

Texas

A  
&  
M

University

N - M - R

Newsletter

Bryan H. Sykes  
No. 172

January, 1973

R. D. Green Polar Solutes in Aromatic Solvents	1
V. M. S. Gil The $\Delta E$ Approximation in Correlations of $^1J_{CH}$ To S-Characters	2
W. Bremser The Water-Welder in NMR	5
J. A. den Hollander and P. C. M. van Rossum Pulsed NMR Program for the PDP-12	6
V. Dimitrov DNMR-Single Operational Parameter Approach	7
J. B. Lambert, D. A. Netzel, R. J. Loyd and J. Larsen A Timer for Delaying Pulses and a Filter for Reducing Transient Response	11
K. L. Williamson Position Available	13
J. Schaefer Offsetting Transmitter and Receiver Reference Frequencies in Fourier Transform Experiments	14
H. L. Retcofsky and R. A. Friedel Carbon-13 Magnetic Resonance in Diamonds, Coals and Graphite	15
E. J. Fendler, J. H. Fendler and O. A. El Seoud Let's Turn Micelles Inside Out or $^1H$ NMR Investigations of Alkylammonium Carboxylate Surfactants in Non-Polar Solvents	18
A. C. McLaughlin, G. G. McDonald and J. S. Leigh, Jr. Measurement of $T_2$ 's in Spin Coupled Spectra	20
F. H. Rummens Chemical Shift Definition, Again and Again	22
J. J. Villafranca and M. Henry Sugar Phosphates and Modifications to a JEOL PS-100-FT	24

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.



# WILMAD

**WORLD'S SUPPLY HEADQUARTERS FOR  
NMR AND EPR SPECTROSCOPY.**

**... EVERYTHING YOU NEED FOR YOUR  
INVESTIGATIONS EXCEPT THE SPECTROMETER**

For more than 18 years, Wilmad precision NMR sample tubes have been the first choice of researchers using the modern investigative techniques of NMR and EPR high resolution spectroscopy.

During those pioneering and developing years, we added such items as:

- large volume sample tubes
- tube holders
- sample filters
- coaxial cells
- micro tubes
- "throwaway" tubes
- pipets
- thermometers
- microcells
- reference capillaries
- precision spinners
- vortex plugs

## **NOW... A MAJOR EXPANSION**

Recognizing the enormous customer advantages in a one-stop, world-wide source for all your NMR and EPR accessories and supplies, we have completed a major expansion of the Wilmad NMR line to include such items as:

- chart paper, binders, & ink
- fountain points & accessories
- NMR reference standards
- specialized coaxial cells
- deuterated solvents, compounds, & reagents
- shift reagents and special solvents
- Carbon-13 enriched compounds, solvents and gases
- Nitrogen-15 enriched compounds
- Oxygen-18 enriched water, both normalized and with deuterium
- lock solvents for Fluorine, Boron, Phosphorous, and Hydrogen

This is a random listing. Be sure you have our latest catalogs.



### **NEW CATALOG SUPPLEMENT**

Write today for our new Cat. Supp 5006-2... 24 pages filled with items you need for your investigations. Write today to Wilmad Glass Company, Inc., Route 40 and Oak Road, Buena, N.J. 08310.



**WILMAD**  
**PIONEER IN GLASSWARE  
FOR NMR SPECTROSCOPY**

Distributors of  
Thompson-Packard products

SPONSORS:

Abbott Laboratories  
 Bruker Scientific, Inc.  
 Digilab, Inc.  
 JEOL, INC.  
 The Lilly Research Laboratories, Eli Lilly and Co.  
 The Monsanto Company  
 Unilever Research (U.K.)

CONTRIBUTORS:

The British Petroleum Co., Ltd. (England)  
 Eastman Kodak Company  
 International Business Machines Corporation  
 Dr. R. Kosfeld, Abt. Kernresonanz, Inst. f. Phys. Chemie, TH Aachen (Germany)  
 The Perkin-Elmer Company  
 The Procter & Gamble Co., Miami Valley Laboratories  
 Shell Development Company  
 Thompson-Packard, Inc.  
 Union Carbide Corporation

ADVERTISERS:

Bruker Scientific, Inc.	- see p. 10
JEOL, INC.	- see inside back cover
Nicolet Instrument Corp.	- see p. 4
Varian Instrument Division	- see outside back cover
Wilmad Glass Co., Inc.	- see inside front cover

CO

C

C

## UNIVERSITI MALAYA

Department of Chemistry  
Lembah Pantai  
KUALA LUMPUR  
MALAYSIA



ALAMAT KAWAT: UNIVSEL  
TALIPON: 54361 (6 Saraf)

Bil. Kami:

8 December 1972.

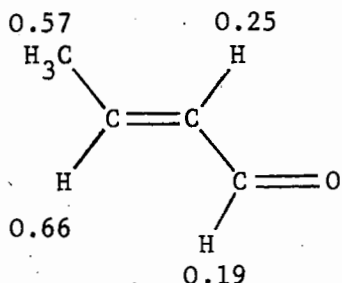
Dr B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas  
U.S.A.

Polar Solutes in Aromatic Solvents

Dear Dr Shapiro:

I was very interested to read of Engler and Laszlo's model for the solvation of carbonyl-containing molecules by aromatic solvents(1). It struck me that the solute chosen by them, bornanone, was rather curious in that the negatively-charged end of the molecular dipole is quite small and readily accessible, whereas the positive charge is more dispersed.

In a molecule with both ends of the molecular dipole fairly small and accessible, it is by no means obvious that solvation of the carbonyl oxygen atom would predict the relative chemical shifts of the protons in the solute molecule. We have found that the shifts induced by aromatic



solvants in the solute molecule 2-butenal (crotonaldehyde) are not at all consistent with solvation at the carbonyl oxygen atom, but rather with solvation near the other end of the molecule. Unfortunately, attempts to define a solvation site anywhere about the molecule which would predict the relative shifts quantitatively have not been successful. The differences in chemical shifts between cyclohexane and benzene solvents (in ppm) are shown on the diagramme.

The general usefulness of the Engler-Laszlo model appears to be less than would be wished for solute molecules having more than one highly-charged site available for solvation.

Yours faithfully,

R. D. Green

(1) E.M. Engler and P. Laszlo, J. Am. Chem. Soc., 1971, 93, 1317.





DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF COIMBRA  
PORTUGAL

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

5.12.1972

Dear Professor Shapiro,

THE  $\Delta E$  APPROXIMATION IN CORRELATIONS OF  $^1J_{CH}$  TO S-CHARACTERS.

Sometime ago (1,2), it was shown (using Pople-Santry theory) that there is no theoretical justification for the neglect of residual delocalization, in the Muller-Pritchard model, between localized MO's defined in terms of the usual carbon hybrid orbitals. The inclusion of delocalization in the simple symmetrical  $CH_n$  systems ( $CH_4$  tetrahedral,  $CH_3$  trigonal planar,  $CH_2$  linear) implies mainly an increase in  $\Delta E$  with carbon coordination number  $n$ . That is, one may write  $J_{CH} = A \rho_{CH} / \Delta E$ , allowing for appropriate changes in  $\Delta E$ .

When going from these systems to the simple hydrocarbons  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , etc. one may, within the same  $n$ , a) keep the hybrid orbital basis the same and allow for changes in  $\Delta E$  associated to variations of delocalization effects; it then turns out that the effective  $\Delta E$  values for  $n=2, 3, 4$  become closer and the Muller-Pritchard formula holds. Alternatively, b)  $\Delta E$  may be kept constant, within the same  $n$ , while  $\rho_{CH}$  is varied. There are indications (3) that the variations in  $\rho_{CH}$  given by the maximum overlap method have the right sign and magnitude to reproduce the results of a). Therefore, a reasonable proportionality relation of  $J_{CH}$  to  $\rho_{CH}$  is expected, within the same  $n$ , but no general proportionality because  $\Delta E$  must then change with  $n$ .

