Texas A & M University N–M–R Newsletter

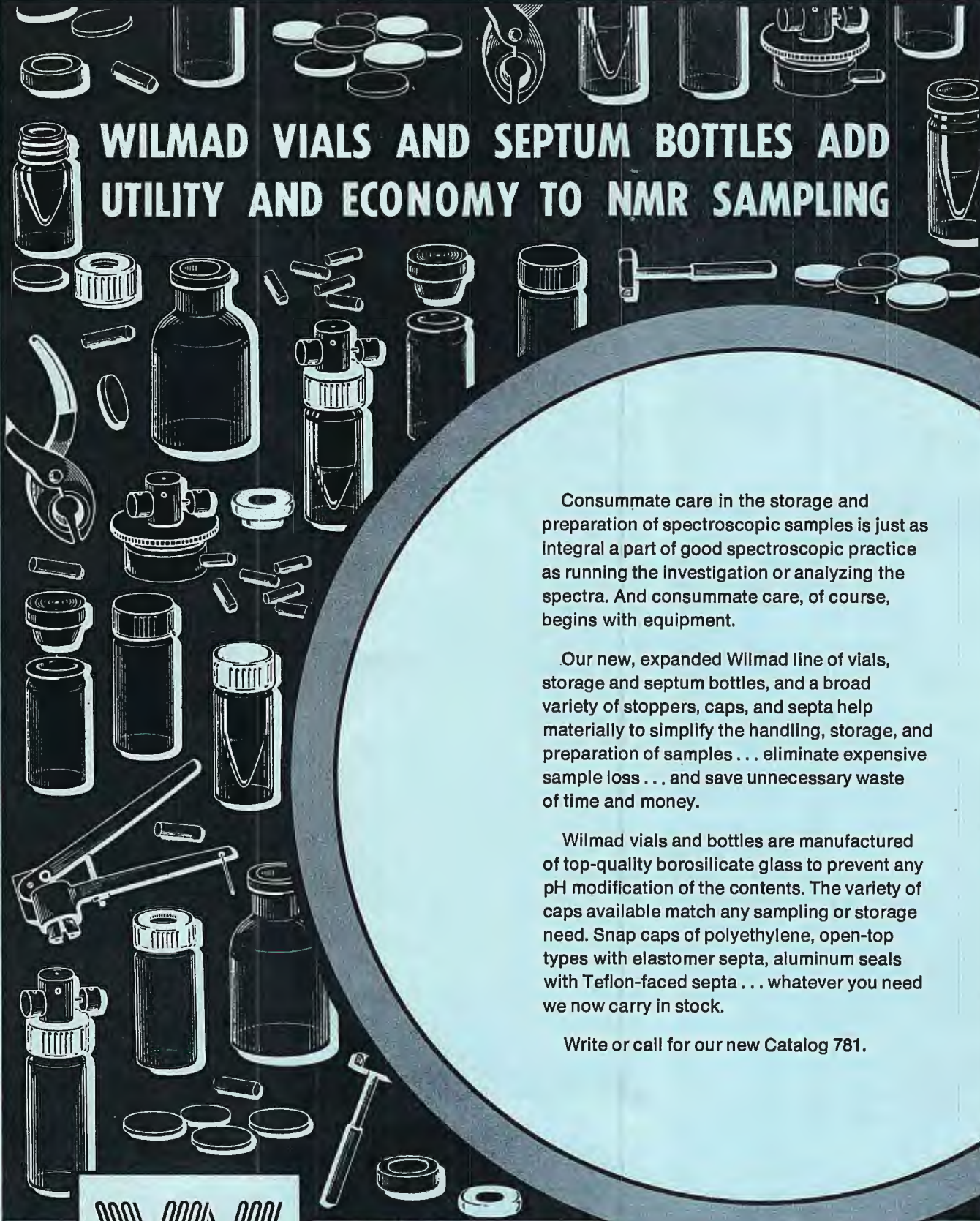No. 244

January, 1979

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All Newsletter Correspondence, Etc. Should Be Addressed To

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

PHYSICAL CHEMISTRY LABORATORY

OXFORD UNIVERSITY

Telephone

OXFORD
(0865-) 53322

SOUTH PARKS ROAD
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26 October 1978

Dear Barry,   "The Emperor's New Clothes"

NMR spectra are often so rich in information that it may well prove worthwhile to employ data manipulation techniques that actually throw away information, revealing the remainder in all its stark simplicity.   Suppose we wish to pick out certain lines in an NMR spectrum and measure their contribution to the total integral.   We need a "mask" which accepts these signals and rejects all others.   In the computer we construct a stick spectrum $S(f)$ by setting the chosen peaks to unit intensity and all other locations to zero.   Fourier transformation of $S(f)$ gives a time-domain signal $S(t)$ which may be exponentially weighted to give a decaying signal $M(t)$.   The Fourier transform of $M(t)$ would be an artificial spectrum $M(f)$ with Lorentzian lines of unit intensity and no noise, which can be thought of as the desired "mask" for the experimental spectrum $E(f)$. In practice this masking operation is carried out in the time domain by multiplying the experimental free induction signal $E(t)$ by the time-domain mask $M(t)$, point-by-point, and then integrating the result.

We describe here only one application: the improvement of the sensitivity of the "J-scaling" experiment (1,2) and the simplification of the resulting spectra. (J-scaling is an alternative to off-resonance decoupling in which heteronuclear spin-spin splittings are scaled down by some predetermined constant factor.) The experiment can be thought of as involving a skew projection (3) of a two-dimensional spectrum of the kind described by Müller, Kumar and Ernst (4), as illustrated for proton-coupled carbon-13 spectroscopy in Figure 1.   The inherent sensitivity of the method is poor, but can be considerably improved by using a suitably weighted projection, such that traces carrying NMR signals make strong contributions to the summations, while traces carrying only noise make no contribution.   This is achieved by using a masking signal $M(t)$ corresponding to a mask spectrum $M(f)$ derived from the noise-decoupled conventional spectrum. Not only does this provide optimum filtration of noise components, but it also permits considerable simplification in crowded spectra.   Overlap of multiplets in the J-scaled spectrum can be eliminated by choosing only a limited number of resonance lines for the mask $M(f)$.   The lowest trace of Figure 2 shows the decoupled carbon-13 spectrum of cholesteryl acetate.   Eight lines have been chosen to construct the mask shown in the central trace, and the resulting J-scaled spectrum in the top trace shows clearly the multiplicities of these eight sites, all other responses having been suppressed.

We call this method "tailored detection" in order to bring out the analogy with tailored excitation (5).   Readers may well think of other applications where key information can be revealed by stripping away the emperor's finery.

Kindest regards,

Gareth Morris *   Ray Freeman.

* Present address: Dept. of Chemistry, University of British Columbia, Vancouver.

