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NMR
NEWSLETTER

No. **290**

November, 1982

Renou, J. P. Water collagen system - Study at different relative humidities.	1	Ackerman, J. L. and Pratt, R. G. Nitrogen-14 Chemical Shifts in Solids via the MASQ Technique	31
Reeves, L. W. Dicarboxylic Acid Micelles.	3	Barieux, J. J. and Duboeuf, M. More about ^{13}C - ^{31}P coupling constant in Phosphonate.	33
Vold, R. R. 24th ENC, Asilomar, California, April 10-14, 1983	5	Ackerman, J. J. H. and Gard, J. K. A P-31 NMR External Reference for Interact Biological Systems	35
Miller, J. M. "Naked" Fluoride Exposed.	8	Cohen, J. S., Foxall, D. L. and Tschudin, R. G. Selective observation of ^{13}C enriched metabolites by ^1H NMR.	37
Marshall, A. G. Pascal Program for DISPA Plots.	9	Lichter, R. L. NMR Supervisor Position Available.	39
Laszlo, P. and Delville, A. Ion Binding or Condensation to Polyelectrolytes ?.	11		
Abraham, R. J. L.I.S. ANALYSIS OF <u>cis</u> and <u>trans</u> 2-DECALONE .	13		
Ackerman, J. L. Postdoctoral Position: Fluorochemical NMR Imaging.	16		
Marks, T. J. and Katahira, D. A. Apparatus for Anaerobic NMR Kinetics.	17		
Earl, W. L., Fukushima, E. and London, R. E. Postdoctoral Positions Available.	20		
Bolton, P. Heteronuclear Multiple Quantum Spectroscopy and Conformations	21		
Evans, C. A. 2-D Exchange Measurements on N, N-Dimethylacetamide	23		
Garroway, A. N., Moniz, W. B., Poranski, C. F. and Resing, H. A. Postdoctoral and Visiting Scientist Programs.	28		
Berlin, K. D. Sensitivity and Installation of the First XL-300 NMR Spectrometer Request for Probe Accessories for a Varian Probe V-4412 for an X.-100	23		

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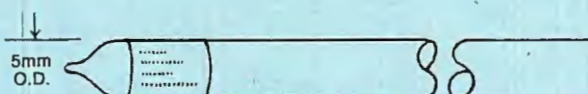
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DEADLINE DATES: No. 291 6 December 1982
 No. 292 3 January 1983

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

Dr. Bernard L. Shapiro
 Department of Chemistry
 Texas A&M University
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AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 290

Abraham, R.J.....	13	Katahira, D.A.....	17
Ackerman, J.J.H.....	35	Laszlo, P.....	11
Ackerman, J.L.....	16	Lichter, R.L.....	39
Ackerman, J.L.....	31	London, R.E.....	20
Barieaux, J.J.....	33	Marks, T.J.....	17
Berlin, K.D.....	23	Marshall, A.G.....	9
Bolton, P.....	21	Miller, J.M.....	8
Cohen, J.S.....	37	Moniz, W.B.....	28
Delville, A.....	11	Poranski, C.F.....	28
Duboeuf, M.....	33	Pratt, R.G.....	31
Earl, W.L.....	20	Reeves, L.W.....	3
Evans, C.A.....	23	Renou, J.P.....	1
Foxall, D.L.....	37	Resing, H.A.....	28
Fukushima, E.....	20	Tschudin, R.G.....	37
Gard, J.K.....	35	Vold, R.R.....	5
Garroway, A.N.....	28		

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Références à rappeler :

Prof. B.L. SHAPIRO
 Department of Chemistry
 College of Sciences
 Texas University

COLLEGE STATION TX 77843
 U.S.A.

Water collagen system -
 Study at different relative
 humidities

Theix, le 8 Octobre 1982

Dear Professor SHAPIRO,

We apply the cross relaxation method (TAMU 281-3) to collagen fibers with different ratios of hydration at different temperatures. The cross relaxation rate T_m^{-1} is determined by $T_m^{-1} = A (W_{DD} + \tau_2^{-1})$; W_{DD} is the contribution of the dipole-dipole interaction between the water and collagen protons, τ_2^{-1} is the magnetization exchange rate. At low temperatures $T < 280^\circ K$, τ_2^{-1} can be disregarded and we observe an increase in T_m^{-1} with a decrease in T . For an increase in Relative Humidity (R.H.), T_m^{-1} decrease; Since τ_1 represents the time required to jump from one site to another are in lattice water, the increase in R.H. must decrease τ_1 and T_m^{-1} as well. The same slope for different ratios of R.H. is obtained at low temperatures.

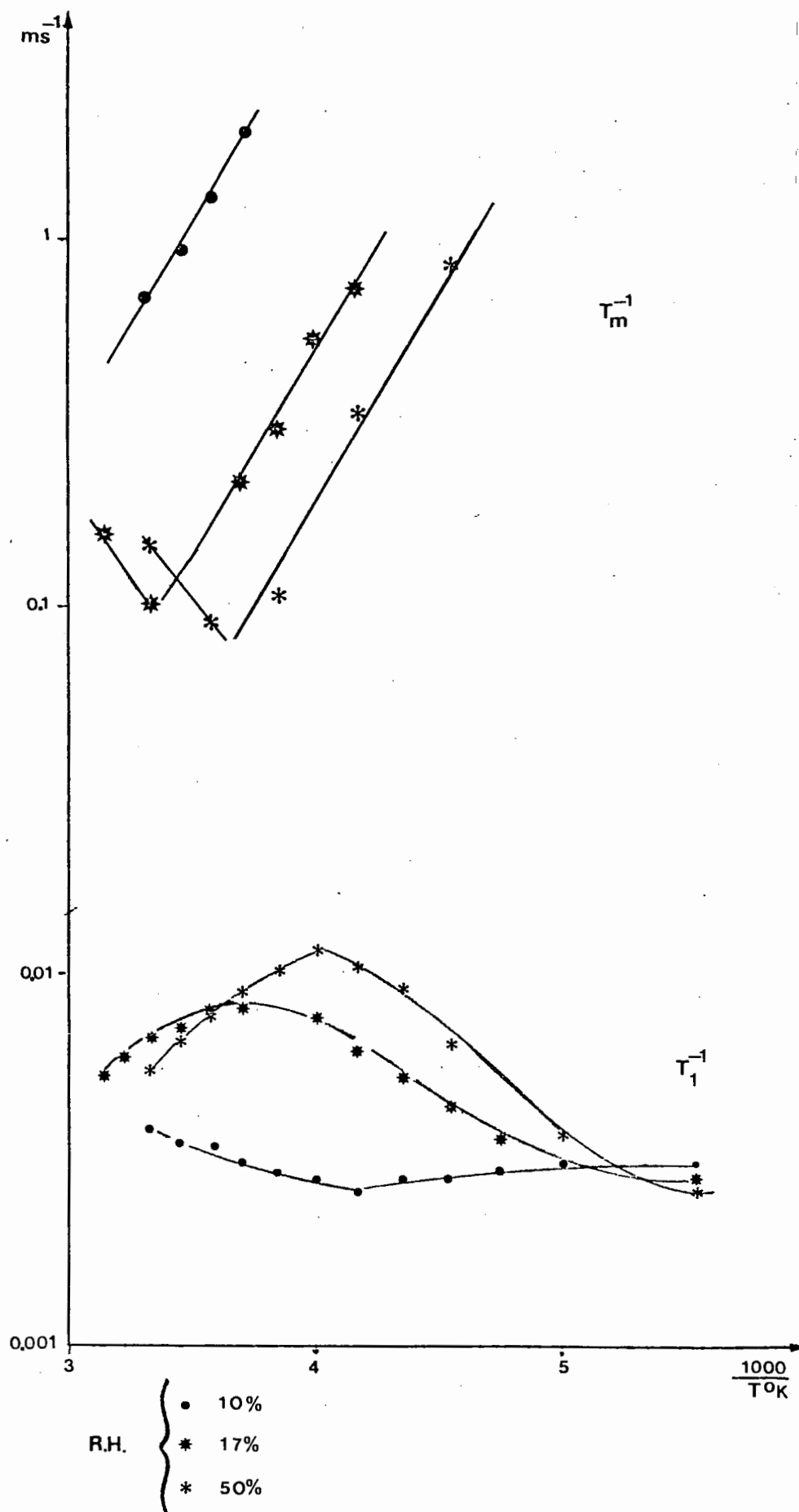
When $T > 280^\circ K$ the contribution from exchange rate is dominant. We observe the first step of the T_m^{-1} increase for the most hydrated collagen. We cannot increase the temperature, without causing the sample to lose water.

The behavior of the spin lattice relaxation rate as a function of temperature varies strongly with the relative humidity. For the most hydrated collagen, when the temperature decreases, T_m^{-1} passes through a maximum at a temperature of $250^\circ K$: we observe probably the motion of the least bound water protons.

This reserach is being carried on with samples at other relative humidities and at different frequencies.

Sincerely yours

J.P. RENOU



University of Waterloo



Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Chemistry
519/885-1211

Dicarboxylic Acid Micelles

September 27, 1982

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

Dear Barry,

I managed to collect the yellow page on passing through Waterloo and I am endeavouring to get my fingers walking. Perhaps the readers of TAMUNMR will be interested in some results obtained with α - ω dicarboxylic acids of varied intermediate chain lengths, immersed at low concentration, in the bilayers of disk-micelles, which are the units of the type II DM nematic systems. The basic notion is that if the methylene chain between the two carboxyl groups is too short to span the bilayer then the polar ends are forced to return to the same interface of the micelle and consequently the methylene chain is in an overall U conformation. The perdeuteration of the chain renders a series of deuterium quadrupole splittings in general one pair for each segment, because of the different constraint angles of the methylene groups to the interface normal and possibly also different motional averaging at each segment. As the methylene chain is lengthened, it must reach the spanning length between opposite planar interfaces of the micelles.

At the spanning length, the most stable conformation is an all-trans chain and all segments should give the same quadrupole splitting. This may be followed by plotting the $-\alpha$ CD_2 -splitting and the lowest quadrupole splitting observed against the number of intermediate methylene groups in the guest compound. When they coincide we have the spanning distance between interfaces in terms of the number of all trans segments. All splittings can be normalized to correspond to the same mesophase by methods we have already published.

Mr. Bernard L. Shapiro

September 27, 1982

The table gives a typical result for mesophases based on carboxylate head groups in the host bilayer micelle. Small amounts of the perdeuteriated (actually partially perdeuteriated) α,ω dicarboxylates were studied in a magnetically aligned potassium decanoate phase.

TABLE

Ratio of $-\alpha \text{ CD}_2-$ to lowest quadruple splitting observed in α,ω dicarboxylates in a decanoate bilayer micelle.

C_{12}	C_{14}	C_{16}	C_{20}	C_{22}
1.235	1.309	1.452	1.000	1.145

The absolute splittings are quite low with the short methylene chains, but became approximately equal to the $-\alpha \text{ CD}_2-$ splitting of the host decanoate chain for C_{20} . The spanning distance corresponds closely to that of the C_{20} all trans chain length.

Kind regards.

Yours sincerely,

Maria Elia Marcondes Helene
for Dr. Reeves.

L.W. Reeves
Professor
Department of Chemistry

LWR/aj

ENC Inc. Twenty-fourth Experimental Nuclear Magnetic Resonance Spectroscopy Conference
Asilomar, California, April 10-14, 1983

290-5

24TH ENC, ASILOMAR, CALIFORNIA, APRIL 10-14, 1983

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

Dear Barry

The next ENC will be held at the Asilomar Conference Center in Pacific Grove, California 93950, April 10-14, 1983. The meeting will have a minimum of formal sessions, opening up more time for discussion. Tentative plans include sessions on solids, polymers and biopolymers, coherence transfer and spin dynamics, experimental tricks-of-the-trade and a medley of special techniques for high-resolution spectroscopy.

There will be poster presentations and the plan is to keep the posters up throughout the meeting. Anyone interested in presenting a poster should submit an abstract to the Poster Session Chairman, Dr. Howard D. W. Hill, Instrument Division, Varian Associates, 611 Hansen Way, Palo Alto, CA 94303 before February 1, 1983. In the event that the number of submitted posters exceeds the available space, we will give preference to posters with a strong emphasis on novel experimental methods.

Registration information and a preliminary program will be sent in January to those on a mailing list consisting of attendees at the last five ENC's; anyone who suspects he/she is not on this list should contact the secretary of the ENC, Robert G. Bryant.

Local Arrangements are being handled by Lynne S. Batchelder.

