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## Delocalized water and fluoride contributions to Dyson orbitals for electron detachment from the hydrated fluoride anion

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The experimental vertical electron detachment energy (VEDE) of aqueous fluoride,  $[\text{F}^-(\text{H}_2\text{O})]$ , is approximately 9.8 eV, but spectral assignment is complicated by interference between  $\text{F}^-$  2p and  $\text{H}_2\text{O}$  1b<sub>1</sub> orbitals. The electronic structure of  $[\text{F}^-(\text{H}_2\text{O})]$  is analyzed with Monte Carlo and *ab initio* quantum-mechanical calculations. Electron-propagator calculations in the partial third-order approximation yield a VEDE of 9.4 eV. None of the Dyson orbitals corresponding to valence VEDEs consists primarily of F 2p functions. These results and ground-state atomic charges indicate that the final, neutral state is more appropriately described as  $[\text{F}^-(\text{H}_2\text{O})^+]$  than as  $[\text{F}(\text{H}_2\text{O})]$ .

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### I. INTRODUCTION

The study of water and the influence of aqueous environments on molecules and ions are topics of widespread interest with special importance in biochemical processes.<sup>1</sup> Understanding aqueous solvation of ionic systems may open large avenues in biochemistry.<sup>2–4</sup> Halide ions have played a central role in several, recent studies of the solvation of anionic systems.<sup>5–7</sup> Of particular interest is the appearance of absorption transitions in water that are absent in the isolated ion. This effect is the so-called charge-transfer-to-solvent (CTTS)<sup>8,9</sup> that has attracted considerable attention in solvated  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . Ionic systems are of importance also because of their possible ability to induce or hinder breaking of hydrogen bonds in water.<sup>10</sup> Also of great and recent theoretical interest are the properties of  $\text{F}^-$  in water.<sup>11–16</sup> There is certainly an enormous change in the properties of water and of  $\text{F}^-$  in the composite solution. For example, the electron detachment energy of isolated  $\text{F}^-$  is known experimentally to be close to 3.4 eV.<sup>17,18</sup> In water, the vertical electron detachment energy (VEDE) of this anion has been measured close to 9.0 eV (Refs. 19 and 20) with a huge, concomitant solvent effect of 5–6 eV. It is this large increase in the electron binding energy of halide anions that allows for the existence of stable excited states that are not possible in the gas phase. This change in the binding energy of the excess electron is thus at the origin of the CTTS states. Investigations of these anions in solution can be divided in two major lines of interest. The first and the most exploited one is the microsolvation of anionic species in clusters.<sup>11–13</sup> The second is oriented toward studies in solution.<sup>14–16,21</sup> For example, there are many investigations devoted both to experiments and calculations<sup>22</sup> on  $\text{F}^-(\text{H}_2\text{O})_n$  clusters where  $n$  is a small, posi-

tive integer. Much has been learned using the microsolvation approach, but extension to liquid solution can be made only with great care. First, by adopting the microsolvation approach, it is not clear how large the cluster should be to allow for comparison with the bulk situation. Of even greater importance for liquid solutions is the large number of possible molecular arrangements around the ion that a rigid, minimum-energy structure cannot represent. In fact, at non-zero temperature a statistical approach should be used and any property will represent a statistical average. Finally, whereas the excess electron in a cluster system also may be on the surface, in the bulk it is confined as an interior state.<sup>13,14,22</sup>

Although theoretical studies have been presented for some halides, it seems that a detailed analysis of the vertical electron detachment of  $\text{F}^-$  in water is still missing. In this work, we theoretically obtain the VEDE of  $\text{F}^-$  in bulk water at room temperature and analyze the electronic structure of the anionic system in solution. We use Monte Carlo (MC) simulation to generate liquid structures of the anionic solution and subsequently submit these structures to quantum-mechanical (QM) calculations. From this strategy, we obtain the electronic configuration of the system, the distribution of the extra charge and the VEDE. For this latter property, we use *ab initio*, electron-propagator methods that have proven reliable in studies of gas-phase molecules and anions such as water and  $\text{F}^-$ . In the present work, good agreement with experiment is obtained but analysis of the molecular orbitals indicates that the fluoride anion's contributions are distributed over many energy levels. In aqueous solution, the valence electrons are highly delocalized over the surrounding water molecules. Water molecules do not constitute a simple solvent and, in fact, most of the ejected electron upon detachment is removed from water, not the fluoride anion.

