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Electric-dipole $4f^N$–$4f^N$ transition intensity parametrizations for lanthanides: multiple indistinguishable parameter sets and 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 removes 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 the previously well-studied system NdODA, we examine and attempt to resolve this local minima problem. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electric-dipole transitions; Lanthanide ions; Multiple indistinguishable parameter sets

1. Introduction

The intensities of transitions within the $4f^N$ configurations of lanthanide ions are strongly dependent on the environment of the ion. The electric dipole transitions that dominate the solid-state spectra are forbidden for an isolated ion, and only become allowed when the symmetry is reduced from the full rotational symmetry of a free ion to the point group symmetry of an ion in a condensed matter environment.

The calculation of integrated transition intensities between *J*-multiplets was made possible by the pioneering work of Judd [1] and Ofelt [2] in the early 1960s. Over the last four decades, the measurement and calculation of *J*-multiplet to *J*-multiplet integrated transition intensities have become commonplace [3–5].

The first completely general intensity parametrization schemes for transitions between crystal-field energy levels were introduced by Newman and Balasubramanian [6] in 1975. These authors proposed two alternative parametrizations, one of which was subsequently adopted (with some reformulation) by Reid and Richardson [7,8]. This parametrization scheme is similar to one employed in earlier work by Axe [9], but has broader applicability insofar as it is not restricted by any a priori assumptions about the local symmetry of the lanthanide–ligand pairwise interactions. This latter feature of the Reid–Richardson parametrization scheme is of paramount importance in dealing with systems where the lanthanide ion is coordinated to structurally complex, polyatomic ligands having highly anisotropic charge distributions. In multiple studies of transition intensities for $Na_3[Ln(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$ (commonly called LnODA) systems, the additional parameters in the Reid–Richardson parametrization scheme have been shown to be vital for the rationalization of the experimental results [10–17].

Burdick et al. [18] showed, however, that when the entire set of Reid–Richardson A^{λ}_{tp} parameters are used, an ambiguity in the parametrization arises, causing parameter sets having significantly different values to yield identical calculated transition intensities. That is, for a uniaxial system such as LnODA (D_3 symmetry), there exist four sets of A^{λ}_{tp} parameters that yield identical calculated transition intensities. This ambiguity can be resolved by

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the use of an alternative $B^{\lambda}_{\ell i}$ ($i=\sigma, \pi$) parametrization that explicitly separates parameters for each unique polarization direction.

This alternative parametrization loosely follows the second, previously unused parametrization of Newman and Balasubramanian [6], that they called the 'vector crystal-field.'

This work represents the first attempt to utilize the alternative 'vector crystal-field' parametrization directly to analyze experimental transition intensities for a complex ligand system. For this calculation, we have chosen the previously well examined system, NdODA, for which extensive polarized intensity and rotatory strength data has been reported [19,14,15].

2. Results

For systems having D_3 point-group site symmetry, such as the NdODA system, the 12 A^{λ}_{tp} parameters may be transformed into separate sets of nine sigma-polarization parameters $B^{\lambda}_{\ell\sigma}$ and three pi-polarization parameters $B^{\lambda}_{\ell\pi}$. The four solutions yielding identical calculated intensities are then resolved as arbitrary overall signs multiplying the $B^{\lambda}_{\ell\sigma}$ and $B^{\lambda}_{\ell\pi}$ parameters. Table 1 presents the transformation between A^{λ}_{tp} and $B^{\lambda}_{\ell i}$ parametrizations for D_3 symmetry.

An advantage of the separated-polarization $B^{\lambda}_{\ell i}$ parametrization is that it allows separate fitting to pi-polarized intensities ($B^{\lambda}_{\ell\pi}$) from the axial intensities and rotatory strengths ($B^{\lambda}_{\ell\sigma}$). In fitting the nine sigma-polarization parameters, $B^{\lambda}_{\ell\sigma}$, we fitted our calculations to 47 experimentally determined axial intensities [19]. We also performed fits that included 31 experimentally determined axial rotatory strengths [15], giving a total of 78 experimental values. For the fitting to pi-polarized intensities, we fit the three pi-polarized parameters, $B^{\lambda}_{\ell\pi}$, to 27 experimentally determined intensities [19].

Since the parametrized fitting to transition intensities is necessarily non-linear in the parameters, the least-squares fitting will always result in multiple local minima. In order to determine the complete set of local minima, we use a method of random starting parameters [20], where different sets of parameter values are used as initial values for each fitting. When this is done for a sufficient number of iterations (ranging from 1000 to 50 000, depending upon the number of local minima) the entire set of local minima can be found.

