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^{19}F and ^{1}H Magnetic Relaxation Dispersion Determination of the Translational Encounter between Ionic Salts and Nitroxide Free Radicals in Aqueous Solution

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Measurements of ^{19}F and ^{1}H nuclear spin−lattice relaxation times from aqueous solutions of PF_6^- and $(H_3C)_4N^+$ containing small concentrations of nitroxide free radicals were made at applied magnetic field strengths ranging from 0.00025 to 7.05 T to directly determine the form of the frequency-dependent spectral densities that modulate relaxation. This magnetic relaxation dispersion (MRD) technique may provide detailed information concerning molecular dynamics over the time scale range from milliseconds to picoseconds. The MRD data compare well to a theory for translational diffusion of hard spheres, one that accounts for the intermolecular electrostatic potential between ionic solutes. Theoretically accessible parameters are extracted, and the treatment of the intermolecular potential as a reduction (increase) in the number of effective translational encounters between ions of like (unlike) charge is discussed. Represented by a mean field, the relatively long range Coulombic interaction does not impose spatial conditions on the diffusion equation through which the short-range magnetic dipole−dipole interactions are correlated. Calculated distances of closest approach are approximately 6.5 Å and are consistent with the dimensions expected for a sterically impeded encounter between the nuclear spin probes and the nitroxide centered paramagnetic spin density. Comparison of the $(H_3C)_4N^+$ and PF_6^- data provides a means of quantifying the Coulombic potential, which has a more dramatic effect on the ^{19}F relaxation of the polarizable PF_6^-.

1. Introduction

The hydrodynamic characteristics of solute species is central to an understanding of the aqueous chemical and biophysical processes of small molecules. Recently, this laboratory has undertaken a systematic study of the molecular dynamics of some solute compounds in order to quantify physically accessible parameters for relatively simple systems, the impetus being to ultimately characterize potentially complicated biophysical environments, such as a membrane surface.[1] Direct experimental investigation of solute chemistries can be difficult because of short interaction time scales and exceedingly small instantaneous concentrations of intimate complexes. However, the dependence of the NMR spin−lattice relaxation time on the applied magnetic field strength is directly attributable to fluctuations at the nuclear or paramagnetic electronic Larmor frequencies. In the presence of organic free radicals with long electron relaxation times, these fluctuations are normally thought to be driven by thermal Brownian motion, resulting in the modulation of both inter- and intramolecular relaxation mechanisms, and thus providing an experimental probe of events occurring on the time scale proportional to the inverse of these Larmor frequencies. Our recent reports of the magnetic relaxation dispersion (MRD) of ^{7}Li have revealed some interesting and unexpected solution chemistry based on an analysis of the contributions to the observed relaxation derived from models of rotational[2] and translational[3] diffusion. For example, our strategy to characterize translational diffusion of lithium at macromolecular and membrane surfaces by exploiting the relaxation induced by nitroxides localized at these surfaces was thwarted by the formation of a complex between Li^+ and aqueous nitroxide radicals, with the resulting MRD curve dominated by the Fermi contact interaction.[4] With the existence of this direct interaction between the paramagnetic center and the nuclear spin probe, it was impossible to resolve the subtle effect of charge localized on the free-radical moiety. Subsequently, we reported a bimolecular association constant for the formation of a $Li^+−Mn^{2+}$ outer sphere cation−cation complex and interpreted the relaxation data in terms of the relevant time scales and geometric constraints.[5] The repulsive Coulombic potential that exists between ions of like charge, which would be a substantial barrier to complex formation in the gas phase, is mitigated in a high dielectric solution, and can be overcome by the formation of hydrogen bonds. In the $Li^+−Mn^{2+}$ case, the repulsive potential was accounted for by a frequency-independent scaling factor interpreted as a reduction in the number of effective translational encounters.

