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Electric-dipole $4f^N$–$4f^N$ transition intensity parametrizations for lanthanides: an examination of multiple local minima

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Abstract

For most symmetries the standard parametrization of one-photon electric-dipole transitions between crystal-field levels of the $4f^N$ configuration of lanthanide ions gives the same predictions for several quite different parameter sets. An alternative parametrization scheme that provides separate parameters for each of the different polarization directions has been shown to remove this anomaly. A second problem arises due to the fact that multiple local minima may fit the data nearly equally well. Through a detailed reexamination of a series of lanthanide oxydiacetate (LnODA, Ln=Nd, Sm, Eu, Dy, and Ho) systems using the new parametrization, we examine the multiple local minima problem, and attempt a determination of the robustness of the global parametrization minimum. © 2001 Elsevier Science B.V. All rights reserved

Keywords: Electric-dipole transitions; Lanthanide ions; Multiple local minima;

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1. Introduction

The intensities of electronic transitions acting within the $4f^N$ configurations of lanthanide ions are strongly dependent on the environment of the ion. Although strictly forbidden for an isolated ion, electric-dipole transitions dominate the solid-state spectra of lanthanide ions. The first theoretical treatment of electric-dipole transition intensities for these ions was developed by Judd [1] and Ofelt [2]. Judd's parametrization formalism has been used extensively [3] to harmonize measured and calculated integrated transition intensities between *J*-multiplets, and was adapted by Axe [4] for examination of transitions between crystal-field levels.

Newman and Balasubramanian [5] showed that Axe's formalism was not the most general one-electron, spin-independent scheme possible, but rather, included implicit assumptions of pairwise independence of lanthanide–ligand interactions (commonly referred to as the 'superposition model'). Newman and Balasubramanian proposed two alternative general parametrizations, one of which was subsequently adopted (with some reformulation) by Reid and Richardson [6,7]. In contrast to the Axe parametrization, the Reid–Richardson parametrization scheme is not restricted by any a priori assumptions about the local symmetry of the lanthanide–ligand interactions. This feature of the Reid–Richardson parametrization is of paramount importance when dealing with systems where the lanthanide ion is coordinated to structurally complex, polyatomic ligands having highly anisotropic charge distributions. In multiple studies [8–16] of transition intensities in $Na_2[Ln(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$ (commonly called LnODA) systems, the restricted parametrization of Axe could not adequately interpret the experimental results, and the additional parameters in the Reid–Richardson parametrization scheme were required in order to rationalize the experimental results.

However, Burdick et al. [17] recently showed that when the entire set of Reid–Richardson A^{λ}_{tp} parameters are used, an ambiguity in the parametrization arises, allowing parameter sets having significantly different values to yield identical calculated transition intensities. Thus, for systems with complex ligands, it is advantageous to use an alternative parametrization, modeled loosely after the 'vector crystal field' of Newman and Balasubramanian. This alternative parametrization separates parameters for each unique polarization direction. Thus, for the case of LnODA (D_3 lanthanide site symmetry), the $B^{\lambda}_{\ell i}$ parameters

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separate into sigma-polarization parameters $B^{\lambda}_{\ell\sigma}$ and pi-polarization parameters $B^{\lambda}_{\ell\pi}$ which may be fit separately to the polarized experimental data. The transformations between Reid–Richardson A^{λ}_{tp} and separated-polarization $B^{\lambda}_{\ell i}$ parameters for D_3 site symmetry have been given previously [18].

A second problem arises due to the fact that the intensity parameters are proportional to the electric-dipole moments of the transitions, rather than being proportional to the intensities themselves. As the intensities are the square moduli of the dipole moments, there is an undetermined phase on each of the moments. The standard overall phase convention makes the magnetic-dipole moments pure real, thus requiring the electric-dipole moments to be pure imaginary, and determining the phase on each of the electric-dipole moments up to an arbitrary sign. Thus, there are 2^N possible combinations (where N is the number of experimental data points observed) of electric-dipole moment signs that can yield identical calculated intensities. However, since the parameters are linear with respect to the electric-dipole moments, there are really only a maximum of 2^P possible local minima (where P is the number of intensity parameters used) that may be determined by fitting. All other combinations of electric-dipole moment signs do not result in stable local minima. Since changing the signs on all the moments does not change the fit, we end up with a maximum of 2^{P-1} possible unique minima. For systems of D_3 symmetry, such as the oxydiacetate systems examined here, there exist nine sigma parameters and three pi parameters. This means we can expect to have at most $2^2 = 4$ local minima when fitting to the pi spectrum, and $2^8 = 256$ unique local minima when fitting to the sigma/axial spectra. In reality, many of these combinations do not lead to stable local minima, so the actual number is usually significantly smaller.

