

THE
NMR
NEWSLETTER

No. 457
October 1996

Magnetic Susceptibility Matching Fluid in Microcoil NMR	Olson, D. L., and Sweedler, J. V.	2
Sideband Suppression by VSMAS	Madhu, Pratima, and Kumar, A.	5
NMR Crystallography	Poupko, R., Zimmermann, H., Olivier, L., Müller, K., Krieger, C., and Luz, Z.	7
Macro for Processing n-Dimensional Data Sets (n>2)	Babcock, D. M., and Gmeiner, W. H.	11
Positions Available	Lee, J. C.	12
Signal Enhancement as a Measure of Molecular Motion in Asphalts	Netzel, D. A., and Miknis, F. P.	15
Internuclear Distances with the Help of Karl Mueller	Reimer, J. A.	19
Suspension NMR Spectroscopy of Phosphines Immobilized on Silica	Blümel, J.	23
NMR Studies of the ISL Homeodomain; Position Available	Behravan, G., Lycksell, P. O., and Wijmenga, S.	24
²⁹ Si CP-MAS NMR Investigation of the <i>In Situ</i> Generation of Silica Reinforcement in Modified Polydimethylsiloxane Elastomers	Prabakar, S., Bates, S. E., Ulibarri, T. A., and Assink, R. A.	29
Xenon-Proton Cross-Polarization	Hitchens, T. K., Hinton, D. P., Bryant, R. G., Brookeman, J., and Berr, S.	33
Solid State Exchange Experiments on Slow Molecular Dynamics in Organic Solids and Polymers	Schneider, H., and Reichert, D.	37
Lability of Polyanion-Gelatin Binding Investigated with PGSE-NMR	Antalek, B.	41
The NMR Newsletter: Policies and Practical Considerations	Shapiro, B. L.	45

A monthly collection of informal private letters from laboratories involved with NMR spectroscopy. Information contained herein is solely for the use of the reader. Quotation of material from the Newsletter is not permitted, except by direct arrangement with the author of the letter, in which case the material quoted must be referred to as a "Private Communication". Results, findings, and opinions appearing in the Newsletter are solely the responsibility of the author(s). Reference to The NMR Newsletter or its previous names in the open literature is strictly forbidden.

These restrictions and policies apply equally to both the actual Newsletter recipient/participants and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium for the exchange of NMR-related information.

The University of Virginia

ROBERT G. BRYANT
Commonwealth Professor

Department of Chemistry
McCormick Road
Charlottesville, VA 22901
Tel. (804)924-1494
RGB4G@Virginia.edu
9 September 1996

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

(received 9/14/96)

RE: XENON-PROTON CROSS-POLARIZATION

Dear Barry:

We have made first attempts to investigate the practical aspects of transferring magnetization from optically pumped ^{129}Xe gas with high nuclear spin polarizations to protons in aqueous solutions. Our experiments were made possible by a collaboration between the Princeton Groups of W. Happer and G. Cates and the University of Virginia Radiology Department (James Brookeman and collaborators) and the pulmonary group headed by Dr. Thomas Daniels for the purpose of imaging human lung. We had access to hyperpolarized ^{129}Xe samples for just over a week and conducted simple experiments following the work in magnetically dilute nonaqueous systems by Pines and collaborators.

^{129}Xe polarized to the level of 2% contained in glass containers treated with dichlorodimethyl silane was shaken rapidly with solutions of L-tyrosine, α -cyclodextrin, β -cyclodextrin, and apomyoglobin. Labile protons were out-exchanged prior to the experiment to minimize ^1H exchange into the D_2O as well as maximize solute ^1H relaxation times. Immediately following a vigorous shaking of the D_2O solution, which was injected into the sample bulb, the 3 mL aqueous sample was placed in a 4.7 T horizontal magnet (SISCO) and the ^1H or ^{129}Xe spectrum recorded within seconds. We were searching for large intensity changes and took ^1H spectra using 5° pulses every 2.1 s for five minutes. In no case did we detect a significant enhancement of the proton spectrum similar to that reported by Navon et al. Science 271, 1846 (1996) for any of the solutes listed.

