of the energy difference between interacting levels, i.e., the energy denominator in the perturbation theory treatment of the quadratic Stark effect [see Eq. (5)]. The largest terms are due to interactions between F levels and G levels. As mentioned earlier, two of the pertinent G levels are known (with uncertain accuracy) and four others must be estimated. Effects due to error in the energy denominator are not simply related to linewidth, but any reasonable estimate of the energies of the G levels leads to differences of 20% at very most. The over-all inaccuracy is then probably about 20%.

In light of the errors involved, the experimental and theoretical agreement is quite good. The average ratio of experimental to theoretical width of 0.99 ± 0.18 is well within either the experimental or theoretical error.

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Effect of Electrostatic Interactions on the Nuclear Magnetic Resonance Dipolar Hyperfine Structure with Strong Correlation-Time Narrowing*

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The effect of electric fields on the nuclear magnetic resonance dipolar hyperfine spectrum of a liquid with correlation-time narrowing is examined. A first-order molecular quadrupole effect and a second-order molecular electric dipole effect (Stark effect) of observable magnitude are predicted. The results are discussed with reference to the proton magnetic resonance in water.

INTRODUCTION

In an experiment for measuring the radio-frequency resonance of nuclear magnetic moments in a liquid, one observes that which is known as a strong narrowing in the limit of short correlation time.[1] The effect is simply that the time domain, the radio-frequency field, sees only the average frequency of the nuclear magnetic resonance (NMR) signal as perturbed by molecular motion. Any orientation-dependent hyperfine structure such as a dipolar hyperfine structure will thus be averaged in time by molecular motion when the correlation time of that motion τ_c is short enough so that the hyperfine frequency $\gamma\hbar\Delta H$ is much less than τ_c^{-1}. The time-averaging process is difficult to imagine, but we may conveniently predict the effect of this time averaging by carrying out an ensemble average at an instant of time. Such an average will properly weight angular positions of the molecule to give a result equivalent to a time average. This point is a bit subtle, but it should be noted that it is necessary to make a distinction between a time average, which the NMR calculations require, and an ensemble average, which allows the ready evaluation of this time average but is not otherwise physically significant.

The import of this paper is to point out that two simple molecular parameters, the molecular electric dipole moment and the molecular electric quadrupole moment, are of fundamental importance in determining the orientation statistical weights and, since they are known for many molecules, the observation of the correlation-time-narrowed NMR spectra of nuclei having dipolar hyperfine structure in these molecules will allow a partial description of the electric fields that the molecule "sees," or conversely, if the fields are known, the possibility of the determination of the first two electric moments of the molecule.

Take, for example, the water molecule H_2O^{16}. The nuclear spin of O^{16} being zero, and the spins of H^1 being 1/2, we have only the interaction terms, because of the proton moment that arises from the spin-spin isotropic and anisotropic coupling, the spin-molecular rotation coupling and the spin-Zeeman term measuring the nuclear coupling with the applied external magnetic field.

In a series of beautiful experiments the splittings in the NMR spectra of the proton and the deuteron in

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[1] A. Abragam, *Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. X.

the water molecule in a crystalline environment have been observed and attributed to a nonuniform probability distribution for the orientation of the water molecule.[2] In our discussion we relate this nonuniformity in probability to the interaction of internal crystalline electric fields with molecular electric moments and predict a new and seemingly paradoxical effect, the Stark effect in NMR dipolar hyperfine-structure resonance caused by the molecular electric dipole moment interacting with an external electric field. To this end, we add to the conventional NMR Hamiltonian cited above the molecular rotational energy terms, and the terms that measure the interaction of the molecular electric moments with the external electric fields, either externally applied or gratuitously supplied by the matrix, lattice, or material containing the molecules whose NMR resonance is being observed. It is the explicit introduction of these terms and the examination of their consequences that is the contribution of this paper.

THEORY

We have said that we shall be making ensemble averages with appropriate statistical weights. We note now that the average that we obtain will be classical, but we may rely on the spectroscopic stability of our quantum-mechanical system[3] to make our classical averages valid. Since the magnetic energies are so small compared with the electrostatic energies and compared with the mean rotational energies, or, that which is the same thing, to $(3/2)kT$, we shall concern ourselves only with the influence of the electrostatic terms on the statistical weights.

