

The MS- X_α Treatment of the Energy Transitions in Uranium(V) Complexes

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(Received March 27, 1987)

Abstract

A relativistic MS- X_α method in combination with the ligand field theory has been applied to locate and assign the electronic transitions in the $5f^1$ species of UOX_5^{2-} ($X = F, Cl$ and Br). The data were compared with previous results obtained by using the ligand field approach. It has been concluded that the distortion in the octahedral structure of UX_6^- due to the replacement of one of the X atoms by an oxygen atom resulted in a compression of the axial ligand rather than elongation. In this respect three tetragonal parameters have been used in treating the tetragonal compression. Spin-orbit coupling terms have been invoked in calculations to improve values for the resulting energy of transitions.

Introduction

A considerable number of pentavalent uranium compounds and complexes are now well characterized. These are mainly halogen, ternary mixed oxides and oxohalogeno derivatives [1]. The chemical, spectroscopic and magnetic data indicate clearly that these compounds contain U(V) and not a mixture of U(IV)–U(VI) [1]. The simple electronic configuration exhibited by $U(V)([Rn]5f^1)$ has initiated over the last two decades experimental [2–6] as well as theoretical investigations [4–7] on its compounds. Meanwhile, considerable success has been obtained in the application of the relativistic MS- X_α method to UX_6^- compounds ($X = F, Cl, Br, I$) [7]. This has been an encouragement to apply the same method in combination with ligand field theory to the oxohalogeno complexes of U(V).

Many investigations have been elaborated in order to combine the ligand field with the MS- X_α method for the metal complexes having a d^n outer configuration [8–11]. Less attention has been given to the metal complexes with f^n outer configuration. It seems important to understand the simple f^1 system, where the electron repulsion may be considered to be absent. In this work, much emphasis has been given to the f – f transitions of the UOX_5^{2-} complexes.

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Method of Calculations

The relativistic MS- X_α method employed has been discussed previously [7, 12, 13]. It differs from the non-relativistic version in the inclusion of the mass-velocity and Darwin terms during the SCF procedure.

The up-dated MS- X_α version due to Cook [14] was used to calculate the electronic structure of the ground state and the f – f electronic transitions of the UOX_5^{2-} ($X = F, Cl, Br$) complexes.

The values of the atomic α -parameters for halogens and oxygen were taken from Schwartz listings [15], whereas α for uranium was taken from the values of Thornton *et al.* [7]. Weighted averages of the atomic α -values in the intersphere and outersphere regions were used. In addition, the sphere radii were selected according to the scheme described by Norman [16]. In order to simulate the effect of the surrounding positive ions, the outersphere region was taken as touching the halogens' sphere, serving as a Watson sphere with a positive charge equal in magnitude to that of the anion, *i.e.* $2+$ charge.

The partial wave expansions were truncated at $l=4$ for the outer sphere, $l=3$ for uranium, $l=2$ for chlorine and bromine, and $l=1$ for oxygen and fluorine. The $6s$ and $6p$ electrons of the uranium atom were included in the SCF calculations as valence electrons. The X_α parameters used in this work are summarized in Table I.

TABLE I. UOX_5^{2-} Parameters Used in the MS- X_α Calculations

	UOF_5^{2-}	$UOCl_5^{2-}$	$UOBr_5^{2-}$
α -Halogen	0.73732	0.72325	0.70606
α -Outer sphere	0.72595	0.71715	0.70641
R_U^a	1.4196	1.4267	1.4374
R_O	0.9324	0.9314	0.9311
R_X	1.0615	1.4005	1.5306
R_{out}	3.2822	3.9410	4.2184
R_{U-X}	2.2200	2.540	2.688
$\alpha_O = 0.7447$ $\alpha_U = 0.6920$ $R_{U-O} = 1.78$			

^aAll radii and bond distances are in Å.

