TEXAS A&M UNIVERSITY

NMR

NEWSLETTER

No. **293**

February, 1983

DEADLINE DATES: No. 294   7 March 1983
                 No. 295   4 April 1983

All Newsletter Correspondence, Etc., Should be Addressed To:

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

THE ROCKEFELLER UNIVERSITY

1230 YORK AVENUE • NEW YORK, NEW YORK 10021-6399

9 December 1982

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

<u>Programming Phase Permutations</u>

Dear Dr. Shapiro:

All TAMU Newsletter readers will be familiar with the importance of phase permutations
in pulse sequences, for cancellation of systematic instrumental errors, for polariza-
tion transfer, for enhancement or cancellation of multiple quantum transitions, for
composite pulses, etc. Recent versions of the NMR operating programs from Nicolet (1)
uses an elegant algebraic representation for the relation between the phase quadrant
in a pulse interval and the number of completed acquisitions. I wanted to use a similar
scheme in programs for numerical simulation of spectra resulting from multiple acquisi-
tions with complex excitation schemes. Since the Nicolet formulae are described (ref.1.
p. 117) in a grammar notation, it seemed worthwhile programming the formula translation
using a compiler directly compatible with this notation, Yacc (2) a UNIX* compiler.
After rather more than the half-hour's effort I had projected, I obtained a general
subroutine which takes in the formula directly and then produces the values of the
various settings for any acquisition number (S in the formulae).

These formulae yield values of the phase letters (on the left, fig) with the operators
having the usual algebraic meaning <u>except</u> that assignment ("=") and parentheses {"(expres-
sion)"} yield the result modulo 4. Figure 1 illustrates a pulse sequence. I shall be
happy to supply listings of the routines to anyone interested, but unless you have a
UNIX operating system with Yacc, these are really only usable for wallpaper.

The grammar for phase permutation prepared by Nicolet is a powerful, general (3), and
complete definition, and should be suitable for reporting permutations in phase sequences.

Sincerely,

David Cowburn

DC:mmh

David Cowburn

(1) NMC-1280 manual, June 1982, Nicolet Magnetics, Fremont CA.

(2) Yacc, Yet-another-compiler-compiler. S. C. Johnson in "UNIX manual", Bell
Laboratories, Inc. 1978. Yacc is rather similar in class of application to the
more familiar LISP, but they differ considerable in style and operating detail.
* UNIX is a trademark of Bell Laboratories.

(3) For example, it would be easy to extend it to phase shifting with n positions
in the 2 π radian range, with n >4.

Figure 1. Programming Phase Permutations - Example

Phase permutation expressions for 13C-13C
satellite detection via double quantum coherence
A. Bax, R.Freeman, S.P.Kempsall, J.Am.Chem.Soc.
1980, 102, 4849-4851.

a=s/8

Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	1	1	1	1	1	1	1	1
2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	3

b=s/8+(2*(s/4)+1)

1	1	1	1	3	3	3	3	2	2	2	2	Ø	Ø	Ø	Ø
3	3	3	3	1	1	1	1	Ø	Ø	Ø	Ø	2	2	2	2

c=s/8+s

Ø	1	2	3	Ø	1	2	3	1	2	3	Ø	1	2	3	Ø
2	3	Ø	1	2	3	Ø	1	3	Ø	1	2	3	Ø	1	2

d=s/8-s

Ø	3	2	1	Ø	3	2	1	1	Ø	3	2	1	Ø	3	2
2	1	Ø	3	2	1	Ø	3	3	2	1	Ø	3	2	1	Ø

Sequence : (1) 90 deg pulse at phase a
            (2) delay
            (3) 180 deg pulse at phase b
            (4) delay
            (5) 90 deg pulse at phase a
            (6) 90 deg pulse at phase c
            (7) acquire at relative phase d
            (8) delay for requilibration
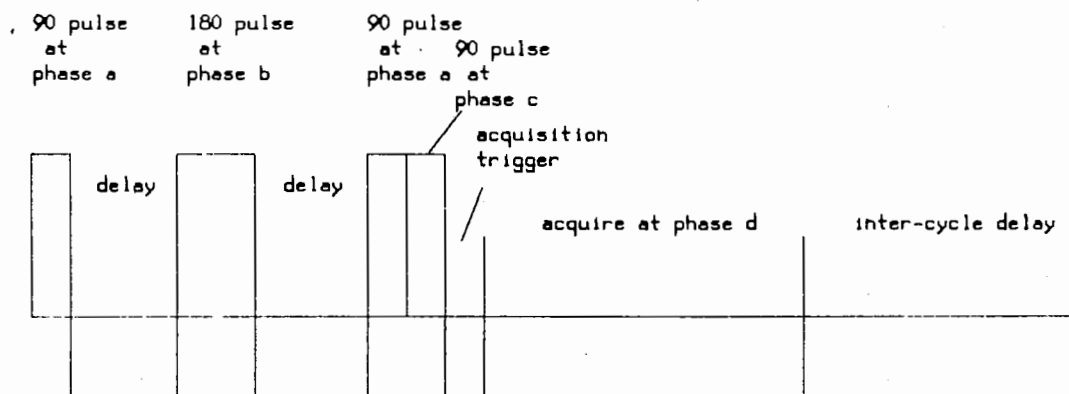
UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

December 20, 1982

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

Dear Barry:

EDITING OF THE ^{15}N NMR SPECTRA OF AMINOGLYCOSIDES BY THE DEPT TECHNIQUE

We have recently applied spectrum editing by the DEPT technique (Distortionless Enhancement by Polarization Transfer; Doddrell et al., J. Magn. Resonance 48, 323, 1982; Bruker literature, 1982) to the structural analysis of aminoglycosides by ^{15}N NMR. In Figure 1 are shown the natural abundance, 40.5 MHz ^{15}N NMR spectra of solutions of isofortimicin in 9:1v/v $CF_3CO_2H:CD_3CO_2H$, a solvent mixture that protonates all nitrogen atoms except that of the amide group, and thereby suppresses the rapid NH proton exchange which occurs at higher pH. For the purpose of a deuterium lock signal for our WM-400 spectrometer, the less expensive CD_3CO_2D solvent was not used, in order to avoid the complication of partially deuterated amino-groups.

The ^{15}N assignments indicated by the proton decoupled NH, NH_2, and NH_3 sub-spectra shown in Figures 1a, 1b, and 1c, respectively, neatly confirm those which we had made earlier by analysis of the multiplicities of the proton coupled, ^{15}N spin multiplets of isofortimicin (see Figure 1e) combined with ^{15}N chemical shift correlations with structural analogues. The work is being done in collaboration with Dr. Jim McAlpine of Abbott Laboratories, and thanks are due Dr. W. E. Hull for his advice.

Yours sincerely,

Bruce

Bruce Coxon
Organic Analytical Research Division
Center for Analytical Chemistry

^{15}N NMR SPECTRUM EDITING BY THE DEPT TECHNIQUE -- LINEAR COMBINATIONS
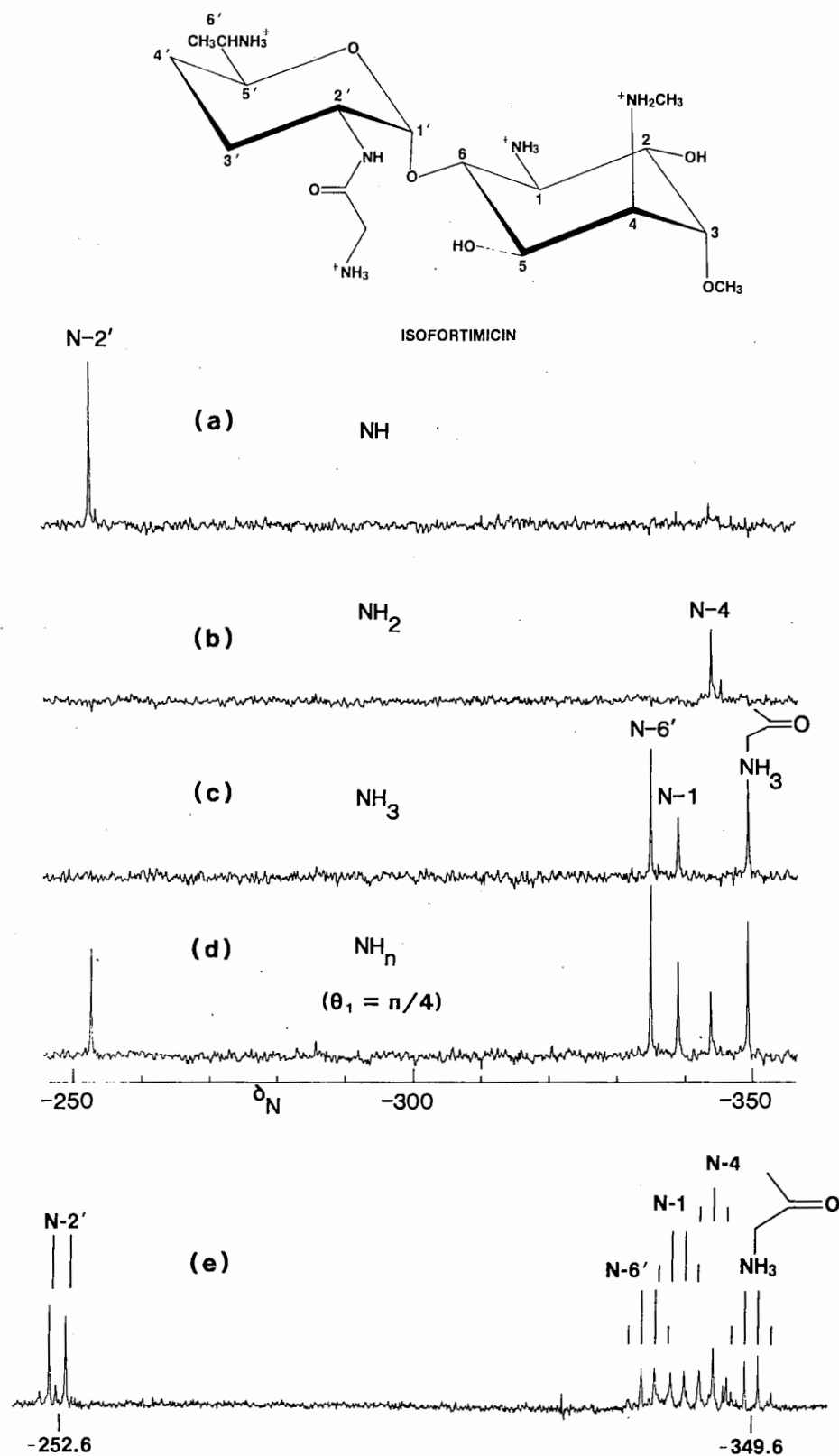
Figure 1.

Chemical shift reference:- saturated aqueous $NH_4{}^{15}NO_3$

TELEPHONE
345 1844

TELEGRAMS
UNIMELB PARKVILLE

University of Melbourne

DEPARTMENT OF ORGANIC CHEMISTRY   *Parkville, Victoria 3052*

21st December, 1982

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

Relaxation Mechanisms of the t-Butyl Cation

Dear Barry,

Despite the existence of a large body of chemical shift and coupling constant data, there are virtually no T_1 data for carbocations in the literature. This fact, together with our observation that cationic carbons often give relatively intense absorptions compared to other non-protonated carbons in the same molecule, prompted us to investigate the relaxation mechanisms of carbocations generated in superacids at sub-ambient temperatures.

The results for the t-butyl cation, generated from the alcohol in excess SbF_5/SO_2ClF (ROH:SbF_5 1:7.$\overline{3}$) with a solution viscosity of 23.6 cp at 213 K are summarized in the Table. The spin rotation mechanism makes no contribution to the relaxation of either carbon nucleus, since plots of $\ln R_1^{OBS}$ against $10^3/T$ give excellent straight lines. Whilst the dipole-dipole mechanisms is the major contributor to relaxation at 14 kG, it contributes only 50% and 20% to the relaxation of the methyl and cationic carbons respectively at 59 kG.

For the cationic carbon, relaxation is by the chemical shift anisotropy mechanism to the extent of 20% at 14 kG and a massive 80% at 59 kG.

Analysis of the relaxation data by the Woessner equations provides a value of the ratio of the rotational diffusion coefficients $D_{11}/D_{\perp} \simeq 6$ but not a value for the internal rotational coefficient Di of the methyl group.

Thus the t-butyl cation in this medium reorients anisotropically, with rotation about the C_{3v} axis being favoured over that of the perpendicular axes by a factor of six.

Full details will be published in the Journal of Magnetic Resonance.

