

Determination of the Signs of Nuclear SpinSpin Indirect Coupling Constants

G. A. Williams and H. S. Gutowsky

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The sound speed a follows:

$$\frac{(RT)^{\frac{1}{2}}}{\varphi} = a = \left[RT \frac{R \frac{DT}{Dt} + T \frac{DR}{Dt} + \frac{DE}{Dt}}{\frac{DE}{Dt}} \right]^{\frac{1}{2}} \quad (12)$$

For a perfect diatomic gas with lagging rotational temperature θ ; $R = \text{const}$ and $E = \frac{3}{2}RT + R\theta$ so that

$$a = \left[RT \frac{\frac{DT}{Dt} + \frac{3}{2} \frac{DT}{Dt} + \frac{D\theta}{Dt}}{\frac{3}{2} \frac{DT}{Dt} + \frac{D\theta}{Dt}} \right]^{\frac{1}{2}} \quad (13)$$

Now if $D\theta/Dt = 0$, $a = [(5/3)RT]^{\frac{1}{2}}$, and if $D\theta/Dt = DT/Dt$, $a = [(7/5)RT]^{\frac{1}{2}}$, for intermediate cases where θ partially follows T we get appropriate intermediate speeds.

For a dissociating diatomic gas with dissociation energy q_0 , vibration and rotation fully excited, with α the fraction of original particles dissociated and R_0 the undissociated gas constant:

$$E = \frac{7-\alpha}{2} R_0 T + \alpha q_0 \quad \text{and} \quad R = (1+\alpha) R_0$$

so that

$$a = \left[RT \frac{(9+\alpha) \frac{DT}{Dt} + T \frac{D\alpha}{Dt} \left\{ 1 + \frac{2q_0}{RT} \right\}}{(7-\alpha) \frac{DT}{Dt} + T \frac{D\alpha}{Dt} \left\{ \frac{2q_0}{RT} - 1 \right\}} \right]^{\frac{1}{2}} \quad (14)$$

Thus the sound speed depends on whether the "inactive" degrees of freedom adjust themselves to induced changes. A smooth transition from one sound speed to another results without the artificial appeal to viscosity or heat conduction.

These considerations are of a characteristic theory for flows of reacting gases.

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Determination of the Signs of Nuclear Spin-Spin Indirect Coupling Constants*

G. A. WILLIAMS AND H. S. GUTOWSKY

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

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A METHOD has been developed for analyzing high resolution nuclear magnetic resonance spectra for the relative signs of the nuclear spin-spin indirect coupling constants.¹ The theory of the coupling mechanism¹⁻³ gives a reliable positive sign for proton-proton coupling; thus the present method makes possible the determination of absolute signs of the coupling between other pairs of nuclei.

The simplest system for which relative signs can be determined contains three nonequivalent nuclei, one with a resonance which is widely separated from the resonances of the others. The Hamiltonian for the system can be written as^{1,2,4}

$$\mathcal{H} = -\hbar(\gamma_1 H_1 I_{z1} + \gamma_2 H_2 I_{z2} + \gamma_3 H_3 I_{z3}) + \hbar(A_{12} \mathbf{I}_1 \cdot \mathbf{I}_2 + A_{13} \mathbf{I}_1 \cdot \mathbf{I}_3 + A_{23} \mathbf{I}_2 \cdot \mathbf{I}_3), \quad (1)$$

where H_i is the static magnetic field at nucleus i , including any chemical shift, and A_{ij} is the coupling constant in cps.

Several examples analyzed consist of a proton and two fluorine nuclei with chemical shift and coupling constant of comparable magnitude. The zero-order nuclear spin states are given in Table I. The matrix elements in the same table show that the fluorine

TABLE I. Zero-order spin functions and matrix elements for the indirect spin-spin coupling of a proton and two chemically shifted fluorine nuclei.

