The Nephelauxetic Effect — Calculation and Accuracy of the Interelectronic Repulsion Parameters

II. Application to $d^3$ and $d^7$ Single Crystal Spectra at Cryogenic Temperatures *

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Expressions are reviewed which may be used to determine $10Dq$ and $B$ from the spin-allowed bands in the optical spectra of $d^3$ and $d^7$ electron systems within octahedral and tetrahedral symmetry. Application to low-temperature single crystal spectra demonstrates that (i) the semi-empirical ligand field theory produces transition energies with sufficient accuracy; (ii) differences in the values of $10Dq$ and $B$ observed with different fitting methods may be attributed to the inaccuracy of experimental data; (iii) there are generally valid values of $B_{2s}$ and $B_{2g}$ for each complex ion.

The semi-empirical ligand field theory provides means to completely determine the electronic $d-d$ spectra of transition metal ions of octahedral symmetry in terms of three parameters: the octahedral splitting parameter $10Dq$ (= $A$) and the inter-electronic repulsion parameters ($= R$) $B$ and $C$ which are linear combinations of the Condon-Shortley parameters $F_2$ and $F_4$. An analogous statement applies to tetrahedral symmetry and one or two additional parameters (e.g. $D_s$ and $D_t$ in tetragonal environment) are required if the symmetry is lower than cubic. In general, the numerical values of the parameters $B$ and $C$, as determined from $d-d$ spectra, are lower than the values in a free transition metal ion. This observation is well known as the nephelauxetic effect

In the first part of this study, the author has recently reviewed and tested methods which may be used to determine $10Dq$, $B$, and $C$ from electronic spectra. To focus the attention on the value of $B$, these methods were applied to the spin-allowed $d-d$ bands in high-spin $d^2$, $d^3$, $d^4$, and $d^9$ complexes of octahedral and tetrahedral microsymmetry. In the expressions of the corresponding transition energies, the parameter $C$ does not occur. In addition, $10Dq$ may always be fixed by a suitable choice of the calculation method. A convenient check on the accuracy of the employed numerical procedure is provided by calculating the extra band energy, if those complex ions are considered where all three spin-allowed $d-d$ bands are observed. Room temperature solution and single crystal spectra of almost fifty complexes and impurity ions of the transition metals were subject of the analysis. The results may be summarized as follows:

(i) The accuracy of $B$ and $10Dq$ depends on the method adopted to their calculation. Consequently, certain methods may be selected which provide the “best” possible fit to the experimental data;

(ii) Given a specific method of calculation, an unsystematic variation in the deviations between calculated and observed transition energies is often encountered. It was suggested that this is due to insufficient accuracy of the experimental room temperature (solution) data.

In the present contribution, the same methods as used previously will be applied to single crystal spectra measured at cryogenic temperatures. It will be demonstrated that results somewhat different from those of room temperature spectra are obtained.

1. Ligand Field Theory of $d^3$ and $d^7$ Ions in Cubic Fields

The general treatment of ligand field theory is adequately covered in several textbooks to which

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* For the first part of this study refer to E. König, Struct. Bonding 9, 175 [1971].
reference is made here. With respect to the single crystal data available at present, we will concentrate on the theory of $d^3$ and $d^7$ ions in cubic fields. The relevant energy expressions have been derived previously.$^4$ For convenience, we will briefly introduce those quantities and list explicitly those expressions which will be needed in the subsequent numerical calculations.

