Free Energy of Rotation About Peptidylprolyl Bonds in Linear and Cyclic Peptides  Bean, J.W.  5
Variable Temperature Work Using a Bruker Minispec  Roberts, D.R.  6
Flat Baselines  Bax, A., Bura, M., Zhu, G., and Kay, L.  9
Mirror Images and Time Extension  yzK, I., uhZ, G., arulk. M., dura xAB, A.  11
Paramagnetic [sic?] Impurities in Solid-State Spectra  Schuld, A., and Merwln, L.  15
Proton Spectra of 1-Bromo-2-phenyl-cyclopropane Isomers  Bladon, P.  19
Fourth Missouri Magnetic Resonance Symposium.  Blum, F.D.  20
13C Shifts of Silylated Exomethylene Cyclobutanes  Ovaska, T.V., and Bailey, W.F.  23
Automation on a JEOL Spectrometer  Krishnaswami, A.  24
Polymer Conformations  Howarth, O.W.  27
International Conference on NMR Microscopy  Kuhn, W., and Bluemich, B.  28
2D 1H NOESY on Pd(II) x-Allyl Complexes  Pregosin, P.S.  31
How to Cope with Dielectric Heating  van der Maarel, J.R.C., Jansen, J., van Kampenhout, G., and Erkelens, C.  32
3H NMR Spectra of a Surfactant Liquid Crystal  Hammond, S.  35
Position Available  Duchamp, D.J.  38
Position Available  Jardetzky, O.  38
Coupling Constants from 2D Spectra of Macromolecules  Senior, M.M., and Dalgarro, D.C.  39
T1-Weighted T2 Measurements for 2D or 3D Relaxation Time Data Sets  Snaar, A., and Van As, H.  43
EPR Simulations on NMR Spectrometers  Astin, D., Gaude, J-P., Lappe-Hutte, A., Jennet, A., and Morat, C.  47
Position Available  Bramwell, M.R.  50
Position Available  Gerig, J.T., and Puloke, W.E.  50

Continued on page 2

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden. These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed open access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.
TABLE I  DEUTERATED SOLVENTS

Need Deuterated Solvents?
WILMAD HAS YOUR SOLUTION!

Cost-conscious quality NMR solvents offered by Wilmad, such as CDCl₃, are frequently priced lower than more traditional sources. Included in this offering are the most common solvents, like Acetone-d₆, Benzene-d₆, D₂O, and DMSO-d₆, as well as some of the most unusual solvents for specialty applications, like 1,1,2,2-
Tetrachloroethane-d₂, Octane-d₆, and Trifluoroacetic Acid-d₃.

<table>
<thead>
<tr>
<th>Cat. No.</th>
<th>Description</th>
<th>Formula</th>
<th>Min. p (atm)</th>
<th>Density g/ml</th>
<th>MP (°C)</th>
<th>BP (°C)</th>
<th>δ-D (ppm)</th>
<th>δ-H (ppm)</th>
<th>X₋₋₋ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-11</td>
<td>Acetone-d₆</td>
<td>C₅H₈O₂D₆</td>
<td>0.0, 0.4</td>
<td>0.996</td>
<td>53</td>
<td>103</td>
<td>1.00</td>
<td>4.11</td>
<td>0.551 (32)</td>
</tr>
<tr>
<td>D-12</td>
<td>Benzene-d₆</td>
<td>C₆H₆D₆</td>
<td>0.0</td>
<td>0.999</td>
<td>90</td>
<td>254</td>
<td>3.27</td>
<td>6.47</td>
<td>0.460 (20)</td>
</tr>
<tr>
<td>D-13</td>
<td>Tetrachloroethane-d₂</td>
<td>C₂Cl₄D₂</td>
<td>0.0</td>
<td>1.27</td>
<td>5.5</td>
<td>79.3</td>
<td>2.70</td>
<td>5.20</td>
<td>0.543 (30)</td>
</tr>
<tr>
<td>D-14</td>
<td>Octane-d₆</td>
<td>C₈H₁₈D₆</td>
<td>0.0</td>
<td>0.946</td>
<td>30</td>
<td>146</td>
<td>2.89</td>
<td>6.47</td>
<td>0.611 (20)</td>
</tr>
<tr>
<td>D-129</td>
<td>Trifluoroacetic Acid-d₃</td>
<td>CF₃COOD₃</td>
<td>0.0</td>
<td>1.19</td>
<td>17.5</td>
<td>135</td>
<td>4.52</td>
<td>8.67</td>
<td>1.740 (20)</td>
</tr>
</tbody>
</table>

VARIAN
BOX/500 SHEETS

Use Plotter Paper and Pens?
WILMAD HAS YOUR CHART!

We provide the largest variety of paper and pens for NMR recorders or plotters available anywhere. Included in these listing are the newest spectrometers from Varian, Bruker, (and IBM), General Electric and JEOI, as well as the latest models, such as the Hewlett Packard 7475A, 7550A, and Thinkjet 2225A, Zeta 8 or 8A, and Western Graphic 4730 plotters and printers.

Searching for the Unusual Requirement?
WILMAD HAS YOUR ANSWER!

