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Transferability of Empirical Crystal-Field Parameters of Ni(II) Complexes of Different Symmetries

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A method of systematic linearization of the crystal-field matrices appropriate for obtaining empirical parameters of transition metal complexes of any symmetry is presented and applied to forty complexes of Ni^{2+} of O_h and D_{4h} symmetries. The method is a generalization of that proposed by L. Pueyo, M. Bermejo, and J. W. Richardson (*J. Solid State Chem.* 31, 217 (1980)) for complexes of O_h symmetry and incorporates the spin–orbit coupling in a very simple manner. Using this method, classical parameters, such as $10Dq$, and punctual quantities, such as the ligand perturbing charges q_i, were obtained for these complexes. The former are transferable within 10% if (a) there are not big changes in the metal–ligand distances and (b) the chemical environments of the ligand atoms are comparable. However, the punctual parameters show variations of 20% or more. Electronic repulsion integrals seem to be nicely transferable by means of addition rules based on the hypothesis of isotropic repulsion in the low-symmetry field. Since one of the fitting parameters is a scaling factor of the $R_{nl}(r)$ metal function, the process of optimization generates an empirical representation, $R_{nl}(\lambda r)$, of the locally perturbed metallic state.

I. Introduction

In a recent work Pueyo *et al.* (*1*) reported a systematic procedure for obtaining crystal-field parameters from the optical spectra of transition metal complexes. The method is based on a linearization of the electrostatic matrices which makes it possible to write down the spectral frequencies as linear functions of $10Dq$ and the Racah electronic repulsion parameters. The optimal linear equations are simpler than those proposed earlier by Boxall *et al.* (*2*) and like those they are restricted to complexes of octahedral symmetry. In these two papers the spin–orbit interaction is neglected.

In this report we present an extension of the method described in (*1*) which is appropriate for dealing with complexes of any symmetry and which is able to incorporate the spin–orbit coupling in a simple way.

We applied the method to a collection of Ni^{2+} complexes of O_h and D_{4h} symmetries with different types of ligand species. In this way, sets of parameters obtained from complexes of different symmetries by means of a systematic and objective method can be compared and analyzed.

An important feature of the present method is the use, as an empirical parameter, of a scaling factor in the metallic radial wavefunction, as proposed by Jørgensen some years ago (*3*). This scaling allows for a substantial reduction in the number of independent parameters without loss of quality in the description of the spectra.

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We chose the Ni^{2+} ion because we are currently interested in the optical spectra and magnetochemistry of species such as the dimer nickel dithiobenzoate (*4, 5*). In dealing with this type of complex an examination of their electronic energy levels in terms of a simple crystal-field treatment could be useful, but in order to do that one needs a good set of appropriate empirical parameters. Then, the question of the transferability of these parameters arises. This matter has been discussed several times in the literature and generally it is believed that the classical parameters, like $10Dq$, are transferable among complexes of a given cation in different symmetries (*6*). This transferability has been observed, for instance, in Cr^{3+} and Co^{3+} complexes by Wentworth and Piper (*6*), in chlorocuprates by Hatfield and Piper (*7*) and by Day (*8*), and in $Ni(py)_4X_2$ compounds by Schreiner and Hamm (*9*).

We also explored the transferability of the punctual parameters, such as the perturbing electric charges or dipole moments associated with the ligands. These parameters appear naturally in our method as functions of the classical ones and the scaled splitting integrals B^k.

From this work we conclude that the classical parameters obtained by linearization of the electrostatic matrices of Ni^{2+} complexes are transferable within 10%, in the worst case. However, the punctual parameters show a more scattered behavior which makes their transferability uncertain. This last result is less satisfactory than that obtained by Glerup *et al.* (*10*) in their analysis of the $Ni(py)_4X_2$ complexes within the Angular Overlap model.

