TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 339

December 1986

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

AUTHOR INDEX ----- TAMU NMR NEWSLETTER, NO. 339, DECEMBER 1986

FORTHCOMING NMR MEETINGS

28th ENC (Experimental NMR Conference) - April 5-9, 1987; Asilomar; Pacific Grove, California; Chairman: Dr. Lynn W. Jelinski, (AT&T Bell Laboratories); For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

8th International Meeting "NMR Spectroscopy" - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V OBN, England. See Newsletter #338, p. 55 for information and application.

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

29th ENC (Experimental NMR Conference) - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

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. 341 (February) ---- 30 January 1987

No. 342 (March) ------ 27 February 1987

INDIANA UNIVERSITY

DEPARTMENT OF CHEMISTRY
Chemistry Building
Bloomington, Indiana 47405
(812) 335-5513

November 4, 1986
(Received November 10, 1986)

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

TITLE IS READER'S CHOICE:

(1) "Soon Your Neighborhood Hardware Store Will Have a More Powerful Computer Than Your 500 MHz NMR Instrument"

(2) "Data Memory Requirements for Fourier Transform NMR in 1987 and Beyond"

Dear Barry:

I quote from an article in the New York Times of August 26, 1986, entitled "New Chip: Vast Power on Horizon": *Perhaps even as soon as next month, a new breed of personal computer will be introduced that is vastly more powerful than any other PC in use today. The new machine will use the Intel 80386 microprocessor, a chip that is likely to be the dominant brain of the best desktop computers at the end of this decade. ...The potential of the chip is so great that its appearance this year signals a major advance in desktop computing. When it is fully supported, the 386 will bring to the average user the same computing power that until now has been associated with mainframes and minicomputers. ...The 386 chip can address much more memory than the current generations of chips - it has a potential capacity of 4 billion bytes (4,000 Megabytes) of main memory and 64 trillion bytes of virtual memory, versus 16 million bytes and 1 billion for the Intel 80286 that powers the PC-AT - it can handle vast databases and other memory-hungry programs with ease.*

I would like to contrast the above example of computer developments with my experience during visits to NMR manufacturers, in connection with the prospective purchase of a 500 MHz instrument. In a nutshell, the manufacturers stated that existing data memory capacity of NMR instruments is adequate for all but "exotic" applications.

Perhaps *now* is the time to do some spectroscopic arithmetic on the subject. In the past, memory cost considerations made such an exercise futile on economic grounds. Today, and even more so tomorrow (=1987) the cost of NMR computer memory *should* become a tiny drop in the large bucket of the half-million dollar cost of a 500 MHz instrument (or even a 300 MHz instrument).

The typical range of chemical shift dispersion on a 500 MHz instrument is about 5,000 and 30,000 Hz for ^{1}H and ^{13}C, respectively. ^{19}F and

(continued on page 5)

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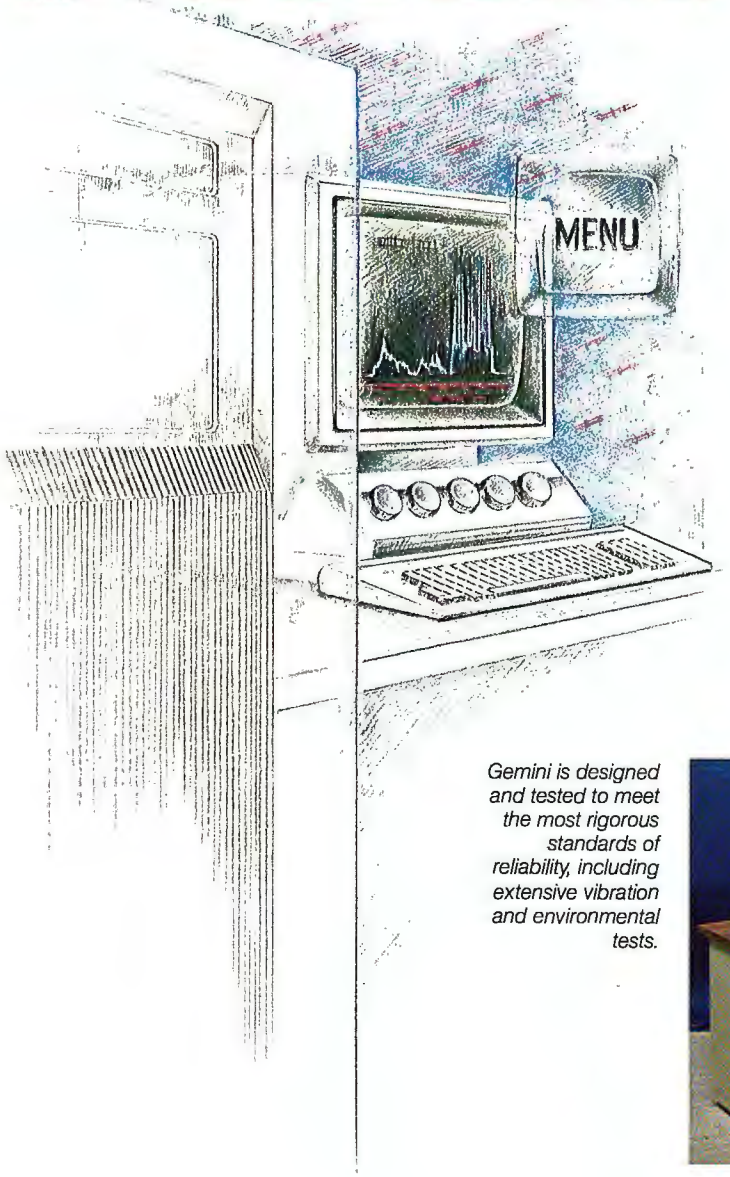

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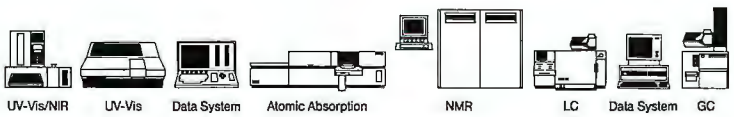

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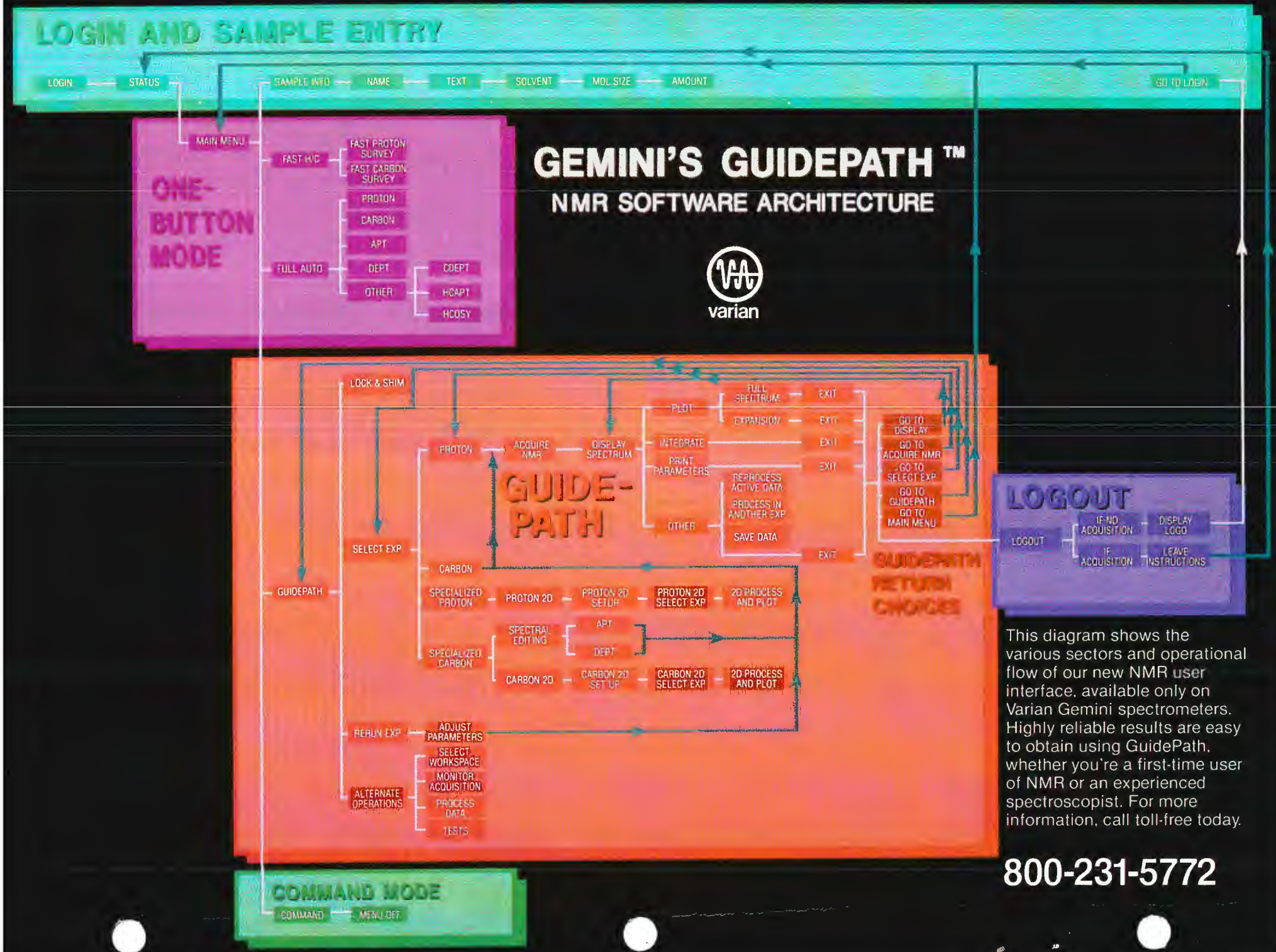

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(continued from page 2)

^{31}P greatly exceed the ^{13}C dispersion (in Hz). The ^{15}N nucleus has a similar range (in Hz) to that of ^{13}C. Therefore, I shall consider here the data memory requirements for ^{13}C NMR on a "500 MHz" instrument (125 MHz ^{13}C resonance frequency). I shall not consider requirements for "ultra-high" resolution NMR, but merely for "ordinary" high resolution NMR.

No one should have to settle for less than 0.1 Hz digital resolution for NMR of spin-1/2 nuclei in liquid samples. This implies 300,000 frequency -domain points for the absorption spectrum, which in turn requires 600,000 data points in the time-domain. Also, a 32-bit word is the minimum desirable for dynamic range purposes. Thus, we are talking about 2.5 Megabytes as a "bare-bones" minimum for data acquisition per spectrum. Furthermore, I believe I can make a convincing case for 2 *Megawords* (8 Megabytes) of data memory for ^{13}C NMR, and 0.5 Megawords (2 Megabytes) for ^{1}H NMR, on the following grounds:

(1) In a recent issue of the Journal of Magnetic Resonance, Delsuc and Lallemand [J. Magn. Reson. *69*, 504 (1986)] show that "oversampling" (dwell time much smaller than required by the Nyquist condition; in other words, much larger spectral width than dictated by chemical shift dispersion) can greatly improve dynamic range for observation of small resonances in the presence of very large ones. In other words, they point out that desired "vertical" digital resolution (per scan) beyond what seems practical now (16 bits) can be substituted by extra "horizontal" resolution, which (as the New York Times illustrates) is quite practical beyond today's NMR requirements.

(2) I have reason to believe that even high-field (500 MHz) magnets are capable of yielding much better homogeneity than manufacturers' specifications. If this is so, 0.1 Hz digital resolution will be inadequate, especially if one wishes to extract T_2 values directly from observed linewidths, which is already feasible at lower fields.[1]

I believe I can back up the above conclusions with more detailed evidence. Please note that the above discussion excludes unforeseen future needs of NMR spectroscopy. Also, it does not take into consideration the advantages of massive data memories for 2D NMR.

Best regards,

Adam

Adam Allerhand
Professor of Chemistry

AA/tam

REFERENCE

[1]A. Allerhand and M. Dohrenwend, *J. Am. Chem. Soc.* 1985, *107*, 6684-6688.

Université de Lausanne — Faculté des Sciences

INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

Place du Château 3, CH-1005 Lausanne (Switzerland)

Dr. Bernard SHAPIRO
Department of Chemistry
Texas A & M University
COLLEGE STATION
Texas 77843
USA

LH/ri/helm 2

October 28, 1986

(Received 6 November 1986)

Concerns : **A Cheap Automatic Control For an Old WP-60**

Dear Professor Shapiro,

In the course of our investigations of slow solvent exchange processes by NMR using an isotopic substitution technique, we needed to record spectra at certain time intervals after mixing of the reacting species. In our case the half-life periods ranged from 26 min. up to 960 hrs ! Our idea was to prepare the sample, put it in the NMR-probe and let the spectrometer work automatically for some hours or days, but we didn't want to tie up our high-field spectrometer for days doing these simple experiments. Thus we decided to use our old 60 MHz (built in 1973) which runs from a BNC-12 computer, but has no automatic facilities.

To overcome this problem we replaced the "stupid" teletype terminal by an "intelligent" Commodore C64 micro-computer and a home-built interface. The C64 now serves as terminal and, in addition, it can be programmed to execute commands in fixed time delays. The limitations are the relatively small number of commands accepted by the BNC-12 and the restricted storage capacity of the floppy diskettes.

As an example, we enclose the result of the exchange of acetonitrile on $Ru(CH_3CN)_6^{2+}$ at 372.8 K. After mixing the normal complex $Ru(CH_3CN)_6^{2+}$ with CD_3CN, ^{1}H-NMR spectra show the increase with time of the intensity of the free CH_3CN signal and the decrease of the bound CH_3CN signal. We fitted the results to well known equations and obtained the following exchange rate : $k_{372.8} = (1.04\pm0.02)\cdot 10^{-5}\ s^{-1}$ ($t_{1/2}$ = 18.5 hrs).

