Vibrational overtones quenching of near infrared emission in Er^{3+} complexes

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Received (in Montpellier, France) 20th January 2009, Accepted 20th February 2009
First published as an Advance Article on the web 9th April 2009
DOI: 10.1039/b901272a

Erbium organic complexes are receiving increasing attention in view of their application in polymeric telecommunication devices, but their use is limited by small emission quantum yield. Non-radiative deactivation of near IR (NIR) transition in Er^{3+} organic complexes is discussed on the basis of the electronic–vibrational energy transfer. Relevant transition matrix elements necessary to predict quenching effects exerted by various bonds located in the Er^{3+} coordination sphere are evaluated on the basis of an anharmonic Morse oscillator model and expressed as analytical functions of the fundamental vibrational intensities. The latter are calculated on the basis of various '*ab initio*' quantum chemical methods, which yield intensity values close to the experimental measurements. Quenching effects in complexes containing a number of common ligands are evaluated and discussed, and a strategy to design highly efficient NIR emitters is proposed.

Introduction

The increasing demand for broadband telecommunications is stimulating the search for novel gain material in the 1.53 μm window for integrated optics and waveguide devices based on Er^{3+} emission. Polymeric matrices possess a number of advantages (over their silica counterparts) because of their low-cost, flexibility, high packaging density and simple processing steps. Instead of ion salts, erbium complexes provide the Er^{3+} emitting ions with the necessary solubility to achieve high concentration in polymeric matrices. Moreover the large absorption cross-section of the ligand makes the indirect excitation of the lanthanide ion possible (emission sensitization), thus circumventing the problems related to the weak and narrow transitions used in the direct optical excitation of the erbium ions. The limiting factor in this kind of system is the very low quantum yield of the lanthanide ion; the conclusions of several early studies on the luminescence quenching of lanthanide ions in organic solutions and also in inorganic glasses suggest that the reason for this low efficiency is the presence of nearby high-energy vibrational centers, in particular O–H and C–H bonds.[1–6] The physical mechanism responsible for the effect is generally identified with a dipole–dipole energy transfer from the electronically excited ion to isoenergetic vibrational states (overtones) of the vibrational center.[7–9] The O–H and C–H bonds most liable for this effect are generally present as functional groups of the organic ligand and/or as residual water (or solvent) molecules from the chemical synthesis of the complexes. The effectiveness of this adverse non-radiative deactivation is indicated by the photoluminescence lifetime of the erbium ion, which from the value of ∼1–10 ms registered in inorganic solids, drops to ∼1 μs or less in most organic complexes. Understandably, most of the recent experimental efforts in this field have been devoted to the synthesis of O–H free and C–H free complexes (by halogenation) and to avoiding contamination with water during the synthesis.[10] By using this strategy, very recently it has been possible to achieve lifetimes of up to ∼300 μs and quantum yields for the ion of 2%. Because the synthesis of fully-fluorinated complexes is chemically very difficult, several studies used deuteration but results were not very encouraging;[11] even if lengthening of the erbium luminescence lifetime was indeed generally observed, it increases at best by a factor 2–3 and not by of the factor of 500–1000 one would ideally want.

In this paper we report a theoretical study of the effectiveness of the quenching effect exerted on the Er^{3+} by various chemical bonds, most frequently encountered in organometallic complexes in order to provide the chemist with a synthetic strategy to obtain ligands with reduced quenching effects.

Theoretical basis

The mechanism of non-radiative quenching in lanthanide ions has been described by Ermolaev and Sveshnikova.[12] This model implies electromagnetic interaction between the downward electronic transition of the lanthanide ion and the oscillator of the vibrational transitions of the groups surrounding the ion with energy matching the electronic transition. This coupling corresponds to the dipole–dipole coupling of the Förster model, with the difference being that the energy acceptor is a purely vibrational oscillator.

