

The g Values of Some Halomolybdenyl, -vanadyl, and -chromyl Complexes¹

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The principal g values of a series of $[MOX_n]^{m-}$ ($M = V^{IV}, Cr^V, Mo^V$; $X = F^-, Cl^-, Br^-$; $n = 4, 5$; $m = 1, 2, 3$) complexes are calculated by the INDO–CI–Stone method. The results agree well with the experimental data and reveal that the traditional models have some limitations in calculating g values for some complexes of this type. © 1999 Academic Press

Key Words: principal g values; metal halide complexes; INDO–CI–Stone model.

INTRODUCTION

The electronic structures of complexes containing the molybdenyl (MO^{3+}) or vanadyl (VO^{2+}) group continue to be of interest largely due to their relevance to the active sites of molybdenum and vanadium oxidoreductase enzymes (1–5), and the vanadyl group attracts more and more attention for its dominant role in crude oil in poisoning hydrodesulfurization catalysts (6, 7). A major contribution to the current understanding of the structures of these metal active sites has come from EPR spectroscopy. The vanadyl, chromyl, and molybdenyl ions (VO^{2+} , CrO^{3+} , and MoO^{3+}) are electronically equivalent. The relatively simple optical and magnetic properties which arise from the simple unpaired d electron and the approximate C_{4v} symmetry have made these systems of particular interest. Simple ligand field models for d^1 systems in axial symmetry predict that the g values should be in the order (8–10)

$$g_e > g_{\perp} (=g_{x,y}) > g_{\parallel} (g_z).$$

However, the anomalously large g values ($g > g_e$) and the “reversed” trend ($g_{\parallel} > g_{\perp}$) are often observed in some metal oxyhalide complexes (11–16). Up to now, all calculations of g values for this type of complex are reported by the use of ligand field theory in which the approximate

expressions of Stone’s formula were adopted (17–23). In such a model, merely the contributions by the lowest-lying excited states of symmetry B_1 and E are included for calculating the g shifts (deviation of g value from g_e). Since some important contributions by the higher lying states may be ignored, most of these works can only approximately interpret the anomalous relationship of “ $g_{\parallel} > g_{\perp}$ ” mentioned above; none of them gave quantitative interpretations of the high g value which is greater than g_e . Here we adopt the CI–Stone formula (24), which is established on Stone’s second-order perturbation theory (25), and configuration interaction to calculate the principal g values of a series of $[MOX_n]^{m-}$ ($M = V^{IV}, Cr^V, Mo^V$; $X = F^-, Cl^-, Br^-$; $n = 4, 5$; $m = 1, 2, 3$) complexes listed in Table 1. The INDOSCI procedure developed by Zerner *et al.* (26–29) is assumed in order to get the multiconfiguration wavefunctions and excitation energies.

CALCULATION

All INDO parameters are taken from the literature (26–30). The Slater orbital exponents of molybdenum are taken as $\xi(4d) = 2.594$ (2.432), $\xi(5s) = 1.447$ (1.429) (26). Values of the ionization potentials, the binding parameters, and the one-centered two-electron integrals are summarized in Tables 1 and 2. All complexes of interest in this paper can be assumed to have C_{4v} symmetry. Their coordination systems are shown in Fig. 1. The geometry parameters of the anions $[MOX_5]^{n-}$ and $[MOX_4]^{n-}$ are given in Table 3. Except for the geometry parameters of $[VOBr_4]^{2-}$, $[CrOBr_4]^-$, and $[CrOBr_5]^{2-}$, which are first estimated in this work, all other parameters are taken from the literature (11–16). Table 4 lists the spin–orbit coupling constants, which are taken from Dunn’s tables (31). λ_{Mo} is taken from Mo^{3+} since the effective charge on molybdenum in the pentahalogeno-oxo-molybdate anions is expected to be less than its oxidation number by about two units (32). The

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TABLE 1
Ionization Potentials I (eV) and Binding Parameters β (eV)

Atom	$-\beta_s$	$-\beta_p$	$-\beta_d$	$-I_s$	$-I_p$	$-I_d$
F	39.0	39.0		39.39	20.86	
O	34.2	34.2		32.90	17.28	
Cl	18.0	18.0		25.23	15.03	6.00
V	1.0	1.0	21.0			
Cr	1.0	1.0	23.0	8.07	5.04	10.66
Mo	1.0	1.0	21.83	(6.97)	(4.06)	(7.43)

