Brian D. Sykes.

No. 346

July 1987

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These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed open access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.



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# TAMU NMR Newsletter

Editor/Publisher: Bernard L. Shapiro

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Telephone: (409) 845-7716

Mailing address after 1 September 1987:

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Department of Chemistry Texas A&M University College Station, TX 77843 U.S.A.

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Telephone: (415) 493-5971.

26 June 1987

#### Implications of the Above Letterhead and Addresses

1. <u>The NMR Newsletter will continue</u>, into the long-term, indefinite future, without significant interruption. It will in fact continue as the <u>TAMU</u> NMR Newsletter, and with the undersigned continuing as Editor/Publisher.

2. <u>New mailing address</u>: effective 1 September 1987, the new address given above should be used for <u>all</u> correspondence, enquiries, etc., including the transmittal of technical contributions, enquiries, and checks. *Please do not send any mail to the Texas A&M University address after 1 September 1987*.

3. <u>Newsletter Policies</u>. The operating policies and procedures for the TAMU NMR Newsletter will not change. After what will, I hope, be a brief period of ironing out logistic problems, the Newsletter will remain in its present form in virtually all respects. As time goes along and we are able to do so, there will be certain cosmetic changes in the appearance of the Newsletter, but these would probably be instituted were I not moving. To reiterate, our Newsletter participants/subscribers/sponsors/advertisers will enjoy the same product, service, opportunities/problems, etc., as at present.

No immediate change of subscription rates is contemplated, and the invoices for the October 1987 - September 1988 year which will be mailed out early in August will be at the same rates as we have been able to maintain for the past three years. The Newsletter will continue to be wholly self-supporting, so we will continue to depend - even more heavily - on the generosity and participation of our loyal Sponsors and Advertisers.

- continued. . .

4. For those who have an active curiosity about such non-cosmic matters, the above changes of geography reflect the fact that as of July 31, 1987, I have elected to participate in Texas A&M University's "Early Retirement Program With Modified Service". The "Modified Service" part consists, *inter alia*, of continuing to serve as Editor/Publisher of the NMR Newsletter as the TAMU NMR Newsletter. (I will also be continuing to serve as a North American Editor of Magnetic Resonance in Chemistry.).

Texas A&M University will be providing the organizational matrix through which the Newsletter will operate, and while funds will need to be <u>mailed to me</u> so that I can keep the appropriate records, etc., the checks will still need to be made out to Texas A&M University, and all funds will be transmitted by me to the University for deposit; check your 1987-88 invoices for details.

5. <u>The Future of the TAMU NMR Newsletter</u>: I hope and expect to operate this Newsletter for many years, with the gradual, incremental type of development which has characterized it for the last twenty-nine years. I do not contemplate any major changes, although suggestions for the continued development and improvement of the Newsletter are, as always, most welcome.

6. I will be away from College Station for the period July 3 - August 11, and will be in the process of moving to California beginning August 20. By approximately September 1, if things go properly, I will be fully in business at the new address indicated above. After that date, communications and visits from old and new friends will be most welcome indeed.

BJ Shapiro.

1 July 1987

#### Notice Concerning Deadline Dates for the TAMU NMR Newsletter.

Please notice on page 3 the advanced schedule of deadline dates for receipt of material for inclusion in forthcoming Newsletters. Basically, we are moving the deadline schedule ahead to the next-to-the-last Friday of each month, so as to optimize the phase relationships of these dates with holidays, printing schedules, etc.

B.L. Shapiro

#### TEXAS A&M UNIVERSITY



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FORTHCOMING NMR MEETINGS

In Vivo NMR Spectroscopy Summer School - August 31-September 5, 1987; University of Orleans, Orleans, France. See page 23 of Newsletter #343, April 1987, for additional information.

Recent Advances in Magnetic Resonance Techniques and Applications - September 10, 1987; Washington University, St. Louis, Missouri. See page 42 of this Newsletter for additional information.

26th Eastern Analytical Symposium - September 13-18, 1987; New York Hilton Hotel, New York, New York; For information, contact J.P. Luongo, AT&T Bell Laboratories, Room 1A-352, Murray Hill, New Jersey 07974, (201) 846-1582.

FACSS XIV - October 4-9, 1987; Detroit, Michigan; For information, contact Dr. Stephen J. Swarin, Publicity Chairman, Analytical Chemistry Department, General Motors Research Labs, Warren, Michigan 48090-9055, 313-986-0806.

Symposium on the High Resolution NMR of Solids - October 15, 1987; Washington University, St. Louis, Missouri. See page 42 of this Newsletter for additional information.

Symposium on Resonance in Perspective - A Tribute to Professor Richard E. Norberg - October 16-17, 1987; Washington University, St. Louis, Missouri. See page 43 of this Newsletter for additional information.

Magnetic Resonance Spectroscopy for Clinicians - October 18, 1987; San Francisco, California; University of California Medical Center, San Francisco, California; For registration information, call (415) 476-5808.

1987 Materials Research Society, Fall Meeting - Nov. 29-Dec. 5, 1987; Boston Marriott Hotel, Boston, Massachusetts. Short course on NMR Spectroscopy - Wednesday, December 2. Course Instructor: James P. Yesinowski (Cal Tech). For further details, contact: Materials Research Society, 9800 McKnight Road, Suite 327, Pittsburgh, Pennsylvania 15237.

Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance - December 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See page 7 of Newsletter #341, February 1987, for additional information.

- <u>NMR-88</u> February 14-18, 1988; Thredbo Alpine Hotel, Thredbo, N.S.W. Australia. Chairman: Dr. L.R. Brown, The Australian National University. For further information, contact: Leslie Harland, Research School of Chemistry, The Australian National University, Canberra, A.C.T. 2601, Australia. Telex: AA62172. Facsimile: (61-62)-49-7817. Telephone: (61-62)-49-2863.
- <u>29th ENC (Experimental NMR Conference)</u> April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For informa-tion, contact Professor Edward O. Stejskal, ENC Secretary, Department of Chemistry Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204; telephone (919) 737-2998.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence Should be Addressed to:

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



DEADLINE DATES No. 348 (September) ---- 21 August 1987 No. 349 (October) --- 25 September 1987

---- NU V 1007



#### THE MILTON S. HERSHEY MEDICAL CENTER THE PENNSYLVANIA STATE UNIVERSITY

P.O. BOX 850 HERSHEY, PENNSYLVANIA 17033

> Department of Radiology 717 531- 6069

June 23, 1987 (Received 25 June 1987)

Professor B. L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843-3255

Dear Professor Shapiro:

Cancer Detection Using High Resolution <sup>1</sup>H NMR

<sup>1</sup>H NMR spectroscopy of blood plasma has been used by Fossel and coworkers (1,2) to diagnose patients with untreated malignant tumors. The mean widths of the lipoprotein methyl and methylene resonance lines were reported to be significantly smaller for these cases. Since then many investigators (3) including ourselves have attempted to reproduce these results. We have now altered some of the NMR methods and observed new parameters, thus allowing a trained observer to distinguish most cancer patients from normal controls.

We used a Bruker AM-400 wide-bore spectrometer. For most samples an inversion recovery pulse sequence with presaturation of the water resonance was implemented. Echo suppression of the short  $T_2$  components was also tested. Parameters and conditions were kept constant during the course of the study so as to allow comparisons of areas and peak heights. Temperature was maintained at 25°C and 10%  $D_20$  was used to ensure a frequency lock. Optimal shimming on the  $H_20$  FID for each sample minimized inhomogeneity errors to within 1 Hz. In cases where lactate was interfering, interpolation was used to correct the line width measurement. A pulse delay of 0.8 secs can be used to null the lactate.

In this study the methylene line width has been found to be the most reliable parameter. Spectra from normal plasma have a characteristic shoulder centered about 0.04 pp: upfield from the tallest components of the methylene envelope (Figure 1A). The  $T_1$  for this shoulder is more than 20% shorter than for the central peak. Spectra from all of the cancer patients could be divided into two classes. The first cancer class (Figure 1B) exhibits a large increase in contributions to the envelope from the central components, resulting in measurement of a smaller line width. The total methylene area may be up to twice as large in this class. In addition, the  $T_1$  is slightly longer for this resonance than for other classes. In particular, the partially relaxed spectra often magnify these effects (Figure 1C) with a moderate to broad line width and areas comparable with normal samples. A shoulder is difficult to distinguish in these cancer cases. Instability in some of the samples has been shown to result in broader line shapes. Refrigeration seems to minimize this problem.

Variations in the distribution of some lipoprotein domains which are composed of phospholipids, cholesterol esters, acylglycerols, glycolipids and free fatty acids should account for the observed differences in the composite NMR methylene and methyl lineshapes. This study and others (4) have shown that there are components present with differing relaxation times. However, it has not been demonstrated that the individual lipid methylene segments have altered mobility (rates of motion) or ordering (amplitudes of motion). Evidence for this would require very detailed investigations (5). It is not likely that measurement of a single parameter, by itself, will provide specificity in diagnosis.

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However more sophisticated spectroscopic methods (2D,  $^{13}$ C T<sub>1</sub>'s and T<sub>2</sub>'s, simulations, use of internal standards, etc.) and chromatographic analysis combined with numerous, but thorough, patient plasma studies should eventually result in acceptable protocols.

#### References

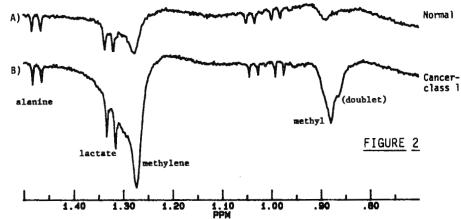
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- Fossel, E.T., Carr, J.M. and McDonagh, J., Clinical Research 35(3), 629A, 1987 (Abst.).
- Fossel, E.T., et al., <u>N. Engl. J. Med.</u>, 316, 1411-1415, 1987 (correspondence).
- Wright, L.C., May. G.L., Dyne, M. and Mountford, C.E. <u>FEBS Lett</u> <u>1986</u>, 203, 164-168, 1986.
- Brown, M.F. and Williams, G.D. J. Biochem. Biophys. Methods, 11, 71-81, 1985.

#### FIGURE 1

Representative methylene line shapes from A) Normal, B) Cancer-class 1 and C) Cancer-class 2 patients. Note that line width values are very sensitive to phasing. No line broadening was applied so as not to mask spectral features.

#### FIGURE 2

Representative inversion recovery spectra with VD = 0.20 secs corresponding to A) Figure 1A and B) Figure 1B.



We would like to acknowledge Drs. David Cunningham, Allan Lipton, William Weidner and Srinivas Kottapally and Sherry Imboden from the Radiology and Oncology Departments for support, consultations and help with sample preparations.

Sincerely,

Genald D. Williams

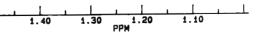
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Gerald D. Williams, Ph.D.<sup>†</sup> NMR Research Associate Kenneth R. Metz, Ph.D.\* Assistant Professor

\*Current address: Department of Radiology, New England Deaconess Hospital, Harvard Medical School, 185 Pilgrim Road, Boston, MA 02215

<sup>†</sup>Please credit to the account of G.D.W.

A) FIGURE 1 A)  $T_1(c) = 0.38 \pm 0.04 \text{ s}$   $T_1(s) = 0.30 \pm 0.02 \text{ s}$  LW = 30 - 43 Hz  $T_1(c) = 0.40 \pm 0.03 \text{ s}$  LW = 19 - 26 HzC) LW = 25 - 37 Hz



#### CALIFORNIA INSTITUTE OF TECHNOLOGY

#### Mail Code 164-80, Pasadena, CA 91125

Professor Bernard L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843

June 5, 1987 (Received 22 June 1987)

#### Homonuclear Dipolar Sidebands in <sup>1</sup>H MAS-NMR Spectra

#### Dear Barry:

It is well-known that inhomogeneous interactions such as chemical shift anisotropy give rise to spinning sidebands in MAS-NMR spectra at "moderate" spinning speeds. Analysis of such sidebands can yield the anisotropic parameters, which are often more sensitive to structural changes and chemical perturbations than is the isotropic chemical shift. It may not be as widely-realized that the homonuclear dipolar coupling between an isolated pair of spins also behaves as an inhomogeneous interaction in the sense of MAS-NMR.<sup>1</sup> Figure 1 shows what we believe is the first experimental demonstration of this behavior, in the 500 MHz <sup>1</sup>H MAS-NMR of water molecules in the zeolite mineral analcite. The envelope of the resultant "dipolar" spinning sidebands, especially at low spinning speeds, is seen to resemble closely the Pake doublet expected for a relatively isolated pair of protons.

We have observed such dipolar sidebands in the <sup>1</sup>H MAS-NMR spectra of numerous other minerals as well,<sup>2,3</sup> although often the resolution is not as good as in the case of analcite, even at spinning speeds of ca. 8 kHz (presumably due to stronger intermolecular dipolar interactions). A point to note is that although 180° "flips" of the H<sub>2</sub>O molecules do not affect the intramolecular dipolar coupling, they presumably contribute to improved resolution by (1) reducing the intermolecular dipolar couplings; and (2) averaging the <sup>1</sup>H chemical shift tensors, which otherwise would result in "powder pattern" lineshapes for the MAS-NMR peaks, as demonstrated by Maricq and Waugh.<sup>1</sup>

We have found that such dipolar sidebands provide valuable structural and dynamical information in a variety of minerals, including those containing low levels of nonstoichiometric water.<sup>3</sup> Particularly encouraging is that spinning speeds of ca. 8 kHz are generally sufficient to achieve resolved peaks, without the need for multiple-pulse line-narrowing methods or isotopic dilution.

