Microsolvation of F^- in Water

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Received: July 4, 2005; In Final Form: September 1, 2005

Microsolvation of F^- in water is studied by ionization and double ionization spectra of $(H_2O)_{1-3}F^-$ calculated by ab initio methods. It is shown that the presence of the fluorine electrons introduces many-body properties in the spectra which cannot be reproduced by the presence of a negative point charge. The increase of the solvation shell increases the complexity in particular of the double ionization spectra. Ionization and double ionization energies slowly increase with continued solvation, and many-body effects in the inner valence spectra become more prominent.

I. Introduction

Microsolvation of halide anions in water has been the subject of theoretical as well as experimental studies for quite some time. Mostly, the solvation process as such has been in focus of interest. Properties such as enthalpy or entropy changes due to solvation have been calculated and measured. The first measurement of enthalpy and entropy changes with continued microsolvation by adding more and more water molecules to clusters dates from the 1970s.[1]

In addition to the study of macroscopic quantities as solvation enthalpies and entropies of microsolvation clusters, the solvation process of halide anions has also been addressed on a more microscopic level. The progress in computational facilities and the development of more and more powerful methods for theoretical simulations made the prediction of ground-state structures possible, which facilitates the interpretation of experimental results. Furthermore, Monte Carlo and molecular dynamics simulations help to elucidate the process of solvation[2−6] as such.

Anionic microsolvation clusters have attracted particular interest, because they provide the possibility to study charge transfer to solvent states. The impact of the geometry of the cluster and of the size of the anion on the excitation energies of charge transfer to solvent precursor states, for example, was studied for the larger halides Cl^-, Br^-, and I^-.[7] The lowest ionized charge transfer to solvent states for the ionized H_2OF^- cluster have been addressed both theoretically[8] and experimentally.[9] Ionized states of small microsolvation clusters H_2OX^-, $X = F^-, Cl^-, Br^-$, are particularly interesting, because the ground-state geometries of the anionic and the ionized systems differ[9,10] and their different properties[10] and reaction dynamics[11] following electron detachment have been studied.

In this contribution, we address the microsolvation of the fluorine anion in water on the microscopic level of ionized and doubly ionized states. Water is certainly one of the most important solvents, and fluorine anions are rather ubiquitous. Fluorine anions are known to interact more strongly with the solvent water than the larger halides chlorine, bromine, or iodine. Whereas the latter are found at the periphery of aqueous microsolvation clusters, fluorine anions are found in a more central position; see ref 12 and references therein. Accordingly, a particularly important influence of fluorine on the properties of the solvent molecules can be expected. We analyze the impact of microsolvation on the fluorine anion and on the solvent molecules by means of ionization and double ionization spectra which are derived by ab inito propagator methods. Photoelectron spectroscopy is a powerful tool for the investigation of the electronic structure of clusters in general and has thus also been applied to study microsolvation clusters. It was applied to investigate microsolvation clusters of halide anion Cl^-, Br^-, and I^-;[13] recent studies are also available for F^-.[9] Photoelectron spectroscopy is a very powerful and useful tool to probe cluster properties. For example, photoelectron spectroscopy probing inner valence ionized states of rare gas clusters has been applied to confirm[14−16] the cluster-specific intermolecular Coulombic decay relaxation mechanism.[17] The interpretation of experimental data gained by photoelectron spectroscopy often needs theoretical calculations because of the complexity of the spectra. Theoretically derived photoelectron spectra are thus helpful to assign experimental data and provide a deep insight into the electronic structure of clusters and molecules.

Besides a detailed investigation of the microsolvation of the fluorine anion by a single water molecule, continued solvation by up to three water molecules is discussed. In addition to the ground-state structure, two slightly energetically higher-lying isomer structures of the cluster containing three water molecules are addressed in this contribution in order to show the impact of different bonding properties and of hydrogen bonds between different solvation shells.

II. Methods and Computational Details

All ionization and double ionization spectra have been calculated by means of propagator methods.[18−22] The third-order algebraic−diagrammatic construction scheme ADC(3)[23−25] has been applied to approximate the one-particle Green's function. Ionization energies and spectral intensities are available as poles and pole strengths, respectively, of this Green's function.

The following nomenclature is applied throughout this contribution. A 1h configuration denotes a configuration which is derived by removing one electron from one of the occupied orbitals of the Hartree−Fock ground-state Slater determinant. A 2h1p configuration denotes a single excitation upon a 1h

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10.1021/jp0536551 CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/25/2005

configuration, such that two electrons are removed from occupied orbitals of the Hartree−Fock ground-state Slater determinant and one electron is added to one of the virtual orbitals. 2p1h, 2h, and 3h1p configurations are to be understood accordingly.

The ADC(3) method reformulates the calculation of the poles and the pole strengths of the Green's function to a matrix eigenvalue problem. The formalism applied is based on the Dyson equation,[18] which leads to a coupling of the ionization and the affinity part of the Green's function. The configuration space from which the ADC(3) matrix is built up comprises all 1h and 2h1p configurations, but also all 1p and 2p1h configurations. The latter configurations determine the dimension of the matrix eigenvalue problem. As the 2p1h block of the ADC matrix mainly describes electron affinities and not ionization and because this block only couples indirectly via the 1p,1h block to the 2h1p block, its dimension can be reduced without loss of information in the ionization spectra by a few block-Lanczos iterations.[25] Ten block-Lanczos iterations have been applied here to reduce the dimension of the problem, such that the number of 2h1p configurations now determines the dimension of the matrix-eigenvalue problem. The aug-cc-pVDZ basis set,[32−34] obtained from a basis set library,[35] on all atoms has been used throughout all calculation for all but the $(H_2O)_3F^-$ cluster in its ground-state geometry. No diffuse functions have been placed at the site of the H-atoms for the latter during the ADC calculation because of limited computational resources. The dimensions of the ADC(3) matrix, after prediagonalization, are in the range between 2000 for H_2OF^- applying the aug-cc-pVDZ basis set and 30 000 for $(H_2O)_3F^-$ applying aug-cc-pVDZ for fluorine and oxygen and cc-pVDZ for the hydrogen atoms. A full diagonalization of the ADC(3) matrix was achieved for $(H_2O)_{1-2}F^-$, whereas the eigenvalues and eigenvectors of the ADC matrix were approximately determined by applying 400 block-iteration of the Lanczos algorithm[25,27,29] for $(H_2O)_3F^-$. The number of block vectors is equivalent to the dimension of the 1h,1p block of the ADC matrix.

In analogy to the ionization spectra, which are computed via the one-particle Green's function, double ionization spectra are derived by evaluating the particle−particle propagator. Double ionization energies are given as poles and spectral intensities as pole strengths of the particle−particle propagator. The problem of determining these quantities is reformulated as a matrix-eigenvalue problem according to a second-order algebraic−diagrammatic construction scheme ADC(2).[27,30] The ADC(2) scheme for the particle−particle propagator comprises all 2h and 3h1p configurations. Because of the large number of 3h1p configurations, the resulting matrix dimensions are very large. Consequently, the ADC(2) matrix is not stored on disk. Matrix elements are calculated when they are required for matrix × vector multiplication in a block-Lanczos diagonalizer.[31] Four hundred iterations of the block-Lanczos algorithm were sufficient to converge the interesting part of the eigenvalue spectra of the ADC(2) matrix.

Self-consistent field (SCF) energies and two-electron integrals from a Hartree−Fock SCF calculation by means of the Gamess-UK program package[26] are calculated as input quantities to the ADC(3) program package[25,27,28] and references therein and to the ADC(2) program package.[31]

III. Cluster Geometries

The geometries of the clusters H_2OF^- and $(H_2O)_2F^-$ have been reoptimized on the MP2 level using the aug-cc-pVDZ basis set mentioned in the preceding section according to the symmetry of the ground-state structures calculated before by several groups; see Baik et al. for a compendium.[36] The fluorine anion tends to be localized in the center of the cluster rather than at its periphery, as already mentioned in the Introduction. Two water molecules are bound to the fluorine anion in the ground-state structure of $(H_2O)_2F^-$. The tendency of the water molecules to bind via one of the H-atoms to fluorine and to build a H-bond to the second molecule by the other H-atom leads to the C_2 symmetric structure depicted in Figure 1. The water−fluorine bond is too strong to allow for a real O−H bond-though. The H_2OF^- cluster has been optimized in its well-known planar structure.

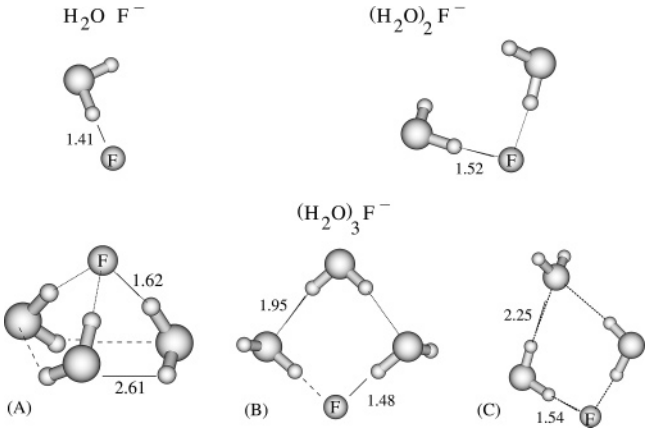

Figure 1. Ground-state geometries of the clusters $(H_2O)_nF^-$, $n = 1, 2, 3$. For $(H_2O)_3F^-$, the C_3 ground-state geometry (A) is shown together with the geometries of two isomers slightly higher in energy. In these, a third water molecule is bound to a $(H_2O)_2F^-$-like cluster by H-donor (B) and H-acceptor (C) bonds, respectively.

