

# THE MAGNETIC DIPOLE TRANSITIONS IN THE OCTAHEDRAL COMPLEXES OF THE TRANSI- TION METAL IONS

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**ABSTRACT.** The oscillator strengths of the magnetic-dipole transitions in the octahedral complexes of the transition metal ions have been calculated using the strong field wave functions. The agreement with experiment is reasonable. More experimental data are needed in order to check the theory more completely.

## INTRODUCTION

It is well known that among the forbidden transitions between the states with the same parity, the following transitions are able to have non-vanishing intensity (Van Vleck 1937; Tanabe and Sugano 1954): (1) the electric-dipole transitions coupled with the odd vibrations (Liehr and Ballhausen 1957; Chakravarty 1968), (2) the magnetic-dipole transitions and (3) the electric-quadrupole transitions (Chakravarty 1967). The oscillator strengths of the electric-dipole transitions observed experimentally ranges between  $10^{-3}$  and  $10^{-5}$ , those of the magnetic-dipole transitions are of the order  $10^{-5}$  and those of the electric-quadrupole transitions are of the order of  $10^{-9}$ . Thus the magnetic-dipole transitions may be of comparable intensity when compared with the electric-dipole transitions coupled with the odd vibrations. In the octahedral complexes of the transition metal ions in which we are interested in this paper, there are situations where both these types of transitions are non-vanishing and comparable in magnitude. It is, therefore, important to know the oscillator strengths of the magnetic-dipole transitions in the different types of complexes of the transition metal ions.

## THEORY

The oscillator strengths of the magnetic dipole transitions are given by (Ballhausen 1962)

$$f = \frac{\hbar\nu k^2}{6mc} \sum_{E_{ac.}} |\langle \psi_{Gr.} | \vec{L} | \psi_{E_{ac.}} \rangle|^2$$

where  $k$  is the orbital reduction factor. Its magnitude generally varies from 0.8 to 0.9 in the type of complexes under consideration (Owen and Thornley 1966). In our calculations we assume  $k = 0.9$ . For a detailed discussion on the covalency and consequently the orbital reduction factor as soon as the ion enters into a crystalline complex one should consult the excellent review article by Owen and Thornley (1966).  $\nu$  is the energy difference between the ground and the excited states in wave numbers, and is known from experiments. The other quantities in the above equation have their usual significance. Tables 1 and 2 give the theoretically calculated oscillator strengths for the  $kd^n$  ( $k = 3, 4, 5$ , and  $n = 1$  through 9) octahedral complexes in the strong field scheme. Though the complexes mentioned in the tables are certainly not strictly octahedral and often have lower symmetries, we perform our calculations by assuming only the octahedral symmetry. Since the oscillator strengths are small, this assumption will not change the values significantly.

## DISCUSSION

It is rather unfortunate that except for  $Ni^{2+}$  complexes (Fergusson *et al.*, 1964) no other experimental data exists in this field. In  $Ni^{2+}$  octahedral complexes the most intense ligand field bands correspond to the electronic transitions between the ground state ( $t^6_{2g} e^2_g$ )  ${}^3A_{2g}$  and two other excited triplet states ( $t^5_{2g} e^3_g$ )  ${}^3T_{2g}$ ,  ${}^3T_{1g}$ , respectively. These transitions are strictly forbidden for pure electric-dipole absorption of radiation but the transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  is allowed for magnetic dipole absorption. It is generally true that the contribution to the absorption intensity by the latter mechanism are smaller by a factor 10—100 than those of the vibronically induced electric-dipole transitions and this may be one of the reasons why it is easy for them to go undetected in the experimental optical absorption spectra. However, Fergusson *et al.* (1964) have reported the evidence from the fluorescence and absorption spectra of  $Ni^{2+}$  in  $KMgF_3$  and  $MgF_2$  which shows that the  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition has appreciable magnetic-dipole intensity in the above compounds of  $Ni^{2+}$ . The experimental value of the oscillator strength of this transition is  $6.7 \times 10^{-6}$  at  $20^\circ K$  and  $7.8 \times 10^{-6}$  at  $300^\circ K$ . The slight temperature dependence of this band indicates that a small part of the total intensity comes from the vibronically allowed electric-dipole mechanism. Our theoretically calculated value of the order  $3 \times 10^{-6}$  agrees favourably with the experimental values, though the agreement is not certainly close. The possible reason of this discrepancy is not known definitely though it can be argued that since some amount of intensity comes from the electric-dipole character, this part has to be subtracted out from the total intensity of  $6.7 \times 10^{-6}$  at  $20^\circ K$  and  $7.8 \times 10^{-6}$  at  $300^\circ K$  before any comparison of our theoretical value can be made. Lastly more and more experimental data are needed very badly to compare our theoretical values with.