The commonly used differential weighting method [21,22], which minimizes the quantity $\Sigma_i[(e_i - c_i)/0.5(e_i + c_i)]^2$, where e_i and c_i are the ith experimental and calculated values, yielded more than 10 000 local minima for the fit to the 47 axial intensities. Most of these minima, however, had standard deviations that were much higher than the best local minimum, with the standard deviations distributed in a Gaussian distribution. If all of the parameter space were randomly sampled without fitting, we would expect the calculated errors of these randomly determined parameters to associate themselves in a Gaussian distribution. Thus, our conclusion is that the vast majority of these 10 000+ solutions come from a random sampling of the error space, rather than having any physical significance.

By contrast to the differential weighting method, use of a standard weighting [23], minimizing the quantity $\Sigma_i[(e_i - c_i)/e_i]^2$, yielded only 37 local minima. These 37 solutions yielded similar parameters and similar standard deviations ($\sigma = 0.61$–0.78) to those achieved by the best 37 solutions of the differential weighting ($\sigma = 0.65$–0.79). However, whereas the best solution was achieved approximately 12% of the time for the standard weighting, the best solution for the differential weighting was found only 0.2% of the time.

Table 1
Transformations between the A^{λ}_{tp} and B^{λ}_{ℓ} parameter sets in D_3 symmetry

	A^2_{20}	A^2_{33}				
$B^2_{1\sigma}$	$1/2$	0				
$B^2_{2\sigma}$	0	$-1/\sqrt{2}$				
	A^4_{33}	A^4_{40}	A^4_{43}	A^4_{53}		
$B^4_{1\sigma}$	0	$1/2$	0	0		
$B^4_{2\sigma}$	$-1/\sqrt{72}$	0	$\sqrt{7/40}$	$-\sqrt{14/45}$		
$B^4_{3\pi}$	$-\sqrt{7/36}$	0	$3/\sqrt{20}$	$4/\sqrt{45}$		
$B^4_{4\sigma}$	$\sqrt{7/18}$	0	$1/\sqrt{10}$	$1/\sqrt{90}$		
	A^6_{53}	A^6_{60}	A^6_{63}	A^6_{66}	A^6_{73}	A^6_{76}
$B^6_{1\sigma}$	0	$1/2$	0	0	0	0
$B^6_{2\sigma}$	$-1/\sqrt{26}$	0	$\sqrt{3/14}$	0	$-3\sqrt{5/182}$	0
$B^6_{3\pi}$	$-3/\sqrt{26}$	0	$\sqrt{3/14}$	0	$2\sqrt{10/91}$	0
$B^6_{4\sigma}$	$\sqrt{15/52}$	0	$\sqrt{5/28}$	0	$\sqrt{3/91}$	0
$B^6_{5\sigma}$	0	0	0	$1/\sqrt{14}$	0	$-\sqrt{3/7}$
$B^6_{6\pi}$	0	0	0	$\sqrt{6/7}$	0	$1/\sqrt{7}$

When the 31 rotatory strengths were included in the calculation, the total number of local minima using the differential weighting method did not decrease. However, when the standard weighting method was used, the total number of local minima decreased from 37 to only three. This improvement in the number of total local minima can be explained by the fact that the parameters are linear with respect to the rotatory strengths, while they are quadratic with respect to the intensities. Thus, if the rotatory strengths were fitted by themselves, a single unique solution would be determined. But this is true only for a standard weighting method. For the differential weighting method, the minimization function includes calculated values in the denominator, which makes the derivative of the minimization function with respect to calculated values non-linear, and thus the linearity of the parameters with respect to the rotatory strengths does not prevent the occurrence of a plethora of local minima.

For the fitting to the pi-polarized intensities, the number of total parameters is much less, and thus the differential weighting method works better. The differential weighting method yields eight local minima for the pi parameters, compared to two solutions for the standard weighting.

In each case examined, the total number of local minima that must be considered is greatly reduced using a standard weighting method versus the differential weighting method. We can thus conclude, for both practical and statistical reasons, that the standard weighting method is to be preferred. For the remainder of this paper, we will present results using only a standard $\Sigma_i[(e_i - c_i)/e_i]^2$ weighting.

For the system examined here, we get different parameter sets yielding different local minima that have nearly identical fitting standard deviations. In order to distinguish which is the better fit, it is not justifiable simply to choose the one with the lowest standard deviation, since small variations in the wavefunctions or in the experimental intensities can very well cause a reordering of these low-lying local minima, so that alternative minima can have lower standard deviations.

