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Structures, Energetics, and Vibrational Frequencies of Microhydrated Hexafluorophosphate, PF6−(H2O)n=1,2 from DFT and Ab Initio Computations

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Structures, Energetics, and Vibrational Frequencies of Microhydrated Hexafluorophosphate, PF$_6^-$$(\text{H}_2\text{O})_{n=1,2}$ from DFT and Ab Initio Computations

by

Yasmeen A. Abdo

A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2019

Approved by

Advisor: Dr. Gregory S. Tschumper

Reader: Dr. Ryan C. Fortenberry

Reader: Dr. Nathan I. Hammer
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Abstract

This study systematically examines an anion commonly used in room temperature ionic liquids, hexafluorophosphate PF$_6^-$, and its non-covalent interactions with up to two explicit water molecules (PF$_6^-$($\text{H}_2\text{O}$)$_n$ where $n = 1, 2$). Initial low-energy configurations are identified via a set of relaxed angular scans across the edges and faces of the PF$_6^-$ octahedron using the global hybrid M06-2X density functional with a triple-$\zeta$ correlation consistent basis set augmented with diffuse functions on all non-hydrogen atoms (cc-pVTZ for H and aug-cc-pVTZ for P, O, F; denoted haTZ). Full geometry optimizations are performed on these initial structures using a variety of common density functionals theory (DFT) methods (B3LYP, B3LYP-D3, M06-2X, and $\omega$B97XD) as well as the MP2 and CCSD(T) ab initio methods with the same haTZ basis set. The corresponding harmonic vibrational frequencies are computed for all identified stationary points. Single point energy computations are also performed on the CCSD(T)/haTZ geometries using the CCSD(T) method with an analogous quadruple-$\zeta$ basis set (haQZ). A new PF$_6^-$($\text{H}_2\text{O}$)$_2$ minimum has been identified that is approximately 2 kcal mol$^{-1}$ lower in energy than any other structure previously reported in the literature. For the PF$_6^-$($\text{H}_2\text{O}$)$_1$ system, DFT computations identify two unique stationary points competing for the lowest energy configuration, which is consistent with prior work. However, only one of these structures is a stationary point on the MP2 and CCSD(T) potential energy surfaces. This result suggests that some DFT methods might not correctly describe the interaction between PF$_6^-$ and H$_2$O.
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1 Introduction

Room Temperature Ionic Liquids (RTILs) are ionic salts that form liquids at or near room temperature.\textsuperscript{1} RTILs are increasingly used as solvents in a wide range of applications because of their low vapor pressures, high conductivities, and low flammability. In addition, by changing the anion-cation combination or adding a co-solvent, the properties of the RTIL can be customized for particular application.\textsuperscript{1}

Water, a common co-solvent and potential impurity, has the potential to change the physical properties of a given RTIL (\textit{e.g.} conductivity, density, solubility, viscosity).\textsuperscript{2–4} The water-RTIL interaction has been studied extensively in the literature both experimentally and computationally. Studies have found that when compared to the cation-water interaction, the anion-water interactions contributed more to the strength of water’s interaction with an RTIL.\textsuperscript{5–9} In addition, several studies found that the anion and water form an alternating Anion-Water-Anion pattern when interacting.\textsuperscript{4,5,10,11}

Compared to other commonly used RTILs, the PF\textsubscript{6}\textsuperscript{−} based RTILs have been shown to form some of the weakest water-anion hydrogen bonds\textsuperscript{5} and have one of the lowest miscibilities with water.\textsuperscript{7,12–14} As such, PF\textsubscript{6}\textsuperscript{−} is one of the least hygroscopic anions for RTILs, and is generally used to make “hydrophobic” ionic liquids.\textsuperscript{15}

