THE NMR NEWSLETTER

No. 438

March 1995

continued on inside back cover

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Iso. Purity (D)	Density (g/cc)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetic Acid-d_4	CD_3COOD	99.5%	1.17	17	118	0.551 (32)
D-120	Acetic Acid-d_4 + TMS		99.5%				
D-13	Acetone-d_6	CD_3COCD_3	99.9%	0.84	-94	57	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129							
D-14							543 (20)
D-21							0.611
D-122							
D-130							
D-28	Choloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

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Cat. No.	Paper Size	Instrument Model	Type
WCV-100 (S-100A)	11" X 26"	HA-100, HA-100D	Gridded-Two Color
WCV-60 (A-60C)	11" X 26"	A-60, A-60A, A-60D	Gridded-Two Color
WCV-XL (XL-100)	11" X 26"	XL-100 (C and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
WCV-20 (CFT-20)	11" X 16 3/4" X 17"	CFT-20, FT-80, FT-80A All Models 16 1/2" or 16	Gridded-Two Color Blank

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FORTHCOMING NMR MEETINGS

Symposium on "*In Vivo* Magnetic Resonance Spectroscopy VIII", North Falmouth, Massachusetts, **March 25 - 26, 1995**; Contact: Radiology Postgraduate Education; Room C-324, University of California School of Medicine, San Francisco, CA 94143-0628; Phone: (415) 476-5731; Fax: (415) 476-9213; For registration, call (415) 476-5808.

Symposium on "Advances in NMR Applications", Boston, MA, **March 26, 1995**; Contact: Victoria Davies at Nalorac, 837 Arnold Drive, Martinez, CA 94553; (510) 229-3501; Fax: (510) 229-1651. See Newsletter 438, 50.

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073.

Keystone Symposia on Molecular and Cellular Biology, Frontiers of NMR in Molecular Biology - IV, Keystone, Colorado, **April 3 - 9, 1995**; Organizers: S. W. Fesik, T. L. James, and G. Wagner; Contact: Keystone Symposia, Drawer 1630, Silverthorne, CO 80498; Phone: (303) 262-1230; Fax.: (303) 262-1525.

International School of Biological Magnetic Resonance, 2nd Course: Dynamics and the Problem of Recognition in Biological Macromolecules, Erice, Trapani, Sicily, Italy , **May 19 - 30, 1995** ***(Note the new dates.)***; Contact: Prof. O. Jardetzky, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94305-5055; Phone: (415)723-6270; Fax: (415) 723-2253; or, Prof. J.-L. Lefèvre, ESBS, CNRS-UPR9003, Univ. Louis Pasteur, Blvd. Sébastien Brant, F67400 Illkirch Graffenstaden, France; Phone: (+33) 88-655269; Fax.: (+33) 88-655343; See Newsletter 438, 54.

Summer School on "Isotope Effects as Tools in Basic and Environmental Research", Roskilde, Denmark, **June 24 - 28 1995**; Contact: Prof. P. E. Hansen, Fax +45 4675-7721, or Phone +45 4675 7781-2432 or +45 4675-7711, ext. 2432; . See Newsletter 438, 39.

Workshop on "Structure Determination from NMR", Pittsburgh Supercomputing Center, Pittsburgh, PA, **June 25 - 28 1995**; Contact: N. C. Blankenstein: blankens@psc.edu or (412) 268-4960. See Newsletter 438, 29.

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

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. W. A. Bubb, Dept. of Biochem., Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-351-4120; Fax: +61-2-351-4726; Email: ismar95@biochem.su.oz.au. See Newsletter 437, 20.

NMR Symposium at the 37th Rocky Mountain Conference on Analytical Chemistry, Denver Colorado, **July 24-27, 1995**; Contact: Dr. Alexander J. Vega, DuPont Central Research and Development, P.O. Box 80356, Wilmington, DE 19880-0356; Tel. (302) 695-2404; Fax: (302) 695-1664; e-mail: vega@esvax.dnet.dupont.com. See Newsletter 432, 34.

continued on p. 53

ABBOTT

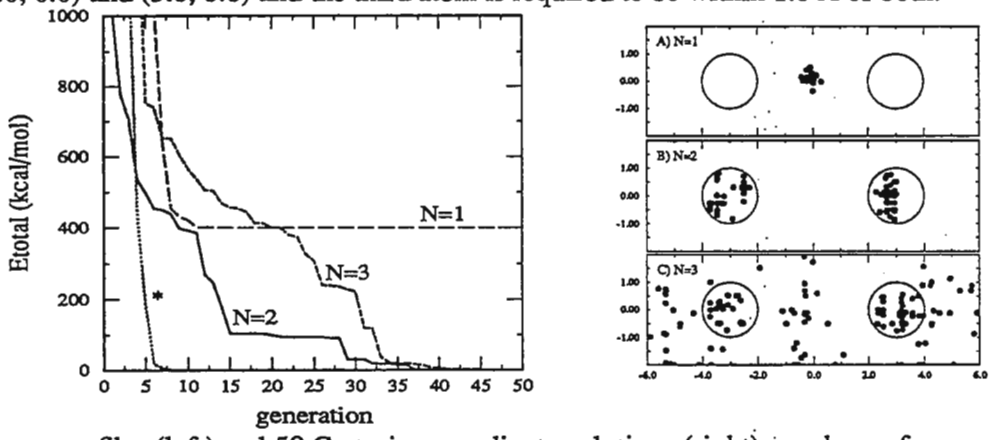
Abbott Laboratories
Pharmaceutical Discoveries Division
Abbott Park, IL 60064

Feb. 16, 1995 (received 2/21/95)
Dr. B.L. Shapiro, Publisher
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

EGADS: An Ensemble Genetic-Algorithm for the Docking of Structures

Dear Dr. Shapiro,

We have recently been investigating methods for determining high-resolution NMR structures of proteins when bound to small, low-affinity ligands. One problem with such an analysis is the possibility that a single structure cannot satisfy all of the NOE-derived distance restraints. Although the use of time-averaged restraints may yield a family of structures which satisfy the restraints, detailed structural information can be lost in the averaging process. As an alternative, we have encoded a genetic algorithm which will perform ensemble r^{-3} averaging over only a user-specified number of structures. The advantage of this approach is that the *minimum number of structures* that fulfill the restraints can be directly investigated. An example is given below for a simple three-atom system in which two atoms have been fixed at (-3.0, 0.0) and (3.0, 0.0) and the third atom is required to be within 1.0 A of both.



Energy profiles (left) and 50 Cartesian coordinate solutions (right) are shown for ensemble averaging over N = 1, 2, and 3 conformations. As expected, when only a single structure was used, the final energies are high (~400 kcal) and the solutions are points equidistant between the two restraints (the allowed space is enclosed by the circles). When two conformations were used (N=2), all solutions fall within the allowed regions of space; however, with three conformations, many solutions are obtained which do not correspond to either of the two restraints. The final energies for the N=2 and N=3 case are indistinguishable (both are essentially zero), and the "aberrant" structures in the N=3 case are allowed because of the r^{-3} averaging process. This simple example demonstrates the loss of detailed structural information when too many conformations are included in the averaging.

We have successfully applied this technique to a protein-ligand complex in our lab and were able to determine that two binding conformations fulfilled all of the NOE restraints. Full conformational flexibility of the ligand was included in these calculations. One disadvantage of the technique is that the GA is best suited for evolving a small number of geometric parameters (typically ~ 20-30), and (except for a small number of sidechains) the protein structure was held rigid.

Sincerely,

Steve Fesik Rob Meadows Phil Hajduk

THE NMR NEWSLETTER

B. L. Shapiro, Publisher
The NMR Newsletter
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Palo Alto, CA 94303

*Tel. (415) 493-5971**
*Fax.(415) 493-1348**

Policies and Practical Considerations

The NMR Newsletter (formerly the **TAMU NMR Newsletter**, the **IIT NMR Newsletter**, and originally, the **Mellon Institute NMR Newsletter**), now in its thirty-seventh year of consecutive monthly publication, continues under the same general policies as in the past. All communication with the Newsletter should be sent to the address above.

1. **Policy**:

The NMR Newsletter is a means for the rapid exchange of information among active workers in the field of NMR spectroscopy, as defined broadly, including imaging. As such, the Newsletter serves its purpose best if the participants impart whatever they feel will interest their colleagues, and inquire about whatever matters concern them. Technical contributions should always contain a significant amount of information that has not already been published or that will appear in the formal literature within a few weeks of the appearance in the Newsletter.

Since the subscriber/participant clearly is the best judge of what he or she considers interesting, our first statement of policy is "We print anything." (This is followed by the reservation, "that won't land us in jail or bankruptcy court.") Virtually no editorial functions are performed, although on rare occasions there is the need to classify a contribution as 'not for credit'. I trust that the reasons for this policy are obvious. The Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is submitted. Foreign participants should not feel obliged to render their contributions in English.

2. **Public Quotation and Referencing:**

Public quotation of Newsletter contents in print or in a formal talk at a meeting, etc., is expressly forbidden (except as follows), and reference to The NMR Newsletter by its present or previous names in the scientific literature is *never* permissible. *In order to quote or use material from the Newsletter, it is necessary, in each individual case, to obtain the prior permission of the responsible author and then to refer to the material quoted as a "Private Communication".* If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted with, and abide by, these statements of policy.

3. **Participation is the prime requisite for receiving the Newsletter: In order to receive the Newsletter, you must make at least occasional technical contributions to its contents.**

We feel that we have to be quite rigorous in this regard, and the following schedule is in effect: Eight months after your last technical contribution, you will receive a "Reminder" notice. If no technical contribution is then forthcoming, ten months after your previous contribution you will receive an "Ultimatum" notice, and then the next issue will be your last, absent a technical contribution. Subscription fees are not refunded in such cases. If you are dropped from the mailing list, you can be reinstated by submitting a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of nine per contribution.

Frequent contributions are encouraged, but no advance credit can be obtained for them. In cases of joint authorship, only one contributor may be credited. Please indicate to whose account credit should be given. Please note that meeting announcements, as well as "Position Available," "Equipment Wanted" (or "For Sale"), etc., notices are very welcome, but only on a not-for-credit basis, *i.e.*, such items do not substitute for a *bona fide* technical contribution. Similar considerations must occasionally be applied to a few (quasi-)technical items.

4. **Finances**: The Newsletter is wholly self-supporting, and its funding depends on Advertising, Sponsorships, and individual Subscriptions. The **Subscription** fee for the October 1994 - September 1995 year is US$170, with a 50% academic or personal subscription discount. Subscriptions are available for a minimum of the twelve monthly issues which end with a September issue. However, a subscription can be initiated at any time, with the price for more than twelve issues being prorated.

Continued

Corporations are also invited to join the list of **Sponsors** of the Newsletter. Sponsors' names appear in each month's Newsletter, and copies of the Newsletter are provided to all Sponsors. The continuation of the Newsletter depends significantly on the generosity of our Sponsors, most of whom have been loyal supporters of this publication for many years. We will be happy to provide further details to anyone interested.

Another major, indeed most essential, source of funds for the Newsletter is **Advertising**. We earnestly encourage present and potential participants of the Newsletter to seek advertising from their companies. Our rates are very modest - please inquire for details.

5. **Practical Considerations**:

a) All technical contributions to the Newsletter will be included in the next issue if received on or before the published deadline dates.

b) Please provide short titles of all topics of your contributions, so as to ensure accuracy in the Table of Contents.

c) Contributions should be on the *minimum* (NOTE!!) number of 8.5 x 11" (21 x 27.5 cm) pages, printed on one side only. Contributions may not exceed three pages without prior approval. Each page must have margins of at least 0.5" (1.3cm) on all four sides. Black ink for typing, drawings, etc., is essential. All drawings, figures, etc., should be mounted *in place* on the 8.5 x 11" pages. We are not equipped to handle pieces of paper larger than 8.5 x 11" (21 x 27.5 cm).

Please do not fold, clip, or staple your pages. Protect the condition of your letters from the ravages of the mails by enclosing what you send in a cardboard or plastic folder, etc.

Foreign subscribers are reminded that regardless of the standard paper length you use, *all material* - letterhead, text, figures, addresses printed at the page bottom, *everything - must not exceed 10" (ca. 25.3 cm) from top to bottom.*

Significant savings of Newsletter pages and total space can be made by exercising close control over the formatting and type sizes of the contributions. **Please consider the following:**

i) Try using a smaller type font. The body of this page is printed in 10 point type, which I believe is adequate for most purposes. Even 11 or 12 point type is acceptable if the particular font is not too large. Those who are computerized can also employ non-integral spacing of lines so that sub- and superscripts don't collide with lines below and above. Type smaller than 7 point should not be used.

ii) **PLEASE** avoid excessive margins. *Instruct your secretaries to avoid normal correspondence esthetics or practices, however time-honored or 'standard'!* This page has margins on both sides of 0.6" (*ca.* 1.55 cm), which is very adequate. Margins of the same size at the top and bottom are sufficient also, but don't worry if there is more space at the end of your document, for I can often use such spaces for notices, etc.

Also, please avoid large amounts of unused space at the top of letters. Give thought to the sizes of figures, drawings, etc., and please mount these so as to use the minimum space on the page.

iii) 'Position Available', 'Equipment Wanted', and Similar Notices. These are always welcome, but not for subscription credit, of course. Such notices will appear, however, *only* if received with these necessarily rigid constraints: a) Single spaced; b) both side margins 0.6 - 0.7" (1.5 - 1.7 cm.)- NOT WIDER; c) the minimum total height, please, but definitely no more than 4.5" (11.5 cm.).

iv) **AVOID DOUBLE SPACING LIKE THE BLACK PLAGUE ! ! !** This is extremely wasteful of space. Even sans computer, small type and 1.5-line (if needed) spacing can be had with a little effort.

6. **Suggestions**: They are always welcome.

B. L. Shapiro

B. L. Shapiro
February 1995

*Telephone: (415) 493-5971. Please confine telephone calls to 8:00AM-10:00PM, *Pacific Coast Time.*
*Fax: (415) 493-1348 (Do not use for technical contributions which are to appear in the Newsletter, for Fax quality is not adequate.)

BRUKER

3-AXIS GRADIENT APPLICATIONS

MAGIC ANGLE GRADIENT DQF-COSY

The introduction of three axis field gradient spectroscopy in high resolution NMR has led to numerous applications including:

- *Gradient shimming...*
  optimization of magnetic fields by using 3D field image mapping
- *Water exchange filter (WEX)* [1]...
  rapid saturation of water to selectively monitor exchangeable protons
- *and now* ***Magic Angle gradient***

It was recently demonstrated[2,3] that residual water can be refocused in multiple quantum experiments when single axis magnetic field gradients are used for coherence selection thereby causing incomplete water elimination. *This refocusing can be removed by applying coherence selection gradients at the magic angle which is simple using triple axis gradients.*

Using the Bruker GRAdient SPectroscopy III (GRASP III) accessory with x,y,z-gradients, an effective gradient at the magic angle (54.74°) can be produced by applying three gradients simultaneously. This greatly improves the elimination of residual water by coherence selection in multiple-quantum-filtered COSY experiments.

This is best illustrated in a comparison of DQF-COSY experiments, one using z-gradient only and the other using magic angle gradient[4].

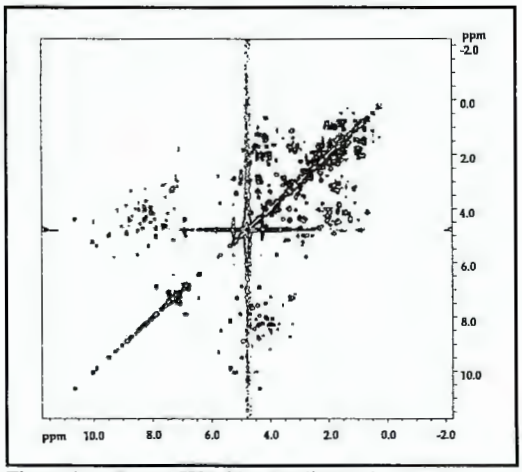


Figure 1: DQF-COSY with z-gradient only

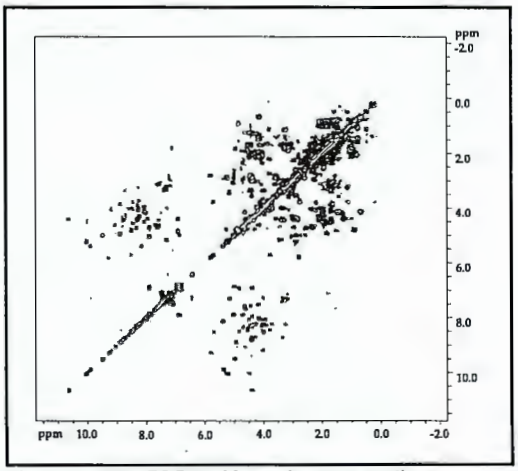
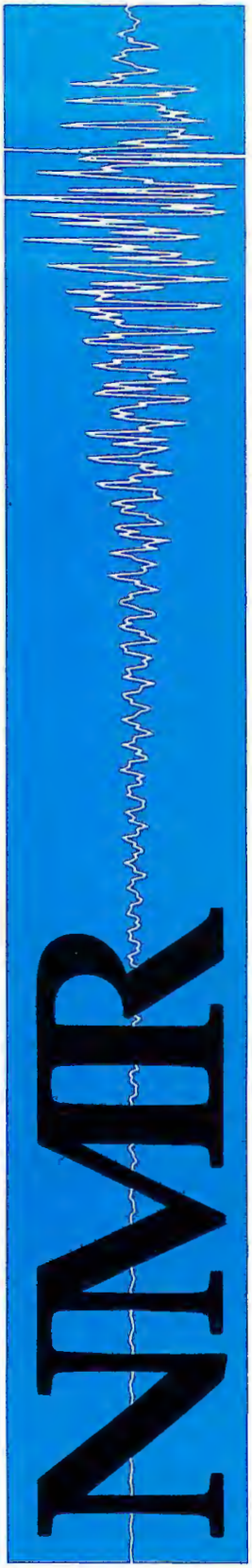


Figure 2: DQF-COSY with magic angle gradient



BRUKER

NMR

Both experiments were acquired on a sample of 1.5 mM BPTI in 90% H_2O/10% D_2O, using a Bruker *AVANCE™* DMX 500 equipped with a 5 mm inverse triple resonance (TXI) probe with GRASP III. The elimination of the water signal is achieved by coherence selection. **No presaturation is used in either experiment!** The only difference is the application of one gradient versus three gradients.

