Molecular dynamics simulation of trivalent europium in aqueous solution: A study on the hydration shell structure

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As a prelude to a spectroscopic investigation of doped wet gels, we have made molecular dynamics simulations of a very dilute $EuCl_3$ solution. The symmetry properties of the first hydration shell of Eu^{3+} have been determined. The 8 water molecules of this shell are roughly arranged according to the square antiprism D_{4d} pseudo-symmetry. Though the arrangement of oxygens is little distorted from regular positions, the orientation of the water molecules themselves is found to be not so well organized at room temperature. © *1996 American Institute of Physics.* [S0021-9606(96)51038-X]

I. INTRODUCTION

It is well known that optical spectra of luminescent ions in materials are very sensitive to the surrounding molecules through the local electrostatic field, that is also known as ligand or crystal field. Thus the interest of luminescent rare-earth ions as a local probe in different structures or materials has been widely demonstrated. Particularly, several works have been done where such probes have been employed in order to follow the densification process of sol–gel material leading to glass.[1–3]

In ordered materials, such as crystals, it is supposed that each doping ion that belongs to a specific site—sites exist in a reduced number—experiences the same field as that of identical ions in identical sites with well determined symmetry. From the spectroscopic features (splitting, intensity, polarization) one can determine structural and even dynamical site characteristics.

In disordered materials, in principle, each ion does not experience exactly the same field as another and therefore the properties of symmetry are roughly absent. Consequently, in such materials it is harder to draw a conclusion on the local structure by means of spectroscopic measurements and crystal field calculations.

To remedy these difficulties, several authors have chosen to simulate models of disordered structures.[4–7] From simulations, statistical data are collected and spectroscopic properties are calculated, reproducing the best structures and properties of materials. One of the most useful techniques of simulation is molecular dynamics (MD).

Our goal is to study each step of the densification process from a sol–gel to a well densified silica glass. In a previous paper we have described the near neighboring of Eu^{3+} ions in a porous silica glass.[7] That was to say in a microscopic structure near to that of a glass not completely densified. We have found a very low coordination number (<4) and explained such a result by the difficulty of the silica structure to satisfy the doping ion. We have also noticed the importance of non-bridging oxygens in porous silica. Now, looking at the other side of the densification process, we have to deal with the wet gel. In this case doping ions are entirely surrounded by water molecules. In conse-

quence, before directly studying wet gel it is preferable to begin with trivalent europium in aqueous solution.

Previous studies of rare-earth in aqueous solution were focused on coordination number, influence of concentration and water exchange reactions.[8–12] Recently Kowal *et al.*[13] have published an investigation of the rare-earth series in aqueous solution showing the change in the coordination number from 8 to 9 according to the ionic radius. However, concerning the trivalent europium cation, the hydration number has never been well established since this cation belongs to the middle of the series. Besides, experimental or simulation conditions are in every case different deciding factors.

In this paper, we present results on the water molecules arrangement within the first hydration shell in the case of a very dilute $EuCl_3$ aqueous solution. By means of MD calculations, we collect a set of data that enables one (i) to carry out a radial ordering study using classical radial distribution functions and (ii) to go further in the analysis of the structural characteristics of the first hydration shell.

Systematic angular ordering analysis led us to display in evidence a regular and specific structural arrangement of the 8-coordinated water molecules of the first hydration shell. This interesting result could present further perspectives, in thinking of the role of symmetry in the spectroscopic properties.

II. MOLECULAR DYNAMICS AND DETAILS OF THE SIMULATIONS

Molecular dynamics calculations are performed with the program MOLDY 2.6.[14] It can handle any assembly of rigid polyatomic molecules, atoms or ions and any mixture thereof. The *link cell* method is used to calculate short-range forces, and the Ewald sum technique to treat long-range electrostatic forces.

Each of our simulations is first equilibrated to lead to a stable total energy and a mean temperature of about 300 K. The MD simulations are then carried out at constant total energy, number of particles and at constant volume.