In order to get a more detailed understanding of the water-anion interaction in PF\textsubscript{6}\textsuperscript{−} based RTILs, two studies focused on the explicit solvation of PF\textsubscript{6}\textsuperscript{−} with one or two water molecules (PF\textsubscript{6}\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n=1,2}) and without the presence of a cation.\textsuperscript{15,16} Wang \textit{et al.} identified a monohydrate structure (denoted as configuration \textit{C\textsubscript{2v}} Edge in Figure 1 of the present study) as well as a dihydrate configuration (denoted as configuration \textit{D\textsubscript{2h}} Edge-Edge in Figure 2 of the present study).\textsuperscript{15} In that study, these structures were 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. In
response to Wang et al., Rodriguez-Otero et al. published a subsequent analysis
that was able to identify the corresponding minima with both the B3LYP and MP2
methods when using the 6-31++G** basis set. In addition, Rodriguez-Otero et al.
identified another monohydrate water structure (denoted as configuration $C_s$ Edge in
Figure 1 of the present study), but only when they did not include diffuse functions
in their basis sets. This present study builds upon these prior works by performing
a more extensive exploration of the possible configurations for the $\text{PF}_6^-(\text{H}_2\text{O})_{n=1,2}$
systems using both DFT and \textit{ab initio} methods.
2 Computational Methods

Relaxed angular scans are performed over several coordinates of PF$_6^-$-$(\text{H}_2\text{O})_n$ (where $n = 1, 2$) using the M06-2X$^{17}$ density functional with Dunning’s correlation consistent triple-$\zeta$ 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 haTZ).$^{18,19}$ The resulting low-energy configurations are then fully optimized with the haTZ basis set using various density functional theory (DFT) methods (B3LYP$^{20}$, B3LYP-D3$^{20,21}$, M06-2X, $\omega$B97XD$^{22}$) as well as the MP2$^{23}$ and CCSD(T)$^{24}$ 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 (the two methods never differed by more than 1.0 cm$^{-1}$). Single point energy computations with the CCSD(T) methods and the corresponding haQZ basis set are performed on the CCSD(T)/haTZ geometries using Molpro. All DFT computations are performed with the Gaussian09$^{25}$ software package with a dense pruned numerical integration grid composed of 175 radical 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.$^{26}$ All electronic energies are performed with pure angular momentum ($5d$ and $7f$) atomic orbital basis functions.
3 Results and Discussion

3.1 Structures and Energetics

Figure 1 and Figure 2 depict the mono- and dihydrate configurations of the PF$_6^-$ (H$_2$O)$_n$ systems, respectively, along with selected intermolecular bond lengths. Configurations $C_{2v}$ Edge, $C_s$ Edge, and $D_{2h}$ Edge-Edge have been previously reported. The remaining unreported configurations included in Figures 1 and 2 originate from a set of relaxed angular scans performed with one or two water molecules on the faces and/or edges of the PF$_6^-$ octahedron. All low-energy mono- and dihydrate configurations identified on the M06-2X/haTZ potential energy surface are fully optimized at the MP2/haTZ, then at the CCSD(T)/haTZ levels of theory. At the CCSD(T) and MP2 levels of theory, several of the initial M06-2X structures collapse to the configurations shown in Figures 1 and 2. These CCSD(T)/haTZ structures remain in similar geometries when optimized using the same basis set with the B3LYP, B3LYP-D3, M06-2X, ωB97XD, and MP2 methods.

For most configurations shown in Figure 1 and 2, either Edge and/or Face hydrogen bonds are observed. The Edge designation denotes the interaction of a water molecule with the two fluorine atoms along an edge of the PF$_6^-$ octahedron while the Face designation denotes the interaction between a water molecule and the three fluorine atoms at the vertices of a face on the PF$_6^-$ octahedron. The instances that involve high symmetry result in equivalent Edge and Face hydrogen bonds. Furthermore, the Face hydrogen bonds are usually shorter than the Edge hydrogen bonds. The $C_s$ WW-Edge-Face configuration differs from the other structures in that the configuration contains a water-water hydrogen bond (OH···O), and its Edge hydrogen bonds are shorter than its Face hydrogen bonds. In addition, the $C_s$ WW-Edge-Face
configuration as a whole exhibits 1 OH···O interaction and 3 OH···F interactions, whereas all other structures exhibit either 2 or 4 OH···F interactions and no OH···O interactions.

![Diagram of structures with bond lengths](image)

Figure 1: Optimized PF$_6^-$-(H$_2$O)$_n$ configurations and intermolecular bond lengths at the CCSD(T)/haTZ level of theory (M06-2X/haTZ for the $C_s$ Edge configuration).

