

- zene with NOPF_6 . However, we assumed that oxygen molecule might be an oxidizing agent in this reaction, since **3** was stable under vacuo. The oxidation mechanism of **3** by oxygen is currently uncertain. An electron transfer from **3** to oxygen, followed by the formation of 1,2-dioxetane might be a possible route to lead **7** and formaldehyde. Refer to the following references: G. A. Olah and N. Friedman, *J. Am. Chem. Soc.*, **88**, 5330 (1966); W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *J. Am. Chem. Soc.*, **96**, 7525 (1974); W. H. Richardson, F. C. Montgomery, P. Slusser, and M. B. Yelvington, *J. Am. Chem. Soc.*, **97**, 2819 (1975).
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Simulation of the Solution EPR Spectra of Mixed-Valence Heteropolyanions Containing Vanadium(IV) and Vanadium(V)[†]

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Modified Bloch equations were used to simulate the solution EPR spectra of mixed-valence heteropolyanions containing vanadium(IV) and vanadium(V). Simulated are the 15-, 22-, 36- and 43-line spectra of α -1,2-[PV(IV)VW₁₀O₄₀]⁶⁻, [P₂V(IV)V₂W₁₅O₆₂]¹⁰⁻, [HP₂V(IV)V₂W₁₅O₆₂]⁹⁻ and α -1,2,3-[HSiV(IV)V₂W₉O₄₀]⁷⁻, respectively. The transition probabilities for the intramolecular electron transfer were determined from the simulations.

Introduction

Recently we have simulated the temperature-dependent EPR spectra of mixed-valence copper(II)-copper(I) complexes,¹ using the modified Bloch equations.^{2,3} The simulation made it possible to determine the transition probability for the intramolecular electron transfer, and the activation energy when spectra at several different temperatures were available.

We have applied the same method to the simulation of the EPR spectra of mixed-valence heteropolyanions containing vanadium(IV) and vanadium(V), which show a variety of interesting EPR spectra. So far four types of solution spectra

have been observed: a 15-line spectrum for [SiV(IV)VW₁₀O₄₀]⁷⁻, [P₂V(IV)VW₁₆O₆₂]⁹⁻, and α -1,2-[PV(IV)VW₁₀O₄₀]⁶⁻; ^{4,6} a 22-line spectrum for [P₂V(IV)V₂W₁₅O₆₂]¹⁰⁻; ⁵ a 36-line spectrum for [HP₂V(IV)V₂W₁₅O₆₂]⁹⁻ in which the VO₆ octahedra are edge-shared; ⁵ and a 43-line spectrum for α -1,2,3-[HSiV(IV)V₂W₉O₄₀]⁷⁻ in which the VO₆ octahedra are corner-shared.⁴ The simulation of these spectra is reported in this paper.

Simulation of the Spectra

The 15-Line Spectrum. When a heteropolyanion containing two equivalent vanadium(V) atoms connected by a bridging oxygen atom is reduced, it shows a 15-line spectrum.^{4,6} In order to simulate the spectrum, we first calculate the positions of eight hyperfine lines expected when the

[†] Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.

unpaired electron is trapped on one vanadium ($I = 7/2$) atom, then calculate the spectrum for each combination of two nuclear spin states using the modified Bloch equations,^{2,3} and finally add up the spectra for all possible combinations of the nuclear spin states.

When the unpaired electron is trapped on one vanadium atom, the positions of the hyperfine lines in the solution spectrum may be calculated by the following equation:⁷

$$B(m) = (1/g\beta) [h\nu - am - (a^2/2h\nu) \{I(I+1) - m^2\}] \quad (1)$$

where $m = -I, -I+1, \dots, +I$, and g and a are the g value and the hyperfine coupling constant, respectively. When an electron is hopping between the two equivalent vanadium atoms, the total complex magnetic moment is given by the following equation:⁸

$$\hat{M} = -\gamma B_1 M_0 \frac{0.5(2\omega - \hat{\omega}_A - \hat{\omega}_B) + 2iP}{\{(\omega - \hat{\omega}_A) + iP\} \{(\omega - \hat{\omega}_B) + iP\} + P^2} \quad (2)$$

$$\hat{\omega}_A = \omega_A - i/T_{2A}; \quad \hat{\omega}_B = \omega_B - i/T_{2B} \quad (3)$$

where P is the transition probability of the electron from one vanadium atom to the other in the unit time, T_{2A} and T_{2B} are the transverse relaxation times of the electron in V_A and V_B , M_0 is the static magnetization, ω_A and ω_B are the resonance frequencies $\times 2\pi$ in the absence of hopping, and other symbols have their usual meaning.