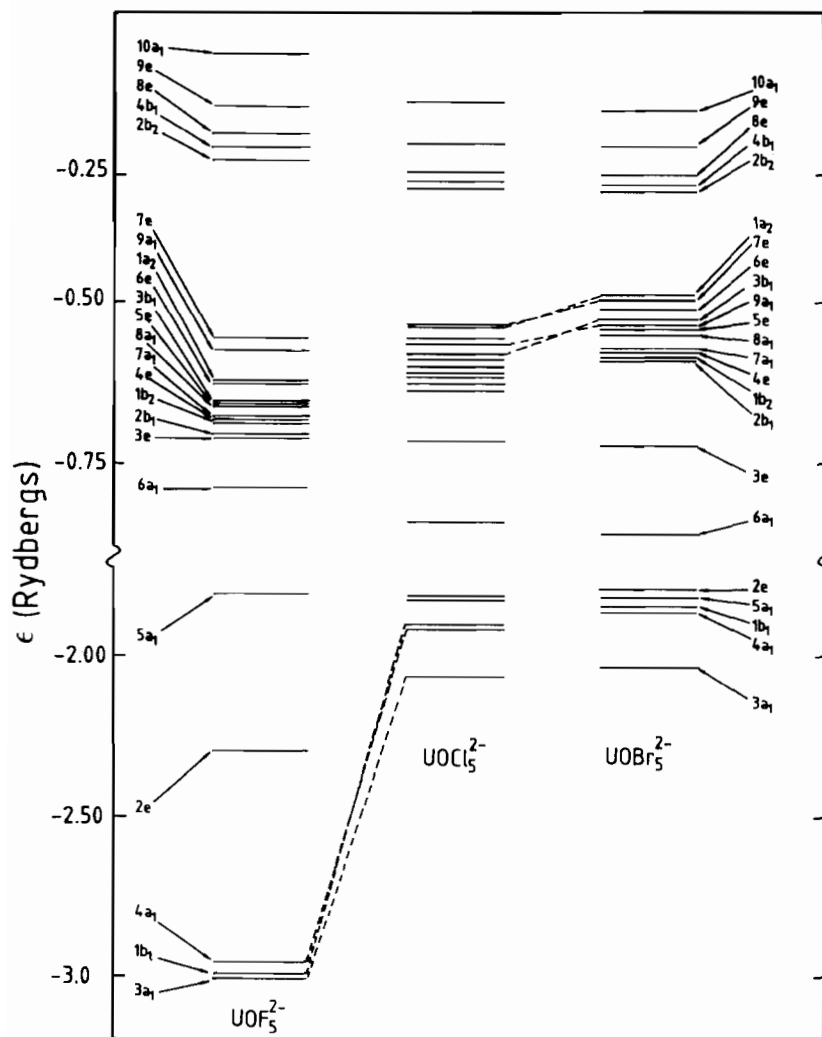


Fig. 1. MO diagram of UOX_5^{2-} complexes. (Core-like MOs $1a_1$, $2a_1$ and $2e$ are not shown.)

Since the X-ray structures of these complexes have not been reported, a distorted octahedral structure was assumed in which one of the halogen ions has been replaced by an O^{2-} ion. Actually, spectroscopic studies [4, 5] were found to be in favour of this assumption. Moreover, X-ray structural determination of the PaOCl_5^{2-} complex has revealed a distorted octahedral structure for the molecule, approximating the C_{4v} symmetry [17].

In this work the U–X bond distances were taken to be similar to that in UX_6^- [7] and a U–O bond distance of 1.78 Å was used in the three complexes. This value was chosen as the average of that expected for a U–O multiple bond distance [17].

Results and Discussions

The relativistic MS- X_α one-electron energies of the ground state of the UOX_5^{2-} complexes are shown in

Fig. 1. It can be seen that the energy spectrum of the MOs for the fluoro complex is more expanded in comparison to the other two complexes, a situation which has been also found in the X_α results of UX_6^- [7]. This may be rationalized on the basis of the strength of the interaction of U with the X moiety, which is stronger in the case of the fluoro compounds than in the other halogen compounds. This result is compatible with the trend found for the heats of formation of halogen compounds of uranium [18].

The highest five MOs in Fig. 1 are the U-5f-like MOs, *i.e.* the ligand-field states in these complexes. The HOMO state is the $2b_2$ which is occupied by a single electron. The splitting patterns follow the order $2b_2 < 4b_1 < 8e < 9e < 10a_1$ in the three complexes.

It is noticed that the trend in the calculated ligand-field splitting (Fig. 1) follows that found

TABLE II. Ligand-field States of UOX_5^{2-} Obtained from X_α Calculations

	UOF_5^{2-}			UOCl_5^{2-}			UOBr_5^{2-}		
	ϵX_α^a	ΔE^b	5f (%)	ϵX_α	ΔE	5f (%)	ϵX_α	ΔE	5f (%)
b_2	-0.2784	0	95.6	-0.3246	0	95.4	-0.3290	0	95.6
b_1	-0.2609	1920	94.2	-0.3150	1056	91.7	-0.3201	977	91.3
$e_{(1)}$	-0.243	3894	89.7	-0.2999	2760	85.2	-0.3057	2605	84.2
$e_{(2)}$	-0.1963	9070	82.6	-0.2550	7700	75.6	-0.2615	7572	74.8
a_1	-0.1165	18167	67.2	-0.1909	15167	60.9	-0.2035	14234	60.7

^a X_α eigenvalues in Rydberg units. ^b X_α transition energies in cm^{-1} .