![Diagram of structures with bond lengths](image)

Figure 2: Optimized PF$_6^-$-(H$_2$O)$_2$ configurations and intermolecular bond lengths at the CCSD(T)/haTZ level of theory

Table 1 reports the relative energetics ($\Delta E$) and the number of imaginary modes...
assigned to each configuration in Figure 1 and 2, calculated from both DFT and \textit{ab initio} methods. For the monohydrate system, CCSD(T) predicts the $C_{2v}$ Edge configuration to be a minimum, while the $C_s$ Face configuration is predicted to be a transition state that is $+0.33$ kcal mol$^{-1}$ higher in energy. MP2 both qualitatively and quantitatively agrees with the CCSD(T) results. While the DFT methods all agree qualitatively that the $C_{2v}$ Edge configuration is the lowest in energy, the predicted difference in energy between the two configurations ranges from $+0.06$ kcal mol$^{-1}$ to $+0.53$ kcal mol$^{-1}$.

Furthermore, despite the qualitative energetic consistency with CCSD(T), the M06-2X and $\omega$B97XD DFT methods differ from CCSD(T) in their assignment of imaginary modes. M06-2X assigns the $C_{2v}$ Edge configuration as a transition state while $\omega$B97XD not only assigns the $C_{2v}$ Edge configuration as a transition state, but also assigns the higher energy $C_s$ Face configuration as a minimum.
Table 1: Relative electronic energies (ΔE in kcal mol$^{-1}$) and number of imaginary modes ($n_i$) of the PF$_6^-$-(H$_2$O)$_{n=1,2}$ configurations at various methods with the haTZ basis set as well as the CCSD(T)/haQZ energy points using the CCSD(T)/haTZ geometries.

<table>
<thead>
<tr>
<th>Structure</th>
<th>CCSD(T)</th>
<th>MP2</th>
<th>B3LYP</th>
<th>B3LYP-D3</th>
<th>ωB97XD</th>
<th>M06-2X</th>
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<tbody>
<tr>
<td></td>
<td>haQZ</td>
<td>haTZ</td>
<td>haTZ</td>
<td>haTZ</td>
<td>haTZ</td>
<td>haTZ</td>
</tr>
<tr>
<td>$C_{2v}$ Edge</td>
<td>ΔE +0.00</td>
<td>+0.00</td>
<td>+0.00</td>
<td>+0.00</td>
<td>+0.00</td>
<td>+0.00</td>
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<tr>
<td></td>
<td>$n_i$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
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<tr>
<td>$C_s$ Face</td>
<td>ΔE +0.38</td>
<td>+0.33</td>
<td>+0.34</td>
<td>+0.53</td>
<td>+0.47</td>
<td>+0.15</td>
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<tr>
<td></td>
<td>$n_i$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
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<tr>
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<td>ΔE +0.00</td>
<td>+0.00</td>
<td>+0.00</td>
<td>+0.00</td>
<td>+0.00</td>
<td>+0.00</td>
</tr>
<tr>
<td></td>
<td>$n_i$</td>
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<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
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<td>ΔE −2.09</td>
<td>−2.09</td>
<td>−2.11</td>
<td>−1.95</td>
<td>−2.36</td>
<td>−2.48</td>
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<tr>
<td></td>
<td>$n_i$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_s$ Edge-Edge</td>
<td>ΔE +0.38</td>
<td>+0.30</td>
<td>+0.35</td>
<td>+0.50</td>
<td>+0.37</td>
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<td></td>
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<td>0</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_s$ Edge-Face</td>
<td>ΔE +0.37</td>
<td>+0.31</td>
<td>+0.32</td>
<td>+0.47</td>
<td>+0.41</td>
<td>+0.16</td>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$C_{2v}$ Edge-Edge</td>
<td>ΔE +0.30</td>
<td>+0.29</td>
<td>+0.28</td>
<td>+0.27</td>
<td>+0.27</td>
<td>+0.30</td>
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<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3 depicts the relaxed angular scan used to rationalize the predictions of the M06-2X and ωB97XD methods. The relaxed angular scan explores the relationship between $C_{2v}$ Edge, $C_s$ Face, and $C_s$ Edge configurations on various potential energy surfaces. The $C_s$ Edge configuration is previously reported to be the monohydrate.
minimum only when the PF$_6^-$-(H$_2$O)$_1$ system is optimized using the B3LYP and MP2 methods with a double-$\zeta$ basis set and no added diffuse functions. The scan, which is performed with the haTZ basis set, shows that the $C_s$ Edge configuration is predicted to be the lowest energy minimum only on the M06-2X and $\omega$B97XD potential energy surfaces and not along the B3LYP, B3LYP-D3, MP2, or CCSD(T) potential energy surfaces. Because this structure does not exist at higher levels of theory, results for the $C_s$ Edge configuration have been relegated to the Supporting Information (SI) along with a handful of other mono- and dihydrate configurations that only appear as stationary points on the M06-2X/haTZ potential energy surface.

