THE NMR NEWSLETTER

No. 441

June 1995

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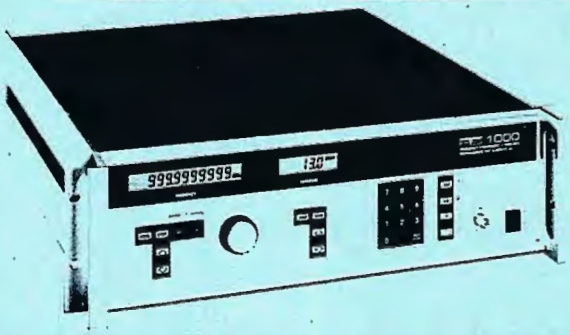
	Frequency Range	Resolution	Switching Time[1]	Phase-Continuous Switching[2]	Rack-Mount Cabinet Dim.[3]	Remote-Control Interface	Price Example[4]
PTS 040	.1-40 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$5,330.00 (1 Hz resol., OCXO freq. std.)
PTS 120	90-120 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$5,330.00 (1 Hz resol., OCXO freq. std.)
PTS 160	.1-160 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$6,495.00 (1 Hz resol., OCXO freq. std.)
PTS 250	1-250 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$7,440.00 (1 Hz resol., OCXO freq. std.)
Type 1 **PTS 310** Type 2	.1-310 MHz	1 Hz	1-20μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	1 Hz resol., OCXO: $6,425.00 1 Hz resol., OCXO: $5,850.00
PTS 500	1-500 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,720.00 (1 Hz resol., OCXO freq. std.)
PTS 620	1-620 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$9,625.00 (1 Hz resol., OCXO freq. std.)
PTS 1000	0.1-1000 MHz	optional .1 Hz to 100 KHz	5-10μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$11,830.00 (1 Hz resol., OCXO freq. std.)
PTS 3200	1-3200 MHz	1 Hz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$14,850.00 (1 Hz resol., OCXO freq. std.)
PTS x10	user specified 10 MHz decade	1 Hz	1-5μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	$3,000.00 (1 Hz resol., OCXO freq. std.)
PTS D310	two channels .1-310 MHz	.1 Hz	1-20μs	standard	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,560.00 (.1 Hz resol., OCXO freq. std.)
PTS D620	two channels 1-620 MHz	.1 Hz/.2 Hz	1-20 μs	standard	5¼"H×19"W	BCD (std) or GPIB (opt)	$13,240.00 (.1 Hz/.2 Hz resol., OCXO freq. std.)



1 Switching Time is dependent on digit (decade) switched; see detailed instrument specifications.

2 For applicable digits, see detailed instrument specifications.

3 Bench cabinets are 17" wide.

4 Prices are U.S. only and include Manual and Remote (BCD) Control; PTS 3200 Digital Front Panel.

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FORTHCOMING NMR MEETINGS

Summer School on "Isotope Effects as Tools in Basic and Environmental Research", Roskilde, Denmark, **June 24 - 28 1995**; Contact: Prof. P. E. Hansen, Fax +45 4675-7721, or Phone +45 4675 7781-2432 or +45 4675-7711, ext. 2432; . See Newsletter 438, 39.

Workshop on "Structure Determination from NMR", Pittsburgh Supercomputing Center, Pittsburgh, PA, **June 25 - 28 1995**; Contact: N. C. Blankenstein: blankens@psc.edu or (412) 268-4960. See Newsletter 438, 29.

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995**; Contact: Dr. J. F. Gibson - See Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. W. A. Bubb, Dept. of Biochem., Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-351-4120; Fax: +61-2-351-4726; Email: ismar95@biochem.su.oz.au. See Newsletter 437, 20.

NMR Symposium at the 37th Rocky Mountain Conference on Analytical Chemistry, Denver Colorado, **July 24-27, 1995**; Contact: Dr. Alexander J. Vega, DuPont Central Research and Development, P.O. Box 80356, Wilmington, DE 19880-0356; Tel. (302) 695-2404; Fax: (302) 695-1664; e-mail: vega@esvax.dnet.dupont.com. See Newsletter 432, 34.

3rd Scientific Meeting, Society of Magnetic Resonance, and 12th Meeting European Society for Magnetic Resonance in Medicine and Biology, Nice, France, **August 19 - 25, 1995**; Contact: Society of Magnetic Resonance, 2118 Milvia St., Suite 201, Berkeley, CA 94704; Tel. (510) 841-1899; Fax: (510) 841-2340.

Western Biotech Conference, San Diego, CA, **October 18 - 21, 1995**; Contact: Western Biotech Conf. Registr'n., c/o Tom Lobl, Tanabe Research, 4540 Towne Centre Court, San Diego, CA 92121; Tel. (619) 622-7035; Fax: (619) 622-7080; E-mail: tjlobl@cerf.net.

37th ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **March 17 - 22, 1996***[sic]*; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073.

38th ENC (Experimental NMR Conference), Orlando, FL, **March 23 - 27, 1997***[sic]*; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073.

Additional listings of meetings, etc., are invited.

SYRACUSE UNIVERSITY

DEPARTMENT OF CHEMISTRY

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Prof. Bernard L. Shapiro
Editor/Publisher
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

May 24, 1995
(received 5/27/95)

Re: Two water signals in DMSO-d_6

Dear Professor Shapiro,

It is well known that in pure DMSO-d_6 there are two water signals; the main signal is accompanied by another, smaller resonance at somewhat lower fields. It seemed to be an interesting question what is the origin of this double signal. There were suggestions (thanks for our colleagues on the ***str-nmr@net.bio.net*** news-group) that it is either a result of strong solvation or simply that of an isotope effect. Although the answer could seem obvious for many, we decided to run a simple experiment. The result is shown on Figure 1.

We have recorded the spectrum of a pure DMSO-d_6 sample (0.5 ml) at 500 MHz and room temperature *(a)*, then added a tiny amount of D_2O (only 0.75 µl). The signal at lower fields increases significantly *(b)*. With more (30 µl) D_2O the signals collapse into one *(c)*. This tells two things: the duplicate signal is indeed a result of isotope shift ($^1H^2HO$), and this is a very sensitive probe for the presence of exchangeable deuterium. Careful analysis of the duplicate signals can reveal kinetics for the process:

$$^1H^1HO + {}^1H^2HO \longleftrightarrow {}^1H^2HO + {}^1H^1HO$$

in this environment. Also, there might be some application of this system as a probe for slow exchange phenomena involving deuterium.

Sincerely, with our best regards,

István Pelczer

Deborah Kerwood

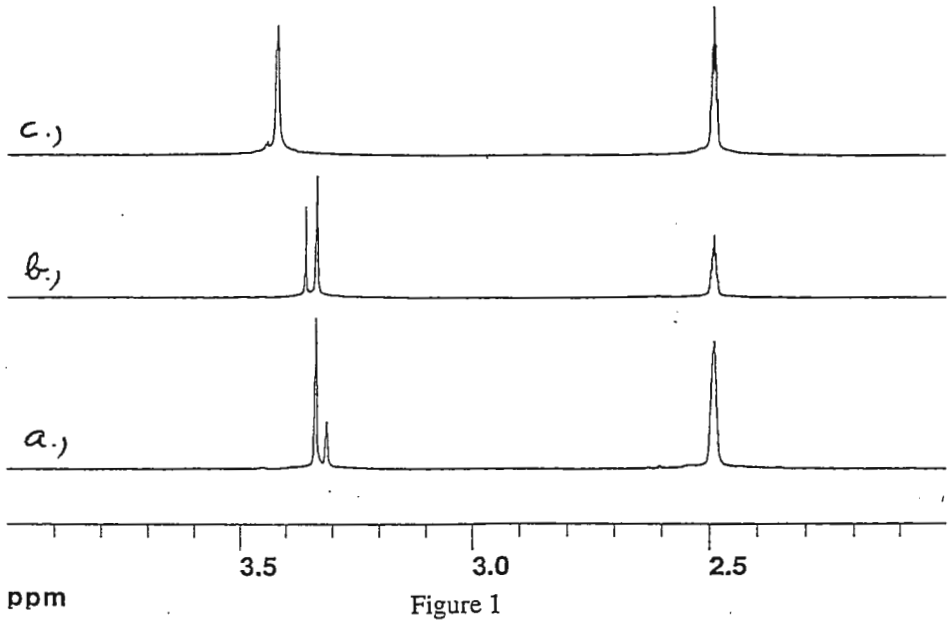
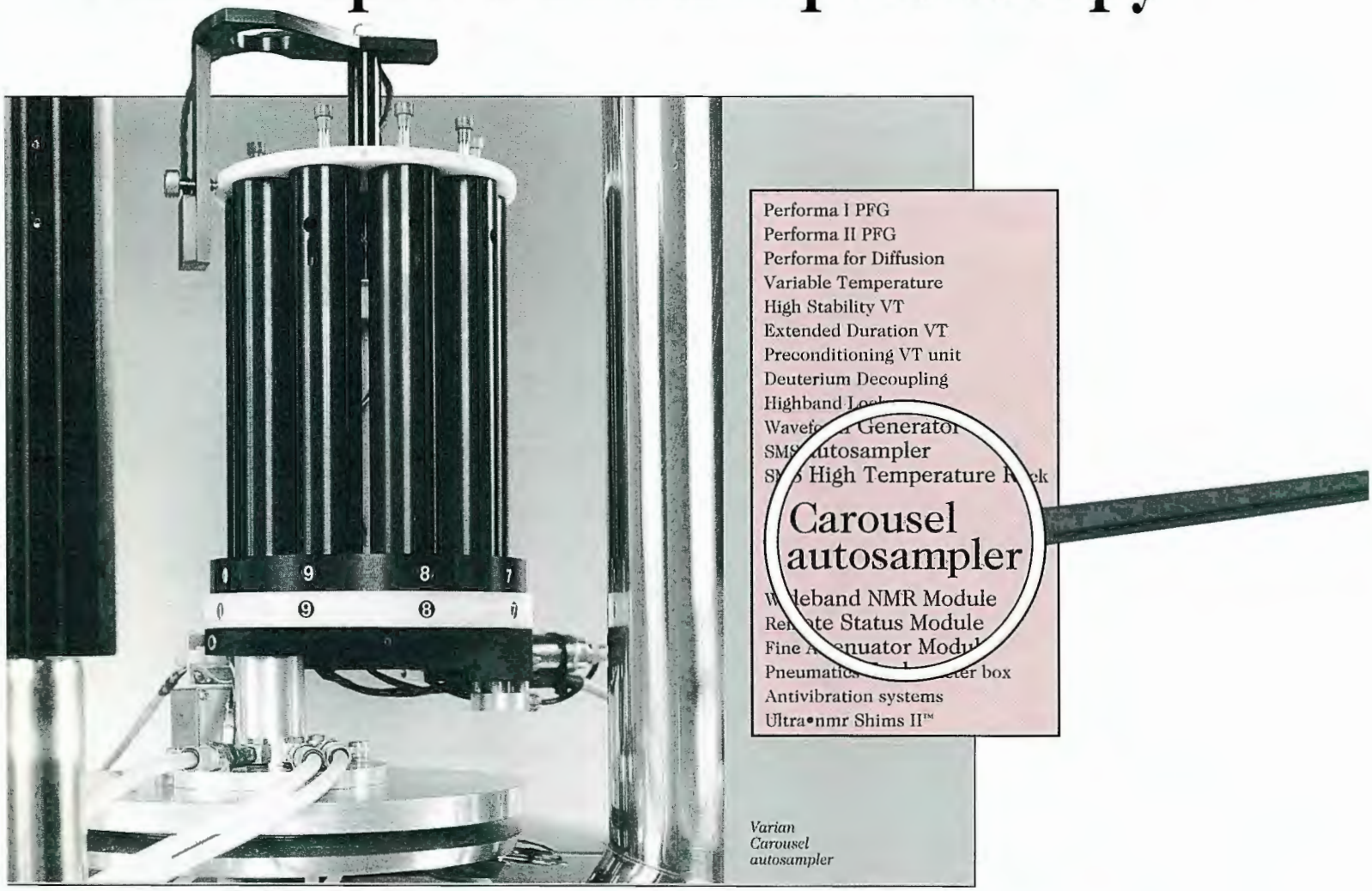


Figure 1

Varian Introduces New Carousel Autosampler for NMR Spectroscopy



Varian Carousel autosampler

The new Carousel autosampler from Varian provides a low-cost, reliable automation solution for a wide variety of NMR laboratory settings. The result of yet another joint development project with Zymark Corporation, the recognized leader in laboratory automation, the Carousel increases productivity with the latest state-of-the-art components.

Capable of running up to nine high resolution samples unattended, the Carousel allows completely random access to all sample locations, providing a more flexible automation system relative to competitive products. Sequential operation is not required and the priority of samples can be changed easily.

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The Carousel autosampler is compatible with all automated NMR consoles from Varian, including XL, VXR, Gemini, *GEMINI 2000*™, UNITY, UNITY*plus*™ and UNITY***INOVA***™. Please contact your local Varian sales representative for ordering information.

The first name in nmr...

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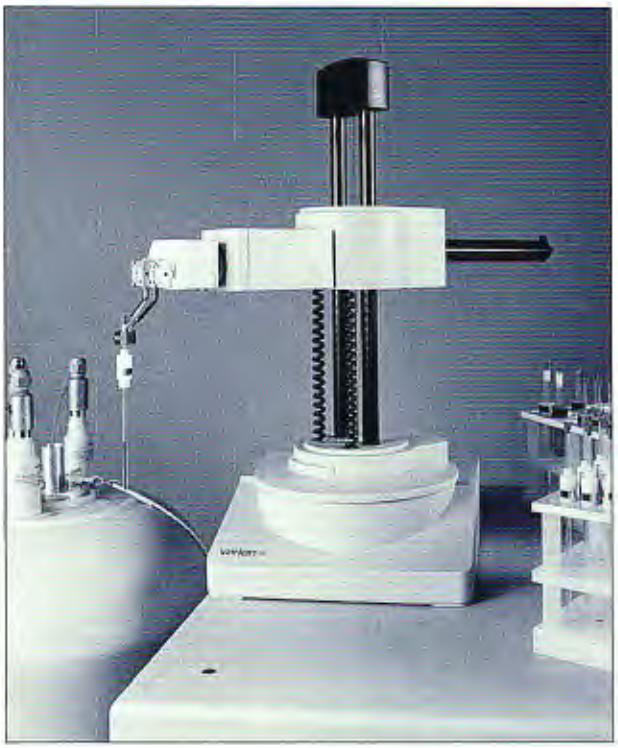

Highest Throughput

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State-of-the-art robotics minimizes the risk to equipment and samples while maintaining dependable automated operation. The self-calibrating system ensures reproducible positional accuracy while a tactile sensing capability provides verification of robot functions. Use of Varian's Auto•nmr™ probes with the SMS autosampler provides the most reliable automated NMR capability available.

Easiest Operation

Data acquisition and robot control are provided by the same computer, allowing users to focus on results, not additional software. Switching between walk-up and automation modes simply requires a single command, and sample submission is possible at any time due to easily accessible sample racks.

Features	Benefits
30-second full cycle sample change time	Fast turnaround of samples; increased productivity.
Self-calibration of autosampler	Reproducible positional accuracy.
Tactile sensing gripper	Securely holds sample during transport.
Integrated with NMR software	Same user interface as NMR console.
Available from 200 to 600 MHz	Many configurations possible.
50 or 100 sample racks	Rack selection can be based on throughput requirements.
Built-in flexibility	Accommodates 5-mm or 10-mm NMR tubes.

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MAG-8406/433

The University of Akron

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May 12, 1995 (received 5/16/95)

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

Solid State ^{33}S NMR

Dear Barry:

Our usual submissions to The NMR Newsletter often reflect the work that we are doing in high-resolution solution NMR of complex polymer systems. This time, I thought I might point out one of the more interesting studies that we are presently involved with which favors solid state NMR techniques.