INDO calculation (without CI) indicates that the ground state of these types of complexes is in B_2 symmetry. The excited states are generated by limited configuration interaction (26, 29) among configurations formed by single-electron excitation from occupied MOs into unoccupied or virtual orbitals determined in INDO calculations. There are five types of relevant configurations shown in Fig. 2 (33, 34). As our calculation shows, the dominant g shifts are contributed by types 0, 1, and 2 in Fig. 2, and each of these configurations corresponds to a single half-filled MO; therefore, for explicitness, we use the same symbol to indicate the half-filled MO and the corresponding configuration. In this paper, we designate lowercase letters (i.e., b_1 , b_2 , and e) to be the indications of MOs and uppercase letters (i.e., B_1 , B_2 , and E) to be the state wavefunctions. Table 5 lists the atomic orbital combination of some important MOs, where n or m can be taken as 1, 2, 3 . . . indicating that MOs of the same symmetry have the same combination, and they are ordered by energy. $1b_1(o)$ indicates the highest-lying occupied MO of b_1 symmetry. $2b_1(o)$ indicates the subhighest

TABLE 2
One-Centered Two-Electron Integrals $\gamma_{\mu\nu}$ (eV)

Atom	γ_{ss}	γ_{pp}	γ_{sd}	γ_{pd}	γ_{dd}
V	5.07	5.07	6.01	6.01	8.91
Cr	5.60	5.60	6.60	6.60	9.81
Mo	5.57	5.57	6.38	6.38	9.25

occupied MO of b_1 symmetry. b_2 is the half-filled MO. $b_1(u)$ is the highest-lying unoccupied (or virtual) MO of b_1 symmetry, and similar indications can be extended to all MOs. θ_{b_2} , θ_{b_1} , ψ_{b_1} , ϕ_{b_1} , $\phi_{e(x,y)}$, etc., are group orbitals of ligands in appropriate symmetry: $\theta_{b_2} = p_{y1} + p_{x2} - p_{y3} - p_{x4}$, $\theta_{b_1} = p_{x1} - p_{y2} - p_{x3} + p_{y4}$, $\psi_{b_1} = p_{z1} - p_{z2} + p_{z3} - p_{z4}$, $\phi_{b_1} = s_1 - s_2 + s_3 - s_4$, $\phi_{e(x,y)} = (p_{x1} + p_{x3}, p_{y2} + p_{y4})$, $\varphi_{e(x,y)} = (p_{z1} - p_{z3}, p_{z2} - p_{z4})$, $\psi_{e(x,y)} = (p_{y1} + p_{y3}, p_{x2} + p_{x4})$.

RESULTS

The principal g values calculated by the INDO–CI–Stone method in this work are given in Table 6, compared with the experimental data and the results of the χ_α method (11). For the lack of experimental EPR data of $[\text{VOBr}_4]^{2-}$, $[\text{CrOBr}_4]^-$, $[\text{CrOBr}_5]^{2-}$, and $[\text{MoOBr}_4]^-$, their calculated g values can be considered to be the predicted parameters. Among these complexes, only the calculation of g value for $[\text{MoOBr}_4]^-$ was reported (11); $[\text{VOBr}_4]^{2-}$, $[\text{CrOBr}_4]^-$, and $[\text{CrOBr}_5]^{2-}$ are calculated for the first time. From Table 6, it can be shown that the INDO–CI–Stone calculations agree well with the experimental data and get some improvement over the χ_α method as a whole.

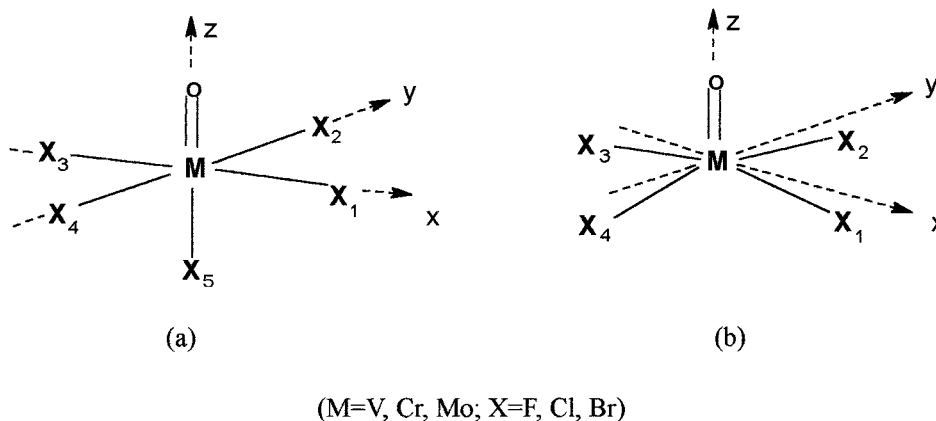


FIG. 1. The coordination systems of $[\text{MOX}_5]^{n-}$ (a) and $[\text{MOX}_4]^{n-}$ (b).

