TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

NO. **299**

AUGUST 1983

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A U T H O R   I N D E X   ---   TAMU NMR NEWSLETTER NO. 299, AUGUST 1983

DEPARTMENT OF CHEMISTRY
TELEPHONE 902-424-3305

DALHOUSIE UNIVERSITY
HALIFAX, CANADA
B3H 4J3

June 30, 1983

Professor B. L. Shapiro
Texas A & M NMR Newsletter
College Station, Texas   77843
U.S.A.

Dear Barry:

1) NO_3^- rotations in solid NH_4NO_3

Ammonium nitrate is known to undergo at least five different solid-solid phase transitions. There has been considerable debate in the literature about the rotational motion of the nitrate ion in the high temperature phase (1). We have carried out a few simple nitrogen nmr experiments which are most useful in characterizing the behaviour of the nitrate ion. Proton-decoupled nitrogen-15 nmr spectra of the solid I (T = 403 K) and solid II (T = 373 K) phases of NH_4NO_3 are shown in fig. 1. The $^{15}NO_3^-$ and $^{15}NH_4^+$ resonances have opposite phases but for easier presentation are both plotted with identical phases. The spectra indicate that in the solid I phase rotations of the nitrate ion are rapid with respect to the ^{15}N chemical shielding anisotropy. A more quantitative measure of the effect correlation time for nitrate ion rotations can be obtained by measuring ^{14}N T_1's. E.G., at 413 K, T_1 (^{14}N) = 14.6 ms which implies $\tau_{eff} \simeq 8$ ps.

2) Unusual Coupling

In a recent letter (294-25) one of your readers suggested $^4J(O\underline{H},\underline{H}_4) \simeq$ 6 Hz in I. If correct I would agree that this is a most unusual coupling being at least an order of magnitude greater than would be expected. I would suggest that the assignment of H_4 and H_6 should be reversed and the 6 Hz coupling be attributed to $^3J(N\underline{H}, \underline{H}_6)$? ?

Best wishes from Nova Scotia.

I

Yours sincerely,

Rod

Roderick E. Wasylishen
Associate Professor
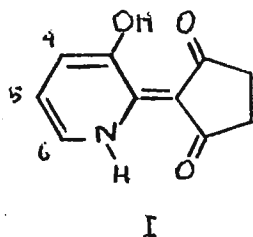
REW/djc

1) G. J. Kearley and S. F. A. Kettle, J. Mol. Struct., <u>79</u>, 319 (1982).

373 K

NO$_3^-$

NH$_4^+$

403 K

Universität Bern

Institut für organische Chemie

CH - 3012 Bern, Freiestrasse 3
Telefon 031 65 43 11
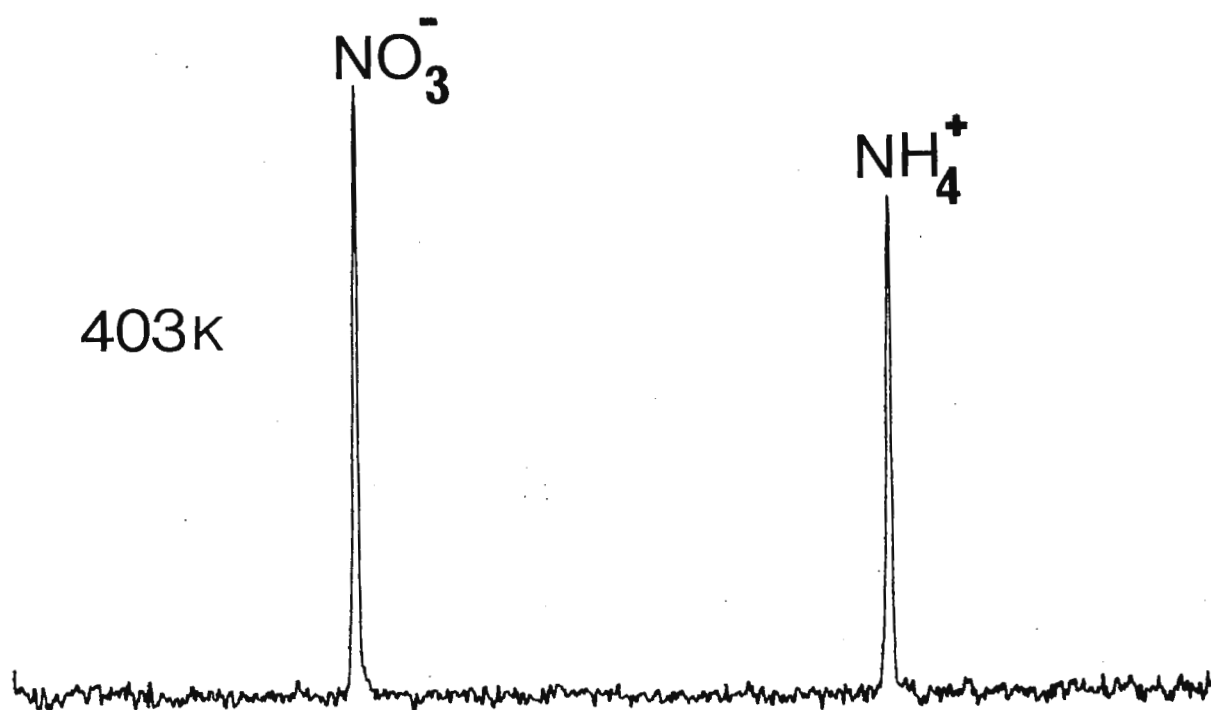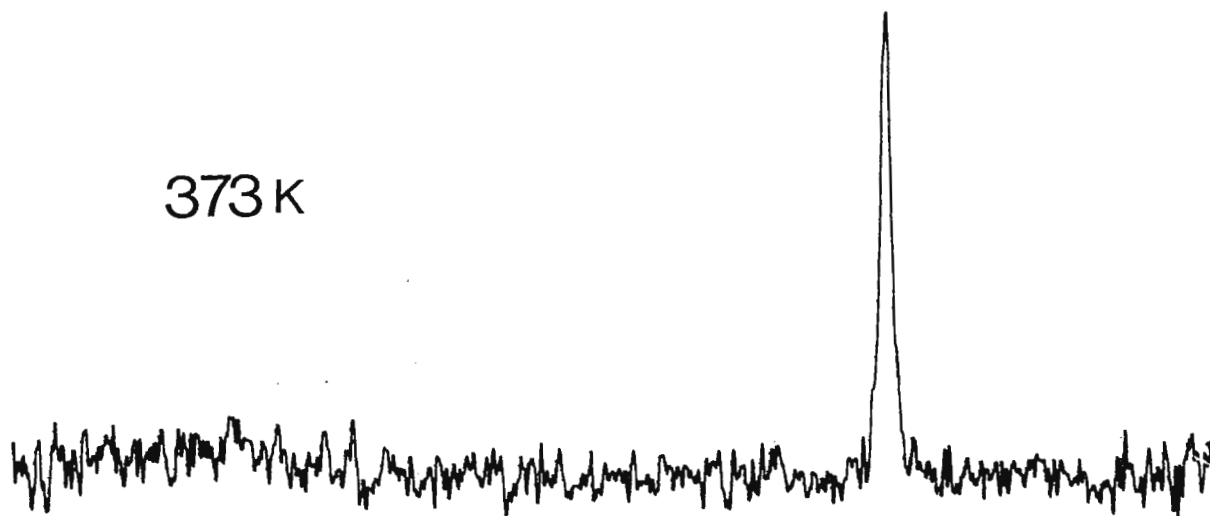
July 8, 1983

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

Dear Prof. Shapiro:

Yet another simple Test for ^{13}C-Multiplicity on a VARIAN XL-100

There exist now some new experiments to determine carbon
multiplicities. In contrast to the well known off-resonance
technique they show almost equal sensitivity compared to the
normal broadband decoupled carbon spectra and don't suffer
from overlap of multiplet lines in spectra with a high density
of signals. Multiplet selection in these new procedures is
based on relative phase and intensity of proton broadband de-
coupled carbon signals, which are different for C, CH, CH_2 and
CH_3.
The attempt to adapt some of the modern pulseschemes on
an older type spectrometer fails mainly due to the fact, that
these machines are not equipped with a rf-90^0-phase-shifter.
Long 90^0-pulsewidths - if not equipped with a pulseamplifier -
and single phase detection mode on the other hand don't
guarantee uniform flip angles over the entire frequency range.
This leads to poor sensitivity for some lines, phasing problems
and thus ambiguities in multiplicity determination. We re-
ferred therefore to the simple one-pulse method with delayed
decoupling as proposed by Le Cocq et al. some time ago [1] .
In contrast to this original version which leads to severe
phasing problems and line shape distortions caused by the
delayed sampling, we start the detection of the FID immediately
after the pulse as visualized in Fig. 1. The first part of the
FID which contains the carbon signal under proton coupled
conditions hardly contributes to the spectrum, which shows only
the signals determined under proton decoupling in the second
part. Simplicity both in setting up the experiment and modifying
the hardware, no problems with phasing and the determination
of 90^0 pulsewidths - we use pulsewidths optimized for maximum
sensitivity - are the main advantages of this variant. Some
slight loss of sensitivity for proton bearing carbons, compared
to a normal broadband decoupled spectrum and some baseline
roll are the disadvantages.
Fig. 2 shows two spectra of Isoquadrone with delays
optimized to show all carbon signals with appreciable sensitivity
a) and set to suppress signals with $^1J_{CH}$=125 Hz b). Spectrum a)
shows CH and CH_3 with negative, C and CH_2 with positive intensities.
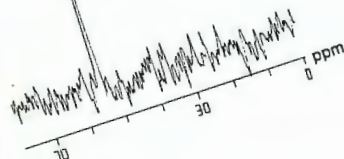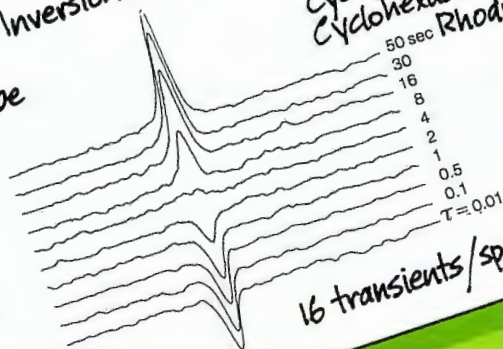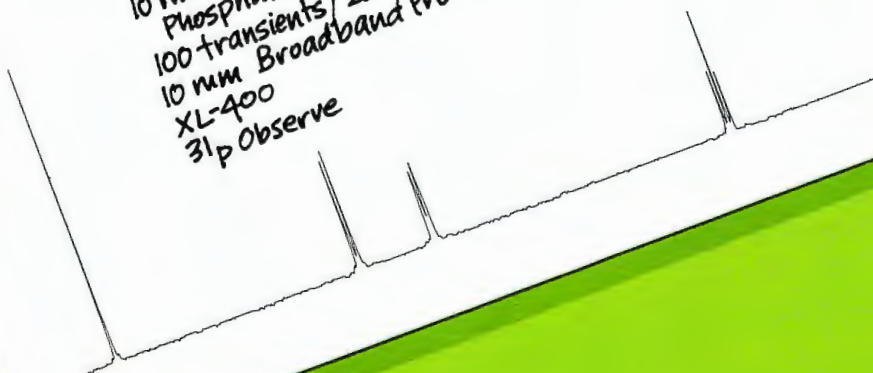
Varian's new XL Series Data System is so advanced...
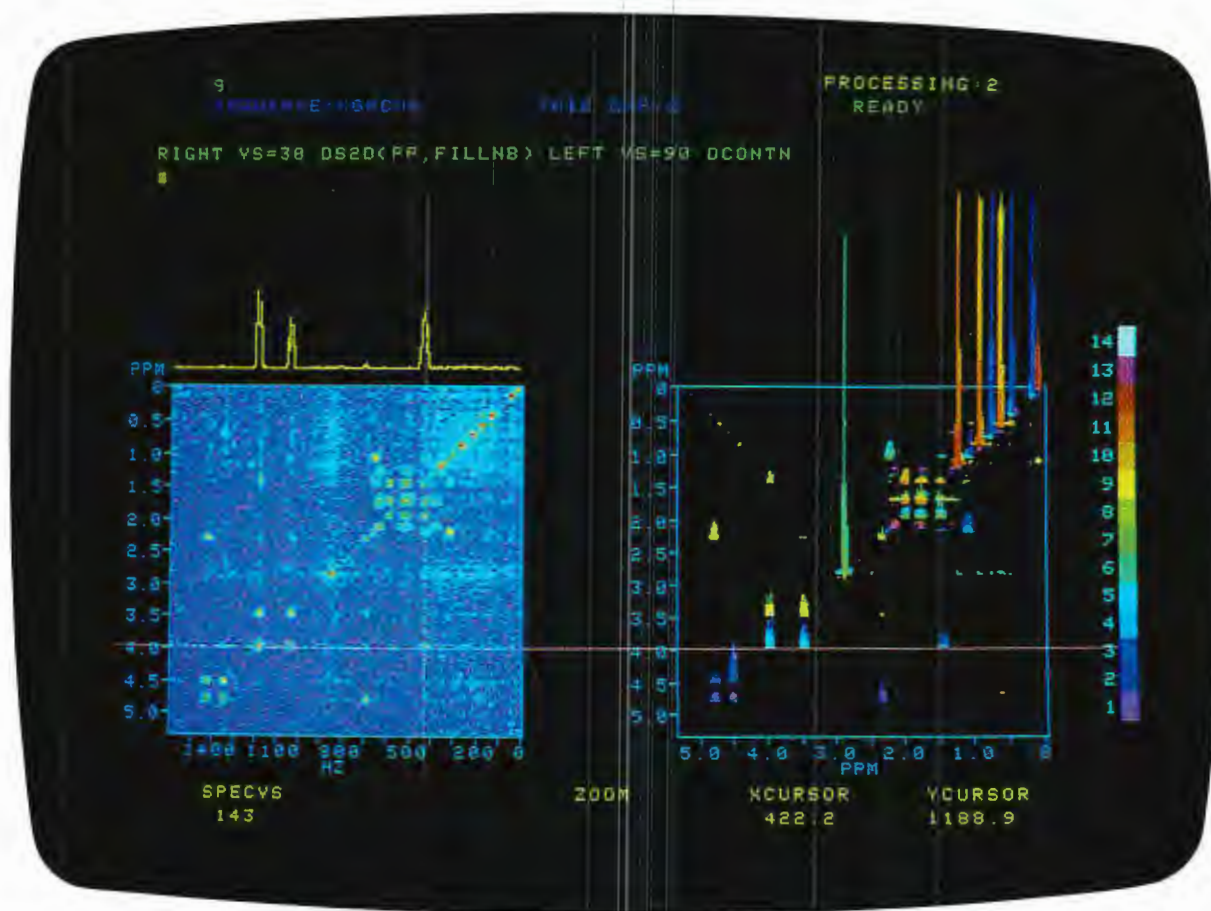
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Dr. George Slomp, The Upjohn Co.
"The use of color in the stacked displays is more than just artistic. It helps correlate peaks in the individual areas."

