamilton, Ontario L8S 4M1
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FAXMAIL (416) 522-2509

May 5, 1993
(received 5/10/93)

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

ARTIFACTS AND SIMULATIONS

Dear Barry,

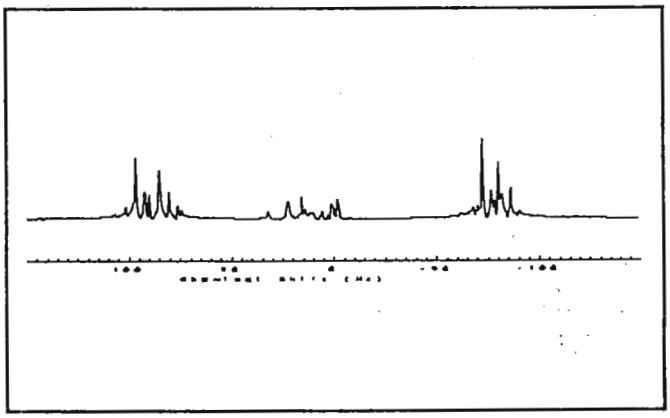
Tim Allman and I am close to finishing the major rewrite of the SIMPLTN (SIMulation of PuLse and Two-dimensional Nmr) spin simulation program, and we will keep your readers informed when the program is ready for release. With considerable help from the group at Monsanto (particularly Joel Garbow), we now have a general, easy-to-use program that will simulate most NMR experiments. It will handle a general spin system (strongly or weakly coupled) and produce data that can be processed by any software package. The program is written in C for essentially any UNIX box, and is intended for general distribution.

As a test case, we have duplicated some of Gareth Morris' virtual coupling artifact spectra on methyl acrylate(1). These occur in a standard HETCOR when a coupled proton overlaps with the ^{13}C satellite of another proton, and show up as a spurious correlation. The figure below shows typical results on a strongly coupled ABCX system, where A, B and C are the vinyl protons and X is the vinylic CH_2 carbon. The peaks in the middle of the spectrum are all artifacts. The simulation of a HETCOR on this system, with 512 points in t_1 and 4 scans per point took about 13 minutes on an old (i.e. one year old) 33 MHz R3000-based SGI INDIGO. We are having fun chasing down these artifacts, and trying to figure out why the Bax-modified HETCOR (with a BIRD pulse) is so good at eliminating them(2). We'll let you know.

Yours truly

Alex Bain

1. G.A. Morris and K.I. Smith, Mol. Phys. **61**, 467 (1987).
2. G.V.T. Swapna, R. Ramachandran, N. Reddy and A.C. Kunwar, J. Magn. Reson. **88**, 135 (1990).



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Dr. B. L. Shapiro

TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

May 20, 1993 (received 5/22/93)

Practical Aspects of Phase-ramped Off-resonance Pulsing

Dear Dr. Shapiro,

We have a 500 Mhz GE system running Omega software, and have implemented triple-resonance 3- and 4-D experiments for our studies of several relatively large proteins. These experiments come in two varieties: those that use only one carbon frequency for magnetization transfer and/or frequency labelling (e.g. HNCA, HNCO) (1) and those that use two carbon frequencies, both Cα and C=O, which are treated as isolated frequency ranges and are pulsed separately (e.g. HN(CO)CA, HCA(CO)NNH) (2,3). Currently, due to hardware limitations, we have to generate both frequencies from a single channel. Off-resonance pulses are generated by varying the phase of the pulse in a time-dependent manner (4-6). A pulse can be broken into 1 μsec intervals by our pulse programmer, and if the phase of each interval is incremented by 5.4°, the effective frequency is shifted by 15 kHz (the difference between the center of the α carbons and the carbonyl carbons). This ability is implemented in the Omega software either as a RAMP command (which applies a formula phase shift) or as the command DF, where you simply provide the Δν. However, the pulse sequences were not working correctly; there was low signal-to-noise, and in some cases there were foldover problems. This is because phase coherence is maintained only at the carrier frequency, not at the shifted frequency. So we now apply a formula to calculate a correction to the phase of every shifted pulse after the first one where phase coherence must be maintained (a decoupling π pulse generally does not require phase coherence), and the phase correction is applied together with the phase of the pulse from the pulse sequence.

As an example, Figure 1 depicts a portion of the 4D HCA(CO)NNH (3) sequence, neglecting the nitrogen channel, which has no pulses during the portion shown. In this sequence, the carrier is placed on the carbonyl resonant frequency,

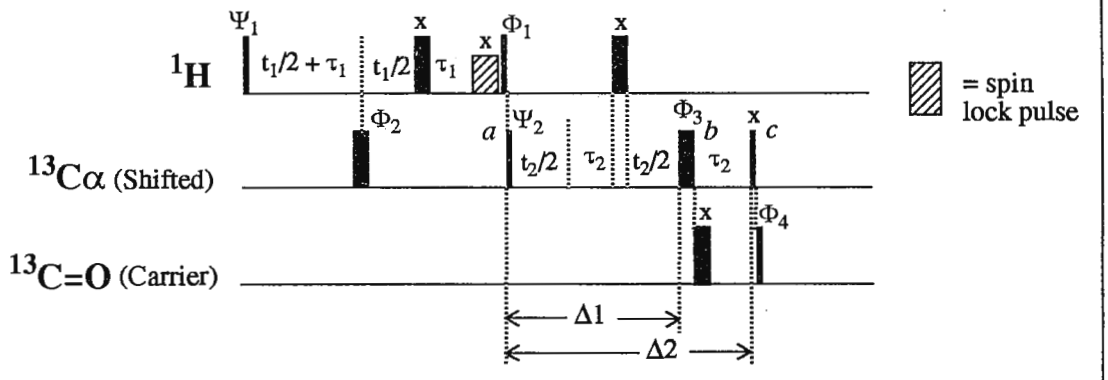


Figure 1: Portion of HCA(CO)NNH sequence, with the carrier is set to the carbonyl region, and the α-carbons selectively excited by means of the ramped phase shift. In this sequence, pulse *a* must be phase-coherent with pulses *b* and *c*. Δ1 is the period between the start of pulse *a* and the start of pulse *b*, and Δ2 the period between pulse *a* and pulse *c*. π/2 and π pulses are indicated in the usual manner by narrow and wide bars, respectively.

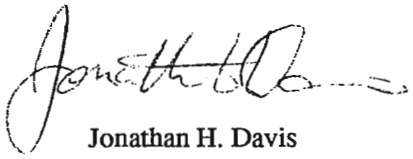
and all Cα pulses are shifted using the phase ramp technique. (Alternatively, the carrier may be placed on the Cα frequency, and the carbonyl pulses shifted). It is not critical that the first π pulse (Φ_2) is in phase, since it is for decoupling only (although it could be coherent with the rest of the pulses by calculating the interval beginning with the Φ_2 pulse). But the remainder of the Cα pulses must maintain phase coherence, so we calculate the delay from the onset of each pulse, where evolution begins, to the onset of the next pulse, where we want to be in phase. Essentially, we are 'following' the evolution, at 15KHz in this case, of the off-resonance spins, so subsequent pulses catch the spins in the proper phase. The beginning of pulse *a* is the start of the period that needs phase correction. We calculate the phase correction for subsequent pulses according to equation 1:

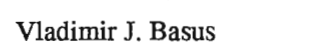
Eqn. 1 $$\Delta\varphi = (\Delta t)\ (\Delta\nu)\ (360 deg/cyc)$$

where $\Delta\phi$ is the phase correction in degrees, Δt is the amount of time elapsed, in seconds, from the beginning of the first pulse in the phase-coherent train, and $\Delta\nu$ is the frequency offset in Hz. In the example cited in Fig. 1, $\Delta\phi_b$ is calculated with $\Delta t = \Delta 1 = c90 + t_2 + \tau_2 + p180$, where c90 and p180 are ^{13}C π/2 and ^{1}H π pulses, respectively. $\Delta\phi_c$ is calculated with $\Delta t = \Delta 2 = \Delta 1 + c180 + \tau_2$. These phase corrections can then be converted to numbers between 0 and 360 with modulo math, and the correction added to the phase of the ^{13}C pulse in question. Since t_2 is incremented over the course of the experiment, Δt, and therefore $\Delta\phi$, must be recalculated for each slice.

We have successfully implemented on the Omega all the sequences mentioned in this letter, as well as other 3- and 4-D triple-resonance sequences, using phase ramping with phase correction. There is no easy way to compare the data with that we would obtain with a fourth channel, but it is encouraging that such experiments are possible on equipment that does not reflect the state of the art. It is possible to program the spectrometer software to calculate and apply the phase correction in a transparent manner, in which case the spectroscopist does not need to worry about the phase correction. But since many groups are implementing new triple-resonance methods on older spectrometers that have been upgraded but do not have all the capabilities of the most advanced instruments, we feel that this information may be useful.

