TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 385
October 1990

TEXAS A&M NMR NEWSLETTER   NO. 385, OCTOBER 1990   AUTHOR INDEX

TEXAS A&M NMR NEWSLETTER   NO. 385, OCTOBER 1990   ADVERTISER INDEX

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FORTHCOMING NMR MEETINGS

1990 Pacific Conference on Chemistry and Spectroscopy, October 31 - November 2, 1990, San Francisco; NMR symposia Thursday and Friday, Nov. 1, 2; Contact: Registration Chairman, Pacific Conference, P. O. Box 561, Palo Alto, CA 94302.

Eastern Analytical Symposium, Garden State Convention Center, Somerset, NJ; NMR Symposia and Poster Sessions on Nov. 13 and 14, 1990; Contact D. C. Dalgarno or C. A. Evans, Schering-Plough Research, 60 Orange St., Bloomfield, NJ 07003; (201) 429-3957; FAX: (201) 429-3916.

Recent Advances in NMR Applications to Porous Media (First International Meeting), November 14 - 16, 1990, Bologna, Italy; Contact: SERCOOP CONGRESSI, Via Massarenti 190, 40138 - Bologna, Italy; Tel. (51) 300811; Fax (51) 309477.

Fourth Annual Missouri Magnetic Resonance Symposium, November 19, 1990, University og Missouri - Rolla; Contact: Frank D. Blum, Univ. of Missouri - Rolla, Dept. of Chemistry, 142 Schrenk Hall, Rolla, MO 65401; See Newsletter 385, 20.

Advanced Tomographic Imaging Methods for the Analysis of Materials, Symposium at the Fall Meeting of the Materials Research Society, Boston, Mass., Nov. 26 - Dec. 1, 1990; See Newsletter 378, 57.

In Vivo Magnetic Resonance Spectroscopy Tutorial and Participatory Workshop, St. Louis, Missouri, April 4 - 7, 1991; See Newsletter 385, 58.

32nd ENC (Experimental NMR Spectroscopy Conference), St. Louis, Missouri, April 7 - 11, 1991; Contact: ENC, 750 Audubon, East Lansing, MI 48823; (517) 332-3667.

1991 Keystone Symposia on Molecular & Cellular Biology, Keystone, Colorado: April 8-14, 1991, *Frontiers of NMR in Molecular Biology*; *Proteolysis in Regulation and Disease*; *Protein Folding, Structure and Function*; See Newsletter 384, 46.

International Conference on NMR Microscopy, Heidelberg, Germany, September 16 - 19, 1991; See Newsletter 385, 28.

Additional listings of meetings, etc., are invited.

Table of Contents, cont'd.

*   *   *   *   *

Mailing Label Adornment: Is Your Dot Red?

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Thank you.

All Newsletter Correspondence

Should Be Addressed To:

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303, U.S.A.

(415) 493-5971

DEADLINE DATES *

No. 387 (December)-------9 November 1990

No. 388 (January)----------7 December 1990

No. 389 (February) --------- 18 January 1991

No. 390 March)-------------15 February 1991

Please note that these deadline dates have been moved a bit forward from those previously in effect.

*   *   *   *   *
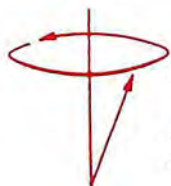
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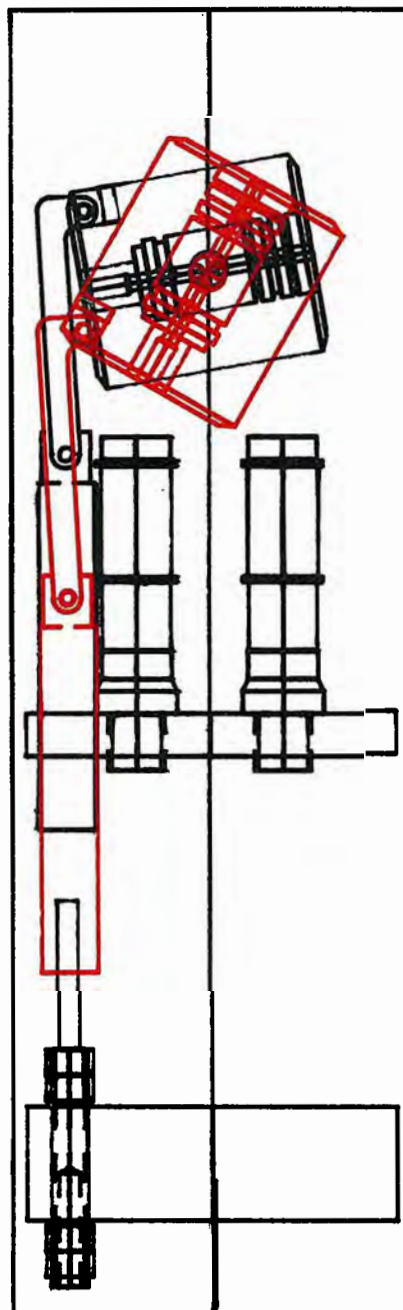
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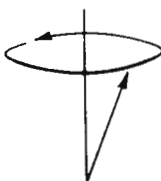
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August 30, 1990 (received 9/1/90)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
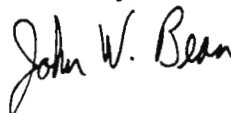
Free Energy of Rotation about Peptidylprolyl Bonds in Linear and Cyclic Peptides

Dear Dr. Shapiro:

Recently, we were interested in determining the free energy of activation for rotation about the peptidylprolyl bond in linear peptides by the saturation transfer method. Using D_2O as the solvent, we determined $\Delta G_{300}^{\ddagger}$ =19.9 +/- 1.7 kcal/mol-K for the hexapeptide acetyl-SQNYPV-amide, and $\Delta G_{300}^{\ddagger}$ = 18.7 +/- 1.7 kcal/mol-K for the nonapeptide acetyl-RASQNYPVV-amide. These values were of the order of magnitude that we had expected, and the $\Delta G^{\ddagger}$ values determined for each peptide can be considered equivalent given the standard deviation. This made us curious to see if the rotation about a peptidylprolyl bond in a cyclic peptide would be equally or perhaps more hindered than in linear peptides. We grabbed a cyclic peptide off the shelf, cyclo(ANAVSGPdF), and dissolved it in dimethylsulfoxide solution. As luck would have it, this cyclic peptide was not soluble in D_2O. By the saturation transfer method we then determined $\Delta G_{300}^{\ddagger}$ = 21.6 +/- 1.0 kcal/mol-K. Considering the standard deviation, this value is not much different than those determined for the linear peptides. We now plan to repeat the saturation transfer experiments on the linear peptides in dimethylsulfoxide solution in order to be better able to compare our results.

Please credit this contribution to Dr. Susanta Sarkar's account.

Sincerely,

John W. Bean

John W. Bean

709 Swedeland Road, PO Box 1539, King of Prussia, PA 19406. Telephone (215) 270 4800. Fax (215) 751 3400.

BP RESEARCH

Dr B L Shapiro
TAMU NMR News Letter
966 Elsinore Ct.
Palo Alto, CA 94303

17th August 1990
(received 8/23/90)

Dear Dr Shapiro,

VARIABLE TEMPERATURE WORK USING A BRUKER MINISPEC

Much of the work we are required to do using our PC110 Minispecs needs to be carried out at non-ambient temperature (40^oC in the case of the Minispec). Bruker can supply variable temperature probes, but the maximum sample diameter is limited to 25mm. Unfortunately this prevents their use for the analysis of 38mm diameter solid samples at room temperature - one of our major Minispec applications.

We have overcome this problem by reducing the temperature of the whole probe (40mm diameter absolute version) rather than just the sample. Nitrogen gas is cooled by its passage through a simple heat exchanger - a copper coil inside an insulated box containing "Cardice". It then flows over an in-line heater and is piped to the probe, fitted with a thermocouple. Temperature control at 27^oC is effected by a standard Bruker VT unit with the gas flowrate set to 850l/hr. The only modifications necessary to the probe were to drill two holes for the gas inlet/outlet fittings and to cut a slot in an internal former - the thermocouple was pushed through an existing screw-hole. The probe is well lagged to prevent overcooling of the Minispec magnetbox and the heaters rewired in parallel to improve temperature stability (see Bruker before making this modification). This system has now been working well for over six months (even during an untypical English summer with temperatures approaching 100^oF) with no adverse affects on instrument performance. The maximum temperature variation throughout the sample cavity is less than 2^oC but this could probably be reduced by repositioning the gas inlet and adding baffles inside the probe. It should be possible to achieve lower temperatures but this has not been attempted to date.

We have studied smaller samples at temperatures between -60^oC and 60^oC using a glass dewar, designed to fit the 40mm probe, where gas flows between the sample and coil. For low temperature work the gas was firstly cooled using a coil immersed in liquid nitrogen and then reheated to the required temperature. For measurements above ambient temperatures nitrogen gas also circulated around the probe to maintain temperature stability in the magnetbox.

Finally, a Bruker 25mm diameter VT ratio probe has been used perfectly satisfactorily at temperatures down to -36^oC using a Julabo FP50-HC bath and a 3M perfluorinated fluid.

I hope these comments will be of interest to Minispec users and apologise to any UK participants at the first Minispec Users' Group meeting in September who will have heard all of this already!

Yours sincerely,

D R Roberts
Spectroscopy Branch

DEPARTMENT OF HEALTH & HUMAN SERVICES

National Institute of Diabetes and
Digestive and Kidney Diseases
Bethesda, Maryland 20892

Dr. Bernard L. Shapiro
Editor
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA94303

August 22, 1990
(received 8/27/90)
Flat baselines

Dear Barry:

Almost as much has been said about baseline correction in NMR as about
more controversial topics such as zero filling or maximum entropy. Here,
we want to add another little bit, hopefully without confusing newsletter
readers even more. As has been correctly pointed out by a large number of
people, baseline distortions in the F_2 dimension of a 2D spectrum are the
result of deviations from ideality of the first few data points, and from
using an incorrect starting point for data acquisition. The latter effect
necessitates the use of a frequency-dependent phase correction after FT.
As Otting and friends (1) correctly pointed out, discrete Fourier
transformation is another source of baseline distortion. In fact, baseline
distortion in the F_1 dimension of a 2D spectrum is entirely due to
incorrect scaling of the first data point and to the delayed sampling in
this dimension. Because of finite pulse widths, the effective duration of
the first t_1 increment ($t_1(0)$) frequently is a significant fraction of a
dwell time (DW) and not zero as desired. Marion (2) suggested setting the
effective delay in sampling to exactly one dwell time, and then using
linear prediction to calculate what the first point should have been,
prior to FT in the t_1 dimension. In addition, scaling of this "linear
predicted" first data point by a factor 0.5 is needed in this case. This
procedure works quite well, but as pointed out below, it is more
complicated than need be for the F_1 dimension. In their original paper,
Otting et al. suggest that a first data point scaling factor equal to
$0.5+(t_1(0))/DW$ would fix both the delayed sampling and the incorrect
scaling problem. Indeed, use of such a scaling factor provides some
relief, but certainly does not result in a perfect baseline. As
illustrated in Fig.1a, Fourier transformation of a simulated FID, delayed
by 1/4 dwell time, with the first data point scaled by the Otting factor
of 0.75, still gives a crooked baseline. Actually, as can be seen in
Fig.1b, a scaling factor of 0.6 is at least equally good/bad, and an ideal
scaling factor does not exist for the general case of an arbitrary
sampling delay. However, for the case where the sampling is delayed by
exactly half a dwell time, no scaling of the first data point results in a
perfect baseline, exactly as good as in the case of no delayed sampling
and scaling by 0.5.
   This latter option, to delay sampling by exactly half a dwell time, has
an additional advantage in the case of folding (aliasing) of complex data.
If the sampling delay is exactly half a dwell time, after phase correction
resonances that are folded (aliased for the purists) are exactly upside
down (Fig.1d). This comes in handy when analyzing our 3D spectra where we
frequently have to use folding in order to keep matrices within acceptable
limits. For some of our most recent and yet unpublished 4D experiments, we

use only 8 complex data points in two of the four dimensions and delaying
the sampling by half a dwell time actually gives an improvement in
resolution of 8.5/8 in both these dimensions, i.e., that's an increase of
a total of (8.5/8)**2 or 12.5% in effective resolution at no extra charge.
There is another advantage to the half a dwell time delay when using
linear prediction, but because of your strict space limits, we'll write to
you about it some other time. *? no!*

Kindest regards,

Ad Bax   Mitsuhiko Ikura   Ghuang Zhu   Lewis Kay

1. G. Otting, H. Wider, G. Wagner and K. Wuthrich, J. Magn. Reson. 66, 187
(1986).
2. D. Marion and A. Bax J. Magn. Reson. 83, 205-211 (1989).
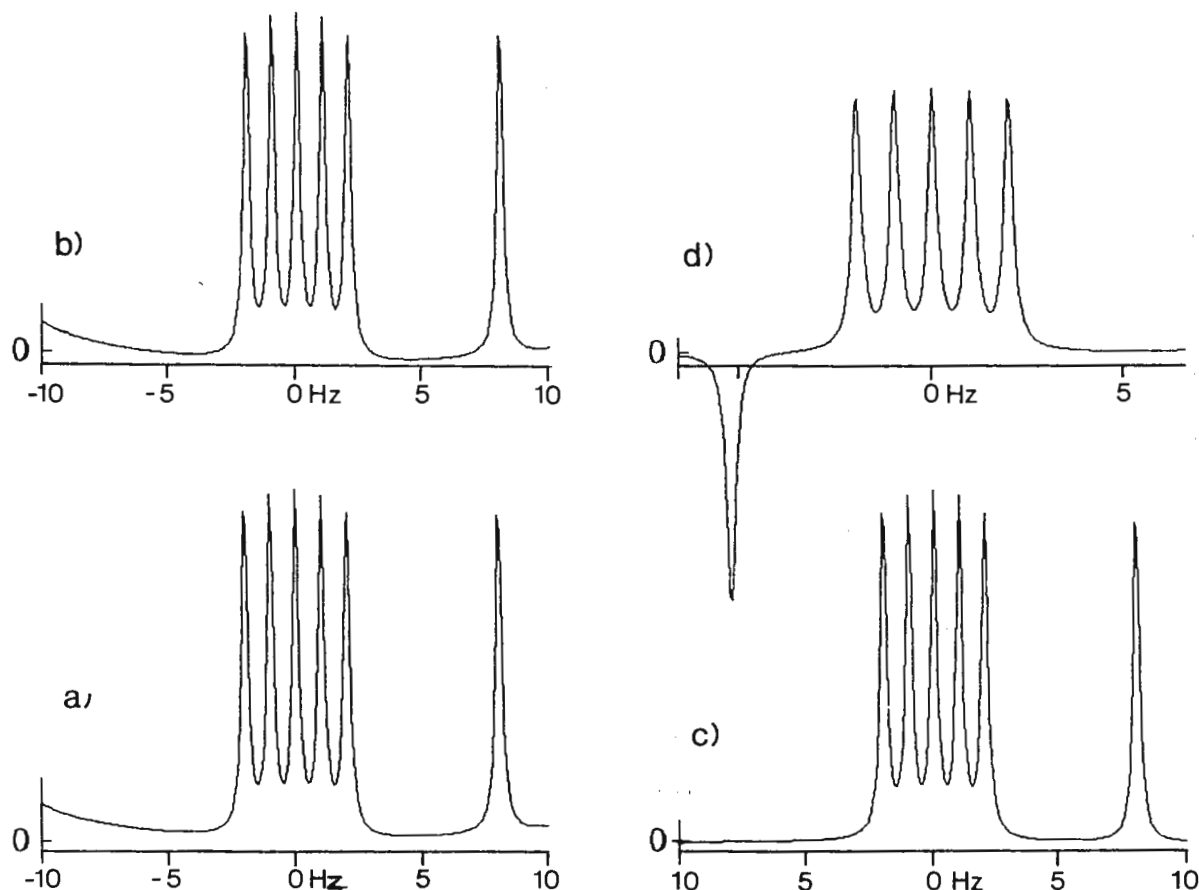
Fig. 1. (a,b) Simulated spectra obtained by Fourier transformation of data
with an initial sampling delay of one quarter dwell time. For (a),
multiplication of the first data point by 0.75 has been used, for (b) the
scaling factor was 0.6. For both (a) and (b) the linear phase correction
was 90° across the spectrum. (c) Spectrum obtained for a sampling delay
equal to one half dwell time, with no scaling of the first data point. (d)
Spectrum obtained if the spectral window is narrowed by 33%, again with a
sampling delay of half a dwell time. The resonance at the right side of
the spectrum is aliased and appears inverted at the left hand side. For
both (c) and (d) the linear phase correction is 180°.

