hydrophobic organic cation. While this explanation is quite feasible for aqueous solutions, it cannot be carried over to much less structured organic solvents used in this investigation.

It seems reasonable to assume that the main reason for the negative entropy of complexation is the decrease in the conformational entropy of the ligand upon the formation of a metal complex. Large macrocyclic ligands such as DB30C10 should be rather flexible in the free state. The degree of flexibility would vary with the solvent, i.e., with the extent of ligand–solvent interaction. The formation of a rigid three-dimensional complex should decrease the conformational entropy of the ligand and thus, perhaps, give rise to a negative entropy of complexation. At the present time, however, thermodynamic data on the formation of macrocyclic complexes in nonaqueous solvents are quite sparse. Additional work is very necessary before the entropy destabilization of macrocyclic ligands in nonaqueous solvents can be explained satisfactorily.

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J-Cross Polarization in Silanes

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Abstract: The first cross-polarization NMR experiment between ^{1}H and ^{29}Si in the liquid state with rare-spin observation is reported. A line-shape-fitting technique is employed to directly measure the spin coupling constant, *J*, from the experimental results of initial magnetization vs. cross-polarization contact time. The technique has been used to enhance sensitivities of ^{29}Si measurements in Si–O - model compounds.

Introduction

The technique of cross polarizing a rare-spin species, S, by an abundant-spin species, I, is well-known.[1,2] In the early 1960s, Hartmann and Hahn[1] developed the theory of polarization transfer in liquids and solids via the coupling of two different nuclear species. They measured the ^{1}H–^{31}P coupling constant in hypophosphorus acid, $HPO(OH)_2$, by observing the magnetization of the abundant spin, ^{1}H, and observed the cross polarization of ^{35}Cl by ^{39}K in solid potassium chlorate, $KClO_3$.

In the early 1970s, Pines et al.[2] developed the cross-polarization technique with high-powered decoupling and rare-spin observation and recorded the first enhanced NMR spectra of rare spins in solids. Recently, Maudsley et al.[3] and Bertrand et al.[4] have utilized scalar coupling to cross polarize ^{13}C by ^{1}H in molecules in the liquid state, with observation of the ^{13}C magnetization.

The static dipolar coupling[1] is the interaction used for polarization transfer between I and S spins in solids. In liquids, the static dipolar coupling is motionally averaged to zero. However, the indirect or scalar coupling which results from the hyperfine interactions of electrons and nuclei remains. This indirect (or scalar, or *J*) coupling provides the means of polarization transfer in liquids.

Cross polarization, whenever possible, offers certain advantages in NMR studies of liquids. First, there is an enhancement in the magnetization of the rare spin, S, for suitable cross-polarization times, by a factor which can be as large as γ_I/γ_S. Second, the repetition period is determined by the longitudinal relaxation, T_1, of the abundant spin, I. The abundant spin's T_1 can be shortened through suitable "doping" with paramagnetic impurities and is usually much less than that of the rare spin.

The liquid *J*-cross-polarization experiment notably differs from that on most solids in that the magnetization will oscillate between the abundant and rare spins. The equations which govern the behavior of the magnetization in the liquid state for the matched Hartmann–Hahn (H–H), on-resonance experiment have been previously reported by Hartmann and Hahn[1] and Bertrand et al.[4] These equations are

S–I
$$M_S = M_I' \sin^2\left(\frac{\pi J\tau}{2}\right) \quad (1)$$

S–I$_2$
$$M_S = M_I'' \sin^2\left(\frac{\pi J\tau}{\sqrt{2}}\right) \quad (2)$$

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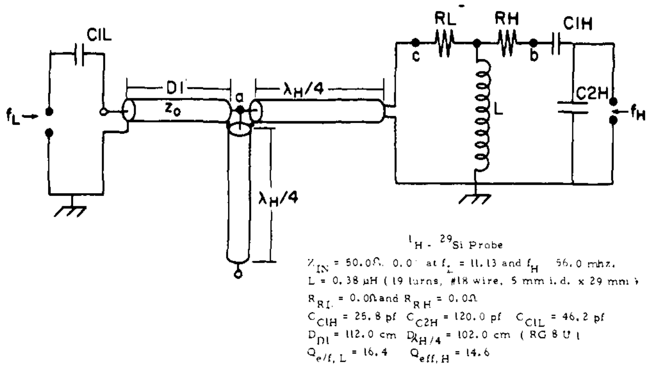

Figure 1. The design of the single coil, double resonance probe used for ^1H-^{29}Si cross polarization.