The quantum mechanical formulation connecting ensemble spin relaxation to the more fundamental power spectral densities is well established[6,7] and there exists a number of recent experimental reports relating the NMR relaxation phenomena of, for example, microporous materials,[8] biological interfaces,[9] and mesophases[10,11] to models of molecular motion. Notably, the electrostatically repulsive translational encounter between

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$(^1H_3C)_4N^+$ and Gd(III) ($S = {}^7/_2$) has been described in terms of the relative diffusion of ions in an exponentially decaying isotropic potential.[13] With *a priori* knowledge of the relative diffusion constant and distance of closest approach for the system, Vigouroux et al. found good agreement between the observed proton relaxation rates and the standard treatment of spin relaxation in the Redfield limit incorporating ion−ion Coulombic potentials that radially oscillate with successive hydration shells. Even though the theoretical account of the proton spin−lattice relaxation was described as parameter-free, given the independent measurement of the bulk hydrodynamic properties of the solutions studied, the model relies upon a relatively detailed description of solvation. Furthermore, the theory is predicated upon the limit of long electronic relaxation times compared to the correlation times for Brownian diffusion. This may be a fair approximation for the aquo complex of Mn(II) which bears spherically symmetrical electron spin density, but in general, electron relaxation rates are dependent upon the point symmetry at the metal center of mass. Reduction of the spherical symmetry results in a zero field splitting (ZFS) of the otherwise spatially degenerate electronic orbitals, and electron relaxation derives primarily from thermal modulation of the ZFS tensor. Transient ZFS are correlated on the time scales of both intra- and intermolecular motions ($\tau_v = 2-10$ ps) associated with collisional and vibrational motions. Static ZFS results from a nonspherical average over all configurations of the coordinate shell, correlated on the time scale of Brownian motion of the entire molecule. In the limit of short electronic relaxation times, T_{ke} ($k = 1,2$), the coupled nuclear relaxation is correlated with the ZFS, and therefore cannot be easily related to the normal geometric and stochastic variables.

The complications of short electron spin relaxation times are absent for molecules bearing $S = {}^1/_2$ spin density. The absence of spin exchange or spin−orbit coupling between unpaired electrons in the $S = {}^1/_2$ system implies exceedingly long electronic relaxation times of order 10^{-6} s, regardless of the symmetry of the molecular crystal field. The nitroxide free radicals are particularly convenient because of their chemical stability and localized paramagnetic spin density. Here we continue our survey of solute nuclear spin relaxation and report the MRD of aqueous solutions of $P^{19}F_6^-$ and $(^1H_3C)_4N^+$ containing small concentrations of ionic nitroxide free radicals, showing the relaxation over a very wide range of frequencies. Corresponding to the dynamical regime ranging from milliseconds to picoseconds (in a paramagnetic sample), the MRD curve provides a reliable test of the validity of models of molecular motion intrinsic to theories of magnetic relaxation. Excellent agreement is found between the MRD data and a translational model for spin−lattice relaxation that assumes a mean intermolecular potential. Radial dependence of the potential, derived from specific short-range interactions between solvated sites, is not specifically precluded. However, important implications follow from the applicability of the mean potential model. Spherical symmetry is consistent with the representation of the solutes as point magnetic dipoles bearing integral charge density; macroscopic relaxation is determined by a weighted geometrically isotropic distribution of solute collisions. Furthermore, the Coulombic interaction is long range compared to the distances over which magnetic dipole−dipole relaxation is effective. Therefore, the Coulomb potential does not affect intermolecular dipole−dipole relaxation *per se*, insofar as it inhibits the formation of intimate collisional pairs, rather than directly influences the short-range dynamics. These approximations are supported by the measured hydrodynamic constraints.

2. Theory

For solutes in aqueous solution, both the ^{1}H and ^{19}F ($I = {}^1/_2$) relaxation is dominated by interaction of the nuclear magnetic dipole moment with the magnetic induction fields generated by surrounding spin-bearing nuclei or paramagnetic electron spin density. In solution, these fields fluctuate on time scales associated with random Brownian rotation or translation, and with chemical exchange. Designated $R_{1D} = T_{1D}^{-1}$, the diamagnetic contribution to the total relaxation of the $I = {}^1/_2$ nucleus is due to dipolar coupling with all other spin-bearing nuclei in the solute molecule and in those inhabiting the outer sphere. This relaxation is concentration dependent, amounting to a baseline shift of the dispersion data, and all data presented are corrected for this diamagnetic contribution. In the absence of any paramagnetic species, the ^{19}F relaxation in PF_6^- will arise from the dipole−dipole interaction with ^{31}P and all other covalently bonded fluorine nuclei, and will be correlated on the time scale of molecular rotation. An analogous situation exists for $(^1H_3C)_4N^+$, which is subject also to rapid methyl group internal rotations. Spin-bearing nuclei associated with the outer sphere solvent cage also generate magnetic induction fields that are modulated by relative translational diffusion. Thus, there are distinct inter- and intramolecular contributions to the observed spin−lattice relaxation rates that are similar in their physical origin.

