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Newsletter

No. **275**

August, 1981

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DEADLINE DATES: No. 276   7 September 1981
                               No. 277   5 October 1981

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.

KEMIAN JA BIOKEMIAN LAITOS
TURUN YLIOPISTO
SF-20500 TURKU 50

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

July 3, 1981

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

Dear Professor Shapiro,

^{13}C NMR Spectroscopy and the Epimer Equilibria of Perhydro-1,3-oxazines

Although perhydro-1,3-oxazines usually exist almost exclusively in the ring form they can exhibit a ring-chain tautomerism similar to that of 1,3-oxazolidines(1,2):

n = 2   1,3-oxazolidine
n = 3   perhydro-1,3-oxazine
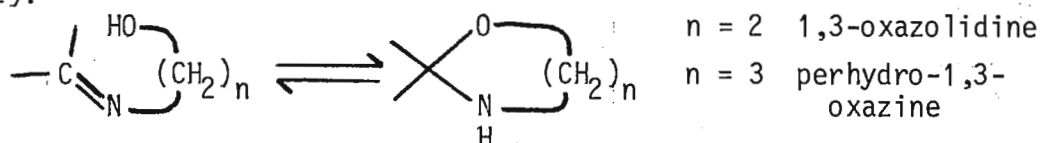
Despite the fact that both forms - if present in reasonable amounts - can be seen separately in a NMR experiment the equilibrium is established fairly fast. Since we know that the amount of the open-chain form remains almost negligible in the case of alkyl-substituted perhydro-1,3-oxazines we concluded that ^{13}C NMR signal intensities can be used to determine the epimer equilibria:

E.g.

<u>cis</u>   (open-chain)   <u>trans</u>
       minor component
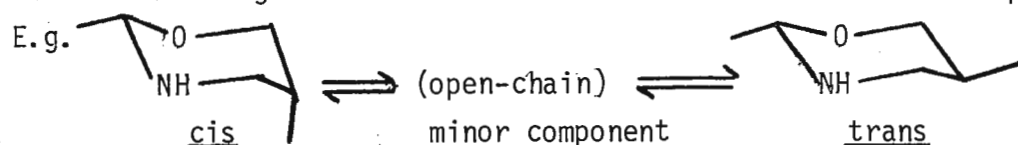
In another study (3) we have used our approach based on the multilinear correlation of ^{13}C chemical shifts with the substitution patterns (4) to carry out a complete conformational analysis of methyl perhydro-1,3-oxazines at 298 K. In the following we will give you three examples of the epimeric equilibria we studied and compare their $\Delta G^{\ominus}$-values with those obtained for the corresponding conformational equilibria using the substituent effects on the chemical shifts (3,4):
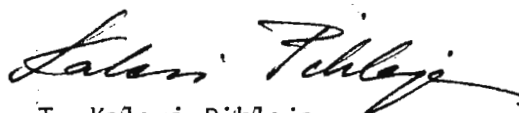
Epimer Equilibrium	$-\Delta G^{\ominus}$/(kJ mol^{-1})	Conformer Equilibrium	$-\Delta G^{\ominus}$/(kJ mol^{-1})
<u>cis</u>-2,5-Me$_2$ $\rightleftharpoons$ <u>trans</u>-2,5-Me$_2$	5.2 ± 0.2	5a-Me $\rightleftharpoons$ 5e-Me	5.4 ± 0.1
<u>r</u>-2,<u>c</u>-4,<u>t</u>-6-Me$_3$ $\rightleftharpoons$ <u>r</u>-2,<u>t</u>-4,<u>c</u>-6-Me$_3$	1.2 ± 0.1	4e6a-Me$_2$ $\rightleftharpoons$ 4a6e-Me$_2$	1.4 ± 0.4
<u>r</u>-2,<u>t</u>-4,<u>t</u>-5-Me$_3$ $\rightleftharpoons$ <u>r</u>-2,<u>c</u>-4,<u>c</u>-5-Me$_3$	5.4 ± 0.1	4a5e-Me$_2$ $\rightleftharpoons$ 4e5a-Me$_2$	5.0 ± 0.2

It is easy to realize that the results are in excellent agreement with each other and this seems to speak both for the accuracy of our approach to use ^{13}C chemical shifts as sensitive structural probes (3,4) and for the usefulness of the signal intensity data in determining the equilibria for epimeric perhydro-1,3-oxazines. In the latter case the experiments are very easy to repeat at various temperatures to determine the other thermodynamic parameters ($\Delta H^{\ominus}$ and $\Delta S^{\ominus}$) although in the case of methyl perhydro-1,3-oxazines we did not, in general, find very palpable entropy differences.

Please credit this contribution to Dr. Pekka Pyykkö's (Åbo Akademi, Turku, Finland) subscription.

1. K. Pihlaja and K. Aaljoki, Finnish Chem. Lett., in press.
2. C.K. Tseng and J.H. Chan, TAMU NMR Newsletter, 239-25.
3. K. Pihlaja and M.-L. Kettunen, Unpublished results on the conformational analysis of methyl perhydro-1,3-oxazines using the method reported in Ref. 4.
4. K. Pihlaja and T. Nurmi, Isr. J. Chem. 20, 160 (1980).

Sincerely yours

T. Kalevi Pihlaja
Professor in Physical Chemistry

ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE ZÜRICH

Laboratorium für anorg. Chemie

July 17, 1981

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CH-8092 Zürich

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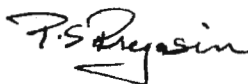
Dear Prof. Shapiro,

Our interest in the homogeneous hydrogenation catalyst containing the $Pt-SnCl_3$ moiety prompted us to investigate the ^{119}Sn NMR characteristics of some of the presumed intermediates. As the data show, $\delta^{119}Sn$ markedly depends on the nature and number of ligands coordinated to Pt. This is interesting since there is no change in the immediate coordination sphere of the tin. We interpret these results in terms of changes in the metal-metal bonding and will expand on this theme at a later time.

Complex	$\delta^{119}Sn[(CH_3)_4Sn]$, ppm
trans-$[PtCl(SnCl_3)(PEt_3)_2]$	- 201
$[Pt(SnCl_3)_3(PEt_3)_2]^-$	- 77
trans-$[Pt(SnCl_3)_2(PEt_3)_2]$	- 41
trans-$[Pt(C_6H_5)(SnCl_3)(PEt_3)_2]$	+ 92

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

Sincerely

P. S. Pregosin

Suggested title: ^{119}Sn Chemical Shifts in $SnCl_3$ Complexes of Platinum.

UNIVERSITY OF GRONINGEN LABORATORY OF PHYSICAL CHEMISTRY

NIJENBORGH 16, 9747 AG GRONINGEN, THE NETHERLANDS

Tel.: 050 - 117087

RK/gl

GRONINGEN, 3th July 1981.

Professor B.L. Shapiro
Texas AGM University
Department of chemistry
College Station Texas 77843 U.S.A.

Dear Barry,

<u>Microsecond time-resolved photo-CIDNP</u>

Application of the photo-CIDNP methode[1] to protein systems has yielded much infor-
mation on the surface structure of proteins and on their interactions with
ligands. However, the information obtained thusfar is qualitative in nature
and for a more detailed and possibly quantitative interpretation of the CIDNP
intensities knowledge of the reaction mechanism and the kinetic parameters of
the polarization process is required.

The time-resolved photo-CIDNP experiment[2], in which the polarization is induced
by a short flash-laser pulse, gives this kinetic information with a time-resolution
basically limited by the rf pulse (a few μsec with a less than 90° rf pulse on our
Bruker HX-360). We use a Phase-R flashlamp pumped dye laser (3 Joule, 0.5 μsec
pulse) for light excitation. The pulse sequence is: [flash - τ - rf - FID
(light) - T - rf - FID(dark) - T]$_n$ where τ is a variable delay and T a waiting
time.

As an example the Figure shows a series of light minus dark difference spectra
obtained with various delays τ for the photo-reaction of flavin (F) with
tryptophan (T). One can clearly see that a lot of information present at short τ
is lost at long delays and therefore also in the conventional cw laser experiment.
For instance, the flavin lines vanish when the FID is taken 100 msec after the
light flash. This is due to a cancellation of "recombination" and "escape"
type polarization inherent in the cyclic reactions normally used to generate
CIDNP in biological molecules. The cancellation is more complete for the flavin
lines, because of additional disproportionation and exchange reactions available
to the flavosemiquinone radicals. From an analysis of the time-evolution for
various concentration of flavin and tryptophan, rate constants for various
reactions and for nuclear spin relaxation in the radicals could be obtained.
A full account of this work will be published shortly.

Best regards,

Robert Kaptein

Robert Kaptein

Peter Hore

Peter J. Hore

P.S. Please credit this letter to the account of Dr. W.D. Weringa.

1. R. Kaptein, K. Dijkstra and K. Nicolay, Nature, 274 293 (1978)
2. G.L. Closs and R.J. Miller, J. Amer. Chem. Soc., 101 1639 (1979)
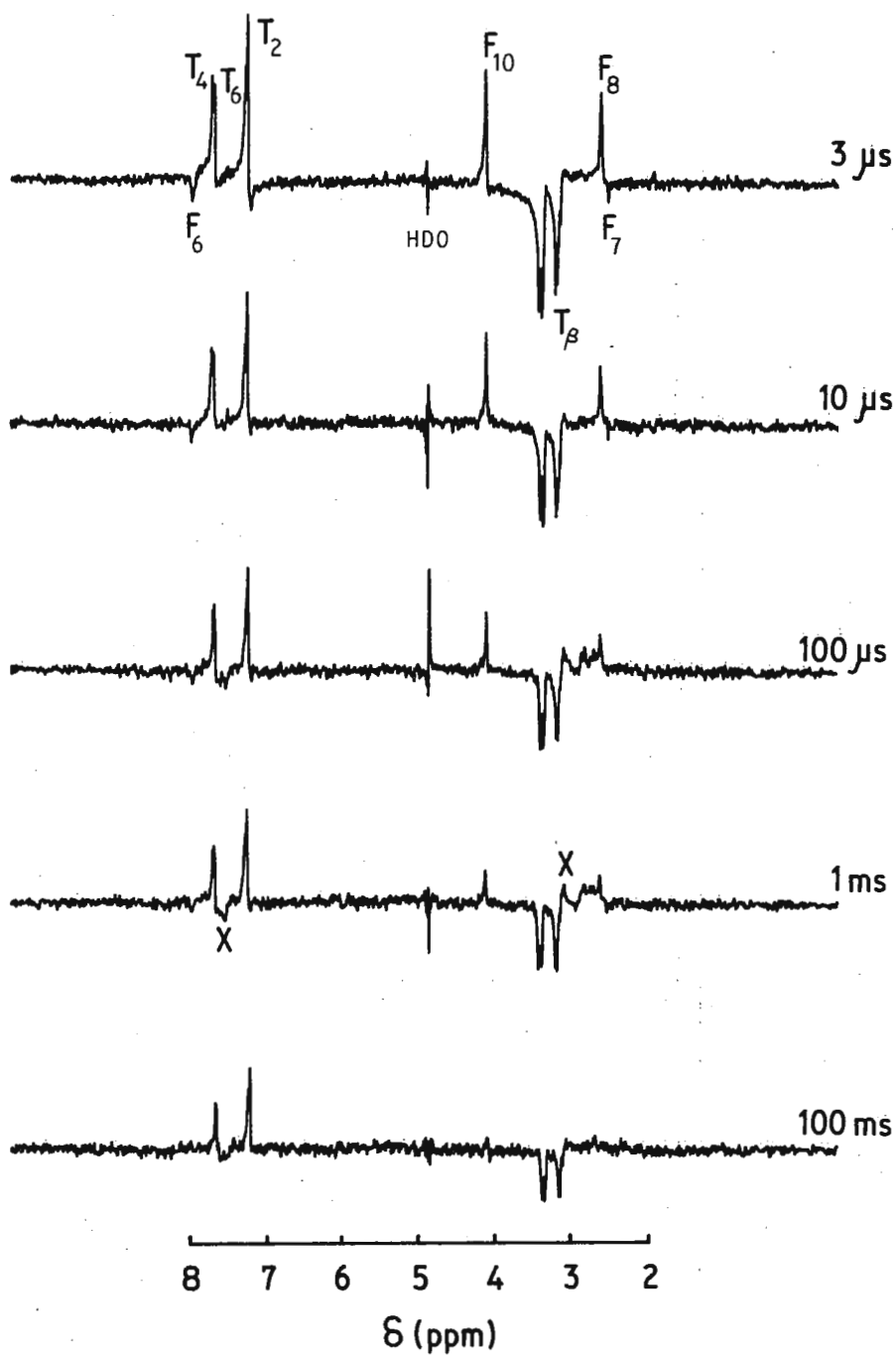
Flash photo-CIDNP spectra of a solution of flavin and N-acetyl tryptophan at various delays τ after the laser pulse. lines indicated by a T belong to tryptophan, those indicated by F to flavin.

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July 23, 1981

Dr. B. L. Shapiro
TAMUNMR Newsletter
College of Science
Texas A&M University
College Station, TX 77843

"Positon Available -- Calculator on your Spectrometer --
Conference Announcements"

Dear Barry:

I have an immediate opening for a chemist/programmer
or programmer/chemist to work on software projects in nmr
and related fields here in Billerica. Some assembly language
experience is required and familiarity with Pascal would be
helpful. The position can be for B.S., M.S. or Ph.D. with
a commensurate salary.

Recently one of our high power pulse applications
people noted that they occasionally must make calculations
in order to define their experiments. Since these are seldom
standard "canned" experiments it is not usually possible to
have a program perform them for you. However, since it is
annoying to hunt up a calculator when a computer is available,
I recently added a calculator module to DISNMR, DISNMRP and
DISCXP which essentially allows all the power of a $50.
calculator for only $250,000.