Table I. Magnetic-Dipole Transitions

Configu- ration	Ion	Complex	Transition ( $g \rightarrow g$ )	Energy difference ( $\text{cm}^{-1}$ )	Oscillator strength $f$ in $10^{-8}$
$3d^1$	$\text{Ti}^{3+}$	$\text{Ti}(\text{H}_2\text{O})_6^{3+}$	${}^2T_2 \rightarrow {}^2E$	20,300	7.97
		$\text{Ti}(\text{urea})_6^{3+}$	${}^2T_2 \rightarrow {}^2E$	16,000	6.28
$3d^2$	$\text{V}^{3+}$	$\text{V}(\text{H}_2\text{O})_6^{3+}$	${}^3T_1 \rightarrow {}^3T_2$	17,100	10.07
			$\rightarrow {}^3T_1$	25,200	4.90
		$\text{V}^{3+}$ in $\text{Al}_2\text{O}_3$	${}^3T_1 \rightarrow {}^3T_2$	17,400	10.24
			$\rightarrow {}^3T_1$	25,200	4.94
		$\text{V}(\text{urea})_6^{3+}$	${}^3T_1 \rightarrow {}^3T_2$	16,250	9.57
		$\rightarrow {}^3T_1$	24,200	4.75	
$3d^3$	$\text{V}^{2+}$	$\text{V}(\text{H}_2\text{O})_6^{2+}$	${}^4A_2 \rightarrow {}^4T_2$	11,800	4.63
		$\text{Cr}^{3+}$	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	${}^4A_2 \rightarrow {}^4T_2$	17,400
		$\text{KCr}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$	${}^4A_2 \rightarrow {}^4T_2$	17,600	6.91
		$\text{Cr}(\text{ox})_3^{3-}$	${}^4A_2 \rightarrow {}^4T_2$	17,390	6.82
		$\text{Cr}(\text{en})_3^{3+}$	${}^4A_2 \rightarrow {}^4T_2$	21,880	8.59
		$\text{Cr}(\text{NH}_3)_6^{3+}$	${}^4A_2 \rightarrow {}^4T_2$	21,500	8.44
$3d^4$	$\text{Cr}^{2+}$	$\text{Cr}(\text{H}_2\text{O})_6^{2+}$	${}^5E \rightarrow {}^5T_2$	14,000	5.49
	$\text{Mn}^{3+}$	$\text{CSMn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	${}^5E \rightarrow {}^5T_2$	21,000	8.24
	$\text{Mn}^{3+}$	$\text{K}_3\text{Mn}(\text{CN})_6$	${}^3T_1 \rightarrow {}^3E^{(1)}$	24,000	4.67
$3d^6$	$\text{Fe}^{2+}$	$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	${}^5T_2 \rightarrow {}^5E$	10,400	4.08
	$\text{Co}^{3+}$	$\text{Co}(\text{en})_3^{3+}$	${}^1A_1 \rightarrow {}^1T_1$	21,400	16.81
		$\text{Co}(\text{ox})_3^{3-}$	${}^1A_1 \rightarrow {}^1A_1$	16,500	12.96
	$\text{Co}(\text{NH}_3)_6^{3+}$	${}^1A_1 \rightarrow {}^1T_1$	21,070	16.55	
$3d^7$	$\text{Co}^{2+}$	$\text{Co}(\text{H}_2\text{O})_6^{2+}$	${}^4T_1 \rightarrow {}^4T_2$	8,200	4.83
			$\rightarrow {}^4T_1$	20,000	3.92
		$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	${}^4T_1 \rightarrow {}^4T_2$	8,350	4.91
			$\rightarrow {}^4T_1$	19,800	3.88
		$\text{Co}(\text{NH}_3)_6^{2+}$	${}^4T_1 \rightarrow {}^4T_2$	9,000	5.30
		$\rightarrow {}^4T_1$	21,1000	4.14	
$3d^7$	$\text{Co}^{2+}$	$\text{Co}(\text{en})_3^{2+}$	${}^4T_1 \rightarrow {}^4T_2$	9,800	5.77
			$\rightarrow {}^4T_1$	21,700	4.26

Table I (Contd.)

