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Spin-Orbit Coupling in Chelates with Conjugated Ligands

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In the paper the spin-orbit coupling in chelates with conjugated ligands has been studied theoretically. The proposed models were used for the calculation of the lifetime of the ${}^3\Gamma_2$ electron-transfer triplet state of the complex ion $\mathrm{Ru(phen)}_3^{+2}$.

Key words: Spin-orbit coupling in inorganic chelates

In the literature there are many papers dealing with the luminescence properties of transition metal complexes. The complexes of $4d^6$ and $5d^6$ elements with π-conjugated ligands has been especially studied in the last ten years because of their unusual luminescence properties [1-15]. Thus, in complexes of Ru(II) with conjugated ligands (e.g. 2,2′-bipyridyl and 1,10-phenanthroline) a $\pi^* \rightarrow d$ emission has been observed [16], and the experiments have shown that the emission occurs from a manifold of three levels of different multiplicity [7, 12, 13, 15]. As has been demonstrated [12], at low temperatures the luminescence exhibits the properties of a phosphorescence, while at high temperatures the radiation obtains an increasing amount of fluorescence character. Spin-orbit coupling plays a dominant role in this process due to the presence of heavier transition elements. In this short note the problem of spin-orbit coupling in complexes of nd^6 metal ions with conjugated ligands is discussed theoretically. For the description of complex particles we have used the "coupled chromophore" model proposed by Longuet-Higgins and Murrell for studies of conjugated π-electron systems [17]. On the basis of this model the matrix elements of the spin-orbit operator are given:

$$\langle ET, \Gamma_i, 0, 0 | H^{S0} | ET, \Gamma_j, 1, 0 \rangle$$
$$= \sum_{h<k} (D_h^{\Gamma_i} D_h^{\Gamma_j} - D_k^{\Gamma_j} D_k^{\Gamma_i}) \frac{\hbar}{2} \xi_M \langle m(p_h) | l_z | m(p_k) \rangle \tag{1}$$

and

$$\langle ET, \Gamma_i, 0, 0 | H^{S0} | ET, \Gamma_j, 1, \pm 1 \rangle$$
$$= \sum_{h<k} (D_h^{\Gamma_i} D_h^{\Gamma_j} - D_k^{\Gamma_j} D_k^{\Gamma_i}) \frac{\hbar}{2} \xi_M \langle m(p_h) | l_x \pm i l_y | m(p_k) \rangle \tag{2}$$

where $D_r^{\Gamma_s}$ are the group transformation coefficients with Γ_s indicating the symmetry properties of the electron-transfer states and r labelling the ligand molecules in which a d-electron from the central metal ion has been excited. For the derivation of these expressions the isomorphism of t_{2g}-electrons with p-electrons was taken into account

[18], i.e. the t_{2g} orbital functions of the metal were formally replaced by p orbital functions

$$m(t_{2g}) = m(p) \tag{3}$$

and

$$\xi_M l_{m(t_{2g})} \cdot s = -\xi_M l_{m(p)} \cdot s \tag{4}$$

The results can be used for the calculation of the natural decay lifetime of the electron-transfer triplet state. The formula for the lifetime τ_P^0 of the triplet state [19] is in the dipole velocity representation of the form

$$\frac{1}{\tau_P^0} = \frac{8\pi\hbar\sigma e^2}{3m^2c^2} \sum_{(ET,0)} \sum_{M_S} \left| \frac{\langle ET, \Gamma_i, 0, 0 | H^{SO} | ET, \Gamma_j, 1, M_S \rangle}{E_{(ET,0)} - E_{(ET,1)}} \right|^2 \times |\langle ET, \Gamma_i, 0, 0 | \nabla | G, \Gamma, 0, 0 \rangle|^2 \tag{5}$$

