with the predicted value of 22. From the slope we calculate that amount of Cu(I) absorbed on platinum at 0.1 V to be 0.15$_8$ mC/cm^2.

In an earlier study in 0.5 *M* HCl solutions known to contain 10^{-6} *M* Cu(I) or less, we found[8] that 0.15 mC/cm^2 of Cu(I) was adsorbed at platinum at 0.0 V. These experiments were performed at a rotating platinum disk electrode using the chronopotentiometric and linear scan voltammetric techniques. The results obtained in this work in concentration range 10^{-4} to 10^{-3} *M* Cu(I) and Cu(II) yield the same value for the amount of adsorbed Cu(I). At millimolar levels of Cu(II), i_d–t curves (Figure 8) suggest the presence of adsorbed Cu(II).

All our results are in agreement with those of Bowles[13] who used a radioisotope technique to demonstrate the adsorption of a monolayer of some copper species at potentials more negative than 0.15 V.

Conclusion

The excellent agreement between the theoretical i_d–t and i_r–t curves for an adsorbed species and the corresponding experimental curves obtained in Cu(I) and Cu(II) solutions in 0.5 *M* HCl suggests that the ring–disk electrode technique will prove to a very powerful and useful method to study adsorption processes at solid electrodes.

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Intermolecular Radical–Solvent Hyperfine Coupling in Fluorocarbons

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Abstract: Experimental dynamic nuclear polarization measurements at 74 G for a large number of fluorocarbon solutions containing free radicals led to four empirical conclusions independent of the system chosen for study: (1) protons in C–H bonds exhibit no detectable contact coupling in any solution; (2) aliphatic fluorocarbons are less positively enhanced than aromatic fluorocarbons in similar solutions; (3) nmr enhancements for aromatic fluorocarbons generally increase with fluorination; and (4) sterically well-shielded radicals give rise to large negative enhancements whereas poorly shielded radicals yield large positive enhancements. These trends are interpreted in terms of differences in intermolecular hyperfine coupling and complexation tendencies based on LCAO–MO calculations for three generalized radical–solvent collision types. Plane–plane collisions between aromatics are shown to be most effective in producing spin density at solvent nuclei; edge-on π collisions are least effective for all types of molecules. In addition, we show that radical–solvent hyperfine couplings are of the order of 1 G for all systems. This leads to the conclusion that differences in solvent spin density of approximately 10^{-3} electrons can account for the entire range of contact coupling observed and demonstrates the usefulness of dynamic nuclear polarization for the study of weak intermolecular interactions.

Recent studies of dynamic nuclear polarization (Overhauser effect) in dilute organic free radical solutions led to a number of interesting conclusions. Ultimate nmr signal enhancements, obtained by pumping radical epr signals, were shown to be sensitive to the nature and detailed chemical environment[1,2] of the resonating nucleus. In particular, protons invariably gave rise to large negative enhancements independent of the free radical or proton-containing solvent used, while for fluorine nuclei in similar solutions a wide range of enhancements was observed. The degree of ^{19}F polarization was then related to steric shielding in the free radical and to molecular properties of the fluorocarbon solvents based on pure dipole–dipole interactions for protons and varying degrees of scalar interaction for fluorine.

Two mechanisms[2] were proposed to account for the different degrees of fluorine scalar coupling: exchange polarization, after the manner of intramolecular coupling on free radicals, and transient complex formation. Physically, both mechanisms should lead to variations in the intensity of scalar interaction and in the scalar correlation time. On the basis of multifield dynamic polarization measurements,[3] we have previously shown that independent fluorine dipolar and scalar correlation times are necessary to characterize radical–fluorocarbon systems and that a relationship exists between scalar correlation time and observed enhancement. The purpose of the present communication is to extend our low-field experimental results to enable us to understand better the degree to which radical and solvent affect enhancement and to offer a molecular orbital interpretation for dynamic nuclear polarization results based on explicit radical–solvent interactions.

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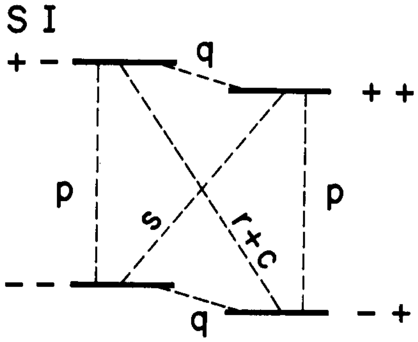

Figure 1. Spin states and relaxation transitions for weak-field electron–nucleus interaction.

Theory

In typical dilute free radical solutions, most solvent nuclei are far removed from a radical at any given time. However, molecular diffusion (collision frequency typically 10^{11} sec^{-1}) brings all solvent molecules near an odd electron several times during the nuclear relaxation time (typically 0.5 sec in our solutions). Hence, except for multiple complex formation, solvent molecules are unaware of their competition for the electron and we may consider a single nucleus interacting with a single electron.

Spin states for a radical–solvent pair during collision, shown in Figure 1, are labeled according to the spin quantum number of the electron (S) and that of the nucleus (I). Pure eigenstates are shown for simplicity; in actuality, they may be more complex. Relaxation transition p corresponds to the epr signal, q to the nmr signal, while r, s, and c are cross relaxations. The transitions may be divided into two types: dipolar and scalar. Dipolar relaxation transitions p, q, r, and s are modulated by translational and rotational motions between radical and solvent dipoles while the scalar or contact transition c is modulated by molecular motions which cause a change in overlap of the electronic and nuclear wave functions as the species collide in solution. Steady-state dynamic nuclear polarization is produced when electron transitions parallel to p are stimulated by a strong radiofrequency source. This tends to equalize the populations n_{+-}, n_{--} and n_{++}, n_{-+}. The nmr signal, which is proportional to the population difference $(n_{+-} + n_{--}) - (n_{++} + n_{-+})$, will now depend upon the relative magnitudes of q, $r + c$, and s according to the relation[2]

$$G = \frac{A}{A_0} - 1 = \frac{\gamma_e}{\gamma_n}\left(\frac{r - s + c}{2q + r + s + c}\right)\left(1 - \frac{T_1}{T_B}\right)S_e(P) \quad (1)$$