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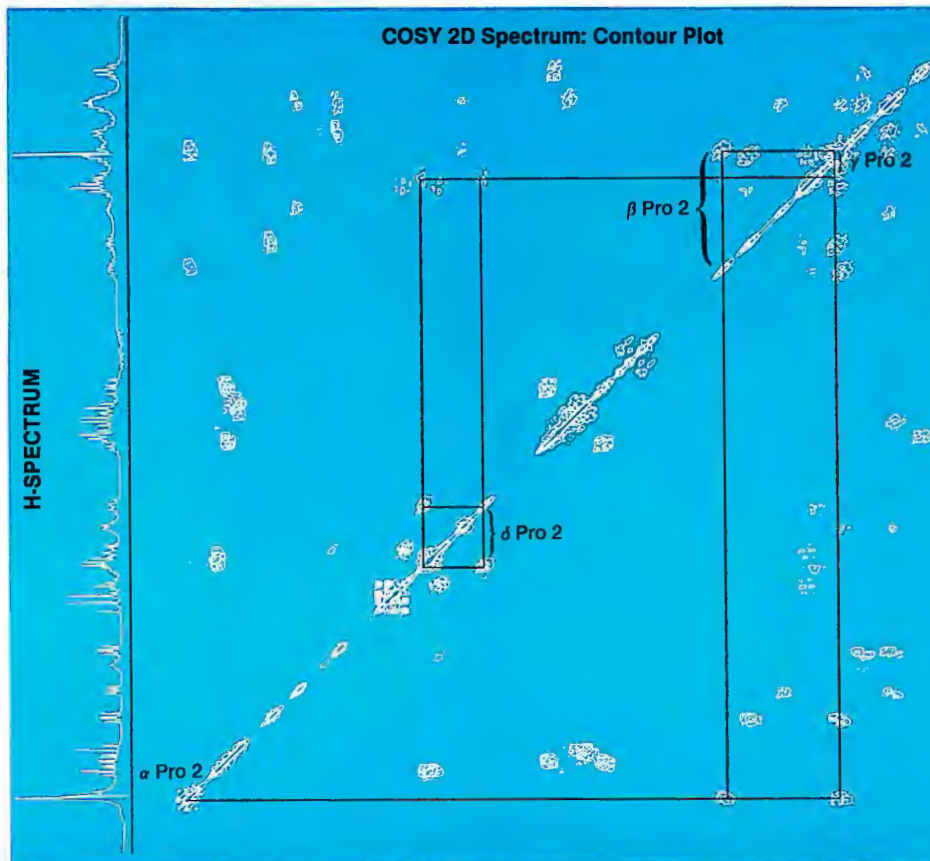
See you there



Regitze R. Vold, Chair 24th ENC
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C₅₀H₇₃N₁₅O₁₁ by 2-D NMR

When complex molecules are submitted to analysis—e.g. the oligopeptide Bradykinin sample in this experiment—two-dimensional spectra such as proton correlated spectroscopy (COSY) can often produce dramatic simplification of seemingly intractable spectra, even at high magnetic field. Here is evidence:



Chemical Shift Assignments Using 2D Proton Correlated Spectroscopy (COSY).

The pulse sequence for COSY is given by:

$$90^\circ_x - t_1 - 90^\circ_{\pm x} - \text{Acq}(t_2) \pm y$$

The chemical shifts of mutually coupled protons can be extracted from over-lapping multiplets by means of a contour plot obtained from the COSY Experiment Data. The normal Proton Spectrum is represented along the diagonal axis, and the symmetrical off-diagonal cross peaks provide the clue to any coupled protons.

The COSY Contour Plot of Bradykinin triacetate (Arg-Pro*-Pro-Gly-Phe-Ser-Pro-Phe-Arg), illustrates the technique on the aliphatic moiety. With the known position of the H α -Pro 2 (*), the chemical shifts of all the six remaining protons (2 β ; 2 γ ; 2 δ) can easily be located as shown by the connecting lines.

(1) Ad Bax and Ray Freeman, JMR 44, p. 542-561 (1981)

Q.E.D. Both spectrum and contour plot of this COSY experiment were produced on a WM 400 at the Bruker Applications Laboratory. The WM Series of high-field NMR spectrometer systems comes with an extensive software system, including programs for 2-D processing display and plotting. A full-color graphic display processor further facilitates speed and clarity of stack and contour plots.

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

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

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



The three new BRUKER brochures.

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

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

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

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

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September 28, 1982.

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

Dear Professor Shapiro:

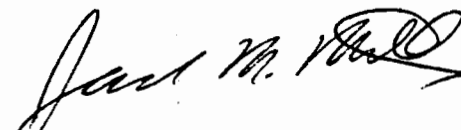
"Naked" Fluoride Exposed

The use of crown ethers to solubilize alkali metal salts in organic solvents is a major area of research. The anions in such systems have been described as "naked".

However, ^{19}F NMR spectra of samples saturated with KF in 0.2 molal 18-crown-6 solutions in organic solvents give broad lines with widths at half height (≈ 6 kHz), line shapes and chemical shifts being similar to powdered solid KF. In benzene, line widths are reduced by only a factor of two on raising the temperature from 303° to 373° K. As RbF and CsF also gave broad lines, we wondered whether quadrupolar coupling to these nuclei was important, but TlF gave similar results, with spin $\frac{1}{2}$ Tl. In aqueous solutions with KF:crown ratio of 1:10, both sharp and broad peaks were observed.

These data suggest that the fluoride is certainly not "naked" or simply "solvated", but has an interaction greater than would be expected for a similar ion pair.

Yours sincerely,



Jack M. Miller,
Professor of Chemistry.

JMM/jh



The Ohio State University

Campus Chemical
Instrument Center116 Johnston Laboratory
176 West 19th Avenue
Columbus, Ohio 43210

Phone 614 422-3446

18 October, 1982

Professor Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77843Pascal Program for DISPA Plots

Dear Barry,

In response to a number of requests, we have written a Pascal program for constructing a dispersion-vs.-absorption (DISPA) curve¹ and its corresponding reference circle from the usual absorption and dispersion data sets obtained by Fourier transformation of a free induction decay. Because the main program is written in Pascal, it should be readily adapted to most computers.

The program flattens both the absorption and dispersion baselines, and fits the absorption line to a polynomial to locate the precise peak height for use as the diameter of the reference circle. The experimental data appear as diamonds and the reference circle as a smooth curve, either on the scope or on an analog plotter. The point spacing on the final DISPA plot is made uniform by deleting superfluous points, in order to reduce computation time and redundancy. We have found all these features to be quite helpful in speeding up the display and minimizing artifacts. The program runs in 2-3 minutes or less for 4K to 8K data sets on a Bruker Aspect 2000 computer.

Examples plotted using the program are shown on the next page. The program returns the expected behavior for the theoretically simulated curves (including b and c, for which the maximum absorption "data" point was not at the center of the absorption envelope). The near-perfect circle for the ²³Na signal from aqueous NaCl (d) simply rotates when the same spectrum is deliberately mis-phased before DISPA display (e). The ²³Na data in (f) for a laurate/lauric acid mixture served as the first experimental demonstration² of dynamic frequency shifts³ in NMR.

The display subroutines are written in assembler for a Bruker Aspect 2000 computer. For anyone with a CDC disk drive, we will write the program onto his/her blank disk and return it. For others, we will send a complete description and listing of the program, which can readily (although more laboriously) be entered from a terminal.

Sincerely,

Alan G. Marshall
Professor, Chemistry & Biochemistry

1. Marshall, A. G. (1982), in Fourier, Hadamard, and Hilbert Transforms in Chemistry, ed. A. G. Marshall (Plenum, N.Y.), pp. 99-123.
2. Marshall, A. G., Lin, T.-C., Cottrell, C. E., and Werbelow, L. G. (1983) J. Amer. Chem. Soc., in press.
3. Werbelow, L. G., and Marshall, A. G. (1981), J. Magn. Reson. 45, 344-351.

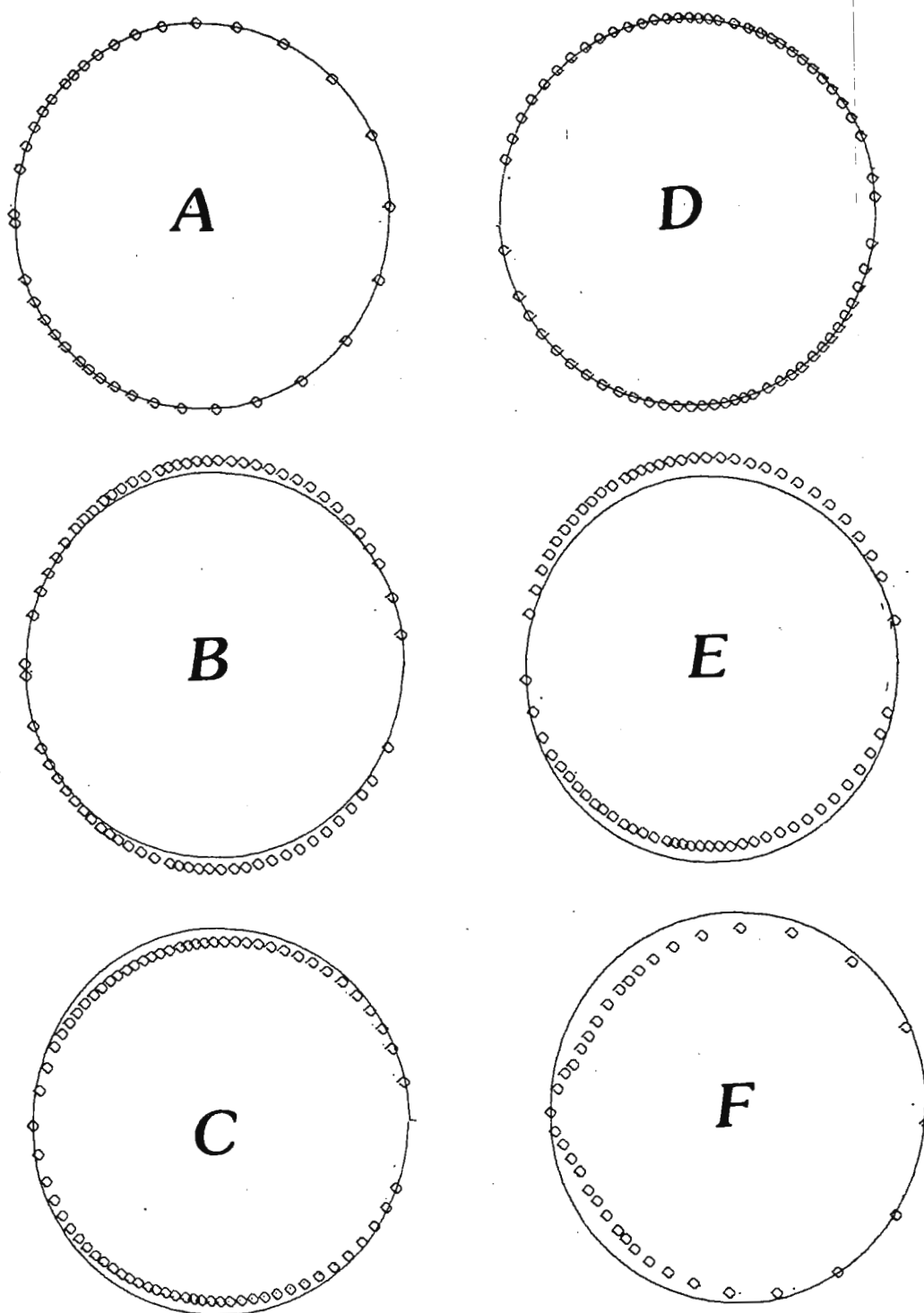


Figure. Dispersion-vs.-absorption (DISPA) plots. (a) Single Lorentzian peak; (b) Two Lorentzians of equal height and width but different frequency; (c) Two Lorentzians of equal height and frequency but different width; (d) ^{23}Na signal from aqueous 1.0 M NaCl in 15:85 mixture of $\text{D}_2\text{O}/\text{H}_2\text{O}$; (e) Same as (d), but deliberately misphased before DISPA display; (f) ^{23}Na from aqueous 1:4 laurate/lauric acid (DISPA shape identifies dynamic chemical shift, corresponding to $\omega_0 \tau_{\text{rot}} = 5.6$).

Professeur PIERRE LASZLO

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

September 23, 1982

Ion Binding or Condensation to Polyelectrolytes ?

