

## Spin-orbit coupling constant in divalent iridium

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**Abstract** The spin-orbit coupling constant in  $5d^7$  divalent iridium ion,  $\xi = (3450 \pm 500) \text{ cm}^{-1}$  is obtained from Electron Paramagnetic Resonance data and molecular orbital calculations.

To our knowledge, **measurements** in free ion divalent iridium do not exist. From an experimental **point** of view, the spin-orbit coupling constant for divalent iridium ion remains unknown. On the other **hand**, Fraga et al.<sup>1</sup> calculated this **parameter** from **Hartree-Fock** wave functions for the configuration  $5d^7$  ( ${}^4F_{9/2,3}$  term) including **relativistic** corrections.

More generally, in the divalent iridium complexes, reports in the literature are also scarce<sup>2</sup>. The first observation of a stable divalent iridium **complex** was reported by Vugman et al. in  $[\text{Ir}(\text{CN})_5]^{3-}$  in KCl host lattice<sup>3</sup>, by Electron **Paramagnetic** Resonance (EPR) spectroscopy. In this paper we **shall** derive the spin-orbit coupling constant for **Ir(II)** from EPR data **and** show that it **lies** between Fraga et al.'s value and the **value** obtained by extrapolation from **Co(II)** and **Rh(II)** spin-orbit coupling constants.

Electron Paramagnetic Resonance spectroscopy in divalent iridium complexes **can** give information about the ratio between the free ion spin-orbit coupling and the difference between molecular energy **levels** mixed by spin-orbit interaction.

For a  $C_{4v}$  or  $D_{4h}$  symmetry low spin  $d^7$  system the unpaired electron occupies a  $d_{z^2}$  orbital ( ${}^2A_1$  ground state). Spin-orbit coupling causes the admixture of the ground state configuration with the  ${}^2E$  excited configurations (only the **first** one is **usually** considered in the calculations). The  $|E'\alpha'\rangle$  components of Kramer's

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doublet for these two configurations, in the complementary scheme, are  $|\tilde{b}_1^2 a_1^+ \rangle$  and  $|\tilde{a}_1^2(1)^- \rangle$ , respectively.

Assuming a LCAO-MO scheme the corresponding antibonding orbitals can be written as

$$a_1 = \alpha \tilde{a}_1 - a' \tilde{\Psi} a_1 \quad \text{and} \quad (1) = \beta(\tilde{1}) - \beta' \tilde{\Psi}_L,$$

where  $\tilde{\Psi} a_1$  and  $\tilde{\Psi}_L$  are linear combinations of the ligand orbitals of appropriated symmetry. The symbol  $\tilde{\phantom{x}}$  indicates an atomic orbital.

After diagonalization of the spin-orbit interaction matrix and evaluation of the components of the g tensor<sup>4</sup> it follows that

$$g_{zz} = g_0 \cos 2\delta + 2k'' \sin^2 \delta \quad (1)$$

$$g_{xx} = g_{yy} = g_0 \cos^2 \delta + \sqrt{6}k' \sin 2\delta \quad (2)$$

where  $k'$  and  $k''$  are orbital reduction factors defined by the following expressions:

$$k' = \langle (1) | l_+ | a_1 \rangle / \sqrt{6} = \alpha\beta - \alpha\beta' S_e - \alpha'\beta S_{a_1} + (\alpha'\beta' / \sqrt{6}) \langle \tilde{\Psi}_L | l_+ | \tilde{\Psi} a_1 \rangle$$

$$k'' = \langle (1) | l_z | (1) \rangle = 1 - \beta'^2 (1 - \langle \tilde{\Psi}_L | l_z | \tilde{\Psi}_L \rangle)$$

The quantities  $S_e$  and  $S_{a_1}$  are the overlap integrals  $\langle \tilde{1} | \tilde{\Psi}_L \rangle$  and  $\langle \tilde{a}_1 | \tilde{\Psi} a_1 \rangle$ , respectively. The angle  $\delta$  is such that

$$\tan 2\delta = \frac{\sqrt{6}k'y}{1 + yk''/2}$$

where

$$y = \xi / (E_2 - E_1),$$

$\xi$  is the spin-orbit coupling constant and  $E_2 - E_1$  is the energy difference between the two mixing configurations. The sign of the spin-orbit coupling constant has already been changed to give the right expressions for  $d^7$ , not  $d^3$ , configuration.

