THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

Cite This: J. Phys. Chem. A 2018, 122, 4902−4908

pubs.acs.org/JPCA

Dissociation Energy of the $H_2O\cdots HF$ Dimer

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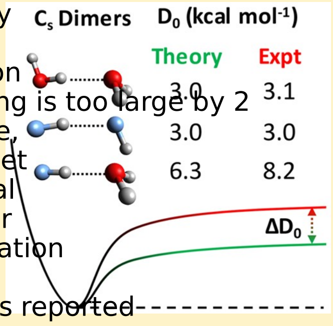
* Supporting Information

ABSTRACT: Even though $(H_2O)_2$ and $(HF)_2$ are arguably the most thoroughly characterized prototypes for hydrogen bonding, their heterogeneous analogue $H_2O\cdots HF$ has received relatively little attention. Herein we report that the experimental dissociation energy (D_0) of this important paradigm for heterogeneous hydrogen bonding is too large by 2 kcal mol^{-1} or 30% relative to our computed value of 6.3 kcal mol^{-1}. For reference, computational procedures similar to those employed here to compute D_0 (large basis set CCSD(T) computations with anharmonic corrections from second-order vibrational perturbation theory) provide results within 0.1 kcal mol^{-1} of the experimental values for $(H_2O)_2$ and $(HF)_2$. Near the CCSD(T) complete basis set limit, the electronic dissociation energy for $H_2O\cdots HF$ is ~4 kcal mol^{-1} larger than those for $(H_2O)_2$ and $(HF)_2$ (~9 kcal mol^{-1} for the heterogeneous dimer vs ~5 kcal mol^{-1} for the homogeneous dimers). Results reported here from symmetry-adapted perturbation theory computations suggest that this large difference is primarily due to the induction contribution to the interaction energy.



■ INTRODUCTION

The dimers of H_2O and HF are among the most widely studied model systems for hydrogen bonding. The mixed dimer has received relatively little attention compared to its homogeneous counterparts $(H_2O)_2$ and $(HF)_2$, both of which have their own CAS registry numbers (25655-83-8 and 30664-12-1, respectively). The $(H_2O)_2$ dimer is particularly well studied, with energetics examined by methods up to coupled cluster with single, double, triple, and perturbative quadruple (CCSDT(Q))[1] excitations and with vibrational modes examined by a variety of methods,[2] including local modes.[3] Recent computational studies have examined heterodimers of HF with other molecules, including CO, CO_2, N_2, Ar, and HCl.[4,5] This study examines the heterodimer of H_2O with HF. Although both HF and H_2O can readily donate a hydrogen bond, their heterodimer exhibits only one low-energy configuration in which the water molecule accepts a hydrogen bond from hydrogen fluoride,[6] denoted here as $H_2O\cdots HF$.

The investigation of the $H_2O\cdots HF$ dimer as a prototypical hydrogen-bonded system dates to 1969, when Kollman and Allen performed the first semiempirical[7] and later *ab initio*[8] studies of $H_2O\cdots HF$. They predicted that a stable dimer would form in quantities large enough to be investigated spectroscopically. Shortly thereafter, Hancock and Green[9] studied the deactivation of vibrationally excited gas-phase HF by H_2O and D_2O. The high deactivation rate and the similarity between the H_2O and D_2O rates led them to suggest the formation of a complex or quasicomplex between H_2O and HF, which lasted for the period of many HF vibrations, in which vibrational energy transfer took place. The existence of the $H_2O\cdots HF$ dimer was confirmed by microwave spectroscopy in 1975 with the observation of a low-frequency intermonomer mode not present in the pure spectra of either monomer alone.[10] Later that same year, an experimental study by Thomas assigned several vibrational modes and made the first attempt at the determination of dissociation energies.[11] Investigations into the rotational spectrum of the $H_2O\cdots HF$ dimer found only a single form in the gas phase: that of water as proton acceptor.[6] However, it was not possible to discern whether the complex had C_s or C_{2v} symmetry. Subsequent investigation of the vibrational spectrum determined that the equilibrium conformation has C_s symmetry, with HF and O defining the plane of symmetry (Figure 1).[12] The C_{2v} structure is a transition state connecting two equivalent C_s minima to form a symmetric double well potential with a low barrier on the order of 0.5 k mol^{-1}.[11,12]

Additional aspects of the $H_2O\cdots HF$ complex have been measured experimentally, including the dipole moment,[6] the in-plane bending potential energy function and barrier to inversion,[12] the nuclear-spin−nuclear-spin hyperfine coupling constants,[13] a Fourier transform infrared (FTIR) spectrum in argon, including evidence for inversion doubling of vibrational peaks,[14] and Stark effects in the rotational spectrum.[15] Force constants for hydrogen-bond stretching and out-of-plane bending potentials were found for the $H_2O\cdots HF$ complex[16] and later confirmed by repeating the experiment with the $D_2O\cdots DF$ complex.[17] A second experimental determination[18] of the dissociation energy (D_0) that includes the zero point vibrational energy (ZPVE) used a method based on intensities of rotational transitions near room temperature in the gas phase[19,20] to obtain a D_0 value of 8.2 ± 0.1 kcal mol^{-1}. The dissociation energy from geometric equilibrium (D_e) was back-