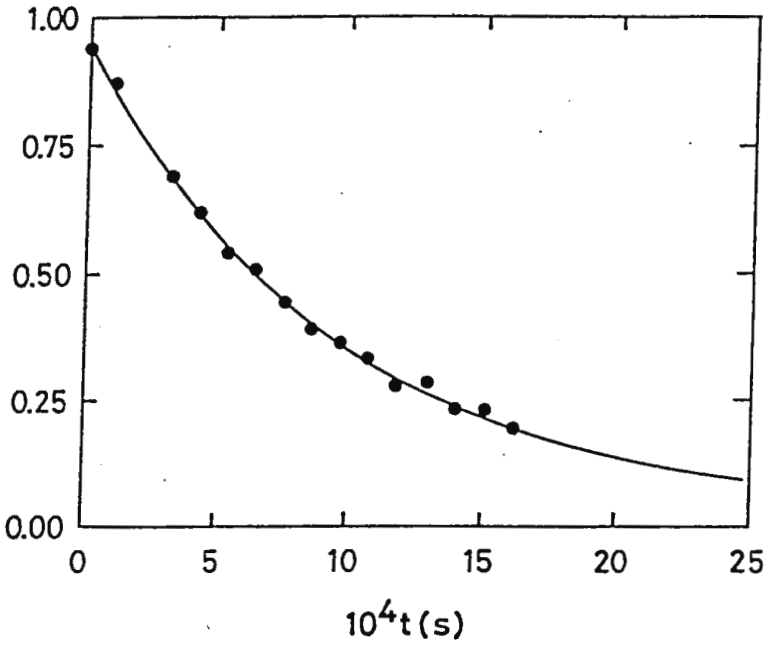
Details on hard- and software will be given on request.

Yours sincerely

I. Rapaport P. Favre L. Helm

P.S. Please credit this contribution to the account of A.E. Merbach.

Figure. Decrease of the mole fraction of the bound CH_3CN with time (T = 372.8 K). The corresponds to the best non-linear least squares fit.



DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF CAMBRIDGE

DIRECT LINE (0223) 333676

Tennis Court Road
CAMBRIDGE CB2 1QW
Telephone: (0223) 337733

17 November, 1986

I have a postdoctoral position available from January, 1987, for 2 years in the field of in vivo N.M.R. The research programme will include ^1H, ^{13}C and ^{31}P spectroscopic studies of cell suspensions and isolated perfused organs. This work will be complemented by imaging studies in intact animals.

Applications are sought from scientists with a background in biological NMR. Salary will be on the U.K. Research Assistant 1A scale. Those interested should send me a full curriculum vitae and the names and addresses of two academic referees.

Yours sincerely,

Dr. P.G. Morris

Lawrence Livermore National Laboratory

November 7, 1986 (Received 25 November 1986)

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

Dear Barry:

After many years we would like to renew our subscription to the Texas A&M NMR Newsletter with this contribution.

We have an interest in determining the homogeneity distribution within low density foam material. Our approach has been to load this material with fluid and use NMR imaging techniques to map the proton density of the fluid throughout the foam. We have made use of the eagerness of commercial instrument manufactures to demonstrate their wares to explore the feasibility of this approach. Figure 1 shows a 2mm slice through a high molecular weight form of polyethylene saturated with duodecanol. The dimensions of the polyethylene was ~4.5x4x4 cm. A white circular duodecanol impermeable plug of ~8mm diameter which extends throughout the material is clearly discernible. This high degree of inhomogeneity was a complete surprise to the polymer chemist.

We have modified a home built 4T, 127mm bore, spectrometer located at Sandia National Laboratory by the addition of commercial gradient coils and driver amplifiers to do small scale imaging. The gradient coils are interfaced to a GE 1280 computer and a 293B pulse programmer by means of an interface system designed along the lines suggested by Dr. Evelyn Babcock at the University of Texas Southwestern Medical School, Dallas, Texas. We are able to obtain 3-4 gauss/cm for each X,Y,Z gradient, but have not yet developed slice selection capabilities. Images are obtained by a 2D echo technique with contour plots for hard copy. Figure 2 is a 2D contour plot of vaseline in concentric cylinders of teflon obtained with a gradient of 2.5 gauss/cm. The widths of the cylinders are 1.6mm with a depth of 3.3mm. This figure illustrates the linearity of the X and Y gradients. Last, but not least, an image of a portion of a chinese chick pea appears in Figure 3. The end of the pod had a bulb with a cracked stem.

If possible, will you please send us copies of the TA&M Newsletter for the entire 1986 year and bill us accordingly. Thanks.

With best regards,

Ray Ward

Ray Ward, Group Leader
Analytical Chemistry, C&MS

RLW:jer
1143R

TITLE: NMR Imaging at LLNL*

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

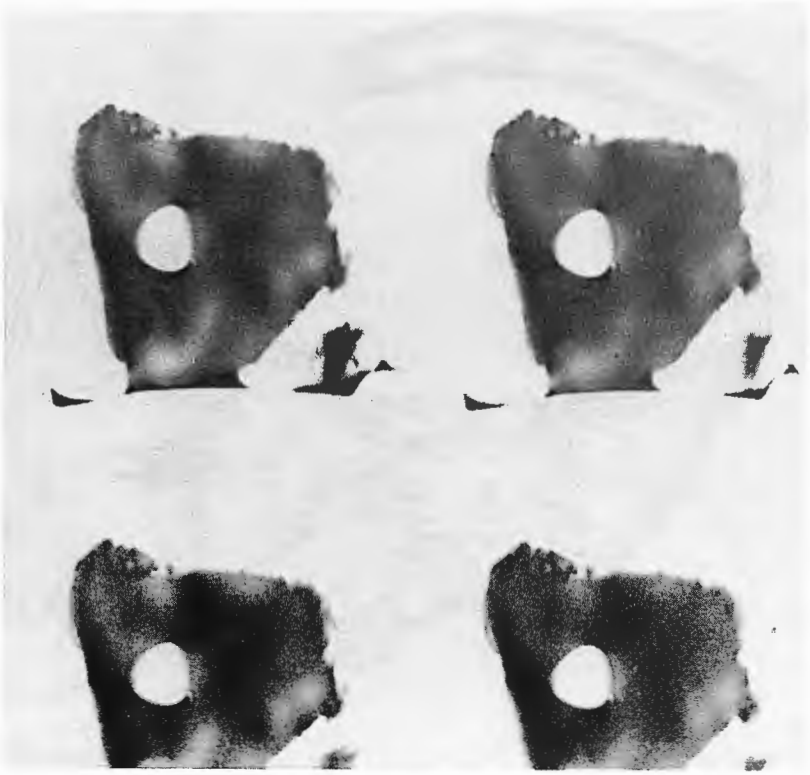


Figure 1 2-3M molecular weight polyethylene foam saturated with duodecanol. A 2mm slice and a FOV of 1cmx1cm, 256x256.

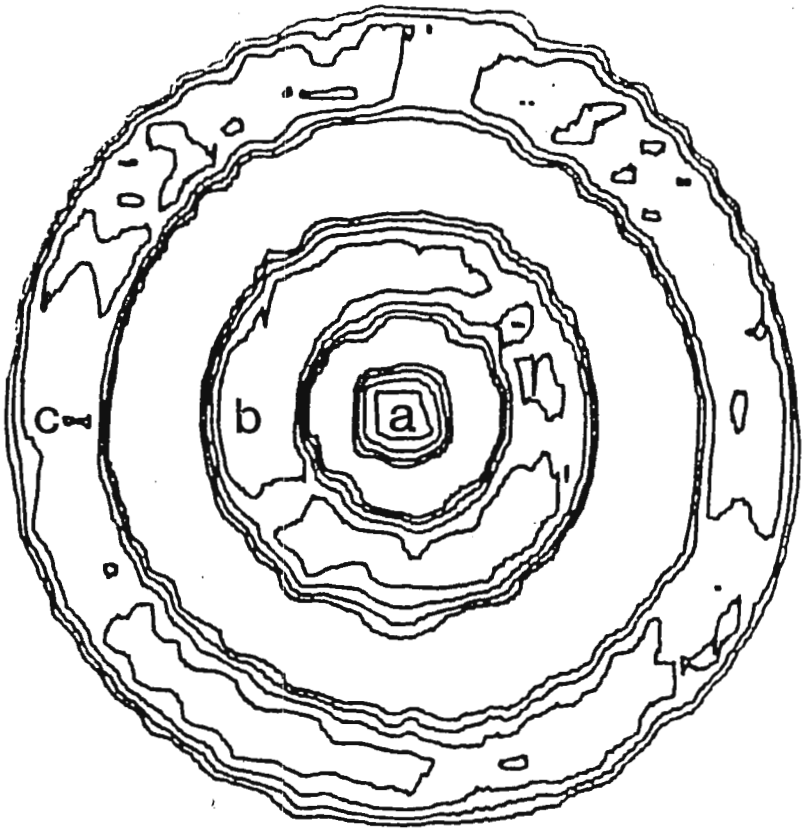


Figure 2 Vaseline in teflon holder, gradient 2.5 gauss/cm, widths 1.6mm, depth 3.3mm.

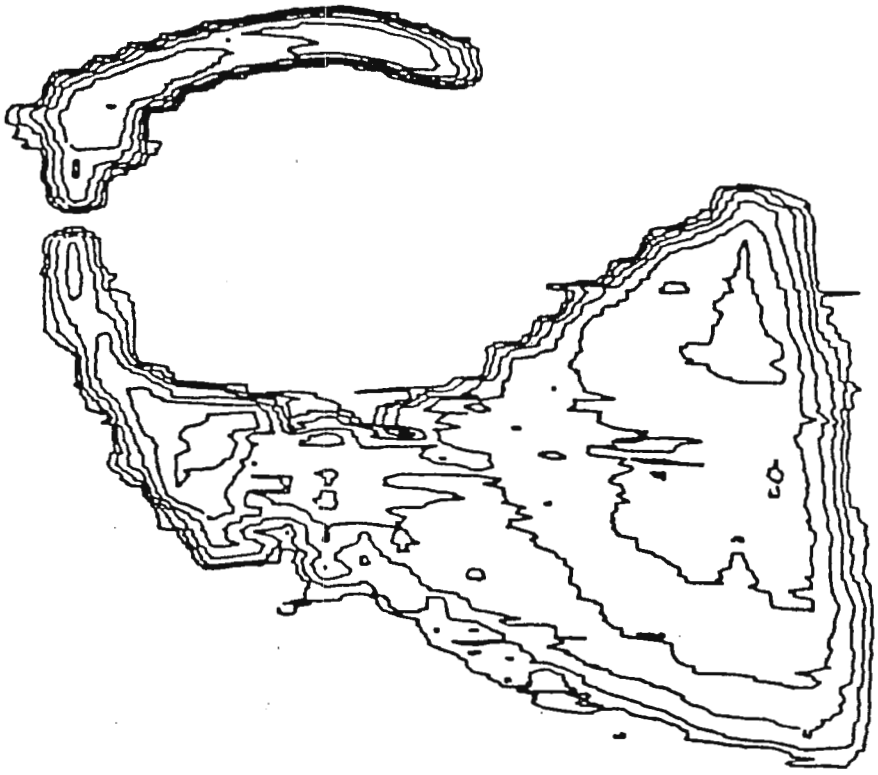


Figure 3 Chinese chick pea at 2.5 gauss/cm. Overall dimensions ~1x1cmx3mm thick.

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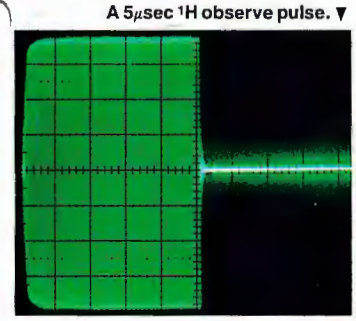
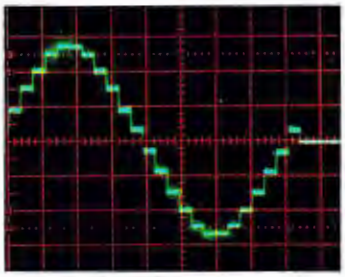


15° phase shift through 360°. ►



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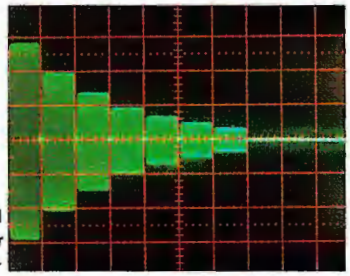
Shaped decoupler pulse. ►



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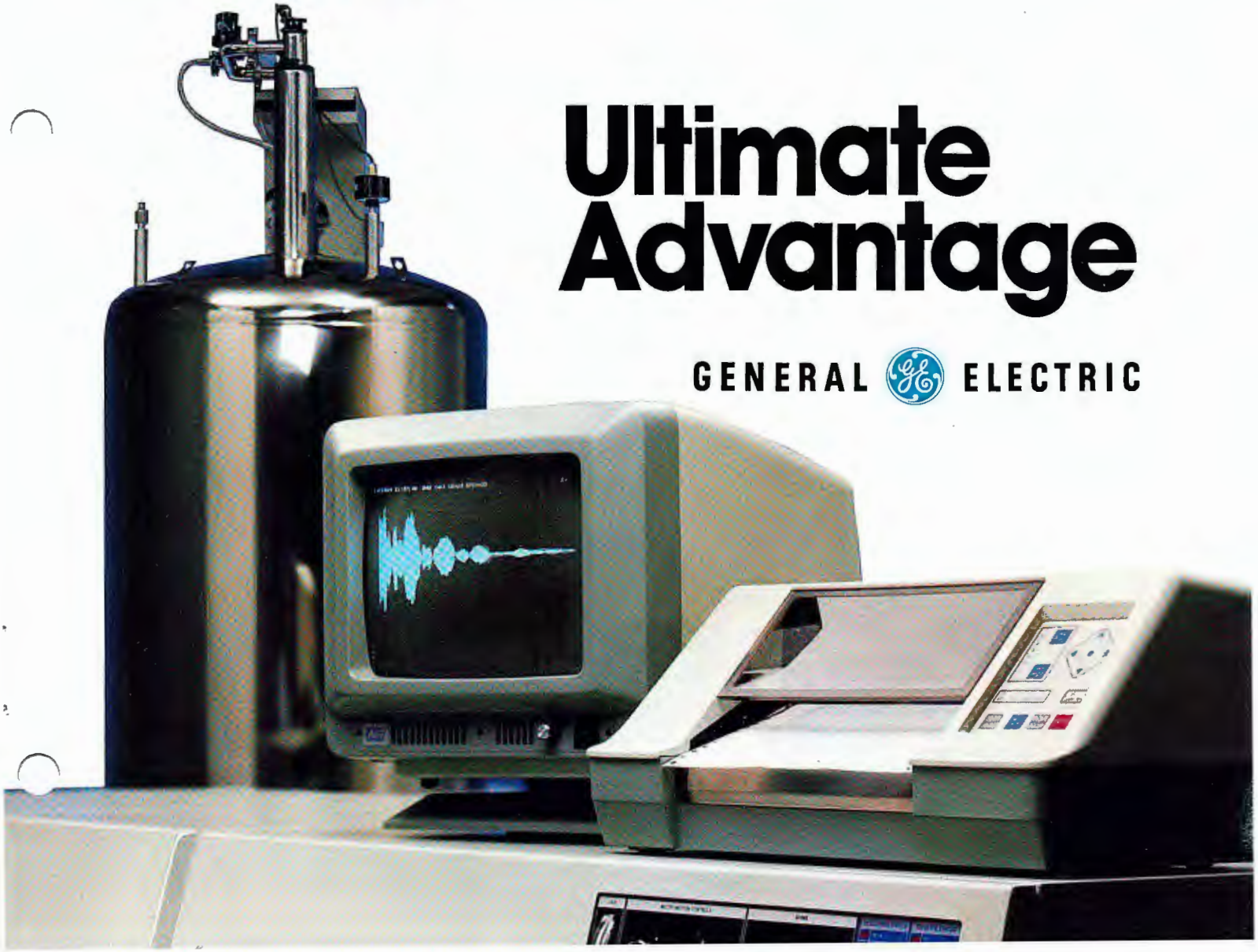