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Following the model proposed by Quochi *et al.* by assuming a continuous and homogeneous distribution ρ_A of acceptor sites the non-radiative deactivation rate constant k_{nr} can be written as

$$k_{nr} = \frac{k_{rad}}{(2\pi n)^4 R_{min}^3} \int F_D(\lambda)\alpha_A(\lambda)\lambda^4 \qquad (1)$$

where R_{min} is the minimum distance between the lanthanide ion and acceptors, below which $\rho_A = 0$.[13] k_{rad} is the radiative emission rate of the erbium ion, n is the refractive index of the medium, $F_D(\lambda)$ is the normalized erbium emission spectrum, and $\alpha_A(\lambda) = \sigma_A(\lambda)\rho_A$ is the vibrational absorption coefficient of the quencher. By assuming that quencher absorption shape can be approximated by a Gaussian peak, eqn (1) can be expressed as a function of the vibrational transition moments $\mathbf{M}_{0n}$ by

$$k_{nr} = k_{rad}\frac{\lambda_{em}^4}{(2\pi n)^4}\frac{\rho_A}{R_{min}^3}\int F(\upsilon)\Gamma(\upsilon)d\upsilon\left(\frac{4\pi^3\upsilon_{0n}}{3h\varepsilon_0 ce^2}\right)|\mathbf{M}_{0n}|^2 \qquad (2)$$

where λ_{em} is the wavelength of the erbium emission peak (1530 nm), $\Gamma(v)$ is the normalized absorption spectrum of the quencher, and υ_{0n} is the frequency of the resonant vibrational absorption peak.

In order to make a quantitative prediction of the extent of the non-radiative decay originating from Förster transfer, the transition moments $\mathbf{M}_{0n}$ of the vibrational overtones in resonance with the ${}^4I_{13/2}$–${}^4I_{15/2}$ electronic transition of the ion must be evaluated. Accurate absolute infrared intensity data are however often difficult to obtain, especially when the intrinsic band intensity is low and in the case of solid samples. For this reason, in this work we will use DFT calculations, which allow us to obtain the intensity of the fundamental normal modes, from which the intensities of the overtone transitions falling in the 1.53 μm region are evaluated by recursive analytical expressions obtained by using the Morse oscillator model.

Results and discussion

Vibrational transition moment for Morse oscillators

The eigenfunctions of the Morse potential are known, so it is possible to obtain explicit formulae for the electric dipole moment matrix elements of $Z = (r - r_e)$, even if the resulting expressions are quite involute.[14,15] For our purposes, we only need the matrix element of Z between the vibrational ground state (0) and the first few excited states (n). Taking $a = (2\mu x_e\omega/\hbar)^{1/2}$ and $k = 1/x_e$, where x_e is the anharmonicity constant, μ the reduced mass, ω the fundamental frequency of the biatomic oscillator, we derived the following expressions in series of x_e, for $\mathbf{M}_{0n}$

$$|\mathbf{M}_{0n}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 |\langle 0|Z|n\rangle|^2 \qquad (3a)$$

$$\begin{aligned}|\mathbf{M}_{0n}|^2 &= \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}\frac{n!k(k-2n-1)(k-1)\Gamma(k-n)}{n^2(n+1-k)^2\Gamma(k)} \\ &= \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}\frac{n!}{n^2}k^{1-n}\left(1+\frac{n(n+1)}{2}k^{-1}+\cdots\right)\end{aligned} \qquad (3b)$$

where the hypothesis of electrical harmonicity is assumed. In particular for the fundamental (eqn (4a)) and first overtones (eqn (4b)–(4f)) we have:

$$|\mathbf{M}_{01}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}(1 + x_e + \cdots) \qquad (4a)$$

$$|\mathbf{M}_{03}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}x_e\left(\frac{1}{2}+\frac{3}{2}x_e+\cdots\right) \qquad (4b)$$

$$|\mathbf{M}_{03}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}x_e^2\left(\frac{2}{3}+4x_e+\cdots\right) \qquad (4c)$$

$$|\mathbf{M}_{04}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}x_e^3\left(\frac{3}{2}+15x_e+\cdots\right) \qquad (4d)$$

$$|\mathbf{M}_{05}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}x_e^4\left(\frac{24}{5}+72x_e+\cdots\right) \qquad (4e)$$

$$|\mathbf{M}_{06}|^2 = \left|\frac{\partial \mathbf{M}}{\partial \mathbf{r}}\right|^2 \frac{\hbar}{2\mu\omega}x_e^5(20+240x_e+\cdots) \qquad (4f)$$

