# The Dipole Polarizability of F<sup>-</sup> in Aqueous Solution. A Sequential Monte Carlo/Quantum Mechanics Study

Sylvio Canuto,<sup>1</sup> Kaline Coutinho<sup>1</sup> and Prasanta K. Mukherjee<sup>1,2</sup>

<sup>1</sup>Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP, Brazil <sup>2</sup>Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

#### Abstract

The sequential Monte Carlo/quantum mechanics methodology is employed to obtain the dipole polarizability of the atomic fluorine anion in an aqueous medium. Using Monte Carlo simulation, the structure of the water around the  $F^-$  anion is generated. Statistically relevant configurations are extracted for subsequent quantum mechanical calculations using the first solvent shell of water molecules and the density-functional theory, within an extensive basis set. The statistically converged result for the dipole polarizability of the  $F^-$  anion in the presence of the first solvation shell of water molecules is  $10.56 \pm 0.66a_0^3$ . This value is considerably reduced compared to the free atomic anion calculated as  $20.59a_0^3$  but still very large compared to the free neutral atom calculated as  $3.88a_0^3$ .

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### 1. INTRODUCTION

The static dipole polarizability is the linear response of an atomic or molecular system to the application of a weak static electric field [1]. It relates to a great variety of physical properties and phenomena [2–5]. Because of its importance, there have been numerous *ab initio* calculations of isolated atomic and molecular polarizabilities [6–14]. Particular theoretical attention has been dedicated to the polarizability of free atomic anions [15–21] because of its fragility and difficulty in obtaining direct experimental results. In recent years theoretical studies have

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been initiated to find the effect of surrounding medium on the electronic properties 48 of atomic or molecular systems. Understanding these solvent effects is important 49 for rationalizing experimental data in general. Some progress has been achieved 50 by treating solvent effects using the so-called continuum models [22-26], where 51 the solvent is described by its macroscopic constants such as the dielectric 52 constant and index of refraction. Solvent effects in dipole polarizabilities and 53 hyperpolarizabilities have been studied using continuum theories [27–31]. 54 Although very successful in some contexts, the statistical nature of the liquid 55 environment is not considered in such models. The proper treatment of liquid 56 systems has to consider its statistical nature [32,33]. Indeed, for nonzero 57 temperature there are many possible geometrical arrangements of the molecules 58 of the liquid with equivalent probability. Thus, liquid properties are best described 59 by a statistical distribution [34–37], and all properties are obtained from statistical 60 averaging over an ensemble. 61

In this paper we use the sequential Monte Carlo/quantum mechanics (S-MC/OM) 62 methodology [38–41] to obtain the dipole polarizability of the atomic fluorine anion 63 in an aqueous medium. We first generate the water environment around  $F^{-}$  using 64 Metropolis Monte Carlo. Next, statistically relevant configurations are separated 65 and submitted to quantum mechanical calculations. Several QM calculations are 66 necessary to obtain the ensemble average that is necessary to characterize the 67 statistical nature of the liquid. Statistically converged results are obtained. In the 68 present study the dipole polarizability of  $F^{-}$  in water is obtained using density-69 functional theory (DFT). We compare the dipole polarizability in the condensed 70 liquid phase with that for the gas phase. Because of the diffuse nature of the ground 71 state of the anionic system, it is expected that the confinement due to the condensed 72 medium will decrease the dipole polarizability. Currently, confined states are of great 73 interest [42,43]. Understanding this confining effect is also of interest in relation to the 74 absorption spectra leading to excited Rydberg states [44]. 75

