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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,
New Era Enterprises, Hitchin, Hertfordshire, SG1 3SA, United Kingdom.
Second International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds - September 3-6, 1985; Kansas
City, Missouri; Dr. Donald Lawrence, 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., 6290 Center Hill Rd.,
Cincinnati, OH 45242, 513-659-6445.
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 responded to the readership survey card which was inserted into Issue No. 317 (February)? If not, please let us know promptly how many people routinely read, or have the opportunity to see 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
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 F₁ 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 F₁ dimension of the two rival sampling schemes which are commonly used in F₂.

TPPI is used here, simply as a means of implementing "Alternate acquisition" (sometimes called Sequential acquisition) in F₁ while the technique of States et al. is a method which we might call "Pseudo Simultaneous Acquisition" in F₁. If we restrict the discussion to quadrature detection in F₂ 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.

Alternate acquisition uses the same sampling rate as single-phase detection. This similarity 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 not 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.
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\textsubscript{1} dimension there are no analog filters, thus the choice of an optimum pre-acquisition delay in F\textsubscript{1} is a moot point. But since T\textsubscript{1} noise and T\textsubscript{1} ridges (7) may be caused by systematic digitization errors or baseline distortions in the spectra recorded with the first few t\textsubscript{1}-values, presumably the choice of the pre-acquisition delay in F\textsubscript{1} (and possibly even in F\textsubscript{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.

C. J. Turner

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, focused on the detection of solid state Pt-195 and the establishment of suitable instrument parameters for routine acquisition 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 $K_2\text{PtCl}_4$. 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 cannot 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

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$_2$PtCl$_6$. 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$_2$PtCl$_4$ 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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Dear Barry,

I do not know if Mr. Piraro from the San Francisco 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

May 12, 1985

BIZARRO / By Piraro

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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 $(SL_x-60°_x-300°_x-SL_x60°_x-300°_x)_n$ mixing period, where $SL_x$ is a short spin lock pulse (1-5 ms).

Figure 1 shows the fingerprint region (NH-C$_2$H) 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 magnetization 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

Fig. 1 The fingerprint region of a 3 mM solution of ribonuclease in D$_2$O. 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.
May 29, 1985

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843
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 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 $\rightarrow$ ATP flux was approximately 2
fmoles/(cell x sec) at 36°C. It is thus concluded that the in vivo kinetics of $31^c$K 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
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 $-ATP$. $5 \times 10^5$ 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.
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 $-76^\circ C$ 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 $-60^\circ C$, with 20% $D_6$ acetone as lock. The spectra of $F_2C=C=CF_2$ (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

Frank J. Weigert
\[ F_2^{13}C=^{12}CF_2 \]

\[ ^{13}C = 142.7 \text{ ppm} \]

\[ ^{19}F = -134 \text{ ppm} \]

| Isotope shifts of \( F_2^{13}C=^{12}CF_2 \) versus \( F_2^{12}C=^{12}CF_2 \) |
|------------------|-----------------|
| \( ^{13}C-F \)  | -0.1 ppm for \( F_2^{13}C= \), -0.05 ppm for \( ^{12}CF_2 \) |

\[ ^1J^{13}C-F = -268.3 \text{ Hz} \]

\[ ^2J^{13}C-F = +50.5 \text{ Hz} \]

\[ J_{F-F \text{ Trans}} = -111.4 \text{ Hz} \]

\[ J_{F-F \text{ CIS}} = +73.3 \text{ Hz} \]

\[ J_{F-F \text{ GEM}} = +124.0 \text{ Hz} \]

---

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 77843-3265

Re: MULTINUCLEAR SELF-DIFFUSION COEFFICIENTS

Dear Barry,

Thank you very much for your recent pink "Reminder"; a "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
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:

\[
\text{CH}_3-O-P-O-\text{CD}_3
\]

\[
O-\text{CH}_3
\]

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:

\[
A_1 = A_0 \text{ exp} \left( -\frac{\gamma^2 G^2 D}{2} \right)
\]

where the A's are the echo intensities, \(\gamma\) the gyro-magnetic ratio, G the gradient strength, D the self-diffusion coefficient and \(\beta\) is a time variable related to the gradient pulse length and the time between the 180° and 90° pulses. The equation suggests a dependence on the nucleus of \(\gamma^2\). This is seen in the figure where the log intensity is plotted against \(\gamma^2\). 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.
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Quadrupole Coupling Constants (?)

