Breakdown of the Energy Gap Law in Molecular Lanthanoid Luminescence: The Smallest Energy Gap Is Not Universally Relevant for Nonradiative Deactivation

Christine Doffek,[†] Jessica Wahsner,[†] Elisabeth Kreidt,[†] and Michael Seitz*,[†]

[†]Department of Chemistry and Biochemistry, Ruhr-University Bochum, 44780 Bochum, Germany

ⓢ Supporting Information

ABSTRACT: For several decades, the energy gap law has been the prevalent theoretical framework for the discussion of nonradiative deactivation of lanthanoid luminescence in molecular coordination chemistry. Here we show experimentally on samarium and dysprosium model complexes that the size of the energy gap ΔE between a lanthanoid emitting state and the next-lower electronic state cannot be considered a reliable and accurate predictor of the quantitative extent of nonradiative deactivation by aromatic C–H and C–D oscillator overtones. Because the energy gap is the central pillar for the entire conceptual framework of the energy gap law, this finding amounts to largely invalidating this theory for the quantitative description of molecular multiphonon relaxation.

The quantitative understanding of radiative and nonradiative processes in light-emitting systems is one of the Holy Grails in photophysics. It would allow far-reaching control of the luminescence properties, e.g., in order to increase or modulate emission characteristics. In this context, the "energy gap law" (EGL) is one of the very few reliable cornerstones for the quantitative assessment of nonradiative deactivation rates k_{nr} of emitting electronic states according to eq 1

$$k_{nr} \propto e^{-[\text{constant}(\Delta E/\hbar\omega_{max})]} \tag{1}$$

where ΔE is the energy gap between the emitting level and the next-lower state and $\hbar\omega_{max}$ is the energy of a high-frequency oscillator that mediates nonradiative deactivation. Originally, the EGL was developed for aromatic hydrocarbons,[1] but it has also been applied for a number of other luminophore classes, such as transition-metal complexes,[2] or lanthanoid ions in solid matrixes[3] and in complexes with organic ligands.[4,5] The great practical appeal of the EGL for lanthanoid luminescence is to a great extent based on the fact that the metal-centered electronic states are largely unchanged in different environments and, consequently, that the energy gap ΔE is a priori known. We have recently shown that predictions of the EGL can fail under special circumstances, e.g., for the anomalously high quenching ability of aromatic C–D oscillators with respect to the $^1D_2$ state of praseodymium.[6] Here, we show in exemplary model systems the very general phenomenon that the energy gap according to the EGL is not a reliable quantity in the context of multiphonon relaxation. The reported very serious breakdown all but invalidates the EGL for the quantitative description of nonradiative decay in molecular lanthanoid complexes, which has been the prevalent theoretical framework for decades.

The starting hypothesis for the present study was that nonradiative deactivation in molecular lanthanoid luminescence is not necessarily determined by the smallest energy gap according to the EGL but rather by the very specific energy of an oscillator overtone. In order to experimentally assess the validity of this basic idea, we chose the two lanthanoids samarium and dysprosium and two different oscillators, aromatic C–H and C–D moieties, often found in successful lanthanoid chelators. Figure 1 depicts the relevant states for this situation.
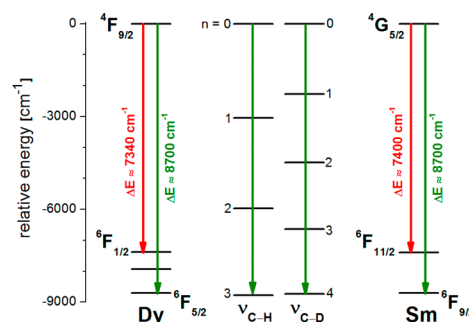
Figure 1. Partial energy-level diagram for dysprosium(III) and samarium(III) showing the energy gaps ΔE according to the EGL (red) and the ones proposed here to be relevant for aromatic C–(H/D) oscillators (green).[7]

A conventional EGL approach would assume the following gaps ΔE to be relevant: Dy, $^4F_{9/2}-{}^6F_{1/2} \approx 7340$ cm^{-1}; Sm, $^4G_{5/2}-{}^6F_{11/2} \approx 7400$ cm^{-1}.[7] In both cases, however, if deactivation is considered to be mediated by the aromatic C–(H/D) oscillators, much larger energy gaps of ca. 8700 cm^{-1} (Figure 1, green arrows) would be in almost perfect resonance with the second C–H overtone ($n = 3$), as well as the third C–D overtone ($n = 4$).[6b] For the practical implementation of this setup, we prepared the suitable lanthanoid complexes shown in Chart 1.

