TEXAS A&M UNIVERSITY

# NMR NEWSLETTER

NO. 335

AUGUST 1986

**Briggs, R.W., Metz, K.R., and Boehmer, J.P.**
$^{23}$Na Rotating Frame Imaging in Two Dimensions; Position Available . . . . 2

**Live, D.**
Deuterium Quadrupole Echo Spectra of Peptides Attached to Resins; Position Available . . . . . 4

**Geoffrion, Y., Morris, P., Forester, G., and Smith, I.C.P.**
Observing a Heart Break the (Ultra)Sonic Barrier Using $^{31}$P NMR . . . . . 8

**Vincendon, M. and Nardin, R.**
COSY Spectrum of Chitin . . . . . 10

**Ray, G.J.**
Position Available . . . . . 11

**Wimperis, S. and Bodenhausen, G.**
Composite Pulses in Multiple-Quantum Experiments . . . . . 12

**DiVerdi, J.A.**
Fast Frequency Switching for PTS Synthesizers . . . . . 16

**Nicolaidis, M., Pickles, S., Cerisier, J., and Le Botlan, D.**
Determination of Water Content of Baker's Yeast by Low Resolution NMR Spectroscopy. . . . . 18

**Canet, D. and Brondeau, J.**
Carbon Connectivities from a Selective INADEQUATE Experiment . . . . 22

**Brevard, C.**
Low $\gamma$ Nuclei, MAS NMR . . . . . 24

**Gerig, J.T., Goldstein, E., and Pinnell, R.P.**
Fluorine-Proton Coupling in Fluorotryptophans . . . . . 26

**Bulthuis, J.**
Position Available . . . . . 29

**Shapiro, B.L. and Kirk, R.R.**
Sponsors and Contributors of the TAMU NMR Newsletter . . . . . 30

**Shapiro, B.L. and Kirk, R.R.**
Advertising in the TAMU NMR Newsletter . . 31

**Burgar, I. and Dragar, C.**
INAPT: A Useful Alternative to 2D $^{1}$H-$^{13}$C Correlation . . . . . 32

**Booth, H. and Readshaw, S.**
Temperature Dependence of $^{1}$J(CH) . . . 34

**Doddrell, D.M.**
Gradient Encoded Volume Selection Techniques for Spectroscopy . . . . . 37

**Shapiro, B.L. and Kirk, R.R.**
Subscription Renewal Notice . . . . . 40

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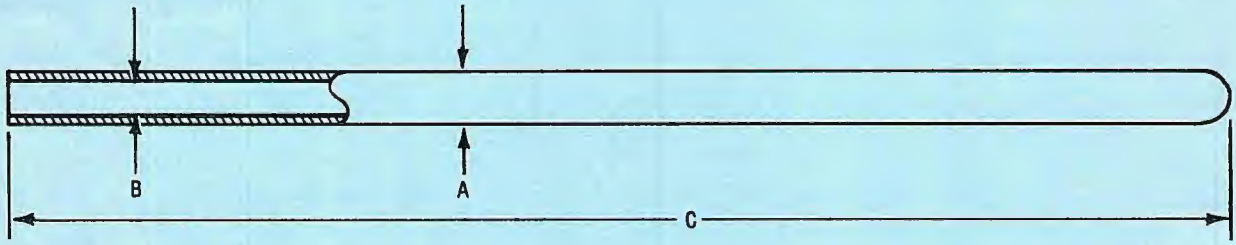


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**AUTHOR INDEX ------ TAMU NMR NEWSLETTER, NO. 335, AUGUST 1986**

Bodenhausen, G. . . . . 12
Boehmer, J.P. . . . . 2
Booth, H. . . . . 34
Brevard, C. . . . . 24
Briggs, R.W. . . . . 2
Brondeau, J. . . . . 22
Bulthuis, J. . . . . 29
Burgar, I. . . . . 32
Canet, D. . . . . 22
Cerisier, J. . . . . 18
DiVerdi, J.A. . . . . 16
Doddrell, D.M. . . . . 37
Dragar, C. . . . . 32
Forester, G. . . . . 8
Geoffrion, Y. . . . . 8
Gerig, J.T. . . . . 26
Goldstein, E. . . . . 26
Kirk, R.R. . . . . 30,31,40
Le Botlan, D. . . . . 18
Live, D. . . . . 4
Metz, K.R. . . . . 2
Morris, P. . . . . 8
Nardin, R. . . . . 10
Nicolaidis, M. . . . . 18
Pickles, S. . . . . 18
Pinnell, R.P. . . . . 26
Ray, G.J. . . . . 11
Readshaw, S. . . . . 34
Shapiro, B.L. . . 30,31,40
Smith, I.C.P. . . . . 8
Vincendon, M. . . . . 10
Wimperis, S. . . . . 12

**ADVERTISERS**

Bruker Instruments, Inc. . . . . 19
General Electric Company, Medical Systems Group, NMR Instruments . . 27, inside back cover
IBM Instruments, Inc. . . . . 5
JEOL . . . . . outside back cover
M-R Resources, Inc. . . . . 13
New Era Enterprises . . . . . 23
Omicron Biochemicals, Inc. . . . 29
Varian. . . . . 33
Wilmad Glass Company, Inc. . . . inside front cover

**FORTHCOMING NMR MEETINGS** (Additional listings are solicited)

**XXIII Congress Ampere on Magnetic Resonance** - September 15-19, 1986; Rome, Italy; XXIII Congress Ampere, Dipartimento di Fisica, Universita de Roma, "La Sapienza," P. le Aldo Moro 5, I-00185 Roma, Italy.

**Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XIII)** - September 28-October 3, 1986; St. Louis, Missouri; Program Manager: Dr. Sydney Fleming, FACSS (Titles), 24 Crestfield Road, Wilmington, Delaware 19810.

**1986 Eastern Analytical Symposium** - October 20-24, 1986; Hilton Hotel, New York; see Newsletter No. 329, p. 23 and Newsletter No. 325, p. 27.

**An International Meeting Sponsored by the British Radiofrequency Spectroscopy Group on New Methods in Magnetic Resonance** - September 6-8, 1986; York, U.K.; Dr. T.K. Halstead, Department of Chemistry, University of York, York YO1 5DD, U.K.

**Third Congress of the European Society for Magnetic Resonance in Medicine and Biology** - September 21-24, 1986; Aberdeen, U.K.; Dr. M.A. Foster, Department of Bio-Medical Physics, University of Aberdeen, Foresterhill, Aberdeen AB9 2ZD, U.K.

All Newsletter Correspondence Should be Addressed to:

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

**DEADLINE DATES**

No. 337 (October) --- 26 September 1986

No. 338 (November) ---- 31 October 1986

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Department of Radiology
717 534-8044

June 5, 1986 (Received June 26, 1986)

$^{23}$Na Rotating Frame Imaging in Two Dimensions; Position Available

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

Dear Barry:

As part of our research program in the area of development and application of rotating frame imaging (RFI) techniques, we have recently extended the method to obtain two-dimensional rather than one-dimensional spatial images. We are particularly interested in $^{23}$Na RFI, because of the importance of $Na^+$ in biological samples and the possible advantages of RFI over conventional NMR imaging with static field gradients for nuclei with short $T_2$'s.

The data were collected from two cylindrical phantoms containing saline (0.9% aqueous NaCl). The cylinders were 7 mm in diameter, spaced 5 mm apart. The 2D image was produced from nine one-dimensional projections (20° rotations of the rf coil assembly) using the algebraic reconstruction technique, or ART (1). For each 1D projection, 64 pulse widths were used, with 40 acquisitions per pulse width. The samples are easily resolved in this image; from images of other phantoms we estimate the resolution to be on the order of 2 mm.

We are currently trying to improve upon these results by using more projections to reduce the artifacts and better define the phantom shapes, and by using Fourier series imaging, or FSI (2), and other techniques to increase the time efficiency of data collection.

We would also like to mention that we have several postdoctoral research positions available in our laboratory. Applicants should have a Ph.D. in chemistry, biochemistry, physiology, or related field with experience in NMR techniques and instrumentation. Knowledge of electronics and computer programming would also be helpful. Excellent collaborative research opportunities exist in biomedical NMR, primarily of heart, brain, kidney, muscle, and tumors. Instrumentation includes a 1.9 T 26-cm spectroscopy/imaging system, a Bruker AM400WB with data station, and a whole-body 0.5 T imaging system (to be upgraded to 2.0 T in the future).

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References

1. R. Gordon, R. Bender, and G. T. Herman, J. Theor. Biol. 29, 471-481 (1970).
2. K. R. Metz and R. W. Briggs, J. Magn. Resonance 64, 172-176 (1985).

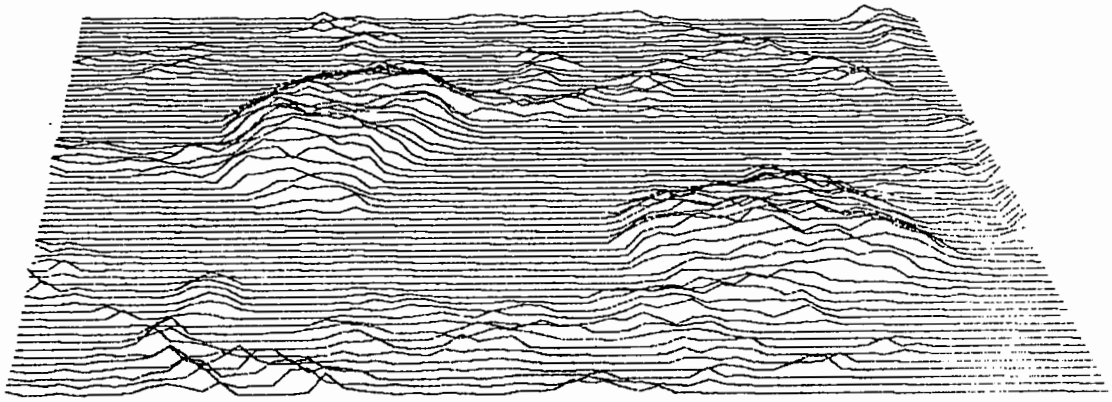

Figure 1. 2D $^{23}Na$ rotating frame image of two saline phantoms.

Sincerely,

Richard W. Briggs

Richard W. Briggs, Ph.D.
Assistant Professor of Radiology
and Biological Chemistry

Kenneth R. Metz

Kenneth R. Metz, Ph.D.
Assistant Professor of Radiology

John P. Boehmer

John P. Boehmer, M.D.
Research Assistant

RWB/jp

EMORY UNIVERSITY
Department of Chemistry

1515 Pierce Drive
Atlanta, Georgia 30322
404/329-6585

Deuterium Quadrupole Echo Spectra of Peptides Attached to Resins; Position Available

July 11, 1986
(Received July 15, 1986)

Dear Barry:

The physical properties of swollen loosely cross linked polystyrene have received some attention because of its use as a support in solid phase synthesis methods. These methods are of great interest because of the impact they are having on molecular biology by facilitating synthesis peptides and oligonucleotides(R. B. Merrifield, Science, V. 232, p.341 (1986)). Because the beads of this polymer used in synthesis give the visual impression of being solids suspended in a solvent, there has been a tendency to think of them as rigid systems. Because of an interest in understanding the properties of these polymers with growing peptides attached, we have previously examined $^{1}H$ and $^{13}C$ NMR spectra of solvent swollen systems (D. Live and S. B. H. Kent in "Elastomers and Rubber Elasticity", ACS Symposium Series 193, J. Mark and J. Lol eds. (1982) and D. Live and S. B. H. Kent in "Peptides: Structure and Function", V. Hruby and D. Rich eds. Pierce Chemical Co. Rockford Ill (1983)). In order to investigate the dynamics of these systems further peptide-resin systems were prepared with oligomers of deuterated glycine on them. The $^{2}H$ spectra of these systems were studied in collaboration with investigators at AT&T Bell Laboratories (A. G. Ludwick, L. W. Jelinski, A. Kintanar, and J. J. Dumais). A quadrupole echo spectrum of a dry peptide-resin sample shows a rigid powder pattern lineshape, where as samples that swell normally in DMF show a single narrow deuterium signal, indicative of rapid motion of a well solvated peptide. These results are consistent with conclusions about motions in swollen peptide resins deduced from the earlier NMR data (see references above). With longer oligoglycines, 7 to 9 residues in length, unusually poor swelling properties of the resins were observed. It was suspected this arose from interchain association of the peptides. Polyglycine chains would be particularly favorable for this since they are homopolymers of units with a minimum of steric hindrance. The result of the interaction is probably to produce non-covalent cross links in the system, which is reflected in an increasing portion of a component with slower motion. The group at Bell Labs was able to show that the length of peptide that produced the onset of the more rigid component was consistent with that needed to provide significant chain overlap. This assumed a random distribution of chains in the resin and a distance/residue derived from X-ray data. It is interesting to note that even in the case where the spectrum shows most restricted motion, the amino acid coupling proceeded to over 98% completion. Apart from the value of this study in understanding solid phase synthesis, this system provides a good model for examining copolymer systems.