Here, A is the enhanced signal amplitude; A_0 is the normal nmr signal; γ_e and γ_n are the magnetogyric ratios of the electron and nucleus, respectively; T_B is the nuclear relaxation time for the pure solvent; T_1 is that for the radical-containing solution. $S_e(P)$ is the electron saturation function and is dependent upon the nature of the epr signal. To place all systems on a comparable scale, values of G are usually extrapolated to infinite power ($S_e(P) \rightarrow 1$) and infinite radical concentration ($T_1 \rightarrow 0$). We then obtain the extrapolated enhancement

$$G_{\infty,\infty} \equiv U_\infty = \frac{\gamma_e}{\gamma_n}\left(\frac{r - s + c}{2q + r + s + c}\right) \quad (2)$$

For a vanishingly small applied field, the frequency spectrum of molecular motions modulating the spin–spin coupling is white; that is, molecular frequencies corresponding to the various energy differences in Figure 1 are all equally present. In that case, q, r, and s are proportional to 3, 2, and 12, respectively, and measurement of U_∞ leads to a unique scalar transition probability c. As the field is increased, the nature of the motion frequency spectrum must be taken into account and the relationship between q, r, and s is less simply defined. We assume that all solutions are characterized by a dipolar correlation time of 3×10^{-11} sec, whence, from dipolar diffusion curves,[4] $(q/3) = (r/1.6) = (s/9.6)$ at 74 G. Now, c at 74 G is uniquely determined *via* eq 2. If $c = 0$, $U_{\infty F}$, the extrapolated enhancement for fluorine nuclei, becomes -330 at 74 G; as $c \rightarrow \infty$, $U_{\infty F} \rightarrow +660$. For protons, the corresponding values are -310 and $+620$.

Two physical models have been proposed to account for the scalar transition probability: diffusion and sticking. The diffusion model[5] leads to a scalar transition probability

$$c(\omega) = \frac{n_s \pi \mathcal{A}^2 d^3}{2\lambda^2 D(\omega\tau_s)^{1/2}} \times \{1 + \exp(\omega\tau_s)^{1/2}[\sin(\omega\tau_s)^{1/2} - \cos(\omega\tau_s)^{1/2}]\} \quad (3)$$

where $\mathcal{A}$ is the isotropic hyperfine coupling constant; d is the radical–solvent distance of closest approach; n_s is the radical concentration per cubic centimeter; D is the average diffusion constant; τ_s is the scalar correlation time; and ω is the Larmor frequency of the transition. The quantity λ describes the rate of energy decline with distance according to the relation

$$\mathcal{A}_{ij} = \frac{\mathcal{A}d}{r_{ij}} \exp[-\lambda(r_{ij} - d)] \quad (4)$$

where $\mathcal{A}_{ij}$ is the instantaneous value of the hyperfine coupling at a radical–solvent distance r_{ij}. At zero field, eq 3 reduces to

$$c(0) = \lim_{\omega \rightarrow 0} c(\omega) = \frac{n_s \pi \mathcal{A}^2 d^3}{2\lambda^2 D} \quad (5)$$

and since $\tau_s \equiv d^2/D$

$$c(0) = \frac{n_s \pi \mathcal{A}^2 d \tau_s}{2\lambda^2} \quad (6)$$

The derivation of eq 6 is based on the assumptions that $\lambda d \gg |\omega\tau_s|^{1/2}$ and that the scalar correlation time equals the corresponding dipolar time, τ_d. We have previously investigated the second assumption and have shown that it is not valid to an order of magnitude for some fluorocarbon systems which show large scalar rates.[3] The first assumption will be considered later when λ is estimated and it will be shown that this assumption may not be valid at high fields. However, since the values we obtain for c at 74 G are close to the corresponding values of $c(0)$, we expect the first condi-

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(4) K. D. Kramer and W. Muller-Warmuth, *Z. Naturforsch.*, **19a**, 375 (1964).

(5) P. S. Hubbard, *Proc. Roy. Soc.* (London), **A291**, 537 (1966).

tion to be satisfield at our field strength. The second assumption becomes less damaging if reasonable values for τ_s can be obtained.

The sticking model[6] leads to a less complicated expression for c

$$c(\omega) = \frac{\mathcal{A}^2\tau_s}{1 + \omega^2\tau_s^2} \qquad (7)$$

which at zero field reduces to

$$c(0) = \mathcal{A}^2\tau_s \qquad (8)$$

Thus, for the low-field approximation, both theories predict the same functional dependence of c upon $\mathcal{A}$ and τ_s. However, a modified diffusion model has been shown[3] to give correlation times which are in better agreement with observed multifield data for a number of systems and we shall rely on it here implicitly whenever comparisons of hyperfine coupling constants are offered.

Coefficients obtained from LCAO-MO calculations have been used extensively to interpret hyperfine coupling constants obtained from epr spectra of organic free radicals.[7] If the odd electron is confined primarily to a radical π MO, the hyperfine coupling of the electron with a given nucleus can be related to the spin densities in the π MO by the expression[8]

$$\mathcal{A}_j = \sum_i Q_i\rho_i \qquad (9)$$

where ρ_i is the spin density in an atomic $2p\pi$ orbital and the Q's essentially describe the attenuation of unpaired spin density in going from the π to the σ system. This intramolecular exchange polarization mechanism has also been used to interpret solvent effects on the epr spectra of organic free radicals.[9,10] There, the solvent was assumed to alter the electronegativity of a radical functional group. Consequently, different radical spin density distributions were obtained for different solvents and these were compared with the observed hyperfine coupling constants *via* eq 9.

We are interested primarily in the delocalization of spin density on solvent nuclei as the species collide and so cannot depend entirely on this simplified intramolecular treatment. Instead, we consider radical-solvent collisions explicitly from which we obtain small spin densities in fluorocarbon π systems; thus the mechanism incorporates "spin transfer." Relative estimates of $\mathcal{A}$ for various systems can then be obtained from eq 9 and compared with observed values for c.