Dr. Jake Stothers, University of Western Ontario
"The number of colors gives you greater dynamic range for contour plots."

Dr. Robert Santini, Purdue University
"It does Fourier transforms so fast that data manipulation is no longer a barrier to the routine use of 2-D...I want one."

Dr. Josef Dadok, Carnegie-Mellon University
"Finally, a company that makes NMR instruments has incorporated the advances that computers have made over the past decade."

Dr. Gheorghe Mateescu, Case Western Reserve
"What amazes me is the speed of the FT. This is essential for opening up new possibilities for research in two-dimensional NMR."

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varian

Another advance in NMR
...from Varian

From spectrum b) one immediately recognizes five signals with relative high intensities, the quaternary ▼ (positive), the two olefinic ■ and the two cyclopropane ✦ methine carbons.

[1]   C. Le Cocq, J.Y. Lallemand, Chem. Communs. , 150 (1981)

Sincerely yours

Peter Bigler

Peter Bigler
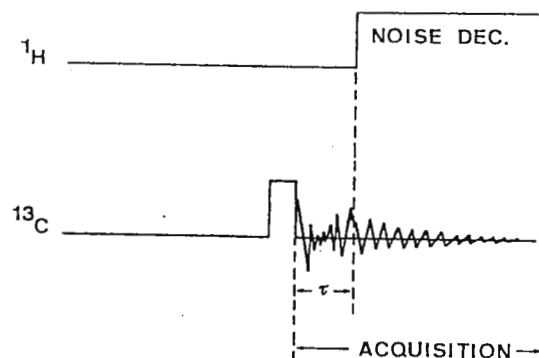
Fig. 1
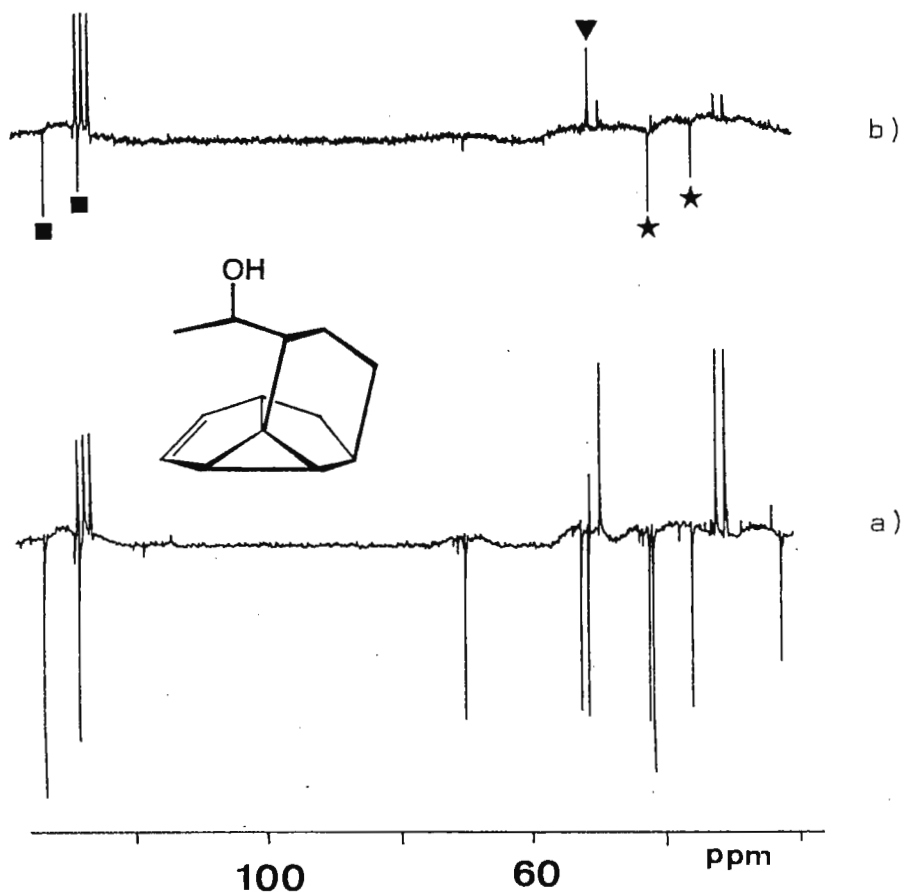
Fig. 2

QUEEN MARY COLLEGE

UNIVERSITY OF LONDON

DEPARTMENT OF CHEMISTRY
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Professor D.C.Bradley, DSc., FRS
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Bernard L. Shapiro,
Editor and Publisher,
TAMU NMR Newsletter,
Texas A&M University,
College Station,
Texas 77843,
U.S.A.

6th July, 1983

Dear Barry,

T_1 Values for ^{17}O in Metallocarbonyls

About five or six years ago we started to look at ^{17}O spectra of some small heterocycles supplied by Rosanna Mondelli from Milan to supplement the ^{13}C and ^{15}N data we had. We used our now defunct Bruker HFX-13 (vintage 1970) and obtained the normal, quite broad, spectra which one had come to expect. One of our other Italian collaborations was with the inorganic chemists at the University of Turin. This had led to our early ^{13}C work on metallocarbonyls and the collaboration was still occasionally activated. Because of this Silvio Aime visited us about 1978 and suggested we should try ^{17}O work on metallocarbonyls – something that had not occurred to us as being useful since we were conditioned to expecting broad lines. We concurred and obtained delightful ^{17}O spectra with narrow lines.[1] This opened up the possibility of high resolution ^{17}O work on metallocarbonyls such as the study we then did[2] on $Co_4(CO)_{12}$, for which ^{13}C work had been enigmatic. By this time we had access to the London University Bruker WH-400.

The latest news is that we have been measuring T_1 values for ^{17}O in metallocarbonyls. Normally the samples are prepared in Turin, enriched in ^{17}O and arrive in London by a variety of means – normally in someone's holiday baggage.

For $Fe(CO)_5$ (measured at natural abundance) we found the ^{17}O T_1 value (toluene solution; 298 K) to be 50 ms. Use of the Stokes-Debye formula gave τ_c as 4.6 ps which compares well with the literature value[3] for the T_1 range in the temperature interval 253-313 K (pure liquid) of 3.5-9.0 ps. The derived value for the ^{17}O quadrupole coupling constant (QCC) is 2.13 MHz. This is smaller than the value for free CO (4.34 MHz)! For other metallocarbonyls we have found T_1 to be in the range 50-8 ms so far, and we have calculated the QCC range to be 2.0-3.3 MHz. Interestingly T_1 varies from one CO to another within the same compound. For example, in $Re_2(CO)_{10}$ we find 29.4 ms for the axial CO s and 13.2 ms for the equatorial CO s. The difference is in the wrong sense for preferred rotation around the Re-Re bond and we deduce that QCC values are structure related. The work has been accepted for publication in Chemical Communication[3] if readers want details.

Other work here has included some saturation transfer experiments which Geoff Hawkes inspired (and did!) to study slow carbonyl exchange in $H_2Os_3(CO)_{10}$ (^{13}C enriched). This let to some elegant 2D-spectra on the same sample to pick up not only the exchange but also the $^{13}C-^{13}C$ coupling, *with the help of du-Yun Lian*.

Not content with all this, Silvio Aime and his colleagues have been producing ^2H enriched hydrido metallocarbonyls and we accordingly have a programme of ^2H work. Until it comes to fruition and your next reminder arrives,

Best wishes from the Group,

Yours sincerely,

Geoff Hawkes,
LuYun Lian

Ed

Professor E.W. Randall

1. S. Aime, L. Milone, D. Osella, G.E. Hawkes and E.W. Randall, J. Organomet. Chem., 1979, 178, 171-175.

2. S. Aime, idem., J. Am. Chem. Soc., 1981, 103, 5920.

3. S. Aime, R. Gobetto, D. Osella, L. Milone, G.E. Hawkes and E.W. Randall J. Chem. Soc., Chem. Commun., 1983, to be published.

Professeur PIERRE LASZLO

Institut de Chimie
Université de Liège
Sart-Tilman par 4000   Liège, Belgique

Professor Bernard L. SHAPIRO
Texas A&M University
Department of Chemistry
College Station, TX 77843, USA   July 11, 1983

Dear Barry,

Condensation of sodium counterions around micelles : experiment and theory.

We had applied successfully earlier a modified Poisson-Boltzmann treatment to systems, synthetic or natural, constituted of cylindrical poly-electrolyte molecules in an ionic atmosphere[1-2]. We have now extended this formalism to micellar aggregates : the concept of counterion condensation, as borrowed from the definition by Westra and Leyte[3], is generalized for this purpose to polyelectrolytes of spherical symmetry. The calculated ionic activities agree very well with experimental activities from the literature.

As yet another test of the model, sodium-23 nmr linewidths are measured for sodium dodecyl sulfate, in the range of <u>ca.</u> 10^{-1} cmc - 10 cmc. They show outstanding agreement with the mean value of the calculated $(efg)^2 = \langle(V_r/r)^2\rangle$: the line broadenings are directly proportional to $\langle(V_r/r)^2\rangle$. From the slope, taken together with a mean viscosity of 9 mP (the entire viscosity range extends from 8.5 to 10.8 mP), we obtain a value of 41 ns for the product $(1 + \gamma_\infty)^2.\tau_c$. Our experimental results are also consistent with the notion of a pre-aggregation, prior to micelle formation, at concentrations below the cmc. Hence, we are confident that the modified Poisson-Boltzmann approach will prove more generally useful in studying micelles.

Otherwise, we are eagerly awaiting delivery at the end of the summer of a new Bruker 300 wide bore spectrometer for our group. Micelles are not the only organized bodies of interest to us. We are also busy investigating ionic

transport across membranes, in relation with the metabolism, both normal and pathological. So that the new instrument will come in handy for these other and more biological studies.

Did you know that Belgium has now three three-stars restaurants in the Michelin Guide ? Which makes your visit here even more overdue !

With best personal regards,

Cordially yours,

A. Delville   P. Laszlo

References :

1.   Delville, A.; Laszlo, P.; Gilboa, H., J. Phys. Chem. 1982, 77, 2045.
2.   Delville, A.; Laszlo, P., Biophys. Chem. 1983, 17, 119.
3.   Westra, S.W.T.; Leyte, J.C., Ber. Bunsenges. Phys. Chem. 1979, 83, 672.

HERCULES

July 12, 1983

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

Dear Professor Shapiro:

CURVE DECONVOLUTION OF ESR SPECTRA ON THE NMR COMPUTER

Our laboratory has two Nicolet-360 WB NMR spectrometers and one Nicolet data station, interfaced to an IBM ER200-D-SRC electron spin resonance spectrometer and (recently) to a Varian EM390 proton spectrometer. All three instruments are based on the Nicolet 1280 computer with CDC-9427H disk drives.

