Isotropic Proton Hyperfine Coupling Constants of Two Cationic Nitroxides

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The isotropic proton hyperfine coupling constants of 2,2,6,6-tetramethylpiperidineoxide–trimethylammonium bromide and 2,2,6,6-tetramethylpiperidineoxide–dodecyldimethylammonium bromide have been determined using a nuclear magnetic resonance technique. The measured coupling constants have been used to generate computer simulated electron paramagnetic resonance (e.p.r.) spectra, which show moderate agreement with experimental e.p.r. spectra. Evidence is presented which indicates that intermolecular exchange effects in the e.p.r. spectra may account for the discrepancies.

Proton hyperfine structure makes an appreciable contribution to the linewidths of solution electron paramagnetic resonance (e.p.r.) spectra of nitroxides, such as the cationics $I(n = 0)$ and $I(n = 11)$. Motional parameters such as correlation times
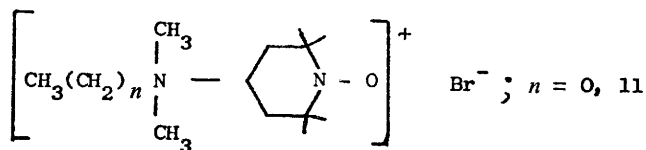
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are related to the linewidth in the absence of proton hyperfine structure; it is this linewidth which must be determined in detailed studies of nitroxide motion. In principle, this linewidth can be obtained from comparisons of computer simulated and experimental spectra.[1]

The proton hyperfine coupling constants necessary for simulating the e.p.r. spectra can be determined from the proton nuclear magnetic resonance (n.m.r.) spectra of concentrated solutions of nitroxides, if the nitroxide concentration is high enough to shorten the electron spin relaxation time to a time shorter than the inverse of the proton hyperfine coupling constant.[2] If the electron spin population follows a Boltzmann distribution and the high temperature limit applies ($g\beta H/kT \ll 1$), then the energy of interaction of a nitroxide proton with the combined magnetic field due to the unpaired electron and the n.m.r. spectrometer will be given by

$$\mathcal{H} = -g_N\beta_N I_z H\left[1 + \frac{g\beta}{g_N\beta_N}\frac{aS(S+1)}{3kT}\right] \qquad (1)$$

where g, g_N, β and β_N are the electron and nuclear g-factors and the electron (Bohr) and nuclear magnetons respectively, H is the applied magnetic field, I_z the nuclear spin quantum number, S the electron spin quantum number, k Boltzmann's constant, T, the temperature in Kelvin, and a the isotropic proton hyperfine coupling constant.

Compared with the nuclear resonance of a similar proton in a diamagnetic compound, the n.m.r. peak of the nitroxide proton is shifted downfield by an amount $g\beta/g_N\beta_N \cdot aS(S+1)/3kT$ if a is positive, and upfield by the same amount if a is negative. From the observed shift the sign and magnitude of the isotropic hyperfine coupling constant can be determined if S and T are known.[3-10]

EXPERIMENTAL

Nitroxides I($n = 0$) and I($n = 11$) were prepared according to a procedure supplied by Dr. W. L. Hubbell of Stanford University for I($n = 11$),[11] modified somewhat for I($n = 0$).[12] The n.m.r. spectra of the diamagnetic (amine) precursors of I($n = 0$) and I($n = 11$) were obtained using a Perkin Elmer R-12A n.m.r. spectrometer while the n.m.r. spectra of the paramagnetic compounds were recorded on a Varian 220 MHz n.m.r. spectrometer. E.p.r. spectra were recorded on a Varian E-4 spectrometer equipped with a variable temperature accessory.

RESULTS

The n.m.r. spectrum of I($n = 11$), dissolved in a minimum amount of D_2O at 60°C and then heated to 97 ± 2°C as measured from the temperature-dependent splitting of a standard ethylene glycol sample, is shown in fig. 1. The resonances marked A, B and C are identified as broadened diamagnetic lines arising from HOD, $(H_3C)_3N$ and the hydrocarbon chain protons respectively. The resonances at D and E decreased as the sample was diluted with D_2O, and hence are due to protons coupled with an unpaired electron. From intensity considerations, the high field line was assigned to the twelve methyl protons, and the shoulder to lower field to the four methylene protons. The spectrum was scanned 10 000 Hz up-field and down-field of the diamagnetic resonances, but no other paramagnetically shifted peaks were observed. This is not surprising, in view of the low intensity of the observed paramagnetically shifted peaks.
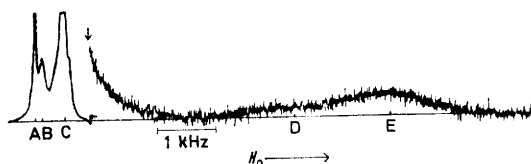

FIG. 1.—N.m.r. spectrum of I($n = 11$) in D_2O. The vertical arrow indicates an amplitude gain for the remainder of the spectrum.