Since the electrostatic potential must satisfy Laplace's equation, we may write the electrostatic terms as irreducible operators by using spherical harmonics. The result is an expansion in a scalar product of molecular electric multipole moments and the corresponding electric field factors. In exact analogy to the development for the nuclear electric moment we have[4]

$$\mathcal{H}_{\mathrm{E}} = -\boldsymbol{\mu}\cdot\mathfrak{E} + \mathfrak{Q} : \nabla\mathfrak{E}^*,$$

where $\boldsymbol{\mu}$ is the molecular dipole moment, $\mathfrak{Q}$ is the molecular electric quadrupole moment tensor, $\mathfrak{E}$ is the electric field, and $\nabla\mathfrak{E}$ is the electric field gradient tensor.

Now, we write the rotational, electrostatic, Zeeman, spin-spin, spin-rotation, etc., energies as

$$\mathcal{H} = \mathcal{H}_{\mathrm{rot}} + \mathcal{H}_{\mathrm{E}} + \mathcal{H}_{\mathrm{Zeeman}} + \mathcal{H}_{\mathrm{s\text{-}s}} + \mathcal{H}_{\mathrm{s\text{-}rot}} + \mathcal{H}',$$

with the contributions ordered as to magnitude, assuming a case in which the electric term $\mathcal{H}_{\mathrm{E}}$ is greater than $\mathcal{H}_{\mathrm{Zeeman}}$, but less than the mean value of the rotational energy $\mathcal{H}_{\mathrm{rot}}$, since this Hamiltonian, in the absence of $\mathcal{H}_{\mathrm{E}}$, is well understood. The direct coupling of electric fields is only with the molecular motion. Hence, $\mathcal{H}_{\mathrm{E}}$ cannot affect the NMR spectrum directly, but only through its effect on the statistical weight used in the ensemble average over the molecular motion of the molecule, i.e., through its effect on the mean value of $\mathcal{H}_{\mathrm{s\text{-}s}}$. There is another possible indirect interaction of $\mathcal{H}_{\mathrm{E}}$ with the NMR spectrum through the chemical effect symbolized by $\mathcal{H}_{\mathrm{s\text{-}rot}}$. However, we shall find the effect of $\mathcal{H}_{\mathrm{E}}$ to be a small perturbation and, since the chemical effect is already a small perturbation, we leave an interaction through this term for consideration elsewhere.

In a representation in which the total spin angular momentum $\mathbf{I}=\mathbf{I}_1+\mathbf{I}_2$, the sum of the spins of the two hydrogen nuclei, and with quantization along the external static magnetic field axis $\mathbf{H}_0$, the main terms of interest in $\mathcal{H}$ (leaving the complication of isotropic coupling, chemical shift, and so on to be added in the usual fashion) are written

$$\mathcal{H}_{\mathrm{s\text{-}s}} = (\mu_p^2/r_{12}^3)[3m_I^2 - I(I+1)](3\cos^2\theta_{12} - 1),$$
$$\mathcal{H}_{\mathrm{Zeeman}} = 2\mu_p m_I H_0.$$

These terms contain the usual physical quantities, and θ_{12} is the angle between the vector $\mathbf{r}_{12}$ joining the two protons in a water molecule and the static magnetic field $\mathbf{H}_0$. Whether or not the spins are identical does not change our conclusions, however.

Recognizing that the principal axes of $\boldsymbol{\mu}$ and $\mathfrak{Q}$ can be coplanar but need not be collinear with $\mathbf{r}_{12}$, we establish the molecular geometry, at $t=0$, as follows: Choose $r_{12}=r_{12}\mathbf{k}$, then $\boldsymbol{\mu}$ and $\mathfrak{Q}$ are determined by giving $\boldsymbol{\mu}=\mu_x\mathbf{i}+\mu_y\mathbf{j}+\mu_z\mathbf{k}$ while $\mathfrak{Q}$ is given by

$$Q_0 = \tfrac{1}{2}\sum_i q_i(3z_i^2 - r_i^2),$$
$$Q_{\pm1} = \tfrac{1}{2}\sqrt{6}\sum_i q_i z_i(x_i \pm iy_i),$$
$$Q_{\pm2} = \tfrac{1}{4}\sqrt{6}\sum_i q_i(x_i \pm iy_i)^2,$$

where x_i, y_i, z_i are the coordinates in the molecular framework for the molecular charge q_i.