Proton function	Fluorine function	Matrix elements of \mathcal{H}
α_1	$\alpha_2 \alpha_3$	$\mathcal{H}_{11} = -\frac{\hbar}{2} [\gamma_H H_1 + \gamma_F (H_2 + H_3)] + \frac{\hbar}{4} [A_{12} + A_{13} + A_{23}]$
α_1	$\frac{1}{\sqrt{2}} (\alpha_2 \beta_3 + \beta_2 \alpha_3)$	$\mathcal{H}_{22} = -\frac{\hbar}{2} \gamma_H H_1 + \frac{\hbar}{4} A_{23}$
α_1	$\frac{1}{\sqrt{2}} (\alpha_2 \beta_3 - \beta_2 \alpha_3)$	$\mathcal{H}_{33} = -\frac{\hbar}{2} \gamma_H H_1 - \frac{3\hbar}{4} A_{23}$
α_1	$\beta_2 \beta_3$	$\mathcal{H}_{44} = -\frac{\hbar}{2} [\gamma_H H_1 - \gamma_F (H_2 + H_3)] - \frac{\hbar}{4} [A_{12} + A_{13} - A_{23}]$
		$\mathcal{H}_{23} = -\frac{\hbar}{2} \gamma_F [H_2 - H_3] + \frac{\hbar}{4} [A_{12} - A_{13}]$
β_1	$\alpha_2 \beta_3$	$\mathcal{H}_{55} = +\frac{\hbar}{2} [\gamma_H H_1 - \gamma_F (H_2 + H_3)] - \frac{\hbar}{4} [A_{12} + A_{13} - A_{23}]$
β_1	$\frac{1}{\sqrt{2}} (\alpha_2 \beta_3 + \beta_2 \alpha_3)$	$\mathcal{H}_{66} = +\frac{\hbar}{2} \gamma_H H_1 + \frac{\hbar}{4} A_{23}$
β_1	$\frac{1}{\sqrt{2}} (\alpha_2 \beta_3 - \beta_2 \alpha_3)$	$\mathcal{H}_{77} = +\frac{\hbar}{2} \gamma_H H_1 - \frac{3\hbar}{4} A_{23}$
β_1	$\beta_2 \beta_3$	$\mathcal{H}_{88} = +\frac{\hbar}{2} [\gamma_H H_1 + \gamma_F (H_2 + H_3)] + \frac{\hbar}{4} [A_{12} + A_{13} + A_{23}]$
		$\mathcal{H}_{67} = -\frac{\hbar}{2} \gamma_F [H_2 - H_3] - \frac{\hbar}{4} [A_{12} - A_{13}]$

triplet and singlet $M=0$ states are mixed by the F, F chemical shift and the $H-F$ coupling. The resulting fluorine spectrum contains two 4-component multiplets, each similar to the spectrum of a two spin system with chemical shift and coupling.^{5,6}

One of the fluorine quartets arises from the proton spin up state and the other from the proton down. The centers of the two quartets are separated by $\frac{1}{2}(A_{12} + A_{13})$ cps. In spectra such as those in Fig. 1, two assignments into quartets are possible: (a) 1357 and 2468 or (b) 1368 and 2457. A choice can not be based upon the observed splittings alone. However, the assignment can be made from the relative intensities, which are symmetrical about the center of each quartet but have different ratios for the two quartets or, in some cases, by observing the field dependence of the spectrum.

The proton resonance is split into four main components by A_{12} and A_{13} . The components, to a good approximation, are displaced by $\pm \frac{1}{2}(A_{12} + A_{13})$ and $\pm \frac{1}{2}(A_{12} - A_{13})$ from the center of the resonance. The fluorine assignment identifies one of the proton

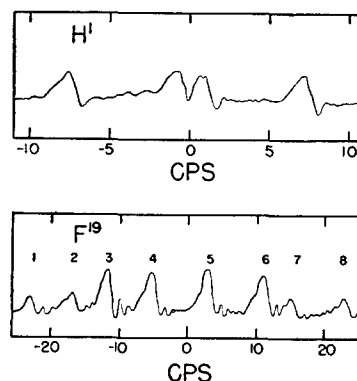


FIG. 1. The proton and fluorine high resolution magnetic resonance absorption spectra of 1,4-difluoro, 2,5,6-trichlorobenzene. The spectra were recorded at fixed frequencies with a permanent magnet at 4165 gauss. The magnetic field sweep gives decreasing fields from left to right.

splittings as $(A_{12} + A_{13})$; the other is $(A_{12} - A_{13})$. In this manner the relative signs of A_{12} and A_{13} are found, as well as approximate numerical values. The numerical values can be refined by a detailed analysis of the fluorine spectrum.