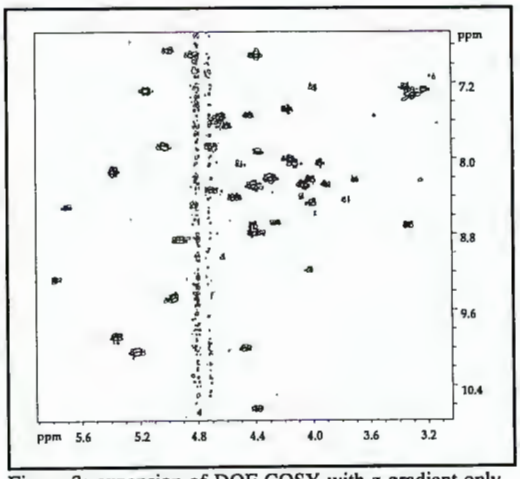


Figure 3: expansion of DQF-COSY with z-gradient only

Result with the z-gradient only...

the residual water ridge is clearly visible and overlaps crosspeaks of interest.

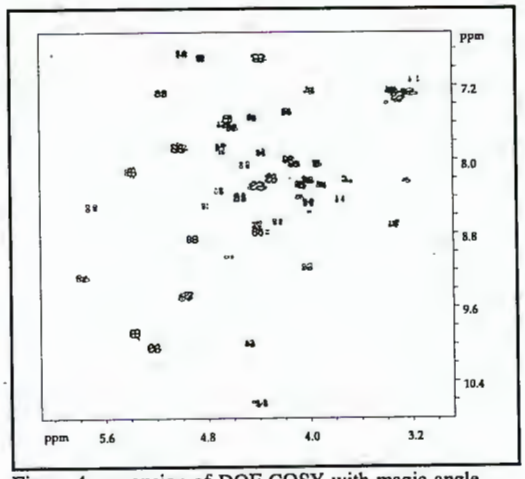


Figure 4: expansion of DQF-COSY with magic angle gradient

Result with magic angle gradient...

the residual water ridge is eliminated! Crosspeaks previously overlapped by the water can be observed and used for correlation assignment.

Magic angle gradient provides a simple and effective method for coherence selection in NMR spectroscopy. Just another example of the flourishing three axis gradient applications.

1. S. Mori, M. O'Neil Johnson et al, J. Am. Chem. Soc. **116**, 1994
2. W. Warren, W. Richter, A. Hamilton Andreotti, B. Farmer, Science, **262**, 2005 (1993)
3. R. Bowtell, R. Bowley, P. Glover, J. Magn. Reson, **88**, 643 (1990)
4. P. van Zijl, M. O'Neil Johnson et al, J. Magn. Reson, in press

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(received 2/6/95)

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

Subject: **Transverse ROESY pulse sequence for the Bruker AMX series.**

Dear Barry,

Bruce Hilton and Gwendolyn Chmurny, at the Frederick Cancer Institute, working with Joseph Paukstelis of Kansas State, have shown[1-4] some impressive results which they obtained using the transverse roesy experiment[5] on a Varian system.

We were interested in using this experiment at Searle on a Bruker AMX-500 system, so I persuaded Bruce Hilton to help me convert the Bruker roesytp sequence to a transverse ROESY sequence. Alan Deese kindly examined the sequence and suggested a useful improvement. Robert Dykstra checked things over and assured us that we would not burn anything out.

We have tested the sequence using both gramicidin S and spironolactone in DMSO and spironolactone in $CDCl_3$. Since there appears to be some general interest in this experiment, we are attaching the Bruker AMX code for others who may wish to use the sequence.

With best personal regards,

Roy H. Bible, Jr. (bible@skcla.monsanto.com) and

Bruce Hilton (hilton@fcs280s.ncifrcrf.gov)

1. B. D. Hilton, Washington Area NMR Group, NIH, Bethesda, MD, June 23, 1992.

2. J. V. Paukstelis*, B. D. Hilton and G. N. Chmurny, Eastern Analytical Symposium, Somerset, NJ, November 15, 1993.

3. B. D. Hilton, Kansas State University, Manhattan, Ks, April 18, 1994.

4. B. D. Hilton* and G. N. Chmurny, Eastern Analytical Symposium, Somerset, NJ, November 16, 1994.

5. A. J. Shaka, J. Am. Chem. Soc., **114**, 3157 (1992).

```
;troesy for Bruker AMX-500
;2D ROESY with Shaka spinlock for mixing.  Phase sensitive using TPPI
;A. Bax & D.G. Davis, J. Magn. Reson 63, 207-213 (1985)
;A. J. Shaka, JACS, vol 114, p. 3157 (1992)
;Adapted to Bruker AMX by Roy Bible under the careful guidance of
;Bruce Hilton with advice from Alan Deese
;The number of loops, l1, required to give the desired mixing time, p15,
;is calculated.  This version limits loops, l1, to 16383.
;Note the possible confusion of the letter l with the number 1!

l1=(p15*0.5/p3);

1 ze
2 d1
3 d12 hl1
  p1 ph1
  d13
  d0
  d12 hl4

;loop for spin locking with 180 deg pulses at transmitter power hl4
4   p4 ph3
    p4 ph4
    lo to 4 times l1

  go=2 ph31
  d1 wr #0 if #0 id0 ip1 zd
  lo to 3 times td1
exit

ph1=0 2 2 0 1 3 3 1
ph3=1 3 1 3 2 0 2 0
ph4=3 1 3 1 0 2 0 2
ph31=0 2 2 0 1 3 3 1

;hl1: ecoupler observe high power level attenuation; typically 6 db
;hl4: ecoupler low power level attenuation for ROESY spinlock,
;     typically 13 db on AMX-500.
;     Power in Hz for p4 should be about 6000 to 7000, or higher if the
;     probe and duty cycle permit.

;p1 :  90 degree observe transmitter high power pulse using
;      hl1 attenuation
;p4 : 180 deg pulse for spin locking using hl4 attenuation.
;     (For gammah1= 6605 Hz, p4=(1/2)*(1/6605)= 75.7u)
;p15: TROESY spinlock time; converted to mixloop by definition

;d0 : incremented delay (2D)                          [3 usec]
;d1 : relaxation delay; 1-5 * T1
;d12: delay for power switching                       [20 usec]
;d13: short delay (e.g. to compensate delay line)     [3 usec]

;in0: 1/(2 * SW) = DW
;nd0: 2
;NS: 8 * n
;DS: 2 or 4
;td1: number of experiments
;MC2: TPPI
```

UNIVERSITY OF DELAWARE

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Professor

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January 27, 1995
(received 2/2/95)
Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Quantification of Solid-state Carbon Spectra, Polymer Relaxation, and Symposium

Dear Barry:

Everyone wants quantification of solid-state carbon cross-polarization spectra! This sounds simple, but we have found it difficult if you want accuracy of 1% or less. We find ratio analysis offers the best means of determining relative quantities and avoids errors associated with short-contact-time deviations from the simple first-order theory of cross polarization (as given in, for example, Mehring's classic book) and variations of the spectrometer that affect intensities. Ratios vary with contact time, but in a much slower and more easily modeled manner than do intensities of individual lines; extrapolation yields accurate ratios from which relative amounts of various carbon types can be determined directly.

One use of cross-polarization curves is determination of $T_{1\rho H}$. From analysis of cross-polarization curves, we (along with Dave Rethwisch and John van Alsten) have found that $T_{1\rho H}$ for polydimethylsiloxane adsorbed on silica is linear in the coverage of polymer. One may understand this dependence in terms of a Huggins-like "intrinsic surface viscosity" which affects the dynamics of polymer segments and is reflected in the spin-lattice relaxation.

Lastly, I point out the 15th Blue Hen NMR Symposium, to be held June 5, 1995. As in years past, we shall have distinguished speakers from the area and around the world spend a whole day living and breathing NMR. Anyone wishing information on the symposium may contact me at the above address or Martha Bruch.

Spectroscopically,

Cecil

Cecil Dybowski
Professor

Lilly

Lilly Research Laboratories
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Lilly Corporate Center
Indianapolis, Indiana 46285
(317) 276-2000

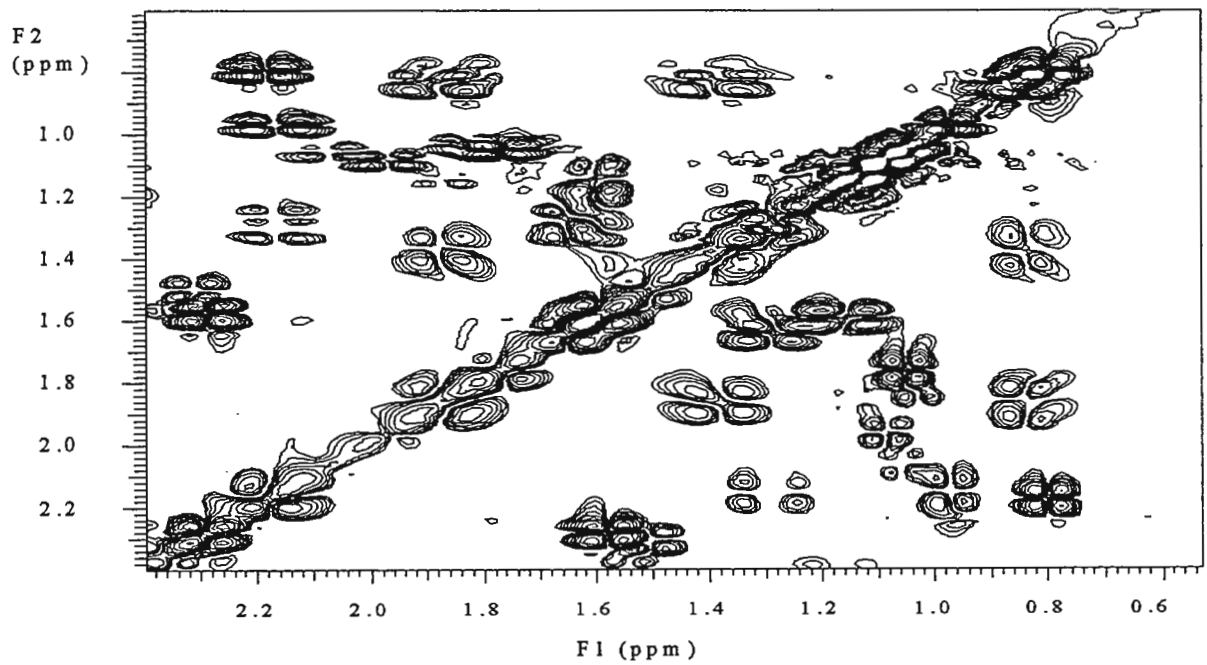
Dr. Bernard Shapiro
the NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

February 16, 1995
(received 2/21/95)

Dear Dr. Shapiro,

It would seem that many NMR spectroscopists are exploring ways to incorporate their spectroscopic data into reports as evidenced by the number of contributions to the Newletter dealing with this topic. To add to the number of choices, and in response to a "Reminder" notice, we would like to offer the following information on how we are importing publication quality spectra into various documents. Currently we are using Varian's VNMR software to process our data and Word 6.0 for Windows running on a 486/66 PC to produce our documents. The first step in the process is to generate an HPGL file which contains the spectrum to include in the document. This HPGL file is transferred to an NT server which connects all of our PC, Macintosh, and UNIX boxes. Once the information is on the NT server it is easily imported directly into Word 6.0 using the HPGL file converter packaged with Word. This procedure produces a publication quality graphic image; however, the size of the spectrum can lead to a very large document when several spectra are included. To get around this problem, we are using a product called HiJaak Pro 2.0 which provides graphic conversion from one format to another. The table at right shows the file size of an HPGL file and the corresponding file size after converting it to various vector graphic file formats. By using HiJaak Pro to convert an HPGL file to a metafile format, either WMF or CGM, the file size can be reduced by about 75%. Once the file has been incorporated into the Word document we use the Microsoft drawing module that comes with Word to easily edit/annotate the spectrum. As an example I have incorporated a spectrum which was converted from HPGL format to WMF format into this Word document. We observe no loss of quality when converting back and forth between file formats, and we have even used HiJaak Pro to convert MacIntosh PICT files to WMF format and incorporated them into documents. The only drawback to this approach is that the text in an HPGL file can be manipulated as text in the drawing module of Word, but in the metafile formats text is recognized as an object.

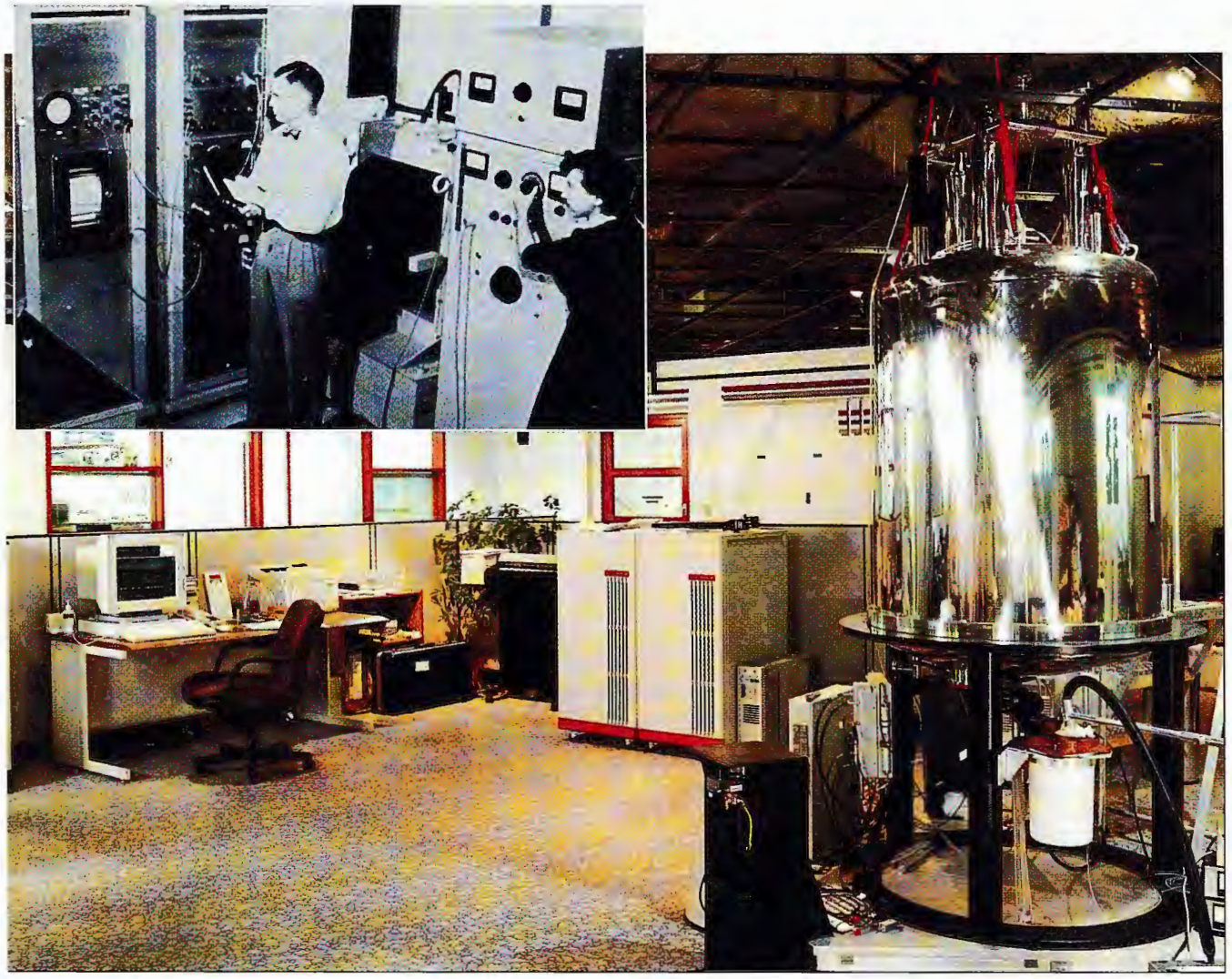
Graphic File Format	Size (Kbytes)
Hewlett Packard Graphic Language (HPGL)	608.3
Windows Metafile (WMF)	146.4
Computer Graphics Metafile (CGM)	140.8
Micrografx Draw (DRW)	184.8
Encapsulated Postscript (EPS)	586.5



Please credit this contribution to Doug Dorman's account.

Steve Maple Steve Maple

Varian: The First Name in NMR



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25 January 1995
(received 1/30/95)

Professor Bernard L. Shapiro
Editor/Publisher TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California
94303 USA

Thiocarbonyl and Carbonyl Carbon Shielding Tensors

Dear Barry:

It is well known that carbon chemical shifts of thiocarbonyls are deshielded relative to those of analogous carbonyl groups. For example, the isotropic chemical shift of the thiocarbonyl carbon of thioacetone is 252.7 ppm while the corresponding value for the carbonyl carbon of acetone is 206.4 ppm. This deshielding has often been ascribed to the smaller $n \rightarrow \pi^*$ electronic energy gap associated with the C=S functional group compared to that of the C=O group. In the Ramsey theory of nuclear magnetic shielding, small values of $\Delta E_{n \rightarrow \pi^*}$ are generally associated with deshielding (however, as noted below, other factors must be considered). In the case of thiobenzophenone and benzophenone the $n \rightarrow \pi^*$ excitations are 16,400 cm^{-1} and 26,800 cm^{-1}, respectively, consistent with this argument. Based on symmetry considerations, $n \rightarrow \pi^*$ rotations lead to deshielding along the C=O(S) bond. Thus, for thioketones, it has been suggested that the small values of $\Delta E_{n \rightarrow \pi^*}$ would lead to the least shielded component of the carbon shielding tensor (δ_{11}) lying along the C=S bond direction.

We have used dipolar-chemical shift NMR to investigate the orientation of thiocarbonyl and carbonyl carbon shielding tensors of several thioamides and amides including acetamide and thioacetamide. Carbon-13 NMR spectra of static powder samples of a representative amide and thioamide are shown in Figure 1; small ^{14}N dipolar splittings are apparent at δ_{11} and δ_{33}. Also, we have carried out GIAO and LORG calculations on several molecules containing the C=S and C=O groups. Both experiment and theory indicate that the least shielded component of the carbon shielding tensors is approximately perpendicular to the C=S(O) group and within the thioamide/amide plane. The deshielding perpendicular to the C=S(O) group is governed by $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ excitations. Along the C=S(O) bond, the *ab initio* MO calculations indicate that deshielding is associated with the C-C and C-N σ-bonds whereas the lone-pair MO's of sulphur and oxygen contribute to shielding!