As the time evolves, $\mathbf{r}_{12}$ moves away from $\mathbf{k}$ through Euler angles θ and ϕ, and hence, in time, since the molecule is rigid, we write

$$\mathcal{H}_{\mathrm{s\text{-}s}} = (\mu_p^2/r_{12}^3)[3m_I^2 - I(I+1)][3\cos^2\theta_{12}(t) - 1].$$

We must express the operator $[3\cos^2\theta_{12}(t)-1]$ with respect to a fixed reference frame, that of the electric field, for the analyses to follow. This is done, of course, simply by using the spherical harmonic addition theorem. There is a large probability of making errors in sign and in the identification of angular variables if this is carried out in too cavalier a fashion, so we develop the relation from first principles.[5] We note that in terms of finite rotation operators, the rotation operator, $\mathfrak{D}^{(l)}(\omega)$, for the rotation of a tensor

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[2] P. Averbuch, P. Ducros, and X. Paré, Compt. rend. **250**, 322 (1960); Y. Ayant, P. Ducros, X. Paré, and M. Soutif, *ibid.* **252**, 550 (1961); P. Ducros, Bull. soc. franç. minéral. et crist. **83**, 85–112 (1960); thèse, Paris, 1960 (unpublished).

[3] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927).

[4] M. W. P. Strandberg, *Microwave Spectroscopy* (Methuen and Company, Ltd., London, 1954).

[5] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), Chap. IV, p. 125.

of order l through Euler angles α, β, $\gamma\equiv\omega$, can be written as a succession of two rotations α_1, β_1, $\gamma_1\equiv\omega_1$, and then α_2, β_2, $\gamma_2\equiv\omega_2$:

$$\mathfrak{D}_{mm'}{}^{(l)}(\omega)=\sum\nolimits_{m''}\mathfrak{D}_{mm''}{}^{(l)}(\omega_2)\mathfrak{D}_{m''m'}{}^{(l)}(\omega_1).$$

Now we note that when $m=m'=0$ and $l=2$ we have

$$\mathfrak{D}_{00}{}^{(2)}(\omega)=1/2(3\cos^2\beta-1)=\mathfrak{D}_{00}{}^{(2)}(0\beta 0);$$

thus,

$$(3\cos^2\beta-1)=2\sum\nolimits_{m''}\mathfrak{D}_{0m''}{}^{(2)}(\omega_2)\mathfrak{D}_{m''0}{}^{(2)}(\omega_1).$$

Now, if the Euler angles of the rotation that takes the Z axis of the intermediate reference frame into $\mathbf{r}_{12}$ are α_2, β_2, $\gamma_2\equiv\omega_2$, then we must identify α_1, β_1, $\gamma_1\equiv\omega_1$ with the inverse Euler rotation that takes the Z axis of the intermediate reference frame into the magnetic field direction. Thus, if ϕ, θ, ψ are the rotation angles with respect to a *fixed* reference frame, we have

$$[3\cos^2\theta_{12}(t)-1]$$
$$=2\sum\nolimits_{n}\mathfrak{D}_{0m}{}^{(2)}(\psi\theta\phi)\mathfrak{D}_{m0}{}^{(2)}(-\phi'-\theta'-\psi'),$$

where ϕ', θ', ψ' are the magnetic field spherical coordinates with respect to the space-fixed X, Y, and Z coordinates having unit vectors $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$, and ϕ, θ, ψ are the spherical coordinates of $\mathbf{r}_{12}$ with respect to the same reference frame. Since quantization is assumed along $\mathbf{H}_0$, $\mathcal{H}_{\text{Zeeman}}$ is invariant in time. We now must represent the time development of $\mathcal{H}_{\text{E}}$, knowing the time development of ϕ, θ, and ψ for $\mathbf{r}_{12}$.