On the basis of previous work,[8,9] the tris(2,2′-bipyridine)-based cryptate [D_0]-Sm and its perdeuterated analogue [D_{30}]-Sm were synthesized.[10] For dysprosium, isotopologic 2,2′-bipyridine-6,6′-dicarboxylates[11] were chosen as ligands because

Chart 1. Lanthanoid Complexes Used in This Study

[D$_0$]-Sm: R = H
[D$_{30}$]-Sm: R = D

[D$_0$]-Dy: R = H
[D$_{12}$]-Dy: R = D
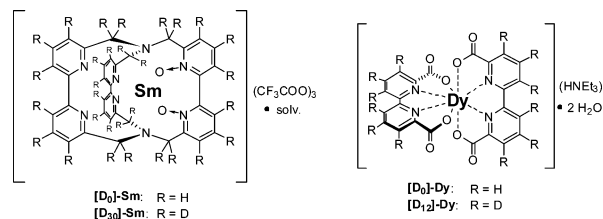
of their high ligand triplet energies ($\approx$23500 cm^{-1}), which are necessary for sensitization of the metal-centered, emitting ^{4}F$_{9/2}$ state ($\approx$21100 cm^{-1}).[7] All complexes show very efficient photoluminescence in solution in the visible and near-IR regions and exhibit well-defined, monoexponential luminescence decays (Figures 2 and 3 and Table 1).
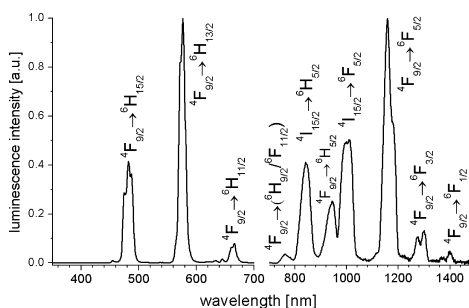
Figure 2. Steady-state emission of [D$_{12}$]-Dy in CD$_3$OD (left, λ_{exc} = 306 nm, 2 nm bandwidth; right, λ_{exc} = 306 nm, 9 nm bandwidth; emission, long pass filter RG780).
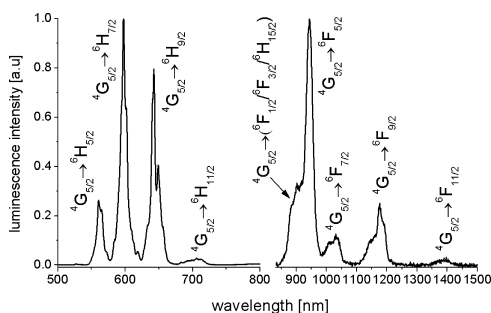
Figure 3. Steady-state emission of [D$_{30}$]-Sm in CD$_3$CN (left, λ_{exc} = 310 nm, 2 nm bandwidth; right, λ_{exc} = 310 nm, 6 nm bandwidth; emission, long pass filter RG780).

Table 1. Luminescence Lifetimes for [D$_x$]-Dy in CD$_3$OD and for [D$_x$]-Sm in CD$_3$CN[a]

| complex	τ_{574} [μs][b]	τ_{940} [μs][c]	τ_{1000} [μs][d]	τ_{1156} [μs][e]	τ_{943} [μs][f]	τ_{1175} [μs][g]
[D$_{12}$]-Dy	194	190	154	189		
[D$_0$]-Dy	107	104	95	105		
[D$_{30}$]-Sm					394	394
[D$_0$]-Sm					30	32

[a]Estimated uncertainties: τ ± 10%; Dy, λ_{exc} = 305 nm, A_{305} $\approx$ 0.20; Sm, λ_{exc} = 310 nm, A_{310} $\approx$ 0.20/ [b]^{4}F$_{9/2}$ $\rightarrow$ ^{6}H$_{13/2}$. [c]^{4}F$_{9/2}$ $\rightarrow$ ^{6}H$_{5/2}$. [d]^{4}I$_{15/2}$ $\rightarrow$ ^{6}F$_{5/2}$. [e]^{4}F$_{9/2}$ $\rightarrow$ ^{6}F$_{5/2}$. [f]^{4}G$_{5/2}$ $\rightarrow$ ^{6}F$_{5/2}$. [g]^{4}G$_{5/2}$ $\rightarrow$ ^{6}F$_{9/2}$.

