BRIAN SYKES

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 322

JULY 1985

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Forthcoming NMR Meetings (Additional listings are solicited)

The Society of Magnetic Resonance in Medicine - August 19-23, 1985; London; Information from either Renee Sauers, Society of Magnetic Resonance in Medicine, 15 Shattuck Square, Suite 204, Berkeley, CA 94704, or Peter Peregrinus Ltd., P.O. Box 26, Hitchin, Hertfordshire, SG5 1SA, United Kingdom.

Second International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds - September 3-6, 1985; Kansas City, Missouri; Dr. Donald Wilk, Symposium Coordinator, University of Missouri-Kansas City, School of Pharmacy, 5100 Rockhill Road, Kansas City, MO 64110-2499.

FACSS (Federation of Analytical Chemistry and Spectroscopy Societies) - 12th Annual Meeting; Philadelphia, PA; September 29 - October 4, 1985. Included are eight sessions on NMR. Contact A.H. Ullman, Procter & Gamble Co., 6250 Center Hill Rd., Cincinnati, OH 45242, 513-659-6445.

1985 Eastern Analytical Symposium - November 19-22, 1985; Penta Hotel, New York; see Newsletter No. 321, pages 17-18.

27th ENC - April 13-17, 1986; Baltimore Hilton; Chairman: R.G. Bryant, Department of Radiology, University of Rochester Medical Center, 601 Elmwood Avenue, Rochester, NY 14642.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed - please make your wishes known.

Have you returned the readership survey card which was inserted into issue No. 317 (February)? If not, please let us know promptly how many people routinely read, inspect, or have the opportunity to use your copy of the Newsletter. Your cooperation will be appreciated.

All Newsletter Correspondence
Should be Addressed to:

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

DEADLINE DATES

No. 324 (September) ---- 26 August 1985

No. 325 (October) --- 27 September 1985

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DEPARTMENT OF CHEMISTRY Havemeyer Hall

TPPI

Dear Barry

I was interested by a recent contribution (TAMU 317-10) which was concerned with the use of TPPI as a method to achieve quadrature detection in the F_1 dimension of 2-D spectra (1), especially because of the suggestion that the major difference between this method and that of States, Haberkorn and Ruben (2) is concerned with the choice between a real or complex Fourier transform routine. I don't buy that ! It seems to me that these two methods are simply analogies in the F_1 dimension of the two rival sampling schemes which are commonly used in F_2.

TPPI is used here, simply as a means of implementing "Alternate acquisition" (sometimes called Sequential acquisition) in F_1 while the technique of States et al. is a method which we might call "Pseudo Simultaneous Acquisition" in F_1. If we restrict the discussion to quadrature detection in F_2 for a moment, these differences become easier to grasp (for me at least !).

The sampling rate in Simultaneous acquisition is equal to the Spectral Width (SW). At each sampling interval, both channel A and channel B are sampled. That is, two samples are taken 90 degrees out of phase with each other at the same moment in time.

The sampling rate in Alternate acquisition is equal to twice the spectral width but the two channels are sampled alternately. That is, at each sampling interval a single sample is taken from either channel A or channel B. The two parts of the FID (the real and imaginary parts) are acquired at slightly different times, which means that the two parts of the FID also have different pre-acquisition delays.

Aternate acquisition uses the same sampling rate as single-phase detection. This simillarity between alternate acquisition and single-phase detection can extend to the data-processing, since it is possible to process data acquired by Alternate acquisition with a real Fourier transform by the use of the so-called "Redfield Trick" (3). However, it is <u>not</u> mandatory to use a real transform as Redfield himself showed in an earlier paper (4). Thus, data acquired by either sampling scheme in quadrature detection can be processed with a complex (real and imaginary) Fourier transform routine.

TPPI

In alternate acquisition the sampling rate is twice that of simultaneous acquisition. A slower sampling rate may allow the use of a longer pre-acquisition delay (5). A careful choice of the pre-acquisition delay may alleviate problems of baseline roll, caused by the transient response of the analog filters (6). This may present problems for data acquired by alternate acquisition since there are effectively different pre-acquisition delays for the real and imaginary parts of the FID.

However, in the F_1 dimension there are no analog filters, thus the choice of an optimum pre-acquisition delay in F_1 is a moot point. But since T_1 noise and T_1 ridges (7) may be caused by systematic digitization errors or baseline distortions in the spectra recorded with the first few t_1-values, presumably the choice of the pre-acquisition delay in F_1 (and possibly even in F_2) could drastically affect the amplitude of these artifacts.

I leave you with a final thought...Why sample data any faster than necessary ?

Best Wishes, and thanks for all your recent help .

Chris

C. J. Turner

(1) D. Marion and K. Wuthrich, *Biochem. Biophys. Res. Commun.*, **113**, 967 (1983)

(2) D. J. States, R. A. Haberkorn, D. J. Ruben, *J. Magn. Reson.*, **48**, 286 (1982)

(3) A. G. Redfield and S. D. Kunz, *J. Magn. Reson.*, **19**, 250 (1975)

(4) A. G. Redfield and R. K. Gupta, *Adv. Magn. Reson.*, **5**, 81 (1971)

(5) E. Fukushima and S. B. W. Roeder, "*Experimental Pulse NMR, a nuts and bolts approach*" Addison-Wesley p.73 (1981)

(6) D. I. Hoult, C.-N. Chien, H. Eden and M. Eden, *J. Magn. Reson.*, **51**, 110 (1983)

(7) W. Denk, G. Wagner, M. Rance and K. Wuthrich, *J. Magn. Reson.*, **62**, 350 (1985)

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10 June 1985

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

Dear Barry,

Platinum-195 Chemical Shielding Anisotropies

The nmr of solid state ^{195}Pt compounds has received considerable attention in our laboratory in the last several months. We are pursuing two rather broad areas of interest: platinum in drug related compounds and platinum compounds for surface catalysis. While the results of these studies will appear elsewhere in their entirety, certain general findings may be of interest for those involved in solution state platinum studies.

Our initial experiments, of course, focussed on the detection of solid state Pt-195 and the establishment of suitable instrument parameters for routine aquisition of spectra. Some results of experiments on chloro compounds are shown in Figure 1. The first four Pt(IV) compounds have anisotropies spanning zero to 1,855 ppm; the four Pt(II) compounds 3,829 to 10,340 ppm. Our findings support Doddrell's anticipation, based on solid state Pt(IV) studies, of larger than part per thousand anisotropies in tetra-coordinated Pt(II) complexes.(1) As most platinum anti-tumor drugs are Pt(II) complexes, a more precise knowledge of shielding anisotropies is required to properly interpret drug related nmr studies.(2,3)

The most anisotropic Pt(II) shielding we have completely analyzed is that of K_2PtCl_4. The MAS spectrum shown in Figure 2 represents a composite of seven individual overlapping spectral windows, each experiment performed at a roughly 3 KHz spinning rate. The shielding elements were calculated using the assistance of the x-ray crystal work.(4) Only one platinum resonance is present and the two elements of the axial tensor were determined from the "powder" edges. This determination has been confirmed with single crystal studies. Judging from this and similar results, Pt(II) anisotropies approaching 1% of applied field strength may be common.

In general, nominal spin-lattice relaxation times of 5-30 seconds and single crystal linewidths of roughly 16-1600 ppm, dominated by dipolar coupling to the quadrupolar chlorine, present no real difficulties to platinum solid state studies. Obtaining three shielding elements from the MAS silhouette spectrum is another matter. Only two pieces of information are immediately accessible. The isotropic sideband connot be located by the usual means of TOSS or varying the spinning rate.(5)

Clearly, platinum nmr in the solid state presents some unusual problems. Obtaining three distinct elements of a single shielding tensor or even the anisotropies of distinguishable tensors requires either single crystal studies or receivers with MHz spectral windows.

Best Regards.

Sincerely,

Steven W. Sparks

Paul D. Ellis

1) D.M.Doddrell, P.F.Barron, D.E.Clegg, and C.Bowie, JCS Chem. Commun., 575 (1982).
2) JY.Lallemand, J.Soulie, and JC.Chottard, JCS Chem. Commun., 436 (1980).
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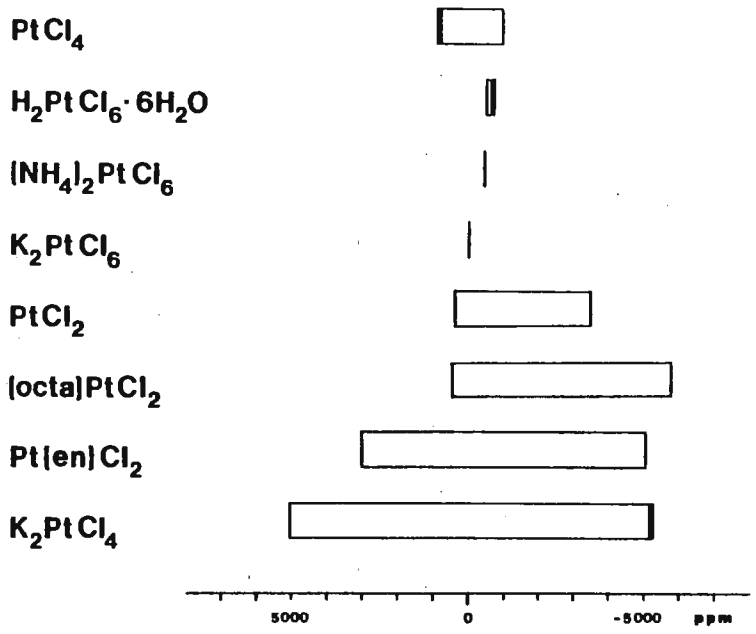

Figure 1. Platinum-195 Chemical Shielding Anisotropies. Static powder, MAS powder, and single crystal determinations of Pt(II) and Pt(IV) shielding anisotropies are shown. Darkened regions indicate non-unique elements of axial tensors. Chemical shifts are relative to isotropically shielded K_2PtCl_6. Abreviations: en = ethylenediamine, octa = 1,5-cyclooctadiene.

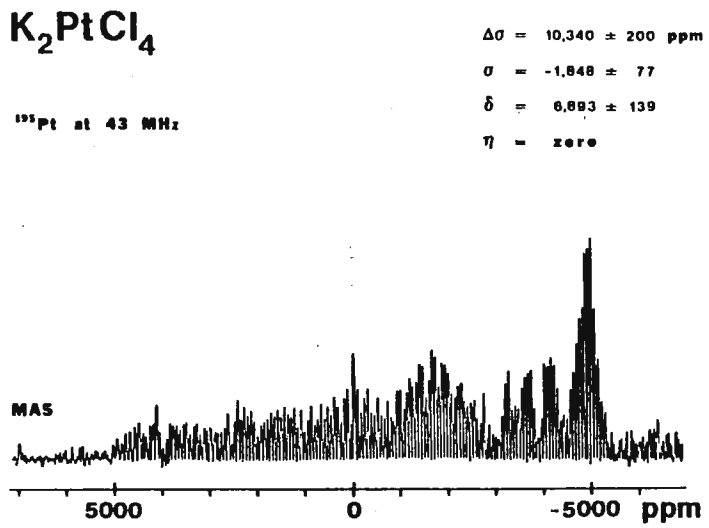

Figure 2. Platinum-195 in Potassium Tetrachloro Platinum(II). The very, very slow MAS spectrum, acquired in seven overlapping spectral windows by Bloch decay, of K_2PtCl_4 is shown. Platinum site symmetry D_{4h} requires the shielding tensor to be axially symmetric. The shielding anisotropy is 1.0% of the applied field strength.

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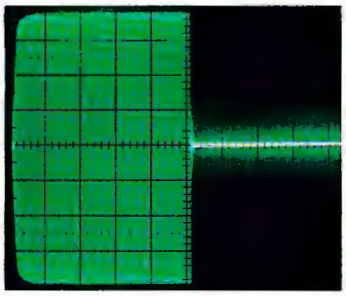
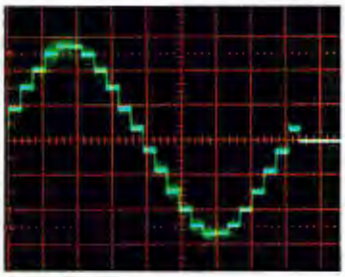
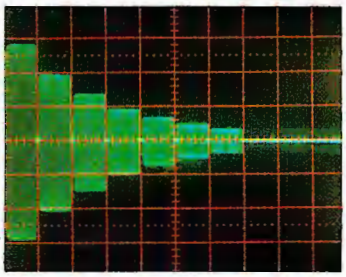




15° phase shift through 360°. ►



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May 12, 1985

Professor B. L. Shapiro
Department of Chemistry
Texas A-M University
COLLEGE STATION, TX 77843

ENC Aftermath

Dear Barry,

I do not know if Mr. Piraro from the San Franciso Chronicle attended the ENC this year, but he certainly caught the spirit, did he not?

Some new and exciting results have been obtained in my lab, and I will send you a more serious (?) contribution in the middle of June.

Yours sincerely,

Jean L. Delayre
Assistant Professor
Director, NMR program

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322-10

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May 24, 1985

2D Homonuclear Hartmann-Hahn Spectroscopy

Dear Barry,

Heteronuclear Hartmann-Hahn type cross polarization is commonly used in solids to enhance the sensitivity of ^{13}C NMR spectroscopy. Muller and Ernst (1) and Chingas et al.(2) demonstrated the use of this technique for liquids to transfer polarization from ^{1}H to ^{13}C. This heteronuclear experiment is on many spectrometers difficult to execute, unless one has a ^{1}H-^{13}C double tuned coil, where rf inhomogeneity is similar for ^{1}H and ^{13}C, and does not introduce a mismatch (2).

A much easier task is to obtain homonuclear Hartmann-Hahn (HOHAHA) cross polarization. A single coherent rf field is used for this purpose, and one does not have to worry about rf inhomogeneity. A simple 2D experiment, based on this principle, is: 90_x - t_1 - spin lock - acquire(t_2). Note that this sequence is very similar to Bothner-By's CAMELSPIN experiment (3), in which we first discovered the Hartmann-Hahn peaks as artefacts. The method is conceptually almost identical to the TOCSY experiment (4).

Although rf inhomogeneity does not affect the CP efficiency, rf offset does. If two spins, A and X, have different absolute values for the offset from the carrier frequency, the effective rf field strengths will differ and a Hartmann-Hahn mismatch is introduced. A simple way around this problem is to use a $(SL_x\text{-}60°_{-x}\text{-}300°_x\text{-}SL_{-x}60°_x\text{-}300°_{-x})_n$ mixing period, where SL_x is a short spin lock pulse (1-5 ms).

Figure 1 shows the fingerprint region (NH-C_αH) of a 3 mM solution of ribonuclease, obtained on a 500 MHz spectrometer in a measuring time of about 80 minutes. A major advantage of the cross polarization method is that net magnetzation transfer is obtained during the mixing period, giving high sensitivity compared to the COSY experiment, especially when couplings are unresolved. The sensitivity of an 8 h. COSY experiment was significantly lower than for the spectrum shown in Fig.1. An additional advantage of net magnetization transfer is that phase-sensitive spectra can be recorded, yielding enhanced resolution. There are a large number of other details to think about when using HOHAHA spectroscopy. A communication is in press in JACS and a full paper will be submitted shortly to the Journal of Magnetic Resonance.

Kindest regards,

Ad Bax Donald Davis Rolf Tschudin

1. L. Muller and R.R. Ernst, Mol. Phys. 41, 95 (1980).
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3. A.A. Bothner-By, R.L. Stephens, J.T. Lee, C.D. Warren, and R.W. Jeanloz, J. Am. Chem. Soc. 106, 811 (1984).
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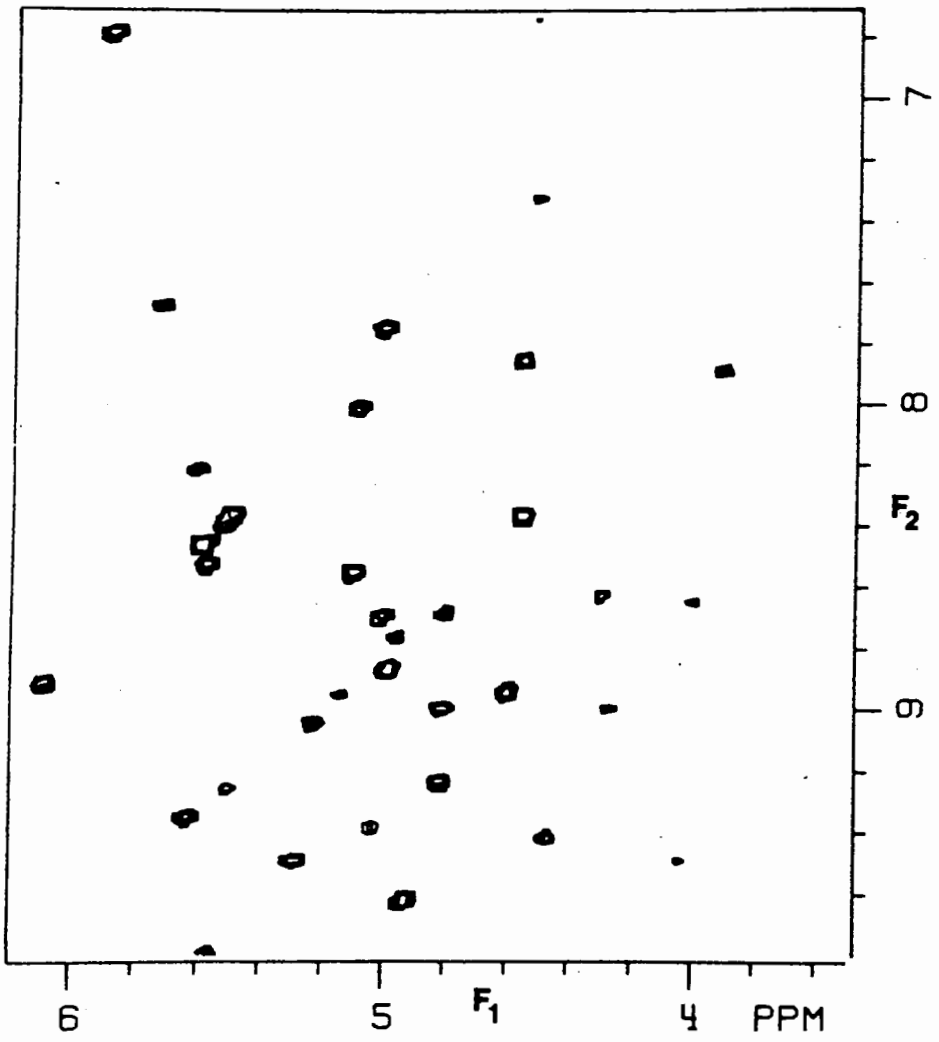

Fig. 1 The fingerprint region of a 3 mM solution of ribonuclease in D_2O. The sample has been prepared several weeks before this spectrum was recorded and all exchangeable amide protons have disappeared. The total measuring time was 82 min. on a NT-500 spectrometer, at 37 °C. 5W rf power was used to generate a 7 kHz rf field, and a mixing time of 27 ms was used.

