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Aqueous Solutions of Europium(III) Dipicolinate Complexes: Estimates of Water Coordination Based on Molecular Dynamics Simulations and Excited State Decay Rate Constants

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The rate constants for decay of the $Eu^{3+}(^5D_0)$ excited state are reported for aqueous $Eu(dipicolinate)_n^{3-2n}$ complexes with $n = 0-3$ in H_2O and D_2O at 295 K. These rate constants are used to estimate water coordination numbers, and the results are compared to parallel molecular dynamics calculations, showing good general agreement. Electronic energy exchange between species with differing numbers of coordinated dipicolinate ligands is examined and is found to be most significant for species of opposite charge.

I. Introduction

Eu^{3+} forms tightly bound complexes with the dipicolinate (2,6-pyridinedicarboxylate) anion, dpa^{2-} in aqueous solution giving species with formulas $Eu(dpa)^+$, $Eu(dpa)_2^-$, and $Eu(dpa)_3^{3-}$. Equilibrium constants for the successive formation of the $Eu(dpa)_n$ complexes at 293 K have been reported by Grenthe[1] as $\log K_1 = 8.84$, $\log K_2 = 7.14$, and $\log K_3 = 5.51$ for an ionic strength, $\mu = 0.5$ M. The constants are large and decrease rapidly with n making it feasible to produce solutions in which a single species predominates. Coordination of the dpa^{2-} ligands results in displacement of coordinated water and thus strongly impacts the decay rate of the excited $Eu^{3+}(^5D_0)$ state. In this work, decay rate constants of the $Eu^{3+}(^5D_0)$ states of the three dpa-coordinated species are reported and results are correlated with molecular dynamics calculations of inner sphere hydration numbers. The outer sphere coordination by water is discussed in a qualitative manner.

An empirical model for the linear dependence of the $Eu^{3+}(^5D_0)$ decay rate constant on the number of directly coordinated water molecules was developed by Horrocks et al.[2] from a fit to Eu^{3+} compounds in crystals for which the number of coordinated H_2O is well defined. The model gives the number of coordinated water molecules, x, as,

$$x = 1.05 \times 10^{-3}\ \mathrm{s} \times (k_{H_2O} - k_{D_2O}) \qquad (1)$$

where k_{H_2O} and k_{D_2O} are the rate constants (s^{-1}) in H_2O and D_2O, respectively. The authors of that work suggest an uncertainty in x derived from eq 1 of ± 0.5 H_2O molecules. Kimura and Choppin[3] developed a modification of this with

$$x = 1.07 \times 10^{-3}\ \mathrm{s} \times k_{H_2O} - 0.62 \qquad (2)$$

which works well when the ligand itself does not strongly quench $Eu^{3+}(^5D_0)$. More recently, Beeby et al.[4] suggested

$$x = 1.2 \times 10^{-3}\ \mathrm{s} \times (k_{H_2O} - k_{D_2O} - k_{outer}) \qquad (3)$$

where $k_{outer} = 250\ s^{-1}$ is the contribution of outer sphere water molecules to the quenching of $Eu^{3+}(^5D_0)$. This correction factor has been determined for a closely related set of complexes and transferability to other complexes may not always be justified (vide infra). Nonetheless, there is good evidence to support a nonnegligible contribution from k_{outer}. May et al.[5] measured an outer sphere contribution of 264 s^{-1} in crystalline $Na_3[Eu(oxydiacetate)_3]\cdot 2ClO_4\cdot 6H_2O$. In aqueous solutions, where there are larger numbers of second sphere waters, we might expect a contribution at least that large. However, the magnitude of the slope, 1.2×10^{-3}, would lead one to conclude that $x = 10$ H_2O's in $Eu^{3+}(aq)$, which is not supported by the experimental evidence[6] or molecular dynamics calculations.[7]

