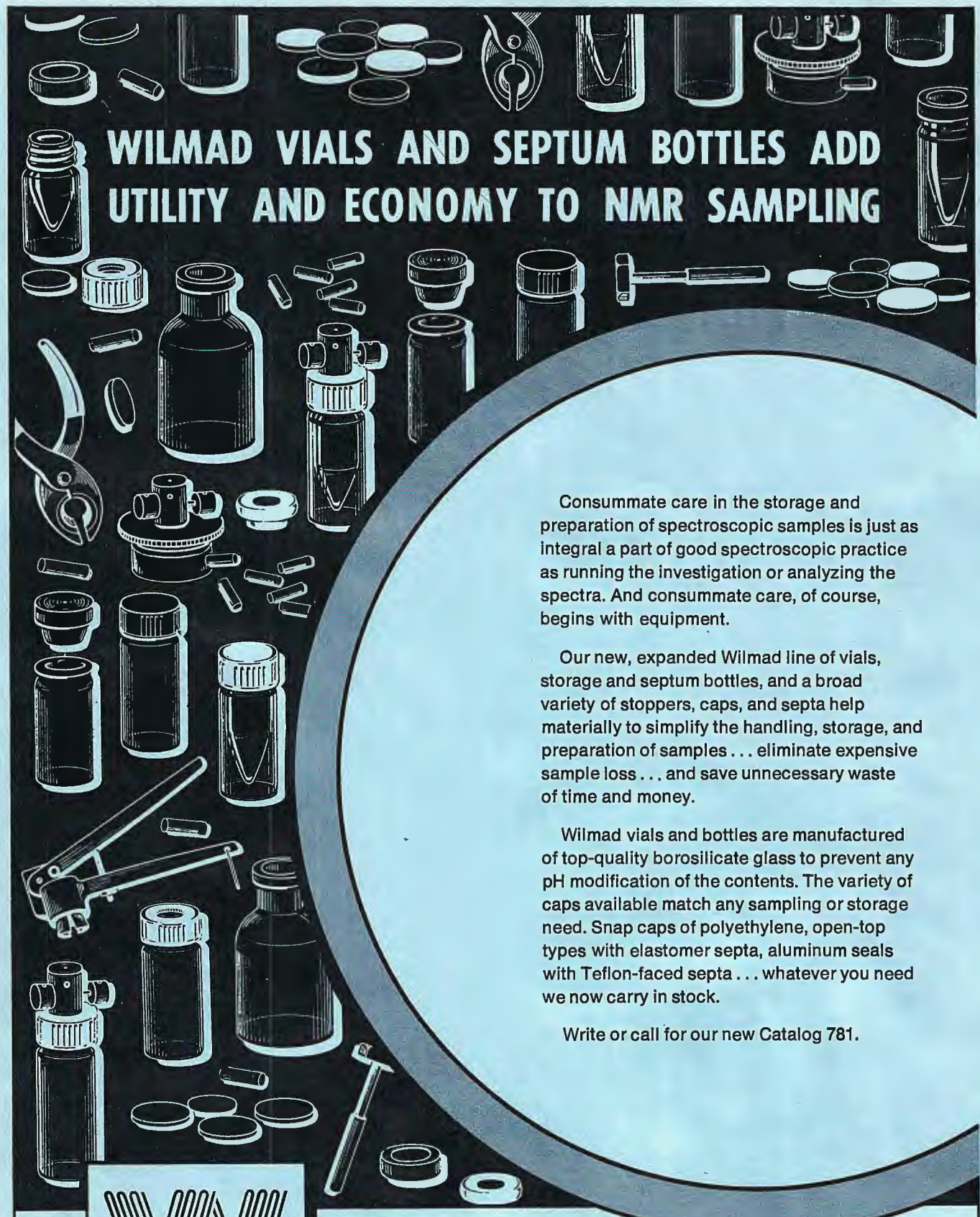
Texas A & M University N-M-R Newsletter

No. 249

June, 1979



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DEADLINE DATES: No. 250: 2 July 1979
No. 251: 6 August 1979

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.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 249

UNIVERSITY OF CALIFORNIA, SAN DIEGO

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30 May 1979

ROBERT W. VAUGHAN: IN MEMORIAM

Robert W. Vaughan was returning to Pasadena, California on May 25, 1979 on American Airlines flight 191. His life was lost in the tragic disaster.

Bob will be especially missed by his friends in the solid state nmr community. His boundless optimism, keen insights, and monumental productivity provided inspiration to all, and will continue to do so in years to come.

For ourselves, and others who were privileged to know Bob well, the loss is doubly tragic. He was one of the finest human beings we have ever known.

We wish to express our deepest sympathy to Bob's wife Sharon and daughter Tena, and to Bob's students, past and present.

Bob & Gritze

Robert L. and Regitze R. Vold

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

April 13, 1979

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

Re: EPR Symposia

Dear Barry:

Enclosed is the preliminary program for the EPR Symposium to be held in conjunction with the 21st Annual Rocky Mountain Conference on Analytical Chemistry at the Denver Convention Complex, Denver, Colorado from July 30 to August 1, 1979.

Both Gareth and I are pleased with the response we have received to our invitations. There are over 100 papers dealing with the applications of magnetic resonances to chemistry and biology and we extend an invitation to all readers of the Newsletter to attend the Conference. Additional information about the Conference can be obtained from either Dr. Gareth Eaton or me.

Dr. Gareth R. Eaton
EPR Symposium Chairman
Department of Chemistry
University of Denver
Denver, Colorado 80280
(303) 753-2507

Dr. Daniel A. Netzel
NMR Symposium Chairman
Laramie Energy Technology Center
P. O. Box 3395, Univ. Station
Laramie, Wyoming 82071
(307) 721-2370

Sincerely,

Daniel A. Netzel
NMR Symposium Chairman

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

G. R. Eaton, Chairman

SESSION I

Monday Morning, July 30

Introductory Remarks - G. R. Eaton

Title to be announced, E. G. Janzen.

ESR DETECTION OF RADICALS PRODUCED IN THE REACTION OF THIOLS WITH NO CONTAINING COMPOUNDS, G. C. Yang and A. Joshi.

INVESTIGATIONS ON THE MUTAGENICITY AND ELECTRON SPIN RESONANCE SPECTRA OF NITROSOFLUORENE-LIPID ADDUCTS, R. Sridhar, M. J. Hampton, J. E. Steward, and R. A. Floyd.

CARCINOGEN AND PARAMAGNETISM OF HEPATIC CELL ORGANELLA, Y. Sakagishi, M. Sonoda, and T. Komoda.

EPR STUDIES ON HUMAN SERUM, E. Kimoto, F. Movishige, T. Takuda, M. Kohno, and T. Yamaguchi.

ESR STUDIES OF TRAPPED ELECTRONS, H. C. Box.

Monday Afternoon, July 30

EPR SPECTRA OF THE LIVERS IN DISEASED STATES, F. Morishige, H. Tanaka, E. Kimoto, and H. Kawasaki.

SPIN-TRAPPING AND LIQUID CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF UNSTABLE RADICALS OF AMINO ACIDS, PEPTIDES, AND NUCLEOTIDES, H. Hatano, K. Makino, N. Suzuki, A. Moryla, and S. Roknshika.

ESR STUDIES OF ION PAIR FORMATION WITH THE TRIPHENYLENE ANION RADICAL, M. T. Jones and R. Ahmed.

Title to be announced, J. Herring.

QUANTITATIVE DETERMINATION OF NITROSYL-HEMOGLOBIN IN THE BLOOD BY EPR, T. Nakajima.

HEME-SPIN-LABELING OF HEMOPROTEINS, T. Asakura and P. W. Lau.

ESR AND VISIBLE ABSORPTION SPECTROSCOPY OF HORSE RADISH PEROXIDASE, FREE AND BOUND TO DONOR SUBSTRATE AT CRYOGENIC TEMPERATURES, M. M. Maltempo.

THE O_2-BINDING SITE OF CYTOCHROME WITH OXIDASE AS REVEALED BY EPR SPECTROSCOPY, S. Chan.

EFFECT OF POLYMER MATRIX ON THE ROTATIONAL MOTION OF SPIN-LABELED PROTOHEMIN COORDINATED TO POLYMER-CHAIN, S. Hata and E. Tsuchida.

ESR OF COPPER COMPLEXES OF SOME DRUG AND BIOMOLECULES, G. Rakhit.

SESSION II

Monday Morning, July 30

EPR OF TRANSITION METAL NITROSYLS, K. F. Preston.

EPR STUDIES OF DEUTERATED NITROXIDE SPIN LABELS, A. Mathew, W. R. Hedrick, and J. D. Zimbrick.

LONG RANGE PROTON HYPERFINE COUPLING IN A NITROXYL RADICAL, M. J. Heinig, G. R. Eaton, and S. S. Eaton.

SPIN ECHO AND CW MEASUREMENTS OF ELECTRON SPIN RELAXATION OF NITROXIDES IN SOLUTION, R. N. Schwartz and M. K. Bowman.

STUDY OF THE PRODUCTS OF COAL HYDROGENATION AND DEUTERATION BY EPR, I. B. Goldberg, H. R. Crowe, J. J. Ratto, L. Heredy, and R. Skowronski.

EPR STUDIES OF OIL SHALE, SHALE OIL, AND SPENT SHALE, B. L. Sidwell, L. E. McKinney, M. F. Bozeman, P. C. Egbujor, G. R. Eaton, S. S. Eaton, and D. A. Netzel.

ESR STUDIES OF HEAVY METAL ENVIRONMENTAL POLLUTANTS, J.K.S. Wan.

Monday Afternoon, July 30

ESR OF F-CENTER IN $BaTiO_3$, M. Tsukioka.

EPR OF E^1 CENTERS IN ULTRAPURE FUZED SILICA, M. Schwab and M. J. Moran.

EPR IN THE STUDY OF RADIATION DAMAGE IN SILICATE GLASSES, M. Schwab and M. J. Moran.

TRAPPING REGIONS FOR ALLYL RADICALS IN IRRADIATE POLYETHYLENE, T. Fujimura, N. Hayakawa, and I. Kuriyama.

ESR OF PHASE TRANSITIONS IN HYDROGEN-BONDED SOLIDS, N. S. Dalal.

ESR STUDIES OF DIFFUSION IN LIQUIDS, M-K Ahn.

RELAXATION SPECTRA OF POLYMERS OBTAINED FROM ESR AND NMR STUDIES, T. Tanigawa, T. Kitahara, S. Shimada, and H. Kashiwahara.

HOLE CENTERS IN THE ALKALINE EARTH OXIDES, J. E. Wertz.

EPR OF Gd^{3+} IONS IN LANTHANIDE HYDROXIDES, H. A. Buckmaster.

Title to be announced, M. Fastman.

EPR OF ORGANIC COMPOUNDS IN AMBIENT TEMPERATURE MOLTEN SALTS, J. S. Wilkes and L. P. Davis.

ESR INVESTIGATIONS OF THE THERMAL DECOMPOSITION OF ENERGETIC MATERIALS, H. L. Pugh, Jr., L. P. Davis, and J. S. Wilkes.

SESSION III

Tuesday Morning, July 31

SOLVENT POLARITY EFFECTS ON CORRELATION TIMES FOR NITROXIDE SPIN PROBES, J. J. Windle.

BIFUNCTIONAL SPIN LABELS DESIGNED FOR SATURATION TRANSFER EPR STUDIES OF ANISOTROPIC MOTION IN MEMBRANES, B. J. Gaffney, G. L. Willingham, M-W Tse, and A. Mahon.

SPIN-LABELING STUDIES OF LIGNINS, P. Tormala.

DIAGNOSTIC APPLICATIONS OF SPIN ASSAY TECHNIQUES, C.J.C. Hsia.

A STUDY OF RIBOSOMES USING THE SPIN LABEL METHOD, H. Dugas, A. Rodrigues, and N. Brisson.

ROTATIONAL MOTIONS OF MUSCLE PROTEINS STUDIED BY SATURATION TRANSFER EPR, J. C. Seidel.

SATURATION TRANSFER EPR OF VIRUSES, M. A. Hemminga.

Tuesday Afternoon, July 31

ELECTRON SPIN POLARIZATION IN PHOTOSYNTHESIS, O. Adrianowycz, K. W. Kinnally, and J. T. Warden.

THE USE OF A NEW SPIN BROADENING AGENT IN THYLAKOID SUSPENSIONS TO MASK EXTERNAL SPIN LABEL SIGNAL, D. M. Nesbitt and S. P. Berg.

APPLICATION OF EPR FOR THE ANALYSIS OF SPATIAL ORGANIZATION OF REDOX COMPONENTS IN MITOCHONDRIAL MEMBRANES, T. Ohnishi.

ELECTRON SPIN RELAXATION IN BACTERIAL PHOTOSYNTHETIC SYSTEMS, M. K. Bowman, J. R. Norris, and C. A. Wraight.

THE PRIMARY EVENTS IN GREEN PLANT PHOTOSYNTHESIS - STUDIED BY TIME-RESOLVED ELECTRON SPIN ECHO SPECTROSCOPY, M. C. Thurnauer and J. R. Norris.

INTERCELLULAR VISCOSITY OF LYMPHOCYTES DETERMINED BY AN ^{15}N SPIN LABEL PROBE, W. R. Hedrick, A. Mathew, and J. D. Zimbrick.

TRANSLATIONAL MOTION OF THE SPIN LABEL TEMPAMINE IN THE INTERNAL AQUEOUS COMPARTMENT OF SPINACH THYLAKOIDS AND RED BLOOD CELLS, P. Morse.

METAL-NITROXYL INTERACTIONS, P. M. Boymel, D. L. DuBois, K. More, G. R. Eaton, S. S. Eaton, and D. J. Greenslade.