#### 2. METHODS

#### 2.1. Monte Carlo simulation

81 The Monte Carlo (MC) simulation is performed using standard procedures [33] 82 for the Metropolis sampling technique in the isothermal-isobaric ensemble, where 83 the number of molecules N, the pressure P and the temperature T are fixed. As 84 usual, we used the periodic boundary conditions and image method in a cubic box 85 of size L. In our simulation, we use one  $F^-$  embedded in 1000 molecules of water in normal conditions (T=298 K and P=1 atm). The F<sup>-</sup> and the water molecules 86 87 interact by the Lennard–Jones plus Coulomb potential with three parameters for each interacting site *i* ( $\varepsilon_i$ ,  $\sigma_i$  and  $q_i$ ). 88

$$U_{ab} = \sum_{i}^{\text{on a}} \sum_{j}^{\text{on b}} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j e^2}{r_{ij}}$$
(1)

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where *i* and *j* are the sites in system a and b, respectively,  $r_{ij}$  is the interatomic distance between the sites *i* and *j*, *e* is the elementary charge,  $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$  and

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 $\sigma_{ii} = (\sigma_i \sigma_i)^{1/2}$ . For the water molecules we used the SPC [45] parameters and for 95 the anion  $F^-$  the OPLS [46] parameters. In the calculation of the pair-wise 96 energy, each molecule interacts with all other molecules within a center of mass 97 separation that is smaller than the cutoff radius  $r_c = L/2$ . For separations larger 98 than  $r_{c}$ , we use the long-range correction of the potential energy [33]. The initial 99 configuration is generated randomly, considering the position and the orientation 100 of each molecule. One MC step is concluded after selecting one molecule 101 102 randomly and trying to translate it in all the Cartesian directions and also rotate it 103 around a randomly chosen axis. The maximum allowed displacement of the 104 molecules is auto-adjusted to give an acceptance rate of new configurations 105 around 50%. The maximum rotation angle is fixed during the simulation in  $\pm 15^{\circ}$ . 106 The simulation was performed with the DICE program [47].

The full simulation involves a thermalization stage of about  $15 \times 10^6$  MC step followed by an averaging stage of  $60 \times 10^6$  MC steps. During the averaging stage, the density was calculated as  $0.989 \pm 0.007$  g/cm<sup>3</sup> in agreement with the result for liquid water. Radial distribution functions (RDFs) and liquid configurations are also generated during the averaging stage in the simulation. After completing the cycle over all 1000 molecules, a configuration of the liquid is generated and separated. Thus, the total number of configurations generated by the MC simulation is 60,000.

As quantum mechanical calculations will be performed on the configurations 115 generated by the MC simulation, it is important to optimize the statistics. 116 Configurations that are statistically very correlated will not give important 117 additional information. Therefore, we calculate the auto-correlation function 118 of the energy, C(i) [38], to obtain the interval of correlation  $\tau$ , where the 119 configurations are statistically uncorrelated, i.e., have less than 13% of statistical 120 correlation [38,39,48,49]. For Markovian processes, C(i) follows an exponen-121 tially decaying function [50,51], that after integration gives the interval of 122 correlation,  $\tau$ . Figure 1 shows the calculated auto-correlation function of the 123





energy calculated for the configurations generated by the anion F<sup>-</sup> in water and 142 the best fit of a doubly exponential decay function. From this exponential 143 function, we obtain the interval of correlation  $\tau \sim 200$ . Therefore, from the 144 60,000 successive configurations generated by the MC simulation, we select 300 145 statistically uncorrelated configurations separated by an interval of 200 that 146 represent the entire simulation [48]. As can be seen, however, the statistically 147 converged result for the dipole polarizability of  $F^-$  is obtained using only 60 148 configurations. 149

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### 2.2. Quantum mechanical calculations

<sup>153</sup> The major interest of this paper is the calculation of the polarizability,  $\alpha$ , of the <sup>154</sup> anion F<sup>-</sup> in an aqueous solution. Using the supermolecular approach, we <sup>155</sup> calculated for several configurations obtained from the simulation, the polariz-<sup>156</sup> ability of F<sup>-</sup> surrounded by the first solvation shell (*n* water molecules) and <sup>157</sup> subtracted the polarizability of these *n* water molecules without the F<sup>-</sup>, i.e.,

$$\alpha(\mathbf{F}^{-} \text{ in solution}) = \alpha(\mathbf{F}^{-} + n\mathbf{H}_2\mathbf{O}) - \alpha(n\mathbf{H}_2\mathbf{O})$$
(2)

Assuming this separability is an approximation that has been successfully used before [30,52].