The most comprehensive offering of "widgets, gadgets and specials" for NMR spectroscopy, including:

- Spatula for 5mm NMR Tubes
- Three types of Valve NMR Tubes
  (including the new J. Young Valve Tube)
- Solvent Jet NMR Tube Cleaners
- pH Electrode for 5mm NMR Tubes
- Taperlok ® NMR Tubes
- A multitude of Coaxial Inserts
- Alumina NMR Tube for Si-29 Studies
- Ultra-thin wall NMR Tubes
- Throwaway "THRIFT" and "ECONOMY" NMR Tubes

Serving the Spectroscopic Aftermarket

WILMAD GLASS COMPANY
Route 40 and Oak Road • Buena, NJ 08310 U.S.A.
609-697-3000 • TWX 510-897-8911
FAX 609-697-0536
Table of Contents, cont'd.

Relative Motions of Ions Within Ion Pairs ............................... 51
Cabral, J., and Fraenkel, G.

Position Available .......................................................... 52
Kline, A. D.

Imaging of Solid Polymeric Films ....................................... 57
Assink, R. A., and Caprihan, A.

In Vivo MR Spectroscopy Tutorial and Participatory Workshop 57
Ackerman, J. J. H., and Matson, G. B.

Mailing Label Adornment: Is Your Dot Red?
If the mailing label on your envelope of this issue is adorned with a large red dot or circle: this decoration means that you will not be mailed any more issues until a technical contribution has been received by me.

Page Length Request Instruction

Attention overseas subscribers: If you must use paper which is longer that 11", please take care that all material (including signatures, addresses - everything!) ends no more than 10" from the top of each of your pages. It is costly to make reductions, and henceforth I reserve the right to chop the excess length off any page, no matter what the result. Beware of the dreaded guillotine! Your cooperation in this matter will be greatly appreciated.

Thank you.

All Newsletter Correspondence
Should Be Addressed To:
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elmore 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.
DAS

FAST FLIPPING VARIABLE ANGLE:

DAS PROBES
Variable angle from 30° to 90°. DAS probes are capable of multinuclear, double-tuned, and variable temperature operation.
DAS is available with all high speed spinning options in wide bore probes. 44 mm diameter DAS probes allow 5 mm high speed spinning options only. Limited variable angle mechanisms can be provided in probes under 44 mm.
Most high speed Doty Scientific MAS probes can be built for DAS operation. For more complete information on DSI probes, please reference our MAS Catalog.

DAS CONTROLLER
The microcomputer controller, motor driver, and software designed to control the DSI DAS probe and servo motor will allow 60° angle change in under 15 ms. Up to 255 angles can be stored to be stepped through in the course of the experiment. The user may edit, store, and retrieve angle files with ultimate operation precision of ±0.2°. An IBM XT/AT compatible computer is required for initial set up and program modifications.
DAS Operation:

The menu-driven software is designed for clarity and ease of use. Angle change is initiated by a 50 μs TTL pulse from the spectrometer. Less than 15 ms later the spin axis has stepped to the next angle in the list. The minimum time between initiating pulses is 40 ms. All angles are referenced to Magic Angle, which can be set precisely by standard NMR techniques. This angle calibration normally is required only once at initial installation.

The software menu includes: Set Magic Angle, Add/Edit Angle Sequence, Run Angle Sequence, and Setup (defines probe type).

300 MHz, Multinuclear, 5 mm,  
High Speed DAS Probe $21,500.  
DAS Controller and Servo Motor 3,500.

(Probes price will vary with frequency. A required XT/AT computer is not provided.)

Doty Scientific, Inc.
600 Clemson Road  
Columbia, S.C. 29223  
USA

Office: (803) 788-6497  
Fax: (803) 736-5495

Sales: (803) 699-3806  
Service: (803) 699-3807
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 $\Delta G_{300}^{0} = 19.9 \pm 1.7$ kcal/mol-K for the hexapeptide acetyl-SQNYPV-amide, and $\Delta G_{300}^{0} = 18.7 \pm 1.7$ kcal/mol-K for the nonapeptide acetyl-RASONYPVV-amide. These values were of the order of magnitude that we had expected, and the $\Delta G$ 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 $\Delta G_{300}^{0} = 21.6 \pm 1.0$ 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

709 Swedeeland Road, PO Box 1539, King of Prussia, PA 19406. Telephone (215) 270 4800. Fax (215) 751 3400.
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°C 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°C 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°F) with no adverse affects on instrument performance. The maximum temperature variation throughout the sample cavity is less than 2°C 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°C and 60°C 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°C 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
The NMR evolution continues:

The new Bruker NMR microscope accessory provides the medical, biological and materials researcher with an exciting new NMR capability: very high resolution NMR imaging on small samples. An unprecedented variety of experiments are now possible using the NMR microscope.

- T1/T2 Imaging
- Multi-Echo
- Multi-Slice
- Volume Selective Spectroscopy
- Chemical Shift Imaging
- Diffusion Imaging
- Multi-Nuclear Imaging

The Bruker NMR microscope accessory comes as a comprehensive package, requires virtually no modification of the standard spectrometer, and includes software and image processor.

Designed to work on Bruker AMX and MSL systems, this versatile new accessory redefines the limits of spatial resolution.

The power of this technique is illustrated by the images shown above, which were obtained using an AM-400WB spectrometer with 9.4 Tesla operating field strength.

Fig. A: Cross sectional image of a philodendron stem. Resolution 19µ x 19µ x 300µ.
Fig. B: Nude mouse abdomen: kidney (lower left), tumor (lower right), liver (darkened area in upper right), and gut. Resolution 130µ x 100µ x 650µ.
Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution 20µ x 20µ x 250µ.
Fig. D: Image of an ovum from laevis (frog egg). Resolution 10µ x 10µ x 250µ.
Fig. E: Diffusion of water through a 4 mm dia. nylon screw. Echo time, (Te), 2.5 msec. Resolution 75µ x 75µ x 2 mm.

