Structure and Stability of Aquotetrafluorouranyl(VI) in the Solid State. Density-Functional Study of $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})][\text{NMe}_4]_2 \cdot 2\text{H}_2\text{O}^\ddagger$

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Abstract

Periodic density functional computations have been performed for solid $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})][\text{NMe}_4]_2 \cdot 2\text{H}_2\text{O}$ at the BLYP level. A model with disordered fluoro and aquo ligands in the uranyl anion is significantly lower in energy than one with a symmetrical assignment of these sites, which was favored in the original X-ray crystallography study. According to optimized energies and Car-Parrinello molecular dynamics (CPMD) simulations, the $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ ion in the solid is stable with respect to loss of the coordinated water molecule. In contrast, CPMD simulations had found this ligand to be unbound in aqueous solution. The role of the counterions in stabilizing the higher coordination number in the crystal is discussed.

[‡]*Dedicated to Prof. Dr. Tom Ziegler on the occasion of his 65th birthday.*

Introduction

Approximate density functional theory (DFT) has fertilized computational transition-metal chemistry tremendously,¹ especially since relativistic methods have been implemented that allow the proper treatment of heavy metals.² Complexes of the heaviest metals, actinides, have been early challenging targets for DFT,^{3,4} and are important benchmarks for calculations of spectroscopic properties such as NMR parameters.⁵ DFT-based molecular dynamics simulations, long established as powerful tools to study elementary reaction steps at transition-metal centers,^{6,7} are now also being applied to actinide chemistry.^{8,9,10,11}

We have been applying Car-Parrinello molecular dynamics (CPMD) simulations to study structure,^{9,10} speciation,¹² reactivities,¹³ and NMR chemical shifts of uranyl(VI) complexes in aqueous solution. A protocol based on constrained CPMD and pointwise thermodynamic integration (PTI) has been shown to capture salient structural and energetic features reasonably well. With the possibility to evaluate changes in free energies under realistic conditions (i.e. taking temperature and solvation effects explicitly into account), this approach often surpasses static quantum-chemical computations with simpler solvation models. For instance, the acidity constant¹⁴ and ligand-exchange barrier¹³ in uranyl hydrate, $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, as well as the free binding energies between the latter and ligands such as nitrate,¹² chloride,¹⁵ and fluoride¹⁶ have all been reproduced within ca. ± 2.5 kcal/mol of experiment, a rather respectable accuracy for present-day DFT.

In our recent study on mixed aquo fluoro uranyl species,¹⁶ an apparent inconsistency between DFT and experiment was noted for the tetrafluoro complex. In two salts with organic counterions, this anion had been characterized as $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ (**1a**) by X-ray crystallography,^{17,18} and evidence for its presence in aqueous solution had been given by EXAFS.¹⁹ In CPMD simulations of pristine **1a**, in contrast, the water ligand turned out to be unbound both in gaseous and aqueous phases, where it spontaneously detaches, affording four-coordinate $[\text{UO}_2\text{F}_4]^{2-}$ (**1b**).¹⁶ Employing the PTI technique and the U-O(water) distance as reaction coordinate, a shallow minimum corresponding to **1a** was

found in water, but the driving force for dissociation of the aqua ligand from **1a** into the bulk was indicated to be substantial, $\Delta A = -7.2 \pm 1.5$ kcal/mol. Even when allowing for the general tendency of DFT to underestimate metal-ligand bond strengths,^{20,21} this result appeared to be at odds with the observation of **1a** in the EXAFS experiment. No experimental value for this dissociation energy is known, but the EXAFS data furnished strong evidence for the presence of two shells in the equatorial plane of the tetrafluoride, corresponding to F and O atoms. Because it was difficult to refine the precise number of coordinated water ligands, in the adopted model this number was fixed to one (as observed in the solid),¹⁹ implying rather strong binding of water (with a positive free energy for dissociation, and, possibly, zero as its lower limit²²).

