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Line-Shape Analysis in EPR Spectra of Nb(IV) Complexes in Solutions and Glasses

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The EPR spectra of a Nb (IV) complex in alcoholic liquid and solid solution are investigated between 293° and 77°K. The spectra exhibit hyperfine structure originating from interaction of one single $4d$ electron with the central Nb$(I=\frac{9}{2})$ nucleus. At 77°K the spectra show a complicated appearance. In order to analyze the observed spectra a formula for the line shape is derived by assuming a Lorentzian shape function, axial symmetry of both the g and a tensor, and completely randomized orientation of the complexes. With the correct transition probabilities and a certain approximation for the resonance field a closed expression for the line shape of a single hyperfine structure line is given, which readily lends itself to numerical calculation. By use of a computer program the components of the g and a tensor are determined for three different alcohols, methanol, ethanol, and isopropanol, as solvents (see Table IV). It is shown that satisfactory agreement between observed and calculated spectra can only be obtained if anisotropy of the Lorentzian line-shape parameter is assumed besides the well-known dependence of this parameter on the magnetic quantum number m.

A. INTRODUCTION

THE analysis of the line shape of EPR spectra is required for the evaluation of the components of the g and a tensors. The line-shape-analysis problem is particularly complicated in cases, where only powders or solutions of noncubic complexes are available for experimental investigation. There are many papers in literature dealing with the problem of line-shape calculations; a list of references is given below in Table I.

In the course of an investigation of EPR spectra of Nb (IV) complexes in liquid and solid solutions it became apparent that the experimentally observed line shapes were strongly influenced by a dependence of the relaxation constants on the orientation of the complex relative to the fields, besides the well-known dependence of the half-width of hyperfine lines on the quantum number m. None of the line-shape calculations published so far seemed to be readily adaptable to this case.

In this paper we derive a closed formula for the calculation of the line shape of a single hyperfine line, assuming a Lorentzian shape function for each $(\frac{1}{2}, m)\rightarrow(-\frac{1}{2}, m)$ transition and perfectly randomized orientation. This formula can easily be applied with a medium size computer. It is then used for the evaluation of the magnetic parameters of Nb (IV) complexes.

B. LINE-SHAPE CALCULATION

1. Brief Review of Previous Work

Table I presents a list of references in line-shape calculations for EPR spectra of isotropic powders and solutions. Most of the earlier and some of the more recent work made use of the δ-type shape function, considering isotropic or anisotropic g- and a tensors. Actual line shapes in isotropic systems with complete Brownian randomization show considerable linewidth, especially in the case of Nb (IV) complexes, so that the δ-shape function model seems questionable. There is little physical argument for preference of either a Gaussian or a Lorentzian shape function. However, the analytical treatment of the Lorentzian being considerably simpler, our investigation is restricted to the latter case. Furthermore, we seek approximations which allow a relatively simple analytical representation of the shape of a hyperfine line in closed form. Formulas of this type have been given by Searl *et al.*[1,2] and Ibers and Swalen.[3] The treatment by the former worker omits hyperfine interaction but includes correct transition probabilities for axial g tensors. Ibers and Swalen treated the problem under similar conditions, arriving at a closed expression for the line shape containing 15 (interrelated) parameters.

2. Present Work

In the present work we give a line-shape calculation assuming the following conditions:

(a) axial g tensor and axial hyperfine interaction tensor, both tensors admitting common principal axes;

(b) for the transition probability the correct expression for the Zeeman term alone is used;

(c) the Lorentzian shape function is used in the form

$$g(h-h_0)=\pi^{-1}h_{\frac{1}{2}}[h_{\frac{1}{2}}^2+(h-h_0)^2]^{-1};$$

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* Part of the work contained in this paper is described in more detail in M. Lardon, Dissertation No. 3530, Swiss Federal Institute of Technology, Zurich, Switzerland.

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[1] J. W. Searl, R. C. Smith, and S. J. Wyard, Proc. Phys. Soc. (London) **74**, 491 (1959).

[2] J. W. Searl, R. C. Smith, and S. J. Wyard **78**, 1174 (1961).