DEPARTMENT OF HEALTH & HUMAN SERVICES

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Dr. Bernard L. Shapiro
Editor
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA94303

August 22, 1990 (received 8/27/90)

Dear Barry: Mirror image and time extension

We recently have had a lot of fun trying to do 4D NMR (1,2). One of the
problems with this type of experiment is, however, that it takes a long time
to record such a data set. Acquiring a small $(32 \text{ complex})^4$ 4D matrix would
require 64^3 scans per step of the phase cycle. Using a modest 4-step phase
cycle, this would result in several weeks of spectrometer time. Therefore,
instead of measuring signals for all these increments in the t_1, t_2 and t_3
dimensions, we rather predict what we would have measured, and Fourier
transform that data set.

Linear prediction algorithms are in principal ideally suited for
predicting the future of a truncated time domain signal. Naively, one might
measure 8 data points in each dimension, and predict the future out to, for
example, 512 data points, giving a 64 fold increase in apparent resolution.
In practice, this does not work, of course. It is basically impossible for a
reasonable signal-to-noise data set to predict its future to more than twice
its original length. A second problem is that linear prediction tries to
calculate four numbers per frequency component: the phase of the signal, its
amplitude, its damping factor (T_2), and its frequency. With four unknowns,
the maximum number of frequency components that can be measured in a
noiseless 8-complex point FID is thus limited to 4. In practice, we may have
more than four components in our truncated FID, however.

For linear prediction of severely truncated NMR data, as encountered in
our higher-D spectra, we know the phase of the signal in the indirectly
detected dimensions, and we also know the damping factors (approximately zero
for the few ms of the truncated time domain). Hence we could try to modify
the linear prediction algorithm to determine only 2 unknowns per frequency
component. In principle, this would permit measurement of up to 8 components
from a 8-complex FID. However, messing with the linear prediction algorithm
appeared pretty hopeless, considering a number of much smarter mathematicians
were only partly succesful in attempting similar things before.

We stumbled on a simpler solution to solve our problem. Since we know the
phase of the signal (zero at time zero) and signal decay is almost
negligeable, we can "calculate" exactly what the signal would have looked
like at negative time ($\cos\omega t = \cos-\omega t$; $\sin\omega t = -\sin-\omega t$). So, one takes the
complex conjugate of the signal, reverses it and puts it in front of the
measured signal. Of course, we now end up with two points for time zero, so
one would have to be deleted. A smarter way of doing things ensures that the
FID starts with exactly half a dwell time delay (didn't I read this before
anywhere ...?). In this case the FID consisting of 8 complex points can be
extended to 16 complex points instead of 15, allowing up to 8 frequency
components to be measured and because our new time domain is twice as long,
we also can predict its future for a longer period of time without running
into problems. This procedure works very well, although, because of the
larger size of the data table it takes significantly longer to do the linear

prediction this way, several days on a CONVEX for a modest 4D data set.

The two panels in Fig.1 show a simple application to a section of a slice of a 3D spectrum illustrating that using the mirror image really improves the linear prediction. In this example, we attempted to extend an 8-complex FID to 32-complex (more than recommended !). For the nearly overlapping resonances of amino acids Q3 and K115, some distortion occurs of the F_1 peak positions relative to their real F_1 coordinates (marked by arrows), but this distortion is significantly less for the mirror-imaged LP data set than for the regular LP-enhanced panel. Comparisons for our 4D data are even more impressive, but will have to wait for reviewers to approve of their relevance.

Doubling the length of the time domain should also keep us safe from your dreaded ultimatum axe till 1992, right ?[HO! HA! HA! Actually, your next R/U letter is due in 1/2 the time, and was due last month. BLS]

Kindest regards,

yaK siweL   uhZ gnauG   arukI okihustiM   xaB dA

(1) L.E. Kay, G.M. Clore, A. Bax and A.M. Gronenborn Science 249, 411 (1990)
(2) L.E. Kay, M. Ikura, G. Zhu and A. Bax J. Magn. Reson. submitted.
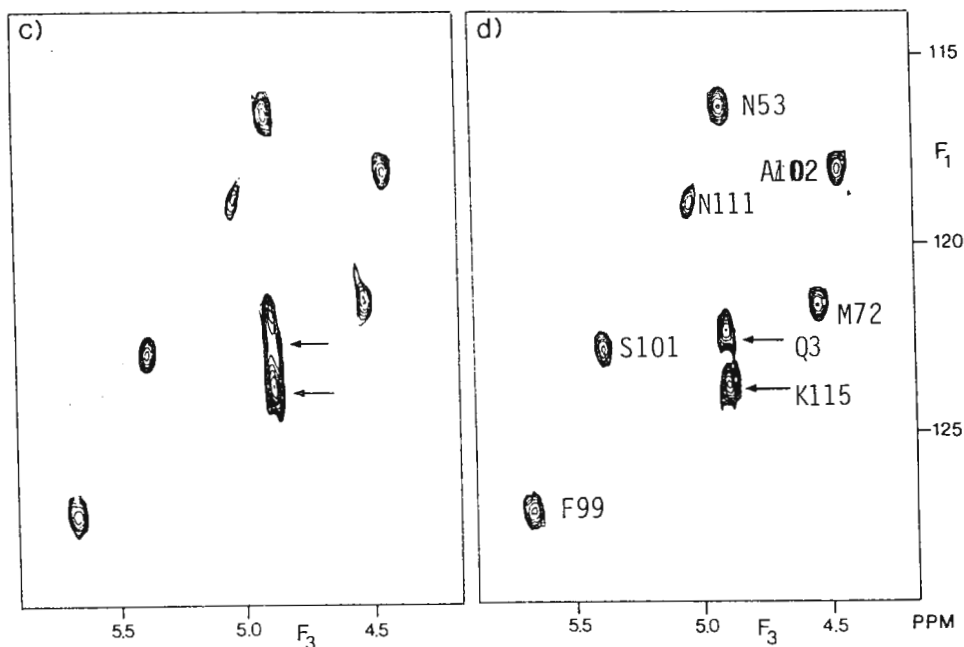
Fig.1. (F_1, F_3) slice of a triple resonance 3D HCA(CO)N relay spectrum, correlating Hα, Cα shifts with the ^{15}N shift of the next residue. Both panels have been processed identically in the F_3 dimension. (c) Spectrum obtained by 9 Hz exponential F_1 line narrowing, linear prediction of the first 8 data points out to 32 followed by $\cos^2$ apodization, zero filling and Fourier transformation. (d) Processed as (c), but using the negative plus positive time domain data points (16 complex data) for linear prediction of the additional 24 data points. The arrows in panels (c) and (d) mark the true F_1 coordinate of the Q3 and K115 resonances.

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September 4, 1990
(received 9/8/90)

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Paramagentic Impurities in Solid-state Spectra

Dear Barry,

Working, as we do, in an institute of geochemistry and geophysics, we have become well acquainted with the pitfalls associated with paramagnetic impurities in solid samples, be they natural or synthetic in origin. Over the past two years now over which we have been up and running, we have been able to successfully convince our synthetic co-workers of such evils and, as a result, have been able to obtain, in general, useful and informative spectra. We were quite surprised several weeks ago, however, when we obtained the pyrope/grossular glass spectrum shown in fig 1a. This spectrum has a severely rolling baseline and an FID with large distortion in the first points, and in general shows all of the characteristics of paramagnetic impurities. We were rather puzzled by this as the sample is one in a series of glasses, all of which had given quite reasonable spectra up to that point. All of the samples had ben prepared by the same careful coworkers using ultra pure starting materials and taking what we thought to be thorough and careful precautions to avoid paramagnetic impurities. At this point the sample was prepared again and produced the rather broad, but nevertheless informative spectra shown in fig. 1b, which was more in keeping with the other spectra in the series.

Now, as we found out, this particular sample, for some reason, was ground in an iron mortar and pestle <u>and</u> subsequently refired. While a strong magnet was passed over the sample to remove any bits of iron, most probably a small amount of iron remained on the surface of the ground, powdered sample. The subsequent refiring process allowed this "surface" iron to be distributed throughout the sample and, thus, to produce the severe distortions noted in the spectrum. Subsequent microprobe analysis showed the Fe impurity to be less than 0.02% Further discussions with our coworkers revealed (much to our horror) that all of the samples had been ground with an iron mortar and pestle. However, further investigation showed that only the sample which had been refired gave a distorted spectrum. Clearly the "surface" Fe did not affect the bulk of the glass material. The moral of the story is that one can't be too careful when paramagnetics in solids are concerned.

Sincerly,

Angelika Sebald

Larry Merwin
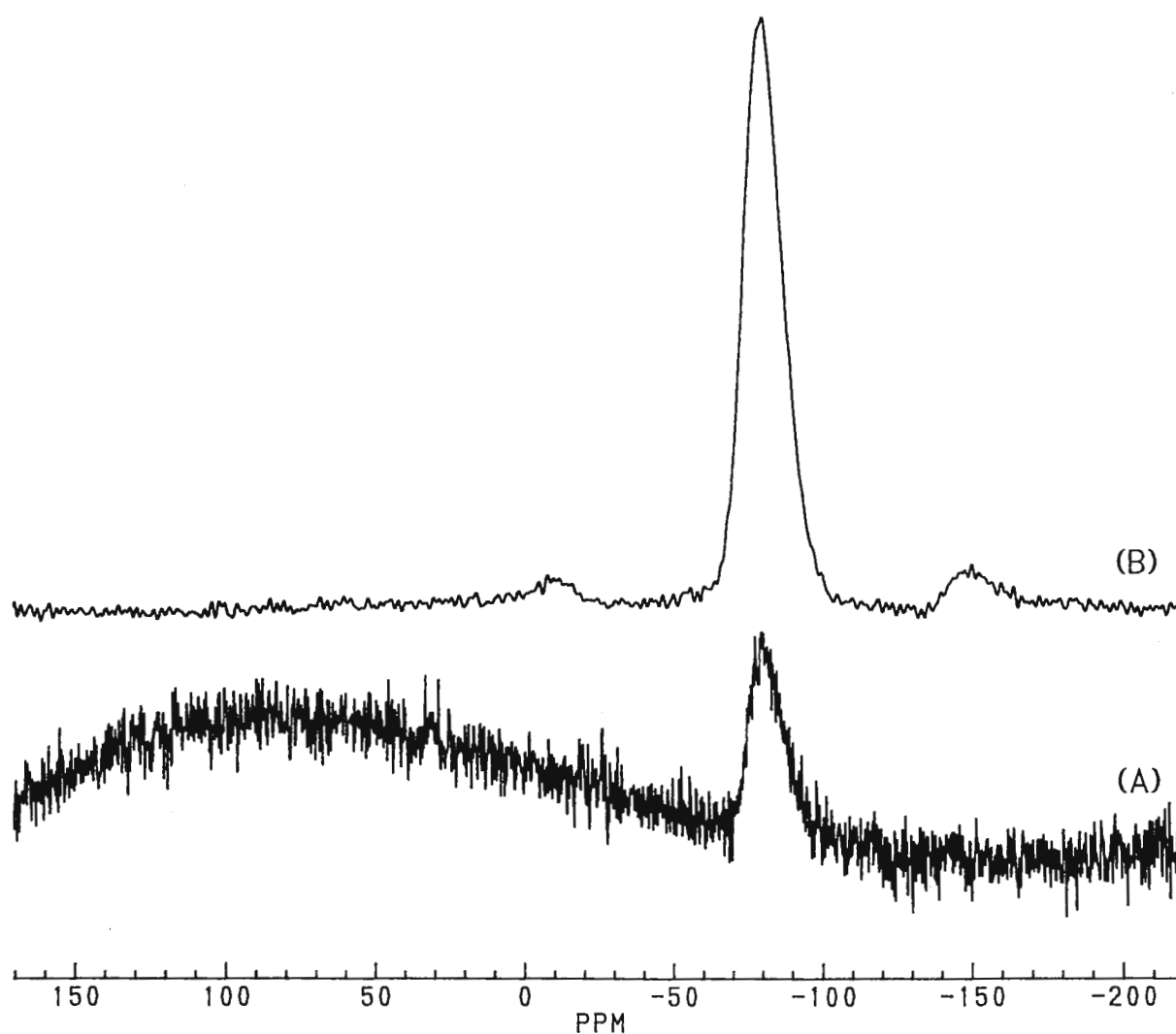
Figure 1: The absolute intensity mode ^{29}Si MAS spectra of glasses having the composition 60% pyrope ($Mg_3Al_2Si_3O_{12}$) 40% grossular ($Ca_3Al_2Si_3O_{12}$). A) Spectrum of sample containing paramagnetic impurites (NS = 2864); and B) spectrum of a newly prepared sample without Fe impurities (NS = 2132). For both spectra the following parameters were used: 2 μs, 36° pulse, recycle delay: 30 sec and 3.8 kHz MAS.

G O S S I P

GOSSIP is a new two-way data transfer program written by FMR for data transfer between IBM compatible PC computers and the Nicolet/GE 1280. Data transfers can be done at rates up to 38.4K baud (about 700 Nicolet Words per second with overhead). This function gives the 1280 user a new spectrum of capabilities:

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🧲 The processed data is immediately available for direct incorporation into many popular **word processing and desktop publishing** packages.

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With the TMON operating system for the 1280, transfers to the PC can be done in two ways.

<u>FILTRN</u> - RS-232 transfers can be done using the Nicolet/GE FILTRN program from the TMON operating system to GOSSIP on the PC. This can be done at rates up to 38.4K baud (about 700 Nicolet Words per second with overhead).

<u>NMR Programs</u> (QE, GN and NT) - Transfers can be done from inside the NMR programs. These programs support foreground and background RS-232 transfers at rates up to 38.4K baud (about 700 Nicolet Words per second with overhead). These transfers can be automated under MACRO control of the 1280 so that when the experiment is finished the data is automatically transferred. Overnight and/or sample changer operations can automatically store copies of the data on a waiting PC.

DEXTER

With the DEXTER operating system for the 1280, transfers to the PC can be done in two ways.

<u>FILTRN</u> - RS-232 transfers can be done using the Nicolet/GE FILTRN program from the DEXTER operating system to GOSSIP on the PC. This can be done at rates up to 38.4K baud (about 700 Nicolet Words per second with overhead).

<u>NMR Programs</u> (NT) - FMR provides a package of software which includes an *overlay for the 1280 NMR program* and the GOSSIP PC program. With this package transfers can be done from inside the NMR program IN BACKGROUND and at rates up to 38.4K baud (about 700 Nicolet Words per second with overhead).
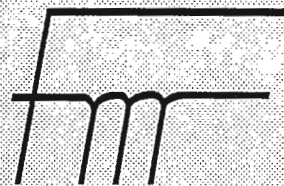
Felix / PC

NMR Data Processing Software

FMR cooperates with Hare Research in providing the NMR community with Felix/PC (tm) NMR data processing software and software utilities for IBM compatible PCs. The software is available in either a 1D or Multi-D package. Felix/PC is a "toolbox" of NMR data processing routines which allow the operator to perform all common and many unusual processing functions. It is an extremely powerful processing package rivaling many packages on "more powerful" computers.

1D Package:
* Full range of apodization routines.
* Forward and reverse transforms.
* On screen "real time" phasing , expansion and difference routines.
* Several types of baseline correction routines.
* Automatic and manual peak picking and labeling.
* Total spectrum and "broken" integration routines.
* 1D data table sizes up to 64K words.
* Complete macro functions.
* "Locate" menuing system.
* Graphics support for HPGL and Postscript.

