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# Assessment of the spherical-averaging approximation for the interpretation of electron spin-echo modulation for cupric ion complexes

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A comparison is made between three methods for the simulation of deuterated ligand modulation from cupric ion complexes as powders using electron spin-echo modulation (ESEM) spectroscopy: (a) the spherical-averaging approximation which assumes both isotropic $g$ and a random distribution of deuterium nuclei about the paramagnetic center, (b) an average which is performed over specific orientations of the field $H_0$ with respect to $g_\parallel$ using analytical expressions for the spin-echo intensity for an axially symmetric $g$ tensor, and (c) a similar approach to (b) but with full geometrical correlation between the deuterium nuclei. Approach (c) is found to be unnecessary because of the degree of freedom of the ligand molecules to rotate about the ligand axis before freezing locks them into a particular configuration. This, in effect, removes any strict correlation between the deuterium nuclei. Approaches (a) and (b) are found to be equivalent when (i) the electron–nuclear distance $r$ is greater than 0.35 nm, (ii) $r$ is less than 0.35 nm but the number of interacting nuclei, $N$, is 6 or greater, and (iii) $r$ is less than 0.35 nm, $N$ is less than 6, and the angle $\theta_I$ between $g_\parallel$ and $r$ is greater than 45°. In all cases microwave irradiation must be near $g_\perp$. When the situation is none of the above, then parameters defined by the spherical-averaging approximation should be interpreted with caution.

## INTRODUCTION

Electron spin-echo modulation (ESEM) spectroscopy has been used extensively to measure weak hyperfine interactions that are often not observed in continuous wave electron spin resonance owing to various line-broadening processes.[1-4] In frozen solution and crystalline powders analytical expressions have been developed which relate the depth of the modulation to the number of interacting nuclei $N$, the electron–nuclear distance $r$, and the isotropic hyperfine coupling $a_0$.[5-13] For an isotropic signal, apart from the constants $N$, $r$, and $a_0$, the echo intensity depends on the angle $\theta$ between the field direction and the electron–nuclear vector. Problems arise when trying to deal with this angle. In the case of a single crystal, $\theta$ is usually fixed for each interacting nucleus and the total echo intensity $(V_{\text{mod}})^N$ for interaction with $N$ nuclei is calculated by expression (1):

$$(V_{\text{mod}})^N = \prod_{i=1}^{N} V_{\text{mod}}(r_i, a_0, \theta_i). \tag{1}$$

In the case of a crystalline powder the situation becomes more complex. If $N = 1$, then because the field may take up any orientation with respect to the electron–nuclear vector, $\theta$ must be averaged over all orientations as in expression (2):

$$\langle V_{\text{mod}} \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} V_{\text{mod}}(\theta) \sin\theta \, d\theta \, d\phi. \tag{2}$$

When $N > 1$, then for each orientation of the magnetic field each vector, $r_i$, will subtend a different angle $\theta_i$ with the field direction. If the vectors $r_i$ are geometrically correlated such that there is a strict relationship between them, then the echo intensity for a given orientation of the field $H_0$ will be given by an expression such as Eq. (1). Averaging over all

orientations of $H_0$ is then performed by expression (3):

$$\langle (V_{\text{mod}})^N \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \prod_{i=1}^{N} \{V_{\text{mod}}(\theta_i)\} \sin\theta \, d\theta \, d\phi. \tag{3}$$

In the case of a frozen solution very often there will be no such geometrical correlation between the nuclei. To treat this case Kevan et al.[8] introduced the "spherical-averaging approximation" which assumed an effective interaction distance where the nuclei are randomly distributed on a sphere of radius $r$. This allows the integration to be performed before the product over all nuclei, as in expression (4):

$$[\langle V_{\text{mod}} \rangle]^N = \left[ \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} V_{\text{mod}}(\theta) \sin\theta \, d\theta \, d\phi \right]^N. \tag{4}$$

It was also demonstrated that for $r > 0.4$ nm and for $N > 4$ that Eqs. (3) and (4) are equivalent. Equation (4) permits an easy determination of the values of $r$, $N$, and $a_0$ for a powder system.