Bruker will be having two conferences this fall of
interest to the nmr community. An Nmr User's Conference
is scheduled for October 28 - 30, with contributions by
both users and Bruker personnel, and a Software course
covering assembly language, disk programming and Pascal
is scheduled for the following week, November 2 - 6.
For more information, call or write BII.

Regards,

James W. Cooper, Ph. D.
Vice President
Software Development

JWC/cs

University of Illinois at Urbana-Champaign

School of Chemical Sciences
505 South Mathews Avenue
Urbana, Illinois   61801

July 9, 1981

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

Dear Barry:

Reducing MHz to PPM

In addition to spinning our wheels, we've recently started to
spin our samples. Although at first glance most of the easy spin
I = 1/2 nuclei seem to have been taken, there are in fact far more
(1/2, -1/2) transitions to play with in quadrupolar systems, i.e.,
for nuclei having spin I=3/2, 5/2, 7/2 and 9/2. Contrary to popular
belief, high resolution NMR of quadrupolar nuclei in solids is possible -
one only has to average dipolar, CSA and second order effects, not
the unpleasantly broad first order quadrupolar patterns associated with
weird systems like ^{2}H, ^{14}N etc.

Figure 1 shows a FID of a spinning V-containing sample (^{51}V
I=5/2). This is an easy one since the broad line spectrum is only
$\sim$ 1.0 MHz wide. The Figure shows spinning beats or "rotational echoes"
since there's a CSA of $\sim$ 1,000 ppm. For larger quadrupoles (and

$$e^2qQ/h = 0.8 \text{ MHz}$$

$$^{51}V \quad I = 5/2, \quad \Delta\sigma \sim 1,000 \text{ ppm}$$

t = 2.5 msec
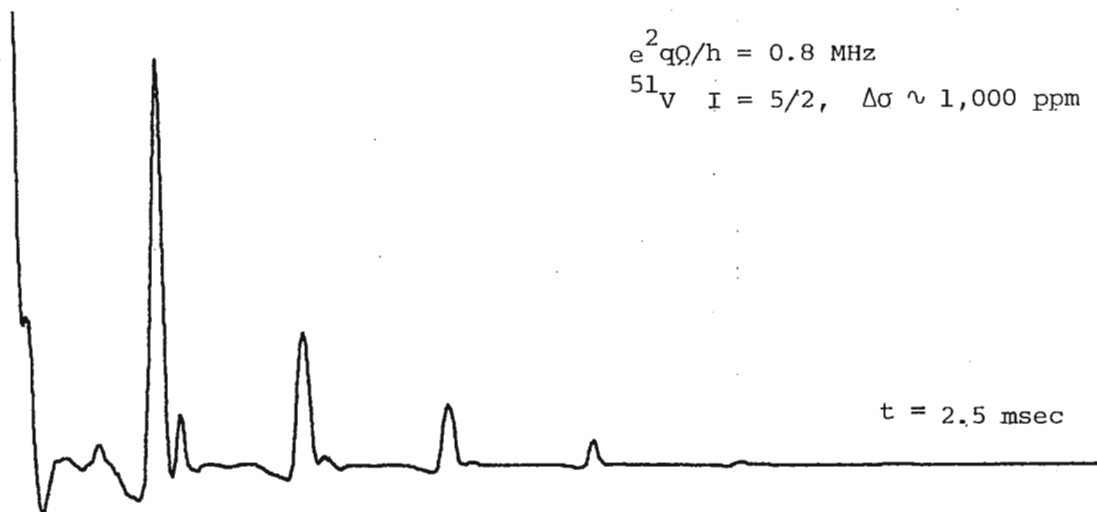
smaller spins) second order effects dominate the (1/2, -1/2) transition, as shown below. Nevertheless, with some effort high resolution spectra may be obtained, Figure 2. In this case, e^2qQ/h was ∿ 2.5 MHz.

$e^2qQ/h = 2.5$ MHz

$W_{1/2}$ ∿ 10 kHz

STATIC

$W_{1/2}$ ∿ 10 ppm

SPINNING
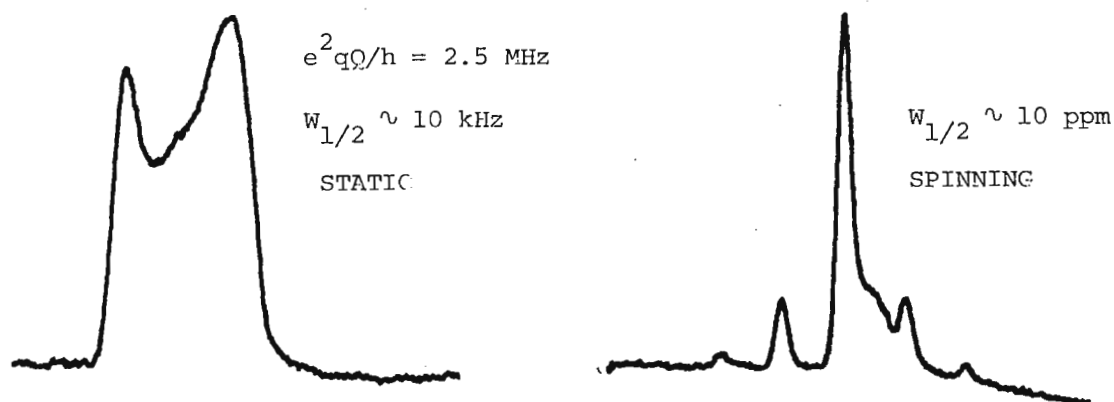
Finally, we went overboard and looked at a system having e^2qQ/h ∿ 20 MHz. We get some averaging, Figure 3, suggesting that high field, high frequency (> 10 kHz) operation will easily give high-resolution spectra of a large number of quadrupolar nuclei in the solid-state.

$e^2qQ/h = 20$ MHz

$W_{1/2}$ ∿ 60 kHz

STATIC

SPINNING
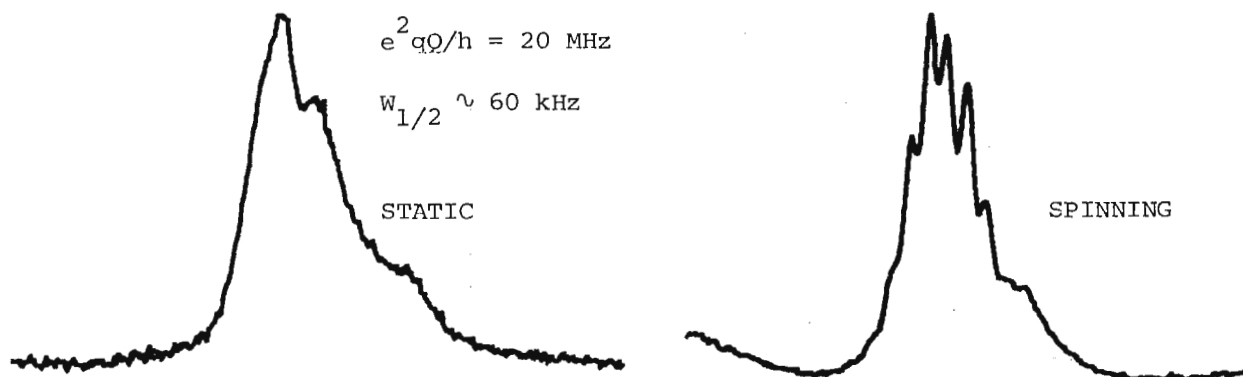
Yours sincerely,

Eric Oldfield

Robert Kinsey

Karen Ann Smith

Robert Skarjune

Tane Ray

Michael D. Meadows

Winfried Boenigk and
Prof. Dr. Gerhard Hägele
Institut für Anorganische
und Strukturchemie

4000 Düsseldorf, 10-7-1981
Universitätsstraße 1
Tel. 0211-311-2288

to

Prof. B. Shapiro

Dept. of Chemistry

Texas A&M University

College Station

Texas 77843   U.S.A.

Dear Professor Shapiro,

we wish to introduce our new program DSYMPLOT to the readers
of TAMU NMR Newsletters. DSYMPLOT allows the calculation of
NMR spectra from symmetric spin systems in isotropic and aniso-
tropic phases. The program covers up to 10 single spins $I=1/2$
using any given symmetry.

e.g. $[AB]_n$ $[AX]_n$ $n = 1 - 5$

   $[[A]_2 X]_m$ $m = 1 - 3$

In this letter we demonstrate a useful application with the
data of 1,3,5-Trifluorobenzene given by S.A.Spearman and J.H.
Goldstein in J. Magn. Res. 26, 237 (1977).
In figures 1 and 2 the low-frequency-half-spectra for ^1H and
^{19}F nuclei are calculated using D_3 symmetry for sym-$C_6H_3F_3$ in
the potassium-laureate metaphase.
DSYMPLOT will conveniently supply the isotropic NMR spectra
setting all dipolar interactions D_{jk} to zero.
DSYMPLOT is the result of a consequent pursuit of ideas started
with our earlier version SYMTRY (TAMU 248 and J. Magn. Res. 26,
505 (1977)).
A complete description of DSYMPLOT and copies on tape are
available from the authors.

Yours sincerely

Winfried Boenigk   G. Hägele

KEYWORD: DSYMPLOT
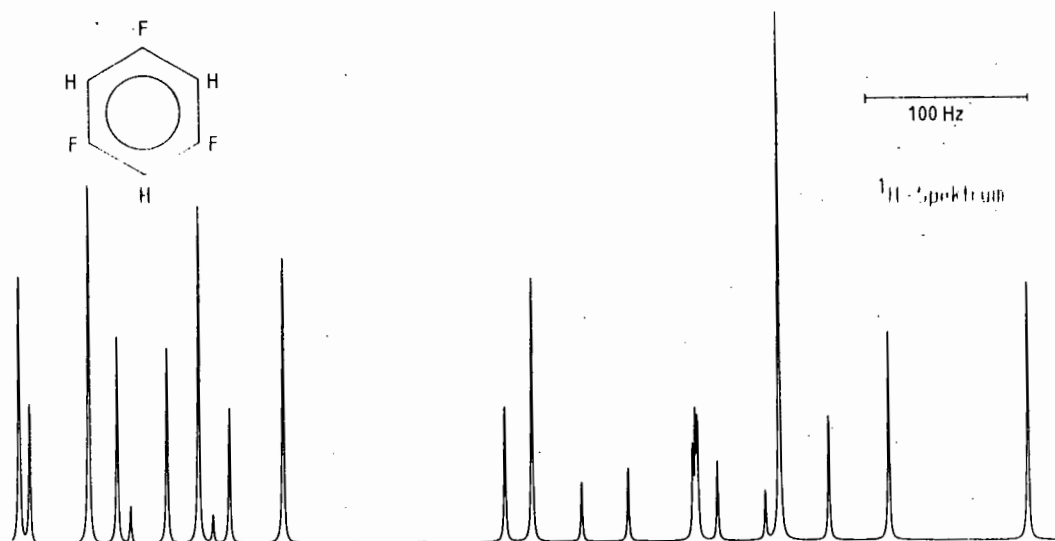
Fig. 1 ^{1}H- low-frequency-half-spectrum of 1,3,5-Trifluoro-
benzene in the potassium-laureate metaphase
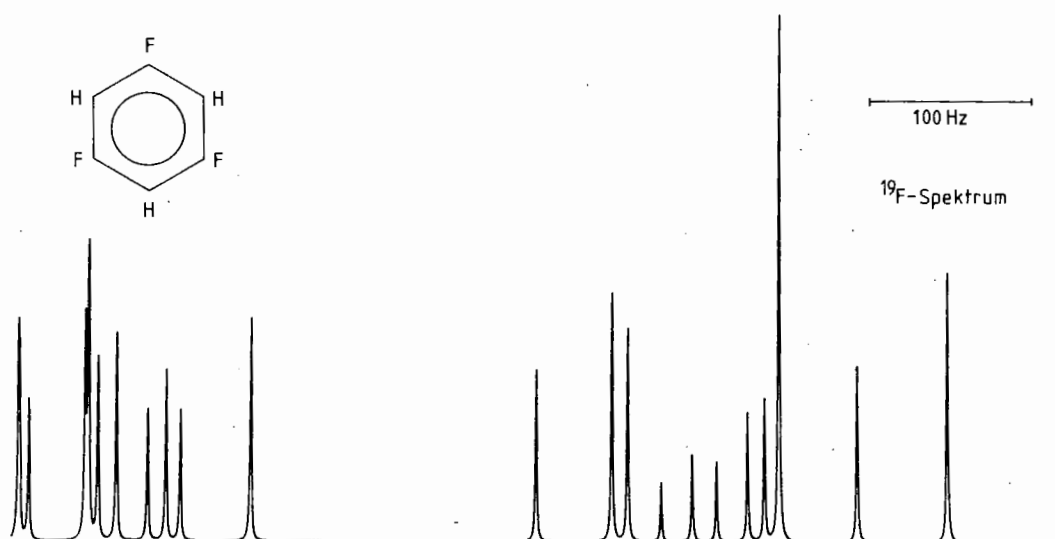
Fig. 2 ^{19}F- low-frequency-half-spectrum of 1,3,5-Trifluoro-
benzene in the potassium-laureate metaphase

Southern Research Institute

KETTERING-MEYER LABORATORY

2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA ███████ 35255
TELEPHONE 205-323-6592

July 1, 1981

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

Title: Rabenstein's SEFT Experiments

Dear Barry:

Many of the Newsletter readers probably saw Dr. Dallas Rabenstein's presentation at ENC in April of this year of his ^{13}C SEFT experiment. It's main interest for me was the apparent ease of distinguishing among methyl, methylene, methine, and quaternary carbons.