Merry Christmas!

Yours sincerely,

D. R. Leslie   D. P. Kelly.

DPK:EC

TABLE I

^{13}C NUCLEAR RELAXATION PARAMETERS FOR THE t-BUTYL CATION 0.75 M IN SbF$_5$/SO$_2$ClF AT 213 K

	CH$_3$		C$^+$	
B$_o$ kG	14.1	58.8	14.1	58.8
T$_1$^{OBS} s^a	3.3 ± 0.1	3.3 ± 0.1	5.0 ± 0.3	1.2 ± 0.04
η	1.6 ± 0.1^b	1.6 ± 0.1	1.0 ± 0.1	0.19 ± 0.06
R$_1$^{OBS} s^{-1}	0.30 ± 0.01	0.30 ± 0.01	0.198 ± 0.005	0.83 ± 0.03
R$_1$^{DD} s^{-1}	0.24 ± 0.02	0.24 ± 0.02	0.10 ± 0.01	0.08 ± 0.03
R$_1$^{CSA} s^{-1}	-	-	0.038 ± 0.002	0.67 ± 0.04
R$_1$$^{OTH^d}$ s$^{-1^c}$	0.06 ± 0.03	0.06 ± 0.03	0.06 ± 0.02	0.08 ± 0.10

a Uncertainties are the standard deviations of the least squares values of T$_1$.

b Estimated maximum uncertainties.

c Uncertainties calculated by propagation of those for T$_1$ and η.

d $R_1^{OTH} = R_1^{OBS} - R_1^{DD} - R_1^{CSA}$

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL   CH - 4056 Basel (Schweiz) Dec 22, 1982

EXPERIMENTELLE KERNPHYSIK

Klingelbergstrasse 82, Telefon 061 - 44 22 80

Prof. Dr. P. Diehl

Prof. Dr. B. Shapiro
Department of Chemistry
Texas A & M University

College Station, Texas 77843

USA

^{13}C Chemical Shift Anisotropies of 2-Butyne

Dear Barry

Although the NMR-spectroscopy of oriented molecules provides an elegant method for the measurement of shift anisotropies, there are various problems steming predominantly from the reference signal which may depend upon temperature in the gradient method, upon the phase in the phase-transition method or upon the change of local effects in the 90° rotation method. These problems are particularly important for measurements of small anisotropies as e.g. of the nucleus ^{1}H. On the contrary, for ^{13}C, the results seem quite reliable as we have demonstrated some time ago for CH_3CN [1] and now for 2-butyne. The results are summarized in the table.

Tab: ^{13}C Chemical Shift Anisotropies of 2-Butyne ($\Delta\sigma$ in ppm)

Method	Solvent	Methyl Carbon	Acetylenic Carbon
gradient	ZLI 1167	15.5 ± 0.3	223.7 ± 0.8
"	EBBA	18.6 ± 0.5	227.6 ± 0.5
NEMIX [1]	ZLI 1132 +ZLI 1167	17.4 ± 1.1	227 ± 1
solid state-NMR [2]			201 ± 10
theory [3]			237.6

Our results for the acetylenic carbon disagree with a recent publication [4] which gave the value 160±7 but was based on spectra of lower quality and on an assumed molecular structure. The agreement with theoretical predictions[3] is very satisfactory.

With best regards, yours sincerely

P. Diehl

F. Moia

References:

1) P. Diehl, J. Jokisaari and F. Moia, J. Magn. Reson. 49, 498 (1982)

2) A. Pines, M.G. Gibby and J.S. Wangh, Chem. Phys.Lett. 15, 373 (1972)

3) K.A.K. Ebraheem and G.A. Webb, Org. Magn. Reson. 9, 241 (1977)

4) K. Hayamizu, O. Yamamato and I.Ando, J. Magn. Reson. 39, 343 (1980)

University of Nottingham

Department of Chemistry

12 January 1983

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

Title: ^{121}Sb and ^{123}Sb nmr linewidths

Dear Professor Shapiro

Although there are reports in the literature (1) of the ^{121}Sb and ^{123}Sb nmr spectra of SbX_6^- (X = F or Cl) in non-solvolysing media, these reports do not give reliable linewidth data. One source (2) has observed broader resonances from ^{123}Sb in SbF_6^- than ^{121}Sb. This is not to be expected and indeed it can be shown that for a given species the ^{121}Sb linewidths should be broader than those of ^{123}Sb by a factor of 1.2. The relevant equation (3) is:

$$W_{\frac{1}{2}} = \frac{3\pi}{10I^2} \frac{(2I+3)}{(2I-1)} \chi^2 \left(1 + \frac{1}{3}\eta^2\right) \tau_i$$

where I is the spin of the nucleus in question (^{121}Sb I = $\frac{5}{2}$, ^{123}Sb I = $\frac{7}{2}$)
χ is the nuclear quadrupole coupling constant and is defined:
$\chi = \frac{e^2 q_{zz} Q}{h}$. In our calculations the electric quadrupole moment Q was substituted for χ as the q_{zz} factor should be constant for each pair of symmetrical octahedral species that we have studied. Similarly the asymmetry factor η should be constant in octahedral species. τ_i is the isotropic tumbling correlation time which is constant in our samples, since we have studied the ^{121}Sb and ^{123}Sb nmr spectra of 1 molar solutions of both $(C_2H_5)_4N^+SbCl_6^-$ and $(C_2H_5)_4N^+SbF_6^-$ in d^3-methyl cyanide. Our experimental results are collected in the table and the ^{123}Sb spectrum of SbF_6^- is also shown.

THE UNIVERSITY OF NOTTINGHAM

12 January 1983

Professor BL Shapiro

The linewidth of the $SbCl_6^-$ signal in its ^{121}Sb spectrum has been previously reported (4) as 300 Hz, whereas we have observed a value of 175 Hz in our work.

The linewidths for ^{123}Sb are indeed narrower than those for ^{121}Sb and it is the larger spin of ^{123}Sb which produces this substantial effect. The ratio $\frac{^1J(^{121}Sb-F)}{^1J(^{123}Sb-F)} = 1.84$ is in good agreement with the ratio $\frac{\gamma_{121Sb}}{\gamma_{123Sb}} = 1.8456$. Although ^{123}Sb nmr spectra do give narrower linewidths, the coupling constant to a given nucleus is smaller by a factor of approximately 2, which could make resolution of overlapping signals more difficult.

Yours sincerely

Dr MFA Dove   JCP Sanders

(1)   R.K. Harris and B.E. Mann, NMR and the Periodic Table, Academic Press, 1978, 380-381 and references cited therein.

(2)   J.V. Hatton, Y. Saito and W.G. Schneider, Can. J. Chem., 12, 1709, 1973.

(3)   Ref. (1), p.17.

(4)   R.G. Kidd and R.W. Matthews, J. Inorg. Nucl. Chem., 37, 661, 1975.

Nucleus	Observing freq./MHz	Compound	Chem.* Shift	^1J(Sb-F) /Hz	Linewidth /Hz
^{121}Sb	59.859	$Et_4N^+SbCl_6^-$	0	–	175
		$Et_4N^+SbF_6^-$	86.7	1938	Septet 85
^{123}Sb	32.415	$Et_4N^+SbCl_6^-$	0	–	110
		$Et_4N^+SbF_6^-$	88.1	1053	Septet 51

* Relative to $SbCl_6^-$

^{123}Sb n.m.r. spectrum of
$Et_4N^+SbF_6^-$ in CD_3CN
(recorded on a WM 250
Bruker n.m.r.
spectrometer).

├─── ┤ = 1053 Hz

New Literature Available from BRUKER

NMR-Tomography

– A simple introduction into a fascinating NMR technique –

The "NMR-Imaging" technique is without any doubt a revolutionary new method for obtaining pictorial information about internal structures e.g. of the human body. The evolution of this method has now reached the state were non-specialists have recognized the extraordinary power of this technique and consequently BRUKER has now available an introductory six-page brochure for those not familiar with this new method. In order to facilitate the understanding of the physical background to this method the basic principles are given in a simplified manner and are illustrated by a large number of figures.

In a short survey it is shown that for the last twenty years the instrumental development in the pulsed NMR field has been synonymous with the name of BRUKER and it is pointed out that the first commercially available Fourier Transformation (FT) spectrometers were developed by BRUKER in 1969. Since NMR tomography is based on both "pulsed" and "FT"-NMR, the unique experience of BRUKER in these fields represents the ideal basis for the recently developed imaging systems.

After a short introduction, the principles of NMR are described in the brochure followed by a short representation of the "Projection-Reconstruction-Technique". Due to the expected extraordinary importance of NMR tomography in the field of diagnostic medicine a comparison of the average X-ray tissue contrast with NMR data is given as well as some remarks about theoretically possible risks for patients. At the end of this brochure an "outlook" is given into new applications and of the expected development of NMR tomography.

The three new BRUKER brochures.

With the general title "BRUKER Info", periodically illustrations of BRUKER's latest results are added to the NMR Tomography brochure.

If you wish to obtain the new brochure containing two "BRUKER Info" illustrations please return the reply card.

Two-Dimensional NMR *aspect 2000*

A practical introduction into this new technique by an experienced spectroscopist.

The common 2-D experiments are described, measuring conditions and microprograms are given. Application examples on various spectrometers demonstrate the capabilities of the method and naturally the outstanding performance of BRUKER spectrometers in 2-D spectroscopy.

DEPT
Distortionless Enhancement by Polarization Transfer

A new method with significant advantages over other polarization transfer techniques is described in a new brochure.

This method developed at the Griffith University by Drs. Bendall, Doddrell and Pegg can be performed on any BRUKER Spectrometer equiped with a CXP or high speed pulse programmer. Using this sequence the sensitivity in coupled spectra can be significantly increased or the multiplicity selection in ^{13}C spectra can be performed without the critical adjustments required for other polarization transfer pulse sequences.

For Your Copy, Please Write to Your Nearest BRUKER Sales Office

ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH

Laboratorium für anorg. Chemie
PD Dr. P. S. Pregosin
Universitätstrasse 6
Telefon 01 32 62 11

January 20, 1983

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

Professor Bernard L. SHAPIRO
Texas A&M University
College of Science
COLLEGE STATION, Texas 77843
U.S.A.

Dear Professor Shapiro,

Some time ago [1] we reported $^1J(^{195}Pt, ^{119}Sn)$ coupling constants in excess of 28,000 Hz and have recently extended this range to > 35,000 Hz [2]. These values are rather large, but to our surprise $^2J(^{119}Sn, ^{117}Sn)$ is even larger, e.g. 37,164 Hz, for trans-$[Pt(SnCl_3)_2(AsEt_3)_2]$ [3]. Moreover, in the past few months Heinz Rüegger has synthesized complexes in which this two-bond spin-spin coupling exceeds 46,000 Hz, e.g. 46,582 Hz for the $[PtCl(SnCl_3)_2(PEt_3)]^-$ anion. It seems likely that we will shortly need a new computer with a digitization rate suitable for ^2J values of 50 KHz or more.

We are not quite certain why these ^2J values are so large, although we have a few ideas, and would certainly welcome further suggestions.

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

Sincerely

Paul Pregosin

1. K.A. Ostoja Starzewski and P.S. Pregosin, Angew. Chemie Int. Ed.
    19, 316 (1980); K.A. Ostoja Starzewski and P.S. Pregosin, "Catalytic
    Aspects of Metal Phosphine Complexes", Advances in Chemistry Series,
    196, 23 (1982)
2. To appear in Inorg. Chim. Acta 1983.
3. K. A. Ostoja Starzewski, P.S. Pregosin & H. Rüegger, Helv. Chim. Acta,
    65, 785 (1982).

Suggested Title Large $^2J(^{119}Sn, ^{117}Sn)$ values.

0410

The Wellcome Research Laboratories

The Wellcome Foundation Ltd

Langley Court
Beckenham
Kent BR3 3BS
telephone 01-658 2211

Wellcome

telegrams and cables
WELLAB BECKENHAM
telex
WELLAB
BECKENHM 23937

BMNC/83/1

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

5th January 1983.

Dear Dr. Shapiro,

SPINNING SPEED MODULATOR

Having completed the construction of an automatic sampling device on our
Bruker WM-360, we have also incorporated a spinning speed modulator to
minimise the appearance of sidebands. The equipment consists simply of
a supplementary gas regulator, a solenoid valve and some associated
electronics.