Sincerely yours,





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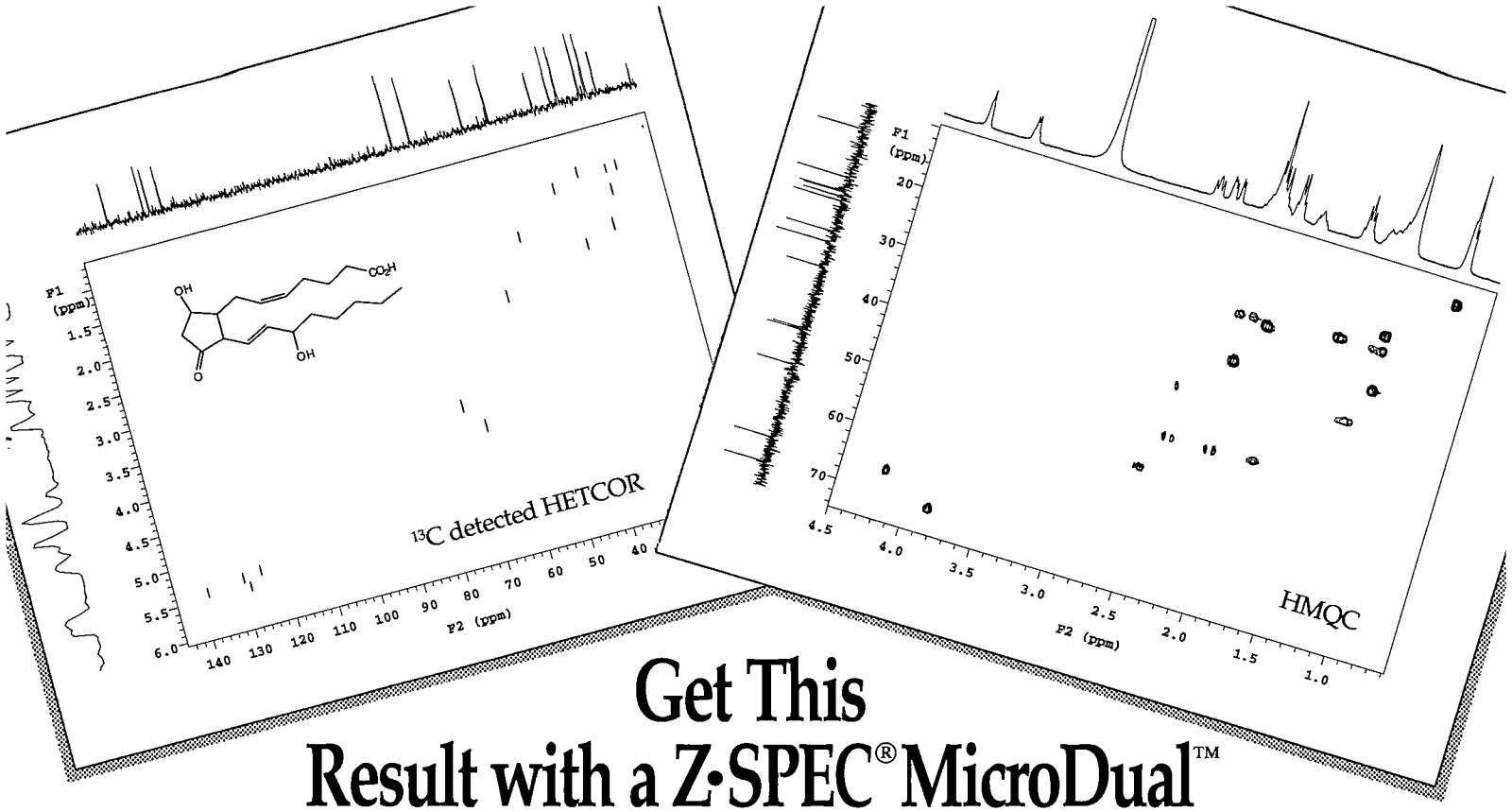

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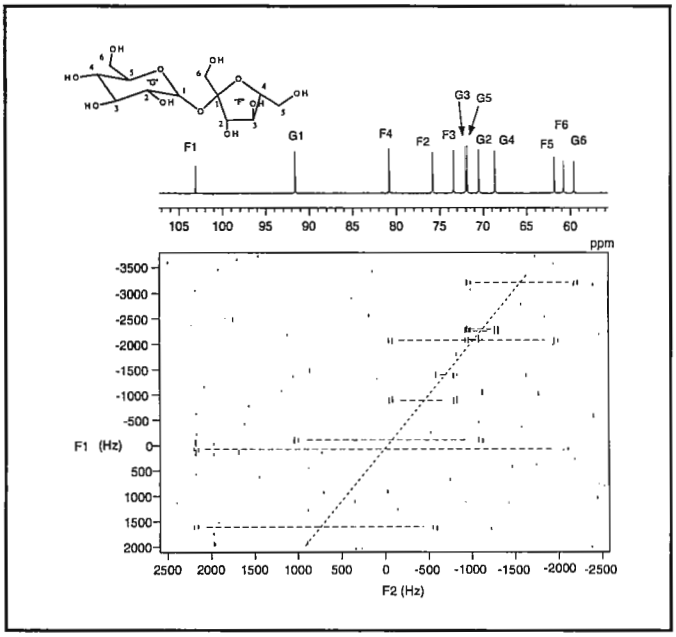

Figure 1: Phase-sensitive INADEQUATE spectrum acquired in 18 hours with 42mg Sucrose sample and Z•SPEC MD 400 probe.

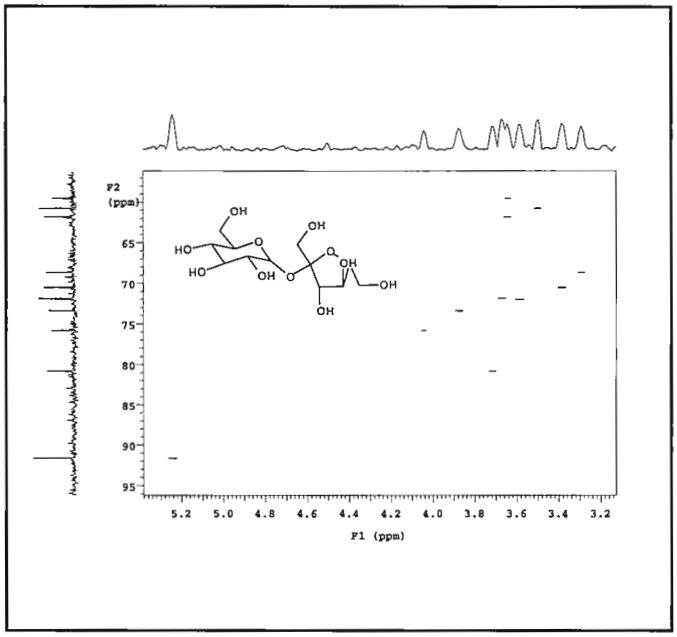

Figure 2: Phase-sensitive HETCOR spectrum of 600µg Sucrose acquired in 2 hours with a Z•SPEC MD 400 probe.

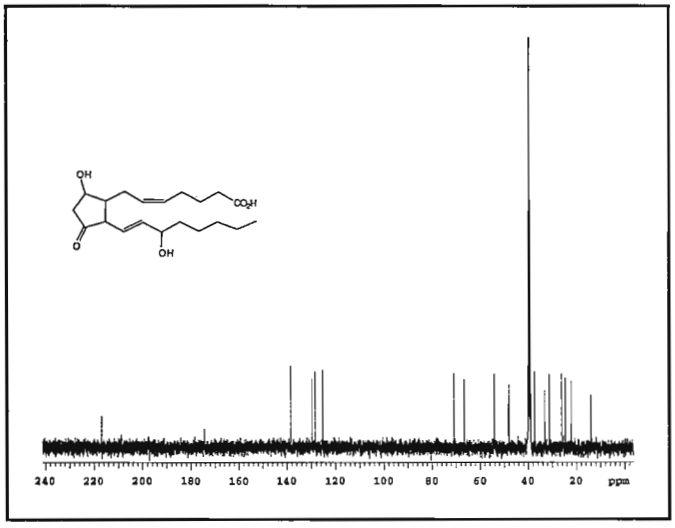

Figure 3: ^{13}C spectrum of 1.0mg Prostaglandin D2 obtained in 2 hours with a Z•SPEC MD 400 probe.

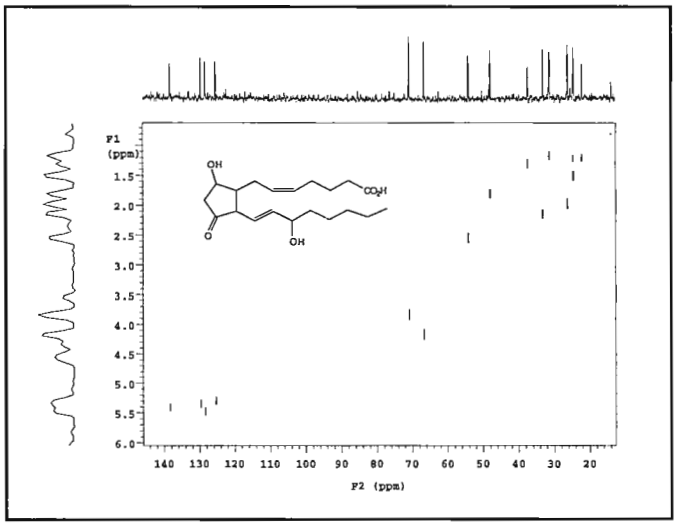

Figure 4: HETCOR of 1.0mg Prostaglandin D2 obtained in 14 hours with a Z•SPEC MD 400 probe.

NALORAC 837 Arnold Drive, Suite 600 • Martinez, CA 94553 • Telephone: (510) 229-3501 • FAX (510) 229-1651

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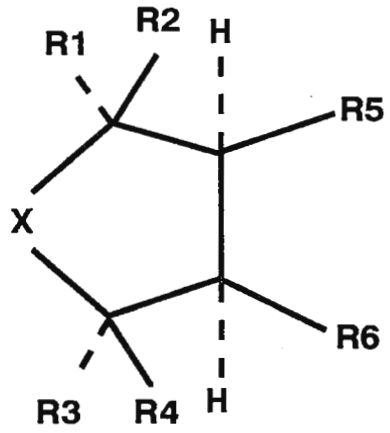
Telephone 041-552-4400 ex 2285

(received 5/12/93)

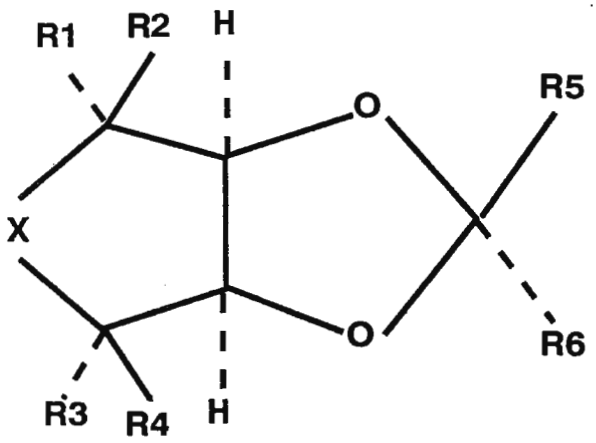
Dear Barry,

Many years ago we reported briefly[1] on the preparation and behaviour of ortho-trifluoroacetates derived from certain 1,2-diols. Regretably the work was never published in full. I have now had the opportunity to perform calculations with a view to establishing the details of the structures proposed.