Dr. Rabenstein graciously supplied me with details of his experiments, which he says are in press with the Journal of Magnetic Resonance, and I have tried them on several samples. Since the times, (τ_2's), chosen for these experiments depend upon the expected values of $^1J_{CH}$, I was concerned about possible ambiguities when working with samples where the values of $^1J_{CH}$ are expected to vary considerably. As a test, I chose to try the simplest experiment on I, a retinoid closely related to those

I
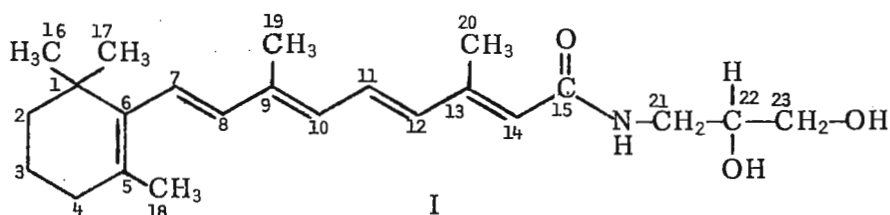
Carbon	δ_C	Carbon	δ_C	Carbon	δ_C
1	34.31	9	138.93	17	29.00
2	39.71	10	*130.16	18	21.75
3	19.31	11	*128.36	19	12.87
4	33.14	12	135.50	20	13.76
5	129.80	13	149.33	21	42.21
6	137.81	14	120.97	22	71.38
7	128.36	15	168.91	23	63.96
8	137.41	16	29.00		

*Assignments may be interchanged.

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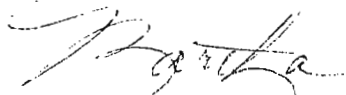
Prof. Shapiro   July 1, 1981

about which I have written to you before.[1]   Since $^1J_{CH}$ for the aliphatic carbons should be about 125 Hz and $^1J_{CH}$ for the olefinic methines should be about 150 Hz, I chose an average value of 137.5 Hz. It was gratifying to find that this gave satisfactory results, as shown in the accompanying spectrum, and that it was not necessary to do two separate experiments, as I had feared. I do not yet know whether the difference spectra he describes will be more sensitive to this problem, though I shall investigate that when time permits. Meanwhile, this simple experiment has confirmed the assignment made on the basis of the work of Gerhard Englert[2] and by comparison with some simple reference spectra. The chemical shifts from this spectrum are in good agreement with those from the conventional spectrum.

Sorry I could not make the deadline of the FINAL ULTIMATUM. I trust this will reinstate us.

Sincerely,

Martha Thorpe
Senior Chemist

MT/cpm

Enclosure

---

[1]TAMU Newsletter No. 230, p. 37, 1977.

[2]Helv. Chim. Acta, 58 (8), 2367-2390, 1975.

^{13}C Spectrum of I with Methyl and Methine Carbons Up, Methylene and Quatenary Carbons Down

TMS

12.87

13.76

19.31

21.75

29.00

33.14

34.31

39.71

42.21

63.96

71.38

CDCl$_3$

120.97

128.36

129.67

129.80

130.16

135.50

137.81

137.41

138.93

149.33

168.91

'The Crown and Sceptre',
Burgess Road - as from

23rd July 1981

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

Professor B.L.Shapiro,
Department of Chemistry,
Texas A.& M. University,
College Station,
Texas 77848, U.S.A.

TEL. 0703-559122
TELEX 47661

Re: DOUBLE QUANTUM NMR ON SINGLE QUANTUM SPECTROMETERS

Dear Barry,

The use of quadrature detection on Fourier transform spectrometers
has led to the provision of 90° phase shifts in the radiofrequency to allow
imbalance in the receivers to be corrected to first order (1). Thus even the
humble one-pulse experiment is usually phase-cycled over four transients.
The 90° shift is sufficient for two-pulse experiments also (2), with four
transients to clean up the excitation, repeated four times to clean up the
detection. The three-pulse experiment, however, may require π/n phase shifts
to separate different orders of multiple quantum coherence (3).

A spectrometer supplying quadrature radiofrequency to the power
amplifier via a multiplexer can be persuaded to give 45° phase shifts, and hence
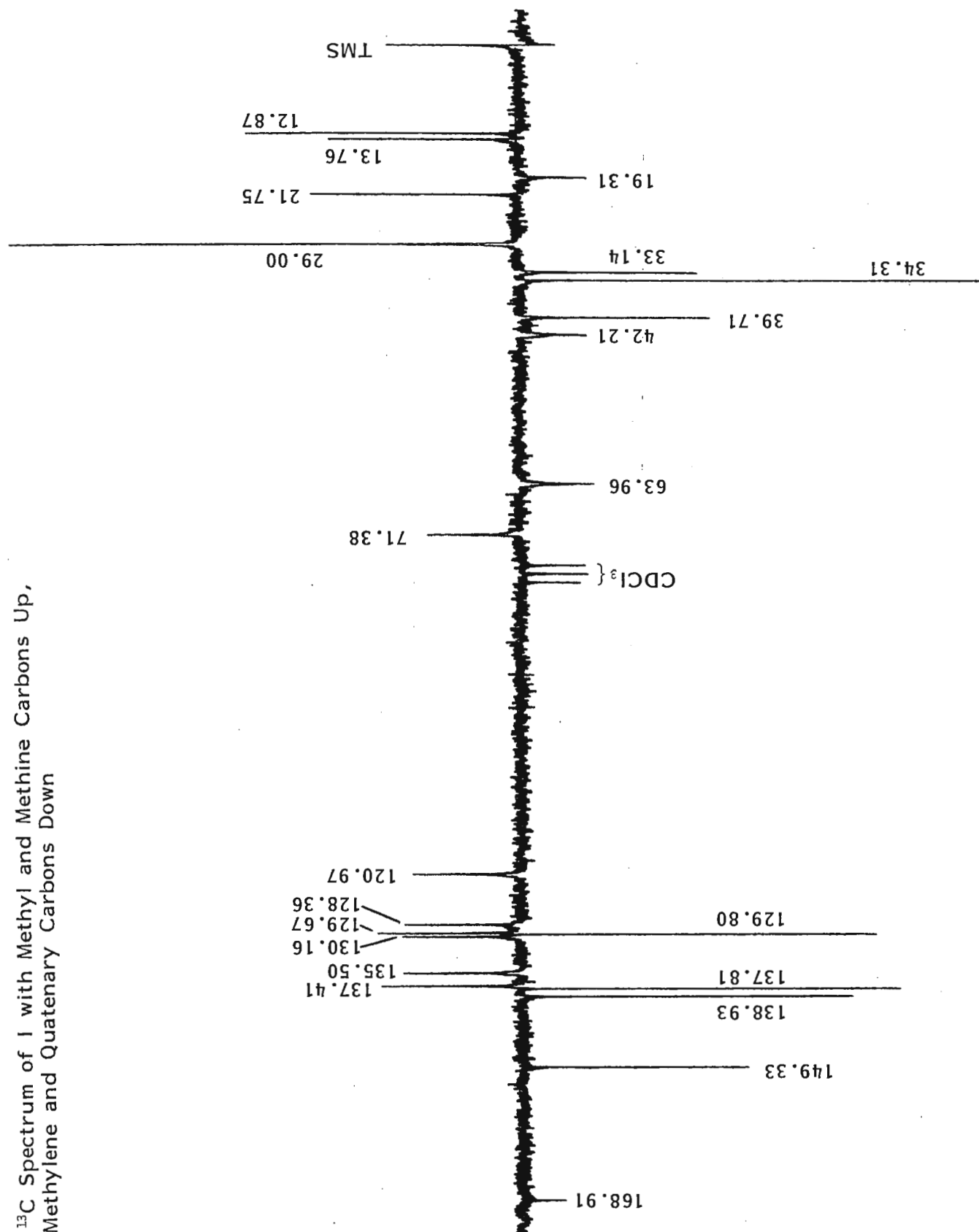tackle double quantum experiments, according to the formula:

$$\sin(\theta) + \sin(\theta + \pi/2) = 2^{\frac{1}{2}}\sin(\theta + \pi/4) \quad .$$

This is demonstrated in the series of spectra below using a CXP-200 spectrometer
in the operational mode and simply specifying either a pure phase (+X or +Y) or
simultaneous quadrature phases (+X and +Y) on one line of the pulse programme.

| X | XY | Y | -XY | -X | -X-Y | -Y | X-Y |
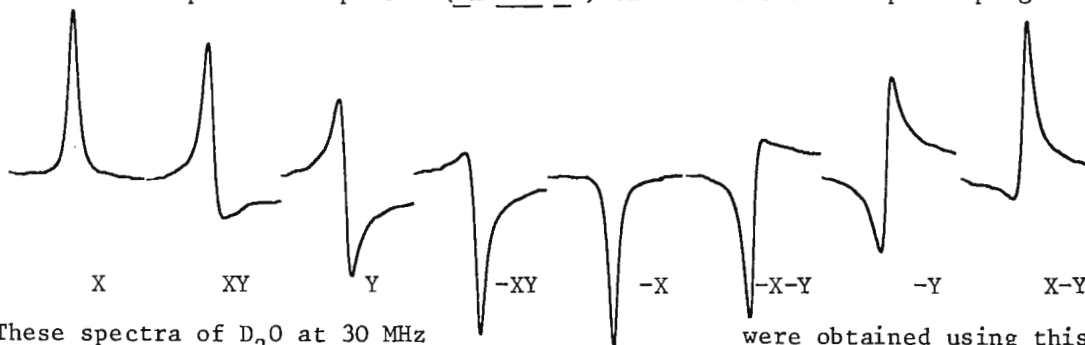
These spectra of D_2O at 30 MHz   were obtained using this
novel method 'PULSENMR' with identical scaling and phase correction. The 90°
pulse used for the pure phases was 14 µsec and 10 µsec for the mixed phases,
though the standard 20 W Amplifier Research driver amplifier is presently under
repair and may not have as linear a response as the ENI broadband amplifier
used in its place.

1. D.I.Hoult and R.E.Richards, Proc.Roy.Soc.Ser. A <u>344</u>, 311 (1975)
2. G.Bodenhausen, R.Freeman and D.L.Turner, J.Magn.Reson. <u>27</u>, 511 (1977)
3. G.Bodenhausen, R.L.Vold and R.R.Vold, J.Magn.Reson. <u>37</u>, 93 (1980)
   G.Drobny,A.Pines,S.Sinton,D.Weitekamp & D.Wemmer, Disc.Faraday Soc. <u>13</u>, 49 (1979)

With best wishes,

J.W.Emsley   Jim   &   D.L.Turner

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

Amsterdam, 15th July 1981
Badhuisweg 3
Tel. via telefoniste (020) 30 91 11
Tel. rechtstreeks (020)
Hr/Mw

Dear Barry,

THE CHARACTERIZATION OF CHEMICALLY MODIFIED SILICA GELS BY HIGH-RESOLUTION
SOLID-STATE ^{13}C NMR

As part of our continuing programme to assess how valuable solid-state
^{13}C NMR might be for the study of surface species, we have examined a
series of well-characterized chemically-modified silica gels, covering a
wide range of organic chemical species[1].

The samples on which we wish to report are six silica gels,
chemically modified with aliphatic chains. All have the general structure

$$
\equiv\!\!-\ O-\!\!\!\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{Si}}\!\!-R
$$
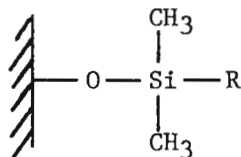
where R is a C_1, C_3, C_6, C_8, C_{18} or propylcyclohexane alkyl chain. The
samples were prepared by the same general route, namely via the reaction
of silica with the respective monochlorosilane. The use of monochlorosila-
nes (which often serve as stationary phases in chromatography columns) re-
sults not only in stable products with high surface loadings but also, more
importantly, in well-defined products. Bi-functional and tri-functional si-
lanes, although frequently used because they give generally higher loadings
than the monofunctional reagents, lead to less well-defined compounds.

The spectra were recorded on a Bruker CXP-300 spectrometer (7.05 T field
and a ^{13}C frequency of 75.45 MHz) using cross polarization and magic angle
spinning. Our spinners were fabricated from coated boron nitride (see
TAMUNMR No. 264, p. 28); the spin rates were between 3 and 4 kHz. Single
cross polarization contacts with contact times between 2 ms and 10 ms were
employed. The recycle time between acquisitions was 5 s, and the acquisi-
tion time was 100 ms using a sweep width of 20 kHz. B_1 field strengths
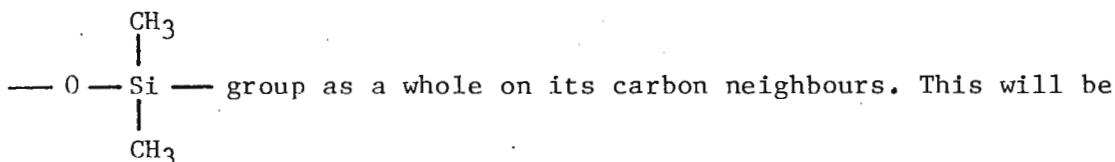were 10 G and 40 G for proton and carbon channels, respectively.

----

1. Samples provided by Dr. G. van der Velden (DSM, Geleen) and
   Prof. Dr. L. de Galan (T.H. Delft).

Koninklijke/Shell-Laboratorium, Amsterdam

d.d.15th July 1981   Pag.

The spectra of three of the chemically modified silica gels are shown in
the Figure. Line widths are in many cases less than 0.6 ppm and it is
extremely promising that we can see all seven types of carbon separately
in the spectrum of the C_6 compound. In the case were R is C_8, we see eight
individual resonances; only the middle two carbons in the chain (C-5 and C-6)
have coincident chemical shifts.

