

# NMR

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Recent issues of the Newsletter have contained a substantial and growing number of "Position Available" notices. While this is most heartening in terms of the implied vigor of the field, the amount of space these notices are taking up has become a burden. In this, as elsewhere, we are trying to keep costs down.

Therefore, all "Position Available" notices should be constructed so as to fit within a space bounded by the frame line drawn around this notice. This space will allow for notices which have a **maximum size of 4.5 inches high x 7.5 inches wide (11.4 cm high x 19.0 cm wide)**. Notices which do not meet this space restriction will be returned for reworking, resulting in a delay in their appearance in the Newsletter.

Please understand that we do not intend for these space restrictions to diminish the number of position available notices which appear in the Newsletter. This number should self-regulate. We must, however, deal with the economic aspects of the issue. Position available notices dated June 15 or later will be expected to meet this new space consideration policy. If you send longer notices between May 1 and June 15, we would appreciate your airmailing us smaller, replacement versions if this is appropriate.

B. L. Shapiro

May 1, 1984

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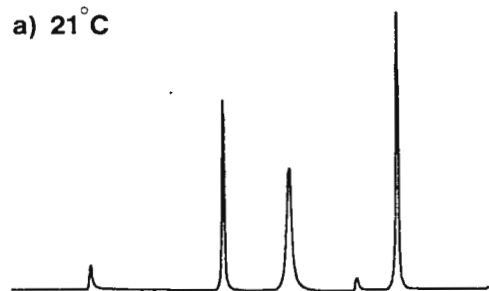
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 Department of Chemistry  
 Texas A&M University  
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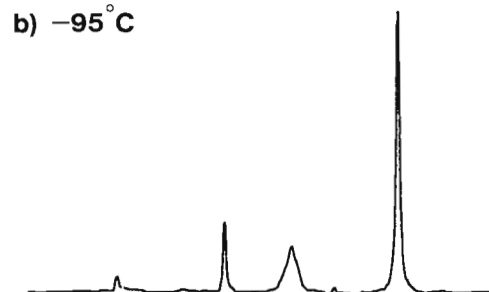
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# Variable Temperature CP-MAS with the GX Series FT NMR Spectrometers

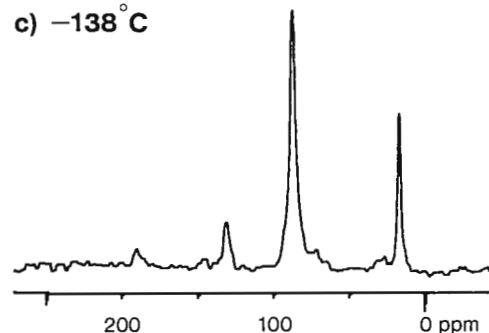
a) 21°C



b) -95°C



c) -138°C



<sup>13</sup>C (50.1 MHz) VT/MAS spectra of hexamethylbenzene. a) and c) <sup>1</sup>H-<sup>13</sup>C cross polarization. b) Bloch decay. The peak at ~ 90ppm is due to the Delrin rotor.

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IN REPLY REFER TO:

6120-166:HAR:mjt  
20 March 1984

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

IMAGING OF  $\text{AsF}_5$  DIFFUSION IN GRAPHITE

Dear Dr. Shapiro:

We are using NMR imaging to study diffusion of the intercalant  $\text{AsF}_5$  in highly oriented pyrolytic graphite (HOPG). A simple model of HOPG is a book, where the pages, the planes of carbon atoms, are impermeable to intercalant. Diffusion is limited to directions parallel to the C-planes (in between the "pages").

We have imaged the intercalation process by means of the pulse FT method in a fixed gradient. To provide axial symmetry we used a thin HOPG disc of ~10 mm diameter, loaded by contact with an  $\text{AsF}_5$  gas reservoir in a dry ice/acetone mix to provide a constant pressure of ~130 torr. The  $^{19}\text{F}$  signal (at ~60 MHz) was monitored as a function of the time of contact. A linear magnetic field gradient of ~10 kHz/cm was applied in one of the radial directions. The radial distribution of  $\text{AsF}_5$  inside the HOPG was derived from the experimental lineshape. For example, a semicircular lineshape implies a uniform radial distribution of  $\text{AsF}_5$  density. The integrated line intensity is proportional to the total amount of  $\text{AsF}_5$  intercalated into HOPG.

We expected that the concentration of  $\text{AsF}_5$  would at first be large near the rim of the disc, so we would be able to image the propagation of the intercalant toward the center. To our surprise, we actually observed a series of consistently semicircular spectra (typically as shown in Fig. 1) which only intensified as time elapsed. The intensity data, as shown in Fig. 2, indicate that intercalation of  $\text{AsF}_5$  into HOPG takes a considerable amount of time. There is an initiation period of the order of a day before the occurrence of any appreciable intercalation. The uniform loadings of intercalant over the entire area, especially at short times, imply that radial migration from the edges is not the rate-limiting process. In fact, from the decay of the spin echo in the imaging field gradient, the radial diffusivity of  $\text{AsF}_5$  in gradient (stage I) is found to be comparable to that in liquids ( $\sim 10^{-5} \text{ cm}^2/\text{sec}$ ).

Possible rate-determining processes may be the penetration of  $\text{AsF}_5$  into the edges of HOPG or the diffusion through grain boundaries from the planar (001) face. Further experiments are needed for clarification of the processes.

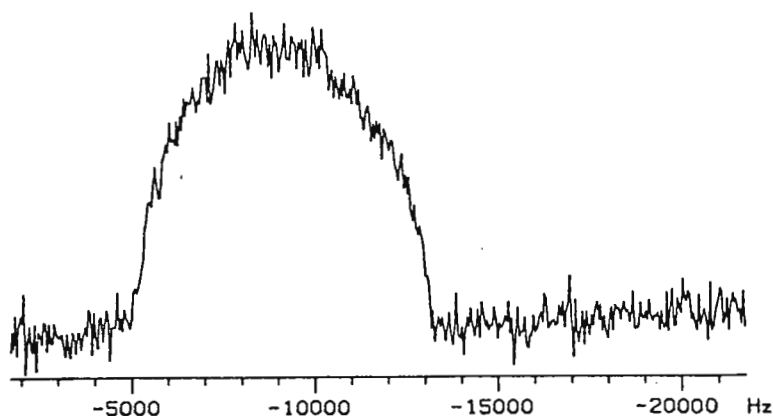


Fig. 1 Typical line shape

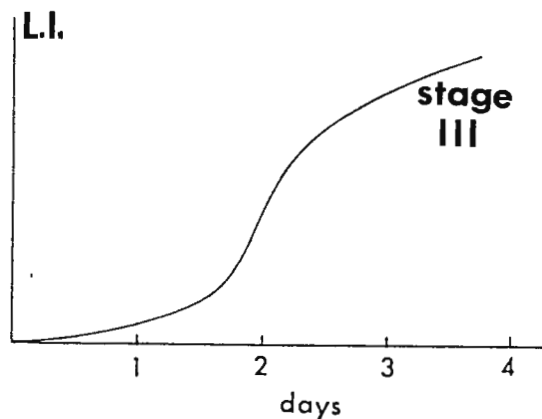


Fig. 2 Line intensity vs. time of exposure

G. C. Chingas

*G. C. Chingas*

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April 3, 1984

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

Dear Berry:

## NMR Thermometer for Variable-Temperature CPMAS NMR

We have recently installed a variable temperature control unit on our 200 MHz CPMAS spectrometer. The temperature of the sample environment can be adjusted to between 0 and 50°C by controlling the temperature of the journal bearing air supply for the magic-angle spinner. This temperature range is sufficient for studies involving viable cells and biological membranes.

In low-power, high-resolution nmr experiments one usually assumes that the sample remains in thermal equilibrium with its environment, so one needs only to measure the temperature near the sample to determine the sample temperature. This is not the case for CPMAS nmr, particularly with biological samples containing ionic buffers. In CPMAS experiments several kilowatts of peak radiofrequency power are required to extract the nmr information. Conductive samples may adsorb a fraction of the rf power and convert it to heat. When the sample becomes a heat source one can no longer assume thermal equilibrium between the sample and the environment. What is needed is a way to determine the temperature of the sample itself. Direct sample temperature measurement is always difficult without degrading the nmr signal. In the case of CPMAS, direct temperature measurement is complicated by the fact that the sample is spinning at 2-3 kilohertz. Of course, physical contact is impossible.

To solve this problem we have adapted a nmr thermometer which has been described previously in the literature.<sup>1</sup> We use a mixture of approximately 3 parts tetramethylsilane (10%-<sup>13</sup>C) and 1 part methyl iodide (60%-<sup>13</sup>C) sealed in a 1.5 mm O.D. by 1 cm capillary. The nmr thermometer is small enough to be inserted along with the sample into the magic-angle rotor (displacing 5% of the sample), and yet sufficiently enriched in carbon-13 for the resonances to be easily detected; the temperature can be determined after about a minute of signal averaging. The chemical shift of the TMS is slightly temperature dependent,<sup>1</sup> but is suitable for use as an internal

chemical shift reference in most applications. The chemical shift of the  $\text{CH}_3\text{I}$  (near -26 ppm) is conveniently upfield of most other carbon-13 resonances and is sensitive to temperature. The chemical shift difference between these two resonances indicate the actual sample temperature. Here the assumption of thermal equilibrium between the sample and the nmr thermometer is good since the thermometer is immersed in the sample and is not itself a source of heat.

Each nmr thermometer capillary must be calibrated since the chemical shift difference between the TMS and  $\text{CH}_3\text{I}$  depends on the composition of the thermometric solution. To calibrate the thermometer we place the capillary in a rotor filled with ethylene glycol. The ethylene glycol serves as a primary ( $^1\text{H}$ ) nmr thermometer. With the rotor spinning at 2kHz, we find that the temperature indicated by the ethylene glycol, a non-conductive fluid, agrees with the temperature of the probe environment to within about one degree. Over the temperature range of 0 to 50°C the chemical shift difference from the  $^{13}\text{C}$  nmr thermometer can be approximated as a linear function of temperature. A one degree change in temperature produces about a one hertz change in the chemical shift. We estimate the accuracy of the capillary thermometer to be about  $\pm 1^\circ\text{C}$  from 0 to 50°C.

