Solvent Dependence of Nuclear Spin–Spin Coupling Constants

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Contents

I. Introduction

A. Scope

Investigations of the solvent dependence of electron-mediated coupling constants in high resolution nuclear magnetic resonance (nmr) spectra fall into two almost mutually exclusive categories. This review will emphasize the solvent dependence of coupling constants for solute molecules in which the relative spatial locations of the coupled nuclei are constrained by the structural features of the molecule. In these cases medium effects on coupling constants arise from electronic changes of the solute molecule owing to differing intermolecular solute–solvent interactions. In the second category fall the wide classes of molecules which can assume two or more conformations by internal rotation or ring interconversions. In these cases medium effects are usually attributed to solvent-induced changes in the relative populations of the rotamers or conformers,[2-5] but it is not generally possible to infer the importance of the first type of solvent effect in such cases.[6]

Of particular interest for the purposes of this review is the development of a conceptual basis for interpreting the mechanisms which lead to the observed effects as an aid in predicting the importance of solvent effects, and their applicability in studies of intermolecular interaction. For these purposes theoretical results for a number of models of varying degrees of complexity are compared with representative experimental data. Since some of the best correlations of experimental and theoretical results are found for the cases of dipolar aprotic solvents,[7] *i.e.*, solvents such as acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide, which do not have the capability of donating protons to form strong hydrogen bonds, greater emphasis will be placed on these types of compounds.

In a general review of solvent effects on nmr spectral parameters, Laszlo[2] included an extensive compilation of experimental data for solvent dependent coupling constants. He concluded that the practice of presenting the "raw data" without interpretation was "rather undigestible fare." However, since the appearance of his review article in 1967, considerable progress has been made in both qualitative and quantitative interpretations of the observed solvent effects. Much of the experimental data have now been compiled in existing review articles,[2,8] including a recent one[8a] which includes 39 tables of experimental data. For this reason it is not our intention to be comprehensive in the present review, which includes references through April of 1972. Only recent and/or representative experimental data are presented here to emphasize the relevant aspects of the qualitative and quantitative models.

B. Experimental Details

In almost all of the cases for which medium-dependent coupling constants are observed, the largest variations between solvents amount to only a few per cent of the total value.[8a] There are some striking exceptions to this statement, however, and many apparent disparities between literature values may be due to unrecognized solvent effects.[9] Geminal H–H coupling constants often exhibit substantial variations. For example, the geminal H–H coupling constant in α-chloroacrylonitrile which has a value of -1.96 Hz in cyclohexane solvent decreases to -3.24 Hz in dimethyl sulfoxide.[10] An even more spectacular example occurs in $AgBF_4$ for which the directly bonded ^{11}B–^{19}F coupling constant changes sign[11] de-

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pending on whether the solvent is water or an aprotic organic medium. The change of more than 100 Hz, which has been observed[12] for the directly bonded $^1H-^{31}P$ coupling in dimethyl hydrogen phosphite, is presumed to be due to solvation of the P=O group.

Electrostatic effects between solute and solvent molecules have been the most frequently cited intermolecular interaction responsible for solvent dependent coupling constants because the observed changes often correlate with some function of the dielectric constant of the medium. However, the problem is much more complicated than this because of the possibility for other types of intermolecular interactions such as specific association effects, especially hydrogen bonding.[13-15] Dispersion effects have been cited as possible contributing factors,[16-19] but usually in those cases in which neither of the coupled nuclei is a proton.

In a number of cases[2,18,20-25] the observed coupling constants are very nearly linear functions of the reaction field parameter,[26] or solvent Stark effect.[27] The series of mono-,[20] di-,[25] and trifluoro-substituted[18] ethylenes provides the basis for a most interesting comparison, which indicates that the geminal H-H and H-F coupling constants are strongly correlated with the solute dipole moment, but the correlation is not as apparent for vicinal coupling constants. In contrast to these coupling constants, vicinal coupling between protons shows a negligible solvent dependence.[2]

It has been suggested[28-30] that the solvent dependence of coupling constants has potential for the determination of the signs of coupling constants without the necessity of using double resonance techniques. However, it should be clear from this review that the complexity of the phenomena make this a very hazardous procedure in those cases in which the mechanism for the coupling are not well understood.

Solvent dependencies of coupling constants are of particular interest for nmr studies in nematic liquid crystals[31] as it has been suggested[32] that conclusions[33] concerning the magnitudes of the anisotropies of the indirect nuclear spin-spin coupling constants[34] cannot be made with any confidence without considering the changes in the values of the indirect coupling constants in the nematic *vs.* the isotropic phase. Similar arguments have been made[35] with regard to chemical shift anisotropies.

In a completely different connection, large changes of geminal coupling constants in ketones have been observed[36] in the presence of a lanthanide-shift reagent,[37] and are indicative of substantial electronic rearrangements in the solute, probably arising from a charge-transfer interaction between the ketones and the shift reagent.

C. Nomenclature

Classification of types of coupling constants in this review corresponds to the usual nomenclature,[38,39] *i.e.*, directly bonded, geminal, vicinal; coupling over four or more bonds is called "long-range." The coupling constant between nuclei N and N′, which are separated by n intervening bonds, is designated by the symbol $^nJ_{NN'}$. With few exceptions the pattern of absolute signs of coupling constants is well established by measurements in nematic liquid crystals[31] and will not be of concern in this review.

Since it is usually not feasible to put precise error limits on experimentally determined coupling constants, it is a frequent practice in the nmr literature merely to cite some average value. With typical nmr instrumentation and careful experimental techniques, errors in the liquid phase are usually cited as ±0.05 Hz and are almost always better than ±0.1 Hz. To avoid excessive repetition of error limits in the experimental data reported here, and where no conclusions are dependent on this assumption, the smaller value will be considered to be applicable.

II. Theoretical Considerations

In the absence of corrections for conformational effects, vibrational motions, and relaxation processes, Raynes[40] envisions four distinct contributions to the solvent change, ΔJ, in the coupling constant in going from the gas at low pressures to the condensed phase

$$\Delta J = J_M + J_W + J_E + J_C \qquad (1)$$

The first term, J_M, corresponds to a magnetic shielding of the nuclear spin-spin coupling by magnetic moments induced in the neighboring molecules by the nuclear dipoles and is given by[23,40]

$$J_M = -(8\pi/3)(\chi_V/ha^3)\hbar^2\gamma_N\gamma_{N'} \qquad (2)$$

where χ_V is the volume magnetic susceptibility of the solution, γ_N and $\gamma_{N'}$ are the magnetogyric ratios of the coupled nuclei, and a is the radius of a spherical cavity with origin at the solute molecule. For coupling between protons in the solute molecule with carbon tetrachloride as solvent at 30°, Raynes estimated a value of J_M =

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+0.1 Hz. This value is much smaller than the values which are often observed experimentally.[2]

The second term in eq 1, J_W, denotes contributions arising from intermolecular dispersion effects, which would be of both the London[41] and second-order exchange[42] types. The third term in eq 1 denotes the effect of intermolecular electrostatic interactions, which will have its smallest value for the case of nonpolar solutes in nonpolar solvents, and will have its greatest value for the case in which both the solute and the solvent are electrolytes. The last term, J_C, arises for those cases in which there may be specific interactions between solute and solvent molecules, such as by charge transfer or hydrogen bonding.

The dissection of solvent effects on coupling constants into the various contributions specified in eq 1 is somewhat artificial in the absence of precise definitions of the various terms. In general, it is not possible to write meaningful mathematical expressions for any but the first term of eq 1. In discussions of intermolecular forces,[43,44] electrostatic and dispersion effects are usually associated with long-range forces, whereas specific interactions would presumably be identified with the short- or intermediate-range interactions.

In the following sections we will review the theoretical basis for the qualitative and quantitative interpretations of the factors which are responsible for solvent-dependent nuclear spin–spin coupling constants. The next section provides a brief review of computational methods for nuclear spin–spin coupling. This is followed by several theoretical models for electrostatic, inductive, and dispersion contributions to the solvent effects on these parameters. These formulations provide the basis for subsequent discussions of mechanisms of solvent effects on directly bonded, geminal, and vicinal coupling constants.

A. Computational Methods for Nuclear Spin–Spin Coupling

Detailed mathematical treatments of the various theoretical formulations for nuclear spin–spin coupling constants are given in the literature references which are cited here, as well as reviews in 1965[45] and 1970.[46] Most theoretical treatments are based on the interpretations of Ramsey and Purcell[47] and the perturbation formulation of Ramsey,[48] who showed that the electrons can provide several mechanisms for coupling since they can interact with the nuclei *via* magnetic dipole–dipole, orbital–dipole, and Fermi contact terms in the electron-nuclear Hamiltonian. Contributions from the contact term provide the major part of the total for coupling involving at least one proton, and almost all discussions have emphasized this mechanism. Recent theoretical studies[49] have shown that the orbital contributions are essential for an adequate description of F–F and C–F coupling constants.

The expression for the contact contribution to the coupling between nuclei N and N′ arises in second-order perturbation theory because the interaction energy is bilinear in the nuclear spins[48]

$$J_{NN'} = -(2/3h)(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times \Sigma_\kappa[E_\kappa - E_0]^{-1}\langle\Psi_0|\Sigma_j\delta(r_{jN})\mathbf{S}_j|\Psi_\kappa\rangle \times \langle\Psi_\kappa|\Sigma_k\delta(r_{kN'})\mathbf{S}_k|\Psi_0\rangle \quad (3)$$

where Ψ_0 and Ψ_κ are the ground and triplet-state wave functions with energies E_0 and E_κ, respectively, and $\delta(r_{jN})$ is the Dirac delta function for electron j at nucleus N. The summation in eq 3 is over all of the triplet levels. Early theoretical work based on eq 3 invoked the "average energy approximation" to eliminate the sum over the triplet levels.[45,46] Although such schemes are occasionally useful for interpreting[50] coupling constant mechanisms, they have been superceded by molecular orbital (MO)[51] and valence-bond[52] descriptions which do not make this simplification. The MO expression[51]

$$J_{NN'} = (4h)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'}\phi_t^2(N)\phi_u^2(N')\pi_{tu} \quad (4)$$

relates the coupling constant to the mutual atom–atom polarizability

$$\pi_{tu} = 4\Sigma_{ij}[\epsilon_i - \epsilon_j]^{-1}c_{it}c_{iu}c_{jt}c_{ju} \quad (5)$$

and has been quite useful in qualitative descriptions of substituent[53-55] and solvent effects[28-30,56-58] on nuclear spin–spin coupling constants. The terms $\phi_t^2(N)$ and $\phi_u^2(N')$ in eq 4 denote the atomic orbital densities at the two nuclear sites. In eq 5 c_{it} and c_{jt} denote the coefficients of atomic orbital t in the ith occupied and in the jth unoccupied molecular orbitals with energies ϵ_i and ϵ_j, respectively. The summation is over both occupied and unoccupied molecular orbitals.

A more recent approach to the spin–spin coupling problem, which has been most successful in correlating conformational and substituent trends, is based on finite perturbation theory (FPT)[59] in the INDO (intermediate neglect of differential overlap) approximation[60] of self-consistent-field molecular orbital (SCF-MO) theory. This method has been applied to a wide variety of spin coupling problems[49,59,61-63] and provides the basis for several theoretical models[58,64,65] for solvent effects on coupling constants. In the SCF-MO-FPT method[58] for contact coupling constants, a perturbation of magnitude

$$\eta_N = (8\pi/3)\gamma_N\phi_s^2(N) \quad (6)$$

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is added to the diagonal element for the s orbital, which is centered on nucleus N, in the Fock matrix corresponding to electrons of α spin, and it is subtracted from the corresponding element of the Fock matrix for electrons of β spin. In the iterative SCF-MO-FPT scheme this has the effect of inducing a small spin density, $\rho_t(\eta_N)$, throughout the molecular electronic system, and the coupling constant is proportional to this spin density

$$J_{NN'} = h(4\beta)^2\gamma_N\gamma_{N'}\phi_s^2(N)\phi_{s'}^2(N')[\rho_t(\eta_N)/\eta_N] \quad (7)$$

where $\phi_{s'}^2(N')$ denotes the s' orbital density at nucleus N'. In another common terminology[66,67] this type of calculation corresponds to the "coupled" Hartree-Fock approximation, and the use of SCF orbitals in eq 4 and 5 corresponds to one type of "uncoupled" Hartree-Fock method.[67]

B. Models for Intermolecular Interactions on Coupling Constants

In general, any satisfactory theoretical calculation of a second-order property such as nuclear spin-spin coupling requires a greater degree of sophistication in the molecular wave function than a first-order property such as the charge density. As a consequence, a realistic approximation to the actual charge distribution of the solute molecule must presumably enter any theoretical model which attempts to provide a quantitative interpretation of solvent effects. However, the same degree of sophistication would not normally be required in the theoretical description of the solvent molecules. The simplest treatments, and those which have been proposed most frequently to account for solvent effects in the absence of specific association effects, are those in which the solvent is treated as a continuum surrounding the solute molecule. Several different models of this type have been proposed[68] to explain solvent effects on electronic spectra, depending on whether the solute and solvent molecules are polar or nonpolar. For example, the reaction field model[26] is applicable to polar solutes dissolved in polar and nonpolar solvents. The solvent Stark effect[27,68] arises from the dipole-induced dipole interactions in cases in which the solute is nonpolar. Continuum model treatments[69] have been used to discuss[70,71] solvent effects on chemical shifts.

Improvements in the continuum models would incorporate corrections for structural features of the solvent molecules. In almost all cases the nuclei which are studied by nmr techniques are near the "surface" of the solute molecule and are more exposed to the individual solvent molecules.[71] Therefore, it seems likely that some improvement could be made by including local effects due to polarization by adjacent solvent molecules. Since it does not appear feasible at this time to combine a rigorous theory of solutions of polar molecules[72-75] with a satisfactory theory of nuclear spin-spin coupling, it will be necessary to consider alternative models of varying degrees of complexity.