Experimental Section

A. Dynamic Polarization. All dynamic polarization measurements were taken at 24 ± 2° in a primary magnetic field of 74 G for which the resonating frequencies of protons, ^{19}F nuclei, and electrons are 319.7 Kc, 300.8 Kc, and 210.7 Mc, respectively. At this low field, all spectra were broad line; that is, no chemical shifts or spin-spin couplings were observed. Radical epr lines were stimulated by a 100-W transmitter, which, at maximum power, gave a secondary field of 0.7 G. A marginal oscillator, usually adjusted for adiabatic rapid passage, was used for nmr detection. Nuclear relaxation times were measured by observing signal growth and decay after switching the transmitter. A detailed treatment of the apparatus is given elsewhere.[1]

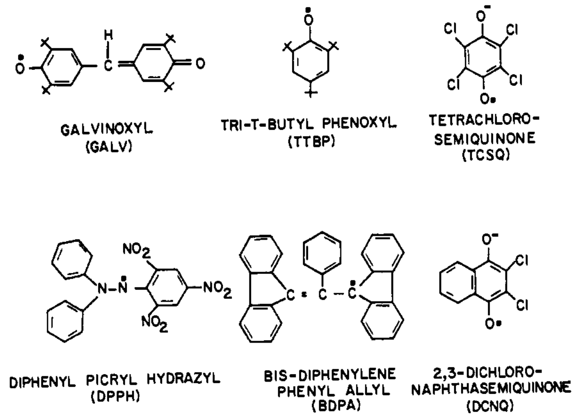

Figure 2. Structures of radicals used.

Six radicals were chosen for tests: galvinoxyl (GALV), 2,4,6-tri-*t*-butylphenoxyl (TTBP), diphenylpicrylhydrazyl (DPPH), bisdiphenylenephenylallyl (BDPA), tetrachlorosemiquinone (TCSQ), and 1,2-dichloronaphthasemiquinone (DCNQ). Structural formulas for these radicals are shown in Figure 2. The radicals were chosen on the basis of preliminary results for hexafluorobenzene and 1,1,1-trichloro-2,2,2-trifluoroethane which led to a wide range of observed enhancements;[1] hence, they should be a useful set for determining the nature of radical-solvent interactions in fluorocarbons. Fluorocarbon solvents were chosen on the basis of their compatibility with the radicals and for the trends they were intended to isolate. Additional solvents were sometimes necessary to dissolve or stabilize the radicals, but the effects of these solvents upon enhancement have been shown[1,2] to be small except for a few cases.[3]

The epr lines from all samples except those containing DPPH were sufficiently narrow so that direct power extrapolations could be performed; for DPPH, the ratio method[2] was used to obtain ultimate enhancements. TTPB, TCSQ, and DCNQ solutions were all nominally 0.1 *M* in the radical precursor, while for GALV, DPPH, and BDPA, 0.01 *M* quantities of the radicals themselves were used. The preparations and properties of GALV, DPPH, BDPA, and TTBP have been discussed previously.[1] TCSQ and DCNQ were prepared by reduction of the appropriate quinone with glucose in basic solution. The preparative procedure was as follows: 0.1 mol of the quinone was mixed with 0.2 mol of glucose in a small quantity of methanol; addition of 0.4 mol of NaOMe then led to a deep red solution which contained free radicals and was stable for a period of days when diluted with fluorocarbons. Other solvents and radical precursors were tried, but the solutions were much less stable and decomposed in a matter of minutes. In particular, stable radicals could not be prepared from benzoquinone,[11] tetrabromoquinone, dichloroquinone, or tetrafluoroquinone. TCSQ prepared by this method gave more concentrated solutions than could be obtained by air oxidation of the hydroquinones; similar experimental results were obtained from both procedures for test samples indicating the presence of the same radical. All samples were degassed and sealed in glass.

B. Molecular Orbital Calculations. Molecular orbital results were obtained using an LCAO-MO method described in detail previously.[12] All overlap and kinetic energy integrals were calculated explicitly. Diagonal potential energy matrix elements (α) were taken from those of smaller, related molecules for which self-consistent field calculations had been performed; values of α used for the various types of bonds encountered are shown in Table I. Slater exponents were used for all orbitals except H_{1s} which was given a value of 1.2. Off-diagonal potential energy matrix elements were evaluated by means of a modified Mulliken approximation using constants given previously.[12] Owing to the size of the systems, the original computer program was modified so that π-only calculations could be performed. For aliphatics, π-only calcula-

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(7) A. Carrington and J. Dos Santos-Veiga, *Mol. Phys.*, **5**, 285 (1962); N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

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Table I. Diagonal Potential Energy Matrix Elements

Bond	Atom	α^a	$\alpha_{2p\sigma}$	Taken from[b]
C–H	H	−0.537		C_2H_6
C–H (aliphatic)	C	−0.364		C_2H_6
C–H (aromatic)	C	−0.146	−0.480	C_2H_4
C–O (aromatic)	C	−0.199	−0.580	H_2CO
C–F (aliphatic)	C	−0.544		HC(O)F
C–F (aromatic)	C	−0.250		HC(O)F
C–O	O	−0.179	−0.503	H_2CO
C–F (aliphatic)	F	−0.462		HC(O)F
C–F (aromatic)	F	−0.472		HC(O)F

[a] Values are $\alpha_{2p\pi}$ for aromatics, α_{2p} for aliphatics, and α_{1s} for hydrogen. [b] SCF calculation from which α was taken.