The chemical shifts in general resemble those that might be expected from
similar molecules in liquid-state NMR; many are directly predictable. For
example, the upfield shift of the silyl methyl groups (C-1) in going from
C_1 to C_3 could be expected from the combination of the extra γ and δ effect
present in the C_3 compound. Similar observations allow one to draw conclu-
sions regarding the effect of the

$$
\begin{array}{c}
CH_3 \\
| \\
--- O --- Si --- \\
| \\
CH_3
\end{array}
\quad \text{group as a whole on its carbon neighbours. This will be}
$$

reported in more detail elsewhere[2]. It also allows the assignments and che-
mical shifts for the C_6 compound to be easily predicted and the C_8, C_{18} and
cyclohexane derivative assignments logically follow. Indeed the tabular for-
mat of chemical shifts and assignments (Table) shows the consistency of
shift for each type of carbon, for example α, β or γ to silicon atom (C-2,
C-3 or C-4). This allows one to assign the longer alkyl chain groups.

Our conclusion is that high-field solid-state NMR can be considered a valid
and routine technique for the study of chemisorbed surface species of these
types. Furthermore, the well-defined series demonstrates that such chemical-
ly absorbed surface species behave, with regard to chemical shifts and hence
assignments, in the same way as if one were dealing with liquid NMR samples.
It is obviously essential to know this before these techniques are extended
to more complicated and less well-defined surface species such as in the
study of catalysts.

                                        Yours sincerely,

                        KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

A.D.H. Clague   G.R. Hays   R. Huis

                        D.S.M. CORPORATE RESEARCH, GELEEN
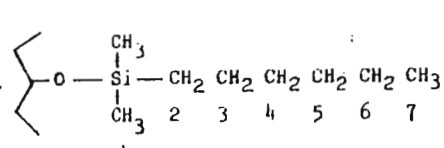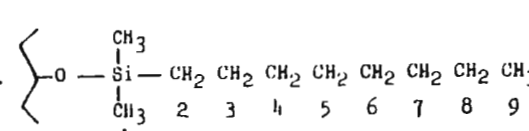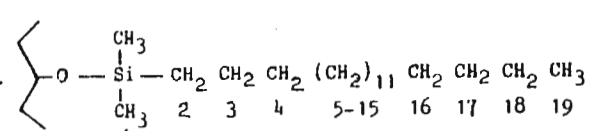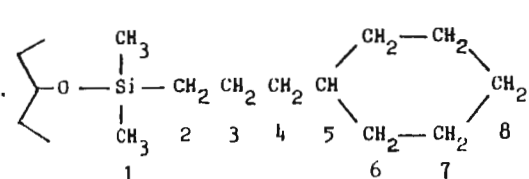
                        G. van der Welden

----
2. G.R. Hays, A.D.H. Clague and R. Huis, submitted to Surface Science.

Table

Chemical shifts and assignments for six surface-modified silica gels

Chemical shifts in ppm relative to TMS

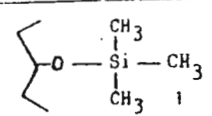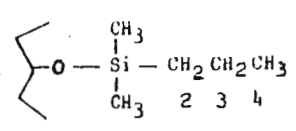| Structure	Chemical shift assignments														
	1	2	3	4	5	6	7	8	9	10	11	12-16	17	18	19
1. }O—Si(CH₃)(CH₃)—CH₃ (1)	1.5														
2. }O—Si(CH₃)(CH₃)—CH₂ CH₂ CH₃ (1,2,3,4)	0.5	21.6	17.7	17.7											
3. }O—Si(CH₃)(CH₃)—CH₂ CH₂ CH₂ CH₂ CH₂ CH₃ (1,2,3,4,5,6,7)	0.8	19.1	24.2	34.4	33.0	23.7	13.2								
4. }O—Si(CH₃)(CH₃)—CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₃ (1,2,3,4,5,6,7,8,9)	0.5	19.0	24.2	34.8	30.7	30.7	33.4	23.8	13.5						
5. }O—Si(CH₃)(CH₃)—CH₂ CH₂ CH₂ (CH₂)₁₁ CH₂ CH₂ CH₂ CH₃ (1,2,3,4,5-15,16,17,18,19)	1.2	19.3	24.7	35.3	←———————— 31.4 ————————→								33.4	23.8	13.5
6. }O—Si(CH₃)(CH₃)—CH₂ CH₂ CH₂ CH—(cyclohexyl ring: CH₂—CH₂, CH₂, CH₂—CH₂) (1,2,3,4,5,6,7,8)	0.7	18.8	21.1	42.3	38.4	34.3	27.0	27.0							

REPRESENTATIVE SOLID-STATE ^{13}C SPECTRA

DELFT UNIVERSITY OF TECHNOLOGY
Laboratory of Organic Chemistry

Julianalaan 136
2628 BL DELFT
The Netherlands

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

U.S.A.

Delft, July 20, 1981

Dear Dr. Shapiro,

Self-association of lanthanide shift reagents

Recently, we have observed that in concentrated solutions of $Ln(fod)_3$ shift reagents complex self-association phenomena occur.[1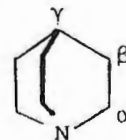] E.g. at $-38\ ^\circ C$ and 300 MHz in the ^1H NMR spectrum of a 2 M solution of $Yb(fod)_3$ in $CDCl_3$ at least 40 peaks were visible. When using lanthanide shift reagents, one usually deals with the fast exchange region, where the measured induced shift is the weighted average of the shifts of the substrate in the free and complexed states. Therefore, the evaluation of bound shifts requires measurements of induced shifts as a function of the molar ratio (ρ) of added shift reagent and added substrate. Then it is difficult to circumvent measurements at high $Ln(fod)_3$ concentrations where the self-association phenomena mentioned might interfere in the determination of bound shifts.

Probably the best way to determine bound shifts is a *direct* measurement of these shifts in the slow exchange region. There, the measurements can be performed under conditions where the self-association can be neglected (low concentration of shift reagent). Moreover, products of self-association might be detected in the spectra obtained. Measurements of $Yb(fod)_3$-induced shifts of quinuclidine under both fast (60 MHz) and slow exchange conditions (300 MHz) show substantial differences (see Table) and demonstrate that great care is needed in the interpretation of the former shifts.

Table. Relative lanthanide induced shifts in quinuclidine

	$Yb(fod)_3$ slow exchange[a]	$Yb(fod)_3$ fast exchange[b]	$Yb(dpm)_3$ fast exchange[c]	
H_α	1.00	1.00	1.00	
H_β	0.43	0.38	0.42	
H_γ	0.37	d	0.39	

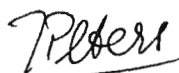[a] 300 MHz, 0.2 M quinuclidine, in $CDCl_3$, shifts ratios constant between -60 and $25\ ^\circ C$. [b] 60 MHz, $35\ ^\circ C$, 2 M quinuclidine in CCl_4, relative induced shifts obtained from a plot of the induced shifts of H_β versus those of H_α at various ρ-values. [c] Ref. 2. [d] Not observed due to coincidence with H_β.

Upon changing the electron donating character of the Yb ligands in the starting reagent the picture can alter as is shown by the results obtained with Yb(dpm)$_3$ under fast exchange[2] (see Table), which are compatible with those obtained with Yb(fod)$_3$ in the slow exchange region. We assume that self-association is less pronounced with Yb(dpm)$_3$ allowing higher concentrations to be applied without oligomerization.
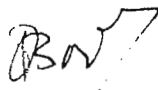
From the bound shifts, obtained from the slow exchange experiments the Yb-N distance in the quinuclidine-Yb(fod)$_3$ adduct was calculated to be 2.63 Å. This is in good agreement with X-ray studies on related complexes.[3]

Often, it is difficult or even impossible to reach the slow exchange region. In these cases it may be useful to check the structural data based on LIS measurements via measurements of ^{1}H and ^{13}C spin-lattice relaxation rate enhancements induced by the related compound Gd(fod)$_3$. These experiments can be performed under conditions where self-association is negligible ($\rho < 10^{-2}$). A drawback is, however, that an accurate correction for intermolecular relaxation (T_{1inter}) is essential. We performed relaxation rate enhancement measurements for quinuclidine and adamantane-1-carbonitrile, using bicyclo[2.2.2]octane and adamantane, respectively, as a probe for T_{1inter}. The Gd-N distances calculated from the corrected relaxation rate enhancements (2.60 Å and 2.53 Å) are in good agreement with X-ray data on related compounds. (P)reprints are available.
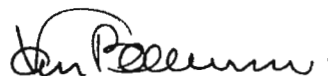
Sincerely yours,

J.A. Peters   W.M.M.J. Bovée   H. van Bekkum

References:
1. J.A. Peters, P.J.W. Schuyl, W.M.M.J. Bovée, J.H. Alberts, and H. van Bekkum, J. Org. Chem., in press.
2. C. Beauté, Z.W. Wolkowski, and N. Thoai, Tetrahedron Lett. 1971, 817.
3. E. Bye, Acta Chem. Scand. A28, 731 (1974).

July 23, 1981

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

SPICE Quantum Mechanized

Dear Barry :

"The time has come", the Walrus said, "to talk of many things...".
But let us discount the Walrus and the Carpenter and concentrate on
that single thing without which there can be no Newsletter contri-
bution, namely a new (in the sense of new wine in old skins) acronym,
constructed by merging the well known triplet SPI with Chemical
Exchange. Here's the skeleton of a Liouville space theory :

$$d\vec{\rho}(t)/dt = \underline{X}\vec{\rho}(t) + \underline{R}(\vec{\rho}(t) - \vec{\rho}_o(t))$$

$$\underline{M} = \underline{X} + \underline{R} \; ; \; \vec{\rho}_o(t) = \vec{\rho}_o(0) = \vec{\rho}_o \; ; \; \underline{X}\,\vec{\rho}_o = 0; \; \vec{\eta}(t) = \vec{\rho}(t) - \vec{\rho}_o$$

$$d\vec{\eta}(t)/dt = \underline{M}\,\vec{\eta}(t)$$

$$\vec{\eta}(t) = \exp(\underline{M}t)\vec{\eta}(0) = \underline{V}\exp(\underline{\Lambda}t)\underline{V}^\dagger\vec{\eta}(0)$$

$$\underline{V}^\dagger\underline{M}\underline{V} = \underline{\Lambda} = \text{diag}[\lambda_1, \lambda_2, \ldots, \lambda_n]$$

$$\exp(\underline{\Lambda}t) = \text{diag}[\exp(\lambda_1 t), \exp(\lambda_2 t), \ldots, \exp(\lambda_n t)]$$

All perfectly clear so far, no need to clutter it up with words !
Now we want to do a special case characterized by

$$\text{I} : [ABCD] \rightleftharpoons [DCBA] \quad \Rightarrow \quad P_I'$$

$$\text{II} : [ABCD] \rightleftharpoons [BADC] \quad \Rightarrow \quad P_{II}'$$

where the processes contribute with statistical factors of $1/3$ and
$2/3$, respectively. What representation should we choose ? Obviously,
the permutation operators P' become trivial (just zeros and ones)
when expressed in a primitive spin product basis in 16-dimensional
Hilbert space. Then

$$\underline{X}' = k\,(P_I' \otimes P_I'/3 + 2\,P_{II}' \otimes P_{II}'/3 - \underline{I})$$

where $\otimes$ denotes a tensor product and $\underline{I}$ is the identity superoperator
in spin Liouville space. But $\vec{\rho}(0)$, and hence $\vec{\eta}(0)$, is only simple in
the eigenbasis of the static Hamiltonian H, for then it suffices to
formulate the equations in the 16-dimensional Liouville subspace
spanned by the diagonal elements of the density matrix and $\vec{\rho}(0)$ is
obtained from $\vec{\rho}_o$ simply by switching the elements corresponding to
the inverted lines, e.g. for a double SPI

$$\vec{\rho}_o{}^\dagger = C(-2,-1,-1,-1,-1,0,0,0,0,0,0,1,1,1,1,2) \Rightarrow \vec{\rho}(0)^\dagger$$

Professor Bernard L. Shapiro

So somewhere along the line we must do a transformation, e.g.

$$U^\dagger H U = E_{diag} \; ; \; \underline{U} = U \otimes U^* \; ; \; \underline{X} = \underline{U}^\dagger \underline{X}' \underline{U}$$

It has recently been brought to our attention that there are still some NMR spectroscopists left who feel uncomfortable in Liouville space. For those dinosaurs we offer an alternative. Instead of performing a unitary supertransformation first calculate

$$P = U^\dagger P' U$$

by an ordinary Hilbert space transformation and then

$$\underline{X} = k(P_I \otimes P_I/3 + 2 \; P_{II} \otimes P_{II}/3 - \underline{I})$$

It's the same thing !

We have recently used this theory for the qualitative purpose of confirming an assignment, for which we took $\underline{R} = -\underline{I}/T_1$ (one shudders !) with a global T_1 of 110 ms and with $k = 26 \; s^{-1}$, both measured independently. There was also a hetero nucleus around which is responsible for additional doublet fine structure (never mind what the molecule is). Computed time-dependent spectra for 2 alternative assignments are shown in Fig. 1 and two experimental spectra in Fig. 2. The double inversion was done by a suitably programmed DANTE. Clearly, the correct assignment is that of the set on the left of Fig. 1, but the agreement is not yet quantitative because there are still 3 things wrong with this simple version of the theory: (1) we must do a better job for $\underline{R}$; (2) the dependence on the flip angle of the observing pulse must be put in explicitly (in Fig. 2 we used 18°); (3) the evolution of the system *during* the DANTE must be taken into account. One of these days we hope to get around to ironing out these defects and then write a paper on the complete story. As everyone who has read this far surely realizes, this is the quantum-mechanical generalization of the classical (and classic !) Forsén-Hoffman theory of saturation transfer, performed of course with selective population inversion rather than saturation.