1D / 2D Package:
* Process up to 4 dimensional without transposition.
* 1D data table sizes up to 32K words.
* 2D data table sizes up to 2K x 2K.
* Color coded contour displays and plots.

Felix/PC *requires* a 100% compatible IBM PC computer (8088, 8086, 80286 or 80386) with an with 640 K of memory, a 80x87 coprocessor, a hard disk and an IBM compatible CGA, EGA or VGA graphics adapter.

If Felix/PC is to be used with data from NMR spectrometers, data format translation is *required.* Data format translation is the responsibility of the buyer. Data format translation software is available as a separate purchase.

Felix software is also available for other computers such as SUN and IRIS systems. Felix/PC and Felix is available from Hare Research for only a small handling charge ($150.00) to all academic and government institutions. Demo software packages are available.

Data Translation Software.

Both Nicolet/GE and Bruker provide Kermit and X-Modem data transfer software for their spectrometers. This software can easily communicate with a PC running any one of the many software communication packages using Kermit or X-Modem transfer protocol at transfer speeds up to 38K Baud.

Once the data is transferred using X-Modem or Kermit protocols, with FMR's GOSSIP or by any other means, data translation software packages are available to convert the Nicolet/GE 1280 20 bit word or the Bruker Aspect 24 bit word into floating point Felix/PC words. Key parameters are also converted from the Nicolet/GE and Bruker integer and floating point header parameters into the respective file headers for Felix/PC:
* Spectrometer Frequency.
* Sweep Width.
* Data Table Size.
* Non-Quadrature / Quadrature Data.

Some Varian conversions are available from other vendors. The capability to process several manufacturers' data with a single software package can make life in a mixed instrument laboratory easier for many users.

Parallel port 1280 to PC transfers are in development.

BXR Data Transfer & Translation Software

BXR is a set of programs that transfers data files from the Bruker Aspect computers to PC computers. BXR stores the data in translated files that Felix/PC can read. Parameters related to data processing are transferred for use by Felix. Transfer rates of up to 19200 baud are usually routine (> 100 KBytes per minute). In normal operation the PC and the Aspect are connected with a communication cable and the BXR transfer program started on the PC. The unattended PC then waits for files to be transferred by the Aspect. There is no need to halt the PC program. You can start and stop the transfer program on the Aspect without stopping and restarting BXR on the PC. Under this condition, the PC waits for additional files from the Aspect until you halt it. This is for convenient data transfers to an unattended PC.

UNIVERSITY OF STRATHCLYDE

Department of Pure and Applied Chemistry

Thomas Graham Building, 295 Cathedral Street
Glasgow G1 1XL Tel: 041-552 4400

Dr. Barry Shapiro,
TAMU NMR Newsletter,
966 Elsinore Court,
Palo Alto, California 94303,   (received 8/27/90)
U.S.A.   17th August 1990

Proton Spectra of 1-Bromo-2-Phenyl-cyclopropane Isomers

Dear Barry,

Faced with the task of deciding which of the two isomers of
1-bromo-2-phenylcyclopropane was which, we recently had recourse
to old-fashioned steam nmr. The two liquid compounds were
separated by column chromatography and had very similar spectra.
However, their 4-spin proton systems in the cyclopropane rings
were susceptible to simulation using Bruker's PANIC program. The
results and assignments for the spectra (in chloroform-d on our
WM-250) are shown below.

For the cis-isomer (slow running on chromatography):-

$\delta 1$ = 2.31, $\delta 2$ = 3.30, $\delta 3a$ = 1.58, $\delta 3b$ = 1.32 ppm.
J12 = 7.63, J13a = 9.49, J13b = 7.60, J23a = 7.55,
J23b = 4.57, J3a3b = -6.81 Hz.

For the trans-isomer (fast running on chromatography):-

$\delta 1$ = 2.39, $\delta 2$ = 3.20, $\delta 3a$ = 1.45, $\delta 3b$ = 1.50 ppm.
J12 = 3.37, J13a = 10.06, J13b = 6.40, J23a = 4.47,
J23b = 7.42, J3a3b = -6.79 Hz.

The crucial difference between the isomers, which allows the
distinction to be made is the presence of the relatively large
vicinal coupling (J13a) in the trans isomer.

Yours sincerely

Peter Bladon

ANNOUNCEMENT
and call for contributed papers

The Fourth Missouri Magnetic Resonance Symposium (MMRS-IV)

Host: Frank D. Blum

Monday, November 19, 1990

Centennial Hall
University of Missouri-Rolla
Rolla, Missouri 65401

The planned one day program includes 5 invited lectures plus a contributed poster session. The list of speakers includes:

Mark Conradi, Washington University
Wilmer Miller, University of Minnesota
Charles Wade, IBM Almaden Research Center
Eric Oldfield, University of Illinois at Champaign-Urbana
Jerome Ackerman, Massachusetts General Hospital

At this time, we are calling for posters for all areas of magnetic resonance.

Registration: $10.00 per person, students free; Symposium luncheon $10.00

If you need further information, contact us at the address below, or mail the attached form.

Frank D. Blum
Department of Chemistry
University of Missouri-Rolla
Rolla, MO 65401
(314) 341-4451
INTERNET: C2828@umrvmb.umr.edu
BITNET: C2828@UMRVMB

____ I (we) plan to attend the Fourth Missouri Magnetic Resonance Symposium.

____ I (we) plan to present a poster entitled _____

_____

_____

____ Please send us further information.   Also send information to the following person(s):

Name:_____   Name:_____

Address:_____   Address:_____

_____   _____

_____   _____

²H EXCHANGE IN THE SOLID STATE

The CD$_3$ groups of dimethyl sulfone-d$_6$ undergo 180° flips about the C$_2$ axis with a rate on the order of 10 msec. The 2D spectrum presented here were obtained on a UNITY-400 in the manner of Blumich and Spiess and show the ellipsoids of motion predicted for this system. Spectrum A is a stacked plot and spectrum B is a contour plot that combines the sine and cosine transforms.

A.

B.

UNIVERSITY OF CONNECTICUT

Department of Chemistry, Box U-60, Storrs, CT 06269-3060

August 24, 1990
(received 8/27/90)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

^{13}C Shifts of Silylated Exomethylene Cyclobutanes

Dear Dr. Shapiro:

In connection with our recent investigation of the intramolecular addition of alkyllithiums to acetylenes [*Tetrahedron Lett.* **1989**, *30*, 3901 and **1990**, *31*, 627] we found that four-membered rings may be easily prepared by 4-exo-dig cyclization of a 6-(trimethylsilyl)-4-pentyn-1-yllithium generated by low-temperature lithium-iodine exchange. As shown below, addition of any of a variety of electrophiles delivers functionalized, silylated exocyclic alkenes.
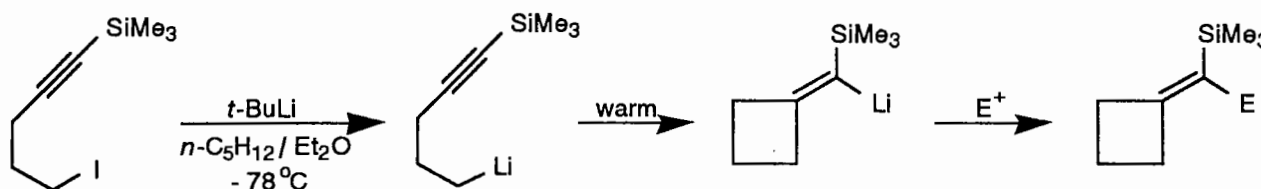
The ^{13}C chemical shifts (ppm from TMS in CDCl$_3$ solution) of the alkene and ring carbons of several of the products are given below.
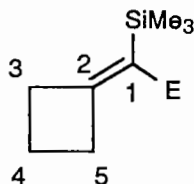
E	C(1)	C(2)	C(3)	C(4)	C(5)
H	118.94	160.23	35.46	16.41	33.42
CO$_2$H	124.85	175.85	34.73	17.06	37.30
CHO	134.75	182.38	33.20	17.37	35.68
CH$_2$CH$_2$OH	125.99	155.46	34.44	16.39	32.23
CO$_2$Et	125.64	169.62	34.43	17.11	36.62
CH$_2$CH(OH)CH$_3$	127.19	155.60	33.23	16.33	32.60

Please credit this contribution to Tom Leipert's account .

Sincerely,

Timo V. Ovaska

William F. Bailey

Anaquest

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A Division of BOC Inc

August 27, 1990
(received 9/4/90)

Anesthesia and
Acute Care
Pharmaceuticals

Dr. Bernard L. Shapiro
TAMU Newsletter
960 Elsinore Court
Palo Alto, CA 94303

Subject: Automation on a JEOL Spectrometer

Dear Dr. Shapiro:

After experimenting with EXE files on a Bruker, the knowledge gained
was extremely helpful in streamling the automation sequences available
on the JEOL spectrometer.

At Anaquest, the GSX-270 is a hands on spectrometer with over 20
chemists obtaining routine spectra. The canned automation programs
used a combination of GLG and STAK files. The use of STAK files **does**
return control of the spectrometer to the user prior to acquisition,
but the instrument is not available for another acquisition till the
plot job is completed.

The present automation routines exclusively uses GLG files with
complete control returned to the user the instant the plot job **begins.**
This has increased the throughput of the instrument by close to 100%.
The instant the plot job commences, the user is prompted to change the
data accumulation area (ACMEA)in the JCPU memory. The routine loops
back to the beginning of the sequence for the next experiment.
Additionall the FID is displayed on the screen during accumulation
which permits the user to terminate acquistion at any point.

Certain automation routines have been written for specific users. To
inform all users of the various automation sequences, a nested GLG
automation sequence reads in a menu of all sequences available.
Included in the sequence is a help screen which highlights the
features of each sequence.

On another note, parameter listings can be customized by editing *.PRT
files in [70,11]. To introduce text in the parameter listing, the
text string should be preceded by an exclamation mark (!); e.g.
!Operator.

The above modifications are available to interested users. Please send
the request along with a formatted 51/4" diskette.

Yours Sincerely,

Ashok Krishnaswami

BOC Health Care

Sadtler ^{13}C NMR Structure Assignment Library

The Sadtler ^{13}C NMR Structure Assignment Library consists of:

The Sadtler Standard ^{13}C NMR Spectra Library
containing entries for 30,000 pure compounds

Sadtler ^{13}C NMR Search Software

Sadtler ^{13}C NMR Molecular Structure Library
(the corresponding 30,000 chemical structures)

Sadtler Molecular Substructure Search Software

STRUCTURE SEARCH CHARACTERIZATION ASSIGNMENT	DISPLAY/PRINT ARCHIVE SPECTRA	DISPLAY/PRINT SPECTRA	STRUCTURE SEARCH	DISPLAY/PRINT PERFORMANCE PROPERTIES

SADTLER SOFTWARE PRODUCTS   **3rd PARTY SOFTWARE**

FT-IR STD SPECTRA	FT-IR COMM. SPECTRA	STD STRUCTURES	^{13}C NMR STD SPECTRA	CORP. FT-IR SPECTRA	CORP. STRUCTURES	CORP. ^{13}C NMR SPECTRA	CORP. ARCHIVAL SPECTRA	CORP. STRUCTURES	CORP. PERFORMANCE PROPERTIES

The assignment library provides a unique access to Sadtler's ^{13}C NMR spectra that correlates molecular properties with chemical shifts. Structure elucidation is facilitated by searching anticipated structural features and measured chemical shifts.

Department of Chemistry
Tel: 523187
DR. OLIVER W. HOWARTH

University of Warwick
Coventry CV4 7AL

Department of Physics
Tel: 523523 Ext. 2403
DR. RAY DUPREE

Dear Barry

30th August 1990
(received 9/7/90)

<u>Polymer Conformations</u>

We are making considerable progress with what has until now been a largely wasted nmr resource - the shifts in the ^{13}C and ^{1}H spectra of polymers which arise from variations in tacticity. Our analyses follow Tonelli's lead[1], but aim to include all a polymer's available resonances in one rotational isomeric state model. The figure shows the ^{13}C-^{1}H shift correlation spectrum of the methyl resonance of polymethyl acrylonitrile, $(-CH_2-C(\underline{C}H_3)CN-)_n$. The clear anticorrelation of the ^{1}H and ^{13}C shifts arises because the methyl carbon shifts decrease when either flanking $\underline{C}(CH_3)CN$ carbon is γ-gauche to it. This nearly always also entails closeness of the CN group, and hence an <u>increase</u> of H shift due to deshielding by the CN bond current. The anticorrelation can only arise because of the comparative simplicity of the shift mechanisms. Alongside the 2D spectrum, and to roughly the same scale, is one of our attempts at predicting the carbon shifts from a conformational model. The solvent-free model is too simple to give a perfect fit, but it does reproduce the triad (eg. mm) and pentad (eg. mrrm) microstructure fairly well using reasonable steric parameters. It also gives a reasonable fit for the C, CN and CH_2 resonance groups. We hope to use the resulting steric energy data for computer modelling.

Yours sincerely

Oliver Howarth

Dr O.W. Howarth

1   A.E. Tonelli "NMR Spectroscopy and Polymer Microstructure",
    V.C.H., New York, 1989.
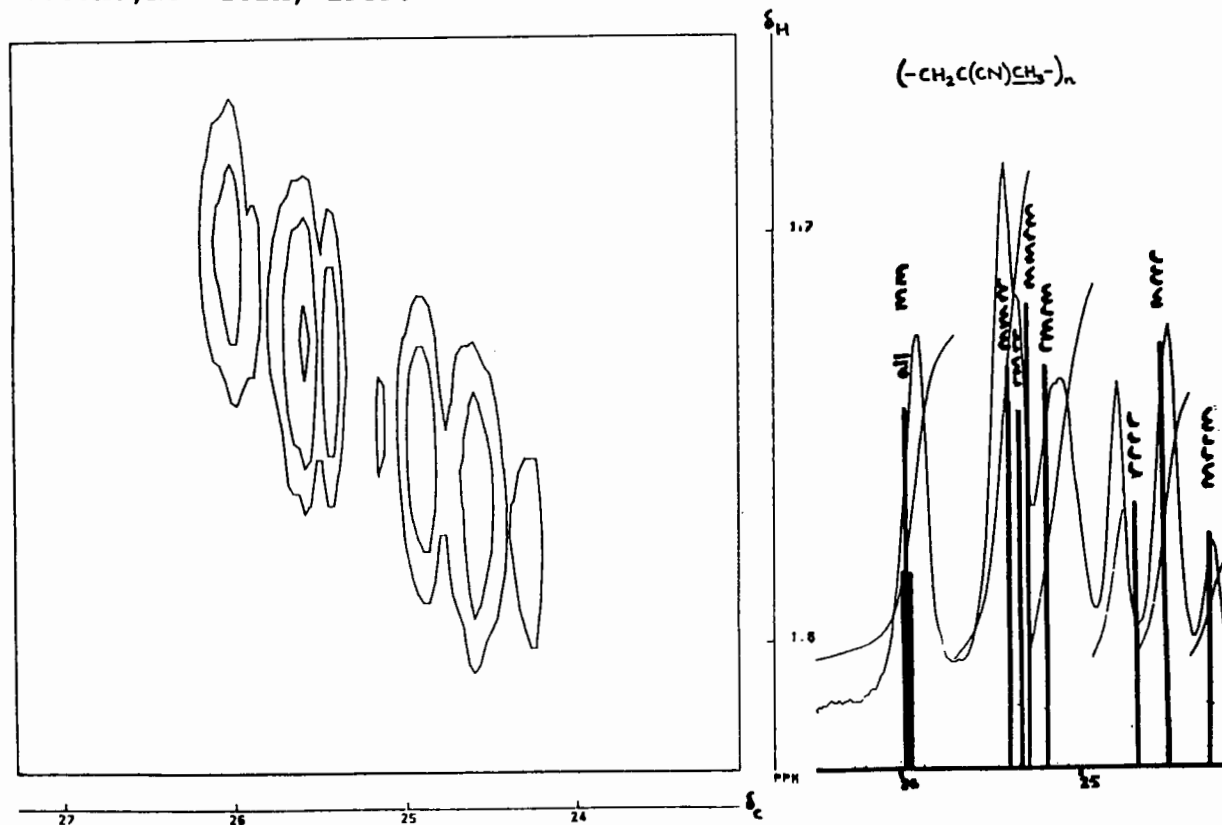
CALL FOR PAPERS

International Conference on NMR Microscopy

September 16 - 19, 1991

Heidelberg, Germany

Scope: The conference provides an interdisciplinary forum for the discussion of recent experimental and theoretical results in NMR microscopy.