The intensity of the spectral line is proportional to v , the imaginary part of \hat{M} . As was shown before,¹ the first derivative of v with respect to the magnetic field B is given by

$$\frac{dv}{dB} = \frac{(\gamma B_1 M_0 \hbar) [(Q'T + R'S)(Q^2 + R^2) - 2(QT - RS)(QQ' - RR')]}{g\beta (Q^2 + R^2)^2} \quad (4)$$

with

$$Q = (B - B_A)(B - B_B) - W_A W_B - p(W_A + W_B) \quad (5)$$

$$R = (B - B_A)(W_B + p) + (B - B_B)(W_A + p) \quad (6)$$

$$S = 0.5(2B - B_A - B_B) \quad (7)$$

$$T = 0.5(W_A + W_B) + 2p \quad (8)$$

$$Q' = (dQ/dB) = 2B - B_A - B_B \quad (9)$$

$$R' = (dR/dB) = W_A + W_B + 2p \quad (10)$$

$$W_A = \hbar/g\beta T_{2A}; \quad W_B = \hbar/g\beta T_{2B} \quad (11)$$

$$p = P\hbar/g\beta \quad (12)$$

The line width is known to vary according to the formula⁷

$$W = c + dm + fm^2. \quad (13)$$

A cubic term may be included to get a closer fit between the measured and calculated line widths, but we have neglected this usually small term.⁷

Preliminary calculations showed that an 8-line spectrum changed gradually to a 15-line spectrum as the P value was increased. But the spacings between the hyperfine lines in the calculated 15-line spectrum did not match those in the measured spectrum. A better simulation could be obtained when the second order energy term in Eq. (1) was reduced to one half of its value. This reduction may be justified by the following argument. When the hopping rate is extremely fast, the system must approach to a system with a delocalized electron. When the electron is delocalized over two vana-

electron. When the electron is delocalized over two vanadium atoms with nuclear spin states m_1 and m_2 , the position of the spectral line is given by

$$B = (1/g\beta) [h\nu - a'(m_1 + m_2) - \frac{a'^2}{2h\nu} \{2I(I+1) - m_1^2 - m_2^2\}]. \quad (14)$$

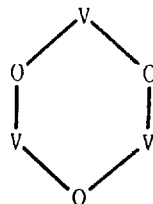
According to the hopping electron model, the average magnetic field for the two nuclear spin states m_1 and m_2 is given by

$$B = (1/g\beta) [h\nu - \frac{a}{2}(m_1 + m_2) - \frac{a^2}{4h\nu} \{2I(I+1) - m_1^2 - m_2^2\}]. \quad (15)$$

In order that the above two equations agree with each other for all combinations of m_1 and m_2 , a' must be $0.5a$ and the second order energy term in Eq. (15) must be reduced to one half of its value. Thus we have introduced a reduction factor r , so that $r=1$ corresponds to the trapped electron and $r=0.5$ to the delocalized electron. It is probable that an intermediate value of r produces the best simulation for an intermediate transition probability.

Thus we have used seven adjustable parameters to simulate the spectrum: g , a , P , c , d , f , and r . The line positions are determined by g , a and r , the relative intensities of the 15 hyperfine lines by P , and the line widths or the peak heights of the hyperfine lines by c , d and f .

The 22-Line Spectrum. $[P_2V_3W_{15}O_{62}]^{9-}$ may be represented by the following abbreviated form.



When one of the vanadium atoms is reduced, a 22-line spectrum is observed.