Dear Barry,

Two rival and seemingly incompatible approaches can be and have been applied to the study of the interaction between ions and polyelectrolytes. One can solve the Poisson-Boltzmann (P-B) equation or a modified form thereof (1) to study the atmospheric condensation (2) of the fully solvated counterions. Or one can use the altogether different formalism of a chemical equilibrium, to determine binding at the various equivalent sites (2) by partly desolvated counterions.

We have applied recently the former treatment to the quantitative understanding of the activity coefficients and of the ^{23}Na nmr linewidths for sodium polystyrene sulfonate in the presence of various added salts (1). We had used five years ago the alternate, site-binding formalism to account for the ^{23}Na nmr linewidths for sodium heparinate, also in the presence of added salts (3).

We have now performed a detailed quantitative comparison of these two treatments, applied to sodium heparinate. It was well worth the effort, since the results gave us the little amused chuckle which is a too rare although redeeming feature of scientific work ! Both treatments converge, rather surprisingly, to quite similar conclusions. We were able to show that a local property such as the nmr relaxation rates for the counterion are determined predominantly by those ions present in the first shell around the polyelectro-

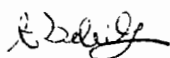
lyte, whose size we take as the diameter of the hydrated ions. For instance, the relative importance of the mean of the square of the efg, $\langle e^2 q^2 \rangle$ has values of 62.042, 0.049, 0.016, 0.005, and $0.002 \cdot 10^{34}$ SI for shells nos. 1-5, respectively; and a total value of 62.116×10^{34} SI for sodium heparinate, without added salt.

Hence, simplified two-states models, whether of the Manning or of the Guéron-Weisbuch (5) type (= condensation (2)) or of the chemical type (3) (= site binding (2)) will provide qualitatively equivalent results to those from the more complete and intellectually more satisfying full P-B treatment.

It was a joy meeting again with Lee and with you in Stirling, and directing you to the outstanding French restaurant there. The following week, I dined in Cahors : if you make it there, do not fail to try out "La Taverne", whose chef is Patrick Lannes (his intercontinental cooking engagements, from Brazil to Japan and China, would put to shame the lecture tours of anyone of us, try catching him when he is in his own kitchen).

With best regards,

Cordially yours,



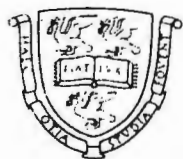
Alfred Delville



Pierre Laszlo

References :

1. A. Delville, H. Gilboa, and P. Laszlo, *J. Chem. Phys.*, 77, 2045 (1982).
2. P. Spegt and G. Weill, *Biophys. Chem.*, 4, 143 (1976).
3. L. Herwats, P. Laszlo, and P. Genard, *Nouveau J. Chimie*, 1, 173 (1977).
4. G.S. Manning, *Acc. Chem. Res.*, 12, 443 (1979).
5. M. Guéron and G. Weisbuch, *Biopolymers*, 19, 353 (1980).



DEPARTMENT OF ORGANIC CHEMISTRY
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX

TEL: 051 - 709 - 6022

The University of Liverpool

6th October 1982

Professor B.L.Shapiro,
Texas A and M University,
College of Science,
College Station,
TEXAS 77843

Dear Barry,

RE: L.I.S. ANALYSIS OF *cis* and *trans* 2-DECALONE

In response to your reminder, Helen Bergen, Derek Chadwick and myself have just finished some work on the conformational analysis of the 2-decalones by the L.I.S. technique. The method involves the use of $\text{Yb}(\text{fod})_3$ to obtain ^1H and ^{13}C L.I.S.; a four-site model of lanthanide binding and an error analysis which avoids the use of a normalising atom (program LIRAS-3).

The angle of pucker of the ketone ring in *trans* decalone is $51 \pm 2^\circ$, identical to that of cyclohexanone, but different from that determined for substituted decalones in the solid state, in which significant flattening of the ring occurs.

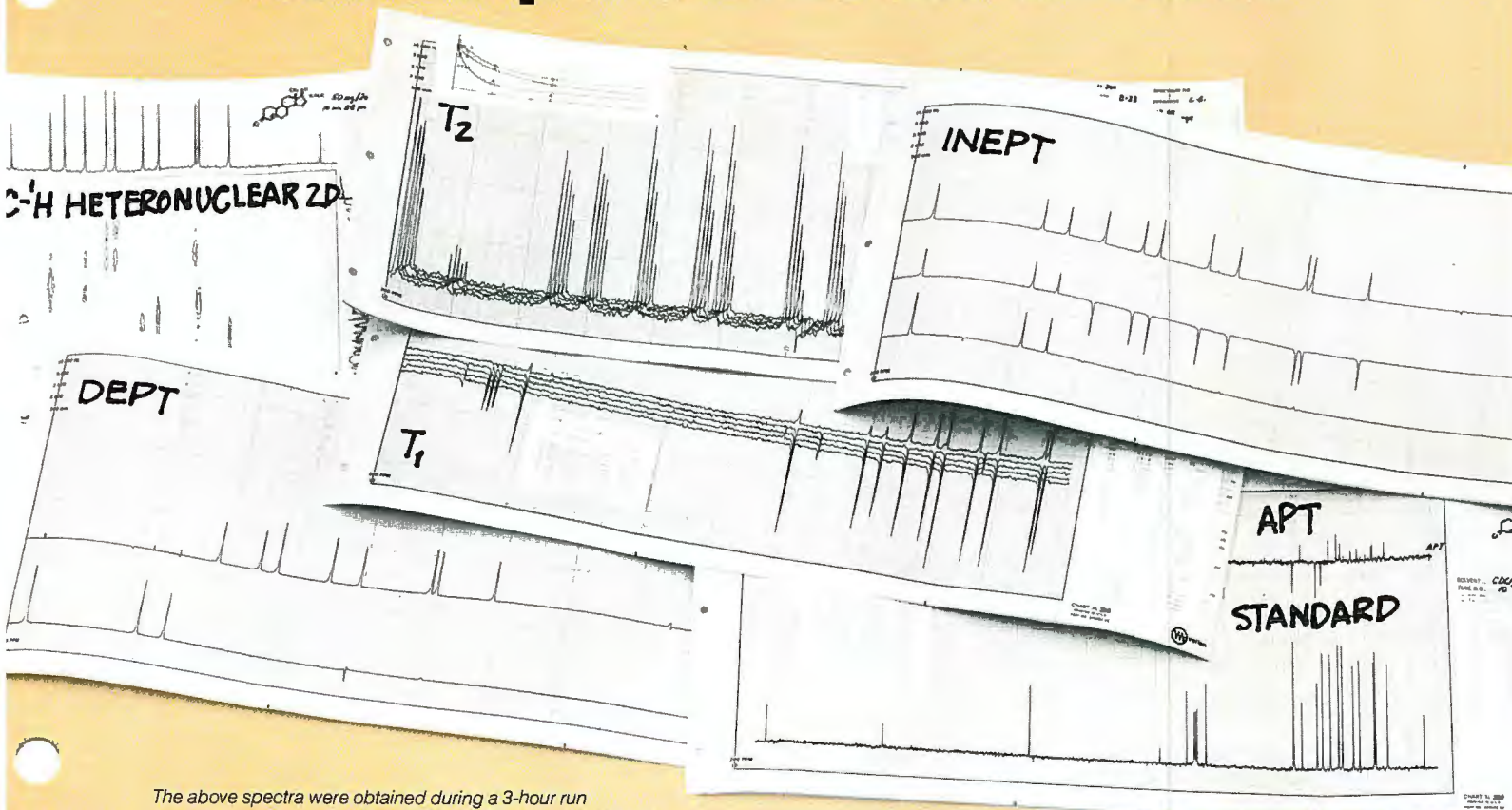
The steroidal conformer of *cis*-2-decalone, when the latter is complexed to $\text{Yb}(\text{fod})_3$ in CDCl_3 , is found to be preferred over the non-steroidal conformer by a ratio of 55:45, in contrast to the preference reported from the low temperature ^{13}C n.m.r. spectrum for the non-complexed ketone in CH_2Cl_2 . The two determinations can be combined to give the enthalpy difference in favour of the non-steroidal conformer of ca. 0.8 kcal mole^{-1} .

With best wishes,

Yours sincerely,

DR. R.J. ABRAHAM

Some manufacturers claim these experiments are difficult



The above spectra were obtained during a 3-hour run on an XL-300 Superconducting FT NMR Spectrometer System.

Varian owners perform them all before lunch

Here's what one XL Series owner says:

Dr. Peter Rinaldi is a chemist at the *Major Analytical Instruments Facility*, Greenwood, Ohio. MAIF is a research and testing facility serving Case Western Reserve University and scientists throughout the Ohio Valley region. All quotes are from the MAIF NEWSLETTER, Vol. 1, Issue 3, March 1982, reprinted courtesy of MAIF.

Software written for chemists: "Special experiments are a standard part of the XL-200 NMR software package," says Dr. Rinaldi. "We have been routinely running experiments such as INEPT, APT, solid state cross polarization, and most of the commonly used 2D-FTNMR experiments. Having run many of these myself, I can personally vouch for the tremendous advantage they offer."

Multi-tasking capabilities: "We need not be concerned about idling the instrument while time-consuming data processing and plotting is being performed; a long acquisition can be run simultaneously. It is not uncommon for the more experienced users to have the XL-200 occupied

doing three or even four tasks simultaneously for extended periods of time."

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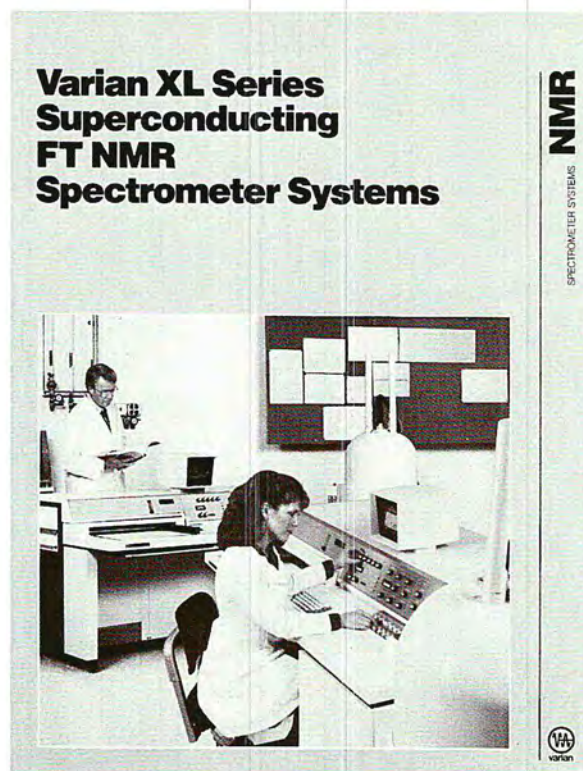
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United States

Varian Instrument Group
611 Hansen Way
Palo Alto, CA 94303



University of Cincinnati

Cincinnati, Ohio 45221
(513) 475-2263

DEPARTMENT OF CHEMISTRY

October 18, 1982

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

Postdoctoral Position: Fluorochemical NMR Imaging

Dear Barry:

We have an immediate opening for a postdoctoral student to work on an NIH-funded three year project devoted to the development and applications of ^{19}F NMR imaging of fluorochemical emulsion blood substitutes. Fluorine-based imaging of these materials introduces complications when compared to the conventional proton modality, but also suggests several exciting possibilities in medical diagnosis that cannot be explored with proton-based techniques.

In addition to myself, there are three other co-principal investigators: Leland C. Clark, Jr., (P.I.; Professor Clark performed the first liquid breathing experiments, and is one of the pioneers of fluorochemical blood substitute science), Children's Hospital Research Foundation; Ronald W. Millard, Pharmacology and Cell Biophysics, University of Cincinnati College of Medicine; and Stephen R. Thomas, Radiology, UCCM.

The responsibilities of this postdoctoral person will include a mix of gathering conventional spectra on Chemistry's NMR, obtaining images on our small scale imaging system, participating in the construction and eventual use of a whole body imager, and possibly some chemical synthesis. He/she will work primarily with Professor Thomas and myself.

Interested parties should submit their vita and arrange for two letters of recommendation to be sent to me at the above address.

The University of Cincinnati is an equal opportunity employer, and especially encourages applications from female and minority candidates.

Regards,

A handwritten signature in cursive script, appearing to read "Jerome".