The mono-trifluoroacetate of cis-tetrahydrofuran-3,4-diol is a solid which exists in the cyclic ortho-ester form (1a). In solution in CH_3CN this is slowly (~30 minutes) converted into an equilibrium mixture containing the second cyclic form (2a) and the normal ester (3a). These three forms of the ester are characterised by three peaks in the ^{19}F nmr spectrum. A question remains as to whether the assignment of the cyclic structures is correct. This has been resolved in part by studying the effect of varying the temperature on the equilibrium mixture, which yields the themodynamic parameters, and also by modelling the structures using semi-empirical calculations (MOPAC - AM1). The results of these studies, on the compounds (1a, 2a, 3a), on the related thia- analogues (1b, 2b, 3b), and the unsymmetrical dimethyl derivatives (1c, 2c, 3c, 4c), are shown in the tables, and lead to the conclusion that the structures are correct as shown.



(A)



(B)

1a B: X = O; R1 = R2 = R3 = R4 = H, R5 = OH; R6 = CF_3

2a B: X = O; R1 = R2 = R3 = R4 = H, R5 = CF_3; R6 = OH

3a A: X = O; R1 = R2 = R3 = R4 = H; R5 = OH; R6 = O.CO.CF_3

1b B: X = S; R1 = R2 = R3 = R4 = H, R5 = OH; R6 = CF_3

2b B: X = S; R1 = R2 = R3 = R4 = H, R5 = CF_3; R6 = OH

3b A: X = S; R1 = R2 = R3 = R4 = H; R5 = OH; R6 = O.CO.CF_3

1c B: X = O; R1 = R4 = H; R2 = R3 = Me; R5 = OH; R6 = CF_3

2c B: X = O; R1 = R4 = H; R2 = R3 = Me; R5 = CF_3; R6 = OH

3c A: X = O; R1 = R4 = H; R2 = R3 = Me; R6 = OH; R5 = O.CO.CF_3

4c A: X = O; R1 = R4 = H; R2 = R3 = Me; R5 = OH; R6 = O.CO.CF_3

Reference 1 P. Bladon and G. C. Forrest, *Chemical Communications*, 1966, p. 481.

Table 1

Structure		δF(*)	Mole fract.(†)	Heat of formation(§)
1a	¶	-85.29	0.71	-333.6
2a		-84.43	0.21	-332.2
3a		-74.80	0.08	-322.3
1b	¶	-85.17	0.39	-289.7
2b		-83.70	0.08	-287.6
3b		-74.95	0.53	-280.5
1c	¶	-84.65	0.56	-341.4
2c		-83.40	0.24	-337.2
3c		-74.20	0.07	-329.6
4c		-74.10	0.13	-331.1

* ppm from CCl_3F in CH_3CN at 297K

† At equilibrium in CH_3CN at 297K

§ Kcal/mole calculated using MOPAC and AM1 parameters

¶ Structure initially present

Table 2

Process	ΔF(*)	ΔH(*)	ΔS(†)	ΔH(*)(Calc.§)
1a → 2a	0.66	0.12	-0.002	1.4
1a → 3a	1.45	5.40	0.013	11.3
1b → 2b	0.79	0.10	-0.002	2.1
1b → 2b	-0.02	3.36	0.011	9.2
1c → 2c	0.65	0.26	-0.001	4.2
1c → 3c	1.51	5.19	0.012	11.8
1c → 4c	1.10	4.90	0.013	10.0

* Kcal/mole

† Kcal/mole/degree

§ From MOPAC calculations

Yours sincerely,

Peter Bladon

Peter Bladon

PETROLEUM RECOVERY INSTITUTE

April 23, 1993
(received 5/3/93)

RGB Monitor Replacement For Mitsubishi Color Displays

Dear Barry,

One of the potentially frightening occurrences that may plague those with expensive color monitors is the failure of that device, followed by a lengthy repair period. Few of us can afford to have spare monitors of this type sitting around. We have found a relatively inexpensive way of using our existing personal computer graphics monitors (VGA/SVGA) in lieu of the Mitsubishi (Model HL6915 SBKV in our case) for such occasions.

The answer is to purchase a 'V50 Composite Sync Decoder' (ca $300 CDN, not including our favourite tax, the GST). The V50 can be set for systems with Horizontal rates from 15 kHz (NTSC/CGA, 320x200 to over 53 kHz (1024 x 768) with an internal trimmer control. The device can handle composite video source from a single connector, source that is RGB with sync on Green and source that is RGB with composite/separate sync. It has a size of 4.25" x 3.75" x 1.0", weighs 5 oz and comes with a 15VDC adaptor.

The better video stores should be able to tell people where to get these; however, if anyone is interested and is having a problem locating the device then they can contact me, preferably via e-mail (axelson@acs.ucalgary.ca).

Sincerely,

Dave

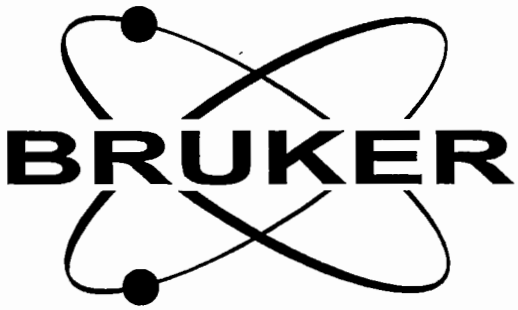
Dr. D E Axelson
Group Leader
Petroleum Recovery Institute
Imaging Centre

We Couldn't Wait!

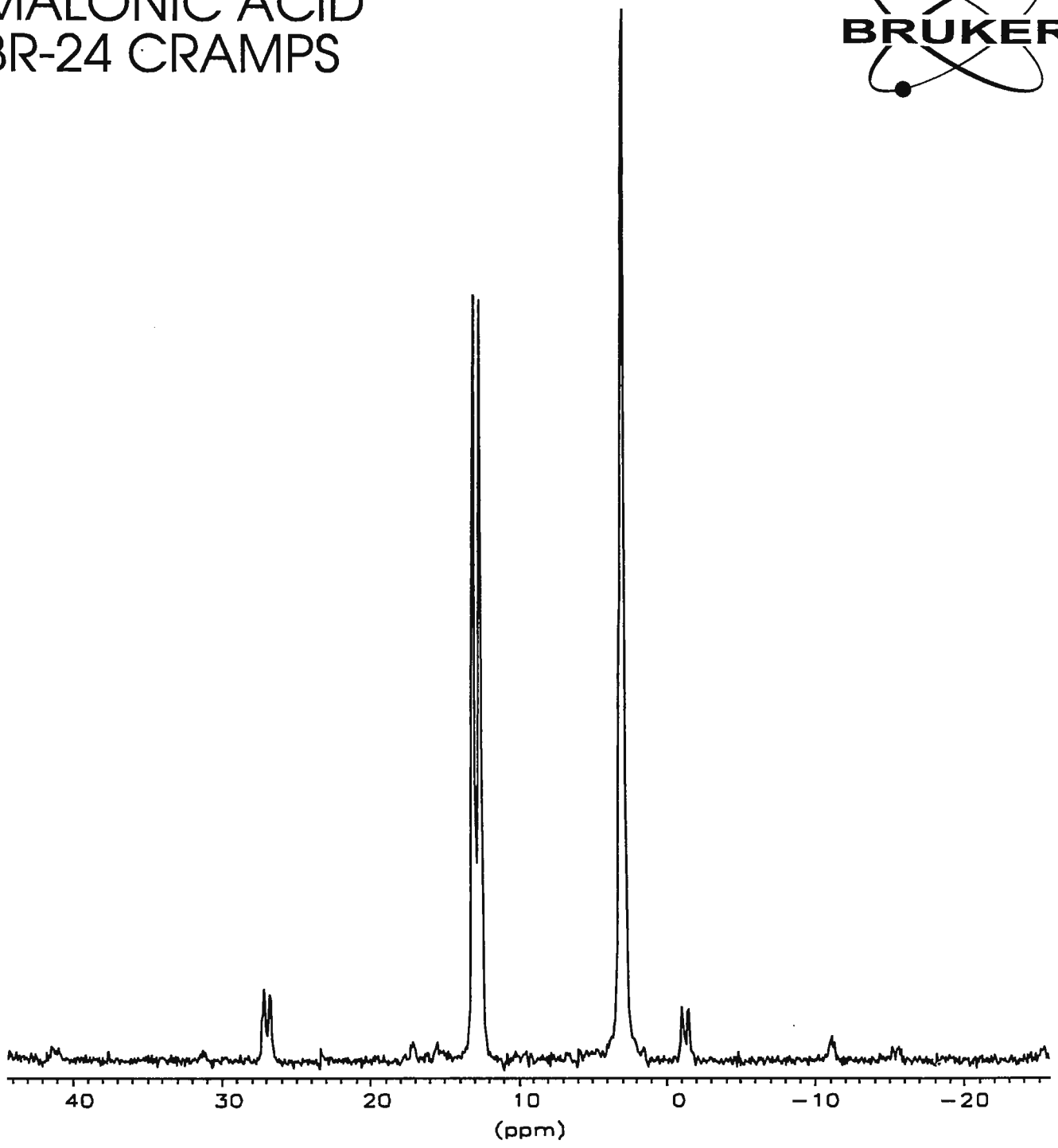
We have so many new features and results in solid state NMR that we just couldn't wait any longer to tell you about them. So we decided not to wait!

Come and join us for a one-day symposium just before the Rocky Mountain conference, July 25, 9:00 AM to 5:30 PM at the Denver Hyatt hotel. Anyone interested in solid state NMR is welcome. You'll have a chance to see our new developments and also find out what some of our users have been doing.