322-12

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May 29, 1985

Professor Bernard L. Shapiro
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U.S.A.

Dear Professor Shapiro:

Creatine Kinase Kinetics in Human Breast Cancer Cells by ^{31}P Magnetization Transfer Techniques

Our current work is mainly devoted to the characterization of metabolic changes associated with estrogen growth promotion of breast cancer cells.

In the uterus, under estrogen stimulation, the induction of the synthesis of a specific protein termed IP represents the earliest observable change in the protein fraction (Notides and Gorski, Proc. Natl. Acad. Sci. USA 56, 230, 1966). Recently Reiss and Kaye (J. Biol. Chem. 256, 5741, 1981) have shown that the major component of IP is the BB isozyme of creatine kinase (CK). Thus an increase in CK-BB activity can serve as a marker for estrogen stimulation. To evaluate whether estrogen response of breast cancer cells involves a similar stimulation of CK activity, we have employed ^{31}P magnetization transfer techniques.

Human breast cancer cells of the T47D line established by Keydar et al. (Europ. J. Cancer 15, 659 (1979) were cultured in monolayers. For NMR measurements cells were trypsinized and then embedded in agarose filaments and perfused constantly with a medium saturated with oxygen. Under constant perfusion rate (4 ml/min) the level of all high energy phosphates including phosphocreatine (PCR) remained stable for at least 20 hr. Both saturation transfer and inversion transfer experiments were performed. Selective saturation was achieved with a DANTE sequence composed of 25000 pulses of 0.5 sec and a time interval of 240 sec. To minimize fluctuations with time a complete saturation experiment included repeated accumulation of selective saturation of 16 scans at the four consecutive frequencies of PCR, -ATP and two corresponding controls (see Fig.). Selective inversion was achieved similarly with 12 to 24 pulses of a composite length corresponding to 180°.

Analysis of the data yielded an estimation of the kinetics of the CK reaction in the cells. The PCR --> ATP flux was approximately 2

fmoles/(cell x sec) at 36°C. It is thus concluded that the <u>in vivo</u> kinetics of CK in estrogen responsive breast cancer cells can be measured by ^{31}P magnetization transfer methods.

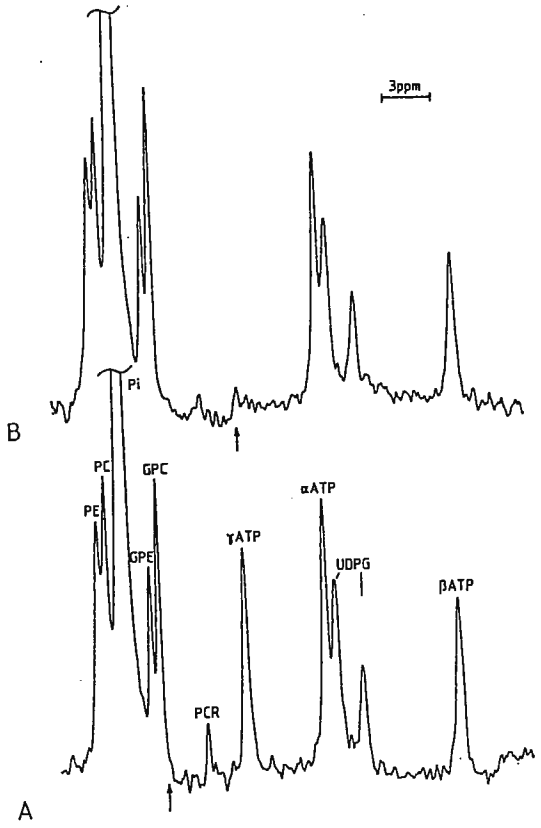
We are looking for postdoctoral fellows. Applicants interested in the above project and related in vivo NMR studies should write directly to H. Degani.

Please credit this letter to Dr. R. Poupko's account.

Yours sincerely,

Michal Neeman E. Rushkin Hadassa Degani

Michal Neeman Edna Rushkin Hadassa Degani



^{31}P saturation transfer experiment at 121.5 MHz in T47D human breast cancer cells. A. Control for -ATP saturation. B. Saturation of -ATP. $5x10^8$ cells were constantly perfused with RPMI medium saturated with 95% O_2 + 5% CO_2. The sample temperature was kept constant at 36°C. Each spectrum includes 1696 transients. The arrows indicate the frequencies of selective saturation.

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1985 March 25

(Received 6/17/85 - BLS)

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

Dear Barry:

Analysis of the NMR Spectrum of Tetrafluoroethylene

Chemical shifts and coupling constants for a large number of fluoroalkanes have been reported but no data on tetrafluoroethylene (TFE), except for its ^{19}F chemical shift, have yet appeared. TFE boils at -76°C at one atmosphere, and under pressure, it can decompose explosively to carbon and carbon tetrafluoride!

Recently, we have measured the 100.6 MHz ^{13}C and 376.5 MHz ^{19}F NMR spectra of a solution of TFE in tetrahydrofuran at -60°C, with 20% D_6 acetone as lock. The spectra of $F_2{}^{13}C={}^{12}CF_2$ (in natural abundance) were analysed as an AA'BB'X pattern, using the program PANIC, developed by Bruker from Castellano and Bothner-By's LAOCOON. Chemical shifts and coupling constants are given in the Table. The simulated spectra were sensitive to the relative spins of all coupling constants.

The geminal and cis F-F coupling constants are substantially greater than any previously reported for fluoroalkenes. Investigations of possible correlations for trifluoroethylenes, including the data for TFE, showed that the cis coupling constants correlate well with the electronegativity of the substituent, while the geminal coupling constants correlate well with the chemical shift of the fluorine atom cis to the substituent. Credit this to the account of D. D. Bly.

Yours Sincerely,

Derick W. Ovenall

Derick W. Ovenall

Frank J. Weigert

Frank J. Weigert

Table

$F_2{}^{13}C{=}{}^{12}CF_2$

^{13}C = 142.7 ppm

^{19}F = -134 ppm

Isotype shifts of $F_2{}^{13}C{=}{}^{12}CF_2$ versus $F_2{}^{12}C{=}{}^{12}CF_2$

-0.1 ppm for $F_2{}^{13}C{=}$, -0.05 ppm for $={}^{12}CF_2$

$^1J^{13}C\text{-}F$	=	-268.3 Hz
$^2J^{13}C\text{-}F$	=	+50.5 Hz
$J_{F\text{-}F}$ Trans	=	-111.4 Hz
$J_{F\text{-}F}$ CIS	=	+73.3 Hz
$J_{F\text{-}F}$ GEM	=	+124.0 Hz

Drexel University

College of Science
Department of Chemistry
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Drexel University • Philadelphia, Pennsylvania 19104

Frank D. Blum
(215)-895-2650

May 23,1985

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

Re: **MULTINUCLEAR SELF-DIFFUSION COEFFICIENTS**

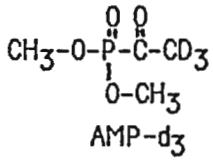
Dear Barry,

Thank you very much for your recent pink ☐ "Reminder"; ☑ "Ultimatum." * Actually I had a contribution ready, but I wanted to see this (beloved/dreaded) piece of colored paper which is the cause of a large fraction of your correspondence. Now that I have you can be sure that my contribution will be prompt in the future. (I hope)

I wish to report the preliminary results of some measurements on the self-diffusion of a molecule that contains protons, phosphorus, carbon and deuterium. The molecule of interest was

* Touché! BLS

synthesized for the self-diffusion measurements by Prof. Marcus Thomsen of Franklin and Marshall College. The structure is shown below and we call it AMP-d_3. Shown in the figure

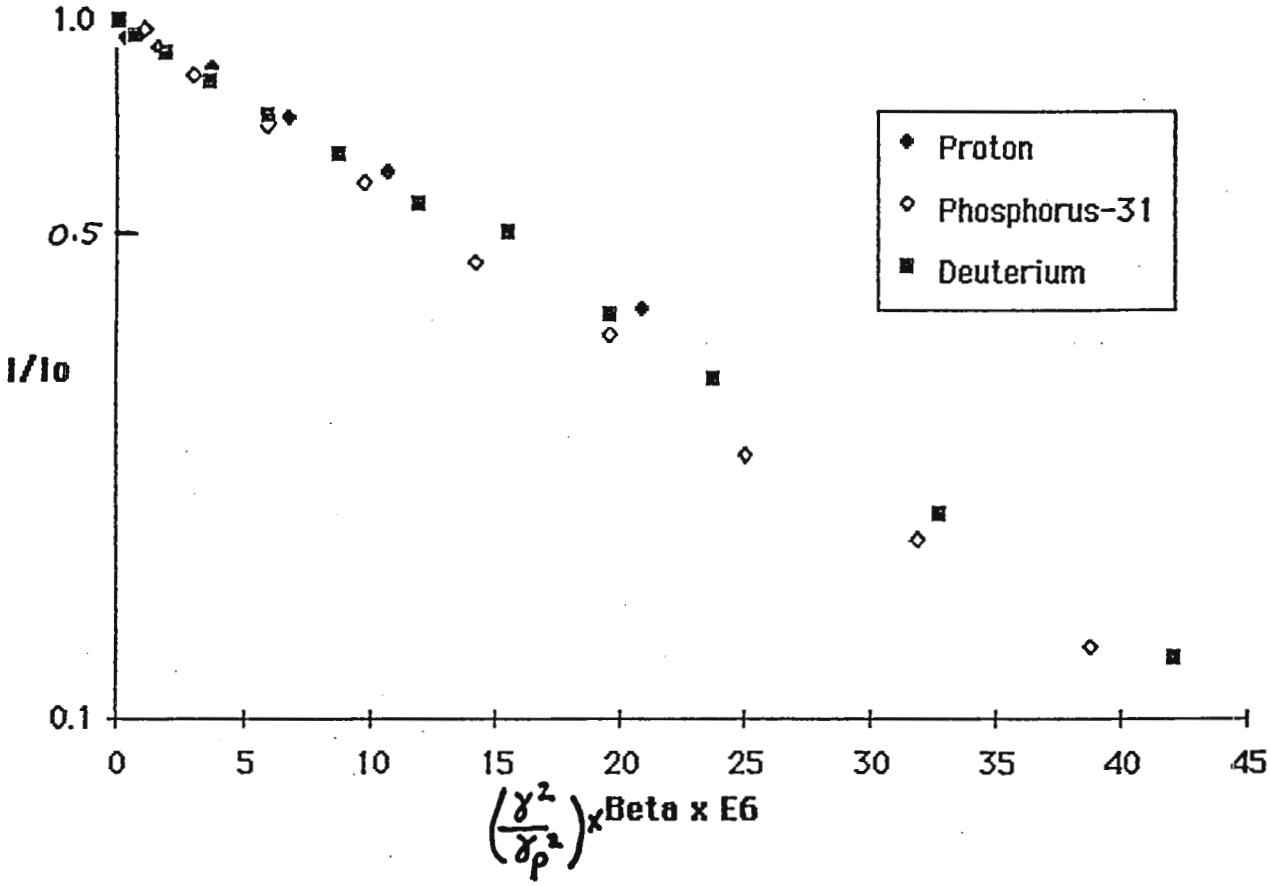


AMP-d_3

is the self-diffusion behavior of this molecule as studied by different nuclei in bulk. We remind the readers that the basic equation governing the Stilbs modification of the pulsed-field gradient spin-echo experiment is:

$$A_i = A_0 K \exp(-\gamma^2 G^2 D \beta)$$

where the A's are the echo intensities, gamma the gyro-magnetic ratio, G the gradient strength, D the self-diffusion coefficient and β is a time variable related to the gradient pulse length and the time between the 180° and 90° pulse. The equation suggests a dependence on the nucleus of gamma squared. This is seen in the figure where the log intensity is plotted against γ^2 β. The calculated diffusion coefficients from each experiment are all in rough agreement as can be seen in the figure. We intend to do some more studies on this system before we compare the numerical results of all three more carefully.



Sincerely,

Frank

Frank D. Blum
Assistant Professor
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DEPARTMENT OF CHEMISTRY, B-014
LA JOLLA, CALIFORNIA 92093

May 30, 1985

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

Quadrupole Coupling Constants (?)

Dear Barry,

Deuterium spin lattice relaxation rates are widely used to probe molecular motion, using formulae such as

$$R_1 = \frac{3\pi^2}{2} (e^2qQ/h)^2[J_1(\omega_o) + 4J_2(2\omega_o)] \qquad (1)$$

where R_1 is the measured relaxation rate, the spectral density functions J_1 and J_2 contain the desired motional information and (e^2qQ/h) is the quadrupole coupling "constant" (QCC). Commonly, QCC values are determined from solid state spectra and used directly in Eq. (1). This procedure introduces a subtle uncertainty which may be especially important for large, slowly moving molecular assemblies such as liquid crystals and membranes.

The solid state measurement of QCC necessarily yields values which are averaged over residual molecular motion in the solid. Such motion includes small-angle librations of the whole molecule about its equilibrium position in the lattice, intramolecular torsional modes, and fast localized vibrational modes. The net effect of such motion is to reduce the apparent QCC value from that which could (in principle, at least) be observed for isolated molecules in the ground rotational and vibrational state.

For purposes of relaxation, motion which produces appreciable spectral density at the Larmor frequency ω_o (or $2\omega_o$) must be omitted from the apparent QCC value to be used in Eq. (1), and it follows that the "proper" QCC value for relaxation is always a bit larger than the solid state value. The problem is, how much larger? How does noe determine which motional modes to include in an effective QCC and which to describe by (model) spectral densities?

In a recent investigation of spin relaxation of nonadecane in a urea clathrate [M.S. Greenfield, R.R. Vold and R.L. Vold, J. Chem. Phys., in press] we were able to show that all modes except zero-point bond vibrations contribute to relaxation, so that the proper "relaxation value" for the CD_2 quadrupole coupling constant in this system is at least 190 kHz -- significantly larger than the 163 kHz which we determined from rotation experiments on a single crystal. Neglect of vibrational averaging effects in this case would lead to errors on the order of $[1 - (163/190)^2]=26\%$ in effective correlation times determined from solid state QCC values and Eq. (1).

In a more general context, partitioning the vibrational modes into those which are "relaxation active" and those which are not requires a reliable model of the motion. In situations where such models are lacking, it seems prudent to regard correlation times determined from Eq. (1) as upper limits.

We trust this note will stave off further polychromatic epistles.

Sincerely,

Bob & Gitte

Robert L. Vold
Regitze R. Vold

P.S. We have just installed in our lab a C1200 computer from Celerity Computing, Inc. This machine runs UNIX Fortran at ∿2.5 times the speed of a VAX 780.

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Schools of Medicine and Dental Medicine
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(716) 831-2700

May 21, 1985

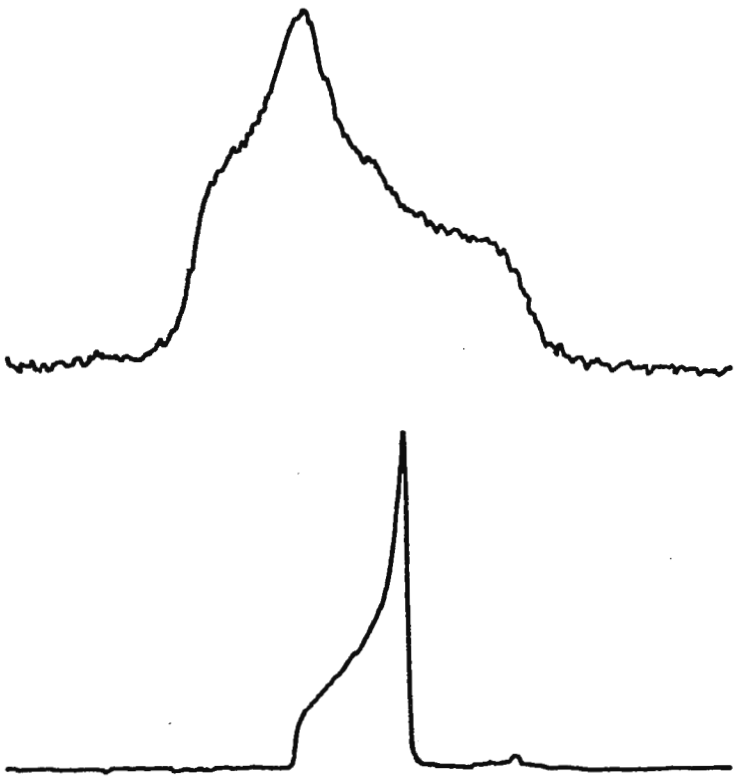
Professor Bernard I. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843-3255

CSA of Phospholipids

Dear Barry:

We have been using P-31 NMR to study phospholipid behavior in membranes for a number of years. In the course of such studies, the residual phosphorus chemical shift anisotropy has been noted to be remarkably similar for phospholipids in the liquid crystal state. Whether one is examining bilayers of pure phosphatidylcholine, or of complex lipid extracts from biological membranes, one obtains almost invariably an axially-symmetric lineshape (due to the rapid rotation of the phospholipid headgroups about an axis approximately perpendicular to the membrane surface) about 40 - 45 ppm wide. During my recent sabbitical with Dr. Bruce Cornell, CSIRO, Australia, we had occasion to examine bilayers of pure phosphatidylinositol, in the

liquid crystal state. The P-31 NMR spectra were obtained on a Bruker CXP 300. Much to our surprise, the phosphatidylinositol powder pattern was about 57 ppm in width (see the figure). The powder pattern of the dehydrated phosphatidylinositol, obtained with cross polarization, is similar to that obtained for other dry phospholipids (see the figure). Thus the motional averaging in the hydrated phosphatidylinositol bilayers is subtly different than in other phospholipid bilayers. Because of the biological importance of PI, this subject is worthy of further investigation. Please credit this to the account of P.L. Yeagle.