1. Freeman and Morris, J. Mag. Res. 29, 173 (1978).
2. T.A.M.U.N.M.R. Newsletter, 232, 17 (1978).
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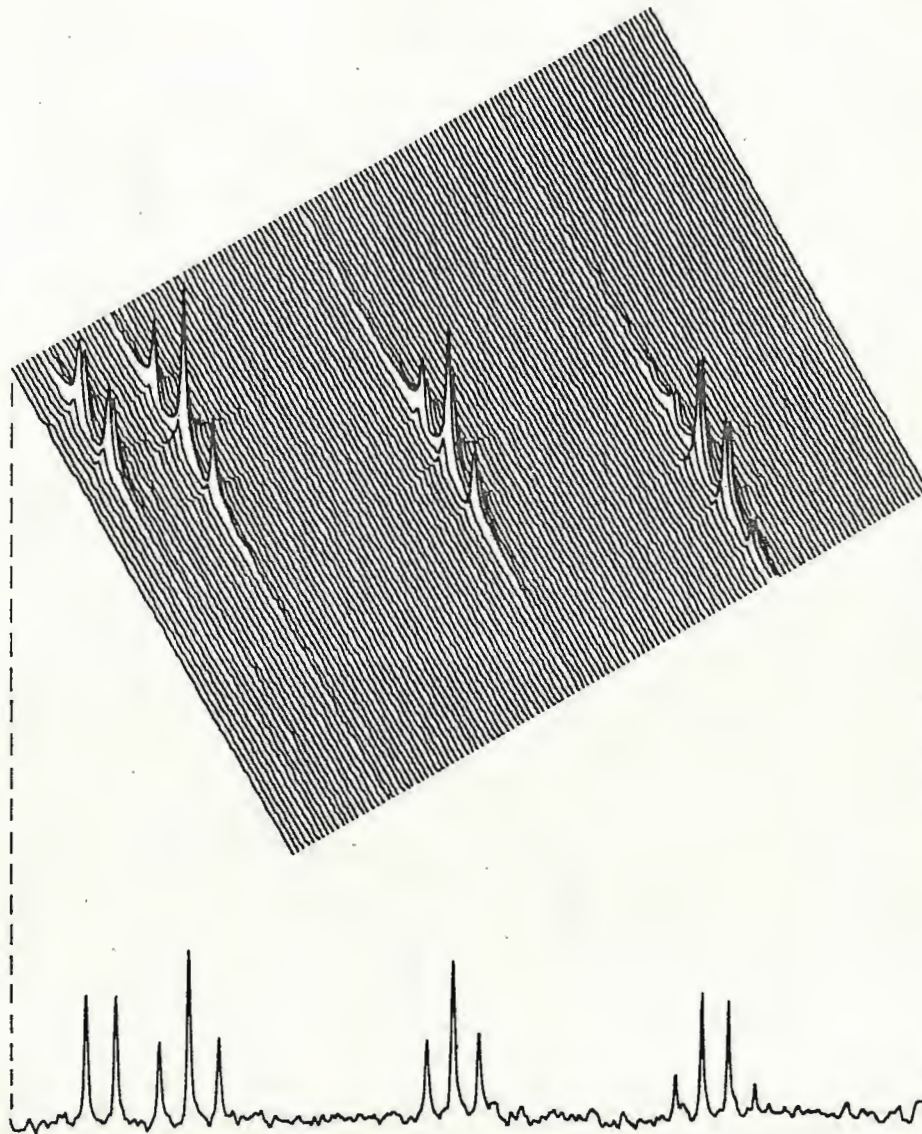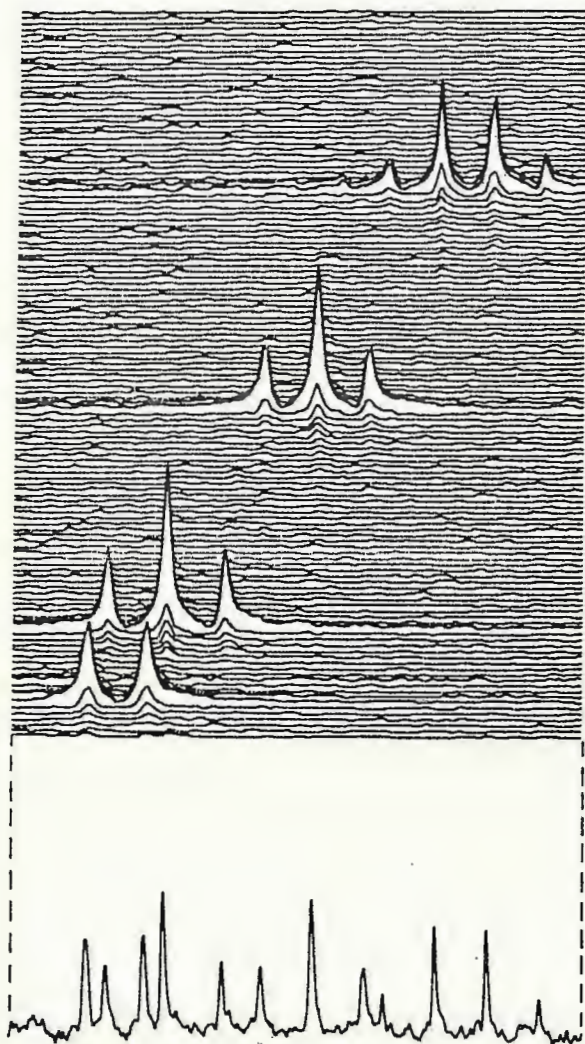
Gareth Morris and Ray Freeman   Figure 1.
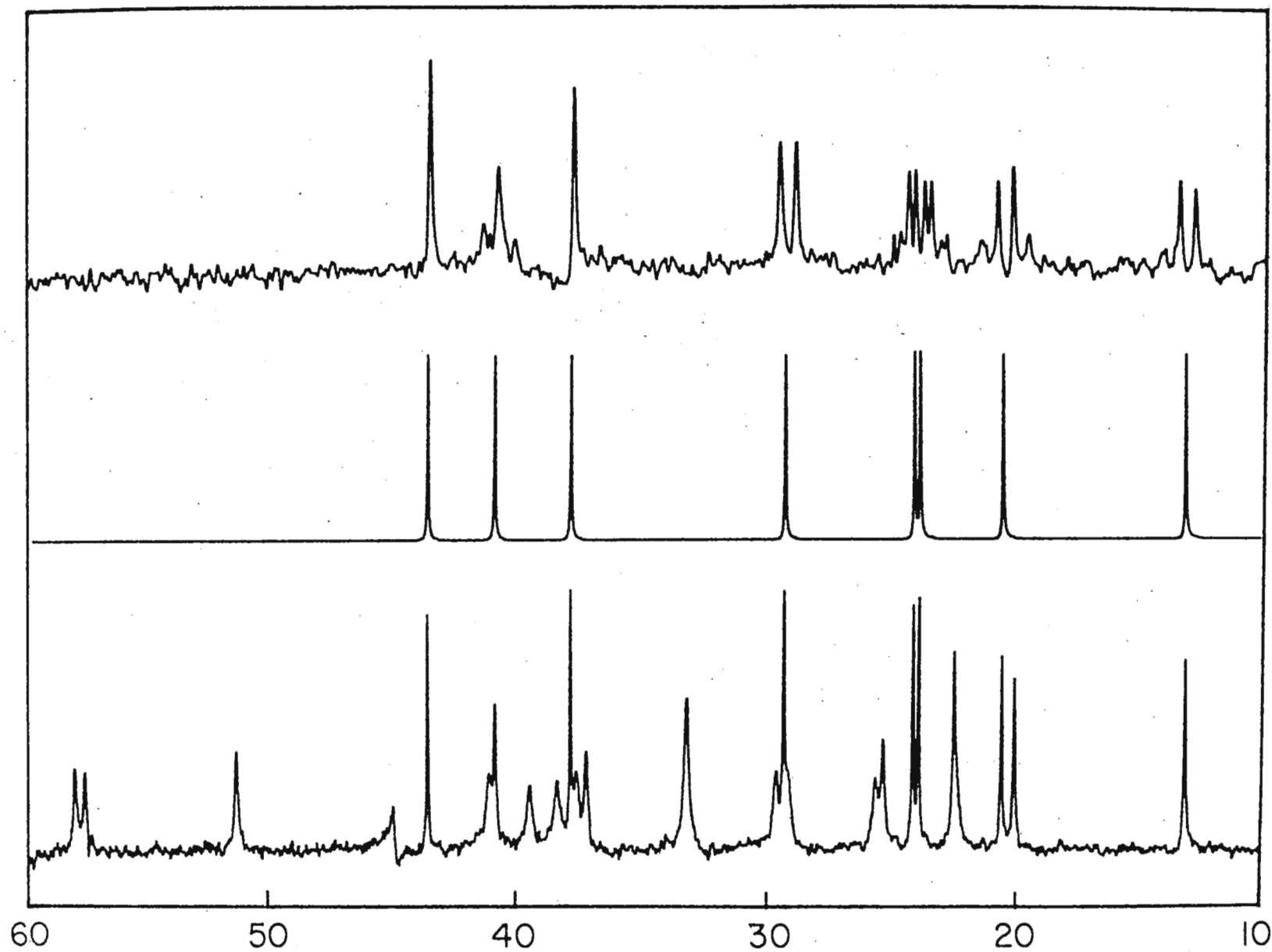
Gareth Morris and Ray Freeman   Figure 2.

ANIXTER
TECH CENTER

November 7, 1978

Professor Barry Shapiro
Dept of Chemistry
Texas A and M University
College Station, Texas. 77843

Dear Professor Shapiro:

Professor Wallace Brey suggested that I write to you regarding some
equipment we have for sale.

