

1 **On the experimental determination of 4f-4f intensity parameters from the**
2 **emission spectra of europium (III) compounds**

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1 **Abstract:**

2 Eu^{3+} complexes and specially β -diketonate compounds are well known and studied in several
3 areas due to their luminescence properties, such as sensors and lightning devices. A unique
4 feature of the Eu^{3+} ion is the experimental determination of the 4f-4f intensity parameters Ω_λ
5 directly from the emission spectrum. The equations for determining Ω_λ from the emission
6 spectra are different for the detection of emitted power compared to modern equipment that
7 detects photons per second. It is shown that the differences between Ω_λ determined by misusing
8 the equations are sizable for Ω_4 (ca. 15.5%) for several $\text{Eu}^{3+}\beta$ -diketonate complexes and leads
9 to differences of ca. 5% in the intrinsic quantum yields $Q_{\text{Ln}}^{\text{Ln}}$. Due to the unique features of
10 trivalent lanthanide ions, such as the shielding of 4f-electrons, which lead to small covalency
11 and crystal field effects, a linear correlation was observed between Ω_λ obtained using the
12 emitted power and photon counting equations. We stress that care should be exercised with the
13 type of detection should be taken and provide the correction factors for the intensity parameters.
14 In addition, we suggest that the integrated intensity (proportional to the areas of the emission
15 band) and the centroid (or barycenter) of the transition for obtaining Ω_λ should be determined
16 in the properly Jacobian-transformed spectrum in wavenumbers (or energy). Due to the small
17 widths of the emission bands of typical 4f-4f transitions, the areas and centroids of the bands
18 do not depend on the transformation within the experimental uncertainties. These assessments
19 are relevant because they validate previously determined Ω_λ without the proper spectral
20 transformation.

21

22 **Keywords:** intensity parameters; Judd-Ofelt; correction factor; emitted power; photon
23 counting.

24

1 **1. Introduction**

2 Lanthanide (or lanthanoid) containing compounds surround us in everyday life in many
3 technologies, from MRI machines to LEDs for lighting or displays [1–3]. These widespread
4 applications arise from their unique properties, especially the photophysical and optical
5 properties of trivalent lanthanide ions (Ln^{3+}), to which professor Marina Popova has made
6 relevant contributions [4–8]. One of these unique features of Ln^{3+} ions is the complete
7 description of the intensities of f-f transitions by only three quantities, known as intensity
8 parameters [9–11]. These parameters are essential to quantify important photophysical
9 properties such as branching ratios and their radiative lifetimes, applications to lasers, and their
10 applications to luminescent materials. Therefore, the proper experimental determination of
11 these intensity parameters is relevant to further developments and improvements of lanthanide-
12 based materials as well as to validate theoretical models [11–14]. Among the elements of the
13 lanthanide series, europium plays a relevant role in photonics and optical applications, in the
14 forms of both Eu^{3+} and Eu^{2+} , each one with its own spectroscopic characteristics. Because of
15 such special electronic structure features of the Eu^{3+} ion, emission spectra of compounds and
16 materials can be employed in determining the intensity parameters [10,12,15]. On the other
17 hand, the Eu^{2+} ion shows dipole allowed 4f-5d transitions and has been applied, for instance, in
18 materials that present the persistent luminescence phenomenon, with the emission colour being
19 tunable due to high ligand field effects [16–18]. However, the Eu^{3+} relevant transitions as well
20 as of most Ln^{3+} ions have a 4f-4f nature and, therefore, are electric dipole forbidden, presenting
21 much lower oscillator strengths and longer excited-state lifetimes, enabling various applications
22 ranging from nanothermometers to safety markers [19–22]. The lower oscillator strengths of
23 the Ln^{3+} 4f-4f transitions can be overcome, as shown by Weissman in 1942 [23], by
24 coordinating Ln^{3+} to chromophores that can absorb light and efficiently populate the excited
25 levels of the ion, thus rendering luminescent materials with high emission intensity.

26 The key to understanding the 4f-4f intensities of the trivalent lanthanide ions are the forced
27 electric dipole (FED) and dynamic coupling (DC) mechanisms. In 1962, Judd and Ofelt in
28 independent works introduced the FED mechanism which explained satisfactorily the nature of
29 4f-4f transitions [24,25]. However, the FED mechanism presented discrepancies to the so-
30 called hypersensitive transitions, giving evidence that another important mechanism could
31 exist. Thus, in 1964, Jørgensen and Judd introduced the “pseudoquadrupole” mechanism to
32 explain the behavior of these hypersensitive transitions [26]. In 1975, Mason *et al.* introduced
33 the formalism of and the term dynamic coupling mechanism [27] which is attributed to the

1 ligand-polarizability dependent effect, however, Judd demonstrated in 1979 that the DC
2 mechanism proposed by Mason *et al.* is formally identical to his previous work with Jørgensen
3 [28].