The n.m.r. spectra of the diamagnetic precursors of I($n = 11$) and I($n = 0$) indicated that the positions of the nitroxide ring methylene protons, the nitroxide ring methyl protons, and the hydrocarbon chain methylene protons were similar, within the accuracy required for the determination of the isotropic hyperfine coupling constant from n.m.r. data. Therefore, the diamagnetic hydrocarbon peak in fig. 1 was taken as the diamagnetic position from which the methyl and methylene peaks had been shifted. Using the measured value of these shifts and the measured temperature of 97 ± 2°C, the isotropic hyperfine coupling constants were calculated, using eqn (1), to be $a_{CH_3} = -42.5\pm1.2\mu$T, $a_{CH_2} = -30\pm3\mu$T.

Since the signals from which these coupling constants were obtained were quite weak, it was thought that more reliable results might be obtained from I($n = 0$), which is easier to solubilize in D_2O. The n.m.r. spectrum of a saturated solution of I($n = 0$) in D_2O is shown in fig. 2. This spectrum was obtained from the oscilloscope

of the 220 MHz n.m.r. spectrometer. The large peaks at the left of the spectrum are the first sidebands of the diamagnetic peaks (the normally recorded spectrum). The central peaks are the paramagnetic peaks, and the right hand peaks the second sidebands of the diamagnetic peaks, shifted from the first sidebands by 10 000 Hz. The coupling constants obtained from the shift from the diamagnetic hydrocarbon peak are $a_{CH_3} = -44 \pm 2 \mu T$, and $a_{CH_2} = -31 \pm 2 \mu T$.
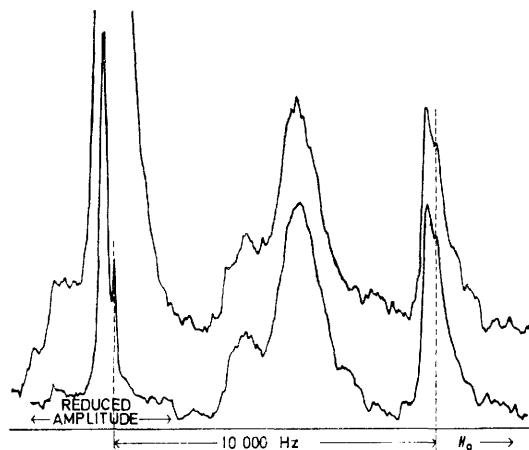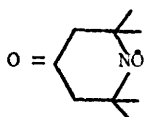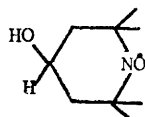

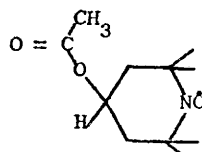FIG. 2.—N.m.r. spectrum of I($n = 0$) in D_2O.

The coupling constants obtained for I($n = 0$) are in reasonable agreement with those obtained for I($n = 11$). The coupling constants found in the literature for other nitroxides, II-VII, are shown in table 1.
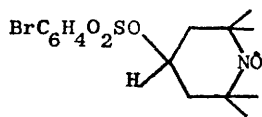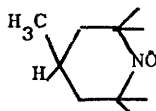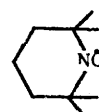

Thus the coupling constants assigned to I($n = 0$) and I($n = 11$) are in reasonable agreement with those which have been found for similar nitroxides.

Studies of radicals II, III, IV and VII have shown [8] that the temperature dependence of the coupling constants is small, especially at temperatures above 35°C. However, the variation in the magnitude of the coupling constants with concentration cannot be measured. It is thought that this may be the cause of small differences, of the order of 5-10 %, between the values of the hyperfine coupling constants determined by n.m.r. and the values necessary to reproduce the observed e.p.r. spectrum.[4, 5, 7, 10]

For this reason, the hyperfine coupling constants determined for I($n = 11$) were varied by up to 10 % of their magnitude in order to obtain a better fit between the observed e.p.r. spectra and the computer simulated spectra.

