TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 414

March 1993

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D-14							[illegible]543 (20)
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FORTHCOMING NMR MEETINGS

High Resolution NMR Spectroscopy (a residential school), University of Sheffield, England, **April 19 - 23, 1993**; Organizer: Dr. B. E. Mann (Sheffield); For information, contact Ms. L. A. Hart, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England; Tel.: 071-437-8656.

Gordon Research Conference: Magnetic Resonance, Wolfeboro, NH, **July 11 - 16, 1993**; Contact: Dr. A. M. Cruickshank, Gordon Research Center. University of Rhode Island, Kingston, RI, 02881-0801; (401) 783-4011 or -3372; FAX: (401) 783-7644.

35th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado: **July 25-29, 1993**; Contact: Patricia L. Sulik, RML, Inc., 456 S. Link Ln., Ft. Collins, CO 80524; Phone: (303) 530-1169.

12th Annual Scientific Meeting and Exhibition of the Society of Magnetic Resonance in Medicine, New York, NY, **August 14-20, 1993**; Contact: SMRM, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Phone: (510) 841-1899; FAX: (510) 841-2340.

1993 FACSS Meeting, Detroit, Michigan, **October 17-22, 1993**; Contact: H. N. Cheng, Hercules, Inc., Research Center, 500 Hercules Road, Wilmington, DE 19808; Phone: (302) 995-3505; Fax:. (302) 995-4117. See TAMU NMR Newsletter 411, 10.

Additional listings of meetings, etc., are invited.

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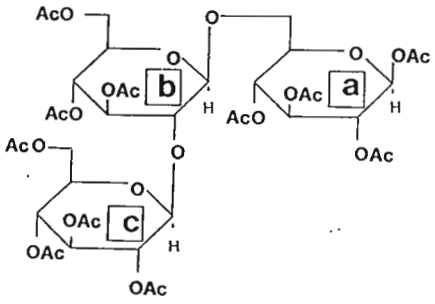
Dr. Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 943030 USA

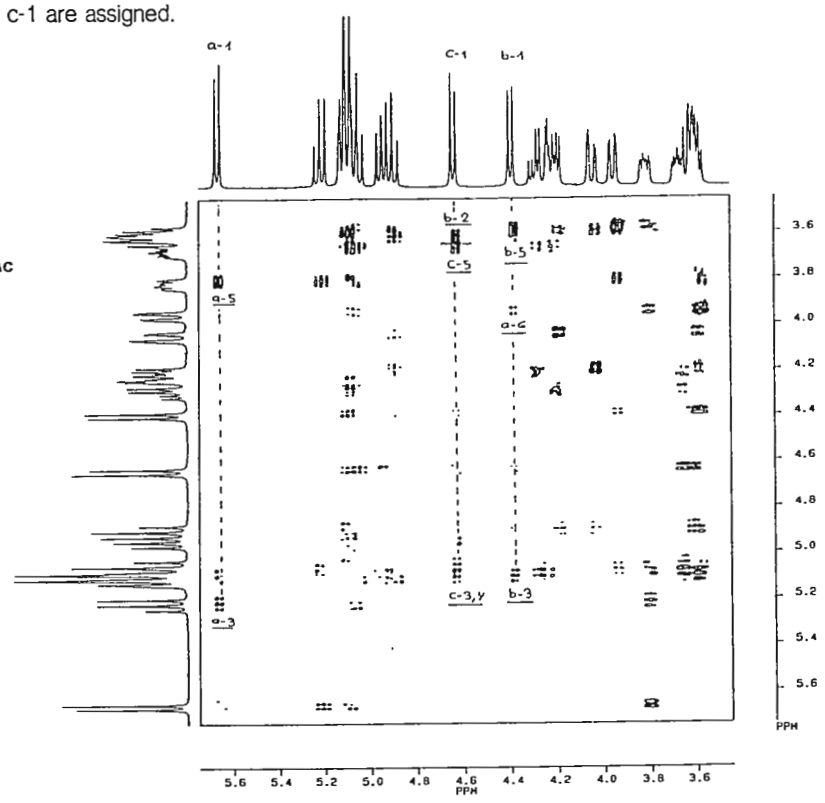
January 29th 1993
(received 2/4/93)

2D TRANSVERSE ROESY SPECTROSCOPY

Dear Dr. Shapiro

It is well known that an annoying problem in ROESY spectroscopy is coherent magnetization transfer by TOCSY that occurs by J-coupling pathways. Although ROESY and TOCSY peaks have opposite phases and may therefore be identified immediately, accidental superpositions of both effects could lead to signal cancellations and will certainly affect quantification of ROESY effects. The problem of unwanted TOCSY peaks is most pronounced between protons with similar resonance frequencies. Most demanding samples to test improvements of the basic ROESY experiment with respect to these TOCSY peaks are therefore oligosaccharides. Very recently a pulsesequence was proposed by HWAN G and SHAKA [1] dedicated to measure transverse rather than the usual "longitudinal" Nuclear Overhauser Enhancements in the rotating frame. We have applied this sequence on our BRUKER AM 400 spectrometer to measure ROEs in a peracetylated trisaccharied composed of glucose units. We found all the expected ROEs within the subunits, i.e. H(1) <---> H(3), H(1) <---> H(5) , ... , a few interresidue effects and probably as the most important result no TOCSY peaks. ROEs for the three anomeric protons a-1, b-1 and c-1 are assigned.





[1] T.L. Hwang and A.J. Shaka, JACS 114, 3157 (1992)

Yours sincerely

Dr. P. Bigler

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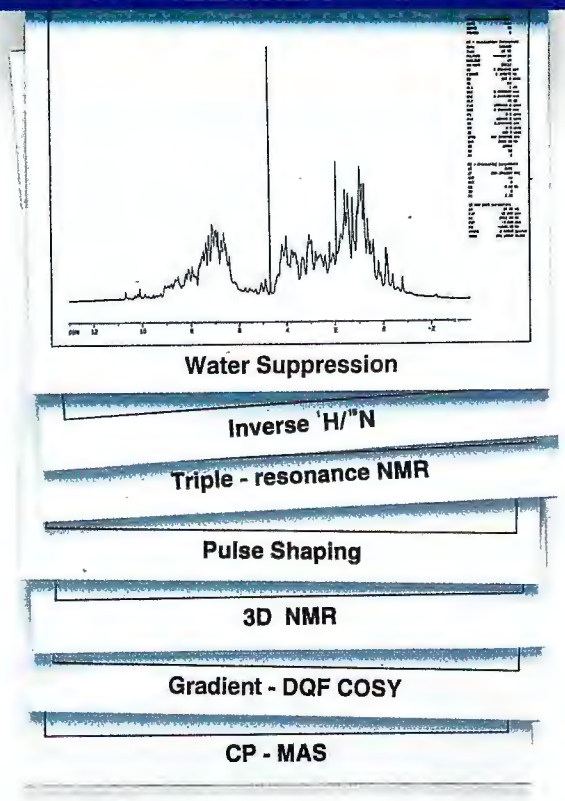

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Probehead	Sample				
Resolution Test					
All 5 mm ^{1}H 5+10 mm ^{13}C	ODCB/C_6H_6	0.2	0.2	0.2	
Lineshape Test					**SSB %**
All 5 mm ^{1}H	10% $CHCl_3$	6/12	7/15	7/15	<1
All 5 (10) mm ^{13}C	80% C_6H_6	3/7 (3/7)	3/7 (3/8)	4/8 (4/8)	<0.5 (<1)
Sensitivity Test					
5 mm ^{1}H Selective	0.1% EB	175	250	450	<10
5 mm ^{1}H Inverse Detection	0.1% EB	135	190	350	<15
5 mm ^{1}H Dual, QNP, VSP	0.1% EB	100	140	200	<15
5/10 mm ^{13}C QNP, Dual	ASTM	100/320	160/450	180/600	<15/<20
5/10 mm ^{13}C QNP, Dual	10% EB	70/200	100/300	150/400	
5/10 mm ^{13}C VSP multinuc.	ASTM	100/320	160/450	180/600	<15/<20
5/10 mm ^{13}C VSP multinuc.	10% EB	70/200	100/260	150/320	
5/10 mm ^{15}N VSP multinuc.	90% Form.	10/35	15/55	20/70	<25/<30

EB = ethylbenzene (for ^{13}C with ^{1}H-dec.);
ASTM = 60% C_6D_6 in dioxane
Form. = formamide (^{1}H-dec. without NOE)
lineshape: ^{1}H = $CHCl_3$ linewidth at ht. of ^{13}C-satellites/at 20^6 this level
^{13}C = C_6H_6 linewidth at 0.55% / 0.11 level (^{1}H-dec.)
SSB = Spinning sidebands measured with 8 transients
QNP: 5 or 10 mm ^{1}H, ^{31}P, ^{13}C, ^{15}N
VSP: 5 mm ^{15}N – ^{13}P; 10 mm ^{109}Ag – ^{31}P.

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January 25, 1993
(received 1/29/93)

Dr. Bernard L. Shapiro
966 Elsimore Court
Palo Alto, CA 94303

Dear Barry:

I am in receipt of your dreadful* *ultimatum* and thus am responding to it. Recently in collaboration with Dr. Arun Chattopadhayay of ICI Explosives in McMasterville, we have been evaluating the utility of NMR microscopy in structural characterization of polycrystalline materials. There is currently no good non-destructive method available to study the structural features of these materials.

We have taken ammonium nitrate prills, which play an important role in fertilizers and commercial explosives, as an example of polycrystalline material. In order to observe NMR signals, we have soaked the ammonium nitrate prills with tetradecane. Three-dimensional NMR images were collected at 9.4 T with resolution of 19 x 19 x 19 μm. A 2D section through the 3D data set is shown below; a network of radially distributed pores within the prills are clearly visible in the image.

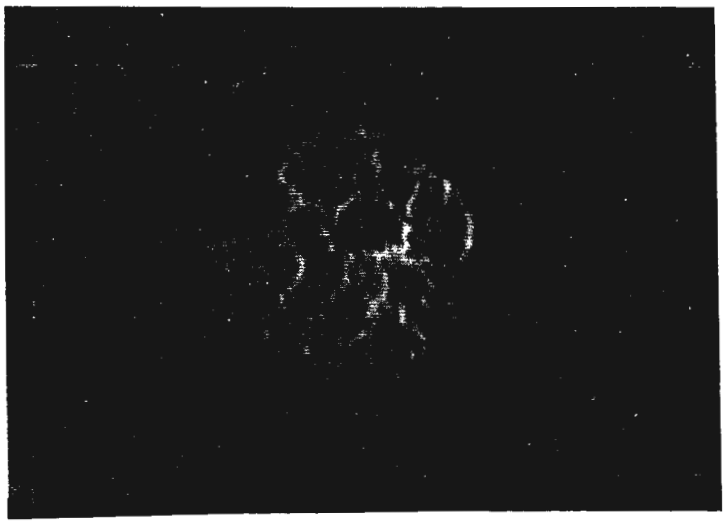
A detailed account of this work is being submitted.

Yours Sincerely

Rasesh.

Rasesh D. Kapadia

Susanta K. Sarkar



*Perhaps he means *dreaded*.
Perhaps not.
BLS

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KTH
(The Royal Institute of Technology)

Dept. of Inorganic Chemistry
Julius Glaser, associate professor

January 22, 1993
(received 1/29/93)

First ^{205}Tl 2D EXSY

Dear Prof. Shapiro,

Recently, we have recorded the first Tl–205 2D spectrum. Believe it or not, the idea was not to be the first, but rather to get an overview of the exchange reactions in a relatively complicated chemical system. We are studying dynamics of ligand exchange for $Tl(CN)_n^{3-n}$ complexes *(n = 0–4)*. In our solutions, also HCN, CN^-, H^+ and H_2O are present and can participate in the exchange processes. This makes nine possible exchange sites, five of which contain Tl. Being newcomers in the 2D EXSY business, and because of the limited spectral window available at our AM400, we started with a solution containing only two Tl–species, $Tl(CN)_3$ and $Tl(CN)_4^-$. However, to complicate the things a little we used C–13 enriched (~100%) cyanide. You can see the result in *Figure 1* below.

