BRIAN SYKES

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 318

MARCH 1985

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Forthcoming NMR Meetings (Additional listings are solicited)

26th ENC - April 21-25, 1985, Asilomar, Pacific Grove, California; Chairman: P. Mark Henrichs, Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

Seventh International Meeting on NMR Spectroscopy - July 8-12, 1985, University of Cambridge.

12th FACSS Meeting - Sept. 30-Oct. 4, 1985, Philadelphia, PA; NMR Program Chairman: Rodney D. Farlee, E.I. du Pont de Nemours & Co., Inc., Experimental Station, Building 328, Wilmington, Delaware 19898; see page 9.

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

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

All Newsletter Correspondence
Should be Addressed to:

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

DEADLINE DATES

No. 320 -------- 5 May 1985

No. 321 ------ 3 June 1985

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USE OF 'COUNTER DIAGONAL' PEAKS IN
DOUBLE QUANTUM FILTERED COSY SPECTRA

Dear Barry,

We have recently been recording several double quantum filtered COSY spectra and one of us (TN) has noticed a rather peculiar, and we think useful, feature often shown by the diagonal peaks in such spectra. This shows up most clearly when the spectra are recorded and processed according to the procedure described by States, Haberkorn and Ruben (1) so as to obtain spectra with pure absorption lineshapes. The spectrum of cedrol, recorded on an XL300 spectrometer, shows the effect nicely. In normal COSY each multiplet gives a neat square on the diagonal, however, in the double quantum filtered version we find instead a 'cross'. Each arm of the cross contains the normal multiplet. One arm lies on, and the other perpendicular to the diagonal. The centre locates the chemical shift. Most usefully the peaks in the two arms of the cross have opposite signs, thus by plotting only positive or negative contours one gets a most striking set of multiplets crossing the main diagonal. We call these the 'counter diagonal peaks', although the heraldic term 'bar sinistra' also seems appropriate.

The lower spectrum of cedrol has been plotted with only the negative levels and shows the counter diagonal peaks. The upper spectrum contains both levels and shows the cross effect. Note that because the couter diagonal peaks are angled to the main diagonal overlap between them is largely avoided.

The explanation for the effect is quite simple. It all arises because all of the observed magnetization has been passed through double quantum coherence. Consider an AMX spin system, and consider just the A spin diagonal peak. There are three contributions to this peak, the A=M and A=X double quantum coherences and the 'indirect' M=X double quantum coherence. Each contribution gives a square array of peaks, but with different patterns of alternating signs among the individual peaks. Cancellation between the A=M and A=X contributions takes place leaving only those peaks lying on or across the main diagonal. The M=X contribution gives a full square, but as it turns out to be in dispersion its peak height is very much less than the absorption contributions from A=X and A=M double quantum = thus the cross becomes the dominant feature. For systems with three resolved couplings the cross is not so perfect, but is still easily visible.

These counter diagonal peaks can be most useful when analysing the spectrum as they point to the chemical shifts in a very direct way. A search can then be made for cross peaks in the appropriate areas. Normally the contour levels are first set quite high so as to pick up just the counter diagonal peaks, when these have been located the contours are lowered to locate the cross=peaks. Combined with the other useful

properties of the double quantum filtered COSY spectrum this makes such spectra much more useful than conventional absolute value COSY spectra.

Toshi James

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Stockholm
Sweden

James Keeler
University Chemical Labs.
Cambridge
England

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

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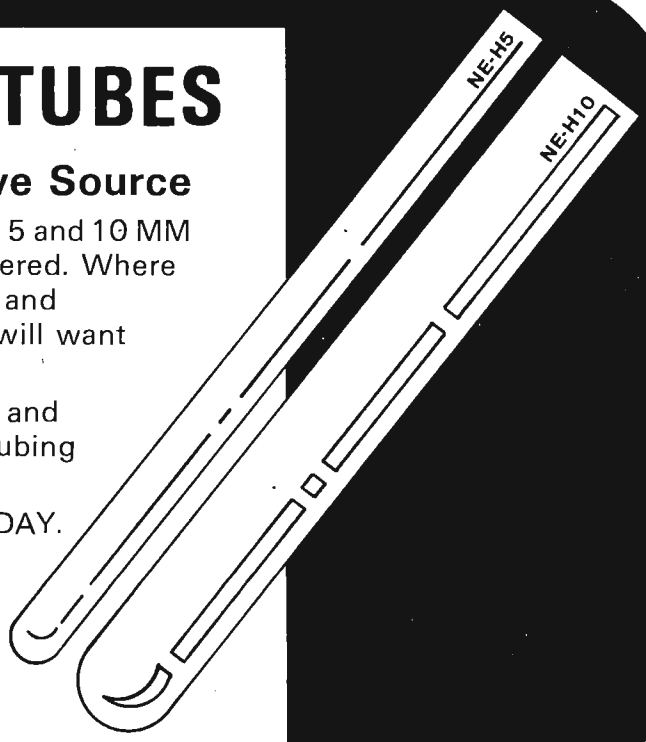

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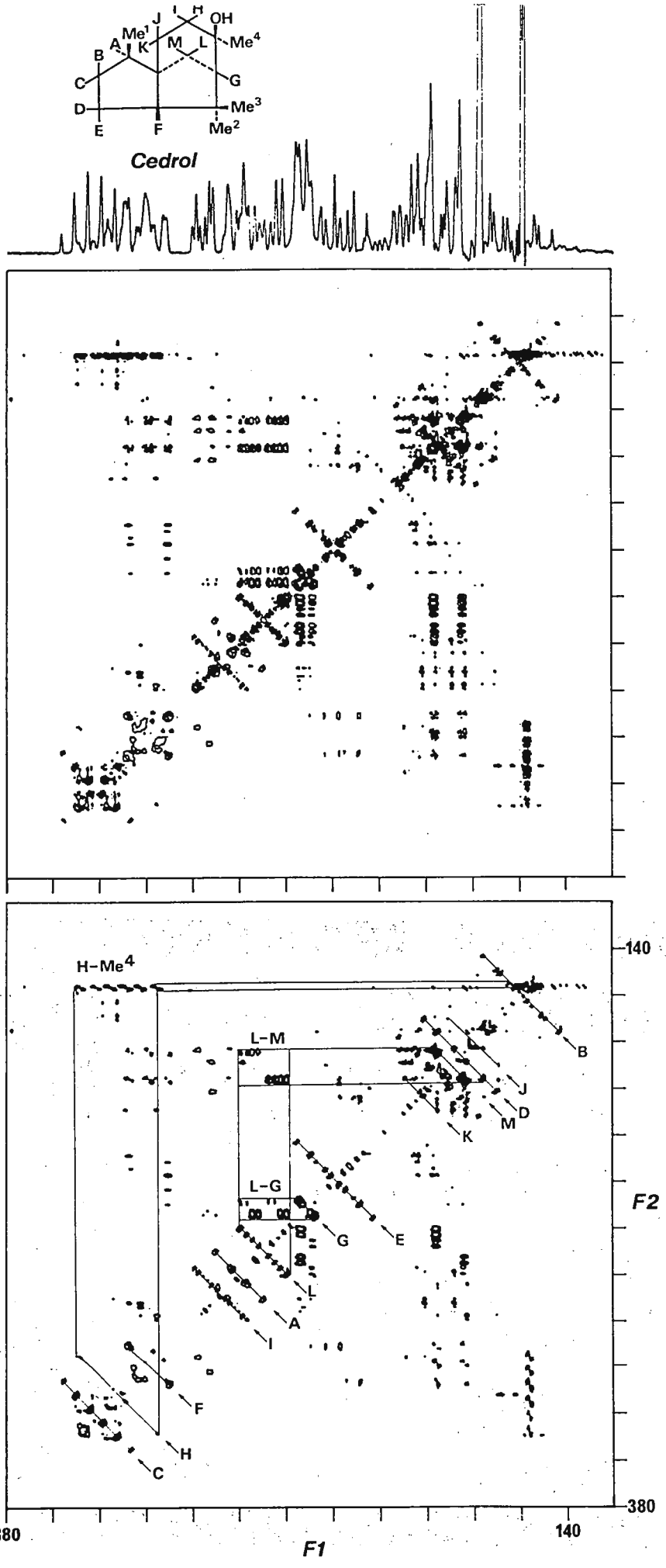
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November 13, 1984

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

Received 18 February 1985

CATION BINDING PROPERTIES OF THE POLYOXYETHYLENE GROUP- STUDIES OF SODIUM COMPLEXATION USING 23Na NMR

Dear Barry:

Sorry that I have been so remiss in responding to your final ultimatum of sometime back. Perhaps the following abstract of a paper being submitted to Journal of Physical Chemistry will redeem us.

A B S T R A C T

23Na NMR spectroscopy has been used to determine the formation constants for the complexation of the sodium cation with low molecular weight polyethylene glycols (PEG's) and polyoxyethylene monoalkyl ethers in methanol at room temperature. The binding constants with pentaethylene glycol (EG-5) have been examined as a function of solvent composition (methanol-water) and temperature. The thermodynamic parameters also have been determined for heptaethylene glycol (EG-7) in methanol. The results indicate that in methanol the formation constants increase monotonically with an increase in PEG chain length, except for diethylene glycol, and that the formation constants are enthalpy determined. The increase in formation constant on going from EG-5 to EG-7 in methanol is the result of ΔH being more exothermic for the latter, with ΔS being nearly equal for the two. For EG-5, the formation constants decrease dramatically with the addition of water and is the result of a decrease in the entropy while the enthalpy is nearly constant with solvent composition. The prediction that complexation of Na+ by PEG's is small ($K<<1$) is corroborated by the data on EG-5 and water mixtures in which it is shown that the 23Na chemical shifts qualitatively fit a solvent exchange (preferential solvation) model, and that the 23Na chemical shifts quantitatively fit a solvent exchange model for ethylene glycol-water mixtures. An examination of the solvent exchange equilibrium constants in this case shows little temperature dependence. There is a change from a solvent exchange model to a complexation model in the treatment of the data at about triethylene glycol (four oxygen atoms).

Yours very truly,

Bob

Robert M. Riddle

RMR-BL
08001

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J. DELMAU

Cher Docteur Shapiro,

ECHANGE D'EAU INTRA ET EXTRA CELLULAIRE DANS LE SANG

Désolés pour notre retard !

La mesure du temps de relaxation transversale T_2 dans le sang fait apparaître une courbe biexponentielle lorsque l'on ajoute des ions paramagnétiques (Mn^{2+}). Ces ions paramagnétiques restent dans le plasma et abaissent alors le temps de relaxation de l'eau extracellulaire. Cette eau s'échange en fait avec l'eau intracellulaire contenue dans les erythrocites.