This is a more fundamental reason why no proportionality of  $J_{CH}$  to  $\rho_{CH}$



UNIVERSIDADE DE COIMBRA  
LABORATÓRIO QUÍMICO DA FACULDADE DE CIÊNCIAS  
COIMBRA - PORTUGAL - TELEF. 22825

given by the maximum overlap method is found (4) than that which invokes the ionic character of C-H bonds (4).

Yours sincerely

*Victor Gil*

Victor M.S. Gil

Professor of Chemistry

1. F.B. van DULJNEVELDT, V.M.S. GIL, and J.N. MURRELL, Theoret. Chim. Acta, 4, 85 (1966).
2. V.M.S. GIL and J.J.C. TEIXEIRA-DIAS, Molec. Phys., 15, 47 (1968).
3. V.M.S. GIL and C.F.G.C. GERALDES, J. Magn. Res. (submitted)
4. Z.B. MAKSIĆ, M. ECKERT-MAKSIĆ and M. RANDIĆ, Theoret. Chim. Acta, 22, 70 (1971).

# the Nicolet 1020A is a time averaging system for magnetic resonance spectrometers that gives you results like these:

The Nicolet 1020A is an easy-to-use time averaging system combining unique data processing capabilities with extremely useful display and readout routines.

Using a normalized signal averaging method, the 1020A presents a true average on its built-in 5" CRT display. The complete spectrum (or any expanded portion of it) is continuously displayed throughout the averaging process.

Thumbwheel switches select sweep times from 60 milliseconds to 1,999 seconds for a 2048-word sweep with 4-digit accuracy. The 1020A can provide sweep current to the spectrometer and can compensate for spectrometer field drift when using the Field Stabilization mode. The calibrated sweep widths are front panel selected and can be matched to any spectrometer.

The analog-to-digital converter (ADC) resolution is 12 bits (one part in 4096) for sweep times over 1 second and 9 bits (one part in 512) for sweep times less than 1 second.

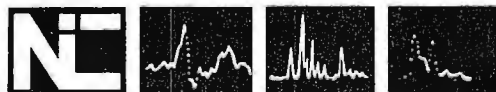
Total memory capacity is 2048 words, 24 bits long. The upper 12 bits store the final average while the lower 12 may be used to store the integral. Averaged spectra may be stored in halves of memory and added to or subtracted from one another.

Digital integration is built-in and does not destroy the original spectrum thus allowing simultaneous display of spectrum and integral. Baseline correction can be accomplished during display of the integral to assure optimal results.

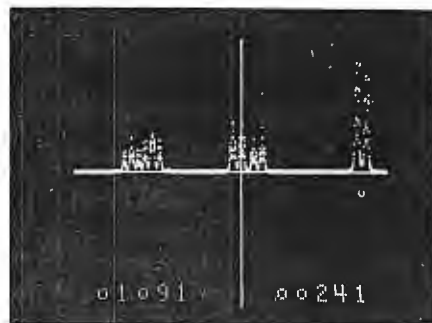
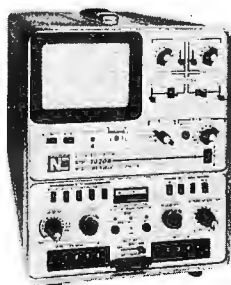
Another unique display feature is the ability to expand the displayed spectrum in both the X and Y axes by factors of 2 up to a total expansion of 64 times. (Typical expansion examples are shown to the right). In addition to this analog display a simultaneous numerical display shows the amplitude and address values of any data point selected by a moveable electronic cursor.

Write or call collect for complete details or to arrange a demonstration in your laboratory.

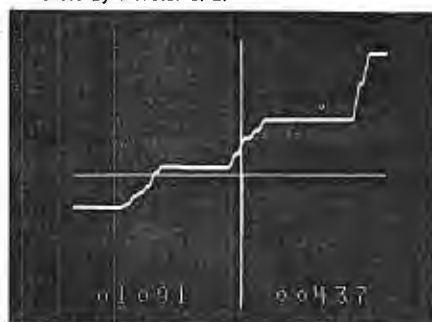
**NICOLET INSTRUMENT CORPORATION**



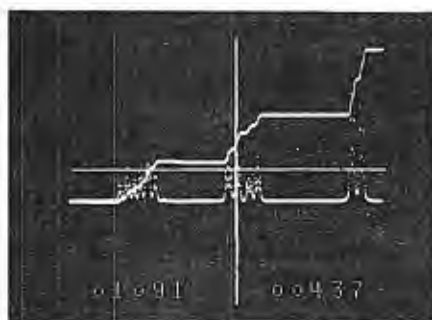
5225 Verona Road, Madison, Wisconsin 53711  
Phone 608/271-3333 TWX: 910-286-2713



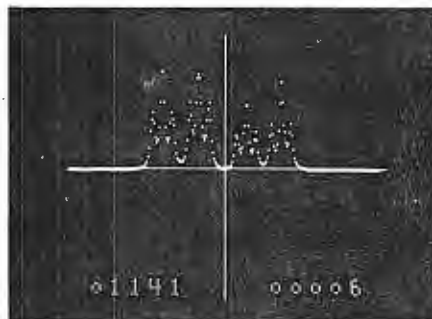
1. Averaged spectrum of 2-butyl-1, 2-dihydropyridene with spectrum expanded on amplitude scale by a factor of 2.



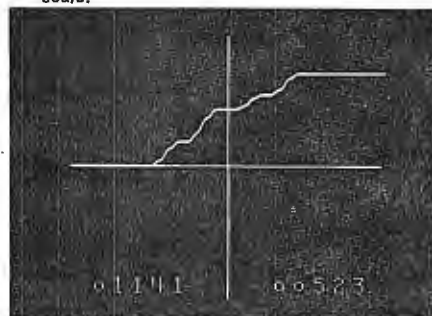
2. Integral of Figure 1 averaged spectrum.



3. Figure 1 spectrum and Figure 2 integral displayed simultaneously.



4. Averaged spectrum expanded by a factor of 4 on both the amplitude scale and the frequency scale.



5. Integral of Figure 4 averaged spectrum.



Dr. W. Bremser c/o

**Badische Anilin- & Soda-Fabrik AG**

Hauptlaboratorium

**BASF**

Telefon (06 21) 601 (Vermittlung)

Telex 464 811 basf d (Zentrale)

Telegramme: BASF Ludwigshafenrhein

Bankverbindung: Landeszentralbank

6700 Ludwigshafen, Girokonto 545 07300

BASF · 6700 Ludwigshafen

Luftpost

Prof. Dr. B.L. Shapiro

Department of Chemistry  
Texas A & M UniversityCollege Station, TX 77843

U S A

Ihre Zeichen

Ihre Nachricht vom

Unsere Zeichen

WH/PV

WBr/Dr

Telefon-Durchwahl

(06 21) 60- 8401

Telex

464-

Ludwigshafen

Dec. 1, 1972

Betreff

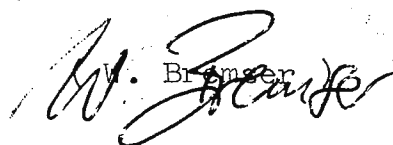
The Water-Welder in NMR

Dear Professor Shapiro,

following your editorial advice I will restrict myself to a short description of the "water-welder". In our laboratory we routinely store all measured samples for possible later reference - except those contained in the valuable high precision tubes used for our superconducting magnet. Thus a fast, precise and easy (for unskilled operators) technique of sealing these sample tubes is essential. Ing. Heft has recently introduced the water-welder, a microwelding instrument from Henes Man. Co., Phoenix, Arizona. The water welder produces the correct oxygen-hydrogen mixture for a hot flame by electrolysis of distilled water. A regulation of the electric current with a potentiometer permits a reproducible, stable and pointed heat of discrete temperature for a moderate price. We found this instrument very useful in practical use and I feel this information might be valid to some of your readers, even though the topic is very close to the good old stories of how to clean magnet coils.

For the European readers I would like to add that the instrument is marketed in Germany by Kager KG, 6000 Frankfurt, Konstanzer Str. 73. There are four models available (M, V, SB, B), we chose model SB with a price of 2210 DM for the complete system.

Sincerely yours,



W. Bremser

CHEMISCHE LABORATORIA  
DER RIJKS-UNIVERSITEIT

Afd.:

Wassenaarseweg.

