# I. CARBON-THIRTEEN INTERACTIONS IN THE ELECTRON RESONANCE OF ORIENTED ORGANIC RADICALS

# II. RATE OF ELECTRON TRANSFER BETWEEN VANADIUM (V) AND VANADIUM (IV) BY NUCLEAR MAGNETIC RESONANCE

Thesis by

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# ABSTRACT

Part I consists of the measurement of the angular dependence of the anisotropic $C^{13}$ hyperfine interactions in the radical $\overset{\circ}{C}{}^{13}D(COOD)_2$. The above radical is formed when perdeutero malonic acid is subjected to x-ray damage. The deuterated radical's EPR spectra are compared with those of the protonated radical. In addition it was possible, because of the large anisotropy in the $C^{13}$ interaction, to identify and determine the orientation of another radical formed. The second radical is $\overset{\circ}{C}D_2COOD$ (or $\overset{\bullet}{C}H_2COOH$) and is found to have two orientations in the crystal lattice.

In Part II the rate of electron transfer between vanadium (IV) and vanadium (V) is determined by $V^{51}$ nuclear resonance line broadening. The rate of transfer was found to be first order in vanadium (IV) and second order in vanadium (V). The rate constant for the exchange reaction in 6.5 F acid solution is $k = 1.5 \times 10^6\ l^2/mole^2$-sec.

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# PART I

# CARBON-THIRTEEN INTERACTIONS IN THE ELECTRON RESONANCE OF ORIENTED ORGANIC RADICALS

## INTRODUCTION

It has been known for many years that the absorption of electromagnetic radiation by certain molecular systems can lead to the formation of unstable or metastable molecules called free radicals or simply radicals. Also countless kineticists have postulated the existence of radicals as intermediates in hundreds of chemical reactions.

Since the discovery of electron paramagnetic resonance (EPR) in 1945 (1) a tremendous number of measurements have been made on free radical systems. An excellent review in the form of a book is available (2) which covers very well the important work done up to 1958.

Until rather recently the free radicals studied were observed in solutions, polycrystalline solids, or in amorphous glasses. The EPR spectra of free radicals in solution are generally much simpler than in the above mentioned solids because the anisotropic hyperfine interactions are averaged to zero by the rapid tumbling motions. In polycrystalline solids and amorphous glasses the anisotropies lead to broadening and overlapping of the resonance lines because of the random orientations of the radicals in the external magnetic field. Because of the above effects, very little knowledge can be gained concerning the anisotropic interactions which can be very instructive in learning about the electronic structure of molecules.

It would be highly desirable to be able to orient free radicals in the external field in order to analyse the anisotropic hyperfine structure. This has been recently done (3-9) by means of subjecting single crystals of organic compounds to bombardment by x-rays or $\gamma$-rays. Thus one is able to form radicals which are trapped in the crystal lattice and examine the anisotropic hyperfine interactions. If the crystal structure of the compound is known one can place the crystal in desired orientations. On the other hand, if the crystal structure is not known, one may learn something about the orientations of the radicals by observing various angular dependences of hyperfine splittings.

Extensive work has been carried out by McConnell et al. (9) on the radical $\dot{C}H(COOH)_2$ formed from x-irradiation of malonic acid $[CH_2(COOH)_2]$. Electron paramagnetic resonance (EPR) studies on this radical have revealed the principal values of the hyperfine tensor for the interaction between the C-H proton and the unpaired electron. This interaction is described by the hyperfine Hamiltonian where $\underset{\approx}{D}$

$$\mathcal{H}_{hf} = \underset{\sim}{S} \cdot \underset{\approx}{D} \cdot \underset{\sim}{I} \qquad (1)$$

is a symmetrical dyadic. Equation 1 can be written in diagonal form for the $R_2\overset{\circ}{C}H$ radical to give

$$\mathcal{H}_{hf} = hAS_zI_z + hBS_xI_x + hCS_yI_y \qquad (2)$$

The set of axes which diagonalize the hyperfine tensor were found (9) and are shown in Fig. 1. The z-axis was chosen parallel to the C-H bond; the x-axis, parallel to the $2p\pi$ orbital; the y-axis is the third

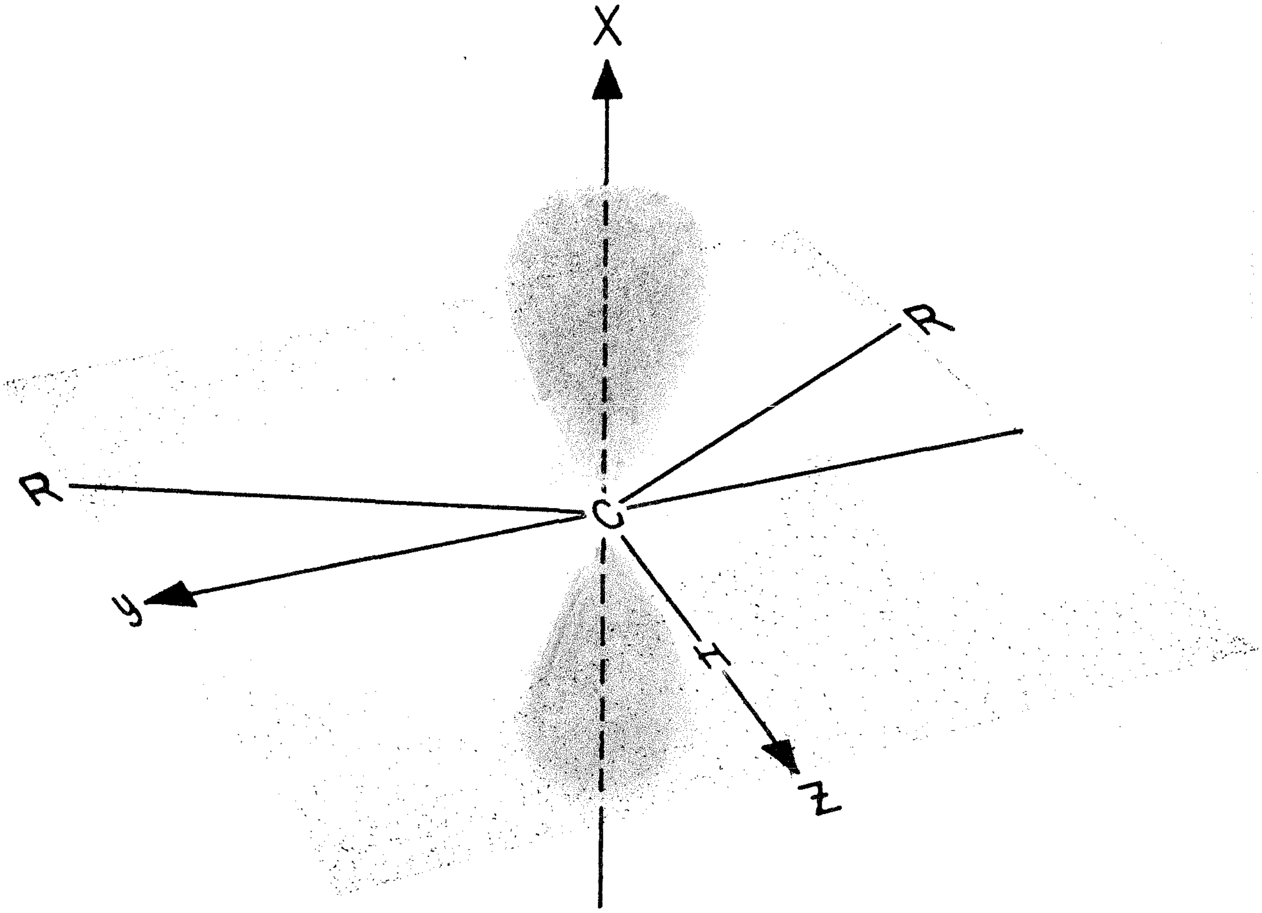

Figure 1. The Cartesian coordinate system which diagonalizes the proton hyperfine interaction

mutually perpendicular axis.

Additional work on this radical species was carried out by McConnell and Fessenden (10) who measured the $C^{13}$ splittings in natural abundance when the magnetic field $H_o$ was directed parallel to the 2pπ cloud (i.e. the x-axis). This splitting was observed to be 210 ± 5Mc. The $C^{13}$ splittings for $H_o$ in the y and z directions were not observed because of interference by other radical species present. These splittings were calculated to be 51 Mc (10,11).

If one makes the reasonable assumption that the interfering radical species is also formed from malonic acid irradiation, then one would expect that by deuterating malonic acid the resulting spectra would be "compressed" because of the smaller magnetic interaction of the deuteron. It was hoped that this compression effect would make it possible to observe the smaller $C^{13}$ splittings along the y and z orientations. In practice it was still not possible to see them. There was still interference from the other radical species and also from the small amount of unexchanged protons left. However, the splittings were followed into this region and the angular dependence was observed. The range studied extended to within 30° of the ± y and ± z axes in the x-y and x-z planes respectively. This angular dependence agrees very well with that calculated for a 2pπ orbital and represents the first real physical evidence of the existence of such orbitals in organic radicals.

## EXPERIMENTAL

Perdeutero-malonic acid was prepared by repeatedly equilibrating malonic acid in $D_2O$ and pumping off the solvent. Complete equilibration of all exchangeable sites is attained in a matter of minutes. The high resolution nuclear magnetic resonance spectrum of malonic acid dissolved in $D_2O$ shows essentially all hydroxylic protons in the short time required to prepare the solution and run the spectrum. The NMR spectrum of malonic acid in water shows both the methylene and the hydroxylic protons. This indicates that the exchange rate for the methylene protons is small compared to their NMR lifetime but fast enough to effect complete exchange within a few minutes. The heavy water used was 99.5% $D_2O$ of Liquid Carbonics Corp.

Single crystals were grown by slow pumping of $D_2O$ from solutions. Crystals were grown at different stages of enrichment. The crystal structure of malonic acid has been determined by Goedkoop and MacGillavry. (12) The crystal is triclinic with unit cell dimensions $a = 5.33$ Å, $b = 5.14$ Å, $c = 11.25$ Å; and angles $\alpha = 102° 42'$, $\beta = 135° 10'$ and $\gamma = 85° 10'$. The unit cell has two molecules related by a center of symmetry. The molecules are hydrogen bonded end-to-end in chains parallel to the crystalline c-axis, the carbon atoms lying approximately in the 210 plane. The carboxyl group nearer the center of the unit cell is inclined 13° from the 210 plane; the other carboxyl group is twisted about 90°. The crystal cleaves easily along the 010 and 100 planes. With the aid of cleavage data and an optical goniometer, the various faces of the crystal grown from $D_2O$ (or water) were identified. These are shown in Fig. 2.

Single crystals were subjected to x-rays from a tungsten target operating at 50 kv and 20 ma for periods ranging from 1 to 16 hours. Electron paramagnetic resonance spectra were taken using a 100 kc field modulation and phase sensitive detection unit built by R. W. Fessenden in this laboratory. The spectra were observed at x-band (9,500 Mc) frequency using the klystron from a Varian Associates V-4,500 Spectrometer. A cylindrical microwave cavity operating on the TE01 mode was employed. The crystals were mounted with wax to a lucite goniometer which fit into the sample cavity. The spectra were calibrated using the $N^{14}$ splittings of peroxylamine disulfonate.

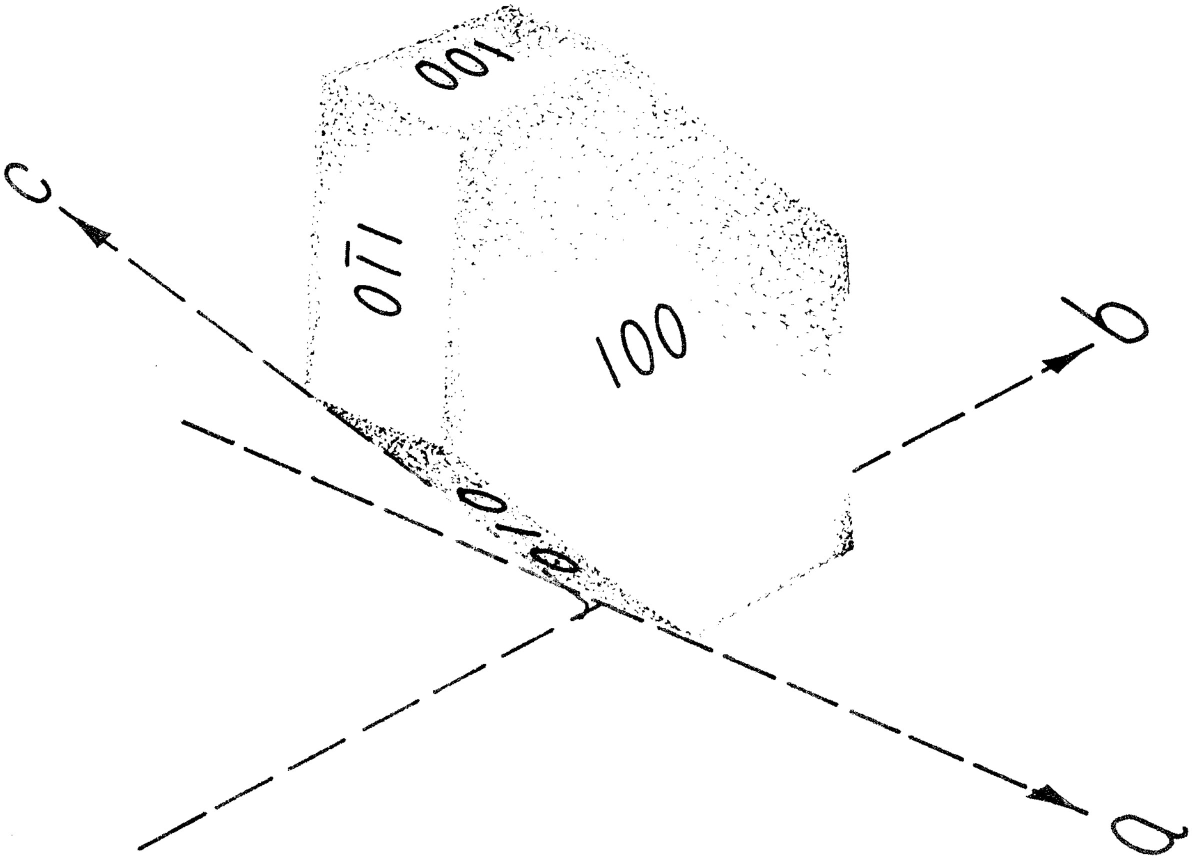

Figure 2. Drawing of the malonic acid crystal as it appears when grown from water. The Miller indices of the plane faces are given.

# THE SPIN HAMILTONIAN

The electron paramagnetic resonance spectra of radical species can be interpreted by means of the spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{hf} \tag{3}$$

In this equation $\mathcal{H}_z$ is called the Zeeman term and refers to the coupling of the electronic and nuclear magnetic moments, $\underset{\sim}{\mu}_e$ and $\underset{\sim}{\mu}_n$ to the external magnetic field, $\underset{\sim}{H}_o$.

$$\mathcal{H}_z = - \underset{\sim}{\mu}_e \cdot \underset{\sim}{H}_o - \underset{\sim}{\mu}_n \cdot \underset{\sim}{H}_o \tag{4}$$

Equation 4 may also be written

$$\mathcal{H}_z = |\beta| \ \underset{\sim}{S} \cdot \underset{\approx}{g} \cdot \underset{\sim}{H}_o - g_n \beta_n \underset{\sim}{I} \cdot \underset{\sim}{H}_o \tag{5}$$

In equation 5, $|\beta|$ is the absolute value of the electronic Bohr magneton, $\beta_n$ is the nuclear Bohr magneton, $g_n$ is the nuclear g-factor, and $\underset{\approx}{g}$ is the spectroscopic splitting factor dyadic. For most organic radicals $\underset{\approx}{g}$ is almost equal to $g_o$ times the unit dyadic; $g_o$ is the g-value corresponding to a spin-only magnetization, $g_o = 2.0023$.

We therefore simplify equation 5 to read

$$\mathcal{H}_z = h\nu_e S_H - h\nu_n I_H \tag{6}$$

Here $\nu_e$ and $\nu_n$ are the electron and nuclear resonance frequencies; $S_H$ and $I_H$ are the components of electron and nuclear spin along the external field direction

$$\nu_e = h^{-1} g_o \, |\beta| \, H_o \tag{7}$$

$$\nu_n = h^{-1} g_n \beta_n H_o \tag{8}$$

The second term in the spin Hamiltonian describes the interaction of the unpaired electron spin with the nuclear spin and is written

$$\mathcal{H}_{hf} = \underset{\sim}{S} \cdot \underset{\approx}{D} \cdot \underset{\sim}{I} + \underset{\sim}{V} \cdot (\underset{\sim}{S} \times \underset{\sim}{I}) \tag{9}$$

The first term in equation 9 includes the (electron-spin)-(nuclear-spin) Fermi contact interaction which arises from a finite electron spin density at the nucleus, and the (electron-spin)-(nuclear-spin) dipole interaction. $\underset{\approx}{D}$ is a symmetric second rank tensor. The second term in 9 describes the magnetic interactions of the electron orbit with the electron spin and the nuclear spin. $\underset{\sim}{V}$ is a pseudovector fixed in the radical. (13,14) The pseudovector interaction comes into play when the set of axes which diagonalizes the g-tensor does not coincide with the set of axes which diagonalizes the dipolar interaction tensor. Obviously, if the g-tensor were completely isotropic, then the pseudovector interaction would be zero. It has been shown (13) that the pseudovector interaction is of the order of $\Delta g$ times the dipolar interaction, $\Delta g$ being the anisotropy in the g-tensor. In the present case and for most organic radicals, typical anisotropies in g are of the order of $10^{-3}$ or less making the second term in equation 9 negligible with respect to the first term. We will thus retain only the first term of equation 9 and rewrite it in the diagonal form

$$\mathcal{H}_{hf} = hAS_zI_z + hBS_xI_x + hCS_yI_y \qquad (10)$$

The x,y, and z axes which diagonalize the dipolar part of $\underset{\approx}{D}$ have been found for $\dot{C}H(COOH)_2$ and are shown in Fig. 1.

The terms A,B,C in equation 10 contain both isotropic and anisotropic parts

$$A = a + A_d \qquad (11)$$

$$B = a + B_d \qquad (12)$$

$$C = a + C_d \qquad (13)$$

The isotropic term, a, arises from the Fermi contact interaction and the anisotropic terms $A_d$, $B_d$, $C_d$ arise from the (electron-spin)-(nuclear-spin) dipolar interaction. The isotropic and anisotropic terms are related to the density of spin angular momentum in the radical, $\hbar \underset{\sim}{S} \rho(\underset{\sim}{r})$. Here $\rho(\underset{\sim}{r})$ is called the spin density distribution function (15)

$$\int \rho(\underset{\sim}{r})\, dv = 1 \qquad (14)$$

Equation 14 is simply a normalization condition for the spin density and when multiplied by $\hbar \underset{\sim}{S}$ it is a statement of conservation of spin angular momentum over the entire paramagnetic molecule.

