Parahydrogen-Induced Hyperpolarization of 15N

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Introduction

The Parahydrogen-Induced Polarization (PHIP)[1] phenomenon qualifies for hyperpolarizing ^{13}C in MRI[2]. If the parahydrogenation occurs in the absence of a static magnetic field, all processes due to chemical shifts are suppressed. Since the efficiency of hyperpolarization transfer mediated by the Nuclear Overhauser Effect (NOE) is inversely proportional to the strength of the static magnetic field, it tends to dominate the transfer either via dipolar or scalar coupling. If the latter dominates, the resulting hyperpolarization will be distributed throughout the molecule via appropriate coherences. This closely resembles 'isotropic mixing', represented by a density matrix under the influence of a Hamiltonian consisting only of the coupling terms. The details of this isotropic mixing between ^1H and ^{15}N strongly depend on the size of the coupling parameters[3], and if the contributions from the first and second former p-H_2 proton have the opposite sign, the NOE-derived hyperpolarization transfer to a heteronucleus at low field may almost cancel.[3]

Method and Results

To efficiently transfer PHIP-derived polarization to ^{15}N, ^{13}C, ^{31}P, and other heteronuclei we have designed optimized pulse sequences such as PH-INEPT.[3] Starting from the time averaged density operator[3] of a 3 spin AA'X system $r(t) = I_{1z}I_{2z} + \sin^2 f\ (ZQ)x + \sin f\cos f(I_{1z} - I_{2z})I_{3z}$ a pulse to the heteronucleus (denoted '3') with a flip angle a and phase y transforms the two-spin order terms $(I_{1z}-I_{2z})I_{3z}$ of this operator into the observable single quantum terms $(I_{1z} - I_{2z})I_{3x}$. During the FID these single quantum terms evolve into observable magnetization. For the optimal flip angle a = p/2 the signal amplitude is proportional to $\cos^2 f\sin f$, whereby maximum signal intensity is achieved[3] if cos f = $(2/3)^{-1/2}$, corresponding to $|JD/J_{12}| = 2^{-1/2}$. At high field the operators can be transferred into a more suitable form simply by applying a 90° pulse followed by a delay and another 90° pulse. Appropriate transformations for ^{15}N and ^{13}C hyperpolarized systems have been worked out.[3]
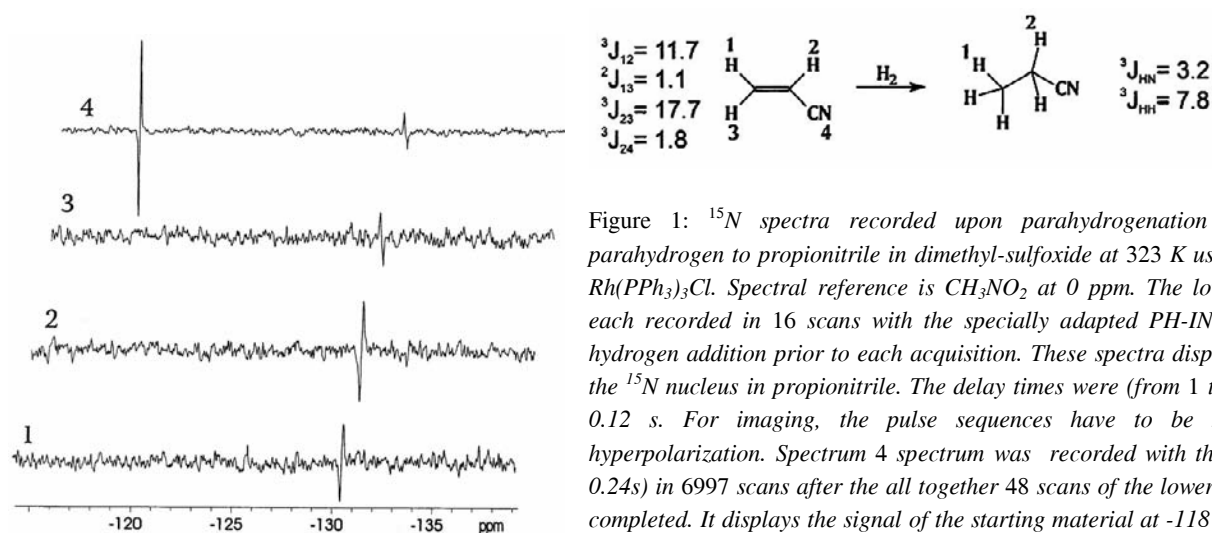

Figure 1: *^{15}N spectra recorded upon parahydrogenation of acrylonitrile with parahydrogen to propionitrile in dimethyl-sulfoxide at 323 K using Wilkinson's catalyst Rh(PPh3)3Cl. Spectral reference is CH3NO2 at 0 ppm. The lower three spectra were each recorded in 16 scans with the specially adapted PH-INEPT sequence and 5 s hydrogen addition prior to each acquisition. These spectra display antiphase signals of the ^{15}N nucleus in propionitrile. The delay times were (from 1 to 3) 0.24 s, 0.16 s, and 0.12 s. For imaging, the pulse sequences have to be modified to yield net hyperpolarization. Spectrum 4 spectrum was recorded with the INEPT sequence (t = 0.24s) in 6997 scans after the all together 48 scans of the lower three spectra had been completed. It displays the signal of the starting material at -118 ppm and the product at -130.5 ppm.*

Discussion and Conclusions

Our ^{15}N spectra prove the efficiency of the PH-INEPT sequence for polarization transfer allowing *in situ* detection of ^{15}N upon few scans. In agreement with theory, the signs of the signals for propionitrile and acrylonitrile are opposite (Fig. 1.4).

References

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