Since all three vanadium atoms are equivalent, only one parameter is needed to represent the transition probability of the unpaired electron. The derivation of dv/dB is essentially the same as the 15-line case. Here only the result is given.

$$\begin{aligned} dv/dB = & -\{\gamma\beta_1 M_0 \hbar / 3g\beta (Q^2 + R^2)^2\} \\ & \times [(Q'R + QR' - R'S - RS') (Q^2 + R^2) \\ & - 2(QT - RS)(QQ' + RR')] \end{aligned} \quad (16)$$

where

$$Q = XYZ - XW_B W_C - YW_A W_C - ZW_A W_B - 3p^2(X + Y + Z) - 2p\{X(W_B + W_C) + Y(W_A + W_C) + Z(W_A + W_B)\} \quad (17)$$

$$R = XYW_C + XZW_B + YZW_A + 2p(XY + YZ + XZ) - W_A W_B W_C - 3p^2(W_A + W_B + W_C) - 2p(W_A W_B + W_A W_C + W_B W_C) \quad (18)$$

$$S = XY + YZ + XZ - W_A W_B - W_A W_C - W_B W_C - 27p^2 - 6p(W_A + W_B + W_C) \quad (19)$$

$$T = X(W_B + W_C) + Y(W_A + W_C) + Z(W_A + W_B) + 6p(X + Y + Z) \quad (20)$$

$$Q' = dQ/dB = (XY + YZ + XZ) - (W_A W_B + W_A W_C + W_B W_C) - 9p^2 - 4p(W_A + W_B + W_C) \quad (21)$$

$$R' = dR/dB = X(W_B + W_C) + Y(W_A + W_C) + Z(W_A + W_B)$$

$$+4p(X+Y+Z) \quad (22)$$

$$S' = dS/dB = 2(X+Y+Z) \quad (23)$$

$$T' = dT/dB = 2(W_A + W_B + W_C) + 18p \quad (24)$$

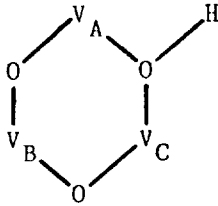
$$X = B - B_A; Y = B - B_B; Z = B - B_C \quad (25)$$

$$W_A = \hbar/g\beta T_{2A}; W_B = \hbar/g\beta T_{2B}; W_C = \hbar/g\beta T_{2C} \quad (26)$$

$$p = P\hbar/g\beta \quad (27)$$

Here the limiting τ value for the extremely fast hopping rate is found to be 1/3.

The 36- and 43-Line Spectra. The heteropolyanions responsible for the 36- or 43-line spectrum may be represented by the following abbreviated form.



Since protonation at a bridging oxygen atom prevents electron transfer effectively,⁹ the above group may also be represented by OH-V_A-O-V_B-O-V_C-OH sequence.

The modified Bloch equations contain two different transition probabilities, P_1 for the transition from V_A (or V_C) to V_B and P_2 for the reverse transition. The derivation of dv/dB is again straightforward and only the result is given below.

$$\begin{aligned} dv/dB = & -\{ \gamma B_1 M_0 \hbar / gB(Q^2 + R^2) \} \\ & \times \{ (Q'R + QR' - R'S - RS') (Q^2 + R^2) \\ & - 2(QT - RS)(QQ' + RR') \} \quad (28) \end{aligned}$$

$$\begin{aligned} Q = & XYZ - X(W_B W_C + p_1 p_2 + p_1 W_B + 2p_2 W_C) \\ & - Y(W_A W_C + p_1^2 + p_1 W_A + p_1 W_C) \\ & - Z(W_A W_B + p_1 p_2 + p_1 W_B + 2p_2 W_A) \quad (29) \end{aligned}$$

$$\begin{aligned} R = & XY(W_C + p_1) + XZ(W_B + 2p_2) + YZ(W_A + p_1) - W_A W_B W_C \\ & - p_1 p_2 (W_A + W_C) - p_1^2 W_B - p_1 (W_A W_B + W_B W_C) - 2p_2 W_A W_C \quad (30) \end{aligned}$$