In summary, our results indicate that the common "textbook" interpretation of thiocarbonyl carbon chemical shifts relative to carbonyl carbon chemical shifts needs to be revised. Furthermore, the importance of examining the shielding tensor as opposed to its trace is clear. Anyone interested in further details can contact us via E-mail at RODW@AC.DAL.CA. Best wishes for 1995.

Yours sincerely,

Rod Mike Lumsden

Rod Wasylishen Mike Lumsden Chris Kirby

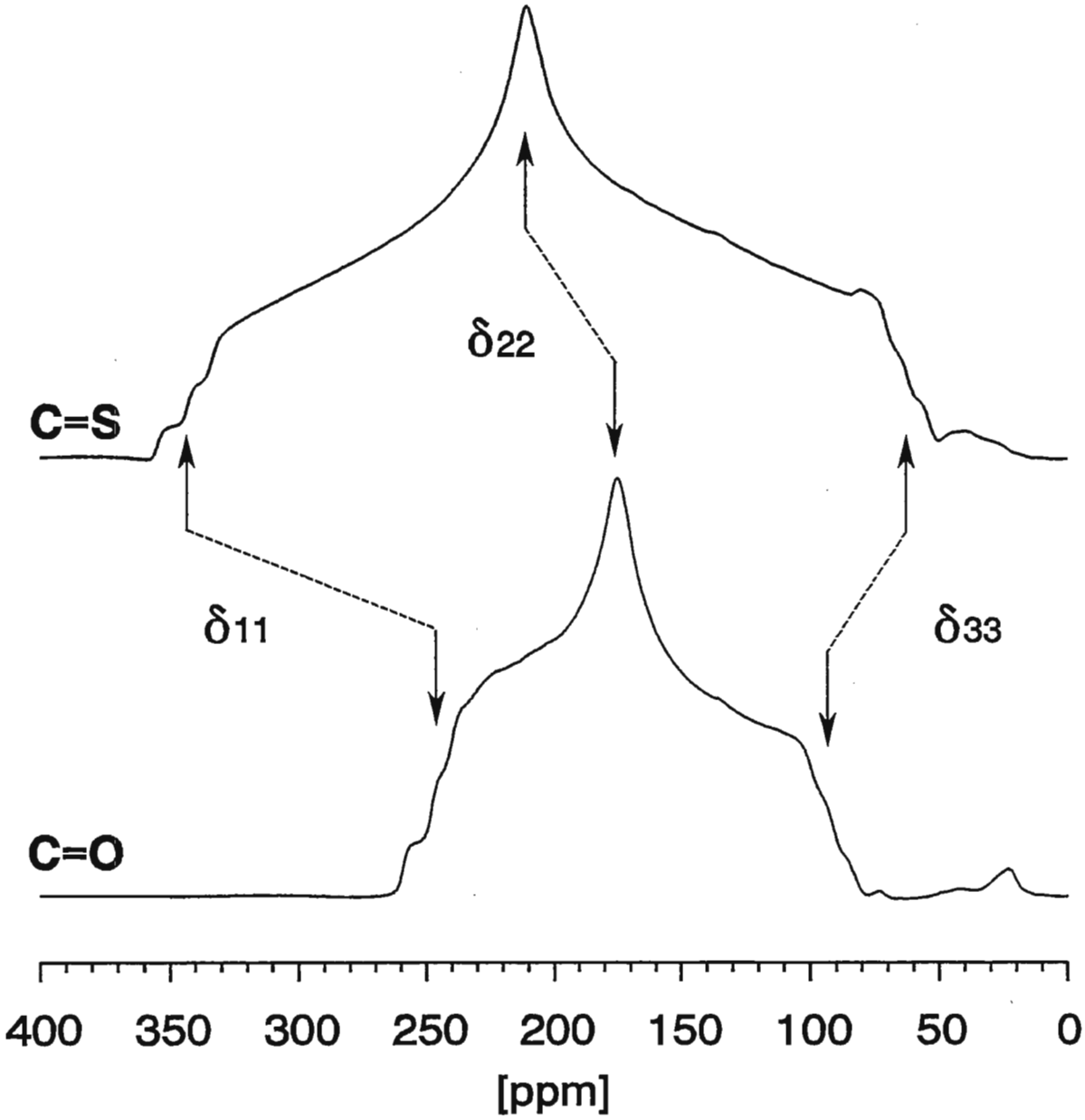

Figure 1. Carbon-13 NMR spectra of static powder samples of 4'-methoxythioacetanilide-^{13}C(CS) (upper) and 4'-methoxyacetanilide-^{13}C(CO) (lower) obtained at 9.40 T. Features apparent in the region 10-80 ppm are due to ^{13}C nuclei in natural abundance. Note that both δ_{11} and δ_{22} are responsible for the average deshielding in thioamides relative to amides while δ_{33} corresponds to greater shielding for the thioamides compared to amides. Analysis of these powder spectra indicate that δ_{22} is very close to the C=S and C=O bond directions while δ_{33} is perpendicular to the thioamide/amide plane.

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Bethesda, Maryland 20892

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

(received 2/15/95)
February 7, 1995

Dear Barry:

Small samples and vespel plugs

Production of isotopically enriched proteins can be quite expensive, depending on how well the expression system works, and what the yield of the purification is. If, on top of that, the protein turns out to be unstable, one really can be in serious financial trouble if the aim is to determine the protein's structure by NMR. The introduction of microcells by Shigemi, one of your regular advertisers, has been a real godsend in this respect, reducing the need for sample volume from 400 to ~200 µl for a 5 mm NMR probe. Shigemi has doped their glass such that the magnetic susceptibility is close to that of water, and the magnetic field discontinuity at the glass-water interface is thereby minimized. The magnetic susceptibility of the glass seems to vary somewhat from one shipment to the next, and most samples require careful shimming of z^4 for obtaining acceptable line shapes.

One problem we had with the Shigemi tubes was to keep the sample perfectly oxygen free, needed to prevent oxidation of free sulfhydryls in one of our proteins. The Shigemi tubes are not very amenable to flame sealing or degassing. Toby Zens told me that of all commercailly available polymers, vespel-2 is closest in magnetic susceptibility to water, within ~2%. Vespel-2 is a polymer made by DuPont, rather expensive but readily machinable, and we therefore decided it was worth while to try the ancient susceptibility plug idea again, pioneered by Varian in the sixties, I believe.

We have gone through various design cycles for the plugs. Initially, we used a bottomless tube and shuffed one plug in from the bottom. The lower half of this plug has a teflon sleeve (Fig.1A) to keep it snugly in place. A round bottom of this plug with a diameter of the OD of the sample tube was needed to prevent destruction of Toby Zens' otherwise spectacular triple resonance gradient 8-mm probehead. For minimizing the effects of the small remaining difference in susceptibility between vespel and water on the sample homogeneity, the top of the plug which contacts the sample has a hemispherical shape (Fig.1A). As each Wilmad sample tube is slightly different in ID, these bottom plugs almost needed to be custom made for the tube, or at least one would have to try a few tubes to find one with a good fit. More recently we've shifted to a simpler design, that fits in the bottom of a regular tube (Fig.1B). This plug has no teflon sleeve. After dropping ~15 µl of H_2O (or D_2O) in the bottom of the tube, this smaller dimater bottom plug is pushed down in the tube as far as it can go, and air is squeezed out from underneath. The sample is put on top of this plug, followed by the top plug (Fig. 1C,D). The top is like an inverted bottom plug, with the only difference that it has a small hole in its center (1/32 ", or 0.8 mm for the more cultured among your readers). The top of the plug has a larger threaded hole, just like the Wilmad vortex plugs, that allows one to slide the top plug in and out (Fig.1E). It has a cylindrical hole drilled down its center (1/16 ") with an orthogonal cylindrical hole reaching it from the side, to let the air escape when pushing down the plug. (Fig.1E). First we used the more advanced design, with a teflon sleeve (Fig.1D), but more recently we also have shifted to vespel-only plugs which are faster to machine. The top plug is also machined to go down relatively easy. To prevent it from sliding down by itself, we just make a small scratch on the side of the plug and that provides it with enough friction not to slip down. Removal of air bubbles from the sample is relatively easy

compared to Shigemi tubes, thanks to the hemispherical contact surface which positions the air bubble right in front of the 1/32 hole.

Proper sample degassing remains a pain, but degassing, filling it up with argon and then pushing down the top plug before flame sealing is a tedious but workable solution. The top plugs are easily recycled; for getting the bottom plug out we have to sacrifice the tube. The shimming is actually somewhat easier than on a regular sample, particularly if the solvent height is ~13 mm (5 mm probe) and 17 mm (8 mm probe), reducing the amount of solvent needed to ~200 and 600 µl, respectively. For very short sample lengths, i.e., with the vortex plugs about 3 mm apart, the line shape is less good (~30 Hz at 0.55 %), but still acceptable for protein NMR. The good news for such an ultrashort sample: Forget about high order z gradient shimming, it has zero effect!

One minor but possibly important detail to your readers: it is worth checking for each probe whether the center of the coil corresponds to the "black line" on the depth gauge. This is easily verified by moving an ultrashort sample up and down, or by moving a regular microcell volume (13 or 16 mm length) and maximizing the initial part of the H_2O FID (on-resonance) after a single pulse of ~30° (for each depth, the probe may need slight retuning). For most of our probes, the center is down by 1-2 mm from what the depth gauge indicates.

Kindest regards,

Frank Ray,
Chief Engineer

Ad Bax

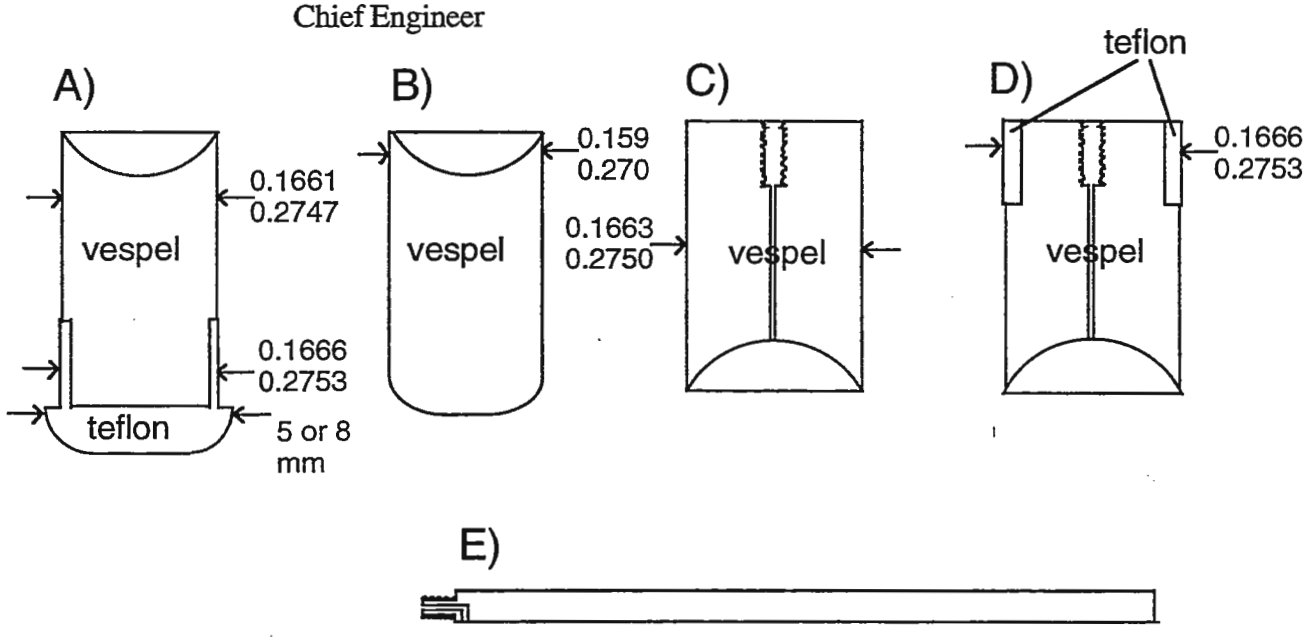

Figure 1. Design of the (A, B) bottom and (C,D) top plugs with (A, C) and without (B, D) teflon sleeves. The length is 11 mm for 5 mm sample tubes, and 12.5 mm for 8 mm tubes. The center hole for C and D has a 1/32" diameter. The top of this hole fits the brass rod. (E) The insertion rod (8", brass, 2-56 thread) for the top plug, with a 1 mm hole drilled down its center (9 mm long) and a side hole reaching the center hole. All dimensions in the figure are in inches; the top number corresponds to the 5 mm sample tube and the bottom to 8 mm.

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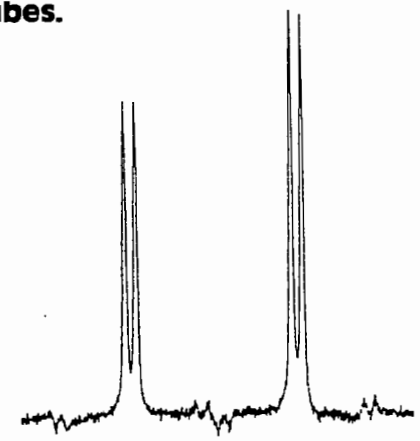
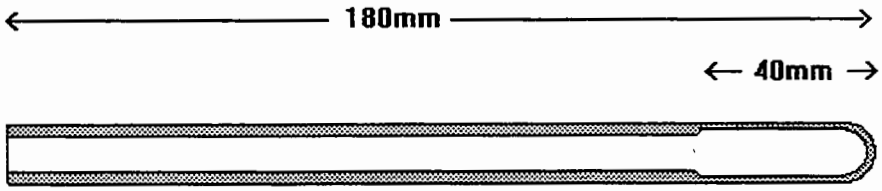
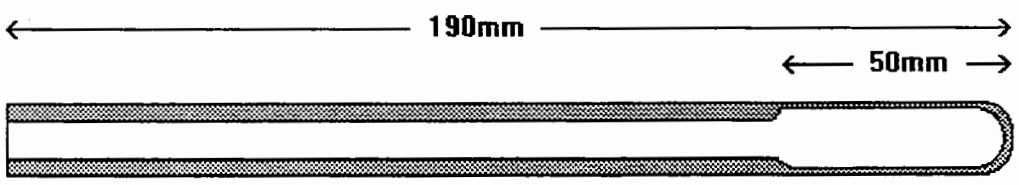


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



PST-001 and PST-002



ST8-001,ST8-002, ST10-001, and ST10-002

O.D. (mm)	Product Number	Wall (mm)	Concen-tricity/Camber (μ)	OD (mm)	ID (mm)	Price Each 1-99	Price Each 100+
5	PST-001	0.21	20/ 8	4.96 + 0.00 - 0.01	4.54 ± 0.01	$15.00	$13.50
	PST-002	0.21	40/15	4.96 + 0.00 - 0.01	4.54 ± 0.01	$13.00	$12.00
8	ST8-001	0.25	40/ 8	8.00 + 0.00 - 0.01	7.52 ± 0.01	$31.00	$28.00
	ST8-002	0.25	50/15	8.00 + 0.00 - 0.01	7.52 ± 0.01	$27.00	$25.00
10	ST10-001	0.25	40/ 8	9.98 + 0.00 - 0.01	9.52 ± 0.01	$36.00	$32.00
	ST10-002	0.25	50/15	9.98 + 0.00 - 0.01	9.52 ± 0.01	$32.00	$28.00

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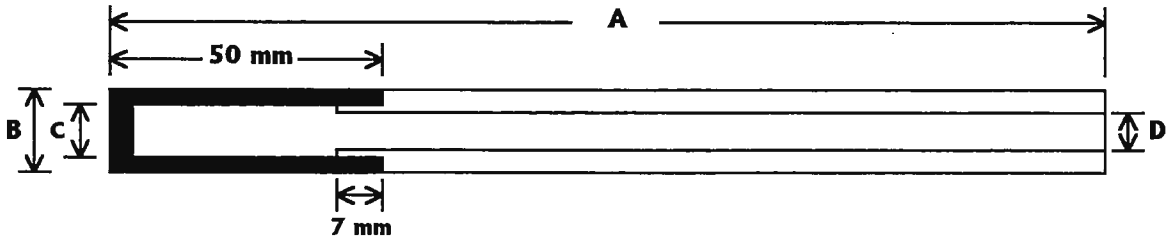

	A Length (mm)	B OD (mm)	C ID (mm)	D OD (mm)	Camber (μ)
Si-005	180	4.965 + 0 − 0.005	4.0 ± 0.1	2.5	± 0.02
Si-010	190	10.0 + 0 − 0.01	9.0 ± 0.1	6.5	± 0.02

Type	Diameter	Price for 5 tubes
Si-005	5 mm	$300.00
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Professor Bernard L. Shapiro
Editor/Publisher *TAMU NMR Newsletter*
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February 13, 1995
(received 2/23/95)

Altered Brain Proton Metabolite Relaxation Properties in Cytotoxic Edema

Dear Barry,

In vivo spectroscopy offers the promise of increased sensitivity for disease detection that may complement or even increase that obtained by MRI alone. However, many properties of metabolite signals have yet to be characterized. One general question that we have recently been interested in is to what extent are proton metabolite relaxation properties altered in pathology. To investigate this question we have used an animal model of cytotoxic edema that provides a global increase in brain water content. Associated with the increase of brain water is a reduction in cerebral perfusion pressure that leads to a mild ischemic condition. These two components (increased water and ischemia) are early pathological events associated with several common diseases, such as stroke and myocardial infarct, and can lead to a wide range of metabolic dysfunction in neuronal tissue. We localized a 125 um^3 volume from rat brain using a modified PRESS(1) sequence and measured relaxation properties from this volume at 7T. Group decay plots are displayed below. As expected, the water proton longitudinal rate constant decreased; from 0.63 ± 0.02 sec^{-1} (mean $\pm$ se) in controls to 0.50 ± 0.03 sec^{-1} in edematous brains. A less pronounced decrease was observed for water apparent transverse relaxation rate constant; from 21.1 ± 0.2 sec^{-1} in controls to 19.8 ± 0.2 sec^{-1} in edematous brains. Interestingly, we also found that the longitudinal rate constant of the resonance at 3.0 ppm (primarily due to methyl protons of Cr and PCr) decreased from 0.63 ± 0.02 sec^{-1} in controls to 0.50 ± 0.03 sec^{-1} in edema. This decrease could be due to a shift in the relative populations of Cr and PCr and intrinsic R_1 differences between these species or perhaps due to reduced exchange through a site efficient in relaxing these spins. The apparent transverse rate constant of the 2.0 ppm resonance (primarily due to methyl protons from N-acetylaspartate) increased from 5.3 ± 0.2 sec^{-1} in controls to 6.6 ± 0.3 sec^{-1} in edematous brain. The mechanism for this increase is not clear but could be related to a change in tissue bulk magnetic susceptibility that accompanies a reduced oxygenation state of hemoglobin associated with the reduced perfusion condition. The transverse relaxation data were collected with relatively long interpulse delays (similar to how MRS data is acquired, and hence the qualifier 'apparent') and diffusion through microscopic field gradients can be a dominant mechanism of signal attenuation (2). These results suggest that metabolite relaxation

properties that accompany tissue pathology can be responsible for substantial alterations of metabolite signal intensities when data are collected with either T1 or T2 weighting (as is usually the case).

