APPLICATIONS OF DSCPCF MODEL IN RARE EARTH COMPLEXES(V)*

—ANALYSIS OF SPECTRA OF THE NEODYMIUM AND ERBIUM TETRA(2-THENOYLTRIFLUOROACETONE) MONO PIPERIDINE COMPLEXES

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Abstract

The complexes, Nd(TTA)$_4$·HP and Er(TTA)$_4$·HP, have been prepared, and their UV-VIS-NIR absorption spectra measured. The matrix element expressions with $J=1/2-15/2$ of $f^9$ and $f^{11}$ configurations in $D_4^+$ symmetry field were derived with the Double Sphere Coordination Point Charge Field Model. And the influence of change in symmetry of the complex unit REO$_5$ on splitting of their levels was discussed. Based on theoretical calculations, the absorption peaks in the spectra were assigned.

Rare-earth-β-diketon complexes have been receiving increased attention recently as a result of their excellent optical and magnetic properties and their importance in many practical applications. However, although a large number of experimental researches on these complexes have been reported, no detailed theoretical study of the relation between their solution absorption spectra and their coordination types has yet appeared in literature, especially no quantitative calculations involving the effect of coordination field. Hence, besides La, Pr and Lu, we synthesized the tetration(2-thenoyltrifluorooacetone) mono piperidine complexes of all lanthanide trivalent ions. In this paper, we report only the theoretical analysis of the UV-VIS-NIR absorption spectra of Nd$^{3+}$ and Er$^{3+}$ complexes and some relative questions.

1. Experiment

1. Materials

HTTA, A. R. was produced by Shanghai No. 3 Reagent Plant. Pure piperidine was made in the West Germany. Nd$_2$O$_3$ and Er$_2$O$_3$ contents were more than 99.9%, produced by Shanghai Yuelong Chemical Plant.

2. Synthesis of Complex

A mixture containing 0.5077 g of Er$_2$O$_3$ and approximate 5 ml of concentrated hydrochloric acid was heated, and then the solution was distilled to slight dry to yield ErCl$_3$ crystal-

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line. Moreover 15 ml of absolute ethanol was added to make the crystalline dissolve. Next, to a solution at about 90°C and containing 2.3776 g of HTTA and 1.05 ml of piperidine in 15 ml of absolute ethanol, the warm filtered solution of ErCl₃ in absolute ethanol was added. The reaction mixture was maintained at ambient temperature for four days, and then filtered. The crystalline product was washed with cold absolute ethanol and vacuum-dried to give the pure product Er(TTA)₄·HP which had a tetragonal-prism crystalline form with a pink-red of color, and its yield was 73%.

The synthetic procedure of Nd(TTA)₄·HP was the same as Er(TTA)₄·HP, and its crystalline form was a tetragonal-prism with a purplish red of color, and its yield was 50%.

3. Elemental Analysis

The contents of carbon, hydrogen and sulphur in the complexes were analyzed by the classical combustion method, and that of metal by the following complexometric titration method: 0.1 g of the complex sample was accurately weighed and moistened with 15 ml of deionized water. After the addition of approximate 0.7 ml of concentrated HNO₃, the solution was heated to boiling to decompose the sample. Then, the solution was diluted, 5 drops of 0.3% of dimethyl phenolic orange indicator were added, and the color of the solution was adjusted to purplish red with 30% of urotropine. Next, an excess of 8 ml of the amine was added, and the stirred mixture was titrated with 0.04151 mol/L of Na₂EDTA standard solution until the sharp end-point change from purplish red to bright yellow occurred. Results of elemental analysis are as follows.

For Er(TTA)₄·HP, the formula is C₃₇H₅₆O₈S₄NF₁₄Er (calc.: Er, 14.70; C, 39.05; H, 2.48; S, 11.27. exp.: Er, 14.56; C, 38.44; H, 2.61; S, 12.46). And for Nd(TTA)₄·HP, the formula is C₃₇H₅₆O₈S₄NF₁₄Nd (calc.: Nd, 12.93; C, 39.85; H, 2.53; S, 11.50. exp.: Nd, 12.88; C, 40.01; H, 3.20; S, 10.51).