There has been a lot of recent interest in the application of ESEM techniques to the study of crystalline powders, especially transition metal cations in zeolites.[14-19] One of the important functions of a zeolite is to act as a shape selective catalyst. The transition metal acts as a catalytic center while microporosity of the zeolite structure provides the basis for molecular sieving. It is of much interest, therefore, to determine both the cation siting of the transition metal along with the number of adsorbate ligands whether they be organic species or water. Information about the numbers of ligands has been obtained by adsorbing deuterated organic species or $D_2O$ and then recording the deuterium modulation by three-pulse ESEM spectroscopy. In order to analyze the data in a manageable fashion the spherical approximation has been widely employed utilizing Eq. (4). The justification

for this approach has been that the results make good chemical sense based on the accumulation of a large amount of data on different transition metal ions and with different types of ligands. For instance, complimentary data obtained by adsorption of $CD_3OH$ and $CH_3OD$ yield the same number of interacting molecules and the different deuterium interaction distances give the orientation of the methanol ligand. Methanol is typically found to be coordinated to the transition metal cation through the hydroxyl oxygen. It is corroborative data such as this which lends credence to the whole approach. The purpose of this work is to investigate further the applicability of the spherical approximation to cupric ion complexes.

Two recent papers[20,21] have addressed the problem of partial excitation of an axially symmetric ESR signal with respect to calculating cesium modulation in $Cu^{+2}$-doped zeolites rho and A. In zeolite rho consideration was given to the problem of an axially symmetric $g$ tensor but not to geometrical correlation between the $Cs^+$ cations.[20] In zeolite A both of these aspects were included because the specific location of the $Cs^+$ cations is known and a quite quantitative description of the ESEM spectra was obtained. There is one account[22] where deuterium modulation was calculated for a $VO^{2+}/D_2O$ complex in frozen solution in which the $g$ anistropy was included. However, no correlation was introduced between the deuteriums because of lack of specific geometrical information and simulations were done at $g_\parallel$ and $g_\perp$ and not at an arbitrary observing field.

## THEORY AND DISCUSSION

The development of the theory for integration of the echo intensity in the case of large $g$ anisotropy where only a small fraction of the spectrum is excited is described elsewhere.[2,20] A set of coordinates is defined such that $g_\parallel$ lies along $z$ and then $x$ and $y$ are chosen such that $r$, the electron–nuclear vector, lies in the $z$, $x$ plane at an angle $\theta_I$ to the $z$ axis.

The $H_0$ may take up any orientation in an annulus cut from a sphere such that $\phi_I$ is the azimuthal angle about $z$ between the $z$, $x$ plane and the $z$, $H_0$ plane and $\theta_0$ is the polar angle between $z$ and $H_0$ in the $z$, $H_0$ plane. The annulus will cover the polar angle range $\theta_0 = \theta_0^c + \delta$ to $\theta_0 = \theta_0^c - \delta$, where $\theta_0^c$ is the specific value of $\theta_0$ defined by the $g$ tensor geometry in a molecular system and $2\delta$ is the range of $\theta_0$ covered by the finite width of the microwave pulse. The average modulation for interaction with one nucleus will be given by Eq. (5):

$$\langle V_{mod} \rangle = \frac{1}{4\pi \sin \theta_0^c \sin \delta} \int_0^{2\pi} \int_{\theta_0^c - \delta}^{\theta_0^c + \delta} V_{mod}(\theta_I, \theta_0, \phi_I)$$
$$\times \sin \theta_0 \, d\theta_0 \, d\phi_I. \tag{5}$$

However, this assumes that $\theta_I$ is constant. Consider the case of an octahedrally coordinated hexaquo $Cu^{2+}$ complex. If the water molecules have a degree of freedom to rotate about the $Cu^{2+}$–O axis then an integration must also be performed over $\theta_I$ from $\gamma_1$ to $\gamma_2$, where $\gamma_1$ and $\gamma_2$ are the upper and lower limits of $\theta_I$, respectively. Then Eq. (5) can be

rewritten as Eq. (6):

$$\langle V_{mod} \rangle = \frac{1}{4\pi(\gamma_2 - \gamma_1) \sin \theta_0^c \sin \delta}$$
$$\times \int_{\gamma_1}^{\gamma_2} \int_0^{2\pi} \int_{\theta_0^c - \delta}^{\theta_0^c + \delta} V_{mod}(\theta_I, \theta_0, \phi_I)$$
$$\times \sin \theta_0 \, d\theta_0 \, d\phi_I \, d\theta_I. \tag{6}$$

For more than one nucleus we will consider two cases. In the first case there is no known geometrical correlation between the nuclei. In this case for a set of $N$ nuclei with the same values of $r$, $a_0$, and $\theta_I$ the modulation $\langle V_{mod} \rangle^N$ will be given by Eq. (7). This is tantamount to assuming the nuclei to be randomly distributed around a ring of radius $r \sin \theta_I$:

$$\langle V_{mod} \rangle^N = \left\{ \frac{1}{4\pi(\gamma_2 - \gamma_1) \sin \theta_0^c \sin \delta} \right.$$
$$\times \int_{\gamma_1}^{\gamma_2} \int_0^{2\pi} \int_{\theta_0^c - \delta}^{\theta_0^c + \delta} V_{mod}(\theta_I, \theta_0, \phi_I)$$
$$\left. \times \sin \theta_0 \, d\theta_0 \, d\phi_I \, d\theta_I \right\}^N. \tag{7}$$