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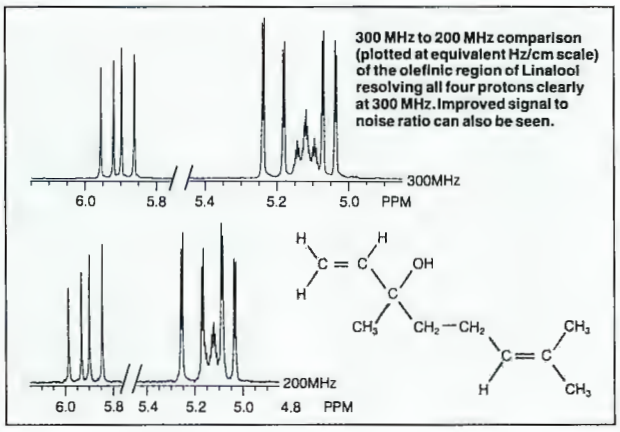

300 MHz to 200 MHz comparison (plotted at equivalent Hz/cm scale) of the olefinic region of Linalool resolving all four protons clearly at 300 MHz. Improved signal to noise ratio can also be seen.

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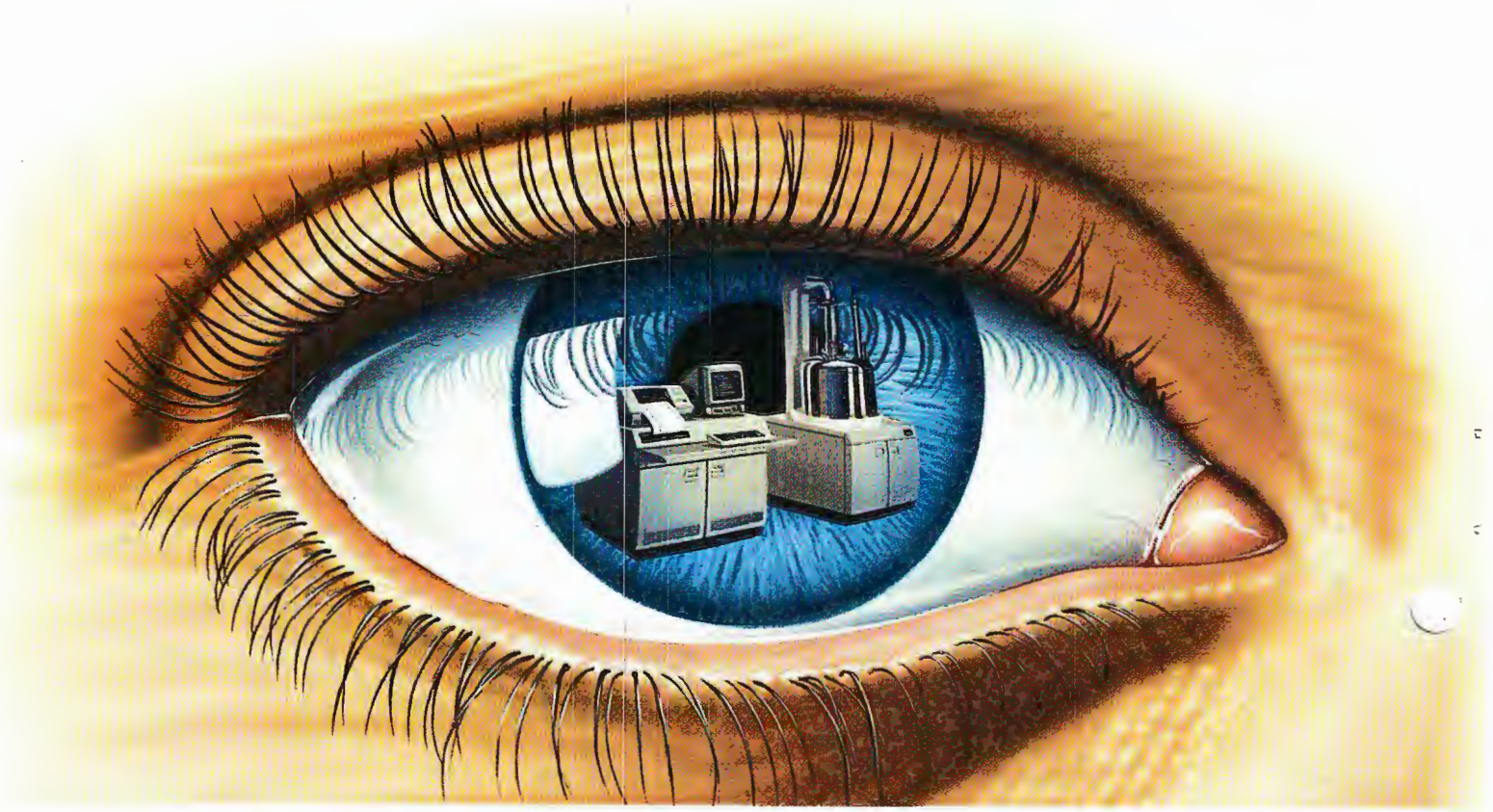

LABORATOIRES DE CHIMIE

Département de Recherche Fondamentale de Grenoble

Grenoble, le 20 octobre 1986
(Received 11 November 1986)

N/référence : DRF/CH/86-169/nb

Professor Bernard SHAPIRO
Department of Chemistry
TEXAS A & M University
College Station, TX 77843
U.S.A

Evaluation of sugar composition and intracellular PH in potato tissue by ^{13}C NMR.

Dear Dr. Shapiro,

Greetings from the Department of Fundamental Research of the Centre d'Etudes Nucléaires in Grenoble France, where I have been spending a most productive six months doing collaborative studies in In Vivo solution and solid state CPMAS ^{31}P and ^{13}C NMR spectroscopy.

In connection with the interest here in Carbohydrate and plant biochemistry we have embarked on a program to examine the effects of different environmental factors on the sugar composition of intact and sectional cores of potato tubers by ^{13}C NMR. As we quickly discovered, the sugar content of this tissue can be easily assesed in the potato tissue in the presence of large amounts of starch as long as the immobility of the starch matrix is preserved i,e, the temperature of the tissue is kept at ambiant.

It is well known that both the maturity and storage conditions of potatoes can influence the relative metabolism of starch to sucrose and the utilization of the latter as a source of glucose and fructose for glycolysis[1]. Thomas and Ratciffe[2] have recently demonstrated that ^{13}C NMR is useful for examining the changes in sugar composition of carrots with storage time.

Here we show two ^{13}C spectra (figure 1) of two different potatoes

Centre d'Etudes Nucléaires de Grenoble, DRF-CH, 85 X, F. 38041 GRENOBLE CEDEX, France.
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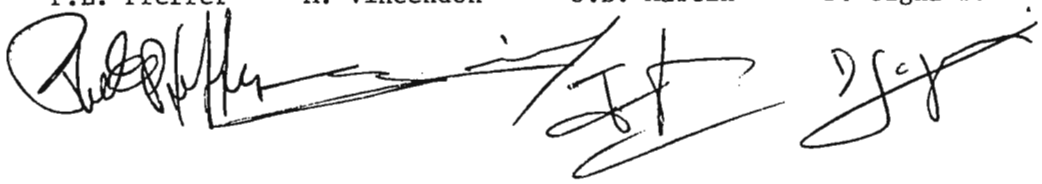
harvested from the same plant, however, stored under slightly different conditions. Spectrum IA shows a clear dominence of sucrose while spectrum IB demonstrates significant hydrolysis of sucrose to glucose and fructose. We also note that many other unidentified compounds whose resonances are on the high field side of the spectrum (IA) have disappeared in IB. In addition to the sugar resonances, we have assigned the peaks at 51.5 and 44.8 ppm to choline (CH_3) and the C_2, C_5 of citrate, respectively, major compounds known to exist in potato tissue[1]. Interestingly enough the citrate resonance shows a respectable PH dependent chemical shift profile (insert fig I) which has potential use for evaluating the intracellular PH environment of such tissue. These spectra, which were taken under anaerobic conditions i.e, no perfusion with oxygenated medium, indicate that the intracellular PH is approximately 5.0. With oxygen perfusion the intracellular PH can be maintained at 7 (δ citrate = 45.8).

Au revoir for now. I will return to the USDA in Philadelphia on Nov. 15, 1986.

Please credit this contribution to Dr. Didier Gagnaire 's account.

Sincerely

P.E. Pfeffer M. Vincendon J.B. Martin D. Gagnaire



References

1) A. Van Es and K-J. Hartmans, "Storage of potatoes"
A. Rastovki, A. Van Es Edit. PUDOC WAGENINGEN 1981 HOLLAND.

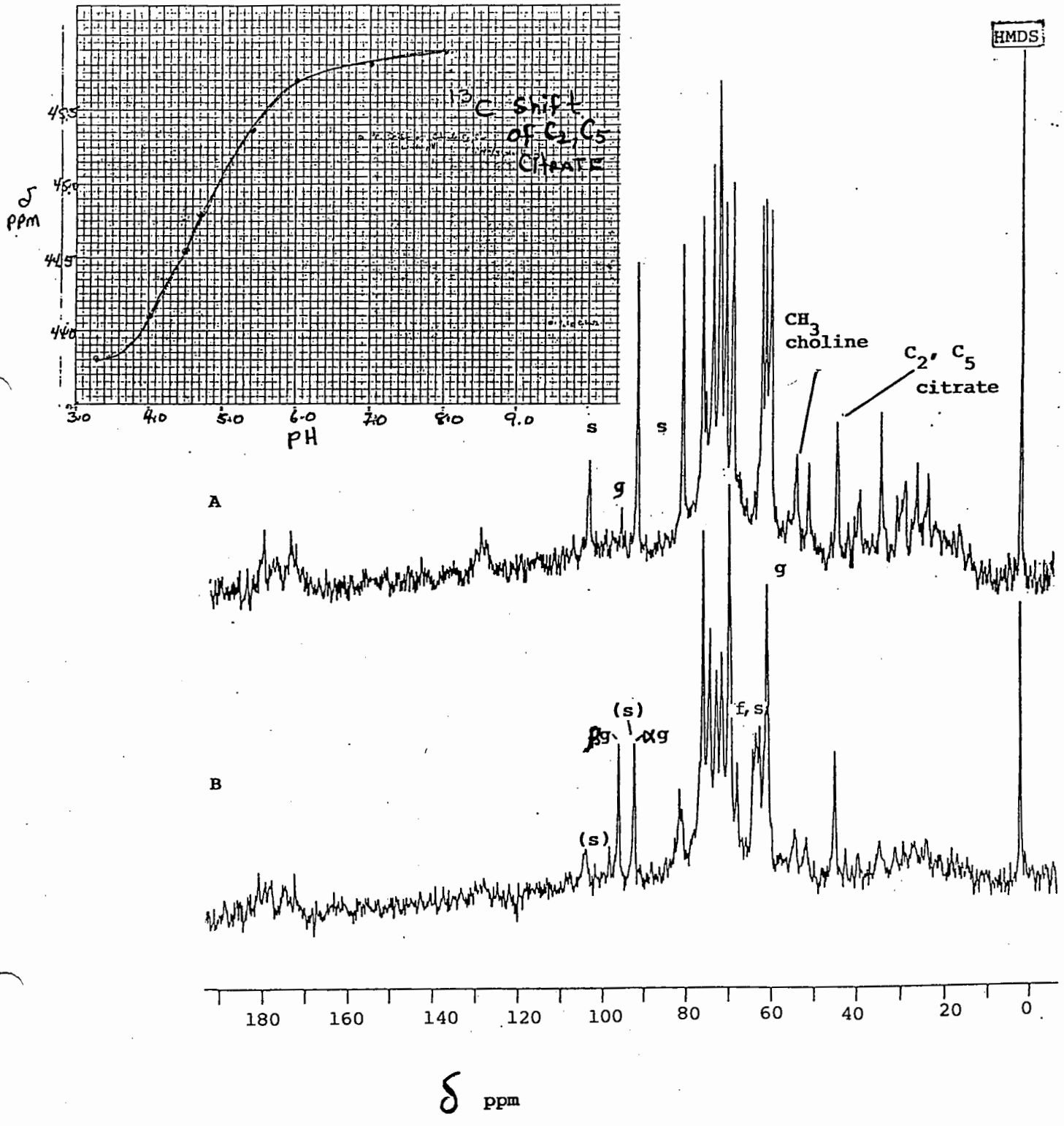
2) T.H. Thomas and R.G. Ratcliffe. Physiol. Plant 63 : 284 (1985).