Leiden

Telefoon 4 83 33

P.O.Box 75,

Leiden,

The Netherlands.

LEIDEN, 7 december 1972

Prof. B.L. Shapiro

Department of Chemistry

Texas A & M University

College Station

TEXAS 77843.

U.S.A.

Pulsed NMR program for the PDP-12.

Dear Dr. Shapiro,

We want to report the availability of a program for pulsed NMR for the PDP-12. This program was developed by us using as a basis a rather primitive program obtained from Digital Equipment Corporation.

This program incorporates a setup-mode, allowing the operator to optimize the spectrometer, an averager for 2K double precision, a FFT subroutine, which transforms 2K data in about 5 seconds, an interactive phase correction using the VR-12 display, and a plotroutine for an Y-T recorder.

Maximum sampling speed is 50 us/point, giving 10KHz frequency range. Furthermore the program can use LINC-tape for storage and retrieval of both free induction decays and spectra.

The minimum hardware required is a PDP-12 with 8K of core memory, hardware multiply/divide, analog to digital converter, real time clock, LINC-tape, and VR12 display.

We have interfaced the PDP-12 with a HA-100 equipped with FT 100.

Only two cables are required: one connecting the signal output of the FT100 to AD channel 10, the other the sync. pulse to the Schmitt trigger input 1 of the real time clock.

One recommended improvement of the program should be the replacement of the FFT routine by a double precision one.

Yours Sincerely,

  
F.C.M. van Rossum.

  
J.A. den Hollander.

БЪЛГАРСКА  
АКАДЕМИЯ НА НАУКИТЕ  
ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

BULGARIAN  
ACADEMY OF SCIENCES

INSTITUTE OF ORGANIC CHEMISTRY  
Sofia 13, Bulgaria

Valentin Dimitrov

Sofia, the 12th of December 1972...

Professor Bernard L. Shapiro

Department of Chemistry  
Texas A&M University

College Station, Texas 77843

DNMR-Single Operational Parameter Approach

Dear Professor Shapiro,

Although single parameter methods for evaluation of rate constants of systems undergoing chemical exchange have been already censured for obvious reasons<sup>1</sup>, an expression for calculation of life time in the two equally populated exchanging sites case, is offered. It is not of course an attempt to resurrect the era of simple, rapid, and (in most cases) erroneous calculations in the realm of DNMR, but I feel it may help sometimes.

Using the Hahn, Maxwell, and McConnell equation, and placing the origin of the coordinate system in the centre of the spectrum, i.e. at the position: a. of the singlet at rapid exchange, or b. of the "valley" between the two signals below coalescence, it is simple to obtain:

$$G_i = A_i \frac{1/T_{2i} + 1/\tau_i}{(1/T_{2i} + 1/\tau_i)/T_{2i} + (\pi\delta)^2} \quad (1)$$

where A is the amplitude factor. The i-index shows that the respective quantities are functions of temperature. G is the amplitude of the central V (from "valley")-point. The other symbols have their usual significance.

Since the amplitude factor A is proportional to static magnetization, which itself is function of temperature, a ratio-g-between the signal under consideration and another one, which is not affected by the exchange process, but whose amplitude depends on the temperature in the same way, is used. A single, sharp line (preferably produced by other nucleus/droup of nuclei of the same compound) is utilized as a second signal.

After some transformations one gets the following formula:

$$\tau_i = \frac{\rho^{-\varepsilon_i}}{(\varepsilon_i(1 + (\pi \rho T_{2i})^2) - \rho) / T_{2i}} \quad (2)$$

where  $\varepsilon_i$  are the above described ratios, and  $\rho = N_s/N_r$ .  $N$  is number of nuclei per unit volume, and  $s$  and  $r$  stand for signal and reference. Since both signal and reference lines are produced by groups of the same compound,  $\rho$  is simply a ratio between the numbers of nuclei in the two groups.

If  $T_2$  is assumed independent of temperature ( $T_{2i} = T_2 = \text{const}$ ), Eq. 2 is rewritten:

$$\tau_i = \frac{\sqrt{\alpha-1}}{\alpha \pi \rho} \frac{\rho^{-\varepsilon_i}}{\varepsilon_i - \rho/\alpha} \quad (3)$$

Here  $\alpha = \varepsilon_{\text{max}}/\varepsilon_{\text{min}}$ , and  $\varepsilon_{\text{max}}$  and  $\varepsilon_{\text{min}}$  are the relative amplitudes at very fast and very slow exchange rates, respectively.

This is a formula, which uses the amplitude of V-point as a Single Operational Parameter-VSOP (not to be confused with the trade name of some spirits-Very Special Old Production)-to evaluate life time in the case of two equally populated exchanging sites.

This approach has been applied to determine the activation parameters of N,N-Dimethyl-methylpropiolamide. The table compares results obtained by the Rogers and Woodbrey's intensity ratio method, total line shape calculations (using iterative procedure) with data produced by this formula.

	RW	TLS <sup>a</sup>	VSOP <sup>b</sup>	VSOP <sup>c</sup>
Activ. enthalpy	8.2 ± 0.9	18.2 ± 0.2	18.9 ± 1.4	20.4 ± 1.1
$\Delta H^\ddagger$ kcal/mol				
Activ. entropy	-32.4 ± 2.6	-3.5 ± 0.7	-1.7 ± 3.6	1.7 ± 3.0
$\Delta S^\ddagger$ e.u.				
Activ. free	17.86 ± 0.19	19.30 ± 0.01	19.37 ± 0.21	19.92 ± 0.17
enthalpy (298.2 °K)				
$\Delta G^\ddagger$ kcal/mol				

<sup>a</sup> Total Line Shape calculations

<sup>b</sup> VSOP, Eq. 2

<sup>c</sup> VSOP, Eq. 3



Please credit this contribution to the Dr.S.L.Spassov subscription.

Greetings and all good wishes for Christmas and the New Year.

Sincerely yours

*Valentin Dimitrov*

Valentin Dimitrov

<sup>1/</sup>G.Binsch, The study of intramolecular rate processes by Dynamic Nuclear Magnetic Resonance, in "Topics in Stereochemistry" ed. by E.L.Eliel and M.L.Allinger, Vol.3, John Wiley & Sons, 1968; and citations therein.

In 1973, more than ever before,  
look to BRUKER for leadership,  
innovation and responsibility to create  
the breakthroughs that will advance the  
techniques of magnetic resonance  
instrumentation and their applications.



#### P-20 SERIES

A pushbutton mini-pulsed NMR spectrometer operating at 20 MHz. For relaxation time measurements, process control and teaching purposes.

#### HX SERIES

Recognized worldwide as the industry standard for multinuclear NMR spectroscopy. Available at 60, 90 and 270 MHz with comprehensive Fourier transform accessories.

#### WH SERIES

Dedicated FT spectrometers, the WH-60 and WH-90 are available for any nucleus with a basic 8K of computer. Memory is fully expandable to 36K plus disk.

The new dimension, comprehensive instrumentation series now ready for your laboratory include:

#### SXP SERIES

Variable frequency pulsed NMR spectrometers, the SXP 4-60 and SXP 4-100 are available with a choice of magnets. Also capable for NQR measurements.

#### BM SERIES

Bruker magnets in the BM series are available up to 22" pole pieces. A range of superconducting cryomagnets are also available to suit your need.

#### BER SERIES

The BER-414 and BER-418 bring performance and reliability to the serious epr spectroscopist for X-band and/or Q-band operation.

#### B-NC SERIES

From the B-NC-8 through to the B-NC-36, these FT systems with 20 bit word length computers and comprehensive software lead the way as the first choice among experts in FT-NMR.

We keep thinking ahead.