In the second case is where there is a known correlation between the azimuthal angles, $\phi_I^i$, for $N$ nuclei with the same values of $r$, $a_0$, and $\theta_I$. In this case the modulation is given by Eq. (8):

$$\langle V_{mod} \rangle^N = \frac{1}{4\pi(\gamma_2 - \gamma_1) \sin \theta_0^c \sin \delta}$$
$$\times \int_{\gamma_1}^{\gamma_2} \int_0^{2\pi} \int_{\theta_0^c - \delta}^{\theta_0^c + \delta} \left\{ \prod_{i=1}^N V_{mod}(\theta_I, \theta_0, \phi_I^i) \right\}$$
$$\times \sin \theta_0 \, d\theta_0 \, d\phi_I \, d\theta_I. \tag{8}$$

Exact analytical expressions for the echo modulation from a nucleus with $I = 1$ in the absence of quadrupolar effects are taken from Dikanov et al.[23] and are as follows:

$$V_{mod}^1$$
$$= \frac{1}{2} \left\{ \frac{1}{2I+1} \sum_{m=-1}^{m=1} \cos m\xi^\alpha \frac{1}{2I+1} \sum_{m=-1}^{m=1} \cos m\xi^\beta \right\}$$
$$= \frac{1}{6} \left\{ 4 \left( \cos^2 \frac{\xi^\alpha}{2} + \cos^2 \frac{\xi^\beta}{2} \right) - 1 \right\}, \tag{9}$$

where

$$\cos \left( \frac{\xi^\alpha}{2} \right) = 1 - 2k \sin^2 \frac{\omega_\alpha(\tau + T)}{2} \sin^2 \frac{\omega_\beta \tau}{2},$$
$$\cos \left( \frac{\xi^\beta}{2} \right) = 1 - 2k \sin^2 \frac{\omega_\beta(\tau + T)}{2} \sin^2 \frac{\omega_\alpha \tau}{2},$$
$$k = \left( \frac{\omega_I B}{\omega_\alpha \omega_\beta} \right)^2, \quad \omega_I = \frac{g_n \beta_n H_0}{\hbar},$$
$$\omega_\alpha = \left[ \left( \frac{A}{2} + \omega_I \right)^2 + \left( \frac{B}{2} \right)^2 \right]^{1/2},$$
$$\omega_\beta = \left[ \left( \frac{A}{2} - \omega_I \right)^2 + \left( \frac{B}{2} \right)^2 \right]^{1/2},$$

$$A = \frac{g g_n \beta \beta_n}{\hbar r^3} \left\{ \left[ \frac{3}{g^2} \right] (g_{\parallel}^2 \cos \theta_0 \cos \theta_I \right.$$

$$+ g_{\perp}^2 \sin \theta_0 \sin \theta_I \cos \phi_I )( \cos \theta_0 \cos \theta_I$$

$$\left. + \sin \theta_0 \sin \theta_I \cos \phi_I ) - 1 \right\} - 2\Pi a_0,$$

$$B^2 = B'^2 + C'^2,$$

$$B' = \frac{g g_n \beta \beta_n}{\hbar r^3} \left\{ \left( \frac{3}{g^2} \right) (g_{\parallel}^2 \cos \theta_0 \cos \theta_I \right.$$

$$+ g_{\perp}^2 \sin \theta_0 \sin \theta_I \cos \phi_I )$$

$$\times (\cos \theta_0 \sin \theta_I \cos \phi_I - \sin \theta_0 \cos \theta_I )$$

$$\left. + \left( \frac{2\pi \hbar a r^3}{g g_n \beta \beta_n} - 1 \right) \left( \frac{g_{\perp}^2 - g_{\parallel}^2}{g^2} \right) \sin \theta_0 \cos \theta_0 \right\},$$

$$C' = \frac{g g_n \beta \beta_n}{\hbar r^3} \left\{ \left( \frac{3}{g^2} \right) (g_{\parallel}^2 \cos \theta_0 \cos \theta_I + g_{\perp}^2 \right.$$

$$\left. \times \sin \theta_0 \sin \theta_I \cos \phi_I )( \sin \theta_I \sin \phi_I ) \right\}.$$

Let us now consider the $Cu^{2+}/D_2O$ complexes that have been found in a zeolitic environment; they are illustrated in Fig. 1. First consider an octahedrally coordinated hexaquo complex with two axial ligands and four equatorial ligands. Assume the water is coordinated through the oxygen with the D–O–D plane containing the ligand axis and that at room temperature it can rotate freely about the ligand