TABLE 1: Hartree−Fock and MP2 Energies of H_2OF^-, $(H_2O)_2F^-$, and the Three $(H_2O)_3F^-$ Clusters Shown in Figure 1, Calculated Using the aug-cc-pVDZ Basis Set

cluster	HF energy [H]	MP2 energy [H]
H_2OF^-	−175.5067	−175.9884
$(H_2O)_2F^-$	−251.5778	−252.2929
$(H_2O)_3F^-$ (A)	−327.6440	−328.5937
$(H_2O)_3F^-$ (B)	−327.6400	−328.5915
$(H_2O)_3F^-$ (C)	−327.6151	−328.5625

The ground-state structure of $(H_2O)_3F^-$ is less obvious, because it is not clear whether the third water molecule preferentially binds to fluorine, such that a C_3 symmetric structure is realized, or a cluster formation via two H-bonds to a $(H_2O)_2F^-$-like cluster fragment is more favorable. Several publications agree that a C_3 symmetric structure with three fluorine−water bonds is the ground-state structure.[12,36−38] We calculated the Hartree−Fock and MP2 energies by applying the aug-cc-pVDZ basis set for all atoms for the optimized structures of C_3 symmetric $(H_2O)_3F^-$ and of two isomers with a H-bond water molecule in the second solvation shell (Table 1). All isomers considered are depicted in Figure 1. Isomer B was also considered in the contributions cited above and found to be slightly higher in energy than isomer A, in agreement with our results. Isomer C, which contains a double H-acceptor bound second-layer water molecule, is less close in energy to the ground state. The comparison of its spectra to those of the two other isomers is, nevertheless, of interest, because it allows us to study the impact of different bonding properties on spectra.

IV. Impact of Solvation by One Water Molecule on Ionization and Double Ionization Spectra

A. The Influence of Microsolvation on Ionization Spectra. In this section, we demonstrate the influence of solvation by a

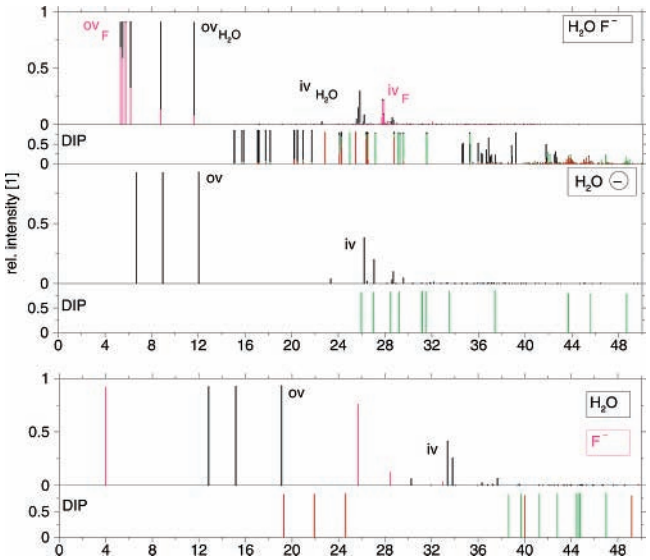

Figure 2. Ionization and double ionization spectra (DIP) of H_2OF^-, $H_2O\ominus$, H_2O, and F^-; the spectra of the latter two are shown in one graph. Each vertical line denotes a state at the ionization energy or double ionization energy indicated. Coloring of the ionization spectra: black, ionization on water; magenta, ionization on fluorine. Coloring of the double ionization spectra: green, double ionization of water; red, double ionization of fluorine; black, distributed hole charges, one electron is removed from water, the other electron from fluorine. "ov" and "iv" stand for ionization out of an outer valence and inner valence orbital, respectively.

single water molecule on the ionization characteristics of the fluorine anion. For completeness, we also investigate the influence of the fluorine anion on the ionization and double ionization of the water molecule. The ionization and double ionization spectra of the isolated water molecule and the fluorine anion as well as those of the cluster H_2OF^- are shown in Figure 2. For the sake of discussion, the corresponding spectra are also depicted for $H_2O\ominus$, which denotes water and a negative charge placed at the site of the fluorine anion in H_2OF^-. The valence ionization energies of these molecules and clusters are collected in Table 2.

1. Outer Valence Spectra. We address the outer valence ionization of the fluorine anion first. The computed outer valence ionization energy of the isolated fluorine anion in the gas phase is 3.97 eV (the experimental value is 3.4 eV[39]). The triple degeneracy of this energy is lifted by solvation as the fluorine p orbitals interact differently with the π orbitals of the water molecule. In H_2OF^-, this energy is strongly shifted upward and clearly splits into three components, 5.32, 5.52, and 5.76 eV. The 1.5 eV shift in H_2OF^- in comparison to the gas-phase fluorine anion is due to charge transfer from the anion to the water molecule in the ground state of the cluster. The component with the highest ionization energy is assigned to the fluorine 2p orbital, which shows the weakest interaction with the water molecule because none of the water outer valence orbitals is well-oriented for interaction. It thus exhibits a nearly pure fluorine character. The component with the lowest ionization energy, on the other hand, is assigned to that fluorine 2p orbital which points to the H-atom of the water molecule and therefore interacts with water. The remaining fluorine 2p orbital is perpendicular to the water−fluorine plane and interacts strongly with that lone pair of the O-atom which is also perpendicular to the water−fluorine plane. The fluorine−water interaction is antibonding for those two fluorine p orbitals which interact with water orbitals. The corresponding ionization energies are consequently the lowest outer valence ionization energies of

TABLE 2: Valence Ionization Energies of All Clusters Discussed[a]

cluster	ov IPs (O) [eV]	ov IPs (F) [eV]	iv IPs (O) [eV]	iv IPs (F) [eV]
H_2O	12.85		33.37	
	15.16			
	19.11			
F^-		3.97		25.68
$H_2O\ominus$	6.67		26.21	
	8.95			
	12.04			
H_2OF^-	6.21	5.32	25.83	27.77
	8.79	5.52		
	11.64	5.76		
$(H_2O)_2F^-$	7.01, 7.13	6.46	26.92, 27.01	29.07
	9.55, 9.78	6.47		
	12.64, 12.80	6.64		
$(H_2O)_3F^-$ (A)	7.50, 7.50, 7.62	7.22	27.71, 27.71, 27.81	30.20
	10.17, 10.17, 10.54	7.28		
	13.23, 13.26, 13.26	7.28		
$(H_2O)_3F^-$ (B)	7.49, 7.60, *7.19*	6.94	27.59, 27.73	29.93
	10.16, 10.23, *9.86*	7.03	*28.11*	
	13.23, 13.40, *13.13*	7.39		
$(H_2O)_3F^-$ (C)	6.44, 6.85, *10.24*	6.09	26.54, 26.64	28.91
	9.00, 9.28, *12.89*	6.12	*30.95*	
	11.82, 12.43, *16.55*	6.14		

[a]The energy of the line with the highest spectral intensity is given for inner valence ionization. For all clusters containing two and more water molecules, the three lowest energy states with large 1h contribution on fluorine were assigned to fluorine 2p ionization in this tabular and throughout this contribution. Numbers in italics are assigned to second-layer water molecules.

H_2OF^-. The overall position of the fluorine valence ionization energy of H_2OF^- reported in this contribution is in good, though not excellent, agreement with experimental data; see ref 9. If one assumes that the error in the calculation is the same as that of the ionization energy of isolated F^-, one obtains approximately 5.0 eV for the center of the three fluorine components. A broad band between 4.5 and 5.5 eV, the maximum being localized at 4.9 eV, was measured by Yang et al. by photodetachment spectroscopy.[9] In the experiment, the individual components discussed above have not been resolved.

Let us now address the influence of microsolvation on the solvent molecule. The outer valence shell of the isolated water molecule is composed of three different energy levels, which may be ionized according to our calculations at 12.85, 15.16, and 19.11 eV, respectively. The highest ionization energy is assigned to the outer valence orbital which forms the O−H bond, whereas the lowest ionization energy is attributed to the oxygen lone pair perpendicular to the H−O−H plane. This pattern is not changed by microsolvation, although the absolute ionization energies are strongly shifted. To better understand the results on the water ionization of the cluster, we have also computed the spectra of $H_2O\ominus$ where the fluorine anion is replaced by a negative point charge (see Table 2 and Figure 2). This allows one to separate the influence of the negative charge on the water ionization spectrum from the influence of the electrons of the fluorine anion. In the calculation, we have retained the fluorine basis set at the site of the negative point charge to ensure comparability.

The outer valence ionization spectrum of $H_2O\ominus$ is rather similar to the water spectrum of H_2OF^-. Corresponding lines are separated by no more than 0.4 eV, which is relatively little in view of the substantial mean shift of 6.5 eV by which the H_2OF^- spectrum has been shifted in comparison to the isolated water molecule. The energetical shift of the water outer valence ionization energies thus mainly derives from the presence of a

negative point charge. However, the impact of the electrons of the fluorine atom also contributes nonnegligibly to the decrease of the water outer valence ionization energy. Having in mind that the spectra of the cationic H_2OLi^+ cluster and of the $H_2O\oplus$ cluster—where Li^+ is replaced by a positive point charge—are almost identical,[41] the influence of the F^- electrons is surprisingly important. One may argue, on the other hand, that the Li^+ cation is so small and thus much closer to a bare positive charge than the fluorine anion to a negative point charge. A comparison of the present results with those for to H_2ONa^+ is, therefore, more appropriate. We have computed water ionization spectra of H_2ONa^+ and $H_2O\oplus$ and found that they do not differ significantly.[42] We conclude that the influence of the electrons of the solute on the ionization energies of the solvent is, in general, more important in the case of anions than in the case of microsolvated cations. This conclusion is further substantiated by our calculations on the water spectra of the clusters H_2OCl^- and H_2ONa^- when compared to the spectrum of the corresponding $H_2O\ominus$ clusters.[42]

We stress here that the water outer valence ionization energy is more greatly influenced by the presence of the fluorine anion than the fluorine energies are influenced by the presence of the water molecule. The formation of the H_2OF^- microsolvation cluster brings the outermost water ionization energy close to that of fluorine. We fully agree with Yang et al., who assign the charge-transfer band at 6.1−6.2 eV in their experimental ionization spectrum to the ionization of the solvent.[9] It is a pity that their experimental spectrum covers only the energy range below 8 eV, such that the next solvent band, which is expected at 8.79 eV (compare to Table 2), is not reported.

The large impact of cluster formation on the water ionization energies is mostly explained by the Coulomb attraction between the hole on water and the negative charge on fluorine. Assuming two isolated point charges, this attraction amounts to 5.9 eV. The result obtained from the full calculation on the $H_2O\ominus$ cluster is 6.1 eV; see the results in Table 2. Interestingly, the electron density on water slightly stabilizes the hole, although the screening of the positive charge decreases the Coulomb attraction to the fluorine anion.