TABLE 1.—THE ISOTROPIC HYPERFINE COUPLING CONSTANTS OF SEVERAL NITROXIDES

ref.	radical	$a_{CH_3}/\mu T$	$a_{CH_2}/\mu T$	$a_{CH}/\mu T$
8	II	-11	-1	
9	II	-12	-2	
8	III	-43	-29	$+9$
9	III	-45	-34	$+7$
8	IV	-41	-29	$+9$
9	IV	-43	-31	$+8$
9	V	-41	-32	$+6$
9	VI	-40	-27	0
8	VII	-22	-39	$+18$
9	VII	-23	-39	$+18$

COMPUTER SIMULATION OF NITROXIDE SPECTRA

The program used to computer-simulate e.p.r. spectra was written by C. S. Johnson, Jr.[13] It has been modified by M. K. Ahn, Yale University and by M. A. Turpin and Mrs. J. C. Savage of Unilever Research.   The program calculates line positions and intensities from assumed hyperfine coupling constants, and then calculates and plots the resultant spectrum.   The individual lines can have either Gaussian or Lorentzian lineshapes, and the spectrum can be calculated in either the adsorption mode or in the first or second derivatives thereof.   The program assumes that each of the hyperfine lines has the same width.   The calculated spectra are first order approximations, and are strict superpositions of their components—*i.e.* any possible exchange between components is not taken into account.
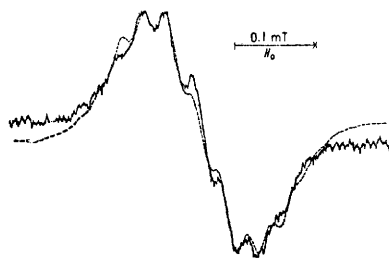

FIG. 3.—Comparison of computed and experimental spectra, ——— experimental spectrum, - - - - - spectrum computed with $a_{CH_3} = 45.8\ \mu T$, $a_{CH_2} = 32.5\ \mu T$, gaussian lineshape, linewidth $= 40\ \mu T$.

This program was used, in conjunction with the proton hyperfine coupling constants determined from n.m.r. spectroscopy, to calculate simulated e.p.r. spectra. It was assumed that only four methylene protons and twelve methyl protons contributed to the spectrum.   When the experimentally determined coupling constants were used, it was found that the experimental spectrum was not reproduced by the program.   For an appropriately low line-width (about 38 μT), 65 Lorentzian lines formed by splitting 13 lines of binomial intensity separated by 42.5 μT each into 5 lines of binomial intensity separated by 30 μT gave a first-derivative spectrum similar to that shown in fig. 4c.   An experimental spectrum of the $M_I = 0$ line, obtained at low modulation amplitude (3.2 μT) from a de-oxygenated sample in order to avoid

extraneous line broadening, is shown in fig. 3 for comparison. It can be seen that the feature numbered 1 on the simulated spectrum is too sharp, while the features numbered 3 and 4 are not sharp enough.   If one keeps the linewidth narrow enough to allow the features of the line, determined by the proton hyperfine structure, to be observable, then the general shape of the line will be determined by the ratio of the proton hyperfine coupling constants, while the absolute distances such as the distance
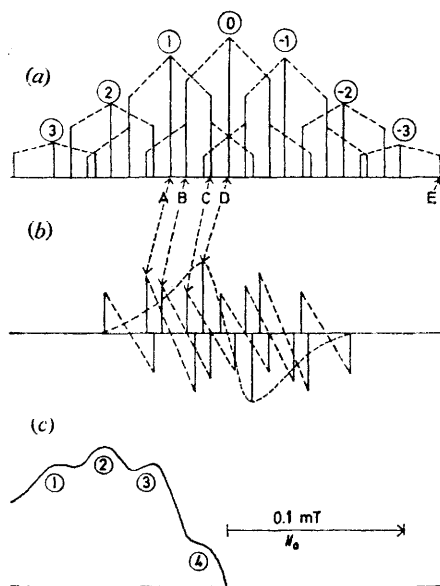