(continued on page 7)

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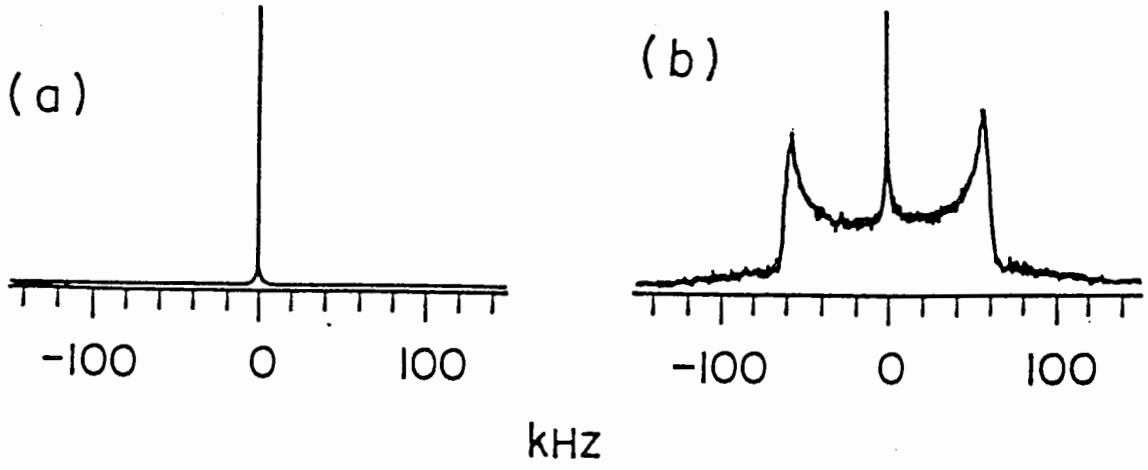


Deuterium quadrupole echo spectrum of gly-$d_2$ peptide resins

a) $(gly\text{-}d_2)_5$-peptide resin swollen in DMF showing only a narrow signal.

b) $(gly\text{-}d_2)_9$-peptide resin swollen in DMF. The sharp line here is from residual deuterium in the solvent.

---

Postdoctoral Opening:

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Yours,

David Live

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Division of Biological Sciences
Division des sciences biologiques

Ottawa, Canada
K1A 0R6

Ottawa, June 24 1986
(Received June 30, 1986)

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

Dear Barry,

OBSERVING A HEART BREAK THE (ULTRA)SONIC BARRIER USING $^{31}$P NMR

One of our ongoing research projects in collaboration with George Forester from Medical Engineering requires that we obtain 31-P NMR spectra of Langendorf perfused rat hearts while pacing and applying ultrasound at low power levels. George could tell you more about the ultimate goals of the study, but we would like to present here some of the NMR results we are now obtaining routinely.

After a few initial trials with a standard probe for 20-mm tubes, we soon realized that the presence of the required pacing wires drove the 31-P NMR signal-to-noise ratio across the noise barrier, with unrecognizable NMR signals from the perfused heart!

The obvious solution to our NMR problem was to build a probe dedicated to this type of experiment. Thanks to Paul (Morris Instruments Inc., Ottawa), the probe now in use for these experiments is yielding spectra showing very good S/N and resolution with, or without, pacing and ultrasound (Figure 1). We are currently using spectra with a physiologically meaningful time resolution (60 s per spectrum), allowing us to follow the time course of the effects of ultrasound on the phosphorus spectrum. Now that experiments can be performed on both sides of the ultrasonic barrier, we are getting a lot of bang (ultrasonic of course) for the bucks invested in the probe.

We regret that you will be denied the pleasure of sending us your colorful correspondence; we are ahead of you this time !

Best regards,

Yves Geoffrion  Paul Morris  George Forester  Ian C. P. Smith

Canada

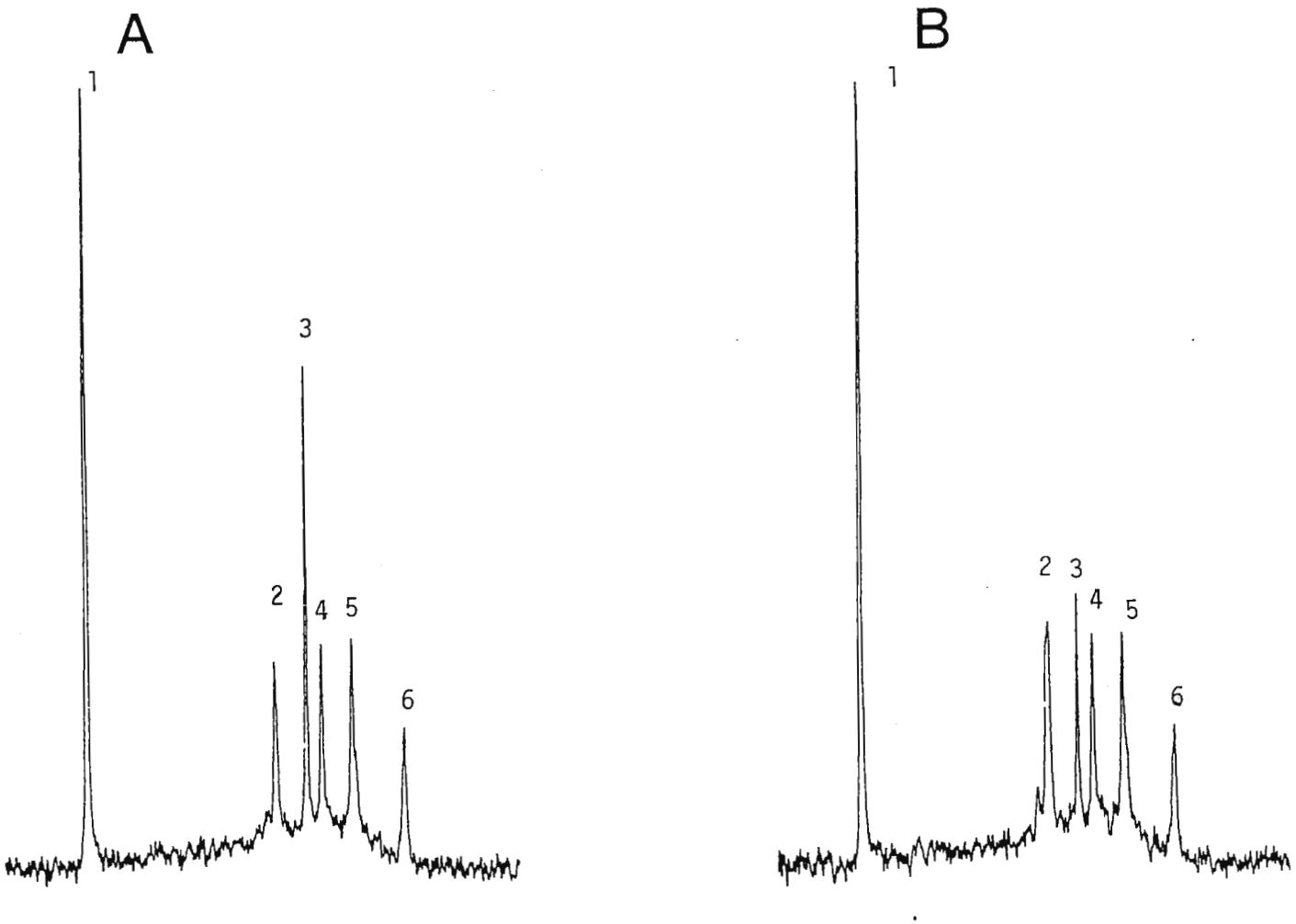


**Figure 1.** $^{31}P$ NMR spectra (145.785 MHz) of a Langendorf-perfused heart (10 mL / min); **A**: without any pacing or ultrasound and **B**: with pacing (300 / min) and ultrasound. Spectral acquisition conditions: 2s recycle delay, 10 μs (60°) pulse, 64 scans, 20 kHz sweepwidth, 4K data points. A 20 Hz line broadening was applied to the spectra before Fourier transformation. Spectra were acquired on a Bruker AM-360 NMR spectrometer. Peak assignments are: 1, dimethylmethylphosphonate (external reference); 2, inorganic phosphate; 3, phosphocreatine; 4, γ-ATP + β-ADP; 5, α-ATP + α-ADP; 6 β-ATP.

335-10

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Département de Recherche Fondamentale de Grenoble

Grenoble, le
19 juin 1986

N/référence : DRF/CH/86-101/mjc

(Received June 30, 1986)

Professor B. SHAPIRO
Department of Chemistry
Texas A and M. UNiversity
COLLEGE STATION, Texas 77843
USA

COSY spectrum of chitin

Dear Professor SHAPIRO,

Chitin, poly B(1→4) N-acetyl-D-glucosamine, is a natural polymer occuring as the main constituent of exo skeletons of crabs, lobsters and shrimps. It might be considered as one of the most difficult natural polymer to dissolve.

N,N-dimethylacetamide containing 5% of LiCl is a non degradative solvent for chitin. Its aprotic nature allows the observation of both hydroxyl and amino proton signals. The proton NMR spectrum of chitin (top of figure, 400 MHz, 70°C) does not reveal any couplings associated with proton signals, due to the high viscosity of the solution (2 % W/V).

The four most clearly deshield signals are assigned to the labile protons - NH-2, OH-3 and OH-6 - and to the anomeric proton H-1. The temperature dependent chemical shift behaviour normally used to distinguish labile NH and OH protons from non labile C-H protons could not be used here due to the close range of both proton types. In addition O-H resonance could not be differentiated from labile protons through deuterium exchange experiments due to its low value.

The 2D-COSY $^{1}H$ NMR spectrum allows the identification of most signals of chitin, starting from the most highly deshielded one (NH-2).

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The unusual behaviour of the OH-3 proton, i.e., low value and small temperature dependent chemical shift, is attributed to the inaccessibility of this OH for solvating LiCl molecules and the formation of an intramolecular hydrogen bond with the ring oxygen of a neighbouring unit (as indicated on formula).

From the NMR study of these solutions, it has been possible to postulate a dissolution mechanism of chitin in this mixed solvent (1).

M. VINCENDON R. NARDIN

(1) M. VINCENDON, Proceedings of the Third International COnference on Chitin and Chitosan, Ancona, Italy, April 1985, Plenum 1986.

---

**Amoco Corporation**
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July 27, 1986

There is an opening starting January 1987 for an electronics technician in the NMR group at Amoco's main research and development facility in Naperville, a suburb of Chicago. Primary responsibilities of the position will include the maintenance, repair, and modification of five spectrometers (JEOL FX60QS, Nicolet NTC-200 & -300, Varian VXR-300 & -400, Chemagnetics CM-200). The design and construction of probes for a variety of solution and solid samples applications will be a key aspect of the position. Training and experience in modern rf circuitry and digital electronics is required, and familiarity with NMR spectrometers and laboratory computers is highly desirable. Salary is commensurate with experience. To reply, please send resume to me.

Sincerely,

Joe Ray

G. Joseph Ray, B-5
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GJR/jh

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

27th June 1986

(Received July 3, 1986)

Dear Dr Shapiro,

Composite pulses in multiple-quantum experiments

Several excellent papers have been written to warn us against the dangers of naively inserting composite pulses into sophisticated pulse sequences (1,2). Recently we have come across a pleasing example that demonstrates the differing consequences of naïveté and true wisdom.

The simple excitation sandwich used in multiple-quantum NMR, i.e. the sequence ($90_x$ - $\tau/2$ - $180_y$ - $\tau/2$ - $90_x$), is known to yield only even orders of coherence, provided the last pulse in the excitation sandwich is accurately calibrated to 90° (Fig.1a). In practice, of course, rf inhomogeneity makes perfect separation of even and odd orders tricky, and deliberate missetting of the flip angle obviously leads to a breakdown of the separation (Fig.1b). Disregarding Levitt's dire warnings, we've tried to replace the last pulse by a composite $90_y90_x$ pulse, which - predictably - failed to relieve our problem (Fig.1c). However, replacing the last excitation pulse by Tycko's $90_0180_{105}180_{315}$ (3) does rescue the even/odd order separation, even if the flip angles are deliberately misset to 80° and 160° respectively (Fig.1d).

