On the Study of Racah Parameter B for Nickel (II) and Cobalt (II) Compounds

Mohamad M.E. Shakdofa[1], Kamal A. Aly[2,3], Pankaj Sharma[4] and Gomaa A. M. Ali[5,*]

[1]Chemistry Department, Faculty of Science and Arts, P.O. Box 80200, 21589 Khulais, University of Jeddah, Jeddah, Saudi Arabia

[2]Physics Department, Faculty of Science and Arts, P.O. Box 80200, 21589 Khulais, University of Jeddah, Jeddah, Saudi Arabia

[3]Physics Department, Faculty of Science, Al-Azhar University, P.O. 71452, Assiut, Egypt

[4]Department of Physics and Materials Science, Jaypee University of Information Technology, Waknaghat, Solan, H.P. – 173234, India

[5]Chemistry Department, Faculty of Science, Al-Azhar University, Assiut branch, Assiut 71524, Egypt

Abstract: The ligand field strength (Dq) and interelectronic repulsion (B) have been calculated for nickel (II) and cobalt (II) compounds by Underhill and Billing [1] based on v_2 and v_3 values. They solved the quadratic equation $340(Dq^2-18(v_2+v_3)$ Dq+ v_2 $v_3=0$ in Dq for octahedral. Then, the B value was determined using the equation $v_2+v_3-30Dq-15B=0$. But, the first equation has real and imaginary solutions and it's difficult to determine the imaginary one. In addition, in many cases there is no solution of this equation as well as in the case of CoO (d^7 oct.). For octahedral, the above two equations can be considered as a system of two equations with two unknowns which can be solved if we have v_2 and v_3 values and vice versa. Similarly, for tetrahedral, the former two equations also can be solved for Dq and B. Using Newton–Raphson iterations, Dq and B values are exactly determined for octahedral and tetrahedral systems. The obtained values of Dq and B were compared with those previously reported.

Keywords: Racah parameter, Metallic composites, Electronic transition.

INTRODUCTION

The spectra of nickel (II) [2-4] and cobalt (II) [5,6] complexes have been used to estimate Racah parameter (interelectronic repulsion parameter, *B*). In octahedral nickel (II) complexes, only the bands of $v_2\left(3A_{2g}-3T_{1g}(F)\right)$ and $v_3\left(3A_{2g}-3T_{1g}(P)\right)$ are observed. The ligand field strength (Dq) and interelectronic repulsion (B) have been estimated by solving the secular equation [7]. Underhill and Billing [1] simplify the problem by solving a quadratic equation in Dq and B only. The equations for calculating Dq and B based on the v_2 and v_3 values for octahedral Ni(II) complexes d^8 are [1]:

$$340Dq^2-18\left(v_2+v_3\right)Dq+v_2v_3=0 \quad (1)$$

$$B=\frac{v_2+v_3-30Dq}{15} \quad (2)$$

Solving the quadratic equation will give two solutions (real and imaginary). It is difficult to determine the imaginary one. To overcome this problem Eq. (2) can be rewritten as:

$$-30Dq+\left(v_2+v_3\right)-15B=0 \text{ or } v_2+v_3=30Dq+15B \quad (3)$$

Then, substituting the term $v_2 + v_3$ into Eq. (1) gives:

$$-200\ \mathrm{Dq}^2-270BDq+v_2v_3=0 \quad (4)$$

These two Eqs. (3) and (4) are contained two unknowns *i.e.* these two equations can be solved for Dq and *B* if we have v_2 and v_3 values and vice-versa. Each of the two systems of the Eqs. (1) and (2) or Eqs. (3) and (4) can be solved for Dq and B for $Ni(3Etpy)_2Br_2$ (d^8, octa.), $NiMbCl_2$ (d^8, octa.), CoO (d^7, octa.) using a rapidly-converging algorithm (Newton–Raphson iterations) [8,9]. The obtained values have been listed in Table **1** and are compared with those reported previously. It has been found that, in the case of CoO (d^7 octa.), there is no solution of quadratic Eq. (1). The two solutions of Eq. (1) are given by:

$$Dq=\frac{18(v_2+v_3)\pm\sqrt{(18(v_2+v_3))^2-4(340)v_2v_3}}{2(340)} \quad (5)$$

Substituting v_2 = 16680 cm^{-1} and v_3 = 18450 cm^{-1} [10], Eq. (5) could be written as:

*Address correspondence to this author at the Chemistry Department, Faculty of Science, Al-Azhar University, Assiut branch, Assiut 71524, Egypt; E-mail: pks_phy@yahoo.co.in

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$$Dq = \frac{632340 \pm \sqrt{3.99x10^{11} - 4.185x10^{11}}}{680} \qquad (6)$$

The value under the square root is negative. Therefore there is no solution of Eq. (1) at these values of ν_2 and ν_3. Thus a high doubt on how it has been solved.

Furthermore, the authors' values of Dq (887 cm^{-1}) and B (780 cm^{-1}) for CoO don't satisfy the Eqs. (1) and / or (3) as one can see Eq. (1) for CoO take the following form:

$$\left(340\times(887)^2\right)-\left(18\times(16680+18450)\times887\right)+\left(16680\times18450\right)\neq 0$$

Similarly, Eq. (2) become:

$$(-30\times887)+(16680+18450)-(15\times780)\neq 0$$

On the other hand, Dq and B values (781 cm^{-1} and 835 cm^{-1}) for $Ni(3Etpy)_2Br_2$ (d^8, octa.) complex does not satisfy Eq. (3) consequently, Eqs. (1) or (4) also can't be satisfied. Although, B (152 cm^{-1}) and Dq (1123 cm^{-1}) values for Ni(3Etpy)2Br2 (d^8, octa.) are satisfied by the Eq. (1), (2) and (3) but these values are far away from those previously reported. Therefore, these values are incorrect. The exact values of Dq and B are given in Table **1**. From Table **1**, it is noted that Dq and B values are very accurate and sensitive, therefore the two Eqs. (1) and (2) or (3) and (4) must be solved exactly.

