

Semiempirical Study of the Electronic and Optical Properties of the Er(8-hydroxyquinolate)₃ Complex

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We use a simple quantum chemical semiempirical procedure to study the electronic properties of organic-lanthanide complexes, taking as a model system Er(8-hydroxyquinolate)₃. Among the problems inherent to such a study is the fact that the lanthanide ion has never been parametrized in any of the standard semiempirical Hamiltonians. To overcome this difficulty, the lanthanide ion is replaced by a different but somewhat similar parametrized ion, or merely by a point charge. Good agreement with experiment, where available, is obtained, particularly in the former case. In fact, the electronic properties of the complex (apart from the emission properties) are seen to be scarcely affected by the nature of the lanthanide ion itself, but the core interactions between the metal ion and the ligand units play a relevant role, also in the calculation of the excitation energies. In particular, the ordering and separation of both singlet and triplet excited states are affected. The main conclusion is that to describe in detail the mechanism of the energy-transfer process occurring in the complex it is essential to take into account the geometry relaxation effects in the excited states.

1. Introduction

Organic-lanthanide complexes are interesting materials for their physicochemical properties and are the object of growing interest due to their importance in technological applications, for example, in the photonic and optoelectronic fields^{1–4} and in telecommunications.⁵ In fact, organolanthanides, based, for example, on the erbium ion Er³⁺,⁶ show emission around 1540 nm (0.83 eV), that is, in the most important telecommunication window, due to the optical transition $^4I_{13/2} \rightarrow ^4I_{15/2}$ of the lanthanide.

In particular, what is attractive for the possible use of these systems in the latter applications is that they possess an emission bandwith broader than that of the lanthanide ion embedded in inorganic matrixes, combined with the high absorption cross sections in the UV–vis spectrum and tunability which is characteristic of the organic chromophores.^{1,2,7–9} In fact, the generally accepted mechanism to explain the sensitized photoluminescence of the organic-lanthanide complex can be schematized in three steps. The first one is the optical excitation of the “antenna”, that is, a conjugated system that could be the ligand itself or a suitable sensitizer attached to it. Starting from the above singlet excited state of the antenna, in a second step, an energetically lower triplet state of the latter can be efficiently populated via intersystem crossing (IC). As a third step, an energy transfer between the antenna and the lanthanide ion takes place. To be more specific, two channels for the energy transfer are conceivable, involving respectively a triplet or a singlet excited state of the antenna and a near resonant state of the lanthanide ion. Recent theoretical work, supported by experi-

mental data,¹⁰ shows however that the preferred channel is the one involving the triplet state of the antenna. According to the Förster–Dexter^{11,12} theory of energy transfer, the intermediate triplet state should have an energy matching with some excited states of the lanthanide ion. Besides the rate of the energy-transfer process itself, a different effect can dramatically influence the overall quantum yield of the organolanthanides, namely, the quenching effect exerted by the overtone stretching modes of the OH (CH) bonds in the first coordination sphere,¹³ in resonance with the erbium emission at about 1500 nm.

Despite the complexity of the different photophysical processes occurring in these systems, the design of efficient sensitizers for the lanthanide emission is an important task to achieve. Systematic quantum chemical studies on the ordering of the excited electronic states, and a correlation with the structural properties of the antenna, could provide an a priori screening of efficient chromophores. To this end, different approaches have been used in recent years, based on the ligand field theory¹⁴ or on the so-called sparkle model,¹⁵ and kinetic models¹⁶ have also been proposed. In these methods, the ground state geometry of the complex is first optimized¹⁵ and then the vertical excitation energies of the lowest singlet and triplet states are usually calculated, with the lanthanide ion being simply modeled as a point charge.

In this paper, we use a similar but somewhat different semiempirical procedure to compute the electronic properties of the complex ErQ₃ [erbium(III) tris(8-hydroxyquinolate), see Figure 1] chosen as a model. In the calculation of the electronic spectra, we make a comparison between two kinds of approaches, in which the lanthanide ion (which is not parametrized in current semiempirical methods) is modeled either by a parametrized one or by a point charge, respectively. Moreover, we believed that the consideration of *vertical* excitations alone would not be able to give a sufficient basis to

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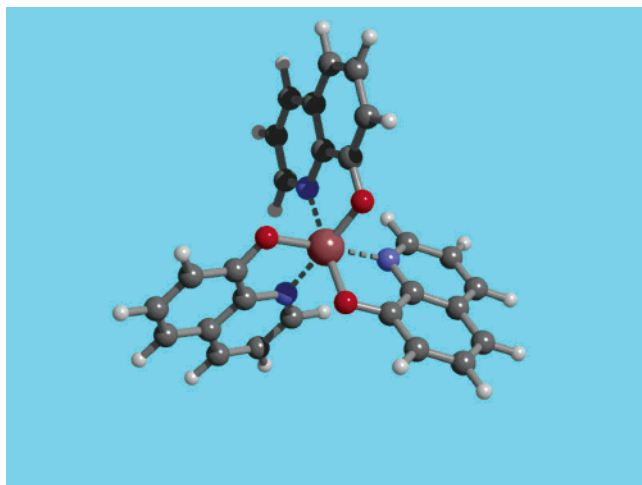


Figure 1. Molecular structure of the erbium(III) tris(8-hydroxyquinolate) complex (named ErQ_3 in the text).

understand what happens in this case. In fact, photoabsorption by the organic chromophores will be followed by geometrical relaxation in the excited states — more marked in the triplet ones — which is potentially important in explaining the body of existing spectroscopic data on these complexes. We have accordingly allowed the geometries of the lowest singlet and triplet excited states to relax to their respective minima, and as expected, this effect has been seen to play a crucial role in the proposed mechanism of the energy-transfer process.