Dr. Bruce Cornell

CSIRO

Dr. Philip L. Yeagle

SUNY/Buffalo

Mobil Research and Development Corporation

June 10, 1985

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EUGENE L. JONES
MANAGER

Dr. B. M. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

CP/MAS OF QUADRUPOLAR NUCLEI

Dear Barry:

Very few papers concerning CP/MAS of quadrupolar nuclei have appeared in the open scientific literature. One possible reason for this paucity is that quadrupolar nuclei usually have short T_1 values so that cross polarization may not be necessary to attain good sensitivity. I have made cursory CP/MAS observations on quadrupolar nuclei such as B-11, Na-23, and Al-27 at 6.35 Tesla.

Although I have not made a detailed study in any case, I have made an observation which may be related to a pulse excitation characteristic of quadrupolar nuclei.

It is well-known that the MAS signal observed from quadrupolar nuclei is ordinarily the central -1/2 to +1/2 transition, since the first-order quadrupole effect on this transition is zero. Also, it is well-known that the effect of a r.f. pulse in exciting observable central transitions is a function of the r.f. pulse amplitude versus the nuclear quadrupole coupling constant. The fundamental question in this context is whether the pulse is sufficiently strong so as to excite all the nuclear spin transitions or is of such a smaller magnitude so as to excite only the central transition. The relative effective pulse amplitude in the second case is (I+1/2) times that for the first case (for half-integer quadrupolar nuclei). For spin 3/2 nuclei, this effect can be most dramatic. An r.f. pulse amplitude which gives a 90° pulse for the first case (maximum signal amplitude) gives a 180° pulse for the second case (zero signal amplitude).

The mineral kernite, $Na_2B_4O_6(OH)_2 \bullet 3H_2O$, has equal numbers of B-11 nuclei in trigonal coordination with quadrupole coupling constant of about 2.4 MHz and B-11 nuclei in tetrahedral coordination with quadrupole coupling constant less that 0.2 MHz. Variable pulse width measurements on aqueous

$NaBH_4$ and solid kernite at ω_{rf} = 3.35 X 10^5 rad/sec indicate that for the tetrahedral borons all the transitions are excited whereas, for the trigonal boron only the central transitions are excited. CP/MAS measurements were made on B-11 of kernite as a function of ω_{rf} (B-11) with ω_{rf} (H-1) = 2.42 X 10^5 rad/sec and a contact time of 0.5 millisecond from ω_{rf} (B-11) = 0.6 X 10^5 to 4.1 X 10^5 rad/sec. At ω_{rf} (B-11) = 2.20 X 10^5, only the tetrahedral borons are observed, whereas at ω_{rf} (B-11) = 2.61 X 10^5 and 1.31 X 10^5 both tetrahedral and trigonal borons are observed with approximately equal integrated intensities (see Fig. 1). [on following page]

These observations suggest that cross-polarization experiments are sensitive to the quadrupole coupling constant of quadrupolar nuclei.

Sincerely,

Don

D. E. Woessner
Senior Research Associate

DEW:dpj
Attachment
cc: E. L. Jones
J. T. Nipper
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Central File (602-815)

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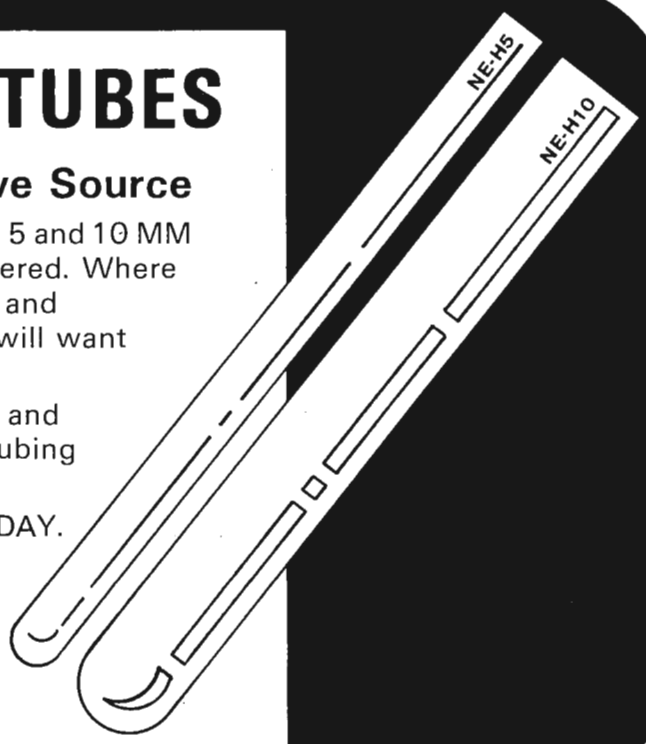

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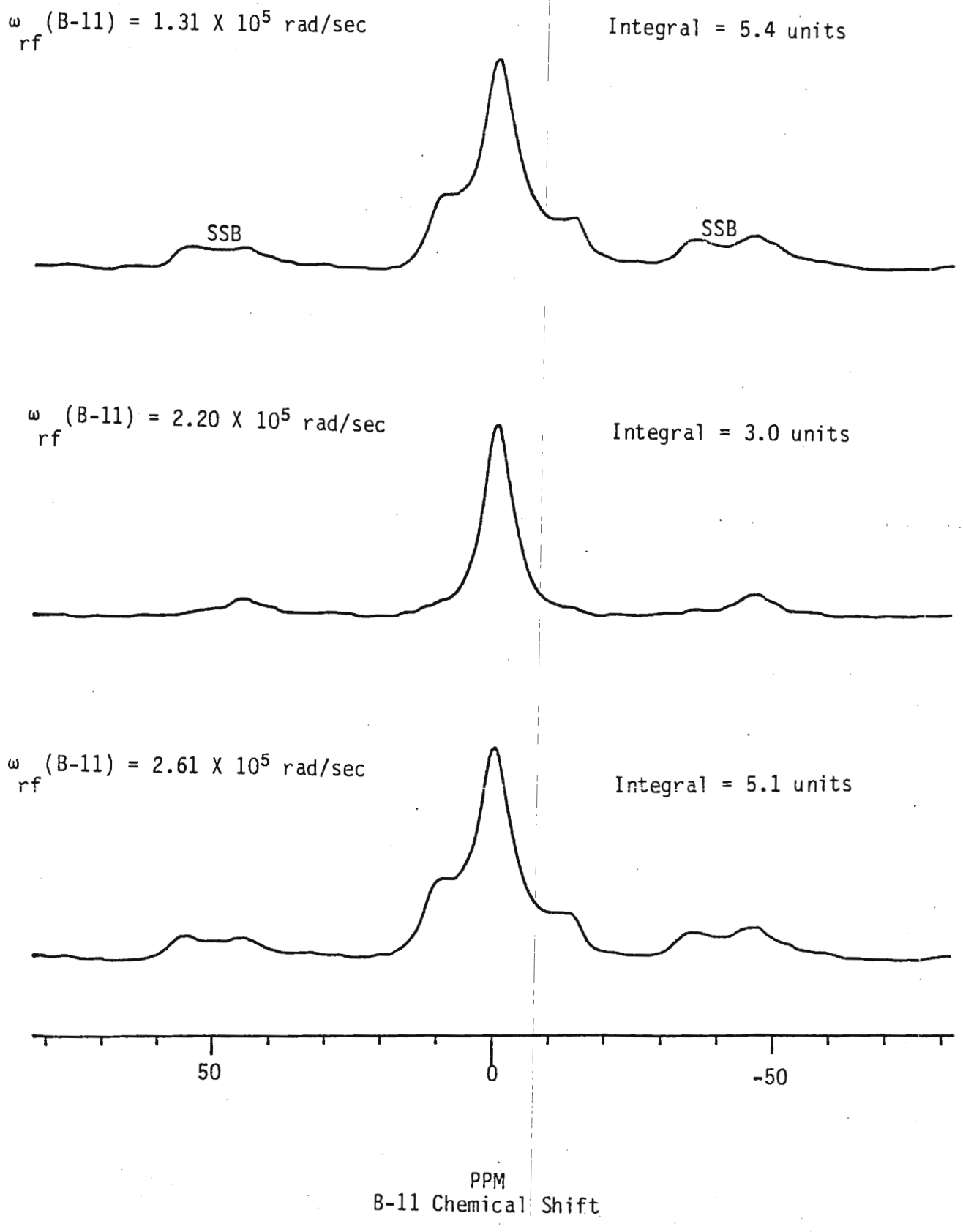
Woessner: CP/MAS of Quadrupolar Nuclei (cont'd)

Figure 1. CP/MAS Signals at 6.35 Tesla
for Boron -11 in Kernite



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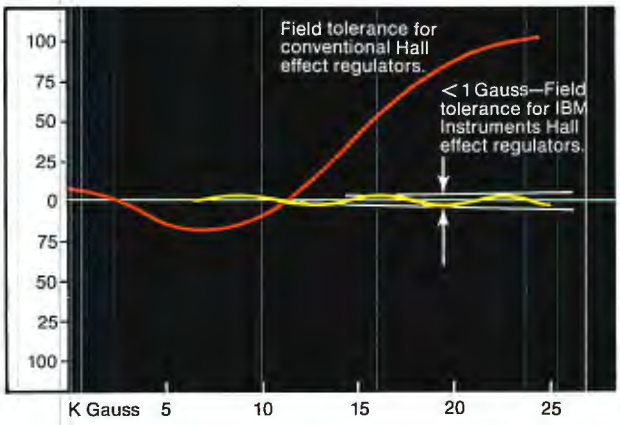

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Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor - **W. B. Smith,** Texas Christian University, Fort Worth, Texas.

Recently the publishing firm of VCH Publishers, Inc. (née Verlag Chemie) initiated a series entitled, "Methods in Stereochemical Analysis," under the guidance of Alan P. Marchand of North Texas State University. Several volumes in the series deal specifically with NMR applications. Two of the early volumes are reviewed here briefly. More detailed reviews of later volumes will follow.

Stereochemical Applications of NMR in Rigid Bicyclic Systems

by
Alan P. Marchand
North Texas State University

VCH Publishers, Inc., 303 N.W. 12th Avenue, Deerfield Beach, Florida 33442-1705
1982; 231 pages; US $92.50

Ideally rigid bicyclic systems should provide the best place to test the utility of NMR as a structural and stereochemical tool. As a consequence, many examples of NMR applications in such systems are available. Published in 1982, this volume provides some 45 tables of NMR data on bicyclic systems. No claim is made that the coverage is exhaustive; rather, data were selected to illustrate points made in the text. Divided into four chapters, the book sets forth as aids to making NMR spectral assignments only lanthanide induced shifts and intramolecular NOEs. Stereochemical applications involving both chemical shift and coupling constant information are presented. The difficulties in utilization of the Karplus relation are reviewed. At forty cents a page, this volume will interest mainly those who work with bicyclic molecules. The index is good.

Carbon-Carbon and Carbon-Proton Couplings

by
James L. Marshall
North Texas State University, and
Motorola, Inc., Fort Worth, Texas

VCH Publishers, Inc, 303 N.W. 12th Avenue, Deerfield Beach, Florida 33442-1705
1983; 241 pages; US $49.95

This volume provides a comprehensive survey of carbon-carbon and carbon-proton coupling constants up to the year 1983. As one of the first persons to recognize the importance of carbon-carbon couplings, the author can speak with authority on their utility. Of particular interest are the various attempts to extend the Karplus relation to the determination of dihedral angles by using three-bond couplings in systems containing carbon, oxygen, and/or protons in a variety of permutations and combinations. Empirically, these seem to work quite well.

The 1D and 2D INADEQUATE techniques were only just being introduced as this volume was being written. They are referenced and briefly discussed. One of the values of this book will be in providing typical coupling constants to use as parameters for the several 2D experiments which require them, i.e., heteronuclear correlation spectra and the 2D INADEQUATE experiment. The general index is ample, and the compound index is most helpful.

W.B.S.

322-28

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DIRECTEUR : PR BERNARD P. ROQUES

Paris, June 5th 1985.

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

Dear Professor Shapiro,

^{31}P assignment of d(^{Me}Cp$_I$Gp$_{II}$ ^{Me}Cp$_{III}$G) in Z form.

In this letter we want to describe some ^{31}P experiments just done on our new Brüker AM 400 MHz equiped with a selective phosphorus probe.

Although it is straightforward to assign ^{31}P in nucleotide using the 2D heteronuclear chemical shift correlated experiment, this method cannot be used with methylated nucleotide since ^{31}P signals disappear probably due to unfavourable relaxation processes. In the case of the d(^{Me}Cp$_I$Gp$_{II}$ ^{Me}Cp$_{III}$G) synthesized in the laboratory of Dr J. IGOLEN (Institut Pasteur), the three ^{31}P signals in B form were assigned by heteronuclear low power decoupling experiments performed on sugar H_3' protons while observing the ^{31}P (figure 1). The possible difficulty caused by overlapping proton resonances can be easily solved by temperature variation.

Addition of ethanol (30%) to a solution of the methylated tetranucleotide induces a conformational equilibrium between B and Z forms which remains slow on the NMR time scale. Owing to the unambiguous assignments of ^{31}P signals in the B form, we have assigned the ^{31}P signals in the Z form by two dimensional homonuclear NOESY experiment (figure 2) in which the mixing time τ_M is set up in the order to the rate of exchange, here 700 msec. Conversely knowledge of the ^{31}P signal in the Z form allows to confirm the assignment of sugar protons in the conformational state.

Yours sincerely.

Bernard P. ROQUES.

Muriel DELEPIERRE.

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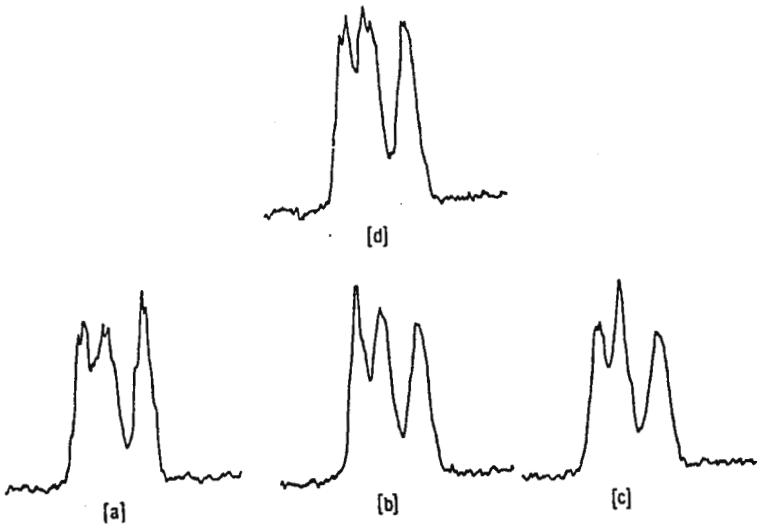

Figure 1. : ^{31}P spectra at 162 MHz of d($^{Me}Cp_I GP_{II}{}^{Me}Cp_{III}G$) 1 mM helix in deuteroacetate buffer 0.1 M, pH 5.5. Low power heteronuclear decoupling experiments at 47°C. (a) ^1H selective irradiation at 4.99 ppm corresponding to G_2H_3'. (b) ^1H selective irradiation at 4.78 ppm corresponding to C_3H_3'. (c) ^1H selective irradiation at 4.64 ppm corresponding to C_1H_3'. (d) ^1H off resonance irradiation for control spectrum.

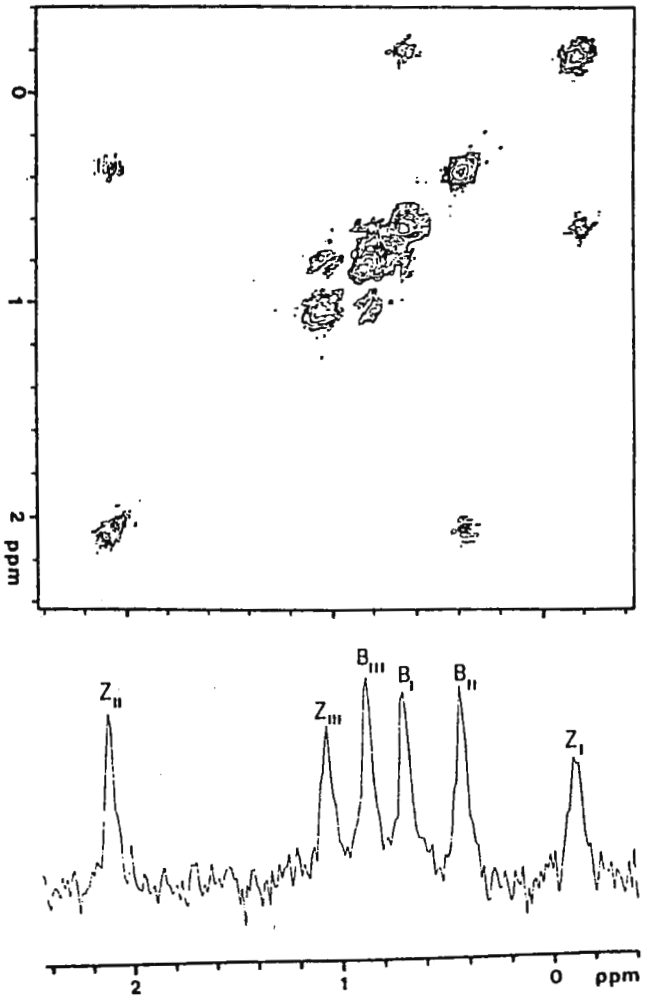

Figure 2. : ^{31}P spectrum at 162 MHz of d($^{Me}Cp_I Gp_{II}{}^{Me}Cp_{III}G$) : homonuclear two dimensional ^{31}P-^{31}P chemical exchange in a mixture of 30% ethanol and deuteroacetate buffer at 5°C. The mixing time τ_m was 700 msec and recycle delay 2 seconds.