Note that if $x_e = 0$ one regains the corresponding harmonic values, *i.e.* $|\mathbf{M}_{01}|^2 = |\partial\mathbf{M}/\partial\mathbf{r}|^2(\hbar/2\mu\omega)$ and all the other matrix elements vanish. The relative intensity of the nth overtone with respect to the intensity of the fundamental transition is given by:

$$\frac{|\mathbf{M}_{0n}|^2}{|\mathbf{M}_{01}|^2} \approx \frac{n!}{n^2}x_e^{n-1} \qquad (5)$$

eqn (5) shows that if the moment associated with the fundamental transition 0 → 1 is known it is possible to predict the intensity of any overtone transition, provided that the value of the anharmonic constant x_e is known. The value of $|\mathbf{M}_{01}|^2$ is related to the integrated infrared intensity of the corresponding absorption band through the equation:[16,17]

$$A = \frac{1}{Cd}\int \ln\left(\frac{I_0}{I}\right)d\upsilon = \xi|\mathbf{M}_{01}|^2\left(\frac{2\omega}{\hbar}\right) = \xi\left|\frac{\partial \mathbf{M}}{\partial \mathbf{Q}}\right|^2 \qquad (6)$$

In this equation, which holds in the hypothesis of mechanical and electrical harmonicity, C and d are, respectively the concentration of the sample and the pathlength in the sample, while ξ is a constant. Infrared intensities are expressed in km mol^{-1} and the units for the dipole derivative ($\partial\mathbf{M}/\partial\mathbf{Q}$) with respect to the normal mode $\mathbf{Q}$ are debye A^{-1} amu$^{1/2}$ (with these units $\xi = 42.2547$). Notice moreover that, in the case of a diatomic oscillator the following relationship holds: $\partial\mathbf{M}/\partial\mathbf{Q} = (1/\mu)^{1/2}\partial\mathbf{M}/\partial\mathbf{r}$. Eqn (6) is used by standard quantum chemical codes for the prediction of infrared intensities of the first order infrared spectra. The order of the overtone transition (n) in resonance with the erbium ion emission can be obtained from the position of the anharmonic (Morse) energy levels:

$$v_n = \frac{v_1 n - v_1 x_e n(n+1)}{1 - 2x_e} \qquad (7)$$

where v_1 is the frequency of the fundamental vibration.[18] Eqn (2) shows that the extent of the quenching effect depends

Table 1 Data relative to the vibrational fundamental frequency v_1 (scaled by 0.97), intensity A and anharmonicity x_e constants are reported for several oscillators. The first two set of data have been estimated with the help of quantum chemical predictions (PBE1PBE/aug-cc-pVTZ), as discussed in the next section

	v_1/cm^{-1}	A/km mol^{-1}	x_e
C–H str. hydroxyquinolate (anion)	3054	48.1	0.0190
C–H str. hydroxyquinolate + Na$^+$	3086	16.4	0.0190
C–H str. CH$_2$O	2844	91.1	0.0190
CH str. CH$_3$CCCN	3005	1.36	0.0190
C–D str. hydroxyquinolate (anion)	2262	23.0	0.0138
C–D str. hydroxyquinolate + Na$^+$	2288	9.1	0.0138
C–D str. CD$_2$O	2108	86.2	0.0138
C–D str. CD$_3$CCCN	2210	0.54	0.0138
C–F str.	1247	307.2	0.0056
C–Cl str.	761	117.7	0.0078
C=C str.	1615	11.5	0.0055
O–H str. hydroxyquinoline	3534	105.9	0.0166
O–D str. hydroxyquinoline	2579	58.2	0.0115

not only on the intensity of the transitions involved, but also on their effective resonance, which is quantified by the so-called *spectral overlap* $\int F(\upsilon)\Gamma(\upsilon)\mathrm{d}\upsilon$. This quantity can vary for each specific case, since it depends on the precise location of the emission and vibrational absorption bands, and on their bandshape.

By using the values of x_e and υ_I reported in Table 1, the computed value of frequency and intensity of the first 5 overtones of the selected, frequently occurring bonds (normalized to the C–H fundamental intensity) are shown in Fig. 1. The figure shows clearly that the most anharmonic vibrations (C–H/O–H) exhibit a lower decrease of the overtone intensity with the order of the process than less anharmonic bonds. This, combined with the fact that for these stretching modes less vibrational quanta are needed to match the Er^{3+} emission energy, makes them the most efficient quenchers.