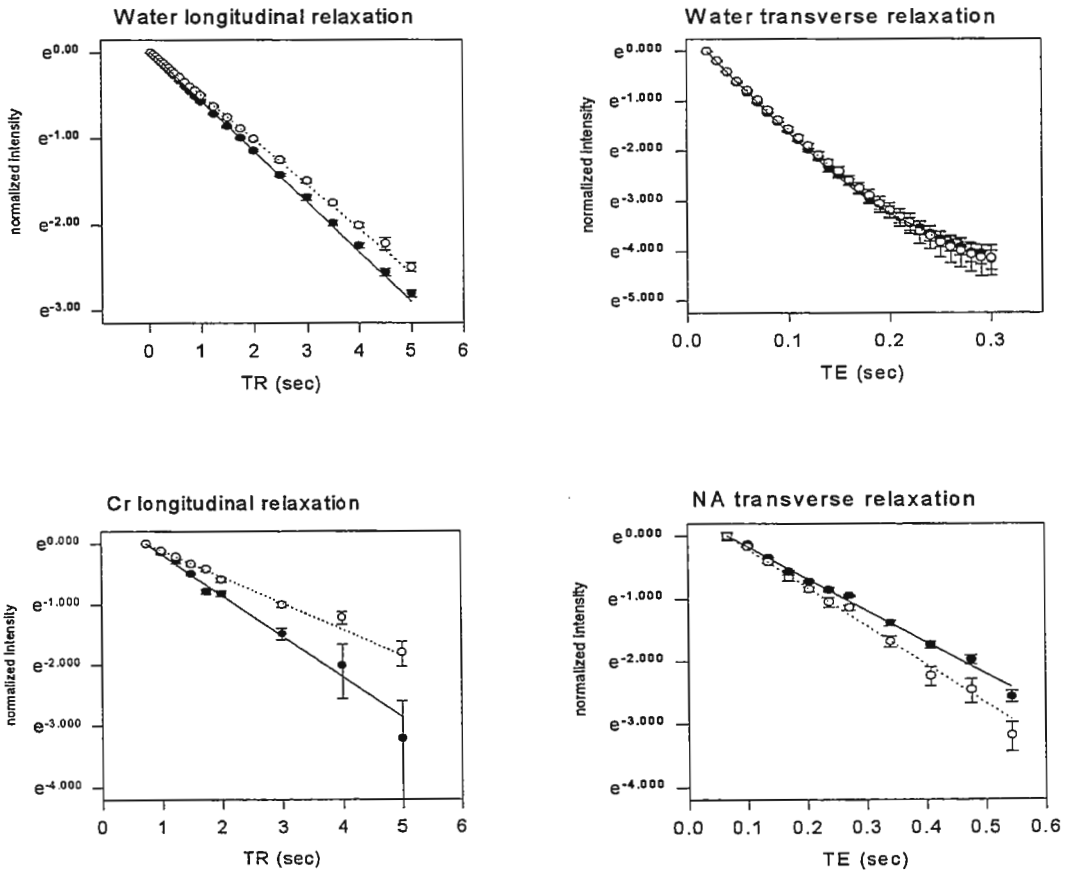
1. P.A. Bottomley, U.S. Patent 4 480 228 (1984)
2. F. Brown, The effect of compartmental location on the proton T2* of small molecules in cell suspensions: a cellular field gradient model. *J. Magn. Reson.* **54,** 385-399 (1983).

Sincerely,

William Rooney
Research Spectroscopist

Michael Weiner
Professor of Radiology
and Medicine

Andrew Maudsley
Professor of Radiology



Normalized group relaxation plots. Filled circles represent control group data and unfilled circled represent data from cytotoxic edema group. Standard error are indicated by vertical bars.

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750	51	15	60	3.8
600	51	10	120	3.4
500	51	10	150	3.2
400	54	8	365	2.8
360	54	8	365	2.8
300	54	3	365	2.8
270	54	2.7	365	2.8
200	54	2	365	2.8
100	54	1	365	2.8
500	89	15	120	3.4
400	89	10	180	2.8
360	89	10	365	2.8
300	89	3	365	2.8
270	89	2.7	365	2.8
200	89	2	365	2.8
100	110	1	119	2.8

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Stockholm, 30 January 1995
(received 2/3/95)

Institutionen för oorganisk kemi
Docent Julius Glaser

Equilibrium Dynamics

Dear prof. Shapiro,

NMR spectroscopy is a powerful tool to study *equilibrium dynamics*. However, one often forgets that both parts, i.e. equilibrium and dynamics, are equally important. This short story is just about it.

Recently, we have studied aqueous solutions of the $(UO_2)_3(CO_3)_3^{6-}$ complex (structure in the Figure below#). As expected, in the ^{13}C spectrum we observed two signals with equal intensity, one for the CENTral and one for the TERMinal carbonates. We have played with magnetization transfer and found that the carbonate exchange between CENT and TERM sites occurs on a time scale of seconds (Fig.1). Parameter fitting by means of the two site exchange equation:

$$\begin{aligned} d[M_{CENT}-M_{CENT}(\infty)]/dt &= -(R_{CENT}+k_{AB})[M_{CENT}-M_{CENT}(\infty)]+k_{BA}[M_{TERM}-M_{TERM}(\infty)] \\ d[M_{TERM}-M_{TERM}(\infty)]/dt &= k_{AB}[M_{CENT}-M_{CENT}(\infty)]-(R_{TERM}+k_{BA})[M_{TERM}-M_{TERM}(\infty)] \end{aligned} \quad (1)$$

gave the relaxation rates R (=$1/T_1$) and the exchange rate constants k with low standard deviations. (M are the values of magnetisation at time *t*, and M(∞) are at time $t = \infty$) Surprisingly, the expected relation $k_{AB} \equiv k_{BA}$ was not fulfilled. The deviation was significantly larger than the experimental error.

Finally, the detailed knowledge of the equilibrium helped us to solve the problem. The thermodynamic data show that minor concentration of free HCO_3^- is present in the studied solutions. This species is in exchange connection with the TERMinal carbonates. The peak of HCO_3^- is hidden because of the low population and large broadening. Furthemore, we found from independent experiment that T_1 of HCO_3^- was 16 s, i.e. much longer than that of the other carbonate species (about 4 s). Therefore, we considered a three-site model:

$$\xleftarrow{R_{CENT}} \text{CENT} \underset{k_{BA}}{\overset{k_{AB}}{\rightleftarrows}} \text{TERM} \underset{k_{CB}}{\overset{k_{BC}}{\rightleftarrows}} HCO_3^- \xrightarrow{R_{HCO_3^-}}$$

$$\downarrow R_{TERM}$$

Full story will appear in *Inorg. Chem.*

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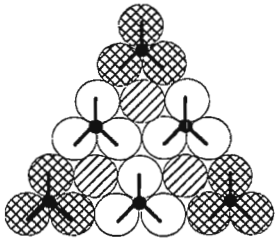
Let us examine the effect of the site HCO_3^-. The relaxation of HCO_3^- is much slower than that of the other sites, so that the latter can be neglected. From the line broadening we know that the exchange between TERM and HCO_3^- is fast compared to the exchange between CENT and TERM.

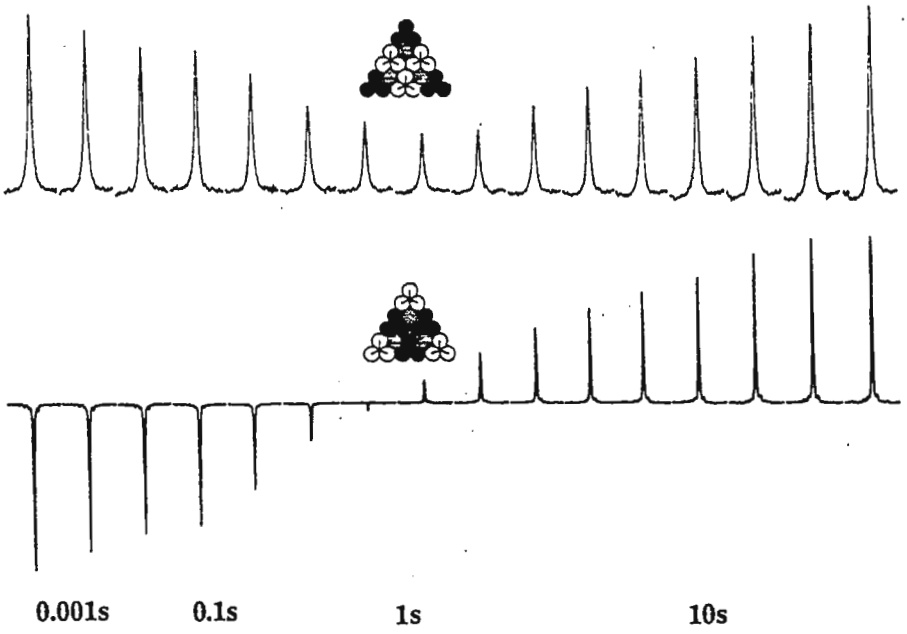


Left:

TERMinal carbonate oxygens

CENTral carbonate oxygens

URANYL groups



Therefore, the chemical equilibration is fast but relaxation occurs only on the sites TERM and CENT. Defining $K = M_{HCO_3^-}/M_{TERM} = k_{BC}/k_{CB}$, the total magnetisation at the site TERM in presence of HCO_3^- can be written as $M'_{TERM} = M_{TERM} + M_{HCO_3^-} = M_{TERM} + KM_{TERM}$. From this equation $M_{TERM} = M'_{TERM}/(1-K)$, by substituting it into the equations above we obtain:

$$\begin{aligned} d\left[M_{CENT}-M_{CENT}(\infty)\right]/dt &= -(R_{CENT}+k_{AB})\left[M_{CENT}-M_{CENT}(\infty)\right]+k_{BA}\frac{1}{1+K}\left[M'_{TERM}-M'_{TERM}(\infty)\right] \\ d\left[M'_{TERM}-M'_{TERM}(\infty)\right]/dt &= k_{AB}\left[M_{CENT}-M_{CENT}(\infty)\right]-(R_{TERM}+k_{BA})\frac{1}{1+K}\left[M'_{TERM}-M'_{TERM}(\infty)\right] \end{aligned} \qquad (2)$$

From these equations the apparent disagreement between the determined "exchange rate constants", k_{AB} and k_{BA}, is readily seen. The form of the equations is the same as that of Eqs. 1. If the concentration of the HCO_3^- is lower, then K is smaller and the two sets of equations become identical.

István Bányai *Julius Glaser* *Imre Tóth*

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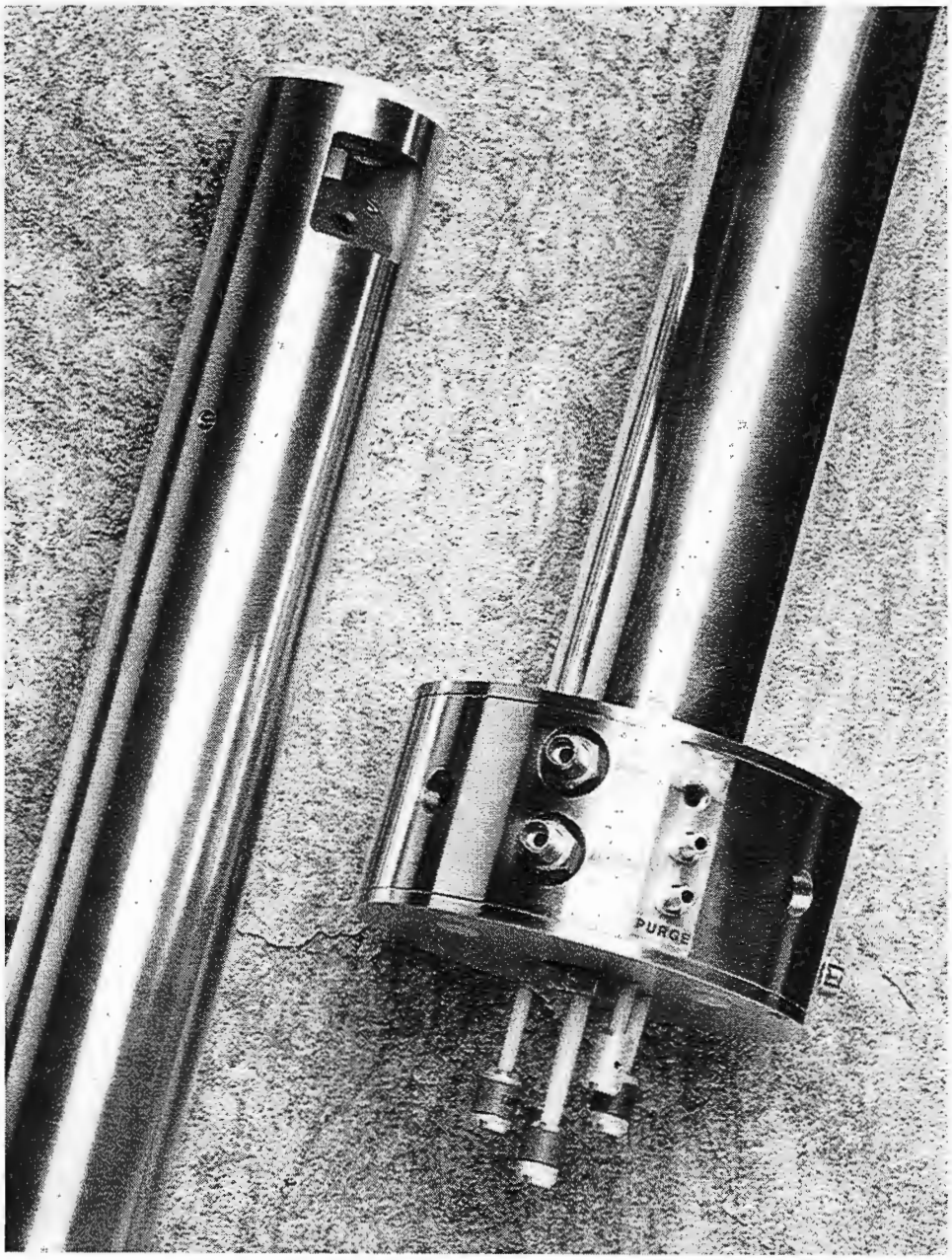
High Speed 4.0 mm Turbo PENCIL™ MAS Probe



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[1] Available in proton/fluorine tuning at proton frequencies ≥ 360 MHz
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[4] Higher speeds can be obtained using rotors with reduced inner diameter.
[5] Available on probes with proton frequencies ≥ 360 MHz
[6] Adamantane sample, ^{13}C, MAS, single pulse.
[7] HMB, 12 scans, ^{13}C, CP/MAS, methyl carbon.
[8] Glycine, 4 scans, ^{13}C, CP/MAS, alpha carbon.
[9] Glycine, 8 scans, ^{15}N, CP/MAS.
[10] Chiraphos, 4 scans, ^{31}P, CP/MAS
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February 6, 1995

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

N-15 CP/MAS NMR of Aromatic Polyamide/imides

Sometime ago we were interested in using N-15 solids NMR to characterize a variety of novel polyamide/imide polymers. These polymers are polycondensation products of diacids (or anhydrides) and diamines. Nylon-66, made from adipic acid and hexamethylene diamine, is perhaps the most famous polyamide known. We, however, were interested in some new classes of amide/imide polymers that were made using aromatic acids and/or diamines. Despite the obvious interest in using solids N-15 NMR to characterize these new classes of polymers, we could not find much information in the literature, e.g., chemical shifts, relaxation times etc. We assumed that this was mostly due to novelty of these materials, but realized only later that it may also be due to experimental difficulties of recording an interpretable spectrum.

The N-15 nuclei in these polymers require relatively long CP contact times to adequately cross-polarize, especially the tertiary (imide) nitrogen, but the protons in these polymers have very short spin-lattice relaxation time in the rotating frame($T_1\rho$). The problems, thus, arise from the difficulty of compromising between the two competing processes. Under normal spectrometer operating conditions, the spin-locked proton magnetization cannot be maintained for effective cross-polarization. Fortunately, however, we found that proton $T_1\rho$ increases with increasing proton rf power for spin locking. But when we used high rf powers during long CP contact times, we ran into horrible probe arcing problems. So finally we compromised at using a somewhat extreme proton rf field of 50KHz and a somewhat less than ideal CP contact time of 2 milliseconds as the experimental conditions. This permitted us to acquire useful N-15 spectra without damaging the probe. All spectra were acquired on our CMX200 spectrometer using a Chemagnetics double resonance MAS probe and ca. 3 KHz spinning speed.