The general signal averaging computer program supplied by Nicolet Instrument Corp. (Madison, Wisconsin) for the ESR data station is called LAB2. This versatile program can accept just about any analog signal as input and then perform a multitude of data handling routines, e.g. Fourier transformation, spectral addition, integration, phase correction, and plotting of spectra. However, there is no provision in the LAB2 program to do curve deconvolution.

The NMC program supplied by Nicolet Magnetics Corp. (Fremont, California) to operate their NMR equipment is capable of doing curve deconvolution. Unfortunately the NMR program will not recognize disk files generated by the LAB2 program. The NMC program recalls a file from the disk by searching for the file name, verifying that the file header is under NMC header, and then loading the file into computer memory. In order to force LAB2 data files into the NMC program, there are a few things that need to be known: (1) our computers contain 128K RAM; (2) the NMC program occupies the first 64K of memory; (3) the data memory is the second 64K of RAM; and (4) the files are stored on disk with the file header at the beginning of the file. Hence if the file can be loaded into the data memory area (second 64K) before the NMC program is loaded, the data should be available for the NMC program. The following diagram will be used to explain how this can be accomplished:

HERCULES

Computer memory

```
        ┌──────────────────────────┬──────────────────────────┐
        │                          │                          │
        │          NMR             │       DATA MEMORY        │   (1)
        │                          │                          │
        └──────────────────────────┴──────────────────────────┘
Actual
address  0                      200000                     400000
                                (64K)
```

File loaded

```
        ┌──────────────────────────────────────────────────────┐
        │                                                      │
        │         header                  data                 │   (2)
        │                                                      │
        └──────────────────────────────────────────────────────┘
        0        177240      200000                      400000
                             (64K)                        128K
```
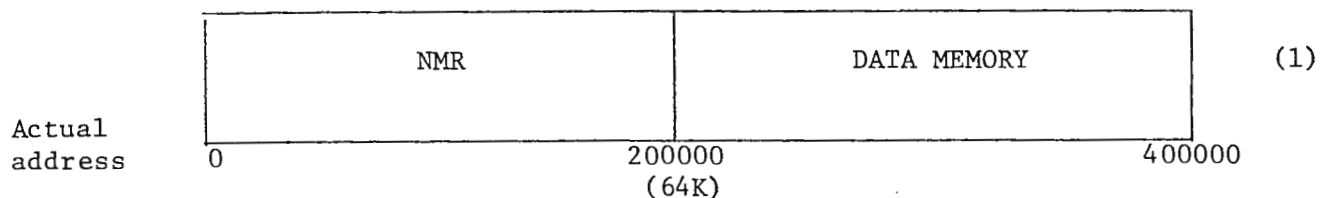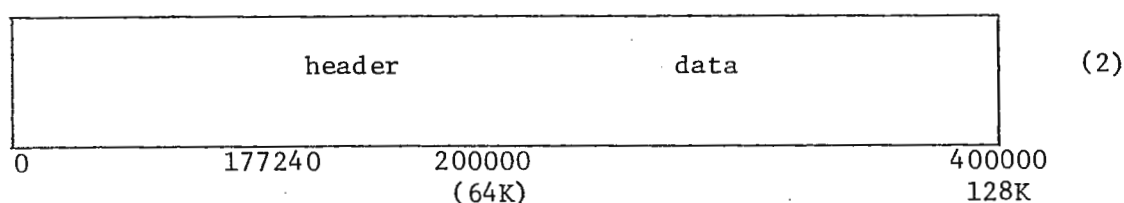
The file is loaded from monitor into computer memory such that the file header is in the first 64K and the data is in the second 64K. When the NMC program is loaded, the header is overwritten by the NMC program, but the data remains intact. The following commands are used:

With the computer in monitor.

* LOAD __ FILE NAME __ 177240 <ret>
* RUN __ NMC <ret>
> CB select the correct block size for your data

Your data will be in block No. 0. If you wish to save the data on disk, use the appropriate NMC command which will create a disk file with an NMC header. Data stored in this manner can be recalled from the NMC program and treated as NMC data. All data handling routines available in NMC may be used, e.g. curve deconvolution, line fitting, IC base line straightening integration, plotting, expansion, etc.

Please credit this contribution to the Hercules Research Center account. I wish to thank Dr. D. L. Dalrymple of NMC for assistance in this work.

Yours very truly,

David A. Smith
Analytical Division

DAS:bjm

Université de Nancy I

LABORATOIRE DE CHIMIE THEORIQUE

D. CANET
Professeur

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

July 13, 1983

About approaches used for interpreting carbon-13 relaxation data in systems involving a fast motion superimposed on a slow motion

Dear Professor Shapiro,

When carbon-13 longitudinal relaxation times of an alkyl chain are frequency dependent, although ranging at relatively high values (of the order of a second), and/or the nuclear Overhauser factor is less than its maximum value, this indicates the presence of a slower motion superimposed on a fast motion due to internal rotations. This situation is encountered is side-chains of polymers or peptides as well as in surfactants engaged in micelles or lyotropic mesophases. Some procedures available for interpreting such relaxation data make use of two correlation times (τ_R and τ_G for the slow and fast motions, respectively). Two of them lead to the same formulae : the "two-step model" originating from the Lund group [1] and the so called "model free approach" of Lipari and Szabo [2] :

$$\frac{1}{T_1} = (\frac{\hbar\gamma_H\gamma_C}{r_{CH}^3})^2 \left\{ \frac{1}{10} S^2 \left[\frac{3\tau_R}{1+\omega_c^2\tau_R^2} + \frac{\tau_R}{1+(\omega_H-\omega_c)^2\tau_R^2} + \frac{6\tau_R}{1+(\omega_H+\omega_c)^2\tau_R^2} \right] + (1-S^2)\, \tau_G \right\} \quad [1]$$

This formula applies for a carbon bonded to a single proton ; all symbols have their usual meaning. S is a "local" (two-step model) or a "generalized" (model free approach) order parameter. Within the frame of the model free approach, [1] is valid provided that $\tau_G<<\tau_R$ and that $(\omega\tau_G)^2<<1$ for any considered ω. If one applies these latter conditions to the well-known Woessner's formula [3], one obtains :

$$\frac{1}{T_1} = (\frac{\hbar\gamma_H\gamma_C}{r_{CH}^3})^2 \left\{ \frac{1}{10} \left[\frac{1}{4}(3\cos^2\theta-1)^2 \right] \left[\frac{3\tau_R}{1+\omega_c^2\tau_R^2} + \frac{\tau_R}{1+(\omega_H-\omega_c)^2\tau_R^2} + \frac{6\tau_R}{1+(\omega_H+\omega_c)^2\tau_R^2} \right] \right.$$

$$\left. + \frac{9}{16}(1+6\cos^2\theta-7\cos^4\theta)\, \tau_G \right\} \quad [2]$$

As a matter of fact, this model can also be used [4] to interpret carbon relaxation data of alkyl chains whose one extremity is attached to a slowly reorienting body (in micelles, for instance). In that case, θ must be considered as the angle between the CH bond and a virtual axis around which the CH vector is assumed to rotate. (This virtual axis is defined according to the cumulative effect of rotations around all C-C bonds). Regarding the slow motion contribution, formulae [1] and [2] are seen to be formally identical provided that $\frac{1}{2}(3\cos^2\theta-1)$ is identified as S^2. The

4
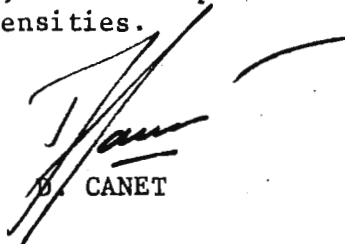
coefficient in front of τ_G in [2] never differs by more than 15% from $[1-\frac{1}{4}(3\cos^2\theta-1)]^2$. Therefore, the interpreting procedures represented by formulae [1] and [2] appear to be very similar.

Finally, it should be mentionned that exponential correlation functions have been assumed throughout. This is far from being warranted for the slow motion especially in micelles or lyotropic mesophases. This problem can be circumveted in the following way. If measurements have been performed at different frequencies, τ_R can be fitted at <u>each</u> frequency using [1] or [2] and its numerical value reinserted in

$$\left[\frac{3\tau_R}{1+\omega_c^2\tau_R^2} + \frac{\tau_R}{1+(\omega_H-\omega_c)^2\tau_R^2} + \frac{6\tau_R}{1+(\omega_H+\omega_c)^2\tau_R^2} \right]$$

This yields numerical values (as a function of the frequency) for what would be the spectral density pertaining to the slow motion. Although this procedure is rather approximate (three different ω are involved), it should provide some insight into the frequency dependence of these spectral densities.

Yours sincerely,

D. CANET

(1) H. Wennerström, B. Lindman, O. Söderman, T. Drakenberg and J.B. Rosenholm
J. Am. Chem. Soc., <u>101</u>, 6860 (1979)

T. Ahlnäs, O. Söderman, C. Hjelm and B. Lindman
J. Phys. Chem. <u>87</u>, 822 (1983)

(2) G. Lipari and A. Szabo
J. Am. Chem. Soc. <u>104</u>, 4546 (1982)
ibid.   <u>104</u>, 4559 (1982)

(3) D.E. Wossner
J. Chem. Phys., <u>36</u>, 1 (1962)

(4) D. Canet, J. Brondeau, H. Nery and J.P. Marchal
Chem. Phys. Lett. <u>72</u>, 184, (1980)
D. Canet, J.P. Marchal, H. Nery, B. Robin-Lherbier and J.M. Cases
J. Colloid Interf. Sci., <u>93</u>, 241 (1983)

PURDUE
UNIVERSITY DEPARTMENT OF CHEMISTRY

July 6, 1983

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

Identification of Polyamines in Plant Viruses by ^{1}H NMR.

A number of plant viruses and bacteriophages are known
to have different amounts of polyamines.
Identification and quantitation of these molecules
involve detailed chemical procedures in combination with
GC/MS methods. We report here a simple and
nondestructive way of identifying polyamines in plant
viruses by ^{1}H NMR.

The figure shows high-field ^{1}H NMR spectra at 470 MHz
of (a) turnip yellow mosaic virus (TYMV) and (b)
spermidine-treated and (c) native belladonna mottle
virus (BDMV). The three broad peaks in spectrum (a)
are assigned to polyamines based on their chemical
shift similarity to those of free spermine/spermidine
and from the chemical information that TYMV contains
about 400 polyamine molecules (predominantly
spermidine) per virion. It is apparent from spectrum
(c) that native BDMV does not contain any polyamine
although it belongs to the same family as TYMV.
However, spermidine is able to penetrate the protein shell
of BDMV and irreversibly bind to the RNA as revealed by
spectrum (b) which was obtained from spermidine-treated
BDMV. We found from ^{31}P NMR and analytical
ultracentrifugation studies that native BDMV is
unstable above neutral pH whereas TYMV is known to be
stable up to pH 11.5. We attribute the instability of
BDMV to the lack of polyamine in the virus particle.
Spermidine-treated BDMV not only gives rise to a
spectrum similar to that of TYMV but is also stable at
high pH (11.5).

Chemistry Building
West Lafayette, Indiana 47907

We hope to utilize these small molecule inclusions as NMR probes to study the behavior of a large system like a virus particle (mol. wt. ~7 million). These results are described in a paper to appear in Virology.

