

Note

Lanthanide coordination compounds modeling: Sparkle/PM3 parameters for dysprosium (III), holmium (III) and erbium (III)

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Abstract

The Sparkle model, recently parameterized for all trivalent lanthanide ions using the AM1 semiempirical quantum chemical model, is now parameterized to PM3 method. In a recent paper [R.O. Freire, G.B. Rocha, A.M. Simas, *Chem. Phys. Lett.* 425 (2006) 138] we defined the Sparkle/PM3 model for Tm(III). Now the Sparkle/PM3 is extended to dysprosium (III), holmium (III) and erbium (III) ions. In the parameterization procedure, we used the same three sets of 15 complexes used to parameterize Sparkle/AM1 for each of these three lanthanide ions, with various representative ligands. The Sparkle/PM3 unsigned mean error, for all interatomic distances between the trivalent lanthanide ion and the ligand atoms of the first sphere of coordination, is 0.072 Å for Dy(III); 0.064 Å for Ho(III); and 0.072 Å for Er(III). These figures are similar to the Sparkle/AM1 ones of 0.066 Å, 0.054 Å, and 0.064 Å, respectively, indicating they are all comparable parameterizations. Moreover, their accuracy is similar to what can be obtained by present-day ab initio effective core potential calculations on such lanthanide complexes. Hence, the choice of which model to use remains with the researcher who must evaluate the impact of either AM1 or PM3 on the quantum chemical description of the organic ligands.

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When Ln(III) complexes exhibit intense luminescence, a wide range of applications becomes possible. Dysprosium (III) displays characteristic transitions leading to blue and yellow emissions at around 484 nm and 575 nm, which can be taken advantage of to create useful luminescent complexes [1–4] – an appropriate tuning of the blue/yellow intensity ratio can be presumed to accomplish a white luminescent system.

Holmium (III) possesses one of the highest magnetic moments of all rare earth metal ions. As such, it may be a choice as a magnetic center in the design and synthesis of single-molecule magnets and molecular-based magnetic materials. A complex of holmium 166 with chitosan is

largely applied in cancer research [5,6]. Ho(III) also displays a near infrared emission at 1197 nm, which has lately received attention [7]. A tuneable near infrared emitting diode, an electroluminescent device, has been made with a porphyrin complex of Ho(III), blended with porphyrin complexes of Yb(III) and Er(III), which emit at 977 nm and 1570 nm, respectively [8].

Trivalent erbium displays an eye safe intra- $4f^{11} \ ^4I_{13/2} \rightarrow \ ^4I_{15/2}$ rather sharp transition at 1.54 μm in the near infrared, which lies at the lowest attenuation and low dispersion window of standard silica based optical fibers. And it is due to the general availability of Er(III)-doped amplifiers, that optical telecommunications networks have developed as much [9].

Hence, due to innumerable applications of lanthanide complexes, there is a need of supporting theoretical techniques to assist in the design of ligands with aforethought

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structures and optimized energy levels with the following aims: of boosting the long term stabilities of the complexes; of enhancing the luminescent quantum yields; of optimizing the lifetimes; and of reducing the quenching mechanisms.

Since 1953, Dexter [10] noticed that the energy transfer rate from the ligands to the lanthanide ion is strongly dependent on the distances between the metal ion and the ligands, with the transfer rate diminishing rapidly at distances larger than 5 Å. Such interatomic distances are indeed the most sensitive geometric variables impacting upon the description of the effect of the surrounding chemical context on the lanthanide ion $4f^n$ configuration [11,12]. So, the ability to predict geometries of lanthanide complexes, more specifically of their coordination polyhedra, is therefore central to luminescent complexes design.

Conceived in 1994 [13,14] and later improved [15], the Sparkle model has since been applied exclusively to Eu(III) complexes. However, recently, we developed a new paradigm for lanthanide complex semiempirical calculations, called Sparkle/AM1 [16], based on a more sophisticated parameterization scheme.