If $\underset{\sim}{r}_n$ is the vector position of the nucleus in question then $\rho(\underset{\sim}{r}_n)$ is the spin density at that nucleus and the isotropic coupling constant a is (15,16,17)

$$a = h^{-1} g_o |\beta| \, g_n \beta_n \frac{8\pi}{3} \rho(\underset{\sim}{r}_n) \qquad (15)$$

McConnell and Strathdee (18) have calculated the dipolar interaction tensor for a distributed spin in $\pi$-electron radicals. The diagonal components of the dipolar tensor are

$$A_d = h^{-1} g_o |\beta| g_n \beta_n \int_\epsilon \rho(\underset{\sim}{r}) \frac{(1-3\cos^2\theta)}{|\underset{\sim}{r}-\underset{\sim}{r}_n|^3} \, dv \qquad (16)$$

$$B_d = h^{-1} g_o |\beta| g_n \beta_n \int_\epsilon \rho(\underset{\sim}{r}) \frac{(1-3\sin^2\theta\cos^2\phi)}{|r-r_n|^3} \, dv \qquad (17)$$

$$C_d = h^{-1} g_o |\beta| g_n \beta_n \int_\epsilon \rho(\underset{\sim}{r}) \frac{(1-3\sin^2\theta\sin^2\phi)}{|r-r_n|^3} \, dv \qquad (18)$$

These equations are straightforward extensions of the classical magnetostatic dipole-dipole interactions where $\underset{\sim}{r}-\underset{\sim}{r}_n$ is the vector connecting the nuclear dipole at $\underset{\sim}{r}_n$ and the electronic dipole at the position $\underset{\sim}{r}$ weighted by the electronic spin density at that position, $\rho(\underset{\sim}{r})$. The angles $\theta$ and $\phi$ are the polar and azimuthal angles of the vector $\underset{\sim}{r}-\underset{\sim}{r}_n$ in the x,y,z axis system. Since the equation describing the interaction between two dipoles is only valid when the distance between them is large compared to their size, a small region about the nucleus, with a volume of the order of the size of an electron $(\hbar/Mc)^3$, is excluded from the integration. The symbol $\epsilon$ indicates the exclusion of this region. In fact it is within this region $\epsilon$ that the isotropic contact interaction arises. (16)

The quantities A,B,C in equation 10 were determined (9) by aligning the crystal so that the magnetic field was parallel to the z,x, and y axes respectively and measuring the doublet splitting due to the proton. The results are

$$A = 29 \pm 2 \text{ Mc} \qquad (19)$$

$$B = 61 \pm 2 \text{ Mc} \qquad (20)$$

$$C = 91 \pm 2 \text{ Mc} \qquad (21)$$

## COMPARISON OF $\overset{\circ}{C}H(COOH)_2$ WITH $\overset{\circ}{C}D(COOD)_2$

The EPR spectrum of an x-irradiated malonic acid crystal containing comparable amounts of protons and deuterons is shown in Fig. 3. The crystal is oriented with the external field parallel to the canonical y-axis (see Fig. 1). The outer doublet arises from the proton interaction in the radicals $R_2\overset{\circ}{C}H$ and the splitting is that measured by McConnell et al. (9) corresponding to the y orientation (i.e. $C_H = 91$ Mc). The inner triplet arises from the deuteron interaction ($I = 1$) in the radical $R_2\overset{\bullet}{C}D$, the splitting between the components being $C_D = 14$ Mc.

When we refer to equations 13, 15, and 18 we see that the relative splittings $C_H/C_D$ should be proportional to the nuclear g-factors $g_{nH}/g_{nD}$ if one assumes no isotope effect in $\rho(\underset{\sim}{r})$ for the two radicals. Indeed the ratio of the splittings agrees with the ratio of the nuclear g-factors to within experimental error.

$$\frac{C_H}{C_D} = 6.5 \qquad (22)$$

$$g_{nH}/g_{nD} = \frac{\mu_H/I_H}{\mu_D/I_D} = \frac{2.79/\frac{1}{2}}{0.857/1} = 6.52 \qquad (23)$$

Any isotope effect in $\rho(\underset{\sim}{r})$ is not detectable. The spectra of this "mixed" crystal show the same feature along the other canonical orientations, the deuterium splittings being 1/6.5 of the proton splittings. The g-values also are the same for both radicals. Those previously measured for $R_2\overset{\circ}{C}H$ are $g_x = 2.0026$, $g_y = 2.0035$, $g_z = 2.0033$.

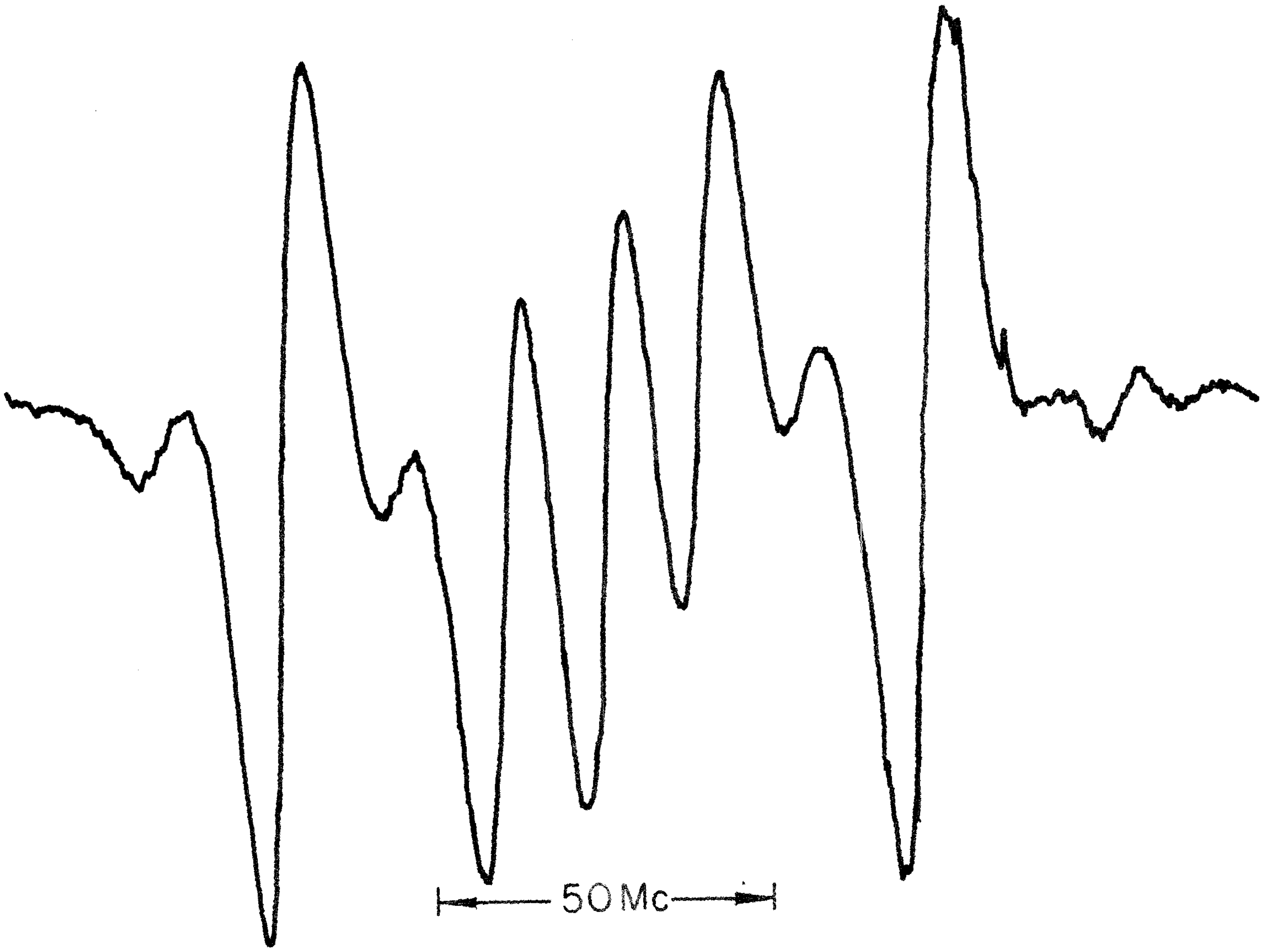

Figure 3. The EPR spectrum of an x-irradiated crystal of malonic acid containing comparable amounts of protons and deuterons. $H_o$ is parallel to the crystalline c-axis

There is however an effect of deuteration on the resonance line width. For a given crystal the deuteron and proton lines have the same peak-to-peak width in the derivative curve spectrum but this width decreases with increasing deuteron concentration. In non-deuterated malonic acid the lines of the proton doublet measure about 11 Mc from peak-to-peak on the derivative curve whereas in $\sim 95\%$ deuterated malonic acid both the proton and deuteron lines have a width of 4.5 Mc. At this point it should also be noted that the saturation properties of both radicals are essentially the same. Local dipolar field effects from neighboring molecules are not sufficiently large to account for this line-narrowing with increased deuteration. If one assumes that a small amount (ca. 2-3%) of the unpaired spin is found on the carboxyl groups then this could interact with the carboxyl protons to give further splitting of the C-H doublet. It might be expected that each line of the doublet would be split into an unresolved triplet by the two carboxyl protons or even further split by some additional interaction with the hydrogen-bonded protons of the adjacent molecules. At any rate, a replacement of the carboxyl protons by deuterons would result in a smaller splitting of the main doublet (or triplet for the $\dot{C}D(COOD)_2$ radical) and lead to an apparent narrowing of the resonance lines.

## THE CARBON-THIRTEEN INTERACTION IN $C^{13}D(COOD)_2$

In our discussion of the $C^{13}$ interaction in malonic acid radical we will be involved with the deuterated species since all the measurements were done on the perdeutero radical. Fig. 4 illustrates a typical spectrum showing the splitting due to $C^{13}$ on the central carbon atom of the radical $\dot{C}^{13}D(COOD)_2$ plus the spectrum of the other radicals without $C^{13}$, $\dot{C}D(COOD)_2$. (The natural abundance of $C^{13}$ is 1.1%). The energy level diagrams corresponding to the spectrum in Fig. 4 are shown in Fig. 5; the strong transitions are labelled. The large inner triplet of the spectrum arises from the bulk of the radicals $R_2\dot{C}D$ whereas the outer pair of triplets is due to the 1% containing $C^{13}$. The distance between the centers of the outer triplets measures the $C^{13}$ interaction and the distance between the individual components of any of the triplets is the deuterium coupling constant for that orientation. Other less intense lines in the central portion of the spectrum are due to the so called "impurity radicals" which will be discussed later.

The $C^{13}$ interaction with a $2p\pi$ electron has been calculated (11) for the external field parallel and perpendicular to the $\pi$-cloud;

$$\text{for } H_o \parallel \quad B_{calc} = 243 \text{ Mc}, \tag{24}$$

$$\text{for } H_o \perp \quad A_{calc} = C_{calc} = 51 \text{ Mc}. \tag{25}$$

The observed value $B_{obs} = 210$ Mc is in good agreement with the calculated value. In 24 and 25, B and A consist of both dipolar

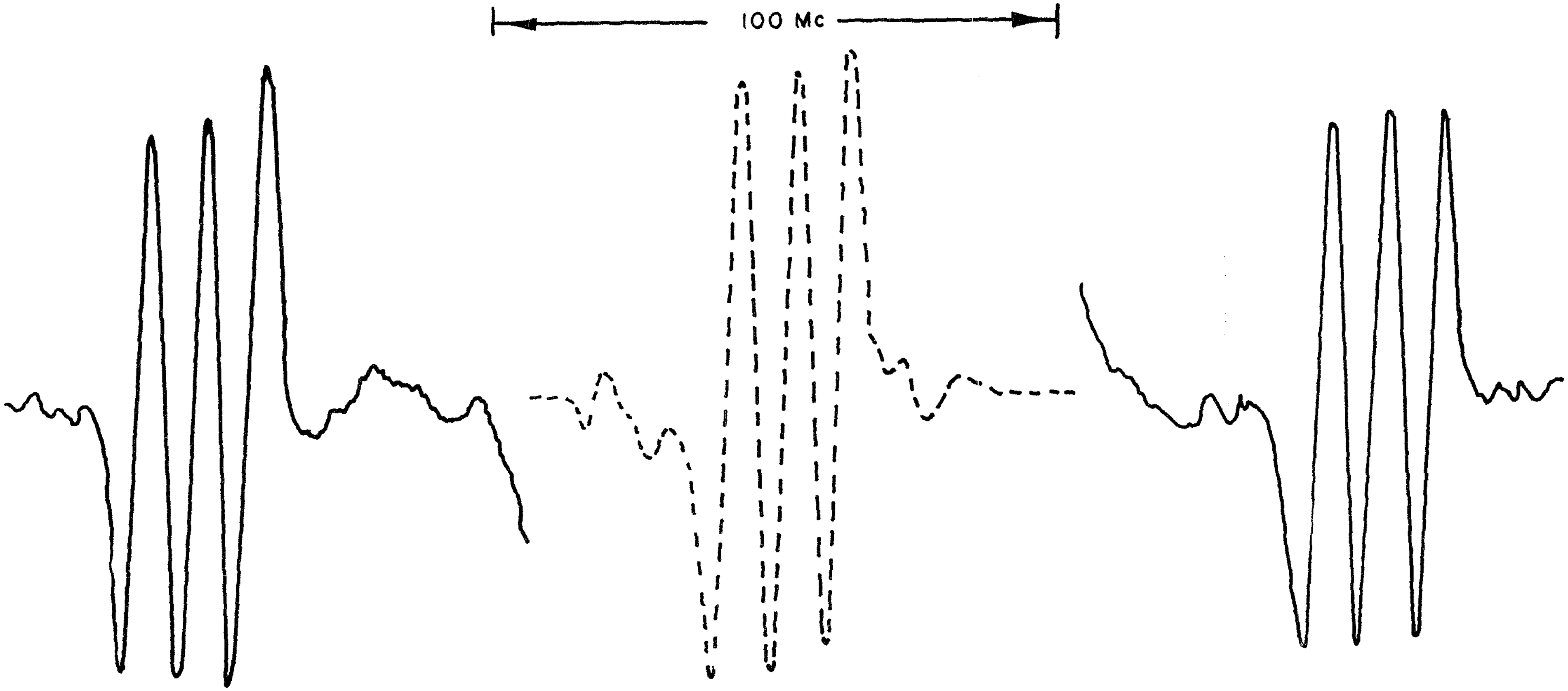

Figure 4. Carbon-13 hyperfine splittings in the EPR spectrum of x-irradiated perdeutero malonic acid. The outer triplets were observed with an increase in gain of about one hundred over that used to observe the central triplet.

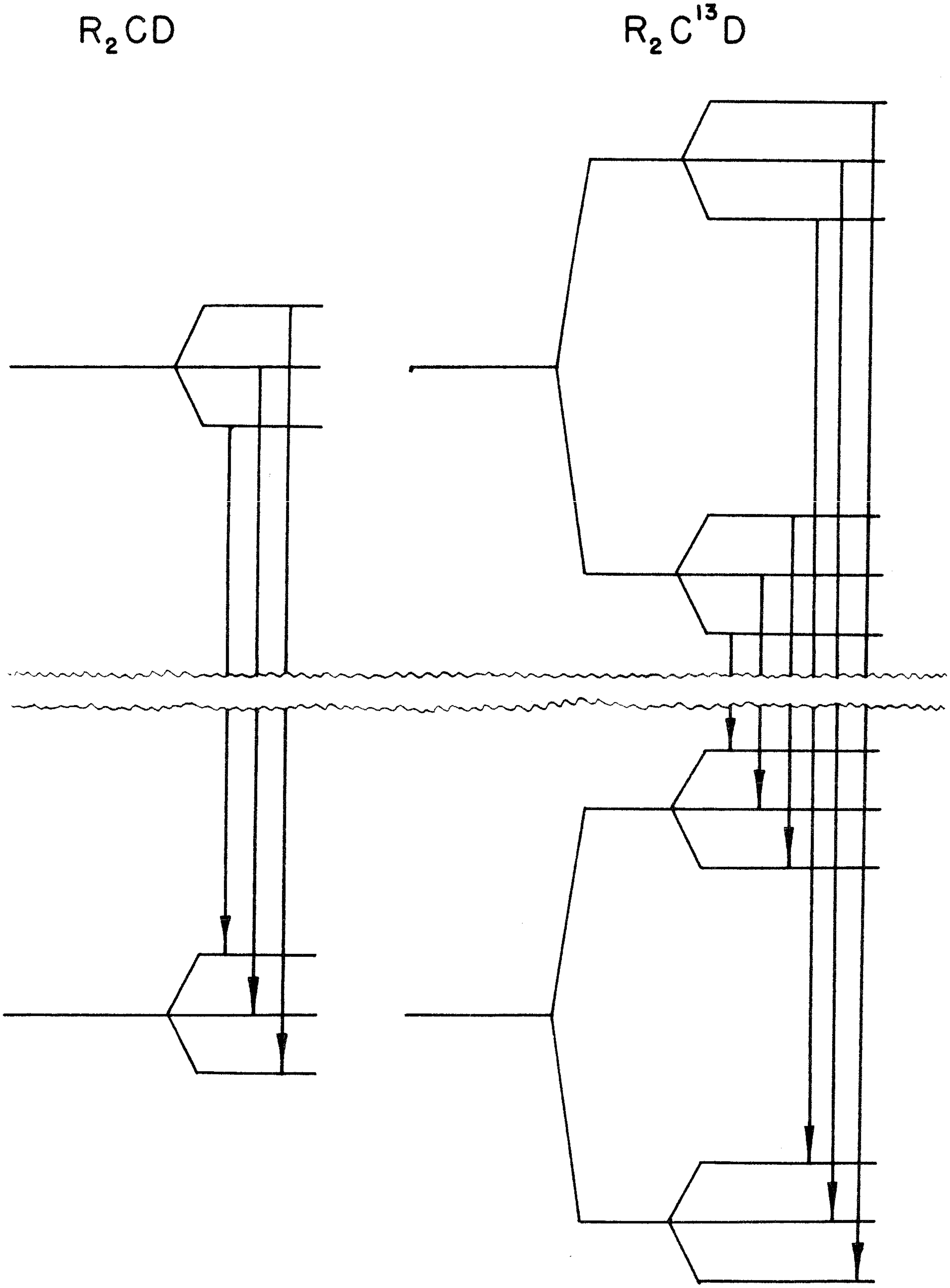

Figure 5. Energy level diagrams for the magnetic interactions in the radicals $CD(COOD)_2$ and $C^{13}D(COOD)_2$. Splittings are not drawn to scale.

and contact terms. It is expected that the contact term is close to that observed for $C^{13}H_3$(19), a = 115 ± 10 Mc. The calculated dipolar contributions are (11) $B_d = 128$ Mc and $A_d = -64$ Mc, hence the values given in equations 24 and 25. We also note that $B_d + 2A_d = 0$. This is a general property of the dipolar tensor; that its trace should vanish.

Since the value of A for $C^{13}$ could not be observed directly because of interference by other radical species, the next best thing was done. The angular behavior of the splittings was observed and compared with the predicted behavior.

Let us write down the spin Hamiltonian for the radical $\dot{C}^{13}D(COOD)_2$ neglecting for a moment the deuterium interaction.

$$\mathcal{H} = h\nu_e S_H - h\nu_c I_H + hB_c S_x I_x + hA_c(S_z I_z + S_y I_y)^* \qquad (26)$$

In 26, $\nu_c$ is the $C^{13}$ nuclear resonance frequency at x-band; $\nu_c = 3.2$ Mc. The subscripts on $A_c$, $B_c$ simply denote that the coupling constants belong to $C^{13}$.

When $|\nu_e| \gg A_c, B_c$ the values of $\underset{\sim}{S}$ perpendicular to $\underset{\sim}{H}_o$ may be neglected and one can write the eigenvalues of the spin Hamiltonian simply

$$E = h\nu_e S_H - h\nu I_u \qquad (27)$$

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* The Cartesian coordinate systems generally used with 2pπ orbitals make the z-axis the long axis of the π-cloud and the x and y axes the cylindrically equivalent axes. Here however we retain the same set of labels used for the axes which diagonalized the proton interaction in $R_2CH$. See Fig. 1.

