Application of Symmetry Coupling Coefficients in the Evaluation of the Electronic Spectra of d^7 Ions

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The optical absorption spectrum of cobalt chloride thiourea has been studied at room and liquid air temperatures. The results have been interpreted using group theoretical methods taking into account all the quartet states and several doublet states. Crystal field, electrostatic, and spin-orbit coupling interactions were included to yield the allowed transitions with the relative transition probabilities. The experimental results were interpreted for the following set of parameters: $B = 750$ cm^{-1}, $C = 3100$ cm^{-1}, $\Delta = 7370$ cm^{-1}, $\delta = -200$ cm^{-1}, $\mu = 500$ cm^{-1}, and $\zeta = 450$ cm^{-1}.

Key words: Electronic spectra of d^7 ions, theoretical calculations of $\sim$

1. Introduction

Over the last few years detailed studies have been carried out examining paramagnetic resonance and optical spectral data of d^3 and d^7 ions. Jesson [1] calculated the zero field splitting and the principal g-values for the Co^{2+} ion when the ground state is orbitally non-degenerate. Perumareddi [2] carried out calculations for all d^3 and d^7 configurations in non-cubic fields. Recently Ferguson et al. [3] reported results of the work on the electronic absorption spectra of tetragonal and pseudo-tetragonal cobalt(II) complexes.

In a previous paper [4] we outlined a concise group theoretical method to evaluate an analytical expression for the zero-field splitting in d^5 ions in a weak crystal field of tetragonal symmetry. In this paper we shall use the same group theoretical methods to evaluate the electronic spectra – the electronic transitions and their relative intensities – for d^7 ions in a weak crystal field of tetragonal symmetry. We shall illustrate how, from a knowledge of the symmetry coupling coefficients for the

octahedral double group [5] and the group theoretical extension of the Wigner–Eckhart theorem, the labour involved in the evaluation of the required matrix elements is significantly reduced.

2. Theory

Initially we shall begin with a crystal field of octahedral symmetry where $\langle t_2|V_{(oct)}|t_2\rangle = -2\Delta/5$ and $\langle e|V_{(oct)}|e\rangle = 3\Delta/5$ where Δ is the crystal field parameter. The states we need consider with the appropriate electronic configuration are:

$t_2^6e:{}^2E,$

$t_2^5e^2:{}^4T_1, {}^2T_1, {}^2T_1, {}^2T_2, {}^2T_2,$

$t_2^4e^3:{}^4T_1, {}^4T_2,$

$t_2^3e^4:{}^4A_2.$

The basic wavefunctions were derived using the appropriate t_2^n and e^m wavefunctions given by Griffith [6]. Using the V symmetry coupling coefficients given in Ref. [5, 7], the wavefunctions were determined from the relationship

$$|\Gamma_1\Gamma_2\Gamma_3c\rangle = \sum_{a,b} \langle\Gamma_1\Gamma_2ab \mid \Gamma_1\Gamma_2\Gamma_3c\rangle|\Gamma_1a\rangle|\Gamma_2b\rangle, \tag{1}$$

where

$$\langle\Gamma_1\Gamma_2ab \mid \Gamma_1\Gamma_2\Gamma_3c\rangle = \lambda(\Gamma_3)^{1/2}(-1)^{2\Gamma_2+\Gamma_3-c}V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma_3 \\ a & b & -(c)\end{pmatrix}.$$

The evaluation of the matrix elements can very simply be carried out through the application of the Wigner–Eckhart theorem which in group theoretical notation and in terms of the V symmetry coefficients may be expressed as

$$\langle\Gamma_3'c'|O(\Gamma_4a)|\Gamma_3c\rangle = \sum_J \left[(-1)^{\Gamma_3'-c'}V\begin{pmatrix}\Gamma_3' & \Gamma_3 & J\Gamma_4 \\ -(c') & c & a\end{pmatrix}\right.$$

$$\left. \times \langle\Gamma_3'\|O(\Gamma_4)\|\Gamma_3\rangle_J\right],$$

where $\langle\Gamma_3'\|O(\Gamma_4)\|\Gamma_3\rangle_J$ are the reduced matrix elements.

It is essential that we use a consistent phase convention throughout this work and, as we require many more additional terms than previously evaluated [1, 6], we shall use the V symmetry coupling coefficients for the O^* group [5] and the method outlined in Ref. [4] to evaluate *all* the matrix elements required. For convenience we shall give the matrix elements in a concise format.