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## II. METHODS

Metropolis MC simulation is performed in the isothermal-isobaric  $NPT$  ensemble using standard procedures.<sup>23</sup> We used periodic boundary conditions and the image method in a cubic box of size  $L$  containing one fluoride anion embedded in 1000 molecules of water in normal conditions ( $T=298$  K and  $P=1$  atm). The fluoride anion and the water molecules interact by the Lennard-Jones plus Coulomb potential with three parameters for each interacting site  $i$  ( $\epsilon_i$ ,  $\sigma_i$ , and  $q_i$ ), where  $i$  and  $j$  are the sites in the system and  $\epsilon_{ij}=(\epsilon_i\epsilon_j)^{1/2}$  and  $\sigma_{ij}=(\sigma_i\sigma_j)^{1/2}$ . For the water molecules, we used the single point charge (SPC)<sup>24</sup> parameters and for the fluoride anion, the optimized parameters for liquid simulation (OPLS)<sup>25</sup> parameters. In the calculation of the pairwise energy, the fluoride anion interacts with all water molecules within a center-of-mass separation that is smaller than the cutoff radius  $r_c=L/2$  (that is approximately 15.5 Å in this case). For separations larger than  $r_c$ , we use the long-range correction of the potential energy.<sup>23</sup> The simulation was performed with the DICE program.<sup>26</sup>

The entire simulation involves a thermalization stage of about  $1.5 \times 10^7$  MC steps followed by an averaging stage of  $6.0 \times 10^7$  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. After the simulation, we sample configurations having less than 13% of statistical correlation.<sup>27–29</sup> Fifty configurations suffice to obtain statistically converged results as will be shown in Sec. III B.

These configurations are submitted to QM calculations and we now discuss the QM model adopted and the size of the supermolecular structures, that is, the number of water molecules around the anion. Because the QM calculations use a reference wave function that is antisymmetric over the entire solute-solvent system, the electron density of the fluoride anion may be delocalized over the water region.

QM calculations of the VEDEs of the anionic system are performed using the electron propagator method in the partial third-order (P3)<sup>30,31</sup> and renormalized partial third-order (P3+) approximations<sup>32</sup> with the 6-311+G(2df) basis set for fluorine and the 6-311G(d,p) basis set for the oxygen and hydrogen atoms. Satisfactory predictions of electron binding energies of closed-shell species have been obtained with these methods, which include orbital relaxation and correlation corrections to canonical, Hartree–Fock orbital energies. For every electron binding energy calculated with electron propagator methods,<sup>33</sup> there is an associated Dyson orbital ( $\Phi^{\text{Dyson}}$ ) defined by

$$\Phi^{\text{Dyson}}(x_1) = N^{1/2} \int \dots \int \Psi_{\text{initial}}(x_1, x_2, x_3, \dots, x_N) \Psi_{\text{final}}^* \times (x_2, x_3, x_4, \dots, x_N) dx_2 dx_3 dx_4 \dots dx_N, \quad (1)$$

where  $N$  is the number of electrons in the initial state ( $\Psi_{\text{initial}}$ ),  $N-1$  is the number of electrons in the final state ( $\Psi_{\text{final}}$ ), and  $x_i$  is the compound, space-spin coordinate of electron  $i$ . In the present P3 and P3+ calculations, relaxation and correlations corrections to Koopmans results are included and each Dyson orbital is proportional to a canonical, Hartree–Fock orbital. The proportionality factor is the square

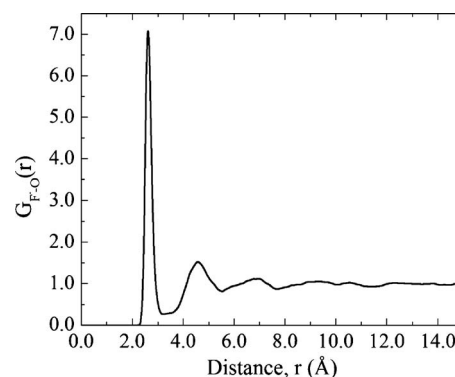


FIG. 1. RDF between the fluorine atom and the oxygen atoms of the water molecule.