Dans ce cas la décroissance de l'aimantation transversale est décrite par une double exponentielle [1].

$$h(t) = P'_a \exp(-t/T'_a) + P'_b \exp(-t/T'_b),$$

$$1/T'_a = C_1 - C_2,$$
$$1/T'_b = C_1 + C_2,$$
$$P'_b = \frac{1}{2} - \frac{1}{4}\left[(P_b - P_a)\left(\frac{1}{T_a} - \frac{1}{T_b}\right) + \frac{1}{\tau_a} + \frac{1}{\tau_b}\right]/C_2,$$
$$P'_a = 1 - P'_b,$$

$$C_1 = \frac{1}{2}\left[\frac{1}{T_a} + \frac{1}{T_b} + \frac{1}{\tau_a} + \frac{1}{\tau_b}\right]$$

$$C_2 = \frac{1}{2}\left[\left(\frac{1}{T_b} - \frac{1}{T_a} + \frac{1}{\tau_b} - \frac{1}{\tau_a}\right)^2 + \frac{4}{\tau_a \tau_b}\right]^{1/2}.$$

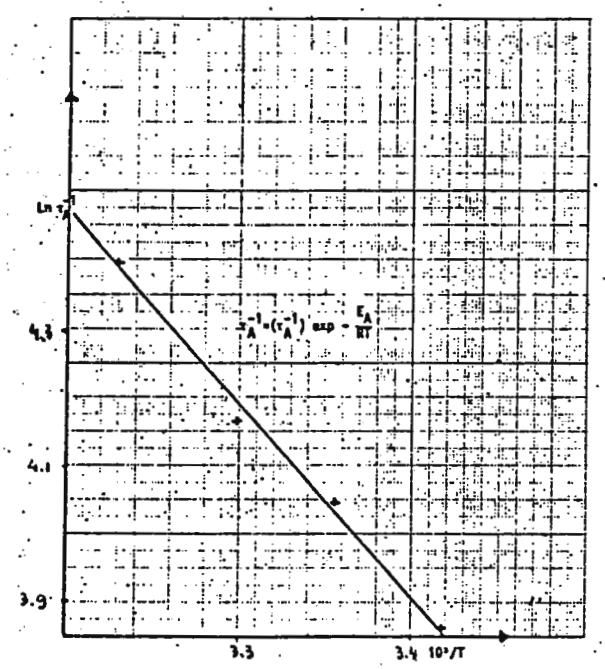
Le temps de résidence τ_A à l'intérieur des érythrocites peut être déterminé à partir d'un échantillon à concentration donnée de Mn^{2+}. On doit pour cela utiliser la mesure du temps de relaxation de l'eau des érythrocites seuls séparés par centrifugation.

Ce temps de résidence a ainsi été mesuré pour quelques températures

	20°C	25°C	30°C	37°C
τ ms	21,5	18,7	15,6	12,5

A partir de ces résultats une énergie d'activation de l'échange peut être estimée à :

$$E_a = 5{,}65 \text{ kcal/mole}$$



Si l'on compare cette valeur à l'énergie d'activation de diffusion de l'eau pure (4,8 kcal/mole), on voit que la membrane des erythrocites apparaît comme pratiquement "transparente" aux échanges d'eau.

Sincèrement.

R. TEISSIER J. DELMAU J.C. DUPLAN

|1| J.L. PIRKLE, D.L. ASHLEY, J.M. GOLDSTEIN
Biophys. J. 25 389-406 (1979)

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February 5, 1985

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

"Does Cell settling get you down; try Stractan Suspension to enjoy an unsettling experience."

Dear Dr. Shapiro:

Like Drs. Brauer and Sykes we have observed settling of Red Cells in the NMR tube during our experiments. We would like to to propose a relatively simple procedure for eliminating the settling in spinnning and nonspinning tubes. The principle behind this procedure is to increase the buoyant density of the suspending solution to match that of the Red Cells. The polysaccharide Stractan "arabinogalactan" ,Sigma Chemical Co.,is a high molecular weight compound that is used in density centrifugation separations of Red Cells. The compound does not appear to effect the Red Cell metabolism, is very soluble in water, and contributes little to the osmolarity of the solution.

Our procedure utilizes a concentrated stock solution of Stractan (100g/100ml H20) which is deionized by mixing with Rexyn Beads, a mixed bed ion exchanger, and filtering. This procedure is repeated as necessary to reduce the osmolarity below 120 mosm/l. This stock solution is then diluted with the appropriate Red Cell suspending solutions to a specific gravity, 1.060 to 1.090. The ideal specific gravity is chosen by mixing Red Cells with the Stractan buffer and centrifuging in a hematocrit centrifuge. The density at which the cells do not separate out is the one selected for our NMR studies.

The details of this procedure will be published in Analytical Biochemistry later this year under the title,"Elimination of the Settling Artifact in the NMR Spectroscopy of Living Cells" by Richard J. Labotka, et al.

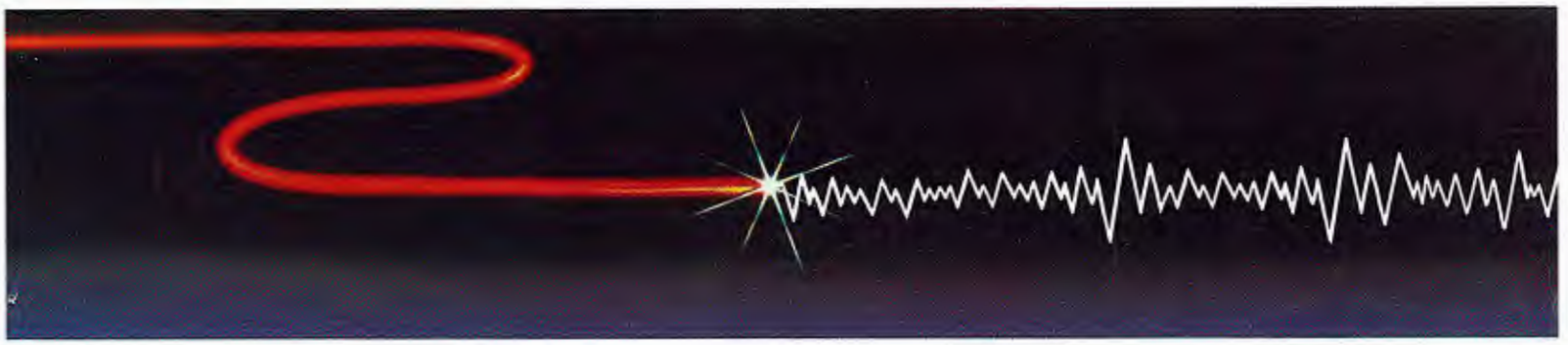
Yours sincerely,

Richard J. Labotka

Richard J. Labotka, M.D.

P.S. Please credit this letter to Dr. Rob Kleps's account.

The NMR evolution continues:



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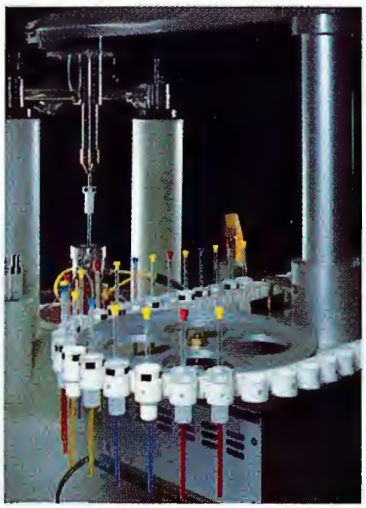

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THE UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NEW MEXICO 87131

January 25, 1985

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

Sixth New Mexico Regional NMR Meetings

Dear Barry:

Thirty seven scientists from throughout New Mexico attended the sixth New Mexico Regional NMR $(NMR)^2$ meeting that was held at the University of New Mexico on November 10, 1984. Professor Joseph J. H. Ackerman presented the morning talk, titled "NMR Spectroscopy of Evolving Metabolism". I gave the afternoon talk on the topic of employing hard and soft pulse sequences for observation of exchangeable protons in 90% ^1H_2O solution. In keeping with the format of these biannual meetings, many people brought posters and there was discussion about these and other NMR topics over a long lunch that was hosted jointly by Wilmad and MSD Isotopes.

As you may know, the purpose of our group is to promote interaction by NMR users within New Mexico. At last count, there were at least 11 research spectrometers in the State and the consistently high attendance at our meetings reflects this growing interest. Our Spring meeting will be hosted by Larry Werbelow at NMIMT in Socorro and I would like to invite everyone interested in NMR in our region to attend. The meeting will take place on April 13, 1985, and the speakers will be Professor David Grant (Utah) and Dr. Beat Meier (LANL).

I would also like to thank MSD Isotopes, Wilmad Glass Co., JEOL Instruments and Nalorac Cryogenics Corp. for their generous and continued support of our group.

Sincerely,

Jim

James D. Satterlee
Associate Professor
Fellow of the Alfred P. Sloan Foundation

P. S. Please credit this to Bill Earl's (Los Alamos National Laboratory) account.

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December 19, 1984

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

Sub: Use of T_1-shortening relaxation reagents for J-modulated spin-echo experiments in C-13 nmr

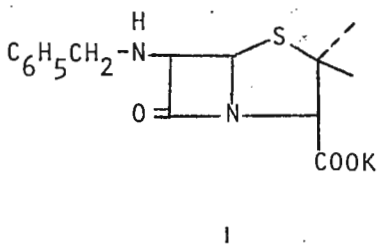
Dear Prof. Shapiro:

Paramagnetic relaxation reagents (PARR's) were popular for some time in C-13 nmr; reagents such as $Cr(acac)_3$ often provided considerable enhancement of intensities of quaternary carbon resonances. Disadvantages were (1) loss of nuclear Overhauser effect (nOE) and consequent decrease in signal intensities of proton-bearing carnbon resonances and (2) large increase in signal intensities of organic solvent carbon resonances which often mask those due to the substrate.

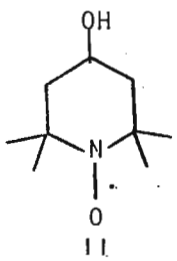
The new J-modulated spin-echo experiments provide instant partial editing of the noise-decoupled C-13 spectra with the C and CH_2's phased one way and the CH and CH_3's phased in the opposite way. In such experiments, deuterated carbon resonances of the solvents were suppressed greatly. However, delays of 4-10 sec are often necessary to observe quaternary carbon resonances. Employment of PARR's in these experiments also decreases the intensities of proton-bearing carbon resonances and increases the intensities of deuterated solvent carbon resonances. Hence, the application of PARR's is almost scarce.

We have tried free radical relaxation reagents in aqueous solutions to enhance quaternary carbon intensities in J-modulated spin-echo experiments. The relaxation delays could be cut substantially and often an overall "acceptable" C-13 spectrum obtained in much shorter times. Loss of nOE causes some decrease in the intensities of proton-bearing carbon resonances.

Illustrative of the above is the case of benzyl penicillin potassium salt(I) (200 mg/1.8 ml D_2O). Spectrum A was obtained with a relaxation delay of 4.0 sec and spectrum B was obtained with a relaxation delay of 1.0 sec. Both A and B took 15.7 min each. Spectra C and D were obtained after addition of 10 mg of Aldrich's 4-hydroxy TEMPO free radical (II). A relaxation delay of 1.0 sec was employed in both C and D. Spectrum C took 15.7 min while D took only 5.7 min. (In all spectra, C and CH_2's are phased up and CH and CH_3's down).