$$\begin{aligned} S = & f_A \{ XY + YZ - 2p_1^2 - 4p_1 p_2 - W_A W_B - W_B W_C \\ & - p_1 (W_A + 2W_B + W_C) - 2p_2 (W_A + W_C) \} \\ & + f_B \{ XZ - W_A W_C - p_1^2 - 2p_1 p_2 - (p_1 + p_2) (W_A + W_C) \} \quad (31) \end{aligned}$$

$$\begin{aligned} T = & f_A \{ XW_B + Y(W_A + W_C) + ZW_B + p_1 (X + 2Y + Z) \\ & + 2p_2 (X + Z) \} + f_B \{ XW_C + ZW_A + (p_1 + p_2) (X + Z) \} \quad (32) \end{aligned}$$

$$\begin{aligned} Q' = & XY + XZ + YZ - \{ W_A W_B + W_A W_C + W_B W_C + 2p_1 p_2 + p_1^2 \\ & + 2p_2 (W_A + W_C) + p_1 (W_A + 2W_B + W_C) \} \quad (33) \end{aligned}$$

$$\begin{aligned} R' = & (X + Y) (W_C + p_1) + (X + Z) (W_B + 2p_2) \\ & + (Y + Z) (W_A + p_1) \quad (34) \end{aligned}$$

$$S' = f_A (X + 2Y + Z) + f_B (X + Z) \quad (35)$$

$$\begin{aligned} T' = & f_A (W_A + 2W_B + W_C + 4p_1 + 4p_2) \\ & + f_B (W_A + W_C + 2p_1 + 2p_2) \quad (36) \end{aligned}$$

$$f_A = f_C = P_2 / (P_1 + 2P_2); f_B = P_1 / (P_1 + 2P_2) \quad (37)$$

$$W_A = \hbar/g\beta T_{2A}; W_B = \hbar/g\beta T_{2B}; W_C = \hbar/g\beta T_{2C} \quad (38)$$

$$p_1 = P_1 \hbar/g\beta; p_2 = P_2 \hbar/g\beta \quad (39)$$

A 36-line spectrum can be obtained when P_1/P_2 is near 3 or 0.25. But only $P_1/P_2 = 3$ produced a correct intensity pat-

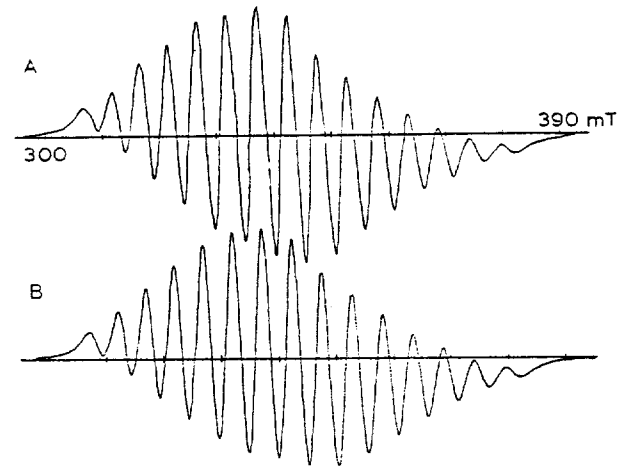


Figure 1. (A) Measured and (B) simulated 15-line EPR spectra of $[PV(IV)VW_{10}O_{40}]^{6-}$ at 336K. $\nu = 0.31489 \text{ cm}^{-1}$.

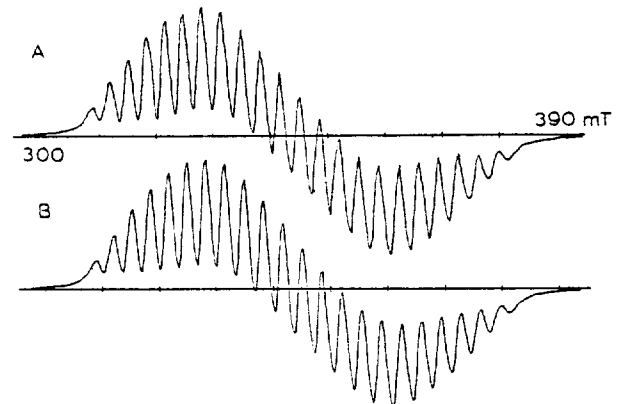


Figure 2. (A) Measured and (B) simulated 22-line EPR spectra of $[P_2V(IV)V_2W_{15}O_{62}]^{10-}$ at 336K. $\nu = 0.31488 \text{ cm}^{-1}$.