#### USA

**Bruker Scientific Inc.**  
One Westchester Plaza  
Elmsford, N.Y. 10523  
Tel. (914) 592-5470  
Tlx. 13-1524

**Bruker Magnetics Inc.**  
1 Vine Brook Park  
Burlington, Mass. 01803  
Tel. (617) 272-9250  
Tlx. 94-9493

**Bruker Scientific Inc.**  
1548 Page Mill Road  
Palo Alto, Calif. 94305  
Tel. (415) 493-3173  
Tlx. 34-5533

#### CANADA

**Bruker Spectrospin Canada Ltd.**  
84 Orchard View Blvd.  
Toronto 12, Ontario  
Tel. (416) 486-7907  
Tlx. 06-22366



## NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

December 4, 1972

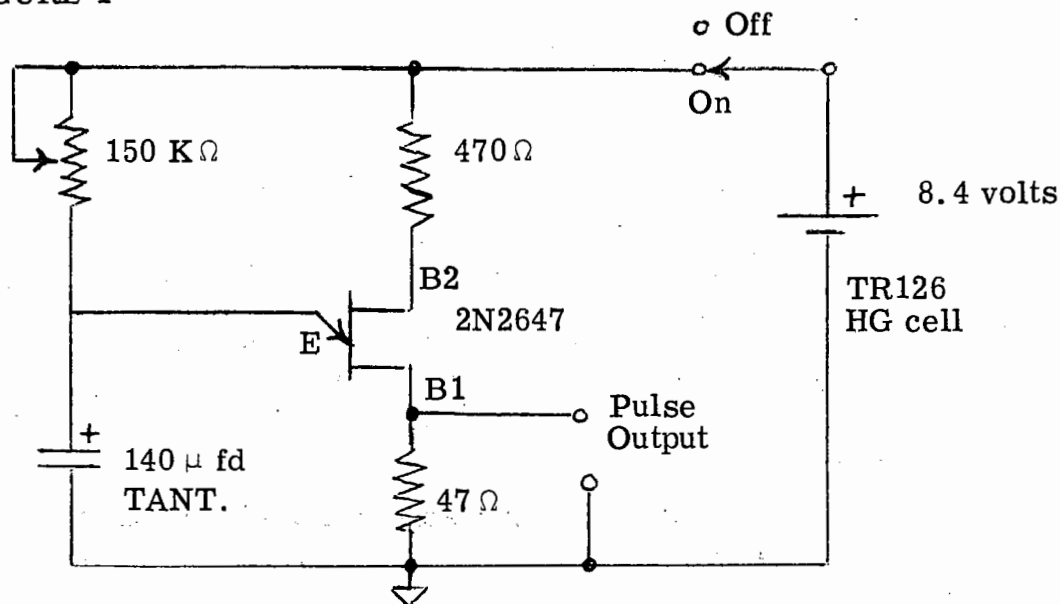
Professor Bernard L. Shapiro  
 Department of Chemistry  
 Texas A & M University  
 College Station, Texas 77843

Dear Barry:

The following modifications to our Bruker may be of interest to your readers:

I. Early models of the Bruker HFX-10, when operating in the pulse mode, were severely limited in pulse programming versatility. In our studies of  $^{13}\text{C}$  Ft-nmr it is sometimes necessary to delay the start of a pulse because of long relaxation times, while still maintaining the frequency range desired. Both the Nicolet 1074 and the Bruker BSV-2 units have facilities for an external trigger. The timer described here (Figure 1) permits the interval between successive rf pulses to be varied up to 35 sec by means of external trigger pulses to the 1074. The components are housed in a small box equipped with banana plugs that fit directly into the Sweep Trigger input of the SW-71 Wide Range Sweep Control of the 1074. The Trigger Switch of the Sweep Control Unit must be set to plus (+), and the plus (+) push button on the Bruker BSV-2 must be pushed in.

FIGURE 1

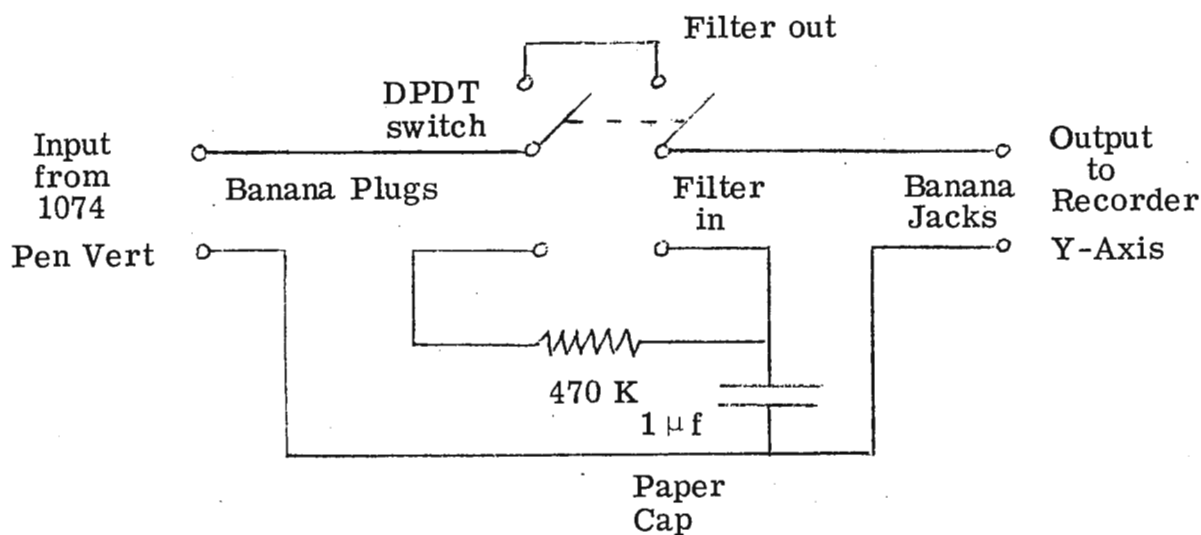


Professor Shapiro

December 4, 1972

II. When the Nicolet #1074 system is used with the Bruker HFX-10 for Ft work, the recorder pen response to the step inputs on the Y-axis is faster than the flow of ink from the pen, so that skipping occurs. To alleviate this problem, the simple low-pass filter shown below (Figure 2) was connected to the Y-axis cable of the recorder. This filter slows down the transients between channels during recording of the spectrum, thereby preventing skipping and in effect dampening the noise relative to the signal. For samples in which the signal-to-noise ratio is low, the vertical display scale of the 1074 can be set to a greater amplitude than normal and the filter is used to dampen the increased noise level. The filter is mounted in a small box with banana plugs and jacks directly on the rear panel "Pen Vert" output terminals of the 1074. A switch is provided on the box to select filter IN and OUT operation. The Pen real-time switch on the SW-71 wide-range sweep control of the 1074 can also be set to the IN position and the dwell time per channel adjusted to give the best spectral presentation.

FIGURE 2



Sincerely,

*JBL*

Joseph B. Lambert

*Daniel A. Netzel*  
Daniel A. Netzel

*Robert J. Loyd*  
Robert J. Loyd

*James Larsen*  
James Larsen

JBL:vc

Title: A Timer for Delaying Pulses and a Filter for Reducing Transient Response



Carr Laboratory, Department of Chemistry

MOUNT HOLYOKE COLLEGE

South Hadley, Massachusetts 01075

Telephone 413 538-2214



11 December 1972

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

POSITION AVAILABLE

Dear Barry:

We have an opening for a Postdoctoral Fellow, beginning immediately, interested in applying  $^{13}\text{C}$  nmr to problems of biological interest and conformational analysis. Our equipment includes an HA-100 with a Digilab IMR-3 pulsed Fourier Transform System, Data General Nova, and 128K disk memory, in addition to a T-60 for proton work.

Sincerely yours,

Kenneth L. Williamson  
Professor of Chemistry

KLW/jrl

# Monsanto

Monsanto Company  
800 N. Lindbergh Boulevard  
St. Louis, Missouri 63166  
Phone: (314) 694-1000

December 5, 1972

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

Dear Barry:

Offsetting Transmitter and Receiver Reference  
Frequencies in Fourier Transform Experiments

It may be desirable in a Fourier transform experiment to operate the transmitter at a slightly different reference frequency relative to that of the receiver. For example, placing the pulsed rf of the transmitter in the center of the expected spectral width results in more efficient use of the available rf power. If the receiver reference frequency is offset sufficiently far from the center of the spectrum, then the Fourier transform experiment can still be performed as usual without loss of information, and without complicated quadrature detection schemes to distinguish upfield from downfield. One way to achieve this offset is to reference the transmitter and the receiver by separate frequency synthesizers which are phase locked but differ in frequency from one another by, say, 5 kHz. The two frequencies are mixed and the audio output is now used as the clock frequency to time repetitive pulses and data accumulation. The mixing ensures the coherent addition of successive free induction decays. For a Bruker system, this mixing can be conveniently accomplished by using external inputs to the mixer-amplifier circuit described as "Frequenzzählung" (as suggested by Rudi Nünlist, Bruker Scientific, Palo Alto).