In one application of the  $^{13}\text{C}$ -nmr thermometer with a conductive sample we discovered that a rf pulse sequence we were using to measure the strength of the C-H dipolar interaction in a lipid dispersion containing 50 wt% water heated the sample 29°C above ambient. We were able to cool the MAS air supply and maintain the sample temperature at 41°C, to study molecular motion just below the gel-liquid crystalline transition temperature.

Please use this contribution to maintain the Monsanto subscription.

(1) D.W. Vidrine and P.E. Peterson, Anal. Chem., **48**, 1301 (1976).

Sincerely,

  
Jake Schaefer

  
Ed Stejskal

  
Bob McKay

  
Mike Sefcik

  
Gary Jacob



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THE UNIVERSITY OF ALBERTA  
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April 18, 1984

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

re: Bruker Power Level Switching

Dear Barry,

We have an early Bruker WH-400 on which the <sup>1</sup>H decoupler power level is controlled by miniature sealed relays. For experiments that required fast decoupler level switching (such as INEPT with refocussing and decoupling), these relays were neither fast enough nor reliable; consequently, we resigned ourselves to using much higher power levels than necessary for decoupling in these experiments.

We were pleased, then, to discover that our newer WM-360 had done away with these pesky relays on the high power decoupler range and better, that it was a simple matter to update our older instrument. A small breadboard circuit incorporating a PROM, a DAC and a dual Op-Amp was piggy-backed onto the Decodage and Attenuator Control Board and our switching problems were solved. The settling time on switching power levels is now about 5 micro sec. with a clean transition; the old relay system had a settling time as long as 10 milli sec. and much contact bounce.

If anyone is interested in making this modification to their own instrument, we would be happy to send them drawings and a more detailed writeup.

Please credit this letter to Tom Nakashima's subscription.

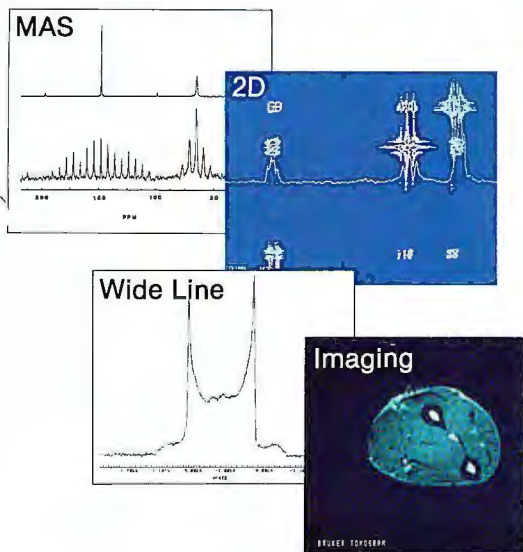
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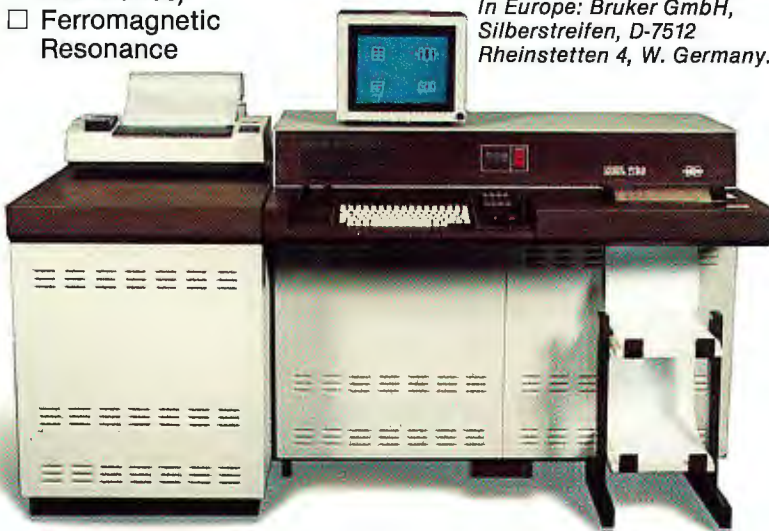
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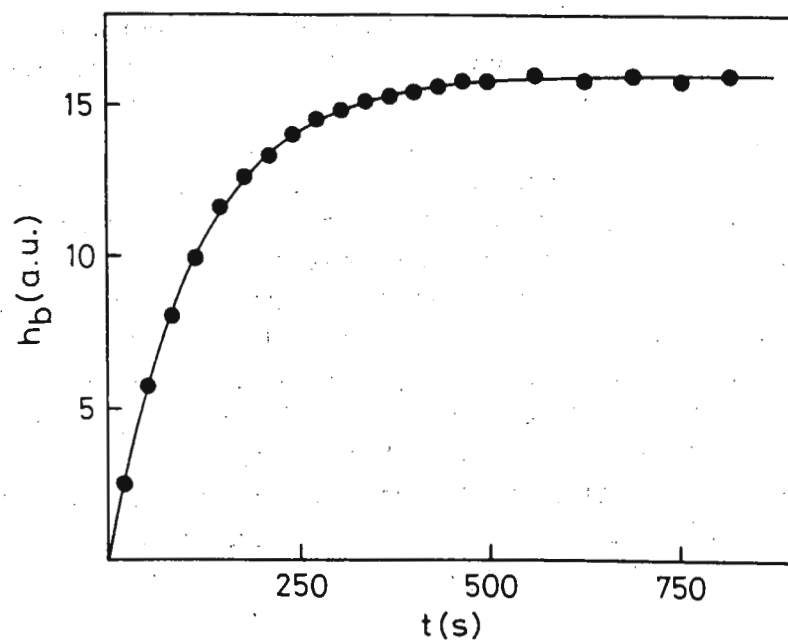
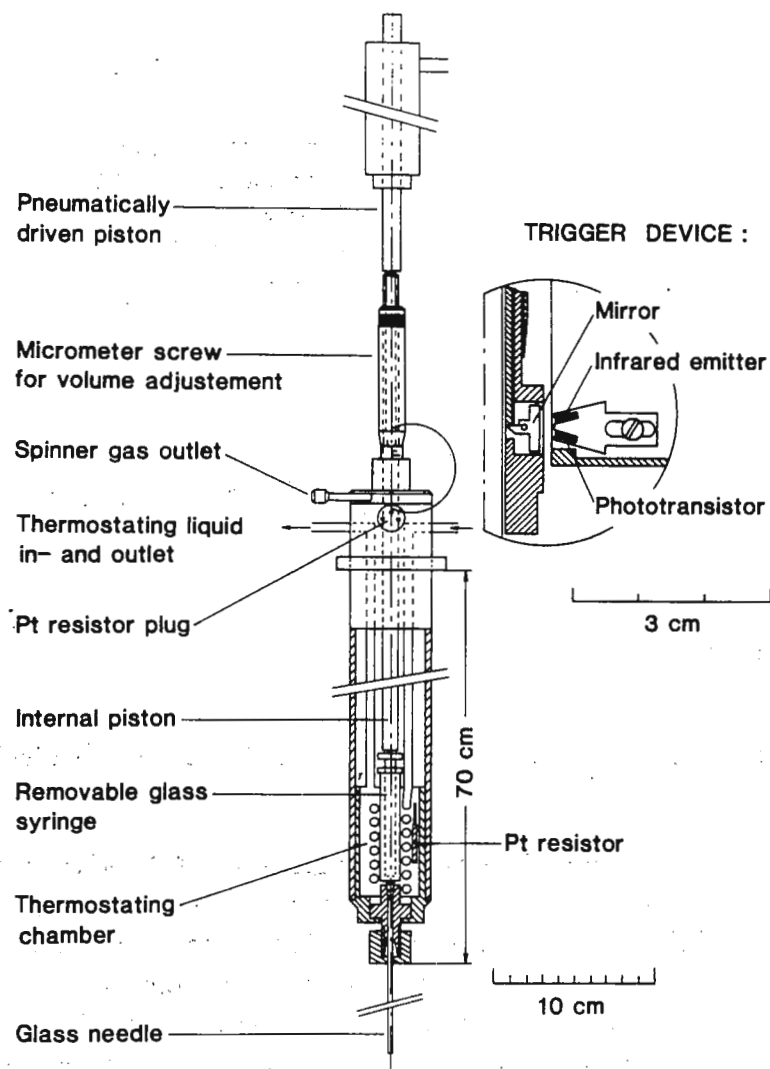
April 6, 1984

Dear Professor Shapiro,

A Thermostated fast injection apparatus for wide-bore superconducting magnets

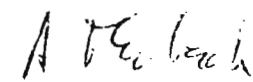
To be able to follow solvent exchange reactions with half-life periods from seconds to several minutes by an isotopic substitution technique (for example  $^1\text{H}$ - $^2\text{D}$  or  $^{16}\text{O}$ - $^{17}\text{O}$ ) we built a thermostated fast injection apparatus Fig. 1. The injector fits into a wide-bore superconducting magnet and is installed in a few minutes. A pneumatically driven piston pushes the internal piston and a syringe piston. The path length of the internal piston is set by a micrometer screw allowing the injection of volumes of up to 1 ml with a precision of 10  $\mu\text{l}$ . The piston displacement causes rotation of a mirror into a vertical position, and the consequent reflection of infrared radiation from an emitter onto a phototransistor triggers the NMR spectrometer. The removable glass syringe is screwed into the bottom of the thermostating chamber through which a thermostating liquid is pumped. The temperature is measured by means of a platinum resistor. The needles, easy to replace, are glass capillaries and fit into the center of 5 or 10 mm diameter NMR tubes. Rotation and thermostatisation of the tube can be carried out using the inbuilt spectrometer facilities. About 5 minutes are needed between experiments, mainly to change and refill the syringes. The thermostatisation time of the solution in the syringe does not exceed 15 minutes even for extreme temperatures (200 K or 370 K). The mixing time of two 1 ml solutions in a 10 mm spinning tube is less than 50 ms.


Figure 2 shows as an example the kinetics of water exchange on aqueous  $[\text{Pt}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$  as followed by the increase in the height  $h_b$  (arbitrary unit) of the bound water  $^{17}\text{O}$ -NMR signal (-124.3 ppm from free water) at



324 K (27.11 MHz). The solution was prepared by injection of 0.7 g of 0.58 m  $[\text{Pt}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$  (3.52 m  $\text{HClO}_4$ ) in normal water into 0.55 g of 20 % enriched water. The accumulation time for one spectrum was 31.8 s. The exchange rate calculated is  $8.6 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$ .