Explore the potential of this technology. Ask your nearest Bruker representative for more details on the new microscope or other NMR products.

Bruker Instruments, Inc.
Manning Park, Billerica, MA 01821
In Europe: Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten, 4, W. Germany
New Micro-Imaging Accessory for AM and MSL Systems.

The standard configuration includes:
1. High resolution image graphics display processor and high resolution B/W monitor
2. Gradient amplifiers (x, y, and z)
3. Gradient pre-emphasis unit and gradient wave form memories
4. Selective Excitation Unit consisting of:
   a. RF wave form memory
   b. RF pulse amplitude modulator
   c. Linear RF amplifier
5. Probehead with integral gradient assembly
6. Imaging software

Micro-Imaging Accessory

Image graphics display processor

Gradient pre-emphasis unit

Wave form memories

Selective Excitation Unit

RF amplitude modulation

Linear-RF amplifier

Fast I/O bus

Control line

Main console

Spectrometer

µ-imaging probehead

Variable temp. air

Main console

USA: BRUKER INSTRUMENTS, INC., Billerica, MA 01821, 508-667-9580
Regional Offices in Chicago, IL, Wilmington, DE, Houston, TX, San Jose, CA
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 F2 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 F1 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 t1 increment (t1(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 t1 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 F1 dimension. In their original paper, Otting et al. suggest that a first data point scaling factor equal to 0.5+(t1(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.

Kindest regards,

Ad Bax  Mitsuhiko Ikura  Zhun Zhu  Lewis Kay


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°.
August 22, 1990 (received 8/27/90)

Dear Barry:

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 complex) 4D matrix would require 64 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 negligible, we can "calculate" exactly what the signal would have looked like at negative time (\( \cos(-\omega t) \); \( \sin(-\omega t) \)). 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,

(1) L.E. Kay, G.M. Clore, A. Bax and A.M. Gronenborn Science 249, 411 (1990)

Fig.1. $(F_1, F_3)$ slice of a triple resonance 3D HCA(CO)N relay spectrum, correlating $\text{Ha}, \text{Co}$ shifts with the $1^{N}$ 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.
Instant Upgrade of RF Amplifier Performance in Your NMR/MRI System

Install an AMT Series 3000 solid-state pulse power amplifier—6–500 MHz at up to 1000 W—into your system. Instant upgrade!

Here’s just one example: AMT’s RF power envelope detection system guarantees full protection. That means you can operate at low-level CW with full-power peaks on demand.

Pre-saturation water suppression? Cross polarization in solids? No problem—now!

Additional Key Features:
- Broadband Frequency Ranges—6–220 MHz, 200–500 MHz
- Key Power for Liquids & Solids—50, 150, 300, 1000 Watts
- Excellent Linearity—(±1.0dB)
- Low Pulse Droop—typically less than 5%
- Fast Low Noise blanking—within 20dB of KTB in 2µS

For full information call your NMR/MRI system manufacturer or call Lowell Beezley at AMT: (714) 680-4936.

Models Available:

<table>
<thead>
<tr>
<th>Model</th>
<th>Frequency Range</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>3205</td>
<td>6–220 MHz</td>
<td>300W</td>
</tr>
<tr>
<td>3200</td>
<td>6–220 MHz</td>
<td>1000W</td>
</tr>
<tr>
<td>3137</td>
<td>200–500 MHz</td>
<td>50W</td>
</tr>
<tr>
<td>3135</td>
<td>200–500 MHz</td>
<td>150W</td>
</tr>
<tr>
<td>3134</td>
<td>200–500 MHz</td>
<td>300W</td>
</tr>
</tbody>
</table>

© 1989 American Microwave Technology Inc.
<table>
<thead>
<tr>
<th>Electrical Specifications:</th>
<th>Models: 3200</th>
<th>3205</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Range</td>
<td>6 - 220 MHz</td>
<td></td>
</tr>
<tr>
<td>Pulse Power (min.) into 50 ohms</td>
<td>1000W</td>
<td>300W</td>
</tr>
<tr>
<td>CW Power (max.) into 50 ohms</td>
<td>100W</td>
<td>30W</td>
</tr>
<tr>
<td>Linearity (+1dB to 200MHz)</td>
<td>0-600W</td>
<td>0-250W</td>
</tr>
<tr>
<td>(To 220MHz)</td>
<td>0-600W</td>
<td>0-200W</td>
</tr>
<tr>
<td>Gain (typ.)</td>
<td>+6dB</td>
<td>+3dB</td>
</tr>
<tr>
<td>Gain Flatness</td>
<td>±4dB</td>
<td></td>
</tr>
<tr>
<td>Input/Output Impedance</td>
<td>50 ohms</td>
<td></td>
</tr>
<tr>
<td>Input VSWR</td>
<td>&lt; 2:1</td>
<td></td>
</tr>
<tr>
<td>Pulse Width</td>
<td>20ns typ.</td>
<td></td>
</tr>
<tr>
<td>Duty Cycle</td>
<td>Up to 10%</td>
<td></td>
</tr>
<tr>
<td>Amplitude Rise/Fall Time</td>
<td>200ns typ.</td>
<td>150ns typ.</td>
</tr>
<tr>
<td>Amplitude Droop</td>
<td>5% to 10ns typ; 7% max</td>
<td></td>
</tr>
<tr>
<td>Phase Change/Power Output</td>
<td>10° to rated power typ.</td>
<td>8° to 10ns duration typ.</td>
</tr>
<tr>
<td>Phase Error Overpulse</td>
<td>4°</td>
<td>11° typ.</td>
</tr>
<tr>
<td>Noise Figure</td>
<td></td>
<td>8dB typ.</td>
</tr>
<tr>
<td>Output Noise (blanked)</td>
<td>&lt; 20dB over thermal</td>
<td>&lt; 5us on, 2us off, TTL signal</td>
</tr>
<tr>
<td>Blanking Delay</td>
<td>&lt; 2us</td>
<td></td>
</tr>
<tr>
<td>Protection</td>
<td>1. VSWR- will withstand infinite VSWR at rated power</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Input overdrive- up to +10dBm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Over duty cycle/pulse width</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. Over temperature</td>
<td></td>
</tr>
</tbody>
</table>