Thus in the octahedral $d^3$ configuration three spin-allowed transitions from the $4A_{2g}$ ground state to the excited states $4T_{2g}$, $4T_{1g}$, and $4T_{1g}$ are expected. Within the approximation considered here, the energy of the lowest transition is always determined as $v_1 (4A_{2g} \rightarrow 4T_{2g}) = 10 Dq$. The energies of the two higher transitions follow from

$$v_{2,3} = \frac{1}{2} (15 B + 30 Dq) \pm \frac{1}{2} [(15 B - 10 Dq)^2 + 12 B \cdot 10 Dq]^{1/2}.$$  \hspace{1cm} (1)

The parameter $B$ may then be obtained according to four different methods:

(a) fitting the second band,

$$B = \frac{1}{2} (v_1 + v_2 - 3 v_3) / (15 v_2 - 27 v_1),$$  \hspace{1cm} (2)

(b) fitting the third band,

$$B = \frac{1}{2} (v_1 + v_3 - 3 v_2) / (15 v_3 - 27 v_1),$$  \hspace{1cm} (3)

(c) fitting the sum of the second and third band,

$$B = (v_2 + v_3 - 3 v_1) / 15,$$  \hspace{1cm} (4)

(d) fitting the difference between the second and third band,

$$B = \frac{1}{75} [3 v_1 \pm (25 (v_3 - v_2)^2 - 16 v_1^3)^{1/2}].$$  \hspace{1cm} (5)

The expressions (1) to (5) apply to tetrahedral $d^7$ ions as well.

In the octahedral $d^7$ configuration, the ground state is $a^3T_{1g}$ and the excited quartet states are, in the order of increasing energy, $4T_{2g}$, $4A_{2g}$, and $4T_{1g}$. The energy of the three spin-allowed transitions is determined according to

$$v_1 (a^3T_{1g} \rightarrow 4T_{2g}) = -\frac{1}{2} (10 Dq - 15 B) + \frac{1}{2} v_2,$$  \hspace{1cm} (6)

$$v_2 (a^3T_{1g} \rightarrow 4A_{2g}) = v_3 + 10 Dq,$$  \hspace{1cm} (7)

$$v_3 (a^3T_{1g} \rightarrow b^4T_{1g}) = \left[ (10 Dq + 15 B)^2 - 12 B \cdot 10 Dq \right]^{1/2}.$$  \hspace{1cm} (8)

There are again four different methods which may be employed to obtain the parameters $10 Dq$ and $B$:

(a) fitting the first and second band,

$$10 Dq = v_2 - v_1,$$  \hspace{1cm} (9)

$$B = (2 v_1^2 - v_1 v_2) (12 v_2 - 27 v_1).$$  \hspace{1cm} (10)

(b) fitting the first and third band,

$$10 Dq = 2 v_1 - v_3 + 15 B,$$  \hspace{1cm} (11)

$$B = \frac{1}{30} [-(2 v_1 - v_3) \pm (-v_1^2 + v_2^2 + v_1 v_3)^{1/2}].$$  \hspace{1cm} (12)

(c) fitting the second and third band,

$$10 Dq = \frac{1}{3} (2 v_2 - v_3) + 5 B,$$  \hspace{1cm} (13)

$$B = 510 [7 (v_2 - 2 v_3) \pm 3 (81 v_3^2 - 16 v_2 (v_2 - v_3))]^{1/2}.$$  \hspace{1cm} (14)

(d) fitting the difference between the first and second band,

$$10 Dq = v_2 - v_1,$$  \hspace{1cm} (15)

$$B = (v_2 + v_3 - 3 v_1) / 15.$$  \hspace{1cm} (16)

II. Application to Single Crystal Spectra

In order to assess the accuracy of the parameter values of $10 Dq$ and $B$, the equations listed in section I will be applied below to some recent low temperature single crystal spectra. Following the first part of this study$^4$ it will be assumed, for the sake of argument, that the three-parameter $(10 Dq, B, C)$ theory is valid exactly. The question then arises about the significance of the calculated transition energies. In ligand field theory, all energy differences are calculated at a constant value of $10 Dq$ (viz. “vertical” transitions in the Tanabe-Sugano diagram). Since the relation $10 Dq \sim R^{-5}$ holds to a reasonable approximation$^{10}$, this is equivalent to a fixed metal-ligand distance, $R$. In the spin-allowed $d-d$ transitions considered here, the states involved originate in different strong field configurations $t_{2g}^6 e_{g}^0$ and, consequently, the potential minima of the excited state and the ground state do not coincide. The calculated transition energy corresponds, therefore, to the energy of a transition from the zero-point vibrational level of the electronic ground state to an excited vibrational level of the excited state (cf. “vertical” transition according to the Franck-Condon principle).