First, we write $\boldsymbol{\mu}\cdot\mathfrak{E}$ in terms of irreducible operators

$$\mu_0=\mu_z;\quad \mu_{\pm1}\mp(\mu_x\pm i\mu_y)/\sqrt{2},$$
$$\mathfrak{E}_0=\mathfrak{E}_Z;\quad \mathfrak{E}_{\pm1}=\mp(\mathfrak{E}_X\pm i\mathfrak{E}_Y)/\sqrt{2},$$

so that

$$\boldsymbol{\mu}\cdot\mathfrak{E}=\sum\mu_m\mathfrak{E}_m{}^*.$$

Since $\mathfrak{E}$ is time-invariant with respect to molecular rotation, we need only the rotational transformation of $\boldsymbol{\mu}$ for a rotational transformation of the molecular framework through the Euler angles ϕ, θ, ψ. This is formally represented as

$$D(\psi\theta\phi)\mu_m=\sum\mu_{m'}\mathfrak{D}_{m'm}{}^{(1)}(\psi\theta\phi).$$

Similarly, we take the field gradients as time-invariant with respect to molecular rotation, that is, as a property of the molecular environment. Since the Q's form an irreducible representation of order 2, we have

$$D(\psi\theta\phi)\mathfrak{Q}_m=\sum\mathfrak{Q}_{m'}\mathfrak{D}_{m'm}{}^{(2)}(\psi\theta\phi).$$

Finally, the statistical weighting factor for the angular variables for the ensemble average is

$$p(\phi\theta\psi)=(8\pi^2\Sigma)^{-1}\sin\theta\exp[-E(\phi\theta\psi)/kT],$$

with

$$\Sigma=(8\pi^2)^{-1}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\sin\theta\exp(-E(\phi\theta\psi)/kT)d\phi d\theta d\psi,$$

where E is the eigenenergy of $\mathcal{H}$. It is apparent, or it will be assumed, that the only nontrivial dependence of the energy with orientation arises from $\mathcal{H}_{\text{E}}$. Thus, we assert that the averages over rotational states implied in this integral can be ignored, or rather replaced by classical averages. This is certainly so in the absence of $\mathcal{H}_{\text{E}}$, since one knows that the observation of a single NMR line in the presence of dipolar hyperfine structure is consistent with averaging the rotation with the simple weighting factor of $(8\pi^2)^{-1}\sin\theta d\phi d\theta d\psi$. That is, the spectra are consistent with averaging E_{rot} classically. We make the same assumption, retaining only the rotation-dependent term $\mathcal{H}_{\text{E}}$. Thus, we have

$$p(\psi\theta\phi)=(8\pi^2)^{-1}\exp(-\mathcal{H}_{\text{E}}/kT)\sin\theta.$$

We expand the exponent, since to be consistent with our assumption of the validity of a classical averaging of E_{rot} we must have $\mathcal{H}_{\text{E}}\ll kT$. Thus, we have the time average of $(3\cos^2\theta_{12}-1)$ represented by the ensemble average

$$\langle 3\cos^2\theta_{12}-1\rangle_t$$
$$=\frac{1}{4\pi^2}\sum\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\mathfrak{D}_{m0}{}^{(2)}(-\phi'-\theta'-\psi')\mathfrak{D}_{0m}{}^{(2)}(\psi\theta\phi)$$
$$\times\Big\{1+\frac{1}{kT}[\langle\mathfrak{E}_{m'}{}^*\rangle\mu_{m''}\mathfrak{D}_{m''m'}{}^{(1)}(\psi\theta\phi)$$
$$+\langle\nabla\mathfrak{E}_{m'}{}^*\rangle Q_{m''}\mathfrak{D}_{m''m'}{}^{(2)}(\psi\theta\phi)]$$
$$+\frac{1}{2k^2T^2}[\sum\langle\mathfrak{E}_{m'v}{}^*\mathcal{E}_{m'}{}^*\rangle\mu_{m''}\mu_m\mathfrak{D}_{m''m'}{}^{(1)}\mathfrak{D}_{m\ m'v}{}^{(1)}$$
$$+\langle\nabla\mathfrak{E}_{m'v}{}^*\nabla\mathfrak{E}_{m'}{}^*\rangle Q_{m''}Q_m\mathfrak{D}_{m''m'}{}^{(2)}\mathfrak{D}_{m\ m'v}{}^{(2)}$$
$$+\langle\nabla\mathfrak{E}_{m'v}{}^*\mathfrak{E}_{m'}{}^*\rangle\mu_{m''}Q_m\mathfrak{D}_{m''m'}{}^{(1)}\mathfrak{D}_{m\ m'v}{}^{(2)}]+\cdots\Big\}$$
$$\times\sin\theta d\phi d\theta d\psi.$$