2. Quantum Chemical Approaches

Optimizing the geometry of ErQ_3 , or in general of a lanthanide complex, is not an easy task whatever *ab initio* or semiempirical methods are used. In the first case, due to the presence of the lanthanide ion carrying a huge number of inner electrons, it is necessary to use a large basis set in association with an effective core potential. Moreover, the presence of 4f open shell electrons requires an approach of the unrestricted type. Since such a procedure frequently produces spin contamination effects,¹⁷ this kind of calculation can hardly be performed in a reasonable time. For this reason, and considering that a main goal of this work is to analyze the relaxation effects in the first excited states of the antennae, with particular attention to triplets and their interactions, we have carried out the geometry optimizations by using the semiempirical PM3 Hamiltonian¹⁸ implemented in the MOPAC code.¹⁹ However, the current semiempirical Hamiltonians are not parametrized to treat f electrons or to use polarization and diffuse functions²⁰ which are needed for a correct description of the ligand/metal interaction. For this reason, Er^{3+} has been replaced by an “effective” atomic center, which implies among other things that the electronic states of the complex having a charge-transfer character (namely, states involving electron donation from the ligands to the metal or vice versa, where 5p and/or 5d orbitals play an important role²⁰) could not be properly taken into account.

A method to choose a suitable effective atom is the so-called sparkle model for the calculation of lanthanide complexes (SMLC),¹⁵ where the sparkle atom at the AM1 level is reparametrized in order to obtain good agreement between the computed geometry and the experimental structural data. In the present work, we have adopted a different approach, on the basis of the following considerations: (i) at a semiempirical level, the geometry of the complex is mainly determined by Coulombic interactions (with an important contribution given by core

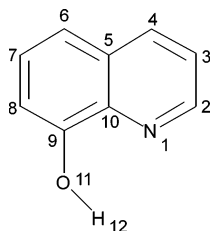
interactions) between the ligands and the coordinating atom; (ii) the absorption properties of the lanthanide complexes are strictly related to those of the ligands, and are practically unaffected by different coordinating metal ions;²¹ (iii) the X-ray photoemission spectra of the complexes are only slightly affected by the nature of the coordinating metal ion;²² (iv) here, we are essentially interested in the absorption properties of the complex, while the photoluminescence and/or electroluminescence ones are obviously strictly connected to the nature of the metal ion. On these grounds, Er^{3+} has been replaced by “equivalent” (i.e., of the same charge) ions, namely, Al^{3+} and Ga^{3+} , for which a parametrization within the PM3 Hamiltonian is available. In this way, (i) reparametrization of a sparkle atom (i.e., a point charge with a “defined ion radius”, which is 0.7 Å in the standard MOPAC code) is avoided; (ii) the spin multiplicity of the system is that of the organic moiety, which bypasses the challenging theoretical problem of a correct treatment of the open 4f5d6s valence shell of the lanthanide atom; (iii) the use of real atoms such as Al and Ga takes into account, at least partially, the core interactions between the coordinating atom and its first neighbors. The latter are expected to significantly affect the charge distribution and distances around the metal ion, as also shown by the applications of the so-called modified SMLC model.²³

The approach described has been used to optimize at the PM3 level the geometry of the ground, first excited singlet, and first excited triplet state of the XQ_3 systems, where the X ions (Al^{3+} and Ga^{3+}) replace the Er^{3+} ion. Relaxation in the excited states (notably in the triplet) has been considered explicitly in order to estimate the extent of the geometry distortions in the latter. Excited state optimizations have been performed by using the standard configuration-interaction procedure implemented in the MOPAC¹⁹ and AMPAC²⁴ packages. On the basis of the above optimized geometries, the excitation energies and the corresponding oscillator strengths have been calculated in the framework of a CIS-INDO/S approach,²⁵ using the ZINDO code²⁶ and an active space of 40 occupied and 40 virtual molecular orbitals (MOs), which includes all of the π type orbitals and the nonbonding orbitals of the system. The two different Hamiltonians are made necessary by the fact that the PM3 one is well suited for geometry optimizations, while the INDO/S Hamiltonian is known to reproduce well the transition energies of organic systems. The energies of the excited states and their ordering in the XQ_3 complexes have been compared with results from the simple model referred to above¹⁵ and with experimental UV–visible absorption spectra of erbium and aluminum complexes.

3. Results

3.1. Geometries. To begin with, in Table 1, we compare with the X-ray data of 8-hydroxyquinoline in the crystal²⁷ (where the repeat unit is a hydrogen-bonded dimer) the corresponding PM3 and *ab initio* HF/6-31G(d,p) results in the dimer itself. In the following, we shall refer to the above PM3 geometry as the “isolated” geometry. Both the semiempirical Hamiltonian and the *ab initio* calculations give results in excellent agreement with the experimental data, with the root-mean-square deviations (ϵ_{rms}) between theoretical and experimental data being 0.024 and 0.019 Å, respectively. It is remarkable that the PM3 Hamiltonian gives a satisfactory result even for the N–O intermolecular distance (2.747 Å versus an experimental value of 2.815 Å and an *ab initio* result of 2.787 Å).