Jerome L. Ackerman
Associate Professor of Chemistry

js

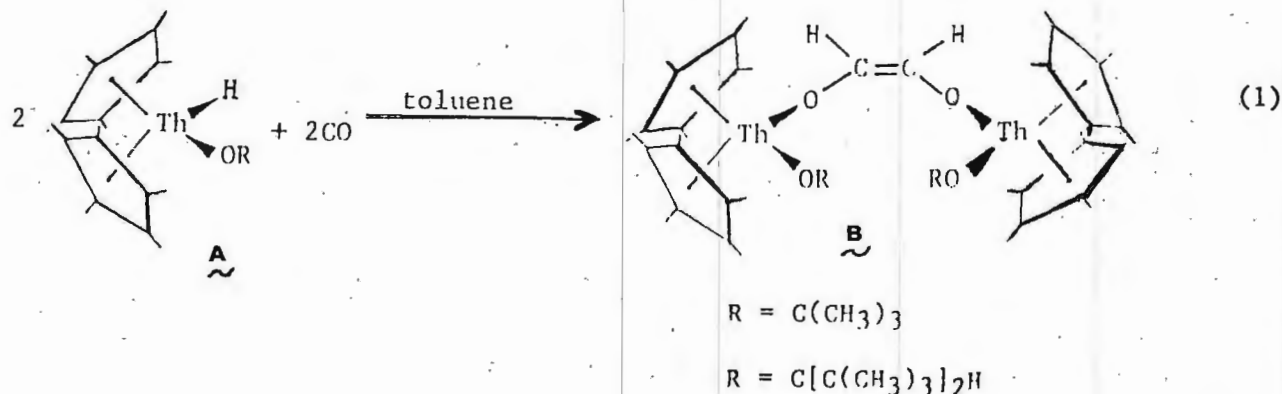
September 30, 1982

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

Apparatus for Anaerobic NMR Kinetics

Dear Barry:

We make heavy use of NMR in our studies of f-element organometallic compounds,¹ and from time to time report various aspects of the molecular dynamics and isotropically shifted NMR spectra (due to unpaired 4f and 5f electrons) in TAMU NMR Newsletter. This time we wish to report our approach to measuring the kinetics of the carbonylation reaction by which certain bis-(pentamethylcyclopentadienyl) thorium hydrides (A) are coupled to yield, via organothorium formyls,² cis-enediolates (B) (eq.(1)).³ We hope that the



apparatus employed will be of interest to other organometallic/NMR types who have mechanistic problems involving gas uptake. The catch in the present study is that the organoactinide compounds involved are extremely oxygen- and moisture-sensitive, that we wish to know the reaction orders in CO and thorium hydride, and that we wish to follow the kinetics by ¹H NMR.

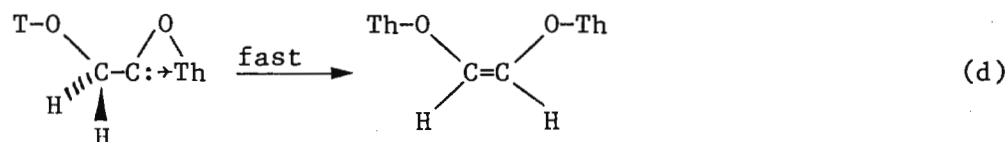
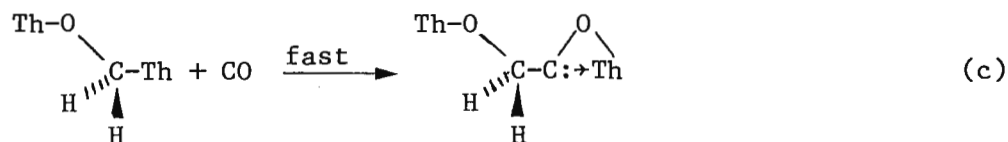
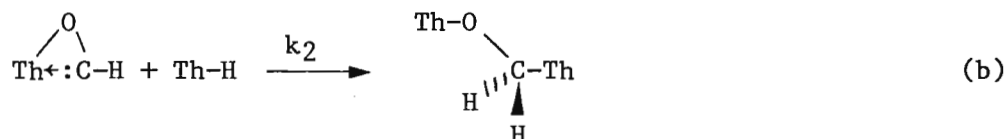
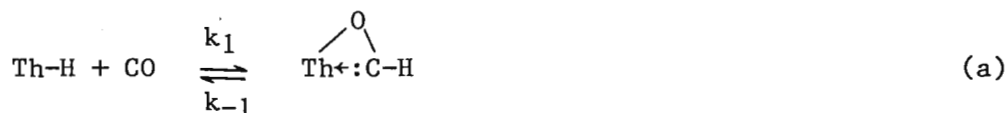
The answer is the apparatus (NMR tube!) shown in the accompanying figure which allows all reagents to be introduced by glove box (Vacuum Atmospheres recirculating type) or vacuum line techniques, and for the kinetics to be measured as a function of CO pressure while under pseudo first-order conditions in CO. The sample preparation/measurement procedure involved flaming the apparatus under high vacuum, transferring to the glove box, filling with a

measured amount of thorium hydride and scrupulously purified toluene-d₈, returning to the vacuum line, freeze-thaw degassing, and filling the vessel to a known pressure with scrupulously purified CO.⁴ The vessel was next sealed and the solution-containing portion of the NMR tube placed in a 30±0.4°C thermostatted bath, shielded from light. Rapid stirring was then initiated with a magnetic stirrer placed under the bath (control experiments established that under the present reaction conditions, variations in the stirring rate did not detectably affect the measured reaction rates).

Kinetic measurements were performed by quickly removing the reaction vessel from the constant temperature bath, transferring the stirring bar to the holding cup with a small magnet, and inserting the NMR tube into the probe (30°C) of our JEOL FX-90Q nmr spectrometer. The instrument had been previously tuned to maximize field homogeneity under non-spinning conditions and linewidths were typically on the order of 10 Hz or less. Proton spectra were recorded (with appropriate precautions to avoid saturation) on disk under previously optimized conditions (non-spinning), the NMR tube removed from the probe, the stirring bar returned to the reaction solution, and the reaction vessel quickly returned to the thermostatted bath. Typically this operation required about two minutes, and the kinetic results were found to be insensitive to whether this time was or was not included in the total reaction time. The kinetic measurements were typically carried out for four or more halflives. Even for the run at lowest CO pressure (155 torr), it was calculated that the CO pressure decreased by no more than 4% during the course of the run, ensuring that essentially constant concentrations of CO were maintained. In this particular problem, quantitative analysis consisted of integrating the Th-H resonance versus the toluene-d₇ aromatic resonance as a function of time.

The reaction in eq.(1) was found to be first-order in CO and second-order in metal hydride, consistent with the mechanism shown in the Scheme below.

Scheme



Together with other results,^{2,3} this work demonstrates that the formyls are key branch points in the reductive CO chemistry which leads to ethylene glycol derivatives (coupling) or methoxide functionalities (hydrogenation).

Although the present apparatus proved satisfactory for the problem at hand, it is easy to envision a second generation design with a magnetically-coupled device for continuous stirring and a jacketed gas bulb for more precise temperature control.

Best wishes.

Dean Katahira

Dean A. Katahira
Postdoctoral Research
Associate

Sincerely yours,

Tobin

Tobin J. Marks
Professor of Chemistry

TJM:vc

P.S. Please credit this contribution to Joe Lambert's account.

References

1. Marks, T.J. Science, 1982, 217, 989-997.
2. Fagan, P.J.; Moloy, K.G.; Marks, T.J. J. Am. Chem. Soc. 1981 103, 6959-6962.
3. (a) Katahira, D.A.; Moloy, K.G.; Marks, T.J. Organometallics, in press.
(b) Katahira, D.A.; Moloy, K.G.; Marks, T.J. Advances in Catalytic Chemistry II, in press.
(c) Fagan, P.J.; Maatta, E.A.; Marks, T.J. ACS Symp. Series 1981, 152, 53-78.
4. The vapor pressure of toluene under these conditions, ca. 20 torr, is relatively small and constant.

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545
Group INC-4, Mail Stop C346

September 30, 1982

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

Dear Dr. Shapiro:

Postdoctoral Positions Available

We would like to point out that Los Alamos National Laboratory has a competitive postdoctoral program. In general, about 10% of the applicants are selected for appointment. The starting salary is about \$23,000 /yr and includes relocation and the usual fringe benefits. Selections are made four times per year.

We have recently consolidated most of the research NMR spectroscopy in one building and we think that our physical facilities and equipment are excellent. We are presently operating four spectrometers: An XL-100 which is primarily used for routine high resolution carbon-13 spectra, a WM-300 widebore which has multinuclear capability and is primarily used for biological studies, a CXP-200 which is used for high resolution, cross polarization nitrogen-15 and proton NMR in solids, and a variable field-variable frequency wideline spectrometer primarily used for solids experiments. This last instrument can be used from essentially zero to 4.7 T in either CW or pulsed modes. It is also significant that Los Alamos is the source of the majority of the enriched stable isotopes of carbon, nitrogen and oxygen so we are often interested in labelling experiments. We are also building a high resolution, solids spectrometer at 1.4 T and have other ongoing problems in NMR instrumentation.

We would be glad to hear from any interested applicants. Los Alamos is, of course, an equal opportunity employer but applicants should be United States citizens.

Sincerely,

Bill

William L. Earl

Eiichi Fukushima

Eiichi Fukushima

Robert E. London

Robert E. London



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DEPARTMENT OF CHEMISTRY

October 17, 1982

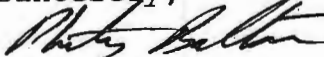
"Heteronuclear Multiple Quantum Spectroscopy and Conformations"

Dear Barry:

For some time now I have been interested in examining the conformations of various phosphate containing compounds by two-dimensional NMR. This has now branched out to the examination of the possible uses of heteronuclear experiments involving many quanta. One attraction of the multiple quantum approach is that the zero quantum heteronuclear spectrum has a multiplicity of one less than the normal spectrum in addition to being insensitive to field homogeneity. This implies that the zero and two quantum spectra of a typical cellular phosphate will not contain the proton-phosphorus-31 coupling which is rarely of interest anyway.

The spectrum shown has the zero and two quantum signals of phosphothreonine obtained with phosphorus-31 detection using a pulse sequence to be named later. The correspondence between the zero quantum and normal, phosphorus-31 decoupled proton spectrum of the sample is also shown. Thus, the multiple quantum experiment allows indirect detection of the phosphorus-31 decoupled proton spectrum. Since the multiple quantum spectrum can be simulated by traditional means the coupling constants so obtained can be related to conformational features by the usual methodology.

