THE JOURNAL OF PHYSICAL CHEMISTRY A

pubs.acs.org/JPCA Article

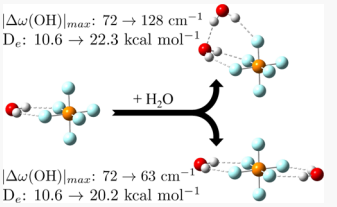
Competition between Solvent−Solvent and Solvent−Solute Interactions in the Microhydration of the Hexafluorophosphate Anion, $PF_6^-(H_2O)_{n=1,2}$

Yasmeen A. Abdo and Gregory S. Tschumper*

Cite This: https://dx.doi.org/10.1021/acs.jpca.0c06466 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: This study systematically examines the interactions of the hexafluorophosphate anion (PF_6^-) with one or two solvent water molecules ($PF_6^-(H_2O)_n$ where n = 1, 2). Full geometry optimizations and subsequent harmonic vibrational frequency computations are performed on each stationary point using a variety of common density functional theory methods (B3LYP, B3LYP-D3, M06-2X, and ωB97XD) and MP2 and CCSD(T) *ab initio* methods with a triple-ζ correlation consistent basis set augmented with diffuse functions on all non-hydrogen atoms (cc-pVTZ for H and aug-cc-pVTZ for P, O, and F; denoted as haTZ). Five new stationary points of $PF_6^-(H_2O)_2$ have been identified, one of which has an electronic energy of approximately 2 kcal mol^{-1}, lower than the only other dihydrate structure reported for this system. The CCSD(T) computations also reveal that the detailed interactions between PF_6^- and H_2O can be quite difficult to model reliably, with some methods struggling to correctly characterize stationary points for n = 1 or accurately reproduce the vibrational frequency shifts induced by the formation of the hydrated complex. Although the interactions between the solvent and ionic solute are quite strong (CCSD(T) electronic dissociation energy ≈10 kcal mol^{-1} for the monohydrate minimum), the solvent−solvent interactions in the lowest-energy $PF_6^-(H_2O)_2$ minimum give rise to appreciable cooperative effects not observed in the other dihydrate minima. In addition, this newly identified structure exhibits the largest frequency shifts in the OH stretching vibrations for the waters of hydration (with $\Delta\omega$ exceeding −100 cm^{-1} relative to the values for an isolated H_2O molecule).



1. INTRODUCTION

The hexafluorophosphate anion (PF_6^-) is frequently used as a component in room temperature ionic liquids (RTILs)[1] and aprotic electrolytes for lithium-based batteries.[2] In the former context, the presence of water as an impurity or as a cosolvent can appreciably alter the physical properties of a given RTIL (*e.g.*, conductivity, density, solubility, and viscosity).[3−6] Compared to other common RTILs, those based on PF_6^- have been shown to exhibit some of the weakest associations with water[7] and some of the lowest miscibilities with water.[8−11] PF_6^- is one of the least hygroscopic anions for RTILs and is generally used to make "hydrophobic" ionic liquids.[12] As such, the interactions between water with the ionic components of RTILs containing the hexafluorophosphate anion have been the focus of a number of experimental and computational studies.[6,7,9,13]

The PF_6^- ion has also played an important role in fundamental studies of ion solvation in aqueous solutions.[14−21] Singly deuterated water (HOD) can provide a sensitive spectroscopic probe of ion hydration. Both Raman and infrared (IR) measurements have shown that PF_6^- shifts the OD stretching frequency of bulk water (2509 cm^{-1})[22] to higher energy by more than +150 cm^{-1} (ca. 2667 cm^{-1}).[14,17] Recent *ab initio* molecular dynamics (AIMD) simulations by Śmiechowski qualitatively reproduced this result with a predicted shift of more than +300 cm^{-1} for the corresponding OH stretch.[21] More importantly, the subsequent distance-dependent analysis of the simulated IR spectrum provided much needed molecular-level insight into the solute−solvent interactions that are the source of these unusual perturbations to the IR spectrum of liquid water.

At the smaller end of the size scale for hydration phenomena, relatively few microsolvation studies of PF_6^- have been carried out with quantum mechanical electronic structure methods based on wave function theory (WFT) or density functional theory (DFT). The authors are not aware of any analogous experimental investigations of small clusters composed of PF_6^- interacting with one or more water molecules. Two computational studies have examined PF_6^- explicitly solvated with one or two water molecules (i.e., $PF_6^-(H_2O)_{n=1,2}$ clusters) to better understand the water−anion interaction in RTILs.[12,23] Wang et al. identified a monohydrate structure (denoted as configuration C_{2v} edge in Figure 1 of the present study) and a dihydrate configuration (denoted as configuration D_{2h} edge−edge at the top of Figure 2 of the

Received: July 15, 2020
Revised: September 9, 2020

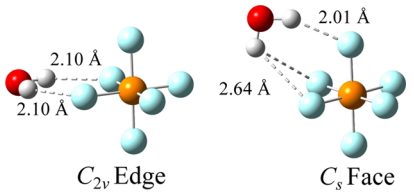


Figure 1. CCSD(T)/haTZ-optimized stationary points of $PF_6^-(H_2O)_1$ with select intermolecular R(H···F) distances in Å.

present study).[12] These structures were previously identified as minima on the HF/6-31G* potential energy surfaces but not with the B3LYP or MP2 methods when using the same 6-31G* basis set. Rodríguez-Otero et al. published a follow-up study that was able to identify the corresponding minima with both the B3LYP and MP2 methods when using the 6-31++G** basis set.[23] In addition, Rodríguez-Otero et al. identified another monohydrate water structure (denoted herein as f3 configuration C_s edge and shown in the inset of Figure 3) but only when diffuse functions were not included in the basis set.

In the broader context of ion hydration, the C_{2v} edge structure (Figure 1) reported for the solvation of PF_6^- with a single water molecule is consistent with the double ionic hydrogen bond (DIHB) motif typically observed for molecular anions in the size regime of three or more atoms with the hydrogen bond acceptors separated by at least 2.2 Å.[24−30] The single ionic hydrogen bond (SIHB) pattern is normally reserved for monohydrated atomic and diatomic anions.[30−39]

The progression to dihydrate systems immediately manifests a competition between anion−water and water−water interactions. In the sequence of halide ion dihydrates ($X^-(H_2O)_2$, where X = F, Cl, Br, and I), for example, there is essentially no evidence of hydrogen bonding between the two water molecules for F^-.[39−44] In contrast, the water···water hydrogen bond is clearly present for the other halide ions, growing in strength from Cl^- to Br^- and I^-,[39,44−49] but the corresponding spectral signatures can vanish with increasing temperature.[50,51] This competition also extends to other atomic and polyatomic anions.[34,52−56] Interestingly, the D_{2h} edge−edge structure (Figure 2) identified for the PF_6^- dihydrate does not display any sort of solvent−solvent interactions. Instead, the two water molecules independently engage in identical DIHB contacts on opposite edges of the hexafluorophosphate octahedron.[12]

It is worth noting that the closely related sulfur hexafluoride anion (SF_6^-) has been reported to deviate from the aforementioned trends for mono- and dihydrated anions.[57] Although SIHB and DIHB SF_6^- monohydrate structures were computed to be nearly isoenergetic (within 0.1 kcal mol^{-1}), for this somewhat challenging open-shell system, the IR spectra are more consistent with the former. Similarly, there is no spectroscopic evidence of water−water hydrogen bonding in the dihydrate even though *ab initio* computations suggest that such a structure lies within 0.2 kcal mol^{-1} of the lowest-energy $SF_6^-(H_2O)_2$ minimum identified in that study.