FIG. 1. Schematic representation showing various hydrated $Cu^{2+}$ complexes that exist within zeolite structures: (a) hexaquo complex with no coordination to the zeolite lattice, (b) octahedral complex coordinated to three water molecules and three lattice oxygens in a zeolite six ring, (c) trigonal-bipyramidal complex, (d) square-based pyramidal complex, and (e) tetrahedral complex.

axis. Then, for the equatorial ligands $\theta_I$ is $90° \pm 16°$ and for the axial ligands $\theta_I = 16° \pm 0°$; see Fig. 1(a). The range in $\theta_I$ is determined from the geometry of a water molecule and a $Cu^{2+}$–O distance of 0.21 nm, assuming that the water molecule is frozen randomly into various orientations at 4 K.

Cupric ions also often have coordination to three zeolite oxygens in a six ring together with coordination to additional water. For interaction with three water molecules the complex will assume near-octahedral stereochemistry, however, the g tensor will not be aligned along a ligand direction as shown in Fig. 1(b). For all interacting deuteriums $\theta_I = 55° \pm 16°$, again allowing for rotation about the ligand axis.

For a cupric ion located in a six ring and coordinated to two water molecules the stereochemistry may be either trigonal-bipyramidal or square-based pyramidal; see Figs. 1(c) and 1(d). For the former case, $\theta_I = 16° \pm 0°$ but for the latter case the g tensor will not be axially symmetric and so will not be considered here. Finally for a cupric ion located in a six ring and coordinated to only one water molecule then the most likely stereochemistry is tetrahedral with $\theta_I = 16° \pm 0°$ as in Fig. 1(e).

Another likely cation position for a cupric ion is a four-ring site where it is coordinated to two zeolitic oxygens. Additional coordination to two, three, or four water molecules will result in square-coplanar, square-based pyramidal, and octahedral stereochemistries, respectively. However, for all these complexes the g tensor will probably not be axially symmetric and so is beyond the scope of this article.

To perform the integration in Eqs. (7) and (8) it is also necessary to derive the width of the microwave pulse in terms of the spread in $\theta_0$. The microwave pulses for an ESEM experiment in our laboratory are typically of 40 ns duration and cover about 18 G at $H_0 = 3150$ G. We will consider a typical axially symmetric g tensor for a $Cu^{2+}$ complex: $g_{\parallel} = 2.396$; $g_{\perp} = 2.064$; $A_{\parallel} = 132 \times 10^{-4}$ cm$^{-1}$; $A_{\perp} = 14 \times 10^{-4}$ cm$^{-1}$. If the field is adjusted to irradiate in the $g_{\perp}$ region at the point of maximum echo intensity then $\theta_0$ is approximately $83° \pm 7°$. This is calculated by simulating a typical powder spectrum using the analytical expressions given by Siderer and Luz.[24] At the maximum echo intensity all four copper hyperfine components near $g_{\perp}$ are excited resulting in a variation in $\theta_0$ of 7°, as quoted above. If the field is tuned to the $m = 3/2$ $g_{\perp}$ hyperfine component then a better choice of $\theta_0$ might be $86° \pm 4°$, however, the echo intensity is about four times smaller resulting in poorer signal to noise.