Sincerely,

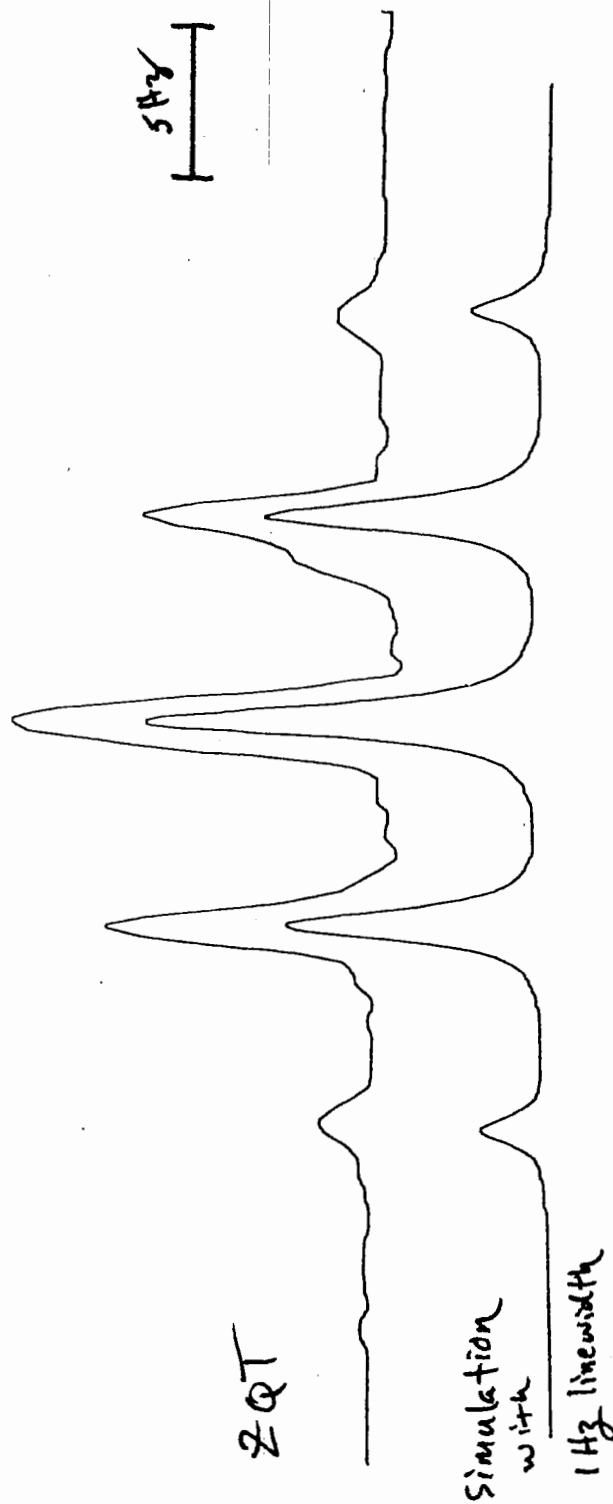
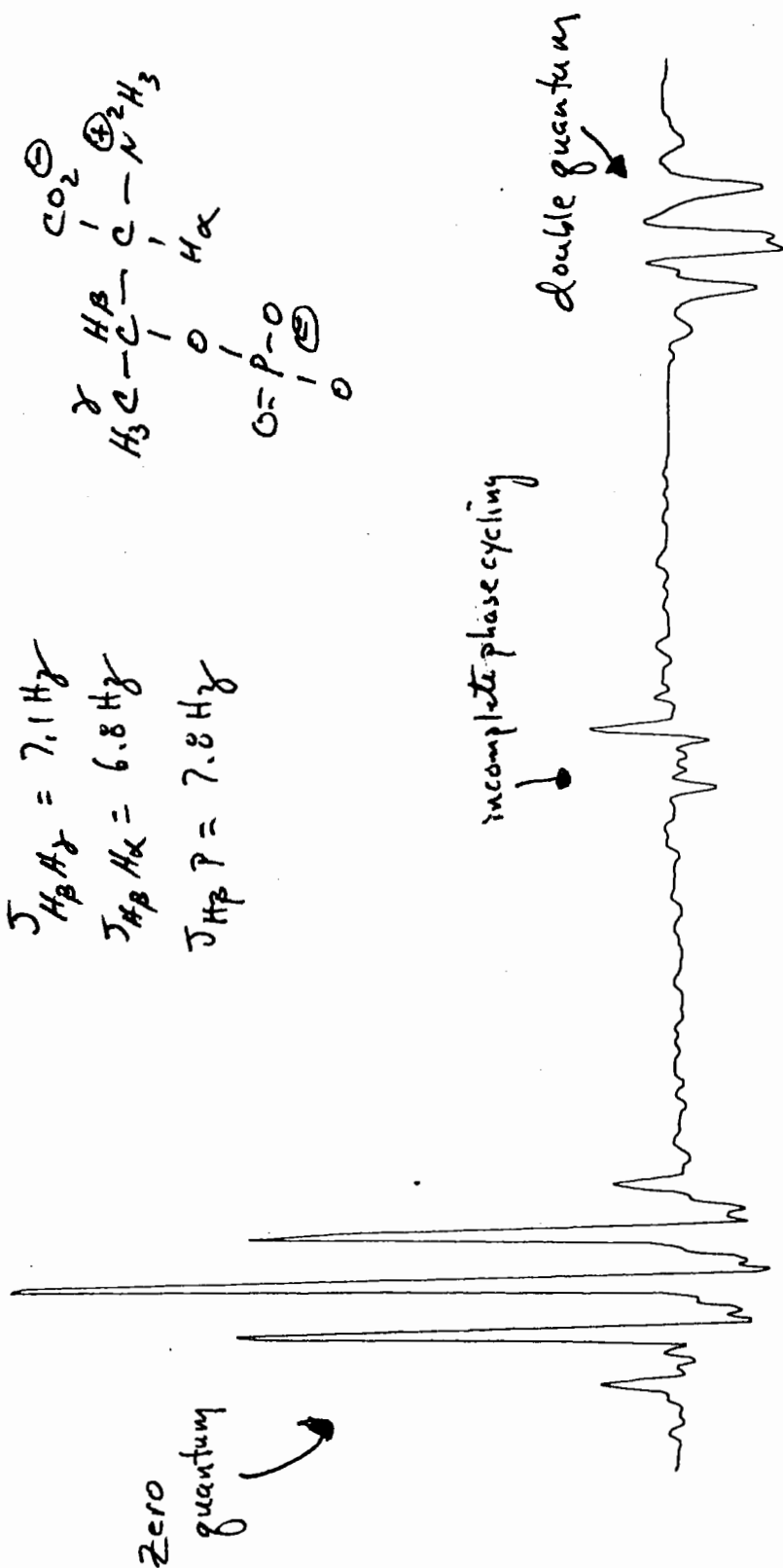
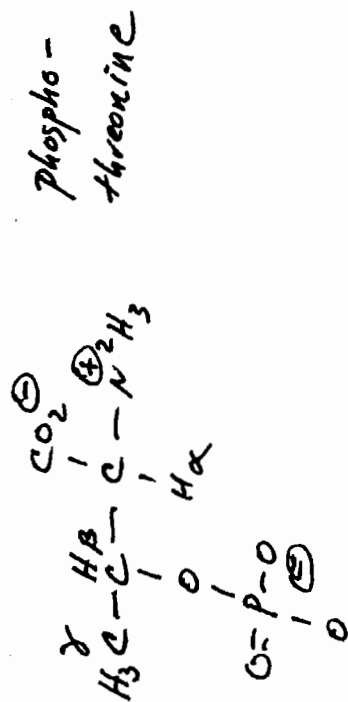


Philip Bolton

$$J_{H_\beta H_\gamma} = 7.1 \text{ Hz}$$

$$J_{H_\beta H_\alpha} = 6.8 \text{ Hz}$$

$$J_{H_\beta P} = 7.8 \text{ Hz}$$





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2-D Exchange Measurements on
N,N-Dimethylacetamide

October 13, 1982

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

Dear Barry:

Two dimensional NMR experiments are ever more commonly reported in the literature. Many spectroscopists not in possession of a modern superconducting NMR system are under the impression that they will have to wait until they have a new SCM NMR before they can enjoy the "2D experience". In this letter, I would like to demonstrate that it is possible to obtain viable 2D-NMR data on an electromagnet based NMR (in this case, an FX-90Q) using floppy disc software. All data matrices shown in this letter are 32K (256 X 128) requiring ~ 20 min. accumulation time.

I have chosen to show results from 2D-Exchange measurements on the classic system, N,N-Dimethyl Acetamide, at 90 MHz proton. A full data matrix is shown as a stacked plot in Fig. 1 with $\tau_m = 1.4$ S. Several partial plots of the N,N-Dimethyl region are shown as a function of τ_m along with a plot of the intensity data. Analysis of this data gives an exchange rate $k_{ex} = 1.04 \pm 0.10$ S.⁻¹ for a probe temperature of ~ 32°C.

It may be remarked that 2D data for rates in the slow exchange regime significantly extend the range over which the rates are measured, which should improve the accuracy in the determination of activation barriers.

Examples of COSY and SECSY measurements on Ethyl Crotonate at 90 MHz are shown in Fig. 2. Both plots are ~ 8 ppm X 8 ppm. Please note I make no claim that one should grab his nearest sample of BPTI for 2D measurement at 90 MHz. However, correlation measurements are possible (and convenient) to do.

Sincerely,

C. Anderson Evans
Manager-Applications Lab

CAE/mjd



"Bringing the Scientist Tomorrow's Capabilities Today."

DIMETHYL ACETAMIDE
2D EXCHANGE τ_m 1.4 Sec.

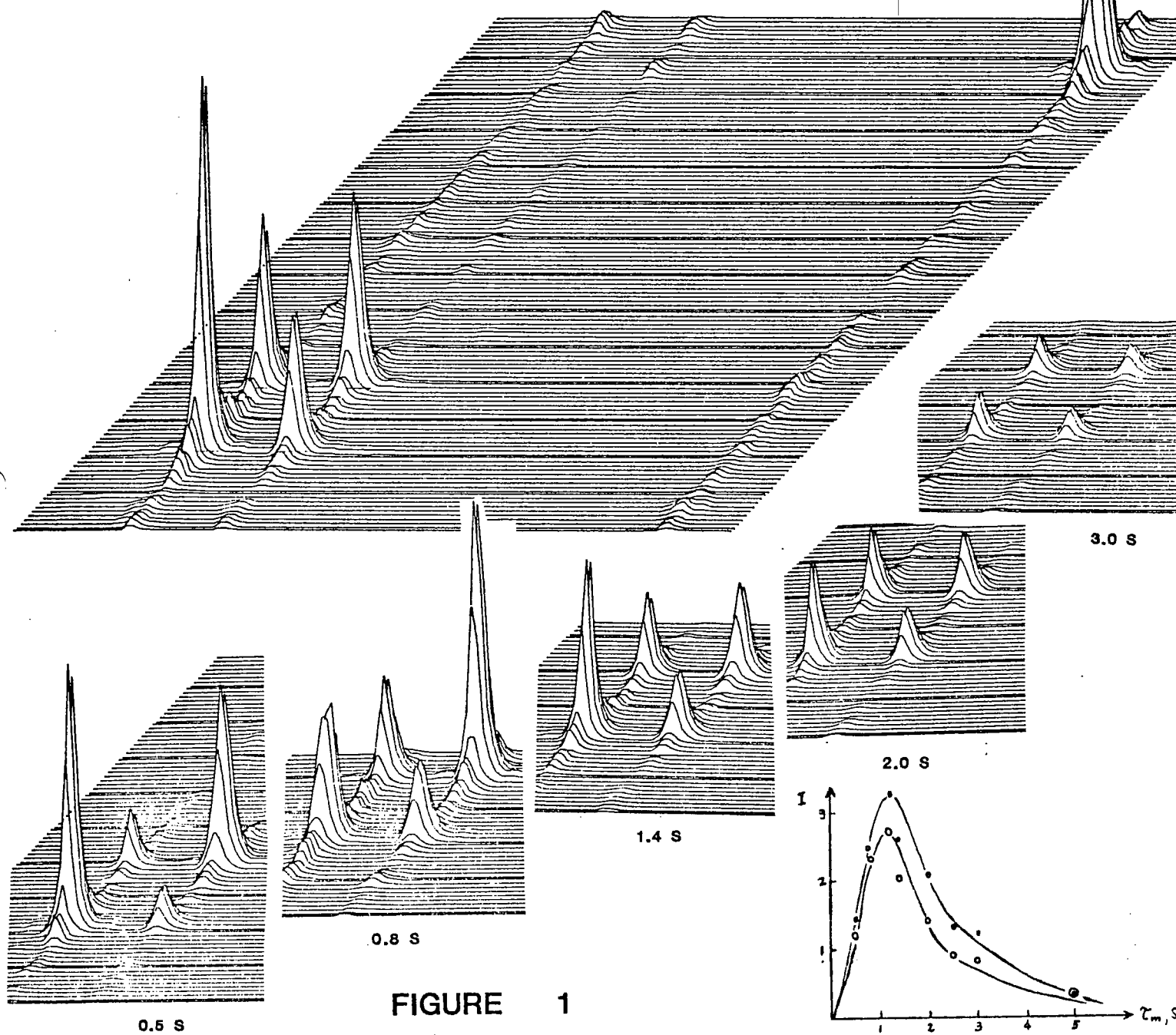
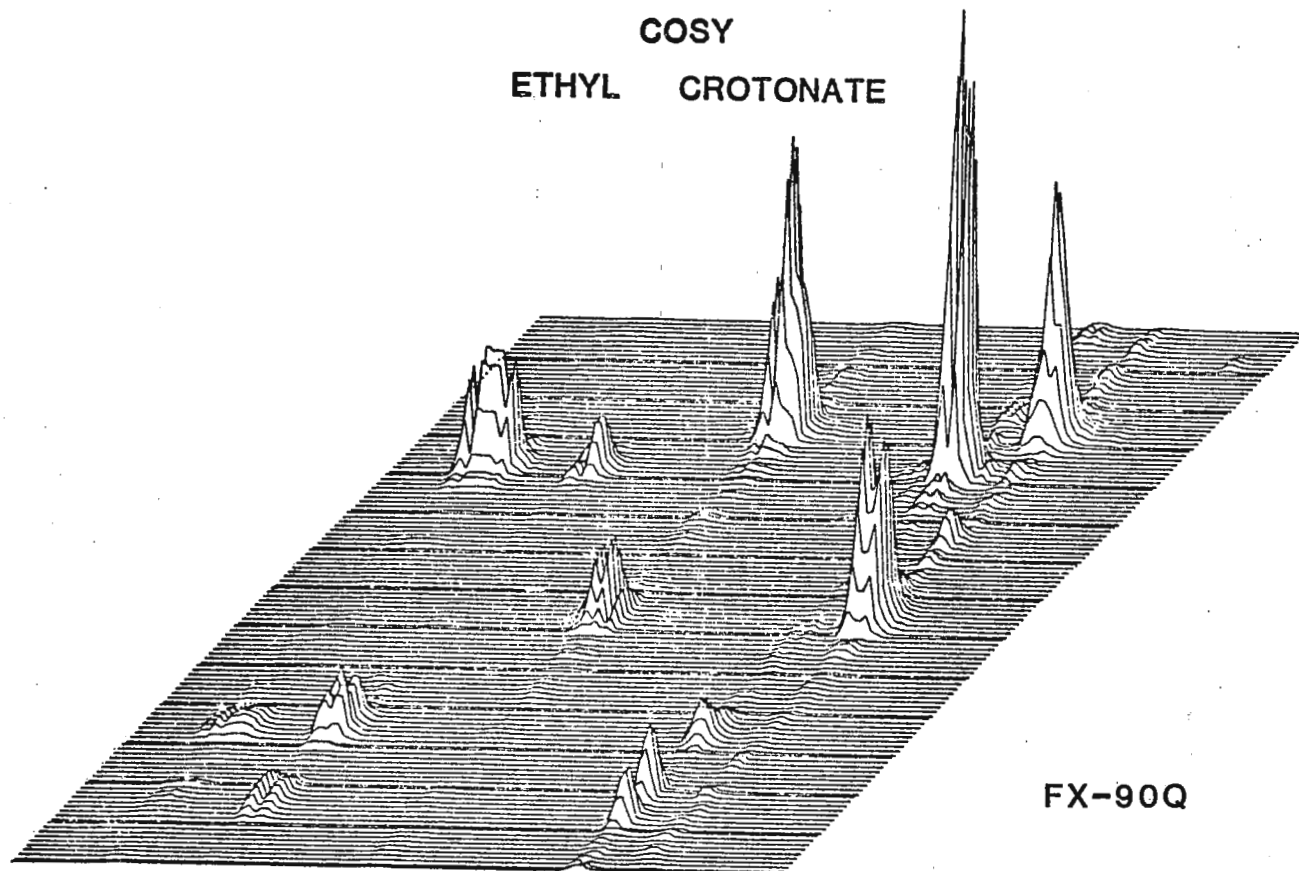