The present study builds upon the earlier WFT and DFT results for the $PF_6^-(H_2O)_{n=1,2}$ systems by performing a more extensive exploration of the possible hydration configurations, particularly those exhibiting water−water interactions for n = 2, utilizing robust *ab initio* methods and correlation consistent basis sets. This investigation also provides a vibrational analysis that complements that of Śmiechowski.[21] Rather than probing spectroscopic perturbations to bulk water, this work examines

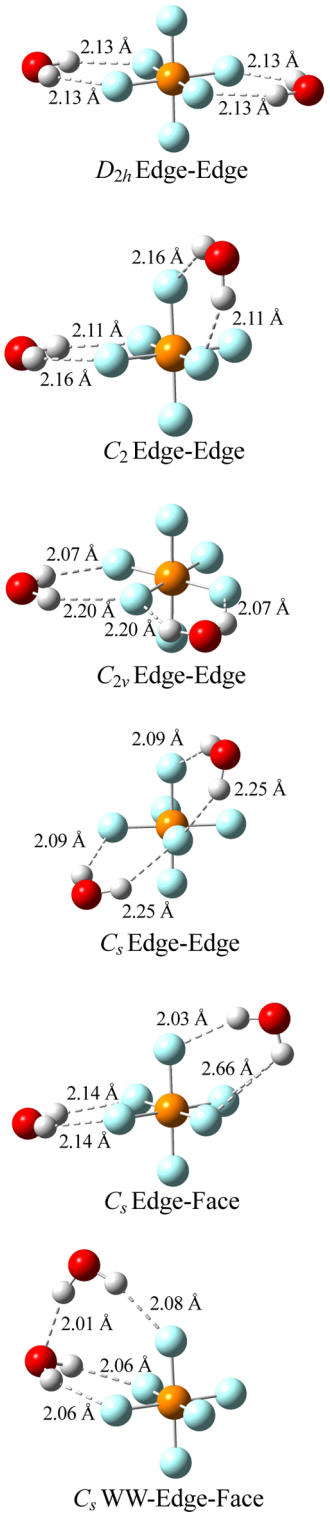


Figure 2. CCSD(T)/haTZ-optimized stationary points of $PF_6^-(H_2O)_2$ with select intermolecular R(H···F) and R(H···O) distances in Å.

the shifts in the OH stretching vibrations of an individual H_2O molecule when it interacts with PF_6^- (as well as a second H_2O molecule when it interacts to form $PF_6^-(H_2O)_2$). In other words, we use an isolated H_2O molecule devoid of intermolecular contacts as the reference for probing the effects of this ionic solute on the (micro)solvent instead of liquid water, which has an extensive network of hydrogen bonds.

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX

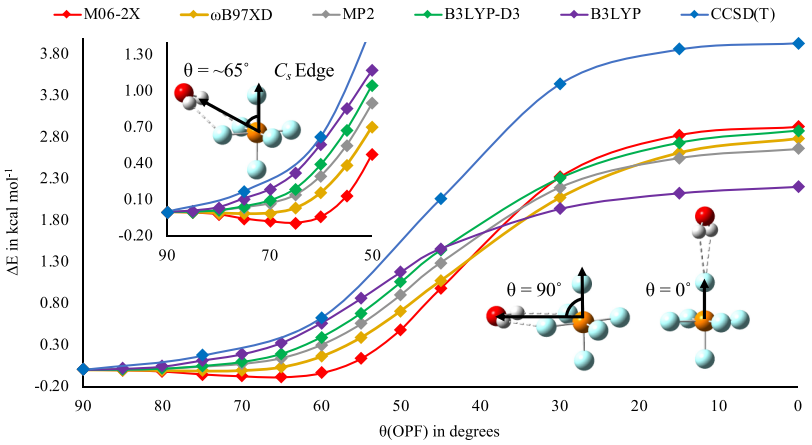


Figure 3. Relaxed C_s scans (with the haTZ basis set) of an H_2O molecule along a face of PF_6^- where the scan angle, θ(OPF), is 90° for the C_{2v} edge configuration (Figure 1) and approximately 65° for the C_s edge configuration (inset).

Table 1. Relative Electronic Energies (ΔE in kcal mol^{-1}) and Number of Imaginary Modes (n_i) of the $PF_6^-(H_2O)_{n=1,2}$ configurations Optimized with Various Methods and the haTZ Basis Set and CCSD(T)/haQZ Relative Energies Computed Using the CCSD(T)/haTZ -Optimized Geometries

		CCSD(T)		MP2	B3LYP	B3LYP-D3	ωB97XD	M06-2X
structure	n_i	haQZ	haTZ	haTZ	haTZ	haTZ	haTZ	haTZ
C_{2v} Edge	0[a]	+0.00	+0.00	+0.00	+0.00	+0.00	+0.00	+0.00
C_s Face	1[b]	+0.38	+0.30	+0.34	+0.53	+0.47	+0.15	+0.06
D_{2h} Edge−Edge	0[c]	+0.00	+0.00	+0.00	+0.00	+0.00	+0.00	+0.00
C_2 Edge−Edge	0	+0.08	+0.08	+0.01	+0.01	+0.01	+0.00	−0.18
C_{2v} Edge−Edge	1[d]	+0.30	+0.29	+0.28	+0.27	+0.27	+0.30	+0.36
C_s Edge−Edge	0	+0.38	+0.33	+0.35	+0.50	+0.37	+0.22	+0.04
C_s Edge−Face	1	+0.37	+0.31	+0.32	+0.47	+0.41	+0.16	−0.04
C_s WW−Edge−Face	0	−2.09	−2.09	−2.11	−1.95	−2.36	−2.48	−2.29

[a] n_i = 1 for ωB97XD and M06-2X. [b] n_i = 0 for ωB97XD. [c] n_i = 3 for ωB97XD and n_i = 2 for M06-2X. [d] n_i = 0 for B3LYP and M06-2X.

Consequently, the OH vibrational frequency shifts reported here are in the opposite direction (to lower energy or red-shifted) from those associated with bulk phase measurements and simulations (to higher energy or blue-shifted).