As a measure of the nonradiative deactivation of a lanthanoid-emitting state, we used the model developed by Ermolaev and Sveshnikova,[12] which provides a convenient expression for k_{nr} via a spectral overlap integral (SOI) of the following form:

$$k_{nr} = \frac{9000 \ln(10)\, k_r \kappa^2}{128\pi^2 n^4 N_A r^6} \int I_{em}(\tilde{\nu})\, \varepsilon_{vib}(\tilde{\nu})\, \tilde{\nu}^{-4}\, d\tilde{\nu} \qquad (2)$$

where I_{em} in the integral is the lanthanoid-based emission spectrum (normalized to unit area) and ε_{vib} is the molar vibrational absorption coefficient, both on the wavenumber scale $\tilde{\nu}$.[13] In general, this expression is rather impractical because of the great experimental difficulty to obtain quantitative spectra $\varepsilon_{vib}(\tilde{\nu})$ for a particular oscillator. In this case, however, we have recently established the relevant vibrational absorption signatures for aromatic C$-$(H/D) overtones in 2,6-substituted pyridine moieties[6b] which allows full analysis of nonradiative deactivation pertaining to the hypothesis of this study.

The advantage of the SOI approach for this study is that, unlike the EGL, it allows evaluation of which spectral region contributes most to nonradiative deactivation. If the smallest energy gap ΔE according to the EGL was relevant, the integrand of the overlap integral would have most of its intensity around this energy value. In stark contrast to this notion, the integrand functions for both lanthanoids and both oscillators show that the overwhelming contributions to the SOIs, and by extension to k_{nr}, come from the region between ca. 8500 and 9000 cm^{-1} (Figure 4) corresponding to much larger energy gaps, in perfect agreement with our hypothesis.
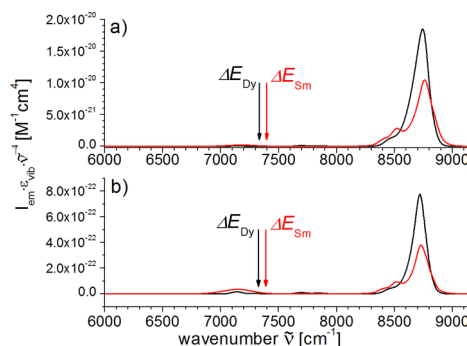

Figure 4. SOI integrand functions for the low-energy emission bands of dysprosium (black) and samarium (red) with the first and second C$-$H overtones (a) and of the second and third C$-$D overtones (b). Smallest ΔE indicated by arrows.[10]

In addition, this phenomenon is not restricted to the discussion of only samarium/dysprosium complexes or C$-$(H/D) oscillators. Effects similar to the ones described here are certainly also operative for other systems. For example, in the light of our own study, we interpret published data on the energetic positions of isotopologic O$-$(H/D) oscillator overtones in methanolic solutions (CH$_3$OH/CD$_3$OD)[10] with respect to the nonradiative deactivation of terbium and europium luminescence, as shown in Figure 5. The O$-$H oscillator overtones are in good resonance with the smallest ΔE values in both lanthanoids (red arrows), while contrary to this, the isotopologic oscillators O$-$D are in almost perfect resonance with the larger energy gaps (green arrows).

In summary, the fact that the smallest energy gaps are not universally relevant for the quantitative discussion of non-radiative decay has a number of important implications and ramifications for the entire field of molecular lanthanoid luminescence in the future:

(a) The most salient result of this study is that the relevant energy gaps for specific lanthanoid/oscillator combinations are
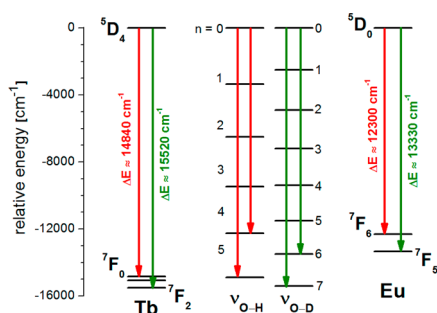
Figure 5. Partial energy-level diagram for terbium(III) and europium-(III) showing the energy gaps ΔE relevant for O−H (red) and for O−D (green) oscillators in methanolic solutions.[10,14]

not known a priori and that the potential differences can be quite substantial (e.g., 7400 cm^{-1} for the EGL in samarium versus the actually operative 8700 cm^{-1}). This largely invalidates the EGL in this area because of the absolute centrality of the energy gap concept for the entire theoretical framework. It remains only a tool for rationalization of the qualitative trends, but it can no longer be considered valid for quantitative analysis of non-radiative deactivation in molecular lanthanoid luminescence because of these serious deficiencies.