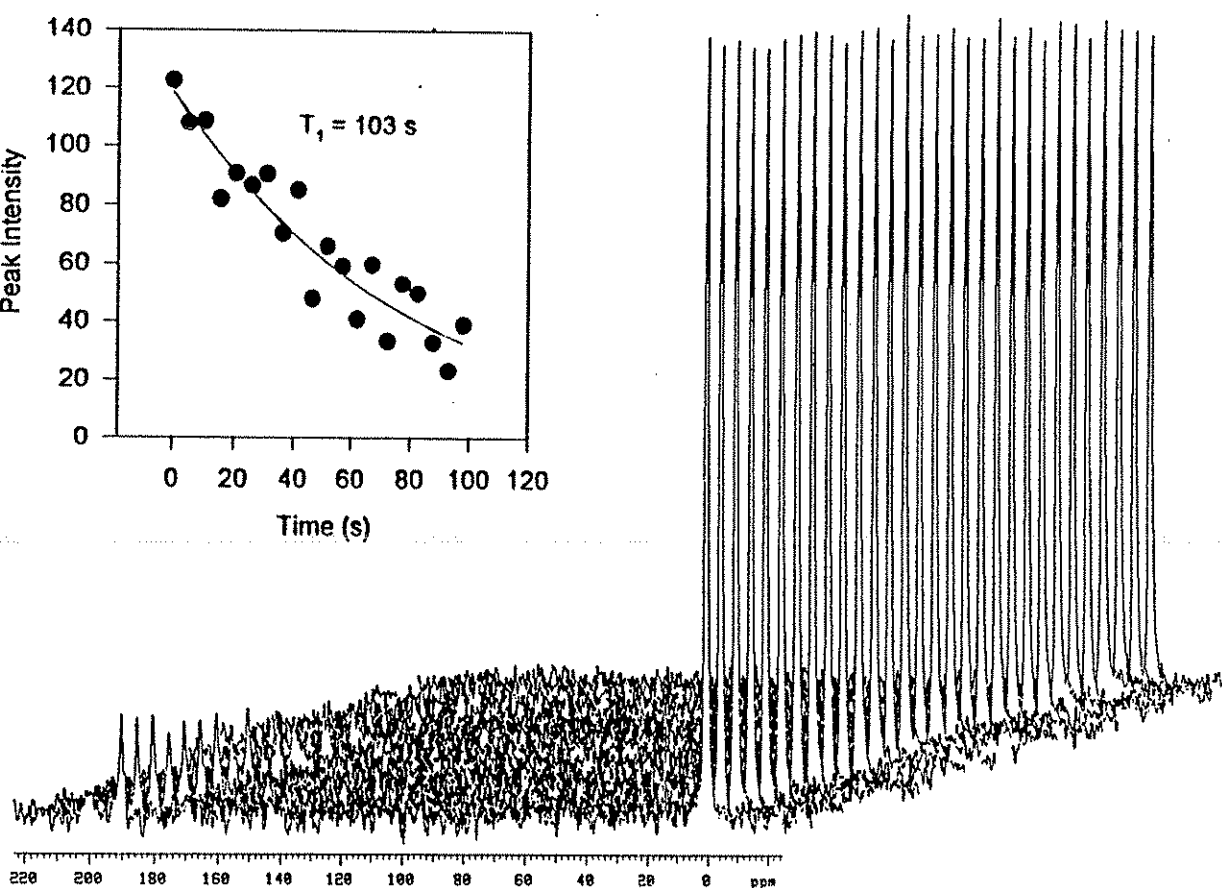
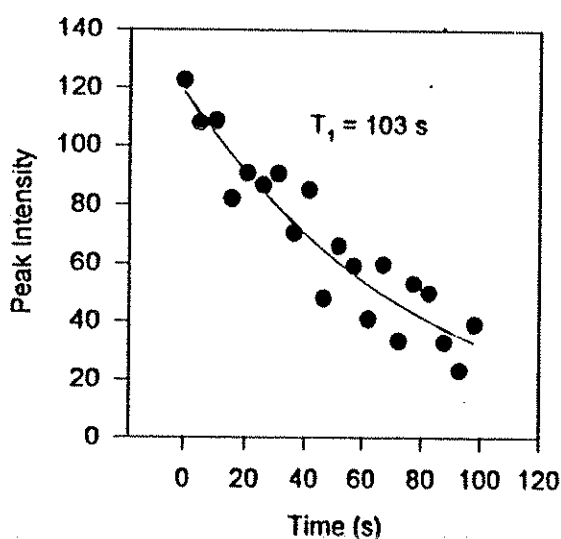
The xenon spectrum was monitored in separate experiments using samples prepared in the same way. The ^{129}Xe T_1 in the D_2O solution was approximately 600 s and the xenon T_1 values in L-tyrosine and β -cyclodextrin solutions were similar and longer than 100 s. The T_1 of the gas phase signal above the D_2O solution was long and the decay dominated by the effects of the 10.8° sampling pulses used to monitor it. Both α -cyclodextrin and myoglobin bind xenon. The relaxation rate of ^{129}Xe in the apomyoglobin solution was so rapid that no ^{129}Xe resonance could be detected in the solution following mixing although the gas phase peak verifies that the polarization was not inadvertently lost at the glass surface. The α -cyclodextrin solution shows a measurable decay of the ^{129}Xe polarization with a T_1 of 103 s as shown in the Figure below. The chemical shift reference is taken as the gas phase signal. These relatively short ^{129}Xe relaxation times demonstrate efficient coupling to the solute protons which serve as relaxation agents for the xenon. In spite of these observations, no proton signal enhancement was observed with single pulse experiments and the finite mixing times employed. Given the solution mixing times and sample positioning times of order 10 seconds, if the proton polarization was enhanced significantly, the solute ^1H polarization relaxed to Boltzmann levels more rapidly than we were able to detect the ^1H spectrum.