Angular brackets have been added to the electric field operators to indicate a spatial average, since an average must be made not only over the angular variables, which involve the molecular operators, but also over the spatial variation of the electric fields available to the molecular translational motion.

Since the $\mathfrak{D}$'s form an orthogonal, normalized set of functions[5] with respect to integrations over the Euler angles, the integrals over the first term in the expansion of the exponential, $1\equiv\mathfrak{D}_{00}{}^{(0)}$, equals zero, a well-known result.

The term linear in $\mathcal{H}_{\text{E}}$, arising from the electric dipole moment, also yields a zero integral, because of the inequality, 1 and 2, of the order of the two $\mathfrak{D}$'s involved. However, the quadrupole contribution is finite and yields a term

$$\frac{2}{5kT}\sum\mathfrak{D}_{m0}{}^{(2)}(-\psi'-\theta'-\phi')\langle\nabla\mathfrak{E}_m{}^*\rangle Q_0.$$

For the terms quadratic in $\mathcal{H}_{\mathrm{E}}$, we have

$$\frac{1}{k^2T^2}\Big\{\sum \mathfrak{D}_{m0}^{(2)}\Big[\langle\mathfrak{E}_{m''}{}^*\mathfrak{E}_{m'}{}^*\rangle\mu_{m''}\mu_m\begin{pmatrix}2 & 1 & 1\\ 0 & m'' & m\end{pmatrix}\begin{pmatrix}2 & 1 & 1\\ -m & m' & m''\end{pmatrix}$$

$$+\langle\nabla\mathfrak{E}_{m''}{}^*\nabla\mathfrak{E}_{m'}{}^*\rangle Q_{m''}Q_m\begin{pmatrix}2 & 2 & 2\\ 0 & m' & m\end{pmatrix}\begin{pmatrix}2 & 2 & 2\\ -m & m' & m''\end{pmatrix}+\langle\mathfrak{E}_{m''}{}^*\nabla\mathfrak{E}_{m'}{}^*\rangle\mu_{m''}Q_m\begin{pmatrix}2 & 1 & 2\\ 0 & m'' & m\end{pmatrix}\begin{pmatrix}2 & 1 & 2\\ -m & m'' & m'\end{pmatrix}\Big]\Big\}.$$

Here, the usual $3-j$ symbol is in brackets; for this Edmonds[5] has given convenient expressions. Obviously, higher terms are available with the use of this method, but the new information that they yield is negligible.

Explicit evaluation of these terms can be readily made. In general,

$$\nabla\mathfrak{E}_0=\tfrac{1}{2}V_{ZZ},\quad \nabla\mathfrak{E}_{\pm1}=\frac{1}{\sqrt{6}}(V_{XZ}\pm iV_{YZ}),$$

$$\nabla\mathfrak{E}_{\pm2}=\frac{1}{2\sqrt{6}}(V_{XX}-V_{YY}\pm2iV_{YX}).$$

Choose as the reference axis the principal axes of the mean electric-field gradient operator with the maximum gradient magnitudes ordered with Z largest, X next, and Y smallest. If the gradients all vanish, the choice is immaterial. The first-order term is then, in general,

$$\frac{Q_0}{10kT}\{(3\cos^2\theta'-1)\langle V_{ZZ}\rangle$$
$$+4\sin\theta'\cos\theta'(\langle V_{ZX}\rangle\cos\phi'+\langle V_{ZY}\rangle\sin\phi')$$
$$+\sin^2\theta'[\langle V_{XX}-V_{YY}\rangle\cos2\phi'+2\langle V_{XY}\rangle\sin2\phi']\}$$

and, on the mean symmetry axes,

$$\frac{Q_0}{10kT}\{(3\cos^2\theta'-1)\langle V_{ZZ}\rangle+\sin^2\theta'\cos2\phi'\langle V_{XX}-V_{YY}\rangle\}.$$

The second-order terms are

Stark.

$$\frac{(2\mu_z{}^2-\mu_x{}^2-\mu_y{}^2)\langle\mathfrak{E}^2\rangle}{30k^2T^2}(3\cos^2\gamma-1),$$

where γ is the angle between $\mathfrak{E}$ and $\mathbf{H}_0$.