One attempt to improve on the continuum models in studies of the solvent dependence of the chemical shift[76] is the collision complex model. An attempt has also been made to combine the latter with a continuum-type model by introducing the reaction field effects on chemical shifts in a virial-type expansion.[77] The collision complex model assumes that there is an equilibrium between solute molecules (A) and solvent molecules (B) and some collision complex (AB)

$$A + B \rightleftarrows AB$$

where the equilibrium constant for this case reflects the fact that there may be a very large number of possible complexes. It is assumed, further, that the complexes are short lived on the nmr time scale and that the interactions probably involve only nearest-neighbor solvent molecules.[76] On the nmr time scale the collision complex would undoubtedly correspond to some type of molecular aggregate in which the solvent molecules are undergoing translational and rotational motions relative to the solute molecule. The properties of the solute would then be some statistical average over all possible collision complexes. The collision complex model, however, can only be expected to work well for atoms on the periphery of the molecule. The excellent correlation of chemical shift data is attributable to the localized interactions at the single atomic sites. In most cases coupling constants involve interactions which are spread over the molecular framework.

An alternative to the collision complex model, which was developed[64] to provide a quantitative model for solvent effects on coupling constants, assumed an oriented clustering of the solvent molecules around the solute molecule. Models of this type[78-80] have been used to interpret solvent effects on electric dipole moments. In terms of existing theories of liquids,[72-75] a possible justification for such a model is the greater statistical weights associated with these preferred orientations of the dipole moments.

1. The Reaction Field Model

In Onsager's original formulation of the reaction field model,[26] the solute molecule was considered to be a polarizable point dipole embedded in a spherical cavity within the dielectric continuum formed by the solvent molecules. The point dipole of the solute polarizes the surrounding medium, thereby producing a secondary field, the reaction field, which is applied to the solute molecule parallel to the dipole moment vector. In the simplest form of the reaction field model, the radius of the spherical cavity is given by

$$r = (3M/4\pi\rho N)^{1/3} \quad (8)$$

where M and ρ are the molecular weight and density of the solute and N is Avogadro's number. The reaction field is given by[26]

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$$\mathbf{R} = [2(\epsilon - 1)(n^2 - 1)\mu]/[3\alpha(2\epsilon + n^2)] \qquad (9)$$

where ϵ is the dielectric constant of the medium and n, μ, and α are the refractive index, dipole moment vector, and polarizability of the solute, respectively. Since the polarizability can be expressed in terms of the refractive index and the radius of the spherical cavity by the expression

$$\alpha = [(n^2 - 1)r^3]/[n^2 + 2] \qquad (10)$$

eq 9 can be rewritten in the form

$$\mathbf{R} = [8\pi\rho N(\epsilon - 1)(n^2 + 2)\mu]/[9M(2\epsilon + n^2)] \qquad (11)$$

The Hamiltonian operator for calculating coupling constants between nuclei N and N′ in the presence of some additional perturbation, Q, is given by[58]

$$\mathcal{H} = \mathcal{H}^0 + Q + \mathbf{H}_{\mathrm{N}}\cdot\mathrm{I}_{\mathrm{N}} + \mathbf{H}_{\mathrm{N}'}\cdot\mathrm{I}_{\mathrm{N}'} \qquad (12)$$

where I_{N} and $\mathrm{I}_{\mathrm{N}'}$, are the nuclear spin operators, $\mathcal{H}^0$ denotes the Hamiltonian operator for the unperturbed electronic system, and $\mathbf{H}_{\mathrm{N}}$ denotes the contact term

$$\mathbf{H}_{\mathrm{N}} = (16\pi\beta\hbar/3)\gamma_{\mathrm{N}}\Sigma_k\delta(\mathrm{r}_{k\mathrm{N}})\mathbf{S}_k \qquad (13)$$

In the case of a homogeneous electric field, **E**, or a reaction field, **R**, such as that specified in eq 11, the perturbation in eq 12 is given by[81]

$$Q = -\mu\cdot\mathbf{E} \qquad (14)$$

In a subsequent section a perturbation formulation is used to present a simple model for directly bonded coupling constants. To first order of perturbation theory the coupling constant is a linear function of the electric field. A better calculation is based on the self-consistent perturbation formalism described in the previous section. The only modification required is the addition of the matrix elements of the operator Q in eq 14 to the one-electron parts of the Fock matrices. The reaction field induced shifts, ΔJ, in the calculated coupling constants, ${}^1J({}^{13}\mathrm{C}\text{-H})$ in fluoroform and ${}^2J_{\mathrm{HH}'}$ in 1,1-difluoroethylene, are plotted in Figure 1 as a function of magnitude of the electric field, **E**. It can be seen that the results are very nearly linear functions over the entire range up to 3 × 10^5 esu/cm^2. It was for this reason that the assumption of linearity of the coupling constant with the magnitude of the electric field was used in calculations based on the reaction field model.[58]

2. The Point Multipole Approximation

Although the solute molecule is necessarily treated in the quantum mechanical descriptions as a collection of discrete charges, there are several possibilities for the solvent molecules which provide greater computational economy. For example, the solvent molecules could be described to good approximation by means of the point multipole expansion with or without motional averaging.[65]

The electrostatic potential due to a discrete distribution of charges is frequently expanded in a series about a single center.[82] The first term in the series is the potential which would be produced at a point by a charge, $q = \Sigma_i e_i$, placed at the origin. The second is that due to an electric dipole moment

$$\mu = \Sigma_i e_i r_i \qquad (15)$$

and is given by $-\mu\cdot\mathrm{grad}(1/r)$, which is the potential caused by a point dipole at the origin. Matrix elements of this operator are given by

$$Q_{jk} = -\langle\phi_j|\mu\cdot\mathrm{r}/r^3|\phi_k\rangle \qquad (16)$$

where the ϕ's denote the atomic orbitals. These integrals can be evaluated analytically using solid spherical harmonic expansions.[83] The third and higher terms in the point multipole expansion, which are associated with quadrupoles, octupoles, etc., are not normally used in simple applications of the multipole expansion.

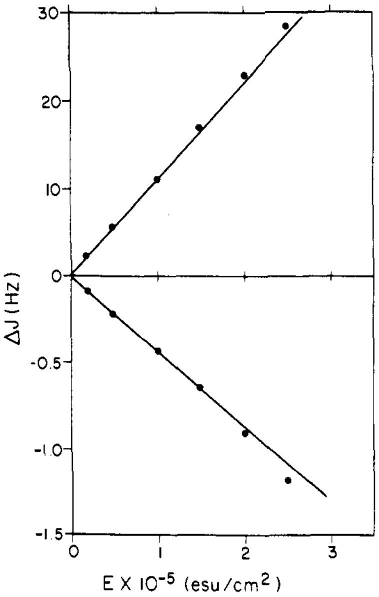

Figure 1. Calculated dependence of electric field induced changes, $\Delta J_{\mathrm{NN}'}$, in coupling constants as a function of the magnitude of the electric field, **E**. The upper plot shows the dependence of the ^{13}C-H coupling constant in fluoroform and the lower plot gives completely analogous data for the geminal H-H coupling in 1,1-difluoroethylene.

3. Electric Field Dependence of Atomic Orbital Densities

It has been suggested[57] that it is a serious approximation to neglect changes of the atomic orbital densities [$\phi_t^2(\mathrm{N})$ and $\phi_u^2(\mathrm{N}')$ in eq 4] in the presence of an external electric field. Since the second-order Stark effect for a hydrogenic atom can be treated quite accurately,[84-86] at least one aspect of this problem can be resolved immediately.

Application of perturbation theory for an electric field of magnitude E_z to a hydrogen atom ground state in parabolic coordinates yields

$$\phi_{1s} = \pi^{-1/2}[1 + \tfrac{1}{8}E_z(\xi^2 - 12\xi - 6)] \times [1 - \tfrac{1}{8}E_z(\eta^2 - 12\eta - 6)] \times \exp[-\tfrac{1}{2}(\xi + \eta)] \qquad (17)$$

At the origin $\xi = \eta = 0$; hence

$$\phi_{1s}^2(0) = \pi^{-1}[1 - \tfrac{9}{16}E_z^2]^2 \qquad (18)$$

which exhibits quadratic and higher order dependence

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[81] This term inadvertently appeared without a negative sign in eq 6 of ref 58.

[82] C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam, 1952, Chapter IV.

[83] R. M. Pitzer, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 267 (1962).

[84] L. D. Landau and E. M. Lifshitz, "Quantum Mechanics," 2nd ed., Pergamon Press, New York, N. Y., 1965, pp 269-274.

[85] L. I. Schiff, "Quantum Mechanics," 3rd ed., McGraw-Hill, New York, N. Y., 1968, pp 263-265.

[86] P. C. Gibbons and N. F. Ramsey, *Phys. Rev.*, **5A**, 73 (1972).

rather than a linear dependence on electric field, E_z, and even for very large fields such as 10^6 esu/cm^2 produces a change of only 0.38% in the orbital density. The other effect, which the authors[57] presumably had in mind as important for the s-orbital densities, is the electric field induced changes in the values of the orbital exponents. This is, of course, a much more difficult problem because the dependence of these parameters on structural and other factors is not clearly understood. Most SCF-MO calculations are based on the assumption of fixed orbital exponents. Calculations of solvent effects which have been performed[58,64,65] do not give any indication that this neglect is a critical approximation.

4. A Perturbation Treatment of Inductive and Dispersive Effects on Spin-Spin Coupling

In this section a group function treatment of the importance of inductive and dispersive effects on nuclear spin-spin coupling is developed in a theoretical formulation which is analogous to that used by Longuet-Higgins and Pople[87] and by McRae[68] to discuss the importance of these factors on electronic spectral shifts in nonpolar solutes. Although the method could be easily generalized to an arbitrary number of solute and solvent molecules, for simplicity we shall consider a single solute (A) and a single solvent molecule (B).

Let the wave functions for the ground and excited states of the solute molecule be denoted by A_α (α = 0, 1, 2, 3, . . .), where the zero subscript denotes the ground state and the nonzero subscripts refer to the excited states. The wave functions for the solvent molecule are designated in a completely analogous way by the symbol, B_β, where β = 0, 1, 2, 3, ... Now consider a new ground-state wave function constructed by configurational mixing of the various product wave functions for the solute and solvent molecules

$$\Psi_0 = [A_0B_0] + \Sigma_\alpha c_\alpha[A_\alpha B_0] + \Sigma_\beta c_\beta[A_0B_\beta] + \Sigma_{\alpha\beta}c_{\alpha\beta}[A_\alpha B_\beta] \quad (19)$$

where $[A_0B_0]$ denotes the wave function for both groups in their ground states, and $[A_\alpha B_0]$ denotes the excited singlet state formed by exciting group A to the αth excited state. Analogous interpretations follow for the next two terms in eq 19. In general, these would be antisymmetrized product functions, but for the case of long-range forces[87] it is not necessary to include this in the calculations. Triplet states, Ψ_κ, can also be constructed by excitation into the triplet manifold of either molecule A or molecule B

$$\Psi_\kappa = [A_1B_0], [A_2B_0], \ldots ; [A_0B_1], [A_0B_2], \ldots \quad (20)$$

where for simplicity subscripts have not been introduced to distinguish between excited singlets and triplets.

The coefficients in eq 19 follow from first-order perturbation theory

$$c_\alpha = -\langle A_0B_0|\mathcal{H}'|A_\alpha B_0\rangle/(E_{\mathrm{A}\alpha} - E_0) \quad (21)$$

$$c_\beta = -\langle A_0B_0|\mathcal{H}'|A_0B_\beta\rangle/(E_{\mathrm{B}\beta} - E_0) \quad (22)$$

$$c_{\alpha\beta} = -\langle A_0B_0|\mathcal{H}'|A_\alpha B_\beta\rangle/(E_{\mathrm{A}\alpha} + E_{\mathrm{B}\beta} - E_0) \quad (23)$$

where $\mathcal{H}'$ denotes the operator for interaction between solute and solvent molecules, and the denominators in eq 21, 22, and 23 denote the excitation energies for group A alone, group B alone, and both groups simultaneously. From these equations it can be noted that the second and third terms in eq 19 correspond to the inductive effect, or dipole-induced dipole terms, whereas the last term corresponds to a mixing of excited states into the ground state by dispersive effects, *i.e.*, induced dipole-induced dipole contributions.