**Supplemental Characteristics:**

- **Connectors (on rear panel):**
  1. Input- BNC (F)
  2. Output- Type N (F)
  3. Blanking- BNC (F)
  4. Interface- 25pin D(F), EMI filtered

- **Indicators, Front Panel:**
  1. Peak power meter
  2. CW Mode
  3. Over temperature
  4. Overdrive
  5. Over pulse width

- **System Monitors:**
  1. Thermal
  2. DC power supply fault
  3. Over duty cycle
  4. Over pulse width

- **Front Panel Controls:**
  1. A.C. power
  2. Pulse width
  3. Duty cycle

- **Cooling:**
  Internal forced air

- **Operating Temperature:**
  +10 to 40°C

- **A.C. Line Voltage:**
  120/240 VAC, ±10%, 50-60Hz
  (3200, 220/240V only)

- **A.C. Power Requirements:**
  2000 watts
  700 watts

- **Package:**
  Rack Mount

- **Size (HWD, inches):**
  12.25x19x24
  5.25x19x24

---

1127 S. Placentia Ave. • Fullerton, CA 92631 • (714) 680-4936 • FAX 714-871-2453
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 been 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 and 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.

Sincerely,

Angelika Sebald
Larry Merwin
Figure 1: The absolute intensity mode $^{29}$Si MAS spectra of glasses having the composition 60% pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_9$) 40% grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_9$). A) Spectrum of sample containing paramagnetic impurities (NS = 2864); and B) spectrum of a newly prepared sample without Fe impurities (NS = 2132). For both spectra the following parameters were used: 2 $\mu$s, 36° pulse, recycle delay: 30 sec and 8 kHz MAS.
GOSSIP

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:

- Inexpensive mass data storage. Once the data is on the PC, large capacity, inexpensive and reliable magnetic and optical disks and tape backups are abundant. 330 MByte disks sell for as little as $2000. This makes long term data backups and personal spectral archives practical.

- Many alternate NMR data processing packages are available for the PC. When GOSSIP is combined with data translation software and one of these data processing packages, convenient and inexpensive desktop NMR processing becomes possible.

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

TMON

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

FILTRN - 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).

NMR Programs (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.

FILTRN - 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).

NMR Programs (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 8087 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.
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):-

\[ \delta_1 = 2.31, \delta_2 = 3.30, \delta_3a = 1.58, \delta_3b = 1.32 \text{ ppm.} \]
\[ J_{12} = 7.63, J_{13a} = 9.49, J_{13b} = 7.60, J_{23a} = 7.55, \]
\[ J_{23b} = 4.57, J_{3a3b} = -6.81 \text{ Hz.} \]

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

\[ \delta_1 = 2.39, \delta_2 = 3.20, \delta_3a = 1.45, \delta_3b = 1.50 \text{ ppm.} \]
\[ J_{12} = 3.37, J_{13a} = 10.06, J_{13b} = 6.40, J_{23a} = 4.47, \]
\[ J_{23b} = 7.42, J_{3a3b} = -6.79 \text{ Hz.} \]

The crucial difference between the isomers, which allows the distinction to be made is the presence of the relatively large vicinal coupling \( J_{13a} \) 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: ______________________________

______________________________________________________________________
UNITY LETS YOU SWITCH FROM ONE TO THE OTHER WITH EASE

Combine high performance capabilities with unparalleled flexibility using Varian’s new UNITY™ NMR spectrometer. This unique spectrometer is a true, multi-capability instrument that performs high resolution microimaging as easily as it analyzes liquid and solid samples.

UNITY’s revolutionary system architecture employs a modular design that addresses all NMR applications with a single instrument.

Analyze liquid samples using a variety of techniques over a wide range of nuclei. Perform CP/MAS, wideline and multipulse for solid samples. Examine microimaging samples with ease. Maximum flexibility has been built in to cover future experimental capabilities for every application.

Resolve problem diversity: invest in the most flexible technology of today to better address the research of tomorrow. Invest in a UNITY NMR spectrometer. For additional information, please call the Varian office closest to you.
The CD₃ groups of dimethyl sulfoxide-d₆ undergo 180° flips about the C₂ 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.
August 24, 1990
(received 8/27/90)

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

13C 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 13C chemical shifts (ppm from TMS in CDCl₃ solution) of the alkene and ring carbons of several of the products are given below.