As the appropriate Boltzmann weights are included in the Metropolis Monte Carlo sampling technique, the average value of the polarizability, or any other property calculated from the MC data, is given as a simple average over all the values calculated for each configuration.

The quantum mechanical polarizability is calculated using the DFT, with B3P86 (Becke's three-parameter functional [53] with the non-local correlation provided by Perdew [54]). The basis set used for the water molecules is 6-311 + +G. Because of the very diffuse nature of the anion F<sup>-</sup>, the basis set used is the specially designed, and very extensive, fully uncontracted 14s 9p 6d 2f Gaussian-type orbitals [55]. All the QM calculations were made with the Gaussian98 program [56].

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### 177 **3. RESULTS**

### 179 **3.1. Solvation shells and the hydrogen bonds**

The molecular structure of liquids is best analyzed using the concept of RDF. 181 This is of particular importance in solute-solvent structures as it defines the 182 solvation shells around the solute molecule. Therefore, we analyzed the solvation 183 of the anion  $F^-$  using the RDF between the anion and the oxygen of the water 184 molecules, as shown in Fig. 2. At least three solvation shells are well defined. 185 The integration of these peaks defines the coordination number, or the number of 186 water molecules in each solvation shell. The first shell that ends at 3.15 Å with a 187 maximum at 2.65 Å has, on average, 6.6 molecules of water. The second shell, 188

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**Fig. 2.** The radial distribution function between  $F^-$  and the oxygen atom of water.

ending on 5.50 Å with a maximum at 4.45 Å, has 25 molecules of water and the third, which goes to 7.60 Å with a maximum at 6.75 Å, has 64 molecules of water.

More detailed analysis of the first solvation shell of the F<sup>-</sup> can be obtained by the identification of the hydrogen bonds (HBs) formed between the water molecules and the anion. A very efficient procedure to identify the HBs in liquids is obtained using a geometric and energetic criteria [49,57–59]. We consider here a hydrogen-bonded structure when the distance  $R_{\rm F}$   $\leq 3.15$  Å, the angle  $\Theta(\text{FOH}) \leq 35^\circ$  and the binding energy is larger than 14.5 kcal/mol. This geometric criterion was obtained from the radial and angular distribution functions. The energetic criterion was obtained from the distribution of the pair-wise energy shown in Fig. 3. In this figure, there is a clear peak in the region of higher energy that characterizes the HBs for interacting energies larger than -14.5 kcal/mol. Thus, using the geometric and energetic criteria, in the 300 MC configurations we 





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**Fig. 4.** Illustration of one structure of the  $F^-$  and 6 hydrogen-bonded water molecules obtained from the simulation of the aqueous solution.

find that in 7% of the configurations the  $F^-$  forms HB with 5 water molecules, in 52% forms 6 HBs, in 39% forms 7 HBs and in only 2% it forms 8 HBs. This gives an average of 6.3 HBs. Therefore, we used all the 156 most probable structures, one  $F^-+6H_2O$  hydrogen bonded, for the subsequent quantum mechanical calculations. Recent simulation of  $F^-$  in water suggested instead a number of 5 water molecules in the first shell [60]. Figure 4 shows, as an illustration, one of the structures obtained here for the first solvation shell. The calculated average of the distance F···H is  $1.68 \pm 0.13$  Å, F···O is  $2.66 \pm 0.12$  Å and the binding energy is  $20.1 \pm 2.6$  kcal/mol. 

