TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 403

April 1992

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FORTHCOMING NMR MEETINGS

Third Annual Workshop on Magnetic Resonance Microscopy and Materials Imaging, Charlestown (Boston), Mass., **May 11-12, 1992**; Contact: NMR Center at (617) 726-5811; fax (617) 726-5819; or email J. L. Ackerman at jerry@nmr-r.mgh.harvard.edu, or L. Garrido at garrido@nmr-r.mgh.harvard.edu. See Newsletter 402, 24.

Sixth Washington University-ENI/Emerson Electric Co. Symposium on NMR, St. Louis, Missouri, **May 18, 1992**; Contact: Karen Klein, Wash. Univ.; (314) 935-6405. See Newsletter 402, 46.

Gordon Research Conference: Magnetic Resonance in Biology and Medicine, Tilton, NH, **July 13 - 17, 1992**; Contact: Dr. A. M. Cruickshank, Gordon Research Center. University of Rhode Isalnd, Kingston, RI, 02881-0801; (401) 783-4011/3372; FAX: (401) 783-7644.

ISMAR 92 (The XIth Meeting of the International Society for Magnetic Resonance), Vancouver, B.C., Canada, **July 19 - 24, 1992**; Chairman: C. Fyfe. Contact: ISMAR 92, Dept. of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. Tel: (604) 822-2293; FAX: (604) 822-2847; EMAIL: ismar@unixg.ubc.ca; BITNET: ismar@ubcmtsg.bitnet.

Science Innovation '92, New Techniques and Instruments in Biomedical Research (sponsored by the AAAS), San Francisco, **July 21-25, 1992**; Workshops on biomedical imaging. chemical and structural NMR; Plenary session on NMR on Fri., July 24. Contact: Science Innovation '92, P.O. Box 630285, Baltimore, MD 21263; fax (202) 289-4021.

34th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, **August 8-14, 1992**; Contact: M. C. Goldberg, P.O. Box 25046 MS 424, Lakewood, CO 80225; (303)236-4728.

Eleventh Annual Scientific Meeting and Exhibition, Society of Magnetic Resonance in Medicine, Berlin, Germany, **August 8-14, 1992**; Contact: S.M.R.M., 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415) 841-1899, FAX: (415) 841-2340.

XV International Conference on Magnetic Resonance in Biological Systems, Jerusalem, Israel, **August 16 - 21, 1992**; Contact: Prof. Gil Navon, XV ICMRBS, P. O. Box 50006, Tel Aviv 61500, Israel.; Tel. (972-3) 5174571, Fax: (972-3) 655674/660325.

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

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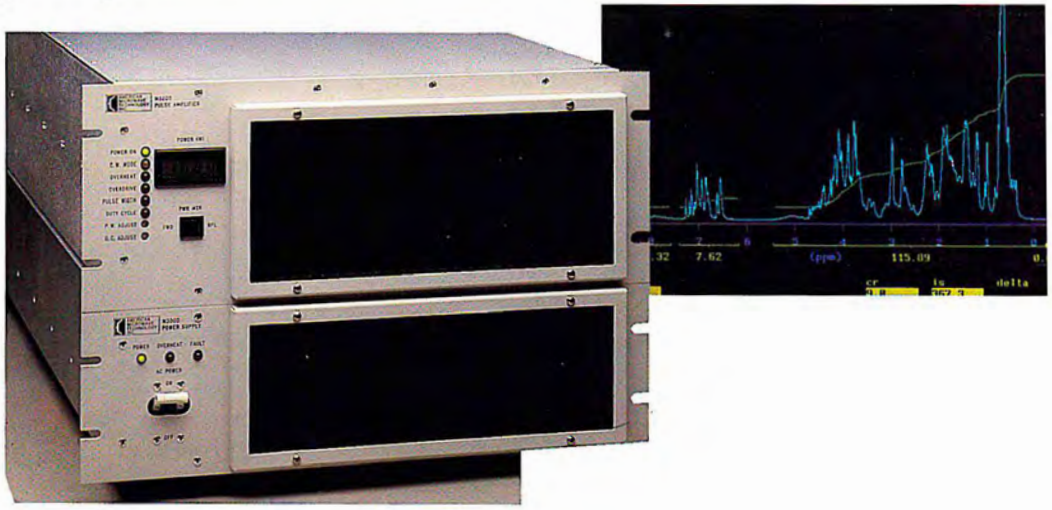

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9 March 92
(received 3/16/92)

RELATIVE SIGN DETERMINATION OF AMX COUPLINGS BY 2D A-X (A-M OR M-X) HETERONUCLEAR SHIFT CORRELATION SPECTROSCOPY

Dear Dr. Shapiro,

For the three spin AMX system the relative signs of all the couplings can be determined by any combination of two 2D heteronuclear shift correlation (HETCOR) experiments. In the A-X HETCOR spectrum a doublet is observed, resulting from the passive coupling with spin M. The resonances of this doublet are located at $(\omega_A + \pi J_{AM}, \omega_X + \pi J_{MX})$ and $(\omega_A - \pi J_{AM}, \omega_X - \pi J_{MX})$. If a line is drawn between the two resonances and the slope of the resulting line is positive then J_{AM} and J_{MX} have like signs. A negative slope would arise from unlike signs of J_{AM} and J_{MX}. However, this is only true if γ_A and γ_X have like signs! It is easily shown that when the signs of γ_A and γ_X are opposite the frequencies of the resonances in the A-X HETCOR spectrum are $(\omega_A + \pi J_{AM}, \omega_X - \pi J_{MX})$ and $(\omega_A - \pi J_{AM}, \omega_X + \pi J_{MX})$. In this case the dependence of the slope of the line connecting the two peaks is reversed; i.e., negative slope for like signs of J_{AM} and J_{MX} and positive slope for unlike signs. An example of this reversal is provided by the ^{29}Si-^{1}H HETCOR spectrum of TMS, ($\gamma_{Si}<0$). In the ^{29}Si-^{1}H correlation map, see Figure 1, an intense singlet and two weak doublets are observed. The singlet is due to TMS molecules void of ^{13}C nuclei, while the two doublets arise from TMS containing one ^{13}C nucleus,

$$(H_3{}^{12}C)_3 - {}^{29}Si - {}^{13}CH_3$$
$$\uparrow \qquad \uparrow \quad \nearrow \nwarrow$$
$$A \qquad X \quad M \; B$$

Although the above molecule is a A_9B_3MX spin system it can be treated as two separate AMX spin systems; $\Delta\upsilon_{AB}$ = 59Hz, J_{AB} = 0.2Hz. The lines connecting the resonances of each doublet exhibit a positive slope which is consistent with $^{1}J_{SiC}$ having the opposite sign compared to $^{1}J_{CH}$ and $^{3}J_{CH}$. Since it is generally excepted that $^{1}J_{CH}$ is positive (+118.4Hz), then $^{1}J_{SiC}$ = -50.9Hz and $^{3}J_{CH}$ =+2.0Hz. For completeness, the ^{13}C-^{1}H HETCOR experiment was also conducted, see Figure 2. In this instance both γ's are positive; therefore, the observed negative slope of the line drawn between the doublet resonances is due to $^{1}J_{SiC}$ and $^{2}J_{SiH}$ having unlike signs, i.e. $^{2}J_{SiH}$ =+6.5Hz. The magnitude as well as the signs of the couplings obtained are in agreement with the results of double resonance experiments[1].

It should be noted that the slope of the line connecting the doublet resonances in the A-X HETCOR spectrum is independent of the sign of γ_H and J_{AX}. Further analysis of the AMX spin system reveals that the 64 possible sign combinations of γ and J produce only 4 different slope combinations for the three 2D HETCOR spectra (3 of the slope combinations are related by symmetry; i.e. interchanging of the spin labels A,M and X). These slope combinations show that if two of the 2D HETCOR spectra have been measured then the slope of the third 2D HETCOR spectrum can be easily deduced.

Dennis L. Hasha

Dennis L. Hasha

[1] H. Dreeskamp and G Stegmeier, Z. Naturforsch. 22a, 1458 (1967).

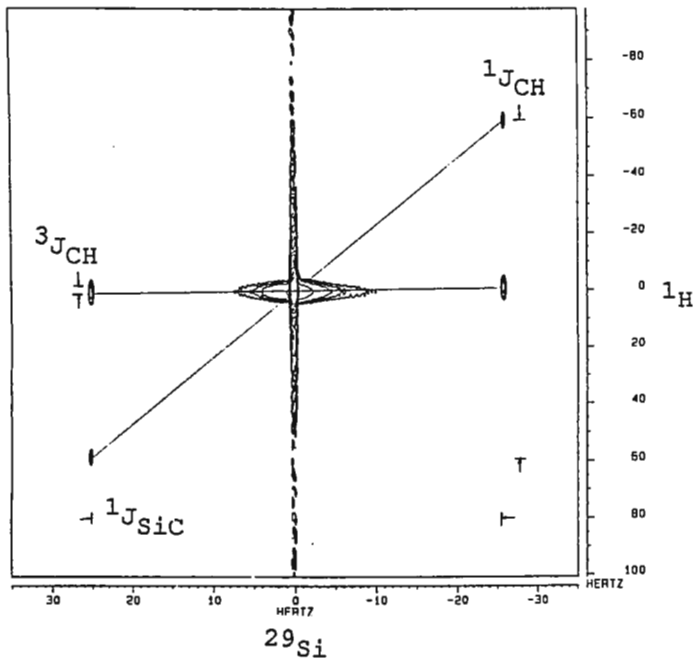

Figure 1. 2D ^{29}Si-^1H HETCOR via INEPT of 40mole% TMS solution based on the long-range coulping $^2J_{SiH}$ = 6.5Hz, τ=D5=1/(4J) and $\Delta/2$=D6=0.047/J. 64 data points in ω_1 dimension, 128 scans with 1s reptition time. Squared sine-bell in both ω_1 and ω_2 with phase shift equal to $\pi/12$.

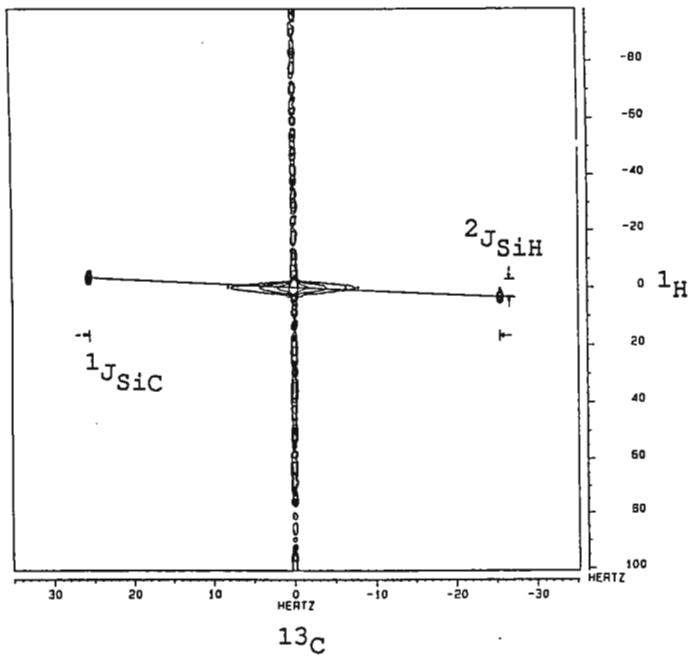

Figure 2. 2D ^{13}C-^1H HETCOR via INEPT of 40mole% TMS solution based on $^1J_{CH}$ = 118.4Hz, τ=D5=1/(4J) and $\Delta/2$=D6=0.098/J. 128 data points in the ω_1 dimension, 16 scans with 1s reptition time. Squared sine-bell apodization in ω_1 and ω_2 with phase shift equal to $\pi/12$.