We have optimized at the PM3 level the geometries of the ground state (S_0) and of the first singlet (S_1) and triplet (T_1)

TABLE 1: Comparison between the Crystal X-ray Data and the Dimer Theoretical Ground State Geometries for 8-Hydroxyquinoline (Bond Lengths in Å)

bond	X-ray ^a	6-31G(d,p)	PM3
N ₁ –C ₂	1.331	1.320	1.332
C ₂ –C ₃	1.389	1.416	1.420
C ₃ –C ₄	1.357	1.377	1.375
C ₄ –C ₅	1.402	1.419	1.422
C ₅ –C ₆	1.410	1.419	1.415
C ₆ –C ₇	1.365	1.379	1.382
C ₇ –C ₈	1.427	1.414	1.404
C ₈ –C ₉	1.371	1.381	1.396
C ₉ –C ₁₀	1.393	1.431	1.432
N ₁ –C ₁₀	1.374	1.360	1.388
C ₅ –C ₁₀	1.428	1.426	1.420
C ₉ –O ₁₁	1.367	1.350	1.361
O ₁₁ –H ₁₂ ^b	1.0	0.978	0.950
ε _{rms} ^c		0.019	0.024

^a Data from ref 27. ^b Assigned crystal value, see ref 27. ^c The root-mean-square deviation between experimental data and theoretical results.

states of the XQ₃ systems, where X = Al³⁺ and Ga³⁺. All of the calculations have been performed both in a C₁ and in a C₃ symmetry, and for S₀, the structures obtained in this way, as well as the associated energies, are identical within the limits of the procedure adopted. This means that for S₀ the C₃ structure is a result of the calculation, and all of the ligands are symmetry equivalent. The most relevant bond lengths for this state are reported in the first two columns of Table 2 (for the atom numbering, refer to Figure 2). No symmetry at all, however, is found in the excited states, with any attempt to attain a C₃ structure for S₁ and T₁ leading at most to a first-order saddle point. In fact, only asymmetric equilibrium structures are obtained for both states, in which two ligands (named I and II in Figure 2) have essentially the same geometry (unchanged with respect to that in S₀), while the third one (named unit III) shows strongly modified bond lengths. In consequence, for S₁ and T₁, only the geometries of units I and III are reported in the last four columns of Table 2. A pictorial representation of a few relevant bond length variations is given (for ligand III) in Figure 3. The upper panel of the latter refers to S₀ and displays the difference between the ligand geometries in AlQ₃ (or in GaQ₃) and the isolated geometry (see Table 1) and that between the ligand geometries in AlQ₃ and GaQ₃ themselves. The lower panel refers to the corresponding variations between the geometries in the S₁ or T₁ states and that in S₀, for AlQ₃ and GaQ₃.

In Table 2, the ligand bond lengths of unit I in states S₀, S₁, and T₁ exhibit a mean deviation as low as 0.01 Å, an exception being given by the C–O bond length of GaQ₃ in S₁. That C–O is a sensible bond is confirmed by the results in the upper panel of Figure 3, where only for this bond a strong length difference is predicted in S₀ with respect to the isolated geometry, an effect whose amount is markedly different in the two complexes. This behavior can be explained by realizing that in the complexes 8-hydroxyquinoline carries a strong negative Mulliken charge, that is mainly localized on the oxygen atom but can be partly

shared with the π system of the ring, thereby giving the C–O bond a variable double-bond character depending on the environment. As a reference, a PM3 geometry optimization of deprotonated 8-hydroxyquinoline gives a charge of –0.486 au on the oxygen atom, with a very short C–O bond length of 1.241 Å. Instead, in the XQ₃ complexes, we can have different charges on the single ligand units, and in consequence different C–O bond lengths, depending on the ionic/covalent ratio of the X–O bond, which in turn is related to the X electronegativity. Such a correlation becomes apparent in Figure 4, which displays the S₀ atomic charges on X, N, and O atoms, and their variations upon going to S₁ and T₁ (unit III). The shortening of the C–O bond between the first and second columns of Table 2 (–0.022 Å) has a clear counterpart in Figure 4 in the increase in S₀ of the positive charge on Ga with respect to Al, and in the (markedly less) increase of the negative charge on the oxygen atom bonded to Ga with respect to that bonded to Al.

From the lower panel of Figure 3, optimization of the geometry of the S₁ and T₁ excited states is seen to give structures substantially different from that of the ground state, a fact that is seldom accounted for in the calculation of the electronic excitations in lanthanide complexes, which are usually based on the ground state geometry only. A point of much interest is the substantial reduction of the distance between unit III (the energy donor) and the erbium ion (the acceptor), because both Förster and Dexter theories predict an inverse dependence of the energy-transfer rate on the donor–acceptor distance.

The same Figure 3 shows that the differences between AlQ₃ and GaQ₃ are small throughout, with the exception in S₁ (lower panel) of the O–X bond and the bonds surrounding the N atom. The absolute variations are greater in the triplet state than in the singlet state (mean values being 0.032 and 0.026 Å, respectively), with a net effect of sensibly increasing the mean quinoid character of the ligand rings in T₁ with respect to S₁.

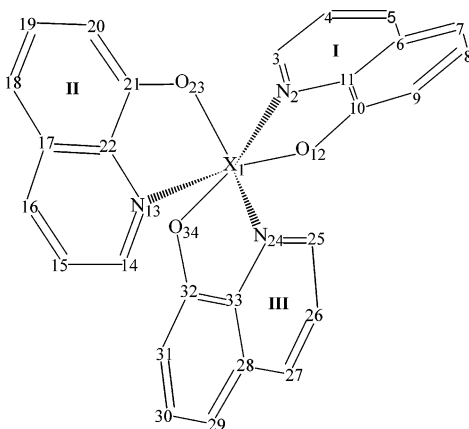
Figure 5 is the counterpart of Figure 3 for what concerns X–N and X–O bonds, in that it displays their bond length variations (ΔR) (ligand III) between AlQ₃ and GaQ₃ in S₀, and between S₁ (or T₁) and S₀ for AlQ₃ and GaQ₃, respectively. The variations in the coordination bond X–N are much greater than those in the “true” bond X–O, and as big as ±0.5 Å, a value that is curiously more or less constant in all cases but the last one (the T₁ state of GaQ₃), in which it is essentially zero. The sign of the X–N and X–O bond length distortions in S₁ and T₁ can be predicted on the grounds of simple electrostatic arguments. In fact, if we consider for each actual bond the product of the atomic charges of the atoms involved (Figure 4), the sign of the difference between the value of this product in the actual excited state and its value in S₀ is the same as the sign of the corresponding ΔR value in all cases but one (the Al–N bond in S₁).