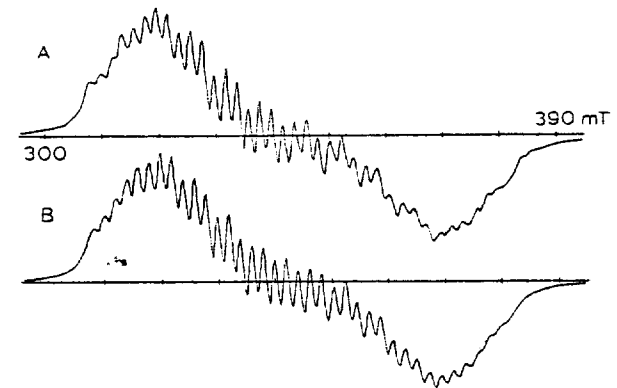


Figure 3. (A) Measured and (B) simulated 36-line EPR spectra of $[HP_2V(IV)V_2W_{15}O_{62}]^{9-}$ at 353K. A small amount of diprotonated species contributes to the spectrum. See the text. $\nu = 0.31472 \text{ cm}^{-1}$.

tern in the calculated spectrum. The limiting τ value for extremely fast electron hopping is found to be 11/25.

A 43-line spectrum can be obtained when P_1/P_2 is near 4. The limiting τ value for extremely fast electron hopping is 1/2.

Results and Discussion

Simulation of the Spectra. The experimental and simulated spectra are shown in Figures 1-4. The parameters

Table 1. Parameters Used for Simulating the EPR Spectra

Type	Compound	Temp. (K)	g	$-a^*$ (cm ⁻¹)	P_1 (or P) (10 ⁹ s ⁻¹)	P_2	r	c (mT)	d (mT)	f (mT)
15-line	[PV(IV)VW ₁₀ O ₄₀] ⁶⁻	336	1.957	0.00944	344	—	0.5	2.046	-0.129	0.074
22-line	[P ₂ V(IV)V ₂ W ₁₅ O ₆₂] ¹⁰⁻	336	1.953	0.0092	22.3	—	0.5	2.026	-0.043	-0.023
36-line	[HP ₂ V(IV)V ₂ W ₁₅ O ₆₂] ⁹⁻	353	1.956	0.00932	72.3	24.1	0.5	1.67	-0.086	0.027
43-line	[HSiV(IV)V ₂ W ₉ O ₄₀] ⁷⁻	357	1.958	0.00944	96.4	24.1	0.5	0.83	-0.057	0.096

* The negative value of a has been assumed. See ref. 7.

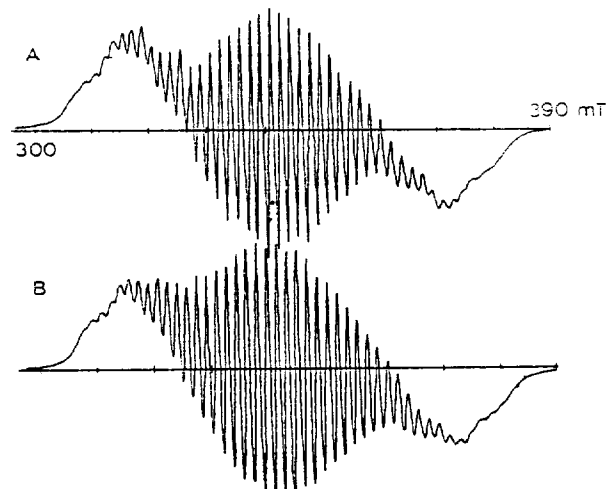


Figure 4. (A) Measured and (B) simulated 43-line EPR spectra of [HSiV(IV)V₂W₉O₄₀]⁷⁻ at 357K. $\nu = 0.31488$ cm⁻¹.