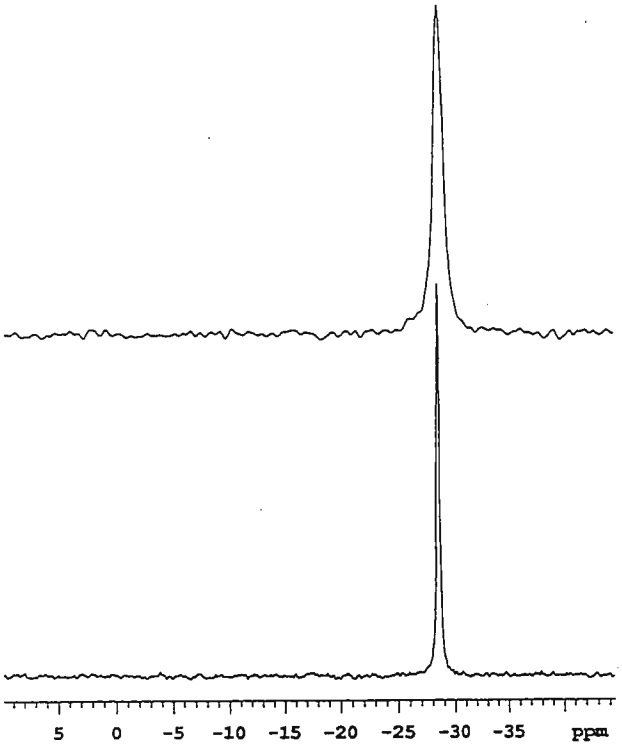
Currently, we are applying the use of our 4.7T and a 14.1T Unity+ systems to the study of ^{33}S in the solid state. As you know, this low gamma, quadrupolar nucleus (I=3/2) is typically observable only in systems with high electronic symmetry about the nucleus. Second-order quadrupolar interactions due to low electronic symmetry can broaden lines into the MHz region. One partial solution in reducing the second-order effects is to observe the nucleus at the highest field strength possible because the second-order quadrupolar broadening is inversely proportional to B_0. Another partial solution is rapid mechanical rotation about the magic angle at the highest speeds obtainable. Neither of these methods completely removes the broadening, but in combination they often have a profound effect on reducing ^{33}S chemical shifts with kHz linewidths, bringing them closer to routine observation.

Consider the spectra of calcium sulfide overlaid in Figure 1. The top spectrum was obtained at 15.34MHz with a MAS rate of 7.2kHz. The bottom spectrum was obtained at 46.02MHz, with a MAS rate of 12kHz. The table below compares some of the ^{33}S spectral properties at the two different field strengths.

One additional benefit of observing ^{33}S at 46MHz is the significant reduction of acoustic probe ringing which severely distorts spectra at lower fields. In fact, the small amount of residual ringing that distorts the first few points in the FID can easily be corrected with simple Linear Prediction (Figure 2). This allows one to avoid the use of multiple pulse sequences which often remove the effects of acoustic ringing, but severely limit the width of the observable spectral window.

Sincerely,

William A. Daunch **Peter L. Rinaldi**



^{33}S Frequency (MHz)	15.34	46.02
FWHH (Hz)	12.7	10.1
T1 (s)	23.8 ± 0.8	23.3 ± 1.3
S/N	58 : 1	146 : 1
sample mass (mg)	220.9	66.7

FIGURE 1: Spectral overlay of calcium sulfide ^{33}S signal observed at (A) 15.34MHz and (B) 46.02MHz. 10240 free induction decays were signal averaged for both using a single pulse experiment, 29 degree flip angles and a 3s recycle delay (Ernst approximation). The low-field sample underwent MAS at 7.2kHz; the high-field sample was spun at 12kHz. Approximate experiment time for both spectra was 9 hours.

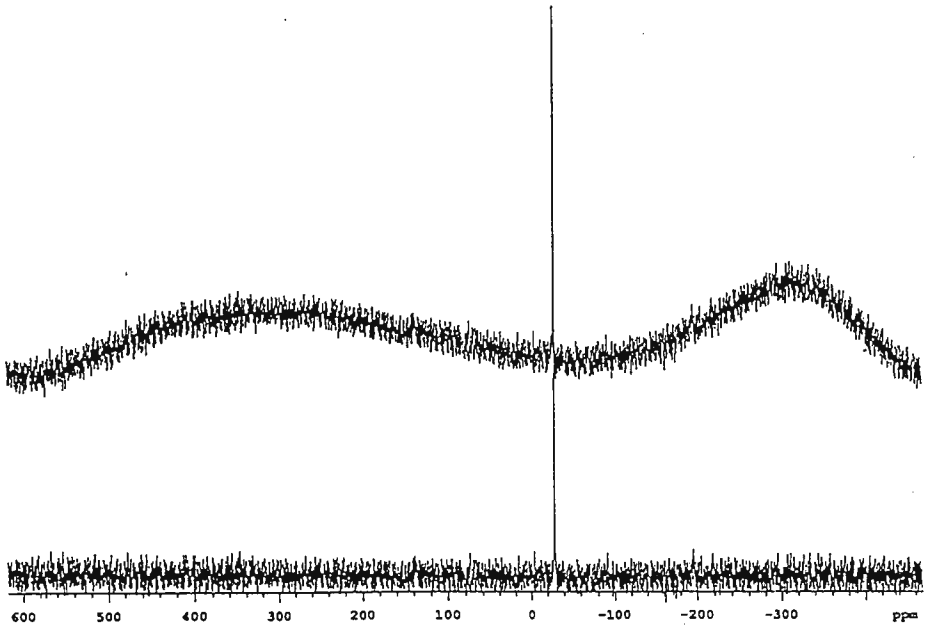


Figure 2: 46.02MHz one-pulse ^{33}S spectra of CaS with and without Linear Prediction of the first few points.

NATURAE SPECIES RATIOQUE

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A joint Institute of the University of Nijmegen and the Netherlands Foundation for Chemical Research

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

(received 5/15/95)
Nijmegen, 10 May 1995

Herzfeld and Berger CSA analysis and error estimates.

Dear Dr. Shapiro,

The Herzfeld and Berger analysis (1) is a convenient and widely used method to retrieve information about the chemical shift anisotropy from the intensities of spinning sideband patterns in Magic Angle Spinning spectra. As the graphical method proposed in the original paper can be somewhat tedious I wrote a PC-based program that minimizes the least squares sum of the errors using a simplex routine. I gave this program to several colleagues who all found it very useful. A few years ago, when Rod Wasylishen from Dalhousie University visited our lab, he also showed some interest in the program. For his purposes the original Herzfeld and Berger tables where far too limited, however, as he studied system displaying large chemical shift anisotropies. He and his student Bill Power therefore extended the tables to include -15 to +15 sidebands and μ-values up to 30. I adapted my program to work with these extended tables and we have been using it to our satisfaction for quite some time now. Triggered by some work on large phosphorus tensors in phosphaalkene compounds I got interested in the accuracy of the method. Surprisingly there is hardly any literature about this except for the paper of Clayden et al. (2) who look somewhat into this problem but to do no systematic error analysis. Therefore I decided to look into this problem, and got some surprising results. I took the approach described in chapter 14 of the Numerical Recipes by Press et al. (3). The program now computes the goodness-of-fit of the model considering the degrees of freedom. I found that this goodness of fit is not very high in many cases when I use the spectral signal to noise ratio to estimate the error in the sideband intensities. The next step was to Monte Carlo simulate a great number of datasets, varying the sideband intensities using the signal to noise ratio. To my surprise the simulation showed hardly any variation of the model parameters μ and ρ, even if I entered noise levels of 10-20% of the central line intensity. This means that the signal-noise is not the main error source in the sideband intensities of the experimental spectra.

Finally I decided to map out the χ^2-plane as a function of μ and ρ for a few examples as is demonstrated in the figure. First I looked at the ^{31}P-tensors in sodium dihydrogen orthophosphate and triphenyl phosphine oxide which where discussed in the paper of Clayden et al. The figure shows four contour levels, $\chi^2_{min}+0.05$, $\chi^2_{min}+1$, $\chi^2_{min}+2$, and $\chi^2_{min}+3$. Their claim that the error in ρ is larger for ρ close to ±1, clearly doesn't hold as it is similar in both cases. Inspection of the Herzfeld and Berger tables shows that the intensity contours run more and more parallel along the ρ-axis for small μ-values, thus the determination of ρ (i.e. the asymmetry) gets less and less accurate with decreasing μ. This is demonstrated for the ^{13}C tensor in polyoxymethylene and the ^{31}P tensor in a phosphaalkene. These tensors happen to have approximately the same ρ-value, but largely different μ. In case of the polyoxymethylene μ is small and there is a substantial spread in ρ. For the phosphaalkene we get a larger variation in μ, whereas ρ is very accurately determined. The χ^2-values obtained here were again calculated using the signal to noise ratio, the resulting distributions in μ and ρ are very small which also

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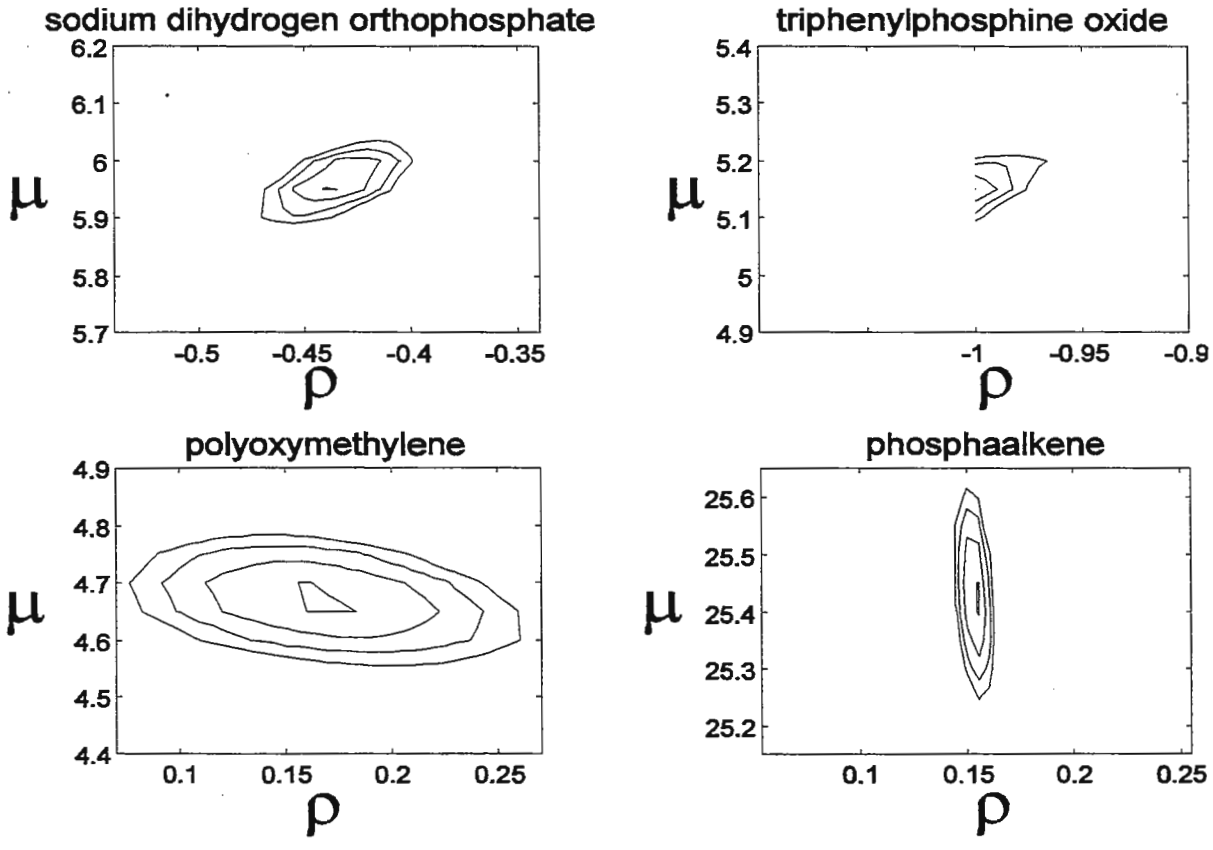
suggest that there must be other sources of errors in the experimental spectra that influence the sideband intensities.
Summarizing I can say that fitting sideband intensity data using the Herzfeld and Berger analysis is a stable procedure. The main sources of errors have yet to be identified, however, before reliable error estimates on the obtained model parameters can be given. I will make the fitting program with the extended tables available to those who are interested. (Please credit this contribution to the account of Prof. E. de Boer.)

Sincerely yours,

Arno Kentgens

(1) J. Herzfeld and A.E. Berger, J. Chem. Phys. **73**, 6021 (1980).
(2) N.J. Clayden, C.M. Dobson, L-Y. Lian and D.J. Smith, J. Magn. Reson. **69**, 476 (1986).
(3) W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, "Numerical Recipes", Cambridge University Press, Cambridge (1986).



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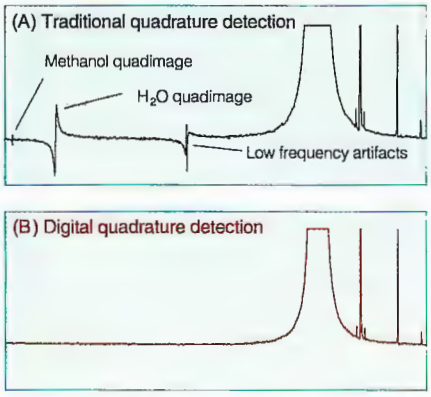

Bruker standard dynamic range sample, obtained with (B) and without (A) DQD

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Digital Quadrature Detection (DQD) is the next evolutionary step from analog to digital NMR. With DQD you can eliminate artifacts such as "center spikes", quad images, flicker noise and 50/60 Hz interference.

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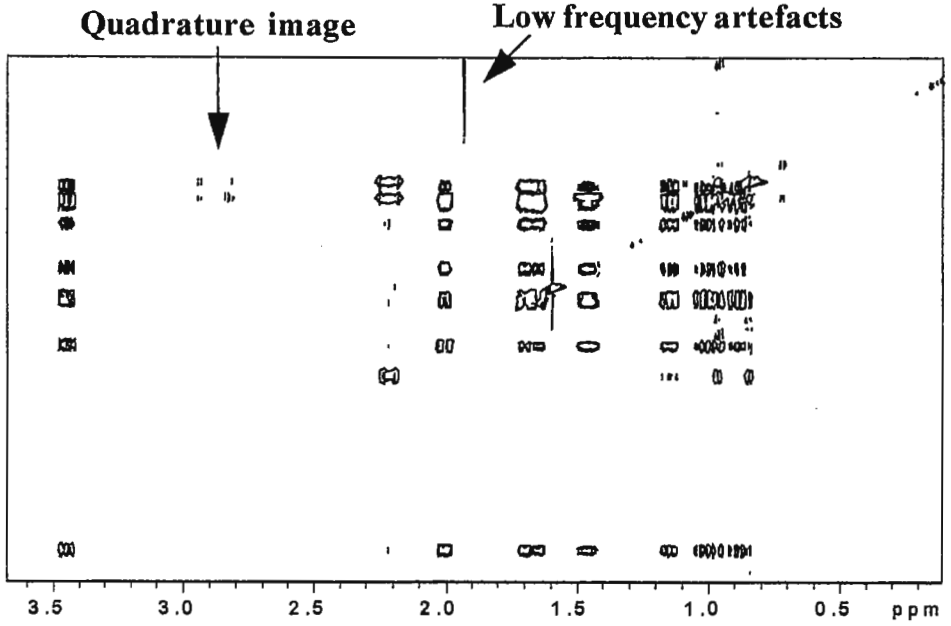

Fig 2d Traditional quadrature detection
1 scan per t1 increment 15 min.