The electrostatic and crystal field matrix elements are well known – see Ref. [6] – but since we are using different wavefunctions based on Eq. (1) there are changes in sign of the required off-diagonal electrostatic matrix elements, namely,

$$\langle t_2^5e^2:{}^4T_1| \sum e^2/r_{ij}|t_2^4e^3:{}^4T_1\rangle = -6B,$$

$$\langle t_2^5e^2({}^1E):{}^2T_1|\sum e^2/r_{ij}|t_2^5e^2({}^3A_2):{}^2T_1\rangle = 2\sqrt{3}B,$$

$$\langle t_2^5e^2({}^1E):{}^2T_2|\sum e^2/r_{ij}|t_2^5e^2({}^1A_1):{}^2T_2\rangle = -10B.$$

Table 1. Spin-orbit coupling matrix elements in units of ζ

U'	1	2	3	4	5	6	7	8	9	10	11	12		
1	$-1/3$												1.	$t_2^5e^2$:$^4T_1U'$
2	0	$1/2$											2.	$t_2^5e^2$:$^4T_{1\frac{5}{12}}U'$
3	$-1/3$	0	$1/6$										3.	$t_2^4e^3$:$^4T_1U'$
4	0	$1/2$	0	$-1/4$									4.	$t_2^4e^3$:$^4T_{1\frac{5}{12}}U'$
5	$-2/5$	$-4/5$	$-1/5$	$-2/5$	$1/6$								5.	$t_2^4e^3$:$^4T_2\phi_1$
6	$-4/5$	$9/10$	$-2/5$	$9/20$	0	$-1/4$							6.	$t_2^4e^3$:$^4T_2\phi_2$
7	0	0	0	0	$\sqrt5/\sqrt3$	0	0						7.	$t_2^3e^4$:$^4T_2U'$
8	0	0	$\sqrt5/\sqrt3$	0	0	0	0	$-1/4$					8.	$t_2^5e^2(^1E)$:$^2T_1U'$
9	$\sqrt5/3$	0	$-\sqrt5/6$	0	$1/2\sqrt5$	$1/\sqrt5$	0	0	$-1/6$				9.	$t_2^5e^2(^3A_2)$:$^2T_1U'$
10	0	0	$-\sqrt3/2\sqrt5$	0	$\sqrt5/2\sqrt3$	0	0	0	0	$1/2$			10.	$t_2^5e^2(^1A_1)$:$^2T_2U'$
11	0	0	$-\sqrt3/\sqrt5$	0	$\sqrt5/\sqrt3$	0	0	$-3/4$	0	0	$-1/4$		11.	$t_2^5e^2(^1E)$:$^2T_2U'$
12	$-1/\sqrt5$	$3/\sqrt5$	0	0	0	0	0	$\sqrt3/2$	$-1/2$	$-\sqrt3/2$	$-\sqrt3/2$	0	12.	t_2^6e:$^2EU'$

E''	1	2	3	4	5		
1	$1/2$					1.	$t_2^5e^2$:$^4T_1$
2	$1/2$	$-1/4$				2.	$t_2^4e^3$:$^4T_1$
3	$1/2$	$1/4$	$5/12$			3.	$t_2^3e^4$:$^4T_2$
4	0	$-\sqrt3/\sqrt2$	$-1/\sqrt6$	-1		4.	$t_2^5e^2(^1A_1)$:$^2T_2$
5	0	0	0	0	$1/3$	5.	$t_2^5e^2(^1E)$:$^2T_2$

E'	1	2	3	4	5		
1	$-5/6$					1.	$t_2^5e^2$:$^4T_1$
2	$-5/6$	$5/12$				2.	$t_2^4e^3$:$^4T_1$
3	$1/2$	$1/4$	$-1/4$			3.	$t_2^4e^3$:$^4T_2$
4	0	$-\sqrt2/\sqrt3$	0	$1/2$		4.	$t_2^5e^2(^1E)$:$^2T_1$
5	$-\sqrt2/3$	0	$1/\sqrt2$	0	$1/3$	5.	$t_2^5e^2(^3A_2)$:$^2T_1$

The spin–orbit coupling interaction may best be handled by coupling the spin and orbital components to derive our basic wavefunctions which transform as irreducible representations of the octahedral group, i.e.

$$^4T_1 \rightarrow E' + E'' + (3/2)U' + (5/2)U',$$

$$^4T_2 \rightarrow E' + E'' + (3/2)U' + (5/2)U',$$

$$^4A_2 \rightarrow U',$$

$$^2T_1 \rightarrow E' + U',$$

$$^2T_2 \rightarrow E'' + U',$$

$$^2E \rightarrow U'.$$

The required spin–orbit coupling matrix elements have been evaluated using the wavefunctions given by (1) and are given in Table 1.