Figure 3: Relaxed $C_s$ scans using the haTZ basis set of an H$_2$O molecule along a face of PF$_6^-$ where the scan angle, $\theta$(OPF), is 90$^\circ$ for the $C_{2v}$ Edge configuration and $\sim$65$^\circ$ for the $C_s$ Edge configuration.

For the dihydrate system, CCSD(T) predicts four minimum configurations ($D_{2h}$ Edge-Edge, $C_s$ WW-Edge-Face, $C_s$ Edge-Edge, and $C_2$ Edge-Edge) and two transition state configurations ($C_s$ Edge-Face and $C_{2v}$ Edge-Edge). The $n_i$ for $C_s$ WW-Edge-Face, $C_s$ Edge-Edge, $C_2$ Edge-Edge, and $C_s$ Edge-Face are based on the CCSD(T)/heavy-
aug-cc-pVDZ computations. The CCSD(T)/haTZ frequency computations are currently in progress. Almost isoenergetic to the $D_{2h}$ Edge-Edge configuration, the literature minimum, is the $C_2$ Edge-Edge configuration which is only about +0.08 kcal mol$^{-1}$ higher in energy. The two transition state configurations, $C_s$ Edge-Face and $C_{2v}$ Edge-Edge as well as the minimum $C_s$ Edge-Edge configuration are all around +0.3 kcal mol$^{-1}$ higher in energy than the $D_{2h}$ Edge-Edge configuration. The CCSD(T) relative energetics presented in the current study predict the $C_s$ WW-Edge-Face structure to be lower in energy than the previously reported lowest energy configuration, $D_{2h}$ Edge-Edge, by 2 kcal mol$^{-1}$. The energy difference may stem from the stabilizing power of the OH···O interaction present only in the $C_s$ WW-Edge-Face configuration.

Most of the MP2 and DFT methods agree with the relative energetics of the configurations predicted by CCSD(T). However, though M06-2X predicts the $C_s$ WW-Edge-Face configuration to be the lowest energy configuration by around 2 kcal mol$^{-1}$, the method disagrees with CCSD(T) on the relative energies of the higher energy configurations.

Several DFT methods disagree with the characterization of the configurations on the CCSD(T) potential energy surfaces. ωB97XD predicts the $D_{2h}$ Edge-Edge configuration to be a higher order stationary point with three imaginary modes. In addition to predicting the $D_{2h}$ Edge-Edge configuration to be a higher order stationary point with two imaginary modes, M06-2X also predicts the $C_{2v}$ Edge-Edge configuration to be a minimum, rather than a transition state. Finally, B3LYP assigns the $C_{2v}$ Edge-Edge configuration to be a minimum rather than a transition state.

Table 2 reports the dissociation energies ($D_e$) for the minimum configurations of both the mono- and dihydrate systems. The monohydrate configuration, $C_{2v}$ Edge is fairly well bound, with a dissociation energy of 10.67 kcal mol$^{-1}$. DFT and MP2 are consistent with CCSD(T) in that they also predict a $D_e$ of around 10 kcal mol$^{-1}$ for the monohydrate system. For the dihydrate system, the $C_s$ WW-Edge-Face configu-
ration has the highest dissociation energy around 22 kcal mol\(^{-1}\) while the other three minimum configurations, \(D_{2h}\) Edge-Edge, \(C_s\) Edge-Edge, and \(C_2\) Edge-Edge all have dissociation energies around 20 kcal mol\(^{-1}\). While both DFT and MP2 qualitatively agree with the CCSD(T) prediction, B3LYP quantitatively underestimates the \(D_e\) by around 3 kcal mol\(^{-1}\).