The Sparkle model replaces the trivalent rare earth ion by a Coulombic charge of $+3e$ superimposed to a repulsive exponential potential of the form $\exp(-\alpha r)$, which accounts for the size of the ion; provides three electrons to the orbitals of the ligands; adds two Gaussian functions to the core–core repulsion energy term; and includes the lanthanide atomic mass. Thus, the sparkle model assumes that the lanthanide trications behave like simple ions, without any angular steric properties. Accordingly, the angular effects of the f orbitals are assumed to be negligible and are not taken into account. The good agreement between various predicted and observed lanthanide ion complexes structures is a powerful evidence for the appropriateness of this concept.

Recent research on lanthanide complexes has indeed indicated that Sparkle/AM1 coordination polyhedron geometries are comparable to, if not better than, geometries obtained with the best contemporary *ab initio* calculations with effective core potentials (*ab initio*/ECP) on such complexes [17]. Besides, Sparkle/AM1 calculations are hundreds of times faster [16]. Indeed, the ability to evaluate many different putative structures of lanthanide complexes in a combinatorial manner, may prove important for luminescent devices design, for single-molecule magnets design, and for telecommunications research.

PM3 [18,19] was introduced in 1989 as a more accurate semiempirical model, giving lower average errors than AM1 [20], mainly for the enthalpies of formation. PM3 also became very popular. In a recent paper [21] we defined the Sparkle/PM3 model for Tm(III). In this note, we introduce the Sparkle/PM3 parameters for Dy(III), Ho(III) and Er(III).

The Sparkle/PM3 parameters for Dy(III), Ho(III) and Er(III) were obtained using essentially the same procedure used in our previous work [16]. Accordingly, we only used

high quality crystallographic structures (R -factor $<5\%$) of complexes taken from the “Cambridge Structural Database 2004” (CSD) [22–24], having found a total of 30 structures of complexes of Dy(III), 27 of Ho(III), and 39 of Er(III). As training sets, we used the same three subsets of 15 complexes each, already chosen for the parameterization of Sparkle/AM1 for the same ions, and described in Fig. 1 of each of the Dy(III) [25], Ho(III) [26] articles, and in Figure S3 of the supplementary material of the Er [27] article.

The Sparkle/PM3 parameters found for the three lanthanide ions are shown in Table 1.

The directly coordinating atoms of the ligands form the coordination polyhedron of the complex, whose faces are the polygonal bases of a set of adjacent pyramids that share the same apex, where the lanthanide ion is located. Each