ESR STUDIES OF DIMERIC COPPER COMPLEXES OF ADENINE, D. Sonnenfroh and R. Kreilick.

ESR DETECTION OF ELECTROLYTICALLY GENERATED UNSTABLE RADICALS, R. D. Allendoerfer and J. B. Carroll.

PHOTOASSISTED ELECTROLYSIS AND THE EPR CONNECTION, J. F. Houlihan and D. P. Madacsi.

SESSION IV

Wednesday Morning, August 1

EPR POSSIBILITIES AT S. BAND (2-4 GHz), J. R. Pilbrow.

ENDOR INVESTIGATIONS IN THE NEMATIC AND SMECTIC PHASE OF LIQUID CRYSTALS, H. Kurveck and B. Kirste.

FIELD THEORETICAL TREATMENT OF THE PROTON hfa IN THE AROMATIC ION RADICALS, S. Aono.

ENDOR ON VANADYL COMPLEXES IN FROZEN SOLUTION, H. Van Willigen.

TWO-WAY EPR CAVITY AND STARK EFFECT IN NO, I. Suzuki.

NANOSECOND TIME-RESOLVED EPR SPECTROSCOPY, A. D. Trifunac.

ENDOR STUDIES OF RADICALS ADSORBED ON SOLIDS, R. B. Clarkson.

Wednesday Afternoon, August 1

COMPUTER GRAPHICS AND THE INTERPRETATION OF EPR DATA, C. E. Klopfenstein.

A DIGITAL ACQUISITION SYSTEM FOR AN ESR SPECTROMETER: APPLICATION TO THE GENERATION OF DISPERSION ABSORPTION PLOTS, F. C. Herring and P. S. Phillips.

COMPUTER SIMULATION OF EPR POWDER SPECTRA, R. L. Belford and M. J. Nilges.

ANALYSIS OF ELECTRONIC REARRANGEMENTS BY EPR, J. H. Ammeter.

DIGITIZED EPR AND ST-EPR SYSTEMS, T. Watanabe, T. Sasaki, K. Sawatari, and S. Fujiwara.

AN EFFICIENT APPROACH TO SIMULATION OF EPR SPECTRA OF HIGH SPIN Fe^{3+} IN RHOMBIC LIGAND FIELDS, M. I. Scullane, L. K. White, and N. D. Chasteen.

CALCULATION OF POWDER ESR SPECTRA WITH HYPERFINE AND QUADRUPOLAR INTERACTIONS, A. Lund.

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Professor Barry Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843
U S A

6 MAR 79

Dear Professor Shapiro

Proton FID behaviour for polymeric fibres

In a previous contribution from our group[1] we described how we were able to isolate the proton T_1 behaviour for 'amorphous' chain segments in wet Nylon 6,6 fibres using a Pulse Gated Integrator attached to our Bruker 322S spectrometer and hence study the influence of penetrating D_2O molecules and Mn^{2+} ions on relaxation.

Since then we have investigated a variety of polymeric fibres; nylon, terylene, orlon, rayons and cottons and have used the proton F.I.D. components to obtain other relaxation data which we could relate to the mobility properties of the amorphous chain segments in these semi-crystalline systems.

The common feature observed in most of the systems studied was the appearance of a longer T_2 component (practically Lorentzian) in the FID's at some temperature depending upon the relative humidity - we have attributed this to the mobilization of some amorphous chain segments above their glass transition temperature, Tg. In wet fibres onset of this motion is encouraged by local plasticization of these segments or groups due to penetration of water molecules and the 'mobile' T_2 component occurs at a lower temperature. Examples of FID's for some fibre systems are given in the FIGURE.

The result which interests us most at this stage is the striking difference in behaviour observed between the synthetic and natural versions of the cellulosic fibres, i.e. rayon and cotton. Both types of fibre are generally considered to have a semi-crystalline morphology, cotton being more crystalline than rayon, yet the FID data demonstrate a surprising absence of 'amorphous-type' T_2 behaviour in the cotton fibres, the FID resembling that of a completely crystalline powder sample.

In future experiments we hope to use FID and T_1 data in conjunction with paramagnetic ions as probes to explore more fully the nature of the accessible polymer chain segments in cellulosic fibres.

I hope this contribution serves as a reminder that good old-fashioned proton T_1 and FID experiments are alive and well and still have a lot to offer in studies of complex solid materials.

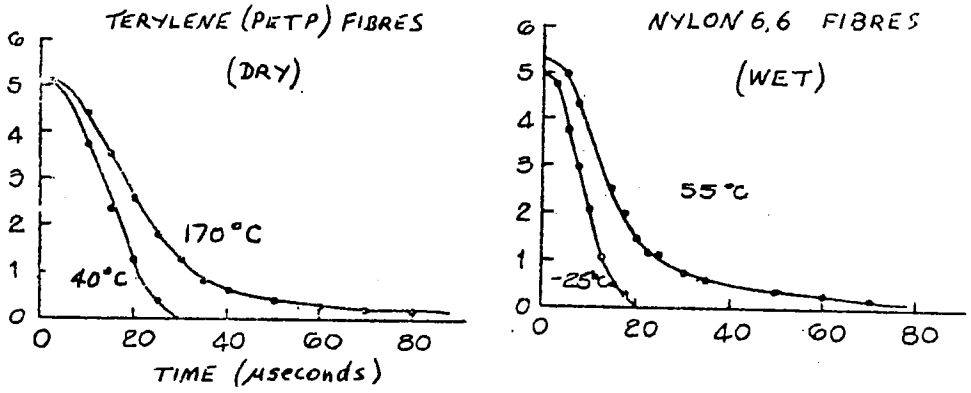
Yours sincerely

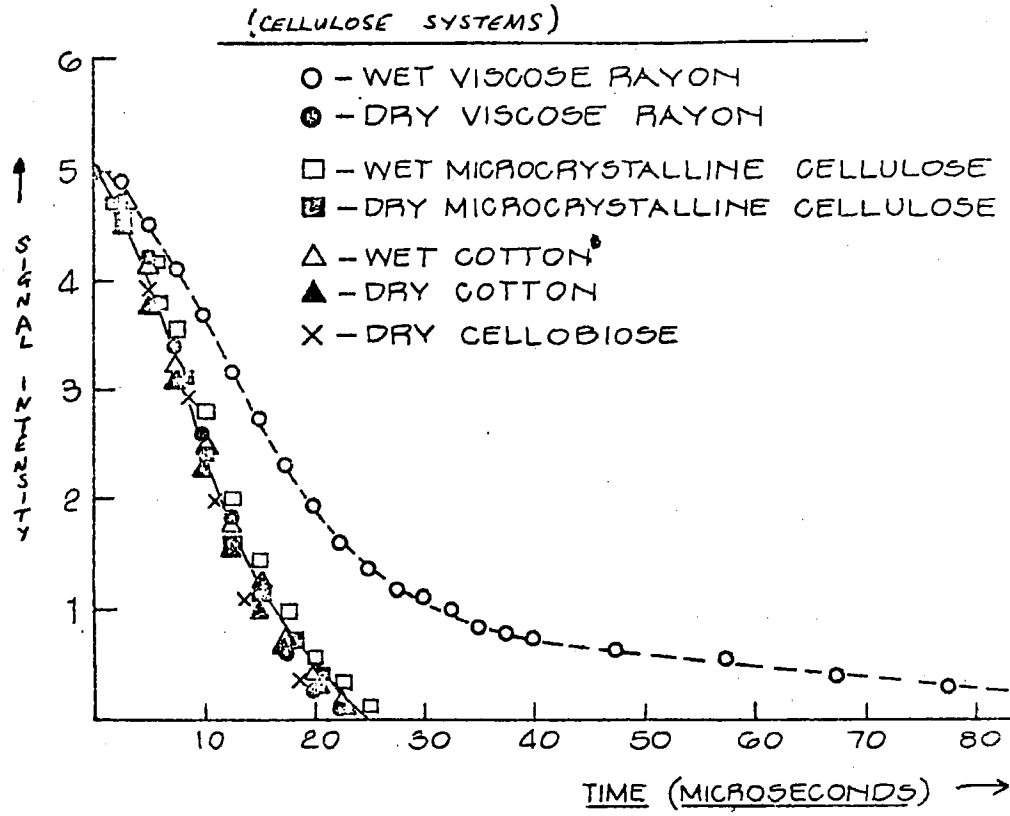
EDWARD G. SMITH

References

i. E.G. Smith. T.A.M.U. N.M.R Newsletter 1976, March, 12

FIGURE 1 : FREE INDUCTION DECAYS FOR POLYMERIC FIBRES.





IBM

RESEARCH LABORATORY

International Business Machines Corporation
5600 Cottle Road
San Jose, California 95193

May 2, 1979

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

Dear Barry:

We have been using magic angle spinning with variable temperature capability (VT-MAS) to obtain highly resolved ^{13}C NMR spectra of solids from -196° to 100°C for the last eighteen months.[1] The results were obtained in a routine manner using a newly developed apparatus.[2] Our prime motivation in VT-MAS experiments has been chemical applications. The initial work has been on frozen liquids,[3] the direct observation of chemical exchange processes in the solid state,[4] and carbonium ions.[5] Since the Colorado meeting, we have obtained data on several other carbonium ion systems in a continuing collaboration with Colin Fyfe at Guelph University.[6] A brief discussion of these results was given at the 20th ENC at Asilomar, California. The spectrum of one such ion is shown in the attached figure. To date, our findings indicate that spectral resolution is adequate for structural assignments, and more importantly, that no large chemical shifts are induced by "solid-state" effects. We feel that the results demonstrate the potential of VT-MAS spectroscopy as a new approach to the study of reactive intermediates in the solid state.

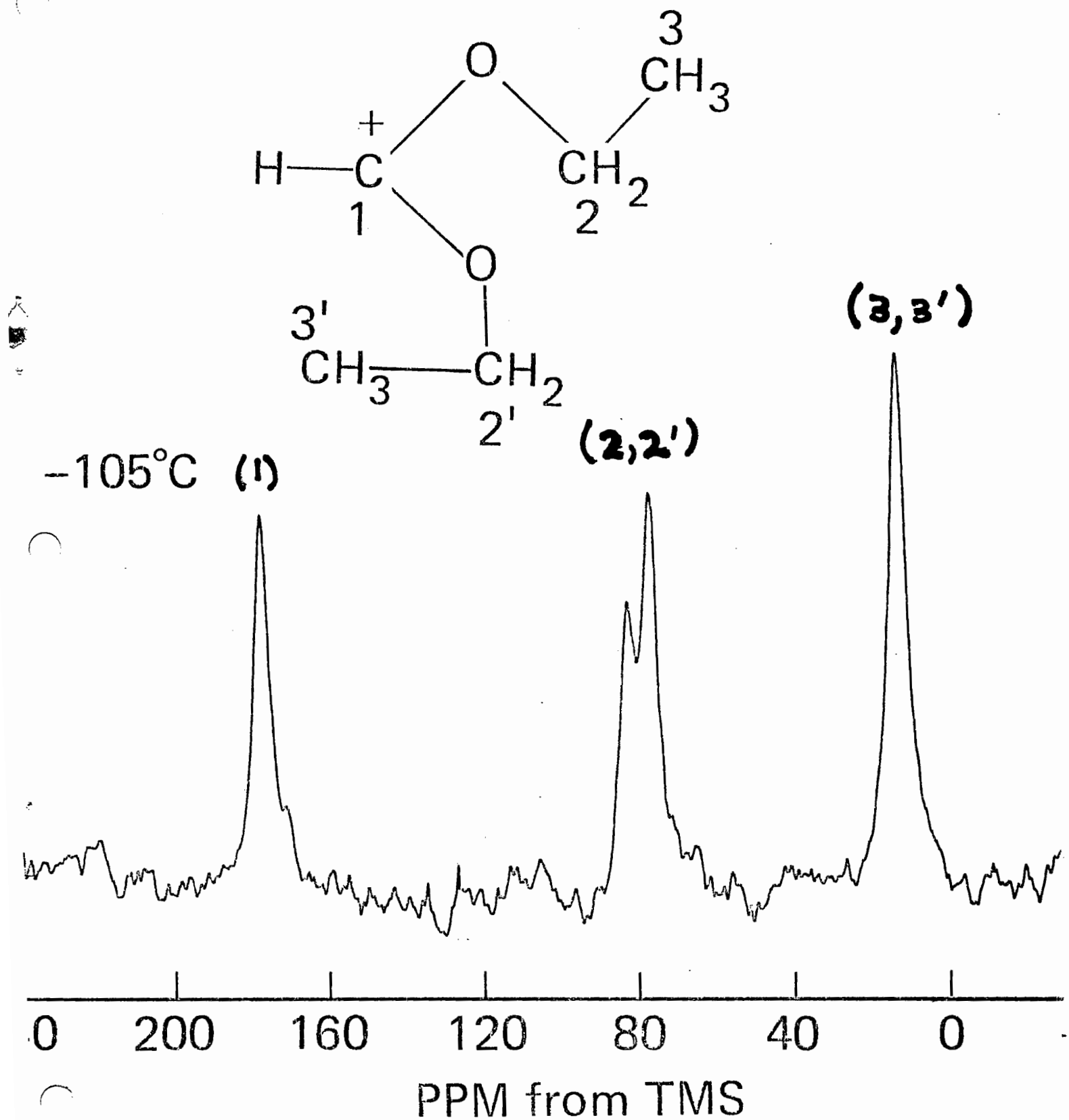
Sincerely yours,

J. R. Lyerla

C. S. Yannoni

JRL:CSY/bwm

1. See TAMU-NMR Newsletter of July 1978 for the spectrum of acetic acid at -196°C.
2. J. Mag. Res. (to be published in October 1979).
3. J. Am. Chem. Soc. 100, 5635 (1978).
4. J. Am. Chem. Soc. 101, 1351 (1979).
5. 20th Rocky Mountain Analytical Conference at Denver, Colorado, in August 1978.
6. Submitted to J. Am. Chem. Soc.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(3,3')
(2,2')
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200
160
120
80
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PPM from TMS

BRUKER

BRUKER announces a new landmark
in low-cost high-resolution
superconducting NMR spectrometers with

^{1}H frequency of 250 MHz

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

Dear Professor Shapiro

Digitization and Dynamic Range

We have recently been evaluating the high field N.M.R. market and have chosen a broad-banded Bruker WH-360 with a wide-bore solenoid, for which we hope to soon place an order.