We have offset the reference frequencies of transmitter and receiver to use wide pulse widths (1-10 msec) in investigating the structure of inhomogeneously broadened lines. The spectral density of the wide pulse varies over the broad line and thereby provides a way of distinguishing the individual components of the line. The position of the transformed line can be fixed in the center of the displayed spectral width even though the pulsed transmitter frequency is varied. Wide pulses such as these can also be used to null intense solvent lines in Fourier transform experiments without interfering cross relaxation effects, as discussed by Redfield in Vol. 5 of Advances in Magnetic Resonance.

Please credit this contribution to the Monsanto subscription.

Sincerely,

*Jack*  
Jack Schofer



# United States Department of the Interior

## BUREAU OF MINES

4800 FORBES AVENUE  
PITTSBURGH, PENNSYLVANIA 15213

December 29, 1972

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

Dear Barry:

Our recent nmr endeavors have been devoted almost exclusively to

### CARBON-13 MAGNETIC RESONANCE IN DIAMONDS, COALS, AND GRAPHITE.

Diamonds and Graphite.---The  $^{13}\text{C}$  nmr spectrum of diamonds (figure 1) yields a chemical shift of  $156 \pm 3$  ppm with respect to neat carbon disulfide. The chemical shift is well within the range of values reported for quaternary carbons in alkanes and not far removed from the average chemical shift observed for solid adamantane. This spectrum, as well as all others reported herein, are broadline spectra presented as first derivatives of the dispersion mode. In the case of figure 1, both the  $\text{CS}_2$  resonance and the diamond resonance are artificially broadened -- operating conditions were chosen for maximum S/N, therefore resolution suffers.

The spectrum of graphite (not shown) is quite similar to that of the very high rank meta-anthracite coal (See figure 2, bottom). The inversion of the resonance relative to that of diamond is believed to result from changes in passage conditions since relaxation times for the two carbon allotropes would be expected to be quite different, i.e., one is a magnetically dilute insulator; the other, a semiconductor.

Coals. Spectra of the four coals examined are shown in figure 2. We feel that the changes in linewidth, chemical shift, and lineshape can be best rationalized in terms of increasing carbon aromaticity with increasing coal rank (carbon content) leading finally to the formation of graphite-like layers within the coal structure.

Sincerely yours,

H. L. Retcofsky

R. A. Friedel

BEST WISHES FOR THE NEW YEAR!

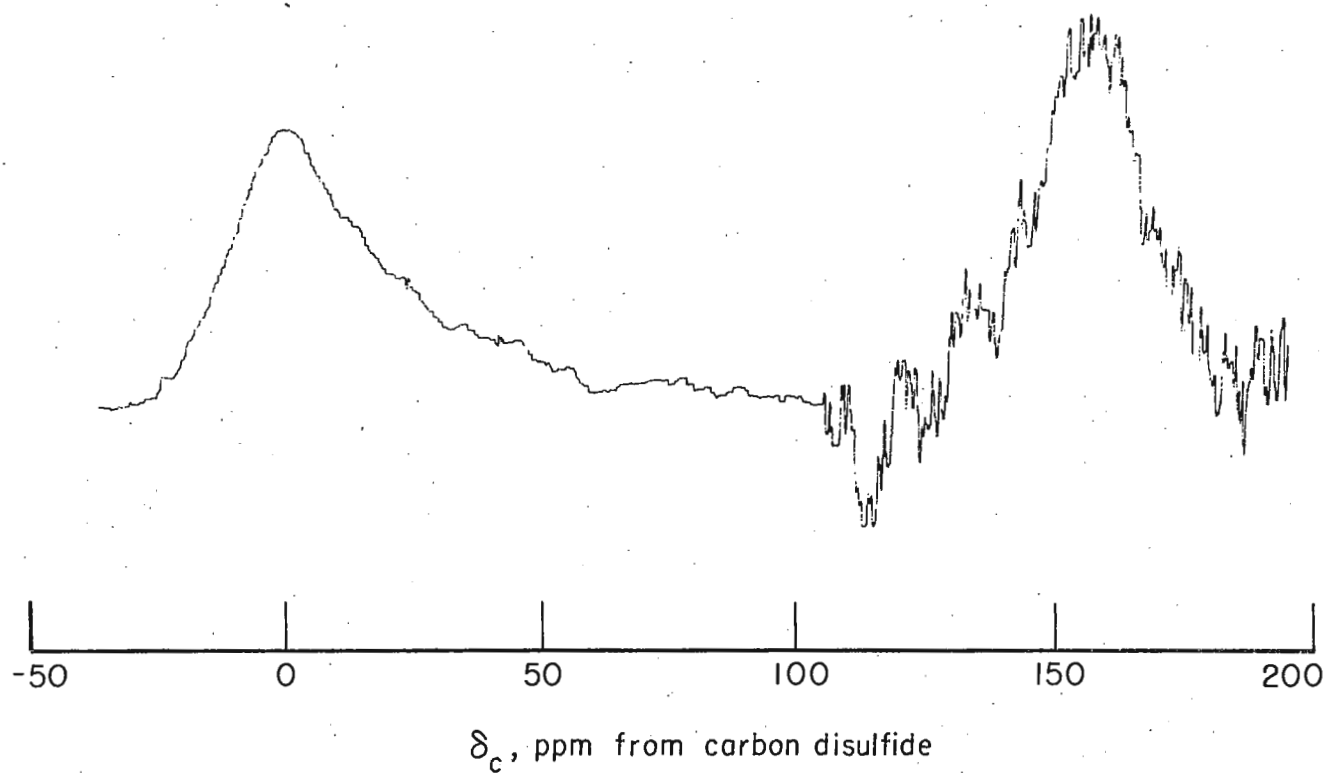


Figure 1.  $^{13}\text{C}$  NMR spectrum of diamond (250 scans)