Sincerely yours,

Eva E. Wille

David S. Stephenson

Gerhard Binsch

P.S. Next time about cabbages - and kings !

Figure 1

Figure 2
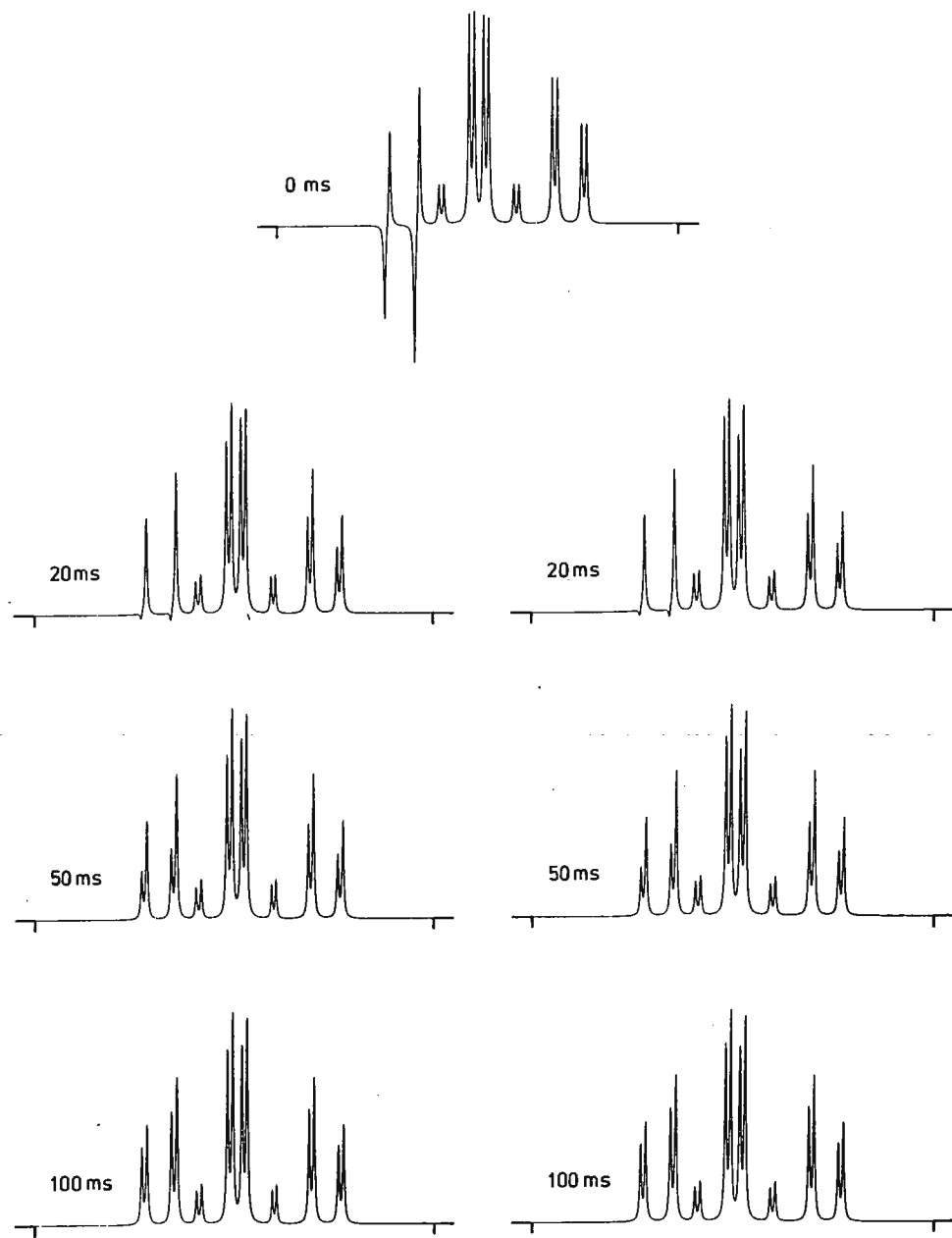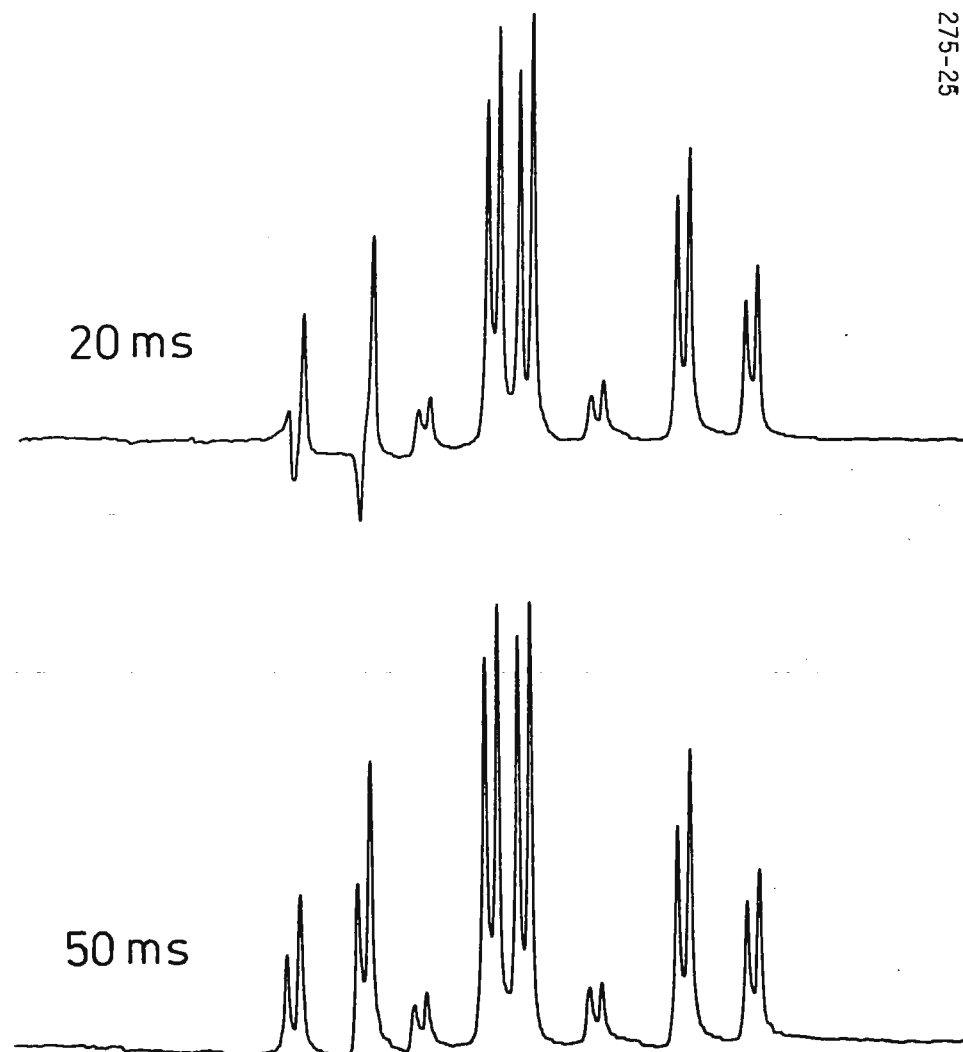
$\frac{\text{Signal}}{\text{Noise}}$ x 2.5 x $2^{®}$ = Varian XL-200

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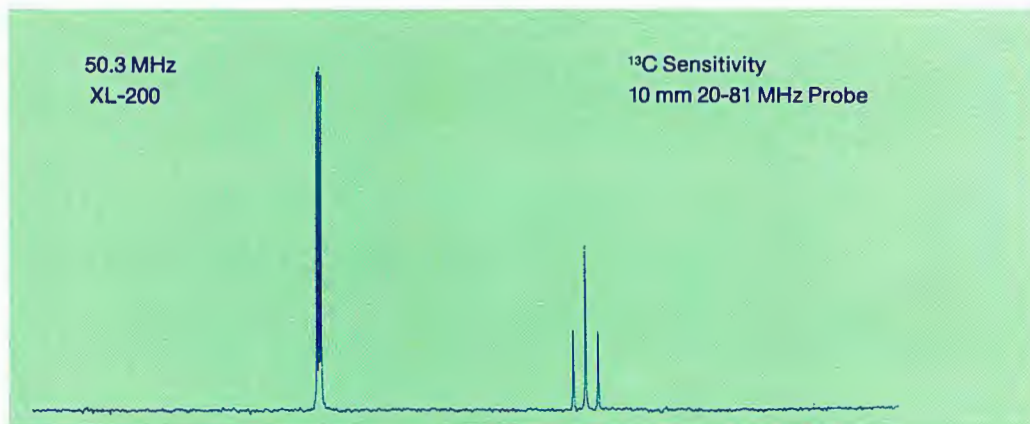
^{13}C Sensitivity Test: Single transient following 90° pulse on 60% C_6D_6/40% dioxane using the 10 mm 20-81 MHz broadband probe.

50.3 MHz
XL-200

Cholesteryl Acetate, 100 mg/ml
10 mm 20-81 MHz Probe

24 Scans

1 Scan
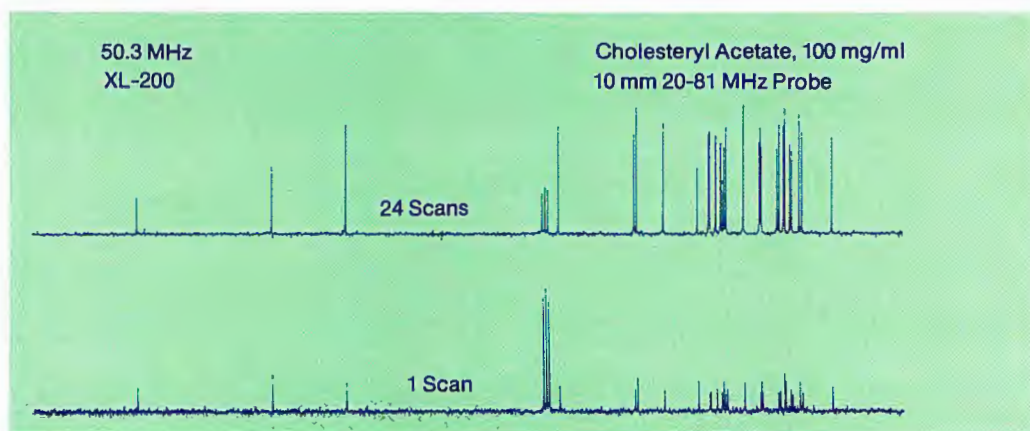
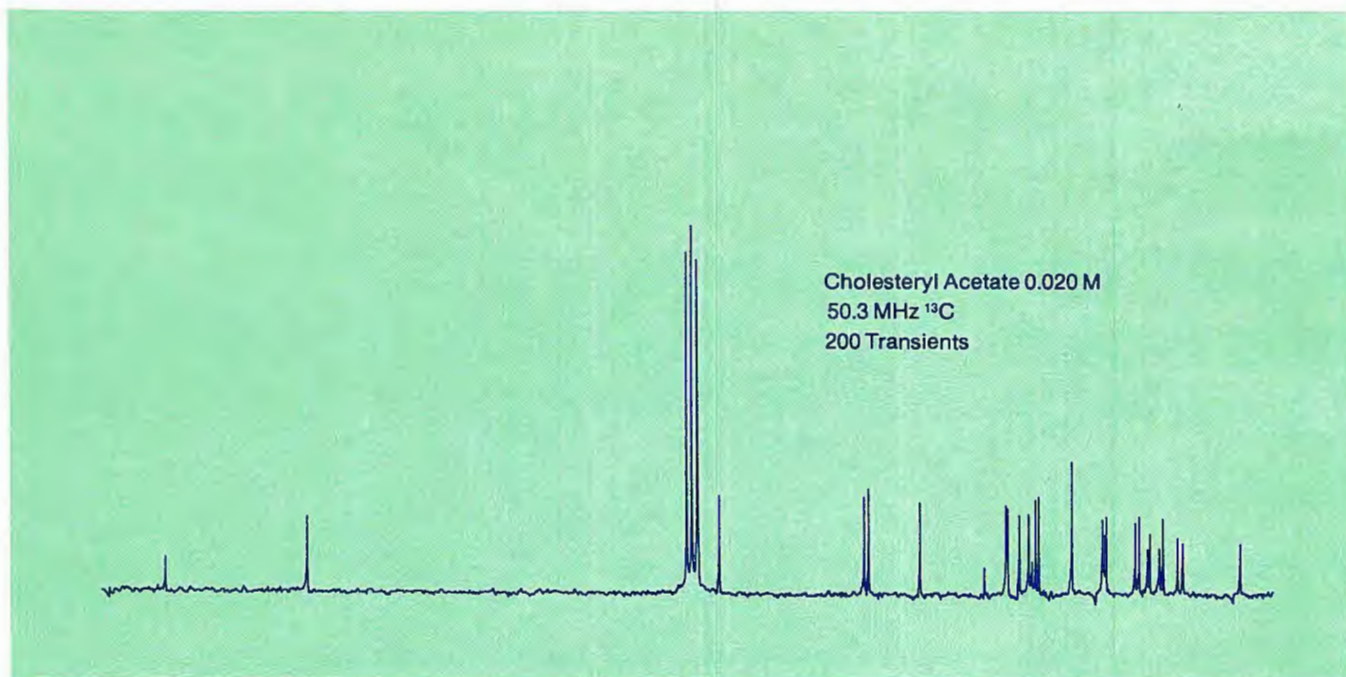*^{13}C Sensitivity Test:* Cholesteryl acetate, 100 mg/ml, 10 mm broadband probe. Transients accumulated using 90° pulses every 2.28 seconds with 0.5 Hz line-broadening.