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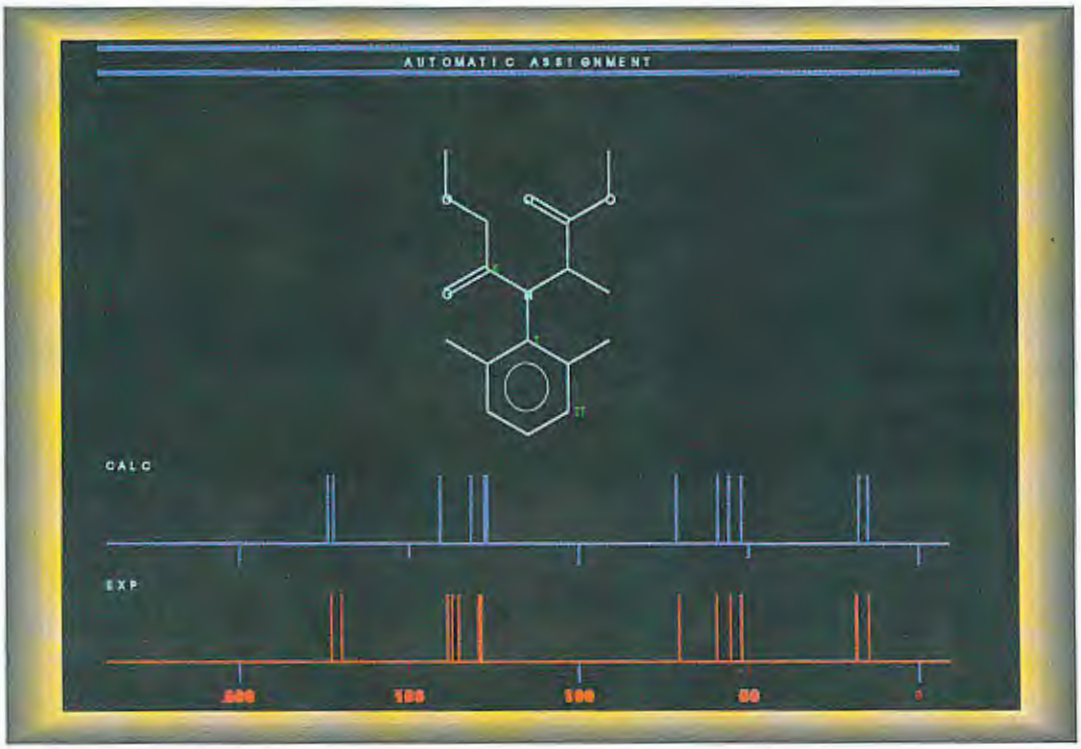

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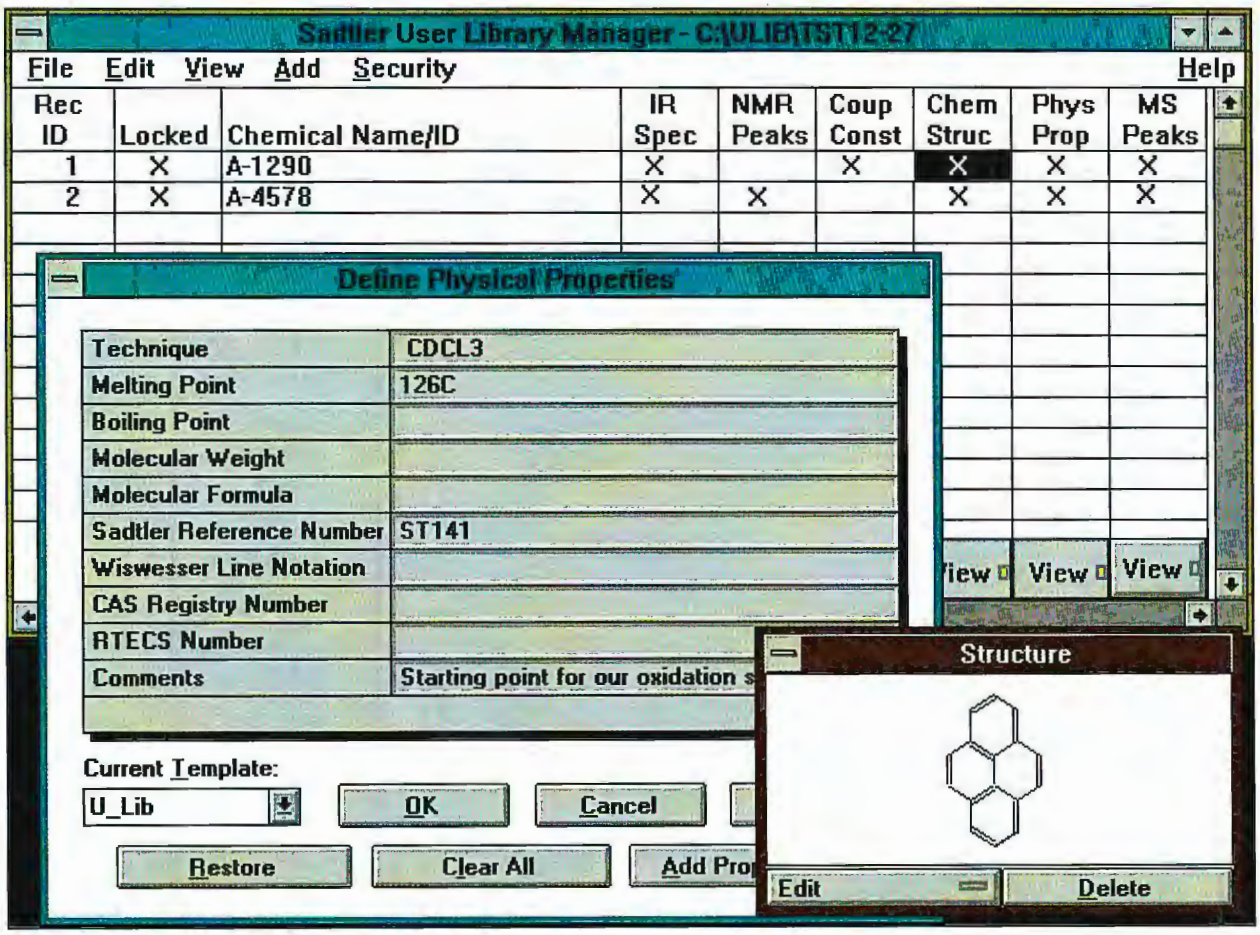

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2 March, 1992
(received 3/14/92)

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

^{13}C NMR OF AQUEOUS MICROEMULSIONS

Dear Dr Shapiro,

As part of a larger research project on the polymerization of microemulsions, some aspects of the carbon-13 NMR spectra of aqueous methyl methacrylate/butyl acrylate/nonionic surfactant (MMa/BA/S) macro- and microemulsions were examined. These were of particular interest to us from a mechanistic point of view because a coarse macroemulsion (particle size >250nm) could be free radically polymerized to a microemulsion (size 50nm) without high shear. The question arose as to whether there was a microemulsion phase present in the coarse emulsion, or whether the polymerized microparticles arose spontaneously from the particular mix of chemicals present as a result of free radical polymerization mechanistics.

A monomer-to-surfactant (M:S) ratio 5:1 coarse emulsion initially gives a fairly broad line ^{13}C spectrum ($w_{\frac{1}{2}}$~20Hz). As the emulsion breaks, the clear lower phase gives a narrow line spectrum ($w_{\frac{1}{2}}$~2Hz) with the cloudy upper phase giving a very similar spectrum to the entire emulsion. The narrow line spectrum of the lower phase is typical of a microemulsion spectrum, and contains about 20% of the original monomer. Fig.1 shows this in an overlay of all 3 spectra (alkene region). Note the chemical shift differences observed for the microemulsion.

The growth of the microemulsion phase can also be followed by a time course examination of the 'window' of emulsion within the receiver coil. Fig.2 shows the change from a broad to a narrow line spectrum over 1.5h for a M:S 5:1 case (40% solids).

For low M:S ratios (eg 2:1), <u>both</u> narrow and broad line peaks are observed in a one-phase system, indicating the coexistence of micro- and macroemulsion in slow equilibrium on the NMR timescale.

Evidence such as this seems to indicate that for high monomer:surfactant ratios, little if any microemulsion phase exists in the sheared emulsion, and that the polymerization mechanism acts by the free radicals nucleating particle growth <u>outside</u> the large monomer droplets and subsequently restricting growth to approx. 50nm, whilst using the larger droplets as monomer reservoirs.

Please credit this contribution to Ian D Rae's account.

Yours sincerely,

Iain Cook Bruce Leary

Iain Cook Bruce Leary (Dulux Australia Pty Ltd)

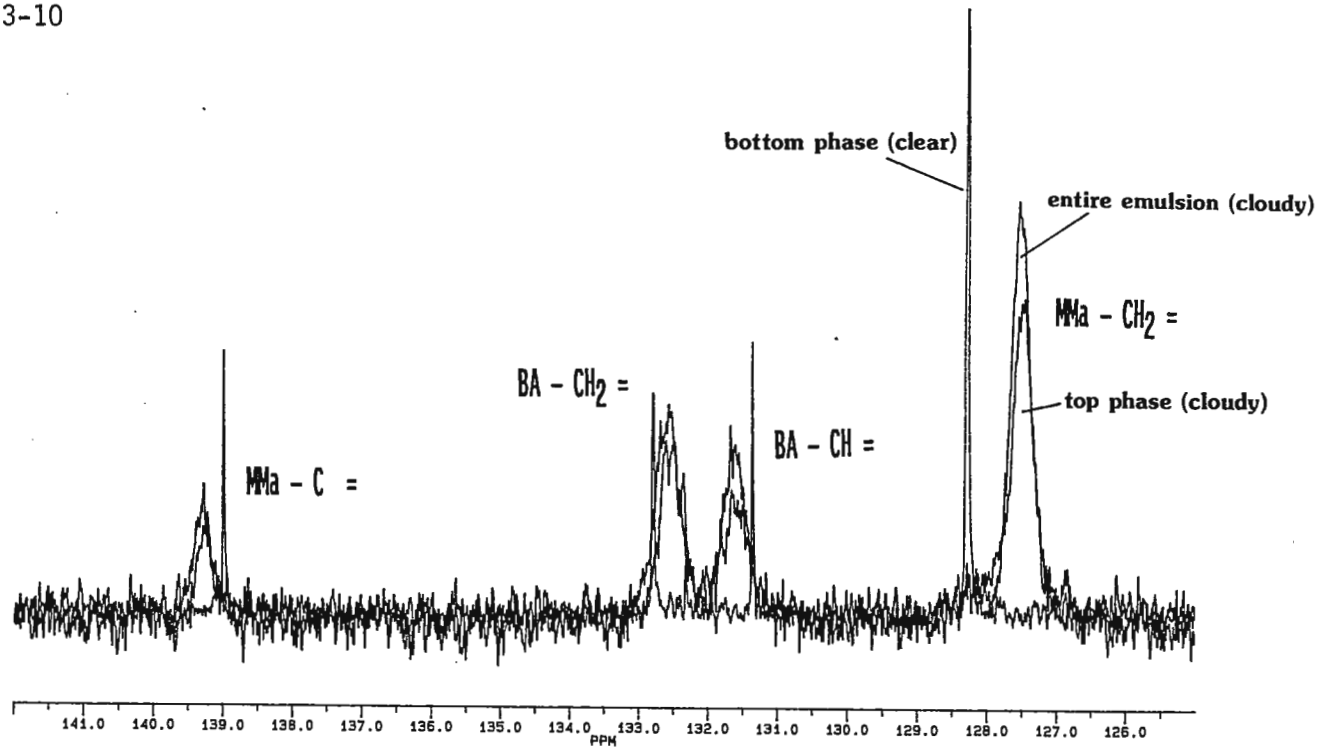


FIG.1 Overlay of ^{13}C alkene peaks of MMa and BA for an intact 5:1 M:S ratio macroemulsion and the top and bottom layers of the broken emulsion 24h after shearing had ceased.