Yours sincerely,

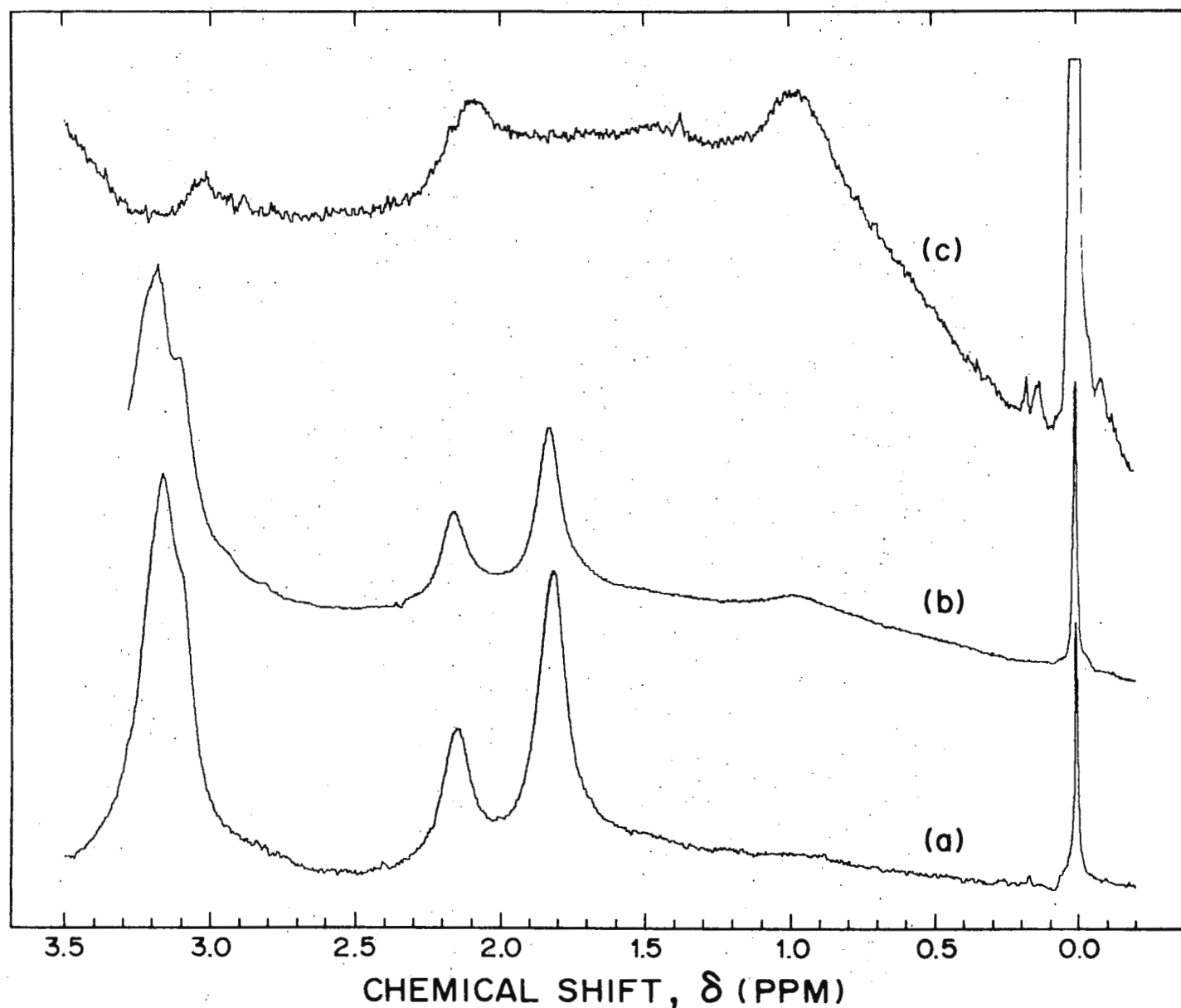J.L. Markley

R. Virudachalam

Figure. ^{1}H NMR spectra (high-field region) at 470 MHz of (a) turnip yellow mosaic virus, (b) spermidine-treated, and (c) native belladonna mottle virus.

WASHINGTON 🛡 UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY
July 6, 1983

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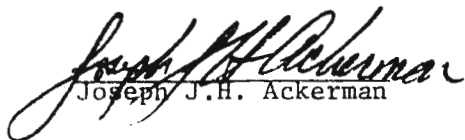Department of Chemistry
College Station, TX 77843
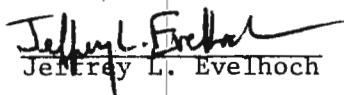
Dear Barry:

OPTIMIZATION OF S/N FOR SURFACE COIL NMR

One never seems to have enough S/N when applying NMR to biological
systems. Sensitivity problems can be especially acute in the case of
intact tissue samples where one confronts not only low concentrations
but also lossy conducting samples and often less-than-optimal r.f.
antennae. A particular case of interest to us has been the use of
surface coil antennae to monitor on going _in_ _vivo_ biochemistry.

To develop techniques for maximization of S/N we let the Washington
University IBM-370 consider the case of an ideal single-turn, flat,
circular surface coil operating in the single-coil mode and placed
against a large homogeneous sample. The results, shown in the
accompanying figure, are remenisant of those in elegant paper by
Becker, Ferretti and Gambhir [Anal. Chem., _51_ 1413-1420 (1979)]. As
with the homogeneous B_1 of conventional coils, a significant increase
in S/N may be obtained with surface coils by optimizing pulse repitition
rate and pulse width. In practice this is straight forward to do
empirically by setting the interpulse spacing T=Aquisition Time $\sim$ 2-3T_2*
and then experimentally determining the pulse width that provides
maximum S/N.

Sincerely,

Joseph J.H. Ackerman

Jeffrey L. Evelhoch
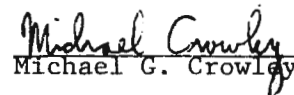
Michael G. Crowley

Figure Caption

A plot of theoretical and experimental maximum integrated S/N per unit
time as a function of pulse repetition period, T/T_1. The curves are the
theoretical results for the sample starting 0.10 radii (solid line) and
0.15 radii (broken line) from the plane of the surface coil. The symbols
represent experimental data at two different frequencies (30 MHz for H-2 and
188 MHz for F-19) for a large homogeneous sample starting 0.10-0.15 radii
from the plane of the surface coil.

Calc; .10r	————
Calc; .15r	————
^{2}H; 150mM NaF	☐
^{19}F; 150mM NaF	◇

Relative Maximum S/N (per unit time)

T/T_1

2.5 2 1.5 1

0.05 0.1 1

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

July 15, 1983

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

New Instrumentation, the 4th Delaware NMR
Symposium, and Surface Chemistry

Dear ~~Professor Shapiro~~ *Barry*:

The Blue Hen NMR Complex continues on its merry way. Lila, Joe, and
Roger continue investigation of interesting problems with solution-state
NMR spectroscopy, while I only scratch the surface of problems in
catalytic chemistry. Most recently, we have held our 4th Delaware NMR
Symposium on June 8. It was a tremendous success. If anyone would like
to be included on future mailings, please contact Lila Gierasch, Joe Noggle,
Roger Crecely, or me and we shall make an effort to notify you of the 5th.

Other recent developments include the installation of our new AM-250
Bruker NMR spectrometer with its Aspect 3000 computer which, in addition
to the WM-250, gives us the capacity we have needed for some time.

A small tidbit of the things you can do at surfaces. Supported metals
are often used for hydrogenations and dehydrogenations. Attached are some
spectra hot off the spectrometer of what you see when you combine benzene
with a supported metal catalust which has previously been treated with
hydrogen and outgassed. You see cyclohexane! We have been able to monitor
kinetics of this reaction with proton NMR in some very recent experiments
over this catalyst. Not all catalysts allow this discrimination, because
the broadening of the resonances of these physically adsorbed species may be
severe depending on the nature of the catalyst. Thus, NMR spectroscopy is
potentially very useful for the study of catalysts.

This communication should be credited to Joe Noggle, whose regards I
send with mine.

Yours truly,

Cecil

Cecil R. Dybowski
Associate Professor of Chemistry

sr
Enclosure

RH/TiO$_2$

A — REDUCED SAMPLE + C$_6$H$_6$
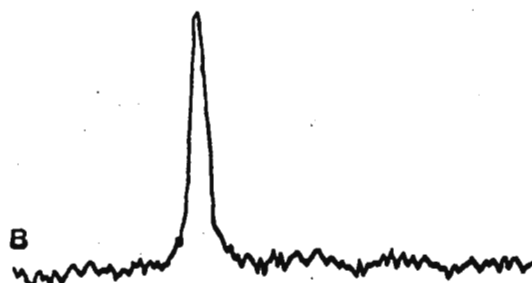
B — CALCINED SAMPLE + C$_6$H$_6$

C — CALCINED SAMPLE + C$_6$H$_{12}$

D — REDUCED SAMPLE + C$_6$H$_{12}$

E — REDUCED SAMPLE + XS C$_6$H$_6$

ppm 10 5 0 -5

DEPARTMENT OF HEALTH & HUMAN SERVICES   Public Health Service

National Institutes of Health
Bethesda, Maryland 20205
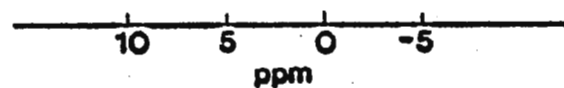
18 July 1983

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

Dear Barry,

In vitro and in vivo Enzyme Catalyzed
Rates of Reactions by 2D FTNMR

We are continuing our studies of in vitro and in vivo
enzyme catalyzed rates of reactions by 2D FTNMR. In our first
study of the anomerization and isomerization of glucose-6-
phophate and fructose 6-phosphate, we were able to obtain the
various reaction rates involved. As a bonus we were also able to
deduce the rate limiting steps in the reaction.

We have expanded our studies to more complex enzyme
systems and have been successful in quantitating our results
for adenylate kinase, creatine phosphokinase, and the carbonic
anhydrase reaction. Most recently we have measured the in vivo
unidirectional flux between creatine phosphate (CrP) and
adenosine triphosphate (ATP) in the leg and head of an
anesthetized rat in a specially constructed probe with
an animal cradle.

$$CrP + ADP + E \rightleftharpoons CrPEADP \rightleftharpoons CREATP \rightleftharpoons Cr + ATP + E$$
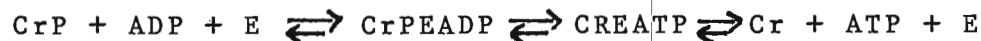
These studies are being acarried out in collaboration with
Drs. Howard Kantor and Robert Balaban, also of the National
Heart, Lung and Blood Institute.

In Figure 1 is the 2D contour plot of the data
obtained from the rat leg with a mixing time of 600 msec.
A single 2D spectrum can be obtained in a few hours. The
volumes of the cross peaks are a direct measure of the exchange
rates in the initial velocity approximation. The experiment
is repeated various times using different mixing periods to
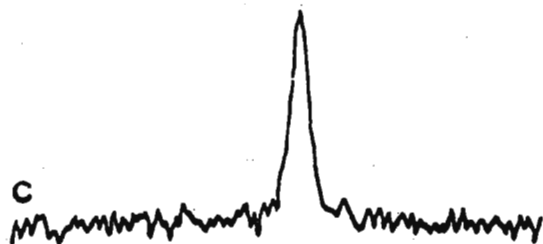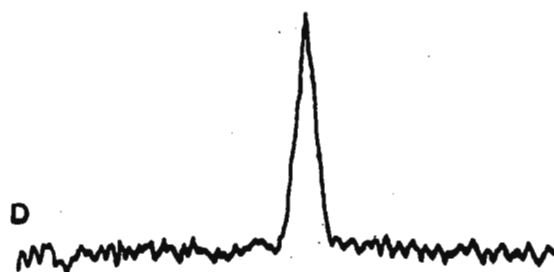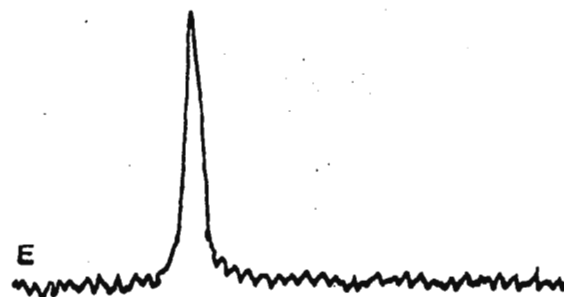obtain the time dependance of the cross peak volumes. These
results are shown in figure 2 for the rat leg. The unidirectional
flux for CrP going to ATP was 13 umoles/g/sec in the leg and
2 umoles/g/sec in the head. Please credit this to the
subscription of Bob Highet, the chagrined recipient of the
notorious yellow reminder.

Sincerely,

Jim

James A. Ferretti
Laboratory of Chemistry
National Heat, Lung and Blood Institute

αATP

γATP

ATP→CrP

CrP

CrP→ATP

F_1

Pi

SP

F_2

FIGURE 1.

Crp → ATP   Rat Leg
Cross Peak

VOLUME

20

10

0

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7   0.8

T_{mix} (sec)

FIGURE 2.

Rensselaer Polytechnic Institute   Troy, New York 12181

July 22, 1983

^{17}O Chemical Shifts of Substituted Uridines.

Dear Barry:

I want to take this opportunity, as my first contribution to the newsletter, to present some interesting ^{17}O NMR data obtained while working in the laboratory of Dr. Steven Danyluk[1] at Argonne National Laboratory. As part of a continuing study[2,3] of ^{17}O NMR of uridine nucleosides, we studied the effects of substitution in the uracil ring on the ^{17}O shifts of the carbonyl oxygens in both protic (H_2O) and aprotic (CH_3CN) solvents. The samples used were synthesized by Dr. Malcolm MacCoss[4] with ~50% ^{17}O enrichment selectively in either the 02 or 04 oxygen. A table of limited results appears below. The data on a more extensive number of compounds is being prepared for publication in the future.

The data in CH_3CN indicate firstly that substitution at the uracil 5 position causes significant effects at 04 but minimal perturbation at 02. This is understandable in terms of an 04-C4-C5-C6 conjugation which does not include 02. The differences in H-bonding to H_2O indicated by the differences Δ are consistent with previous experimental[3] and theoretical[5] data indicating only one lone pair is available for H bonding to solvent at 02, but both are available on 04.