4. Measurement of Absorption Spectrum

The UV-VIS-NIR absorption spectra of the complexes in acetonitrile solution were measured in the region of 190--2500 nm with a Shimadzu UV-365 double-monochromator record-

![Absorption spectrum of Nd(TTA)₄·HP](image_url)
ing spectrophotometer (made in Japan), by using 1-cm sample cells at room temperature. The results of measurement showed that the complex Nd(TTA)_4·HP had fifteen characteristic absorption bands of f-f transition centered in the region of 420—920 nm, and beyond 920 nm none of these absorption bands were observed. An example of these absorption bands is given in Fig. 1. And the complex Er(TTA)_4·HP had nine intra-f transition absorption bands centered in the region of 480—1580 nm. An example is shown in Fig. 2. Besides, all complexes exhibited strong bands at wavelengths below 420 nm, corresponding primarily to absorption by the organic ligands. The infrared spectra of their solid samples were measured in the region of 400—4000 cm⁻¹ with a Unicam-SP 1100 type infrared spectrophotometer, by using KBr as a disperser. The results are as follows: for HTTA, ν_{s=2>C=O} is 1662 cm⁻¹(s) and 1644 cm⁻¹(s); ν_{s=2>C=C} is 1521 cm⁻¹(w). For Nd(TTA)_4·HP, ν_{s=2>C=O} 1609 cm⁻¹(vs), ν_{s=2>C=C} 1538 cm⁻¹(s). And for Er(TTA)_4·HP, ν_{s=2>C=O} 1612 cm⁻¹(vs), ν_{s=2>C=C} 1537 cm⁻¹(s).

II. Spectral Analysis

1. The DSCPCF Perturbation Energy Levels of the Ed^{3+} and Er^{3+} Ions in D₄* Symmetry Field

In coordination field, the energy operator of the Nd^{3+} and Er^{3+} ions is \( \hat{H} = \hat{H}_0 + \hat{H}_e \), where \( \hat{H}_0 \) is the free-ion Hamiltonian including spin-orbit coupling (the corresponding part of its experimental eigenvalues is shown in the middle of Figs. 4 and 5) and \( \hat{H}_e \) represents the DSCPCF perturbation potential.

It may be seen from the above infrared spectra that with the formation of the complexes, the vibrational absorption peaks of the group \( \nu_C=O \) of HTTA not only become a single peak from original double peaks, but also shift to red by \( \sim 45 \) cm⁻¹. This result shows not only that four ligands of the complex RE(TTA)_4·HP are all coordinate to the metal ion RE^{3+} with...
double teeth, but also that the two groups \( \gamma C=O \) and \( \gamma C=O^- \) are equal for the formation of the long conjugate \( \pi \)-bonds. In addition, in reference to Ref. [2], we may assume that the coordination type of RE(TTA)₄·HP in solution may alter between a square antiprism \( (D_{4h}^s) \) and a square prism \( (D_{4v}^s) \). Suppose the complex unit REO₈ has a general coordination type shown in Fig. 3, the coordinates of 8 ligand oxygen atoms are then as follows:

\[
\begin{align*}
(R, \Theta, \frac{\pi}{4} + \alpha), & \quad (R, \Theta, \frac{3\pi}{4} + \alpha), \\
(R, \Theta, \frac{5\pi}{4} + \alpha), & \quad (R, \Theta, \frac{7\pi}{4} + \alpha), \\
(R, \pi - \Theta, \frac{\pi}{4} - \alpha), & \quad (R, \pi - \Theta, \frac{3\pi}{4} - \alpha), \\
(R, \pi - \Theta, \frac{5\pi}{4} - \alpha), & \quad (R, \pi - \Theta, \frac{7\pi}{4} - \alpha).
\end{align*}
\]

**Fig. 3.** Arrangement of atoms in complex unit REO₈.

If \( 2\beta \) is used to represent the bond angle \( \angle O(1)-\text{RE}-O(5) \), the following relation among the angles \( \Theta, \alpha \) and \( \beta \) can be found:

\[
\sin \Theta \cos \alpha = \cos \beta. \tag{1}
\]

Then, for the coordination type of the square antiprism, \( 2\alpha = 45^\circ \); if \( \alpha = 0^\circ \) and the distances are \( O(1)-O(2) \neq O(1)-O(5) \), the complex unit is the square prism; when the angle \( 2\beta \) is fixed and the angle \( \alpha \) changed it has a \( D_{4h}^s \) symmetry. And the ligand-field splitting of levels of the complexes in \( D_{4h}^s \)-field and \( D_{4v}^s \)-field may be dealt with as that in \( D_{4v}^s \)-field.

In a \( D_{4v}^s \) symmetry field, the DSCCPF perturbation potential \( \hat{H}_c \) can be expanded in the form:

\[
\hat{H}_c = \sum_{i=1}^{N} \left\{ A_{3}^2 r_{i}^2 C_{6}^0(i) + A_{3}^4 r_{i}^4 C_{6}^0(i) + A_{0}^3 r_{i}^3 C_{6}^0(i) \right. \\
+ \left. A_{4}^3 r_{i}^3 [ C_{4}^4(i) + C_{-4}^4(i) ] + A_{4}^5 r_{i}^5 [ C_{4}^4(i) + C_{-4}^4(i) ] \right\}, \tag{2}
\]