TABLE 3
Geometry Parameters

Anions	$M-O(\text{\AA})$	$M-X_{\text{eq}}(\text{\AA})$	$M-X_{\text{ax}}(\text{\AA})$	$\angle O-M-X_{\text{eq}}(^{\circ})$	Ref.
$[\text{VOF}_4]^{2-}$	1.63	1.97		98.5	11
$[\text{VOF}_5]^{3-}$	1.63	1.97	2.16	90	11
$[\text{VOCl}_4]^{2-}$	1.63	2.42		98.5	12 ^a
$[\text{VOCl}_5]^{3-}$	1.63	2.42	2.67	90	11
$[\text{VOBr}_4]^{2-}$	1.65	2.52		98.5	This work
$[\text{CrOF}_4]^{-}$	1.519	1.79		104.5	11
$[\text{CrOF}_5]^{2-}$	1.519	1.79	2.01	90	11
$[\text{CrOCl}_4]^{-}$	1.519	2.24		104.5	13 ^a
$[\text{CrOCl}_5]^{2-}$	1.519	2.24	2.389	90	11
$[\text{CrOBr}_4]^{-}$	1.549	2.34		104.5	This work
$[\text{CrOBr}_5]^{2-}$	1.549	2.34	2.349	90	This work
$[\text{MoOF}_4]^{-}$	1.61	1.88		105.2	11
$[\text{MoOF}_5]^{2-}$	1.61	1.88 ^b	2.02	90	14 ^a
$[\text{MoOCl}_4]^{-}$	1.61	2.39 ^b		105.2	13 ^a
$[\text{MoOCl}_5]^{2-}$	1.61	2.39	2.59	90	15 ^a
$[\text{MoOBr}_4]^{-}$	1.64	2.49		105.2	11
$[\text{MoOBr}_5]^{2-}$	1.64	2.49	2.49	90	16 ^a

^a Crystal structures.

^b $M-X_{\text{eq}}$ is taken as the average value over the four equatorial bond lengths.

The residual errors (Er) can be applied to compare the calculations of the two methods,

$$\text{Er}_{\parallel} = \sum_i [g_{\parallel}(\text{cal})_i - g_{\parallel}(\text{exp})_i]^2 / \sum_i [g_{\parallel}(\text{exp})_i]^2$$

$$\text{Er}_{\perp} = \sum_i [g_{\perp}(\text{cal})_i - g_{\perp}(\text{exp})_i]^2 / \sum_i [g_{\perp}(\text{exp})_i]^2,$$

where the summation is over all comparable complexes for which the experimental data and the calculated values by two methods are available. The Er_{\parallel} and Er_{\perp} given by the INDO–CI–Stone method are 2.2×10^{-4} and 1.7×10^{-4} , which are several times smaller than those given by χ_{α} , 1.1×10^{-3} and 1.3×10^{-3} , correspondingly.

DISCUSSION

Tables 7a–7f list the CI coefficients of the dominant excited states and their contributions to g shifts. Since the g shifts

contributed by the listed states occupy more than 95% of the total g shifts, which include the contributions from all calculated states (more than 20), the contributions of other states can be neglected. From Table 7, we can see that the excited states of symmetry B_1 only contribute to g_{\parallel} shift, and the states of symmetry E only contribute to g_{\perp} shift. This is because the excited states contribute to g shift only by mixing with the ground state B_2 . With the exception of

$$\langle B_2 | \ell_z | B_1 \rangle \neq 0$$

$$\langle B_2 | \ell_x | E_x \rangle \neq 0$$

$$\langle B_2 | \ell_y | E_y \rangle \neq 0,$$

TABLE 4
Spin–Orbit Coupling Constants λ (cm^{-1})

V(IV)	Cr(V)	Mo(V)	O	F	Cl	Br
210	300	890	151	272	587	2460

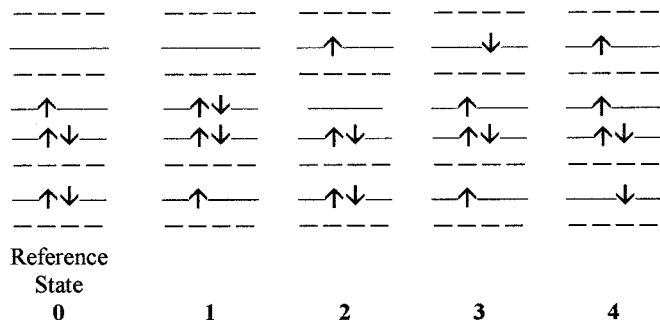


FIG. 2. The five types of configurations of interest in the calculation.

TABLE 5
Combinations of the Important MOs

MO	Combination	
	Metal	Ligand
b_2	d_{xy}	θ_{b_2}
$b_1(u)$	$d_{x^2-y^2}$	θ_{b_1}
$nb_1(o)$	$d_{x^2-y^2}$	$\theta_{b_1}, \Psi_{b_1}, \phi_{b_1}$
$e_{(x,y)}(u)$	d_{xz}, d_{yz}	$\phi_{e(x,y)}, \varphi_{e(x,y)}, \psi_{e(x,y)}$
$me_{(x,y)}(o)$	d_{xz}, d_{yz}	$\phi_{e(x,y)}, \varphi_{e(x,y)}, \psi_{e(x,y)}$

the other angular momentum operator matrix elements are zero because of the unmatched symmetry.