Table II. ^{19}F Nmr Enhancements for Aliphatic Fluorocarbons[a]

	CF_3CCl_3			Perfluorodecalin			$CF_3C_6H_5$		
Radical	Additional solvent	$U_{\infty F}$	c_F	Additional solvent	$U_{\infty F}$	c_F	Additional solvent	$U_{\infty F}$	c_F
TTBP	80% acetone	−280	1.0	5% acetone, 90% CCl_4	−275	0.9	80% acetone	−240	1.5
GALV	80% acetone	−225	1.9	5% acetone, 90% CCl_4	−225	1.9	80% acetone	−230	1.8
DPPH	50% acetone	−235	1.8	5% acetone, 90% CCl_4	−200	2.4	80% acetone	−180	2.8
BDPA	80% acetone	−165	3.6				80% acetone	−135	3.8
DCNQ	80% methanol	−195	2.5				80% methanol	−110	4.6
TCSQ	90% acetone	−240	1.6				80% acetone	−150	3.6
TPPY	80% acetone	−80	5.4				50% acetone	−30	7.0
WBPC	75% acetone	+40	9.5				50% acetone	+120	13.1

[a] TPPY = triphenylpyrylyl; WBPC = Wurster's blue perchlorate.

Table III. ^{19}F Nmr Enhancements for Halo-Substituted Fluorobenzenes[a]

	C_6F_5Cl		C_6F_5Br		C_6F_5I	
Radical	$U_{\infty F}$	c_F	$U_{\infty F}$	c_F	$U_{\infty F}$	c_F
TTBP	−180	2.8	−185	2.7	−200	2.4
GALV	−185	2.7	−160	3.3	−120	4.4
DPPH	−25	7.2	−35	6.8	−50	6.3
	p-C_6H_4FCl		p-C_6H_4FBr		p-C_6H_4FI	
TTBP	−195	2.5	−180	2.8	−140	3.8
GALV	−170	3.1	−160	3.3	−155	3.4
DPPH	−145	3.7	−145	3.7	−155	3.4

[a] Additional solvent 50% benzene in all cases.

tions were not feasible and the full minimum basis set (1s for H; 1s, 2s, and 2p for C, O, and F) was used. For aromatic systems which were strictly coplanar, the π-only procedure gave the same results as would the original program since the π and σ systems are symmetry distinct.

Of the parameters used, those for F are most likely to be inaccurate; for this element, 3d electrons may be important and the model SCF compound somewhat inappropriate. In addition, the free radical parameters used came from neutral compounds and therefore the energy of the orbital containing the odd electron is likely to be inaccurate. But, since the coefficients should give results at least as accurate as those obtained by Hückel calculations, and since we are only interested in comparisons between fluorocarbons with the same radical, we may expect to obtain the correct order of magnitude for the intermolecular hyperfine interaction and an order for fluorocarbons which compares favorably to that found experimentally.

Results and Chemical Interpretation

Ultimate extrapolated enhancements and fluorine scalar rates calculated from eq 2 assuming $(q/3) = (r/1.6) = (s/9.6)$ are shown in Table II for a selection of saturated fluorocarbons with the six radicals. Similar results for some halo-substituted fluorobenzenes and for a series of fluorobenzenes are given in Tables III and IV, respectively. Proton ultimate enhancements, measured for all proton-containing systems, were found to cluster about the dipolar limit within experimental error and are not shown. Thus there is still little evidence for intermolecular proton scalar coupling in solutions of this type and dipolar interpretations of the coupling suffice. (Scalar coupling has been observed[13] in proton-containing solutions where chemical exchange can occur, but these systems should be treated separately.) For F nuclei, we shall relate observed enhancements to the degree of exchange polarization and complexation.

The results for CF_3CCl_3 and perfluorodecalin show large negative ^{19}F enhancements which vary from radical to radical, but for all systems there is some scalar coupling (scalar rates range from 0.9 to 3.6). For all cases except GALV, enhancements for $CF_3C_6H_5$ are more positive than those for CF_3CCl_3 and perfluorodecalin. On the basis of π-system interactions, this result would be anticipated since we have previously suggested[2] that π interactions are important for the interpretation of dynamic nuclear polarization results. Orbitals of π symmetry are not available for interactions by electron delocalization or complex formation except for $CF_3C_6H_5$. That GALV shows no variation in polarization for these three solvents is consistent with our earlier suggestion[2] that, for that radical, π interactions are expected to be minimal.

Radicals such as TTBP, GALV, and DPPH, which contain well-shielded odd electrons, give rise to more negative polarizations with aliphatic fluorocarbons than do the poorly shielded BDPA, TCSQ, and DCNQ, indicating that steric effects are important. In fact, since aliphatic fluorocarbons are not expected to complex readily with radicals, the enhancement observed for a radical–aliphatic fluorocarbon system may be related to the availability of the odd electron at the radical edge. A steric factor obtained from low-field scalar rates could then be compared semiquantitatively with appropriately averaged radical spin density values obtained from epr spectra. Inversions of the pattern

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(13) R. A. Dwek, J. G. Kenworthy, and R. E. Richards, *Mol. Phys.*, 10, 529 (1966).

Table IV. ^{19}F Nmr Enhancements for Fluorobenzenes

Radical	Additional solvent	C_6H_5F		o-$C_6H_4F_2$		1,2,4-$C_6H_3F_3$		1,2,3,4-$C_6H_2F_4$		C_6F_5H		C_6F_6	
		$U_{\infty F}$	c_F	$U_{\infty F}$	c_F	$U_{\infty F}$	c_F	$U_{\infty F}$	c_F	$U_{\infty F}$	c_F	$U_{\infty F}$	c_F
GALV	None	−195	2.5	−205	2.3	−200	2.4	−205	2.4	−215	2.1	−200	2.4
TTBP	None	−190	2.6	−195	2.5	−155	3.4	−155	3.4	−145	3.7	−120	4.4
DPPH	None	−170	3.1	−170	3.1	−155	3.4	−130	4.0	−95	5.0	−2	8.0
BDPA	None	−115	4.5	−100	4.8	−65	5.8	−55	6.2			+20	9.2
TCSQ	80% methanol	−80	5.4	−110	4.6			−50	6.3			+130	13.5
DCNQ	80% methanol	−105	4.8	−110	4.6			+45	9.7			+310	28.0

obtained might then be related to the degree of complexation for a given system; any trends toward complexation could then be compared to calculated scalar correlation times. Such a treatment would provide a further test of the proposed mechanisms for the interaction and could lead to a better understanding of steric influences and weak tendencies toward molecular aggregation in solution.