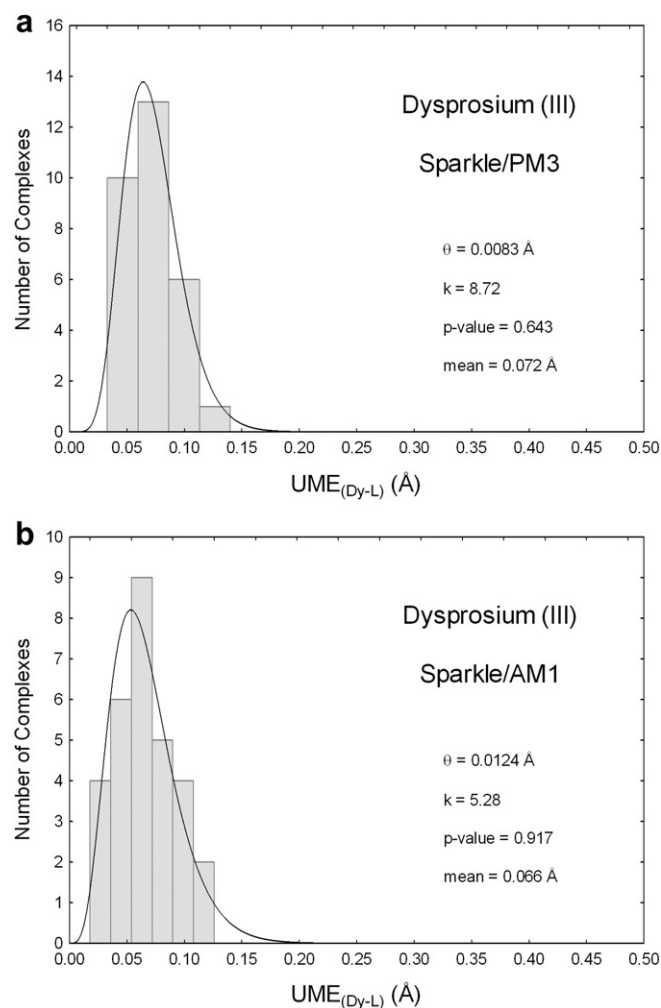


Fig. 1. Probability densities of the gamma distribution fits of the $UME_{(Ln-L)S}$ for the Dy(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 30 Dy(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the p -value is a measure of the significance of the gamma distribution fit; and mean is the expected value of the fitted gamma distribution, which is set to be equal to the arithmetic mean value of the 30 $UME_{(Ln-L)S}$.

Table 1
Parameters for the Sparkle/PM3 model for the Dy(III), Ho(III) and Er(III) ions

	Sparkle/PM3		
	Dy(III)	Ho(III)	Er(III)
GSS	55.7563629021	58.0161995449	58.0537274879
ALP	2.4630183002	3.7240820504	3.6824732031
a_1	1.3287435702	1.0370243923	0.5361755749
b_1	7.9816784235	8.7236664457	8.7390296713
c_1	1.7080927380	1.7412327388	1.7856436299
a_2	0.3332412720	0.5175396118	0.0776867913
b_2	9.7816147381	10.6247030904	8.6267120701
c_2	2.9323938165	3.0090983082	2.9875549001
EHEAT ^a (kcal mol ⁻¹)	1001.3	1009.6	1016.15
AMS (amu)	162.5	164.9303	167.26

^a The heat of formation of the Dy(III), Ho(III) and Er(III) ions in Sparkle/PM3 and Sparkle/AM1 models were obtained by adding to the heat of atomization of each respective lanthanide, their first three ionization potentials.

two adjacent pyramids share one triangular face, and therefore, also one side of their polygonal bases.

We used the average unsigned mean error for each complex i , UME_i as geometry accuracy measures. In Eq. (1) n_i is the number of ligand atoms directly coordinating the lanthanide ion.

$$UME_i = \frac{1}{n_i} \sum_{j=1}^{n_i} |R_{i,j}^{CSD} - R_{i,j}^{calc}| \quad (1)$$

Two cases have been examined: (i) UMEs involving the interatomic distances R_j between the lanthanide central ion and the atoms of the coordination polyhedron, as well as the interatomic distances R_j between all atoms of the coordination polyhedron, and (ii) $UME_{(Ln-L)}$ s involving only the interatomic distances R_j between the lanthanide central ion and the atoms of the coordination polyhedron. Tables 1S, 2S and 3S of the supplementary data present the $UME_{(Ln-L)}$ s and UMEs and for both Sparkle/PM3 and Sparkle/AM1 for Dy(III), Ho(III), and Er(III), respectively.

Assuming that the sparkle model is a good representation of the lanthanide ion, as well as of its interactions with the ligands, the distribution of these UMEs should be random around a mean, whose value can be used as a measure of the accuracy of the model. Since the UMEs are positive, defined in the domain $(0, \infty)$, they should follow the gamma distribution which has the probability density function $g(x; k, \theta)$,

$$g(x; k, \theta) = x^{k-1} \frac{e^{-x/\theta}}{\theta^k \Gamma(k)} \quad (2)$$

where $x > 0$ stands for the UMEs, $k > 0$ is the shape parameter, $\theta > 0$ is the scale parameter of the gamma distribution, and $\Gamma(k)$ is the gamma function of k . The expected value of the gamma distribution is simply $k\theta$. To obtain the gamma distribution fit of the UME data, we have to estimate the shape and scale parameters. To obtain these estimates we used the method of maximum likelihood.

Fig. 1a presents a gamma distribution fit of the $UME_{(Ln-L)}$ data for the Sparkle/PM3 model for Dy(III).