Using the existing regulator inside the spectrometer console, a minimum
flow rate is set which, with the needle valve on the front, is adjusted
to say a 5 Hz spin rate. The new regulator is set to give a maximum flow
rate to enable say a 50 Hz spin rate. The electronics then accomplishes
two things. It causes the solenoid valve to close at variable time
intervals so as to avoid any coherence with the data collection. It also
detects when the spin speed falls below 20 Hz and causes the valve to open.
The natural inertia of the system does the rest.

The apparatus was built by Kevin Brooks following Alan Strutt's design,
who can provide more details if anyone is interested. The diagram shows
an example of the suppression achieved.

Yours sincerely,

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

Enc.

JCL/ag

STY E 43/ The Wellcome Foundation Ltd 183 Euston Road London NW1 2BP Registered in England No 194814

Optimised field

Spin rate: 27Hz

SSB = 0.20%
64 scans (3.5min)

13C

* * *
SSB

impurity. 13C

* * *
SSB

X20

Optimised field

Modulated spin rate: 20-50Hz
Cycle time ≅ 25sec

64 scans (3.5min)
SSB <0.03%

13C

impurity 13C

X20

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P.O. BOX 39175
CINCINNATI, OHIO 45247

HAHN SPIN ECHOES AND SPIN-DIFFUSION IN ^{19}F MAS-NMR OF FLUORIDATED HYDROXYAPATITE SURFACES

Dear Barry:

We have been using high-field ^{19}F MAS-NMR to study the fluoridation of hydroxyapatite surfaces, with the goal of better understanding the mechanism of dental enamel fluoridation. One long-standing problem has been the need to quantitatively distinguish between the formation of calcium fluoride and fluoro-apatite ($Ca_5F(PO_4)_3$). Although both compounds have similar ^{19}F chemical shifts, at moderate (4kHz) spinning speeds only the inhomogeneously-broadened resonance from fluoroapatite is significantly narrowed and exhibits spinning sidebands. Figure 1a shows the spectrum of a hydroxyapatite sample exposed to aqueous fluoride; both the broad peak of calcium fluoride and the sharper peak with sidebands characteristic of fluoroapatite can be observed. Since calcium fluoride has a T_2 orders of magnitude shorter than that of fluoroapatite, a Hahn spin echo can be used to eliminate the calcium fluoride signal and clearly reveal the fluoroapatite component (Figure 1b).

We have used ^{19}F MAS-NMR to study the effects of fluoride solution concentra-tion and solid-state transformations upon the form of fluoride at the surface. One example of the intriguing information available from the technique concerns the ultrastructural relationship between calcium fluoride and fluoroapatite at the surface.

The results of an inversion-recovery measurement of T_1 in a surface-treated sample containing both calcium fluoride and fluoroapatite are shown in Figure 2 for three delay values. The existence of a null for both components at the same delay value (1.6s) demonstrates that the T_1 values are identical. Unless this equality is fortuitous (which is not supported by measurements on the bulk compounds), spin-diffusion between the calcium fluoride and fluoro-apatite spin systems appears to be responsible. Thus, we can conclude that the fluoroapatite and calcium fluoride at the surface are in intimate contact at the molecular level.

A note describing preliminary results has been submitted for publication (J. P. Yesinowski and M. J. Mobley, "^{19}F MAS-NMR of Fluoridated Hydroxy-apatite Surfaces"). Further data is included in the proceedings of an ACS Symposium on the Adsorption on and Surface Chemistry of Hydroxyapatite, to be published by Plenum Press in 1983 (J. P. Yesinowski, R. A. Wolfgang, and M. J. Mobley, "New NMR Methods for the Study of Hydroxyapatite Surfaces"). A manu-script on the detailed characterization of bulk model compounds is in preparation (J.P.Y.).

Sincerely yours,

THE PROCTER & GAMBLE COMPANY
Research & Development Department

James P. Yesinowski
(513) 977-2551

Figure 1: a) ^{19}F MAS-NMR spectrum of hydroxyapatite treated with 33 mM fluoride, 0.73% total fluoride uptake, 30° pulses, 3.7 kHz spinning speed.

b) Hahn spin-echo with 273 μs delay time (= one rotation period) of same surface sample, showing only fluoroapatite component.

Figure 2: ^{19}F MAS-NMR spectra obtained with inversion recovery sequence to measure T_1 of surface fluoride signals (unequal amplitudes of short and long delay time spectra are probably due to rf inhomogeneity).

DOW CORNING

January 11, 1983

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

Dear Professor Shapiro,

"The ^{29}Si NMR Spectrum of a Constrained Molecule"

Recent investigations of siloxane polymers resulted in the isolation of a white crystalline solid which sublimed at approximately 60-70°C.

The ^{29}Si NMR spectrum of the solid was obtained using a Varian XL-200 NMR spectrometer operating in the Fourier transform mode at 39.75 MHz with broad band decoupling to remove all (SiH) scalar couplings (Figure 1). The deuterated chloroform solvent was used for the internal field frequency controlled lock system. The decoupler was gated off during the pulse delay and the sample was doped with 0.1 M tris(acetylacetonato)chromium to allow maximum relaxation of the nuclear spins. The spectrum showed two peaks one at -14.64 ppm and the other at -58.35 ppm relative to tetramethylsilane in a 3:2 intensity ratio. This information in conjunction with the mass spectrum of the solid (m/e: M+ -15 = 341, 94.9%) indicated the following chemical structure:

$$
\begin{array}{c}
Me_2 \\
Si \\
O \qquad\qquad O \\
Me_2 \\
MeSi - O - Si - O - SiMe \\
O \qquad\qquad O \\
Si \\
Me_2
\end{array}
$$

$$D_3\ T_2$$

The Me_2SiO and $MeSiO_{3/2}$ units are shifted downfield from the -20 and -65 ppm chemical shifts normally observed for these units, respectively.

Such downfield chemical shifts have been noted for strained siloxane ring systems (Table 1). This is the first time such downfield shifts have been noted for rotationally-hindered or constrained molecules.

Sincerely yours,

Sunny Lo, Ph.D.
Elastomers and Engineering
Industries Research

[1] G. Engelhardt, M. Maggi and E. Lippmaa, _J. Organmetal. Chem._, _54_, 115(1973).

[2] H. Jancke, G. Engelhardt, M. Magi and E. Lippmaa, _Z. Chem._, _13_, 435 (1973).

TABLE 1

Siloxane Chemical Shifts in ppm Relative to TMS

	D	T
D_3[1]	-9.2	
D-T, D-T / with D [2]	-8.6	-55.2
	-19.4	

P.S. Please credit this contribution to Tom Carr's account.

aw/h/glb
enclosure (1)

Figure 1: ^{29}Si NMR spectrum of $(MeSiO_{3/2})_2 (Me_2SiO)_3$ in $CDCl_3$. Chemical shifts are in ppm from TMS.

Send today for this XL Series brochure.

Varian XL Series Superconducting FT NMR Spectrometer Systems

NMR SPECTROMETER SYSTEMS

Call or write now to receive your copy of the XL Series brochure on Varian Superconducting FT NMR Spectrometer Systems. This publication includes information concerning 2-D NMR, pulse sequence generation, dot matrix displays, new software capabilities, user programming and other valuable input for NMR spectroscopists.

To receive your copy, or to have a Varian Sales Representative call on you, please contact the Varian Sales Office nearest you. A listing of both U.S. and international offices appears below.

varian

Varian U.S. Sales Offices

California
9901 Paramount Blvd.
Downey, CA 90240
(213) 927-3415

375 Distel Circle
Los Altos, CA 94022
(415) 968-8141

Colorado
4665 Kipling, Suite 1
Wheatridge, CO 80033
(303) 425-0413

Georgia
6650 Powers Ferry Road
Suite 100
Atlanta, GA 30339
(404) 955-1392

Illinois
205 W. Touhy Avenue
Park Ridge, IL 60068
(312) 825-7772

Maryland
4701 Lydell Drive
Cheverly, MD 20781
(301) 772-3683

Massachusetts
83 Second Avenue
Burlington, MA 01803
(617) 272-4152

Michigan
3721 W. Michigan
Suite 300
Lansing, MI 48917
(517) 321-5000

New Jersey
25 Hanover Road
Florham Park, NJ 07932
(201) 822-3700

New York
6489 Ridings Road
Syracuse, NY 13206
(315) 437-6464

Texas
505 Julie Rivers Road
Suite 150
Sugar Land, TX 77478
(713) 491-7330

Varian International Sales Offices

Australia
Varian Pty. Ltd.
679 Springvale Road
Mulgrave, Victoria,
Australia 3170

Brazil
Varian Industria e Comercio Ltda.
Av. Dr. Cardosa de Melo, 1644
CEP 04548, Sao Paulo, SP, Brazil

Canada
Varian Canada, Inc.
45 River Drive
Georgetown, Ontario,
Canada L7G 2J4

Europe/Near East/Africa
Varian AG
Steinhauserstrasse
CH-6300 Zug, Switzerland

Japan
Analytica Corporation
3rd Matsuda Building
2-2-6 Ohkubo
Shinjuku, Tokyo 160,
Japan

Mexico
Varian S.A.
FCA Petrarca 326
Mexico City, Mexico 5, DF

Southeast Asia
Varian Pacific
East Commercial Center
Room 1103
393-407 Hennessy Road
Wanchai, Hong Kong

United States
Varian Instrument Group
611 Hansen Way
Palo Alto, CA 94303

DE GUIGNÉ
TECHNICAL CENTER
WESTERN RESEARCH

Stauffer | CHEMICALS

Stauffer Chemical Company

1200 S. 47th St. / Richmond, CA 94804 / Tel. (415) 233-9361 / TWX (910) 382-8174

January 6, 1983

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

Subject: "Long Range H-F and C-F Coupling Constants
            in Fluorinated Cinnamates"

Dear Barry:

We have recently studied the NMR spectra of butyl esters of o-(trifluoromethyl)cinnamic acid(I) and o-fluorocinnamic acid(II). No coupling was observed between the vinyl protons and the fluorine nucleus in II. On the other hand, a 5-bond coupling between the β-vinyl proton and fluorines was observed in I. The H-F coupling constant is 2.2 Hz. We believe the H-F coupling constant is transmitted "through-space" rather than through bonds. The result implies that the conformation of I is Ia rather than Ib. Apparently,

Ia   Ib

interaction between the α-vinyl proton and the trifluoromethyl group destabilizes conformer Ib.

The H-F and C-F coupling constants between the vinyl group and the fluorine nucleus are listed in the table.

Long Range H-F and C-F Coupling Constants*

	$J(H_\beta F)$	$J(C_\beta F)$	$J(C_\alpha F)$
I	2.2	2.0	~0
II	~0	3.2	6.5

*Expressed in Hz. Solvent is $CDCl_3$.

Sincerely,

C. K. Tseng

D. A. Bowler

P. A. Foliv

AMHERST COLLEGE

AMHERST • MASSACHUSETTS • 01002

Department of Chemistry
Telephone 413-542-2342

January 10, 1983

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

Dear Barry:

I've switched from deuterons to protons since our last communication on bile salt-lecithin (BS/L) mixed micelles — am taking advantage of the National Magnet Lab's 500 MHz spectrometer while on leave in Mary Roberts' lab at M.I.T.'s Department of Chemistry. ^1H chemical shift and linewidth studies for BS, L headgroup, and L backbone resonances are a nice complement to our ^2H relaxation work on L acyl chains (1); and together they provide important new information on the molecular arrangement and surface features of these aggregates.

The most intriguing observation so far is a peak splitting for the lecithin choline methyl groups (see Figure 1), which appears at a variety of compositions as the total lipid concentration is decreased. Two populations are present in slow chemical exchange; they could be inner and outer monolayers of large phospholipid vesicles, or else both vesicle layers plus the BS/L micelles. Formation of single walled vesicles (along with BS monomers) has been proposed from quasielastic light scattering measurements (2) and is understandable in terms of the model in Figure 2: dilution pulls BS molecules from the disk perimeter and also forces the bile salts below their critical micelle concentration in the bulk solution.

Further experiments are in progress, focusing particularly on peak susceptibility to lanthanide reagents and quantitative characterization of a mixed micelle–vesicle equilibrium. Among the more obvious flies in the ointment: (a) formation of metastable states and (b) probable enhancement of inner–outer vesicle flip-flop rates by the presence of bile salts. More to follow as the picture becomes clearer ...

Sincerely yours,

Ruth

Ruth E. Stark
Assistant Professor of Chemistry

P.S. to all NATO Rowdies: Hope to stage reunion at E.N.C. Please bring slides, giggles, thirsty throats and dancin' shoes.