The electronic magnetic moment is nearly 3 orders of magnitude larger than any nuclear counterpart, so the situation changes dramatically in the presence of even a small amount of paramagnetic species. The magnetic induction fields generated by the presence of unpaired electron spin density provide much more efficient relaxation mechanisms, particularly for those nuclei in close proximity to the paramagnetic center. In the event that a direct chemical bond is formed between the nuclear probe and the paramagnetic spin, as has been observed for the interaction between $^7Li(H_2O)_n^+$ and nitroxides,[4] the existence of a fixed intermoment vector induces a Lorentzian contribution to the magnetic dipole−dipole interaction that is correlated by a well-defined molecular rotation. Should a significant steady state concentration of such complexes be maintained, relaxation will likely be dominated by the spatially invariant Fermi contact interaction that is correlated by the lifetime of the covalently bonded complex. Yet, as is the case for the intermolecular solvent contribution to the diamagnetic relaxation, the translational diffusive motions of the free radicals in solution generate significant fields, regardless of any chemical binding event.

Liquid phase intermolecular correlation functions are appropriately treated in the classical limit, and for the dipolar interaction between spins I and S are written

$$G_m^{IS}(t) = \int d^3\mathbf{r} \int d^3\mathbf{r}_0 D_{0m}^{(2)\dagger}(\Omega_r) D_{0m}^{(2)}(\Omega_{r_0}) P(\mathbf{r}_0|\mathbf{r}, t) \frac{g(r_0)}{r^3 r_0^3} \qquad (1)$$

Wigner rotation matrices of second rank, $D_{0m}^{(2)}(\Omega_r)$, subtending the solid angles Ω_r represent the unitary transformation from the molecular coordinate axes to the laboratory fixed frame. Radial probability distributions $P(\mathbf{r}_0|\mathbf{r}, t)$ determine the likelihood that an initial intermoment vector $\mathbf{r}_0$ will evolve into $\mathbf{r}$ after some time t *via* a diffusive flux, and as solutions to a stochastic differential equation

$$\frac{\partial P(\mathbf{r}_0|\mathbf{r}, t)}{\partial t} = D\nabla\cdot\left[\nabla P(\mathbf{r}_0|\mathbf{r}, t) + \frac{1}{kT} P(\mathbf{r}_0|\mathbf{r}, t)\nabla U(R)\right] \qquad (2)$$

with initial condition $\lim_{t\to 0} P(\mathbf{r}_0|\mathbf{r}, t) = \delta(r-r_0)$ determine the time evolution of Brownian motion. The solvent cage mean field potential

$$U(R) \propto C_{ij}(R) = \frac{q_i}{4\pi\epsilon_0\epsilon_r}\sum_j \frac{q_j}{R_{ij}} \tag{3}$$

will oscillate with consecutive solvent shells at very close interionic separation but should be well represented by a scalar parameter, C, that accounts for the local dielectric properties and apparent mean separation of point charges, yet bears no explicit radial dependence. The pair correlation functions $g(r_0)$ describe the initial equilibrium pair distribution and are related to the intermolecular potential of averaged forces between the spin bearing molecules

$$f_0 = \exp[\{-C(q_1q_2/4\pi\epsilon_0)\}/kT] \tag{4}$$

and to the number density of S spins N in an infinitesimal volume contained by $\mathbf{r}$ centered about the spin I.