[3] J. A. Ibers and J. D. Swalen, Phys. Rev. **127**, 1914 (1962).

TABLE I. Literature on line-shape calculations of polycrystalline substances.

Line shape[a]	g[b]	a[c]	Reference	Comment
δ	axial	$\cdots$	d,e	
δ	axial	axial	f	
δ	isotropic	$\cdots$	g	$S=\frac{3}{2}$
δ	axial	axial	h	
δ	axial	axial	i	
$\delta+G$	$\cdots$	$\cdots$	j	NMR
$\delta+G$	anisotropic	anisotropic	k	
$\delta+G$	isotropic	anisotropic	l	
$\delta+G$	anisotropic	$\cdots$	m	
$\delta+G$	isotropic	anisotropic	n	
$\delta+G$	isotropic	anisotropic	o	
$\delta+G$, P	axial	$\cdots$	p	$S>\frac{1}{2}$
$\delta+G$	axial	axial	q	
$\delta+L$	isotropic	isotropic	r	
G	isotropic	axial	s	
L	axial	$\cdots$	1	closed-form expression
G	isotropic	anisotropic	t	
L	anisotropic	$\cdots$	u	
G	isotropic	anisotropic	v	
G	anisotropic	anisotropic	w	
L, G, P	axial	$\cdots$	2	
L, P	axial	$\cdots$	3	closed-form expression
L, G, P	axial	axial	x	
G, P	isotropic	$\cdots$	y	$S=1$, $S_3=2$
G, L	anisotropic	anisotropic	z	
L, P	axial	axial	Present work	closed-form expression

[a] *Line-shape function* δ delta-function, G Gaussian, L Lorentzian, $\delta+G$ delta function with Gaussian broadening, P orientation-dependent transition probability (intensity included).

[b] Symmetry of the g tensor.

[c] Symmetry of the a tensor.

[d] B. Bleaney, Proc. Phys. Soc. (London) **A63**, 407 (1950).

[e] B. Bleaney, Proc. Phys. Soc. (London) **75**, 621 (1960).

[f] R. H. Sands, Phys. Rev. **99**, 1222 (1955).

[g] L. S. Singer, J. Chem. Phys. **23**, 379 (1955).

[h] R. Neimann and D. Kivelson, J. Chem. Phys. **35**, 156 (1961).

[i] H. R. Gersmann and J. D. Swalen, J. Chem. Phys. **36**, 3221 (1962).

[j] G. E. Pake, J. Chem. Phys. **16**, 327 (1948).

[k] D. E. O'Reilly, J. Chem. Phys. **29**, 1188 (1958).

[l] S. M. Blinder, J. Chem. Phys. **33**, 748 (1960).

[m] F. K. Kneubühl, J. Chem. Phys. **33**, 1074 (1960).

[n] H. Sternlicht, J. Chem. Phys. **33**, 1128 (1960).

[o] N. W. Lord and S. M. Blinder, J. Chem. Phys. **34**, 1693 (1961).

[p] F. K. Kneubühl and B. Natterer, Helv. Phys. Acta **34**, 710 (1961).

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[u] A. K. Chirkov and A. A. Kokin, Soviet Phys.—JETP **12**, 964 (1961) [Zh. Eksperim i Teor. Fiz. **39**, 1381 (1960)].

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[y] P. Kottis and R. Lefebvre, J. Chem. Phys. **39**, 393 (1963).

[z] J. A. Weil and H. G. Hecht, J. Chem. Phys. **38**, 281 (1963).

h, h_0, and $h_{\frac{1}{2}}$ are the variable field strength, the resonance-field, and the half-width of line in suitable units, respectively;

(d) line-shape calculation is made for the case constant frequency–variable field, using the expression of second-order perturbation theory for the resonance field strength.