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

\[ R_1 = \frac{3}{2} \left( \frac{e^2 q Q}{h} \right)^2 \left[ J_1(\omega_0) + 4J_2(2\omega_0) \right] \]

where \( R_1 \) is the measured relaxation rate, the spectral density functions \( J_1 \) and \( J_2 \) contain the desired motional information and \( (e^2 q Q/h) \) 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 \( \omega_0 \) (or \( 2\omega_0 \)) 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 \[ 1 - (163/190)^2 \approx 26\% \] 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,

Robert L. Vold
Regitze R. Vold

P.S. We have just installed in our lab a CI200 computer from Celerity Computing, Inc. This machine runs UNIX Fortran at ~2.5 times the speed of a VAX 780.
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
CP/MAS OF QUADRUPOLAR NUCLEI

April 10, 1985

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

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 $(1+1/2)$ 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 $90^\circ$ pulse for the first case (maximum signal amplitude) gives a $180^\circ$ pulse for the second case (zero signal amplitude).

The mineral kerinite, Na$_2$B$_4$O$_6$(OH)$_2$•3H$_2$O, 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 than 0.2 MHz. Variable pulse width measurements on aqueous
NaBH₄ and solid kernite at \( \omega_{rf} = 3.35 \times 10^5 \text{ rad/sec} \) 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 \( \omega_{rf} \) (B-11) with \( \omega_{rf} \) (H-1) = 2.42 \( \times 10^5 \) rad/sec and a contact time of 0.5 millisecond from \( \omega_{rf} \) (B-11) = 0.6 \( \times 10^5 \) to 4.1 \( \times 10^5 \) rad/sec. At \( \omega_{rf} \) (B-11) = 2.20 \( \times 10^5 \), only the tetrahedral borons are observed, whereas at \( \omega_{rf} \) (B-11) = 2.61 \( \times 10^5 \) and 1.31 \( \times 10^5 \) 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,

D. E. Woessner
Senior Research Associate

DEW:dpj
Attachment
cc: E. L. Jones
J. T. Nipper
P. M. Wilson
Central File (602-815)
Woessner: CP/MAS of Quadrupolar Nuclei (cont'd)

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

\[ \omega_{rf}(\text{B-11}) = 1.31 \times 10^5 \text{ rad/sec} \]

Integral = 5.4 units

\[ \omega_{rf}(\text{B-11}) = 2.20 \times 10^5 \text{ rad/sec} \]

Integral = 3.0 units

\[ \omega_{rf}(\text{B-11}) = 2.61 \times 10^5 \text{ rad/sec} \]

Integral = 5.1 units

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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.
Dear Professor Shapiro,

$^{31}$P assignment of $d(^{10}$Cp$_{\text{II}}^{\text{Me}}$Cp$_{\text{III}}^{\text{Me}}$G) in Z form.

In this letter we want to describe some $^{31}$P experiments just done on our new Bruker AM 400 MHz equipped 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 $d(^{10}$Cp$_{\text{II}}^{\text{Me}}$Cp$_{\text{III}}^{\text{Me}}$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 $\tau_M$ 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 DELEPIEIRE.
Figure 1: $^{31}$P spectra at 162 MHz of $d^{(\text{Cp}_{\text{I}}\text{Cp}_{\text{II}}\text{Cp}_{\text{III}})}$ 1 mM helix in deuteroacetate buffer 0.1 M, pH 5.5. Low power heteronuclear decoupling experiments at 47°C. (a) $^1$H selective irradiation at 4.99 ppm corresponding to $\text{G}_{2}\text{H}_3^1$. (b) $^1$H selective irradiation at 4.78 ppm corresponding to $\text{C}_{3}\text{H}_3^1$. (c) $^1$H selective irradiation at 4.64 ppm corresponding to $\text{C}_{1}\text{H}_3^1$. (d) $^1$H off-resonance irradiation for control spectrum.