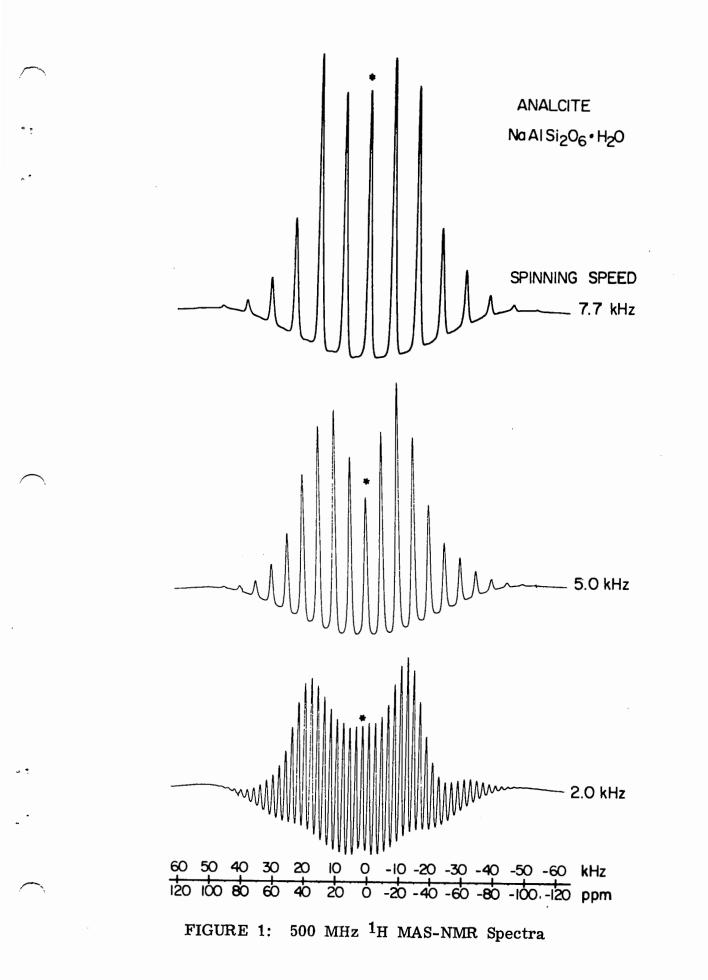
- 1. M.M. Maricq and J.S. Waugh, J. Chem. Phys., 1979, 70, 3300.
- 2. J.P. Yesinowski and H. Eckert, J. Am. Chem. Soc., in press.
- 3. J.P. Yesinowski, H. Eckert and G.R. Rossman, manuscript in preparation.

James Nesimouski H. S. S. S.

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Southern California Regional NMR Facility



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Department of Chemistry Tel: 523187 DR. OLIVER W. HOWARTH

University of Warwick Coventry CV4 7AL Department of Physics Tel: 523523 Ext. 2403 DR. RAY DUPREE

5 June 1987 (Received 12 June 1987)

Professor B L Shapiro Department of Chemistry Texas A & M University College Station TEXAS 77843 USA

Dear Professor Shapiro

VANADIUM-51 COSY OF MOLYBDOVANADATES

Although Peter Domaille has reported<sup>1 51</sup>V COSY spectra of decavanadate and of tetradecaphosphovanadate, he comments a little pessimistically that the single observed cross-peaks in each spectrum "are very weak and approach the spectrometer artefact levels". I am happy to report that the prospect is now considerably brighter. In collaboration with Lage Pettersson's group at Umea I have been studying molybdovanadates. The main species in the low-molybdenum part of the system have not yet proved possible to crystallise, and so we are dependent on n.m.r. for their identification. Fortunately, almost all the inter-species equilibria are slow on the n.m.r. timescale, so that we can obtain useful narrowing of lines by working at 99°C. The main part of our study has been by straightforward 1D nmr and stoicheiometry, and has yielded excellent results using our WH400. Oxygen-17 n.m.r. is also proving very informative. But the purpose of this note is to report that  $^{51}$ V COSY at 99°C has also been successful. Figure 1 shows the crowded part of the  $^{51}$ V COSY-90 spectrum of the molybdovanadate system at pH 5.72, 0.05M in Mo and V, using sinebell windows. The main species present (M) is monomolybdononavanadate,  $[V_0Mo0_{28}]^5$ . Also present is about 10% of dimolybdo-octavanadate species (D) and about 20% of an as yet unidentified molybdovanadate (U). The M peaks are labelled as in the structural diagram, and show clearly that M retains the decavanadate structure with a molybdenum substituted for a vanadium atom at a "capping" site.

In Figure 2 the same data is replotted to full scale after processing with Gaussian windows. The crowded region is of course messier due to the increased weighting of early FID points. However, two cross-peaks from the central vanadiums are now clearly visible, which was not the case with the sinebell windows. In fact, the only missing cross-peaks are those from the "capping" atoms V4, 5 and 6 to each other and to V1. The absence of V4 - V6 casts doubt upon the idea that M-O-M couplings are largest for linear bridges.

At lower pH we have found that a second Mo replaces another capping V. Surprisingly, the "cis" and "trans" isomers form in roughly equal proportions, whereas the "geminal" isomer is not found.

1. P.J. Domaille, J. Amer. Chem. Soc. (1984) 106, 7677-7687.

Yours sincerely

Ouver Howart

Oliver Howarth

(continued on page 11)

346-8

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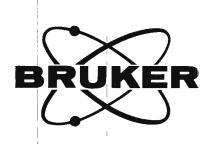
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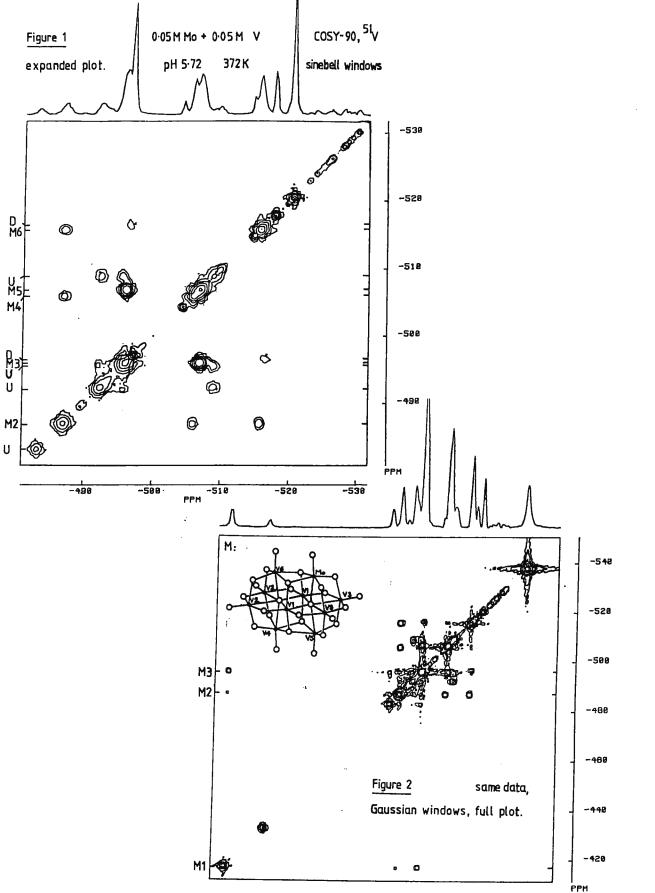
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CHALMERS TEKNISKA HÖGSKOLA OCH GÖTEBORGS UNIVERSITET INSTITUTIONEN FÖR BIOKEMI & BIOFYSIK DEPARTMENT OF BIOCHEMISTRY & BIOPHYSICS

> May 25, 1987 (Received 12 June 1987)

Professor B L Shapiro Department of Chemistry Texas A & M University College Station, TX 77843

Dear Prof. Shapiro,

INTERACTION BETWEEN CYTOCHROME c AND CARDIOLIPIN

In an effort to gain further knowledge of the effects of ischemia / reperfusion in muscle tissue, we have undertaken an NMR study of the interaction between ferricytochrome c and cardiolipin. When the oxygen supply is restored in the tissue highly reactive radicals are produced. These affect many of the enzymic activities found in the mitochondrion. The decreased activities may be due to direct damage of the proteins involved or indirectly through destruction of different lipid components in the membrane. Of these, cardiolipin has been implicated as being essential for the cytochrome c oxidase activity, although it is not known whether it is directly so or indirectly through an enhanced binding of cytochrome c to the oxidase (1).

Lecithin liposomes do not significantly perturb the spectral features of ferricytochrome c at 270 MHz. However, with increasing amounts of cardiolipin a strong overall broadening of the spectrum is observed. The interaction between this negatively charged lipid and ferricytochrome c is mainly electrostatic in nature and the line-broadening is due to the increased rotational correlation time of bound cytochrome c in rapid exchange (for most resonances) with the free protein. Destruction of cardiolipin by addition of varying amounts of superoxide radicals results in reduced binding of the protein. It is thus clear that intact cardiolipin is required for binding of cytochrome c to the membrane surface.

Adress Chalmers tekniska högskola Inst för biokemi och biofysik 412 96 GÖTEBORG Tel, 031 - 81 01.00 Address Chalmers University of Technology Department of Biochemistry and Biophysics S-412 96 GÖTEBORG (Sweden)

We have also found some specific effects of cardiolipin on the cytochrome c structure, the most important being the disappearance of the heme methyl resonance at 10.1 ppm. Concomitantly a very broad feature, which presumably corresponds to the bound environment of the disappearing resonance, centred around 14.5 ppm, appears, thus suggesting a slow exchange behavior between these two resonances. Actually, this finding agrees well with a previous EPR investigation showing a shift of the g-value from 1.25 to 1.54 (2) since the direction of this g-tensôr component is towards the heme methyl group on which the NMR effect was seen. These results indicate that cardiolipin induces conformational changes at the exposed heme edge in cytochrome c, a conclusion which is further supported by changes in the T values of different heme resonances. The results are also in accord with the finding that the oxidase interacts with ferricytochrome c at the solvent exposed heme edge (3,4). Since one or two cardiolipin molecules are tightly bound to the former protein, it may well be that cardiolipin contributes in the binding of cytochrome c to the oxidase and that damage of this lipid results in a decreased activity.

Yours sincerely,

Jours Agel Barran form

Jonas Ångström

Bassam Soussi

Please credit this letter to Lars Baltzer's subscription.

#### References

- Vik, S. B., Georgevich, G. & Capaldi, R. A. (1981) Proc. 1. Natl. Acad. Sci. U.S.A. 78, 1456-1460.
- Vincent, J. S., Kon, H. & Levin, I. (1987) Biochemistry 2. 26, 2312-2314.
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# Medical College of Virginia Virginia Commonwealth University

May 27, 1987 (Received 1 June 1987)

Professor Bernard L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843-3255

Title: INTERFACING THE N.M.R. SYSTEM WITH A SONOMICROMETER

Dear Professor Shapiro:

Our interests are in defining the relationships between regional cardiac metabolism and mechanical function in the open-chested dog with LAD occlusion; this model was chosen because of the huge amount of published experience with it. Our metabolic studies include serial 31P NMR spectroscopic measurements (Bruker Biospec) with a surface coil placed on the heart during coronary occlusion and reperfusion. During these NMR measurements of ischemic zone metabolism, we simultaneously monitor mechanical function in this region (wall thickening or segmental shortening, depending on the protocol) as well as in a distant, non-ischemic region using a Triton 120 Sonomicrometer (Triton Technology, Inc., San Diego, Calif).

Obtaining the NMR measurements requires an environment free of RF noise at the Larmor frequency of the nucleus of interest; for 31P in our system this is 40 MHz. There are two sources of RF noise introduced by the addition of the sonomicrometer to the NMR system: (1) harmonics produced by the sonomicrometer itself, and (2) ambient RF noise which is picked up from the laboratory environment by the sonomicrometer leads and carried into the magnet ("antenna effect"). In our lab, either one of these is sufficient to obliterate the NMR signal, but the effects of both can be virtually elimin-Each NMR acquisition is gated so as to be acquired at end-inspiration ated. via a microswitch/cam assembly mounted on the animal ventilator. This assembly also triggers a monostable multivibrator with a time constant of just over one second; the multivibrator pulse turns off the sonomicrometer clock during the one second in four when NMR data is actually being acquired, and thus eliminates the first source of RF noise. We have eliminated the antenna effect by (1) using double-shielded twinaxial cables (Alpha 9814) between the sonomicrometer and the magnet, (2) installing an aluminum bulkhead on the face of the magnet through which all connections are made, and (3) routing our cables over a copper mesh groundplane installed along the floor between our magnet and equipment rack.

We currently experience no degradation of the 31P NMR signal by insertion of the sonomicrometer leads and apparatus into the system, and operation of the NMR spectrometer produces no degradation of the sonomicrometer signal. I would be happy to provide a more detailed account of (1) the gating electronics and their connection to the sonomicrometer, (2) the design of our bulkhead, or to answer any questions regarding the marriage of the sonomicrometer and NMR spectroscopy. My address and phone number are Box 1 - MCV Station, Richmond, VA 23298-0001, (804) 786-8263.

Division of Radiation Physics • P. O. Box 72 • Richmond, Virginia 23298 • (804) 786-7233

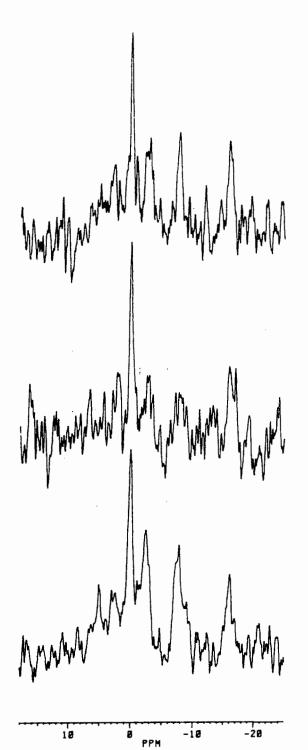
Figure 1:

 (a) Spectrum without any sonomicrometer connections, no bulkhead;

 (b) Shielded cables, 95% shield, no bulkhead, sonomicrometer operating with gating;

(c) Shielded cables (100% shield), bulkhead in place, sonomicrometer operating with gating.

> (NOT SHOWN): sonomicrometer operating without gating: NO spectral detail visible.



Best regards,

NMR RESEARCH FACILITY DEPARTMENT OF RADIOLOGY

Roger Rehr, M.D.

Clarke, Ph.D. Geof rey

WASHINGTON RSITY UNT

#### ST. LOUIS, MISSOURI 63130

DEPARTMENT OF PHYSICS

May 28, 1987 (Received 2 June 1987)

Self Decoupling in HD

Professor Bernard L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843

Dear Professor Shapiro,

We have been using an 8.5 T spectrometer to study the 55 MHz deuterium NMR of HD. In the liquid at 19°K, the J coupling to the proton gives rise to a 43 Hz doublet. As the temperature is reduced into the solid (melting point =  $16.6^{\circ}$ K) the lines broaden, coalesce, and then the single averaged line sharpens. The full width at half maximum is 83 Hz at 15.4°K and this narrows to 54 Hz at 14.0°K. (See figure.) This is the classical exchange behavior, but the apparent exchange rate increases as the temperature drops!