Contact Doug Burum at (508) 667-9580 for more details. See you there!



MALONIC ACID
BR-24 CRAMPS



The Bruker ASX offers many features that make it ideal for CRAMPS, including 50 nsec phase switching time, 1 kW droop-free 1H rf and a receiver with 4 MHz bandwidth and 451 MHz IF frequency. As a result, the ASX consistently produces high quality CRAMPS spectra that are well resolved and nearly artifact free.

The above spectrum was obtained using a quadrature detection technique developed at Bruker. The rf carrier was at approximately 10 ppm.

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Fri May 14 1993

(received 5/18/93)

Dear Barry:

I am pleased to be able to write you about some of the recent results ***Stu Adler*** has obtained using ^{17}O NMR to probe atomic motion in barium indium oxide (Fig. #1). These measurements, in conjunction with high-temperature x-ray diffraction and thermal analysis, provide information about the onset and rate of oxide-ion motion in this layered, perovskite-related material. The NMR and thermal analysis show that at 925C there is an order-disorder transition which involves the oxygen atoms in the tetrahedral layers. However, both NMR and x-ray diffraction show that the material retains an orthorhombic (layered) structure until ~1075C, where the material becomes cubic. The number of mobile oxygen atoms in the structure increases continuously between 925C and 1075C, and only above 1075C does the full population of anions become mobile. These results imply that vacancies become mobile primarily within the tetrahedral layers at the order-disorder transition, and contribute to transport "two-dimensionally".

Measurements of high-temperature oxygen-17 NMR were made using homebuilt water-cooled NMR probe which is a modification of a design described previously(Rev.Sci.Instr. **61** 3368,1990). The probe has the advantage that the radio-frequency electronics, including the NMR coil, remain at room temperature, ensuring constant receiver sensitivity and power delivery. The furnace, which rests inside a water-cooled NMR coil, has been redesigned to minimize temperature gradients (max. 7C at 900C), and improve filling factor (~48%). The circuit has also been redesigned to improve power delivery and sensitivity, and can now produce a 9μs, $\pi/2$ pulse for ^{17}O in water at 24.58 MHz. The circuit stability of the probe allows direct comparison of nutation rates and signal intensities at different temperatures.

Figure 2 shows the reciprocal of the linewidth (*T2) between 700 and 1200C, along with measured values of T2 and T1 at selected temperatures. The linewidth is roughly independent of temperature below 850C, and is best described as a Gaussian. Above 800C, however, the lineshape begins to acquire a Lorentzian shape, and the time constants *T2, T2, and T1 converge. This change from a Gaussian line to a lifetime-broadened line suggests an increase in MHz frequency motion.

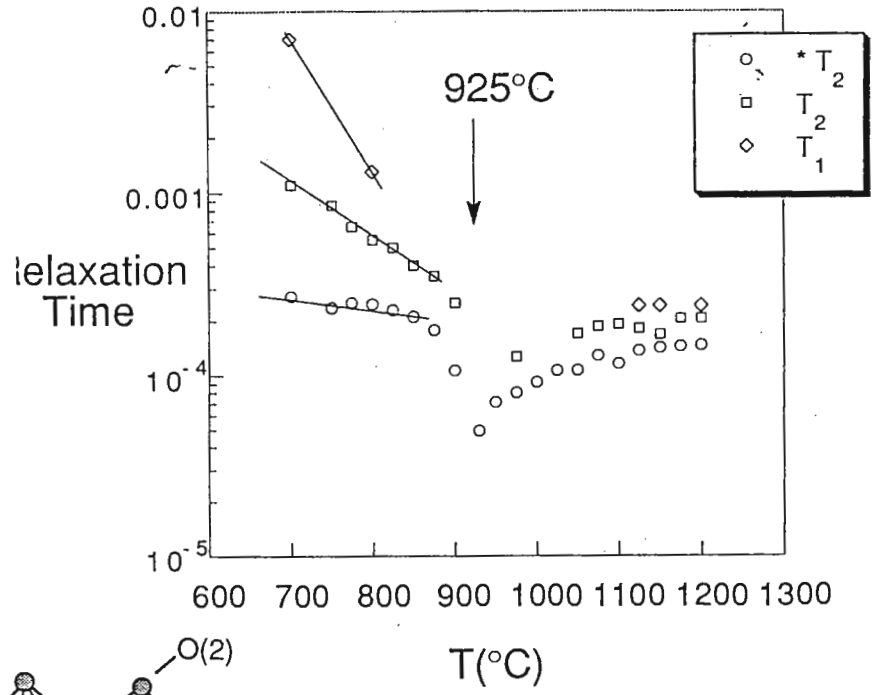
At 925C there is a sharp maximum in the linewidth, and at the same temperature both T2 and T1 become too short for us to measure (<100μs). Both these facts indicate that the lineshape becomes lifetime broadened, and that there is a sharp maximum in the relaxation rate. Singularities in the relaxation rate similar to this one are commonly observed at order-disorder transitions in solids, and indicate critical slowing-down of phonon modes at the critical temperature. This "slowing" of lattice vibrations to MHz frequencies results in an increased coupling of the spin system to the lattice, and therefore a singularity in the spin-lattice relaxation rate. This maximum occurs at the same temperature as an endotherm in a DTA and an extraordinary jump in ionic conductivity. Together, these

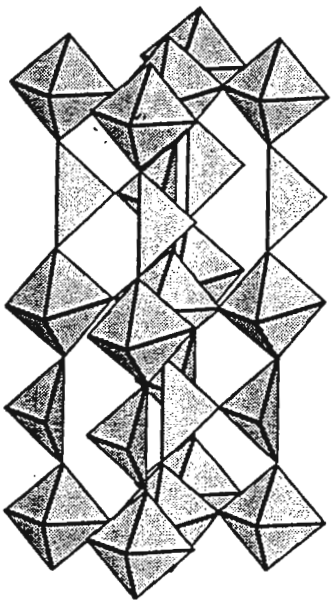
measurements are very strong evidence for an order-disorder transition at 925C. Despite this transition, however, it is clear from the X-ray powder diffraction that the disordering of the vacancies is not isotropic until above 1000C.

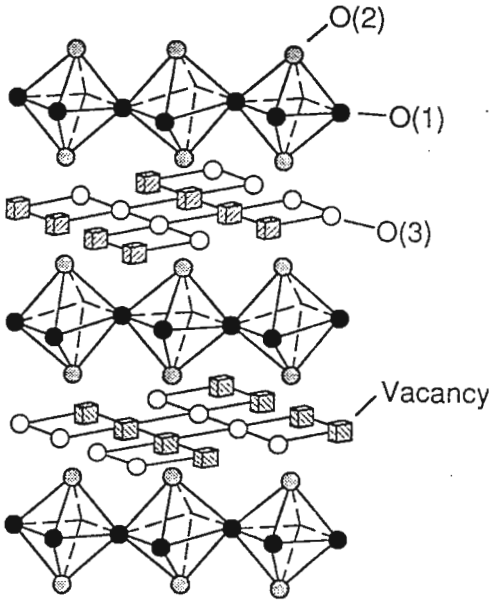
I am also pleased to announce that Stu has received an NSF-NATO Postdoctoral Fellowship and will be joining Brian Steele's group at Imperial College for a year.

Best regards,

p.s. Please credit this contribution to the Raychem account!







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Dear Dr Shapiro

Theix, 1993 april 20
(received 4/28/93)

T2 MAPPING OF WATER IN RABBIT MUSCLE. EFFECT OF BRINE INJECTION

Water-holding capacity is enhanced when meat is treated with salt. ^{31}P spectroscopy, ^{1}H and ^{23}Na NMR micro-imaging have been used to investigate the effects of brine injection. One part of this study reported here, concerns the *post mortem* evolution of the transverse relaxation time (T_2) of the water proton in rabbit muscle during a period of 1000 min after muscle excision.

Rabbits were anesthetized, the *biceps brachii* muscle exposed and its axillary arteries and veins ligated and cut. Brines (0.5 ml, 3M or 5M NaCl at 0°C) were arterally injected. The muscle (3-4g) was then excised, wrapped in parafilm and transferred in the micro-imaging probe head maintained at 4°C. NMR experiments were recorded on a Bruker AM 400 spectrometer equiped with the AM imaging accessory. A multiecho spin-echo sequence was used. The echo time was 11.5 ms and the repetition time was 3 s. Data matrix was 128x128 pixels giving a pixel size of 157 µm. The slice thickness was 2 mm. Total acquisition time to acquire a set of 8 images was 15 min for 2 scans. T_2 images were generated from this set by exponential fit, pixel by pixel.