The BLYP density functional was used in the simulations. Rather well suited to describe the properties of liquid water and aqueous solutions,^{23,24} it is not the first choice for geometries of transition-metal complexes in general.²⁵ BLYP is a typical member of the GGA family, i.e. pure, gradient corrected functionals, which are sometimes outperformed by hybrid variants when it comes to reaction energies involving actinides.²⁶ As mentioned above, in the CPMD/PTI studies of aqueous uranyl complexes BLYP has performed quite well so far, but if it turns out to fail for the aquo tetrafluoro complex, the predictive power of this approach may be at stake. An utter failure would for instance be the incorrect prediction that **1a** should also be unstable in the environment of a known, stable crystal. In the present paper, initial investigations to that effect are reported, including, to the best of my knowledge, the first CPMD simulations of a uranyl complex in the solid state.

Of the two solids containing **1a**, $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})][\text{NMe}_4]_2 \cdot 2\text{H}_2\text{O}$ (**2**)¹⁸ was chosen as target, because it has the smaller unit cell. In addition, an ambiguity in the assignment of the atomic positions had been noted during analysis of the crystal structure, which will be addressed as well.

Computational Details

All computations used the CPMD program²⁷ and the same settings as in the previous gas-

phase and solution studies (BLYP functional,^{28,29} Troullier-Martins pseudopotentials,^{30,31} 80Ry plane-wave cutoff). Starting point were the heavy-atom coordinates as deposited in the Cambridge Structure Database (refcode DAPWUM).¹⁸ A simple orthorhombic cell with lattice constants fixed to the experimental values ($a = 7.006 \text{ \AA}$, $b = 8.938 \text{ \AA}$, $c = 13.619 \text{ \AA}$) and two formula units in the unit cell were used (affording a total of 100 atoms). Unfortunately, the current version of the CPMD program does not allow optimization of lattice constants for systems containing f-electrons. Hydrogen atoms were placed on the water oxygen atoms (pointing toward potential H-bond acceptors, but otherwise arbitrarily) and their positions relaxed both at the Γ -point and using 2, 2, and 1 k-points along the reciprocal a , b , and c axes, respectively.³² Attempts to use more k-points resulted in severe convergence problems or, where wavefunctions could be converged, in relatively minor changes in total energies. Unless otherwise noted, results from the 2x2x1 k-point calculations are discussed in the following. CPMD simulations were performed at the Γ -point, however (see discussion below), using a fictitious electronic mass of 600 a.u., a time step of 0.121 fs, and the deuterium mass for H atoms. Starting from the Γ -point optimized coordinates, the system was equilibrated for 0.5 ps, during which a temperature of $320 \pm 50 \text{ K}$ was maintained via velocity rescaling, and then propagated for 3 ps without constraints in the NVE ensemble. For population analysis, the orbitals represented in plane waves were projected onto suitable atomic orbitals, which were taken from the pseudo wavefunctions involved in construction of the pseudopotentials, except for hydrogen, where a standard Slater function was used.³³

Results and Discussion

In the refinements of the X-ray data of **2** an ambiguity concerning the location of F and O atoms was noted, and the simplest model had been adopted (denoted Model 1 here), in which an O atom of the coordinated water ligand (O2 in Figure 1) resides on a symmetry plane.¹⁸ Because the resulting U-O2 distance would be exceptionally short, however, this assignment was later questioned¹⁹ and it was suggested that this O2 position would rather be occupied by an F atom, and that the O atom would be disordered over the F1 and F1^a sites, a possibility that was already mentioned in the X-ray study. This alternative assignment would be more consistent with the rather long bond distances between

uranium and the F1 and F1^a sites. A corresponding model (denoted Model 2) was constructed by exchanging F and O in the F1^a and O2 sites in both uranyl moieties of the unit cell.

Figure 1: Labeling of atoms in the original X-ray crystallography study (reference 18, W denotes O atoms of crystal water).