From eqn (5) we get that the ratio $|\mathbf{M}_{03}|^2$(C–D)/$|\mathbf{M}_{02}|^2$(C–H) is approximately given by:

$$\frac{|\mathbf{M}_{03}|^2_{\mathrm{CD}}}{|\mathbf{M}_{02}|^2_{\mathrm{CH}}} \approx 0.42 x_e^{\mathrm{CH}} \tag{8}$$

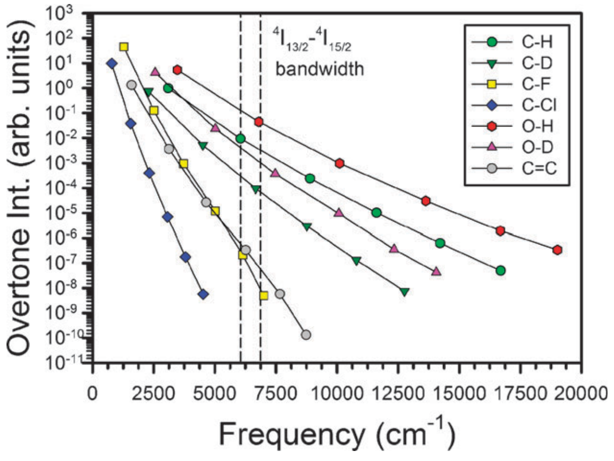


Fig. 1 Overtone relative intensity for the bonds reported in Table 1 normalized for the C–H fundamental intensity.

As shown by eqn (8), in principle deuteration should reduce the quenching considerably. This is not always the case since the spectral overlap is usually larger for the C–D bond. Fig. 1 shows that upon deuteration of the C–H bond the first overtone (n = 2) is no longer in resonance with the near IR erbium emission, but on the other end we have seen that the second overtone (n = 3) falls at about 6500 cm^{-1} and becomes resonant with the ion luminescence; so in many practical cases deuteration reduces the quenching by less than an order of magnitude. Similar considerations hold for the quenching by O–H/O–D stretching modes. Since O–H is usually more polar than the C–H bond, its fundamental intensity is somewhat larger (16.4/105.9 km mol^{-1} for charge-compensated quinolate$^-$–Na$^+$ system) while the scaling of the intensity with the order of the process is the same because these two bonds possess the same anharmonicity, so we can expect that O–H/O–D vibrations quench more efficiently than C–H/C–D bonds. Interesting for practical applications is also the case of the ubiquitous C=C bond. In the most unfavourable case the C=C double bond fundamental stretching vibration falls at *ca.* 1600 cm^{-1}. This bond is only weakly polar and its fundamental intensity is rather low (see Table 1), moreover since we would need to go to the third overtone (n = 4) to meet the resonance condition with erbium emission, we can predict from Fig. 1 that the quenching effect will be four orders of magnitude lower compared with that of the C–H bond, even supposing a perfect match of the spectra. Hence we can probably forget about the quenching coming from the omnipresent C=C bonds. Similar considerations hold for the halogenated bonds. For C–F (C–Cl) groups five (eight) vibrational quanta are needed to meet the resonance conditions with a corresponding reduction of the oscillator strength of the transition of six (> ten) orders of magnitude with respect to the C–H overtone.

Predictions of fundamental infrared intensities: the case of C–H stretching modes

We present in this section the results obtained through *ab initio* and DFT simulations of the IR spectrum of model molecules which would mimic the organic fragments of the erbium complexes. The calculation of fundamental absorption intensities combined with eqn (4) can be used to theoretically predict quenching effects exerted by bonds falling in the Er^{3+} first coordination sphere. In the following we report the results on the erbium tris-hydroxyquinoline (ErQ$_3$) complex which is used here as a test case, since the effect of quenching due to resonance with its C–H stretching first overtone (n = 2) levels is a well recognized phenomenon.[19,20] Moreover, the availability of the experimental FT-IR spectrum of this complex in its crystalline solid state will allow us to check the reliability of our predicted intensities by comparison between theoretical and experimental intensity ratios. Both Hartree–Fock (RHF) and DFT calculations have been carried out with some different basis sets, as reported in Table 2. For DFT calculations, the PBE1PBE exchange–correlation functional was used.[21] All the calculations were carried out with Gaussian03 code.[22]