The method used to compare the spherical-averaging approach of Eq. (4) with that of using Eq. (7) was first to generate a modulated echo decay curve using Eq. (7) with reasonable values of r and $a_0$. This simulated curve was then treated as if it were experimental data using ratio analysis[9] with the spherical-averaging approximation to obtain the best fit parameters, N, r, and $a_0$. The ratio analysis procedure compares the ratios of the maxima to minima of the modulation envelope as a function of interpulse time T to cancel out the unknown relaxation decay function.[9] These derived parameters are then compared to the ones in the original simulation to assess the validity of the spherical-averaging approximation.
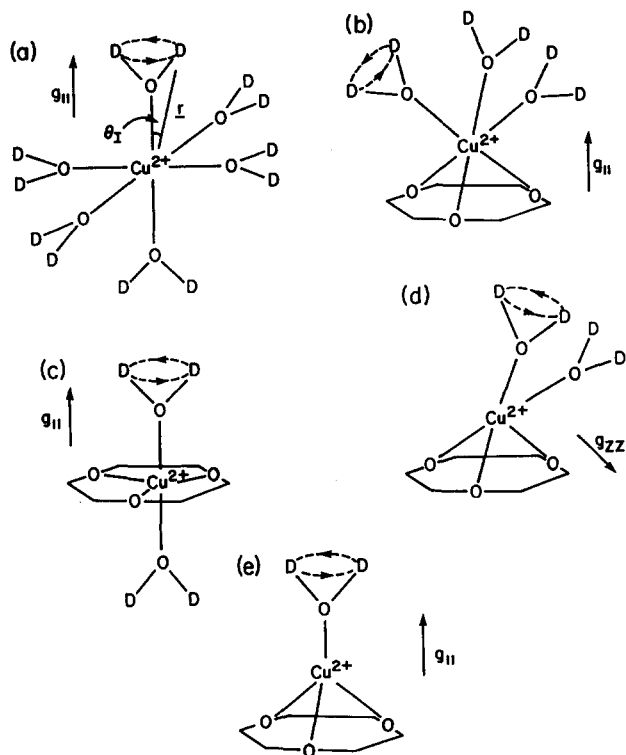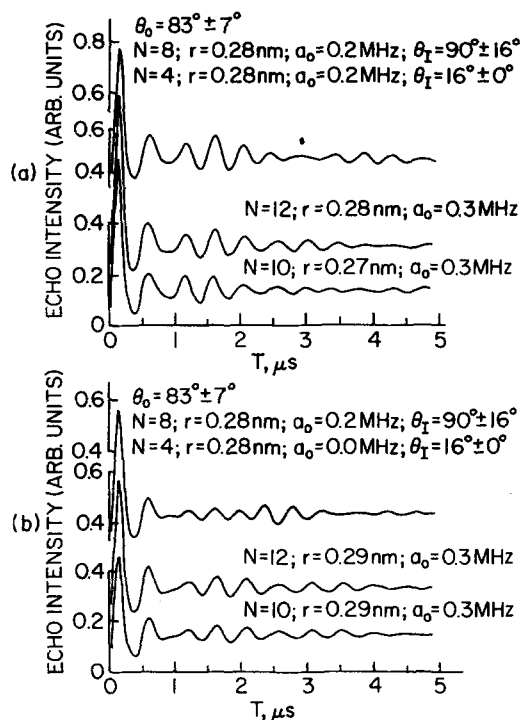
FIG. 2. Calculated three-pulse ESEM spectra of a hexaquo complex. (a) Top spectrum calculated by Eq. (7) using two sets of interacting nuclei: $N = 8, r = 0.28$ nm, $a_0 = 0.2$ MHz, $\theta_I = 90° \pm 16°$ and $N = 4, r = 0.28$ nm, $a_0 = 0.2$ MHz, $\theta_I = 16° \pm 0°$; lower spectra are two simulations calculated using the spherical-averaging approximation. (b) Same as (a) except that the second set of nuclei for the top spectrum has $a_0 = 0.0$ MHz.

Figure 2 shows two three-pulse ESEM spectra calculated using Eq. (7) for an octahedrally coordinated hexaquo species. In both cases the distance $r$ was 0.28 nm for all deuteriums regardless of whether the water molecule was in an axial or equatorial position. Figure 2(a) was calculated with $a_0 = 0.2$ MHz for all the deuteriums and Fig. 2(b) with $a_0 = 0.2$ MHz for the equatorial deuteriums and 0.0 MHz for the axial deuteriums. This latter example will probably be closer to the true situation because the unpaired electron in such a complex will reside somewhere near the equatorial plane. The possibility of orbital overlap with the axial deuteriums is therefore negligible. Such a situation was postulated previously for a $VO^{2+}/D_2O$ complex by Dikanov *et al.*[22] In case (a) the spherical averaging gave a best fit with $N = 12, r = 0.28$ nm, and $a_0 = 0.3$ MHz although a possible fit with $N = 10$, $r = 0.27$ nm, $a_0 = 0.3$ MHz could not be ruled out. The spherical approximation gives a good replication of the data yielding closely similar values for $N$, $r$, and $a_0$. In case (b) the best fit was either $N = 12, r = 0.29$ nm, and $a_0 = 0.3$ MHz or $N = 10$, $r = 0.29$ nm, and $a_0 = 0.3$ MHz. Although the fits are not precisely the same between the two approaches the spherical approximation is accurate enough to determine direct coordination to either five or six water molecules. Then with additional information such as the values of $g_\parallel, g_\perp, A_\parallel$, and $A_\perp$, and also the behavior of the ESR signal with temperature, the choice between fivefold and sixfold coordination should be possible. Other values of $r$ and $a_0$ were chosen for the calculation using Eq. (7) but in all cases the spherical average always gave a fit indicating
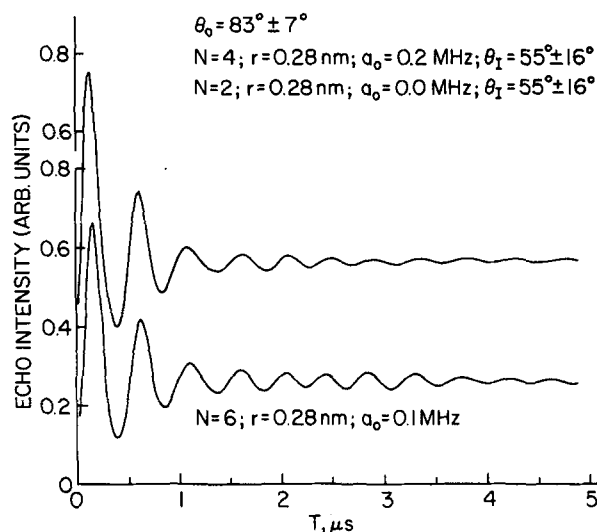