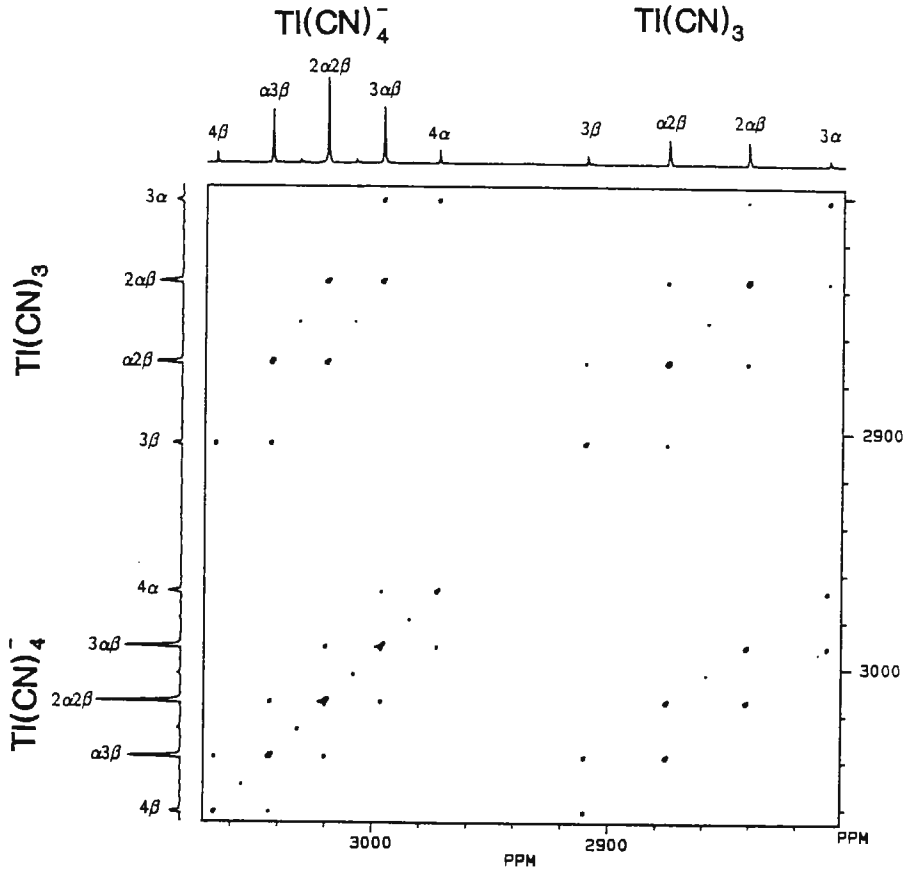

Figure 1. 231 MHz Tl–205 2D EXSY spectrum of a 38 mM solution containing two Tl–species: $Tl(CN)_3$ and $Tl(CN)_4^-$, and HCN. Mixing time, τ_m = 20 ms.

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The appearence of the 1D spectrum was not a surprise,[1] but we didn't expect such a peculiar 2D pattern. Look at it for a moment: although it's clear that there is a cyanide exchange between $Tl(CN)_3$ and $Tl(CN)_4^-$, some of the cross peaks are just not there.

After assigning the different combinations of the carbon-13 spins to the signals in the 1D spectrum (see Fig. 1), the 2D pattern was not so surprising any more. It shows that only such ligand exchange reactions occur in which a single cyanide ion jumps between the exchanging sites. Certainly, for a chemist it is quite a reasonable condition.

The chemical shift range for Tl(III) complexes is large, some thousand ppm, so it took some time to persuade our AM400 (certainly not born for this type of experiments) to hang on. Still, the digital resolution was poor and the Fourier transform (4K·4K) took a few hours. We have used the 2D data to calculate the rate matrix, **R**:

$$-\mathbf{R} = \ln\mathbf{A} \;/\; \tau_m$$

A is the normalized intensity matrix for the mixing time τ_m.

A										R									
0	0	0	16	15	0	0	4	x		0	0	0	29	28	0	0	3	x	
0	0	49	48	0	0	8	x	3		0	0	27	26	0	0	2	x	1	
0	46	49	0	0	5	x	8	0		0	25	26	0	0	2	x	2	0	
14	16	0	0	0	x	4	0	0		26	26	0	0	0	x	5	0	0	
0	0	0	7	x	0	0	0	10	⟹	0	0	0	3	x	0	0	0	34	
0	0	21	x	6	0	0	37	12		0	0	2	x	1	0	0	26	8	
0	20	x	20	0	0	41	39	0		0	2	x	2	0	0	17	17	0	
6	x	20	0	0	15	39	0	0		1	x	3	0	0	9	26	0	0	
x	6	0	0	0	14	0	0	0		x	4	0	0	0	39	0	0	0	

In fact, the relative values of the rate constants (= the off-diagonal elements of the rate matrix) can be predicted. For example, let's look at the $Tl(CN)_4^-$ species with carbon spin-label $\alpha 3\beta$ (1 α-carbon and 3 β-carbons). It can loose a cyanide and form $Tl(CN)_3$ with two sets of carbon labels 1.) $\alpha 2\beta$ – probability 75% or 2.) 3β – probability 25%, giving the exchange probability ratio 3:1. This ratio appears also for the appropriate elements of the rate matrix: 26/9.

Another example could be the complex $Tl(CN)_3$, labeled $\alpha 2\beta$. It can absorb a cyanide from other species present in the solution, but now there is an equal probability for a reaction with an α-cyanide leading to a $2\alpha 2\beta$-$Tl(CN)_4^-$, and for β-cyanide forming $\alpha 3\beta$-$Tl(CN)_4^-$. This is in good agreement with the ratio 26/25 in the rate matrix.

Yours sincerely,

Gyula Batta István Bányai Julius Glaser

[1] Blixt, J., Györi, B., Glaser, J. J. Am. Chem. Soc. 111 (1989) 7784.

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Secretary: Dr Bill Bubb

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4 February, 1993

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

Dear Professor Shapiro,

ISMAR 1995 in SYDNEY

The International Society of Magnetic Resonance will hold its 1995 conference in Sydney, Australia at the University of Sydney from 16-21 July, 1995. The conference will incorporate the biennial Australian Magnetic Resonance meeting and commemorate the 50th anniversary of the discovery of NMR.

The conference will provide an extensive scientific program in Australia's number one tourist destination. Sydney also offers accommodation to cater for all budgets and good international and domestic transport connections. Further details may be obtained from Dr. Les Field, Chair ISMAR-95 (E-mail: ismar-95@biochem.su.oz.au).

Yours sincerely,

W.A. Bubb

Bill Bubb

For the **ISMAR-95 Committee:**

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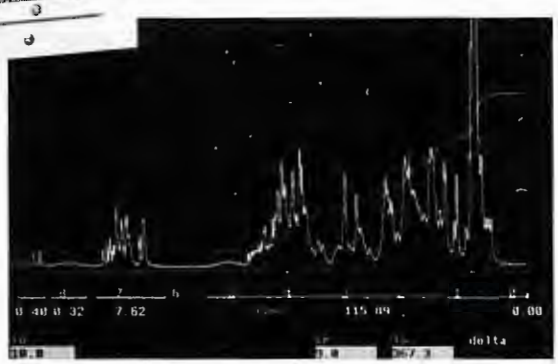

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Frequency range	10–90 MHz
Pulse power (min.) into 50 ohms	1000 W
CW power (max.) into 50 ohms	100 W
Linearity (±1 dB)	0–900 W
Gain (typ.)	65 dB
Gain flatness	± 2 dB
Input/Output impedance	50 ohms
Input VSWR	< 2:1
Pulse width	20 ms
Duty cycle	Up to 10%
Amplitude rise/fall time	250 ns typ.
Amplitude droop	5% to 20 ms typ.
Phase change/output power	10° to rated power, typ.
Phase error overpulse	4° to 20 ms duration, typ.
Noise figure	11 dB typ.
Output noise (blanked)	< 20 dB over thermal
Blanking delay	< 2 μs on/off, TTL signal
Protection	1. VSWR: infinite VSWR 2. Input overdrive: up to 10 dB 3. Over duty cycle/pulse width 4. Over temperature

Supplemental characteristics:

Connectors, rear panel	1. RF input: BNC (F) 2. RF output: Type N (F) 3. Noise blanking: BNC (F) 4. Interface: 25 pin D(F), EMI filtered
Indicators, front panel	1. AC power on 2. Peak power meter 3. Over pulse width 4. Over duty cycle 5. Over temperature 6. Over drive 7. CW mode
System monitors	1. Forward/Reflected RF power 2. Over pulse width/duty cycle 3. DC power supply fault 4. Thermal fault
Front panel controls	1. AC power 2. Pulse width 3. Duty cycle
Cooling	Internal forced air
Operating temperature	+10 to 40°C
AC line voltage	208/230 VAC, ±10%, 50–60 Hz
AC power requirements	2000 watts
Package	Rack mount
Size (HWD, inches)	8.75×19×20.25
Net weight	100 lbs.

03/92

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Brandeis University

Graduate Department of Biochemistry

Waltham, Massachusetts 02254-9110

January 21, 1993
(received 1/30/93)

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

Dear Barry,

Here are some things we have been trying on our custom-built 500 MHz system. It is now based on an 80486 computer with a Symmetric Research Coprocessor board which has 640 KB on-board memory. There is a nearly identical data station in the lab which has 32 MB memory, and both are Etherneted to a cluster of SGI's, and are sneakernetted directly to each other via 5" floppies. The latter each hold, typically, about 600 k 32 bit data words using special NMR-oriented compression software I wrote, usually enough to archive one or two 2D runs. 3D runs are archived on data tapes by a SGI. The C language programs are run by Pharlap DOS Extender.

1. I have just set up what might be called diagonal data truncation for certain types of 3D runs (those, like NOESY-HMQC that don't involve "constant time" methods). Instead of taking a full set of FIDs with $0 \le t_1 \le t_{1\,max}$, $0 \le t_2 \le t_{2\,max}$, the computer takes no data when $(t_1/t_{1\,max}) + (t_2/t_{2\,max}) > 1$; instead it replaces entire FIDs by zeros (this wastes space but was expedient). If, for example, $t_{1\,max}$ and $t_{2\,max}$ are picked to equal the T_2's for the respective coherences, we thereby avoid taking data which has relaxed by more than 1/e times its $t_1 = t_2 = 0$ size. I have not yet evaluated or simulated this method as compared to the usual way, but initially it looks promising, with no weird distortion. It would be easy to try other restrictions on the data set. Whatever the merits of this truncation may be, it must surely not be optimum to take data over a rectangular domain in the t_1, t_2 plane. Obviously this strategy might be extended to higher dimension or to the observe dimension, for slightly greater efficiency.

2. The coprocessor board we use is based on an AT&T DSP32C chip which does ~ 1K FT's in 10-20 millisec and can do it while the AT is doing something else. Now we are working on interfacing it as a buffer to two high-speed A/D's, to replace our old input buffer. Besides FT's, the coprocessor also formats data lines for a fast 2D raster display, again time sharing formatting (including gain changing and color formatting) of the (n-1)'th line while the AT draws the n'th line. Elegance is sacrificed for speed and utility, and it draws a 512 point by 350 line data set, with cursor-directed slices, in < 1 second. Our current super-VGA is already obsolete and we could do better. Our next step will be to oversample our data by about twenty-fold and then digitally filter the spectral region(s) of interest to get a FID or FIDs that emulate

what we now get from our slow A/D's. The input center frequency will be offset from zero, to eliminate any possible image problem. The combination of a 486 AT and a coprocessor board is potent, and there is lots more that can be done. Symmetric Research now sells an 8 MB version, which could take an entire 2D run or slice of a 3D run, and another version with four independent 1 MB units, for 3D processing. This kind of technology is not entirely irrelevant to people who already own NMR machines: such a computer could be used as a front end of an existing system, "fooling" it into thinking it was getting data from a conventional A/D, without great difficulty.

3. Previously in TAMU, we described use of a "gain changer" and water suppression analogue filter system. (The gain is reduced by 4 for the first 20 or so points, by analog circuitry, just before the A/D, and is correspondingly increased by software just after it arrives in the computer. This treats the large initial transient that is emitted by the filter with reduced digitization accuracy, with little side effect.) We just want to report that this method has been well-proven over several years here. It gives you 12 db extra dynamic range in setting the receiver gain in H_2O work.

4. We have modified an old Class A ENI 25 W amplifier to be gated off in ~ 200 μsec, useful for high resolution NMR if you don't need time-shared homodecouple, and your gating system doesn't completely take out the noise from your amplifier. It gates the power supply and is simple.

5. We built yet another phase shifter for our system which is satisfactory and supersimple, using eleven TTL chips, a PAL, a pot, and a commercial 5 MHz low pass filter. It takes a 4 X IF clock and divides by 4, followed by a data selector and synchronizing JK flip flops to get precise 90° shifts at 3.85 MHz, and generates also an unshifted reference. Then fine shifts are generated by adding to a square wave a differentiated version of itself, using the pot. This passes through the filter to a TTL gate acting as a comparator.

6. Like many biochemical labs, we use a commercial air dryer, feeding a copper tubing coil immersed in a Neslab bath and cold-finger to get probe temperature to O°C. The bath gets so cold that the coil blocks with water. We avoid this by using a commercial temperature regulator of the type used to regulate meat freezers, costing about $100. You dunk the copper sensor in the bath, put the switch in series with the cold finger power, and set the temperature to around 0°F. That's it!

Details of these things are available on request.

Best wishes,

Sara + Al

Sara Kunz and Al Redfield

CLARK UNIVERSITY
950 Main Street Worcester Massachusetts 01610-1477

Gustaf H. Carlson School of Chemistry
Internet: "chemistry@vax.clarku.edu"

Telephone (508) 793-7116
FAX (508) 793-8861

February 15, 1993
(received 2/20/93)

Dr. B.L. Shapiro
TAMU NMR Newletter
968 Elsinore Court
Palo Alto, CA 94303

Semi-Painless Shimming of Samples for High-Resolution NMR

Dear Barry:

We have developed a manually-implemented, sample-shimming algorithm on our Varian Unity 500 that both works well and appeals to common sense. The method is really quite simple and requires only a little patience and concentration. It goes as follows:

1). Insert the sample, spin it at 20 Hz , obtain the lock (keep the lock gain high and the lock power low). Collect four transients and transform. We typically collect 32k of data and zero fill to 64k. Set the receiver gain. Find the peak on which you wish to shim, measure its linewidth, and save these shim values as something simple like "temp".