In this work, the first-order decay rate constants, k_n for $Eu^{3+}(^5D_0)$ with n coordinated dpa^{2-} ligands in dilute aqueous (H_2O and D_2O) solution are reported. The rate constant, k_0, for $Eu^{3+}(aq)$, has been reported by several authors[8] and our results confirm the earlier measurements. Richardson[9] has reported k_3 in both H_2O and D_2O and our results are in good agreement with his. Horrocks[10] reported values for k_1 and k_2 in H_2O measured in a 1 mM solution with a mixture of $Eu(dpa)^+$ and $Eu(dpa)_2^-$. Though, as was pointed out in that work, energy exchange between the species at that concentration is slow, we find that it has a nonnegligible impact on the measured rate constants. Spectral overlap of the two excitation features also impacts the measurement and thus we report numbers that differ from his. There have been no earlier reports of k_1 and k_2 in D_2O.

Molecular dynamics (MD) calculations on each of the four species $Eu(dpa)_n$, $n = 0-3$, are reported here and the calculated numbers of directly coordinated water molecules are compared to the numbers deduced from the decay rates invoking the Horrocks[2] and Beeby[4] models.

II. Experimental Section

To measure the decay rate constants for the individual $Eu(dpa)_n$ species, aqueous solutions with Eu^{3+}:dpa^{2-} ratios of 1:1, 1:2, and 1:3 were prepared with total Eu^{3+} concentrations of 5 or 10 mM from stock solutions of 0.08 M Na_2dpa and

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0.20 M $EuCl_3$. The pH of the mixtures was adjusted to approximately 6 with dilute aqueous Na_2CO_3. A 0.1 M $EuCl_3$ solution was prepared to measure the decay rate constant for Eu^{3+}(aq).

Excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition were measured to assess the number of chemical species present. The $^5D_0$ decay rate constant was measured for each of the four solutions by exciting directly into the $^5D_0$ state of the dominant species and monitoring luminescence decay on the $^5D_0 \rightarrow {}^7F_2$ transition (6144 Å). For each of the three solutions containing dpa^{2-}, successive 2-fold dilutions were made and the decay curves were remeasured after each dilution.

Excitation (5780−5800 Å) was provided by a N_2-pumped dye laser (Laser Photonics UV12/DL14); emission was selected by a 0.47 m monochromator (Jobin Yvon HR460) and detected by a Hamamatsu R2949 phototube connected to a Stanford Research Systems SR430 multichannel scaler.

To assess the importance of energy exchange between species of different dpa^{2-} coordination number, solutions with Eu:dpa ratios of 1:0.3, 1:0.5, 1:1.5, and 1:2.5, were prepared with total Eu^{3+} concentrations of 10 mM. As before the pH was adjusted to approximately 6. Excitation spectra on the $^7F_0 \rightarrow {}^5D_0$ transition were measured. $^5D_0$ luminescence decay curves were measured for each of the solutions exciting into each of the two dominant species. For example, for the 1:1.5 solution, one decay curve was measured after exciting $Eu(dpa)^+$ at 5792 Å and a second curve was measured after exciting into $Eu(dpa)_2^-$ at 5797 Å. See Figure 1. Successive dilutions of the solutions were made and the decay curves were remeasured after each dilution.

III. Molecular Dynamics and Molecular Modeling Calculations

Initial structures as well as visualizations were carried out with Quanta 97.[11] The MM and MD calculations were run with CHARMM 24.[12] Parameters were taken from Quanta 97 and point charges were assigned with the charge template option in Quanta. The ligand was charged to −2, with a small "excess" charge smoothed to nonpolar carbons and hydrogens. The parameters for the europium cation were $\epsilon = 0.050$ kcal/mol and $\sigma = 3.30$ Å. The starting structures were minimized by ABNR (Adopted-Basis set Newton−Raphson) until the RMS on the energy gradient was ≤ 0.001 kcal·mol^{-1}·Å^{-1}. No cutoff on the nonbonded interactions was applied in the gas-phase minimizations of the complexes. A constant dielectric constant with an ϵ of 1 was used. The structure of the complex $[Eu(dpa)_2 \cdot 3H_2O]^-$ was manually created by replacing the three coordinated atoms of one dpa in the minimized structure of $Eu(dpa)_3^{3-}$ by waters, followed by minimization. Similarly, the complex $[Eu(dpa) \cdot 6H_2O]^+$ was created by replacing two dpa^{2-} anions by six waters.