Topics are   - instrumental and methodical developments
              - applications in   materials sciences
                                    biology
                                    agriculture and
                                    medicine
covering polymers and ceramics, plants, tissue samples and animals.

The program includes plenary lectures as well as oral and poster contributions selected from submitted papers. The papers will be judged solely on the basis of an abstract.

Organizing and program committee:

Jerome L. Ackerman, Boston
Bernhard Blümich, Mainz
Paul T. Callaghan, Palmerston
Alan N. Garroway, Washington D. C.
Lynn W. Jelinski, Murray Hill

Winfried Kuhn, St. Ingbert
Gheorge Mateescu, Cleveland
Jim Pope, Sydney
Vassili Sarafis, Sydney

Preregistration deadline: April 30, 1991

For further information please write to Dr. Winfried Kuhn, Fraunhofer Institute, Ensheimer Str. 48, D-6670 St. Ingbert, Germany, phone +49-6894-89738, FAX +49-6894-89750 or Dr. Bernhard Blümich, Max-Planck Institute for Polymer Research, Postfach 3148, D-6500 Mainz, Germany, phone +49-6131-379125, FAX +49-6131-379100

Name and Degree:.....................................
Affiliation:..
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mail to

    Dr. Winfried Kuhn
    Fraunhofer Institute
    Ensheimer Str. 48

    D-6670 St. Ingbert
    Germany

O   I intend to participate
O   I intend to submit a paper

    subject of interest:
O   materials sciences
O   biology
O   agriculture and plants
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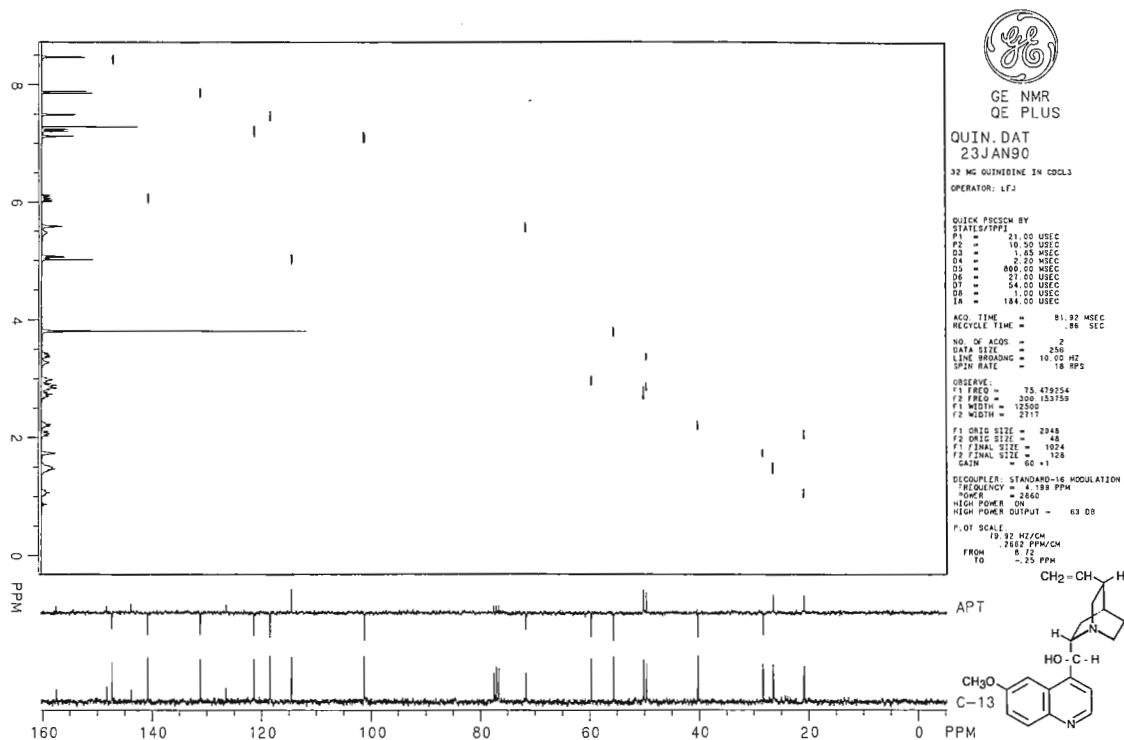
An automated run using MACRO mode operation on a sample of 32 mg of quinidine in 0.5 ml chloroform-d (0.20M). Data were obtained using the 5 mm broadband probe. ^{1}H, ^{13}C, APT and phase sensitive 2D data were collected, processed and plotted—including the 2D contour—in only 8.2 min.

ETH
EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE ZÜRICH

Laboratorium für anorganische Chemie
Prof. Dr. P.S. Pregosin

Universitätstrasse 6

Telefon Durchwahl-Nr. 01/256 29 15
            Telefonzentrale 01/256 22 11
            Fax   01/252 89 35
Postadresse
Laboratorium für anorganische Chemie
ETH-Zentrum
CH-8092 Zürich

August 22, 1990
(received 8/28/90)

2513

Prof. B.L. SHAPIRO
966 Elsinore Court
Palo Alto, California 94303
USA

Dear Barry,

Since optically active π–allyl complexes of Pd(II) are often precursors in organic synthesis, it is useful to recognize how the chiral ligand encroaches on the π–allyl. In our studies[1] of spartein, a ligand with four chiral centers, 2–D NOESY has been helpful in providing 3–D structural data in solution. The 2–D–^{1}H spectrum clearly reveals that the π–allyl proton on C–33 (δ ca. 4) interacts with an aliphatic ring proton of the type NCH$_2$CH$_2$, on C–3, δ ca. 1.2, thereby allowing a determination of the relative orientations of the two halves of each ligand. Please credit this contribution to the account of L.M. Venanzi.
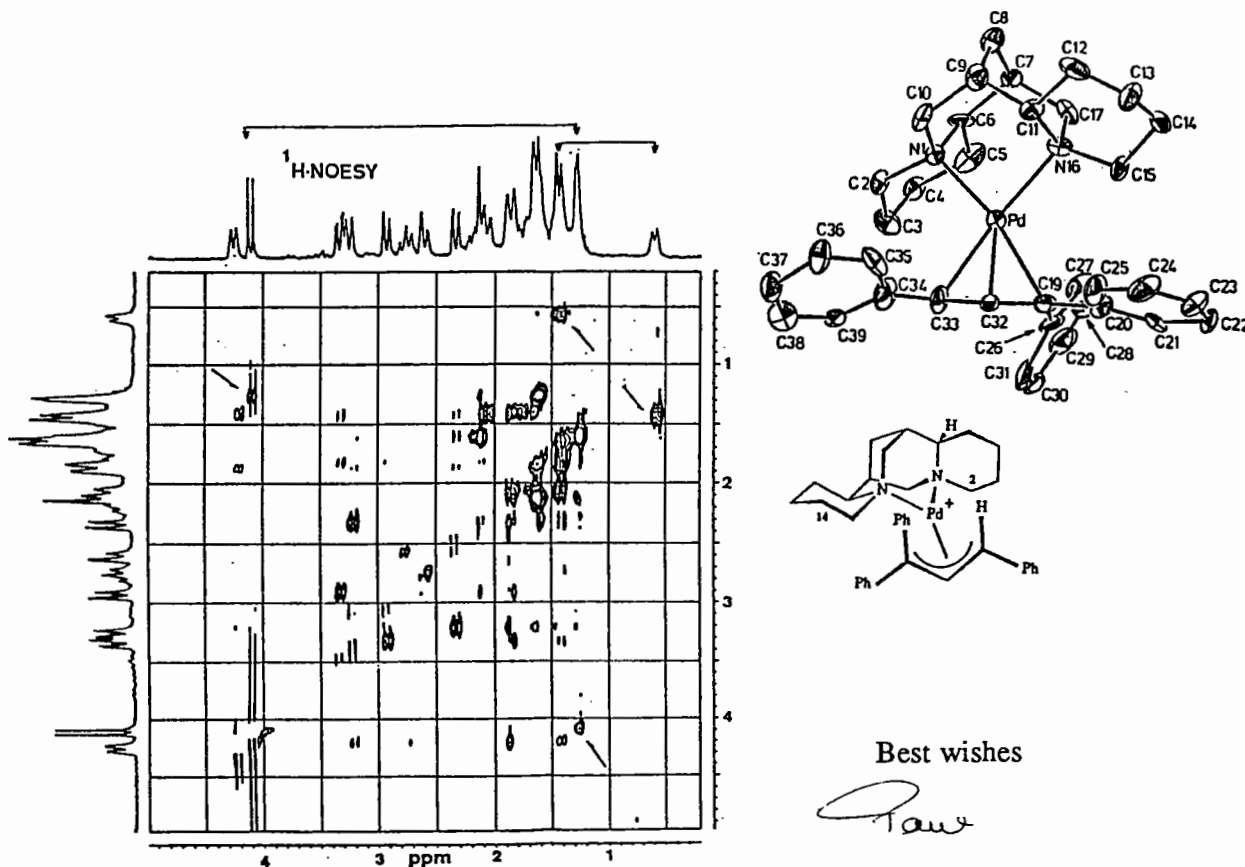
Best wishes

[1] A. Togni, G. Rihs, P.S. Pregosin and C. Ammann, *Helv. Chim. Acta*, **1990**, *73*, 723.

Suggested Title: 2–D ^{1}H–NOESY on Pd(II) π–allyl Complexes

LEIDEN UNIVERSITY

DEPARTMENT OF CHEMISTRY

GORLAEUS LABORATORIES

Dr. B.L. Shapiro
Editor TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

August 16 1990
(received 8/29/90)

Dear Dr. Shapiro:

How to cope with dielectric heating

We are exploring the use of a spin–lock experiment to study slowly fluctuating electric field gradients experienced by spin 3/2 nuclei in aqueous macromolecular electrolyte solutions (e.g. ^{23}Na in DNA or ion exchange resins [1,2]). The electrolyte samples show a considerable amount of heat dissipation during the spin–lock period. Without taking any preventions, the sample may be brought to boil or even explode when it is sealed in a glass ampoule. This heating is due to the parasitic capacitors formed by the proximity of the turns on a solenoid (distributed capacitance, [3]), combined with the high conductivity of the samples. This effect can be minimized by applying a Faraday shield mounted around the sample inside the coil [4]. This shield consists of a set of parallel wires parallel to the spin–lock field and at one side connected to ground. Furthermore, we built a high power probe in which the temperature can be controlled using a fluid (Fluorinert, 3M Co.) thermostat. For this purpose we used an old Bruker wide bore probe from which the interior was removed (a generous gift from the Unilever company). A schematic drawing of the probe is presented in Fig. (1). The probe is characterized by an inhomogeneity broadening of 12 Hz (for sodium). In a 0.1 molal NaCl solution no significant sample heating could be detected.

Cordially,

J.R.C. van der Maarel, J. Jansen, G. van Kampenhout, and C. Erkelens

[1] J.R.C. van der Maarel, J. Chem. Phys. 91 (1989) 1446.
[2] J.R.C. van der Maarel, R.H. Tromp, J.C. Leyte, J.G. Hollander, and C. Erkelens, Chem. Phys. Letters 169 (1990) 585.
[3] The ARRL handbook for the radio amateur, American Radio Relay League, (1990), Ed. 67
[4] H. Förster, private communication.

PS. Please credit this contribution to the account of J. Lugtenburg.

1	DEMPINGRESISTORS
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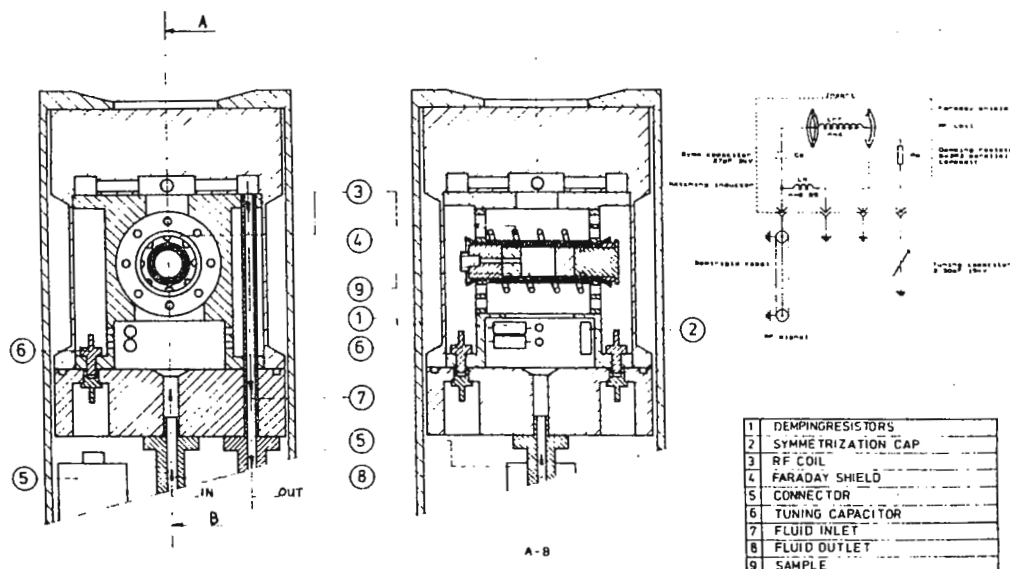
Fig. 1

mAcSPECT

Aspect 2000 Replacement for Bruker Spectrometers
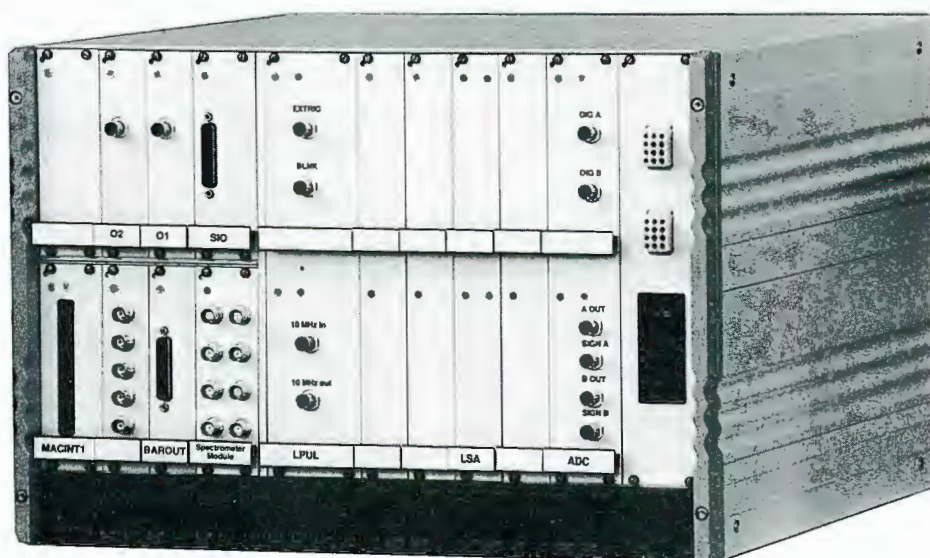
The mAcSPECT™ is a Real Time NMR Station. Coupled with a Macintosh™ II computer, the mAcSPECT has been specifically designed to replace the Aspect™ 2000A computer used on Bruker™ NMR spectrometers. Replacing an Aspect 2000A with a mAcSPECT can be accomplished in minutes with no special tools.