As we are interested in working in H_2O, the question of the highest dynamic range is vitally important. Current machines usually provide a 12 or 13 bit digitizer as standard and because of the high sensitivity of the cavity-type probes and low noise design amplifiers, the ADC becomes the main limiter of dynamic range.

Bruker have cooperated in our testing by incorporating a 16 bit ADC into a WH-400 and although the dynamic range on 90% H_2O is not increased by the full four bits, a very valuable factor of X9 is observed. Using this 16 bit ADC it was possible to detect 1.5 ppm of t-butanol in 90% H_2O in a single transient, which because of the different linewidths, is only a dynamic range of 126,000 in the frequency domain. The equivalent spectrum using a 12 bit ADC gave a figure of 14,000. All this applies to a single transient with only a 0.25 Hz line broadening exponential weighting factor, the result being improved by multi-scan signal summation.

Bruker's Aspect 2000 computer used on their FT instruments has a 24 bit word and consequently it is possible to average 256 transients using a 16 bit ADC before overflow. At this stage the dynamic range will have increased to 2,076,000 after about 5-10 minutes accumulation. Is this enough? No? Then it is possible to acquire into double precision on disc (or use a 32 bit acquisition processor) and transform in floating point or double length format. Left shifting the noise out of the least significant bits after accumulation such that the data is normalized to 24 bits can only give a dynamic range in the time domain of 2^{23} or 8,388,608 which is clearly inadequate even though the dynamic range in the frequency domain will in general be much higher!

Yours sincerely

J. C. Lindon

A. G. Ferrige

StonyBrook

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May 4, 1978

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

HOT SPECTROSCOPY: TRITIUM NMR

Dear Barry,

Spring has arrived on Long Island and the grey of winter has been replaced by Nature's full spectrum of colors—including the esthetically pleasing hues of your reminder notices. We would like to remind readers that the Facility for Biomedical NMR on Radioactive Samples is in full operation and we invite prospective users to contact us regarding potential projects. At present there is no charge for non-profit organizations.

Among the many uses of tritium nmr is the ability to analyse the labelling patterns of compounds to be used in tracer studies. A recent example of this is the analysis of the compound N (methyl ethyl)-azobenzene, the structure of which is shown in the Figure. While we already knew that the sample was tritiated on the unsubstituted ring, it was important to determine the amount, position(s) and multiplicity of labelling. The percent of unlabelled compound in the sample is large, thus conventional proton nmr is of no use. The $^{3}H\{^{1}H\}$ spectrum, however, reproduced in (a), clearly shows two resonances at 8.15 and 7.11 ppm. As no J_{T-T} is observed, it can immediately be concluded that all of the labelled compound is monotritiated. Assignment of the resonances is facilitated by the proton coupled spectrum, (b) which shows the resonance at 8.15 ppm split into a doublet of triplets and the resonance at 7.11 into a triplet of triplets. Based on the above, the resonance at 8.15 ppm, accounting for 73% of the labelled compound, is assigned to the 2´6´ position and the resonance at 7.11 ppm, accounting for 27% of the labelling, to the 4´ position.

These spectra also suggest the interesting possibility of using tritium nmr as a means to assign coupling constants in the more complex proton spectrum, a problem we are now working on.

We wish to thank Dr. Bill Duncan of Midwest Research Institute for permission to publish this data.

Sincerely,

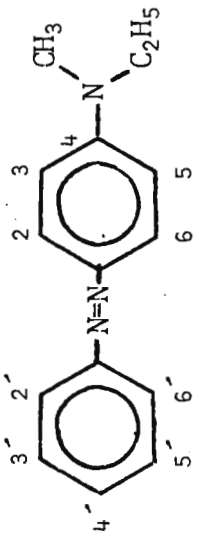
Dave Bailey

David B. Bailey
Facility Manager

Paul

Paul C. Lauterbur
Professor of Chemistry

DBB:rd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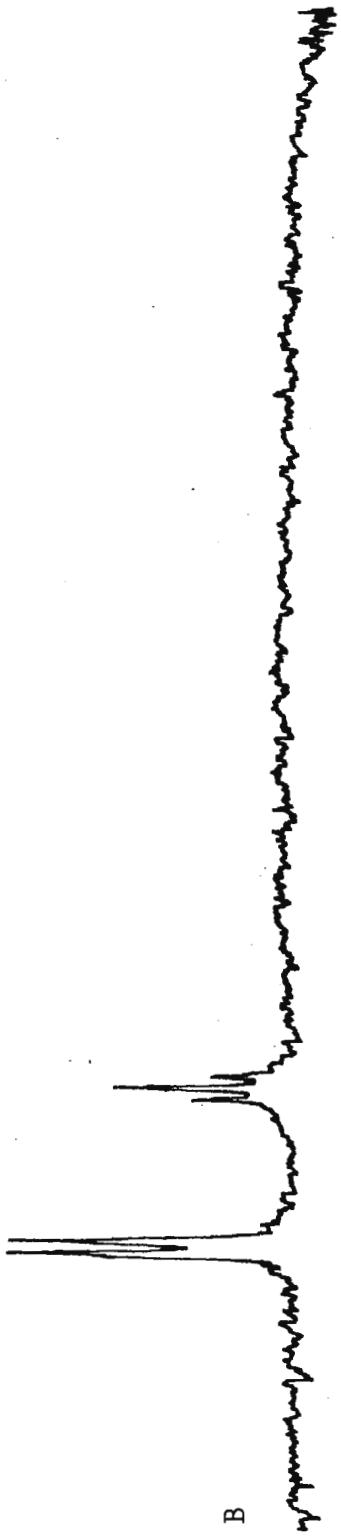

B


A

McMASTER UNIVERSITY
Department of Chemistry
1280 Main Street West, Hamilton, Ontario, L8S 4M1
Telephone: 525-9140

May 10, 1979

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

McMaster Enters the Second Dimension

Dear Barry,

With some help from Nicolet, we have been convincing our Nicolet FT-IR instrument that it really is an NMR machine. It has an 1180 computer and we have the NMR software, so provided it gets data from somewhere we can get spectra out.

We've written a BASIC program which simulates the 2D NMR experiments on an ABX spin system. It calculates a series of fake FIDs, which are then processed like real data. Some of the results are shown in the figure. Using "superspin" (our name for angular momentum in Liouville space(1,2,3)), the program can simulate any pulse flip angle, so that we can simulate ghosts, phantoms and other spectral features.

The figure shows 2D spin echo spectra with "good" and "bad" pulses applied to a system for which $\nu(A)=166.3$ Hz, $\nu(B)=155.1$ Hz and $\nu(X)=136.9$ Hz. The coupling constants are $J(AB)=4.3$ Hz, $J(AX)=0$ and $J(BX)=4.8$, so the system is similar to the ribose protons in 5'AMP which are labelled 2',3' and 4'. Now that we can simulate all the bumps in a 2D spectrum, we can use the program to assign a real spectrum.

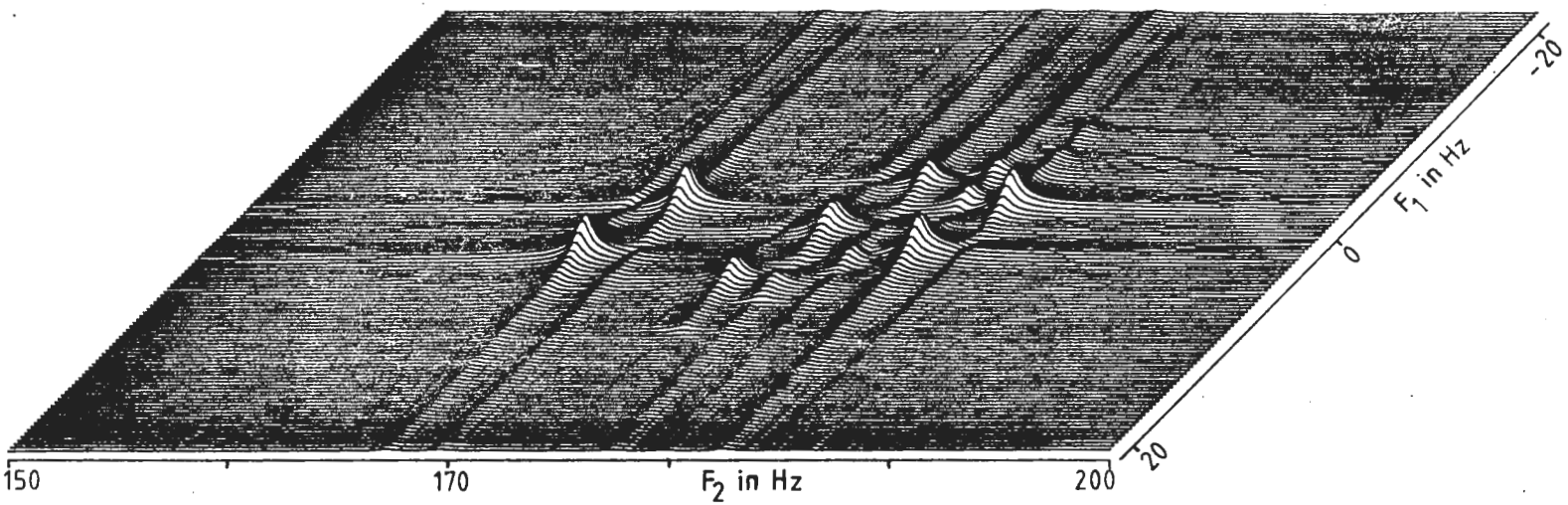
Please credit this contribution to J.I.A. Thompson's account.

Yours truly,

Alex D. Bain

1,2. A.D. Bain and J.S. Martin, J. Magn. Resonance 29, 125 and 137 (1978).
3. A.D. Bain, Chem. Phys. Letters 57, 281 (1978).

ABX SYSTEM 90-T-180-ECHO SEQUENCE



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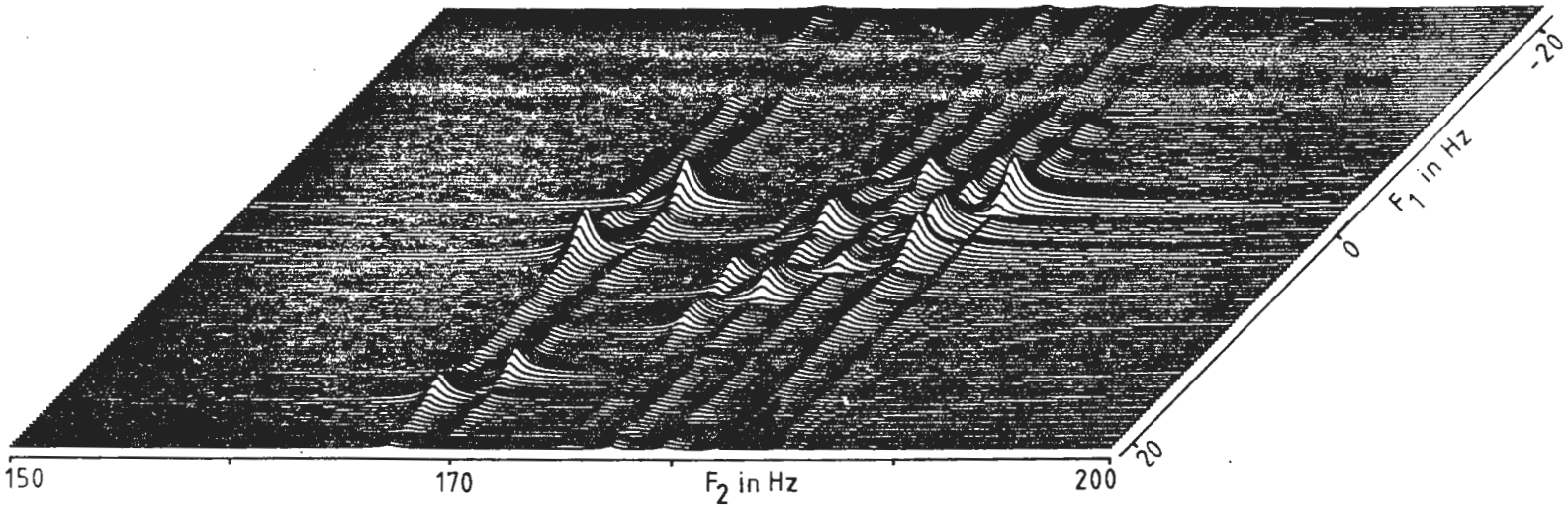


JEOL (U.S.A.), INC. • ANALYTICAL INSTRUMENTS DIVISION
235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016
TELEX NO. 13-8840 • (201) 272-8820

April 30, 1979

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

SUBJECT: "A VERTICAL PPM SCALE FOR NMR"

Dear Barry,

The interesting note from George Gray on dynamic range limitations (TAMU NMR Newsletter, 245, 35, 1979) prompted us to investigate the dynamic range limits of the foreground/background software on our FX-90Q NMR Spectrometer.

We have been using our double precision, D.P., software for about two years now, and thought the readers might wish to share in some of our experiences.