The ^{129}Xe - ^1H cross-relaxation rate for these samples is that appropriate to the fringe field of the 40 cm-4.7 T magnet. The remaining contact occurs at 4.7 T. No match conditions were created, either at zero

field or using rf fields (Hartmann-Hahn) both of which may make the transfer rate more favorable. In the β -cyclodextrin and L-tyrosine solutions, no effective magnetic coupling was observed. Thus, transient or collisional interactions are unlikely to be effective as practical cross-relaxation vehicle for proton rich solutes.

Although these experiments were disappointing, they do not by any means eliminate the possibility that significant enhancements may be observed with higher xenon polarization, more efficient sample mixing, and a magnetization transfer conducted under some kind of matched resonance condition.

Exponential Fit for ^{129}Xe in 20mM α -Cyclodextrin/ D_2O



T. Kevin Hitchens

T. Kevin Hitchens

Denise P. Hinton

Denise P. Hinton

Robert G. Bryant

Robert G. Bryant

James Brookeman

James Brookeman

Stuart Berr

Stuart Berr

THE
NMR
NEWSLETTER

No. 459
December 1996

Failed Failure	Pines, A.	2
CORVUS, Computations On Randomly Vitalized Uplifted Spins	Woessner, D. E.	5
Combined 1D Z-Filtered Gradient TOCSY and Homonuclear Decoupling	Doss, G. A.	8
X-Filtered 2D Spectroscopy Revisited	Silber, S. K.	11
¹³ C Relaxation Measurements in Cardiac N-Troponin C	Spyracopoulos, L., Gagné, S., and Sykes, B. D.	15
Position Available	Spencer, R. G. S.	16
"Double-WURST" Decoupling for ¹⁵ N- and ¹³ C-Labeled Proteins in a High Magnetic Field	Zhang, S., and Gorenstein, D. G.	19
¹²⁹ Xe NMR Studies of Polystyrene Microgels	McGrath, K. J., Roland, C. M., Antonietti, M., and Neese, M.	21
Use of a 10mm Probe for RNA Structure Determination	Yao, L., Schmitz, U., and James, T. L.	25
Field of Dreams, V. A Letter to Santa	Shaffer, K.	26
Direct Coupling of HPLC, NMR Spectroscopy and Mass Spectrometry	Nicholson, J., and Lindon, J. C.	27
Fluorinated Gases in Lungs Are More Like Solids Than Liquids	Kueth, D. O., Caprihan, A., Fukushima, E., Gach, H. M., and Lowe, I. J.	31
UNIX Scripts	Silber, S. K.	35
Solids or Liquids?	Tjandra, N., and Bax, A.	39
Position Available	Burke, J. M.	42
Primary and Secondary Isotope Effects in Perylenequinones	Mondelli, R., and Scaglioni, L.	45
A Wish-List for Automation	Stanley, P. P. D.	49