It is now possible to make use of eq 3 and 19 to write down an expression for the inductive and dispersive contributions to the solvent effect on the contact nuclear spin-spin coupling constant. Note that a term can be subtracted corresponding to the coupling constant of the unperturbed solute and that matrix elements in the numerator of eq 3 between Ψ_0 and Ψ_κ vanish for functions specified by the last term of eq 15. In this approximation the shift in the contact coupling constant, $\Delta J_{\mathrm{NN}'}$, is given by eq 24. Therefore, the only contribution from the London dispersion interactions, corresponding to induced dipole-induced dipole interactions, will arise from the modifications in the energy denominators in eq 24.

$$\begin{aligned}\Delta J_{\mathrm{NN}'} = -(2/3h)(16\pi\beta\hbar/3)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N}'} \times \\ \Sigma_\kappa[E_\kappa - E_0]^{-1} \times \\ \{\Sigma_\alpha c_\alpha\langle A_0B_0|\Sigma_j\delta(\mathrm{r}_{j\mathrm{N}})\mathbf{S}_j|A\ B_0\rangle \times \\ \langle A_\kappa B_0|\Sigma_k\delta(\mathrm{r}_{k\mathrm{N}'})\mathbf{S}_k|A_\alpha B_0\rangle + \\ \Sigma_\beta c_\beta\langle A_0B_0|\Sigma_j\delta(\mathrm{r}_{j\mathrm{N}})\mathbf{S}_j|A_0B_\kappa\rangle \times \\ \langle A_0B_\kappa|\Sigma_k\delta(\mathrm{r}_{k\mathrm{N}'})\mathbf{S}_k|A_0B_\beta\rangle\}\end{aligned} \quad (24)$$

It should be noted, however, that if interactions between the triplets of the solute and solvent molecules were considered, then there would be additional contributions to eq 24 corresponding to spin coupling of the triplets to singlets.[88] In this case there would be some additional terms occurring in eq 24 in which the mixing coefficients were proportional to the intermolecular exchange integrals. These would correspond to the second-order exchange contributions to the dispersion interaction,[42] which are more important in the intermediate than in the long-range. As a consequence, it appears that there is a reasonable theoretical basis for assuming that interactions of the dispersion type are not particularly important for contact coupling. This seems also to be the case experimentally and will be discussed in the next section. It is suggested that solvent effects on coupling constants between nuclei involving at least one proton can be adequately accounted for by the *polarization* effects on the contact term as in eq 24. However, for coupling constants such as F-F and C-F and Si-F, where orbital terms become important,[49] it appears that dispersion effects can become important.

First-order contributions from intermolecular interactions of the London type specified in eq 19 do not occur in the expression for the contact coupling constant because matrix elements of the one-electron spin operators *vanish identically if more than one group has a different spin multiplicity.* The same is true for the other coupling constant terms which arise in second-order perturbation theory. There is, however, an orbital contribution which occurs in first order given by eq 25. Since this equation

$$\begin{aligned}J_{\mathrm{NN}'}{}^{(1\mathrm{a})} = (4/3h)\,(e^2h^2/2mc^2) \times \\ \langle\Psi_0|\Sigma_k \mathrm{r}_{k\mathrm{N}}\mathrm{r}_{k\mathrm{N}'}r_{k\mathrm{N}}{}^{-3}r_{k\mathrm{N}'}{}^{-3}|\Psi_0\rangle\end{aligned} \quad (25)$$

gives nonvanishing contributions from both the inductive and dispersive terms, if eq 19 is substituted into eq 25 there is a theoretical basis for the experimental data which indicate a correlation between the importance of

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[87] H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, **27**, 192 (1957).

[88] M. Barfield, *J. Chem. Phys.*, **49**, 2145 (1968).

TABLE I. Representative Experimental Values for Directly Bonded Coupling Constants in the Gas and in the Liquid Phases

			Gas		Liquid
No.	Solute	Solvent	$^1J_{NN'}$, Hz	ρ_g, mol/l.	$^1J_{NN'}$, Hz
1	CH_3Cl	CH_3Cl	147.5 ± 0.3[a]	0.14	148.6 ± 0.2[a]
2	$(CH_3)_3N$	$(CH_3)_3N$	131.5 ± 0.2[a]	0.08	131.7 ± 0.1[a]
3	CH_4	CH_4	125.34 ± 0.16[b]	1.32	
			125.45 ± 0.15[b]	6.63	
4	SiH_4	SiH_4	201.90 ± 0.47[b]	1.31	
			201.72 ± 0.17[b]	9.74	
5	SiH_4	C_6H_6			202.5 ± 0.2[c]
6	SiF_4	SiF_4	169.3 ± 0.2[d]	0.4–0.6	
			169.00 ± 0.08[e]	1.2	
			169.87 ± 0.10[b]	3.50	
			169.6 ± 0.15[f]	4.37	
			169.8 ± 0.15[f]	4.61	
			170.0 ± 0.15[f]	6.03	
			169.9 ± 0.15[f]	7.30	
			170.2 ± 0.15[f]	7.69	
7	SiF_4	$(CH_3)_4Si$			174.8[g]
		$(C_2H_5)_2O$			173.7[g]
		CCl_3F			175.0[g]
		CCl_4			176.8[g]
8	PF_3	PF_3	1404[h]		
9	PF_3	$Sn(CH_3)_4$			1411[h]
		$Si(OC_3H_5)_4$			1415[h]
		$CHCl_3$			1418[h]
		CCl_4			1423[h]

[a] Reference 95. [b] Reference 91. [c] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962). [d] Reference 89. The density was calculated from the estimated pressure of 10–15 atm assuming ideality. [e] Reference 93. The pressure was estimated to be about 30 atm. The density in the table was calculated assuming ideality. [f] Reference 92. [g] Reference 94. The values correspond to 15 mol % of SiF_4 in the indicated solvent. [h] Reference 23.

dispersive effects and of orbital contributions to the coupling constants. In general, both effects are most important for heavier elements and negligible for hydrogen atoms. Furthermore, since coupling constants involving at least one proton are almost invariably well accounted for by the contact mechanism, the failure to observe any correlation with dispersive effects in such cases is not unexpected.

If $\mathcal{H}'$ in eq 21–23 corresponds to the long-range interaction between a pair of oscillating dipoles, then the assumption of an average over isotropic molecules may cause all of the terms in eq 24 and 25 to vanish. However, in the absence of detailed calculations the discussion of this section is speculative and serves only as a hypothesis for interpreting the data in subsequent sections.

III. Solvent Effects on Directly Bonded Coupling Constants

A. Density Dependence

A few measurements have been performed for directly bonded coupling constants in the gas phase[89-92] and for the changes from the gas to the liquid phase.[23,93-95] Representative experimental values in the gas and liquid phases are compiled in Table I. For the gas-phase values, the densities, ρ_g in moles/liter, are included in the table. In some cases these were calculated from the ideal gas equation with very crude estimates of the pressures of the gas. The only clearly defined density dependence in the gas phase is that for $^1J(^{29}Si-^{19}F)$ in SiF_4. The experimental values from Table I are plotted in Figure 2 as a function of the density, ρ_g in moles/liter. Although there is no theoretical basis for assuming that

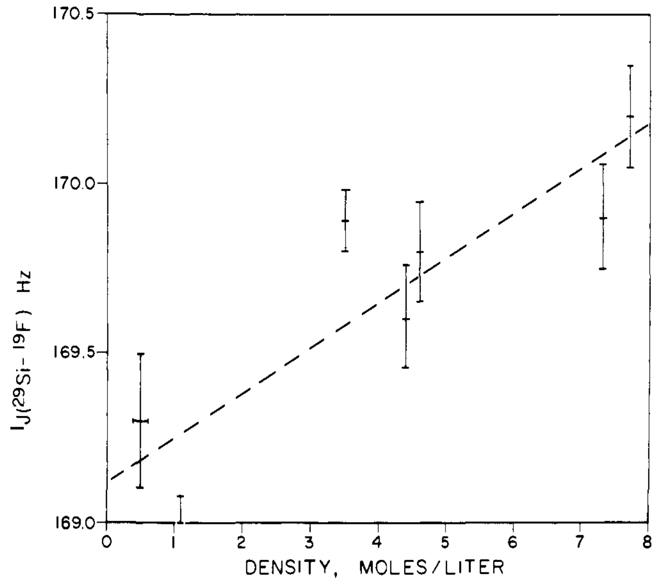

Figure 2. Experimental values of $^1J(^{29}Si-^{19}F)$ coupling constant in SiF_4 in the gas phase plotted as a function of the density in moles per liter. The dashed line corresponds to the linear least-squares fit of the experimental data.

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(89) R. J. Gillespie and J. W. Quail, *J. Chem. Phys.*, **39**, 2555 (1963).

(90) A. K. Jameson and J. P. Reger, *J. Phys. Chem.*, **75**, 437 (1971).

(91) J. P. Reger, M.Sc. Thesis, Loyola University of Chicago, 1971.

(92) A. K. Jameson, private communication, 1972.

(93) T. D. Coyle, R. B. Johannesen, F. E. Brinckman, and T. C. Farrar, *J. Phys. Chem.*, **70**, 1682 (1966).

(94) R. B. Johannesen, F. E. Brinckman, and T. D. Coyle, *J. Phys. Chem.*, **72**, 660 (1968).

(95) A. W. Douglas and D. Dietz, *J. Chem. Phys.*, **46**, 1214 (1967).

the coupling constant is a linear function of the density, a good linear least-squares fit of the experimental points is obtained and gives an intercept of 169.1 Hz. Jameson and Reger[90] extrapolated the data for $^1J(^{29}Si-^{19}F)$ in the SiF_4 mixtures with CO_2, HCl, and CH_4 to the densities of the liquid solvents, and obtained the values $^1J(^{29}Si-^{19}F)$ = 172, 174, and 175 Hz, respectively. As these values were in the range found by Coyle, *et al.*,[93] it was concluded[90] that it would not be necessary to invoke any additional assumptions to explain the gas-phase coupling constants. Within the experimental errors no density dependence was observed[90] for the directly bonded coupling constants in CH_4, SiH_4, and PF_3.

In all of the cases in Table I for which experimental data are available, the coupling constants increase in magnitude in going from the gas phase to the condensed phase. However, it is only for the nonpolar solute, SiF_4, that it is necessary to suggest that the dispersion interaction is an important factor for solvent dependence of the coupling constants. Furthermore, this solute is one of the two in the table for which it is also reasonable to expect that orbital mechanisms will give greater contributions than contact mechanisms. At a very speculative level, therefore, the solvent dependence of $^1J(^{29}Si-^{19}F)$ can be associated with contributions from the orbital term in eq 25 and dispersion contributions corresponding to the last term of eq 19.

Since PF_3 is strongly polar, contributions might also be expected from dipole-dipole and dipole-induced dipole contributions to the $^{31}P-^{19}F$ coupling constant. The second of these corresponds to the first term of eq 24. From the other data in Table I it can only be presumed that dispersion effects have little or no effect on the directly bonded coupling constants in which the contact mechanism is dominant, *i.e.*, those coupling constants involving a proton. This is consistent with our speculations in the preceding section, but careful experimental work on appropriate systems is clearly needed to put bounds on this assessment.

In the absence of experimental data for the gas phase molecules, the usual reference state for solvent effects is a dilute solution of the solute in nonpolar solvents such as CCl_4 or aliphatic hydrocarbons, *i.e.*, cyclohexane. As a consequence, the reported values are somewhat smaller than would be expected if the low-pressure gas served as the reference. In those cases in which the reference solvent is in a condensed phase, solvent effects should be less sensitive to dispersion effects than to electrostatic interactions. This viewpoint is consistent with the experimental data which show only small changes in the chemiquite different dispersion energies.[96a] More recent work[96b] shows a substantial solvent shift for nonpolar solutes in nonpolar solvents.

Since the heat of vaporization of a liquid at its boiling point is a crude measure of the dispersion free energy,[69] attempts have been made to correlate coupling constants of the solute with the heat of vaporization for the solvent.[16-18] Since there does not appear to be any theoretical basis for assuming that *solvent effects on coupling constants* should be linear functions of the dispersion free energy, the apparent correlations with heat of vaporization of the solvent is interesting but does not yet provide a theoretical model for interpreting solvent effects on coupling constants.

TABLE II. Solvent Effects on Directly Bonded Coupling Constants in Representative Molecules[a,b]

No.	Solute	Solvent	$^1J_{CH}$, Hz	ΔJ_{CH}, Hz	Mol % solute
1	CH_3Cl	C_6H_{12}	148.58	0.00	19.22
		Neat	149.64	1.06	100.00
		DMF	150.40	1.82	21.68
2	CH_3Br	C_6H_{12}	150.54	0.00	26.07
		Neat	151.44	0.90	100.00
		DMF	151.59	1.60	23.20
3	CH_3I	C_6H_{12}	150.31	0.00	23.42
		Neat	151.09	0.78	100.00
		DMF	151.59	1.28	23.20
4	CH_2Cl_2	C_6H_{12}	176.48	0.00	24.02
		Neat	178.11	1.63	100.00
		DMF	180.55	4.07	22.35
5	CH_2Br_2	C_6H_{12}	177.74	0.00	23.61
		Neat	179.22	1.48	100.00
		DMF	181.63	5.15	21.17
6	CH_2I_2	C_6H_{12}	171.93	0.00	24.28
		Neat	172.92	0.99	100.00
		DMF	173.80	1.87	21.25
7	$CHCl_3$	C_6H_{12}	208.11	0.00	22.53
		Neat	208.91	0.80	100.00
		DMF	216.46	8.35	24.36
8	$CHBr_3$	C_6H_{12}	204.31	0.00	25.19
		Neat	205.40	1.09	100.00
		DMF	211.60	7.29	25.19
9	CH_3CCl_3	C_6H_{12}	133.25	0.00	22.37
		Neat	133.46	0.25	100.00
		DMF	133.77	0.52	24.16
10	*cis*-$C_2H_2Cl_2$	C_6H_{12}	197.1	0.0	50.0
		Neat	197.9	0.8	100.0
		DMF	200.1	3.0	50.0
11	*trans*-$C_2H_2Cl_2$	C_6H_{12}	198.4	0.0	50.0
		Neat	198.9	0.5	100.0
		DMF	200.8	2.4	50.0
12	1,1-$C_2H_2Cl_2$	C_6H_{12}	166.3	0.0	50.0
		Neat	166.5	0.2	100.0
		DMF	167.0	0.7	50.0

[a] Values for items 1–9 were taken from reference 15. [b] Values for items 10–12 were taken from V. S. Watts, J. Loemker, and J. H. Goldstein, *J. Mol. Spectrosc.*, **17**, 348 (1965).