L-11511



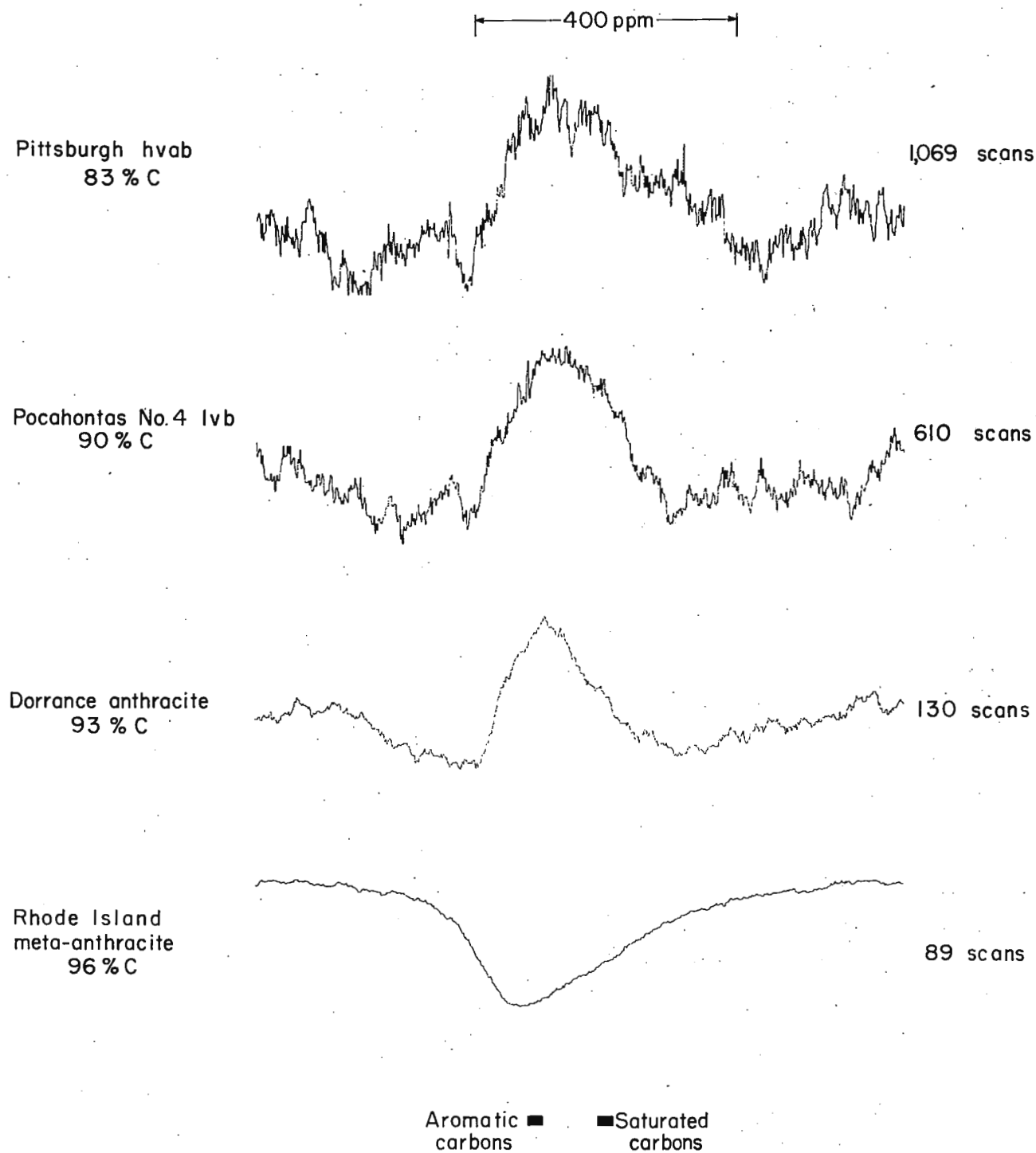


Figure 2. 15.085 MHz  $^{13}\text{C}$  NMR spectra of selected coals.

L-11341

## TEXAS A&amp;M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

December 26, 1972

Department of  
CHEMISTRY

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

Dear Barry,

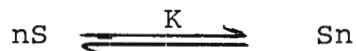
Let's Turn Micelles Inside Out

or

<sup>1</sup>H Nmr Investigations of Alkylammonium Carboxylate Surfac-  
tants in Non - Polar Solvents

We have been investigating the properties of alkylammonium carboxylate surfactants in non-polar solvents by <sup>1</sup>H nmr to provide structural information essential to the elucidation of rate enhancements of several reactions by these surfactants.

Assuming an idealized situation, the formation of aggregates can be represented by :



where S and S<sub>n</sub> are the concentrations of monomeric and micellar surfactant, K is the equilibrium constant for the formation of the micelle and n is the aggregation number. Changes in the chemical shifts of the magnetically distinct protons of the alkylammonium carboxylates as functions of their concentration were treated according to :

$$\delta = \delta_M + \frac{CMC}{C_D}(\delta_m - \delta_M)$$

where  $\delta$ ,  $\delta_M$  and  $\delta_m$  are the observed, micellar and monomeric

chemical shifts of the protons, respectively,  $C_D$  is the stoichiometric surfactant concentration and CMC is the critical micelle concentration. Furthermore, the concentration of the monomeric surfactant can be calculated from :

$$[S] = \frac{C_D (\delta_M - \delta)}{\delta_M - \delta_m}$$

which allows the calculation of  $n$  and  $K$  by treating the data according to :

$$\log(C_D - [S]) = \log nK + n \log [S]$$

Briefly our findings are :

(1) Alkylammonium carboxylates form small ( $n = 3-8$ ) reversed micelles with the ammonium and carboxylate groups in the interior and the hydrocarbon chain extending into the bulk solvent pseudo-phase in  $C_6H_6$ ,  $C_6H_5Cl$ ,  $CCl_4$ ,  $CDCl_3$  and there is some solvent penetration into the micelle.

(2) Except in  $CCl_4$ ,  $\log CMC$  values decrease linearly with an increasing number of carbon atoms in the alkylammonium group but they increase with an increasing number of carbon atoms in the carboxylate group.

(3) The CMC of the surfactant for butyl, hexyl, octyl, and dodecylammonium propionate correlates well with both the reciprocal dielectric constant and the solvent polarity parameter  $E_T$ . Not unexpectedly, increasing solvent polarity retards micelle formation.

These results are being fully reported in the open literature.

Sincerely,

Omar A. El Seoud  
Omar A. El Seoud

E. J. Fendler  
E. J. Fendler

J. H. Fendler  
J. H. Fendler

## UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

*The School of Medicine*

JOHNSON RESEARCH FOUNDATION  
DEPARTMENT OF  
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

December 20, 1972

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

Dear Dr. Shapiro:

Measurement of  $T_2$ 's in Spin Coupled Spectra

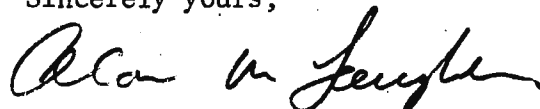
We have recently been playing with techniques of  $T_2$  measurement with FT-NMR. Perhaps the simplest method we have tried is a simple "90° pulse- $\tau$ -180° pulse- $\tau$ " sequence using short, non-selective RF pulses. Transformation of the "echo" yields a (partially)  $T_2$  relaxed spectrum. However in first order, homonuclear, spin-coupled spectra the phase of lines within a multiplet distorted. During the total waiting time  $2\tau$ , each line in a complex spectrum accumulates a phase error corresponding to its shift from the center of the multiplet (since the 180° pulse inverts all the spin states). This effect is shown in Figure 1. The sample is neat ethyl acetate, not degassed. The lower spectrum is taken with  $\tau = 1/2J$ . The other spectra are taken at times  $\tau = 5/8J$ ,  $6/8J$ ,  $7/8J$  and  $1/J$  respectively. Note that the non-spin coupled acetate peak shows no phase errors. The inner peaks of the quartet accumulate phase errors at a rate  $\pm 2\pi 3J/2$ . Within the triplet, the central unshifted line shows no phase errors and the outer lines accumulate phase errors at a rate  $\pm 2\pi J$  rad/sec.

Two simple expedients can remove this "phase error". (1) take  $T_2$  relaxed spectra only at times  $\tau$  which are integral multiples of  $1/J$  or (2) use a "absolute value" plot (square root of the sum of squares of the sine and cosine transforms). Figure 2 shows the absolute value representation of the series of spectra shown in Figure 1. Semi log plots of spectra using the absolute value plot give " $T_2$ " values of 0.6, 0.9 and 1.9 sec. for the  $\text{CH}_2$ , acetate  $\text{CH}_3$  and ethyl  $\text{CH}_3$  peaks respectively at 21°C. It is worth noting that the absolute value presentation cannot be used with severely overlapping lines.

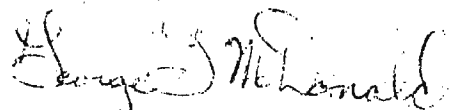


With a 5 mm sample tube serious amplitude modulation of the spectra with a period equal to the reciprocal of the spinning frequency were noted but use of a 2 mm capillary reduced this distortion to less than 5%.

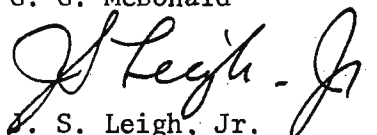
Sincerely yours,



A. C. McLaughlin



G. G. McDonald



J. S. Leigh, Jr.



## UNIVERSITY OF SASKATCHEWAN, REGINA CAMPUS

REGINA, CANADA

S4S 0A2

DEPARTMENT OF CHEMISTRY

January 4, 1973

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

Dear Barry:

Chemical Shift Definition, Again and Again

I would like to respond to Rolf Johannesen's letter (TAMU-NMR 166 32 (1972)).