Finally, we briefly address the fine structure of the water outer valence ionization spectra. The third water molecular orbital is strongly involved in the O−H bond and points directly to the fluorine anion. The corresponding ionization energy shows the largest decrease due to cluster formation among the three lines. Consequently, the energetical gap to the neighboring lower-lying ionization line has also shrunk in comparison to the free water molecule by as much as 1 eV. On the other hand, the gap between the lowest-lying water ionization line and the next one increases by 0.3 eV.

2. Inner Valence Spectra. The inner valence ionization of H_2OF^- is particularly interesting. The first interesting observation is that the fluorine inner valence ionization becomes higher in energy than that of the water monomer. The opposite is true for the isolated anion and molecule. The interchange of the two inner valence ionization energies is mainly a result of the decrease of the inner valence ionization energy of the cluster's water by 7.5 eV in comparison to that of the isolated water molecule. The fluorine inner valence ionization energy, on the other hand, increases by 2 eV as a consequence of cluster formation. Both these energetical shifts are slightly larger than the respective shifts of the outer valence ionization energies. As discussed above, the water ionization energies are very much influenced by the Coulomb attraction between the hole on water and the negative charge on fluorine. Naturally, the Coulomb attraction is lowered by enlarging the water−fluorine distance. Indeed, we find that for fluorine−hydrogen distances larger than 1.8 Å the ordering of the fluorine and the water inner valence ionization groups changes to that of the isolated cluster compounds. Interestingly, the estimation of the crossing distance by considering one point charge on O and one on F results in a somewhat larger F−H distance of about 2.6 Å. This result indicates that the impact of the electron density distribution is by far not negligible.

The appearance of both the fluorine and the water inner valence ionization groups in the cluster spectrum differs substantially from the corresponding groups in the spectra of the isolated monomers. Moreover, the water spectrum of H_2OF^- also differs substantially from that of the $H_2O\ominus$ cluster. The latter resembles the spectrum of the gas-phase water molecule despite the energetical difference between them. The appearance of the inner valence spectrum of the microsolvation cluster, on the other hand, is not explained by the presence of the negative charge and has to be attributed to the presence of the electrons of the fluorine anion.

To facilitate the understanding of this result, we have analyzed the inner valence ionized states of water and the fluorine anion in the different systems by means of a 1h+2h1p population analysis. This method of analysis is described in detail in ref 43. The idea of the population analysis is the following. The ionization energies and the corresponding eigenvectors are obtained by the ADC method by solving a matrix eigenvalue problem. Each eigenvector consists of the coefficients of the 1h configurations and of the 2h1p configurations which contribute to the respective ionized states. The 1h+2h1p population analysis is a Mulliken-like population analysis of these contributions for each eigenvector and assigns the contributions to particular atomic orbital (AO) basis functions and hence to the atoms or fragments of the system investigated.

For our purpose, we grouped the diffuse basis functions on fluorine and water together. The remaining nondiffuse functions were subdivided into functions on water and functions on fluorine. For $H_2O\ominus$, the basis set placed at the site of the negative charge is treated separately and divided into diffuse and nondiffuse functions. The Mulliken-like population analysis delivers excess charges with respect to the ground-state occupation for each of the predefined groups of basis functions. The results for the inner valence ionization range of H_2O, $H_2O\ominus$, and H_2OF^- are shown in Figure 3. We first discuss the findings for H_2O and $H_2O\ominus$. The most intense states in the inner valence spectrum of the gas-phase water molecule (see Figure 2) are found in the energy region between 33 and 35 eV. According to the bottom panel of Figure 3, these states are composed of 1h and 2h1p configurations without electron density in diffuse functions. Only some of the states describing weak satellite lines at higher energies show 2h1p character with two holes localized on oxygen and one electron excited to diffuse functions. The water inner valence energy region of $H_2O\ominus$ exhibits the same characteristics. The states with the majority of the spectral intensity are found in the energy region between 24 and 28 eV. Interestingly, the basis functions on the site of the negative point charge do not contribute to the density.

Many more states appear because of the inner valence ionization of the H_2OF^- cluster, and these states exhibit completely different characteristics than in H_2O and $H_2O\ominus$. In the energy range between 24 and 27 eV, most of the states appear because of water ionization. The vast majority of them exhibits 2h1p character where one particle is in diffuse functions on water and the two holes are delocalized, i.e., one hole is

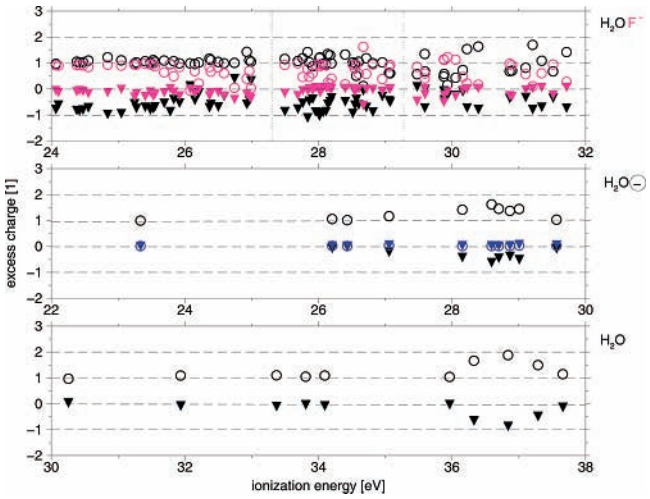

Figure 3. Results of the 1h+2h1p population analysis for the ionic states of H_2OF^-, $H_2O\ominus$, and H_2O. The charge difference between an ionized state and the ground state of the cluster is shown for all iv states. This excess charge is broken up into contributions in nondiffuse functions on water (black circles), contributions in diffuse functions on water (black triangles), nondiffuse functions on fluorine (magenta circle), diffuse functions on fluorine (magenta triangles), and diffuse and nondiffuse functions on the site of the negative point charge of $H_2O\ominus$ (blue). The corresponding states of water and $H_2O\ominus$ (note that the energies are shifted and one of the states of $H_2O\ominus$ is out of the scale of the figure) show similar excess charge distributions. States with different characteristics appear for H_2OF^- due to hole charge delocalization over both molecules. Details are given in the text.

localized on oxygen and the other one is localized on fluorine. Similar characteristics are found for the states arising from the fluorine inner valence ionization in the energy region between 27.2 and 29.2 eV. Interestingly, the particle is mostly found in diffuse functions placed on the water molecule. Satellite states arising because of water or fluorine inner valence ionization are seen in Figures 2 and 3 in the energy range above 29.3 eV. Most of them exhibit 2h1p characteristics with both holes on water and the particle being in diffuse functions on water. These states resemble the satellite states found for H_2O and $H_2O\ominus$. The inner valence ionized states characterized by one hole on fluorine, one hole on water, and one particle in diffuse functions are probably indications of secondary electron emission by intermolecular Coulombic decay (ICD). Secondary electron emission via the ICD process is a possible relaxation process of inner valence ionized states if the initial state is above the double ionization threshold of the cluster.[17,43,44] From Figure 2, one sees that the water and fluorine inner valence ionization are indeed above the H_2OF^- double ionization threshold. Most of the energetically lower-lying states in the double ionization spectrum are characterized by one hole on water and one on fluorine. Electronic relaxation of inner valence ionized states to these cationic states is simulated in the computed ionization spectra by 2h1p states with two holes distributed over the two monomers and a particle in diffuse functions, as discussed in detail in ref 43. Intermolecular Coulombic decay of $(H_2O)_nF^-$ microsolvation clusters is only briefly mentioned here.

We conclude that the nature of the water inner valence and fluorine inner valence ionized states has substantially been changed upon cluster formation. This nature cannot be explained for the water inner valence states by the influence of a negative point charge instead of the full fluorine anion, but rather by inter-monomeric interactions which open intermolecular electronic decay channels.

B. Comparison of the Double Ionization Spectra of H_2OF^-, F^-, and H_2O. Microsolvation has an important effect on the composition of the double ionization spectrum. Whereas the respective double ionization spectrum of the monomers composing the cluster naturally shows only one-site states, two-site states with delocalized holes appear as soon as a cluster is formed. Doubly ionized states with both holes localized at the same molecule are called one-site states in the following. If the holes are on two different molecules forming the cluster, they are denoted two-site states. The presence of two-site states changes the double ionization spectrum substantially and leads to a dramatic decrease of the double ionization potential (compare Table 3). The appearance of two-site states cannot be simulated by placing a negative point charge at the site of a cluster anion and is thus a unique result of cluster formation. Of course, two-site states are not found in the spectrum of $H_2O\ominus$. Its double ionization spectrum mainly illustrates the influence of the negative charge on the double ionization of the water molecules and is helpful to assign the water one-site spectrum of H_2OF^-.

TABLE 3: One-Site Double Ionization Energies (in eV) on Water and on Fluorine and Two-Site Double Ionization Energies with One Hole on Fluorine and One Hole on Water and with Two Holes on Water, Each on a Different Water Monomer[a]

cluster	F^{-2}	H_2O^{-2}	H_2O^{-1}/F^{-1}	H_2O^{-1}/H_2O^{-1}
H_2O		39.69		
F^-	19.31			
$H_2O\ominus$		25.97		
H_2OF^-	22.83	24.04	15.05	
$(H_2O)_2F^-$	25.74	26.19	16.26	15.73
$(H_2O)_3F^-$ (A)	27.49	27.46	17.51	17.18
$(H_2O)_3F^-$ (B)	27.04	27.43, *26.97*	17.01, *16.02*	16.37, *17.62*
$(H_2O)_3F^-$ (C)	24.66	25.21, *33.14*	15.25, *17.15*	14.56, *18.84*

[a] Numbers in italics symbolize one hole on the water molecule in the second solvation shell.

The following nomenclature and abbreviations are applied in the following: ov is used to abbreviate outer valence and iv to address inner valence; ov/ov denotes a double ionized state with two outer valence holes and iv/ov denotes a double ionized state with one inner valence and one outer valence hole. S/T-split addresses the energetical gap between the triplet and singlet states of the same double hole characteristic. S and T are used to denote singlet and triplet states, respectively.