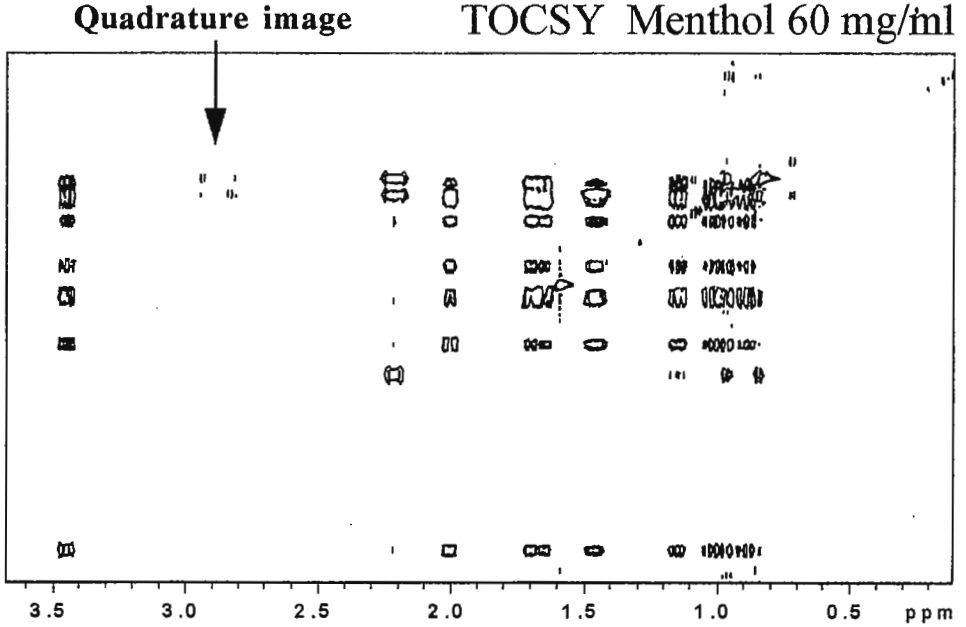

Fig 2c Traditional quadrature detection
2 scan per t1 increment 30 min.

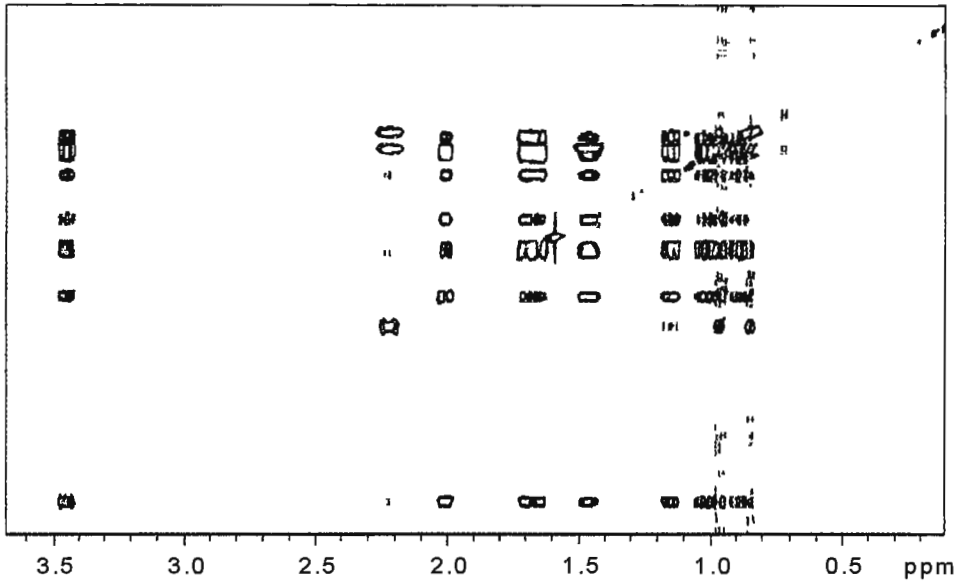

Fig 2a Digital quadrature detection
1 scan per t1 increment 15 min.

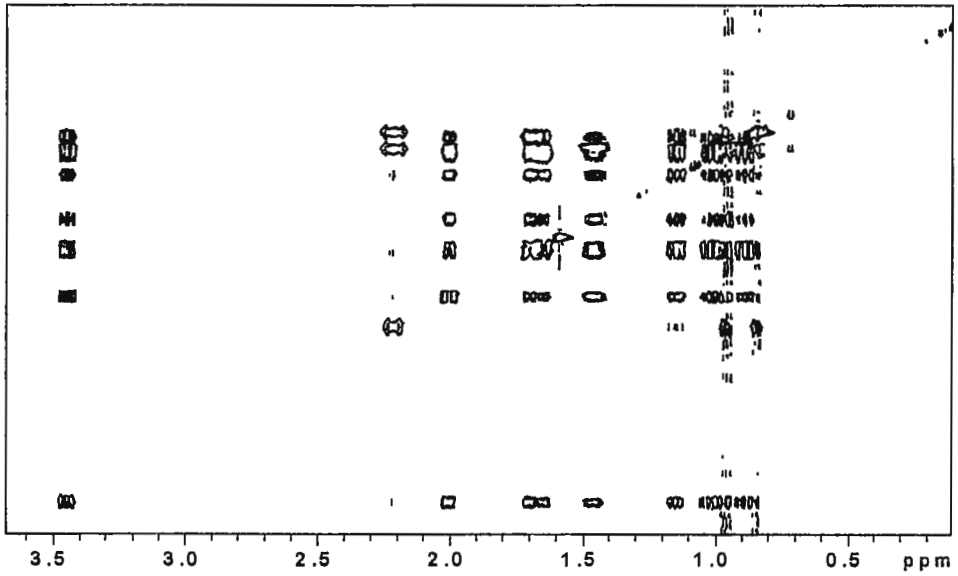

Fig 2b Traditional quadrature detection
4 scan per t1 increment 60 min.

NATIONAL TAIWAN UNIVERSITY

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

May 7, 1995
(received 5/15/95)

Re: **An evolution of ^{23}Na NMR spectra at an annealing of C_{60} fulleride intercalated by Na from sodium azide.**

Dear Dr. Shapiro:

The use of sodium azide (NaN_3) instead of Na vapor for the doping of C_{60} led to a formation of a superconducting $Na_xN_yC_{60}$ phase[1-3]. A superconductivity in Na-intercalated C_{60} strongly depends on annealing conditions: an annealing at moderate temperature (about 200 °C) improves it, while an annealing at high temperatures (≥300 °C) destroys superconductivity.

An evolution of ^{23}Na static and "magic angle spinning" (MAS) solid state NMR spectra of a Na-doped C_{60} with a nominal composition Na_1C_{60} prepared by the sodium azide thermal decomposition is studied in dependence on the annealing time and temperature. The ^{23}Na static NMR spectra (Fig.1) showed two lines at 51.6~52.2 ppm and at –2.8~4.2 ppm with respect to Na^+ in 1 M NaCl aqueous solution. The former line did not change position in MAS NMR spectra (Fig.2) and had 50.0 ppm shift. This line is assigned to Na^+ in tetrahedral interstitial site of the C_{60} lattice. The second line at –2.8~4.2 ppm was split in MAS spectra into several components, respectively, at 7.3 ppm, 5.0 ppm and –3.7 ppm, intensities of which were changed with an annealing. These lines are assigned, respectively to Na^+ ion, Na cluster, and undecomposed sodium azide, all possibly located in octahedral interstitial site.

1. K. Imaeda, I.I. Khairullin, K. Yakushi, M. Nagata, N.Mizutani, H. Kitagawa and H. Inokuchi, Solid State Commun. 1993, V.87, pp.375.
2 I.I. Khairullin, K. Imaeda, K. Yakushi and H.Inokuchi, Physica C 231 (1994) 26.
3. N. Yamasaki, H. Araki, A.A. Zakhidov and K. Yoshino, Solid State Commun.92 (1994) 547.

Sincerely,

I.I. Khairullin — Ilias. I. Khairullin

Lien-Tsung Chang — Wen-Tsung Chang

Lian-Pin Hwang — Lian-Pin Hwang

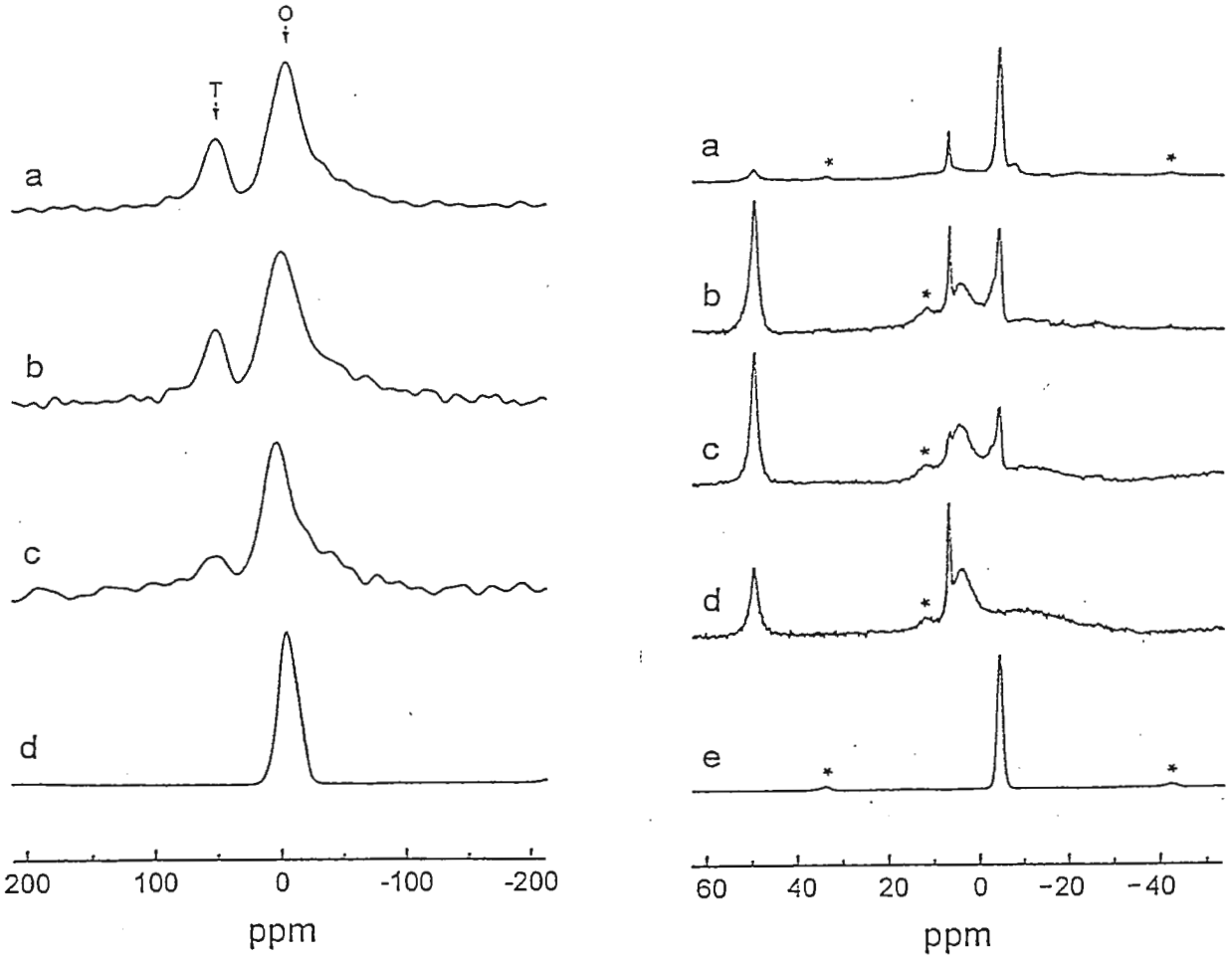

Fig. 1. Room temperature solid state ^{23}Na static NMR spectra displayed at different annealing stages for Na-doped C_{60} with a nominal compostion Na_1C_{60} prepared by sodium azide: a) after annealing first in dynamic vacuum of $5x10^{-5}$ torr at 470°C for 10 min, then at 350°C for 2.5 hours, and finally in a sealed tube at 200 °C for 2 days; b) after annealing at 200°C for 3 days; c) after annealing first in dynamic vacuum at 470 °C for 20 min, then in sealed tube at 200 °C for 5 days; d) the bottom spectrum is of NaN_3.

Fig. 2. Room temperature solid state ^{23}Na magic angle spinning (MAS) NMR spectra displayed at different annealing stages: a) after the first annealing at 200°C for 48 hours performed after the azide decomposition; b) after the second annealing first in dynamic vacuum of $5x10^{-5}$ torr at 470°C for 10 min, then at 350°C for 2.5 hours, and finally in a sealed tube at 200 °C for 2 days; c) after the third annealing at 200 °C for 3 days; d) after the fourth annealing first in dynamic vacuum at 470 °C for 20 min, then in a sealed tube at 200 °C for 5 days; e) the bottom spectrum is of NaN_3. Asterisks mark the spinning sidebands.

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UNIVERSITY OF OREGON

Dr. Barry Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

March 21, 1995
(received 5/11/95)

Dear Dr. Shapiro,

We have recently resurrected 3-pulse-2D ^{15}N-^{1}H correlation (1), (fig. 1a) for reasons outlined by Griffey and Redfield (2). This technique was abandoned because the spectra must be displayed in absorption mode which limits resolution. We append a z-filter to the original 3-pulse-2D experiment to eliminate the phase skew of the proton spins accumulated during t_1 and the two 1/2J delays. However, the z-filter destroys half of the signal so although this technique is simple, it is not sensitive. Resolution enhancement techniques introduced by Rance (3) allow us to both regain that signal and observe it in pure phase. We eliminate the gradient and use the z-filter pulses as a 180 degree proton pulse toggled on and off (fig. 2). Please credit this to the account of Rick Dahlquist.

Sincerely, David F. Lowry

References:

1) Bax, A., Griffey, R. H., and Hawkins, B. L. (1983). *J. Magn. Reson.* **55**, 301-315.
2) Griffey, R. H. & Redfield, A. G. (1987) *Quart. Rev. Biophys.* **19**, 51-82.
3) Cavanagh, J., & Rance M. (1993). *Annual Reports on NMR Spectroscopy* **27**, 1-58.