One final observation is the relative effects the substituents have on the conjugated π electron system as evidenced by the 04 shifts in CH_3CN.
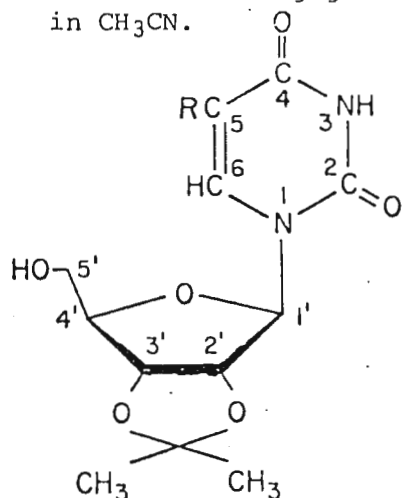
I.   R = H   2',3'-O-ISOPROPYLIDENEURIDINE
II. R = CH$_3$ 2',3'-O-ISOPROPYLIDENERIBOSYLTHYMINE
III. R = F   2',3'-O-ISOPROPYLIDENE-5-FLOUROURACIL
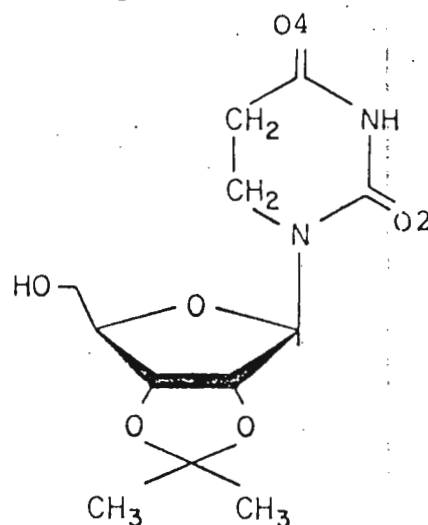
IV.   2',3'-O-isopropylidene-5,6-dihydrouridine

^{17}O Chemical Shifts[a]

	Labeled Compound	CH_3CN	H_2O	Δ[b]
$[4-^{17}O]$	I	333 ± 2	294 ± 6	39
$[4-^{17}O]$	II	333 ± 2	288 ± 8	45
$[4-^{17}O]$	III	323 ± 3	288 ± 4	35
$[4-^{17}O]$	IV	374 ± 3	344 ± 3	30
$[2-^{17}O]$	I	259 ± 1	246 ± 4	13
$[2-^{17}O]$	II	250 ± 2	234 ± 7	16
$[2-^{17}O]$	III	255 ± 3	239 ± 3	16
$[2-^{17}O]$	IV	260 ± 2	246 ± 4	14

a. Chemical shifts are reported in ppm downfield from H_2O (29°C).

b. $\Delta \quad \delta_{CH_3CN} - \delta_{H_2O}$

Best regards,

Dr. Herbert M. Schwartz
Director, Major Instrumentation Center

1. Current address; Domtar Inc., Senneville, Quebec, H9X 3L7, CANADA.

2. H. M. Schwartz, M. MacCoss and S. S. Danyluk, Tetrahedron Letters, 21, 3837 (1980).

3. H. M. Schwartz, M. MacCoss and S. S. Danyluk, JACS (1983) in press.

4. Current address; Merck Sharp and Dohme Research Laboratory, P.O. Box 2000, Rahway, NY 07065.

5. S. Scheiner, Biopolymers, 22, 731 (1983).

TOKYO COLLEGE OF PHARMACY

1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

July 1, 1983

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

Title: Internal Motion of DNA in Hydrated Fibers

Dear Barry:

It is a little surprise to us that a rapid internal motion
with a large amplitude occurs in DNA fibers at high relative humi-
dity, just as observed for DNA in solution. Figure 1 shows the ^{31}P
solid -state NMR spectra (40.3 MHz) and the observed relaxation
times of T_1 and T_2 of B-DNA fibers at 98% relative humidty, for wich
the fibers are oriented paralle and perpendicular and 45° relative
to the magnetic field. Clearly, these relaxation times reveal
anisotropic effects: the relaxation times for parallel orientation of
of DNA fibers is about twice shorter than those for the perpendi-
cular.

We have shown[1] that the interpretation for these anisotropic
effects requires the following motional modes within a DNA: two-
site jump as a simplified rapid internal motion, rotation about
the helical axis and bending or wobbling motion of the DNA strands.
For two-site jump the rate of 6×10^9 sec^{-1} and the amplitude of ±40°
were estimated, the diffusion rate of about 10^5 sec^{-1} for the rota-
tional motion about the helical axis and the amplitude of about ±25°
for the bending motion.

There are many NMR studies on the internal motion of DNA
in solution and most of the results are consistent with each other
in that a rapid internal motion has a correlation time of nanosec.
Therefore, we can state that the dynamic behaviors of DNA in solution
is very much similar to that of DNA in hydrated fibers.

$T_1 = 1.17$ s $T_1 = 2.10$ s

$T_2 = 1.78$ ms $T_2 = 2.61$ ms

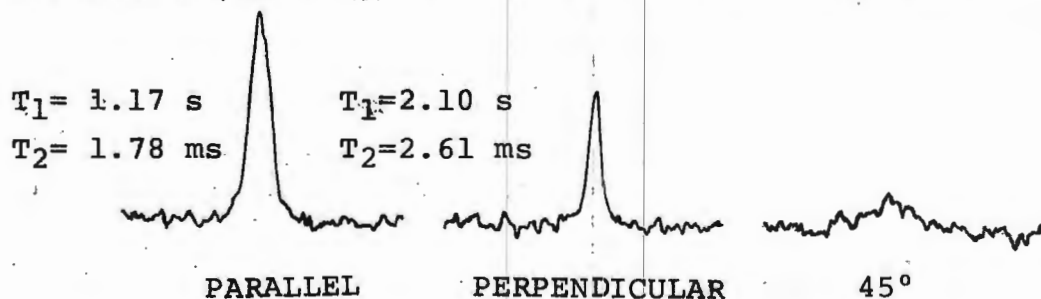PARALLEL   PERPENDICULAR   45°

Fig. 1. Cross-polarized ^{31}P spectra of DNA fibers
at different orientations relative to H_O.

Ref. 1) Shindo, H. et al. (1983) The 16th Juerusalem Symposium
in Quantum Chemistry and Biochemistry, 1983.

Sincerely Yours

Heisaburo Shindo

Prof. Dr. D. Leibfritz
Universität Bremen
Fachbereich Chemie/Biologie

NW 2 Leobenerstraße
2800 Bremen 33
Telefon (04 21) 218-2818/28 41
2817

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

5-7-1983

Title:

"Geminal Methylgroups"

Dear Dr. Shapiro,
    Recently we analyzed the structure of a tricyclic derivative of barbituric acid (A)
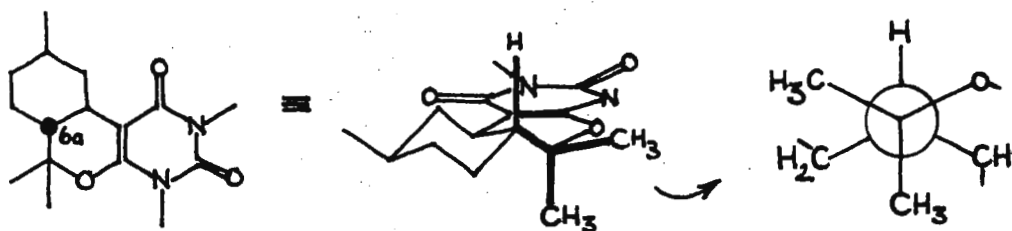
Geminal methyl groups exhibit couplings which are less frequently encountered in the literature. The most intense cross peak in the COSY spectrum connects these methyl signals. From the J resolved spectrum, we take the constant $^4J_{HH} = 0.65$ Hz, not a negligible quantity in spectrum simulation. As a matter of fact it is exactly one third of the four bond W-coupling in a rigid molecular backbone (f.e. 1.5 - 2.0 Hz in steroids),

The carbon signals of these methyl groups are split by three bond coupling between the protons of the geminal CH_3 and 6a-H. The latter coupling amounts to 4 Hz with the upfield methyl carbon and 3 Hz with the downfield methyl carbon. Hence, if we assume a Karplus type dependence of $^3J_{CH}$, we have criteria for the axial vs equatorial assignment.

Yours sincercly

KEMIAN JA BIOKEMIAN LAITOS
TURUN YLIOPISTO
20500 TURKU 50

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
UNIVERSITY OF TURKU
SF-20500 TURKU 50 FINLAND

Turku, July 6th 1983

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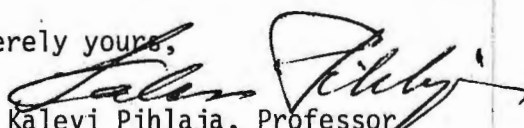Texas A&M University, College Station,
Texas 77843, U.S.A.

Dear Professor Shapiro,

"The First Nordic Symposium on NMR Spectroscopy"

Some of the newsletter readers might be interested to know the date and venue of the First Nordic Symposium on NMR Spectroscopy which will take place on June 12-June 15th 1984 in Turku, Finland. The programme will consist of both basic problems and practical applications although the general theme will emphasize new applications rather than techniques. One invited lecture from each Scandinavian country will be included in addition to some keynote lectures, posters and possibly a couple of discussion groups. The keynote lectures will be selected (20 min. each) from the most novel topics offered by the potential participants. The participation will be limited to 100-120 people. The conference language will be English.

Nordic colleagues will get the first circular about this meeting through their departments and/or the local chemical papers (like Kemia-Kemi in Finland) but other interested readers should contact the undersigned as soon as possible.

Sincerely yours,

Kalevi Pihlaja, Professor
Chairman, Section of NMR Spectros-
copy, the Association of Finnish
Chemical Societies

P.S. In mutual agreement with Professor Pekka Pyykkö, I shall hereby take over his former subscription to the TAMU NMR Newsletter for the shared University of Turku - Abo Akademi NMR facility which by the way will in this year be a new multinuclear Jeol GX-400 system.

Buenos Aires, july 6, 1983.

UNIVERSIDAD DE BUENOS AIRES

FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Prof. Bernard L. Shapiro.

Texas A. & M. University.

Dept. of Chemistry
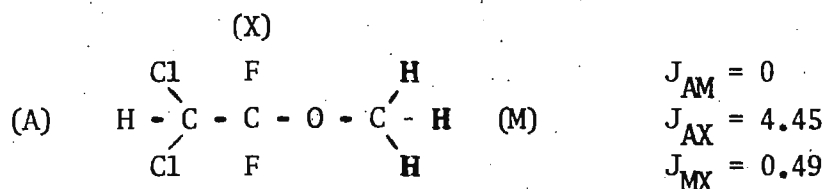
College Station, Texas 77843.

U.S.A.

Title: The Signs of the J's in Flurane.

Dear prof. Shapiro:

The theoretical group of our local NMR team led by prof. Ruben Contreras got used to bring us, experimentalists, some odd questions like e.g. " what is the relative sign of J_{AX} in an ABCX system in which J_{AX} is the only non-zero X coupling?"

Usually we do not mind their questions but what we do mind is their getting used to have us answering them!

The last question they brought us was: "what are the relative signs of J_{AX} and J_{MX} in flurane (formula shown) taking into account that, besides being this a degenerate system, $J_{AM} = 0$!?"

$$(X)$$

$$
(A) \quad
\begin{array}{ccccccc}
Cl & F & & H & \\
\backslash & & & / & \\
H - C - C - O - C - H & (M) \\
/ & & & \backslash & \\
Cl & F & & H &
\end{array}
$$

$J_{AM} = 0$

$J_{AX} = 4.45$

$J_{MX} = 0.49$

It took some brain-squeezing and some engineering work to be able to give them the answer, through a triple resonance experiment: "Both are the same ! "

But we do hope that they are not going to ask us the absolute sign of these constants, since we are not so sure of being able to answer them that question!

Yours, sincerely

V.J.Kowalewski.

P.S. Thank's for the remainder!

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

Professor B.L. Shapiro

Department of Chemistry

Texas A & M University

College Station, Texas 77843

· U.S.A.

Uw ref.:

Onze ref.:   AG   **1179**

Amsterdam, July 18th, 1983
Badhuisweg 3
Tel. via telefoniste (020) 30 91 11
Tel. rechtstreeks (020)
　　Hr/Mw

Dear Professor Shapiro,

SOLID-STATE NMR SPECTRA OF THE ZEOLITE ZSM-5

Since our last contribution we have continued with our solid-state NMR
work, studying all manner of nuclei, spinning at every imaginable angle,
in as many different field strengths as possible.

In particular we have continued our work on organic ligands chemically
bound to silica gel surfaces[1] and have used ^{27}Al magic angle spinning
techniques at 130.3 MHz (11.75 T, Bruker WM-500 spectrometer) to charac-
terize transitional aluminas[2].

A suitable subject for this communication, however, would appear to be the
^{29}Si NMR spectra of the zeolite ZSM-5, in which everyone seems to be
interested.

In general, two types of ^{29}Si ZSM-5 spectra have been published:

(a) a poorly resolved spectrum with Si(OAl) resonances centered around
　　-113 ppm[3], and

(b) a spectrum exhibiting a number of Si(OAl) resonances between -109
　　and -117 ppm[4].

We have monitored the preparation and activation of such catalysts step-by-
step using solid-state ^{29}Si NMR[5], and a typical example of our results (for
a ZSM-5 having an initial Al content of 0.32 %w) is shown in the attached
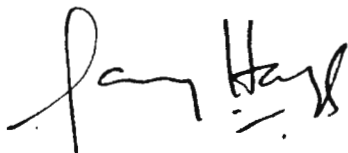figure.