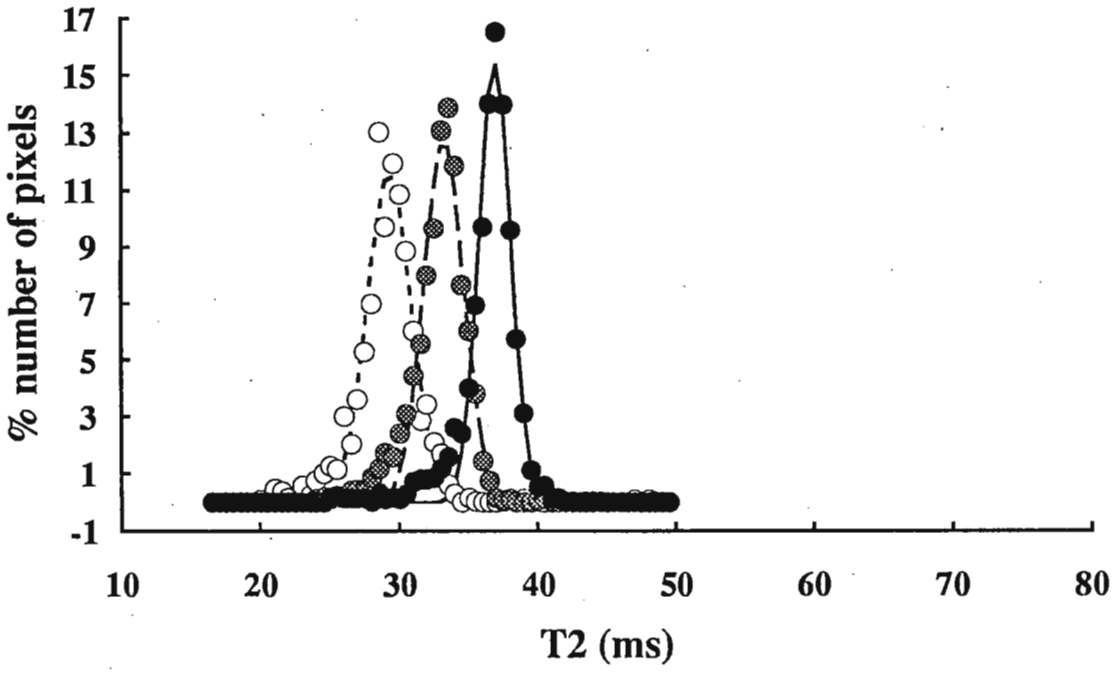
Fig.1-a,b are histograms, respectively for intact and salted (5M) muscles, in which the percentage of pixels in a T_2 interval is plotted against T_2 for 40, 220 and 1000 min *post mortem*. These data can be used to determine the mean value, peak width (for symmetrical distribution) or skewness and kurtosis parameters (for asymmetrical distribution).

From these experiments, a number of important points emerge. (i) For intact muscle, the T_2 distribution is symmetric, the values are relatively homogeneous and increase with time *post mortem* to reach an equilibrium value of about 36 ms. (ii) For injected muscles, the distributions are always asymmetric with a great spatial heterogeneity of T_2 values. (iii) At first, the highest T_2 values correspond to the proximity of injection site (artery). Then NaCl diffusion allows an homogenization of T_2 values but were still more variable than in the intact muscle.

Sincerely yours

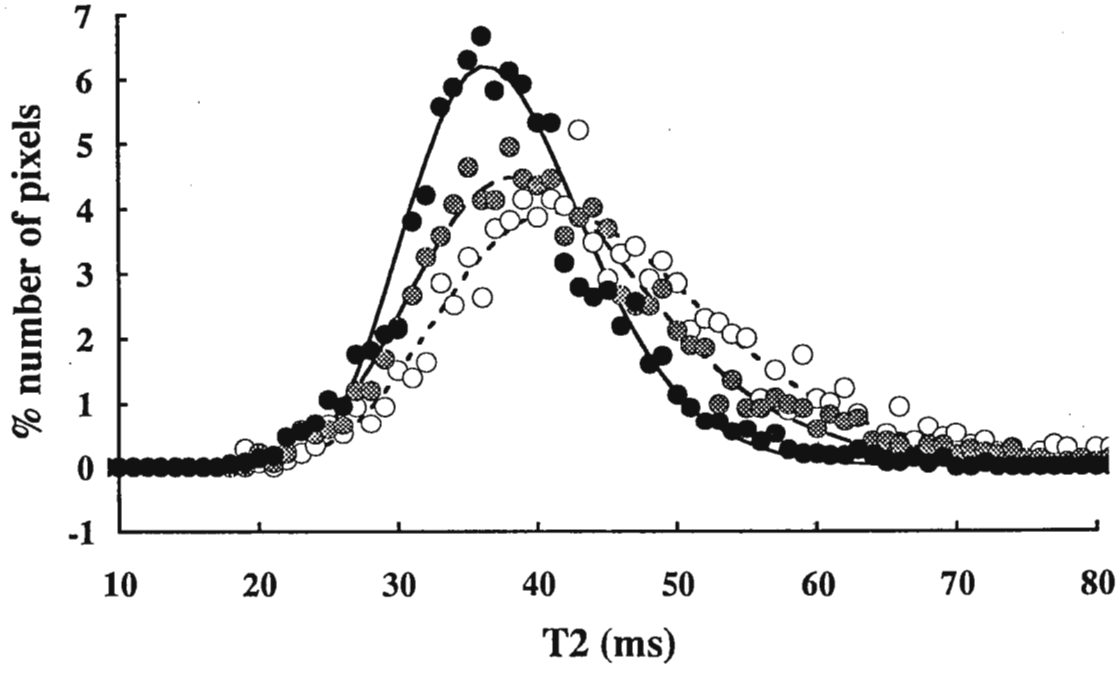
L. FOUCAT G. BIELICKI A. TRAORE J.P. RENOU

Fig.1-a



40 220 1000 min post mortem

Fig.1-b



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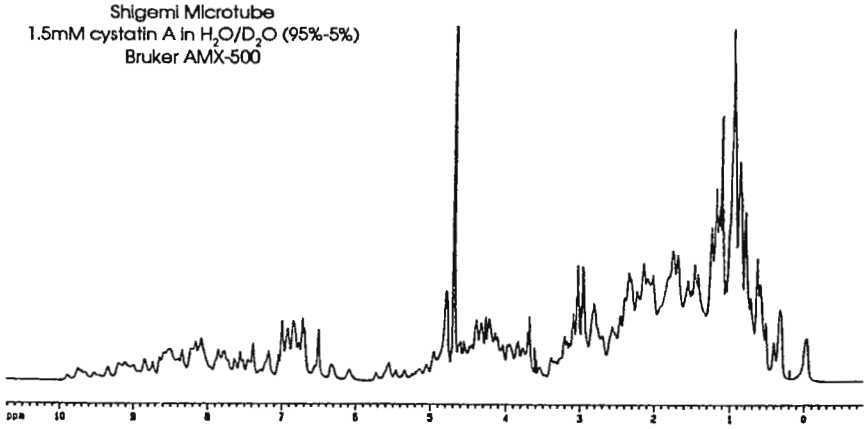

Figure 1: 1D spectrum of 1.5 mM protein dissolved in 250µl H_2O solution.

A protein, 11kDa, was dissolved in 250µl H_2O solution (pH 3.8) containing 5% D_2O for frequency lock and packed into the Shigemi Microtube. This spectrum was measured at 37°C on a Bruker AMX500 spectrometer with scan times 64. The solvent signal was suppressed by using low power RF irradiation.

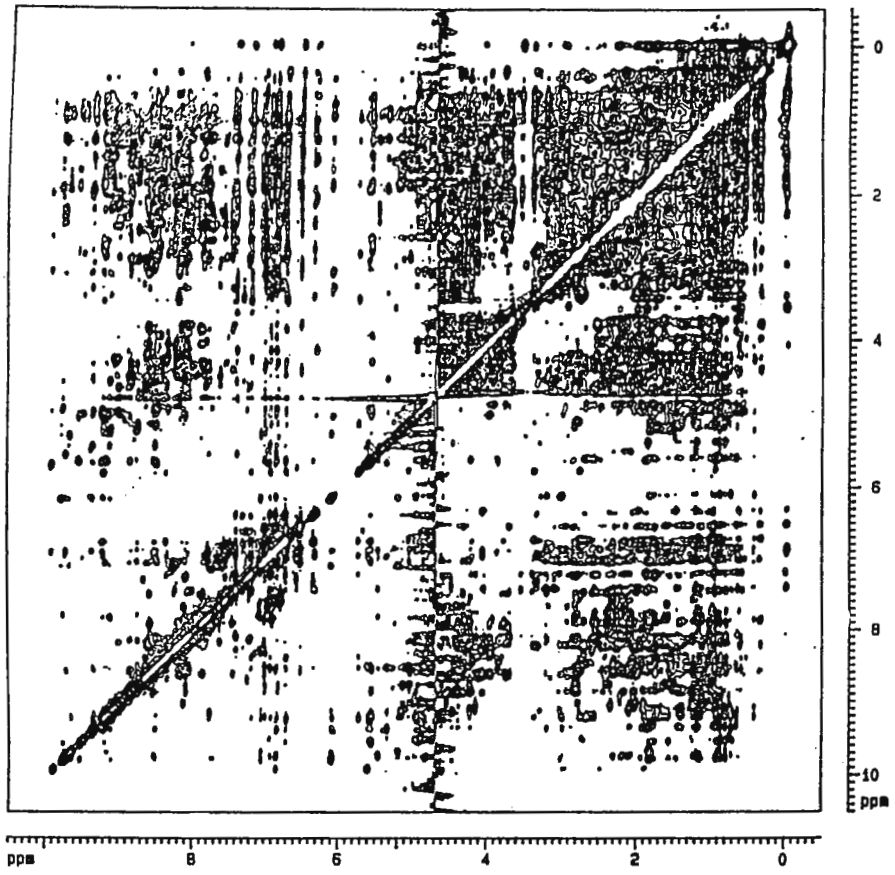

Figure 2: 2D NOESY spectrum of the same sample in Shigemi Microtube.

This 2D NOESY spectrum (τm=150 msec) of the protein in 250µl H_2O solution was measured with scan times 32 on a Bruker AMX500 spectrometer. The observed data matrix size was 1024 (t_2) x 200 (t_1) complex points. This matrix was processed with zero filling along t_2 dimension and resulted in a final data matrix of 1024 (F2) x 512 (F1) real points. It should be noted that baseline correction and digital processing were **not** applied to remove the water signal.