The attached figure shows some selected N-15 CP/MAS spectra to highlight the correlation between N-15 chemical shift and the chemical structure. From the data collected on a variety of these polymeric materials, we were able to classify N-15 chemical shifts in four categories related to the nature of the three attached groups as:

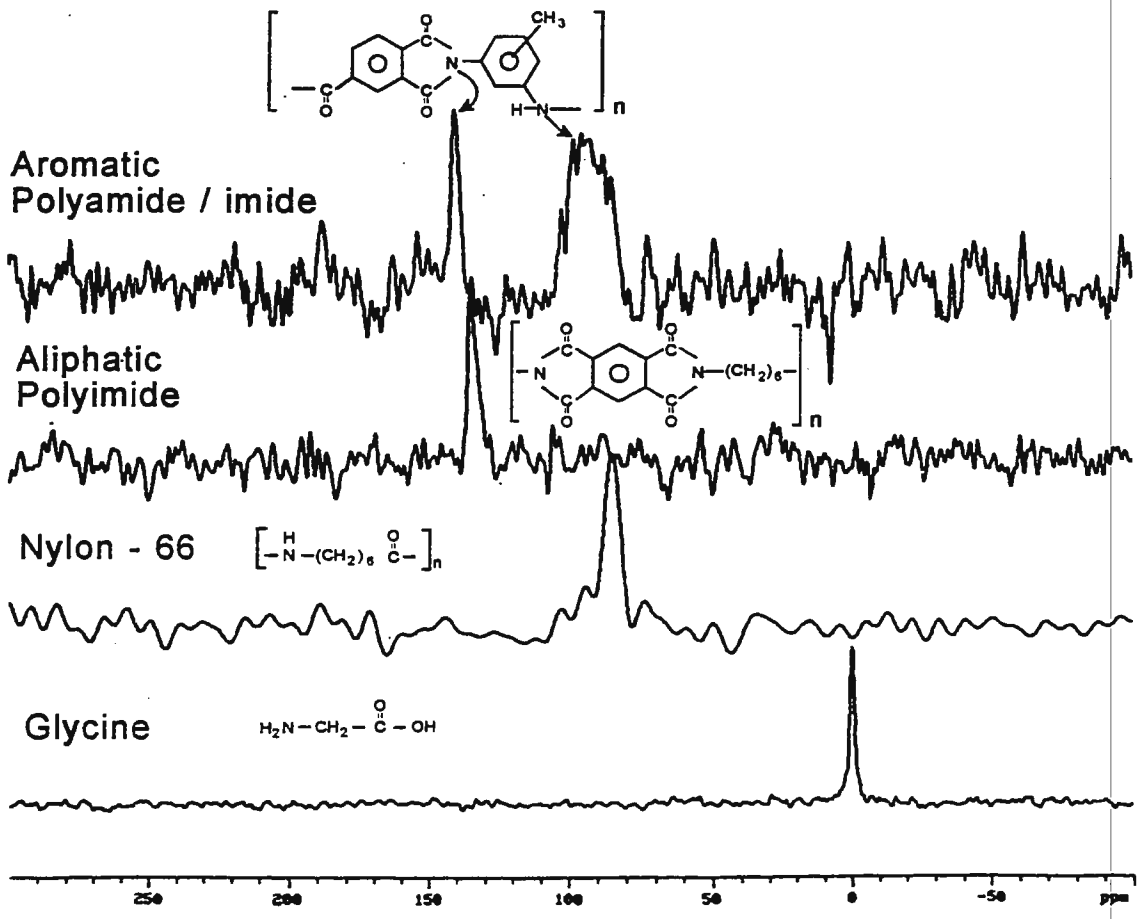
Three attached groups	Nitrogen Functionality	Chemical shift (ppm)
H, H, Aliphatic	[glycine]	0 (reference)
H, Carbonyl, Aliphatic	Aliphatic Amide	84
H, Carbonyl, Aromatic	Aromatic Amide	96
Carbonyl, Carbonyl, Aliphatic	Aliphatic Imide	134
Carbonyl, Carbonyl, Aromatic	Aromatic Imide	140

N-15 chemical shifts were found to be mostly insensitive to chemical groups two or more bonds away, e.g., substituents on the aromatic ring or the length of the aliphatic chain showed negligible effect on chemical shifts, or perhaps the effect was less than the linewidth. So we could only classify chemical shift in the broad categories shown in the table.

We believe that this is the first time characterization of aromatic polyamide/imides with natural abundance solids N-15 NMR and a first attempt at establishing chemical shift vs. structure criterion for these materials. Besides chemical shifts, peak linewidths may provide additional information. For instance, for a sample that contains both aromatic amide and imide nitrogen (top trace), the amide peak is much broader than the imide peak. It may be postulated that the amide hydrogens are involved in interchain hydrogen bonding causing amide group to be locked in a variety of conformations which leads to inhomogeneous broadening of the peak. Since, the imide groups can not participate in hydrogen bonding, the imide peak remains relatively narrow.

Regards,

Naresh K. Sethi
Research Scientist



STRUCTURE DETERMINATION FROM NMR

Pittsburgh Supercomputing Center
Biomedical Initiative
June 25-28, 1995

Pittsburgh Supercomputing Center (PSC) is offering biomedical researchers a workshop on "Structure Determination From NMR." The objective is to introduce participants to different techniques for elucidation of solution structures of biological macromolecules from nuclear magnetic resonance data. The workshop is suitable for researchers who are beginning or who are in the process of analyzing their experimental data. It is recommended also for more experienced investigators who have challenging problems to discuss with the instructors. No prior supercomputing experience is necessary.

Workshop leaders are: Dr. David Case, The Scripps Research Institute; and Drs. Thomas James, Julie Newdoll and Uli Schmitz, University of California, San Francisco.

Problems and challenges encountered during the process of structural elucidation from NMR data will be discussed. The programs AMBER, Mardigras and MidasPlus will be taught through lectures and extensive hands-on sessions. During the hands-on sessions, participants will be able to work on the examples provided or on their own experimental data.

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- Structure derivation from restraints
- Problems with pseudoatoms
- Distances and torsion angles restraints
- Motion
- Relaxation matrix
- R factors
- Distance geometry
- Energy minimization and restrained molecular dynamics

This workshop is funded by a grant from the Biomedical Research Technology Program, National Center for Research Resources, National Institutes of Health. Travel, meals and hotel accommodations for researchers affiliated with U.S. academic institutions are supported by this grant. Enrollment is limited to 20. Deadline for applications is: **April 28, 1995**.

For more information and an agenda please see URL:

http://pscinfo.psc.edu/biomed/workshops95.html

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Pittsburgh, PA 15213

Direct inquiries to: Nancy Blankenstein, Biomedical Administrator: blankens@psc.edu or (412) 268-4960.

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LESZEK POPPE, Ph.D.
Research Scientist
Carbohydrate Research

(received 2/4/95)

Prof. Dr. B. L. Shapiro
TAMU-NMR Newsletterm
966 Elsinore Court
Palo Alto, CA 94303

Selective Measurements of Inter-glycosidic ^{13}C-^{1}H Coupling Constants by ^{13}C-filtered experiments with DANTE pulses

Dear Dr Shapiro,

In certain oligosaccharides interglycosidic ^{13}C-^{1}H coupling constants can be measured by ^{13}C-filtered dipolar correlated experiments provided the anomeric and aglyconic protons are close in space (< 2.5 Å). Based on this new selective methods were developed and applied to β(1-2)-D-glucan, cyclic molecule, built out of seventeen β-D-glucose units connected between C1 and C2' carbon atoms. Due to the symmetry of the molecule the ^{1}H (see trace A) and ^{13}C ground spectra are degenerate. Traces B and C show 1D NOESY spectra (250 ms mixing time) obtained by selective excitation of ^{13}C satellites of the anomeric proton (arrows indicate the position of rf offset during the pulse sequences). Selective excitations in carbon and proton domains were achieved by DANTE-z and DANTE-180 pulse trains respectively (sequence B, where ϕ1=x, ϕ2=x, ϕ3=x, -x, -x, x, ϕ4=4x, 4y, ϕ5=8x, 8(-x), ϕ6=x, ϕ7=x, -x, -x, x, -x, x, x,-x, -x, x, x, -x, x, -x, -x, x; the delay Δ and pulse train on carbon were each 2 ms long, the proton selective pulse was 20 ms). The long-range C1-H? couplings are equal to the differences in chemical shifts of the corresponding proton multiplets in traces C and B.

The intraresidual $^{2}J_{C1H2}$ coupling constant was measured by pulse sequence A (ϕ1=0, ϕ2=0 ϕ3=x, -x, -x, x, ϕ4=y, ϕ5=x, -x, -x,x), where the DANTE pulse train on proton was tuned to produce selective HOHAHA magnetization transfer (traces D and E).

The complete set of coupling constants: $^{2}J_{C1H2}$=-6.5 Hz, $^{2}J_{C2H1}$=0 Hz, $^{3}J_{C1H2'}$=4.7 Hz, $^{3}J_{C2'H1}$=2 Hz, was obtained in less than two hours.

Sincerely yours,

Leszek Poppe

Leszek Poppe, Ph.D.

Amgen Inc., 1840 DeHavilland Drive, Thousand Oaks, California 91320-1789
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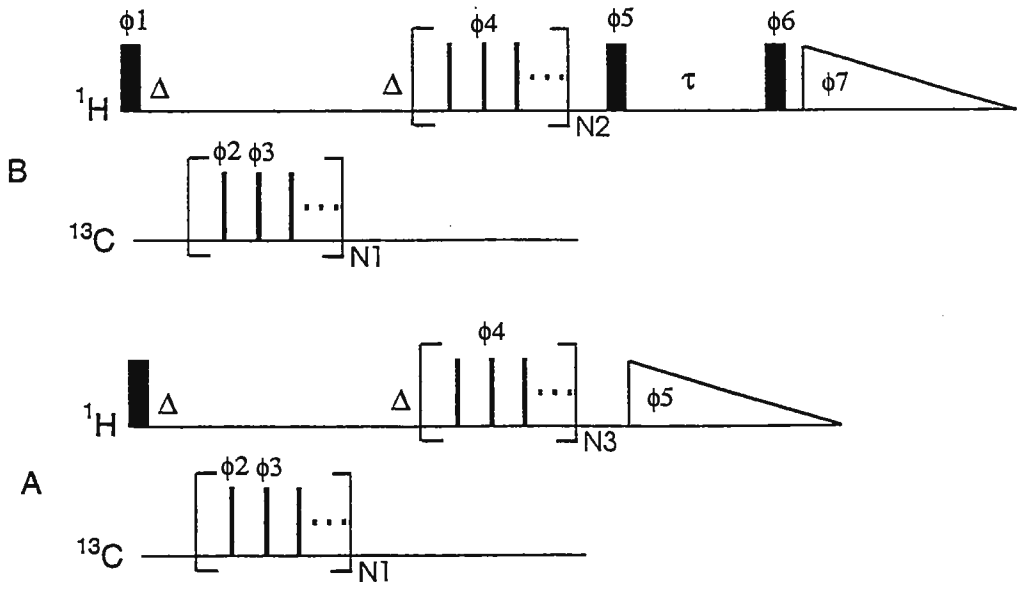
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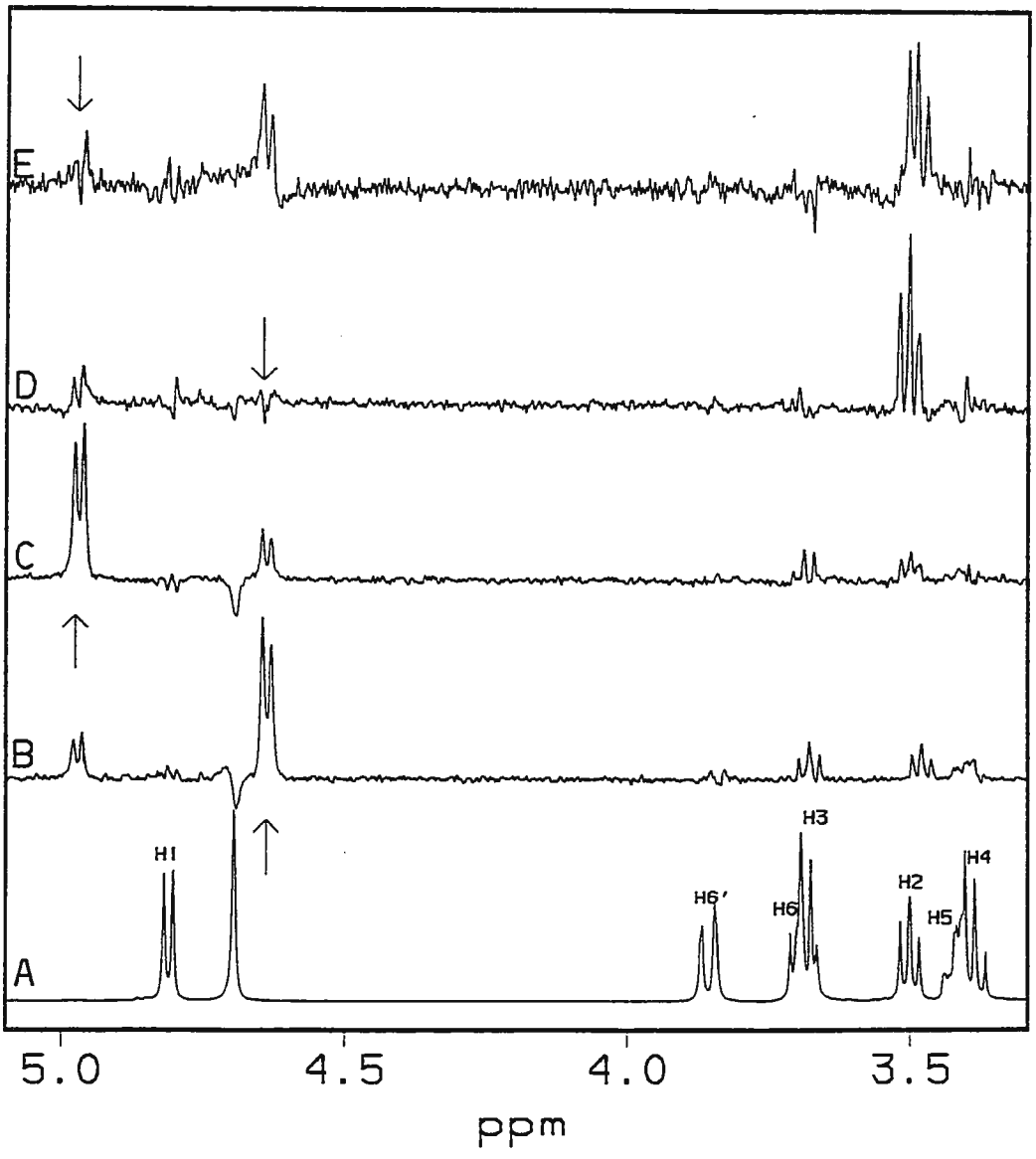
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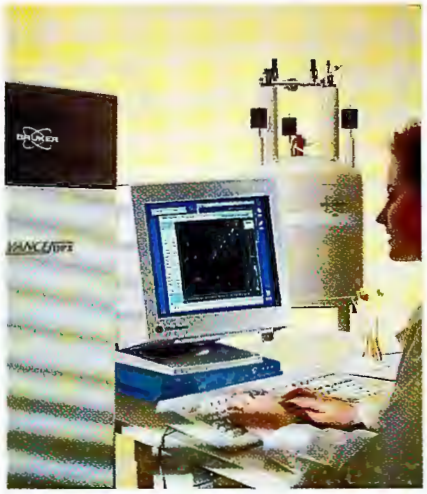

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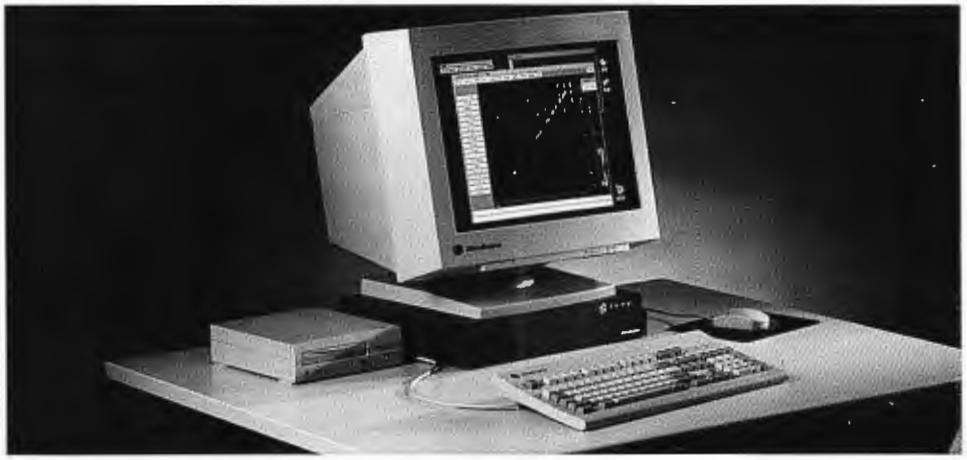

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Prof. Dr. B. Blümich

Tel.: 0241/80 6421
Fax: 0241/8888 185
e-mail: bluemich@rwth-aachen.de
Datum: 08.02.1995

RWTH, Makromolekulare Chemie, SB Chemie
Worringer Weg 1, D-52056 Aachen

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

^{2}H-Spectroscopic images of a stretched rubber sample

Dear Barry,

Many authors discuss the influence of external strain to an elastomer network in terms of changes in chain mobility and/or alignment. NMR imaging is a sensitive probe to study changes in molecular dynamics and orientation due to differences in local strain. This has been demonstrated by T_2-parameter images of strained PMDS samples [1,2], which map the local network mobility. This technique can be refined to the detection of orientation and mobility effects by ^{2}H-imaging. The dependence of quadrupole splittings in stretched deuterated rubbers on the external strain was subject of many spectroscopic investigations [3].

We have combined both methods and acquired spectroscopic images of stretched natural rubber samples doped with 1,4-deuterated poly(butadiene) oligomers. It has been shown earlier, that oligomers (M_w=1000) show nearly the same strain induced orientation as the network chains [3]. Additionally the use of oligomers has the advantage that most elastomers can be doped with them and that they are easier to synthesize.

In a ^{2}H-spectroscopic investigation of a homogeneously stretched rubber band it could be confirmed that the quadrupole splitting of the co-aligned oligomers is proportional to the orientation parameter of the network. Thus, by measuring a spatially resolved ^{2}H-spectrum of the rubber, we have direct access to strain inhomogeneities which result from physical or chemical network imperfections.