The explanation of this lies in the proton flip-flops. At high temperatures, the rapid diffusion averages away the intermolecular proton-proton dipolar interaction. A measure of the flip-flop rate is the proton  $T_2$ , which is 10 msec near the melting point.<sup>1</sup> As the temperature decreases, T<sub>2</sub> gets shorter - approximately 2 msec near 15.4°K - and the proton flip-flops become more rapid. Eventually, in the rigid lattice limit the flip-flop rate will be  $5/9 T_{2RL}^{-1}$ , roughly  $10^5 \text{ sec}^{-1}$ , fast enough to average out the scalar couplings. This is an unusual example of the AgF effect discussed by Abragam and Haeberlen ("self decoupling").<sup>2,3</sup>

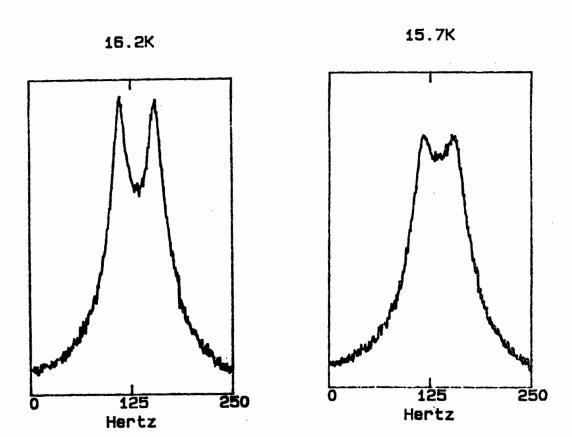
Sincerely,

Joseph Ganem

kreph samen 1227/02000 R. E. Norberg Mark S. Conradi

**References:** 

1. Bloom, M., Physica 23 (1957) 767. 2. Abragam, A., Principles of Nuclear Magnetism, Oxford University Press, (1961) 122. 3. Haeberlen, U., High Resolution NMR in Solids Selective Averaging, Academic Press, (1976) 87.

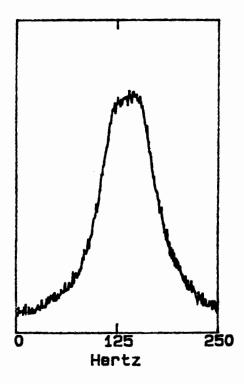


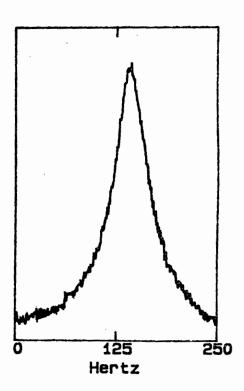
15.4K

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UNIVERSITY OF LUND PHYSICAL CHEMISTRY 2 Lund, June 5, 1987 (Received 16 June 1987)

Prof. B.L. Shapiro Department of Chemistry Texas A&M University College Station Texas 77843 USA

<sup>31</sup>P NMR study

Dear Barry,

In several parts of Europe it is obvious that the forest is not very healthy and therefore the acid rain has become a major concern for many biologists during the last few years.

The acid rain is certainly not the only, maybe not even the main, reason to the unhealthy state of our forests. However, any experiment that may help to clarify what is causing this problem is valuable. I have therefore been helping Paul Jensén at the Department of Plant Physiology with some <sup>31</sup>P NMR studies on beech roots. He has been interested in the effect on the phosphate uptake caused by increasing amounts of  $Al^{3+}$  ions, dissolved at acidic pH. Small beech plants have been grown in a medium at pH 4. 0.1 or 1 mM AlCl<sub>3</sub> was added to the medium at various times before the NMR experiment. The roots were rinsed and the thin roots were cut off and placed in an NMR tube, 0.5 - 1.0 g, with some D<sub>2</sub>O. The <sup>31</sup>P spectra were run on our Nicolet 360 WB spectrometer with good S/N ratio after 1000 transients.

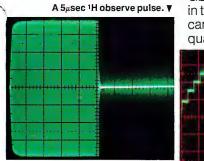
The shift of the obtained <sup>31</sup>P signal shows that the compartments of the roots we are observing are the vacuols, pH 5.5. For the roots grown with 1 mM AlCl<sub>3</sub> in the medium we observed significantly less intence <sup>31</sup>P signals than when no AlCl<sub>3</sub> or 0.1 mM AlCl<sub>3</sub> was present. For the plants that had been in the 1 mM AlCl<sub>3</sub> medium for 3 weeks the roots contained only 30 % of the NMR observable phosphate as compared to beech plants grown in AlCl<sub>3</sub> free medium. The presence of dissolved Al<sup>3+</sup> ions in the soil may therefore have a serious effect on the phosphate balance in beech. These simple experiments show that also NMR may be of some help in studies on our changing environment. Please credit this contribution to the account of Prof. Sture Forsén.

Best regards

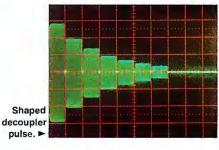
Torb jorn Drakenberg

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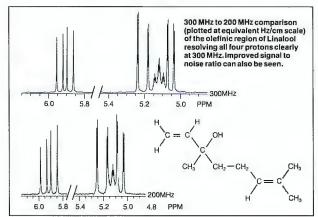
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DEPARTMENT OF CHEMISTRY SANTA BARBARA, CALIFORNIA 93106

26 May 1987 (Received 1 June 1987)

Professor B. L. Shapiro TAMU NMR Newsletter Department of Chemistry Texas A & M University College Station, TX 77843

"Two-dimensional H-F NOE Studies of a Carbonic Anhydrase-Inhibitor Complex"

#### Dear Barry,

Two-dimensional proton-fluorine nuclear Overhauser effect experiments can provide new information about chemically modified proteins and protein-small molecule complexes (1-3). We have recently become involved in studies of complexes formed between human carbonic anhydrase and a variety of fluorinated benzenesulfonamides (4) and describe here some initial results of application of the 2D H-F NOE experiment to these systems. Pentafluorobenzenesulfonamide forms a tight complex with the enzyme. Aromatic ring rotation is slow within this complex and the fluorine nmr spectrum consists of five multiplets of equal integrated intensity, spread over about 25 ppm. Steady state proton irradiation experiments show that each of these fluorine nuclei relax predominantly by proton-fluorine dipole-dipole interactions. The Figure shows the results of a 2D NOE experiment with this complex. Presuming that the binding site for the inhibitor is the active site of the enzyme, a contention we are presently seeking to support, these results indicate that the ortho and meta fluorines of the inhibitor interact strongly with aromatic protons in this site. X-ray studies of other inhibitor complexes of these enzyme suggest that the most likely candidate for these protons are those of phe-91. Interactions with other protons are seen and we are attempting to analyze these and related observations to come up with a detailed structure for the complex.

In the sample used to produce the data shown in the Figure the inhibitor concentration was approximately 4 mM and the human carbonic anhydrase B concentration approximately 1 mM. Small signals for the free inhibitor present in the 1D fluorine spectrum are not apparent because they have essentially no proton NOE. Sixty four t1 values were used; about 100 hrs. were required for the experiment.

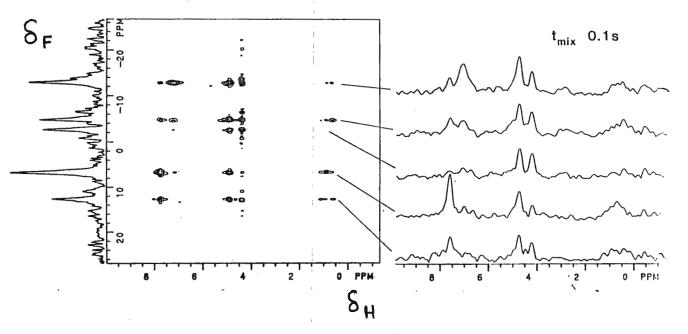


Figure 1. Proton-fluorine two-dimensional nuclear Overhauser effect obtained at a proton frequency of 300 MHz using a GN-300 spectrometer. From top to bottom, the slices shown correspond to the two fluorines <u>meta</u> to the sulfonamide group, followed by the <u>para</u> fluorine, and the <u>ortho</u> fluorines.

Sincerely,

L. B. Dugad Research Associate

J. T. Gerig Professor of Chemistry

J. T. Gerig and S. J. Hammond, J. Am. Chem. Soc. 106 8244 (1984).
 M. Cairi and J. T. Gerig, J. Magn. Reson. 62 131 (1985).
 Dr. A. R. Jacobson, work in progress.
 J. T. Gerig and J. M. Moses, J. Chem. Soc. Chem. Commun. (6) 482 (1987).

#### UNIVERSITY OF CALIFORNIA, SANTA CRUZ

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DEPARTMENT OF CHEMISTRY

SANTA CRUZ, CALIFORNIA 95064

Professor Barry Shapiro Department of Chemistry College Station, TX 77843-3255 May 29, 1987 (Received 2 June 1987)

SUBJECT: ZETA 8 Digital Plotter - It pays to read the User's Manual

Dear Barry:

At times one would like to slow the ZETA 8 Pen Plotter speed down to prevent "skipping" when recording narrow line multiplutes. Switch option (Side Access Door) SW1-1, according to the manual, allows you to select half speed for the pen. On both of our ZETA 8's, SW1-1 does absolutely nothing to the pen plotter speed, but there is a way.

Although I read the section on Parameter Mode Select (PMS) operation carefully, it took me a while to grasp the technique (SECTION V). For those who cannot follow instructions like myself, here is the "Trained Monkey" version of how to change Pen speed on the ZETA 8:

- 1. Hit the CLEAR bottom (took me awhile to figure this out)
- 2. Hit the DOT (Fast) control and PAUSE button simultaneously. If the PAUSE indicator light is "blinking" you are in the PMS mode.
- 3. Using the PEN SELECT button, select the pen # corresponding to the first digit of the Function # (i.e. Pen #3) and press RETURN. Notice that the Pen Select lights are now in "Reverse" video.
- 4. Move the PEN SELECT to the second digit of the Function # (i.e. Pen #4). Only Select Light #4 will be extinguished, all the rest will be illuminated. Press RETURN.
- 5. Hit the PAUSE and DOT (Fast) control simultaneously. The Pen Speed should now be at 50% of normal.
- 6. To return to the normal speed, hit CLEAR.

Below is a listing of Pen Speed function numbers:

<u></u>	<u></u>	
31	Set Speed 1/	<b>'</b> 8
32	2/	<b>'</b> 8
33	. 3/	<b>'</b> 8
34	4/	<b>'</b> 8
35	5/	<b>'</b> 8
36	6/	'8
37	7/	'8
38	(100%) 8/	8

FUNCTION

Sincerely,

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Professor B.L. SHAPIRO Department of Chemistry Texas A & M University College Station

SADIS BRUKER SPECTROSPIN, Bolte Postele N 67160 WISSEMBOURG

Texas 77843 U.S.A.

87 05 112 CB/AFWissembourg, le25 mai 1987(31p)-13C Correlated Experiments(Received 1 June 1987)

Dear Barry,

Organometallic chemists are gaining more and more from the experiments devised by their "organic" colleagues.

Spectra shown are examplifying the usefulness of  $\{P31\}$  - C13 correlated experiments.

Spectrum 1 was recorded with the standard 5.5 pulse sequence using P31 to C13 polarization transfer.

Spectrum 2 is a  $\{P31\}$  - C13 heteroCOSY with no "a priori" guess on  ${}^{n}J_{C13-P31}$  :more correlations show up, clearly telling that all the carbons of the organo-palladium compound are coupled to the phosphorus atom.

Experimental :

- AC 300
- triply tuned 10 mm probe : H1, P31, C13 and H2 lock
- heterodecoupler BSV 3/BX

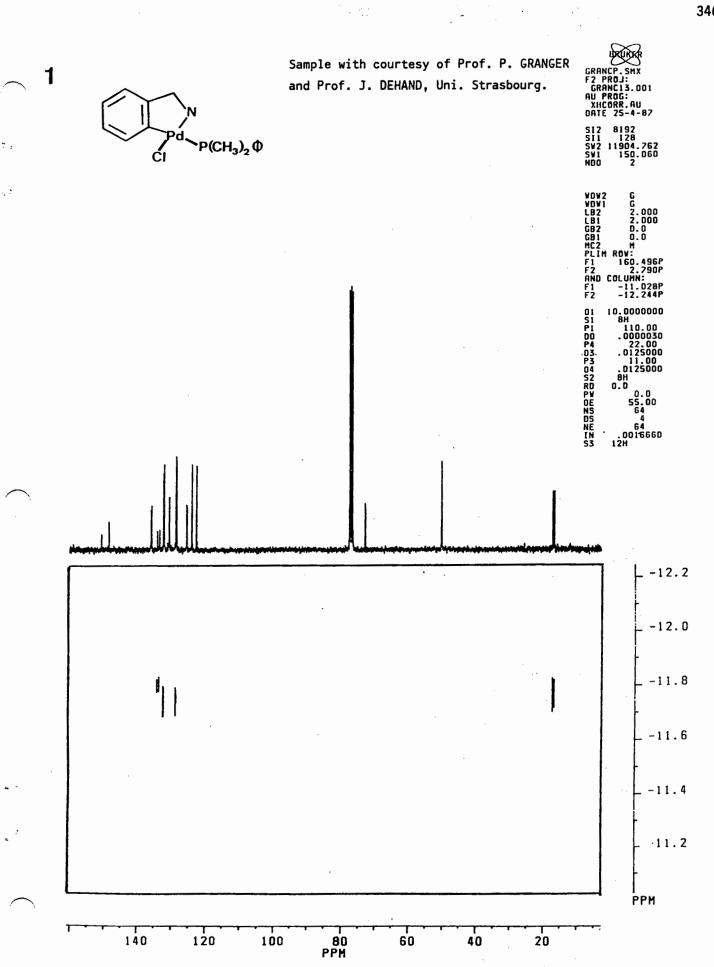
Sorry again for the delay.