Another problem that is apparent in the spectra of Fig.1 is the asymmetry of the signals corresponding to opposite orders of coherence p and -p. These signals have been separated by time-proportional phase incrementation (there is no actual evolution period in our experiments), and the asymmetry of these signals must be attributed to the imperfections of the 'read' pulse used to reconvert the multiple-quantum coherences into observable magnetization immediately after the excitation sequence. This asymmetry, which would prevent one from obtaining pure two-dimensional absorption peakshapes by computing a real (cosine) transform with respect to $t_1$, can also be cured with Tycko's composite pulse (Fig.1d), but not with the $90_x90_y$ composite pulse (Fig.1c). The even/odd order separation and the symmetry of the signals in this type of experiment may be used as criteria for the practical usefulness of various composite recipes.

Yours sincerely,

Steve Wimperis

Geoffrey Bodenhausen

(continued on page 15)

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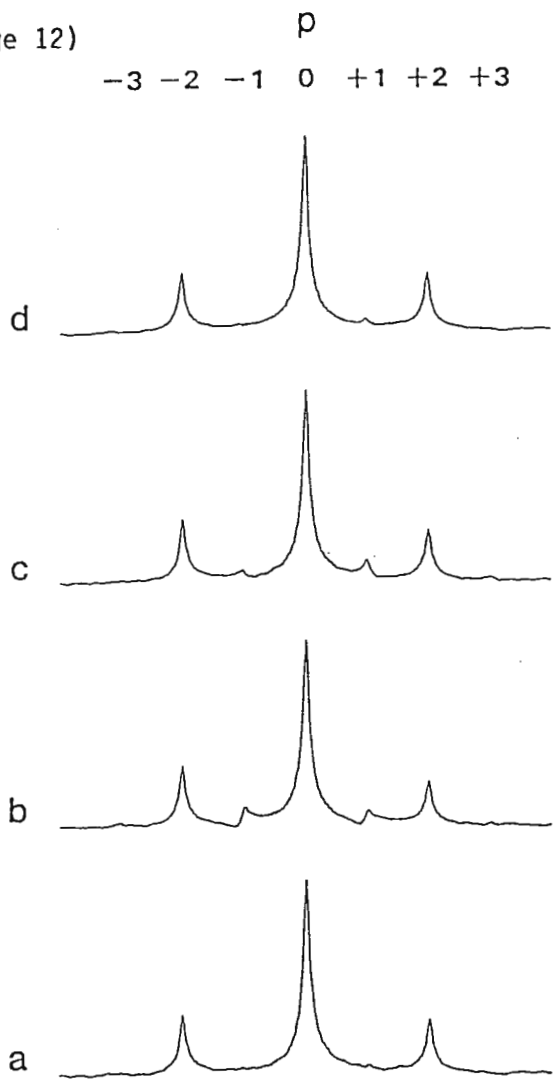


Figure caption: Projections onto the $\omega_1$ axis of absolute value two-dimensional spectra of the AMX system of 2,3-dibromopropionic acid recorded with the multiple-quantum filtration experiment:

$$(90_x - \tau/2 - 180_y - \tau/2 - \beta_x)_\varphi \; \beta_x \quad \text{Acquire}$$

where the phase $\varphi$ was incremented according to the TPPI scheme (phase increment $45^\circ$) for the purpose of separating the various orders of coherence p in $\omega_1$. In (a) the last two pulses were accurately set to $\beta = 90^\circ$; only even orders of coherence are observed and the amplitudes of the p = +2 and −2 peaks are nearly equal. In (b) the last two pulses were set to $\beta = 80^\circ$, and now odd orders can be clearly seen and the amplitudes of the p = +2 and −2 peaks are unequal. Spectrum (c) shows the result when the last two pulses are replaced with $80_y80_x$ and $80_x80_y$ respectively. These composite pulses have <u>failed</u> to remove the effects of the pulse flip angle error. Use of Tycko's composite pulse $80_0160_{105}160_{315}$ in (d), however, restores the experiment to full health despite the deliberate pulse misset.

(1) M.H.Levitt and R.R.Ernst, Mol.Phys. <u>50</u>, 1109 (1983).
(2) M.H.Levitt, Progr.NMR Spectrosc. <u>18</u>, 61 (1986).
(3) R.Tycko <u>et al</u>. J.Magn.Reson. <u>61</u>, 90 (1985).

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July 18, 1986

(Received July 28, 1986)

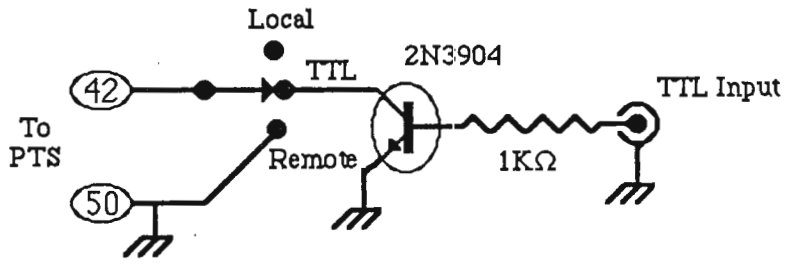
Bernard L. Shapiro, Ph.D.
Department of Chemistry
Texas A&M University
College Station, TX 77843

FAST FREQUENCY SWITCHING FOR PTS SYNTHESIZERS

Dear Professor Shapiro:

There are a number of contemporary NMR experiments that require fast switching of the transmitter frequency. These include water supression by presaturation in High Resolution Solution NMR and Separated Local Field Spectroscopy using Magic Angle Decoupling in High Resolution Solid State NMR. This letter describes a method for toggling any PTS synthesizer between two independently selectable frequencies.

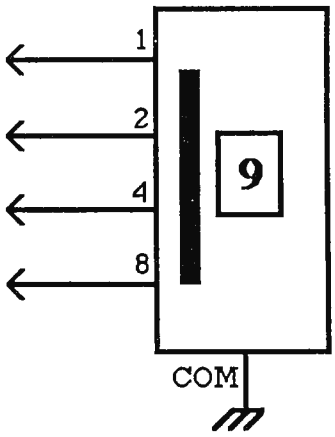
This method utilizes the remote programming input connector in the rear panel of the PTS synthesizer. One frequency is entered on the front panel (local) controls and the second is entered into a set of thumbwheel switches connected to the remote programming inputs. The synthesizer is then switched between the remote and local controls via a TTL control line interfaced to the remote enable input, also on the rear panel. The TTL control circut is as follows:



The three position switch affords manual control of the frequency selection for test and setup purposes. Any NPN switching transistor can be used.

The thumbwheel switch circut is somewhat more complex but conceptually simple. Each digit of the remote frequency is controlled by a single BCD (binary coded decimal) thumbwheel switch, *e.g.*, Imlec #MF-21/MF-EP (Newark Electronics, Cornwells Heights, PA). Any digit can be permanently set by hardwiring it. We typically hardwire all of the MHZ and Hz digits and only control the KHz digits because no more resolution is necessary and it simplifies the wiring. Pins 23,24,25,46 and 47 must be connected to ground (pin 50). The pin assignments are as follows:

| MHz | | | KHz | | | Hz | | |
|---|---|---|---|---|---|---|---|---|
| 100 | 10 | 1 | 100 | 10 | 1 | 100 | 10 | 1 |
| 43 | 15 | 17 | 1 | 3 | 5 | 7 | 9 | 11 |
| 44 | 16 | 18 | 2 | 4 | 6 | 8 | 10 | 12 |
| 49 | 40 | 19 | 26 | 28 | 30 | 32 | 34 | 36 |
| -- | 41 | 20 | 27 | 29 | 31 | 33 | 35 | 37 |




The PTS manual specifies the switching time as 20 µsec to within 0.1 rad of the new frequency. Our measurments have born this out *when measured at the synthesizer output.* It is important to realize that the time response of any tuned circut(s) after the synthesizer will be convoluted into this switching time, thereby degrading the specification.

Sincerely,

Joseph A. DiVerdi, Ph.D.
Associate Senior Investigator

NANTES. le 30 Juin 1986 (Received July 7, 1986)

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Professor Bernard SHAPIRO
TAMU NMR Newsletter
Department of Chemistry
Texas A and M University
College station
TEXAS 77843

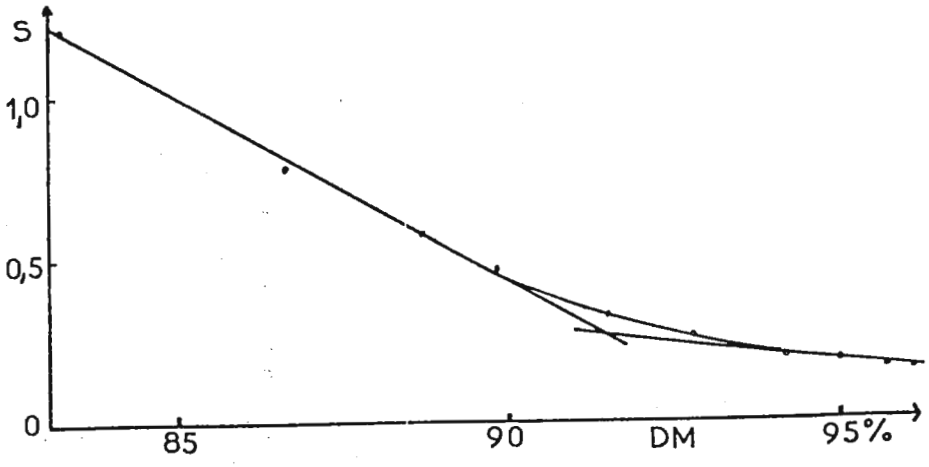
**Determination of water content of baker's yeast by low resolution NMR spectroscopy**

Dear Professor SHAPIRO

We have recently been studying the possibility of using low resolution NMR (the spectrometer BRUKER MINISPEC PC 20) for the determination of water content in dry baker's yeast. The conventional method for carrying out these determinations consists of drying the yeast in an oven at 105°C for 5 hours. This method is long and does not allow a result to be used for subsequent modification of the drying process in progress. On the contrary, low resolution NMR, after calibration of the spectrometer, gives a result in a few minutes under the condition that the sample must be at the same temperature as those used for constructing the calibration curve.

Commercial dry yeast contains approximately 5 % water by mass and it was either dehydrated or hydrated to obtain a range of samples from 83 % to 98 % dry matter. The signal in volts per gram of sample was plotted against the dry matter DM of the sample and the graph 1 was obtained. Two distinct straight lines are seen either side of 91.5 % DM :

| | | |
|---|---|---|
| S = 10.4 - 0.111 DM | r = 0.998 | DM < 91.5 % |
| S = 3.6 - 0.036 DM | r = 0.966 | DM > 91.5 % |

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(continued on page 21)

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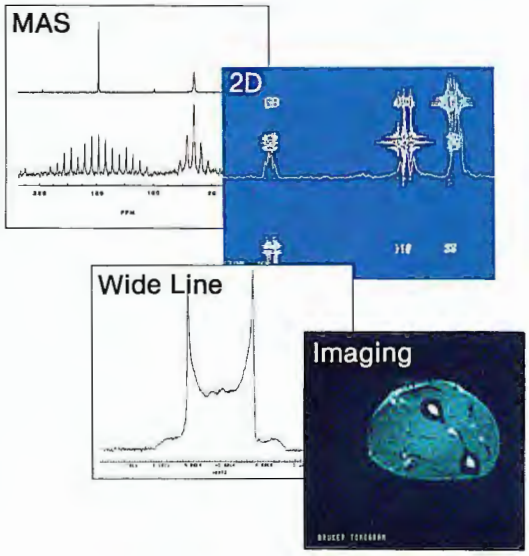


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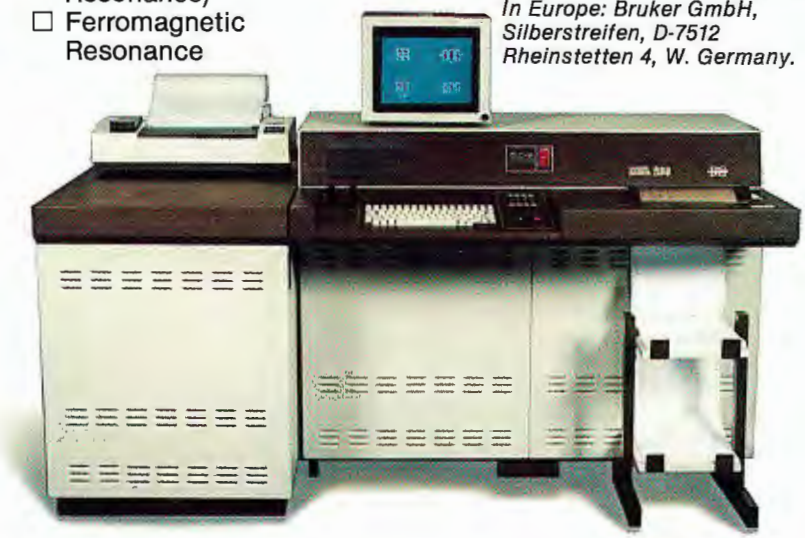