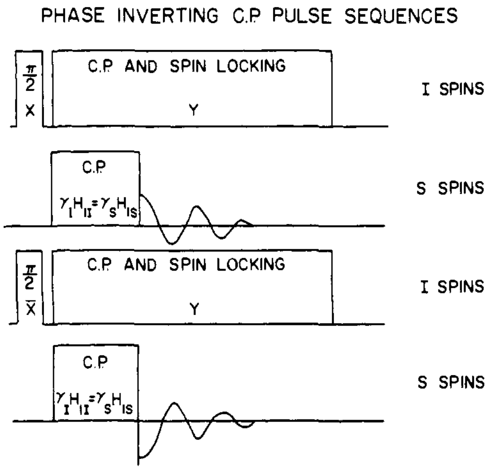

Figure 2. The rf pulsing sequences used to produce phase inversion of the ^{29}Si FID following cross polarization (CP).

$$\text{S-I}_3 \qquad M_S = M_I''' \left(\frac{1}{2} \sin^2 \left(\frac{\pi J \tau}{2} \right) + \frac{1}{2} \sin^2 \left(\frac{\pi J \tau \sqrt{3}}{2} \right) + \frac{1}{4} \sin^2 (\pi J \tau) \right) \quad (3)$$

In the above equations, S refers to the rare spin and I to the abundant spins. Also, J refers to the scalar coupling constant between the S and I spins and is equivalent for all S-I bonds. The quantities M_I', M_I'', and M_I''' refer to the initial magnetization of the abundant spins obtained by direct polarization. When this relatively large magnetization is transferred to the rare spin, the rare spin's magnetization is enhanced by a factor which can be as large as γ_I/γ_S (ratio of gyromagnetic ratios) times that obtained by direct polarization.

Furthermore, as can be seen in the above equations, the magnetization is modulated as a function of cross-polarization time by frequencies proportional to the spin coupling constant J.

Both Maudsley et al.[3] and Bertrand et al.[4] have used the J-cross-polarization technique with rare-spin observation to measure ^1H-^{13}C coupling constants.

Maudsley et al.[3] describe techniques for the transfer of polarization by both oscillations in the rotating frame and pulse-interrupted free precession. The technique developed by Bertrand et al.[4] relies on the oscillatory transfer of polarization in the rotating frame. Both Maudsley et al.[3] and Bertrand et al.[4] use two-dimensional Fourier transforms to generate frequency spectra from which the spin coupling constant, J, can be inferred. The present work uses the oscillatory transfer of polarization in the rotating frame and reports the first use of the J-cross-polarization technique[4] on a ^1H-^{29}Si spin system with rare-spin observation. The method is used to measure ^1H-^{29}Si spin coupling constants for three different ^1H coupling multiplicities in the compounds: triethylsilane, $(CH_3CH_2)_3SiH$, diethylsilane, $(CH_3CH_2)_2SiH_2$, and phenylsilane, $C_6H_5SiH_3$.

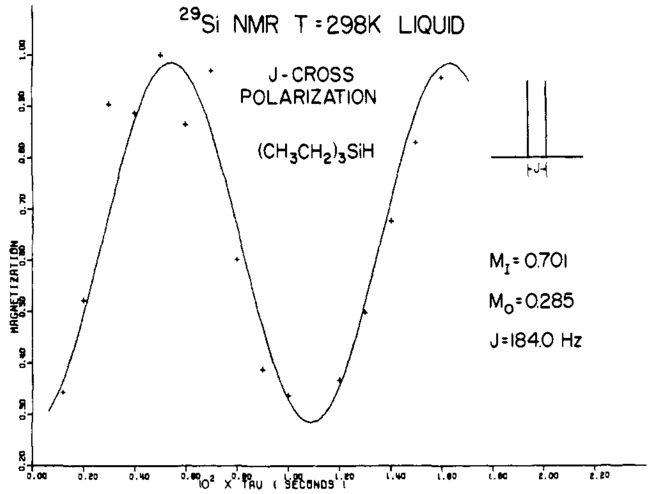

Figure 3. A graph of the ^{29}Si magnetization (arbitrary units) vs. cross-polarization time, τ, for triethysilane. The nonlinear least-squares fit to eq 1 is superimposed.

A line-shape-fitting technique is used to fit the theoretical equations (1, 2, 3) to the experimental data. The nonlinear least-squares algorithm iterates a "best fit" to the experimental data (modified Levenberg-Marquardt method[5]) and yields the value of the spin coupling constant, J, directly.