After relaxation of the H positions, Model 2 is lower in energy than Model 1 by ca. 125 kcal/mol, after full optimization (with fixed lattice constants) it is still favored by 13.4 kcal/mol. This result is thus in complete accord with the suggested revision of the atomic positions in the crystal and the concomitant disorder.³⁴

In the following only results for Model 2 will be discussed. Figure 2 shows perspective drawings of solid **2** after H-relaxation (top) and full optimization (bottom). To illustrate the packing more clearly, 8-fold unit cells with doubled lattice constants are displayed. The most notable change upon full optimization is that the O atoms of the two crystal water molecules move somewhat above and below the equatorial uranyl plane (which is a plane of symmetry in the point group of the crystal), and that the uranyl fluoride moieties rotate somewhat about the O=U=O axis. This can be seen in Figure 3, an overlay of X-ray and optimized coordinates (both sets of coordinates are supplied as supporting information for 3D visualization).

Figure 2: Stereoviews of the solid after H-relaxation (top) and full optimization (bottom), showing 8 unit cells (over doubled lattice parameters).

Figure 3: Overlay of X-ray derived (red) and optimized (blue) positions of the non-hydrogen atoms, viewed along the a -, b -, and c -axes (from left to right).

These changes could to some extent be due to the initial choice of the location of the H atoms, which would induce a bias for a particular H-bond pattern. An exhaustive search of all possible such patterns would be very involved and was not conducted at this point. It is rather noted that the overall features of the observed solid-state structure are reasonably well preserved in the DFT-optimized crystal, in particular if one allows for disorder in the former. Observed and correspondingly averaged computed bond distances are found to be in good accord, except for the U-F(O2) distance, the experimental value of which appears to be rather short also for an U-F bond (compare Expt. and CP-opt values in italics in Table 1).

Table 1: Observed and simulated uranium-ligand distances in the uranyl aquo fluoro anion **1a** [in Å]. Labeling see Figure S1, with F(O2) and O(F1^a) indicating the atoms that have been switched in model 2.^a

Bond	Expt. ^b	CP-opt	Γ -opt ^c	CPMD ^{c,d}
U-O(F1 ^a)		2.52	2.54	2.58(10)
<i>> mean</i>	<i>2.39(1)</i>	<i>> 2.39</i>	<i>> 2.40</i>	<i>> 2.42(10)</i>
U-F1		2.26	2.26	2.27(9)
U-F(O2)	<i>2.11(2)</i>	2.28	2.28	2.28(8)
U-F2		2.28	2.28	2.27(7)
<i>> mean</i>	<i>2.28(1)</i>	<i>> 2.29</i>	<i>> 2.29</i>	<i>> 2.28(7)</i>
U-F2 ^a		2.29	2.29	2.29(7)

^aIn italics: average of the denoted bonds assuming disorder of the O atom over F1 and F1^a sites (see text). ^bFrom reference 18. ^cUsing Γ -point integration only (see Computational Details). ^dMean values (in parentheses: standard deviations) over 3 ps of unconstrained MD.

In CPMD simulations of a single $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ anion, both in gaseous and aqueous phases, the water ligand has detached spontaneously from the complex.¹⁶ To test if the same would happen in the crystal, CPMD simulations were performed for solid **2**. Unfortunately, CPMD simulations are not possible using k-point integration. The usual procedure is to use supercells large enough that calculations at the Γ -point are sufficient.

In the present case, this would mean that the lattice constants a and b would have to be doubled, which would render the simulations rather expensive. On the other hand, the structural parameters of the uranyl complex are very similar whether the solid is optimized using k -points or at the Γ -point only (compare CP-opt and Γ -opt entries in Table 1). It is thus to be expected that the artifacts of just using the Γ -point would not be too severe. In fact, if anything, neglect of the k -points appears to weaken the U-O(water) interaction, as evidenced by the increase of the U-O(F1^a) distance on going from the CP-opt to the Γ -opt value (by 0.02 Å, Table 1). CPMD simulations were therefore performed at the Γ -point for the regular unit cell, bearing in mind that this procedure might artificially weaken the binding of the water ligands. Nonetheless, the five-coordinated uranyl complexes remain stable during a total simulation time of 3.5 ps (including equilibration) at a mean temperature of 314 K. Except for the U-O(water) distance, which increases noticeably by 0.04 Å, only minor changes are found on going from equilibrium to thermal averaged bond distances (compare Γ -opt and CPMD values in Table 1).