On the other hand, the corresponding relations for ions with d^2 or d^7 configuration in an octahedral filed or with a d^3 or d^8 configuration in a tetrahedral filed [1]:

$$340Dq^2 + 18(\nu_3 - 2\nu_2)Dq + \nu_2^2 - \nu_2\nu_3 = 0 \qquad (7)$$

$$B = \frac{\nu_3 - 2\nu_2 + 30Dq}{15} \qquad (8)$$

Rewriting Eq. (8) in the form of:

$$30Dq + (\nu_3 - 2\nu_2) - 15B = 0 \quad or$$
$$\nu_3 - 2\nu_2 = 15B - 30Dq \qquad (9)$$

Substituting the term ν_3−$2\nu_2$ into Eq. (7) gives:

$$-200Dq^2 + 270BDq + \nu_2^2 - \nu_2\nu_3 = 0 \qquad (10)$$

Similarly, the two Eqs. (9) and (10) have been solved using Newton–Raphson iterations [8, 9] in Dq and B for $NiMp_5Cl_2$(d^8, tetra.) and $Cs_3[CoCl_2]Cl$ (d^7, tetra.). The obtained values are listed in Table **1**. In comparison with previously reported results, it has been found that, the Dq, B, ν_2 and ν_3 values don't satisfy Eq. (9) where the term ν_3-$2\nu_2$ isn't equal to the term *15B−30Dq* (Table **1**). In the case of $Cs_3[CoCl_2]Cl$

Table 1: Calculated Values of Dq and B (ν_2, ν_3 Dq and B in cm^{-1})

Compound	Ref.	ν_2	ν_3	Dq	B	ν_2+ν_3	*30Dq+ 15B*	ν_3−$2\nu_2$	*15B−3 0Dq*	Dq	B	Reported values	
		Ref. 1				octa		tetra		This study ++		Dq	B
$Ni(3Etpy)_2Br_2$ (octa.)	[1, 2]	12970	23000	781 1123	835 152	35970	35950 35970	-2940	-10905 -31410	781.262	835.472	789	830
$NiMbCl_2$ (octa.) *+	[1,3]	13150	23000	795 1118	819 173	36150	36140 36140	-3300	-11565 -30945	795.29	819.42	794	825
CoO (octa.)	[1, 10]	16680	18450	887-98	780 ---	35130	38310 20790	- 14910	-14910 ---	884.298	781.403	888	780
2.5-$DmpNiC1_2$ (octa.) *+	[3]	13000	22750	------	1190 ---	35750	--- ---	-3250	--- ---	786.088	811.156	786	811
$NiMb_5Cl_2$ (tetra.)	[1,3]	9200	15620	497-350	--- 808	24820	--- ---	-2780	--- 22620	496.829	808.325	500	810
$Cs_3[CoCl_4]Cl$ (tetra.)	[1,6]	5580	14800	320 759	-884 719	20380	--- ---	3640	-22860 ---	304.397	851.46	320	719
Mp_5NiBr_2 (tetra)	[3]	8600	15470	--- ---	-159 ---	24070	--- ---	-1730	--- ---	465.16	814.987	465	820
Mp_5NiI_2 (tetra)	[3]	8100	15400	--- ---	--- ---	23500	--- ---	-800	--- ---	438.741	824.149	435	825

3Etpy is 3-ethyl pyridine, Mp is Methyl pyrazine, Dmp is Dimethyl pyrazine, * Bridging Halogen, + Bridging pyrazine, ++ These values satisfy that the term $\nu_2 + \nu_3 = 30Dq+15B$ for octahedral and the term $\nu_2 - 2\nu_2 = 15B$ for tetrahedral.

(d^7, tetra.), solving the Eqs. (9) and (10) gives Dq and B values as 304.397 cm^{-1} and 851.46 cm^{-1}. These values of Dq and B are in excellent agreement when we solve the quadratic Eq. (7) in Dq according to the Ref [1] authors. The solutions for Dq are 304.397 cm^{-1} and - 497.1 cm^{-1}. Substituting Dq values into eq. (8) gives B values of 851.46 cm^{-1} and -751.54 cm^{-1} while, the authors of the Ref. [1] reported that Dq = 320 cm^{-1} and B = 719 cm^{-1}. In the case of $NiMbCl_2$ (d^8, tetra.) a small difference has been observed, but the exact values that satisfies the system of Eqs. (9) and (10) are needed.

For clarity and confirmation Dq and B values for octa 2.5-$DmpNiC1_2$, tetra Mp_5NiBr_2 and tetra Mp_5NiI_2 have been calculated based on v_2 and v_3 values from Ref [3] (see Table **1**) and also compared with the reported data [3]. Small difference is observed between the reported values and the present study. Furthermore, the exact values of Dq and B according to the present study satisfy the pairs Eqs. (1) and (2) or/and (3) and (4) for ions with octahedral field and also satisfy the pairs Eqs. (7) and (8) and/or (9) and (10) for ions with tetrahedral field.

HIGHLIGHTS

- In the previous reports Dq and B for oct. and tet. compounds were determined by solving the secular equation only.
- The secular equation has real and imagery solutions, it's difficult to determine the imaginary one.
- The present study concerns with precisely determination of both Dq and B using Newton–Raphson iterations.

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