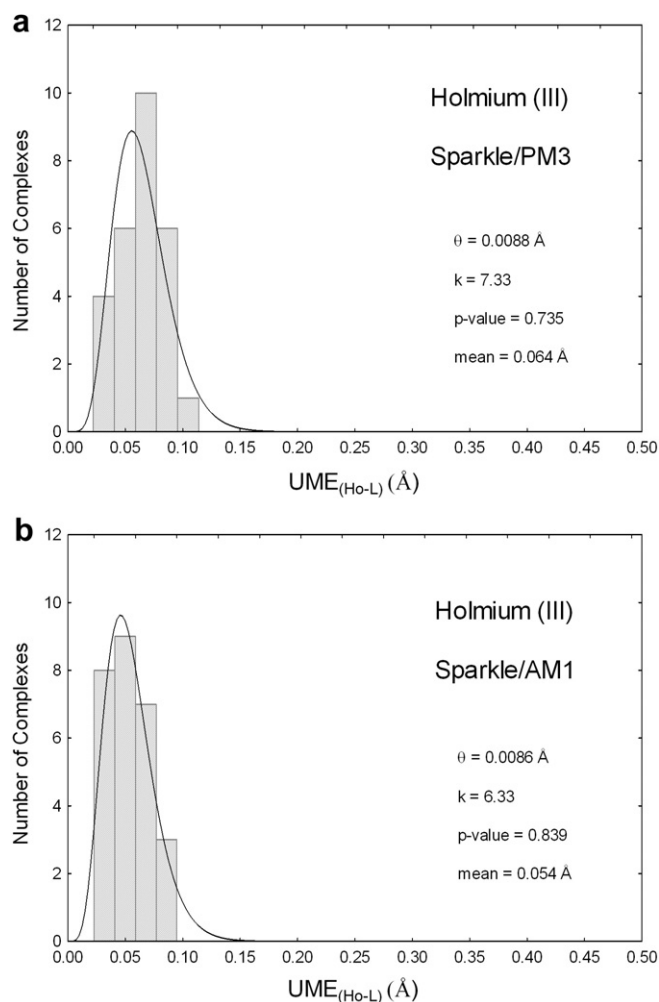


Fig. 2. Probability densities of the gamma distribution fits of the $UME_{(Ln-L)}$ s for the Ho(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 27 Ho(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the p -value is a measure of the significance of the gamma distribution fit; and mean is the expected value of the fitted gamma distribution, which is set to be equal to the arithmetic mean value of the 27 $UME_{(Ln-L)}$ s.

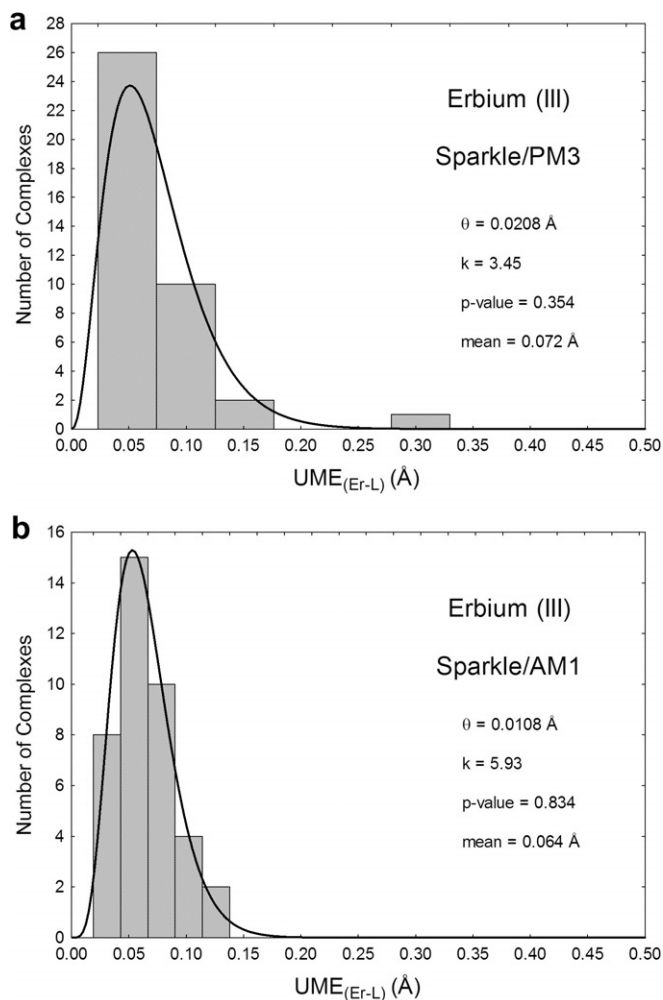


Fig. 3. Probability densities of the gamma distribution fits of the $UME_{(Ln-L)S}$ for the Yb(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 47 Yb(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the p -value is a measure of the significance of the gamma distribution fit; and mean is the expected value of the fitted gamma distribution, which is set to be equal to the arithmetic mean value of the 47 $UME_{(Ln-L)S}$.