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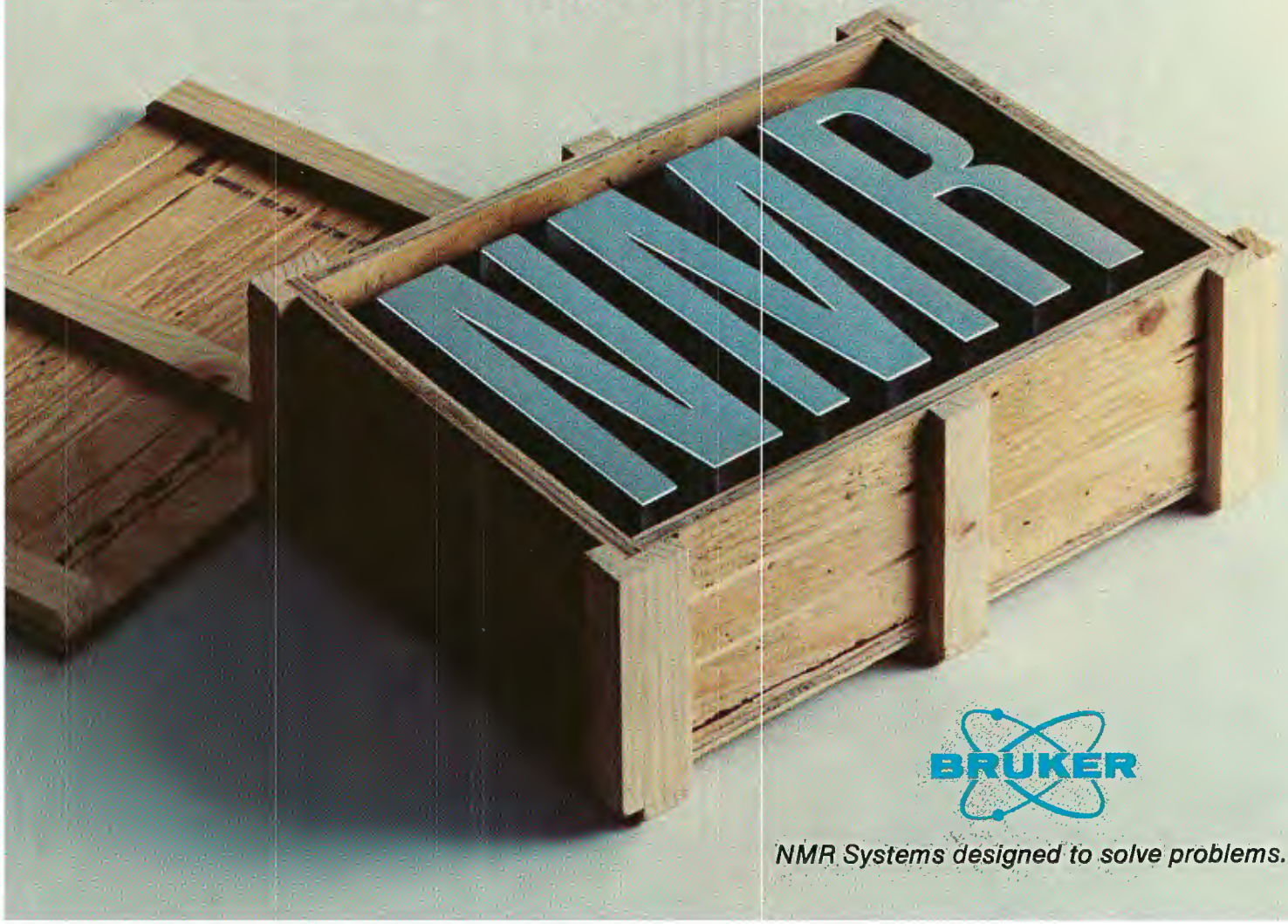


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***NMR Systems designed to solve problems.***

(continued from page 18)

Note that the second straight line gives a signal of zero at DM = 100 %.

In order to explain the break at 91.5 %, we measured the transversal relaxation times $T_2$ of the water in 6 samples. We have shown that there exist 2 different values of $T_2$ of 0.2 ms and 4 ms which appear constant for the samples with a dry matter of more than 91.5 %. These values correspond to those generally found for bounded and free water (also called freezable water 1,2).

On the contrary, for the yeast samples with a dry matter of less than 91.5 % it is noted that the $T_2$ increases slightly for the free water (from 4.5 to 5.3 ms) and more sharphy for the bounded water, rising from 0.3 ms to 0.46 ms.

The variation of the value of the $T_2$ of the bonded water is attributed to an exchange phenomenon with the free water, the $T_2$ measured in this case not being the true $T_2$ but the apparant $T_2$.

The signal obtained at a time t is given by the relation

$$I = a_B \exp\left(\frac{-t}{T_2B^*}\right) + a_L \exp\left(\frac{-t}{T_2{}^*L}\right)$$

and as the measurement is made at 50$\mu$s, an increase in the value of $T_2B^*$ of the bonded water could explain a larger value for the slope in presence of exchange for dry matter content below 91.5 %.

Please, credit this account to Dr G. MARTIN

Sincerely yours.

M. NICOLAÏDIS, S. PICKLES, J. CERISIER and D. LE BOTLAN

References

1 - E. BROSIO, G. ACTOBELLI, SHI YUN YU and A. DI NOLA
J. Fd. Technol. 18, 219, 1983.

2 - P.N. GAMBHIR and A.K. AGARWALA, J. Amer. Oil Chem. Soc. 62, 103, 1985.

Université de Nancy I

**Laboratoire de Méthodologie RMN**

D. CANET
Professeur

Professor B.L. SHAPIRO
TEXAS A & M University
Department of Chemistry
COLLEGE STATION
Texas 7784-3255
U.S.A.

Title : Carbon connectivities from a selective INADEQUATE experiment.

July 10, 1986 (Received July 18, 1986)

Dear Professor Shapiro,

The two dimensional version of the INADEQUATE experiment is often hampered by a prohibitive measuring time. Furthermore, in a carbon-13 spectrum, many resonances can readily be assigned on the basis of chemical shift arguments. Instead of running the INADEQUATE sequence as many times as needed by a second dimension, we proposed to selectively apply it only to those resonances whose assignment is unknown or ambiguous.

The following sequence :

$$(\tfrac{\pi}{2})_{x} - \tau - (\tfrac{\pi}{2})_{-x} - (\tfrac{\pi}{2})_{\phi} - (Acq)_{\psi}$$

with the carrier positionned at the A nucleus resonance makes it possible to transfer polarization from A towards any nucleus X, provided it is J-coupled to A. A maximal effect occurs for $\tau = 1/2\ J_{AX}$ . A proper phase cycling, derived from the one of the INADEQUATE sequence, permits the elimination of all parent signals in a natural abundance carbon-13 spectrum

| $\phi$ | $\psi$ |
|---|---|
| y | -y |
| -y | y |
| x | x |
| -x | -x |

Selectivity can be achieved by varying $\tau$ . In our case $\tau$ is incremented from $0.8/2\ J_{AX}$ to $1.2/2\ J_{AX}$ step by step in order to fulfill the Nyquist criterium ($\Delta\tau < 1/2|\nu_A - \nu_X|_{max}$).

Resulting free induction decays are coadded. Selectivity is effective in a range of ca. 20 Hz around the A frequency.

Concerning parent elimination (polarization transfer is necessarily of good quality since it flows from resonances close to the carrier), the proposed phase cycling does compensate for rf field inhomogeneity but not for off-resonance effects. The latter are greatly reduced by replacing the last $\pi/2$ pulse by a cluster devised by Levitt and Ernst (Mol.Phys., 50, 1109 (1983)).

With this letter, we hope to be back on your mailing list.

Yours sincerely,

D. CANET

J. BRONDEAU

SOCIETE ANONYME DE DIFFUSION DE L'INSTRUMENTATION SCIENTIFIQUE
**BRUKER SPECTROSPIN** - 34, Rue de l'Industrie 67160 Wissembourg **FRANCE**

July 16, 1986

LOW $\gamma$ NUCLEI, MAS NMR

(Received July 24, 1986)

Dear Barry,

Thank you for your two reminders plus ultimatum, your file keeping system is quite efficient !

I would like to briefly present some W 183 solid state results we obtained in MAS observation. As a matter of fact, we are actively exploring the area of low $\gamma$ , CP/MAS or MAS only experimental conditions.

For these low frequency isotopes, we tune the magic angle setting via the side bands spectrum of a Cl35 sample ( Fig. 1) or better, through the sharpening of the $^{*}NO_3$ signal in enriched $^{*}NH_4\ ^{*}NO_3$.

Fig. 2 shows some characteristic MAS/W 183 spectra of solid $Na_2\ WO_4$ and W(CO)6.

The solid state isotropic shift of W(CO)6 correlates quite well with the liquid state result (see TAMU N° 292 p 27 ) : - 3447 ppm/$WO_4$