The Back Panel Emulator (BPE), an integral part of the mAcSPECT system, allows the Macintosh II computer to take control of all the peripherals normally attached to a Bruker spectrometer. Two DB25 connectors on the BPE unit replace the Slow Device Channel and the Level/Sense connectors located on the Aspect computer. Observe and decoupling frequencies and Fourier filters can be set directly from the "dashboard" of the Macintosh II computer. Temperature, receiver gains and decoupling modes can be set as well.
mAcSPECT also has sixteen BNC connectors to emulate the signals found on the Aspect computer, such as PULSE's, PF's and SPF's signals, and offset oscillators O1 and O2. These two offset oscillators are now locked on the 10 MHz Master Clock.

Based on the design used in the Tecmag LIBRA™ system, the mAcSPECT incorporates the following:
- one 100 ns resolution pulse programmer with 5 loop counters, 2048 steps and 70 control lines.
- one 128K x 32-bit of memory signal averager.
- two 2μs per complex point, 12-bit simultaneous sampling Analog-to-Digital Converters (standard).
- one Back Panel Emulator to control the peripherals already present on the Bruker spectrometers.

mAcSPECT has been designed for any type of experiments and can be expanded to accommodate such options as a 100 MHz pulse programmer, a pulse programmer extension, up to 4-channels of waveform generators, different types of ADC.

mAcSPECT uses MacNMR™, the same powerful software that has made the success of LIBRA. Regular upgrades insures the user of always having state-of-the-art software applications.

Specifications

PULSE PROGRAMMER

Minimum Pulse Width:	100 ns
Maximum Pulse Width:	430 s
Time Resolution:	100 ns
Loop Counters:	5
Memory Size:	2048 x 128 bits

SIGNAL AVERAGER

ADC Resolution:	12 bits
No. of Channels:	2
Min. Sampling Time:	2 μs /channel
Max. Bandwidth:	500 kHz (± 250 kHz)
Memory Size:	128 k-Word x 32 bits

Shell Development Company

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Westhollow Research Center
P.O. Box 1380
Houston, TX 77251-1380

<u>²H NMR Spectra of a Surfactant Liquid Crystal</u>

8/20/90
(received 9/12/90)

Dear Dr. Shapiro

We have been dabbling with the use of deuterium NMR in the study of surfactant phase behaviour. Since this is a new area for us we chose to initially look at a system for which there is considerable previous work, the alkyl polyoxyethylene surfactant $C_{12}H_{25}(OCH_2CH_2)_3OH$ (usually abbreviated to $C_{12}EO_3$) in D_2O [1].

$C_{12}EO_3/D_2O$ forms a lamellar mesophase (liquid crystal), over a broad region of composition and temperature, that is characterised by a deuterium powder pattern. For example, in the attached figure, (A) shows the ²H NMR spectrum of a sample 3:1 $C_{12}EO_3$ to D_2O, by weight, at 30°C. The unusual feature to note about this spectrum is the pair of small peaks (labelled *) apparently superimposed on the main quadrupolar powder pattern. For some time we entertained a number of (wild?) ideas about the origin of these peaks - was there another anisotropic phase present? or could there be a peculiar type of motion distorting the bandshape in this system? The answer turned out to be rather more mundane and only surfaced after another unexpected observation.

(B) shows the spectrum of the same sample after it has been heated to 42°C and allowed to cool in the magnet. A sharp quadrupolar doublet is formed due to alignment of the mesophase in the 4.7T magnetic field. This does not occur after days in the magnet at 30°C. At 42°C the ²H NMR spectrum contains a single sharp peak showing that the sample becomes an isotropic solution at this temperature. Numerous liquid crystals orient in a magnetic field but in this case it appears that the activation energy for alignment is such that it can only occur on cooling the sample from the isotropic phase. This phenomenon was not evident in earlier work [1], possibly due to the lower magnetic field that was used, but we subsequently found that it has been described for at least one other surfactant system [2]. Interestingly, the pair of small peaks remain after alignment. A careful look at (B) also shows that this pair of peaks is not centered at the same frequency as the center of the major doublet - the measured shift difference is 50 Hz (1.7 ppm). This gave us a clue to the identity of the peaks.

A small amount of aqueous base was added to the sample and the small peaks 'disappeared', as shown in (C). This behaviour suggests that the peaks are due to the hydroxyl groups of the surfactant. The appearance of the hydroxyl deuterons as a separate resonance from the D_2O, as in (A), requires that the rate of exchange of deuterons between the surfactant and water is slow relative to the difference in splitting between the two deuteron sites (about 1 kHz).

[1] K.Rendall and G.T.Tiddy, J.Chem.Soc. Faraday Trans. I, 80, 3339 (1984).
[2] A.Johansson and T.Drakenberg, Molecular Crystals and Liquid Crystals, 14, 23 (1971).

Yours sincerely,

Stephen Hammond

P.S. Please credit to the subscription account of Dr. Larry Sterna.

Deuterium NMR spectra, at 30°C, of the mesophase formed by C12EO3: D2O
(A) initially
(B) after heating to 42°C and cooling in the magnet
(C) after the addition of a few drops of aqueous base and mixing

A

B

C

3000   2000   1000   0   -1000   -2000   -3000
HERTZ

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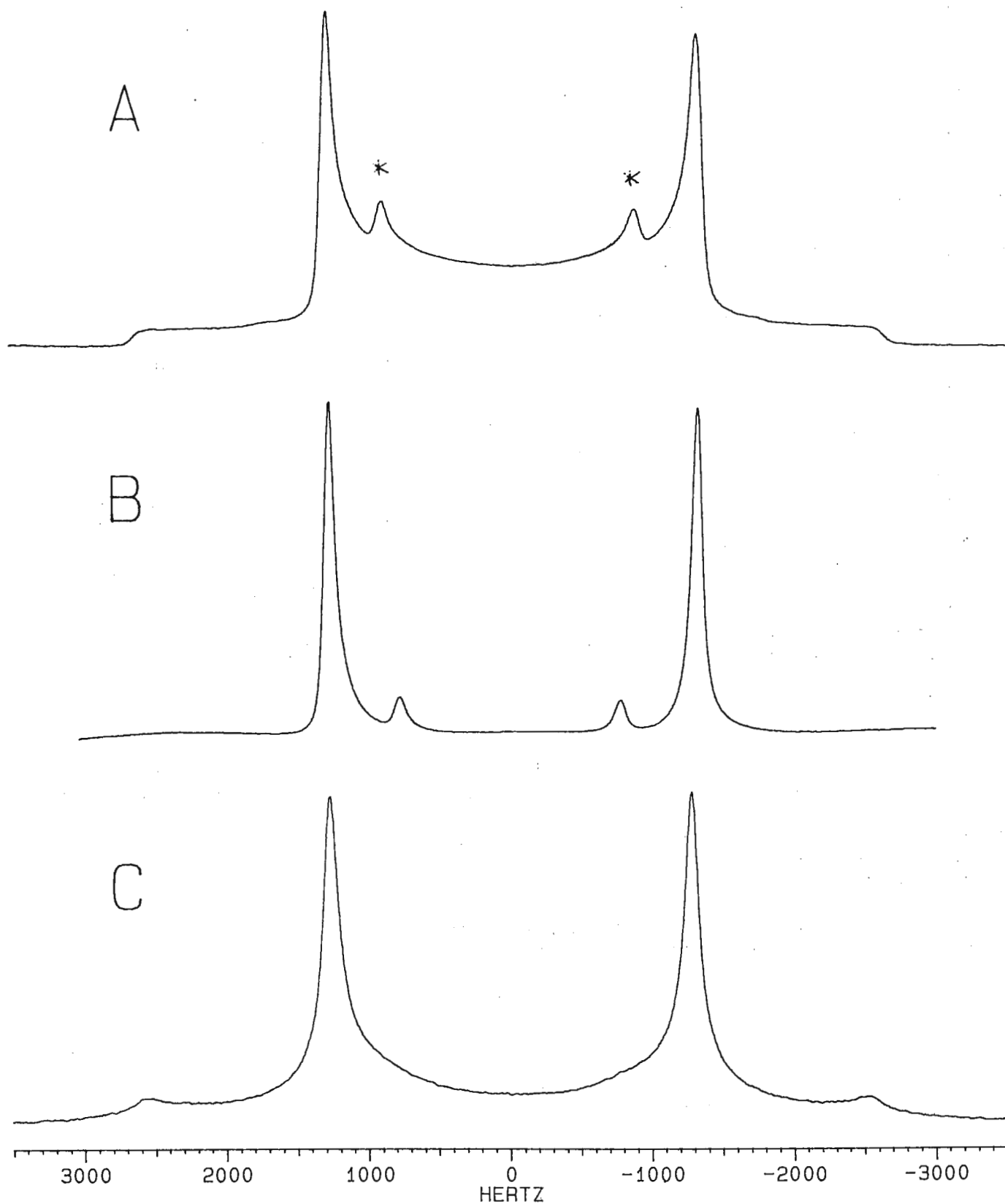
PTS 040

Range: 0.1-40 MHz	Output: +3 to +13dBm; 50ohm	Freq. St'd: OCXO, TCXO, Ext.
Resolution: 0.1Hz-100KHz (opt)	Spurious Outputs: −75dB	Interface: BCD par. or GPIB
Switching: 1-20µs	Phase Noise: −75dBc (0.5Hz-15KHz)	Price: $4,800.00*

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Range: 90-120 MHz	Output: +3 to +10dBm; 50ohm	Freq. St'd: OCXO, TCXO, Ext.
Resolution: 0.1Hz-100KHz (opt)	Spurious Outputs: −75dBc	Interface: BCD par. or GPIB
Switching: 1-20µs	Phase Noise: −75dBc (0.5Hz-15KHz)	Price $4,800.00*

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Switching: 1-20µs	Phase Noise: −63dBc (0.5Hz-15KHz)	Price: $5,850.00*

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Range: 1-250 MHz	Output: +3 to +13dBm; 50ohm	Freq. St'd: 0CXO, TCXO, Ext.
Resolution: 0.1Hz-100KHz (opt)	Spurious Outputs: −70dB	Interface: BCD par. or GPIB
Switching: 1-20µs	Phase Noise: −63dBc (0.5Hz-15KHz)	Price: $6,700.00*

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Phase Continuous: 1Hz-100KHz steps	Phase Noise: −68dBc (0.5Hz-15KHz)		−63dBc

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Interface: BCD par. or GPIB	
Price: Type 1 / Type 2	$5,800.00* / $5,300.00*

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Range: 1-500 MHz	Output: +3 to +13dBm; 50ohm	Freq. St'd: OCXO, TCXO, Ext.
Resolution: 0.1Hz-100KHz (opt)	Spurious Outputs: −70dB	Interface: BCD par. or GPIB
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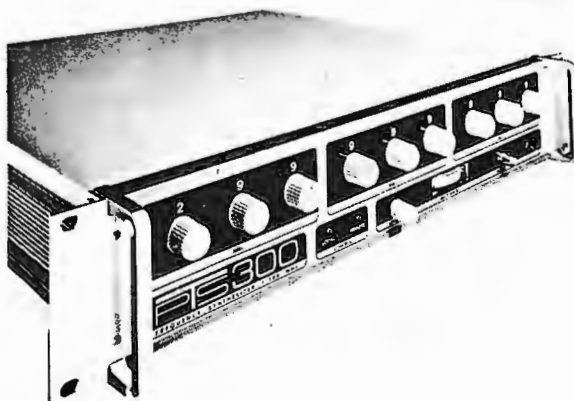
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385-38

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July 13, 1990
(received 9/8/90)

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California, 94303

Re: Measurements of spin-spin coupling constants from 2D spectra of macromolecules

Dear Dr. Shapiro,

The problems associated with extracting coupling constant information from 2D spectra of macromolecules are well known., e.g. direct measurement of $^3J_{NH\alpha}$ values from DQF-COSY spectra results in artificially large values due to cancellation effects [1,2]. We would like to share our experiences with extracting the NH-CHα coupling constants from a 26 amino acid peptide in 50% TFE/water solution. We have adapted the method described by Kim and Prestegard [3] to obtain accurate $^3J_{NH\alpha}$ values using a calculation programmed into a hand held calculator.

In the published work of reference 3, absorption extrema were measured from phase sensitive COSY spectra by taking the difference between the maximum and minimum intensity of the antiphase doublets, whereas dispersive extrema were measured from the difference in the initial and final baselines of the dispersion peak. The authors expressed the extrema values in mathematical terms by setting the first derivatives of equations describing absorption and dispersion lines to zero. From these equations an expression in J dependent on the extrema values was derived.

We applied the Newton-Raphson method to the above expression to obtain accurate $^3J_{NH\alpha}$ values. The algebra was programmed into a Hewlett-Packard 42S calculator. The program asks for the absorptive and dispersive extrema values and a first guess J value as input, and then iterates until it converges to a solution. We obtained absorption and dispersion peak to peak separations from TPPI-DQF-COSY data. We processed the data using FTNMR [4] two separate times (we have been told that only one transform is necessary using the FELIX [4] "sep" command); once as an absorption spectrum and then with a 90° phase shift. Data sets were zero filled to 4K x 2K. We found that it was important to make the dispersion extrema measurement carefully as described in reference 3. Selecting the initial and final baseline points too close to the dispersion peak resulted in extrema values which iterated to unrealistic J values. Table I shows our results compared to analytical solutions obtained by Kim and Prestegard for an α-helical segment of ACP [3].

Table 1
$^3J_{NH\alpha}$ Values for the second α-Helical segment of ACP
[from *JMR 84* 9-13, 1989]

Residue	$J_{published}$	$J_{N-Raphson}$
36	5	4.7
39	4	3.6
48	4	4.0
50	11	11.2

Table I shows that there is excellent agreement between the J values calculated from the two
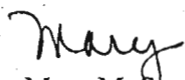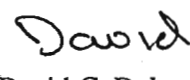
methods. The coupling constants in Hz obtained for the 26 residue peptide by direct measurement (J_{app}) from the antiphase doublets and from the Newton-Raphson method are listed in Table II.

Table II
$^3J_{NH\alpha}$ Values for a 26 Residue Peptide

Residue	$J_{N\text{-}Raphson}$	J_{app}	Residue	$J_{N\text{-}Raphson}$	J_{app}
1	3.4	5.7	14	5.7	7.9
3	6.0	6.6	15	4.7	7.0
4	6.0	9.0	16	6.2	8.8
5	5.7	8.2	17	3.8	10.4
6	5.9	7.4	18	6.6	8.0
7	5.5	9.3	19	3.0	6.2
8	5.9	9.3	20	6.6	8.9
9	4.7	7.0	21	5.4	7.3
10	6.0	7.1	22	3.3	7.0
11	3.9	6.8	23	4.1	7.2
12	5.5	8.8	24	4.4	7.2
13	4.1	8.1	25	8.3	9.3
			26	8.9	9.3

The coupling constants calculated from the iteration method indicate that most of this peptide exists as a helix under these solution conditions. These values agree with other data we have on this peptide suggesting it is in a helical conformation in solution.

Sincerely,

Mary M. Senior   David C. Dalgarno

The authors would like to thank YangMee Kim and Jim Prestegard for their advice in processing the TPPI data.
A listing of the HP-42S program is available upon request.
Please credit this contribution to Andy Evans' account.

(1) Bystrov, V.F. (1976) *Prog. NMR Spect. 10* , p.41.
(2) Pardi, A., Billeter, M., & Wuthrich, K. (1984) *J. Mol. Biol. 180* , p.741.
(3) Kim, Y. & Prestegard, J. (1989) *J. Mag. Res. 84* , p.9.
(4) Hare Research, Woodinville, WA.