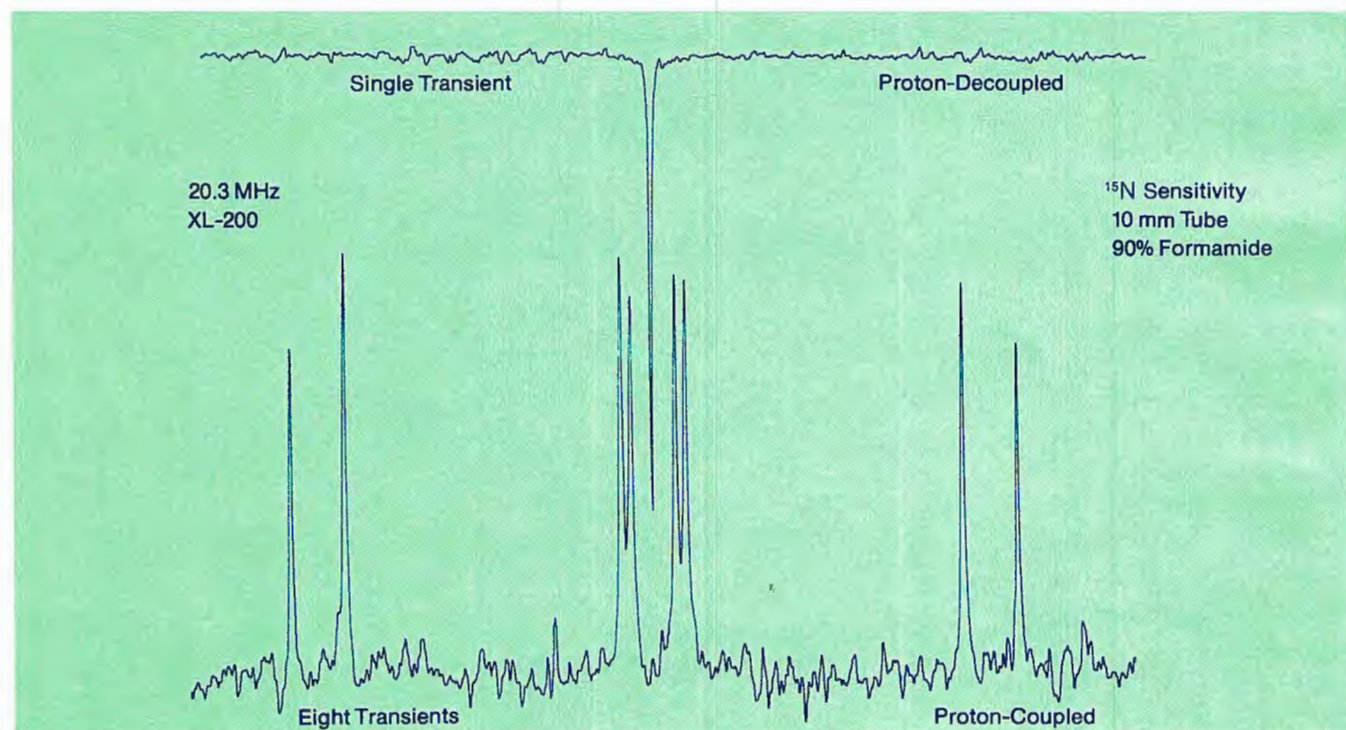*Additional spectra appear on the following page*

Cholesteryl Acetate 0.020 M
50.3 MHz ^{13}C
200 Transients

^{13}C Sensitivity Test: *0.02 molar cholesteryl acetate in a 16 mm tube, 200 transients.*

Single Transient

Proton-Decoupled

20.3 MHz
XL-200

^{15}N Sensitivity
10 mm Tube
90% Formamide

Eight Transients

Proton-Coupled

^{15}N Sensitivity Test: *90% Formamide in dmso-d$_6$, 10 mm 20-81 MHz broadband probe. Upper trace: single-transient (with NOE) proton-decoupled. Lower trace: eight transients, coupled (with NOE) 8-second acquisition time, 20-second delay time.*

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DEPARTMENT OF CHEMISTRY   DAVIS, CALIFORNIA 95616

July 24, 1981

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

Field Strength Effects on Dipolar Shifts

Dear Barry:

My apologies for the need for the many reminders. I trust this will rein-
state our subscription!

It is now recognized that a slight ordering of the average orientation can
be imposed on a molecule tumbling in solution, due to the interaction of molec-
ular magnetic anisotropy and an external magnetic field. This field dependent
ordering has been detected in ^2H NMR of aromatic (1) and paramagnetic (2) com-
pounds, where this partial ordering causes a splitting in the quadrupolar
nucleus' signal. Less well recognized is the fact that the paramagnetic dipolar
shift (3) should also be dependent on the rotational averages in solution, which
will depend on field strength. Hence dipolar shifts are, in principle, neces-
sarily field dependent. Analysis of the dipolar shift equation, replacing
isotropic trigonometric averages with averages under partial ordering, shows the
field dependent contribution to the chemical shift to be additive. This field
dependent shift has the form $\delta(\frac{\chi_{\parallel}+\chi_{\perp}}{2})$, with δ the ordering parameter $\alpha \ \Delta\chi B_o^2/kT$.

The field-dependent shift of cobalt trispyrazolylphenylborate has been
investigated in our laboratory. This compound has a large anisotropy with axial
symmetry (4), but exhibits substantial linewidths. At -35°C, the field dependent
portion of the ortho-H shift is calculated as ~20 Hz upon increasing the field
strength from 4.7 T to 8.4 T. This is a very small effect for a molecule with a
large anisotropy. Although measurements confirm a trend to larger shifts at
higher fields at very low temperatures, the shift uncertainty because of the
great linewidth is always greater than the measured difference. Hence magnetic
field ordering influences on the magnitude of dipolar shifts should be negligible
for all systems studied to date.

Sincerely,

Robert D. Johnson   Gerd N. La Mar

1. J.A.B. Lohman and C. MacLean, Chem. Phys. 35, 769 (1978).
2. P.J. Domaille, J. Am. Chem. Soc. 102, 5392 (1980).
3. J.P. Jesson, in NMR of Paramagnetic Molecules (La Mar, Horrocks and Holm,
   Eds.), Academic Press, 1973, Chapter 1.
4. J.P. Jesson, J. Chem. Phys. 45, 1049 (1966).

UNIVERSITÄT TÜBINGEN

PHYSIKALISCHES INSTITUT

Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den 20.07.1981

Morgenstelle

Telefon (0 70 71) 29 67 14

Professor B.B. Shapiro

Department of Chemistry
Texas A & M University

College Station

Texas 77843

U.S.A.

Some NMR data on the heteronucleus ^{50}V

Dear Dr. Shapiro,

The element vanadium has two isotopes which are accessible to
NMR spectroscopy, ^{50}V and ^{51}V, where the first has a natural
abundance of only 0.24 % and a nuclear spin of $I = 6$.

We have investigated some NMR properties of this low receptive
nucleus (1):
The ratio of the Larmor frequencies of ^{50}V and ^{51}V have been
measured very accurately in a strongly basic aqueous solution
containing VO_4^{3-}. Further we found no primary isotope effect of
magnetic shielding for ^{50}V and ^{51}V in VO_4^{3-} and $VOCl_3$, which
compounds show a chemical shift of $\delta = (-537.15 \pm 0.04) \cdot 10^{-6}$.
For both isotopes T_1 has been measured in $VOCl_3$ at room tem-
perature. From these data, a ratio of the quadrupole moments
$|Q(50) / Q(51)| = 3.99 \pm 0.14$ could be derived if the assumption
is made, that the quadrupolar interaction governs the relaxation
process. This result is in very good agreement with that of
Meisel et al. (-4.03 $\pm$ 0.03) measured by the method of atomic
beam magnetic resonance detected by Laser-induced resonance
fluorescence (2) and also with that of Bleaney et al. (4.07 $\pm$ 0.03)
derived from the quadrupole splitting of the NMR signal in
solid $SmVO_4$ (3).

(1) O. Lutz, W. Messner, K.R. Mohn, P. Kroneck
    Z. Physik A 300, 111 (1981)
(2) W. Ertmer, V. Johann, G. Meisel
    Phys. letters 85B, 319 (1979)
(3) B. Bleaney, A.C. de Oliveira, B.M. Wanklyn, M.R. Wells
    Phys. letters, to be published.

Sincerely yours

O. Lutz   W. Messner, K.R. Mohn   P. Kroneck
                                                 (Konstanz)

Université de Nancy I   LABORATOIRE DE CHIMIE THEORIQUE

Professor B.L. SHAPIRO
TEXAS A & M UNIVERSITY
Department of Chemistry

COLLEGE STATION, Texas 77843

U.S.A.

Suggested title :
Selective polarization transfer

July 23, 1981

Dear Professor Shapiro

Your "final ultimatum" prompts us to describe to your readers a sequence which allows selective polarization transfers *via* J couplings. It consists mainly in exciting a given A nucleus of high gyromagnetic ratio with an appropriate semi selective pulse (or preferably a DANTE sequence (1))followed by a A non selective $\pi/2$ pulse, phase shifted by 90°. A subsequent $\pi/2$ non selective X pulse allows to observe the polarization transfer which only affects the X nucleus (or nuclei) J-coupled to the A nucleus previously excited. A refocussing sequence (2) can be used in order to obtain decoupled spectra.
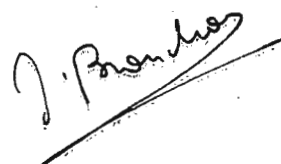
This method represents a way of performing polarization transfer which seems experimentally easier than SPT (3) or INEPT (4) sequences. Also, it can be used for establishing chemical shift correlations between A and X nuclei ; the joined spectra show the maximum of each carbon-13 signal of glutathione (CH and CH_2) as a function of the frequency of the proton selective excitation.

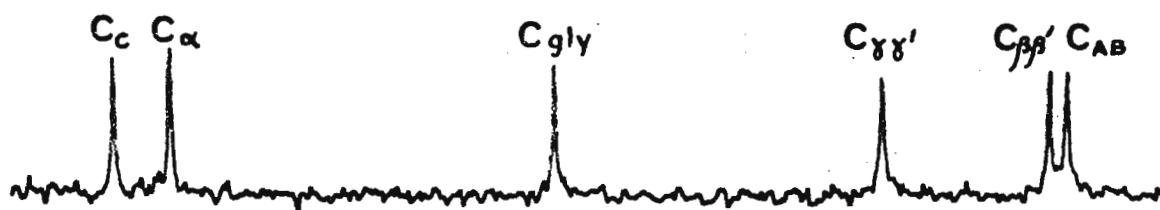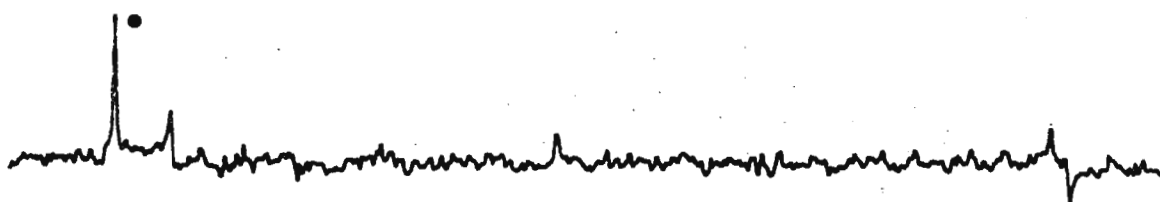Details about this method will be published soon.
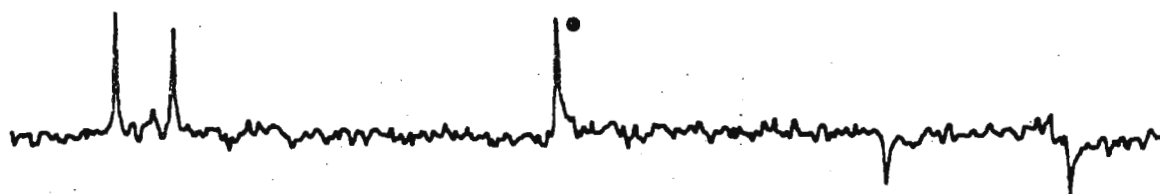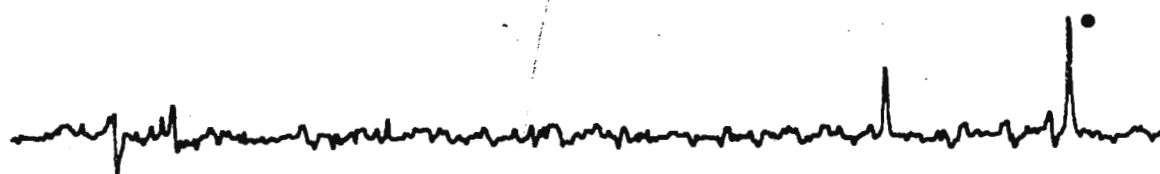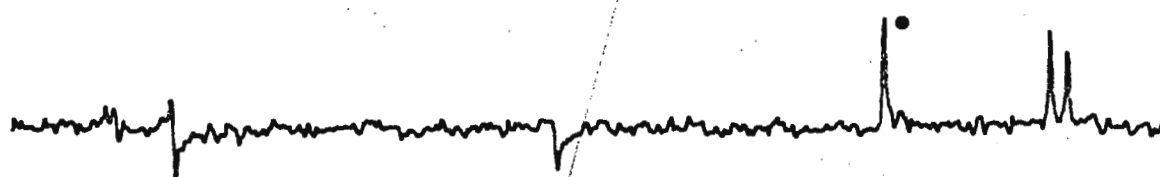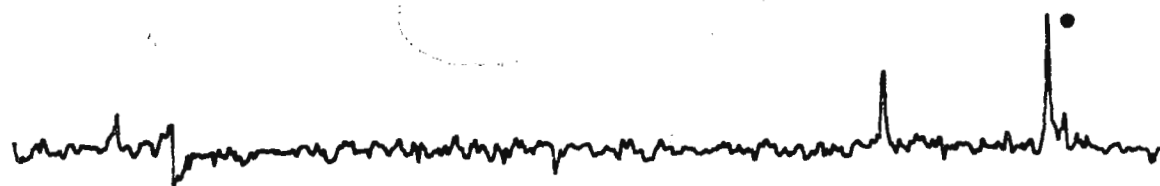
Yours sincerely