A dominant reason for the present work is the fact that alkylated silanes are probes of the molecular environment of oxygen in relatively complicated molecules.[6] Since the primary mechanism for cross polarization of ^{29}Si is by nearest-neighbor ^1H in liquids, the present work represents a basis on which to enhance sensitivities of ^{29}Si NMR measurements in studies of $(R)_n$-(SiH_{3-n})-O-R′ model compounds. The chemical shifts of ^{29}Si in these -Si-O- model compounds will provide a basis for understanding the structure of organic oxygen (in the form of alkylated silyl ethers) in much more complicated systems such as derivatives of coals. A somewhat similar study using ^1H NMR has been made by Schweighardt et al.[6]

Experimental Section

The spectrometer used in these experiments was constructed in this laboratory and has been previously described.[7,10] Resonant frequencies for ^1H and ^{29}Si were 56.021 and 11.129 MHz, respectively. A single-coil probe doubly tuned at both frequencies[8-10] was used. The construction of this probe has been described in detail elsewhere.[10]

When the H-H condition was matched, approximately 0.39 and 1.27 rms W were required to achieve H_1's of 1 and 5 G at frequencies of 56.021 and 11.129 MHz, respectively. The $\pi/2$ pulse width of 62.5 μs for protons was sufficiently short to ensure uniform excitation of all frequencies of the ^1H multiplets by the preparation pulses. A simplified tuning procedure for critically adjusting rf power levels has been described in detail elsewhere.[10]

Figure 2 shows the pulse sequences used. A 180° phase inverted $\pi/2$ pulse was alternately applied to the ^1H spin, resulting in an alternating, 180° phase-inverted ^{29}Si FID. Every other FID was subtracted from the computer's memory buffer so that only magnetization from J-cross polarization was observed. All measurements were made within 50 Hz of proton resonance. Sample spinning was not used.

Preparation of Dimethylsilyl Ethers. These silyl derivatives were prepared from the corresponding alcohols by adding 0.40 mol of the alcohol to a 50-mL round-bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer. Liquid alcohols were added neat, but solid alcohols were dissolved in a minimum amount of benzene prior to addition. After the system was purged with nitrogen, 0.20 mol of tetramethyldisilazane and 1 drop of dimethyl-

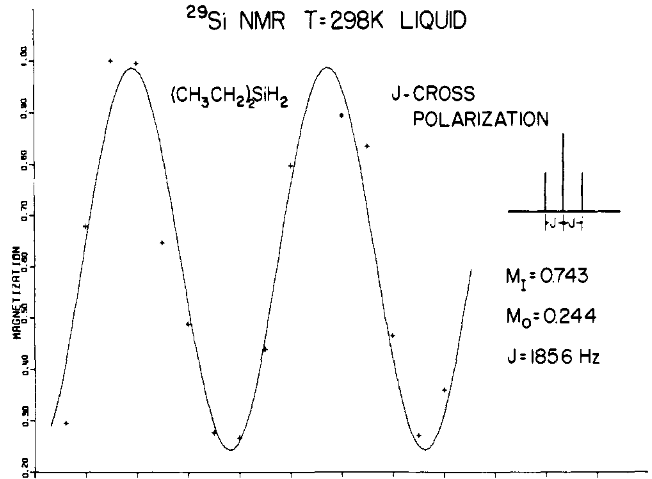

Figure 4. A graph of the ^{29}Si magnetization (arbitrary units) vs. cross-polarization time, τ, for diethylsilane. The nonlinear least-squares fit to eq 2 is superimposed.

Table I. Parameters Obtained by Nonlinear Least-Squares Fitting of Equations 1-3[a]

compd	M_I	M_0	J, Hz ($\pm$10)	J, Hz $\pi/2$, ($\pm$5)	Δ, Hz ($\pm$12)
$(CH_3CH_2)_3SiH$	0.701	0.285	184.0	195.4	66
$(CH_3CH_2)_2$-SiH_2	0.743	0.244	185.6	195.4	61
$C_6H_5SiH_3$	0.698	0.211	198.8	205.6	52

[a] M_I is the initial amplitude of the abundant-spin magnetization. M_0 is the base-line constant. J is the value of the spin coupling constant obtained by J-cross polarization while $J_{\pi/2}$ is that value obtained by excitation with a $\pi/2$ pulse. Δ is an estimate of the mismatch of the Hartmann-Hahn condition.

chlorosilane were added to the flask. The reaction mixture was refluxed for 8-12 h. The crude silyl ethers were separated from the reaction mixture by distillation through a short-path, microdistillation apparatus. Samples for ^{29}Si NMR were purified by preparative gas chromatography on 5% OV-101 or 10% Carbowax 20M. Infrared, mass spectral, and ^{1}H NMR analyses of purified dimethylsilyl ethers were used to confirm the authenticity of these materials.

