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The University of Virginia

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9 September 1996

(received 9/14/96)

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

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.

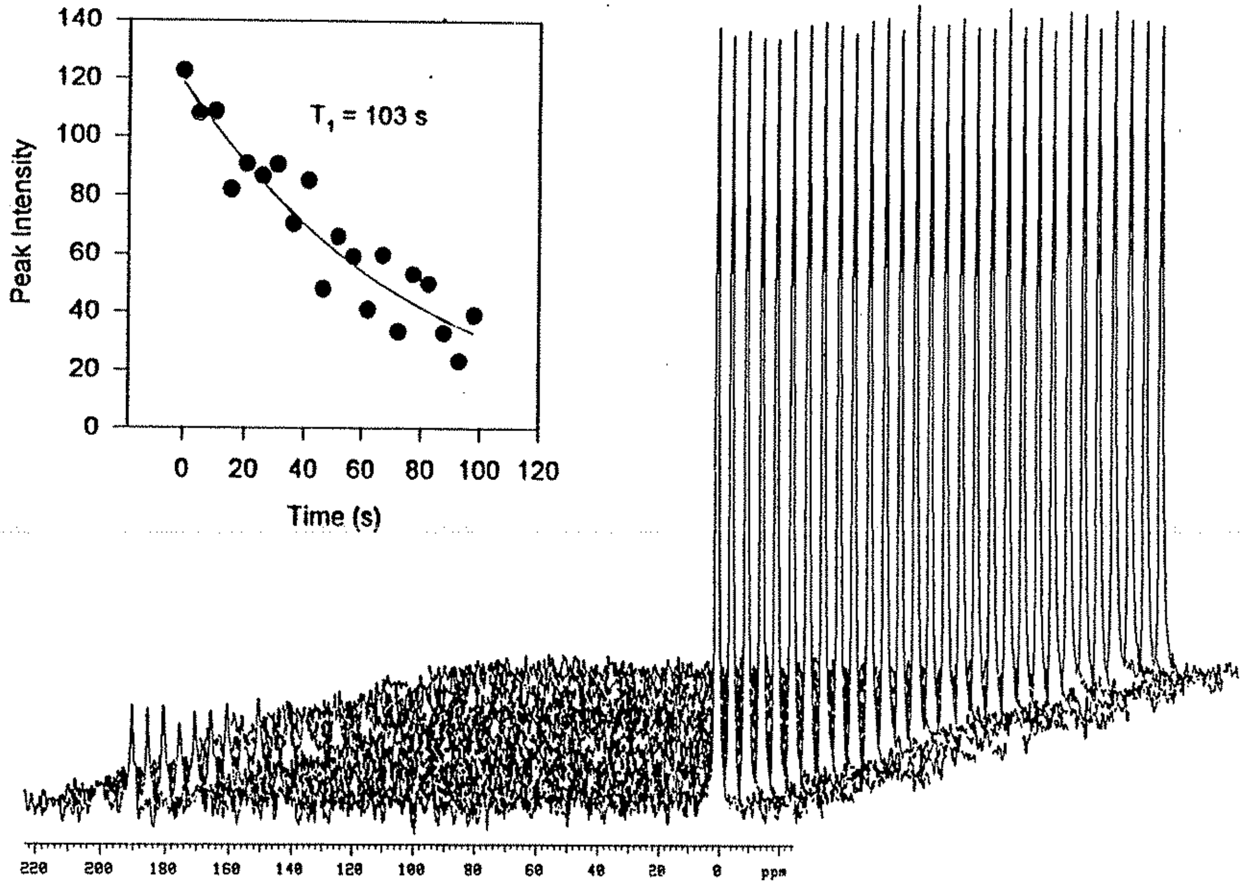
^{129}Xe polarized to the level of 2% contained in glass containers treated with dichlorodimethyl silane was shaken rapidly with solutions of L-tyrosine, α-cyclodextrin, β-cyclodextrin, and apomyoglobin. Labile protons were out-exchanged prior to the experiment to minimize ^{1}H exchange into the D_2O as well as maximize solute ^{1}H relaxation times. Immediately following a vigorous shaking of the D_2O solution, which was injected into the sample bulb, the 3 mL aquous sample was placed in a 4.7 T horizontal magnet (SISCO) and the ^{1}H or ^{129}Xe spectrum recorded within seconds. We were searching for large intensity changes and took ^{1}H 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 at 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 ^{1}H polarization relaxed to Boltzmann levels more rapidly than we were able to detect the ^{1}H spectrum.

The ^{129}Xe-^{1}H 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



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November 13, 1996
(received 11/15/96)

Barry Shapiro, Esquire
The NMR Newsletter
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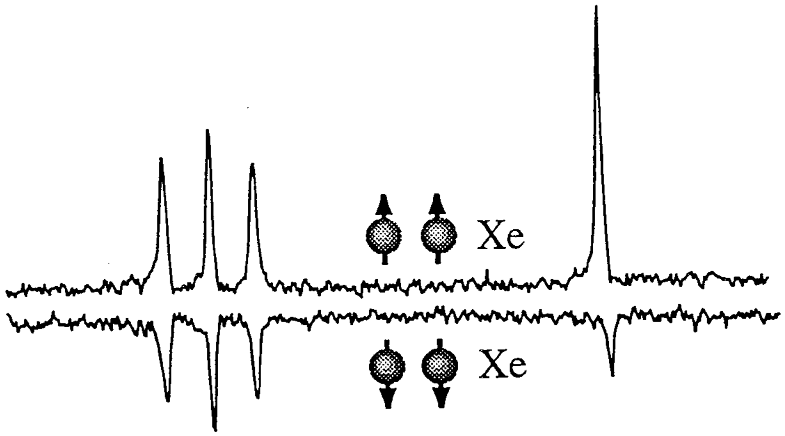
Dear Barry:

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