I



II

Sincerely yours,

P. R. Srinivasan

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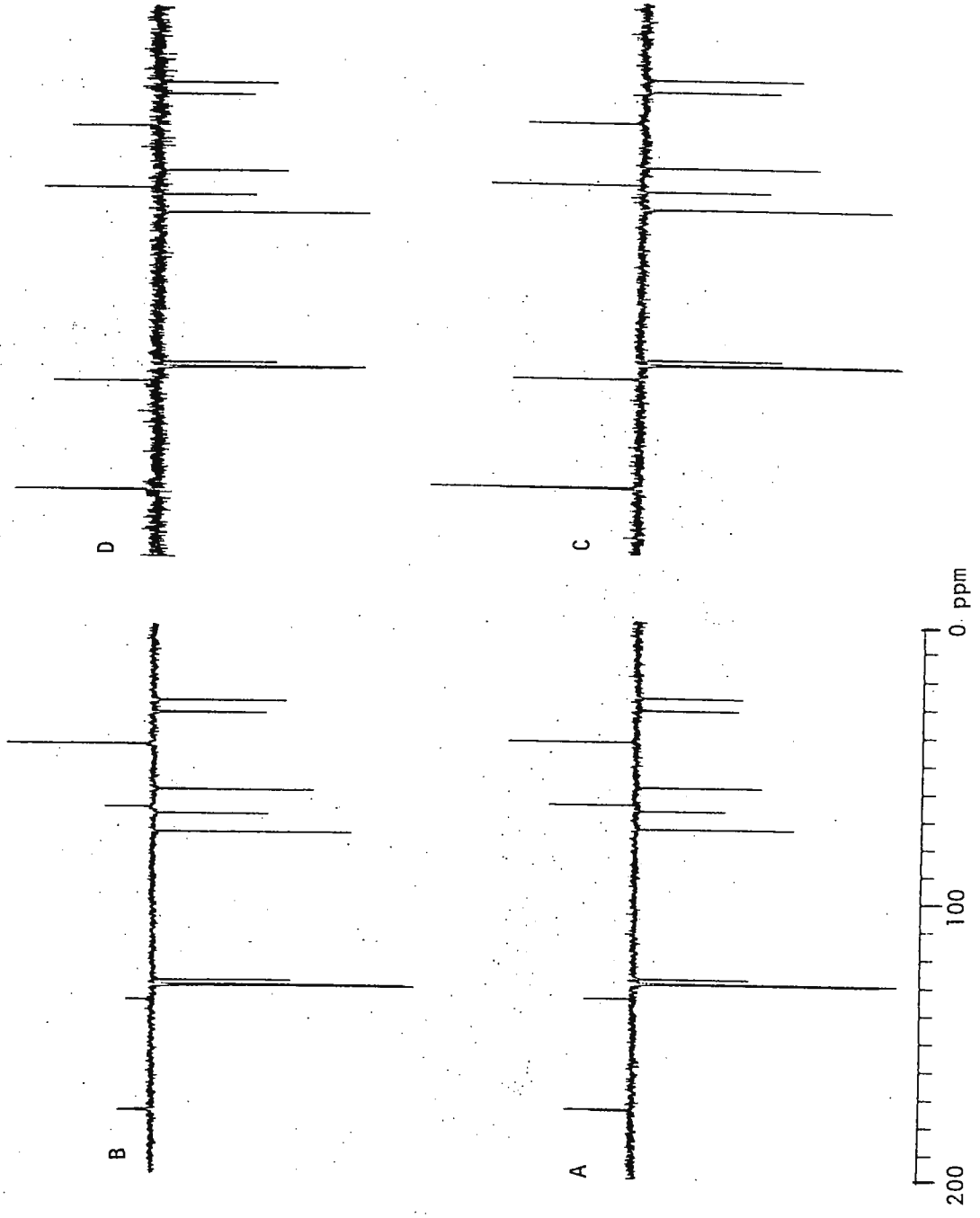
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B
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Telefoon 030 - 882311

Prof. B.L. Shapiro
Dept. of Chemistry
Texas A and M University
College Station
Texas 77843
U.S.A.

Datum January 22, 1985
Uw kenmerk
Ons kenmerk
Onderwerp Solvent dependency of coupling constants. Acetonitril and Methoxy-acetylene

Dear Prof. Shapiro,

Within the space of one week we received your kind green reminder, as well as your more ultimative yellow reminder of our obligation to contribute to TAMU, in order to continue our subscription, although you sent both reminders almost one month apart. Transatlantic postal services are thus full of surprises.

In december 1983 (TAMU 303, p.29) we reported on the solvent dependency of direct proton-carbon coupling constants. We found then direct evidence that the solvent induced changes in these couplings arise from the reaction field. The effect was similar, in a range of solutions with varying dielectric constants, in $CHCl_3$, CH_2Cl_2 and paraldehyde. For paraldehyde we found that in addition a solvent Stark-effect contributes to the total internal electric field in the solution. This total field is ultimately responsible for the observed changes in coupling constants.

When we extended our study to acetonitril, a very polarizable molecule with a large permanent dipole moment, the results were disappointing, in that we didn't find the expected relatively large change in the $^1J(CH)$ coupling with the changing dielectric constant of the solution, but a much smaller one (fig. 1). The change in the carbon-carbon coupling (studied in enriched acetonitril) is much larger, but with opposite sign, than that of the carbon-proton coupling (fig. 2). It is obvious that the carbon-carbon coupling is linearly dependent on the reaction field, but at large values of the dielectric function $R(\varepsilon)$ $(=(\varepsilon-1)/(\varepsilon+\frac{1}{2}))$ the reaction field saturates and another contribution takes over, which we again ascribe to the solvent Stark-effect.

At first sight, it is to be expected that the slopes for the reaction field dependency of $^1J(CH)$ and $^1J(CC)$ are of opposite sign, as follows. When we assume that the increase of the carbon-proton coupling reflects an increase in s-character of the C-H bond, the s-character of the $C(sp^3)$-C(sp) bond decreases, causing a decrease in the carbon-carbon coupling. In this way the increase in CH-coupling reflects the increase of the substituent (C≡N-group)-electronegativity caused by the internal electric field. However, the decrease in CC-coupling is larger than expected, solely on this basis, hence the sp-carbon hybridisation has to change too. This can be explained

(Continued on page 17.)

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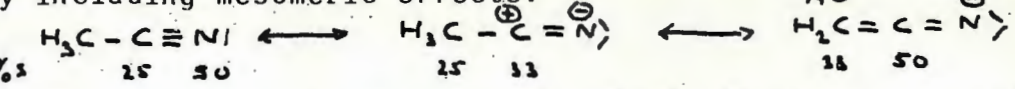
(Continued from page 14.)

by assuming a change in the hybridisation of the sp-carbon, from a purely sp-hybridisation towards an sp^2 hybridisation, by including mesomeric effects:



In methoxy-acetylene both the $^1J(C(sp^3)-H)$ and the $^1J(C(sp)-H)$ coupling constants increase linearly with an increase of the reaction field dielectric function $R(\varepsilon)$ (fig. 3,4), but at high values of this function the reaction field saturates and the solvent Stark-effect seems to take over, as at high values of the dielectric constant ε of the solution the couplings increase linearly with the Stark effect dielectric function $S(\varepsilon)$ $(=(\varepsilon-1)(2\varepsilon+1)/\varepsilon)$.

The observed increases of the one-bond couplings in methoxy-acetylene with the mentioned dielectric functions can be explained by assuming an increase in the electronegativity of the oxygen, caused by the electric field, which is felt in both oxygen-carbon bonds. The observed magnitude of the effects seems to indicate that the molecular dipole-moment bisects the carbon-oxygen-carbon angle, contrary to the normally accepted direction, which is almost perpendicular to this direction (Drenth et al.: Recl.Trav. Chim.Pays-Bas, 79,1056(1960)).

ONE BOND COUPLING CONSTANTS AS A FUNCTION OF $R(\varepsilon)$

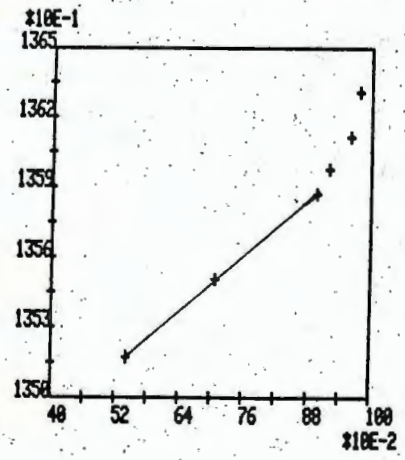
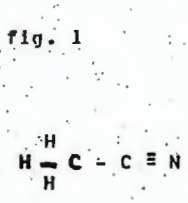


fig. 1



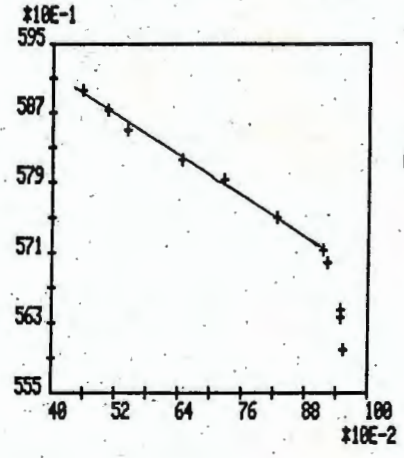
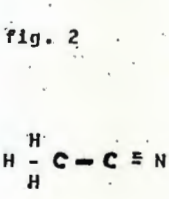


fig. 2



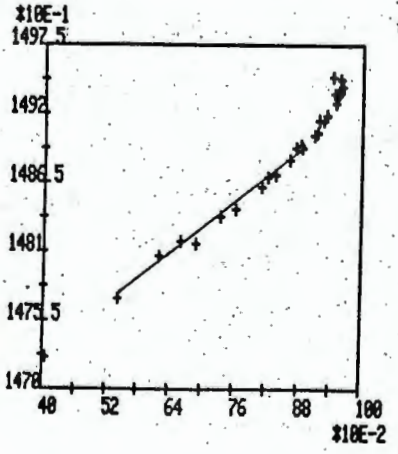
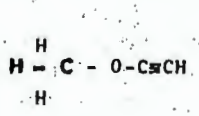


fig. 4



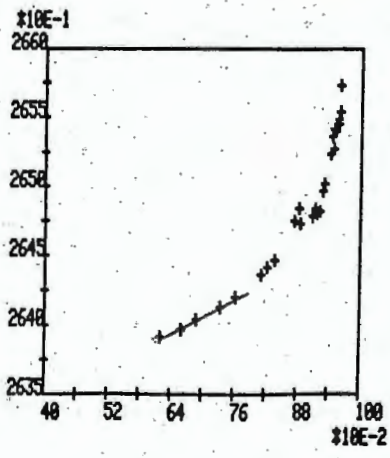
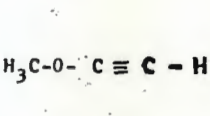


fig. 3



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February 6, 1985

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

NMR Spectrum Generating/Plotting Programs for the IBM PC

Dear Barry:

It is hoped that you will not be too much shocked, but this communication is being sent long before receipt of a green "warning" form.

In the midst of other things, I recently found the necessity for getting an NMR spectrum generating/plotting program for my IBM PC. Having found myself dissatisfied with most options available I decided to take the law (or at least the Hamiltonian) into my own hands. The result was a package of programs called (with great use of imagination): NMR.

Programs in this package will do the following, among other things:

1) Calculate NMR spectra of up to 7 spins, given chemical shifts and coupling constants.
2) Plot spectra as stick plots or Lorentzians (sample enclosed).
3) Print out the Hamiltonian, all eigenvalues and eigenvectors, and--of course--the line frequencies and intensities.
4) Draw energy level and Fz diagrams with or without the transitions being connected.