in which \( C_{m}^k(i) = \sqrt{\frac{4\pi}{2k+1}} Y_{m}^{k}(\theta_{i}, \varphi_{i}) \), and is an irreducible tensor operator defined by Racah; \( (r_{i}, \theta_{i}, \varphi_{i}) \) are the coordinates of 4f electrons; and \( N \) is the number of 4f
electrons. According to the DSCPCF model, the ligand field parameters $A_{m}^{k}$ are:

$$A_{m}^{k} = \sum_{j=1}^{n} \sqrt{\frac{4\pi}{2k+1}} \left( \frac{q_{j}}{r_{j}^{k+1}} - \frac{Z_{j}^{*}}{R_{j}^{k+1}} \right) Y_{m}^{k*} (\Theta_{j}, \Phi_{j}),$$  \hspace{1cm} (3)

where $r_{j}$ is the distance of the $j$th bond charge $q_{j}$ from the central ion RE$^{3+}$, and $q_{j}$ and $r_{j}$ are given in Eqs. (1) and (2) in Ref. [4], respectively. $(R_{j}, \Theta_{j}, \Phi_{j})$ are the coordinates of the $j$th ligand oxygen atom; $Z_{j}^{*}$ is its effective nuclear charge and $Y_{m}^{k*} (\Theta_{j}, \Phi_{j})$ a complex conjugate spherical harmonic of degree $k$ evaluated at the position $(R_{j}, \Theta_{j}, \Phi_{j})$.

In accordance with Fig. 3 and the corresponding coordinates of ligand oxygen atoms (for bond charges, their coordinates are $(r_{j}, \Theta_{j}, \Phi_{j})$), the specific form of $A_{m}^{k}$ can be obtained by Eq. (3), they are:

$$A_{0}^{0} = 4 \left( \frac{a}{r^{3}} - \frac{Z_{0}^{*}}{R^{3}} \right) \cdot (3\cos^{2}\Theta - 1),$$

$$A_{0}^{1} = \left( \frac{a}{r^{3}} - \frac{Z_{0}^{*}}{R^{3}} \right) \cdot (35\cos^{4}\Theta - 30\cos^{2}\Theta + 3),$$

$$A_{1}^{0} = \frac{1}{2} \left( \frac{a}{r^{7}} - \frac{Z_{0}^{*}}{R^{7}} \right) \cdot (231\cos^{6}\Theta - 315\cos^{4}\Theta + 105\cos^{2}\Theta - 5),$$

$$A_{1}^{1} = -\sqrt{35} \left( \frac{a}{r^{3}} - \frac{Z_{0}^{*}}{R^{3}} \right) \cdot \sin 4\Theta \cos 4\alpha,$$

$$A_{1}^{2} = -\frac{3}{4} \sqrt{14} \left( \frac{a}{r^{7}} - \frac{Z_{0}^{*}}{R^{7}} \right) \cdot (11\cos^{2}\Theta - 1) \cdot \sin 4\Theta \cos 4\alpha.$$  \hspace{1cm} (4)

In order to reduce the calculations of energy levels, it is necessary to make a linear transformation for the L-S coupling wavefunctions $|\tau SLJM\rangle$ (abbreviated as $|JM\rangle$ below), to give the basis functions for the irreducible representations of $D_{4h}$ group:

$$|J\Gamma\rho\rangle = \sum_{M} S_{M,\tau JL}^{J\Gamma\rho} |JM\rangle.$$  \hspace{1cm} (5)

Here, $S_{M,\tau JL}^{J\Gamma\rho}$ are transformation coefficients and can be found from the tables of Tang Aoqing, Griffith and Lai Shantao, in which, the basis functions for the irreducible representations of the $D_{4h}$ group are classified by three symbols $J, \Gamma$ and $\rho$, which are respectively the irreducible representation symbols of $R(3)^{*}, O^{*}$ and $D_{4h}^{*}$ groups; and $\rho$ is a raw label of the $\rho$.

Matrix element expressions of the operator $H_{c}$ in $D_{4h}$-field can be derived from the above equations, and are tabulated in Appendix as linear combination of $T_{m}^{k}$, where $T_{0}^{0} = aA_{0}^{0}(r^{3}), T_{4}^{0} = bA_{0}^{0}(r^{4}), T_{0}^{6} = cA_{0}^{0}(r^{6}), T_{4}^{6} = dA_{0}^{0}(r^{4}),$ and $T_{4}^{6} = eA_{0}^{0}(r^{6})$. And the coefficients $a, b$ and $c$ for configurations $f^{3}$ and $f^{4}$ are given in Table 1. Coefficients $d$ and $e$ are respectively in relation to $b$ and $c$: for the levels with total angle moment $J < 15/2$, there are $d = \sqrt{70} b, e = \sqrt{14} c$; for that with $J = 15/2, d = \sqrt{2} b, e = \sqrt{2} c$.