In Table 1

$$|t_2^4 e^2 : {}^4T_2\phi_1 U'c'\rangle = -\frac{9}{5\sqrt{5}} |{}^4T_2 \tfrac{3}{2} U'c'\rangle - \frac{2\sqrt{29}}{5\sqrt{5}} |{}^4T_2 \tfrac{5}{2} U'c'\rangle,$$

$$|t_2^4 e^2 : {}^4T_2\phi_2 U'c'\rangle = -\frac{8}{5\sqrt{5}} |{}^4T_2 \tfrac{3}{2} U'c'\rangle - \frac{\sqrt{29}}{5\sqrt{5}} |{}^4T_2 \tfrac{5}{2} U'c'\rangle.$$

Table 2. The distortion matrix elements in units of $\langle \Gamma_i \| E \| \Gamma_j \rangle / \sqrt{3}$

	1	2	3	4	5	6	
1	$-2/5$	$-3/10$	$-3/2\sqrt{5}$	$-2/5$	$-3/10$	$1/2\sqrt{5}$	1. $^4T_1 U'\kappa'$
2	$-3/10$	$2/5$	$-1/2\sqrt{5}$	$-3/10$	$2/5$	$-3/2\sqrt{5}$	2. $^4T_1 \tfrac{5}{2} U'\kappa'$
3	$-3/2\sqrt{5}$	$-1/2\sqrt{5}$	0	$3/2\sqrt{5}$	$1/2\sqrt{5}$	0	3. $^4T_1 E''\beta''$
4	$2/5$	$3/10$	$-3/2\sqrt{5}$	$-2/5$	$-3/10$	$-1/2\sqrt{5}$	4. $^4T_2\phi_1 U'\kappa'$
5	$3/10$	$-2/5$	$-1/2\sqrt{5}$	$-3/10$	$2/5$	$3/2\sqrt{5}$	5. $^4T_2\phi_2 U'\kappa'$
6	$-1/2\sqrt{5}$	$3/2\sqrt{5}$	0	$-1/2\sqrt{5}$	$3/2\sqrt{5}$	0	6. $^4T_2 E''\beta''$

	1	2	3	4	5	6	
1	$2/5$	$3/10$	$-1/2\sqrt{5}$	$2/5$	$3/10$	$3/2\sqrt{5}$	1. $^4T_1 U'\lambda'$
2	$3/10$	$-2/5$	$3/2\sqrt{5}$	$3/10$	$-2/5$	$1/2\sqrt{5}$	2. $^4T_1 \tfrac{5}{2} U'\lambda'$
3	$-1/2\sqrt{5}$	$3/2\sqrt{5}$	0	$1/2\sqrt{5}$	$-3/2\sqrt{5}$	0	3. $^4T_1 E'\alpha'$
4	$-2/5$	$-3/10$	$-1/2\sqrt{5}$	$2/5$	$3/10$	$-3/2\sqrt{5}$	4. $^4T_2\phi_1 U'\lambda'$
5	$-3/10$	$2/5$	$3/2\sqrt{5}$	$3/10$	$-2/5$	$-1/2\sqrt{5}$	5. $^4T_2\phi_2 U'\lambda'$
6	$-3/2\sqrt{5}$	$-1/2\sqrt{5}$	0	$-3/2\sqrt{5}$	$-1/2\sqrt{5}$	0	6. $^4T_2 E'\alpha'$

	1	2	3			1	2	3	
1	$1/2$	$1/2$	$1/\sqrt{2}$	1. $^2T_1 U'\kappa'$	1	$-1/2$	$-1/\sqrt{2}$	$-1/2$	1. $^2T_1 U'\lambda'$
2	$-1/2$	$1/2$	$-1/\sqrt{2}$	2. $^2T_2 U'\kappa'$	2	$-1/\sqrt{2}$	0	$1/\sqrt{2}$	2. $^2T_1 E'\alpha'$
3	$-1/\sqrt{2}$	$-1/\sqrt{2}$	0	3. $^2T_2 E''\beta''$	3	$1/2$	$-1/\sqrt{2}$	$-1/2$	3. $^2T_2 U'\lambda'$

	1			1	
1	$\sqrt{3}/2$	1. $^2E U'\kappa'$	1	$-\sqrt{3}/2$	1. $^2E U'\lambda'$

Only very few of the required spin–orbit coupling matrix elements have been given by Griffith [6] and we note that there are sign differences due to the definitions of the wavefunctions.

The tetragonal distortion component of the crystal field may be defined by the parameters δ and μ in terms of the one-electron complex notation.

$$\langle \varepsilon | V_{\text{tetr}} | \varepsilon \rangle = -\langle \theta | V_{\text{tetr}} | \theta \rangle = \tfrac{3}{2}\mu$$

and

$$\tfrac{1}{2}\langle \zeta_1 | V_{\text{tetr}} | \zeta_1 \rangle = -\langle \pm 1 | V_{\text{tetr}} | \pm 1 \rangle = \delta.$$