1. Two-Site Spectra. Let us discuss the composition of the two-site double ionization spectrum of H_2OF^- first. For H_2OF^-, it is obvious that one hole must be located on fluorine and the other one on water to form a two-site state. We have seen in the discussion of the outer valence ionization spectrum of H_2OF^- that the three fluorine outer valence levels are no longer equivalent. Nevertheless, these levels are still quite close in energy in the sense that the energy gaps between the different water outer valence orbitals exceed the gaps between the fluorine levels by far. Consequently, one can roughly distinguish in the double ionization spectrum of H_2OF^- between three (rather widespread) groups of ov/ov two-site states, which are defined by their water ov contributions. They are separated from each other by energy gaps of 2 and 5 eV.

The first group is composed of T and S states with one hole in one of the three fluorine ov levels and one hole in the outermost water ov level. The first three distinguishable lines in the spectrum of Figure 2 belong to this group. The first line hides three other lines behind it. Two of the lines represent two-site S states with one hole in one of the two lower fluorine ov levels; the other states are the corresponding T states. The S/T-split is very small for these states. Interestingly, the S states are slightly lower in energy here because of mixing with

configurations characterized by two holes in the same orbital. The second and third distinguishable two-site lines are characterized by one hole on water and one hole in the highest occupied fluorine level. The S/T-split is resolved for these states. The T state appears at lower double ionization energies. The energy of the doubly ionized states with one hole in the highest occupied level of fluorine is slightly higher than that of the corresponding states with one hole in one of the other fluorine ov levels throughout the two-site spectrum, because the highest fluorine orbital points to the water molecule such that the hole−hole repulsion of the corresponding two-site states is increased.

The second group of two-site states is characterized by one hole on fluorine and one in the second ov level of water. The first four lines are very close together and not resolved. They represent S and T states characterized by a fluorine hole in one of the two lower fluorine ov levels. Those lines related to states with one hole in the highest fluorine level are 0.7 eV higher in energy, and their T/S gap is well-resolved.

The third group is formed by one line representing the unresolved T states with one hole charge in the water molecular orbital (MO) forming the OH-bond and the second hole in the lower-lying fluorine ov levels. The next line represents the corresponding unresolved S states. The S and T states with hole contributions in the highest ov level of fluorine are resolved in the computed spectrum shown in Figure 2. The S state is lower in energy than the T state because of configuration mixing with configurations which do not have a triplet counterpart. The corresponding two lines complete the ov/ov two-site double ionization spectrum of H_2OF^-.

A large gap of 12 eV separates the ov/ov two-site spectrum from the onset of the iv/ov two-site double ionization spectrum. We have seen above that the inner valence ionization energy of water is smaller than that of fluorine. Naturally, the lowest-lying states in the iv/ov two-site double ionization spectrum are characterized by a water iv hole and a fluorine ov hole. The first four lines appearing at approximately 34 eV are not well-resolved. Their fluorine ov holes are found in one of the lower fluorine levels. S and T energies are very similar. The corresponding states with a hole in the highest fluorine level are higher in energy, and the S and T energies differ by 2 eV for these states. The T line is nearly hidden behind a green water one-site line at 35 eV; the following black line belongs to the corresponding S state. The next four unresolved lines are satellites of the first four lines of the ov/iv two-site spectrum.

The fluorine iv/water ov part of the ov/iv two-site spectrum is energetically more widespread. It starts at 37 eV, and the individual T and S lines are resolved. Some satellites of the water iv/fluorine ov spectrum discussed above precede the next lines of the fluorine iv/water ov spectrum. They are found between 38 and 39 eV, and their T and S states are again well-resolved. The second hole is found in the second water ov level for these lines. The last T line of this part of the two-site spectrum appears above 40 eV. The corresponding S component at approximately 42 eV already shows a pronounced breakdown of the MO picture, i.e., it is broken into many states which share its intensity.[45] The second hole of these lines is situated in the MO forming the OH-bond.

This iv/ov two-site line group, the one-site line group preceding it, and all following one-site line groups exhibit characteristics of the breakdown of the MO picture with pronounced line bundling. The appearance of line bundling in electronic spectra is, as already mentioned above, an indication for the relaxation of the corresponding state by electronic decay. Electronic decay of a doubly ionized state by electron emission is operative if there exist energetically lower-lying triply ionized states. We have calculated the triple ionization threshold of H_2OF^- as the energy difference between the electronic ground state and the lowest triple ionized state by QCISD(T)[46] methods using the *Gaussian 03* program package.[47] The resulting threshold is found to be at 41 eV. This threshold is difficult to compute accurately. Furthermore, the method used is very different from those used above to calculate the doubly ionized and singly ionized states, and there may be a nonnegligible relative energetic shift when relating the different results. In any case, the onset of the triple ionization spectrum may be expected to be such that most of the high-energy states in Figure 2 with pronounced breakdown character, if not all of them, are above the triple ionization threshold. The line bundling of these states may, therefore, at least partially be attributed to the electronic decay of the dicationic states to tricationic ones.

2. One-Site Spectra. In the following, we discuss the changes in the one-site spectra of water and of the fluorine anion induced by cluster formation. The one-site states in the double ionization spectrum of H_2OF^- are found above 22 eV. The ov/ov one-site part of this spectrum is situated below 36 eV. We discuss the fluorine one-site states first. The fluorine ov/ov one-site states are found in the energy range between 22 and 30 eV. The corresponding states of the isolated fluorine anion are found between 19 and 25 eV. Cluster formation thus increases the energy of these states and slightly enlarges the interval in which they are found because of the lower symmetry of the cluster. The fluorine energy levels are no longer degenerate as discussed above.

Only three lines appear in the double ionization spectrum of the isolated fluorine anion. The first line is triply degenerate and describes all three T states deriving from fluorine/fluorine ov ionization. The second line is fivefold degenerate, representing five of the six ov/ov singlet combinations. The lacking sixth combination represented by the last line is a linear combination of configurations characterized by two holes in the same orbital.

All these degeneracies are lifted in the double ionization spectrum of H_2OF^-. The ordering of the lines is preserved in that the first two lines—the second one is hiding a third line behind it—are related to T states. The line with a minor hole contribution in the highest fluorine level has a smaller energy than the two lines with considerable hole charge in this fluorine level. The next two lines are unresolved in Figure 2 and represent two of the six above-mentioned S combinations. Three of the remaining states are clustered around 26.5 eV, whereas the last S state is found at approximately 29 eV. This state shows strong hole contributions on the highest fluorine level. We conclude that microsolvation leads to noticeable changes in the one-site ov/ov double ionization spectrum of fluorine. The double ionization energies increase, and their degeneracies are lifted.

The onset of the iv/ov one-site double ionization spectrum of fluorine is increased by microsolvation from 40 eV in the spectrum of the isolated fluorine anion to 44 eV. Its composing groups in the cluster spectrum are subject to a strong breakdown of the molecular orbital picture, because they are above, or at least near, the triple ionization threshold; see the discussion above. The two line groups shown are T states. The corresponding S states appear at about 53 eV and are outside the range of Figure 2.

The water one-site double ionization spectrum of H_2OF^- may be assigned by comparison to the lines in the spectrum of $H_2O^{\ominus}$. All lines of H_2OF^- are shifted by approximately 1.5 eV with respect to the corresponding lines of the $H_2O^{\ominus}$ spectrum. We

remind that the overall appearance of the latter is not very different from the double ionization spectrum of an isolated water molecule, except for a 12.5 eV energy shift; see Figure 2.

The first line is related to a T state with a hole in each of the two highest water levels. The next line represents a S state with both holes in the highest water level, followed by the S state corresponding to the lowest-lying T state. The next two lines are characterized by one hole in the highest and one hole in the lowest water ov level. The T/S-split between them is 3 eV. The S state coincides with the T state of the lowest/second ov level combination. The corresponding S state is preceded by the second level/second level S state. The S state at 36 eV in the spectrum of H_2OF^- with two holes in the third water orbital concludes the water one-site ov/ov double ionization spectrum.

The iv/ov states are found above 42 eV below the corresponding fluorine one-site states. The first three groups represent T states which have a counterpart in the spectrum of $H_2O\ominus$. Their different appearance is, however, interesting. These states exhibit strong breakdown characteristics in the spectrum of H_2OF^-, but they are well-characterized by 2h configurations in that of $H_2O\ominus$. These states are, like we have demonstrated above for the fluorine iv/ov one-site states, above the triple ionization threshold. The double ionization spectrum reflects, as already discussed for the ionization spectrum in section 4.1, the importance of the fluorine−water interaction in the cluster. This interaction introduces excited configurations into the wavefunctions which strongly modify the double ionization spectrum.

We have seen in this section that the formation of an anionic microsolvation cluster severely influences the electronic structure of both anion and solvent molecule. The effects of microsolvation can by analyzed by the help of ionization and double ionization spectra. It is particularly interesting to note that the fluorine−water interaction is directly reflected in the ionization and double ionization spectra, such that the modifications of the solvent part of the spectra may not be satisfactorily simulated by a negative point charge. The inner valence part of the spectra, in particular, cannot be understood without taking fluorine−water interaction via excited configurations into account. The appearance of two-site states in the double ionization spectrum is the most prominent characteristic of cluster formation. These states may, in particular, be fingerprints of the availability of decay channels for singly ionized states.

V. The Influence of Continued Solvation on Outer Valence Ionization Spectra

In this section, we address the outer valence ionization spectra of the clusters $(H_2O)_nF^-$, paying particular attention to the impact of increasing microsolvation.