Sincerely yours

  
A.E. Merbach

  
L. Helm

---

**NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIST.** University of Lausanne, Switzerland

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UNIVERSITÄT TüBINGEN  
PHYSIKALISCHES INSTITUT  
Prof.Dr.O.Lutz

D-7400 TüBINGEN 1, den 04.04.1984  
Morgenstelle  
Telefon (0 70 71) 29 67 14

Physikalisches Institut, Morgenstelle, D-7400 Tübingen 1

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

Ihr Zeichen

Unser Zeichen

Ihre Nachricht vom

Lu/Sc

Some Remarks on  $^{53}\text{Cr}$  NMR Parameters

Dear Barry,

$^{53}\text{Cr}$  is one of the hetero-nuclei which has not often been investigated by NMR Spectroscopy (1,2,3). This is due to the small NMR receptivity of  $8.6 \times 10^{-5}$  (proton  $\cong 1$ ), the low Larmorfrequency, and the fact that quadrupolar interactions govern the relaxation mechanism in liquids.

We have been interested in the spin-lattice relaxation rates of the central quadrupolar nuclei in tetrahedral oxoanions like  $\text{CrO}_4^{2-}$  (4). In the figure, a stacked plot of a  $T_1$  measurement of  $^{53}\text{Cr}$  is presented together with experimental parameters.

As a function of concentration of  $\text{K}_2\text{CrO}_4$  in  $\text{H}_2\text{O}$ , the range of the  $T_1$ 's of  $^{53}\text{Cr}$  is about from 42 ms to 55 ms.

These are relatively small values compared with those for other central nuclei in oxoanions (4). But this is no longer surprising since Ertmer et al. (5) have recently published a convincing measurement of the quadrupole moment of  $^{53}\text{Cr}$ :

$$Q = -0.15 \cdot 10^{-28} \text{ m}^2.$$

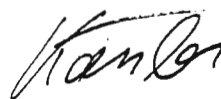
(The value recommended in the tables of G. Fuller (6) was:

$$Q = 0.03 \cdot 10^{-28} \text{ m}^2!).$$

Sincerely yours

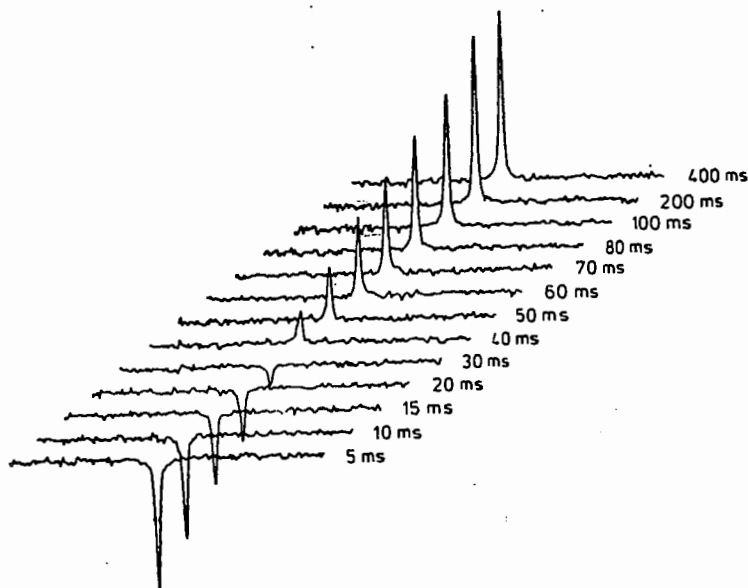


(Otto Lutz)



(Günther Kössler)

- 1) Y. Egozy, A. Loewenstein  
J. Mag. Res. 1, 494 (1969)
- 2) B.W. Epperlein, H. Krüger, O. Lutz, A. Nolle, W. Mayr  
Z. Naturforsch. 30a, 1237 (1975)
- 3) H. Günther, P. Schmitt, Z. Naturwiss., in press
- 4) E. Haid, D. Köhnlein, G. Kössler, O. Lutz, W. Schich  
J. Mag. Res. 55, 145 (1983)
- 5) N. Ertmer, V. Johann, R. Mosmann, Z. Phys. A309, 1 (1983)
- 6) G. Fuller, J. Chem. Phys. Ref. Data 5, 835 (1976)



Stacked plot of a Fourier transform inversion recovery measurement of the longitudinal relaxation time of  $^{53}\text{Cr}$  in a 2.5 molal solution of  $\text{K}_2\text{CrO}_4$  in  $\text{H}_2\text{O}$ :  $T_1 = (45 \pm 2)$  ms. For each signal 4000 free induction decays have been accumulated; the waiting times between the  $180^\circ$  and  $90^\circ$  pulses are given. The whole measuring time was 5.5 hours. Larmor frequency: 5.09 MHz.

# PURDUE UNIVERSITY

BIOCHEMICAL MAGNETIC RESONANCE LABORATORY

April 2, 1984

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

Dear Professor Shapiro,

## Pulse Sequence Simulations and Graphics on a Microcomputer

Do you ever get tired waving your arms when you explain a pulsed NMR experiment to someone? Do you ever get odd stares when your arms are frantically trying to follow the magnetization vectors in some new fangled pulse sequence and finish tied up in knots? Well, I got tired of doing semaphore to explain or understand pulse sequences (figure 1) especially since it generally only served to confuse myself and others.

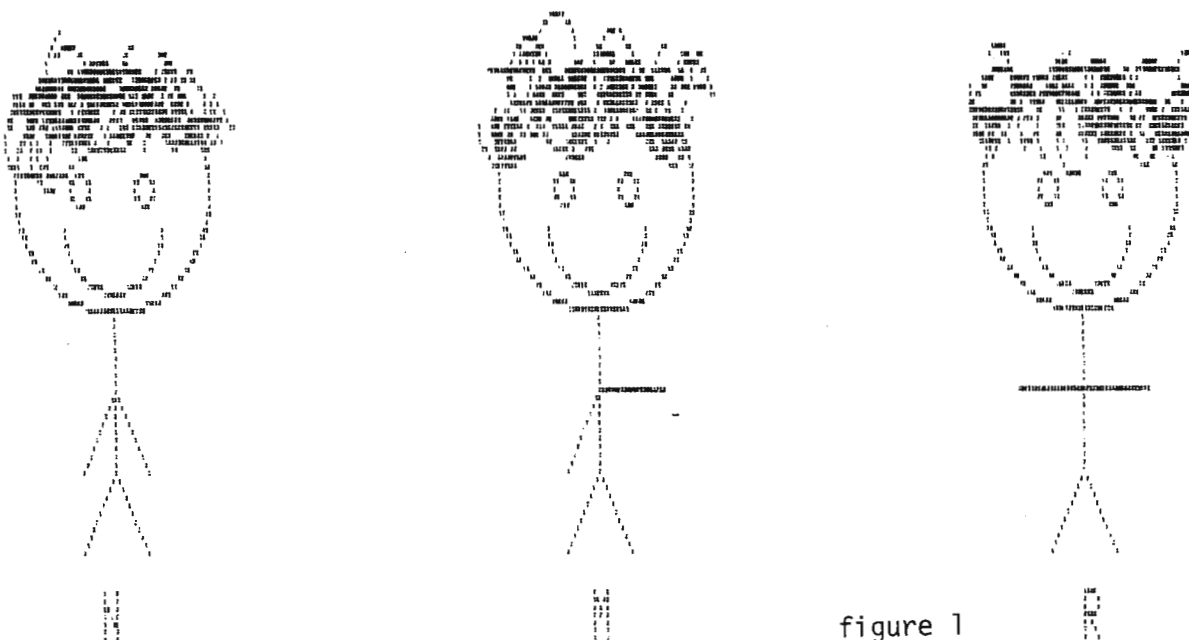


figure 1

Having a Zenith-100 microcomputer in our lab (courtesy of a grant from Allied Corporation), it made inherent sense to me to use its computing ability and excellent color graphics to save my arms and



Chemistry Building  
West Lafayette, Indiana 47907  
(317) 494-5283  
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(317) 494-5287



at the same time add clarity to the descriptions of pulse sequences. The program uses the standard Bloch equations to calculate the fate of magnetization vectors that are subjected to a series of pulses of various phases and delays between the pulses. Rotation matrices are used to calculate the final position of eighty vectors of different frequencies. Off resonance effects and finite transmitter power are described in terms of effective fields. The user supplies the following inputs to the program: 1) the time required for a 90 degree pulse; 2) the range of spectral frequencies; and 3) the pulse sequence including pulse angle, pulse phase, and delays between pulses. The output of the program is routed to a graphics program that displays the results of the simulation program on the RGB monitor of the Zenith-100 microcomputer. Instead of using a single three dimensional projection of the the vector positions, views down each of the three coordinate axes (x,y,z) are displayed; also, a plot of z magnetization versus resonance offset is displayed. We have used the pulse sequence simulation program to evaluate and optimize water suppression techniques and composite pulses. The program is also useful to introduce various concepts such as pulse angles and spin echoes to novice NMR users of our facility.

Figure 2 shows the output generated from a WALTZ pulse sequence (90x:180-x:270x) for a 40 microsecond 90 degree pulse and a sweep width of plus and minus one and one half times the magnitude of the irradiating field. For the sake of clarity, only the tips of the vectors are displayed.

Please credit this article towards the subscription of John L. Markley.