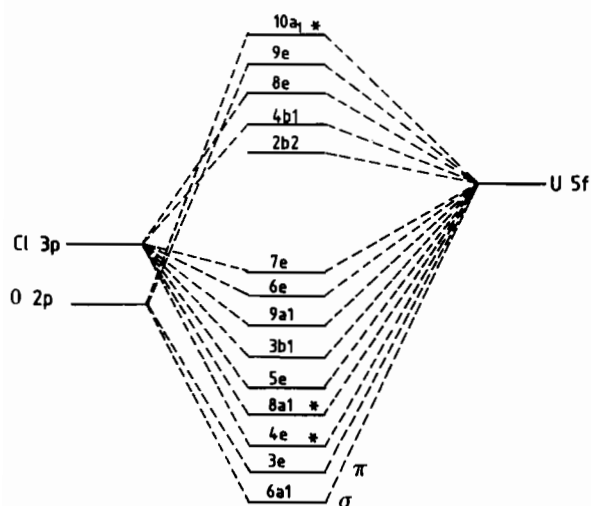


Fig. 2. Portion of the MO diagram of UOCl_5^{2-} showing only the MOs of significant U-5f contributions. * indicates MOs involving axial chlorine ligands.

experimentally [4, 5] and that which should be expected from the spectrochemical series.

In Fig. 2 a portion of the MO diagram of UOCl_5^{2-} is reproduced where the MOs involving significant bonding between the 5f orbitals of uranium and the p orbitals of the ligand are shown. The results obtained from this diagram indicate that the uranium–oxygen bonding (one σ and two π bonds) is stronger than the uranium–chlorine bonding. This was also the case for the X_α results of the oxohalo complexes of transition metal ions [19]. The π -bond shortening in U–O may cause this strong interaction. The frequency of the U–O stretching vibration is in quite good agreement with the presence of such U–O π -bonding [2]. The same conclusion can be deduced for the other fluoro and bromo complexes under consideration.

Ligand Field Spectrum

The X_α one-electron energies of the ligand-field states of the UOX_5^{2-} complexes, together with the atomic population of the U-5f orbitals are depicted in Table II. Also shown in this Table are the energies

of the four possible transitions calculated according to the Slater transition state procedure [20]. These transition energies cannot be compared directly to the experimental electronic spectra of these complexes because up to this point the spin–orbit coupling effect has not been included in the X_α calculations. The importance of the spin–orbit coupling effect for the 5f ligand-field states of the actinide complexes is evidently due to the relatively large value of the parameter $\xi(5f)$. This parameter varies from 1600–2700 cm^{-1} for the actinide series [21]. Theoretical calculations predict a value of 2113 cm^{-1} for 5f [21] of the pentavalent uranium ion (U^{5+}).

In the following discussion, a proposed scheme is introduced to include the spin–orbit coupling effect in the X_α results.

The ligand-field wave functions of the $5f^1$ system in C_{4v} symmetry can be represented as

$$b_2 : -1/\sqrt{2} \quad (|+2\rangle - |-2\rangle) \quad (1)$$

$$b_1 : 1/\sqrt{2} \quad (|+2\rangle + |-2\rangle) \quad (2)$$

$$e_{(1)} : C_1 | +3\rangle + C_2 | -1\rangle \quad (3)$$

$$e_{(2)} : -C_2 | +3\rangle + C_1 | -1\rangle \quad (4)$$

$$a_1 : |0\rangle \quad (5)$$

(ignoring at this point the ligand contributions in these 5f-like MOs), where C_1 and C_2 are mixing coefficients depending on the strength of the tetragonal distortion of the octahedral environment. These coefficients were taken from the X_α ground-state eigenvectors of the UOX_5^{2-} complexes.

In order to construct the necessary matrices for the c_{4v} double group, the effect of the spin–orbit coupling on the above wave functions was calculated by using the operator $\xi(r)(l_s)$.