Fig 1

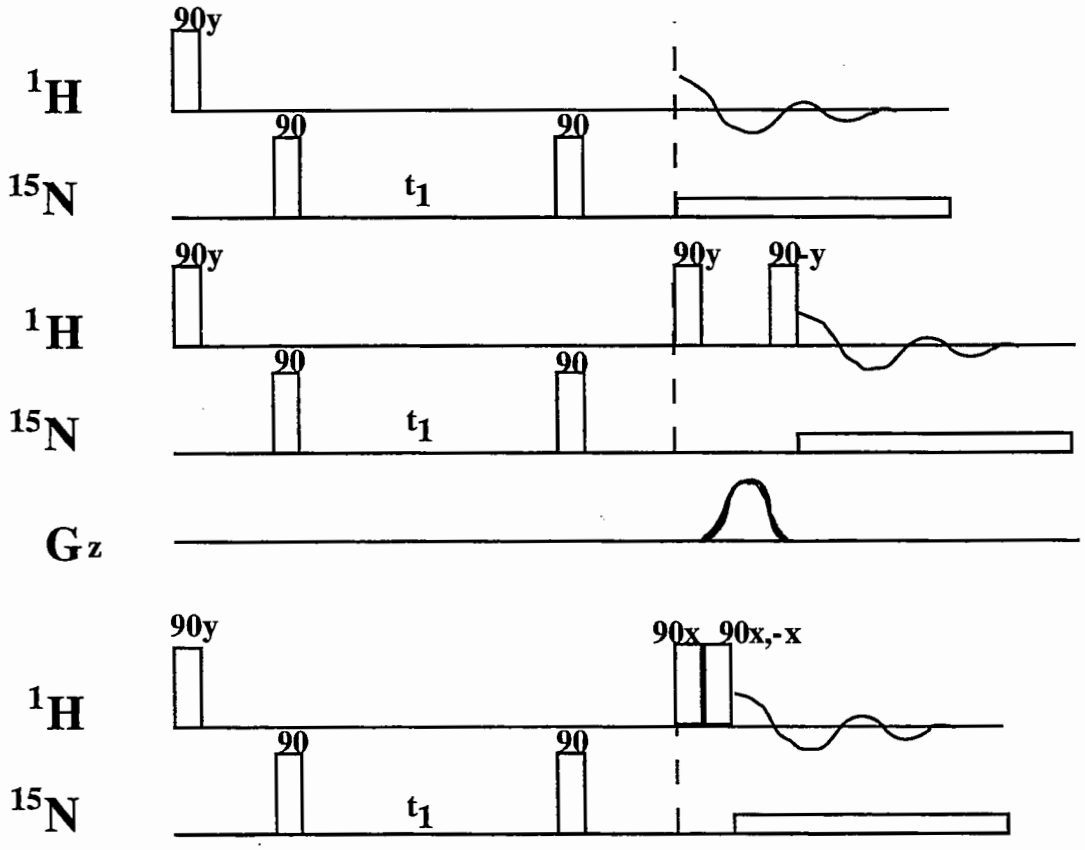

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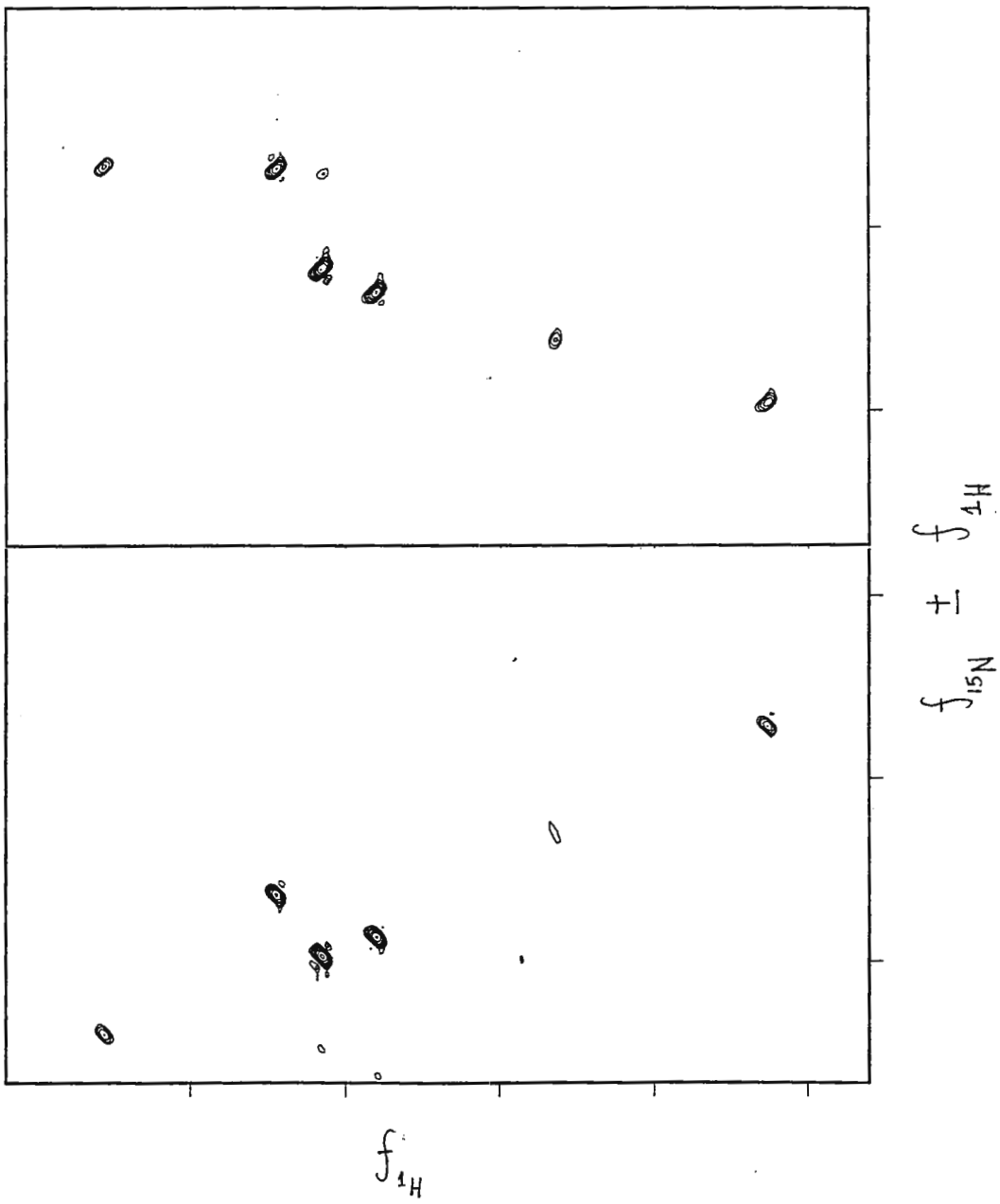
Figure 2



Pure ^{1}H-^{15}N sum and difference frequencies observed in pure phase with the sequence in figure 1c. The sample was [^{15}N]-methionine labeled CheY from E. coli at 17° C.

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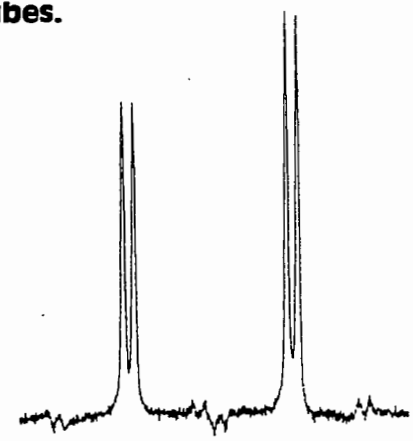
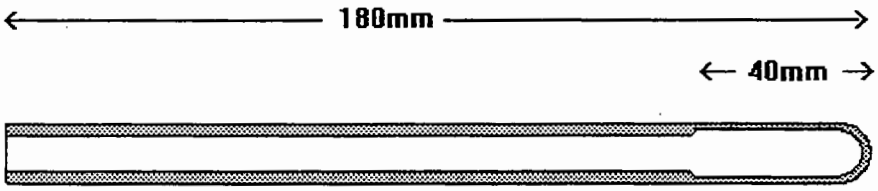


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



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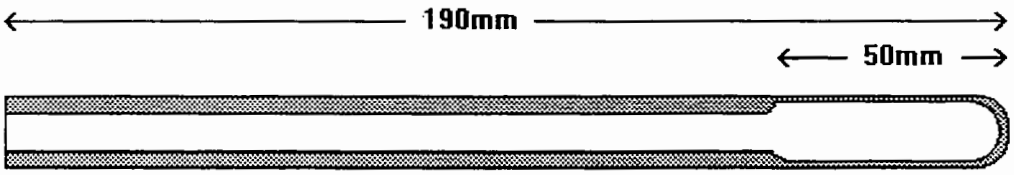

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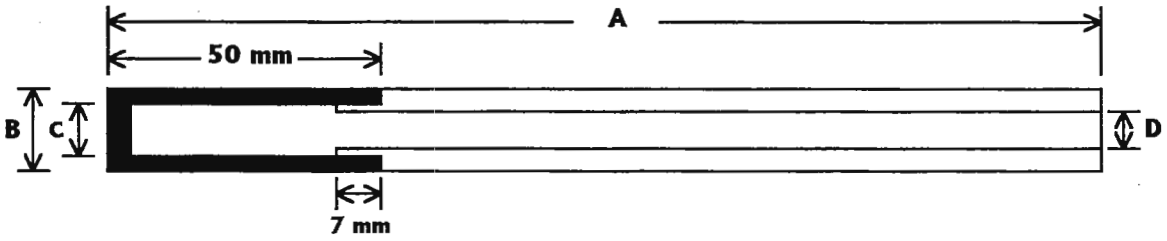

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IN REPLY REFER TO:

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

May 8, 1995
(received 5/10/95)

NMR Studies of Polyisoprene/Poly(vinylethylene) Miscible Blends

Dear Barry:

Miscible polymer blends are an exciting area for research, not only as a route to new materials, but also because they exhibit interesting behavior and may potentially reveal new physics. It is often most fruitful to investigate systems in which the structure and dynamics are not complicated by specific (chemical) interactions. There are a number of known miscible polymer blends; one which we have studied extensively over the past several years is the mixture of polyisoprene (PIP) and poly(vinylethylene) (PVE). Surprisingly, miscibility occurs over the entire composition range of this van der Waals mixture. A small angle neutron scattering study indicates that the interaction parameter, χ, which provides a measure of all noncombinatorial entropy contributions to the mixing free energy, is *negative*, despite the absence of specific interactions [1].

The origin for this negative enthalpy is revealed by measurement of the cross polarization cross relaxation rate T_{IS}^{-1}[2], as shown in the attached figure for the downfield vinyl carbon of PVE; similar results were found for the upfield vinyl carbon and the backbone carbons of ^{2}H PVE. By using dipolar dephasing to eliminate the complication of *intra*chain cross polarization, we are able to quantitatively compare *inter*chain separations in the blend versus the pure components. Specifically, we characterize the rate of cross polarization from protonated PVE or protonated PIP to perdeuterated PVE. The distance separating the carbon nuclei (of perdeuterated PVE) and hydrogen nuclei (of protonated PVE or PIP) is found to be *reduced* by blending. The reduction of *inter*chain distances in the blend results in a stronger van der Waals interaction and hence a negative interaction parameter.

A noteworthy feature of miscible blends is that the components can exhibit very different dynamics, notwithstanding the homogeneous morphology. "Dynamic heterogeneity" was in fact first observed in this same PIP/PVE blend using ^{13}C MAS solid state NMR spectroscopy [3]. This NMR technique is sensitive to the shape of the relaxation spectrum, as well as its temperature dependence [4].

A model was proposed [5,6] based on the idea that both the intrinsic mobility differences of the constituents and the distribution of local environments in a blend arising from concentration fluctuations give rise to the dynamic heterogeneities. This model predicts many of the well-known anomalies seen in miscible blends, such as broad glass transitions and the breakdown of the time-temperature superposition principle. Through combined mechanical and dielectric spectroscopies, the individual relaxation times for the PVE and PIP components were actually determined, and shown to be consistent with the blend model [7]. These results have recently been confirmed by two-dimensional deuteron exchange NMR measurements on the same system [8].

Regards,

K.J. McGrath J.B. Miller K.L. Ngai C.M. Roland

References:

[1] Tomlin, D.W.; Roland, C.M. *Macromolecules* **1992**, *25*, 2994.
[2] Roland, C.M.; Miller, J.B.; McGrath, K.J. *Macromolecules* **1993**, *26*, 4967.
[3] Miller, J.B.; McGrath, K.J.; Roland, C.M.; Trask, C.A.; Garroway, A.N. *Macromolecules* **1990**, *23*, 4543.
[4] McGrath, K.J.; Ngai, K.L.; Roland, C.M. *Macromolecules* **1995**, *28*, 2825.
[5] Roland, C.M.; Ngai, K.L. *Macromolecules* **1991**, *24* , 2261.
[6] Roland, C.M.; Ngai, K.L. *J. Rheology* **1992**, *36*, 1691.
[7] Alegria, A.; Colmenero, J.; Ngai, K.L.; Roland, C.M. *Macromolecules* **1994**, *27*, 4486.
[8] Chung, G.-C.; Kornfield, J.A.; Smith, S.D. *Macromolecules* **1994**, *27*, 5729.

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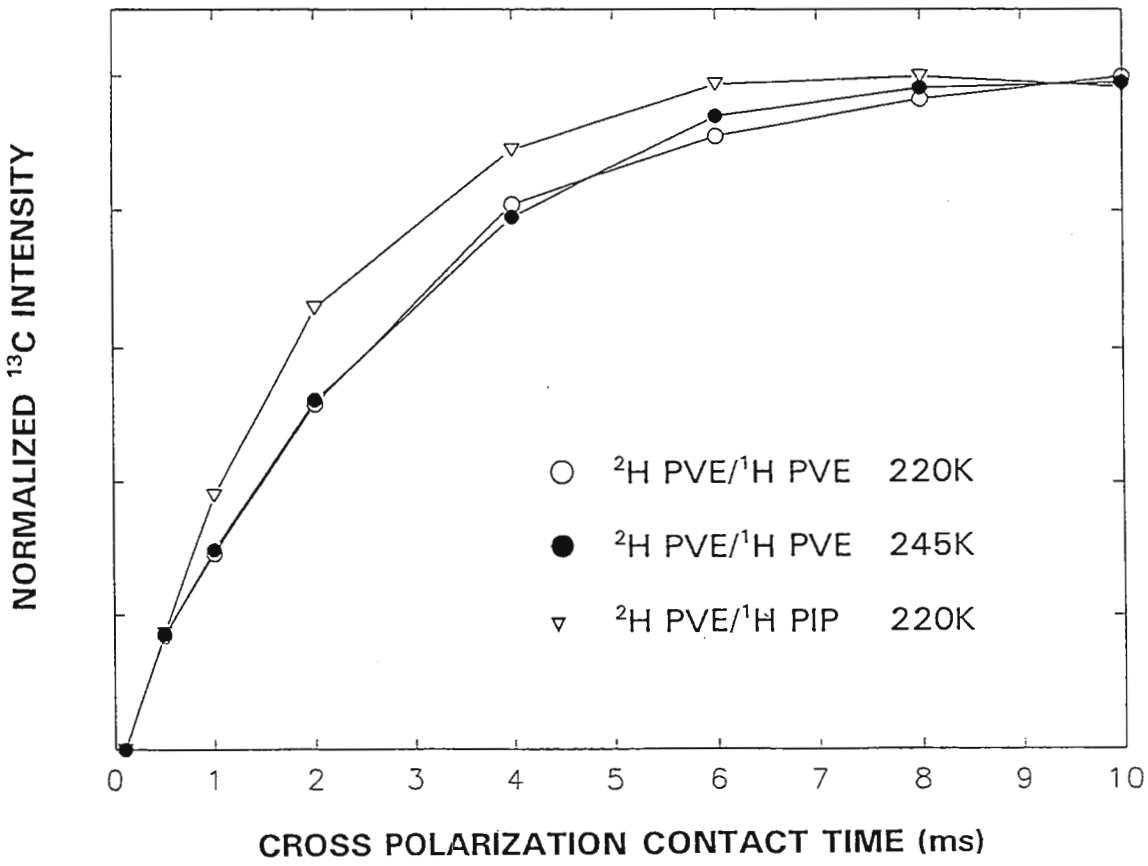