The appropriate distortion matrix elements in terms of the appropriate reduced matrix elements are given in Table 2. The required reduced matric elements are:

$$\langle t_2^5 e^2 {:}^4 T_1 \| E \| t_2^5 e^2 {:}^4 T_1 \rangle = 2\sqrt{3}\,\delta$$

$$\langle t_2^4 e^3 {:}^4 T_1 \| E \| t_2^4 e^3 {:}^4 T_1 \rangle = -\frac{\sqrt{3}}{2}\{4\delta + 3\mu\}$$

$$\langle t_2^4 e^3 {:}^4 T_2 \| E \| t_2^4 e^3 {:}^4 T_2 \rangle = \frac{\sqrt{3}}{2}\{4\delta - 3\mu\}$$

$$\langle t_2^4 e^3 {:}^4 T_1 \| E \| t_2^4 e^3 {:}^4 T_2 \rangle = \frac{3\sqrt{3}}{2}\mu$$

$$\langle t_2^4 e^2 ({}^3A_2){:}^2 T_1 \| E \| t_2^5 e^2 ({}^3A_2){:}^2 T_1 \rangle = 2\sqrt{3}\,\delta$$

$$\langle t_2^5 e^2 ({}^1E){:}^2 T_1 \| E \| t_2^5 e^2 ({}^1E){:}^2 T_1 \rangle = 2\sqrt{3}\,\delta$$

$$\langle t_2^5 e^2 ({}^3A_2){:}^2 T_1 \| E \| t_2^5 e^2 ({}^1E){:}^2 T_1 \rangle = 0$$

$$\langle t_2^5 e^2 ({}^1A_1){:}^2 T_2 \| E \| t_2^5 e^2 ({}^1A_1){:}^2 T_2 \rangle = -2\sqrt{3}\,\delta$$

$$\langle t_2^5 e^2 ({}^1A_1){:}^2 T_2 \| E \| t_2^5 e^2 ({}^1E){:}^2 T_2 \rangle = 3\sqrt{3}\,\mu$$

$$\langle t_2^5 e^2 ({}^1E){:}^2 T_2 \| E \| t_2^5 e^2 ({}^1E){:}^2 T_2 \rangle = -2\sqrt{3}\,\delta$$

$$\langle t_2^5 e^2 ({}^1A_1){:}^2 T_2 \| E \| t_2^5 e^2 ({}^1E){:}^2 T_1 \rangle = 3\sqrt{3}\,\mu$$

$$\langle t_2^5 e^2 ({}^1A_1){:}^2 T_2 \| E \| t_2^5 e^2 ({}^3A_2){:}^2 T_1 \rangle = 0$$

$$\langle t_2^5 e^2 ({}^1E){:}^2 T_2 \| E \| t_2^5 e^2 ({}^1E){:}^2 T_1 \rangle = 0$$

$$\langle t_2^5 e^2 ({}^1E){:}^2 T_2 \| E \| t_2^5 e^2 ({}^3A_2){:}^2 T_1 \rangle = 0$$

$$\langle t_2^6 e {:}^2 E \| E \| t_2^6 e {:}^2 E \rangle = 3\mu$$

$$\langle t_2^3 e^4 {:}^4 A_2 \| E \| t_2^3 e^4 {:}^4 A_2 \rangle = 0$$

In addition $\langle T_1 \| E \| T_2 \rangle = -\langle T_2 \| E \| T_1 \rangle$.

Combining all the matrix elements we have two 17×17 matrices, one matrix containing the $U'\kappa'$ and $E''\beta''$ terms and the other the $U'\lambda'$ and $E'\alpha'$ terms. The eigenvalues of these matrices give the energy level scheme.

The relative d–d transition probabilities have been determined by considering the transitions

$$t_2^5 e^2 {:}^4 T_1 \rightarrow t_2^4 e^3 {:}^4 T_1$$

Table 3. The matrix elements $\langle ^4T_1\Gamma'a|T_{10}|^4T_1\Gamma a\rangle$ and $\langle ^4T_1\Gamma'a|T_{1x}|^4T_1\Gamma a\rangle$ in terms of the reduced matrix element $\langle T_1\|T_1\|T_1\rangle$. The bra vectors correspond to the $t_2^5e^2$ configuration. The ket vectors correspond to the t_2e^3 configuration

T_{10}	$|^4T_1U'\kappa'\rangle$	$|^4T_{1\frac52}U'\kappa'\rangle$	$|^4T_1E''\beta''\rangle$
$\langle ^4T_1U'\kappa'|$	$\sqrt2/5\sqrt3$	$-1/5\sqrt6$	$-1/\sqrt{30}$
$\langle ^4T_{1\frac52}U'\kappa'|$	$-1/5\sqrt6$	$-11/15\sqrt6$	$2\sqrt2/3\sqrt{15}$
$\langle ^4T_1E''\beta''|$	$-1/\sqrt{30}$	$2\sqrt2/3\sqrt{15}$	$1/3\sqrt6$