The programs were quite easy and fun to do. Anyone wishing to have a copy is welcome to one provided he sends me a blank DS/DD diskette and a stamped, self-addressed envelope to return a copy of the program with. Running requires an IBM-PC with (preferably) DOS 2.1, 256K of memory, and two floppy disk drives. Having access to a fixed or RAM disk would also be helpful along with ownership of the IBM BASIC compiler (the program runs with interpreted BASIC but is then excruciatingly slow).

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Associate Professor

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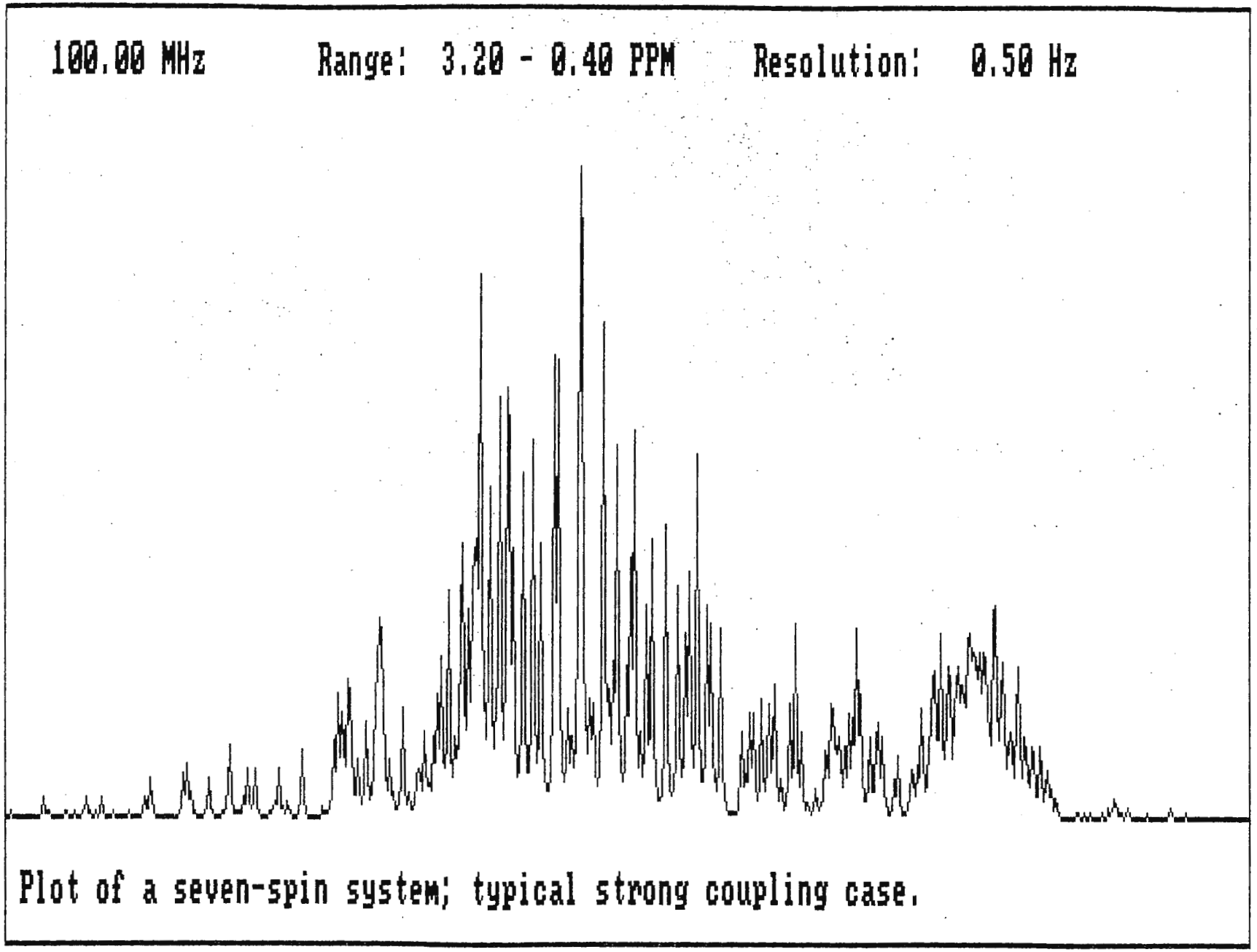

Plot of a seven-spin system; typical strong coupling case.

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TEL. (02) 293.662

7th February, 1985

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

Dear Barry,

Trying not to "expire". NMR of seeds, roots phytotoxins and other matters

We apologize for the delay in answering your "warning" letters, but the arrival of your last threatening pink ultimatum prompted me to try...

One reason for my delay was the change of my position in the University of Milano and my moving from the Politecnico to the Agriculture Faculty. Please acknowledge my new address.

The real truth of my delay is that I did not work very much in the last year!

Now, my first approach to the Agriculture Faculty was to try NMR of seeds, roots and other vegetable materials. We have measured ^{31}P spectra of the negatively photoblastic seed of Phacelia tanacetifolia under different condition of germination, in order to monitor any change in intracellular pH. As spectra must be accumulated for relatively long periods, it was necessary to keep the seeds alive by using perfusion techniques.

Our research on the stereodynamic properties in solution of substances with phytotoxic activity, has progressed. They are metabolites of some species of fungi (namely Cercospora, Cladosporium, Elsinoè), of which several are pathogenic for many plants. We have last year, reported on a conformational study of several of these substances, containing a perylenequinone ring, with helical chirality. One other interesting aspect of these systems is the quinone-phenol tautomerism, which has been investigated in detail for chloroform and acetone solutions. As this process is fast, compared with NMR times, the relative amount of one or the other tautomers has been estimated by the values of the long range ^{13}C-H coupling constants. It was thus necessary a complete assignments of all the carbon atoms, that has been performed by selective decoupling and NOE experiments.

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The results showed that the position of the tautomeric equilibrium depends, not only on the solvent and the concentration, but is depending on the helicity of the perylenequinone system, the substituents, and the possibility to form aggregates in solution. The conformation of the side-chains does not seem to be an important factor, unless it does not influence the aggregative process. For one compound, the aggregation is relevant, due to a particular geometrical situation. From a detailed investigation (dilution experiments), the structure of the aggregate could be determined. This study is in progress.

One of us (E.R.) spent two years in Oxford and in Lund at prof. R.J.P. Williams and prof. Forsén laboratories working on interesting problems:

- *"Calcium binding proteins" (in Lund) and*
- *"^{59}Co NMR studies of cobalt hexacyanide binding to horse ferricytochrome-c" (in Oxford).*

Some results have just been published on J.Inorg.Biochem. 21, 253 and 295 (1984).

Dr. A. Arnone
C.N.R. Center of
Natural Substances
at the Politecnico (Milano)

Dr. E. Ragg

Prof. R. Mondelli

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

January 30, 1985

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

Dear Barry,

^{19}F NMR of 2-Fluoro-2-deoxy-D-Glucose (2FDG) In Vivo

Phosphorus-31 NMR coupled with surface coil technology is a remarkably informative technique for the study of an important but limited number of phosphorus containing metabolites involved with bioenergetics in vivo. However, not all metabolites of interest contain a phosphorus moiety and so many researchers in the in vivo NMR community have recently focused on other NMR active nuclides in addition to ^{31}P. This is evidenced by the recent applications both in vitro and in vivo of ^{1}H NMR to examine brain metabolism, the use of ^{19}F NMR to study fluorine labeled anesthetics in a wide range of tissues, and use of ^{13}C NMR to study liver glycolysis, glycogenesis and glycogenolysis. Recent ^{19}F studies of the cancer drug 5-Fluorouracil have been reported as well.

Motivated by such studies our attention has recently been directed to the use of ^{19}F NMR to study fluorine labeled substrates that serve as precursors for further metabolism in vivo. The NMR sensitivity of fluorine (a 100% naturally occuring spin 1/2 nuclide) is much more akin to ^{1}H than ^{13}C with ^{19}F having a Larmor frequency only 6% lower than ^{1}H. Another advantage of ^{19}F is its negligible endogenous concentration in vivo which greatly reduces background spectral interference. Thus, in principle one can follow ^{19}F labeled substrates at lower concentrations (~ 0.1 mM) than typically studied using ^{31}P NMR (~ 1 mM) during a similar data aquisition period (~ 1 min).

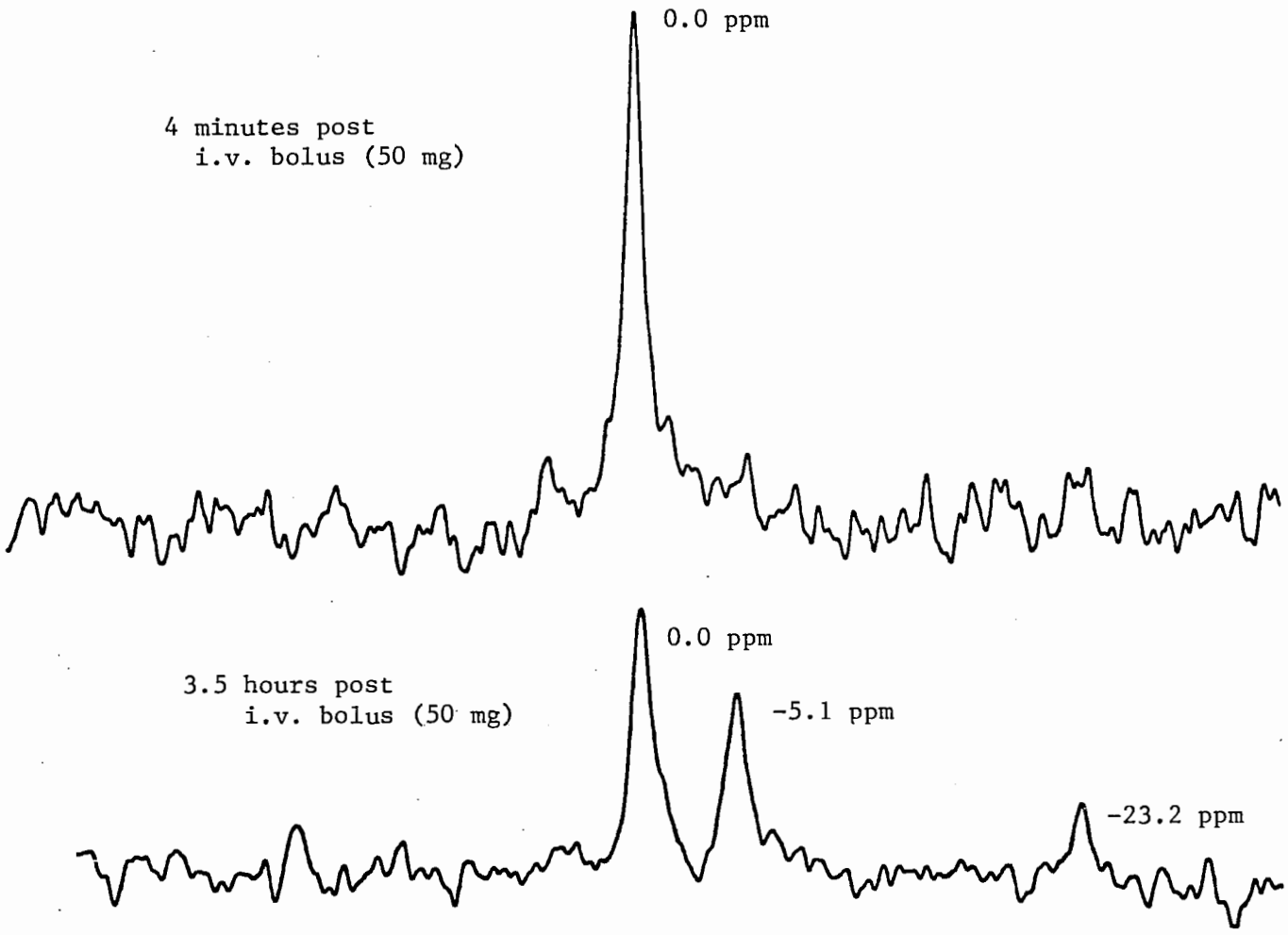
The top spectrum shows the brain ^{19}F resonance observed in vivo from a fluorinated glucose analog, 2FDG, injected as an i.v. bolus into a rat that had been fasted for 24 hours. The excellent sensitivity of this technique is clearly realized. At a later time, the bottom spectrum demonstrates the ability of ^{19}F NMR to follow the in vivo metabolic products of 2FDG in brain tissue of the intact rat. Powerful radiological imaging techniques using ^{18}F labeled 2FDG generally assume that 2FDG and its phosphorylated metabolic product 2-fluoro-2deoxy-D-glucose-6-phosphate are exclusively substrates for only the phosphorylation and dephosphorylation reactions, respectively. Thus, the appearance of the additional resonances, seen in the bottom spectrum, is somewhat of a surprise and points to the promising potential that ^{19}F NMR coupled with fluorine labeled substrates has to offer in studies of metabolism in vivo.