where the first summation runs over all singlet electron transfer excited states, σ is the wave number of the emission transition and e, $\hbar$, m, and c have their usual meanings. We applied Eq. (5) for the calculation of the lifetime of the triplet states originating using spin-orbit coupling mechanism from the $^1\Gamma_3$ electron-transfer state of the complex ion Ru(phen)_3^{+2} (phen = 1,10-phenanthroline) (i.e. the electron-transfer state having the lowest energy [20]). The only non-zero matrix element of the operator H^{SO} is $\langle ET, \Gamma_3, 0, 0 | H^{SO} | ET, \Gamma_2, 1, 0 \rangle$. For the solution of this matrix element Eq. (1) has been used. The formally introduced p orbitals were transformed like p orbitals of the ligand molecules into which the metal electron is excited (see Fig. 1). Thus, the p orbitals of the first, second and third ligand transform like p_z, p_y and p_x, respectively. The calculated value of the matrix element is

$$\langle ET, \Gamma_3, 0, 0 | H^{SO} | ET, \Gamma_2, 1, 0 \rangle = i \frac{1}{\sqrt{6}} \xi_{\text{Ru}}$$

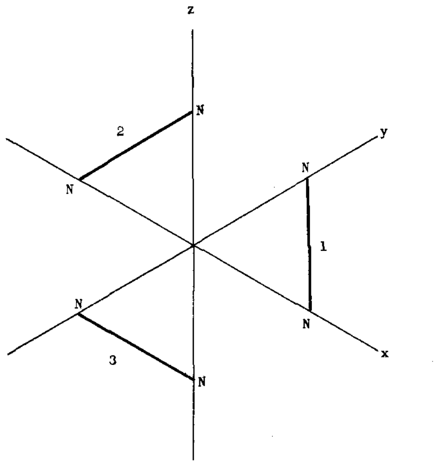

Fig. 1. The coordinate system of Ru(phen)_3^{+2}

Table 1. Interatomic distances in $Ru(phen)_3^{+2}$

M-X	Bond Length in Å	M-X	Bond Length in Å
$Ru-N_1$ $Ru-N_{10}$	2.1	$Ru-C_5$ $Ru-C_6$	5.17
$Ru-C_2$ $Ru-C_9$	3.24	$Ru-C_{11}$ $Ru-C_{12}$	2.79
$Ru-C_3$ $Ru-C_8$	4.41	$Ru-C_{13}$ $Ru-C_{14}$	4.13
$Ru-C_4$ $Ru-C_7$	4.79		

where

$$\xi_{Ru} = 1000 \text{ cm}^{-1} \text{ (see [21])}.$$

The matrix elements of the operator ∇ were calculated using the same procedure as published in the literature [22]. The necessary distances of the carbon and nitrogen atoms from the central metal ion are given in Table 1. The carbon and nitrogen functions were taken in mono-ξ form [23], the atomic ruthenium function is the same as that published by Richardson *et al.* [24]. In addition the SCF molecular orbitals given for 1,10-phenanthroline by Ito *et al.* were used [25]. With $\sigma = 17\,550 \text{ cm}^{-1}$ and with $E_{(ET,0)} - E_{(ET,1)} = 4050 \text{ cm}^{-1}$ (see [26]) we finally obtained the value of the lifetime of the $^3\Gamma_2$ metal-to-ligand electron-transfer state $\tau_P^0 = 4.8 \cdot 10^{-5}$ sec, while the experimentally observed value is of the order of 10^{-5} sec.

In spite of good agreement of the theoretical and experimental values, the whole luminescence process is not simple, as was shown by Crosby *et al.* [7, 12, 13, 15], and to understand them more study must be done about the electronic structure of these types of complex compounds. From our study the limitation for the non-zero spin-orbit coupling in complexes with conjugated ligands results. The condition for the mixing of singlet and triplet electron-transfer states via the spin-orbit coupling mechanism is the non-coplanar arrangement of two or more coordinated ligand molecules, as is seen from Eqs. (1) and (2). In connection with this statement are the phosphorescence properties caused due to the electron-transfer transition, i.e. only molecules with non-coplanar coordinated π-electron ligands are able to produce (neglecting triplet-triplet mixing) $\pi^* \rightarrow d$ emission.

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