The halo-substituted pentafluorobenzenes (Table III) give rise to an interesting effect. For TTBP and DPPH, the order of increasing polarization is $C_6F_5I < C_6F_5Br < C_6F_5Cl$, whereas for GALV, the order is inverted. Our initial interpretation[2] of the order of polarization for these compounds was based on results for DPPH alone. We suggested that the order for DPPH might be due to a steric effect since the larger halogens should be least able to interact with the π system and therefore should give rise to low scalar rates. The results for GALV indicate that the effects are more subtle. This is supported by the results for the p-halo-substituted fluorobenzenes (Table III). For these compounds, the halogen atoms are not in sterically forced positions and therefore we would expect only small differences in polarization. Small differences are observed for GALV and DPPH, but the order of increasing scalar rate changes from p-C_6H_4FCl < p-C_6H_4FBr < p-C_6H_4FI for GALV to p-C_6H_4FI < p-C_6H_4FBr = p-C_6H_4FCl for DPPH. Much larger differences in extrapolated enhancements are observed for TTBP and the same fluorocarbons, while the order of enhancement is similar to that for GALV. Over-all, the results in Table III indicate that subtle substituent effects are highly dependent upon the exact nature of the system. Additional measurements will be necessary to interpret existing trends.

Another measure of the importance of radical and solvent upon enhancement is provided by the results for the fluorobenzenes with the six radicals (Table IV). In general, there is an increase in scalar rate as one goes from mono- to hexafluorobenzene. Further, the spread in contact coupling when the radical is varied becomes greater as polysubstitution is increased: C_6F_6 accentuates radical differences more than C_6H_5F, but the order of increasing scalar rate remains essentially the same regardless of the choice of radical. Thus fluorocarbon molecular properties should be useful for a description of these systems. Polyfluorinated species allow for induced transmission of spin information through the fluorocarbon π system to F atoms removed from the point of radical contact. Also, for relatively planar radicals, collisions for which both molecular planes are eclipsed and parallel could lead to simultaneous intense polarization of all fluorine nuclei and hence to large scalar rates for polyfluorinated species. On a steric basis, both possibilities are supported by the observed results since well-shielded radicals give rise to small variations in nuclear polarization. In the following section, we shall demonstrate that the polyfluorinated benzenes can receive more intense polarization than C_6H_5F during both edge-on and plane–plane collisions.

Our previous results, coupled with those presented here, lead to four general conclusions concerning dynamic nuclear polarization in fluorocarbon solutions which appear independent of the system chosen for study: (1) protons exhibit no detectable scalar coupling in any solution, (2) all aliphatic fluorocarbons are less positively enhanced than aromatic fluorocarbons in similar solutions, (3) enhancements for aromatics generally increase with fluorination, and (4) well-shielded radicals give rise to large negative enhancements while poorly shielded radicals to large positive enhancements. The following discussion is an attempt to interpret these experimental conclusions in terms of the molecular properties of appropriate systems and the theory presented above.

Discussion

Differences in scalar rate for radical–fluorocarbon systems may be attributed to changes in correlation time, hyperfine coupling, or distance of closest approach (eq 6). We have previously shown[3] that fluorocarbon systems with strong scalar coupling are associated with long scalar correlation times in contrast to similar systems with weak scalar coupling where the reverse is true. Here, we attempt to determine the importance of the remaining parameters in eq 6 and to generalize the properties of the radical–solvent encounter.

Ideally, a detailed interpretation of dynamic nuclear polarization results would require an average over many collision attitudes; such a procedure would necessitate Monte Carlo types of calculations which are not feasible for systems of the size considered here. Instead, we distinguish three types of collisions which we consider representative of all types encountered: π collisions, where the solvent and radical molecules are coplanar; σ collisions, where the contact axis passes through nuclei at the edge of solvent and radical molecules and is perpendicular to the radical plane; and, for aromatics, plane–plane collisions, where the molecular planes are eclipsed. The three types are illustrated schematically in Figure 3 for benzosemiquinone interacting with fluorobenzene; notice that, for π collisions, overlap of the 2p electrons comprising the radical π system with the $F_{2p\pi}$ orbital is of the (2p–2p) π type, whereas, for σ collisions, it is (2p–2p)σ. A crude assessment of the relative effectiveness of σ and π collisions for the transmission of spin density to solvent nuclei

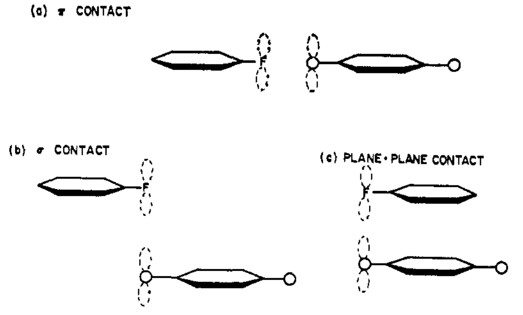

Figure 3. Generalized collision attitudes for fluorobenzene and benzoquinone.

can be obtained from Table V which shows (2p–2p) σ and (2p–2p) π overlap integrals for a F atom separated by a distance r_{ij} from an O atom. At the F···O van der Waal's distance (2.75 Å[14]) where intermolecular effects become important, σ overlap is some nine times greater than π overlap. As a consequence of the angular part of the 2p wave function, this ratio decreases regularly with r_{ij}, but it is always greater than 1. Hence, if spin density is transmitted to F nuclei *via* π-system overlap, we would expect σ collisions to be more effective than π collisions in producing large scalar rates.

