Table I. Temperature Dependence of Microscopic Viscosities at 0.02 M Detergent

deter-gent	microscopic viscosities, cp					
	1 °C	10 °C	20 °C	30 °C	40 °C	50 °C
HDTBr	81	60	39 (30,[a] 151[b])	22	14	9
HDTCl	70	49	31	18	13	8
SDS	17	13	9 (16,[c] 193[b])	6	6	7

[a] Depolarization of fluorescence. (ref 5a at 27 °C). [b] Excimer dynamics (ref 6 at 24 °C). [c] Depolarization of fluorescence (ref 5c at 25 °C).

In the case of intermolecular excimer formation the probe molecules (naphthalene or pyrene[6]) may or may not distribute themselves among the available micelles in a manner that is accurately described by statistical methods.[4] Whatever the detailed nature of this distribution, a strict correlation between the measured values of I_{ex}/I_m for micellar systems and those for homogeneous solution is not expected. In other words, the statistical methods that are valid for homogeneous solution are unlikely to be appropriate for analyzing data and deriving microviscosity parameters for micellar systems. In the case of DNP, however, excimer formation is possible at low enough concentration to avoid interference from intermolecular excimer formation, and the unimolecular nature of excimer formation avoids the problem of explicitly including the distribution of probe molecules in deriving microviscosities from I_{ex}/I_m ratios. We thus feel that the use of excimer dynamics, per se, is a valid method for determining microviscosities,[13,14] but that the intermolecular method presents problems because of the difficulties of explicitly including a distribution of probe molecules in the derivation of micelle parameters from experimental parameters.

Acknowledgment. The authors thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research. The authors thank Dr. Ed Chandross of Bell Laboratories for his generous gift of a sample of DNP.

References and Notes

(1) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, London, 1970, pp 403–491.
(2) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975, pp 254–304.
(3) (a) Th. Forster and B. Selinger, *Z. Naturforsch., A*, **19**, 38 (1964); (b) G. Reske, *ibid.*, **24**, 17 (1969).
(4) (a) R. C. Dorrance and T. F. Hunter, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1572 (1974); (b) U. Khuanga, B. Selinger, and R. McDonald, *Aust. J. Chem.*, **29**, 1 (1976).
(5) (a) M. Shinitzky, A. C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, **10**, 2106 (1971); (b) M. Grätzel and J. K. Thomas, *J. Am. Chem. Soc.*, **95**, 6885 (1973); (c) Y. Kubota, M. Kodama, and M, Miura, *Bull. Chem. Soc. Jpn.*, **46**, 100 (1973).
(6) H. J. Pownall and L. C. Smith, *J. Am. Chem. Soc.*, **95**, 3136 (1973).
(7) P. Mukerjee and K. J. Mysels, "Critical Micelle Concentration of Aqueous Surfactant Systems", NSRDS–NBS 36, U.S. Government Printing Office, Washington, D.C., 1971.
(8) B. Stevens and T. Dickinson, *J. Chem. Soc.*, 5492 (1963).
(9) Time-resolved spectra were recorded by single photon counting: R. R. Hautala, N. E. Schore, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 5508 (1973).
(10) E. C. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970).
(11) P. Avouris, J. Kordas, and M. A. El-Bayoumi, *Chem. Phys. Lett.*, **26**, 373 (1974).
(12) A. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 3272 (1971); K. Kalyansundaram, *J. Am. Chem. Soc.*, **99**, 2039 (1977).
(13) During the process of refereeing of this manuscript, a publication has appeared employing 1,3-bis(pyrenyl)propane as an intramolecular excimer forming probe for deriving micellar viscosities: K. Zachariasse, *Chem. Phys. Lett.*, **57**, 429 (1978). The results of that investigation is consistent with our results and those of Emert: J. Emert, C. Behrens, and M. Goldenberg, *J. Am. Chem. Soc.*, preceding paper in this issue.
(14) For discussions of the problems in quantitative analysis of bimolecular kinetics in micellar solutions, see B. K. Selinger and A. R. Watkins, *Chem. Phys. Lett.*, **56**, 99 (1978), and M. Maestri, P. P. Infelta, and M. Grätzel, *J. Chem. Phys.*, **69**, 1522 (1978).
(15) A. Yekta thanks the Arya-Mehr University of Technology and the Iranian Ministry of Sciences for a Visiting Research Fellowship for the period of 1977–1978.