root of the pole strength ( $p$ ), which equals the norm of the Dyson orbital according to

$$p = \int |\Phi^{\text{Dyson}}(x)|^2 dx \quad (2)$$

and may vary between zero and unity. For all outer valence (orbitals 15–35) VEDEs presented below, the pole strengths exceed 0.9 and therefore confirm the validity of the approximations that are inherent in the P3 and P3+ approximations.<sup>30–32</sup>

Some additional calculations also are done with second-order perturbation theory (MP2), the coupled-cluster singles and doubles approximation (CCSD)<sup>34</sup> and with density-functional theory using the hybrid exchange-correlation parameters of the B3LYP functional.<sup>35,36</sup> The QM calculations were performed with the GAUSSIAN-03 program.<sup>37</sup>

## III. RESULTS

### A. Solvation shells

Figure 1 shows the  $G_{F-O}(r)$  radial distribution function (RDF) that is used to characterize the structure of the water molecules around the anion. In this RDF, three solvation shells are well defined. The integration of these peaks defines the coordination number, or the number of water molecules in each solvation shell. The first shell, that ends at 3.15 Å, with a maximum at 2.65 Å, has, on average, six molecules of water. The second shell, ending at 5.50 Å with a maximum at 4.45 Å, has 25 water molecules and the third, which goes to 7.60 Å with a maximum at 6.75 Å, has 66 water molecules. Most of the QM calculations use six explicit water molecules electrostatically embedded in the field of the 60 remaining water molecules (treated as classical point charges). We thus consider all molecules within a distance of 7.60 Å from the anion. For some intermediate results, we also limit the calculations to the second solvation shell, thus including six explicit water molecules in the electrostatic embedding of the 19 remaining water molecules.

The structural properties of  $F^-$  in water have been subjected to several previous studies.<sup>14–16,38–40</sup> The results are variable. Heuft and Meijer<sup>16</sup> obtained the first peak position of the RDF at 2.66 Å and from this a coordination number of 5.1 water molecules. Koneshan *et al.*<sup>38</sup> obtained 6.3 molecules in the first coordination shell. Tongraar and Rode<sup>39</sup>

TABLE I. Vertical electron detachment energies of  $F^-$  in gas phase and in bulk water. Uncertainties are statistical errors.

System	Method	VEDE (eV)	Experiment
$F^-$	MP2 ( $\Delta E_{\text{total}}$ )	3.44	3.40, <sup>a</sup> 3.45 <sup>b</sup>
$F^-$	B3LYP ( $\Delta E_{\text{total}}$ )	3.46	
$F^-$	P3	3.73	
$F^-$	P3+	3.23	
$F^-+6H_2O$	P3+	$6.78 \pm 0.03$	8.7, <sup>c</sup> 9.8 <sup>d</sup>
$F^-+6H_2O$	P3	$6.95 \pm 0.03$	
$F^-+6H_2O+60H_2O(PC)$	P3	$9.41 \pm 0.05$	
$F^-+6H_2O$	Koopmans's theorem	$8.61 \pm 0.01$	
$F^-+25H_2O$	Koopmans's theorem	$9.03 \pm 0.01$	
$F^-+6H_2O+19H_2O(PC)$	Koopmans's theorem	$10.28 \pm 0.01$	
$F^-+6H_2O+19H_2O(PC)$	B3LYP HOMO energy	$5.88 \pm 0.05$	
$F^-+6H_2O+19H_2O(PC)$	B3LYP ( $\Delta E_{\text{total}}$ )	$8.18 \pm 0.04$	

<sup>a</sup>Reference 17.<sup>b</sup>Reference 18.<sup>c</sup>Reference 19.<sup>d</sup>Reference 20.

obtained 4.6 and Öhrn and Karlström<sup>15</sup> obtained 4.7 molecules in the first coordination shell. Our results are very similar to those obtained by Xantheas and Dang<sup>14</sup> that also obtained a first peak with a maximum at 2.7 Å and a first coordination shell composed of six water molecules. This result also is in agreement with experiment.<sup>40</sup> Thus the present simulation gives a reliable structure for subsequent QM calculations. As expected, each of the neighboring water molecules has one of its OH bonds pointing to the center where the fluoride anion is located.