The g_{\perp} shifts contributed by $E(u)$ and $nE(o)$ ($n = 1, 2, 3$) are given in Table 8. It can be shown that g_{\perp} shift is dominantly contributed by $E(u)$ in negative; only a small positive g_{\perp} shift is contributed by $E(o)$ (except for $[\text{CrOBr}_4]^-$ and $[\text{CrOBr}_5]^{2-}$). As a result, for these complexes, the relationship is “ $g_{\perp} < g_e$,” which is in agreement with the simple ligand field theory. In the reported ligand field MO models (21–23), only $E(u)$ is included for calculating g_{\perp} components of $[\text{MOX}_n]^{m-}$, and now it is proved to be a reasonable approximation in most cases, except for

$[\text{CrOBr}_4]^-$ and $[\text{CrOBr}_5]^{2-}$, where it would give the underestimated g_{\perp} components.

From Table 8 we can get the total g_{\perp} shifts simply by adding up the g_{\perp} shifts contributed by $E(u)$ and $E(o)$. It can be shown that the complexes with the same metal center have close g_{\perp} shifts, which indicates that the varieties in the halogen ligand make little difference to their g_{\perp} components. For the same reason, as the penta-coordinated complex and the analogous six-coordinated complex with the same metal and halogen ligand have close g values, it is revealed that the halogen atom in the second axial position has little effect on the magnetic properties.

Table 9 lists the g_{\parallel} shifts contributed by $B_1(u)$ and the overall g_{\parallel} shifts contributed by $nB_1(o)$ ($n = 1, 2, \text{ or } 3$). First let us look at the fluorides. The positive g_{\parallel} shifts contributed by $B_1(o)$ are far less than the negative g_{\parallel} shifts contributed by $B_1(u)$, so the ignorance of $B_1(o)$ in the ligand field MO models (21–23) still gives reasonable results in calculating g_{\parallel} components of the fluorides. Second, for the bromides, the situation is contrary. The positive g_{\parallel} shifts contributed by $B_1(o)$ are far greater than the negative g_{\parallel} shifts contributed by $B_1(u)$, so the bromides have g_{\parallel} components greater than g_e . Especially for the chromium bromides, the small g_{\parallel} shift contributed by $B_1(u)$ is negligible

TABLE 6
Calculated and Experimental g Values

Complex	g_{cal} (INDO–CI–Stone)		g_{cal} (χ_{α})		g_{exp}		Ref. ^a
	g_{\parallel}	g_{\perp}	g_{\parallel}	g_{\perp}	g_{\parallel}	g_{\perp}	
$[\text{VOF}_4]^{2-}$	1.9397	1.9771	1.938	1.955	1.932	1.973	35
$[\text{VOF}_5]^{3-}$	1.9412	1.9850	1.937	1.944	1.937	1.977	36
$[\text{VOCl}_4]^{2-}$	1.9331	1.9808	1.948	1.968	1.948	1.979	37
$[\text{VOCl}_5]^{3-}$	1.9485	1.9904	1.947	1.962	1.945	1.985	38
$[\text{VOBr}_4]^{2-}$	2.0039	1.9885					
$[\text{CrOF}_4]^-$	1.9665	1.9751	1.959	1.967	1.959	1.968	36
$[\text{CrOF}_5]^{2-}$	1.9622	1.9695	1.963	1.943	1.961	1.975	39
$[\text{CrOCl}_4]^-$	2.0033	1.9758	2.040	1.980	2.006	1.979	36
$[\text{CrOCl}_5]^{2-}$	1.9906	1.9752	2.043	1.966	2.008	1.977	40
$[\text{CrOBr}_4]^-$	2.0730	1.9812					
$[\text{CrOBr}_5]^{2-}$	2.0630	1.9776					
$[\text{MoOF}_4]^-$	1.8883	1.9332	1.898	1.927	1.895	1.925	35
$[\text{MoOF}_5]^{2-}$	1.8838	1.9293	1.903	1.869	1.874	1.911	36
$[\text{MoOCl}_4]^-$	1.9693	1.9428	1.994	1.946	1.965	1.947	35
$[\text{MoOCl}_5]^{2-}$	1.9551	1.9369	1.980	1.917	1.963	1.940	36
$[\text{MoOBr}_4]^-$	2.0812	1.9426	2.141	1.947			
$[\text{MoOBr}_5]^{2-}$	2.0925	1.9418			2.090	1.945	23

^a References for the experimental data.