<table>
<thead>
<tr>
<th>E</th>
<th>C(1)</th>
<th>C(2)</th>
<th>C(3)</th>
<th>C(4)</th>
<th>C(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>118.94</td>
<td>160.23</td>
<td>35.46</td>
<td>16.41</td>
<td>33.42</td>
</tr>
<tr>
<td>CO₂H</td>
<td>124.85</td>
<td>175.85</td>
<td>34.73</td>
<td>17.06</td>
<td>37.30</td>
</tr>
<tr>
<td>CHO</td>
<td>134.75</td>
<td>182.38</td>
<td>33.20</td>
<td>17.37</td>
<td>35.68</td>
</tr>
<tr>
<td>CH₂CH₂OH</td>
<td>125.99</td>
<td>155.46</td>
<td>34.44</td>
<td>16.39</td>
<td>32.23</td>
</tr>
<tr>
<td>CO₂Et</td>
<td>125.64</td>
<td>169.62</td>
<td>34.43</td>
<td>17.11</td>
<td>36.62</td>
</tr>
<tr>
<td>CH₂CHOHCH₃</td>
<td>127.19</td>
<td>155.60</td>
<td>33.23</td>
<td>16.33</td>
<td>32.60</td>
</tr>
</tbody>
</table>

Please credit this contribution to Tom Leipert's account.

Sincerely,

Timo V. Ovaska

William F. Bailey
Subject: Automation on a JEOL Spectrometer

Dear Dr. Shapiro:

After experimenting with EXE files on a Bruker, the knowledge gained was extremely helpful in streamlining 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 JCUP memory. The routine loops back to the beginning of the sequence for the next experiment. Additionally, the FID is displayed on the screen during accumulation which permits the user to terminate acquisition 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
When faced with a tough analytical problem . . .

**QUESTION**

How do you find all the thiophenol derivatives matching YOUR CARBON SPECTRUM?

**ANSWER**

Sadtler Structure Assignment Library

**STEP 1**

Search For Thiophenol Derivatives.

**STEP 2:**

Match Those Derivatives With Your Spectrum.

YOUR SEARCH IS OVER!

. . . look to SADTLER for the knowledge to end your search.

---

BIO-RAD

Sadtler Division

3316 Spring Garden Street,


Telephone: (215) 382-7800.

Telefax: (215) 662-6865.

TWX: 710 670-1186.
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.
Dear Barry

Polymer Conformations

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, 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(CH$_3$)CN-)$_n$. The clear anticorrelation of the $^1$H and $^{13}$C shifts arises because the methyl carbon shifts decrease when either flanking C(CH$_3$)CN carbon is $g$-gauche to it. This nearly always also entails closeness of the CN group, and hence an increase 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

O. W. Howarth

Dr O.W. Howarth

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. Garraway, 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: ................................................
Street: ........................................................
City: ...........................................................
Country: .....................................................

mail to

Dr. Winfried Kuhn
Fraunhofer Institute
Ensheimer Str. 48
D-6670 St. Ingbert
Germany

I intend to participate
I intend to submit a paper

subject of interest:
materials sciences
biology
agriculture and plants
medicine

please send
registration forms
abstract forms
second circular
Seven days a week, twenty-four hours a day. For over three years, a QE automated NMR analytical spectroscopy system ran experiments at Searle Labs in Chicago with only a few hours of downtime.

This sterling work record helped Searle gather high quality data from both fully automated macro and manual routine experiments. Today, two QE automated systems:
► Accommodate the experiments of over 30 chemists
► Operate 24 hours a day, seven days a week
► Perform both manual and fully automatic macro experiments during the day
► Perform fully automatic macro programs at night and on weekends
► Adapt to a demanding user schedule of 15 and 30 minute time slots

**Work smarter with the new QE Plus**

With more speed and efficiency, the new QE Plus does the job even better—to meet your needs for automated performance day after day, year after year.

For more information on the new QE Plus, write 255 Fourier Ave., Fremont, CA 94539 for a full color QE Plus brochure. Or call 800-543-5934.

And get to work.
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.
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 NH(CH\(_2\))\(_2\) 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.

---


Suggested Title: 2-D \(^{-1}\)H–NOESY on Pd(II) π-allyl Complexes
Dear Dr. Shapiro:

We are exploring the use of a spin-lock experiment to study slowly fluctuating electric field gradients experienced by spin \( \frac{3}{2} \) nuclei in aqueous macromolecular electrolyte solutions (e.g. \(^{23}\text{Na}\) 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 precautions, 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


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

Aspect 2000 Replacement for Bruker Spectrometers

distributed in the USA by: MR RESOURCES
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

<table>
<thead>
<tr>
<th>PULSE PROGRAMMER</th>
<th>SIGNAL AVERAGER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Pulse Width: 100 ns</td>
<td>ADC Resolution: 12 bits</td>
</tr>
<tr>
<td>Maximum Pulse Width: 430 s</td>
<td>No. of Channels: 2</td>
</tr>
<tr>
<td>Time Resolution: 100 ns</td>
<td>Min. Sampling Time: 2 µs / channel</td>
</tr>
<tr>
<td>Loop Counters: 5</td>
<td>Max. Bandwidth: 500 kHz (± 250 kHz)</td>
</tr>
<tr>
<td>Memory Size: 2048 x 128 bits</td>
<td>Memory Size: 128 k-Word x 32 bits</td>
</tr>
</tbody>
</table>

*Pulse and Aspect are trademarks of Bruker Analytik GmbH.
*Macintosh is a trademark of Apple Computer, Inc.
*MacNMR, LIBRA and mAcSPECT are trademarks of Tecmag, Inc.
© Copyright 1990 Tecmag, Inc. All rights reserved (295).
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 C₁₂H₂₅(CH₂CH₂O)₃0H (usually abbreviated to C₁₂E₀₃) in D₂O [1].