In the complex under study three quinolate anions are interacting with an Er^{3+} ion. Two simple models have been

Table 2 Values of total intensities of CH stretching bands ($I_{CH}{}^{tot}$), reference bands (I^{ref}) and of the ratio ($I^{ref}/I_{CH}{}^{tot}$) (see text) for the two models shown in Fig. 1

	Anion			Na^+–anion		
	$I_{CH}{}^{tot}$	I^{ref}	$I^{ref}/I_{CH}{}^{tot}$	$I_{CH}{}^{tot}$	I^{ref}	$I^{ref}/I_{CH}{}^{tot}$
PBE1PBE/6-311 + + G(d,p)	296.7	550.4	1.86	100.3	246.4	2.46
PBE1PBE/aug-cc-pVTZ	288.4	514.0	1.78	98.0	222.4	2.27
RHF/6-311 + + G(d,p)	304.4	751.2	2.47	136.2	212.9	1.56
RHF/6-311 + + G(3df,3pd)	293.8	716.7	2.44	131.4	206.2	1.57
Experimental			$I^{ref}/I_{CH}{}^{tot} = 2.1 \pm 0.2$			

used to simulate such a complex: in the first case, calculations have been performed on the negatively charged quinolate ligand (isolated anion) while in the second case a neutral complex has been studied where the quinolate anion is interacting with a Na^+ cation. This last model complex has been chosen in order to test the sensitivity of the calculation to the presence of an interacting counter-ion which should mimic the effect of the electrostatic interaction taking place between the erbium ion and each quinolate anion. A more realistic model would also consider the presence of the other two ligands and a counter-ion^{3+}; however, we prefer to focus on a simpler model which allows us to make use of extended basis set, required for a reliable description of IR intensities. The relative position of the two ions has been obtained by geometry optimization of the whole complex. Both systems are sketched in Fig. 2.

From the computed IR spectrum, the total intensity of the C–H stretching bands (km mol^{-1}) was obtained. In order to compare predicted values with the experimental results (only relative intensities are experimentally available) we have chosen as internal reference the intensity of the two strong IR bands ascribed to vibrations assigned to C–O and C–N stretching modes. These bands can be identified in the experimental spectrum of the complex at 1600 and 1573 cm^{-1}, respectively. The sum of the intensities (I^{ref}) of these two bands has been used to determine the experimental ratio $I^{ref}/I^{tot}{}_{CH}$ (where $I^{tot}{}_{CH}$ is the sum of the intensities assigned to C–H stretching modes): this value was then compared with the corresponding one obtained by RHF and DFT calculations. The results of our different computations are reported in Table 2 for the two models. In the case of the isolated quinolate anions, a good agreement is found both for RHF and PBE1PBE calculations. However, in spite of the fact that most of the theoretical intensity ratios reported in Table 2 show quite a good agreement with the experimental one the values of the absolute C–H stretching intensities are seen to be strongly sensitive to the presence of a counter-ion. A remarkable increase of the C–H stretching intensity is indeed always predicted for the isolated anion for all the theoretical approaches adopted; for instance, in the case of PBE1PBE/aug-cc-pVTZ calculations, a total C–H stretching intensity of 288 km mol^{-1} is found for the anion, while a value of 98 km mol^{-1} is obtained for the neutral complex with Na^+. Since the quenching of luminescence due to vibrational overtones depends on the intensity value of the fundamentals, the difference between the prediction for the isolated anion and that of the complex cannot be neglected.

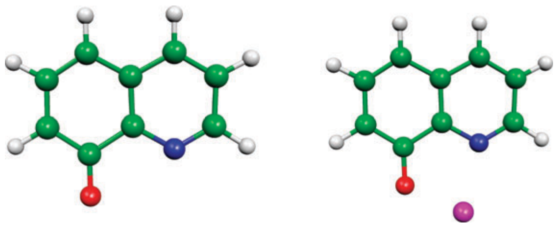


Fig. 2 Sketch of the two models investigated by first principle calculations as reported in the text. (Left) Isolated quinolate$^-$ anion. (Right) Neutral complex quinolate$^-$–Na^+.