used in the simulation are listed in Table 1. The g and a values are similar to those of [PV(IV)W₁₁O₄₀]⁵⁻ ($g = 1.952$, $a = 0.00907$ cm⁻¹) or [SiV(IV)W₁₁O₄₀]⁷⁻ ($g = 1.957$, $a = 0.00877$ cm⁻¹) which has only one vanadium atom.¹⁰

For the 15-line spectrum of α -1,2-[PV(IV)VW₁₀O₄₀]⁶⁻ (PV(IV)V), the best overall fit could be obtained for a very large value of P . In fact, $P = 344 \times 10^9$ s⁻¹ = 12.6 T is so large that the spectrum changes only slightly when the P value is increased beyond this value. The heights of some middle lines could not be simulated correctly.

The 22-line spectrum of [P₂V(IV)V₂W₁₅O₆₂]¹⁰⁻ (P₂V(IV)V₂) could be simulated quite nicely; see Figure 2. Here the resulting $P = 22.3 \times 10^9$ s⁻¹ = 0.816 T is much smaller than that of the 15-line spectrum, but still about ten times the spacing between the two outermost lines.

We could simulate the general feature of the 36-line spectrum of [HP₂V(IV)V₂W₁₅O₆₂]⁹⁻ (HP₂V(IV)V₂) using $P_1 = 3P_2 = 72.3 \times 10^9$ s⁻¹. However, the line heights in the simulated spectrum changed monotonically without the irregularity observed in the measured spectrum. The irregular feature could be obtained when the calculated 15-line spectrum in Figure 1 was superimposed on the 36-line spectrum. This indicates that a species showing a 15-line spectrum coexists with the species responsible for the 36-line spectrum. We believe this is the diprotonated species, [H₂P₂V(IV)V₂W₁₅O₆₂]⁸⁻, which should show a 15-line spectrum just as [H₂PV(IV)V₂W₉O₄₀]⁵⁻ does.⁹ The amount of this diprotonated species was found to be only 2% by the simulation.

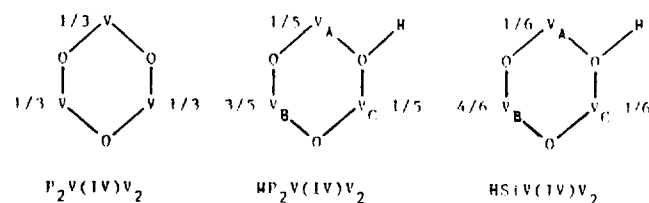
The simulation of the 43-line spectrum of [HSiV(IV)V₂W₉O₄₀]⁷⁻ (HSiV(IV)V₂) is not very satisfactory. Although we could simulate the line positions and general shape of the spectrum using $P_1 = 4P_2 = 96.4 \times 10^9$ s⁻¹, the relative heights

of some lines did not match those in the measured spectrum.

We have found a reduction factor $r = 0.5$ gives good line positions for all four cases. This value is the limiting value for 15- and 43-line spectra, for which the transition probabilities are large. For the 22-line spectrum $r = 0.5$ generates better line positions than the limiting value, 0.33. The relatively small value of P for this system justifies an intermediate reduction factor. For the 36-line spectrum $r = 0.5$ generates better line positions than the limiting value, 0.44. This may again be attributed to the relatively small values of P for this system.

Transition Probabilities. Since the transition probabilities are large compared with the spacing between the two outermost lines, the spectral change is not very sensitive to the P values. Thus it was not possible to determine the P values accurately, the estimated error being $\pm 10\%$. In addition, the spectra are not well-resolved at room temperature.¹¹ These two factors, namely inaccurate P values and the narrow temperature range to observe well-resolved spectra prevented us from studying the temperature dependence of the transition probability.