The system contains 252 water molecules, 1 ion Eu^{3+} and 3 ions Cl^- within a cubic box of $20 \times 20 \times 20$ Å (that corresponds to a very dilute solution since concentration is

TABLE I. Interaction potential parameters.

water–water	σ_{oo} (Å)	ε_{oo} (kcal mol^{-1})	charge
O (H$_2$O)	3.1536	0.155042	
M (H$_2$O)			-1.04
H (H$_2$O)			$+0.52$
ion–water	σ_{io} (Å)	ε_{io} (kcal mol^{-1})	charge
Eu^{3+}	2.4647	0.879130	$+3$
Cl$^-$	3.7854	0.135137	-1
ion–ion^a	σ_{ij} (Å)	ε_{ij} (kcal mol^{-1})	charge
Cl$^-$–Cl$^-$	4.4172	0.117788	
Eu^{3+}–Cl$^-$	3.0965	0.766267	

^{a}Parameters concerning Eu^{3+}–Eu^{3+} interaction are not necessary since only one cation is present in the MD box.

0.22 molal). We treat the water molecules as rigid bodies with a monomer geometry and pair potential that corresponds to the TIP4P model.[15] In this model the charges on H are situated at 0.9572 Å from the Lennard-Jones center at O. The negative charge is at site M located 0.15 Å away from O along the bissector of the H–O–H angle of 104.52°.

The interaction potentials between water and ion have the TIPS form:[15,16]

$$V_{iw}(r_{io}) = 4\varepsilon_{io}\left[\left(\frac{\sigma_{io}}{r_{io}}\right)^{12} - \left(\frac{\sigma_{io}}{r_{io}}\right)^6\right] + \sum_{j \in w} \frac{e^2}{4\pi\epsilon_0} \cdot \frac{q_i q_j}{r_{ij}}.$$

Here, ε_{io} and σ_{io} are Lennard-Jones parameters between oxygen on a given water molecule and an ion i, q_j is the charge at site j in water, and q_i is the charge on ion i. In addition, r_{io} and r_{ij} are the distances between ion i and an oxygen site of a water molecule and between ion i and a charge site j in water, respectively. In the same way one can define the interaction potential between two water molecules as

$$V_{ww}(r_{oo}) = 4\varepsilon_{oo}\left[\left(\frac{\sigma_{oo}}{r_{oo}}\right)^{12} - \left(\frac{\sigma_{oo}}{r_{oo}}\right)^6\right]$$
$$+ \sum_{i \in w_1} \sum_{j \in w_2} \frac{e^2}{4\pi\epsilon_0} \cdot \frac{q_i q_j}{r_{ij}}.$$

Finally, between two ions, the interaction potential reads

$$V_{ij}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{q_i q_j}{r_{ij}}.$$

All potential parameters are given in Table I. The parameters describing TIP4P water–ion interactions are from Refs. 15 for Cl$^-$ and 12, 16, 17 for Eu^{3+}. Parameters concerning ion–ion interactions are deduced from the usual Lorentz–Berthelot rules[18]

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2,$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}}.$$

A first run is carried out with a time step of 0.5 fs for 20 000 time steps (10 ps). The configurations of molecules and ions are considered every 20 time steps for radial distri-
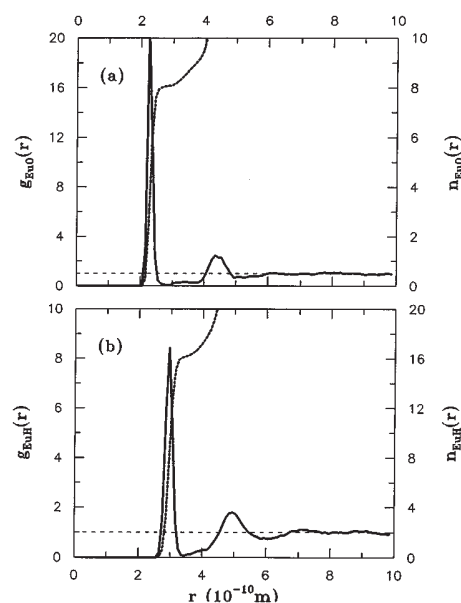

FIG. 1. Radial distribution functions (—) and corresponding running integration numbers (– –), for (a) Eu–O pair, (b) Eu–H pair.

bution functions calculations. A second run with the same time step is then performed for 200 000 steps (100 ps) where 200 configurations are stored for further analysis every 1000 steps (0.5 ps).