TABLE 7a
The Dominant Contributions to g Shifts for $[\text{VOX}_4]^{2-}$ ($X = \text{F, Cl, Br}$)

X	State	Composition of configuration and MO (%)	Excitation energy (cm^{-1})	g_{\parallel} shift ($\times 10^{-3}$)	g_{\perp} shift ($\times 10^{-3}$)
F	B_2	98[86 d_{xy}]	0	0	0
	$B_1(\text{u})$	100[79 $d_{x^2-y^2}$ 18 θ_{b1}]	16200	-68.10	0
	$B_1(\text{o})$	97[18 $d_{x^2-y^2}$ 80 θ_{b1}]	87890	5.19	0
	$E_x(\text{u})$	97[69 d_{xz} 18 p_{xo} 7 d_{xz}]	12067	0	-27.40
	$E_x(\text{o})$	73[12 d_{xz} 61 p_{xo} 23 φ_{ex}] + 25[12 d_{yz} 61 p_{yo} 23 φ_{ey}]	34990	0	2.16
Total g -shift				-62.6	-25.2
Cl	B_2	92[79 d_{xy} 21 θ_{b2}] + 8[21 d_{xy} 77 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[79 $d_{x^2-y^2}$ 18 θ_{b1}]	12269	-90.29	0
	$1B_1(\text{o})$	54[18 $d_{x^2-y^2}$ 67 θ_{b1}] + 46[85 θ_{b1}]	23700	17.59	0
	$2B_1(\text{o})$	46[18 $d_{x^2-y^2}$ 67 θ_{b1}] + 54[85 θ_{b1}]	34078	3.37	0
	$E_x(\text{u})$	81[62 d_{xz} 14 p_{xo} 10 d_{yz}]	14267	0	-23.20
	$E_x(\text{o})$	77[44 ψ_{ex} 37 ϕ_{ex} 13 φ_{ex}]	36044	0	0.86
Total g shift				-69.2	-21.5
Br	B_2	90[74 d_{xy} 25 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[79 $d_{x^2-y^2}$ 19 θ_{b1}]	18975	-28.56	0
	$1B_1(\text{o})$	47[19 $d_{x^2-y^2}$ 67 θ_{b1}] + 53[88 θ_{b1}]	41437	22.64	0
	$2B_1(\text{o})$	53[19 $d_{x^2-y^2}$ 67 θ_{b1}] + 47[88 θ_{b1}]	43690	7.4	0
	$E_x(\text{u})$	91[50 d_{xz} 19 d_{yz}]	14267	0	-17.40
	$E_x(\text{o})$	85[81 φ_{ex} 11 ϕ_{ex}] + 12[11 φ_{ex} 81 ϕ_{ex}]	36044	0	2.80
Total g shift				1.7	-13.3

TABLE 7b
The Dominant Contributions to g Shifts for $[\text{CrOX}_4]^-$ ($X = \text{F, Cl, Br}$)

X	State	Composition of configuration and MO (%)	Excitation energy (cm^{-1})	g_{\parallel} shift ($\times 10^{-3}$)	g_{\perp} shift ($\times 10^{-3}$)
F	B_2	99[71 d_{xy} 29 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[71 $d_{x^2-y^2}$ 26 θ_{b1}]	23390	-45.51	0
	$B_1(\text{o})$	97[21 $d_{x^2-y^2}$ 61 θ_{b1}]	90766	8.67	0
	$E_x(\text{u})$	88[64 d_{xz} 28 p_{xo}] + 12[64 d_{yz} 28 p_{yo}]	12340	0	-29.35
	$1E_x(\text{o})$	100[25 p_{xo} 67 φ_{ex}]	64667	0	1.17
	$2E_x(\text{o})$	100[41 p_{xo} 32 d_{xz} 10 ϕ_{ex} 15 φ_{ex}]	96057	0	0.88
Total g shift				-35.8	-27.2
Cl	B_2	92[62 d_{xy} 38 θ_{b2}] + 8[38 d_{xy} 61 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[67 $d_{x^2-y^2}$ 27 θ_{b1}]	20540	-49.11	0
	$1B_1(\text{o})$	97[77 ψ_{b1} 21 θ_{b1}]	23000	11.03	0
	$2B_1(\text{o})$	96[28 $d_{x^2-y^2}$ 52 θ_{b1} 19 ψ_{b1}]	25680	37.62	0
	$3B_1(\text{o})$	100[96 ϕ_{b1}]	51293	1.43	0
	$E_x(\text{u})$	71[66 d_{xz} 21 p_{xo} 9 ϕ_{ex}] + 28[66 d_{yz} 21 p_{yo} 9 ϕ_{ey}]	13500	0	-30.57
$E_x(\text{o})$	95[87 ψ_{ex} 6 p_{xo}]	36044	0	2.1	
Total g shift				1.0	-26.5
Br	B_2	90[58 d_{xy} 41 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[66 $d_{x^2-y^2}$ 29 θ_{b1}]	23000	-1.4	0
	$1B_1(\text{o})$	95[77 ϕ_{b1} 16 θ_{b1}]	32153	25.2	0
	$2B_1(\text{o})$	95[30 $d_{x^2-y^2}$ 49 θ_{b1} 19 ϕ_{b1}]	39963	46.5	0
	$E_x(\text{u})$	93[62 d_{xz} 25 θ_{ex}]	15000	0	-32.5
	$E_x(\text{o})$	100[82 φ_{ex} 10 θ_{ex}]	29106	0	12.0
Total g shift				70.7	-21.3