Dynamic range between sample peaks has been a minor use of double precision for us. We find that we can obtain greater sensitivity on very small samples (micro probe) or on very dilute spins (nitrogen-15) by using D.P. With these samples, the dynamic range problem is between the large noise and the very small sample signals. D.P. allows one to fill, or nearly fill, the ADC on every pulse but yet the FID never has to be scaled. On our system with a 12 bit ADC never means at least $2^{32-12} = 2^{20} = 1{,}048{,}576$ scans.

To date, we have never approached any dynamic range limitation with the 32 bit word and integer math. Of course, we had previously never encountered a sample with a signal-to-signal dynamic range greater than 10,000 to 1; for which we had to pulse only long enough to yield a signal-to-noise of about 131,000 to 1. Hence, we prepared a test sample (See Table 1) and diluted it 8:2 with D_2O for lock just prior to running:

COMPOUNDS	ml	%PROTONS	DYNAMIC RANGE RATIO	RELATIVE CONCENTRATION BY WEIGHT	RELATIVE CONCENTRATION BY PROTONS
Water	800	100%	1	1	1
DMSO	0.70	0.0665%	1,504	962ppm	665ppm
Acetonitrile	0.06	0.0039%	25,641	58ppm	39ppm
t-butanol	0.01	0.0011%	90,909	10ppm	11ppm
DMSO ^{13}C Satellite	-	0.00037%	273,411	5ppm	4ppm

TABLE 1. PREPARATION OF SAMPLE

A run of 196,340 pulses (20° flip angle) was performed giving a 8192 word, double precision FID (32 bit word).

Perhaps here we should point out that there is some confusion in terminology. A double precision (32 bit) accumulation does not automatically imply double precision (32 bit) transform mathematics. Our software allows both single precision (16 bit) integer transform and double precision (32 bit) integer transform of an FID which has been accumulated in 32 bit words.

The test FID was first transformed with single precision mathematics. This single precision result, as expected, exhibited digitzation:

$$\frac{\text{Signal Intensity}}{\text{Digitization}} = \frac{245}{3} \times 250 \text{ gain} = 20{,}416$$

This is in keeping with the maximum dynamic range of 2 exp (16-1) = 32,768 available in single precision for a 16 bit word. The acetonitrile and t-butanol peaks were not observed since their dynamic range is below this digitization level.

The original FID was then transformed in double precision (32 bit word) and the results are shown in the accompanying figure. As you can clearly see, all three minor components were observed. In addition, the upfield ^{13}C satellite of the DMSO is visible on the 2 exp 15 (x32768) expansion ($^{1}J_{CH}$DMSO = 138Hz reported value, $^{1}J_{CH}$DMSO = 138.7Hz observed). This peak corresponds to an observation level of about 5ppm. Our measured signal to noise is 8,700,000:1 for the H_2O.

It is further interesting to point out that we observe an acetone peak (marked * in the figure). It presumably originates from the acetone used in washing the bottle in which the sample was prepared. The bottle was flushed with dry nitrogen, but not oven dryed. Judging from the size of the peak it corresponds to roughly 1.8ul/800ml water or less than 2ppm!

The consideration of a maximum dynamic range obtainable is a complex one. After all, not too many years ago, it was generally believed that dynamic range was limited to only slightly more than the digitizer (ADC) resolution, here 4096 (See: "Topics in Carbon-13 NMR" Levy, Volume II CH7, 1976). Thus, theoretically we should not have seen the acetonitrile, butanol, DMSO ^{13}C satellites or the acetone impurity.

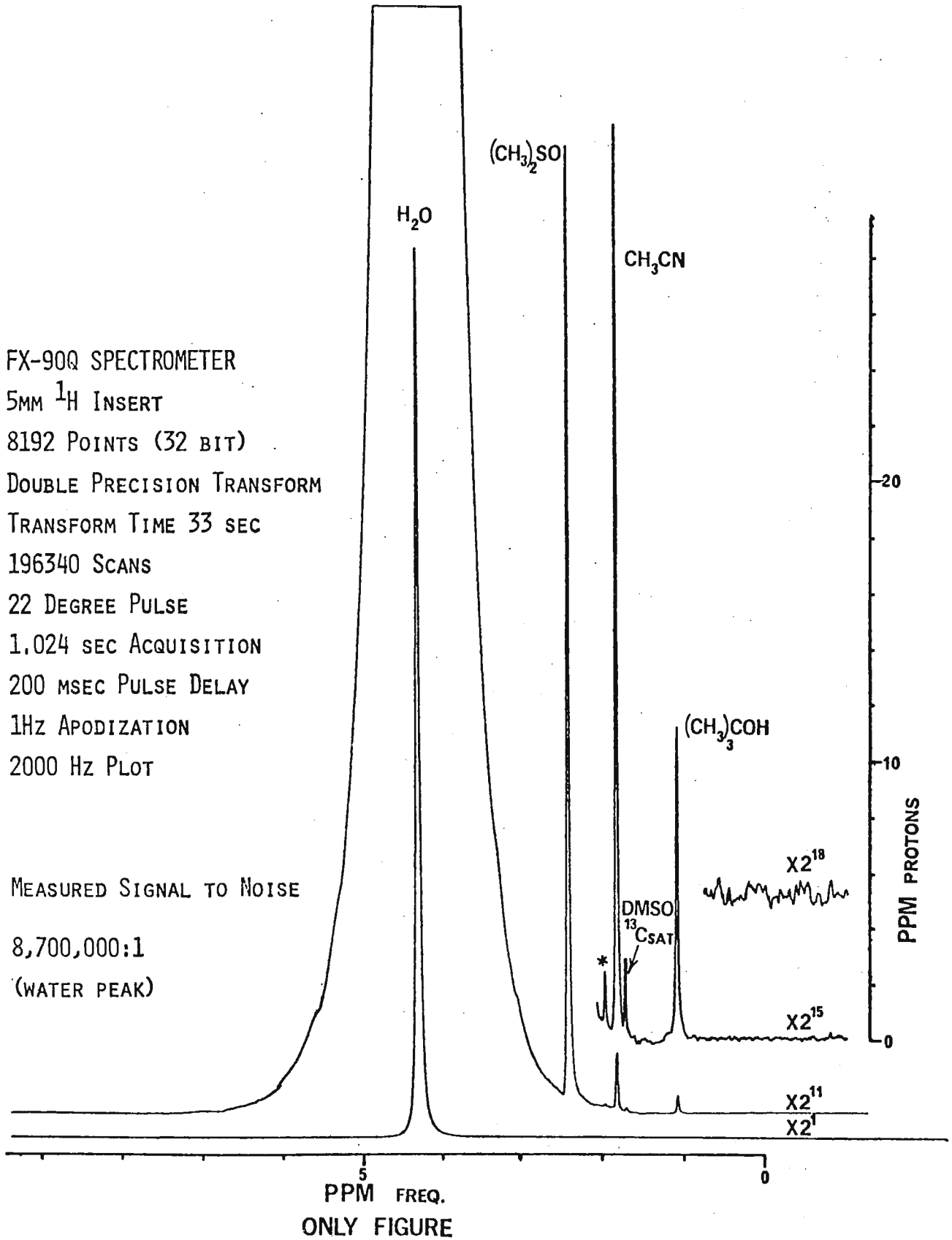
We believe that the time domain (FID) acquisition is inherently integer - as long as one is using a digitizer (ADC) to collect the data. Therefore, the ultimate limiting factor is the word length in the time domain (for a 32 bit word this is considerable - 4.3×10^9) from this we must now subtract round off transform errors, noise amplitudes, etc. Perhaps floating point can define greater dynamic range, but any number greater than the dynamic range of the FID seems meaningless.

We do not have precise answers to the problems here raised and invite further comments from the readers.

Sincerely yours,

M. J. Albright K. Goto R. Obenauf

/njc


FX-90Q SPECTROMETER
5MM 1H INSERT
8192 POINTS (32 BIT)
DOUBLE PRECISION TRANSFORM
TRANSFORM TIME 33 SEC
196340 SCANS
22 DEGREE PULSE
1.024 SEC ACQUISITION
200 MSEC PULSE DELAY
1HZ APODIZATION
2000 HZ PLOT
MEASURED SIGNAL TO NOISE
8,700,000:1
(WATER PEAK)
H2O
(CH3)2SO
CH3CN
(CH3)COH
DMSO
13CSAT
*
X2^18
X2^15
X2^11
X2^1
20
10
0
PPM PROTONS
5
0
PPM FREQ.

ONLY FIGURE

RICHMOND
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May 15, 1979

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

SUBJECT: "Dibromotriphenoxyphosphorane"

Dear Barry:

Recently, we have reinvestigated the reaction of triphenyl phosphite and bromine utilizing phosphorus-31 NMR spectroscopy. When 1/4 molar equivalent of bromine was added to triphenyl phosphite, $(PhO)_4PBr$ (+22.5 ppm, relative to 85% phosphoric acid), $(PhO)_2PBr$ (-175.3 ppm) were observed. When 1/2 molar equivalent of bromine was added to triphenyl phosphite, $PhOPBr_2$ (-199.4 ppm) was observed in addition to the aforementioned compounds. When 3/4 molar equivalent of bromine was added to triphenyl phosphite, the phosphorus compounds observed were $(PhO)_4PBr$, $(PhO)_2PBr$, $PhOPBr_2$, and PBr_3 (-228.2 ppm). It is interesting to note that when a molar equivalent of bromine was added slowly into a chloroform solution of triphenyl phosphite, only $(PhO)_4PBr$ and PBr_3 were observed. However, when a molar equivalent of triphenyl phosphite was added quickly into the bromine solution, the major product observed was $(PhO)_3PBr_2$ (-4.5 ppm) in addition to two minor products, $(PhO)_4PBr$ and PBr_3. Dibromotriphenoxyphosphorane, a pale yellow solid, became liquid on contact with air to form triphenyl phosphate (+17.7 ppm).

Sincerely,

CKTseng

C. K. Tseng

USSR Academy of Sciences
Shemyakin Institute
of Bioorganic Chemistry

Ul. Vavilova 32
Moscow 117312 USSR

May 16, 1979

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

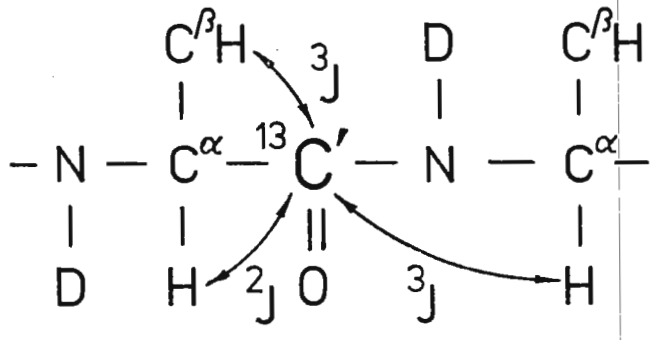
Title: Heteronuclear $^{13}C/^{1}H$ Double Resonance Assignments of Peptide Signals

Dear Barry,

The starting point for any meaningful application of NMR to the conformational study of peptides and proteins is resolution of the NMR signals and their assignments to given amino acid residues. Since, in general, the primary structure contains most of the different amino acid residue more than once, two levels of NMR resonance identification had to be considered

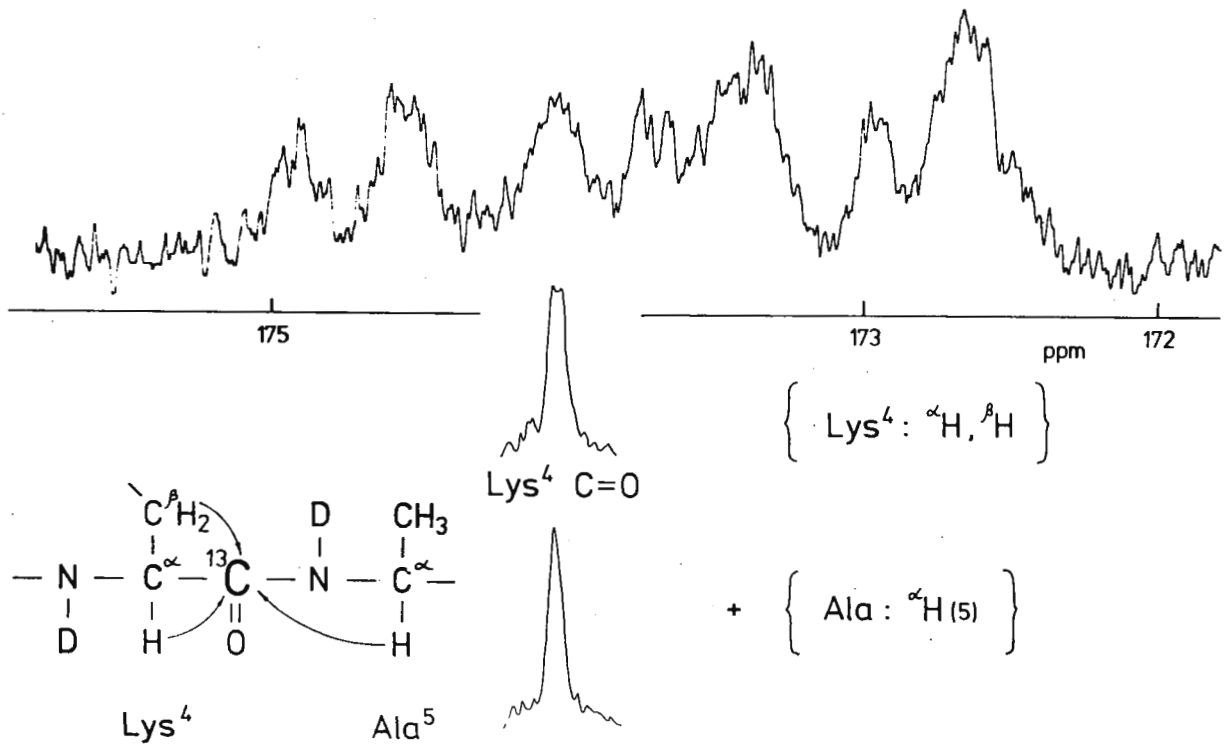
First, the proton signals and spin systems of different types of amino acids have to be distinguished by homonuclear spin decoupling experiments. Second level implies assignment of the individual spin systems to the specific position in the amino acid sequence.