As far as the comparison between theoretical and experimental energies is concerned, two limiting conditions may be distinguished:

(i) In centrosymmetric (e.g. octahedral) complexes, all $d-d$ transitions are rigorously forbidden on the basis of parity. The forbidden electronic transitions may gain intensity through coupling to odd vibrations (vibronic mechanism$^{11}$). At low
temperatures, each band thus consists of a progression in one or more even vibrations superimposed upon one quantum of the odd ("permitting") vibration. The no-phonon \((0'' \rightarrow 0')\) band is absent or of very weak intensity. Therefore, within reasonable approximation, the calculated vertical transition energy should be associated with the maximum of the vibronic band determined, in principle, at 0 °K.

(ii) In non-centrosymmetric (e.g. tetrahedral) complexes, the \(d-d\) transitions become partly allowed on account of mixing with odd-parity states of the central ion (e.g. p states). One observes, at low temperatures, a progression in the totally symmetric vibronic mode originating in the no-phonon \((0'' \rightarrow 0')\) band. Normally, the highest intensity would be expected in one of the higher vibrational sub-bands \(0'' \rightarrow n' v_{\text{even}}\). However, in the example studied at present\(^{13,14}\), the most prominent band is associated with the no-phonon transition. This situation is encountered if ground and excited state potential minima occur at the same internuclear distances. It has been suggested\(^ {13}\), therefore, that the geometry of the Co\(^ {2+}\) ion in the relevant excited states is not greatly different from that in the ground state. Here it may be more appropriate to approximate the calculated vertical transition energy by the average of the energies of the no-phonon bands in the most intense spin-orbit components determined again, in principle, at 0 °K.

If the temperature is increased, in both cases higher vibrational levels of the electronic ground state become successively populated and the corresponding band in the electronic spectrum is progressively shifted to lower energy. The magnitude of the shift is dependent on the distribution of the vibrational levels in the electronic ground state and on the intensity of the resulting hot bands and will differ from compound to compound. Therefore, in general, spectra measured at higher than cryogenic temperatures cannot compare favorably with theory.

### III. Results and Discussion

Results of the present analysis are compiled in Tables 1 to 3. For each compound, experimental transition energies determined according to section II are listed in line 1. Subsequent lines contain the calculated transition energies, their deviation from the corresponding experimental value, \(\delta v = v_{\text{calc}} - v_{\text{exp}}\) (in cm\(^{-1}\) and in percent), and the values of the parameters \(B_{35}\) and \(\beta_{35}\). In Table 2, values of \(10 Dq\) and of the deviation, \(\delta(10 Dq)\), from the value of \(v_2 - v_1\) are listed in addition. Each line applies to a different method marked with reference to section I.

In the octahedral \(d^3\) configuration, the only well evidenced low-temperature single crystal spectrum where the \(4A_{2g} \rightarrow b^4T_{1g}\) transition has been unequivocally assigned is that of VCl\(_4\). If the quasi-molecular model is assumed type (i) behaviour is expected. No fine structure has been observed in the \(4A_{2g} \rightarrow 4T_{2g}\) and \(4A_{2g} \rightarrow a^4T_{1g}\) bands, and thus the band maxima listed in Table 1 are associated with the vertical transition energies. In the \(4A_{2g} \rightarrow b^4T_{1g}\) band where a vibrational progression in a mode of \(\sim 234\) cm\(^{-1}\) is encountered, the first prominent vibrational component (viz. 22,244 cm\(^{-1}\)) seems to well approximate the centroid of the band (viz. Fig. 1 of I. c.\(^ {18}\)). The parameter values calculated by Kim et al.\(^ {16}\) are incorrect, since applying eq (1) the fit was based on the estimated energy of the no-phonon transition. No suitable data on the \(d^3\) configuration in tetrahedral environment are known.