Our results seem to be consistent with a sharp variation of $10Dq$ with the bondlength, R_{ML} (*7*). Such variation destroys any possibility of transference when there are large changes in geometry. On the other hand, differences in the chemical environment of the donor atom give rise to differences of even 35% in the classical parameters. These changes should be taken into account in any attempt of transferability of parameters.

In the next section we detail the characteristics of our method. Section III contains the results and the discussion.

II. Methodology

In this paper we will deal with the usual crystal-field matrices whose elements can be written down as (*11*)

$$H(i,j) = \sum_k a(i,j,k)\, F(k) + \sum_k \sum_l b(i,j,k,l)\, \mu(l)\, B(k,l), \quad (1)$$

where the linear coefficients $a(i,j,k)$ and $b(i,j,k,l)$ are known numbers, $F(k)$ the Slater–Condon interelectronic repulsion integrals (*12*), $\mu(l)$ the dipole moment associated with the lth ligand species, and $B(k,l)$ the radial splitting integral of order k defined as (*13*)

$$B(k,l) = dG(k,l)/dR_{ML}. \quad (2)$$

In Eq. (2), R_{ML} is the internuclear distance between the metal ion and the lth ligand and

$$G(k,l) = \langle R_{nl}(r) \left| \frac{r_<^k}{r_>^{k+1}} \right| R_{nl}(r) \rangle, \quad (3)$$

where $r_<$ is the lesser and $r_>$ the greater of r and R_{ML}. $R_{nl}(r)$ is the radial metallic wavefunction of the nl state.

The Racah parameters $A = F(0) - 49F(4)$, $B = F(2) - 5F(4)$, and $C = 35F(4)$ (*14*) are commonly used instead of the Slater–Condon integrals. The splitting interactions are generally collected in the form of the well-known quantities Dq, Ds, Dt appropriate for dealing with fields of octahedral, tetragonal, trigonal, and cylindrical symmetries (*15*).

As is well known, in complexes of octahedral symmetry only one splitting parameter appears, the familiar $\Delta = 10Dq$. In fields created by arbitrary arrangements of arbitrary types of ligand species the general expression (1) will contain different values of $\mu(l)$ and different orders, k, and distances, R_{ML}, in $B(k,l)$.

In our previous work (*1*), we used the classical parameter $10Dq$ without delving into the details of its structure. In this work we considered this structure for two reasons. First, we are interested in the possibility of obtaining reliable empirical punctual parameters associated with a given ligand. Second, we can argue that we can understand the fitting of the crystal-field matrices to the observed spectrum as a method of obtaining an empirical nl metal wavefunction. This function will determine all the electronic repulsion integrals as well as the $B(k,l)$ splitting integrals once the geometry of the complex is specified. In doing that all the $B(k,l)$ become interrelated and the number of splitting parameters is noticeably reduced.

The empirical nl wavefunction discussed in this paper will have the form

$$\Psi_{nlm}(r,\theta,\phi;\lambda) = R_{nl}(\lambda r)Y_{lm}(\theta,\phi), \quad (4)$$

where $Y_{lm}(\theta,\phi)$ are the spherical harmonics, $R_{nl}(r)$ is any reference normalized radial wavefunction, and λ is the scaler that will be considered as a fitting parameter. Once a numerical value is given to λ all the $F(k)$ integrals are determined by the relationship

$$F(k,\lambda) = \lambda F(k,1), \quad (5)$$

$F(k,1)$ being the $F(k)$ integral computed with the reference function $R_{nl}(r)$. The splitting integrals will need, also, the geometry of the complex, the reference function, and a value of λ in order to be fully determined. We will write, then, $B(k,l,\lambda)$ for $B(k,l)$.

Now, the number of independent parameters will be equal to the number of different ligand species plus one, λ. The description of the spectrum of a complex like the *trans*-$\mathrm{Ni(py)_4Cl_2}$, formed by a pseudooctahedron of four equatorial nitrogen atoms and two chloride ions in the C_4 axis, will need three parameters, say, Δ_{xy}, Δ_z, λ, instead of the usual set formed by Dq, Ds, Dt, B, and C.