Table V. Overlap Integrals for F···O System

r_{ij}	S_σ	S_π	$\lvert S_\sigma/S_\pi \rvert$
2.00	−0.05615	0.00980	5.74
2.25	−0.02839	0.00417	6.81
2.50	−0.01367	0.00173	7.90
2.75	−0.00633	0.00070	9.08
3.00	−0.00284	0.00028	10.2
3.25	−0.00124	0.00011	11.3

A more detailed analysis of the collision process is afforded by analysis of the results listed in Table VI. There, we list appropriate molecular parameters for selected solvents in collision with benzosemiquinone. We limit ourselves primarily to collisions which occur between an O atom of the radical and solvent magnetic nuclei. This is reasonable since the O atoms in quinone and phenolic radicals are associated with large spin densities.[15] Further, this choice allows for the direct interpretation of steric effects associated with large bulky radical side groups. Results for four representative solvents, C_6H_5F, C_6F_6, CF_4, and CH_4, in the three collision attitudes are listed. The quantity r_{ij} describes the distance between the O atom and the nearest solvent magnetic nucleus, d is the molecular center-to-center distance, S_{ij} is the overlap integral for the $O_{2p\pi}$ orbital and the appropriate orbital of the magnetic nucleus (2p for F, 1s for H), and ΔE is the increase in energy of the radical orbital during collision. Spin density on the solvent is measured by the extent to which the radical orbital delocalizes over solvent nuclei; spin densities at F obtained from products of the coefficients of the radical orbital are listed.

Estimation of λ. An estimate of λ can be obtained from the spin densities in Table VI in conjunction with eq 4 and 9. To accomplish this, we should obtain values for $\mathcal{A}_{ij}$, the instantaneous value of the hyperfine coupling at an electron–nuclear distance r_{ij}. These cannot be obtained directly; however, by taking the ratio of $\mathcal{A}_{ij}$ for two values of r_{ij}, the dependence on $\mathcal{A}$ and d can be removed and we obtain

$$\frac{\mathcal{A}_{ij}}{\mathcal{A}_{ij}'} = \frac{r_{ij}'}{r_{ij}} \exp[-\lambda(r_{ij} - r_{ij}')] \qquad (10)$$

From eq 9 we infer that $\mathcal{A}_{ij}$ is proportional to the $F_{2p\pi}$ spin density if that term dominates the sum. Coupling parameters at F have been shown[16] to be some ten times as large as those at C for the C–F bond and this assumption therefore is reasonable. We then obtain the relation

$$\frac{\rho_F}{\rho_F'} = \frac{r_{ij}'}{r_{ij}} \exp[-\lambda(r_{ij} - r_{ij}')] \qquad (11)$$

Average values of λ obtained using eq 11 are shown in Table VII. Reasonable exponential fits of spin density to distance of closest approach could be obtained in all cases except C_6F_6 (σ collision) and CH_4 (π collision). For the former, spin densities at F did not vary monotonically with r_{ij} due perhaps to electronic π interactions between F atoms or difficulties inherent in the MO technique, while for CH_4 (π), the H atom was in the radical orbital node and did not overlap the odd electron. π collisions give rise to values of λ of the order of 6 which are independent of fluorocarbon type, whereas, for σ collisions, the "negative" fluorocarbon CF_4 gives a value of λ larger than that obtained for the more positive C_6H_5F. Plane–plane collisions lead to relatively small λ values, consistent with the "positive" behavior of systems where this type of collision is expected to be present.

From Table VII, an average value of λ for all collision types is approximately 5. This, coupled with the center-to-center distances of closest approach (Table VI) for the various collisions, leads to values of λd in the neighborhood of 30 and permits an evaluation of the assumption that $\lambda d \gg |\omega\tau|^{1/2}$ used to derive results for the diffusion model. At 74 G, ω_e = 211 Mc/sec and, assuming $\tau = 10^{-10}$ sec, $|\omega_e\tau|^{1/2} \cong 0.1$, justifying the assumption. At higher fields, the assumption will not be valid. It has previously been suggested[17] on the basis of high-field dynamic nuclear polarization results that λd must be >1000 in order to justify the approximations made in evaluating scalar spectral densities by the diffusion model. That this is not so may explain the difficulties[3] we have had fitting field-dependent experimental results to this model, particularly for F-containing systems which gave large positive enhancements at low field.

Hydrogen *vs.* Fluorine. To a first approximation, we might expect the intensity of scalar interaction to be related to the square of the isotropic coupling strength of the atoms. For protons, $\mathcal{A}$ = 508 G; for F, 17,200.[18] On this atomic basis, proton scalar cou-

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Table VI. Molecular Orbital Results for Selected Solvents in Collision with Benzosemiquinone[a]

r_{ij}	d	S_{ij}	ρ_H	ρ_F	ρ_{F_o}	ρ_{F_m}	ρ_{F_p}	ΔE rad
a. CH_4 (π)								
2.00	6.40	0	0					0.02864
2.25	6.65	0	0					
b. CF_4 (π)								
2.00	6.02	0.00980		6.95				0.00044
2.25	6.27	0.00417		1.40				0.00008
2.50	6.52	0.00173		0.25				0.00002
2.75	6.77	0.00070		0.05				0.00001
c. C_6H_5F (π)								
2.00	7.39	0.00980		8.5				0.00068
2.25	7.64	0.00417		1.7				0.00014
2.50	7.89	0.00173		0.3				0.00003
2.75	8.14	0.00070		0.05				0.00001
d. C_6F_6 (π)								
2.00	7.39	0.00980		19.1	2.5	0.05	3.0	0.00098
2.25	7.64	0.00417		3.7	0.45	0	0.6	0.00019
2.50	7.89	0.00173		0.7	0.10	0	0.1	0.00004
2.75	8.14	0.00070		0.1	0	0	0	0.00001
e. CH_4 (σ)								
2.00	4.28	0.08431	56.6					0.01656
2.25	4.40	0.05297	26.6					0.00244
2.50	4.53	0.03263	12.5					0.00087
2.75	4.67	0.01979	4.9					0.00028
f. CF_4 (σ)								
2.25	4.60	−0.02839						
2.50	4.72	−0.01367		6.2				0.00039
2.75	4.86	−0.00633		0.50				0.00000
3.00	5.01	−0.00284		0				−0.00002
g. C_6H_5F (σ)								
2.00	5.74	−0.05615		234.4				0.01415
2.25	5.82	−0.02389		49.2				0.00258
2.50	5.93	−0.01367		8.7				0.00029
2.75	6.04	−0.00633		1.2				−0.00002
3.00	6.16	−0.00284		0.05				−0.00001
3.25	6.28	−0.00124		0				0
h. C_6F_6 (σ)								
2.00	5.74	−0.05615		252.8	0.4	0	0.45	0.01420
2.25	5.82	−0.02839		28.7	3.1	0.1	3.8	0.00196
2.50	5.93	−0.01367		0.9	4.7	0.2	5.8	0.00087
2.75	6.04	−0.00633		0.35	3.3	0.1	4.1	0.00036
3.00	6.16	−0.00284		0.85	1.7	0	2.1	0.00016
3.25	6.28	−0.00124		0.65	0.7	0	0.85	0.00009
i. C_6H_5F (plane–plane)[b]								
2.50		−0.01367		133.8				0.04596
2.75		−0.00633		66.8				0.02329
3.00		−0.00284		30.2				0.01102
3.25		−0.00124		12.7				0.00492
3.50		−0.00053		5.1				0.00208
3.75		−0.00022		1.95				0.00084
4.00		−0.00009		0.75				0.00033
j. C_6F_6 (plane–plane)[b]								
2.50		−0.01367		292.5	19.4			0.06367
2.75		−0.00633		181.0	16.6			0.03290
3.00		−0.00284		96.2	10.9			0.01571
3.25		−0.00124		45.1	5.9			0.00704
3.50		−0.00053		19.4	2.8			0.00298
3.75		−0.00022		7.8	1.2			0.00121
4.00		−0.00009		3.0	0.5			0.00047