2). Zero all of the shims. Be sure you do not lose the lock (you may have to increase the lock power). If specific shims on your magnet consistently have optimal values well away from the zero values, you may wish to use these as your starting points instead.

At this point we introduce the method for the shimming and the premise on which it is based. Analogous to least-squares methods, it is assumed that the lock level exhibits a parabolic dependence on each individual shim. Rather than trying to find the top of the parabola by subtly roaming around on the top of the curve, it is faster and easier to alter a given shim value until a significant decrease in the lock level is realized (individuals can decide what significant means, we typically use a change of 0.5 to 1.0%). Note this shim setting and then proceed past the maximum until the same decrease is observed. Now simply set this shim to halfway between the current point and the previously noted value. From now on the verb adjust is used to denote this procedure.

(3). Adjust the coarse Z1 and Z2 shims to maximize the lock level. This may require four or five iterations but should only take a couple of minutes.

(4). Adjust the higher order axial shims (Z1-Z5). After adjusting Z3, go back and redo Z1. After adjusting Z4, go back and adjust Z2. After adjusting Z5, adjust Z1, Z3, Z1 and Z2 in that order.

(5). Acquire a spectrum and measure the linewidth of the previously selected peak. This value should be comparable or better (smaller) than the value measured in step 1. Save these shim values as "temp2" (or "temp" if the newly acquired spectrum looks better than the old).

(6). Stop the sample spinning and adjust the non-spinning shims. Do only the lower order shims initially (X1, Y1, XZ, YZ, XY, X2Y2). Respin the sample and check the linewidth. An increase in linewidth indicates that either the axial shims need to be redone or one of the non-spinning shims is causing problems. Save your best two or three shim sets at all times.

(7). Repeat step 6, adjusting the higher-order, non-spinning shims. Chances are that the linewidths may increase if large changes in these shims are made. You may wish to reduce the magnitudes of these changes if the linewidth gets worse after this step.

(8). Adjust the axial shims one last time as outlined in step 4. Be sure to save the best set of shims with a name other than "temp".

Caveats and Pointers:

The D/A converter on the shim power supply can sometimes exhibit a discontinuous jump when more significant bits are flipped (e.g. in going from 255 to 256). Watch for unusual jumps in the lock level when changing shim settings. When these discontinuities are encountered, try not to cross them when bracketing the lock signal maximum, as these jumps will skew the determined midpoint.

Realizing too large a change in the lock level will poorly locate the maximum. Recall that the parabolic dependence of the lock level on a given shim is only an approximation, one that becomes more and more valid near the maximum value. In practice, use the smallest change that you can distinquish from the random fluctuations of the lock signal.

Beware of using too high lock power (you may wish to turn it down after an initial shimming)- this may give rise to oscillatory behavior and lock instability that will hinder your efforts.

Do not go by lock level and linewidth alone. Towards the end of the shimming process, pay more attention to line shape, in particular to anomolous bumps near the baseline (below where the canned routines measure linewidth).

If you have an autoshimming routine on your spectrometer, give it a try after you have completed your own shimming. We find that autoshimming on Z1-Z5 at the end of a manual shim can improve the spectrum but be sure to save what you have worked to obtain before letting the computer try it - we have seen the autoshimming algorithm on our spectrometer make things worse.

Using the algorithm above, it should be possible to obtain linewidths of less than 1 Hz for a typical sample in perhaps ten or twenty minutes once you get the hang of it.

Sincerely,

Jeffrey H. Simpson

Paul T. Inglefield

GRIFFITH UNIVERSITY
FACULTY OF SCIENCE & TECHNOLOGY
Nathan, Brisbane, Queensland, 4111 Australia

Phone: 61-7-875-7825
Fax: 61-7-875-7656
e-mail: S.Berners-Price @sct.gu.edu.au

12th February, 1993

Dear Dr Shapiro,

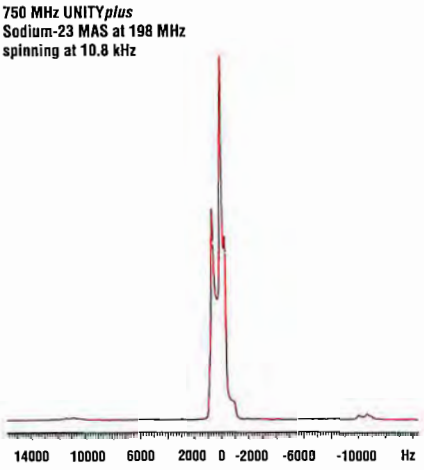
Following the recent upgrade of the NMR instrumentation at Griffith University we are seeking an experienced NMR Spectroscopist to take responsibility for the operation and maintenance of this new Facility. The instrumentation currently comprises a Bruker CXP-300 spectrometer and newly installed Varian Gemini-200 and UNITY-400 spectrometers. The latter includes a 3-channel RF system and Solids module. An order has been placed for a 600 MHz UNITY spectrometer due to be installed in late 1993. The Facility will be supported by a network of UNIX-based workstations. The position requires a relevant PhD together with extensive NMR experience and familiarity with the operation and maintenance of state-of-the-art NMR instrumentation including some contact with UNIX. The position will be a continuing appointment at the level of Research Fellow or Senior Research Fellow depending on qualifications and experience. Interested candidates should contact me as soon as possible for further details.

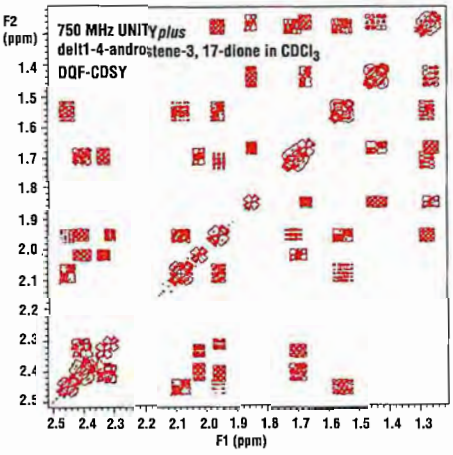
Yours sincerely,

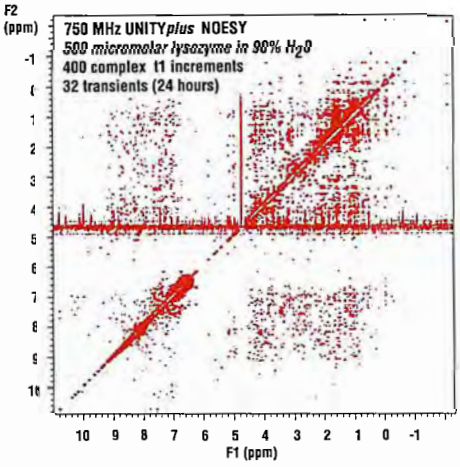
Sue Berners-Price.

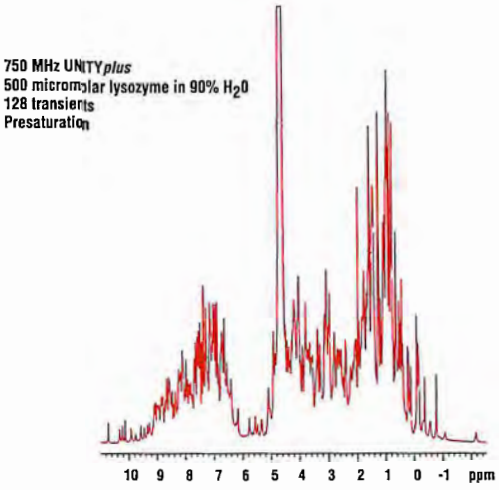
Dr Sue Berners-Price

Varian Delivers 750 MHz Results.









These spectra were obtained on a Varian 750 MHz UNITYplus™ NMR spectrometer.

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MAG-6055/569

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NMR Applications Laboratory

February 12, 1993 (received 2/24/93)

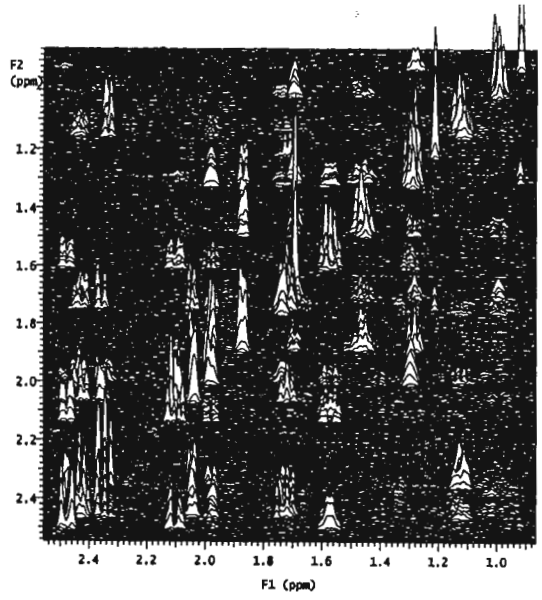
Dr. Barry Shapiro
966 Elsinore Court
Palo Alto, CA 94303

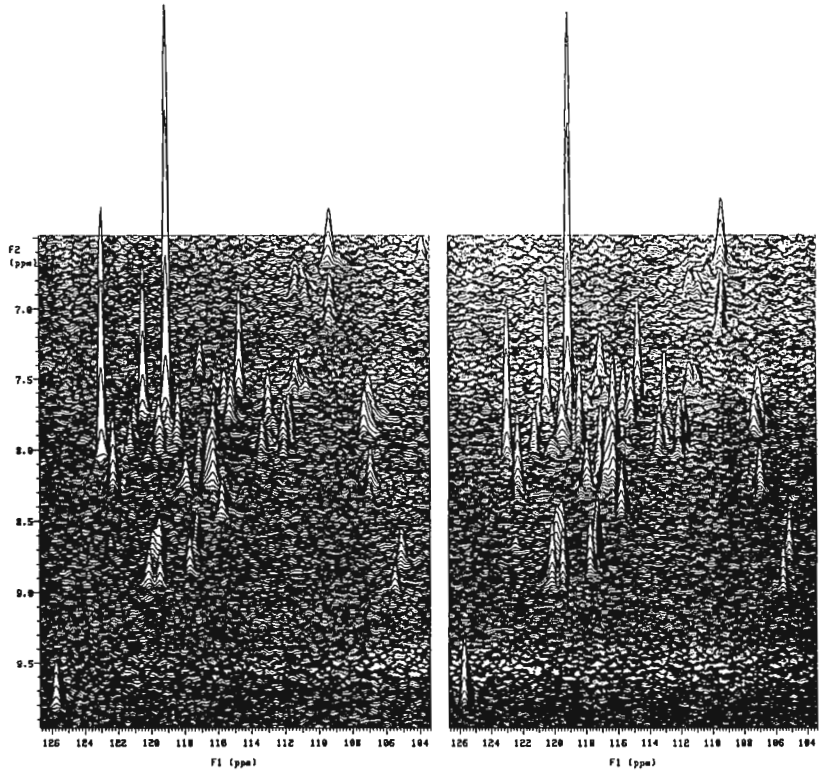
Indirect Detection and Pulsed Field Gradients at 750 MHz

Dear Barry,

We have recently carried out ^{15}N-^{1}H HSQC experiments on a UNITY*plus* 750 using a triple-resonance probe equipped with Actively-shielded Pulsed Field Gradient capability.We are sure that there is considerable interest as to the performance of these very important experimental capabilities at 750 MHz and would like, therefore, to report the current state of progress. The UNITY*plus* console was equipped with our standard low-noise transconductance current amplifier.

Figure 1 shows a 256 increment pfg-dqcosy spectrum in which only a single scan per increment was acquired- total time 6 minutes for this chloroform solution of an androstane derivative. Figure 2 shows a comparison of expansions for phase-sensitive HSQC data sets run under identical conditions for a 90% H2O solution of an approximately 1mM ^{15}N-enriched protein. The left data set is from the pulsed field gradient version using no presaturation. It is clear that both experiments give essentially the same quality data. The lack of water saturation does result in increased sensitivity for some of the NH's in the PFG version. The high quality of the data speaks well of the utility of these experiments, particularly the PFG versions, even at the highest magnetic field available.





Sincerely Yours,

George Gray
Applications Lab,Palo Alto

PETER

Peter Sandor
Applications Lab,Darmstadt

Ali Behbin
Probe R&D, Palo Alto

414-18

ATI INSTRUMENTS

February 5, 1993
(received 2/16/93)

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

Dear Barry:

We were excited to see the various 750 MHz spectra presented in the January issue and thought your readers would be interested in seeing what's being done in the real world at the other end of the frequency spectrum.