Bruce A. Berkowitz

Joseph J.H. Ackerman

JJHA/kk
enclosures

^{19}F NMR Spectra of Rat Brain in Vivo : 2FDG Metabolism



All animals were fasted 24 hours, anesthetized with nebutol, and given an i.v. bolus of 50mg 2FDG in one ml of 0.9% saline. The top spectrum represents a 4.4 minute aquisition time taken directly after i.v. bolus injection with a 1 turn, 1 cm OD surface coil tuned for 188.154 MHz and placed on the rat's head. The bottom spectrum is of a different rat taken with a 13.2 min. aquisition time 3.5 hours after injection with a 1 turn, 2 cm OD surface coil.

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February 8, 1985

COMPUTER CAPABILITIES FOR
BROAD PROTON SPECTRA IN SOLIDS

Prof. B. Shapiro
Dept. of Chemistry
Texas A&M University
College Station, TX 77843-3255

Dear Barry:

We have been interested recently in looking at some broad proton spectra in solids. Since we only have a NIC-80 computer with ADCs capable of 50 kHz data rates, it was necessary to interface a transient digitizer to the spectrometer. We got hold of a Biomation Model 8100 with a 100 MHz sampling rate and are using it after working out the bugs of the interface. The following key steps were taken to make the system work:

(1) An adapter card to interface the NIC-80 I/O bus to the Biomation digital control was built according to the specificaitons in the NIC-80 instruction manual on interfacing.

(2) The appropriate software [BIGADC routine in the NTCFT program (DIN overlay)] was modified to drive the BIOMATION-8100 instead of the BIGADC option for the Nicolet 1080.

Anyone interested in details should write or call Ray Kendrick at (408) 256-7854.

Best regards,

C. S. Yannoni

R. D. Kendrick

/ph

Standard Oil Company (Indiana)
Amoco Research Center
Post Office Box 400
Naperville, Illinois 60566
312-420-5111

February 1, 1985

Dr. B. L. Shapiro
TAMU NMR Newsletter
College Station, TX 77843

^{133}Cs NMR in Inorganic Solids

Dear Barry:

Recently we obtained ^{133}Cs NMR spectra of several cesium salts in the solid state and the spectra of Cs_2SO_4 were of particular interest. The MAS spectrum of a powdered Cs_2SO_4 obtained on an NTC-300 is shown in Figure 1B. The spectrum consists of two discrete resonances at -122 and -154 ppm relative to solid CsCl which indicates that there are two magnetically nonequivalent cesium atoms in a unit cell. The resonance at -122 ppm has rapidly attenuating spinning sidebands while the resonance at -154 has sidebands that extend to ±40, kHz (in an expanded spectrum). The reason for this sideband behavior becomes clear with the static spectrum shown in Figure 1A. The peak at -154 ppm (now seen as a shoulder) clearly has 6 satellite peaks due to quadrupolar coupling while the -122 ppm peak has a smaller coupling constant which from this spectrum can be estimated to be <1 kHz. The separation between the peak centered at -154 ppm and its nearest satellites was measured to be 9.1 kHz which gives a value for ν_Q of 18.2 kHz.

Haase[1] reported a chemical shift of -136 ppm for Cs_2SO_4 but did not report seeing two resonances. Further the reported value of ν_Q was 38 kHz, nearly double the value we obtain.

Some of the high frequency satellites in the static spectrum appear to have "doublet" characteristic which we were not able to explain. Therefore we grew single crystals to see if they could shed any light on this problem. Figure 1C shows the spectrum obtained for the single crystal when two of its axes were perpendicular to the magnetic field. The spectrum consists of two overlapping heptets -- one centered at -119 ppm has a peak separation of 0.9 kHz and one centered at -171 ppm with a peak separation of 8.9 kHz. A sharp signal at -200 ppm is due to a hydrated cesium ion. Rotation of the crystal by 5° about its long axis resulted in a doubling of the satellite peaks symmetrically displaced from the -171 ppm peak with peak separations of 8.3 and 9.0 kHz. We believe this indicates that there are two different cesium atoms in the unit cell and that each has a symmetry related site which accounts[2] for the doubling of the satellite lines.

Sincerely,

Joe Ray

G. J. Ray, B-5
(312) 420-5217

JH19:GJR/TA&M
59-4000
Attachment

[1] A. R. Haase, et al., Z. Naturforsch, 32a, 952 (1977).
[2] H. E. Petch and K. S. Pennington, J. Chem. Phys. 36, 1216 (1962).

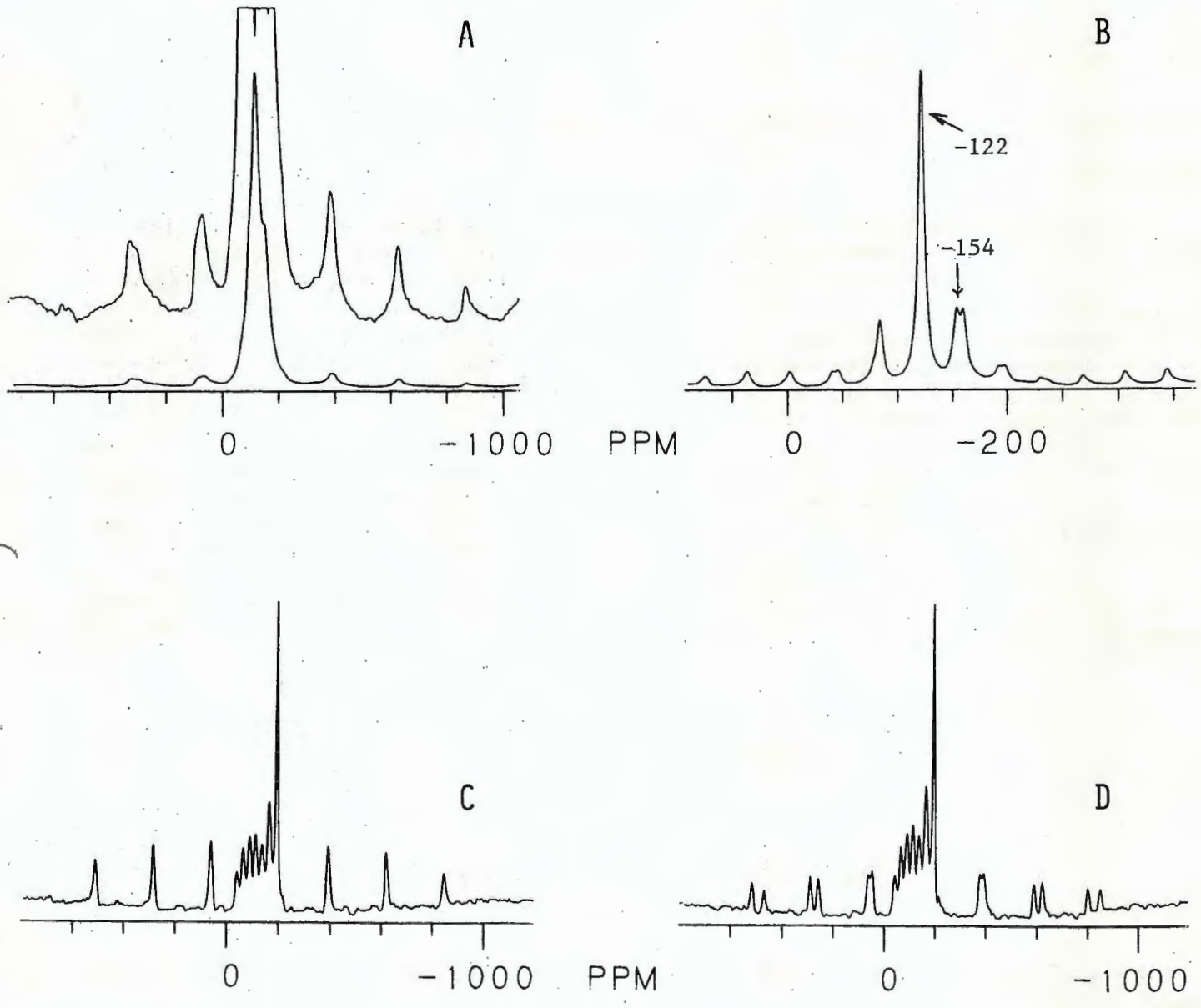


Figure 1. A) Static ^{133}Cs NMR spectrum of powdered Cs_2SO_4.
B) MAS spectrum of the powder.
C) Static spectrum of a single crystal of Cs_2SO_4 oriented with two crystallographic axes perpendicular to the magnetic field.
D) Static spectrum of the single crystal obtained after a 5° rotation about the crystals long axis. The singlet near 1-200 ppm is due to an impurity presumed to be due to hydration.

Department of Chemistry
University of Denver
Denver, CO 80208
303-871-2980

February 4, 1985

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

Re: Kinetic Studies of Paramagnetic Samples on the A200.