We have the following items available and we are open to an
offer for any or all of the items:

```
lea Varian NMR probe S/N 1403... 4.33 MHz
 "    "      "     "    "  1100    8.1  "
 "    "      "     "    "   733    60   "     Varian Type 4331 A probes.
 "    "      "     "    "   825    60   "
```

```
1 ea Varian NMR Probe type V-4230B  S/N 240..... 2-4 MHz
 "    "      "     "     "     "      "  241     4-8  "
 "    "      "     "     "     "      "  242     8-16 "
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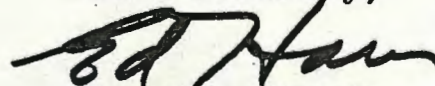
These probes are in almost new condition.

In addition we have a Varian V-4004, 4 inch variable air gap, 4-5 K gauss
magnet with V-2300A power supply and & V-2301 Regulator. This unit has
an extra set of tapered pole pieces.

I understand that you publish an NMR Newsletter monthly and would appreci-
ate it if you could place this information in the newsletter. Also
would like to get a copy and if you have a subscription setup, etc
we would like to subscribe.

Thank you for your consideration.

Yours sincerely,

Edward F. Harris
V.P. R and D
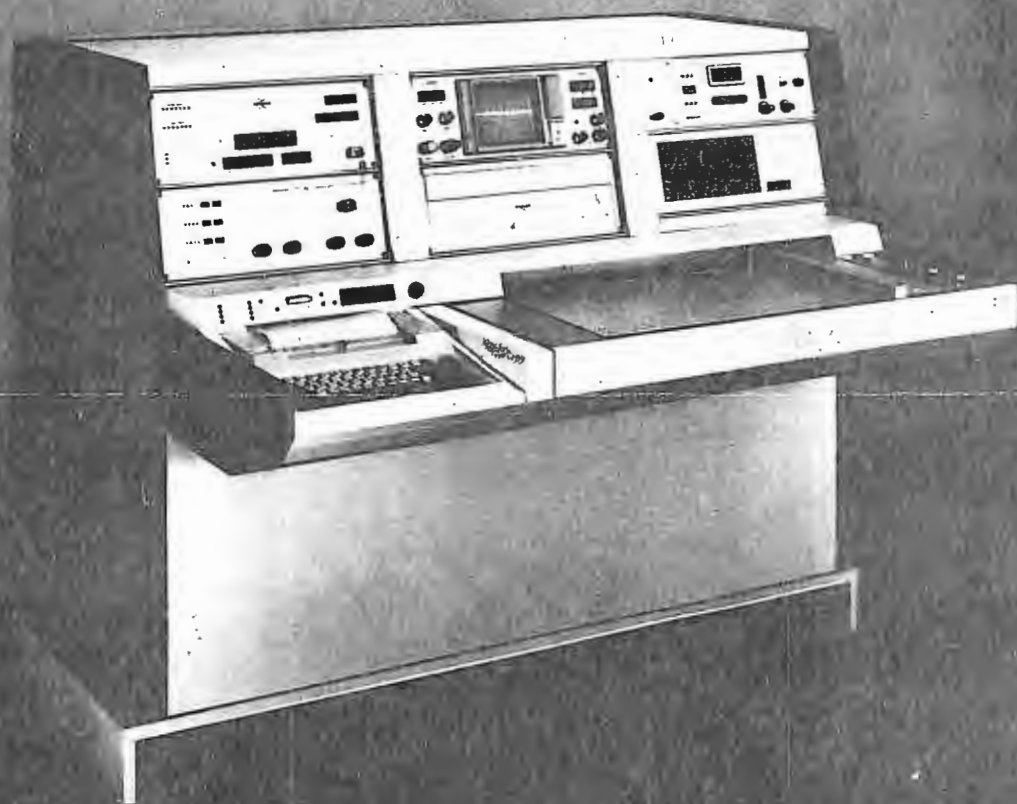
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Department of
Chemistry

416/684-7201

Glenridge Campus
St. Catharines,
Ontario L2S 3A1
Canada

December 4, 1978.

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

Dear Barry:

Brain Waves or What to do on Sleepless Nights

Shortly after installation of our Bruker WP60 FT NMR
several years ago, Paul Tyson of our Psychology Department
approached us concerning crude FT analysis of some electro-
encephalogram (EEG) tapes. After installation of our disk
interface two years ago, we were able to automate the input and
processing of the data to a considerable extent.

Multivariate techniques have recently been employed to
isolate the experiences that were maximally correlated with
changes in the spectral characteristics of the EEG during
biofeedback for alpha (8-13 Hz) and theta (4-8 Hz) waves. A
10 Hz or 6 Hz, 50μV calibration signal and the raw EEG were
recorded on a Vetter FM tape recorder and these signals were
connected to the ADC input of the WP-60 spectrometer via an
active low pass filter and attenuator. After Fourier transform-
ation the absolute power spectral density between 0-30 Hz was
integrated within five frequency bands (1-4 Hz, 4-8 Hz, 8-10.5
Hz, 10.5-13 Hz and 13-30 Hz) and then rescaled relative to the
calibration signal to yield the mean amplitude in microvolts.
These integrated amplitudes were later cross-correlated with
the principle components of experience using canonical correl-
ations to yield the adjectives that were maximally correlated
with changes in these frequency bands.

To enable a reasonably fast rate of accumulation and
processing, we modified the disk based TI/II program. This not
only allows consecutive storage of the data on disk, but also
enables the analyst to study individual files and thus screen
cases where noise or transient species have reached unacceptable
levels. The other advantage of this program is that the pro-

cessing step automatically scales the data to an absolute level to maintain consistency between runs. The software modifications involved three small segments within the TIPROC module. The first replaced the memory phase correction with a magnitude calculation to give the power spectrum of the FT/d block. The second and third changes alter the EP (expansion) routine to allow
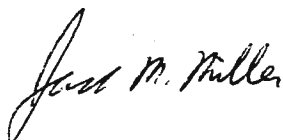
  (i)   the setup of 5 frequency blocks
  (ii) integration and lineprinter output of the block
        intensities.

Typically the analyst will accumulate one hundred files of data including the calibrating signal, process the first file (usually calibration) manually and then process his data files using the automatic processor mode. Since a number of timing structures are available within the T /II program, it is possible to signal average data or do some type of selective sampling.

Presentaly, we are implementing this sort of technique on a demand basis for evenings when the WP-60 is on a sensitive nucleus not needing overnight runs since it has been in almost constant day and night use over the last two years. This may give some readers a clue towards using their NMR/data systems for other types of analysis when chemists aren't lurking about.

Best Regards,
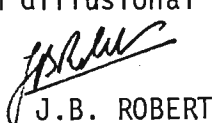
J. M. Miller,   T. Jones,   P. Tyson,
Department of Chemistry   Department of Chemistry   Department of
                                                        Psychology.

- The ^{13}C T_1 is essentialy dipolar, and the plot of log T_1 vs. the inverse temperature is better described by two Arrhenius straight lines which may reflect the charge of molecular motion from diffusional to inertial.

Sincerely yours,

J.B. ROBERT   C. TAIEB   J. TABONY

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Dr. SHAPIRO
Department of Chemistry
Texas A. & M. University
College Station, Texas
U.S.A.

RÉFÉRENCE A RAPPELER
G/COP-78-513/mjc

VOTRE RÉF.

VOTRE LETTRE DU

GRENOBLE, LE December 19, 1978

Dear Dr. Shapiro,

T_1 Measurements on small organophosphorus molecules.

Compared with other spin 1/2 nuclei, there have been relatively few n.m.r. spin lattice relaxation time measurements of ^{31}P containing liquids. In order to examine the contribution of the different mechanisms to the ^{31}P relaxation and to study the molecular motion of organophosphorus molecules, we initiated a program on the study of the relaxation time measurements of the different nuclei of small and symmetrical organophosphorus compounds.

As a first example, the ^{13}C and ^{31}P T_1 values have been measured on $P(CH_3)_3$, a simple symmetric top molecule in which the parameters needed for a quantitative study are known : the geometry (microwave), the phosphorus chemical shift anisotropy and the rotation barrier around the C-P bond.

From the measurements, which have been performed between -100° and 60°C, the following results are obtained :

- For the ^{31}P nucleus, the dipole-dipole mechanism is dominant at low temperature, and the spin-rotation dominates at high temperature.

- The molecular motion may be described in the rotation diffusion scheme at low temperature and becomes inertial at high temperature.

- The rotation is highly anisotropic and is faster around the symmetry axis than around an axis perpendicular to it.

IBM

RESEARCH LABORATORY

International Business Machines Corporation

5600 Cottle Road
San Jose, California 95193

November 29, 1978

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

Dear Barry:

For some time now, we have been making an effort to try to
develop a complete theory for a line-narrowing method
developed here at IBM.[1] In the process, Richard Johnson,
who recently completed a postdoctoral year, has written