Sincerely,



W. Milo Westler  
Operations Director

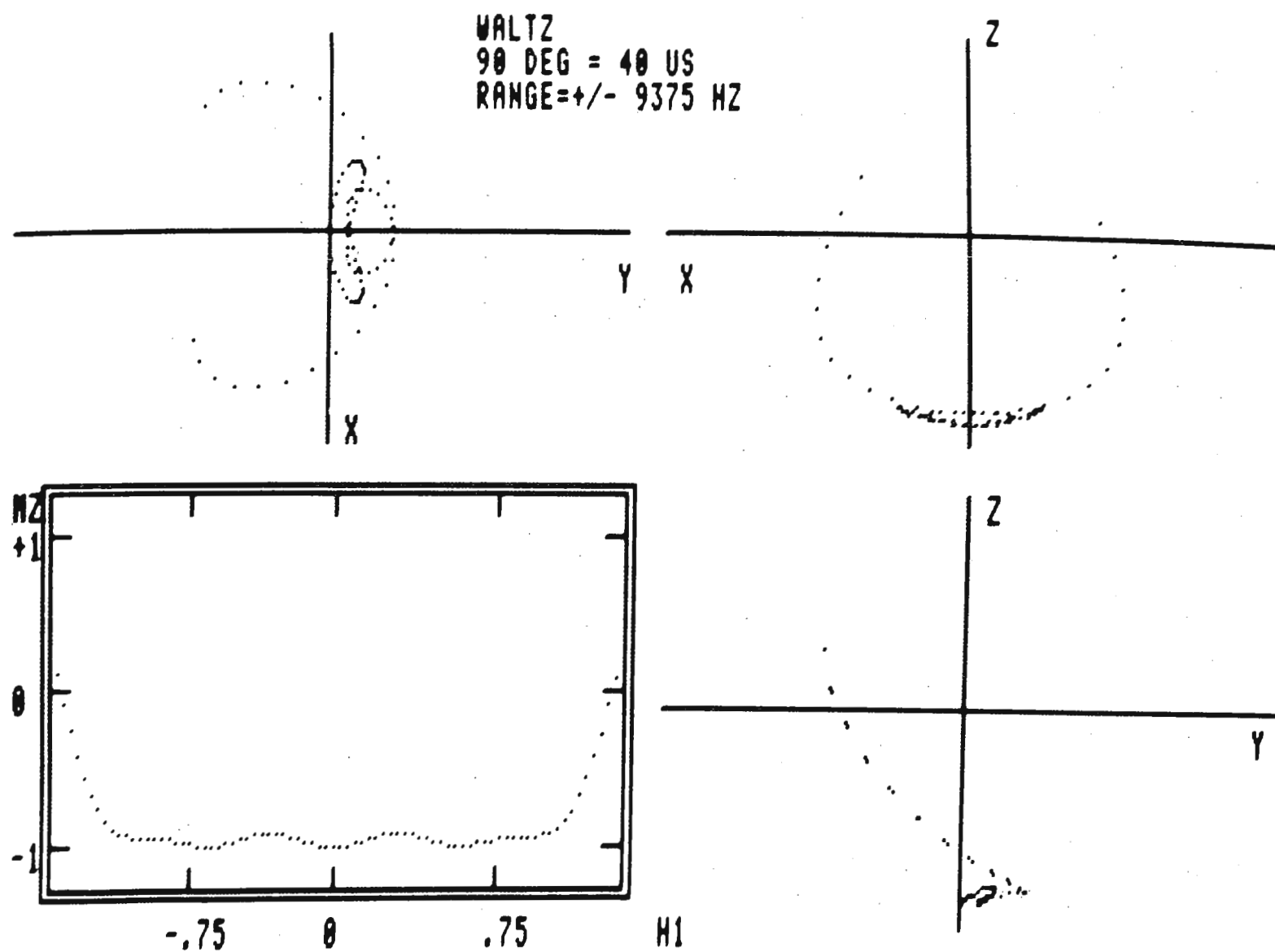


figure 2

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RESEARCH LABORATORY K34/281

International Business Machines Corporation

5600 Cottle Road  
San Jose, California 95193  
(408) 256-5590

April 17, 1984

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

Dear Barry:

We dinosaurs who still use electromagnets have to resort to various stratagems to keep them going because of tube obsolescence (in this case a 5693). We have recently replaced the entire chopper amplifier circuit in the V2100B power supply of our high impedance 1.4T magnet with a single IC op-amp (Burr-Brown Model 3583AM). The 210V floating supply was used to power the op-amp. This necessitated changing the voltage regulator tubes to semiconductor Zener diodes to supply a regulated +50/-150V to the op-amp. We also replaced the 5Y3(V814) rectifier tube with semiconductor diodes (this was not a necessary operation, but did eliminate the last remaining tube in the circuit).

We have been using the magnet for a month, and the system stays locked overnight and over weekends with no apparent difficulty to date.

Sincerely yours,

Ray Kendrick

Nino Yannoni

Replacement of the Chopper Amplifier in the V2100B Electromagnet Power Supply



## UNIVERSITY OF SOUTH FLORIDA

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DEPARTMENT OF CHEMISTRY  
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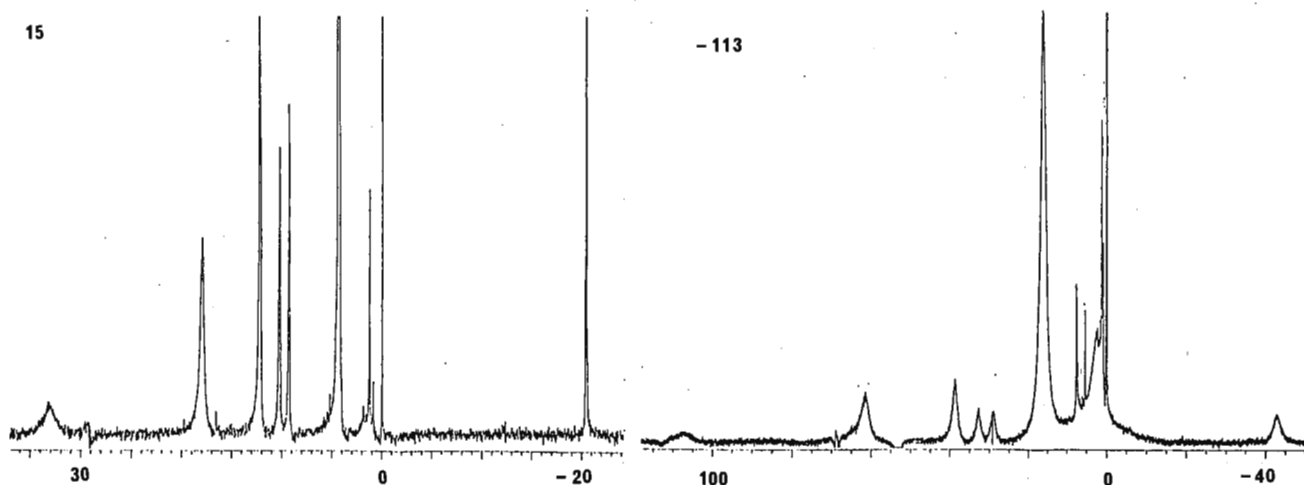
April 18, 1984

Dear Barry:

While working together last summer at the Delft University of Technology, we carried out an extensive study of adamantanone with a variety of different lanthanide shift reagents (LSR). All the work was done with a Nicolet NT-200 WB spectrometer, and one of the experiments we conducted was to look at the low temperature spectra of adamantanone in the presence of  $\text{Yb}(\text{fod})_3$ .

At temperatures below  $-100^\circ\text{C}$  we were able to observe slow exchange of free and complexed adamantanone, and this is the first time that slow exchange has been observed for a ketone with a shift reagent. The success of the experiment can be attributed to a large association constant that results from using a strongly binding shift reagent,  $\text{Yb}(\text{fod})_3$ , and a nonpolar solvent ( $\text{CFCl}_3$ ). This solvent also permitted us to use very low temperatures (below its freezing point in the presence of solute).

The spectra at ambient temperature and at  $-113^\circ\text{C}$  are shown below for a sample with  $\text{LSR/ketone} = 0.7$ . Signals for the 5 different hydrogens of adamantanone appear at 9-33 ppm at ambient temperature, and these shift to 29-109 ppm in the low temperature spectrum. The important difference between the spectra is the presence of the peaks at 2-3 ppm corresponding to free adamantanone. This allows direct measurement of the bound shifts, and these are in good agreement with values calculated for spectra at different LSR/ketone ratios under fast exchange conditions.



Sincerely,

*J.A. Peters*

J.A. Peters

*Douglas J. Raber*

Douglas J. Raber



INSTITUTE FOR CANCER RESEARCH ■ 7701 BURHOLME AVENUE ■ PHILADELPHIA, PENNSYLVANIA 19111

215/728-6900

April 12, 1984

Professor Bernard L. Shapiro  
Chemistry Department  
Texas A and M University  
College Station, Texas 77843-3255

RE: I. In vivo probe. II. LASER/NT-300 interface

Dear Professor Shapiro:

I. In vivo probe

A special probe for in vivo  $^{31}\text{P}/^1\text{H}$  NMR studies in rats or mice has recently been constructed here. Interchangeable 4mm and 9mm id coil formers have been made for mice or rat tails, respectively. The coil is a solenoid having an inductance of about 0.3 microhenry, and a Q of 90. The 90 degree pulse width at 121 MHz is 12.5 microseconds for the 9mm id sample coil.

We have followed the example of others (1,2) to transplant tumors subcutaneously on the tail of a rat (mouse).

Results from the first day of  $^{31}\text{P}$  (at 121 MHz) testing are shown in the Figure. 96 accumulations using 50 degree flip-angle pulses took about 5.4 minutes on our NT-300 WB. 30 Hz line broadening was used. Additional work is planned to optimize sensitivity, establish  $^1\text{H}$  T1 values, and to incorporate a surface coil.

1. R. E. block, B. C. Parekh and R. Menditto. J. Magn. Reson. **53**, 509 (1983).

2. I. D. Weisman, L. H. Bennett, L. R. Maxwell, M. W. Woods and D. Burk. Science **178**, 1288 (1972).

## II. LASER/NT-300 interface

In anticipation of planned photo-CIDNP experiments, we have interfaced a LASER (Coherent, Inc., Innova 90-5) to the NT-300 computer. By installing an operational amplifier (Analog Devices, Inc., type 284J) on the LASER interface board, remote control by an external 0 to +5 volt dc signal is made possible. A coaxial cable has been connected to a BNC connector on the LASER power supply from the NT-300 293 pulse programmer.