Following the approach suggested by Goursat *et al.* [11], the reduction in the spin–orbital coupling parameter $\xi(5f)$ due to molecular orbital formation is allowed for by introducing the fraction of the charge ρ_i of the atomic U-5f orbital of each MO in the derivation of the spin–orbit coupling matrices (see Appendix). After adding the X_α -calculated

TABLE III. Theoretically Calculated f-f Transitions Including Spin-Orbit Coupling

	UOF ₅ ²⁻		UOCl ₅ ²⁻		UOBr ₅ ²⁻	
	Calculated	Found ^a	Calculated	Found ^b	Calculated ^a	Found ^a
Γ ₇ ← Γ ₇	1855	2380	1203	1555	1105	1490
Γ ₇ ← Γ ₇	6638	6792	6000	5050	5926	4865
Γ ₆ ← Γ ₇	6972	6837	6511	6161	6454	6080
Γ ₆ ← Γ ₇	10943	11448	9370	8584	9115	8163
Γ ₇ ← Γ ₇	12064	12420	11080	10616	10995	10460
Γ ₆ ← Γ ₇	20640	18660	18002	16835	17049	16194

^aRef. 15; ^bRef. 14.

transition energies (Table II) to the diagonal elements of the matrices given in the Appendix, the transition energies including the spin-orbit coupling effect can be calculated. By this method, the f-f transition energies were determined using a value for $5f$ equal to 2000 cm^{-1} for the UOX_5^{2-} complexes (Table III). The experimental transition energies also are shown in the same Table. For the sake of clarifying the effect of the magnitude of $\xi(5f)$ on the splitting pattern, a plot of transition energies as a function of $\xi(5f)$ are displayed in Fig. 3a for UOCl_5^{2-} , starting from the X_α spin-orbit coupling free results ($\xi = 0$). It is clear from Fig. 3a that the relative orders of the excited states are not affected over a wide range of ξ values, and only above $\xi = 2300$ is a reverse in the order of the second and third transitions observed. The theoretically calculated g factor of the ground state of UOCl_5^{2-} is also plotted as a function of $\xi(5f)$ in Fig. 3b (notice that $g = 0.77$ at $\epsilon = 2000 \text{ cm}^{-1}$ compared to the experimentally determined value of 1.09 [4]). It is calculated [22] from the ground-state doublet wave functions Γ_7^\pm which was obtained (after diagonalization) as follows:

$$g_{\parallel} = 2 \langle \Gamma_7^+ | (L_z + 2S_z) | \bar{\Gamma}_7 \rangle$$

$$g_{\perp} = 2 \langle \Gamma_7^+ | (L_x + 2S_x) | \bar{\Gamma}_7 \rangle$$

$$\langle g \rangle = \frac{1}{3} g_{\parallel} + \frac{2}{3} g_{\perp}$$

The assignment given in Table III of the electronic transitions of the UOX_5^{2-} complexes are based on the X_α results in combination with the spin-orbit coupling scheme. These are not in accord with the previous tentative assignments of Selbin *et al.* [4, 5], especially for the first excited state, where they proposed a $\Gamma_6 \leftarrow \Gamma_7$ transition. Although these authors [4] have reached these assignments based on some approximations and assumptions, it is not claimed here that the assignments in Table III (which are based on theoretical grounds) are in favour of their predictions. However, it demonstrates that our assignments are also acceptable; unfortunately there