The best example we have found is 1,4-difluoro, 2,5,6-trichlorobenzene for which the proton and fluorine spectra were first observed by Holm.⁷ Inspection of the line intensities in the fluorine spectrum shows that the quartets are 1357 and 2468; the assignment is confirmed by calculation of the relative intensities. This assignment of the fluorine spectrum gives $A_{\theta}^{\text{HF}} + A_m^{\text{HF}} = 14.7$ cps, where the subscripts designate *ortho*- and *meta*-orientations. Therefore, the 2.3 cps splitting in the proton spectrum is $A_{\theta}^{\text{HF}} - A_m^{\text{HF}}$. The final result for the absolute values is $A_{\theta}^{\text{HF}} = 8.5$ cps and $A_m^{\text{HF}} = 6.2$ cps; the signs of the coupling constants are alike.

Similar analyses have been made of the spectra of several other fluorobenzenes. The general method can be used to determine relative signs of the coupling constants in $\text{CF}_2 = \text{CFCl}$ and several other fluoroethylenes,⁸ work on which is in progress. A more detailed report, including determination of numerical values of H-H, H-F and F-F coupling constants for *ortho*-, *meta*-, and *para*-orientations,⁷ is being prepared.

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Anisotropic Chemical Shielding and Nuclear Magnetic Relaxation in Liquids

H. M. McCONNELL* AND C. H. HOLM
Shell Development Company, Emeryville, California
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THE purpose of this note is to suggest that anisotropic chemical shielding can sometimes provide significant nuclear spin-lattice relaxation in liquids. We consider first the theory of anisotropic chemical shielding.

Let \mathbf{H}_0 be the external field applied to a molecule containing a nucleus N ; \mathbf{H}_0 is the z direction of a system x, y, z fixed in the laboratory. The field at N , \mathbf{H}_N , is related to \mathbf{H}_0 by the shielding tensor σ ,

$$\mathbf{H}_N = \mathbf{H}_0 - \sigma \cdot \mathbf{H}_0. \quad (1)$$

An equation for σ can be obtained by extending Ramsey's shielding theory¹ to the anisotropic case. In Ramsey's notation,¹

$$\sigma = (1/2m)(e/c)^2 \langle \sum_i (\mathbf{I} r_i^{-1} - \mathbf{r}_i \mathbf{r}_i^{-3}) | o \rangle \langle \sum_j \mathbf{m}_j^p | n \rangle - 2 \sum_n 1/(E_n - E_0) \{ \langle n | \sum_j \mathbf{m}_j^p r_j^{-3} | o \rangle \langle o | \sum_j \mathbf{m}_j^p | n \rangle + \langle o | \sum_j \mathbf{m}_j^p r_j^{-3} | n \rangle \langle n | \sum_j \mathbf{m}_j^p | o \rangle \}, \quad (2)$$

where \mathbf{I} is the unit tensor.

For simplicity consider a molecule axially symmetric at N ; (2) becomes

$$\sigma = \lambda \Delta \sigma + \mathbf{I} \sigma_{\perp}, \quad (3)$$

where σ_{\perp} is the shielding perpendicular to the symmetry axis λ (a unit vector) and $\Delta \sigma$ is the difference between the shielding parallel to the symmetry axis and σ_{\perp} . The Fourier spectrum of the x, y components of \mathbf{H}_N , i.e.,

$$H_{Nz} = \sin \vartheta(t) \cos \vartheta(t) \cos \varphi(t) \Delta \sigma H_0 \quad (4)$$

can have components of the proper frequency, $\nu_0 = (2\pi)^{-1} \gamma H_0$, to give spin-lattice relaxation. ϑ and φ give the orientation of λ relative to x, y, z . The procedure of Bloembergen, Purcell, and Pound² gives for T_1 , for nuclei of spin $\frac{1}{2}$,

$$T_1^{-1} = (8\pi^2/15) (\Delta \sigma)^2 \nu_0^2 \tau_c (1 + 4\pi^2 \nu_0^2 \tau_c^2)^{-1}. \quad (5)$$