322-30

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service
National Institutes of Health

National Institute of Arthritis,
Diabetes, and Digestive and
Kidney Diseases
Bethesda, Maryland 20205
Building: 2
Room : 109
(301) 496- 2848

May 24, 1985

A "rotating" 90° rf localization pulse

Dear Barry,

To keep our various subscriptions to your newsletter going, we describe a new sort of pulse. This pulse is rather similar to the rf selective 180° pulses, proposed by Shaka and Freeman (1) and by Tycko and Pines (2), and is also related to the Depth pulses of Bendal and Gordon (3). Our new pulse, $\alpha_x, \alpha_y, \alpha_{-x}, \alpha_{-y}$ has the effect to turn all magnetization from z to z for small α values (linear system approximation) whereas for α=90°, the four-pulse pulse produces a rotation from z to x. Standard recipes (1,2) for improving the rf selectivity of this particular 90° pulse don't work, but some of the other Freeman/Levitt ideas are applicable. One such improvement gives: $\alpha_x, \alpha_y, \alpha_{-x}, \alpha_{-y}, \alpha_{-x}, \alpha_{-y}, \alpha_x, \alpha_y$. For α=45°, this pulse leaves $(13+2\sqrt{2})/16 \sim 99\%$ of the z magnetization along the z axis.

The advantage of our new pulse over other localization pulses is that they do not require phase cycling to eliminate unwanted parts of the signal, and hence, dynamic range requirements are reduced. This probably makes these pulses useful for some kind of in vivo spectroscopy or another.

We use the new pulse for water suppression on our NT-500 spectrometer. The poor design of the old 500 MHz resonator coil causes a significant amount of signal to be picked up by the leads of this coil. This "lead signal" comes from an inhomogeneous region of the H_o field and gives rise to a broad hump in the spectrum with an amplitude of ~ 0.2 % of the main signal. This hump is a particular nuisance when one is working in H_2O solution since saturation of the H_2O resonance does not saturate the water in the inhomogeneous H_o region. Fortunately, the rf field strength in the inhomogeneous H_o region is significantly lower than inside the resonator and our new pulse $90_x, 90_y, 90_{-x}, 90_{-y}$ can be used to reject most of this unwanted signal (Fig.1). Figure 2 shows what rf localization can do on our 270 MHz spectrometer, where the hump is due to a poor H_o field profile and not to poor coil design. Here a combination of our four-pulse with the "conventional methods" (1-3) has been used to select signals originating from the center of the receiver coil.

Unfortunately, on our console it is impossible with the current design to adjust the rf phase differences between x and y, etc., to exactly 90° without introducing some amplitude imbalance. Although the rotating pulse is very sensitive to such errors, a significant amount of suppression is obtained nevertheless. However, with the current phase misadjustments it does not appear useful to use some of the more compensated 8- and 16-pulse sequences.

The rotating 90° pulse can directly be used to replace a normal 90° pulse in any one- or two-dimensional experiment that is sensitive to rf inhomogeneity without introducing the need for extra phase cycling.

Kindest regards,

Ad Bax Rolf Tschudin Donald Davis

1. A.J. Shaka and R. Freeman, J. Magn. Reson. 59, 169 (1984).
2. R. Tycko and A. Pines, Chem. Phys. Lett. 111, 462 (1984).
3. M.R. Bendal and R.E. Gordon, J. Magn. Reson. 53, 365 (1983)

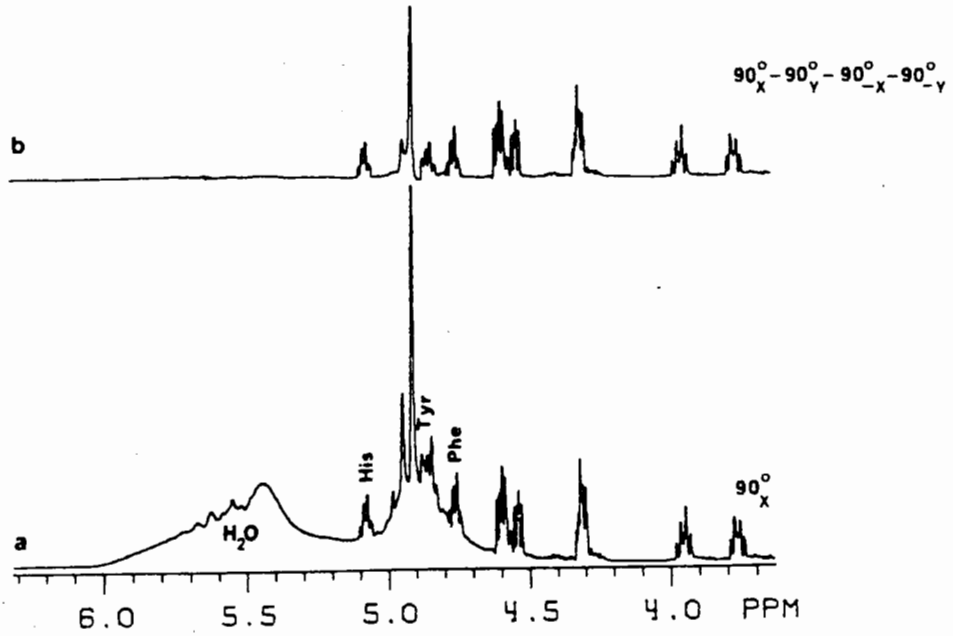

Fig.1 (a) 500 MHz spectrum of angiotensin-II in H_2O, obtained with presaturation of the H_2O with a 12 Hz rf field. (b) Spectrum obtained under exactly identical conditions as (a), but with the $90_x, 90_y 90_{-x} 90_{-y}$ excitation pulse. Signals from "low rf field strength regions" are effectively suppressed by the rotating pulse.

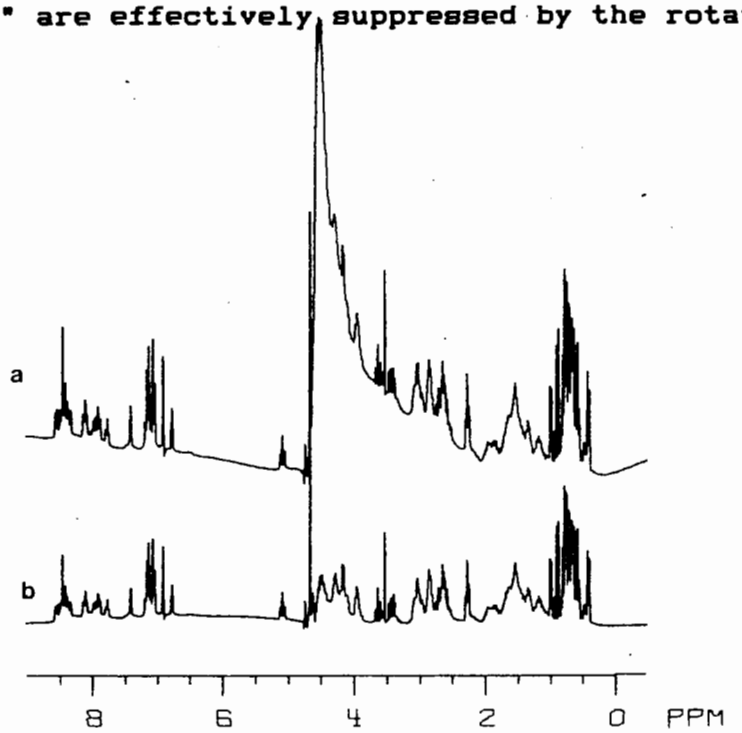

Fig.2. 270 MHz spectra of bacitracin in H_2O. (a) regular spectrum using presaturation and (b) spectrum obtained by using the composite four-pulse in combination with exorcycling of the Shaka/Freeman rf selective 180° pulse.

322-32

Wageningen

Department of Molecular Physics

Your reference
Your letter of
Our reference 85/266/cd/mk
Date June 11th, 1985
Enclosure(s)

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

Subject

RESOLVED CHLOROPHYLL ^{1}H RESONANCES OF CHLOROPHYLL-PROTEINS

Dear dr. Shapiro,

We present this contribution to illustrate the use of ^{1}H NMR for structural studies of hydrophobic chlorophyll-proteins isolated from plants. As yet, no crystals of these proteins are available.

We have investigated 29 kD monomer and 70 kD oligomer solutions (0.1 mM) of the light-harvesting complex (LHC), containing chlorophyll-a and -b, from barley in D_2O buffer by 500 MHz ^{1}H NMR, using DASWEFT [1] to suppress HDO resonances. Monomer and oligomer solutions were prepared from Chl-a/b particles obtained from Drs. D. von Wettstein and B.M. Møller, Carlsberg Laboratories, Copenhagen. Because the detergent Triton X-100, used in these preparations, strongly promotes aggregation of the LHC particles, it was completely replaced by 99% perdeuterated SDS. Addition of SDS to the oligomer solution shifts the oligomer/monomer equilibrium sufficiently towards the monomer side to obtain a considerable increase in resolution.

Under optimal conditions we observe resolved resonances assigned to Chl-a α(9.1 ppm), β(9.5 ppm) and δ(8.5 ppm) methine protons and the Chl-b formyl proton (11.0 ppm). The corresponding in vitro values are found to be 9.4, 9.7 and 8.5 ppm for Chl-a and 11.3 ppm for Chl-b [2], thus no large ligand-shifts are observed for these resonances. No resonances of Chl-b α- and β-methine-protons were observed, presumably due to heterogeneous broadening in accordance with Raman data [3] which also report a larger heterogeneity for the Chl-b species, as compared to Chl-a. No high-field shifted ligand resonances are observed. To our knowledge, this is the first ^{1}H NMR studie of a hydrophobic chlorophyll-protein, exhibiting resolved chromophore resonances.

Yours sincerely,

Cor Dijkema Geoff F.W. Searle Tjeerd J. Schaafsma

[1] C.A.G. Haasnoot, J. Magn. Res. 52, 153-158 (1983).
[2] G.L. Closs, J.J. Katz, F.C. Pennington, M.R. Thomas and H.H. Strain, J. Am. Chem. Soc. 85, 3809 (1963).
[3] M. Lutz, J.S. Brown and R. Remy, "Resonance Raman Spectroscopy of Chlorophyll-Protein Complexes" in Ciba Foundation Symposium 61 (1977) Chlorophyll Organization and Energy Transfer in Photosynthesis, pp. 105-125.

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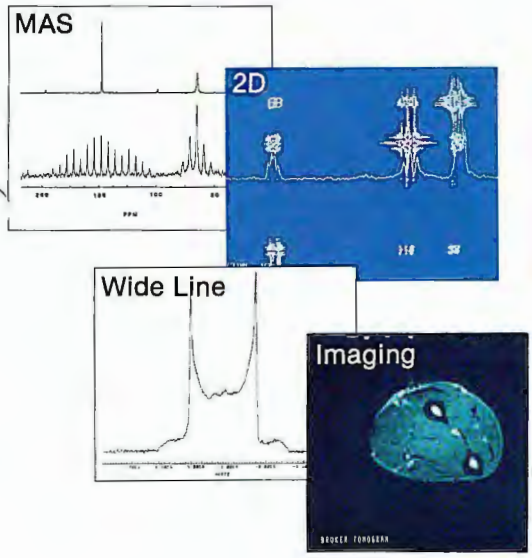

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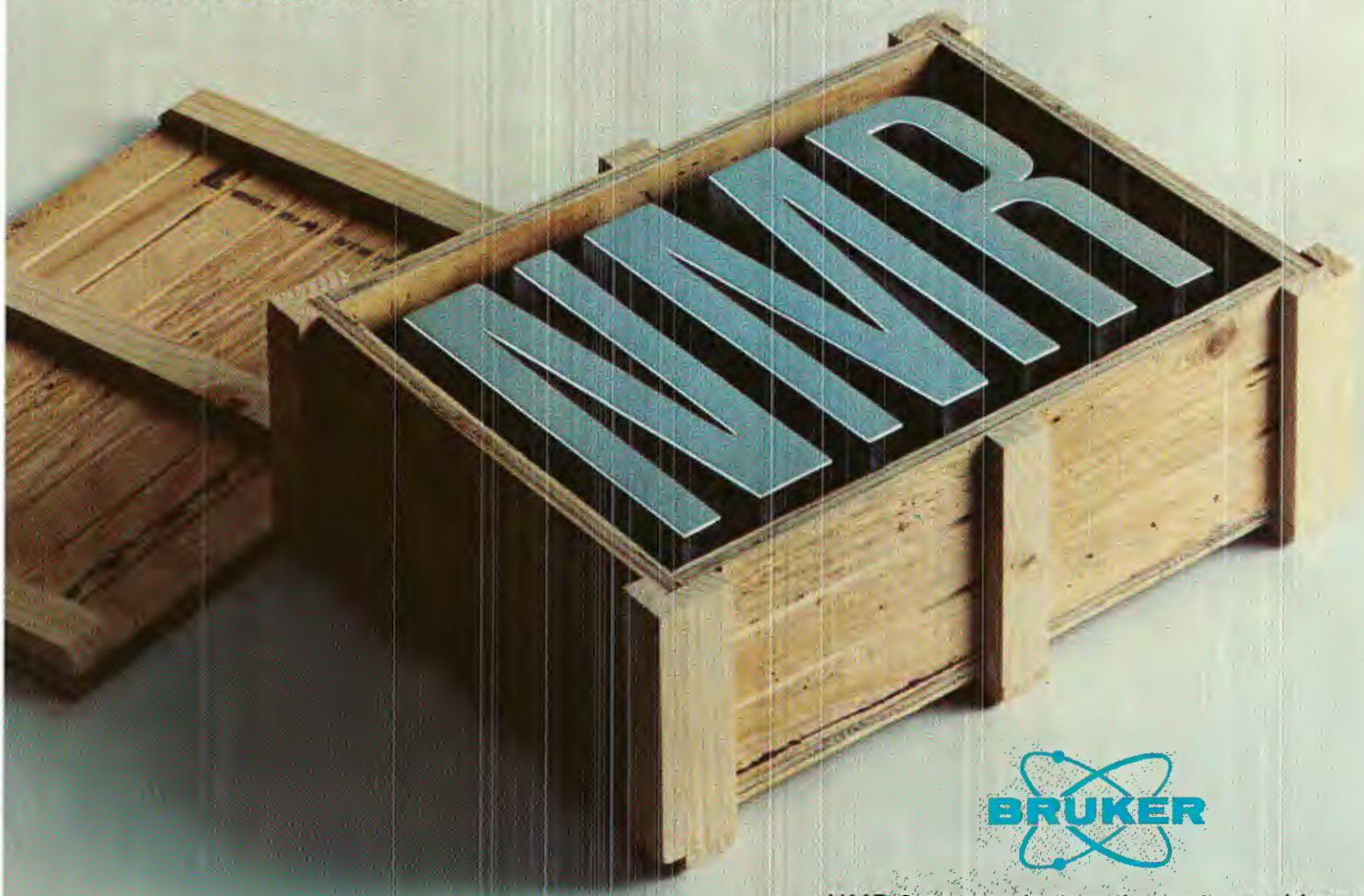

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Klingelbergstrasse 82, Telefon 061 - 44 22 80
Prof. Dr. P. Diehl

CH-4056 Basel (Schweiz) June 11, 1985 322-35

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

A simple test for solvent effects on the structure of oriented molecules

Dear Barry

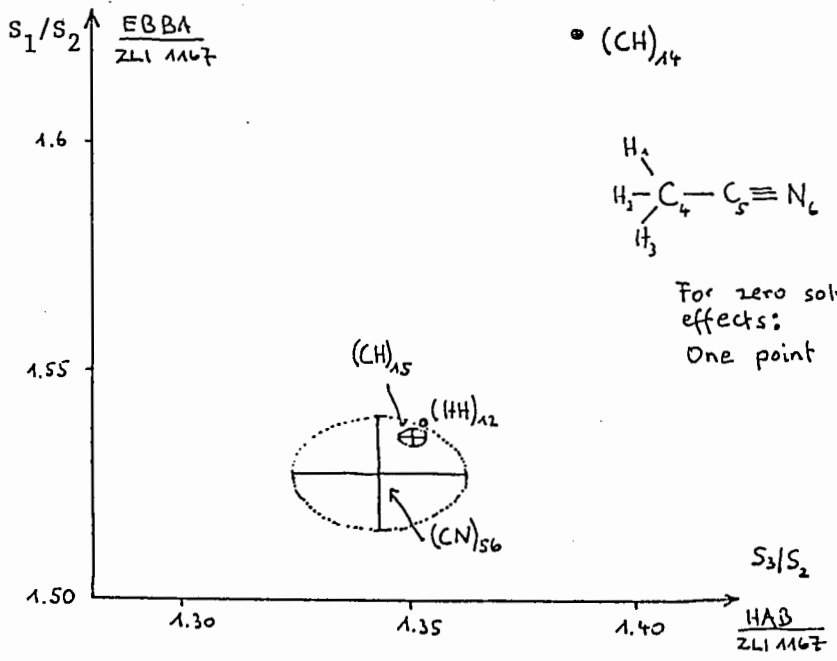
Solvent effects on the structure of oriented molecules have been observed for many years, but only lately the theory [1] has been published which explains the effects and allows the correction. For future structure determinations it will be important to use several solvents and get a quick idea on how large the effects are and on which coupling they are located. For molecules of high symmetry (one degree of order) I suggest a simple test which consists of measuring the direct couplings in three different solvents and to make a plot of [(D_{ij} in solvent 1)/(D_{ij} in solvent 2)] versus [(D_{ij} in solvent 3)/(D_{ij} in solvent 2)]. As these ratios measure the ratios of degrees of order of the molecule in the various solvents they should be independent of the coupling i.e. all the points should coincide. In fact the scatter, as shown in the example (CH_3CN) below, indicates the inconsistency of the data with a considerable solvent effect on $D(CH)_{14}$ but small effects on the remaining couplings. For molecules with lower symmetry, similar tests are being developed.

With best regards, yours sincerely

Peter

(Peter Diehl)

1) J. Lounila, P. Diehl, Y. Hiltunen and J. Jokisaari, Magn.Reson. 61, 272(1985)



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DEPARTMENT OF BIOCHEMISTRY

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AUSTRALIA

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5 June 1985

Professor Bernard S. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas 77843 U.S.A.