Of course, the apparent stability of five-coordination in the solid during the CPMD simulations might just be caused by the confines of the fixed unit cell. In order to estimate how strongly the aquo ligand would be bound in the solid, a coordinated water molecule was removed from one of the optimized uranyl complexes in the unit cell (the other complex retaining five-coordination). The combined total energies of the fragments, i.e. that of the unit cell without one water and that of the water molecule in the same empty box, is 23.2 kcal/mol above that of the full, optimized solid (k -point results). Upon relaxation of these fragments, in the course of which the four-coordinated $[\text{UO}_2\text{F}_4]^{2-}$ moiety with its vacant coordination site optimizes to the usual approximately square-bipyramidal conformation of **1b**, this energy difference reduces to 7.9 kcal/mol. Thus, a substantial binding energy is indicated for the water ligand in the solid. Because the lattice constants were fixed throughout, this value is only to be used as a rough guide. It is quite possible that the "dehydrated" crystal would have a slightly smaller unit cell than the intact one or, more likely, that it would adopt a different, more stable morphology altogether. In particular the latter question is impossible to address at present because the sheer size of the system precludes a true ab-initio prediction of its crystal structure.

In any event, the estimated water dissociation energy of ca +8 kcal/mol within the constraints of the solid is noteworthy, as it contrasts with the results obtained for free **1a** in the gas phase or in solution, where the water ligand is indicated to be unbound, with a computed dissociation energy of ca. -7 kcal/mol (ΔE at the BLYP/SDD(+)/PCM level or ΔA from constrained CPMD and PTI).³⁵ To shed more light on the possible reasons for the apparent stabilization of $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ in the solid,³⁶ a single such anion was retained in the fully optimized crystal and all other atoms deleted. The resulting slabs of $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ moieties approaching each other with their equatorial ligands are highly unphysical because of the strong Coulomb repulsion between them, but are an instructive model for comparison with the estimated water binding energy discussed above for the full crystal. When this "pristine" $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ moiety is further separated into $[\text{UO}_2\text{F}_4]^{2-}$ and H_2O fragments (again with the same unrelaxed structures in the otherwise empty cell), the combined energies of these fragments are 9.7 kcal/mol above that of the $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ slabs. Upon relaxing the fragments, their combined energies drop below that of the complex (in its structure adopted in the full crystal), namely to -12.8 kcal/mol. In other words, it costs more energy (ca. 13 kcal/mol) to distort the separated fragments, **1b** and water, into the structures they adopt in the complex than is released upon binding between these distorted fragments (ca. -10 kcal/mol). Without the counterions (and the crystal water), the water ligand in **1a** is thus indicated to be unbound. Apparently, the interactions with the counterions are instrumental for the stability of **1a** in the solid, where each of these complexes is surrounded by eight NMe_4^+ ions (forming two "crowns" above and below the equatorial plane, see Figure 2).

In order to assess the effect of this polar environment on the overall charge distribution, Mulliken population analysis has been performed for the whole crystal and for the periodic $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ slabs cut out thereof. The results are summarized in Table 2. While the absolute numbers should not be over-interpreted,³⁷ the general trend is interesting: Upon removing the neighbors around **1a**, the overall charge density on the UO_2F_4 unit increases significantly, i.e. this fragment becomes more negative (by more than a fourth electronic charge unit, see last entry in Table 2). This additional negative

charge is shared roughly equally between terminal oxo and equatorial fluoride ligands, but also the U atom becomes slightly less positive. Apparently, this increased negative charge makes the uranyl moiety less electrophilic toward the fifth water ligand, consistent with the computed drop in dissociation energy of the latter (from ca. 23 kcal/mol to 10 kcal/mol using the unrelaxed fragments, see above). Similarly, the Mayer bond orders between U and the water O atom decrease from 0.19 in the full crystal **2** to 0.15 in the slabs of **1a**.