In our scheme the spin–orbit coupling can be incorporated without further increase in the number of parameters, since the spin–orbit coupling constant has the property

$$\zeta_{nl}(\lambda) = \lambda^3 \zeta_{nl}(1). \quad (6)$$

The general form of the perturbing matrix element can then be written as

$$H(i,j) = a(i,j)\lambda + b(i,j)\lambda^3 + \sum_k \sum_l c(i,j,k,l)\mu(l)B(k,l,\lambda). \quad (7)$$

In this expression the first term collects all the electronic repulsion normally written as $\alpha B + \beta C$, the second represents the spin–orbit contribution, and the double sum the splitting terms. The coefficients a, b, and c are all predetermined by the angular integrations and the reference values, ($\lambda = 1$), of the correspondent radial integrals.

We now want to linearize the eigenvalues of the hamiltonian matrix H in a systematic manner. In order to do that, we define a splitting parameter $\Delta(l)$ for each different ligand species,

$$\Delta(l) = -5\mu(l)\, B(k^\circ,l,\lambda)/3, \quad (8)$$

where k° is any convenient value of k. We chose $k^\circ = 4$ in order to have $\Delta(l) = 10Dq$ in the octahedral case. Then, we assume that the eigenvalues of H can be expressed as linear functions of λ and all the $\Delta(l)$, plus a cubic term in λ. If this linearization is possible, any transition energy, $\Delta E(i)$, will adopt the form

$$\Delta E(i) = \alpha(i)\,\lambda + \beta(i)\,\lambda^3 + \sum_l \gamma(i,l)\,\Delta(l). \quad (9)$$

The problem now is to obtain the best

values of $\alpha(i)$, $\beta(i)$, $\gamma(i,l)$, λ, and $\Delta(l)$ for a given spectrum.

The working procedure for solving this problem follows the lines described in (*1*). First, we adopt a geometry for the complex and a reference function $R_{nl}(r)$. Some trial values for λ and $\Delta(l)$ are taken, and according to Eq. (8) the dipole moments $\mu(l) = -3\Delta(l)/5B(4,l,\lambda)$ are calculated. Then, all the splitting terms are generated by the equations

$$\mu(l)B(k,l,\lambda) = -3\Delta(l)B(k,l,\lambda)/5B(4,l,\lambda), \quad k \neq 4. \quad (10)$$

The perturbing matrix can now be completely calculated and diagonalized giving rise to a set of computed transition energies.

Next, we compute the coefficients $\alpha(i)$, $\beta(i)$, $\gamma(i,l)$ by generating new sets of transition energies with the correspondent parameters incremented in a small amount. For instance, we compute the matrix $H(\ldots\ \Delta(l)\ \ldots)$, its eigenvalues $E(i, \ldots \Delta(l) \ldots)$, and the transition energies $\Delta E(i, \ldots \Delta(l) \ldots)$. Then, we increment $\Delta(l)$ to $\Delta(l) + \delta\Delta(l)$ and compute the matrix $H(\ldots \Delta(l) + \delta\Delta(l) \ldots)$, its eigenvalues $E(i, \ldots \Delta(l) + \delta\Delta(l) \ldots)$, and the transition energies $\Delta E(i, \ldots \Delta(l) + \delta\Delta(l) \ldots)$, having

$$\gamma(i,l) \simeq \{\Delta E(i, \ldots \Delta(l) + \delta\Delta(l) \ldots) - \Delta E(i, \ldots \Delta(l) \ldots)\}/\delta\Delta(l). \quad (11)$$

Once we have the coefficients we perform a least-squares fitting to the experimentally observed frequencies, using Eq. (9). With the new values of λ and $\Delta(l)$ a second cycle of calculations can be executed. An iterative sequence of calculations follows. The cycles stop when the parameters and the coefficients are reproduced within a given stability threshold (10^{-5} in this work). We obtain, in that way, an optimum set of classical parameters, $\Delta(l)$, a correspondent set of punctual parameters, from Eq. (8), and an optimum scaler that gives rise to an optimum empirical $R_{nl}(r)$ wavefunction.

