Inorganic Applications of Polarization Transfer NMR

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Polarization transfer in NMR spectroscopy is a process by which the magnetization of one nuclear species, S (usually protons) is transferred to another nuclear species, I, through a scalar coupling, J_{IS}. This results in a signal enhancement of the I nuclei by γ_S/γ_I, where γ is the gyromagnetic ratio.

Several methods of bringing about polarization transfer have been put forth [1]. One of the most popular and successful methods thus far is called "Insensitive Nuclei Enhanced by Polarization Transfer" (INEPT). This pulse sequence was first proposed by Morris and Freeman [2] and can be described as follows:

$$\begin{aligned} S:&\quad (\pi/2)_x - \tau - (\pi)_x - \tau - (\pi/2)_{y,-y} \\ I:&\qquad\qquad\quad (\pi) - \tau - (\pi/2) - \text{acquire} \end{aligned}$$

In addition to the signal gain due to population transfer, a savings in spectrometer time also results, since the rate at which the sequence can be repeated depends on the usually short proton relaxation times, rather than those of the I nucleus. The sequence yields a spectrum with peak ratios distorted from their expected binomial distribution, as can be seen in Figure 1b. If, however, a waiting period, Δ, is introduced following the final pulses, the peak phases will change relative to each other, which allows normal decoupling procedures to be employed [3], and selective enhancement of I nuclei with specific multiplicities (e.g., CH carbons) [4].

Polarization transfer enhancement has been found to persist in the presence of paramagnetic relaxation agents, whereas nuclear Overhauser enhancement does not. This makes it an effective tool for recording C-13 NMR of paramagnetic transition metal complexes [5]. The technique has been applied to simple Sn-119 and Si-29 compounds by Doddrell, Pegg, Brooks, and Bendall [6]. Experimentally determined enhancement factors compared well with those predicted by theory for a nucleus coupled to many protons [7]. Helmer and West [8] have reported enhancement factors of 2.9 to 9.3 for a wide variety of Si-29 spectra with Si-H couplings of up to three bonds. Some very impressive examples of Ag-109 and Rh-103 NMR spectra have been published by Brevard, van Stein, and van Koten [9]. Time saving factors were estimated at up to 400 for Ag-109 and 900 for Rh-103. Brevard and Schimpf have demonstrated INEPT results by transferring magnetization from P-31 instead of protons, to coordination complexes of Rh-103, W-183 and Fe-57 containing phosphine ligands [10].

In mid-1982 an alternative to the INEPT pulse sequence was proposed by Doddrell, Pegg, and Bendall [10]. The technique, "Distortionless Enhancement by Polarization Transfer" (DEPT), provides the same theoretical enhancement as does INEPT, but with multiplets in their "undistorted" binomial distribution. An example

is shown in Figure 1c. The basic DEPT pulse sequence is:

$$S: \quad (\pi/2)_y - 1/2J - (\pi)_y - 1/2J - (\theta)_{x,-x} - 1/2J - \text{decouple}$$
$$I: \quad\quad\quad\quad (\pi/2)_y - 1/2J - (\pi)_{x,-x} - 1/2J - \text{acquire}$$

The variable length θ pulse has the same functional form as does the waiting period, Δ, in INEPT and determines what coupling multiplicities will be enhanced. The DEPT sequence has been applied to Si-29 and Pt-195 with enhancement factors slightly less than those obtained with INEPT [12]. This is attributed to T_2 relaxation of the I nucleus during the longer time needed for the DEPT sequence. A commercially available routine, "Automatic DEPT" (ADEPT) can sample a C-13 spectrum at four different values of θ and, using appropriate combinations, generate subspectra of only CH, CH_2, or CH_3 carbons [13].

Though recently developed, these techniques have already been shown effective on a multitude of compounds of interest to the inorganic chemist. The techniques are straightforward in operation and require no special instruments or modifications. Their recent commercial availability could be an indication of widespread future use in NMR.

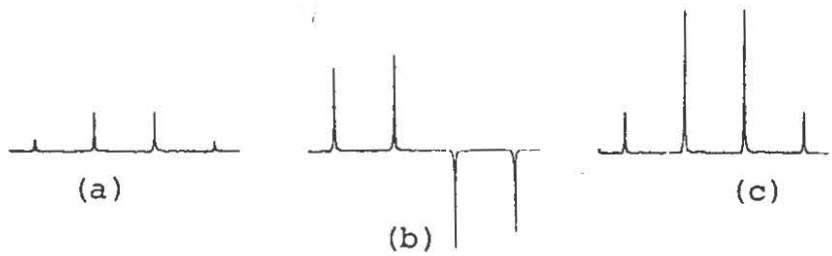

Figure 1: (a) Normal FT; (b) INEPT; and (c) DEPT C-13 NMR spectra of the methyl carbon in acetic acid.

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