Details of the MD simulations were as follows. The minimized complexes were placed in a cubic box of approximately 31 Å dimensions, initially filled with 1000 TIP3P (as implemented in CHARMM).[13] Solvent molecules that overlap with the complexes were removed (based on heavy atom interatomic distances ≤ 2.3 Å). This in general resulted in removal of one water per one non-hydrogen atom of the systems under study. Full periodic boundary conditions were imposed. Before running the MD simulations the system was minimized by steepest descent, to remove the worst contacts, until the RMS on the energy gradient was ≤ 1.0 kcal·mol^{-1}·Å^{-1} or a maximum of 1000 steps was reached. During the simulation the nonbonded list was updated every 20 time steps with a cutoff of 12 Å. The van der Waals interactions were treated with a switch function between 10 and 11 Å, whereas the shift function was applied to the electrostatic interactions (cutoff 11 Å). A constant dielectric constant and an ϵ of 1 were applied. The system was heated to 300 K in 5 ps, followed by 10 ps equilibration with scaling of the velocities within a temperature window of 10 degrees. After equilibration no scaling of the velocities was applied. No systematic deviation from the average temperature was observed. The production phase consisted of 500 or 1000 ps, and coordinates were saved regularly, i.e., every 500 time steps, for subsequent analysis. The verlet/leapfrog algorithm was used for the numerical integration. The SHAKE algorithm[14] on bonds involving hydrogen was applied, allowing a time step of 1 fs. The RDFs were calculated from the saved coordinates with a resolution of 0.05 Å and were averaged over the duration of the MD.

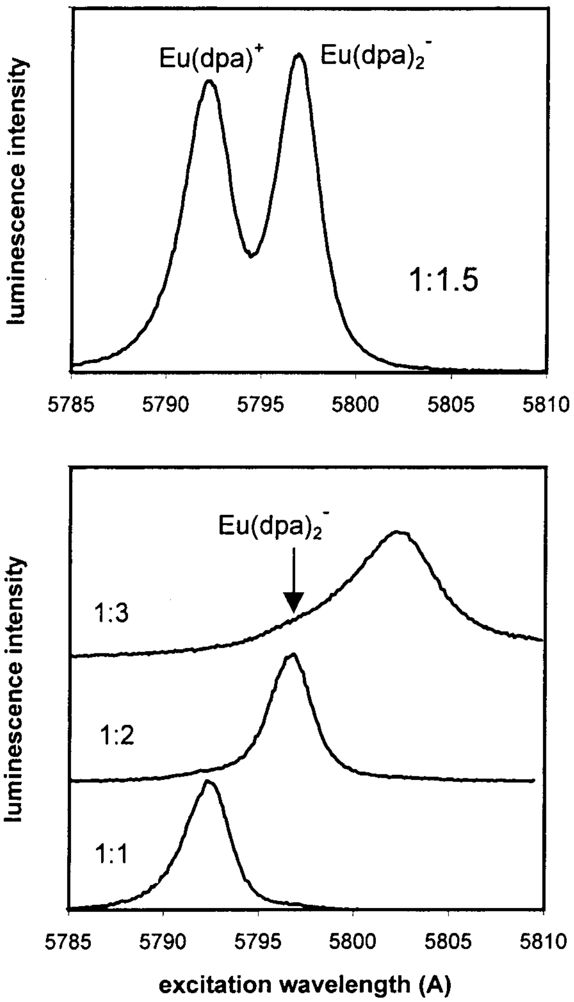

Figure 1. Excitation spectra on the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} for aqueous $Eu(dpa)_n$ solutions with Eu^{3+}:dpa^{2-} ratios of 1:1, 1:2, 1:3, and 1:1.5. Emission is monitored on the $^5D_0 \rightarrow {}^7F_2$ transition at 6144 Å.