Department of Molecular Physics

Dr. H. Van As

Landbouwuniversiteit **Wageningen**

Your reference :	"Ultimatum"
Your letter of :	
Our reference :	
Enclosure(s) :	(received 9/13/90)
Date :	6 September 1990

Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
USA

T_1-weighted-T_2 measurements for 2D or 3D Relaxation Time Data Sets

Dear Dr Shapiro,

By accurate (relaxation) decay curve measurements (FID, T_2, T_1 sequences) in combination with proper analysis strategies (multi-exponential decay curve fitting up to four exponentials), even low field NMR on water in plant tissue can provide us with high resolution information. Invariably, we observe multi-exponential T_1 and T_2 decay curves at 10 and 20 MHz. The different relaxation times can be assigned, more or less uniquely, to water in the different cell compartments: vacuole, cytoplasm and cell wall/extracellular space (1). In general, accurate T_1 measurements by Inversion Recovery or Saturation Recovery are time consuming: between each data point the recovery time should be about 4 à 5 times T_1, resulting in a TR of typically 10 s. However, by combining the SR sequence with the T_2-CPMG sequence, this recovery time can be used in a effective way, and a 2D or 3D Relaxation Time Data Set is obtained.
The SR-CPMG sequence consists of a

$$90_{x,y}°(\text{composite})\text{-spoil gradient pulse-}t_1\text{-}90_x°\text{-}(\text{TE-}180_y°\text{-TE-echo})_n.$$

The amplitude of each echo is sampled, and each echo train is measured as a function of the delay time t_1. TE can either be constant (2D) or variable (3D). Here we discuss the constant TE case.
The data can be analysed on different ways: e.g. the amplitude of the first point of the echo train (the FID after the second 90° rf pulse) as a function of t_1 results in the standard $T_1(\text{SR})$; the envelope of the echo train as a function of 2nTE results in the standard $T_2(\text{CPMG})$. More interestingly, in the case of multi-exponential behaviour, corresponding T_1 and T_2 values can be obtained, by first analysing the T_2 decay curves, resulting in $T_{2,i}$ and A_i, the amplitudes of each exponential, and then analysing the A_i's as a function of t_1, resulting in a corresponding observed T_1 value with each $T_{2,i}$ (see Figs. 1 and 2).
This latter approach is demonstrated on two phantoms: 1. two tubes containing different Mn^{2+}-solutions (no exchange between the tubes!); 2. a piece of apple fruit tissue, containing water in compartments, with proton exchange between the compartments. Typically 8192 echoes are acquired, and 80 variable t_1 increments were used (from 5 ms to 8 s). TE is 0.34 ms.
The results for $T_2(\text{CPMG})$, $T_1(\text{SR}, 100$ data points) and T_1,T_2-combination(SR-CPMG) on the separate tubes of phantom 1, and on the total phantom 1 are:

sample	$T_2(s)$ (CPMG)	fraction (SR)	$T_1(s)$ $T_2(s)$	fraction fraction	T_1-weighted-T_2(SR-CPMG) $T_1(s)$		
tube 1	0.82	1	1.79	1			
tube 2	0.21	1	0.49	1			
phantom 1	0.81	0.835	1.58	1	0.82	0.833	1.83
	0.22	0.165			0.22	0.167	0.49

These results clearly demonstrate the improved T_1 result for the multi-exponential behaviour of the phantom, due to *a priori* knowledge of the amplitudes of the fractions resulting from the more accurate T_2 measurements.

For phantom 2 we observe three T_2's (CPMG) and two T_1's(SR, 500 data points). The SR-CPMG sequence results again in three T_2's and in three T_1's, each of which corresponds with a particular T_2:

	$T_2(s)$ (CPMG)	fraction (SR)	$T_1(s)$	fraction $T_2(s)$	T_1-weighted-T_2(SR-CPMG) fraction	$T_1(s)$	
A1	1.02	0.752			1.01	0.746	1.37
A2	0.19	0.164			0.19	0.17	0.68
A3	0.03	0.084			0.03	0.084	0.35
a1			1.48	0.8			
a2			0.32	0.2			

The steps involved in obtaining the SR-CPMG results are depicted in Figs. 1 and 2. In Fig. 1 part of the the result of the analysis of the T_2 decay curves with CONTIN, resulting in a T_2 spectrum, are plotted vs. t_1. The amplitude of each T_2 as a function of t_1 is plotted in Fig. 2.
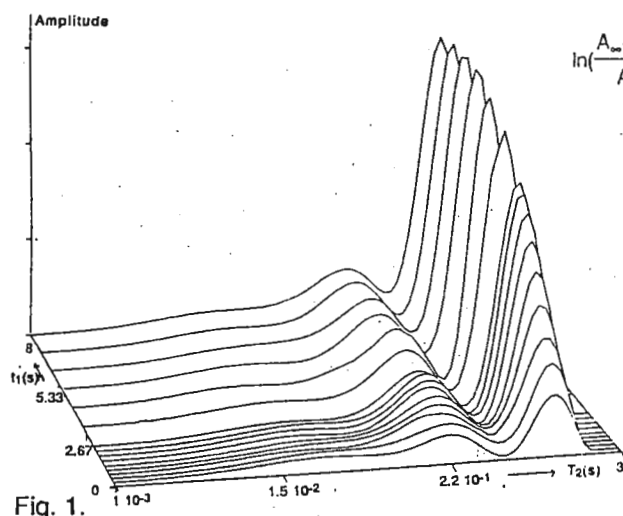
Fig. 1.
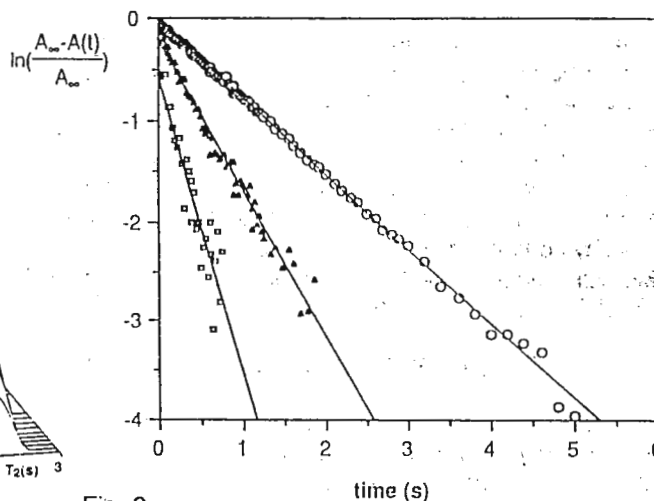
Fig. 2.

For NMR relaxation time measurements the effect of exchange is defined with respect to the relaxation times of the exchanging sites. For example, this exchange can be fast at the time scale of T_1, resulting in a single exponential for a two site situation, but slow or intermediate with respect to T_2, resulting in multi-exponential T_2 decay curves. This situation is met in phantom 2. The SR-CPMG results in T_1 values based on the T_2 analysis, and therefore these T_1 values contain exchange information with respect to T_1 **and** T_2. This results in this phantom 2 in different number of observed T_1's and different values with respect to the SR results.

Other analysis strategies can be applied to the 2D Relaxation Time Data Set, resulting in different exchange effects on the observed relaxation times, giving access to the exchange rates it self.

(1). H. Van As, J.E.M. Snaar, ^{1}H NMR relaxation times of water in plant cells: on the origin of fractions, book of abstracts XIV ICMRBS, Warwick, 1990; J.E.M. Snaar, H. Van As, Water permeability of plant cell membranes studied with in vivo ^{1}H NMR, book of abstracts 10th Int. Biophys. Conf., Vancouver, 1990.

Please credit this contribution to the account of Prof. T.J. Schaafsma.

Sincerely,

Angelien Snaar   Henk Van As

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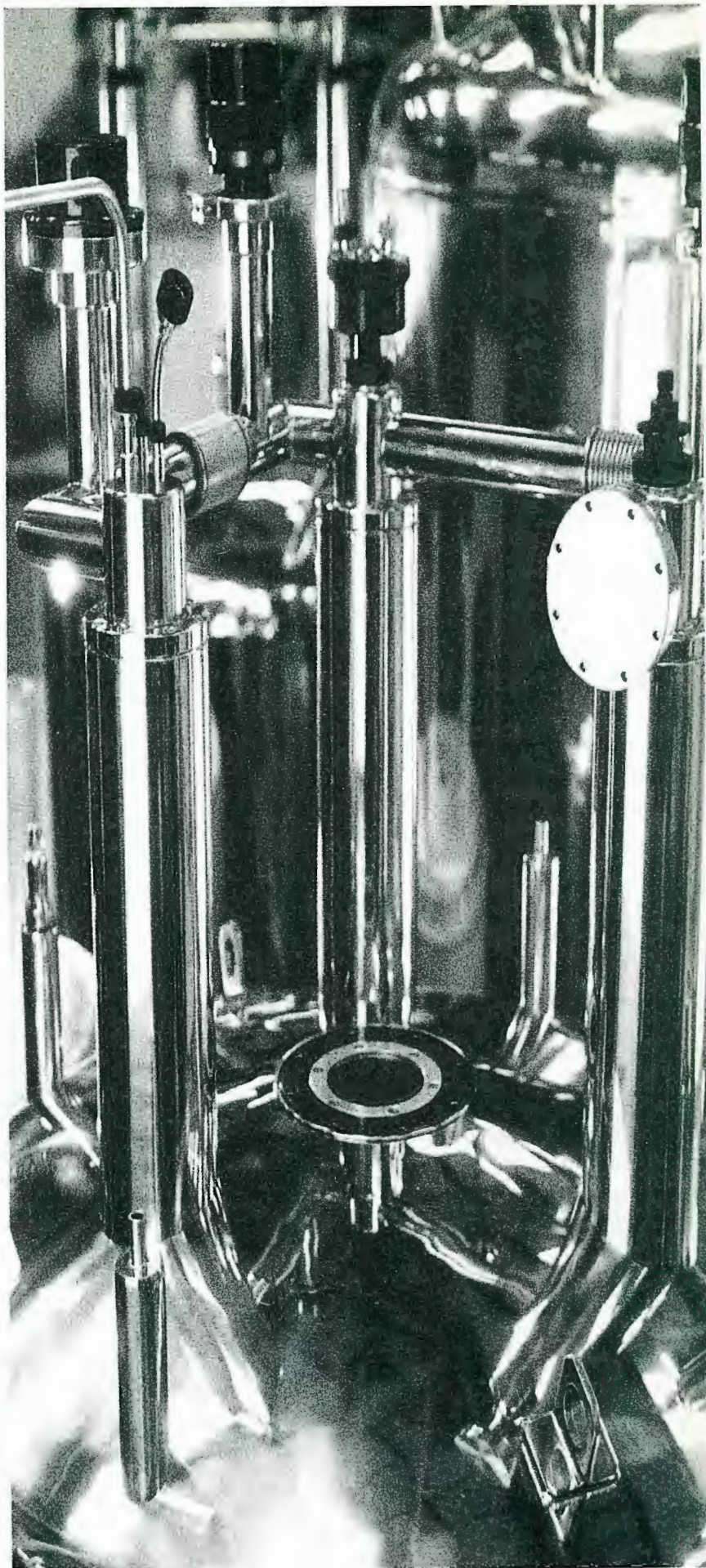
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Grenoble 8/17/90
ST-MARTIN-D'HÈRES, LE   (received 9/11/90)

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Objet

Professor B.L.Shapiro
TAMU Newsletter
966 Elsinore Court
Palo Alto,CA 94303
USA

ESR   simulations   on   NMR   spectrometers

Dear Professor Shapiro,

The LAOCOON type programs for simulating NMR experimental spectra are widely used in routine applications.The corresponding PANIC program for BRUKER users is particularly efficient with its 24-bits wordlength.
Lately,due to a "tape-crash" inside our H.P.computer(!),used for simulating ESR spectra obtained with our non computerized spectrometers (BRUKER ER 100D and VARIAN E102-still going strong !-),we tried to use PANIC.Surprisingly results were quite good (figures 1 & 2)and did not require too much time (less than 3 min calculation time for 3 sets of nuclei:figure 1).
The a_N or a_H values,in gauss,were entered as indirect coupling constants,in Hz,and the δ values corresponding to the different kinds of nuclei coupled to the impaired electron were entered at the same Hz values and assuming weak couplings (X-approximation in BRUKER language)
The snag is that PANIC does not allow first derivation corresponding to ESR experimental spectra! We circumvent this problem by copying the simulated spectra on to disk and then recalling them in the DISNMR program for final derivation.

Sincerely,

Duc Astin   Jean-Pierre Gaude   Aimé Lappe-Hutte

André Jeunet   Claude Morat

1 a

1b

2 a

2b

Figures 1 & 2:experimental(a) and simulated(b) spectrum.

1a: TEMPO in dmso

2a: mixture of 2 nitroxydes.

NMR IN BIOMEDICINE: THE PHYSICAL BASIS

Editor: Eiichi Fukushima

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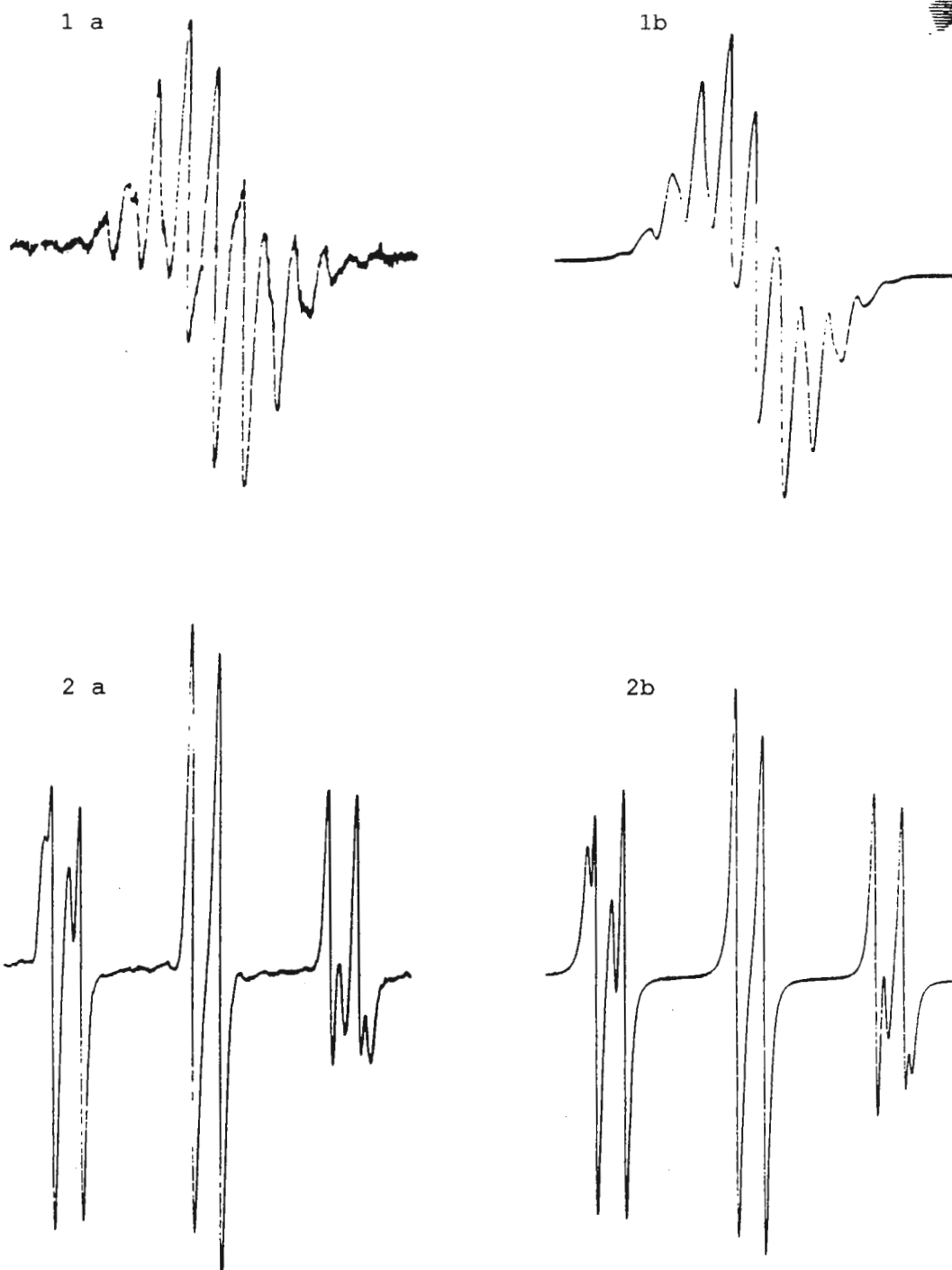
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September 11, 1990

Prof. Bernard L. Sharpiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

We have recently been awarded a grant for a project involving the development of the
theory and corresponding computer programs for describing nmr results for molecular
systems away from the extreme-narrowing limit. A postdoctoral position is available in our
labs beginning January 1. The work will require writing code for the IBM 6000 to simulate
an arbitrary pulsed nmr experiment on a multi-spin sample. Dipole-dipole, csa, and other
sources of relaxation and including cross-correlation effects will be included. It is intended
that programming generated will interface smoothly to FTNMR and other nmr analysis
programs. While these developments are general in nature the specific applications we
have in mind are protein and nucleic acid systems. Some initial results of this work have
been described [*Bull. Magn. Reson.* **11** 210 (1989)]. Persons interested should contact
either of us.