1) Lai Shantao et al., Transformation coefficients of the basis vectors of irreducible representations for the SO(3)—O Groups, 1983.
### Table 1

<table>
<thead>
<tr>
<th>J</th>
<th>( ^{4}S_{3/2} )</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>J</th>
<th>( ^{4}G_{5/2} )</th>
<th>a</th>
<th>b</th>
<th>c</th>
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<td>3/2</td>
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<td>0</td>
<td>9/2</td>
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<td></td>
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<tr>
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<td>( ^{4}G_{7/2} )</td>
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<td></td>
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<td>17</td>
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Note: For the levels with total angle moment \( J = 1/2 \), these coefficients are all zero.

Now, it may be seen that the matrix elements of \( \hat{H}_c \) are the functions of arguments \( r, q, R, Z_0^*, \langle r^k \rangle, \Theta \) and \( a \). For the Nd(TTA)\(_4\) \cdot HP complex, the bond length \( R \) of the Nd—O bond is assumed as 4.60\( a_0 \); and radial parameters \( \langle r^k \rangle \) have the values\(^{[2]}\) that \( r^2 = 1.001a_0^2 \), \( r^4 = 2.401a_0^4 \), \( r^6 = 12.396a_0^6 \). In addition, the effective nuclear charge \( Z_M^* \) of the ion Nd\(^{3+}\) is\(^{[3]}\) 19.40\( e \), and that of the coordination oxygen atoms is assumed as \( Z_0^* = 1.50e \). Thus, we have \( q = 0.9183e \) and \( r = 3.5991a_0 \). For the Er(TTA)\(_4\) \cdot HP complex, these parameters are as follows: \( R = 4.42a_0 \); \( \langle r^3 \rangle = 0.666a_0^3 \), \( \langle r^4 \rangle = 1.126a_0^4 \), \( \langle r^6 \rangle = 3.978a_0^6 \); \( Z_M^* = 24.60 \) \( e^{[3]} \), \( Z_0^* = 2.00e \); thus \( q = 1.2109e \) and \( r = 3.4393a_0 \). Besides these, let \( 2\alpha = 45^\circ \) and \( \Theta = 61.873^\circ \) (this corresponds to the \( D_{4h}^2 \) coordination), the DSCPCF perturbation energy levels of the ions Nd\(^{3+}\) and Er\(^{3+}\) are then obtained by diagonalizing the matrix of \( \hat{H}_c \) and displayed in Figs. 4 and 5 respectively. Here, for the sake of comparison, the energy levels of them calculated by the Electrostatic Crystal Field Model (ECF model) are also displayed on the left of both the figures. In these calculations the negative charges of the coordination oxygen atoms for the complexes Nd(TTA)\(_4\) \cdot HP and Er(TTA)\(_4\) \cdot HP are respectively 0.56\( e \) and 0.62\( e \).

It should be pointed out that the two levels \( ^{4}F_{5/2} \) and \( ^{4}F_{7/2} \) of Er\(^{3+}\) are close to each other in energy; hence, the term interaction of them should be taken into consideration in the calculations. The matrix elements relevant to this with \( J = J' \) can be found in Appen-
Fig. 4. Coordination-field energy levels of Nd(TTA)_4. b. HP (cm⁻¹).

dix, and those of non-zero with $J \neq J'$ are as follows:

$$\langle F_{J''} U'_e | \hat{H}_c | F_{J''} U'_e \rangle = -\sqrt{6} (T_0 + T_0),$$
Fig. 5. Coordination-field energy levels of Er(TTA)·HP (cm⁻¹).

\[
\langle F_{3/2} U'e'' | \hat{H}_c | F_{5/2} E'' e'' \rangle = -\sqrt{30} T_0^0 + \frac{5}{\sqrt{6}} T_0^1 - \frac{1}{\sqrt{30}} T_4^1,
\]

\[
\langle F_{3/2} U'e'' | \hat{H}_c | F_{3/2} U'e'' \rangle = \frac{1}{\sqrt{6}} (6 T_0^0 - T_0^1 - T_4^1),
\]

where \( T_0^0 = \frac{3}{175} A_0^0(r^2) \), \( T_0^1 = \frac{1}{42} A_1^1(r^4) \), \( T_4^1 = \frac{\sqrt{70}}{42} A_4^1(r^4) \). The splitting of the two levels considering the term interaction is shown in the upper right of Fig. 5. For the ion
Nd\textsuperscript{3+}, although the energy difference between \textsuperscript{4}G_{5/2} and \textsuperscript{2}G_{7/2} is very small, too, no term interaction occurs because the total spin angle moments of them are different. And the term interactions between the levels \textsuperscript{4}S_{3/2} and \textsuperscript{4}F_{7/2} are also not in existence because the reduced matrix element between them is zero.