In order to distinguish between the true global minimum and spurious low-lying local minima we have examined the 'robustness' of the solutions. That is, if the minimum does not change significantly upon small changes in the wavefunctions or the measured intensity values, then the minimum can be said to be robust. In order to examine the 'robustness' of our local minima, we have chosen three similar, but not identical, sets of wavefunctions for our calculation. These three sets are, (1) the standard crystal-field parametrization, (2) the standard crystal-field parametrization with the addition of three correlation–crystal-field (CCF) parameters [24,22], and (3) the standard crystal-field parametrization with the addition of only one delta-function CCF parameter [25,26]. The addition of CCF parameters improves the overall root-mean-square (rms) calculation error for 116 experimentally determined energy levels from 14.4 cm^{-1} down to 9.0 cm^{-1} for the three-parameter CCF (10.8 cm^{-1} for the one-parameter CCF) Hamiltonian [27]. The majority of this improvement comes from the well-known anomalous multiplet $^2H(2)_{11/2}$. Inclusion of CCF parameters does not significantly affect the values of the other atomic and crystal-field parameters, and thus has only a small effect upon the wavefunctions used for the intensity calculations.

Fig. 1 presents the parameter values for the lowest fits to 47 axial intensities using the three different sets of wavefunctions. Each solution presented here has a two-fold degeneracy, as the overall signs of all parameters can be reversed without changing the calculated intensity values. The solutions presented in each panel have standard deviations within 0.01 of each other, and so cannot be distinguished by standard deviation values alone. Notice that except for the anomalous parameter set CCF #3, all the parameter sets presented in this table follow very similar parameter value trends. The CF #2 parameter set corresponds to the previously reported parametrization of May et al. [14]. This parameter set closely follows the other five parameter sets (ignoring the anomalous CCF #3 set) presented here, except for a value of the parameter $B^2_{1\sigma}$ which seems to be too large. However, $B^2_{1\sigma}$ is the least-well defined parameter, with parameter uncertainties that are larger than the magnitude of the parameter for most of the fits. The left two columns of Table 2 compares the 'best' CF #1 solution with the 'average' of the six parameter sets (omitting CCF #3). The uncertainties presented for the CF #1 solution are determined by the curvature of the error space at the position of the local minimum, while the uncertainties presented for the 'average' solution are calculated from the standard deviations of the six-parameter values from the mean. Notice that these very different calculations yield similar uncertainties.

When the 31 axial rotatory strengths are added to the fit, the two-fold degeneracy of parameter sets is removed. That is, the overall signs of the $B^{\lambda}_{\ell\sigma}$ parameters are explicitly determined. Also, the large numbers of local minima disappear, and there remain only three local minima for the CF and delta-function CCF parametrizations, and only two local minima for the three-parameter CCF parametrization. Most importantly, each of these local minima lie within a standard deviation of 0.01 of the best local minima, meaning that every local minima found must be considered when choosing the globally minimum parameter set. All eight of these parameter sets are presented in the three panels of Fig. 2. Notice in contrast to Fig. 1, the deviation between parameter sets is smaller, and there are no remaining 'spurious' solutions. The right two columns of Table 2 present the 'best' CF #1 solution along with the 'average' of the eight solutions, using the same format as for the left two columns.

Fig. 3 presents fitted parameter sets for the 27 pi-polarized intensities. The complete search of the parameter space yielded two CF solutions, three CCF solutions, and four delta-function CCF solutions. The five solutions that have the lowest standard deviation are presented in the three panels of Fig. 3. As was the case for the 'axial-only'