Discussion

For 0.25 mL of doped triethylsilane (4×10^{19} ^{29}Si spins), a bandwidth of 5 kHz, and repetition rate of 3 s, a maximum $(S + N)/N \cong 2$ was obtained with one scan. The observed $(S + N)/N$ is consistent with an enhancement of 5 $(=\gamma_I/\gamma_S)$ over that obtained with a $\pi/2$ pulse. All $(S + N)/N$ ratios refer to initial amplitudes of the FID.

Figures 3-5 show the magnetization (arbitrary units) of ^{29}Si as a function of cross-polarization time, τ. The plotted values are the initial amplitudes of the FID following the cross-polarization pulse. Each value is the average of two measurements and the maximum value of each graph has been normalized to 1.0.

Superimposed on each graph is the line shape of the nonlinear least-squares fit. A constant, M_0, was added to each equation (1, 2, 3) to account for the experimental artifact of dc offset. There are three parameters in each fit: the amplitude of the abundant magnetization, M_I, the base line constant, M_0, and the spin coupling constant, J. The convergence condition for each fit was that the residual sum of errors squared changed by less than 0.001 for two consecutive iterations of the parameters. Table I contains the values of the parameters for each fit. Also included in this table is the value of the spin coupling constant, $J_{\pi/2}$, measured by the conventional method of $\pi/2$ excitation and Fourier transform. The quantity Δ ($\cong |J_{\pi/2}{}^2 - J^2|^{1/2}$) is an estimate[3] of the mismatch in the H-H condition.

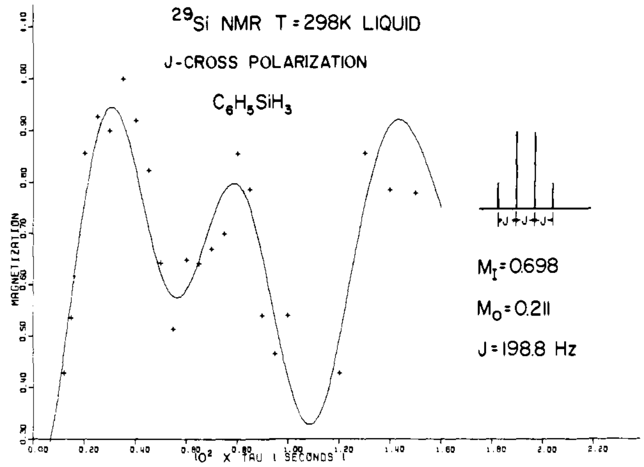

Figure 5. A graph of the ^{29}Si magnetization (arbitrary units) vs. cross-polarization time, τ, for phenylsilane. The nonlinear least-squares fit to eq 3 is superimposed.

Table II. ^{29}Si Chemical Shifts of Silyl Ether Model Compounds, R = $(CH_3)_2HSiO$-, and Other Compounds[a]

structure	empirical formula	shift, ppm ($\pm$0.3)
R-*n*-butyl	$SiOC_6H_{16}$	−3.6
R-*tert*-butyl	$SiOC_6H_{16}$	−0.5
R-*n*-pentyl	$SiOC_7H_{18}$	−3.3
R-phenyl	$SiOC_8H_{12}$	−4.6
R-α-naphthyl	$SiOC_{12}H_{14}$	−5.8
R-β-naphthyl	$SiOC_{12}H_{14}$	−5.3
$(RCH_2\text{-})_2$	$Si_2O_2C_6H_{18}$	−4.9
$((CH_3)_2HSi)_2NH$	$Si_2NC_4H_{15}$	+10.1
$(CH_3)_2HSiCl$	$SiClC_2H_7$	−11.1

[a] Shifts are reported with respect to Me_4Si and negative shifts are downfield.

The spin coupling constants determined by this method agree within experimental error with those of the conventional method. The time evolution of the magnetization does appear to follow the oscillatory behavior expressed in eq 1-3.

Of course, measurements of spin coupling constants via their dependence on τ are time consuming. In fact, the amount of time can be comparable to that of the conventional method—even with shorter T_1's and signal enhancement. Clearly the most rapid means of measuring J would be to use J-cross polarization for a suitable τ without abundant-spin decoupling. The coupling constant will modulate the FID and be directly measurable in the Fourier domain while the advantages of favorable T_1's and signal enhancement would be retained.