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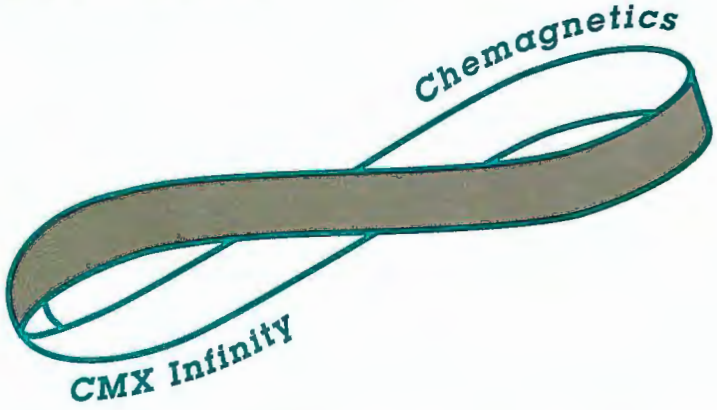

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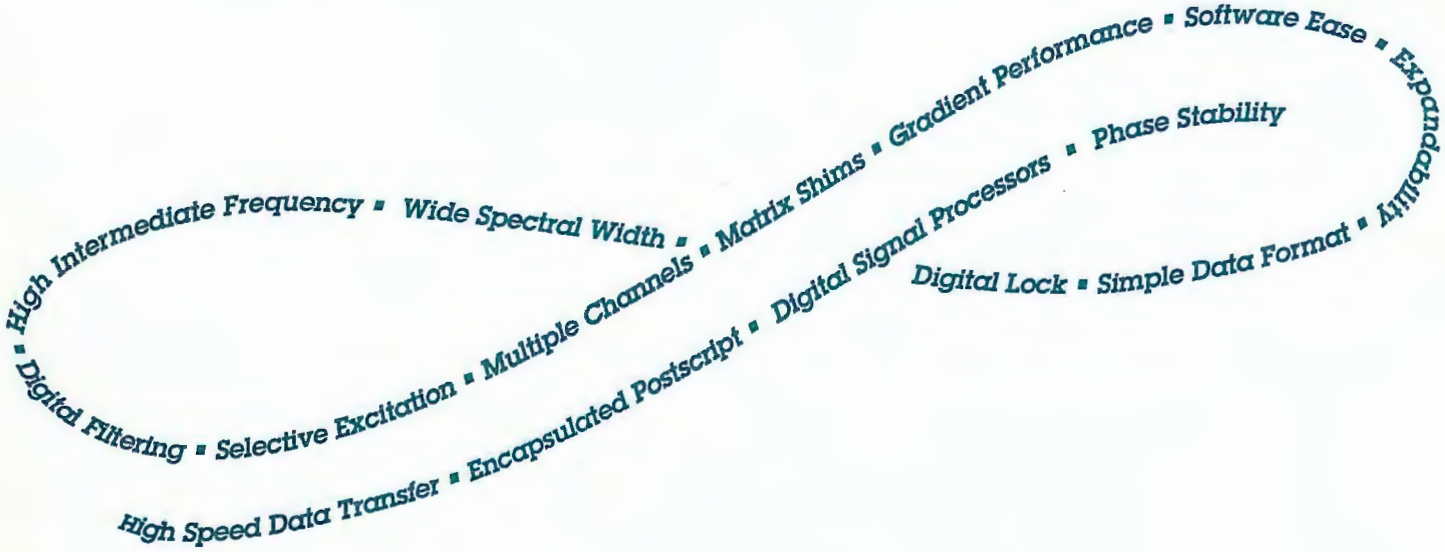

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From: Dr F. G. Riddell

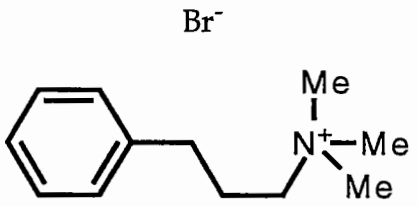
19 - 04 - 95
(received 4/25/95)

Prof. B. L. Shapiro,
The NMR Newsletter,
966 Elsinore Court,
Palo Alto, CA 94303,
USA

Dear Barry,

!Amazing molecular motions in a crystalline ammonium salt!

Whilst it is generally recognised that there are many examples of rotation and diffusion of whole molecules in the solid state it is less generally recognised how widespread examples of large-amplitude molecular motions are in molecular solids. We have recently come across an amazing example in which all parts of a crystalline ammonium salt display dynamic effects in its ^{13}C CP/MAS spectra attributable to large-amplitude molecular motions: trimethyl(3-phenylpropyl)ammonium bromide.

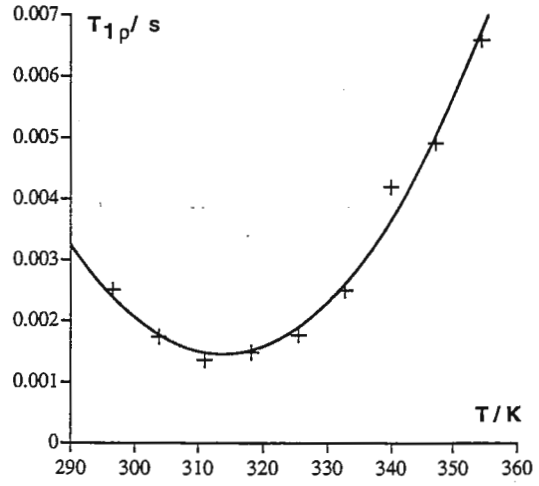


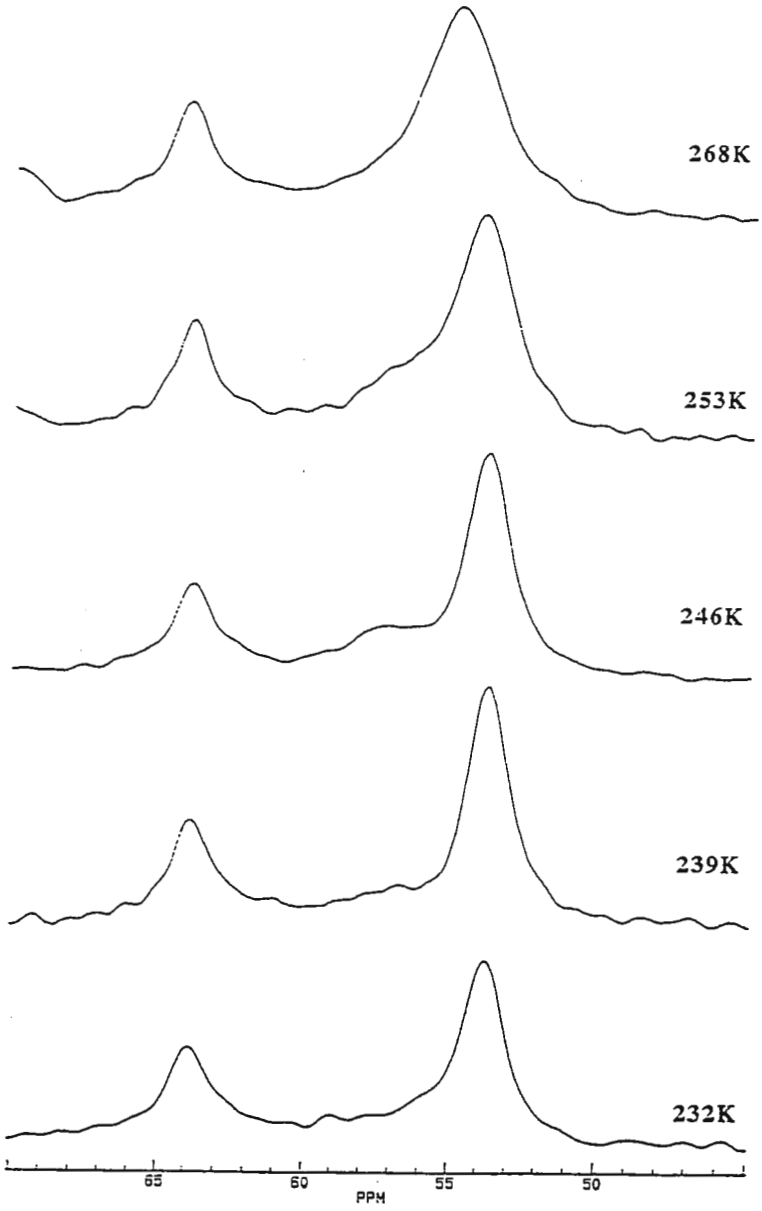
Firstly there is a coalescence of the carbon resonances in the phenyl group at ca 305K attributable to phenyl group rotation with an estimated $\Delta G^{\neq}_c$ of 55 kJ.mol^{-1}. Then at lower temperatures (ca 246K) there is a coalescence of the trimethylammonium group in which a shoulder splits off to the high frequency (LHS) of the main resonance $\Delta G^{\neq}_c$ ca 43.4 kJ.mol^{-1}. This coalescence arises from rotation of the trimethylammonium group. As the temperature is lowered further the shoulder broadens and reduces in intensity until it disappears. This is consistent with maximum dipolar broadening of the methyl resonance and an associated reduction in $T_{1\rho}$ giving a broadened signal with very poor cross polarisation efficiency. These in turn arise from the rate of rotation of the methyl group becoming similar to the precessional frequency of the nuclei in the decoupler and spin lock fields. With a decoupler field of ca 50kHz and a $T_{1\rho}$ minimum at 200K this gives an estimated $\Delta G^{\neq}_c$ of 30 kJ.mol^{-1}. The other methyls must be rotating more rapidly and have lower barriers to rotation.

It is possible to measure $T_{1\rho}$ values for the methyl group carbons at temperatures between ambient and 354K. A minimum for $T_{1\rho}$ is observed and the data allow an estimate of the energy of activation for the trimethyl ammonium group (Ea = ca 42 kJ.mol^{-1}) in good agreement with the free energy of activation from the coalescence.

Thus, this compound shows three dynamic processes in its ^{13}C CP/MAS NMR spectrum associated with complete rotation of essentially all parts of the molecule. In order of increasing activation energy they

are methyl rotation ($\Delta G^{\neq}_{200K}$ ca 30 kJ.mol^{-1}), trimethylammonium rotation (Ea = 41.6 kJ.mol^{-1}, $\Delta G^{\neq}_{246K}$ ca 43.4 kJ.mol^{-1}) and phenyl rotation ($\Delta G^{\neq}_{305K}$ ca 55 kJ mol^{-1}). The other two methyl groups must be rotating faster than the one we observe to broaden. The fact that all sections of the molecule in an ionic molecular solid that does not have globular molecules exhibit substantial rotations shows that commonly held prejudices about the rigidity of molecules in the solid phase need revision.





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Yours sincerely,

Frank

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Slobodan I. Macura, Ph.D.
Biochemistry and Molecular Biology

May 24, 1995
(received 5/30/95)

Heteronuclear Editing of Cross-Relaxation Networks

Dear Barry:

Recently, we have examined analytically the effects of various NMR magnetization exchange network editing (MENE) procedures, starting from equilibrium or nonequilibrium conditions, on generalized systems that undergo magnetization exchange (cross-relaxation and/or chemical exchange)[1]. Also, we described a new class of heteronuclear editing experiments in which the system starts from a nonequilibrium state and is edited during the mixing period. In an experimental application of this approach to the spectral analysis of a small protein, recombinant human ubiquitin (M_r 8565) labeled uniformly with ^{15}N and ^{13}C, we demonstrated how the cross-relaxation network of the protein can be decomposed simultaneously into subnetworks of ^{15}N-bound protons, aliphatic ^{13}C-bound protons, aromatic ^{13}C-bound protons, and ($^{12}C/^{14}N/O$)-bound protons. Such a decomposition permits the measurement of slower magnetization exchange rates, including those that are masked in conventional cross-relaxation experiments.

Figure 1 shows isotopically-assisted NOESY pulse sequences. (a) *[^{1}H-^{15}N]HMQC-NOESY.* the HMQC part of the sequence makes only the ^{15}N bound protons, which are labeled by their respective ^{15}N frequencies, observable during the evolution period. Signals from other protons are eliminated in repeated scans by virtue of the subtractive nature of the phase rotations. However, the magnetization from these invisible protons is finite during the mixing time, and thus contributes to spin-diffusion just as it would if the direct signals were visible. (b) *[^{1}H-^{15}N]HMQC-[^{1}H-^{13}C]BD-NOESY.* BIRD sequences during the mixing time selectively invert the ^{13}C-bound protons. Spins from protons attached to ^{15}N are only brought into the transverse plane for the period $k \cdot 2\tau_2$, where k is the number of BIRD sequences (inversions) during the mixing time. This effectively decomposes the cross-relaxation network into a submatrix of ^{15}N-bound protons and a submatrix of ^{13}C-bound protons. Since only the ^{15}N-bound protons are selected during the evolution period, the [^{1}H-^{15}N] HMQC-[^{1}H-^{13}C] BD-NOESY spectrum contains only cross and diagonal peaks from the amide region. Phase rotations were: φ_1 = 0000 2222; φ_2 = 02; φ_3 = 0022; receiver = 0220 2002. Delays: $\tau_1 = 1/(2J_{NH})$; $\tau_2 = 1/(2J_{CH})$. Quadrature in the evolution dimension was accomplished by time proportional phase incrementation (TPPI) of φ_2.

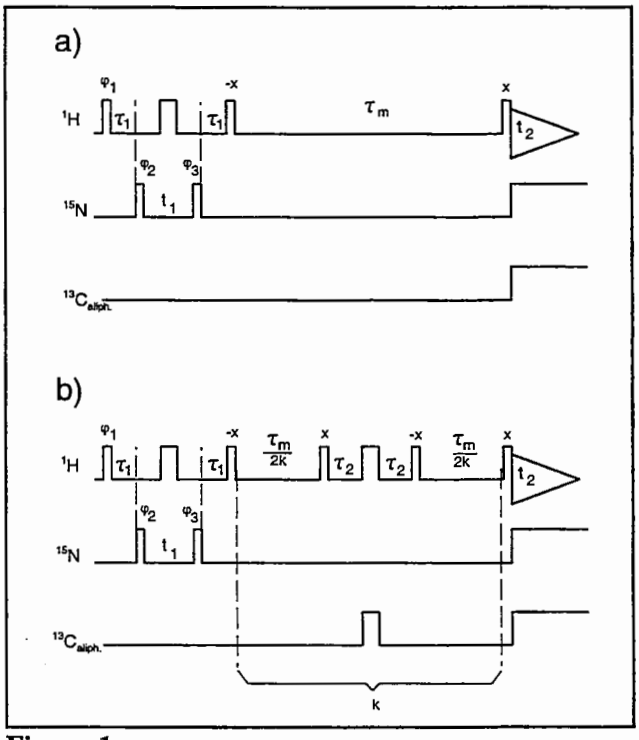


Figure 1

Figure 2 shows isotopically-assisted NOESY spectra of a small protein (recombinant human ubiquitin) labeled uniformly with ^{13}C and ^{15}N. (a) [^{1}H-^{15}N]HMQC-NOESY spectrum (mixing time τ_m = 300 ms) obtained by the pulse sequence from fig. 1a. The spectral width in the acquisition domain was 11 ppm and in the evolution domain 77 ppm. In the evolution 256 t_1 values were collected, each recorded with 128 scans and 1024 t_2 data points. The delay τ_1 was set to 5.2 ms. (b) [^{1}H-^{15}N]HMQC-[^{1}H^{13}C]BD-NOESY spectrum recorded with the pulse sequence from fig. 2b. All experimental settings were as in 3a, except that data were recorded with 256 scans. The delay τ_2 was set to 3.7 ms; the inversion pulse at ^{13}C(aliphatic) was semi-selective (70 μs). (c) Enlargements of the boxed regions of the spectra shown in 3a (left) and 3b (right). Comparison of the two panels shows how [^{1}H-^{13}C]-block decoupling (right) leads to attenuation of the cross-peaks G47/A46 and G47/K48 (left), which arise from the spin diffusion pathways depicted in 3a.