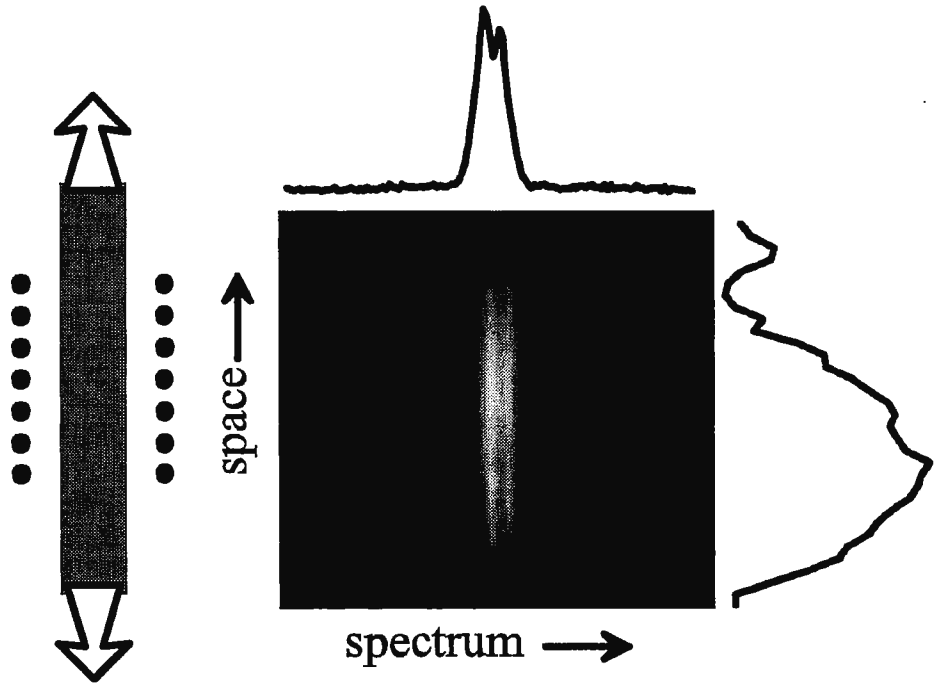
As shown in the figures, we have investigated a strained rubber sample (λ=3) before and after two cuts were made into its sides. Figure a) reveals the homogeneity across the whole sample; the quadrupole splitting is constant. Figure b) shows the stress distribution introduced by the cuts. The highest strain is found in the middle of the sample where the quadrupole splitting is clearly present and the signal intensity is reduced. As we move along the projection axis we get less strain which then overlaps with the isotropic signal from the two unstressed lobes of the cut material. At the bottom and top of the spatial axis the signal again reveals a small quadrupolar splitting from the less strained areas beyond the lobes. Additionally, the signal intensity decreases due to B_1 field imperfections towards the end of the rf coil.

The pulse sequence used in both cases was a solid echo (to obtain refocussing of quadrupole interactions) with an echo time of 5 ms and a phase encoding gradient, applied for 0.5 ms between the pulses, which was varied from -150 mT/m to +160 mT/m in 32 steps. For each step 80 acquisitions were accumulated. The sample length inside the B_1 coil was ca. 10 mm.

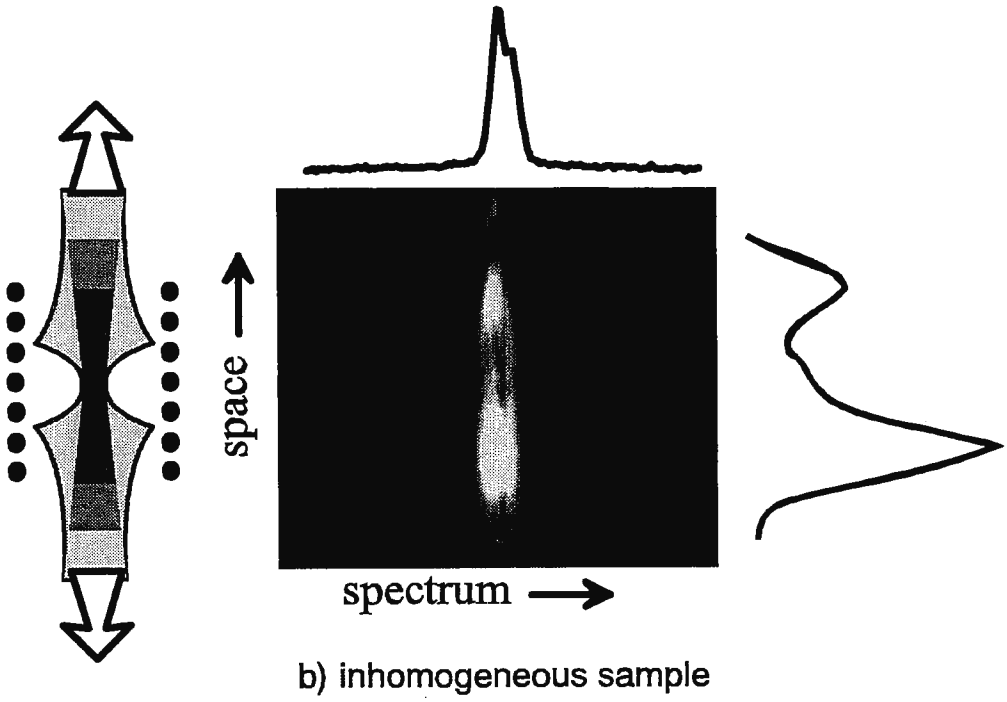
Sincerely yours,

Maurice Klinkenberg Peter Blümler Bernhard Blümich

[1] P. Blümler, B. Blümich, *Acta Polymer.* **44** (1993) 125.
[2] P. Blümler, B. Blümich, E. Günther, and G. Schauss *Bruker Report* **2** (1990) 22.
[3] W. Gronski, R. Stadler, and M. M. Jacobi, *Macromolecules* **17** (1984) 741.



a) homogeneous sample



b) inhomogeneous sample

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For further information, please contact Dr. Brian J. Stockman, The Upjohn Co., MS 7255-209-0, 301 Henrietta St., Kalamazoo, MI 49001. Telephone (616) 385-7582.

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Richard A. Komoroski, Ph.D.
Professor

UAMS MEDICAL CENTER

February 6, 1995
(received 2/9/95)
Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Title: *In Vitro* NMR of Alzheimer Brain

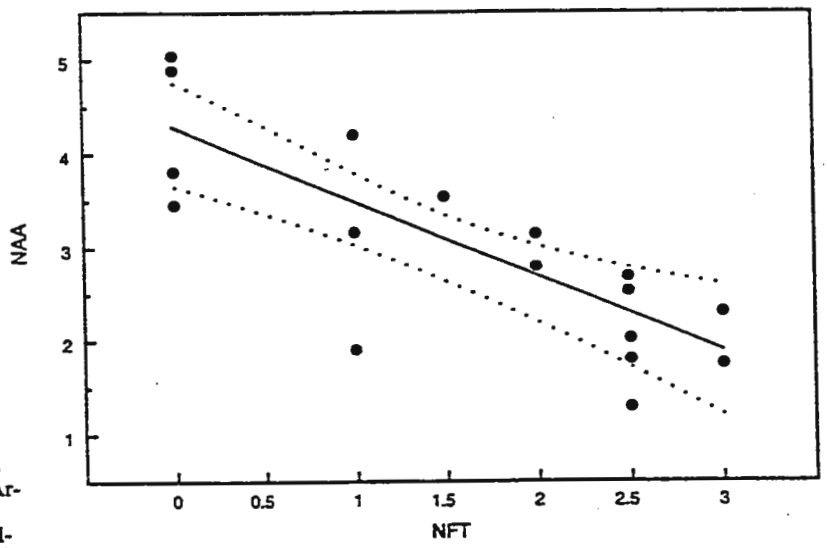
Dear Barry:

We have been using high resolution ^{1}H NMR to follow changes in metabolite levels postmortem in the brains of individuals suffering from Alzheimer disease (AD). At present there is no gold standard for the antemortem diagnosis of AD, and many laboratories are working on localized *in vivo* ^{1}H NMR in this context. There is some disagreement as to which metabolites change in AD relative to normal, aged brain, but all workers see a reduction in N-acetyl aspartate (NAA), the putative neuronal marker. Our *in vitro* work is meant to elucidate the changes seen *in vivo*. For the temporal cortex in postmortem AD brain, we saw significant reductions relative to controls for NAA, GABA, and creatine, but not glutamate or inositol. The reductions in NAA and GABA are consistent with neuronal loss in temporal cortex in AD. Similar results were obtained in other brain regions except for creatine, for which no differences were observed. Within the group of AD brains studied, we observed a correlation of NAA concentration determined by NMR and a semiquantitative estimate of the level of neurofibrillary tangles (NFT), a histologic indicator of the presence of AD. Below is a plot of NAA vs. NFT for temporal cortex. The details of some of this work will appear shortly (P. Mohanakrishnan, A.H. Fowler, J.P. Vonsattel, M.M. Husain, P.R. Jolles, P. Liem, and R.A. Komoroski, *Exp. Brain Res.*, in press.)

Sincerely,

Richard A. Komoroski
Professor

P. Mohanakrishnan



N-acetyl aspartate (*NAA*) concentration versus estimate of tangles (*NFT*). Arbitrary scores of 1, 2, and 3 were assigned for mild, moderate, and severe presence of tangles. For nondemented cases a score of 0 was given. The *dotted curves* represent the 95% confidence limit for the negative linear correlation ($r = -0.67$; $P < 0.004$)

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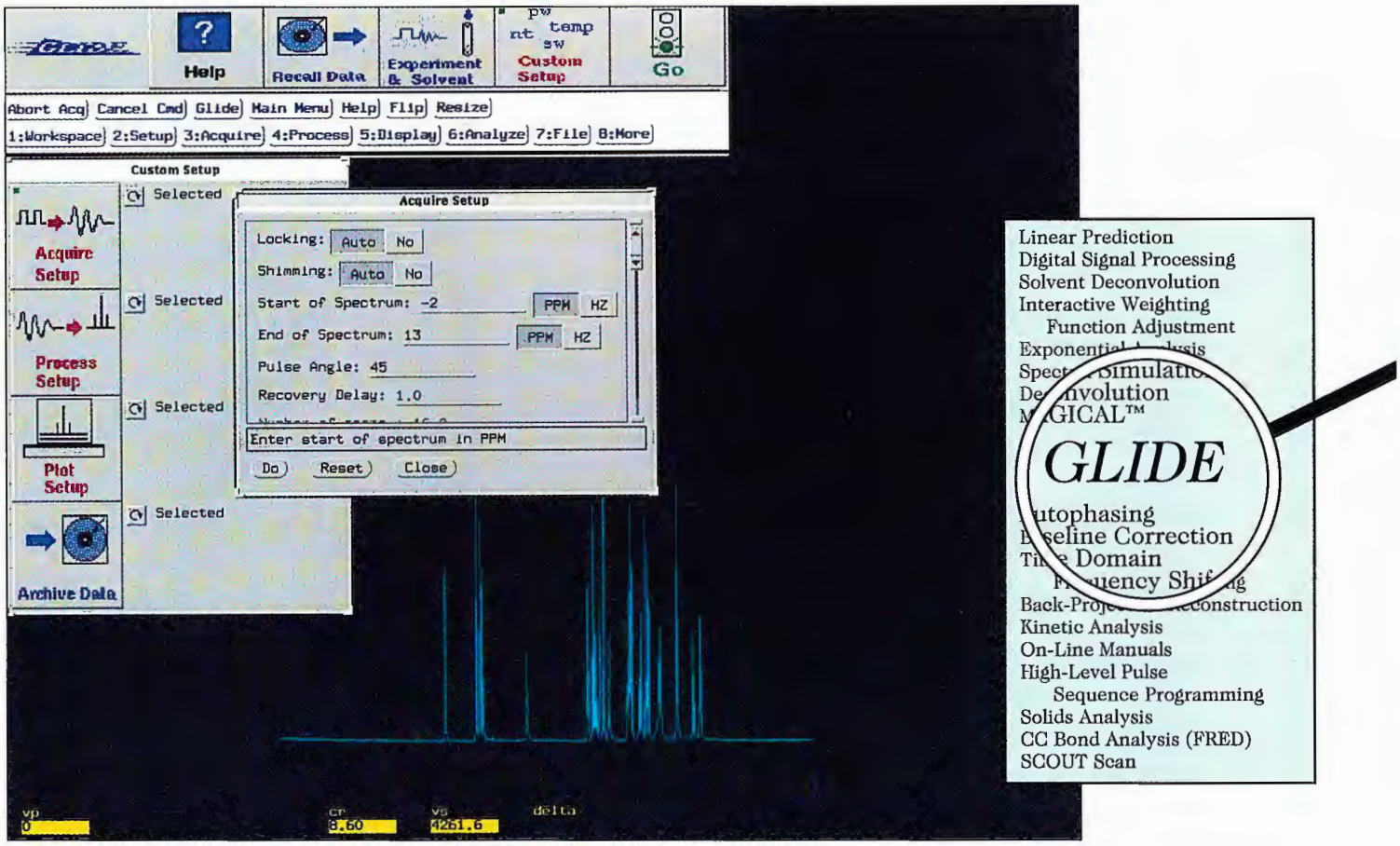

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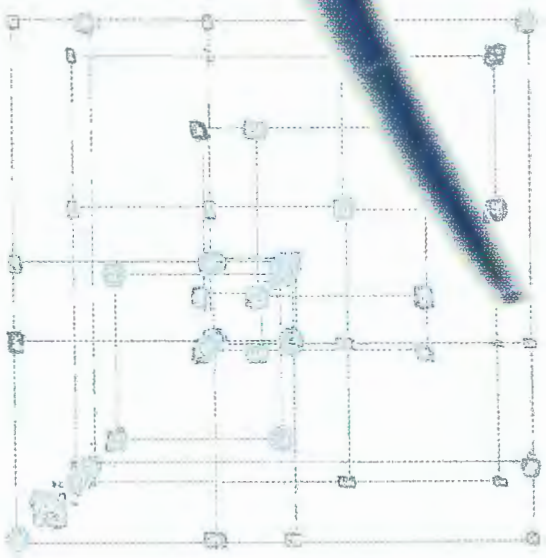

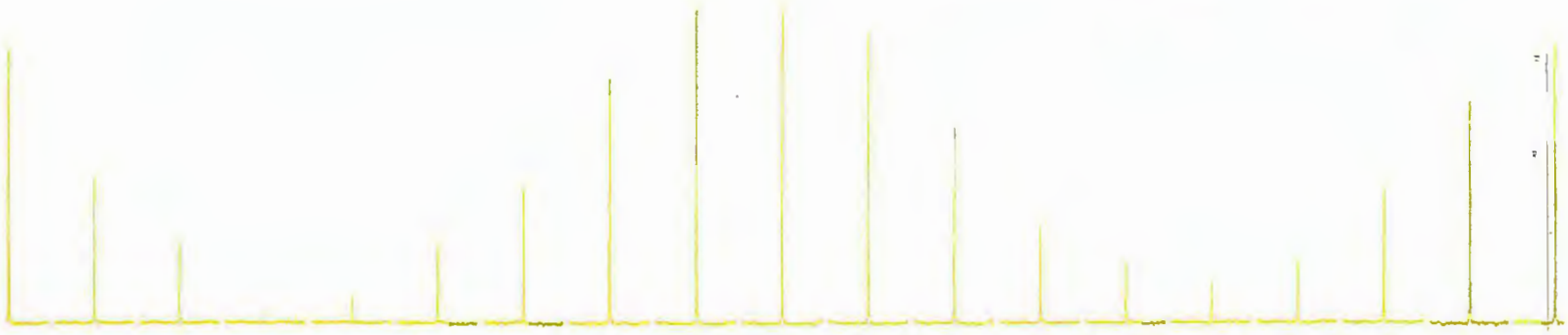

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February 15, 1995

Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elisnore Court
PALO ALTO, California
U.S.A. 94393

Re: Gradient Instability

Dear Barry:

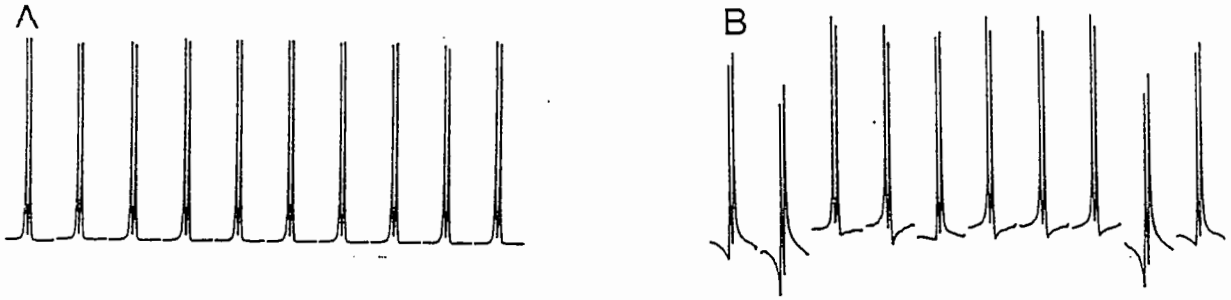
In July 1993 we installed a Pulsed Field Gradient accessory on our Varian Unity 500 Spectrometer. Recently we noticed that even though the standard gradient calibration experiments (the gradient recovery and the profile test that measures the gradient strength) worked properly, some gradient experiments (the gradient hmqc, for example) led mainly to t_1 stripes. The problem turns out to be instability (the cause of which is unknown) of the gradient amplitude at the sample. The easiest way to determine if the gradient instability exists is by performing a series of spin echo experiments with equal gradients placed before and after the 180° pulse. The phase and amplitude of the resulting spectra should all be constant as shown in A if the gradients (strength ≈ 10G/cm) are stable or variable as in B if there is some type of instability.

Sincerely,

Tom

Tom Nakashima

TTN:lf



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February 3, 1995
(received 2/4/95)

INSTITUTE OF ANALYTICAL RESEARCH

Bernard L. Shapiro, Ph.D.
966 Elsinore Court
Palo Alto, CA 94503

Dear Barry,

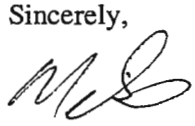
Treatment of 1,3-naphthalene-diol with triflic anhydride in dichloromethane gives rise to three products. The desired product was the 3-triflate-1-ol. The chemist who carried out the reaction measured his own ^{1}H spectra on the open shop spectrometer and then came to me with the question, "which one is it?" If one compares the ^{13}C spectra of the diol and the two mono-triflates, an assignment is possible but it leaves some doubt. Measuring the ^{13}C spectra in DMSO with 1 μL D_2O does however permit an unambiguous assignment of the position of the phenolic group. In the 1-triflate, carbons 2, 3, and 4 were observed to shift upfield by 0.09, 0.17, and 0.07 ppm respectively when D_2O was added to the DMSO solution. Best technique is, of course, to use only 0.5 eq. or less D_2O since signals due to both OH and OD species are observed[1]. In the 3-triflate, carbons 1, 2, and 8a were observed to shift upfield by 0.22, 0.05 and 0.09 ppm respectively. As in the acetates,[2] there is an upfield shift of the oxygen bearing carbon when forming the ester.