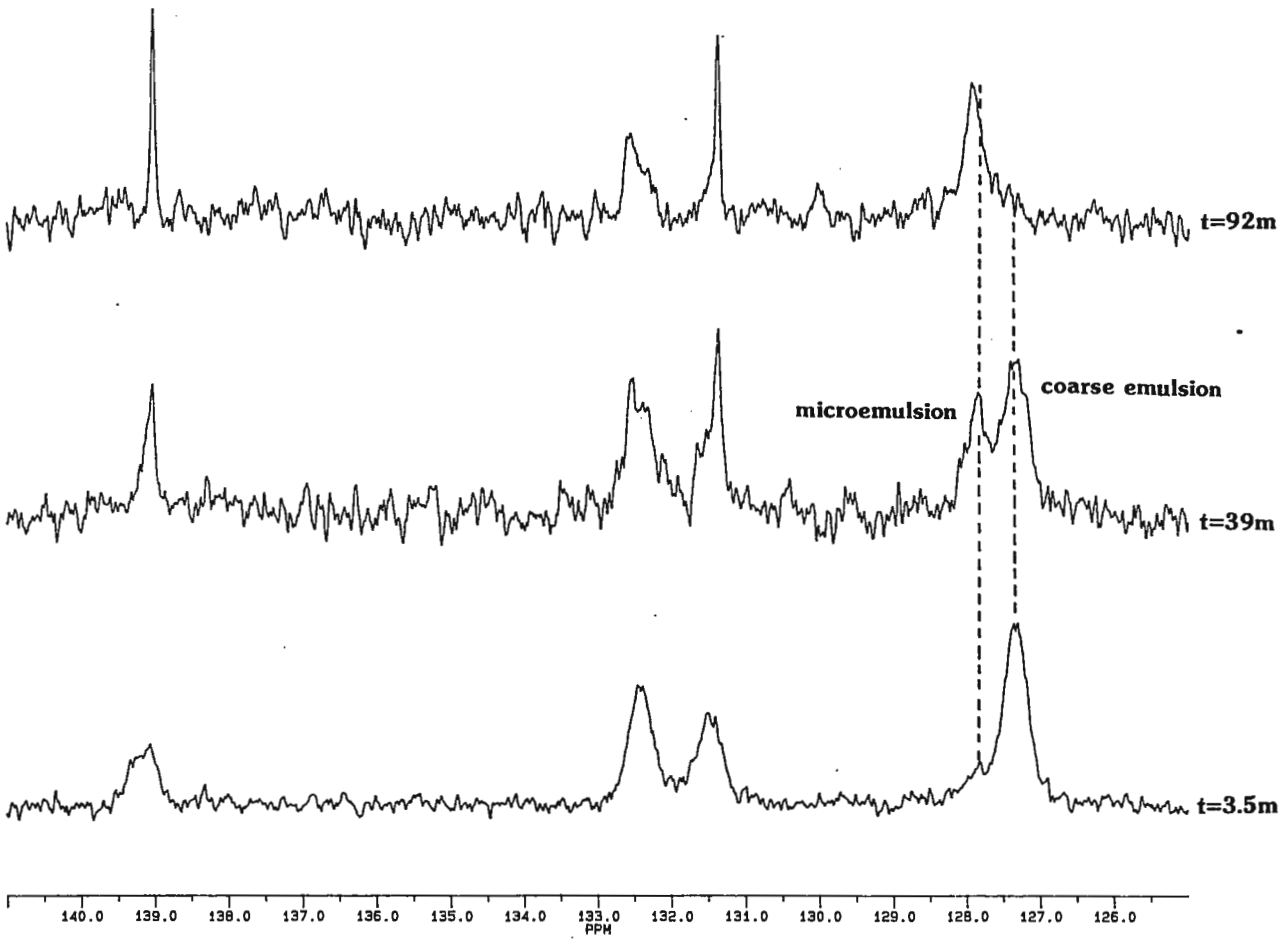
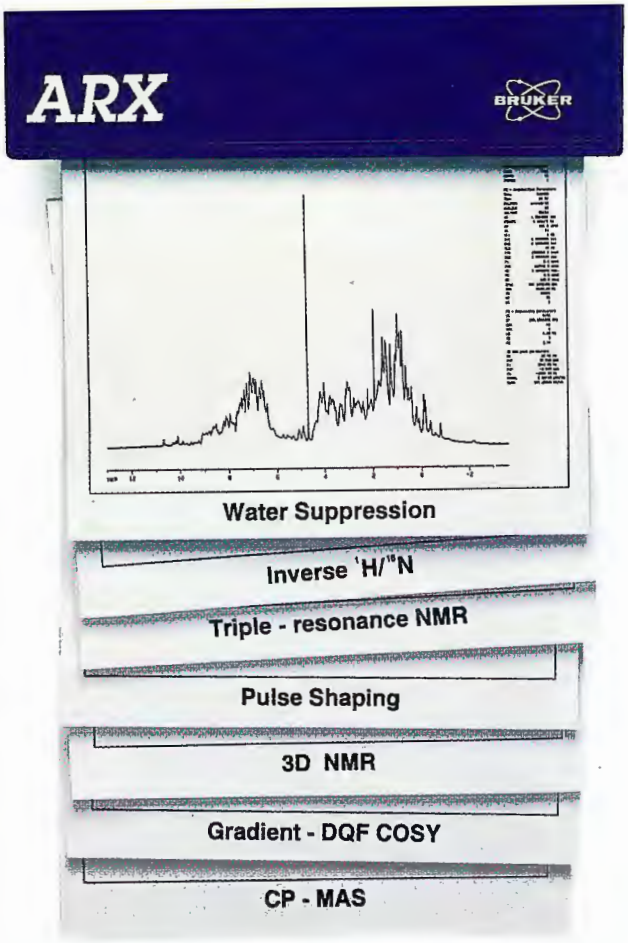


FIG.2 Growth of sharp microemulsion peaks and concurrent loss of broad macroemulsion peaks during the breaking of a 5:1 emulsion.



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Prof. P. Diehl
Direct Dial Number +41 61/ 2673703

Electronic Mail Address:
diehl@urz.unibas.ch

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

March 16, 1992
(received 3/23/92)

Field corrections for finite sample size

Dear Barry,

Lately we studied gas-to-solution shifts of ^{3}He dissolved in various liquid solvents. If the gas and solvent samples are prepared with equal glass containers, then the following relation holds

$$\delta_{solv} - \delta_{gas} = -\sigma_m + (\frac{4\pi}{3} + g)\,\chi_{solv}$$

where δ_{gas} is an extrapolated value for zero pressure and σ_m is the medium shift. g is equal to 0 for an infinetely long cylindrical solvent column, that lies parallel to the field. For a finite geometry g is different from 0, but usually not very important in the determination of σ_m, unless we deal with shifts of light atoms such as protons or ^{3}He, for which the finite size correction $g \cdot \chi_{solv}$ can be about 20% of the medium shifts. For our nonspinning samples g was then calculated for a geometry of a cylinder rounded off at the bottom as is shown in Fig.1. This was done first order in the solvent susceptibility, which has the advantage that one can avoid the solution of the Laplace-equation for magnetostatics. Simple integrations over magnetic charges at the poles of the cylinder are sufficient to obtain the additional magnetic field. Only its z component gives a first order correction to $\delta = g\chi_{solv}$. As that component doesn't vary much in the xy-plane (for usual h/d-ratios), we present here the correction for the cylinder axis:

$$g(\zeta) = 2\pi \left(\frac{(2+x)(1-\zeta)}{\sqrt{(2+x)^2(1-\zeta)^2 + x^2}} + \frac{\sqrt{[(2+x)\zeta - x]^2 + x^2}\;\left([(2+x)\zeta - x]^2 - 2x^2\right) + 2x^3}{3\left((2+x)\zeta - x\right)^3} - \frac{4}{3} \right)$$

where we introduced ζ=z/h and x=$d/(h - d/2)$. The z dependence of g is shown in Fig.1 for various x values (in the direction of the doublelined arrow they are: 1/20, 1/15, 1/10, 1/8, 1/6 and 1/5). To avoid nasty asymmetric and broadened lines when one works at a constant shim, as it is necessary for measurements of gas-to-solution shifts, x should be less than 1/10 and the coil should be placed between 0.4 and 0.6 of the solvent column's length (in commercial probeheads the coil is usually too low). Then it is possible to extract a more or less z independent g value. Otherwise a lineshape calculation must be done. This was tested for a water sample with 9mm inner diameter and filling heights of 7.6 and 3.7cm. The evaluated field corrections according to the above formula in the coil region (between 1.3 and 2.9cm from the tube's bottom) are demonstrated in Fig.2. These profiles of course are for a magnet field that is completely homogeneous, when no sample is loaded. But now for the sample with 7.6cm of water the shim was adjusted such that the water line showed no asymmetry. Then the field profile for the second measurement with 3.7cm is the difference between the two calculated for homogeneous field.

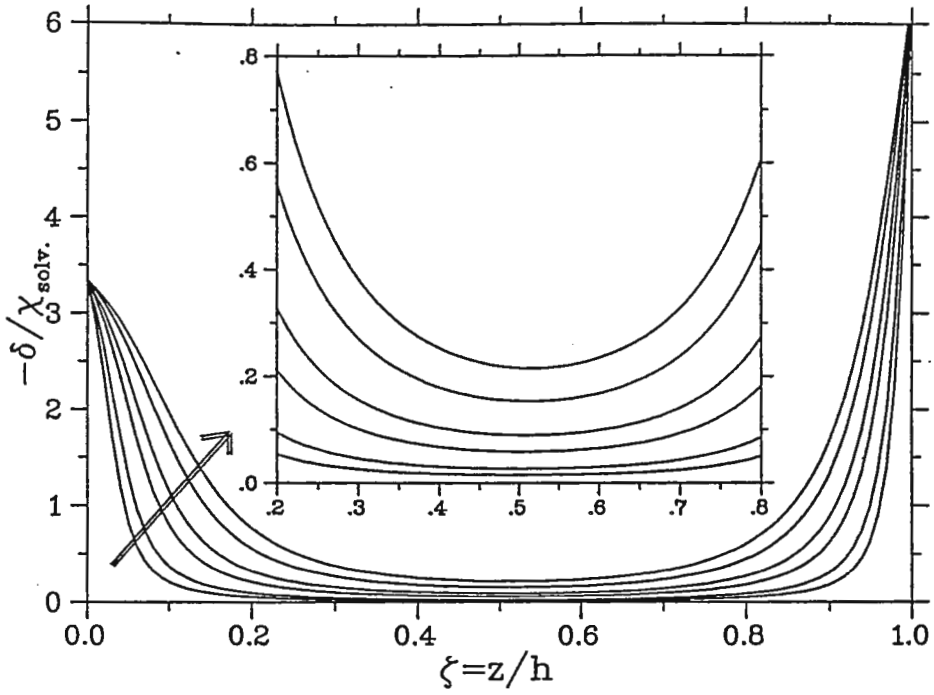


Fig. 1

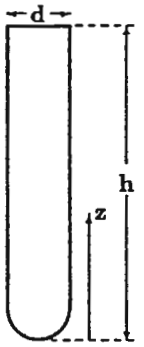


Fig. 2

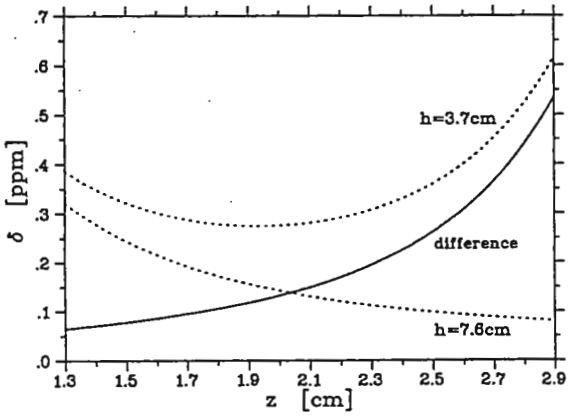
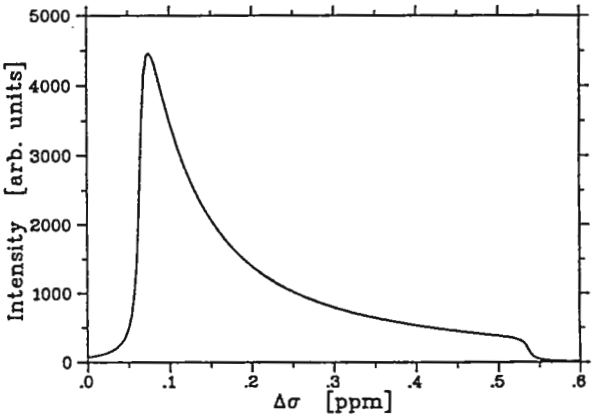


Fig. 3



The such extracted theoretical lineshape is shown in Fig.3. The peak appears at 0.078 ppm downfield from the '7.6cm sample' and the line is affected with an asymmetry of about 0.47 ppm. The experiment showed a peak at 0.088 ppm and an asymmetry of 0.44 ppm. At least our procedure seems to provide a more reasonable geometry correction than that for an ellipsoid [1], which would predict a 4.7 times higher value for the peak position and cannot account for the observed asymmetry.

With kind regards

Roberto Seydoux & P. Diehl

[1] J.A. Osborn, *Physical Review* **67**(11,12), 351 (1945).

ACTIVELY SHIELDED GRADIENT PROBES

Gradient-Enhanced Spectroscopy (**GES**), Pulsed-Field Gradient (**PFG**) measurement of diffusion coefficients, and Magnetic Resonance Imaging Microscopy (**MRI-M**) all benefit greatly from actively shielded gradient coils. DSI was the first to offer actively shielded gradient coils, and we continue to lead the way with such features as wound-kevlar reinforcing, computer numerical modeling, and computer controlled manufacturing methods for minimum vibration, high linearity, and minimal eddy currents.