III. Results and Discussion

Our main interest in this calculation has been the comparison of the splitting and repulsion parameters of Ni^{2+} complexes of O_h and D_{4h} symmetries. We analyzed 29 NiL_6 clusters, 20 with L = oxygen, 8 with L = nitrogen, and 1 with L = sulfur. The spectrum of the NiS_6 compound was taken from Tarantelli *et al.* (*16*), the spectra of all the other NiL_6 complexes from Reedijk *et al.* (*17*).

We used R(Ni–O) = 2.05 Å in the 20 NiO_6 complexes, R(Ni–N) = 2.11 Å in the 8 NiN_6 complexes, and R(Ni–S) = 2.45 Å in NiS_6 (*18*). As examples of clusters of D_{4h} symmetry we took seven $Ni(stien)_2^{2+}$ complexes (stien = 1,2-diphenylethylenediamine) whose spectra have been reported by Zink and Drago (*19*) and two NiS_4X_2 complexes studied by Tarantelli *et al.* (*16*). The $Ni(stien)_2^{2+}$ compounds were analyzed in this work with R(Ni–N) = 2.084 Å and R(Ni–O) = 2.102 Å and the NiS_4X_2 with R(Ni–S) = 2.48 Å and R(Ni–X) = 2.45 Å (*18*).

These spectra do not show fine structure and accordingly we have not included the spin–orbit coupling in the analysis. As reference wavefunction for the Ni^{2+} $3d$ states we used the double-ζ function of Richardson *et al.* (*22*).

A sample of the calculation performed in the complexes of octahedral symmetry is presented in Table I. Table II contains our results in the D_{4h} group. First, we note that these calculations reproduce the observed spectra within 200–400 cm^{-1} in the O_h group and within 300–700 cm^{-1} in the D_{4h} group. Results of the NiS_4X_2 complexes are worse. In all these cases the method shows a good convergence in 10–15 iterations. We recall that we describe the four octahedral transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, ^1E_g, a^3T_{1g}, b^3T_{1g} with only two parameters, Δ and λ, and the

TABLE I

SELECTED RESULTS OF THE FITTING CALCULATIONS IN OCTAHEDRAL COMPLEXES

Compound[a]	R^{a}_{ML} (Å)	Δ (kK)	μ (D)	λ (a.u.)	rms (kK)
1. $Ni(AcOH)_6(ClO_4)_2$	2.05	7.90	4.03	0.729	0.31
2. $Ni(EtOH)_6(ClO_4)_2$	2.05	8.00	4.13	0.733	0.34
3. $Ni(MeOH)_6(ClO_4)_2$	2.05	8.09	4.28	0.740	0.38
4. $Ni(H_2O)_6(ClO_4)_2$	2.05	8.21	4.51	0.749	0.36
5. $Ni(CH_3CN)_6(ClO_4)_2$	2.11	10.40	5.17	0.686	0.28
6. $Ni(NH_3)_6(ClO_4)_2$	2.11	10.78	5.01	0.667	0.13
7. $Ni(en)_3(ClO_4)_2$	2.11	10.54	4.64	0.624	0.20
8. $Ni(stien)_3(ClO_4)_2$	2.11	11.42	4.89	0.643	0.20
9. $Ni(dbtu)_6I_2$	2.50	8.74	3.42	0.400	0.38

[a] The spectra of compounds 1–7 were taken from Ref. (*17*); the spectrum of compound 8 from Ref. (*20*) (stien = 1,2-diphenylethylenediamine); and the spectrum of compound 9 from Ref. (*16*) (dbtu = dibutylthiourea).