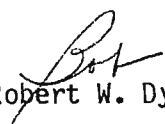
An example of an acquisition sequence for difference spectra follows:

1. Delay
2. LASER pulse (variable in amplitude and time)
3. Delay
4. Transmitter pulse (X)
5. Acquire data
6. Delay
7. Transmitter pulse (-X)
8. Acquire data

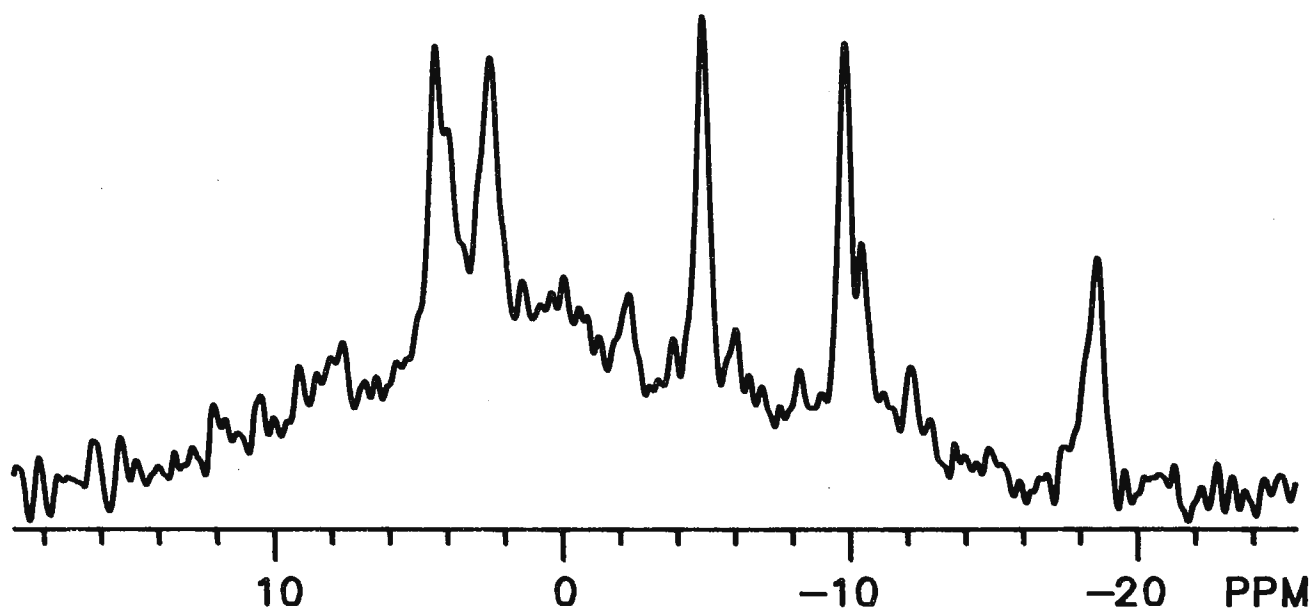
The 180 degree phase shift of the two transmitter pulses provides automatic subtraction of the "light" and "dark" signals. A list of up to 32 values for either LASER pulse time or the delay between the LASER pulse and signal acquisition can be used to automate a series of spectra.

Please credit this contribution to the subscription of Dr. Mildred Cohn.

Sincerely yours,

  
Robert W. Dykstra

RWD/m







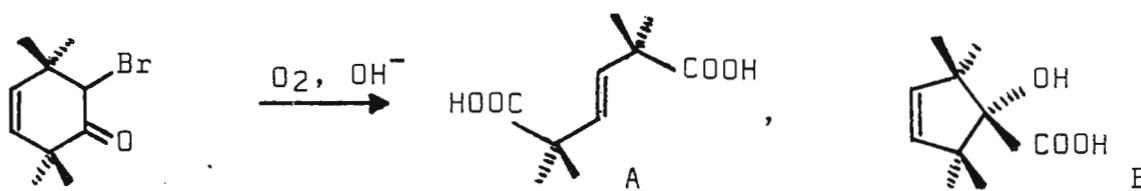
April 11, 1984

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

Dear Dr. Shapiro

ABX-Analysis using ( $^{13}\text{C}$ -) X subspectra measured under different  $^1\text{H}$ -off resonance decoupling conditions

In the course of the reaction



two products A and B are formed. To prove the expected trans configuration at the double bond of compound A, I was primarily interested in the value of the vicinal coupling constant of the olefinic protons, although  $^3J_{\text{C}(3)\text{H}(4)}$  in comparison to literature data would give the answer as well.

Since the proton spectrum of the main  $^{12}\text{C}$  isotopomer of this class of compounds bears no coupling information, the  $^1\text{H}$  spectra of the  $^{13}\text{C}$  isotopomers are normally recorded. From the proton spectrum of the  $^{13}\text{C}(3)$  isotopomer the vicinal coupling constant of the olefinic protons could eventually be measured, if the problems arising from the strong peak of the  $^{12}\text{C}$  isotopomer and the signals of impurities are circumvented.


From the well known expressions for the analysis of ABX spin systems a set of modified analytical expressions for the parameters  $J_{AX}$ ,  $J_{BX}$ ,  $J_{AB}$  and  $\Delta\delta_{AB}$  can be derived, which take into account the influence of the  $^1\text{H}$  decoupling field on coupling constants (hetero- and homonuclear) and chemical shifts (Bloch-Siegert effect).

From the analysis of three carbon spectra - two measured under  $^1\text{H}$ -off resonance decoupling conditions with different decoupler offsets, one without decoupling - the following parameters could be evaluated. The large vicinal coupling ( 13.6 Hz ) of the olefinic protons for compound A clearly confirms its trans configuration. Comparison of the two  $^2J_{\text{CH}}$  shows the positive contribution due to the larger angle between the corresponding bonds in compound B.

Hz	A	B
$J_{AX}$	165.2	162.6
$J_{BX}$	-1.6	+1.0
$J_{AB}$	13.6	5.9
$\Delta\delta_{AB}$	9.2	12.2
$\chi_{\text{H}_1}$	3050	2890

The figure on the next page shows the good agreement between the experimental and the simulated spectra for compound A

Yours sincerely



Peter Bigler

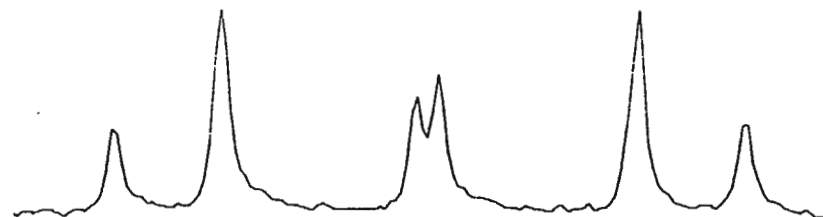
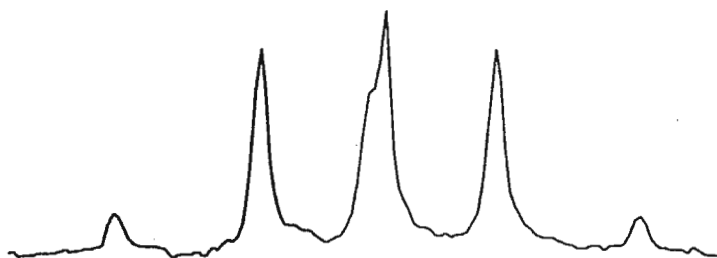
Experimental and simulated off resonance decoupled  $^{13}\text{C}$  spectra of compound A using two  $^1\text{H}$  decoupler offsets.

Decoupler  
offset

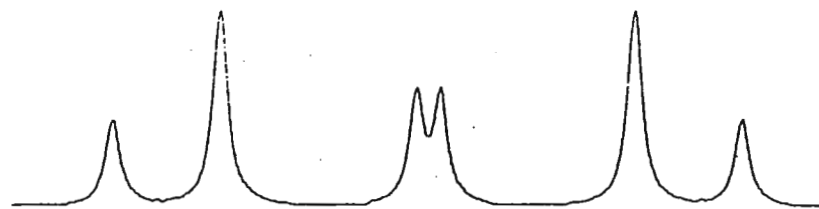
275.7 Hz

475.7 Hz

experimental



simulated



10 Hz



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in St. Louis, June 4-7!*



3

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## NMR SPECTROSCOPIST

The M.I.T. Francis Bitter National Magnet Laboratory is seeking a Ph.D. physical scientist with demonstrated extensive experience in state-of-the-art NMR, preferably in the application of solution state high resolution NMR to problems in biology and biochemistry. Will undertake independent research to conceive and apply new NMR techniques to the study of biomacromolecules. Position offers excellent opportunity for collaboration and the use of advanced instrumentation such as 500 MHz/photo-CIDNP, wide bore 360 MHz and 600 MHz spectrometers. Send resume and three letters of recommendation to: Dr. L.J. Neuringer, M.I.T., Francis Bitter National Magnet Laboratory, 170 Albany Street, Cambridge, MA 02139. M.I.T. is an equal opportunity affirmative action employer.

**"Position Available" Notices**

Recent issues of the Newsletter have contained a substantial and growing number of "Position Available" notices. While this is most heartening in terms of the implied vigor of the field, the amount of space these notices are taking up has become a burden. In this, as elsewhere, we are trying to keep costs down.

Therefore, all "Position Available" notices should be constructed so as to fit within a space bounded by the frame line drawn around this notice. This space will allow for notices which have a **maximum size of 4.5 inches high x 7.5 inches wide (11.4 cm high x 19.0 cm wide)**. Notices which do not meet this space restriction will be returned for reworking, resulting in a delay in their appearance in the Newsletter.

Please understand that we do not intend for these space restrictions to diminish the number of position available notices which appear in the Newsletter. This number should self-regulate. We must, however, deal with the economic aspects of the issue. Position available notices dated June 15 or later will be expected to meet this new space consideration policy. If you send longer notices between May 1 and June 15, we would appreciate your airmailing us smaller, replacement versions if this is appropriate.

B. L. Shapiro

May 1, 1984

UNIVERSITY OF DELAWARE  
NEWARK, DELAWARE  
19716

DEPARTMENT OF CHEMISTRY

April 17, 1984

Professor B.L. Shapiro  
TAMU NMR Newsletter  
Department of Chemistry  
Texas A & M University  
College Station, TX 77843-3255

Mating Catalysis with NMR

Dear Professor Shapiro:

In response to your letter, Joe Noggle has turned over the fate of the University of Delaware's subscription to me. As you know, one of the principal interests of my group has been the use of NMR spectroscopy to investigate catalysis. Aside from the many other difficulties which accompany such foolhardy adventures, one is faced with the question of how to contain the sample, since the basic character of catalysis is kinetic, and still be able to examine the sample with NMR spectroscopy at various stages of treatment. One solution is to seal off samples into tubes so as to make "permanent" samples which can then be investigated with NMR spectroscopy. Unfortunately, such a technique can complicate the life of a chemist who is used to thinking of catalytic change as an evolutionary process. Although we use this technique at times, our preference has been to marry the flow techniques of classical kinetic studies to NMR spectroscopy. In essence, we perform a stopped-flow experiment in a reactor with an NMR tube sidearm (Figure 1), designed originally by Tom Apple and Patricio Gajardo, which has a cross-section that allows the sealed reactor-NMR sample tube to fit into the electromagnet (Unfortunately, we do not yet have a superconducting magnet in which to perform these experiments). This reactor has been used in a variety of experiments in our laboratory. A modification which places the U tube and NMR tube axes parallel should allow one to perform similar experiments in a superconductive magnet.