C₁₂E₀₃/D₂O 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 C₁₂E₀₃ to D₂O, 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 bandsape 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 D₂O, 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).


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 C12E03: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
# HIGH-PERFORMANCE DIRECT SYNTHESIZERS

Accurate, stable, quiet frequencies on command, fast. For NMR, imaging, SATCOM, surveillance, ATE. Sources adapting to your needs with options. High demonstrated reliability. Thousands in use.

## PS 040

- **Range:** 0.1-40 MHz
- **Output:** 3 to +13dBm; 50ohm
- **Spurious Outputs:** -75dB
- **Phase Noise:** -75dBc (0.5Hz-15KHz)
- **Switching:** 1-20µs
- **Frequency Synthesizers**

## PS 120

- **Range:** 0.1-120 MHz
- **Output:** 3 to +10dBm; 50ohm
- **Spurious Outputs:** -75dBc
- **Phase Noise:** -75dBc (0.5Hz-15KHz)
- **Switching:** 1-20µs

## PS 160

- **Range:** 0.1-160 MHz
- **Output:** 3 to +13dBm; 50ohm
- **Spurious Outputs:** -63dBc
- **Phase Noise:** -63dBc (0.5Hz-15KHz)
- **Switching:** 1-20µs

## PS 250

- **Range:** 0.1-250 MHz
- **Output:** 3 to +13dBm; 50ohm
- **Spurious Outputs:** -70dBc
- **Phase Noise:** -70dBc (0.5Hz-15KHz)
- **Switching:** 1-20µs

## PS 300

- **Range:** 0.1-300 MHz
- **Output:** 3 to +13dBm; 50ohm
- **Spurious Outputs:** -63dBc
- **Phase Noise:** -63dBc (0.5Hz-15KHz)
- **Switching:** 1-20µs

## PS 500

- **Range:** 0.1-500 MHz
- **Output:** 3 to +13dBm; 50ohm
- **Spurious Outputs:** -70dBc
- **Phase Noise:** -70dBc (0.5Hz-15KHz)
- **Switching:** 1-20µs

## PS x10 NEW

- **Range:** 10 MHz band, selected decade 0.1-100 MHz
- **Output:** 3 to +13dBm; 50ohm
- **Spurious Outputs:** -85 to -90dBc
- **Phase Noise:** -70dBc (0.5Hz-15KHz)
- **Switching:** 1-5µs
- **Phase Continuous:** 2 MHz band, even or odd steps

**OTHER OPTIONS:** Programmable Attenuator 0-90dB (or 0-99dB with GPIB) n x 10 MHz output (20-140 MHz) or any 10 MHz line

*Prices are US only, and include manual & remote (BCD) control, 1 Hz resolution, OCXO std.

---

**NEW! MORE CLEAN MHZ PER DOLLAR COMING. . . . . . . PTS 620**
Macromolecular NMR Spectroscopist

The Physical and Analytical Research Unit of Upjohn Laboratories has an opening for an NMR spectroscopist. Applicants should have a Ph.D. in chemistry, biochemistry or related field preferably with post-doctoral experience, and the ability to apply modern NMR techniques (2-D and 3-D) for the structure elucidation of macromolecules. Experience in molecular computational methods is desirable. The scientist will characterize both the structure of proteins that are targets for therapeutic intervention and the complexes of these proteins with substrate analogs and inhibitors. He will also assist in the development of heteronuclear multidimensional spectroscopy.

Successful candidates will join an NMR team that is equipped with an AMX-600, AM-500 and two SGI workstations. He will collaborate closely with biological, synthetic, and computational chemists in a range of projects. Qualified candidates should send a curriculum vitae to:

Dr. David J. Duchamp, The Upjohn Company, 301 Hentietta St., Kalamazoo, Michigan 49001

STANFORD MAGNETIC RESONANCE LABORATORY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305-5055

October, 1990 - Position Open - RESEARCH AFFILATE

A postdoctoral research position is currently open at Stanford Magnetic Resonance Laboratory for a computational Biophysicist. The work involves primarily the implementation and testing of computer programs developed within SMRL for protein structure determination by NMR. The applicant will be working on testing, refining and extending algorithms designed with other SMRL researchers and will perform computational tasks and analysis of results. The applicant should be experienced in computational chemistry and familiar with nuclear magnetic resonance theory and the theoretical evaluation of molecular structures.

Apply to: Dr. Oleg Jardetzky, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94305-5055, USA.
(415) 723-6270

Stanford is an EO/AA employer.
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 \(^1\). We would like to share our experiences with extracting the NH-CH$_{\alpha}$ 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 FfNMR \(^4\) 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 $\alpha$-helical segment of ACP \(^3\).

<table>
<thead>
<tr>
<th>Residue</th>
<th>$J_{published}$</th>
<th>$J_{N-Raphson}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>5</td>
<td>4.7</td>
</tr>
<tr>
<td>39</td>
<td>4</td>
<td>3.6</td>
</tr>
<tr>
<td>48</td>
<td>4</td>
<td>4.0</td>
</tr>
<tr>
<td>50</td>
<td>11</td>
<td>11.2</td>
</tr>
</tbody>
</table>

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

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.

(4) Hare Research, Woodinville, WA.
FALL

NMR SOLVENT OFFER

(Valid until December 15, 1990)

Take 10% off catalog prices for all solvent orders over $200.*

Take 15% off catalog prices for all solvent orders over $400.*

*Deuterium Oxide and multiple package units, i.e. 3x(10x1g); 3x(10x10g) not included.