3. Derivation of Line-Shape Integral

Bleaney[4] has shown that the spin Hamiltonian

$$\mathcal{H}=\beta_e[g_3H_3S_3+g_1(H_1S_1+H_2S_2)] +A_3S_3I_3+A_1[S_1I_1+S_2I_2] \quad (1)$$

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[4] B. Bleaney, Phil. Mag. **42**, 441 (1951).

in the crystal system leads to the following expression for the resonance field of the $(\frac{1}{2}, m)\rightarrow(-\frac{1}{2}, m)$ transition:

$$h_0=g^{-1}-cg^{-2}m-\tfrac{1}{4}a_1^2g^{-1}[1+(a_3gc^{-1})^2][I(I+1)-m^2]$$
$$-\tfrac{1}{2}(a_3^2-a_1^2)^2(g_1^2g_3^2c^{-2}g^{-3})z^2(1-z^2)m^2. \quad (2)$$

In (2) h_0 represents the dimensionless resonance field

$$h_0=h_0(z)=\beta_eH_0(\hbar\omega)^{-1},$$

and

$$g^2=g_1^2+(g_3^2-g_1^2)z^2, \quad (2')$$

$$c^2=a_1^2g_1^2+[a_3^2g_3^2-a_1^2g_1^2]z^2,$$

$$a_i=A_i(\hbar\omega)^{-1}. \quad (2'')$$

$\beta=\cos^{-1}z$ is taken as the second Eulerian angle.[5]

Introducing the dimensionless relative field strength $\alpha=h/h_{\frac{1}{2}}=H/H_{\frac{1}{2}}$ and using the fact that the transition probability is proportional to (with γ taken as the third Eulerian angle)[6]

$$P=(g_1/g)^2[g_3^2+(g_1^2-g_3^2)\sin^2\beta\sin^2\gamma], \quad (3)$$

one obtains, for the power absorbed by one-spin system in the (β, γ) orientation at the field strength α the equation

$$A(\alpha)=Pg(\alpha-\alpha_0). \quad (4)$$

When (4) is integrated over all orientations of the crystal system, assuming isotropic distribution, one obtains the integral

$$\langle A(\alpha, m)\rangle_{\text{Av}}=\left(\frac{g_1^2}{h_{\frac{1}{2}}}\right)\int_0^1\left[1+\left(\frac{g_3}{g}\right)^2\right][1+(\alpha-\alpha_0)^2]^{-1}dz, \quad (5)$$

which is proportional to the total power absorbed at the variable field strength α. To evaluate the integral (5), Formula (2) has to be inserted in the integrand. Although the resulting integral can be expressed in elliptic integrals, the evaluation is too tedious for practical purposes. Instead we proceed by the following approximation. Remarking that the second factor $[1+(\alpha-\alpha_0)^2]^{-1}$ of the integrand depends solely on z^2, one is tempted to approximate α_0 by a polynomial of the type $c_0'+c_2'z^2$. The constants c_0' and c_2' can be chosen such that

$$h_{\frac{1}{2}}c_0'=h_0(z=0); \qquad c_2'h_{\frac{1}{2}}=h_0(z=1)-h_0(z=0).$$

This choice means that the approximation polynomial coincides with the correct value of the resonance field h_0 at the extremes $\beta=\pi/2$ and $\beta=0$ of the domain of the angle β. It is suggested by the fact that these two extreme orientations of the spin system are contributing mainly to the low-field and high-field parts of the line shape. Numerical calculation shows that the approximation produces deviation of less than 1% from the correct value of h_0. However, the error of the line-shape integral resulting from the polynomial approximation may be larger for certain h values, but the discussion of the deviations is quite complicated.

When the foregoing approximation is used, the integral (5) may be evaluated in a relatively simple closed form. It is convenient to introduce two complex parameters v and w:

$$v=[(\alpha-c_0'+i)/c_2']^{\frac{1}{2}}, \quad 0<|\arg v|<\tfrac{1}{2}\pi,$$
$$0<|\arg(v+1)/(v-1)|<\pi, \quad (6')$$

$$w=g_1(g_1^2-g_3^2)^{-\frac{1}{2}}. \quad (6'')$$

Using Eqs. (6) one obtains three cases:

(a) $g_1>g_3$, w real

$$\langle A(\alpha, m)\rangle_{\text{Av}}\propto-\frac{g_1^2}{h_{\frac{1}{2}}}\left(\operatorname{Im}\left\{\frac{1}{2vc_2'}\left[1+\left(\frac{g_3^2}{g_3^2-g_1^2}\right)\left(\frac{1}{v^2-w^2}\right)\right]\right.\right.$$
$$\left.\times\log\frac{v+1}{v-1}\right\}+\frac{g_3^2}{g_3^2-g_1^2}\,\frac{1}{(c_2')^2}$$
$$\left.\times\frac{\log[(w+1)/(w-1)]}{2w[w^4-2w^2\operatorname{Re}(v^2)+|v|^4]}\right). \quad (7')$$

(b) $g_1<g_3$, w pure imaginary

$$\langle A(\alpha, m)\rangle_{\text{Av}}\propto-\frac{g_1^2}{h_{\frac{1}{2}}}\left(\operatorname{Im}\left\{\frac{1}{2vc_2'}\left[1+\left(\frac{g_3^2}{g_3^2-g_1^2}\right)\left(\frac{1}{v^2-w^2}\right)\right]\right.\right.$$
$$\left.\times\log\frac{v+1}{v-1}\right\}-\operatorname{Re}\left[\frac{g_3^2}{g_3^2-g_1^2}\,\frac{1}{(c_2')^2}\right.$$
$$\left.\left.\times\frac{\log[(w-1)/w]}{w[w^4-2w^2\operatorname{Re}(v^2)+|v|^4]}\right]\right). \quad (7'')$$

(c) $g_1=g_3$, this case represents an isotropic g tensor and results in a particularly simple formula

$$\langle A(\alpha, m)\rangle_{\text{Av}}\propto-\frac{g^2}{h_{\frac{1}{2}}}\left\{\operatorname{Im}\left[\frac{1}{vc_2'}\log\frac{v+1}{v-1}\right]\right\}. \quad (7''')$$

Formulas (7′), (7″), and (7‴) can easily be programmed in FORTRAN language and actually a program has been written for numerical calculation on an IBM 1620 computer. By numerical differentiation the first derivative of the line shape is obtained and provision is made for composition of the whole spectrum from any number of hyperfine lines.

The accuracy for Approximation (7′), (7″) was tested for small anisotropy of Tensor g by comparison with exact numerical integration. Both for Lorentzian line shape and δ-shape function about 100 line contours

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[5] For definition of Eulerian angles see E. P. Wigner, *Group Theory and Atomic Spectra* (Academic Press Inc., New York, 1959).

[6] Formula (3) is obtained by applying the Bleaney transformation to the interaction operator of the spin system with the microwave magnetic field perpendicular to the Zeeman field.

with anisotropy $3(g_3-g_1)/(2g_1+g_3)<0{,}2$ were calculated by both procedures. The relative maximum deviation of Approximation (7′), (7″) from numerical integration was observed to never exceed 3%. With δ-shape function errors of up to 30% were found in many cases as well as noticeable errors in the magnetic constants.

C. EPR SPECTRA OF Nb IV COMPLEXES

1. Review of Previous Work on Optical and EPR Spectra of Nb (IV) Compounds

Only very little work seems to have been done on EPR spectra of Nb (IV) complexes. Garif'yanov *et al.*[7] obtained EPR spectra from ethanolic solutions of niobium pentachloride reduced by zinc and hydrochloric acid. At room temperature they observed a four-line spectrum, whereas at 77°K a 20-line spectrum was found. No attempt was made apparently by these workers to analyze the spectra.

Nb (IV) complexes represent $4d^1$ systems with either strong or medium crystal field, analogous to Ti^{3+} or V^{4+} complexes. In aqueous or alcoholic solutions with high concentration of hydrochloric acid Nb^{4+} complexes are slightly red colored which is attributed by Cozzi and Vivarelli[8] to originate from sixfold coordination with the chloride ion. At lower hydrochloric acid concentration fivefold coordination is assumed by these workers, resulting from the formation of the complex ion $NbOCl_4^{2-}$, deeply blue colored.