Received: April 10, 2018
Revised: April 18, 2018
Published: April 18, 2018

DOI: 10.1021/acs.jpca.8b03397

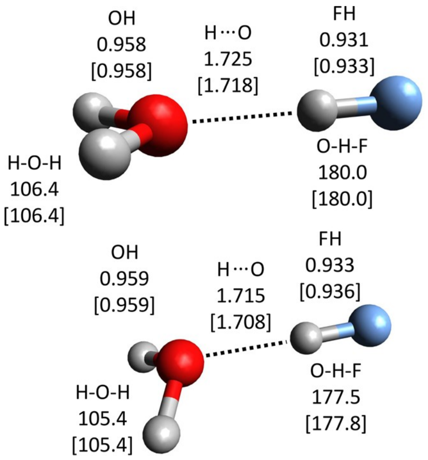


Figure 1. Select CCSD(T)/ha5Z optimized bond lengths (Å) and angles (deg) for the C_{2v} transition state (top) and C_s global minimum (bottom) of the $H_2O\cdots HF$ dimer with corresponding MP2/ha5Z values in square brackets.

calculated based on the harmonic approximation for assigned modes and a quartic potential for the double well mode, giving D_e = 10.3 ± 0.2 kcal mol^{-1}. These are the most current experimentally derived values for D_0 and D_e of $H_2O\cdots HF$.

For the $H_2O\cdots HF$ dimer, computational work[21] provided assistance for the reassignment of the experimental[22,23] fundamental frequency for the HF bond stretch from 3608 to 3634 cm^{-1}. This reassignment invalidated the D_0 for $H_2O\cdots HF$ determined by Thomas,[11] as that value for D_0 was computed based on the intensity of a mis-assigned HF stretch. After reassigning this peak, Bulychev et al.[22] suggested that additional experimental and theoretical investigation of the system was needed, including additional anharmonic calculations. There have also been some more recent high-level computational investigations of D_e for the $H_2O\cdots HF$ dimer dissociation. In 1999, Halkier et al. reported D_e = 8.5 kcal mol^{-1} from counterpoise corrected CCSD(T) and a two-point extrapolation to the complete basis set limit (CBS) from aug-cc-pVQZ and aug-cc-pV5Z values.[24] In 2007, Boese et al. determined the dimerization energy of a number of dimers with the W2 method, giving D_e = 8.7 kcal mol^{-1} for the $H_2O\cdots$HF dimer.[25] Most recently, Demaison and Liévin[26] calculated the dimerization energy at CCSD(T)/aug-cc-pV5Z as D_e = 9.20 kcal mol^{-1} and noted that there was a significant difference between their results and the experimental value for D_e. They speculated that the deviation was due to the difficulty reliably modeling the vibrational energy for the double well potential and noted that the experimental D_0 value seemed compatible with their D_e value. These computed D_e values for $H_2O\cdots HF$ are considerably larger than those found in the $(HF)_2$[27] and $(H_2O)_2$ dimers[28] (4.6 and 5.0 kcal mol^{-1}, respectively).

The large discrepancy between the experimentally inferred equilibrium dissociation energy (D_e = 10.3 kcal mol^{-1})[18] and recent theory for the $H_2O\cdots HF$ dimer is somewhat surprising given that the experimental dissociation energies of the two closely related homogeneous dimers $(H_2O)_2$ and $(HF)_2$ were well described by CCSD(T) computations with quadruple-ζ quality basis sets when anharmonic effects were evaluated with second-order vibrational perturbation theory (VPT2).[29] For the $(H_2O)_2$ and $(HF)_2$ homogeneous complexes, that computational procedure provided computed D_0 values within 0.01 kcal mol^{-1} of the experimental values for the latter and 0.06 kcal mol^{-1} for the former, while the differences between theoretical and experimental donor stretching frequencies were 3 cm^{-1} for $(H_2O)_2$ and 1 cm^{-1} for $(HF)_2$.

The aforementioned experimental D_0 values for $(H_2O)_2$ and $(HF)_2$ were determined by vibrational predissociation (VPD) methods. Other examples exist in the literature, where D_0 or experimentally inferred D_e values from VPD of similar weakly bound complexes are in excellent agreement with modern theoretical methods,[30] for example, $H_2O\cdots HCl$[31,32] and $N_2\cdots$HF.[33,34] When only harmonic ZPVEs were used, moderate agreement between theory (CCSD(T) D_e and MP2 ZPVE) and experiment (various molecular beam techniques) was found for D_0 values for 10 hydrogen-bonded complexes of aromatic chromophores and small molecules.[35] Reasonable agreement has also been found between theoretical and experimental VPD fragmentation patterns for HCCH complexes with HCl, DCl, HF, and OH radical.[36] D_0 values for the small-molecule trimers $(H_2O)_3$ and $(HCl)_3$ determined by VPD also have good agreement with modern computational techniques.[37,38] For the $(HF)_2$ and $(HCl)_2$ dimers, a gas-phase equilibrium method based on intensities of vibrational transitions[39] provided measurements in line with VPD results, although VPD results had smaller error bars.[40,41] In contrast, the most recent experimental D_0 for $H_2O\cdots HF$ was measured[18] using a gas-phase equilibrium technique based on absolute intensities of rotational transitions.[19,20] For the similar HCN··· HF dimer, D_0 values determined by absolute intensities of rotational transitions[19] or by relative FTIR intensities[42] have been later found to be significantly different from those give by more reliable VPD techniques.[43]