Dear Barry:

We have been obtaining spectra on our Chemagnetics Magnachem A200 for about 6 months so we thought it was time for our progress report. Much of our work to data has been on ^1H NMR of paramagnetic complexes of Fe(III), Cr(III), and Ni(II). We routinely use sweep widths up to 95 ppm. One of the questions that we have examined is the mechanism of dimerization of iron(III) tetratolylporphyrin hydroxide (FePOH) to the corresponding μ-oxo-bridged dimer, $(FeP)_2O$ in CCl_4 solution. FePOH was prepared by vigorously stirring the CCL_4 solution with aqueous base. We monitored the signal from the para-methyl groups as a function of time as shown in the accompanying figure. The methyl signal from FePOH is at 4.85 ppm (26 Hz linewidth) and the methyl signal from $(FeP)_2O$ is at 2.81 ppm (6 Hz linewidth). The broad signal at 0 to 1 ppm is due to water that is slowly exchanging with water attached to FePOH. Water does not bind to $(FeP)_2O$ so the position of the water signal shifts as a function of the extent of reaction. We studied the rate of the reaction as a function of the initial concentration of FePOH and as a function of the concentration of base in the aqeuous phase. We also studied FePOD. The combined data support the following mechanism. The rate of the second step was about five times slower for FePOD than for FePOH.

$$FeTTPOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeTTP^+ + OH^- \qquad (1)$$

$$FeTTP^+ + FeTTPOH \xrightarrow{k_2} (FeTTP)_2O + H^+ \qquad (2)$$

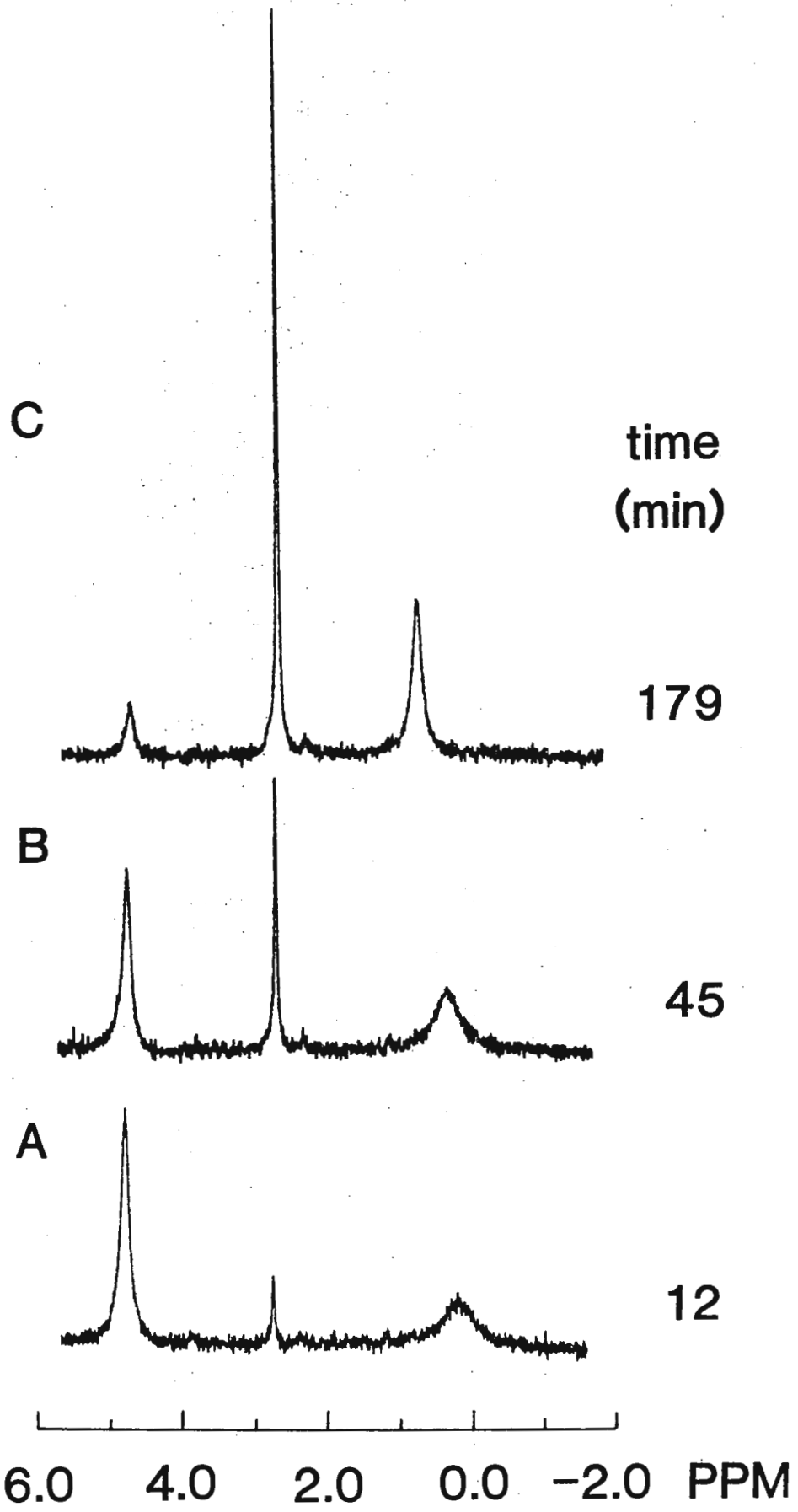
A paper reporting the details of this work will be submitted to Inorganic Chemistry.

Sincerely,

Gareth R. Eaton
Professor

Sandra S. Eaton
Visiting Professor

The spectra in the accompanying figure were obtained on a solution with an initial 1 mM concentration of FePOH. 200 acquisitions were used for each spectrum.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PROF. C.L. KHETRAPAL

Ref No.

Date 14.2.85

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

Title : Another confusion in NMR literature!

Dear Professor Shapiro,

The already confused readers of the TAMU-NMR News letter may be interested in getting further confused! The orientation of tetrahedral molecules in liquid crystals has posed so many problems of theoretical and experimental interest that no clear cut picture about the mechanism of orientation has yet emerged even though many Scientists have earned their bread and butter from such studies! The proton NMR spectra of tetramethylsilane (TMS) oriented in a mixture of two liquid crystals of opposite diamagnetic anisotropies around the "Critical" concentration at various temperatures are shown in figure 1. The two liquid crystals used are EBBA and ZLI-1167. Near the "Critical point", TMS provides two spectra (essentially triplets) separated by 0.42 ppm (at 288 K) and the component with larger dipolar coupling ("EBBA-like" orientation) appears at the lower field. Whether it is a "true coexistence" or some sort of inhomogeneities are responsible for the appearance of the two spectra is a different question but the fact that the two spectra separated by 0.42 ppm are observed under these conditions poses interesting theoretical questions and demands further investigations.

As is clear from the letterhead, I have now moved over to the Sophisticated Instruments Facility at the Indian Institute of Science. It is a National Facility available to scientists from all over the country. The Facility which already has a WH-270 FT-NMR spectrometer equipped with an ASPECT-2000 computer will shortly have an MSL-300 equipment for carrying out work in solid state NMR. With these facilities and colleagues like Professor Anil Kumar, we may create more "confusions" not only in the solid and liquid state NMR but also in development of the "Techniques".

Yours sincerely,

C. L. Khetrapal

(C.L. KHETRAPAL)

(Continued on page 33)

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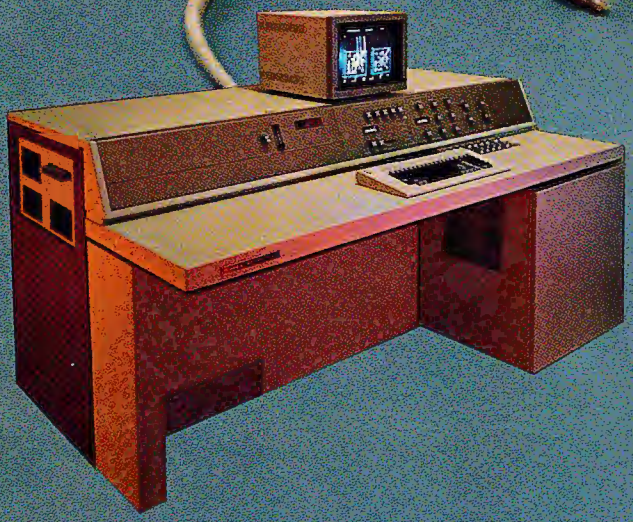

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(Continued from page 30)

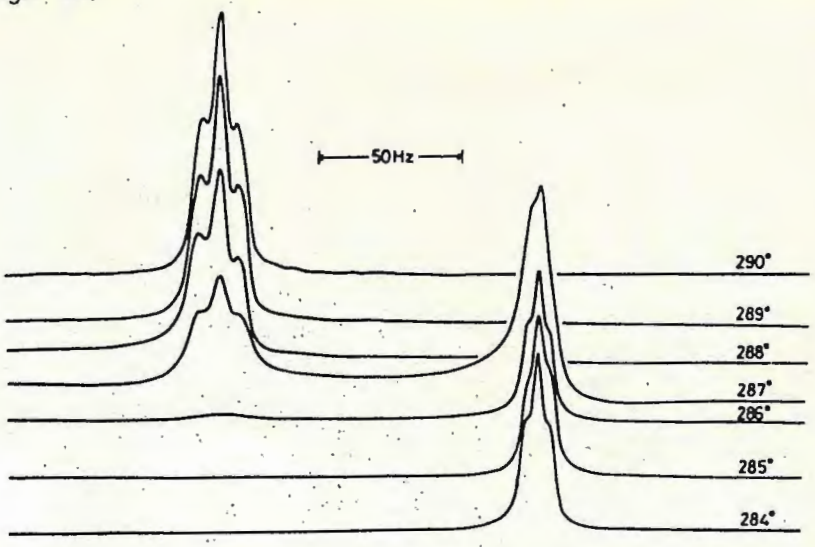

Fig.1 Proton magnetic resonance spectra of tetramethylsilane at various temperature in 0.3 : 1.0 mixture (by weight) of EBBA : ZLI-1167 ; solute concentration : 3% (by weight) ; spectrometer frequency : 270 MHz ; No. of scans : 240.

POSTDOCTORAL POSITION IN BIOLOGICAL NMR
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A position is available immediately for an nmr spectroscopist in a group of biochemists and spectroscopists interested in metabolic studies using sophisticated nmr techniques. A specific problem under consideration is the use of nmr to determine intracellular concentrations of metal ions in genetically modified cells. A person is sought with a strong background in nmr spectroscopy having a demonstrated interest in biological problems. The Stable Isotopes and Structural Chemistry Group, INC-4, has a strong program in metabolic studies using ^{13}C and ^{15}N labelled substances in conjunction with sophisticated nmr facilities. Collaborative arrangements for clinically related studies are available through the Center for Non-invasive Diagnosis at the University of New Mexico Medical School in Albuquerque. United States citizens preferred. Please contact: Dr. James A. Fee, Division of Isotope and Nuclear Chemsitry, INC-4, C-345, Los Alamos National Laboratory, Los Alamos, NM 87545, 505/667-5324.

318-34

UPPSALA UNIVERSITET
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Uppsala, February 13, 1985

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

"Organic counterion binding to micelles"

Dear Professor Shapiro,

Thank you for the reminder. While waiting for delivery of an XL-300 (hopefully at the end of March 1985) we continue our search for chemical applications of the Fourier-transform pulsed-gradient spin-echo multicomponent self-diffusion FT-PGSE-MC-SD (!) technique. Enclosed is a figure from a recently submitted paper (co-authored by M.Jansson) concerning the micellization of "organic" surfactants, i.e. ionic surfactants with organic counterions (rather than Na^+, Cl^- etc). The Figure nicely illustrates that in a competive situation (and also in a single ion-type situation) the most highly hydrophobic counterion is the most strongly bound. It is difficult to imagine any other technique that could provide similar information in such a clear-cut way.