4 For non-centrosymmetric systems, the effect of the odd components of the crystal field acts
5 as a perturbation on the free-ion Hamiltonian. As a result, the perturbed wavefunctions of 4f
6 states have components with opposite parity such as 5d, 6d, 5g, etc [24,25]. This leads to the
7 expressions for transition rates that translate this configuration mixture caused by the ligand
8 field in the so-called Judd-Ofelt intensity parameters (or intensity parameters) often labeled as
9 Ω_λ ($\lambda = 2, 4,$ and 6), which can be experimentally measured. The DC mechanism states that the
10 exciting radiation induces oscillating electric fields on the ligand atoms, proportional to the
11 polarizabilities. The induced field can, therefore, promote the 4f-4f transitions and the final
12 equation for the transition rates is analog to the Judd-Ofelt Theory, i.e. one cannot discriminate
13 by experiment the contributions of each mechanism to the intensity parameters Ω_λ [11]. The
14 experimental determination of these intensity parameters is of great importance in the study of
15 the local environment of the lanthanide ion; combined with ligand field models, one can obtain
16 information about structure and bonding between the ion and the first coordination sphere, such
17 as charge factors, polarizabilities and covalency [14,29]. In some compounds, it was even
18 reported long-range structural sensitivity for the Ω_λ parameters [12].

19 In the case of the Eu^{3+} ion, experimental determination of these intensity parameters is made
20 easy due to the energy level structure. Because the emitting $^5\text{D}_0$ level has zero total angular
21 momentum and of the selection rules, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ intensity is influenced only by the Ω_2 , the
22 $^5\text{D}_0 \rightarrow ^7\text{F}_4$ by the Ω_4 , and the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ by the Ω_6 . Moreover, Eu^{3+} ions present the $^5\text{D}_0 \rightarrow ^7\text{F}_1$
23 transition that is practically only allowed by magnetic dipole, which makes this transition nearly
24 independent on the ligand field, depending on the refractive index. This transition can be taken
25 as an internal reference to calculate the spontaneous emission rates of the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions
26 ($J = 2, 4$ and 6).

27 One of the most efficient Eu^{3+} luminescent compounds is β -diketonate-based complexes
28 [10]. This class of compounds is extensively studied because they usually present high emission
29 intensities when excited at the ligands excitation band due to their efficient sensibilization of
30 the Eu^{3+} ions, which can lead to quantum yields up to around 80%, albeit most complexes
31 cannot sustain UV irradiation for a long time [9,20,21,23,30–33]. Even when new ligands are
32 synthesized, in many cases the core of the luminescent complex is based on β -diketone-type
33 ligand [34].

1 However, most parameters calculated from the emission spectra for Eu^{3+} compounds in the
2 last two decades considered detection of emitted power, while most of the modern equipment
3 detect the number of emitted photons per second [35–42]. In addition, all determinations of the
4 intensity parameters, the integrated intensities and centroids are obtained as the areas of the
5 bands in the emission spectra recorded in wavelengths. However, a proper determination of
6 these areas would be from emission spectra in wavenumber (or energy) scales, which require
7 transformation of the signal [43,44]. In this work, several Eu^{3+} β -diketonate complexes were
8 prepared and their photoluminescence spectra recorded. From the emission spectra, the
9 experimental 4f-4f intensity parameters Ω_λ were determined using the proper expressions for
10 photon-counting detectors and compared to the data obtained using the emitted power equation
11 as well as taking into consideration the proper transformed spectra to wavenumbers.

14 2. Experimental

16 2-Thenoyltrifluoroacetone (Htta, 99%), benzoyltrifluoroacetone (Hbtfa, 99%), 1,10-
17 phenanthroline (phen, 99%), tetraethylammonium chloride (Et_4NCl , >98%), and 1-ethyl-3-
18 methylimidazolium chloride (C_2mimCl , >98%) were all purchased from Merck and used
19 without further purification. Eu_2O_3 was purchased from CSTARM (99,99%) and converted to
20 $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ according to the procedure previously reported in the literature [36].

21 Microanalyses were carried on a Perkin-Elmer 2400 series II, the ESI-MS spectra were
22 recorded in an Amazon speed ETD Bruker Daltonics spectrometer with Ion Trap detection,
23 utilizing a 4500 V electrospray ionization source under flow of hot N_2 gas ($300\text{ }^\circ\text{C}$, 5 L min^{-1}).
24 Emission spectra measurements were recorded in an Edinburgh FLS980 instrument utilizing a
25 450 W Xe arc lamp as the excitation source.