B. Electrostatic Interactions

The influence of intermolecular, electrostatic interactions between solute and solvent molecules on coupling constants, which is a widely observed experimental phenomenon, is amenable to qualitative mechanistic interpretation and theoretical calculation in a number of cases. In this regard the discussion of electrostatic solvent effects on coupling constants can be put on a better theoretical basis than solvent effects on chemical shifts.[71,97,98] because of the greater degree of confidence in the theoretical treatment of coupling constants, especially contact coupling.[45,46]

Representative values for directly bonded coupling constants are entered in Table II for several molecules in a number of solvents of widely varying polarity. The solvent-induced shifts, $\Delta J_{NN'}$, in the coupling constants in Table II were obtained as the difference between the value measured in the indicated solvent and the value obtained in cyclohexane. For general reference in this review, the dielectric constants and abbreviations of representative solvent molecules are entered in Table III.

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(96) (a) P. Laszlo, A. Speert, R. Ottinger, and J. Reisse, *J. Chem. Phys.*, **48**, 1732 (1968); (b) W. T. Raynes and M. A. Raza, *Mol. Phys.*, **17**, 157 (1969); **20**, 555 (1971).

(97) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(98) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

TABLE III. **Representative Solvents and Their Dielectric Constants**

No.	Solvent	ϵ^a
1	Tetramethylsilane (TMS)	1.91
2	Cyclohexane	2.02
3	*p*-Dioxane	2.20
4	Carbon tetrachloride	2.22
5	Benzene	2.26
6	Bromotrichloromethane	2.38
7	Carbon disulfide	2.61
8	Propionic acid	3.30
9	Diethylamine	3.60
10	Bromoform	4.28
11	Diethyl ether	4.34
12	Bromodichloromethane	4.47
13	Chloroform	4.63
14	Chloroform-*d*	4.80
15	Fluorobenzene	5.32
16	Bromobenzene	5.33
17	Acetic acid	6.22
18	Methyl acetate	6.57
19	Dibromomethane	7.04
20	Tetrahydrofuran (THF)	7.85
21	Bromochloromethane	8.41
22	Dichloromethane	8.75
23	Cyclopentanone	16
24	Acetone	20
25	Ethanol	24.3
26	2-Nitropropane	25.5
27	Methanol	33.6
28	Nitrobenzene	33.9
29	Dimethylformamide (DMF)	35
30	Acetonitrile	35.8
31	Nitromethane	35.9
32	Trifluoroacetic acid	39.5
33	Dimethyl sulfoxide (DMSO)	46
34	Formic acid	59
35	Propylene carbonate	64
36	Water	80
37	Formamide	109

[a] National Bureau of Standards, Circular No. 514, 1951. Values are for 35°C, a typical probe temperature for 60-MHz nmr spectrometers.

1. Mechanisms

Qualitative discussions[24,30] of $^1J(^{13}C\text{-}H)$ based on eq 4 and 5 attributed the electric field dependence to a change in the s character of the bonding orbital for the C-H bond, whereas solvent effects on C-F coupling constants were rationalized in terms of changes in the mutual atom-atom polarizability. Since eq 4 and 5 lead to calculated coupling constants, which are not necessarily of the right order of magnitude,[58] qualitative discussion of solvent effects in terms of these equations may be of questionable significance.

Raynes and Sutherley[56] have discussed the electric field dependence of $^{13}C\text{-}^1H$ coupling constants in terms of the variations in the mutual atom-atom polarizabilities in a MO treatment similar to the one used by Gil and Teixeira-Dias[54] to examine substituent effects on directly bonded coupling constants. In eq 4 the coupling constant is proportional to the mutual atom-atom polarizability which is defined by eq 5. The latter can be related to the empirical resonance and Coulomb integrals of simple Hückel MO theory.[54] Inclusion of the electric field dependence of these empirical parameters leads to a theoretical estimate of the solvent dependence of $^1J(^{13}C\text{-}^1H)$ which is of the right order of magnitude.[56] However, it will be shown below that this is a fortuitous result, and more detailed calculations for an isolated C-H bond give results of the right order of magnitude but of the wrong sign. The difficulty is shown to arise because of the failure to consider transfer of electron density *out* of the C-H bonding region.

Consider a C-H bond, for which the ground-state wave function can be written in the generalized geminal form[99]

$$^1\Psi_0 = \Lambda[t(1)h(2) + h(1)t(2) + \lambda t(1)t(2)]^1\Theta_0 \qquad (26)$$

where t denotes a hybrid orbital on carbon directed toward the hydrogenic 1s orbital, h, Λ is a normalizing factor

$$\Lambda = [2 + 2S^2 + \lambda^2 + 4\lambda S]^{-1/2} \qquad (27)$$

$^1\Theta_0$ is a singlet spin function

$$^1\Theta_0 = 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (28)$$

λ is a parameter which determines the charge distribution, and S is the overlap integral. Perturbation by an electric field will mix the ground state with the excited singlet state

$$^1\Psi_1 = \mathbf{K}[t(1)t(2) - \kappa h(1)h(2)] \qquad (29)$$

where $\mathbf{K}$ is the normalizing factor

$$\mathbf{K} = [1 + \kappa^2 - 2\kappa S^2]^{-1/2} \qquad (30)$$

and κ is chosen so that the two singlet functions are orthogonal. Matrix elements in the numerator of eq 3 require triplet-state functions

$$^3\Psi_m = [2(1 - S^2)]^{-1/2}[t(1)h(2) - h(1)t(2)]^3\Theta_m \qquad (31)$$

where $^3\Theta_m$ denotes the three components of a triplet spin function

$$^3\Theta_m = \alpha(1)\alpha(2), 2^{-1/2}\alpha(1)\beta(2) + \beta(1)\alpha(2)\}, \beta(1)\beta(2) \qquad (32)$$

corresponding to $m = +1, 0$, and -1, respectively.

If the electric field perturbation is directed along the positive z axis with magnitude E_z, then the perturbing Hamiltonian is

$$\mathcal{H}' = -eE_zz \qquad (33)$$

The convention used here corresponds to that in which the dipole moment is directed from positive to negative charge along the z axis. This further requires that the electric field be directed from negative to positive charge. This convention is just opposite to the one most commonly used by physicists,[82] but retains the chemist's intuitive ideas regarding the effects of substituents on dipole moments.[80]

The perturbation due to the electric field will mix $^1\Psi_0$ and $^1\Psi_1$

$$^1\Psi_0' = {}^1\Psi_0 + c_1{}^1\Psi_1 \qquad (34)$$

where

$$c_1 = eE_z\langle^1\Psi_0|z|^1\Psi_1\rangle/(^1E_1 - {}^1E_0) \qquad (35)$$

where $^1E_1$ and $^1E_0$ are the energies of the excited singlet and of the ground states, respectively. Substitution of the various terms into eq 3 yields the following expression for the shift, ΔJ_{CH}, in the coupling constant on application of an external field

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(99) M. Karplus and D. M. Grant, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1269 (1959).

TABLE IV. Calculated Electric Field Induced Changes in the Directly Bonded Coupling Constant in Formaldehyde

	$\lvert\mathbf{R}\rvert = 0$		$\lvert\mathbf{R}\rvert = 10^5$ esu/cm^2	
Excitation	$\epsilon_j - \epsilon_i$, au	$^1J_{CH}(i \rightarrow j)$, Hz	$\epsilon_j - \epsilon_i$, au	$^1J_{CH}(i \rightarrow j)$, Hz
$1a_1 \rightarrow 4a_1$	1.8755	13.09	1.8846	12.50
$1a_1 \rightarrow 5a_1$	2.0835	−0.97	2.0930	−0.92
$2a_1 \rightarrow 4a_1$	1.2861	161.87	1.2812	162.19
$2a_1 \rightarrow 5a_1$	1.4940	−11.43	1.4896	−11.40
$3a_1 \rightarrow 4a_1$	0.9135	−42.89	0.9189	−39.28
$3a_1 \rightarrow 5a_1$	1.1215	2.86	1.1274	2.61
	$^1J^0_{CH} = 122.53$		$^1J_{CH} = 125.70$	

$$\Delta J_{CH} = {}^1J_{CH} - {}^1J_{CH}{}^0 = c_1{}^1J_{CH}{}^0(\mathbf{K}/\Lambda)[\{S/(1 + \lambda S)\} - \kappa S] \quad (36)$$

where $^1J_{CH}{}^0$ is the coupling constant in the absence of the field, and c_1 is the mixing coefficient given in eq 35. Substitution of reasonable values for the various terms in eq 35 and 36[56,99] leads to a value of ΔJ_{CH} which is of the right order of magnitude, but which is of the wrong sign!

Changes in the orbital densities of formaldehyde and methyl fluoride due to an electric field of 10^5 esu/cm^2 parallel to the dipole moment vector, *i.e.*, a strong solvent reaction field, are depicted in Figure 3. The charge densities for each of the valence orbitals were obtained in the INDO approximation[60] of SCF-MO theory. Charge densities in the presence of the electric field were calculated by self-consistent perturbation theory[58,59] in the same approximation. Numerical values in Figure 3 denote the *differences* between the two sets of results. In the case of formaldehyde in Figure 3a, the greatest change due to the electric field is the transfer of charge density from the carbon to the oxygen *via* the π-electron system. For methyl fluoride in Figure 3b much less charge is transferred from the carbon to the fluorine because of the cancellation of the effects from the orbitals which are perpendicular to the bond direction.

The example of the formaldehyde molecule will be discussed in more detail since it exhibits all of the features which lead to solvent-dependent coupling constants. Formaldehyde has ten orbitals in the valence shell. The nodal behavior of these MO's is depicted schematically in Figure 4a and labeled by the symmetry designations appropriate to C_{2v} symmetry. The ordering of the MO energies in Figure 4b follow from the results of the INDO approximation of SCF-MO theory. Transitions from occupied to unoccupied MO's, which lead to nonvanishing contributions to $^1J_{CH}$ according to eq 4 and 5, are all of a_1 symmetry. There are six transitions of this type. The energy separations and contributions of each to the directly bonded C-H coupling constant are entered in Table IV. Calculated values are given for external, uniform fields of zero and of 10^5 esu/cm^2. The difference between these two values corresponds to $\Delta J_{CH} = +3.17$ Hz, which is in good accord with the sign and magnitudes for the representative directly bonded coupling constants in Table II.

From Table IV it can be seen that the major changes in $^1J_{CH}$ are due to the $3a_1 \rightarrow 4a_1$ transition. In the presence of the solvent reaction field the $4a_1$ orbital, which is unoccupied in the ground state, will be relatively insensitive to the electric field. However, the effect of the electric field is to produce a substantial decrease in the coefficient of the 2s orbital on carbon in the $3a_1$ MO. Since the contribution of the $3a_1 \rightarrow 4a_1$ transition to $^1J_{CH}$ is negative in sign, the net effect is to produce a positive shift in the directly bonded coupling constant. Therefore, the mechanism for this type of coupling is not implicit in the consideration of an isolated CH bond or even a CH_2 moiety, but arises from a polarization of the electrons which extend over the entire molecule.

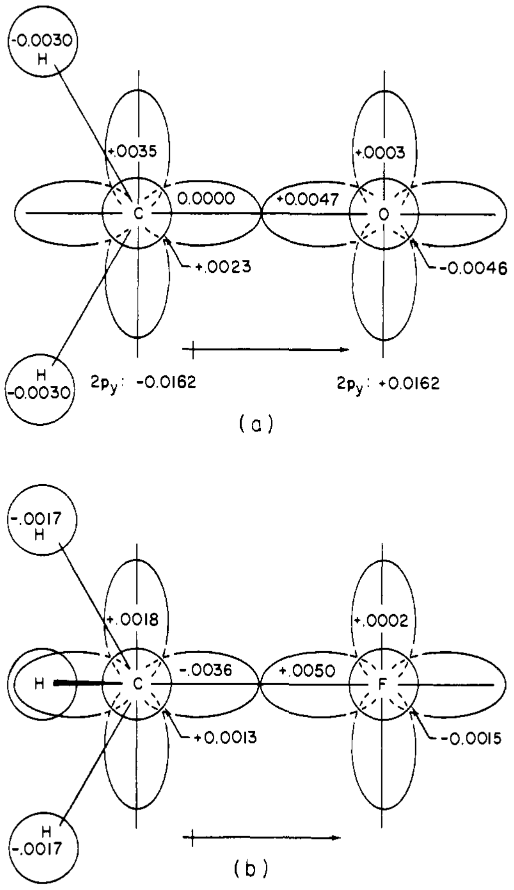

Figure 3. Calculated INDO-SCF-MO results for the *changes* in the orbital densities for (a) formaldehyde and (b) methyl fluoride due to a uniform electric field of 10^5 esu/cm^2. The field is parallel to the dipole moment vector.

2. Results of Theoretical Models

Numerical results based on the theoretical models described in section II.B are entered in Table V along with the experimental results. The experimental results for purposes of comparison represent differences between the values measured in the indicated solvent and the value obtained for cyclohexane as the reference solvent. Calculated and experimental results for solvent effects on the directly bonded C-F coupling constants were included in the table even though the calculated results do not include contributions from the orbital terms, which are expected to dominate this type of coupling.[49] In contrast to the reasonable correlation between experimental and theoretical results for the directly bonded C-H coupling constants in Table V, in several cases the calculated results for ΔJ_{CF} are not even of the correct sign!