2. COMPUTATIONAL DETAILS

Preliminary relaxed angular scans are performed over several coordinates of $PF_6^-(H_2O)_1$ and $PF_6^-(H_2O)_2$ using various DFT methods (B3LYP,[58] B3LYP-D3,[58,59] M06-2X,[60] and ωB97XD[61]) with Dunning's correlation consistent triple-ζ basis set augmented with diffuse functions on all nonhydrogen atoms (cc-pVTZ for H and aug-cc-pVTZ for P, O, and F; denoted haTZ).[62,63] The resulting low-energy configurations are then fully optimized with the haTZ basis set and all four functionals and the MP2[64] and CCSD(T)[65] *ab initio* methods. All optimizations are computed using analytical gradients. DFT harmonic vibrational frequencies are computed analytically for each stationary point, whereas the CCSD(T) Hessians are obtained from the finite difference of analytical gradients. To validate the finite difference procedure, MP2 frequencies are computed both analytically and from the finite difference of analytical gradients, and the results never differed by more than 0.1 cm^{-1}. Single-point energy computations with the CCSD-(T) method and the corresponding haQZ basis set are performed on the CCSD(T)/haTZ geometries using Molpro. All DFT computations are performed with the Gaussian09[66] software package with a dense pruned numerical integration grid composed of 175 radial shells and 974 angular points per shell for H, O, and F and 250 radial shells with 974 angular points per shell for P corresponding to the superfine keyword in Gaussian09. MP2 computations are performed using both Gaussian09 and CFOUR, whereas the CCSD(T) computations are performed with CFOUR.[67]

Analogous optimizations and single-point energy computations were also performed on the isolated fragments (PF_6^- and H_2O) in order to evaluate the electronic dissociation energies of the complexes ($D_e = E[PF_6^-] + nE[H_2O] - E[PF_6^-(H_2O)_n]$). This scheme for computing the dissociation energy and related quantities introduces an inconsistency from the use of finite basis sets that was identified as early as 1968 by Kestner[68] and later dubbed basis set superposition error (BSSE).[69] To help assess the impact of this inconsistency on the D_e values reported in this work, we apply the popular counterpoise (CP) procedure developed independently by Jansen and Ros in 1969[70] and Boys and Bernardi in 1970[71] to the lowest-energy minima identified for n = 1 and 2. The extension of the procedure to systems with ≥3 fragments is not uniquely defined. For the $PF_6^-(H_2O)_2$ system, we follow the protocol described in detail elsewhere[72] for flexible (not rigid) fragments.

3. RESULTS AND DISCUSSION

When a water molecule interacts with PF_6^-, two common structural motifs are observed for the mono- and dihydrate stationary points shown in Figures 1 and 2. The "edge" label for the structures indicates that water has formed two (often

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX

symmetric) OH···F contacts with a pair of fluorine atoms along an edge of the PF_6^- octahedron. The "face" label denotes that water is effectively interacting with the three fluorine atoms at the vertices of a face on the PF_6^- octahedron via one short and two significantly longer bifurcated OH···F contacts.

When two water molecules are present, OH···O contacts between the water molecules can also occur, which is indicated by the "WW" designation. This paper will also use the term hydrogen bonding when referring to these OH···F and OH···O contacts even though the associated geometrical parameters might sometimes fall outside the typical ranges associated with hydrogen bonds involving ions.

3.1. Monohydrate Structures and Relative Energies. In addition to the C_{2v} edge minimum reported by Wang, Li, and Han[12] (left side of Figure 1), a second stationary point has been identified in the current work for the monohydrated PF_6^- system (right side of Figure 1). The C_s face configuration is a transition state lying approximately 0.3 kcal mol^{-1} above the C_{2v} structure according to the MP2 and CCSD(T) electronic energies (ΔE values in Table 1).

Geometry optimizations with the M06-2X functional and haTZ basis set readily identify a C_s edge structure that was reported in an earlier study when the basis set was not augmented with diffuse functions[23] (shown in the inset of Figure 3). However, all subsequent haTZ geometry optimizations with the other methods employed in this study collapse to the C_{2v} edge configuration. The relaxed angular scans shown in Figure 3 along the coordinate connecting the C_{2v} and C_s edge structures conclusively demonstrate that the C_s edge structure does not correspond to a stationary point on the MP2, CCSD(T), B3LYP, B3LYP-D3, and ωB97XD potential energy surfaces computed with the haTZ basis set. Consequently, the C_s edge configuration is not discussed elsewhere in this report.

The scans presented in Figure 3 clearly indicate that some methods struggle to reliably describe the nature of the interaction as H_2O adopts different orientations around the hexafluorophosphate anion. Prior observations[12,23] indicate that the computational results can also be sensitive to the quality of the basis set, particularly the presence or absence of diffuse functions in small double-zeta quality basis sets. In this work, minor discrepancies are also observed in the number of imaginary vibrational frequencies (n_i) computed for the two stationary points of this simple monohydrated ion (see footnotes *a* and *b* in Table 1). The Cartesian coordinates and harmonic vibrational frequencies for both stationary points are reported in the Supporting Information for readers interested in more details.

The distance between the F atoms interacting with H_2O in the C_{2v} edge structure of $PF_6^-(H_2O)_1$ (≈2.3 Å in Figure 1) is compatible with the distance-based guidelines, suggesting a propensity for DIHB monohydrate motifs when the atoms accepting the hydrogen bonds in a polyatomic anion are separated by at least 2.2 Å.[24] In contrast, SF_6^- seems to violate this relationship because the IR spectrum of its monohydrate is more consistent with a SIHB structure even though SF_6^- is structurally similar to PF_6^- and even has a slightly larger distance between adjacent F atoms (≈2.7 Å).[57] It is also interesting to note that the F···HO angle about the hydrogen bond in the C_{2v} edge structure of $PF_6^-(H_2O)_1$ (≈142° in Figure 1) is quite similar to a collection of analogous angles for other DIHB monohydrates (146 ± 2° degrees from ref 24) despite being optimized with rather different methods and basis sets.

3.2. Dihydrate Structures and Relative Energies. In addition to the D_{2h} edge−edge minimum characterized in prior studies,[12,23] five new stationary points have been identified for the $PF_6^-(H_2O)_2$ system that have not been reported elsewhere to the best of our knowledge. All six configurations are shown in Figure 2. In four of the six structures, both waters bridge an edge of the PF_6^- octahedron. This group includes the D_{2h} edge−edge minimum, and the other three edge−edge structures (C_{2v}, C_2, and C_s) are simple symmetry unique permutations of the two water molecules along the different edges of PF_6^-. Another dihydrate structure (C_s edge−face in Figure 2) was generated from the D_{2h} edge−edge configuration by moving one of the water molecules from the edge to an adjacent face. Other permutations of this hydrogen bonding motif may exist, but our preliminary optimizations of other edge−face structures collapsed to one of the aforementioned edge−edge configurations or to the C_s WW−edge−face structure. This new C_s WW−edge−face configuration exhibits a completely different hydrogen bonding topology with one OH···O hydrogen bond between the water molecules along with three relatively short OH···F hydrogen bonds between the water molecules and the hexafluorophosphate anion.