Here $S_H$ is one of the eigenvalues of the electron spin ( $\pm\ ^1/_2$ ) along the external field direction, $I_u$ is one of the eigenvalues ( $\pm\ ^1/_2$ ) of the nuclear spin operator along the net field direction (applied plus hyperfine) acting at the $C^{13}$ nucleus. This net field direction is defined by the unit vector $\underset{\sim}{u}$, and the frequency $\nu$ is the $C^{13}$ nuclear resonance frequency in the net magnetic field. Furthermore, $\nu$ and $\underset{\sim}{u}$ depend on the eigenvalue $S_H$

$$\nu \underset{\sim}{u} = \nu_c \underset{\sim}{u}_H - S_H \left[ \underset{\sim}{i}\ B_c \sin\theta \cos\phi + A_c(\underset{\sim}{j} \sin\theta \sin\phi + \underset{\sim}{k} \cos\theta) \right] \tag{28}$$

In equation 28 $\underset{\sim}{u}_H$ is a unit vector in the external field direction and $\underset{\sim}{i}$, $\underset{\sim}{j}$, $\underset{\sim}{k}$ are unit vectors along the positive x, y, z axes. The angles $\theta, \phi$ define the direction of $\underset{\sim}{H}_o$ in the xyz coordinate system. From 28 we easily obtain an expression for

$$\nu = \left[ (\nu_c - S_H B_c)^2 \sin^2\theta \cos^2\phi + (\nu_c - S_H A_c)^2 (\cos^2\theta + \sin^2\theta \sin^2\phi) \right]^{1/2} \tag{29}$$

McConnell et al. (9) have presented the above equations in their analogous treatment of the proton interaction in $\dot{C}H(COOH)_2$ and in addition have given the spin eigenfunctions and electron resonance transition frequencies in terms of $\nu_e$ and $\nu$. Suffice it to say here that the pair of electron resonance lines which arise from the $C^{13}$ interaction will have transition frequencies

$$E_1 h^{-1} = \nu_e - \tfrac{1}{2} (\nu' + \nu'') \tag{30}$$

$$E_2 h^{-1} = \nu_e + \tfrac{1}{2} (\nu' + \nu'') \tag{31}$$

The number $\nu'$ is that value of $\nu$ in 29 for which $S_H = + \frac{1}{2}$ and $\nu''$ is the corresponding value for which $S_H = - \frac{1}{2}$. We see then that the splitting of the $C^{13}$ doublet is $E_2 - E_1$ or $\nu' + \nu''$. Hence from equation 29 we can calculate the $C^{13}$ splitting for any orientation of the radical in the external magnetic field if we know $A_c$ and $B_c$.

The inclusion of the deuterium interaction in the spin Hamiltonian, 26, merely effects a splitting of the $C^{13}$ doublets each into a triplet of splittings corresponding to the deuterium hyperfine coupling for that orientation. As before mentioned the spectrum of $\dot{C}^{13}D(COOD)_2$ will consist of two triplets separated by the appropriate $C^{13}$ splitting.

The $C^{13}$ splittings have been calculated from equation 29 using the measured value of $B_c = 210$ Mc and different values of $A_c$ near the theoretically predicted value. The values of $A_c$ used are 62 Mc, 52 Mc and 42 Mc. The reader is referred to Figs. 6 and 7 where the angular dependence of the $C^{13}$ splittings is shown for $H_o$ in the x - z plane and the x - y plane. In each case the solid curves are those calculated from equation 29 and the points are the experimentally measured quantities. It can be seen that the angular dependence of the spectra is in good agreement with that expected. On the basis of the data presented in Figs. 6 and 7 we take the value of $A_c$ to be $A_c = 52 \pm 10$ Mc.

From the above obtained values of $A_c$ and $B_c$ we can calculate the contact and dipolar contributions. Remembering that the trace of the dipolar tensor is zero we have

$$A_c = a_c + A_d \qquad (32)$$

$$B_c = a_c + B_d \qquad (33)$$

$$B_d + 2A_d = 0 \qquad (34)$$

Then the contact term for the $C^{13}$ interaction is

$$a_c = 104 \text{ Mc}, \qquad (35)$$

and the dipolar terms are

$$B_d = 106 \text{ Mc} \qquad (36)$$

$$A_d = - 53 \text{ Mc}. \qquad (37)$$

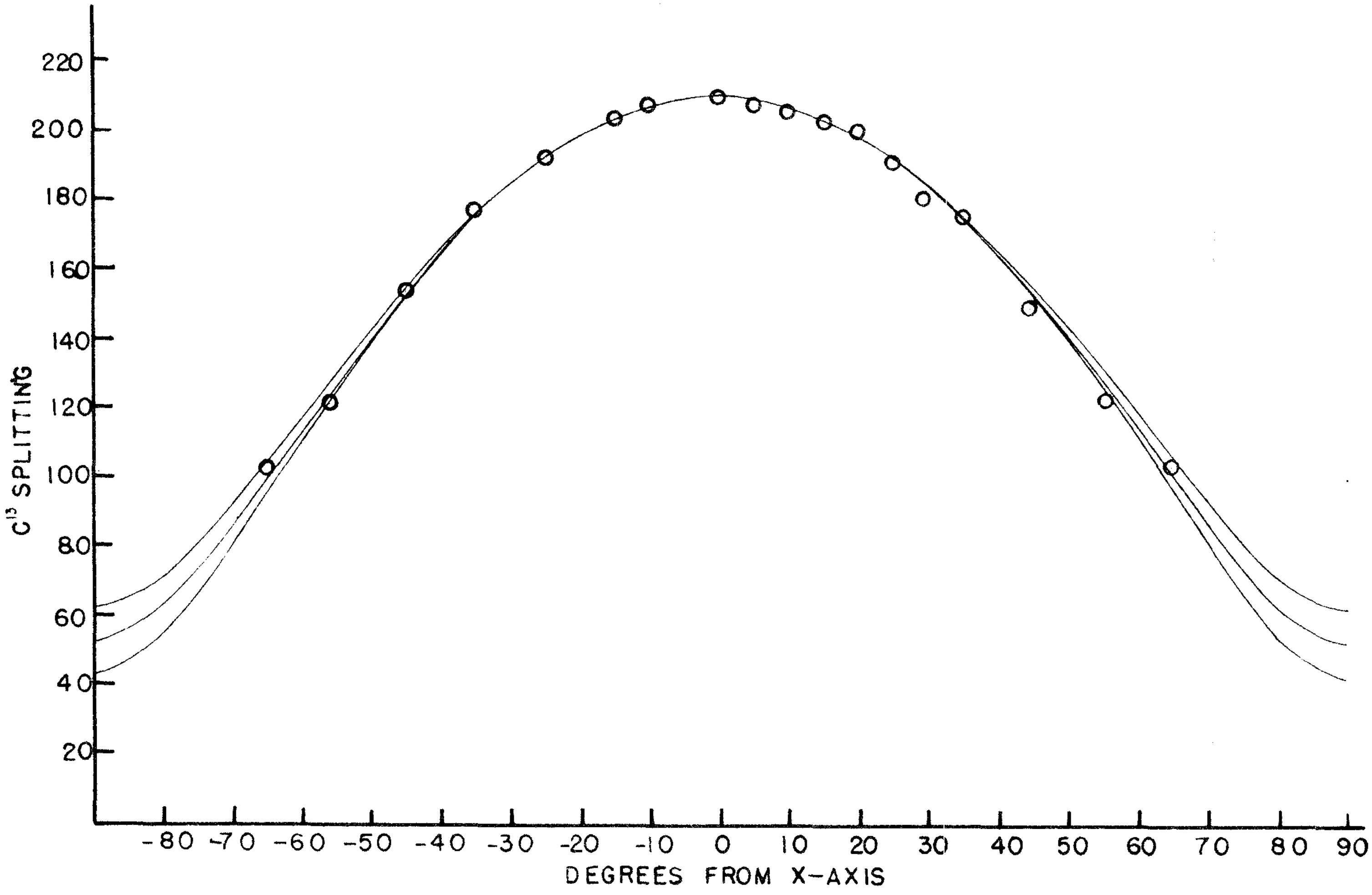

Figure 6. The angular dependence of the $C^{13}$ splittings in $C^{13}D(COOD)_2$ for rotation about the y-axis ($H_o$ in the x-z plane). The solid curves are the calculated dependence; the points are the experimental results.

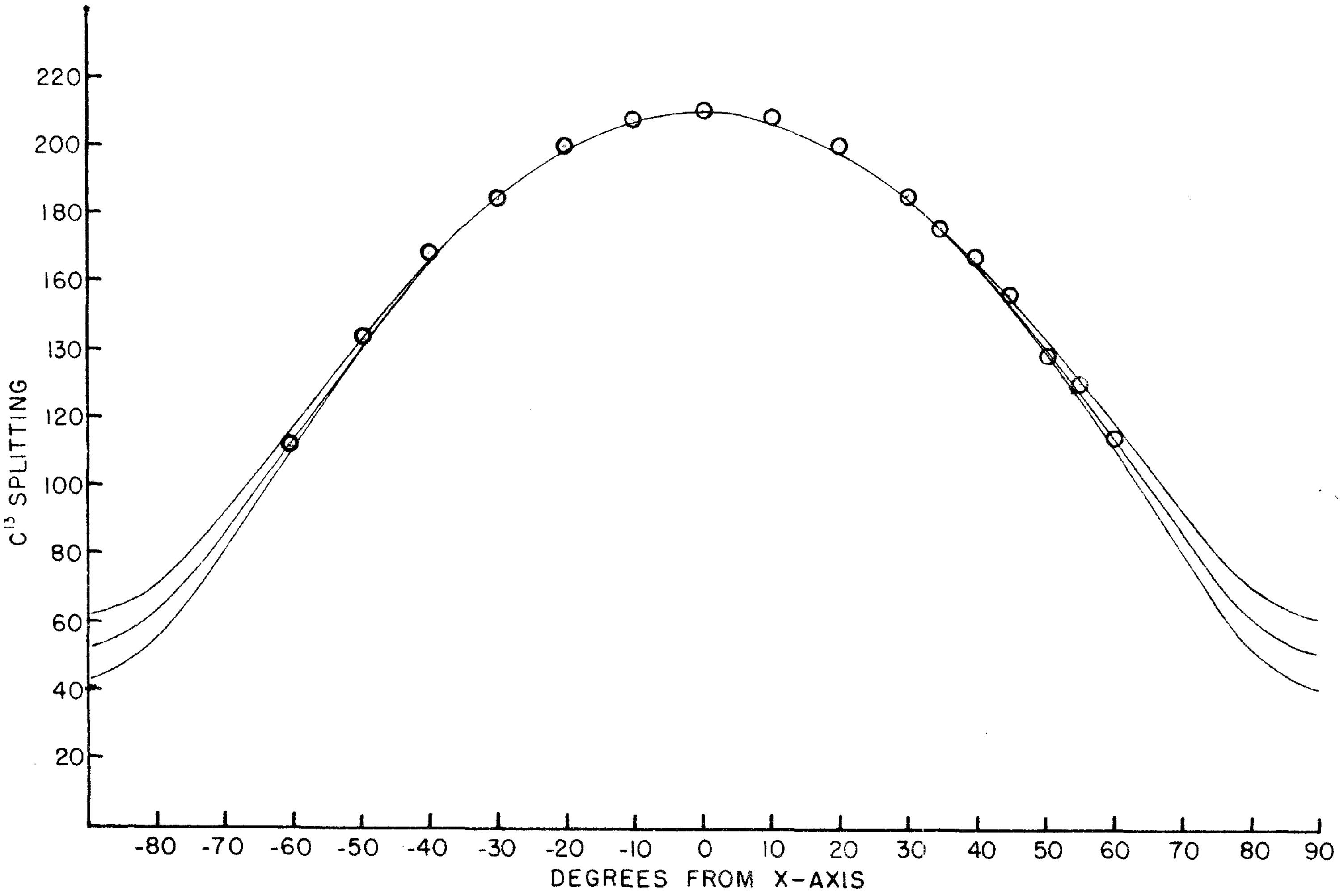

Figure 7. The angular dependence of the $C^{13}$ splittings in $C^{13}D(COOD)_2$ for rotation about the z-axis ($H_o$ in the x-y plane). The solid curves are the calculated dependence; the points are experimental results.

# THE SECOND RADICAL SPECIES

It was noted by McConnell et al. (9) in their study of x-irradiated malonic acid that a large amount of some other radical species was formed. This second species was found to diminish when the crystal was allowed to stand at room temperature for a few weeks. In addition it was found that one could considerably reduce the concentration of the second radical by annealing the crystal for about 24 hours at 50°-60° C. We also note that the resonance of the "secondary" radical was more difficult to microwave saturate than that of $\dot{C}H(COOH)_2$.

At some orientations the spectrum of the second radical appeared as a triplet and it was suspected to arise from a radical containing a $CH_2$ group, for instance $\dot{C}H_2COOH$. However the spectra at other orientations were more complicated and not easily interpreted. The first real clues for identifying the other radicals and their orientations arose from the $C^{13}$ studies in perdeutero malonic acid.

The observations of the $C^{13}$ splittings in $\dot{C}^{13}D(COOD)_2$ were carried out on a crystal which was annealed to the point where the concentration of the secondary radicals was about 10% that of the main radical. During the annealing process the radical $\dot{C}D(COOD)_2$ also diminishes in concentration, but not so fast as the secondary radicalsspecies. If one anneals for a long time the secondary radicals disappear but also the concentration of the radical $\dot{C}D(COOD)_2$ has diminished to the point where it is no longer possible to observe the 1% which contain $C^{13}$. Thus one must choose annealing conditions such that the secondary radical concentration is as small as possible, commensurate with being able to observe the desired $C^{13}$ splittings. To achieve this condition the crystals were annealed for 24 hours at 60° C.

Early experiments on crystals which had a larger concentration of secondary radicals (i.e. which were annealed for shorter times) showed a somewhat different set of spectra for the $C^{13}$ interaction. First, when the crystal was rotated about the y or z axis there was not always a pair of simple triplets in the outer region of the spectra but additional lines as well which sometimes overlapped with the triplet and complicated the spectra. Apparently we were observing $C^{13}$ splittings of some of the secondary radicals as well as $\dot{C}^{13}D(COOD)_2$.

When the crystal is rotated so that $H_o$ moves in the y-z plane of the radical $\dot{C}D(COOD)_2$ one would expect to observe a constant $C^{13}$ splitting of 51 Mc because of the cylindrical symmetry of the $\pi$-cloud. (Of course the 51 Mc splitting was not observed because of the interference mentioned earlier.) Instead there was observed a pair of outer quintets of approximate intensities 1:2:3:2:1, the distance between the centers of which varied in a similar fashion to that of the $C^{13}$ splittings of $\dot{C}D(COOD)_2$. See Figs. 8 and 9. The maximum separation of the outer quintets (190 Mc) was found to occur about 30° from the z axis in the y-z plane. It would seem from the above information that we were observing the $C^{13}$ splittings of a radical containing a $CD_2$ group with a $2p\pi$ orbital lying very nearly

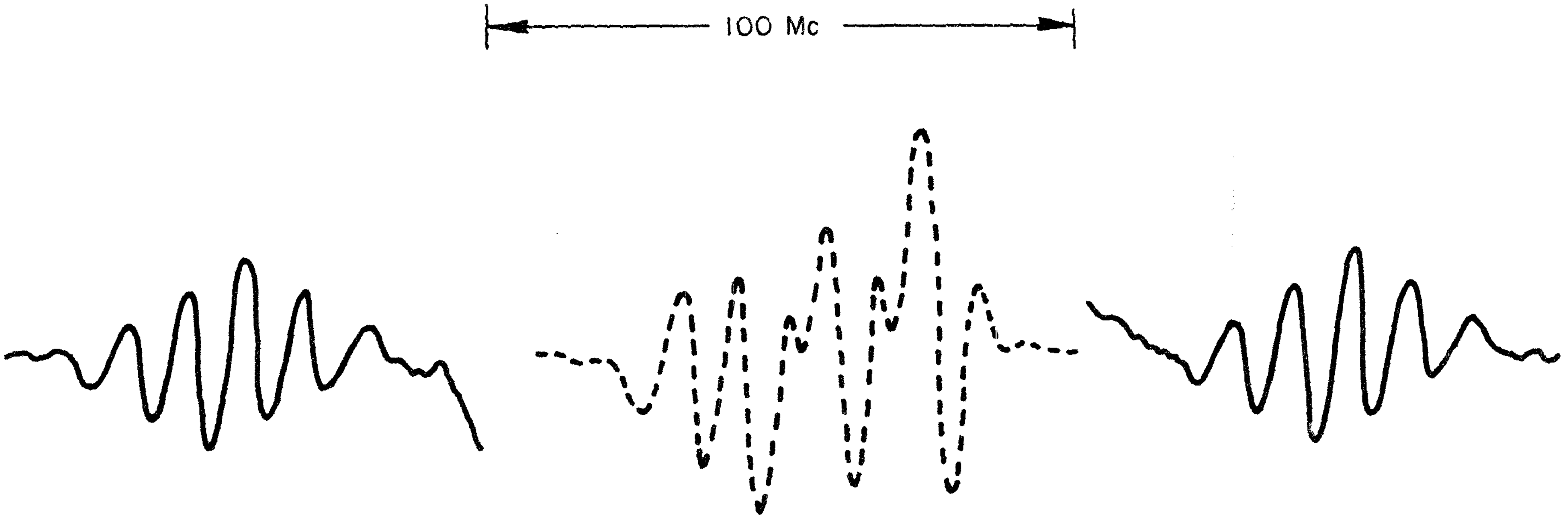

Figure 8. $C^{13}$ splittings in perdeutero malonic acid showing an outer quintet due to a radical $RC^{13}D_2$.

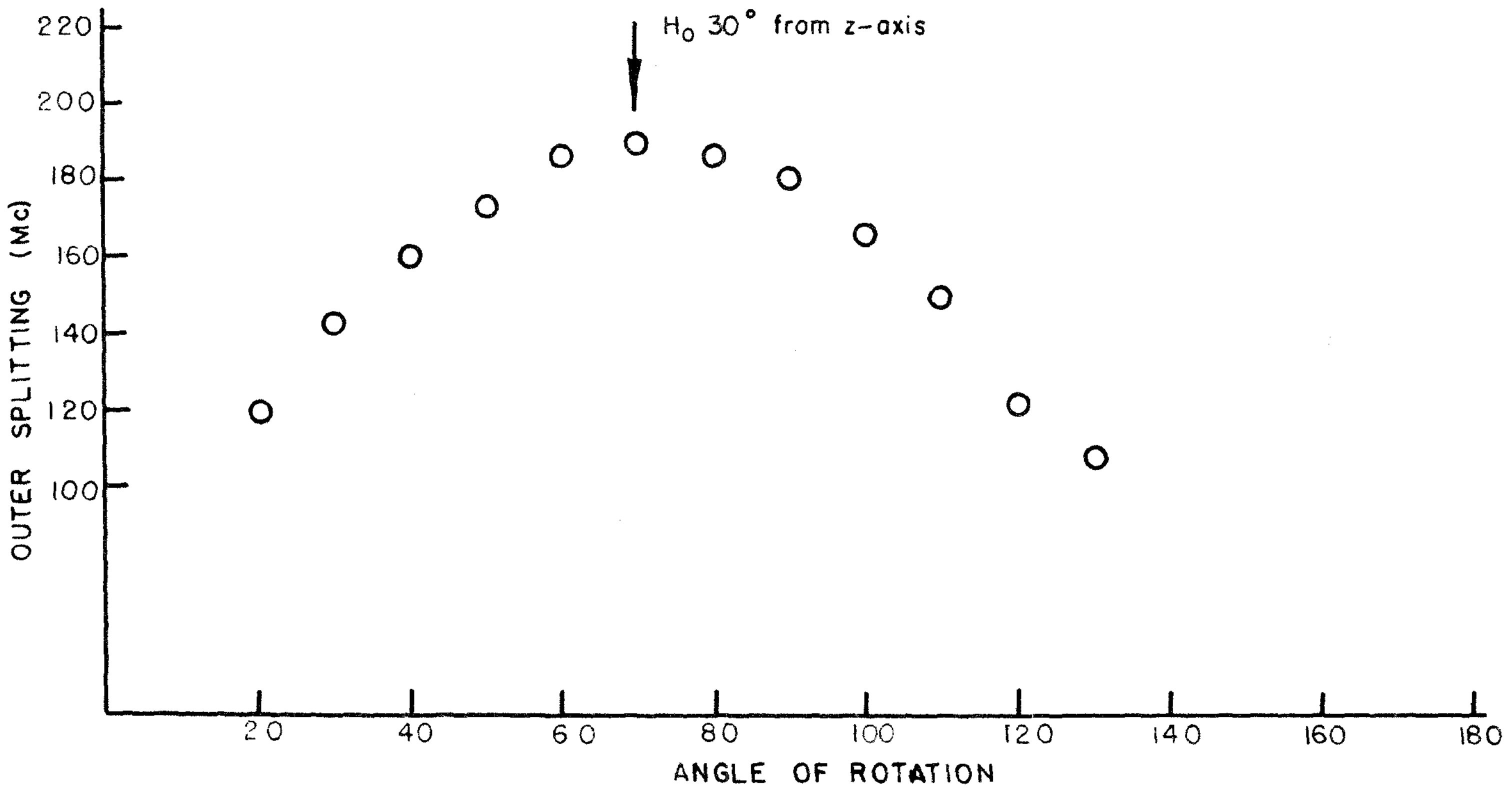

Figure 9. Angular dependence of quintet $C^{13}$ splittings in a slightly annealed crystal. $H_o$ is in y-z plane

in the y - z plane of the $\dot{C}D(COOD)_2$ radical. Moreover the π-cloud of this second radical has its symmetry axis make an angle of 30° with the z-axis of the main radical.