27 2.1 Synthesis of the $[\text{Eu}(\beta\text{-dik})_3(\text{L})_n]$ complexes

29 All complexes were synthesized following the same methodology, adapted from the
30 literature [9,15]. Initially, a solution of 3 mmol of NaOH in 10 mL of deionized water was
31 added dropwise to an ethanolic solution of 3 mmol of the β -diketone (Htta or Hbtfa) with
32 constant stirring at $60\text{ }^\circ\text{C}$. Following, an aqueous solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol in 10 mL of
33 deionized water) was added dropwise to the previous mixture. After partial evaporation of the

1 ethanol, the $[\text{Eu}(\beta\text{-dik})_3(\text{H}_2\text{O})_n]$ complex was formed as an oil, originating two phases from the
2 initial ethanolic solution. Then, 20 mL of deionized water were added under vigorous stirring
3 to precipitate the solid $[\text{Eu}(\beta\text{-dik})_3(\text{H}_2\text{O})_n]$. The complex was filtered and dried at 50 °C for 72
4 h.

5 The water ligands were replaced by 1,10-phenanthroline as: 0.5 mmol of the $[\text{Eu}(\beta\text{-}$
6 $\text{dik})_3(\text{H}_2\text{O})_n]$ was dissolved in 20 mL of ethanol, followed by the dropwise addition of an
7 ethanolic solution of 1,10-phenanthroline (1 mmol in 10 mL of ethanol) with constant stirring.
8 The $[\text{Eu}(\beta\text{-dik})_3(\text{phen})]$ complex precipitated almost instantaneously. The mixture was stirred
9 for 2 h and then placed in an ice bath to precipitate any dissolved complex. The formed
10 compounds were filtered and dried at 50 °C for 72 h.

11 $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ ESI(+) MS: m/z $[\text{M}+3\text{H}]^+ = 852.91$, ca. 852.91. Anal. calcd. for
12 $\text{C}_{24}\text{H}_{16}\text{EuF}_9\text{O}_8\text{S}_3$:
13 C 33.85, H 1.89%, found: C 34.06, H 1.85%.

14 $[\text{Eu}(\text{btfa})_3(\text{H}_2\text{O})_2]$ ESI(+) MS: m/z $[\text{M}+3\text{H}]^+ = 835.01$, ca. 835.05. Anal. calcd. for
15 $\text{C}_{30}\text{H}_{20}\text{EuF}_9\text{O}_7$:
16 C 43.23, H 2.66%, found: C 43.10, H 2.68 %.

17 $[\text{Eu}(\text{tta})_3(\text{phen})]$ ESI(+) MS: m/z $[\text{Eu}(\text{tta})_2(\text{phen})_2]^+ = 953.11$, ca. 953.03 . Anal. calcd. for
18 $\text{C}_{36}\text{H}_{20}\text{EuF}_9\text{N}_2\text{O}_6\text{S}_3$: C 43.43, H 2.02, N 2.81%, found: C 43.23, H 1.99, N 2.82 %.

19 $[\text{Eu}(\text{btfa})_3(\text{phen})]$ ESI(+) MS: m/z $[\text{Eu}(\text{btfa})_2(\text{phen})_2]^+ = 941.20$, ca. 941.12. Anal. calcd. for
20 $\text{C}_{42}\text{H}_{26}\text{EuF}_9\text{N}_2\text{O}_6$: C 51.60, H 2.68, N 2.87%, found: C 51.27, H 2.73, N 2.99 %.

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22 2.2 Synthesis of the $Q[\text{Eu}(\beta\text{-dik})_4]$ complexes

23 All complexes were synthesized following the methodology reported previously by our
24 group [21]. To an isopropanol solution of 2-thenoyltrifluoroacetone, Htta, (20 mmol in 40 mL
25 of iPrOH) with stirring at 60 °C an aqueous solution of sodium hydroxide, NaOH (20 mmol in
26 10 mL of H_2O) was added dropwise. Following, 10 mL of an isopropanol solution of
27 tetraethylammonium chloride, $\text{Et}_4\text{N}^+\text{Cl}^-$ (6 mmol) was added. Finally, an aqueous solution of
28 europium (III) chloride (4 mmol in 10 mL of water) was added and a precipitate of $Q[\text{Eu}(\beta\text{-}$
29 $\text{dik})_4]$ was formed. After stirring at around 70 °C for 2h, the mixture was filtered, washed with
30 cold ethanol and dried under reduced pressure for 5h. ESI-MS analyses were performed in
31 negative mode to scan for the $[\text{Eu}(\beta\text{-dik})_4]^-$ anion.