The D_{2h} edge−edge structure is adopted as the reference for the dihydrate relative energies in Table 1 because it has been previously identified as a minimum for $PF_6^-(H_2O)_2$.[12,23] The MP2 and CCSD(T) relative electronic energies in Table 1 indicate that the one edge−face and five edge−edge stationary points are separated by less than 0.4 kcal mol^{-1}. The D_{2h} edge−edge structure consistently has the lowest electronic energy, but the nearly isoenergetic C_2 edge−edge lies within 0.1 kcal mol^{-1}. However, the electronic energy of the newly identified C_s WW−edge−face dihydrate structure is significantly lower than that of the D_{2h} edge−edge by 2.1 kcal mol^{-1} according to the results of the MP2 and CCSD(T) data reported in the last row of Table 1. These results suggests that the OH···O (solvent−solvent) interactions between water molecules may be just as important as the OH···F (solvent−solute) interactions between water and PF_6^- when characterizing the hydration of this ion.

MP2 and CCSD(T) harmonic vibrational frequencies indicate that all of the edge−edge stationary points are minima except the C_s edge−edge structure for which $n_i = 1$. The C_s edge−face configuration is also a transition state, whereas the C_s WW−edge−face structure appears to be a strong candidate for the global minimum of the $PF_6^-(H_2O)_2$ system. As with the monohydrated ion structures, there are some discrepancies in the number of imaginary vibrational frequencies computed for the high-symmetry D_{2h} and C_{2v} edge−edge dihydrate stationary points. (See footnotes *c* and *d* in Table 1.) The Cartesian coordinates and harmonic vibrational frequencies for all six dihydrate structures are provided in the Supporting Information.

As with the hydration of other molecular anions, water−water interactions become significant as soon as a second water molecule is introduced.[34,52,53,55,56] For $PF_6^-(H_2O)_2$, the configuration exhibiting water−water hydrogen bonding (C_s WW−edge−face) lies ≈2 kcal mol^{-1} below that involving only water−ion interactions. Despite the structural similarities between PF_6^- and SF_6^-, the energetics of the dihydrate systems are quite different. With $SF_6^-(H_2O)_2$, the IR spectrum is not consistent with water−water hydrogen bonding, and a

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX

Table 2. Dissociation Energies (D_e in kcal mol^{-1}) of the PF_6^- Monohydrate and Dihydrate Minima Computed with Various Methods and the haTZ Basis Set and the CCSD(T)/haQZ D_e Computed Using the CCSD(T)/haTZ-Optimized Geometries

	CCSD(T)		MP2	B3LYP	B3LYP-D3	ωB97XD	M06-2X
structure	haQZ	haTZ	haTZ	haTZ	haTZ	haTZ	haTZ
C_{2v} Edge	10.55	10.67	10.44	9.16	10.68	10.22	11.00
D_{2h} Edge−Edge	20.17	20.43	19.96	17.43	20.41	19.53	21.00
C_2 Edge−Edge	20.09	20.35	19.95	17.41	20.40	19.53	21.18
C_s Edge−Edge	19.80	20.10	19.61	16.92	20.04	19.31	20.96
C_s WW−Edge−Face	22.26	22.52	22.07	19.38	22.78	22.02	23.29

Table 3. Shifts in the Harmonic OH Stretching Frequencies ($\Delta\omega$ in cm^{-1}) Induced by Hydrogen Bonding in the PF_6^- Monohydrate and Dihydrate Minima Relative to the Symmetric (a_1) and Antisymmetric (b_2) OH Stretches for an Isolated Water Molecule (ω in cm^{-1}) Computed with the haTZ Basis Set

irreps[a]		CCSD(T)	MP2	B3LYP	B3LYP-D3	ωB97XD	M06-2X
			H_2O Frequencies (ω)				
	a_1	3814	3825	3801	3801	3882	3872
	b_2	3924	3952	3904	3904	3989	3976
			C_{2v} Edge Frequency Shifts ($\Delta\omega$)				
a_1	a_1	−17	−27	−27	−27	−32	−28
b_2	b_2	−72	−86	−83	−87	−90	−87
			D_{2h} Edge−Edge Frequency Shifts ($\Delta\omega$)				
b_{3u}	a_1	−13	−22	−22	−22	−26	−24
a_g	a_1	−12	−22	−21	−21	−26	−23
b_{1g}	b_2	−63	−76	−73	−76	−80	−77
b_{2u}	b_2	−62	−75	−72	−75	−79	−76
			C_2 Edge−Edge Frequency Shifts ($\Delta\omega$)				
b	a_1	−15	−23	−22	−22	−27	−25
a	a_1	−14	−22	−22	−21	−26	−24
a	b_2	−61	−76	−72	−75	−79	−76
b	b_2	−61	−75	−71	−75	−78	−75
			C_s Edge−Edge Frequency Shifts ($\Delta\omega$)				
a″	a_1	−26	−26	−37	−24	−32	−25
a′	a_1	−25	−24	−35	−23	−31	−24
a″	b_2	−89	−72	−61	−71	−72	−75
a′	b_2	−86	−69	−58	−67	−69	−72
			C_s WW−Edge−Face Frequency Shifts ($\Delta\omega$)				
a′	a_1	−104	−118	−140	−138	−219	−94
a′	a_1	−46	−48	−47	−47	−128	−49
a′	b_2	−128	−118	−105	−114	−199	−117
a″	b_2	−121	−110	−106	−109	−195	−107

[a]Irreducible representations[76] of the OH stretching mode in the complex (left) and reference mode in H_2O (right).

dihydrate structure without solvent−solvent interactions was computed to lie ≈0.2 kcal mol^{-1} lower than any configuration with water−water hydrogen bonding.[57] This study did, however, see spectroscopic evidence emerge for water−water hydrogen bonding in $SF_6^-(H_2O)_3$.

3.3. Dissociation Energies.

Table 2 reports the dissociation energies (D_e) for the minimum configurations of both the mono- and dihydrate systems (i.e., the relative energy of the isolated, optimized fragments: one PF_6^- ion and n H_2O molecules). The MP2 and CCSD(T) computations reported here and in ref 23 indicate that the monohydrate minimum (C_{2v} edge) has a dissociation energy exceeding 10 kcal mol^{-1}. For comparison, the D_e of the water dimer[73,74] is approximately 5 kcal mol^{-1} when computed with similar methods and basis sets. Together, these results suggest that the interaction between water and the hexafluorophosphate anion is significantly stronger than the interaction between two neutral water molecules.