and tested a general computer program which calculates
spin dynamics, oriented especially toward testing the
efficiency of line narrowing pulse sequences. We have
obtained results for the well known sequences using both
delta function pulses and finite pulse widths. We are
in the process of writing something on this in collaboration
with Robert Wind from Delft, who collaborated with us on
this during the summer.

Best regards,

C. S. Yannoni

/aj
Short Title: Spin Dynamics by Computer
1. a) TAMU NMR Newsletter #218, by R. F. Johnson and C. S. Yannoni
   b) C. S. Yannoni and H.-M. Vieth, Phys. Rev. Lett. $\underline{37}$,
      1230 (1976).

Department of Chemistry   **The Florida State University**
Tallahassee, Florida 32306

November 29, 1978

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

Dear Barry:

ACS Short Course/Workshop on Multi-Nuclei FT NMR

Frank Anet, Pierre Laszlo, and I are conducting two sessions of a special
ACS Short Course/Workshop this next June. The two sessions will be held June 6-8,
1979 in Los Angeles at UCLA and June 13-15, 1979 in Tallahassee, Florida at
FSU. The program of the Workshop/Short Course is given below. The level of
treatment will be appropriate for those having at least reasonable familiarity
with standard ^1H nmr concepts, etc.

The number of participants at each of the sessions will be restricted so as
to allow individualized discussions and experimentation. The UCLA and FSU supercon
NMR spectrometers will be used for multi-nuclei demonstrations and service operation.
Participants will be encouraged to bring samples to the Workshop for analysis.

The American Chemical Society will start to advertise this Short Course/
Workshop this spring. We wanted to give prior notice to the nmr community so
that anyone interested could be assured of participation.

The Program

Day 1 Introduction
    Concepts of Fourier Transform NMR
    Modern Carbon-13 NMR Spectroscopy
    Demonstration
    Fourier Transform NMR Instrumen-
      tation
    Dynamic NMR Spectroscopy
    NMR Services in evening

Day 2 Quadrupolar Nuclei
    Deuterium NMR
    Nitrogen-15 NMR
    Demonstration
    Computer Methods in FT NMR
    Discussion
    NMR Services continued
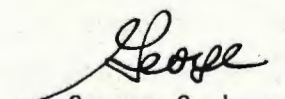
Day 3 Sodium-23 and other "Light"
      Metal Nuclides
    Heavy Metal Nuclides
    High Resolution in Solids
    NMR of Biopolymers: Special
      Opportunities
    Binding of Ions to Biomolecules
    Panel Discussion
    NMR Services continued

Fees, Registrations
    ACS Members, $250; non-members $300

For reservations contact Professor
F.A.L. Anet (UCLA Session) or Professor
G.C. Levy (FSU Session) or The
Continuing Education Department, Short
Course Division, American Chemical
Society, 1155 16th Street, N.W.,
Washington, D.C.   20036

Yours sincerely,

George C. Levy
Professor

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL   CH-4056 Basel (Schweiz) December 5, 1978

EXPERIMENTELLE KERNPHYSIK

Klingelbergstrasse 82, Telefon 061 - 44 22 80

Prof. Dr. P. Diehl

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

Re: Nuclear Relaxation, Quadrupole Coupling Constants
    and Vibrational Averages.

Dear Barry,

Your blue letter has reminded me of a letter which had appeared
in TAMUN NMR Newsletters 231-25 (1) last year and which I had
planned to answer but forgot to. In this letter the authors had
pointed out that the neglect of vibrational averaging can lead
to large uncertainties in estimating correlation times from
relaxation rate measurements. Unfortunately they based their
arguments on a formula which we had used earlier for vibration
corrections in direct coupling constants (D) of oriented mole-
cules (2):

$$r_D = r_e + <\Delta z> + \frac{2}{r_e} \{ \frac{<\Delta x^2>+<\Delta y^2>}{2} - <\Delta z^2> \} \qquad (1)$$

In this formula the effects of averaging internuclear distances
as well as degrees of order are included. The formula which con-
siders exclusively the internuclear distances and which is cor-
rect for relaxation (R) is the following:

$$r_R = r_e + <\Delta z> + \frac{1}{r_e} \{ \frac{<\Delta x^2>+<\Delta y^2>}{2} - \frac{21}{6}<\Delta z^2> \} \qquad (2)$$

Both equations are excellent approximations for simple molecules
like e.g. chloroform and agree with a full normal mode analysis.

Numerically there is a large difference between the two. Whereas
formula (1) shows that a measurement of the chloroform C-H bond
length from an uncorrected direct coupling in the oriented mole-
cule provides a distance which is too long by approximately 1.6%,
formula (2) demonstrates that in relaxation phenomena the uncor-

rected chloroform C-H bond length is too short by roughly 0.7%. This means that the uncorrected correlation time is too long by 4.1% and not too short by 13% as the authors had feared. The corresponding result for benzene C-H is a correlation time too long by 1.1%. It consequently seems that in relaxation, vibration corrections are not so important.-

On the contrary in NMR of oriented molecules vibration correction is an absolute necessity for directly bonded nuclei. A typical example demonstrating what can go wrong if corrections are neglected appeared in the literature some months ago (3). Some authors suggested to measure deuterium quadrupole coupling constants from natural abundance ^{13}C-satellites in the ^2H-spectra. They used the direct couplings D(CD) in benzene uncorrected, i.e. neglecting the increase of roughly 8%. Their result of Q_D = 207 kHz is consequently too high but can easily be corrected for vibration. The corrected value turns out to be 192 kHz which is in excellent agreement with our own latest measurements (4).

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     S. Sýkora, J. Vogt, H. Bösiger and P. Diehl, submitted to J. Magn. Reson.

(3) J.B. Wooten, A.L. Beyerlein. J. Jacobus and G.B. Savitsky, J. Magn. Reson. 31, 347 (1978).

(4) P. Diehl and M. Reinhold, Mol. Phys. 36, 143 (1978).

With best wishes,
Yours sincerely

Peter

P. Diehl

UNIVERSITÉ RENÉ DESCARTES (PARIS V)

UER DES SCIENCES PHARMACEUTIQUES ET BIOLOGIQUES

DÉPARTEMENT DE CHIMIE ORGANIQUE

(CNRS) ERA 07.613

PROFESSEUR B. P. ROQUES

PARIS, LE   December 7^{th}, 1978

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

Dear Professor Shapiro,

In response to your multicolored letters we went to talk you about the ^{13}C NMR assignments in cyclopeptides. In fact, we had some desagreement when studying the conformational behavior of Iturin A, an antibiotic from Bacillus subtilis (1) with antifungal activity (2). Iturin A has a cyclic peptidolipidic structure with the following sequence : cyclo(L.Ser-$\beta_{NC14,C15}$-L.Asn-D.Tyr-D.Asn-L.Gln-L.Pro-D.Asn). The lipidic moiety is a mixture of 3-amino 12-methyl tridecanoic acid (β_{NC14}) and 3-amino 12-methyl tetradecanoic acid (β_{NC15}).