Stark-quadrupole.

$$\frac{\sqrt{3}}{30ik^2T^2}[\mu_1Q_{-1}-\mu_{-1}Q_1]\{(\sin^2\theta'\sin2\phi')$$
$$\times\langle(V_{XX}-V_{YY})\mathfrak{E}_Z\rangle+\tfrac{3}{8}\sin\theta'\cos\theta'\sin\phi$$
$$\times\langle V_{ZZ}-\tfrac{1}{4}(V_{XX}-V_{YY})(\mathfrak{E}_X{}^2+\mathfrak{E}_Y{}^2)^{\frac{1}{2}}\rangle\}.$$

Quadrupole. It is unimportant, since first-order quadrupole terms will dominate, if this term is nonvanishing.

DISCUSSION

Several generalities can be stated from inspection of the results.

(a) A molecule with an electric quadrupole moment placed in an electric field with lower than cubic symmetry should have with correlation-time narrowing an NMR proton resonance split by an amount proportional to the field gradients, if a nuclear dipolar hyperfine structure exists.

(b) This quadrupole splitting should vary as T^{-1}, in addition to any implicit temperature dependence of the electric field.

(c) If uniform electric fields of sufficient magnitude are applied to a polarizable system that otherwise possesses statistically, spherical symmetry such as a liquid, a splitting arising from a dipolar hyperfine structive should be observable in the absence of narrowing by chemical exchange. In other words, a molecule possessing a permanent electric moment, for which isotropic exchange hyperfine structure of a few cycles per second has been observed, can exhibit a second-order Stark splitting of this fine structure if a dipolar hyperfine-structure term exists. This effect is proportional to T^{-2}, in addition to any implicit temperature dependence of the electric field.

As an example: If one applies an electric field of 10 kV/cm to a liquid water sample at 300°K, parallel to H_0, a splitting of 0.0057 cps results. This splitting varies as $\mathfrak{E}^2\mu^2T^{-2}$ and can be increased by (1) increasing $\mathfrak{E}$, (2) choosing a molecule with a larger $\boldsymbol{\mu}$, and (3) a lower freezing point to use a lower T. Thus, a change of each of these factors by 2 yields a splitting of 2^6 greater, or approximately 0.5 cps which should be readily measurable with some precision. In any case, such a splitting may not be observable because of chemical exchange.

Note that a linear Stark effect exists in molecules having high electrical asymmetry placed in a region of high-field gradients so that a first-order quadrupole splitting exists. In this case the second-order quadrupole-dipole cross terms give a term that is linear in $\mathfrak{E}$ which can be many orders of magnitude greater than the second-order pure dipole terms if the quadrupole energy is of the order of kT.

The disadvantages of this Stark-effect method of measuring electric dipole moments are numerous and apparent. Not the least is the magnitude of the electric field required. However, the advantages are obvious also, since the dipole moment may be measured independently of the purity of the sample, and in liquids at a single temperature, if its orientation is known; or its orientation in the molecule can be determined if the magnitude of the moment is known.

But to the experimentalist the greatest advantage is, undoubtedly, that we have, apparently, a new probe—the electric field—with which to investigate molecular and nuclear properties.

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APPENDIX A

From the considerations above, one can understand the variation of the splitting observed in zeolite[2] with the number of water molecules in the "cage" as the effect of the electric susceptibility of the water molecule on the internal, crystalline fields. This must certainly be so, since the only other factor, the molecular quadrupole moment, is a molecular constant sensibly invariant with its surroundings; that is, the electronic and nuclear distributions involve energies of the order of electron volts. To consider this shielding problem with all analytical rigor is not appropriate here because it would certainly lead us too far afield; for the solution depends too intimately on the specific details of the situation. Instead, we shall present an approach to an understanding of the effect in a handwaving fashion, and without apology.