Also if one rotates the same crystal about the y-axis one observes, instead of the simple picture of Fig. 6, an angular dependence which indicates that there are two π-clouds being observed. See Fig. 10. In Fig. 11 is seen the angular dependence of the $C^{13}$ splittings when the crystal is rotated about an axis perpendicular to both π-clouds. Here are observed two maxima about 80° apart. The circles on the plot correspond to the separation of outer triplets whereas the triangles refer to outer quintets.

Let us make the following assertions concerning the second radical species in x-irradiated malonic acid.

a. The radicals are $\dot{C}H_2COOH$ (or $\dot{C}D_2COOD$), formed by loss of $HO\dot{C}O$ (or H· and $CO_2$) from malonic acid.

b. The positions of the carbon and oxygen atoms in the unit cell are very nearly the same for the radicals as they were for the undamaged malonic acid molecules before the radicals were formed.

c. There are two orientations for the radical $\dot{C}H_2COOH$ depending on which carboxyl group is lost. See Fig. 12.

d. The carbon-hydrogen bonds in the radical will move so as to give the expected trigonal $sp^2$ configuration for the $CH_2$ carbon atom.

e. The plane of H-C-H in $\dot{C}H_2COOH$ will coincide with the carboxyl plane so that the carboxyl π-clouds will be parallel to the π-cloud on the $CH_2$ group. (This is very likely the position of

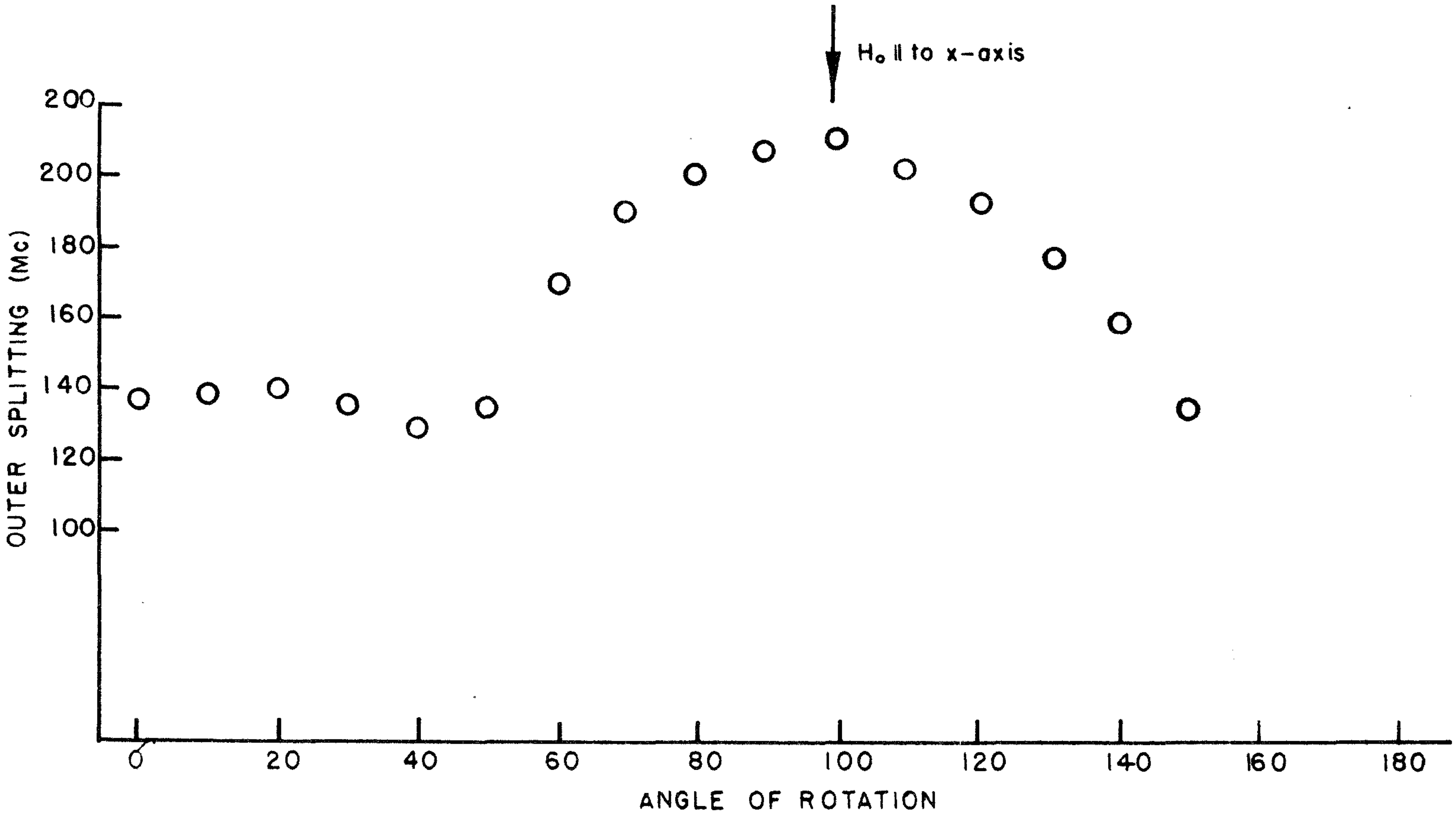

Figure 10. Angular dependence of $C^{13}$ splittings of a slightly annealed crystal. Crystal was rotated about the y-axis ($H_o$ in x-z plane). The large "hump" consists of spectra with outer triplets, the small one, outer quintets

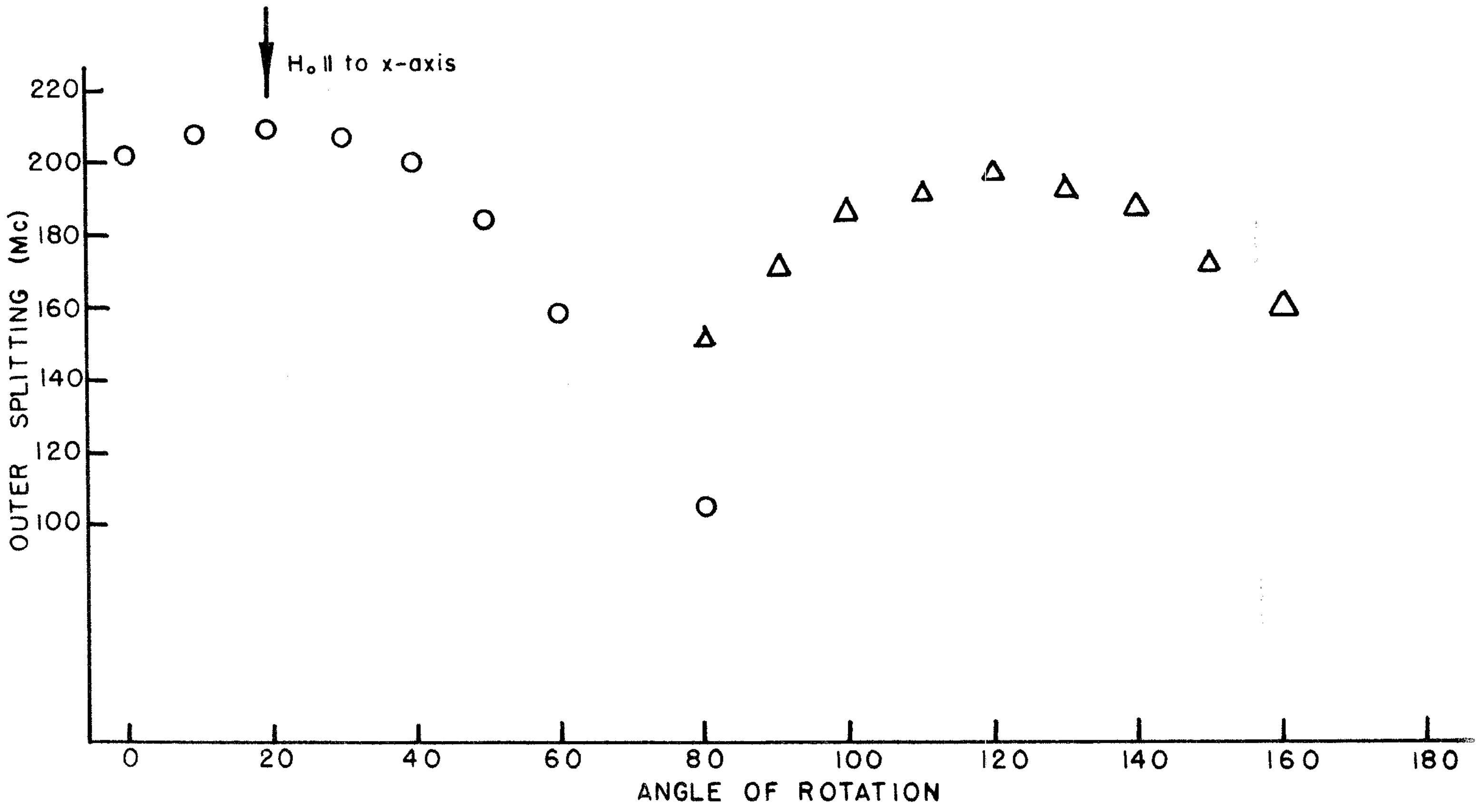

Figure 11. $C^{13}$ Angular dependence when the crystal is rotated about an axis perpendicular to both $\pi$-clouds. The circles correspond to the separation of outer triplets, the triangles, to outer quintets.

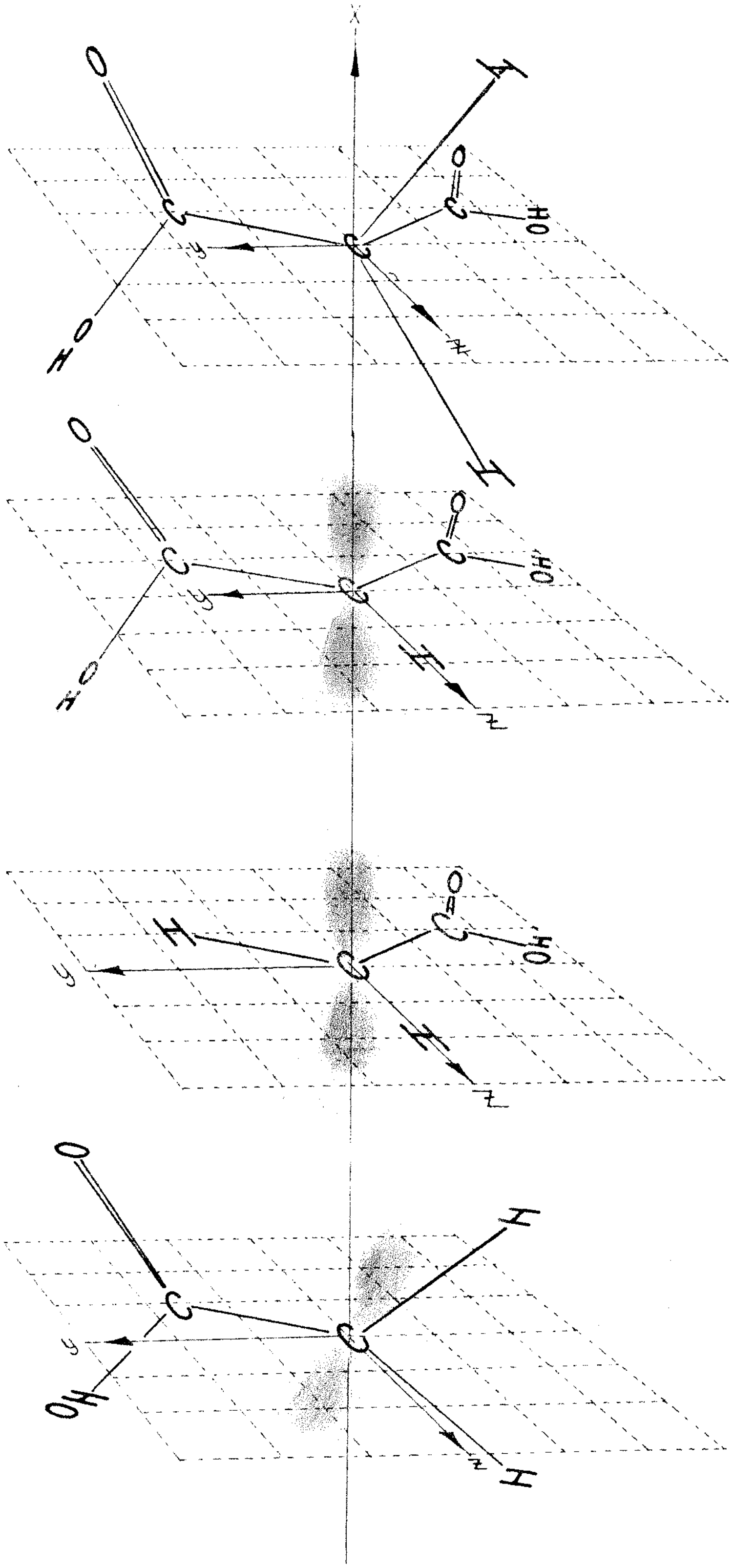

Figure 12. Drawings of the orientations of the parent malonic acid molecule and the three radicals formed with respect to the xyz canonical axis system of $CH(COOH)_2$.

minimum energy from $\pi$-overlap considerations.)

We recall that in malonic acid one carboxyl group lies quite near the C-C-C plane while the other carboxyl group is perpendicular to the plane of the three carbon atoms. Thus we would expect that one of the $\dot{C}H_2COOH$ radicals will be oriented so that its $\pi$-cloud is essentially parallel to that of the radical $CH(COOH)_2$ (i.e. along the x-axis). On the other hand the second $\dot{C}H_2COOH$ radical would be oriented such that its $\pi$-cloud would lie in the y - z plane of $\dot{C}H(COOH)_2$ making an angle of 35° with the z-axis. Indeed this is the $\pi$-cloud whose angular behavior was observed in the quintet $C^{13}$ spectra of the deuterated radicals.

The radicals formed in x-irradiated malonic acid will be referred to as in Fig. 12 with roman numerals I, II, III. Radical I is $\dot{C}H(COOH)_2$ or the corresponding deuterated radical. The other two numerals refer to the radical $\dot{C}H_2COOH$; II to the radical whose $\pi$-cloud is essentially parallel to that of $\dot{C}H(COOH)_2$, and III to the radical whose $\pi$-cloud is perpendicular to the others.

Using the orientations of radicals I, II, and III as seen in Fig. 12 it is possible to calculate the paramagnetic resonance spectrum of all three radicals for any general orientation of the crystal in the external magnetic field. We will do this by assuming that the hyperfine coupling constants A, B, C for the $CH_2$ protons in $\dot{C}H_2COOH$ are the same as those for the proton interaction in $\dot{C}H(COOH)_2$. Now, however, there is no single set of axes which diagonalizes the hyperfine interaction. Instead there are two sets of canonical axes, both centered on the $CH_2$ carbon atom, each with its z-axis pointing along one of the C-H bonds, and both with their x-axes parallel to the 2p$\pi$ orbital. The hyperfine Hamiltonian, 10, will now contain three more terms corresponding to the components of $\underset{\sim}{S}$ and $\underset{\sim}{I}$ along the second set of axes.

Again an equation analogous to 27 can be developed in a very straightforward manner the eigenvalues of the spin Hamiltonian being

$$E = h\nu_e S_H - h(\nu_1 I_{1_u} + \nu_2 I_{2_u}) \qquad (38)$$

where the subscripts correspond to the two methylene protons in $\dot{C}H_2COOH$. In 38, $\nu_1$ and $\nu_2$ are defined by equations similar to equation 29. For example,

$$\begin{aligned}\nu_1 = [(\nu_p - S_H A)^2 \cos^2\theta_1 \\ + (\nu_p - S_H B)^2 \sin^2\theta_1 \cos^2\phi_1 \\ + (\nu_p - S_H C)^2 \sin^2\theta_1 \sin^2\phi_1]^{1/2}\end{aligned} \qquad (39)$$

where again the subscripts on $\theta$ and $\phi$ refer to the coordinate system for the particular proton involved.

In general there will be four strong transitions corresponding to $\Delta S_H = \pm 1$ and $\Delta I_{1u} = 0$. The frequencies are

$$E_1 h^{-1} = \nu_e - 1/2 \; (\nu_1' + \nu_1'') - 1/2 \; (\nu_2' + \nu_2'') \qquad (40)$$

$$E_2 h^{-1} = \nu_e - 1/2 \; (\nu_1' + \nu_1'') + 1/2 \; (\nu_2' + \nu_2'') \qquad (41)$$

$$E_5 h^{-1} = \nu_e + 1/2\ (\nu_1' + \nu_1'') - 1/2\ (\nu_2' + \nu_2'') \qquad (42)$$

$$E_6 h^{-1} = \nu_e + 1/2\ (\nu_1' + \nu_1'') + 1/2\ (\nu_2' + \nu_2'') \qquad (43)$$

The prime and double prime symbols on the $\nu_i$'s correspond to those values of $\nu_i$ for which $S_H$ equals + 1/2 and - 1/2 respectively. Clearly if $\nu_1' = \nu_2'$ and $\nu_1'' = \nu_2''$, then the paramagnetic resonance spectrum will consist of a triplet of intensities 1:2:1; otherwise the resonance will be a quartet.

The paramagnetic resonance spectra for radicals I, II, and III have been calculated for the cases where the external field is aligned along the x,y, and z canonical axes of radical I, $\dot{C}H(COOH)_2$. These are compared with spectra of a freshly irradiated crystal of malonic acid in the above mentioned orientations. See Figs. 13, 14, and 15. The quite satisfactory agreement between the calculated and observed spectra further substantiates the assertions as to the identification of the radicals and their orientations.