[b] See Ref. (*18*).

six tetragonal transitions $^3B_{2g} \rightarrow a^3E_g$, $^3B_{1g}$, a^3A_{2g}, b^3E_g, b^3A_{2g}, c^3E_g with three parameters, Δ_{xy}, Δ_z, and λ. In these circumstances, the rms deviation obtained here seems to be good.

In order to examine the transferability of the crystal-field parameters obtained in this calculation we summarized our results in Table III. In this table we present the average values of the best punctual and classical parameters obtained in all the octahedral and tetragonal complexes studied in this work. In Table III we observe that in the group of octahedral complexes Δ is stable with relative deviations of about 6–7%. Still better is the stability of Δ(O) and Δ(N) in the tetragonal complexes, with deviations smaller than 5%. We discuss below the significative influence of R_{ML} in Δ. The influence of R_{ML} on the electronic repulsion parameters is in all probability much smaller and we will neglect it in this analysis. Accordingly, we will enter into the analysis of the transferability of λ without

TABLE II

RESULTS OF THE FITTING CALCULATIONS IN COMPLEXES OF D_{4h} SYMMETRY

Compound[a]	Δ_{xy} (kK)	Δ_z (kK)	μ_{xy} (D)	μ_z (D)	λ (a.u.)	rms (kK)
1. $Ni(stien)_2Ac_2$	11.61	9.76	5.24	6.00	0.711	0.38
2. $Ni(stien)_2(ClAc)_2$	11.01	9.67	3.73	4.11	0.614	0.30
3. $Ni(stien)_2(Cl_2Ac)_2$	11.38	9.41	5.64	5.70	0.731	0.47
4. $Ni(stien)_2(Cl_3Ac)_2$	11.77	8.96	5.17	6.50	0.730	0.50
5. $Ni(stien)_2(\phi-COO)_2$	11.41	9.57	4.38	5.04	0.667	0.71
6. $Ni(stien)_2(Cl-\phi-COO)_2$	11.74	10.35	4.23	4.64	0.632	0.69
7. $Ni(stien)_2(CH_3-\phi-COO)_2$	11.38	9.69	5.64	6.35	0.733	0.40
8. $Ni(dbtu)_4Cl_2$	9.23	8.60	4.69	4.56	0.518	1.30
9. $Ni(dbtu)_4Br_2$	9.40	8.71	4.28	4.16	0.486	1.47

[a] The spectra of complexes 1–7 (R_{xy} = 2.084, R_z = 2.102 Å) were taken from Ref. (*19*); the spectra of compounds 8–9 (R_{xy} = 2.480, R_z = 2.450 Å) taken from Ref. (*16*).

TABLE III

AVERAGE VALUES OF THE BEST PARAMETERS OBTAINED IN THIS WORK

Parameter	Group O_h	Group D_{4h}
$\bar{\mu}$(O)	3.93(7.4)	5.48(15.3)
$\bar{\mu}$(N)	4.83(5.5)	4.86(14.3)
$\bar{\lambda}$(O)	0.714(3.3)	0.688(6.8)
$\bar{\lambda}$(N)	0.661(3.4)	
$\bar{\Delta}$(O)	8.13(7.1)	9.63(4.0)
$\bar{\Delta}$(N)	10.62(6.4)	11.47(2.1)

Note. Dipole moments are in Debye units, λ in atomic units, and Δ in kK. The variation coefficients $\sigma/\bar{x}$ (%) are in parentheses.

taking into account the differences in $R_{\rm ML}$ in the calculations collected in Table III. In these circumstances, the scaling parameter seems to be transferable according to the addition rule

$$\lambda(\mathrm{NiN_4O_2}) \simeq \{2\lambda(\mathrm{NiN_6}) + \lambda(\mathrm{NiO_6})\}/3 \qquad (12)$$

as can be seen in Table III for the average values of λ. This result suggests that the usual assumption of isotropy of the electronic repulsion in fields of low symmetry (*6*) is satisfied in the complexes explored here up to 7%. Our results on the transferability of the classical parameters, even without considering the effects of the changes in $R_{\rm ML}$, are quite comparable with those reported by Wentworth and Piper in monoacido and diacidopentamine complexes of Co^{3+} and Cr^{3+} (*6*), and by Day in chlorocuprates (*8*).