Inclusion of experimentally determined rotatory strengths helps to further reduce the total number of local minima. This is due to the fact that the experimental rotatory strengths, being products of electric-dipole and magnetic-dipole moments, are linear with respect to the electric-dipole moments, and thus linear with respect to the intensity parameters. If only rotatory strengths were included in the fit of sigma intensity parameters, there would always be a single unique solution [19]. However, when rotatory strengths are included for only part of the experimental intensities, usually more than one local minima appears, due to the fact that the moment signs are still arbitrary for those experimental intensities without experimentally determined rotatory strengths.

The purpose of this work is to reexamine the experimental intensities and rotatory strengths previously reported for NdODA [12,20,21], SmODA [8,9,22], EuODA [10,11], DyODA [23], and HoODA [13,14,24], in order to understand and rationalize the apparent trends previously observed in the parameter values, and to determine whether these trends are in fact real, or whether they are the result of finding local minima that appear to match the values expected.

2. Results

In order to locate all of the local minima for each system, we randomly generated sets of starting parameters for use in a standard non-linear least squares algorithm [25] that finds the closest minimum. Repeating this process for a sufficient number of iterations (up to 10 000 times for sigma parameters and 2000 times for pi parameters) allows determination of the complete set of local minima. Standard deviations reported for each local minimum refer to the following standard weighted error:

$$\sigma = \sqrt{\frac{\sum_i [(e_i - c_i)/e_i]^2}{N - P}} \tag{1}$$

where e_i and c_i are the ith experimental and calculated values, respectively, N is the number of data points, and P is the number of parameters.

2.1. Neodymium

Values for the nine sigma-polarization parameters were determined using 47 experimentally determined axial unpolarized intensities [12]. This yielded 37 local minima, each of which is doubly degenerate, due to the arbitrary overall sign on the parameters. These 37 local minima have standard deviations ranging from 0.6105 to 0.7813. When 31 experimentally determined axial rotatory strengths [21] are added to the fit, the overall sign on the parameters becomes determined, and the total number of local minima is reduced to three, with nearly identical parameter values and standard deviations.

Values for the three pi-polarization parameters were determined using 27 experimentally determined pi-polarized intensities [12]. This yields only two local minima, each of which is doubly degenerate, due to the arbitrary overall sign on the parameters. Of these two local minima, one has a very low standard deviation ($\sigma = 0.5526$) and the other one has a very high standard deviation ($\sigma = 0.7994$). We can therefore conclude that the first local minimum corresponds to the true global minimum, and the second minimum is a spurious minimum coming from a non-optimized set of signs on the electric-dipole moments.

2.2. Samarium

The sigma-polarization parameters for SmODA were determined using 45 experimentally determined axial unpolarized intensities [8], resulting in 17 doubly-degenerate local minima, with standard deviations ranging from 0.4169 to 0.7525. However, only the lowest two fits have comparable standard deviations, as the standard deviation of the third-lowest fit is 0.5659. These two lowest fits have very similar parameter values, and differ only in the sign of the electric-dipole moments for two experimental transitions. When 52 experimentally determined axial rotatory strengths [9] are added to the fit, only one local minimum is produced. The reduction of multiple local minima down to a single solution is to be expected any time the number of included experimental rotatory strengths equals or exceeds the number of experimental intensities included in the fit.

The pi-polarization parameters for SmODA were determined using 31 experimental pi-polarization intensities [8]. The fits result in three local minima, the lowest one having a standard deviation of 0.7644 and the higher two having standard deviations of 0.8300 and 0.9010. The second and third minima appear to be spurious, coming from non-optimized sets of signs on the electric-dipole moments.

2.3. Europium

The smallest published data set, and correspondingly the largest number of local minima found, is for EuODA. Fitting to 24 experimental axial unpolarized intensities [10] results in 153 different local minima, ranging from a standard deviation of 0.4856 up to 0.7367. This is the only system we examined where the total number of local minima approaches the theoretical limit of 256. Inclusion of 13 experimental axial rotatory strengths [11] only reduces the total number of local minima down to 101, with standard deviations ranging from 0.6201 for the best solution to 0.9598 for the worst.