Koninklijke/Shell-Laboratorium, Amsterdam

The spectrum of sample A in Figure 1 exhibits two broad resonances at -102 and -112 ppm. The -102 ppm resonance is due mainly to silanol groups (as shown by cross-polarization experiments, which we regard as <u>essential</u> in solid-state ^{29}Si NMR studies), most of which are located inside the zeolite (lattice defects). As can be seen, upon calcination and ion exchange followed by further heat treatments, a better resolved spectrum is obtained. This is because silanol groups are removed by ring closure, which the presence of Na^+ and tetrapropylammonium (TPA^+) ions otherwise inhibits. As a consequence of this final ring closure, the ZSM-5 lattice becomes more homogeneous, which is reflected by line narrowing in the spectrum, leading to the well-resolved spectrum of sample E in Figure 1.

We trust that this missive keeps our subscription open!

Yours sincerely,

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

(G.R. Hays)   (N.C.M. Alma)

1) G.R. Hays, A.D.H. Clague, R. Huis and G. van der Velden, Appl. Surf. Sci. <u>10</u> (1982) 247.

2) C.S. John, N.C.M. Alma and G.R. Hays, Appl. Catal. (in press). With thanks to Dr. A. Samoson (Tallinn, USSR) for the design and construction of the probe and help with carrying out the 130.3 MHz experiments, and to Bruker Analytische Messtechnik and Dr. W.E. Hull for the opportunity to use their WM-500 spectrometer in August 1982.

3) J.B. Nagy, Z. Gabelica and E.G. Derouane, Chem. Lett. (1982) 1105.

4) C.A. Fyfe, G.C. Gobbi, J. Klinowski, J.M. Thomas and S. Ramdas, Nature <u>296</u> (1982) 530.

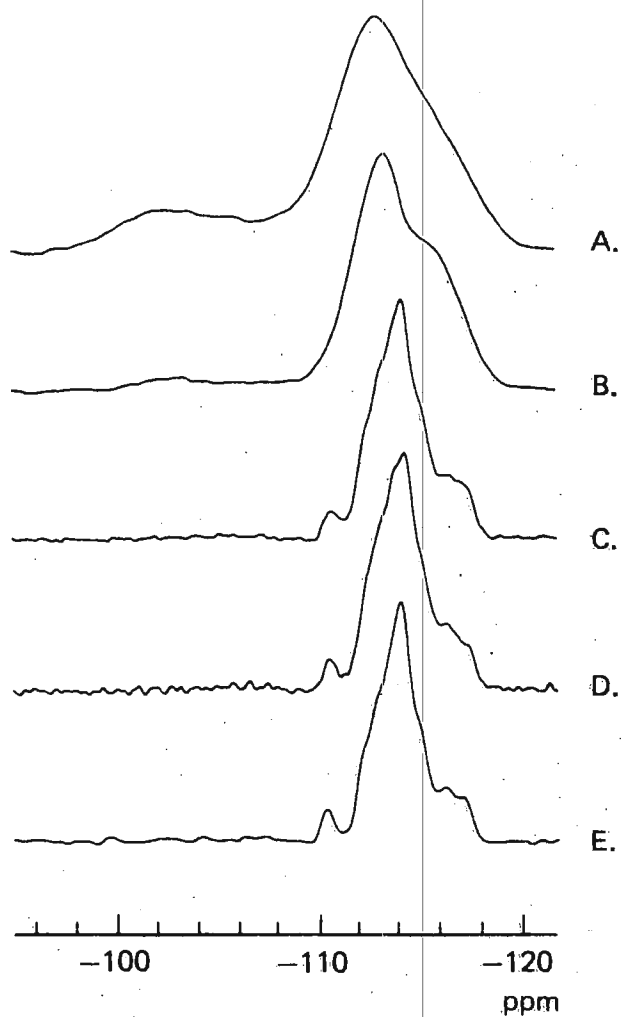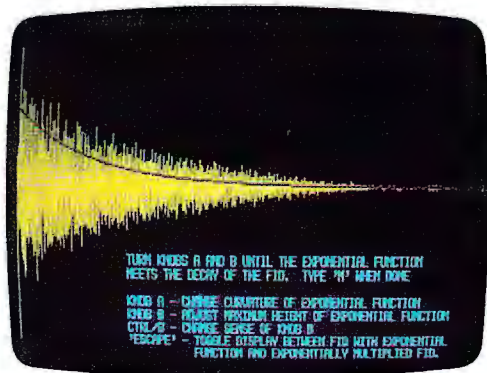5) G. Boxhoorn, A.G.T.G. Kortbeek, G.R. Hays and N.C.M. Alma, Zeolites (in press).

Encl.: 1 Figure

FIG. 1: ^{29}Si SOLID—STATE NMR OF ZSM—5

A. Na$^+$, TPA$^+$ ZSM—5 AFTER DRYING AT 120 $^\circ$C
B. Na$^+$, H$^+$ ZSM—5 AFTER 500 $^\circ$C CALCINATION OF A
C. NH$_4^+$, H$^+$ ZSM—5 AFTER Na$^+$ EXCHANGE OF B
D. H$^+$ ZSM—5 AFTER 500 $^\circ$C CALCINATION OF C
E. H$^+$ ZSM—5 AFTER 800 $^\circ$C HEAT TREATMENT OF D

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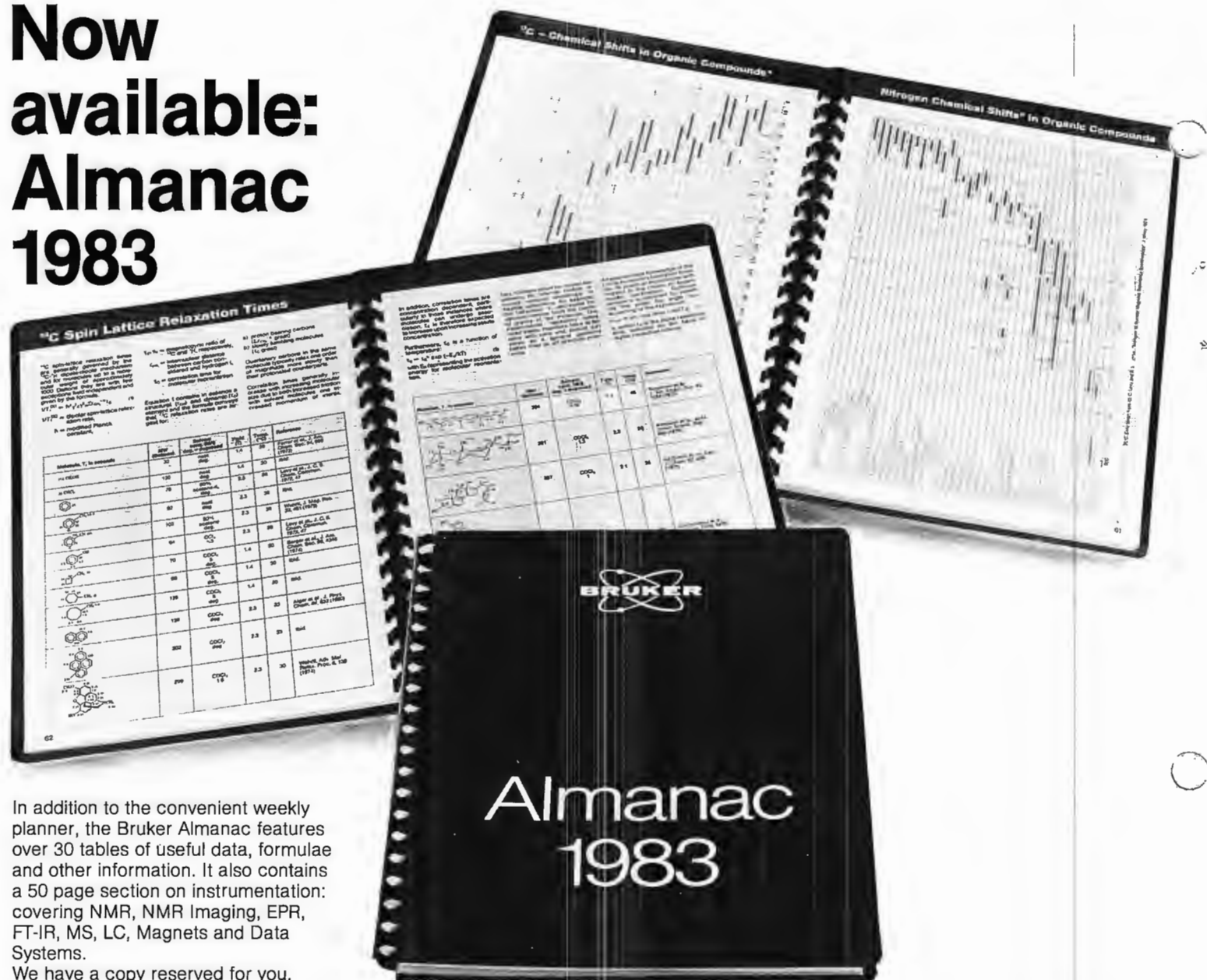
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University of Waterloo

July 18, 1983

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

<u>Order Profiles in Bilayers</u>

Dear Barry:

Thank you for your reminders. The world is now falling
back into its original place for me and I shall make a contri-
bution along the lines of a comment on Ed Samulski's letter <u>297</u>
19 (1983). In his last paragraph he alludes to the difficulty
of incorporating deuteriated phospholipid in nematic solvents,
but predicts an unchanged order profile for the lipid. In fact
Bruce Forrest was able to get phospholipid guests in a
lyotropic nematic host some years ago and similar profiles were
obtained to biological situations. The results were published
in Chem. Phys. Lipids <u>24</u> 183 (1979). In comparing order pro-
files, it is possible to detect changes along the lines sugges-
ted by us in recent papers. Order profiles may look the same
but in bilayer situations they are sensitive to the changes in
bilayer thickness. Two recent papers from our laboratory
illustrate this sensititivity of order profiles. J. Phys.
Chem. <u>85</u> 718 (1981) and J. Am. Chem. Soc. <u>105</u> 1469 (1983).

We continue to work in the area of lyotropic aqueous
cholesterics and nematics with NMR as the principal tool.

Yours sincerely,

Leonard W. Reeves,
Professor of Chemistry.

LWR/ee

VRIJE UNIVERSITEIT

VAKGROEP FYSISCHE CHEMIE
SUBFACULTEIT DER SCHEIKUNDE

Verzoeke bij beantwoording ons kenmerk te vermelden en slechts één zaak per brief te behandelen

1081 hv amsterdam
de boelelaan 1083
telefoon 020 - 548

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

uw kenmerk	uw brief van	ons kenmerk	datum	bijlage(n)
		CM/BHR/UH/IS	July 22, 1983	

onderwerp

^{14}N Quadrupole Coupling Tensor of Pyridine
and Pyrimidine in the Liquid Phase

Dear Barry,

When a strong d.c. electric field is applied over a polar liquid sample the molecules become partially oriented with their dipole-moments along the direction of the applied field. In the NMR spectrum anisotropic interactions between the spins will be manifest. In the case of (quadru-polar) I = 1 nuclei (e.g. ^{14}N and ^{2}H) the resonance-lines appear as doublets. The splitting ($\Delta\nu$) of a doublet depends on the nuclear quadrupole moment (eQ), the field-gradient along the dipole moment (V_{zz}) and the extent of orientation by the electric field (called the alignment, $<\frac{3}{2} \cos^2\theta - \frac{1}{2}>_E$):

$$\Delta\nu = \frac{3}{2} \frac{eQ}{h} V_{zz} <\frac{3}{2} \cos^2\theta - \frac{1}{2}>_E \qquad (I)$$

Note that V_{zz} is the gradient in a molecular frame (xyz), adapted to the symmetry of the molecule. The principal frame, in which the field gradient tensor is diagonal, is denoted by (x'y'z'). To express V_{zz} in the principal components, $V_{x'x'}$, $V_{y'y'}$ and $V_{z'z'}$, an appropriate transformation has to be performed.