Table 2: Mulliken charges in the uranyl aquo fluoro anion **1a**.^a

Atoms	full crystal (2)	only 1a ^b
U	2.32	2.29
O(H ₂ O)	-0.90	-0.90
F (mean)	-0.64	-0.67
O(uranyl)	-0.63	-0.69
Σ UO ₂ F ₄ ^c	-1.48	-1.75

^aAt the Γ -point, CP-opt geometry for Model 2. ^b[UO₂F₄(H₂O)]²⁻ slabs from single **1a** unit retained in the unit cell (not relaxed). ^cTotal charge of this fragment.

Apparently, when pristine **1a** is immersed in water, the environment is not polar enough to increase the electrophilic character of the uranyl center to the same extent as the counterions do in the crystal. At this point it is tempting to speculate if counterions in solution, which were not included in the CPMD simulations so far, could be more efficient in that respect. In the EXAFS experiments, a considerable excess of NaF (ca. 9-fold) had been used to produce solutions that contain **1a** as major uranyl component.¹⁹ It is possible that the notable concentration of Na⁺ ions about **1a** in water (or the increased ionic strength) could result in an increased affinity between the tetrafluoro uranyl complex and the water ligand, which could eventually help to reconcile the apparent discrepancy between the DFT and EXAFS results. More work should be directed toward this question.

Conclusion

According to periodic DFT/BLYP computations for solid $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})][\text{NMe}_4]_2 \cdot 2\text{H}_2\text{O}$, a model with disordered fluoro and aquo ligands in the uranyl anion is significantly lower in energy than the originally adopted symmetrical assignment of these sites. This result supports the proposed revision of this structural detail that was based on a critical analysis of the refined bond distances. Thus, DFT computations akin to those presented here can be helpful in X-ray crystallography of uranyl complexes, when, as in the present case, competing structural models cannot be proved or disproved based on the diffraction data alone.

In these static model computations and in dynamic (CPMD) simulations, the water ligand in the $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$ anion (**1a**) is indicated to be bound. There is no evidence that the DFT-based approach employed, including the BLYP functional, would fail utterly for **1a** in the sense that it would incorrectly predict an unbound water ligand in the solid state. This finding therefore does not invalidate our previous results for gaseous and aqueous phases, according to which the free tetrafluoride does not bind this fifth water ligand and should be formulated as four-coordinated $[\text{UO}_2\text{F}_4]^{2-}$ (**1b**), in apparent contrast to EXAFS experiments, which favor the formulation as five-coordinated **1a** in solution. Computational evidence has been presented suggesting that it is the crystal environment that stabilizes the higher coordination number in the solid. Studies are underway to explore if counterions in the aqueous solution, so far neglected in the simulations, could also increase the propensity of free **1b** to bind an additional water ligand, which would help to resolve the apparent discrepancy between theory and experiment on the structure of uranyl tetrafluoride in water.

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References

- (1) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651-667.
- (2) Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743-761.
- (3) Wezenbeek, E. M.; Baerends, E. J., Ziegler, T. *Inorg. Chem.* **1995**, *34*, 238-246.
- (4) Denning, R. G. *J. Phys. Chem. A* **2007**, *111*, 4125-4143.
- (5) Schreckenbach, G.; Wolff, S. K., Ziegler, T. *J. Phys. Chem. A* **2000**, *104*, 8244-8255.
- (6) Woo, T. K.; Margl, P. M.; Lohrenz, J. C. W.; Blöchl, P. E.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 13021-13030.
- (7) De Angelis, F.; Fantacci, S.; Sgamellotti, A. *Coord. Chem. Rev.* **2006**, *250*, 1497-1513.
- (8) Infante, I.; Visscher, L. *J. Comput. Chem.* **2003**, *25*, 386-392.
- (9) Bühl, M.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.* **2005**, *127*, 13506-13507.
- (10) Bühl, M.; Kabrede, H.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.* **2006**, *128*, 6357-6368.
- (11) Nichols, P.; Bylaska, E. J.; Schenter, G. K.; de Jong, W. *J. Chem. Phys.* **2008**, *128*, 124507.
- (12) Bühl, M.; Golubnychiy, V. *Inorg. Chem.* **2007**, *46*, 8129-8131.
- (13) Bühl, M.; Kabrede, H. *Inorg. Chem.* **2006**, *45*, 3834-3836
- (14) Bühl, M.; Kabrede, H. *ChemPhysChem* **2006**, *7*, 2290-2293.
- (15) Bühl, M.; Sieffert, N.; Golubnichiy, V.; Wipff, G. *J. Chem. Phys. A* **2008**, *112*, 2428-2436.
- (16) Bühl, M.; Sieffert, N.; Wipff, G., submitted to *Chem. Phys. Lett.*
- (17) Ivanov, S. B.; Davidovich, R. L.; Mikhailov, Y. N., Shchelokov, R. N. *Koord. Khim.* **1982**, *8*, 211.
- (18) Mak, T. C. W., Yip, W.-H. *Inorg. Chim. Acta* **1985**, *109*, 131-133.
- (19) Vallet, V.; Wahlgren, U.; Schimmelpfennig, B.; Moll, H.; Szabo, Z.; Grenthe, I. *Inorg. Chem.* **2001**, *40*, 3516-3525.
- (20) Rotzinger, F. R. *J. Phys. Chem. B.* **2005**, *109*, 1510-1527.
- (21) For recent validation studies in context with associative vs. dissociative water exchange in uranyl hydrate see reference 13 and a) Gutowski, K. W.; Dixon, D. A. *J.*