The MP2 and CCSD(T) data in Table 2 show that when two edge contacts form in the C_s, C_2, and D_{2h} edge−edge dihydrate minima, the D_e increases by a factor of ≈1.9 relative to the corresponding value for the monohydrate minimum. As such, the interactions are close to being perfectly additive, but they fall about 5% short of doubling the D_e of the C_{2v} edge structure. In contrast, the C_s WW−edge−face minimum displays cooperative effects that enhance D_e by roughly 5% to a value slightly larger than 22 kcal mol^{-1}.

When the CP procedure is applied to the lowest-energy structures identified for the monohydrate and dihydrate systems (C_{2v} edge and C_s WW−edge−face, respectively), the CCSD(T)/haQZ dissociation energies decrease by less than 3% for both. The dissociation energies computed with the CP procedure for these two minima can be found in the Supporting Information, and when they are combined with the CCSD(T) data reported in Table 2, the results indicate that the D_e of the C_{2v} edge minimum for $PF_6^-(H_2O)_1$ will be near 10.4 kcal mol^{-1} at the CCSD(T) complete basis set limit

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX

(where the BSSE must vanish by definition) and that of the C_s WW−edge−face minimum for $PF_6^-(H_2O)_2$ will be near 22.0 kcal mol^{-1}.

3.4. Vibrational Frequencies. The harmonic symmetric (a_1) and antisymmetric (b_2) OH stretching frequencies (ω) computed for an isolated water molecule are listed in the first two rows of data at the top of Table 3. When a water molecule binds to an edge of the PF_6^- octahedron, the formation of the OH···F hydrogen bonds perturbs the OH stretching vibrations of the water molecule, inducing a shift in the corresponding frequency ($\Delta\omega$). In the C_{2v} edge monohydrate structure, for example, the energy of the symmetric a_1 stretching mode decreases by 17 cm^{-1} and that of the antisymmetric b_2 mode decreases by 72 cm^{-1}, according to the CCSD(T)/haTZ results reported in the first column of numbers in Table 3. All of the other methods predict larger shifts with the haTZ basis set (by approximately 10 cm^{-1}). The tabulated MP2 and DFT $\Delta\omega$ values for the C_{2v} edge minimum range from −27 to −32 cm^{-1} for the a_1 mode and from −83 to −90 for the b_2 mode.

DIHB structures tend to induce less-pronounced OH stretching frequency shifts in H_2O than their SIHB counterparts,[24,25] and the data presented here suggest that the C_{2v} edge minimum for $n = 1$ is no exception. In fact, the magnitudes of the computed harmonic shifts for $PF_6^-(H_2O)_1$ in Table 3 are appreciably smaller than the readily assignable shifts from the DIHB series analyzed by Robertson et al. by more than a factor of two.[24] This result is, however, consistent with a proton affinity of only 280 kcal mol^{-1} for the hexafluorophosphate anion[75] based on the qualitative relationship between this quantity and the OH frequency shifts (see Figure 2 of ref 24, e.g.).

For the dihydrate systems, the irreducible representations associated with the coupled OH stretching vibrations of the two water molecules are listed in the first column of Table 3.[76] Even when they do not necessarily directly correlate to the a_1 and b_2 irreducible representations of the C_{2v} point group, each mode is dominated by a synchronous or asynchronous OH stretching motion that can be used to assign the H_2O reference mode for calculating $\Delta\omega$ (indicated by the a_1 or b_2 entries tabulated in the second column of Table 3).

When two water molecules bind to different edges of the anion octahedron in the dihydrate edge−edge minima (D_{2h}, C_2, and C_s), the magnitudes of the vibrational frequency shifts are quite similar to those observed for the monohydrate. In the three edge−edge minima, the symmetric OH stretch shifts to slightly lower energy by − 19 ± 7 cm^{-1} according to the CCSD(T)/haTZ harmonic vibrational frequencies. The corresponding shifts for the antisymmetric OH stretch also fall into a fairly narrow range of $\Delta\omega$ values of −75 ± 14 cm^{-1}. The similarity of the frequency shifts for the monohydrate minimum and edge−edge dihydrate minima is consistent with the lack of cooperative effects observed for the corresponding D_e values in Table 2.

With a qualitatively different hydrogen bond topology, the C_s WW−edge−face structure exhibits much larger OH stretching frequency shifts than the three Edge−Edge minima. According to the CCSD(T)/haTZ harmonic vibrational frequencies, only one OH stretching mode shifts by less than 100 cm^{-1}; $\Delta\omega$ is only −46 cm^{-1} for the mode predominated by the synchronous OH stretching motion in the water molecule that accepts the OH···O hydrogen bond. In contrast, the corresponding shift in the donor of the OH···O hydrogen bond is −104 cm^{-1} (both relative to the a_1 stretch of an isolated H_2O molecule). The CCSD(T)/haTZ $\Delta\omega$ values are −128 and −121 cm^{-1} for the asynchronous stretching modes primarily associated with the donor and acceptor of the OH··· O hydrogen bond, respectively.

The solvent−solute interactions also induce vibrational frequency shifts in the PF stretching modes of the hexafluorophosphate anion, but they tend to be much smaller (Table S13 in the Supporting Information). When a single water molecule interacts with PF_6^- to form the C_{2v} edge monohydrate structure, the CCSD(T)/haTZ harmonic vibrational frequencies indicate that one PF stretching frequency shifts by −12 cm^{-1} to lower energy, while another shifts by +16 cm^{-1} to higher energy, while the four other PF stretching modes shift by no more than ±7 cm^{-1}. The latter nearly doubles in magnitude to +30 cm^{-1} in the D_{2h} edge−edge local minimum when a second water molecule is added to the opposite side of the PF_6^- octahedron. However, the CCSD-(T)/haTZ frequency shifts do not exceed ±6 cm^{-1} for the lowest-energy structure identified for $PF_6^-(H_2O)_2$ (the C_s WW−edge−face minimum). The vibrational frequency shifts for the PF stretches are tabulated in the Supporting Information along with all of the computed harmonic vibrational frequencies and corresponding IR intensities.

4. CONCLUSIONS

Low-energy configurations of the $PF_6^-(H_2O)_{n=1,2}$ system have been identified via a set of relaxed angular scans across the edges and faces of the PF_6^- octahedron. Two low-lying stationary points have been found for the $PF_6^-(H_2O)_1$ system with the CCSD(T) *ab initio* method, the C_{2v} Edge minimum and the C_s transition state. For the $PF_6^-(H_2O)_2$ system, four minima and two transition states have been identified, with the lowest energy minimum being approximately 2 kcal mol^{-1} lower than that of any other structure yet identified.