Figure I. 62.9 MHz proton bilevel decoupled ^{13}C spectra of potato sections obtained in 75 min (15000 scans, 0.30 sec recycle time) in a 15 mm probe.

A) Freshly spring harvested potato stored for 3 weeks at 9°.

B) Another potato from the same harvest after storage 3 weeks at 9° and then at 2° for 16 hours.

S indicates sucrose ; g, glucose and f, fructose. The insert shows the PH, chemical shift dependence of the C_2 and C_5 resonance of citrate.



DEPARTMENT OF CHEMISTRY
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HALIFAX, CANADA
B3H 4J3

October 29, 1986 (Received November 5, 1986)

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

Dear Barry,

RE: CP/MAS ^{13}C nmr spectra of NH_4NCS

In order to obtain the maximum resolution in ^{13}C CP/MAS studies of solids, it is important to set the angle between the applied magnetic field and the spinning axis, β, as close to $54^{\circ}\ 44'$ as possible. Several techniques have been suggested (1,2), one of the most convenient is that of Frye and Maciel (3) who point out that the magic angle can be set by maximizing the intensity of the sidebands of ^{79}Br resonance in KBr.

We have found that carbon nuclei which are directly bonded to ^{14}N often give rise to spectra which are quite sensitive to β. This, of course, is particularly true when the ^{14}N quadrupolar coupling constant, χ, is not much greater than the ^{14}N Zeeman interaction. For example, in the case of NH_4NCS where $\nu(^{14}N)/\chi(^{14}N) \simeq 6.33$ for the MSL-200, one obtains the spectra shown in figure 1. The sensitivity of the observed spectrum to β has been predicted by theory (4-6), in particular, see fig. 4 of ref. 4. Although we do not advocate that one use this method of setting the "magic angle" we felt that the spectra in fig. 1 clearly illustrate that care must be taken in adjusting β if one is attempting to obtain estimates of r_{CN} or χ from observed high-resolution ^{13}C nmr spectra of solids.

Yours sincerely,

Rod

Mike McKinnon

Roderick Wasylishen

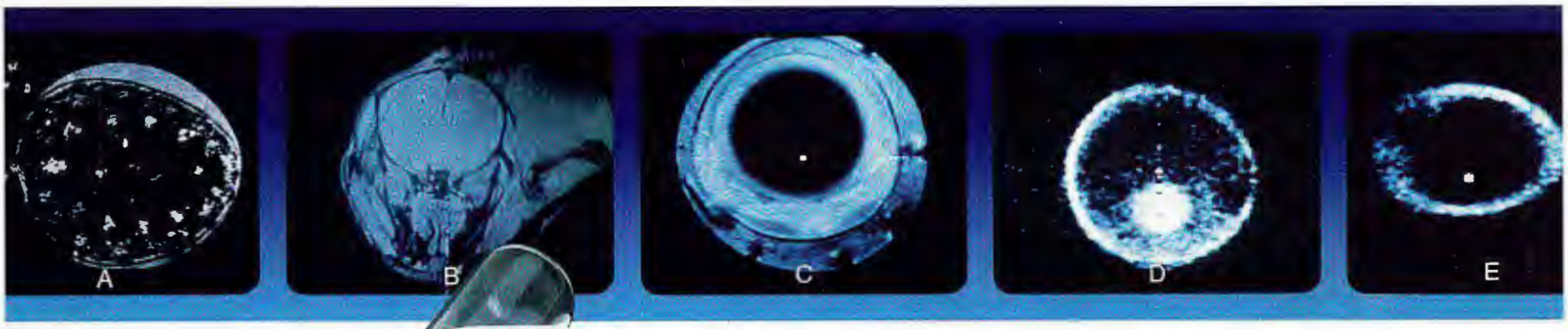
Mike McKinnon

References

1. C.A. Fyfe, "Solid State NMR For Chemists", C.F.C. Press, Guelph, Ontario (1983).
2. D.E. Axelson, "Solid State Nuclear Magnetic Resonance of Fossil Fuels" Multiscience Publications Ltd., Ottawa (1985).
3. J.S. Frye and G.E. Maciel, J. Magn. Reson. 48, 125 (1982).
4. N. Zumbulyadis, P.M. Henrichs and R.H. Young, J. Chem. Phys. 75, 1603 (1981).
5. A. Naito, S. Ganapathy and C.A. McDowell, J. Magn. Reson. 48, 367 (1982).
6. J.G. Hexem, M.H. Frey, and S.J. Opella, J. Chem. Phys. 77, 3847 (1982).

(continued on page 19)

The NMR evolution continues:



New visions through NMR microscopy.

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Fig. A: Cross sectional image of a philodendron stem. Resolution 19μ x 19μ x 300μ.
Fig. B: Cross sectional image of a mouse brain tumor. Resolution 100μ x 100μ x 500μ.
Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution 20μ x 20μ x 250μ.
Fig. D: Image of an ovum from laevis (frog egg). Resolution 10μ x 10μ x 250μ.
Fig. E: Diffusion of water through a piece of nylon. Resolution 50μ x 50μ x 1000μ.

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(continued from page 16)

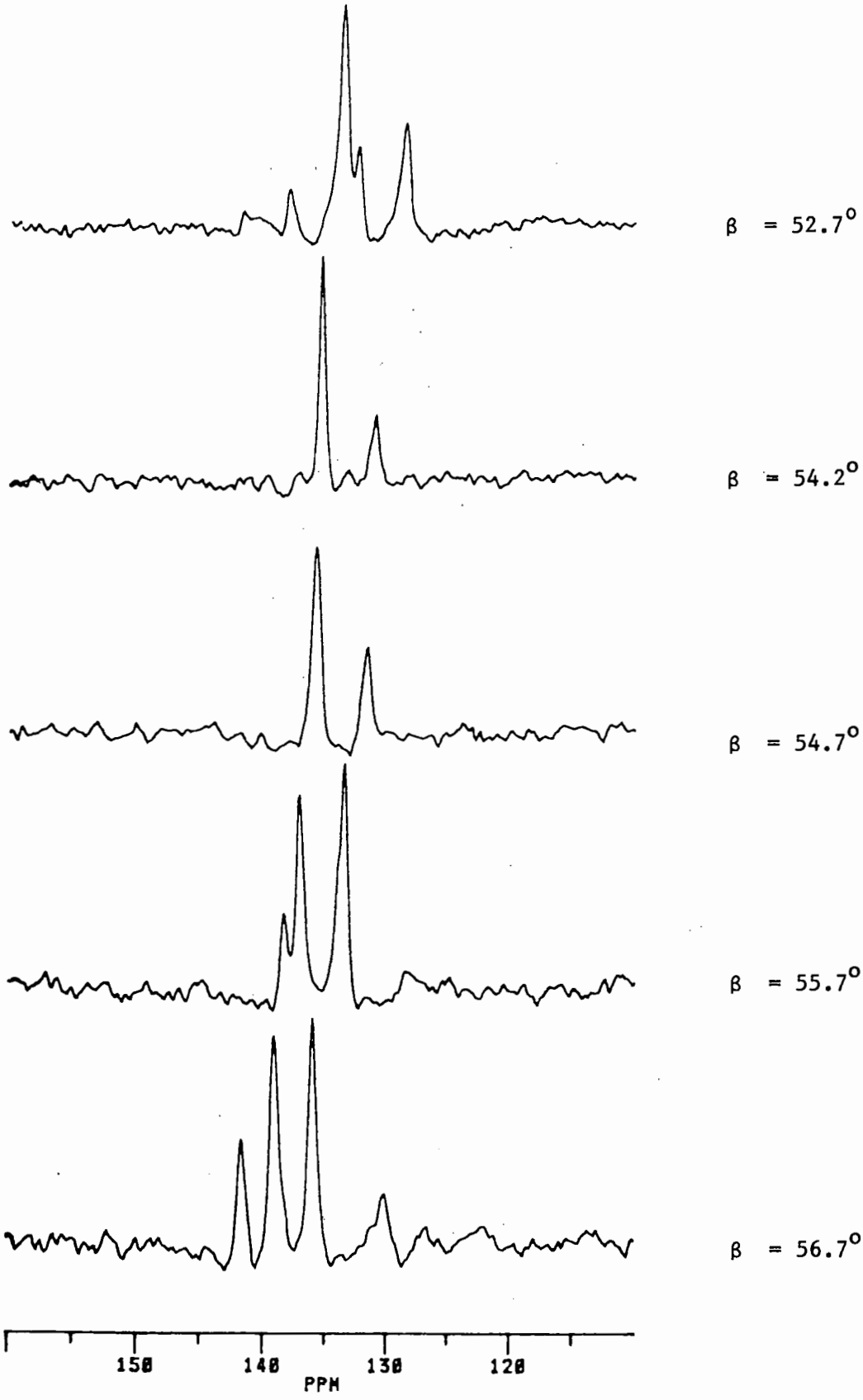

Figure 1. Carbon-13 CP/MAS nmr spectra of NH_4NCS as a function of β. The error in our estimate of β is approximately ± 0.3°.

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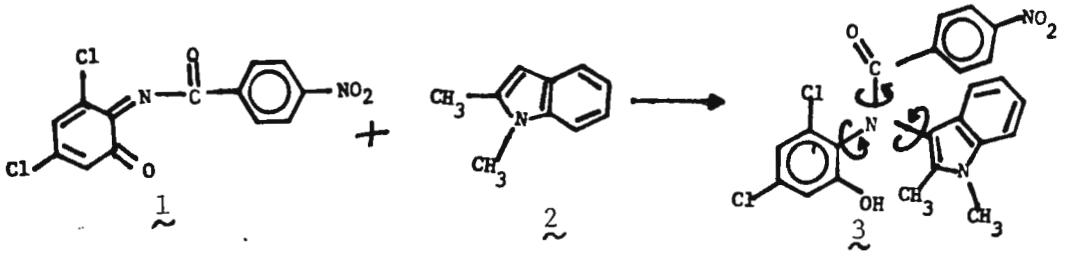
November 5, 1986
(Received 17 November 1986)

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

Title: Observation of Restricted Rotation in Adducts of an o-Quinone Monoimide with Methyl Indoles

We are continuing to use ^{13}C NMR extensively to elucidate the structures of adducts formed by reaction of the o-quinone monoimide 1 with electron rich alkenes. This work, which is conducted in collaboration with



1 2 3

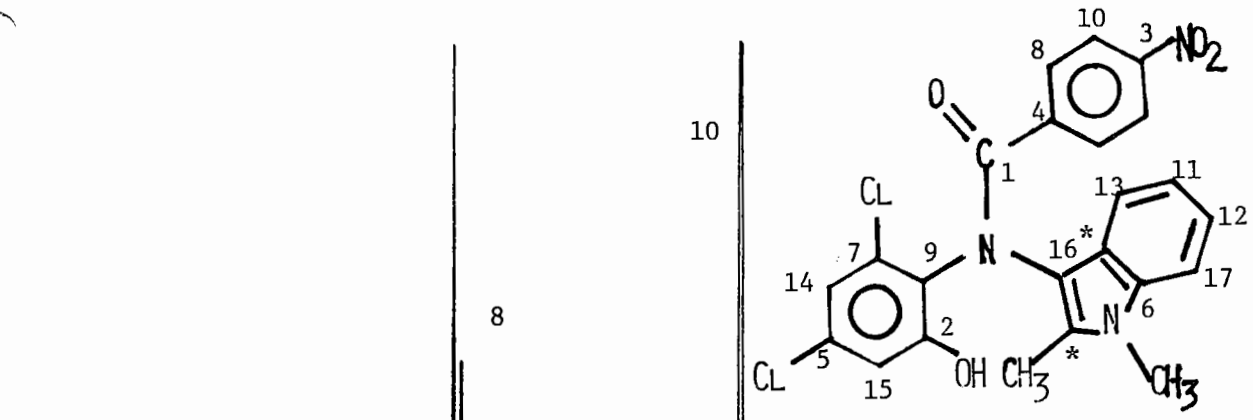
Professor Harold Heine of Bucknell University, has produced some quite sterically crowded molecules which exhibit a variety of conformational and rotational isomers (up to six distinct species in one case). An example is the electrophilic substitution reaction shown above with 1,2-dimethylindole (2). The ^{13}C NMR spectrum (75.4 MHz) of 3 at room temperature is shown in the Figure. Three resonances are resolved for almost every carbon atom in the molecule. These can arise from restricted rotation about the amide nitrogen-carbonyl bond and the nitrogen-aryl carbon bonds (labelled with arrows in 3). At 140°C complete coalescence has not been achieved, and one process is still slow on the NMR time scale. The 2-methyl substituent on the indole ring must be necessary to inhibit rotation since the 2-methylindole adduct behaves identically to 3, but N-methylindole only shows amide isomerism. Some of this work will appear shortly in the Journal of Organic Chemistry.

On another topic - our recently purchased GN-300 with a Chemagnetics CPMAS probe has been installed and is working beautifully. We should have some interesting results for the newsletter soon.