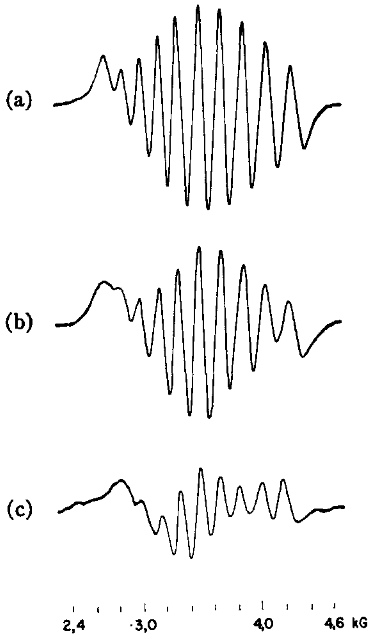

FIG. 1. Room-temperature spectra of Nb^{4+} complexes in solution. (a) methanol (b) ethanol (c) i-propanol.

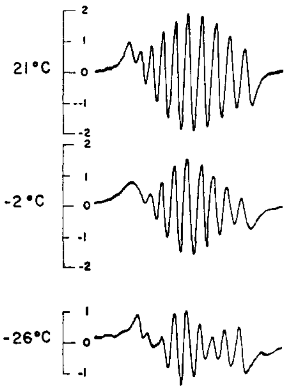

FIG. 2. Temperature dependence of Nb^{4+} complex in methanolic solution.

2. Present Work

In this paper work is reported on the EPR spectra of Nb^{4+} complexes, obtained by electrolytical reduction of niobium pentachloride in alcoholic solutions saturated with hydrochloric acid. The spectra were studied under conditions where $NbCl_6^{2-}$ ions should exist predominantly. From the spectra information should be derived about the symmetry of the crystal field, aiming at a decision between a cubic or axial symmetry field.

3. Experimental

Methanol, ethanol, and isopropanol containing approximately 25% water were chosen as solvents. Approximately $0.3M$ solutions of $NbCl_5$ in these solvents were saturated at 0°C with dried HCl gas and reduced electrolytically at a mercury cathode directly to Nb^{4+},[9] carefully excluding oxygen. EPR spectra were measured with a Hilger Microspin-X-band spectrometer equipped with 100-kc/sec modulation at room temperature and at 77°K. Furthermore, the temperature dependence of the line shape was studied on a Varian V4500 spectrometer, from room temperature to 170°K. The variable field was measured by a proton resonance magnetometer.

4. Results

The observed EPR spectra are shown in Figs. 1, 2, and 3. At room temperature a striking influence of the solvent alcohol on the shape of the spectra is found (Fig. 1). The temperature dependence of the spectrum in methanolic solution (Fig. 2) suggests that the solvent effect originates almost completely from the viscosity of the solvent alcohol. This is demonstrated clearly

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[7] V. N. Fedotov, N. F. Garif'yanov, and B. M. Kozyrev, Dokl. Akad. Nauk SSSR **145**, 1318 (1962).

[8] D. Cozzi and S. Vivarelli, Z. Anorg. Allg. Chem. **279**, 165 (1955).

[9] Detailed description of the reduction procedure will be published in Helv. Chim. Acta.