The technique we are using for the second level assignment consists of heteronuclear double resonance C-13 {H-1} in the peptide fragment [1,2], shown on Fig. 1, where the proton spin systems of neighbour amino acid residues are connected via carbonyl C'-13 carbon.



In the proton spectrum of apamin (18-membered peptide with two disulfide bridges, isolated from bee venom) [2] the H^{α} and H^{β} resonances of lysine-4 residue were selectively irradiated by two r.f fields, while observing the

C-13 NMR spectrum in the carbonyl region (Fig. 2). The carbonyl signal of this residue becomes a doublet due to vicinal coupling



with H^{α} proton of neighbour alanine-5 residue. The apamin contains three alanines; Ala-5, Ala-9 and Ala-12. Only when, by trial, the Ala-5 H^{α} resonance is irradiated, the Lys-4 carbonyl signal transforms into singlet.

The described technique allows to assign almost all the proton and carbonyl C-13 signals of apamin to the individual amino acid residues in the primary structure. In general it isn't necessary to choose as a starting point the assigned proton spin system. Instead, by trial and error, one could find a pair correspondence of the neighbour residues.

With best wishes,

Yours sincerely,

Vladimir

Vladimir Bystrov

1. V.F.Bystrov, Yu.D.Gavrilov, V.T.Ivanov, Yu.A.Ovchinnikov, Eur. J. Biochem. 78, 63 (1977).
2. V.F.Bystrov, A.S.Arseniev, Yu.D.Gavrilov, J. Magn. Res. 30, 151 (1978).

UNIVERSITY of PENNSYLVANIA
PHILADELPHIA 19174

The School of Medicine
DEPARTMENT OF BIOCHEMISTRY

May 24, 1979

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

Broadband Transmit/Receive Circuit

Dear Barry:

I'm not sure how the big boys build their Transmit/Receive(T/R) circuits for multinuclear NMR, but we've found that the circuit here is a pretty hot performer (or cold, if you prefer). Its Noise Figure(NF) with preamplifier is 2 dB in the frequency range where I've measured it (10...70 MHz) and should be as good at higher and lower frequencies. It's similar to a circuit published a bit too soon in RSI, which had a NF of 3 dB.[1]

The PIN diodes KS9377 (KSW Corp., Burlington, MA) are kept turned on during receive time by a total current of 30 mADC from the transistor 2N5551. All other diodes (IN914) are not conducting during the receive time. The transmission line transformer[2] is 5 turns of a twisted pair wound on a Stackpole ferrite toroid type 57-9322. The wire size is probably not critical, although it does determine the characteristic impedance of the transformer. During receive time, with one transformer input wire effectively grounded by the PIN diodes, the transformer provides simple broad band coupling of the probe output to the preamplifier input. We installed the T/R circuit in the same housing as the preamplifier. The input transistor of the preamplifier is an NEC type NC921, common emitter, with I_C = 5 mA, which claims to give a max. NF of 1.5 dB when it looks back at a resistance of 50 ohms. We measured 1.5 dB without the T/R circuit. Take care that the transmitter noise is not leaking into the preamplifier via the crossed

diodes, especially at higher frequencies. PIN diodes might be helpful here, because of their lower capacitance.

During the transmitter pulse time the high RF voltage is peak detected at the 50 pF capacitor, the 2N5551 stops conducting, and -100 V turns the PIN diodes hard off. The transformer input looks like a high impedance RF choke, so that most of the transmitter power is well coupled through the crossed diodes into the 50 ohm probe. A helpful feature here is that the timing of the switching of the PIN diodes does not depend upon any external timing pulses except for the transmitter pulse itself. The dead time due to this circuit is about 1.5 μsec -- a lot shorter than our receiver recovery time.

I'd like very much to hear from anyone who wants to try this circuit, or has tried it.

Sincerely,

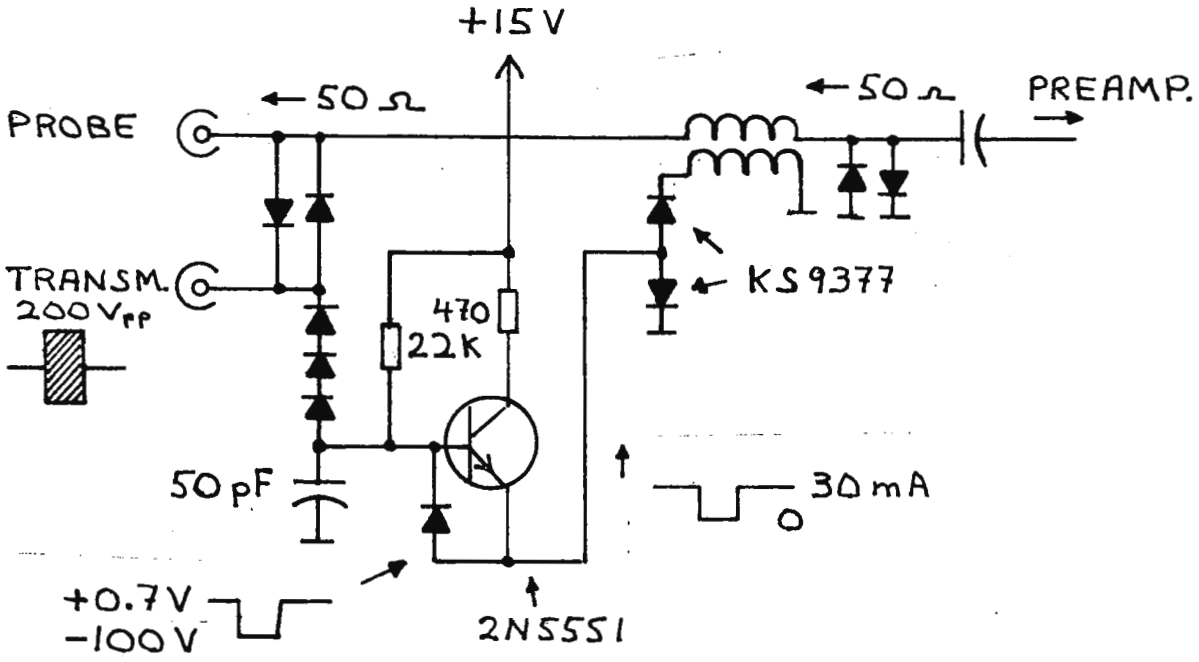
Jim

James L. Engle

[1]Rev. Sci. Instrum. 49(9), 1356(1978)

[2]C.L. Ruthroff, Proc. IRE 47, 1337(1959)

P.S. Please credit this to Dr. Mildred Cohn's subscription.



BROADBAND T/R CIRCUIT

UNIVERSITY OF SOUTH FLORIDA
TAMPA • ST. PETERSBURG • FORT MYERS • SARASOTA

DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

813:974-2144
SUNCOM: 574-2144

10 May, 1979

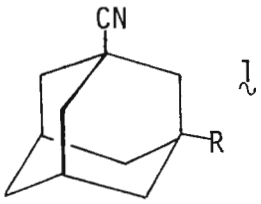
STRUCTURES OF EUROPIUM SHIFT REAGENT COMPLEXES WITH ORGANIC NITRILES.

Dear Barry:

Our work with a variety of organic nitriles and $Eu(fod)_3$ permits a few observations which may be of some interest:

We have come to the conclusion that the nitrogen-europium bond length in the complexes of organic nitriles is not the 1.89 Å which we suggested several years ago. A review of the crystallographic literature (of both lanthanide and transition metal complexes) leads to the conclusion that the bond length must be approximately 2.5 Å. While the original bond length gave good agreement between experimental and calculated values of the induced shifts, the revised value affords even better results.

One of the advantages of studying nitriles is that the europium is expected to lie on a linear extension of the carbon-nitrogen bond, thus leading to less uncertainty in the structural calculations. Although the linear relationship is clearly appropriate in the case of 1-adamantanecarbonitrile (1, R = H) which has a threefold axis of symmetry, a linear C-N-Eu arrangement is not required in the less symmetrical cases where the R group of 1 corresponds to an alkyl group. In fact our shift reagent studies indicate a slight but progressive deviation from linearity along the series where R is methyl, ethyl, i-propyl and t-butyl, with the largest deviation being approximately 5°.

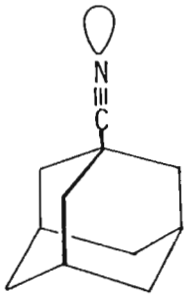


1

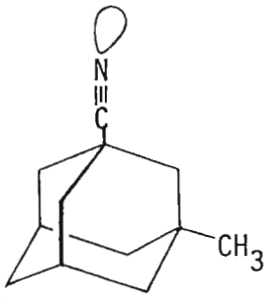
We have obtained supporting evidence for this view from MO calculations on the parent nitrile and the methyl derivative. MINDO/3 calculations indicate that the nitrogen "lone pair" is indeed colinear with the cyano group of the unsubstituted nitrile (2). However, the presence of the methyl group of 3 causes a small distortion in the direction of the alkyl substituent. This is precisely the direction of the nonlinear distortion which gives the best fit for our shift reagent data.

Best regards,

Douglas J. Raber



2



3

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Tel. (01) 32 62 11

May 16/1979

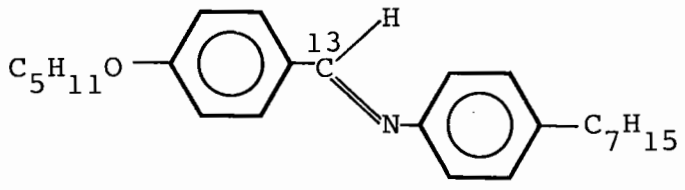
Professor B.L. S H A P I R O
Department of Chemistry
College of Sciences
Texas A & M University
COLLEGE STATION
Texas 77843 U S A

Two-Dimensional Carbon-13 Powder Spectra

Dear Barry,

Those scientists who have tried to grow single crystals large enough to do NMR spectroscopy on them understand the desire to work with powders. Powders are simply bought in the grocery store, poured into an NMR tube and measured in seconds. Several attempts have been undertaken to make the usually rather dull looking powder spectra more attractive to those spectroscopists accustomed to more curvaceous shapes. One possibility is spinning at the magic angle to strip the lines naked of their dipolar dress.

Another powerful technique to unveil the hidden appeal of a spectrum is spreading it out in a second frequency dimension. Such a two-dimensional spectrum of a powder is shown in the figure. It represents the carbon-13 spectrum of the liquid crystal molecule 507,



^{13}C-enriched at the benzylidene position. The vertical frequency axis presents the chemical shielding anisotropy in the form of an axial tensor while along the horizontal frequency axis a doublet splitting is caused by the dipolar interaction with the benzylidene proton. The splitting is of course angular-dependent. It collapses at the magic angle position and causes the sensual erection in the center of the figure.

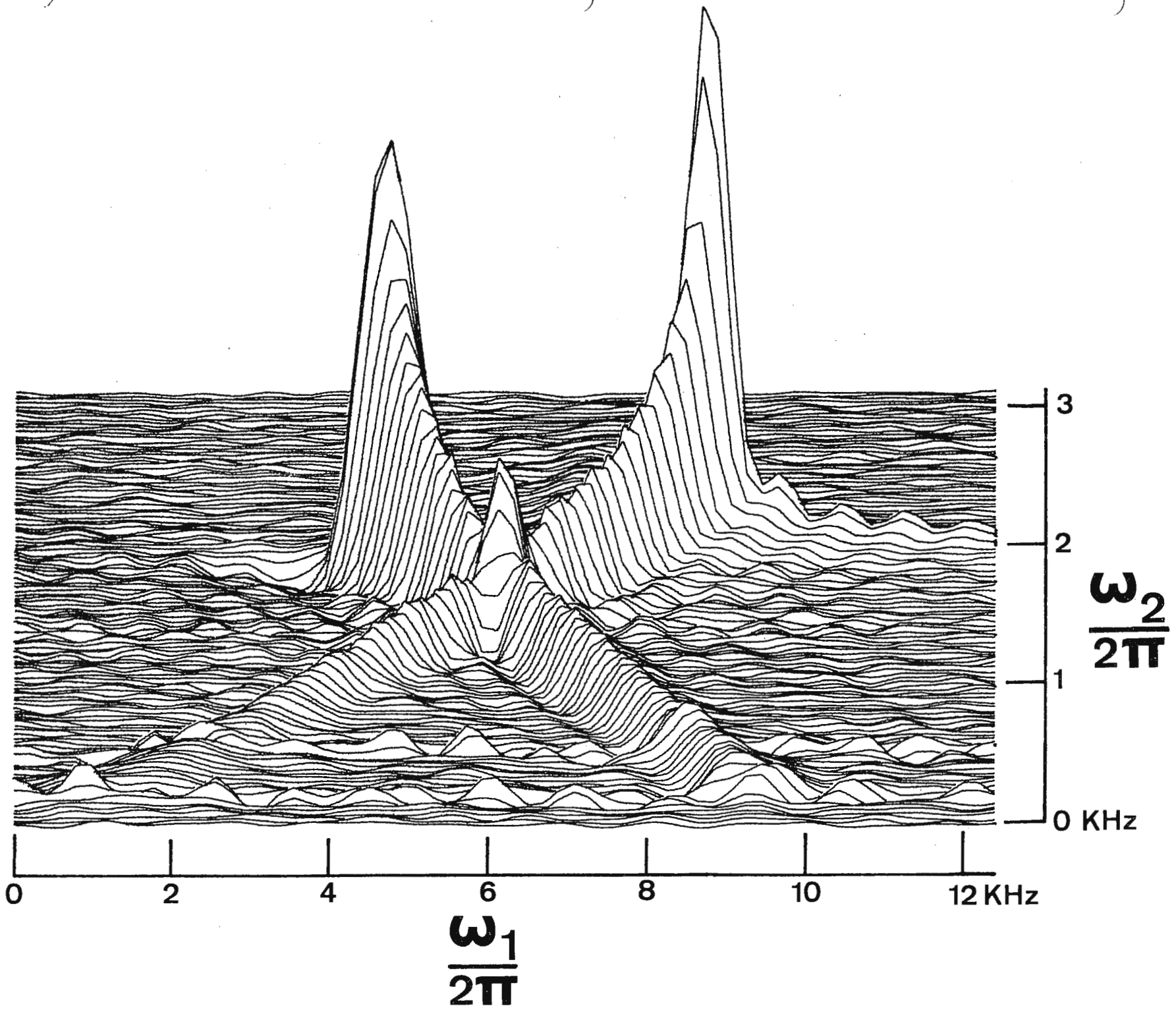
In addition to providing separate information on the chemical shielding tensor and on the dipolar interaction, this representation allows one to relate the two tensors. In this particular case, one finds that the two tensors are coaxial, with the rotation axis of the chemical shielding tensor coinciding with the rotation axis of the dipolar interaction tensor. The coincidence is not astonishing in this spectrum as it is the result of molecular rotation about the director axis in the smectic B_c phase from which this spectrum has been obtained. However, in other examples real geometric information can be gained.