¹³ C NMR Study of Dihydrofuro[2,3-b]indoles Containing a Push-Pull Ethylene System	Suárez-Castillo, O. R., Morales-Rios, M. S., and Joseph-Nathan, P.	51

A monthly collection of informal private letters from laboratories involved with NMR spectroscopy. Information contained herein is solely for the use of the reader. Quotation of material from the Newsletter is *not* permitted, except by direct arrangement with the author of the letter, in which case the material quoted *must* be referred to as a "Private Communication". Results, findings, and opinions appearing in the Newsletter are solely the responsibility of the author(s). Reference to The NMR Newsletter or its previous names in the open literature is strictly forbidden.

These restrictions and policies apply equally to both the actual Newsletter recipient/participants and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium for the exchange of NMR-related information.

UNIVERSITY OF CALIFORNIA, BERKELEY
Department of Chemistry

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO

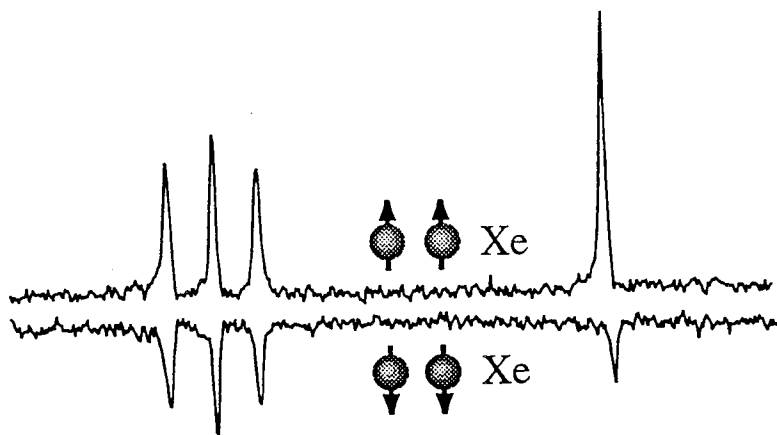


SANTA BARBARA • SANTA CRUZ

Professor Alexander Pines
The President's Chair
University of California
Berkeley, CA 94720-1460Tel: (510)642-1220
Fax: (510) 486-5744
E-mail: Pines@cchem.berkeley.eduNovember 13, 1996
(received 11/15/96)Barry Shapiro, Esquire
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

We read with interest the recent letter reporting negative results on xenon-proton cross-polarization in solution (NMR Newsletter 457-33). We attempted the experiments described but, despite fervid efforts, we were unable to replicate their failure. On the contrary, we noted differential effects for the proton lines of p-nitrotoluene/benzene following the introduction of laser-polarized xenon into solution:



Proton NMR spectrum of p-nitrotoluene/benzene in benzene- d_6 after introduction into solution of laser-polarized xenon-129 with spins "up" or "down". The proton and xenon resonances were perturbed with π pulses in order to exhibit primarily the SPINOE effect over a period of two seconds. (Courtesy of Y.-Q. Song, B. M. Goodson, R. E. Taylor, G. Navon)

Although these experiments were disappointing, they do not by any means eliminate the possibility that insignificant enhancements may be observed with low polarization and reduced concentration.

Divertingly yours,

Alex Pines