For optimal savings, ask about our blanket solvent quotations based on annual solvent usage.

CIL
CAMBRIDGE ISOTOPE LABORATORIES
20 Commerce Way, Woburn, Massachusetts 01801
800-322-1174 (Toll-free) 617-938-0067 (in Mass) 617-932-9721 (Fax)
Dear Dr Shapiro,

By accurate (relaxation) decay curve measurements (FID, T2, T1 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 T1 and T2 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 T1 measurements by Inversion Recovery or Saturation Recovery are time consuming: between each data point the recovery time should be about 4 to 5 times T1, resulting in a TR of typically 10 s. However, by combining the SR sequence with the T2-CPMG sequence, this recovery time can be used in an effective way, and a 2D or 3D Relaxation Time Data Set is obtained.

The SR-CPMG sequence consists of a

\[ 90^\circ x,y^-(\text{composite})-\text{spoil gradient pulse}-t_1-90^\circ y^-(\text{TE}-180^\circ y^--\text{echo})_n \]

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 T1(SR); the envelope of the echo train as a function of 2nTE results in the standard T2(CPMG). More interestingly, in the case of multi-exponential behaviour, corresponding T1 and T2 values can be obtained, by first analysing the T2 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 T1 value with each \( T_{2,i} \) (see Figs. 1 and 2).

This latter approach is demonstrated on two phantoms: 1. two tubes containing different Mn2+-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 T2(CPMG), T1(SR, 100 data points) and T1,T2-combination(SR-CPMG) on the separate tubes of phantom 1, and on the total phantom 1 are:

<table>
<thead>
<tr>
<th>sample</th>
<th>( T_2(s) ) (CPMG)</th>
<th>fraction</th>
<th>( T_1(s) ) (SR)</th>
<th>( T_1(s) ) (SR)</th>
<th>( T_1)-weighted-T2(SR-CPMG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tube 1</td>
<td>0.82</td>
<td>1</td>
<td>1.79</td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td>tube 2</td>
<td>0.21</td>
<td>1</td>
<td>0.49</td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td>phantom 1</td>
<td>0.81</td>
<td>0.835</td>
<td>1.58</td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.165</td>
<td>0.82</td>
<td>0.167</td>
<td>0.49</td>
</tr>
</tbody>
</table>

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 $T_2$:

<table>
<thead>
<tr>
<th>$T_2(s)$ fraction</th>
<th>$T_1(s)$ fraction</th>
<th>$T_1$-weighted-$T_2$(SR-CPMG) fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_2(s)$ (CPMG)</td>
<td>$T_1(s)$</td>
<td>$T_1$-weighted-$T_2$(SR-CPMG)</td>
</tr>
<tr>
<td>(SR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>1.02</td>
<td>1.01</td>
</tr>
<tr>
<td>A2</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>A3</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>$a_1$</td>
<td>1.48</td>
<td>0.8</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.32</td>
<td>0.2</td>
</tr>
</tbody>
</table>

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.

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 itself.


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

Sincerely,

Angelien Snaar

Henk Van As
More people specify Oxford Instruments NMR magnets than any other

SO WHAT IS THE BIG ATTRACTION?

Oxford Instruments have been the foremost manufacturer of highly homogenous superconducting magnets for high resolution NMR applications since 1968.

A track record which could only have been achieved by a constant search for excellence in every aspect of NMR magnet design. Which is why, in our extensive range of magnets from 200MHz to 600MHz, we painstakingly ensure that every single one is balanced to at least the eighth order on-axis, giving the ultimate in NMR performance.

A performance which is also typified by the stability of the fields produced, thanks to our ability to achieve truly superconducting joints - whatever the superconductor. What is more, we design and build the long hold cryostats in which they're installed to the same exacting standards.

But simply producing magnets of such quality isn’t all of the story, for we back them with installation and service centres that provide high quality advice and support worldwide.

Innovation, design, quality and service, just some of the reasons why we’ve remained so attractive for so long.

OXFORD
NMR Division

The future demands the best

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-bit 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 \( \delta \) 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 recalculating them in the DISNMR program for final derivation.

Sincerely,

Due Astin Jean-Pierre Gaude

Aimé Lappe-Hutte

André Jeunet Claude Morat
Figures 1 & 2: experimental (a) and simulated (b) spectrum.

1a: TEMPO in DMSO
2a: mixture of 2 nitroxides.
NMR IN BIOMEDICINE: THE PHYSICAL BASIS

Editor: Eiichi Fukushima

Hardcover. ISBN 0-88318-603-9. $45.00 list price/$36.00 member price*
Paperback. ISBN 0-88318-609-8. $32.00 list price/$25.60 member price*

NMR in Biomedicine: The Physical Basis offers a rich source of historical and technical papers, supplying background for scientists in physics, chemistry, biology, engineering, medicine, and other disciplines.

Contents

General, Historical

Instrumentation and Technique

RF Field Effects on Biological Samples
RF Magnetic Field Penetration, Phase Shift and Power Dissipation in Biological Tissue: Implications for NMR Imaging, P.A. Bottomley, E.R. Andrew; The Sensitivity of the Zeugmatographic Experiment Involving Human Samples, D.J. Hoult, P.C. Lauterbur; Radiofrequency Losses in NMR Experiments on Electrically Conducting Samples, D.G. Gadian, F.H. Robinson; An Efficient Decoupler Coil Design which Reduces Heating in Conductive Samples in Superconducting Spectrometers, D.W. Alderman, D.M. Grant; A Large-Inductance, High-Frequency, High- Q, Series-Tuned Coil for NMR, B. Cook, I.J. Lowe; An In Vivo NMR Probe Circuit for Improved Sensitivity, J. Murphy-Boesch, A.P. Koretsky.