Sincerely,

J. T. Gerig
Professor of Chemistry
Telephone: 805/893-2113
E-mail: Gerig@VOODOO

W. E. Palke
Professor of Chemistry
Telephone: 805/893-3392
E-mail: Palke@VOODOO

September 5, 1990

Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elsimore Court
Palo Alto, CA 94303

**Relative Motions of Ions
Within Ion Pairs**

(received 9/10/90)

Dear Barry:

On the basis of NMR studies of different solvated silylithium compounds such as exo-1-trimethylsilylallyllithium and exo, exo-1,3-bis(trimethylsilyl)allyllithium we decided these species are contact ion-pairs in which coordinated lithium is unsymmetrically sited with respect to the allyl counterion. Further, rotation of the coordinated lithium relative to the anion is slow at 160 K compared to the NMR time scale. Then the ^{13}C NMR line-shape changes we observed with increasing temperature above 160 K were most reasonably ascribed to progressively faster rotation of coordinated Li^+ with respect to the anion. We say most reasonably because there are other interpretations.[1,2]

Lately, we found another system which exhibits similar rotational intra ion-pair dynamics to these described above and more clear cut. This system is a silylallyllithium with pendant potential lithium ligand attached to the silyl side chains, I, prepared by Horvath and Chan.[3] NMR shows this to be a monomeric contact ion-pair in which Li^+ is tridentately complexed to the pendant ligand. In toluene the system exists as an exo/endo mixture, 88/10. Of particular interest is the non-equivalence of all carbons on the pendant ligand. At low temperature, 160 K. Line-shape analysis of the ^{13}C signal averaging which takes place with increasing temperature, Δ with Δ, o with o, with and the two methoxy carbons, reveals that the exchange rates responsible for these line-shape changes are all the same with $\Delta H^{\neq} = 7.6$ kcal and $\Delta S^{\neq} = -15$ eu. These effects must be the result of rotation of the solvated lithium with its ligand around the allyl loop, see II.

The above dynamic results for I are similar to those encountered before hence strengthen the proposal that we are observing the dynamics of ion motion within ion-pairs. Surely such effects will be observed in other ion-paired salts if attention is paid to the NMR behavior of coordinated ligands.

Best wishes to you and TAMU.
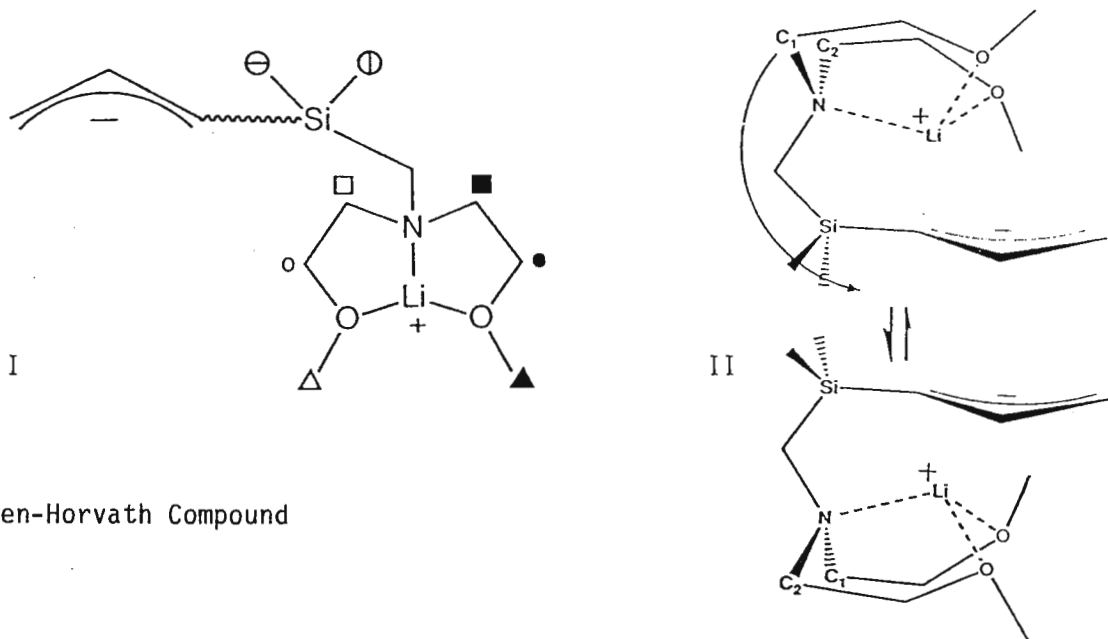
Jose Cabral
Research Associate

Yours sincerely,

Gideon Fraenkel
Professor of Chemistry

GF:jlp

[1] Fraenkel, G.; Chow, A.; Winchester, W.R.   J. Am. Chem. Soc. 1990, 112, 2582-2585.

[2] Fraenkel, G.; Chow, A.; Winchester, W.R.   J. Am. Chem. Soc. 1990, 112, 1382-1386.

[3] Horvath, R.F.; Chan, R.H.   J. Org. Chem.   1989, 54, 317-327.

Chen-Horvath Compound

Macromolecular NMR Spectroscopist

The **Lilly Research Laboratories**, a division of Eli Lilly and Company, has an opening for an Associate Scientist who will collaborate with established groups from several disciplines to study the structure of proteins and their interactions with other biologically active molecules.

Candidates for the position should have a Masters degree or a bachelors degree with equivalent experience. Specific training in modern multi-dimensional NMR techniques is required. A strong background in biological and computer sciences is desirable.

The Lilly NMR laboratory is exceptionally well equipped for macromolecular studies and includes a UNITY-500 spectrometer, a Silicon Graphics workstation, and the necessary software for advanced NMR processing and molecular calculations. These facilities are housed in a newly completed suite of laboratories which also include x-ray crystallography, vibrational spectroscopy and computational chemistry.

Qualified candidates should send a curriculum vitae to:

Dr. Allen D. Kline
Lilly Research Laboratories
Lilly Corporate Center
Indianapolis, Indiana 46285-0403

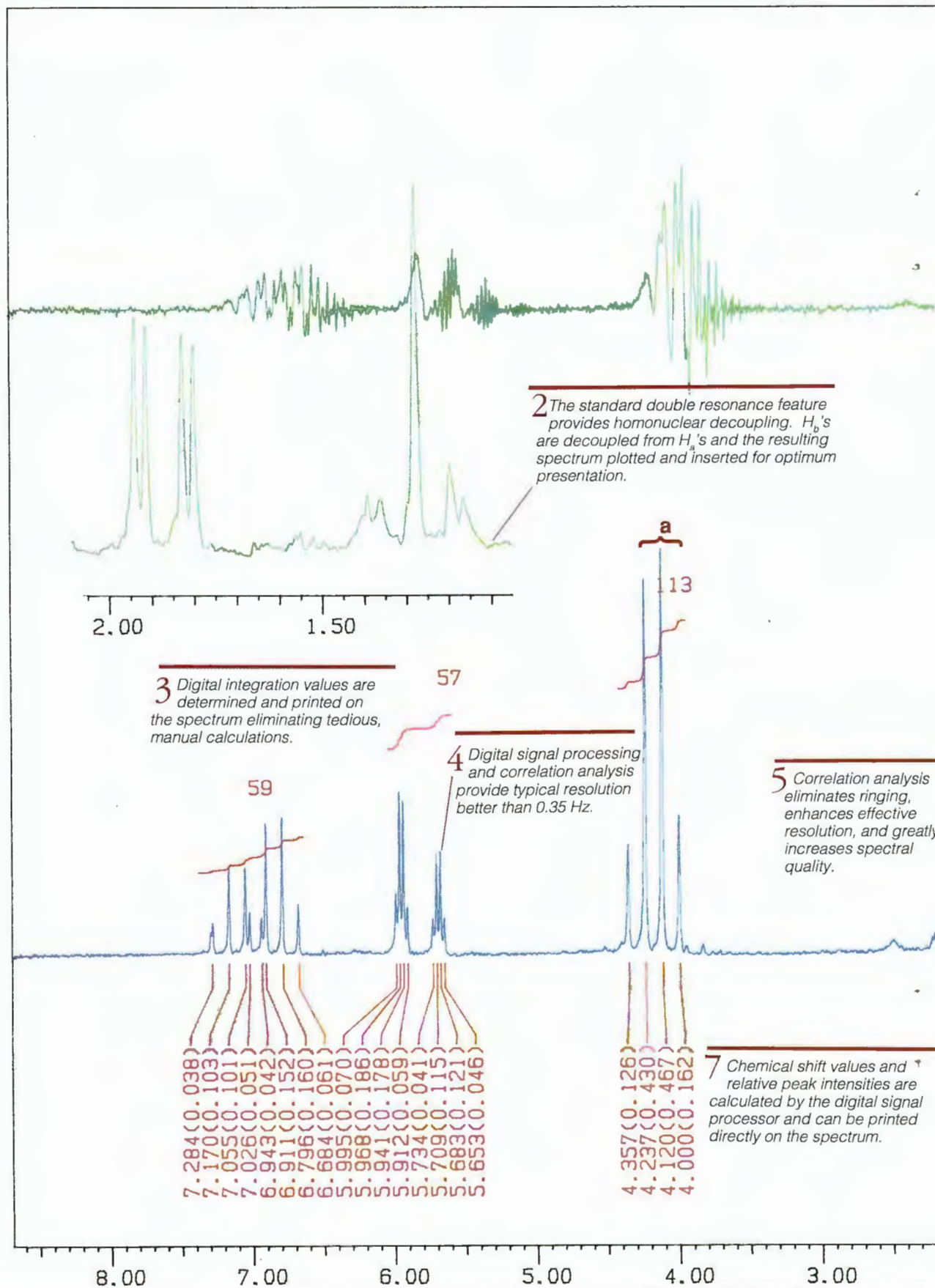# Model R-1200 Rapid Scan 60 MHz NMR Spectrometer

The Model R-1200 Rapid Scan, 60 MHz NMR Spectrometer scans 10-20 times faster than conventional cw instruments. Performance is enhanced significantly and features, available only with more expensive, higher field instruments are included as standard .

- **Scan times are ten to twenty times faster** than conventional cw instruments. Total microprocessor control provides superior performance and a new level of user convenience for 60 MHz NMR.

- **Digital signal processing ensures drift free operation** and eliminates the need for rescanning and tedious tuning of the instrument. Spectra are obtained faster and more conveniently.

- **Our unique Field Cure™ corrects field drift** and allows the accumulation of multiple spectra for improved signal-to-noise ratios faster than the time required for a single scan with a conventional instrument.

- **Correlation analysis eliminates ringing** and its interference with peak discrimination and chemical shift calculations. Effective resolution is significantly enhanced.

- **Chemical shift values are calculated by the microprocessor** and can be printed directly on the NMR spectrum, eliminating time consuming manual measurements.

- **Digital integration eliminates phasing** problems and the need to reintegrate if field drift occurs.

- **Post-run processing of stored spectra** allows the user to select any peak as a reference for correct chemical shift calculations.

- **Maximum resolution is set in less than one minute** by a single keystroke, eliminating the tedious and time consuming procedure required by conventional instruments.

- **A high quality, 4-pen printer/plotter** provides publishable spectra including, chemical shift values, operating parameters, and spectral data.
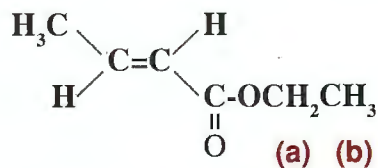
2 *The standard double resonance feature provides homonuclear decoupling. H_b's are decoupled from H_a's and the resulting spectrum plotted and inserted for optimum presentation.*

a

113

57

59

3 *Digital integration values are determined and printed on the spectrum eliminating tedious, manual calculations.*

4 *Digital signal processing and correlation analysis provide typical resolution better than 0.35 Hz.*

5 *Correlation analysis eliminates ringing, enhances effective resolution, and greatly increases spectral quality.*

7 *Chemical shift values and relative peak intensities are calculated by the digital signal processor and can be printed directly on the spectrum.*

2.00   1.50

7.284(0.038)
7.170(0.103)
7.055(0.101)
7.026(0.051)
6.943(0.042)
6.911(0.152)
6.796(0.160)
6.684(0.061)
6.995(0.070)
5.968(0.186)
5.941(0.178)
5.912(0.059)
5.734(0.041)
5.709(0.115)
5.683(0.121)
5.653(0.046)

4.357(0.126)
4.237(0.430)
4.120(0.467)
4.000(0.162)

8.00   7.00   6.00   5.00   4.00   3.00

SAMPLE & SOLUTION

(a) (b)

Ethyl Crotonate

1 *Uncorrelated spectrum scanned in 25 seconds shows the negative interference of ringing on peak discrimination and effective resolution.*

** ACQUISITION PARAMETER **

SPECTRUM WIDTH :	10.00	ppm
FILTER :	100.00	Hz
AMPLITUDE		
SPECTRUM :	8	
SWEEP RATE :	25	sec
NO. OF ACCUMU. :	25	
H1 LEVEL :	NOR	
H2 LEVEL :		
H3 LEVEL :		

** PROCESSING PARAMETER **

SCALE EXP. :	10.00	ppm
AMPLITUDE		
SPECTRUM :	8	
INTEGRAL :		
MEMO :		

6 *Field Cure™ on the TMS peak allows multiple accumulation of spectra (25 for this example) and improved signal-to-noise ratios while maintaining optimum resolution.*

8 *Acquisition and processing parameters are stored and can be printed automatically so that data and operating conditions are linked.*

OPERATOR :

DATE :

168   b   182

1.911(0.570)
1.827(0.550)
1.800(0.530)
1.392(0.497)
1.275(1.000)
1.155(0.440)
0.000(0.204)