## B. Vertical electron detachment energies

We first briefly analyze the electron detachment energy of isolated  $F^-$ . We use three theoretical methods to obtain the detachment energy, as seen in Table I. Using differences of MP2 total energies, we obtain an ionization energy of 3.44 eV, in excellent agreement with the experimental values<sup>17,18</sup> of 3.40 and 3.45 eV. With the B3LYP exchange-correlation functional, we obtain an energy difference of 3.46 eV. Using the partial third-order approximation of electron propagator theory gives a value of 3.73 eV. Extending this third-order result to the renormalized P3+ level,<sup>32</sup> we obtain 3.23 eV. A recent coupled-cluster calculation obtained 3.31 eV.<sup>5</sup> Overall, the theoretical results for the isolated anion are seen to be in good agreement with the experimental values, suggesting that these electronic structure approximations and basis sets are appropriate for describing the diffuse nature of the outer valence electrons.

Now we turn to the aqueous anion. There are two available experimental results.<sup>19,20</sup> Böhm *et al.*<sup>19</sup> obtained the He(I) photoelectron spectrum from the surface of a concentrated aqueous solution of CsF and observed signals that were identified as originating from  $F^-$ . From this, the detachment energy of  $F^-$  in aqueous solution was suggested to be 8.7 eV.<sup>19</sup> More recently, Faubel<sup>20</sup> estimated a value of 9.8 eV. There is some uncertainty in this VEDE. As pointed out in Ref. 5, the fluoride anion seems to be slightly off the trend

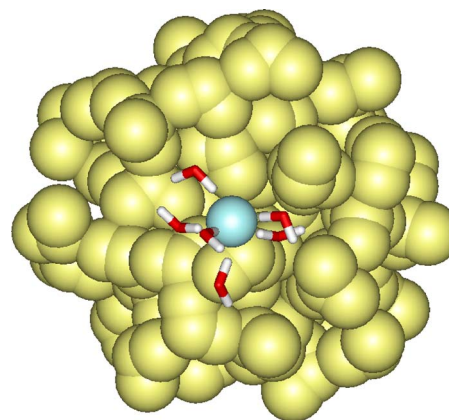


FIG. 2. Illustration of a configuration involving the fluoride anion surrounded by six explicit water molecules and electrostatically embedded in the field of the remaining 60 water molecules. All water molecules within 7.60 Å of the fluoride anion are included.

expected from results on  $Cl^-$ . Winter *et al.*<sup>5</sup> also remarked that there is a strong spectral overlap of the  $F^-$  2p levels and the location of the  $1b_1$  ionization in liquid water.

Results for the VEDE of the fluoride anion in water are presented in Table I where there is a comparison with values inferred from experiment. We discuss first the results obtained with electron propagator calculations, which are expected to be more accurate. For the anion and the six water molecules in the first solvation shell, the renormalized P3+ method gives 6.78 eV, which seems to be an underestimate. This result does not differ much if one uses the simpler P3 method. In this case, the result is slightly higher but still below the expected experimental region. The results improve considerably with the inclusion of electrostatic embedding that considers all 66 water molecules within a distance of 7.60 Å from the anion. The first six are explicitly included and the remaining outer 60 molecules are represented only by point charges. Figure 2 depicts one of these configurations. The result of 9.41 eV is our best estimate and it compares very favorably with the indirect experimental results, also shown in Table I.

Figure 3 (top) demonstrates that the average result of 9.41 eV obtained here for the detachment energy of  $F^-$  in aqueous solution is statistically converged with fifty configurations. In addition, Fig. 3 (bottom) shows a histogram and the corresponding Gaussian distribution of the calculated values.

Table I also shows some results obtained at the Hartree-Fock and B3LYP levels that will be useful in the qualitative discussions of the next section. Using total energy differences, the B3LYP calculations give an electron detachment energy of 8.18 eV, which can be considered a good, but slightly underestimated result.

Comparison of P3 and Koopmans (canonical, Hartree-Fock orbital energies) results in Table I indicate that relaxation and correlation effects on the lowest VEDE are large. These corrections also are large for higher VEDEs. However, for all outer valence transition energies corresponding to orbitals 15–35, the pole strengths exceed 0.9. Such results indicate that the Dyson orbitals strongly resemble canonical,