FIG. 3. Calculated three-pulse ESEM spectra of an octahedral complex coordinated to three water molecules and three lattice oxygens. Top spectrum calculated by Eq. (7) using two sets of nuclei: $N = 4, r = 0.28$ nm, $a_0 = 0.2$ MHz, $\theta_I = 55° \pm 16°$ and $N = 2$, $r = 0.28$ nm, $a_0 = 0.0$ MHz, $\theta_I = 55° \pm 16°$. Lower spectrum calculated using the spherical-averaging approximation.

interaction with five or six water molecules. The value of $a_0$ obtained with the spherical-averaging approach is largely a fitting factor and should not be considered as particularly physically significant.

Figure 3 shows the three-pulse ESEM spectrum calculated using Eq. (7) for an octahedrally coordinated species with three water ligands and three ligands to zeolitic oxygen. This example shows results calculated with $r = 0.28$ nm, $a_0 = 0.2$ MHz for the four equatorial deuteriums and $r = 0.28$ nm, $a_0 = 0.0$ MHz for the two axial deuteriums. In this case the best fit using the spherical-averaging approximation was $N = 6$, $r = 0.28$ nm, and $a_0 = 0.1$ MHz. With
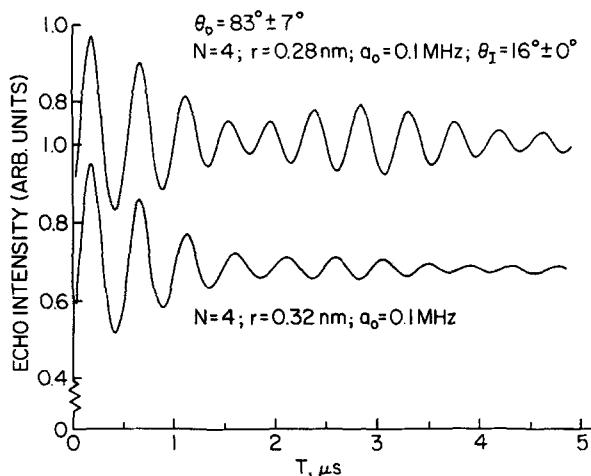


FIG. 4. Calculated three-pulse ESEM spectra of a trigonal-bipyramidal complex coordinated to two axial water molecules and three equatorial lattice oxygens. Top spectrum calculated by Eq. (7) using $N = 4, r = 0.28$ nm, $a_0 = 0.1$ MHz, $\theta_I = 16° \pm 0°$. Lower spectrum calculated using the spherical-averaging approximation.

the spherical-averaging approximation the value of $N$ was unambiguous and the value of $r$ correct indicating interaction with three water molecules. Again $a_0$ is some average fitting parameter but the important information, from a chemical standpoint, of $N$ and $r$ is obtained from the spherical-averaging approximation.

Figure 4 shows the three-pulse ESEM spectrum for a trigonal bipyramidal species coordinated axially to two water molecules. This particular spectrum was calculated with Eq. (7) using $r = 0.28$ nm and $a_0 = 0.1$ MHz. The best fit using the spherical-averaging approximation is $N = 4$, $r = 0.32$ nm, and $a_0 = 0.1$ MHz. However, the fit is still rather poor. Clearly there is a significant discrepancy in $r$ indicating that the spherical-averaging approximation breaks down in this case. This is not surprising considering that the field is directed at 90° to $g_{\parallel}$ whereas the electron–nuclear vector is tilted only 16° from $g_{\parallel}$. As $\theta_I$ approaches 0°, $\theta_0$ approaches 90° and from Eqs. (9) $k$ goes to zero so that the modulation is completely suppressed whereas the spherical-averaging approximation predicts no change in the modulation depth with $\theta_I$. For the same reason a similar problem is encountered in the interpretation of a tetrahedral species coordinated to one water molecule and three zeolitic oxygens as shown in Fig. 5.