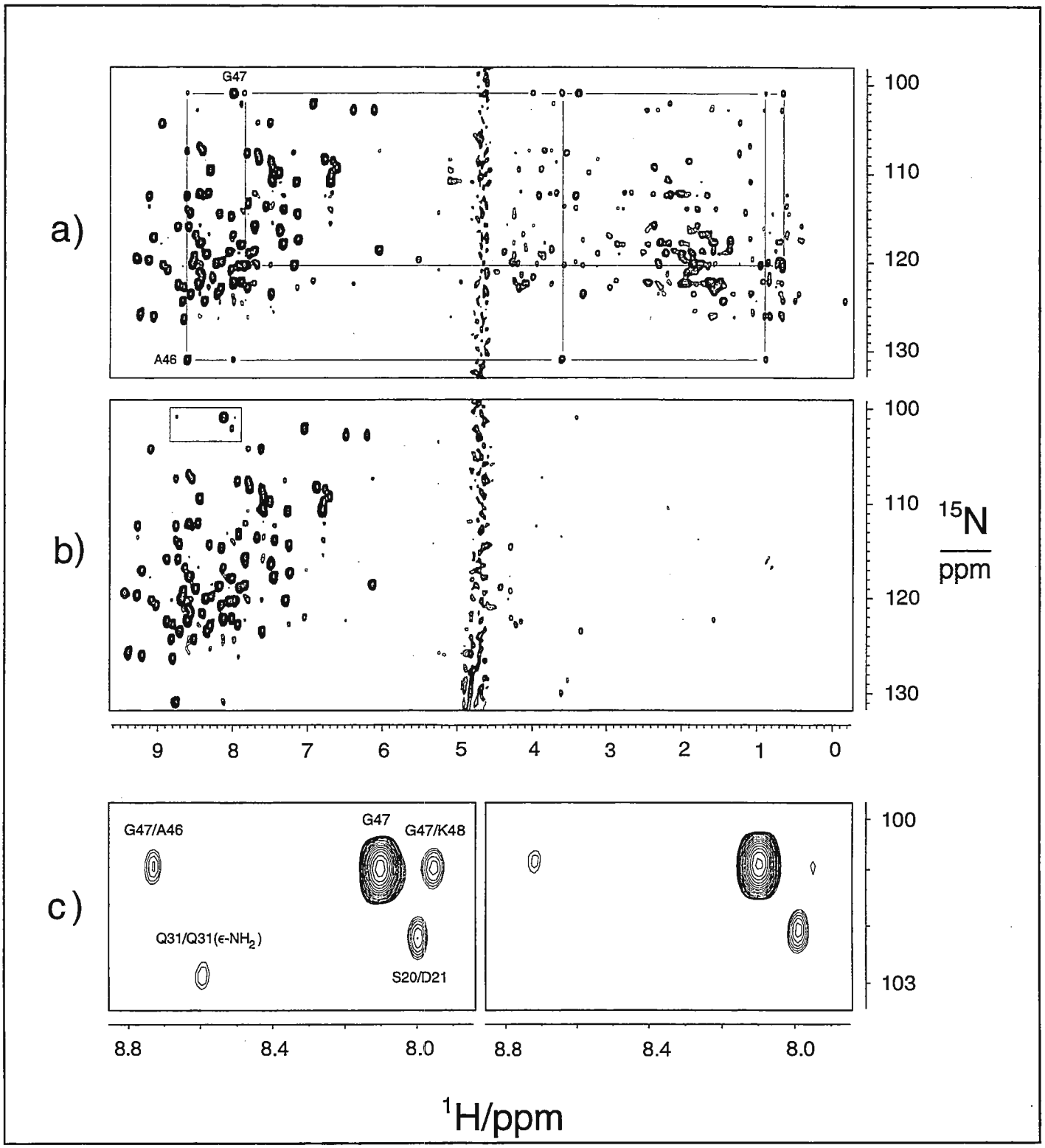


Figure 2

1. Zs. Zolnai, N. Juranić, J. L. Markley and S. Macura, Chemical Physics, in press

Sincerely yours,

Zsolt Zolnai, zsolt@kosi.nmrfam.wisc.edu
Nenad Juranić, juranic@mayo.edu
John L. Markley markley@barka.nmrfam.wisc.edu
Slobodan Macura macura@mayo.edu

SLOW MAGIC ANGLE TURNING IN SOLIDS

Chemical Shift Anisotropy (CSA) is an important indicator of the symmetry around nuclear sites. The CSA gives information about chemical structure, and can be used to determine structural parameters such as molecular conformation and protonation states.

The ideal experiment for obtaining CSA information in solids is a 2D measurement that presents spinning side band CSA patterns in the first dimension, and separates them according to their isotropic chemical shifts in the second dimension. Thus in ^{13}C spectra containing multiple resonances, the overlapping CSA patterns can be separated.

It is possible to design a 2D experiment that yields such a result, by rotating the sample at very slow speeds and synchronizing the 2D evolution time with the rotation period. Such so-called magic angle "turning" experiments require highly stable spinning at very slow speeds, typically only a few hundred Hz.

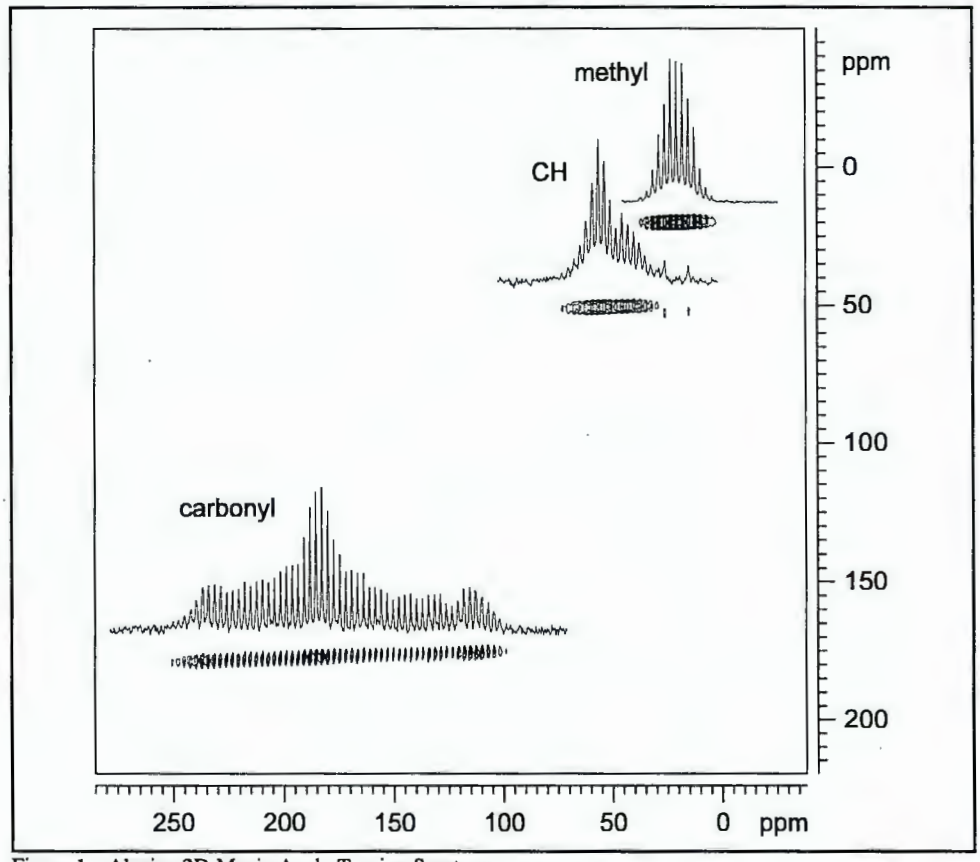
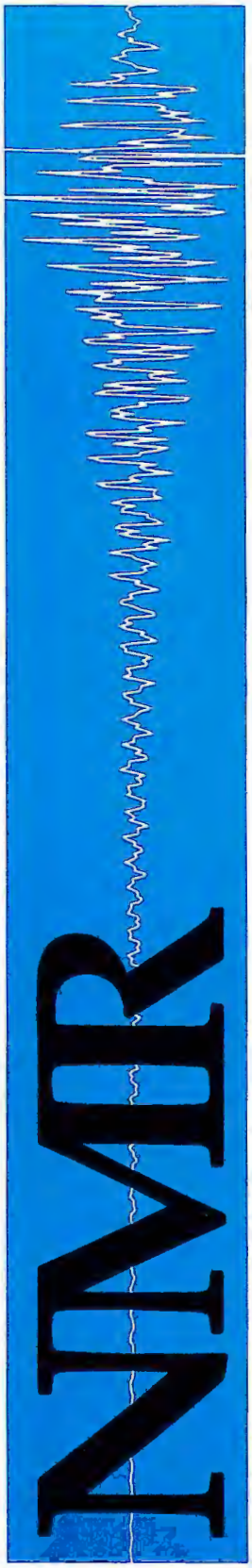


Figure 1: Alanine 2D Magic Angle Turning Spectrum

Figure 1 presents a 2D magic angle turning spectrum of alanine obtained on an *AVANCE* DSX-300 with a 7 mm MAS rotor spinning at 204 Hz. A rotor cap without drive flutes was used to allow better stability at low speeds.



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NMR

The pulse program used for the experiment is shown in Figure 2[1]. The evolution time consists of a fixed interval (T) set equal to the time it takes for the rotor to make several complete rotations (i.e. rotor periods). This interval is divided into six equal sub-intervals and contains five 180° pulses. Instead of varying the total evolution time (T), the timing of the pulses within the evolution interval (T) is varied according to the variable t_1 shown in the figure.

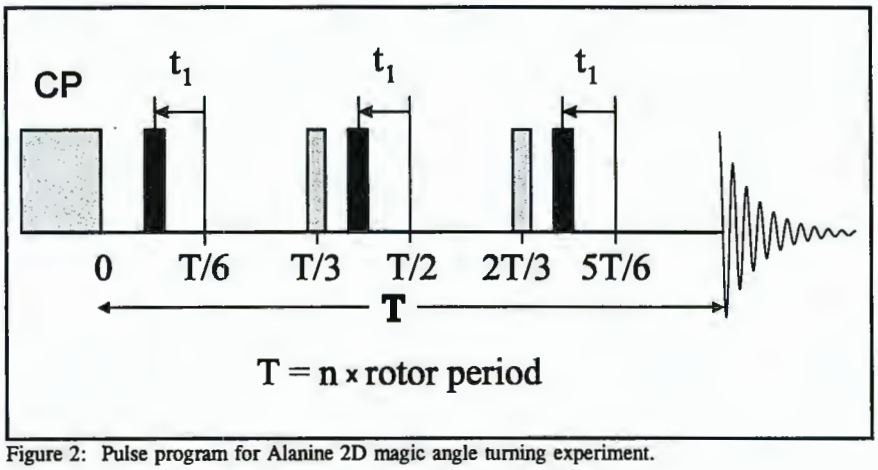

Figure 2: Pulse program for Alanine 2D magic angle turning experiment.

Any Bruker system equipped for CPMAS with the Bruker microprocessor controlled pneumatic unit can perform the magic angle turning experiment shown here. The Bruker microprocessor controlled pneumatic unit is ideal for MAS turning because the microprocessor uses active feedback to regulate the spinning speed, providing a very stable spinning rate. The only special item needed is a Bruker 7 mm rotor cap without flutes (Bruker P/N B200181), which can be ordered from your local Bruker representative.

[1] J.Z. Hu, D.W. Alderman, C. Ye, R.J. Pugmire and D.M. Grant, J.Magn.Res. A 105, 82 (1993)

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May 17, 1995
(received 5/22/95)

SCHOOL OF SCIENCE

IUPUI

Dr. B. L. Shapiro, Publisher
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Correlation Functions Derived from Complex Molecular Motion

Dear Dr. Shapiro,

It has been calculated that the relaxation correlation function obtained from the dipole-dipole interaction

$$H = \sum_{q=-2}^{q=2} F^q(\theta,\varphi)A^q(\underline{I}_1,\underline{I}_2)$$

for molecular motion consisting of the diffusional rotation of a spherical molecule superimposed on the independent diffusional rotation inside a conical region of the spherical molecule with the boundary condition that the probability = 0 on the boundary of the conical region gives rise to three different correlation functions: $G_1(t)$, $G_2(t)$ and $G_3(t)$. These correlation functions -- each of which is non-exponential -- are shown in Fig (1). These results contrast with previous calculations (1, 4) using different boundary conditions where a single non-exponential correlation function was obtained.

Our results are being recalculated using the b.c. that the diffusion current = 0 on the boundary. The qualitative result (three different correlation functions) is expected to be similar to those shown in Fig (1).

DEPARTMENT OF PHYSICS

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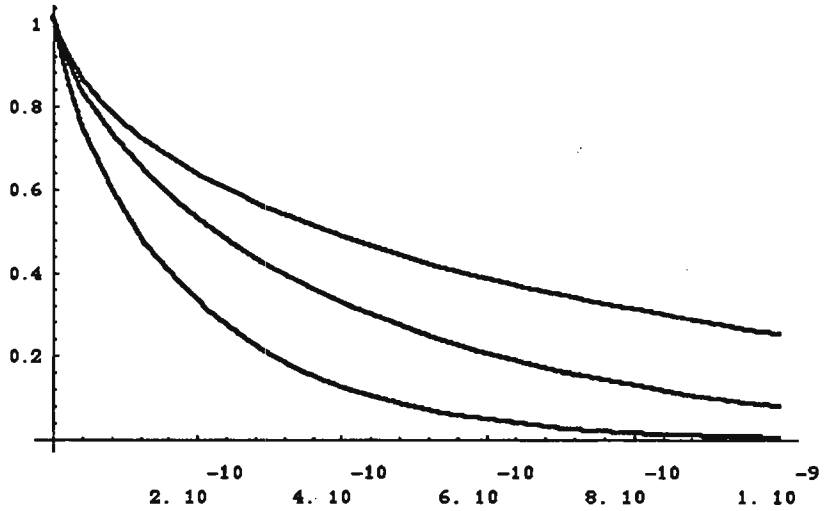

Figure (1) Correlation functions $G^{(0)}$, $G^{(1)}$ and $G^{(2)}$

(1) is for $G^{(1)}(t)$, (2) is for $G^{(2)}(t)$ and (0) is for $G^{(0)}(t)$.

References

1. James Tropp, J. Am. Chem. Soc., **72**, 6035 (1980).

2. R. E. London and J. Avitabile, J. Am. Chem. Soc., **100**, 7159 (1978).

3. R. J. Wittebort and Attila Szabo, J. Chem. Phys., **69 (4)** , 1722 (1978).

4. Rafael Gruschweiler and Peter E. Wright, J. Am. Chem. Soc., **116**, 8426-8427 (1994).

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Professor

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THE COLLEGE OF STATEN ISLAND
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May 19, 1995
(received 5/19/95)
Dr. Bernard Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Using Commercial Hardware to Measure REDOR Distances in Peptide Hormones

Dear Barry:

As part of our ongoing studies of peptide hormone structure and function, we have been using Rotational Echo Double Resonance (REDOR) and molecular modeling to determine the solid-state conformation of a series of selectively labeled α-factor tridecapeptides.[1] Recently we have begun to carry out these experiments at CUNY's College of Staten Island (CSI), using our widebore Varian Unity*plus* 300 spectrometer and a 5 mm triple-tuned Supersonic HXY probe from Doty Scientific. Shown below are the pulse sequence[2] we use for ^{15}N-observed REDOR and our preliminary data for both doubly labeled glycine and the yeast mating hormone WHWLQLKPGQPNLeY. These results provide an excellent prospectus for the measurement of ^{13}C-^{15}N distances in the 4-5 Å range.