32 $\text{Et}_4\text{N}^+[\text{Eu}(\text{tta})_4]$ ESI(-) MS: m/z $[\text{Eu}(\text{tta})_4]^- = 1036.87$, ca. 1036.96 Anal. calcd. for
33 $\text{C}_{40}\text{H}_{36}\text{EuF}_{12}\text{NO}_8\text{S}_4$: C 41.17, H 3.11, N 1.20%, found: C 41.10, H 3.10, N 1.24 %.

1 C₂mim[Eu(tta)₄] ESI(-) MS: m/z [¹⁵³Eu(tta)₄]⁻ = 1036.94, ca. 1036.96 Anal. calcd. for
2 C₃₈H₂₇EuF₁₂N₂O₈S₄: C 39.76, H 2.37, N 2.44%, found: C 39.77, H 2.34, N 2.44 %.

3. Results and discussion

6
7 Elemental analysis results of the samples are in excellent agreement with the the proposed
8 formulas compounds. The ESI-MS results (**Figure S1-S10**) also indicate that we obtained the
9 desired complexes, while it is worth mentioning that lanthanide complexes may react during
10 ionization even at mild conditions such as electrospray ionization, as it seems to have occurred
11 with [Eu(β-dik)₃(phen)] compounds [45]. A ligand exchange reaction is suggested, such as
12 2[Eu(β-dik)₃(phen)] → [Eu(β-dik)₂(phen)₂]⁺ + [Eu(β-dik)₄]⁻, due to the presence of [Eu(β-
13 dik)₄]⁻ ions in the ESI (-) spectrum of the phenanthroline complexes (Figures **S3** and **S10**),
14 although further investigation is necessary.

15 The emission spectra for all complexes are presented in **Figure 1**. The data were recorded
16 in the solid state (powdered samples) at room temperature (298 K) from 570 to 720 nm under
17 excitation at the most intense excitation band of the ligand. All compounds showed the the
18 hypersensitive ⁵D₀ → ⁷F₂ signal as well as the other typical Eu³⁺ ⁵D₀ → ⁷F_{0,1,3,4} transitions as
19 narrow emission bands. An interesting feature of the *tetrakis* complexes is the absence of the
20 ⁵D₀ → ⁷F₀ transition, suggesting a non-C_{n(v)} point group. It is also noteworthy that the
21 Et₄N[Eu(tta)₄] presents an almost monochromatic ⁵D₀ → ⁷F₂ transition, with a FWHM of 1.250
22 nm (33 cm⁻¹). The excitation spectra for the compounds are presented in **Figure S11**.

23 From the emission spectra complexes, it is possible to calculate the 4f–4f intensity
24 parameters Ω_λ for the Eu³⁺ ion (**Table 1**). To express the difference between the parameters
25 obtained using an emitted power formula in a photon counting detector, it is useful to first derive
26 the well-known equations for the determination of such parameters, starting from the definition
27 of the spectral intensity of a transition in terms of emitted power, I^P (**Eq. 1**), and photons per
28 seconds, I^C (**Eq. 2**):

$$30 I_{0j}^P = NA_{0j} \hbar \omega_{0j} = 2\pi NA_{0j} \hbar c \sigma_{0j} \quad (1)$$

$$32 I_{0j}^C = NA_{0j} \quad (2)$$

1 where N is the population of the emitting level, A_{0j} is the spontaneous emission coefficient for
 2 the ${}^5D_0 \rightarrow {}^7F_j$ transition, ω_{0j} is the angular frequency, σ_{0j} is the transition centroid in
 3 wavenumbers (in cm^{-1}), \hbar is the reduced Planck constant, and c is the speed of light.

4 From the Judd-Ofelt and dynamic coupling theories, we can obtain the expressions for the
 5 spontaneous emission coefficients for electric dipole transitions of the Eu^{3+} ion as:

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$$7 \quad A_{0\lambda} = \Lambda \sigma_{0\lambda}^3 \Omega_\lambda, \quad \Lambda = \frac{32\pi^3 e^2 \chi}{3\hbar} |\langle {}^5D_0 || U^{(\lambda)} || {}^7F_\lambda \rangle|^2 \quad (3)$$

8

9 where e is the elementary charge, χ is the Lorentz local field correction factor, Ω_λ is the 4f-4f
 10 intensity parameter and $\langle {}^5D_0 || U^{(\lambda)} || {}^7F_\lambda \rangle^2$ is the reduced matrix element of the unitary tensor
 11 operator of rank λ , with values of 0.0032 for $\lambda = 2$ and 0.0023 for $\lambda = 4$ for the Eu^{3+} ion [46].
 12 It should be noted that a misprinted value of 0.032 for the matrix element for $\lambda = 4$ has been
 13 detected in references of wide use and citation [19,47].