[a] All spin densities are times 10^4. All energies are given in atomic units (1 au = 27 eV). ΔE rad is the increase in energy of the free radical orbital when the radical is at a distance r_{ij} from the solvent. For C_6H_6 collisions, ρ_{F_o}, ρ_{F_m}, and ρ_{F_p} are spin densities at F atoms *ortho*, *meta*, and *para*, respectively, to the F atom nearest the radical. [b] The r_{ij} column is equal to d.

Table VII. Average Values of λ for Various Fluorocarbons and Collision Types

	CH_4	CF_4	C_6H_5F	C_6F_6
π		6.2	6.4	6.6
σ	2.8	9.8	6.6	
Plane–plane			3.2	3.4

pling is expected to be some three orders of magnitude smaller than corresponding F coupling. Observed proton ultimate enhancements range from −330 to −270 leading to a range of 0.0 to 0.9 for c_H(O). Corresponding values for F in varying chemical environments[1,2] are −275 to +530 with c_F(O) ranging from 0.9 to approximately 100. Hence, atomic coupling parameters give the correct order of polarization but cannot account for more subtle differences in polarization.

For the molecular case, we assume that the odd electron becomes delocalized primarily in the solvent π system during the collision. Now, the hyperfine coupling at a given magnetic nucleus may be related to the spin density in the π MO *via* eq 9. For protons, $Q_C(CH)$ is estimated[16] to be approximately 25 G/electron; that is, one electron in a $2p\pi$ orbital about C would produce a hyperfine splitting of 25 G at the proton in a C–H bond. With F, the situation is more complicated. Spin density in the $F_{2p\pi}$ orbital must be considered and estimates[16] of the coupling parameters vary from -37.5 to -147 for $Q_C(CF)$ and from $+371$ to $+1440$ for $Q_F(CF)$. These π–σ parameters show that F is particularly effective for electron–nuclear coupling and lead to relative estimates of 32–3100 for F scalar rates as compared with H for equal spin densities in all orbitals. If F is considered to be more polarizable than H or if the effect of the $F_{2p\sigma}$ orbitals is considered, the ratio of effective coupling increases. Thus on the molecular level, too, F should give rise to much larger scalar rates than H.

An additional demonstration of the differences between F and H is afforded by examination of the results listed in Table VI. For the edge-on π collisions, H cannot overlap the radical π system by symmetry; hence, for π collisions, spin density can arise at H only through indirect coupling with the electrons at C. For F, π collisions lead to appreciable spin densities at F for distances of closest approach between the sum of the covalent and van der Waal's radii of O and F. These distances are expected[19] to be approached by reasonably energetic collisions. Hence, for well-shielded radicals where π collisions would be favored, the difference in behavior between F and H can be readily understood on the basis of differences in the intensity of scalar interaction.

For σ collisions, the H_{1s} orbital can overlap the radical electron and an appropriate value of $Q_H(CH)$ would be of the order of 500 G/electron, the atomic coupling parameter.[18] Now, Table VI shows that induced spin densities at H for $CH_4(\sigma)$ are comparable to those for fluorocarbons. Since H and F coupling parameters are now comparable, we would expect comparable hyperfine interaction for both systems and comparable scalar rates; however, small scalar rates are observed for H in contrast to F. From Table VII, λ_H is comparable to λ_F for this collision attitude and further, there is no *a priori* reason to assume different correlation times for molecules containing H or F, respectively. We note, however, that the σ collision attitude is only one of three representative types considered and that the other two show F to have markedly stronger scalar coupling.

To conclude, we may expect H atoms bound to C to have small scalar rates in the majority of cases.[20] Where π collisions are dominant, $\mathcal{A}_H$ is vanishingly small; where σ collisions are important, $\mathcal{A}_H$ should be significant. Hyperfine interactions at H, then, need not always be small and the existence of systems where appreciable scalar coupling exists is not precluded.