Table 2: Dissociation energies (\(D_e\) in kcal mol\(^{-1}\)) of the PF\(_6^-\)(H\(_2\)O)\(_n=1,2\) configurations at various methods with the haTZ basis set as well as the CCSD(T)/haQZ energy points using the CCSD(T)/haTZ geometries indicated in parentheses.

<table>
<thead>
<tr>
<th>Structure</th>
<th>CCSD(T) haQZ</th>
<th>CCSD(T) haTZ</th>
<th>MP2 haTZ</th>
<th>B3LYP haTZ</th>
<th>B3LYP-D3 haTZ</th>
<th>ωB97XD haTZ</th>
<th>M06-2X haTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{2v}) Edge</td>
<td>10.55</td>
<td>10.67</td>
<td>10.44</td>
<td>9.16</td>
<td>10.68</td>
<td>10.22</td>
<td>11.00</td>
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<tr>
<td>(D_{2h}) Edge-Edge</td>
<td>20.17</td>
<td>20.43</td>
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<td>21.00</td>
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<tr>
<td>(C_s) WW-Edge-Face</td>
<td>22.26</td>
<td>22.52</td>
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<td>22.78</td>
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<td>23.29</td>
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<td>(C_s) Edge-Edge</td>
<td>19.80</td>
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<td>20.04</td>
<td>19.31</td>
<td>20.96</td>
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<tr>
<td>(C_2) Edge-Edge</td>
<td>20.09</td>
<td>20.35</td>
<td>19.95</td>
<td>17.41</td>
<td>20.40</td>
<td>19.53</td>
<td>21.18</td>
</tr>
</tbody>
</table>

In order to assess the effects of the inconsistencies produced by the basis set superposition error (BSSE)\(^{27,28}\), the Boys-Bernardi counterpoise correction procedure\(^{29,30}\) is applied to the lowest energy minimum of each system. Table 3 reports both the uncorrected and counterpoise corrected dissociation energies for the lowest energy monohydrate minimum, \(C_{2v}\) Edge, and the lowest energy dihydrate minimum, \(C_s\) WW-Edge-Face. The gap between the corrected and uncorrected dissociation energies is 0.6 kcal mol\(^{-1}\) for the \(C_{2v}\) Edge configuration according to CCSD(T)/haTZ. This gap between the uncorrected and corrected \(D_e\) shrinks as expected when computed using the CCSD(T)/haQZ energy point, which predicts the gap to be 0.27 kcal mol\(^{-1}\). While MP2 agrees with both CCSD(T) results, DFT underestimates the BSSE and predicts the gap between the uncorrected and corrected dissociation
energies to be around 0.2 kcal mol\(^{-1}\). The BSSE increases when computed for the dihydrate system. CCSD(T)/haTZ and the CCSD(T)/haQZ energy points predict a BSSE of 1.4 kcal mol\(^{-1}\) and 0.59 kcal mol\(^{-1}\) respectively. While MP2 is consistent with these predictions, DFT again underestimates the BSSE, predicting it to be around 0.4 kcal mol\(^{-1}\).

Table 3: Uncorrected (\(D_e\) in kcal mol\(^{-1}\)) and counterpoise corrected (\(D_{e}^{cp}\) in kcal mol\(^{-1}\)) dissociation energies for the lowest energy monohydrate structure \(C_{2v}\) Edge, and the lowest energy dihydrate configuration, \(C_s\) WW-Edge-Face, at various methods with the haTZ basis set as well as the CCSD(T)/haQZ energy points using the CCSD(T)/haTZ geometries.

<table>
<thead>
<tr>
<th>Method</th>
<th>(C_{2v}) Edge</th>
<th>(C_s) WW-Edge-Face</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_e)</td>
<td>(D_{e}^{cp})</td>
<td>(D_e)</td>
</tr>
<tr>
<td>CCSD(T)/haQZ</td>
<td>10.55</td>
<td>10.28</td>
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<tr>
<td>CCSD(T)/haTZ</td>
<td>10.67</td>
<td>10.06</td>
</tr>
<tr>
<td>MP2/haTZ</td>
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<td>B3LYP/haTZ</td>
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<td>B3LYP-D3/haTZ</td>
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<td>10.49</td>
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<td>(\omega)B97XD/haTZ</td>
<td>10.22</td>
<td>10.03</td>
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<tr>
<td>M06-2X/haTZ</td>
<td>11.00</td>
<td>10.83</td>
</tr>
</tbody>
</table>