IV. Results and Discussion

A. Decay Rate Constants. Figure 1 shows $^7F_0{-}^5D_0$ excitation spectra of Eu−dpa solutions with Eu:dpa ratios of 1:1, 1:2, and 1:3, and 1:1.5. In the lower panel the individual spectra are scaled relative to each other to give equal peak intensities. In the 1:3 ratio spectrum $Eu(dpa)_2^-$ is evident. The $Eu(dpa)_3^{3-}$ species dominates in concentration but the $^7F_0{-}^5D_0$ transition is symmetry forbidden for this D_{3h} complex and the luminescence signal is therefore quite weak.

TABLE 1: Extrapolated Rate Constants, k_n (s^{-1}) in H_2O and D_2O[a]

n	$k_n(H_2O)$	$k_n(D_2O)$	$x(1)$[b]	$x(3)$	$x(MD)$[c]	$r(Eu-O)$[d]	$r(Eu-H)$
0	8950 ± 40	252 ± 1	9.1	10.1	9.0 ± 0.01	2.47	3.09
1	6030 ± 50	281 ± 7	6.0	6.6	6.5 ± 0.1	2.50	3.18
2	3110 ± 35	306 ± 1	2.9	3.1	3.1 ± 0.2	2.46	3.15
3	600 ± 4	301 ± 8	0.3	0.1	0.2 ± 0.2	2.54	

[a] Also given are the calculated number of first coordination sphere water molecules, x, predicted by eqs 1 and 3 and by the molecular dynamics simulation. The last two columns give the Eu−O and Eu−H distances in Å, calculated from the radial density functions produced by the MD simulation. [b] The accuracy of $x(1)$ has been estimated as ± 0.5 H_2Os. See ref 2. [c] Precision in $x(MD)$ is estimated by calculating x for each of the 100 ps intervals of the simulation and evaluating the 95% confidence limits from the standard deviation of the mean. [d] The precision in $r(Eu-O)$ is ≤ 0.01 Å. This is estimated from the standard deviation of the approximately Gaussian RDF.

TABLE 2: Effective Single Exponential Rate Constants, k_n(eff) (s^{-1}), for Binary Mixtures of $Eu(dpa)_n$ Complexes with the Specified Total Eu^{3+} Concentrations[a]

Eu:dpa ratio	k_n(eff)	concentration (mM) 10	5	2.5	1.2	0.6	0.3	0.15
1:0.3	k_1(eff)	6855	6885	6790	6827			
1:0.5	k_1(eff)	6587	6635	6503	6528	6537		
1:1.5	k_1(eff)	3912	4270	4590	4661	5062	5304	5426
	k_2(eff)	3830	3670	3439	3416	3321	3274	3202
1:2.5	k_2(eff)	2850	2875	2893	2912			
	k_3(eff)	860	837	829	819			

[a] Significant scatter in the data results from fitting these non-single exponential decay curves with effective single exponential rate laws. From the concentration dependence of the rate constants it can be seen that only $Eu(dpa)^+$ and $Eu(dpa)_2^-$ exhibit significant energy exchange at concentrations below 10 mM.