It is interesting to note that the transferability is worse when we look at the punctual parameters μ(O) and μ(N), in Table III. This is not surprising if we recall that the final value of μ is affected by the variations in λ, which, in turn, are mainly determined by the electronic repulsion terms. This difficulty in dealing with punctual parameters seems to be avoided in the Angular Overlap model, where a nice transferability in the quantities Δ'_σ and Δ'_π, associated with the pyridine in $\mathrm{Ni(py)_4}X_2$, is observed (*10*).

Our results in Table III give rise to an interesting observation concerning the influence of the geometry and the chemical environment in the stability of the empirical parameters. If we assume that the empirical Δ changes with $R_{\rm ML}$ as $R_{\rm ML}^{-5}$, as the theoretical Δ does, we can write for the empirical parameters the equation

$$\Delta(R') = \Delta(R)(R/R')^5. \qquad (13)$$

Equation (13) could then be used in comparing the values of Δ since they were obtained at different values of $R_{\rm ML}$. For instance, the $\bar{\Delta}$(O) in Table III (8.13 kK) was calculated at $R_{\rm ML}$ = 2.05 Å. According to Eq. (13) this value becomes 7.17 kK at $R_{\rm ML}$ = 2.102 Å, the distance of the D_{4h} complexes. This corrected value has to be compared with the tetragonal $\bar{\Delta}$(O) = 9.63 kK, some 35% larger. The same correction transforms $\bar{\Delta}$(N) = 10.62 kK, in Table III, into $\bar{\Delta}$(N) = 11.30 kK, which has to be compared with the tetragonal $\bar{\Delta}$(N) = 11.47 kK in Table III. Now, one can argue that if the known changes in geometry were taken into account by means of the $\Delta = \Delta(R_{\rm ML}^{-5})$ law, the residual discrepancies in the analysis of the transferability could be assigned to changes in the chemical environment of the ligand atom. If this hypothesis is accepted and the $R_{\rm ML}^{-5}$ law is valid, we find an insignificant effect of the chemical environment in passing from $\mathrm{NiN_6}$ to $\mathrm{NiN_4}X_2$ complexes, whereas a rather remarkable contribution of 2.46 kK is obtained in the group of oxygen complexes. These results seem reasonable when we recall that most of the $\mathrm{NiN_6}$ complexes studied here are formed by amines and all the tetragonal $\mathrm{NiN_4}X_2$ are amine complexes too. On the other hand, the $\mathrm{NiO_6}$ complexes contain six neutral oxygens as ligands, whereas the tetragonal complexes have the charged oxygens of two carboxylate anions as axial ligands.

If our analysis is correct, we can conclude that when dealing with transference of empirical parameters, changes in geometry and chemical environment of the ligand species could be significant factors which should be taken into consideration as carefully as possible. For instance, a large reduction in R_{ML} can produce an increase in Δ big enough to change the ground state of a complex. This is, of course, the crystal-field interpretation of the diamagnetism of the tetracoordinated NiS_4 complexes (R(Ni–S) = 2.23 versus 2.50 Å in NiS_6 (*4*)) and many other Ni^{2+} complexes, like the yellow Ni(stien)$_2$(Cl$_2$CH–COO)$_2$ reported by Nyburg and Wood (*21*). Evidently, the exact way in which the empirical Δ varies with R_{ML} has to be found from a large number of parameter determinations in clusters of different geometries. We have not attempted to answer this problem in this report.