FIG. 4.—Computer simulation of nitroxide spectra.   (a) Stick diagram, (b) first derivatives, (c) top half of simulated spectrum.   Symbols explained in the text.

of any feature from the centre of the spectrum can be fixed by adjusting the magnitudes of the coupling constants after their ratio has been determined.   In an attempt to improve the spectral simulation, the methyl coupling was fixed at $45.5\ \mu T$ and the methylene coupling constant allowed to range from $20.0\ \mu T$ to $45.5\ \mu T$ in steps of $0.1\ \mu T$.   No significant improvement was observed.   Since experimental lineshapes are intermediate between Lorentzian and Gaussian, the computer-simulations were repeated using Gaussian instead of Lorentzian lines.   The best result of this simulation is shown in fig. 3.   One can see that the feature numbered 1 is still too sharp, while the feature numbered 4 is not sharp enough.

Since the Gaussian character of e.p.r. lines is often due to the presence of unresolved hyperfine structure, it was thought that a small coupling due to the proton in the γ position might be causing both the Gaussian lineshape and the lack of agreement between the computed and the experimental spectra.   To check this assumption, each of the 65 lines in the simulated spectrum was split into two lines of equal intensity, separated by coupling constants ranging from $0.01\ \mu T$ to $0.2\ \mu T$ in steps of $0.01\ \mu T$, from $0.2\ \mu T$ to $2.0\ \mu T$ in steps of $0.2\ \mu T$, and from $2.0\ \mu T$ to $15.0\ \mu T$ in steps of $0.5\ \mu T$.   The lineshapes in these simulations were Lorentzian.   No significant improvement in the computed spectra resulted.   Thus it was concluded that the possible Gaussian character of the lineshape was not due to the presence of a small hyperfine splitting due to the γ proton.

DISCUSSION

In a study of Heisenberg spin exchange,[14] Freed and co-workers have shown that, when the strongest nuclear spin-dependent relaxation processes are due to exchange, in the slow exchange region the width of each hyperfine line depends upon the degeneracy of that line, according to eqn (2).

$$[\delta_M - \delta_M(0)] = \frac{2}{\sqrt{3}} W_{HE}\left(\frac{N - 2D_M}{N}\right). \tag{2}$$

Here $\delta_M - \delta_M(0)$ is the increase, in Hz, in the width of the line of spectral index number M and degeneracy D_M caused by Heisenberg spin exchange at frequency W_{HE}. N is the total number of transitions. Since different nitroxide proton hyperfine lines will have different degeneracies, if exchange is present the widths of the lines will not be the same.

In fig. 4(a) a stick diagram is shown which contains the more intense (10 % of the most intense line or greater) proton hyperfine lines. The encircled numbers above some of the lines are the nuclear magnetic moments of the methyl protons—for all of these lines the methylene proton magnetic moment is zero. Dashed lines connect these lines to other lines with the same methyl proton coupling but different methylene proton couplings. Of the lines shown here the one labelled by the encircled zero is the most degenerate, containing 6 out of 16 possible methylene states and 924 out of 4096 possible methyl states for a total degeneracy of 5544 out of 65 536. For this line the degeneracy factor $(N - 2D_M)/N$ will be 0.83. Thus this line will have 0.83 of the width of a similar but non-degenerate line, if $\delta_M(0)$ is zero and the linewidth is determined entirely by Heisenberg spin exchange. If the inherent linewidth is greater than zero, the reduction in linewidth and accompanying increase in the height of the line will be less, with the maximum possible peak height being 1.45 times the height of a similar but non-degenerate peak.

TABLE 2.—NUMBER OF STATES AND DEGENERACY FACTORS FOR SOME NITROXIDE LINES

line	M_{CH_3}	M_{CH_2}	no. of states	$(N - 2D_M)/N$
A	+1	0	4752	0.855
B	0	+1	3696	0.887
C	+1	−1	3168	0.903
D	0	0	5544	0.831
E	−3	−1	880	0.973

Fig. 4(b) shows some first derivative maxima and minima obtained from some of the lines in the stick diagram. Only the most intense line is indicated by a Lorentzian curve; for the other lines a diagonal connecting the maximum and the minimum is used to indicate the Lorentzian lineshape. The degeneracies of the lines labelled A to E and the degeneracy factors $(N - 2D_M)/N$ are given in table 2.