Fitting the pi-polarization parameters to 15 experimental pi-polarized intensities [10] results in four local minima, each of which is doubly degenerate due to the arbitrary overall sign. This equals the theoretical limit for a three-parameter fit. Of these four local minima, two have almost identical parameter values and standard deviations ($\sigma = 0.3865$ vs. $\sigma = 0.3914$), and the other two also have parameter values similar to each other, with higher standard deviations ($\sigma = 0.5491$ and $\sigma = 0.5608$).

2.4. Dysprosium

Fitting 39 experimentally determined axial unpolarized intensities for DyODA [12] produces 12 local minima, ranging from a standard deviation of 0.6247 to 0.6982. The lowest two minima have almost identical standard deviations and parameter values ($\sigma = 0.62469$ vs. 0.62471), and have significantly lower standard deviations than do the other 10 local minima. Inclusion of eight experimental rotatory strengths [26] reduces the total number of local minima down to six.

No experimentally determined pi-polarization studies have been reported for DyODA, and thus we do not have any pi-polarized parameters to report.

2.5. Holmium

Fitting 36 experimental ground state axial unpolarized intensities for HoODA [24], we get 34 local minima, the lowest one ($\sigma = 0.4554$) being much better than the other 33 ($\sigma = 0.5010$ to 0.7384). When 21 experimentally determined rotatory strengths [14] were included in the fit, the number of local minima reduced to two, with standard deviations very close to each other ($\sigma = 0.7352$ vs. 0.7398).

The pi-polarization parameters for HoODA were determined using 14 experimental ground state pi-polarization intensities [24]. The fits result in three local minima, the lowest one having a standard deviation of 0.4960 and the higher two having much worse standard deviations of 0.7383 and 0.7583. Thus, we can conclude that the second and third minima are spurious, coming from non-optimized sets of signs on the electric-dipole moments.

3. Analysis

Table 1 presents the sigma-polarized parameter values for the best fits to experimental axial intensities and rotatory strengths for each of the five systems examined. Columns labeled ‘Ax’ include only the experimental axial intensities, while columns labeled ‘Ax + Rot’ include experimental rotatory strengths along with the axial intensities. Parameter uncertainties (given in parentheses) are calculated from the local curvature of the minimum, and represent the change in the parameter that would produce an increase in the standard deviation by a factor of $\sqrt{2}$, assuming the curvature of the local minimum to be quadratic in shape [25]. Pi-polarized intensity parameters are presented in Table 2 for the best fits to the four systems with published pi-polarization intensities. In each of these tables, a consistent similarity of parameter values is shown.

In order to allow comparison with previously published Reid–Richardson intensity parameters, the ‘Ax + Rot’ parameters of Table 1 and the pi-polarization parameters of Table 2 are transformed into Reid-Richardson A_{tp}^{λ} parameters in Table 3. The ‘Set 1’ columns present the transformation using the pi-polarized parameters of Table 2; the ‘Set 2’ columns present the transformation using opposite signs for the pi-polarized parameters. There is an arbitrary overall sign on the pi-polarization parameters, and since ortho-axial circular dichroism measurements are infeasible, there is no way to experimentally determine which of the two sets of A_{tp}^{λ} is the most physically meaningful set. However, there is a reasonable degree of correlation between the ‘Set 2’ A_{tp}^{λ} parameters and previously published comparisons of electric-dipole intensity parameters [13].

Table 1

Intensity parameters (in 10^{-12} cm^2) for the best local minima obtained from experimentally determined axial unpolarized transition intensities (Ax) and axial unpolarized transition intensities and rotatory strengths (Ax+Rot)

Parameter	NdODA		SmODA		EuODA		DyODA		HoODA	
	Ax	Ax+Rot	Ax	Ax+Rot	Ax	Ax+Rot	Ax	Ax+Rot	Ax	Ax+Rot
$B^2_{1\sigma}$	−48(14)	10(15)	125(26)	67(26)	−95(30)	56(38)	−137(89)	−27(56)	132(22)	54(38)
$B^2_{2\sigma}$	−9(12)	−46(9)	18(24)	32(18)	−151(23)	148(29)	−317(55)	−7(39)	90(29)	57(44)
$B^4_{1\sigma}$	−23(13)	−42(10)	−5(14)	55(13)	30(21)	50(26)	−130(28)	128(18)	16(22)	144(23)
$B^4_{2\sigma}$	124(12)	105(13)	235(26)	67(20)	128(25)	140(30)	−72(22)	46(25)	152(21)	24(40)
$B^4_{4\sigma}$	−23(14)	−41(9)	−91(33)	−60(28)	−30(16)	−6(19)	−34(42)	−87(33)	37(14)	−55(23)
$B^6_{1\sigma}$	−52(19)	−13(21)	84(19)	9(21)	23(19)	46(24)	71(28)	21(23)	28(14)	87(19)
$B^6_{2\sigma}$	19(16)	−29(19)	−93(19)	−93(25)	−61(15)	−58(18)	33(27)	−110(17)	−23(17)	−58(21)
$B^6_{4\sigma}$	199(18)	157(21)	487(22)	235(27)	314(30)	301(38)	205(26)	93(30)	201(12)	107(16)
$B^6_{5\sigma}$	91(25)	−10(23)	92(20)	−25(25)	110(11)	125(14)	87(33)	−71(15)	71(10)	71(17)
N[a]	47	78	45	97	24	37	39	47	36	57
σ[b]	0.6105	0.7909	0.4169	0.7250	0.4856	0.6201	0.6247	0.7399	0.4554	0.7352
n[c]	37	3	17	1	153	101	12	6	34	2
n'	4	3	2	1	14	3	5	2	1	2