For reasons which should be obvious, one might wish to have the flow reactor (and the reaction) in the spectrometer. One way to do this is to build a probe with the reactor as an integral part of the probe. Because we need to use our spectrometer for other experiments, we would prefer not to have exchange probe bodies. It was with this constraint in mind that David Mesaros of this laboratory designed a flow reactor which could be inserted into the spectrometer and removed easily. The concept of having concentric inlet and outlet tubes was the important idea in developing this device. It has now been used by David in a number of experiments.

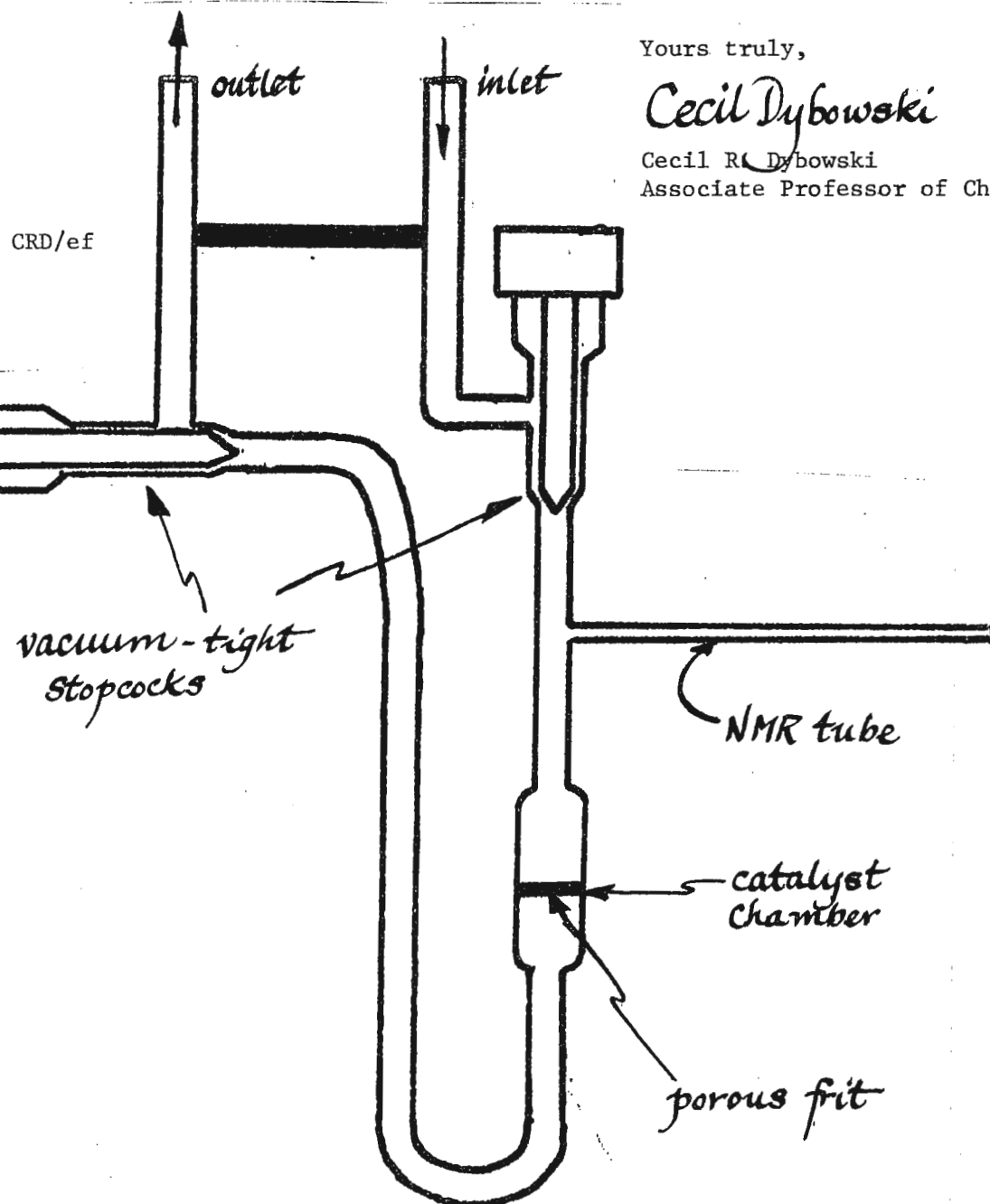
The marriage of the catalytic devices with NMR spectroscopy is important to utilize NMR as a tool in catalytic science, in the same fashion that infrared

spectroscopy has been adapted to use in this field. I am quite sure that designs similar to those used by us must have been used by others. If so, I would like to hear of their designs. A number of investigators have asked for the designs of our reactors; I shall be happy to supply further information for those wish to write me.

Yours truly,

*Cecil Dybowski*

Cecil R. Dybowski  
Associate Professor of Chemistry





Dr. Peter Stilbs  
Institute of Physical Chemistry  
Uppsala University  
Box 532  
S-75121 Uppsala , Sweden

Tel: \*\*\*46-18-183646

Uppsala 24 April 1984

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

"Mononucleotide Aggregation from FT-PGSE Self-diffusion Data;  
Equipment bought (Diablo and JEOL FX-").

Dear Professor Shapiro:

Thank you for your reminders; I hope that this letter will reach you before the ultimate deadline date.

For some time Roger Rymdén and myself have studied the feasibility of diffusion-based investigations of different aggregation processes in solution, including those of mononucleotides in aqueous solution.

The project turned out to be very much more difficult than initially anticipated; computer simulations on the basic monomer-n-mer models did not satisfactorily reproduce the experimental data. A slightly more complex, indefinite monomer-n-mer aggregation model with appropriate accounting for changes in aggregate geometry with aggregate size and obstruction effects, however, fits the observed data quite well (Figure 1). We are presently preparing the paper for publication

We will soon get a new supercon NMR in the 300 MHz-range, but we still hope to keep the JEOL FX-100 alive for many years. Most current problems concern the cooling system, and are of corrosion-related nature. The Diablo 24-sector MHD disc drive is malfunctioning, and needs a motor replacement. Generally, we would like to hear from anybody that has any FX-100, FX-60 or FX-90Q-related equipment (whole spectrometer systems or just spare parts) for sale. A Diablo disc drive is needed immediately.

Yours sincerely,

/ Peter Stilbs /



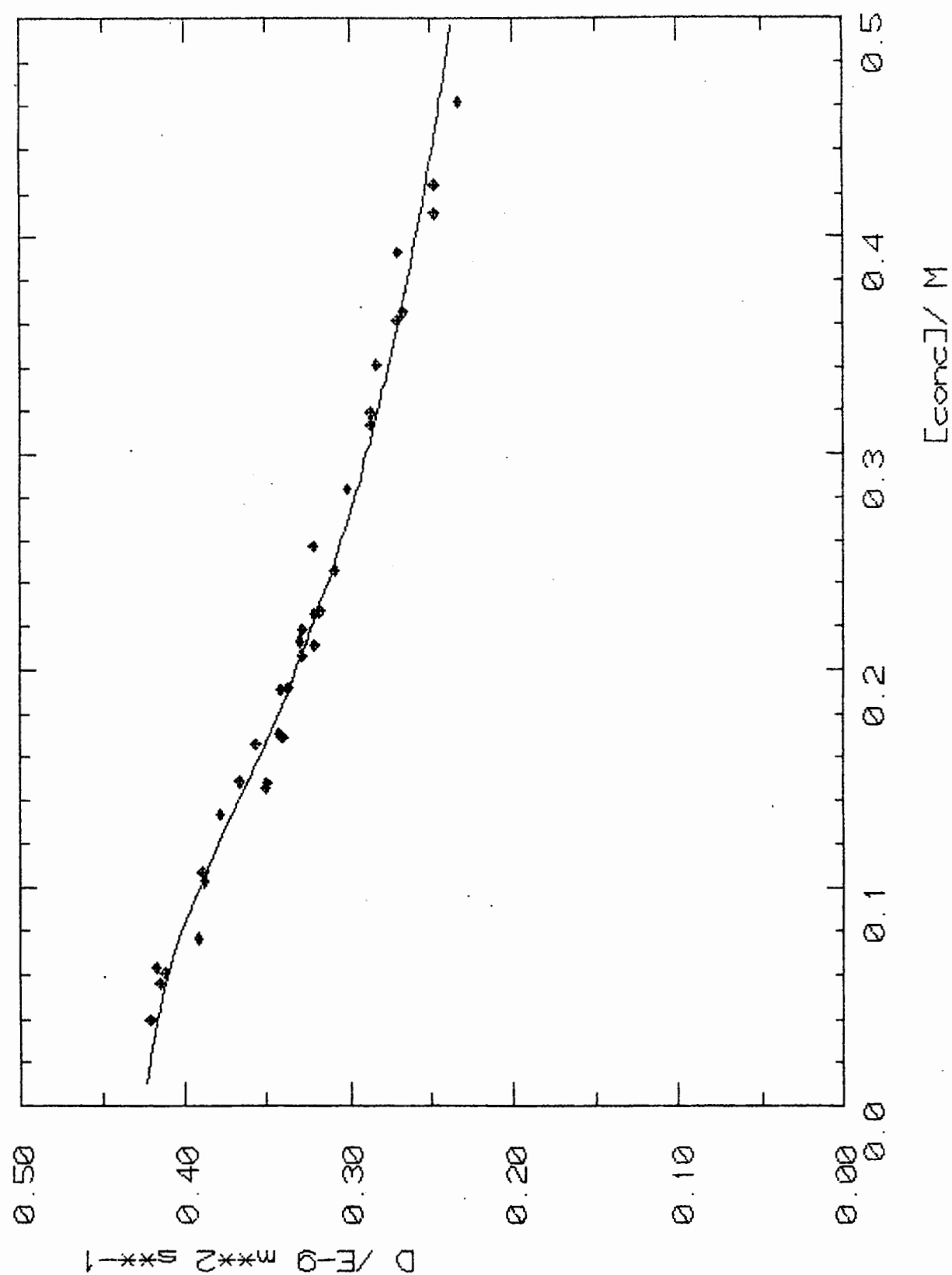


Figure 1. Typical mononucleotide self-diffusion behaviour in water ( $D_2O$ ) and the result of a computer simulation of an indefinite aggregation process.

## RAMAN RESEARCH INSTITUTE

BANGALORE - 560 080, INDIA

Professor C.L.Khetrapal

March 27, 1984

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

Title: The use of two liquid crystals in the determination of molecular structure of systems providing deceptively simple spectra.