D. CANET   J. BRONDEAU

(1) G.A. Morris and R. Freeman, J.Magn.Resonance, 29, 433 (1978)
(2) D.P. Burum and R.R. Ernst, J.Magn.Resonance, 39, 163 (1980)
(3) S. Sørensen, R.S. Hansem and H.J. Jakobsen, J.Magn.Resonance, 14, 243 (1974)
(4) G.A. Morris and R. Freeman, J.Amer.Chem.Soc., 101, 774 (L979)

C_c C_α $\quad\quad\quad\quad\quad$ C_{gly} $\quad\quad\quad\quad\quad$ $C_{\gamma\gamma'}$ $\quad\quad\quad$ $C_{\beta\beta'}$ C_{AB}

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

July 25, 1981

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

Relative Analysis of LIS Data

Dear Barry,

Analysis of molecular geometries using lanthanide shift reagents is normally carried out by using the initial slope of the shift vs. concentration curve as the limiting shift, regardless of the fact that more than one complex may be formed. In a recent review, Inagaki et al. (1) favor the ratio method (where one signal of the substrate is taken as a reference signal) for geometry calculations. Also, Abraham et al. (2) have derived a new agreement factor.

The advantages and disadvantages of the use of a relative analysis are described in detail by Roth and Rewicki (3), and we will only give a short summary here:

(a) If just a 1:1 complex is formed, the relative chemical shifts are strictly linear, provided both the observed and the reference nuclei are part of the same compound.

(b) Given (a), the slope of the shift vs. shift plot will be equal to the ratio of the geometry factors and independent of the total substrate concentration, impurities and the concentration ratio (L/S).

(c) Bifunctional substrates will also give straight lines, but the slopes are not then equal to the geometry-factor quotient.

We report here extension of the relative method when both 1:1 and 1:2 complexes are formed simultaneously. Fig. 1 shows the chemical shifts of two nuclei when both complexes have large complex formation constants ($K_1 = 500$, $K_2 = 400$). The limiting shifts used for this calculation were $\Delta_1^i = 40$, $\Delta_2^i = 15$, $\Delta_1^r = 40$ and $\Delta_2^r = 20$. The initial slope is given by (1)

$$\frac{\delta^i - \delta_0^i}{\delta^r - \delta_0^r} = \frac{\Delta_1^i + 2K_2[S_0]\Delta_2^i}{\Delta_1^r + 2K_2[S_0]\Delta_2^r} \approx \frac{\Delta_2^i}{\Delta_2^r}$$

and the slope at high lanthanide concentrations can be approximated by

$$\frac{\Delta\delta^i}{\Delta\delta^r} \approx \frac{\Delta_1^i - \Delta_2^i}{\Delta_1^r - \Delta_2^r}$$

The nature of the shift-shift curve will depend on the complex formation constants and on the ratios Δ_1^i/Δ_2^i. If the limiting shift ratios are the same for all nuclei in the molecule, or if $\underline{K}_2$ is small, the plot will be linear over the whole concentration range. In this circumstance, the slope will be identical to the ratio of the limiting shifts of the 1:1 complex. This way of treating the data is clearly useful to determine whether more than one complex (with different geometries) is formed.

With all good wishes,

Sincerely yours,

Hans Bauer

Hans Bauer

Jack

John D. Roberts

(1) E. Inagaki and T. Miyazawa, Progr. in NMR Spectr., 14, 111 (1981).
(2) R. J. Abraham, D. J. Chadwick and F. Sancassan, Tetrahedron Lett., 2139 (1981)
(3) K. Roth and D. Rewicki, Kontakte (Merck), 1978 (2), 9.
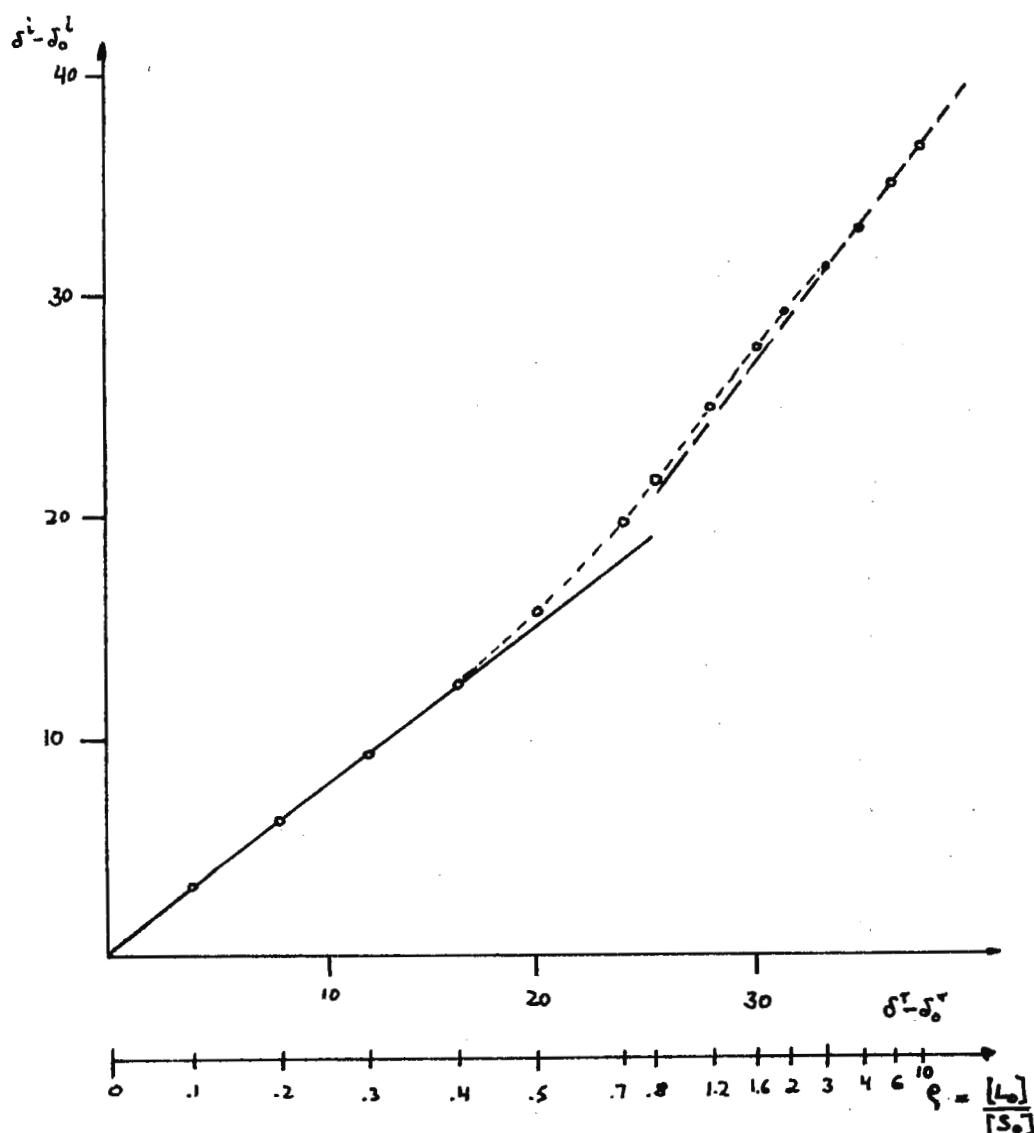
LABORATORIUM VOOR FYSISCHE CHEMIE

Toernooiveld
6525 ED   Nijmegen
Telefoon (080) 55 88 33

FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN, NEDERLAND

Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION, Texas 77843
U.S.A.

Uw kenmerk	Uw brief van	Ons kenmerk	
		U5511/WV/dw	Datum July 31, 1981

Onderwerp
—

Dear Professor Shapiro,

Solid state proton NMR of zeolites

Since the pioneering work of Andrew and coworkers [1], it is well
known that in some cases magic angle spinning alone substantially narrows
NMR lines. A new example of such a case is the proton spectrum of a so-
called H-ZSM zeolite. These zeolites, first synthesized by Mobil, possess
unusual catalytic properties. For instance, methanol can be selectively
converted to high quality gasoline over a ZSM-5 class of catalysts [2,3].
The proton spectrum of the non-spinning sample is shown in figure A.
It is believed that the line is due to the protons in the zeolite hydroxyl
groups and/or water molecules adsorbed by the material. The line is
relatively narrow because the hydroxyl groups are far apart and the water
molecules presumably undergo rapid reorientations. Magic angle spinning
at less than 3 kHz is sufficiently fast to narrow the spectrum considerably
(fig. B). Absorption of ethylene drastically changes the broad line at low
field, showing that this line must be assigned to either the OH groups
at the catalytically active sites and/or water molecules surrounding these
groups [3]. Outgassing the sample for a couple of hours at 250°C decreases
the signal by an order of magnitude but does not change the pattern except
for a slight broadening. This suggests that the signals are due to water
molecules and not to OH groups. The presence of more than one line shows
the existence of several clearly distinct sites.
Spectra B and C are both from H-ZSM-5 samples but which were prepared
from Na-ZSM in two different ways: in sample B Na was exchanged with H
by HCl, in sample C by ammonium nitrate solution. This clearly makes a
difference for the spectra.

Finally, spectrum D shows what happens when NH_3 is absorbed by sample C. The assignment of the lines needs some more work, however, we think the spectra show that with a simple spectrometer (low power proton + magic angle spinner [4]) reasonable resolution in this kind of system can be achieved.

[1] E.R. Andrew, in Progress in Nuclear Magnetic Resonance Spectroscopy, 8, p. 1, eds. J.W. Emsley, J. Feeney, L.H. Sutcliffe.

[2] C.D. Chang and A.J. Silvestri, J. Catalysis, 47 (1977) 249.

[3] E.G. Derouane, P. Dejaifve, J.B. Nagy, J.H.C. van Hooff, B. Spekman, C. Naccache and J.C. Védrine, J. Catalysis, 53 (1978) 40.
J.C. Védrine, A. Auroux, V. Bolis, P. Dejaifve, C. Naccache, P. Wierzchowski, E.G. Derouane, J.B. Nagy, J.-P. Gilson, J.H.C. van Hooff, J.P. van den Berg and J. Wolthuizen, J. Catalysis, 50 (1979) 248.