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### 3.2. Polarizability in solution

The dipole polarizability of the free F<sup>-</sup> anion has been of substantial interest in the past [61–64] and the accurate result is estimated between 18 and  $21a_0^3$ , after inclusion of the very important electron correlation effects. The use of pre-fabricated basis is not recommended in this case. The Hartree-Fock (HF) and second-order MP2 results for the dipole polarizability of the free F<sup>-</sup> anion, using the aug-cc-pVTZ basis [65], are only 7.09 and  $8.89a_0^3$ , respectively. All calcula-tions described next were made with the 14s 9p 6d 2f basis set [55]. The HF result with this basis is  $10.9a_0^3$ , in good agreement with the estimated numerical HF result of  $10.7a_0^3$  [66]. The MP2 result using the same basis is  $17.2a_0^3$  [61]. The use of density-functional methods in this basis gave a better performance. Hybrid functionals, such as the popular B3LYP, B3PW91 and B3P86, gave results of 21.95, 21.20 and  $2.59a_0^3$ , respectively. For the calculations of the polarizability in solution we selected the B3P86 functional. Using the configurations extracted from the MC simulation, composed of the  $F^-$  anion and the six surrounding water molecules, corresponding to the first solvation shell, we calculated the dipole polarizability. Figure 5 shows the calculated results for the polarizability in solution. The converged result in water is  $10.56 \pm 0.66a_0^3$ . The uncertainty of  $0.66a_0^3$  is the standard deviation As the result indicates, there is a considerable 

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**Fig. 5.** Convergence of the average value of the polarizability of  $F^-$  in aqueous solution with respect to the number of MC structures included in the quantum calculation. Statistical error is also shown.

reduction of the dipole polarizability compared to the free atomic anion. For reference, the calculated dipole polarizability of free neutral F, using the same theoretical method, is  $3.88a_0^3$ , in good agreement with the experimental value of  $3.8a_0^3$  [5]. The polarizability change from  $20.59a_0^3$  to  $10.56\pm0.66a_0^3$  corresponds to a very large reduction (~49%). This reduction is similar to the case of  $Cl^{-}$ studied by Morita and Kato [52] who obtained a reduction of 37%. Our theoretical estimate uses only the interaction with the first solvation shell. Inclusion of the outer shells may still affect the result. The standard deviation for the dipole polarizability in solution reflects the large variation seen in the liquid case. Figure 6 shows the statistical distribution of such values. 





The changes in the dipole polarizabilities in solution using continuum theories have been questioned by van Duijnen et al. [67,68]. While most continuum theories yield an increase in the dipole polarizability, their studies suggest a reduction, compared to the isolated gas phase result. The present  $F^-$  anion case is interesting in this aspect because of the diffuse nature of this reference solute system. A considerable decrease is obtained here and the trend shows similarity with the results for the diffuse anionic atomic system  $Cl^{-}$  [52].

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## 4. CONCLUDING REMARKS

341 The sequential Monte Carlo/quantum mechanics methodology has been employed 342 to obtain the dipole polarizability of the atomic fluorine anion in liquid water. 343 Using Monte Carlo simulation, the structure of the water around the  $F^-$  anion 344 is generated. The auto-correlation function of the energy derived from the 345 simulation is calculated and analyzed. From this, statistically relevant configura-346 tions are extracted for subsequent quantum mechanical calculations. Using the RDF we separate the first solvation shell of water molecules around the anion. 347 348 Density-functional calculations within the hybrid B3P86 exchange correlation functional have been performed using an extensive basis set. Statistically 349 converged result for the dipole polarizability of the F<sup>-</sup> anion in the presence of 350 the first solvation shell of water molecules is  $10.56 \pm 0.66a_0^3$ . This value is 351 considerably reduced compared to the calculated free atomic anion calculated as 352  $20.59a_0^3$  but still very large compared to the free neutral F calculated as  $3.88a_0^3$ . 353 This reduction can be understood in terms of liquid confinement, which in general 354 355 reduces the diffuseness of the electronic charge cloud of the solute molecule.

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