Optics and Spectroscopy, 2025, Vol. 133, No. 11

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Modified Judd–Ofelt method for analysis of optical transition intensities of rare earth ions

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Received May 04, 2025
Revised June 28, 2025
Accepted October 24, 2025

A modification of the Judd–Ofelt method for analyzing the spectra of rare-earth ions is proposed. It consists in the transition from considering the absolute oscillator strengths of transitions to the oscillator strengths of transitions normalized to the oscillator strength of the reference transition, which contains a significant magnetic dipole component. Due to the presence of the magnetic dipole component, it becomes possible to carry out the Judd–Ofelt analysis without knowing the concentration of optically active ions of the rare-earth element in the sample and the sample thickness. The proposed method is used to analyze the absorption spectrum of $LiNbO_3$ doped with Er^{3+}.

Keywords: modified Judd–Ofelt method, rare earth elements, erbium, $LiNbO_3$.

DOI: 10.61011/EOS.2025.11.62909.8020-25

In the early 1960s, the Judd–Ofelt theory emerged, enabling description of optical transition intensities between excited states within the $4f$-shell of rare-earth element (RE) ions [1]. It describes the intensities of such transitions for trivalent RE ions using just three Judd–Ofelt parameters (Ω_2, Ω_4, Ω_6), which encapsulate all information about the ion's interaction with its environment.

The Judd–Ofelt theory facilitates calculation of radiative transition probabilities between states within the $4f$-shell, radiative lifetimes of excited states, and branching ratios [1]. This theory provides acceptable descriptions of both absorption and luminescence spectra. Currently, it is widely applied to analyze intensities of spectra from trivalent RE ions in diverse materials, including crystals, glasses, solutions, powders, films, and nanoparticles [1].

In the standard Judd–Ofelt method, analysis begins with the sample's absorption coefficient spectrum, where transitions from the ground state to excited states within the trivalent RE ion's $4f$ shell appear as narrow bands. The analysis requires knowledge of the concentration of optically active RE ions in the 3+ charge state and the sample thickness. However, determining these parameters can be challenging in certain cases — for instance, with inhomogeneous, powdered, porous samples, irregularly shaped microparticles, or when some RE atoms exist in states where their optical properties are not described by standard Judd–Ofelt theory (e.g., due to symmetry-forbidden electric dipole transitions from inversion center presence [2] or ions bearing different charges, such as 2+ instead of 3+). Moreover, determining RE ion concentrations typically involves additional measurements that yield only total ion concentrations, without accounting for charge states or lattice positions.

To overcome this difficulty, various modifications of the standard Judd–Ofelt method have been proposed [3,4]. These require supplementary measurements: radiative lifetimes of individual excited states, emission spectra, and diffuse scattering spectra. The present work proposes a Judd–Ofelt modification that enables analysis based solely on the transmission spectrum, without using data on optically active RE ion concentration and sample thickness.

Within standard Judd–Ofelt theory, the oscillator strength f^{calc} of a transition between initial state $(^{2S+1}L_J)$ and final state $(^{2S'+1}L'_{J'})$ in the RE ion's $4f$ shell is given by

$$f^{\text{calc}}(J \to J') = \frac{8\pi^2 mc}{3h\lambda_m(2J+1)n^2}\{\chi_{ed}S_{ed} + \chi_{md}S_{md}\}, \quad (1)$$

where m — electron mass, c — speed of light, h — Planck's constant, J — total angular momentum of the initial state, λ_m — mean transition wavelength, n — refractive index, $\chi_{ed} = n(n^2+2)^2/9$, $\chi_{md} = n^3$ — Lorentz local field correction factors for electric dipole (ed) and magnetic dipole (md) transitions, S_{ed} — intensity of the electric dipole transition line:

$$S_{ed} = \Sigma_{t=2,4,6}\Omega_t|\langle[\alpha SL]J||U^{(t)}||[\alpha' S'L']J'\rangle|^2,$$

Ω_t $(t = 2, 4, 6)$ — Judd–Ofelt intensity parameters, $\langle[\alpha SL]J||U^{(t)}||[\alpha' S'L']J'\rangle$ — reduced matrix elements of rank t unitary tensor operators $U^{(t)}$ (their calculated values are given in [5], S, L, J — spin, orbital, and total momentum values, α —additional quantum number. In this formula, environmental dependence is contained in the three fitting parameters Ω_2, Ω_4, Ω_6 determined from the experimental absorption spectrum, while all angular dependencies reside in theoretically calculated matrix elements. S_{md} — intensity of the magnetic dipole transition line,

$$S_{md} = \left(\frac{\hbar}{2mc}\right)^2 |\Sigma_{\alpha SL,\alpha' S' L'} C(\alpha SL) C(\alpha' S' L') \langle [\alpha SL] J|$$
$$\times |\hat{L} + 2\hat{S}||[\alpha' S' L'] J'\rangle|^2,$$