T_{10}	$|^4T_1U'\nu'\rangle$	$|^4T_{1\frac52}U'\nu'\rangle$	$|^4T_1E''\alpha''\rangle$
$\langle ^4T_1U'\nu'|$	$-\sqrt2/5\sqrt3$	$1/5\sqrt6$	$-1/\sqrt{30}$
$\langle ^4T_{1\frac52}U'\nu'|$	$1/5\sqrt6$	$11/15\sqrt6$	$2\sqrt2/3\sqrt{15}$
$\langle ^4T_1E''\alpha''|$	$-1/\sqrt{30}$	$2\sqrt2/3\sqrt{15}$	$-1/3\sqrt6$

T_{10}	$|^4T_1U'\chi\rangle$	$|^4T_{1\frac52}U'\chi\rangle$	$|^4T_1E'\alpha'\rangle$
$\langle ^4T_1U'\chi|$	$\sqrt2/15\sqrt3$	$\sqrt3/5\sqrt2$	$\sqrt5/3\sqrt6$
$\langle ^4T_1U'\chi|$	$\sqrt3/5\sqrt2$	$1/5\sqrt6$	0
$\langle ^4T_1E'\alpha'|$	$\sqrt5/3\sqrt6$	0	$-1/3\sqrt6$

T_{10}	$|^4T_1U'\mu'\rangle$	$|^4T_{1\frac52}U'\mu'\rangle$	$|^4T_1E'\beta'\rangle$
$\langle ^4T_1U'\mu'|$	$-\sqrt2/15\sqrt3$	$-\sqrt3/5\sqrt2$	$\sqrt5/3\sqrt6$
$\langle ^4T_{1\frac52}U'\mu'|$	$-\sqrt3/5\sqrt2$	$-1/5\sqrt6$	0
$\langle ^4T_1E'\beta'|$	$\sqrt5/3\sqrt6$	0	$1/3\sqrt6$

T_{1x}	$|^4T_1U'\nu'\rangle$	$|^4T_{1\frac52}U'\nu'\rangle$	$|^4T_1U'\chi\rangle$	$|^4T_{1\frac52}U'\chi\rangle$	$|^4T_1E'\alpha'\rangle$	$|^4T_1E''\alpha''\rangle$
$\langle ^4T_1U'\kappa'|$	0	$-1/2\sqrt6$	$\sqrt2/15$	$1/10\sqrt2$	$-\sqrt5/6\sqrt2$	$-1/2\sqrt{30}$
$\langle ^4T_{1\frac52}U'\kappa'|$	$-1/2\sqrt6$	$-1/3\sqrt6$	$1/10\sqrt2$	$-\sqrt2/15$	0	$\sqrt2/3\sqrt{15}$
$\langle ^4T_1U'\mu'|$	$\sqrt2/15$	$1/10\sqrt2$	$2\sqrt2/15\sqrt3$	$-\sqrt3/10\sqrt2$	$\sqrt5/6\sqrt6$	$-1/2\sqrt{10}$
$\langle ^4T_{1\frac52}U'\mu'|$	$1/10\sqrt2$	$-\sqrt2/15$	$-\sqrt3/10\sqrt2$	$-\sqrt3/5\sqrt2$	0	$\sqrt2/3\sqrt5$
$\langle ^4T_1E'\beta'|$	$\sqrt5/6\sqrt2$	0	$-\sqrt5/6\sqrt6$	0	$-1/3\sqrt6$	0
$\langle ^4T_1E''\beta''|$	$1/2\sqrt{30}$	$-\sqrt2/3\sqrt{15}$	$1/2\sqrt{10}$	$-\sqrt2/3\sqrt5$	0	$-1/3\sqrt6$

and

$$t_2^5 e^2 : {}^4T_1 \rightarrow t_2^4 e^3 : {}^4T_2$$

in terms of the reduced matrix elements $\langle T_1 \| T_1 \| T_1 \rangle$ and $\langle T_1 \| T_1 \| T_2 \rangle$. For the $t_2^5 e^2 : {}^4T_1 \rightarrow t_2^4 e^3 : {}^4T_1$ transition the matrix elements are of the form

$$\langle t_2^5 e^2 : {}^4T_1 \Gamma' a' | T_{10} | t_2^4 e^3 : {}^4T_1 \Gamma a \rangle$$

and

$$\langle t_2^5 e^2 : {}^4T_1 \Gamma' a' | T_{1x} | t_2^4 e^3 : {}^4T_1 \Gamma a \rangle.$$

Table 4. The matrix elements $\langle {}^4T_1 \Gamma' a' | T_{10} | {}^4T_2 \Gamma a \rangle$ and $\langle {}^4T_1 \Gamma' a' | T_{1x} | {}^4T_2 \Gamma a \rangle$ in terms of the reduced matrix element $\langle T_1 \| T_1 \| T_2 \rangle$. The bra vectors correspond to the $t_2^5 e^2$ configuration. The ket vectors correspond to the $t_2^4 e^3$ configuration