Dear Professor Shapiro,

This is in response to the green reminder for a Scientific Contribution to the TAMU NMR Newsletter.

It is well known that the NMR spectra of *oriented molecules* of the type AA'BB' or AA'BB'X where the dipolar couplings  $D_{AB}(D_{A'B'})$  are much larger than the other coupling constants and  $D_{AA'} \approx D_{BB'}$ , it is not possible to determine all the spectral parameters to any reasonable precision due to *deceptive simplicity* reasons. Such a situation is usually encountered in the proton spectra of *p*-disubstituted benzenes in general and *p*-substituted fluorobenzenes in particular in thermotropic solvents. In such AA'BB'X systems, the spectra are quite insensitive to the chemical shift  $\delta_{AB}$ ,  $(D_{AX} - D_{BX})$  and  $(D_{AA'} - D_{BB'})$  and hence one can obtain only  $D_{AB}(D_{A'B'})$ ,  $D_{AB'}(D_{A'B})$ ,  $(D_{AA'} + D_{BB'})$  and  $(D_{AX} + D_{BX})$ . Such a system needs 2 order parameters for the specification of molecular orientation and 3 relative interproton distances for the fixation of relative nuclear positions. Consequently, 5 geometrical and orientational parameters are required to be determined whereas the system in a single experiment provides only 4 dipolar parameters. If, however, the studies are carried out in two different solvents providing substantially different relative order parameters, the number of dipolar coupling parameters doubles (becomes 8) and only two additional order parameters are required to be determined assuming that the molecular geometry does not change with the solvent. Such experiments, therefore, enable the determination of molecular structure in cases providing deceptively simple spectra. The use of the method has been actually demonstrated<sup>1</sup> for 2-(*p*-bromophenyl) 4,6-dichloropyrimidine where the geometrical parameters have been derived.

<sup>1</sup> C.L.Khetrapal, A.C.Kunwar and S.Arumugam, *Org. Mag. Res.* (to be published).

Yours sincerely,

C.L.Khetrapal

UNIVERSITÉ PARIS VII



INSTITUT DE TOPOLOGIE ET DE DYNAMIQUE DES SYSTEMES  
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ORGANIQUE PHYSIQUE

J.-E. DUBOIS, *Directeur*

B. ANCIAN, Professeur  
Poste 57.87.

PARIS, April, 26th, 1984.

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

TEXAS 77843

U.S.A.

Dear Professor,

Thank you for having published the first circular about the French NMR Summer School (R-2D) to be held in Orléans (France).

A final program has now been established with some minor modifications in the timing. Can you publish the final circular in the next edition of your journal with the mention :

Inquiries and inscriptions **before July 1st, 1984** to :

Bernard ANCIAN  
ITODYS - Université Paris VII  
1, rue Guy de la Brosse,  
75005 - PARIS  
FRANCE.

Phone. (1) 336.25.25. extension 57.87

Thank you, with my best regards.

Sincerely yours,

A handwritten signature in black ink, appearing to be 'B. Ancian', written in a cursive style.

B. ANCIAN.

**Programme ECOLE D'ETE**  
**RMN à 2 dimensions R.2D.2**

Orléans 29 Août - 5 Septembre 1984

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**Comité d'Organisation :** B. ANCIAN (Paris) , D. CANET (Nancy), P. GRANGER (Rouen),  
 J.Ph. GRIVET (Orléans), J.Y. LALLEMAND (Gif sur Yvette),  
 G. POUZARD (Marseille)

**MERCREDI 29 AOUT**

**Matin : Prof. G. POUZARD : Les outils de la RMN impulsionnelle.**

I Matrice densité	2 h.
Travaux Dirigés	1 h.

**Après-Midi : Prof. G. POUZARD : II Applications** 2 h.

Travaux Dirigés 2 h.

**JEUDI 30 AOUT**

**Matin : Prof. D. CANET : Les outils de la RMN impulsionnelle.**

III Opérateurs densité	2 h.
Travaux Dirigés	1 h.

**Après-Midi: Dr. J.Y. LALLEMAND :**

VI Applications aux séquences d'impulsions	2 h.
Travaux Dirigés	1 h.

**VENDREDI 31 AOUT**

**Matin : Prof. R. FREEMAN : Spectroscopie J-Echos et Modulation des Echos**

INEPT. Introduction à la RMN à 2 dimensions.	2 h.
Travaux Dirigés et Travaux Pratiques	1 h.

**Après-Midi : Dr. J.Y. LALLEMAND : Application des séquences d'échos -**

Séquences DEPT, APT et SEMUT	2 h.
Travaux Pratiques	2 h.



**SAMEDI 1er SEPTEMBRE**

Matin	: Dr. G. BODENHAUSEN : Transfert de Polarisation (SPT,SPI)		
		Cyclage de phase et détection en quadrature en RMN 2D.	2 h.
		Travaux Pratiques et Travaux Dirigés	1 h.
Après-Midi	: Dr. G. BODENHAUSEN : Transfert de Polarisation par couplage scalaire - Corrélations $\delta$ - $\delta$ homo et hétéronucléaires (COSY, SECSY). Spectroscopie par transfert de cohérence relayée.		
			2 h.
		Travaux Pratiques et Dirigés	2 h.

**DIMANCHE 2 SEPTEMBRE**

Libre

avec Visite des Châteaux de la Loire prévue  
ou Séances Supplémentaires de Travaux Pratiques

**LUNDI 3 SEPTEMBRE**

Matin	: Dr. G. BODENHAUSEN : Corrélations de sites par Effet Overhauser		
		Nucléaire et Echange Chimique.	2 h.
		Travaux Pratiques et Travaux Dirigés	1 h.
Après-Midi	:	Travaux Pratiques	4 h.

**MARDI 4 SEPTEMBRE**

Matin	: Prof. R. FREEMAN : RMN multiquanta INADEQUATE 1D et 2D.		
		Travaux Pratiques	1 h.
Après-Midi	: Prof. R. FREEMAN : Applications de la RMN multiquanta		
		Travaux Pratiques et Dirigés	2 h.

**MERCREDI 5 SEPTEMBRE**

Matin	: Dr. M.H. LEVITT : Impulsions Composites et Découplage		
		large bande	2 h.
		Travaux Pratiques et Dirigés	1 h.
Après-Midi	: Dr. O.W. SORENSEN : Filtres multiquanta et de Spin.		
		Impulsions de "Purge"	2 h.
		Travaux Pratiques et Dirigés	1 h.



## THE UNIVERSITY OF ADELAIDE

ADELAIDE, SOUTH AUSTRALIA, 5001

DEPARTMENT OF ORGANIC CHEMISTRY  
TELEPHONE 228 5487

19th April, 1984.

Professor Bernard L. Shapiro,  
Department of Chemistry,  
Texas A. & M. University,  
COLLEGE STATION. TEXAS. 77843.  
U.S.A.

Dear Professor Shapiro,

<sup>19</sup>F Relaxation in Cyclodextrin Complexes

During the course of our <sup>19</sup>F n.m.r. study of  $\alpha$ -cyclodextrin ( $\alpha$ -CD) (I) complexes of fluorinated cinnamates (1), we investigated a number of trifluoromethyl substituted cinnamates and, in the case of para-CF<sub>3</sub> cinnamates, observed quite dramatic chemical shift changes accompanied by unusually severe line broadening. We believe  $\alpha$ -CD forms consecutive 1:1 and 2:1 complexes with the cinnamates, and as can be seen in Fig.1 for  $\alpha$ -Fluoro-p-CF<sub>3</sub>-cinnamate, these effects occur over a relatively narrow  $\alpha$ -CD concentration range, indicative of a high stability constant for at least one of the complexes, probably the 2:1 complex.

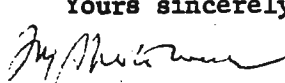
The linewidth of the CF<sub>3</sub> resonance of p-CF<sub>3</sub>-cinnamate reached almost 500 Hz and then narrowed with increasing  $\alpha$ -CD concentration. (m-CF<sub>3</sub>-cinnamate showed no broadening and a relatively small chemical shift variation.) It is unlikely that this enormous broadening is due to a very efficient T<sub>1</sub> relaxation mechanism such as spin-rotation, since the reorientational correlation time for similar  $\alpha$ -CD complexes is known to be too short (2). It seems more probable that the effect arises from an exchange process of the substrate between two or more equilibrium sites. Computer simulation of the lineshape arising from such a system gives linewidths of the order of magnitude observed, and the width variation over the  $\alpha$ -CD concentration range is also consistent with this explanation. However, to further complicate the issue, on cooling the samples the linewidths narrow markedly, possibly due to a shift in equilibrium position.

So Joe Lambert (TAMU NMR newsletter no. 301, p.20 1983) is not alone in the perplexing world of <sup>19</sup>F relaxation and we also would appreciate any clues your readers may provide.

Please credit this to the account of E.H. Williams,

Yours sincerely,

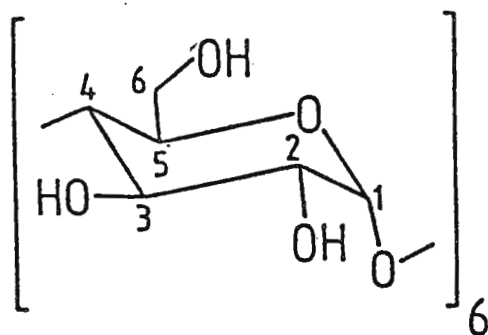
  
I.M. BRERETON

  
T.M. SPOTSWOOD

S.F. LINCOLN

Ref: 1. I.M. Brereton, T.M. Spotswood, S.F. Lincoln and E.H. Williams,  
J.C.S. Faraday 1, in press.