8 Hz

Total lipid concentration

(g/dL)

0.08

25 Hz

25

$N(CH_3)_3$

26

— 0.16

— 0.31

0.62

1.25

3.5   3.0

CHEMICAL SHIFT (ppm)

Figure 1. 500 MHz proton NMR spectra (partial traces) of 70:30 mol %
taurocholate-egg lecithin solutions as a function of total
lipid concentration. Chemical shifts are referenced to DSS;
resolution enhancement by the correlation difference technique
was applied to the top trace.

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2 - C - O - CH_2$

$CH_1(CH_2)_7 - CH = CH - (CH_2)_7 - C - O - CH$

$CH_2 - O - P - O - CH_2CH_2N^{+} \genfrac{}{}{0pt}{}{CH_3}{CH_3}$

CH_3

taurocholate

1-palmitoyl-2-oleoyl-phosphatidylcholine (POPC),
the major constituent of egg yolk lecithin.

Figure 2. Molecular structures of the components and schematic model
for one proposed structure of the bile salt–lecithin mixed
micelle, shown in longitudinal and cross section.

(1) R.E. Stark, J.L. Manstein, W. Curatolo, and B. Sears, submitted to
     Biochemistry.

(2) P. Schurtenberger, N.A. Mazer, W. Känzig, and R. Preisig,
     International Symposium on Surfactants in Solution, Lund,
     Sweden, 1982.

UNION CARBIDE

UNION CARBIDE CORPORATION

P. O. BOX 8361, SOUTH CHARLESTON, W. VA. 25303
RESEARCH AND DEVELDPMENT DEPARTMENT
Technical Center

January 17, 1983

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

Dear Professor Shapiro:

Re: Reflected-Wave Detector/Interlock

In NMR spectrometers used for studies of solids, dielectric breakdrown resulting from high humidity in the NMR probe in the presence of the intense radiofrequency excitation pulse, and disintegration of the sample rotor due to forces caused by high rotation rates are two of several conditions that may be expected in normal use which will cause adverse effects in the radiofrequency transmission path and may result in damage to spectrometer parts.

An electronic circuit which detects reflected-waves in a radiofrequency transmission path and a simple interface to the spectrometer computer has been incorporated into our Nicolet NT-200 NMR spectrometer. The circuit protects expensive equipment (transmitter, probe, receiver preamplifier) from prolonged exposure to excessive reflected voltages (and preserves the collected data) by automatically causing an experiment in progress to stop when adverse conditions occur.

A block diagram of the rf reflected-wave detector is shown in Figure 1. The voltage comparator circuit provides a user selectable variable sensitivity from 50 mW to 100 W. The detection circuit has been tested over a frequency range from 10 to 500 MHz making it suitable for a variety of existing spectrometers. A full report is scheduled to appear in the April, 1983 issue of Journal of Magnetic Resonance.

Cordially,

Robert W. Dykstra

RWD/lc

Attachment

<u>FIGURE 1</u> - Block diagram of the essential ingredients of the reflected-wave detector, and the simple change required to interface the circuit to an NMR spectrometer. (The specific dual directional coupler used should be selected for the frequency range of interest.)

University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

17th January, 1983

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

Dear Barry,

Some preliminary work done in collaboration with Dr. Graham Knox and Debbie Willison on the iron carbonyl derivative (1) may be of interest. This is one compound among many formed by the reaction of $Fe_3(CO)_9$ and $Me_2N.NO$.

(1)

The molecular formula was found initially by mass spectrometry, but the presence of four non-equivalent methyl groups is confirmed by peaks in the ^1H (δ 2.65, 3.10, 3.90, 4.00) and in the ^{13}C n.m.r. spectrum (δ 33.9, 39.2, 51.5 and 53.0). At 383K the carbon spectrum shows seven separate carbonyl peaks (δ 210.2, 213.0, 213.1, 213.5, 213.7, 214.6, and 215.9) and a low field quaternary carbon atom (δ 328.15).

That the compound is fluxional is indicated by the fact that three of the carbonyl peaks coalesce at 313K, while there are indications (despite decomposition occurring) that all the carbonyls are exchanging at 353K.

We presume that the more ready process involves NMe_2 groups exchanging roles, with movement of the three carbonyl groups attached to the iron atom (A), while the higher temperature process involves movement of a carbonyl group from one iron atom (B) to the other (A) (via a bridging intermediate). We must admit that the proposed structure is rather strained and we are considering others for this compound which is still under investigation.

Yours sincerely,

Peter Bladon

Peter Bladon

^{13}C spectrum of $Fe_2(CO)_7C(NMe)_2$ in toluene d_8.

Solvent peaks marked (S)

WM-250 at 62.9 MHz

303K

283K

215

210

(S)

TMS

(S)

400   300   200   100   0

(p.p.m.)

293-30

DEPARTMENT OF BIOCHEMISTRY

THE UNIVERSITY OF ALBERTA
MEDICAL SCIENCES BUILDING
EDMONTON, CANADA   T6G 2H7

PHONE: (403) 432 −5460

January 20, 1983

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

Title: Alterations to VT Apparatus on NT-300WB

Dear Barry:

With the arrival of your yellow notice I must spring into action. We
have been checking out our new Nicolet 300WB spectrometer over the last couple of
months although this has been made difficult because of pile driving going on just
outside our building. Anyone interested in the frequency spectrum of our building
in response to periodic pulsed excitation and its analysis as a driven damped
haromonic oscillator can contact me.

One of the things we are impressed with on the spectrometer is the
computer controller VT. However, we like to time aver_age for days at slightly
low temperatures (0-4°C for biological systems) and I have always hated the coil
in the ice bath/slush approach so we immediately converted over to using a NESLAB
Cyro Cool unit as a cooling source [Model CC-100 lowest temperature range is -100°C
probe]. For our limited temperature range we find it is sufficient to just pass
the dry air over the probe which is placed inside a relatively loosely fitted, in-
sulated copper tube.

We also modified the Nicolet VT stack by having the glassblower put a bend in the QUARTZ
tube where the inlet air is attached and bringing this out through the bottom of
the probe where the AIR tube is attached using nylon swage lock fittings. This we
think is simpler and more reliable than trying to pull the VT air tube off each
time.

Speaking of reliability, the results of having a leak in the system
just before the VT stack are interesting. We obtained the following aberrant
behaviour with a leak that resulted in insufficient air passing out the heater
coil so that it repeatedly overheated and then took too long to cool.

. . . .

Bernard L. Shapiro,   January 20, 1983

TEMPERATURE
DEG C

60

40

10   20   time
                        (mins)

What one really needs as a safety device in these systems is a flow
detector on the exit air.

Best regards,

Brian Sykes

Gerard McQuaid

Tom Williams

THE UNIVERSITY OF LEEDS

Department of Physical Chemistry
Coal Research Group
Leeds
LS2 9JT   England
Telephone 31751

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

11th January, 1983

Dear Professor Shapiro,

Distribution About the NMR-determined Average Structures of Coal-derived Asphaltenes

Asphaltenes comprise some of the higher molecular mass (MM, 200-3000) constituents of coal liquefaction products, and are of interest both as precursors of the more tractable oil fractions and intrinsically as substrates for further processing to fuels and chemical feedstocks.

^{1}H and ^{13}C NMR methods of determining the statistically averaged structures of coal-derived asphaltenes are well established[1] but, because of the very localised nature of the chemical-shift parameter on which they are based, there is no direct way of knowing how well such average structures represent the extremely large number of individual constituents actually present. Moreover, since the asphaltene fraction contains molecules with a wide range of masses, and the proposed structures are averages over all of these, information concerning the variation of structure with MM is also lacking.

In cooperation with Terry Martin and Colin Snape of the National Coal Board Coal Research Establishment, we have addressed the first of these problems in two ways. Firstly, the agreement between NMR averages[2,3] and the results[2,4] of GC and GC/MS analyses which allow identifications of many hundreds of compounds in low − MM coal-derived mixtures engenders some confidence in extrapolations to the fractions of higher MM. More directly, differential pulse voltammetry of the asphaltenes enables[5,6] many of the aromatic nuclei linked together in the structures (e.g. naphthalenes, fluorenes, anthracenes, phenanthrenes, pyrenes etc.) to be identified; for high-yield extracts obtained from coals of different rank by a variety of methods, agreement with NMR-determined average structures is good in all cases so far examined.[5,6]

^{1}H and ^{13}C NMR of almost monodisperse preparative size-exclusion chromatographic sub-fractions of coal-derived asphaltenes[7] revealed considerable variations about the average structure determined for the whole asphaltene fraction. With increasing MM, the following trends were observed: aromaticity decreased, but the degree of condensation of aromatic nuclei did not vary significantly; the size of aliphatic substituents increased.

Please credit this contribution to the Bradford University subscription.

Yours sincerely,

Keith D Bartle   Norman Taylor   Derry W. Jones

References

1. K.D. Bartle and D.W. Jones in C. Karr Jr. ed. 'Analytical Methods for Coal and Coal Products' Vol. II, Ch. 23 (Academic, New York, 1978).

2. K.D. Bartle, D.W. Jones and H. Pakdel in E.L. Fuller Jr. ed. 'Coal and Coal Products: Analytical Characterization Techniques', ACS Symposium Series No. 205, Ch. 2, p.27, 1982.

3. Z. Stompel and K.D. Bartle, in preparation.

4. Z. Stompel, K.D. Bartle and B. Frere, Fuel, 61, 817 (1982).

5. K.D. Bartle, C. Gibson, D. Mills, M.J. Mulligan, N. Taylor, T.G. Martin, and C.E. Snape, Anal. Chem., 54, 1730 (1982) and further unpublished work.

6. K.D. Bartle and M. Zander, Erdöl, Kohle, Erdgas, Petrochemie, in the press.

7. D.G. Richards, C.E. Snape, K.D. Bartle, C. Gibson, M.J. Mulligan and N. Taylor, Fuel, submitted.

DATA 28.1.1983

VS. RIF

NS. RIF.

TEL. DIRETTO

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A.&M. University
College Station
TX 77843 - U.S.A.

Title: NMR investigation of the reaction between
diketene and methanol.

Dear Prof. Shapiro,

Diketene reacts with alcohols according to the
following scheme[1]:

$$CH_2=\underset{\underset{O-C=O}{|}}{C}-\underset{|}{CH_2} \quad + \; ROH \; \longrightarrow \quad CH_3COCH_2COOR$$

I   II

The reaction is catalysed by bases and acids.
We have studied by pulse 'HNMR the kinetic of the
reaction of diketene with methanol using triethyl-
amine as catalyst (deuteroacetone as solvent).Under
our conditions the reaction gives yields of $> 95\%$ of
II indicating that the alcoholysis is essentially
complete. The experimental data obtained at several
temperatures and concentrations of the reagents, in
absence of water, can be interpreted according to
the general equation:

$$\frac{d\,[A]}{dt} = - K\,[A]\,[B]$$

where $[A]$, $[B]$ are the concentrations of diketene
and methanol respectively. The data show also the
linear dependence of the reaction rate, K, on the
catalyst's amount (fig. 1), so that the reaction

./.

is first order in all three components. The Arrhenius plot (fig. 2) let us calculate an energy of activation of 8.5 kcal/mole.

The NMR spectra of the reacting system in presence of water (0.5 mol. 1^{-1}) do not show any significant side reactions such as hydrolysis of diketene to aceto acetic acid which can decarboxylate to acetone[2]. The kinetic of the reaction is lower than that one in absence of water. The experimental data are not described by the previous equation so that the reaction mechanism could be different in the two cases.
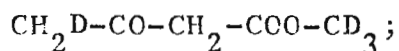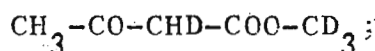
Using deuteromethanols several reaction products can be recognized in the reaction mixture. The products differ in the deuterium position. According to the ^{1}H and ^{13}CNMR spectra the following structures have been assigned:

$$CH_2D-CO-CH_2-COO-CD_3; \qquad CH_3-CO-CHD-COO-CD_3; \qquad CH_2D-CO-CHD-COO-CD_3$$

  III   IV   V

Compound III is initially produced, however, at the end of the reaction, compound IV is the main reaction product. The production of III is explained by the following scheme:

$$diketene + CD_3OD \longrightarrow \left[CH_2\!\!=\!\!\underset{OD}{\overset{|}{C}}-CH_2-COO-CD_3 \right] \longrightarrow III$$

As II (and III, ...) is a β-ketoester, the CH_2 protons are strongly acidic and can be easily exchanged with deuterium[3]. Infact an ^{1}HNMR investigation of the system II + CD$_3$OD with NEt$_3$ as catalyst (deuteroacetone as solvent) shows that the CH_2 protons are exchanged with deuterium several orders of magnitude faster than methyl protons, reaching the equilibrium in a short time. The final extent of deuteration is a function of the relative concentrations of mobile protons and deuteriums.