It can be seen from Figs. 4 and 5 that the splittings of all levels calculated by the two models are different, especially for the levels \textsuperscript{4}F_{3/2}, \textsuperscript{4}F_{5/2}, \textsuperscript{4}F_{7/2} and \textsuperscript{4}G_{7/2} of Nd\textsuperscript{3+}. The case is which splitting is reasonable. For this question we shall lay stress on discussing it later.

2. Comparison of Calculated Results With Observed Spectra

According to the electric-dipole selection rules of the \textit{D}_4\textsuperscript{*} symmetry and considering the effect of population number and some other factors, we may assign the absorption peaks in spectra of the complexes. Results of the assignments show that for all the absorption peaks, the calculated absorption wavelengths by the DSCPCF model are in good agreement with the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ndtta_absorption.pdf}
\caption{Assignments of part absorption bands of Nd(TTA)\textsubscript{4} - HP. (The absorption bands of the transitions \textsuperscript{4}S_{3/2} \rightarrow \textsuperscript{4}F_{7/2} and \textsuperscript{4}S_{3/2} \rightarrow \textsuperscript{4}S_{3/2} overlapped each other)}
\end{figure}
observed ones. Because of the limit space, only several examples of the assignments are displayed in Figs. 6 and 7.

![Diagram](image)

**Fig. 7.** Assignments of part absorption bands of Er(TTA)$_4$·HP.

3. The Influence of Change in Symmetry of the Complex Unit REO$_8$ on the DSCPCF Splitting

It has been pointed out that the above calculations carried out are on the basis of the assumption that the symmetry of the complex unit REO$_8$ is $D_{4h}^*$. Actually, the symmetry of the complex unit in solution may deviate from the strict $D_{4h}^*$ symmetry because of steric repulsion among the ligands. In order to analyze the influence of this distortion of the complex unit on the DSCPCF splitting, we took the Nd(TTA)$_4$·HP complex as an example and calculated the variation of its DSCPCF splitting with the $\alpha$ angle at $2\beta=70.87^\circ$. The results obtained are shown in Fig. 8. From Fig. 8, we may see that in the vicinity of $2\alpha=45^\circ$, the variations of the DSCPCF splittings of all levels, except those of the levels $^2P_{1/2}$, $^1G_{1/2}$ and $^1S_{1/2}$, with angle $\alpha$ are very obvious. This may not only interpret the lower resolution and some wider overlapped bands of the observed spectra, but also shows that the symmetry of the complex unit REO$_8$ is basically $D_{4h}^*$, though it is not the strict $D_{4h}^*$, or else the good agreement given above would not be obtained.

III. DISCUSSION

It was pointed out before that when the splittings of the ground levels are basically the
Fig. 8. The variation of the DSCPCF energy levels (in cm⁻¹) with the angle α.
same, the differences between those of excited levels calculated by the DSCPCF and the ECF models are very big. For example, for the three levels $^4F_{3/2}$, $^4F_{5/2}$, and $^4G_{7/2}$ of the Nd(TTA)$_4$·HP complex the ratios of their DSCPCF to ECF splittings are respectively 0.745, 0.720 and 2.891. Because the observed spectra have been interpreted by the DSCPCF model in the above, it is obvious that the ECF splittings are not very reasonable.

Hüfner\textsuperscript{[s]} pointed out that for the rare earth compounds, the values of $A^k_m$ calculated by the ECF model were the largest for $k=2$ terms, in the right order of magnitude for $k=4$ terms, and too small in an order of magnitude for $k=6$ terms. This defect of the ECF model can be overcome by the DSCPCF model. We shall take the complex Nd(TTA)$_4$·HP as an example and explain this as follows.

Let $A^k_m(D)$ represent the coordination field parameters calculated by the DSCPCF model, and $A^k_m(E)$ by the ECF model. Thus, the ratios of $A^k_m(D)$ to $A^k_m(E)$ are:

$$R(k) = A^k_m(D)/A^k_m(E) = Z^k_0/Z^k_{M}Q[(1 + \sqrt{Z^k_0/Z^k_M})^{k-1} - 1],$$

where $Q$ represents the charges of coordination oxygen atoms used in the ECF model. Substituting the relative parameters into the above equation, we have $R(2) = 0.7448$, $R(4) = 2.9133$, $R(6) = 6.4555$.

Using the DSCPCF model we can make the calculated value of $A^k_m$ decrease and that of $A^k_m$ increase. This is just the advantage of the DSCPCF model over the ECF model.