Dear Professor Shapiro

Re: "Saturation Transfer NMR Spectroscopy of Carbonic Anhydrase Catalysed Reactions".

We are using ^{1}H and ^{13}C saturation transfer NMR to study the kinetics of carbonic-anyhydrase-catalysed hydration reactions. The principal biological function of the enzyme is the reversible hydration/dehydration of CO_2/H_2CO_3. It also catalyses the hydration/dehyration of acetaldehyde/hydrate at a slower rate.

$$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2$$

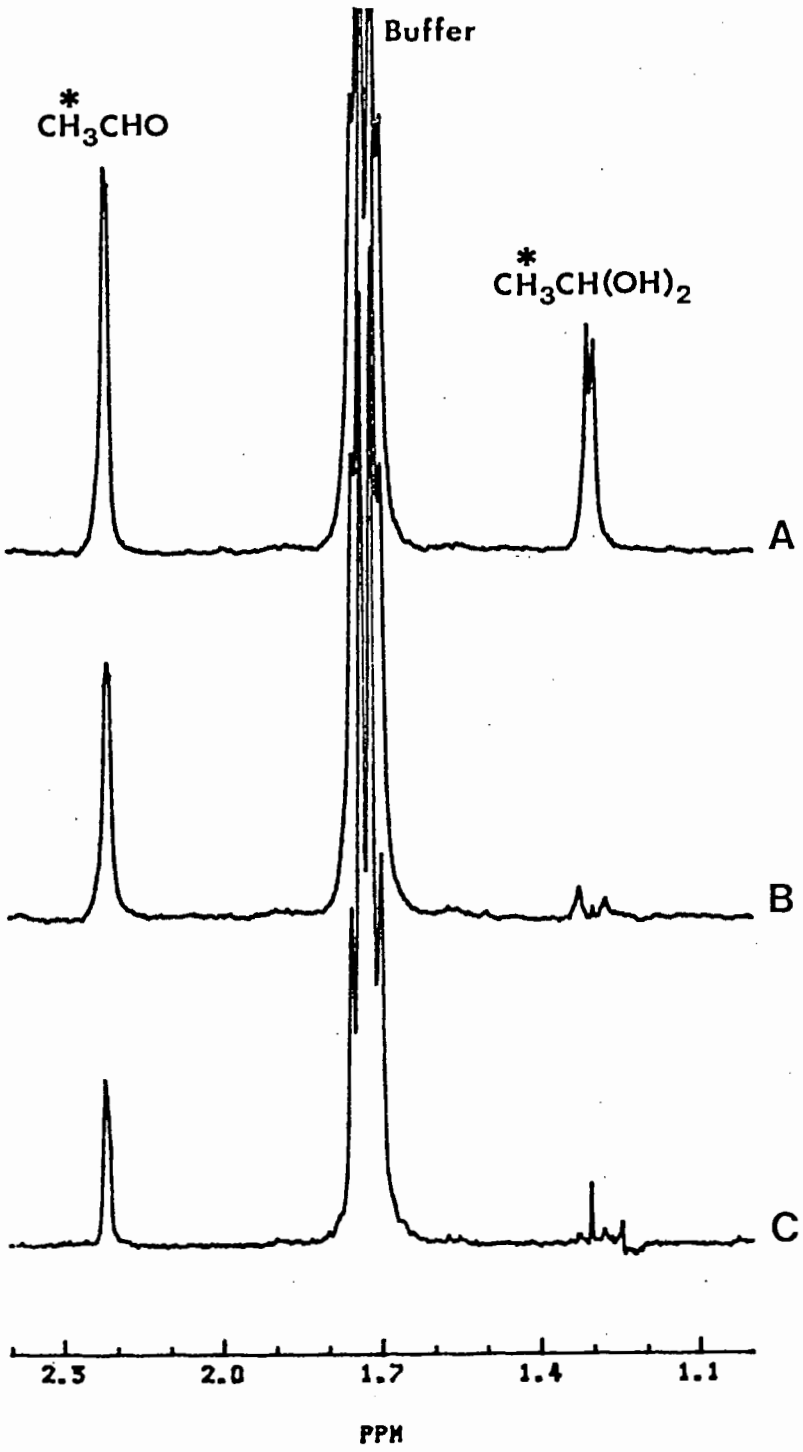
Figure A shows the equilibrium mixture of aldehydrate/hydrate formed for 50mM acetaldehyde in 0.1M diethylmalonic acid buffer, pH 7.5 at 37°C. Saturation of the hydrate methyl peak results in a transfer of saturation to the aldehyde methyl peak (Fig. B). Addition of 2×10^{-5}M carbonic anhydrase results in an increased saturation transfer (Fig. C).

We have calculated the rates of the uncatalysed reaction over a range of temperatures and determined the ΔG of the reaction. As free aldehyde is the substrate of the degradative enzyme, aldehyde dehydrogenase, the significance of carbonic anhydrase in aldehyde removal can be quantified.

Yours faithfully

B. E. CHAPMAN

P.W. KUCHEL


Buffer
*CH3CHO
*CH3CH(OH)2
A
B
C
2.5
2.0
1.7
1.4
1.1
PPM

322-38

ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH

Laboratorium für anorg. Chemie
PD Dr. P.S. Pregosin
Universitätstrasse 6
Telefon 01 ~~326211~~ 256 29 15 (28 51)

Postadresse:
Laboratorium für anorg. Chemie
ETH-Zentrum
CH-8092 Zürich

June 6, 1985

Professor B.L. SHAPIRO
Department of Chemistry
Texas A&M University
COLLEGE STATION,
Texas 77843-3255
USA

Suggested Title: Large and (Relatively) Small $^{1}J(^{195}Pt,^{119}Sn)$ Values.

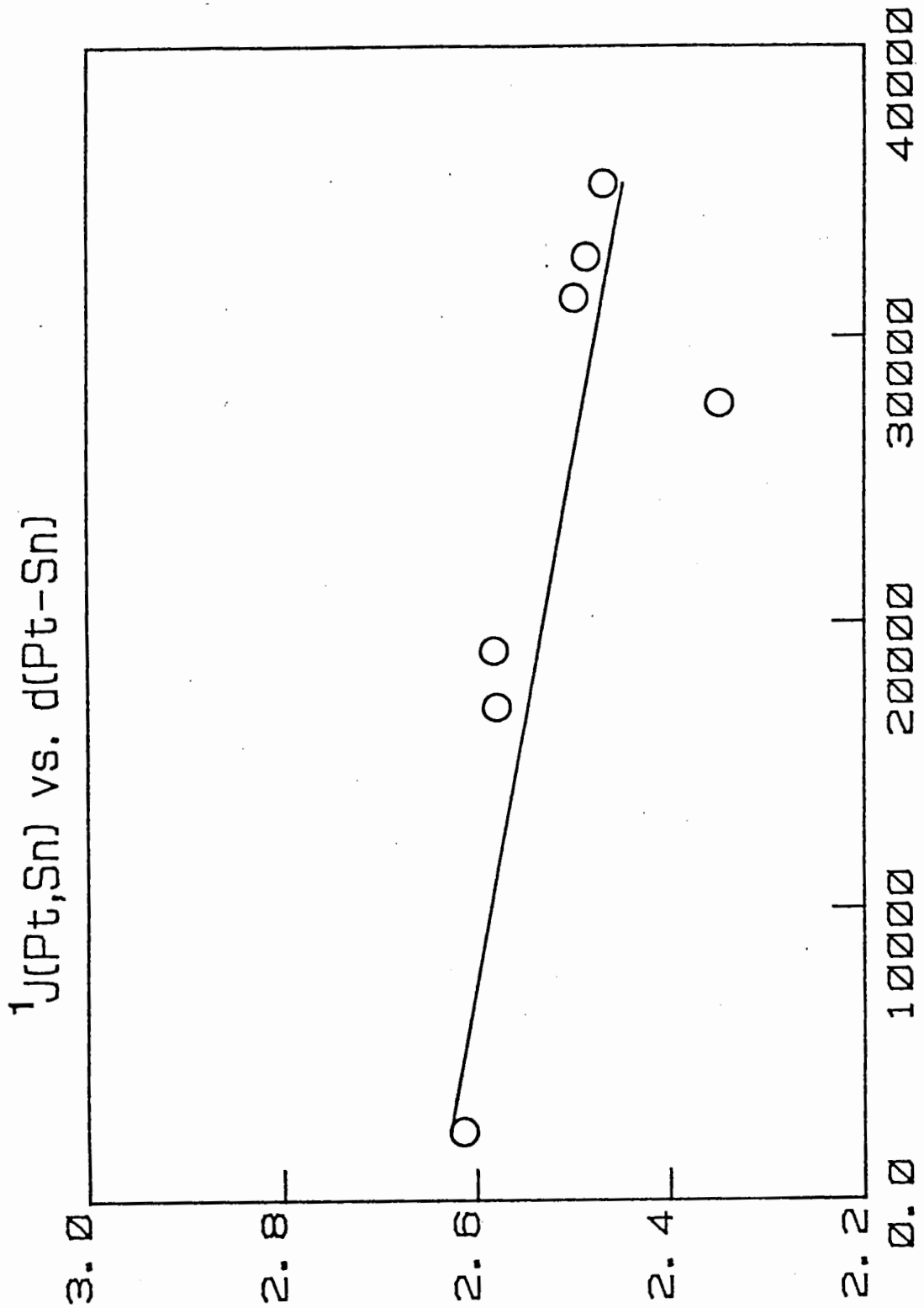
Dear Professor Shapiro,

Heavy metals provide valuable probes as their NMR parameters are quite sensitive to structural change. We have been concerned with the "Pt-$SnCl_3$" moiety for some time and find that $^{1}J(^{195}Pt,^{119}Sn)$ can be as large as ca. 36,000 Hz and as "small" as 2300 Hz, a considerable range. Moreover, there seems to be a reasonable correlation of ^{1}J with the Pt-Sn bond distance (see figure). The point far from our line shows considerable distortion within the $SnCl_3$ ligand (X-ray data) relative to the other complexes. Considering that the contact term need not be the only contributor where metals are concerned, it is reassuring to find an example when ^{1}J can be understood in terms of relatively simple hydridization arguments.

Please credit this contribution to the account of L.M. Venanzi.

Sincerely

P.S. Pregosin


^{1}J(Pt,Sn) vs. d(Pt-Sn)
3.0
2.8
2.6
2.4
2.2
d(Pt-Sn) (Å)
0.0
10000
20000
30000
40000
^{1}J(Pt,Sn) (Hz)

322-40

STATE UNIVERSITY LEIDEN - THE NETHERLANDS
GORLAEUS LABORATORIES - DEPARTMENT OF CHEMISTRY

P.O. Box 9502, 2300 RA Leiden

Phone: 71-148333, extension: 3921

Your letter:
Your ref.:
Our reference: J.Lugtenburg

Subject: ABC ^{13}C NMR spectrum of 10,11,14-$^{13}C_3$ retinal

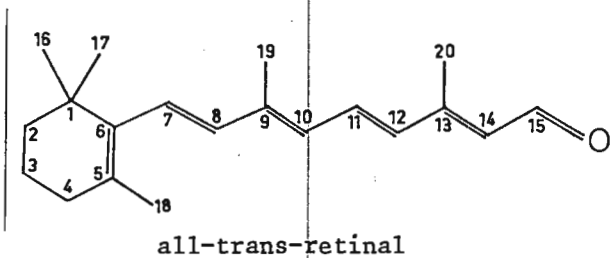
LEIDEN. May 30, 1985

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

USA

Dear Professor Shapiro,

We prepared 10,11,14-$^{13}C_3$ retinal for our investigations on vision and bacteriorhodopsin photochemistry (92% ^{13}C incorporation on 10, 11 and 14).



all-trans-retinal

The noise decoupled 50.2 MHz ^{13}C NMR spectrum was recorded on a JEOLCO FX 200 (shown in Figure). The spectrum was simulated with the PANIC-84 program on the Bruker ASPECT 2000 Computer with the following parameters:

Chemical shifts		Coupling Constants		
C_{10}	129.3 ppm	$^1J_{10-11}$	58.0	Hz
C_{11}	132.5 ppm	$^4J_{10-14}$	0.0	Hz
C_{14}	129.0 ppm	$^3J_{11-14}$	7.3	Hz

^{13}C incorporation

92% on 10, 11 and 14 each

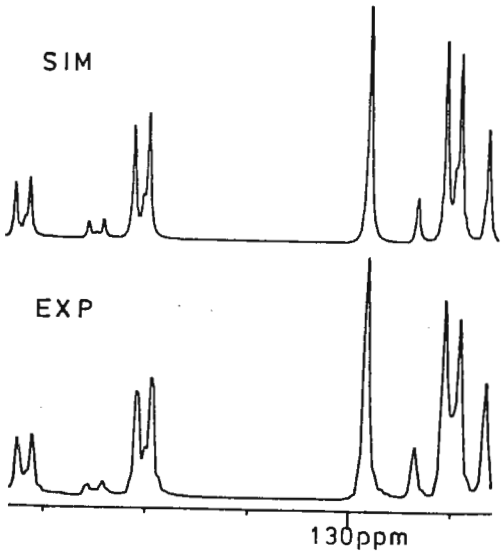


FIGURE :

Sincerely yours,

Irene Hornung, Rob van der Steen, Fons Lefeber, Cees Erkelens, Johan Lugtenburg

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StonyBrook

June 13, 1985

POSITION AVAILABLE - DEPARTMENTAL NMR COORDINATOR

The Chemistry Department at SUNY/Stony Brook invites applications for Departmental NMR Coordinator. The ideal candidate will have extensive NMR and electronics experience, will supervise and maintain existing instruments, train new users, and would participate in Chemistry research programs. We currently have a 300 MHz spectrometer, a stand-alone data station, and several lower field instruments. Acquisition of a 500 MHz spectrometer is anticipated. Send a curriculum vita, a statement on capability in NMR, electronics, research interests, and the names of three references by 1 September 1985 to Professor C. S. Springer, Department of Chemistry, SUNY/Stony Brook, Stony Brook, New York 11794-3400. The State University of New York is an equal opportunity/affirmative action employer.

Vacancy for a Research Associate. I expect to have a vacancy after July 1 for someone to work in the area of proton-detected heteronuclear NMR and its biological applications involving ^{13}C, ^{15}N and ^{31}P. We have a 300 MHz widebore spectrometer equipped for this work, and will shortly order a higher field system. Ideally, the applicant should be a recent Ph.D. with extensive NMR experience in instrumentation and modern 2-D techniques. Applicants should send a biographical sketch and names of references to:

David Cowburn
The Rockefeller University
1230 York Avenue
New York, New York 10021-6399

322-44

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
TEXAS 77843
Verenigde Staten

Uw ref.:

Onze ref.: IS/22 2751

Amsterdam, 6th June 1985
Badhuisweg 3
Tel. via telefoniste (020) 30 9111
Tel. rechtstreeks (020)
Hr/Mw

Re: Quantitative aluminium solid-state NMR

Dear Professor Shapiro,

Aluminium solid-state magic-angle-spinning NMR is now a routine method for discriminating between octahedrally and tetrahedrally co-ordinated Al ions.
When attempting to extract quantitative information from aluminium spectra however, one has to exercise the greatest care in view of the severe spectral distortion that can occur for nuclei with an associated electric quadrupole moment such as ^{27}Al.

An understanding of the underlying theory together with some experimental adaption can allow the determination of the absolute amount of aluminium contributing to the tetrahedral aluminium signal from aluminosilicates for example.
If for the solid only the $(\frac{1}{2}, -\frac{1}{2})$ transition is observed, as is usually the case for aluminosilicates, and under the condition that the spectrum is recorded using small pulse angles, the intensity of the ^{27}Al soild-state signal is factor $4I(I+1)/3(I+\frac{1}{2}) = 35/9$ smaller than that of a liquid-state signal of the same number of nuclei.

A liquid-state internal standard (aqueous $AlCl_3$ solution) can therefore be used, which is added to the sample in a narrow cylindrical holder as shown in the figure. The holder is then kept in the centre of the spinner by a close-fitting circular bottom plate. Knowledge of the weight of the sample allows the amount of aluminium to be calculated from the ^{27}Al intensity ratio. Measurement at high magnetic fields ($\geq$ 9.4T) is sometimes also mandatory for certain samples.

Koninklijke/Shell-Laboratorium, Amsterdam

Application of this method has resulted in the determination of the framework aluminium content of a number of aluminium-poor zeolites (< 3%) where the silicon solid-state spectra are no longer capable of yielding this information.

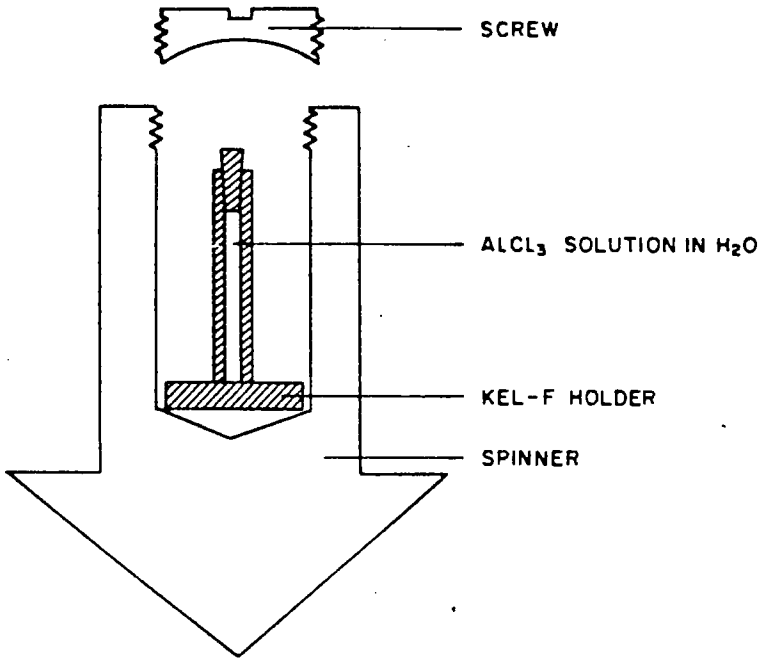
Yours sincerely,

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

G.R. Hays

N.C.M. Alma

A.E. Wilson



SPINNER FOR QUANTITATIVE SOLID-STATE ^{27}Al MAS NMR MEASUREMENTS

322-46

CSIRO

Division of Applied Organic Chemistry
506 Lorimer Street, Fishermens Bend, Victoria.