Yours sincerely,

(E. Santoro)   (P.L. Cantini) (L.Rivolta)

MONTEDIPE

FIG. **1**

CATALYST (C): NEt₃ $2.1 \cdot 10^{-2}$ (mol. l⁻¹)

DIKETENE : 2.0 (mol. l⁻¹)

CH₃OH : 5.4 (mol. l⁻¹)

SOLVENT : deuteroacetone

WATER : $< 0.15 \cdot 10^{-2}$ (mol. l⁻¹)

TEMPER : 28 °C

REACTION RATE (K) VS. CONCENTRATION OF THE CATALYST [C]

FIG. **2**

CATALYST (C): NEt₃ $2.1 \cdot 10^{-2}$ (mol. l⁻¹)

DIKETENE : 2.0 (mol. l⁻¹)

CH₃OH : 5.4 (mol. l⁻¹)

SOLVENT : deuteroacetone

WATER : $< 0.15 \cdot 10^{-2}$ (mol. l⁻¹)

REACTION RATE (K) VS. INVERSE OF THE TEMPERATURE ($1/_T$)

REFERENCES

1) T. Kato, Accounts Chem. Res., 7, 265 (1974)

2) J.M. Briody and D.P.N. Satchell, J.Chem. Soc., 3378 (1965)

3) R. Brouillard and J. Dubois, "J. Org. Chem." 39, 1137 (1974)

Maximization of Spectral Data Throughput with the Multi-Terminal GX PLEXUS System...

The JEOL Theory of NMR Productivity:
Multi-terminals are better than one...

Over the last decade, the contribution that FT NMR spectroscopy has made for the chemical analysis community is enormous. Some scientists have even claimed that NMR spectral data is the single most important source of structural information available to the organic chemist. NMR spectroscopy provides information on structural analysis, quantitation, the behavior of molecules in various environments and the nature of an environment.

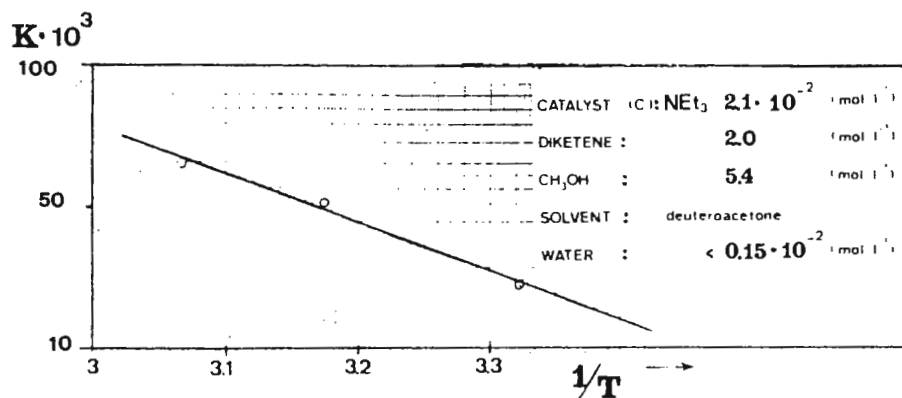Until recently, NMR spectral throughput was dependent upon the sensitivity limits of the NMR spectrometer hardware. For example, ten years ago a simple carbon spectrum could take hours to collect. Nowadays, that same experiment takes only several minutes (See Figure 1). Hence, the profusion of routine and complex data now being generated by modern, commercially available NMR spectrometers has placed an ever increasing demand for high quality spectral throughput.

The Throughput Dilemma

In many cases, a spectroscopist can collect spectral data at the same rate or faster than the data can be processed and output. Continuing advances in NMR signal detection and high sensitivity probe design have created a "throughput dilemma."

The typical single operator/single terminal data system available in most NMR spectrometer systems cannot efficiently handle such fast rates of data acquisition.

In a typical single access scenario, operators must wait in line in order to collect data from that single terminal. One by one, each operator takes his or her turn at the instrument, places a sample in the probe, collects data and finally works up the results for hardcopy output.

Any operation (such as FFT, integration, printing and plotting of spectra) which takes place after spectral accumulation is data system intensive. However, they all cause unnecessary and costly dead time on the system. The spectrometer cannot be utilized in any matter until the operator currently using it completes his or her work and allows the next operator in line to have physical access to the instrument.

This scenario, of a typical single terminal instrument, effects a tremendous waste of
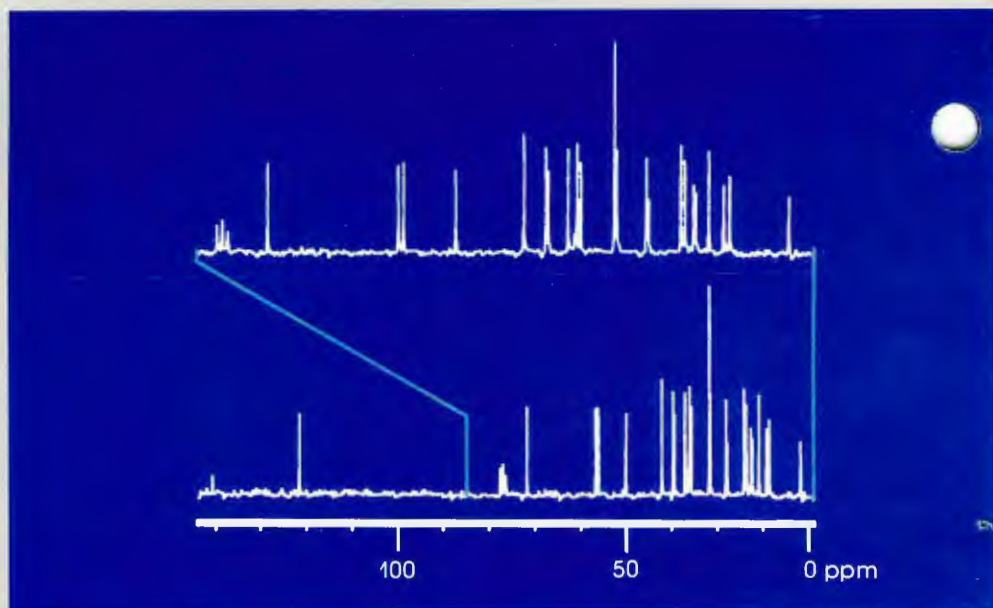

Figure 1. Carbon-13 spectrum of 5 mg. of cholesterol, acquired in five minutes at 50.0 MHz using the *MICRO-TILT PROBE* especially designed for high S/N when sample amounts are limited.

valuable time. The waste is magnified when the cost of commercially available NMR systems is considered.

To solve the throughput dilemma, the most efficient and logical recourse would be to increase operator access to the spectrometer thereby eliminating costly dead time. In other words, the answer is the PLEXUS solution.

The PLEXUS Solution

The GX Series of FT NMR spectrometers with the PLEXUS data system, offers multiple user access to maximize operator interaction and data throughput. JEOL has achieved the unique position of offering multi-terminal spectrometer systems by incorporating the unsurpassed expertise of DEC hardware. The GX multiple-user access systems include a DEC LSI 11/23 microprocessor with the RSX multi-terminal/multi-tasking operating system, and a 32-bit word, high speed "NMR processor." This data system package yields the uncompromising speed and efficiency demanded by today's sophisticated NMR market.

The advantages of a multi-terminal/multi-tasking NMR spectrometer are numerous as well as obvious. When an operator is actively collecting data and maintaining privileged control of the spectrometer, it is possible for other operators to manipulate previously accumulated data (e.g., process two-dimensional spectra, write pulse programs or request FFT operations on two or more different sets of data). A typical three-terminal PLEXUS system is illustrated in Figure 2 below.

Here Terminal One is being used to collect and display a Free Induction Decay (FID). This implies temporary spectrometer control by Terminal One. Concurrently, Terminal Two is involved with data manipulation of a previously accumulated data set. The data set could have been accumulated minutes before on Terminal Two or weeks before and read from a disc. Terminal Three is being used for pulse program editing.

Consequently, the often time-consuming job of writing novel pulse sequences or experimental menus can be achieved without

Figure 2. Two JEOL graphics terminals and one DEC terminal being used simultaneously, with the RSX-11M Multi-terminal/Multi-tasking operating system.

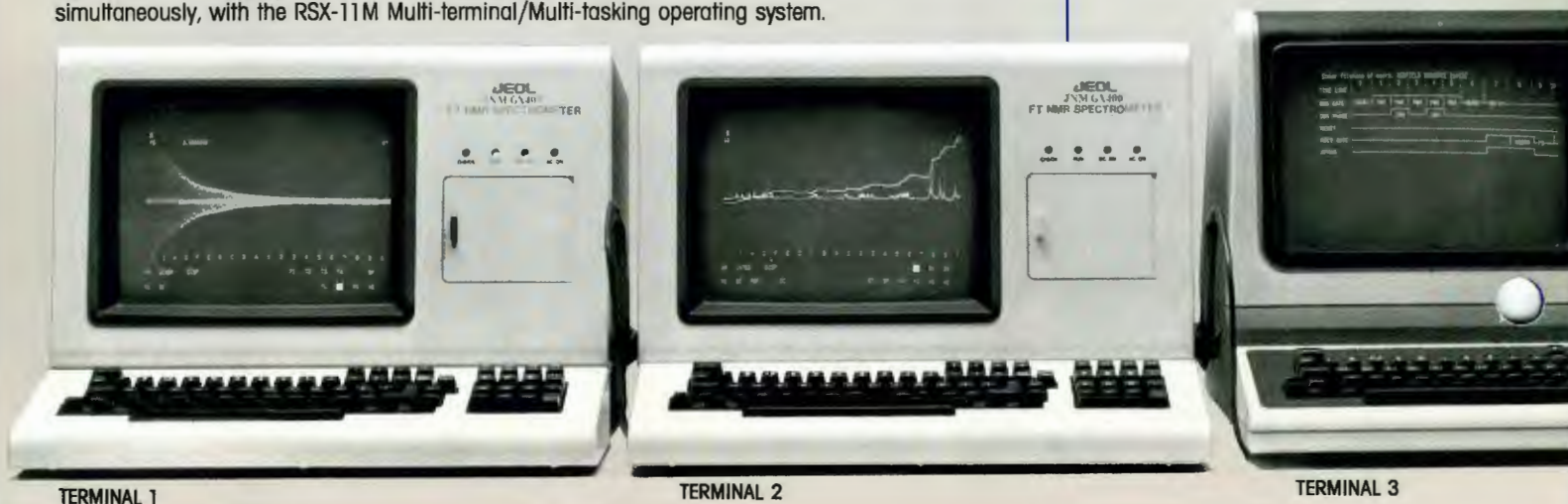TERMINAL 1   TERMINAL 2   TERMINAL 3

Figure 3. Redfield water suppression pulse program generated with PEGS (Pulse Editing Graphic Software).

taking up valuable instrument time. In short, the activities of Terminal One, Two, and Three can be accomplished simultaneously with only one spectrometer and data system.

Advantages Over Conventional NMR Systems

The operational configuration of a multi-terminal system has distinct logistical benefits over non-instrument interactive satellite stations. First of all, in a multi-terminal system, there is no time wasted by the transfer of data through a RS-232 interface or by physically moving a disc from the spectrometer to a work station. Secondly, there is no difference in software from one terminal to another; since the entire data system uses a one multi-terminal monitor program.

Thirdly, and most importantly, each JEOL graphics terminal has potential control of spectrometer operation. This fact alone eliminates the bottleneck of single-user interaction as shown in the maximized throughput scheme of Figures 4a and 4b. The throughput of a multi-terminal system is double that of a single terminal spectrometer without a satellite station. When compared to a single terminal system with a satellite station, the throughput of a multi-terminal station is still faster. Under the best of circumstances, transfer time is usually several minutes for each spectrum. When large data sets, such as 2-D data, are relocated, transfer time may approach one-half hour.

A further benefit (and one that shouldn't be overlooked), is a psychological benefit. In a multi-terminal set-up, each operator at the spectrometer remains at one terminal for the full duration of the experiment. This continuity allows for greater concentration on each job without the distraction of moving from the spectrometer to a satellite station for final data processing.

RSX Operating Systems

RSX systems allow realtime activities to execute concurrently with less-time-critical activities. Through priority-based scheduling, the assigned priority and activities of a task determine the level of service it needs. With an RSX system, each terminal can operate independently of others in the system. That way, each terminal can run a different task and each can run more than one task.