[a] Number of experimental intensities included in the data fits.

[b] Statistical standard deviation between calculated and observed transition intensity data (in cm^2) calculated from Eq. (1) in the text.

[c] Total number of local minima found is given by n, while n' gives the number of statistically significant local minima (σ within 5% of the lowest minimum).

Table 2

Intensity parameters (in 10^{-12} cm^2) for the best local minima obtained from experimentally determined pi-polarized transition intensities

Parameter	NdODA	SmODA	EuODA	DyODA[d]	HoODA
$B^4_{3\pi}$	155(15)	237(38)	223(25)	[211]	231(25)
$B^6_{3\pi}$	262(23)	227(40)	408(27)	[278]	218(44)
$B^6_{6\pi}$	72(17)	−78(22)	32(3)	[30]	93(32)
N[a]	27	31	15		14
σ[b]	0.5526	0.7644	0.3865		0.4960
n[c]	2	3	4		3
n'	1	1	2		1

[a] Number of experimental intensities included in the data fits.

[b] Statistical standard deviation between calculated and observed transition intensity data (in cm^2) calculated from Eq. (1) in the text.

[c] Total number of local minima found is given by n, while n' gives the number of statistically significant local minima (σ within 5% of the lowest minimum).

[d] Experimental intensities have not been reported for DyODA. Averages of the other four systems are used.

Table 3

Reid–Richardson intensity parameters (in 10^{-12} cm^2) for the best local minima obtained from experimentally determined pi-polarized and axial unpolarized transition intensities and rotatory strengths, corresponding to the separated polarization parameters of Tables 1 and 2. 'Set 1' uses pi-polarized parameters from Table 2, 'Set 2' uses reversed signs for pi-polarized parameters

Parameter	NdODA		SmODA		EuODA		DyODA		HoODA	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
A^2_{20}	20	20	133	133	112	112	−54	−54	312	312
A^2_{33}	65	65	−45	−45	−209	−209	10	10	192	192
A^4_{33}	−144	−8	−195	14	−139	58	−212	−26	−85	118
A^4_{40}	−84	−84	110	110	100	100	256	256	200	200
A^4_{43}	166	−42	177	−141	263	−36	125	−158	203	−107
A^4_{53}	−33	−218	54	−228	−24	−290	56	−195	96	−179
A^6_{53}	26	334	155	422	106	586	−21	307	−15	242
A^6_{60}	−26	−26	18	18	92	92	42	42	−2	−2
A^6_{63}	227	−15	218	7	390	12	105	−152	215	13
A^6_{66}	61	−72	−85	59	96	37	−10	−66	90	−82
A^6_{73}	260	−88	328	27	437	−104	327	−41	166	−123
A^6_{76}	40	−14	3	62	−152	−176	104	82	26	−44

4. Conclusion

The presence of multiple local minima in the non-linear least squares fitting of transition intensities provides challenges to the determination and interpretation of calculated intensity parameters. However, we have shown that through a method of random searching, it is possible to identify all relevant local minima, and to determine which parameter values may be reliably used. Through a more rigorous examination of previously published intensity and rotatory strength data, we have shown that consistent parameter trends do occur, which may be useful in future analysis and interpretation of the mechanistic details of the transition intensities. However, any theoretical analysis of the phenomenologically determined A_{tp}^{λ} values must take into consideration the experimental indistinguishability between the 'Set 1' and 'Set 2' parameter.

Inclusion of rotatory strength data in the fitting of intensity parameters, something that was not done in previous analyses, always reduces the total number of local minima which must be considered, and thus produces a more reliable set of intensity parameters.

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