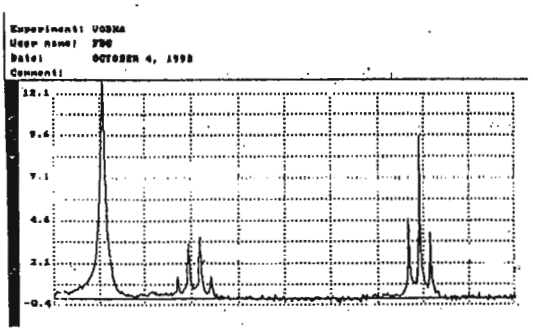
We've been on the road with the ATI Series 2000 portable NMR preaching the gospel of high resolution FT NMR for process control. To that end, we've run proton, fluorine, and phosphorus samples of process streams in both continuous flow and batch sample modes.

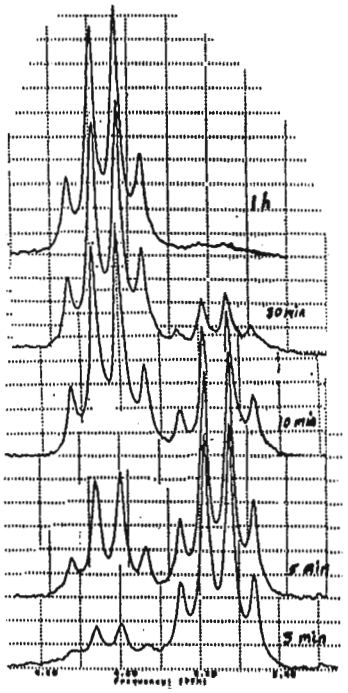
We have also simulated some processes in our own lab; two examples are shown below. The first is simply the esterification of absolute ethanol with excess TFA, basically duplicating, in a fairly casual manner, an experiment designed for the teaching lab. The other is following the curing of a two component epoxy adhesive. We've also included a spectrum of one of our favorite samples.

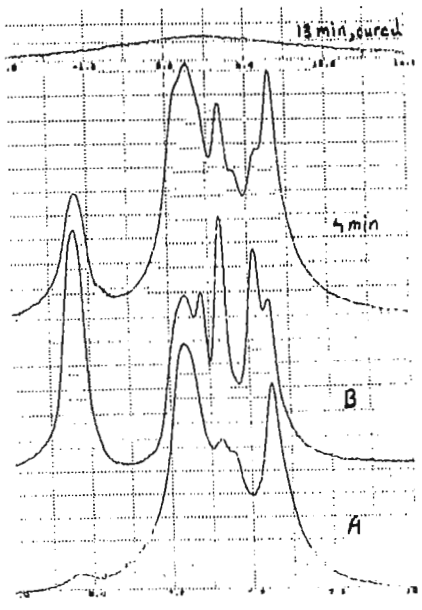
We have successfully demonstrated the use of NMR for water balance control of a polymerization process and are making some progress with FT NMR as a detector for HPLC in process control. We hope to be able to report on these processes in future communications. 60 MHz is alive and well!

Best regards,

Myra Gordon Frank Contratto Tal Cohen Matthew Blakley







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Eileen K. Jaffe, Ph.D.
Member

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January 27, 1993 (received 1/30/93)

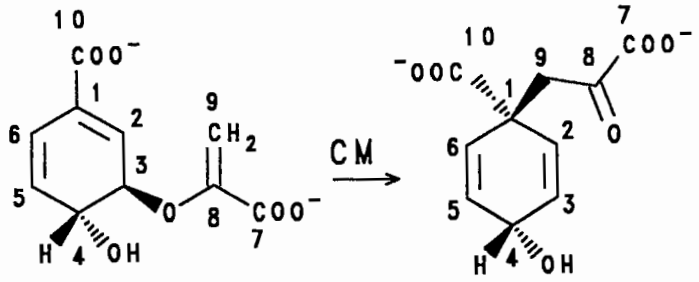
Professor Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

RE: ^{13}C NMR Studies on Enzyme-Product Complex of *B. subtilis* Chorismate Mutase

Dear Professor Shapiro:

Greetings from Philadelphia. As new subscribers, we wish to introduce our area of research to TAMU NMR Newsletter readers. Our group has been using multinuclear NMR to look at enzyme-bound substrates, products or intermediates; in some cases the enzymes are as large as 280 KDa. One of the smaller enzymes that intrigues us is chorismate mutase - an enzyme that catalyzes the rearrangement of chorismate to prephenate illustrated below; this is the first committed step in aromatic amino acid biosynthesis. Recently, we have assigned the ^{13}C NMR spectrum of prephenate bound to *B. subtilis* chorismate mutase using [U-^{13}C]chorismate as substrate. The enzyme-bound prephenate undergoes remarkable changes in chemical shifts compared to free prephenate as shown in the table below. We have also observed some changes in J_{CC}'s when prephenate binds chorismate mutase. The olefinic carbons undergo major chemical shift changes and they are non-degenerate in the presence of enzyme (C_2 and C_6 or C_3 and C_5 of prephenate are degenerate in the absence of enzyme). We have carried out model studies (pH titrations and solvent effects) which suggest that the changes in chemical shifts and coupling constants cannot be adequately described simply in terms of changes in pKa or hydrophobic solvation at the active site of the enzyme.

CHORISMATE MUTASE REACTION



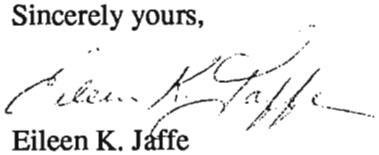
Chorismate Prephenate

^{13}C NMR chemical shifts of bound and free [U-^{13}C]prephenate

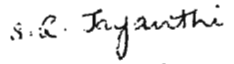
Carbon	Free (ppm)	Bound (ppm)	Change in Chemical Shift ($\Delta\delta$)	ΔJ_{CC} (bound-free)
C_1	48.6	49.0	0.4	
C_2	131.7	129.4	-2.3	
C_3	127.9	129.4	1.5	
C_4	61.6	59.8	-1.8	$^1J_{C7,C8} = 0\pm1$ Hz
C_5	127.9	133.5	5.6	
C_6	131.7	125.1	-6.6	
C_7	170.1	166.5	-3.6	$^1J_{C8,C9} = +4.5\pm1.5$ Hz
C_8	204.3	202.9	-1.5	
C_9	48.1	46.2	-1.9	
C_{10}	180.0	177.9	-2.1	$^1J_{C10,C1} = +5\pm1$ Hz

We should also like to bring the published ^{13}C NMR characterization of [U-^{13}C]chorismate, [U-^{13}C]prephenate and [U-^{13}C]hydroxyphenylpyruvate (Rajagopalan, J.S., Chen, L.-C. and Jaffe, E.K. *Bioorg. Chem.* **20:** 115-123, 1992) to the attention of your readers. We found it possible to obtain one, two and three bond J_{CC}'s for the above compounds and would like to utilize these J_{CC}'s to elucidate conformational information. As novices to computational chemistry, we solicit advice and/or collaboration in this endeavor.

Sincerely yours,



Eileen K. Jaffe
(e-mail) EK_Jaffe@fccc.edu



Jayanthi S. Rajagopalan

EKJ,JSR/msw

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Reads ^{13}C NMR peak tables directly

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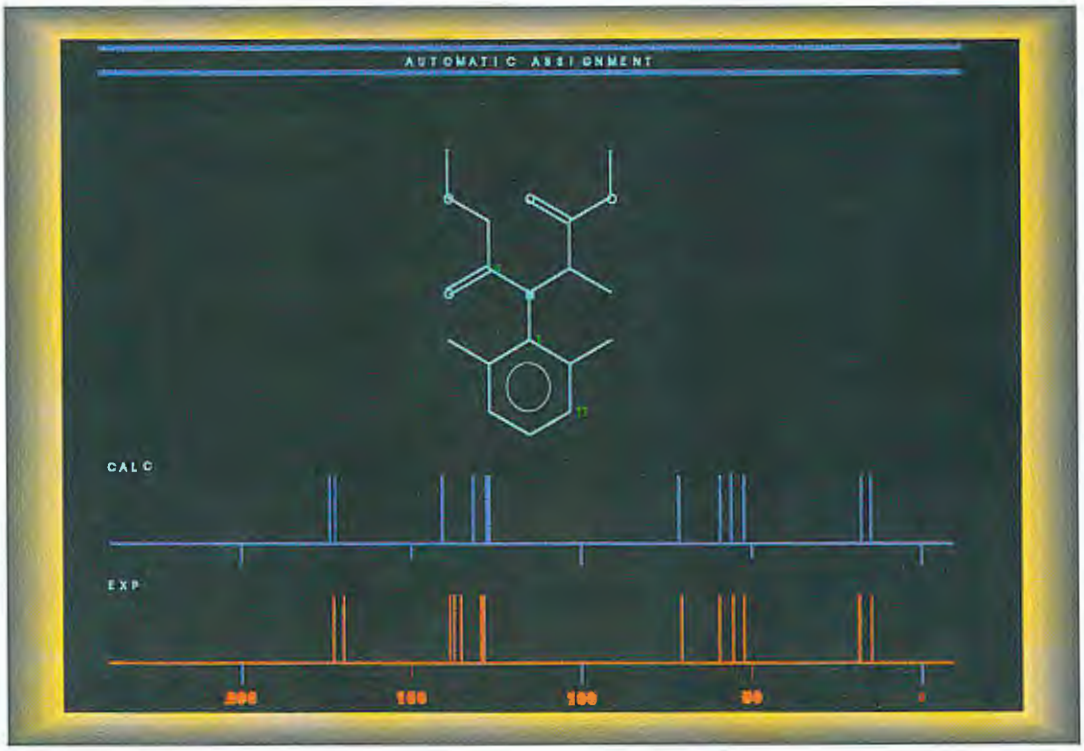
Comparison of the calculated spectrum of a proposed structure with its measured spectrum. The intelligence of CSEARCH is demonstrated by favorable comparison for a structure not contained within the database of 52,000 spectra.



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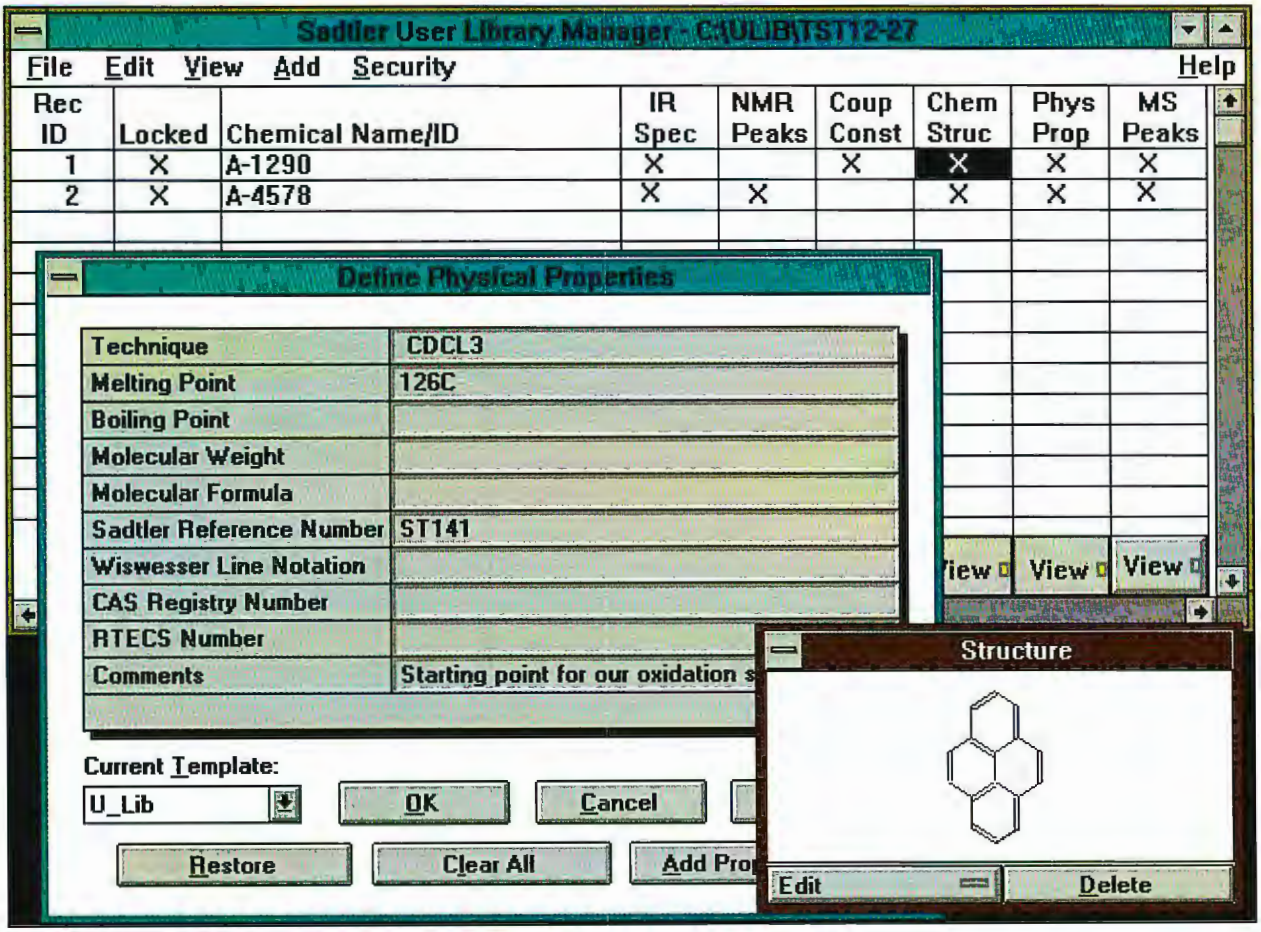

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TCU
TEXAS CHRISTIAN UNIVERSITY
Box 32908
Fort Worth, Texas 76129
817-921-7195

Department of Chemistry

2/12/93
(received 2/19/93)

Dear Barry:

Recently Mike Barfield and I searched for examples of $^3J_{HH}$ couplings in rigid molecules where one could hope to model accurate C-C-H and H-C-C-H angles. The purpose was to parameterize an updated verson of the Karplus equation (JACS, **114**,1574 (1992)). In checking earlier work we were unable to identify any case where people had found reliable examples of torsion angles near 180°.