Table 1. ^{13}C NMR Chemical Shifts in $CDCl_3$

Assignment	3-triflate	diol	1-triflate
1	153.34	153.79	146.11
2	102.87	100.88	110.42
3	146.66	154.09	152.41
4	111.66	101.86	110.21
5	127.97	126.18	126.51
6	128.28	126.99	128.00
7	126.47	122.52	125.39
8	121.99	121.96	120.78
4a	135.63	135.63	135.17
8a	123.74	120.47	121.75
CF_3	118.81		118.75
$^{1}J_{CF}$	320.5		320.4

1. Y. Nakashima, T. Teranishi, T. Suzuki, T. Sone and K. Takahashi, *Magn. Reson. Chem. 32*, 578 (1994) and references therein.
2. P. Granger and M. Maugras, *Org. Magn. Reson. 7*, 598 (1975)

Sincerely,



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January 25, 1995

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

Orderly NMR

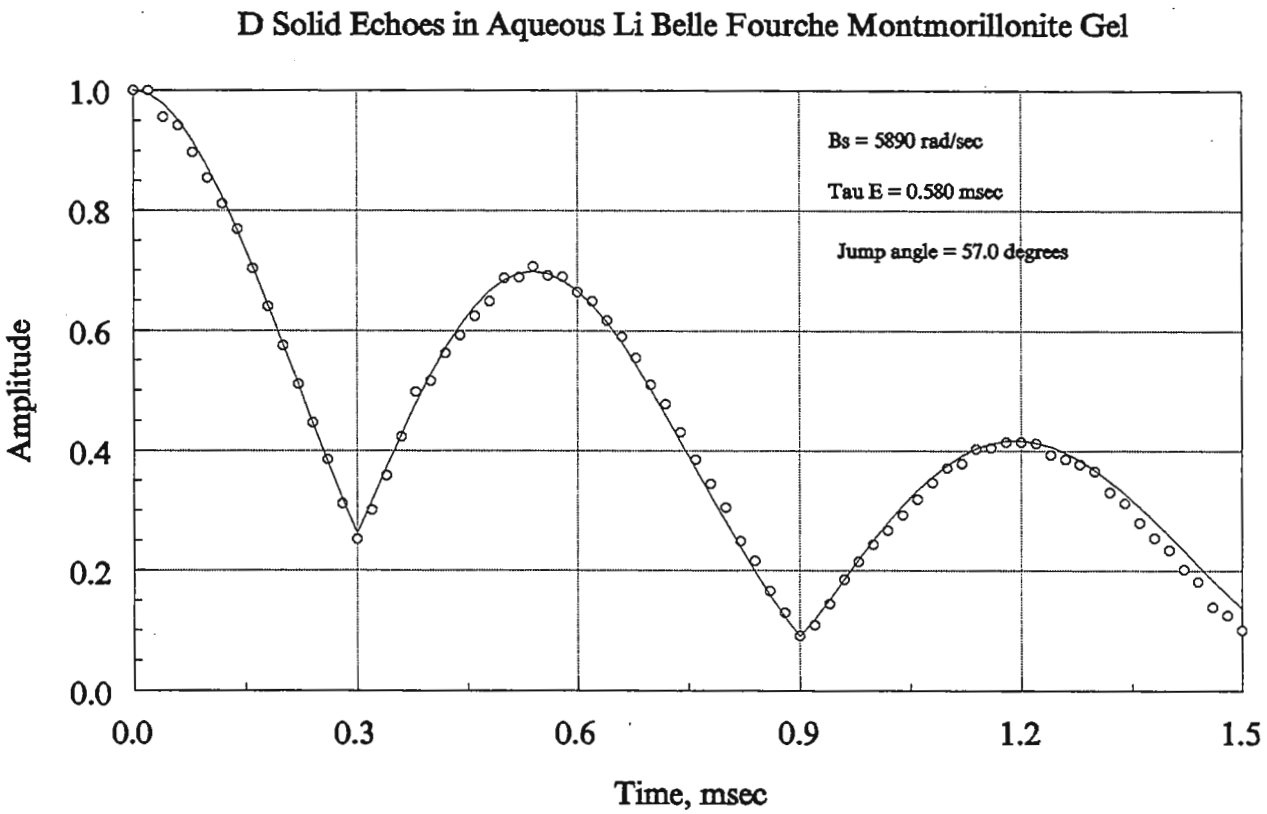
Dear Barry,

In my relentless pursuit of structural and motional information on aqueous heterogeneous systems that we can get from NMR relaxation measurements, I have stumbled across some interesting items that I mention later in this letter. The idea behind my pursuit is to use the interactions of water molecules with the "solid" components in the system to encode structural information about the geometrical arrangement of these components. Of course, the pertinent interactions are those that can affect the NMR signal of nuclei in the water molecule. Because of these interactions, the water molecules at a local interface are preferentially oriented with a director that is normal to the local interface. This preferential orientation results in residual deuteron quadrupolar splitting for D_2O (or proton dipolar splitting for H_2O) that depends on the orientation of the director in B_0. Let me illustrate this by an elementary example - water in contact with a planar surface. While a water molecule is in the interface at the planar surface, it is preferentially oriented so that it has a residual quadrupolar (or dipolar) splitting that depends on the orientation of the plane in B_0. Chemical exchange of water molecules at the interface with those in the "bulk" phase away from the surface is rapid compared to the splitting. All of the water spends part of the time at the interface so that it has a splitting that is equal to the splitting at the interface multiplied by the fraction of time F_i that it experiences the interface. The splitting S depends on the orientation of the plane in B_0 as given by the magical relationship $S = B_s \times (3 \times \cos^2\theta - 1)$, where θ is the angle between B_0 and the director (the normal to the plane) and B_s is the splitting constant that is equal to $B_i \times F_i$ in which B_i is the splitting constant at the interface.

Under what conditions can we observe the conseqences of this splitting? If we have a system of many parallel planes, all of the directors point in the same direction. If the diffusion of the water is sufficiently fast and the lateral dimensions of the planes are sufficiently small, all of the water molecules will have the same value of S. The NMR spectrum will be a doublet with splitting that has the magical relationship to orientation in B_0. When many molecular layers of water are in contact with the planes, the splitting will be inversely proportional to the water content of the sample.

Consider the opposite extreme of ordering of the planes: neighboring planes have random relative orientations. As a water molecule diffuses rapidly among these planes, it experiences spectral splitting that averages to zero during the time $1/B_s$. We will not observe a splitting in the NMR spectrum; the only consequence of the local preferential orientation will be a slight broadening of the NMR peak.

These extremes are uninteresting. I am concerned with intermediate cases, of which there are many. Let us take the first case and decrease the degree of ordering by allowing neighboring planes to tilt slightly by relatively small, random angles so that the average director orientation is the same as originally. The doublet splitting will obey the magic angle, but the value of the splitting constant will be reduced because of the reduced order of the orientations

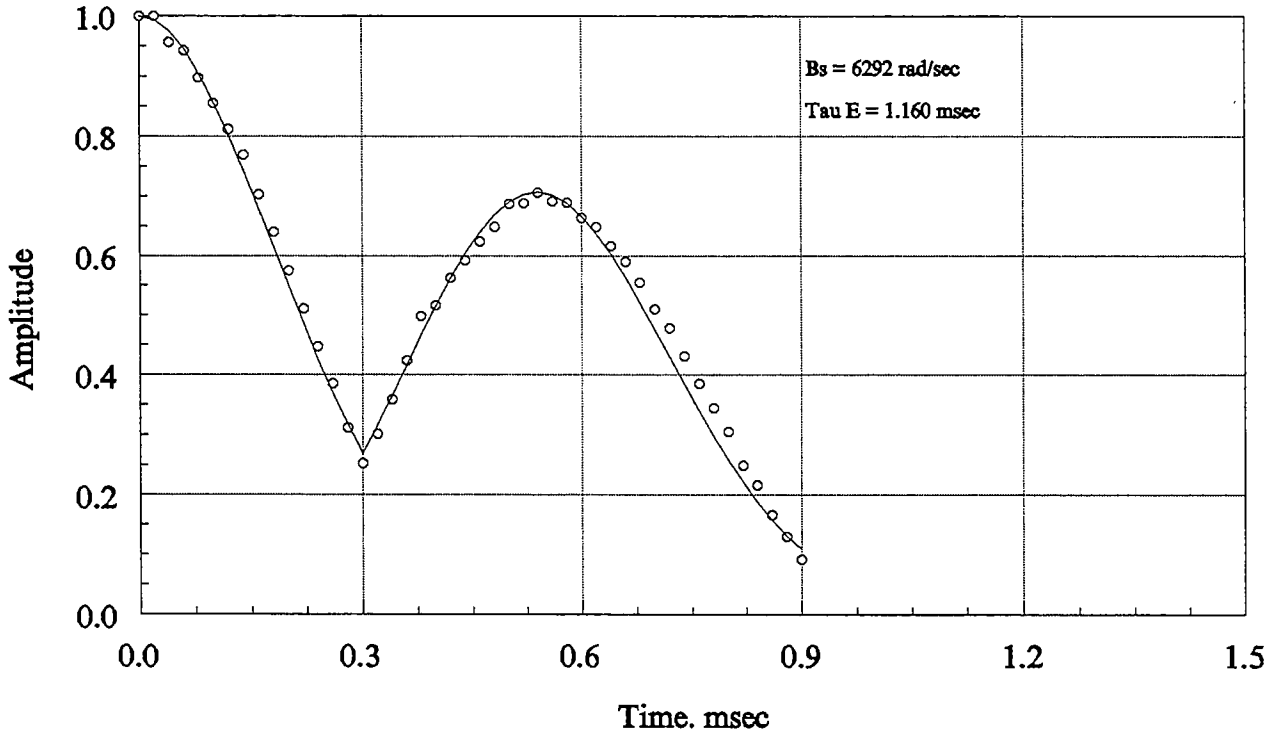


of the planes. All very interesting. Let us consider another case of reduced order in the sample. Let the sample consist of many randomly oriented isolated "crystallites." Each "crystallite" comprises many parallel planes that are evenly-spaced with the interlamellar space filled with water molecules. Globally, the sample is completely disorderd. Locally, the sample is perfectly ordered. The time-domain NMR signal from this sample is the Fourier Transform of the Pake powder pattern. But if the crystallites are not isolated, water molecules can diffuse between crystallites of different orientations in B_0 and the Pake pattern is distorted. Let τ_e be the average lifetime of a water molecule in a given crystallite. When τ_e is very long, the solid echoes in two- and three-pulse sequences are at the expected times. When τ_e decreases, but still obeys the condition $B_s \times \tau_e \approx 1$, the solid echoes can be observed when the pulse spacings are of the same order-of-magnitude as τ_e but some echoes are shifted to shorter times. If 90° pulses are applied at times t = 0 , τ and 3τ, the peak of the first echo is shifted to a time that is less than 2τ but the peak of the second echo occurs at its expected time (4τ). How do I know this? By experimental observation supported by NMR simulations. The circles in the first figure (τ = 0.30 msec) illustrate this echo shift. They are values measured on a smectite clay gel that closely approximates the ideal crystallite system described above. Aqueous smectite samples that are properly prepared closely approximate the various cases, as verified by both NMR and other kinds of measurements.

I have found John Waugh's simulation program ANTIOPE to be very useful in analyzing such data to obtain values of B_s and τ_e (we can use these values to obtain information on the degree of order and on the range of order in heterogeneous systems). The solid line in the first figure represents results from ANTIOPE with B_s = 5890 rad/sec and τ_e = 0.580 msec. In using ANTIOPE, a random 3-dimensional "jump" of 57 degrees was used (the closest to 1 radian that ANTIOPE was happy with). The agreement with experiment is gratifying. Both experiment and ANTIOPE show the same echo positions. It would be good to have an analytical expression for the shift of the first echo to estimate τ_e from an experimental echo shift.

A gaussian diffusion model, although simplistic, gives a fair, but inferior, fit to the experimental data, as shown in the second figure, with B_s = 6292 rad/sec and τ_e = 1.160 msec. The value of B_s is different from ANTIOPE because of the difference between a gaussian distribution and the Pake powder pattern. The value of τ_e is twice that for ANTIOPE because the gaussian model assumes small differences in consecutive splitting values, which corresponds

D Solid Echo in Aqueous Li Belle Fourche Montmorillonite Gel



to small "diffusional" jumps. This model is useful for making a quick analysis of data to provide initial values for ANTIOPE and it provides an analytical expression for the echo shift: $t_m = \tau_e \times \ln[2 \times \exp(\tau/\tau_e) - 1]$, where t_m is the time of the maximum of the first echo. Because this expression does not include the splitting, it enables a quick estimate of τ_e from the experimental time shift of the echo.

These results and physical model show how structure and order of the immobile material in aqueous heterogeneous systems can affect NMR phenomena. I have observed comparable NMR behavior in aqueous biopolymer gels. (If we consider a local segment of a macromolecule to be a cylinder, the splitting is reduced by a factor of 1/2 and the director is along the axis of the cylinder.) The main points are (1) that water is preferentially oriented at an interface, and (2) that if the interface is nonrandomly oriented over a sufficiently long range, the local preferential orientation is extended so that spectral splitting effects cause changes in the NMR line shape and transverse relaxation. The observable effects depend on the order of the aqueous interface; physical treatment of the sample that changes this order also affects these NMR parameters. The whole question is too vast for this letter. The interested reader who missed the original publications or has deficient pre-natal memory can consult the articles listed below and forthcoming encyclopedic and pedagogic articles.

Sincerely,

Don

Donald E. Woessner
Adjunct Assistant Professor
Department of Radiology

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Practical Aspects of Gradient-Enhanced Heteronuclear Correlation Experiments with Small Molecules
R.C. Crouch, Ann O. Davis, & Gary E. Martin, Burroughs Wellcome Co.

Triple Resonance Isotope Edited Spectroscopy: A New Method for Metabolite Identification
W.C. Hutton, J.K. Gard, J.R. Garbow, & J.J. Likos
Monsanto Corporate Research

Susceptibility Plugs - Theoretical Considerations
Toby Zens & Jim Moore, Nalorac

Microcells or Susceptibility Plugs at 5 & 8mm
Ad Bax, Frank Ray, & Stephan Grzesiek, N.I.H.

Spin-Locks, ^{2}H Decoupling, and Other Protein Spin Gymnastics at 8mm
R. Andrew Byrd, Amanda S. Altieri, & Donna M. Baldisseri
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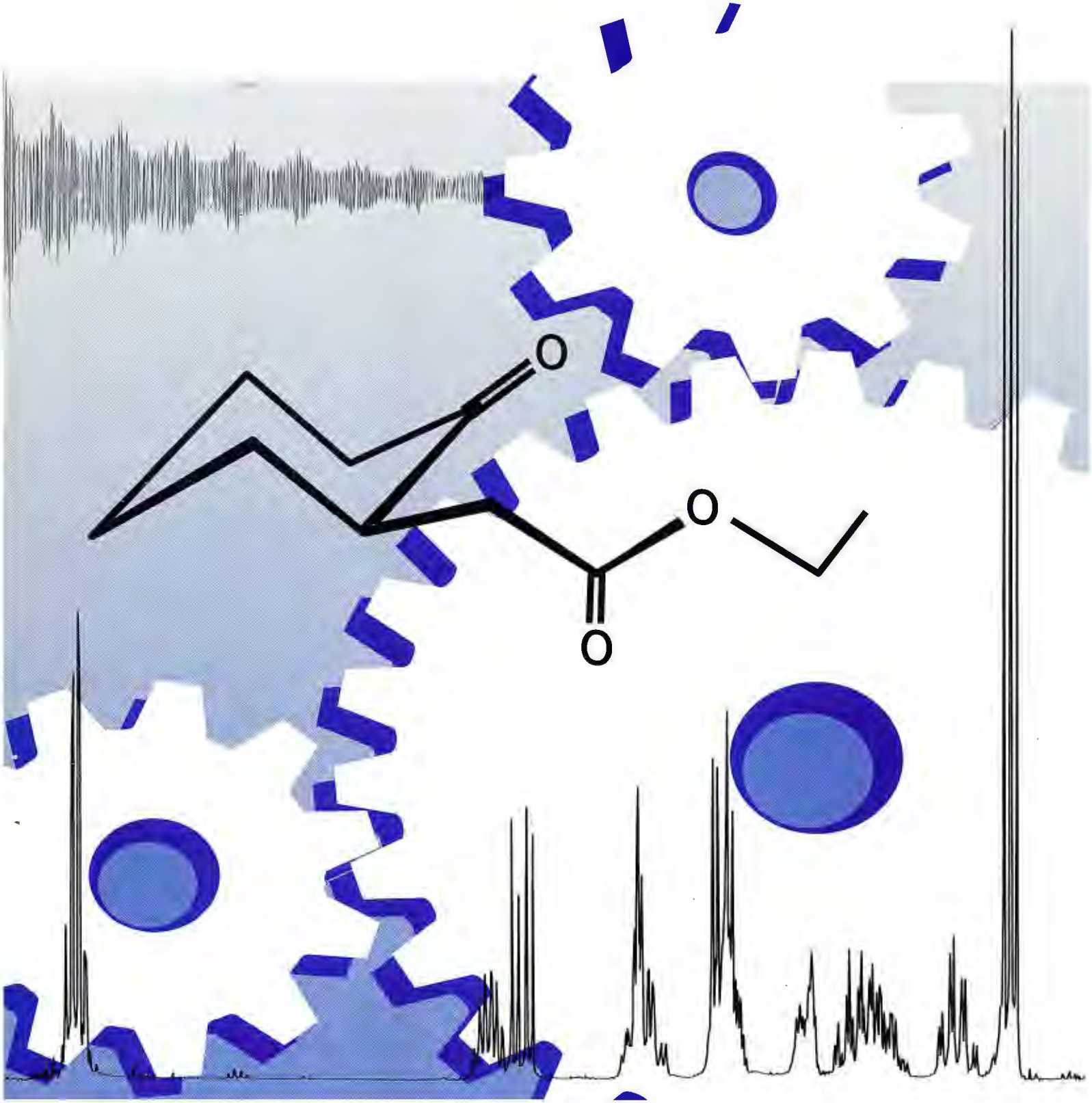

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Plus ça change (2) . . .

Beginning with the February 1995 issue, this publication is continuing privately under its new name, *The NMR Newsletter.*

It must be emphasized that the only change (other than a few cosmetic matters) is the name. The Newsletter policies and operation continue as in the past, except that *all* aspects are now handled here in Palo Alto, at the unchanged address and telephone numbers given above. Subscription, sponsorship, and advertising funds that have already been paid for the October 1994 - September 1995 Newsletter year will, of course, be honored. No changes or interruptions in the publication schedule are expected.