The above results support our previous hypotheses about the effects of the coordinating ion on the geometry optimizations of the complex. First of all, we have shown that in AlQ₃ and GaQ₃ the effect of the coordinating atom on the geometries of the ligands aggregate (the complex minus the central ion) is small and practically concentrated on its nearest neighbors. A further key point is that electrostatic effects play a central role, the bond length variations in the X–N and X–O bonds, as well as the atomic charges on the Al, Ga, N, and O atoms, being only related to the electronegativity of the metal ion. For instance, an atomic charge of +1.14 and +2.12 is obtained for Al and Ga, respectively, versus a formal value of +3. In the literature,²⁸ an effective charge of about +2.4 is estimated for the Er³⁺ ion, which could suggest that our model ions are not

TABLE 2: Computed Geometries for the Ground State (S_0) and the First Excited Singlet (S_1) and Triplet (T_1) States of the XQ_3 Complex (Bond Lengths (R) in Å)

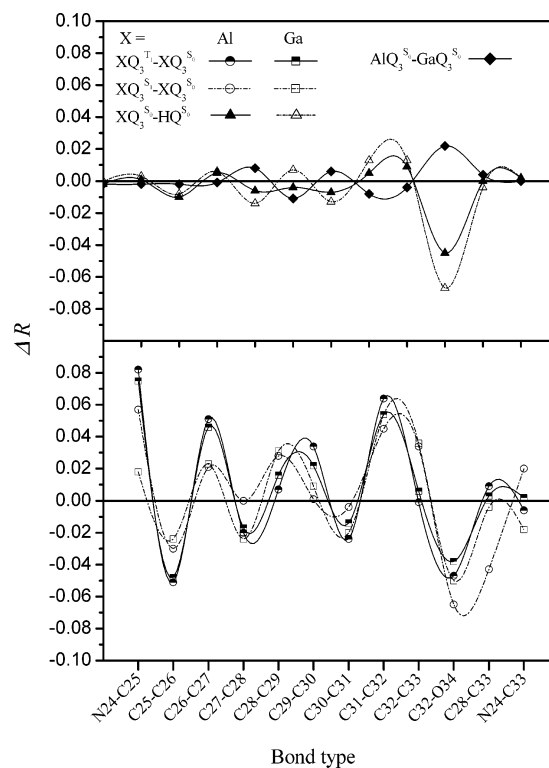
R	S_0 (C_3)		S_1 (C_1)		T_1 (C_1)	
	X = Al	X = Ga	X = Al	X = Ga	X = Al	X = Ga
	Unit I ^{a,b}					
X ₁ -N ₂	2.390	1.909	2.479	1.861	2.443	1.901
X ₁ -O ₁₂	1.787	1.842	1.773	1.824	1.787	1.844
N ₂ -C ₃	1.330	1.332	1.331	1.341	1.341	1.340
C ₃ -C ₄	1.421	1.423	1.418	1.408	1.416	1.419
C ₄ -C ₅	1.365	1.367	1.369	1.387	1.376	1.377
C ₅ -C ₆	1.427	1.428	1.420	1.412	1.422	1.424
C ₆ -C ₇	1.409	1.401	1.400	1.401	1.410	1.405
C ₇ -C ₈	1.378	1.389	1.396	1.395	1.386	1.393
C ₈ -C ₉	1.397	1.391	1.383	1.389	1.396	1.391
C ₉ -C ₁₀	1.401	1.409	1.412	1.406	1.412	1.415
C ₁₀ -C ₁₁	1.441	1.445	1.434	1.422	1.436	1.440
C ₁₀ -O ₁₂	1.316	1.294	1.316	1.327	1.310	1.295
C ₆ -C ₁₁	1.420	1.416	1.431	1.428	1.426	1.420
N ₂ -C ₁₁	1.390	1.390	1.374	1.392	1.383	1.386
	Unit III ^a					
X ₁ -N ₂₄			1.876	2.436	1.929	1.904
X ₁ -O ₃₄			1.927	1.849	1.887	1.848
N ₂₄ -C ₂₅			1.387	1.350	1.412	1.407
C ₂₅ -C ₂₆			1.391	1.399	1.370	1.375
C ₂₆ -C ₂₇			1.386	1.390	1.416	1.413
C ₂₇ -C ₂₈			1.427	1.404	1.407	1.411
C ₂₈ -C ₂₉			1.437	1.432	1.416	1.417
C ₂₉ -C ₃₀			1.379	1.398	1.412	1.411
C ₃₀ -C ₃₁			1.393	1.371	1.373	1.377
C ₃₁ -C ₃₂			1.446	1.463	1.465	1.463
C ₃₂ -C ₃₃			1.475	1.481	1.440	1.451
C ₃₂ -O ₃₄			1.251	1.244	1.269	1.256
C ₂₈ -C ₃₃			1.377	1.412	1.429	1.419
N ₂₄ -C ₃₃			1.410	1.372	1.384	1.392

^a See Figure 2. ^b In S_1 and T_1 , units I and II have the same geometry within a few units $\times 10^{-3}$ Å.

**Figure 2.** Atom numbering in the XQ_3 complex.

electropositive enough to effectively model the Er^{3+} ion. However, a more significant parameter to describe the strength of the Coulombic interactions is known to be given by the charge/ionic radius ratio of the ion. With ionic radii for Al^{3+} , Er^{3+} , and Ga^{3+} of 0.675, 1.03, and 0.76 Å,²⁹ respectively, we obtain for the above ratio corresponding values of 1.70, 2.33, and 2.78. That is, for what concerns the description of the Coulombic interactions, the erbium case lies (at least to first order) in the middle of a tight range which is bounded by two very similar extrema given by aluminum and gallium. This seems to be a clear demonstration that substituting the lanthanide ion with an already parametrized one, without looking for a new specific rare earth parametrization, can be a satisfactory procedure, at least to give geometry predictions.