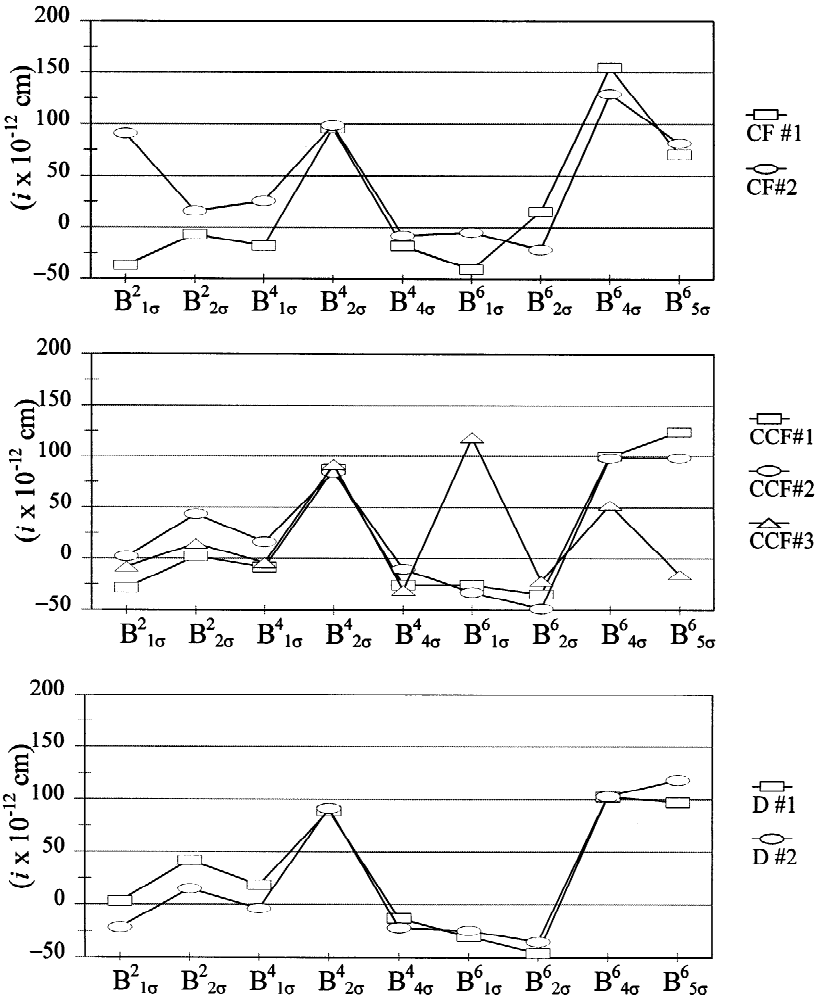

Fig. 1. $B^{\lambda}_{\ell\sigma}$ parameter values for the best local minima fit to 47 axial intensities using crystal-field (CF) parametrized wavefunctions (CF, top panel), CF plus three-parameter CCF parametrized wavefunctions (CCF, second panel), and CF plus one-parameter delta-function CCF parametrized wavefunctions (D, third panel). Fitting standard deviations are 0.6105 (CF ≠1), 0.6160 (CF ≠2), 0.6438 (CCF ≠1), 0.6483 (CCF ≠2), 0.6487 (CCF ≠3), 0.6319 (D ≠1), 0.6398 (D ≠2).

Table 2
Fitted $B^{\lambda}_{\ell\sigma}$ parameters, best fit and average parameter set for axial intensities only and for axial intensities plus rotatory strengths[a]

	Axial		Axial + rotatory	
	CF ≠1	Average of six	CF ≠1	Average of eight
$B^2_{1\sigma}$	−37(11)	2(43)	8(12)	−18(22)
$B^2_{2\sigma}$	−7(9)	19(19)	−36(7)	−45(10)
$B^4_{1\sigma}$	−18(10)	5(16)	−33(8)	−31(4)
$B^4_{2\sigma}$	96(10)	91(5)	82(10)	79(3)
$B^4_{4\sigma}$	−18(11)	−16(6)	−32(7)	−28(5)
$B^6_{1\sigma}$	−41(15)	−27(11)	−10(16)	−4(11)
$B^6_{2\sigma}$	15(13)	−29(21)	−22(15)	−44(18)
$B^6_{4\sigma}$	155(14)	115(21)	122(16)	104(22)
$B^6_{5\sigma}$	71(20)	99(19)	−8(18)	−17(9)
σ	0.6105		0.7909	

[a] All values are given in units of $i \times 10^{-12}$ cm, values in parenthesis are uncertainties. Standard deviation is given by the expression:

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

where N is the number of data points and p is the number of parameters.

fits, there is an arbitrary overall sign on the parameter sets, making each solution two-fold degenerate. The five solutions presented here follow similar trends, but there are some distinct differences between the CF solution and the other solutions. Unfortunately, rotatory strengths do not tell us anything about the pi-polarization parameters, since it is technically infeasible to perform ortho-axially oriented circular dichroism measurements. Table 3 presents the 'best' CF ≠1 solution along with the 'average' of the five solutions, using the same format as for Table 2.