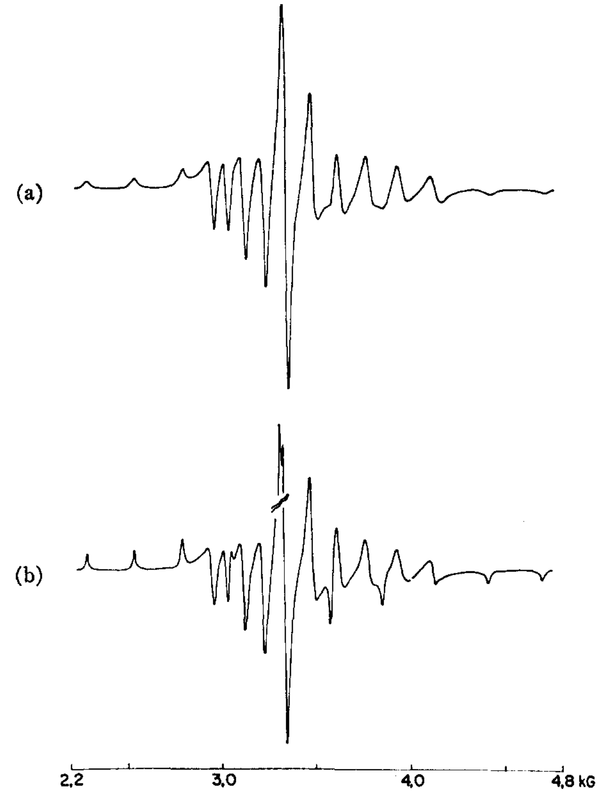

FIG. 3. Spectra of Nb^{4+} complexes in frozen solution. (a) ethanol (b) i-propanol.

by the following compilation of viscosity data of the three alcohols

Temp.	MeOH	EtOH	*i*-PrOH
20°C	1.9	3.0	3.7 cP
− 6°C	3.0		
−16°C	3.7		

It is concluded that the solvent alcohols do not produce a remarkable individual influence on the EPR signal under comparable conditions.

TABLE II. Dependence of Lorentzian half-width parameter of hyperfine lines at 273°K for Nb^{4+} complex in methanolic solution.

m	$H_{\frac{1}{2}}(m)$ (estimated)	$H_{\frac{1}{2}}(m)$ (accurate)
4.5	76.2 G	128.6 G
3.5	72.1	106.4
2.5	68.0	89.6
1.5	64.7	78.2
0.5	62.0	70.7
−0.5	60.7	69.4
−1.5	62.7	72.8
−2.5	68.0	80.8
−3.5	80.2	93.0
−4.5	98.3	106.4

In the spectra of methanolic solutions at room temperature only hyperfine interaction between the electron and the central Nb nucleus ($I=\frac{9}{2}$) is observed. In no case hyperfine interaction with the ligand nuclei was detected. As is seen from the isotropic spectra, the half-width of the hyperfine structure lines is approximately 70 G. It is strongly dependent on m, as is shown by Table II under the column "estimated values" taken directly from the solution spectrum at 273°K. This dependence may be represented analytically by a quadratic polynomial in m, giving the half-width parameter based on line-shape analysis

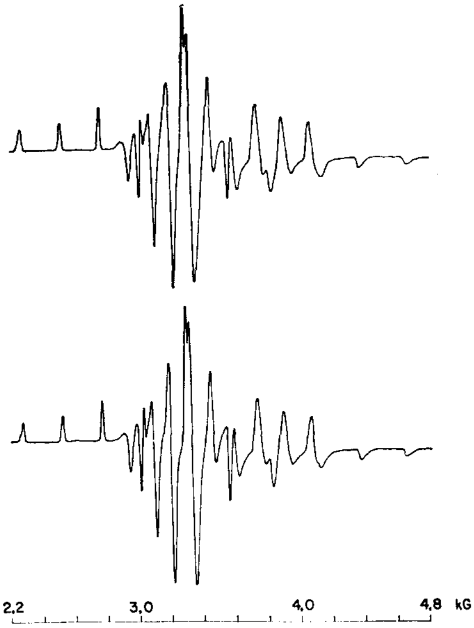

FIG. 4. Calculated spectra of Nb^{4+} complexes in solid solution. (a) optimum synthetic line shape of ethanol glass spectrum calculated with line-shape parameters from Table IV. (b) optimum synthetic line shape of *i*-propanol glass spectrum calculated with anisotropic line-shape parameters given in Table IV.

$$H_{\frac{1}{2}}=69.5+1.72m+2.54m^2 \text{ (gauss)}.$$

Furthermore, from the 293°K spectra in methanol values for g and A constants are derived as follows

$$g=1.892\pm0.001,$$

$$A=3.109\pm0.002\times10^{-18} \text{ erg}$$

(corresponding to 177.4 G).

D. ANALYSIS OF LINE SHAPES OBSERVED AT 77°K

Our measurements showed that the EPR spectra are essentially independent of temperature between 170° and 77°K, but they are considerably more complex

TABLE III. g and A tensors of Nb^{4+} complexes in different alcoholic glasses (77°K).