FIGURE 1

COSY
ETHYL CROTONATE



FX-90Q

SECSY
ETHYL CROTONATE

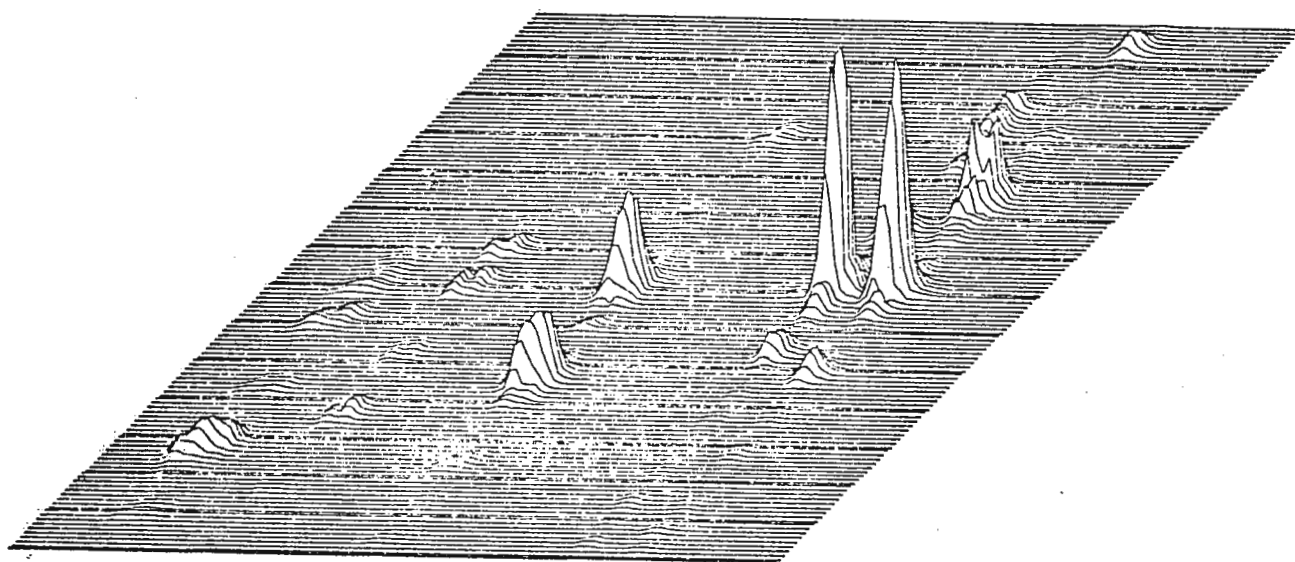


FIG. 2

GX Report #2

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6 October 1982

Postdoctoral and Visiting Scientist Programs

The Naval Research Laboratory has programs for both postdoctoral and visiting scientists. We are writing, on behalf of the Polymer Diagnostics Section, to inform TAMUN Newsletter readers of some of these opportunities.

The NRL postdoctoral program is administered by the National Research Council (NRC) and the applications are approved on a competitive basis. The present stipend is \$23,500 per year. Relocation expenses and a professional travel allowance are provided. The applicant must be a U.S. citizen. Appointments are for two years. The following attraction has been added recently; a third year of contractual support may be available from the Office of Naval Research for selected NRC associates who continue research in post tenure positions at academic institutions. Application and research proposal forms are available from NRC at the following address and must be completed and returned to NRC by 15 January 1983.

Associateship Office, JH 610-PC
National Research Council
2101 Constitution Avenue, N.W.
Washington, D. C. 20418

Announcement of awards is usually made in April with tenure normally beginning within six months of the awards, but not later than 1 February 1984.

The Laboratory also has a program for visiting faculty members on sabbatical or leave, under the provisions of the Intergovernmental Personnel Act (IPA). Depending on the circumstances, supplemental or full support may be available. An IPA agreement may cover any period from a few months to two years. Allowances are provided for moving expenses, travel to scientific meetings, etc.

Within the Section are the following opportunities for research under the NRC program.

Molecular Characterization of Polymers
13C NMR Solid State Spectroscopy of Polymers and
Surfaces
NMR Imaging for Nondestructive Evaluation
NMR in Electroactive Polymers and Graphites

The NRC deadline is 15 January. Please encourage anyone interested to contact us directly and informally. Your assistance in publicizing these postdoctoral and visiting scientist programs is greatly appreciated.

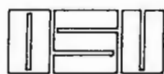
Sincerely,

AI
A. N. Garroway
(202) 767-3239

Bill
W. B. Moniz
(202) 767-2323

C. F. Poranski, Jr.
(202) 767-2488

H. A. Resing
(202) 767-2025



Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74078

October 19, 1982

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

Title: Sensitivity and Installation of the First XL-300 NMR Spectrometer
Request for Probe Accessories for a Varian Probe V-4412 for an XL-100
Dear Barry:

Sorry that you had to remind me about our contribution. We have been very busy with the installation of the first Varian XL-300 NMR spectrometer. All went extremely well with highly competent personnel from Varian doing a first class job. We have begun to do some tests and checks of our own and thought that some might be interested in the S/N ratio we obtain on the $^1\text{H}/^{19}\text{F}$ probe using the old standard of 1% ethylbenzene. You will note that the S/N ratio as calculated on the enclosed sheet was 1400/1 almost twice what the specifications provide. We have found the instrument performs quite well and is highly sensitive to the less commonly observed nuclei such as ^{15}N , ^{17}O , ^{33}S , etc. We are only beginning to test the capability of this spectrometer but so far it really looks superb.

We are also seeking someone who might have a Varian V-4412 probe as we are interested in it for our old XL-100 spectrometer which is still turning out data at a steady rate. If some one has such a probe which they might consider for sale, I would be pleased to hear from them.

I trust this will satisfy for our contribution this time and we shall do better in the future. Best regards.

Sincerely yours,

K. D. Berlin
Regents Professor

$$S/N = \frac{168}{3} \times 2.5 \times 10 = 1400 : 1$$

200-mm

3,000

1,500

1,200

300

2,000

1,000

500

200

1,000

500

400

100



University of Cincinnati

Cincinnati, Ohio 45221
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DEPARTMENT OF CHEMISTRY

Nitrogen-14 Chemical Shifts in Solids via the MASQ Technique

October 19, 1982

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

Dear Barry:

Who was that MASQ-ed nucleus (see following page)?? Why, that was nitrogen-14, whose isotropic chemical shift spectrum was obtained by synchronous sampling^{1,2} of the FID from a magic angle experiment.

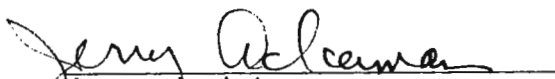
Since no new experiment will be accepted in the NMR community without a catchy acronym, we submit as a general handle for the rash of recent studies of spins $I > \frac{1}{2}$ -- magic not necessarily being limited to 54.7° -- the following: Magic Angle Spinning of Quadrupoles.

Of prime importance for integral spin nuclei, of which the most useful are likely to be ^2H and ^{14}N , is the settability and stability of the angle. The static quadrupolar powder widths of both compounds whose spectra appear overleaf are on the order of 50 kHz. Taking the entire isotropic linewidth (.7 ppm, 13 Hz) as due to angle variation suggests that the maximum angle deviation is less than 11 millidegrees. Other important linewidth contributions could be residual proton couplings (no decoupling was employed), ^{14}N homonuclear couplings, second order quadrupole coupling, susceptibility anisotropy, and a distribution of isotropic shifts.

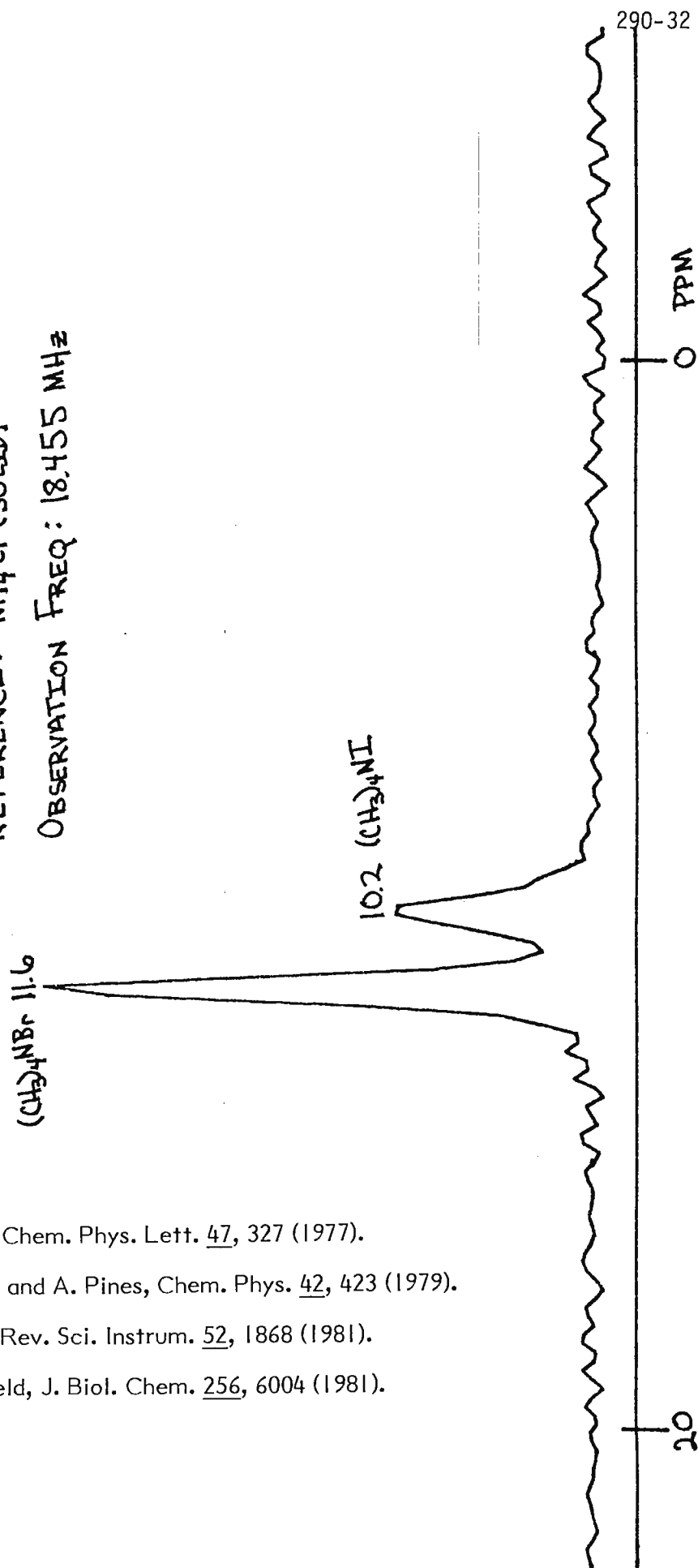
Our spinner is specially optimized for these experiments, having a gas-lubricated journal bearing³ for axis stability, and a differential screw arrangement for obtaining angle settability on the order of 3 millidegrees.