3. Conclusions

As can be seen from these results, the problem of multiple local minima appears to be an endemic feature of the non-linear intensity parametrization, and cannot be completely eliminated. However, through the use of multi-

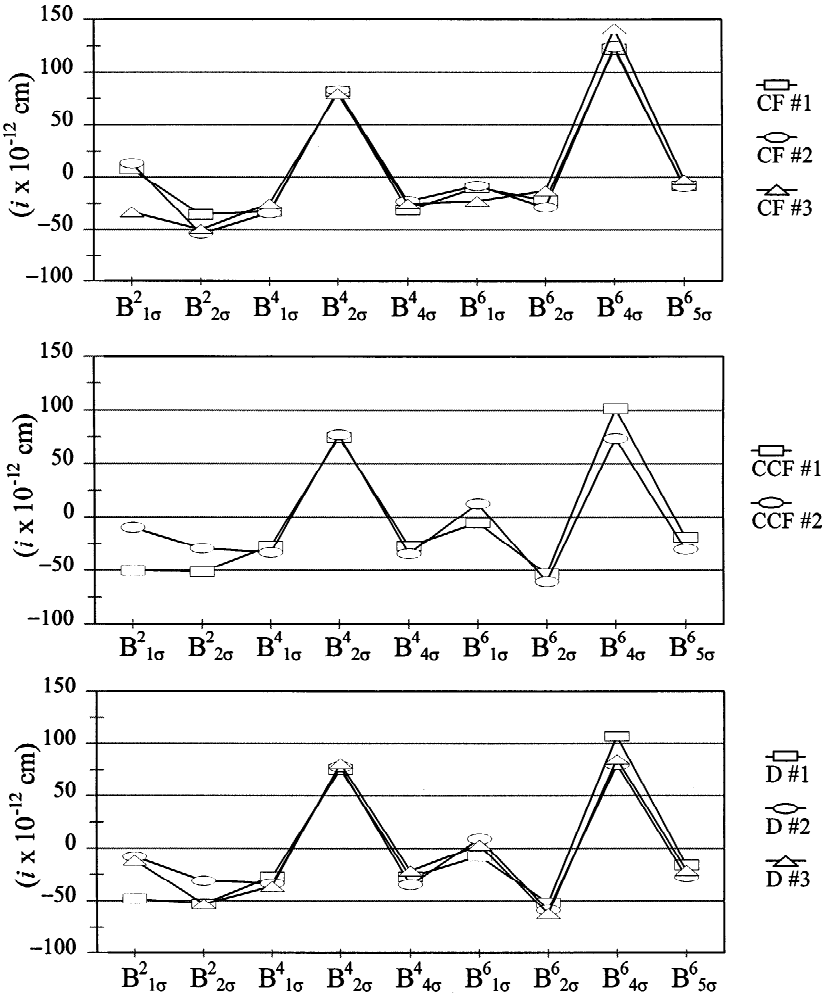

Fig. 2. $B^{\lambda}_{\ell\sigma}$ parameter values for the best local minima fit to 47 axial intensities plus 31 rotatory strengths using crystal-field (CF) parametrized wavefunctions (CF, top panel), CF plus three-parameter CCF parametrized wavefunctions (CCF, second panel), and CF plus one-parameter delta-function CCF parametrized wavefunctions (D, third panel). Fitting standard deviations are 0.7909 (CF ≠1), 0.7967 (CF ≠2), 0.8098 (CF ≠3), 0.7966 (CCF ≠1), 0.8025 (CCF ≠2), 0.7903 (D ≠1), 0.7953 (D ≠2), 0.7997 (D ≠3).

ple (similar but not identical) sets of wavefunctions, and by identification of the complete set of local minima, it is possible to distinguish between physically robust minima and other spurious minima that may have similar fitting standard deviations. These physically robust minima provide a more reliable set of parameters.

The use of the separated sets of $B^{\lambda}_{\ell i}$ ($i=\sigma,\ \pi$) parameters, rather than the complete set of A^{λ}_{tp} parameters, helps to reduce the total number of parameters fit at one time, and thus makes the identification of local minima a more tractable task. By separation of the two sets of polarized data in the fitting, it is also possible to identify which polarized data set provides the greatest difficulties with regard to multiple local minima.