	MeOH	EtOH	*i*-PrOH
g_1	1.892±0.001	1.891±0.001	1.891±0.001
g_3	1.925	1.922	1.925
$\frac{1}{3}(2g_1+g_3)=\langle g\rangle_{Av}$	1.903	1.901	1.902
10^2a_1	3.674±0.006	3.654±0.006	3.648±0.006
a_3	7.711±0.012	7.698±0.012	7.678±0.012
$\frac{1}{3}(2a_1+a_3)=\langle a\rangle_{Av}$	5.020±0.008	5.005±0.008	4.991±0.008
$A_1\times10^{18}$erg	2.296±0.004	2.283±0.004	2.279±0.004
$A_3\times10^{18}$ erg	4.818±0.008	4.810±0.008	4.795±0.008
$\langle A\rangle_{Av}=\frac{1}{3}(2A_1+A_3)\times10^{18}$erg	3.317±0.005	3.127±0.005	3.118±0.005

than at room temperature. To analyze these spectra the formulas (7′), (7″), (7‴) were calculated numerically for different sets of parameters g_1, g_3, a_1, a_3, and $H_{\frac{1}{2}}$ as a function of m including differentiation of the absorption curve. By comparison with the observed spectra the parameters were adjusted until the extrema in the low- and high-field parts, and the zeros in the central part of the spectra coincided optimally with the derivative curve.

It was found from this calculation, that the observed shape of each hyperfine structure line can only be reproduced if a pronounced dependence of the Lorentzian half-width parameter on the orientation of the complex, in particular on the angle β, is taken into account. Figure 4 demonstrates this behavior. Figure 4(a) was calculated using an individual but constant half-width parameter for each hyperfine line whereas in Fig. 4(b) for each hyperfine line two different half-width parameters were used, one for that part of the line resulting from $\beta=0$ and a different one for the part around $\beta=\pi/2$. By comparison of Fig. 3(b) and 4(b) a considerable improvement of agreement between observed and calculated spectra is obvious. This result is not a consequence of the approximate line-shape calculation method. Using correct numerical integration for (5) the same result is obtained.

TABLE IV. Lorentzian half-width parameter of low-temperature spectra of Nb^{4+} complexes in alcoholic glasses (77°K).

m	MeOH	EtOH	*i*-PrOH $\beta=\pi/2$	*i*-PrOH $\beta=0$
4.5	31.9 G	21.0 G	20.9 G	7.4 G
3.5	30.6	20.7	20.1	8.1
2.5	29.9	21.0	20.1	8.7
1.5	29.4	22.0	20.9	9.4
0.5	29.9	23.4	22.1	10.1
−0.5	30.7	25.2	24.0	10.7
−1.5	31.4	29.0	26.9	11.4
−2.5	33.2	32.7	30.6	12.1
−3.5	35.2	37.3	35.2	12.8
−4.5	37.8	42.9	41.3	13.4

In Table III sets of the magnetic constants of the Nb^{4+} complex are given for 77°K. It is seen that the g tensor is the same within the limits of error for the three alcohols considered, whereas a slight but definite dependence of the coupling tensor on the solvent alcohol is observed.

Since no definite knowledge exists about the chemical formula of the Nb complexes investigated in this work, it cannot be decided at present whether the axial symmetry results from Jahn–Teller effect or from either non chemically equivalent ligands or fivefold coordination.

From the analysis of the spectra at low temperature also follows Table IV, giving the Lorentzian half-width parameter of the individual hyperfine lines at 77°K. In the case of isopropanol values of $H_{\frac{1}{2}}$ are given for both $\beta=\pi/2$ and $\beta=0$, showing that the assumption of strong anisotropy of the half-width parameter within a hyperfine line considerably improves the approximation of experimental line shapes.

No attempt could be made to analyze the linewidth dependence on m according to the method given by Kivelson,[10] since no data on the viscosity of the alcohol–hydrochloric mixtures used as solvents in this work seem to be available.

ACKNOWLEDGMENTS

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[10] R. N. Rogers and G. E. Pake, J. Chem. Phys. **33**, 1107 (1960).