The calculated results in Table V were based on three models: the reaction field model,[58] a cubic closest packed cluster model,[64] and a point dipole model with rotational averaging.[65] The theoretical basis for these various models was discussed briefly in section II.B. Because the limited amount of data in Table V does not exhibit the salient features of these various models, and because the calculated results for directly bonded coupling

TABLE V. Comparison of Calculated and Experimental Values for Solvent Effects on Directly Bonded Coupling Constants

					$\Delta J_{NN'}$, Hz			
No.	Solute	Solvent	Dielectric constant	Coupled nuclei, NN′	Experiment[a]	Reaction field[b]	Cluster model[c]	Dipole model[c]
1	CH_2F_2	Neat	5[d]	CH	2.9	0.89	2.95	1.44
				CF	1.78	1.23	−1.39	10.28
	CH_2F_2	Acetone	20	CH	2.70	2.28	0.86	1.52
				CF	3.80	3.13	−1.05	12.19
	CH_2F_2	DMSO	46	CH	4.40	2.48		
				CF	4.46	3.39		
2	CHF_3	Acetone	20	CH	7.25	4.05		
				CF	0.10	3.02		
	CHF_3	DMSO	46	CH	9.20	4.38		
				CF	−1.00	3.28		

[a] Experimental values from ref 24 were obtained as the differences between the value observed in the indicated solvent and value in cyclohexane. [b] The calculated values are from ref 58 and 64 and correspond to the difference between the coupling constants calculated for a molecule in a solvent with the indicated dielectric constant and a solvent with the dielectric constant of cyclohexane. [c] Calculated values from ref 64 and 65 correspond to the coupling constant differences between the solute surrounded by six solvent molecules and the value for the isolated molecule. [d] Estimated from bond polarizability and dipole moment data.

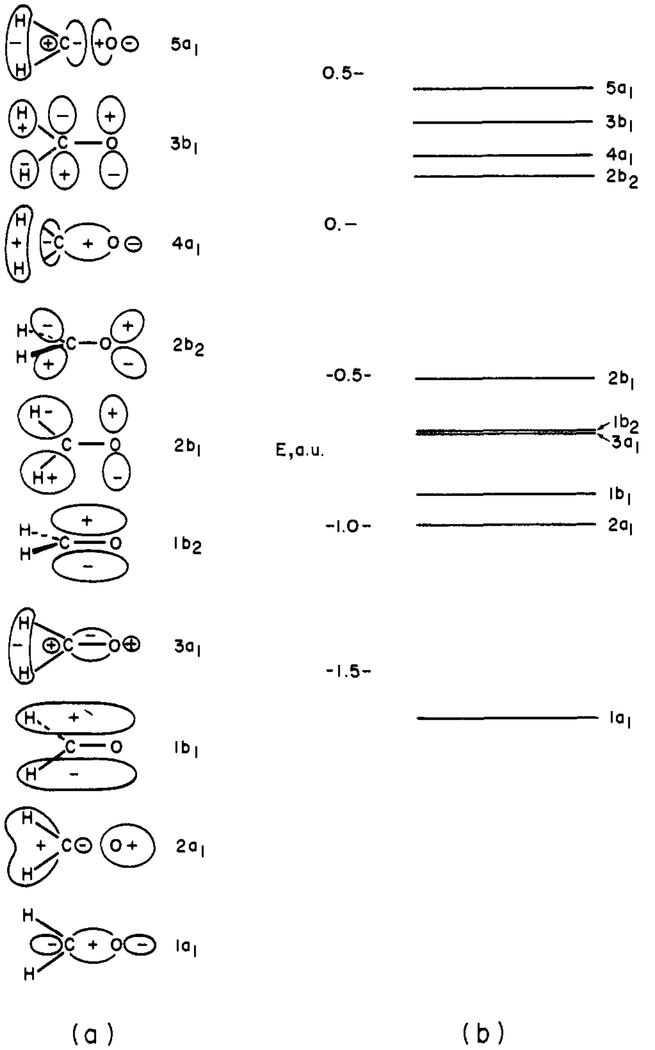

Figure 4. (a) Nodal behavior and symmetry designations for the ten molecular orbitals of formaldehyde. (b) Ordering of the MO energy levels for formaldehyde based on the INDO-SCF-MO calculations.

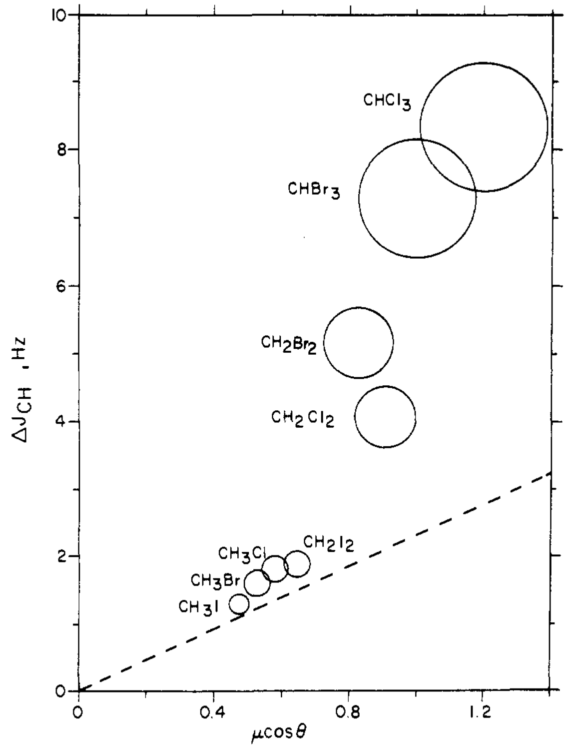

Figure 5. A plot of the experimental values for solvent shifts, ΔJ_{CH}, in the directly bonded coupling constants of the halomethanes as a function of μ cos θ, where μ is the dipole moment and θ is the angle between the dipole moment direction and the C–H bond. The dashed line is based on the theoretical reaction field results from Table V.

constants are not much better than those based on the semiquantitative models of the previous section, discussion of the computational aspects of these models will be deferred to the sections on geminal and vicinal coupling constants. Fortunately, the overall agreement of the various models is generally better than is suggested by the limited results in Table V.

For a given solvent and solutes which do not differ greatly in size, reaction fields based on eq 11 are not widely different. With this assumption solvent effects determined in the same solvent should be approximately linear functions of the quantity μ cos θ. The experimental data for directly bonded $^{13}C-^{1}H$ coupling constants from Table II for the various substituted methanes in dimethylformamide are plotted in Figure 5 as a function of the quantity μ cos θ. Dipole moments, μ, were taken from the compilation of McClellan,[100] and the angles, θ, mea-

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[100] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

sured between the dipole moment axis and the C–H bond were taken from the compilations of Sutton.[101] In the absence of specific association effects, the applicability of the reaction field model would require that the experimental points fall on a straight line passing through the origin. The dashed line in Figure 5 is based on the theoretical results for CH_2F_2 and CHF_3 from Table V. The substantial deviations from this line in Figure 5, which occur for $CHCl_3$ and $CHBr_3$, are probably attributable to specific association effects. It should be noted that the errors associated with the experimental data plotted in Figure 5 are enormous as the least concentration of the solute was 19 mol %. Perhaps, with the possibility of much greater signal to noise available by Fourier transform techniques,[102] the experimental data can be substantially improved because much lower solute concentrations will be possible, thereby eliminating solute–solute interactions as a factor in the observed medium effects.

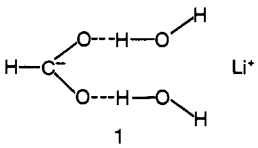
C. Specific Association Effects

In the context of this review *specific association* implies that the solute and solvent molecules have preferential sites of affinity. In such cases classical electrostatics is not generally sufficient to describe the interaction because the solute–solvent "complex" must be treated as a distinct entity. The formation of new chemical species, such as by charge transfer or hydrogen bonding would be expected to lead to much greater changes in the molecular electronic structure than the longer range electrostatic interactions discussed in the previous section. Furthermore, this has the effect of producing more dramatic changes in the coupling constants.

The increases in the ^{13}C–H coupling constants in $CHCl_3$ and in $CHBr_3$ in going from cyclohexane to dimethylformamide solvents were noted in the previous section and have been attributed to the effects of weak hydrogen bonding.[13] This may be true for the other compounds in Figure 5 for which the solvent effects deviate significantly from the reaction field results suggested by the dashed line.

The increase in the directly bonded ^{13}C–H coupling constant in acetone has been attributed[14] to hydrogen bonding between the carbonyl group and the solvent, and in acidic solutions the change is attributed to protonation of the acetone molecules. It is interesting to note that the directly bonded ^{13}C–H coupling constants of acetone in cyclohexane and dimethylformamide are identical, thereby ruling out any type of long-range electrostatic model of the type considered in the previous section. However, considerable caution should be used in interpreting these results because of the possibility of internal motion in acetone.[2]

The effects of hydrogen bonding on $^1J(^{13}C\text{–}H)$ have been investigated theoretically by Maciel, *et al.*,[61] using self-consistent perturbation theory in the INDO approximation. In the case of formic acid the authors performed the calculation for the molecular cluster **1** and obtained a value of $^1J(^{13}C\text{–}H)$ = 178.8 Hz, compared with a value of 106.5 Hz for the isolated formate ion. It was concluded[61] that the inclusion of hydrogen bonding effects and the electrostatic field of the cation bring the calculated results into reasonable agreement with the experimental value of 194.8 Hz.[103] It is most interesting to note that similar calculations, which attempted to include hydrogen bonding effects on the ^{13}C–H coupling constant in formaldehyde, gave no improvement.[61] This is consistent with the results of the previous section in which solvent effects of the right order of magnitude were obtained by means of electrostatic models.



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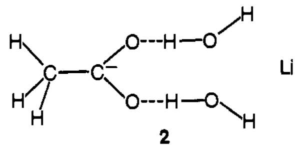
Calculations[61] for the acetate ion in solution with the hydrogen bonding configuration **2** gave a value of ^1J(C–C) = 71.1 Hz, which is substantially larger than the calculated value of 46.0 Hz for the isolated acetate ion. The experimental value of 51.6 Hz[104] in aqueous solution is intermediate between the two calculated values. Calculations for acetic acid were based[60] on the dimer **3**, which gave $^1J_{CC}$ = 80.7 Hz in comparison with the monomer value of 83.2 Hz, and an experimental value of 56.7 Hz.[104]



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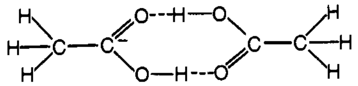

3

The directly bonded ^{15}N–H coupling constant in aniline increases regularly from 78.0 Hz in C_6D_{12} to 82.3 Hz in DMSO-d_6.[105] This increase has also been observed[106] for substituted anilines and is attributed to the hydrogen-bonding ability of the solvent.[105] It appears[107] that the directly bonded ^{15}N–^{13}C coupling constant in pyridine changes sign on protonation of the nitrogen.

In several cases solvent effects on directly bonded coupling constants have been observed for ionic solutes. A most interesting example is the ^{11}B–^{19}F coupling constant of the BF_4^- ion. This coupling constant depends on the nature of the cation as well as the concentration and the solvent.[108] The concentration dependence of the coupling constant, which varies between 1.1 and 4.8 Hz in aqueous solutions of $NaBF_4$, was ascribed to ion pair formation between Na^+ and BF_4^- ions. More recent work[11] has shown that $^1J(^{11}B\text{–}^{19}F)$ in $AgBF_4$ has an opposite sign in water than it has in aprotic solvents. The very small magnitude of $^1J(^{11}B\text{–}^{19}F)$ in comparison with other directly bonded coupling constants is indicative[51,108] of a cancellation between large terms of opposite sign. The situation is completely analogous to that for geminal H–H coupling for which a cancellation of this type combined with inadequacies in the integrals led to calculated values of the wrong sign.[45,46]

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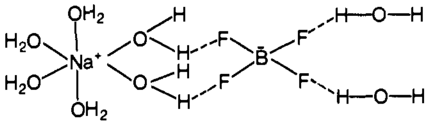
Haque and Reeves[109] have proposed that solvent effects on $^1J(^{11}B-^{19}F)$ are due to hydrogen-bonding effects instead of ion pair formation; *i.e.*, all changes are attributable to B—F•••H—O hydrogen bonding. Gillespie, *et al.*,[11] argue against discarding an inner-sphere ion pair. The authors[11] propose that structure **4** is possible for the ion pairs in solution, and that there are small differences between this and **5**, which could cause changes in the $^{11}B-^{19}F$ coupling constant. It was argued[11] that for the ion pair **4**, the B-F bonds should be more polar than in **5**. As a consequence, the contribution of the corresponding excitation becomes more positive,[29] and the coupling constant should become more positive. Solvent dependence of the $^{11}B-^{19}F$ coupling constant has been noted for some boron trifluoride adducts.[110]



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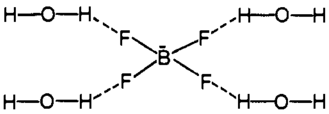

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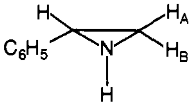
Large solvent-dependent coupling constants have been observed for $^1J(^{119}Sn-^{19}F)$ in $SnF_6{}^{2-}$ in $(C_2H_5N)_2SnF_6$. This coupling constant changes from 1557 Hz in H_2O to 1593 Hz in dimethyl sulfoxide.[111] The apparent reversal of the usual trend arises here because of the negative sign of the magnetogyric ratio for ^{119}Sn. Studies of $^1J(^{75}As-^{19}F)$ coupling in $AsF_6{}^-$ ions[112,113] suggest association with cations rather than with solvent molecules.

The 100-Hz variation of $^1J(^{31}P-H)$ in dimethyl hydrogen phosphite was noted previously.[12] The influence of hydrogen bonding has also been noted[114] to produce an increase in $^1J(^{31}P-H)$ coupling in dialkyl phosphonates. In addition, the change in the ratio $^1J_{PH}/^1J_{PD}$ with solvent indicates different hydrogen bonding effects for the deuterated and the nondeuterated species.