Inclusion of rotatory strengths in the calculation has been shown to improve the determination of the $B^{\lambda}_{\ell\sigma}$ parameters in two ways. First, since the rotatory strengths are linear with respect to the parameters, their inclusion in the fit allows determination of the overall sign of the $B^{\lambda}_{\ell\sigma}$ parameters. Second, their inclusion helps to reduce the overall number of local minima to a smaller, better determined set of minima. Unfortunately, inclusion of rotatory strengths cannot help the fitting to the $B^{\lambda}_{\ell\pi}$ parameters, since it is not technically feasible to take rotatory strength measurements in the ortho-axial direction. In the case of NdODA examined here, inclusion of rotatory strengths decreased the total number of local minima for the fitting of the nine $B^{\lambda}_{\ell\sigma}$ parameters from 37 to 3 (39 to 2 and 44 to 3 for the two sets of CCF wavefunctions), with the resulting local minima very close to each other in parameter space. Since the standard deviations of the fits to experiment are very similar for each of these remaining local minima, it is impossible to determine a unique global minimum. However, this is not required, as each of the remaining local minima are very similar to each other, and thus we can use the averages of the parameter values for the eight local minima as the most reliable parameter set.

It will be important to expand this analysis to other

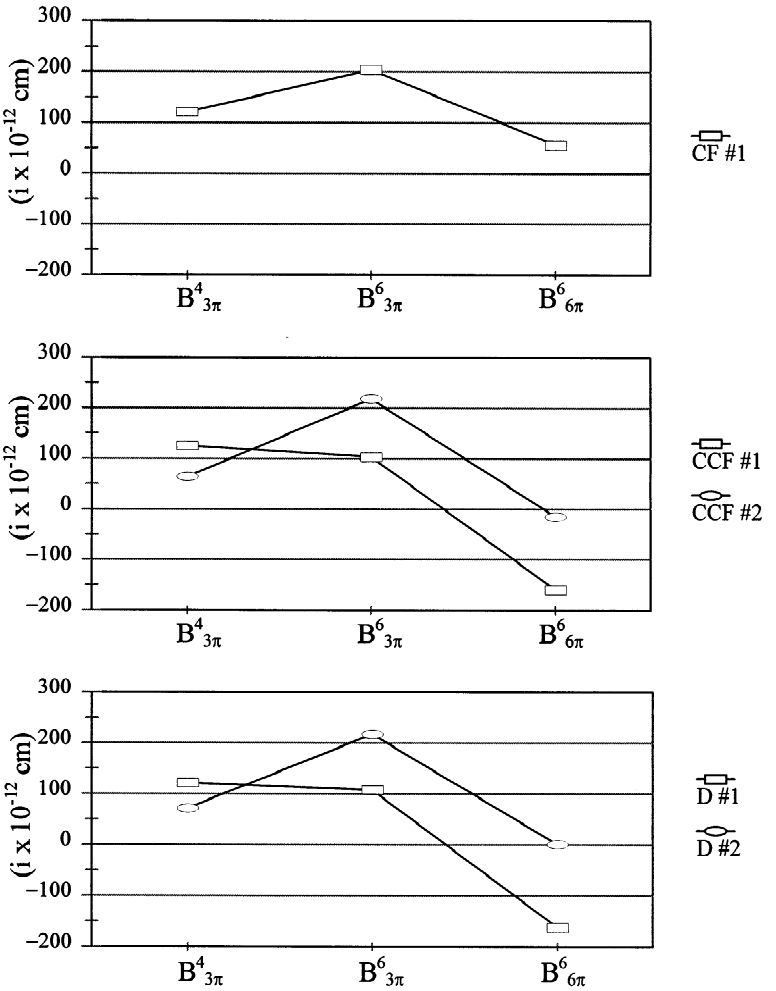

Fig. 3. $B^{\lambda}_{\ell\pi}$ parameter values for the best local minima fit to 27 pi-polarized intensities using crystal-field (CF) parametrized wavefunctions (CF, top panel), CF plus three-parameter CCF parametrized wavefunctions (CCF, second panel), and CF plus one-parameter delta-function CCF parametrized wavefunctions (D, third panel). Fitting standard deviations are 0.5526 (CF ≠1), 0.6506 (CCF ≠1), 0.7171 (CCF ≠2), 0.6503 (D ≠1), 0.6898 (D ≠2).

LnODA systems to see if the same trends found for NdODA hold true across the LnODA series.

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Table 3
Fitted $B^{\lambda}_{\ell\pi}$ parameters, best fit and average parameter set for pi intensities. All values are given in units of $i\times10^{-12}$ cm, values in parenthesis are uncertainties. Standard deviation is given as in Table 2

	Pi-polarized	
	CF ≠1	Average of five
$B^4_{3\pi}$	121(12)	101(27)
$B^6_{3\pi}$	204(18)	170(53)
$B^6_{6\pi}$	56(14)	−56(89)
σ	0.5526	

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