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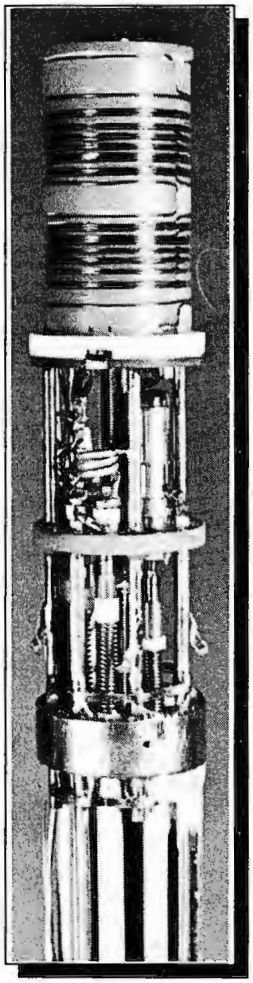

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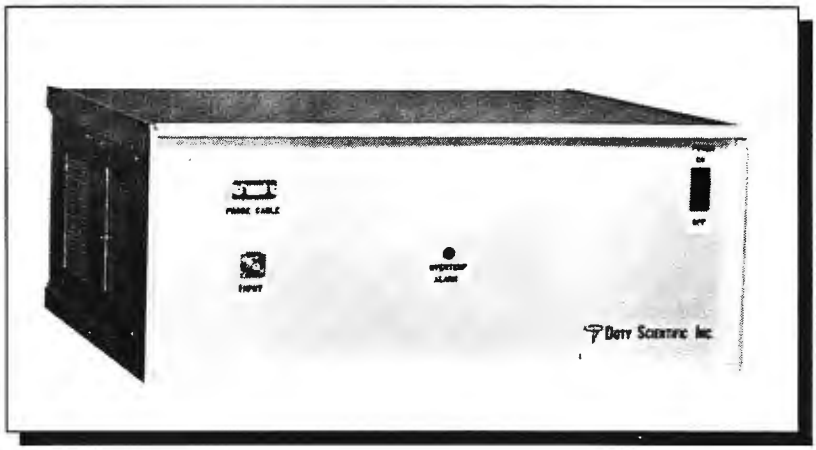

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National Center for NMR Applications

Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Subjects: (1) NATO ASI in Turkey, Aug. 23-Sept. 4, 1992;
(2) NMR Services Available; (3) DNP of C_{60} and Diamond Films

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

March 4, 1992
(received 3/5/92)

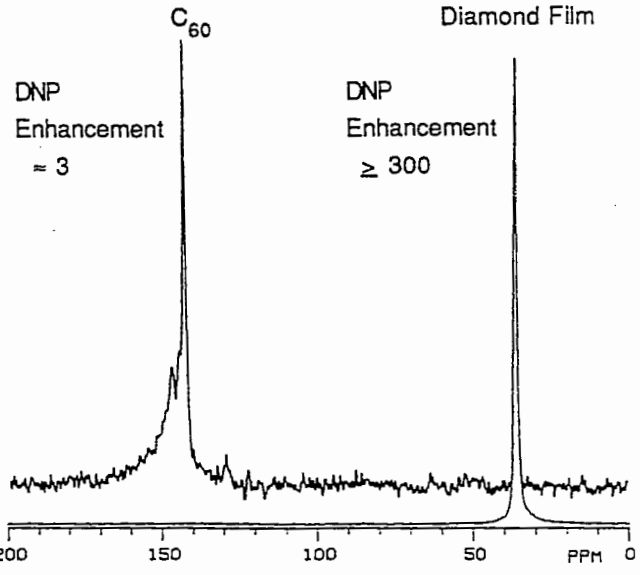
Dear Barry:

Here is our tardy contribution. I'll try to cram as much into this as I can in one page.

1. A **NATO Advanced Study Institute** will be held in Turkey (near Dalaman and Mugla) from August 23 through September 4, 1992. The theme is "NMR in Modern Technology", or "what is NMR doing to support industrial technology and what could NMR do in the future". The program includes NMR basics, modern liquid-sample and solid-sample NMR techniques and applications and NMR in quality control/process control. The speakers tentatively include R. Dupree (Warwick, U.K.), G. Erbatur and O. Erbatur (Çukurova, Turkey), R. Freeman (Cambridge, U.K.), C. Fyfe (British Columbia), G. Hatfield (W.R. Grace), B. Hawkins (Colorado State U.), L. Jelinski (Cornell), G. Maciel (Colorado State U.), A. Pines (Berkeley), H. Pfeifer (Leipzig, Germany), E. Randall (London), J. Ray (Amoco), A. Samoson (Tallinn, Estonia), W. Veeman, (Duisburg, Germany), J. Waugh (M.I.T.), C. Yannoni (IBM) and A. Zambelli (Salerno, Italy). Those interested in attending should contact me for additional information and application forms.

2. The **National Center for NMR Applications** (formerly the NSF-funded Regional NMR Center) continues to expand its capabilities, with 10 spectrometers from 0.5 T to 1.4 T performing solid-state, liquid-sample and process-control/quality-control studies on a service or project basis. Interested laboratories should contact me or Dr. Bruce Hawkins (303-491-6455), the Center's manager.

3. **Dynamic Nuclear Polarization (DNP)** studies on a variety of solids continue here. On the right are shown natural-abundance ^{13}C DNP spectra of a diamond film (sample provided by Dr. Curtis Johnson of the Naval Weapons Laboratory, China Lake) and C_{60} (sample provided by C.S. Yannoni of IBM), obtained by graduate student, Herman Lock. Spectra that are impractical to obtain without DNP (e.g., the diamond film) often are obtained easily with DNP.



Sincerely,

Gary E. Maciel
Professor

OSU

Oklahoma State University

DEPARTMENT OF CHEMISTRY
COLLEGE OF ARTS AND SCIENCES

STILLWATER, OKLAHOMA 74078-0447
PHYSICAL SCIENCES 106
405-744-5920

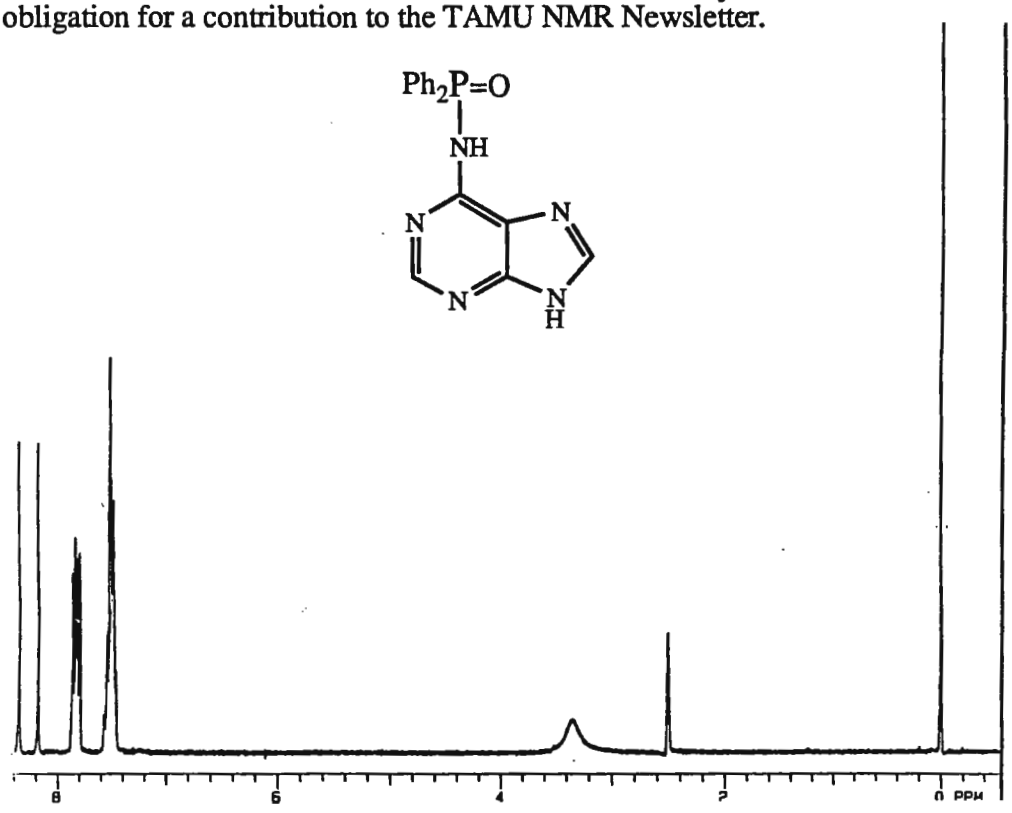
2/21/92
(received 2/24/92)

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

TITLE: Phosphorylated Adenine

Dear Dr. Shapiro:

Some of our recent work has required a phosphorylated derivative of adenine which is drawn below. The proton NMR spectrum was very interesting in that we could clearly see both H(2) and H(8) of the adenine ring without any P-coupling. Admittedly, the $^{5}J_{PH(2)}$ coupling might be small but we thought it worth evaluating. The shifts for H(2) and H(8) are 8.18 and 8.36 ppm, respectively, and do *not* exhibit any P-H coupling that is detectable even when the signals are enlarged at 400 MHz. We did not expect to see a $^{6}JP_{P\text{-}H(8)}$ coupling. The proton on nitrogen is around 3.8 ppm while the aromatic proton signals are bunched at 7.5 and 7.82 ppm. There is a residual signal from the solvent (DMSO-d_6) which is evident at 2.24 ppm. These phosphorylated systems seem to be novel as a search of the literature revealed very few are known. We trust this meets our obligation for a contribution to the TAMU NMR Newsletter.



Sincerely yours,

K. Darrell Berlin
Regents Professor

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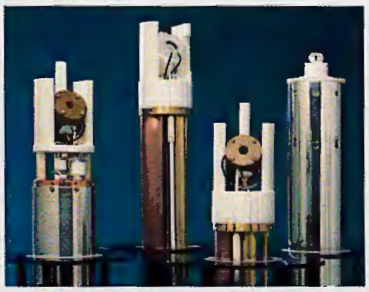

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Telephone 071 975 5555
Fax 071 975 5500
Telex 893750

18th March 1992 (received 3/21/92)

Dear Barry,

Queen Mary's Images: **Nitrogen and Soil Water**

The SISCO 4.7T (33 cm bore) imaging spectrometer has been operational here since 1990. It is under the management of Dr. Steve R. Williams (who should not be mistaken for Steve R. Williams down at the Royal College of Surgeons) and is used by a variety of research groups in the University.

My own main interest has been with soils and also with the imaging of nitrogen. Concerning the latter we started with ^{14}N and tested out the line width problems: how wide a line could we image? With our modest maximum gradient of 2 G cm-1, the answer was about 150 Hz which would be increased (courtesy of Dr. F. Howe at St. George's Hospital Medical School) to about 500 Hz using their shielded gradient set (10 G cm^{-1}). A report of this work will appear soon in J. Magn. Reson.

We next imaged ^{15}N at natural abundance as befits the traditions of the group. We set up on our standard laboratory sample, 99% enriched ammonium nitrate - $^{15}N_2$, which has horribly long relaxation times (51s for $^{15}NH_4^+$ and 106s for $^{15}NO_3^-$) and then proceeded directly to image liquid - N_2 at natural abundance (n.a.). I had remembered my experience with Geoff Hawkes when testing out a Bruker 180 in 1975. We obtained very good signal to noise with one pulse.[1] The instrument was destined for Jack Roberts' lab., so we thought it only proper to put his name on the paper. This sample is the best for n.a. work since it consists only of nitrogen and gives a useful gain in sensitivity because of the low temperature. We then went on to image aniline, phenyl hydrazine, and hydrazine hydrate among other things before digging out some of our ^{15}N enriched samples from our '^{15}N bank'.

Incidentally, one sample of liquid - N_2 was so contaminated with liquid - O_2 that we would not initially contain it in an open-topped dewar during insertion into the bore of the magnet. We now call this the Kinchesh effect after Paul the post-doc. on the project, who observed that the liquid was pulled into the bore and was not pushed out of it.

More recently we have shortened the imaging times by use of sensitivity enhancements, including NOE experiments and indirect detection.

As for soils, we visited Klaus Zick at Bruker near Karlsruhe and persuaded him to apply the STRAFI technique developed for soilds to look at liquids in solids. The very large stray field gradients on his Bruker MSL 400 (15 kG cm^{-1}) mean one can get images on ^1H water lines which are 15 kHz wide, and can reduce the magnetic susceptibility distortions to negligible proportions. There is a note in preparation for J. Magn. Reson. We also imaged plant material in the soil with no distortions.

I send best wishes from Geoff Hawkes in whose name the subscription is currently held, and from the rest of the NMR community here.

Yours sincerely,

Ed

Edward Randall

[1] C.H. Bradley, G.E. Hawkes, E.W. Randall and J.D. Roberts, J. Amer. Chem. Soc., 97, 1958 (1975).

Mount Holyoke College
Kenneth L. Williamson
Carr Laboratory
South Hadley, Massachusetts 01075
Telephone 413-538-2349
Fax 413 538 2327

Dear Barry,

Mount Holyoke College is searching for an nmr spectroscopist to fill a tenure track faculty position. Mount Holyoke is a liberal arts college for women, enrollment 1700 with a chemistry faculty of eight The department has four working spectrometers, a T-60, a JEOL FX 90 Q, a Bruker 250 and an IBM/Bruker 270. The latter spectrometer, equipped with a 10 mm multinuclear probe and 5 mm C/H probe, array processor, variable temperature, large disk and flatbed recorder will be turned over to the new faculty member. The Bruker 250 with a 5 mm C/H probe is used for routine analytical work and teaching. The JEOL is also available for research. The department has four electronics technicians who do all maintenance on the spectrometers as well as design and build apparatus.

Interested candidates should write to Prof. Sheila Browne, Chairman, as soon as possible with a CV, statement of research plans and arrange for three letters of reference to be sent.