From (2), and from solid-state studies on anisotropic chemical shielding,³ we infer that $\Delta \sigma$ is sometimes of the order of σ itself, i.e., $10^{-2} - 10^{-6}$. Numerical estimates using (2), (5), and empirical shielding data can thus support the idea that anisotropic tensor coupling of the x, y components of the nuclear magnetization to the external field \mathbf{H}_0 yields strong spin-lattice relaxation in some molecules. According to (5), T_1 always decreases with increasing ν_0 . Exactly the opposite behavior is expected for magnetic dipolar relaxation.

The foregoing discussion is further supported by our finding of experimental evidence for (a) a short T_1 (~ 60 sec) for C^{13} in unenriched oxygen-free CS_2 , and (b) an apparently long T_1 for C^{13} in CCl_4 . For (a) the chemical shift relaxation must be dominant because of the virtual absence of magnetic nuclei in CS_2 . In (b) the chemical shift is isotropic by symmetry and cannot contribute to T_1^{-1} .

* Address after August 24, 1956: Department of Chemistry, California Institute of Technology, Pasadena, California.

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Hyperfine Structure in Paramagnetic Resonance Absorption Spectra

H. S. JARRETT

E. I. du Pont de Nemours and Company, Wilmington 98, Delaware
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ISOTROPIC proton hfs in paramagnetic resonance absorption spectra of solutions of aromatic organic free radicals has been shown in order of magnitude calculations by McConnell¹ and Bersohn² to arise from configuration interaction. It is the purpose of this note to show that a calculation similar to that of McConnell, if carried to completion without neglect of certain terms, leads to a value of the hfs splitting in excellent agreement with experiment.

Valence bond calculations were made on the three-electron system consisting of two σ electrons and one unpaired π electron of an aromatic CH fragment. In second order, other orbitals do not give rise to hfs and were not considered. Configuration interaction between the two doublet states in conjunction with the Fermi³ isotropic hyperfine interaction yields a hyperfine splitting

$$\Delta H = \frac{16\pi}{3} \frac{\mu_H \mu_{\sigma}}{\mu_B} \frac{[h^2(r_H) - \sigma^2(r_H)] \lambda}{1 - S_{\sigma h}},$$

where $h^2(r_H)$ and $\sigma^2(r_H)$ represent the squares of the magnitude of the hydrogen electron wave function and the carbon σ wave function at the position of the proton and $S_{\sigma h}$ is the overlap integral. The configuration interaction constant, $\lambda = (J_{\sigma\pi} - J_{\pi h})/\Delta E$, where the energy separation between the doublets $\Delta E = \sqrt{2} \{ (J_{h\pi} - J_{\sigma\pi})^2 + (J_{h\pi} - J_{\sigma h})^2 + (J_{\sigma\pi} - J_{\sigma h})^2 \}^{1/2}$. The part of ΔH involving $h^2(r_H)$ is just the hfs of a free hydrogen atom and is equal to 510 gauss. The σ bond contribution at the proton can be determined from the self-consistent field calculations of Torrance⁴; viz., $\sigma^2(r_H)/h^2(r_H) = 0.17$, and $\Delta H = 423\lambda/(1 - S_{\sigma h}^2)$ gauss.

The matrix element, $J_{h\pi} = 0.745$ eV, which is a two-center integral, was obtained by Altmann⁵ with use of Slater wave functions. Although Slater wave functions are not a faithful representation of the actual radial wave functions where an appreciable contribution to this integral is expected.

$J_{\sigma\pi}$, which is an atomic integral, is also given by Altmann. However, his value is too large because the Slater functions do not represent the inner parts of the actual radial wave function where