The outer valence ionization spectra are shown in Figure 4. The valence ionization energies are also given in Table 2. Let us first restrict the discussion to the clusters in their respective ground-state geometries. A glance at the figure reveals an interesting result of microsolvation: both water and fluorine outer valence ionization energies increase with increasing number of water molecules in the cluster. The fluorine ionized states partly exhibit strong admixtures of water 1h contributions. The fluorine outer valence ionization energies increase by a mean value of 1.6 eV in H_2OF^- compared to F^-; an additional 1.0 eV and finally 0.7 eV are contributed by the second and third H_2O molecules, respectively. The increase of the fluorine outer valence ionization energies thus slows down with increasing cluster size. We remind that, in comparison to isolated water,

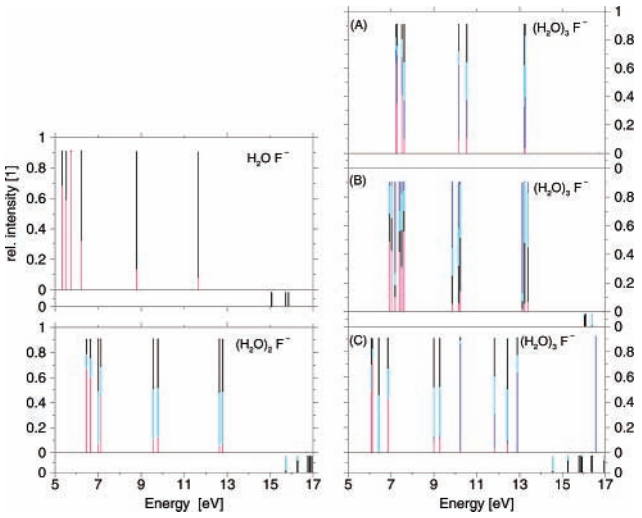

Figure 4. Outer valence ionization spectra of H_2OF^-, $(H_2O)_2F^-$, and the three $(H_2O)_3F^-$ isomers shown in Figure 1. Coloring of the spectra: black, cyan, blue, 1h contribution of the ionized state localized on different water molecules; magenta, 1h contribution to the ionized state localized on fluorine. All water molecules composing the clusters $(H_2O)_2F^-$ and $(H_2O)_3F^-$ (A) are symmetry equivalent. For the $(H_2O)_3F^-$ isomers (B) and (C), the 1h contributions on the water molecule which is not directly bound to F^- are shown by blue colors. The remaining water molecules are equivalent. The small figures below the outer valence ionization spectra show the onset of double ionization for those clusters for which the double ionization potential is below 17 eV.

the water outer valence ionization energies of H_2OF^- have decreased by a mean value of 6.8 eV. Increasing the number of water molecules in the cluster further, however, increases the ionization energies by 0.9 and 0.5 eV, respectively. Again, the increase of the water ionization energies slows down with increasing cluster size. The energy increase is slightly smaller than that found for the fluorine energies.

The fluorine and the water outer valence ionization energies increase by a comparable amount due to continued solvation. It is thus probable that the growing charge transfer from fluorine to water in the ground state of the clusters is responsible for these changes. The charge transferred per water monomer decreases with increasing cluster size, and hence with it the local impact on the ionization. The increase of the outer valence ionization energies slows down. In addition, the Coulombic attraction between the hole charge on the water molecules created by ionization and the negative charge of the anion decrease slowly with increasing cluster size, because the fluorine−water distance increases.

We will now turn to the outer valence ionization spectra and discuss their evaluation with advancing solvation in detail. We have seen in the previous section that the p orbitals of the fluorine anion are no longer degenerate in the H_2OF^- cluster because of their different orientations with respect to the water molecule. Electrons in the p orbital pointing to water are more readily ionized than those occupying the lone pair perpendicular to the plane which is spanned by the water molecule. The ionization energy of the latter is smaller than the energy necessary to ionize the electrons from the remaining fluorine p orbital, which is localized in the plane spanned by the water molecule but does not interact with the water molecule.

The situation is different for the $(H_2O)_2F^-$ cluster ionization spectrum. Only two lines assigned to fluorine outer valence ionization are resolved in Figure 4. The line emerging from the lowest ionization energy hides the second line. The second resolved line is thus the third line assigned to fluorine outer

valence ionization. To explain the fluorine outer valence ionization spectrum of this cluster, it is helpful to recall the cluster geometry, which is shown in Figure 1. Like the water molecule of H_2OF^-, both water molecules of $(H_2O)_2F^-$ are bound to the fluorine anion by H-donor bonds. Unlike the water molecule and the fluorine of H_2OF^-, the water molecules of $(H_2O)_2F^-$ are not in the same plane as the fluorine anion. The planes which are spanned by the water molecules are mutually twisted in order to minimize H−H interaction. Both water molecules are equivalent by symmetry; consequently, the fluorine anion cannot be situated in any of the planes spanned by the water molecules. According to this geometry, it is not possible to distinguish between a p level of fluorine pointing to a water molecule and a p level in the water plane, but not interacting with water as is the case for H_2OF^-. These two levels become rather similar from the point of view of interaction with water monomers. Nevertheless, there exist two linear combinations with a resolved energy gap in Figure 4. They appear because of a bonding and antibonding combination of the fluorine AOs with the water lone pairs which are perpendicular to the plane spanned by the respective water molecule.

The hidden line in the ionization spectrum of $(H_2O)_2F^-$ can be assigned to the p orbital of fluorine which corresponds to the fluorine lone pair perpendicular to the water molecular plane in H_2OF^-. Although this fluorine lone pair is no longer exactly perpendicular to any of the water molecular planes of $(H_2O)_2F^-$ and $(H_2O)_3F^-$, it shall still be addressed as "fluorine lone pair perpendicular to water" for convenience. This fluorine p orbital strongly interacts with lone pairs on water. As its ionization energy is very close to the lower ionization energy of one of the "fluorine p orbitals in plane", it is justified to conclude that the interaction with water is comparable for these levels.

In comparison to the ionization spectrum of H_2OF^-, all fluorine levels have been stabilized in the spectrum of $(H_2O)_2F^-$. The "fluorine in plane not interacting with water" level of H_2OF^- obtains a slightly smaller energy shift than the other levels.

The energetical ordering of the three lowest ionized states of $(H_2O)_3F^-$ (A) obeys a principle similar to that of the spectrum of $(H_2O)_2F^-$. All three levels are very close in energy, closer than for $(H_2O)_2F^-$. Different from the suggestions of the SCF calculation, the level, which may be considered the "fluorine lone pair perpendicular to water" in the sense established above, obtains the lowest ionization energy. The other two levels are energetically degenerate because of the symmetry of the cluster. They are formed from the "fluorine in plane" levels and water admixtures. The decrease of the energy gap between the three levels may also be attributed to the symmetry of the cluster which leads to a stronger mixture of water and fluorine p orbitals for all levels. For this cluster, the three lowest ionized states may be assigned to fluorine ionization, but an important fraction of the hole charge is localized on water. The assignment should also be regarded as a "formal assignment" for the fourth resolved line in the spectrum of $(H_2O)_2F^-$, which is assigned to water ionization although showing strong fluorine 1h admixtures.

We now return to the outer valence ionization spectrum of $(H_2O)_2F^-$ to discuss the lines assigned to water outer valence ionization. The third and fourth resolved lines in the outer valence ionization spectrum of $(H_2O)_2F^-$ are assigned to linear combinations of the water lone pairs perpendicular to the respective water molecular plane. The bonding combination strongly mixes with the fluorine p orbital "perpendicular to the water planes", such that it gains electron density from fluorine. The energy gap to the antibonding combination, which has a smaller ionization energy, is therefore small in comparison to bonding and antibonding linear combinations of the other water ov orbitals. The fifth and sixth lines are assigned to ionization from water lone pairs in their respective molecular planes, and the seventh and eighth lines derive from ionization of linear combinations of the OH bond. The ionization energies of the latter are increased slightly more in comparison to the ionization energy of the corresponding state of H_2OF^- than those of the other lines.

Because of the symmetry of the cluster, two of the three lines emerging because of ionization of equivalent water p orbitals of $(H_2O)_3F^-$ (A) are energetically degenerate. One linear combination of three equivalent water p orbitals is characterized by equivalent contributions from each of the composing orbitals. The other two linear combinations obtain different contributions from the water monomers, such that the sum of the contributions to these levels is equivalent for all three water monomers. The linear combination with equal contributions from all water molecules is bonding for all but the OH bond orbitals. Consequently, its ionization energy is higher than that of the energetically degenerate linear combinations for all but the OH bond lines. The linear combinations of the lone pairs in the respective water molecular planes show the largest energy gap between the level with equivalent contributions and the degenerate levels. This is due to the fact that these orbitals have a relative orientation which is more suitable for a bonding interaction than that of the other water p levels. The gaps between lines of the other outer valence groups are rather small. The increase of the ionization energies of $(H_2O)_3F^-$ with respect to their counterparts in the $(H_2O)_2F^-$ spectrum is comparable for all three groups of water ov ionization.

In addition to $(H_2O)_3F^-$ in its ground-state structure, two low-lying isomers have been calculated. These isomers do not exhibit a direct bond of the third water molecule to the fluorine anion; see Figure 1. The third water molecule is bound to the first-layer water molecules by H-donor bonds in $(H_2O)_3F^-$ (B) and by H-acceptor bonds in $(H_2O)_3F^-$ (C). The outer valence ionization spectra of these two clusters are also shown in Figure 4.

Interestingly, corresponding lines show up at very similar energies in the ionization spectra of $(H_2O)_3F^-$ (A) and $(H_2O)_3F^-$ (B). The fine structure of corresponding line groups differs though. The similarity of the outer valence ionization energies of (A) and (B) may be explained as follows. For structure (A), all water molecules are equivalent and directly bound to the fluorine anion. All of them are therefore influenced by the electronic density of the fluorine anion. Two of the water molecules of (B) are also directly bound to the fluorine anion. From this alone, it may be expected that the ionization energies of the first-layer water molecules of (B) are similar to those of $(H_2O)_2F^-$. In reality, the water ionization energies of (B) are closer to those of (A) than to those of $(H_2O)_2F^-$. The differences between fluorine−water distances of the first-layer water molecules of these three cluster is negligible and does not explain this phenomenon. It can thus be concluded that the charge transfer via the two H-bonds of (B) is the reason for the unexpectedly high ionization energies of the first-layer water molecules of (B). The electron density transfer via the H-bonds to the second-layer water molecule is even so important that the ionization energies of the third water molecule approach those of the water molecules which are directly bound to fluorine. The impact of hydrogen bonding on ionization energies has been shown before at the example of the second solvation shell water molecule of $(H_2O)_5Li^+$, which is expected to have

a smaller ionization energy than the first solvation shell molecules, but has in reality a larger ionization energy than any of the other water molecules of the cluster.[41]

It is very interesting that the three groups of ionized states of (A) and (B) appear at similar energies and that the spread of these groups is, however, different. This overall appearance has the drawback that unresolved experiments may not be suitable to make a distinction between the two cluster geometries. One should also keep in mind that the computed levels will be broadened by nuclear dynamics not considered here.