Recently, low temperature single crystal spectra of RbCoCl\(_3\) and of the Co\(^ {2+}\) ion in several chloride lattices became available.\(^ {19}\) The \(a^4T_{1g}\) ground state of the octahedral \(d^7\) configuration is split by spin-orbit interaction into the \(T_6, T_8^a, T_8^b\) and \(T_7\) levels in the order of increasing energy. Since \(T_6\) and \(T_7\) are Kramers doublets, the \(a^4T_{1g}\) term

| Compound | Method | \(v_1\) cm\(^{-1}\) | \(v_2\) cm\(^{-1}\) | \(v_3\) cm\(^{-1}\) | \(v_{\text{calc}}\) cm\(^{-1}\) | \(\delta v\) | \(B_{35}\) cm\(^{-1}\) | \(\beta_{35}\) |
|----------|--------|----------------|----------------|----------------|-----------------|----------------|----------------|
| VCl\(_2\) (22°K) | exp | 9300 | 14,220 | 22,244 | 22,231 | - 7 | 0.03 | 570.1 | 0.74 |
| a | 10 | 14,226 | fitted | 22,231 | + 6 | 0.04 | 571.3 | 0.75 |
| b | 10 | 14,224 | fitted | 22,240 | + 4 | 0.02 | 570.9 | 0.75 |
| d | 10 | 14,231 | fitted | 22,255 | + 11 | 0.06 | 572.3 | 0.75 |

Table 1. Observed and Calculated Transition Energies of Octahedral Vanadium(II) \((B_{\text{free}} = 766\) cm\(^{-1}\)).
has been effectively stabilized against the action of the Jahn-Teller effect. Thus, assuming type (i) conditions, the experimental energies included in Table 2 were obtained directly from the reported spectra. If a vibrational structure was observed (viz. the $a_{4}T_{lg} \rightarrow 4T_{2g}$ band in CsMgCl$_3$: Co$^{2+}$ and in LiCl : Co$^{2+}$), the centroid of the vibronic band was estimated. It should be observed that, due to its low intensity (“two-electron jump”), a high experimental uncertainty should be assumed for the $a_{4}T_{lg} (t_{2g} e_{g}^{2}) \rightarrow 4A_{2g} (4 e_{g}^{4})$ band.

In the single crystal spectra of tetrahedrally co-ordinated Co$^{2+}$ ions, type (ii) conditions are prevalent and the experimental energies are determined...
accordingly. Thus, in ZnO: Co$^{2+}$, it is the energies of the highest intensity (no-phonon) vibrational bands which are listed in Table 3, since individual vibrational components at higher energies are considerably weaker in intensity. In ZnAl$_2$O$_4$: Co$^{2+}$, the transition energies employed in Table 3 are mean values of the most intense no-phonon bands in each of the electronic transitions. It should be kept in mind that, due to the complicated structure of the bands, the totality of the weak vibrational transitions may still contribute a significant fraction to the overall transition energy.

Inspection of the results which have been collected in Tables 1, 2, and 3 reveals considerable differences to the results from room temperature (solution) spectra. If those results are disregarded which were obtained by the most unfavorable methods [viz. (a) in Table 3], the agreement between calculated and observed transition energies is surprisingly good. On the other hand, there is not much that could be gained by choosing between methods (b), (c), and (d) in octahedral $d^3$ and tetrahedral $d^3$ spectra. Most important, the deviation between the values of $B_{35}$ calculated by different methods is negligible and that of $\beta_{35}$ is practically non-existent. In Table 2, differences between results obtained by methods (b), (c), and (d) are somewhat larger but still considerably smaller than in the room temperature spectra. In addition, the smallest differences are encountered in those spectra where the best resolution in the $a^3T_{1g} \rightarrow 4A_{2g}$ band has been achieved, cf. CsCdCl$_3$: Co$^{2+}$ and LiCl: Co$^{2+}$. Thus, if the complications inherent in the data are taken into account, the results of octahedral Co$^{2+}$ ions are similar to those discussed above.