Sincerely yours,

Ken Williamson

Postdoctoral Position - Molecular Dynamics

A postdoctoral position is available in the laboratory of Professor Lian-Pin Hwang at the Institute of Atomic and Molecular Sciences, Taipei. Current research interests involve the development of NMR methods to study molecular dynamics and their application to chemical and biological systems. The laboratory has Bruker MSL 300 and MSL 90 spectrometers and will soon install a 400 MHz spectrometer and the Institute has already purchased a 500 MHz spectrometer. Candidates for this position should have graduated with a Ph.D. within the last three years. Candidates with a strong background may be eligible for financial support from the National Science Council. The period is for one year in the first instance but may be renewed upon mutual agreement. Interested individuals should send a curriculum vitae and names of three referees to:

Professor Lian-Pin Hwang
Institute of Atomic and Molecular Science
Academia Sinica
P.O. Box 23-166
Taipei,
TAIWAN 10764
FAX: (02) 3620200

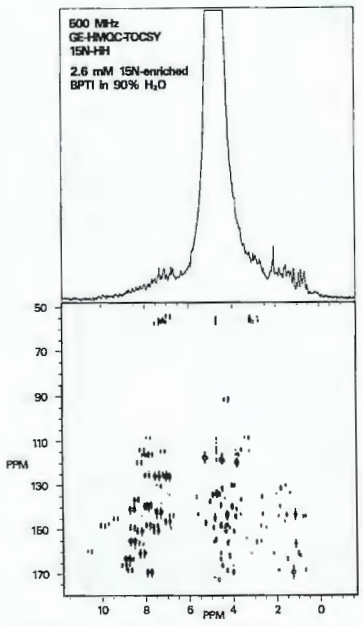
NMR UPDATE

Gradient Enhanced Spectroscopy: a new, practical answer

By Frank Huang, PhD, Paul Calderon, MS, and Boban John, PhD

Making Gradient Enhanced Spectroscopy (GES) a viable method for high resolution spectroscopy has long been of interest to researchers. The obvious benefits in speed and information content were too often overshadowed by the drawbacks of signal loss and distortion.

Technology developed at GE NMR Instruments has overcome these challenges. The S-17 Gradient Enhanced Spectroscopy Accessory with integrated inverse probehead makes GES practical for a broad range of applications in 1D, 2D, 3D and 4D experiments.



Gradient Enhanced Spectroscopy technique applied to an HMQC-TOCSY experiment demonstrates excellent water suppression without the need for presaturation or selective excitation.

Research Implications

- Speed without phase distortion or signal loss.
- Practical for 1D, 2D, 3D and 4D experiments.
- Accommodates proton and heteronuclear GES techniques.

A better design

The use of a three-axis, actively-shielded gradient set allows GE to overcome the inherent drawbacks of previous GES technology —most notably, phase distortion and signal loss:

Active shielding. Eddy current effects are the major source of phase distortion in GES spectra. Active shielding prevents interaction of strong gradients with magnet and shim components—the source of eddy current effects.

Fast, strong gradients. Short gradient pulses in excess of 20 G/cm minimize signal loss during pulse sequences.

Applications advantages

With its integral inverse probehead, the S-17 Accessory can accommodate proton as well as heteronuclear GES techniques.

Gradient fields in excess of 20 G/cm are able to suppress water in aqueous samples and to improve performance in heteronuclear experiments. Other applications advantages:

- Eliminates phase cycle requirements and subtraction error.
- Reduces T1 noise.
- Reduces collection times for 2D, 3D and 4D data sets.
- Provides lineshape independent water suppression in multiple quantum coherence selection experiments.
- Provides lineshape independent water suppression via diffusion differences for large molecular weight samples.
- Improves water suppression in experiments using selective time reversal RF pulses.
- Separates cross-correlation and exchange phenomena in NOESY experiments.
- Distinguishes chemicals inside the cell from those outside in whole cell applications.

For additional information on the S-17 GES Accessory, write to GE NMR Instruments, 255 Fourier Ave., Fremont, CA 94539.
Or call toll free:

1-800-543-5934

GE NMR Instruments

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Gradient-Enhanced ^{15}N HMQC

The pulse sequence and the coherence pathway diagram for a ^{15}N GE-HMQC are shown in Fig. 1. The pulse sequence was a standard ^{13}C GE-HMQC experiment (1) with different gradient amplitudes to account for the difference between the gyromagnetic ratios of ^{13}C and ^{15}N. The 90° proton pulse creates transverse magnetization which evolves into an anti-phase state with respect to J(NH) coupling at the end of the period Δ (where $\Delta = \frac{1}{2}J$ (NH)). The antiphase components are converted into heteronuclear zero- and double-quantum coherence by the ^{15}N 90° pulse and the multiple quantum coherences are allowed to evolve during t_1. The 180° ^1H pulse in the center of the evolution period serves to eliminate the ^1H chemical shift evolution, yielding pure ^{15}N chemical shifts along that axis. The zero- and double-quantum signals are then *coherence-order labeled* by the gradient pulses G1 and G2. After conversion into antiphase proton magnetization by the last ^{15}N 90° pulse, the desired components are refocused by the gradient G3 and detected. The application of a gradient pulse results in a phase factor being applied to the magnetization which is dependent upon gradient strength, duration, the distance from the gradient isocenter, the gyromagnetic ratios of the coupled nuclei, and the desired coherence order. The relative amplitudes of the labeling and refocusing gradient pulses will determine the selection of a specific coherence pathway and are calculated to suppress magnetization components arising from the solvent and other protons not coupled to ^{15}N spins.

The fundamental principle of coherence selection using gradients is that for a pathway to be detected, the cumulative phase factor during the acquisition must be zero:

$$G_1p'1 + G_2p'_2 + G_3p'_3 = 0. \quad [1]$$

The subscripts denote steps in the pulse sequence where p′ defines a composite coherence order for the heteronuclear case which includes the gyromagnetic ratios of the coupled nuclei:

$$p' = {}^{p1}H + (\gamma^{15}N/\gamma^{1}H)^{p15}N \quad [2$$

and ^{p1}H and ^{p15}N are the coherence orders for the ^1H and ^{15}N spins respectively.

In the coherence pathway diagram, the relevant values of p' are given to the left and the relative gradient areas (gradient strength x duration) are given next to each gradient pulse. The following pathway (shown in *Fig. 1*):

$$H(+1) \rightarrow H(+1)N(0) \rightarrow H(+1)N(+1) \rightarrow H(-1)N(+1) \rightarrow H(-1)N(0)$$

is detected using a 5:5:1 ratio of gradient areas, since according to Equation 2:

$$5(1.1) + 5(-0.9) + 1(-1.0) = 0 \quad [3]$$

where the numbers in the parentheses refer to the composite coherence orders. Using these relative gradient areas, protons not coupled with ^{15}N spins may pass through an alternate pathway:

$$H(+1) \rightarrow H(+1) \rightarrow H(+1) \rightarrow H(-1) \rightarrow H(-1)$$

which results in a net phase factor:

$$5(1.0) - 5(-1.0) + 1(-1.0) = -1 \quad [4]$$

Thus, signals from this pathway remain defocused during the acquisition.

A 2D ^{15}N GE-HMQC spectrum of ^{15}N enriched BPTI is shown in *Fig. 2*. The spectrum was collected using a 5 mm inverse probe on an Omega™ PSG 500 spectrometer equipped with an S-17 gradient accessory. Half-sinusoid shaped gradient pulses were applied simultaneously along the X, Y, and Z axes with a maximum gradient strength of ≈20 Gauss/cm and a duration of 3.5 ms. A matrix size of 2048 × 128 resulted in 3.5 Hz resolution in the ω_2 dimension and 10 Hz in the ω_1 dimension. No decoupling was applied.

Gradient-enhanced experiments provide a viable alternative to traditional phase-cycling methods for the selection of coherence pathways. In cases where the sensitivity is adequate, gradient selection can substantially reduce the collection time in multi-dimensional experiments. The ^{15}N GE-HMQC data presented here has none of the t_1-noise from cancellation artifacts usually present in phase-cycled versions of the HMQC experiment. In addition, since the suppression of the single-quantum signals is done prior to acquisition, the receiver gain may be increased, which results in a substantial increase in signal-to-noise. For these reasons, gradient pulses should be the method of choice for coherence selection in HMQC experiments.

Reference

1. R.E. Hurd and B. K. John, *J. Magn. Reson.* **91,** 648 (1991).

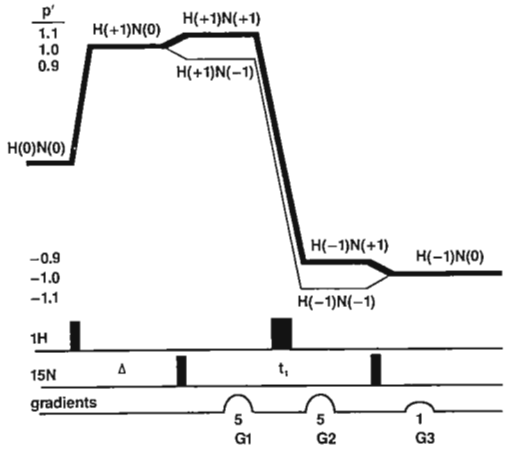


Fig. 1

Pulse Sequence and the coherence pathway diagram for a 15N GE-HMQC experiment.

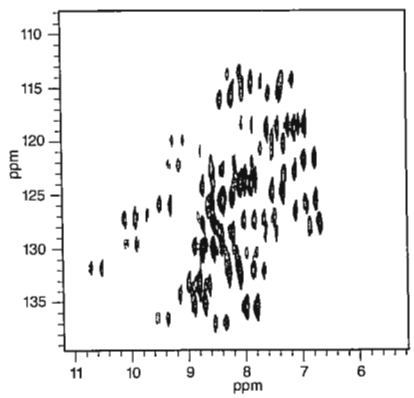
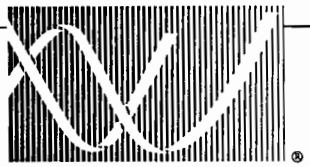


Fig. 2

A 2P Ge-HMQC spectrum of 15N enriched BPTI. The sample was 2.6mM in 90% H2). The data collection time was 2.6 hours.



C A B M

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679 Hoes Lane • Piscataway, NJ 08854-5638 • 908/463-5300

March 10, 1992
(received 3/20/92)

Initial Results with Pulsed Field Gradients

Dear Dr. Shapiro,

Two common ways of selecting multiple quantum coherence in NMR experiments are phase cycling and pulsed field gradients (PFG's). The PFG approach exploits the fact that homonuclear N-quantum coherence will defocus (or refocus) in an inhomogeneous magnetic field N-times more rapidly than single quantum coherence. PFG methods for MQ coherence selection have many potential applications in biological NMR including suppression of single-quantum solvent coherences and selection of heteronuclear coherences. They can provide more efficient MD-NMR data collection by minimizing phase cycling requirements, and can improve dynamic range by allowing selection of MQ-filtered pathways in a single scan.

We have recently carried out some hetero- and homonuclear MQ-filtered experiments using new pulsed field gradient hardware available from Varian NMR. PFG-HMQC spectra were obtained using the following sequence:

$$90°(H) - \tau - 90°(C) - [(t1/2) + \Delta] - 180°(H) - [(t1/2) + (G4+)] - 90°(C) - \tau - (G5-) - \text{acquire}$$

where $\tau = 1 / [2 * J_{CH}]$, G4+ is a positive PFG with area 4, G5 – is a negative PFG with area 5, and Δ is a delay equal in length to the G4+ PFG. The pulse sequence was tested on a 1% sample of 60% - enriched $^{13}CH_3I$ in $CDCl_3$, containing 0.2% Cr[acac] and 1% tetramethyl phosphate (Wilmad #WGH84582). Shown in Fig 1 are ^1H 1D spectra recorded using this pulse sequence (t1 = 0 sec, G4 = 1 ms) with either zero power on the field gradients (Fig 1A) or with a 6 Gauss / cm PFG (Fig 1B). In a single scan, we observe good suppression of the protons bound to ^{12}C (the center peak), with retention of signals for the protons bound to ^{13}C. This result was highly reproducible as shown by five repetitions of the same PFG experiment (Fig 1C), each run with a single scan.