The last example of a $(H_2O)_3F^-$ structure, labeled (C), may be considered a counterpart to (B), because the third water molecule is bound to each of the other two water molecules by a H-acceptor bond instead of the donor bond of (B).

In accordance with our discussion of the properties of the ionization spectrum of (B) above, the two water molecules which are directly bound to the fluorine of water (C) are ionized at energies similar to those of $(H_2O)_2F^-$. This statement holds true for each of the different groups of first-layer water molecules. The third water molecule, which is more likely to donate electron density to the other two water molecules than to receive electron density, is ionized at significantly higher energies than the other water molecules of the cluster. Its ionization energies are nevertheless still approximately 2.5 eV lower than those of the neutral isolated water molecule. The fact that this water molecule is part of a negatively charged cluster has a visible impact on the ionization energies even of this water molecule because of the Coulombic attraction between the hole on water and the fluorine anion.

The cluster (C) is the only cluster containing three water molecules for which the fluorine ionization energies are smaller than for $(H_2O)_2F^-$. The fluorine−water distance is similar for (C) and for $(H_2O)_2F^-$, such that the explanation for this result has to be found elsewhere. The fluorine ionization energy of (C) is smaller than those of $(H_2O)_2F^-$, which means that the electron density of fluorine is larger for (C) than for $(H_2O)_2F^-$. On the other hand, the ionization energies of corresponding water molecules are very similar for both clusters. This leads to the conclusion that electron density is indeed transferred via the H-bond from the third water molecule to the water molecules bound to fluorine, such that the density transfer from fluorine to the first-layer water molecules may be smaller than that realized for $(H_2O)_2F^-$, although similar water ionization energies are found for the two clusters.

We would like to mention here that the spectra of (A) and (B) are in agreement with the experimentally obtained result[9] in which the intensity of the charge-transfer band increases with increasing number of water molecules in the cluster. All outer valence ionization spectra shown agree with a third experimental result stated in ref 9: the CT band approaches the fluorine ionization band with increasing cluster size. We thus conclude that a $(H_2O)_3F^-$ isomer close to (A) or (B) has probably been produced by means of electrospray techniques by Yang et al.

VI. The Development of the Inner Valence Spectra with Continued Solvation

The inner valence ionization spectra of the clusters discussed here are collected in Figure 5. As already discussed in section 4, the properties of the inner valence spectrum of H_2OF^- are dictated by the strong mixture of the 1h determinants describing the inner valence holes with 2h1p configurations where the two holes are distributed over F^- and H_2O. The resulting states form the line bundles showing up in the water and in the fluorine inner valence spectra. Similar line bundles are present in the

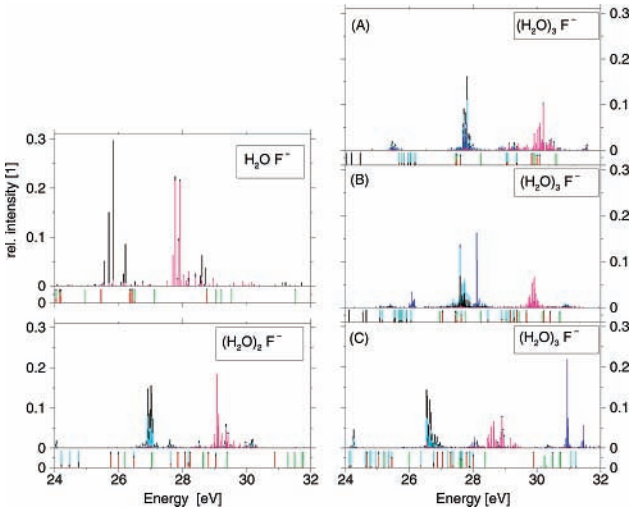

Figure 5. Inner valence ionization spectra of H_2OF^-, $(H_2O)_2F^-$, and the three isomers of $(H_2O)_3F^-$ shown in Figure 1. Coloring of the spectra: black, cyan, blue, 1h contribution of the ionized state localized on different water molecules; magenta, 1h contribution to the ionized state localized on fluorine. All water molecules composing the clusters $(H_2O)_2F^-$ and $(H_2O)_3F^-$ (A) are symmetry equivalent. For the $(H_2O)_3F^-$ isomers (B) and (C), the 1h contributions on the water molecule which is not directly bound to F^- are shown by blue colors. The remaining water molecules are equivalent. The small figures below the outer valence ionization spectra show the double ionization spectra of the molecules.

inner valence ionization spectra of the larger clusters. These bundles are much denser than for H_2OF^-. In $(H_2O)_2F^-$ and $(H_2O)_3F^-$ (A), all water molecules are equivalent, and essentially only two dominant energetically resolved bundles appear in the inner valence ionization spectra: one for fluorine and one for water. The spectra of clusters (B) and (C) show an additional dominant bundle due to the ionization of the water molecule in the second layer.

Let us first address the fluorine inner valence ionization of the clusters. It is observed that the intensity of the individual lines in a bundle diminishes with increasing cluster size and that the bundle broadens. This behavior reflects the growing admixture of more and more available 2h1p configurations. For $(H_2O)_3F^-$, this statement holds true regardless which geometry of the cluster is used to derive the spectrum.

The situation is slightly more complicated for the water inner valence ionized groups. Obviously, the intensity of the individual lines decreases in the spectrum of $(H_2O)_2F^-$ compared to that of H_2OF^-. No further decrease of the intensity is achieved in the spectrum of any of the three isomers of $(H_2O)_3F^-$ discussed here. In the case of (A), we have to keep in mind that the spectrum was calculated without using diffuse functions on the H atoms because of limited computing capacities. A quantitative comparison of line fine structures of this spectra to that of the other spectra is, therefore, not fully legitimate. The spectra of (B) and (C) are calculated including diffuse functions on hydrogen, and it seems that the third water molecule does not contribute significantly to the excited states on the other water molecules, i.e., on the $(H_2O)_2F^-$ subunit. Unfortunately, we could not compute the 2h1p populations for these very complex states, to enable us to carry out a more detailed analysis.

The line shape of the peak corresponding to the second-layer water molecule is rather sharp, but not without line bundling characteristics. The admixture of 2h1p configurations with one hole on the fluorine atom is naturally less important for this bundle than for the inner valence ionized states of the other water molecules. We have discussed in section 4 at the example

of H_2OF^- the importance of charge delocalization to fluorine for the inner valence ionized states of water bound to F^-. For H_2OF^-, a more detailed population analysis is available. The sharp structure of the bundles of the water molecule in the second layer of $(H_2O)_3F^-$ (B) and (C) may thus be due to the lack of direct contact to fluorine. The satellites and the line bundles which appear in the inner valence ionization spectra of the second-layer water molecules of (B) and (C) thus appear because of the interaction with the neighboring first-layer water molecules.

We have seen above that the inner valence ionized states of H_2OF^- are above the double ionization threshold and that ICD is operative for them. All line groups in each of the calculated inner valence spectra of the larger clusters are also above the double ionization threshold, which is shown in Figure 5. The ICD process, which becomes more efficient with an increasing number of water molecules in the cluster, leads to line bundling in the inner valence ionization spectra. Line groups become broader, and the spectral intensity of the composing lines decreases with increasing efficiency of the ICD process, in agreement with the evolution of the iv spectra with increasing cluster size. The kinetic energy distribution of the ICD electrons depends crucially on the energy gap between the initial decaying states and the final states of the decay as well as on the efficiency (partial widths) of these decay channels. Obviously, the number of water molecules in the cluster and the geometry of the cluster influence the ICD process.

It is interesting to note here that the inner valence ionization energy of the water molecule of (B) bound by an H donor is slightly larger than that of the other water molecules of this cluster. The respective ionization energy of the H-acceptor bound water molecule of (C) is surprisingly large. It is even larger than the inner valence ionization energy of fluorine in the same cluster, whereas all the ionization energies of the other water molecules in all clusters are below the respective fluorine ionization energies. The energetical shifts of the inner valence ionization energies with increasing solvation resemble those of the outer valence ionization energies, such that the energies of fluorine and water in the first solvation shell are more similar for (A) and (B), while the energies of (C) are close to those of $(H_2O)_2F^-$.

VII. Double Ionization and Microsolvation

In this section, we discuss the development of the double ionization spectra with continued microsolvation of F^- in water. We have already seen above that cluster formation of F^- and one water molecule changes the double ionization spectrum with respect to the double ionization spectra of the isolated monomers considerably. New two-site states appear, and some of the one-site states, which are well-described by 2h contributions in the spectra of the isolated cluster components, show breakdown characteristics due to fluorine–water interaction via excited states.

Figure 6 shows the double ionization spectrum of H_2OF^- in comparison to the double ionization spectra of the ground-state structures of $(H_2O)_2F^-$ and $(H_2O)_3F^-$. All three spectra look very complicated at first sight. We have seen above how the double ionization spectrum of H_2OF^- is composed of two-site states and different one-site states. The double ionization spectrum of $(H_2O)_2F^-$ contains an additional class of two-site states which increases the complexity of the spectrum. As two water molecules are part of the clusters, it is possible to form water/water two-site states, which are not present in the H_2OF^- double ionization spectrum by definition.