Basing on classical off-resonance experiments and literature data (for L.Amino acids) we recently proposed (3) the following assignments for the Cα resonances (in DMSO-d_6 ppm from TMS as internal reference). L.Ser = 56.2 ; L.Asn = 50.8 ; D.Tyr = 56.2 ; D.Asn = 49.8 ; L.Gln = 50.8 ; L.Pro = 60.8 ; D.Asn = 49.8 ; $\beta_{NC14,C15}$ = 47.2.

As an ambiguity arised in ^{1}H sprectrum assignments for the Hα protons of Tyrosine and the Hα of the lipidic moiety respectively, we decided to record the ^{13}C NMR spectra of Iturin A with systematic selective low power ^{1}H irradiation of the Hα region. These experiments permitted us to rise the ambiguity but moreover we had to revise our first ^{13}C assignments. We are now proposing another set of assignments : L.Ser = 56.2* ; L.Asn = 56.2 ; D.Tyr = 50.8 ; D.Asn = 49.8 ; L.Gln = 50.8 ; L.Pro = 60.8* ; D.Asn = 49.8 ; $\beta_{NC14,C15}$ = 45.7.

What is noticeable in the results of Iturin A is the very large deshielding of the Cα in the residue L.Asn (56.2 ppm) and the shielding of the Cα in the D.Tyr one (50.8 ppm) compared to the chemical shift of aminoacid Cα's in extended "random coil" structure (4) [L.Ser = 54.8 ; L.Pro = 59.1 ; L.Asn = 49.3 ; L.Tyr = 53.9 in ppm from TMS in DMSO-d_6]

It is difficult to correlate these data with the secondary structure proposed by ^{1}H NMR (two β-turns involving for the first one the residues L.Asn, D.Tyr, D.Asn and L.Gln with an hydrogen bond between the CO of L.Asn and NH of L.Gln, and for the second, the residues L.Gln, L.Pro, D.Asn and L.Ser involving the CO of L.Gln and NH of L.Ser) unless the resonances of L.Pro and L.Ser be reversed. In that case, the important shielding of the D.Tyr and L.Pro residues could be related to their position (i+1) in the β-turns.

* *These values may be reversed.*

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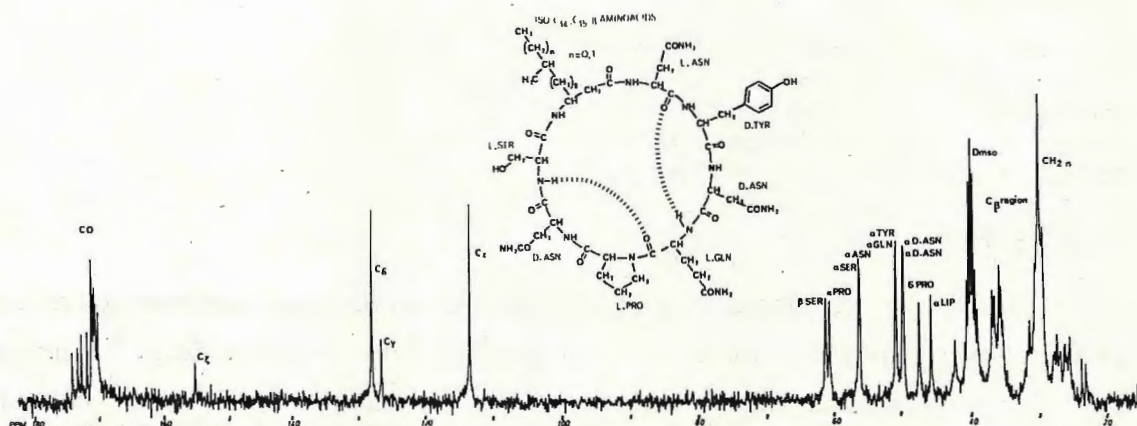
^{13}C Spectrum of Iturin A.

Finally, we would like to focus your attention on the necessity to beware of too simple assignments of ^{13}C NMR resonances, in such very constrained cyclopeptide.

Sincerely yours.

Ch. Garbay

C. GARBAY-JAUREGUIBERRY

B. Roques

B.P. ROQUES.

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4. K. Wüthrich, NMR in biological research ; peptides and proteins. North-Holland publishing Company Amsterdam. Oxford. (1976) Chapter 5, p. 177-178.

NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

"Cross-Polarization in Liquids: the Ptolemaic Perspective;

Intrinsic Error in S/N Measurements"

Dr. Barry Shapiro
TAMUNN Newsletter
Department of Chemistry
Texas A and M University
College Station, TX 77843

Dear Barry:

Recently we have applied rather standard cross-polarization techniques to liquids utilizing the J coupling;[1] indeed the first results were reported by Hartmann and Hahn[2] on hypophosphorous acid in 1962. There are the usual advantages: an enhanced magnetization and a repetition rate determined by the T_1 of the "abundant" spin. Most of the behavior in JCP (J Cross-Polarization) is intuitively satisfying: as a function of cross-polarization time, magnetization transfer is oscillatory rather than thermal, since spins in liquids couple to form systems which are small in a thermodynamic sense. Several discrete frequencies (in integer or non-integer multiples of J) can enter when the spin 1/2 nucleus (e.g. ^{13}C, ^{15}N, ^{29}Si) is coupled to more than one proton.

There was one surprise however. Seen in the doubly rotating frame, each carbon has a longitudinal component of magnetization along the rf axis as well as a transverse component, perpendicular to B_1, which is correlated with transverse proton polarization. The transverse components seen in the lab frame turn out to be equal and opposite for carbons coupled to protons with equal and opposite $I_z = \pm M$ quantum numbers. With decoupling, the transverse components cancel, and the longitudinal components combine, to give a single line in phase with the rf. In the undecoupled spectrum (coupled spectrum according to WBM), the phase of each component can be measured and in general varies with cross-polarization time.

We anticipated a rather simple phase relationship. In Fig. 1 is plotted the complex ^{13}C magnetization of the upfield inner component of the undecoupled spectrum of the methyl group in methanol, parameterized by the cross-polarization time (in ms) for Hartmann-Hahn cross-polarization.

A calculation[3], shown as the solid curve in Figure 1, qualitatively reproduces the behavior. The open circles denote ms increments in cross-polarization time (for J = 140 Hz) and 5 ms intervals are indicated by x's. The plot is not symmetrical about the rf axis (horizontal axis): it is in principle not even periodic as the frequencies involved are $J/2$, J and $\sqrt{3}\, J/2$.

We find these results anticipated in the epicycles of the cosmology of Ptolemy,[4] Fig. 2. In that figure monthly intervals are indicated.

On a related matter, we looked into the (Nicolet) definition of signal-to-noise ratio to understand the reproducibility of a S/N measurement. The "signal" S is defined as the maximum in the peak and is not averaged over any adjacent channels. The rms noise σ is then computed and the S/N defined as $S/2\sigma$ i.e. the signal-to-(twice rms) noise ratio. Hence, the standard deviation in the measurement of S is σ while the rms deviation is very well defined and so the signal-to-noise ratio should be reported as

$$S/N = \frac{S \pm \sigma}{2\sigma} = \left(\frac{S}{2\sigma}\right) \pm \frac{1}{2}$$

i.e. S/N ratios are always determined with an intrinsic error of ± 1/2 unit. We apologize in advance to those for whom this relation is common knowledge.

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4. Camille Flammarion, "Astronomic Populaire," Flammarion, Paris (1955) p. 257.

Dick
Gerry
Al
Bill

R. D. Bertrand*
G. C. Chingas**
A. N. Garroway
W. B. Moniz

Polymer Diagnostics Section
Code 6110
Chemistry Division

*   U. Michigan - Dearborn. Work performed while on sabbatical leave at NRL under the Intergovernmental Personnel Act.
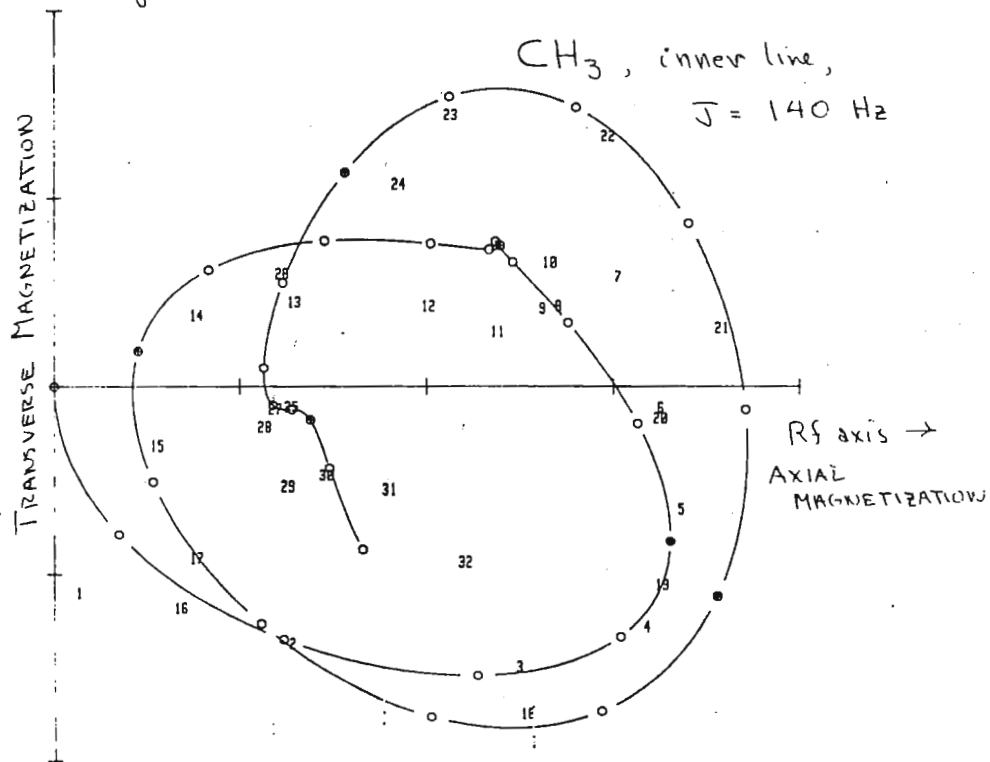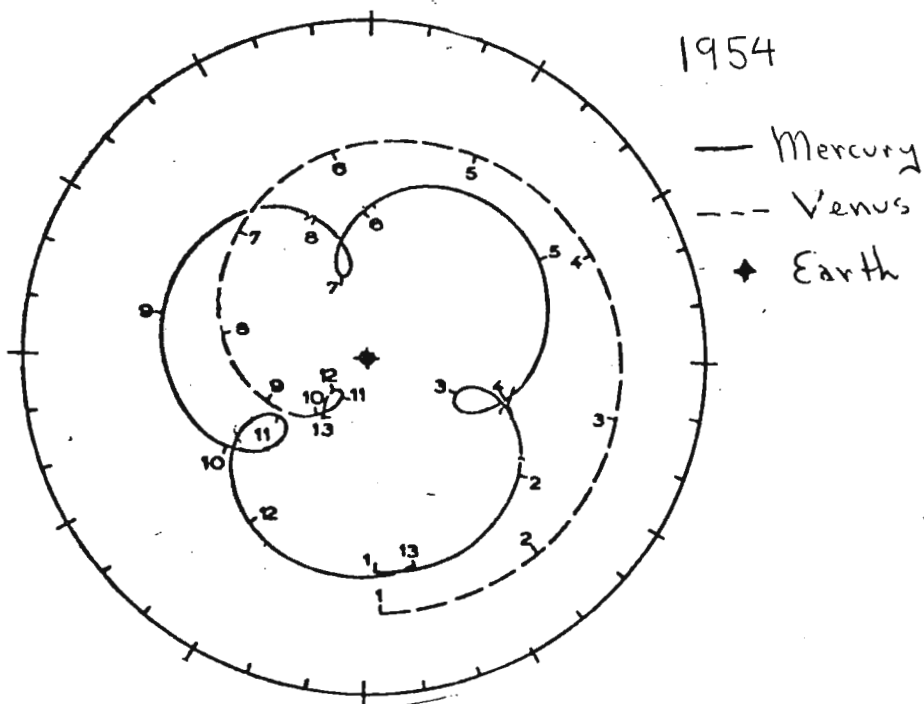
** Contract employee of the University of Utah.

Figure 1

CH₃ , inner line,
J = 140 Hz

Figure 2

1954

—— Mercury
--- Venus
✦ Earth

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FACHBEREICH CHEMIE UND PHARMAZIE
Institut für Chemie

R. Küspert

8400 REGENSBURG. 20.12.78
Universitätsstraße 31 – Postfach
Telefon (0941) 9431
Telex: 065658 unire d

A⇋B-Austausch im symmetrischen, ungekoppelten AB-System.
Exakte, explizite Berechnung der Parameter.

Sehr geehrter Herr Professor Shapiro,

Für die von Gutowsky, McCall und Slichter[1] angegebene Linien-
form symmetrischer, ungekoppelter AB-Systeme mit A⇋B-Austausch
gibt es offenbar bisher keine exakte analytische Lösung zur