The CCSD(T) electronic dissociation energy is slightly larger than 10 kcal mol^{-1} for the C_{2v} edge minimum of the monohydrate, and this interaction is almost perfectly additive in the D_{2h}, C_2, and C_s edge−edge minima of $PF_6^-(H_2O)_2$. However, appreciable cooperative effects are observed when the two hydrating water molecules are able to interact with each other, and the CCSD(T) D_e increases to approximately 22 kcal mol^{-1} for the C_s WW−edge−face structure. In comparison, the corresponding D_e is approximately 5 kcal mol^{-1} for $(H_2O)_2$,[73,74] and it approaches 16 kcal mol^{-1} for $(H_2O)_3$.[77]

These solvent−solute interactions also induce significant shifts in the OH stretching vibrational frequencies of the hydrating water molecule(s) relative to the corresponding a_1 and b_2 values for an isolated H_2O molecule. The CCSD(T)/ haTZ symmetric and antisymmetric OH stretching frequency shifts by − 17 and −72 cm^{-1}, respectively, in the C_{2v} edge monohydrate minimum, and very similar $\Delta\omega$ values are observed in the D_{2h}, C_2, and C_s edge−edge minima of $PF_6^-(H_2O)_2$. However, the most significant vibrational perturbations occur when the solvent molecules are able to interact with each other and the ion. In the C_s WW−edge−face structure, the CCSD(T)/haTZ frequencies shift by as much as −104 cm^{-1} for the synchronous and −128 cm^{-1} for the asynchronous OH stretching modes. The lowest-energy harmonic OH stretching frequency for the C_s WW−edge− face minimum of $PF_6^-(H_2O)_2$ is computed to be 3721 and 3661 cm^{-1} at the CCSD(T)/haTZ and B3LYP/haTZ levels of theory, respectively. The latter harmonic value is only 36 cm^{-1}

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX

larger than the results from recent DFT AIMD simulations that predicted a shift of more than +300 cm^{-1} relative to bulk water.[21] The present work demonstrates that solvent−solute interactions alone do not provide a complete picture of PF_6^- hydration, and it highlights the importance of the solvent−solvent interactions that must also be considered to identify the lowest-energy structures and to capture the associated spectroscopic perturbations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c06466.

Cartesian coordinates, electronic dissociation energies computed with the CP procedure, harmonic vibrational frequencies, and IR intensities (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Gregory S. Tschumper − *Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677-1848, United States;* orcid.org/0000-0002-3933-2200; Phone: +1 662 915 7301; Email: tschumpr@olemiss.edu; Fax: +1 662 915 7300

Author

Yasmeen A. Abdo − *Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677-1848, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpca.0c06466

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation (CHE-1338056 and CHE-1664998). The Mississippi Center for Supercomputing Research (MCSR) is also thanked for a generous allocation of time on their computational resources.

■ REFERENCES

(1) Wang, Y.-L.; Li, B.; Sarman, S.; Mocci, F.; Lu, Z.-Y.; Yuan, J.; Laaksonen, A.; Fayer, M. D. Microstructural and Dynamical Heterogeneities in Ionic Liquids. *Chem. Rev.* **2020**, *120*, 5798−5877.

(2) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303−4418.

(3) Seddon, K. R.; Stark, A.; Torres, M.-J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(4) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Phase Behavior of Ionic Liquid/CO_2 Systems. *J. Phys. Chem. B* **2001**, *105*, 2437−2444.

(5) Rogers, R. D.; Seddon, K. R. CHEMISTRY: Ionic Liquids–Solvents of the Future? *Science* **2003**, *302*, 792−793.

(6) Danten, Y.; Cabaço, M. I.; Besnard, M. Interaction of Water Highly Diluted in 1-Alkyl-3-methyl Imidazolium Ionic Liquids with the PF_6^- and BF_4^- Anions. *J. Phys. Chem. A* **2009**, *113*, 2873−2889.

(7) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. Molecular States of Water in Room Temperature Ionic Liquids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192−5200.

(8) Ghatee, M. H.; Zolghadr, A. R. Local Depolarization in Hydrophobic and Hydrophilic Ionic Liquids/Water Mixtures: Car-Parrinello and Classical Molecular Dynamics Simulation. *J. Phys. Chem. C* **2013**, *117*, 2066−2077.

(9) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156−164.

(10) Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. On the solubilization of water with ethanol in hydrophobic hexafluorophosphate ionic liquids. *Green Chem.* **2002**, *4*, 81−87.

(11) Hanke, C. G.; Lynden-Bell, R. M. A Simulation Study of Water-Dialkylimidazolium Ionic Liquid Mixtures. *J. Phys. Chem. B* **2003**, *107*, 10873−10878.

(12) Wang, Y.; Li, H.; Han, S. A Theoretical Investigation of the Interactions between Water Molecules and Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 24646−24651.

(13) Schenk, J.; Panne, U.; Albrecht, M. Interaction of Levitated Ionic Liquid Droplets with Water. *J. Phys. Chem. B* **2012**, *116*, 14171−14177.

(14) Walrafen, G. E. Raman Spectral Studies of the Effects of Solutes and Pressure on Water Structure. *J. Chem. Phys.* **1971**, *55*, 768−792.

(15) Paquette, J.; Jolicoeur, C. A near-infrared study of the hydration of various ions and nonelectrolytes. *J. Solution Chem.* **1977**, *6*, 403−428.

(16) Kristiansson, O.; Lindgren, J.; de Villepin, J. A Quantttatlve Infrared Spectroscopic Method for the Study of the Hydration of Ions in Aqueous Solutions. *J. Chem. Phys.* **1988**, *92*, 2680−2685.

(17) Śmiechowski, M.; Gojło, E.; Stangret, J. Ionic Hydration in $LiPF_6$, $NaPF_6$, and KPF_6 Aqueous Solutions Derived from Infrared HDO Spectra. *J. Phys. Chem. B* **2004**, *108*, 15938−15943.

(18) Son, H.; Nam, D.; Park, S. Real-Time Probing of Hydrogen-Bond Exchange Dynamics in Aqueous $NaPF_6$ Solutions by Two-Dimensional Infrared Spectroscopy. *J. Phys. Chem. B* **2013**, *117*, 13604−13613.

(19) Nam, D.; Lee, C.; Park, S. A Quantttatlve Infrared Spectroscopic Method for the Study of the Hydration of Ions in Aqueous Solutions. *Phys. Chem. Chem. Phys.* **2014**, *16*, 21747−21754.

(20) Śmiechowski, M. Anion-water interactions of weakly hydrated anions: molecular dynamics simulations of aqueous $NaBF_4$ and $NaPF_6$. *Mol. Phys.* **2016**, *114*, 1831−1846.

(21) Śmiechowski, M. Unusual Influence of Fluorinated Anions on the Stretching Vibrations of Liquid Water. *J. Phys. Chem. B* **2018**, *122*, 3141−3152.