The high intensity value occurring in the case of the anion can be justified on the basis of the fact that an excess of electron charge is present in the molecule, possibly enhancing charge fluxes, which are responsible for IR intensities of C–H bonds.[23] When a counter-ion is present, some pinning of the electronic charge transferred to the organic fragment is expected by coulomb interaction with the cation: as result the charge transferred becomes more localized and less mobile, thus showing lower charge fluxes during vibrations and consequently lower IR intensities. On the other hand, the case of the isolated anion (that should result as the most efficient in terms of quenching ability) seems to be a quite unrealistic model for mimicking real Er^{3+} organic complexes. In these cases the erbium acts as a counter-ion, making the whole complex a neutral species. Furthermore, recent theoretical studies by Ottonelli *et al.* on organic complexes involving erbium demonstrated that, in order to make the computational problem affordable, it is possible to replace Er^{3+} with another lighter element (in ref. 24 the Al^{3+} ion replaced Er^{3+}), still obtaining very satisfactory results, in agreement with the experimental structural data obtained for the organic ligand.[24,25] These results justify our approach and indicate that the most likely values for the C–H stretching intensities are those obtained for model 2.

Another way to give an estimate of the effectiveness of C–H overtones in the quenching of the luminescence is simply to consider the range of variation of the C–H stretching intensity obtained (both experimentally and theoretically) for a wide ranging series of small organic molecules (Fig. 3). Much experimental data are reported in the literature:[23] accordingly, we find that the C–H stretching intensity per oscillator (*i.e.* the total C–H stretching intensity normalized to the number of C–H oscillators in a given molecule) ranges from 1.2 km mol^{-1} in the case of CH_3CCCN to 77 km mol^{-1} for CH_2O. Recent theoretical DFT predictions of the infrared intensities of these same small molecules show that a very good quantitative agreement with the experimental data can be reached with

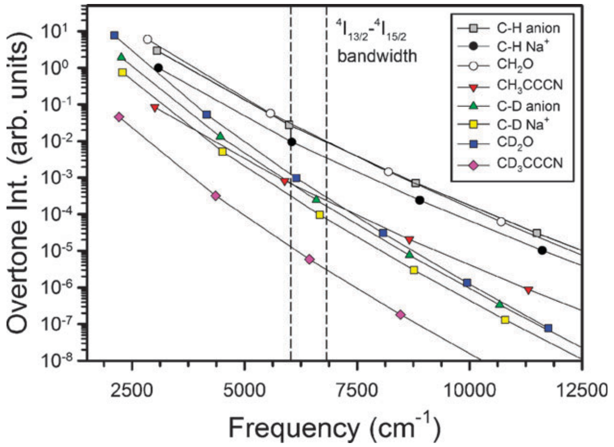


Fig. 3 Overtones relative intensity for the typical C–H oscillators stretching modes.

PBE1PBE/aug-cc-pVTZ calculations, thus supporting the computational approach adopted in this paper.[25] Considering this relatively wide range of C–H intensity data we can make the following observations:

I. C–H oscillators in different chemical environments can lead to relatively different quenching efficiencies according to their characteristic intensity.

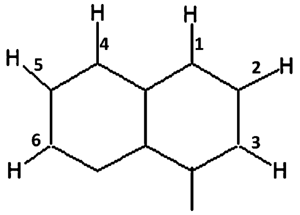
II. The case of CH_3CN and that of formaldehyde can be taken as lower and upper limits for the infrared intensity of a C–H oscillator.