$$g(r_0) = (5/4\pi)N\,f_0 \tag{5}$$

Note the distinction between the separation of centers of mass $\mathbf{r}$ and that of the centers of charge density R. The nuclear relaxation will represent the ensemble response of all spin pairs in all molecular orientations, so that given the symmetry of both the solute spin probes in this study, the magnetic dipole coincides with the molecular center of mass. The Coulombic potential is represented by an idealized parameter which probably does not accurately reflect the complex geometry of the local fields or the local dielectric properties. It is anticipated, then, that polarizable molecules such as PF_6^-, wherein the surplus charge density is delocalized to the fluorine ligands, will be more sensitive to the presence of a Coulombic potential than those such as $(^1H_3C)_4N^+$ in which the positive charge in effect increases the apparent charge separation. By ignoring the radial dependence of the intermolecular potential, we recognize that the observed nuclear relaxation is derived primarily from those solute molecules that are in close proximity to the paramagnetic centers. Since the magnetic dipole−dipole interaction is relatively short range compared to the Coulombic interaction, a static value of the mean field at these short molecular dimensions is a fair approximation of a complicated potential energy surface; while the details of the solvated ion pair electrostatic fields will have important implications as regards the solution of eqs 1 and 2, they are not likely to be resolved by NMR relaxation methods. In this sense, the effect of the Coulombic potential on magnetic relaxation is indistinguishable from a steady state concentration gradient localized at the solute molecule *vis a vis* eq 5. Following Ayant and Freed,[3] Torrey's description of molecular motion as a sequence of random jumps between nodes of a discrete lattice[12] is modified to exclude mutual penetration of hard spheres during a translational encounter. Taking the limits of continuous diffusion and $T_{ke}\omega \gg 1$, one obtains for the force free model

$$J(\omega) = \left(\frac{1 + \frac{5z}{8} + \frac{z^2}{8}}{1 + z + \frac{z^2}{2} + \frac{z^3}{6} + \frac{4z^4}{81} + \frac{z^6}{648}}\right) \tag{6}$$

with

$$z = \left(2\omega\frac{b^2}{D}\right)^{1/2} \tag{7}$$

where $D = D_I + D_S$ is the relative diffusion constant between the two spin-bearing molecules, and b is the distance of closest translational approach. The resulting contribution to spin-latticerelaxation is[6]

$$\frac{1}{T_{1\mathrm{trans}}} = \frac{32\pi}{405}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2\gamma_S^2\hbar^2 S(S+1)\,\frac{N}{bD}\,f_0[J(\omega_S - \omega_I) + 3J(\omega_I) + 6J(\omega_S + \omega_I)] \tag{8}$$

A correlation time of random Brownian translation can be defined

$$\tau_{\mathrm{trans}} = \frac{\overline{\lambda^2}}{6D} = \frac{b^2}{6D} \tag{9}$$

in terms of the mean squared displacement λ, which we approximate by b.

3. Experimental Section

Relaxation time measurements were made as a function of magnetic field strength on an instrument to be described elsewhere that was assembled in this laboratory and utilizes a 7.05 T Magnex superconducting solenoid in close proximity to a GMW 4-in. electromagnet which is isolated magnetically from the higher field by an iron shield. The sample is stored in the high field, moved pneumatically to the variable lower field for various relaxation delay periods, then returned pneumatically to the high field where the remaining magnetization is measured with a 90° pulse or other sequence. Small aliquots of sodium hydroxide or hydrogen chloride solutions were used to adjust the pH prior to addition of nitroxide. The liquid sample is degassed with an Ar stream and sealed in a threaded Delrin cylinder. The sample movement is controlled by a Tecmag Libra system controlled by a MacIntosh Quadra 800 computer, which activates dual dc solenoid valves to control the air/vacuum pressure that drives the sample through the field cycle. The magnetic resonance probes were constructed in this laboratory employing commonly used LRC single resonance circuits, and provide field homogeneity sufficient to resolve the tetramethylammonium and residual water proton peaks. All experiments were performed at ambient temperature which was maintained near 294 K.

The nitroxide free radicals 4-hydroxy-TEMPO, 4-amino-TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl), and 3-carboxy-PROXYL (2,2,5,5-tetramethylpyrrolidine-*N*-oxyl) were used as received from SIGMA. Sodium hexafluorophosphate and tetramethylammonium chloride were used as received from Aldrich.