As a final remark, we note that the computed PM3 ground state geometry of the 8-hydroxyquinolate unit is in good

**Figure 3.** Bond length variations (ΔR , angstroms) for ligand unit III of XQ_3 in S_0 with respect to the isolated geometry of the ligand in the dimer (upper panel) and in S_1 and T_1 with respect to S_0 (lower panel). In S_1 and T_1 , unit III is by far the most distorted one.

agreement with the experimental structural data of the same unit in a few different complexes such as GaQ_3 ,³⁰ AlQ_3 ,³¹

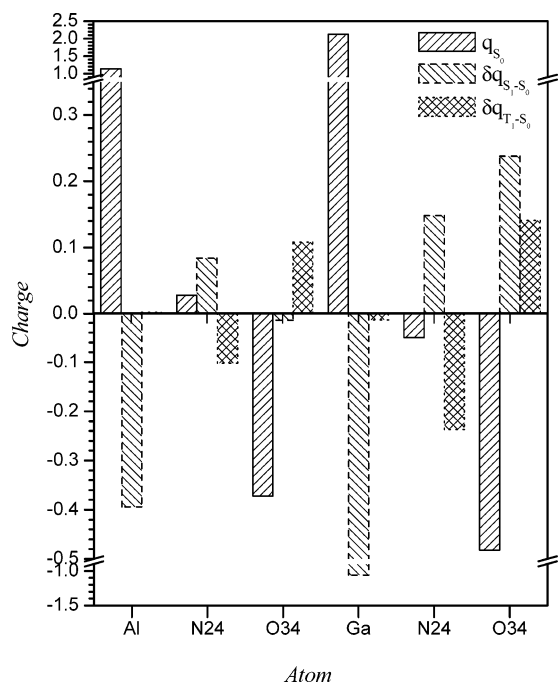


Figure 4. Atomic charges (atomic units) in S_0 and their variations in the S_1 and T_1 states for unit III. In the left (right) part of the figure, the central ion and the coordinated atoms of the AlQ_3 (GaQ_3) complex are depicted.

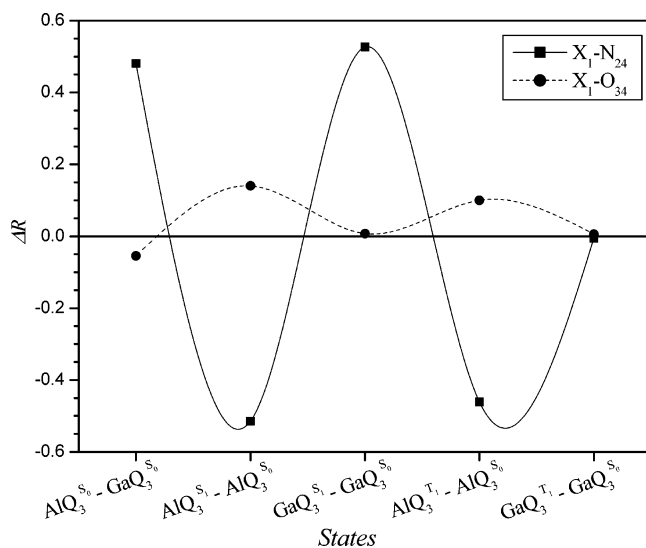


Figure 5. Variation (ΔR , angstroms) of the distances from the coordinating ion X (Al^{3+} or Ga^{3+}) to its nearest neighbors (ligand III). The differences are taken between AlQ_3 and GaQ_3 in S_0 and between different Q_3 states and S_0 .

CuQ_2 ,³² and ZnQ_2 ,³³ and that a similar approach to the geometry optimization of organic-lanthanide complexes has given good results in the study of europium complexes.³⁴

3.2. Excited States and Transition Energies. The main goal of this work is to try to understand which effect the geometry relaxation in the excited states has on transitions energies, on the ordering of the states, and consequently on the luminescence properties of the complex. In the previous section, we showed that the geometries of the ground and excited states of the complex are only slightly affected by the nature of the coordinating metal ion. For this reason, and due to the availability of experimental absorption spectra to which theoretical results can be compared, we take electronic excitations in AlQ_3 as a model for those in ErQ_3 .

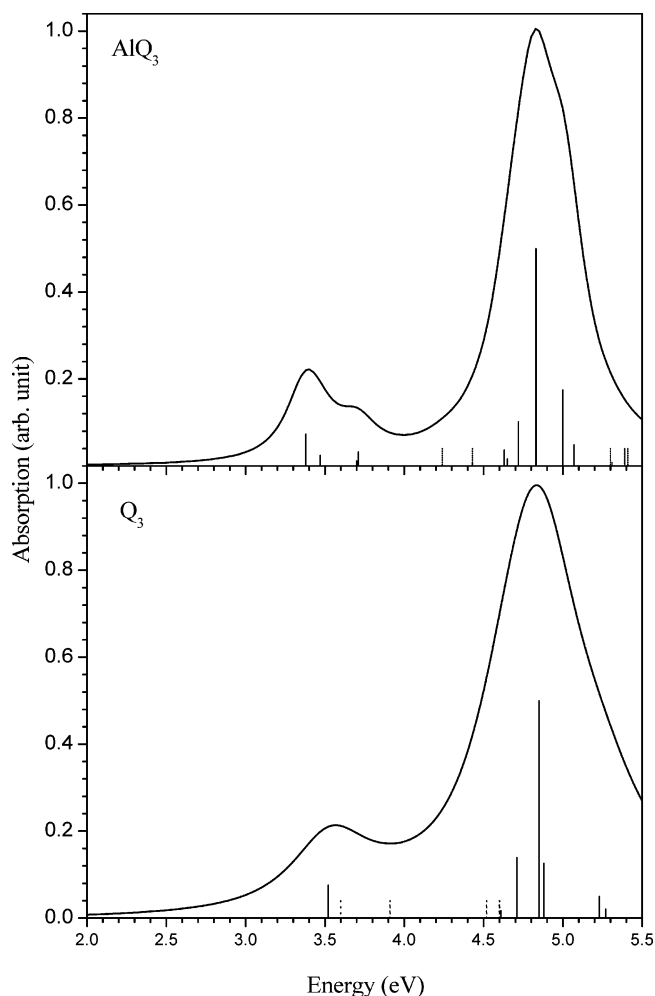


Figure 6. Absorption spectra of the complex computed at the AlQ_3 optimized ground state geometry. In the CIS-INDO/S computation of the spectra, the coordinating center has been assumed to be an Al^{3+} ion (upper panel) or a 3+ point charge (lower panel). Sticks are proportional to the oscillator strength of the transition, and dotted sticks refer to dark transition

