

High-Field, Multifrequency EPR Study of the Vanadium(III) Hexaaqua Cation

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The vanadium(III) cation possesses the [Ar]3d² electronic configuration and forms stable six-coordinate complexes which constitute model systems for the study of the combined effects of a ligand field and interelectronic repulsion. The coordination geometry of vanadium(III) complexes is often axial leading to a splitting of the ³T_{1g} (F) (*O_h*) ground term into ³A_g (*S₆*) and ³E_g (*S₆*) components. The ³A_g (*S₆*) ground term is split to second-order by spin-orbit coupling, and the precise determination of the zero-field splitting (zfs) provides a stringent test of any theoretical model developed to describe the system. Most determinations of this parameter have been made indirectly by modeling the variation of the magnetic susceptibility with temperature,¹ while conventional X-band EPR has been confined to the detection of the Δ*M_s* = ±2 transition.² However, high-field, high-frequency EPR measurements³ and far-infrared Zeeman spectroscopy⁴ can be employed to provide a very precise direct measure of the zfs and ground state *g* values, as demonstrated by very elegant work conducted on vanadium(III)-doped Al₂O₃.^{3,4} In this paper, high-field, multifrequency EPR data for the [V(OH₂)₆]³⁺ cation are presented. The use of more than one frequency allows the detection of a large number of EPR resonances, which affords the determination of the spin-Hamiltonian parameters of the ³A_g ground term to unprecedented precision. This permits the characterization of a pronounced isotope effect, the nature of which cannot be adequately explained using a conventional ligand field model.

High-field, high-frequency EPR experiments were performed on samples of vanadium(III) doped into CsGa(SO₄)₂·12X₂O (Cs-[Ga:V]X) where X = D or H. These alum systems are cubic (Pa3) with the trivalent cation lying on sites of trigonal (*S₆*) symmetry.⁵ The vanadium alums were selected for study as they have been characterized extensively using a wide range of physical techniques; these include magnetic susceptibility measurements⁶ and electronic Raman spectroscopy,^{7–9} which provides a direct measure of the trigonal field splitting, Δ (Δ ≡ E(³E_g) – E(³A_g)) = ca. 1940 cm⁻¹).

Samples of Cs[Ga:V]SX were prepared by cocrystallization of the gallium and vanadium salts (CsGaSX, CsVSX) in solutions of X₂SO₄ (1 M) in which vanadium(III) constituted ca. 1% of the total trivalent cation concentration. EPR spectra were obtained

at the high-field, high-frequency EPR facility in Grenoble, France. Excitation frequencies of ca. 95, 190, and 285 GHz were employed in conjunction with a static field ranging from 0 to 12 T. Spectra were recorded between 5 and 20 K on single-crystal and powdered samples. The experimental setup has been described previously.¹⁰

Representative features from the EPR spectra are presented in Figure 1. The EPR spectra were interpreted using the spin Hamiltonian for an axial (*S*, *I*) = (1, 7/2) spin system,¹¹

$$\hat{H}_s = g_{\parallel}\mu_B B_Z \hat{S}_Z + g_{\perp}\mu_B (B_X \hat{S}_X + B_Y \hat{S}_Y) + A_{\parallel} \hat{S}_Z \hat{I}_Z + A_{\perp} (\hat{S}_X \hat{I}_X + \hat{S}_Y \hat{I}_Y) + D \left\{ \hat{S}_Z^2 - \frac{1}{3} S(S+1) \right\} \quad (1)$$

which is valid for the ³A_g (*S₆*) component of ³T_{1g} (*O_h*) being much lower in energy compared to ³E_g (*S₆*). The parameters *g_∥*, *g_⊥*, *A_∥*, *A_⊥*, and *D* were extracted from the experimental spectra by solving the spin Hamiltonian (eq 1) numerically and minimizing the function

$$\chi^2 = \sum_{i=1}^N \left[\frac{B_{\text{obs},i} - B_{\text{calc},i}}{\sigma_i} \right]^2 \quad (2)$$