14 For the magnetic dipole allowed and electric dipole forbidden ${}^5D_0 \rightarrow {}^7F_1$ transition ($\Delta J = 1$),
 15 the spontaneous emission rate can be expressed as:

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$$17 \quad A_{01} = \kappa \sigma_{01}^3 \quad (4)$$

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19 where $\kappa = 0.31 \times 10^{-11} n^3$, with n being the refractive index of the medium (see **Supporting**
 20 **information**). In this work n was considered as 1.5 for all compounds.

21 With A_{01} being known, it is possible to calculate all others $A_{0\lambda}$ from the ratio of the emission
 22 intensities, which are proportional to the integrated areas in the emission spectrum, namely

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$$24 \quad \frac{I_{0\lambda}^P}{I_{01}^P} = \left(\frac{S_{0\lambda}}{S_{01}} \right) = \left(\frac{A_{0\lambda}}{A_{01}} \right) \left(\frac{\sigma_{0\lambda}}{\sigma_{01}} \right) = \frac{\Lambda}{\kappa} \frac{\sigma_{0\lambda}^4 \Omega_\lambda^P}{\sigma_{01}^4} \quad (5)$$

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$$26 \quad \frac{I_{0\lambda}^C}{I_{01}^C} = \left(\frac{S_{0\lambda}}{S_{01}} \right) = \left(\frac{A_{0\lambda}}{A_{01}} \right) = \frac{\Lambda}{\kappa} \frac{\sigma_{0\lambda}^3 \Omega_\lambda^C}{\sigma_{01}^3} \quad (6)$$

27

28 where $S_{0\lambda}$ is the area of the emission band corresponding to the ${}^5D_0 \rightarrow {}^7F_\lambda$ ($\lambda = 2, 4$ or 6)
 29 transitions, the superscript P and C denote the areas from the spectrum measured as photons per

1 second but calculated by the mathematical formulation for emitted power and photon counting
 2 per second, respectively.

3 The intrinsic emission quantum yield Q_{Ln}^{Ln} is a quantity that defines the internal efficiency of
 4 the Ln^{3+} ion as an emitting center. Thus, Q_{Ln}^{Ln} can be calculated as follows:

$$6 \quad Q_{Ln}^{Ln} = \frac{A_{rad}}{A_{rad} + A_{nrad}} = A_{rad}\tau \quad (7)$$

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 8 where A_{rad} is the sum over all radiative rates and A_{nrad} is the non-radiative decay rate. The
 9 sum of these rates is related to the inverse of the lifetime ($A_{rad} + A_{nrad} = \tau^{-1}$) in absence of
 10 energy transfer processes involving the emitting level. The obtained values of the 5D_0 lifetimes
 11 for the studied compounds are presented in **Table S1 and Figure S12**. For the case of the
 12 compounds containing the Eu^{3+} ion, **Eq. 7** can be rewritten as:

$$14 \quad Q_{Ln}^{Ln} = \tau \sum_{\lambda} A_{0\lambda} \quad (8)$$

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 16 Thus, depending on what the type of detections considered in the calculations of such $A_{0\lambda}$,
 17 the Q_{Ln}^{Ln} could also present errors (mainly in the A_{02} and A_{04} emission coefficients) if the
 18 corrected formula is not applied. **Table 1** shows, for instance, that the values of Q_{Ln}^{Ln} using the
 19 emitted power formula for emission spectra obtained from photon-counting equipment. This
 20 could lead to an overestimation of 5% of the correct $Q_{Ln}^{Ln}(C)$ values (**Figure S13**).

21 It is important to stress that the linear behaviours observed for the correlations in **Figure 2**
 22 are due to the shielding effect provided by the filled 5s5p subshells in the Ln^{3+} ions. So, the 4f-
 23 electrons are subjected to extremely small ligand field effects and vanishing covalency effects,
 24 thus rendering the 4f-4f transitions centroids very localized. As a result, the ratio between the
 25 centroids does not suffer significant changes when comparing different compounds, making the
 26 existence of a linear correction factor possible.

27 The correction factor is obtained by a direct comparison between the emitted power and
 28 photon counting mathematical expressions for the recorded intensity as the ratio between **Eqs.**
 29 **5 and 6**, which yields the following expression for the correction factor:

$$31 \quad \Omega_{\lambda}^C = \Omega_{\lambda}^P \left(\frac{\sigma_{0\lambda}}{\sigma_{01}} \right) \quad (9)$$

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where $\sigma_{0\lambda}$ is the centroid of the ${}^5D_0 \rightarrow {}^7F_\lambda$ transition, with $\lambda = 2, 4$ or 6 .

For the Eu^{3+} β -diketonate complexes analyzed here, we obtain the average correction factor with an extremely low uncertainty due to the low covalency and crystal field effects of $4f$ electrons, namely $\langle \frac{\sigma_{02}}{\sigma_{01}} \rangle = 0.9636 \pm 0.0008$ and $\langle \frac{\sigma_{04}}{\sigma_{01}} \rangle = 0.8478 \pm 0.0007$.