The experimental technique used to obtain such spectra is a modification of a procedure proposed by J.S. Waugh (Proc. Natl. Acad. Sci. USA 73, 1394 (1976)).

Sincerely yours

M. Linder, Dr. A. Höhener* and R.R. Ernst

*) Ciba-Geigy AG, Basel


3
2
1
0 KHz
$\frac{\omega_2}{2\pi}$
0
2
4
6
8
10
12 KHz
$\frac{\omega_1}{2\pi}$

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER STATION
ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

May 8, 1979

Professor Barry Shapiro
Chemistry Department
Texas A & M University
College Station, Texas 77834

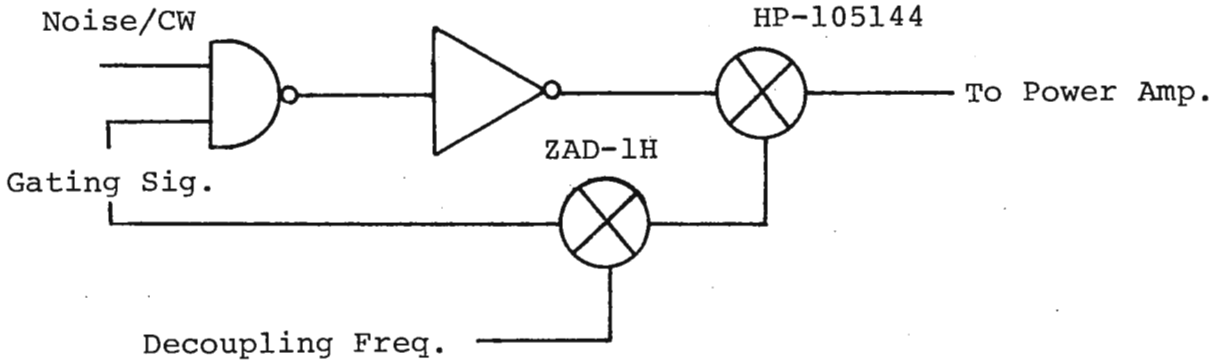
Dear Barry:

We have made a modification to do Homo/Hetero Gated decoupling on our six years old PFT-100 FT-NMR. During the course of our modifications which involves adding a simple gate (ZAD-1H from Minicircuit Lab) and control logics in the decoupler frequency source, we've encountered a problem with redisual decoupling effect on the NOE mode.

As this turned out, the problem was caused by a RF leakage due to an inadequate isolation (Specification-40 DB) on the gate used in the decoupler.

To eliminate the difficulty without using better isolation but more expensive device, we put a NAND gate (using all spares existed in the PC board) on the Noise source and the signal that gates the decoupler. This turns off noise or CW modulating signals for HP-10514A mixer and in effect increased the isolation ratio to the degree where there are no problems.

A brief diagram is given below.



Sincerely,

Yukio Kuroda

YK/rsh

University of Houston
Central Campus
Houston, Texas 77004

Department of Medicinal Chemistry and Pharmacognosy
College of Pharmacy

May 7, 1979

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

Dear Barry,

We have made two modifications to the Nicolet TT760 decoupler provided by Nicolet for our XL-100 system. As originally configured, this unit will modulate a 100MHz rf signal with pseudorandom binary sequence and provides for gating the signal off during data acquisition or off during the pulse delay.

The first modification is the addition of a 555 timer and a 7400 Nand gate to provide a 75Hz square wave. See Figure 1.

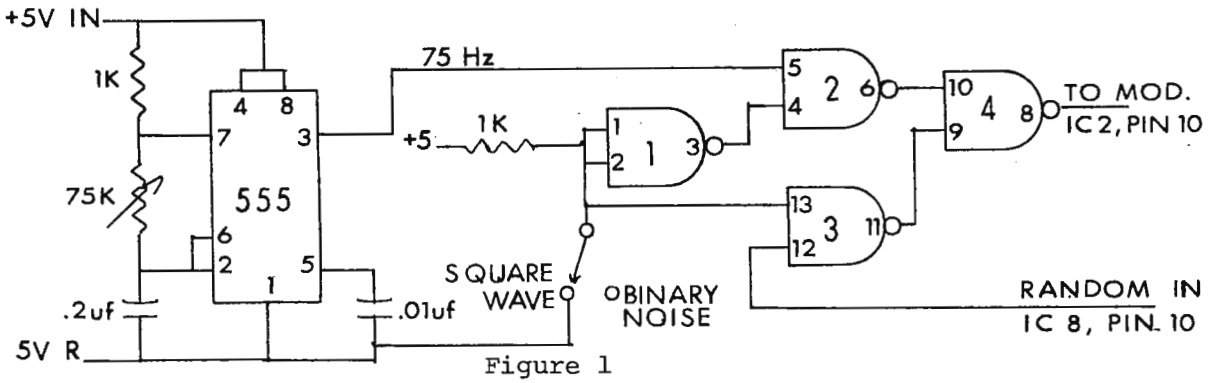
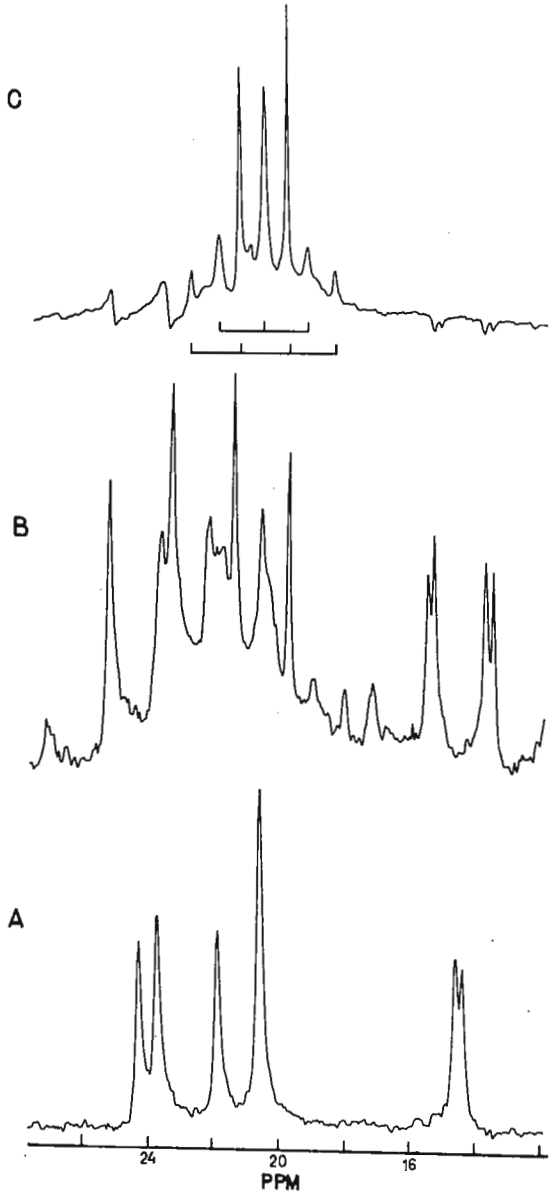


Figure 1

The 555 timer generates the square wave. The input to gate 1 can be switch selected to provide either square wave or binary modulation. A low selects the square wave. Gate 1 is used as an inverter to enable either Gate 2 (square wave) or Gate 3 (binary). Gate 4 acts as a NOR gate since the disable gate is held high enabling Gate 4. The output of Gate 4 drives the normal modulator circuit. (IC3-7400).

The second modification permits gating the modulation on and off rather than the decoupler power. Thus, the spin system can be pulsed under full noise decoupling and the FID collected with single frequency decoupling. This is especially useful in conjunction with the selective excitation sequence of Bodenhausen, Freeman and Morris (J. Mag. Res., 23, 171 (1976)) providing selective excitation with single frequency off-resonance decoupling (SESFORD) (G.E. Martin, et al., J. Am. Chem. Soc., 101, 1888 (1979)). A single line in the decoupled spectrum can be excited and the FID collected to provide a subspectrum containing reduced J values without interference from neighboring spin-multiplets. See Figure 2.

The circuit used for this modification requires only half of a 7400 Nand gate. See Figure 3. If the noise switch is off, R1 enables Gate 1 and the sweep flag controls the noise, off during acquisition and on during the delay. If a normal single frequency decoupled spectrum is desired, turning the noise off still results in the noise being on during the delay which will not effect the off-resonance spectrum. Further, this configuration will also probably provide a more univorm NOE across the entire spectrum, although we have not checked



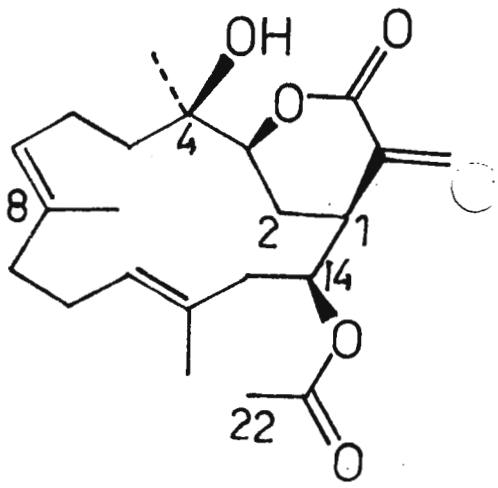


Figure 2. 25.2 MHz spectrum of crassin acetate; A, fully decoupled trace of a portion of the methylene region; B, conventional SFORD; C, SESFORD trace of the degenerate 2 methylene and 22 methyl resonances located at 20.1 ppm. From G. E. Martin, J. A. Matson, J. C. Turley and A. J. Weinheimer, JACS, 101, 1888 (1979)

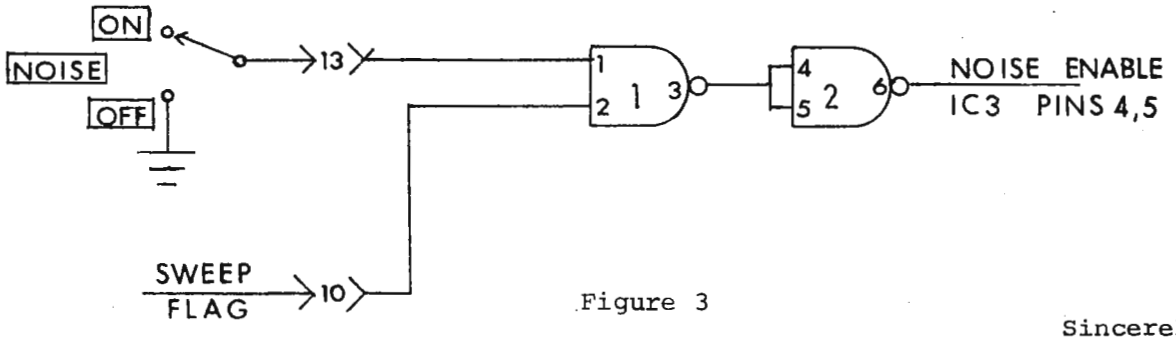


Figure 3

Sincerely,

Garv E. Martin

Steve Silber

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

Rome, May 23rd 1979

Proton magnetic relaxation studies of liposomal model membranes, sensitized with O-stearoyldextrans.

Dear Prof. Shapiro,

a number of information already available on the epitope size and molecular structure of dextrans have proposed these polysaccharides as a useful model system, for studying the molecular mechanisms that are likely to control some immunological properties of thymus-independent multivalent antigens. In particular it seems that a more detailed knowledge of the extent to which the epitope units of the chains are available to the interaction with immunoglobulin receptors of B lymphocytes, should provide a better understanding of the role of epitope structure and density on the immunogenic and tolerogenic activities of these antigens. Since little is known about the three-dimensional structure of dextrans in solution, we have thought that a useful approach to our problem might be provided by a) inducing well defined conformational modifications on the segmental organization and flexibility of the dextran chains and b) subsequently studying the effects of these changes on the antigenic and immunogenic properties of these polysaccharides.

The use of liposomal model membranes as non covalent carriers of dextrans has appeared to be suitable to these purposes, in view of the possibility of modulating the dynamical structure of the system, by varying the chemical composition of the lipid bilayer.