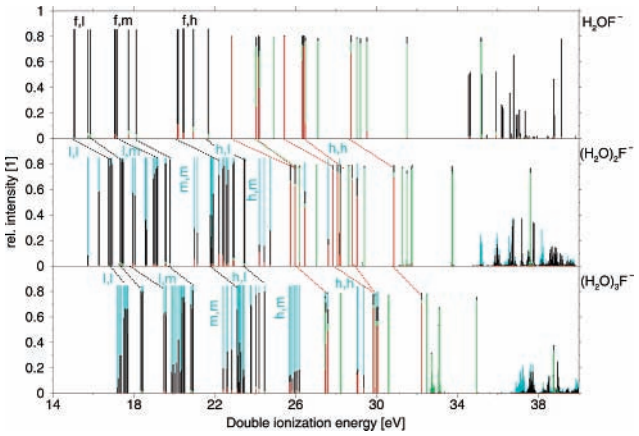

Figure 6. Double ionization spectra of $(H_2O)_nF^-$, $n = 1-3$, at their ground-state geometries. Each dicationic state is presented as a stick at the respective double ionization energy. The height of each stick is given by the overlap of the state with the 2h space, and the various colors indicate the contribution of specific 2h combinations. Coloring of the lines: red, one-site states with two holes on fluorine; green, one-site states with two holes on water; black, two-site states with one hole on water and one on fluorine; turquoise, two-site states with two holes on different water molecules. The black and red additional dotted lines connect vertical lines of similar hole character in different spectra. Note that only the first and last lines of a group of lines with certain hole–hole characteristics are connected with their counterparts. Water/water two-site states, water one-site states, and iv/ov lines are not connected. The labels of water/water two-site states and fluorine/water two-site states are explained in the text.

As already discussed in the context of the ionization spectra, the assignment of lines, and even of MOs to either fluorine or water, is a rather "formal" one. It neglects the fact that the fluorine levels mix with the two highest water levels such that some MOs have similar contributions from water and from fluorine. This level of mixing results in lines in both the ionization and double ionization spectra which may not be unambiguously assigned to one of the different subspectra of the individual monomers. This complicates the discussion of the double ionization spectrum particularly. One-site states are less affected by unambiguous water and fluorine contributions and are more readily assigned and discussed.

A. Two-Site Spectrum of $(H_2O)_2F^-$. What changes appear in the ov/ov two-site spectrum of $(H_2O)_2F^-$ in comparison to that of H_2OF^-? Let us address the water ov/water ov two-site subspectrum first, which has no counterpart in the spectrum of H_2OF^-. The line succession of this subspectrum may be understood by estimating the energy of all possible Hartree–Fock MO combinations. As discussed above, three energetically well-separated groups of water ov levels are distinguishable for $(H_2O)_2F^-$. These groups—each containing two members—are addressed as low, medium, and high ionizing energy levels in the following. According to the HF energies, we expect the energetical ordering as follows: low/low < low/medium < medium/medium < low/high < medium/high < high/high of corresponding two-site states formed from these groups. This building principle is realized in the two-site water ov/water ov double ionization spectrum of $(H_2O)_2F^-$. The energy of the corresponding states is even rather close to the sum of the HF energies. The first line in the double ionization spectrum of $(H_2O)_2F^-$ and also the water/water contributions to the next—mixed—lines may be assigned to low/low states. The following lines are water/fluorine two-site states, which will be discussed later on. The next members of the water/water subspectrum are contributions to a line with mixed 2h character at about 18 eV and the following group of four lines at 18.5 eV. They all reveal

low/medium character. The energy gap between low/low and low/medium states is approximately 2 eV. Another 2.5 eV above the low/medium states, one finds the next two lines belonging to the water/water two-site subspectrum. They are characterized as one triplet and one singlet medium/medium combination. The next group at 21.5 eV contains the low/high two-site states. The gap to the medium/high combinations is again approximately 2 eV. The remaining high/high combinations are embedded in the one-site subspectrum around 28 eV.

It is interesting that the lowest line in the double ionization spectrum of $(H_2O)_2F^-$ is a two-site water/water line, although most of the negative charge of the cluster is localized on fluorine. The reason for this line succession is that the hole−hole repulsion is minimized by placing the charges on the two water molecules. Furthermore, these states are stabilized because of Coulombic attraction between the two water molecules carrying a positive hole charge and the fluorine anion. Fluorine−water two-site states, on the other hand, are characterized by two neutral cluster components, the ionized fluorine anion and one of the water molecules, and one positively charged water molecule. No additional strong stabilizing attraction between different monomers is created by double ionization.

Fluorine−water two-site states which show the second lowest double ionization energies are discussed next. As already stated above, the water outer valence levels may be divided into low, medium, and high ionizing levels with considerable energy gaps between different groups. This means that the fluorine−water two-site states may also be divided into three groups according to their water outer valence character, because the energy gap between fluorine levels is comparatively small. We have already shown above that the two-site double ionization subspectrum of H_2OF^- exhibits this structure. This group structure is not easily spotted in the spectrum of $(H_2O)_2F^-$. The first group contains all fluorine−water lines between 16 and 17.5 eV. The second group is composed of the lines between 17.8 and 20 eV, whereas all fluorine−water lines between 21 and 24 eV compose the last group. Obviously, the energetical gaps between different groups are small. Each group with similar water ov hole characteristic in the two-site water/fluorine spectrum of $(H_2O)_2F^-$ is composed of three subgroups with different fluorine hole character. Two groups with holes in the highest occupied fluorine level embrace one group composed of states with holes in the other fluorine ov levels. The first of these line groups is further characterized by strong admixtures of water/water two-site character.

B. One-Site Spectrum of $(H_2O)_2F^-$. The analysis of the one-site ov/ov part of the double ionization spectrum of $(H_2O)_2F^-$ is somewhat easier than that of the two-site spectrum, because the lines can be assigned by comparison to the spectrum of H_2OF^-. The assignment of the water one-site states corresponds exactly to that of the H_2OF^- spectrum. The main difference between the water ov/ov one-site subspectra of the two clusters is the increase of the double ionization energies by approximately 1.5 eV. Furthermore, all lines in the $(H_2O)_2F^-$ spectrum hide close-lying lines sharing their characteristics where only one line is found in the spectrum of the smaller cluster. The reason for the formation of multiple lines is the presence of two water molecules in the cluster.

The fluorine one-site spectrum of $(H_2O)_2F^-$ shows fewer similarities with that of H_2OF^- than the water one-site spectra of the two clusters. The ordering of the lines is nevertheless preserved. The composition of the spectrum of different line groups of triplet and singlet states is less obvious, because the energy gaps between lines are different. The first three lines belong to the triplet states. These lines are slightly closer together than the corresponding lines in the spectrum of H_2OF^-. The first triplet line approaches the other two, which are themselves separated by a larger energy gap. The first five lines of altogether six singlet lines are distributed over an interval of the same energy width as that in the spectrum of the smaller cluster. The energy gaps between the lines are more regular, though. The sixth line is found at larger energies, similar to the situation in the spectrum of H_2OF^-.

C. Low-Lying States of the iv/ov Subspectrum. Some states belonging to the iv/ov two-site double ionization spectrum of $(H_2O)_2F^-$ are shown in Figure 6 above 34.5 eV. The lowest ionization energy of the two-site iv/ov spectrum is assigned to a water/water state, the ov hole being localized in the outermost water level. The S/T-split is not resolved. The next group of the water iv/water ov spectrum reveals the same hole characteristics. The last group of this subspectrum shown in Figure 6 belongs to the "iv/medium" water iv/water ov spectrum. All fluorine/water lines shown are part of the water iv/fluorine ov spectrum. The fluorine hole charge is localized in the highest fluorine level for the first and third groups and in the other levels for the second group. The last group shown in the double ionization spectrum of $(H_2O)_2F^-$ contains satellites to previous groups. The ordering of the fluorine ov/water iv groups is similar to that of the H_2OF^- spectrum. A major difference concerning the iv/ov two-site spectra of H_2OF^- and $(H_2O)_2F^-$ is the pronounced line bundling from energies of 34 eV on in the spectrum of the latter. We have discussed for several groups with similar appearance that they are subject to ICD relaxation by electron emission. Interestingly, the triple ionization threshold of $(H_2O)_2F^-$ is in the range of 35 eV. This means that the appearance of line bundling coincides with the triple ionization threshold. The decrease of the triple ionization threshold with respect to that of H_2OF^- is explained by the possibility to delocalize the three hole charges over three cluster monomers, such that the two positive charges are further apart than for H_2OF^-.

D. Double Ionization Spectrum of $(H_2O)_3F^-$ in its Ground-State Geometry. The double ionization spectrum of $(H_2O)_3F^-$ contains no new class of states. More states of each of the different groups composing the previously discussed double ionization spectra are present in that of $(H_2O)_3F^-$ because of the additional water molecule. The spectrum is build up according to the same principles as the spectrum of $(H_2O)_2F^-$. Some of the lines in the spectrum of $(H_2O)_3F^-$ may thus be assigned by comparison to the spectrum of $(H_2O)_2F^-$. The water one-site spectrum, in particular, is very similar to that of $(H_2O)_2F^-$; corresponding lines are shifted by approximately 1.5 eV. The fluorine one-site spectrum of $(H_2O)_3F^-$ is much more compact than that of $(H_2O)_2F^-$ because of the higher symmetry of the cluster. The interaction of the different fluorine p orbitals with water molecules is rather similar for all MOs. The fluorine one-site spectrum of $(H_2O)_3F^-$ is therefore close in appearance to that of F^-, although the energies of corresponding states differ by approximately 8 eV.

The assignment of the two-site spectrum of $(H_2O)_3F^-$ by the help of comparison to that of $(H_2O)_2F^-$ is somewhat more tedious, because the different groups of the fluorine/water spectrum are not well-separated in the spectrum of the smaller cluster. The energy gaps between groups with low water ov ionization energy, medium, and high water ionization energies are more pronounced in the spectrum of $(H_2O)_3F^-$ because of its symmetry. The lines with dominant water/fluorine character between 17 and 19 eV belong to the first, those between 19

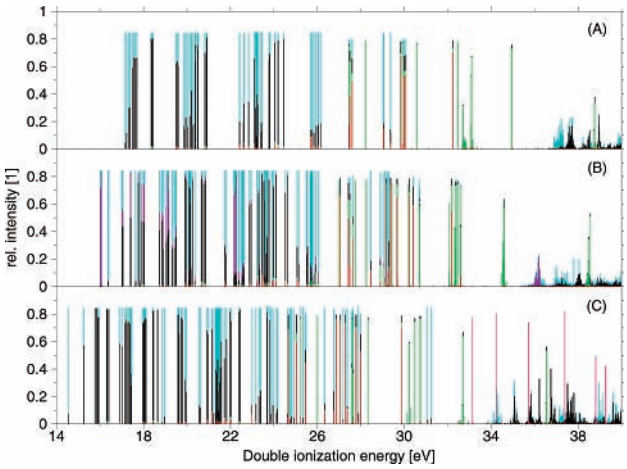

Figure 7. Double ionization spectra of the three isomers of $(H_2O)_3F^-$ (A), (B), and (C); see Figure 1. Each dicationic state is presented as a stick at the respective double ionization energy. The height of each stick is given by the overlap of the state with the 2h space, and the various colors indicate the contribution of specific 2h combinations. Coloring of the lines: red, one-site states with two holes on fluorine; green, one-site states with two holes on water; black, two-site states with one hole on water and one on fluorine; turquoise, two-site states with two holes on different water molecules; violet (only for (B)), two-site states with one hole on fluorine and one hole on the second-layer water molecule; magenta (only for (C)), one-site states with both holes on the second-layer water molecule.

and 22 eV to the second, and finally those between 22 and 25 eV to the third group. Two groups belonging to the fluorine ov/water iv spectrum are shown above 37 eV.