Best regards, A. PAGELOT

BREVA

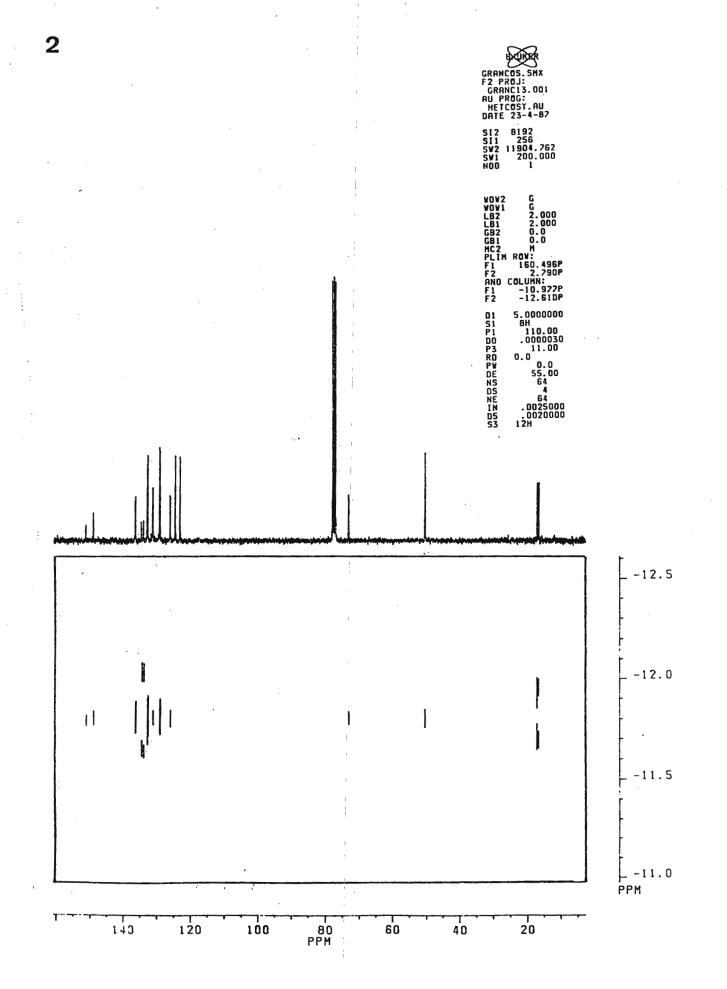


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#### MATERIALS RESEARCH SOCIETY SHORT COURSE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The Materials Research Society will present a program of 29 short courses in conjunction with the MRS 1987 Fall Meeting to be held November 29-December 5, 1987 at the Boston Marriott Hotel and Westin Hotel, Copley Place, Boston, Massachusetts. The one day course on 'Nuclear Magnetic Resonance Spectroscopy' will be presented on December 2 by Dr. James P. Yesinowski, Caltech.

#### WHO SHOULD ATTEND

This one day course is intended to acquaint the scientist, student, engineer, or manager with the basic ideas and range of applications of modern nuclear magnetic resonance (NMR) spectroscopy, with special emphasis on new solid state NMR techniques. The objectives of the course will be to develop an awareness of the types of problems to which NMR can provide answers, to provide an overview of recent developments in the field, and to explain the basis of the technique in order that the attendee can interact effectively with specialists in the field.

#### COURSE DESCRIPTION

The fundamental principles of pulsed Fourier transform nuclear magnetic resonance spectroscopy (NMR) will be presented. The reasons for the distinctions drawn between solid state NMR and solution state NMR will be explained. The information which can be obtained from various multinuclear NMR parameters will be discussed. Examples of the applications of NMR to problems of molecular structure, chemical purity, solid state dynamics, structure, solid solution behavior and the surface characterization of amorphous solids will be given.

#### TOPICAL OUTLINE

Origin of NMR phenomenon Vector magnetization picture in rotating frame Experimental set-up and conditions needed Quantitative aspects of the NMR experiment Origin and measurement of NMR parameters Solution state NMR vs solid state NMR Methods for improving the resolution of solid state NMR Applications of NMR

Tuition for preregistrants: \$320

For further details concerning the MRS Short Course Program and MRS Meeting, contact the Materials Research Society, 9800 McKnight Rd, Suite 327, Pittsburgh, PA 15237. Telephone (412) 367-3003

#### UNIVERSITE SCIENTIFIQUE, TECHNOLOGIQUE et MEDICALE de GRENOBLE LABORATOIRE D'ETUDES DYNAMIQUES ET STRUCTURALES DE LA SELECTIVITE (L.E.D.S.S.)

#### ASSOCIE AU CNRS Nº 332

(Received 12 June 1987)

Saint-Martin-d'Hères, le june 3, 1987

.

Professor Bernard Shapiro TAMU NMR NEWSLETTER Department of Chemistry Texas A&M University College Station, Texas 7.7843

#### DANTE sequence calibration : N\*Pw/N#Pw

Dear Professor Shapiro :

N/REF. CM/jc 87.40

V/REF.

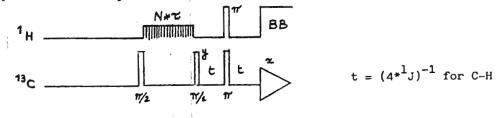
OBJET.

The DANTE sequence<sup>(1)</sup> consisting of N hard mini-pulses (Pw/N) spaced by  $\mathcal{C}$  ms is largely used where one needs to create a soft pulse of N\*t length.

Its use is widespread in Heteronuclear Spectroscopy for the selective excitation of a small part of the proton range while observing X nucleus. The main advantages over a soft pulse is that <u>i</u> it is always easier to calibrate a hard pulse (by a DEPT sequence for instance) on the decoupling coil than a soft one, <u>ii</u> one gets rid of the difficulties in switching between low and high power decoupling modes when acquiring the proton decoupled X nucleus.

We (D.A. and I) were interested in working on the selective 2D-J spin-flip Heteronuclear sequence<sup>(2)</sup> in order to measure long-range<sup>13</sup>C-H coupling constants. We found that, unlike some manufacturers' claims, the mini-pulse of  $P_{180}/N$  value does not correspond to the optimum S/N when we selectively invert a proton resonance in this sequence. In other words :  $N*P_{180}/N \neq P_{180}$ 

We readily found the optimum minipulse value ( $P_{opt}$ ) giving the corresponding soft  $\pi$  pulse by a Selective Population Inversion (SPI) sequence modified by HARRIS<sup>(3)</sup>:



Domaine universitaire de SAINT MARTIN D'HERES – Bâtiment 52 CHIMIE RECHERCHE Adresse postale : B.P. 68 F. 38402 SAINT MARTIN D'HERES CEDEX – Tél : 76.51.46.00 By selectively exciting  ${}^{1}J/2$  Hz away from a particular proton, we observe the corresponding decoupled  ${}^{13}C$  line, keeping the full magnetisation transfer expected ( $\cancel{F}$  H/ $\cancel{F}^{13}C \sim 4$ ) in the simple SPI sequence (the first  $\Pi$  /2 pulse almost completely suppresses the z magnetisation. The complete microprogram for Bruker's users will be send upon request).

Fig.1 and 2 show the powered spectra of the  ${}^{13}C$  line corresponding to the  ${}^{1}H$  excitation using this sequence with AM 300 and AM 400 Bruker spectrometers respectively as a function of .1  $\mu$ s increments in the mini-pulse value.

One can see that the  $P_{opt}$  is ~ 20-30 % higher (depending on spectrometer hardware) and that the progression of the mini-pulses is far from regular ! We found also that the  $P_{opt}$  depended on N and  $\sim$  values. So, the time spent in calibration (~1/2 hour) is worthwile for obtaining the best S/N !

Sincerely yours,

Claude MORAT

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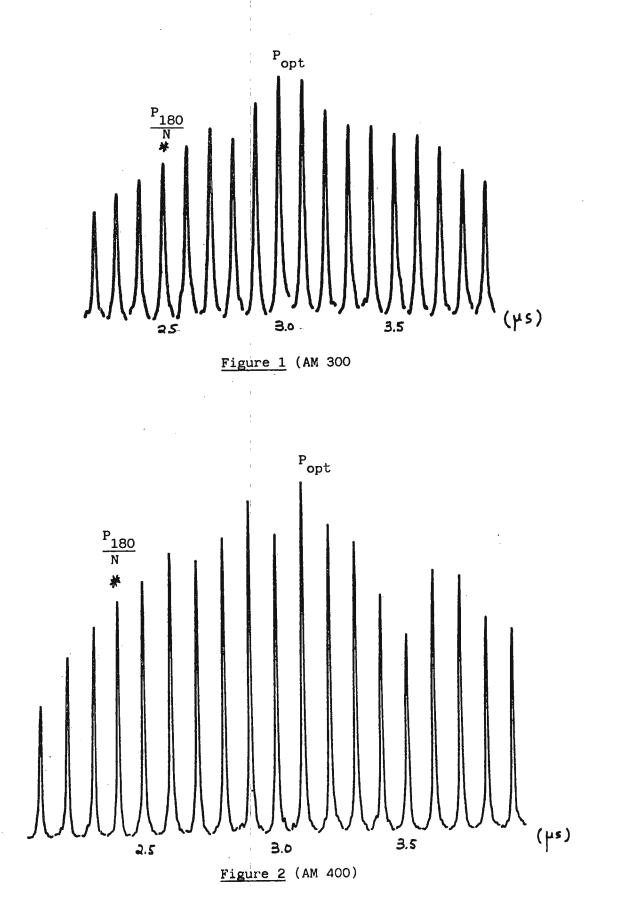
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(1) G. BODENHAUSEN, R. FREEMAN, G.A. MORRIS, J. Mag. Reson., 1976, <u>23</u>, 171.

(2) A. BAX, R. FREEMAN, J. Am. Chem. Soc., 1982, 104, 1099.

(3) R.K. HARRIS, NMR Spectroscopy, Pitman, London, 1983, p. 172.



DANTE sequence used : N = 60 ; Decoupling Power = 7H (AM 300) ; 6H (AM 400) ; t = 0.4 ms ; Acquisition : NS = 64 ; TD = 8K Processing : SI = 32K ; LB = 3

4



# Cornell University

Department of Chemistry Baker Laboratory Ithaca, New York 14853-1301 USA

June 2, 1987 (Received 5 June 1987)

Professor Bernard Shapiro Department of Chemistry Texas A&M University College Station, TX 77843

NMR SPECTROMETERS FOR SALE

Dear Professor Shapiro,

In order to make room for new equipment, the Cornell University Department of Chemistry is offering for sale a Varian EM-390 NMR Spectrometer and a Fourier transform JEOL FX900 NMR Spectrometer.

The EM-390 is a 90 MHz continuous wave <sup>L</sup>H NMR spectrometer with a permanent magnet, and it can provide convenient, low cost, routine proton NMR spectra.

The JEOL FX90Q is a 90 MHz proton and full multinuclear Fourier transform spectrometer. This instrument is equipped with Foreground/ Background capability, variable temperature, and inserts for 1.7mm, 5mm, and 10mm tubes. The purchaser might equip this instrument for CPMAS solids with equipment from JEOL Inc.

Both spectrometers are offered in full working condition by the Cornell Chemistry Department. Service for both instruments is available from the respective manufacturers. For details and information about price, please contact David Rice 607-255-7593.

ncere

David M. Rice, Ph.D. Director, NMR Facility

Notice Concerning Invoices for the 1987-88 TAMU NMR Newsletter Subscription Year.

Invoices for the 1987-88 TAMU NMR Newsletter year will be mailed out on 3 August 1987. Please notify us if you do not receive an invoice by 1 September 1987. Be sure to use the address given below:

Dr. Bernard L. Shapiro Editor/Publisher TAMU NMR Newsletter 966 Elsinore Court Palo Alto, CA 94303 U.S.A.

#### MCMASTER UNIVERSITY DEPARTMENT OF GEOLOGY



1280 Main Street West, Hamilton, Ontario, L8S 4M1 Telephone: (416) 525-9140 Telex: 061-8347 June 4, 1987 (Received 22 June 1987)

Prof. B.L.Shapiro Department of Chemistry, Texas A & M University, College Station, Texas 77843-3255, U.S.A

#### Sodium-23 nmr of fluid inclusions in beryl and guartz

Dear Barry:

We have been investigating the potential of nmr in the analysis of fluid inclusions in minerals. These are usually microscopic and contain trapped fluids either from the original crystallization of the mineral or from a later metamorphic episode and therefore contain information about the history of the mineral. Chemical analysis is extremely difficult due to their small size, and also the difficulty of breaking them open without losing, contaminating or changing the state of their contents. Nmr may allow analysis of fluid inclusions in situ.

In the course of MAS nmr studies of a series of alkali beryls from the Tanco pegmatite deposit in Manitoba (1), we observed a narrow  $^{23}$ Na peak at 0 ppm (the aqueous NaCl peak position) as well as a broad doublet (Fig.1a). In the static spectrum of the same samples this peak is broadened only slightly (from **90** Hz in fig 1a to 540 Hz in fig 1b), compared to the major resonances which arise from the immobilized sodium of the beryl channel site. The narrow peak at 0 ppm is also present in the  $^{23}$ Na MAS nmr of a sample of quartz which was intergrown with one of the beryl samples. Microscopic examination of both the beryl and quartz samples show a large number of fluid inclusions.

We were unable to obtain a signal from the anion; qualitative chemical ana lyses show that this is probably carbonate or bicarbonate.

Recently Yesinowski has reported seeing very small <sup>1</sup>H MAS nmr signals from fluid inclusions in feldspar samples (2). Anyone carrying out MAS nmr studies of minerals should be aware of the possibility that unexpected relatively sharp signals might arise from fluid inclusions.

Difficulties arise from the low concentration of fluid inclusions, which usually make up much less than 1% of the mineral. The best results we obtained were from samples containing about 15% fluid inclusions and using a highly sensitive and 100% abundant nucleus. As instrument sensitivity improves, nmr could become a valuable technique for the study of chemical composition of fluid inclusions These spectra were obtained on the Bruker WH400 instrument of the South Western Ontario High Field Nmr Centre with the assistance of Dr R.E. Lenkinski and colleagues. Mineral specimens were provided by Prof F.C.Hawthorne of the Dept. of Geology, University of Manitoba.