A Division of the Institute of Industrial Technology

G.P.O. Box 4331, Melbourne, Vic. 3001, Australia.

Telephone (03) 647 7222
Cables and Telex AA 33951

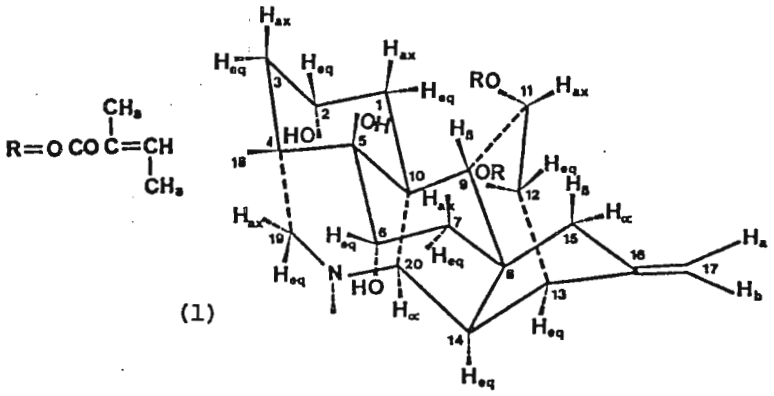
Professor B.L. Shapiro,
Department of Chemistry,
Texas A.& M. University,
College Station, Texas 77843

6th June, 1985.

DETECTION OF COUPLINGS, UNOBSERVABLE IN 1D SPECTRA, BY 2D COSY

Dear Professor Shapiro,

We have recently used the 2D COSY technique to assign the complete ^1H spectrum of the alkaloid, anopterine (1)[1].



(1)

In the 1D spectrum (Fig.1) the signals from H-20 and Me-18 appear as singlets (linewidths 2.5Hz and 2.2Hz, T_1's 0.5s and 0.3s respectively). Although the dihedral angle between the vicinal H-20/H-14 is approximately 90^0, with an expected negligible coupling, the 2D COSY spectrum (Fig.2) shows cross peaks corresponding to this connectivity. More interestingly, cross peaks corresponding to a connectivity between Me-18 and H-2eq indicate a small 5 bond planar coupling between these protons. Such data are of immense assistance in the assignment of structure to complex molecules.

The 2D COSY spectrum also allows accurate assignment of the chemical shifts of overlapping multiplets, e.g. H-7eq, H-3ax, H-14eq, H-9, H-7ax and H-1eq, which are not readily assignable in the 1D spectrum.

Please credit this contribution to the account of Dr. D.P. Kelly, University of Melbourne.

Yours sincerely,

S.R. Johns and R.I. Willing

1. S.R. Johns, J.A. Lamberton, H. Suares and R.I. Willing, Aust. J. Chem., 1985, in press.

Fig.2

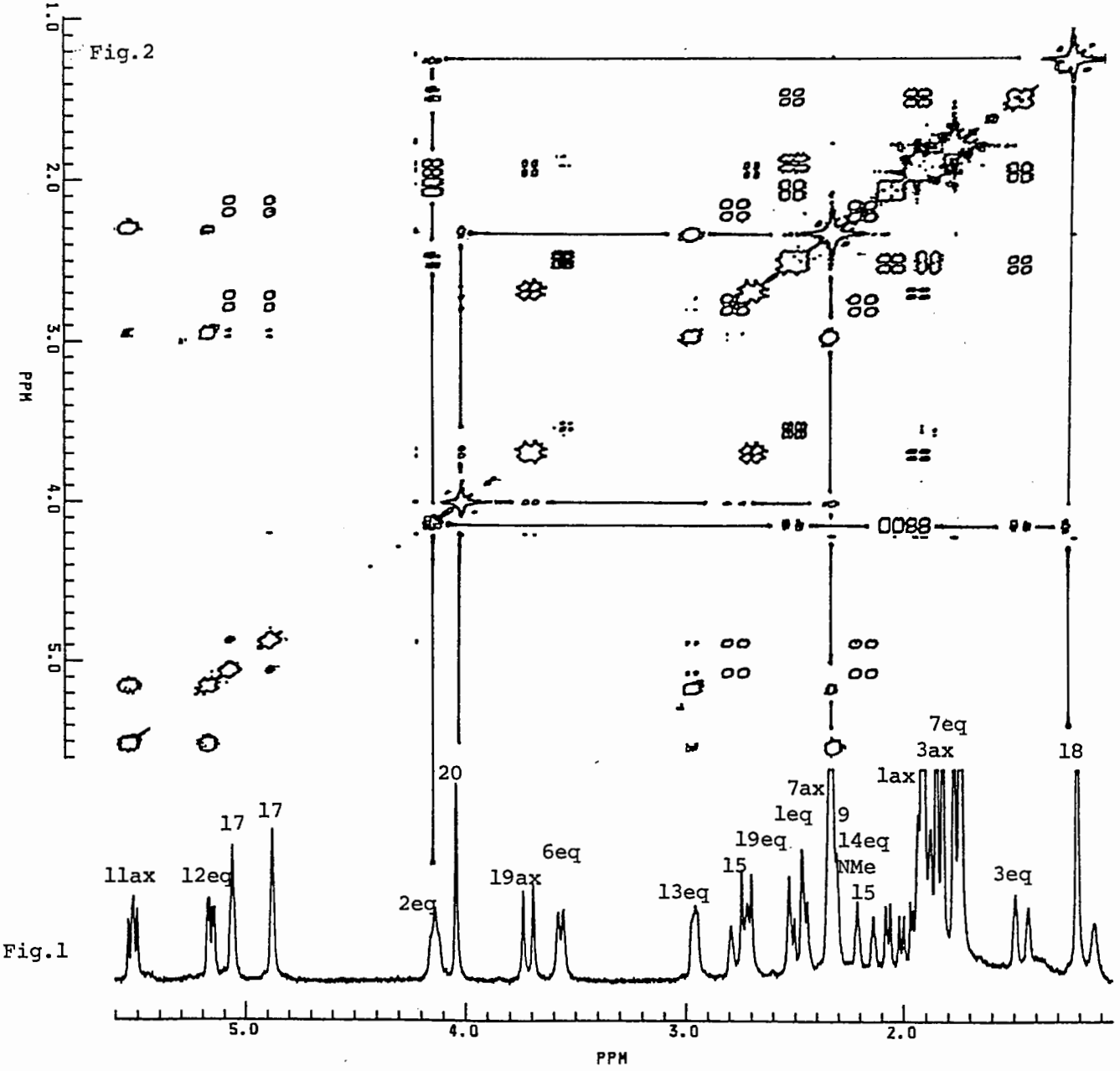
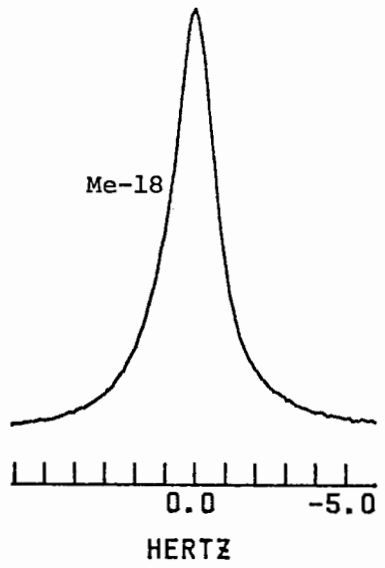
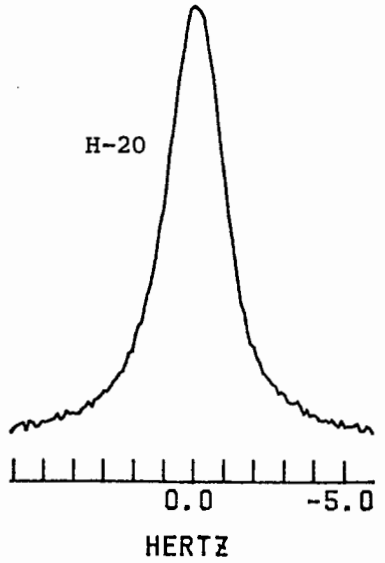

1.0
2.0
3.0
4.0
5.0
PPM
11ax
12eq
17
17
2eq
20
19ax
6eq
13eq
15
19eq
7ax
1eq
9
14eq
NMe
15
1ax
3ax
7eq
3eq
18
5.0
4.0
3.0
2.0
PPM

Fig.1


Me-18
0.0
-5.0
HERTZ


H-20
0.0
-5.0
HERTZ

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DEPARTMENT OF BIOLOGICAL CHEMISTRY

TELEPHONE 955-5000
AREA CODE 301

June 7, 1985

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

Dear Barry:

Effects of Subways on High Resolution NMR

The planned extension of the Baltimore Metro to the Johns Hopkins Medical Campus, and the problems in obtaining high resolution NMR spectra recently noted at Columbia University, prompted us to make a detailed study of the effects of subways on NMR. Problems result from the fact that subways are powerful DC systems which generate large and slow changes in magnetic fields, primarily during the starting up and departure of trains. They also set up sizeable mechanical vibrations. We summarize our findings and recommendations to the Hopkins Administration and to the Maryland Transit Authority, in order that serious problems might be avoided.

1. The New York Experience:

Columbia Medical School which is 600 and 750 feet from two superficial N.Y. subway lines and Columbia University which is 700 feet from one subway line have been unable to do high resolution NMR involving long data accumulation. This problem has not yet been solved after one year. Less than optimal NMR imaging has been possible with expensive magnetic shielding of one room at a cost of ~$80,000. At Rockefeller University, which is 2,700 feet from one subway line, no problems were noted.

2. The NIH Experience:

According to Dr. Ad Bax, high resolution NMR has not been harmed at all by the recently completed NIH limb of the Washington Metro. The trains run along Rockville Pike, 920 feet from NMR instruments but very deeply (120 feet) below ground, according to the Washington, D.C. Transit Authority. The trains run through cast concrete, reinforced by a steel cage. Throughout the Washington Metro, these steel reinforcements are connected to each other for electrical continuity and shielding. No other special features exist near the NIH.

3. Mechanical Vibrations:

At the University of Delft, Holland, mechanical vibrations from streetcars interfered with high resolution NMR. According to the Washington, D.C. Transit Authority, shock mounting can reduce mechanical vibrations by 20 dB. It consists of an 18 inch neoprene base under the subway, installed at the time of building.

According to the Maryland Transit Authority, such mounting has been installed and works well on the Baltimore Metro beneath a movie theater, between the Charles Center and Lexington Stations. Half as much mechanical attenuation can be accomplished less elaborately by appropriate mounting of the ties.

4. Tolerable Magnetic Field Fluctuations:

Measurements were made of the fluctuating magnetic fields in the environment of Mildvan's NMR instruments, using a recording Flux-Gate Magnetometer. The maximal deflections noted were 1-2 milligauss concomitant with the operation of a Sorvall RC 2B centrifuge in the adjacent laboratory.

NMR data collected during the operation of this centrifuge showed no loss of resolution. This is surprising, since 2 milligauss in 58.75 K gauss is 0.034 ppm or 8.5 Hz. We must conclude that the (Oxford) NMR magnet provides shielding against such relatively small fluctuations.

5. Magnetic Fields Generated by the Baltimore Metro:

Magnetic field measurements were made on the 4th floor of a building which is 300 feet from the Charles Center Terminus of the Baltimore Metro. The trains run 70 feet below ground at Charles Center. Small magnetic fluctuations, 0.4-0.8 milligauss, were detected at two perpendicular directions, concomitant with the departure of trains. These fluctuations are about half the size of those noted in Mildvan's laboratory during the operation of nearby centrifuges, the effects of which are tolerable.

We next measured the magnetic fluctuations at the Charles Center Metro Station in a room 50 feet from the trains and at the same level as the trains. Here, very large fluctuations, up to 24 milligauss, were detected during the departures of trains. Moderately large fluctuations, 2.4 milligauss, were detected on the departure of trains from the next (Lexington) station, 1,200 feet away, probably due to the depth of our location. Interestingly, a 4-car subway train gave about twice the deflection as a 2-car train, which convinced us of the validity of our measurements.

6. Conclusions and Recommendations:

(A) Distances from NMR instruments to subway stations of a half mile or greater cause no problems. Closer distances, down to 300 feet, may be safe, provided the subway is installed as deeply as possible, at least 70 feet below ground, or ideally, 120 feet below ground, as was done at the NIH.

(B) A steel tube or at least a steel cage reinforcement of the concrete should be used and continuously connected throughout the system for maximal electromagnetic shielding.

(C) Shock mounting should be seriously considered to minimize mechanical vibrations. Such vibrations can be transmitted over large distances if the rock formation is appropriate.

A.S. Mildvan
V.P. Chacko

322-50

The British Petroleum Company p.l.c.

BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN

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

Our reference	Your reference	Telephone Sunbury-on-Thames (09327) 6	Date
S/SYB/268/85		2168	30th May 1985

Dear Barry

With the trend in off-line data processing and networked spectrometers continuing in industrial and analytical NMR, we found a pressing need to link our JEOL GX400 output with the extensive VAX network available at Sunbury.

As an interim measure, until the networking is complete, we have effected a simple and efficient transfer method using a floppy disk. The RSX-11 operating system and the RL02 disk drive of the JEOL GX400's DEC 11/23 computer creates disk-based records which are transparent to the RX02 unit under VAX/VMS version 4. A simple command routine (in DCL) employing the DUMP utility restructures the file in order that the complex pairs of the FID record may be accessed with confidence. FORTRAN 77 READ statements using T-format specifiers lift the data from the dumped record. The JEOL software is not violated.

The speed of transfer is not our prime concern because the remote off-line manipulation is submitted as a batch job for overnight computation. However, we do require a method that is safe, reliable and that can be implemented quickly without infringing JEOL software.

Further details of the coding are available on request.

Yours truly

A.I. Grant
Spectroscopy Branch

AIG/TCW

The Ohio State University

Department of Chemistry
140 West 18th Avenue
Columbus, Ohio 43210-1173
Phone 614-422-2251

13 June, 1985

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

Effect of Signal-to-Noise Ratio upon Precision in Peak Width, Position, and Height

Dear Barry,

When the spectral line shape is known, it is theoretically possible to predict the precision in peak width ($\Delta\nu$), position (ν_0), and height (A) from the signal-to-noise ratio (S/N) and number of data points per linewidth (K) for a single data set:

$$P(i) = c(i)\ (S/N)\cdot\sqrt{K} \qquad [1]$$

in which c(i) is a constant which depends upon the line shape and i = A, ν_0, or $\Delta\nu$. Posener (J. Magn. Reson. 14, 121 (1974)) has computed c(i) for simulated absorption-mode Lorentzian and Gaussian line shapes, for P(A) and P(ν_0), assuming that $\Delta\nu$ is precisely known. We have extended the theory to include absorption-mode sinc as well as magnitude-mode Lorentzian and sinc line shapes, and have computed P(i) when all three parameters are initially unknown.

Equation 1 predicts that a plot of P(i) vs. $(S/N)\cdot\sqrt{K}$ should give a straight line of slope, c(i). Although simulated spectra to which noise has been added follow Eq. 1 (see top figure), experimental FT/ion cyclotron resonance (middle figure) and FT/NMR (bottom figure) precisions for these parameters can be significantly poorer (e.g., up to a factor of 5) than the theoretical predictions. In those plots, the straight lines are those predicted by Equation 1, and each data point is the precision computed directly from the variance of 20-30 independent data sets.

Although we do not have a complete explanation of these observations, the discrepancy between predicted and measured precision in peak position could point to noise in the abscissa (i.e., "horizontal" noise) in addition to the usually reported ordinate noise (i.e., "vertical" noise)--perhaps due to timing jitter...? In any case, our results suggest that experimental measurements of Fourier transform spectral line shape parameters may be much less precise than previously suspected, for reasons related to the fundamental nature of noise in the experiment. We are collecting additional data to reduce the scatter in the attached figures.

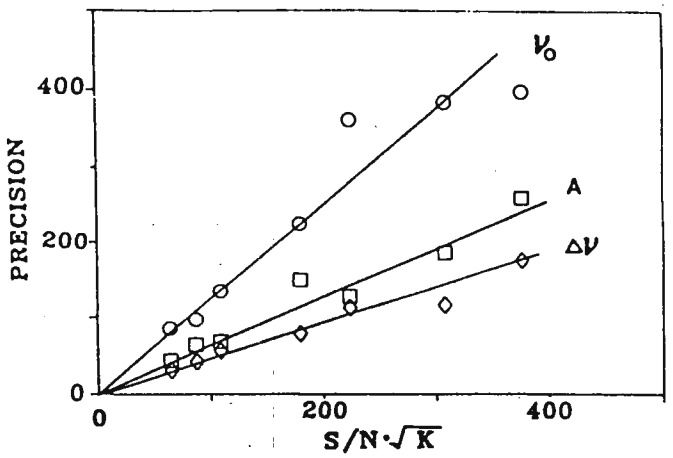
Sincerely,

Alan Marshall Ling Chen Charles E. Cottrell

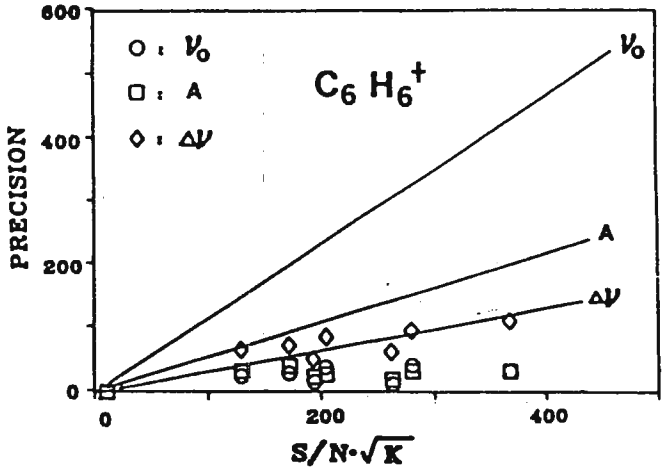
Alan G. Marshall* Ling Chen Charles E. Cottrell

* to whose account this contribution should be credited

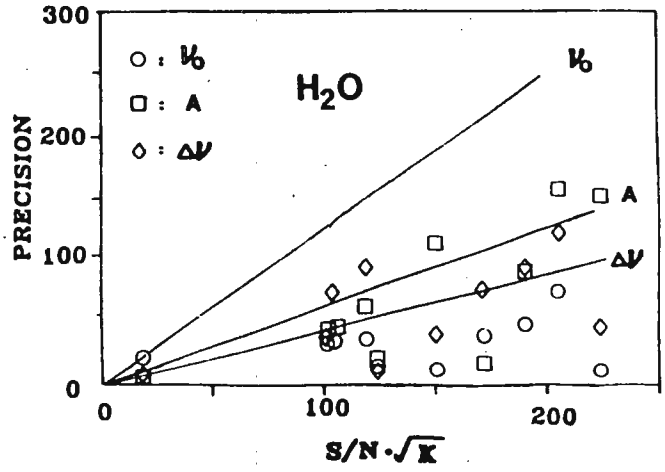
SIMULATED ABSORPTION-MODE LORENTZIAN



EXPERIMENT: FT/MS MAGNITUDE-MODE



EXPERIMENT: FT/NMR ABSORPTION-MODE



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June 10, 1985

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

MAS 2D NMR Detection of Solanesol in Tobacco

Dear Dr. Shapiro:

Your multicolored reminders started arriving a few weeks ago when we were operating at zero field. We had to banish one magnet for recalcitrant behavior and discipline another while a third magnet was just being commissioned. Fortunately, the ranks are returning to service and just in time to do a hasty experiment for the Newsletter.