It is worth to mention that the intensity parameters Ω_λ themselves are not influenced by the type of detector, because those parameters are physical observables, they cannot depend on the measurement. The correction factor should be applied to intensity parameters obtained with photon-counting detectors but were calculated using the emitted power formula, which was the case for various works in the past 20 years. That is, the parameters calculated with the proper equations from a spectrum measured in emitted power should be the same as those calculated from a spectrum recorded from a photons per second detector, provided that the correct equations for each case are used.

As it can be observed in all equations employed in the demonstrations above, the areas and most importantly the barycenters (or centroids) used to obtain radiative rates and intensity parameters should be determined from the spectrum in wavenumbers (or energy or frequency). However, because the spectra are usually recorded wavelengths, it needs to be converted to wavenumbers, for instance, and the signal transformed by the so-called Jacobian transformation [43,44]. For broad emission bands, this transformation has a significant impact in the relative intensities, maximum positions and lineshapes. For instance, the gaussian lineshape observed in the emission spectrum of $\text{Ba}_2\text{WO}_3\text{F}_4$ in wavenumbers becomes remarkably asymmetric in wavelengths [48]. In addition, $\lambda_{\text{max}} = 490 \text{ nm}$ (maximum in the wavelength spectrum), which corresponds to 20408 cm^{-1} , whereas $\tilde{\nu}_{\text{max}} = 19700 \text{ cm}^{-1}$ (maximum in the wavenumber spectrum), see *Appendix 4: Plotting Emission Spectra* in Ref. [48], yielding a significant difference (ca. 700 cm^{-1}) between these maxima determined in the proper spectrum compared to the spectrum in wavelengths. To our knowledge this transformation has never been used in the determination of the intensity parameters from emission spectra, which has motivated us to investigate the effects of this transformation.

The relationship between energy, E , or frequency, ν , or angular frequency, ω , or wavenumber, $\tilde{\nu}$, represented generically by σ and the wavelength, λ , can be expressed as $\sigma = a\lambda^{-1}$, with $a = 10^7$ for $\sigma \equiv \tilde{\nu}$, λ in nm, $a = hc$ for $\sigma \equiv E$, or $a = c$ for $\sigma \equiv \nu$. Therefore, the conversion of λ into σ is straightforward, however, it should be noted that because this is a nonlinear relationship, evenly spaced data acquisition in λ will result in strongly unevenly

1 spaced data in σ , which might result in differences when performing numerical integrations.
2 By the chain rule [43,44], one can write: $f(\sigma) = f(\lambda)d\lambda/d\sigma$, where $f(\lambda)$ is the signal observed
3 in the original acquisition in wavelength, where $f(\sigma)$ is the transformed signal when the
4 wavelength is converted into σ . Combining these two equations, it is possible to obtain $f(\sigma) =$
5 $-a\sigma^{-2}f(\lambda)$, where the original $f(\lambda)$ should be multiplied by a factor $-a\sigma^{-2}$, called the
6 Jacobian transformation, to provide the proper transformed spectrum. In particular, for the
7 conversion to wavenumbers: $\tilde{\nu}$ (cm^{-1}) = $10^7/\lambda$ (nm) and $f(\tilde{\nu}) = -10^7 f(\lambda)/\tilde{\nu}^2$.

8 We calculated the areas of the transitions of interest employing the original spectrum
9 recorded as photons per second as a function of the wavelength as well as with the Jacobian-
10 transformed spectrum in wavenumbers. The differences between these areas were smaller than
11 1%, which is lower the experimental uncertainties in such measurements or even the uncertainty
12 in the limits of integration. In addition, the centroids, $\sigma_{0\lambda}$, of the $^5\text{D}_0 \rightarrow ^7\text{F}_\lambda$ transitions were not
13 significantly affected by the spectral transformation (see **Table S2**). As a result, the determined
14 values of the intensity parameters were, within the experimental uncertainties, independent of
15 the Jacobian transformation. These are important assessments because they validate all data and
16 values obtained previously for the intensity parameters from emission spectra, which have not
17 employed the Jacobian transformation. This insensibility to the transformed spectrum is mainly
18 due to the small widths of the emission bands typical of Ln^{3+} -based compounds.