We expect that most practitioners of NMR might rapidly tire of looking at tetraalkylammonium salts. Although we can never hope to fully narrow the resonances of nitrogens in "normal" environments (where quadrupole couplings could run to 4 or 5 MHz), one potential area of applicability could be in nitrogen chemical shift experiments in phospholipids⁴ or other systems where molecular motion has reduced couplings to manageable values.


Ronald G. Pratt


Jerome L. Ackerman
Associate Professor

SAMPLE: $(\text{CH}_3)_4\text{NBr} / (\text{CH}_3)_4\text{NI}$ (50/50 BY VOL)
 NUMBER SCANS: 500 RECYCLE DELAY: 5 SEC
 SPECTRAL WIDTH: $-/+ 1620 \text{ Hz}$
 LINE BROADENING: -4 Hz (0.22 PPM)
 REFERENCE: NH_4Cl (SOLID)
 OBSERVATION FREQ: 18.455 MHz



1. M. Maricq and J. S. Waugh, Chem. Phys. Lett. 47, 327 (1977).
2. J. L. Ackerman, R. Eckman and A. Pines, Chem. Phys. 42, 423 (1979).
3. F. D. Doty and P. D. Ellis, Rev. Sci. Instrum. 52, 1868 (1981).
4. T. M. Rothgeb and E. Oldfield, J. Biol. Chem. 256, 6004 (1981).

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

TEXAS 77843

U.S.A.

N/réf. JJB/SL

V/réf.

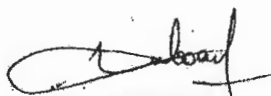
PIERRE-BÉNITE, 10 October 18th, 1982

Dear Professor SHAPIRO,

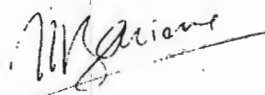
More about ^{13}C - ^{31}P coupling constant in Phosphonate

The magnitude of the coupling of carbon to phosphorus, especially J_{CP} , varies greatly with carbon hybridization. Some typical values in phosphonate series are given in Table I.

Recently, we have been concerned with a series of diethylpyrimidinylphosphonate and the ^{13}C spectrum of a representative compound is shown in figure 1. Some interesting features can be noticed: the high magnitude of J (226 and 271 Hz) bridging the gap between aryl and acetylenylphosphonate and the general larger value for long range coupling constant through hetero atoms (J_{P6C2} , $J_{\text{P2C6}} = 19$ and 17 ; $J_{\text{P6C4}} = 6$ Hz).



M. DUBOEUF



J.J. BARIEUX

	^1J	^2J	^3J	^4J	^5J	Ref.
	137	8.7	6.8	2.9	3.6	(2)
	199					(3)
	184	10	13	2.5		(3)
	190	-	-			(3)
	188	2	18	6	2	(4)
	{ 226(C_4, C_6) 271(C_2)		23	19(P_6C_2) 17(P_2C_4) 6(P_6C_4)	4	(3)
	294	51				(5)
	304	54				(6)

(1) coupling constants in Hz ; only absolute value is given

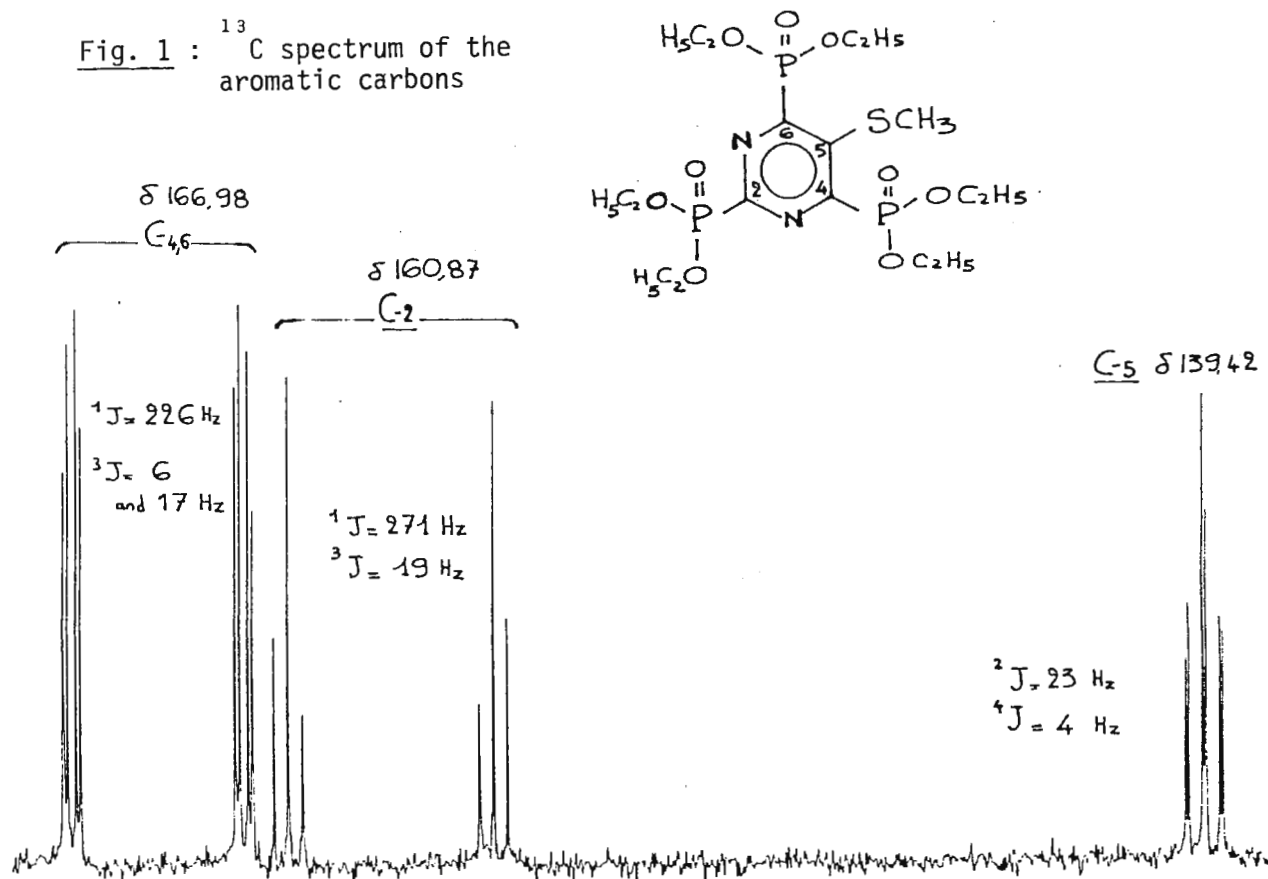
(2) L. Ernst, Org. Magn. Res. 1977, 9, 35

(3) Results from our laboratory

(4) G.A. Krudy, R.S. Macomber, J. Org. Chem., 1978, 43, 4656

(5) R.M. Lequan, M.J. Pouet, M.P. Simorin, Chem. Comm., 1974, 475

(6) G. Mavel, M.J. Green, Chem. Comm., 1968, 742

Fig. 1 : ^{13}C spectrum of the aromatic carbons

WASHINGTON UNIVERSITY



ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

October 19, 1982

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

Dear Barry:

A P-31 NMR External Reference for Intact Biological Systems

As our efforts to establish an NMR facility for the study of intact biological systems begin to reach completion we have recognized the need for a convenient external P-31 reference that is appropriate for the phosphorus metabolite spectral region. After much searching and with the help of Stephen Kinney at Monsanto, we have found what should be a generally useful reference compound for both P-31 NMR intensity and chemical shift measurements on intact tissue and cell preparations.

Hexachlorocyclotriphosphazene (HCCTP), has a chemical shift of 22.9 ppm relative to phosphocreatine and 19.9 ppm relative to 85% H_3PO_4 ; this places it close to but not on top of the metabolite spectral region, figure 1. HCCTP has a narrow linewidth in the absence of proton decoupling (ca. 12 Hz at 145.8 MHz) and has a chemical shift that is quite insensitive to temperature changes around 37°C.

We have been using chromic acetylacetonate doped benzene solutions of HCCTP primarily as an intensity reference with good results for both perfused and in vivo tissue P-31 NMR experiments. A 1 M HCCTP solution in C_6D_6 with 62 mM chromic acetylacetonate gives a T_1 of 0.24 seconds without appreciable line broadening; this is reduced greatly from the natural T_1 of ca. 16 seconds at 145.8 MHz.

HCCTP is available from Aldrich Chemical Co. as phosphonitrilic chloride trimer.