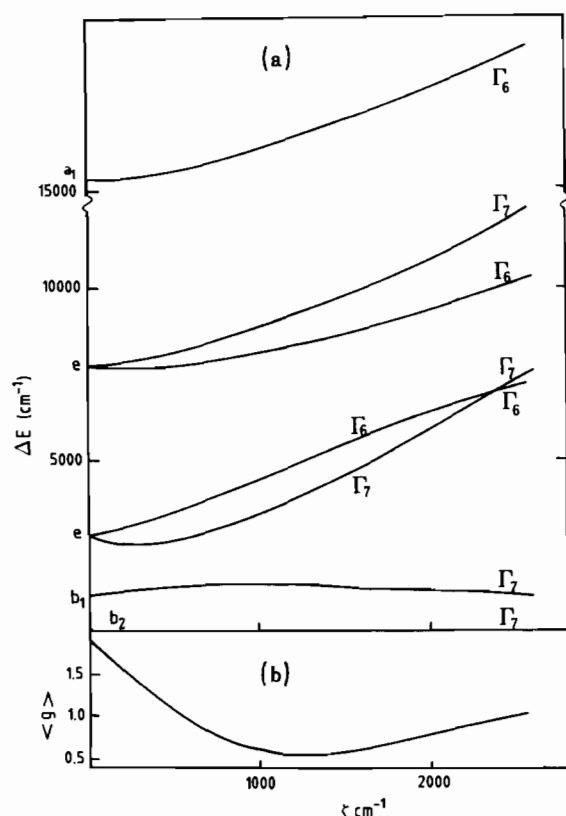


Fig. 3. (a) Variation of the X_α transition energies as a function of the magnitude of the spin-orbit parameter $\xi(5f)$. (b) The g -factor of the ground state of UOCl_5^{2-} as a function of $\xi(5f)$.

are no MCD data available for the UOX_5^{2-} complexes to settle the problem. On the other hand, the MCD of the $\text{NpO}_2\text{Cl}_4^{2-}$ complex [23] (a $5f^1$ system) is in favour of our assignment, namely that the first and second transitions are of the $\Gamma_7 \leftarrow \Gamma_7$ type. Here the similarity of the $\text{NpO}_2\text{Cl}_4^{2-}$ complex with U(V) complexes is not complete, because in $\text{NpO}_2\text{Cl}_4^{2-}$ one expects a large axial distortion of the ligand field due to the grouping $[\text{O}=\text{Np}=\text{O}]^{2+}$.

It is worth mentioning here that the muffin-tin form of the potential usually used in MS- X_α introduces an error in the X_α orbital energies of about the same magnitude as the spin-orbit coupling effect [7], but one hopes that much less error is involved in orbital energy differences. Nevertheless, the matching of the theoretically calculated transition energies (Table III) with experimental values is fairly good, if one of course accepts the assignment based on the X_α results.

Tetragonal Distortion of the Octahedral Field

In order to estimate the amount of tetragonal distortion in the complexes under consideration, X_α results for the 5f-like MOs of the UOX_5^{2-} complexes were combined with the ligand field theory.

In a coordinate system in which the axial oxygen and halogen atoms are oriented in the z axis, while the four equatorial halogen atoms are located in the x-y plane, the following crystal-field Hamiltonian can be formulated:

$$V_{C_{4v}} = V_{oh} + V_{tet}$$

$$V_{tet} = aY_2^\circ + bY_4^\circ + cY_6^\circ$$

where Y_l^m are the spherical harmonics of order $l = 2, 4$ and 6 . Following the approach of Selbin *et al.* [4], the three tetragonal parameters τ , γ and δ are related to the above Hamiltonian by: $\tau = 15a$, $\gamma = 33b$ and $\delta = 429/5c$. The τ , γ and δ parameters can be factorized into contributions from the axial and equatorial ligands as follows:

$$\tau = 30[\langle B_2 \rangle_o - \langle B_2 \rangle_x] \quad (6)$$

$$\gamma = 66[\langle B_4 \rangle_o - \langle B_4 \rangle_x] \quad (7)$$

$$\delta = 858/5[\langle B_6 \rangle_o - \langle B_6 \rangle_x] \quad (8)$$

where $\langle B_n \rangle$ is a radial integral defined by:

$$\langle B_n \rangle = Ze^2 \left\langle \frac{r^n}{R^{n+1}} \right\rangle$$

Utilizing the irreducible representations of the 5f orbitals in C_{4v} symmetry (eqns. (1-5)) and the explicit form of the ligand-field operator $V_{C_{4v}}$ the following transition energies can be formulated:

$$\Delta E (b_1 \leftarrow b_2) = \Delta \quad (9)$$

$$\Delta E (e_{(1)} \leftarrow b_2) = \Delta + \frac{1}{2}\theta - \tau + 9\gamma - 14\delta - \frac{1}{2}\beta \quad (10)$$

$$\Delta E (e_{(2)} \leftarrow b_2) = \Delta + \frac{1}{2}\theta - \tau + 9\gamma - 14\delta - \frac{1}{2}\beta \quad (11)$$

$$\Delta E (a_1 \leftarrow b_2) = \Delta + \theta + 4\tau + 13\gamma + 14\delta \quad (12)$$

where Δ and θ are the Reisfeld and Crosby parameters [24] for the octahedral field and

$$\beta = [(\theta/4 - 8\tau + 2\gamma + 14\delta)^2 - (15/16)\theta^2]^{1/2} \quad (13)$$

From the orthogonality relation between the wave functions of the orbitals $e_{(1)}$ and $e_{(2)}$ (eqns. 3 and 4) one can obtain the equation:

$$\langle e_{(2)} | V | e_{(1)} \rangle = 0 =$$

$$(C_1^2 - C_2^2)(\sqrt{15/8})\theta - C_1 C_2(\theta/4 - 8\tau + 2\gamma + 14\delta) \quad (14)$$

The sign of the τ , γ and δ parameters is obviously dependent on the magnitude of the axial field strength relative to the equatorial one; *i.e.* τ is positive if $\langle B_2 \rangle_o$ is greater than $\langle B_2 \rangle_x$.