T_{10}	$|{}^4T_2 \phi_1 U' \kappa' \rangle$	$|{}^4T_2 \phi_2 U' \lambda' \rangle$	$|{}^4T_2 E'' \beta'' \rangle$
$\langle {}^4T_1 U' \kappa' |$	$-2\sqrt{2}/15$	$-1/5\sqrt{2}$	$1/3\sqrt{10}$
$\langle {}^4T_1 \tfrac{5}{2} U' \kappa' |$	$7/15\sqrt{2}$	$-1/15\sqrt{2}$	$\sqrt{2}/3\sqrt{5}$
$\langle {}^4T_1 E'' \beta'' |$	$1/3\sqrt{10}$	$\sqrt{2}/3\sqrt{5}$	$-1/3\sqrt{2}$

T_{10}	$|{}^4T_2 \phi_1 U' \nu' \rangle$	$|{}^4T_2 \phi_2 U' \nu' \rangle$	$|{}^4T_2 E'' \alpha'' \rangle$
$\langle {}^4T_1 U' \nu' |$	$2\sqrt{2}/15$	$1/5\sqrt{2}$	$1/3\sqrt{10}$
$\langle {}^4T_1 \tfrac{5}{2} U' \nu' |$	$-7/15\sqrt{2}$	$1/15\sqrt{2}$	$\sqrt{2}/3\sqrt{5}$
$\langle {}^4T_1 E'' \alpha'' |$	$1/3\sqrt{10}$	$\sqrt{2}/3\sqrt{5}$	$1/3\sqrt{2}$

T_{10}	$|{}^4T_2 \phi_1 U' \lambda' \rangle$	$|{}^4T_2 \phi_2 U' \lambda' \rangle$	$|{}^4T_2 E' \alpha' \rangle$
$\langle {}^4T_1 U' \lambda' |$	$2\sqrt{2}/15$	$-7/15\sqrt{2}$	$1/3\sqrt{10}$
$\langle {}^4T_1 \tfrac{5}{2} U' \lambda' |$	$1/5\sqrt{2}$	$1/15\sqrt{2}$	$\sqrt{2}/3\sqrt{5}$
$\langle {}^4T_1 E' \alpha' |$	$1/3\sqrt{10}$	$\sqrt{2}/3\sqrt{5}$	$1/3\sqrt{2}$

T_{10}	$|{}^4T_2 \phi_1 U' \mu' \rangle$	$|{}^4T_2 \phi_2 U' \mu' \rangle$	$|{}^4T_2 E' \beta' \rangle$
$\langle {}^4T_1 U' \mu' |$	$-2\sqrt{2}/15$	$7/15\sqrt{2}$	$1/3\sqrt{10}$
$\langle {}^4T_1 \tfrac{5}{2} U' \mu' |$	$-1/5\sqrt{2}$	$-1/15\sqrt{2}$	$\sqrt{2}/3\sqrt{5}$
$\langle {}^4T_1 E' \beta' |$	$1/3\sqrt{10}$	$\sqrt{2}/3\sqrt{5}$	$-1/3\sqrt{2}$

T_{1x}	$|{}^4T_2 \phi_1 U' \nu' \rangle$	$|{}^4T_2 \phi_2 U' \nu' \rangle$	$|{}^4T_2 \phi_1 U' \lambda' \rangle$	$|{}^4T_1 \phi_2 U' \lambda' \rangle$	$|{}^4T_2 E' \alpha' \rangle$	$|{}^4T_2 E'' \alpha'' \rangle$
$\langle {}^4T_1 U' \kappa' |$	$-2\sqrt{2}/15$	$3/10\sqrt{2}$	0	$-1/2\sqrt{6}$	$-1/2\sqrt{30}$	$1/6\sqrt{10}$
$\langle {}^4T_1 \tfrac{5}{2} U' \kappa' |$	$-1/30\sqrt{2}$	$-1/15\sqrt{2}$	$1/2\sqrt{6}$	0	$-1/\sqrt{30}$	$1/3\sqrt{10}$
$\langle {}^4T_1 U' \mu' |$	0	$-1/2\sqrt{6}$	$-4/15\sqrt{2}$	$-1/30\sqrt{2}$	$1/6\sqrt{10}$	$1/2\sqrt{30}$
$\langle {}^4T_1 \tfrac{5}{2} U' \mu' |$	$1/2\sqrt{6}$	0	$3/10\sqrt{2}$	$-1/15\sqrt{2}$	$1/3\sqrt{10}$	$1/\sqrt{30}$
$\langle {}^4T_1 E' \beta' |$	$1/2\sqrt{30}$	$1/\sqrt{30}$	$-1/6\sqrt{10}$	$-1/3\sqrt{10}$	$1/3\sqrt{2}$	0
$\langle {}^4T_1 E'' \beta'' |$	$-1/6\sqrt{10}$	$-1/3\sqrt{10}$	$-1/2\sqrt{30}$	$-1/\sqrt{30}$	0	$1/3\sqrt{2}$