In the calculated spectra of Figs. 13, 14, and 15, all three radicals were given a priori the same g-value even though in the actual spectra some are shifted with respect to others. In addition, the intensities of the lines of one radical relative to the others were chosen to agree approximately with the observed spectra. Of course, the relative intensities within a group of lines for a given radical is meaningful. The theoretical spectra predict only the splittings of the lines and not the g-values nor the absolute

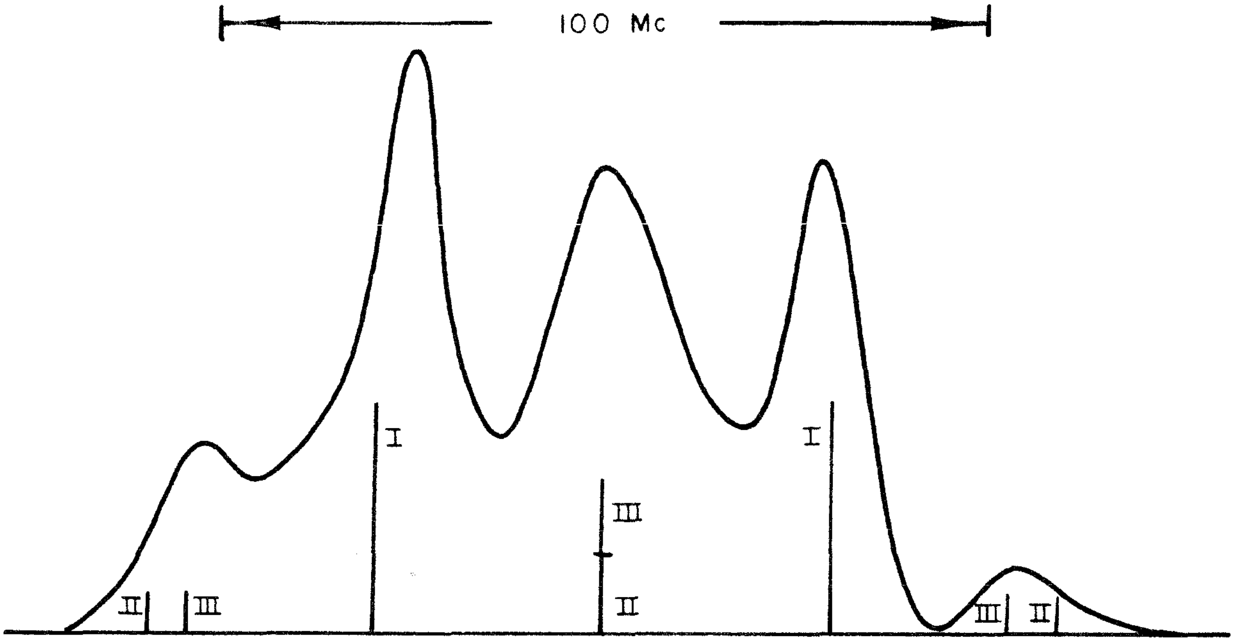

Figure 13. The EPR spectrum of radicals I, II, and III with $H_0$ parallel to the x-axis of radical I, $CH(COOH)_2$. The crystal used was a freshly irradiated, non-deuterated malonic acid crystal. The spectrum is an integration of the recorded derivative spectrum. Calculated spectra are also shown.

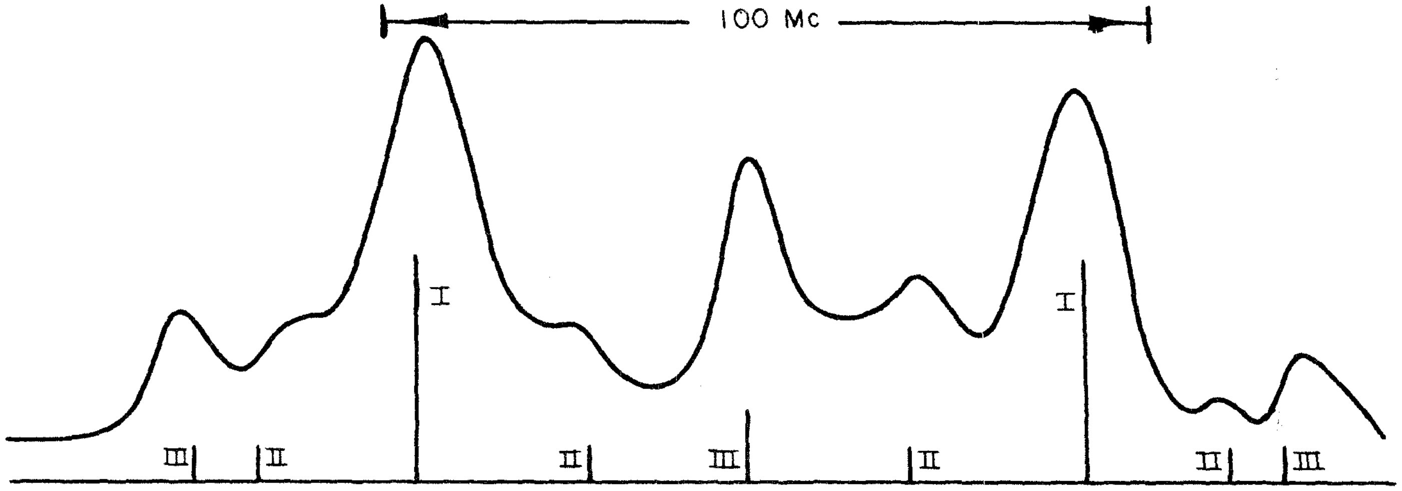

Figure 14. The calculated and observed EPR spectra of radicals I, II, and III with $H_o$ parallel to the y-axis of radical I.

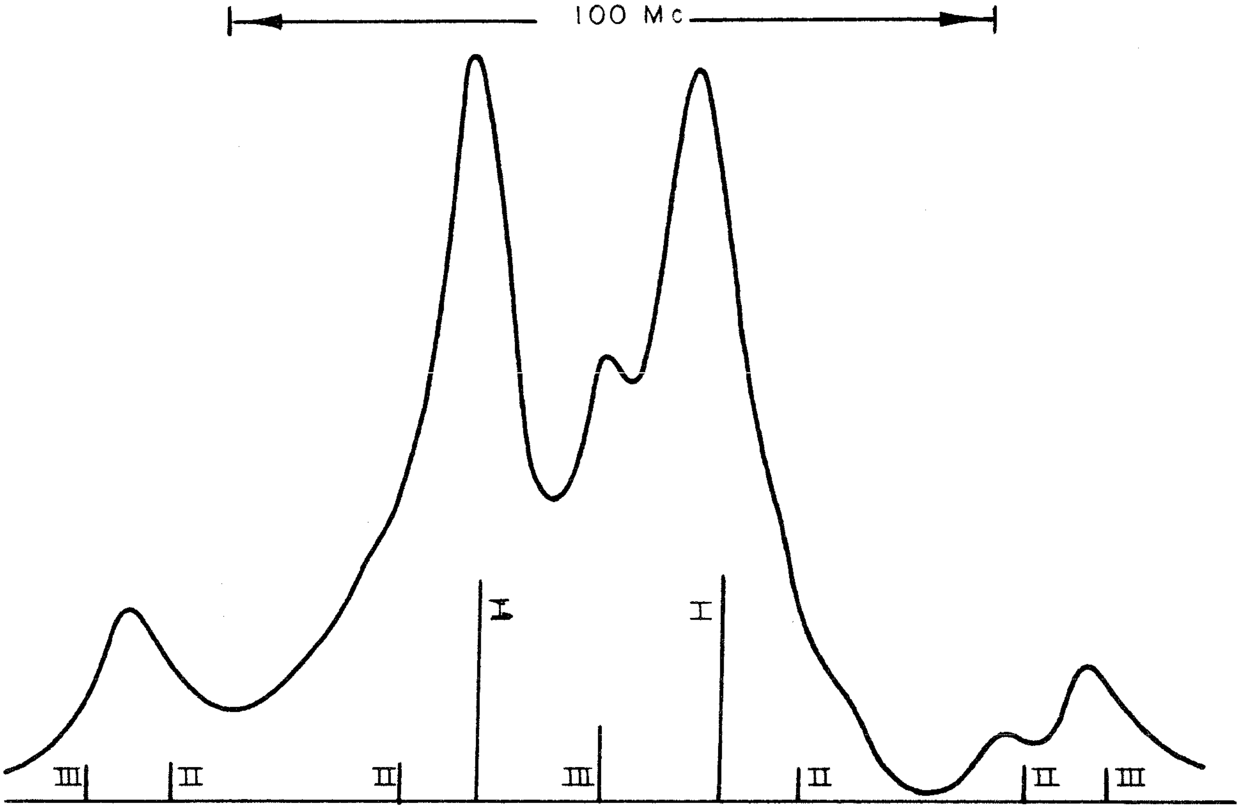

Figure 15. The calculated and observed EPR spectra of radicals I, II, and III with $H_o$ parallel to the z-axis of radical I.

intensities. Previous work on the theory of g-factors in $\pi$-electron radicals (20) has pointed out that $g_{\parallel}$ would be close to the free spin g-value and that $g_{\perp}$ would be slightly greater than the free spin g-value. Here $g_{\parallel}$ and $g_{\perp}$ refer to those g-values for $H_0$ parallel and perpendicular to the $2p\pi$ orbital respectively. Radicals I and II would be expected to have g-values close to each other for a given spectrum whereas radical III might be expected to deviate more because of the different orientation of its $\pi$-cloud. The relative centers of the spectra in Figs. 13, 14, and 15 are consistent with this notion. It is especially apparent in Fig. 15 where the g-values of I and II are seen to be greater than that for radical III which is the expected behavior.

## CONCLUSION

As is evident from the above work, the $C^{13}$ spectra of simple $\pi$-electron radicals can be used to good advantage to gain insight concerning unidentified radicals and their orientations. The malonic acid system, a case in point, shows a rather complex group of lines in the central region of the spectrum. The $C^{13}$ interaction at certain orientations effectively promotes to the extreme outer regions, only the spectra of those radicals whose $\pi$-clouds are parallel or close to parallel to the external field direction, so that in perdeutero malonic acid at some orientations one clearly saw the triplet splittings due to $R_2\dot{C}D$ while at others the quintet spectrum of $R\dot{C}D_2$ was observed in the $C^{13}$ splitting. Thus we have in the $C^{13}$ interaction, because of the large anisotropy of the splittings, a potentially powerful means for unscrambling the spectra of mixtures of oriented $\pi$-electron radicals.

# PART II

## RATE OF ELECTRON TRANSFER BETWEEN VANADIUM (V) AND VANADIUM (IV) BY NUCLEAR MAGNETIC RESONANCE

### INTRODUCTION

The rates of certain fast electron transfer reactions can sometimes be measured under steady state conditions when one of the reactants is diamagnetic and the other is paramagnetic. Thus, the nuclear resonance of $^{63}$Cu in cuprous-cupric hydrochloric acid solution has been used (21) to obtain the rate of electron transfer between these two oxidation states of copper. Similarly, Bruce et al. (22) have studied aromatic proton resonance in mixtures of N,N'-tetramethylparaphenylenediamine and N,N'- tetramethylparaphenylenediamine positive ions in order to obtain the rate of electron transfer between these two molecules. A theory for this technique has been developed in detail by McConnell and Berger. (23) The basic idea of the method is that the nuclear resonance of a molecule or ion in the diamagnetic state is interrupted by the large magnetic hyperfine field when it is converted to the paramagnetic state. The hyperfine field arises from unpaired electrons in the paramagnetic species. In this theoretical work (23) it was shown that if hyperfine splittings can be observed in the paramagnetic resonance of a solution containing a nucleus X in both a diamagnetic molecule D and in a paramagnetic molecule P, then the nuclear resonance line width of X is a direct measure of the lifetime of the diamagnetic molecule or ion.

The purpose of the present work is to show the applicability of this method to a determination of electron exchange rates between vanadium (IV) and vanadium (V) in acid solutions containing chloride ion. The idea that this exchange process might be extremely fast came from the earlier work of Tewes et al., (24) who studied the rate of exchange between vanadium (IV) and vanadium (V) in acid solution using isotopic labelling techniques. They found essentially 100 percent exchange in separation times of the order of 1 sec.

## EXPERIMENTAL AND RESULTS

All reagents were CP grade and no attempt was made at further purification. Pervanadyl stock solutions were prepared by dissolving weighed amounts of ammonium metavanadate in slightly more than one equivalent of sodium hydroxide solution and then gently heating until ammonia evolution ceased. The solution of sodium vanadate was then added to acid very slowly with rapid stirring. Rapid addition gives a red precipitate of vanadium pentoxide which does not dissolve.

All nuclear resonance spectra were made using a Varian wide line NMR spectrometer. Phase-sensitive detection was employed and the observed spectra are the derivatives of the absorption curve. Measurements were made at room temperature with unthermostatted samples. Resonances were observed at approximately 5.6 Mc/s and at applied fields of 5000 gauss. Representative spectra are given in

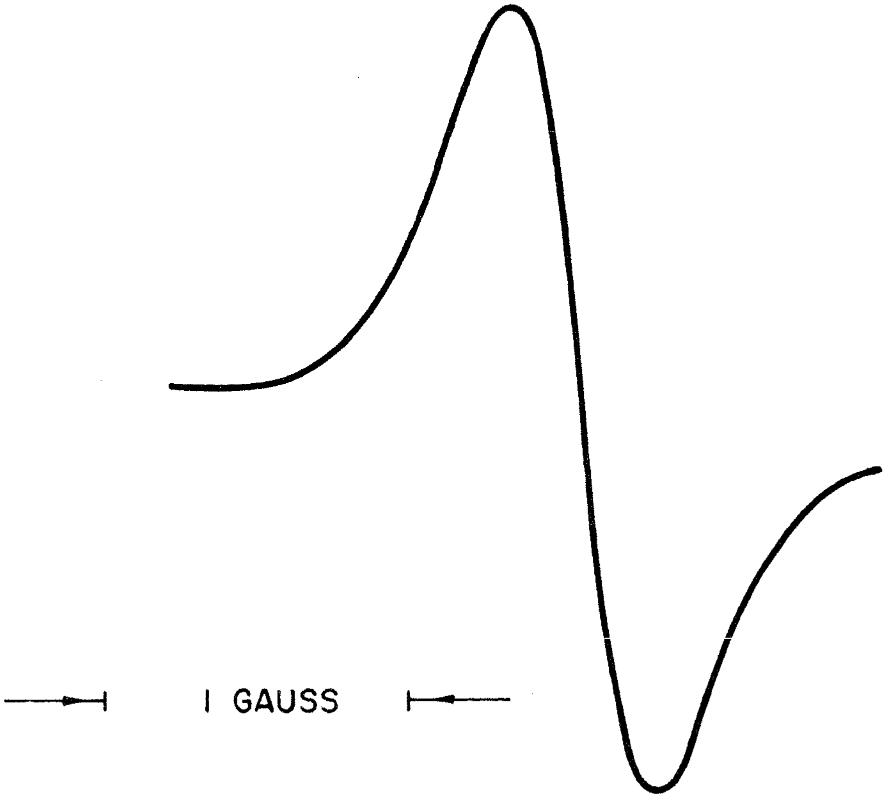

Figure 16. $^{51}V$ nuclear resonance of 0.20 F vanadium (V) in a solution containing 2.8 F $Cl^-$ (as HCl), 6.50 F $H^+$ (as HCl + $HClO_4$).

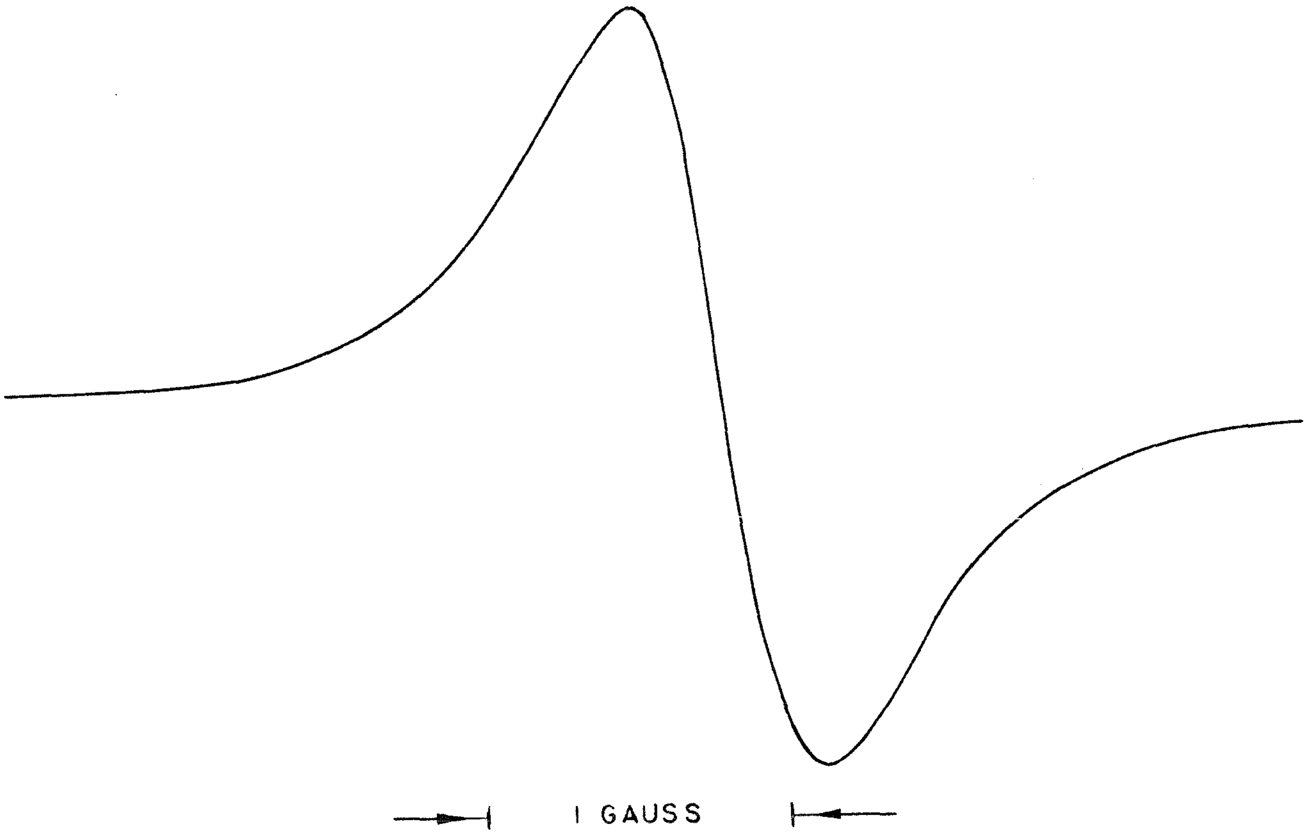

Figure 17. $^{51}V$ nuclear resonance of 0.36 F vanadium (V) in a solution containing 0.10 F vanadium (IV) in 4.7 F HCl.

Figs. 16-19. The line shapes are nearly Lorentzian; the ratios of the maximum positive slopes to the maximum negative slopes are all 4.0 ± 0.2. This line shape is required by the theory, since the theory involves the use of the Bloch equations. (23) Transverse relaxation times $T_2$ were obtained directly from the spectra from the peak to peak separations $\Delta H$ (in gauss):

$$1/T_2 = \sqrt{3}/2(\gamma \Delta H) \qquad (44)$$

In 44, $\gamma$ is the magnetogyric ratio of vanadium; $\gamma = 7.05 \times 10^3$ $\text{sec}^{-1}$ $\text{gauss}^{-1}$. For acidic pervanadyl solutions, the transverse relaxation time $T_2$ is $4 \times 10^{-4}$ sec. This corresponds to a peak to peak separation of 0.42 gauss. Magnetic field inhomogeneity may make an appreciable contribution to this line-width. The rate of electron exchange, however, is related to the increase in the $1/T_2$ relaxation frequency associated with the addition of vanadium (IV), and thus an absolute value of $T_2$ for pure pervanadyl solutions in a perfectly uniform field need not be known. Thus, the quantity of experimental interest is $\delta(1/T_2)$ which is related to the increment in the peak to peak line-width due to the addition of vanadium (IV) to a solution containing a fixed amount of vanadium (V).