*AIP American Institute of Physics Satisfaction Guarantee: AIP invites you to examine any of the books listed for 30 days without risk or obligation. If you are not completely satisfied for any reason, return all materials still in saleable condition, along with a copy of the invoice marked "cancel", to:

American Institute of Physics, c/o AIDC, 64 Depot Road, Colchester, VT 05446.

*Discount: Members of the following AIP Member Societies receive a 20% discount on book purchases for personal use only. To be eligible for this discount, you must indicate your society affiliation by circling one of the following: APS, OSA, ASA, SOR, AAPT, ACA, AAS, AAPM, AVS, AGU, SPS.

To order, call toll-free 1-800-445-6638 (in VT 802-878-0315) FAX: 802-878-1102.

Send orders to: American Institute of Physics c/o AIDC 64 Depot Road, Colchester, VT 05446.


Please Send Me: NMR in Biomedicine: The Physical Basis

Subtotal $ ____________

Less 20% Discount $ ____________

Shipping $ ____________

Total $ ____________

Name ____________________________
Title ____________________________
Organization ____________________________
Address ____________________________
Home Business ____________________________
City ____________________________ State ____________
Zip ____________ Tel ____________________________

TAMU-NMR-9/90

METHOD OF PAYMENT

Check enclosed (payable in U.S. dollars to the American Institute of Physics, drawn on a bank in the U.S.)

Charge my credit card: AMEX MasterCard Visa

Account No. ____________ Exp. Date ____________

Signature ____________________________ (credit card orders must be signed)

Purchase Order No. ____________

Bill my organization ____________________________
We have immediate openings for:

A)  Technical sales representative for the nmr product line in the Western United States.

B)  Field Service Engineer(s) for the Western United States.

If you have interest in either of these positions, please contact the undersigned at your earliest convenience.

Dr. M. R. Bramwell
Bruker Instruments, Inc.
2880 Zanker Road, Suite 106
San Jose, CA 95120

phone: (408) 434-1190

An equal opportunity employer

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
Dear Barry:

On the basis of NMR studies of different solvated silyllithium compounds such as exo-1-trimethylsilylallyllithium and 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.

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 silyllallyllithium with pendant potential lithium ligand attached to the silyl side chains, I, prepared by Horvath and Chan. 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, $\Delta$ with $\Delta$, $\phi$ with $\phi$, with and the two methoxy carbons, reveals that the exchange rates responsible for these line-shape changes are all the same with $\Delta H' = 7.6$ kcal and $\Delta S' = -15$ 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.

Yours sincerely,

Gideon Fraenkel
Professor of Chemistry

GF:jlp
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
The Model R-1200 Rapid Scan, 60 MHz NMR Spectrometer scans 10-20 times faster than conventional \textit{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 \textit{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.
The standard double resonance feature provides homonuclear decoupling. \( H_i \)'s are decoupled from \( H_a \)'s and the resulting spectrum plotted and inserted for optimum presentation.

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

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

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

Chemical shift values and relative peak intensities are calculated by the digital signal processor and can be printed directly on the spectrum.
Uncorrelated spectrum scanned in 25 seconds shows the negative interference of ringing on peak discrimination and effective resolution.

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.

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

Nucleus | ¹H or ¹⁹F or ³¹P
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
Sweep System | 50, 100, 200, 300, 400, 500 Hz
Sweep Time | Digital Scan
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

For More Information Please Call or Write:
Hitachi Instruments, Inc.
44 Old Ridgebury Road
Danbury, CT 06810
(203)748-9001 - (800)548-9001
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 Å² 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 Å². 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


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 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 water. The water resonance has been broadened by introducing a large 21 current in the probe temperature shims. The half-Gaussian pulse width is 200 ns and the width of the "burned hole" is 12 Hz.

Top spectrum (C) is a 1D TOCSY spectrum when the anomeric proton at 4.86 ppm has been selectively irradiated with a half-Gaussian pulse.

Middle spectrum (B) is a 1D TOCSY spectrum, where anomeric proton at 4.43 ppm has been selectively irradiated with a half-Gaussian pulse.

Bottom spectrum (A) is a simple one pulse spectrum. TOCSY of Lactose (10 mM in D2O).

© Copyright 1990 General Electric Company
AFTER THE WORK IS FINISHED...
THE OTHER CPF COMES OUT TO PLAY

When all of the day's production samples have been run and the piles of spectra plowed through, JEOL's CPF can quickly switch operation modes. This same highly automated machine which is used for all of the production work can produce very high quality research data for those non-routine problems that always seem to appear. In many cases all that is necessary to make the change is to log into the research account. This changes the CPF from an automated, limited instrument into a wide-open research-grade spectrometer. With the addition of the appropriate accessories the low cost CPF is capable of running the most sophisticated research type experiments including CP MAS solids. Now that the CPF is available at a field strength of 400 MHz in addition to the very popular 270 MHz, the high field research spectrometer has become very affordable. The above 400-CPF data is a reverse detection 13-C experiment run on Angiotensin-II. The instrument used for this experiment is a standard CPF with the addition of the optionally available reverse detection Broad Band probe. This data clearly shows that the routine need never be the only thing you can do.

For more information please contact:

JEOL
11 Dearborn Road, Peabody, MA 01960
(508) 535-5900 (Phone) 
(508) 535-7741 (FAX)