Yours sincerely

Borbore L. SI

Barbara L. Sherriff,

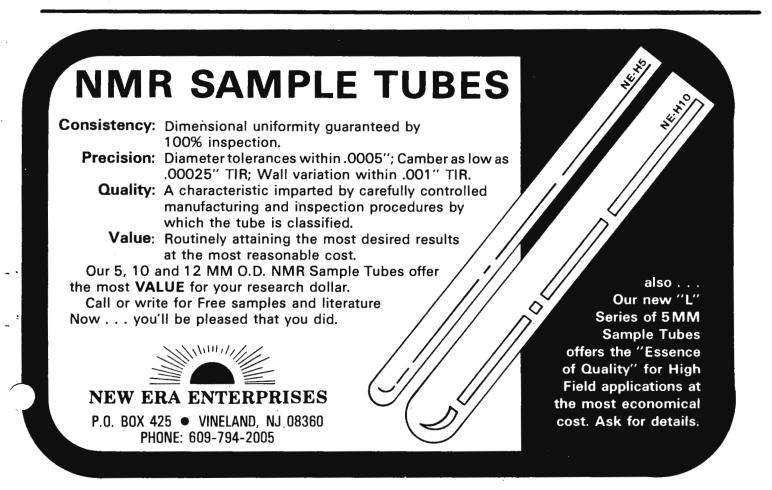
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J.Stephen Hartman (Dept. of Chemistry, Brock University)

1 B.L.Sherriff, H.D.Grundy & J.S.Hartman (1986): High-resolution MAS nmr of alkali beryls <u>Geol. Assoc. of Can. Mineral. Assoc.</u> <u>Can. Program Abstr.</u> 8, 74.

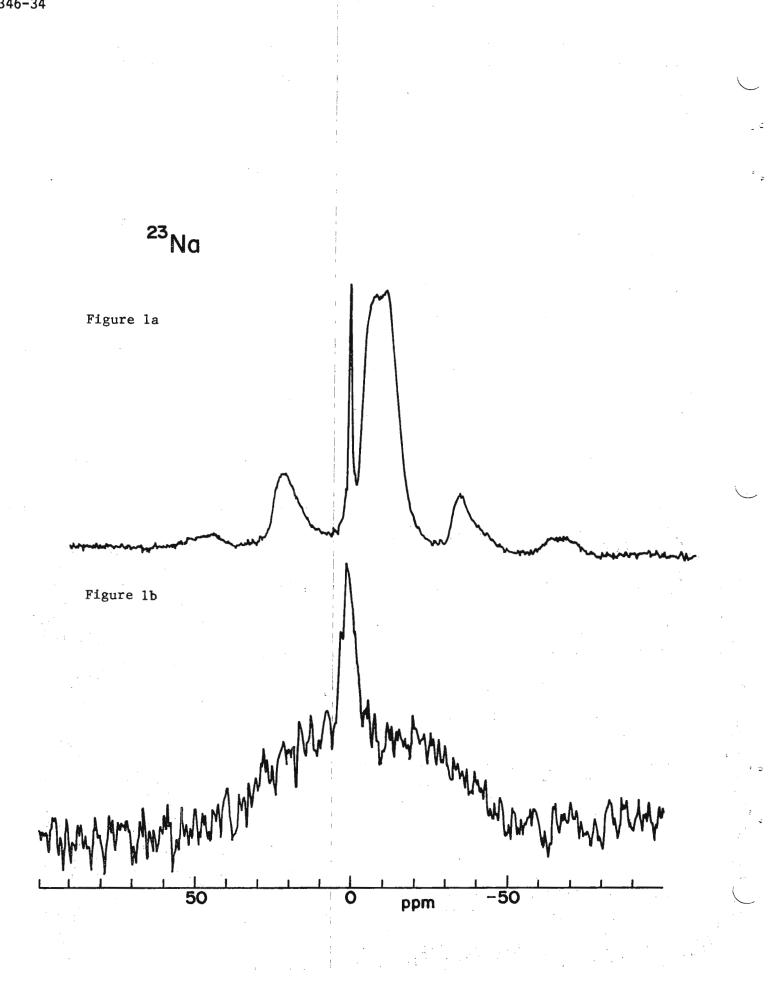
2 J.P.Yesimowski, H.Eckert & A.Nayeem (1987): High-speed <sup>1</sup>H MAS nmr of inorganic solids and paramagnetic compounds, <u>28th</u> <u>Experimental nmr conference abstr.</u>

Figure 1 105.8 MHz  $^{23}$ Na MAS nmr spectrum of beryl sample T-24 (a)spinning (b) nonspinning.



H. Dur, In Gony

H. Douglas Grundy,



#### CALIFORNIA INSTITUTE OF TECHNOLOGY

#### Mail Code 164-30, Pasadena, CA 91125

Professor Bernard L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843 June 16, 1987 (Received 22 June 1987)

#### NMR SPECTROSCOPIST POSITION AVAILABLE

Dear Barry:

The Southern California Regional NMR Facility at Caltech will have an opening for an NMR Spectroscopist beginning in September to replace Dr. Hellmut Eckert, who will be taking up a position as Assistant Professor in the Chemistry Department at UC Santa Barbara.

The NSF-funded Facility has a recently-upgraded Bruker AM-500 spectrometer completely equipped for multinuclear solution NMR studies as well as solid-state capabilities, including a high-power <sup>2</sup>H probe, a <sup>1</sup>H MAS probe, and a multinuclear CP-MAS probe. In addition, a home-built spectrometer for solids based on an Oxford 200 MHz wide-bore magnet and Nicolet 1280 computer with a Nicolet 293B pulse programmer is also available for multiple-pulse <sup>1</sup>H MAS and CP-MAS experiments.

Research carried out at the Facility includes a large number of high-resolution studies on the AM-500 by users in the Southern California region; five student operators assist users in obtaining data. An important part of both the Manager's and Spectroscopist's efforts involves collaborative projects in both the solutions and solids areas, in addition to core research (development and application of new NMR methods and instrumental capabilities).

We are looking for an outstanding NMR spectroscopist interested in developing and applying new NMR methods in a stimulating environment. The salary will depend upon the experience and level of the applicant, but will be competitive. Persons interested in further details should contact me at (818) 356-6241 or the above address. Applications consisting of a c.v., publications list, and the names of three references, should be sent as soon as possible to me at the above address. Please bring this notice to the attention of anyone who may be interested.

Sincerely yours,

James Nesmonski

James P. Yesinowski Manager, SCRNMRF

## Columbia University in the City of New York | New York, N.Y. 10027

DEPARTMENT OF CHEMISTRY

Havemeyer Hail

June 10 1987 (Received 12 June 1987)

Professor B. L. Shapiro Department of Chemistry Texas A&M University College Station Texas 77843-3255

#### Assymetric Spinning Sidebands

Dear Barry:

I was intrigued by a recent letter (TAMU 340-44) on the problems of assymetric spinning sidebands. We have also suffered from this problem and found the experience very frustrating. The spinning sidebands that normally concern us obviously arise from the inhomogeneity of the <u>magnetic</u> field, however the <u>RF</u> field will not be completely homogeneous, and thus can cause spinning sidebands which are not affected by shimming.

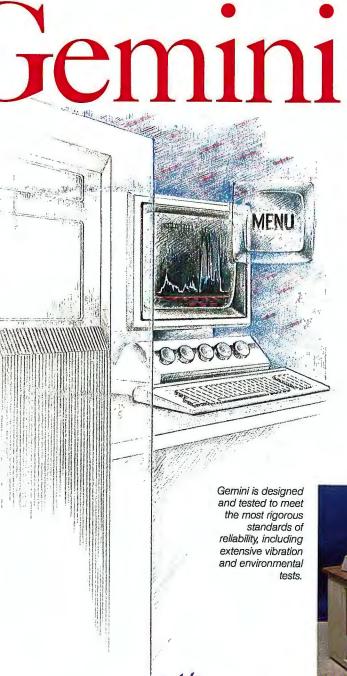
An interesting question is how to reliably distinguish between these two different effects. I am afraid I cannot give you chapter and verse on this issue. However, in my experience, the most common position for RF spinning sidebands is at twice the spinning speed on the RHS of the peak. RF spinning sidebands are often affected by probe tuning, since this changes the homogeneity of the RF field, however retuning the probe will also change the magnetic field slightly, thus the magnetic field must be optimized before one jumps to any conclusions.

The most intriguing issue here is whether one could, in some way, use the magnitude of these artifacts to quantify the RF inhomogeneity. I don't believe this to be possible at present, but would welcome further correspondance on this issue.

Best Wishes

C. J. Turner

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MAG-4615/338



DEPARTMENT OF CHEMISTRY

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Joy Through Pinkies, or Down With Phase Distortions

Professor B L Shapiro Texas A & M University College Station TEXAS 77843-3255 U.S.A.

UNIVERSITY OF QUEENSLAND

2 9 MAY 1987

(Received 4 June 1987)

Dear Barry,

Thank you for the pinkies, they have helped to brighten up my day(s).

You and your readers may be interested in the following rather simple procedure to eliminate phase distortions and thus baseline roll from "binomial" solvent suppression pulse sequences.

Except for the carrier frequency position where there is a phase "jump", the phase shift across the spectral response of all "binomial" excitation sequences is linear. Thus, this phase shift can be eliminated using a  $\pi$  refocussing pulse, an echo being formed following a time  $\tau_{\rm R}$  where  $\tau_{\rm R} = d\beta/d\Delta\omega$ . Here  $\beta$  is the phase shift and  $\Delta\omega$  the frequency offset. A typical "binomial" sequence is thus:

 $\bar{\pi} - (\bar{1}3\bar{3}1) - \pi - \tau_{R} - Acq.$  [A]

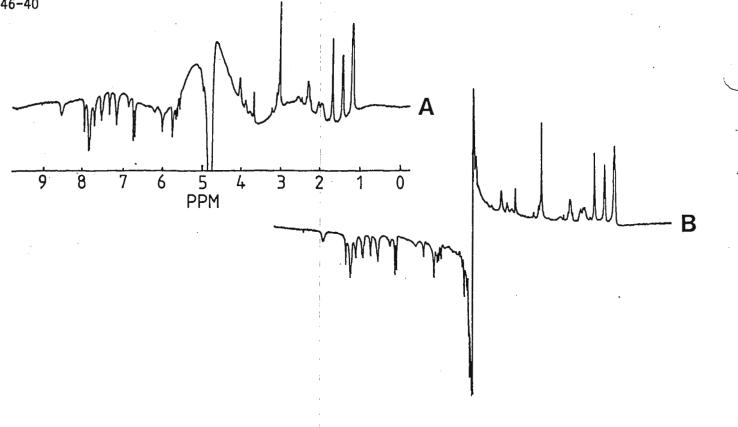
The first  $\pi$  pulse is used to eliminate radiation damping effects from the second  $\pi$  pulse which forms the echo. The figure shows 400 MHz <sup>1</sup>H spectra of 10mM Vancomycin in neat H<sub>2</sub>O using the pulse sequence :

$$\bar{\pi}$$
-(1-2 $\tau$ -5 $\bar{\cdot}$ 4- $\tau$ -5.4-2 $\tau$ -1)- $\pi$ - $\tau_{p}$ Acq. [B]

 $\tau_{\rm p}$  is approximately half the length of the "binomial" sequences.

Yours sincerely,

DAVID M DODDRELL



#### ESONANCE INST AGNET

410 W. Dickinson St. San Diego. CA 92103 Local: (619) 294-6148 In CA: (800) 325-6614



May 26, 1987 (Received 1 June 1987)



Dr. Bernard L. Shapiro Texas A&M University Dept. of Chemistry College Station, Texas 77843

Barry Dear Bernie:

Eddy Current Effects of 1 G/cm Gradient Pulses

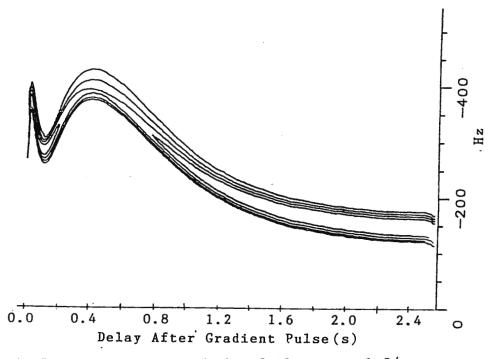
We have been using a number of different schemes to perform localized spectroscopy on our 2.0T G.E. imager/spectrometer. All of these techniques require frequency selective rf pulses and pulsed magnetic field gradients. As one might expect, we have observed distortion of spectra due to eddy currents induced by gradient pulses. These distortions include resonance offsets and phase artifacts (which appear as "birdies" on the sides of peaks). We have been able to obtain reasonable spectra from phantoms, but only after a large amount of tweaking. The difficulties which we have encountered have motivated us to start making measurements of eddy current effects; with the hope of curing or reducing distortion.

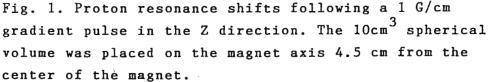
A simple and widely used technique for observing eddy current distortion is to apply a rectangular gradient pulse followed by a delay followed by a 90° pulse. The eddy currents are then characterized by varying the delay time. The result of one such experiment is shown in Fig. 1. The 1 G/cm gradient pulse was left on for 1s to ensure that transients induced by the leading and trailing edges did not cancel. The results show that large resonance( $B_0$ ) shifts occur well beyond 1s. Fortunately, the shorter gradient pulses used in most localized sequences produce some cancellation of these effects. Even so, it is necessary to use caution when acquiring and interpreting these spectra.

In order to obtain reasonable spectra, gradient pulses should be made as short as possible and, unfortunately, the selected volume should be very close to the center of the magnet. In addition, signal acquisition should occur as long as possible after the last gradient pulse. In lieu of actively shielded gradient coils, we hope that these considerations, in combination with careful measurements of the eddy currents, will allow us to obtain reproducible localized spectra.

Sincerely,

Joel F. Martin





#### FIRST SYMPOSIUM ANNOUNCEMENT

## RECENT ADVANCES IN MAGNETIC RESONANCE TECHNIQUES AND APPLICATIONS

#### September 10, 1987

### Washington University

St. Louis, Missouri

A symposium on applications and new methods in NMR spectroscopy will be held September 10, 1987 at the Department of Chemistry, Washington University, St. Louis, Missouri. This symposium marks the official dedication of the Washington University High Resolution NMR Facility.

#### INVITED SPEAKERS INCLUDE:

A. Bax, National Institutes of Health, Bethesda, MD.
W. C. Hutton, Monsanto Co., St. Louis, MO.
G. N. LaMar, University of California, Davis, CA.
A. G. Redfield, Brandeis University, Waltham, MA.
I. C. P. Smith, National Research Council, Ottawa, Canada.
J. S. Taylor, Washington University, St. Louis, MO.