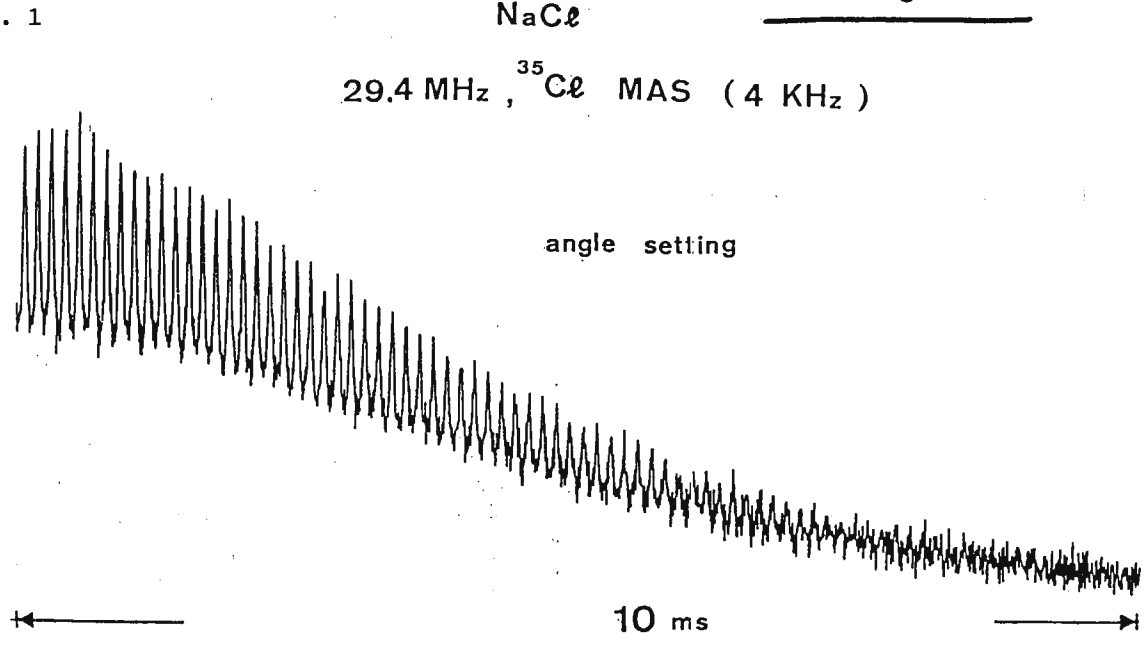
With my best regards,

A bientôt

Christian BREVARD

Christian

Fig. 1



$WO_4$

12.5 MHz, $^{183}W$ MAS

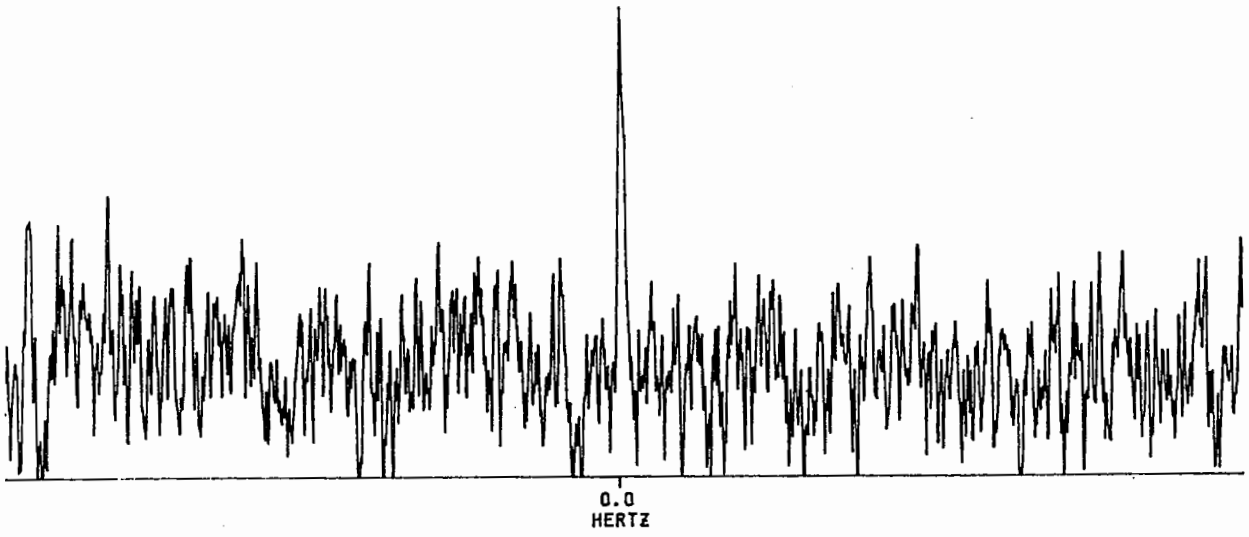
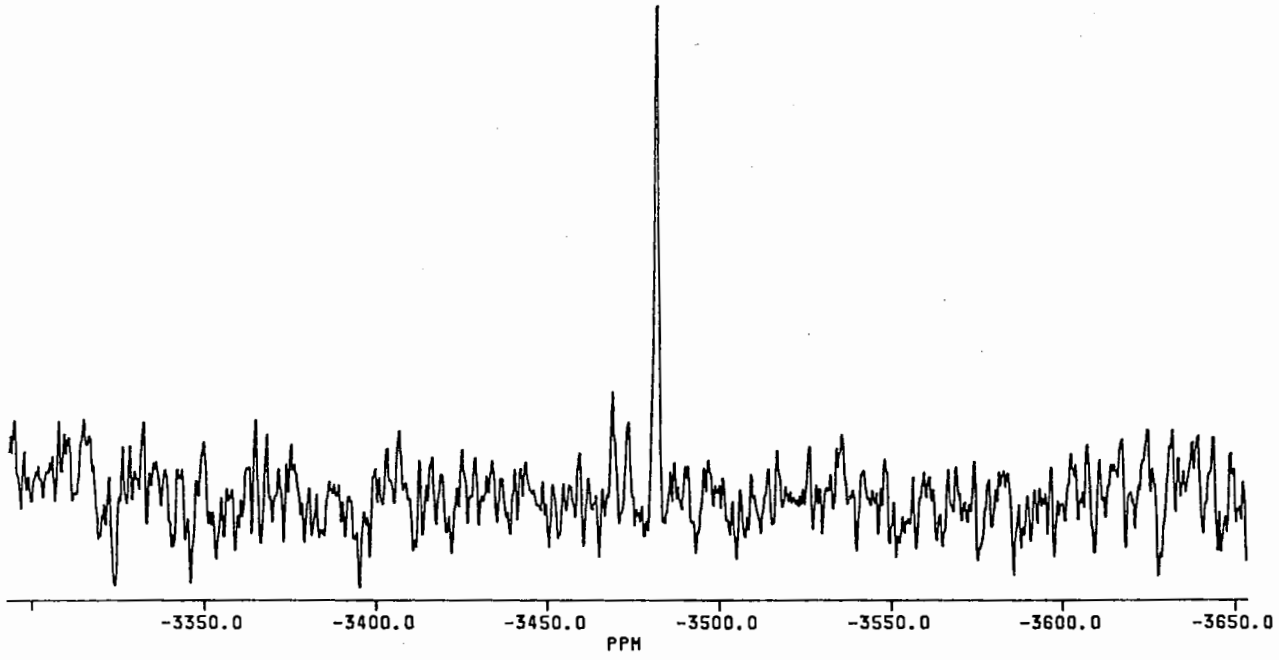



Fig 2 : W183, MAS spectra

W04 : 80 scans, 240 seconds interpulse waiting time
W(CO)6 : 800 scans, 60 seconds interpulse waiting time

$W(CO)_6$

12.5 MHz, $^{183}W$ MAS



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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

16 July 1986 (Received July 21, 1986)

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

"Fluorine-Proton Coupling in Fluorotryptophans"

Dear Barry,

In the course of the preparation and study of peptides containing various fluorotryptophans we had occassion to analyze the pmr and fmr spectra of 4-, 5-, and 6-fluorotryptophan for chemical shift and scalar coupling parameters, using standard techniques. The results at two field strengths agreed well. Comparisons to data for unsubstituted tryptophan indicated that replacement of hydrogen on the indole ring by fluorine results in a significant increase in the four-bond coupling constant between the hydrogens ortho to the fluorine. For example, $J_{46}$ in the 5-fluoro isomer is about twice a large as the corresponding coupling constant in tryptophan (2.48 Hz vs. 1.14 Hz). Similar observations have been reported for 7-fluoroquinoline and 6-fluorobenzofuran.

Within the LCAO approximation the spin coupling constant $J_{AB}$ between two nuclei can be shown to be proportional to the mutual polarizability ( $_{AB}$) of the atoms (cf. Murrell, Prog. NMR Spectroscopy **6** 1-61 (1970).). We have calculated mutual polarizabilities using both the CNDO/2 and MINDO/3 approximations; the $_{AB}$ parameters from both are in close agreement. Figure 1 shows a correlation of observed H-H coupling constants with the computed polarizabilities. It is noteworthy that the theory predicts the enhancement in the four-bond couplings.

Calculated proton-fluorine coupling constants were in poor agreement with experiment.

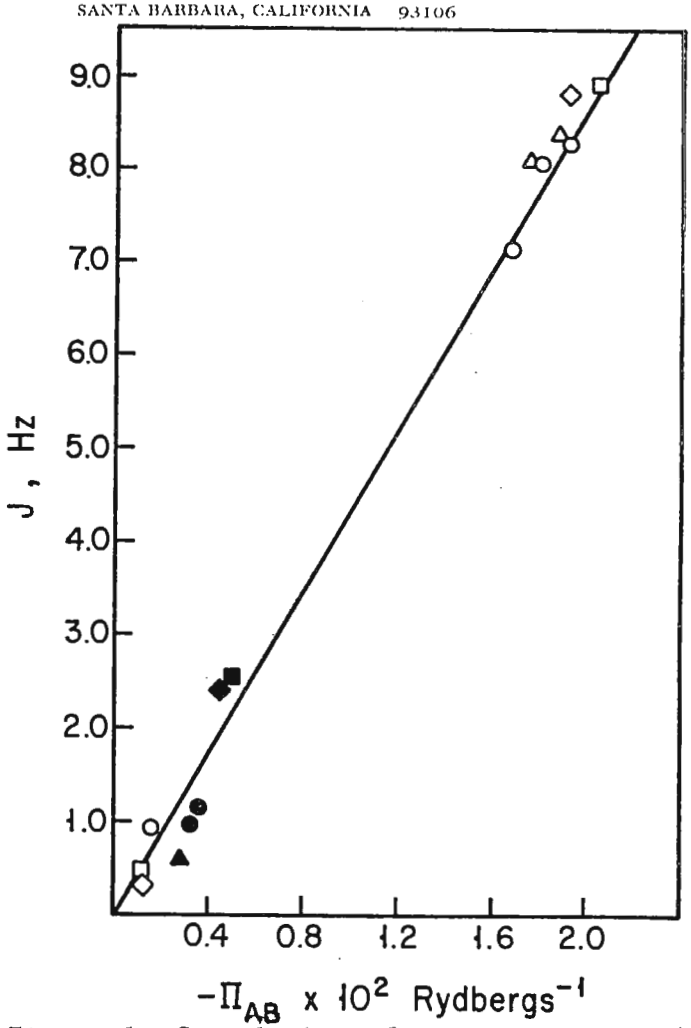


*Figure 1. Correlation of proton-proton spin coupling constants with mutual polarizabilities as computed by the CNDO/2 method. Data for tryptophan, 4-, 5-, and 6-fluorotryptophan are represented by circles, triangles, squares and diamonds, respectively. The slope of the correlation line shown is 5.9 x $10^3$ Hz·ev, which compares well with the theoretical value expected, 6.2 x $10^3$ Hz·ev (cf. Clarke, Tetrahedron **24** 2663 (1968).).*

Sincerely,

Tom

J. T. Gerig
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Joint Science Department
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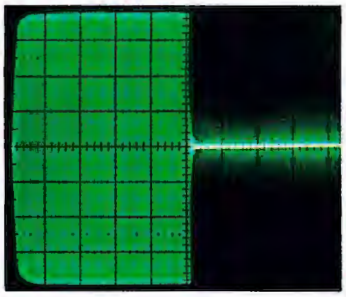
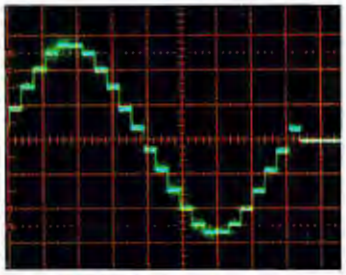
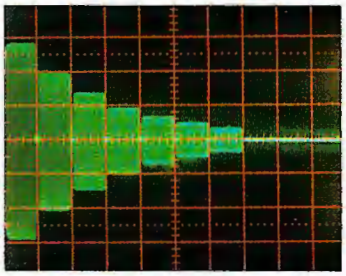




15° phase shift through 360°. ►



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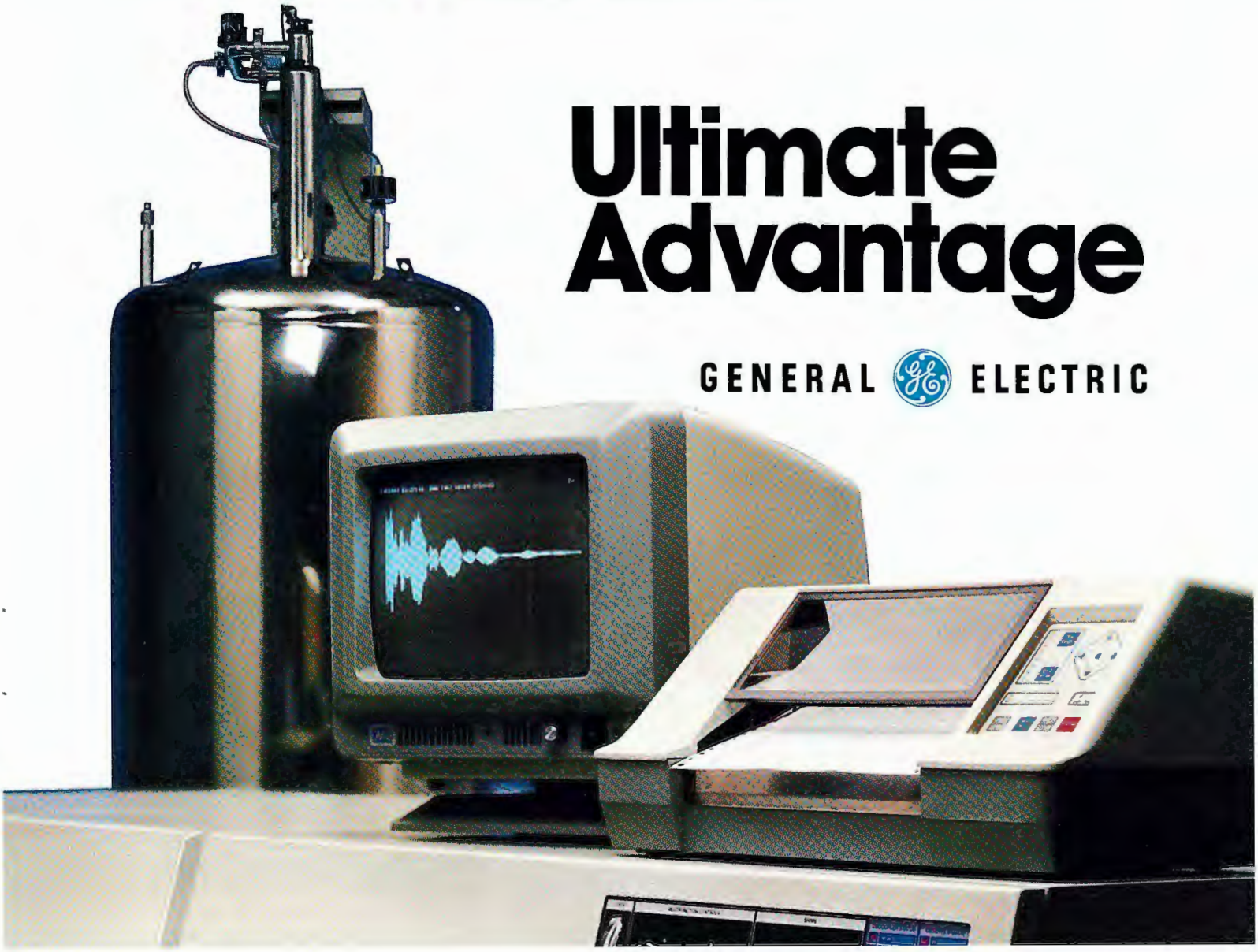