TOKYO METROPOLITAN UNIVERSITY
Department of Chemistry, Faculty of Science
1-1, Minami-Ohsawa, Hachioji, Tokyo 192-03
Japan

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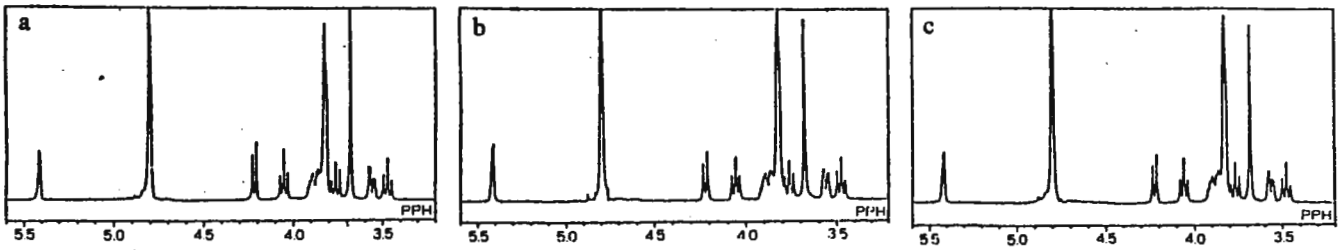
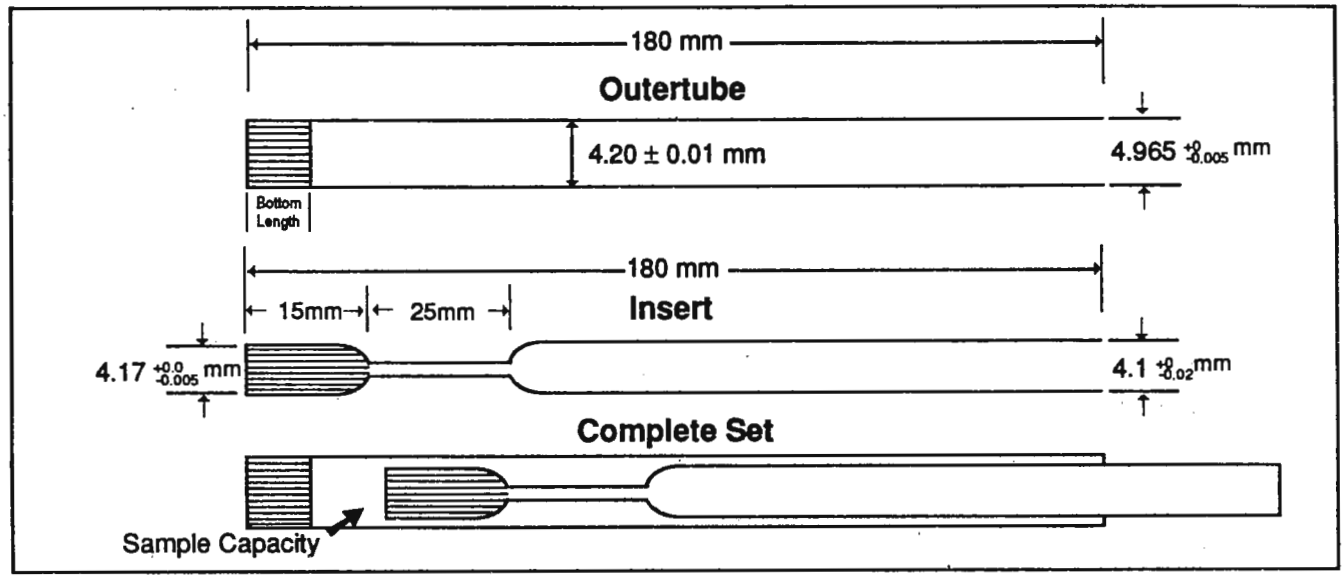


The 400-MHz 1H-NMR spectra of 10mM Sucrose in D_2O with varying sample height in the Symmetrical microtube. a) 5mm (49 µl); b) 3mm (41 µl); c) 2mm (28 µl)



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Professor Bernard L. Shapiro
TAMU NMR Newsletter
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19 April 1993
(received 4/30/93)

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A Simple Method for Obtaining Accurate Volumes for Partially Overlapping Crosspeaks in 3D Through-Space Correlated Experiments

Dear Professor Shapiro:

We are evaluating multi-dimensional NMR methods for determining solution conformation of proteins and polypeptides on mid-field instruments. In our initial studies, we have found that on a 300 MHz instrument, 3D homonuclear experiments for delineating through-space connectivities provide sufficient spectral dispersion to assign individual ^{1}H resonances to specific protons. To obtain distance constraints from these 3D experiments (NOESY-NOESY, HOHAHA-NOESY, NOESY-HOHAHA), we must be able to quantitate cross-peak volumes. To obtain accurate volumes using algorithms which rely on the summation of the intensities of all points in a 3D region, a crosspeak must be well resolved in all three frequncy dimensions. We have found, however, that in 3D experiments obtained on mid-field instruments a cross-peak is often well resolved in only two of the three frequency dimensions. Figure 1 shows an example of such a crosspeak.

An alternative approach for obtaining cross-peak volumes in 2D experiments was proposed by Holak, et al. (1). In this approach the volume of a cross-peak was defined to be:

$$A_{ab} = \frac{I_a I_b}{i_{ab}}. \tag{1}$$

In expression 1, A_{ab} is the cross-peak volume; I_a and I_b are the integrals of intersecting one-dimensional cross sections through the cross-peak, and i_{ab} is the intensity at the intersection of these cross sections. This approach offers several advantages for 2D experiments. For instance, it permits the determination of accurate cross-peak volumes in cases where cross-peak overlap would prevent the determination of accurate volumes by summation of all points in a two-dimensional region. This method, however, requires that the peaks in the 1D cross sections through a 2D cross peak be well resolved to obtain accurate volumes.

This protocol can easily be extended to higher-dimensional NMR experiments. We have found that the volume of a three-dimensional cross-peak is given by:

$$A_{abc} = \frac{I_a I_b I_c}{i^2_{abc}}. \tag{2}$$

In expression 2, A_{abc} is the cross-peak volume; I_a, I_b and I_c are the integrals of intersecting one-dimensional cross sections through the cross peak, and i_{abc} is the intensity at the intersection. These one-dimensional integrals

can be obtained via the use of peak fitting algorithms such as those contained in Felix 2.05B. The use of these peak fitting algorithms permits us to obtain accurate one-dimensional integrals even in cases of rather severe resonance overlap. Consequently, this method enables us to obtain accurate 3D cross-peak volumes in cases where crosspeaks are not well resolved in all three frequency dimensions.

In table I, we present a summary of the volume integration data obtained with the use of expression 2 on crosspeak **1** in Figure 1. Integrals were calculated at points **A**, **B** and **C** in Figure 1b. These data indicate that the values of the volume integrals obtained at these three points agree within ≈30% which corresponds to an error in the corresponding interproton distance of ≈5%.

(1) Holak, T.A.; Scarsdale, J.N. & Prestegard, J.H. (1987) *J. Magn. Reson.*, 74:546–549.

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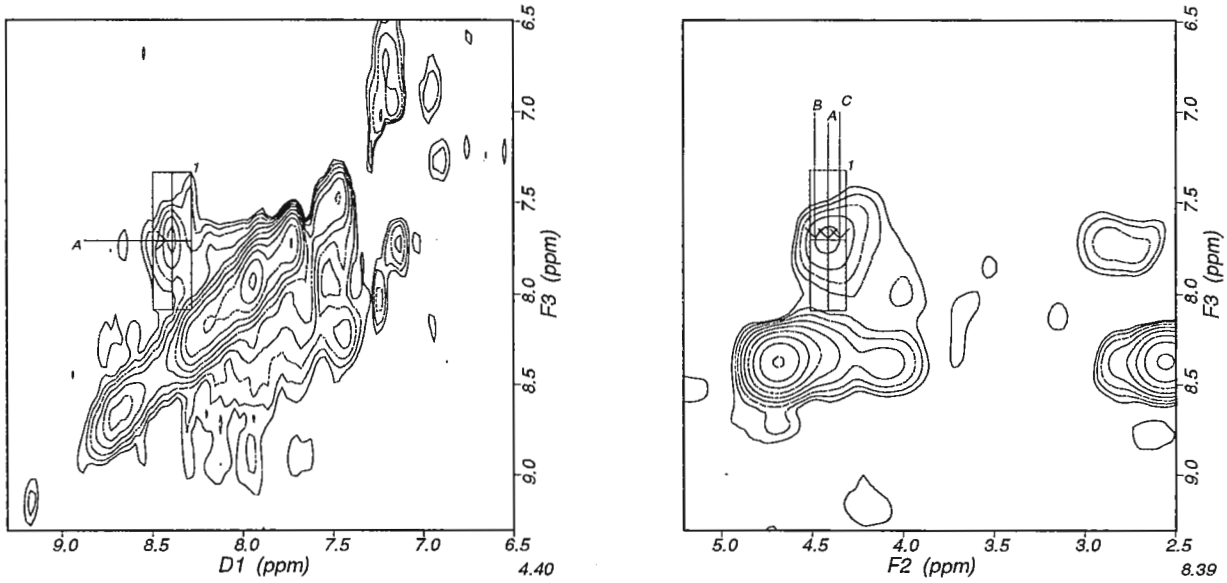

Figure 1: Contour plots of (A) F1,F3 slice taken through $C_\alpha H$ resonance at 4.40 ppm and (B) F2,F3 slice taken through NH resonance at 8.39 ppm from 300 MHz HOHAHA-NOESY data set on 31 residue peptide comprising the prekallikrein binding domain of high-molecular weight kininogen. The highlighted crosspeak corresponds to an interresidue NH,C_αH connectivity. This peak is an example of a crosspeak for which it would be difficult to obtain an accurate volume using volume integration algorithms which rely on summation of all points within a given region.

Table I: Summary of Integration Data For Crosspeak 1

slice	I_a	I_b	I_c	i_{abc}	A_{abc}
A	26.9	93.6	91.6	7.88	3714
B	25.3	93.6	116.	8.54	3769
C	27.1	93.6	113.	7.79	4723

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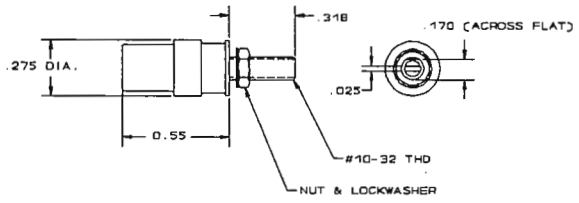

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PETROLEUM RECOVERY INSTITUTE

April 27, 1993
(received 5/3/93)

Variable Temperature Magnetic Resonance Imaging

Dear Barry,

The Petroleum Recovery Institute Imaging Centre has had considerable need for the ability to image materials under non-ambient conditions (eg, high temperature and pressure). To this end we have designed and constructed several (commercially available) non-magnetic sample holders capable of being used to image materials at up to 5000 psi at about 100C. Sample sizes (again depending on temperature / pressure ratings can be up to 3 1/2 inches in diameter and about 19 cm in length (although longer lengths are also possible). In addition to these devices we have also designed and constructed a complete variable temperature system (also to be made commercially available) for use in large bore horizontal superconducting magnets. This system has been in operation for several months now and this letter provides a brief overview of the possible applications of these devices.