For additional information, contact the departmental secretary, Carol Brown, at (314) 889-6530.

# NON UNVERSITY IN STILLUS

#### FIRST ANNOUNCEMENT

# SYMPOSIUM ON THE HIGH-RESOLUTION NMR OF SOLIDS

October 15, 1987

Washington University St. Louis, Missouri

A symposium on the high-resolution NMR of solids will be held October 15, 1987 at the Department of Chemistry, Washington University, St. Louis, Missouri. Participants in this symposium will discuss the development of new experimental NMR approaches to the study of the solid state, as well as how the results of recent experiments are affecting our understanding of the structure and dynamics of many solids, particularly complex biological materials. The symposium will also mark the formal opening of Professor Jacob Schaefer's solids NMR laboratory in the Chemistry Department of Washington University.

### The symposium will feature invited papers by:

R. G. Griffin, Massachusetts Institute of Technology
G. E. Maciel, Colorado State University
J. A. McCammon, University of Houston
A. Pines, University of California at Berkeley
C. S. Yannoni, IBM

For additional information, contact the departmental secretary, Carol Brown, at (314) 889-6530.



#### FIRST ANNOUNCEMENT

# SYMPOSIUM ON RESONANCE IN PERSPECTIVE - A TRIBUTE TO PROFESSOR RICHARD E. NORBERG -

#### October 16-17, 1987

#### St. Louis, Missouri

The Symposium on Resonance in Perspective will be held October 16-17, 1987 at Department of Physics, Washington University, St. Louis, Missouri. This symposium is being organized to review the impact magnetic resonance techniques have had on Condensed Matter Physics and other fields. In addition, the meeting is being convened to honor the contributions of Professor Richard E. Norberg on the occasion of his 65th birthday.

The symposium will consist of a number of invited and contributed presentations; the following have agreed to give invited talks:

Dr. M. Bloom, University of British Columbia

Dr. E. L. Hahn, University of California-Berkeley

Dr. D. F. Holcomb, Cornell University

Dr. G. E. Pake, Xerox PARC

Dr. C. P. Slichter, University of Illinois-Urbana

The conference enjoys the sponsorship of the Washington University Graduate School of Arts and Sciences and the Technilab Corporation.

For further information please contact:

Professor Mark Conradi Department of Physics, Box 1105 Washington University One Brookings Drive St. Louis, Missouri 63130

The General Chairman of the symposium is Dr. William M. Yen, University of Georgia-Athens. The Program Chairman is Dr. W. W. Warren, AT&T Bell Laboratories. The Chairman in charge of social events is Dr. J. R. Gaines, Ohio State University.



8th June 1987 (Received 16 June 1987)

Professor B L Shapiro Department of Chemistry Texas A & M University College Station Texas 77843 U S A

#### A Fallacy Explored

Roche Products Limited · PO Box 8 · Welwyn Garden City · Hertfordshire AL7 3AY Telephone Welwyn Garden 328128 Telex 262098 ROCHEW

#### Dear Barry

The purpose of this letter is to point out a fairly common fallacy in the setting up of 1D steady-state NOE difference experiments. In such experiments, the NOE is built up during a period of pre-irradiation (t), which is followed by a pulse and acquisition of the FID. Because the NOE takes quite a long time to build up and decay, often much longer than the acquisition time AQ, it is sometimes argued that for subsequent pulses, shorter periods of pre-irradiation would suffice, because the NOE would only require 'topping up' by the small amount that it had lost during AQ. This argument leads to a scheme in which, of the 8 or 16 scans acquired at each frequency, only the first need employ the full period t, with subsequent pre-irradiations being reduced in length. This is quite wrong. The fallacy in this argument is that it neglects the effect of the observe pulse on the populations. A 90° pulse completely equalizes the populations. In creating the transverse signals actually detected, it thus eliminates completely the NOE (i.e, the non-equilibrium population distribution) present at the end of t. and the next preirradiation faces the full task of creating the NOE from scratch, just as did the first pre-irradiation.

If the pulse length is reduced, then a proportion of the NOE survives, in proportion to the z component remaining after the pulse. To this extent it might be thought that a time-saving scheme such as that above might be possible if a reduced pulse angle were used. There is some truth in this, but the gain in signal made by acquiring more transients in a given time is in practice more than offset by the signal loss resulting from the smaller pulse angle.

This is illustrated by the simulations in the figure, which are for a linear system  $\{A\}$  -B-C, with B midway between A and C; the T<sub>1</sub> values of A,B and C are approximately 1, 0.5, and 1s respectively. The curves in graph (a) show the enhancements observed after four dummy scans (a pseudo-steady state), using 90° pulses (dashed lines) or 30° pulses (solid lines), as a function of the pre-irradiation time t. These curves are redrawn in graph (b) to give an idea of the enhancement

obtained per unit time, by dividing the enhancement by (AQ + t)(assuming AQ = 2s, and no relaxation delay). Although larger percentage enhancements are indeed seen with a 30° pulse, the reduced pulse angle of course only gives half the signal intensity (sin 30°), and therefore the intensity of the difference NOE signal is considerably worse than with the 90° pulse.

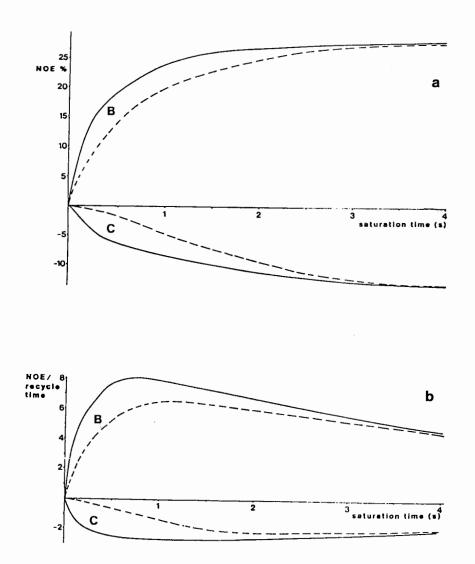
From this simulation, the optimum value of t would appear to be about twice  $T_1$ . Further details are given in a forthcoming book (D Neuhaus & M P Williamson, 'The NOE in Structural and Conformational Analysis' VCH Publishers Inc, New York, 1988).

Please credit this contribution to Tony Thomas' account.

Yours sincerely

Mile





### BIRKBECK COLLEGE University of London

### Department of Chemistry

011-44-1631-6253

### Malet Street London, WC1E 7HX

9th June 1987. (Received 16 June 1987)

Prof. B. L. Shapiro, Dept. of Chemistry, Texas A&M University, College Station, Texas, USA.

Dear Prof. Shapiro,

#### 3D-NMR SPECTROSCOPY

2D-NMR spectroscopy openned up a new dimension in NMR when it was proposed<sup>1</sup> in 1970. The logical extension was 3D-FT NMR spectroscopy, the theory of which was published<sup>2,3</sup> in 1980. However, practical application of 3D-NMR was precluded until recently<sup>4</sup> by the requirement for a large dataset.

The 3D experiment in this work is three dimensional correlated spectroscopy (T-COSY). Using the following pulse sequence

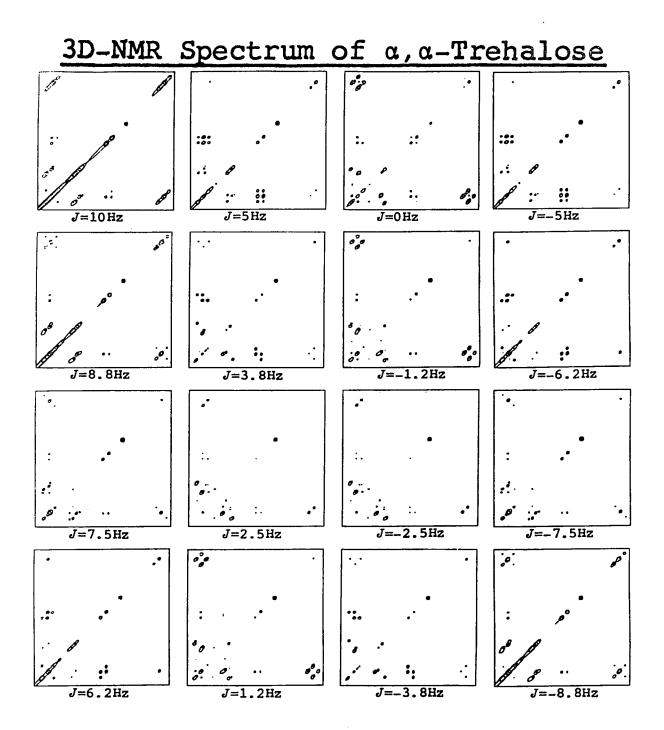
90° +1 +3/2 90° +3/2 180° +3/2 90° +3/2 +2

leads to a spectrum, upon 3D Fourier transformation, with a shift-correlated spectrum in the  $f_1$  and  $f_2$  directions and coupling in the  $f_3$  direction. A sinebell window was applied in all three dimensions prior to 3D Fourier transformation. The resulting matrix after magnitude Fourier transformation was 64 x 64 x 16 real points.

The spectrum shows the H2 to H5 region of alpha, alpha-trehalose in  $D_20$  solution as a series of slices. Presentation of 3D spectra in 2 dimensions poses a problem so alternatives need to be developed eg. optical synthesis (gray scale presentation of the intensity of the spectrum when viewed at an angle). Processing techniques, such as window functions, symmetrisation<sup>5</sup>, and tilting used for 2D spectra should also be applicable to 3D spectra.

A promising use of 3D-NMR would be in determining conformation from long-range heteronuclear couplings. A heteronuclear T-COSY could determine the coupling constant of each correlation in one experiment whereas several experiments would be required to obtain similar data using 2D techniques. The experiment could be modified to select only long range couplings with considerable savings in data size and aquisition time. Several experiments would be required to obtain similar data using 2D techniques.

Please credit this to Dr. D. B. Davies's account.



#### REFERENCES

- 1) J. Jeener, Ampere Int. Summer School, Basko Polje, Yugoslavia, 1971.
- 2) B. Blumich and D. Ziessow, Ber. Bunsenges, Phys. Chem., 1980, 84, 1090.
- 3) B. Blumich and D. Ziessow, J. Chem. Phys., 1983, 78, 1059.
- 4) R. R. Ernst, London University 150th Anniversary Lecture, 1987.
- 5) R. Baumann, G. Wider, R. R. Ernst, and K. Wuthrich, J. Magn. Res., 1981, 44, 402.

Yours sincerely, R.E.HOJSMON, R.E.HOFFMAN.



Ottawa, Canada K1S 5B6

June 15, 1987. (Received 23 June 1987)

Professor B.L. Shapiro Editor TAMU NMR Newsletter Dept. of Chemistry Texas A & M University College Station, Texas, U.S.A. 77843-3255

<u>Title:</u> "Solid Phase Stereochemical Dynamics of 18-Crown-6 Ether and its KNCS Complex "

In solution, 18-crown-6 shows a single  ${}^{1}$ H and  ${}^{13}$ C resonance at all normally accessible low temperatures (<u>i.e.</u> to 143K in our hands). However, x-ray data (1) reveal that the molecule possesses only a centre of symmetry, with six unique carbon environments present. The torsional angles experienced by these carbons differ substantially.

The 45.3 MHz  $^{13}$ C CPMAS spectra of solid 18-C-6 as a function of temperature are shown below.

Department of Chemistry D Steacie Building D (613) 564-2760

346-49

At 295K a broad singlet with linewidth of <u>ca</u>. 150 Hz is observed. No higher temperature was possible due to sample melting. At 210K a "slow exchange" spectrum is obtained with four resonances  $\mathbf{m}$  a ratio of 1:1:2:2 and an overall chemical shift range of 5.6 ppm. We attribute this behaviour to slow torsional angle averaging in the solid on the NMR timescale at 210K.

For the KNCS complex, the x-ray data (2) reveal <u>pseudo</u>  $D_{3d}$  symmetry, with only minor (<10<sup>0</sup>) differences in torsional angles present at individual carbon sites. In this case we see at 295K, and in the low temperature limit, two lines in a 2:1 ratio, whose chemical shift separation is just 1.5 ppm. The geometry of this complex is much more "rigid" than for the free crown ether. This seems to be intuitively reasonable, since K <sup>+</sup> complexation is deemed to anchor the 18-C-6 into the "ideal" complexation geometry.

Sincerely, Ju Ben

G.W. Buchanan, Professor of Chemistry.

References

1. J.D. Dunitz and P. Seiler. Acta Cryst. B30 2739 (1974).

2. P. Seiler, M. Dobler and J.D. Dunitz. Acta Cryst. <u>B30</u> 2744 (1974).

1 July 1987

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Dr. Bernard L. Shapiro Editor/Publisher TAMU NMR Newsletter 966 Elsinore Court Palo Alto, CA 94303 U.S.A.

#### Notice Concerning Deadline Dates for the TAMU NMR Newsletter.

Please notice on page 3 the advanced schedule of deadline dates for receipt of material for inclusion in forthcoming Newsletters. Basically, we are moving the deadline schedule ahead to the next-to-the-last Friday of each month, so as to optimize the phase relationships of these dates with holidays, printing schedules, etc.

B.L. Shapiro



CP-MAS of Biopolyesters in the

Skin of Limes

Professor Bernard L. Shapiro Texas A&M University Department of Chemistry College Station, Texas 77843-3255

Dear Barry:

Our latest foray into the realm of biopolymers has involved cutin, the polyester structural component of the protective cuticle in terrestrial plants. Although the insolubility of this material has hampered investigations of how its monomeric units are linked together, we found it to be an excellent candidate for investigation by  $^{13}$ C CP-MAS methods (Figure 1). So far, we've been able to verify that lime cutin is derived from hydroxylated and oxo-fatty acids; spectral editing experiments have also allowed us to identify aromatic moieties related to the lignin polymer in woody plants. Cutin rigidity (or lack thereof) probably plays an important role in the structural integrity of the plant's protective casing; a series of DP-MAS and  $^{13}$ C T<sub>1</sub> experiments suggests that the structure contains everything from immobilized methine crosslinks to very floppy methylene chains.