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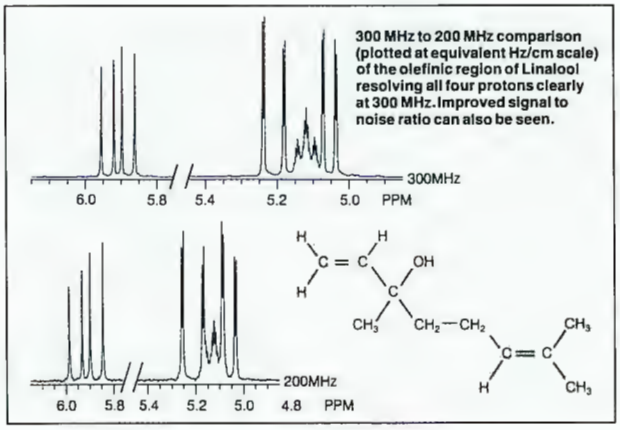


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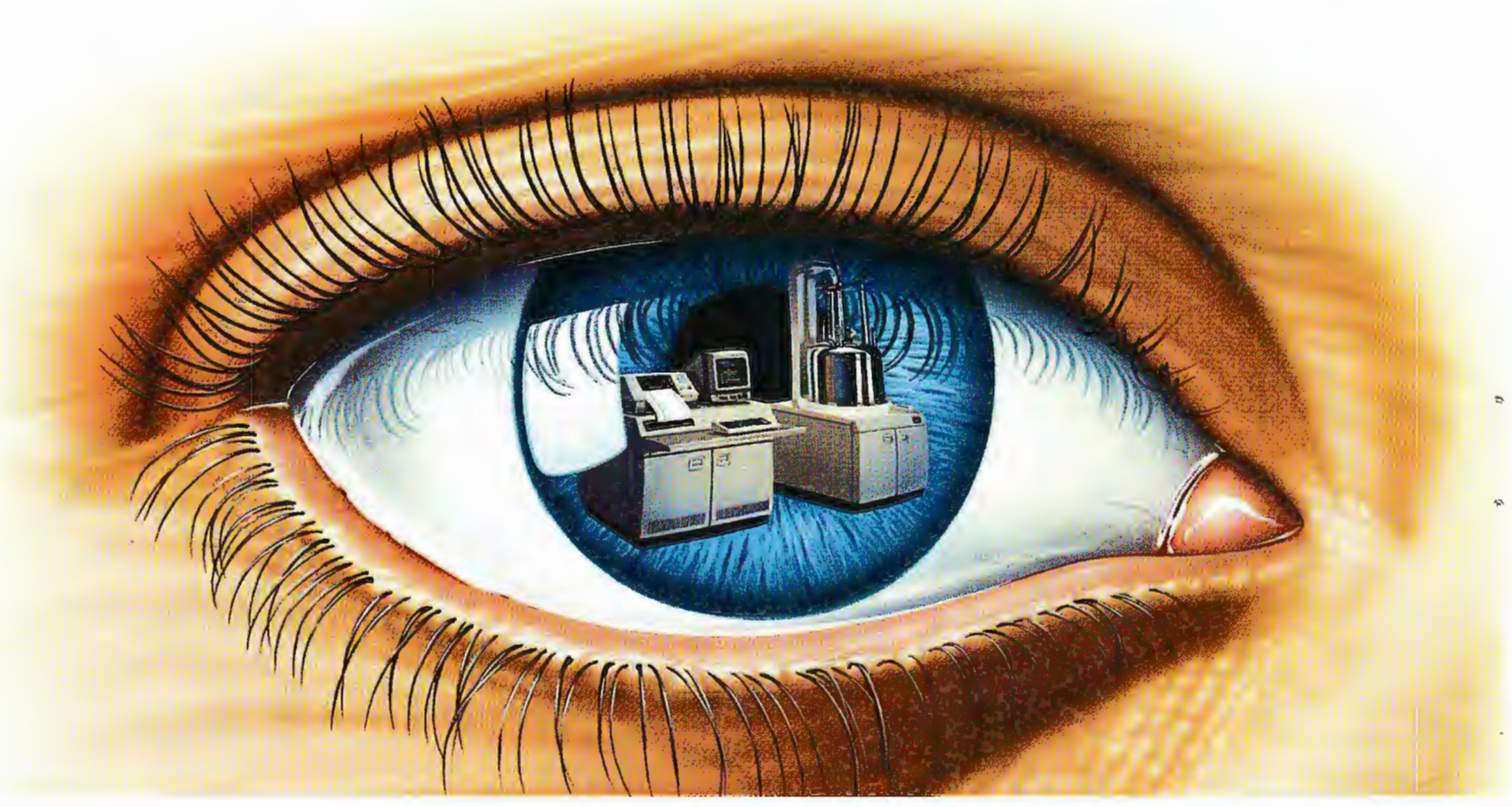

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Dr. J. Bulthuis
Department of Physical and
Theoretical Chemistry
Free University
de Boelelaan 1083
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The Netherlands

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Bernard L. Shapiro
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Russel R. Kirk
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TAMU NMR Newsletter

Department of Chemistry
Texas A&M University
College Station, Texas 77843

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(Received July 29, 1986)

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

INAPT - A useful alternative to 2D $^{1}H$-$^{13}C$ correlation

Dear Professor Shapiro,

Late last year the Central Science Laboratory of the University of Tasmania, took delivery of a Bruker AM300 spectometer, equipped with a 5mm dual probe, a 10mm multinuclear probe and a solid-state probe. This replaced the Chemistry Department's aged Jeol JNM-4H-100, which had served us for many years. It had become quite inadequate for the tasks we wished to perform (even homonuclear decoupling experiments were looked upon as something of an achievement in those days!). Most of the work carried out so far on our new instrument, has been involved with structural assignment of organic and organometallic compounds prepared in the Chemistry Department. However, other Departments are also slowly beginning to show interest in applying NMR to their research problems.

Combined use of homonuclear and heteronuclear, 1D and 2D methods has made the full spectral assignment of complex molecules a matter of routine. One of us (C.D.) has been working on the synthesis and structural elucidation of natural products for some time and recently we completed the structural determination of a new alkaloid from Papaver somniferum. This dimeric morphinan, containing O-demethyl-14-hydroxycodienone and thebaine moieties, is the first alkaloid of its type reported. Using both 1D and 2D NMR techniques, its structure (Figure 1) was established. However, the results of long-range $^{1}H$-$^{13}C$ correlation spectra (COLOC and XHCORR) were not entirely satisfactory in terms of $F_2$ resolution and S/N, which resulted in several important correlations being unobserved. To improve these spectra, substantially increasing the experiment time and/or fine tuning the delay periods was required. Because only several correlations needed to be checked, we tried the 1D INAPT experiment[1], with excellent results. Setting up the experiment[2] was straightforward and more than ten individual INAPT experiments could be performed in the time required for one long-range 2D XHCORR experiment. It was found that about three times the number of scans needed for a good proton decoupled $^{13}C$ spectrum gave a comparable S/N. The results of four of the INAPT experiments are shown in Figure 2. Correlations which were not observed in the 2D experiments are marked with an asterisk. A paper describing the full structural determination, including assignment of the relative configuration of the eight chiral centres by NOE methods, is in preparation.

Yours Sincerely,

Iko Burgar

Charles Dragar

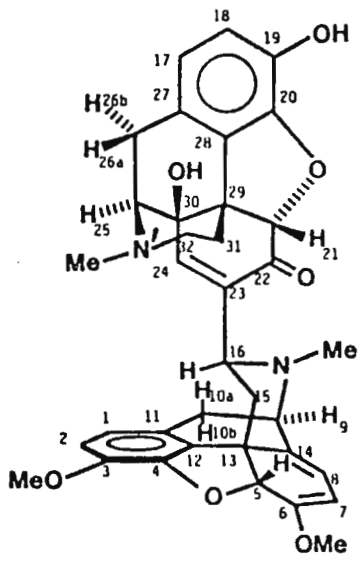


FIGURE 1

$^{13}$C Spectrum

| | |
|---|---|
| C22 | 192.84 CO |
| C6 | 152.57 q |
| C23 + C24 | 144.99 q + CH |
| C4 | 144.70 q |
| C20 | 143.18 q |
| C3 | 142.68 q |
| C19 | 138.65 q |
| C12 | 133.03 q |
| C14 | 131.41 q |
| C28 | 130.74 q |
| C11 | 127.10 q |
| C27 | 124.34 q |
| C1 | 120.11 CH |
| C17 | 119.51 CH |
| C18 | 118.12 CH |
| C2 | 113.08 CH |
| C6 | 111.96 CH |
| C7 | 95.63 CH |
| C5 | 88.51 CH |
| C21 | 86.20 CH |
| C30 | 67.55 q |
| C25 | 64.06 CH |
| C9 | 62.19 CH |
| 3-MeO | 56.39 $CH_3$ |
| 6-MeO | 56.90 $CH_3$ |
| C16 | 50.67 CH |
| C13 | 46.68 q |
| C29 | 46.42 q |
| C32 | 44.91 $CH_2$ |
| N'-Me | 42.62 $CH_3$ |
| C15 | 42.42 $CH_2$ |
| N-Me | 37.16 $CH_3$ |
| C26 | 29.87 $CH_2$ |
| C31 | 29.31 $CH_2$ |
| C10 | 22.22 $CH_2$ |

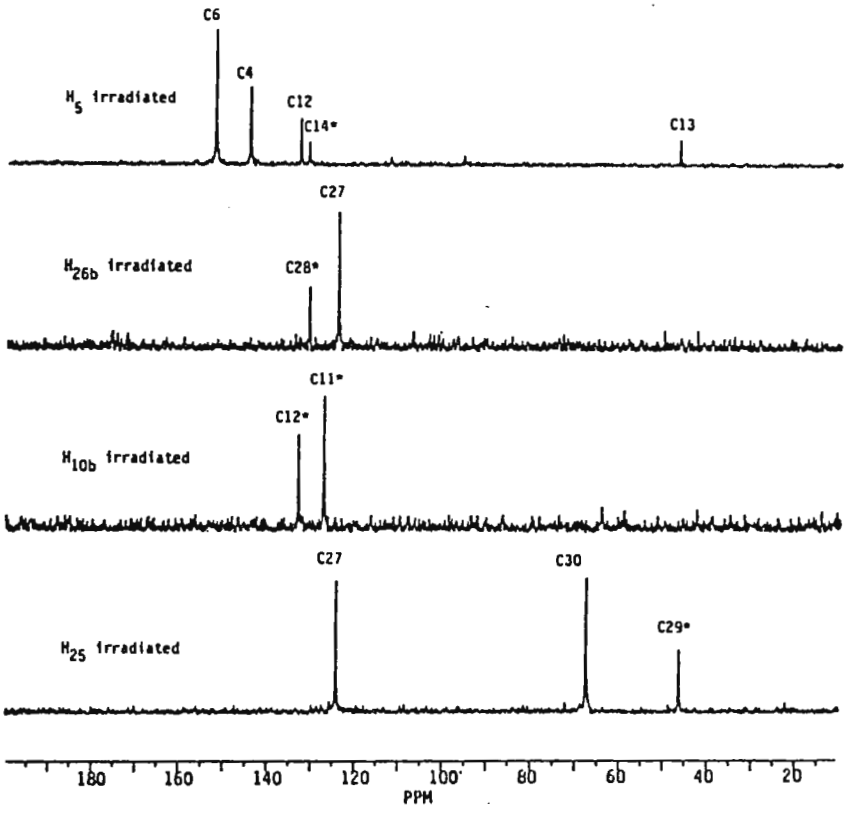


FIGURE 2

## References

1. Abdel-Sayed, A.N. and Bauer, L., Tett. Letters, 1986, 27, 1003, and references cited therein.

2. Bax, A., J. Mag. Res., 1983, 52, 76.

University of Nottingham

Department of Chemistry

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HB/JL

1st July 1986
(Received July 7, 1986)

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

Dear Professor Shapiro,

Temperature Dependence of $^1J(CH)$

If J values are to be used in conformational analysis, their sensitivity to temperature variation is an important consideration.[1] Some of our recent measurements are listed in the Table.