Nicholas J. Turro,* Masayuki Aikawa, Ahmad Yekta[15]
Chemistry Department, Columbia University
New York, New York 10027
Received June 16, 1978

Sensitivity Enhancement in Natural Abundance Proton-Coupled ^{15}N NMR Spectra Using the Selective Population Transfer Method

Sir:

The convenient observation of natural abundance ^{15}N nuclear magnetic resonance spectra promises to open to the areas of organic chemistry, bioorganic chemistry, and inorganic chemistry a structural tool comparable in significance with those afforded by two other spin $^1/_2$ nuclei, ^1H and ^{13}C. Furthermore, the spectra obtained will be of greater value if they yield spin-coupling information rather than merely chemical-shift data.[1,2]

Most of the spin-coupling values for ^{15}N currently available have been obtained from ^{15}N-enriched samples;[3,4] indeed, many coupling constants to hydrogen have been measured only from the ^1H spectra of enriched molecules.[2] Low abundance (0.365%), low sensitivity (6.54×10^{-2} relative to ^{13}C), long spin-lattice relaxation times (up to 250 s for nitrobenzene and 500 s for benzonitrile),[5-7] and the possible partial loss of nuclear Overhauser effect (NOE) because of relaxation mechanisms other than dipolar, a loss especially disasterous for a nucleus with negative magnetogyric ratio, combine to make the observation of natural abundance ^{15}N spectra tedious and time consuming.

We report here the direct observation of proton-coupled ^{15}N NMR spectra using the selective population transfer (SPT) π-pulse technique,[8] which is found to yield dramatic improvements in sensitivity, often as much as a ten- to onehundredfold increase in signal-to-noise ratio with corresponding time saving of between two and four orders of magnitude for repetitive pulse experiments. Indeed, proton-coupled natural abundance ^{15}N NMR spectra of high concentration samples

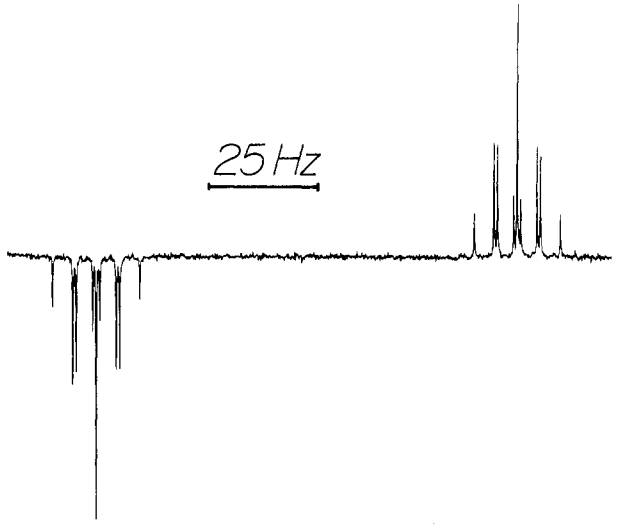


Figure 1. Natural abundance proton coupled ^{15}N SPT FT NMR spectrun. of pyrrole, **1** (85% v/v in benzene-d_6; 512 transients. 8-s acquisition time, no line broadening). The ^1H π pulse ($\gamma_{H_2}/2\pi$ = 8.00 Hz, τ = 0.06 s) was applied at the center of the high-frequency multiplet (triplet of triplets, $^3J_{H(1)-H(2)}$ = 2.59 and $^4J_{H(1)-H(3)}$ = 2.46 Hz)[17] for the ^{15}N satellite in the $^1H(1)$ spectrum ($^1J_{^{15}N-H(1)}$ = −96.40, $^2J_{^{15}N-H(2)}$ = −5.36, and $^3J_{^{15}N-H(3)}$ = −4.55 Hz).