His data on the difference in "chemical shift" between field sweep and frequency sweep spectra are not only qualitatively but also quantitatively in accordance with my "theory" (1). Eq. 24 of reference (1) calculates differences of 1.5 and 6.0 Hz, for the circumstances where Johannesen experimentally finds 1.4 and 6.1 Hz respectively. Although this is gratifying, it only proves that he is a good experimenter and that I did not make any algebra errors. It does not prove any law or hypothesis being either correct or incorrect. The differences arise solely from definitions, which in turn predetermine certain experimental conditions.

Unbeknownst to me, Radeaglia (2) prior to my own work, discussed the difference between field and frequency sweep, his conclusion being that (apart from a sign) there is no difference. His claim (private communication) that my algebra was faulty is now sufficiently disproved. I would leave it to the readers to find the two errors in Radeaglia's derivations.

Johannesen also finds that in the field sweep mode the line separation apparently depends on whether the upfield or the downfield peak is taken as the zero-point (and that in the latter case the separation is equal to that in the frequency sweep mode with the down-frequency peak as zero). This is really only an apparent effect; expressed in Gauss (which is really what one should do in field sweep) the choice of reference does not matter at all. The discrepancy arises because of the conversion to frequency units. In field sweep the difference of resonance frequencies is of course zero so that one is relegated to comparison of larmor frequencies. If we have an upfield signal at  $H_r$  and a downfield signal at  $H_s$  then, when  $r$  is at resonance (i.e. larmor frequency  $\nu_r$  equals  $\nu_o$ ), the field at  $s$  which this happens is

$$H_r = H_o / \mu_g (1 + \sigma_b - \sigma_r) \quad (1)$$

Professor B.L. Shapiro  
January 4, 1973

At the same time the larmor frequency of s is given by  $\nu_s = H_r \nu_o / H_s$  and the difference in larmor frequencies then is

$$(\nu_r - \nu_s) H_r = \nu_o (\sigma_s - \sigma_r) / (1 + \sigma_b - \sigma_r) \quad (2)$$

If we now look at s at resonance we have  $\nu_s = \nu_o$  and  $\nu_r = \nu_o H_s / H_r$  leading to

$$(\nu_r - \nu_s) H_s = \nu_o (\sigma_s - \sigma_r) / (1 + \sigma_b - \sigma_s) \quad (3)$$

Combining Eqs. (2) and (3) then results in

$$\frac{(\nu_r - \nu_s) H_r}{(\nu_r - \nu_s) H_s} = \frac{1 + \sigma_b - \sigma_s}{1 + \sigma_b - \sigma_r} \approx (1 - \sigma_s + \sigma_r) \quad (4)$$

which is exactly the same result as obtained before (eq. 24 ref (1)) for the ratio  $\delta_v / \delta_H$ , comparing frequency to field sweep  $\delta$ 's. Q.E.D.!

Finally, I would like to rise to Johannesen's challenge to propose a pragmatic chemical shift definition. I propose to maintain the set of self-consistent definitions as given before (1), but with one major addition; rather than using a bare nucleus in vacuo as a standard I propose to use zero-pressure ethane in an air filled gap as the standard, at least for proton work. The only effect this has is to drop the permeability term in the afore mentioned definitions; the difference between a bare proton and the protons in ethane at zero-pressure is a constant, which never even needs to be known. In actual practice one would need of course a pressured ethane sample, but fortunately the temperature and pressure dependence of ethane is not only small but is also very accurately known (3) so that a correction to zero-pressure (at any temperature) can be easily calculated. Conversion from other references, say internal TMS, would also be simple; if the ethane sample is made up in an inner tube of a coaxial cell (available from Wilmad) it suffices to fill the annular space between inner and outer tube with the solution and measure the TMS-Ethane difference. Making up gas samples is no trivial matter, but if one laboratory which has the expertise would agree to produce (and sell) such samples one has the additional advantage of inter-comparability between all NMR laboratories.

For other nuclei a similar procedure could be chosen. For example Mohanty and Bernstein's very accurate data on pressure and temperature dependence of  $CF_4$  shifts (4) could be used as a  $^{19}F$  standard. One additional experiment could link this  $^{19}F$  standard to the ethane  $^1H$  standard.

Best Wishes for 1973



F.H.A. Rummens, D.Sc.  
Professor of Chemistry

- (1) F.H.A. Rummens, TAMU NMR Newsletter 125, 36 (1969).  
Org. Magn. Res. 2, 209 (1970).
- (2) R. Radeaglia, Monatsberichte 8 (3), 205 (1966).
- (3) F.H.A. Rummens, Mol. Phys. 21, 535 (1971).
- (4) S. Mohanty, H.J. Bernstein, J. Chem. Phys. 54, 2254 (1971).

## THE PENNSYLVANIA STATE UNIVERSITY

152 DAVEY LABORATORY  
UNIVERSITY PARK, PENNSYLVANIA 16802College of Science  
Department of Chemistry

January 4, 1973

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

Dear Professor Shapiro:

Title: Sugar Phosphates and Modifications to a JEOL PS-100-FT

The pink letter caught up with us. We have been rather busy lately with our new (6 months old now) JEOL PS-100-FT equipped with a Nicolet 1085 computer. I believe we are, as yet, the only installation with a Diablo disc and a Kennedy tape drive. The former is a delight to work with and I shudder to think of the FID's we would have "blown" if we could not have stored them on our disc for later manipulation. The overall system has been a delight to work with and I can't say enough about the excellent assistance we have received from Tom Farrar, Gary Samuelson, Vic Bartuska, Mr. Harra and the rest of the gang at JEOL in Cranford.

One area of current interest with us is a determination of  $T_1$  relaxation times of natural abundance  $^{13}\text{C}$  nuclei in various sugar phosphates and the locus of Mn(II) when chelated to the sugar phosphates in solution. We were rather surprised to find that distances within the Mn- $\beta$ -pyranose and  $\beta$ -furanose complexes of fructose-1-phosphate are consistent with metal ion-ligand binding involving both phosphoryl oxygens and hydroxyls at C-2 and C-3 of the sugar. The dissociation constant of  $\sim 1 \text{ mM}$  would not suggest multiple liganding in F-1-P and this is causing us to reexamine the  $K_D$  value(s) of Mn-F-1-P over a wider range of Mn and F-1-P concentrations. After this its on to some  $^{13}\text{C}$  studies in the presence of the enzyme fructosyl,6-diphosphatase.

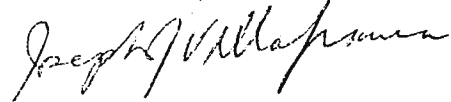
A few helpful tips for JEOL PS-100-FT users. We have installed a safety interlock to protect the probe from "cremation" by the decoupler power in the event of cooling air failure or absence. A pressure switch controls a relay that interrupts the AC line voltage to the decoupler and pulse generator-receiver section. The removal of decoupler power protects the probe but to halt data accumulation the pulse generator-receiver portion was also disabled - originally only the pulse generator was disabled but this "unclamped" the receiver - an undersirable condition for prolonged periods. An air flow control would be superior but a properly chosen and located pressure switch provides adequate protection with simplicity and economy.

For intermediate temperature ranges 0-35°C we find air through a heat exchange coil in a dry ice-ethanol bath gives a more reproduceable temperature control and adjustment than was experienced using the liquid N<sub>2</sub> boil off system supplied by JEOL. Below 0°C the boil off system is excellent and offers better liquid N<sub>2</sub> economy than heat exchange systems.

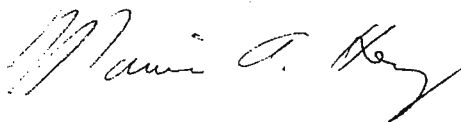
We feel a note of warning is in order for anyone using liquid N<sub>2</sub> boil-off temperature control systems. In our laboratory we apparently had an appreciable quantity of liquid O<sub>2</sub> present in the "boil-off" Dewar and an explosion and fire occurred in the dewar and head assembly - fortunately no damage other than "sooting" occurred in the transfer tube or probe. We think this potential hazard should be brought to the attention of others.