IV. Solvent Effects on Geminal Coupling Constants

A large amount of experimental data for solvent effects on geminal couplings constants has been obtained for H-H, H-F, and F-F coupling constants in substituted ethylenes. Solvent-dependent geminal H-H coupling constants have also been observed in 4-methyl-1,3-dioxolane,[28] hexachlorobicyclo[2.2.1]heptenes,[115] dichlorocyclopropylbenzene,[116] styrene oxide,[117] and styreneimine.[118] In most of these cases the geminal coupling constants decrease in solvents of increasing dielectric constant in agreement with the observations made in unsaturated systems. For this reason it was suggested[115] that the hybridization of the carbon atom was not an important factor for $^2J_{HH'}$. This suggests, further, that solvent effects on geminal coupling constants in flexible systems arise primarily from a direct solvent effect rather than from conformational changes. Similar conclusions were based on the results obtained[119] for the open-chain ethoxy group of dichloroacetal.

It has been suggested that the solvent effect on geminal H-H and H-F coupling constants can be used as a criterion for the determination of absolute signs.[20] For the "normal" direction of the dipole moment vector, *i.e.*, pointing away from the CH_2 moiety, geminal H-H coupling constants should decrease with increasing polarity of the solvent. Thus, positive values decrease in magnitude and negative values become more negative as the dielectric constant of the solvent increases. Possible exceptions have been reported recently for styreneimine,[118] **6**, and the series[120] **7**, in which $^2J(H_A-H_B)$ become more positive with increasing dielectric constant. In the case of **6** it was speculated[118] that specific association effects have the effect of overriding the reaction field effects.



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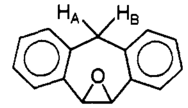
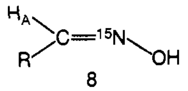


7, X = H, CN, etc.

The signs of the geminal $^{15}N-^{1}H$ coupling constants in the anti, **8**, and the syn ^{15}N-aldoximes, **9**, are opposite,[121,122] as are the solvent effects for the two couplings. The original argument that this effect is opposite to the solvent effect for geminal H-H coupling constants has been reinterpreted in terms of a dipole orientation effect.[8a]



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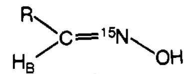

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Experimental work by Laszlo and Speert[19] indicates that the $^{207}Pb-C-H$ and $^{119}Sn-C-H$ geminal coupling constants in tetramethyllead and tetramethyltin are well correlated with interactions of the dispersion types. Measurements were performed in compounds which differed markedly in their refractive indices, but differed only slightly in dielectric constant. The magnitudes of the effects are of the same order of magnitude as the reaction field effects on other types of geminal coupling constants. Thus, the correlation with the "dispersion factor" is excellent, but the reasons for this are obscure.

A. Mechanisms for Electrostatic Interactions

Qualitative descriptions[28-30] of solvent effects on geminal coupling constants have been based on the qualitative molecular orbital model for a CH_2 fragment, which was proposed by Pople and Bothner-By[53] to discuss substituent effects on this type of coupling. Although the conclusions of the earlier descriptions[28-30] are unchanged, the arguments are somewhat modified here to

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TABLE VI. Geminal H–F Coupling Constants (Hz) in Mono-, Di-, and Trifluoroethylenes Dissolved in Solvents of Increasing Polarity

No.	Solvent	$H_2C{=}CHF^a$	*cis*-$HFC{=}CHF^b$	*trans*-$HFC{=}CHF^b$	$HFC{=}CF_2{}^b$
1	Cyclohexane	84.67	71.84	75.10	70.51
2	Carbon tetrachloride		71.80	75.05	70.59
3	Carbon disulfide		71.76	75.06	70.58
4	Chloroform-*d*	85.49	72.01	75.14	70.61
5	Dichloromethane		72.73	75.17	70.73
6	Acetone	86.14	72.73	75.10	70.39
7	2-Nitropropane		72.56		70.43
8	Dimethylformamide	86.47	72.76		70.08
9	Acetonitrile		72.80	75.30	
10	Nitromethane		72.63		70.55
11	Trifluoroacetic acid	86.31	72.50	75.46	70.92
12	Dimethyl sulfoxide	86.54	72.67	75.03	69.93

[a] Reference 20. [b] Reference 25.

take account of the solvent-induced changes which would be expected in the total electronic distribution of the solute molecules. These discussions are based on all-valence electron calculations in the semiempirical INDO approximation.[60] As representative examples, consider formaldehyde and fluoromethane, for which the charge redistributions in a uniform (reaction) field of 10^5 esu/cm^2 are depicted in Figure 3. The numbers in each case denote the *changes* in the calculated charge densities with and without the applied field, which is in the same directions as the dipole moment vectors. In the case of formaldehyde the greatest effect of the field is to move charge density from the $2p_x$ orbital on carbon to the $2p_x$ orbital on oxygen *via* the π bond, which is out of the plane of the figure. Within the CH_2 moiety the major effect is transfer of charge from the region of the hydrogen atoms to the $2p_y$ orbital of carbon.

The example of formaldehyde provides a particularly interesting case since it exhibits all of the features associated with geminal H–H coupling and provides a critical test of the applicability of the reaction field model. The nodal behavior of the ten molecular orbitals is crudely depicted in Figure 4a. The ordering of the energy levels in Figure 4b was based on the INDO calculations,[58] and the orbital designations are those appropriate to C_{2v} symmetry.

As noted previously,[58] the major effect of applying a uniform electric field parallel to the C–O bond arises from the contributions of the $1b_1 \rightarrow 4a_1$ and $1b_1 \rightarrow 3b_1$ virtual excitations which occur in the perturbation sum in eq 4 and 5. Contributions from these virtual excitations are of positive and negative sign, respectively. From Figures 3 and 4a it should be clear that the application of an electric field along the C–O bond will have the effect of removing electron density from the region of the two hydrogens of formaldehyde. This will decrease the coefficients of the 1s atomic orbitals in the $1b_1$ MO in Figure 4a. Because of the orthonormality of the MO's, the coefficients in the other MO's of the same symmetry will be increased accordingly. As a result, the $1b_1 \rightarrow 4a_1$ virtual transition will make a greater contribution than the $1b_1 \rightarrow 3b_1$ transition to the overall value of $^2J_{HH'}$. Thus, the effect of the field will be to give a less positive value of the coupling constant. This is in agreement with the experimental data.[123] On this basis it could be concluded[28-30] that the geminal coupling constant should always be shifted toward more negative values for a solvent reaction field pointing away from the CH_2 (or CH_3) group. From Figure 3 it can be seen that the reaction field has an almost negligible effect on the oxygen lone pair in contrast to the implications of the original qualitative picture.[28]

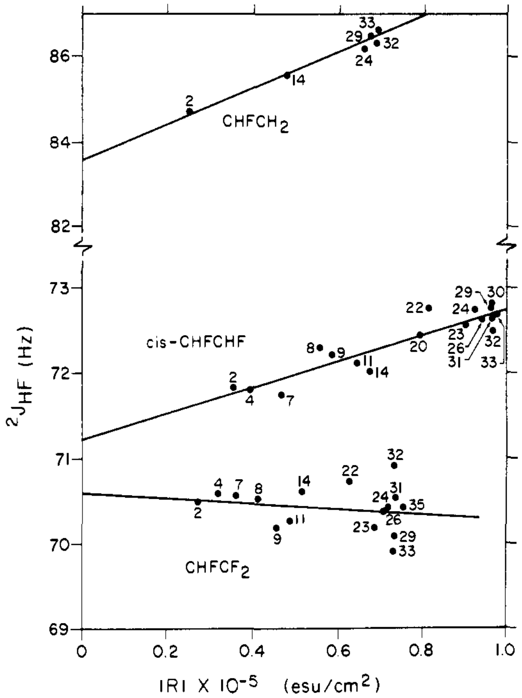

Figure 6. Geminal H–F coupling constants in hertz for fluoroethylene, *cis*-1,2-difluoroethylene, and trifluoroethylene plotted as a function of the magnitude of the reaction field. The numbers for the experimental points designate the various solvents which are identified in Table III. Solid lines are least-squares fits of the experimental points.

The proportionality of the reaction field to the dipole moment vector in eq 11 implies a dipole orientation requirement for this model. In fact, it has been suggested[20] that this may be the main factor controlling solvent effects on geminal coupling constants. This conclusion is based in large part on the solvent effects on $^2J_{HF}$ in the series of fluoroethylenes.[20,25] The experimental data for geminal H–F coupling constants in the series of mono-, di-, and trifluoroethylenes in a variety of solvents of varying dielectric constant are compiled in Table VI and are plotted as a function of the reaction field parameter in Figure 6. The experimental data points are for the various solvents which are numbered according to the scheme in Table III. The solid lines are the least-square fits of the experimental data points. There is an excellent correlation of the experimental data for fluoroethylene and *cis*-

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(123) B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *J. Chem. Phys.*, **39**, 3154 (1963).

1,2-difluoroethylene with the reaction field parameter. Furthermore, for *trans*-1,2-difluoroethylene, which has zero dipole moment, there is essentially no solvent dependence of the geminal H-F coupling constant in Table VI.

The dipole moment orientations of the various fluoroethylenes, which were determined by the SCF-MO method in the INDO approximation, are depicted in Figure 7. Although the results in Table VI exhibit some sort of dipole orientation dependence, there is no theoretical reason for assuming[25] a linear relationship between the solvent shift and the angle between the dipole moment vector and the C-C axis. In terms of the theoretical discussions of section II.B, it would seem that the geminal coupling constant would give a much better correlation with the cosine function of some angles between the dipole moment vectors and the bonds containing the coupled nuclei. Unfortunately there are insufficient data to establish a correlation of this type.

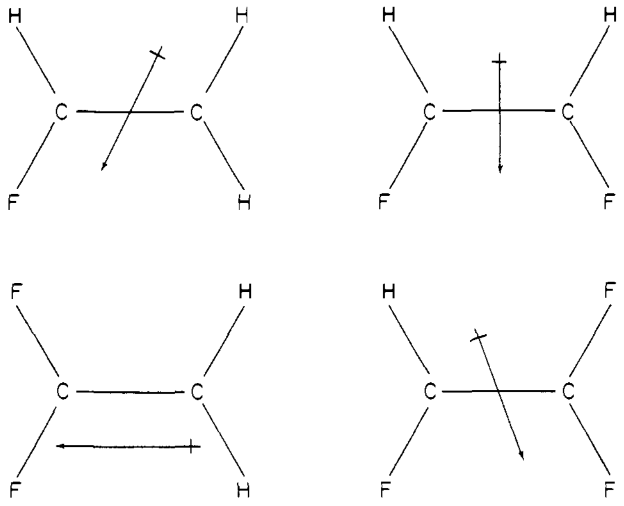

Figure 7. Schematic diagram of the dipole moment orientations in fluoroethylene, 1,1-difluoroethylene, *cis*-1,2 - difluoroethylene, and trifluoroethylene. Dipole moments were calculated by the INDO-SCF-MO method.

B. Results of Theoretical Models

In this section the results of several theoretical models for electrostatic effects on coupling constants are compared with the experimentally inferred data for geminal H-H and H-F coupling constants. In all cases coupling constants were calculated by self-consistent perturbation theory in the INDO approximation of unrestricted SCF-MO theory.[59,60] The electrostatic perturbations due to the solvents were also included as self-consistent perturbations.[58,64,65] The various models for the solvent effects on the coupling constants differ in the assumptions about the nature of the solute-solvent interactions. The details of the various models will be reviewed in the subsequent sections.

A comparison of the calculated results of the various models with the available experimental data is given in Table VII for representative solutes in solvents of widely different polarity. Experimental values in the table are indirect as they were obtained by subtracting the value of the coupling constant measured in cyclohexane from the value measured in the indicated solvent. An exception is the value given for formaldehyde as the reference solvent was tetramethylsilane.[123]

1. The Reaction Field Model

The mathematical details of the reaction field model were discussed in section II.B.1, where it was shown (Figure 1) that coupling constants calculated by self-consistent perturbation theory were very nearly linear functions of the reaction field, **R**. As a consequence, solvent effects were calculated[58] from the equation

$$\Delta J_{\mathrm{NN'}} = 10^{-5}[|\mathbf{R}| - |\mathbf{R}_0|](\Delta J_{\mathrm{NN'}})_E \qquad (37)$$

where $|\mathbf{R}|$ and $|\mathbf{R}_0|$ are the magnitudes of the reaction field in the solvent of interest and in a reference solvent (usually cyclohexane), respectively, and $(\Delta J_{\mathrm{NN'}})_E$ is the difference in the coupling constant calculated for the isolated molecule and that due to the addition of an electric field of 10^5 esu/cm^2.

Calculated reaction field results for solvent effects[58] are entered in the sixth column of Table VII. For many of the solutes in solvents of low dielectric constant the calculated values are within the experimental error (±0.05 to ±0.10 Hz). The results are not as good for more polar solvents such as acetonitrile, dimethylformamide, and dimethyl sulfoxide, but this was not unexpected since the reaction field model is a less satisfactory model for solvents of higher dielectric constant.[26]

A major disparity between the results of the reaction field model and the experimental data in Table VII occurs for formaldehyde (item 1), as the calculated value is an order of magnitude too small and is of the wrong sign. Also, it should be noted that the magnitudes of the geminal H-H coupling constants in 1,1-difluoroethylene and the geminal coupling constants in fluoroethylene are underestimated by the reaction field model. The negative value for $^2J_{\mathrm{HF}}$ of trifluoroethylene (item 8 in Table VII) in dimethyl sulfoxide appears to be spurious, since it is not only inconsistent with the theoretical results, but also with the other experimental values, which are positive. Unfortunately, the sign of this particular solvent effect is crucial for Smith and Ihrig's[20,25] arguments for the dipole orientation requirements in the fluoroethylene series. Dimethyl sulfoxide appears to be different from other aprotic solvents in its electrostatic and dispersion effects.[7]

The correspondence between the results of the reaction field model and the experimental values in Table VII is excellent considering the approximations which are implicit in the model. For example, the assumption of a field which is linear over the dimensions of the solute molecule cannot be applicable in many cases, especially when the coupled nuclei are in widely separated parts of the molecule. Furthermore, the model completely ignores the structure of both the solute and the solvent molecules. Indeed, the only property of the solvent which does enter into the reaction field equations is the dielectric constant of the medium. As a consequence, solvents of the same dielectric constant lead to the same calculated values for the solvent effect. For example, the calculated values of $\Delta J_{\mathrm{HH'}}$ for 1,1-difluoroethylene (item 5 in Table VII) are identical for the solvents dimethylformamide, acetonitrile, and nitromethane. Therefore, an improvement in the reaction field model would include corrections for the nonlinearity of the fields experienced by the coupled nuclei as it seems likely that local effects due to polarization by nearby molecules could lead to electrostatic effects which are quite non-uniform.