Looking to our results for the quinolate taken as a prototype of efficient quencher among the organic ligands, we can conclude that the theoretical intensities obtained according to the two models (intensity data in Table 1, divided by the number of 6 C–H oscillators present in the molecule) give an average C–H intensity per oscillator that lies in the experimental range discussed above. For instance, in the case of the PBE1PBE/aug-cc-pVTZ calculations, the total stretching intensity normalized to a single C–H oscillator turns out to be 48.1 km mol^{-1} (anion) and 16.4 km mol^{-1} (complex), respectively. In Table 1, we also reported the computed intensities for fundamental transitions relative to normal modes involving stretching vibrations of different chemical bonds commonly found in organometallic complexes. In order to make use of the simple relationships previously discussed (eqn (5) and (7)) these modes are considered as localized biatomic oscillators. In some cases, and in particular when one considers stretching vibrations of bonds like C–F and C–Cl, this approximation is very rough due to their strong mixing with other vibrations of the organic fragment (*e.g.* bending vibrations, C=C stretching, *etc.*). The values reported in Table 1 for C–H and C–D oscillators are directly obtained from calculations on the two quinolate anion models (and their deuterated form) by averaging all of the frequencies and intensities of the six C–H normal modes. O–H and O–D values were obtained by calculations on the hydroxyquinoline molecule and its deuterated derivative; C–Cl and C–F were obtained as contribution per C–X oscillator to the total stretching band of CCl_4 and CF_4. The intensity value of a C=C oscillator was derived from the computed infrared intensities of butadiene.

Theoretical investigation of isolated C–H bonds

As already noted, C–H stretching vibrations are extremely sensitive to their closer intramolecular environment and this effect causes a large variation in both their vibrational frequencies and intensities.[23,26] Due to the R^{-6} dependence of the quenching rate constant in Förster RET (see eqn (1) and (2)), the presence of different, possibly unequivalent, C–H oscillators cannot be overlooked: this is of fundamental importance when considering the quenching ability of a specific C–H stretching vibration located at a given position in the molecule and therefore at a given distance from the lanthanide ion. This difference in the C–H stretching intensity behavior is even more important considering the fact that overtone transitions of C–H stretching vibrations are usually assigned to "local oscillators" as a consequence of the strong anharmonicity of these bonds.[27–29] In the case of the quinolate ligand, the C–H stretching normal modes involve simultaneous vibrations of all the C–H bonds, for symmetry reasons and by dynamical coupling; the analysis previously reported did not focus in particular on the peculiar characteristic of any given C–H bond.

However, if a more realistic study on a particular complex is requested, we can evaluate the stretching frequency and the infrared intensity of any individual isolated C–H bond by decoupling its oscillation from the stretching of all the other C–H bonds. This can be done by carrying out a frequency calculation for a model molecule where all the hydrogen masses are substituted by heavy masses (*e.g.* 100 amu) except the hydrogen belonging to C–H bond under study. In this way the oscillation of the selected C–H bond results in being dynamically isolated. This technique is the theoretical counterpart of the deuteration technique proposed by McKean for an experimental study of *non-equivalent* isolated C–Hs.[30] The procedure has been applied here in order to separately study each C–H oscillator that is present in the quinolate molecule. The resulting values for the frequencies and intensities are reported in Table 3.



As shown in Table 3 and as expected on the basis of the above discussion, each C–H oscillator shows different values of both frequency and intensity. Therefore, from the point of view of quenching ability, each C–H oscillator is expected to have a behaviour which is dependent not only on its distance from the emitter, but also on its intrinsic 'character'. Notice that the average values of both the frequency and intensity of all the 'isolated' C–H bonds are the same of those found by averaging the 'real' normal modes. The intrinsic character of the C–H bond becomes important in the case of fluorinated (possibly perfluorinated) complexes often employed to reduce the effect of the vibrational quenching.[31] Due to synthetic difficulties in obtaining a

Table 3 Computed values (PBE1PBE/aug-cc-pVTZ) of vibrational frequencies (scaled by 0.97) and intensities of isolated C–H stretching (see text for details) for the two model (Fig. 2) of Er^{3+}–hydroxiquinoline

	Anion		Anion–Na^+	
	Frequency/cm^{-1}	Intensity/km mol^{-1}	Frequency/cm^{-1}	Intensity/km mol^{-1}
CH-1	3071	30.5	3098	9.1
CH-2	3033	67.1	3078	23.1
CH-3	3072	38.8	3098	13.2
CH-4	3054	33.4	3084	9.8
CH-5	3070	48.0	3109	9.7
CH-6	3018	70.8	3049	32.2

complete fluorination, some residual C–H bonds are left in the molecules and can affect the emission efficiency. For example, in the case of 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Hacac–F_6, the model systems are shown in Fig. 4), three different situations can occur:

(a) a C–H bond in CF_2H end group in *trans* conformation

(b) a C–H bond in CF_2H end group in a '*gauche*-like' conformation

(c) a C–H bond bound to the central sp2 carbon atom

Therefore, this is a peculiar and real case where a single isolated C–H oscillator can be involved in the quenching of luminescence. We can also consider in this case the model of the anion and the model of a neutral complex where a Na^+ ion is added to closer simulate the real lanthanide complex (Fig. 4). The values of frequency and intensity for all these cases are reported in Table 4. Again, a large range of variation is found: first of all changes in the conformation of a terminal C–H bond have a non-negligible effect on the computed intensities; in the case of model c) a very small value of the C–H stretching intensity is found (ten times less for the neutral complex), thus implying that a hydrogen impurity in this location has implicitly a negligible quenching ability. Experimental measures are planned on these molecules in order to verify the accuracy of the computational predictions. The above example clearly shows that, according to DFT predictions, there is a remarkable dependence of C–H stretching frequencies and intensities on the molecular environment. These results point out that the quenching effect due to C–H stretching overtones should be evaluated by considering both the distance R of energy transfer and the intrinsic nature (in terms of its IR intensity) of the C–H oscillator involved.

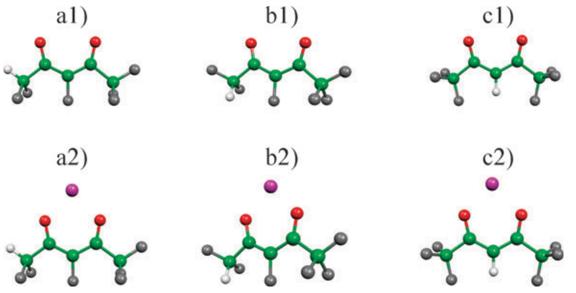


Fig. 4 Sketch of the different cases occurring for the anion (1) and neutral complex 2, (anion–Na^+). (a) C–H impurity in the terminal groups in *trans* conformation. (b) C–H impurity in the terminal group in '*gauche*'-like conformation. (c) C–H impurity in the middle of the molecule.

Table 4 Computed values (PBE1PBE/aug-cc-pVTZ) of vibrational frequencies (scaled by 0.97) and intensities of C–H stretching for the model shown in Fig. 4

	Frequency/cm^{-1}	Intensity/km mol^{-1}
C–H a1	2994	50.2
C–H b1	3004	34.8
C–H c1	3157	0.4
C–H a2	3004	30.4
C–H b2	3025	15.0
C–H c2	3169	3.0

Conclusions

The adverse effects of the presence of high energy vibrations (such as C–H and O–H) groups in the Er^{3+} ions first coordination sphere in complexes were already recognized at a qualitative level. Overcoming of this problem has been attempted by several authors, through the full halogenation of the complex. In order to guide further chemical approach to obtain efficient NIR emitters, we have developed a theoretical model quantitatively predicting the quenching efficiencies of various vibrational groups frequently occurring in organometallic complexes. This model combines the analytical treatment of the anharmonic vibration at the level of Morse potential with the '*ab initio*' evaluation of their fundamental infrared intensities. We have confirmed that C–H and especially O–H bonds are mostly responsible for the low emission quantum yield observed in these systems. We have found that C–H bonds exert a quenching effect that is strongly (about one order of magnitude) dependent on their chemical environment. Since omnipresent C=C bonds do not appreciably affect the non-radiative decay, it appears that the halogenation of the C–H bonds combined with the total elimination of the coordinated water should produce complexes with strongly enhanced emission quantum yield suitable for telecom applications in plastic-based devices.

Acknowledgements

This work was supported by MIUR-FIRB RBNE0357X7 Synergy project and by RTN-NANOMATCH Grant no. MRTN-CT-2006-035884 project. This work has been partly supported by grants from the Italian Ministry of Education, University and Research through FIRB projects 'Molecular compounds and hybrid nanostructured materials with resonant and non resonant optical properties for photonic devices' (RBNE033KMA), and by PRIN projects 'Molecular materials and nanostructures for photonics and nanophotonics' (2004033197) and 'Organic functionalized organized materials: characterization, organization processes and advanced technological applications' (2006034121).

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