Table

| | T/K | $^1J(CH)$ in $OCH_3$/Hz |
|---|---|---|
| t-2-methoxy-4-methyltetrahydropyran | 293* | 141.43 |
| ditto | 162* | 141.77 |
| c-2-methoxy-4-methyltetrahydropyran | 293* | 142.01 |
| ditto | 162* | 142.41 |
| c-2-methoxy-3-methyltetrahydropyran | 293* | 141.47 |
| ditto | 162* | 141.81 |
| t-1-methoxy-2-methylcyclohexane | 293* | 140.00 |
| ditto | 162* | 140.39 |
| ditto | 270** | 140.17 |
| ditto | 175** | 140.64 |

* Solvent $CD_2Cl_2$ ** Solvent $CDCl_3$ : $CFCl_3$ (1:1 v/v)

Bearing in mind digitisation error (± 0.15 Hz, 64 K points over 10.000 Hz), the effect of temperature change is only just significant; however, the general trend in $^1J(CH)$ is always in the same direction, namely, an increase in $^1J$ with a decrease in temperature.

Yours sincerely,

Harold Booth

S.A. Readshaw

Simon Readshaw.

Reference:
1. J.C.J. Barna and M.T.J. Robinson, Magnetic Resonance in Chemistry, 1985, 23, 192.

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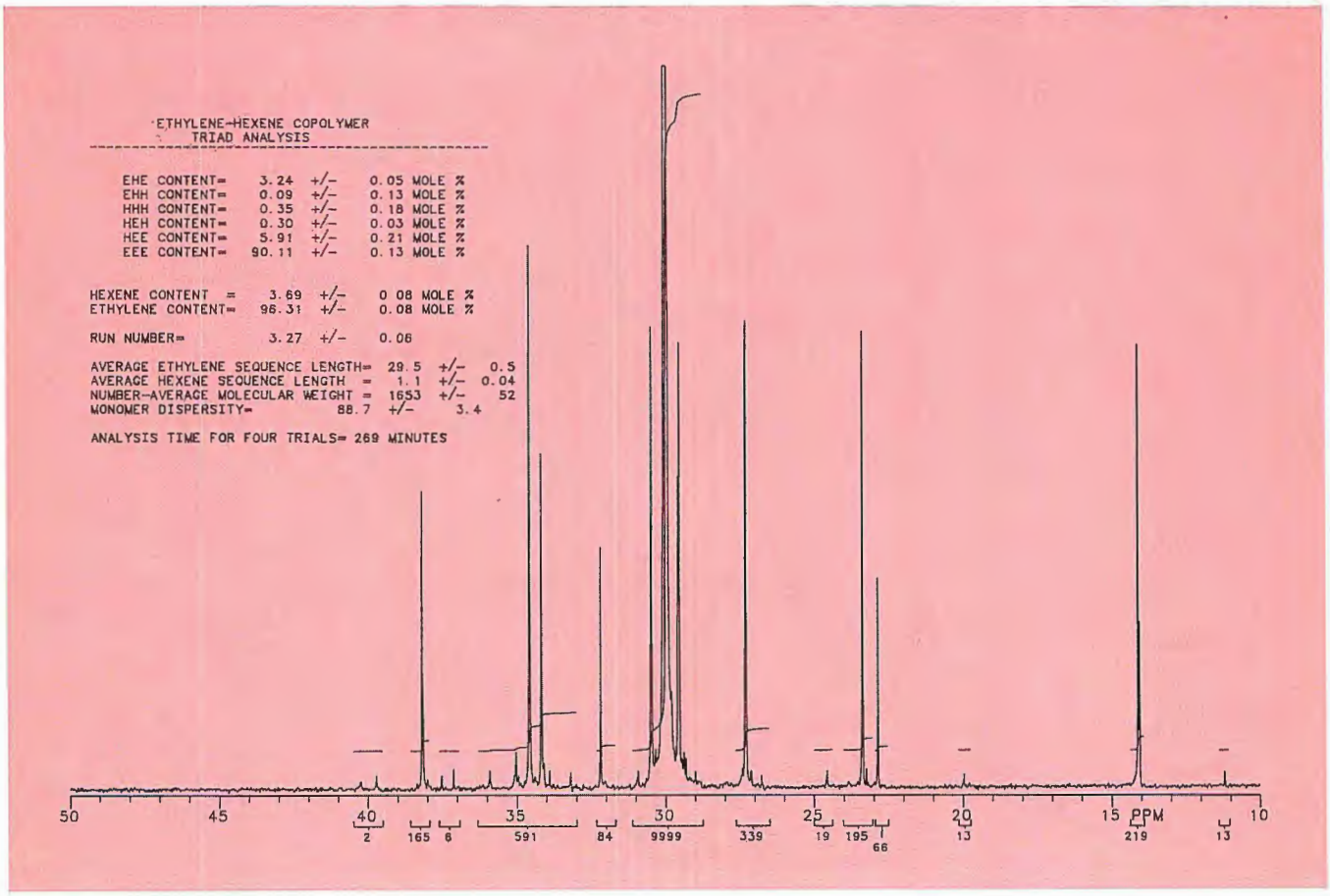


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DEPARTMENT OF CHEMISTRY

FOR ENQUIRIES REGARDING THIS LETTER TELEPHONE:

July 7, 1986 (Received July 17, 1986)

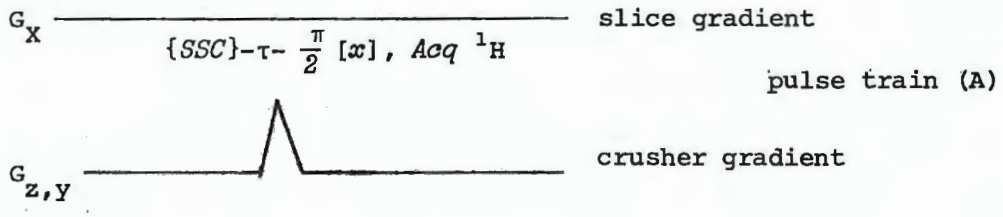
Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station, 77843,
U.S.A.

Gradient Encoded Volume Selection Techniques for Spectroscopy

Dear Barry,

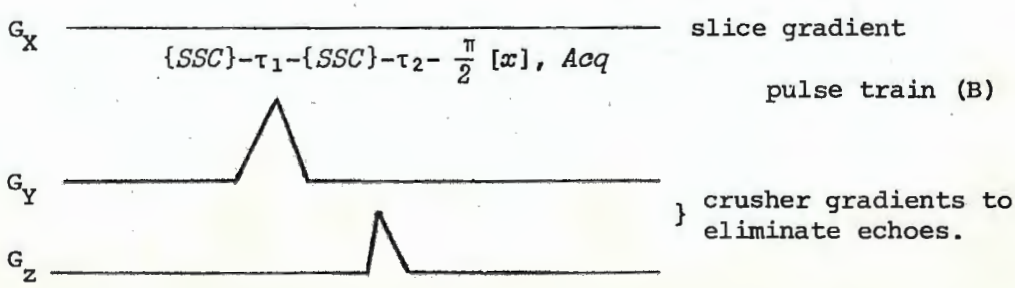
Please note the change of address for me; in future the newsletter and colourful reminders should be sent to the above address.

The group has been spending a lot of time looking at gradient encoded volume selection techniques for spectroscopy. Z-Slicing appears by far to offer the best of all worlds, however, the accuracy of the z-slice is critical. We have used a sin-sinc pulse [waveform $F(t) = sin\alpha t sin\beta t/\beta t$] to excite the $^1H$ NMR spectrum of a cube of water in the presence of a field gradient. The pulse sequence is




With pulse train (A) the z-magnetization profile is shown in figure 1(c); figure 1(A) is the calculated magnetization profile.

The slice definition can be improved by repeating the sin-sinc, {SSC}, pulse. The pulse train is now



Magnetization profiles are shown in Figures 1(B) and 1(D). Note the excellent slice definition. These "spectra" were recorded using $\alpha = 3.0$ and $\beta = 3.5$. Setting $\alpha = 7.0$ and $\beta = 7.5$ yields the slice profile shown in Figure 2. Volume selected spectroscopy is now performed by turning the gradient off and reading the magnetization using a hard pulse.

Your readers may be in some pulse power requirements: a 22cm homemade saddle coil was used (tuned to 100 MHz), a 6.0 kwatt hard pulse yielded a 90° pulse of 32 μseconds. A 2.048 msecond {*SSC*} pulse with pp power of 800 watts was used when $\alpha = 7.0$ and 7.5.

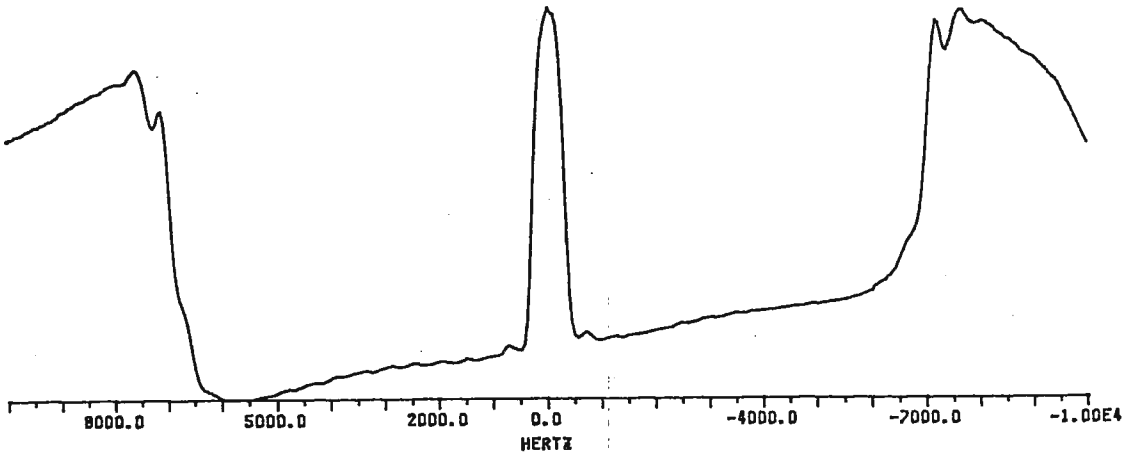
I trust this note will stop all the colourful lists of paper - at least for a short time.

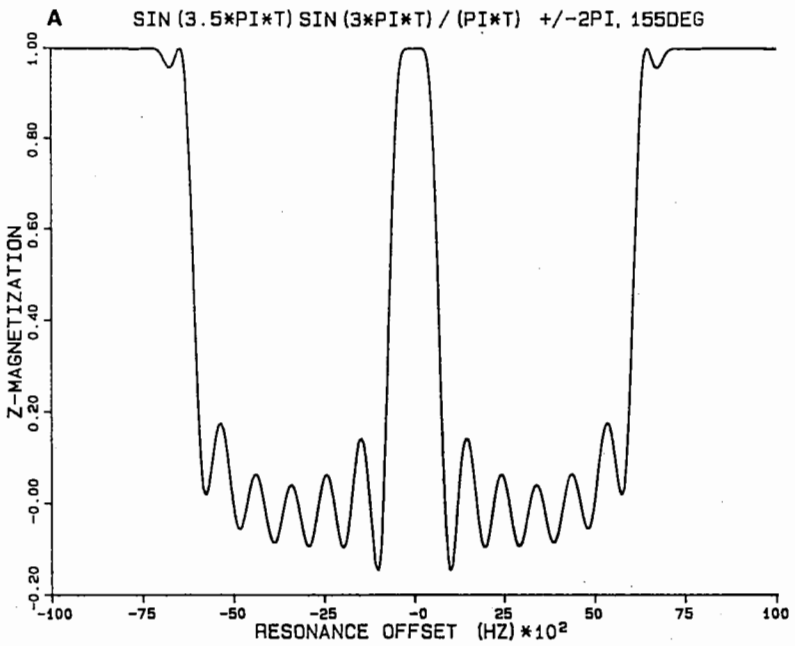
I wrote this letter, Bill Brooks, Graham Galloway did the experiments, Chad Field built the probe and rebuilt the Bruker MSL-100 and Mark Bulsing and the computing centre did the calculations.

A preprint is available,

Best regards,

D.M. DODDRELL
Professor of Chemistry.