T_{1x}	$|{}^4T_2 \phi_1 U' \kappa' \rangle$	$|{}^4T_2 \phi_2 U' \kappa' \rangle$	$|{}^4T_2 \phi_1 U' \mu' \rangle$	$|{}^4T_2 \phi_2 U' \mu' \rangle$	$|{}^4T_2 E' \beta' \rangle$	$|{}^4T_2 E'' \beta'' \rangle$
$\langle {}^4T_1 U' \nu' |$	$-2\sqrt{2}/15$	$3/10\sqrt{2}$	0	$-1/2\sqrt{6}$	$1/2\sqrt{30}$	$-1/6\sqrt{10}$
$\langle {}^4T_1 \tfrac{5}{2} U' \nu' |$	$-1/30\sqrt{2}$	$-1/15\sqrt{2}$	$1/2\sqrt{6}$	0	$1/\sqrt{30}$	$-1/3\sqrt{10}$
$\langle {}^4T_1 U' \lambda' |$	0	$-1/2\sqrt{6}$	$-4/15\sqrt{2}$	$-1/30\sqrt{2}$	$-1/6\sqrt{10}$	$-1/2\sqrt{30}$
$\langle {}^4T_1 \tfrac{5}{2} U' \lambda' |$	$1/2\sqrt{6}$	0	$3/10\sqrt{2}$	$-1/15\sqrt{2}$	$-1/3\sqrt{10}$	$-1/\sqrt{30}$
$\langle {}^4T_1 E' \alpha' |$	$-1/2\sqrt{30}$	$-1/\sqrt{30}$	$1/6\sqrt{10}$	$1/3\sqrt{10}$	$1/3\sqrt{2}$	0
$\langle {}^4T_1 E'' \alpha'' |$	$1/6\sqrt{10}$	$1/3\sqrt{10}$	$1/2\sqrt{30}$	$1/\sqrt{30}$	0	$1/3\sqrt{2}$

In this case we note that

$$\langle t_2^5 e^2 : {}^4T_1\Gamma' a' | T_{1c} | t_2^4 e^3 : {}^4T_1\Gamma a \rangle = \langle t_2^5 e^2 : {}^4T_1\Gamma a | T_{1c} | t_2^4 e^3 : {}^4T_1\Gamma' a' \rangle.$$

The matrix elements, in units of $\langle T_1 \| T_1 \| T_1 \rangle$ are summarized in Table 3.

For the $t_2^5 e^2 : {}^4T_1 \rightarrow t_2^4 e^3 : {}^4T_2$ transition the matrix elements are of the form

$$\langle t_2^5 e^2 : {}^4T_1\Gamma' a' | T_{10} | t_2^4 e^3 : {}^4T_2\Gamma a \rangle$$

and

$$\langle t_2^5 e^2 : {}^4T_1\Gamma' a' | T_{1x} | t_2^4 e^3 : {}^4T_2\Gamma a \rangle.$$

The matrix elements, in units of $\langle T_1 \| T_1 \| T_2 \rangle$ are summarized in Table 4.

We shall, in the next section, use these results to interpret the bands in the optical absorption spectrum of cobalt chloride thiourea.

3. Results and Discussion

In this section we shall examine the optical absorption spectrum of cobalt chloride thiourea. The crystal structure of cobalt chloride thiourea has been determined by Forstat *et al.* [8]. The crystals are tetragonal with point symmetry $4/m(C_{4h})$ and space group P_42/n. The unit cell dimensions are $a = 13.52$ Å and $c = 9.10$ Å with four formula units per unit cell.

The observed spectrum at room temperature consists of two bands in the near infrared at 5850 cm^{-1} and 7520 cm^{-1}, and three in the visible at $17,510$ cm^{-1}, $20,165$ cm^{-1}, and $20,317$ cm^{-1}. (The two infrared bands were recorded at 300 K on a Unicam SP-700 recording spectrophotometer at the Indian Institute of Science, Bangalore, and the visible and ultraviolet bands were recorded at room and liquid air temperatures at the Sri Venkateswara University in the wavelength region on a Hilger medium quartz spectrograph. The photographically recorded spectra were calibrated against the iron arc standard lines – see Pappalardo [9] and Lakshman *et al.* [10].)

On cooling the crystal, the width of the band at $17,510$ cm^{-1} decreased, while that at $20,165$ cm^{-1} increased. Further, the band at $20,317$ cm^{-1} became extremely sharp and the band at $17,510$ cm^{-1} showed a violet shift of $(17,655-17,510)$ 145 cm^{-1}. Two more bands have also been observed at liquid air temperature, one intense band at $20,519$ cm^{-1} and another weak band at $14,970$ cm^{-1}. In the near infrared, however, no observation could be made at liquid air temperature, as there is no provision in the spectrophotometer (Indian Institute of Science, Bangalore) for mounting the cryostat.