Experiments showed that addition of vanadium (IV) to vanadium (V) solutions in the presence of chloride but at relatively low acid concentrations had essentially no effect on the vanadium resonance line-width. See Fig. 17. It was found, however, that in solutions containing large concentrations of both hydrochloric and perchloric acids the vanadium (IV) had a strong effect on the vanadium

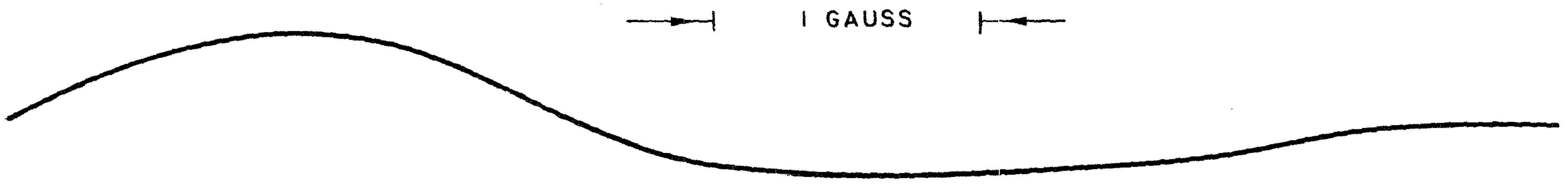

Figure 18. $^{51}V$ nuclear resonance of 0.22 F vanadium (V) in a solution containing 0.06 F vanadium (IV), 2.6 F $Cl^-$ (as HCl) and 7.5 F $H^+$ (as HCl + $HClO_4$).

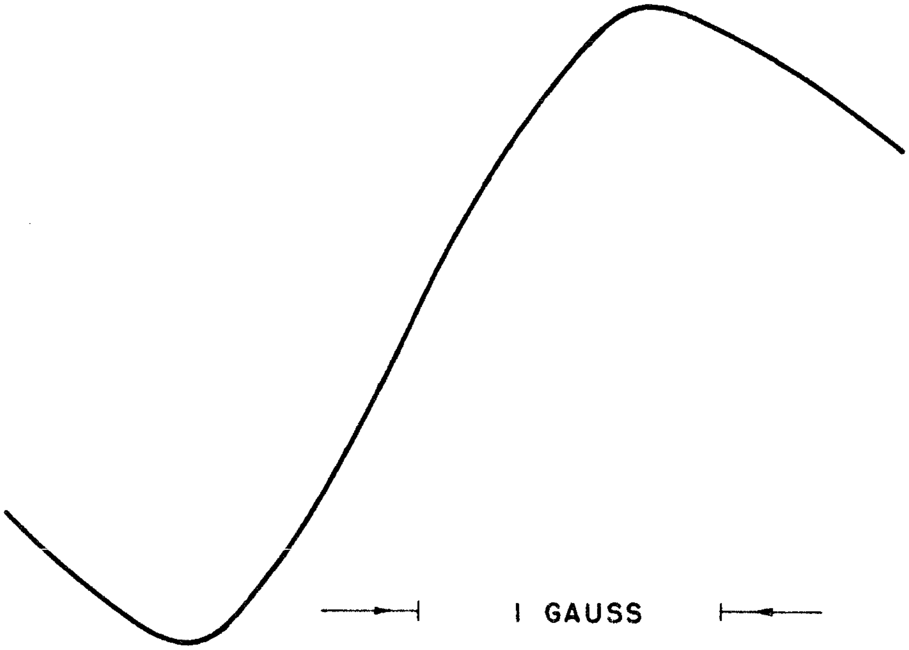

Figure 19. $^{51}V$ nuclear resonance of 0.20 F vanadium (V) in a solution containing 0.025 F vanadium (IV), 2.8 F $Cl^-$ (as HCl), and 6.50 F $H^+$ (as HCl + $HClO_4$).

(V) nuclear resonance line-width. A series of experiments was carried out in solutions having hydrogen ion concentrations from 6.5 to 7.2 F and chloride ion concentrations of 3 F. The results are summarized in Fig. 20, which gives a plot of $\delta(1/T_2)$ vs. the formal concentration of vanadium (IV) for two different concentrations of vanadium (V).

In the region of acidity where this study was made, chloride ion is oxidized by vanadium (V) although the extent of this reaction is quite small in the time required to make our measurements. The rate of the chloride oxidation is strongly acid-dependent (in concentrated HCl, chlorine is rapidly evolved); hence we were limited to acid concentrations less than 8 F. Attempts to make stock solutions of vanadium (V) at these relatively high concentrations (0.4 F) in the absence of chloride ion failed. This strongly suggests that vanadium (V) is somehow complexed with chloride.

## DISCUSSION

It is highly unlikely that the line broadening illustrated in Figs. 18 and 19 is due to paramagnetic dipole broadening of the vanadium (V) nuclear resonance by magnetic fields of the vanadium (IV) ions. The large effect of the hydrogen ion concentration on the vanadium (V) nuclear resonance line-width in the presence of vanadium (IV), as indicated in comparison of Figs. 17 and 18, strongly supports this data. Moreover, one would expect that if the line broadening were dipole in origin, then the vanadium (V) nuclear resonance line-width would be independent of the vanadium (V) concentration,

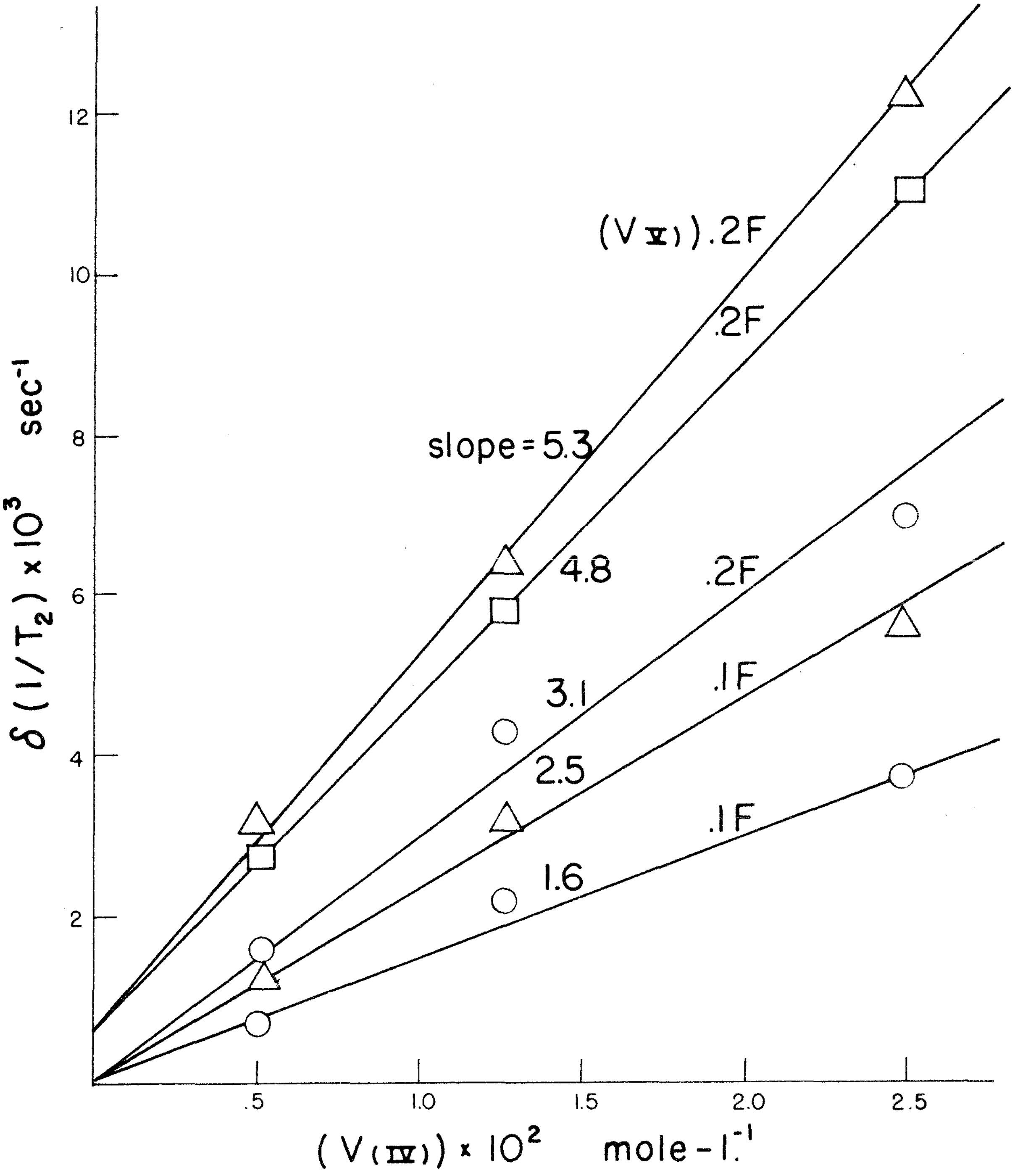

Figure 20. Plot of $\delta(1/T_2)$ vs. [V(IV)] for two different concentrations of vanadium (V) in solutions containing:

○ 2.8 F $Cl^-$ (as HCl) and 6.5 F $H^+$ (as HCl + $HClO_4$),

△ 3 F $Cl^-$ and 6.7 F $H^+$, □ 3 F $Cl^-$ and 7.2 F $H^+$.

whereas, as we shall see below, the line-width does depend on the vanadium (V) concentration. Thus, in the following discussion we attribute the line broadening of the vanadium (V) nuclear resonance to a lifetime limiting process associated with electron transfer between vanadium (V) and vanadium (IV).

According to the theory, (23) if $\tau_D$ is the lifetime of the vanadium (V) species with respect to the electron exchange reaction, then

$$1/\tau_D = \delta(1/T_2). \tag{45}$$

Necessary conditions for the validity of this equation have been discussed previously (23) and essentially involve the requirement that the paramagnetic resonance of solutions containing both vanadium (IV) and vanadium (V) show resolved vanadium hyperfine splittings. This is indeed the case, as illustrated in Fig. 22 which gives the paramagnetic resonance spectrum of the solution whose nuclear resonance is given in Fig. 19.

If we write the rate of electron exchange in a solution containing (D) moles per litre of vanadium (V) and (P) moles per litre of vanadium (IV) as

$$R = k(P)^n(D)^m, \tag{46}$$

where R is the number of moles of electrons transferred per litre per second then it follows that the lifetimes of vanadium (IV) and vanadium (V), $\tau_P$ and $\tau_D$ are

$$\tau_D = \frac{1}{k(P)^n(D)^{m-1}}$$

$$\tau_P = \frac{1}{k(P)^{n-1}(D)^m} \tag{47}$$

From equation 45, it follows that Fig. 20 is actually a plot of $1/\tau_D$ vs. (P). The linearity of the plots indicates that the rate of exchange is first order with respect to vanadium (IV) (n = 1) and values of the slopes for two different concentrations of vanadium (V) show that m = 2. That is, the rate of electron transfer is second order in the vanadium (V) concentration. The number of moles per litre of electrons transferred per second in a solution containing vanadium (IV) and vanadium (V) is therefore $k(P)(D)^2$, where the value of k obtained from the plots in Fig. 20 is $k = 1.5 \times 10^6 \, l^2/\text{mole}^2 \, \text{sec}$ at 6.5 F acid concentration and 3 F chloride concentration.

It was found that the line broadening and hence the rate of the reaction was very sensitive to hydrogen ion concentration. This is illustrated in Fig. 21 where k varies directly as $[H^+]$ in the small range of acidity shown. Measurements were made at high acid (7 F) in the absence of chloride ion, and it appears that the rate of electron exchange is rapid. Because of the low sensitivity, however, we did not attempt to determine the rate constant or the order with respect to vanadium (V) under these conditions. This suggests that there is a path for exchange not involving chloride, although under the conditions of our measurements the vanadium cations are almost certainly complexed to some extent by chloride ions.

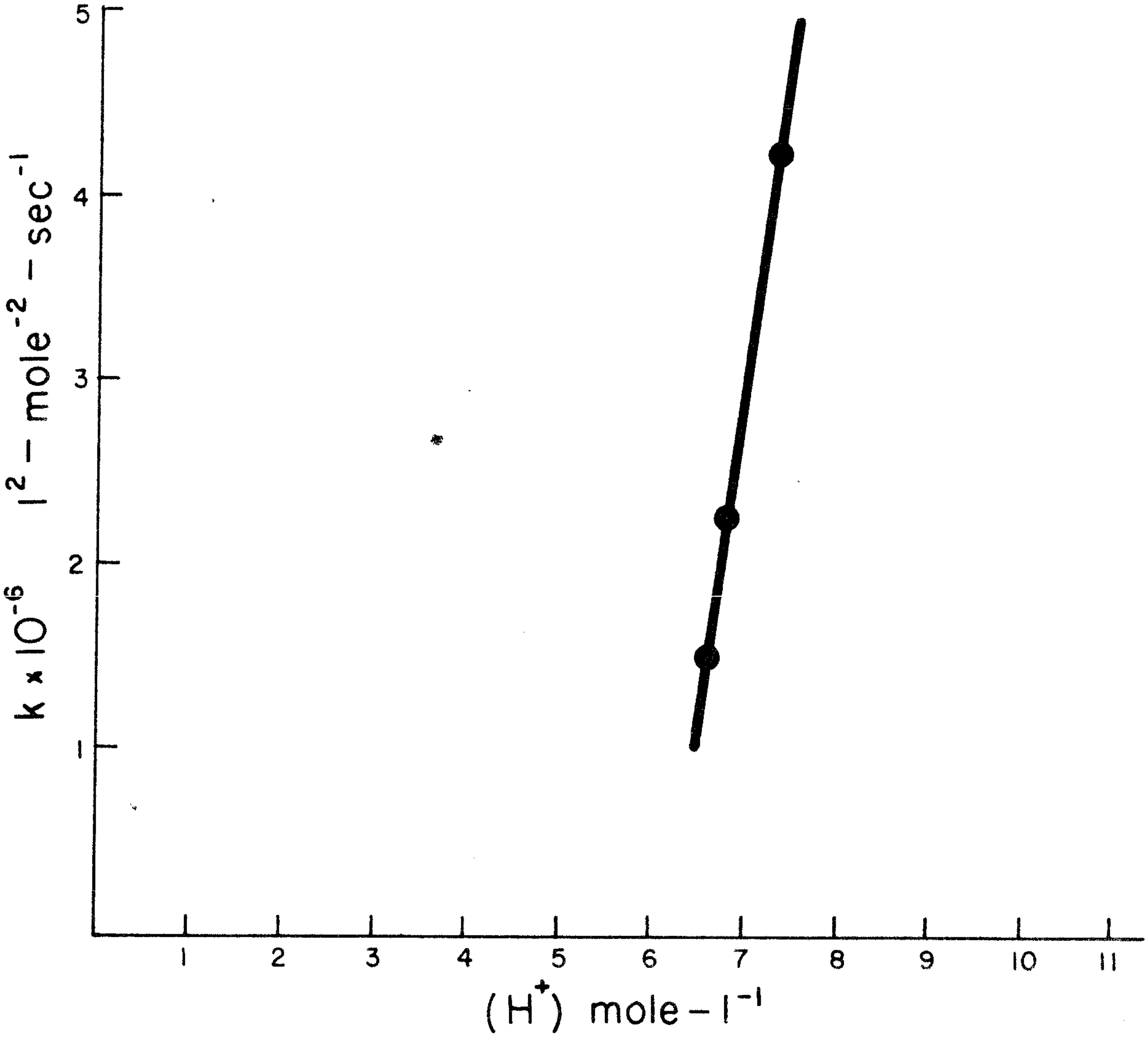

Figure 21. Plot of k vs $[H^{+}]$, k obtained from slopes of plots in Fig. 20

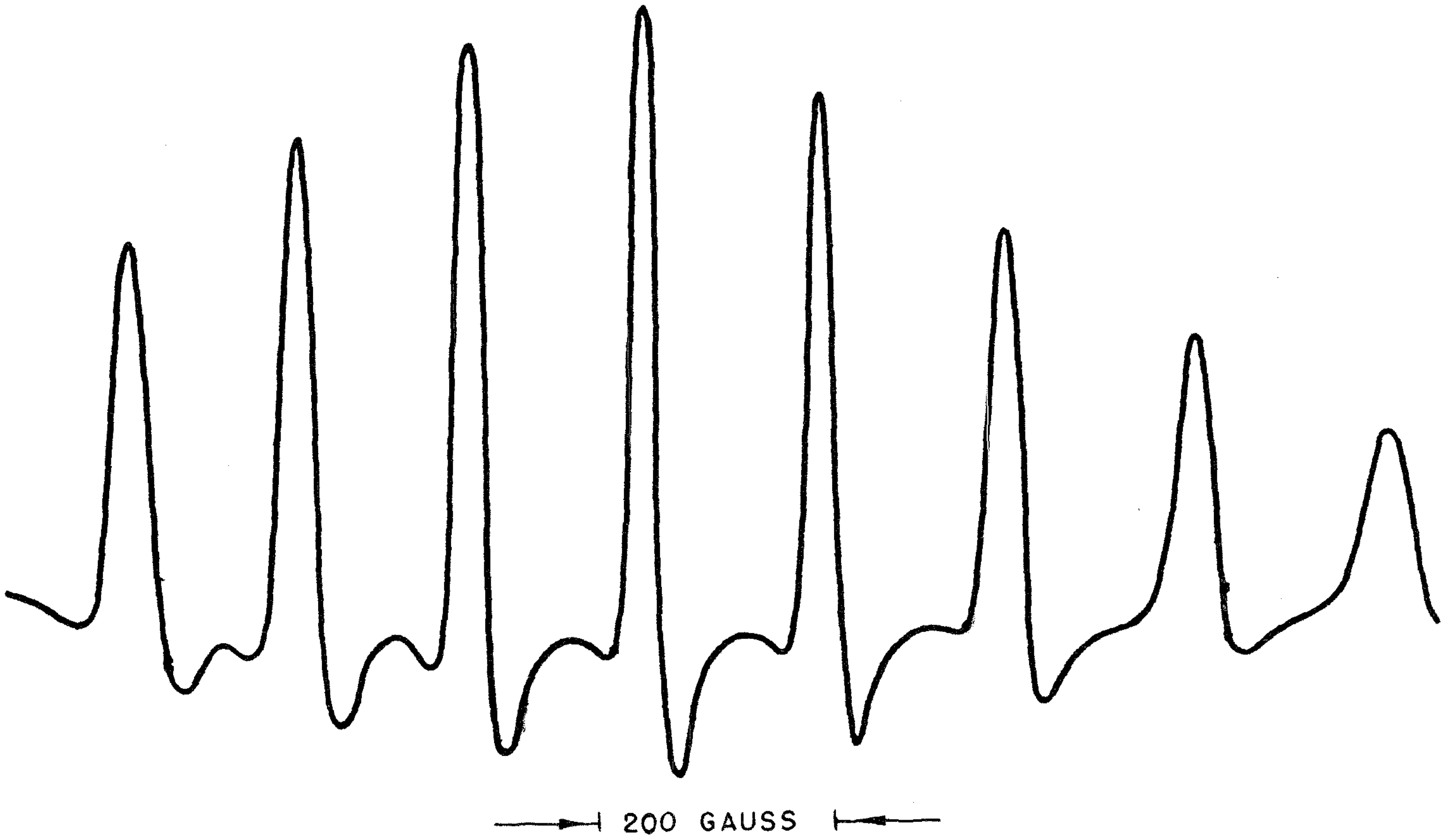

Figure 22. Electron paramagnetic resonance spectrum of 0.025 F vanadium (IV) in a solution containing 0.20 F vanadium (V), 2.8 F $Cl^-$ (as HCl), and 6.50 F $H^+$ (as HCl + $HClO_4$). Klystron frequency is 9500 Mc. and g = 2.0.

## EXCHANGE MECHANISM

The mechanism of this exchange reaction is by no means evident to us. If one assumes that there exists a rapid monomer-dimer equilibrium involving vanadium (V) where the monomer is the predominant species and where the dimer is much more reactive with respect to electron exchange than the monomer, one obtains a mechanism consistent with the rate equation.

$$2V(V) \rightleftharpoons (V(V))_2 \qquad (48)$$

$$(V(V))_2 + V(IV) \longrightarrow (V(V))_2 + V(IV) \text{ (electron exchange)} \qquad (49)$$

We hesitate to speculate as to why the dimer should be more reactive than the monomer with respect to this transfer.