III. STRUCTURAL RESULTS

A. Radial ordering

Herein, we discuss the hydration shell structure mainly by means of atom–atom radial distribution functions $g_{\alpha\beta}(r)$ and the corresponding running integration numbers $n_{\alpha\beta}(r)$ defined as

$$n_{\alpha\beta}(r) = 4\pi\rho_\beta \int_0^r g_{\alpha\beta}(r')r'^2 dr',$$

where ρ_β is the number density of species β in the system. The value of this integral up to the first minimum of the g function is referred to as the coordination (hydration) number of species α by species β.

Figure 1 displays $g(r)$ and $n(r)$ functions concerning the Eu^{3+}-water radial arrangement. Due to the high ionicity of Eu^{3+}, the first peaks are very sharp and the minima are large and deep. This clearly displays the first hydration sphere and allows us to consider values of calculated hydration numbers as accurate ones. The oxygens of water molecules belonging to this first sphere are located from 2.01 to 2.85 Å away from the Eu^{3+} cation, whereas hydrogens are located from 2.60 to 3.45 Å. The sharpness of the hydrogen first peak and its position with respect to that of the oxygen can give some indication about the orientation of the water molecules, that is discussed further in the angular ordering section. Not so clearly but appreciably, a second hydration sphere appears in the 4–6 Å range. Concerning the counte-

rions Cl^-, they are found to remain far from Eu^{3+}, in such a way that they do not perturb significantly the first hydration shell.

The value of the $n_{Eu-\alpha}(r)$ integral up to the first minimum of the $g_{Eu-\alpha}$ function corresponds, to a very good precision, to the hydration number of Eu^{3+} by atoms α (oxygen or hydrogen). We find clearly 8.08 for oxygen and 16.15 for hydrogen. One should note that the hydration number of hydrogen is almost twice as that of oxygen, that supports the existence of a very well defined and stable first hydration shell.

Except a MD simulation of Auffinger et al.,[12] and x-ray diffraction measurements in concentrated EuCl₃ aqueous solution by Habenschuss et al.,[19] there exist no other results to our knowledge. In order to verify the validity of our simulation, we compare the simulated results with the experimental ones obtained by Habenschuss. The total structure function can be expressed as a sum of weighted partial structure functions[20] $h_{\alpha\beta}(k)$

$$H(k) = \sum_{\alpha \leqslant \beta} c_{\alpha\beta}(k) h_{\alpha\beta}(k),$$

which are related to the simulated $g_{\alpha\beta}(r)$ through

$$h_{\alpha\beta}(k) = \rho \int_0^R 4\pi r^2 [g_{\alpha\beta}(r) - 1] \frac{\sin(kr)}{kr} dr,$$

where ρ is the total density of the system and R the cut-off radius that is taken as half the MD box sidelength (10 Å). The weighted function $c_{\alpha\beta}(k)$ can be written in the form

$$c_{\alpha\beta}(k) = \left[(2 - \delta_{\alpha\beta}) x_\alpha x_\beta f_\alpha(k) f_\beta(k) \right] \Big/ \left[\sum_\alpha x_\alpha f_\alpha(k) \right]^2$$

with

$$\sum_{\alpha \leqslant \beta} c_{\alpha\beta}(k) = 1$$

and x_α and $f_\alpha(k)$ the mole fraction and the scattering amplitude for a particle of type α, respectively.

The scattering amplitudes are the fitted analytical functions obtained by Waasmaier et al.,[21] and the mole fractions are taken as those of the experimental solution (3.23 mol kg^{-1}). As justified by Pálinkás et al.,[20] it is more appropriate to treat the EuCl₃ solution as a three components system for the comparison between MD and x-ray diffraction results. Moreover, when evaluating the weighting functions $c_{\alpha\beta}(k)$, one could realize that the ion–ion contribution is negligible compared to those including the water. $H(k)$ consists then of only three partial structure functions: $h_{Eu^{3+}-H_2O}$, $h_{Cl^--H_2O}$, and $h_{H_2O-H_2O}$ where the water molecule is marked off by means of the point M already defined as the location of the negative charge of the molecule according to the TIP4P model. This fit to the simulation, where also ion–ion partial radial distribution functions are not significant enough because of poor statistics. The total x-ray weighted radial distribution function is then obtained through[22]