2. A Cubic Closest Packed Cluster Model

The second model, which was proposed to provide quantitative information of solvent effects on coupling

TABLE VII. Comparison of Calculated and Experimental Results for Solvent Effects on Geminal Coupling Constants

					$\Delta J_{NN'}$, Hz			
No.	Solute	Solvent	Dielectric constant	Coupled nuclei, NN′	Experiment[a]	Reaction field[b]	Cluster model[c]	Dipole model[d]
1	CH_2O[e]	THF	7.85	HH	−1.72	0.07		
		CH_3CN	35.8	HH	−2.20	0.11	−2.39	−2.58
2	CH_2F_2[f]	Neat	5[g]	HF	0.0	0.14	0.87	0.38
		Acetone	20	HF	0.35	0.35	0.46	0.39
3	CHF_3[f]	Acetone	20	HF	0.	0.77		
		DMSO	46	HF	0.05	0.83		
4	CH_2CHF[h]	$CDCl_3$	4.8	HF	−0.28	−0.05		
				HF	0.82	0.08		
		Acetone	20	HH	−0.26	−0.09	−0.32	−0.09
				HF	1.47	0.14	1.71	1.50
		DMF	35	HH	−0.33	−0.09	−0.09	−0.10
				HF	1.80	0.15	1.76	1.66
5	CH_2CF_2[i]	CS_2	2.6	HH	−0.08	−0.04		
		$CHBr_3$	4.3	HH	−0.24	−0.11		
		$CHCl_3$	4.6	HH	−0.22	−0.12		
		DMF	35.0	HH	−0.76	−0.22	−1.18	−0.14
		CH_3CN	35.8	HH	−0.62	−0.22	−0.85	−0.53
		CH_3NO_2	35.9	HH	−0.64	−0.22	−1.56	−0.66
6	*cis*-CHFCHF[j]	CS_2	4.8	HF	0.06	0.07		
		$CDCl_3$	4.8	HF	0.31	0.07		
		Acetone	20	HF	1.03	0.34		
		DMF	35	HF	1.06	0.37		
		CH_3CN	35.8	HF	1.10	0.37		
		CH_3NO_2	35.9	HF	0.93	0.37		
		DMSO	46	HF	0.97	0.38		
7	*trans*-CHFCHF[j]	CS_2	2.6	HF	−0.04	0.00		
		$CDCl_3$	4.8	HF	0.04	0.00		
		Acetone	20	HF	0.00	0.00		
		CH_3CN	35.9	HF	0.20	0.00		
		DMSO	46	HF	−0.07	0.00		
8	CF_2CHF[h]	CS_2	2.6	HF	0.07	0.06		
		$CDCl_3$	4.8	HF	0.10	0.38		
		TFA	39.5	HF	0.41	0.72		
		DMSO	46	HF	−0.56	0.72		
9	CH_2CHCN[k]	DMF	35	HH	−0.24	−0.06		

[a] With the exception of item 1 "experimental" values were obtained as the differences between the value measured in the indicated solvent and the value measured in cyclohexane. [b] Reference 58. Results for item 6 are previously unpublished results by M. Barfield. [c] Reference 64. [d] Reference 65. [e] Reference 123. [f] Reference 24. [g] See footnote *d*, Table V. [h] Reference 20. [i] Reference 18. [j] Reference 25. [k] Reference 10.

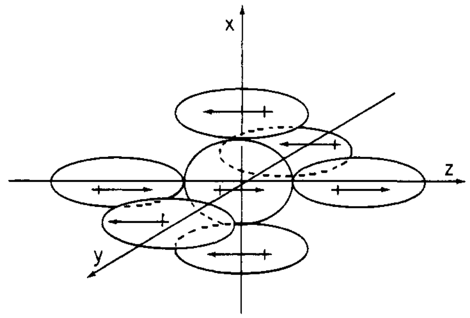

Figure 8. A typical cubic closest packed cluster used in the calculations. The solute molecule is centered at the origin of the coordinate system with its dipole moment vector parallel to the *z* axis. The solvent molecules are arranged around the solute with their dipole moments in the directions indicated.

constants, assumed that the solvent molecules are arranged around the solute molecule in a cubic closest packed array.[64] This arrangement is depicted in Figure 8. Solvent molecules along the *z* axis have their dipole moment vectors parallel to the solute dipole, whereas the solvent molecules along the other two axes have their dipole moments oriented in the opposite direction. Models of this type have been used to discuss[78-80] solvent effects on dipole moments. Although this is an oversimplified model, which ignores the dynamic aspects of the structure of liquids,[72-75] it is one for which computations can be performed with available computational techniques.

For the computational details the original literature reference[64] should be consulted. In its basic form the method includes matrix elements of the perturbation *Q* in eq 12 arising from the attraction integrals between electrons of the solute and the nuclei of the solvents and the intermolecular Coulomb repulsion integrals. Intermolecular exchange integrals were small in comparison with Coulomb integrals for the interatomic distances involved. In all cases the solute and solvent molecules were assumed to be separated by the sum of the van der Waals radii of the closest atoms. Calculated results for representative solute molecules in representative solvents are entered in column seven of Table VII.

It is important to realize the basic differences between this type of calculation[64] and those of Maciel, *et al.*[61] Although self-consistent perturbation theory in the INDO approximation was used throughout, there is a very fundamental difference in the manner in which the intermolecular interactions are included. In the calculations based on the cluster model, the solute and solvent molecules were recognized as distinct groups with strong orthogonality,[124] and the integrals were evaluated explicitly over Slater-type orbitals. In contrast, in the calculations of directly bonded coupling constants by Maciel, *et al.*, the intermolecular interactions are calculated in the same way as the intramolecular interactions in the INDO scheme; *i.e.*, the atomic orbitals are assumed to be orthogonal, but semiempirical parameterization is based on proportionality to overlap integrals.

In most cases the results of the cubic closest packed cluster model are in better agreement with the experimental results than the reaction field values. It is significant to note that the calculated value for formaldehyde in acetonitrile solvent is not only of the right sign, but it is also of the right order of magnitude. The reason for this improvement is of particular interest because the incorrect sign of the reaction field model indicates that a more complex mechanism must be operative in this case. The calculated value for formaldehyde in acetonitrile was -2.35 Hz,[64] which is the difference between the value obtained for the geminal H-H coupling constant in formaldehyde surrounded by six acetonitrile molecules and the value calculated for an isolated formaldehyde molecule. The corresponding changes in the orbital densities for formaldehyde are depicted in Figure 9. A comparison of the calculated densities in Figure 9 with those in Figure 3a, which were based on the assumption of a uniform reaction field, indicates that the electronic density at the hydrogen atoms is increased instead of decreased!

The reaction field model is based on the assumption that polarization occurs only along the *z* axis, *i.e.*, the dipole moment axis. This model can be crudely approximated by performing calculations in which solvent molecules are placed only along the positive and negative *z* axes. For the acetonitrile-formaldehyde-acetonitrile trimer with this geometrical relationship the calculated value for the solvent effect on the geminal H-H coupling constant was 0.50 Hz,[64] which is the same (incorrect) sign obtained by the reaction field model. *A negative sign for the solvent change in the geminal H-H coupling constant for formaldehyde arises only on including the contributions from the solvent molecules which are situated along the other two axes.*

Substantial improvements are also noted for the calculated values of ΔJ_{HF} based on the cubic closest packed cluster model in Table VII. In contrast to the reaction field results, calculated values for ΔJ_{HF} in fluoroethylene are in excellent agreement with the experimental values for the cases of acetone and dimethylformamide as solvents. The series of calculations for 1,1-difluoroethylene are of particular interest. The calculated reaction field results for the geminal H-H coupling constant for this solute dissolved in dimethylformamide, acetonitrile, and nitromethane in Table VII are identical as the three solvents have nearly identical dielectric constants. Although the magnitudes of the experimental values are several times larger, they exhibit a similar constancy. The results of the cluster model calculations exhibit a wider variation than either the reaction field or experimental results. Since the cubic closest packed cluster model gives generally better agreement than the reaction field model, a source of this inadequacy could be that the model is too specific in the interactions between the solvents and the solute molecule. One possible improvement would allow for the effects of rotational and translational motion of the solvent molecules relative to the solute molecule.

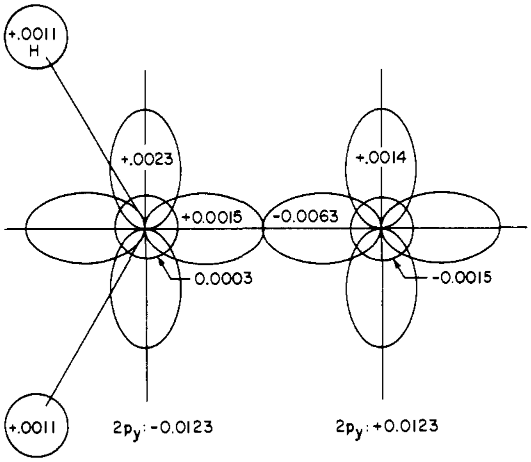

Figure 9. Calculated changes in the orbital densities for formaldehyde when placed in a cluster of six acetonitrile molecules in the arrangement depicted in Figure 8.

3. A Cluster of Rotating Dipoles

A computationally feasible alternative to the cubic closest packed cluster model is one in which the solvent molecules in the cubic closest packed cluster arrangement of Figure 8 are treated as point dipoles. With this simpler description of the solvent molecules, the resulting one-electron integrals can be evaluated analytically. Matrix elements of the operator Q in eq 12 are given by eq 16 with the dipole moment operator located at the centroid of electrical charge of the solvent molecules. The calculated results[125] of such a model greatly overestimate the experimental values and are not reproduced here.

In the next set of calculations[65] a Boltzmann average was taken over all possible orientations of the solvent dipoles; *i.e.*, it was assumed that the solvent dipoles could undergo free rotation about the centroid of electrical charge. These results, which are entered in the last column of Table VII, were obtained as the differences between the values calculated for the solute in the solvent dipole cluster and the values calculated for the isolated solute molecule. Calculated results for this model in Table VII are at least as good as those based on the cubic closest packed model in the previous column.

The results for geminal H-H coupling in 1,1-difluoroethylene (item 5 in Table VII) in the solvents acetonitrile and nitromethane are in better agreement with the experimental values than either of the first two models. This strongly suggests the need for motional averaging effects in any more sophisticated theoretical description of solvent effects. In contrast, the calculated value of $^2J_{\mathrm{HH'}}$ of 1,1-difluoroethylene in dimethylformamide is not in as good agreement as the result of the previous model. One explanation that could be given for the disparity of the results in the three solvents is based on the differences in the shapes of the solvents. Space-filling models indicate that acetonitrile and nitromethane are more nearly spherical than dimethylformamide; hence the assumption of free rotation in the solvent shell should be a much better approximation for the first two. In the case of dimethylformamide restriction of rotation to the plane of the solute gives a much better result (-0.63 Hz[125]) than any of the other models.

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V. Solvent Effects on Vicinal and Long-Range Coupling Constants

In contrast to geminal H–H coupling constants, vicinal H–H coupling constants exhibit a negligible solvent dependence in the absence of solvent-induced changes in conformational populations.[2] The reason for this may be related to the fact that the most important mechanism for vicinal H–H coupling[50] is not sensitive to any type of large cancellation between terms of opposite sign as was the case for directly bonded ^{11}B–^{19}F and geminal H–H coupling constants. Solvent-dependent vicinal H–H coupling constants have been noted in 2,2-dichlorocyclopropylbenzene[116] and in dioxolanes.[6]

The possibility for solvent-induced changes in the populations or rotamers and conformers in nonrigid molecules on vicinal and long-range coupling constants introduces a complexity with which we have not, heretofore, been concerned. In the first section vicinal coupling in essentially rigid systems will be examined. The second section will briefly review the problems associated with solvent effects on vicinal coupling constants in substituted ethanes. Some theoretical estimates will be given of the importance of solvent effects on the coupling constants of some individual rotamers.

Solvent-dependent long-range coupling constants, *i.e.*, coupling over four or more bonds,[55] have been observed in several cases.[14,126,127] However, interpretations of the mechanism for solvent effects on these long-range coupling constants are complicated by the possibilities for conformational equilibria as well as uncertainties regarding the conformational and substituent dependence.[55] As a consequence, there are not yet sufficient experimental data to make any definitive statements about the solvent dependence of long-range coupling constants. However, there is a similarity between geminal coupling and coupling over four bonds in saturated fragments,[128] as several mechanisms of different sign are operative.[55,63] This leads to analogies between substituent effects[128] for the two types of coupling, and perhaps to solvent effects as well.