Metal ions are known to polymerize in aqueous solution,(25-28) but all of the work done has been carried out at relatively low acidities and thus would not apply directly to our situation. In addition, dimer and polymer formation is always favoured toward low acidities in hydrolysis type equilibria as in the case of Fe(III): (27)

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ (K_{eq} = 1.2 \times 10^{-3}) \qquad (50)$$

It is conceivable however that oxygenated cations such as those formed by vanadium (IV) and (V) could act as bases as well as acids:

$$2VO_2^+ + 2H^+ \rightleftharpoons V_2O_3^{4+} + H_2O \qquad (51)$$

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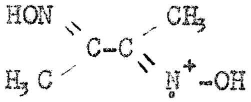
# PROPOSITION I

An EPR study of $\gamma$-irradiated single crystals of dimethylglyoxime by Gordy (1) has revealed the hyperfine coupling between a nitrogen nucleus and an unpaired electron spin. The nuclear coupling was found to be anisotropic with the values of the principal components of the hyperfine tensor being

$$A_1 = 45 \text{ gauss } (126 \text{ Mc})$$

$$A_2 = 25 \text{ gauss } (70 \text{ Mc})$$

The proposed radical species was a positive ion arising from the loss of an electron from the lone-pair $sp^2$ orbital of nitrogen.



Thus, one would expect the odd electron to be located in an $sp^2$ orbital on nitrogen. From the observed values of $A_1$, $A_2$, and $A_3$, it is possible to calculate the s and p character of the wave function if one assumes a mixture of 2s and 2p orbitals. Gordy has done this, and he obtains 19% s-character for the orbital of the unpaired spin. This is in qualitative agreement with the above postulated radical.

It is not unreasonable to expect that the ionized dimethylglyoxime molecule would result in an unpaired spin in an $sp^2$ orbital. The nitrogen in the undamaged molecule presumably has three $sp^2$ orbitals, two used for $\sigma$-bonding with carbon and hydroxyl and one non-bonding orbital containing a lone pair of electrons. In addition there is one p orbital used for $\pi$-bonding with carbon. Thus an ionization of one of the lone pair electrons would result in an unpaired spin in essentially an $sp^2$

orbital.

There is also the possibility of making a "nitrogen radical" where the unpaired spin is located in a p-orbital. In fact, this has been done (2) by passing ammonia through a microwave discharge and trapping the resulting products at liquid helium temperatures. Jen and coworkers (2) observed $NH_2$ radicals which were freely rotating at 4°K. The evidence for the $2p\pi$ spin distribution in $NH_2$ is two-fold. First, the magnitude of the nitrogen hyperfine splittings (only the isotropic component was observed because of rotation) was much smaller than the isotropic contribution observed by Gordy in dimethylglyoxime. The numbers are 29 Mc versus 89 Mc. (The isotropic contribution a, is related to the principle elements of the hyperfine tensor by the equation

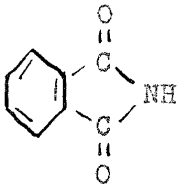
$$3a = A_1 + A_2 + A_3 ).$$

Secondly, McConnell (3) has pointed out, from the proton hyperfine intensities of $\dot{N}H_2$ at 4°K, that the electronic wave function must be antisymmetric with respect to a reflection through the H-N-H plane. This arises from the fact that the singlet nuclear spin state for the protons is not allowed when the $NH_2$ radical is in its zeroth rotational state.

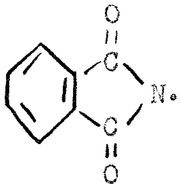
No one has yet reported the anisotropic hyperfine interaction in a free radical containing essentially unit spin density in a p-orbital of nitrogen. This has been done in the case of carbon-13 in x-irradiated malonic acid. (See part I of this thesis.) In the case of $C^{13}$ in damaged malonic acid radicals, $\dot{C}H(COOH)_2$, it was found that the electron-nuclear dipole-dipole interaction is very close to what one might expect from a Hartree orbital on carbon (4).

One of the motivations for observing the analogous interaction for a nitrogen radical would be to see whether the Hartree solutions would be close to the real behavior of the system. In addition one would be learning about the wave function of the radical under study and might, with the proper choice of a system, be able to extend his results in application to other systems. Finally the worth of such an experiment would be manifested by the interest which EPR spectroscopists would hold in its result.

For the above reasons, it is proposed that a study be conducted to measure the principle components of the hyperfine tensor of a nitrogen radical containing essentially unit spin density in a $2p\pi$-orbital of nitrogen. The proposed system for this study is phthalimide,



It is reasonable to expect that one could remove the imido-hydrogen by irradiation to form a radical quite analogous to $\dot{C}H(COOH)_2$. Certainly if there were a loss of a hydrogen atom it would be most likely to come from the nitrogen than from the aromatic ring. Aromatic systems are notorious for their high stability with respect to damage by high energy irradiation. One could envision an opening of the imido-ring, but this would probably close again unless a group were lost in the process. The principle interaction with the unpaired spin in this radical,



would be with the nitrogen. One can see by writing resonance structures that there will be no first-order conjugation with the aromatic ring. Thus the spin density on the benzene ring should be extremely small.

The space group of phthalimide has been determined (5). It is sufficient for our purposes to state that there are two magnetically different molecules in the monoclinic unit cell. (There are actually four molecules in the unit cell but the members of each pair are related by a center of symmetry.)

Smith et al. (4) give the results of calculations of the dipolar coupling of a nitrogen nucleus and an unpaired spin in a 2p orbital. The dipolar coupling constant, which we will call $B_d$, is given by the dipolar part of the spin Hamiltonian, $\mathcal{H}_d$

$$\mathcal{H}_d = g\beta g_n \beta_n \int \left[ \frac{3(\underset{\sim}{S}\cdot\underset{\sim}{r})(\underset{\sim}{I}\cdot\underset{\sim}{r})}{r^5} - \frac{\underset{\sim}{S}\cdot\underset{\sim}{I}}{r^3} \right] |\Psi_{(r)}|^2 \, dv \qquad (1)$$

For an axially symmetric wave function

$$\left\langle \frac{x^2}{r^5} \right\rangle = \left\langle \frac{y^2}{r^5} \right\rangle \qquad (2)$$

Expanding 1, one obtains

$$\mathcal{H}_d = g\beta g_n \beta_n [2(\alpha - 3\beta) I_z S_z - (\alpha - 3\beta)(I_x S_x + I_y S_y)] \qquad (3)$$

where $\alpha = \left\langle \frac{1}{r^3} \right\rangle$ , $\beta = \left\langle \frac{x^2}{r^5} \right\rangle$

Thus,

$$B_d = \alpha - 3\beta = \left\langle \frac{z^2 - \frac{1}{2}(x^2 + y^2)}{r^5} \right\rangle_{2p} \qquad (4)$$

From the Hartree solutions of the free atom (6) and $\left\langle \frac{1}{r^3} \right\rangle$ averages computed from spectroscopic data (7) one obtains from Smith et al. (4)

$$B_d = \frac{2}{5} \left\langle \frac{1}{r^3} \right\rangle_{2p} = 1.01 \text{ a.u.} \qquad (5)$$

Conversion to megacycles gives

$$B_d = 38.3 \text{ Mc.} \qquad (6)$$

One would expect the Fermi-contact interaction to be close to that observed for $NH_2$ (i.e. 30 Mc). The expected principle components of the hyperfine tensor are,

$$A_1 = a + 2B_d = 96 \text{ Mc} \qquad (7)$$

$$A_2 = A_3 = a - B_d = -8\text{Mc} \qquad (8)$$

$A_1$ is the coupling constant for the external magnetic field parallel to the $\pi$-cloud, and $A_2$ , $A_3$ are the interactions with the field perpendicular to the $\pi$-cloud. Note that since the principle coupling constants have opposite sign the triplet hyperfine spectrum will be expected to collapse to one line at certain orientations.

There is, of course, no assurance that the desired radical will be formed from x-irradiation of phthalimide. One could perhaps substitute tritium in the desired position with the expected resultant radical formed after decay to $H_e^3$. The recoil energy as a result of the decay of tritium is at most 60 kv, which is comparable in energy to x-ray sources used in this laboratory. Other possible systems for this purpose are diketopiperazine and succinimide.

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# PROPOSITION II

In a recent publication, Taube has distinguished between water of hydration in solutions of several diamagnetic cations by means of $O^{17}$ NMR in $H_2O^{17}$. Addition of a paramagnetic ion, such as $Co^{+2}$ or $Fe^{+3}$, to water causes the $O^{17}$ resonance to undergo a paramagnetic shift of about $10^4$ cps from that of ordinary $H_2O^{17}$. It was found that when certain diamagnetic cations (e.g. $Be^{+2}$, $Al^{+3}$) were added to the solutions containing the paramagnetic ion, there appeared two resonance lines, one shifted, and one unshifted. The interpretation of these results was that the bulk water exchanges rapidly with the paramagnetic ion resulting in the shift, but the water in the coordination sphere of the diamagnetic cation does not become exposed to the hyperfine field of the paramagnetic ion. The necessary condition for the observation of this phenomenon is that the lifetime of the hydration sphere water be long compared to the inverse paramagnetic shift, i.e. $10^{-4}$ sec. Thus for ions which exchange their hydrated water faster than $10^{-4}$ sec, only the shifted spectrum will be observed. It was also pointed out that, in cases where both lines are observed, the relative intensities of the shifted to the unshifted lines could give a measure of the coordination number for the diamagnetic cation.

The purpose of this proposition is to suggest some experiments which might elucidate the hydration structure of ions in solution. In these experiments, useful information may be gained if certain limiting conditions are fulfilled, whereas no information will be forthcoming if these conditions do not prevail. It is felt, however, that these experiments are worth performing in view of their potential value to physical and inorganic chemists.

The first part of this proposal deals with the phenomenon observed by Taube (1) as applied to square planar complex ions such as formed by platinum and palladium. Using directed bond notation, the hybridization for square planar complexes is $d\,sp^2$. Platinum, palladium and nickel are among the ions which are known to exhibit square planar complex formation in the divalent state. Among the proposed mechanisms for substitution reactions on these square planar complexes is one where the attacking ion becomes coordinated in an axial position, weakening one of the equatorial bonds, and then moves into the position vacated by one of the original ligands. This idea was put forth by Taube (2) who pointed out that with $d\,sp^2$ bonding, there is a p-orbital left over for possible weak bonding in the axial positions.

It is proposed that an $O^{17}$ NMR study be carried out where one looks for an unshifted line due to coordination of $H_2O^{17}$ in the axial positions of such complex ions as $Pt(NH_3)^{+2}$, $Pt(Cl)_4^{-2}$, etc. These ions are "inert" with respect to substitution in the square ligand positions. That is, the lifetime for substitution of the ligands is of the order of many hours to days.

In these experiments one would prepare solutions of the complex ion under investigation and add $Co^{+2}$ ion to about 0.2 M. The $O^{17}$ resonance line of the bulk water would be shifted paramagnetically while those attached to the diamagnetic complex ion would not be shifted. For greater sensitivity, the experiments would be carried out in water which was enriched in $O^{17}$, which is commercially available.

The necessary condition for the observation of this effect is that the lifetime of the water in the axial position of the complex ion be greater than $10^{-4}$ sec. This was the case in Taube's study for $Al^{+3}$ and $Be^{+2}$ but not for $Mg^{++}$.

It is not known whether the lifetime of the axially coordinated water in square planar complexes would be long enough to observe the above described effect. If the effect were not observed, one would at least have a lower limit for the exchange rate of water in these ions.

The second part of this proposition deals with another aspect of hydration properties of ions, this time paramagnetic transition metal ions. When small concentrations ($10^{-3}$ M) of paramagnetic ions are added to water, the $O^{17}$ nuclear resonance is not shifted, but merely broadened. The broadening has been attributed to the entrance of solvent water into the first coordination sphere of the ion and exchanging rapidly with the bulk water. Chromic ion, for example, is known to be inert with respect to exchange of its coordinated water with the solvent. The broadening of the $O^{17}$ nuclear resonance in water by chromic ion is several orders of magnitude less than the broadening caused by $Co^{+2}$, $Fe^{+3}$, $Mn^{+2}$, or $Cu^{+2}$, all of which exchange their waters rapidly with the solvent. Thus, the water must enter into a chemical bond with the paramagnetic ion, giving rise to a large hyperfine field at the oxygen nucleus. This large internal magnetic field causes the oxygen to lose its phase coherence with the oxygens in bulk water. Thus if the exchange between the paramagnetic and diamagnetic environments is of the right order of magnitude, a broadening of the $O^{17}$ nuclear resonance will be observed. The conditions for obtaining rate information have been discussed by McConnell and Berger (4) and these are essentially observed by Connick and Poulson. Lower limits for exchange lifetimes for the reactions

$$M(H_2O^*)^{+n} + H_2O \rightleftharpoons M(H_2O)^{+n} + H_2O^*$$

range from about $10^{-4}$ sec for $Ni^{+2}$ to $10^{-7}$ sec for $Mn^{+2}$.

There is very good evidence (5) that the cyanide complex of $Co^{+2}$ has the composition $Co(CN)_5{}^{-3}$ as opposed to $Co(CN)_6{}^{-4}$ in aqueous solution, but the pentacyanide may be $Co(CN)_5H_2O^{-3}$. It is proposed that $O^{17}$ NMR in water be used to investigate the hydration properties of this complex ion. It may be possible, through a measurement of the broadening of the $O^{17}$ resonance to distinguish between the pentacyano- or the aqua-pentacyano complex.

If one were not to observe a broadening of the $O^{17}$ nuclear resonance in aqueous solutions containing pentacyano cobalt (II), it would be a good indication that water was not entering the coordination sphere of the cobalt. If a broadening of the $O^{17}$ NMR signal were observed there could be two interpretations:

1. The broadening is due to $Co(CN)_5(H_2O)^{-3}$ exchanging water rapidly with the solvent water.

2. It is known that the cyanides on $Co(CN)_5{}^{-3}$ are extremely labile with respect to exchange with radio-cyanide (5). The broadening of the $O^{17}$ resonance could be caused by the entrance of water into the coordination sphere as a labile cyanide ion leaves. The latter possibility could be investigated by examining the $O^{17}$ broadening as a function of cyanide concentration. A study of this dependence would give a measure of the competition of water with cyanide for the coordination of cobalt, a measurement of great value to physical inorganic chemists.

The study of water competition with other ligands for the coordination spheres of labile complex ions could be extended to other systems as well as $Co^{+2}$. For example one could study the competition of water with fluoride ion in $FeF_6^{-3}$ and $MnF_6^{-4}$.

In determining rate constants for water exchange, Connick and Poulson assumed that the coordination number of water in the aquated ions was six. If one assumes that the rate constant for the exchange of coordinated water is independent of the nature of the other five ligands in a labile complex, then the relative $O^{17}$ broadening for a given concentration of paramagnetic ions will give a measure of the effective coordination number of water. Thus, if the broadening of the $O^{17}$ NMR in a solution of say $10^{-3}$ M $FeF_6^{-3}$ were half as great as the broadening for the same concentration of $Fe^{+3}$, one could say in this simple approach that the effective coordination number of water was three.

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# PROPOSITION III

Recently, Gordy (1) has reported the electron paramagnetic resonance spectra of radiation damaged single crystals of alanine, $CH_3CH(NH_2)COOH$. He reports the radical formed to be $CH_3\dot{C}HR$ where R is a non-interacting group. The assignment of the above radical, which we will call I, was based on the knowledge of the molecular structure of alanine plus the observed spectra. The spectra, many of which are displayed in the article, can be interpreted in terms of a doublet (from the C-H proton) each component of which is split into a quartet. The quartet arises from the equal contributions of the three methyl protons. The intensity ratios of the components are also in agreement with the assigned radical species.

Gordy reports the principle components of the hyperfine tensor for the interaction of the C-H proton with the unpaired spin.

$$\mathcal{H}_{hf} = \underset{\sim}{S} \cdot \underset{\approx}{A} \cdot \underset{\sim}{I} \qquad (1)$$

A cylindrical symmetry is reported about the C-H bond.

$$A_1 = \pm 7 \text{ gauss} \qquad (2)$$

$$A_2 = A_3 = \pm 27 \text{ gauss} \qquad (3)$$

From the above data and the fact that the trace of the dipolar contribution to A is zero, Gordy gives the Fermi contact and dipolar coupling constants.

$$A_f = \pm 20 \text{ gauss} \qquad (4)$$

$$A_d = \pm 7 \text{ gauss} \qquad (5)$$

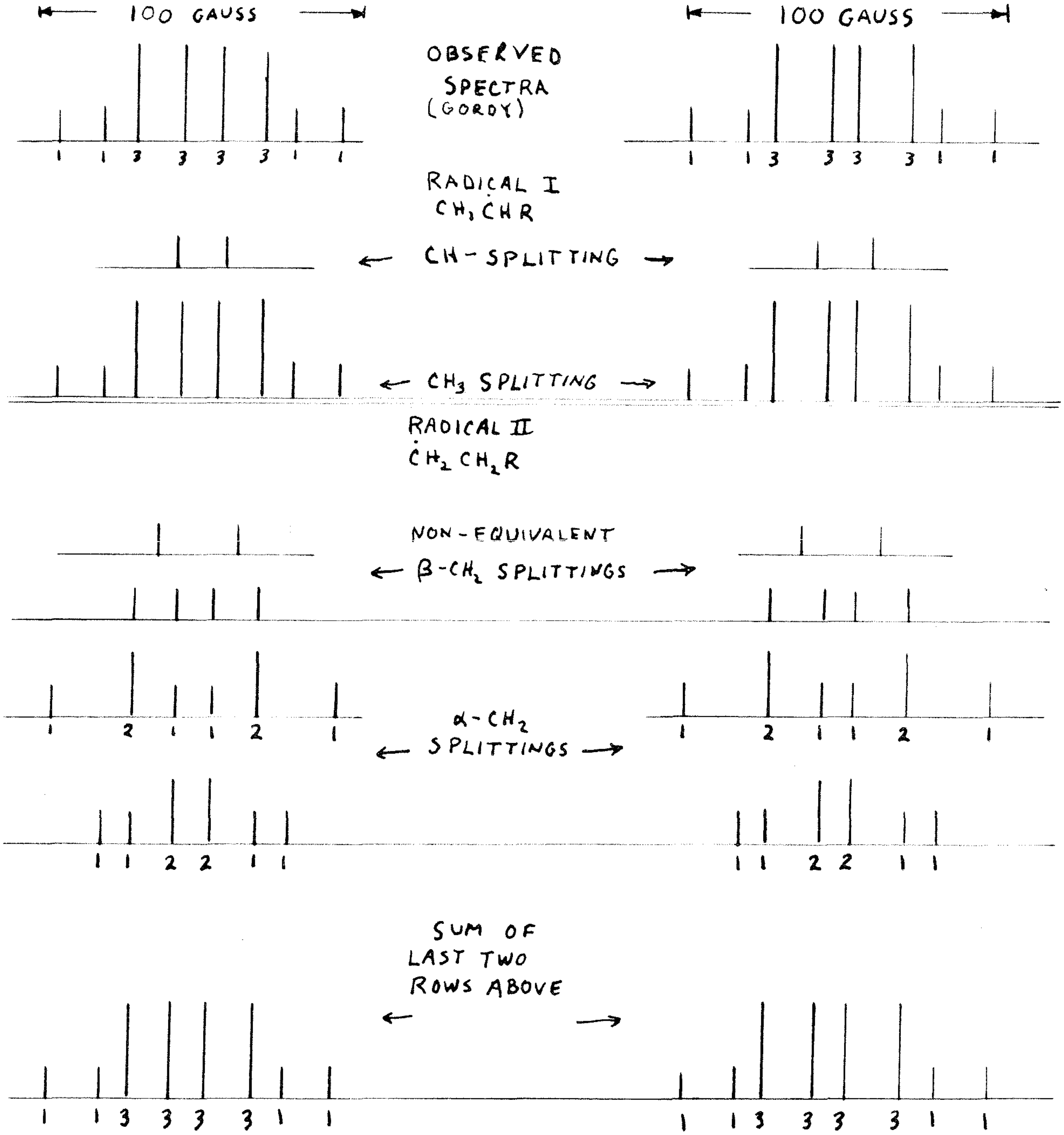
Gordy also discusses second order effects which arise from the fact that the coupling of the C-H proton to the externally applied field is comparable in magnitude with the coupling to the anisotropic hyperfine field of the unpaired spin. These second order contributions give rise to a change in the transition selection rules for certain orientations. The spectrum for the C-H fragment will consist of a pair of doublets of different intensities. The separations between these two doublets are denoted by Gordy as d+ and d-. The development of the equations leading to the splittings d+ and d- are given in a straightforward manner in equations 6 through 15 of Gordy's paper and will not be presented here. One point to be made here is that Gordy uses the values d+ and d- as obtained from spectra to calculate quantities of importance in the Spin Hamiltonian, namely the principle components of the hyperfine tensor. Let us emphasize here that Gordy has reported the principle values of the A-tensor with the assumption the methyl group gives rise to a symmetrical quartet which is superimposed upon the C-H splittings, thus with the assumption that the radical is $CH_3\dot{C}HR$.