$$G(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^K kH(k) M(k) \sin(kr) dk,$$
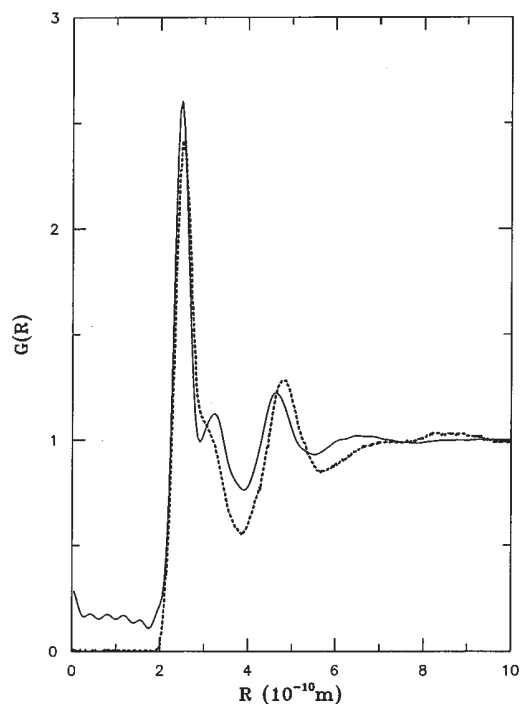

FIG. 2. Total x-ray weighted radial distribution function from simulation (—) and experiment (– –).

where $M(k)$ is the same modification function as used by Habenschuss,[19] which is put as $M(k) = \exp(-0.01k^2)$ in order to eliminate the truncation error of the Fourier transform and to minimize the uncertainty of the $kH(k)$ value at higher k values.

The total x-ray weighted radial distribution functions $G(r)$ obtained from the MD simulation and the experiment[19] are compared in Fig. 2. The superposition of the simulated and experimental first peaks reveals a very good agreement concerning the $Eu^{3+}-H_2O$ distances in the first hydration shell. The maxima of both simulated and experimental $G(r)$ are situated at 2.45 Å, that substantiates the values of 2.25 and 2.95 Å for the $Eu^{3+}-O$ and $Eu^{3+}-H$ distances, respectively, stemmed from the simulated partial radial distribution functions.

The second peak is assigned to the Cl^--H_2O distance. There is still a good agreement concerning the position, but its shape is more pronounced than for the experimental one. As in previous cases[8,23] the simulated system thus appears to be more structured than the experimental one. One also notices that positions discrepancies appear beyond 4 Å. As Meier[8] and Probst[23] explain, it is characteristic for the MD curve that the ion–water contributions appear in form of shoulders while in the experimental $G(r)$ they are hidden under the predominant water–water contribution. This seems to result from the too small sidelength of the MD box and from the fact that the ion–ion contributions are neglected because of their consequential poor statistics. Moreover, our partial radial distribution functions are stemmed from a low concentrated simulated solution because the purpose of this

work is to study the first hydration shell structure attempting to avoid the possible perturbation due to high concentration effects. This involves that the comparison with the concentrated experimental solution of Habenschuss presents some disagreements as observed especially for the long range $G(R)$. One has also to consider the experimental uncertainties and the fact that the Eu^{3+}–water potential model has not been widely tested in comparison with the water potential. However, for the short range structure (<4 Å) the comparison with x-ray diffraction can attest the validity of the simulation, and particularly the radial ordering of the first hydration shell of Eu^{3+}.

From experimental studies,[24] the hydration numbers of lanthanides are generally believed to be around 9 for the lighter ions and changing over to 8 somewhere between Nd^{3+} and Tb^{3+}. Concerning the hydration number of Eu^{3+}, many different values have so far been reported. Some authors have found a concentration dependence, but this is strictly true only at concentrations above 2 molal. From x-ray diffraction studies,[19] Habenschuss has obtained hydration number of 8.3. By the EXAFS method, Yamaguchi *et al.*[10] tend to 8.6 in an aqueous perchlorate solution and from luminescence decay constants in water a value of 9.6 has been determined by Horrocks *et al.*[24] This latter value is, however, given with an estimated error of 0.5, whereas the value of Habenschuss, that is also closer to ours (8.3 compared to 8.1), is given with an error of 0.1. The 9.6 value obtained by Horrocks is discussed by Tanaka[25] who considers, drawing on his own similar luminescence decay measurement, that a lower value is more probable. To sum up, it appears clearly that the experimental hydration numbers are slightly higher than the simulated one. Refinements to the MD simulation—such as improvement of the potential—able to lead to more accurate predictions, can be also envisaged; however, the agreement of our results with experimental data can ensure the relevance of the simulation and thus allow us to look further in dealing with the angular ordering study of the 8-coordinated first hydration shells.