Phys. Chem. A **2006**, *110*, 8840-8856; b) Rotzinger, F. P. *Chem. Eur. J.* **2007**, *13*, 800-811; c) Tsushima, S. *J. Phys. Chem. A* **2007**, *111*, 3613-1617.

(22) Grenthe, I, private communication.

(23) See for instance: Sprik, M.; Hutter, J.; Parrinello, M. *J. Chem. Phys.* **1996**, *105*, 1142-1152.

(24) See however: VandeVondele, J.; Mohamed, F.; Krack, M.; Hutter, J.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **2005**, *122*, 014515 and references cited therein.

(25) Bühl, M.; Reimann, C.; Pantazis, D. A.; Bredow, T.; Neese, F. *J. Chem. Theory Comput.* **2008**, *4*, 1449-1459.

(26) Shamov, G. A.; Schreckenbach, G.; Vo, T. N. *Chem. Eur. J.* **2007**, *13*, 4932-4947.

(27) CPMD Version 3.13.1, Copyright IBM Corp. 1990-2008, Copyright MPI für Festkörperforschung Stuttgart 1997 - 2001.

(28) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

(30) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993-2006.

(31) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425-1428.

(32) k-points are special integration points used to sample the first Brillouin zone in reciprocal space. When the unit cell is large enough, that zone is small and integration using just its center (the Γ -point) is sufficient.

(33) We note in passing that this type of Mulliken population analysis in a plane-wave basis is plagued by an incomplete partitioning of the total electron density onto the atomic pseudo-orbitals. The total amount of this “unassigned charge” is on the order of ca. 1% of the total number of electrons (similar to findings in other ionic solids, see e.g.: Haiber, M.; Ballone, P.; Parrinello, M. *Amer. Mineral.* **1997**, *82*, 913-922), which is most probably contained in regions of a more diffuse density shared by all atoms.

(34) To model the actual disorder, larger supercells with a 50:50 distribution of water molecules over the F1 and F1^a sites would have to be employed. This was not pursued, because the concomitant effect on structural parameters and energies are expected to be too small to affect the qualitative conclusions.

(35) According to the relative energies at the SDD(+)/PCM level, water dissociation

from **1a** is less endothermic with B3LYP than with the BLYP functional, but only by 2 kcal/mol (Table 3 in reference 16).

(36) Quantitatively, a "water sublimation energy" from the crystal of ca. 8 kcal/mol (which should be close to the corresponding enthalpy of sublimation) is not indicating a particularly high stability, as it is slightly smaller than the enthalpy of desolvation of a single water molecule from the bulk liquid, 10.0 kcal/mol at 25°C (cf. Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016-2027).

(37) Wiberg, K. B.; Rablen, P. R. *J. Comp. Chem.* **1993**, *14*, 1504-1518.

Table of Contents