We are presently carrying out parallel studies on the molecular structure and immunological properties of liposomal model membranes sensitized with O-stearoyldextrans (OSD). These dextran derivatives - containing increasing amounts of stearoyl groups esterified at the C-3 position of the glucose units - have been synthesized from a fraction of dextran B 512, a near linear glucose polymer with 96% $\alpha(1\rightarrow6)$ and 4% $\alpha(1\rightarrow3)$ linkages ($MW \simeq 7 \cdot 10^4$)[1]. We have recently verified that these derivatives can be stably adsorbed on the surface of liposomal model membranes, through the incorporation of their stearoyl residues within the hydrophobic region of the lipid bilayer.

Since FT NMR relaxation methods have been shown to be very sensitive to alterations of the intra- and intermolecular mobility of the chemical components of liposomal membranes, at the level of their individual chemical groups, we are employing this technique for studying the organization and dynamical structure of OSD-sensitized liposomes, above the phase transition of the lipid alkyl chains.

Spin-lattice proton magnetic relaxation times and linewidths have been measured at 37 °C on egg lecithin:dicetylphosphate vesicles (mole ratio 10:1), sensitized with OSD containing increasing amounts of stearoyl groups(from 1.4 up to 3.9% w/w). The actual content of adsorbed polysaccharide in the vesicle aqueous suspensions has been determined spectrophotometrically by the phenol-sulfuric acid method.

T_1 s and linewidths, measured at 100 MHz on the proton signals of the lipid components, have indicated that the interaction with OSD induces a remarkable decrease of the rotational mobility of the lecithin headgroups at the level of the $N^+(CH_3)_3$ groups. Preliminary studies on proton signals of the adsorbed polysaccharides have indicated that a) the T_1 of the anomeric protons as well as those of some ring protons (not obscured by the lecithin spectrum) are practically the same as found in the free dextran in solution;[2] b) the linewidths increase with the content of the stearoyl groups esterified to the adsorbed polysaccharide. On the other hand electron microscopy measurements have shown that the vesicle size is practically the same in all the systems studied.

These preliminary results would suggest that, although adsorption on the carrier decreases the overall segmental flexibility of the dextran chain, the local rotational mobility around the $\alpha(1\rightarrow6)$ linkages is not appreciably restricted with respect to that found in the free chains. Further studies should be carried out at higher frequency in order to confirm these conclusions.

^{31}P NOE measurements are presently carried out to further elucidate the mechanisms of the intramolecular interactions between the glucose units of the adsorbed OSD and the lecithin headgroups.

Sincerely,

Franca Podo Carlo Ramoni Carlo Pini

(Franca Podo) (Carlo Ramoni) (Carlo Pini)

(1) Svensson, S., Vicari, G. and Wilkinson, S.J., Immunol. Methods 9, 315-321 (1976).

(2) Podo, F. Ramoni, C. Vicari, G., Texas A & M University NMR Newsletter, 237, 31-32 (1978).

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May 28, 1979

Prof. B.L. Shapiro
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U.S.A.

Dynamic Range in Hadamard - Fourier Transform Spectroscopy

Dear Barry:

Prof. Ziessow's letter in TAMU 246-29 and your blue reminder combined to stimulate the following comments.

We wish to compare the rms signal/rms noise ratio in two spectra. Spectrum I is obtained from the FT of the pulse-stimulated FID. Spectrum II results from the FT of the FID computed as the Hadamard transform of the response to a pseudorandom binary sequence. Conditions shall be comparable: the same number of scans is used with the same sample for signal averaging, the repetition period of the pulses is equal to the period of the pseudorandom sequence and not much longer than the greatest T_2, the acquisition time equals the repetition period, the width of the single pulse equals the width of the pseudorandom pulses, the pulse amplitude is adjusted to an optimum for each experiment. The last condition is ill defined since "optimum" depends on non-linear effects, and these are different in the two cases. We argue that conditions are comparable when the amount of energy absorbed by the spin system in 1 repetition period is the same in the two experiments. Since both experiments utilize the same frequency channels of the sample, and since modes must be reasonably orthogonal for the Hadamard method to give the linear spectrum, the energy of the stimuli and of the responses must also be the same per period in the two experiments. For the stimuli, this condition gives the ratio of the peak powers for the RF transmitters required. For the responses, it says that the rms signal amplitudes are the same. Thus, when obtained from comparable experiments, the bottom and middle traces in Figure 1 of Prof. Ziessow's letter have the same rms signal amplitude. They also have the same rms noise amplitude since they come from the same detector through the same bandwidth. Thus, the rms S/N ratio of the analog data acquired from the spectrometer is the same in the two experiments.

Next, Parseval's theorem says that the Fourier transform leaves the rms S/N ratio unchanged, and so does the Hadamard transform. Thus, if we can neglect computer noise, the two spectra, the two FID's, and the pseudorandom response all have the same rms S/N ratio. If we determine this ratio for the largest signal that does not get chopped by overflow, clipping, blowing fuses, etc., we have the dynamic range, except for niceties hinging on the definition of the smallest observable peak signal/rms noise ratio.

The premise of Prof. Ziessow's comments is that the large-signal-chopping occurs in the A/D converter. The rms noise, generated in his computer experiment by truncation after scaling to the simulated A/D resolution, is (presumably) the same for the FID and for the pseudorandom response. The spectra in his Fig. 2 show about a 1 bit, i.e. factor 2, advantage in the rms S/N ratio of the Hadamard method II over method I. From the foregoing, this implies that, for the same peak amplitude, the pseudorandom response shown in the bottom trace of his Fig. 1 should have about twice the rms value of the FID shown in his middle trace. This appears responable for the traces shown but depends on the particular spectrum. For example, one might be able to simulate a reasonable nmr spectrum such that the FID looks pseudorandom and the pseudorandom response looks FID-like. The rms S/N advantage would then be reversed.

In other words, our arguments make us believe that the dynamic range advantage of one method over the other is equal to the factor by which the rms/peak ratio of the signal to be digitized is greater in one method than in the other. It appears that nmr signals are usually such that the rms/peak ratio is somewhat greater in the pseudorandom response than in the FID. For a given peak amplitude, more signal energy can then be transmitted on the pseudorandom signal than on the FID.

Sincerely yours,

Reinhold

R. Kaiser

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VANCOUVER, B.C., CANADA
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DEPARTMENT OF CHEMISTRY

26 May, 1979

Professor Bernard L. Shapiro
TAMU Newsletter
Dept. of Chemistry
Texas A & M University
College Station, TX 77843 USA

Title. DISPA: Dispersion versus Absorption in NMR, ESR, and ...?

Dear Barry,

I have recently proved analytically[1] that a plot of dispersion versus absorption (DISPA) provides a simple way to distinguish line-broadening due to two or more Lorentzians of different resonant frequency (DISPA data points fall outside the reference circle that would be obtained for a single Lorentzian) and two or more Lorentzians of different line width (DISPA data points inside the reference circle). This proof generalizes the results from DISPA analysis of several previously treated particular line-broadening mechanisms.[2,3]

In this note, we report the extension of DISPA analysis to EPR line shape (see Fig. 1). In this case, we first digitize the EPR derivative spectrum, then flatten the baseline, integrate to obtain a digitized absorption spectrum, then Hilbert transform to produce a digitized dispersion spectrum, and finally construct the DISPA plot. In this way, we avoid any need for direct detection of the dispersion spectrum, and we lose a factor of $\sqrt{2}$ in signal-to-noise ratio compared with separate detection of absorption and dispersion.

Fig. 2 shows an application to detection of modulation broadening in EPR. From the displacement of the DISPA data of Fig. 2b from the reference circle (compare to 2a, with no modulation broadening), we immediately establish that the line shape is overmodulated, with a modulation amplitude of about one natural line width. In contrast, the circular DISPA plot of Fig. 2c shows that the exchange-broadened spectrum there is still Lorentzian in shape.[4]

Finally, it should be noted that the algorithm of Fig. 1 will produce a correctly scaled DISPA plot for any spectrum (NMR, EPR, NQR, ion cyclotron resonance, rotational, vibrational, etc.) for which an absorption-mode signal is available. There is thus no need for separate measurement of the dispersion spectrum.

Alan G. Marshall

D. C. Roe
P. S. Phillips
F. G. Herring

References:
1. A. G. Marshall, J. Phys. Chem. 83, 521 (1979).
2. A. G. Marshall and D. C. Roe, Anal. Chem. 50, 756 (1978); D. C. Roe, A. G. Marshall, and S. H. Smallcombe, ibid. 50, 764 (1978).
3. A. G. Marshall and D. C. Roe, J. Magn. Reson. 33, 551 (1979).
4. F. G. Herring, A. G. Marshall, P. S. Phillips and D. C. Roe, J. Magn. Reson., in press (1979/80).

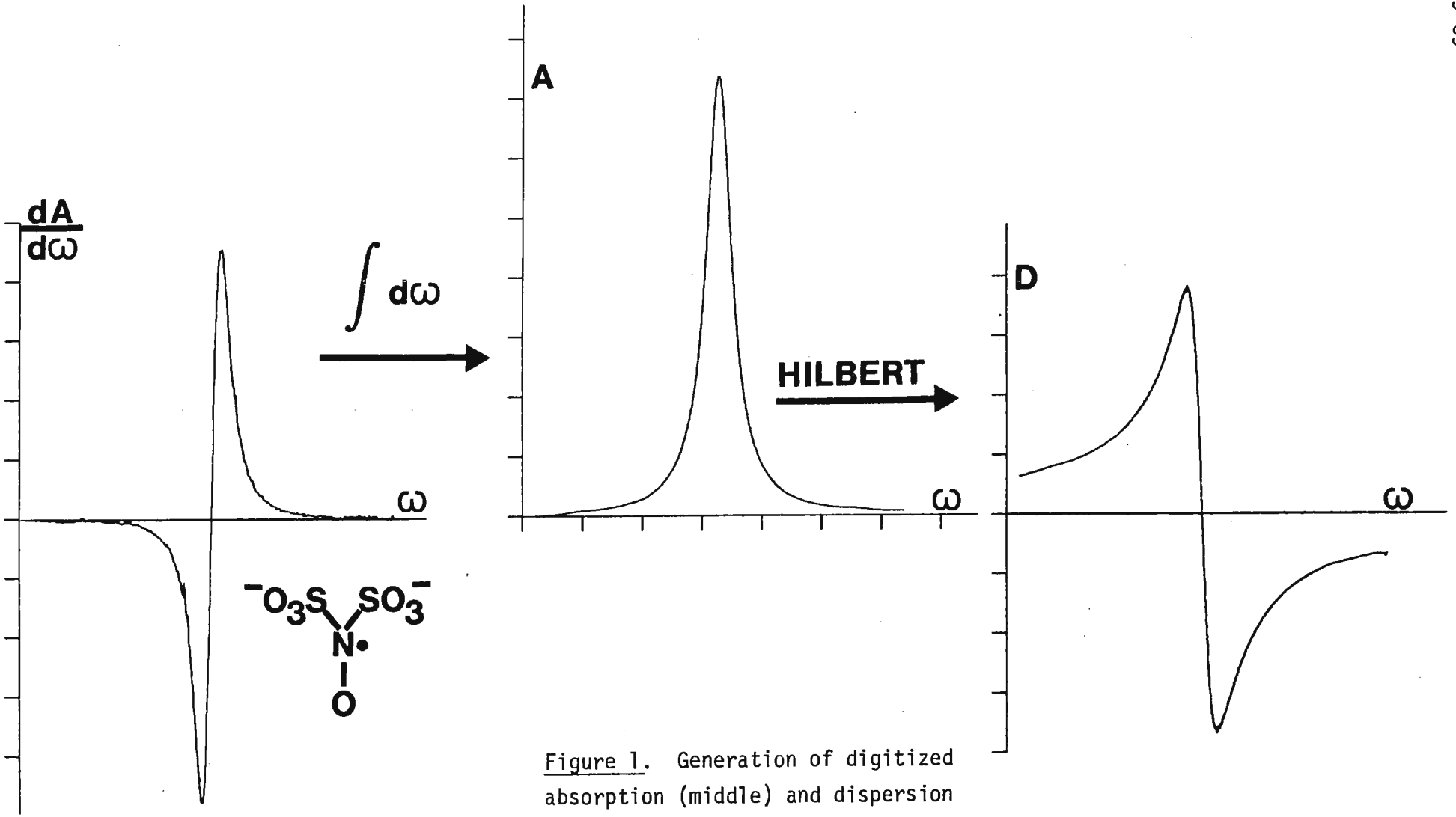

Figure 1. Generation of digitized absorption (middle) and dispersion (right) spectra from an experimental EPR v-mode derivative spectrum (left) of peroxylamine disulfonate (m_I = 0 line).