[4] P.A.S. van Dijk, W. Schut, J.W.M. van Os, E.M. Menger and W.S. Veeman, J. Phys. E : Sci. Instrum. 13 (1980) 1309.
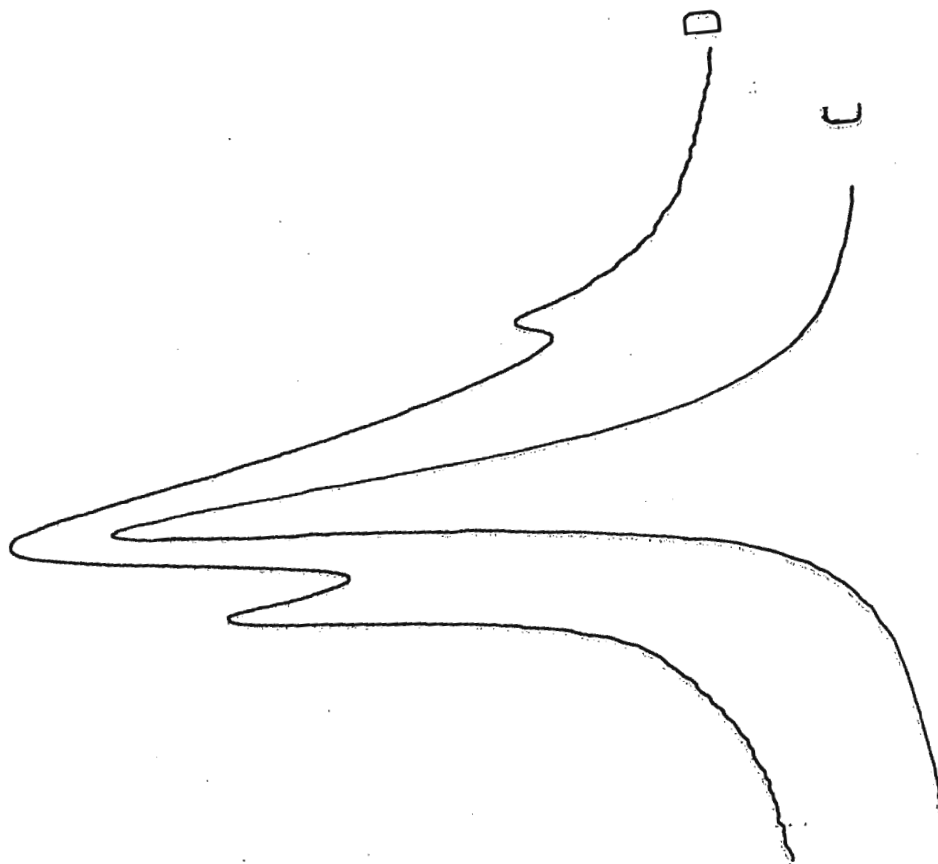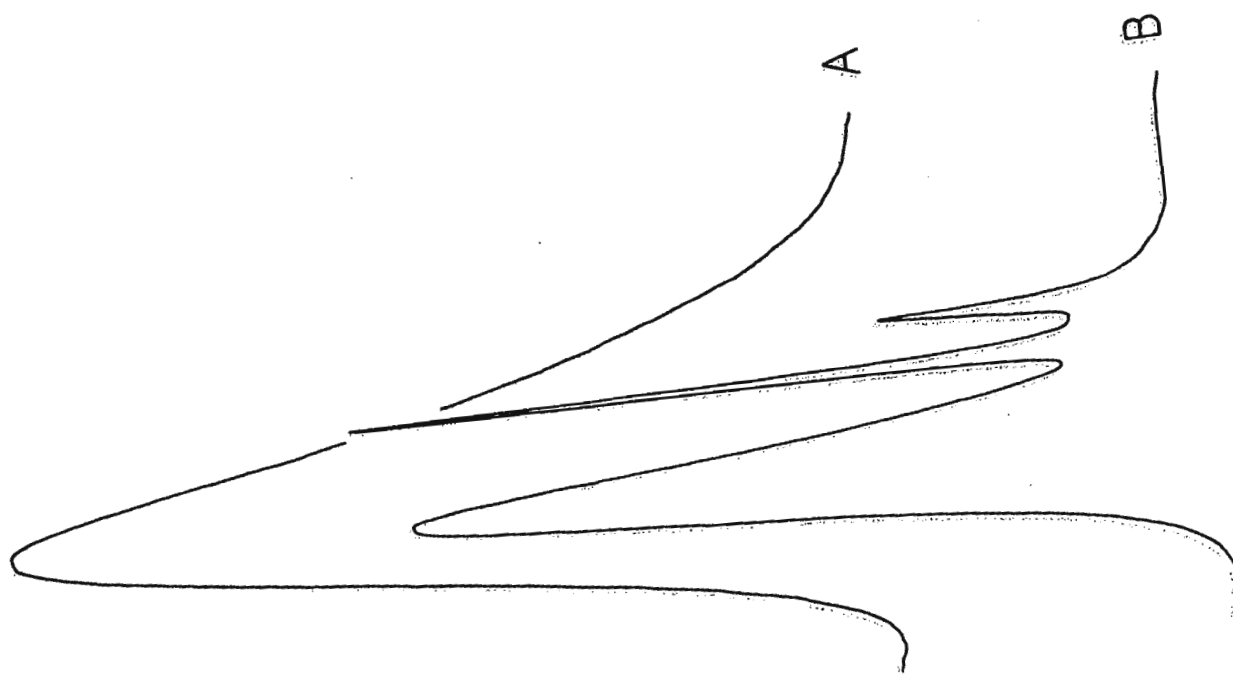
Sincerely yours,

W.S. Veeman   M. Scholle

P.S. Please credit this contribution to the subscription of Prof. E. de Boer.
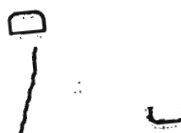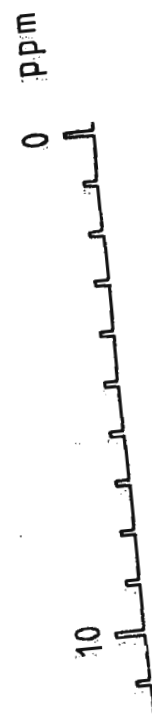
UNIVERSITY OF MINNESOTA
TWIN CITIES

Department of Chemistry
Kolthoff and Smith Halls
207 Pleasant Street S.E.
Minneapolis, Minnesota 55455

June 26, 1981

Barry L. Shapiro
Dept. of Chemistry
Texas A&M university
College Station, TX   77843

Dear Barry:

I have a postdoctoral position available for the study of macromolecular
dynamics using a variety of nuclear magnetic resonance techniques including
NMR dispersion, multinuclear and solid state NMR techniques. This work will
focus on protein systems and protein model systems, and will initially involve
deuterium, proton, and carbon measurements in semisolid systems. We have a
variety of equipment to work with including two multinuclear NMR instruments
operating at 60 MHz for protons on which much of the cross polarization work
will be done, a NMR dispersion instrument which I expect to complete this
August, and a 300 MHz multinuclear Nicolet instrument operating with a wide
bore Oxform magnet. We are also working on alkaline earth metal in - protein
interactions. It will be useful if the candidate has some experience in
either NMR or biochemistry.

Salary is negotiable but is generally tied to NIH postdoc levels. The
initial appointment is for one year, but extension is possible based on
satisfactory performance and continued grant funding. Candidates must be
willing to prepare and submit fellowship applications to NIH and other suit-
able agencies.

The University of Minnesota is an equal opportunity educator and employer
and specifically invites and encourages applications from women and minorities.

Please have interested applicants send me a biographical sketch, list of
publications, summary of research experience and interests and the names of
three references. Thank you in advance for your help in identifying suitable
candidates.

Sincerely,

Robert G. Bryant
Robert G. Bryant
Professor of Chemistry

RGB/mkb

University of East Anglia

Professor R.K. Harris

School of Chemical Sciences
University of East Anglia
Norwich, NR4 7TJ, ENGLAND

Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH

RKH/JH

3rd July, 1981.

Dear Barry,

<u>Vacancy for a Senior Research Associate</u>

This University expects to acquire a Bruker CXP 200 spectrometer, with
facilities for both high-resolution and high-power work in the near future.
In connection with this system there is a vacancy for a post-doctoral Senior
Research Associate (SRA) for three years as from 1.10.81. or thereabouts.
The position will involve day-to-day responsibility for the CXP 200, with a small
amount of service work for organic and inorganic chemists, but the major
involvement will be with two research projects:-

1. The development and application of high-resolution ^{1}H (and ^{19}F) NMR of
   solids, using multiple-pulse (WAHUHA etc.) techniques with magic-angle
   rotation (MAR).

2. Multinuclear studies of quadrupolar nuclei in solution, with the emphasis
   on obtaining accurate representations of broad lines.   Transition metals
   such as ^{59}Co and ^{63}Cu, together with ^{17}O and ^{33}S, are of particular interest.

The first project involves Dr. Ken Packer and me jointly, and the SRA would have
access to our home-built cross-polarization/MAR spectrometer for high-resolution
^{13}C studies on solids, as well as use of the CXP 200 for similar work on ^{29}Si and
^{31}P.   The School also has, inter alia, a Varian XL 100 and two JEOL FX 100
spectrometers.

Salary will depend to some extent on experience but should commence at
ca.£6000 p.a., with increments each August.   Suitably qualified applicants who
wish to spend three years (working hard) in the delightful historic environment
of Norwich should write to me, sending a curriculum vitae, as soon as possible.

With best wishes,

Yours sincerely,

Robin

University of Cincinnati

Cincinnati, Ohio 45221
(513) 475-2263

DEPARTMENT OF CHEMISTRY

July 21, 1981

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

Dear Professor Shapiro:

The Chemistry Department of the University of Cincinnati has an immediate opening for an Instrumentation Specialist to manage the Departmental NMR facilities. Responsibilities for this position include maintenance, operation and supervision of several spectrometers, training of student operators, and running of samples for infrequent users.

A Ph.D. level person is preferred, but full consideration will be given to anyone with sufficient knowledge and experience. Knowledge of electronics and some experience in NMR is essential (we can provide more extensive NMR training). The annual salary range is on the order of $18-22,000; salary will be commensurate with qualifications and experience.

Our NMR equipment will shortly include a high field (250-300 MHz) instrument (to be purchased). Existing equipment includes a 90/260 MHz homebuilt instrument equipped for high resolution solids work as well as for liquids, two Varian HA-100 spectrometers (only one is now in operation; the other is to be converted to FT), and a Varian T60 spectrometer.

The Department has 28 full time faculty members, two visiting professors, and about six postdoctoral and 120 graduate students. Other professional support people include a Mass Spectrometer Specialist, and an Electronics Specialist. One faculty member acts as a half-time computer specialist. The facilities of an electronics shop, as well as special high frequency test equipment specifically for the NMR's, are available to the NMR Specialist.

Direct and active participation of the NMR Specialist in research programs is encouraged. The University of Cincinnati is an Equal Opportunity/Affirmative Action employer, and especially encourages applications from minority and female candidates.

Applicants should submit vitae and arrange for three letters of reference to be sent to me at the above address.

Sincerely,

Jerome L. Ackerman
Assistant Professor
 of Chemistry

js

SYRACUSE UNIVERSITY

DEPARTMENT OF CHEMISTRY | 108 BOWNE HALL | SYRACUSE, NEW YORK 13210

TELEPHONE 315/423-2925

August 3, 1981

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

"NEW NIH RESOURCE FOR MULTI-NUCLEI NMR AND (SPECTRAL) DATA PROCESSING" ☐ ☐ ☐

Dear Barry:

I have just received word from NIH that our proposal to set up a new Resource for Multi-Nuclei NMR and Data Processing will be funded, starting this month. This new Resource will specialize in two areas:

1 - High sensitivity ^{13}C, ^{15}N, ^{31}P, and multi-nuclei NMR studies of complex biomolecules.

2 - New laboratory data processing techniques including remote user access to powerful spectral data processing capabilities at the Resource. This will include inexpensive hardware graphics units available on loan from or purchased through our facility.
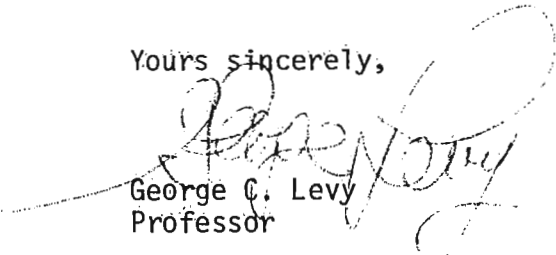
To develop and provide these services the NIH is funding essentially half the costs of a new Bruker WM-360 widebore 8.5 Tesla multi-nuclei NMR and a powerful 32-bit computer with microcomputers and other peripherals. The laboratory will also operate a 3.5 Tesla widebore NMR spectrometer, and, next year, a 5.8 Tesla narrowbore system.

Initial NMR services from the Resource are expected to be phased in early this fall, with new data processing capabilities coming on-line this winter. The Resource will have in-coming WATS lines to the large computer, allowing inexpensive dial-up for all users.

➤Please consider this an invitation to learn more about the new Resource and its capabilities, services, etc. Write to me at the above address and you will be placed on our (computerized - sorry) mailing list and receive further bulletins, information, etc.

➤Appended to this letter is a sheet describing staff positions open at the new Resource. I would appreciate very much if you would alert promising candidates to these openings and suggest that they write to me as soon as possible.

With my best personal regards,

Yours sincerely,

George C. Levy
Professor

GCL:sd

SYRACUSE UNIVERSITY

DEPARTMENT OF CHEMISTRY | 108 BOWNE HALL | SYRACUSE, NEW YORK 13210

TELEPHONE 315/423-2925

NIH RESOURCE FOR MULTI-NUCLEI NMR AND DATA PROCESSING

Operations Staff

Postdoctoral-NMR

In addition to basic research activities this person will run service and collaborative samples for users, instruct new operators, and generally supervise spectrometer operations (Salary Level, $16,000).

Postdoctoral-Biochemist

This person will design biochemical aspects of user collaborative projects and be involved in core and collaborative studies as a biochemical consultant. Additionally this person will operate spectrometers (ca. 30% time). (Salary Level, $15,000).

Computer Programmer

This person will have primary responsibilities for Resource Software development, including primarily higher level language (FORTRAN) and assembly and systems programming. Some time will be spent helping users adapt programs to the Resource Computer. This person will also supervise part-time and student programmers. (Salary Level, $21,000).

Instrument Designer

Responsibilities include design and construction of nmr spectrometer r.f. subsystems including versatile probes for high sensitivity nmr and, with the Operations Director, maintenance of Resource instrumentation. This position is fully funded by the University. The holder will work up to one-third time on Departmental instrumentation projects, in conjunction with a full-time electronics technician (Instrument Designer Salary Level, $25,000).

Operations Director (position filled: Dr. Charles Dumoulin)

Dr. Dumoulin has responsibility for overall Resource Operations, including r.f. instrumentation, computer hardware and software design, scheduling, and general administration.

Federation
of
Analytical Chemistry and Spectroscopy Societies

FACSS

Address reply to: Mary A. Kaiser
E. I. du Pont de Nemours & Co.
Experimental Station
CR&D Dept. E228/200
Wilmington, DE 19898

July 28, 1981

Dr. Bernard Shapiro
Department of Chemistry
Texas A&M University NMR Newsletter
College Station, TX 77840

Dear Dr. Shapiro:

Please include information on the NMR symposia which
will be presented at the FACSS-VIII meeting in Philadelphia, PA,
on September 20-25, 1981.

- Sept. 23, Multinuclear Cross Polarization Magic-Angle
  Spinning Solid State NMR I, II, arranged
  by Phil Pfeffer, USDA.

- Sept. 24, Novel Applications of NMR: NMR Studies of
  Surfaces, Coals, Films and Hydrides;
  Studies of Polymers, arranged by Cecil
  Dybowski, University of Delaware.

Sincerely yours,

Mary A. Kaiser
Program Chairman, FACSS-VIII

MAK/bmw
Encl.