Figure 2: $^{31}$P spectrum at 162 MHz of $d^{(\text{Cp}_{\text{I}}\text{Cp}_{\text{II}}\text{Cp}_{\text{III}})}$: homonuclear two dimensional $^{31}$P-$^{31}$P chemical exchange in a mixture of 30% ethanol and deuteroacetate buffer at 5°C. The mixing time $\tau_m$ was 700 msec and recycle delay 2 seconds.
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, \( a_x, a_y, a_{-x}, a_{-y} \), has the effect to turn all magnetization from \( z \) to \( z \) for small \( a \) values (linear system approximation) where as for \( a=90° \), 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:

\[
ax, ay, ax, ay, ax, ay, ax, ay
\]

For \( a=45° \), this pulse leaves \((13+2\sqrt{2})/16=99.9\%\) 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 \( H_0 \) field and gives rise to a broad hump in the spectrum with an amplitude of \( \sim 0.2 \% \) 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 \( H_0 \) region.

Fortunately, the rf field strength in the inhomogeneous \( H_0 \) region is significantly lower than inside the resonator and our new pulse \( 90x, 90y, 90_{-x}, 90_{-y} \) 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 \( H_0 \) 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

![Diagram](image)

**Fig. 1** (a) 500 MHz spectrum of angiotensin-II in H$_2$O, obtained with presaturation of the H$_2$O with a 12 Hz rf field. (b) Spectrum obtained under exactly identical conditions as (a), but with the 90°, 90°, 90°, 90° excitation pulse. Signals from 'low rf field strength regions' are effectively suppressed by the rotating pulse.

![Diagram](image)

**Fig. 2.** 270 MHz spectra of bacitracin in H$_2$O. (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.
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 kDa monomer and 70 kDa 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 DASWFT [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. Möller, 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 a(9.1 ppm), a(9.5 ppm) and δ(6.5 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 a- 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 study of a hydrophobic chlorophyll-protein, exhibiting resolved chromophore resonances.

Yours sincerely,

Geoff F.W. Searle


Agricultural University/Transitorium, De Dreijen 11/6703 BC Wageningen/The Netherlands/Tel. (08370) 82044/82634
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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 \( \frac{(D_{ij} \text{ in solvent 1})}{(D_{ij} \text{ in solvent 2})} \) versus \( \frac{(D_{ij} \text{ in solvent 3})}{(D_{ij} \text{ in solvent 2})} \). 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\(_3\)CN) below, indicates the inconsistency of the data with a considerable solvent effect on \( D(\text{CH})_{14} \) but small effects on the remaining couplings. For molecules with lower symmetry, similar tests are being developed.

With best regards, yours sincerely

( Peter Diehl )

---

\(^1\) J. Lounila, P. Diehl, Y. Hiltunen and J. Jokisaari, Magn. Reson. 61, 272(1985)
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-anhydrase-catalysed hydration reactions. The principal biological function of the enzyme is the reversible hydration/dehydration of \(\text{CO}_2/\text{H}_2\text{CO}_3\). It also catalyses the hydration/dehydration of acetaldehyde/hydrate at a slower rate.

\[
\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH(OH)}_2
\]

Figure A shows the equilibrium mixture of aldehyde/hydrate formed for 50\,mM 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 \times 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 \(\Delta G\) 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
CH$_3$CHO

CH$_3$CH(OH)$_2$

Buffer

A

B

C

PPM
Suggested Title: Large and (Relatively) Small $^{1}J(^{195}\text{Pt},^{119}\text{Sn})$ 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 $^{1}J(^{195}\text{Pt},^{119}\text{Sn})$ 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 hybridization arguments.

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

Sincerely,

[Signature]
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).

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**

<table>
<thead>
<tr>
<th>(C_{10})</th>
<th>(^{13})C ppm</th>
<th>(J_{10-11}) Hz</th>
<th>(J_{10-14}) Hz</th>
<th>(J_{11-14}) Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{10})</td>
<td>129.3 ppm</td>
<td>58.0 Hz</td>
<td>0.0 Hz</td>
<td>7.3 Hz</td>
</tr>
<tr>
<td>(C_{11})</td>
<td>132.5 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{14})</td>
<td>129.0 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{13}\)C incorporation

92\% on 10, 11 and 14 each

Sincerely yours,

Irene Hornung, Rob van der Steen, Fons Lefeber, Cees Erkelens, Johan Lugtenburg
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David Cowburn
The Rockefeller University
1230 York Avenue
New York, New York 10021-6399
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 adaptation 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 ($\frac{3}{2}, -\frac{3}{2}$) 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 solid-state signal is factor $4(1+1)/3(1+\frac{1}{3}) = 35/9$ 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 ($\geq 9.4$T) is sometimes also mandatory for certain samples.
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
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). In the 1D spectrum (Fig.1) the signals from H-20 and Me-18 appear as singlets (linewidths 2.5Hz and 2.2Hz, T1's 0.5s and 0.3s respectively). Although the dihedral angle between the vicinal H-20/H-14 is approximately 90°, 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.