Radial Steric Effects. Experimentally, well-shielded free radicals such as GALV and TTBP lead to low scalar rates with a variety of fluorocarbons. This may be contrasted with dynamic nuclear polarization results for relatively planar radicals such as TCSQ and TPPY which contain no bulky shielding groups and have appreciable spin density about their peripheries. For these systems, large scalar rates are observed. Assuming that the half-thickness[14] of an aromatic molecule is 1.7 Å, plane–plane collisions are expected to become important for interplanar distances of the order of 3.4 Å. From Table VI, spin densities for plane-plane collisions of C_6H_5F and C_6F_6 with benzosemiquinone become significant at about 4 Å. Increases in the radical orbital energy indicate that r_{ij} for these collisions will not decrease below about 3.5 Å, at which point induced spin densities at F are quite large. Assuming the radius of a methyl group[14] to be 2.0 Å, a *t*-butyl group will extend, on the average, some 3.1 Å above and below the radical plane. The van der Waal's contact for a plane–plane collision between a well-shielded radical containing such groups (TTBP) and a planar fluorocarbon would then be approximately 4.8 Å and induced spin densities for plane–plane collisions are essentially zero. In a similar manner, σ collisions with radical C atoms are eliminated and σ collisions with the radical O atoms are reduced in effectiveness considerably. Hence, for well-shielded radicals, π-collisions should be most effective in producing spin density at solvent nuclei and low scalar rates are expected. Since the effect is purely steric, similar large negative enhancements would be expected for well-shielded fluorocarbons and poorly shielded radicals, but no such systems have been studied to date.

Effect of Polyfluorination. The Fluorobenzene Series. In going from mono- to hexafluorobenzene, ^{19}F nmr enhancements generally become more positive (Table IV). The increase in contact coupling with polyfluorination is more pronounced for poorly shielded radicals than for well-shielded radicals. We attribute this effect to two causes which are illustrated by comparison of collision paths for C_6H_5F and C_6F_6 (Table VI). First, induced spin densities at F for C_6H_6 are inherently larger than those for C_6H_5F in comparable orientations. For well-shielded radicals where π collisions are most important, this effect is smallest, in accord with the small increase in contact coupling for those systems. Induced spin densities at remaining F nuclei for polyfluorinated species in π collision are much smaller than the primary density at the F atom nearest the radical and do not lead to appreciable scalar relaxation. Just the reverse is true for poorly shielded radicals and polyfluorinated benzenes. There, the total induced spin density at additional F atoms for σ and plane–plane collisions equals or exceeds the primary density. This is particularly true for plane–plane collisions where simultaneous intense polarization of all F nuclei occurs.

Aliphatic *vs.* **Aromatic Fluorocarbons.** Comparison of induced spin densities for C_6H_5F and CF_4 in π and σ contact shows that $\rho_F(C_6H_5F)$ is slightly greater than $\rho_F(CF_4)$ for a given increase in the radical orbital energy (system energies cannot be compared since different basis sets were used for each fluorocarbon). For C_6F_6, the comparison is more striking. Thus there appears to be a slight preference for additional hyperfine coupling in aromatics as compared with aliphatics. It would be of interest to determine correlation times for a number of systems containing aliphatic fluorocarbons and compare them with those obtained for

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aromatic systems. Intuitively, we would expect radical–solvent combinations with available π systems to have longer correlation times than those without delocalized π systems. This too could account for aliphatic–aromatic differences.

Order of Magnitude of the Coupling Constant $\mathcal{A}$. Several estimates of the magnitude of the intermolecular coupling constant (eq 6 and 8) have been reported previously. For C_6F_6 with TTBP,[17] use of the modified sticking model and high-field dynamic polarization measurements led to $\mathcal{A}$ = 0.53 Mc (~0.1 G). The diffusion model only permits $\mathcal{A}/\lambda d$ to be evaluated and the same system gave[17] $\mathcal{A}$ = 410 Mc/sec for λd = 1000. Use of the more reasonable value of 30 for λd gives $\mathcal{A} \cong$ 15 Mc/sec. A different author[21] found an average value of about 1 Mc/sec for the intermolecular coupling constant; he performed multifield measurements on a number of "negative" systems. We have previously suggested,[1] on the basis of low-field double-resonance measurements for both negative and positive systems, that $\mathcal{A}$ should be in the range 0.5–1.5 G. Thus, experimentally, the order of magnitude of $\mathcal{A}$ seems reasonably well established.

Assuming that r_{ij} for a thermal collision will not be much smaller than the sum of the atomic van der Waal's radii, it is possible to obtain an estimate of $\mathcal{A}$ (from Table VI) and insight as to the total number of electrons which must be present on the solvent to produce significant contact relaxation *via* hyperfine coupling. At distances 0.25 Å smaller than the van der Waal's radii, spin densities at the F atom nearest the radical range from 2×10^{-5} to 8×10^{-3} electron for σ and π collisions. Use of an average value of Q_F(CF) of about 700 G/electron then leads to expected hyperfine coupling in the range 0.014–5.6 G which spans the experimental estimates. If spin density at all solvent nuclei is considered, a total of less than 0.01 electron need be transferred from radical to solvent during collision to produce the wide range in observed enhancement exhibited by F-containing systems. More important, spin density differences at F of the order of 10^{-3} electrons can change $\mathcal{A}$ by an order of magnitude and c_F by two orders of magnitude (eq 7 and 8), indicating the sensitivity of dynamic nuclear polarization results to small differences in intermolecular interactions.

Conclusions

For all aspects of the interaction which we have studied, differences in ^{19}F nmr enhancements due to scalar coupling can be interpreted qualitatively in terms of exchange polarization and transient complex formation with attendant charge transfer.[1,2] Alternatively, enhancement differences may be related to changes in $\mathcal{A}$ or τ_s, the two most important parameters which characterize the scalar interaction. In many respects, these views are complimentary since the degree of exchange polarization and the strength of transient complex formation may reflect parallel factors which govern both $\mathcal{A}$ and τ_s. Thus the two views may be considered different ways of approaching the same physical situation. Clearly, other parameters, such as radical–solvent distance of closest approach, and other mechanisms, such as direct overlap of electronic and nuclear wave functions, could also be important for a more detailed description of the collision process.

Both existing models for the time dependence of the scalar interaction contain assumptions which, we feel, are not generally valid for all fluorocarbon systems over the entire frequency spectrum of molecular motions. Thus the assumption that $\tau_s \ll \tau_d$, used for an early sticking model, breaks down when molecular complexation is important. The assumption that $\lambda d >> |\omega\tau_s|^{1/2}$, used for the diffusion model, will not be valid at high fields for all fluorocarbon systems. Removal of these assumptions would lead to greater flexibility and more promising correlations between theory and experiment.

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