0002-7863/79/1501-0774$01.00/0

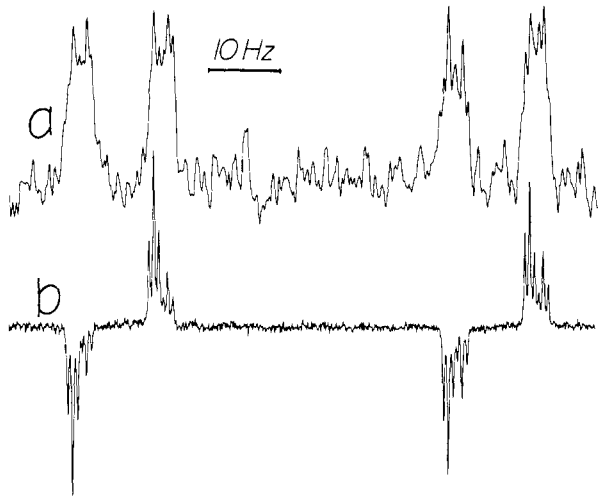
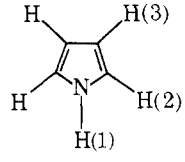
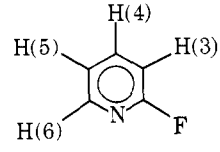


Figure 2. Natural abundance coupled ^{15}N FT NMR spectra of 2-fluoropyridine, **2** (85% v/v in acetone-d_6). (a) Normal coupled spectrum (no gated decoupling, 15 000 transients, 0.35-Hz line broadening). (b) $^{15}N\{H(6)\}$ SPT spectrum obtained after 2000 transients (no line broadening; $\gamma_{H_2}/2\pi = 0.5$ Hz and $\tau = 1.0$ s).

can often be observed from a single transient. The SPT π-pulse method is a powerful technique for intensity enhancement, especially with spin systems having degenerate ^1H transitions, as well as for sign determination of coupling constants and for spin-lattice relaxation studies.[9-12] In $^{15}N\{^1H\}$ SPT experiments, the ratio $|\gamma_{^1H}/\gamma_{^{15}N}| \approx 10$ is very favorable for intensity enhancements. For example, a ^{15}N nucleus coupled to six equivalent hydrogen nuclei would show a septet containing lines of which six may be enhanced, if the relaxation times and acquisition conditions are favorable,[8,9,13,14] by ratios of 20 to 40. A great advantage of the SPT method is that, for repetitive experiments, the *^{15}N NMR spectrum may be sampled with a repetition rate determined by the usually much greater relaxation rate of the irradiated protons rather than by the often very slow relaxation of the observed ^{15}N nucleus.* In fact, this experiment has several of the advantages of the proton-enhanced nuclear spectroscopy method introduced by Pines et al.[15] to observe rare spins in solids and recently also applied to liquids.[16] Natural abundance ^{15}N spectra for pyrrole (**1**) and 2-fluoropyridine (**2**) in Figures 1 and 2 demonstrate the power of the SPT method.



1



2

Spectra were obtained at 10.15 MHz on a Varian XL-100-15 spectrometer equipped with a Varian Gyrocode decoupler (used to generate the SPT π pulses at 100.06 MHz), Nicolet computer system, MONA multinuclear assessory, and 18-mm probe (however, without quadrature detection or single side-band filter). Free induction decays were stored into 16K data points using a spectral width of 1000 Hz and an acquisition time of 8 s. A 90° flip angle (28 μs) was used for $^{15}N\{^1H\}$ SPT π-pulse spectra and a 40° flip angle for normal spectra. All sample solutions were 85% v/v solutions in acetone-d_6 or benzene-d_6.

For the natural abundance ^{15}N NMR spectrum of pyrrole (**1**) in Figure 1, the S/N ratio is ~1.5 times that of a published spectrum[3] obtained from neat 96% ^{15}N-enriched pyrrole in a 5-mm-o.d. tube using the same number of transients (512) and the same acquisition time (8 s). With different irradiation frequencies and lower power, we have established that $^2J_{^{15}N\text{-}H(2)} \times {}^3J_{H(1)\text{-}H(2)} < 0$ and $^3J_{^{15}N\text{-}H(3)} \times {}^4J_{H(1)\text{-}H(3)} < 0$, thus confirming earlier observations and assumptions.[17] In Figure 2 the usual coupled ^{15}N spectrum of 2-fluoropyridine (**2**) obtained with 15 000 transients in 37 h is compared with an SPT spectrum obtained with 2000 transients in 5 h.