The choice of the cross-polarization time, τ, is important if the entire enhancement is to be realized. For chemical systems in which the approximate J values are known, 1-3 can be used to predict the optimum cross-polarization times. Also, this technique may be useful in resolving two shifts that overlap—provided that the overlapping lines have different spin coupling constants. A suitable τ is chosen such that a minimum magnetization occurs for one line, thereby producing a resolved spectra of the other line, and vice versa.

The origin of the large dc offset terms, M_0, is very interesting. Since the value of the dc term (or base-line constant) is very similar in all three fits (Figures 3-5), its origin appears instrumental since all measurements were made using a virtually identical procedure.

Additional and subsequent measurements in this laboratory have shown that the value of M_0 is mainly determined by two factors: (1) the signal-to-noise of the initial point of the FID and (2) the accuracy of the rf phases. Furthermore, when larger data averagings are used to improve $(S + N)/N$ and rf phases are critically adjusted, the value of this dc offset is reduced substantially.

Finally, Table II contains the ^{29}Si chemical shifts of silyl ether model compounds and other compounds used in this research. Nuclei were excited via the JCP technique. The values of shifts are tabulated with respect to Me_4Si_2 and negative shifts are downfield.

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Determination of NMR Spin Coupling Constants Using *J*-Cross Polarization. A Comment on "*J*-Cross Polarization in Silanes" [1]

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Abstract: In NMR, a coupled I and S spin system can interchange polarizations by *J*-cross polarization (JCP). If the S spectrum is observed without I decoupling, the relative phases of the lines within the S multiplet vary with cross-polarization time. A PCJCP sequence (phase corrected *J*-cross polarization) is demonstrated which removes the phase variation; this facilitates determination of the spin coupling constant *J* directly from the cross-polarization spectrum.

Introduction

To scrutinize the theory of the transfer of spin polarization during *J*-cross polarization, Murphy[1] et al. (preceding paper) extract the NMR spin coupling constant *J* by curve fitting their experimental data to the theoretical relation. They find good agreement and are able to infer the magnitude of Hartmann-Hahn[3] mismatch from their effective value of *J*. They hasten to add that such a procedure can be time consuming when contrasted to the more conventional determination of *J* and recommend using *J*-cross polarization without (I) spin decoupling at a single value of cross-polarization time τ.

We have found[4] certain complications when the S cross-polarized magnetization is observed without decoupling. In the coupled spectrum (i.e., without I decoupling), during cross polarization the magnetization associated with each line in the S multiplet does not necessarily grow just along the rf axis. In fact, the magnetization is complex, with a longitudinal component along the rf axis and a transverse component perpendicular to both the rf and static field B_0 directions. The transverse magnetization arises from correlations between the I and S polarizations. We find that, for $I = 1/2$, the transverse components are equal and opposite for S resonances associated with up and down I spins;[4] that is, the respective upfield and downfield lines have equal and opposite transverse magnetizations. These transverse components will cancel under I decoupling but manifest themselves in the coupled spectrum as phase shifts of the multiplet resonance lines which are, in general, dependent on cross-polarization time τ.

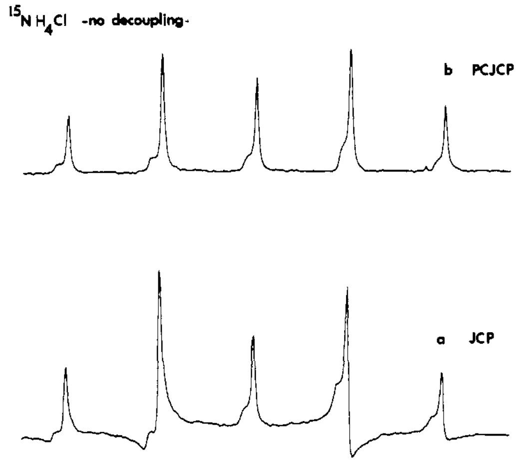

Figure 1. ^{15}N resonance via the JCP pulse sequence with τ = 4 ms in aqueous NH_4Cl. No proton decoupling is used during signal acquisition. In the conventional JCP experiment (a), the relative phases of the lines in the multiplet vary with cross-polarization time τ. In PCJCP at the end of the cross-polarization process, application of an additional $\pi/2$ pulse to I spins (as in (b)) or S spins removes the out-of-phase component so that the relative phases are independent of cross-polarization time. This facilitates measurement of spin coupling constant *J* with the PCJCP sequence. Note also that, in JCP and PCJCP, the multiplet amplitudes are not in the usual quintet ratio of 1:4:6:4:1. In (b) the I extension pulse is in phase with the I cross-polarization rf; if the extension pulse is shifted by 90°, the multiplet amplitudes are altered from (b) but their phases are still independent of τ.