2D PFG-HMQC results for a ca. 20 mM sample of 35% ^{13}C-enriched algal amino acids in water (MSD Isotopes) are shown in Fig 2. We have compared HMQC spectra recorded in D_2O solvent with 2 transients per FID with either phase-cycled (Fig 2A) or PFG (Fig 2B) selection of heteronuclear coherence. In the phase-cycled experiment, quadrature detection in $\omega 1$ is done by hypercomplex data collection, while in the PFG experiment the p- pathway is selected by the G4+ and G5- pulses. The gradient pulses used (G4 = 1 ms) were 6 Gauss / cm in amplitude. These spectra were recorded with broadband ^{13}C-decoupling during detection and plotted in absolute value mode. The vertical band of noise in Fig 2A is due to the residual HOD solvent signal, which was not preirradiated and is not completely cancelled by the phase cycling. Since this artifact arises from 1Q coherence, it is completely eliminated in the PFG version of the experiment (Fig 2B). Artifacts due to decoupler modulation sidebands in the phase-cycled experiment are also eliminated in the PFG-HMQC. This same PFG-HMQC experiment was also run on a similar algal amino acid mixture dissolved in 90% H_2O, using 30 Gauss / cm field gradients and G4 = 1.4 ms. These spectra had excellent solvent suppression with minimal attenuation of signal-to-noise (Fig 2C). Representative $\omega 2$ cross sections through these spectra at the frequency indicated by the dashed lines are shown in Fig 3. No residual water resonance (at 4.8 ppm) was observed in these PFG-HMQC spectra.

Homonuclear PFG 2Q-Spectra can also be obtained using the pulse sequence:

$$90° - \tau - 180° - \tau - 90° - [t1 + (G1+)] - 90° - [G2+] - \text{acquire.}$$

An example of a 2Q-Spectrum of 5 mM hen lysozyme in 90% H_2O acquired using τ = 18 ms, G1 = 2.4 ms, G2 = 4.8 ms, field gradient of 30 Gauss / cm, and one transient per increment is shown in Fig. 4. These spectra have excellent suppression of solvent signal and no t1 noise.

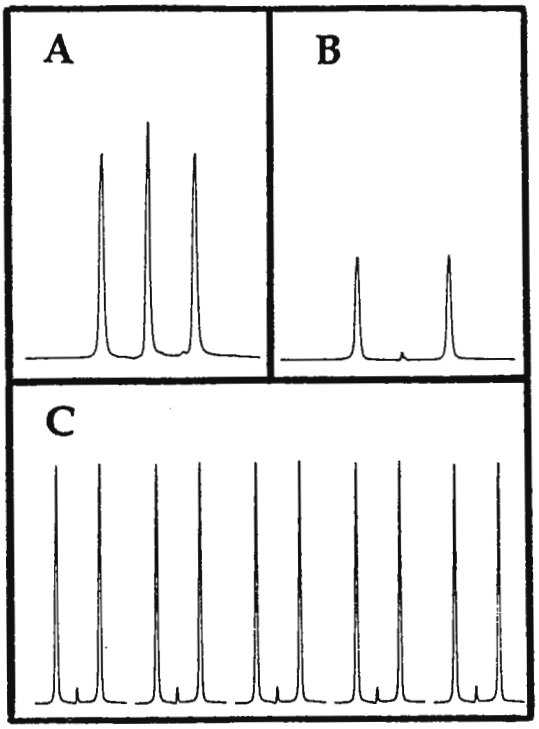

Figure 1

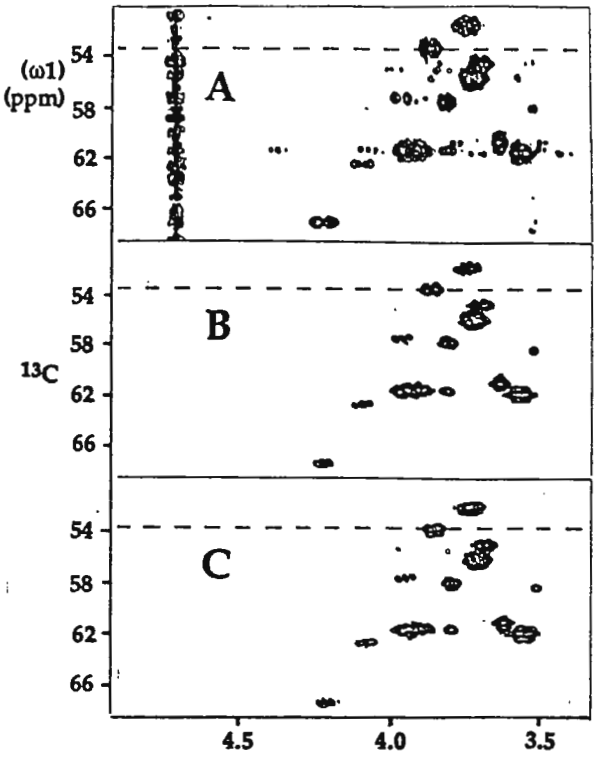

Figure 2

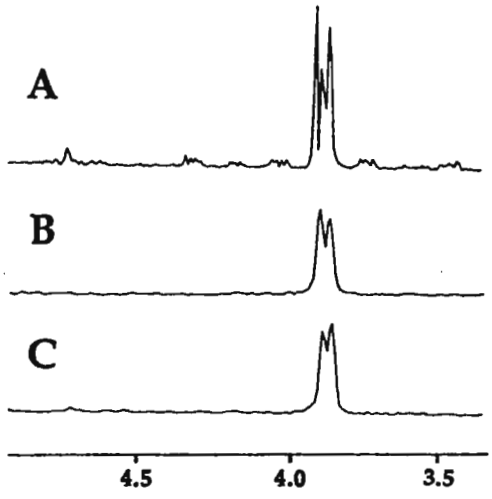

Figure 3

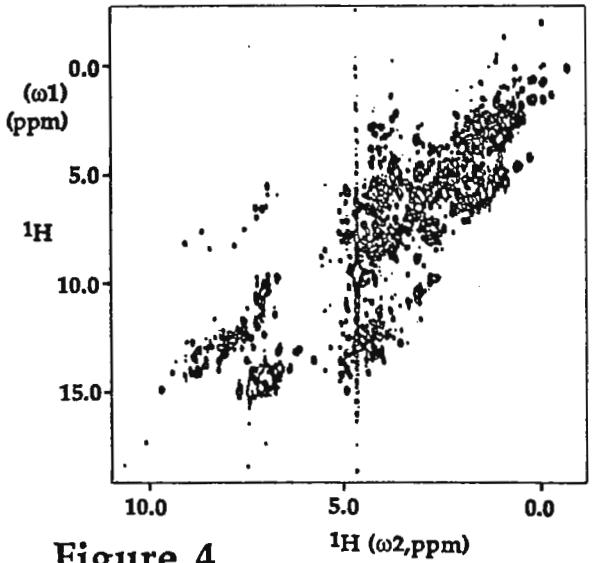

Figure 4

Steven Donald Emerson
CABM - Rutgers University
679 Hoes Lane
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Gaetano T. Montelione
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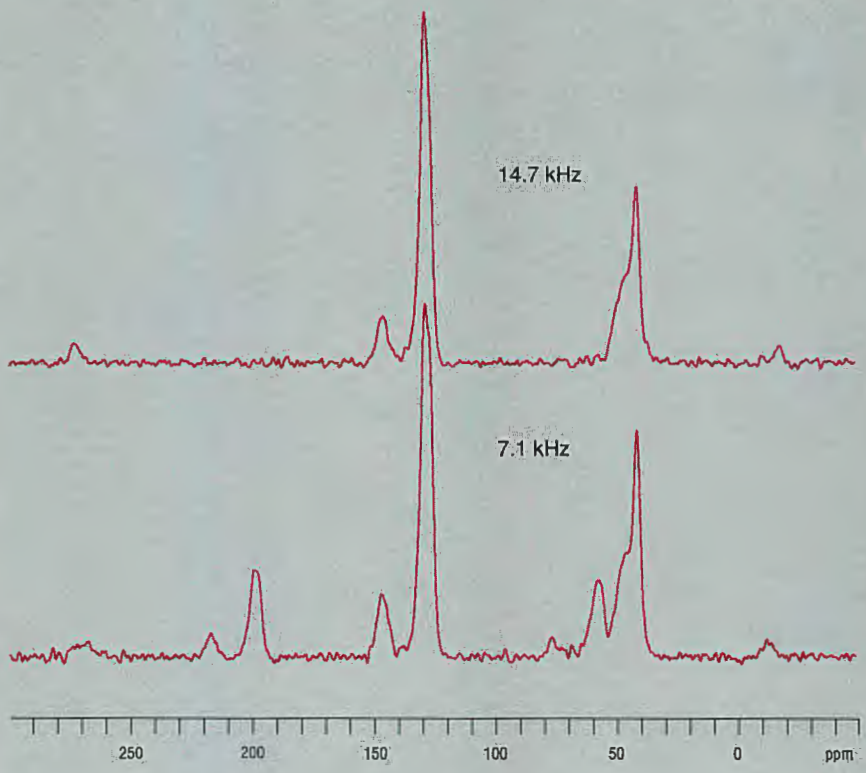
Piscataway, NJ 08854

Tim Saarinen
Varian Associates, NMRID
3120 Hansen Way, Bldg 4
Palo Alto, CA 94304

Varian introduces a 5mm variable temperature CP/MAS probe with a spinning advantage.



The above ^{13}C CP/MAS spectra of non-uniform cylindrical polystyrene beads (approximately 3mm length and 2mm diameter) were run on a UNITY-400 MHz NMR spectrometer. These spectra were easily obtained over a range of spinning speeds, up to 15 kHz. The spectrum shows maximum signal intensity at the isotropic chemical shifts and minimum spinning sideband intensities.*

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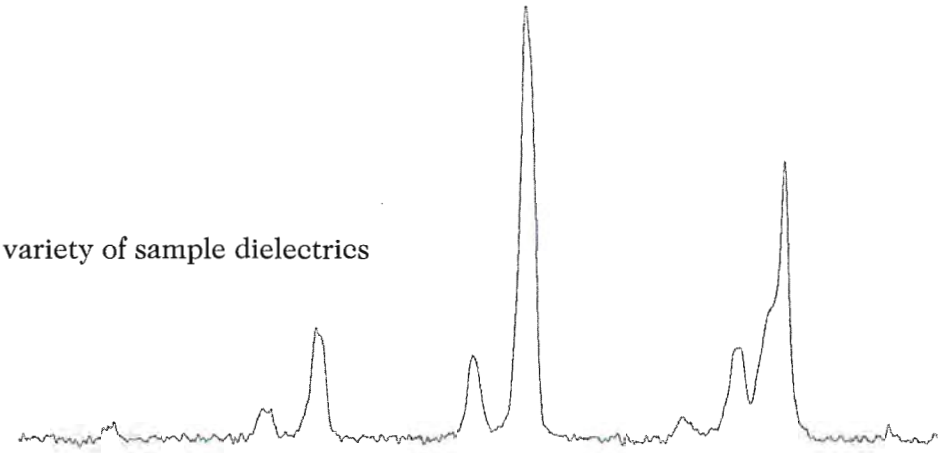

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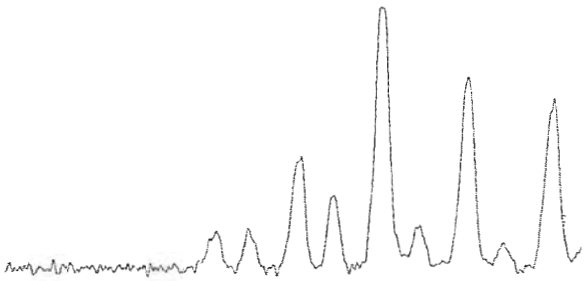

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March 9, 1992
(received 3/12/92)

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

3D NMR Microscopy

Dear Barry:

Thanks for your gentle 'reminder'.

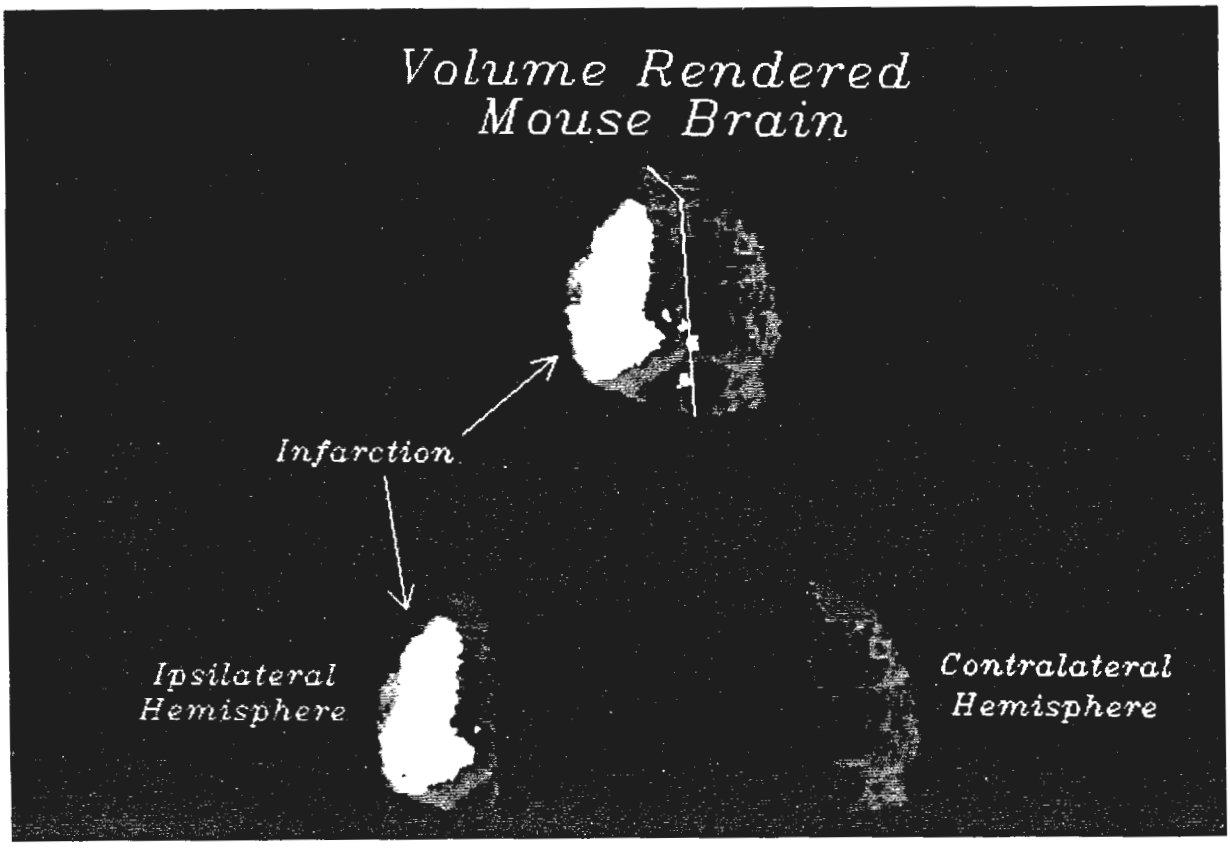
We have been interested to extend the NMR microscopy techniques to 3 dimensions. 3D volume imaging and rendering significantly enhances the display and quantification of structures of interest in the images.