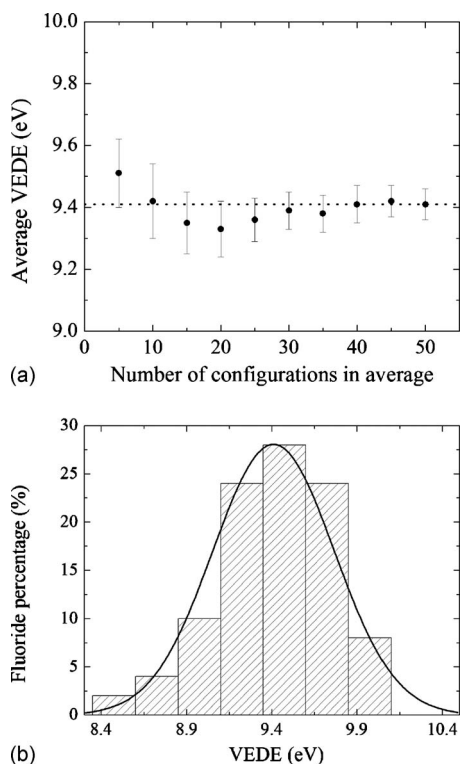


FIG. 3. Above: statistical convergence of the P3 electron propagator result for the  $F^- + 6H_2O + 60H_2O(PC)$  model. See Table I. Below: histogram and associated Gaussian distribution of the calculated values.

Hartree–Fock orbitals. The latter functions therefore may be used to qualitatively analyze changes in electronic structure that accompany electron detachment.

### C. Electronic structure changes upon ionization

Our previous calculations allowed us to provide an estimate for the VEDE of the hydrated  $F^-$  system. It is now important to discuss the corresponding changes in electron density. This discussion will rely on the analysis of the electron populations of all the occupied orbitals. In the present electron propagator calculations, Dyson orbitals corresponding to each electron binding energy are proportional to occupied, canonical, Hartree–Fock orbitals of the anion.

The QM system we are now considering consists of a fluoride anion surrounded by six water molecules. This choice leads to 70 electrons in 35 doubly occupied molecular orbitals. Figure 4 (top) shows the participation of fluorine basis functions in these orbitals. We clearly identify the two core electrons of the fluorine atom. The innermost orbital is F 1s and orbital number 8 in Fig. 4 corresponds to F 2s. (Six O 1s orbitals lie in between and do not have any electron density on the fluorine atom.) Excluding now the F 1s and 2s levels, there are thus six remaining valence electrons of the fluoride anion. The outermost occupied orbital [highest occupied molecular orbital (HOMO)], number 35, is seen to have less than 1% participation from fluorine basis functions. Hence the outermost occupied orbital is entirely located on the water environment. Figure 4 shows that there is not a single valence orbital that is primarily located on the fluorine. The first valence orbital that shows some appreciable

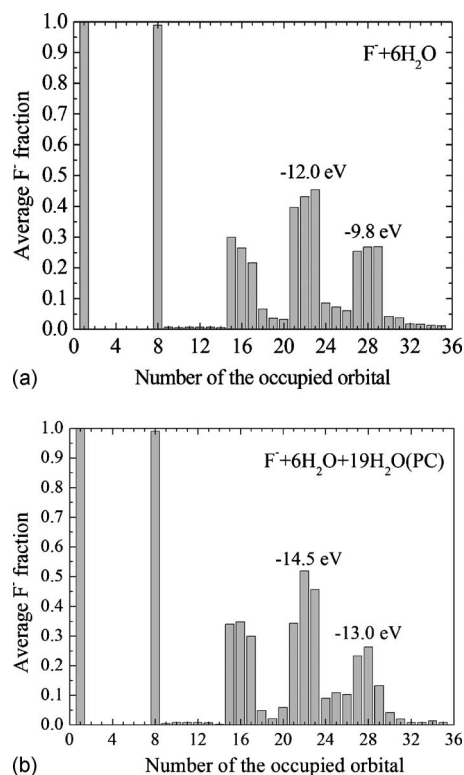


FIG. 4. Distribution of the 10 electrons of the fluoride anion among all 35 occupied orbitals of  $F^- + 6H_2O$  with (bottom) and without (top) electrostatic embedding.

population from  $F^-$  is number 29 (HOMO-6) with a participation of only approximately 25%. Actually, orbital 23 (HOMO-12) has the largest participation from the fluorine atom and this one in particular is seen to be only 45% localized on the fluorine. Figure 5 shows orbitals 35 and 23 and illustrates the distribution of the electron in the water environment. These results show that the valence electrons of the unsolvated fluoride anion are delocalized over the water environment. The six valence electrons of the unsolvated anion are distributed over many occupied orbitals (from 15 to 35) of the supermolecular system composed of  $F^-$  and six water molecules. Results obtained with electrostatic embedding (Fig. 4, bottom) show some numerical differences but do not change the qualitative picture just discussed. Clearly, valence electron detachment transitions in this system remove negative charge chiefly from water molecules.