As further modifications of our JEOL are made we will keep you informed.

Joseph J. Villafranca



Maurice Henry



AUTHOR INDEX

Bremser, W.	. . . . .	5
Dimitrov, V.	. . . . .	7
El Seoud, O. A.	. . . . .	18
Fendler, E. J.	. . . . .	18
Fendler, J. H.	. . . . .	18
Friedel, R. A.	. . . . .	15
Gill, V. M. S.	. . . . .	2
Green, R. D.	. . . . .	1
Henry, M.	. . . . .	24
den Hollander, J. A.	. . . . .	6
Lambert, J. B.	. . . . .	11
Larsen, J..	. . . . .	11
Leigh, J. S.	. . . . .	20
Loyd, R. J.	. . . . .	11
McDonald, G. G.	. . . . .	20
McLaughlin, A. C.	. . . . .	20
Netzel, D. A..	. . . . .	11
Retcofsky, H. L.	. . . . .	15
van Rossum, P. C. M.	. . . . .	6
Rummens, F. H. A.	. . . . .	22
Schaefer, J..	. . . . .	14
Villafranca, J. J.	. . . . .	24
Williamson, K. L.	. . . . .	13



# JEOL

PS-100  
Console-  
Spectrum:  
25.1 MHz  
 $^{13}\text{C}$  Solid  
Natural  
Rubber



## Give your pulse a heart.

**For the kind of pulse required in tomorrow's NMR research, we have the perfect heart today. It's our PFT-100 Fourier Transform system. A system designed with incredible power, unusual versatility.**

The PFT-100 is capable of a 15  $\mu\text{sec.}$  pulse sufficient to produce a  $90^\circ$   $^{13}\text{C}$  magnetization vector tipping. Complete controls permit fine adjustments to regulate Pulse Width, Interval and Repetition. The system design allows you to select single or multiple pulse programs such as FT, DEFT, SEFT and more. Plug-in hard board program modules make it all possible.

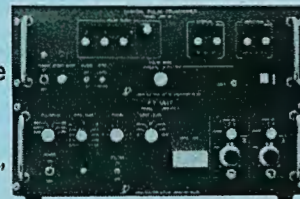
The magnet and CW/FT probe is also at the state of the art. It features a dual cross coil detection system with Deuterium ( $^2\text{H}$ ) Internal lock. It has a hetero-nucleus External lock, as well. You choose a fixed or replaceable insert probe which permits 5, 8 and 10mm/OD variable temperature sample tubes.

There's more. Push button controls and the solid state design of the PS-100 CW/NMR. There is also complete compatibility with most existing FT data reduction systems. They combine to make it a total research NMR system.

### At the heart of NMR research.

JEOL provides worldwide service and knowledge that are unsurpassed in the NMR field. With our MH-60, C-60HL, MH-100 and the PFT-100, we offer a broader range of equipment and locations than any other firm.

Information and demonstrations are available through our offices in Tokyo, London, Paris and Sydney. As well as the newest laboratory in the United States devoted to NMR research at JEOL, 235 Birchwood Avenue, Cranford, N.J. 07016.



NMR Spectrometers/Mass Spectrometers/ESR Spectrometers/Laser Raman Spectrophotometers/Laboratory Computers/Scanning Electron Microscopes/Electron Microscopes/X-ray Diffractometers/Amino Acid Analyzers.

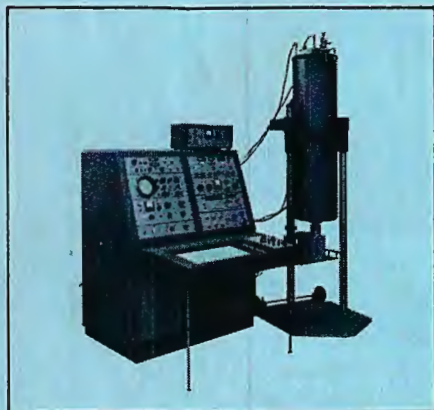


# When You Need an NMR System, See Varian First.

Varian, world leader in magnetic resonance spectroscopy, offers a complete selection of NMR spectrometer systems; from low cost systems designed to solve the typical problems of industrial and academic laboratories to the ultimate in research NMR systems.

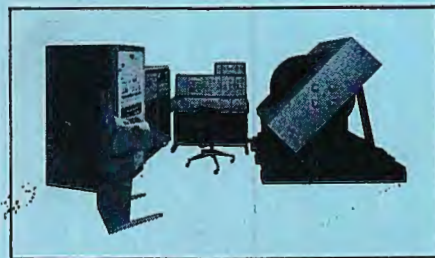
Our basic systems are briefly described here. Ask us what's new for any one, since we're continually expanding the flexibility and research capability of NMR instrumentation.

## HR-220 and HR-300



These offer the highest performance in commercially available high resolution NMR spectrometers. The HR-220 (220 MHz) and HR-300 (300 MHz) spectrometers are engineered for use in those applications requiring the highest magnetic field strengths such as liquid crystal, biological, biopolymer, and biochemical studies. Accessories are available for observation of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}$ , and  $^2\text{H}$  in both the continuous wave and Fourier transform modes.

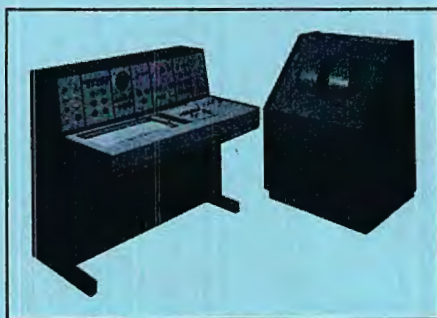
## XL-100



A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz, and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments.

Locking flexibility for homo- or heteronuclear internal lock on  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^2\text{H}$ , and external lock on  $^1\text{H}$  and  $^{19}\text{F}$  are provided. Fourier transform operation,  $T_1$  measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

## NV-14



A moderately priced 14-kG,  $^{13}\text{C}$  research spectrometer offering the highest performance per dollar of any NMR system now available. Accessories include Fourier transform for  $^{13}\text{C}$ , and other nuclei such as  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$ . It is a solid state, frequency swept spectrometer ideal for either high performance routine tasks, or for those research requirements demanding state-of-the-art capabilities along with versatile lock, spin decoupling, and variable temperature capability using 8mm sample tubes.

## New System T-60A



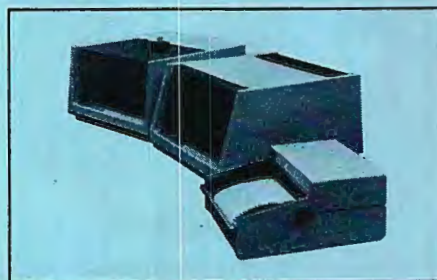
The T-60A is the newest Varian NMR system, a new system with a heritage, a solid tradition of fine workmanship and reliability inherited from its predecessor, the renowned System T-60. T-60A sensitivity is in excess of 30:1, and resolution is better than 0.3 Hz. Modular accessories include internal lock, variable temperature, wide sweep, and spin decoupling.

## EM-360



A 60-MHz instrument which embodies Varian Anaspect's expertise in producing low cost spectrometers and Varian technical leadership in resonance spectroscopy. The result is an instrument which is far ahead of the field in combining economy and performance, flexibility and simplicity. The newest Varian NMR system, it's the low cost leader in the 60-MHz field, yet it delivers high priced performance. Guaranteed sensitivity of 18:1 signal-to-noise and 0.6-Hz resolution are performance features which suit this instrument to a wide variety of routine and research applications.

## EM-300



A rugged, low priced 30-MHz spectrometer giving excellent results with minimum effort. The EM-300 can easily handle routine proton applications. The instrument's ability to offset, expand or integrate have made it the preferred system in hundreds of teaching laboratories. Other owners have found the EM-300 to be just as useful in simple, routine control applications.

Write: 611 Hansen Way, Palo Alto,  
California 94303

**varian instruments** 

Brand names: ANASPECT™ • CARY® • MAT • VARIAN®  
VARIAN AEROGRAPH® • VARIAN TECHTRON