Sincerely,

Paul Donahue Joanne Smith Liz Williams
MATERIALS CHARACTERIZATION & ENGINEERING SUPPORT OPERATION

/ldr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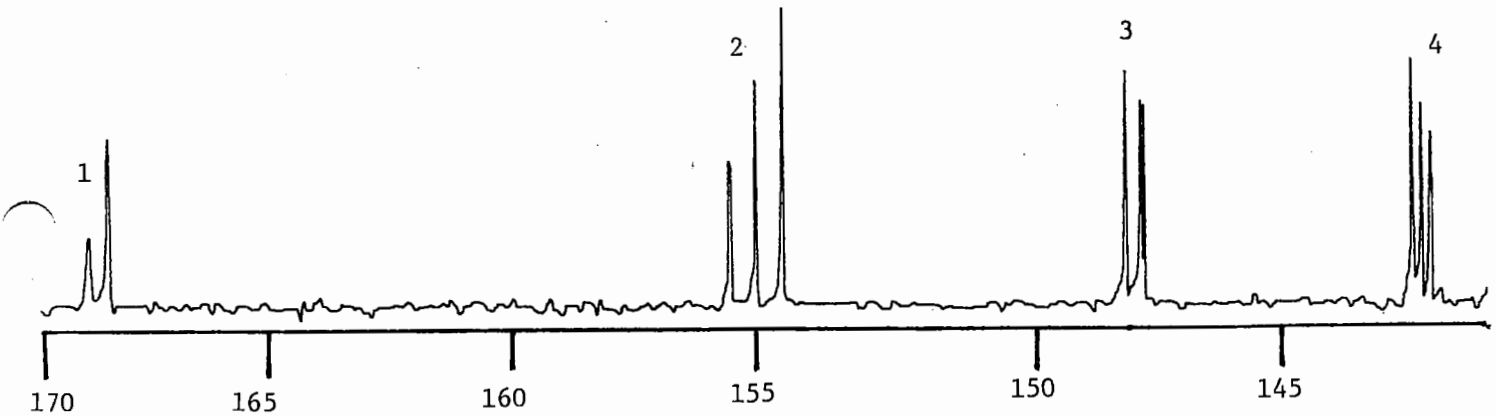
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Naperville, Illinois 60566

November 11, 1986 (Received 17 November 1986)

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

PURPOSEFUL WALKS THROUGH LIOUVILLE SPACE

Dear Professor Shapiro:

Recently we have become interested in modeling multiple-quantum excitation dynamics in large strongly coupled systems of spin-½ nuclei in order to understand the experimental patterns observed in solids and liquid crystals. Any realistic approach to this problem, however, demands that some approximations be made, since an exact solution for N spins requires knowledge of up to N(N-1)/2 coupling constants and the diagonalization of a 2**N x 2**N density matrix. Typically, both analytic and numerical solutions become impossible when N exceeds 6, and even when the system is relatively small, the problem often must be simplified by high symmetry for any such "exact" methods to be practical.

Our approach is to shrug off the complexity by recognizing that "all large systems look alike," at least when the response elicited from them is regarded superficially. For example, the conventional single-quantum spectrum of a dipolar solid (where N is effectively infinity) certainly is complicated, with frequency components corresponding to each of the numerous allowed transitions, but the complexity usually is not obvious in the final product - the well-known "single broad line" or, alternatively, the "featureless blob," which has long inspired the writers of introductory sections of papers on coherent averaging and dilute spin double resonance techniques. The quasi-continuous distribution of frequencies allows the free induction little choice but to decay, for any oscillations are rapidly damped by the interference among the various components. All that remains to characterize the spectrum is perhaps one parameter, say a line width, which summarizes the information contained in the N(N-1)/2 coupling constants.

Accordingly, we are attempting to treat the dynamical evolution of a large system as a universal phenomenon, with any dependence on the actual structure of the material separable from some basic pattern. Before making this approximation, however, we identify the degrees of freedom, i.e., the operators in Liouville space, available to the system and the coherence transfer selection rules rigorously allowed under a particular Hamiltonian. Here the operators may be organized into families of K-spin/n-quantum terms, within which no distinctions need be made. Hence for N spins there are multiple-spin operators containing from K = 1 to K = N angular momenta, connecting states differing by n quanta, where $0 \leq |n| \leq K$. Under the approximation noted above, the evolution of the density operator from one family Kn to another family K'n' can be modeled as a multisite exchange process in Liouville space, described by a rate equation. Such a process is suggested by the diagram in Figure 1, drawn for N = 6 and a double-quantum Hamiltonian (see below). The rates for hopping between sites reflect the

(continued on page 27)

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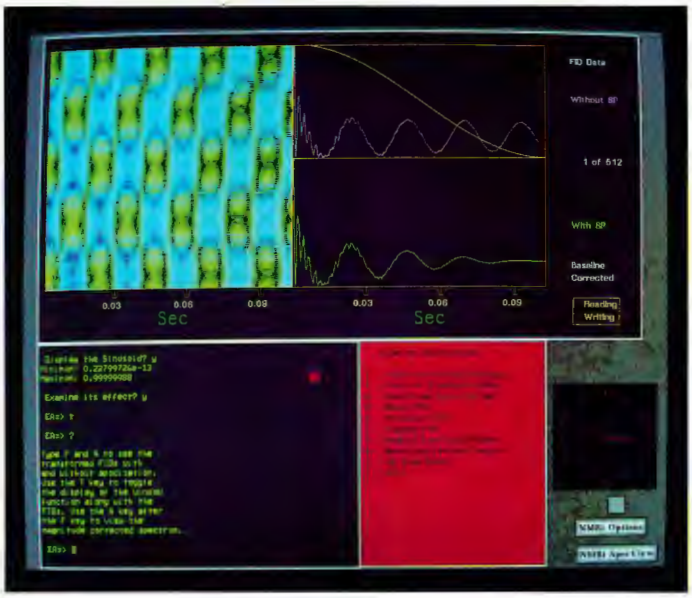
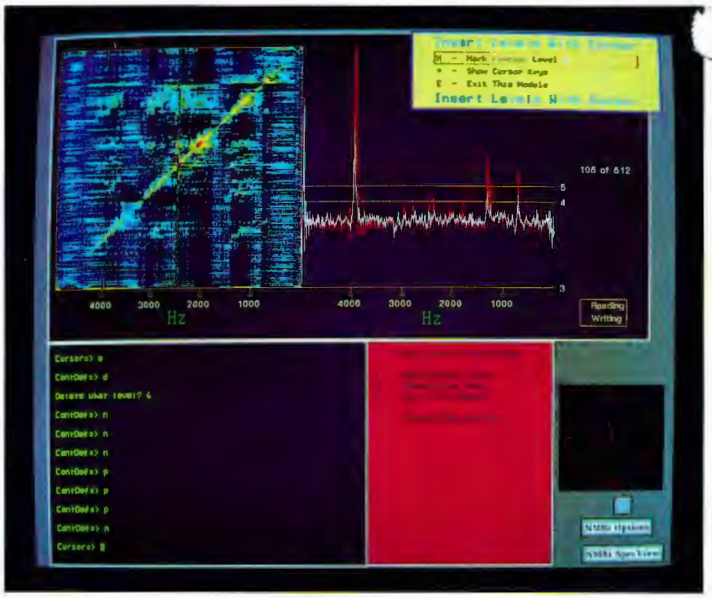


View 1. SpecStation™ multi-window display, showing **NMR2** at initiation of a processing session. The data are from a phase-sensitive 2D NOE experiment obtained with a nucleic acid. A density plot of the two dimensional free induction decay (FID) is displayed in the upper left. The upper right of the display shows the Examine Apodization Module, one of many modules which allow the user to specify processing parameters interactively. The lower left window is a terminal area; the red window supplies an options menu of currently valid commands.



View 2. The Fourier transformed data, shown in the upper left, are first plotted with many levels so that all spectral features are visible. The **NMR2** Contour Level Definition Module is shown in the upper right. It allows the user to interactively select contour levels relative to slices and projections from the data. Levels are selected by moving a mouse-adjustable cursor bar to the desired location. SpecStation™ options and commands can be instantly accessed through mouse-activated pop-up menus. The pop-up *active* menu for this module is shown in yellow at the top right corner.

View 5. In the upper left, **NMR1** displays an *in vivo* surface coil ^{31}P spectrum of a human brain, with the integral trace shown in red. The baseline distortion, characteristic of this type of experiment, makes such quantitation unusable. In the upper right, the continuing **NMR2** session displays a plot of the 2D NOE experiment, enhanced by noise ridge subtraction followed by symmetrization. **NMR2,** now in the 2D Zoom Module, shows a user selected region for viewing. This region (red box) is selected graphically with the mouse.

View 6. At the left, the **NMR1** Baseline Conditioning Module shows the human brain spectrum along with proposed baseline correction, which the program has automatically calculated. The module has colored the spectrum according to the spectral 'states' it has determined (i.e., baseline segment, beginning of peak, crest, down slope, etc). In the upper right, **NMR2** shows a contour plot of the user selected zoom region from the previous frame. Pop-up menus for the programs currently operating are activated depending on the screen location of the mouse cursor. Here the user has selected peak analysis of the zoomed 2D region.

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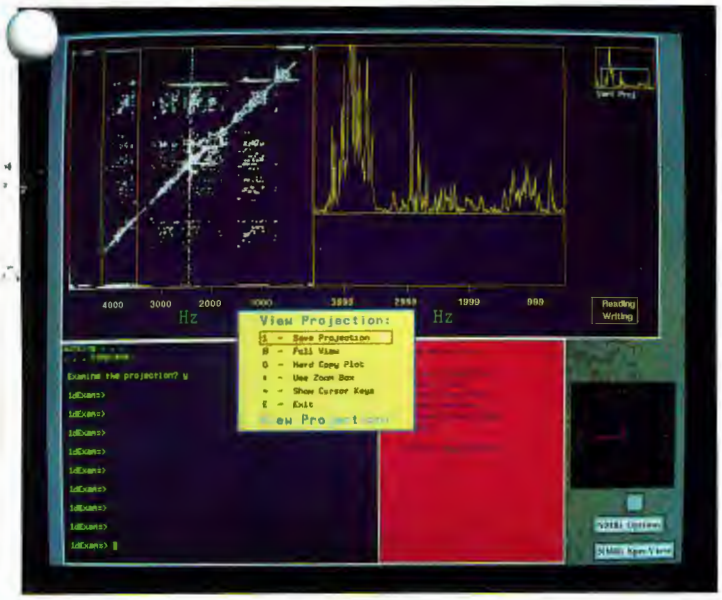

View 3. A single color plot of the data, made with the user-selected contour levels. Effective choice of contour levels has provided a plot where important spectral features are visible. In the upper right, the Projection Module displays expanded and full views of a skyline projection from the vertical band outlined in the 2D display. Shown at the center is another pop-up menu. Icons for an inactive **NMR1** process are visible beneath a clock display on the lower right.

View 4. A free format SpecStation™ display, showing simultaneous execution of **NMR1** and **NMR2.** The **NMR1** windows are clustered in the left half of the display, **NMR2** windows on the right. The **NMR1** graphics window shows the projection from the phase-sensitive 2D NOE spectrum of the nucleic acid, which has automatically been converted into an **NMR1** compatible data set. The projection is shown undergoing **NMR1** Automatic Peak Analysis.

View 7. On the left, **NMR1** now shows the baseline corrected spectrum, with dramatically improved automatic integration. On the right, **NMR2** execution continues at the Peak Analysis level. **NMR2** has located the peaks in the 2D zoom region, and indicated their presence by crosses whose color and dimensions relate to the height and two dimensional widths of each peak. In this case, the user is about to integrate the selected 2D region, as outlined by a red box in the 2D display.

View 8. In this SpecStation™ display the upper right window shows a stacked plot of the zoom region from the phase sensitive 2D NOE experiment. The upper left of the display shows the result of automatic Gaussian curve fitting of the human brain spectrum and the lower right shows the result of maximum entropy Fourier self-deconvolution of the same data. In this case, three separate programs are running simultaneously.

Views of a processing session on SpecStation™.

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(continued from page 22)

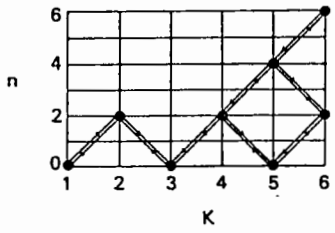
different numbers of operators in each family, and depend explicitly on N, K, and n but not on the coupling constants. Differences between materials show up only as an overall scaling of all the rates by some parameter that incorporates the coupling constants.

This strategy works remarkably well, as perhaps can be appreciated by the results shown in Figure 2. The curves track the development of n-quantum coherence in systems of 6 and 21 spins excited with a pure double-quantum dipolar Hamiltonian, governed by the selection rules $\Delta K = \pm 1$ and $\Delta n = \pm 2$. At left are the predictions for generic systems; at right are the experimental results obtained for (top) a molecule with 6 protons in a dilute solid solution and (bottom) a molecule with 21 protons in a nematic phase. (Experimental data from J. Baum and A. Pines, J. Am. Chem. Soc. 108, in press; November 12, 1986 or subsequent issue) The different time scales needed to match the simulations to the experimental results reflect differences in structure and molecular motion between the two systems. Nevertheless, the overall pattern depends only on N. After long periods of excitation, a steady state is attained under which the coherence amplitudes are described by a Gaussian distribution, proportional to exp(-n**2/N). This outcome is a statistical consequence of assuming that all K-spin/n-quantum modes are equally accessible to the density operator.

Sincerely yours,

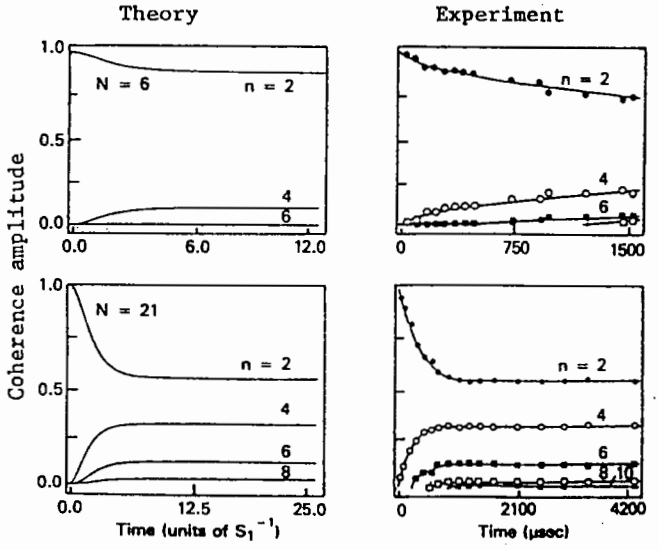
M. Munowitz (Amoco) A. Pines (Berkeley) M. Mehring (Stuttgart)

Figure 1



(initial condition αI_z: K=1, n=0)

Figure 2



(S_1 = scaling parameter)

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RESEARCH AND DEVELOPMENT

November 14, 1986 (Received 24 November 1986)

Automation of EM-390 Spectrometer
Wha-02-86

Professor Bernard Shapiro
Texas A&M University
College Station, Texas

Dear Dr. Shapiro:

For several years we have been using an HP-21MX computer for control and automation of a Varian EM-390. When this elderly system showed signs of imminent senility, we felt it was time to replace the computer with one slightly more up-to-date. In order to safeguard this same computer senility and hedge any bets on software compatibility in the future, we replaced our old computer with an IBM-PC compatible, an FD-1000 from PC Designs (Tulsa, OK). The NMR operating system was initially written in GWBASIC and converted to IBM compiled BASIC.