**Appendix**

**The Matrix Element Expressions in a $D_{4}^\text{h}$ Symmetry Field (for $J = J'$)**\textsuperscript{1}

\[
J = \frac{1}{2} : \langle E'\varepsilon' \| E'\varepsilon' \rangle = 0; \\
J = \frac{3}{2} : \langle U'\varepsilon' \| U'\varepsilon' \rangle = -T_6^3; \\
\langle U'\varepsilon'' \| U'\varepsilon'' \rangle = T_6^3; \\
J = \frac{5}{2} : \langle U'\varepsilon' \| U'\varepsilon' \rangle = 24T_6^3 + 132T_6^4; \\
\langle E''\varepsilon'' \| E''\varepsilon'' \rangle = -154T_6^3 - 22T_6^4, \\
\langle U'\varepsilon'' \| U'\varepsilon'' \rangle = -22T_6^3 + 22T_6^4 + 22T_6^5, \\
\langle E''\varepsilon'' \| U'\varepsilon'' \rangle = 2\sqrt{5} \left( -3T_6^3 + 22T_6^4 - \frac{22}{5} T_6^5 \right); \\
J = \frac{7}{2} : \langle E'\varepsilon' \| E'\varepsilon' \rangle = 147T_6^3 + 5T_6^4 + 21T_6^5 - 5T_6^6, \\
\langle U'\varepsilon' \| U'\varepsilon' \rangle = -10T_6^3 + 141T_6^4 + 3T_6^5 - 21T_6^6 + 5T_6^7, \\
\langle E'\varepsilon' \| U'\varepsilon' \rangle = \sqrt{35} \left( -5T_6^3 - 3T_6^4 - T_6^5 + \frac{3}{5} T_6^6 - \frac{1}{7} T_6^7 \right), \\
\langle E''\varepsilon'' \| E''\varepsilon'' \rangle = -189T_6^3 + 3T_6^4 - 27T_6^5 - 3T_6^6; \\
\]

\textsuperscript{1} a. Since matrix elements bear no relation to the row labels of the irreducible representations of group $D_{4}^\text{h}$, the row labels $\rho$ have been left out.

b. In the above matrix element expressions the operator $\hat{H}_e$ has been omitted to simplify the expressions. Besides, for the matrix element expressions with $J \leqslant 13/2$, the labels $J$ also have been left out.
\[ \langle U'\varepsilon'' \parallel U'\varepsilon'' \rangle = 10T_0^4 - 99T_6^4 - 11T_8^4 + 27T_4^4 + 3T_2^4, \]

\[ \langle E'' \varepsilon'' \parallel U'\varepsilon'' \rangle = \sqrt{3} \left( -5T_0^4 - 45T_6^4 + 7T_8^4 + 9T_4^4 + T_2^4 \right); \]

\[ J = \frac{9}{2} : \langle (1)U'\varepsilon'' \parallel (1)U'\varepsilon'' \rangle = -T_0^4 + 102T_6^4 + 20T_8^4, \]

\[ \langle (2)U'\varepsilon'' \parallel (2)U'\varepsilon'' \rangle = -3T_0^4 - 18T_6^4 + 12T_8^4, \]

\[ \langle (1)U'\varepsilon'' \parallel (2)U'\varepsilon'' \rangle = -\sqrt{3/7} (30T_4^4 + 8T_2^4), \]

\[ \langle E'\varepsilon' \parallel E'\varepsilon' \rangle = -98T_0^4 - 8T_6^4 - 14T_8^4 + 8T_4^4, \]

\[ \langle (1)U'\varepsilon' \parallel (1)U'\varepsilon' \rangle = T_0^4 + 177T_6^4 - 15T_8^4 + 17T_4^4 - 5T_2^4, \]

\[ \langle (2)U'\varepsilon' \parallel (2)U'\varepsilon' \rangle = 3T_0^4 - 3T_6^4 - 3T_8^4 - 3T_4^4, \]

\[ \langle E'\varepsilon' \parallel (1)U'\varepsilon' \rangle = \sqrt{2} \left( -\frac{5}{2} T_0^4 - 25T_6^4 - \frac{7}{2} T_8^4 + 5T_4^4 - \frac{1}{2} T_2^4 \right), \]

\[ \langle E'\varepsilon' \parallel (2)U'\varepsilon' \rangle = \sqrt{42/2} \left( -T_0^4 + 10T_6^4 - 3T_8^4 - 2T_4^4 - \frac{3}{7} T_2^4 \right), \]

\[ \langle (1)U'\varepsilon' \parallel (2)U'\varepsilon' \rangle = \sqrt{21} \left( -25T_4^4 + 2T_6^4 + \frac{5}{7} T_8^4 - \frac{6}{7} T_2^4 \right); \]

\[ J = \frac{11}{2} : \langle E'\varepsilon' \parallel E'\varepsilon' \rangle = -1911T_0^4 - 13T_6^4 - 273T_8^4 + 13T_4^4, \]