(22) Stangret, J.; Gampe, T. Ionic Hydration Behavior Derived from Infrared Spectra in HDO. *J. Phys. Chem. B* **2002**, *106*, 5393−5402.

(23) Rodríguez-Otero, J.; Cabaleiro-Lago, E. M.; Peña-Gallego, Á. Comment on: A Theoretical Investigation of the Interactions between Water Molecules and Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 13465−13466.

(24) Robertson, W. H.; Price, E. A.; Weber, J. M.; Shin, J.-W.; Weddle, G. H.; Johnson, M. A. Infrared Signatures of a Water Molecule Attached to Triatomic Domains of Molecular Anions: Evolution of the H-bonding Configuration with Domain Length. *J. Phys. Chem. A* **2003**, *107*, 6527−6532.

(25) Woronowicz, E. A.; Robertson, W. H.; Weddle, G. H.; Johnson, M. A.; Myshakin, E. M.; Jordan, K. D. Infrared Spectroscopic Characterization of the Symmetrical Hydration Motif in the $SO_2^-\cdot H_2O$ Complex. *J. Phys. Chem. A* **2002**, *106*, 7086−7089.

(26) Surber, E.; Ananthavel, S. P.; Sanov, A. Nonexistent electron affinity of OCS and the stabilization of carbonyl sulfide anions by gas phase hydration. *J. Chem. Phys.* **2002**, *116*, 1920−1929.

(27) Myshakin, E. M.; Jordan, K. D.; Sibert, E. L.; Johnson, M. A. Large anharmonic effects in the infrared spectra of the symmetrical $CH_3NO_2^-\cdot(H_2O)$ and $CH_3CO_2^-\cdot(H_2O)$ complexes. *J. Chem. Phys.* **2003**, *119*, 10138−10145.

(28) Schneider, H.; Vogelhuber, K. M.; Weber, J. M. Infrared spectroscopy of anionic hydrated fluorobenzenes. *J. Chem. Phys.* **2007**, *127*, 114311.

(29) Kelly, J. T.; Ellington, T. L.; Sexton, T. M.; Fortenberry, R. C.; Tschumper, G. S.; Asmis, K. R. Communication: Gas Phase Vibrational Spectroscopy of the Azide-Water Complex. *J. Chem. Phys.* **2018**, *149*, 191101.
(30) Bentley, J.; Collins, J. Y.; Chipman, D. M. Dissociation of Ozonide in Water. *J. Phys. Chem. A* **2000**, *104*, 4629−4635.
(31) Johnson, M. S.; Kuwata, K. T.; Wong, C.-K.; Okumura, M. Vibrational spectrum of $I^-(H_2O)$. *Chem. Phys. Lett.* **1996**, *260*, 551−557.
(32) Ayotte, P.; Weddle, G. H.; Kim, J.; Johnson, M. A. Vibrational Spectroscopy of the Ionic Hydrogen Bond: Fermi Resonances and Ion-Molecule Stretching Frequencies in the Binary $X^-{\cdot}H_2O$ (X = Cl, Br, I) Complexes via Argon Predissociation Spectroscopy. *J. Am. Chem. Soc.* **1998**, *120*, 12361−12362.
(33) Weber, J. M.; Kelley, J. A.; Nielsen, S. B.; Ayotte, P.; Johnson, M. A. Isolating the Spectroscopic Signature of a Hydration Shell With the Use of Clusters: Superoxide Tetrahydrate. *Science* **2000**, *287*, 2461−2463.
(34) Weber, J. M.; Kelley, J. A.; Robertson, W. H.; Johnson, M. A. Hydration of a structured excess charge distribution: Infrared spectroscopy of the $O_2^-{\cdot}(H_2O)_n$, $(1 \le n \le 5)$ clusters. *J. Chem. Phys.* **2001**, *114*, 2698−2706.
(35) Robertson, W. H.; Johnson, M. A.; Myshakin, E. M.; Jordan, K. D. Isolating the Charge-Transfer Component of the Anionic H Bond Via Spin Suppression of the Intracluster Proton Transfer Reaction in the $NO^-{\cdot}H_2O$ Entrance Channel Complex. *J. Phys. Chem. A* **2002**, *106*, 10010−10014.
(36) Robertson, W. H.; Johnson, M. A. Molecular Aspects of Halide Ion Hydration: The Cluster Approach. *Annu. Rev. Phys. Chem.* **2003**, *54*, 173−213.
(37) Schneider, H.; Boese, A. D.; Weber, J. M. Unusual hydrogen bonding behavior in binary complexes of coinage metal anions with water. *J. Chem. Phys.* **2005**, *123*, 084307.
(38) Roscioli, J. R.; Diken, E. G.; Johnson, M. A.; Horvath, S.; McCoy, A. B. Prying Apart a Water Molecule with Anionic H-Bonding: A Comparative Spectroscopic Study of the $X^-{\cdot}H_2O$ (X = OH, O, F, Cl, and Br) Binary Complexes in the 600−3800 cm^{-1} Region. *J. Phys. Chem. A* **2006**, *110*, 4943−4952.
(39) Kim, J.; Lee, H. M.; Suh, S. B.; Majumdar, D.; Kim, K. S. Comparative ab initio study of the structures, energetics and spectra of $X^-{\cdot}(H_2O)_{n=1-4}$ [X = F, Cl, Br, I] clusters. *J. Chem. Phys.* **2000**, *113*, 5259−5272.
(40) Xantheas, S. S.; Dunning, T. H. Structures and Energetics of $F^-(H_2O)_n$, $n = 1 - 3$ Clusters from *ab Initio* Calculations. *J. Phys. Chem.* **1994**, *98*, 13489−13497.
(41) Xantheas, S. S.; Dang, L. X. Critical Study of Fluoride-Water Interactions. *J. Phys. Chem.* **1996**, *100*, 3989−3995.
(42) Ayotte, P.; Nielsen, S. B.; Weddle, G. H.; Johnson, M. A.; Xantheas, S. S. Spectroscopic Observation of Ion-Induced Water Dimer Dissociation in the $X^-{\cdot}(H_2O)_2$ (X = F, Cl, Br, I) Clusters. *J. Phys. Chem. A* **1999**, *103*, 10665−10669.
(43) Chaban, G. M.; Xantheas, S. S.; Gerber, R. B. Anharmonic Vibrational Spectroscopy of the $F^-(H_2O)_n$ Complexes, $n = 1, 2$. *J. Phys. Chem. A* **2003**, *107*, 4952−4956.
(44) Baik, J.; Kim, J.; Majumdar, D.; Kim, K. S. Structures, energetics, and spectra of fluoride-water clusters $F^-(H_2O)_n$, $n = 1 - 6$: Ab initio study. *J. Chem. Phys.* **1999**, *110*, 9116−9127.
(45) Combariza, J. E.; Kestner, N. R.; Jortner, J. Microscopic solvation of anions in water clusters. *Chem. Phys. Lett.* **1993**, *203*, 423−428.
(46) Combariza, J. E.; Kestner, N. R.; Jortner, J. Energystructure relationships for microscopic solvation of anions in water clusters. *J. Chem. Phys.* **1994**, *100*, 2851−2864.
(47) Xantheas, S. S. Quantitative Description of Hydrogen Bonding in Chloride-Water Clusters. *J. Phys. Chem.* **1996**, *100*, 9703−9713.
(48) Ayotte, P.; Weddle, G. H.; Kim, J.; Johnson, M. A. Mass-selected "matrix isolation" infrared spectroscopy of the $I^-{\cdot}(H_2O)_2$ complex: making and breaking the inter-water hydrogen-bond. *Chem. Phys.* **1998**, *239*, 485−491.
(49) Bajaj, P.; Zhuang, D.; Paesani, F. Specific Ion Effects on Hydrogen-Bond Rearrangements in the Halide-Dihydrate Complexes. *J. Phys. Chem. Lett.* **2019**, *10*, 2823−2828.
(50) Dorsett, H. E.; Watts, R. O.; Xantheas, S. S. Probing Temperature Effects on the Hydrogen Bonding Network of the $Cl^-(H_2O)_2$ Cluster. *J. Phys. Chem. A* **1999**, *103*, 3351−3355.
(51) Wolke, C. T.; Menges, F. S.; Tötsch, N.; Gorlova, O.; Fournier, J. A.; Weddle, G. H.; Johnson, M. A.; Heine, N.; Esser, T. K.; Knorke, H.; et al. Thermodynamics of Water Dimer Dissociation in the Primary Hydration Shell of the Iodide Ion with Temperature-Dependent Vibrational Predissociation Spectroscopy. *J. Phys. Chem. A* **2015**, *119*, 1859−1866.
(52) Myshakin, E. M.; Jordan, K. D.; Robertson, W. H.; Weddle, G. H.; Johnson, M. A. Dominant structural motifs of $NO^-{\cdot}(H_2O)_n$ complexes: Infrared spectroscopic and ab initio studies. *J. Chem. Phys.* **2003**, *118*, 4945−4953.
(53) Robertson, W. H.; Diken, E. G.; Price, E. A.; Shin, J.-W.; Johnson, M. A. Spectroscopic Determination of the OH^- Solvation Shell in the $OH^-{\cdot}(H_2O)_n$ Clusters. *Science* **2003**, *299*, 1367−1372.
(54) Chipman, D. M.; Bentley, J. Structures and Energetics of Hydrated Oxygen Anion Clusters. *J. Phys. Chem. A* **2005**, *109*, 7418−7428.
(55) Wang, X.-B.; Kowalski, K.; Wang, L.-S.; Xantheas, S. S. Stepwise hydration of the cyanide anion: A temperature-controlled photoelectron spectroscopy and ab initio computational study of $CN^-(H_2O)_n$, $n = 2 - 5$. *J. Chem. Phys.* **2010**, *132*, 124306.
(56) Gorlova, O.; DePalma, J. W.; Wolke, C. T.; Brathwaite, A.; Odbadrakh, T. T.; Jordan, K. D.; McCoy, A. B.; Johnson, M. A. Characterization of the primary hydration shell of the hydroxide ion with H_2 tagging vibrational spectroscopy of the $OH^-{\cdot}(H_2lO)_{n=2,3}$ and $OD^-{\cdot}(H_2lO)_{n=2,3}$ clusters. *J. Chem. Phys.* **2016**, *145*, 134304.
(57) Schneider, H.; Weber, J. M. Infrared spectra of $SF_6^-{\cdot}(H_2O)_n$ ($n = 1 - 3$): Incipient reaction and delayed onset of water network formation. *J. Chem. Phys.* **2007**, *127*, 244310.
(58) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785.
(59) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
(60) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.
(61) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.
(62) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(63) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796−6806.
(64) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-electron Systems. *Phys. Rev.* **1934**, *46*, 618−622.
(65) Bartlett, R. J. Coupled-cluster Theory and its Equation-of-motion Extensions. *WIREs Comput. Mol Sci.* **2012**, *2*, 126−138.
(66) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian09* Revision D.01; Gaussian Inc.: Wallingford CT, 2009.
(67) Matthews, D. A.; Cheng, L.; Harding, M. E.; Lipparini, F.; Stopkowicz, S.; Jagau, T.-C.; Szalay, P. G.; Gauss, J.; Stanton, J. F. Coupled-cluster techniques for computational chemistry: The CFOUR program package. *J. Chem. Phys.* **2020**, *152*, 214108.
(68) Kestner, N. R. He-He Interaction in the SCF-MO Approximation. *J. Chem. Phys.* **1968**, *48*, 252−257.