In addition, RSX systems are highly reliable. They feature data integrity and increased system availability. For example, in a multi-user/multi-programming environment, the LSI-11 micro-computer processor provides protection as well as multiple access.

Multi-Programming

Multi-programming is the simultaneous execution of two or more tasks that reside in memory. Since task execution usually involves more than the central processor unit (CPU), multi-programming is feasible. For example, a realtime task that initiates a procedure and then waits for the completion of the procedure, may not need access to the CPU while it is waiting. Therefore, with multi-programming
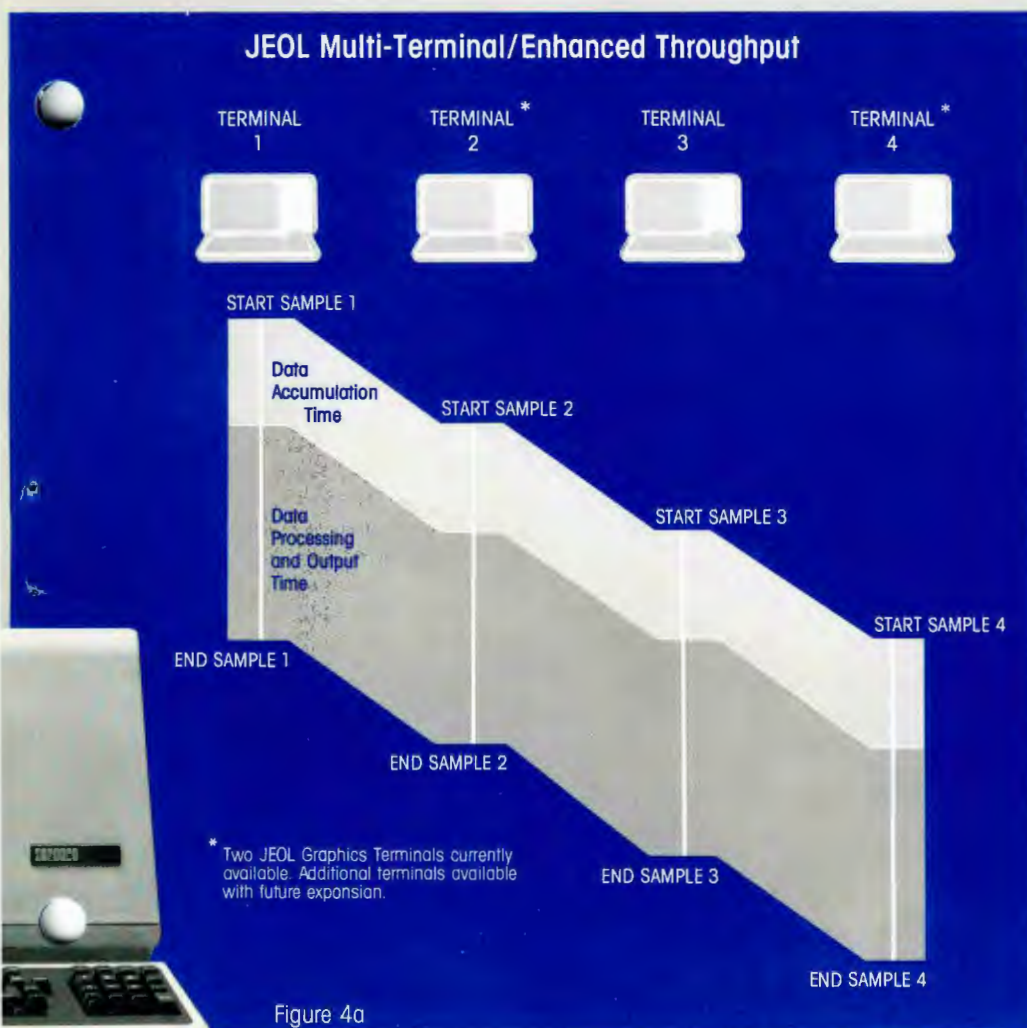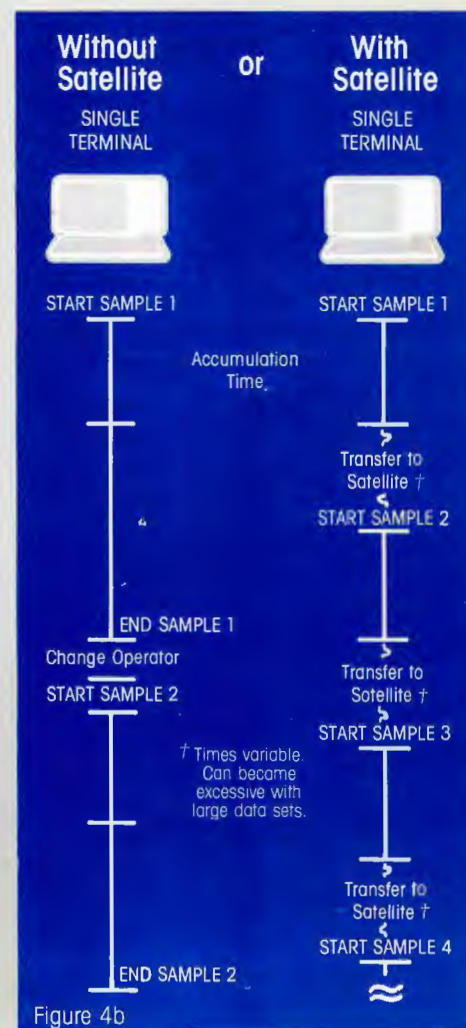

Figures 4a and 4b. Time and motion schematic of enhanced throughput of Multi-terminal/Multi-tasking NMR system vs. conventional configurations.

PLEXUS data system equipped with two JEOL graphics terminals and one DEC terminal.

capability, while one task waits for an event to finish, the control of the CPU can be given to another task. Tasks are multi-programmed by logically dividing available memory into a number of named positions. The transition of task control occurs so rapidly, it appears that many individual users have control of the CPU at the same time.

The System for Today and Tomorrow

Throughput is just one of the many problems confronting today's spectroscopists. The growing field of NMR spectroscopy has created new demands and the GX series meets those demands . . . head on.

Pulse Programming

Advances in pulse programming techniques have opened up new areas in NMR research.

JEOL has developed the PGX-300 multi-pulse programmer and incorporated it into the GX series to give NMR users the ultimate in spectrometer control and programming flexibility. A few of the PGX-300's specifications are: 2048 programming steps, 16 loop counters, 4096 counts each, 27 dynamically programmable output channels, and 5 statically programmable output channels.

To intensify the spectrometer's ability to create novel pulse programs with the PGX-300, JEOL has also developed PEGS (Pulse Editing Graphic Software). This software package enables the user to enter and edit pulse programs in the same fashion as the sequences are reported in the literature (e.g., simple timing diagrams for pulses, decoupling and other hardware triggers). PEGS eliminates the need for abstract codes and mnemonics in generating pulse programs. The visual representation of the pulse program makes sequence generation straightforward and easy to understand. An example of this programming technique, a Redfield water suppression sequence, is shown in Figure 3.

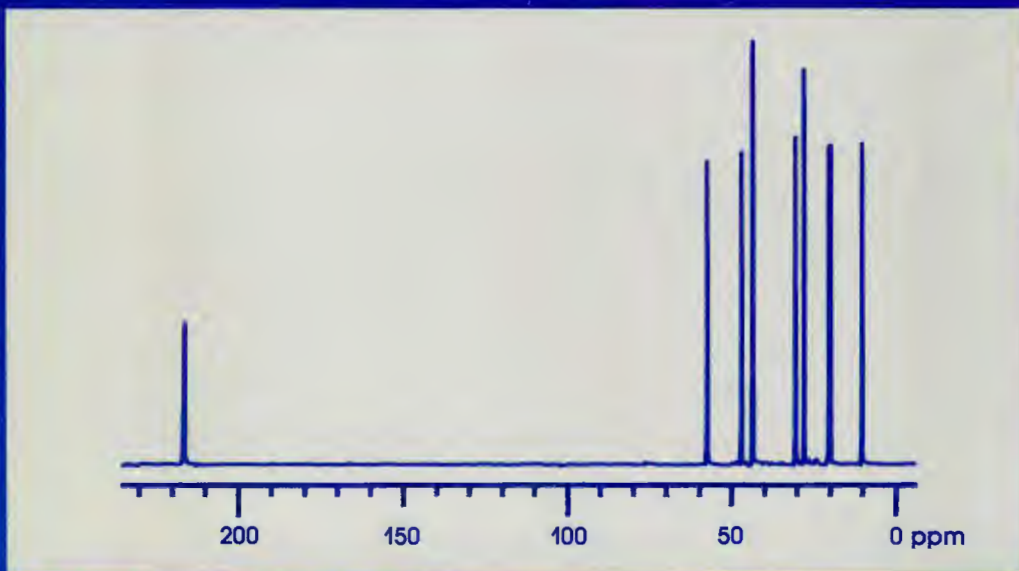### Liquids and Solids Probes

In addition to a comprehensive repertoire of high performance liquids observation probes, the GX series also offers a variety of solids sample probes. For example, cross polarization/magic angle spinning solids probes are available for specific nuclei (e.g., C-13, Si-29 and Al-27), and nuclear ranges at both ambient and variable temperatures.

Optional Magnets

The magnetic field strength options for the GX series allow for proton observation at 270, 400, 500 and 600MHz. The 270 and 400 MHz solenoids are also available as wide bore (89mm) systems.

For further discussion on multi-terminal operation, please contact us at

JEOL (USA) Inc.
Analytical Instruments Division
235 Birchwood Avenue
Cranford, NJ 07016
201—272-8820

Carbon-13 spectrum of solid camphor at 67.5 MHz. Total accumulation time was 8.5 minutes.

JEOL
Serving Advanced Technology

U.S. Department of Energy
Laramie Energy Technology Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

February 2, 1983

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

Dear Barry:

RE: AWU POSTDOCTORAL APPOINTMENT

The Laramie Energy Technology Center has announced a postdoctoral posit-
ion in NMR Spectroscopy to be filled immediately. This position is sponsored
through the Associated Western Universities, Inc. (AWU) and is for a maximum
of two years.

Applicants should have experience in the operation of FT-NMR spectro-
meters and should have the ability or interest to perform spin-echo, polari-
zation transform, and 2D-NMR spectroscopic techniques and apply these to the
analytical characterization of fossil fuels.

The starting stipend is approximately in the $18,000-20,000/year range
with some paid transportation and relocation expenses. An orientation visit
to the Center could also be arranged for qualified candidates.

Applicants may contact me or may write directly for application forms to:

Program Administrator
Associated Western Universities, Inc.
142 East 200 South--Suite 200
Salt Lake City, UT 84111
(Telephone: 801/364-5659)

Sincerely,

Dan

Daniel A. Netzel
Section Supervisor, Spectroscopic
 Research and Chemical Analyses
 Section
(Telephone: 307/721-2370)

GENANL/p/2-83

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO   SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA   93106

January 17, 1983

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

$H^1-{}^{19}F$ Chemical Shift Correlations in Macromolecules

Dear Barry:

Two-dimensional heteronuclear chemical shift correlation experiments are now being applied to large molecules including proteins. Given our interests in proteins containing the fluorophenyl group we thought that this type of experiment might provide the chemical shifts of the protons of the fluorophenyl reporter group, results that would not be available by direct observation. Crucial to the success of such a correlation experiment is the ratio of the heteronuclear coupling constant (J_{AX}) to the transverse relaxation rates (R_2) for either spin A or spin X; the larger J_{AX} is relative to R_2, the better the odds for a successful experiment. In the fluorophenyl system J_{AX} is relatively small (~ 5 or ~ 9 Hz) and, because of the csa contribution, R_2 for the fluorine resonances can be quite large at high magnetic fields.