The computer/spectrometer interface consists of a DT-2801 board from Data Translations tied to several relays used in selecting the sweep direction and control. The sweep time is controlled via insertion of a 2-pole relay into the recorder time base. The time base source is switched from the normal internal spectrometer clock to an external TTL pulse generated under software control. The nmr signal is intercepted on the recorder amplifier board and routed to one of the DT-2801 A/D op amps.

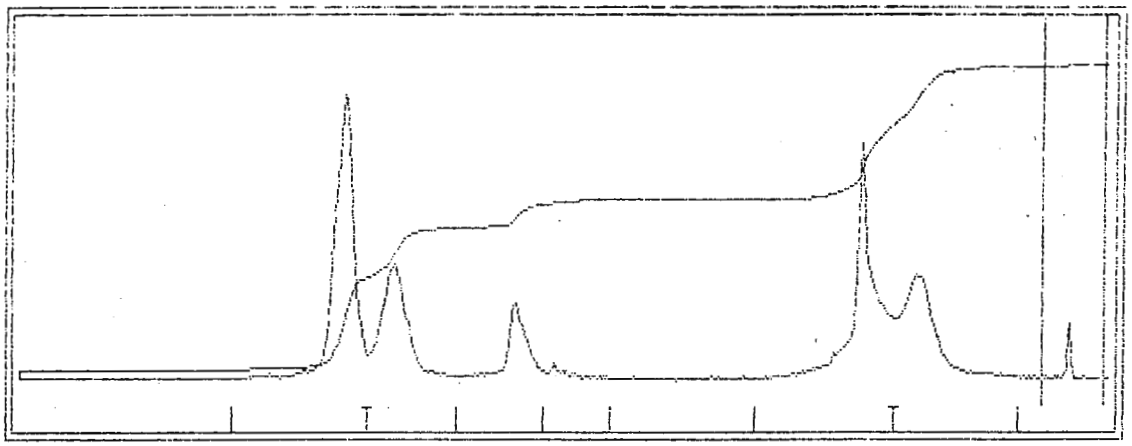
Our current software allows data acquisition/display, horizontal and vertical expansions, integration, data storage and retrieval, signal averaging, plotting on an HP-9872C, labeling of the spectrum, baseline correction, and computer aided phasing adjustment.

We are in the process of completing the automation of the phasing adjustment and spectrum amplitude. This will allow a complete novice to obtain a high quality spectrum, barring major homogeneity problems. With the addition of a turntable it will allow unattended operation. Since quite a few of our samples are oils, differences in homogeneity here will be minimal. Screen dump utilities in the graphics software allow the generation of nmr spectra as shown in Figure 1 Since the areas of interest are already integrated and measured, the hardcopy produced is sufficient to satisfy our needs to actually see the spectrum.

Sincerely,

S. M. Wharry

SMW:rk



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1) Spectrum #	= E-6268	7) Temperature	= Amb.
2) A.B. Number	= 6019651	8) Nucleus	= H-1
3) Customer	= C. Combs	9) Spec. ampl.	= 550
4) Sample number	= Butadiene/styrene	10) Filter	= 0.85
5) Solvent	= CDCl3	11) R.f. Power	= 0.04
6) Reference	= TMS		

Change Item (0=Label,(-1)=Exit) = {

Normalization regions for E-6268
Sample Number = Butadiene/styrene

Region # 1:	8.20 ppm to	6.86 ppm	= 30.34%
Region # 2:	6.86 ppm to	6.00 ppm	= 15.94%
Region # 3:	6.00 ppm to	5.15 ppm	= 7.85%
Region # 4:	5.15 ppm to	4.50 ppm	= 1.25%
Region # 5:	3.10 ppm to	1.71 ppm	= 25.58%
Region # 6:	1.71 ppm to	0.50 ppm	= 19.04%

FACSS XIV - 1987 DETROIT

PRELIMINARY ANNOUNCEMENT - FACSS XIV - 1987 DETROIT

The 1987 FACSS meeting will be held at Cobo Hall and the Westin Hotel in Detroit, Michigan. From October 4 until October 9 the Federation of Analytical Chemistry and Spectroscopy Societies, FACSS, will hold their fourteenth annual meeting. Stay tuned for further information on the premier scientific meeting devoted exclusively to spectroscopy and analytical chemistry.

As in the past, workshops and short courses will be offered prior to, during, and after the conference. The FACSS Employment Bureau will again be available to conference attendees. Centrally located at the meeting will be an exhibition of scientific instrumentation, services, and publications. For further information contact the publicity chairman, Dr. Steve Swarin.

Dr. Stephen J. Swarin
Publicity Chairman
Analytical Chemistry Dept.
General Motors Research Labs
Warren, MI 48090-9055
313 - 986-0806

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DEPARTMENT OF BIOPHYSICS

November 14, 1986
(Received 24 November 1986)

Solid State Pulse Protection Circuit for CP Spectrometers

Dear Barry:

Over the last two years or so we have had a couple of mishaps in our laboratory in which high levels of continuous rf power damaged our probes used for cross polarization and proton decoupling in solids. These accidents occurred because the operator accidentally applied a pulse of greater than several seconds or because of AC power interruption usually associated with bad weather. We have recently constructed a solid state pulse protection circuit that disables the pulses going into our Vari-L SS-30 rf gates and further into high power amplifiers. The pulses are enabled only when no AC power disruption has occurred and the pulse length has not exceeded a preset value (we have set this to 400 msec in our circuit). Otherwise the pulses are disabled so that rf gates are not open and the power amplifiers sit in their idle state. This strategy is superior to a simple fuse in the transmitter line.

Figure 1 shows the pulse protection circuit which we have implemented on our 1.32 and 4.7 Tesla CP spectrometers (1). These spectrometers currently employ a Nicolet 293-B pulse programmer in conjunction with a 1280 data system. We have chosen to protect pulses P, B, C and N, designated so in the 293-B pulse program software. Operator error is unimportant for pulse P since its default unit is microseconds and so we do not protect it against long pulse length. However, all the pulses are protected when power failure occurs.

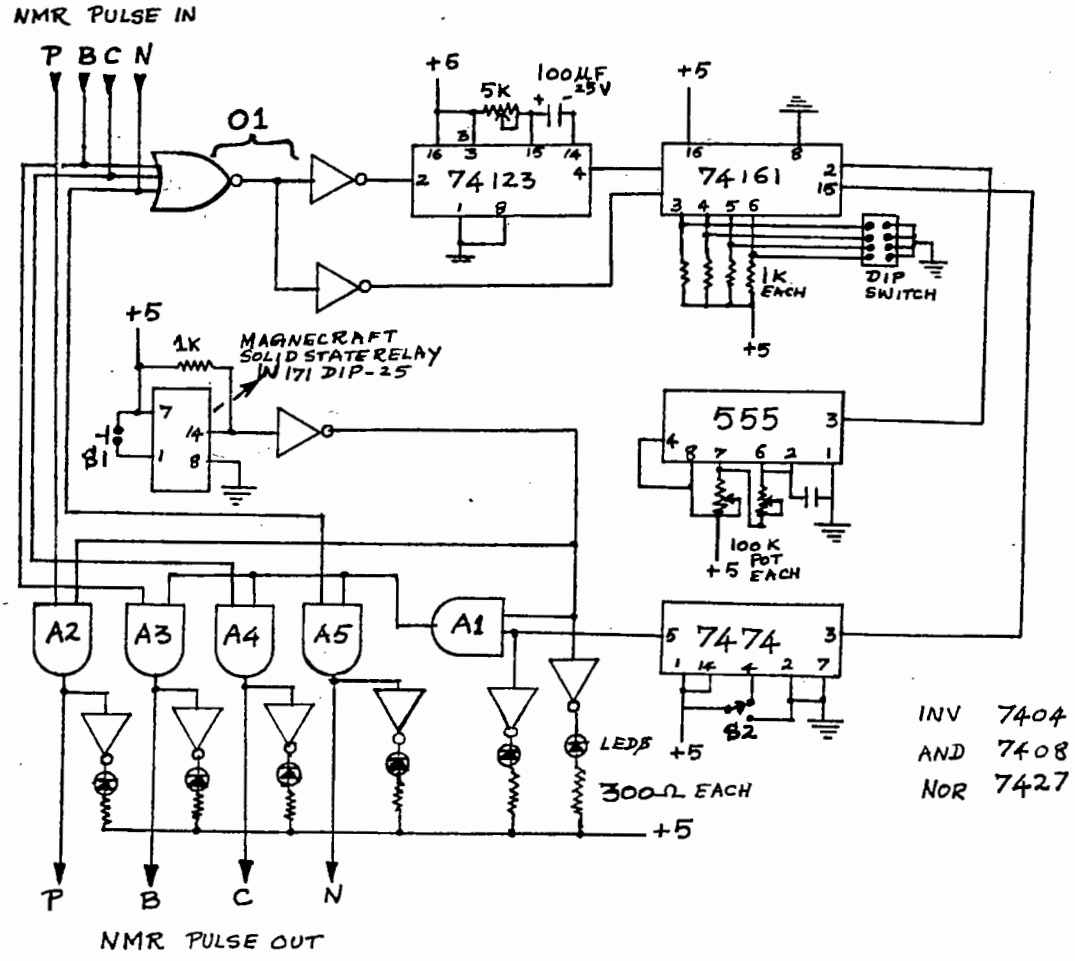
Essentially, the pulses P,B,C and N are enabled through AND gates A2, A3, A4 and A5, respectively. The control signal of A2 is the output of a solid state relay circuit, which is always at logic 1 unless changed to 0 in the event of a power disruption. This relay output controls AND gate A2 to enable or disable pulse P. In order to protect against long pulse lengths, B, C and N pulses are ORed and used to trigger a counting circuit. The counting circuit is clocked by a 555 timer (25 msec period) and is configured to count up to 400 msec using DIP switches. If the NMR pulse length exceeds 400 msec, the output of the counting circuit, normally "high" = logic 1 goes "low" = to logic 0. This output and the relay output are ANDed and then used to control the AND gates A3, A4 and A5 whose other inputs are tied to the NMR pulses B, C and N, respectively. Thus, pulses B, C and N are enabled only when no power disruption has occurred and a pulse length of 400 msec has not been exceeded.

Switches S1 and S2 are used to reset the relay and counter circuits, respectively. Protection of more pulses can be achieved by adding more OR gates and AND gates preceding and following the counting circuit, respectively.

Sincerely,

Robert G. Bryant S. Ganapathy Scott D. Kennedy

(1) T. L. Ceckler, Ph.D. Thesis, Dept. of Chemistry, University of Rochester (1985).



UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
McCORMICK ROAD
CHARLOTTESVILLE, VIRGINIA 22901

November 21, 1986
(Received 25 November 1986)

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

Intramembrane Location of Hydrophobic Ions

Dear Professor Shapiro:

The hydrophobic ions tetraphenylboron (TPB^-) and tetraphenylphosphonium (TPP^+) have been used extensively to study the electrical properties of biomembranes. One important factor in obtaining information about membrane electrostatics is a knowledge of the intramembrane location of the bound hydrophobic ions. We have examined the intramembrane position of the ions by performing a variety of ^1H NOE measurements and simulations. The measurements were made on small vesicles containing egg phosphatidylcholine and TPB^- or TPP^+. The simulations, based on the method used by Dobson et al. (1), indicate that even though some spin diffusion takes place, the steady state NOE's will be sensitive to internuclear distances. Shown in Figure 1 are hydrophobic ion - membrane phospholipid steady state NOE's. The NOE profile indicates that the ions are located in the hydrocarbon region of the membrane. The intramembrane hydrophobic concentrations used here are similar to those used in experiments in which the ions act as probes of membrane electrostatics. When present at higher concentrations, TPB^- binds primarily to the choline headgroup of the membrane phospholipid.

In order to further localize the ions, we performed truncated NOE experiments (2) (Figure 2). The initial NOE build-up rates have the following order $h > g > i > 1 \approx f$. Factors important in determining the build-up rates include number of protons saturated per lipid, internuclear distance and spin diffusion. A more complete discussion of the results and their interpretation in terms of hydrophobic ion location will be presented soon. Briefly, the NOE results and those of a recent thermodynamic analysis of hydrophobic ion-membrane interactions (3) suggest that the intramembrane location of the hydrophobic ions, when present at $\leq$ 10 mol%, is that shown in Figure 3.

Sincerely,

Jeff Ellena, Raymond Dominey, Sharon Archer,
Zhen-Chen Xu, David Cafiso

1) Dobson, C.M., Olejniczak, E.T., Poulsen, F.M. and Ratcliffe, R.G. (1982) J. Mag. Res. 48, 97.

2) Wagner, G. and Wüthrich, K. (1979) J. Mag. Res. 33, 675.

3) Flewelling, R.F. and Hubbell, W.L. (1986) Biophys. J. 49, 541.