In deuterated pyridine (fig. 1a), in which the C-^{2}H axis of the para-deuteron is along the dipole moment, V_{zz} is identical to $V_{z'z'}$; the quadrupole coupling constant, $\frac{eQ}{h} V_{z'z'}$, is known to be 186 kHz (1). For the nitrogen spin V_{zz} is also identical to $V_{z'z'}$ (the field gradient along the lone pair). Then, from the ratio of the ^{2}H and ^{14}N line-splittings $\frac{eQ}{h} V_{z'z'}$ for the nitrogen nucleus can be calculated (-5,06 MHz). The situation in deuterated pyrimidine (fig. 1b) is identical as far as the oo- and mm-deuterons are concerned. For the nitrogen spins V_{zz} is a linear combination of the in-plane principal components:

$$\frac{eQ}{h} V_{zz} = \frac{eQ}{h} [\cos^2\theta_{zx'} V_{x'x'} + \cos^2\theta_{zz'} V_{z'z'}] \qquad (II)$$

Under the assumption that ^{14}N principal field gradients are equal in magnitude and are oriented in the same way in the two molecules (i.e. $V_{z'z'}$ along the lone-pair, $V_{y'y'}$ perpendicular to the plane of the molecule) it is possible to solve eq. (II). The l.h.s. is given by the ratio of the ^{2}H and ^{14}N line-splittings in pyrimidine; in the r.h.s. $\frac{eQ}{h} V_{z'z'}$ is already known from the experiment on pyridine. $\frac{eQ}{h} V_{x'x'}$ can be calculated after substitution of the values for $\theta_{zx'}$ and $\theta_{zz'}$. The latter quantities can be derived from the molecular structure of pyrimidine (2) by identifying the bisector of the inner CNC-angle as the direction of the lone-pair (the z'-axis). The third principal component follows from the traceless character of the tensor.

The final results are: $\frac{eQ}{h} V_{x'x'} = +1.17\,\text{MHz}$, $\frac{eQ}{h} V_{y'y'} = +3.89\,\text{MHz}$ and $\frac{eQ}{h} V_{z'z'} = -5,06\,\text{MHz}$. The asymmetry parameter, η, is calculated to be 0.54. From microwave data on pyridine, Sørensen (3) found the values +1.43, +3.45 and −4.88 MHz respectively, giving $\eta = 0.41$. Our value for $\frac{eQ}{h} V_{z'z'}$, −5.06 MHz is increased by about 10% compared to the crystal value from NQR (4). This behaviour has previously been found for nitrobenzene (5). There is reasonable agreement between the gasphase microwave data and the present results.

Sincerely yours,

C. MacLean   B.H. Ruessink   U. Hofstra

(1) H.H. Mantsch, H. Saitô and I.C.P. Smith, Progress in NMR spectroscopy, Vol. 11, p.211 (Pergamon, Oxford, 1977).

(2) P. Diehl, T. Bjorholm and H. Bösiger, J. Magn. Res. 42 (1981) 390
     L. Fernholt, C. Rømming, Acta Chem. Scand. A32 (1978) 271.

(3) G. Sørensen, J. Mol. Spectr. 22 (1967) 325.

(4) E.A.C. Lucken, Nuclear Quadrupole Coupling Constants, Ch. 11 (Academic Press, London, 1969).

(5) T.M. Plantenga, H. Bulsink, F.J.J. de Kanter and C. MacLean, Chem. Phys. 65 (1982) 71.

(a)

(b)
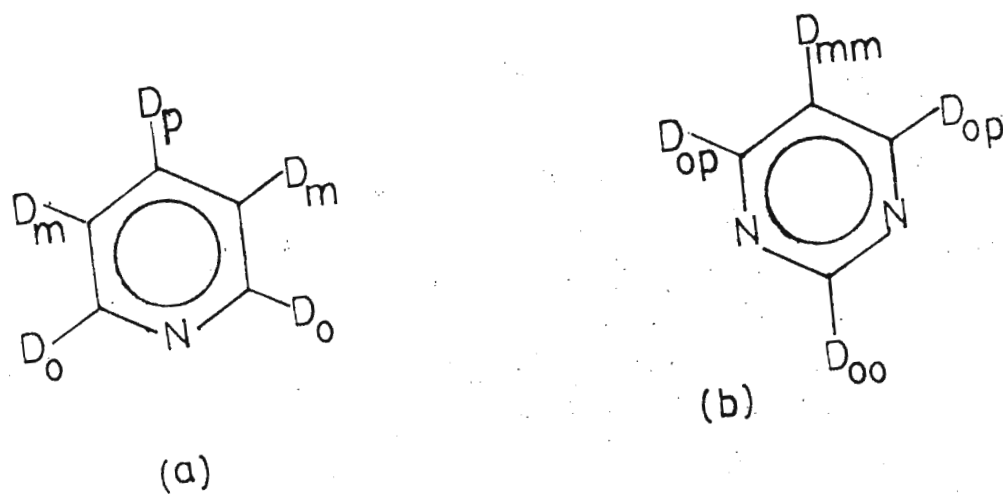
FIG 1
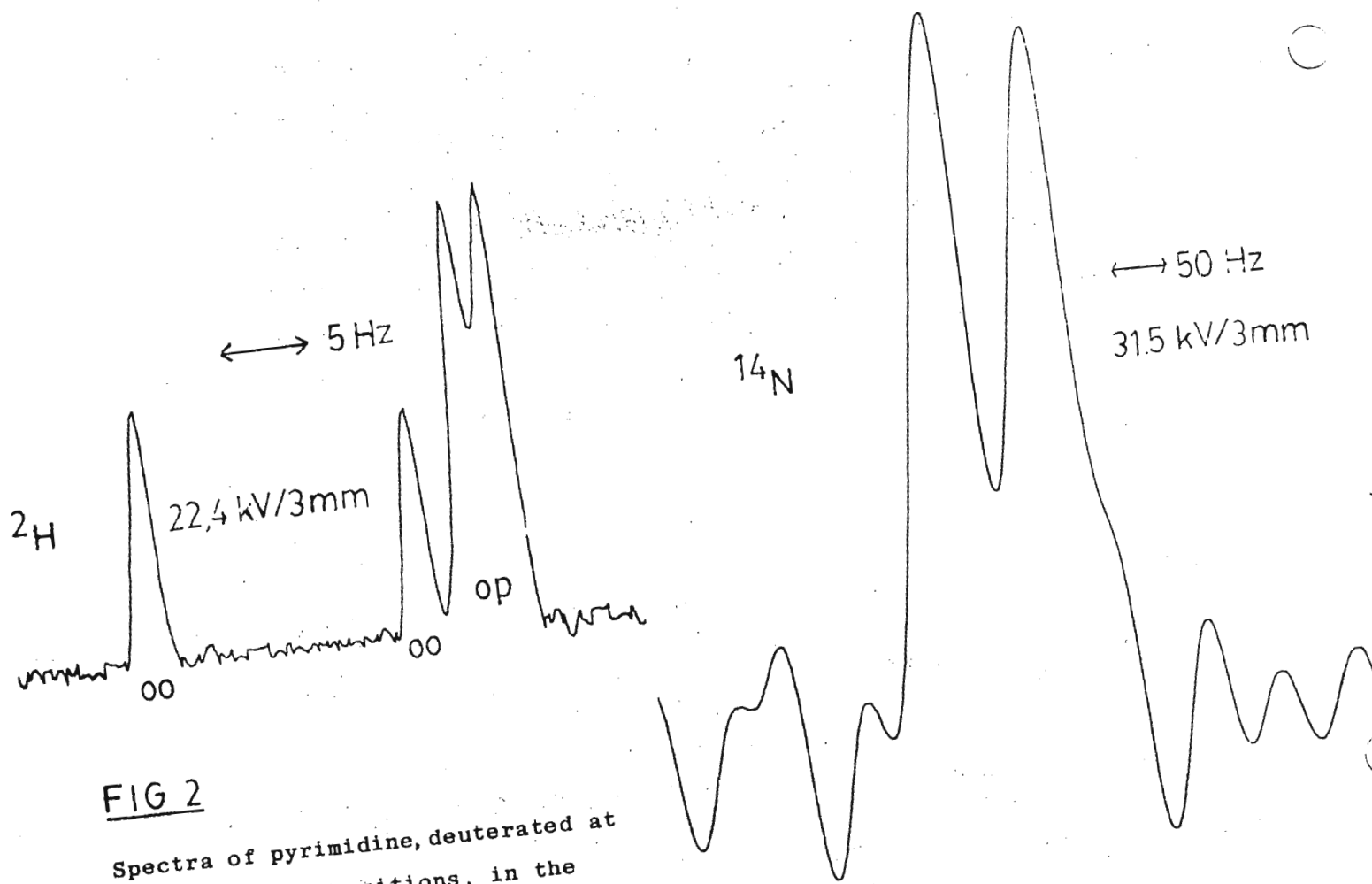
FIG 2

Spectra of pyrimidine, deuterated at
the oo- and op-positions, in the
presence of an electric field.

Shell Development Company

A Division of Shell Oil Company

July 26, 1983

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

SUBJECT: MAGNETIC RESONANCE SPECTROSCOPIST

Dear Dr. Shapiro:

The Analytical Department at the Shell Development Westhollow Research Center in Houston, Texas has an opening for a PhD level magnetic resonance spectroscopist. The position will emphasize applications of multinuclear solution and solid-state NMR, NMR imaging and ESR in support of both oil and chemical R&D efforts. Applicants should have a firm grasp of the fundamentals of magnetic resonance. ESR experience is desirable. Qualified applicants should send resumes to:

> Research Recruitment
> Shell Development Company
> P. O. Box 1380
> Houston, TX 77001

Yours truly,

for   M. J. O'Neal, Manager
Analytical Department

TBM/pkm

Drexel University • Philadelphia, Pennsylvania 19104

Drexel University

College of Science
Department of Chemistry
(215) 895-2638, 2639

July 26, 1983

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

Dear Barry,

Re: Self-Diffusion Measurements on the FX-90Q and Diffusion of Water
     in Planar Smectic Liquid Crystals.

    Thanks for the multicolored reminders. Sorry we took so long to write.
We would like to report some recent progress at Drexel in the measurement
of self-diffusion coefficients. The technique used is the pulsed-gradient
spin-echo (PGSE) method previously described by Stilbs (1,2) for FX series
spectrometers. We have written a pulse program DIFUS which we believe to
be an improvement over those previously reported. Since the sequence uses
the homospoil accessory for the field gradient, no instrumental modification
is necessary for FX-90Q owners with FG/BG and homospoil capability. In
addition, one can, by adjusting the power to the coils gain a factor of about
4 in field gradient. We would be happy to share this program and write up
of the experiment with your readers.

    One example of work we have done using this technique is shown in the
figure for the diffusion of water in smectic liquid crystals of the sodium
4-(1'-heptylnonyl) benzene sulfonate-(SHBS)-water system. In this system
the water is believed to be in between planar bilayers separated by the
$10\overset{o}{A}$ water layer. The loop values shown are related to the amount of time
the pulsed gradient is on. Shown as an inset is a plot of the ln(intensity)
vs. β ', where β is related to the total echo time and pulsed gradient
time (1,2). It is interesting to note that for this system it is possible
to observe a water echo for an unoriented system and that the decay is clearly
non-exponential (as observed in the inset). We are currently interpreting
these results.

                                        Sincerely,

        Erik   *Frank*

        E. Cheever   F. D. Blum

References:
1. P. Stilbs, JEOL News, 18A, 12-13(1982).
2. P. Stilbs, J. Colloid Interface Sci., 87, 385(1982).

75% SHBS — 25%H₂O

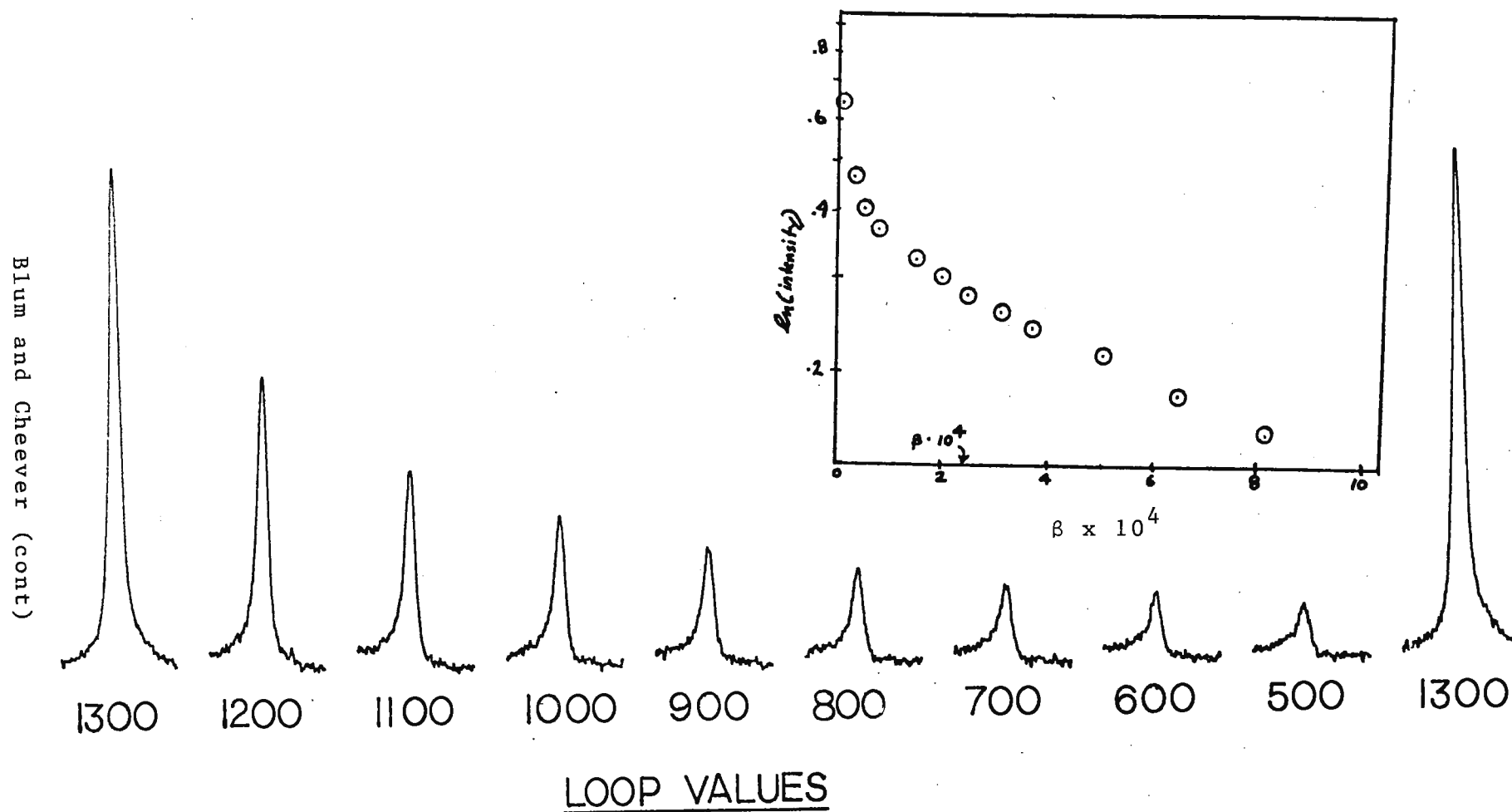1300   1200   1100   1000   900   800   700   600   500   1300

LOOP VALUES

Figure shows the echo attenuated water signal as a function of loop values(related to the field gradient pulse). Also shown is a plot of the intensity vs. β (related to the echo time and field gradient pulse. The decay is clearly non-expontial.