TABLE 7c
The Dominant Contributions to g Shifts for $[\text{VOX}_5]^{3-}$ ($X = \text{F, Cl}$)

X	State	Composition of configuration and MO (%)	Excitation energy (cm^{-1})	g_{\parallel} shift (10^{-3})	g shift (10^{-3})
F	B_2	99[89 d_{xy}]	0	0	0
	$B_1(\text{u})$	100[75 $d_{x^2-y^2}21_{b1}$]	17520	-72.21	0
	$B_1(\text{o})$	97[19 $d_{x^2-y^2}80_{b1}$]	99230	7.45	0
	$E_x(\text{u})$	99[67 $d_{xz}22p_{x0}$]	11410	0	-31.52
	$E_x(\text{o})$	84[41 $p_{x0}23_{ex}19d_{xz}$]	29130	0	3.09
Total g shift				-64.5	-28.4
Cl	B_2	91[78 $d_{xy}21_{b2}$] + 8[21 $d_{xy}78_{b2}$]	0	0	0
	$B_1(\text{u})$	99[76 $d_{x^2-y^2}20_{b1}$]	14628	-101.21	0
	$1B_1(\text{o})$	47[35 $d_{x^2-y^2}47_{b1}$] + 53[72 $b1$]	83450	29.12	0
	$2B_1(\text{o})$	53[35 $d_{x^2-y^2}47_{b1}$] + 47[72 $b1$]	34078	1.39	0
	$E_x(\text{u})$	69[62 $d_{xz}14p_{x0}10_{ex}$] + 30[62 $d_{yz}14p_{y0}10_{ey}$]	21281	0	-26.35
	$E_x(\text{o})$	89[39 $_{ex}45_{ex}$]	31550	0	1.29
Total g shift				-70.1	-24.7

TABLE 7d
The Dominant Contributions to g Shifts for $[\text{CrOX}_5]^{2-}$ ($X = \text{F, Cl, Br}$)

X	State	Composition of configuration and MO (%)	Excitation energy (cm^{-1})	g_{\parallel} shift ($\times 10^{-3}$)	g_{\perp} shift ($\times 10^{-3}$)
F	B_2	98[74 $d_{xy}27\theta_{b2}$]	0	0	0
	$B_1(\text{u})$	100[71 $d_{x^2-y^2}25\theta_{b1}$]	22746	-49.25	0
	$B_1(\text{o})$	100[21 $d_{x^2-y^2}74\theta_{b1}$]	87656	9.16	0
	$E_x(\text{u})$	98[67 $d_{xz}23p_{x0}$]	11310	0	-36.55
	$E_x(\text{o})$	88[46 $p_{x0}39\varphi_{ex}11\phi_{ex}7d_{xz}5p_{x0}$]	27845	0	3.35
Total g shift				-40.1	-32.3
Cl	B_2	92[62 $d_{xy}36\theta_{b2}$] + 8[37 $d_{xy}64\theta_{b2}$]	0	0	0
	$B_1(\text{u})$	100[69 $d_{x^2-y^2}29\theta_{b1}$]	20904	-48.70	0
	$B_1(\text{o})$	100[27 $d_{x^2-y^2}71\theta_{b1}$]	30322	36.80	0
	$E_x(\text{u})$	69[44 $d_{xz}18d_{yz}14p_{x0}$] + 29[44 $d_{yz}18d_{xz}14p_{y0}$]	13783	0	-30.48
	$E_x(\text{o})$	43[25 $_{ex}44\varphi_{ex}11\varphi_{ex}12p_{y5}$] + 27[16 $\phi_{ex}55p_{x5}$]	26000	0	1.14
Total g shift				-11.7	27.1
Br	B_2	91[59 $d_{xy}41\theta_{b2}$]	0	0	0
	$B_1(\text{u})$	100[67 $d_{x^2-y^2}31\theta_{b1}$]	26720	0.19	0
	$1B_1(\text{o})$	100[100 ϕ_{b1}]	38011	0.25	0
	$2B_1(\text{o})$	100[29 $d_{x^2-y^2}71\theta_{b1}$]	43969	60.24	0
	$E_x(\text{u})$	92[34 $d_{xz}42\theta_{ex}$]	14762	0	-37.33
	$1E_x(\text{o})$	78[58 $\theta_{ex}8\varphi_{ex}$] + 18[45 $p_{x5}41\varphi_{ex}$]	19081	0	2.80
	$2E_x(\text{o})$	66[45 $p_{xy}41\varphi_{ey}$] + 12[58 $\theta_{ey}8\varphi_{ey}$] + 14[34 $d_{xz}42\theta_{ex}$]	25234	0	10.56
Total g shift				60.7	-24.7