Current efforts in this area include: (a) determining the polymer structure via partial depolymerization strategies; (b) locating a suitable solvent for intact cutin; and (c) finding good recipes for all the limes, once we've stripped off the skin.

Please credit this contribution to the C.U.N.Y. NMR Facility account, and take us off your tardy list.

Best wishes for your upcoming move,

THE CITY UNIVERSITY OF NEW YORK

ST. GEORGE CAMPUS 130 STUYVESANT PLACE

June 16, 1987

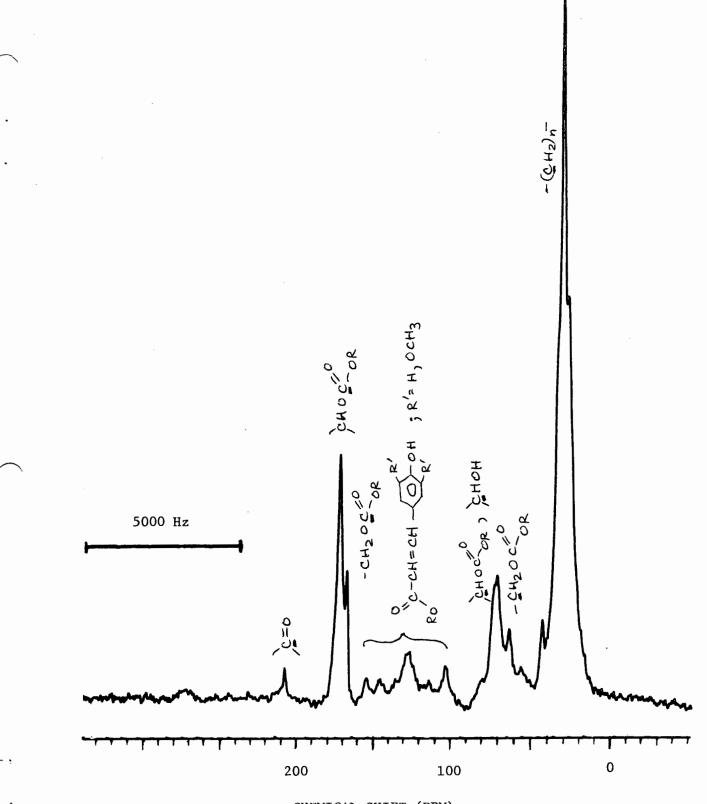
STATEN ISLAND, NEW YORK 10301

(Received 24 June 1987)

Ruth E. Stark Associate Professor of Chemistry

RES:hm

Enclosures



CHEMICAL SHIFT (PPM)

Figure 1. 50.33 MHz <sup>13</sup>C CP-MAS spectrum of the cutin polyester. Tentative peak assignments are as noted; the broad feature at 273 ppm is a spinning sideband of the carboxyl resonances.

346-51

HMRI HUNTINGTON MEDICAL RESEARCH INSTITUTES

> June 17th 1987 (Received 23 June 1987)

Professor Bernard L. Shapiro, Department of Chemistry, Texas A and M University, College Station, Texas 77843-3255

#### "Line shapes in Localised Spectroscopy Experiments"

Dear Professor Shapiro,

This letter is intended to initiate our subscription to the Texas A&M University NMR newsletter. The Huntington Medical Research Institutes (HMRI) operates a Diasonics MT/S 0.15T whole-body imager, a General Electric 4.7T CSI spectrometer/imager, and two high resolution NMR spectrometers (180 and 360 MHz). HMRI was one of the first units in Southern California to perform clinical NMR imaging, and the thrust of the research has been towards clinical and biochemical applications of NMR imaging and spectroscopy.

We are interested in optimising the technology for recording spatially localised <sup>31</sup>P NMR spectra; one of the most promising methods (brought to our attention by the NMR Unit of the Hammersmith Hospital, London, U.K.) appears to be the use of "phase-encoding" pulsed field gradients, first proposed by Brown et. al. (1), and used by several other groups. Our initial implementation of this method revealed problems in recording spectra with pure absorption line shapes - the phase-encoding field gradients resulted, after two-dimensional Fourier transformaton, in a "phase-twist" line shape. This problem may be easily overcome by using both positive and negative polarity gradients - the signal is symmetric with respect to a gradient amplitude of zero, so that on Fourier Transformation, the dispersion component of the line shape is eliminated. The Fourier transform routines on most NMR computers assume that the first data point corresponds to zero time (or gradient amplitude), so this procedure produces a large first order phase error which in fact results in every second point being negated. Hence inverting every second point in this dimension restores the desired line shape. As an example of the improvements that can be gained, the figure compares an absolute value and phase-sensitive display of a data set recorded using a surface coil placed over the scalp of a rabbit; the spectra were recorded at 82 MHz (31P) on a G.E. CSI (4.7T) spectrometer,

yours sincerely,

PB. Barker

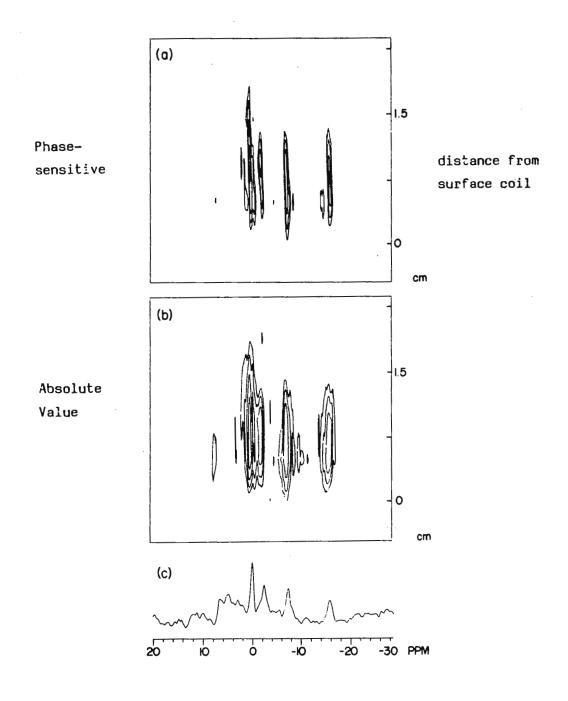
Peter B. Banken

Advanced Neurosurgury Laboratory Research CT, MR Imaging and MR Spectroscopy Center 10 Pico St, Pasadena, CA 91105-3201 Neurosurgery, CT, Imaging (818) 578-8560 Spectroscopy (818) 578-8532

# HMRI

# HUNTINGTON MEDICAL RESEARCH INSTITUTES

(1) T.R. Brown, B.M. Kincaid and K. Ugurbil, Proc Natl. Acad. Sci. USA 79, 3523 (1982)



Advanced Neurosurgury Laboratory Research CT, MR Imaging and MR Spectroscopy Center 10 Pico St, Pasadena, CA 91105-3201 Neurosurgery, CT, Imaging (818) 578-8560 Spectroscopy (818) 578-8532

### XEROX RESEARCH CENTRE OF CANADA

2660 Speakman Drive Mississauga, Ontario Canada L5K 2L1 (416) 823-7091

June 22, 1987 (Received 25 June 1987)

Professor Bernard L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843

#### SOLID STATE <sup>13</sup>C T<sub>1</sub>'s OF POLYCARBONATE

Dear Professor Shapiro:

As our first contribution to the TAMU NMR Newsletter from XRCC, we would like to describe some recent solid state <sup>13</sup>C NMR studies on polycarbonates.

Molecular motion in solid polycarbonates has been studied by a number of NMR techniques<sup>1</sup>. Many of these studies have lead to a heterogeneous model for the motion of the phenyl rings, where a mobile fraction of the phenyl groups undergoes rapid  $\pi$  flips about the phenyl C<sub>1</sub>-C<sub>4</sub> axis. We would like to have an estimate of the size of the mobile fraction in polycarbonates of different chemical structures or molecular weights. Heterogeneous behavior has been noted in the <sup>13</sup>C T<sub>1</sub>'s of the protonated aromatic carbons of polycarbonate<sup>2</sup>, where two components can be used to fit the T<sub>1</sub> relaxation decays. If the shorter T<sub>1</sub> represents the mobile fraction of the phenyl groups, the <sup>13</sup>C T<sub>1</sub> measurements could provide a rapid means of assessing dynamic heterogeneity in various polycarbonates.

The response of the <sup>13</sup>C T<sub>1</sub>'s to variations in the relative fraction of  $\pi$ -flipping phenyl groups was examined by varying the temperature and by the addition of p-dichlorobenzene to the polycarbonate matrix. Increasing the temperature should increase the fraction of  $\pi$ -flippers, while the addition of pdichlorobenzene is known from <sup>2</sup>H NMR studies to decrease this fraction<sup>1a</sup>. Variable temperature <sup>13</sup>C T<sub>1</sub> measurements were carried out on bisphenol-A polycarbonate (BPA) and at 25°C for mixed samples containing p-dichlorobenzene in BPA. The T<sub>1</sub> decays for the protonated aromatic carbons were fit using a two component model via non-linear regression.

The regression analysis yields the two  $T_1$  values and their relative contributions to the total  $T_1$  decay. Little variation was noted in the 'fast'  $T_1$  value (0.4 ± 0.05 sec.) for all the conditions used. The 'slow'  $T_1$  value varied considerably, increasing from 7.1 to 12.3 sec. in BPA as the temperature was decreased from 25°C to -27°C and increasing from 7.1 to 10.6 sec. as the p-dichlorobenzene content was added up to a concentration of 30 mole% relative to the BPA repeat unit. The relative contribution of each component was also determined.

Assigning the 'fast' component to the mobile,  $\pi$ -flipping fraction leads to the expectation that the contribution of this component should increase with increasing temperature and decrease as p-dichlorobenzene is added to the BPA. As seen in Figure 1, the 'fast' fraction varies by a factor of 2 over the 50°C range studied. The effect of p-dichlorobenzene addition is less dramatic, (Figure 2), but shows the expected decrease in the contribution of the 'fast' component with increasing content of this additive.

These observations give us confidence that the  ${}^{13}CT_1$  measurements provide a good indication of the heterogeneity of the phenylene dynamics in solid polycarbonate. We have used these measurements in comparing polycarbonates of different molecular weights and also for structural variants, where, for example, the isopropylidene methyl groups have been replaced by other functions.

References:

1. For example: 1a. Fischer et al., Makromol. Chem., Suppl. 12, 189, (1985).

1b. Roy et al., Macromolecules 19, 1356, (1986).

1c. Schaefer *et al.*, Macromolecules **18**, 368, (1985).

2. Gupta et al., J. Poly. Sci.: Poly. Lett. Ed. 21, 211, (1983).

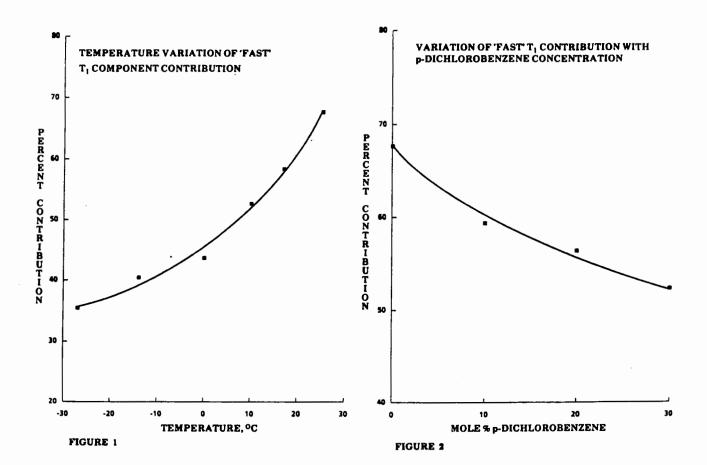
Sincerely,

**Mike Taylor** 

Gord Hamer

BITNET Addresses: Mike\_Taylor.XRCC-NS@XEROX.COM

Gord\_Hamer.XRCC-NS@XEROX.COM



LOVELACE MEDICAL FOUNDATION

22 June 1987 (Received 26 June 1987)

Professor B. L. Shapiro Department of Chemistry Texas A&M University College Station, TX 77843

Dear Professor Shapiro,

#### A PICKUP LOOP WHICH IS SENSITIVE ONLY TO RF MAGNETIC FIELD

The popularization of NMR of large samples in a large magnet bore space has increased the need for a convenient measurement of the magnitude and direction of the rf magnetic field generated by a coil. This is true, for example, in constructing birdcage coils to see if the correct oscillation mode is being generated.

The measurement of the rf magnetic field is best performed by the use of a loop of wire in which a current proportional to the rate of change of the magnetic field is induced. For a sinusoidally varying magnetic field, the induced current is proportional to the magnetic field intensity (with a phase shift).

The major problem with measuring the rf magnetic field with a loop of wire is the sensitivity of the loop to the local rf electric field. In particular, the electric field which is generated by the current in the coil must be accounted for.A crude way to do this is to make two measurements, one with the loop and another with the loop shorted, and subtract the results.

We have been using a variation of the loop which automatically cancels the electric field signal(1) and report its construction here because it seems not to be well known in the NMR community.

#### <u>Design</u>

The figure shows a diagram of the loop and its accompanying circuit. We used RG-174/U coaxial cable with a #26 stranded center conductor for the loop and stem. The plastic jacket is stripped off so that we can minimize the contribution to the total probe area that the stem makes.

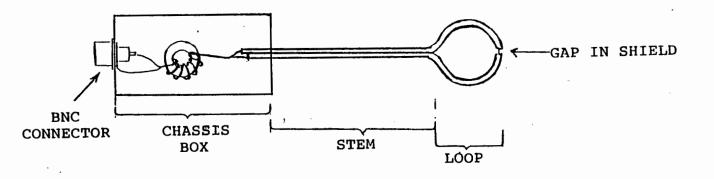
The loop is made by wrapping the cable around a 7/8 in. outside diameter slice of a plexiglass tube as a form. A gap is made in the shield to let the inner conductor "see" the rf magnetic field. It is important to have the stem long enough to be able to keep the chassis box out of the field generated by the coil that's being measured in order that the loop assembly not detune the coil. Ideally, the stem contributes no area to the total loop area. We soldered most of the stem and then used shrink tubing to minimize the area along the stem length. We could have also twisted the two wires in the stem to cancel the net flux passing between them. The loop is sensitive to both electric and magnetic fields, but we are interested only in the magnetic field response. A balun is used to remove the signal caused by the changing electric field. Following Roleson(1), we used #24 enameled wire bifilar wound seven times around a small ferrite core.