IV. Summary and Conclusions

We have reviewed expressions which were derived previously, on the basis of the semi-empirical ligand field theory, to determine $10Dq$ and $B$ from the spin-allowed bands of $d^3$ and $d^7$ electron systems of octahedral and tetrahedral stereochemistry. These equations were applied to low-temperature single crystal spectra of suitable compounds and the extra band energy was calculated.

Provided the spectral data employed are representative for most systems of the studied electron configuration, the conclusions arrived at are as follows:

(i) the semi-empirical ligand field theory reproduces quite accurately the transition energies, at least in spin-allowed bands of $d^3$ and $d^7$ systems of cubic symmetry;

(ii) the differences in the parameter values $10Dq$ and $B$ resulting from the application of different fitting methods are due essentially to inaccuracy of the experimental data;

(iii) there exist generally valid values of the inter-electronic repulsion and nephelauxetic parameters $B_{35}$ and $\beta_{35}$ for each complex ion which, however, may be determined only if sufficiently accurate experimental data are available.

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Auswertung nmr-spektroskopischer Messungen
der Mischassoziation von Nucleosid-Derivaten bei vergleichbaren
Konzentrationsverhältnissen

Evaluation of NMR-spectroscopical Results about Co-association of Nucleoside Derivatives in Comparable Concentrations

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In this paper we described a method how to calculate from NMR the association — caused by H-bonds — of two components. These components may be present in equal concentration and may be partially self-associated.

The may act as H-donors and acceptors. The method is demonstrated using some nucleoside derivatives as examples.

In einer vorangehenden Arbeit haben wir über NMR-spektroskopische Untersuchungen zur Mischassoziation von vier Nucleosid-Derivaten berichtet 1. Die Auswertung erfolgte mit Hilfe einer modifizierten Benesi-Hildebrand-Auftragung:

\[ \frac{1}{v_a - v_{mb}} = \frac{1}{v_{xb} - v_{mb}} + \frac{1}{(v_{xb} - v_{mb}) \cdot K_x \cdot c_{ma}}. \]  

Hierin bedeuten: \( v_b \) gemessene chemische Verschiebung der Komponente b, \( v_{mb} \) extrapolierte chemische Verschiebung des Monomeren b, \( v_{xb} \) berechnete chemische Verschiebung der Mischassoziate, \( K_x \) Mischassoziations-Konstante in \( 1/Mol \), \( c_{ma} \) Monomerenkonzentration der Komponente a.

\( c_{ma} \) läßt sich leicht berechnen, wenn die zugehörige Eigenassoziations-Konstante bekannt ist.


Herleitung der Auswertemethode

In den beiden Molekülen eines Mischassoziatos befinden sich die sauren Protonen in chemisch verschiedener Umgebung, es müssen also auch zwei verschiedene chemische Verschiebungen für das „reine“ Mischassoziat existieren, die jeweils die Lage der zwei beobachteten Signale beeinflussen. Sie gehen dabei mit dem einfachen Gewicht der Mischassoziations-Konzentration ein, wenn ein 1:1-Mischassoziat vorliegt. Die folgende Abb. 1 veranschaulicht dies. Dabei bedeuten die gestrichelten Linien die hypothetischen Signale der einzelnen Spezies, und die ausgezogenen Linien entsprechen

Abb. 1. Schematisches Spektrum der H-Brücken-Protonensignale für die Mischassoziation. \( v_a, v_{nb}, v_{mb} \) gemessene Verschiebungen, Eigenassoziat-Verschiebung, Monomerenverschiebung, \( c, c_n, c_m \) Einwaage-, Eigenassoziat- und Monomerenkonzentration.

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