We note that the density of water in the zeolites with full hydration is approximately that of liquid water. Thus, the possible variation of molecular density is from that of water to 10% of this density. Since water is a polar molecule, we are plagued, in determining total fields, with the necessity of considering not only the modification of the applied field by the molecular polarizability but also the additional fields contributed by the other molecular water dipole fields. For a sphere of material having cubic lattice symmetry in a uniform electric field, these factors give no difficulty. The dipole sum is zero and the internal field is simply calculated with the depolarization factor, $4\pi/3$, for the sphere. But the zeolite cage does not have cubic symmetry, the fields supplied by the gross lattice are not uniform, and the short-range symmetry of liquid water, or of liquids in general, is not cubic because the molecules have more complicated shapes than that of a sphere. A masterful discussion of these factors for liquids of great extension has been given by Mueller.[6] The reader seeking edification is urged to search there and elsewhere.

For enlightenment we assume a uniform medium, having other than spherical symmetry. We assume that the dielectric properties of water are given, and merely scale the susceptibility with density. A large fraction of the susceptibility $(\kappa-n^2)/\kappa$, where κ is the dielectric constant, and n is the index of refraction, arises from dipolar orientation which is temperature-dependent. We must take the empirical temperature dependence of the electrical susceptibility as given also, that is, a decrease of 0.5%/°K.[7]

From the definition of the Lorentz lattice factor $\mathbf{L}$, we have

$$L_g P_g = \mathfrak{E}_{\text{applied }g} - \mathfrak{E}_{\text{int }g} = L_g \frac{N}{N_0}(\epsilon-1)\mathfrak{E}_{\text{int }g}$$

and $\sum_g L_g = 4\pi$. Here we have written the polarization P_g in terms of the electric susceptibility of water $\epsilon-1$ with the density scaled, and the internal field component $\mathfrak{E}_{\text{int }g}$ in the direction g.

The resultant internal field is thus

$$\mathfrak{E}_{\text{int }g} = \mathfrak{E}_{\text{applied }g}\left[1+L_g\frac{N}{N_0}(\epsilon-1)\right]^{-1},$$

and it is dependent upon the field direction and cavity shape through L_g, on the molecular density through N, and on the temperature through the temperature dependence of ϵ. Note also that L_g includes the lattice fields, as well as the cage-shape factor, and hence is not, in general, equal to the depolarizing factor. Mueller[6] gives calculations of the useful values of L_g, and we only note here that, for example, L_Z, in a hexagonal lattice with $c/a \leq 1$ is $L_Z \simeq (4\pi/9)(a/c)^2$.

In any case, since, as we have said, N/N_0 is approximately the number of molecules in the zeolite cage n and since L_Z is approximately 1, we expect the internal fields to vary inversely with n and nearly directly with T. From this point of view, the implicit temperature dependence of the internal fields can be strong enough to cancel the explicit temperature dependence of the first-order quadrupole splitting term.

We have said that this discussion is inadequate and we must now make a more careful study of these mutual interactions terms, quite possibly including in $\mathcal{H}_E$, from the start, electric dipole-dipole interaction terms. We are investigating this matter, but the success of this effort is still unpredictable.

APPENDIX B

Application to Water Molecules

The water molecule is a symmetrical triangular molecule with an H–O–H angle of 104° and the H–O

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[6] H. Mueller, Phys. Rev. **50**, 547 (1936).