where *N* is the number of observations, *B_{obs,i}* and *B_{calc,i}* the *i*th observed and calculated resonance magnetic fields, respectively, and *σ_i* the measurement error associated with the *i*th resonance magnetic field. There are two main sources which contribute to *σ_i*: an error *w_i* related to the bandwidth of the *i*th resonance and an error *e_i* related to uncertainties in the field calibration:

$$\sigma_i^2 = w_i^2 + e_i^2 \quad (3)$$

w_i for derivative-like and absorption-like resonances was set to half the peak-to-peak width and half the width at half-height, respectively. *e_i* was estimated by measuring the resonance field position of DPPH at the three frequencies 95, 190, and 285 GHz and comparing the data to field values calculated using the literature value of *g* = 2.0036. For the deuterated sample, 32 powder and 24 single-crystal hyperfine lines were used to determine the spin-Hamiltonian parameters. For the hydrated sample, 40 hyperfine lines from powder spectra were used. The spectra suggest no deviation from axial symmetry. All the resonances which were used in the fits correspond to the external magnetic field being either parallel or perpendicular to the *S₆* axis of vanadium(III); the transitions are depicted in Figure 2. The parameters and their associated standard deviations, as determined from the fits, are presented in Table 1; the precision and accuracy were estimated by respectively neglecting and including the second term in eq 3. It is seen from Table 1 that the hyperfine

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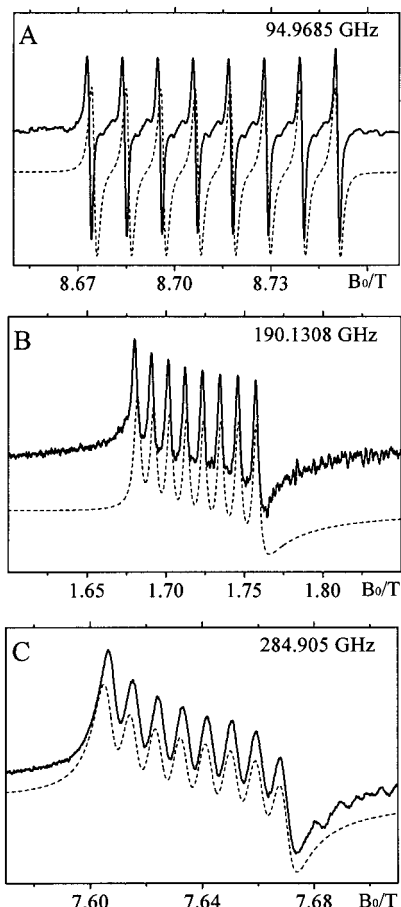


Figure 1. Representative single-crystal (A) and powder (B, C) EPR spectra (solid lines) of Cs[Ga:V]SD (A, B) and Cs[Ga:V]SH (C). Spectral simulations are shown in broken lines and were calculated using the spin-Hamiltonian parameters presented in Table 1.

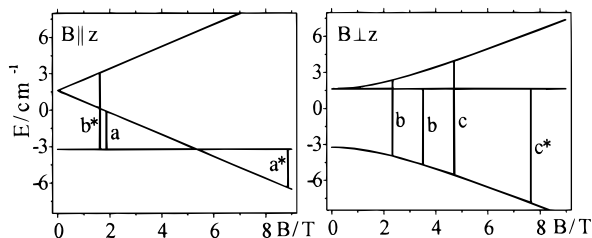


Figure 2. Energy level diagram showing the observed EPR transitions (vertical lines) between states of the $^3A_g(S_6)$ ground term; a, b, and c correspond to frequencies of 95, 190, and 285 GHz, respectively; EPR spectra corresponding to transitions marked * are displayed in Figure 1.