Yours sincerely,

Peter Stilbs

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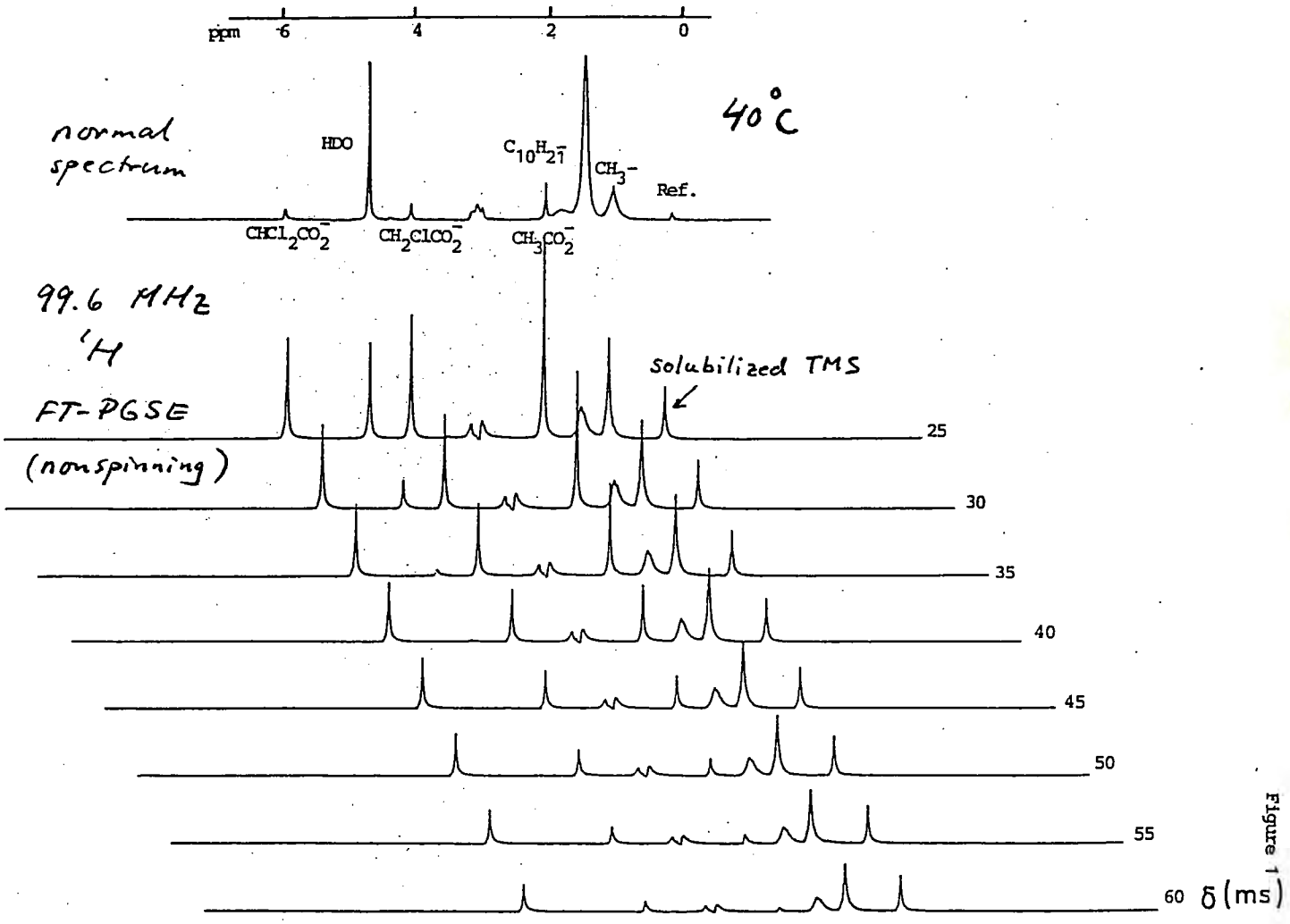


Figure 1

Equimolar mixture of 3 surfactants in D_2O (above CMC) of the $C_{10}H_{21}NH_3^+RCOO^-$ type.

$$A_i = A_0 \exp\left(-(\gamma G \delta)^2 D_i (\Delta - \delta/3)\right)$$

(303)491-6480
Colorado State University
Fort Collins, Colorado
80523

Department of Chemistry

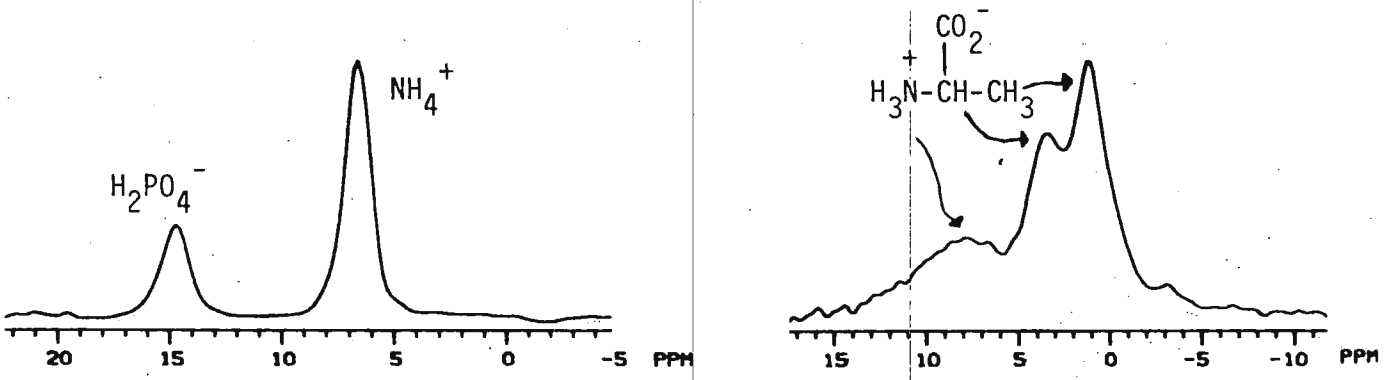
February 12, 1985

^1H Multiple Pulse Experiments. New Staff Position.

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

Dear Barry:

There are a couple of developments in our N.S.F.-sponsored Regional NMR Center that may be of interest to readers of the Newsletter. First, we (i.e., Bruce Hawkins and Chuck Bronnimann) have made considerable progress in ^1H multiple pulse techniques. The spectra below show results obtained



with the CRAMPS experiments (Combined Rotation And Multiple Pulse Spectroscopy) using the MREV-8 sequence and MAS at about 2 kHz. The experiments were carried out on a severely modified NT-200 spectrometer to which a new phase shifter and additional pulse programming capabilities were added. Current efforts are underway to extend these capabilities to the NT-360 (also requiring major modifications).

In addition, the Center is planning to add a new staff member within the next few months. We are looking for a scientist, engineer or technician with strong abilities and interest in NMR instrumentation, preferably with substantial NMR experience. Applicants should send a resume and arrange to have sent three letters of recommendation to me. Our deadline for applications is April 30, 1985, and we hope to have someone in place by June. Colorado State University is an EEO/AA employer.

Sincerely,

Gary E. Maciel
Professor

Instruments Inc.

Orchard Park
PO Box 332 Danbury CT 06810

Telephone: 203 796 2500

February 20, 1985

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

Subject: Quantitative Analysis of Severely Overlapping Resonances

Dear Professor Shapiro:

I am enclosing some preliminary work which compares three methods for extracting structural information from NMR resonances which severely overlap. Illustrations of each of the three methods are shown in Figure 1.

The first method (top of Figure 1) simply involves measuring the heights of the peaks. This method can only be considered accurate if 1) the peaks do not overlap; 2) the peak contours are known to be the same type (i.e. Lorentzian, Gaussian, etc.) and 3) the full widths at half heights are the same. When the peaks severely overlap, as they do here, some or all of the criterion described above are violated. Therefore, quantitative estimates made by this method are usually not very accurate.

The second method (middle of Figure 1) uses the technique of resolution enhancement to artificially narrow the lines. Numerical integration is then used to make quantitative estimates. Resolution enhancement involves multiplying the FID by some apodization function. In the present method, which is known as the Lorentzian-Gaussian transformation, the function has the general form: $y(t) = \exp(-a(t-b)^2 + ab^2)$, $a>0$, $b>0$. The user chooses the values of the parameters a and b in order to optimize the resolution.

If the resonances severely overlap, as they do here, this method may artificially enhance the area under some peaks with respect to those of other peaks. Again, caution should be used when interpreting the numerical estimates.

The third method (bottom of Figure 1) shows the technique of spectral simulation, also known as spectral deconvolution. The method involves selecting lineshapes, in this case, Lorentzian absorptions of the general form: $y(f) = c/(1+a(f-b)^2)$, $a>0$ and optimizing the various parameters (c, a and b) so as to minimize the total error between the synthetic spectrum and the experimental data.

Choosing an improper lineshape, such as Gaussian instead of a Lorentzian, can lead to some uncertainty. Baseline artifacts are potential problems. Fortunately, the error-minimization technique usually results in the best estimate even when conditions are not perfect.

At this time, I feel that the third method produces the best accuracy when NMR resonances severely overlap. Please credit this letter to the account of Richard E. Schwemm.

Cordially,

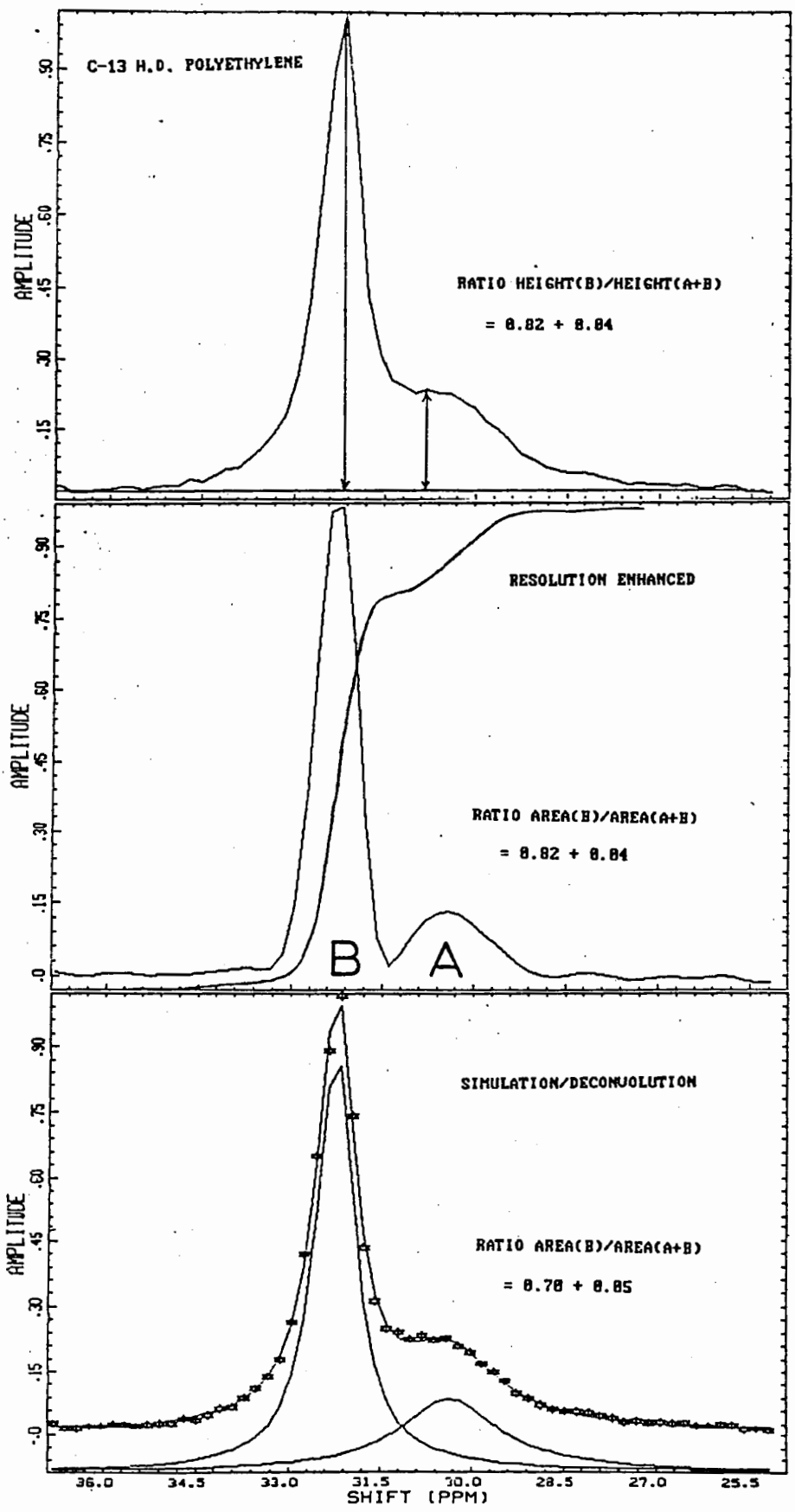
Paul D. Murphy

Paul D. Murphy

/ejk

Figure 1. Examples of three techniques for extracting numerical estimates from severely overlapping resonances:

Top: the height method; Middle: resolution enhancement ; Bottom: spectral simulation.