A
SIN (3.5*PI*T) SIN (3*PI*T) / (PI*T) +/-2PI, 155DEG
Z-MAGNETIZATION
1.00
0.80
0.60
0.40
0.20
-0.00
-0.20
-100
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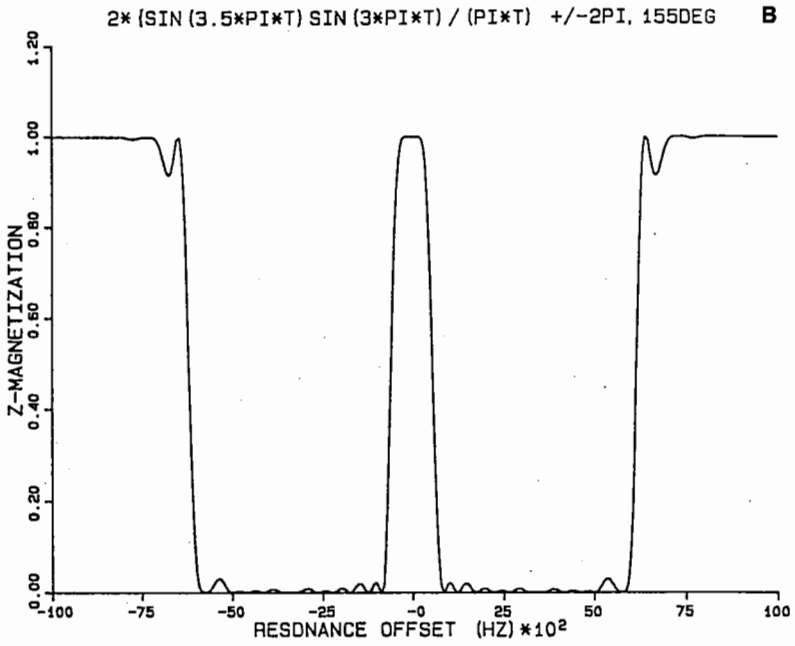
75
100
RESONANCE OFFSET (HZ) *10²


2* (SIN (3.5*PI*T) SIN (3*PI*T) / (PI*T) +/-2PI, 155DEG
B
Z-MAGNETIZATION
1.20
1.00
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0.60
0.40
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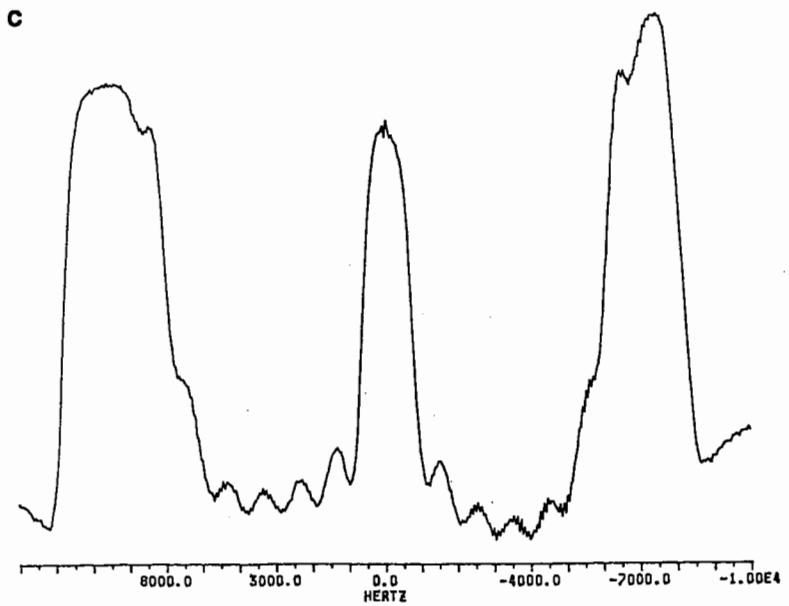
RESONANCE OFFSET (HZ) *10²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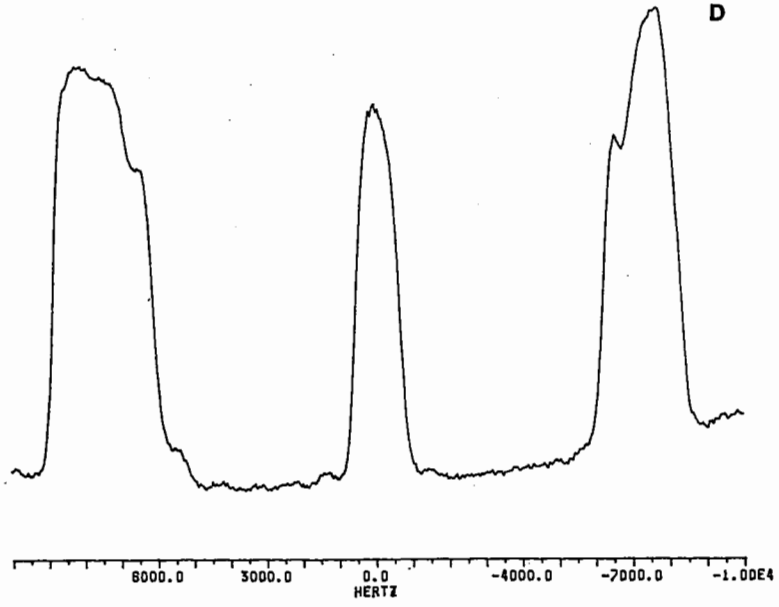
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HERTZ

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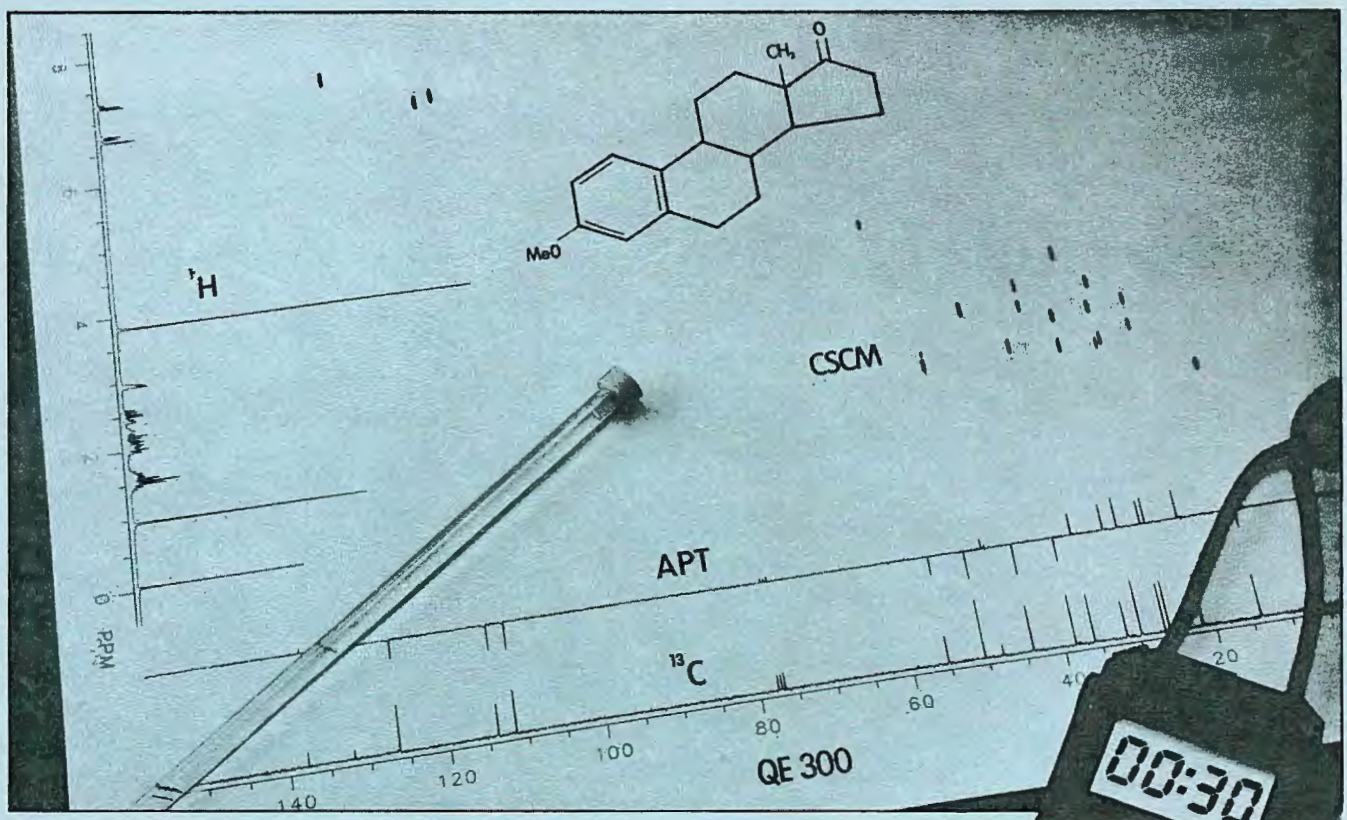


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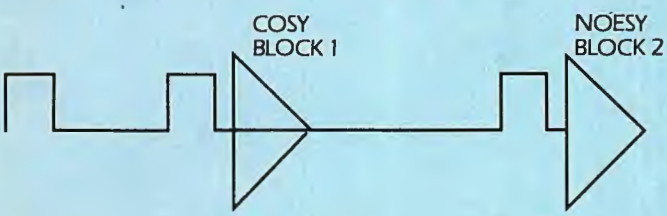


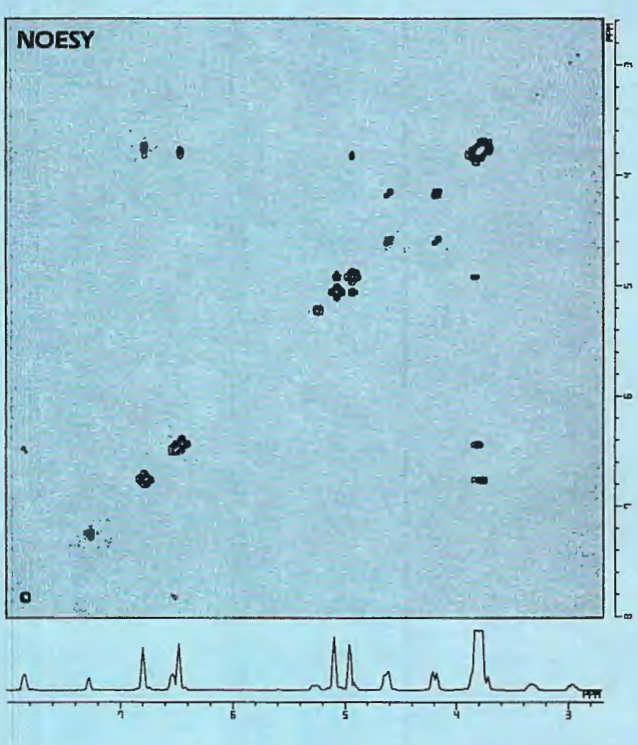


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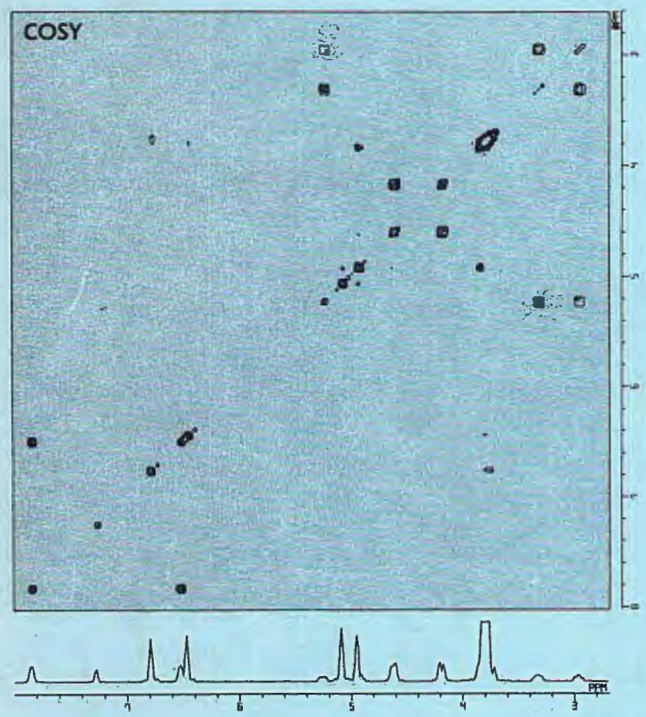


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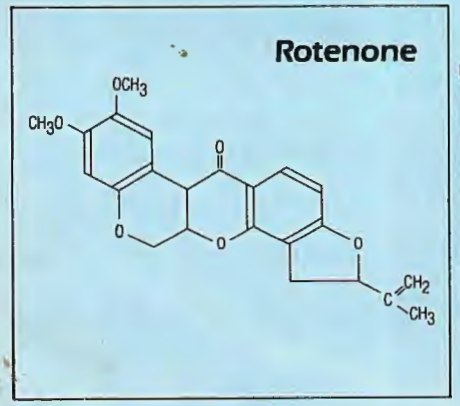

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