Table 1. Spin-Hamiltonian Parameters for $[V(OX_2)_6]^{3+}$ -Doped $CsGa(SO_4)_2 \cdot 12X_2O$ ($X = D$ or H) Determined from Analysis of High-Field, High-Frequency EPR Data^a

	D	H
D/cm^{-1}	4.7735 (3) [2]	4.8581 (4) [4]
$g_{ }$	1.9549 (4) [1]	1.9500 (6) [5]
g_{\perp}	1.8690 (5) [2]	1.8656 (4) [2]
$A_{ }/10^4 cm^{-1}$	99 (1) [1]	98 (2) [2]
$A_{\perp}/10^4 cm^{-1}$	78 (3) [2]	78 (3) [2]

^a The accuracy with which the parameters are determined is given in curved brackets and the precision in squared brackets.

coupling constants are the same for the hydrated and deuteriated samples, but the respective values of $g_{||}$, g_{\perp} , and D differ markedly.

The angular overlap model (AOM) provides a useful framework for the interpretation of the electronic structure of transition metal hydrates.^{12–14} Recent UV/vis and electronic Raman measurements on $RbV(SO_4)_2 \cdot 12H_2O$ (RbVSH) have allowed the estimation of

the AOM bonding parameters ($e_o = 6950 cm^{-1}$, $e_{\pi\perp} = 930 cm^{-1}$, $e_{\pi||} = 0$), and the Racah parameters ($B = 644 cm^{-1}$, $C = 2960 cm^{-1}$) for the $[V(OH_2)_6]^{3+}$ cation in that system.⁹ RbVSH¹⁵ is isostructural with CsVSH⁵ and CsGaSH,⁵ and there is very little change in the absorption spectra upon caesium for rubidium substitution or deuteration.¹⁶ Furthermore, there is little change in the position of the electronic Raman band, which was also measured in doped crystals of Cs[Ga:V]SH down to concentrations of 6% V(III), 94% Ga(III).^{7–9} On this basis, therefore, it would be expected that the electronic structure of $[V(OX_2)_6]^{3+}$ in Cs[Ga:V]SX should be described by bonding parameters similar to those previously employed in the study of RbVSH.

AOM calculations were performed using the program LIGFIELD.¹⁷ The angles needed as input for this modeling were calculated using the fractional coordinates of CsVSD.⁹ Using these angles and the aforesaid bonding parameters, the zfs of the 3A_g ground term, determined from the EPR study of Cs[Ga:V]SD, can be reproduced by setting ζ , the spin-orbit coupling parameter, to ca. $164 cm^{-1}$ (ca. 80% of the free ion value). The g values can then be reproduced, but only by employing anisotropic orbital reduction factors,¹⁸ $k_{||} = 0.910$, $k_{\perp} = 0.866$.

The change in the spin-Hamiltonian parameters upon exchange of hydrogen for deuterium is considerable, precisely defined, and must be accounted for within a self-consistent framework. The hyperfine coupling constants are sensitive to the form of the 3d wavefunction and do not change upon isotopic substitution. No radical change in ζ or the bonding parameters would be expected therefore, a conclusion supported by the insensitivity of the $^3A_g(S_6) \rightarrow ^1E_g(S_6)$ transition upon deuteration.¹⁶ It is likely, therefore, that the isotope effect observed results from a small structural change, which could arise from differences in hydrogen bonding. By altering the values of the AOM angles slightly, it is possible to reproduce the value of the zfs determined for the hydrated sample. However, the calculated changes in the g values, which accompany the change in the zfs, are in poor agreement with experiment. It is found that the g values for the hydrated complex can be reproduced only by employing anisotropic orbital reduction factors that differ considerably from those found to reproduce the deuteriated data. Such a dramatic change in these parameters upon isotopic substitution is not supported by other experimental data; consequently, no physical significance can be attached to the values of $k_{||}$ and k_{\perp} used to model the data. The failure to explain adequately the isotope effect suggests that a more comprehensive model is required to describe the electronic structure of the vanadium(III) hexaaqua cation; work in this area is currently in progress.

In summary, high-field, multifrequency, EPR measurements of a vanadium(III) complex have been reported. It has been shown that these measurements enable the very precise determination of the spin-Hamiltonian parameters pertaining to the $^3A_g(S_6)$ ground term, and so set a new standard to which theoretical models should be compared.

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- $k_{||}$ and k_{\perp} premultiply the orbital Zeeman operators \hat{L}_Z and $\{\hat{L}_X, \hat{L}_Y\}$, respectively; a different factor is used to scale ζ .