The 3-dimensional images could be generated either by 3D FT volume acquisition or by rendering the 2D contiguous slices with or without interpolation. We have been extending 3D NMR microscopy technology using both the approaches for application to systems of biological and non-biological interest. To date, we have obtained images with resolution of 80 x 80 x 80 mm for live mouse and with resolution of 35 x 35 x 35 mm for non-living samples, at 9.4 T. A 3D rendered volume image of a live mouse brain with infarction is shown below.

Yours sincerely,

Rasesh D. Kapadia
Postdoctoral Fellow
Physical & Structural Chemistry

Susanta K. Sarkar
Associate Fellow
Physical & Structural Chemistry



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950 Main Street Worcester Massachusetts 01610-1477

Department of Chemistry

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

(received 3/6/92)

Differential Chemical Shifts in the ^{13}C-NMR Spectra of Aminophosphines

Dear Barry:

In our studies of aminophosphines we have prepared a series of compounds of the general formula Ph(RR'N)PCl [R, R' = Me, Et, Bz, ^{i}Pr, cHex) and examined their ^{13}C-NMR spectra at low temperature. At sufficiently low temperatures these compounds show slow rotation about the P-N bond and the chemical shifts of the carbons adjacent to the N-atom are resolved into two sets signals representing the syn and anti conformers (with respect to the P-lone pair). In comparing the chemical shifts of a particular carbon in the syn position to its own shift in the anti position we note that the chemical shift difference ($\Delta\delta$) is independant of the substituent for both R,R' = small, and conclude that the average value of 5.2 ± 0.5 ppm represents the differential shielding effect of the P-lone pair for this system. The differential chemical shift data is presented below.

Change in Chemical Shift ($\Delta\delta$) Required to Convert δR_{syn} to δR_{anti} (in ppm) As a Function of (R') in Ph(RR'N)PCl

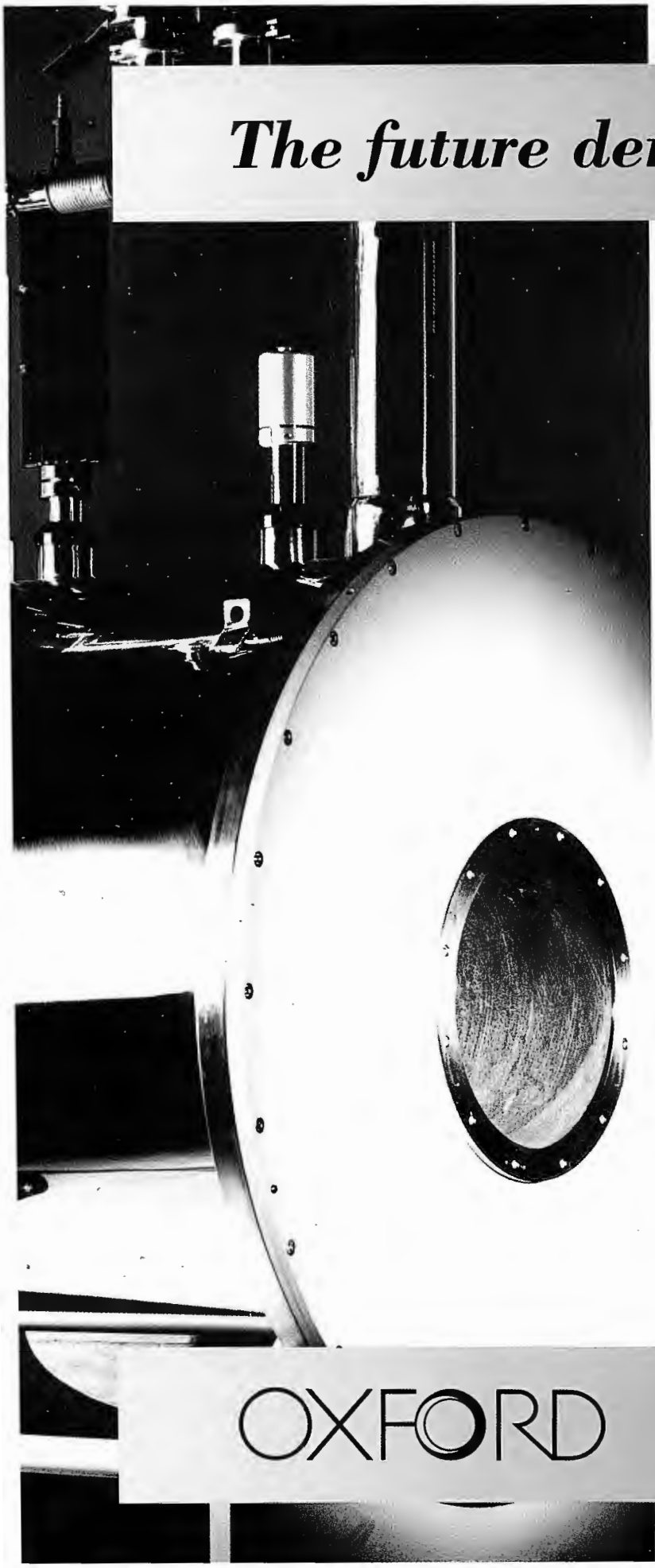
R	(R')	$\Delta\delta$	R	(R')	$\Delta\delta$	R	(R')	$\Delta\delta$
Me	(Me)	-5.5	Me	(Et)	-5.2	Me	(Bz)	-4.9
Et	(Me)	-5.4	Et	(Et)	-4.8	Et	(Bz)	-4.5
Bz	(Me)	-5.7	Bz	(Et)	-6.0	Bz	(Bz)	-5.2

Please credit this contribution to Paul Inglefield's account.

Sincerely,

Mark M. Turnbull

Mark M. Turnbull



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Spurious Outputs: –70dBc
Phase Noise: –63dBc (0.5Hz–15KHz)

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Switching: 5–10μs

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Phase Noise: –60dBc (0.5Hz – 15KHz)

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GEORGETOWN UNIVERSITY MEDICAL CENTER

(received 2/24/92)

Cancer Pharmacology Section
Department of Pharmacology

INCREASE IN THE ATP SIGNAL AFTER TREATMENT WITH CISPLATIN IN TWO DIFFERENT CELL LINES STUDIED BY 31P NMR SPECTROSCOPY

Dr. Barry Shapiro,
Editor, NMR Newsletter

Dear Barry:

Acquired resistance to chemotherapeutic agents is one of the most important problems in cancer treatment. Studies of metabolic changes which occur when tumor cells become drug resistant may contribute to the understanding of the resistant phenotype, and help in designing means to overcome it.

Cisplatin [*cis*-diamminedichloroplatinum(II)] has activity against many solid tumors. The mechanism of action of cisplatin is not completely understood, though its cytotoxicity is believed to result from the adducts it forms with nuclear DNA. It has been shown that mitochondrial morphology and function in some cisplatin resistant cell lines are different than that observed in the sensitive line. Recent studies also indicate that cisplatin and its analogues produce alterations in the structure and function of isolated mitochondria. In other cells, the post-treatment concentration of platinum in mitochondria was higher than in the other subcellular compartments.

^{31}P NMR spectroscopy constitutes a non-invasive technique that is very useful for monitoring high energy and phospholipid metabolism. We have previously described a procedure for continuously perfusing cells under controlled conditions. This technique has been used to demonstrate alterations in basal levels of high energy phosphate and phospholipids in resistant cells and shifts in these levels in response to drug exposure.

We have compared the ^{31}P nuclear magnetic resonance (NMR) spectra of two different cisplatin resistant cell lines, one derived from human ovarian carcinoma and the other from rat lymphoma, and their respective cisplatin sensitive parental cells lines. Comparisons were made between the baseline spectra and after perfusion of the cells with 20 - 50 μM cisplatin for 16 - 20 hours. While no obvious differences were found between baseline spectra of sensitive and resistant cells, during cisplatin perfusion the sensitive cells had an increase in their ATP signals. The resistant cells also exhibited increases in their ATP signals during cisplatin perfusion but to a lesser extent than the sensitive cells. Although the significance of these ATP elevations towards the cellular pharmacology of cisplatin are not presently known, our studies demonstrate that ^{31}P NMR spectroscopy may be useful for elucidating differences in phosphate metabolism in cells expressing the cisplatin resistant phenotype.

Yours sincerely,

Jesus O. Ruiz-Cabello Jack S. Cohen 3/18/92

4 Research Court Rockville MD 20850 USA

Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor:

William B. Smith, Texas Christian University, Fort Worth, TX 76129

" Basic One- and Two-Dimensional NMR Spectroscopy"

by **Horst Friebolin**

VCH Publishers, Suite 909, 220 East 23rd Street, New York, NY 10010-4606;
xxi + 344 pp.; 1991; $45.00 (paper); ISBN 0-89573-972-0.

The selection of a beginning textbook in NMR spectroscopy for an entering group of organic chemistry graduate students in not easy. There are several excellent texts which deal with modern pulse sequences and 2D NMR. However, the number which address spectral analysis and the correlation of NMR parameters with molecular structure is quite limited. Thus, the addition of the Friebolin text is particularly welcome. Originally published in a German edition in 1988, the current text has been updated and put forth in an excellent English translation. The diagrams are clearly drawn, the text reads well, and there is a lovely index of compounds for which spectral information is given, along with the usual subject index.

The subject matter covered is indicated by the chapter headings: 1. The Physical Basis of NMR Spectroscopy; 2. The Chemical Shift; 3. Indirect Spin-Spin Coupling; 4. Spectrum Analysis and Calculations; 5. Double Resonance Experiments; 6. Assignments of ^{1}H and ^{13}C Signals; 7. Relaxation; 8. One-Dimensional NMR Experiments Using Complex Pulse Sequences; 9. Two-Dimensional NMR Spectroscopy; 10. The Nuclear Overhauser Effect; 11. Dynamic NMR Spectroscopy; 12. Chemical Shift Reagents; 13. Macromolecules; 14. NMR Spectroscopy in Biochemistry and Medicine. Each chapter concludes with a useful bibliography.

One realizes that such a lengthy list of subjects cannot be covered in complete detail. Consequently, it is inevitable that your favorite subject is not there in all the glory you would have preferred. I think that the text would have been enhanced with two or three problems at the end of most of the chapters, with answers at the back of the book.

W. B. S.

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(received 3/18/92)
10 March 1992

Using ^{35}Cl NMR Null Point Experiments to Characterize the Binding of Chloride ions to Human Serum Albumin

Dear Barry,

We have previously used null point spectra from inversion-recovery experiments to determine the fluctuation correlation time of the electric field gradient at the nucleus and the quadrupolar coupling constant for ^{7}Li in a sample composed of LiCl dissolved in isopropanol-d_8/D_2O solution [1]. We then extended the theory to include two-site exchange and using ^{35}Cl null point studies to characterize the binding of chloride ions to human serum albumin (HSA) in the presence of sodium dodecyl sulfate (SDS) [2]. HSA has two classes of chloride binding sites: strong (s) and weak (w). SDS inhibits the binding of chloride ions to the strong sites.