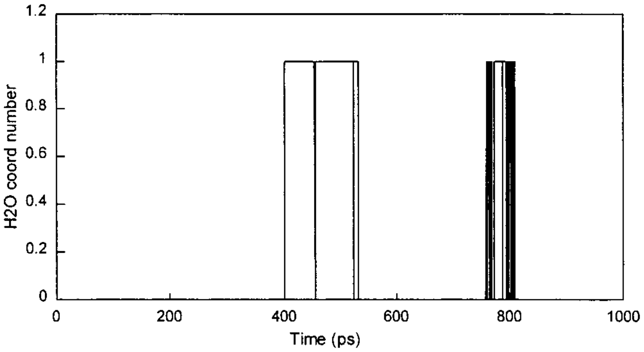

Figure 2. Molecular dynamics simulation. Number of waters coordinated to Eu^{3+} in $Eu(dpa)_3^{3-}$ as a function of time.

Successive dilutions of the 1:1, 1:2, and 1:3 Eu:dpa solutions were performed in order to identify effects due to energy exchange with minor species. Table 1 gives the best estimate of the rate constants, k_n, extrapolated to infinite dilution from the effective rate constants measured at each concentration. The error limits on k_n represent the 95% confidence limits for the extrapolated 0 M concentration intercept. The rate constants, k_n in D_2O are quite similar for all four species and for the most part represent the radiative contribution to the rate constant.

Estimates of the inner sphere water coordination, x derived from eqs 1 and 3 and based on the k_n of the previous columns are given in Table 1.

Table 2 gives the effective rate constants for species in solution with mixtures of $Eu(dpa)_n$ complexes. The k_n(eff) are measured by exciting into the $Eu(dpa)_n$ species selectively and analyzing the decay curve as a single exponential with a single "effective" decay constant. The experimental curves for these mixtures, in fact, show significant deviation from single exponential, but this treatment yields an average decay rate constant and illuminates underlying energy exchange processes.

For the 1:2.5 Eu:dpa ratio, which creates a solution with a mixture of $Eu(dpa)_2^-$ and $Eu(dpa)_3^{3-}$, k_2(eff) and k_3(eff) are clearly different than k_2 and k_3. However these effective rate constants are rather insensitive to dilution. This suggests that energy exchange between $Eu(dpa)_2^-$ and $Eu(dpa)_3^{3-}$ is not important but that the difference between k_n and k_n(eff) results from the less than perfect selectivity in the excitation of the species. The decay curves are in fact much better fit by a double exponential form with $k_2 = 3100$ s^{-1} and $k_3 = 600$ s^{-1} and with the relative magnitude of the preexponential factors depending on excitation selection. There is however a trend in the rate constants vs concentration data suggesting some contribution from an energy exchange process that is slow on the time scale of the luminescence.

For the 1:0.5 and 1:0.3 ratios, giving a mixture of Eu^{3+} and $Eu(dpa)^+$ in solution, the dilution data again indicate that energy exchange is not significant and that k_1(eff) differs from $k_1 = 6030$ s^{-1} because $Eu(dpa)^+$ excitation is accompanied by Eu^{3+}(aq) excitation and the decay curve simply represents the luminescence of species in proportion to their relative degrees of excitation.

In contrast, the data in Table 2 for the 1:1.5 Eu:dpa ratio show a strong concentration dependence indicating that energy exchange between $Eu(dpa)_2^-$ and $Eu(dpa)^+$ is significant at a concentration as low as 0.3 mM. The values of k_1(eff) and k_2(eff) are quite close at 10 mM and diverge toward k_1 and k_2, respectively, as dilution increases. They would not be expected to reach those values precisely since lack of resolution in the excitation will still be a factor in this case. It is not surprising perhaps that energy exchange is most important between species of opposite charge and is much less so between Eu^{3+} and $Eu(dpa)^+$ or between $Eu(dpa)_2^-$ and $Eu(dpa)_3^{3-}$.

In light of the effect that other $Eu(dpa)_n$ species have on the evaluation of k_n(eff), values in Table 1 are those derived from dilute solutions of as nearly a single species as is achievable. For k_1 and k_2 this value is best derived from solutions with Eu:dpa ratios of 1:1 and 1:2, respectively. For k_3 a better value is obtained by shifting the equilibrium with a slight excess of dpa^{2-}.