The change in electronic structure that accompanies the

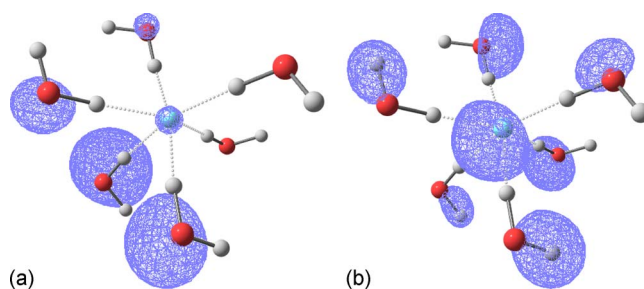


FIG. 5. Electron density of the HOMO (highest-occupied) and HOMO-12 molecular orbitals from a HF calculation on  $[F^- + 6H_2O]$ . These orbitals have 1% and 45% fluorine charges, respectively. See also Fig. 4.

TABLE II. Total charges on fluorine and surrounding water molecules for the anionic  $[\text{F} 6(\text{H}_2\text{O})]^-$  and the neutral  $[\text{F} 6(\text{H}_2\text{O})]$  systems.  $[(\text{B})-(\text{A})]$  indicates the total amount of charge removed in the ionization process. Several electron population analyses were used to estimate the charges.

Method	System	Site	HF			B3LYP		
			CHELPG	MK	Mulliken	CHELPG	MK	Mulliken
(A) $[\text{F} 6(\text{H}_2\text{O})]^-$		F	-0.826	-0.931	-0.843	-0.758	-0.862	-0.805
		$6(\text{H}_2\text{O})$	-0.174	-0.069	-0.157	-0.242	-0.138	-0.195
(B) $[\text{F} 6(\text{H}_2\text{O})]$		F	-0.675	-0.776	-0.816	-0.700	-0.790	-0.793
		$6(\text{H}_2\text{O})$	0.675	0.776	0.816	0.700	0.790	0.793
$[(\text{B})-(\text{A})]$		F	0.151	0.155	0.027	0.058	0.072	0.012
		$6(\text{H}_2\text{O})$	0.849	0.845	0.973	0.942	0.928	0.988
			0.841 <sup>a</sup>	0.835 <sup>a</sup>	0.970 <sup>a</sup>	0.914 <sup>a</sup>	0.899 <sup>a</sup>	0.983 <sup>a</sup>
			0.843 <sup>b</sup>	0.837 <sup>b</sup>	0.970 <sup>b</sup>	0.918 <sup>b</sup>	0.902 <sup>b</sup>	0.984 <sup>b</sup>

<sup>a</sup>The system was embedded in the electrostatic field of  $19\text{H}_2\text{O}(\text{PC})$ .

<sup>b</sup>The system was embedded in the electrostatic field of  $60\text{H}_2\text{O}(\text{PC})$ .

lowest VEDE can be elucidated by comparing the total electron populations of the  $\text{F}^-$  and water subsystems for a single configuration extracted from the simulation. Electron population may be analyzed using several charge localization procedures. First, we consider the simple Mulliken population analysis.<sup>41</sup> Next, we use charges from electrostatic potentials using a grid-based method (CHELPG)<sup>42</sup> and the Merz–Singh–Kollman<sup>43,44</sup> electrostatic fit (MK). These charges are obtained from Hartree–Fock and B3LYP calculations using the same basis set as before. The results are shown in Table II. First, we note that the original anionic  $[\text{F}(\text{H}_2\text{O})]^-$  system has its negative charge on the  $\text{F}^-$  anion. Upon removal of an electron, the  $[\text{F}(\text{H}_2\text{O})]$  system still has a negative charge on the F atom. The difference between the total charges for these two situations,  $[(\text{B})-(\text{A})]$ , indicates whence the electron has been removed. This difference is shown in Table II. The final  $[(\text{B})-(\text{A})]$  results demonstrate that in all theoretical schemes, the electron is removed from the water subsystem. For example, using the B3LYP level and the CHELPG procedure, our results indicate that approximately 94% (or 92%) of the negative charge has been removed from the water subsystem when calculations are carried out without (or with) electrostatic embedded. The final fluoride-water system is more appropriately described as  $[\text{F}^-(\text{H}_2\text{O})^+]$  than as  $[\text{F}(\text{H}_2\text{O})]$ . Spectral features associated to charge transfer states in small clusters of  $[\text{F}^-(\text{H}_2\text{O})_{n=1-4}]$  have been observed experimentally.<sup>11</sup> Considering the experimental values of 9.9 and 10.1 eV (Refs. 45 and 46) for the ionization energy of liquid water, it seems that in the case of the  $\text{F}^-$  anion in water, the first VEDE refers more to the  $1b_1$  orbitals of water molecules than to the F 2p orbitals. Our results also suggest that the ionization energy of water is only slightly perturbed by the fluoride anion.