B. Angular ordering

The analysis of RDF and associated running integrals has allowed us to obtain quantitative information about radial arrangement of water molecules around the Eu^{3+} cation. It appears interesting now to go further and attempt to get more indications about the spatial arrangement of the water molecules belonging to the first hydration shell.

To this purpose, we store a set of consecutive configurations, saving all coordinates of particles in order to study minutely the spatial ordering of the molecules. The choice of a suitable time interval between each stored configuration has been defined in considering the root mean squared displacements (RMSD) of the different compounds contained in the MD box. From those calculations, we have established that an interval of 0.5 ps ensures enough difference between two consecutive configurations. We have then performed a 100 ps run and saved all particles coordinates every 0.5 ps, that points out a set of 200 successive configurations.
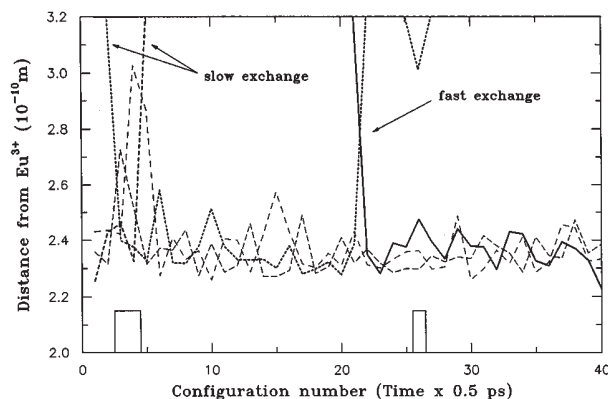
As a preliminary work, we evaluate the hydration num-

FIG. 3. Distance between oxygen of the water molecules and Eu^{3+} within the first hydration shell for a 20 ps time interval. For reasons of clarity only trajectories of water molecules have been included that present significant fluctuations with respect to the mean Eu–O distance. The lower steps indicate time intervals when the coordination number is 9.

ber using this set of configurations. To this purpose, a cut-off radius of 3.1 Å is considered and the water molecules contained inside the corresponding sphere are counted for each configuration. For this count the water molecules are marked off by means of a point G located 0.293 Å away from O along the bisector of $\angle$ H–O–H. We find an average value of 8.18 with a standard deviation of only 0.4, that is relevant with the value obtained from the partial RDF's.

In Fig. 3, we display the radial positions of oxygens for the first forty consecutive configurations. One can distinguish two kinds of cause for the increase of the hydration number from 8 to 9.

The first could be the temporary and superficial entry of a molecule as shown for the 26th configuration in Fig. 4. The second cause seems to result from a relatively slow exchange between two water molecules. One can easily see that, at the beginning of the sequence, a molecule enters into the hydration shell whereas another one leaves it approximately 1 ps later. During this time interval a hydration number of 9 is of course registered. Moreover, we note that another type of exchange is possible, whose swiftness does not permit us to point out an increase of the hydration number from 8 to 9. Finally, this set of establishments makes us to believe that the configurations with a hydration number of 9 are only transient stages and cannot correspond to a stable and significant feature. Thus we neglect those few configurations in order to perform a systematic study of the spatial arrangement for the configurations that present 8 water molecules in their first hydration sphere.

In order to discern a particular geometric arrangement, we evaluate the distribution of the O–Eu–O angles in the first hydration shell of the 8-coordinated configurations. As shown in Fig. 4(a) three preferential angles appear. The only polyhedron that presents similar angles is the regular square antiprism [Fig. 4(b)]. The similitude becomes remarkable when this regular square antiprism is slightly flattened in the direction of its quaternary axis [Fig. 4(c)].