Fig. 4(c) shows the top half of a spectrum simulated from the stick diagram, assuming all lines are Lorentzian and are of equal width. If one looks at the first derivatives in fig. 4(b) which combine to form feature 4, one can see that a narrowing of peaks in the order D > A > B > C > E would raise the peak of feature 4 (dominated by the positive half of line D), and increase the depression between that feature and feature 3 (dominated by the negative half of line A). Since, in general, peaks (3) and (4) would be sharpened relative to peaks (1) and (2), the general effect of this

mechanism would be to increase the correspondence between simulations such as that shown in fig. 4(c) and the experimental spectrum.

The above discussion requires that Heisenberg spin exchange be present in a 2.0×10^{-5} mol dm^{-3} de-oxygenated nitroxide solution. Extrapolation from literature results for 2.8×10^{-5} mol dm^{-3} di-t-butyl nitroxide in dimethoxyethane [13] indicates that an exchange-dominated linewidth of 36μT could be expected for 2.0×10^{-5} mol dm^{-3} I($n = 11$), a result in reasonable agreement with the linewidths indicated by the computer-simulation procedure. Thus it is reasonable to say that Heisenberg spin exchange is present in the 2×10^{-5} mol dm^{-3} I($n = 11$) system, and that because of this the widths of the hyperfine lines are not the same, but will be given by eqn (2), in which $\delta_M(0)$ may be zero and must be less than δ_M.
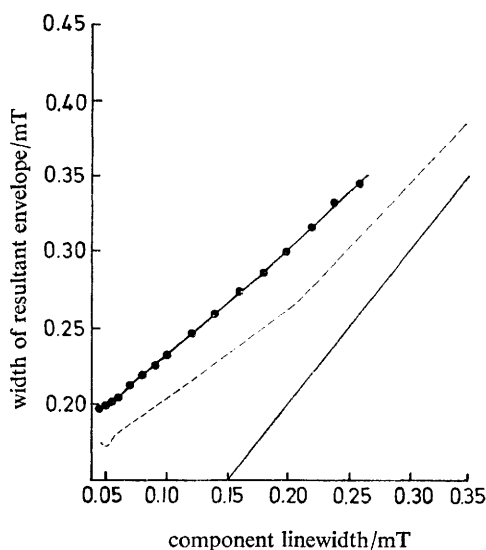

FIG. 5.—Envelope linewidth plotted against component linewidth. $a_{CH_3} = 45.8 \mu$T, $a_{CH_2} = 32.5 \mu$T. - - - - - = gaussian lineshape, ●—● = lorentzian lineshape, ——— = line of equal broadening.

The computer-simulation procedure produced other evidence that exchange is probably present in the system. If one ignores the probable variation in the widths of the proton hyperfine lines and assumes that the computed spectrum shown in fig. 3 adequately represents the experimental spectrum, then by increasing the width of the individual lines one can computer-simulate a series of spectra whose envelope linewidths can be correlated with the individual hyperfine linewidths by means of a graph similar to fig. 5.[1] The points shown in fig. 5 do not follow a smooth curve, especially in the region of low hyperfine component linewidth. The computer simulation program had a vertical sensitivity of one part in 10^8, however, and it was felt that one could only measure the maximum of an experimental spectrum to about one part in 10^2. An apparent maximum, defined as the mean on the horizontal scale of all points within 1 % of the magnitude of the true maximum, was therefore calculated and its value used to define the lines shown in fig. 5. The real and apparent maxima for several linewidths are shown in more detail in fig. 6. The horizontal sensitivity of the calculation is $\pm 1.0 \mu$T, which is about half the experimental error. These two figures show that it is possible to correlate the measured envelope linewidth with a width of the component lines only for envelope linewidths greater than 185μT.

In fig. 5, the points obtained for a similar graph using Lorentzian component linewidths are also shown. These points define a much smoother curve than that obtained with Gaussian lineshapes, and the resultant envelope linewidths are larger than for Gaussian component lines. One would, therefore, expect a lineshape intermediate between Lorentzian and Gaussian to yield widths intermediate between the widths shown here.
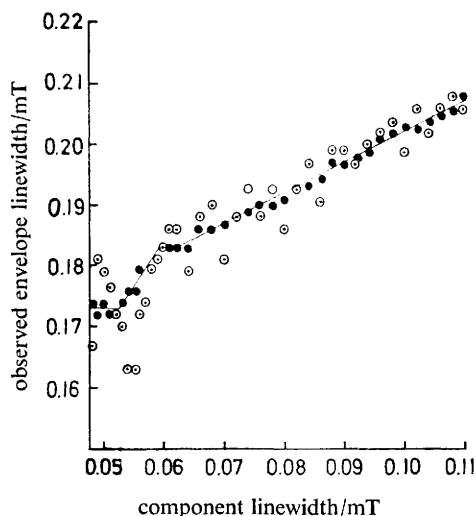

FIG. 6.—Expansion of gaussian lineshape data from previous figure. ○ = real maximum, ● = apparent maximum.