With  $y$  determined from EPR data and the energy difference  $E_2 - E_1$  measured, the  $\xi$  may be evaluated. Direct measurement of  $E_2 - E_1$  requires optical spectroscopy experiments in divalent iridium complexes. These complexes are formed

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by radiation damage in diamagnetic  $5d^6$  Ir(III) complexes, e.g.  $[\text{Ir}(\text{CN})_6]^{3-}$ , in alkali halide host lattices. However, besides the simultaneous formation of several paramagnetic species (for a review see ref. 5), the optical absorption spectrum of each paramagnetic species lies under the stronger absorption bands of the remaining diamagnetic complex.

In order to obtain the energy difference  $E_2 - E_1$  in  $[\text{Ir}(\text{CN})_6]^{3-}$  complex we have carried out molecular orbital calculations employing the extended Hückel method improved with self-consistency in charge and configuration as described in detail elsewhere<sup>6</sup>. The diagonal elements of the Hamiltonian matrix were approximated by the Valence Orbital Ionization Potentials (VOIPs). In general, the dependence of the VOIPs on the charge and configuration of the atom may be obtained from measurements of atomic spectra<sup>7,8</sup>. However, for the  $5d$  transition elements the experimental data are very scarce. For this reason, we have obtained the VOIPs for Iridium by atomic self-consistent relativistic numerical Dirac-Slater calculations, in the local density approximation. The Kohn-Sham-Gaspar local exchange potential was employed<sup>10</sup> and the "transition state" concept<sup>11</sup> was used to define Ionization Potentials. Calculated VOIPs for Ir are given in table 1. The energies of the orbitals  $\sigma(\text{CN})$ ,  $\pi(\text{CN})$  and  $\pi^*(\text{CN})$  were taken from ref.12.

The non-diagonal elements of the Hamiltonian matrix were approximated by the geometrical average of the diagonal elements

$$H_{ij} = -FG_{ij}(H_{ii} \cdot H_{jj})^{1/2}$$

in which  $G_{ij}$  are the group overlap integrals<sup>13</sup> and F is an empirical parameter obtained by approximately fitting the electronic transitions of  $[\text{Ir}(\text{CN})_6]^{3-}$ ,<sup>14</sup>. We adopted the values  $F_\sigma = 2.4$  and  $F_\pi = 2.0$ . Atomic analytic Slater-type functions for Ir used in the evaluation of the overlap integrals were obtained from the literature<sup>15</sup>; for the CN ligands, molecular LCAO functions were employed<sup>12</sup>.

The calculated values for  $E_2 - E_1$  is  $12070 \text{ cm}^{-1}$ , assuming the inter-atomic distances Ir - C = 2.00 Å and C - N = 1.16 Å. The minimum energy is obtained when the Ir ion lies above the equatorial plane, the metal - equatorial cyanides forming a  $101.5^\circ$  angle with the principal symmetry axis of this  $C_{4v}$  penta-coordinated

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complex. We estimate that the accuracy in our calculated value is of the order of 10%.