Some initial results with atactic poly(p-fluorostyrene) dissolved in $CDCl_3$ are shown in the Figure. The proton and fluorine transverse relaxation rates were estimated and used to define optimum delays in the conventional experiment (See A. D. Bax, "Two-dimensional NMR in Liquids", D. Reidel, Boston (1982), p. 60). Although the directly observed fluorine or proton spectra of this polymer are essentially featureless at lower fields and have very little structure at 282/300 MHz., the correlation map and its projections to the ${}^{19}F$ and ${}^{1}H$ axes clearly show that there are many magnetically distinguishable environments for the fluorophenyl ring, presumably due to various local stereochemical situations. How strongly each of these contributes to the spectra depends on transverse relaxation times as well as the intrinsic concentration of each form. Sorting these out will likely keep us occupied for some time.
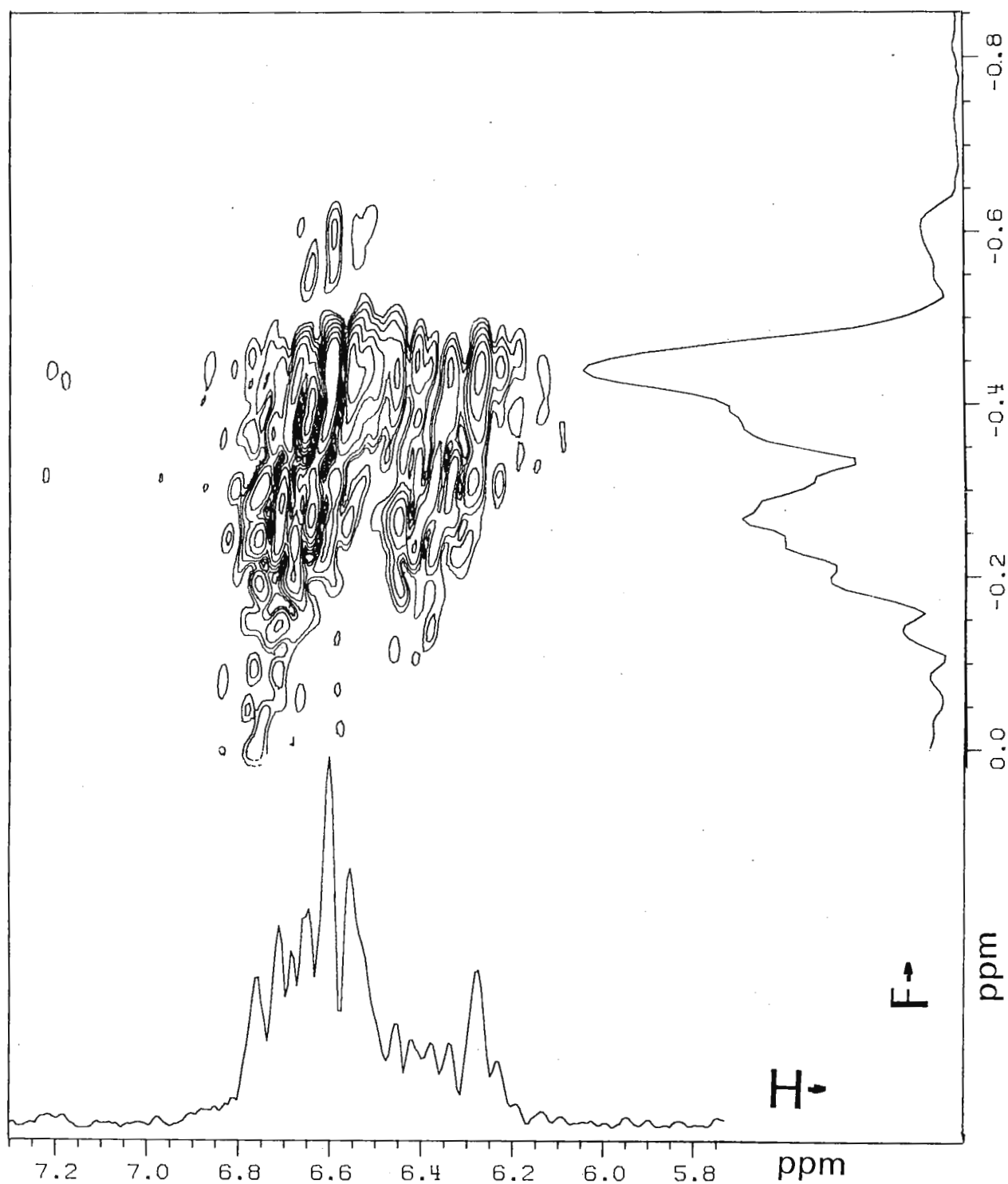
Concurrently, similar experiments are underway with a chymotrypsin derivative containing the fluorophenyl ring and we have been able to produce a correlation map for this system even though the proton R_2 values (~ 70 sec^{-1}) and fluorine R_2 value (~ 200 sec^{-1}) are large.

Sincerely,

Tom

J. T. Gerig
Professor of Chemistry

JTG:mlr

Caption for Figure. $^1H - ^{19}F$ Chemical shift correlation in poly(p-fluorostyrene) obtained at 25°, on a Nicolet NT-300 instrument. The proton chemical shifts are referenced to TMS at 0 ppm.

UAB

The University of Alabama in Birmingham
Comprehensive Cancer Center
205/934-5696

Dr. Bernard L. Shapiro   January 24, 1983
Department of Chemistry
Texas A&M University
College Station, TX 77843

RE: Shielded Solenoidal Probe For In Vivo Studies of Tumors

Dear Barry:

We previously reported that a Faraday shield employed in conjunction
with a surface coil permits spectra of subcutaneously implanted tumors
to be monitored without interference from normal tissues outside the
tumor (1). Surface coils, however, have two disadvantages – low
sensitivity, which limits detection to tumors larger than $\sim$0.6gm, and
rf field inhomogeneity, which complicates experiments such as inver-
sion recovery, spin echo and magnetization transfer. Replacing the
surface coil with a solenoidal coil while retaining the Faraday shield
substantially improves sensitivity and effectively eliminates rf field
inhomogeneity while still eliminating spurious signals from normal
tissues.

The probe design is schematically depicted in Figure 1. The sole-
noidal coil, constructed from gauge 16 copper wire insulated with
vinyl tubing, consists of a 4-turn coil with a diameter of 15.5mm and
a length of 13mm. This coil has a 90° pulse width of 22 μsec and a
Q-value of 87.2 at 80.96 MHz. The other materials employed in con-
structing the probe have been described elsewhere (1).

This probe design yields about a three-fold improvement in sensitivity
over a surface coil of the same diameter. The effect of the Faraday
shield on spectra obtained with a solenoidal coil is illustrated
in Figure 2. No ^{31}P signals were detected from a tumor-free C_3H/He
mouse monitored in the shielded solenoidal probe (Figure 2a), but
signals were detected when the grounded copper cage was replaced by
a polyethylene cage (Figure 2b). The ^{31}P NMR spectrum of a mammary
16/C adenocarcinoma ($\sim$0.6gm) implanted in a C_3H/He mouse was measured
with a polyethylene cage (Figure 2c) and with a grounded copper cage
(Figure 2d). The larger phosphocreatine (PCr) peak observed without
the Faraday shield probably reflects resonance contributions from
normal tissues in the body of the host. All spectra were collected
with a 3 sec repetition time, 13 min total accumulation time.

Sincerely yours,

Thian C. Ng

Jerry D. Glickson

References:
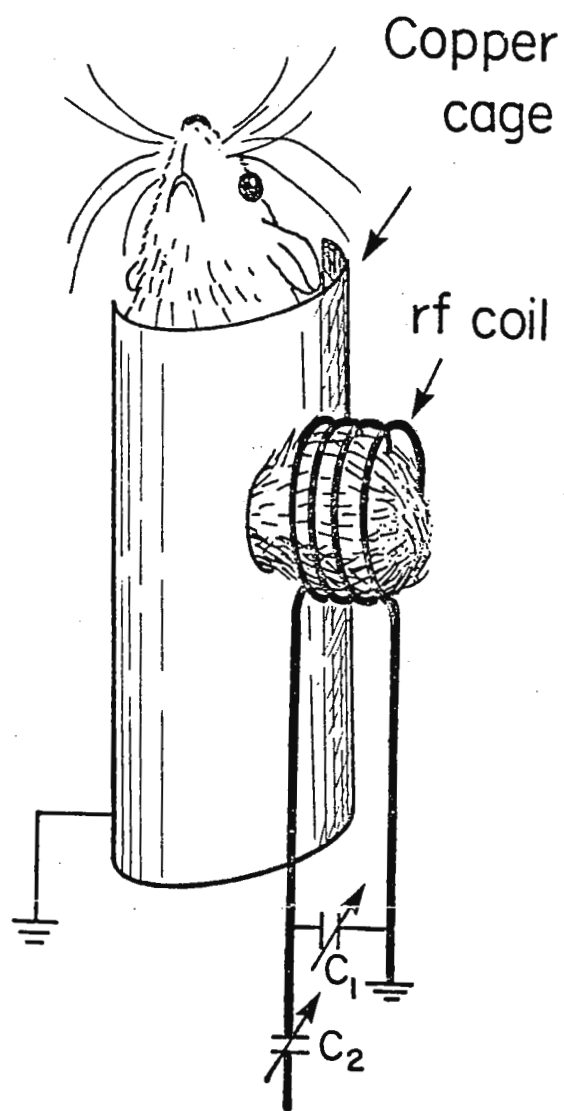1.   T.C. Ng, W.T. Evanochko and J.D. Glickson, J. Magn. Reson. 49,
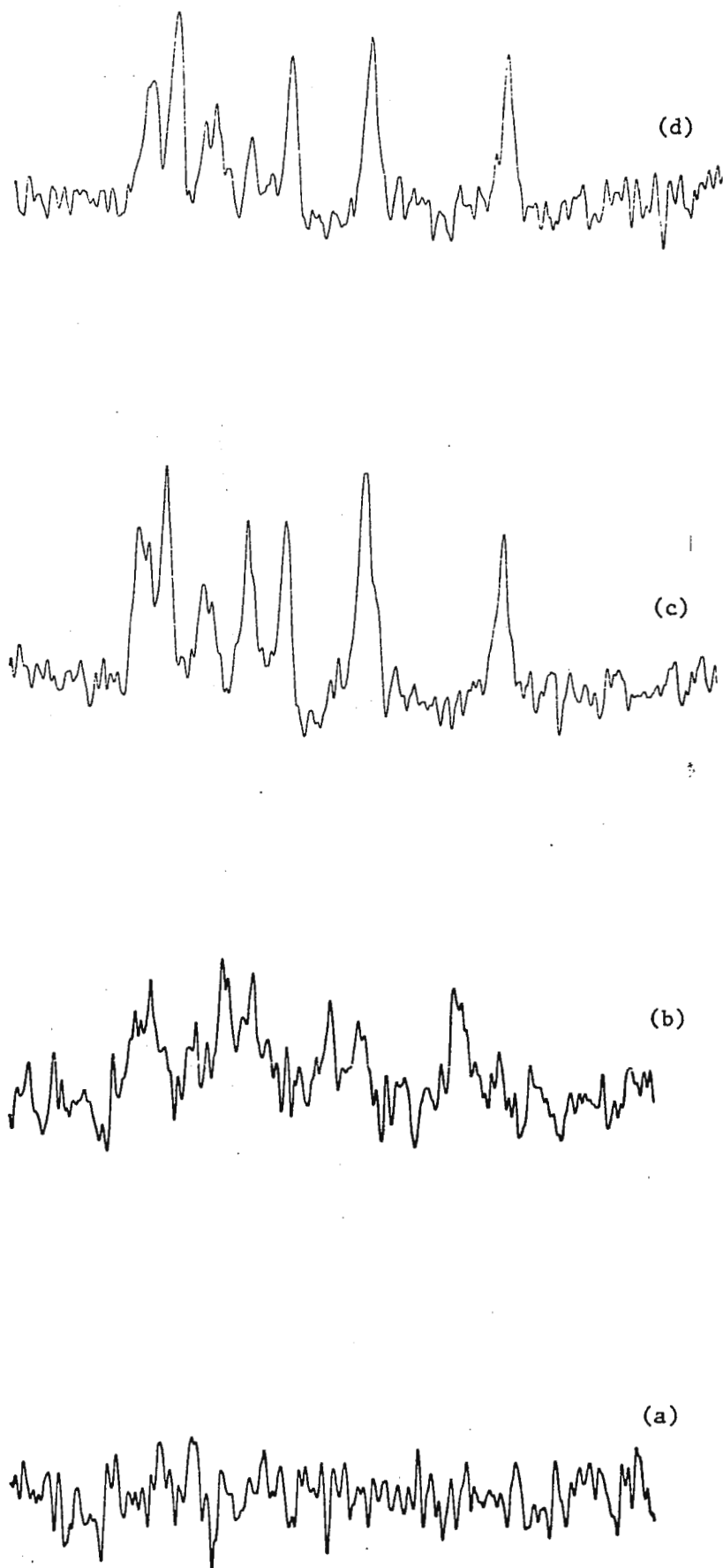   526-529 (1982).