Configuration	Ion	Complex	Transition ( $g \rightarrow g$ )	Energy difference ( $\text{cm}^{-1}$ )	Oscillator strength $f$ in $10^{-6}$	
$3d^8$	$\text{Ni}^{2+}$	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$	8,500	3.33	
		$\text{Ni}(\text{NH}_3)_6^{2+}$	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$	10,750	4.22	
		$\text{Ni}(\text{en})_3^{2+}$	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$	11,200	4.39	
		$\text{MgNiF}_2$	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$	7,600	2.98	
$3d^9$	$\text{Cu}^{2+}$	$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	${}^2\text{E} \rightarrow {}^2\text{T}_2$	12,600	4.94	
		$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	${}^2\text{E} \rightarrow {}^2\text{T}_2$	13,000	5.10	
		$\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$	${}^2\text{E} \rightarrow {}^2\text{T}_2$	12,500	4.90	
$4d^1$	$\text{Nb}^{4+}$	$\text{Nb}(\text{Cl})_6^{3+}$	${}^2\text{T}_2 \rightarrow {}^2\text{E}$	20,900	8.20	
$4d^2$	$\text{Nb}^{3+}$	$\text{Nb}(\text{Cl})_6^{3+}$	${}^3\text{T}_1 \rightarrow {}^2\text{T}_2$	18,900	11.13	
			$\rightarrow {}^3\text{T}_1$	22,500	4.41	
$4d^{3+}$	$\text{Nb}^{2+}$	$\text{Nb}(\text{Cl})_6^{2+}$	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$	22,700	8.91	
$4d^5$	$\text{Ru}^{3+}$	$\text{Ru}(\text{Cl})_6^3$	${}^2\text{T}_2 \rightarrow {}^2\text{A}_2$	19,200	2.51	
		$\text{Ru}(\text{Br})_6^{3-}$	${}^2\text{T}_2 \rightarrow {}^2\text{A}_2$	15,300	2.00	
$4d^6$	$\text{Rh}^{3+}$	$\text{Rh}(\text{H}_2\text{O})_6^{3+}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	25,500	20.03	
		$\text{Rh}(\text{ox})_3^{3-}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	25,100	19.71	
		$\text{Rh}(\text{NH}_3)_6^{3+}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	32,700	25.68	
		$\text{Rh}(\text{en})_3^{3+}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	33,200	26.08	
		$\text{Rh}(\text{Cl})_6^3$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	19,300	15.16	
		$\text{Rh}(\text{Br})_6^{3-}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	18,100	14.28	
$5d^6$	$\text{Ir}^{3+}$	$\text{Ir}(\text{Cl})_6^{3-}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	24,100	18.93	
		$\text{Ir}(\text{Br})_6^{3-}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	22,400	17.59	
		$\text{Ir}(\text{en})_3^{3+}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	40,200	31.58	
	$\text{Pt}^{4+}$	$\text{Pt}(\text{Cl})_6^{2-}$	${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$	28,300	22.23	
$3d^1$	$\text{Ti}^{3+}$	$\text{TiCl}_6^3$	${}^2\text{T}_2 \rightarrow {}^2\text{E}$	10,000a	4.51	
				13,000		
$3d^2$	$\text{V}^{3+}$	$\text{VCl}_6^{3-}$	${}^3\text{T}_1 \rightarrow {}^3\text{T}_2$	1,000b	6.48	
			$\rightarrow {}^3\text{T}_1$	18,020a	3.53	
		$\text{V}(\text{CN})_6^{3-}$	${}^3\text{T}_1 \rightarrow {}^3\text{T}_2$	22,200c	13.07	
		$\rightarrow {}^3\text{T}_1$	28,600c	5.61		
$3d^3$	$\text{V}^{2+}$	$\text{VCl}_6^{4-}$	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$	7,200a	2.82	
		$\text{Cr}^{3+}$	$\text{CrCl}_6^{3-}$	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$	12,500a,d	4.90
		$\text{CrF}_6^{3-}$	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$	14,600e	5.73	

The chloride complexes are in LiCl-KCl eutectic at 400°C and fluoride complexes are in LiF-NaF-KF eutectic at 650°C.