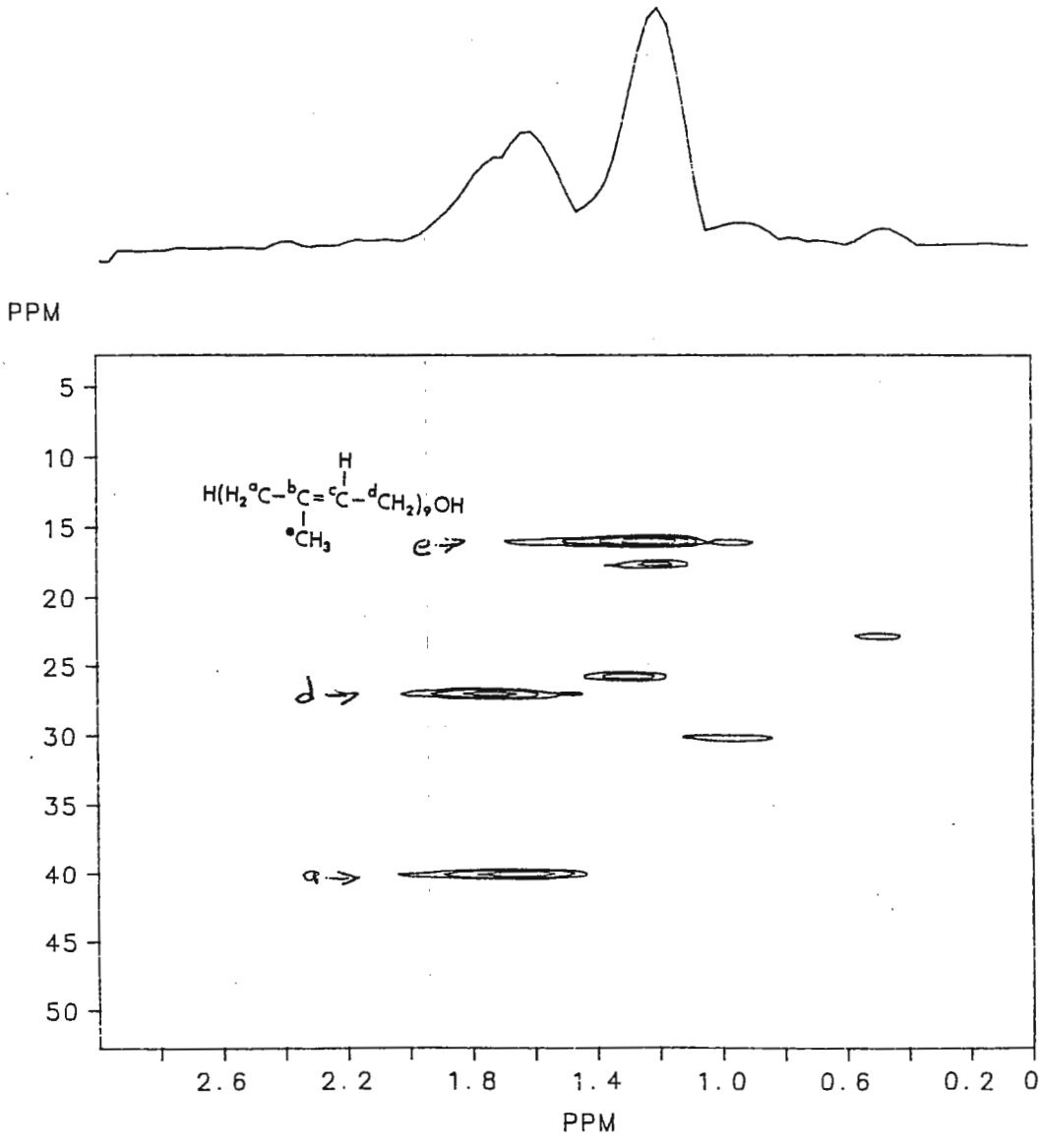
Polyisoprenoid alcohols are nearly ubiquitous in living organisms including higher plants, mammalian tissues and microorganisms. Solanesol is an alcohol containing nine trans-isoprene units that is synthesized in the chloroplasts of the tobacco plant. Some time ago I found that I could detect solanesol directly in the plant tissue by either ^{13}C or ^{1}H NMR if I used magic angle sample spinning to remove the resonance broadening from the variation in the bulk susceptibility within the sample. Even so, the proton linewidths are very broad and badly overlapping at 200 MHz. A considerable improvement in the proton resolution can be achieved by performing a two-dimensional ^{1}H-^{13}C correlation experiment. As shown in Figure 1, the two methylene signals in solanesol and several minor components are easily resolved when exploded by their associated carbon shifts. The unassigned signals may be due to the acyl chains of triglyceride fatty acids which, like the polyisoprene chain in solanesol, exhibit rapid segmental motion that greatly reduces the severe broadening from dipolar interactions and chemical shift anisotropy.

Sincerely,

Jan Wooten

Jan B. Wooten

Figure 1. Aliphatic signals in the ^{1}H-^{13}C heteronuclear correlation 2D spectrum of bright tobacco obtained with magic angle spinning. The spectrum at the top is the projection in the proton dimension.



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DEPARTMENT OF RADIOLOGY
BOX J-374

AREA CODE 904
PHONE 392-8005
Lab 392-3087

13 June 1985

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

Short title: Pulse gradient controller

Dear Professor Shapiro:

We would like to make our inaugural contribution to TAMU NMR Newsletter and briefly introduce ourselves to your readers. Presently our group consists of Raymond Andrew, Jeff Fitzsimmons, Tom Mareci, Kate Scott, one soon-to-arrive post-doc and three graduate students. We have two open positions; one for a spectroscopist and one for a biochemist. Recently our group received an N.I.H. grant (K.N. Scott, P.I.) to establish us as a resource for NMR Imaging and in vivo spectroscopy. We have a Technicare 0.15 T whole-body imager, 2.0 T 31 cm GE-NMR CSI imager/spectrometer and 7.1 T NT-300 high-resolution spectrometer.

We have modified our spectrometers to allow pulse control of x-, y- and z-gradients for either the RT shims or an external gradient system. This allows us to perform both imaging and localized spectroscopy experiments which require pulsed field gradients (PFG). The modification consists of inserting the PFG control circuit, as diagrammed, between the output of the computer controlled spectrometer shim DAC's and the input to the RT shims and/or gradient system. With the select toggle switch closed the control circuit is transparent to the system allowing shimming in the normal manner. With the toggle switched open (PFG mode), the DAC outputs to x, y and z are gated through U3 and U4 dependent on the state of the TTL inputs U, V and W. Three unused shim DAC outputs provide the capability for x-, y- and z-gradients to assume another value or opposite polarity. These are switched by TTL inputs U^1, V^1 and W^1. The TTL gate signals are derived from extra level controls from the pulse programmer thus placing pulsed gradients under direct pulse sequence control (see pulse sequence). Software to control DAC values was written in Nicolet 1280 assembly language and values loaded dynamically before each execution of a pulse sequence. These allow the performance of Fourier imaging techniques (see figures) and several localized spectroscopy experiments. One precaution must be kept in mind. Problems could develop if U and U^1 or V and V^1 or W and W^1 are gated on simultaneously. If any of these pairs are of opposite polarity, the gates could be damaged by induced current flow when the pairs are gated to the "on" state.

We will be glad to discuss the details of this with any interested party. Our programming is specific to the Nicolet 1280 system but this approach should work with most systems with computer control of RT shims.

Sincerely yours,

Tom K.N. Scott

T.H. Mareci, R.G. Thomas, J.R. Fitzsimmons and K.N. Scott

P.S. Please credit the account of T.H. Mareci

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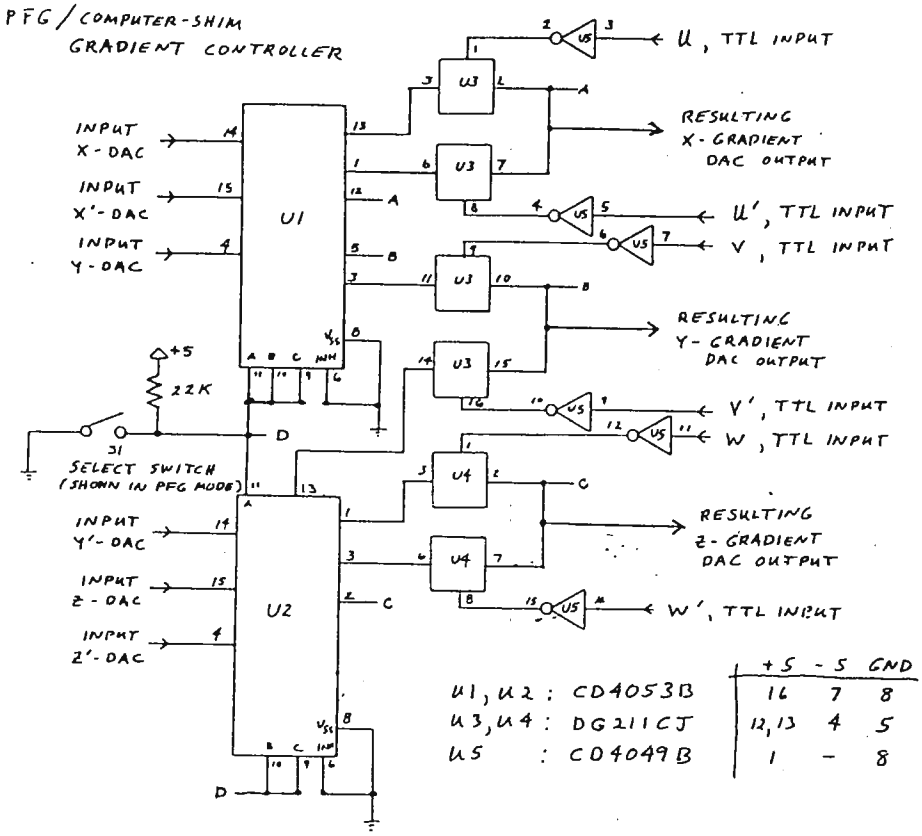

U1, U2 : CD4053B
U3, U4 : DG211CJ
U5 : CD4049B

	+5	-5	GND
U1, U2	16	7	8
U3, U4	12, 13	4	5
U5	1	–	8

Gradient control circuit

Pulse sequence

```
TRANSX
SPIN WARP SEQ W X-GRAD ACQ
#   1: D5
#   2: P1/@A
#   3: D3.U.V,W
#   4: D4
#   5: P1/@B+1
#   6: P2/@B+2
#   7: P1/@B+1
#   8: D8
#   9: A.U
#  10: D2.U  JUMP TO #    1

PHASE A=0
PHASE B=2+S
```

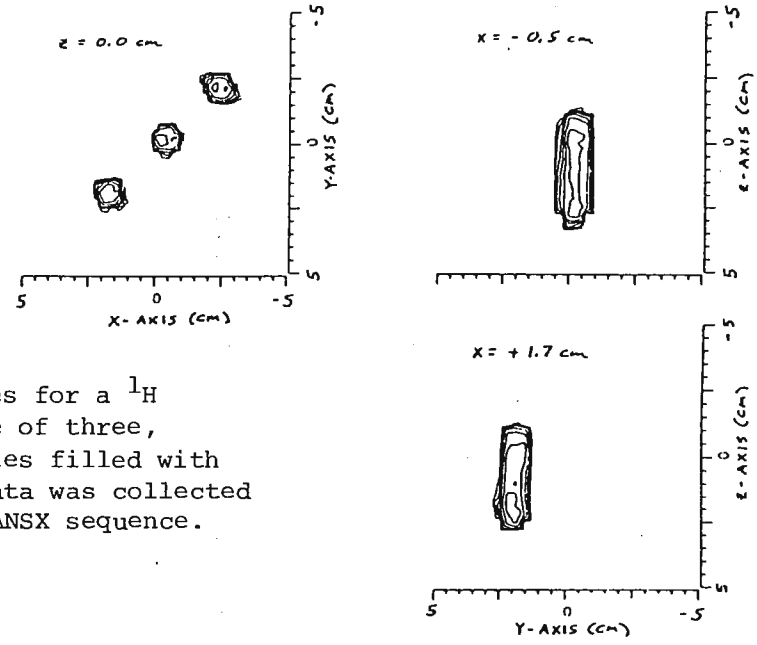

Figure Planar slices for a ^1H volume image of three, 2 dram bottles filled with H_2O. The data was collected with the TRANSX sequence.

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May 28, 1985
HJJ/BHN

Professor BERNARD L.SHAPIRO
Department of Chemistry
Texas A&M University
COLLEGE STATION - Texas 77843-3255
U S A

A High Speed MAS/CP Probe for the Varian XL-300 Spectrometer

Dear Barry,

For the past several months extensive work has been going on in our laboratory towards the design and construction of a high speed magic angle spinning/cross polarization probe for our Varian XL-300 spectrometer equipped with the standard 51 mm bore magnet. We are quite enthusiastic in reporting to you on the successful achievements of (several of) our goals set out for the probe. A report on the failures of some of our ideas is another story.

The spinner assembly uses a cylindrical rotor (7 mm o.d.) with only one end cap which has a cone-shaped top for the air drive. The stator contains a double air bearing system and has a 10 mm hole through its center perpendicular to the spinning axis. This leaves space for inserting the NMR coil (a 4 1/2 turn flattened Cu-wire), a self-supporting coil mounted on a small piece of circuit board. A radial clearance between the rotor and coil of only about 0.1 mm is achieved in this way. The radial clearance between the rotor and stator is 0.015 mm and results in a high stiffness for the air bearing which is considered a critical factor (1). Our present stator (originally intended for nuclei other than ^{13}C) is machined from PMMA and has a thin inner lining of bronze at the two ends constituting the air bearing. For long term time averaging in ^{13}C NMR it may be necessary to employ stators made from Macor of Kel-F although we have experienced no problem with ^{13}C stator CP background even for several thousands of accumulations (probably a profit from the coil hole). Our initial rotors have been machined from Macor (1 mm wall thickness) or delrin and have an optimum NMR active volume of about 0.25 cc. To cope routinely with the highest spinning speeds obtainable we plan to use Al_2O_3 or PSZ (2) cermaics for future rotors. With its present configuration and Macor rotors we obtain speeds of about 5 KHz, which is about the maximum safe speed for this rotor material. However, in routine applications we prefer to operate the Macor rotor around 4 KHz. The spinning speed, which is continuously measured using a light reflection emitter/sensor array, fiber optics, and a frequency counter, is extremely stable, reliable, and routinely obtained. Samples are easily packed and we have had no problems with stator vibrations as a result of unbalanced packed rotors. Apparently the high stiffness of the air bearing and the rather thick-walled rotors prevent the common problems arising from unbalanced rotors. Most importantly, once adjusted the magic angle setting is insensitive to the spinning speed employed (see Fig.2) and sample changes.

Until now we have had the coil double tuned for ^{1}H decoupling/CP at 300 MHz and observation of either ^{113}Cd (66.5 MHz) or ^{13}C (75.4 MHz). With the standard XL-300 amplifiers for solid state NMR we can generate a ^{1}H decoupling field B_{1H} = 16 gauss using approximately 90 watts of power; the 90° pulses for ^{113}Cd (8.5 μsec) and ^{13}C (8.2 μsec) were generated by field strengths of B_{1Cd} = 31 gauss and B_{1C} = 28 gauss and both obtained with 100 watts of power. Using an additional ^{13}C amplifier we have also generated a 90° ^{13}C pulse in 3.5 μsec.

The accompanying figures illustrate the performance and excellent S/N ratios for our probe in ^{113}Cd (350 mg of $Cd(NO_3)_2 \cdot 4\ H_2O$) and ^{13}C (150 mg of hexamethylbenzene) CP/MAS solid state NMR studies.