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21 4. Conclusions

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23 Several Eu^{3+} β -diketonate complexes were synthesized, with general formulas $[\text{Eu}(\beta$ -
24 $\text{dik})_3(\text{L})_n]$ and $Q[\text{Eu}(\beta\text{-dik})_4]$, which were confirmed by elemental and ESI-MS analyses. The
25 emission spectra were recorded in the solid state with a photon counting detector and the
26 experimental 4f-4f intensity parameters Ω_λ were determined using the well-known emitted
27 power, $\Omega_\lambda^{\text{P}}$, and the photons per second, $\Omega_\lambda^{\text{C}}$, equations. The differences between $\Omega_\lambda^{\text{P}}$ and $\Omega_\lambda^{\text{C}}$ are
28 systematic, with $\Omega_\lambda^{\text{P}} > \Omega_\lambda^{\text{C}}$ and Ω_2^{P} being 3.4 to 3.9% larger than Ω_2^{C} , whereas Ω_4^{P} is 15.0 to
29 15.6% larger than Ω_4^{C} . These small and systematic differences are due to the small covalency
30 and the low ligand field effects, yielding an excellent linear correlation between the parameters
31 $\Omega_\lambda^{\text{P}}$ and $\Omega_\lambda^{\text{C}}$. So, for these compounds, correction factors were obtained that allows the
32 conversion $\Omega_2^{\text{P}} \leftrightarrow \Omega_2^{\text{C}}$ and $\Omega_4^{\text{P}} \leftrightarrow \Omega_4^{\text{C}}$. In addition, because the shielding effects, the 4f-4f
33 transitions produce are very narrow emissions, so the areas calculated with the spectrum

1 recorded in wavelengths are practically the same as those obtained from the spectrum converted
2 to wavenumbers and the signal transformed by the Jacobian. We therefore suggest an extra care
3 with the type on detection on the determination of the intensity parameters and provide the
4 correction factors for parameters determined from spectra recorded in photons per seconds but
5 calculated assuming emitted power detection. Such correction factors could be practically used
6 for any Eu^{3+} complex with oxygen or nitrogen bonding atoms.

7 8 **Declaration of competing interest**

9
10 The authors declare that they have no known competing financial interests or personal
11 relationships that could have appeared to influence the work reported in this paper.

12 13 **Author Contributions**

14
15 **L Blois:** Conceptualization, Methodology, Investigation, Formal Analysis, Visualization, Data
16 Curation, Writing – original draft, Writing – review & editing. **A.N. Carneiro Neto:**
17 Conceptualization, Methodology, Formal Analysis, Validation Writing – original draft, Writing
18 – review & editing. **R.L. Longo:** Formal Analysis, Validation, Writing – original draft, Writing
19 – review & editing. **I.F. Costa:** Methodology, Visualization, Data Curation, Writing – original
20 draft, Writing – review & editing. **T.B. Paolini:** Methodology, Writing – review & editing.
21 **H.F. Brito:** Conceptualization, Methodology, Visualization, Data Curation, Supervision,
22 Funding Acquisition, Project Administration, Writing – original draft, Writing – review &
23 editing. **O.L. Malta:** Conceptualization, Methodology, Formal Analysis, Visualization,
24 Supervision, Writing – original draft, Writing – review & editing.

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9

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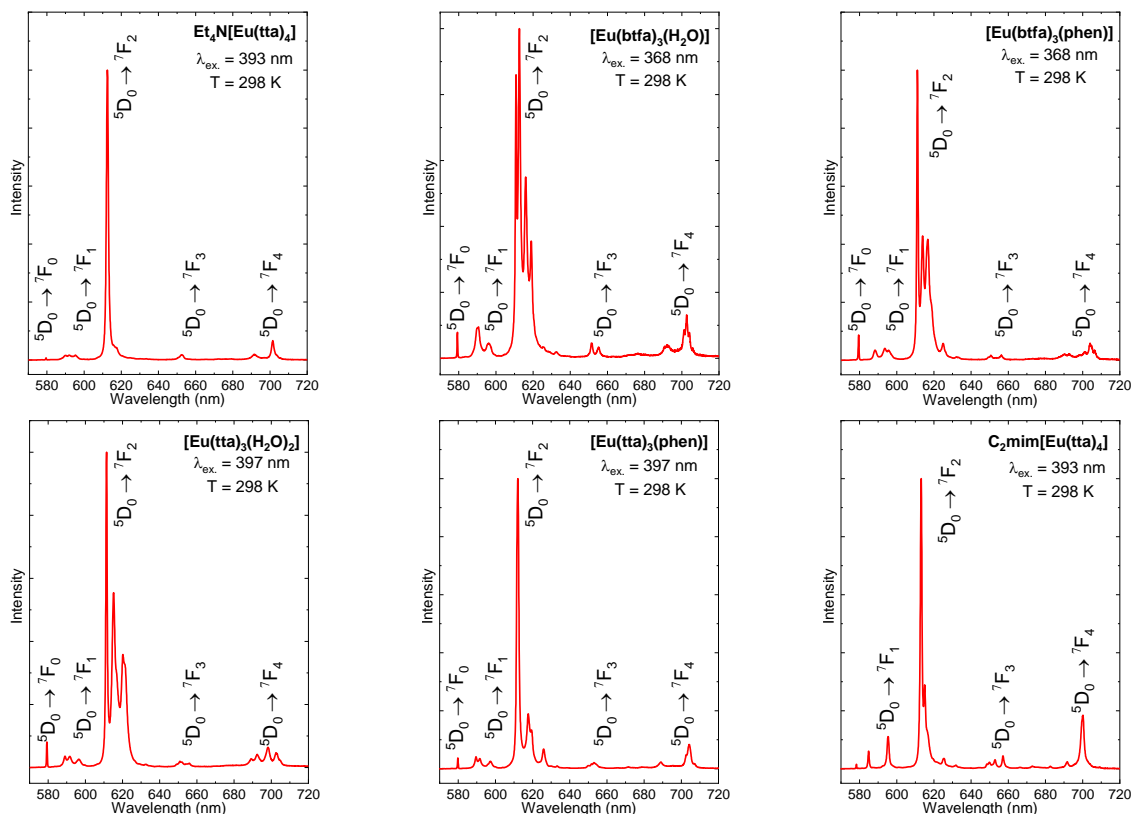
1 **Table 1:** Experimental 4f–4f intensity parameters (in 10^{-20} cm²) obtained by using the
2 expressions for emitted power, Ω_{λ}^P , and photon counting, Ω_{λ}^C , and the corresponding percentual
3 intrinsic quantum yield, Q_{Ln}^{Ln} .