\[ \langle (1)U'\varepsilon' \parallel (1)U'\varepsilon' \rangle = 58T_0^4 - 669T_6^4 + 347T_8^4 + 189T_4^4 - 75T_2^4, \]

\[ \langle (2)U'\varepsilon' \parallel (2)U'\varepsilon' \rangle = -175T_0^4 + 84T_6^4 + 186T_8^4 + 84T_4^4 + 62T_2^4, \]

\[ \langle E'\varepsilon' \parallel (1)U'\varepsilon' \rangle = \sqrt{455} (-9T_0^4 + 39T_6^4 - 4T_8^4 - 39/5T_4^4 - 4/7T_2^4), \]

\[ \langle E'\varepsilon' \parallel (2)U'\varepsilon' \rangle = \sqrt{91/2} (-10T_0^4 + 195T_6^4 + 59/2T_8^4 - 39T_4^4 + 59/14T_2^4), \]

\[ \langle (1)U'\varepsilon' \parallel (2)U'\varepsilon' \rangle = \sqrt{10} (-99T_0^4 + 1173/2T_6^4 - 35/4T_8^4 + 483/10T_4^4 - 29/4T_2^4), \]

\[ \langle E'' \varepsilon'' \parallel E'' \varepsilon'' \rangle = 1001T_0^4 - 143T_6^4 + 143T_8^4 + 143T_4^4, \]

\[ \langle (1)U'\varepsilon'' \parallel (1)U'\varepsilon'' \rangle = -58T_0^4 + 991T_6^4 - 129T_8^4 - 143T_4^4 - 143T_2^4, \]

\[ \langle (2)U'\varepsilon'' \parallel (2)U'\varepsilon'' \rangle = 175T_0^4 + 504T_6^4 - 248T_8^4, \]

\[ \langle E'' \varepsilon'' \parallel (1)U'\varepsilon'' \rangle = \sqrt{145} (-29T_0^4 - 5T_6^4 + 7T_8^4 + T_4^4 + T_2^4), \]

\[ \langle E'' \varepsilon'' \parallel (2)U'\varepsilon'' \rangle = \sqrt{1450} (-9T_0^4 - 69/2T_6^4 - 7/4T_8^4 + 69/10T_4^4 - 1/4T_2^4), \]

\[ \langle (1)U'\varepsilon'' \parallel (2)U'\varepsilon'' \rangle = \sqrt{10} (99T_0^4 + 759/2T_6^4 + 77/4T_8^4 + 897/10T_4^4 - 13/4T_2^4); \]

\[ J = \frac{13}{2} : \langle E'\varepsilon' \parallel E'\varepsilon' \rangle = 449631T_0^4 + 7930T_6^4 + 64233T_8^4 - 7930T_4^4, \]

\[ \langle (1)U'\varepsilon' \parallel (1)U'\varepsilon' \rangle = 21T_0^4 + 219051T_6^4 + 886337T_8^4 - 521557T_4^4 - 22265T_2^4, \]