Starting from the above optimized geometries of the S_0 , S_1 , and T_1 states, two types of calculations have been performed, the first on the complex as such, while in the second one (which from now on will be named Q_3 and is the only one which has been considered in the literature¹⁵) the Al^{3+} ion is replaced by an equivalent point charge. In this way, we will be able to get an estimate of the effects on the electronic excitations of the core interactions between the coordinating atom and its neighbors. We stress that here and throughout the paper *in both cases* the energy calculations are performed on the basis of the geometries obtained for AlQ_3 .

In Figure 6, the computed UV-visible absorption spectra for S_0 in the two cases are displayed. Despite the general resemblance of the spectra shapes, the stick spectra (where both allowed and forbidden transitions appear) show the ordering of the singlet excited states and their oscillator strengths to be rather different. Two absorption peaks are found, as convolutions of different excitations, at 3.38 (3.52) and 4.83 (4.85) eV for AlQ_3 (Q_3), where the excitations at lower energy are doubly degenerate and those at higher energy have the highest oscillator strength. The allowed excitation energies in the AlQ_3 and Q_3 systems are very close, especially for the high-energy peak, and the nature of the excitations is similar, as can be seen in Table 3, which collects the main single-excitation contributions to the CIS excited wave functions and the corresponding MO energies.

TABLE 3: Main Single-Excitation Contributions to the CIS Excited Wave Functions and Corresponding MO Energies (eV) for Selected Electronic Transitions of the Q₃ and AlQ₃ Systems

singly excited configuration	CI coefficient	
	Q ₃	AlQ ₃
electronic transitions at (eV):	3.52	3.38
HOMO-2 → LUMO	-0.545	0.482
HOMO-1 → LUMO	-0.348	-0.410
HOMO → LUMO+1	-0.348	-0.410
HOMO → LUMO+2	0.557	-0.535
electronic transitions at (eV):	3.52	3.38
HOMO-2 → LUMO+1	-0.545	0.482
HOMO-1 → LUMO+1	0.348	0.410
HOMO-1 → LUMO+2	0.557	-0.535
HOMO → LUMO	-0.348	-0.410
electronic transitions at (eV):	4.85	4.83
HOMO-6 → LUMO+2	0.332	-0.417
HOMO-5 → LUMO		-0.386
HOMO-3 → LUMO+1		0.386
MO Energy		
HOMO-6	-9.789	-8.607
HOMO-5, HOMO-3	-9.758	-8.596
HOMO-2	-8.852	-7.189
HOMO-1, HOMO	-8.803	-7.061
LUMO, LUMO+1	-1.714	-0.229
LUMO+2	-1.706	-0.215

In this respect, the most significant variation induced by the explicit considerations of the core interactions is in the absolute energies of the molecular orbitals. In particular, in the point-charge case the presence of new potential terms in the Hamiltonian, globally acting as an attractive Coulombic term, lowers the MO energies of the system with respect to those of AlQ₃. Also, the nature of the MOs could be seen to be different in the two cases, especially for the virtual ones. In fact, in the LUMO, LUMO+1, and LUMO+2 orbitals of AlQ₃, the weights of the N-atom orbitals result to be increased with respect to those in Q₃.

The theoretical absorption spectra are in excellent agreement with the experimental data obtained for a methanol solution of AlQ₃ (peaks at 3.32 and 4.83 eV,³⁵ where the latter is the more intense one). It is remarkable that the additional weak band, which is predicted at 3.7 eV only in the case of AlQ₃, finds an experimental counterpart in the weak absorption peak experimentally found around 3.8 eV.³⁶ It has to be stressed that the presence of more electronic transitions in the lowest absorption band is an important point in view of the correct interpretations of the radiative lifetimes and luminescence properties³⁶ of the complex. Even more gratifying is the good agreement obtained by comparing the present results with the partial absorption spectra (recorded up to 4 eV) of a 1,1,1-trichloromethane solution of ErQ₃,⁶ which show a lowest absorption peak at 3.30 eV. Where comparison is possible, the latter experimental spectrum is very close to that of AlQ₃, with the main difference being a sharp absorption line with a very low intensity, which is observed in ErQ₃ at 2.38 eV and assigned to an Er³⁺ transition involving a ²H_{11/2} or ⁴S_{3/2} excited state.

All of these results nicely confirm our initial hypothesis that the influence of the lanthanide ion on the absorption and electronic properties (and consequently on the ground state geometries) of the complex is a small effect. A further important point is that taking into account, at least partially, the core interactions between the metal ion and its neighbor atoms appreciably improves the quality of the theoretical results.