B. Molecular Dynamics. The molecular dynamics simulation of $Eu(dpa)_3^{3-}$ gave a complex that was a nine-coordinate species with no water coordination most of the time but for two short periods of time one water entered the first coordination sphere (Figure 2). The average number of waters in the first coordination sphere was 0.17.

The $Eu(dpa)_2^-$ complex changed occasionally form a nine-coordinate species to a ten-coordinate species, i.e., with three and four coordinated waters, respectively, leading to an average of 3.15 (Figure 3). The $Eu(dpa)^+$ complex changed very frequently from a nine- to a ten-coordinate species, i.e., with six and seven coordinated waters, respectively, giving an average of 6.50 waters in the first coordination sphere (Figure 3). The exchange rate of the coordinated waters was much higher than in the previous two cases.

Without dpa^{2-} coordination, the Eu^{3+} ion was a nine-coordinate species most of the time with only two very brief periods where a ten-coordinate species existed, giving an average of 9.004 waters in the first coordination sphere (see Figure 3). These coordination numbers are summarized in Table 2 in the column labeled $x(MD)$.

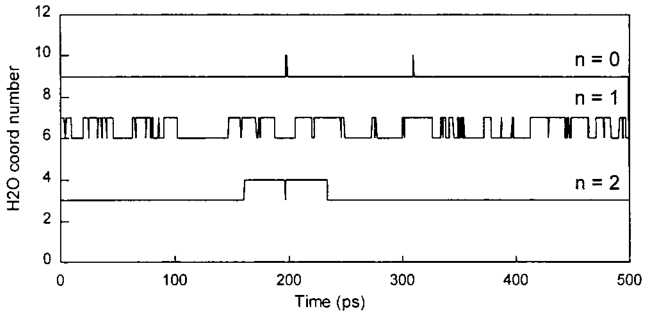

Figure 3. Molecular dynamics simulation. Number of waters coordinated to Eu^{3+} in $Eu(dpa)_n$ as a function of time: bottom trace, $Eu(dpa)_2^-$; middle trace, $Eu(dpa)^+$; upper trace, Eu^{3+}.

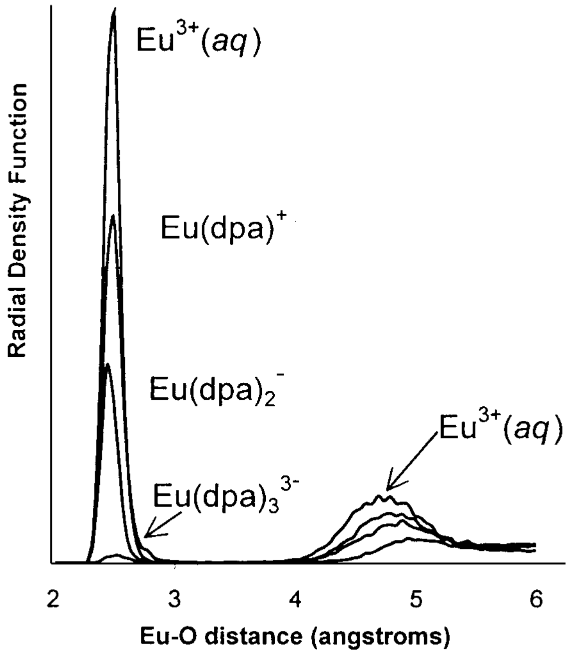

Figure 4. Calculated radial density functions for $Eu(dpa)_n$ with $n = 0-3$ showing an europium−oxygen (water) distance for the first coordination sphere at about 2.5 Å. The less well-defined peaks around 4.8 Å represent oxygen atoms of water molecules in the second coordination sphere.

The last two columns of Table 1 give the molecular dynamics calculation of the Eu−O and Eu−H distances of the coordination for each of the $Eu(dpa)_n$ complexes. The distances were calculated from radial density functions (RDF) for H and O shown in Figures 4 and 5.