There are numerous advantages and applications of variable temperature MRI, including, for instance those related to: accurately reproducing process conditions, making fewer assumptions and extrapolations for data analysis and correlations, curing, crystallization, phase transitions(primary, secondary), chemical reactions, oxidation, reproduce thermal history, storage conditions, exchange processes, diffusion, degradation, aging, polymerization, reactor design and operation, freezing/drying/thawing, rheological studies of composites/plastics, alter experimental conditions to make data acquisition easier (higher temperature -> longer T_2 -> longer echo time TE). It can also be used to enhance contrast among phases / components characterized by different relaxation time regimes and activation energies and to characterize multiple / competing processes in complex systems.

Our hardware is characterized by the following features: sufficiently non-magnetic to be used within 1 meter of a 2.35T magnet (with no detectable change in resonance frequency for an unlocked 1H acquisition), designed for easy access / modification / maintenance and easy sample (re)placement, no increased noise due to pumps/fans/electrical devices, vacuum-jacketed & water-cooled glass insert into which probe is placed to keep probe at ambient temperature, several fail-safe devices to shut down device in case of insufficient air/water flow rates, extremely well thermally insulated to maintain constant temperature (temperature setpoint = sample temperature due to design), accurate temperature maintenance, and reasonable equilibration times (<20-45 minutes) (depending on accuracy required and magnitude of change in temperature). All data were acquired on a Bruker Biospec 24/30 equipped with an X32 computer system.

Figure 1 gives a schematic representation of the variable temperature accessory. and Figure 2 illustrates the relationship between the setpoint temperature and actual sample temperature. Figure 3 shows the variation in T_2 versus temperature for an EPDM rubber. The T_2 of EPDM increases from 5.1 ms at 16C to 28 ms at 100C, corresponding to a significant increase in relative signal intensity for images acquired with a fixed echo time (TE) of = 12 ms in this case. The results in Figure 4 compare the T_2 vs temperature behaviour of a polyvinylchloride (a carbon-black filled pipe) with that of a fluid in a porous medium, namely, water-saturated Berea sandstone cores. The PVC T_2 exhibits a small monotonic increase in temperature from 1.5 ms at 16C to 2.8 ms at 100C, whereas the water in the core displays a more complex variation with temperature over the same temperature range, but does not change significantly even though the temperature has been changed by about 80C. We have generally found that fluids in a variety of porous media are insensitive to, or decrease with, an increase in temperature. Furthermore, as shown in Figure 5, this behaviour also extends to quadrupolar nuclei in the same porous media. In this experiment we measured the ^{23}Na relaxation times in the brine used to saturate the Berea core.

Best Regards,
Dave
D. E. Axelson

Petroleum Recovery Institute
3512 - 33 Street N.W., Calgary, Alberta, Canada
T2L 2A6

Telephone: (403) 282 - 1211 Fax: (403) 289 - 1988

Figure 1. Schematic representation of variable temperature accessory.
Figure 2. Set point temperature versus sample temperature.
Figure 3. T_2 versus temperature for an EPDM rubber.
Figure 4. T_2 versus temperature for a PVC pipe and a water saturated Berea core.
Figure 5. Variation in T_2 versus temperature for ^{23}Na in brine saturated Berea sandstone core.

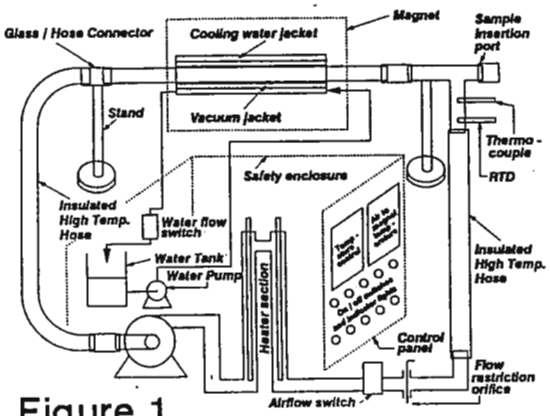
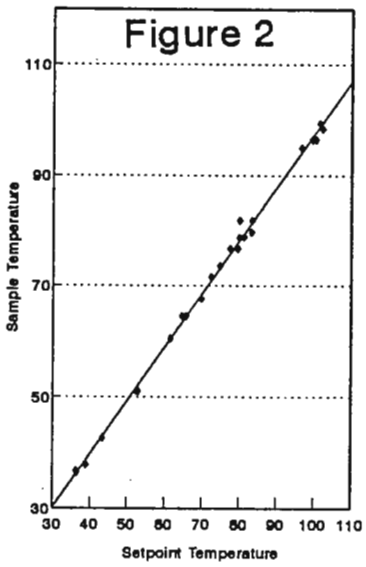


Figure 1



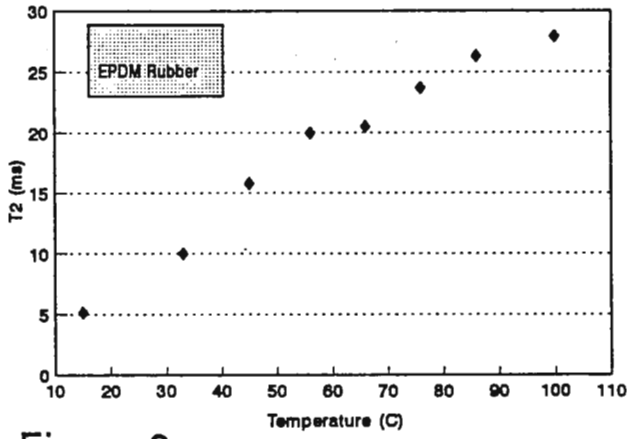
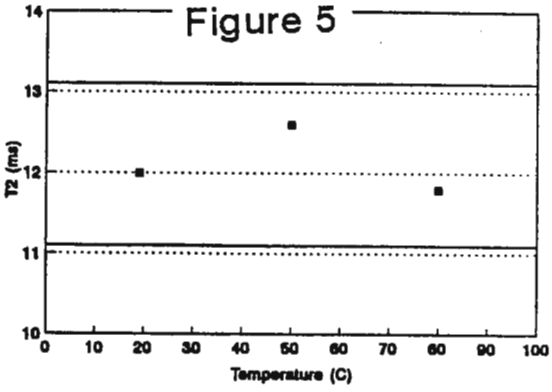


Figure 3



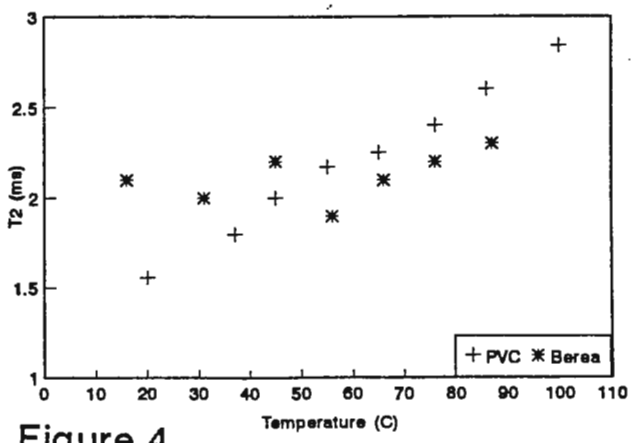


Figure 4

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TAMU NMR Newsletter
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U S A

Zürich, May 13, 1993
(received 5/22/93)

Direct Measurement of Xenon Exchange between Gas and Liquid Phase by 2D NMR

Dear Barry,

We have recently investigated the liquid–gas phase equilibrium and dynamics in xenon. The coexistence of liquid and gas phase below the critical point (T_c=290 K, P_c=59 bar) can easily be monitored in the ^{129}Xe NMR spectrum, because of the different chemical shifts in the two phases. Two–dimensional ^{129}Xe exchange experiments directly reveal the interface crossing of xenon atoms and show the microscopic dynamics under macroscopic conditions and provide information on the diffusive or interfacial control of the exchange.

The measurements were performed at different temperatures under isochoric conditions. The sample tube has an inner diameter of 6 mm and a length of 15 mm and fits into a horizontal 9 mm diameter solenoid coil. All experiments were performed on a home–built spectrometer with a proton resonance frequency of 220 MHz. It is visible in Fig. 1 that coexistence of the two phases is possible between 230 and 280 K for our sample. The exchange of ^{129}Xe nuclei between liquid and gas phase at 256 K is observed in the 2D exchange spectrum of Fig. 2 for a mixing time of 10 s. The cross–peak build–up as a function of the mixing time is shown in Fig. 3.

Information on the kinetic control of the transfer between the phases is obtained from the exchange behavior at short mixing times. We describe the particle transfer between the two phases by the decay of an initial concentration distribution that is represented by a spatial step function. The concentration profiles $C_{liquid}(x,t)$ and $C_{gas}(x,t)$ at different mixing times τ_m can be calculated analytically for a one–dimensional model of infinite dimensions [1]:

$$C_{liquid}(x,t) = \frac{1}{1+k\sqrt{\frac{D_{gas}}{D_{liquid}}}}\left[1+k\sqrt{\frac{D_{gas}}{D_{liquid}}}\,erf\left(\frac{x}{2\sqrt{D_{liquid}\,t}}\right)\right] \quad , \quad C_{gas}(x,t) = \frac{1}{1+k\sqrt{\frac{D_{gas}}{D_{liquid}}}}\left[erfc\left(\frac{|x|}{2\sqrt{D_{gas}\,t}}\right)\right] \qquad (1)$$

where k is given by ρ_{liquid}/ρ_{gas}, the ratio of the two densities at 256 K and D_{gas} and D_{liquid} are the self-diffusion coefficients.