From the nature and position of the bands, it is assumed that the ion responsible for the absorption spectrum is that of Co^{2+}. The observed bands may be interpreted as arising from a d^7 ion in a crystal field environment given by $\Delta = 7370$ cm^{-1}, $\delta = -200$ cm^{-1}, and $\mu = 500$ cm^{-1}. The transitions and their relative intensities were calculated using the results given in the previous section. The Racah B and C parameters were chosen at 750 and 3100 cm^{-1} respectively and the spin–orbit coupling constant ζ as 450 cm^{-1}. The parameters Δ, δ and μ were varied until the calculated transitions and their intensities matched the experimental results.

Table 5. The experimental bands and oscillator strengths at 300 K and the theoretical transitions with the relative intensities

Transition		Type of transition	Relative intensity	Bands at 300 K	Oscillator strengths at 300 K
5870	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0591	5850	3.7×10^{-5}
5947	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0086		
7494	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.1136		
7494	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0022		
7552	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0048	7520	3.5×10^{-5}
7552	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0046		
7585	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0059		
7728	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0006		
13656	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0005		
14000	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0006		
14000	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0004	14970^a	—
14340	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0009		
14589	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0007		
14756	∥	$\lambda', \alpha' \to \lambda', \beta'$	0.0029		
16625	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0001		
17206	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0001		
17206	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0005		
17427	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.1072	17510	6.2×10^{-5}
17427	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0021		
17784	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0485		
17855	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0046		
17855	⊥	$\lambda', \alpha' \to \mu', \beta'$	0.0081		
20036	⊥	$\lambda', \alpha' \to \kappa', \beta''$	0.0013	20165	5.5×10^{-7}
20089	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0003	20317	4.8×10^{-7}
20728	∥	$\lambda', \alpha' \to \lambda', \alpha'$	0.0014	20519	5.2×10^{-7}

^{a} Observed at 80 K.

Under these conditions the ground state is primarily a $t_2^5e^2:{}^4T_1U'\lambda'E'\alpha'$ wavefunction. The relative intensities were determined for the case when $\langle T_1\|T_1\|T_1\rangle = \langle T_1\|T_1\|T_2\rangle$. The calculated transitions using these parameters with a relative intensity greater than 1×10^{-4} are given in Table 5.

The bands at 5850 cm^{-1} and 7520 cm^{-1} arise from transitions to wavefunctions primarily of $t_2^4e^3:{}^4T_2$ character. The band at 14,970 cm^{-1} arises from transitions to wavefunctions primarily of $t_2^5e^2:{}^2T_1$ and ${}^2T_2$ character. The transitions to the wavefunction primarily of $t_2^3e^4:{}^4A_2$ character give bands at 14,470 cm^{-1} (⊥), 14,479 cm^{-1} (∥) and 14,479 cm^{-1} (⊥) with relative intensities 6×10^{-6}, 3.5×10^{-5}, and 6.2×10^{-5} respectively.

Hence the identification of the ${}^4T_1 \to {}^4A_2$ transition as predicted by Koide [11] may be masked by more intense transitions including ${}^4T_1 \to {}^2T_1$ and ${}^4T_1 \to {}^2T_2$ type transitions.

The band at 17,510 cm^{-1} arises from transitions to wavefunctions primarily of $t_2^4e^3:{}^4T_1$ character and the last three bands in Table 5 from transition to wavefunction primarily of $t_2^5e^2:{}^2T_1$ character.

The relative intensities of the bands may be estimated from the relative intensities of the various transitions yielding for the three main bands at 5850, 7520, and 17,510 cm^{-1} relative intensities of 0.0451, 0.0483, and 0.0768 respectively. The relative intensities compare well with the relative oscillator strengths for the various bands.

The energy level above the ground state is separated by 220 cm^{-1} and is also primarily a $t_2^5 e^2$:$^4T_1 U' \lambda'$ $E' \alpha'$ wavefunction. This level will be sufficiently populated at room temperature to observe transitions from this level of at least the relatively more intense transitions. Hence we would expect that the bands which are made up of a large number of relatively intense transitions such as the band at 17,510 cm^{-1} will show a positive shift of less than 220 cm^{-1} with a decrease in temperature. This is observed. (A detailed study of the temperature dependence of the various bands would need to consider the temperature dependence of the various parameters.)

The experimental results obtained from the optical absorption spectrum of cobalt chloride thiourea have been interpreted, using group theoretical methods to determine both the d–d transitions and the relative transition probabilities, as due to the Co^{2+} ion in a crystal field of tetragonal symmetry.

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