The 15- or 22-line spectrum could be simulated with one P value. This indicates that the unpaired electron spends equal time on each vanadium atom in PV(IV)V or P₂V(IV)V₂. Two different parameters P_1 and P_2 were needed to simulate the 36- or 43-line spectrum. The fraction of time the unpaired electron spends on each vanadium atom in HP₂V(IV)V₂ or HSiV(IV)V₂ can be calculated by Eq. (37). The results are summarized below:



It is noted that the electron spends more time on V_B than V_A (or V_C) for both HP₂V(IV)V₂ and HSiV(IV)V₂. If the unpaired electron is described as hopping among three potential wells located at the three vanadium atoms, $f_B > f_A$ means that the potential well at V_B is the deepest. Thus, the electron is expected to get trapped on V_B at a low temperature. But the low-temperature spectrum of HP₂V(IV)V₂ consists of eight broad lines, some of which show eight superhyperfine lines.⁵ This is possible only when the electron is trapped on V_A or V_C. The reason for this discrepancy is not understood now.

It is noted that the P_2 values of 36- and 43-line spectra are similar to the P value of the 22-line spectrum. This indicates that the depth of the potential well at V_B is similar at three

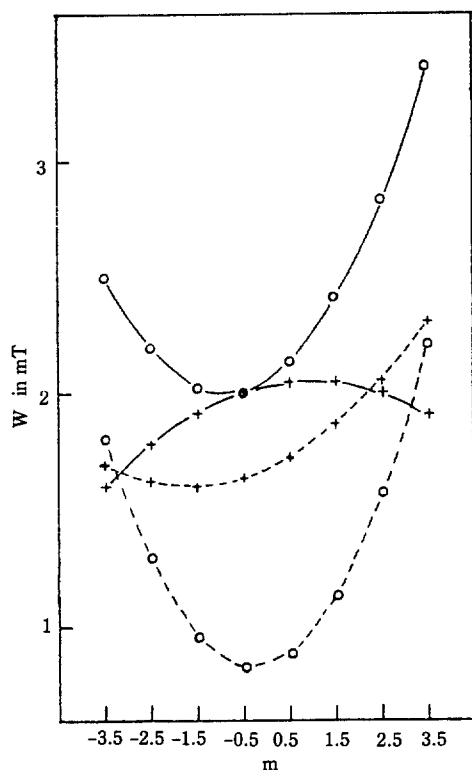


Figure 5. The line width parameters against m . —○— 15-line, —×— 22-line, -○-○- 36-line, -×-×- 43-line spectrum.

systems. When one oxygen atom is protonated, the potential wells at V_A and V_C become shallower, as are shown by $P_1 > P_2$ or $f_B > f_A$ for $HP_2V(IV)V_2$ and $HSiV(IV)V_2$.

Line Width Parameters. The line width parameters resulting from the simulations are plotted against m in Figure 5. Since these parameters represent the widths of the hyperfine lines when the electron is trapped on one vanadium atom, they should be similar to the EPR line widths of a Keggin- or Dawson-structure heteropolyanions containing one vanadium(IV) atom. The parabolas representing the line width variations of the Keggin-structure anions, $PV(IV)V$ and $HSiV(IV)V_2$, are similar to those¹² of $[PV(IV)W_{11}O_{40}]^{5-}$, but the absolute values are in poor agreement. The agreement is even worse, when the line width parameters of Dawson-structure anions, $P_2V(IV)V_2$ and $HP_2V(IV)V_2$, are compared with the line widths¹² of $[P_2V(IV)W_{17}O_{62}]^{8-}$. The dependence of the line width on m for $P_2V(IV)V_2$ is an inverted parabola with broader middle lines. This kind of behavior has not been observed for $[P_2V(IV)W_{17}O_{62}]^{8-}$. It seems that another factor, which was not taken into account explicitly in

our spectral simulation, contributes to the line shape.

Concluding Remarks

We have shown that the solution EPR spectra of various mixed-valence heteropolyanions containing vanadium(IV) and vanadium(V) can be simulated, using a hopping electron model. Although some details are not simulated exactly, the general contours of the spectra are correctly generated. This can not be achieved with a delocalized electron model. Since the transition probabilities are quite large at 63-84°C, and the spectra are not so well resolved at room temperature, it was not possible to study the temperature dependence of the transition probabilities. The temperature dependence could be seen clearly at the polycrystalline spectra¹³ of $H_2PV(IV)V_2$ at 300-100K. Simulation of these polycrystalline spectra would allow us to determine the activation energy for the intramolecular electron transfer. This remains as the most challenging problem.

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