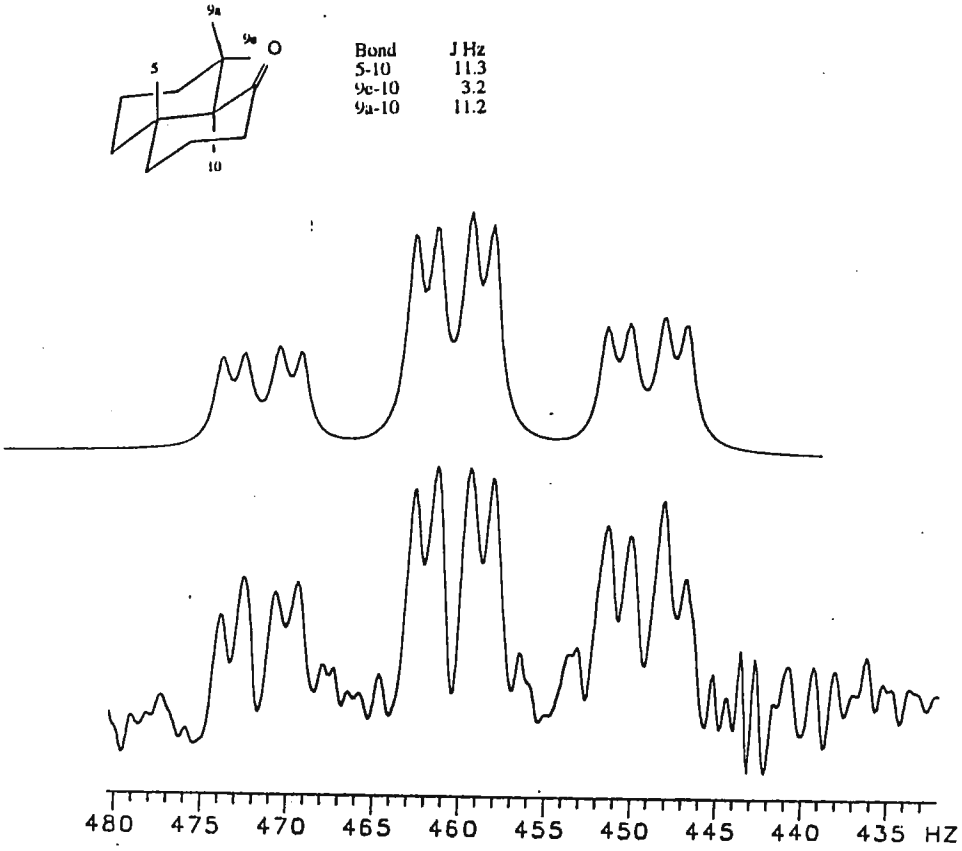
In thinking about this problem at greater length, it struck me that commercially available *trans* 1-decalone might provide the desired situation. When examined, however, it became clear that the two methines in this compound were hopelessly buried in the methylene envelope to a point where it was unlikely that even the highest field machines known could resolve the spectrum. Borrowing an experiment from early days ^{13}C NMR, I resorted to a partially relaxed proton spectrum. A series of 180-τ-90 pulses were essayed to define conditions where the methylene protons were just nulled in the baseline, and the slower relaxing methines were down pointing. These were then rephased for normal presentation. The downfield methine adjacent to the carbonyl is shown below.

A set of trial couplings were generated by modelling the molecule with PCMODEL and using the embedded Altona equation to approximate the couplings to adjacent protons. Refinement via Laocn5 indicated a long range coupling (1.3 Hz) was required. Presumeably, this was across the ring to one of the C-2 protons. When this was taken into account an RMS fit of 0.058 Hz was achieved. The simulated spectrum and coupling values are given in the figure. It is a nice case since we got two values in the desired torsion angle range. A revised parameterization of our initial equation is in press in MRC.

Regards,

Bill

William B. Smith



Two additional items:

1. We have an FX-60 which has not been operational for several years. JEOL apparently no longer services machines that old. The problem is buried somewhere in the electronics. Much of the machine-magnet, computer probes, etc are still ok. Anyone who wants is invited to come haul it away free of charge. There is a ^{1}H-^{13}C switchable probe as well as a deuterium-phosphorous probe.
2. Does anyone out there run COLOC on an XL-300. We would be interested in having a copy of the appropriate software to do this experiment.

Department of Chemistry

Head of Department:
Dr K.D. Sales BSc PhD

Departmental Fax 081 981 8745

UNIVERSITY OF LONDON

Queen Mary and Westfield College
Mile End Road
London E1 4NS

Telephone 071 975 5555
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Telex 893750

Professor B.L. Shapiro,
968 Elsinore Court,
Palo Alto, CA 94303, USA

27th January 1993
(received 2/5/93)

Dear Barry,

Deceptively Simple 2-D Exchange Spectra

Large quantities of very pure phosphine gas are used in the vapour phase deposition of indium phosphide films for semiconductor devices. It was recently demonstrated that the phosphine adduct with *tris*-(pentafluorophenyl)borane provides a relatively safe method for the fixation and storage of the highly toxic phosphine, which can be released from the adduct by moderate heating. We have observed that in toluene solution, in the temperature range 243 - 263 K, the adduct undergoes slow exchange (by NMR - see spectrum **a**) with excess phosphine:

$$(C_6F_5)_3B\text{-}PH_3 \quad + \quad {}^*PH_3 \quad \rightleftharpoons \quad (C_6F_5)_3B\text{-}{}^*PH_3 \quad + \quad PH_3$$

Because we like messing around with NOESY data, we first sought to quantify the exchange process by analysis of the ^1H NOESY spectrum as function of mixing time, and in so doing we obtained the spectra (among many others) **b** - **d**. We were intrigued by the appearance and disappearance of some of the peaks which, in a hand-waving manner, could be explained by changes in the relative amounts of exchange and 31P spin-lattice relaxation occurring during the elapsed mixing time. However we soon realised that a full quantitative analysis of these 2-D spectra would involve an **L** - matrix (the sum of the kinetic and relaxation matrices) with dimensions 32 x 32 (2^4 basis functions for each site) and include many (unknown) relaxation parameters. Faced with this we reverted to obtaining the desired information via the selective inversion of the free phosphine signal in the $^{31}P\text{-}\{^1H\}$ spectrum. The parameters we obtained from this analysis were the spin-lattice relaxation rates of the two ^{31}P sites and the pseudo first order exchange rates (k) at 243, 253, and 263 K. The relaxation rates were in the range 1.75 to 3.75 s^{-1}, and the quality of our simulated data in our iterative fitting procedure was rather insensitive to the actual value. The analyses were however sensitive to the final value of k. For a series of three samples, between which the excess phosphine concentration was varied and the adduct concentration held constant, the value of k did not change and we therefore take this to mean that k is a true first order rate coefficient and that the above equilibrium proceeds in a stepwise fashion with a slow initial dissociation of the adduct into borane + phosphine followed by rapid reaction of the borane to form the adduct, i.e. the reaction is comparable to a S_{N1} process rather than a concerted S_{N2}. For the same sample at 243, 253, and 263 K we obtained values for k of 0.27, 3.48, and 31.4 s^{-1} respectively which gave a value of ca. 126 kJ mol^{-1} for the activation energy of the proposed dissociation of the adduct.

One final point of interest (to us at least) is that the installation of the new University of London NMR service machines is proceeding well with the AMX-600 (with solids) here at QMW and AMX-400 at King's.

Best wishes.

Yours sincerely,

Dr. G.E. Hawkes

Dr. K.D. Sales

Deceptively simple 2-D exchange spectra

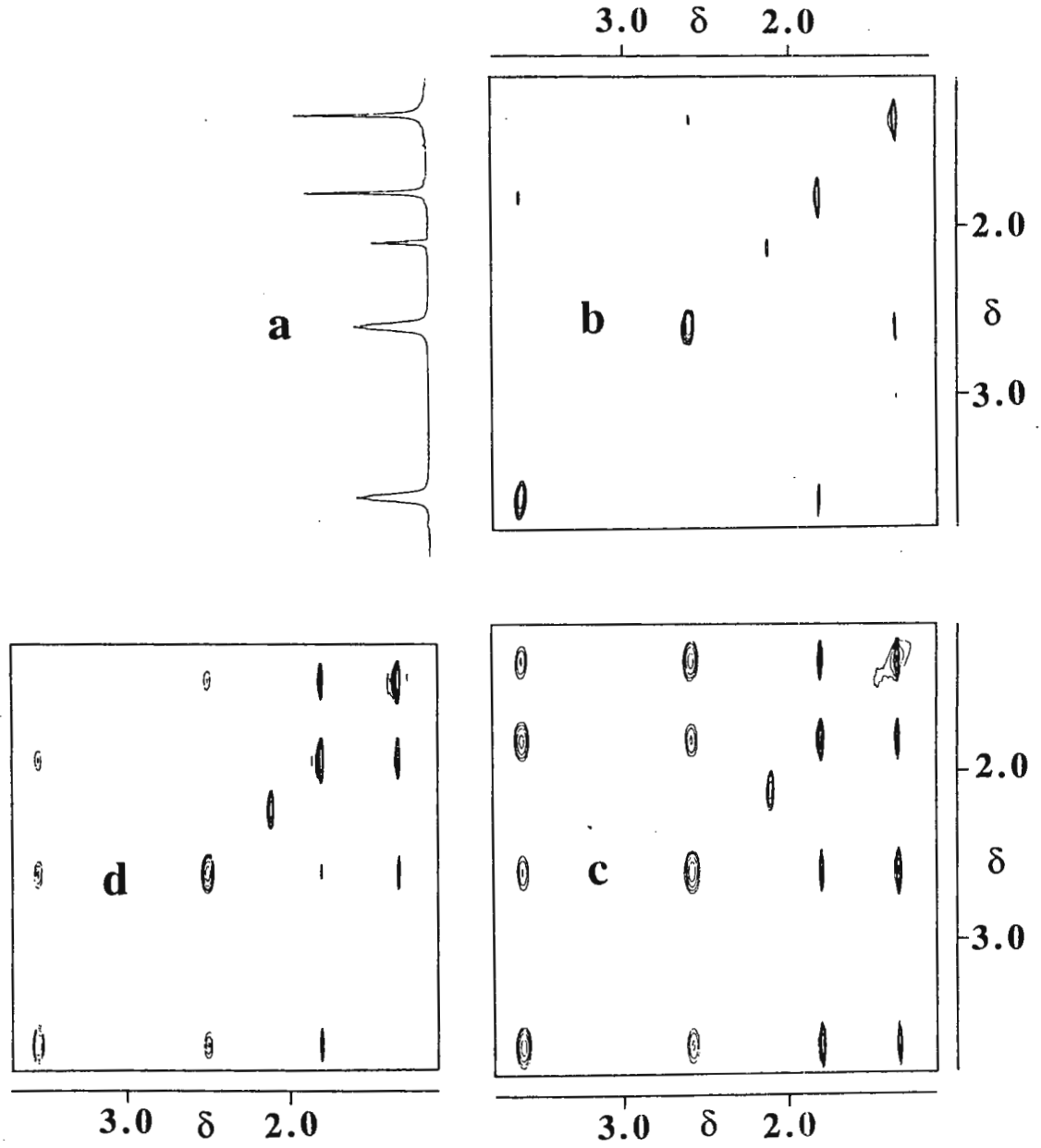

Figure. 400 MHz ^{1}H NMR spectra of a mixture of the adduct (δ 3.0) and free phosphine (δ 1.55) in toluene-d_8; (a) 1-dimensional spectrum at 253 K; (b) and (c) 2-dimensional NOESY spectra at 253 K with mixing time τ_m = 50 ms and 0.6 s respectively; (d) 2-dimensional NOESY spectrum at 243 K, τ_m = 0.6 s.

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These spectra of AlPO-11 below illustrate these effects. The top spectrum shows single resonance DOR at 625 Hz spinning. The bottom trace shows significant improvement at 980 Hz; note especially the appearance of the octahedral peak at 30 ppm. The middle trace shows 625 Hz DOR with proton decoupling; the peaks are narrower than at 980 Hz, especially the octahedral signal.