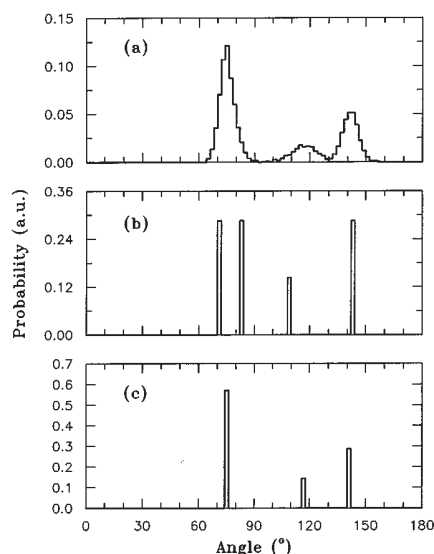One can notice that the resulting polyhedron corresponds

FIG. 4. Distribution of the O–Eu–O angles (a) for the first hydration shell of the 8-coordinated configurations, (b) for a regular square antiprism, and (c) for a regular square antiprism slightly flattened.

FIG. 5. Shot of a configuration stemmed from the simulation. One can easily see the arrangement of the 8 water molecules around the Eu^{3+} cation like the vertices of a square antiprism that are connected with dashed lines.

to the best steric arrangement that can be achieved by close packing of 8 spheres equidistant from a central point. In the present case, there is a perfect adjustment between the peak positions of the distribution and the characteristic angles of the modified square antiprism. In addition, the amplitudes are proportionally very similar.

From this first establishment, it seems that for the 8-coordinated hydration shells, the oxygens could be arranged like the vertices of a square antiprism. It becomes clearer when visualizing any configuration among the available set. A shot is displayed in Fig. 5 for an extremely weak distortion and therefore the regular arrangement is obvious.

With regard to the 8-coordinated complexes, the two common structures are the square antiprism and the dodecahedron: both may be considered as distortions of the simple cube resulting in reduced ligand–ligand repulsions. The ligand field stabilization energies of both structures are comparable and the choice between the two is a delicate balance of forces. At present there has been no satisfactory treatment of the problem of proper selection of geometry for 8-coordination.[26] Concerning aqueous solution, MD simulations allow us to display the square antiprism structure for the first hydration shell of the Eu^{3+} cation.

It is now interesting to orient every configurations in such a way that they get superposed to a maximum degree and then to evaluate the average distortion with respect to the square antiprism feature. The elaboration of a systematic method is a hard task because all the oxygen sites are equivalent. From symmetry considerations, the identification of a couple of oxygen's atoms belonging to a same plane perpendicular to the D_{4d} axis is enough to appoint the others. For each configuration we choose as characteristic angle the value that is the closest to 118°. This angle is assumed to correspond to a couple of vertices belonging to one of the two perpendicular planes described above. The bissector of

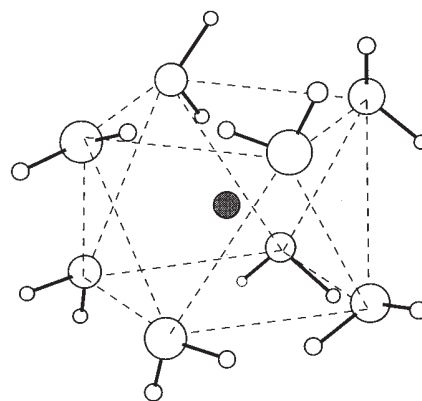the angle is then considered as the new quaternary axis, and the 6 oxygens left are marked therefrom. In this way, each configuration is rotated in order to mark every molecule of the first hydration shell. A finer rotation is finally performed to minimize the root mean square deviation between the real positions of oxygen's sites and the vertices of the reference square antiprism.

In every case, the distortion remains very weak. Considering the set of hydration shells, the mean distance between the position of an oxygen atom and its ideal location is less than 0.2 Å, with a standard deviation of 4.94×10^{-2} Å. That means clearly that the oxygens of water molecules are arranged like the vertices of a square antiprism polyhedron.

Consequently, the first hydration shell is supposed to present a D_{4d} pseudo-symmetry of interest. Particularly, concerning the study of ligand field parameters, most of them should be cancelled therefrom. Thus it seems interesting to verify whether the geometric center of the water molecules are so symetrically arranged as the oxygen sites.