2. J.P. Behr and J.M. Lehn, J. Am. Chem. Soc., 98, 1743 (1976).



I

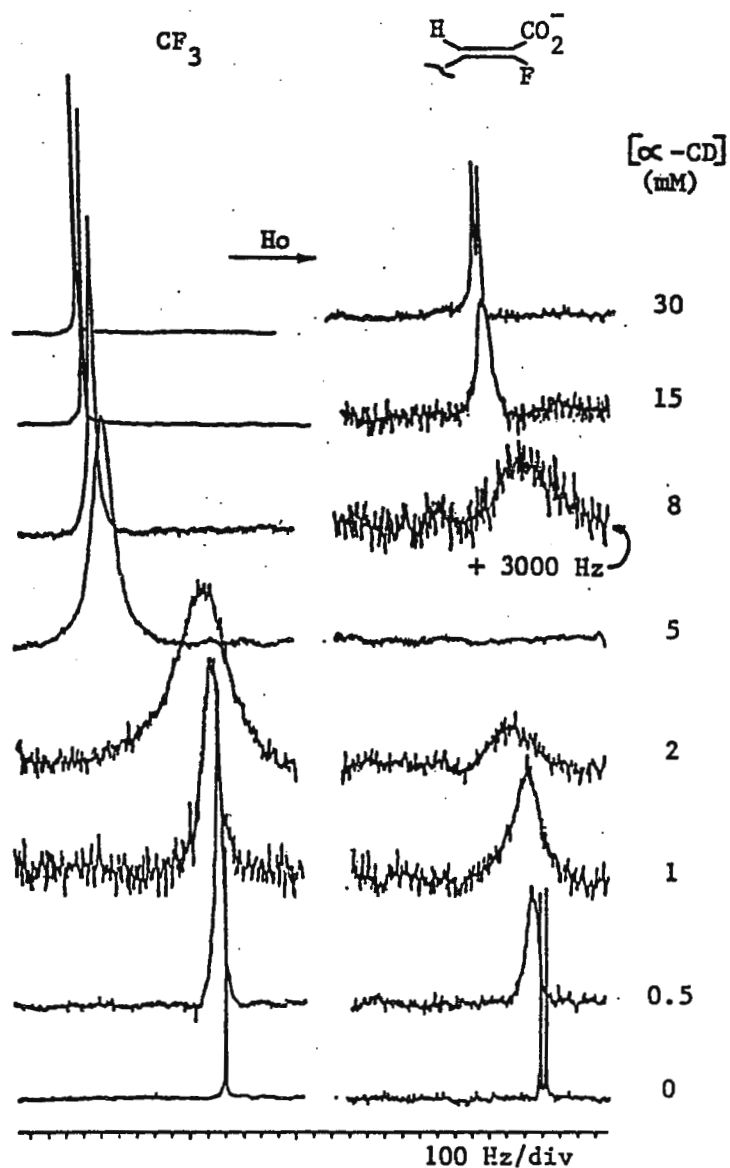


Fig.1. 282.35 MHz <sup>19</sup>F Spectra of Sodium α-F-p-CF<sub>3</sub>-cinnamate (1.0 mM) in the presence of varying amounts of α-CD.



ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

April 11, 1984

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

### Phosphorus-31 $T_1$ Values of Rat Tissue In Vivo

Dear Barry:

The use of horizontal geometry, wide-bore (ca. 30 cm), low to intermediate field (1.9 T to 4.7 T) superconducting magnets is receiving increasing attention for the application of high resolution chemical-shift NMR spectroscopy to living animals. These magnets facilitate the study of larger animals (i.e. rabbits, monkeys and dogs, compared with rats and mice in 'conventional' magnets) in the physiologically-natural, horizontal orientation. However, the cost of such magnets increases substantially with increasing field strength and therefore the relationship between magnetic field strength and sensitivity in intact biological systems is of importance. Because the spin-lattice relaxation time ( $T_1$ ) is related to the sensitivity per unit time and its field dependence is thus of practical import in selection of a spectrometer, we have used surface coils to measure the P-31  $T_1$  values of rat tissue in vivo at magnetic field strengths of 1.89 T, 4.7 T and 8.45 T.

The P-31  $T_1$  values of two important high energy phosphorus metabolite resonances, phosphocreatine (PCr) and the  $\beta$ -phosphate of ATP were determined in rat leg muscle, brain and liver in vivo and are reported in Table 1. The general trend in the rat leg muscle and brain is for a decrease in the  $T_1$  value of PCr and the  $\beta$ -phosphate of ATP with increasing field strength. This suggests that chemical shift anisotropy contributes significantly to the relaxation process at high magnetic field strength. However, in the rat liver in vivo the  $T_1$  value of the  $\beta$ -phosphate of ATP does not differ significantly at 4.7 T and 8.45 T and, in addition, is considerably shorter than in brain or muscle tissue. Rapid relaxation here may reflect dominant paramagnetic contributions. It should also be noted that we have observed a roughly linear dependence of the linewidth (increasing) with field strength in the tissue examined and that in all cases  $T_2^* \ll T_1$ .

In general, consideration of  $^{31}\text{P}$  spin-lattice relaxation times suggests that higher magnetic field strengths are advantageous in the study of animals by  $^{31}\text{P}$  NMR spectroscopy. Considering only the apparent linear relationship between

linewidth and magnetic field strength, the  $^{31}\text{P}$  signal-to-noise vs.  $\omega_0$  relationship is expected to be no greater than  $\omega_0^{3/4}$ , or  $\omega_0^{5/4}$  with matched exponential filter, in intact biological systems. The shorter  $^{31}\text{P}$   $T_1$  values at higher fields will further increase this signal-to-noise gain (on a per unit time basis).

Sincerely,

*Jeffrey L. Evelhoch*

Jeffrey L. Evelhoch

*Richard W. Briggs*

Richard W. Briggs\*

*Joseph J.H. Ackerman*

Joseph J.H. Ackerman

JJHA/kk

enclosure

\*Department of Radiology

The Milton S. Hershey Medical Center

Pennsylvania State University

Hershey, PA 17033

**Table 1. Rat Tissue  $^{31}\text{P}$   $T_1$  Values In Vivo**

[mean  $\pm$  SD (n)]<sup>a</sup>

<u>Tissue</u>	<u>Resonance</u>	<u>8.45 T</u>	<u>4.7 T</u>	<u>1.89 T</u>
Leg	PCr	2.61 $\pm$ .52(4)	4.29 $\pm$ .37(4)	5.42 $\pm$ .59(7)
Leg	$\beta$ -phosphate of ATP	1.23 $\pm$ .10(4)	2.05 $\pm$ .21(4)	2.43 $\pm$ .66(7)
Brain	PCr	2.74 $\pm$ .57(4)	4.21 $\pm$ .28(4)	3.82 $\pm$ .65(12)
Brain	$\beta$ -phosphate of ATP	0.69 $\pm$ .10(4)	1.54 $\pm$ .04(4)	2.15 $\pm$ .90(5)
Liver <sup>b</sup>	$\beta$ -phosphate of ATP	0.31 $\pm$ .08(4)	0.24 $\pm$ .01(4)	—

a) Error estimation given as standard deviation (SD) of the  $T_1$  values determined independently on n rats; it does not refer to the average precision in fitting the magnetization recovery data.

b) The liver does not contain significant amounts of PCr and therefore no  $T_1$  value is reported for this metabolite.



## Job Description

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We seek a person to be in charge of the Molecular Spectroscopy Laboratory of the School of Chemical Sciences (SOCS). This academic professional position, with the title of Spectroscopist, requires a broad range of professional, research, and educational skills. Minimum qualifications include an MS degree in physical science or engineering, and experience related to the responsibilities of the position. The ideal candidate would hold a Ph.D. in Chemistry or Physics with extensive experience in modern NMR spectroscopy and with demonstrated managerial skills.

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Inquiries should be addressed to:

Professor J. Jonas, Director  
School of Chemical Sciences  
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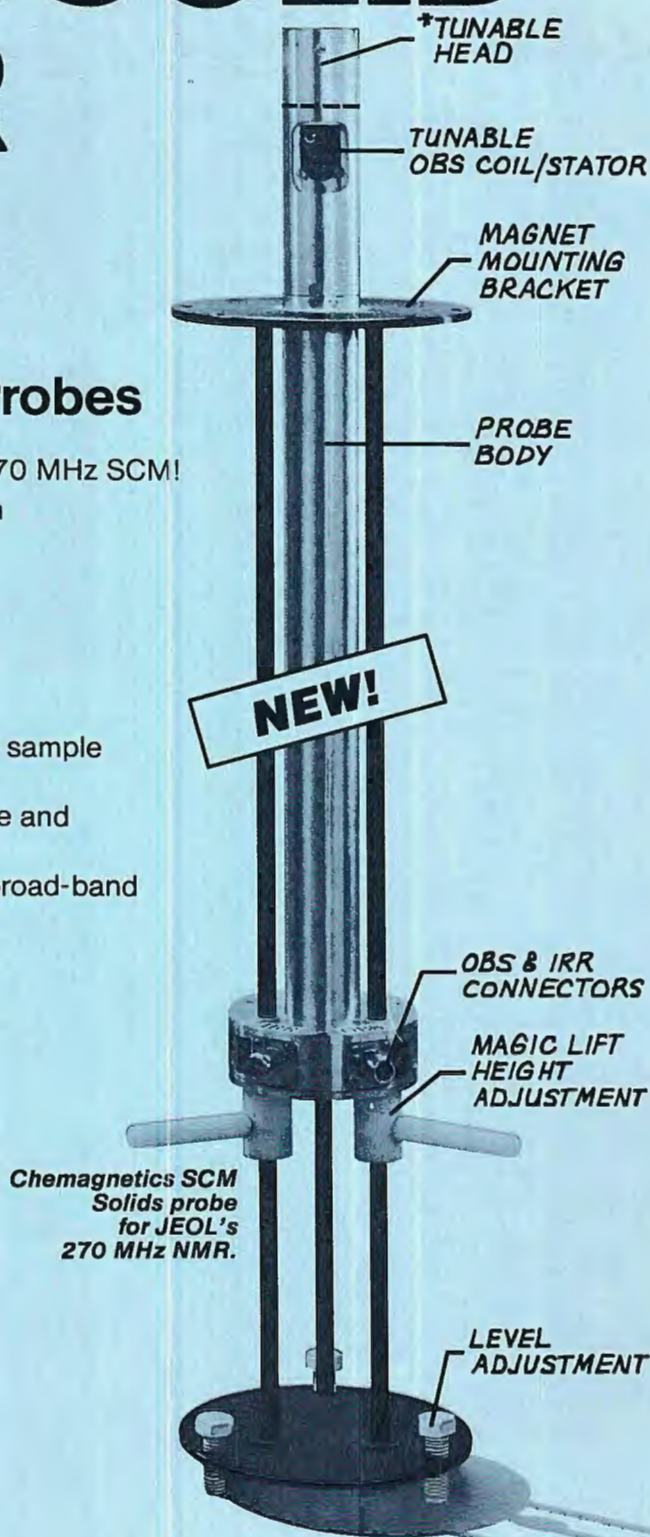
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