This method of sensitivity enhancement will also be applicable to larger molecules, which have shorter ^1H and ^{15}N T_1 values. The short proton T_1 values may afford an advantage, for their only effect is to permit more rapid pulsing. Results reported for ^{15}N relaxation times in proteins indicate that these are of the order of several tenths of a second or longer, a time sufficient to permit a substantial portion of the SPT gain to be preserved during acquisition. Furthermore, in the range of longer correlation time, it is not possible to increase sensitivity by utilizing the Overhauser effect, for the enhancement factor lies between 0 and −1, so that the SPT method should be of special advantage.

Acknowledgments. We thank the Danish Ministry of Education for a NATO travel grant to H.J.J. to visit the University of Florida and the University of South Carolina, and the Instrument Program, Chemistry Division, National Science Foundation, for assistance in the purchase of the Nicolet FT system and multinuclei accessory.

References and Notes

(1) I. Yavari and J. D. Roberts, *J. Am. Chem. Soc.*, **100**, 4662, 5217 (1978).
(2) For reviews on $^{15}N/^{14}N$ NMR spectroscopy, see R. L. Lichter in "Determination of Organic Structures by Physical Methods", Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, 1971, p 195; "Nitrogen NMR", M. Witanowski and G. A. Webb, Ed., Plenum Press, New York, 1973; M. Witanowski, L. Stefaniak, and G. A. Webb in "Annual Reports on NMR Spectroscopy", Vol. 7, G. A. Webb, Ed., Academic Press, New York, 1977, p 117.
(3) J. M. Briggs, E. Rahkamaa, and E. W. Randall, *J. Magn. Reson.*, **11**, 416 (1973).
(4) L. Ernst, E. Lustig, and V. Wray, *J. Magn. Reson.*, **22**, 459 (1976).
(5) E. Lippmaa, T. Saluvere, and S. Laisaar, *Chem. Phys. Lett.*, **11**, 120 (1971).
(6) D. Schweitzer and H. W. Spiess, *J. Magn. Reson.*, **15**, 529 (1974); *ibid.*, **16**, 243 (1974).
(7) G. C. Levy, C. E. Holloway, R. C. Rosanske, and J. M. Hewitt, *Org. Magn. Reson.*, **8**, 643 (1976).
(8) H. J. Jakobsen and H. Bildsoe, *J. Magn. Reson.* **26**, 183 (1977), and references therein.
(9) H. J. Jakobsen, S. Aa. Linde, and S. Sorensen, *J. Magn. Reson.*, **15**, 385 (1974).
(10) S. Aa. Linde, H. J. Jakobsen, and B. J. Kimber, *J. Am. Chem. Soc.*, **97**, 3219 (1975).
(11) S. Sorensen, R. S. Hansen, and H. J. Jakobsen, *J. Magn. Reson.*, **14**, 243 (1974); A. A. Chalmers, K. G. R. Pachler, and P. L. Wessels, *Org. Magn. Reson.*, **6**, 455 (1974).
(12) C. L. Mayne, D. W. Alderman, and D. M. Grant, *J. Chem. Phys.*, **63**, 2514 (1975); C. L. Mayne, D. M. Grant, and D. W. Alderman, *ibid.*, **65**, 1684 (1976).
(13) H. Bildsoe, *J. Magn. Reson.*, **27**, 393 (1977).
(14) K. G. R. Pachler and P. L. Wessels, *J. Magn. Reson.*, **28**, 53 (1977).
(15) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
(16) R. D. Bertrand, W. B. Moniz, A. N. Garroway, and G. C. Chingas, *J. Am. Chem. Soc.*, **100**, 5227 (1978).
(17) H. Fukui, S. Shimokawa, and J. Sohma, *Mol. Phys.*, **18**, 217 (1970); E. Rahkamaa, *ibid.*, **19**, 727 (1970).
(18) Department of Chemistry, University of Aarhus, 8000 Aarhus C., Denmark.

Hans J. Jakobsen, *[18] **Wallace S. Brey***
Department of Chemistry, University of Florida
Gainesville, Florida 32611
Received September 13, 1978

A Time-Dependent Cyclodextrin Induced Perturbation of Ionic Equilibria across a Carbohydrate Membrane[1]

Sir:

Molecular transgression across heterogeneous boundaries is currently a focal issue in many areas of chemistry.[2] Explo-

0002-7863/79/1501-0775$01.00/0