In Table I, the energy differences have been collected from various sources. In this connection see Ballhausen (1962) and also Desai and Chakravarty (1968).

- (a) Gruen, D. M., and McBeth (1962a)
- (b) Gruen, D. M., *et al.*, 1962b
- (c) Perumareddi, J. R., *et al.*, 1963.
- (d) Harrington, G., and Sundheim, 1960.
- (e) Young, J. P., and White, 1960.

Table 2. Expressions for the oscillator strengths for the lowspin  $kd^4$ ,  $kd^5$  and  $kd^7$  complexes

Configuration ( $k$ b = 4, 5)	Transition $g \rightarrow g$	Energy difference ( $cm^{-1}$ )	Oscillator strength
$kd^4$	${}^3T_1 \rightarrow {}^3A_1$	$\nu^3T_1 \rightarrow {}^3A_1$	$\frac{6h\nu}{9mc}$
	$\rightarrow {}^3E^{(1)}$	$\nu^3T_1 \rightarrow {}^3E^{(1)}$	$\frac{6h\nu}{9mc}$
	$\rightarrow {}^3E^{(2)}$	$\nu^3T_1 \rightarrow {}^3E^{(2)}$	$\frac{6h\nu}{9mc}$
	$\rightarrow {}^3T_1^{(1)}$	$\nu^3T_1 \rightarrow {}^3T_1^{(1)}$	$\frac{3h\nu}{2mc}$
	$\rightarrow {}^3T_1^{(2)}$	$\nu^3T_1 \rightarrow {}^3T_1^{(2)}$	$\frac{3h\nu}{6mc}$
	$\rightarrow {}^3T_2^{(1)}$	$\nu^3T_1 \rightarrow {}^3T_2^{(1)}$	$\frac{3h\nu}{6mc}$
	$\rightarrow {}^3T_2^{(2)}$	$\nu^3T_1 \rightarrow {}^3T_2^{(2)}$	$\frac{3h\nu}{2mc}$
$kd^5$	${}^2T_2 \rightarrow {}^2A_2$	$\nu^2T_2 \rightarrow {}^2A_2$	$\frac{6h\nu}{9mc}$
	$\rightarrow {}^2E^{(1)}$	$\nu^2T_2 \rightarrow {}^2E^{(1)}$	$\frac{6h\nu}{9mc}$
	$\rightarrow {}^2E^{(2)}$	$\nu^2T_2 \rightarrow {}^2E^{(2)}$	$\frac{6h\nu}{9mc}$
	$\rightarrow {}^2T_1^{(1)}$	$\nu^2T_2 \rightarrow {}^2T_1^{(1)}$	$\frac{3h\nu}{6mc}$
	$\rightarrow {}^2T_1^{(2)}$	$\nu^2T_2 \rightarrow {}^2T_1^{(2)}$	$\frac{3h\nu}{2mc}$
	$\rightarrow {}^2T_2^{(1)}$	$\nu^2T_2 \rightarrow {}^2T_1^{(1)}$	$\frac{3h\nu}{2mc}$
	$\rightarrow {}^2T_2^{(2)}$	$\nu^2T_2 \rightarrow {}^2T_2^{(2)}$	$\frac{3h\nu}{6mc}$
$kd^7$	${}^2E \rightarrow {}^2T_1^{(1)}$	$\nu^2E \rightarrow {}^2T_1^{(1)}$	$\frac{6h\nu}{3mc}$
	$\rightarrow {}^2T_1^{(2)}$	$\nu^2E \rightarrow {}^2T_1^{(2)}$	$\frac{3h\nu}{2mc}$
	$\rightarrow {}^2T_2^{(1)}$	$\nu^2E \rightarrow {}^2T_2^{(1)}$	$\frac{3h\nu}{2mc}$
	$\rightarrow {}^2T_2^{(2)}$	$\nu^2E \rightarrow {}^2T_2^{(2)}$	$\frac{3h\nu}{2mc}$

As already remarked in the introduction, the total intensity of the optical absorption spectra consists of intensities coming from both the vibronically allowed electric-dipole and the magnetic-dipole transitions. Therefore to compare our theoretical oscillator strengths of vibronically allowed electric-dipole transitions with the experiment, we have to subtract out the magnetic-dipole part from the total observed intensities. The paper containing the oscillator strengths of the vibronically allowed electric-dipole transitions will be published elsewhere very soon (Chakravarty, 1968).

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