Bestimmung der Parameter experimenteller Kurven.

Die folgenden drei Methoden genügen dieser Anforderung und können
in verschiedenen Bereichen angewandt werden. Zur Klassifizierung
der Anwendungsbereiche definieren wir:

$$r_{max} = \frac{\text{maximale Intensität}}{\text{Intensität in der Symmetrieachse}} \text{ der Kurve.}$$

1) **Exact-Intensity-Ratio (EIR) Method** für $r_{max} \lesssim 10$

Diese Methode stellt eine Fortsetzung der Bemühungen von
Rogers und Woodbrey[2] (Intensity-Ratio Method) und Dimitrov[3]
(NIR = New-Intensity-Ratio Method) dar. Durch geeignete Wahl
der zweiten Meßstelle (α) gelang es, exakte Gleichungen für die
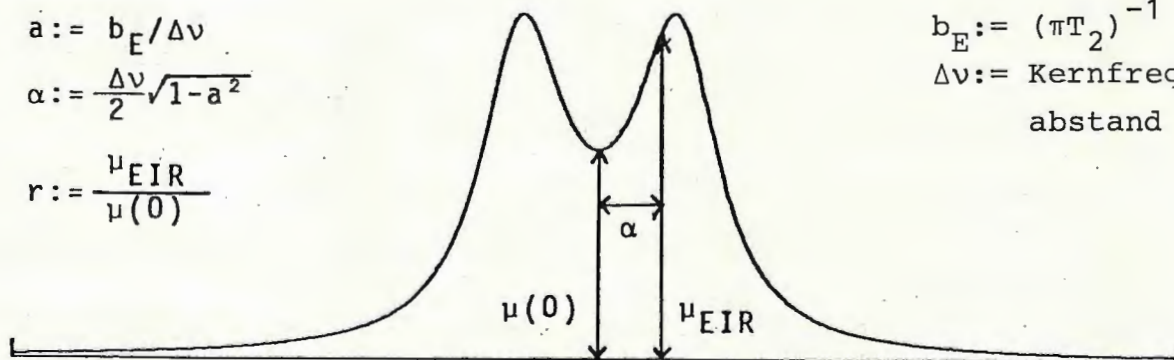Geschwindigkeitskonstante k und ihren Fehler anzugeben:

$$a := b_E/\Delta\nu$$
$$\alpha := \frac{\Delta\nu}{2}\sqrt{1-a^2}$$
$$r := \frac{\mu_{EIR}}{\mu(0)}$$

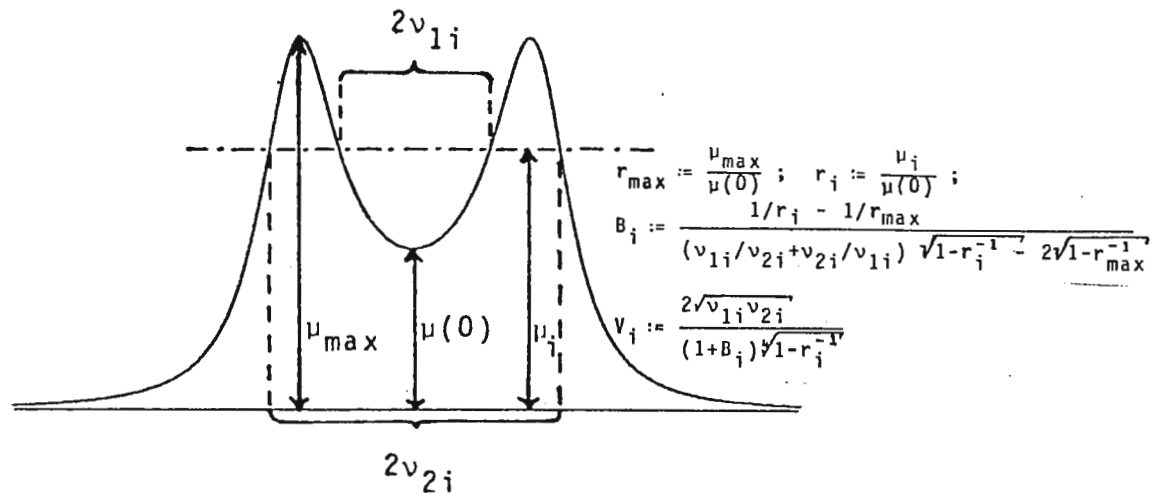$$b_E := (\pi T_2)^{-1}$$
$$\Delta\nu := \text{Kernfrequenz-abstand}$$

$$k = \frac{\pi}{4}b_E\left\{2\frac{1-a^2}{r-a^2}-3+\sqrt{1+\frac{4r}{a^2}\left(\frac{1-a^2}{r-a^2}\right)^2}\right\}$$

2) $\underline{T}$otal $\underline{A}$nalysis of $\underline{P}$arameters by $\underline{I}$ntensity $\underline{R}$atio$\underline{s}$ (TAPIRS)

für $1{,}1 \lesssim r_{max} \lesssim 10$

Für diesen Bereich wurde eine Methode entwickelt, die alle drei Prameter ($\Delta\nu$, b_E, k) einschließlich ihrer Fehler ohne Näherung ermittelt.

$$r_{max} := \frac{\mu_{max}}{\mu(0)} \; ; \quad r_i := \frac{\mu_i}{\mu(0)} \; ;$$

$$B_i := \frac{1/r_i - 1/r_{max}}{(\nu_{1i}/\nu_{2i}+\nu_{2i}/\nu_{1i}) \sqrt{1-r_i^{-1}} - 2\sqrt{1-r_{max}^{-1}}}$$

$$V_i := \frac{2\sqrt{\nu_{1i}\nu_{2i}}}{(1+B_i)\sqrt{1-r_i^{-1}}}$$

$$b_{Ei} = V_i \sqrt{r_{max}^{-1} B_i^{-1} + 2 - 2\sqrt{1-r_{max}^{-1}}} \; ;$$

$$\Delta\nu_i = V_i(B_i + \sqrt{1-r_{max}^{-1}}) ;$$

$$k_i = \pi b_{Ei}(B_i - 1)/2.$$

μ_i ist in den Grenzen $\mu(0) < \mu_i < \mu_{max}$ frei wählbar. Deshalb kann man beliebig viele μ_i wählen, für jedes μ_i die Parameter $\Delta\nu_i$, b_{Ei} und k_i berechnen und aus allen Werten für jeden Parameter den Mittelwert und seinen statistischen Fehler berechnen.

3) $\underline{D}$etermination of $\underline{E}$xchange-$\underline{R}$ate by $\underline{T}$hree-$\underline{F}$requencies-$\underline{A}$nalysis (DERTFA) für $r_{max} \gtrsim 2$

Definiert man ν_1 und ν_2 wie ν_{1i} und ν_{2i} für $\mu_i = \frac{\mu_{max}}{2}$ bei TAPIRS, sowie $2\nu_m$ als den Abstand der Maxima, so erhält man

$$\frac{2k}{\pi} = \sqrt{4\nu_1^2 + 4\nu_2^2 - 16\nu_m^2 + 2\Delta\nu^2 - b_E^2} - b_E.$$

Hieraus folgt auch sofort der Fehler von k.

Zusammenfassung

Da TAPIRS in seinem Bereich alle drei Parameter objektiv bestimmt, liefert es eine ausgezeichnete Inter- bzw. Extrapolationsbasis für $\Delta\nu$ und b_E. Bei genügend kleiner Überlappung, d.h.

kleinem k, können b_E und $\Delta\nu$ unmittelbar dem Spektrum entnommen werden. Eine Interpolation zwischen diesen Werten und den entsprechenden TAPIRS-Ergebnissen liefert als Funktion der Temperatur die Werte, die benötigt werden, um mit Hilfe von DERTFA auch solche k-Werte zu ermitteln, die zu klein sind, um nach TAPIRS berechnet werden zu können.

Größere k-Werte als für TAPIRS zulässig erhält man mit EIR. Hierfür muß man $\Delta\nu$ aus dem Tieftemperatur- und dem TAPIRS-Bereich extrapolieren. b_E kann man sogar interpolieren, wenn b_E-Werte für genügend hohe Temperatur (wo b_E = Halbwertbreite) vorliegen.

Folgende EDV-Software ist beim Autor erhältlich:
a) ein FORTRAN-Programm für TAPIRS einschließlich Statistik
b) Programme für den Taschen- bzw. Tischrechner HP 67/97 für alle drei Methoden einschließlich der Fehlerrechnungen.

Die Erprobung der drei Verfahren an experimentellen Spektren ist in Arbeit.

Gegenwärtig werden in unserem Arbeitskreis folgende weiteren NMR-Probleme bearbeitet: Innere Rotation in Butadienen[4], Acetophenonen[5] und Benzamiden[5], enantiomere Reinheit von Diaziridinen[6]; diastereomere Elektronen-Donor/Akzeptor-Assoziate[7] und Kation/Anion-Assoziate.

Mit freundlichem Gruß

R. Kirpert

1) H.S.Gutowsky, D.W.McCall, C.P.Slichter, J.Chem.Phys. 21, 279 (1953).
2) M.T.Rogers, J.C.Woodbrey, J.Phys.Chem. 66, 540 (1962).
3) V.S.Dimitrov, Org.Magn.Reson. 8, 132 (1976).
4) G.Becher, T.Burgemeister, H.-H.Henschel, A.Mannschreck, Org.Magn. Reson. 11, 481 (1978).
5) M.Holík, A.Mannschreck, Org.Magn.Reson., im Druck.
6) H.Häkli, A.Mannschreck, Angew.Chem.Internat. Edit. 16, 405 (1977); H.Häkli, M.Mintas, A.Mannschreck, Chem.Ber., im Druck.
7) A.Mannschreck, P.Roza, H.Brockmann jr., T.Kemmer, Angew.Chem. Internat. Edit. 17, 940 (1978).

Lh Wageningen

Department of Molecular Physics

Your reference BLS/lmk
Your letter of 1978-10-18
Our reference 937 TS/jw
Date 1978-12-08
Enclosures

Prof.B.L. Shapiro
Texas A&M University
Dept. of Chemistry
College Station
TEXAS 77843 - U.S.A.

Subject General information

Dear Professor Shapiro,

Since this is the first time you receive contribution to TAMU NMR
Newsletter, I might as well give you some general information on
the research program currently pursued at the Laboratory of Mole-
cular Physics of the Agricultural University at Wageningen, Holland.

Our group employs ^{1}H NMR at 15, 100 and 360 MHz and ^{13}C NMR at
90,5 MHz, the latter two frequences being available at the national
facility at Groningen University, to which we have access. Corres-
pondingly, three projects are carried out with these machines: the
study of

(i) motion and geometry of chlorophyll-dimers in solution using a
Varian XL-100 FT and a Bruker SPX 360 spectrometer, in support of a
program aiming at defining properties of biologically important ag-
gregates in solution. We make use of relaxation parameters of suit-
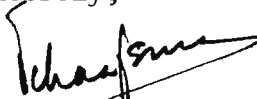able nuclei as probes for rotational diffusion of such aggregates.

(ii) waterflow in tubes by pulsed NMR, diffusional and net transport
of water in parts of plants and the effect of water content on re-
laxation parameters of water plants. This study is carried out using
a home-built 15 MHz pulsed spectrometer and a Varian 100 MHz FT spec-
trometer.

(iii) Finally we have worked on isotopically enriched plantviruses,
applying ^{13}C NMR (90.5 MHZ) to solutions of tobacco mosaic virus and
^{1}H NMR to a number of other viruses. All studies are carried out in
conjunction with electron resonance in zero and high magnetic field,
employing spin-label and triplet probes. I refer to four recent pa-
pers for results. The main results of the chlorophyll NMR prospects
are: a proposal for the geometry of a chlorophyll-dimer, which has been
suggested as the building block of the chlorophyll antenna pigment of
plants, and a description of the motion of chlorophyll in solution.

As you can judge for yourself, agriculture provides a rich and inviting field for the application of NMR.