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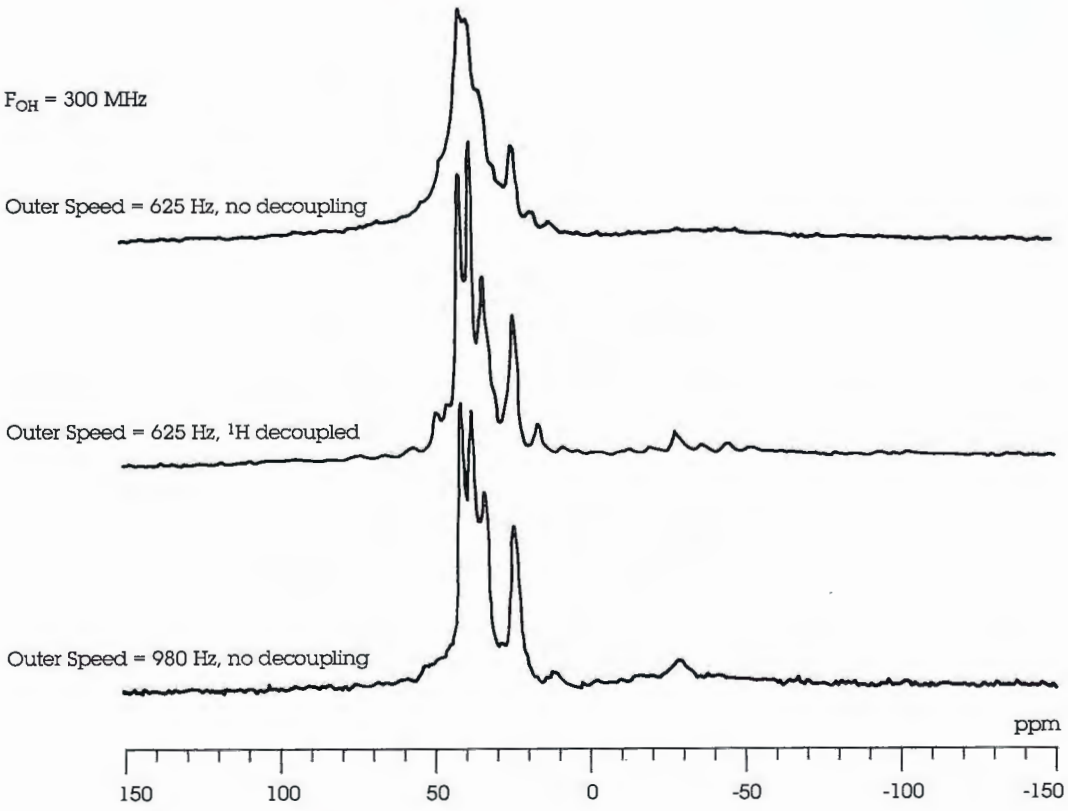


Chemagnetics

KARL-FRANZENS-UNIVERSITÄT GRAZ
Institut für Organische Chemie
Dr.Heinz Sterk

A-8010 Graz, 26.1.92
Heinrichstraße 28
Tel. (0316) 380 — .....

Unser Zeichen:

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

(received 2/6/93)

"Monochromatic" SynchronousNutation - another way to measure cross correlation

Dear Dr. Shapiro :

The effects of cross-correlation between chemical shift anisotropy (CSA) and dipolar coupling (DD) has been widely studied in the past[1-6]. In the laboratory frame, this interference term leads to a partial conversion of Zeeman order into longitudinal two-spin order, which can be detected, notably in proton systems, via double-quantum filtered two-dimensional exchange spectroscopy (DQF-NOESY)[5]. To improve selectivity and restrict the dissipative evolution of the spin system to certain pathways, a selective spin-locking experiment[7] has been proposed recently. Transverse magnetization I_x^A is excited by a self-refocusing 270° Gaussian pulse. The evolution under the scalar coupling is refocused by a G^3 Gaussian cascade applied at the chemical shift Ω_A. At the end of the t_1-period we thus have pure in-phase magnetization. Since time-proportional phase increments (TPPI) have been used, a single in-phase signal is obtained at the center of the ω_1-domain. This transverse magnetization is turned back to the z-axis and subsequently driven to nutate in the y-z plane by a string of square pulses. During the nutation period, Zeeman polarization I_z^A will partly be converted into longitudinal two-spin $2I_z^A I_z^X$ order under the action of CSA/DD cross-correlation. This spin ordered state can be directly detected by applying a 270° Gaussian pulse to spin X, leading to an anti-phase multiplet in ω_2 and a single line in the ω_1-domain. Fig.2 shows the time-dependence of longitudinal two-spin order $2I_z^A I_z^X$ obtained with the sequence in Fig.1.

Figure 1

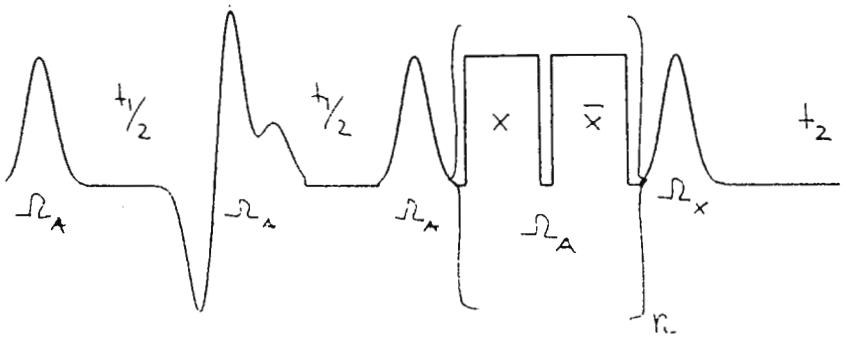
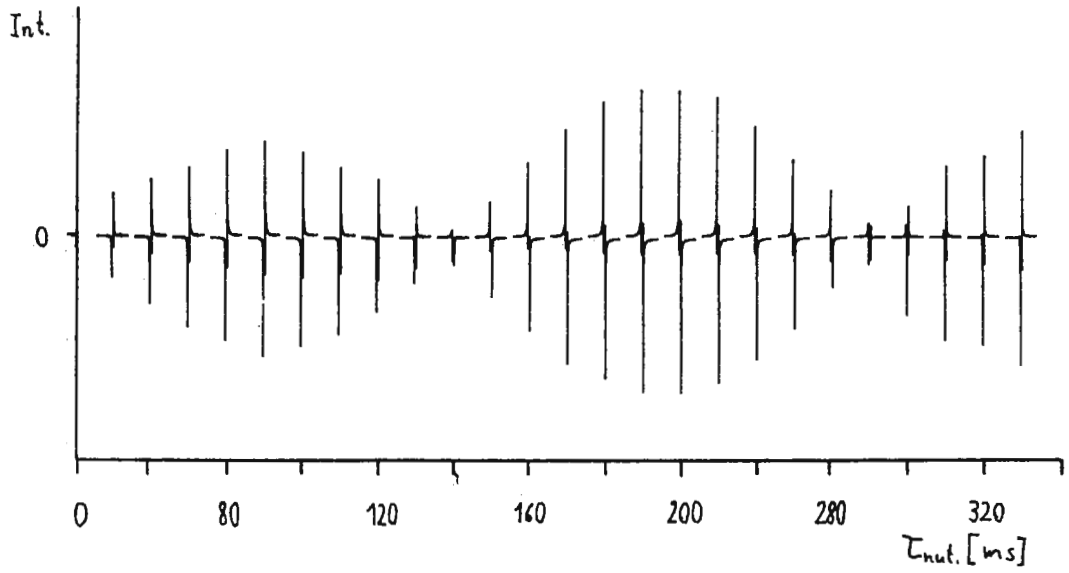


Figure 2



Yours sincerly

H.Sterk G.Zieger R.Konrat

(1) H.Shimizu, J.Chem.Phys.,40, 3357 (1964)
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Mailing Address:
THE JOHNS HOPKINS HOSPITAL
DEPT OF RADIOLOGY/MRI 110
600 N. WOLFE STREET, BALTIMORE, MD 21287
U.S.A

January 22, 1993
(received 2/4/93)

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

Proton Detection of {1-^{13}C}-Glucose Metabolism of Perfused Glioblastoma Cells.

Dear Dr. Shapiro,

we presently have the availability of a 400 MHz GE/Bruker NMR Machine equipped with shielded gradients, which allows indirect detection of labelled compounds using heteronuclear gradient-enhanced spectroscopy (1-5). Although a factor of two in signal is lost with respect to phase-cycled experiments, the gradient experiments provide complete frequency-independent water suppression, allowing artifact-free detection of metabolites at the water frequency with optimum dynamic range, which may actually increase sensitivity. We are using the gradient-enhanced HMQC to detect products of 13C-labelled glucose in perfused cells. The Figure shows 1H-detected 13C spectra of glucose consumption of perfused glioblastoma cells. At the start of the experiment, glucose in the perfusion medium (12 mM) is replaced by 1-13C-glucose, after which 3-13C-lactate was formed by the cells. When 13C-glucose infusion is stopped, both lactate and glucose disappear from the spectrum. The probe used was a 5mm 1H observe/transmit coil-13C decoupling coil. Perfusion into the bottom of a 5mm perfusion apparatus and out of the top of this apparatus assured optimum volume occupancy and perfusion. This was possible due to the specially-designed temperature coil that can accomodate tubing through the bottom of the probe. We are presently interpreting the results and improving time resolution. A series of studies on tumors of different grade is underway. Please contribute this letter to Jack Cohen's account.

Yours sincerely,

Jesus Ruiz Cabello[1], Delphine Davis[2], Jack Cohen[1], Peter van Zijl[2].

1) Georgetown University Medical school, Dept. of Pharmacology, 4 Research Court, Rockville, MD 20285. 2) Johns Hopkins University Medical School, Dept. of Radiology/MRI 110, 600 N. Wolfe Street, Baltimore, MD 21287

[1] A. Knüttel, R. Kimmich and K.-H. Spohn, J. Magn. Reson. **86**, 526 (1990).
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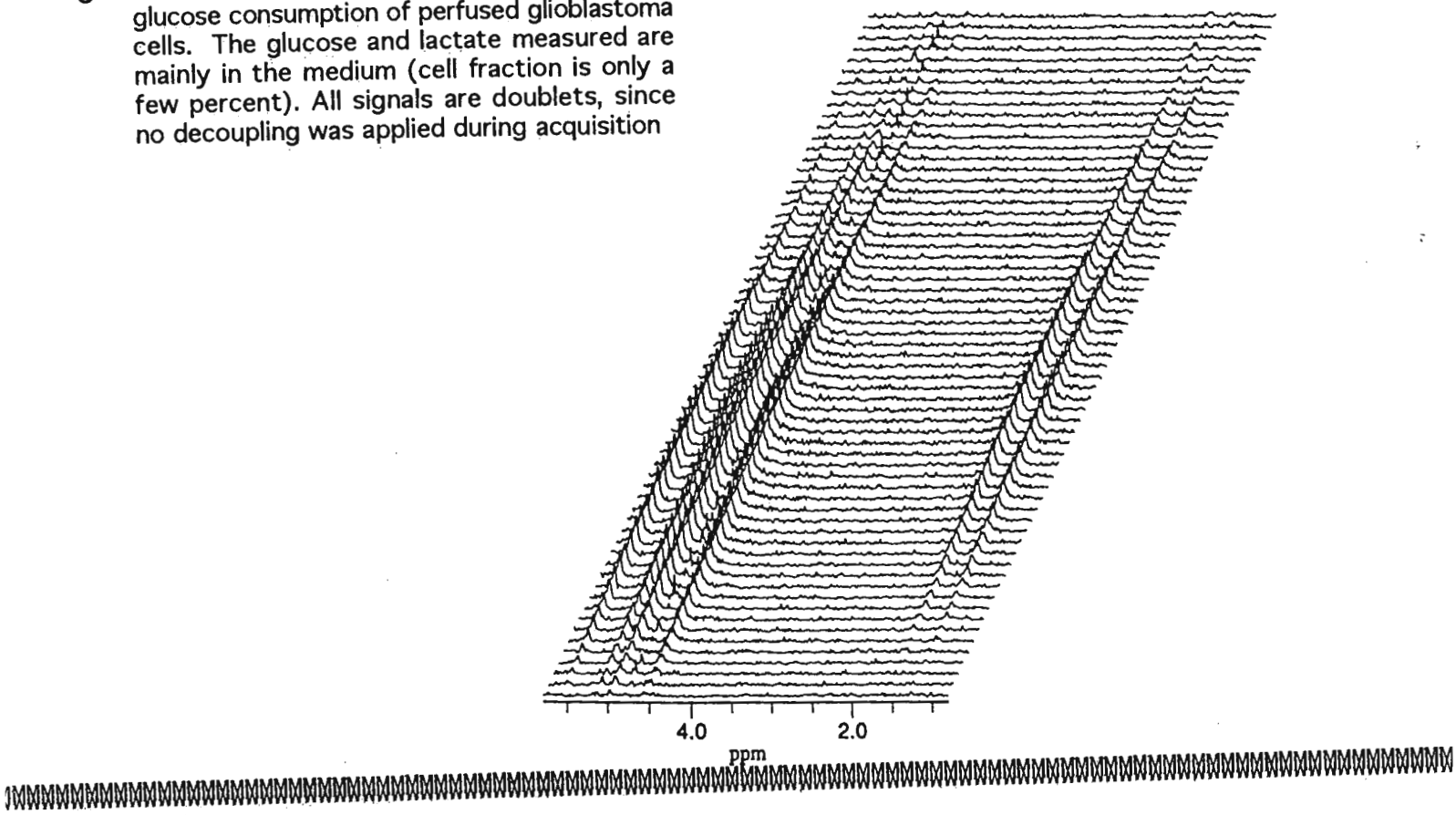
[5] J. Ruiz-Cabello et al., J. Magn. Reson., **100**, 282 (1992).