3.2 Vibrational Frequencies

Table 4 reports the frequency shifts (\(\Delta \omega\) in cm\(^{-1}\)) of the mono- and dihydrate configurations’ symmetric and asymmetric water stretches relative to the reported isolated water monomer’s symmetric (\(a_1\)) and asymmetric (\(b_2\)) frequencies. The CCSD(T) frequency calculations for the \(C_s\) WW-Edge-Face, \(C_s\) Edge-Edge, and \(C_2\) Edge-Edge are currently in progress. For the \(C_{2v}\) Edge configuration, when the complexed wa-
water is stretching symmetrically, the shift is taken relative to the symmetric stretch frequency of an isolated water monomer and is found to be $-17$ cm$^{-1}$. The analogous method is used to calculate the shift of the asymmetric stretch in the $C_{2v}$ Edge configuration which is found to be $-72$ cm$^{-1}$. 
Table 4: Harmonic vibrational frequencies for the symmetric (a\textsubscript{1}) and asymmetric (b\textsubscript{2}) stretches of an isolated water molecule (ω in \textit{cm}^{-1}) and the Frequency shifts (Δω in \textit{cm}^{-1}) of the complexed water relative to the former, all computed using the haTZ basis set.

<table>
<thead>
<tr>
<th>Structure</th>
<th>H\textsubscript{2}O Ref.</th>
<th>CCSD(T)</th>
<th>MP2</th>
<th>B3LYP</th>
<th>B3LYP-D3</th>
<th>ωB97XD</th>
<th>M06-2X</th>
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<tr>
<td>H\textsubscript{2}O</td>
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For the dihydrate $D_{2h}$ Edge-Edge, $C_s$ Edge-Edge, and $C_2$ Edge-Edge configurations, highly coupled vibrational modes between the two water molecules are observed. For any given water stretch, both water molecules are stretching either symmetrically or asymmetrically with respect to the individual water molecule, regardless of the overall symmetry of the configuration. The shift for the water’s symmetric stretch for these dihydrate systems is found to be 20-30 cm$^{-1}$, while the shift for the asymmetric stretch is found to be 70-80 cm$^{-1}$.

However, the presence of the water-water hydrogen bond within the $C_s$ WW-Edge-Face configuration affects the overall frequency shifts. This can be seen in the dramatic difference between the two symmetric shifts, where a $-118$ cm$^{-1}$ shift is observed when the hydrogen bond donor O-H stretch has a larger amplitude than the acceptor water molecule’s symmetric stretching. When both water molecules have similar stretching amplitudes, a frequency shift of $-48$ cm$^{-1}$ is observed. The asymmetric stretches are not as highly coupled as the symmetric stretches resulting in separate asymmetric stretching shifts for the hydrogen bond donor ($-118$ cm$^{-1}$) and the acceptor ($-110$ cm$^{-1}$). The MP2 shifts are reported here and will be updated when the CCSD(T) computations finish.
4 Conclusions

Low energy configurations of the PF$_6^-(\text{H}_2\text{O})_{n=1,2}$ system are identified via a set of relaxed angular scans across the edges and faces of the PF$_6^-$ octahedron. Two low lying stationary points are found for the PF$_6^-(\text{H}_2\text{O})_1$ system by the DFT methods; however, only configuration $C_{2v}$ Edge is found with the MP2 and CCSD(T) \textit{ab initio} methods. Additionally, the identification of $C_{2v}$ Edge as the minimum for the PF$_6^-(\text{H}_2\text{O})_1$ system is in agreement with the previous literature.$^{15,16}$ For the PF$_6^-(\text{H}_2\text{O})_2$ system, four minima and two transition states are identified, with the lowest energy minimum being approximately 2 kcal mol$^{-1}$ lower than any other structure identified in the current study or in previous literature. Though the previously reported $D_{2h}$ Edge-Edge configuration is identified, the lower energy $C_s$ WW-Edge-Face configuration found agrees with what is already known about the hydration of PF$_6^-$ with only 2 H$_2$O molecules: the water$\cdots$water interactions are already competitive the OH$\cdots$F interactions in the system.$^{14}$ In conclusion, MP2 consistently agrees with the CCSD(T) benchmarks for energetics. The M06-2X and $\omega$B97XD methods disagree with the CCSD(T) characterization of structures as minima or transition states. An in-depth frequency analysis that will be conducted once the CCSD(T) frequency computations finish will allow further comparison between DFT and \textit{ab initio} methods.
References


Appendix
Table A1: Harmonic vibrational frequencies ($\omega$) and IR intensities for H$_2$O using the haTZ basis set.