4. Results and Discussion

Figures 1 and 2 present the MRD data showing the frequency dependence of the solute spin−lattice relaxation rates collected from solutions containing 0.5 M P^{19} F_6^- and 0.5 M $(^1H_3C)_4N^+$ in the presence of dilute concentrations of nitroxide free radicals: □, 4-OH-TEMPO at pH 7.0; ○, 4-NH2-TEMPO at pH 4.0; △, 3-COOH-PROXYL at pH 10.0. These data are normalized to the nitroxide concentration and are corrected for T_{1D}; the error bars represent the 95% confidence interval about a Gaussian distribution. The pH was adjusted accordingly with aliquots of dilute acid or base, in order to shift the

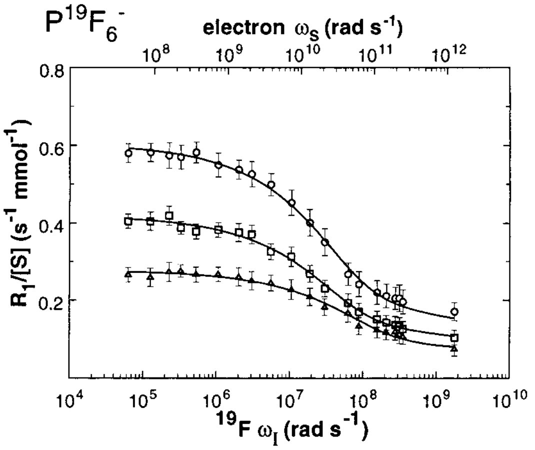

Figure 1. ^{19}F MRD curve describing the translational encounter between the PF_6^- ion and substituted nitroxide free radicals: (□) 4-OH-TEMPO at pH 7.0, (○) 4-NH_2-TEMPO at pH 4.0, (△) 3-COOH-PROXYL at pH 10.0. The solid lines are least-squares fits to the normalized data from a theory of translational diffusion that represents the intermolecular Coulombic potential as a mean field. The calculated mean field parameter is consistent to within 6% for all three sets of data. Other parameters are summarized in Table 1.

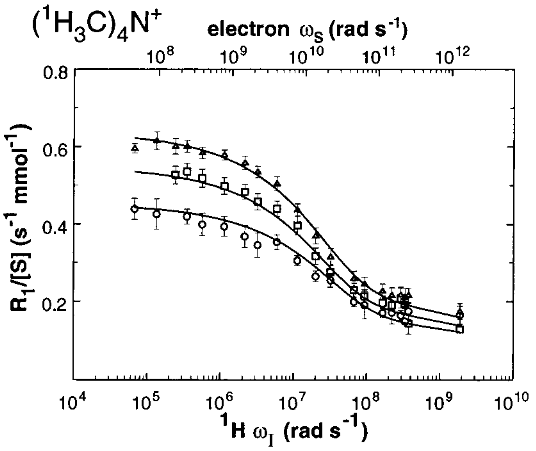

Figure 2. ^{1}H MRD curves from the $(Me)_4NCl$/nitroxide systems suggesting that the relaxation is modulated by relaxation mechanisms that are similar in origin to those inferred from the fluorine data: (□) 4-OH-TEMPO at pH 7.0, (○) 4-NH_2-TEMPO at pH 4.0, (△) 3-COOH-PROXYL at pH 10.0.

chemical equilibrium toward the formation of ionized free-radical moiety.

It is expected that the characteristics of the translational encounter between the center of paramagnetic spin density on the nitroxide and the nuclear spin probe will be affected byany intermolecular electrostatic potential that exists between the collisional pair. Indeed, both sets of data show that the translational contributions to the relaxation rates are increased by interactions between solutes for which there is an attractive electrostatic potential and are conversely decreased when this potential is repulsive. It is also immediately apparent from the relative ^{1}H and ^{19}F molar relaxivities that the effect of this Coulombic interaction is more dramatic for the $P^{19}F_6^-$ ion than for $(^1H_3C)_4N^+$. This is consistent with the disposition of charge density throughout the solute molecules, with a larger mean Coulombic field experienced by the fluorine ligands upon which the negative charge is delocalized.