Fig: 1H-detected 13C spectra (32 scans, 48s) of glucose consumption of perfused glioblastoma cells. The glucose and lactate measured are mainly in the medium (cell fraction is only a few percent). All signals are doublets, since no decoupling was applied during acquisition



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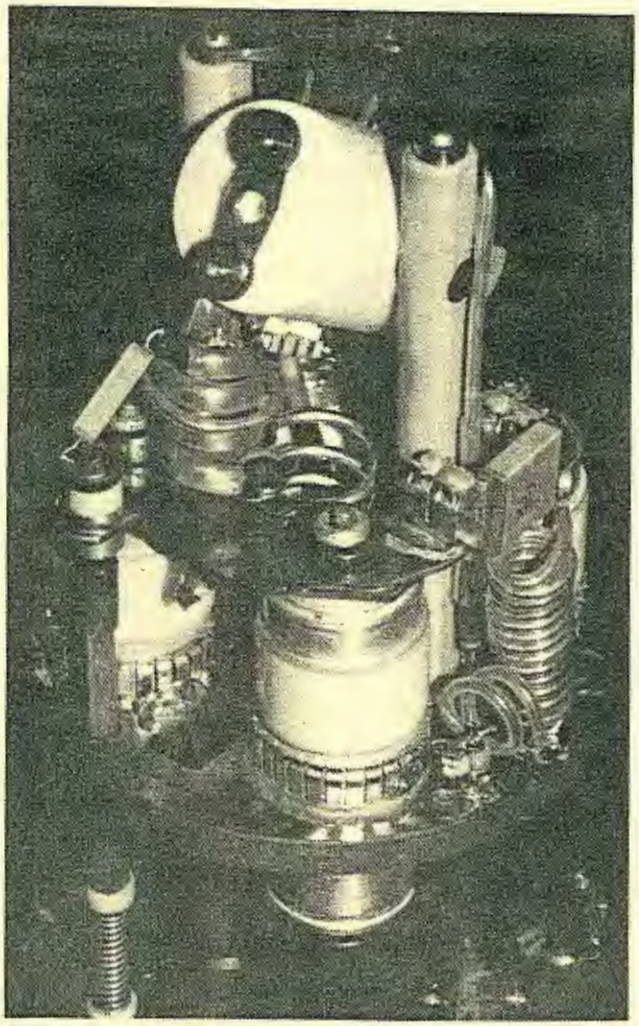

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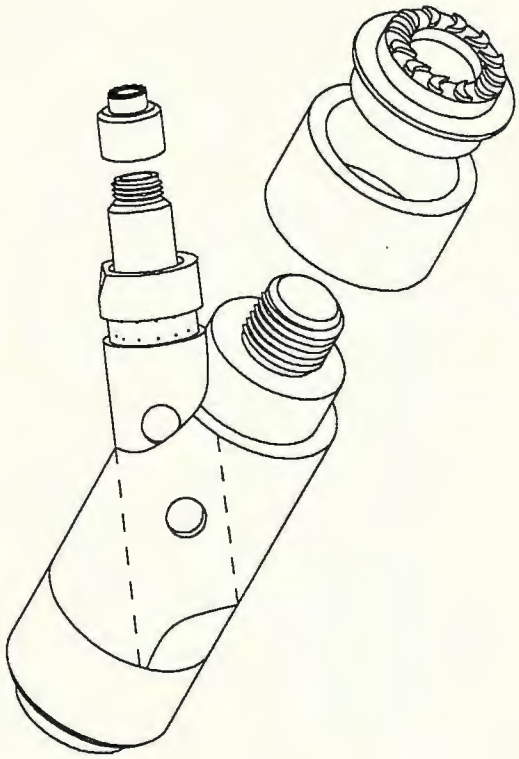
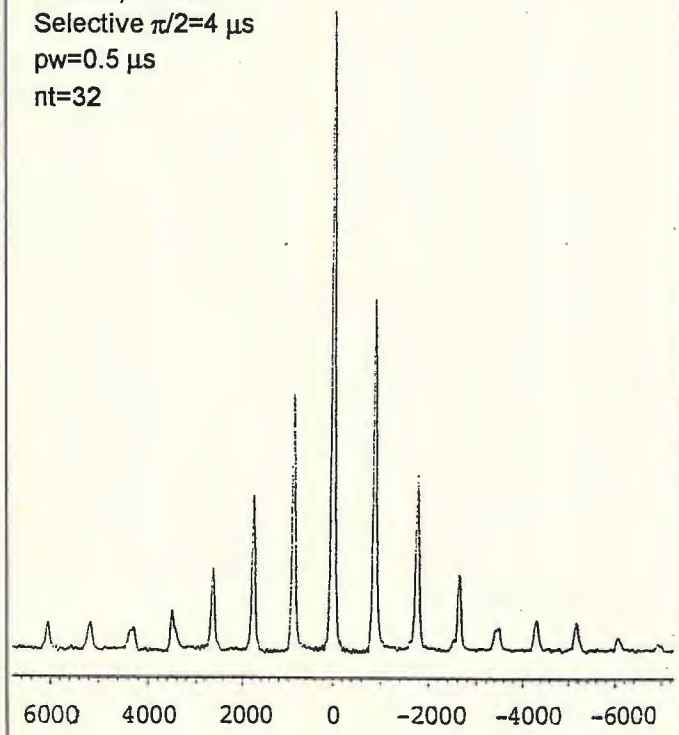
Dual spin rate detection	No	**Yes**
Acoustic noise	deafening	**quiet**
VT range		**-140 to +180°C**



Na_2SO_4 DOR Spectra without side-band suppression

870 Hz, 4500 Hz
Selective $\pi/2$=4 µs
pw=0.5 µs
nt=32



Spectra provided by Dr. Laima Baltusis and Varian Applications Lab, Palo Alto, California

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9.4	^{17}O	54	20 µs	600	4.5

* Ringdown (20τ) when matched to typical preamp.
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(received 1/30/93)

Diffusion-Based Solvent Suppression in 2D Experiments

Dear Barry,

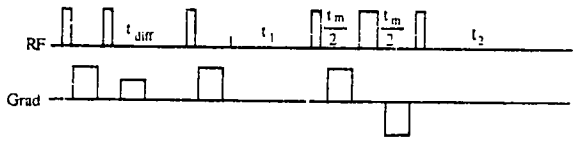
We recently acquired a gradient accessory for our GE Omega 500 MHz NMR spectrometer, and we've been exploring the many applications of the technology. In properly designed gradient-based experiments, solvent is automatically suppressed if gradients are used to select for multiple-quantum coherence, or for heteronuclear coherence transfer. In protein solutions, solvent can also be suppressed by taking advantage of the large diffusion rate differences between solute and solvent (Zilj and Moonen, J.M.R., **87**, 18-25). We've been working on combining diffusion-based solvent suppression with homonuclear two-dimensional experiments which could not otherwise use gradient methods for solvent suppression, such as COSY, TOCSY, and NOESY.

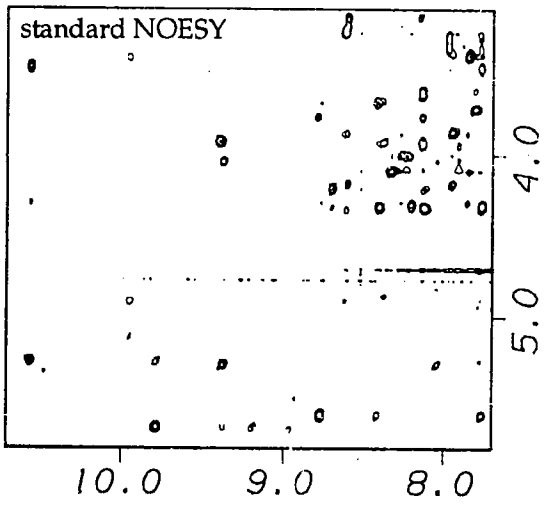
There are a couple of problems with implementing these experiments. First, when water magnetization gets inverted, it can give off a burst of signal, apparently because of a MASER effect. To avoid this you need to be careful not to let a strong water signal become inverted. Second, in diffusion-based solvent suppression, the water signal decreases much faster than the protein signal, but the protein signal still decreases due to both diffusion and relaxation. If you rigorously suppress the solvent, you pay a big price in signal loss from the protein. To get the best data, you must compromise and tolerate some residual water signal.

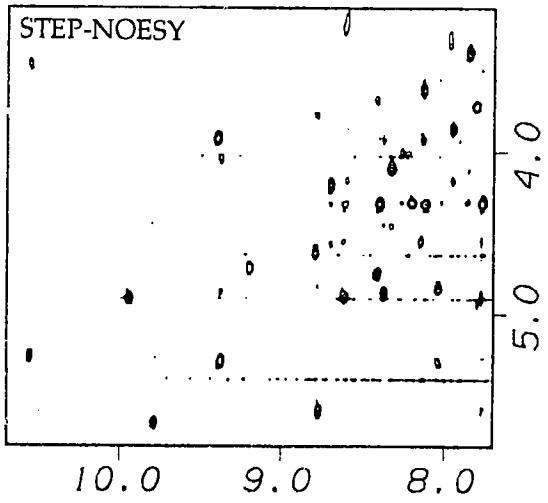
As an example, the figure shows part of a NOESY spectrum of 6 mM BPTI acquired with diffusion-based solvent suppression, compared to a NOESY spectrum which uses solvent presaturation and a gradient pulse for longitudinal magnetization selection during the mixing time. In the diffusion-based version of the experiment, the preparation pulse is replaced with a stimulated echo pulse sequence (STEP) to suppress solvent. The r.f. and gradient pulses applied during the mixing time eliminate water signal that grows in during the mixing time, and select for longitudinal magnetization. The STEP-NOESY has lower sensitivity, but peaks near the water resonance are present which are inadvertently suppressed in the standard NOESY experiment.

Charlie Eads

Charles D. Eads







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Professor B.L. Shapiro
TAMU Newsletter
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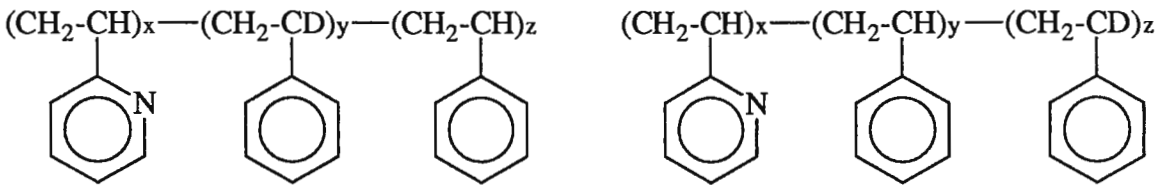
Palo Alto, CA 94303

January 30, 1993
(received 2/6/93)

Do Surfaces Slow Down or Speed Up Polymer Dynamics?

Dear Barry:

The answer to the above "trick" question is that it depends. Generally, polymers adsorbed at interfaces move more slowly than those in bulk or solution states. One could think of solvent-less polymers at interfaces as having a higher T_g than the bulk polymer. In one case that we have studied, part of a polymer at the interface moves faster than it would in solution. Specifically, we have studied the adsorption and dynamics of VPDSS and VPSDS as shown below:



VPDSS **VPSDS**

In a solvent like toluene, these polymers adsorb on silica with the VP group attached and the styrene segments hanging off in a brush-like arrangement. We have used deuterium NMR relaxation times to probe the dynamics of the terminally-attached polymers in the presence of different solvents. For the polymers in a toluene dispersion with silica and in solution, the relaxation times are shown below (Blum, Sinha, Schwab, *Macromolecules*, 1990, **23**, 3592.) If we use the ratio of the relaxation times as a measure of the local dynamics, the local segmental dynamics appear more isotropic or faster than in solution! For solvents which are poorer (thermodynamically) for styrene, the reverse is observed (Sinha, Blum, Schwab, in preparation). Thus the result is solvent dependent.

material		T_1, ms	T_2, ms	T_1/T_2
VPDSS	surface	3.63	3.38	1.07
	solution	3.63	2.75	1.32
VPSDS	surface	3.94	3.60	1.09
	solution	3.94	3.25	1.21

Sincerely,

Frank D. Blum

Frank D. Blum
Professor of Chemistry
and Senior Investigator
Materials Research Center

P.S. As your orange reminder suggested, I have avoided double spacing. However, the "Black Plague", which only exists here in the southwest US, is not deadly if treated with antibiotics. In order to have the impact you desire, I respectfully submit that you update your list of threatening maladies to ones which might better intimidate your modern technologically audience. You could even do it in a way which doesn't impute anyone's lifestyle, *e.g.* the occurrence of a "system error" or computer virus. Alternatively, AIDS, second-hand smoke, or benzene exposure could be used.