2.00   1.00   0.00   -1.00 PPM
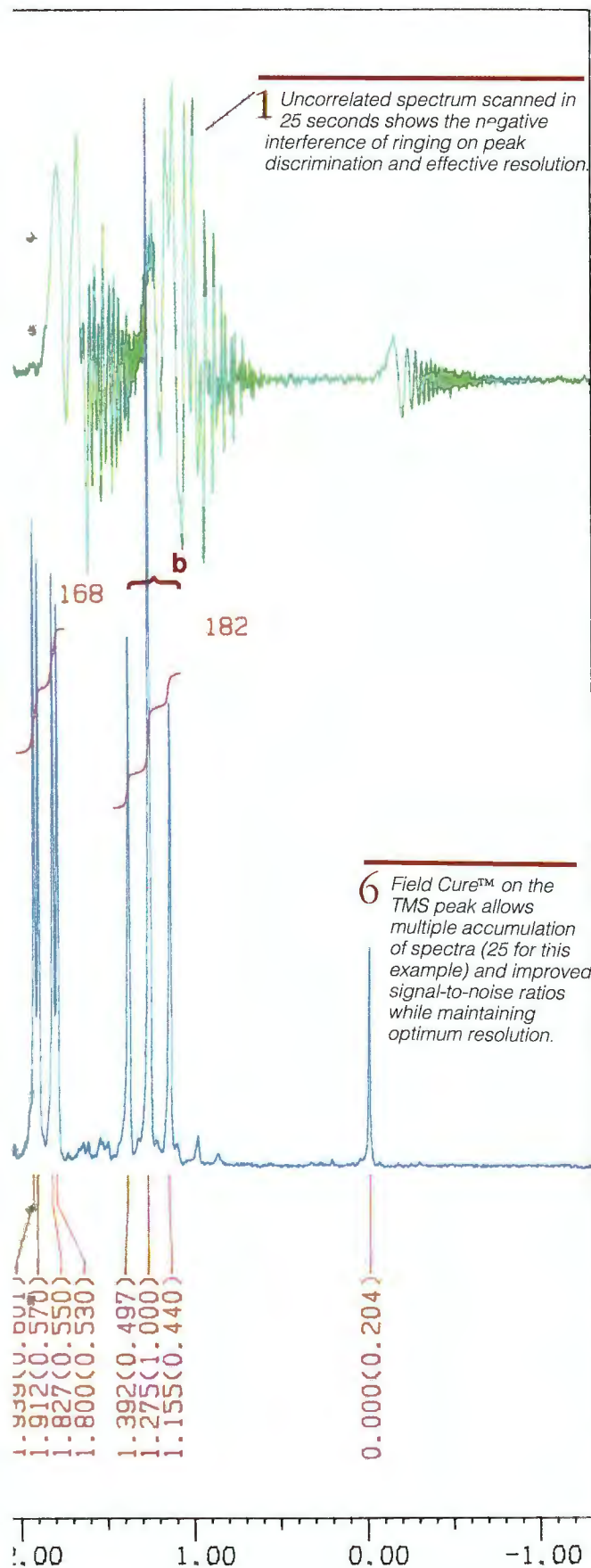
Technical Specifications

Nucleus	^{1}H or ^{19}F or ^{31}P
Resonance Frequency	60 MHz
Field Intensity	1.41 Tesla with Permanent Magnet
Resolution	0.4 Hz or less (full line width at half height of TMS signal).
Sensitivity	30:1 single scan of 1% ethyl benzene 180:1 sixty scans of methylene quartet
Integrator	Digital integration
Filter	100, 10, 5, 2.5, 1, 0.5, 0.25 Hz
Sweep Width	10, 20, 100 PPM 50, 100, 200, 300, 400, 500 Hz
Sweep System	Digital Scan
Sweep Time	1-1000 sec.
Field Lock	Proton internal lock
Double Resonance	Standard
Triple Resonance	Optional
Data Density	4096 points/scan
Interface	RS232C standard
Monitor	Oscilloscope
Recorder	4-pen, multicolor, printer/plotter for A3 chart size. Effective recording width is 270 x 400 mm

Installation Specifications

Room Temperature	16-30°C with <2°C/hr. fluctuation
Power Supply	115 V ± 10%, 60 Hz. 4-5 Amp.
Magnet Weight	250 kg (550 lbs.)
Dimensions	1450 mm(4'8") x 840 mm(2'8") x 800 mm(2'6") high

Order Information

435-2491 R-1200 Rapid Scan 60 MHz NMR Spectrometer

435-2546 Oscilloscope

AN0-0166 Sample tube 0.5 mm OD Pkg/100

AN0-0167 Sample tube caps-red Pkg/100

AN0-0168 Sample tube caps-white Pkg/100

435-2500 Triple Resonance Accessory

◉ **HITACHI**

Sandia National Laboratories

Albuquerque, New Mexico 87185

September 6, 1990
(received 9/10/90)

Dr. B. L. Shapiro, Editor
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Imaging of Solid Polymeric Foams

Dear Dr. Shapiro,

We have been attempting to characterize the shape of low density glassy polymeric foams by NMR imaging techniques. Since conventional imaging methods are not appropriate for these rigid materials, we have been evaluating alternate approaches. One technique is to immerse the foam in water and image the density of the water. This technique does not appear promising for very low density foams. For example, for a 0.05 g/cc foam one would need to accurately resolve the difference between 0.95 and 1.00 g/cc of water. We are presently exploring the potential of imaging foams by exposing them to a low vapor pressure gas with a high hydrogen content and then imaging the location of these hydrogens, which are relatively mobile. We expected that the gas concentration would be proportional to the foam density. Our initial results and subsequent calculations show that we are imaging gas molecules adsorbed on the foam surface and thus are imaging the surface area of the foam.

Figure 1 shows the geometrical arrangement of the experiment. A polyacrylonitrile foam sample with a density of 0.12 g/cc had a diameter of 4.4 cm and a length of 4.0 cm. A 1.5 cm depression was molded in the top of the sample in addition to an inverted conical cavity. The sample was placed in a glass jar and exposed to butane gas at ambient pressure. After approximately 20 minutes of exposure, the jar was sealed and placed in the horizontal bore of a spectrometer described previously [1]. Figure 2 shows the resulting image using a conventional 2-dimensional Fourier imaging pulse sequence [2]. The external shape of the foam has been reasonably reproduced by the imaging process. The somewhat larger circle of intensity intermediate to that of the foam sample and the background corresponds to the free butane gas in the glass jar.
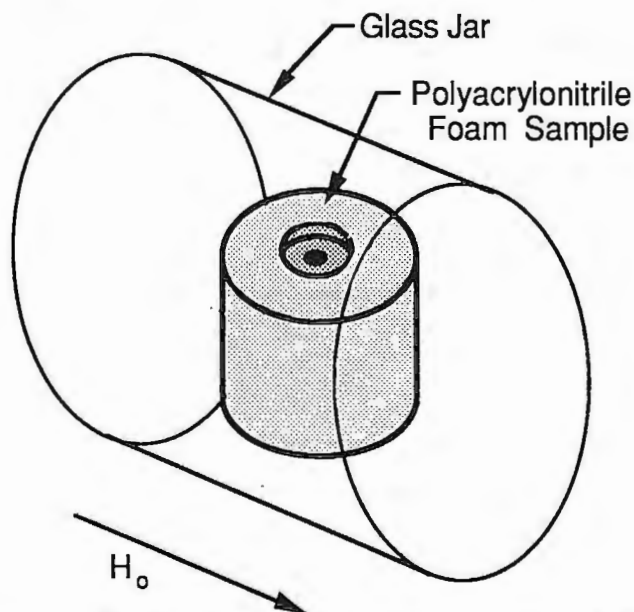

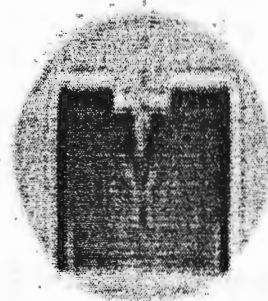Figure 1. The geometric arrangement of the sample cell.

Figure 2. 2-dimensional image
of the polyacrylonitrile foam sample

We have analyzed the butane signal intensity from a series of polyacrylonitrile foams with densities of 0.04, 0.08 and 0.16 g/cc. We found that the butane signal intensities for these three foams were proportional to the surface areas of the foams as determined by BET measurements. We were also able to show that each butane molecule is associated with approximately 30 $Å^2$ of surface area. The molar volume of liquid butane to the 2/3 power, a first-order approximation to the cross sectional area of a butane molecule, is also equal to 30 $Å^2$. We interpret these observations to mean that monolayer adsorption rather than absorption is the primary interaction between the butane and the foam sample. Thus, we are imaging the surface area contours of the sample. This method is being investigated as a tool for examining internal defects in foam material.

Sincerely,

Roger A. Assink
Sandia National Laboratories
Albuquerque, NM 87185

Arvind Caprihan
Lovelace Medical Foundation
Albuquerque, NM 87108

Please credit this contribution to the account of P. Cahill

REFERENCES
[1] R. A. Assink, A. Caprihan and E. Fukushima, AIChE Journal 34, 2077 (1988).
[2] P. G. Morris, Nuclear Magnetic Resonance Imaging in Medicine and Biology, Oxford, Clarendon (1986).

IN VIVO MAGNETIC RESONANCE SPECTROSCOPY

TUTORIAL AND PARTICIPATORY WORKSHOP

April 4 - 7, 1991 - just prior to ENC meeting at the Ritz-Carlton Hotel - St. Louis, Missouri

April 4:   *Tutorial for clinicians and scientists new to in vivo MRS.*

April 5 - 7: *Participatory Workshop which is open to all scientists working in the field. Presentations from all interested scientists are solicited.*

For Registration Information contact: University of California, San Francisco School of Medicine - Radiology, Postgraduate Education - San Francisco, CA 94143-0628

To make scientific presentations at the Workshop, contact: Dr. Joseph J.H. Ackerman - Washington University - Chemistry Department/Campus Box 1134 - St. Louis, MO 63130

Dr. Gerald B. Matson - Magnetic Resonance Unit (11M) - VA Medical Center 4150 Clement Street - San Francisco, CA 94121 OR Dr. Michael W. Weiner - Magnetic Resonance Unit (11M) - VA Medical Center - 4150 Clement Street - San Francisco, CA 94121

# Omega
Pulse Shaping Made Simple

Omega PSG (Pulse Sequence Generator) boards provide very flexible control of both amplitude and phase on each transmitter channel. Through a unique combination of instruction and waveform memory, waveform libraries can be easily created by the user. Normalized waveforms can be recalled and modified in amplitude or duration by a single instruction resulting in very efficient pulse programs.

Wave Shaping on the Omega 500 PSG
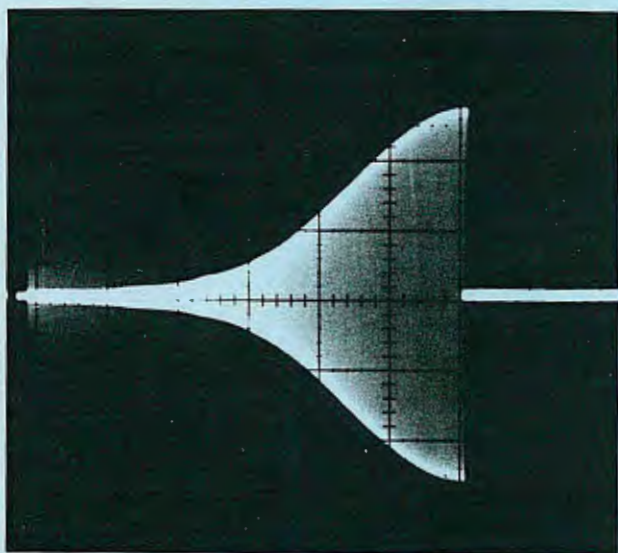
An oscilloscope trace of a half-Gaussian pulse. The pulse is defined by 250 points and the duration is 10 ms.
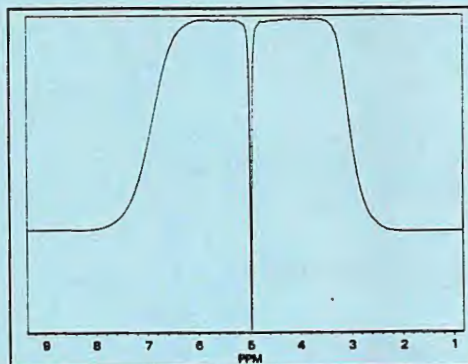
The result of applying a 180° half-Gaussian pulse to a sample of doped water. The water resonance has been broadened by introducing a large Z1 current in the room temperature shims. The half-Gaussian pulse width is 200 ms and the width of the "burned hole" is 12 Hz.

1D HOHAHA OF LACTOSE
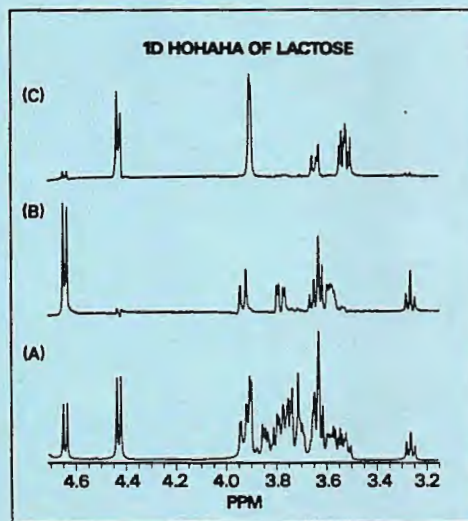
TOCSY of Lactose (10mM in D_2O).
Bottom spectrum (A) is a simple one pulse spectrum. Middle spectrum (B) is a 1D-TOCSY spectrum, where anomeric proton at 4.43 ppm has been selectively irradiated with a half-Gaussian pulse. Top spectrum (C) is a 1D-TOCSY spectrum when the anomeric proton at 4.65 ppm has been selectively irradiated with a half-Gaussian pulse.
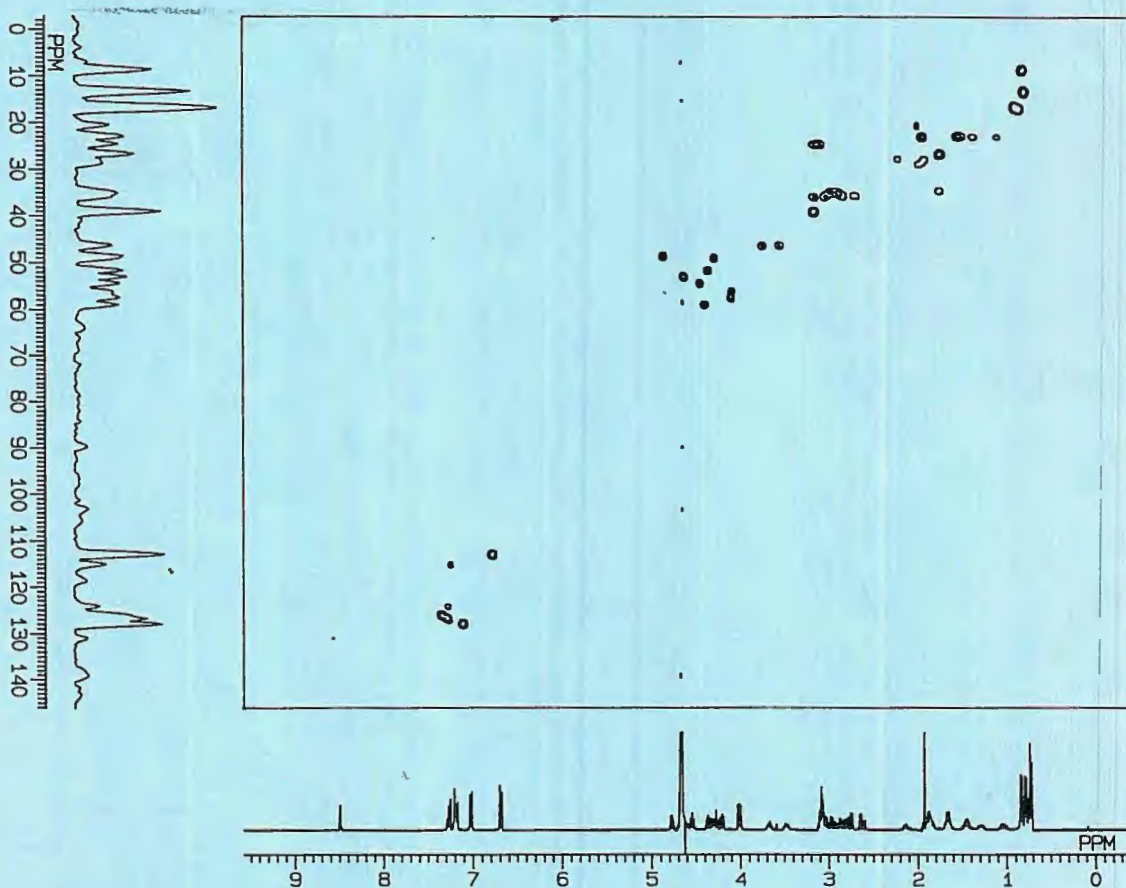
GE NMR Instruments

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