(continued on page 35)

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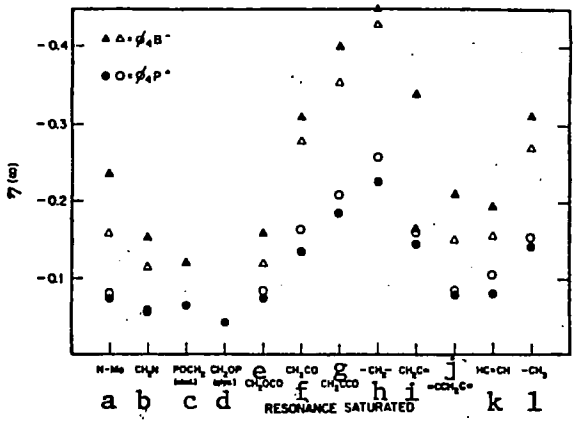
(continued from page 32)

Figure 1.



closed symbols - 10 mol%

open symbols - 4 mol%

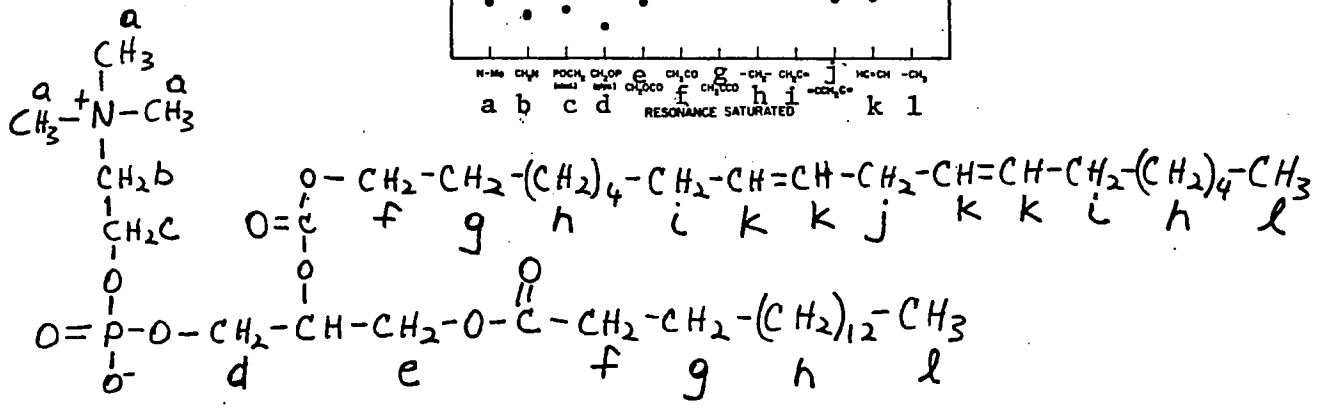


Figure 2.

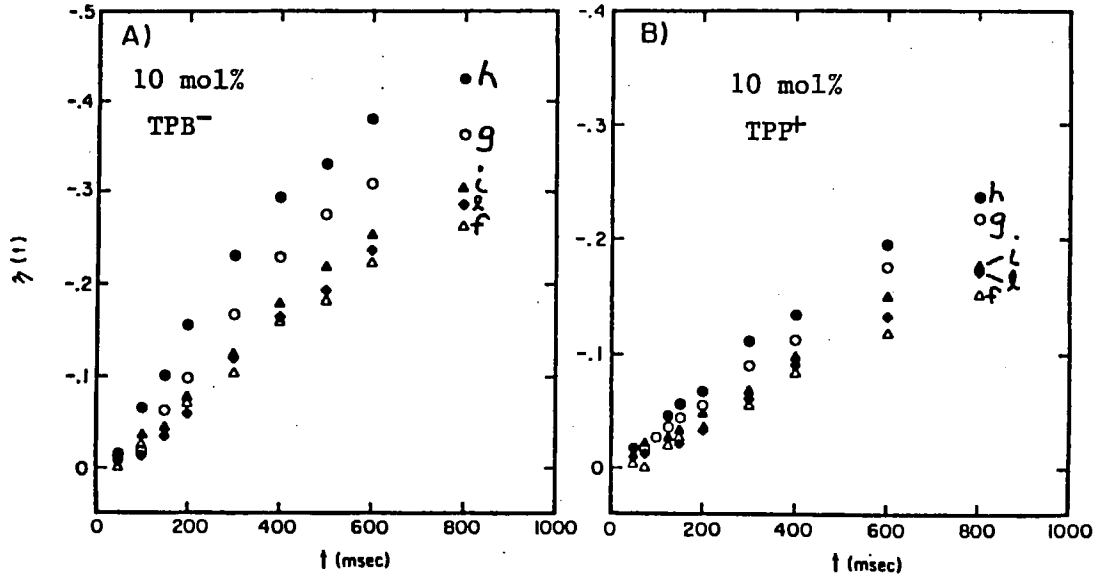
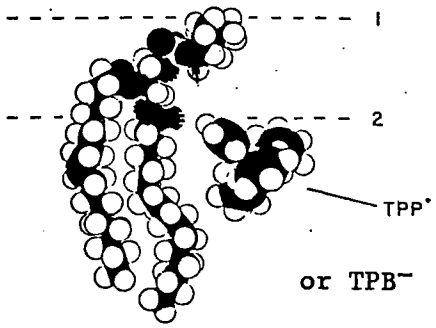


Figure 3.



1 Membrane - Solution Interface

2 Water - Hydrocarbon Interface

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Milano, 7th November, 1986

(Received 25 November 1986)

Prof. Bernard L. SHAPIRO
Texas A&M University
Department of Chemistry
COLLEGE STATION, TEXAS 77843-3255
U.S.A.

Transient NOE Experiments on N-Acetyldaunomycin

Dear Barry,

The nuclear Overhauser effect has been used for quite some time to obtain information about molecular dynamics and conformation[1]. These studies were mainly based on analysis of steady state NOEs. The quantitative use of NOE values to obtain interatomic distances is more difficult; recent methods, which take into account the time development of the NOE[2], or are based on two-dimensional spectroscopy (NOESY) have been presented.

We performed transient NOE experiments, i.e. NOEs generated by selective 180° pulses, to determine glycosidic linkage geometries. This method is shown to give, in the case of N-acetyldaunomycin, a good estimate of the cross-relaxation rates, σ from which the interproton distance ratios are obtained, with an accuracy comparable to X-ray method. The problem of the conformational preference of the sugar with respect to the aglycone in solution is of primary importance, in the study of structure-activity correlation for the anticancer agents of this family. NOE transient experiments were performed with a Bruker CXP-300 spectrometer in $CDCl_3$. The decoupler pulse length was optimized in order to achieve the best inversion[3] compatible with selectivity; the inversion factor was better than 90%; the average duration of an experiment (8-10 data points) was ca 10 h. The cross-relaxation rates (σ) and the relaxation rates (ρ) were obtained by a non-linear least-squares fit of all the experimental points, to the equation:

$$[\eta(t)] = [T] \exp[-Dt] [T]^{-1} [\eta(t)]_{t=0}$$

where T is the matrix formed by the eigenvectors of the relaxation rates matrix, and D is the diagonalized relaxation matrix.

The whole curves have been analyzed with a "two spin approximation". In order to estimate the validity of this approach, we performed a set of calculations which simulate transient NOEs, assuming different geometries. We concluded that the deviation from the multispin treatment is evident in the second part of the curves but negligible in the first part up to 200 ms, thus leading to a good estimate of σ, and a less satisfactory values of ρ, for geometries close to those expected for daunomycin. As we have obtained for 1'-H and 7-H the σ values from all neighbouring protons, we can compare the sum of these values ($\Sigma\sigma$) with the difference of non-selective and selective relaxation times, obtained by separate measurements. The agreement is satisfactory taking account of the error involved in the determination of T_1: $\Sigma\sigma_7 = 0.44 \pm 0.02$ vs 0.33 ± 0.08 s^{-1}, $\Sigma\sigma_{1'} = 0.50$ vs 0.41 s^{-1}.

Experimental transient NOE following inversion of 5'-H (A), 1'-H (B,C) and 7-H (D).

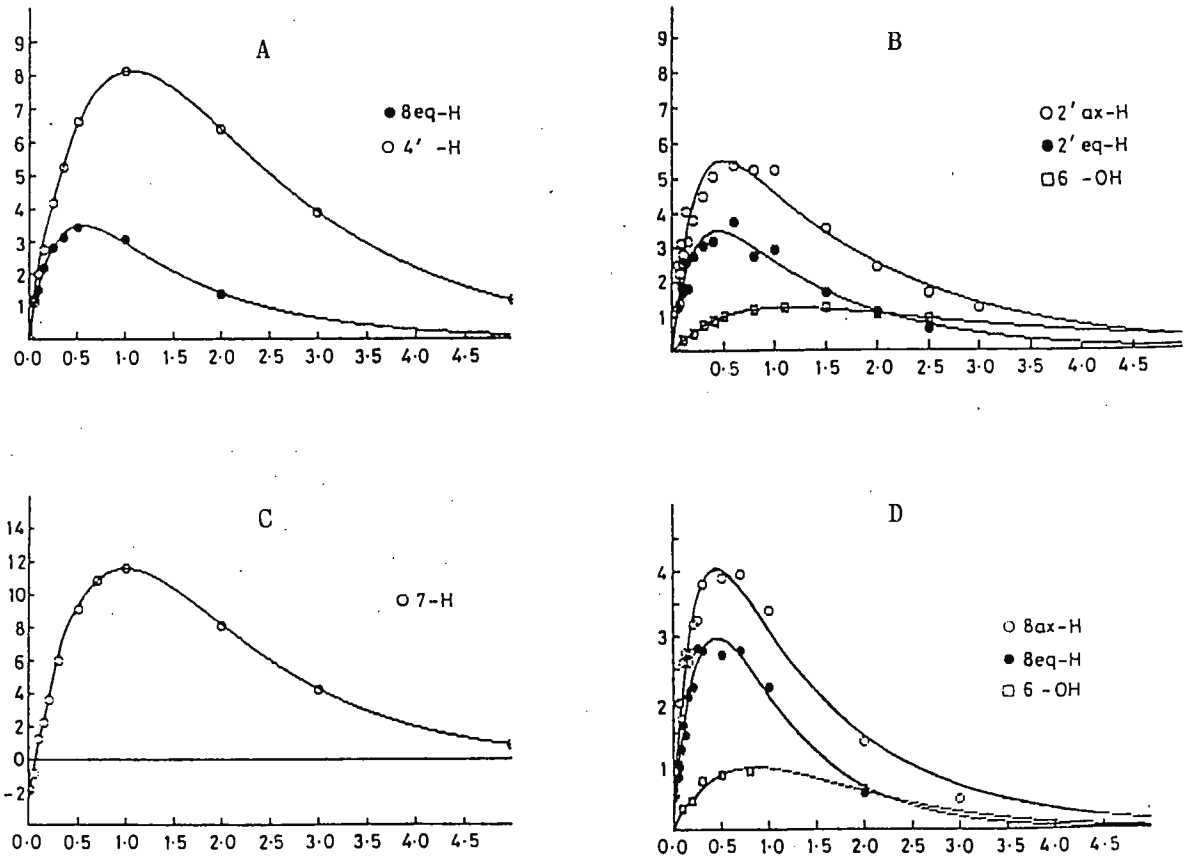


Table.- Cross-relaxation rates (s^{-1}) and interproton distances (Å).

Protons i-j	Cross relax. rates σ_{ij}	Distance ratios $\sigma_{i,j}/\sigma_{4',5'}$	Interproton distances r_{ij} NOE		X-ray[e]	
H(1')-H(2'ax)	0.1769 ± 0.0151[a]	0.940 ± 0.015[b]	2.21 ± 0.03[b,c]	2.34	2.47	2.40
H(1')-H(2'eq)	0.1207 ± 0.0107	1.002 ± 0.016	2.35 ± 0.04	2.39	2.55	2.14
H(1')-H(7)	0.1859 ± 0.0042	0.933 ± 0.005	2.19 ± 0.01	2.20	2.22	2.20
H(1')-OH(6)	0.0171 ± 0.0004	1.388 ± 0.007	3.26 ± 0.02	3.15		
H(7)-H(8ax)	0.1411 ± 0.0125	0.977 ± 0.016	2.30 ± 0.04	2.33	2.38	2.22
H(7)-H(8eq)	0.0948 ± 0.0051	1.044 ± 0.011	2.45 ± 0.03	2.42	2.46	2.54
H(7)-OH(6)	0.0175 ± 0.0022	1.383 ± 0.031	3.25 ± 0.07	3.42		
H(5')-H(8eq)	0.1073 ± 0.0046	1.022 ± 0.010	2.40 ± 0.02	2.59	2.54	2.59
H(5')-H(4')	0.1224 ± 0.0010	1.000	2.35[d]	2.33	2.38	2.57

[a]Standard deviations. [b]Uncertainties calculated from the standard deviations of σ values through the error propagation law. [c]A more realistic estimate of the error, which also takes into account the uncertainty in the reference distance value ($r_{4'-5'}$) is within ± 0.1 Å. [d]Reference value, obtained by the average of X-ray results. [e]Calculated from X-ray atomic coordinates: refs. C.Courseille et al. Acta Cryst., 1979, B35, 764; S.Neidle et al. Biochim.Biophys. Acta, 1977, 479, 450; R.Angiuli et al. Nature New Biol., 1971, 234, 78, respectively. As the standard deviation reported by Courseille et al. for C-H distances is ± 0.09 Å, a reasonable estimated deviation for interproton distances in the crystal phase is larger than ± 0.1 Å.

Since each σ value was obtained by independent experiments, this result is evidence for the good quality of the experiments performed for the determination of σ parameters.

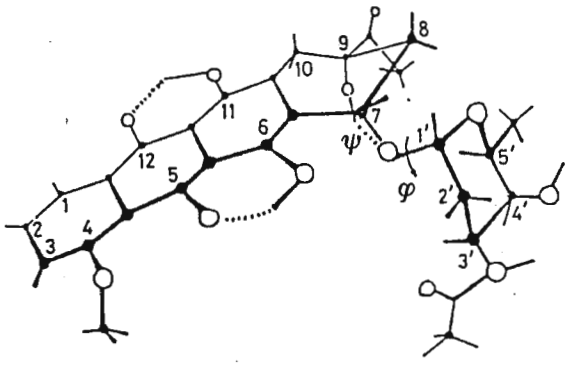
The experimental transient NOE experiments are reported in Figures A-D; the cross-relaxation σ_{ij} and the interproton distances r_{ij} are given in the table.

The similarity of σ values for the corresponding distances in the fragments CH_2(8)-CH(7) and CH_2(2')-CH(1'), and the agreement with X-ray data, allowed us to confirm the validity of the assumption that different interproton vectors like H(1')-H(2'eq) and H(7)-H(8eq) or H(1')-H(2'ax) and H(7)-H(8ax) have the same effective correlation time.

The preferred conformation is presented in the last figure, together with the values of the rotational angles φ and ψ. These values obtained with a geometrical program (HILDE) from NOE data, rely on the assumption that the molecule exists preferentially as a single conformation. Actually NOE distances are $(\langle r^{-6} \rangle)^{1/6}$ means. However, in the present case a good fit of φ and ψ to the NOE distances, functions of these angles, could not be reached, if the magnitude of internal motion was large. Since librational motions of low amplitude are relatively ineffective in perturbing the relaxation rates, we must conclude that the internal motions are small, in order to accommodate a difference of only $\pm$ 0.1 Å between experimental and calculated distances. It is particularly significant that the σ values obtained (-5°) correspond to the optimum geometry ($-10° \leq \psi \leq 0°$) for the 9-OH...O(7) intramolecular hydrogen bond, which was also proved by dilution experiments.