Sincerely,

P. Daugaard Vagn Langer Hans J. Jakobsen

PREBEN DAUGAARD VAGN LANGER HANS J.JAKOBSEN

1. F.D.Dotty and P.D.Ellis, Rev.Sci.Instrum. 52, 1868 (1981)

2. D.J.Cookson and T.Mundy, TAMU NMR Newsl. 315, 7 (1984).

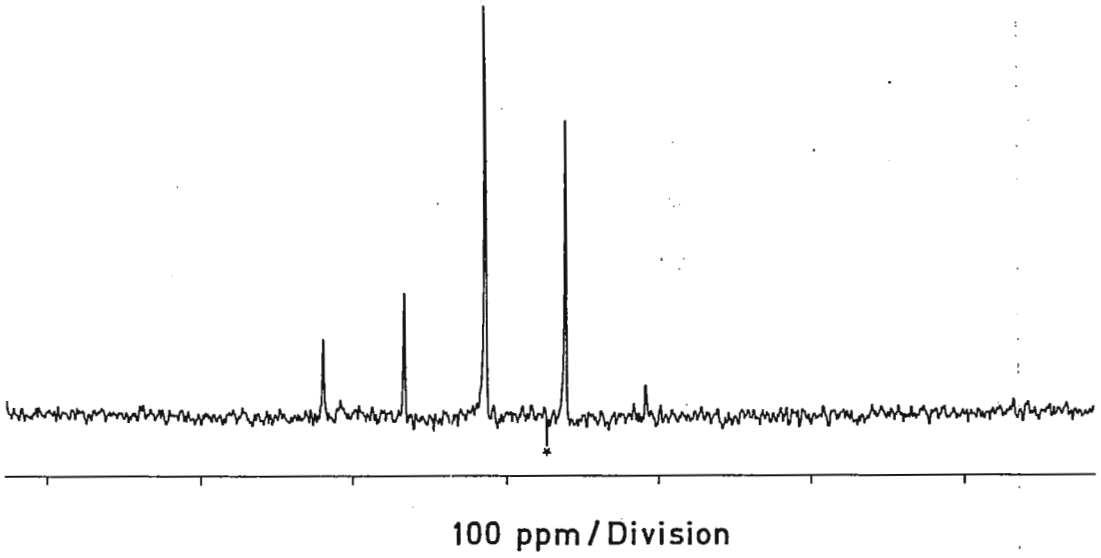

FIG. 1. ^{113}Cd CP MAS NMR spectrum (66.5 MHz) of $Cd(NO_3)_2 \cdot 4\ H_2O$ (350 mg); 1 scan; spin rate 3.5 KHz; (*) indicate carrier frequency.

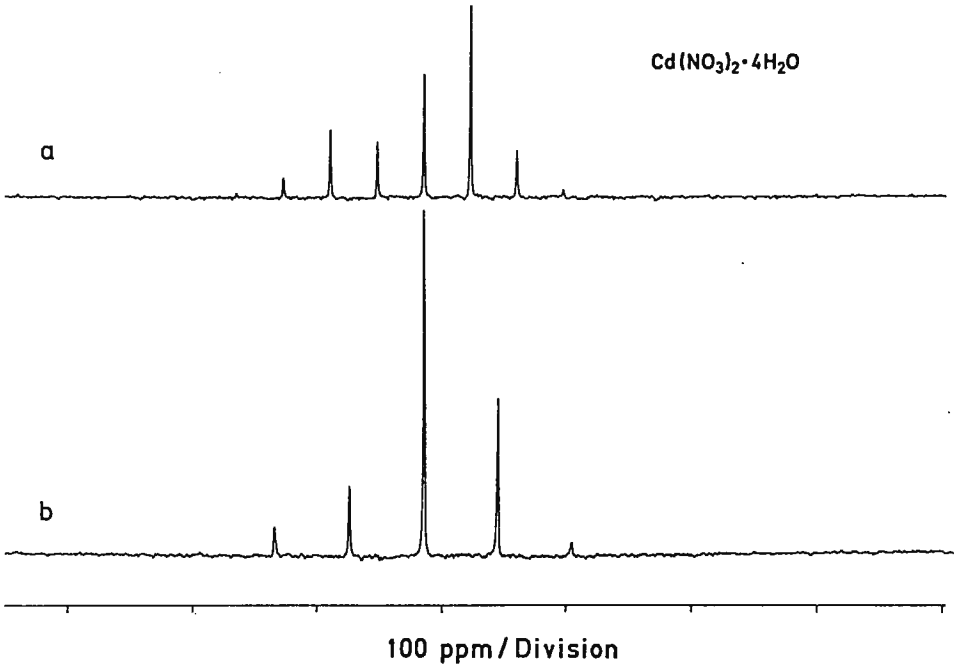

FIG. 2. ^{113}Cd CP MAS NMR spectra (66.5 MHz) of $Cd(NO_3)_2 \cdot 4 H_2O$ (350 mg) obtained in 16 scans. Spin rate (a) 2.5 KHz and (b) 4.0 KHz. Linewidth without linebroadening is 45 Hz; LB = 45 Hz has been applied. No adjustments to the magic angle have been done between the two experiments.

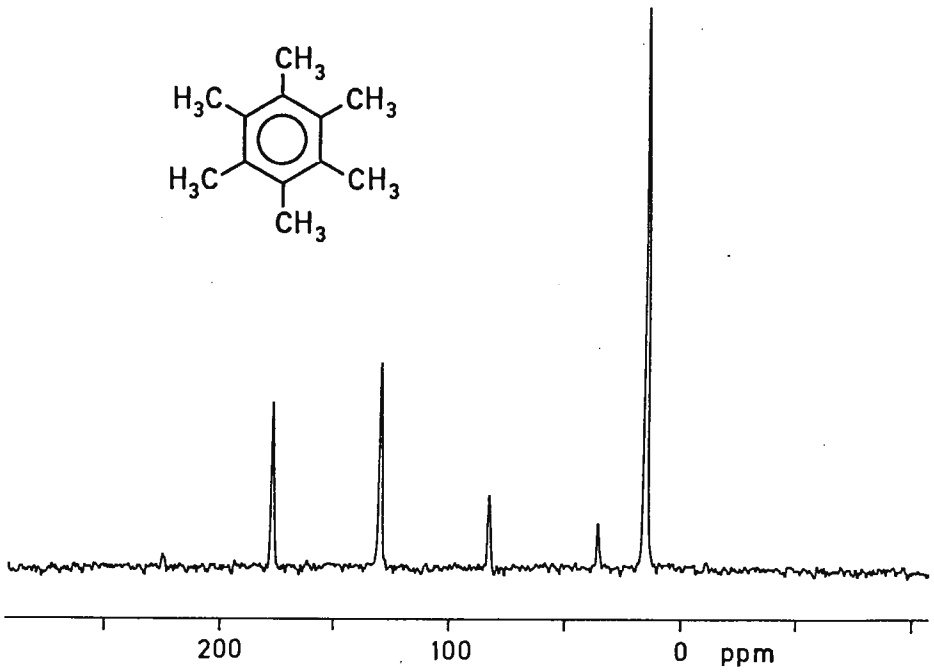

FIG. 3. ^{13}C CP MAS NMR spectrum (75.4 MHz) of hexamethylbenzene (150 mg); 4 scans; spin rate 4 KHz. The S/N ratio based on the CH_3 resonance is about 110:1.

322-64

GRIFFITH UNIVERSITY

Nathan, Brisbane, Queensland, Australia, 4111.

Telephone (07) 275 7111. Telegrams Unigriff Brisbane Telex AA40362

Brisbane NMR Centre
Director: Prof. D. M. Doddrell
Operator/Consultant: Dr. P. Barron

Ref: WB:klj
Please Contact:
Telephone: 2757332

6th June, 1985

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

TITLE: Can you spin-lock a rat?

Dear Professor Shapiro,

Much has been made of the use of variations in relaxation parameters to give contrast in the new field of NMR imaging. Small changes in the clinical state of tissue often result in drastic changes in the relaxation rates of the proton signal arising from such tissue. In our research into applications of NMR to metabolic studies, we have measured ^{31}P relaxation times of the high energy carrying phosphates - phosphocreatine (PCr), adenosine triphosphate (ATP), inorganic phosphate (Pi) and sugar phosphate (SP) - involved with muscle metabolism, in the hind legs of healthy rats. Although T_1's are relatively straightforward to measure, the T_2's of homonuclear coupled systems like adenosine triphosphate (ATP) are not. This is because homonuclear coupling is not refocussed by π-pulses during a spin-echo experiment. Furthermore, the rate of dephasing due to this coupling is of similar order to the estimated spin-spin relaxation rate.

To overcome these problems associated with measuring transverse relaxation we have reverted to measuring $T_{1\rho}$'s - a parameter we believe to be previously unreported in intact tissue for phosphorus metabolites. Of course care must be taken to ensure that the heating effect of the spin-locking pulse is not sufficient to cause hyperthermia.

To measure these parameters, we used a homebuilt probe with a solenoid coil mounted at 45° to the field axis so that larger animals could be fitted into the confines of our 110 mm diameter magnet bore. The high quality spectra obtained from only 8 scans result in each relaxation parameter being determined in a little over an hour.

The interesting upshot of this study was the relative ratio of the ^{31}P relaxation times *in vivo*. For PCr T_1/T_2 was 22 while for the phosphate resonances of ATP it was in excess of 300. $T_1/T_{1\rho}$ was of a similar order of magnitude. The relatively fast transverse relaxation of ATP compared with PCr is paralleled in the other metabolites (Pi and SP) leading to the interesting possibility that by appropriate use of delay times, imaging of phosphocreatine may be possible. This is of particular interest to the study of ischaemic tissue diseases in which it is well known that PCr levels are markedly changed.

Please credit this contribution to David Doddrell's account.

Yours sincerely,

W. Brooks

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

11 June 1985

Dear Professor Shapiro,

AREA MEASUREMENT OF OVERLAPPING BANDS

A recent communication has painted a somewhat pessimistic picture of the use of resolution enhancement methods to obtain accurate area measurements from severely overlapped bands (318-37). This reminded us of some investigations which we pursued about three years ago in connection with the enhancement of U.V. spectra where the lineshape is nearer to Gaussian than Lorentzian. We took simulated bands consisting of a superposition of five lines with intensities and widths as given in the Table, both for Lorentzians and Gaussians. Clearly estimation of the relative areas from the inflection points on the integrals is highly

inaccurate and imprecise for both lineshapes. However by taking the Fourier transforms, applying a resolution enhancing weighting function (either Gaussian-Gaussian or Lorentzian-Gaussian as appropriate) and transforming back it is possible to obtain more reliable valley positions. Given these positions it is then possible to read off from the enhanced integral the relative areas between these points. This, as is seen from the Table, gives relative areas for the Gaussians accurate to about 4% on average with the Lorentzians being somewhat less accurately determined with an average 5% error, due we suspect to the much wider tails of the Lorentzian lineshape causing non equal contributions to the overlap when the relative intensities are very different.

RELATIVE AREAS OF OVERLAPPING BANDS

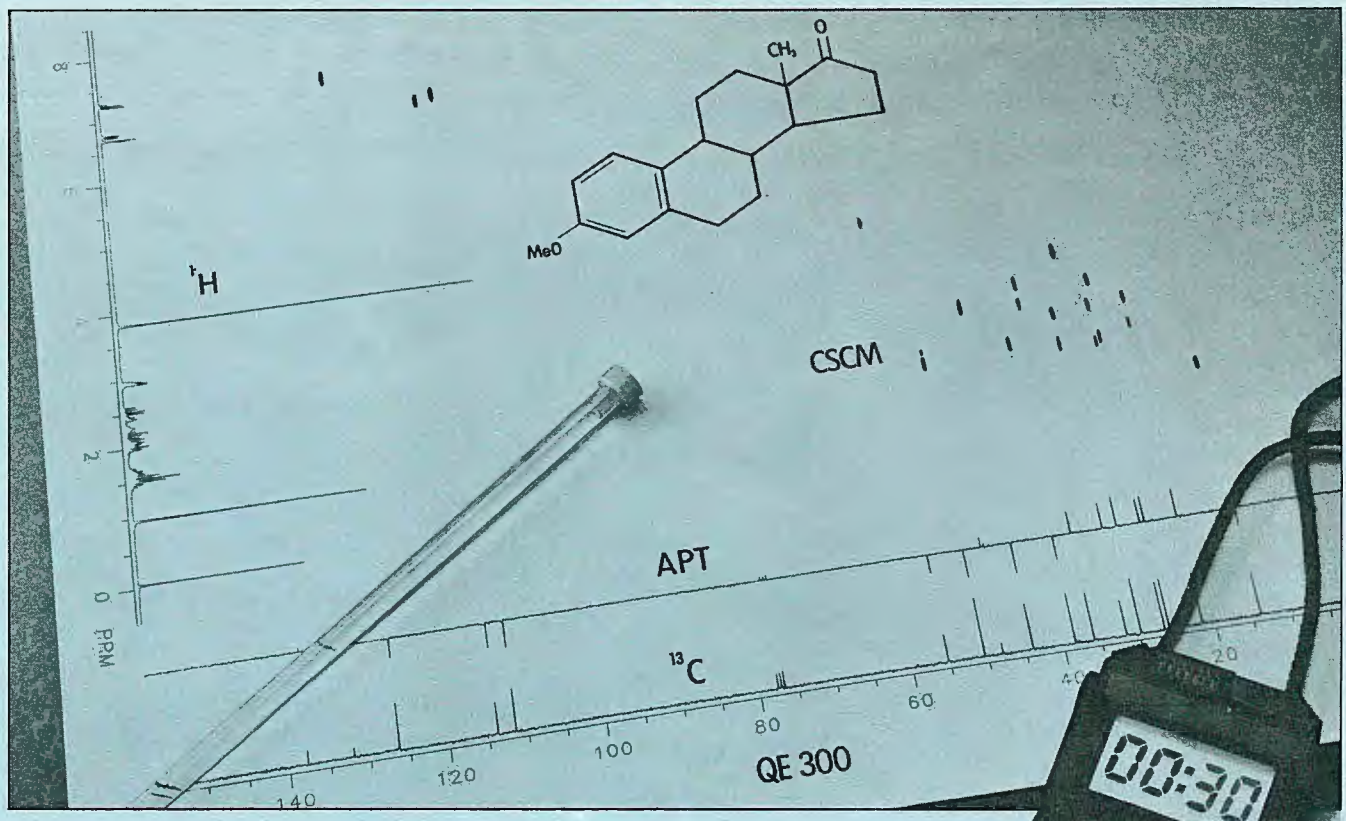
Relative Linewidth	1.0	1.15	1.30	1.45	1.60
True Area	4.00	6.00	5.00	3.00	1.00
Areas from inflections in integral, original Lorentzian	5.13	4.48	4.43	3.10	1.86
Areas from true Valley positions (Lorentzians)	4.31	5.93	4.79	2.89	1.08
Areas from inflections in integral, original Gaussians	3.88	7.10	4.72	2.50	0.81
Areas from true Valley positions (Gaussians)	4.09	6.17	4.90	2.96	0.88

Yours sincerely,

J.C. LINDON A.G. FERRIGE
Department of Physical Chemistry

Enc.

JCL/ag



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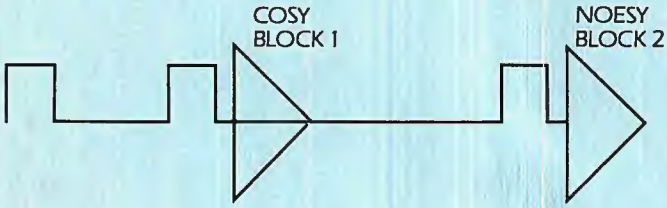

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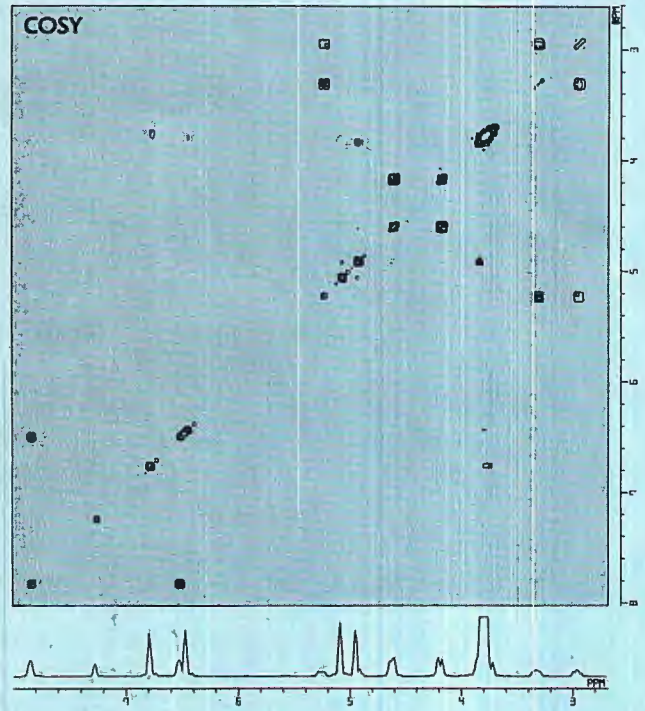

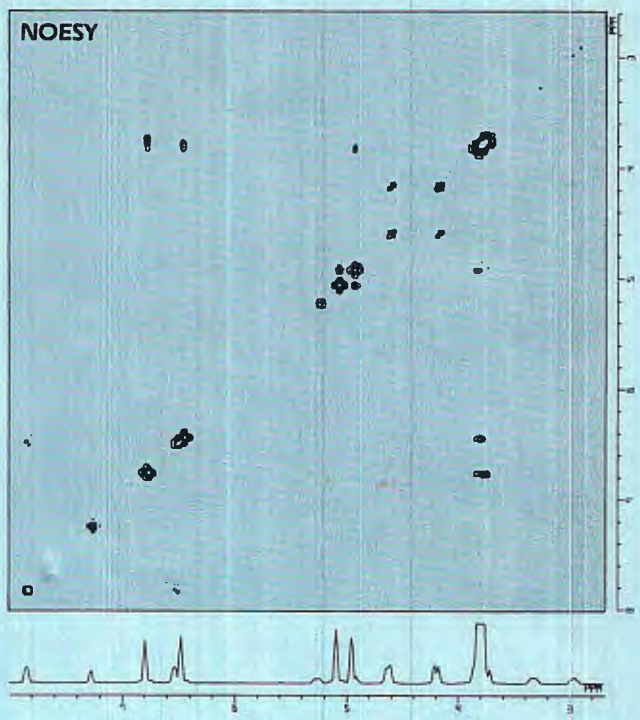

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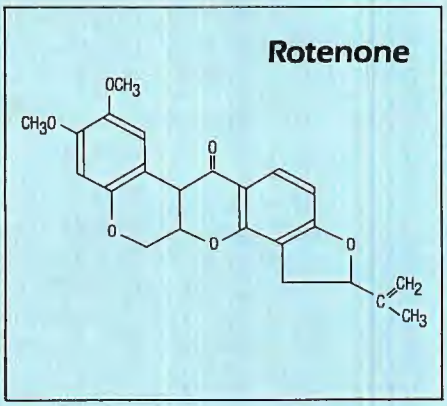
*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])



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