#### <u>Use</u>

The shielded loop antenna is simple to use. Drive the coil to be tested with a cw or pulse signal at the frequency of interest. Attach the shielded loop antenna to a high impedance input of an oscilloscope and make measurements of the relative field strength and direction by comparing the magnitudes of the rf that is being detected by the probe. With our particular birdcage coil, we see 20 volts peak-to-peak into the scope for an effective B field of 0.175 gauss which gives rise to a proton  $\pi/2$  pulse of about  $350\mu$ s. With this high sensitivity, it is easy to test a coil which is excited by a weak cw source. This is convenient for us because the high power transmitter of the NMR apparatus is often not available when the coil is being developed. A loop to be used with high power pulses can be smaller and thus have better spatial resolution.

One test of how well this loop works for measuring the rf magnetic field is to rotate it in the rf coil to be tested. A maximum in the magnitude of the rf detected corresponds to an orientation with the plane of the probe cutting the most field lines, whereas a minimum corresponds to an orientation with the loop cutting no field lines. If the loop-coil system is working well, this minimum will be a zero, but if the electric field is not cancelled fully, there will be a residual signal at minimum.

1. Scott Roleson, "Evaluate EMI Reduction Schemes With Shielded-Loop Antennas," EDN, 203-207; May 17, 1984.



Sincerely,

foll Warkins

Joel C. Watkins and Elichi Fukushima

## EMORY UNIVERSITY

Department of Chemistry

1515 Pierce Drive Atlanta, Georgia 30322 404/727-6585 June 25, 1987 (Received 26 June 1987)

Prof. Bernard L. Shapiro Department of Chemistry Texas A & M University College Station, TX 77843

#### Application of HSA-EDTA-Mn and HSA-EDTA-Gd Compress to Erythrocyte Water Exchange

The NMR detection of water exchange across erythrocyte membranes requires the use of relaxation agents to distinguish the intracellular and extracellular compartments. Although Mn(II) has been quite effective for the above requirements, situations in which an alternate reagent is desired which produces similar relaxation affects, but different chemical and physical properties arise. Examples include studies involving substances which bind or precipitate Mn(II), lengthy studies during which time-unbound Mn(II) enters the intracellular compartment. Possible reagents for this purpose are paramagnetic metal ions bound to macromolecules that are unable to traverse the erythrocyte membrane. Additionally, the metal-macromolecule complex should be incapable of promoting aggregation of red blood cells.

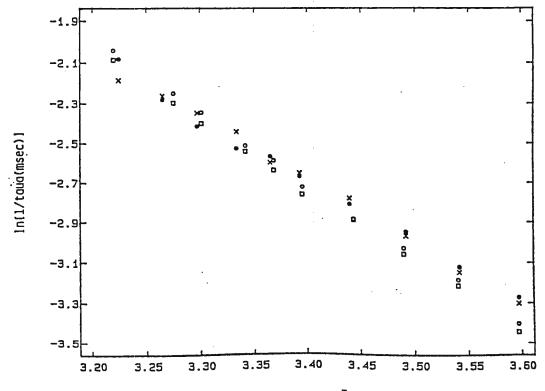


Figure 1.

 $1/T(K) \times 10^3$ 

Recently, our group (G. H. Caines, C. F. Morgan, J. H. Goldstein and R. C. Long, Jr.) has added both Mn(II) and Gd(III) to bovine serum albumin via ethylenediaminetetraacetic acid as originally shown by R. B. Lauffer and T. J. Brady (Magn. Reson. Imaging <u>3</u>, 11 (1985)) and employed these in red cell aggregation studies.

Figure 1. gives an Arhenius plot of  $\ln (1/\tau_a)$  versus  $1/T(^{OK}) \times 10^3$  for these reagents compared to MnCl<sub>2</sub>. (Cross Mn(II) 2.2mM, 42 mg/ml HSA; closed circle Mn(II) 2.6mM, 25mg/ml HSA; square HSA-EDTA-Mn, 42mg/ml). The activation energys were 6.2±.1, 6.1±.2, 6.9±.1 and 7.1±.1 in Kcal/mol. The differences between these values appear to be significant and are under investigation at this time.

The concentration of HSA in human blood is in the order of 3.5 to 4.5%. The relaxation times obtained at these concentrations of HSA-EDTA-metal reagent in buffered saline are essentially the same as the relaxation times obtained with 2mM Mn(II). Therefore, these HSA reagents should prove to be effective extracellular relaxation agents for RBC studies with NMR.

Please credit this to David Live's account.

Sincerely,

Robert C. Sry JE.

Robert C. Long, Jr. Assistant Professor of Radiology

# Monsanto

Monsanto Company 800 N. Lindbergh Boulevard St. Louis, Missouri 63167 Phone: (314) 694-1000

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Sincerely,

Thegong Ler

Gregory Leo, Ph.D. Manager, MAC NMR Facility

### UNIVERSITY OF LEICESTER BIOLOGICAL NMR CENTRE

MEDICAL SCIENCES BLGD UNIVERSITY OF LEICESTER UNIVERSITY ROAD LEICESTER LE1 7RH Telephone (0533) 551284x 523055

Prof. G. C. K. Roberts Dr. L. Y. Lian

Professor Bernard L. Shapiro, Dept. of Chemistry, Texas A & M University, College Station, Texas 77843. U.S.A.

## REVERSE MODE ON AM500 FOR SPIN-LOCK EXPERIMENTS

Dear Professor Shapiro,

We received delivery of our Bruker AM500 spectrometer nearly a year ago, and it has been a rather exciting year in terms of getting 'trendy' experiments to work properly.

The spectrometer is supplied with an f2 board which facilitates 'Reverse' experiments to be done, i.e. using the decoupler channel for data acquisition since it is now phase-locked to be observe channel. This capability of using the decoupler channel for acquisition also means that we can vary our 'transmitter' power within a microprogram with relative ease. For example, in a spin-lock experiment (HOHAHA) with solvent suppression, one would perhaps require three power settings - for pulsing, spin-locking and solvent suppression. These can be conveniently incorporated in one microprogram.

We enclose an example of our initial success - a MLEV17 HOHAHA experiment of the decapeptide Gramicidin S (20mM) in DMSO, with all the scalar connectivities shown (experimental time = 90 minutes).

Yours sincerely,

Lu Yun Lian

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5,,82 terli . 2 5, 52 â ۵ 8 9 ProHA ProHA 0 ProH Orn ٥ 3 HB. A. Sinis Phe Ho Prov Val Hol-HA 2 Val H & K ۵ leur HØ ٥ LouH 6 - - ' DrnH a (AINH55-2.-HA Om HX Leu NH 4HO( ġн Om NH' Orn HA Y хн P.A.H

346-61



Department of Chemistry State University of New York at Stony Brook Stony Brook, New York 11794-3400 NEW PHONE NO: 516 632-7923

June 10, 1987 (Received 16 June 1987)

Re: 2D2Q NMR Spectroscopy of Isolated Spin 3/2 Systems

Professor Bernard L. Shapiro Texas A&M University NMR Newsletter Department of Chemistry Texas A&M University College Station, Texas 77843-3255

#### Dear Barry:

A system consisting of isolated spin 3/2 nuclei can exhibit one or more of four possible types of NMR spectral behavior: (a) single crystal, (b) powder pattern, (c) homogeneous biexponential relaxation, and (d) extreme narrowed. These are determined by the "order" in the sample and the relationship between the various correlation times (of the electric field gradient magnitude-orientation product at the nucleus) and the time-averaged value of the static angular guadrupolar frequency. We have recently been studying the generation of double quantum (2Q) coherence by pulse techniques for <sup>23</sup>Na NMR spectra of the first three types. The standard pulse sequence  $(90_x-\tau/2-180_y-\tau/2-90_x-t_1-90_x-t_2)$ , with phase cycling to select for 2Q works quite well. Figure 1 shows the stacked plot (1a) and contour plot (1b) of a 2D2Q spectrum (obtained with an unmodified NT-300 NB spectrometer), of an unoriented liquid crystalline sample consisting of 38% (w/w) sodium dodecylsulfate, 12% n-decyl alcohol, and 50% deuterium oxide. The skew diagonal ( $v_1 = 2v_2$ ) is also shown in Figure 1b (note the small offset in  $v_2$ ). Figure 2 shows the projection on to the  $v_2$  axis (2a and 2b) and on to the  $v_1$  axis (2c). In Figure 2b, the tops of some of the sharp t<sub>1</sub> noise peaks, evident in 1a, 1b, and 2a, have been cut off. The projection on to v<sub>2</sub> represents the 1Q spectrum and it is clear that this system exhibits a type (b) axial powder pattern. The projection on to  $v_1$  represents the 2Q spectrum and it is clear that it is also, as expected, an axial powder pattern. The stacked plot makes evident an important aspect. All of the 2Q spectral information is contained in the  $v_1$ modulation of the central transition (1/2 to -1/2) in v<sub>2</sub> which is usually sharp and easily detectable. In addition, there is no dead time in the t<sub>1</sub> time domain, and thus quite broad 2Q spectra should be easily detectable, albeit with low spectral resolution, even if the satellite portion of the 1Q spectrum is hard to detect (Figure 2a). Another interesting feature is seen in Figure 2. The breadth of the 2Q powder pattern is identical to that of the 1Q powder pattern. This is in contrast to the situation with the analogous CW experiment. There, the 2Q powder pattern is one half the width of the 1Q powder pattern (G. Lindblom, H. Wennerström, and B. Lindman, J. Magn. Res. 23, 177 (1976)). This is because the CW experiment excites 2Q coherence with two isochromatic photons whereas the pulse experiment employs two photons of different wavelengths. We have submitted for publication a full paper describing these studies.

Charles S. Springer, Jr. Professor

Best regards. Villiam D. Rooney

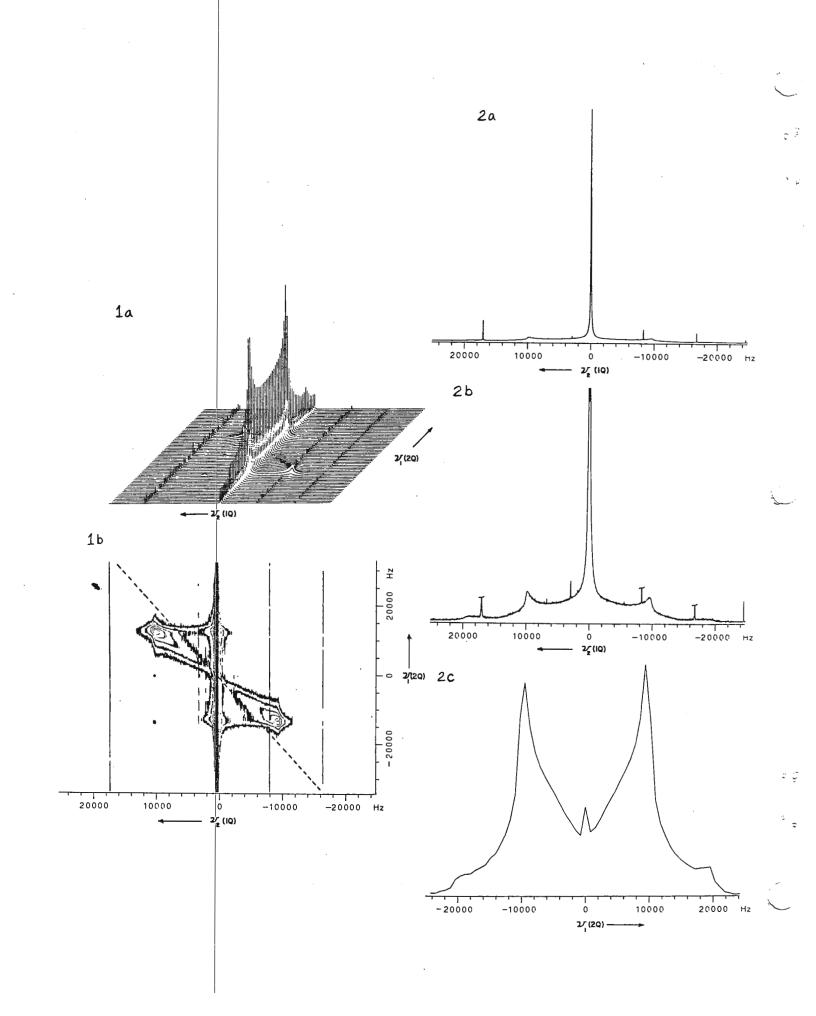
Research Assistant

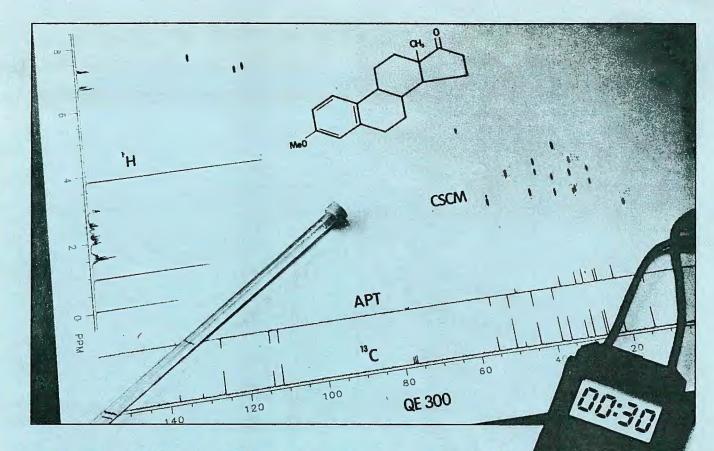
Thomas M. Barbara NMR Coordinator

P.S. CSS wishes to express the Chemistry Department's pleasure in welcoming our new NMR colleagues: Tom Barbara (NMR Coordinator), Gerry Harbison (Assistant Professor), and Bob Lichter (Adjunct Professor and Vice Provost for Research and Graduate Studies). We are happy to have them and hope that their arrival and our newly approved State funding for two high-field, wide-bore spectrometers will encourage your readers to advise their good undergraduates to consider graduate work at Stony Brook.

CSS:mcd







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# **Subject: Automation**

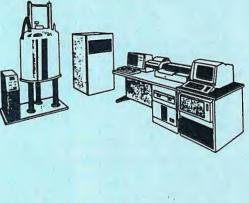
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