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX

(69) Liu, B.; McLean, A. D. Accurate Calculation of the Attractive Interaction of Two Ground State Helium Atoms. *J. Chem. Phys.* **1973**, *59*, 4557−4558.
(70) Jansen, H. B.; Ros, P. Non-Empirical Molecular Orbital Calculations on the Protonation of Carbon Monoxide. *Chem. Phys. Lett.* **1969**, *3*, 140−143.
(71) Boys, S. F.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553−566.
(72) Tschumper, G. S. Reliable Electronic Structure Computations for Weak Non-Covalent Interactions in Clusters. *Rev. Comput. Chem.* **2009**, *26*, 39−90.
(73) Tschumper, G. S.; Leininger, M. L.; Hoffman, B. C.; Valeev, E. F.; Schaefer, H. F.; Quack, M. Anchoring the Water Dimer Potential Energy Surface with Explicitly Correlated Computations and Focal Point Analyses. *J. Chem. Phys.* **2002**, *116*, 690−701.
(74) Howard, J. C.; Gray, J. L.; Hardwick, A. J.; Nguyen, L. T.; Tschumper, G. S. Getting down to the fundamentals of hydrogen bonding: Anharmonic vibrational frequencies of the hetero and homogeneous dimers of HF and H_2O from ab initio electronic structure computations. *J. Chem. Theory Comput.* **2014**, *10*, 5426−5435.
(75) Newton, K. A.; He, M.; Amunugama, R.; McLuckey, S. A. Selective cation removal from gaseous polypeptide ions: proton vs. sodium ion abstraction via ion/ion reactions. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2710−2717.
(76) The Gaussian09 conventions for molecular orientation and irreducible representation assignments were adopted whenever they differed from the conventions in CFOUR.
(77) Anderson, J. A.; Crager, K.; Fedoroff, L.; Tschumper, G. S. Anchoring the Potential Energy Surface of the Cyclic Water Trimer. *J. Chem. Phys.* **2004**, *121*, 11023−11029.

https://dx.doi.org/10.1021/acs.jpca.0c06466
J. Phys. Chem. A XXXX, XXX, XXX−XXX