<table>
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<th>B3LYP</th>
<th>B3LYP-D3</th>
<th>B97XD</th>
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Table A2: Harmonic vibrational frequencies ($\omega$) and IR intensities for PF$_6^-$ using the haTZ basis set.

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<th>MP2 IR Intensity</th>
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<th>B3LYP IR Intensity</th>
<th>B3LYP-D3 $\omega$</th>
<th>B3LYP-D3 IR Intensity</th>
<th>$\omega$B97XD $\omega$</th>
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Table A3: Harmonic vibrational frequencies ($\omega$) and IR intensities for the $C_2$ Edge configuration using the haTZ basis set.

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Table A4: Harmonic vibrational frequencies (ω) and IR intensities for the \( C_s \) Face configuration using the haTZ basis set.

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Table A6: Harmonic vibrational frequencies ($\omega$) and IR intensities for the $C_s$ WW-Edge-Face configuration using the haTZ basis set.

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Table A7: Harmonic vibrational frequencies ($\omega$) and IR intensities for the $C_s$ Edge-Edge configuration using the haTZ basis set.

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Table A8: Harmonic vibrational frequencies ($\omega$) and IR intensities for the C$_2$ Edge-Edge configuration using the haTZ basis set.

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Table A9: Harmonic vibrational frequencies ($\omega$) and IR intensities for the $C_s$ Edge-Face configuration using the haTZ basis set.

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Table A10: Harmonic vibrational frequencies ($\omega$) and IR intensities for the $C_{2v}$ Edge-Edge configuration using the haTZ basis set.

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Table A11: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge complex with the M06-2X method using the haTZ basis set.

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Table A12: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge complex with the ωB97XD method using the haTZ basis set.

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Table A14: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge complex with the B3LYP method using the haTZ basis set.

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Table A15: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge complex with the MP2 method using the haTZ basis set.

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Table A16: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge complex with the CCSD(T) method using the haTZ basis set.

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Table A17: Cartesian coordinates in Angstroms (Å) for the \( C_s \) Edge complex with the M06-2X method using the haTZ basis set.

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Table A18: Cartesian coordinates in Angstroms (Å) for the \( C_s \) Edge complex with the \( \omega \)B97XD method using the haTZ basis set.

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Table A19: Cartesian coordinates in Angstroms (Å) for the $C_s$ Face complex with the M06-2X method using the haTZ basis set.

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Table A20: Cartesian coordinates in Angstroms (Å) for the $C_s$ Face complex with the ωB97XD method using the haTZ basis set.

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Table A21: Cartesian coordinates in Angstroms (Å) for the $C_s$ Face complex with the B3LYP-D3 method using the haTZ basis set.

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Table A22: Cartesian coordinates in Angstroms (Å) for the $C_s$ Face complex with the B3LYP method using the haTZ basis set.

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Table A23: Cartesian coordinates in Angstroms (Å) for the $C_s$ Face complex with the MP2 method using the haTZ basis set.

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Table A24: Cartesian coordinates in Angstroms (Å) for the $C_s$ Face complex with the CCSD(T) method using the haTZ basis set.

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Table A25: Cartesian coordinates in Angstroms (Å) for the $C_s$ WW-Edge-Face complex with the M06-2X method using the haTZ basis set.

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Table A26: Cartesian coordinates in Angstroms (Å) for the $C_s$ WW-Edge-Face complex with the ωB97XD method using the haTZ basis set.

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Table A27: Cartesian coordinates in Angstroms (Å) for the $C_{s}$ WW-Edge-Face complex with the B3LYP-D3 method using the haTZ basis set.