The values of the principle components of the hyperfine tensor for the C-H proton-electron interaction are in disagreement with those calculated by McConnell and Strathdee (2) and also with those observed by McConnell, Heller, Cole, and Fessenden (3). The above workers observed the hyperfine interactions in the radical $R_2\dot{C}H$ formed from x-irradiated single crystals of malonic acid. They observed the principle components for the C-H proton-electron hyperfine interaction and showed that they were indeed the diagonal components because of the constancy of the splittings at two different applied fields. (The doublet splitting along a non-canonical orientation is dependent upon the applied field strength).

The principle values of the hyperfine tensor quoted by McConnell et al. are 29, 61, and 91 Mc or roughly 10, 20, and 30 gauss. The deviation from axial symmetry about the C-H bond is to be expected if one places the unpaired electron in a carbon 2p orbital.

In order to reconcile the conflicting results it is proposed that further work be carried out on the alanine system. First, it is possible to explain the spectra presented in Gordy's paper on the basis of a radical of the formula $\mathring{C}H_2CH_2R$ (II), where again R is a non-interacting group. As is discussed in this thesis, the β-methylene protons are in general non-equivalent for a given orientation of the radical in the externally applied field. Let us examine the spectra presented in Figs. 2 and 3 of Gordy's paper where the magnetic field is oriented along the 001, 100, and 010 directions in the orthorhombic crystal of d-alanine. It is along these three directions that the four molecules in the unit cell are magnetically equivalent. In other directions there are generally four non-equivalent molecules and the spectra are not easily interpretable.

The spectrum for $H_o$ in the 001 direction shows five lines, equally separated of intensity ratios 1:4:6:4:1 which can arise from four equivalent protons interacting with the electron spin, each with a coupling of about 25 gauss. This is consistent with both radicals I and II. For the orientations along the 010 and 100 directions the dual interpretation is shown in the accompanying sketch. Line drawings of the observed spectra are shown in addition to the interpretations consistent with both radicals I and II. In addition, the magnitudes of the splittings are reasonable on the basis of radical II both for the anisotropic β-methylene

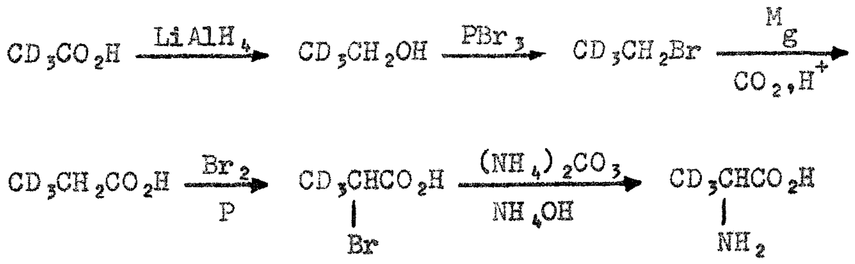

100 GAUSS
100 GAUSS
OBSERVED SPECTRA (GORDY)
1 1 3 3 3 3 1 1
1 1 3 3 3 3 1 1
RADICAL I
$CH_3\dot{C}HR$
CH - SPLITTING
CH₃ SPLITTING
RADICAL II
$\dot{C}H_2CH_2R$
NON - EQUIVALENT
β-CH₂ SPLITTINGS
1 2 1 1 2 1
1 2 1 1 2 1
α-CH₂ SPLITTINGS
1 1 2 2 1 1
1 1 2 2 1 1
SUM OF LAST TWO ROWS ABOVE
1 1 3 3 3 3 1 1
1 1 3 3 3 3 1 1

protons and the isotropic α-methylene protons.

It is certainly easier to postulate a mechanism for the formation of radical I than for radical II. One merely has to invoke a loss of $HCO_2$ or $NH_2$. (More likely $NH_3^+$ or $CO_2^-$ is lost as a first step since the molecules are probably zwiterions in the crystal). There is no simple way in which radical II can be formed in one step. M. W. Hanna has grown crystals of D-alanine from $D_2O$ and found no change in the EPR spectra. This indicates that the carboxyl and amino hydrogens contribute nothing to the hyperfine pattern. One possible process for the formation of radical II is a primary damaging at the α-carbon site to form $CH_3\dot{C}HR$, followed by a proton migration to give $\dot{C}H_2CH_2R$. There is no justification for postulating such a rearrangement. On the other hand it is often difficult to predict the result of bombarding organic systems with high energy radiation. The purpose of this proposition is not to suggest a mechanism for the formation of radical II, but merely to show that the spectra are consistent with it.

A proposed means of distinguishing between radicals I and II is to deuterate the methyl protons of alanine and look at the damaged species formed. Radical I would be $CD_3\dot{C}HR$, whereas radical II would be $\dot{C}D_2CHDR$. The EPR spectra of these two radicals would now be distinguishable. Radical I would still give rise to a large doublet. Each component of the doublet would be split into seven lines. The deuterium splittings would be isotropic and the proton splittings anisotropic. In the case of radical II, there would be observed isotropic proton splittings, whereas the splittings of deuterium would be both isotropic and anisotropic depending upon which carbon atom they are located.

$CD_3$ alanine can be prepared from $CD_3CO_2H$, which is available commercially, by the following method. (4)



$$CD_3CO_2H \xrightarrow{LiAlH_4} CD_3CH_2OH \xrightarrow{PBr_3} CD_3CH_2Br \xrightarrow[CO_2,H^+]{Mg}$$

$$CD_3CH_2CO_2H \xrightarrow[P]{Br_2} \underset{Br}{CD_3CHCO_2H} \xrightarrow[NH_4OH]{(NH_4)_2CO_3} \underset{NH_2}{CD_3CHCO_2H}$$

The DL mixture can be resolved with acylase I (5) to give pure D-alanine.

Actually DL-alanine could be used since its crystal structure is well known (6) whereas for D- or L-alanine the atomic coordinates on the unit cell are not known. (7) There is no assurance, however, that the radicals formed in the DL-crystal will be the same as those in D- or L-alanine. In addition it is much simpler to grow large single crystals of D- or L-alanine than for the DL mixture. (8)

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## PROPOSITION IV

The reduction of $Fe(CN)_6^{-3}$ by $Co(CN)_5^{-3}$ in neutral solution gives a very unusual binuclear complex ion (1)

$$[(CN)_5Fe^{+2}-CN-Co^{+3}(CN)_5]^{-6} \qquad (A)$$

This ion can be oxidized with $I_2$, $Br_2$, or $MnO_4^-$ to give

$$[(CN)_5Fe^{+3}-CN-Co^{+3}(CN)_5]^{-5} \qquad (B)$$

Compound A is diamagnetic. Compound B is paramagnetic with a susceptibility corresponding to one unpaired electron spin. The formula as written in B assigns the unpaired spin to the iron, but it is also possible to write

$$[(CN)_5Fe^{+2}-CN-Co^{+4}(CN)_5]^{-5} \qquad (B')$$

The plus four oxidation state of cobalt is known to exist in certain binuclear complexes of cobalt (1,2,3).

$$[R_5Co^{+3}-O-O-Co^{+4}R_5]^{+5-10\,Z_R} \qquad (C)$$

In the above compound $Z_R$ is the charge of the ligand, R. The ligands in such complexes are, for example, $NH_3$, and $CN^-$.

The valence structure of such compounds as C was given several interpretations. Werner (2) suggested that the cobalts were of different oxidation states. An extended interpretation was given (4) where the valence of each cobalt resonated between three and four. On the basis of molecular orbital calculations Dunitz and Orgel (5) suggested that the two cobalts were trivalent, joined by an $O_2^-$ bridge. In a previous proposition this worker suggested an EPR study to attempt to distinguish between the various possibilities. Recently, Ebsworth and Weil (6) have carried out EPR studies on several binuclear μ-peroxo cobalt complexes. Although there is rather complicated dependence of the observability of hyperfine structure on acidity and viscosity, the hyperfine structure, wherever observed, shows equal interaction of the unpaired spin with both cobalts. The hyperfine structure showed fifteen lines of spacing equal to about 13 gauss. (Each cobalt has spin of 7/2, giving a total effective nuclear spin of 7, hence fifteen lines.) Thus the unpaired spin is equally distributed between both cobalts. The spin density on the bridging peroxo group is not known from the above work. The authors mention the possibility of substituting $O^{17}$ on the bridge to investigate the matter.

Magnetic resonance studies on compound B above are proposed to investigate the spin distribution in this unusual complex ion. It is conceivable that some resonance may exist between "states" B and B', in which case, there is a possibility of observing cobalt hyperfine structure. Comparison of the hyperfine splittings to those obtained by Ebsworth and Weil will give a rough measure of the relative coefficients of states B and B'.

In the case of compound C let us write

$$\Psi_C = \frac{1}{\sqrt{2}} (C + C') \qquad (1)$$

where C and C' denote the structures where first one cobalt, then the other has the plus four oxidation state. The contact hyperfine coupling constant A is

$$A_C = \frac{8\pi}{3} g_n \beta_n |\Psi_C(o)|^2 = \frac{8\pi}{3} g_n \beta_n (\tfrac{1}{2} C(o)^2 + \tfrac{1}{2} C'(o)^2) \quad (2)$$

By the equivalence of both cobalts, $C(o)^2 = C'(o)^2$ so that

$$A_C = \frac{8\pi}{3} g_n \beta_n C(o)^2 \quad (3)$$

In 2 and 3, $g_n \beta_n$ are the nuclear g-factor for cobalt and the nuclear magneton. In compound B let us assume

$$\Psi_B = aB + bB' \quad (4)$$

where B and B' refer to the states as illustrated above. Since the most abundant isotopes of iron have no spin, the hyperfine coupling constant $A_B$ will depend only on the spin density at the cobalt nucleus.

$$A_B = \frac{8\pi}{3} g_n \beta_n b^2 B'(o)^2 \quad (5)$$

The ratio of the hyperfine constants in compound B to compound C is

$$\frac{A_B}{A_C} = \frac{b_2 B'(o)^2}{C(o)^2} \approx b^2 \quad (6)$$

The validity of the above treatment is certainly questionable since it assumes that the nature of the ligands and bridging groups does not effect the relative density of spin at the cobalt nucleus. However it should certainly be correct to give an order of magnitude estimate of a and b in equation 4 of this very simple approach. Continuing along this treatment, we see that we can approximate the effective oxidation state of cobalt in compound C as 3.5. From the magnitude of the hyperfine interaction in compound B, and from equation 6, we can assign an effective oxidation state to cobalt of $3 + b^2$, and to iron of $3 - b^2$. The above treatment also depends upon the observability of cobalt hyperfine structure in the electron resonance.

If cobalt hyperfine structure is not observable it may be possible to get a measure of the magnetic interaction of the unpaired spin with cobalt by cobalt NMR. One might observe a shift of the cobalt nuclear resonance in compound B over that of diamagnetic compound A. The shift, if observable, is a measure of the magnetic field acting at the cobalt nucleus due to the unpaired spin.

Nitrogen nuclear resonance of the cyanide ligands could also be informative in determining the nature of the spin distribution in the binuclear complex. Shulman (7) has observed paramagnetic shifts of nitrogen resonance in ferricyanide ion. If the complex, B, were essentially completely $Fe^{+3}$ and $Co^{+3}$ then the ligands on the cobalt side of the complex would be in essentially a diamagnetic environment, whereas the ligands near the iron would experience the magnetic field due to the unpaired spin on the iron. One might expect to observe actual chemical shifts between the different kinds of cyanides. The line widths for cyanide nitrogen observed by Shulman were about 2.5 gauss at $10^4$ gauss applied field, while the shifts were of the order of 3-10 gauss from the $N^{14}$ resonance of liquid nitrogen.

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## PROPOSITION V

Many metal ions are known to form dimers and polymers in aqueous solutions. In all of the cases studied the formation of the polymeric species is favored by low acidities. For example, ferric ion forms a dimer in a hydrolysis type equilibrium (1).

$$2Fe^{+3} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{+4} + 2H^+ (K_{eq} = 1.2 \times 10^{-3}$$

Also oxygenated cations such as $VO_2^+$ and $UO_2^{++}$ are hydrolyzed to form dimeric and polymeric species (2,3).

$$10VO_2^+ + 8H_2O \rightleftharpoons H_2V_{10}O_{28}^{-4} + 14H^+ \text{ (log K = -6.75)}$$

$$2UO_2^{++} + H_2O \rightleftharpoons U_2O_5^{++} + 2H^+$$

It is conceivable that oxygen-containing cations such as are formed by vanadium, uranium, neptunium and other metals could have an amphoteric nature in extremely high acid solution. Kinetic information in part II of this thesis shows that the rate of electron exchange between vanadium(IV) and vanadium(V) is second order in vanadium(V). This is consistent with a mechanism

$$2V(V) \rightleftharpoons [V(V)]_2$$

$$[V(V)]_2 + V(IV) \longrightarrow [V(V)]_2 + V(IV) \qquad \text{(electron exchange)}$$

where the dimer is much more reactive than the minomer with respect to electron exchange and where its concentration is small compared to that of the monomer. As mentioned in this thesis, it is not unreasonable that the $VO_2^{++}$ ion could act like a base in high acid solution to give

$$2VO_2^+ + 2H^+ \rightleftharpoons V_2O_3^{+4} + H_2O$$

No one has reported such behavior, but no one has worked with these ions at very high acidities (6-12 N). It is proposed, on the basis of the above kinetic evidence that the basic behavior of $VO_2^+$ and other oxygenated cations is feasible, and that investigations be conducted to determine the extent of dimerization of such ions in highly acidic solutions. The motivation in this proposal arises from the observation of an unexpected kinetic result and the natural curiosity to investigate further into this phenomenon. In addition, the investigation involves the search for an undiscovered chemical species which in itself is of scientific importance.

One means for ascertaining the existence of such dimers or polymers is to investigate the various systems spectrophotometrically. $VO_2^+$, for example, absorbs light quite strongly from 2400 to 3200 Å. The molar extinction coefficient in this range of wave length goes from $10^3$ to $10^2$ $cm^{-1}$ $M^{-1}$. It was in this range of wave length that Newman and Quinlan (4) carried out an investigation of the hydrolysis of $VO_2^+$ to $H_2V_{10}O_{28}^{-4}$.

The following is a possible analysis of spectrophotometric data in highly acidic solutions of, say $VO_2^+$. For the sake of specificity let us say the dimeric species in high acid is $V_2O_3^{+4}$. The absorbancy of light at a given frequency, A will be

$$A = \epsilon_1[VO_2^+] + \epsilon_2[V_2O_3^{+4}] \tag{1}$$

where $\epsilon_1$ and $\epsilon_2$ are the extinction coefficients for the monomer and dimer respectively. The total vanadium concentration $V_T$ is

$$V_T = [VO_2^+] + 2[V_2O_3^{+4}] \qquad (2)$$

The absorbancy in regions of acidity where no dimer is formed is

$$A_o = \epsilon_1 V_T \qquad (3)$$

Let us write down a feasible acid-base equilibrium reaction for the dimerization of $VO_2^+$.

$$2VO_2^+ + 2H^+ \rightleftharpoons V_2O_3^{+4} + H_2O \qquad (4)$$

$$K = \frac{[V_2O_3^{+4}]}{[VO_2^+]^2 [H^+]^2} \qquad (5)$$

Solving 1, 2, and 3 for $[VO_2^+]$ and $[V_2O_3^{+4}]$ we obtain

$$[VO_2^+] = \frac{2A - \epsilon_2 V_T}{2\epsilon_1 - \epsilon_2} \qquad (6)$$

$$[V_2O_3^{+4}] = \frac{A - A_o}{\epsilon_2 - 2\epsilon_1} \qquad (7)$$

We substitute these values into equation 5.

$$K = \frac{(A - A_o)(\epsilon_2 - 2\epsilon_1)}{(2A - \epsilon_2 V_T)^2 [H^+]^2} \qquad (8)$$

or rearranging

$$2A - \epsilon_2 V_T = \frac{(A - A_o)^{1/2} (\epsilon_2 - 2\epsilon_1)^{1/2}}{[H^+] K^{1/2}} \qquad (9)$$

$$A = \left[\frac{\epsilon_2 - 2\epsilon_1}{K}\right]^{1/2} \frac{(A - A_o)^{1/2}}{2[H^+]} + \frac{\epsilon_2 V_T}{2} \qquad (10)$$

Now a plot of A vs $(A - A_o)^{1/2}/2[H^+]$ will give a straight line of slope $[(\epsilon_2 - 2\epsilon_1)/K]^{1/2}$ and intercept $\frac{1}{2}\epsilon_2 V_T$. Thus, a systematic deviation from Beer's law behavior can give an indication of polymeric species in equilibrium with the monomer. An addition qualitative investigation could be carried out by simply looking for some changes in the gross features of the absorption spectrum as a function of acidity and vanadium concentration. If the dimer has a high absorption in a region where that due to the monomer is small, then this will cause a systematic change in the absorption spectrum as the acidity and vanadium concentration are changed.

Another means of detecting possible dimer formation is by electrochemical techniques, which have been extensively employed by a large number of workers. One could, in short, measure the vanadium(V)-vanadium(IV) redox potential as a function of acidity and vanadium concentration. The expected behavior of the measured potential can be theoretically predicted from Nernst's equation, and deviations from this behavior can be correlated to possible dimer formation. These techniques are best suited, however, when the concentrations of the species giving rise to the potential are small so that one can approximate activities with concentrations. Since the hydrogen ion concentration plays a part in the vanadium(V)-vanadium(IV) redox potential, potentiometric measurements at high acidities will require large corrections to go from hydrogen ion concentration to activity. In addition, Rossotti and Rossotti (2), in their electrochemical measurements on vanadium(V) polymerization, found it impossible to obtain reproducible results in attempting to measure vanadium(V)-(IV) redox potentials for a large number of electrodes. They base their conclusions essentially on some very precise pH measurements in titrating $VO_2^+$ with $OH^-$ to obtain the equilibrium constant for the hydrolytic polymerization reaction to form the deca-polymer.

Thus, it is expected that a series of spectrophotometric measurements will be more effective to this end, than electrochemical ones.

If the basic premise of this proposition is feasible (i.e. that oxy-cations can act like bases in high acid), then there are a large number of systems which can be investigated for possible dimer formation. Among the metals which form oxy-cations are vanadium, uranium, neptunium, molybdenum, zirconium, and titanium.

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