From our previous discussion concerning the stronger bonding involved between uranium and oxygen, it seems more likely that $\langle B_n \rangle_o$ is greater than $\langle B_n \rangle_x$, so τ and the other parameters should be positive in these systems, corresponding to a tetragonal compression of the octahedron.

By this approach the ligand-field parameters of the UOX_5^{2-} complexes were calculated by fitting eqns. (9)-(14) to the theoretically calculated transition energies (Table II). They are given in Table IV. The positive sign of the tetragonal parameters τ , γ and δ is another confirmation to the tetragonal compression of the ligand field of these complexes.

TABLE IV. Ligand-field Parameters Derived from X_α Results for UOX_5^{2-}

	UOF_5^{2-}	$UOCl_5^{2-}$	$UOBr_5^{2-}$
Δ	1920 ^a	1056	977
θ	4158	3084	2878
τ	247	98.4	44
γ	629	607	587
δ	209	195	184

^aAll parameters are in cm^{-1} .

The ligand-field parameters of the UOX_5^{2-} complexes increase in the order $Br < Cl < F$, which is in good agreement with the spectrochemical series.

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Appendix

Matrices of Spin-Orbit Coupling using the Irreducible Representations of the C_{4v} Points Groups for the f^1 System

The f orbitals in C_{4v} span the irreducible representations $a_1 + b_1 + b_2 + 2e$. Ignoring the ligand contributions the f-like MOs can be expressed as:

$$b_2 = \sqrt{\rho_1} f_{b_2}, \quad b_1 = \sqrt{\rho_2} f_{b_1}$$

$$e_{(1)} = \sqrt{\rho_1} f_{e(1)}, \quad e_{(2)} = \sqrt{\rho_4} f_{e(2)} \quad \text{and}$$

$$a_1 = \sqrt{\rho_5} f_{a_1}$$

where ρ_i is the fraction of the U-5f charge involved in this MO.

Using the explicit form of the U-5f orbitals (eqns. (1-5)) the following matrices are constructed:

$\Gamma_6 =$

$$\begin{vmatrix} e^+_{(1)} & e^+_{(2)} & a_1^- \\ \rho_3(\frac{3}{2}C_1^2 - \frac{1}{2}C_2^2)\xi & -2C_1C_2\sqrt{\rho_3\rho_4}\xi & \sqrt{3}C_2\sqrt{\rho_3\rho_5}\xi \\ 0 & \rho_4(\frac{3}{2}C_2^2 - \frac{1}{2}C_1^2)\xi & \sqrt{3}C_1\sqrt{\rho_4\rho_5}\xi \\ 0 & 0 & 0 \end{vmatrix}$$

$$+ = +\frac{1}{2} \text{ spin} \quad - = \frac{1}{2} \text{ spin}$$

$\Gamma_7 =$

$$\begin{vmatrix} e_{(1)}^- & e_{(2)}^- & b_2^+ & b_1^+ \\ \rho_3(\frac{1}{2}C_2^2 - \frac{3}{2}C_1^2)\xi & 2C_1C_2\sqrt{\rho_3\rho_4}\xi & (\sqrt{5}C_2 - \sqrt{3}C_1)\sqrt{\rho_1\rho_3}\xi/2 & (\sqrt{5}C_2 + \sqrt{3}C_1)\sqrt{\rho_2\rho_3}\xi/2 \\ 0 & \rho_4(\frac{1}{2}C_1^2 - \frac{3}{2}C_2^2)\xi & (\sqrt{5}C_1 + \sqrt{3}C_2)\sqrt{\rho_1\rho_4}\xi/2 & (\sqrt{5}C_1 - \sqrt{3}C_2)\sqrt{\rho_2\rho_4}\xi/2 \\ 0 & 0 & 0 & -\sqrt{\rho_1\rho_2}\xi \\ 0 & 0 & 0 & 0 \end{vmatrix}$$