(b) The failure shown here is expected to be most prominent for systems with high-energy oscillators that themselves have large gaps between their vibrational overtones. This situation sometimes allows for the smallest energy gap ΔE not to be in resonance with a particular overtone, resulting in the potential irrelevance of ΔE as utilized in the EGL. For this reason, low-phonon lanthanoid-doped solids with very densely spaced oscillator overtones are most likely not affected and the validity of the EGL in this area is unquestioned by our findings.

(c) Future experimental work on multiphonon relaxation mediated by high-energy oscillators (e.g., X−H with X = O, N, C) has to focus on the precise energetic overtone positions in order to identify relevant resonances in specific lanthanoid/oscillator combinations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and analytical data for [D_x]-Dy and [D_x]-Sm, spectroscopic details, and SOI calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: michael.seitz@rub.de.
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145−164. (b) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187−1203.

(c) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1973; Vol. *I*, pp 153−237.

(2) (a) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630−632. (b) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Köhler, A.; Friend, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 9412−9417. (c) Whittle, C. E.; Weinstein, J. A.; George, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053−4062. (d) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447−457.

(3) (a) Basiev, T. T.; Orlovskii, Yu. V.; Pukhov, K. K.; Auzel, F. *Laser Phys.* **1997**, *7*, 1139−1152. (b) Malkin, B. Z. In *Spectroscopic Properties of Rare Earths in Optical Materials*; Liu, G., Jacquier, B., Eds.; Springer Series in Material Science Vol. 83; Springer: Hamburg, Germany, 2005; pp 130−190. (c) van Dijk, J. M. F.; Schuurmans, M. F. H. *J. Chem. Phys.* **1983**, *78*, 5317−5323.

(4) Bünzli, J.-C. G.; Eliseeva, S. V. In *Comprehensive Inorganic Chemistry II*; Reedijk, J., Poeppelmeier, K., Eds.; Elsevier: Oxford, U.K., 2013; Vol. 8; pp 339−398.

(5) For selected examples, see: (a) Brandner, A.; Kitahara, T.; Beare, N.; Lin, C.; Berry, M. T.; May, P. S. *Inorg. Chem.* **2011**, *50*, 6509−6520. (b) Reinhard, C.; Güdel, H. U. *Inorg. Chem.* **2002**, *41*, 1048−1055. (c) Haas, Y.; Stein, G.; Würzberg, E. *J. Chem. Phys.* **1974**, *60*, 258−263. (d) Stein, G.; Würzberg, E. *J. Chem. Phys.* **1975**, *62*, 208−213. (e) Stein, G.; Würzberg, E. *Z. Phys. Chem.* **1976**, *101*, 163−170.

(6) (a) Scholten, J.; Rosser, G. A.; Wahsner, J.; Alzakhem, N.; Bischof, C.; Stog, F.; Beeby, A.; Seitz, M. *J. Am. Chem. Soc.* **2012**, *134*, 13915−13917. (b) Doffek, C.; Alzakhem, N.; Bischof, C.; Wahsner, J.; Güden-Silber, T.; Lügger, J.; Platas-Iglesias, C.; Seitz, M. *J. Am. Chem. Soc.* **2012**, *134*, 16413−16423.

(7) Energy levels for the aqua species: Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4424−4442.

(8) Nondeuterated cryptand: Lehn, J.-M.; Roth, C. O. *Helv. Chim. Acta* **1991**, *74*, 572−578.

(9) Doffek, C.; Alzakhem, N.; Molon, M.; Seitz, M. *Inorg. Chem.* **2012**, *51*, 4539−4545.

(10) For details, see the Supporting Information.

(11) (a) Bünzli, J.-C. G.; Charbonniere, L. J.; Ziessel, R. F. *J. Chem. Soc., Dalton Trans.* **2000**, 1917−1923. (b) Wahsner, J.; Seitz, M. *Inorg. Chem.* **2013**, *52*, 13301−13303.

(12) Review: (a) Sveshnikova, E. B.; Ermolaev, V. L. *Opt. Spectrosc.* **2011**, *111*, 34−50. Selected examples: (b) Ermolaev, V. L.; Sveshnikova, E. B. *Chem. Phys. Lett.* **1973**, *23*, 349−354. (c) May, P. S.; Richardson, F. S. *Chem. Phys. Lett.* **1991**, *179*, 277−281.

(13) k_r = radiative rate; κ = orientational factor; n = refractive index; N_A = Avogadro's number; r = distance Ln−oscillator.

(14) Energy levels: (a) Eu: Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4450−4455. (b) Tb: Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4447−4449.