[7] *Dielectric Materials and Applications*, edited by A. H. von Hippel (John Wiley & Sons, Inc., New York, 1954).

distance crudely 10^{-8} cm. From symmetry,

$$\boldsymbol{\mu}=\mu\mathbf{i},$$

$$Q_{\pm 1}=Q_{\pm 2}=0,$$

$$Q_0=\tfrac{1}{2}\textstyle\sum_i (3z_i^2-r_i^2)q_i\neq 0.$$

If we assume, for example, an a $+e/2$ charge at each proton and a $-e$ charge at the oxygen, we find

$$Q_0=2er^2\sin^2 52°\simeq 4.8\times 10^{-26}\text{ esu},$$

$$\mu=er\cos 52°\simeq 2.4\times 10^{-18}\text{ esu}.$$

This is obviously crude, since $\mu=1.85\times 10^{-18}$. We note that Q_0 is approximately 10^{10} that of the deuteron, or approximately 10^8 that of a large *nuclear* quadrupole moment. Since the available internal crystalline fields will be the same, we conclude that the molecular quadrupole coupling energy for water can be approximately 10^8 times that of typical nuclear coupling energies. If we take, as typical of nuclear coupling energies, 10^5 cps or $10^{-8}\,kT$ at room temperature, then the water-molecular coupling energy can, under favorable conditions, be of the order of kT. The experiments for measuring the splitting of the proton resonance in zeolite,[2] if indeed, as it seems likely, the splitting is to be described by the analysis presented here, can be used: (a) If the splitting is due to the molecular quadrupole moment, to define the mean electric field symmetry, that is, $\langle V_{XX}-V_{YY}\rangle/\langle V_{ZZ}\rangle$, or to measure the mean electric field gradients, since the electric quadrupole moment of water is reasonably well known,[8] and to measure the spatial variation of the electric field gradients from the observed linewidth, since the linewidth will be proportional within a constant, to factors such as $\langle V_{ZZ}^2\rangle-\langle V_{ZZ}\rangle^2$, $\langle V_{XY}^2\rangle-\langle V_{XY}\rangle$ and $\langle(V_{XX}-V_{YY})^2\rangle-\langle V_{XX}-V_{YY}\rangle^2$; or (b) If the splitting is the result of the dipole terms, to measure the mean-squared electric field, since the electric dipole moment is well known, to define the mean direction of the electric field, and to measure the spatial variation of the electric field, since the linewidth will depend upon $\langle\mathfrak{E}^4\rangle-\langle\mathfrak{E}^2\rangle^2$.

For example, one finds, by using conventional theory,[1] that the linewidth should vary as

$$\delta\omega=\alpha\tau_c[\langle\omega^2\rangle-\langle\omega\rangle^2],$$

where α is a constant of the order of unity, τ_c is the correlation time, and ω is the nuclear resonance frequency.

For a first-order quadrupole term, one finds, by using the general expression for ω, and with mean axial symmetry so that $\langle V_{XX}-V_{YY}\rangle=0=\langle V_{XY}V_{YZ}\rangle$, that the expression for the linewidth is

$$\delta\omega=\alpha\frac{\tau_c}{16}[\gamma\Delta H]^2\left\{(3\cos^2\theta-1)^2\left[\frac{\langle V_{ZZ}^2\rangle}{\langle V_{ZZ}\rangle^2}-1\right]\right.$$
$$+\frac{\sin^4\theta}{\langle V_{ZZ}\rangle^2}[\cos^2 2\phi\langle(V_{XX}-V_{YY})^2\rangle+4\langle V_{XY}^2\rangle\sin^2 2\phi]$$
$$\left.+16\sin^2\theta\cos^2\theta\frac{\langle V_{XZ}^2\rangle}{\langle V_{ZZ}\rangle^2}\right\},$$

where ΔH is the maximum total observed splitting in gauss, and γ is the nuclear magnetic resonance factor in radians or cps per gauss.

Note that a variation of linewidth with $n\phi$ requires an electric field with symmetry such that $\langle\nabla\mathfrak{E}_{\pm q}\nabla\mathfrak{E}_{\pm(n-q)}\rangle$ be nonvanishing, since the dependence of linewidth on angle is of the form

$$\langle\nabla\mathfrak{E}_{\pm q}\nabla\mathfrak{E}_{\pm(n-q)}\rangle Y_{\pm q}{}^{(2)}(\theta,\phi)Y_{\pm(n-q)}{}^{(2)}(\theta,\phi).$$

The term $Y_m{}^{(l)}(\theta,\phi)$ is the spherical harmonic of order l. This means, for example, that an angular dependence of 3ϕ can be observed only for angles θ not equal to 0 or $\pi/2$.

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[8] W. W. Smith and R. Howard, Phys. Rev. **79**, 132 (1950).