4

	Ω_2^P	Ω_2^C	Ω_4^P	Ω_4^C	$Q_{Ln}^{Ln}(P)$	$Q_{Ln}^{Ln}(C)$
[Eu(tta) ₃ (H ₂ O) ₂]	33	32	8.0	6.8	32	30
[Eu(tta) ₃ (phen)]	22	21	5.0	4.2	63	60
[Eu(btfa) ₃ (H ₂ O) ₂]	20	19	7.1	6.0	33	32
[Eu(btfa) ₃ (phen)]	24	23	5.8	4.9	63	60
Et ₄ N[Eu(tta) ₄]	30	28	9.5	8.0	98	93
C ₂ mim[Eu(tta) ₄]	15	14	10	8.6	52	49

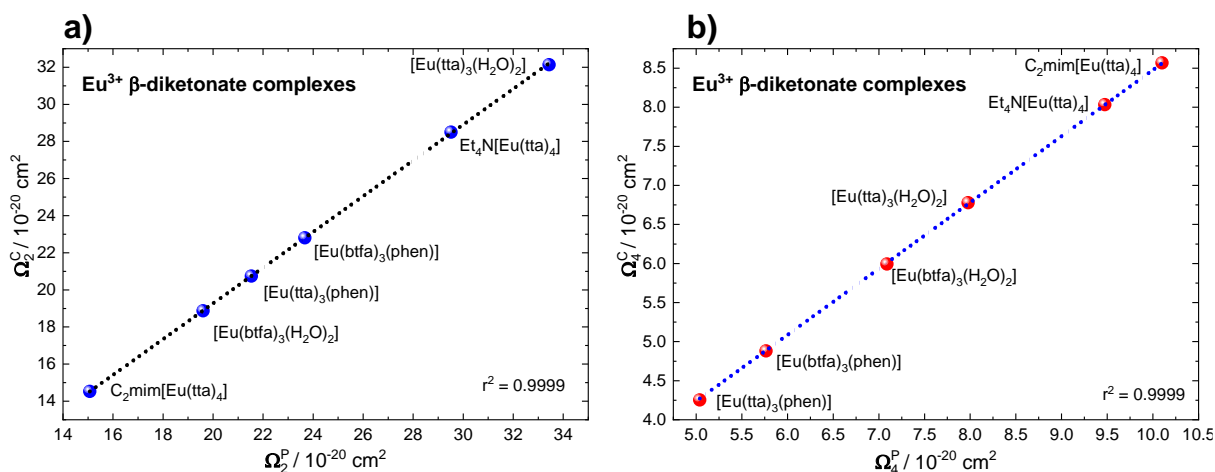
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1
2 **Figure 1:** Emission spectra for the $[\text{Eu}(\beta\text{-dik})_3(\text{L})_n]$ and $\text{Q}[\text{Eu}(\beta\text{-dik})_4]$ complexes with
3 excitation at the maximum of excitation band of the ligand recorded in the solid state at 298 K.

4
5
6



7
8 **Figure 2:** Correlation between 4f–4f intensity parameters for Eu^{3+} β -diketonate complexes
9 calculated with the emitted power (Ω^{P}) and photon counting (Ω^{C}) expressions.

10