414-38

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DR. RAY DUPREE

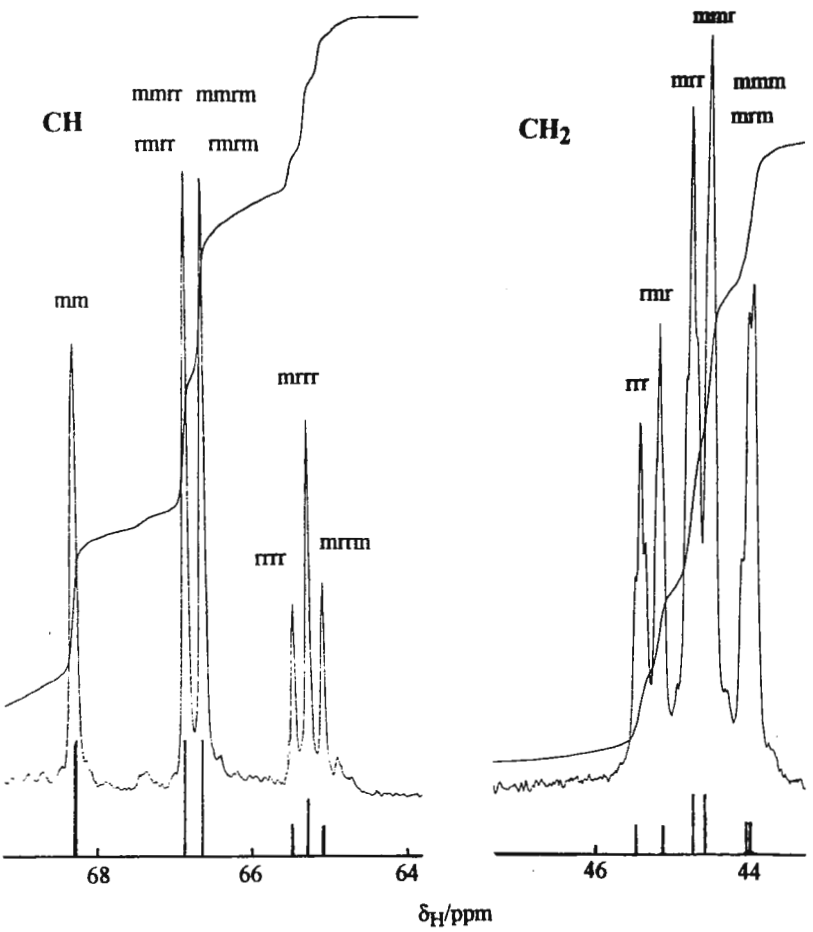
A Very Twisted Polymer

10th Feb 93
(received 2/16/93)

Dear Barry,

One of our recent interests has been in using carbon NMR to predict the conformations of polymers. Alan Tonelli has pioneered this use of γ-*gauche* shifts, and we have attempted a few improvements. One is to distinguish between the different *syn*-axial interactions that must occur in any polymer chain, i.e. between atoms separated by 4 bonds but by only small distances. Another is to loop the process of calculating the carbon shifts from the various conformer weightings, so as to calculate weightings from shifts. This enables us to tackle polymers which are currently impossible to model, because of strong internal repulsions or attractions.

We have obtained good results, fitting to 9 polymer spectra so far. The example shown here is the spectrum of poly(vinyl alcohol), which is particularly interesting because of the myriad possible internal H-bonds. The predicted shifts are shown as sticks, in the correct order. In this case, uniquely, we calculate that neighbouring OH groups prefer to lie mutually parallel, despite their steric repulsions. We also calculate that there is not much energetic disadvantage when the chain suffers a pentane effect, i.e. a chain-chain 1,5 *syn*-axial interaction. The result is unusually tight coiling of the polymer chain. The energy gains from hydrogen bonding can explain both these conclusions.



Observed and fitted (stick) carbon NMR peaks for poly(vinyl alcohol)

Hawk-eyed readers may spot additional, small peaks due to incomplete hydrolysis of acetate groups. Poly(vinyl alcohol) is made commercially from the hydrolysis of poly(vinyl acetate). Thereby hangs a tale. It is experimentally impossible to remove the last few acetate groups, even under forcing conditions. Perhaps this can be explained by our prediction of a tightly coiled chain, for this would serve to protect the last acetate groups from chemical attack.

Yours sincerely

Oliver Howarth

Acorn NMR

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Laboratoire de RMN et Modélisation Moléculaire - UMR 50 CNRS/Bruker/ULP
Institut de Chimie, BP296/R8, 67008 Strasbourg Cedex, France *January 29, 1993*

Simple formulas for the simulation of MAS spectra of Quadrupolar nuclei

Dear Barry,

It is well known that, in the presence of anisotropic shift (λ = CS) or quadrupolar (λ = Q) interactions under sample spinning with a frequency $\nu_r = \omega_r / 2\pi$, the orientation dependent frequencies ω_λ are written to first order [1]

$$\omega_\lambda(t) = \omega_\lambda^{is} + \frac{\omega_\lambda^{an}}{2}\left\{K^\lambda\left(3\cos^2\Theta - 1\right) + \left[C_1^\lambda \cos(\gamma + \omega_r t) + S_1^\lambda \sin(\gamma + \omega_r t)\right]\sin 2\Theta \right.$$
$$\left. + \left[C_2^\lambda \cos 2(\gamma + \omega_r t) + S_2^\lambda \sin 2(\gamma + \omega_r t)\right]\sin^2\Theta\right\} \qquad (1)$$

where

$$K^\lambda = 3\cos^2\beta - 1 - \eta_\lambda \sin^2\beta \cos 2\alpha = f_0^\lambda(\alpha,\beta)$$

$$C_1^\lambda = -\left(3 + \eta_\lambda \cos 2\alpha\right)\sin 2\beta = f_1^\lambda(\alpha,\beta) \qquad S_1^\lambda = 2\eta_\lambda \sin\beta \sin 2\alpha = f_2^\lambda(\alpha,\beta)$$

$$C_2^\lambda = \left(3 + \eta_\lambda \cos 2\alpha\right)\sin^2\beta - 2\eta_\lambda \cos 2\alpha = f_3^\lambda(\alpha,\beta) \qquad S_2^\lambda = 2\eta_\lambda \cos\beta \sin 2\alpha = f_4^\lambda(\alpha,\beta)$$

Θ is the angle between the magnetic field $\mathbf{B_0}$ and the spinner axis and (α, β, γ) are the Euler angles as defined by Spiess [2] giving the orientation of the λ tensor in the spinner frame. When the principal axes of the Q and S tensors are noncoincident, the shift interaction is expressed in the PAS of the Q tensor (or vice-versa). Recently, Skibsted *et al* [3] gave $\omega_\lambda(t)$ for this case. However, their expressions are quite complicated. Here, we give much more compact expressions which are useful for lineshape calculation. Indeed, $\omega_\lambda(t)$ for noncoincident tensors is simply obtained by substituting the following equations into Eq (1)

$$K^\lambda = \frac{1}{2} f_0^\lambda(\psi,\chi)\left(3\cos^2\beta - 1\right) + \left[f_1^\lambda(\psi,\chi)\cos\Gamma + f_2^\lambda(\psi,\chi)\sin\Gamma\right]\sin\beta\cos\beta$$
$$+ \frac{1}{2}\left[f_3^\lambda(\psi,\chi)\cos 2\Gamma + f_4^\lambda(\psi,\chi)\sin 2\Gamma\right]\sin^2\beta$$

$$C_1^\lambda = \left[f_1^\lambda(\psi,\chi)\cos\Gamma + f_2^\lambda(\psi,\chi)\sin\Gamma\right]\left(2\cos^2\beta - 1\right)$$
$$+ \left[f_3^\lambda(\psi,\chi)\cos 2\Gamma + f_4^\lambda(\psi,\chi)\sin 2\Gamma - 3 f_0^\lambda(\psi,\chi)\right]\sin\beta\cos\beta$$

$$S_1^\lambda = \left[f_2^\lambda(\psi,\chi)\cos\Gamma - f_1^\lambda(\psi,\chi)\sin\Gamma\right]\cos\beta$$
$$+ \left[f_4^\lambda(\psi,\chi)\cos 2\Gamma - f_3^\lambda(\psi,\chi)\sin 2\Gamma\right]\sin\beta$$

$$C_2^\lambda = \frac{1}{2}\left[f_3^\lambda(\psi,\chi)\cos 2\Gamma + f_4^\lambda(\psi,\chi)\sin 2\Gamma\right]\left(1 + \cos^2\beta\right) - \frac{3}{2} f_0^\lambda(\psi,\chi)\sin^2\beta$$
$$- \left[f_1^\lambda(\psi,\chi)\cos\Gamma + f_2^\lambda(\psi,\chi)\sin\Gamma\right]\sin\beta\cos\beta$$

$$S_2^\lambda = \left[f_1^\lambda(\psi,\chi)\sin\Gamma - f_2^\lambda(\psi,\chi)\cos\Gamma\right]\sin\beta$$
$$+ \left[f_4^\lambda(\psi,\chi)\cos 2\Gamma - f_3^\lambda(\psi,\chi)\sin 2\Gamma\right]\cos\beta$$

with $\Gamma = \alpha + \xi$

The first tensor is transformed by the Euler angles (ψ, χ, ξ) from its PAS into the PAS of the second tensor which is itself related to the rotor frame by the Euler angles (α, β, γ).

1. M. Mehring *Principles of High Resolution in solids*, 2nd ed. (Springer, Berlin, 1983)
2. H. W. Spiess In *NMR Basic Principles and Progress* Vol 15, p 55 (Springer, Berlin, 1978)
3. J. Skibsted, N. C. Nielsen, H. Bildsoe, H. J. Jakobsen *Chem. Phys. Lett.* **188**, 405 (1992)

J. Hirschinger P. Granger

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* * * * *

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Palo Alto, CA 94303, U.S.A.

(415) 493-5971

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No. 416 (May) ----------23 April 1993
No. 417 (June)----------21 May 1993
No. 418 (July)---------- 25 June 1993
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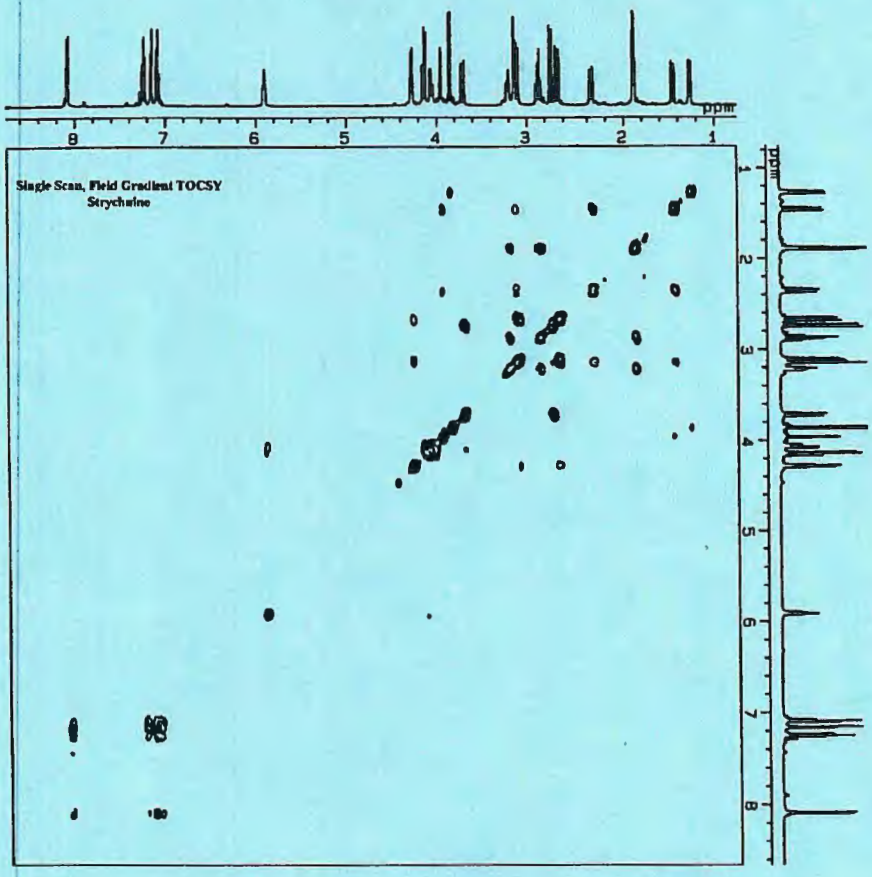

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