TABLE 7e
The Dominant Contributions to g Shifts for $[\text{MoOX}_4]^-$ ($X = \text{F, Cl, Br}$)

X	State	Composition of configuration and MO (%)	Excitation energy (cm^{-1})	g_{\parallel} shift ($\times 10^{-3}$)	g_{\perp} shift ($\times 10^{-3}$)
F	B_2	100[71 d_{xy} 29 θ_{b2}]	0	0	0
	$B_1(\text{u})$	99[71 d_{x2-y2} 21 θ_{b1}]	21000	-155.0	0
	$1B_1(\text{o})$	99[20 d_{x2-y2} 59 θ_{b1} 18 ϕ_{b1}]	50135	33.0	0
	$2B_1(\text{o})$	98[88 d_{x2-y2}]	82311	6.66	0
	$E_x(\text{u})$	98[58 d_{xz} 4 d_{yz} 24 p_{x0}]	13000	0	-75.69
	$1E_x(\text{o})$	99[41 p_{x0} 30 ϕ_{ex} 5 ϕ_{ex}]	32190	0	3.54
	$2E_x(\text{o})$	100[21 p_{x0} 27 d_{xz} 23 ϕ_{ex} 18 ϕ_{ex}]	80927	0	2.5
Total g shift				-114.0	-69.1
Cl	B_2	94[58 d_{xy} 41 θ_{b2}] + 6[42 d_{xy} 58 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[66 d_{x2-y2} 27 θ_{b1}]	24600	-111.83	0
	$1B_1(\text{o})$	100[28 d_{x2-y2} 18 ψ_{b1} 52 θ_{b1}]	34003	67.27	0
	$2B_1(\text{o})$	100[77 ψ_{b1} 21 θ_{b1}]	29000	8.64	0
	$3B_1(\text{o})$	100[5 d_{x2-y2} 95 ψ_{b1}]	98023	2.86	0
	$E_x(\text{u})$	70[35 d_{xz} 29 d_{yz} 12 p_{x0} 10 p_{y0}]	14300	0	-67.66
	$E_x(\text{o})$	96[30 d_{xz} 64 p_{x0}]	32800	0	4.29
Total g shift				-33.0	-59.7
Br	B_2	93[55 d_{xy} 45 θ_{b2}] + 7[45 d_{xy} 55 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[64 d_{x2-y2} 29 θ_{b1}]	25730	-59.84	0
	$1B_1(\text{o})$	100[76 ψ_{b1} 21 θ_{b1}]	26000	26.01	0
	$2B_1(\text{o})$	100[49 θ_{b1} 31 d_{x2-y2} 18 ψ_{b1}]	35000	109.70	0
	$E_x(\text{u})$	44[48 ψ_{ex} 32 ϕ_{ey}] + 21[48 ψ_{ex} 32 ϕ_{ex}] + 25[54 d_{yz} 32 ψ_{ey}] + 10[54 d_{xz} 32 ψ_{ex}]	16810	0	-63.82
	$E_x(\text{o})$	34[48 ψ_{ex} 32 ϕ_{ex}] + 62[54 d_{xz} 32 ψ_{ex}]	19000	0	3.0
	Total g shift				78.9

TABLE 7f
The Dominant Contributions to g Shifts for $[\text{MoOX}_5]^{2-}$ ($X = \text{F, Cl, Br}$)