1. J.L. de Wit and T.J. Schaafsma, FEBS Lett., $\underline{92}$, 273(1978).

2. J.L. de Wit, M.A. Hemminga, T.J. Schaafsma, J. Magn. Res. $\underline{31}$, 97 (1978).

3. P.A. de Jager, M.A. Hemminga, A. Sonneveld, Rev. Sci. Instr. $\underline{49}$, 1217 (1978).

4. M.A. Hemminga, P.A. de Jager, A. Sonneveld, J. Magn. Res. $\underline{27}$, 359 (1977).

Sincerely,

(Tjeerd J. Schaafmsma,
Professor of Mol. Physics)

address:

Dept. of Molecular Physics
Agricultural University
de Dreijen 6,
6700 EP WAGENINGEN
The Netherlands

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2

UM

December 15, 1978.

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

Dear Barry,

<u>What, another cyclohexane?!</u>

Your pink letter and your twentieth anniversary issue prompted recollection
of the days before the Karplus rule (1959) was in wide use and abuse; in
fact, of the days when Lemieux, Kullnig, Bernstein and Schneider (JACS <u>79</u>,
1005 (1957)) were using 40 MHz machines in finding stereospecific ^3J values
in cyclohexane derivatives. How long ago it seems!

Of course, the inversion in cyclohexane also yielded to nmr techniques,
culminating in the work of Anet and Bourn (1967). Many of these authors
began their nmr work in Ottawa in the days when a Canadian dollar amounted
to something; not to speak of other dollars.

Since those early days, the free energy difference between axial and equatorial
conformers has been found for many derivatives of cyclohexane, 1,3-dithiane, and
of 1,3-dioxane. In such derivatives, e.g., phenylcyclohexane and the 2-phenyl
derivatives of 1,3-dithine and 1,3-dioxane, information about the preferred con-
formation and the barrier to rotation about the exocyclic C-C bond is relatively
sparse. An exception is the equatorial dioxane derivative, for which molecular
mechanics calculations and calorimetric and x-ray studies indicate essentially
free internal rotation (JACS <u>98</u>, 6798 (1976); <u>100</u>, 2202 (1978).

Werner Danchura and Walter Niemczura have now applied the J method (JACS <u>99</u>,
1033 (1977)) to show that the preferred conformation of 3,5-dichlorophenyl-
cyclohexane and of the 2-(3,5-dichlorophenyl) derivatives of 1,3-dioxane and
1,3-dithiane (all equatorial) is as in <u>1</u>
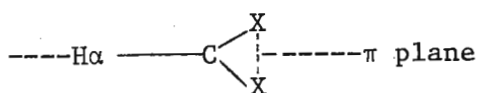
$$X = CH_2,\ 0,\ S$$
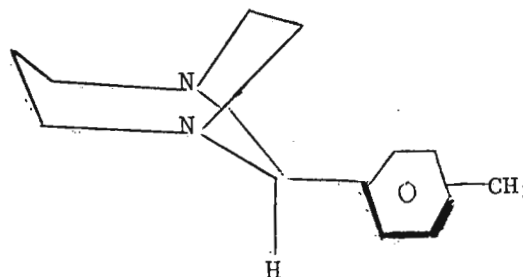
<u>1</u>   <u>2</u>

and that the essentially twofold barrier about the exocyclic C-C bond is 2.0 ± 0.3, 0.4 ± 0.2, 2.2 ± 0.3 kcal/mol for X = CH_2, O, S, respectively. In other words, CH_2 is as "big" as S and O is very small (sic); in agreement with the previous experimental, theoretical work.
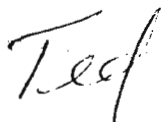
On the other hand, in 2 the C-Hα bond prefers to lie perpendicular to the benzene plane, as expected if N is "small" and the 5-membered ring is also locked as shown.

In 1 (X = CH_2), for example, we have the pretty picture of the benzene plane rotating many times before the cyclohexane ring inverts. In the very small fraction (ambient temperatures) of axial isomers, however, the C-Hα bond lies perpendicular to the benzene plane and the now (presumed) relatively large V_2 slows the phenyl rotation dramatically. The Maxwell demons who prefer a quiet inner life will occupy this isomer.

Watch for it in Can. J. Chem.! Someday, maybe we will convince even Dr. Bothner-By that the J method works....Do you remember his remarkable propene spectrum and analysis of 1961?

Long may you and the Newsletter flourish!

Yours sincerely,

Ted

Ted Schaefer.
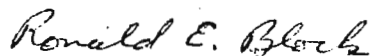
December 1, 1978

Used FT NMR Equipment Sought

We are interested in obtaining (by purchase or donation) some used FT NMR equipment with proton and ^{13}C capabilities. Either a complete system or a console + probes would be satisfactory. The latter would be used with a variable field Varian wide gap magnet. Interested persons should contact me as soon as possible at (305)324-5572 ext. 24 or 25.

Sincerely yours,

Ronald E. Block

Ronald E. Block, Ph.D.
Associate Scientist

מכון ויצמן למדע

THE WEIZMANN INSTITUTE OF SCIENCE

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December 15, 1978

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

Dear Barry:

Bat Sheva Workshop on Magnetic Resonance Spectroscopy

I would be grateful to you if you printed in one of the first TAMU-NMR issues of 1979 the following announcement on the "Bat-Sheva Workshop on Magnetic Resonance Spectroscopy".

Sincerely yours,

Zeev Luz

Zeev Luz

BAT-SHEVA WORKSHOP ON MAGNETIC RESONANCE SPECTROSCOPY SEPTEMBER 2-13, 1979.

THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOT, ISRAEL.

Sponsored by: The Bat-Sheva de Rothschild Foundation for the Advancement of Science in Israel.

Organized by: The Weizmann Institute of Science

Purpose:

The Workshop is intended for graduate students and senior scientists interested in Magnetic Resonance Spectroscopy.
The program will consist of nine series of (6-8) lectures and discussions on current topics in this field. Each topic will be built up from its basic concepts to its latest development. Emphasis will be placed on principles and methodology rather than review of results.

Lecturers and Topics

G. Binsch (Munich)	Dynamic NMR
W. McFarlane (London)	Multiple Resonance in High Resolution NMR in Liquids.
R. Freeman (Oxford)	Fourier Transform and Two Dimensional Spectroscopy
P. Mansfield (Nottingham)	Spin Imaging
J. Schmidt (Leiden)	Optical Magnetic Resonance and Zero Field Experiments
P.W. Atkins (Oxford)	CIDEP and CIDNP
M. Mehring (Dortmund)	Double Resonance NMR Spectroscopy in Solids
U. Haeberlen (Heidelberg)	Multiple Pulse Experiments in Solids
A. Pines (Berkeley)	Multiquantum Spectroscopy

Local Organizing Committee:

Z. Luz (Chairman), A. Achlama, S. Vega, Rehovot - S. Alexander, H. Levanon, Jerusalem
G. Navon, M. Sheinblatt, Tel Aviv - A. Lowenstein, B. Silver, Haifa.
Coordinator: Y. Berman.

General Information:

The Workshop will cover a period of two weeks (10 working days). The first week's sessions will be held on the campus of the Weizmann Institute, the second week's in Kibutz Guesthouse Nof Ginossar by the Sea of Galilee. The weekend (September 7-8) will be free for optional touring.

The language of the Workshop will be English.

There is a participation fee of $180.- which will cover accommodation (on a double room basis) and full board for the period of the Workshop.

Applicants should apply by letter specifying: name, title and position (graduate and postdoctoral acholars, please give name of supervisor), address and affiliation, and send it together with a $50.- deposit to: PROFESSOR ZEEV LUZ, DEPARTMENT OF ISOTOPE RESEARCH, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOT, ISRAEL. Cheques should be made out to "Bat-Sheva Workshop on Magnetic Resonance".

Deadlines:

For applications and deposits: April 30, 1979

For notification of acceptance: May 30, 1979

The number of participants is limited. In the case of non-acceptance, deposits will be refunded.

5FU

SIMON FRASER UNIVERSITY, BURNABY 2, B.C., CANADA
DEPARTMENT OF CHEMISTRY; 291-3345

December 21st, 1978

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

Dear Prof. Shapiro:

<u>Re: Data Link from Nicolet 1080 to IBM 370</u>

It is frequently desirable to have the capability to transfer data
from a FT NMR computer to a larger mainframe. This makes possible such
obvious applications as elaborate calculations, archival storage, and
use of peripherals which may not be available on the smaller computer.

At Simon Fraser, the main computer is an IBM 370/155. The first
problem with a data link is that there must be some permanently
resident program in the 370 with which communication can be established.
Our interface is via the Wylbur system, an interactive text editing
system written at the Stanford Computing Centre. This normally interacts
with users at RS-232 type terminals, and has the capability to create
and edit files on disk, and to submit jobs into the 370 batch stream.
Since this program is always available on the 370, we establish our
data link by making the Nicolet 1080 look like a Wylbur terminal.

The 1080 has to have the teletype board replaced by a dual I/O
board, which provides an additional RS-232 input-output channel. As
received from the manufacturer, this board is unsatisfactory, in that
it has a hardware delay which occurs whenever a carriage return is
transmitted. This initially led to data losses, and was cured by a
minor re-wiring which caused this delay to operate on the teletype
channel only.

We have written a program for the 1080 which interfaces with the
DEMON II monitor system, and provides the necessary appearance of a
terminal to the 370. The heart of this program is simply a buffering
system which takes data from the teletype at 110 baud and transmits to
the data link at 1200 baud, and vice versa. Thus, an operator at the
1080 teletype has the impression that he is operating a terminal on the
Wylbur system. With a few minor exceptions, he can issue any normal

Prof. B. L. Shapiro   December 21st, 1978

Wylbur command, and receive the normal reply. In addition, the 1080
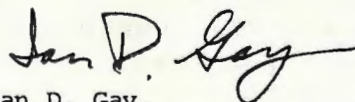program provides a series of special commands to perform data transfer
operations.

The presently available operations ara as follows:

a) Binary or ASCII transmission between 1080 disk files and
    the Wylbur active file.
b) Binary transmission between the 1080 data memory region
    and the Wylbur active file.
c) 1080 Disk directory listing to Wylbur active file (for
    subsequent high-speed printing).

Our present program occupies or uses as buffers most of the first
4K of 1080 program memory, leaving data memory and monitor head untouched.
There is room for a moderate number of additional routines. The binary
transmission referred to above is not really binary, as the Wylbur
system will not accept as data all possible 7-bit codes. Thus we break
each 20-bit 1080 word into four 5-bit chunks, encode each as one of 32
printable ASCII characters, transmit the four characters and decode on
the 370. This achieves nearly a 2-fold speed advantage over transmission
of the seven characters which would be required for a decimal representa-
tion of the 20-bit word.

Further details are available from the author.

Yours sincerely,

Ian D. Gay,
Associate Professor

IDG:vw

P.S. Please credit this communication to the continuance of Bob Cushley's
      subscription.

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SADIS BRUKER SPECTROSPIN, Boîte Postale N 67160 WISSEMBOURG

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

COLLEGE STATION Tex. 77843
USA

N./Réf.   78 12 500 CB/MCH

V./Réf.

Wissembourg, le   December 21th 1978

Dual observation monofrequency probe or how to get more from one pulse

Dear Prof. Shapiro,

Low frequency and low sensitivity nuclei are actually easily observed with multinuclear FT systems.

However, some important parameters which are needed for NMR experiments such as 90°· pulse value are obtained at the expense of very long spectrometer time utilization because of sometimes long T_1 and always bad signal to noise.

Such is the case for ^{109}Ag (sensitivity : 10^{-4} compared to proton, resonance frequency : 3, 72 MHz at 18.8 kG, spin 1/2), although this nuclide may give elegant solutions to ions - ligands equilibrium studies (cf MACIEL and al JACS 99, 8 . 2544 - 1977).

Having this problem in mind, we noticed Potassium 39 has a resonance frequency very close to Silver 109, its sensitivity being 9,5 times higher, a value sufficient to give a one pulse spectrum. It is then a question of seconds for obtaining Potassium 39, α^{90} value, with the probe tuned for Silver 109 observation. The number found being also the α^{90} pulse for Silver.

Spectrum 1 examplified this dual detection of Potassium 39 and Silver 109 resonances with 12 000 Hz spectral width on a WP 80 DS.

Spectrum 2 shows how to null the Silver resonance simply by irradiating the protons of H_2O solvent ! This discourageing result due to the negative gyromagnetic ratio of Silver should be very promising indeed as one could then probe the microstructure of the hydration sphere of the cation from T_1 and NOE determination.

^{39}K and ^{109}AG spectrum of a solution of Ag NO$_3$ in H$_2$O, 10 mm tube, KcL in D$_2$O in concentric 2 mm capillary. 10.000 scans - Spectrum 2 is with proton irradiation.
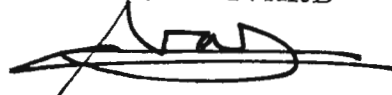
1

840 Hz

2
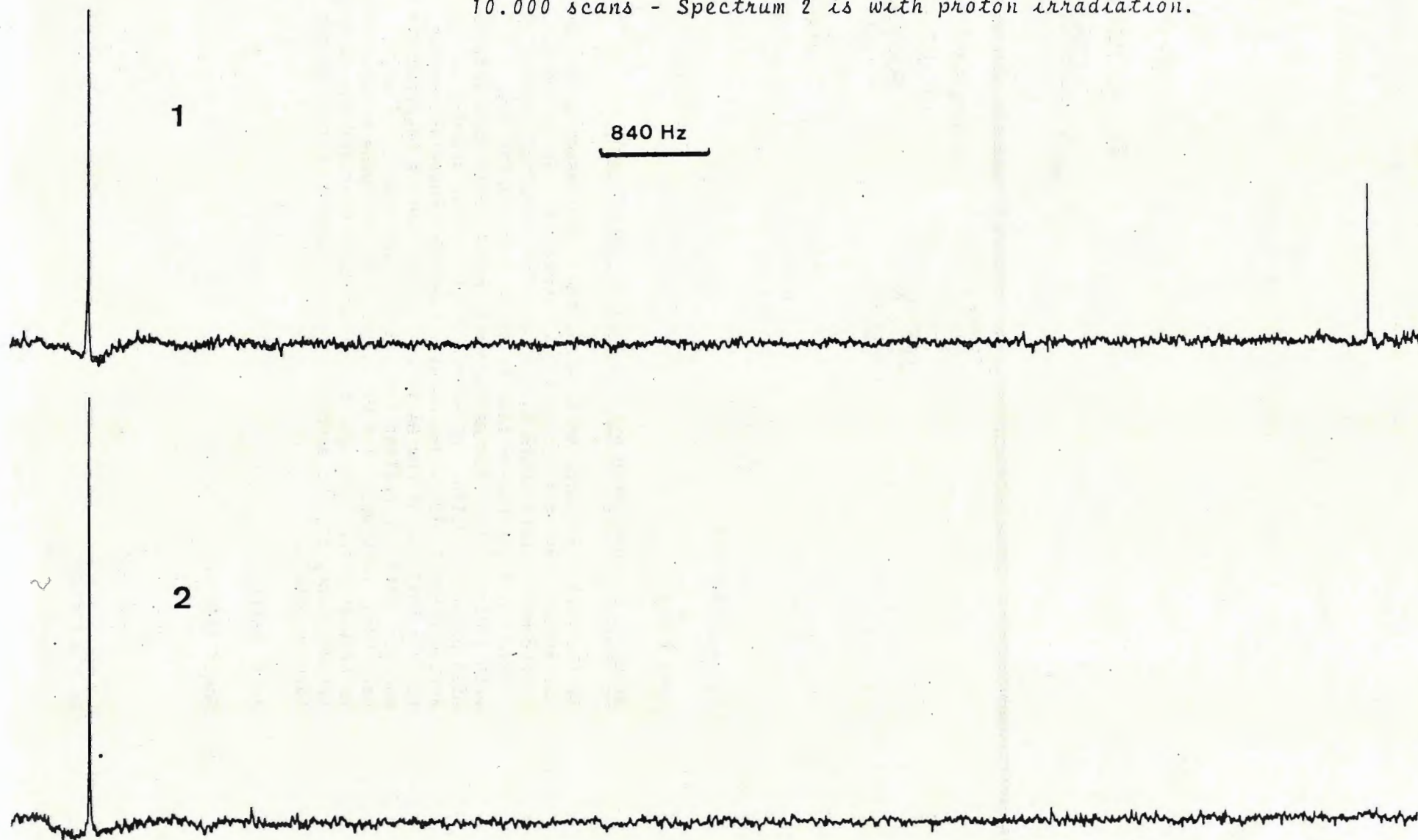
We are currently undertaking such a study in Wissembourg.

I do hope te be able to welcome you sometimes in Alsace, Perhaps in 1979 !

With my best wishes for this new year,

Sincerely yours,

Dr. C. BREVARD

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

TEL. 0703-559122
TELEX 47661

14 December 1978

Dear Barry

Bring in the new, move out the old: HA 100 for sale

In the past six months we have had the time-consuming but very satisfying task of buying a new spectrometer. We wanted a spectrometer which would be the best for recording spectra of liquid crystals, and we finally chose a Bruker CXP 200, with a disc, ^{13}C proton enhancement, magic angle spinning, and high power decoupling accessories. The CXP is now due to arrive early in 1979, and we will then find ourselves unable to make full use of our HA 100. This has been a magnificent machine, giving excellent service over ten years, and still performing very well, but we do not have the space or manpower to keep it going. So, we are prepared to consider any reasonable offers to buy it, and anyone interested should contact me for further details.

Best wishes,

Yours sincerely

Jim.

DR J W EMSLEY