Agreement between the MD calculation of the number of coordinated water molecules, x and the luminescence based calculation, $x(1)$ is quite good. The largest difference is for the $x(MD) = 6.5$ and $x(1) = 6.0$ for $Eu(dpa)^+$. It might be noted however that the simulated radial distances r(Eu−O) and r(Eu−H) are greater for this complex, presumably due to the increased average total coordination number (9.5) and thus the impact of the coordinated water on the luminescence decay might be expected to be attenuated. A calculation of x based on the luminescence decay constant under these circumstances would be expected to underestimate the true water CN. This suggests that one of the sources of the ±0.5 H_2O uncertainty in eq 1 is the slight variability in the Eu(III)−H_2O coordination distance which exists even for water molecules that are considered to be directly coordinated.

It is interesting to note the differences between the RDFs in Figures 4 and 5 for the peaks representing the waters in the second coordination sphere. Clearly, the number of water molecules and the average coordination distance are variable quantities and any contribution, k_{outer}, to the decay rate constant for the $Eu^{3+}(^5D_0)$ state would likewise be expected to be variable.

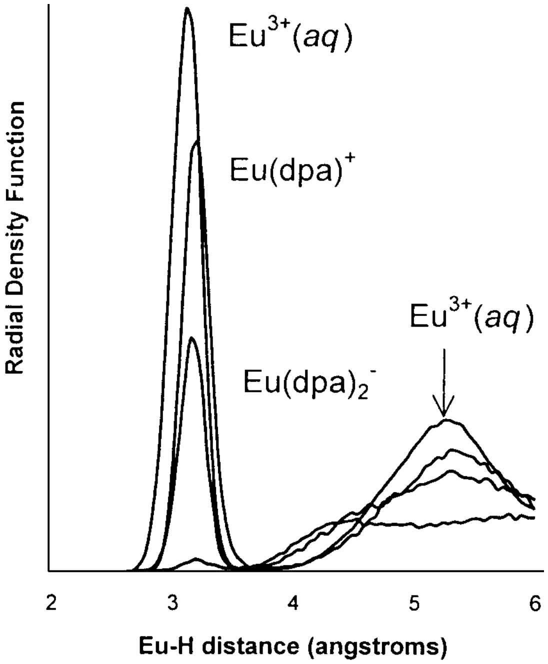

Figure 5. Calculated radial density functions for $Eu(dpa)_n$ with $n = 0-3$ showing an europium−hydrogen distance for the first coordination sphere at about 3.1 Å. The less well-defined peaks around 5 Å represent hydrogen atoms of water molecules in the second coordination sphere.

V. Conclusion

The rate constants for decay of the $Eu^{3+}(^5D_0)$ excited state have been measured for $Eu(dpa)_n$ with $n = 0-3$ in H_2O and D_2O. The differences in the rate constants, $k_n(H_2O) - k_n(D_2O)$ reflect the sequential displacement of approximately three water molecules with addition of each dpa^{2-} ligand. Parallel molecular dynamics calculations show good general agreement.

Evidence for electronic energy exchange between $Eu(dpa)^+$ and $Eu(dpa)_2^-$ that is significant on the time scale of the excited-state lifetime (10^{-4} s) is also presented. Eu^{3+}(aq) and $Eu(dpa)^+$ do not appear to exchange energy on this time scale for the mM concentrations used in this work. Likewise energy exchange between $Eu(dpa)_2^-$ and $Eu(dpa)_3^{3-}$ does not appear to be efficient, though a trend in the measured lifetimes of the individual species with dilution of a mixture indicates some slow exchange. The relative greater efficiency of electronic energy exchange between the $Eu(dpa)^+$ and $Eu(dpa)_2^-$ is likely attributable to the more favorable approach of these oppositely charged species.

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