Sincerely,

Janice Koles Gard
Janice Koles Gard

Joe
Joseph J.H. Ackerman

JJHA/kk

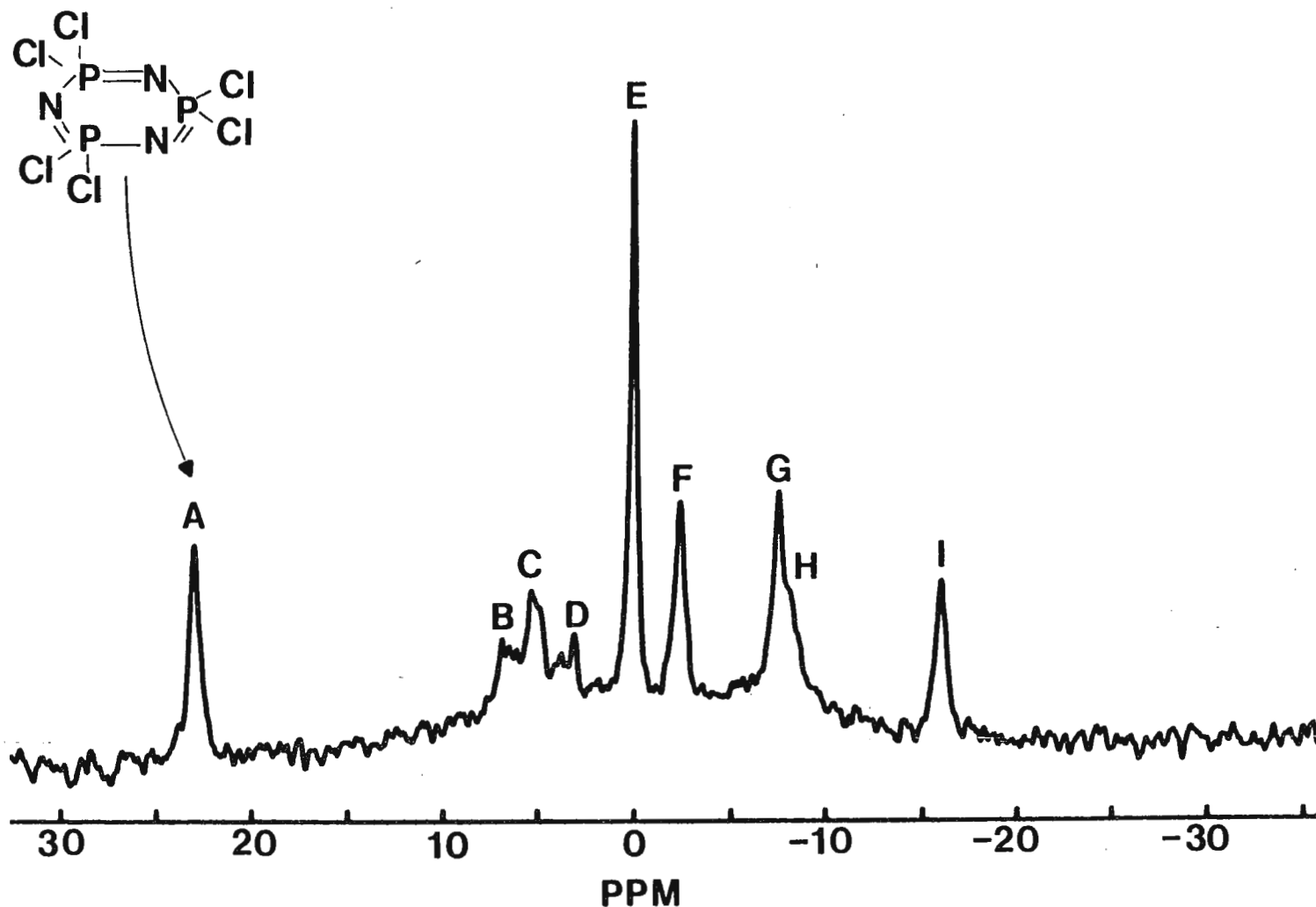


Fig. 1 $P-31$ NMR spectrum of Langendorff perfused, isovolumic rabbit heart (ca. 6 grams, 37°C) at 145.8 MHz. Spectrum represents four minutes of data averaging (240 scans, 45° pulses, 10,000 Hz spectral width, 1024 total data points, zero filled to 2048 points, 25 Hz exponential line broadening filter applied). No proton decoupling was employed. Intracellular phosphocreatine (PCr) is taken as 0.0 ppm and IUPAC convention is used to define chemical shifts. Peak assignments are: A) external hexachlorocyclotriphosphazene, 1 M in C_6H_6 , contained in a Wilmad spherical microcell of ca. 35 μl volume and placed in the left ventricle; B) sugar phosphates; C) inorganic phosphate; D) phosphoesters; E) PCr, 0.0 ppm; F) γ -phosphate of ATP and β -phosphate of ADP; G) α -phosphate of ATP and ADP; H) NAD and NADH; I) β -phosphate of ATP.



DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service
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Bethesda, Maryland 20205

October 20, 1982

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

Title: Selective observation of ^{13}C enriched metabolites by ^1H NMR

Dear Barry:

We are happy to respond to your annual reminder with a report of a method to overcome the low sensitivity of ^{13}C NMR applied to metabolic studies.

Recently, Sillerud *et al.* (1) utilized $^1\text{H}\{^{13}\text{C}\}$ double resonance difference spectroscopy to follow the aerobic metabolism of ^{13}C -acetate in yeast. But, this method with ^{13}C decoupling has a number of disadvantages. We have adapted spin echo $^1\text{H}\{^{13}\text{C}\}$ difference spectroscopy, described by Freeman *et al.* (2,3) and Bendall *et al.* (4) for organic compounds, to a study of $[1-^{13}\text{C}]$ glucose metabolism in yeast. In order to avoid enzyme-catalyzed C-H exchange in D_2O medium we presaturated the H_2O using a DANTE sequence (5). The modified pulse sequence may be written:

PROTONS $[\theta^\circ(\text{Y})-\Delta_1-\text{I}_\text{N}-\Delta_2-90^\circ(\text{X})-\tau-180^\circ(-\text{X})-\tau-\text{AQ}]$
CARBON $180^\circ(\text{ON/OFF})$

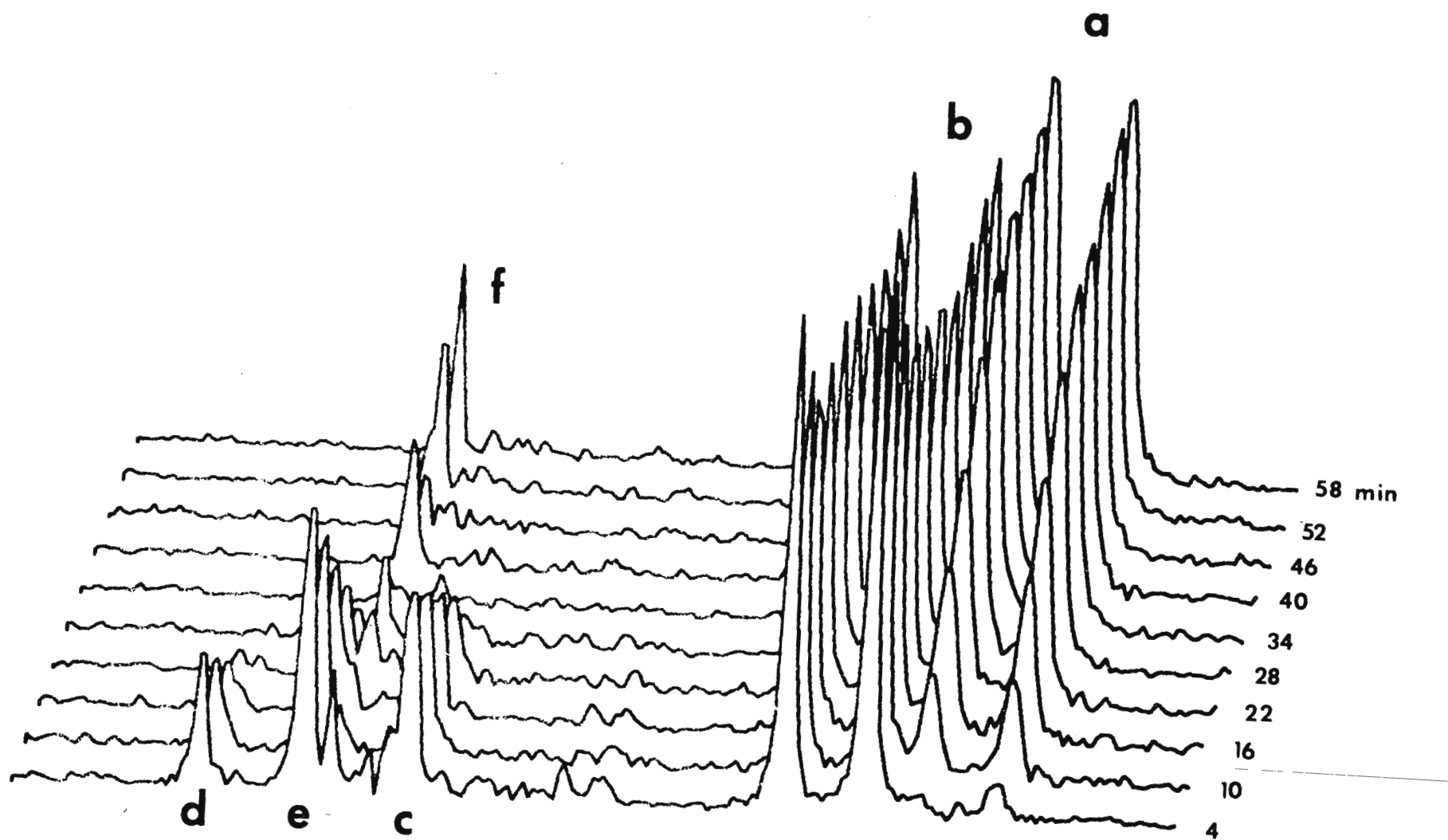
The parameters θ , N , and Δ_1 control the selectivity of the presaturation, and Δ_2 is a switching delay. The delay τ is chosen to be equal to $1/2\langle\text{J}_{\text{CH}}^1\rangle$ to obtain optimum difference signals. The 180° carbon pulse was obtained by modifying our 270 MHz Nicolet NMR spectrometer; the gated output of the decoupler synthesizer at 78 MHz was mixed with a gated 10 MHz master clock signal. After a filter and intermediate amplifier the observe broad band amplifier was used to obtain the final pulse at 68 MHz ($\gamma\text{B}_1/2\pi=36$ kHz). The receiver coil of our 5 mm $^1\text{H}/^{13}\text{C}$ double tuned probe was used in these experiments.

With the $^1\text{H}\{^{13}\text{C}\}$ spin echo difference method we have followed the anaerobic conversion of $[1-^{13}\text{C}]$ glucose to ethanol (Fig. 1) (6). This method is approximately 20 times more sensitive than direct ^{13}C observation and twice as sensitive as the $^1\text{H}\{^{13}\text{C}\}$ decoupling method. In addition, while $^1\text{H}\{^{13}\text{C}\}$ decoupling results in positive and negative components that can be difficult to interpret, the $^1\text{H}\{^{13}\text{C}\}$ spin echo difference method gives a simple doublet for each set of ^{13}C - ^1H satellites. We believe this method will have many potential applications where ^{13}C -labelling is used, particularly in metabolic studies.

Yours sincerely,

Jack Cohen *D.L. Foxall* *R. Tschudin*

Jack S. Cohen, David L. Foxall, Rolf G. Tschudin



References

1. L. O. Sillerud, J. R. Alger and R. G. Shulman, J. Mag. Res. **45** 142 (1981).
2. R. Freeman and H. D. W. Hill, J. Chem. Phys. **54** 30 (1971).
3. R. Freeman, T. H. Mareci and G. A. Morris, J. Mag. Res. **42** 341 (1981).
4. M. R. Bendall, D. T. Pegg, D. M. Doddrell and J. Field, J. Am. Chem. Soc. **103** 934 (1981).
5. G. A. Morris and R. Freeman, J. Mag. Res. **29** 433 (1978).
6. D. Foxall, J. S. Cohen and R. G. Tschudin, submitted for publication.

Figure Legend

A stacked plot of spectra obtained by the $^1\text{H}\{^{13}\text{C}\}$ spin echo difference method during the conversion of $[1-^{13}\text{C}]$ glucose to ethanol by a 24% suspension of yeast in a medium that contained 80% H_2O by volume (20% D_2O was included in the sample to provide a field-frequency lock). The concentrations of reagents present in the sample were $[1-^{13}\text{C}]$ glucose, 90mM; $[2-^{13}\text{C}]$ acetate, 30mM and pyrophosphate buffer, 36mM pH 5.5. The assignment of the resonances was as follows; (a) $[2-^{13}\text{C}]$ ethanol, (b) $[2-^{13}\text{C}]$ acetate, (c) β - $[1-^{13}\text{C}]$ glucose, (d) α - $[1-^{13}\text{C}]$ glucose, (e) overlapped resonances from α and β anomers of glucose and (f) residual water resonance. The time assigned to each spectrum is the time elapsed at the midpoint of each acquisition after the addition of $[1-^{13}\text{C}]$ glucose.

HUNTER COLLEGE

of The City University of New York

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Dear Barry:

Title: NMR Supervisor Position Available

In conjunction with our anticipated acquisition of a high-field (oops, sorry: moderate field, i.e., 270-300 MHz) spectrometer, we seek to appoint an individual to supervise its operation. Duties include determination of service spectra, training of authorized operators, schedule management, collaboration/consultation with researchers, implementation of new hardware and software techniques, and troubleshooting. Because we have a good electronics engineer, no detailed hardware experience is required, but some familiarity with hardware would be preferred. Depending on the individual's preference and available time, opportunities for independent or collaborative research exists. The salary will be competitive and liberal fringe benefits are provided. Those interested should send me a curriculum vitae and three letters of reference at the above address. We are an affirmative action - equal opportunity employer.

Best regards,

Bob
Robert L. Lichter
Professor of Chemistry

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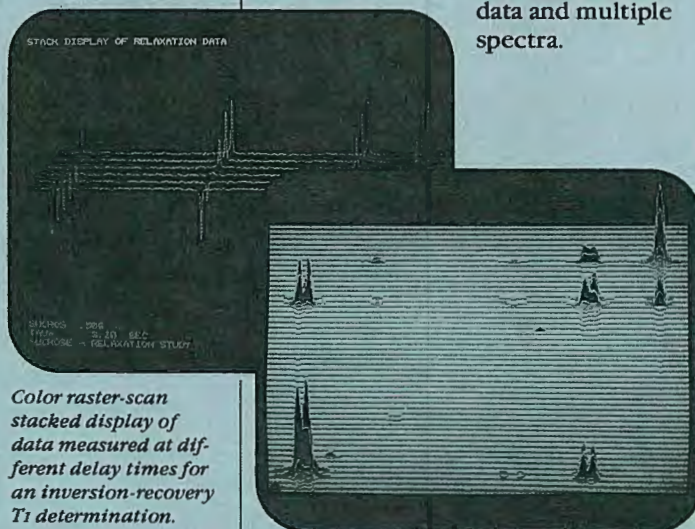
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