A 2D COSY spectrum also allows accurate assignment of the chemical shifts of overlapping multiplets, e.g. H-7eq, H-3ax, H-14eq, H-5, 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

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 Sorval 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
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 affected a simple and efficient transfer method using a floppy disk. The RSX-11 operating system and the ELO2 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
When the spectral line shape is known, it is theoretically possible to predict the precision in peak width ($\Delta \nu$), position ($\nu_0$), and height ($\Delta$) from the signal-to-noise ratio ($S/N$) and number of data points per linewidth ($K$) for a single data set:

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

in which $c(i)$ is a constant which depends upon the line shape and $i = \Delta \nu$, $\nu_0$, or $\Delta$. Posener (J. Magn. Reson. 14, 121 (1974)) has computed $c(i)$ for simulated absorption-mode Lorentzian and Gaussian line shapes, for $P(\Delta \nu)$ and $P(\nu_0)$, assuming that $\nu$ 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 G. Marshall*  
Ling Chen  
Charles E. Cottrell

* to whose account this contribution should be credited
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Professor Barry Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843  

June 10, 1985  

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.
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 postdoc 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 UP, V DOWN and W. 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 P or V and V DOWN or W and W 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,

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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Figure Planar slices for a $^1$H volume image of three, 2 dram bottles filled with H$_2$O. The data was collected with the TRANSX sequence.
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Another"

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INSTRUMENT
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$_2$O$_3$ 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 $^1\text{H}$ decoupling/CP at 300 MHz and observation of either $^{113}\text{Cd}$ (66.5 MHz) or $^{13}\text{C}$ (75.4 MHz). With the standard XL-300 amplifiers for solid state NMR we can generate a $^1\text{H}$ decoupling field $B_{1\text{H}} = 16$ gauss using approximately 90 watts of power; the 90° pulses for $^{113}\text{Cd}$ (8.5 µsec) and $^{13}\text{C}$ (8.2 µsec) were generated by field strengths of $B_{1\text{Cd}} = 31$ gauss and $B_{1\text{C}} = 28$ gauss and both obtained with 100 watts of power. Using an additional $^{13}\text{C}$ amplifier we have also generated a 90° $^{13}\text{C}$ pulse in 3.5 µsec.

The accompanying figures illustrate the performance and excellent S/N ratios for our probe in $^{113}\text{Cd}$ (350 mg of Cd(NO$_3$)$_2$ $\cdot$ 4 H$_2$O) and $^{13}\text{C}$ (150 mg of hexamethylbenzene) CP/MAS solid state NMR studies.

Sincerely,

PREBEN DAUGAARD

VAGN LANGER

HANS J. JACOBSEN


FIG. 1. $^{113}\text{Cd}$ CP MAS NMR spectrum (66.5 MHz) of Cd(NO$_3$)$_2$ $\cdot$ 4 H$_2$O (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$_3$)$_2$ • 4 H$_2$O (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.
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 $^3$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 $T_{1p}$'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. $T_1/T_1p$ 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,

[Signature]

W. Brooks

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. $T_1/T_1p$ 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.

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Yours sincerely,

[Signature]

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Please credit this contribution to David Doddrell's account.

Yours sincerely,

[Signature]

W. Brooks

The Wellcome Research Laboratories
The Wellcome Foundation Ltd
BMNC/85/15

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

The Wellcome Research Laboratories
The Wellcome Foundation Ltd
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Professor Bernard L. Shapiro,
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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.

<table>
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<th>Relative Linewidth</th>
<th>1.0</th>
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<th>1.30</th>
<th>1.45</th>
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<td>True Area</td>
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<td>6.00</td>
<td>5.00</td>
<td>3.00</td>
<td>1.00</td>
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<tr>
<td>Areas from inflections in integral, original Lorentzian</td>
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<td>4.48</td>
<td>4.43</td>
<td>3.10</td>
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<td>2.89</td>
<td>1.08</td>
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<td>7.10</td>
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<td>6.17</td>
<td>4.90</td>
<td>2.96</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Yours sincerely,

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

Enc.

JCL/ag
The GE QE-300 does it all—faster than any other NMR spectrometer.

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

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