X	State	Composition of configuration and MO (%)	Excitation energy (cm^{-1})	g_{\parallel} shift ($\times 10^{-3}$)	g_{\perp} shift ($\times 10^{-3}$)
F	B_2	100[71 d_{xy} 28 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[71 d_{x2-y2} 23 θ_{b1}]	22000	-134.4	0
	$B_1(\text{o})$	100[49 d_{x2-y2} 41 θ_{b1}]	106073	16.0	0
	$E_x(\text{u})$	88[38 d_{yz} 27 d_{xz}] + 12[38 d_{xz} 27 d_{yz}]	13100	0	-77.4
	$E_x(\text{o})$	52[d_{xz} 55 θ_{ex}] + 46[6 d_{yz} 55 θ_{ey}]	60006	0	2.0
Total g shift				-118.5	-73.0
Cl	B_2	94[69 d_{xy} 23 θ_{b2}] + 6[40 d_{xy} 60 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[67 d_{x2-y2} 29 θ_{b1}]	23000	-122.6	0
	$1B_1(\text{o})$	100[27 d_{x2-y2} 71 θ_{b1}]	32100	75.5	0
	$2B_1(\text{o})$	100[81 θ_{b1} 14 d_{x2-y2}]	36363	1.8	0
	$E_x(\text{u})$	100[41 d_{yz} 17 d_{xz} 37 p_{y0} 24 p_{x0}]	13800	0	-71.9
	$1E_x(\text{o})$	87[61 p_{y0} 29 d_{yz}] + 13[61 p_{x0} 29 d_{xz}]		0	1.0
	$2E_x(\text{o})$	10[42 ϕ_{ey} 30 ϕ_{ey} 15 ϕ_{ey} 22 p_{y5}] + 41[42 ϕ_{ex} 30 ϕ_{ex} 15 ϕ_{ex} 22 p_{x5}] + 40[86 p_{x5}]	72610	0	2.5
Total g shift				-47.2	-65.4
Br	B_2	92[56 d_{xy} 44 θ_{b2}] + 7[43 d_{xy} 57 θ_{b2}]	0	0	0
	$B_1(\text{u})$	100[56 d_{x2-y2} 44 θ_{b1}]	21280	-75.1	0
	$B_1(\text{o})$	100[29 d_{x2-y2} 67 θ_{b1}]	26530	165.1	0
	$E_x(\text{u})$	89[27 d_{xz} 24 d_{yz} 13 p_{x5} 12 p_{y5}]	14290	0	-77.6
	$E_x(\text{o})$	94[58 p_{x0} 28 d_{xz}]	24100	0	15.2
Total g shift				90.7	-60.3

TABLE 8
 g_{\perp} Shift Contributed by $E(u)$ and $E(o)$ ($\times 10^{-3}$)

Complex	X = F		X = Cl		X = Br	
	$E(u)$	$E(o)$	$E(u)$	$E(o)$	$E(u)$	$E(o)$
MoOX ₄ ⁻	-75.69	6.04	-67.66	4.29	-63.82	3.00
MoOX ₅ ²⁻	-77.4	2.00	-71.90	3.50	-77.6	15.20
CrOX ₄ ⁻	-29.35	2.05	-30.57	2.10	-32.50	12.00
CrOX ₅ ²⁻	-36.55	3.35	-30.48	1.14	-37.33	13.36
VOX ₄ ²⁻	-27.40	2.16	-23.20	0.86	-17.40	2.80
VOX ₅ ³⁻	-31.52	3.09	-26.35	1.29		

compared with that of $B_1(o)$. Therefore, $B_1(o)$ must be included in the calculation of g_{\parallel} components of bromides; otherwise we would get erroneous results for " $g_{\parallel} < g_e$," which is contrary to the experimental data. Last, in the chlorides, the g_{\parallel} shift from $B_1(o)$ is between that of fluorides and bromides. In the molybdenum chloride complex, the g_{\parallel} shift by $B_1(o)$ is more than half of that by $B_1(u)$, and even in the chromium analogue, the two terms are equivalent, so we cannot ignore the contributions by $B_1(o)$ in calculating the g_{\parallel} component of molybdenum or the chromium chloride complex. But in the vanadium chloride complex, the g_{\parallel} shift by $B_1(o)$ is far less than that of $B_1(u)$, so $B_1(o)$ can be safely ignored.

Summarizing the analyses above, we come to the following conclusions:

(1) For the vanadium and fluorine complex, the calculation of g_{\parallel} with only the inclusion of $B_1(u)$ may give the qualitative explanation of the EPR data, but for the chromium (or molybdenum) chlorine (or bromine) complex, $1B_1(o)$, $2B_1(o)$, . . . must be included.

(2) In the calculation of g_{\perp} for all the complexes in this series, only the lowest-lying $E(u)$ need to be included.

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TABLE 9
 g_{\parallel} Shifts Contributed by $B_1(u)$ and Overall g_{\parallel} Shifts by $nB_1(o)$ ($\times 10^{-3}$)

Complex	X = F		X = Cl		X = Br	
	$B_1(u)$	$nB_1(o)$	$B_1(u)$	$nB_1(o)$	$B_1(u)$	$nB_1(o)$
VOX ₄ ²⁻	-68.10	5.19	-90.29	17.59	-28.56	22.64
VOX ₅ ³⁻	-72.21	7.45	-101.21	29.12		
CrOX ₄ ⁻	-45.51	8.67	-49.11	50.08	-1.40	71.70
CrOX ₅ ²⁻	-49.25	9.16	-48.70	36.80	0.19	60.49
MoOX ₄ ⁻	-155.00	39.66	-111.83	78.77	-59.84	135.71
MoOX ₅ ²⁻	-134.40	16.00	-122.60	77.30	-75.10	165.10

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