Let me take this opportunity to thank you - the advertisers, sponsors, and subscriber/participants - for your interest in and loyalty to the Newsletter over its 438 issues during 36+ years. Some of you have been involved with the Newsletter for two decades or more, and there are even a few - perforce a dwindling number - who have been contributing to and receiving the Newsletter since its inception in the fall of 1958. We share in what must be a useful activity, which I feel has also managed to persist with only a minimum of formality, stuffiness, and ossification. I look forward to our continuing - for a long time, I hope.

Barry Shapiro
1 March 1995

Forthcoming NMR Meetings, *continued from page 1.*

37th ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **March 17 - 22, 1996***[sic]*; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073.

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

Additional listings of meetings, etc., are invited.

International School of Biological Magnetic Resonance, 2nd Course: Dynamics and the Problem of Recognition in Biological Macromolecules

ETTORE MAJORANA CENTRE FOR SCIENTIFIC CULTURE
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NOTE Date Change!!! ⟶ 19-30 May 1995

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NOTE some program changes ⟶ **Program and Lecturers**

Basic Principles	
Introduction	Oleg Jardetzky, Stanford University, USA
Basic Principles of NMR	Hartmut Oschkinat, EMBL Heidelberg, Germany
Basic Principles of Protein Crystallography	Rudolf Ladenstein, Karolinska Inst., Stockholm, Sweden
Solid State NMR	Stanley Opella, University of Pennsylvania, USA
Isotopic Labeling of Biomolecules	John L. Markley, University of Wisconsin, USA
Basic Theory of Relaxation	Robert G. Shulman, Yale University, USA
Internal Dynamics and Empirical Determination of Spectral Density Functions	Jean-François Lefèvre, Louis Pasteur University, France
Hydrogen Exchange and Internal Dynamics	Oleg Jardetzky, Stanford University, USA
Molecular Recognition	
Recognition Processes Studied on Oligomeric Enzymes & a DNA Binding Protein	Rudolf Ladenstein, Karolinska Inst., Stockholm, Sweden
Protein A and G Interactions with Antibodies	Gordon C. K. Roberts, University of Leicester, UK
Structure of Glycoproteins	Gerhard Wagner, Harvard Medical School, USA
Antigen and Superantigen Recognition by MHC Class II Receptor	Theodore Jardetzky, Northwestern University, USA
Enzyme-Ligand and Inhibitor Interaction	Gordon C. K. Roberts, University of Leicester, UK
Ligand Design	Martin Karplus, Harvard University, USA
Structural and Dynamical Consequences of Ion Binding on Metalloproteins	Sture Forsén, University of Lund, Sweden
NMR Studies of Protein-Membrane Interaction	Stanley Opella, University of Pennsylvania, USA
Inhibitor-Protease Interactions	Tad Holak, Max-Planck-Institut, Munich, Germany
Solution Structure of LSIII, a Neurotoxin from the Venom of *Laticauda semifasciata*	Jeffrey C. Hoch, Rowland Institute, USA
Molecular Dynamics	
Simulating Protein and Nucleic Acid Molecular Dynamics	Michael Levitt, Stanford University, USA
Dynamics of Peptides Observed by NMR and Other Physical Methods	Rudolf Rigler, Karolinska Inst., Stockholm, Sweden
Structure and Dynamics of Glycogen	Robert G. Shulman, Yale University, USA
H/D Fractionation Studies of Protein Structure and Dynamics	John L. Markley, University of Wisconsin , USA
Nucleic Acids and Protein-Nucleic Acid Interactions	
Plasticity of DNA Structure and Mutagenesis	Jean-François Lefèvre, Louis Pasteur University, France
Structure and Dynamics of RNA	Cornelius Hilbers, University of Nijmegen, NL
Interaction between *trp* Repressor and *trp* Operator	Oleg Jardetzky, Stanford University, USA
NMR Studies of Protein-Nucleic Acid Complexes	Rolf Boelens, Utrecht University, NL
Protein Folding	
Pathways of Protein Folding	Christopher M. Dobson, Oxford University, UK
Simulations of Protein Folding: From Native to Denatured State and Back Again	Martin Karplus, Harvard University, USA
Thermodynamic Studies of Folding	Walter Englander, University of Pennsylvania, USA
Kinetic Studies of Folding	Walter Englander, University of Pennsylvania, USA

PURPOSE OF THE SCHOOL

The School will be devoted to the analysis of the dynamic behavior of biological macromolecules by Nuclear Magnetic Resonance and the implication of dynamics on the mechanism of recognition between macromolecules or macromolecules and small substrates. The subjects listed above will be explored in detail during the course. Students are encouraged to submit abstracts and some student research will be selected for presentation in workshops.

NMR has reached the stage where both three-dimensional structure of macromolecular complexes and dynamics can be studied quite accurately. An integrated approach between these two aspects should be utilized more and more in future research. The proposed course will bring together the interesting features of such an integrated approach.

VENUE

The Ettore Majorana Centre for Scientific Culture was founded in 1963 in the pre-medieval mountain town of Erice near Palermo as a Conference Centre, taking its inspiration from the Italian Physicist, Ettore Majorana. The Centre's lecture halls are located in two restored monasteries and the ancient Palazzo Ventimiglia. School participants are housed in the Centre Institutes or local hotels and meals are taken at local restaurants.

GENERAL INFORMATION

Prospective participants should apply to either:

Prof. Oleg Jardetzky
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fax: +415/723-2253
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stating: (1) date and place of birth, nationality, qualifications and present position; (2) address, fax and phone numbers and email address; and (3) list of publications.

Applicants interested in submitting unpublished results should send the title and an abstract of about 200 words. Selected papers will be presented and discussed in special sessions.

The total fee, including full board and lodging (arranged by the School) will be US $1,000. Limited financial aid available. Participants should arrive by 5 p.m. on the 19th.

THE CLOSING DATE FOR RECEIPT OF APPLICATIONS IS MARCH 20, 1995. NO APPLICATION FORM IS REQUIRED.

Attendance will be limited to ~75 students, to be selected by the Co-Directors. Further details will be mailed with the acceptance letter.

Oleg Jardetzky
Co-Director of the School

A. Zichichi
Director of the Centre

Jean-François Lefèvre
Co-Director of the School

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

February 23, 1995

Dear Barry,

ADRF cross polarization spectroscopy of calcium phosphates

We are currently investigating methods to perform solid-state NMR spectroscopy of bone mineral *in vivo*. It is known that the HPO_4^{2-}/PO_4^{3-} ratio provides information on the maturity of bone mineral, which is of clinical importance in the study of fracture healing as well as disease states that affect the turnover of bone mineral. It has been shown that it is possible to detect the presence of HPO_4^{2-} in the large PO_4^{3-} background present in bone mineral, using spin-lock cross polarization (SL-CP) ^{31}P-^{1}H NMR with MASS[1].

These techniques are inapplicable *in vivo*, due to the high RF power deposition of the SL-CP technique and the inadvisability of spinning a patient at upwards of 5kHz. In addition, the *in vivo* studies will be performed with a surface coil which produces large inhomogenieties in the B_1 field. We have returned to the early days of NMR and resurrected ADRF-CP (adiabatic demagnetization in the rotating frame cross polarization) in an attempt to overcome these difficulties, as well as potentially improve the efficiency of the magnetization transfer.

Experiments are currently being performed on the synthetic calcium phosphates, brushite ($CaHPO_4 \cdot 2H_2O$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). We are studying powdered samples with a surface coil in a GE-Omega 4.7T horizontal bore magnet. The cylindrical samples were placed in the center of the coil, with the sample radius much smaller than the coil radius, in order to keep B_1 fairly homogenous, though the samples did extend above and below the plane of the coil.

We were able to observe Strombotne-Hahn oscillations in both samples tested. The amplitude of the ^{31}Phosphorus B_1 field was varied in order to test the dependence of the oscillation frequency on the field strength. These oscillations represent a transient oscillatory exchange of polarization between the dipolar and Zeeman reservoirs[2, 3]. The dynamics of the cross-polarization process can provide information on the dipolar fluctuation spectrum and thus the local microstructure of the spins. Figure 1 outlines the pulse sequence used, while figure 2 shows some of the results obtained with a sample of powdered brushite. We used a linear ramp to demagnetize the spin-locked protons instead of a true adiabatic demagnetization.

We are in the process of fitting the results obtained to theoretical predictions, and are testing the applicability of the theory [4] (developed for rare S spins) to an abundant S spin system.

Jerome L. Ackerman

Chandrasekhar Ramanathan

References

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Figure 1. ADRF cross polarization experiment

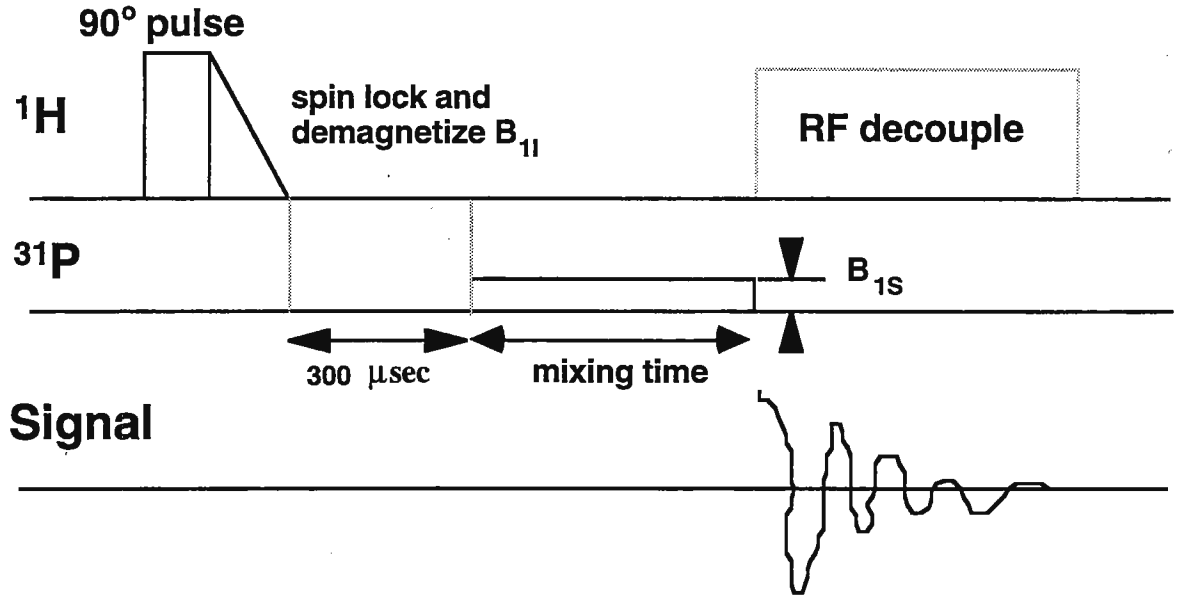
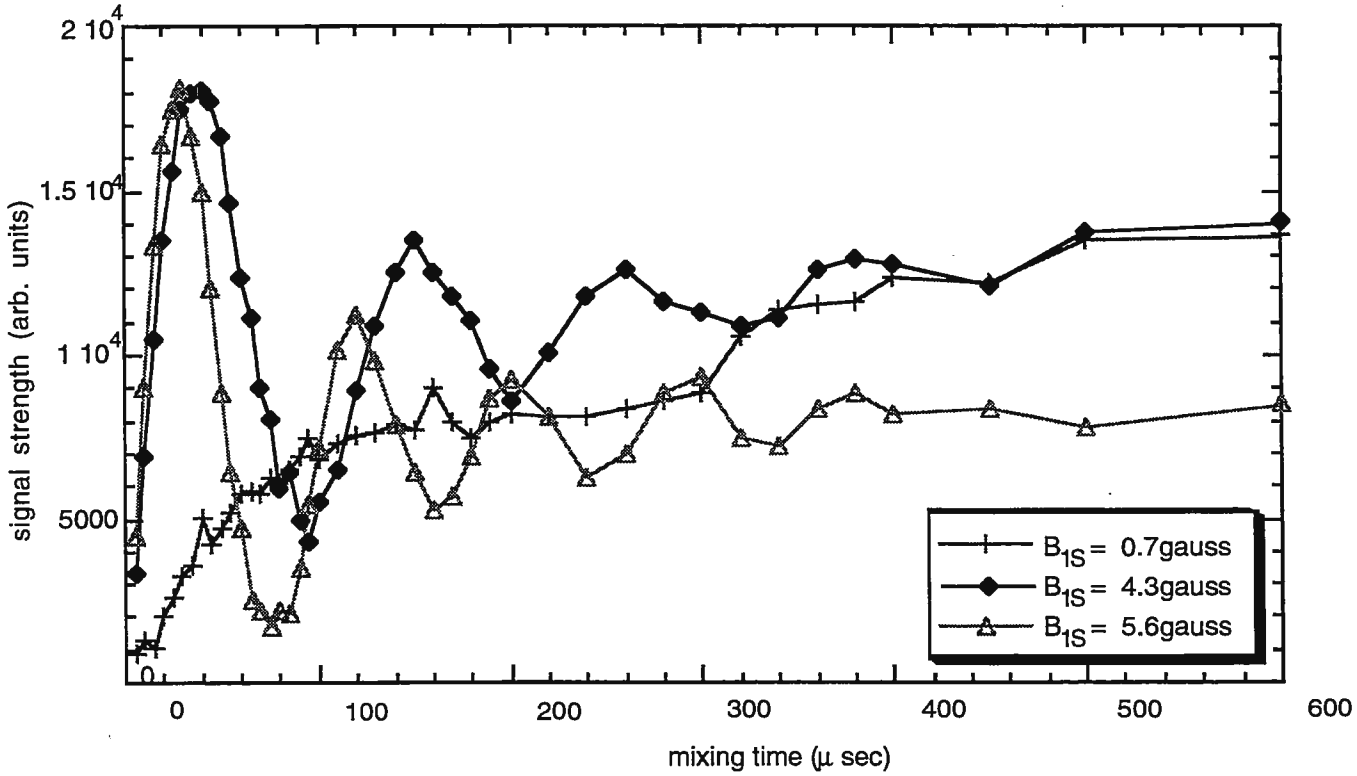


Figure 2. Oscillations observed in brushite during ADRF cross polarization



Each data point represents the average of 64 acquisitions

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Dr. B. L. Shapiro
The NMR Newsletter
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(415) 493-5971* - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

Deadline Dates

No. 439 (April)	24 March 1995
No. 440 (May)	21 April 1995
No. 441 (June)	26 May 1995
No. 442 (July)	23 June 1995
No. 443 (August)	21 July 1995

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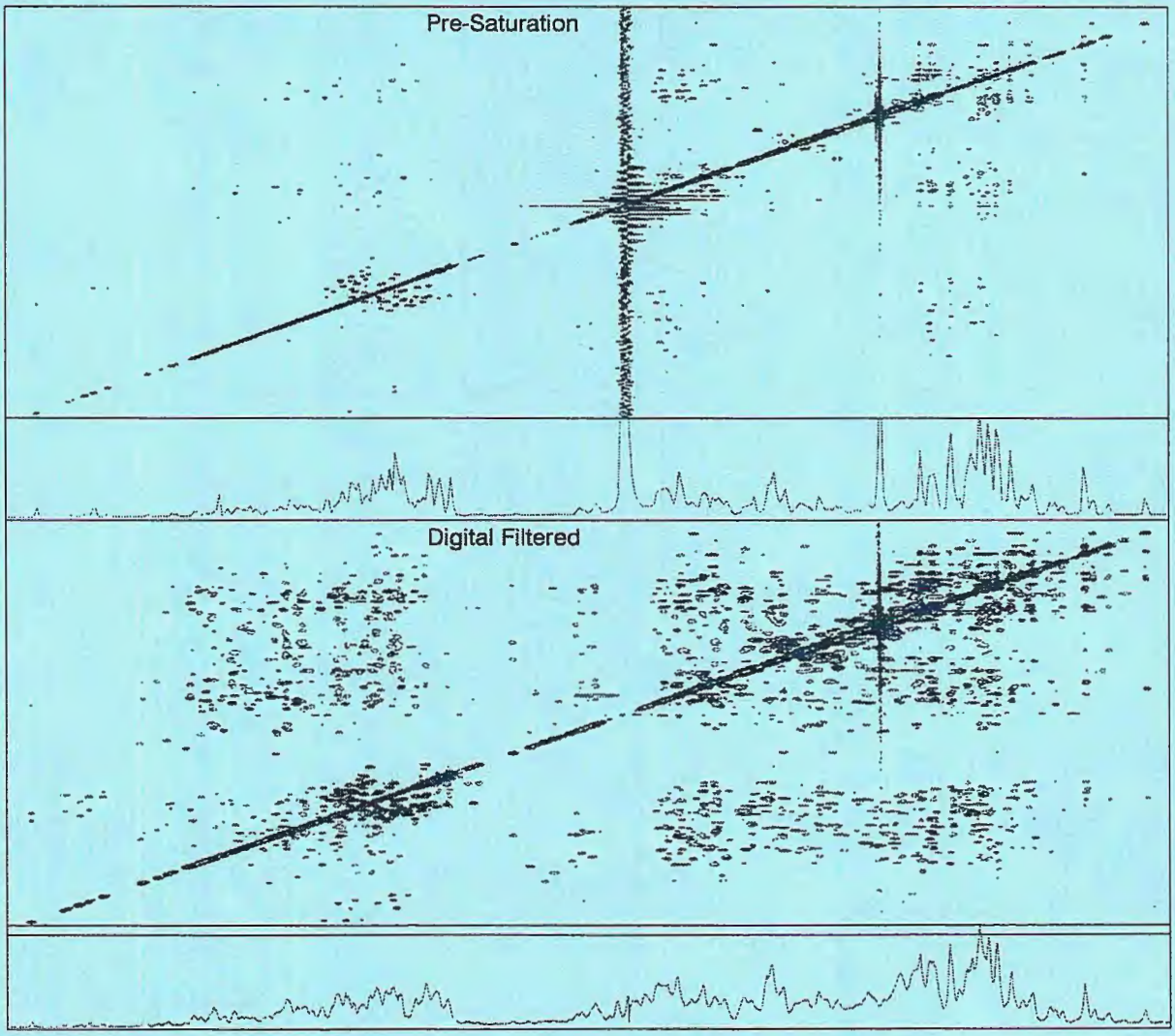
ECLIPSE NMR Advantage: Digital Filtering



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