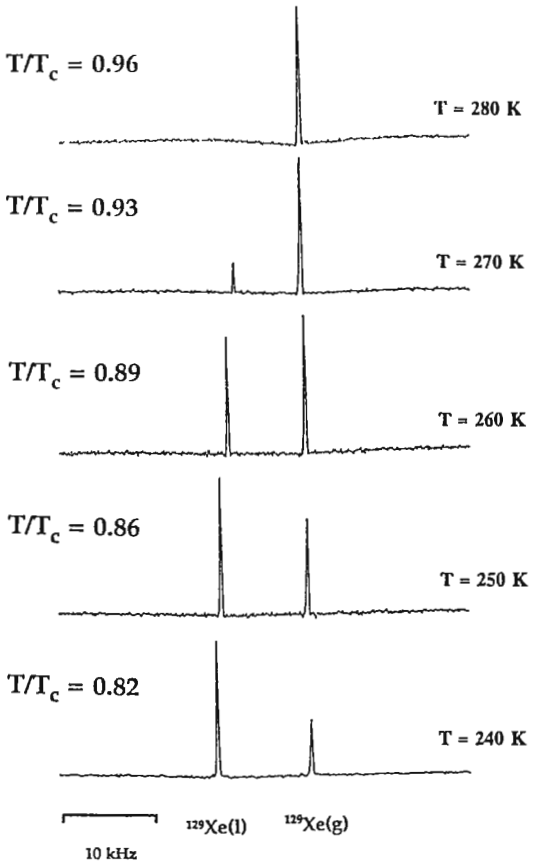

Fig.1: Single-pulse ^{129}Xe NMR spectra in the coexistence region of the Xe(l)⇌Xe(g) system. The reduced temperatures (T/T_c) are indicated in the figure.

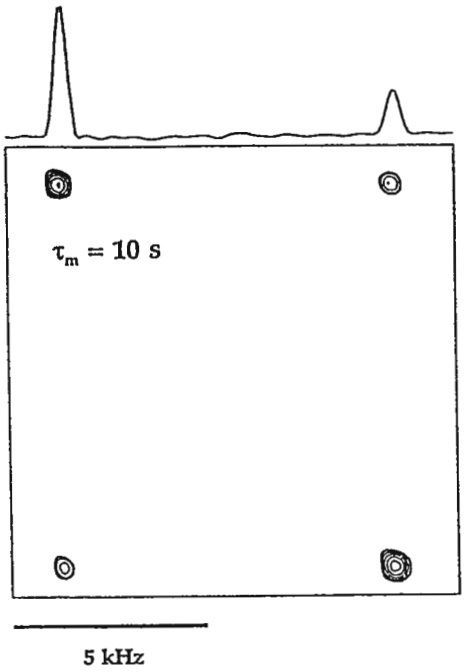

Fig.2: 2D spectrum of ^{129}Xe inter-phase diffusion recorded at 256 K. The mixing time τ_m is indicated on the spectrum. The 1D spectrum represents a horizontal slice through $^{129}Xe(l)$ diagonal peak and the corresponding cross peak.

The solid curve in Fig. 3 represents a numerical integration of the expressions above over the spatial coordinate x. No adjustable parameters are used. The agreement with experimentally determined values for t→0 shows that no barrier at the interface has to be taken into account to describe the experimental exchange behavior. The xenon self-diffusion coefficients in the two phases are taken from independent measurements in the literature [2] (D_{liquid}(256 K)=(8.3±0.3) 10^{-3} mm^2/s and D_{gas}(256 K)=(1.1±0.2) 10^{-1} mm^2/s).

We want to point out that the applied simple one-dimensional model is only valid for short mixing times. The deviation from the experimental points at longer mixing times is determined by the finite size of the system, where the boundary conditions have to be taken into account. A comparison of calculations and experiments indicates that no significant barrier for the crossing between phases exists in the present system.

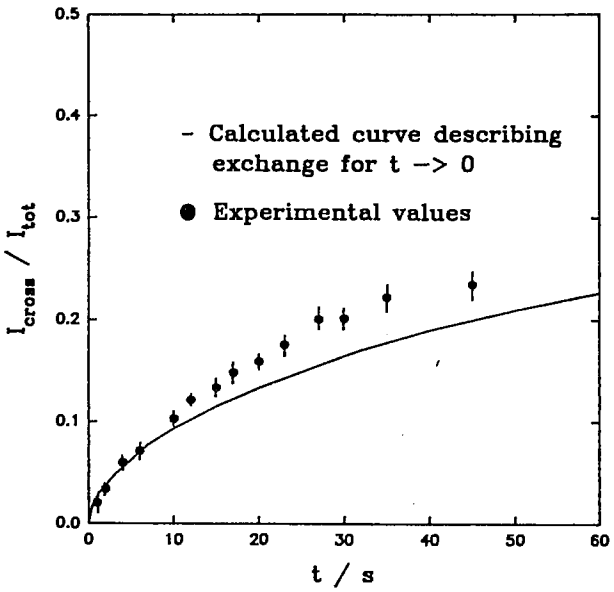

Fig.3: Build-up of cross-peak intensity with increasing mixing time at T=256 K. The points represent experimental values while the curve is a prediction according to the integrated formulae (1).

In summary, we have shown that ^{129}Xe NMR spectroscopy can be used to study thermodynamic and kinetic characteristics in the gas-liquid coexistence region. At 256 K and for the given dimensions of the NMR tube, the liquid-gas transfer process can be well explained by diffusive control in the gas phase. The characteristic time needed to diffuse to the interface from within the gas-phase is 22±7 s. This is the rate-limiting step of the exchange process.

Best wishes.

M. Tomaselli B.H. Meier P. Robyr U.W. Suter R.R. Ernst

[1] J. Crank, "The Mathematics of Diffusion", Clarendon Press, Oxford (1975).
[2] P.W.E. Peereboom, H. Luigjes, and K.O. Prins, Physica A *156* (1989) 260.

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* * * * *

All Newsletter Correspondence

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No. 421 (October) -------24 September 1993
No. 422 (November) -------22 October 1993

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 of this issue is adorned with a large **red dot** or circle: this decoration means that you will not be mailed any more issues until a technical contribution has been received by me.

PLEASE

Page Length Instruction

Attention overseas subscribers: If you must use paper which is longer that 11", *please* take care that all material (including signatures, addresses - everything!) ends no more than 10" from the top of each of your pages. It is costly to make reductions, and henceforth I reserve the right to chop the excess length off any page, no matter what the result. Beware of the dreaded guillotine! Your cooperation in this matter will be greatly appreciated.

We'll supply the isotope. The rest is up to you.

The first privately funded Isotope Research Grant Program.

CIL is proud of its leadership role in the field of stable isotopes. As a measure of our commitment to the advancement of research utilizing stable isotope labeled compounds, CIL has set aside up to $100,000 of Carbon-13 labeled materials to be granted to support novel research in the use of stable isotopes.

CIL recognizes that economic conditions are limiting the scope of many valuable research projects. We are seeking proposals from researchers interested in developing new applications or new detection methods for stable isotopes as well as from synthetic chemists who wish to pursue novel synthetic routes for organic materials.

We hope that this program represents the best in cooperative research between private industry and the scientific community.

Please call for information on how to apply for one of ten $10,000 research grants.

CIL

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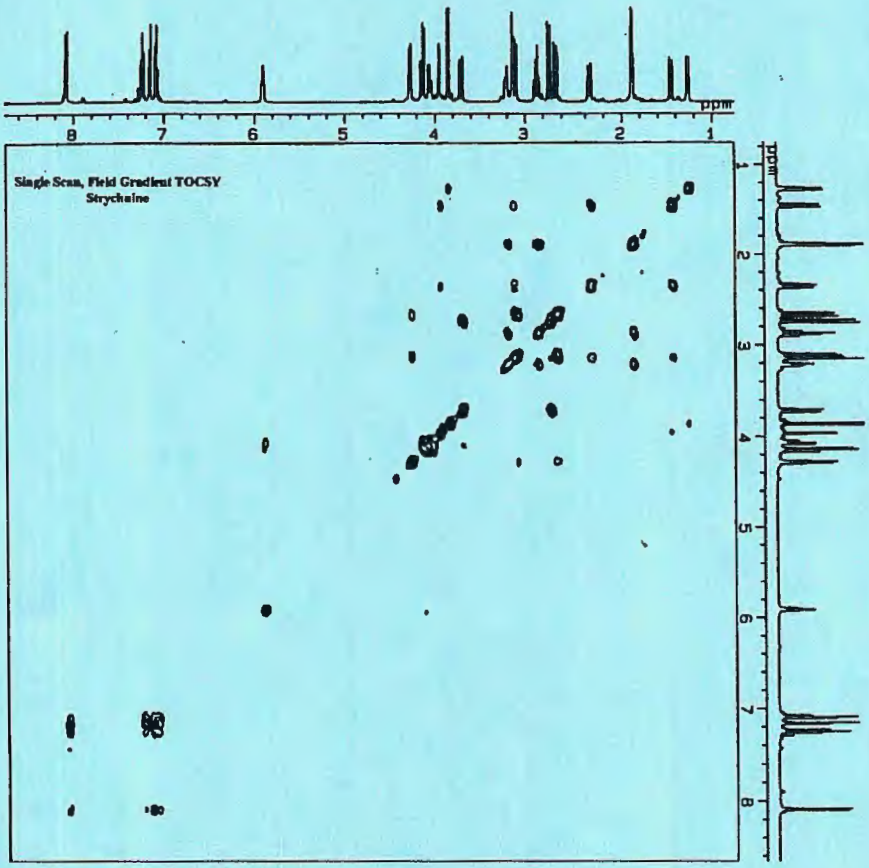
FROM JEOL USA

Gradient Probes



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

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