Fig. 7 shows experimental linewidths obtained as a function of temperature from a de-oxygenated solution of 5.5×10^{-3} mol dm^{-3} I($n = 11$) in the presence of 1.5×10^{-3} mol dm^{-3} of its diamagnetic precursor. As the temperature is increased, the number of collisions between paramagnetic molecules should increase, thus increasing
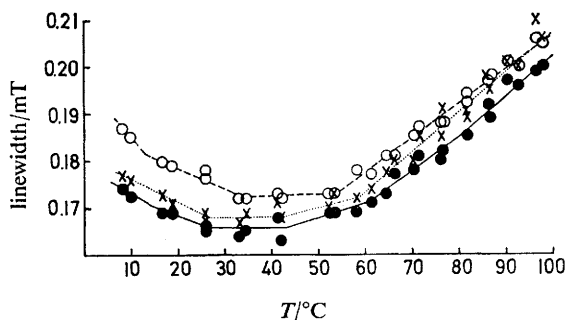

FIG. 7.—Measured linewidth plotted against temperature for 5.5×10^{-3} mol dm^{-3} I($n = 11$) in the presence of 1.5×10^{-3} mol dm^{-3} of its diamagnetic precursor. . . . × . . . = $M_I = +1$, —●— = $M_I = 0$, -- ○ -- = $M_I = -1$.

the Heisenberg spin exchange broadening of the nitroxide lines. Thus fig. 7 should be roughly equivalent to fig. 5 and 6. Since the nitroxide lines are not of equal height, the fast-tumbling limit has not been reached and it is conceivable that increasing the temperature could cause a linewidth decrease, especially to the high field line.

The behaviour of the solutions at the higher temperatures shows that Heisenberg spin exchange broadening dominates the linewidth behaviour in that region. The minimum linewidth obtained for the three lines is $165 \pm 2\ \mu T$ for $M_I = 0$, $167 \pm 2\ \mu T$ for $M_I = 1$ and $172 \pm 2\ \mu T$ for $M_I = -1$. Experimental spectra of $I(n = 11)$ with lower linewidths have been observed—a de-oxygenated 1×10^{-3} mol dm^{-3} sample which on heating loses the hyperfine structure on the central peak between 86 and 96°C, has a width of $135 \pm 5\ \mu T$ at 96°C. This indicates that broadening due to the slower tumbling rate probably dominates the lower temperature region of fig. 7.

The computer-simulated spectra show hyperfine structure at envelope linewidths below $173\ \mu T$ for a Gaussian lineshape and $197\ \mu T$ for a Lorentzian lineshape. They clearly do not approach the experimentally observed width of around $135\ \mu T$. However, spectra have been simulated with coupling constants of smaller magnitude but in the same ratio—reducing the methyl and methylene coupling constants from $45.8\ \mu T$ to $43.0\ \mu T$ and from $32.5\ \mu T$ to $30.5\ \mu T$ respectively reduces the minimum envelope linewidth from $173\ \mu T$ to $167\ \mu T$. Clearly, a much greater reduction in the coupling constants is needed to reduce the minimum to the experimentally observed value.

A reduction in the observed value of the proton hyperfine coupling constants is consistent with the presence of exchange between the proton hyperfine lines, since an exchange frequency of the order of magnitude of the separation of the hyperfine lines would cause the lines to move toward each other, thus reducing the apparent hyperfine coupling constants. Since the hyperfine coupling constants are of the same order of magnitude as the individual linewidths, which seem to be dominated by an exchange-broadening component, exchange effects will be important in the experimental e.p.r. spectra. Thus is is necessary to use a computer-simulation procedure which includes the effects of Heisenberg spin exchange in order to determine accurate motional parameters from observed e.p.r. linewidths.

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