Best wishes, sincerely yours,

E. Ragg G. Fronza R. Mondelli



$\psi = C_{1'}-O_7-C_7-H_7 = -5° \pm 5°$

$\varphi = H_{1'}-C_{1'}-O_7-C_7 = 40° \pm 5°$

1) J.H. Noggle, R.E.Shirmen. "The Nuclear Overhauser Effect", Academic Press, N.Y. 1971.

2) C.M. Dobson et al., J.Magn.Reson. 48, 97 (1982), ibidem 64, 199 (1985); R.R. Ernst et al., J.Am.Chem.Soc. 103, 3654 (1981).

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November 14, 1986

(Received 17 November 1986)

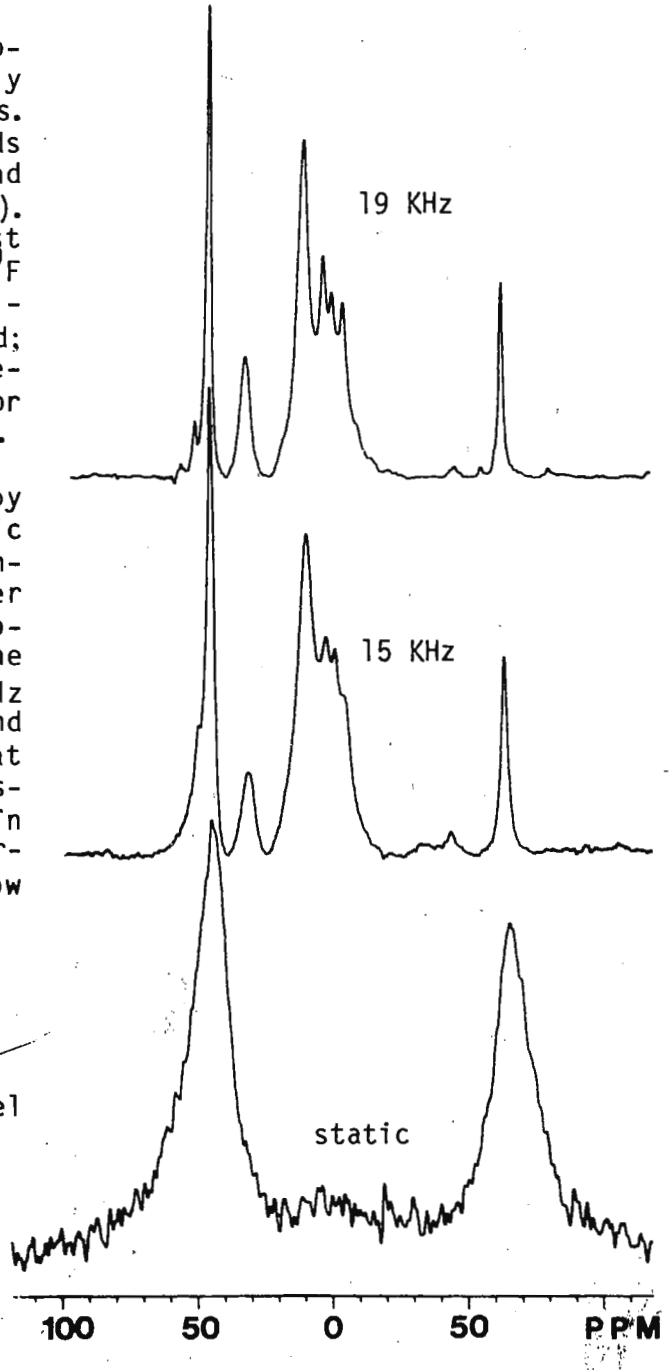
Prof. B.L. Shapiro
TAMU NEWSLETTER
Chemistry Department
Texas A&M University
College Station, TX 77843

Title: High Speed MAS with ^{19}F

Dear Barry:

One of the areas of technical development in which we have made progress recently is magic-angle spinning at very high speeds. So far, spectra have been obtained at speeds up to 23 KHz (S. Dec, R. Wind, G. Maciel and F. Anthonio, J. Magn. Reson., in press). One of the dividends of spinning this fast is the ability to obtain useful ^{1}H and ^{19}F spectra of solids. For both cases, sensitivity is high, so small rotors can be used; also for both cases, homonuclear dipole-dipole broadening is a serious problem. For ^{19}F, the CSA effect can also be very large.

The spectra shown below, obtained by Steve Dec and Robert Wind, are the static spectrum and MAS spectra obtained with spinning at 15 KHz and 19 KHz on a polymer system generated from the following monomers: $F_2C{=}CH_2$, $CF_3C(F){=}CF_2$, $F_2C{=}CF_2$. One can readily see that spinning at 19 KHz provides a substantial line narrowing beyond what is achieved at 15 KHz. Spinning at speeds of at least 10 KHz seems to be necessary for obtaining useful fine structure in the CF_2 region for these types of fluorocarbon polymers. Work is continuing to see how far we can push this approach.



Sincerely,

Gary E. Maciel
Professor

GEM:lb

P.S. We are looking for a postdoc to work in the area of DNP.

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Professor Bernard Shapiro
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Silicon-29 NMR of Aerospace Materials

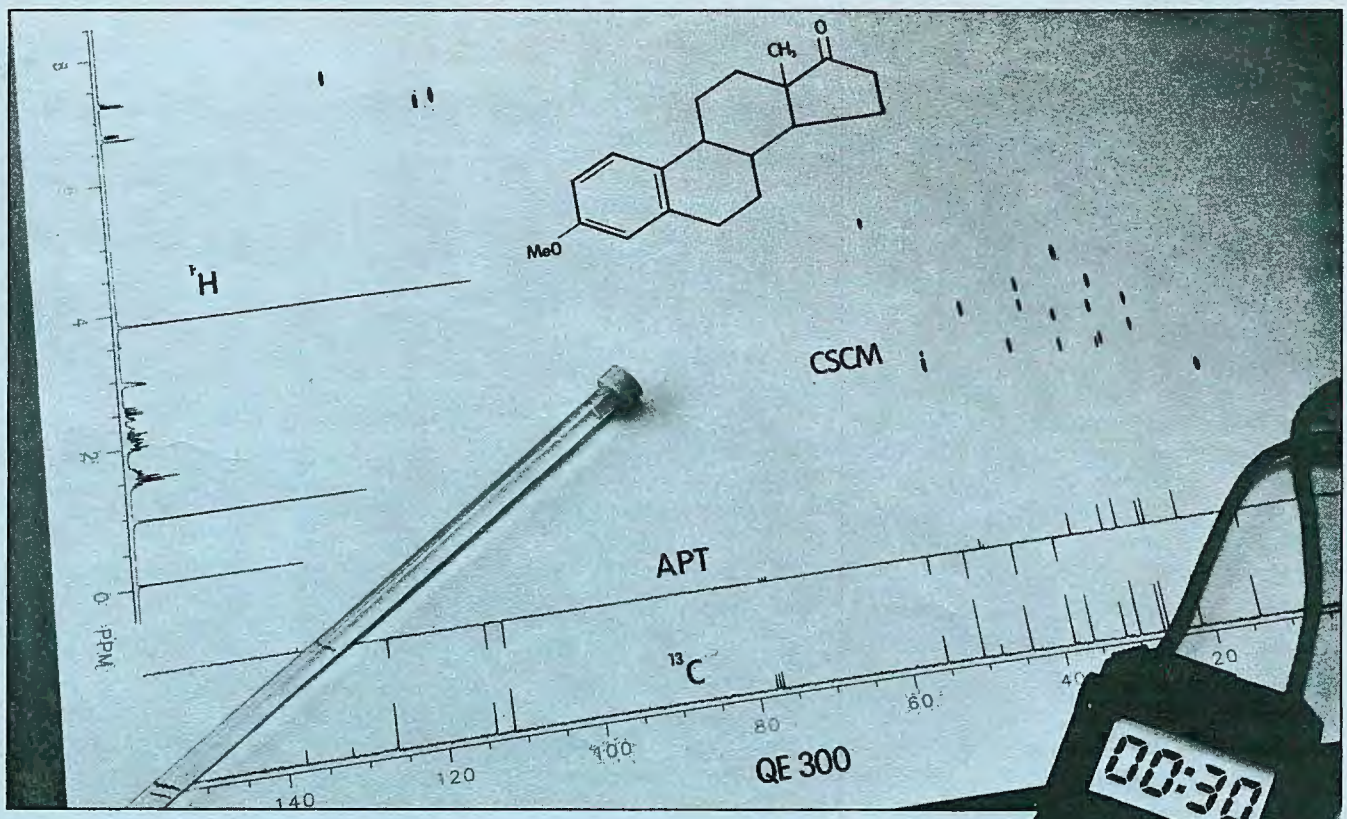
Dear Sir,

We use silicon-29 NMR in chemical characterization of silicone adhesives and primers used in aerospace materials. Tetraalkyl orthosilicates are active ingredients in these materials. Observation and quantitation of these resonances is complicated by the glass absorption from the probe insert and NMR tubes utilized in high resolution work. We compared Wilmad 513-7PP pyrex and quartz 10 mm NMR tubes with a new alumina tube, also made by Wilmad. The quartz and alumina tube give no observable background enhancement of the probe signal (Varian 10 mm BB probe tuned to 59 MHz) in silicon-29 studies. A thin-walled pyrex tube can give enhancement of the insert background signal, but a pyrex insert is by far the most significant interference of the two. The probe must be tuned properly as the difference in dielectric constants between the tube materials is large. Use of appropriate software for baseline correction, such as the Varian MAGICAL spline-fit BC command, can eliminate the glass absorption in this region of the spectrum. For best silicon-29 spectra use a non-pyrex containing probe (quartz is satifactory) and thin-walled quartz or alumina NMR tubes.

Sincerely,

Barbara L. Myers-Acosta

Barbara L. Myers-Acosta



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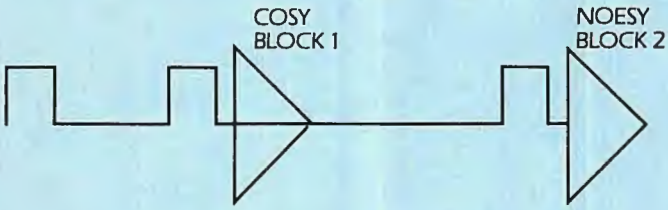

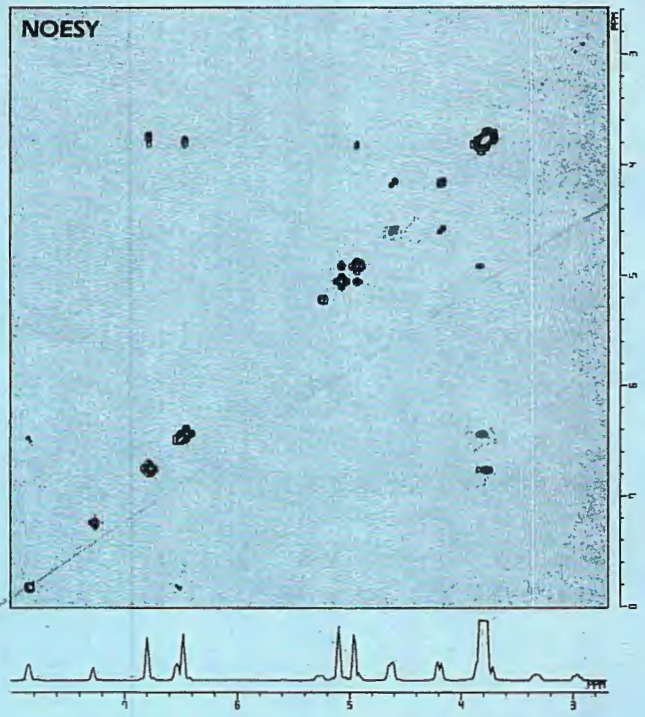

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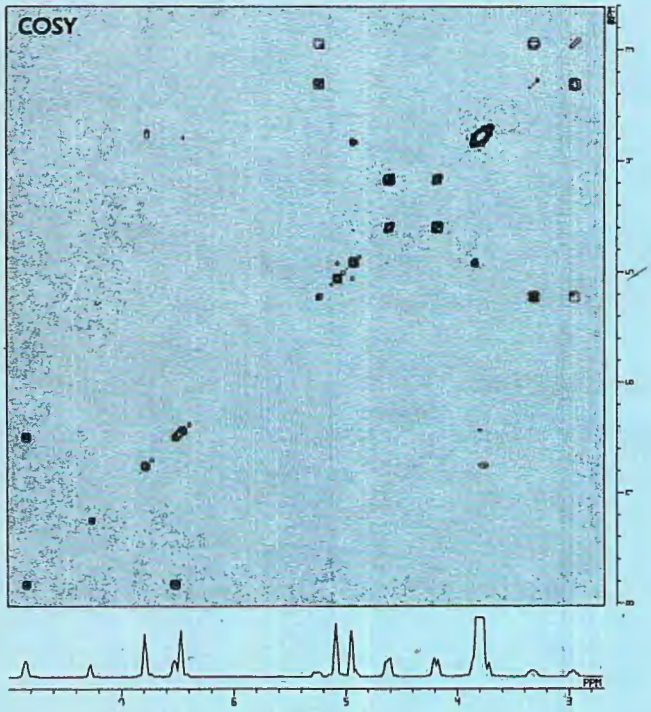

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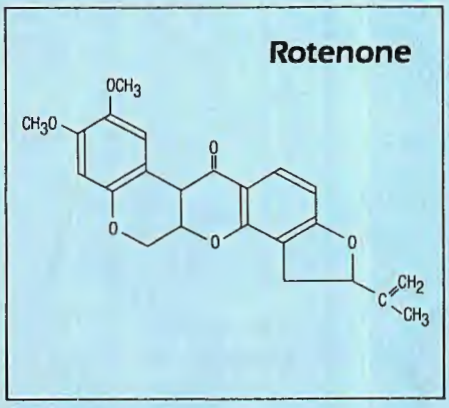

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