$C(\alpha SL)$ —intermediate mixing coefficients for state $|[\alpha SL]J\rangle$, $\hat{L}+2\hat{S}$ — magnetic dipole transition operator, $\hat{L}$ — orbital angular momentum operator, $\hat{S}$ — spin momentum operator, $\hbar$ — reduced Planck's constant [3]. The electric dipole component of the oscillator strength depends on the rare-earth ion's environment field, whereas the magnetic dipole component exhibits very weak environmental dependence and can be considered practically constant and calculated precisely [3,6].

The experimental values $f^{\exp}$ of the oscillator strengths of the transitions are derived from the sample's experimental absorption spectrum:

$$f^{\exp} = \frac{mc^2}{\pi e^2 N} \int_{band} \alpha(\nu) d\nu,$$

where N — concentration of optically active RE ions, $\alpha(\nu)$ — absorption coefficient, ν — energy in cm^{-1} integration over the transition line band. Thus, the oscillator strength $f^{\exp}$ is directly proportional to the line area Y on the absorption spectrum ($Y = \int_{band} \alpha(\nu) d\nu$) and inversely proportional to the concentration of active RE ions and sample thickness.

Judd–Ofelt intensity parameters Ω_2, Ω_4, Ω_6 are found by minimizing the root-mean-square deviation δ between calculated oscillator strengths f^{calc} and experimental values $f^{\exp}$:

$$\delta = \left[\frac{1}{r-p} \sum_{i=1}^{r} \left(\frac{f_i^{\exp} - f_i^{\text{calc}}}{f_i^{\exp}}\right)^2\right]^{1/2},$$

where $p = 3$ — number of varied parameters (Ω_2, Ω_4, Ω_6), r — number of transition lines included in the analysis, summation over all selected lines for analysis [1]. The computed Ω_2, Ω_4, Ω_6 values enable calculation of radiative transition probabilities between $4f$-shell states, radiative lifetimes of excited states, and branching ratios. Since all experimentally determined oscillator strengths are inversely proportional to RE ion concentration and sample thickness, knowledge of these parameters is required.

We propose (in cases where ion concentration and/or sample thickness are unknown or difficult to determine) to move on to considering to relative oscillator strengths of transitions, which are independent of RE ion concentration and sample thickness. The relative oscillator strength of a given transition is defined as the ratio of its absolute oscillator strength to that of a selected reference transition. Logically, the reference transition should be the one least dependent on the rare-earth ion's environment. Such transitions are magnetic dipole transitions. All trivalent RE ions have one or more transitions from the ground state to excited states within the $4f$-shell containing a significant magnetic dipole component, calculated theoretically [6].

Similar approach was previously applied to analyze Eu^{3+} ion spectra [7]. The Eu^{3+} emission spectrum includes the ${}^5D_0 \rightarrow {}^7F_1$ transition, which has purely magnetic dipole character. This transition's intensity is independent of the Eu^{3+} ion environment and calculable precisely. In Judd–Ofelt analysis for Eu^{3+} this transition serves as reference for other electric dipole emission transitions originating from the ${}^5D_0$ state [7]. This feature of Eu^{3+} ions, stemming from their matrix elements, enables Judd–Ofelt analysis using not absorption spectrum lines from ground to excited states, but emission spectrum lines corresponding to transitions from excited to lower-lying states.

The distinction of our proposed approach from the method used for Eu^{3+} lies in employing the absorption spectrum rather than luminescence spectrum for analysis. Thus, our approach can be applied to various trivalent RE ions, whereas the [7] method applies only to Eu^{3+}. The proposed modified method involves selecting, among all observed transitions in the trivalent RE ion absorption spectrum, one with maximum-intensity magnetic dipole component as reference. Relative oscillator strengths of all other transitions are calculated as the ratio of the transition's oscillator strength to that of the reference transition (for the i-th transition: $f_{\text{rel},i} = f_i / f_{\text{ref}}$). Theoretical oscillator strengths are computed using equation (1). Experimental relative oscillator strengths are calculated as (for the i-th transition) $f_{\text{rel},i}^{\exp} = Y_i^{\exp} / Y_{\text{ref}}^{\exp}$, where $Y_i^{\exp}$ — area under the i-th transition line on the absorption spectrum or optical density ($OD = \alpha d \ln(10)$, where α — absorption coefficient, d — sample thickness), $Y_{\text{ref}}^{\exp}$ — area under the reference transition line on the same spectrum.