As indicated in the figure, the p -value is 0.643, thus indicating that the UMEs are indeed significantly randomly dis-

tributed around the mean through a gamma distribution. In order to simply give a pictorial idea of this and also of where and how the actual UMEs occurred. For comparison purposes, Fig. 1b presents the same gamma distribution fit for the $UME_{(Ln-L)}$ data for the already published Sparkle/AM1 model for Dy(III) [25], which presents a p -value of 0.917. Fig. 1 also presents superimposed histograms of the data with the number of bars chosen to best adjust the histogram to the curve obtained from the gamma distribution fit.

Fig. 2 presents a gamma distribution fit of the Sparkle/PM3 as well as for previously published Sparkle/AM1 models for holmium [26]. For the holmium ion the p -values are 0.735 and 0.839, respectively.

Finally, Fig. 3 presents a gamma distribution fit of the respective $UME_{(Ln-L)}$ for trivalent erbium ion. For this case, the p -value is 0.354 Sparkle/PM3 model and 0.834 for previously published Sparkle/AM1 model [27]. In all cases the respective p -values were well above the critical value of 0.05, ranging from 0.143 to 0.971, thus validating the usage of the sparkle model for both PM3 and AM1 for the prediction of lanthanide complexes geometries.

Table 2 summarizes the accuracies of the three parameterizations, displaying the UMEs for all distances involving the central lanthanide ion, Ln(III), and the ligand atoms of the coordination polyhedron, L, for all complexes considered in the present paper. The numbers indicate that the Sparkle/PM3 and Sparkle/AM1 models for Dy(III), Ho(III) and Er(III) possess the same accuracies and that the parameterizations are equalized.

In conclusion, Sparkle/PM3 parameters for Dy(III), Ho(III) and Er(III) are defined here at the same level of quality of the previously introduced Sparkle/AM1 parameters that generate geometries of a quality comparable to present-day rare earth complex ab initio calculations [17]. The decision of which of the equivalent models to adopt, either Sparkle/PM3 or Sparkle/AM1, rests with the user who must conjecture the influence of either AM1 or PM3 on the quantum chemical description of the specific ligands under investigation, and the ensuing impact on the property of interest. In short, many possibilities open up for scientists involved in complex design when, sometimes, it may

Table 2

Sparkle/PM3 and Sparkle/AM1 unsigned mean errors for all distances involving the central lanthanide ion, Ln, and the ligand atoms of the coordination polyhedron, L, for 30 Dy(III) complexes; 27 Ho(III) complexes and 39 Er(III) complexes considered

Model	Unsigned mean errors for specific types of distances (Å)					
	Ln-Ln	Ln-O	Ln-N	L-L'	Ln-L and Ln-Ln	Ln-L, Ln-Ln and L-L'
<i>Dysprosium (III)</i>						
Sparkle/PM3	0.129	0.066	0.099	0.162	0.072	0.147
Sparkle/AM1	0.187	0.069	0.036	0.210	0.066	0.179
<i>Holmium (III)</i>						
Sparkle/PM3	0.163	0.065	0.057	0.184	0.064	0.164
Sparkle/AM1	0.211	0.056	0.041	0.226	0.054	0.195
<i>Erbium (III)</i>						
Sparkle/PM3	0.186	0.072	0.051	0.164	0.072	0.140
Sparkle/AM1	0.137	0.068	0.036	0.206	0.064	0.172

be important to evaluate a series of different ligands in a combinatorial manner, which Sparkle/AM1 now makes feasible.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.01.029](https://doi.org/10.1016/j.jorganchem.2008.01.029).

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