To get information about the possibility of energy transfer between the 8-hydroxyquinolate units and the erbium ion, a

schematic representation of the CIS-INDO/S energies for excited singlet and triplet states is shown in Figure 7. As before, calculations use an active space of 40 occupied and 40 virtual MOs. We have considered an energy range of 4.0 eV, taking as the baseline the ground state energies of the Q₃ and AlQ₃ complexes at the S₀ geometry and reporting results based on the optimized geometries of the ground state (S₀) and of the first triplet state (T₁) of AlQ₃. In the figure, we indicate these results in a self-explanatory way as Q₃^{S₀}, AlQ₃^{S₀}, and AlQ₃^{T₁}. No results for Q₃ based on the T₁ geometry are shown, because the CIS-INDO/S calculations give unphysical results in this case. For comparison, the state energies of 8-hydroxyquinoline based on the ground state (Q₁^{S₀}) and on the first triplet state geometries (Q₁^{T₁}) are also reported (in this case, a 15/15 active space was used). The double degeneracies in the third and fourth columns arise from the fact that here we have used the S₀ geometry of AlQ₃ which, having been obtained without imposing any symmetry constraint, results to be not exactly symmetric. Comparing the results for the cases of Q₁^{S₀}, Q₃^{S₀}, and AlQ₃^{S₀}, we note that intermolecular interaction causes throughout a small decrease in the excitation energies. This amounts approximately to 0.4 eV for the excited singlets and to 0.15 eV for triplets, with the highest decreases being found for AlQ₃^{S₀}. These results, and the degeneracy computed in the complex, suggest that the effect of the molecular interactions consists mainly of the stabilization of the excited state by the surrounding 8-hydroxyquinoline units in their ground states, rather than of an excitonic coupling between the transition electronic densities of the units or of exchange/charge-transfer effects. The comparison between the Q₃^{S₀} and AlQ₃^{S₀} results confirms what we have previously observed in the discussion of their electronic spectra; that is, also for the triplet states, taking into account the core interactions involving the metal ion (in our model, Al³⁺) changes the ordering and spacing of the excited states, which in turn can affect the energy-transfer process between the antennae and the emitting ion. In this respect, it is interesting to compare the results obtained from the calculations based on the optimized geometry of the first triplet state (Q₁^{T₁} and AlQ₃^{T₁}). The presence in the complex of one distorted unit (the one carrying the triplet) destroys the degeneracy of the excited levels, and moreover, the variations in the ordering of the excited states are more marked than those in the Q₃^{S₀} and AlQ₃^{S₀} systems. This fact deserves some mention, as it depends on the strong negative charge all 8-hydroxyquinoline units carry in the complex, different from the isolated neutral unit. In fact, it gives rise to a driving force that tends to displace the like spins from the regions where the negative charge concentrates, thus appreciably modifying the structure and energy of the triplet state³⁷ with respect to that found in the isolated ligand. This in turn makes it clear that any reasoning which considers only the triplet states of the isolated ligand can be subject to question.

The excitation energies of S₁ and T₁ at the optimum geometries of S₀ (T₁) are the vertical (relaxed) excitation energies of these states, and their values are seen from Figure 7 to be 3.38 (2.30) eV for S₁ and 1.64 (1.79) eV for T₁. The numerical values cannot be taken too literally, however, as signaled by the fact that the relation between the two T₁ values is of course slightly wrong, due to the difference in the Hamiltonians used in the geometry optimizations and in the calculation of the excitation energies. In fact, the vertical and 0-0 excitation energies of T₁ as obtained at the PM3 level result to be 2.76 and 2.22 eV (i.e., in the correct order), respectively, and on the other hand the excitation energy for T₁ compares favorably with the experimental value 2.11 eV found for AlQ₃.³⁸

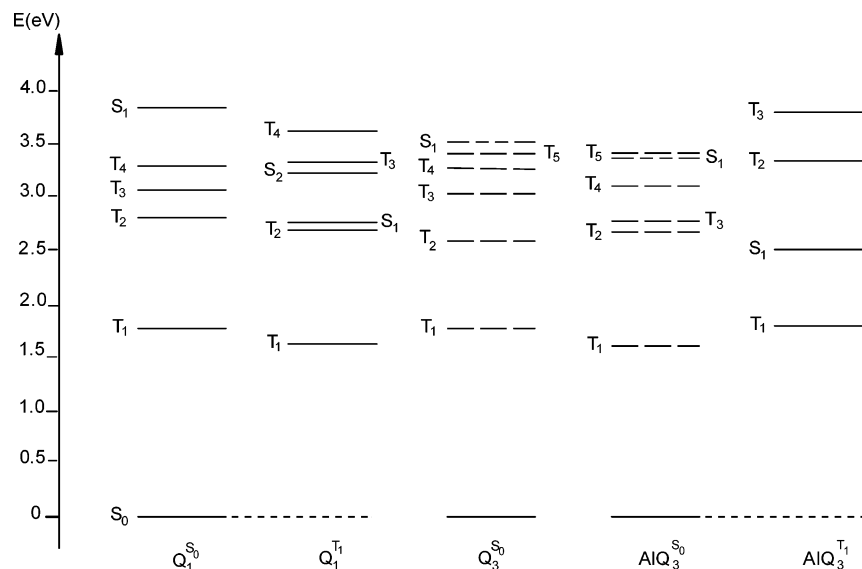


Figure 7. Scheme of the CIS-INDO/S energies of the states for 8-hydroxyquinoline (Q_1), the complex where the coordinating ion has been replaced by an equivalent point charge (Q_3), and the AIQ_3 complex. The baseline is the ground state energy of 8-hydroxyquinoline (first and second columns), Q_3 (third column), and AIQ_3 (fourth and fifth columns). The transition energies in the first (second) column are computed on the basis of the optimized geometry of the S_0 (T_1) state of Q_1 , and those in the third or fourth (fifth) column are computed on the basis of the optimized geometry of the S_0 (T_1) state of AIQ_3 . Dashed (dashed–short dashed) lines indicate triply (doubly) degenerate levels.