\[ \langle (2)U'\varepsilon' \parallel (2)U'\varepsilon' \rangle = 31T_0^4 - 116754T_6^4 - 83875T_8^4 - 12078T_4^4. \]
\[
\langle E' \varepsilon'\| (1) U' \varepsilon' \rangle = \sqrt{\frac{13}{4}} (-T_0^5 + 71370 T_0^6 + 52521 T_0^8 - 14274 T_0^4 + 7503 T_0^8),
\]
\[
\langle E' \varepsilon'\| (2) U' \varepsilon' \rangle = \sqrt{\frac{429}{8}} (-3 T_0^5 + 47580 T_0^6 + 2135 T_0^8 - 9516 T_0^4 + 3057 T_0^8),
\]
\[
\langle (1) U' \varepsilon'\| (2) U' \varepsilon' \rangle = \sqrt{\frac{33}{8}} (9 T_0^5 - 193980 T_0^6 - 54229 T_0^8 - 22692 T_0^4 - 4331 T_0^8),
\]
\[
\langle (1) E'' \varepsilon''\| (1) E'' \varepsilon'' \rangle = 39949 T_0^5 + 47515 T_0^8 + 5707 T_0^4 - 47515 T_0^8,
\]
\[
\langle (2) E'' \varepsilon''\| (2) E'' \varepsilon'' \rangle = -234234 T_0^5 - 42757 T_0^8 - 33462 T_0^4 + 42757 T_0^8,
\]
\[
\langle (1) U' \varepsilon''\| (1) U' \varepsilon'' \rangle = -21 T_0^5 - 267729 T_0^6 - 27511 T_0^8 + 45201 T_0^4 - 38857 T_0^8,
\]
\[
\langle (2) U' \varepsilon''\| (2) U' \varepsilon'' \rangle = -31 T_0^5 - 89914 T_0^6 + 10065 T_0^8 - 17446 T_0^4 + 43615 T_0^8,
\]
\[
\langle (1) E'' \varepsilon''\| (2) E'' \varepsilon'' \rangle = \sqrt{4290} \left( -3185 T_0^5 + \frac{4459}{4} T_0^8 - 455 T_0^4 \right.
\]
\[
\left. - \frac{4459}{4} T_0^8 \right),
\]
\[
\langle (1) E'' \varepsilon''\| (1) U' \varepsilon'' \rangle = \sqrt{11895} \left( -\frac{7}{122} T_0^5 - 1869 T_0^4 + 889 T_0^8 + \frac{1869}{5} T_0^4 + 127 T_0^8 \right),
\]
\[
\langle (1) E'' \varepsilon''\| (2) U' \varepsilon'' \rangle = \sqrt{87230} \left( \frac{37}{244} T_0^5 + 227 T_0^8 + \frac{1561}{4} T_0^8
\]
\[
\left. - \frac{227}{5} T_0^4 + \frac{223}{4} T_0^8 \right),
\]
\[
\langle (2) E'' \varepsilon''\| (1) U' \varepsilon'' \rangle = \sqrt{1342} \left( -\frac{96}{61} T_0^5 + 1365 T_0^4 - \frac{1911}{4} T_0^8
\]
\[
\left. - 273 T_0^4 - \frac{273}{4} T_0^8 \right),
\]
\[
\langle (2) E'' \varepsilon''\| (2) U' \varepsilon'' \rangle = \sqrt{183} \left( \frac{91}{122} T_0^5 + 20020 T_0^8 - 7007 T_0^8
\]
\[
\left. - 4004 T_0^4 - 1001 T_0^8 \right),
\]
\[
\langle (1) U' \varepsilon''\| (2) U' \varepsilon'' \rangle = \sqrt{66} \left( \frac{9}{4} T_0^5 + 41175 T_0^4 - \frac{48251}{4} T_0^8
\]
\[
\left. + 7137 T_0^4 - \frac{10309}{4} T_0^8 \right).
\]

\( J = \frac{15}{2} \): Take directly \(|JM\rangle\) as the basis functions. Matrix elements about \(\varepsilon\):
\[
\left\langle \frac{15}{2} \pm \frac{15}{2} \right| \frac{15}{2} \pm \frac{15}{2} \right\rangle = -35T^2_0 - 273T^4_0 - 65T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{9}{2} \right| \frac{15}{2} \pm \frac{9}{2} \right\rangle = T^2_0 + 201T^4_0 - 59T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{7}{2} \right| \frac{15}{2} \pm \frac{7}{2} \right\rangle = 9T^2_0 + 101T^4_0 - 87T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{1}{2} \right| \frac{15}{2} \pm \frac{1}{2} \right\rangle = 21T^2_0 - 189T^4_0 + 75T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{15}{2} \right| \frac{15}{2} \pm \frac{7}{2} \right\rangle = -7\sqrt{39}T^4_0 - 5\sqrt{195}T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{7}{2} \right| \frac{15}{2} \pm \frac{1}{2} \right\rangle = -14\sqrt{165}T^4_0 + 6\sqrt{33}T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{1}{2} \right| \frac{15}{2} \pm \frac{9}{2} \right\rangle = -21\sqrt{55}T^4_0 - 3\sqrt{11}T^6_0;
\]

matrix elements about \(\varepsilon''\):
\[
\left\langle \frac{15}{2} \pm \frac{13}{2} \right| \frac{15}{2} \pm \frac{13}{2} \right\rangle = -21T^2_0 + 91T^4_0 + 11T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{11}{2} \right| \frac{15}{2} \pm \frac{11}{2} \right\rangle = -9T^2_0 + 221T^4_0 + 39T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{5}{2} \right| \frac{15}{2} \pm \frac{5}{2} \right\rangle = 15T^2_0 - 23T^4_0 - 45T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{3}{2} \right| \frac{15}{2} \pm \frac{3}{2} \right\rangle = 19T^2_0 - 129T^4_0 + 25T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{13}{2} \right| \frac{15}{2} \pm \frac{5}{2} \right\rangle = -7\sqrt{143}T^4_0 - 3\sqrt{715}T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{5}{2} \right| \frac{15}{2} \pm \frac{3}{2} \right\rangle = -42\sqrt{21}T^4_0 + 6\sqrt{105}T^6_0,
\]
\[
\left\langle \frac{15}{2} \pm \frac{3}{2} \right| \frac{15}{2} \pm \frac{11}{2} \right\rangle = -\sqrt{15015}T^4_0 - \sqrt{3003}T^6_0.
\]

REFERENCES
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