Calculation of Spin Orbit Coupling of Tungsten (III) Complexes: A DFT Application

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ABSTRACT

Making use of DFT, we could calculate Spin Orbit Coupling Constant ($\lambda_{complex}$) values of the five tungsten (III) complexes which were difficult to arrive at experimentally since there would always occur errors during the determination of their contributing parameters like CFSE and (A_{ten}).

Keywords: Spin Orbit Coupling, *ZORA* commands, *Collinear*

INTRODUCTION

Unlike the 1st transition series metal ion complexes, there had, hardly, been any study done on the calculation of Spin Orbit Coupling ($\lambda_{complex}$) of the corresponding complexes of 2nd and 3rd transition series. The limitation would arise because high $\lambda_{complex}$ values[1] of their complexes caused errors both in the exact determination of their Crystal Field Stabilization Energies (CFSE) as well as the ESR parameters (especially A_{ten}). They would, further, cause errors in the g values if determined by experimental methods. We applied Density Functional Theory (DFT) implemented in ADF 2012.02 software to its ESR/EPR Program which was run by giving *Single Point, LDA, Default,* *Spin Orbit, Unrestricted, None, Collinear* and *ZORA* commands using *TZP Basis set* with *Nosym* symmetry after definite *Pre-optimization* of five W (III) complexes to obtain their g_{iso} values[2-4]. Five known relations (a-e) were used in a sequence. Magnetic moments (μ_{ADF}) arising from the First Order Zeeman Effect were calculated from the g_{iso} values (a). Magnetic moment values arising from the Second Order Zeeman Effect [Temperature Independent Paramagnetic Moments (μ_{tip})] were calculated by (c) from their paramagnetic susceptibilities (χ_{tip}) as calculated by (b). Sum of μ_{ADF} and μ_{tip} would give effective magnetic moments (μ_{eff}) (d). CFSE values of W (III) complexes were $\approx$1.75 times the reported CFSE values of the corresponding Cr (III) complexes[5-7]. $\lambda_{Complex}$ values[8] of W (III) complexes

Table 1: Various Parameters and Spin Orbit coupling (λ complex) of Tungsten(III) Complexes

Complex ($^4A_{2g}$)	Point group	g_{iso}	CFSE(cm^{-1}) of Corresponding Cr(III) Complex	Approximate CFSE (cm^{-1}) of W(III) Complex*	μADF [a] (B.M)	χtip [b] ** μ tip [c] (B.M)	μ eff [d] (B.M.) (cm^{-1})	λcomplex [e]
[W F6]-3	Oh	1.80193	14900[7]	26075.0	3.489	76.19 0.047	3.536	567.21
[WCl6]-3	-do-	1.868252	13920[8]	24360.0	3.6179	85.71 0.053	3.671	317.79
[W Br6]-3	-do-	1.893263	13224[6]	23142.0	3.6663	90.23 0.0559	3.7222	225.27
[W(OH2)6]+3	C1	1.859795	17400[6]	30450.0	3.6014	68.57 0.0425	3.644	450.30
[W(NH3)6] +3	-do-	1.925022	21750[7]	38062.5	3.7278	54.91 0.034	3.7618	273.21

were calculated by (e).

*Multiply CFSE of corresponding Cr (III) Complex by 1.75

**Multiply by 10^{6} c g s

$\mu_{s.o} = 3.8729$ B.M and $\chi_{s. o.} = 6250 \times 10^{-6}$ cgs for 3 unpaired electrons

(a) $\mu_{ADF} = [g_{iso}^2 s(s+1)]^{1/2}$

(b) $\chi_{tip} = 8N\beta^2/10Dq$

(c) $\mu_{tip} = \chi_{tip} \times \mu_{s.o}/\chi_{s.o}$

(d) $\mu_{t = \mu ADF + \mu tip}$

(e) $\mu_{eff} = \mu_{so} (1 - \sigma \times \lambda_{complex}/10Dq)$

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