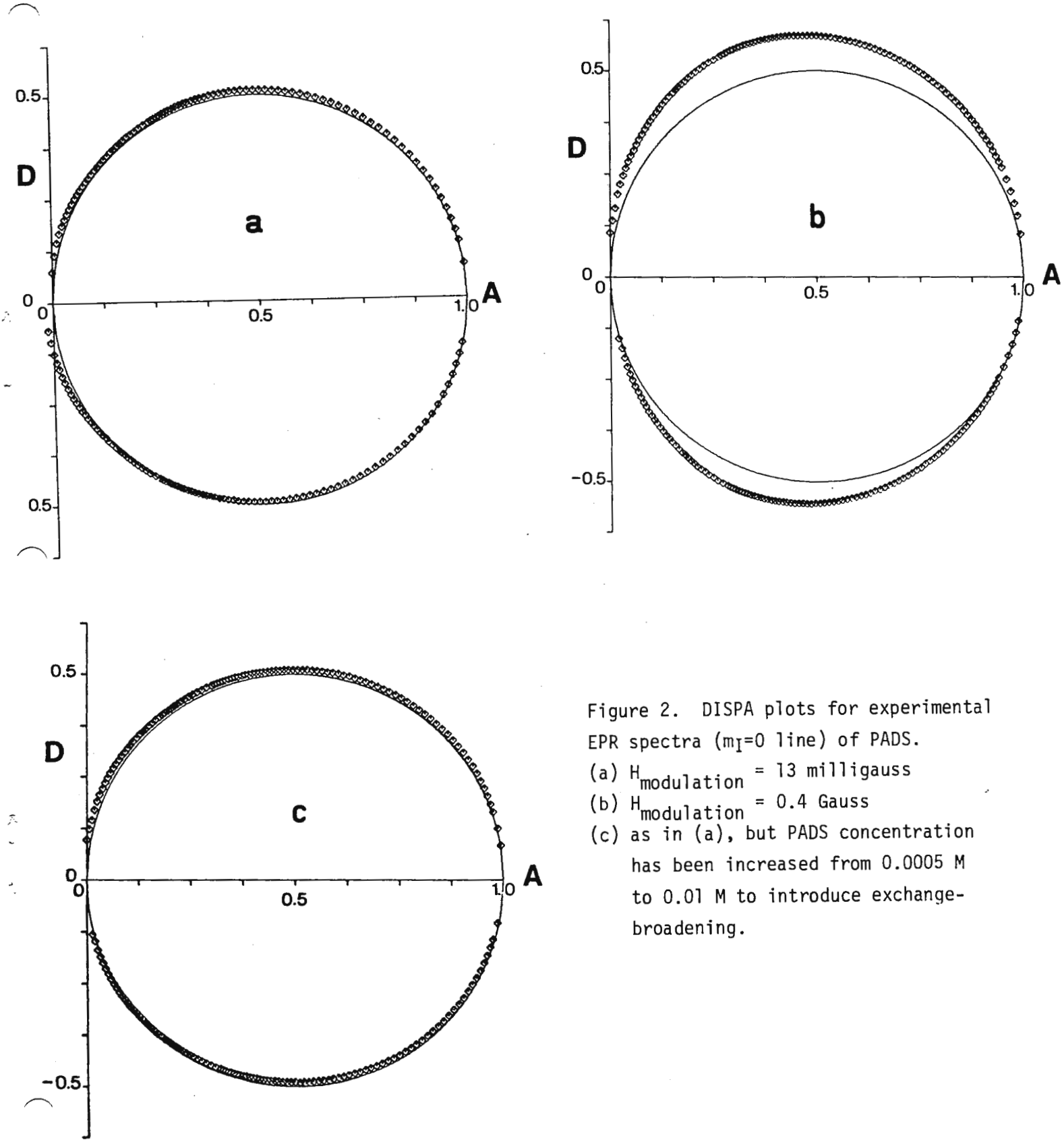

Figure 2. DISPA plots for experimental EPR spectra (m_I=0 line) of PADS.
(a) $H_{modulation}$ = 13 milligauss
(b) $H_{modulation}$ = 0.4 Gauss
(c) as in (a), but PADS concentration has been increased from 0.0005 M to 0.01 M to introduce exchange-broadening.

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Professor B.L. Shapiro
Departmnet of Chemistry
Texas A&M University
College Station, Texas 77483

^{2}H NMR Studies of Nitrogenase-Catalyzed Reduction of Cyclopropene

Dear Barry:

The nitrogenase-catalyzed reduction of cyclopropene in D_2O gives two major products which were isolated and identified as cyclopropane and propene. The ir spectrum of the cyclopropane product on comparison with published spectra of cis-and trans-1,2-d_2-cyclopropane indicates that the predominant product (>95%) corresponds to the cis-isomer. The ir spectrum of the propene product shows that a mixture of d_2-isomers is present but the presence of 1,2-$d_2$propene at greater than 1-2% can be ruled out. The 220 MHz ^{2}H-decoupled ^{1}H nmr spectrum confirms the existence of a complex mixture with multiplets at δ1.67-1.70, δ4.87-5.04, and δ5.74-5.87.

The 30.7 MHz ^{1}H-decoupled ^{2}H nmr spectrum of the propene product can be readily analyzed. The 2,3-d_2-isomer has a methine-d at δ5.7; the cis-1,3-d_2-isomer has a cis-vinyl-d at δ5.0; the trans-1,3-d_2-isomer has a trans-vinyl-d at δ4.8; and all isomers have methyl-d at δ1.7. Because the ^{2}H are present as dilute spins, the ^{2}H nmr spectrum is more readily analyzed than the ^{1}H nmr spectrum.

Sincerely,

Kenneth L. Servis
Associate Professor of Chemistry

Charles E. McKenna
Assistant Professor of Chemistry

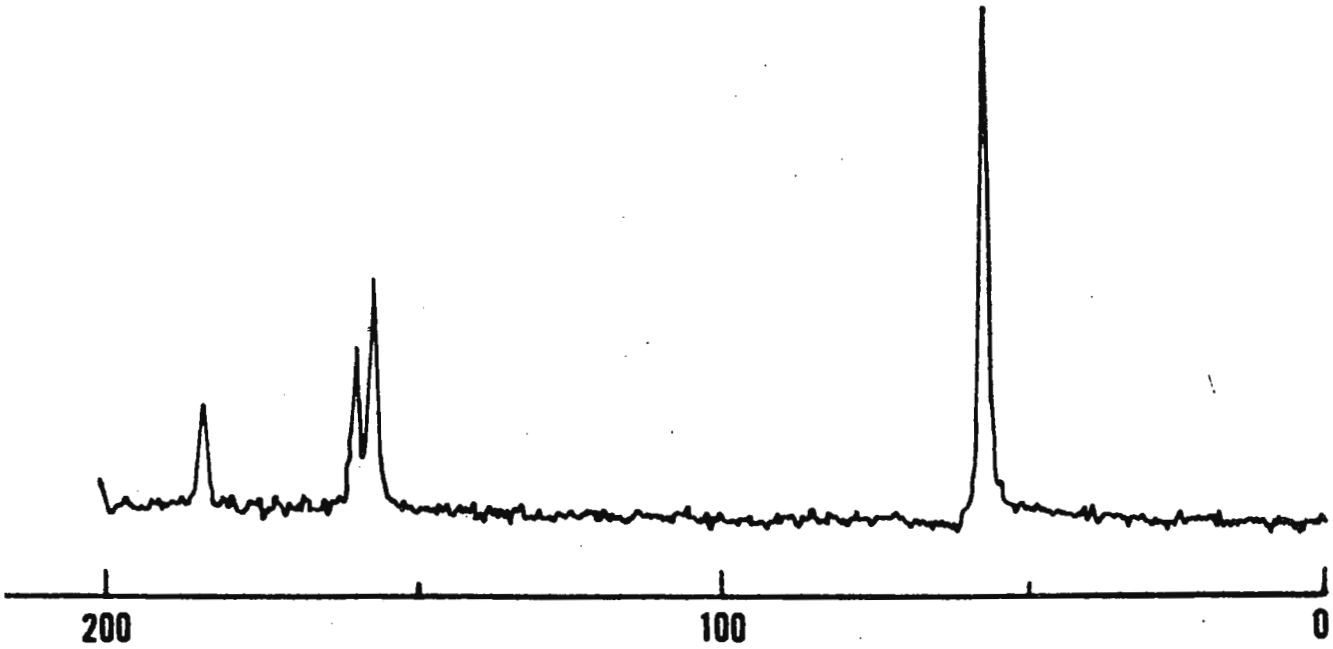

Figure ^{1}H-decoupled 30.7 MHz ^{2}H NMR spectrum of propene isolated from nitrogenase/ $^{2}H_2O$ reduction of cyclopropene. The spectrum was plotted after 400 transients (pulse width 15 μsec, acquisition time 2 sec., no pulse delay) over a 1000-Hz sweep width with the abscissa scale zero 222 Hz upfield from $C^{2}HCl_3$. The spectrometer time on the XL-200 was made available through the courtesy of Varian Associates, Palo Alto, Ca.

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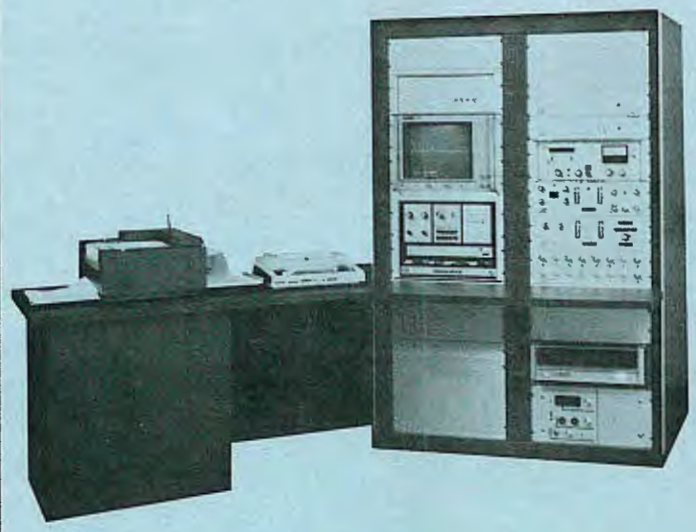

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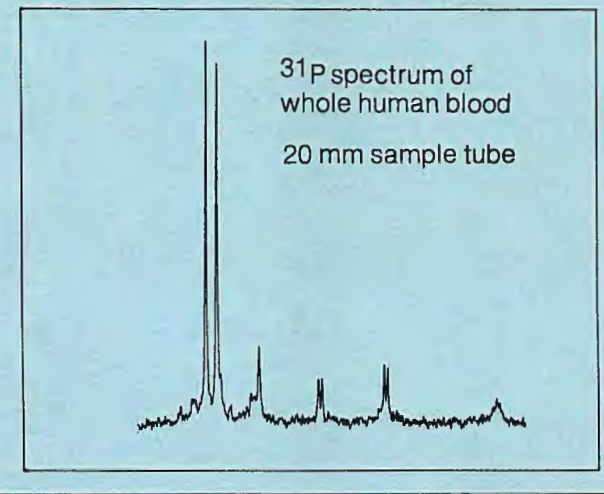

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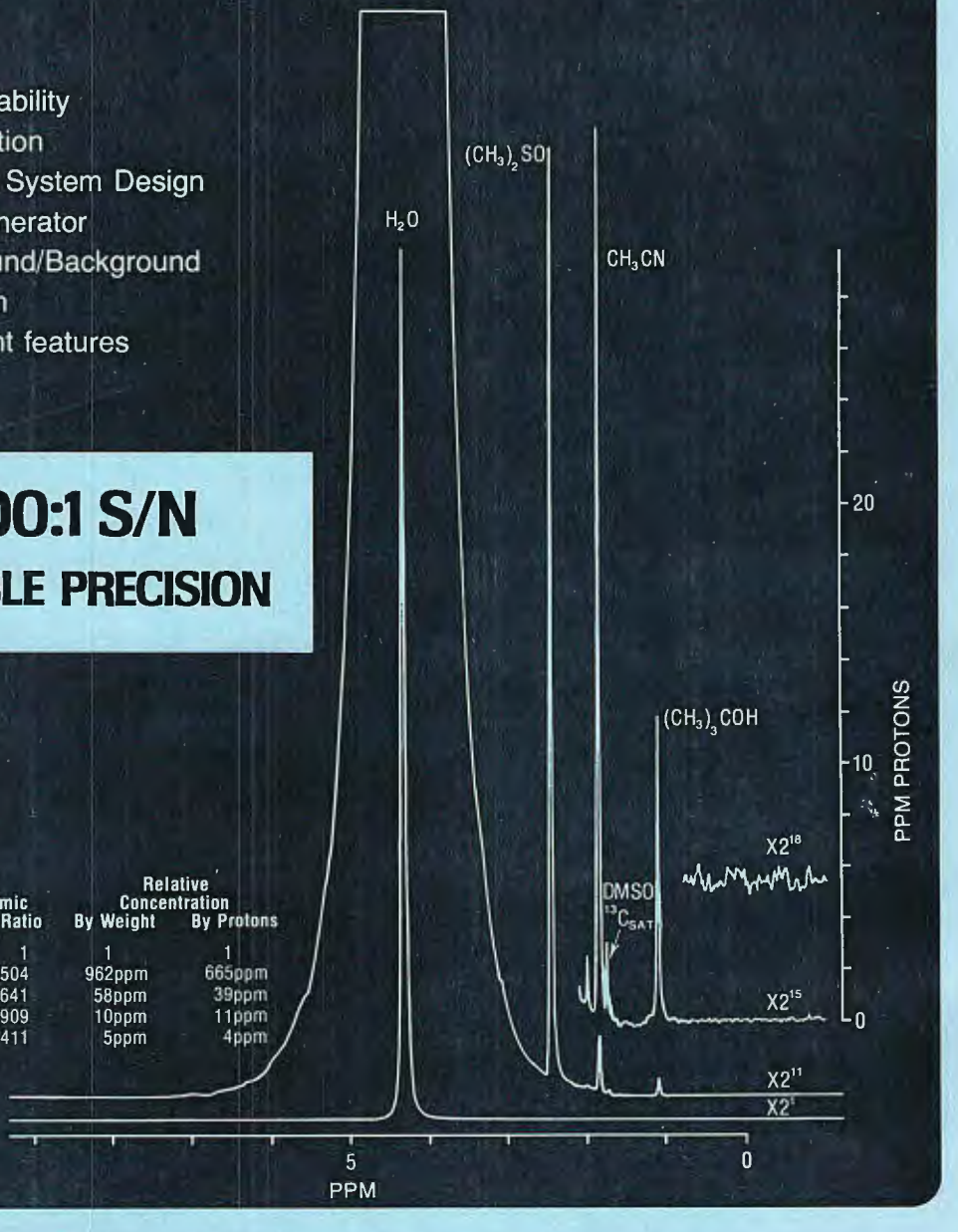

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