As $\theta_I$ increases the agreement between the two approaches improves, however, there may still be an ambiguity in the number of water molecules. Chemical intuition might well remove some of the ambiguity. For instance, in the case of $Cu^{2+}$ directly coordinated to a water molecule the predicted electron–deuterium distance based on ionic radii of $Cu^{2+}$ and $O^-$ is 0.26 to 0.28 nm. Therefore, if the ambiguity is between two deuterons at 0.28 nm and four deuterons at 0.32 nm and we expect direct coordination to explain the ESR data then we would opt for the former distance. When $\theta_I$ is small (less than 45°) and $N$ is small (less than 6), the parameters determined from the spherical-averaging approximation can be somewhat inaccurate and must be evaluated with caution.

Another way to determine the appropriateness of the spherical-averaging approximation is to determine the range of angle $\theta$ between $r$ and $H_0$. For instance, if $\theta_I = 54° \pm 16°$ and $\theta_0 = 83° \pm 7°$ then $\theta$ will range from 6° to 52°. In the spherical-averaging approximation integration over $\theta$ is performed from 0° to 90°, disregarding the portion from 90° to 180° which is related by symmetry. Therefore, in the example considered above the fraction of the area of the sphere being integrated is 0.4. If $\theta_I$ is $16° \pm 0°$ and $\theta_0 = 83° \pm 7°$ then $\theta$ ranges from 60° to 70° covering only 0.2 of the sphere. This example suggests that integration over at least 0.4 of a sphere is necessary before the spherical approximation gives meaningful results.

A geometrically correlated model was also investigated using Eq. (8). For an octahedral hexaquo complex the equatorial deuteriums were taken with $\theta_I = 90° \pm 0°$. This gives the values of $\phi_I^i$ to be $\phi_I^1 = \phi_I$; $\phi_I^2 = \phi_I + 32°$; $\phi_I^3 = \phi_I + 90°$; $\phi_I^4 = \phi_I + 122°$, etc. The axial deuteriums were assumed not to be correlated with the equatorial deuteriums. Using this approach the three-pulse ESEM spectrum was calculated, however, many new frequency components were added to the spectrum. Since such multiplicity of frequencies have not been observed in zeolite systems it appears that there is enough disorder owing to differences in rotation about the ligand axis that the approach described by Eq. (7) is adequate.

The effect of having different values of $r$ and $a_0$ for different deuteriums within one aquo-complex was also examined. Often in octahedral complexes the axial ligands will be longer than the equatorial ligands due to a Jahn–Teller distortion. Varying $r$ between 0.26 and 0.30 nm had very little effect on the overall modulation. However, the modulation is quite sensitive to variations in $a_0$. Neither parameter seemed to affect the conclusions derived so far about the applicability of the spherical approximation which always gives a mean value.

Probably more important than the aquo complexes in zeolites are the complexes formed upon adsorption of organics such as: $CD_3OH$, $CH_3OD$, $C_2D_4$, $ND_3$, $C_6D_6$, $CH_3CH_2OD$, and $CH_3CD_2OH$. For alcohols with the deuterium on the hydroxyl group the electron–nuclear distance is usually the same as for the aquo complexes. Therefore the same rules apply for using the spherical approximation as outlined above. For $CD_3OH$ and $CH_3CD_2OH$ the average electron–nuclear distance will be about 0.36 nm. Similar or longer distances would be expected for $C_2D_4$ and $C_6D_6$. For interaction distances above about 0.35 nm little difference was found between using the two approaches, Eqs. (2) or (7). It is difficult to determine ranges of $\theta_I$ for such complexes owing to the variety of different orientations of the ligands. However, one example is shown in Fig. 6 for a complex containing one molecule of $C_2D_4$. The worst case for agreement between Eqs. (2) and (7) is usually when $\theta_I$ is small. To this end $g_{\parallel}$ was chosen directed towards the center of the ethylene molecule with the C=C bond axis perpendicular to $g_{\parallel}$. This gives reasonable values for $\theta_I$ like $25° \pm 0°$ with $N = 4$, $r = 0.36$ nm, and $a_0 = 0$ MHz. The best fit using
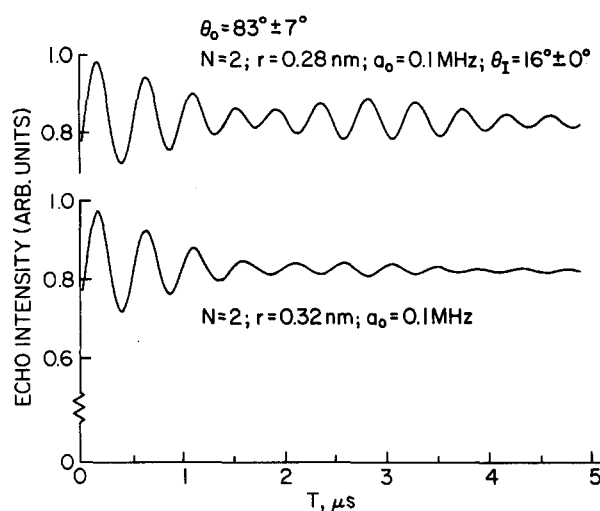