Finally, we will comment on some interesting results of the fitting process that are particularly clear when a method of linearization of the spectral frequencies is used. We present in Table IV the observed and computed spectral frequencies, with our best parameters, of Ni(stien)$_3$(ClO$_4$)$_2$ and Ni(stien)$_2$(CH$_3$–COO)$_2$. The linear coefficients $\alpha(i)$, $\gamma(i,l)$ of Eq. (9) at convergence are also presented. If the coefficients of λ, $\alpha(i)$ are expressed in units of the reference Racah parameter $B(1)$ = 1334 kK, we obtain for the two $\alpha(^3T_{1g})$ of Ni(stien)$_3$(ClO$_4$)$_2$ 3.3733 and 11.6267, respectively. These two numbers add to 15, as they should (*1*), and they are closer to the diagonal-only values, 3 and 12, than those of NiF_6^{4-} (*1*). In Ni(stien)$_3^{2+}$ these two triplets become strongly mixed via configuration interaction, as the coefficients of Δ reveal: 1.331 and 1.669 versus the diagonal-only values

TABLE IV

OBSERVED AND CALCULATED SPECTRAL FREQUENCIES (IN kK) AND LINEAR EXPANSION COEFFICIENTS FOR Ni(stien)$_3^{2+}$ (O_h) AND Ni(stien)$_2$Ac$_2$ (D_{4h})

A. Ni(stien)$_3$(ClO$_4$)$_2$ $\Delta E(i) = \alpha(i)\lambda + \gamma(i)\Delta$

Transition	Obsd.[a]	Calcd.	$\alpha(i)$	$\gamma(i)$
$^3A_{2g} \rightarrow {}^3T_{2g}$	11.11	11.42	0.0	1.0
$\rightarrow {}^1E_g$	12.70	12.85	19.45	0.0305
$\rightarrow a^3T_{1g}$	18.08	18.09	4.500	1.331
$\rightarrow b^3T_{1g}$	29.24	29.03	15.15	1.669
rms deviat.	—	0.20		

Best parameters: Δ = 11.42 kK; λ = 0.643 a.u.

B. Ni(stien)$_2$(CH$_3$–COO)$_2$ $\Delta E(i) = \alpha(i)\lambda + \gamma(i,xy)\Delta_{xy} + \gamma(i,z)\Delta_z$

Transition	Obsd.[b]	Calcd.	$\alpha(i)$	$\gamma(i,xy)$	$\gamma(i,z)$
$^3B_{2g} \rightarrow a^3E_g$	10.01	10.53	0.1450	0.3432	0.6604
$\rightarrow {}^3B_{1g}$	12.19	11.61	0.0	1.0	0.0
$\rightarrow a^3A_{2g}$	16.89	16.51	5.509	0.0278	1.257
$\rightarrow b^3E_g$	18.18	18.38	2.320	1.330	0.1324
$\rightarrow b^3A_{2g}$	28.98	29.23	14.51	1.140	0.5818
$\rightarrow c^3E_g$	29.85	29.73	17.56	1.243	0.2880
rms deviat.	—	0.38			

Best parameters: Δ_{xy} = 11.61 kK; Δ_z = 9.76 kK; λ = 0.711 a.u.

[a] Data drawn from Ref. (*21*).

[b] Data drawn from Ref. (*19*).

of 2.0 and 1.0. Notice that these two numbers add to 3. From Table IV the near independence of the ^1E_g from Δ is also clear. This is a well-known characteristic of this singlet whose equation in Ni(stien)$_2^{2+}$ and NiF$_6^{4-}$ is almost the same (*1*).

In the tetragonal complex shown in Table IV we observe, first, that the energy of the $^3B_{1g}$ state, coming from the octahedral $^3T_{2g}$, is controlled only by Δ_{xy}. Therefore, the $^3B_{2g} \rightarrow {}^3B_{1g}$ frequency gives Δ_{xy} directly even after the mixture. The lower excited state a^3E_g, however, is a big mixture of Δ_{xy} and Δ_z and it shows a small dependence on λ. Second, we know that the octahedral a^3T_{1g} gives rise to the a^3A_{2g}, b^3E_g states in the tetragonal clusters; from Table IV we see that these two triplets are controlled by the axial and equatorial perturbations, respectively. Finally, the two triplets coming from the b^3T_{1g} are strongly dependent on λ. They mainly determine the value of the empirical electron repulsion parameter. As in octahedral complexes (*1*), the coefficients in Eq. (9) are easily obtainable indicators of the configurational character of the multiplets. That, indeed, is an advantage of this systematic calculation of the crystal-field parameters.