Considering the removal of the electron from water, instead of the fluoride, one might consider the spin density distribution. The same calculations above indicate that the net spin of the neutral  $[\text{F}(\text{H}_2\text{O})]$  is located in water.

CCSD calculations also have been performed on the same  $\text{F}^-(\text{H}_2\text{O})_6$  and  $\text{F}(\text{H}_2\text{O})_6$  structures used in Table II. The norms of the  $T_1$  vectors are 0.009 and 0.02 for the anionic and uncharged species, respectively. The norms of the so-called A vectors are 1.2 in both cases. Therefore, correlation

effects have no qualitatively important effects on the electron densities that correspond to the Hartree–Fock reference states in the CCSD calculations. For the electron detachment from anionic to uncharged ground states, changes in Hartree–Fock, Mulliken atomic charges confirm the conclusion reached above: very little of the electron density differences corresponds to F 2p orbitals.

#### IV. DISCUSSION

Recent electron propagator calculations<sup>47</sup> on  $\text{F}^-(\text{H}_2\text{O})$  and  $\text{F}^-(\text{H}_2\text{O})_2$  carried out with large basis sets and the BD-T1 approximation have produced accurate assignments of photoelectron spectra. The BD-T1 approximation employs a Brueckner doubles (BD)<sup>48</sup> coupled cluster reference state and the entire  $f_3$  manifold of ionization operators and has been shown to produce accurate VEDEs for the fluoride anion and the water molecule. Complete geometry optimizations at the BD level with polarized, diffuse-augmented basis sets were employed in the calculation of VEDEs. At this level of theory, relatively flat profiles for proton motion between O and F are generated. The Dyson orbitals from these calculations were delocalized over F 2p and O 2p orbitals for the lowest transition energies. Dyson orbitals that were localized on F correspond to higher VEDEs.

Similar conclusions on delocalization of orbitals were reported in Ref. 12 for  $\text{F}^-(\text{H}_2\text{O})_n$  with  $n=1, 2$ , or 3. In this study, electron propagator calculations at the ADC(3) level were reported for anionic structures that were obtained with MP2 and augmented, double-zeta plus polarization basis sets. Dyson orbitals for the lowest VEDEs were delocalized over F and O centers. Only for higher VEDEs did the Dyson orbitals resemble F 2p functions.

These works indicate that the delocalization of Dyson orbitals corresponding to the lowest VEDEs of aqueous fluoride is not an artifact produced by unrealistic geometries near the anion that follow from the use of approximate intermolecular and ion-molecular potentials. Calculations of VEDEs based on full QM geometry optimization of small, anionic species also produce Dyson orbitals that are not confined to F 2p functions for the lowest final states.

## V. CONCLUSIONS

Vertical electron detachment from fluoride in water was studied using a sequential MC/quantum mechanics methodology. Statistically converged results obtained from P3 and P3+ electron propagator calculations on 50 configurations gave an average detachment energy of 9.4 eV, in agreement with experimental data. However, not a single Dyson orbital for electron detachment in the valence region is primarily built of F 2p functions. Atom charge analysis of the initial, anionic, and final, neutral systems indicates that the electron is ejected from water and that the final state is more appropriately described as  $[\text{F}^-(\text{H}_2\text{O})^+]$  rather than  $[\text{F}(\text{H}_2\text{O})]$ . This qualitative conclusion applies for the final state that corresponds to the lowest VEDE and for valence excited states of the uncharged system.

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