Table 1 - Parameters for VOIP curves of Ir as a function of charge  $q$   
 $\text{VOIP} = \text{A}q^2 + \text{B}q + \text{C}$  in  $10^3 \text{ cm}^{-1}$  units

Config.	V.O. <sup>a</sup>	A	B	C	Calculated VOIP Ir <sup>0</sup>	Experimental <sup>b</sup> VOIP Ir <sup>0</sup>
563	d	6.45	74.2	55.7	55.7	56.1
5d <sup>8</sup> 6s	d	5.59	79.2	68.4		
5d <sup>8</sup> 6p	d	6.37	76.9	78.9		
5d <sup>8</sup> 6s	s	4.19	64.1	66.5	66.5	67.8
5d <sup>7</sup> 6s <sup>2</sup>	s	4.23	66.0	73.0		
5d <sup>7</sup> 6s6p	s	4.76	64.0	80.5		
5d <sup>8</sup> 6p	p	5.17	52.3	31.3		
5d <sup>7</sup> 6p <sup>2</sup>	p	4.76	55.1	40.2		
5d <sup>7</sup> 6s6p	p	4.51	55.8	34.8		

<sup>a</sup>V.O. stands for valence orbital and config. for configuration.

<sup>b</sup>Calculated from atomic data available in refs. 18, 19, 20 and 21.

In order to calculate  $y$ , we have used relations (1) and (2). The  $g$ -values measured in RbCl ( $g_x = 1.9642$  and  $g_{xx} = g_{yy}2.2210$ )<sup>16</sup> may be chosen among the data for [Ir(CN)<sub>5</sub>]<sup>3-</sup> species in alkali halide host lattices because it shows the proper axial symmetry. Relations (1) and (2) describe a system with two equations and three unknowns. For this reason, we have chosen to ascertain values to  $k^n$ , the least important parameter in these relations. The value of  $k^n$  can be approximated to  $(1 - \beta'^2)$ , assuming that the integral  $\langle \Psi_L | l_z | \Psi_L \rangle$  is small. From the calculations we find  $\beta'^2 = 0.23$  so  $k^n \cong 0.77$ , resulting in  $y = 0.284$  and  $\xi_{\text{Ir(II)}} = 3450 \text{ cm}^{-1}$ . The estimated uncertainty in  $\xi_{\text{Ir(II)}}$  is within  $\pm 500 \text{ cm}^{-1}$ , arising from an estimated uncertainty of 0.05 in the determination of  $k^n$  and from the estimated accuracy on the energy difference calculation.

In order to compare our result with previous investigations we shall make an extrapolation from the reported  $\xi$  values<sup>17</sup> for 3d<sup>7</sup> Co(II) and 4d<sup>7</sup> Rh(II) ions. Assuming that for non-hydrogenic atoms  $\xi_{nl} \propto (Z - \sigma)^4$ , where  $\sigma$  is a screening constant to be taken from Fraga et al.<sup>1</sup>, the estimated value for  $\xi_{\text{Ir(II)}}$  is 3236

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$\text{cm}^{-1}$ . On the other hand, the value obtained by Fraga et al. for  $\xi_{\text{Ir(II)}}$  is  $4056 \text{ cm}^{-1}$ . Another guiding principle<sup>17</sup> is that

$$\xi_{n\ell}[M(0) d^{n-2} s^2] \approx \xi_{n\ell}[M(I) d^{n-2} s] \approx \xi_{n\ell}[M(II) d^{n-2}].$$

Therefore, a comparison of our result  $\xi_{5d} [\text{Ir(II)}5d^7] = (3450 \pm 500) \text{ cm}^{-1}$  with the value obtained by Childs et al.<sup>18</sup>,  $\xi_{5d} [\text{Ir(0)}5d^7 6s^2] = (3585 \leq \pm 54) \text{ cm}^{-1}$ , strongly suggests that the former value should be used for the **Ir(II) (5d<sup>7</sup>) spin-orbit coupling constant**.

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**Resumo**

A constante de acoplamento spin-órbita para o ion Irídio divalente, em configuração  $5d^7$ , é obtida dos dados experimentais de Ressonância Paramagnética Eletrônica e de cálculos de orbitais moleculares e vale  $(3450 \pm 500) \text{ cm}^{-1}$ .