A similar study is then performed with the G sites of the water molecules previously defined. The resulting establishment is that the square antiprism structure still remains, but is slightly more distorted. The mean distance between real and ideal positions of a site G amounts to 0.3 Å, with a standard deviation of 7.75×10^{-2} Å. This is simply due to the different orientation of each water molecule. Even if the oxygens are well arranged, the positions of sites G still depend on the orientation of the molecules. In the first hydration shells, the water molecules seem not to be enough aligned by the cation field: in such a way the symmetry is partially broken. Fig. 6 displays the distributions of cos ϕ for the first hydration shell, the second one, and the bulk water, where ϕ is the angle between the Eu–O direction and the bissector of $\angle$H–O–H. It is clear that the molecules of the first hydration shell are mainly oriented outwards, as it was already observed by means of the partial RDF. To some extent, this preferential orientation is still acceptable but significantly less prevalent. Nevertheless, the cation field is patently not strong enough, compared to the rotational kinetic
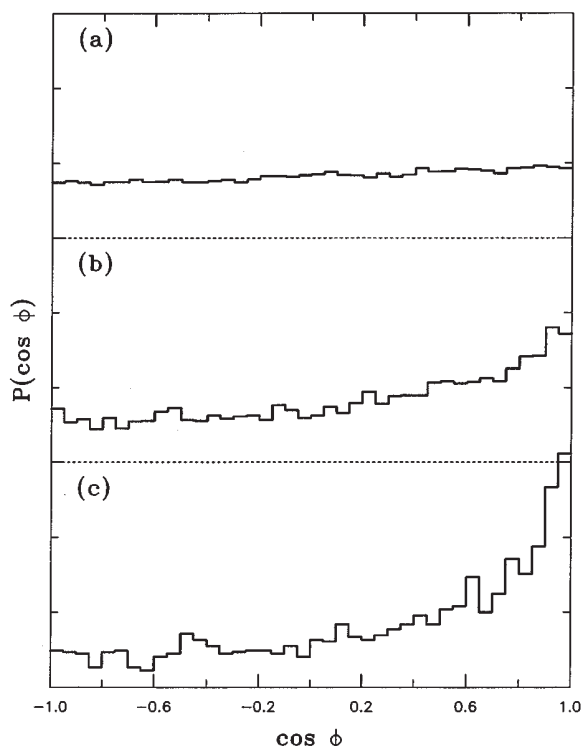
FIG. 6. Distribution of cos ϕ for the water molecules around the Eu^{3+} cation. ϕ is the angle between the Eu–O direction and the bissector of H–O–H. (a), (b), and (c) correspond, respectively, to the bulk water ($r>5.5$ Å), the second hydration shell ($3.1<r<5.5$ Å), and the first hydration shell ($r<3.1$ Å).

energy, to avoid that a non-negligible proportion of water molecules are disaligned even in the first hydration shell. In an ideal situation, the distribution of Fig. 6(c) should have gone to zero in the negative area of cos ϕ.

However, this angular ordering study has allowed us to display in evidence the geometry of the first hydration shell of Eu^{3+}. The square antiprism appears indeed like a remarkably stable arrangement. Besides, very recently, there came to our knowledge a paper by Kowall et al.,[27] where the structure of the first hydration shells of some trivalent lanthanides is also studied, and where the square antiprism is assigned for octaaqua ions.

IV. CONCLUSION

Beyond the scope of the study of the densification process from a sol–gel to a well densified silica glass, we had to make inquiries into the trivalent europium in aqueous solution before studying the wet gel structure. Important information has been obtained from a MD simulation of a very dilute EuCl₃ solution using the TIP4P potential for the water molecules.

A radial ordering analysis has enabled us first to validate the simulation by a satisfactory comparison with an x-ray diffraction experiment and then to display in evidence a well defined hydration shell composed of 8.1 water molecules. In order to get more indications about the spatial arrangement, we have performed a systematic angular ordering study that has revealed a clear specific structure. The water molecules of the first hydration shell are arranged like the vertices of a square antiprism polyhedron. This stable organization, especially for the oxygen atoms, has pointed out a D_{4d} pseudo-symmetry. This symmetry is of course partially broken because of the orientation of the water molecules that are not enough aligned by the cation field at room temperature.

Even if these remarkable symmetrical properties are limited to the very close environment of Eu^{3+}, it could have interesting consequences with regard to ligand field parameters calculations and therefrom to the spectroscopic properties of the cation used as a luminescent probe in the silica wet gel. Such investigations are in progress using both MD simulations and experimental data.

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