University Station / Birmingham, Alabama 35294
An Affirmative Action / Equal Opportunity Employer

Copper
cage

rf coil

C_1

C_2

FIG. 1

(d)

(c)

(b)

(a)

FIG. 2

מכון ויצמן למדע

THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOT 76100 · ISRAEL   ישראל · 76100 רחובות

ISOTOPE DEPARTMENT

מחלקת איזוטופים

Direct phone: (054) 8

(054) 8

טלפון ישיר:

27 January, 1983

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

Biaxiality in the discotic, D_{rd}, mesophase

Dear Professor Shapiro,

During the last three years or so we have been applying (with Z. Luz and H. Zimmermann) deuterium NMR, of deuterated guest as well as host compounds, to study discotic mesophases. Our current topic of interest is biaxiality in the discotic D_{rd} and Dt mesophases.

In a single domain the deuterium NMR spectrum exhibits a doublet whose spacing $\Delta\nu(\theta_o\phi_o)$ depends on the orientation $\theta_o\phi_o$ of the magnetic field, on the average interaction constant ν_Q^{LC} and on the asymmetry parameter η^{LC} of the quadrupole tensor:

$$\Delta\nu(\theta_o,\phi_o) = \frac{3}{4}\nu_Q^{LC}[(3\cos^2\theta_o - 1) + \eta^{LC}\sin^2\theta_o\cos2\phi_o]$$

In multidomain powder samples, the observed spectrum consists of a super position of such doublets weighted by the domains distribution. The parameters ν_Q^{LC} and η^{LC} can then readily be obtained from the characteristic features in the spectrum lineshape. In particular η^{LC} can be computed from the splittings corresponding to the three canonical orientations x,y,z of the liquid crystalline phase.

$$\eta^{LC} = [\Delta\nu(\pi/2,0) - \Delta\nu(\pi/2,\pi/2)]/\Delta\nu(0,0)$$

This parameter depends in general on a large number (25) of molecular motional constants and on the asymmetry parameter η^p of the deuterium quadrupole tensor in its principal frame. However, for certain molecular and mesophase symmetries, some predictions on η^{LC} can be made without actually knowing the motional constants. Specifically for a biaxial orthorhombic phase the following will apply:

(i) For a uniaxial molecule (i.e. having a C_n axis with n>3) the parameter η^{LC} depends only on the ratio of two motional constants and it should there-fore be the same for all tensorial properties. In particular two or more inequivalent deuterons should exhibit the same η^{LC}.

(ii) For a molecule with D_{2h} or lower symmetry η^{LC} will depend on four or more motional constants as well as on the molecular geometry and the corresponding η^P. Therefore in such a moleculer, inequivalent deuterons will in general exhibit different η^{LC} parameters.

These rules are demonstrated in the attached figure showing the isotropic powder spectra of two probes i.e. mesitylene and p-xylene dissolved in the orthorhombic D_{rd} phase of hexadecanoyloxytriphenylene (THA9). In mesitylene which is axial, η^{LC} for both the aliphatic and the aromatic deuterons has the value of 0.13, while for p-xylene the two deuterons have different η^{LC} values, 0.17 and 0.07 respectively.

Please credit this contribution to the account of Dr. Rafi Poupko.

Sincerely

Daniella Goldfarb
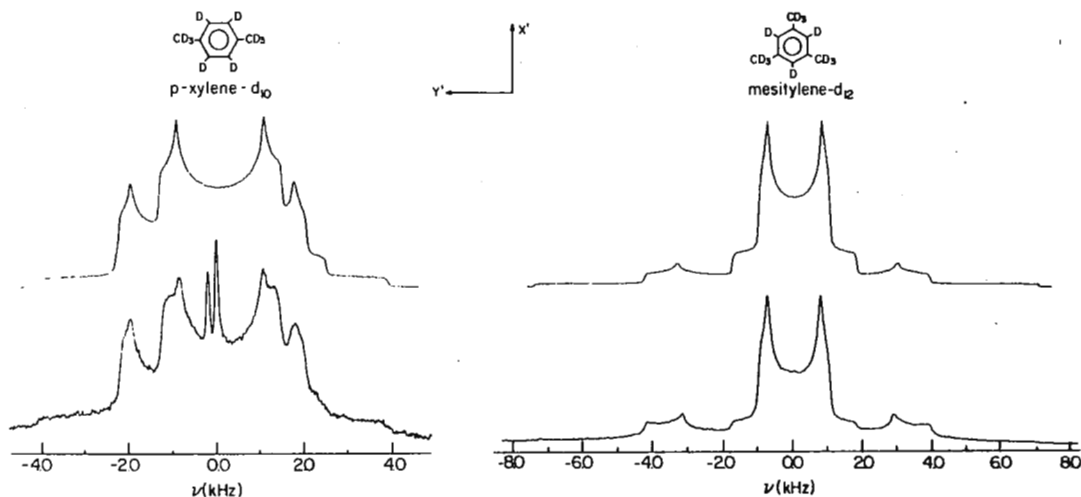
Deuterium NMR spectra of p-xylene and mesitylene (4.7 wt%) in the D_{rd} phase of THA9. The lower traces are experimental and were recorded at $T_c-T=4°C$ and 41°C respectively. The upper traces are theoretical spectra computed with the η^{LC} indicated above.

The Florida State University
Tallahassee, Florida 32306

Department of Chemistry

January 31, 1983

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

^{19}F NMR with ^{31}P Decoupling

Dear Barry,

In attempts to better understand various facets of mixed metal carbonyl-trifluorophosphine complex chemistry, we have performed a variety of NMR experiments. There are a number of reasons for studying these mixed metal carbonyl-trifluorophosphine species by NMR, either individually or as mixtures. However, the extreme similarity of PF_3 and CO as ligands toward lower valent metals is one of the complications present.

The ^{95}Mo NMR spectra of $Mo(PF_3)_x(CO)_{6-x}$ species are first order, but the species are not chemically shifted from each other. Any NMR studies involving mixtures would be virtually impossible.

Simple ^{19}F or ^{31}P NMR spectra are complicated to an extreme degree by higher order couplings. For example, a triphosphine like $Fe(PF_3)_3(CO)_2$ which is classified as an $AA'A''X_3X_3'X_3''$ system presents an incomprehensibly broad spectrum as illustrated in Figure 1b.

The ^{19}F decoupled ^{31}P NMR spectra (the "normal" decoupling experiment) again demonstrates the extreme similarity of PF_3 and CO by yielding super-imposed spectra for all species except the monophosphine for the iron complexes $Fe(PF_3)_x(CO)_{5-x}$.

Dr. Bernard L. Shapiro

Our most recent experiments have taken advantage of the previous simple ^{19}F spectra which implied that there was adequate chemical shift between species if the problem of the higher order couplings could be resolved. A new variable temperature probe has been constructed for FSU's Seminole Spectrometer (3.5T) which decouples ^{31}P (@60.7Mhz) while observing ^{19}F (141.1Mhz).

Figure 1 is an example of its performance on a preparative-scale, GC-separated $Fe(PF_3)_3(CO)_2$ sample. Note the small amounts of $Fe(PF_3)_2(CO)_3$, $Fe(PF_3)_4(CO)$ and $Fe(PF_3)_5$ disproportionation products which are somewhat obscured in the coupled spectrum (Figure 1b).

This experimental approach will greatly aid in on-going studies of these complexes in diverse areas such as photocatalysis, stereochemical non-rigidity, and nuclear hot-atom work.

Sincerely,

Dr. Thomas Gedris
Dr. Ronald J. Clark
Dr. M. F. Menoufy
Richard C. Rosanske

(b)

(a)
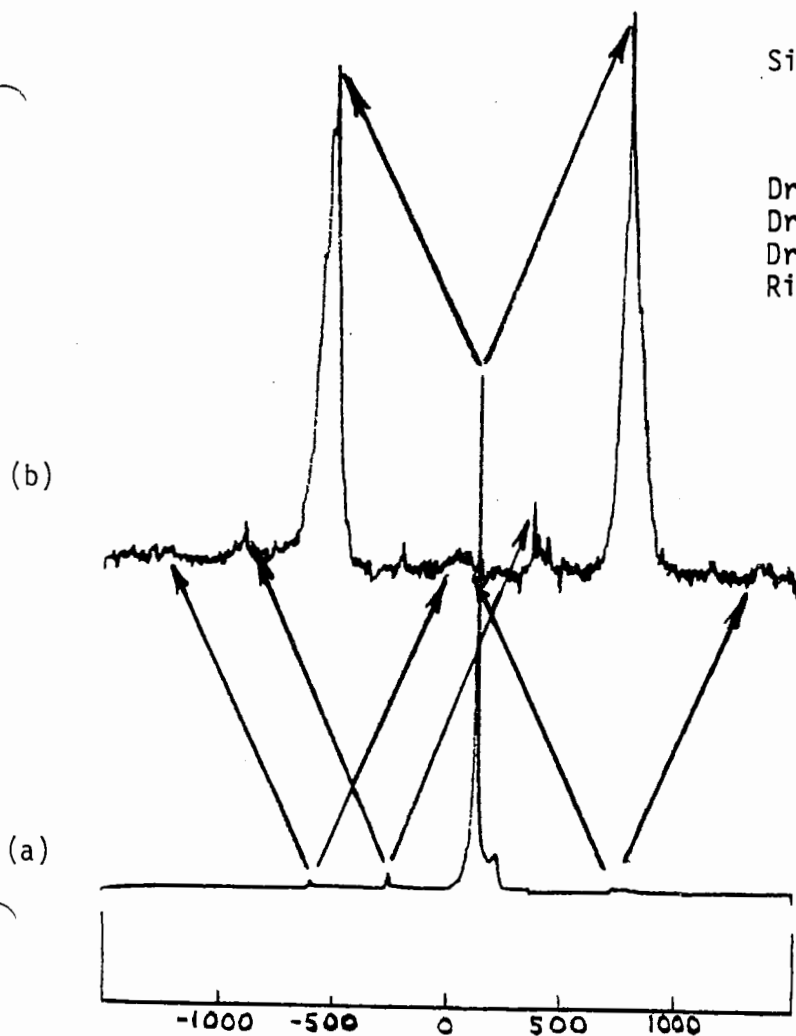
Figure 1. ^{19}F spectra, at 3.5T, for $Fe(PF_3)_3(CO)_2$ sample a) ^{31}P decoupled and b) coupled.
Note the $Fe(PF_3)_2(CO)_3$, $Fe(PF_3)_4(CO)$ and $Fe(PF_3)_5$ disproportionation impurities seen clearly in a.

-1000   -500   0   500   1000

Federation
of
Analytical Chemistry and Spectroscopy Societies

Los Alamos National Laboratory
Los Alamos, New Mexico 87545
January 24, 1983

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

Dear Dr. Shapiro:

FACSS Meeting Philadelphia, Pennsylvania September 25-30, 1983.

I would like to point out that the Federation of Analytical Chemistry and Spectroscopy Societies is having their Tenth Annual Meeting in Philadelphia this Fall. I will be arranging a two day NMR Spectroscopy program. At the present we are planning to have four half day symposia:

Symposium	Chairman
NMR in Solids	Dr. Michael T. Melchior
Two-dimensional NMR	Prof. Ian Armitage
Multinuclear NMR	Prof. George C. Levy
Instrumentation	Dr. William L. Earl

The deadline for submission of titles is April 8, 1983 and the deadline for submission of abstracts is June 15, 1983. Title submission forms can be obtained from any of the symposia chairmen, from myself at the above address or from Dr. John O. Lephardt, Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261 (Program Chairman).

I think that the meeting should be an excellent one and I encourage anyone interested in presenting a talk or simply attending to contact myself or the program chairman for further information.

Sincerely,

William L. Earl.

Title submission form enclosed.

FACSS X
TITLE SUBMISSION FORM

Title:

Categories:

Author(s):

Address:

Phone:

Affiliation: ACS ___ SAS ___ ANACHEM ___ DVCF ___ ASTM ___

ISA ___ COBLENTZ ___

CATEGORIES

1. Atomic Spectroscopy (Absorption, emission, fluoresence, etc.)
2. Infrared and Raman Spectroscopy
3. NMR Spectroscopy
4. Mass Spectrometry
5. Chromatography (gas, liquid, ion, etc.)
6. Electrochemistry
7. Thermal Analysis
8. Particle/Surface Analysis (microscopy, ESCA, XRF, etc.)
9. Data Processing/Computerization/Lab Automation
10. Biological/Clinical/Forensic Analysis
11. Environmental Analysis
12. New Analytical Techniques

SUBMISSION DEADLINE APRIL 8, 1983

If you are not submitting a paper but wish to receive the preliminary program, please check here ☐ and provide your name and address above.

Return to: FACSS X Program Chairman
John O. Lephardt
Philip Morris Research Center
P.O. Box 26583
Richmond, VA 23261