We have now extended the theory to encompass three site exchange and are using this theory to study chloride ion binding to HSA in the presence and absence of SDS. In the absence of SDS, the binding of chloride ions to HSA becomes a three site exchange system. In extending the theory to cover three site exchange, the principle of detailed balance was used along with the following two assumptions: (1) There are n_w equivalent weak binding sites and n_s equivalent strong binding sites per HSA molecule. (2) The exchange between s and the free site (f) and between w and f occur independently (i.e., f $\leftrightarrow$ s and f $\leftrightarrow$ w) since the population of the free site is much greater than the population of the bound sites and the exchange is extremely slow since it would be limited by the Cl^- ion diffusion rate on the protein surface.

The null point spectra are simulated using a complete formulation of the relaxation processes (i.e., both transverse and longitudinal) occuring throughout the inversion-recovery pulse sequence and the subsequent acquisition period. The relaxation equations used to interpret the relaxation processes and analyze the lineshapes were simplified by expressing the spin density matrix in terms of state multipoles [3]. As an example, the density matrix equation for transverse relaxation including exchange between the free, strong and weak sites is then described by the following rate equation

$$\frac{d}{dt}\begin{bmatrix}\rho_f\\ \rho_s\\ \rho_w\end{bmatrix} = \begin{bmatrix}-R_f-(k_{fs}+k_{fw})I-i(\omega_0-\delta_f)I & k_{sf}I & k_{wf}I\\ k_{fs}I & -R_s-k_{sf}I-i(\omega_0-\delta_s)I & 0\\ k_{fw}I & 0 & -R_w-k_{wf}I-i(\omega_0-\delta_w)I\end{bmatrix}\begin{bmatrix}\rho_f\\ \rho_s\\ \rho_w\end{bmatrix}$$

where I is the unit matrix, the k_{ab} (where $a,b = f,s,w$) terms are microscopic rate constants for transfer from site a to b. R_f, R_s and R_w are the Redfield relaxation matrices for the transverse components of the state multipoles in the three classes of sites [1,2], ω_0 is the Larmor frequency and δ_f, δ_s and δ_w are the chemical shifts of the three classes of sites. The column density matrices ρ_f, ρ_s, ρ_w of state multipoles σ_m^k (k is the rank and m is the tensorial component of the state multipole) are defined by,

$$\tilde{\rho}_f \equiv \left[\left(\sigma_1^1\right)_f, \left(\sigma_1^3\right)_f\right], \quad \tilde{\rho}_s \equiv \left[\left(\sigma_1^1\right)_s, \left(\sigma_1^3\right)_s\right] \text{ and } \quad \tilde{\rho}_w \equiv \left[\left(\sigma_1^1\right)_w, \left(\sigma_1^3\right)_w\right].$$

We were able to simulate the binding at the weak site using only one correlation time. However, for binding at the strong site a minor modification of the approach of Halle and Wennerström [4] was used, thus for the strong site two correlation times and an order parameter are needed. The spectral lineshape is related to the real part of the Fourier-Laplace transform of the $\left(\left(\sigma_1^1\right)_f + \left(\sigma_1^1\right)_s + \left(\sigma_1^1\right)_w\right)$ term (n.b. the multipoles are population weighted), which evolves during the acquisition period. Some experimental and simulated ^{35}Cl null point spectra from a sample of chloride ions binding to HSA in the absence of SDS are given in Figure 1.

In the future we hope to extend the null point method to the study of quadrupolar nuclei with $I > 3/2$.

Yours sincerely,

Lian-Pin Hwang William S. Price Nien-Hui Ge Luan-Ze Hong

(1) Price, W. S., N. H. Ge, and L. P. Hwang. *J. Magn. Reson.* **1992,** in press.
(2) Ge, N. H., W. S. Price, L. Z. Hong and L. P. Hwang. *J. Magn. Reson.* **1992,** in press.
(3) Sanctuary, B. C. *J. Magn. Reson.* **1985,** *61,* 116 and pertinent references therein.
(4) Halle, B., and H. Wennerström. *J. Chem. Phys.* **1981,** *75,* 1928.

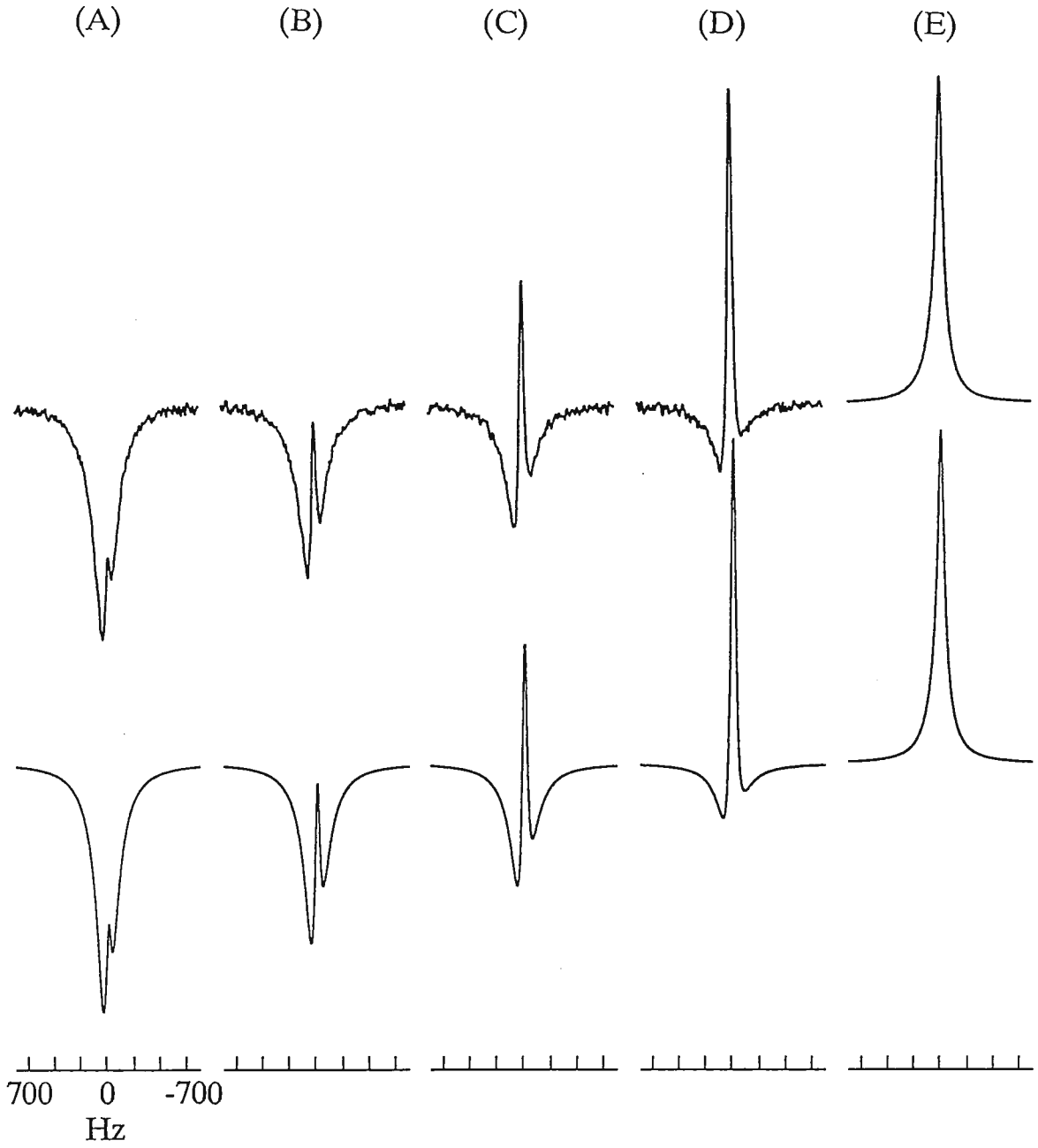

Figure 1. Experimental (top) and simulated (bottom) ^{35}Cl null point spectra of a HSA/saline sample (HSA 0.45 mM; NaCl 1M; Tris-buffer 50 mM) at 298 K. The interpulse delay times in the inversion recovery pulse sequence and ordinate magnifying factors are given respectively by (A) 5.10 ms, 32; (B) 5.20 ms, 32; (C) 5.30 ms, 32; (D) 5.45 ms, 32; (E) 200 ms, 1. The fluctuation correlation times at the free and weak and strong sites were set to 3 ps and 3.5 ns, respectively. The two correlation times for the strong site and the order parameter were 0.8 ns, 43.0 ns and 0.47, respectively. The quadrupolar coupling constants for the free site was set to 1743 kHz and and the population times the (quadrupolar coupling constant)^2 was set to 7981 and 16867 (kHz)^2 for the weak and strong sites, respectively. Since the bound populations are not known accurately, the quadrupolar coupling constants could not be separated from the population terms for the bound sites.

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Indirect Detection ^{1}H Observe, ^{15}N-^{31}P Decouple	ID200	ID250	ID270	ID300	ID360	ID400	ID500	ID600
Triple Resonance Indirect Detection: ^{1}H, (^{13}C, ^{15}N)				IDT300	IDT360	IDT400	IDT500	IDT600
Microsample Indirect Detection				MID300	MID360	MID400	MID500	MID600
Broadband ^{15}N-^{31}P Observe	BB200	BB250	BB270	BB300	BB360	BB400	BB500	BB600
Dual Broadband ^{1}H/^{15}N - ^{31}P Switchable	DB200	DB250	DB270	DB300	DB360	DB400	DB500	DB600
Dual ^{1}H/^{13}C Switchable	D200	D250	D270	D300	D360	D400	D500	D600
^{1}H/^{19}F Observe BB Decoupling of ^{1}H or ^{19}F	H-F200	H-F250	H-F270	H-F300	H-F360	H-F400	H-F500	H-F600
^{1}H/^{19}F Observe	HF200	HF250	HF270	HF300	HF360	HF400	HF500	HF600
Microsample ^{1}H/^{19}F Observe	MHF200	MHF250	MHF270	MHF300	MHF360	MHF400	MHF500	MHF600

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3D spectra were obtained using a 256 x 128 x 128 matrix for sucrose (Fig. 2) and a 512 x 128 x 128 matrix for menthol (Fig. 3). With a predelay time of 1s, total data collection time was approximately 6 hours.

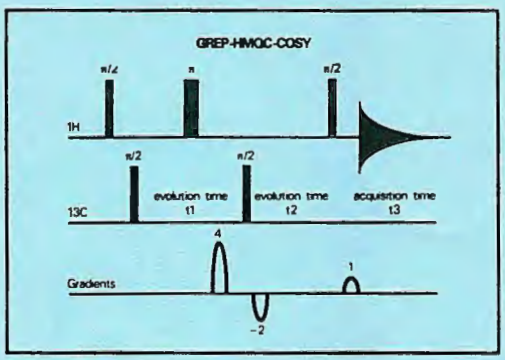

Fig. 1
Gradient-enhanced Relay Edited Proton, GREP-HMQC-COSY pulse sequence.

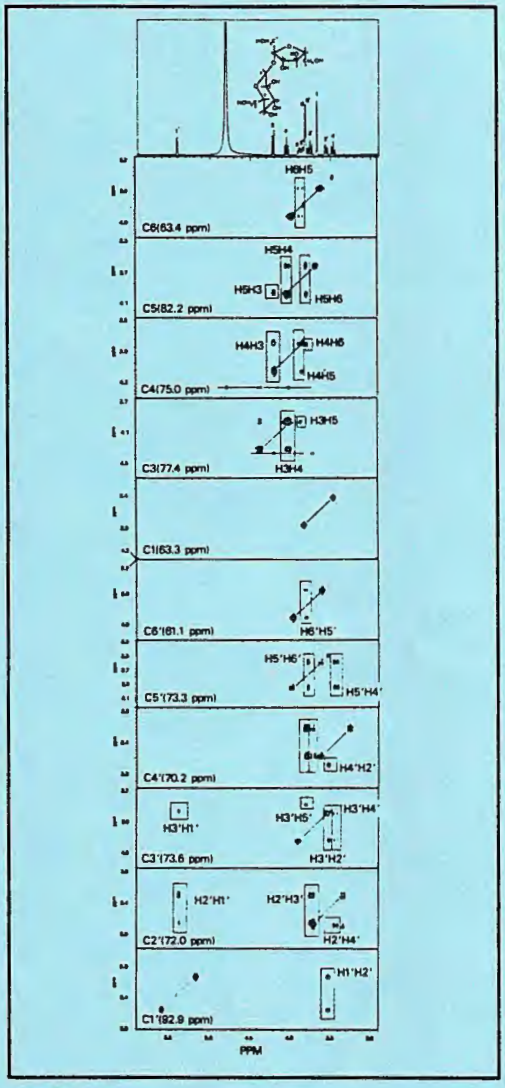

Fig. 2
Contour plots of eleven protonated carbon planes (ω_2, ω_3 planes at the appropriate ^{13}C chemical shifts in ω_1). Individual planes are identified by carbon and the chemical shift position in ω_1. The horizontal lines in C3 and C4 are at zero frequency in ω_2.

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