C-13 H.D. POLYETHYLENE
AMPLITUDE
RATIO HEIGHT(B)/HEIGHT(A+B)
= 0.82 + 0.04
RESOLUTION ENHANCED
RATIO AREA(B)/AREA(A+B)
= 0.82 + 0.04
B
A
SIMULATION/DECONVOLUTION
RATIO AREA(B)/AREA(A+B)
= 0.78 + 0.05
36.0
34.5
33.0
31.5
30.0
28.5
27.0
25.5
SHIFT (PPM)

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Ottawa, Canada
K1A 0R6

23 January 1985

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

Caution in Reporting Ξ (Xi)Values

Dear Barry,

The modern broad-banded FT spectrometers make it easy to look at less common nuclei in reactive systems where direct referencing may be difficult. The design of the spectrometers is usually such that the final RF frequency cannot be measured directly with a frequency counter. If all frequencies are determined as ratios of a standard reasonably accurate frequency the final Ξ values should be quite good since errors tend to compensate. Unfortunately this is not the case with the "Bruker AM series" of spectrometers.

The proton frequency in our spectrometer is obtained from an average quartz crystal, which after addition of an audio-frequency offset, is multiplied by six. One may obtain an acccurate basic spectrometer frequency by counting the continuous frequency for different audio offsets, extrapolating to zero offset, and multiplying that frequency by six. The initialization system in the software will display correct proton frequencies after it is calibrated in this manner.

One still does not get correct frequencies for other nuclei. These frequencies are obtained by subtracting four times the synthesizer frequency from the basic spectrometer frequency. The operating software assumes that the nominal synthesizer frequency is correct regardless of the basic frequency calibration. It is also necessary to manually correct for any inaccuracies in the synthesizer frequency. These corrections require an accurate and well calibrated frequency counter, but the actual measurements need only be done occasionally.

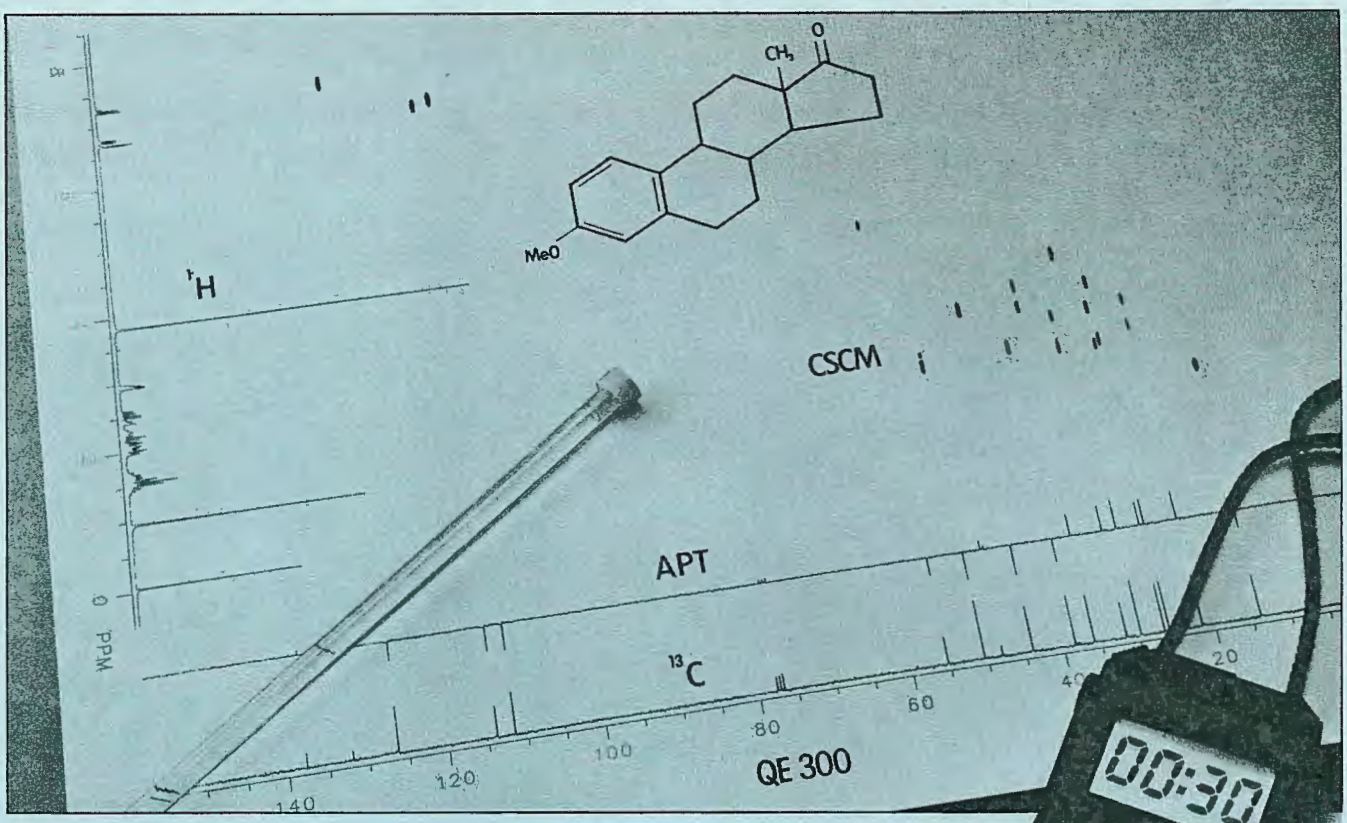
The net result is that for this type of spectrometer, as received from the manufacturer, one cannot obtain accurate Ξ values without both a calibration and correction procedure. The simplest way around the problem is to replace the 10 MHz quartz oscillator with a 10 MHz rubidium frequency standard. Once the basic spectrometer frequency has been calibrated all frequencies should remain accurate.

With best wishes,

S. Brownstein

/mr

Canada



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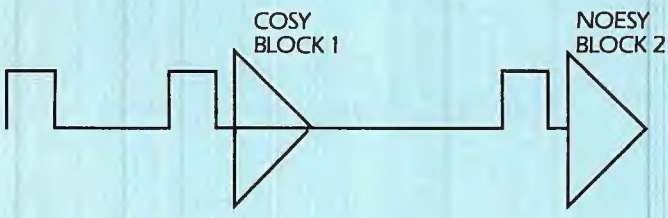

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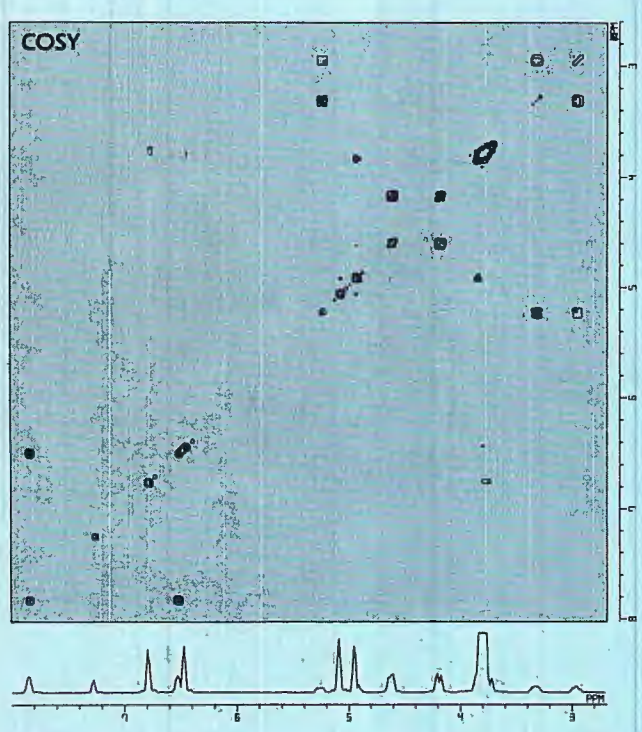

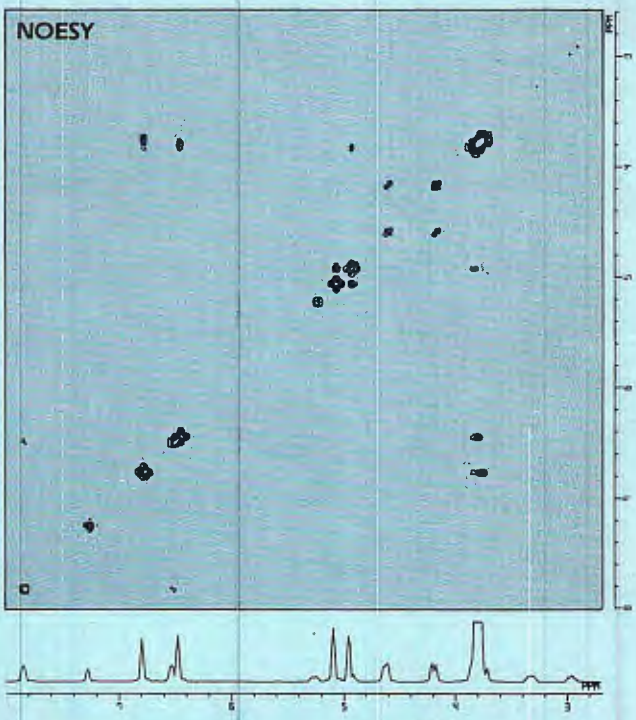

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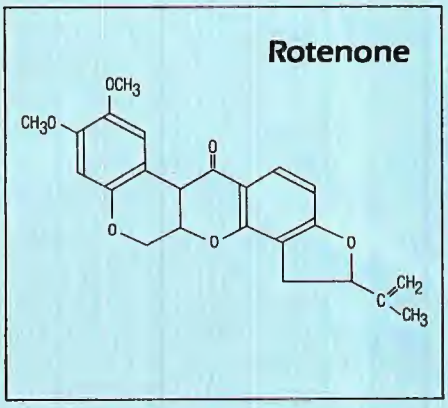

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