In a typical experiment using the pulse sequence shown in **Figure 1**, we do magic-angle spinning at 4000 Hz and use a REDOR evolution period of 0 to 256 rotor cycles (0 to 64 ms) during which rotor-synchronized π pulses are applied to both the observe channel (usually ^{15}N) and the third channel (^{13}C). As shown in **Figure 2**, the ^{15}N spectra from each REDOR experiment are interleaved with controls in which the ^{13}C pulses are omitted (echo intensities reflect T_2 decay but not ^{15}N-^{13}C dipolar coupling). These spectra were obtained on about 40 mg of doubly labeled peptide using up to 512 transients; the total time required to generate the displayed spectra was about 4 hours. Both ^{13}C and ^{15}N fields were 50 kHz (5 μs π/2 pulses); the ^{1}H field was 50 kHz during CP and signal acquisition, but 95 kHz during the REDOR evolution period.

In the control spectra, 85% of the ^{15}N signal intensity is retained after 128 rotor cycles, so that excellent signal-to-noise ratios are obtainable even in experiments for which less sample is available and/or one wishes to measure bond lengths as large as 5 Å. We attribute this heartening result to our use of ^{1}H decoupling field strengths close to 100 kHz during the evolution period, though we're also helped out by looking at ^{15}N-labeled proline, which has no attached protons and thus a relatively long value of T_2. (For [2-^{13}C,^{15}N]glycine diluted with unlabeled glycine and examined under similar conditions, 70% of the intensity is retained after 64 cycles.)

Once we have a set of REDOR echo intensities (S) and control spectra (S_o), we plot $(S_o-S)/S_o$ vs. the product of the number of cycles and rotor periods (**Figures 3 and 4**). As expected,[3] the curves approach 1 as the number of cycles increases. To obtain a distance estimate for the tridecapeptide, we correct the dipolar coupling for interactions with natural-abundance ^{13}C nuclei on the proline ring and for high-frequency molecular vibrations or librations.[1] In comparison with prior 48-cycle experiments that yield a distance of 4.7 Å,[1] our present data from the 32 to 64 rotor cycle portion of the REDOR curve yield distances between 4.3 and 4.7 Å. After all is said and done, these and other measured distances indicate that the central region of this peptide is not in an extended conformation; rather the distances are consistent with a distorted Type-I β-turn conformational model.

Is this 'REDOR for Everyone' in the making? We hope so! For their continuing advice and sharing of expertise, we thank Joel Garbow at Monsanto, Jake Schaefer at Washington University, and Bruce Scruggs at Doty Scientific.

Very truly yours,

Ruth Stark	Dave Rice	Octavian Antohi	Fred Naider	Hsin Wang
Professor	Applications Chemist	Ph.D. Student	Professor	Facility Manager
CSI	Varian NMR	CSI	CSI	CSI

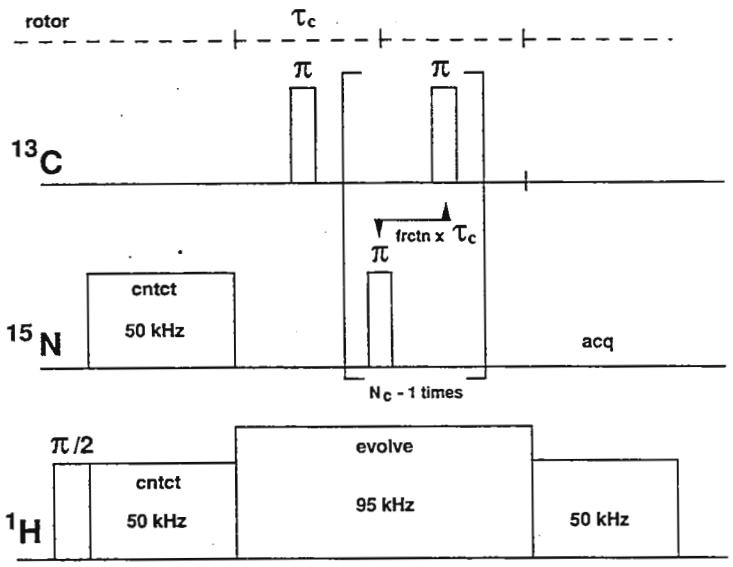

Figure 1. Pulse sequence used for ^{15}N-observe REDOR NMR. The ^{13}C π pulses are either included or omitted on alternate acquisitions, and the resulting data sets are Fourier-transformed to obtain echo intensities S and S_o, respectively.

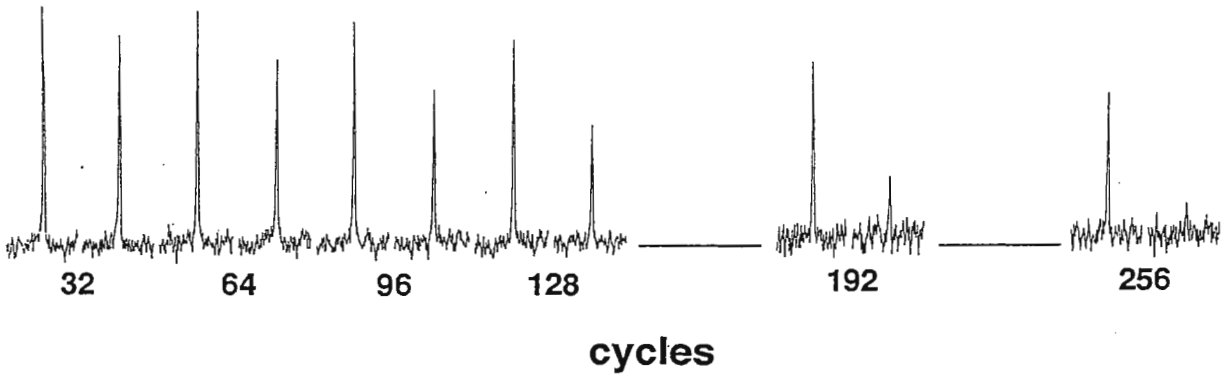

Figure 2. 30-MHz ^{15}N spectra of WHWLQLKPGQPNLeY, obtained in REDOR experiments conducted with the pulse sequence in Figure 1.

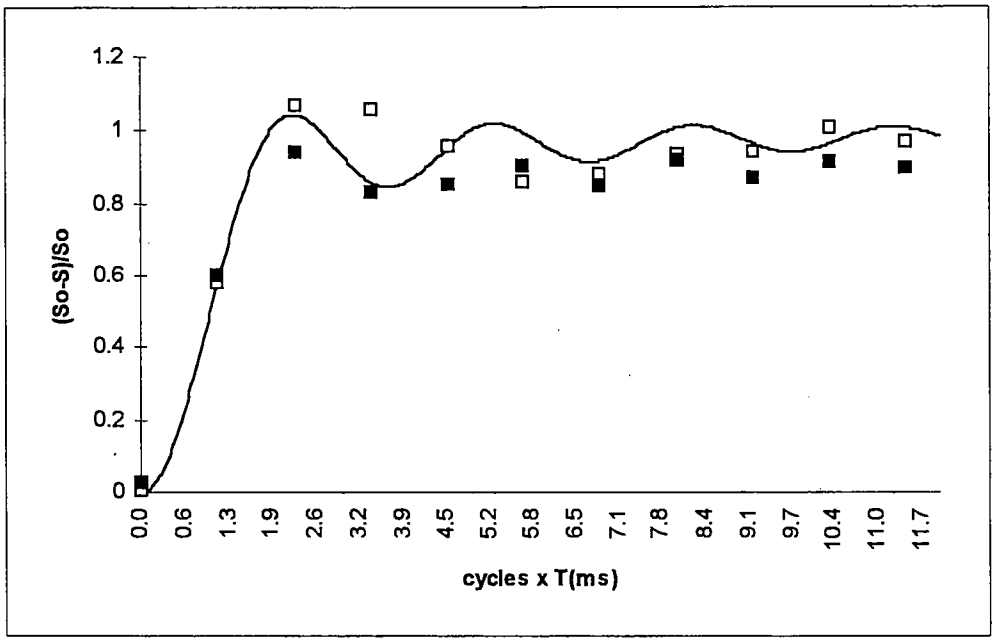

Figure 3. Normalized REDOR difference intensities for about 50 mg of [2-^{13}C,^{15}N]glycine diluted 1 part in 9 with natural-abundance glycine, plotted as a function of the product of number of cycles and spinning period. Data are shown for 4-transient ^{13}C-observe (□) and ^{15}N-observe (■) REDOR experiments, respectively. The curve is calculated from standard formulas, assuming a dipolar coupling of 740 Hz.[3] The number of cycles was varied between 0 and 256; data are shown for 0 to 40 cycles.

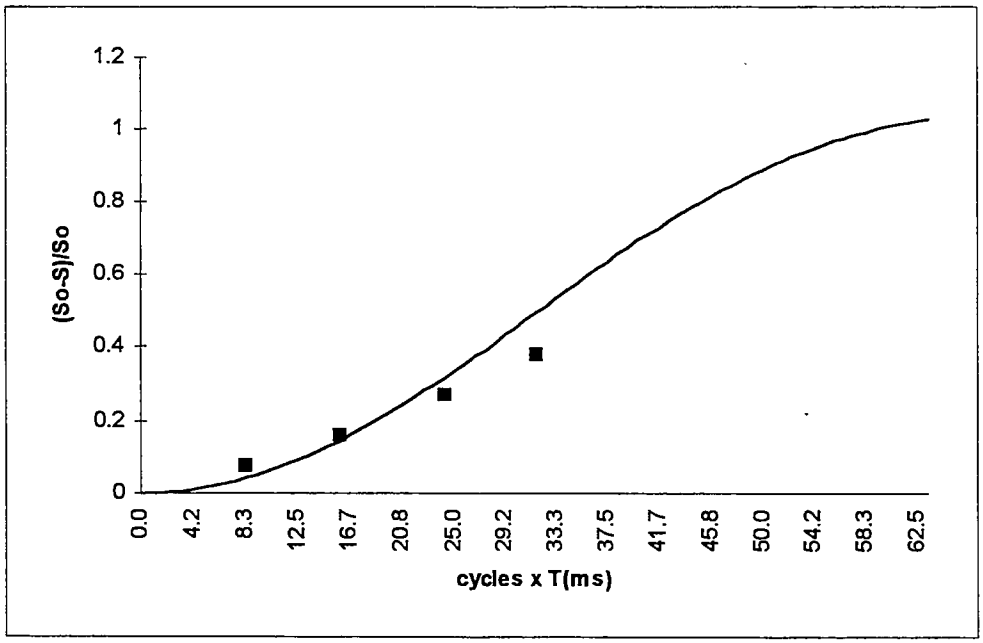

Figure 4. Normalized REDOR difference intensities (■) for WHWLQLKPGQPNLeY, plotted as a function of the product of number of cycles and spinning period. The curve is calculated from standard formulas,[3] assuming a distance of 4.7 Å correcting the data as described by Garbow, et al.[1].

Refererences: [1] J.R. Garbow, M. Breslav, O. Antohi, & F. Naider (1994) *Biochemistry* **33**, 10094-10099; [2] J.R. Garbow & C.A. McWherter (1993) *J. Am. Chem. Soc.* **115**, 238-244; [3] T. Guillion & J. Schaefer (1989) *Adv. Magn. Reson.* **13**, 57-83.

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E-Mail JRALPH@FACSTAFF.WISC.EDU
May 25, 1995
(received 5/26/95)

Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

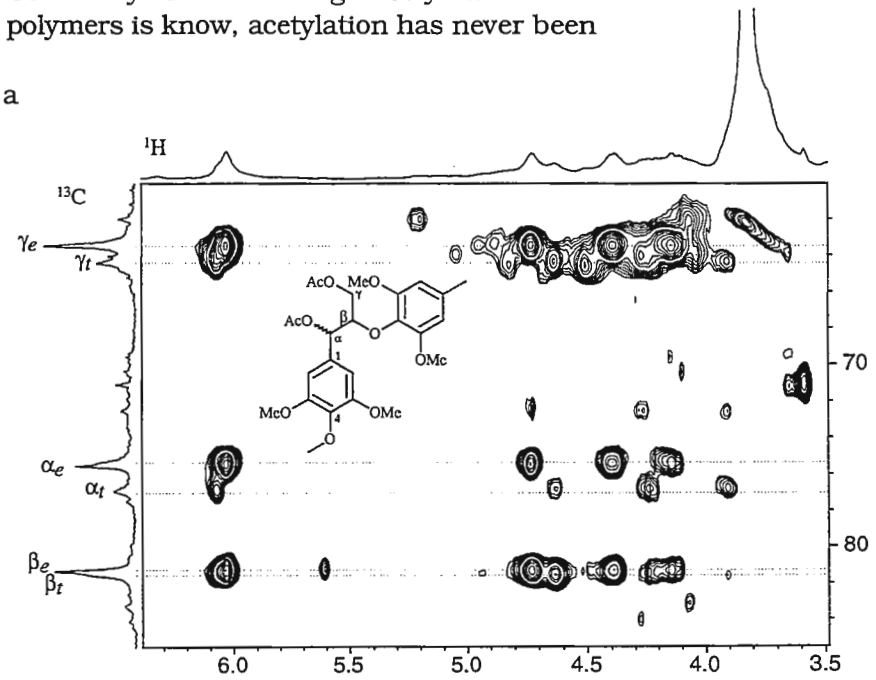
Dear Dr. Shapiro,

NMR of Kenaf Lignin

Don't you just love NMR!! We recently had occasion to prepare and characterize the lignin from Kenaf (a fiber source that is experiencing a resurgence). Lignin is that enigmatic polydisperse natural polymer with no regularity and no repeating units. It if far removed from those other polymers people write about in TAMU that were just made for NMR (proteins!). But, despite its complexity, and the hopelessly broad and featureless proton spectrum, correlative NMR is surprisingly revealing.

NMR showed two amazing features of Kenaf lignin. Firstly, its lignin is substantially derived from sinapyl alcohol monomers, giving a lignin that is more syringyl-rich than any other reported lignin. Without boring you with the details, this gives a significantly simpler and more linear lignin and makes for very nice NMR spectra, at least relative to normal lignins. The other amazing thing is that it is ca. 50% acetylated — although acetylation of saccharides in plant cell wall polymers is know, acetylation has never been reported on native lignins.

Anyway, the figure shows a section of an HMQC-TOCSY experiment (an under-utilized 2D experiment in my view) in which the two isomers of the β-aryl ether syringyl units have their α-carbons beautifully resolved and showing gorgeous correlations to the α-, β- and γ-protons (which agree perfectly with model data). The observation that *erythro*-syringyl β-ethers predominate over their *threo* counterparts has been noted previously and is certainly borne out here.



Aliphatic region of an HMQC-TOCSY experiment on acetylated Kenaf lignin showing β-ether units and the excellent disperison of isomers.