In order to compare our results with those currently available a final remark should be made. The values of Δ in the octahedral complexes and those of Δ_{xy} in the tetragonal complexes are directly comparable with $10Dq$. On the other hand, the parameter λ contains information about the nephelauxetic effect in the complex but it is not, by itself, a direct measure of such effect. The reason is clear: λ measures the expansion of the reference radial function necessary to have a best representation of the complex spectrum. This expansion has to be compared with the expansion that the reference function experiences when a best description of the free metal ion is required. This means that, given a reference function, we have a λ_{opt} (free-ion) and a λ_{opt} (complex). The obtention of the former is straightforward since the free-ion spectral frequencies have the form

$$\bar{\nu}(i) = \sum_k a(i,k)F(k) \qquad (14)$$

and, according to Eq. (5),

$$\bar{\nu}(i) = \sum_k a(i,k)F(k,1)\lambda = A(i)\lambda. \qquad (15)$$

Therefore,

$$\lambda_{\text{opt}}(\text{free-ion}) = N^{-1} \sum_i^N \{\bar{\nu}(i;\ \text{exptl})/A(i)\}, \qquad (16)$$

where $\bar{\nu}(i;$ exptl) are the observed values of the free-ion frequencies and N the number of frequencies. Using formula (16), the approximate Hartree–Fock function of Richardson *et al.* (*22*) used here as reference function $\{B(1) = 1334\ \text{cm}^{-1},\ C(1) = 4943\ \text{cm}^{-1}\}$ gives λ_{opt} (free-ion) = 0.797. The transitions $^3F \rightarrow {}^1D$ (13,038 cm^{-1}), $\rightarrow {}^3P$(15,836 cm^{-1}), $\rightarrow {}^1G$ (20,813 cm^{-1}) are taken from Shenstone (*24*) and the $\rightarrow {}^1S$ (51,538 cm^{-1}) from García-Riquelme (*25*).

The nephelauxetic effect (independent of the reference radial function) is then given by

$$\beta = \lambda_{\text{opt}}(\text{complex})/\lambda_{\text{opt}}(\text{free-ion}). \qquad (17)$$

Using formula (17) and the values of $\bar{\lambda}$ in Table III, we obtain the following average nephelauxetic effects: $\bar{\beta}$(O) = 0.896 for the NiO$_6$ complexes and $\bar{\beta}$(N) = 0.829 for the NiN$_6$ group. We find β(S) = 0.501 in the NiS$_6$ complex. These estimations of the nephelauxetic effect are in very good agreement with those given by Jørgensen (*23*).

Summary

A systematic method for obtaining optimum crystal-field parameters is presented. The method is easy to apply and produces parameters that describe well the observed optical spectrum of 40 complexes of Ni^{2+}. The usual information about orbital splitting and nephelauxetic effect is readily obtainable. The fitting variables in this method are the ligand perturbing charges (or dipole moments) and the shape of the metallic radial $3d$ function. The method describes the spectral frequencies by means of a linear transformation of the best parameters. The elements of the transformation matrix give immediate information on the configurational character of the multiplets involved in the fitting.

The method is appropriate for analyzing the transferability of the parameters among complexes of different symmetries, since it works as an objective and systematic tool. Our study on complexes of Ni^{2+} has shown that the classical parameters can be transferred within 10% if the metal–ligand distances and the chemical environment of the ligands do not suffer big changes. On the other hand, the transferability of the punctual parameters seems to be uncertain.

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