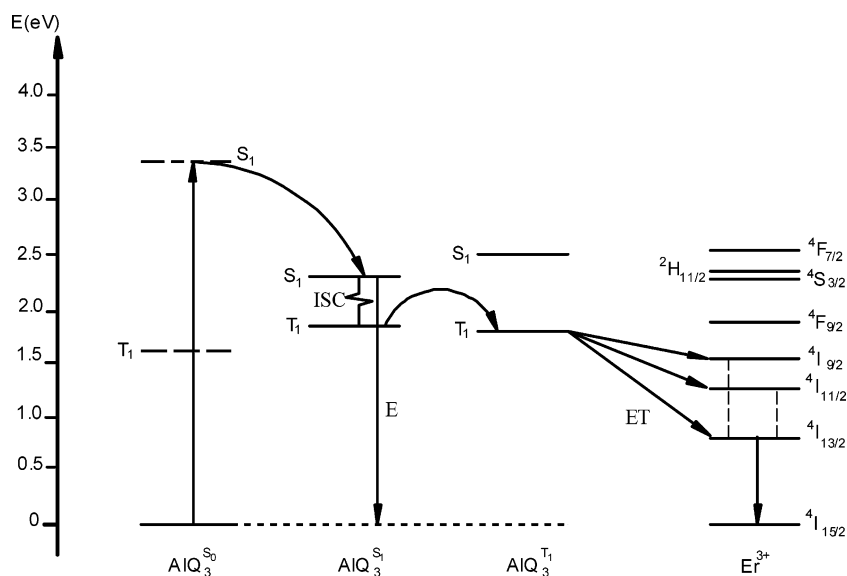


Figure 8. Scheme of the CIS-INDO/S energies of the states for the AIQ_3 complex at the optimized geometry of the ground ($AIQ_3^{S_0}$), the first excited singlet ($AIQ_3^{S_1}$), and the first excited triplet ($AIQ_3^{T_1}$) states. For each case, only the first excited singlet and triplet states are shown, and the atomic levels of the Er^{3+} ion (see ref 37) are also reported. Dashed lines indicate triply degenerate levels, and dashed–short dashed lines, doubly degenerate levels.

Anyway, although Figure 7 does not show the results at the optimum S_1 geometry (see below), it seems unquestionable that, contrary to what frequently happens, in this case, the singlet relaxation energy must be expected to be fairly larger than the triplet one. This implies that relaxation sensibly lowers the S_1 – T_1 energy difference, which in turn means that the probability of a transfer of the excitation between these states through intersystem crossing would be grossly underestimated if it were computed only on the basis of vertical excitations computed at $AIQ_3^{S_0}$. The difference in behavior (in an unusual sense) between S_1 and T_1 can be traced back to the fact that in the former state the excitation can be partially smeared out over all of the many ligands present in the complex, while the like spins in the triplet tend of course to localize themselves on just one of the three units. As we have found in the preceding section,

this implies a particularly increased amount of quinonization of this specific unit, which is well-known to be highly energy costly.

Figure 8 depicts the energy-transfer process in Er(8-hydroxyquinolate)₃ according to our results obtained on the AIQ_3 model system. The positions are reported of the first excited singlet and triplet of AIQ_3 calculated at the optimal geometries of S_0 , S_1 , and T_1 , and the atomic levels of the Er^{3+} ion³⁹ are also shown. The process begins with the excitation to the first vertical singlet that, since the initial geometry has practically a C_3 symmetry, is triply degenerate. This step is followed by the relaxation to the optimal geometry for this state, in which one of the ligand units undergoes sensible variations in the bond lengths, which give rise to some quinoid structure of the rings. The relaxation removes the degeneracy of the S_1 levels and

markedly lowers the energy, and subsequently, the system can radiatively decay to the ground state (emission process), with a computed Stokes shift of 1.08 eV, which compares well with the experimental value 0.93 eV obtained for the ErQ₃ complex.⁴⁰ At this point, three factors can favor an efficient transfer of the excitation to the triplet state; namely, (i) the S₁–T₁ energy difference is only one-half of an electronvolt, (ii) the energies of T₁ at the S₁ and T₁ optimal geometries are practically the same, and (iii) the optimum geometries of the S₁ and T₁ states are strictly correlated, as discussed in the preceding section. A further consequence of the singlet relaxation is that at the S₁ optimal geometry the only intersystem crossing of interest involves T₁, with the higher triplets (e.g., T₂, T₃, and T₄) lying above S₁. In this respect, note that considering only results relative to the S₀ geometry (see Figure 7) could instead suggest the latter states as alternative candidates to the transfer of the excitation.

Finally, the excited triplet state (which is localized on a unit that now gets much closer to the emitting center) can interact with the manifold of the lanthanide ion atomic levels, and the energy transfer can take place.

4. Conclusions

Despite the complexity of the energy-transfer process, we believe that theoretical hints can be given for designing suitable ligands and antennae in order to obtain lanthanide complexes with good emission properties. In this paper, a simple and low-cost theoretical procedure useful for obtaining such hints has been applied to the ErQ₃ complex. We have shown the importance of studying the nature and ordering of the excited states not only at the geometry of the ground state but also at the geometry of at least the first excited singlet and triplet states. The effect of the lanthanide ion on the geometric and electronic structure of the ligands (but not of course on the emission properties of the complex) is negligible to first order, but the core interactions between the metal ion and the neighbor atoms of the ligand units are not. For the excited states (in particular in the triplet case), the bond length distortions are localized on a single ligand, and the unit carrying the triplet gets closer to the emitting metal ion. According to Förster theory,¹¹ which predicts the transfer rate to be proportional to the inverse sixth power of the metal–ligand distance, this implies a net increase of the rate with respect to the value that would be obtained by using the ground state geometry for the triplet.

The excitation energies obtained compare well with experimental data where available, and we believe that although the relative position of the ligand excited levels with respect to those of the emitting ion is only a necessary condition (not a sufficient one) to obtain an efficient emitting complex, our procedure could provide valuable help in finding the most favorable channel for the energy-transfer process and give suggestions in the ligand design to improve this pathway.

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