Best Wishes

John Ralph

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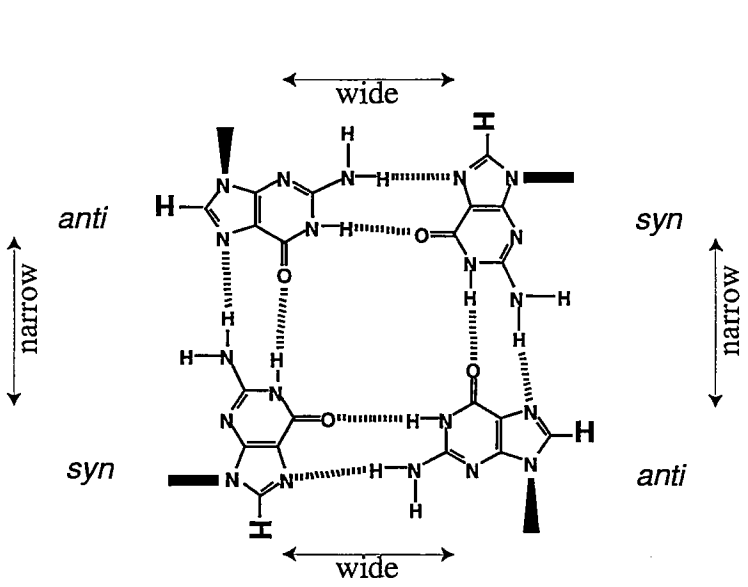
Metal Ion Binding of DNA Quadruplexes (& Adobe Illustrator Tips)

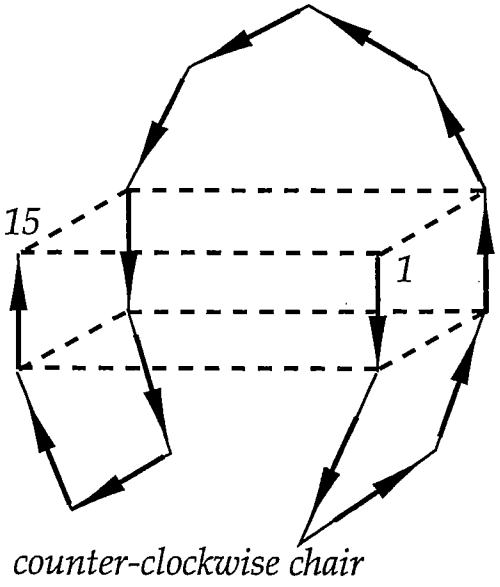
Tuesday, May 9, 1995
(received 5/12/95)

Barry Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

For sometime now we have been interested in the structural and other properties of DNA molecules which form quadruplexes. The 15mer d(GGTTGGTGTGGTTGG) forms a quadruplex structure, shown below, and binds to and inhibits thrombin both *in vitro* and in animal models. One of the features of this structure is that there are two narrow grooves and two wide grooves. The narrow grooves are 7-9 Å across and hence are expected to produce a large, negative electrostatic potential. This electrostatic potential is thought to be important in the binding of this DNA apatamer to thrombin.



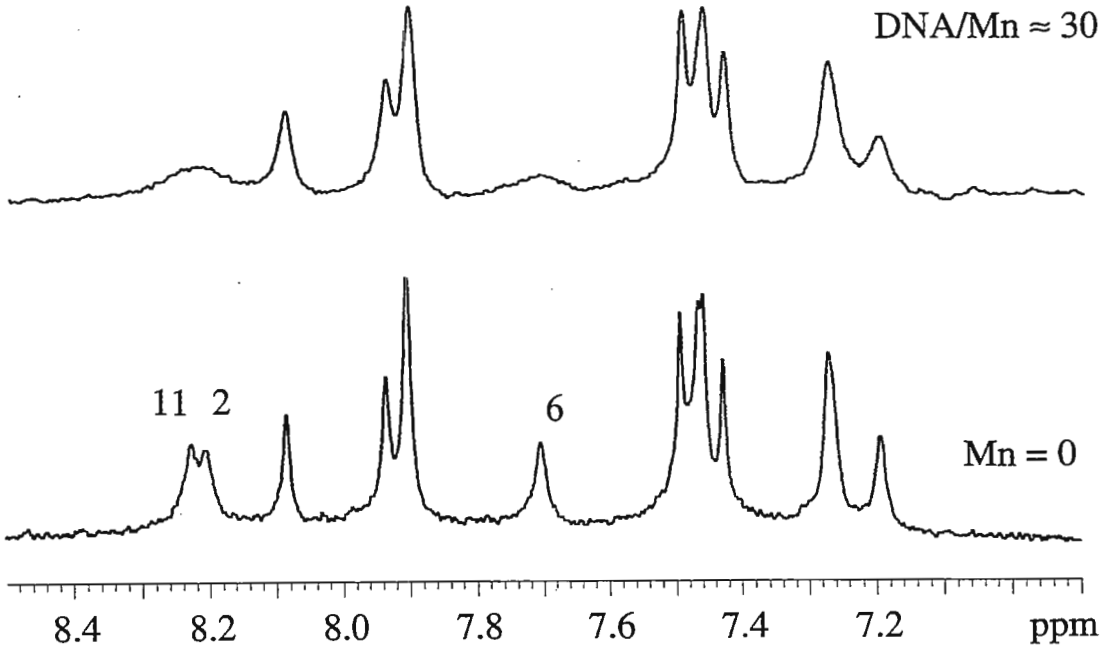


We have been proceeding along the following line of research. We have collected the usual NMR data on this DNA and used this to obtain a refined solution state structure for the DNA. This refined solution state structure has been used to predict the electrostatic potential of the DNA. This electrostatic potential can be used to predict the

binding sites of the paramagnetic probe manganese. The predicted binding site can then be compared to the location of the experimentally determined binding site. The goals of this line of research are to learn more about the electrostatic potential of this DNA which is a key feature of its activity as well as to determine how well we are doing the structure determination. The electrostatic potential is a straightforward consequence of the structure. The information on the electrostatic potential will be used in additional studies on the thrombin-aptamer complex. If the refined structure is correct then the electrostatic potential predicted by this structure should be correct. This would provide an independent check of the structure.

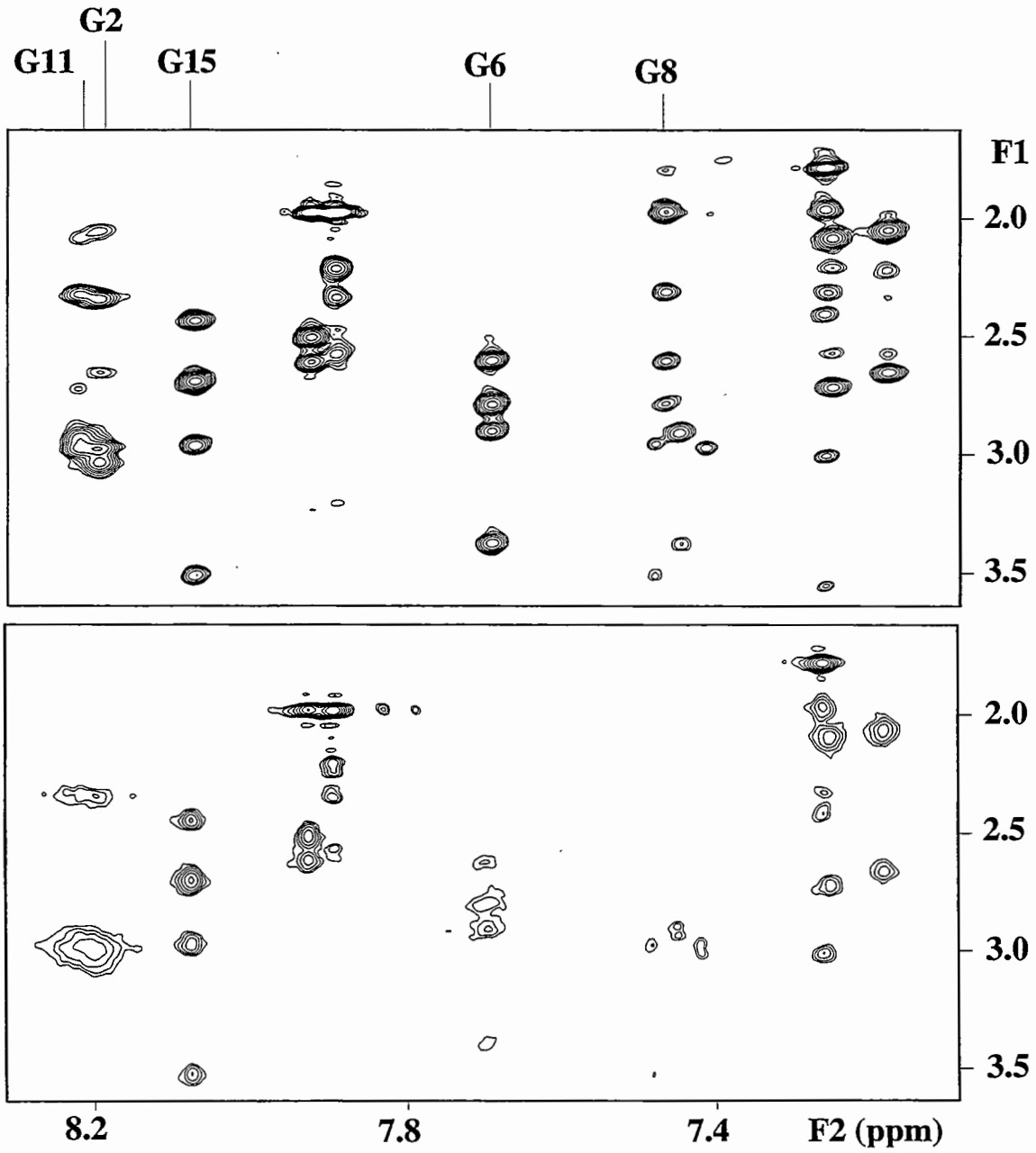
In a recent article we showed how one-dimensional NMR can be used to monitor the location of the manganese binding sites. The H8 protons of the anti G residues of the quartets are in the narrow grooves whereas those of the syn G residues are not and hence selective broadening would allow mapping out of which groove the manganese binds to. The approach we started with is fairly simple minded. We titrated the DNA with manganese and looked for the resonances which were broadened the most. The approximate locations of the manganese binding sites could be determined by the combination of a little knowledge of the structure and which sites were affected by the presence of manganese. A typical titration is shown below and the manganese appeared to be binding in the narrow grooves just as we expected that it would. The approximate binding sites of a DNA quadruplex with a different structure have also been determined.

two of the spectra from the titration of d(GGTTGGTGTGGTTGG)



However, this does not offer very precise information about the location of the manganese binding sites. Thus, we decided to obtain more information. The

experiments we have carried out have been standard NOESY experiments. The NOESY data has been obtained as a function of a titration of the sample with manganese. The additional relaxation induced by the manganese reduces the intensities of cross-peaks from protons near the manganese binding sites. The extent of loss of cross-peak intensity as a function of manganese concentration, rather than the more familiar build up of cross-peak intensity as a function of mixing time, has been used to obtain psuedo-distance constraints. This psuedo-distance constraints can then be incorporated into X-PLOR to obtain the location of the manganese binding sites. The pseudo-distance constraints that we are using are quite similar to the strong, medium and weak types used in protein structure determinations. The spectra shown below compare the intensities in one region of the NOESY map with and without manganese.



The advantage of the collection of NOESY data is that about twenty times as many constraints on the location of the manganese can be obtained. While the one-dimensional titrations are very clean with highly selective broadening observed only the data in the highly resolved aromatic region can be analyzed. In the two-dimensional data broadening of dozens of cross-peaks can be observed. The two-dimensional data has allowed much more clear identification of the binding sites. Even with a one-dimensional spectrum as resolved as that of this aptamer the manganese binding near residue 8 could not be ascertained from the one-dimensional data due to spectral overlap.Unlike the usual case with NMR data this is a highly overdetermined structure refinement since we are determining the posiiton of a couple of metals ions with forty to fifty constraints. The same procedure has also been applied to the quadruplex formed by dimers of d(GGGGTTTTGGG). The details of the comparison of the predicted and experimentally determined binding sites will be presented in a manuscript we are now preparing as well as how all of this relates to the binding of the aptamer to thrombin.

Sincerely,

Ke Yu Wang Vasilios Marathias Philip Bolton

ps. Those of you using Adobe Illustrator on the Macintosh for figure preparation should check http://www.abobe.com for an updated filter for converting pdf files into Illustrator files. Also, if you are taking images from Illustrator and putting them into Word it is better to first save the image as an EPS and then open the EPS in Word rather than going through the clipboard using command-option-C. For reasons unknown the EPS route reduces the size of the image by about 40%, improves the output quality and vastly decreases the time required to print the Word document. The command-option-C route goes through AICB (Adobe Illustrator ClipBoard) format which is erratic and uses a lot of disk space.

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B. L. Shapiro
1 June 1995

Address all Newsletter correspondence to:

Dr. B. L. Shapiro
The NMR Newsletter
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Palo Alto, CA 94303.

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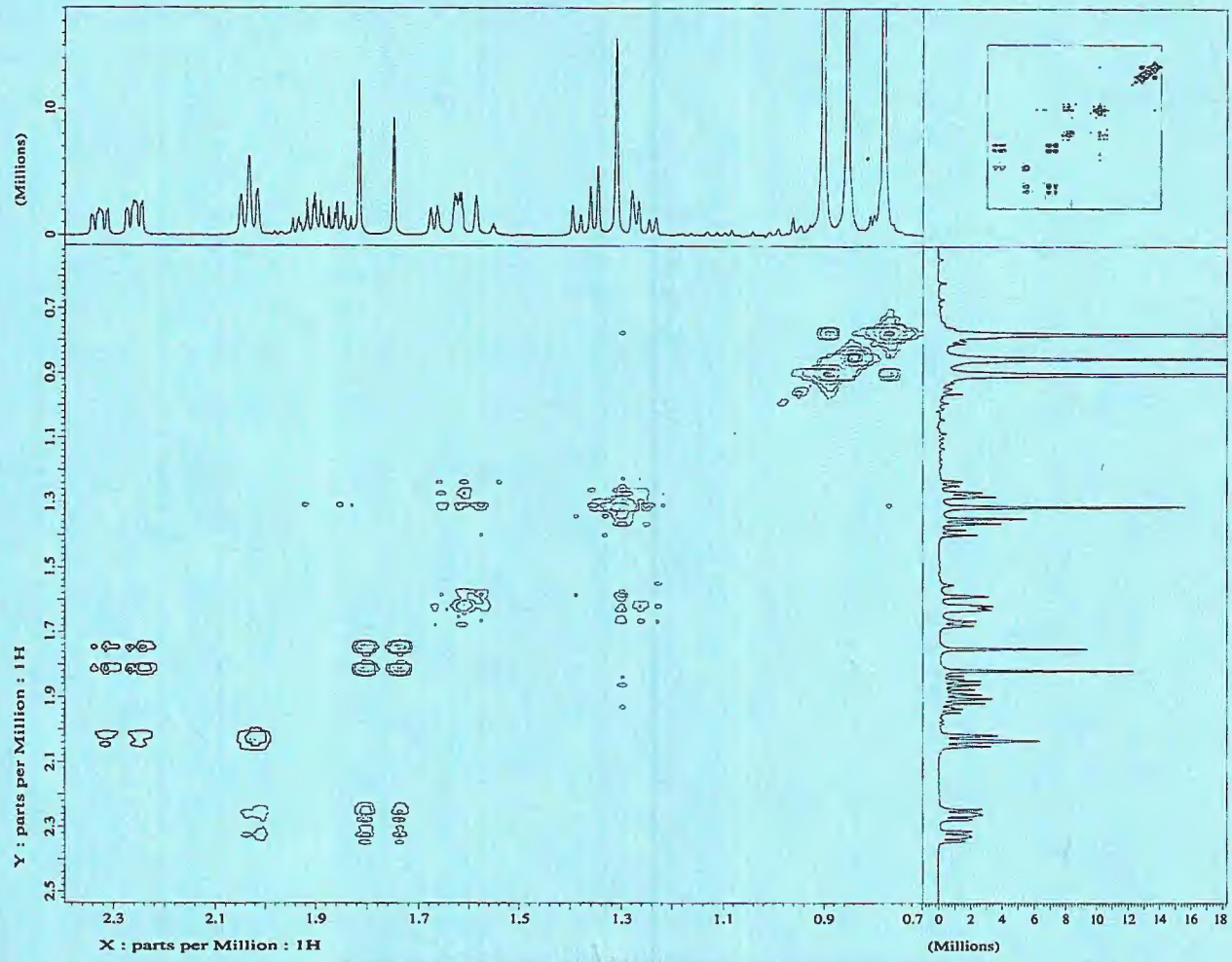

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