A. Mechanisms for Molecules of Rigid Geometry

1. Substituted Ethylenes

Representative experimental data for cis and trans vicinal H–H and H–F coupling constants for substituted ethylenes in a variety of solvents of different polarity are compiled in Table VIII. From the table it is noted that vicinal H–H coupling constants are essentially solvent invariant, whereas the corresponding H–F coupling constants exhibit substantial variations. The largest solvent effect on $^3J_{HH'}$ in Table VIII is -0.24 Hz for acrylonitrile in dimethylformamide (item 6 in Table VIII). Because of the inadequacies in the theoretical results for F–F coupling constants, these data were not included in the table.

The trends in the vicinal coupling constant solvent effects are remarkably well reproduced by the various theoretical models which were used in the previous sections. The reaction field results in the sixth column seem to be completely adequate to account for all of the features of cis and trans H–H and H–F coupling with the possible exception of the cis H–F coupling constants in *trans*-1,2-difluoroethylene for which vanishing coupling constants would be expected because of the zero value for the dipole moment of the solute, and a value as large as 0.77 Hz is found in dimethyl sulfoxide. Disparate results are also noted for trans H–F coupling constants in $CDCl_3$ and trifluoroacetic acid in Table VIII.

Smith and Ihrig have suggested[20,25] that the solvent variations for vicinal coupling constants arise from a common origin since surprisingly linear correlations are obtained when the vicinal coupling constants are plotted as a function of each other. Actually, the larger magnitudes and similarities for H–F coupling solvent effects in the fluoroethylene series are not surprising if it is realized that the major effects of the solvent are to polarize the π-electron system. Although protons interact with the π-electron system by a σ–π configuration interaction mechanism, the interaction of the 2p orbitals of the fluorine atoms with the π-electron system could conceivably provide a mechanism for much larger solvent effects. However, the calculated results based on the INDO approximation indicate that the application of the solvent reaction field has an almost negligible effect on the charge densities of the fluorine 2p orbitals which are perpendicular to the planes of the molecules. Much larger effects are observed in the σ-electron framework.

In the case of trans H–F coupling in $CH_2{=}CHFCl$, there is no direct dependence on dielectric constant of the medium,[17] as it was shown that the coupling constant is primarily dependent on some type of dispersion interaction. Since this was not the case for 1,1-difluoroethylene, it would appear that the C–Cl bond is of primary importance in determining the nature of the solvent effect for $CH_2{=}CHFCl$.

2. Aromatic Compounds

With few exceptions[129] coupling constants between protons in aromatic compounds are independent of solvent.[130] However, a number of investigations of fluorinated aromatic compounds[131-136] have been performed. The ortho, meta, and para H–F coupling constants in fluorobenzenes and in substituted fluorobenzenes increase with increasing polarity of the solvent, with variations as large as 0.80 Hz observed for the ortho H–F coupling constant.[136]

Substantial coupling constants between fluorines have been reported[9,131-136] in fluorinated aromatics. An extensive discussion was given recently for the solvent dependence of $^3J_{FF}$, $^4J_{FF}$, and $^5J_{FF}$ in a number of fluorobenzenes.[132] The authors concluded that the mechanism was complex and that it would be unwise to attribute all of the observed variations to a single mechanism.[132]

B. Solvent Effects and Conformational Equilibria

Almost all coupling constants are sensitive to changes in molecular conformation. In particular, the angular de-

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TABLE VIII. Comparison of Calculated and Experimental Results for Solvent Effects on Vicinal Coupling Constants[a]

No.	Solute	Solvent	Dielectric constant	Coupled nuclei NN′	$\Delta J_{NN'}$, Hz			
					Experiment	Reaction field	Cluster model	Rotating point dipole
1	CH_2CHF	$CDCl_3$	4.8	HH (cis)	0.	0.03		
				HH (trans)	−0.12	0.00		
				HF (cis)	0.90	0.65		
				HF (trans)	2.85	3.90		
		Acetone	20	HH (cis)	−0.04	0.04	0.01	−0.03
				HH (trans)	−0.19	0.00	−0.03	−0.02
				HF (cis)	1.42	1.14	0.87	1.69
				HF (trans)	2.85	3.90	3.77	4.68
		DMF	35	HH (cis)	−0.07	0.05	0.01	−0.03
				HH (trans)	−0.21	0.00	0.00	−0.03
				HF (cis)	1.93	1.22	1.39	1.89
				HF (trans)	3.64	4.19	3.64	5.25
2	CH_2CF_2	CS_2	2.6	HF (cis)	0.13	0.12		
				HF (trans)	0.32	0.59		
		$CHBr_3$	4.3	HF (cis)	0.14	0.30		
				HF (trans)	0.81	1.50		
		$CHCl_3$	4.6	HF (cis)	0.17	0.33		
				HF (trans)	0.61	1.62		
		DMF	35	HF (cis)	0.69	0.62	0.85	1.00
				HF (trans)	2.31	3.12	3.36	3.81
		CH_3CN	35.8	HF (cis)	0.50	0.62	0.58	1.36
				HF (trans)	1.71	3.12	1.70	5.69
		CH_3NO_2	35.9	HF (cis)	0.53	0.62	1.08	1.19
				HF (trans)	1.80	3.12	4.80	5.21
3	*cis*-CHFCHF	CS_2	2.6	HH (cis)	0.07	0.00		
				HF (trans)	0.41	0.63		
		$CDCl_3$	4.8	HH (cis)	0.04	0.00		
				HF (trans)	0.68	1.82		
		Acetone	20	HH (cis)	0.02	0.01		
				HF (trans)	1.45	3.23		
		DMF	35	HH (cis)	0.06	0.01		
				HF (trans)	1.86	3.45		
		CH_3CN	35.8	HH (cis)	0.02	0.01		
				HH (trans)	1.46	3.45		
		CH_3NO_2	35.9	HH (cis)	0.04	0.01		
				HF (trans)	1.40	3.45		
		DMSO	46	HH (cis)	0.12	0.01		
				HF (trans)	2.31	3.52		
4	*trans*-CHFCHF	CS_2	2.6	HH (trans)	0.00	0.00		
				HF (cis)	0.04	0.00		
		$CDCl_3$	4.8	HH (trans)	−0.02	0.00		
				HF (cis)	0.16	0.00		
		Acetone	20	HH (trans)	−0.03	0.00		
				HF (cis)	0.56	0.00		
		CH_3CN	35.9	HH (trans)	0.03	0.00		
				HF (cis)	0.53	0.00		
		DMSO	46	HH (trans)	−0.05	0.00		
				HF (cis)	0.77	0.00		
5	CF_2CHF	CS_2	2.6	HF (cis)	−0.05	−0.02		
				HF (trans)	0.24	0.56		
		$CDCl_3$	4.8	HF (cis)	−0.05	−0.04		
				HF (trans)	0.27	1.60		
		TFA	39.5	HF (cis)	−0.07	−0.06		
				HF (trans)	0.11	3.04		
		DMSO	46	HF (cis)	−0.11	−0.06		
				HF (trans)	1.80	3.12		
6	CH_2CHCN	DMF	35	HH (cis)	−0.24	−0.06		
				HH (trans)	−0.01	−0.07		

[a] References to the data in this table are given in footnotes to Table VII.

pendence of the vicinal coupling constant has been most widely used to ascertain molecular conformation. In conformationally nonrigid molecules, such as substituted ethanes containing two or more polar groups, the relative population of the most polar species typically increases in going from a medium of low dielectric constant to one of high dielectric constant.[3-5] A theory of medium effects on conformational equilibria in such systems has been developed and applied extensively by Abraham and coworkers.[3,4] The original references[3-5] should be consulted for the mathematical details and further literature references.

Because vicinal H-H coupling constants are essentially solvent independent, little error is introduced into the analyses which ignore the solvent effects on the coupling constants of the individual rotamers. However, for geminal H-H, vicinal H-F, and F-F coupling constants, this is certainly not true, but such effects are difficult to ascertain along with those associated with conformational equilibria. To provide some indications of the importance of solvent effects on the individual rotamers, the reaction field method was applied to the calculation of the vicinal H-F coupling constants in 1,1,1-trifluoroethane.

With the assumption of the staggered conformation **10** for 1,1,1-trifluoroethane, trans and gauche coupling constants were calculated by the methods described previously,[58] and the results are entered in Table IX. Since the populations of the rotamers for this molecule should be equal, the solvent dependence of the vicinal H-F coupling constant can be obtained from the equation

10

$$\langle \Delta J_{\mathrm{HF}} \rangle_{\mathrm{av}} = (1/3)[\Delta J_{\mathrm{HF}}{}^{\mathrm{trans}} + 2\Delta J_{\mathrm{HF}}{}^{\mathrm{gauche}}] \quad (38)$$

Average results based on eq 38 are entered in the last column of Table IX. The solvent dependence of $^3J_{\mathrm{HF}}$ in saturated systems is by no means negligible, and it is very strongly conformation dependent. Since the calculated reaction field results for cis and trans H-F coupling in substituted ethylenes are seldom in error by more than a factor of 2, even in solvents of high dielectric constant, it is reasonable to expect a comparable degree of confidence for the theoretical results in Table IX.[137] Therefore, in contrast to vicinal H-H coupling constants in ethanic systems, it is essential to consider the solvent effects on the vicinal H-F coupling constants in conformationally nonrigid systems.

VI. Summary

Substantial progress has been achieved in understanding the factors which are responsible for solvent dependence of nuclear spin-spin coupling constants. In most cases solvent effects amount to only a few per cent of the total value of the coupling constant. However, the large solvent variations which are observed in cases such as the directly bonded ^{11}B-^{19}F coupling in BF_4^- and the geminal H-H coupling in α-chloroacrylonitrile are attributable to the fact that the small values for these constants are due to cancellations between large terms of opposite signs. Since the solvents effect these terms differently, there is a large change in the coupling constants. In other cases large solvent effects arise because of the electronic rearrangements associated with specific association of solute and solvent molecules.

TABLE IX. Calculated Solvent Dependence of the Vicinal H-F Coupling Constant in 1,1,1-Trifluoroethane (Reaction Field Model)

No.	Solvent	$\Delta J_{\mathrm{HF}}{}^{\mathrm{trans}}$, Hz	$\Delta J_{\mathrm{HF}}{}^{\mathrm{gauche}}$, Hz	$\langle \Delta J_{\mathrm{HF}} \rangle_{\mathrm{av}}$,[a] Hz
1	Carbon disulfide	0.40	0.02	0.15
2	Chloroform-*d*	1.16	0.07	0.44
3	Acetone	2.05	0.13	0.77
4	Dimethylformamide	2.19	0.14	0.82
5	Acetonitrile	2.20	0.14	0.82
6	Nitromethane	2.20	0.14	0.82
7	Dimethyl sulfoxide	2.24	0.14	0.84

[a] Calculated results based on eq 38 and the theoretical methods of ref 58.

Dispersion effects on coupling constants are especially important in cases in which the orbital terms in the electron-nuclear Hamiltonian are expected to make a substantial contribution to the coupling constant. In general, it appears that contact coupling constants, *i.e.*, H-H, H-F, and C-H coupling constants can be adequately interpreted in terms of either electrostatic effects, specific association effects, or both.

If specific association effects are not of major importance, the solvent dependence of directly bonded C-H coupling constants can be interpreted both qualitatively and quantitatively in terms of electrostatic models for the interaction between solute and solvent. However, the mechanism for directly bonded coupling is not implicit in the consideration of an isolated C-H bond or a CH_2 fragment since it is necessary to include the effects of removal of electron density from the C-H bonding region. Some progress has been made also in the interpretation of specific association effects. For example, the effects of hydrogen bonding can be examined by means of approximate self-consistent perturbation theory in which the intermolecular interactions are placed on the same approximate quantum mechanical footing as the intramolecular interactions.

The solvent dependence of geminal H-H and H-F coupling constants are well correlated with the reaction field model. However, the use of this property as a criterion for absolute signs must be applied cautiously in the light of recent exceptions to the general trend. Formaldehyde provides an interesting exception to the generally favorable theoretical results obtained by means of the reaction field model and SCF-FPT theory, but the solvent dependence of the geminal coupling in formaldehyde is adequately reproduced by the cubic closest packed cluster model. The good agreement is attributable to the fact that the solvent molecules perpendicular to the solute dipole moment give a sufficiently negative contribution to more than cancel the positive value arising from solvent molecules aligned along the dipole moment axis.

The solvent effects on the geminal H-H coupling of 1,1-difluoroethylene in the solvents dimethylformamide, acetonitrile, and nitromethane constitute a most interesting series. The reaction field results for this case are identical in magnitude, but are several times smaller than the experimental values, whereas the cubic closest packed cluster model exhibits a spread in values. The inclusion of motional averaging of the solvent molecules brings the results into better agreement.

The vicinal coupling constant solvent dependence can be adequately correlated by the various theoretical mod-

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(137) After this article was submitted for publication Dr. S. L. Smith pointed out the existence of some previously unpublished experimental results[138] for $\Delta J_{\mathrm{HF}}{}^{\mathrm{trans}}$ for some bicyclo[2.2.1]heptanes in Table 25 of ref 8a. For example, a value of 1.21 Hz is reported for the vinyl fluoride Diels-Alder adduct in dimethyl-d_6 sulfoxide.

(138) A. M. Ihrig, Ph.D. Thesis, University of Kentucky, 1968.

els. In contrast to geminal H–H coupling, vicinal H–H coupling constants in unsaturated and aromatic systems exhibit a negligible solvent dependence. This is consistent with the fact that vicinal H–H coupling constants are rather well accounted for by a single mechanism. Because of the insensitivity of vicinal H–H coupling constants to solvent, it is a good approximation to neglect this factor in those cases in which conformational equilibria is possible. However, vicinal H–F coupling constants exhibit a substantial solvent dependence, and the neglect of this in such studies would give spurious results.

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