299-42

United States
Department of
Agriculture

Agricultural
Research
Service

Northeastern Region
Eastern Regional
Research Center

600 East Mermaid Lane
Philadelphia
Pennsylvania
19118

7/11/83

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

Dear Barry:

DIETARY FIBER SORPTION AS PROBED BY ^{13}C CPMAS NMR

Numerous animal and human feeding studies suggest that "non-nutritive" dietary
fiber binds bile acids in the gut and thereby initiates a biochemical cascade
which ultimately reduces serum cholesterol levels.

In our recent investigations of the characterization and interactions of
dietary fibers, we examined the dynamics of bile acid sorption to the surface
of insoluble vegetable (fiber) via ^{13}C CPMAS NMR.

Alcohol insoluble dietary fibers composed primarily of polysaccharides
containing neutral saccharides i.e., glucose, arabinose, mannose and
galactose, ($\sim$70%), and uronic acid residues, ($\sim$20%), are incubated with
solutions containing 95% ^{13}C$_{24}$-O enriched cholate at pH 7.3. After a
thorough washing, these fibers were examined by ^{13}C CPMAS as a function of
proton T_1 spin lattice relaxation times. Figure 1 shows the proton
relaxation profile via the carbon resonances of the polysaccharide fiber from
carrot with approximately three weight percent physically sorbed cholate. The
sharp carbonyl resonances seen at 177 and 183 ppm correspond to the protonated
and ionic forms of the sorbed cholic acid, respectively. While the pure
amorphous cholate has a proton T_1 of 192 ms and the protonated form a value
of 62 ms, the physically bound cholic acid (found in both states), have an
average T_1 value of 485 ms. Crystalline cholic acid has a T_1 value of
1200 ms. The rapid proton spin diffusion throughout the fiber gives a uniform
proton T_1 value for all the polymer carbons of 172 ms.

Similar measurements made for cholate ionically linked to cholestyramine (a
cross linked polystyrene polymer containing quaternary amine exchange sites)
clearly demonstrated rapid mutual spin diffusion between the synthetic polymer
proton and cholate proton pool to yield a common proton T_1 of 140 ms.
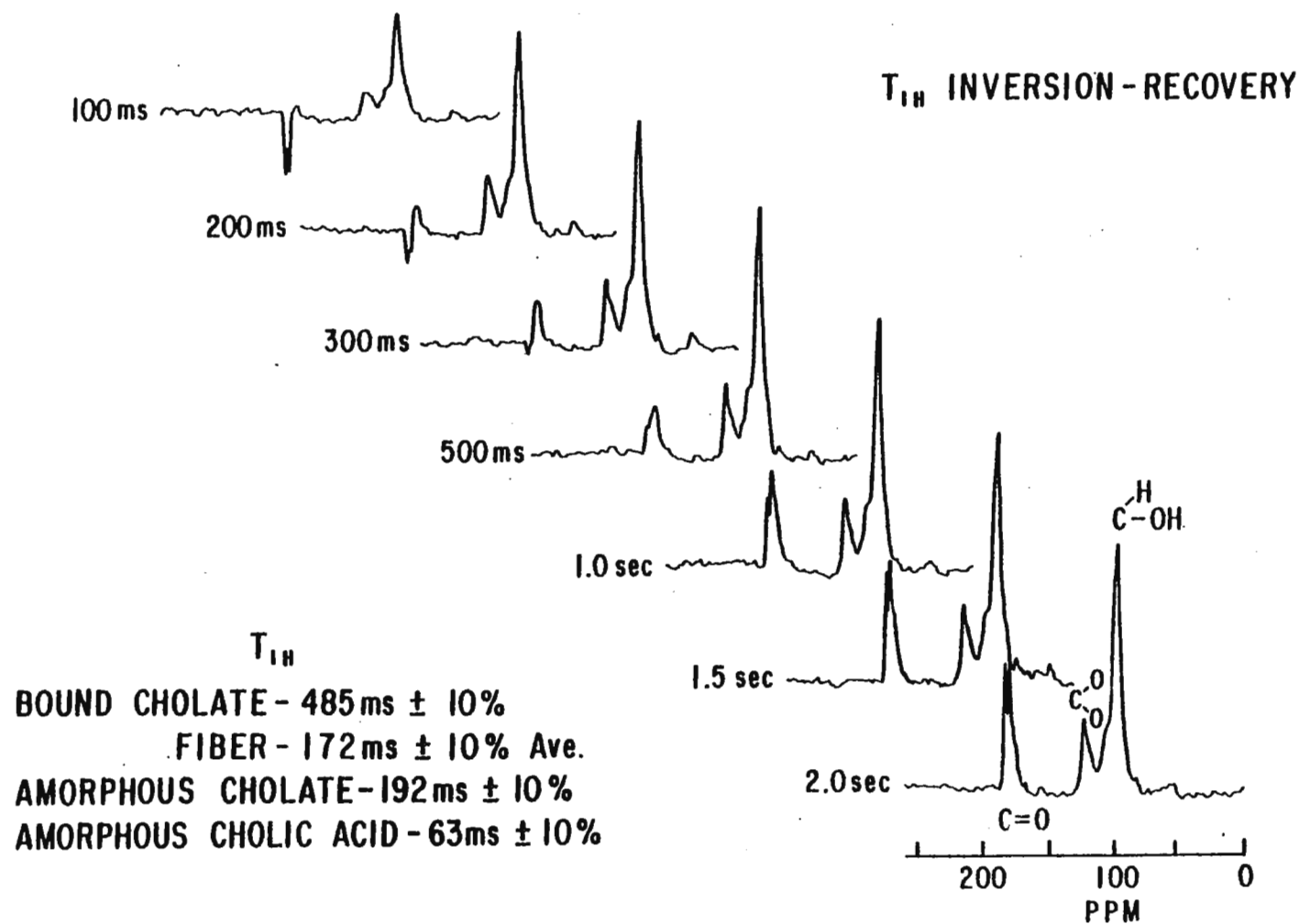
From these experimental results it is evident that the fiber matrix provides
structural rigidity for the bile acid, in both the protonated and ionic states
aligned on the surface or perhaps within the fiber matrix.

It is obvious from this result that ^{13}C CPMAS NMR is a useful tool for
evaluating the nature of small molecule-polymer interactions.

PHILIP E. PFEFFER
Research Leader
Physical Chemistry and
  Instrumentation Laboratory

PETER D. HOAGLAND
Research Chemist
Food Science Laboratory

CARROT RESIDUE WITH 3% SORBED $^{13}C_{24}$ CHOLATE pH = 7.3

T_{1H} INVERSION-RECOVERY

100 ms

200 ms

300 ms

500 ms

1.0 sec

1.5 sec

2.0 sec

T_{1H}
BOUND CHOLATE - 485 ms ± 10%
FIBER - 172 ms ± 10% Ave.
AMORPHOUS CHOLATE - 192 ms ± 10%
AMORPHOUS CHOLIC ACID - 63 ms ± 10%

C-OH (with H above C)

C=O (with two O)

C=O

200   100   0
PPM

Princeton University   DEPARTMENT OF CHEMISTRY

PRINCETON, NEW JERSEY 08544

July 28, 1983

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

Dear Professor Shapiro:

Please excuse my too-long silence. We find ourselves in the perhaps enviable position of having several NMR's, all at different field strengths. This poses an annoying problem for those who want to measure probe temperatures using either CH_3OH or $\{CH_2OH\}_2$ shifts, as the published calibration curves are for 60 MHz instruments. Your readers may find the following two equations useful in similar situations:

For CH_3OH – $T = 403 - \dfrac{29.5}{M} \{\Delta\nu\} - \dfrac{23.81}{M^2} \{\Delta\nu\}^2$
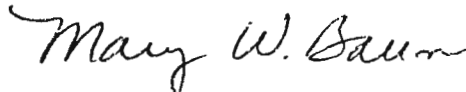
For $\{CH_2OH\}_2$ – $\quad T = 466.4 - \dfrac{100.5}{M} \{\Delta\nu\}$

where T is temperature in degrees K
M is field strength in MHz
$\Delta\nu$ is chemical shift difference in Hz

Sincerely,

Mary W. Baum

Mary W. Baum

gc

cSu

(303) 491-6480

Colorado State University
Fort Collins, Colorado
80523

Department of Chemistry

July 25, 1983

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

Position available,
^{15}N CP/MAS, ^{109}Ag MAS.

Dear Barry:

Below is an announcement for a position in the Colorado State University Regional NMR Center. We hope that some of the Newsletter's readers might be interested.

NMR SPECIALIST

COLORADO STATE UNIVERSITY NMR CENTER

Research Associate position in the NSF-sponsored regional instrumentation facility in nmr. Position available by December 1, 1983.

REQUIREMENTS: Advanced degree in chemistry, physics or electrical engineering. Strong preference for applicants experienced in modern nmr techniques, especially for solids.

SALARY: Negotiable, dependent upon qualifications and experience.
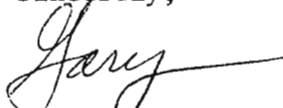
APPLICATION DEADLINE: September 15, 1983.

Send applications with complete resume, including publications, three references and statement of interests to:

Professor Gary E. Maciel
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

Progress in the Center has focussed recently on solid-state NMR applications in a variety of areas. For example, we have been very happy with the information we have been able to get from ^{15}N CP/MAS experiments regarding the interactions of amines with surfaces. We are also beginning to get useful MAS data on ^{109}Ag.

Sincerely,

Gary E. Maciel
Professor

GEM:lb

EASTERN ANALYTICAL SYMPOSIUM, INC.*

November 16-17-18, 1983

July 28, 1983

EAS announces for the NMR spectroscopists a day of advances in this rapidly expanding field with the following program sheduled for Thursday, November 16, 1983:

Advances in NMR: Chairperson, Dr. Gwendolyn N. Chmurny, Frederick Cancer Research Facility, 9:00 a.m. to 12:00 noon.

1. Dr. Roy H. Bible, Jr., G.D. Searle Company
    "An Introduction and Overview of Two-Dimensional High-Resolution NMR Spectroscopy"

2. Dr. Robert E. Santini, Purdue University
    "A Technical Review of High Field NMR Spectrometer Capabilities with a Projection of Future Developments in Biomedical Applications"

3. Dr. Robert S. Balaban, National Institutes of Health
    "Two-Dimensional NMR Studies of Enzymatic Reactions in Vitro and in Vivo"

Advances in NMR Imaging: Chairperson, Prof. Paul C. Lauterbur, 2:00 p.m. to 4:30 p.m.

1. Prof. Paul C. Lauterbur, State University of New York at Stony Brook
    "NMR Zeugmatographic Imaging of Solids, Liquids and Gases"

2. Dr. Ian L. Pykett, Massachusetts General Hospital
    "NMR Chemical Shift Imaging"

3. Dr. W.P. Rothwell, Shell Development Company
    "Industrial Applications of NMR Imaging"

This is part of the Twenty-Second Eastern Analytical Symposium, November 16-18, 1983. For further information, contact Dr. S. David Klein, EAS Publicity, Merck and Company, Inc., P.O. Box 2000, R80 L106, Rahway, NJ 07065.

*New York Statler, New York City