The solid lines are nonlinear regression least-squares fits of eq 8 to the MRD data, for which there are only three independent parameters. $\{f_0\}$ and $\{D,b\}$ are not statistically independent, so the distance of closest approach and diffusion constant are initially found for the 4-hydroxy-TEMPO data which represent an electrostatically neutral interaction between solutes wherein $f_0 = 1$. These initial values for b and D produce an approximation of f_0 for each of the 3-carboxy-PROXYL and 4-amino-TEMPO data sets, which in turn is used to find the unique values of b and D upon which eq 8 converges. The parametric results and calculated standard errors of this procedure are summarized in Table 1. For both the $P^{19}F_6^-$ and $(^1H_3C)_4N^+$ sets of data, the calculated values of b and D are identical within a 95% confidence interval and are therefore insensitive to the presence of a Coulombic potential at this level of approximation. Solution diffusive phenomena will be dependent upon the thermally activated interactions between solvent and solute molecules. Yet, while it is not reasonable to expect homogeneous diffusive flux in all chemical environments experienced by the solute spin probes, Table 1 shows that the measured bulk diffusion constant is not perturbed by the small concentration of charged nitroxide radicals. Therefore, any local effect produced by the presence of intermolecular potentials between the solute species might not be accounted for by spatial variables in a local diffusion function. It is also interesting to note that the measured values for the distance of closest approach between the centers of nuclear and electronic spin density b apparently do not represent the sum of van der Waals' radii for oxygen and either ^{1}H or ^{19}F, which would be of the order of 2−2.5 Å. As formulated, the distance of closest approach represents the weighted integral over all intermoment vectors between spin pairs of interest, since the second-order magnetic dipole−dipole contribution to the relaxation varies as $1/r^6$. Therefore, b is a reasonably accurate measure of the closest separation between magnetic point dipoles during a site specific interaction at the nitroxide moiety.

TABLE 1: Parametric Results and Standard Errors from Nonlinear Regression Fit of Eq 8 to the MRD Data[a]

solute	nitroxide	D ($\times 10^{10}$ m^2 s^{-1})	b ($\times 10^{10}$ m)	f_0	τ_{trans} (ps)
	R-OH	8.4 ± 0.3	6.5 ± 0.2	1	83 ± 6
PF_6^-	R-NH_3^+	8.9 ± 0.3	6.3 ± 0.1	1.46 ± 0.01	75 ± 6
	R-COO^-	8.6 ± 0.3	6.5 ± 0.1	0.70 ± 0.02	82 ± 6
	R-OH	7.1 ± 0.2	7.1 ± 0.2	1	120 ± 10
$(H_3C)_4N^+$	R-NH_3^+	7.9 ± 0.5	6.6 ± 0.3	0.81 ± 0.01	93 ± 14
	R-COO^-	7.3 ± 0.3	7.0 ± 0.2	1.17 ± 0.02	113 ± 11

[a] Recursive least-squares procedure described in the text.

A further test of the theory developed here for the translationally modulated paramagnetic relaxation of solute spin probes can be garnered from comparison of the measured values of the scaling factor f_0. This term is expected to be a function of the mean intermolecular Coulombic field defined by eq 4. Comparison of the calculated values of f_0, which are obtained independently from separate measurements, show that the mean field approximation is consistent for both the repulsive and attractive encounters to within 20% for $(^1H_3C)_4N^+$ and 6% for the $P^{19}F_6^-$. Since it would be naive to expect a realistic solution phase intermolecular potential to be accurately described by a single spatially invariant parameter, this level of precision is somewhat fortuitous. However, the quality of the fit of the mean field theory to the experimental data suggests that magnetic relaxation measurements lack the resolution required to further explore the details of a solvent-mediated translational encounter. While it is conceptually possible to build a model of solvation incorporating the spatially variant electrostatic fields and diffusive properties, introduction of the concomitant parameters to the relaxation theory is probably not justified.

5. Conclusion

We have shown that the NMR relaxation data derived from the interaction of ionic solute with charge-bearing paramagnetic nitroxide free radicals is adequately accounted for by a theory of translational diffusion that describes the intermolecular Coulombic potential by a single parameter mean field. This parameter is consistent for each of the two sets of data to within 20%, suggesting that the mean field approximation is sufficient for the characterization of magnetic relaxation phenomena. Conversely, it is unlikely that magnetic relaxation data alone will produce a more detailed description of local electrostatic fields between solutes. This limitation derives from the fact that the Coulombic interaction is relatively long range in nature, and so the relaxation induced by the short-range magnetic dipole−dipole interaction is insensitive to the details of the spatially dependent field.

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