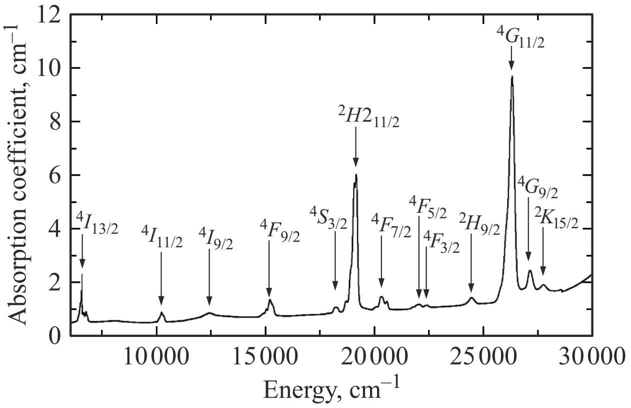
Judd–Ofelt intensity parameters Ω_2, Ω_4, Ω_6 are then found by minimizing the root-mean-square deviation δ_{rel} between theoretically calculated relative oscillator strengths and their experimental values:

$$\delta_{\text{rel}} = \left[\frac{1}{r-p} \sum_{i=1}^{r} \left(\frac{f_{\text{rel},i}^{\exp} - f_{\text{rel},i}^{\text{calc}}}{f_{\text{rel},i}^{\exp}}\right)^2\right]^{1/2}. \qquad (2)$$

Inclusion of magnetic dipole transitions among analyzed lines is essential, as otherwise (considering only electric dipole transitions, whose oscillator strengths are homogeneous functions of Ω_2, Ω_4, Ω_6) only mutual ratios of parameters Ω_2, Ω_4, Ω_6 could be determined, not their absolute values.

Consider application of the proposed method to the Er^{3+} ion in lithium niobate crystal (LiNbO_3). Congruent LiNbO_3 crystals were grown from melt using the Czochralski method [8]. Er^{3+} ions in the LiNbO_3 lattice occupy Li^+ ion sites possessing C_3 symmetry [9].

The Er^{3+} ions do not occupy inversion center symmetry sites, so the proposed modified method is applicable. The sample absorption spectrum (figure) clearly shows lines corresponding to transitions from ground to excited Er^{3+} states within the $4f^{11}$-shell. When performing the Judd–Ofelt analysis using the modified method, the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition was taken as the reference transition for Er^{3+}.



Absorption coefficient spectrum for $LiNbO_3$ sample doped with Er^{3+}. Arrows indicate absorption lines corresponding to transitions from ground state to excited states in the $4f^{11}$-shell. Final states are labeled above arrows.

The oscillator strength of the magnetic dipole $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition was calculated in [6]: $f = 6.817 \cdot 10^{-7}$. Transitions to excited states $^2H2_{11/2}$, $^4G_{11/2}$, $^4S_{3/2}$, $^4F_{3/2}$, $^4I_{9/2}$, $^4G_{9/2}$, $^2K_{15/2}$ were excluded from analysis, as they contain significant high-energy states (above $\sim 32000\,\mathrm{cm}^{-1}$) [10].

Judd–Ofelt analysis using the modified method (equation (2)) with selected transitions $^4I_{15/2} \rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4I_{11/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2} \rightarrow {}^4F_{7/2}$, $^4I_{15/2} \rightarrow {}^2H_{9/2}$ gave the following values of the Judd-Offelt intensity parameters: $\Omega_2 = 5.05 \cdot 10^{-20}$, $\Omega_4 = 0.753 \cdot 10^{-20}$, $\Omega_6 = 0.690 \cdot 10^{-20}\,\mathrm{cm}^2$ with root-mean-square deviation $\delta_{\mathrm{rel}} = 0.0031$. These computed Judd–Ofelt parameters closely match values obtained in [3] for Er^{3+} in $LiNbO_3$: $\Omega_2 = 6.19 \cdot 10^{-20}$, $\Omega_4 = 2.17 \cdot 10^{-20}$, $\Omega_6 = 0.97 \cdot 10^{-20}\,\mathrm{cm}^2$. For all lines selected for analysis, deviations between calculated oscillator strengths (using the above Ω_2, Ω_4, Ω_6 values) and experimental values do not exceed 0.3 %, confirming high analysis accuracy and validating applicability of the proposed modified Judd–Ofelt method for RE ion spectrum analysis.

Conflict of interest

The author declares that he has no conflict of interest.

Funding

The work was performed under state assignment № FFUG-2024-0017.

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Translated by J.Savelyeva