In contrast to the fluorine/water two-site spectrum, line groups with similar character of the water/water two-site spectrum are rather more widespread for $(H_2O)_3F^-$ than for the smaller cluster. More lines are resolved. The "l/l" (low/low) lines are found below 18 eV, followed by the "l/m" (low/medium) lines around 20 eV. "M/m" lines show up at 22.5 eV, closely followed by "h/l" lines. The "h/m" (high/medium) lines around 26 eV and the "h/h" lines at about 29 eV complete the water ov/water ov two-site spectrum of $(H_2O)_3F^-$. The lowest group of triplet states of the water iv/water ov two-site spectrum is shown at 37 eV.

Interestingly, one of the one-site groups below 34 eV shows pronounced line bundling. All groups above 34 eV also show line bundling characteristics. The triple ionization threshold of $(H_2O)_3F^-$ is calculated to be close to 33.5 eV. It might thus be that, even the first group with line bundling patterns is above the triple ionization threshold, those groups above 37 eV are surely subject to electronic decay processes.

E. Double Ionization Spectra of the Isomers $(H_2O)_3F^-$ (B) and (C). We have seen, though less drastic than for the highly symmetric microsolvation clusters of cations,[41] that the symmetry of the microsolvation cluster is reflected in the double ionization spectrum. As it is well-known that $(H_2O)_3F^-$ has a local minimum which is energetically close to the ground state, but very different from the point of view of the geometry, it is most interesting to compare its double ionization spectrum to that of the ground-state cluster. Additionally, the double ionization spectrum of isomer (C) is considered.

In Figure 7, we compare the double ionization spectra of the three isomers of $(H_2O)_3F^-$. We have seen above that the ionization spectra of (A) and (B) are rather similar concerning energies, but that the higher symmetry of (A) is reflected by the line distribution and the appearance of the spectrum. Considering the double ionization spectra, energies of corresponding one-site states are still very close. Energies of corresponding two-site lines, on the contrary, are no longer very close, because contributions of the second solvation shell water molecule mix with those of the first solvation shell water molecule. These admixtures lead to a decrease of the double ionization energy, in particular for fluorine/water two-site states, because the hole charge on fluorine is farther away from the second solvation shell water molecule than from those of the first solvation shell. The minimization of hole repulsion is not the only reason for different double ionization energies of corresponding lines. The outer valence ionization energies of $(H_2O)_3F^-$ (B) are slightly smaller than those of comparable states of (A). The lines without second-layer water hole admixture of isomer (B) are thus also energetically below their counterparts in the spectrum of (A). Second- and first-layer water/fluorine states are shown in different colors in Figure 7 to make clear that the lowest double ionization energy is obtained by a second-layer water/fluorine two-site state because of the minimization of hole−hole repulsion. The same minimization of hole−hole repulsion is achieved by the corresponding states of (C), such that it is rather surprising that the lowest line of the double ionization spectrum shows water/water hole character, both holes being localized in the first solvation shell. We have seen above that the second solvation shell water molecule of (C) obtains comparatively large ionization energies because of its H-acceptor bonds to the rest of the cluster. The decrease of hole−hole repulsion is not sufficient to make up for this comparatively high water ionization energy, such that the lowest states are all dominated by first-layer and fluorine hole contributions. Corresponding states of (C) with holes on the second-layer water molecule are found at approximately 2 eV higher energies if the second hole is localized on fluorine. An energy difference of 4.5 eV is stated if the second hole is on a water molecule from the first shell, and a gap of approximately 8 eV is found between corresponding water one-site states. The different orientation of the H-bonds is thus crucial for the character of the double ionization spectrum.

Those parts of the double ionization spectrum of $(H_2O)_3F^-$ (C) without important hole contributions on the second-layer water molecule are very similar in appearance to the double ionization spectrum of $(H_2O)_2F^-$. The similarity is not obvious in Figure 6 because of the presence of lines with important contributions localizing hole charge on the second-layer water molecule. These lines modify the overall appearance of the double ionization spectrum of $(H_2O)_3F^-$ considerably and make it difficult to recognize similarities to the spectrum of $(H_2O)_2F^-$. Unfortunately, it is not helpful, but confusing, to mark all contributions with hole charge on the second-layer water molecule by different colors. A different color for first- and second-layer water molecules has thus only been chosen for one-site states localizing both holes on water in the spectrum of $(H_2O)_3F^-$ (C). They are shown in magenta colors to distinguish them from their lower-lying counterparts in the one-site spectrum of first-layer water. Their 2h character is much more pronounced than that of the first-layer water one-site states. We have discussed a similar result in the context of inner valence ionization spectra. The similarity in appearance of that part of the double ionization spectrum without important hole charge contributions on the second-layer water molecule to the spectrum of $(H_2O)_2F^-$ is not surprising if we keep in mind that the ionization spectra are very similar, as discussed previously. The energy of the lines with hole charge on first-layer water is lower for (C) than for $(H_2O)_2F^-$. This is not surprising if we

keep in mind that the water ionization energies of the latter clusters are slightly higher than those of (C).

VIII. Conclusion

We have shown by analyzing the ionization and double ionization spectra of a series of aqueous microsolvation clusters of the fluorine anion how the process of microsolvation influences the electronic structure of the anion and the solvent. In the first part of this contribution, the effect of the formation of the H_2OF^- cluster on the spectra of the composing monomers F^- and H_2O is described. Whereas the ionization energies of F^- are increased because of cluster formation, those of water are substantially decreased. The decrease of the water ionization energies could be mainly attributed to the presence of the negative charge by comparison of the H_2OF^- spectrum to the ionization spectrum of a cluster where F^- is replaced by a negative point charge. But, interestingly, the electron density of F^- also contributes nonnegligably to the decrease of the water ionization energy.

Concerning the double ionization spectra, a new class of states, the so-called two-site states, which is characterized by distributed hole charges, appears as a consequence of cluster formation. The double ionization potential decreases considerably because of these states, because their hole−hole repulsion is small.

The presence of several energetically low-lying double ionized states has a strong impact on the character of the inner valence ionized states of both cluster monomers, F^- and water. These states are mainly composed of excited configurations with distributed hole charges, because they are energetically close or even above some of the two-site states.

Summarizing, we have shown in the first part that the presence of the fluorine anion in a cluster of water molecules may by no means be reduced to the presence of a negative charge, because many-body effects are introduced because of its electrons. The influence of the fluorine electrons on the spectrum is particularly large for those parts for which no description whatsoever neglecting many-body effects is adequate. Even those parts of the H_2OF^- ionization and double ionization spectra which are predominantly described by electron removal from water are not well reproduced by replacing fluorine by a negative charge. This is in contrast to our findings for positively charged microsolvation clusters.[41] The presence of fluorine electrons should therefore not be neglected when constructing models for the microsolvation process.

In the second part of the article, we analyze the development of ionization and double ionization with ongoing solvation. The first important result is the increase of both F^- and water ionization energies with increasing number of water molecules. Whereas the ionization energies of the anion show a monotonic increase by cluster formation and ongoing solvation, the ionization energies of water are decreased by the formation of H_2OF^- and then increased by continued solvation. Interestingly, the ionization energies of anionic clusters show a development opposite to that of cationic microsolvation clusters increasing the solvation shell. The ionization energies of the cation decrease monotonically with increasing solvation shell, and the solvent ionization energies are increased by cation−water cluster formation and then decreased with ongoing solvation.[41]

More pronounced differences than in the ionization show up in the double ionization spectra with continued solvation, on one hand because the influence of gaps between different energy levels is doubled and on the other hand because additional classes of lines appear with increasing cluster size, which make the spectra more and more complex. The double ionization potential is further decreased by the formation of these water/water two-site states, because their hole−hole repulsion is comparatively small. Besides, the increasing number of monomers has a particularly interesting influence on those parts of the spectra where many-body effects play an important role. These are mainly inner valence ionization spectra, where pronounced breakdown of the MO picture is stated, and those parts of the double ionization spectra for which hole charge is localized in inner valence orbitals. This part of the double ionization spectrum of $(H_2O)_2F^-$ and $(H_2O)_3F^-$ differs considerably from that of H_2OF^- because of a lower triple ionization threshold which guarantees a large number of excited states in the energy region of the two-hole configurations of these double ionized states. Accordingly, the corresponding parts of the double ionization spectra are characterized by bundles of low-intensity lines.

Finally, we compare the spectra of three different isomers of $(H_2O)_3F^-$. The comparison reveals that the ionization spectrum of the isomer A with C_3 symmetric ground-state geometry is rather similar from the energetical point of view to that of the isomer B with one H-donor-bound second solvation shell water molecule. Interestingly, this concerns all water molecules, including the one being part of the second solvation shell of F^-. This result is astonishing, because the C_3 symmetric ground-state geometry is very different from the other two geometries considered. The double ionization spectra of all three isomers are more different, though, because of the possibility of farther hole delocalization in the two isomers including a water molecule in the second solvation shell.

The ionization energies of the waters in the first solvation shell of isomer C with H-acceptor-bound second solvation shell water are closer to—and even slightly below—those of $(H_2O)_2F^-$. The ionization energies of the water molecule in the second solvation shell, on the other hand, are considerably higher. This result is a consequence of the strong impact of the H-bond on the electron density distribution. The electronic structure of aqueous microsolvation clusters depends particularly strongly on the nature of H-bonds building the cluster geometry.

Acknowledgment. Financial support by DFG is greatly acknowledged.

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