FIG. 5. Calculated three-pulse ESEM spectra of a tetrahedral complex coordinated to one water molecule and three lattice oxygens. Top spectrum calculated by Eq. (7) using $N = 2$, $r = 0.28$ nm, $a_0 = 0.1$ MHz, $\theta_I = 16° \pm 0°$. Lower spectrum calculated using the spherical-averaging approximation.
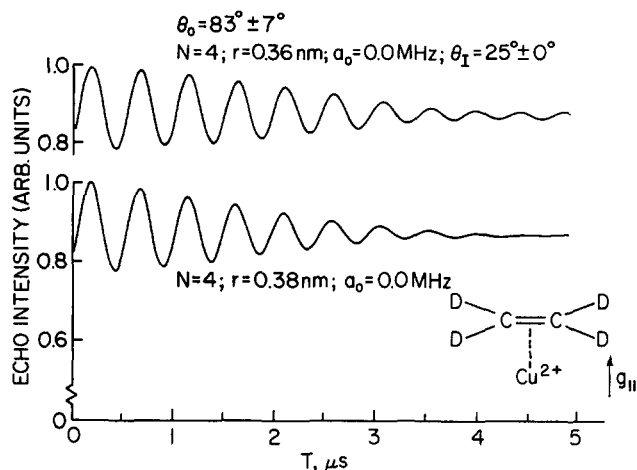
FIG. 6. Calculated three-pulse ESEM spectra of a complex containing one molecule of $C_2D_4$ where $g_\|$ is directed towards the center of the C=C double bond. Top spectrum calculated by Eq. (7) using $N = 4$, $r = 0.36$ nm, $a_0 = 0.0$ MHz, $\theta_I = 25° \pm 0°$. Lower spectrum calculated using the spherical-averaging approximation.

the spherical approximation is with $N = 4$, $r = 0.38$ nm, and $a_0 = 0$ MHz. Even for this worst case the spherical approximation gives a good interpretation of the data.

The agreement between simulation approaches is even better for $C_6D_6$, $CD_3OH$, and $CD_3CD_2OH$. Therefore, in the case of alcohol molecules, it is best to have the deuterium substitution at positions other than the hydroxyl group for optimum applicability of the spherical approximation.

All the calculations discussed so far have involved irradiation near $g_\perp$, $\theta_0 = 83° \pm 7°$. However, using Eq. (7) the modulation may be determined at any value of $\theta_0$. As $\theta_0$ approaches 0° tending towards $g_\|$, the agreement between Eq. (7) and the spherical approximation becomes poor. The reason for this is that at $g_\|$, $\theta_0$ no longer has any meaning and effectively the system resembles that of a single crystal. For easy interpretation of data using the spherical-averaging approximation it is best to observe the echo at a magnetic field near $g_\perp$.

Consideration has been given in detail only to three-pulse spin-echo experiments because in zeolite systems two-pulse echo experiments with deuterated absorbates always exhibit mixed deuterium and aluminum modulation. However, since the applicability of the spherical-averaging approximation rests mainly on the method of integration, parallel arguments can be drawn for both two- and three-pulse echo experiments. Also, the conclusions drawn are applicable to transition metals other than $Cu^{2+}$.

## CONCLUSIONS

A comparison has been made between three types of simulation procedures for the interpretation of deuterium modulation associated with cupric ions in ESEM spectroscopy: the spherical-average approximation for isotropic $g$; a circular-average approximation for axially symmetric $g$ with correlation only between $\theta_I$; and a completely correlated circular averaging for axially symmetric $g$. The last approach is found unnecessry for both deuterated water ligands and deuterated organic ligands. The agreement between the first two approaches is satisfactory for electron–nuclear distances greater than 0.35 nm, as is the case for ligands such as $CD_3OH$, $CD_3CD_2OH$, $C_2D_4$, and $C_6D_6$. When the electron–nuclear distance is less than 0.35 nm, then the two approaches are similar when (a) $N$ is 6 or greater or (b) $\theta_I$ is greater than about 45°. In all cases irradiation should be close to $g_\perp$ rather than $g_\|$. When $\theta_I$ for all deuteriums is less than about 45° and the electron–nuclear distance is less than 0.35 nm, the spherical-averaging approximation should be used with caution.

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