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Table A28: Cartesian coordinates in Angstroms (Å) for the $C_{s}$ WW-Edge-Face complex with the B3LYP method using the haTZ basis set.

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Table A29: Cartesian coordinates in Angstroms (Å) for the $C_s$ WW-Edge-Face complex with the MP2 method using the haTZ basis set.

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Table A30: Cartesian coordinates in Angstroms (Å) for the $C_s$ WW-Edge-Face complex with the CCSD(T) method using the haTZ basis set.

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Table A31: Cartesian coordinates in Angstroms (Å) for the Cs Edge-Edge complex with the M06-2X method using the haTZ basis set.

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Table A32: Cartesian coordinates in Angstroms (Å) for the Cs Edge-Edge complex with the ωB97XD method using the haTZ basis set.

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Table A33: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Edge complex with the B3LYP-D3 method using the haTZ basis set.

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Table A34: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Edge complex with the B3LYP method using the haTZ basis set.

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Table A35: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Edge complex with the MP2 method using the haTZ basis set.

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Table A36: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Edge complex with the CCSD(T) method using the haTZ basis set.

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Table A37: Cartesian coordinates in Angstroms (Å) for the $C_2$ Edge-Edge complex with the M06-2X method using the haTZ basis set.

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Table A38: Cartesian coordinates in Angstroms (Å) for the $C_2$ Edge-Edge complex with the ωB97XD method using the haTZ basis set.

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Table A39: Cartesian coordinates in Angstroms (Å) for the $C_2$ Edge-Edge complex with the B3LYP-D3 method using the haTZ basis set.

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Table A40: Cartesian coordinates in Angstroms (Å) for the $C_2$ Edge-Edge complex with the B3LYP method using the haTZ basis set.

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Table A41: Cartesian coordinates in Angstroms (Å) for the \( C_2 \) Edge-Edge complex with the MP2 method using the haTZ basis set.

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Table A42: Cartesian coordinates in Angstroms (Å) for the \( C_2 \) Edge-Edge complex with the CCSD(T) method using the haTZ basis set.

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Table A43: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Face complex with the M06-2X method using the haTZ basis set.

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Table A44: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Face complex with the ωB97XD method using the haTZ basis set.

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Table A45: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Face complex with the B3LYP-D3 method using the haTZ basis set.

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Table A46: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Face complex with the B3LYP method using the haTZ basis set.

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Table A47: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Face complex with the MP2 method using the haTZ basis set.

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Table A48: Cartesian coordinates in Angstroms (Å) for the $C_s$ Edge-Face complex with the CCSD(T) method using the haTZ basis set.

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Table A49: Cartesian coordinates in Angstroms (Å) for the $D_{2h}$ Edge-Edge complex with the M06-2X method using the haTZ basis set.

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Table A50: Cartesian coordinates in Angstroms (Å) for the $D_{2h}$ Edge-Edge complex with the ωB97XD method using the haTZ basis set.

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Table A51: Cartesian coordinates in Angstroms (Å) for the $D_{2h}$ Edge-Edge complex with the B3LYP-D3 method using the haTZ basis set.

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Table A52: Cartesian coordinates in Angstroms (Å) for the $D_{2h}$ Edge-Edge complex with the B3LYP method using the haTZ basis set.

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Table A53: Cartesian coordinates in Angstroms (Å) for the $D_{2h}$ Edge-Edge complex with the MP2 method using the haTZ basis set.

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Table A54: Cartesian coordinates in Angstroms (Å) for the $D_{2h}$ Edge-Edge complex with the CCSD(T) method using the haTZ basis set.

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Table A55: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge-Edge complex with the M06-2X method using the haTZ basis set.

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Table A56: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge-Edge complex with the ωB97XD method using the haTZ basis set.

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Table A57: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge-Edge complex with the B3LYP-D3 method using the haTZ basis set.

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Table A58: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge-Edge complex with the B3LYP method using the haTZ basis set.

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Table A59: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge-Edge complex with the MP2 method using the haTZ basis set.

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Table A60: Cartesian coordinates in Angstroms (Å) for the $C_{2v}$ Edge-Edge complex with the CCSD(T) method using the haTZ basis set.

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Figure A1: Low energy configurations identified as a result of the M06-2X/haTZ relaxed angular scans that collapsed to one of the configurations focused on in this study.