To resolve the aforementioned discord between experimentally and theoretically derived values for D_e and D_0 of $H_2O\cdots HF$, the present study determines an accurate zero-poin corrected dissociation energy as well as fundamental vibrati frequencies using similar methods to those that were succes for $(H_2O)_2$ and $(HF)_2$.[29] These results can be directly compared with future experiments to help resolve this discrepancy. Although several groups have reported D_e values computed by high-level methods[24−26] and another group has computed an anharmonically corrected HF stretching frequency,[21] this work is the first to report a fully theoretical calculation of D_0 for the dissociation of the $H_2O\cdots HF$ dimer with ZPVE modeled by VPT2 with correlated ab initio electronic structure methods and large correlation consisten basis sets.

■ COMPUTATIONAL DETAILS

The CFOUR package[44] was used to perform all of the coupled cluster computations in this study with single, double, and perturbative triple excitations (i.e., the CCSD(T)[45,46] method), whereas second-order Møller−Plesset perturbation theory (MP2)[47] calculations were performed with CFOUR as well as Gaussian 09.[48] MP2 and CCSD(T) geometry optimizations and harmonic frequency calculations were performed using analytic gradients and Hessians, with mixed basis sets, using Dunning's correlation consistent basis sets[49,50] cc-pVXZ on hydrogen atoms and the corresponding set augmented with diffuse functions (aug-cc-pVXZ) on heavy (non-hydrogen) atoms, with X = T, Q, 5 (abbreviated as haXZ). Additional calculations were performed with Dunning's fully augmente basis sets aug-cc-pVXZ (with X = T, Q, 5, 6, abbreviated aXZ). The subset of data obtained with the larger aXZ basis sets is tabulated in the Supporting Information, and the results are

DOI: 10.1021/acs.jpca.8b03397
J. Phys. Chem. A 2018, 122, 4902−4908

Table 1. Harmonic Vibrational Frequencies (in cm^{-1}) and ZPVEs (in kcal mol^{-1}) for the C_s Form of the $H_2O \cdots HF$ Heterogeneous Dimer as well as the Corresponding Anharmonic Corrections and Estimates from VPT2

	harmonic		ΔVPT2 correction				VPT2
	MP2	CCSD(T)	MP2	MP2	MP2	CCSD(T)	anharmonic
mode	ha5Z	ha5Z	haTZ	haQZ	ha5Z	haTZ	estimate[a]
1	223	222	−46	−51	−53	−46	169
2	245	242	−34	−34	−33	−39	209
3	264	263	−79	−78	−79	−80	184
4	712	704	−105	−104	−103	−110	601
5	837	827	−113	−112	−111	−117	716
6	1634	1651	−54	−46	−59	−46	1592
7	3736	3782	−139	−145	−146	−138	3636
8	3835	3833	−167	−169	−170	−169	3663
9	3953	3936	−178	−180	−181	−183	3755
ZPVE	22.07	22.10	−0.50	−0.50	−0.51	−0.52	21.60

[a] CCSD(T)/ha5Z harmonic values with MP2/ha5Z ΔVPT2 corrections.

very similar to those from the haXZ basis sets. In addition, second-order vibrational perturbation theory (VPT2)[51−54] analyses were performed with CFOUR to estimate anharmonic effects for the minimum-energy structures of the HF and H_2O monomers and the $H_2O \cdots HF$ dimer. Force constants needed for VPT2 were calculated numerically from finite differences of analytic second derivatives.[55] These anharmonic frequency calculations were performed with basis sets up to haTZ for CCSD(T) and ha5Z for MP2. In all cases, the frozen-core approximation was used, and spherical harmonic functions (i.e., 5d,7f) were used instead of Cartesian functions. All Cartesian forces associated with optimized structures have been converged to less than 1.0×10^{-7} Hartree $Bohr^{-1}$ for structures optimized by CFOUR and less than 1.0×10^{-5} Hartree $Bohr^{-1}$ for structures optimized by Gaussian 09.

The use of finite basis sets in the computation of dissociation or interaction energies via the supermolecular method introduces an inconsistency commonly referred to as basis set superposition error (BSSE).[56,57] The effects of this inconsistency were assessed through the application of the counterpoise (CP) procedure for dimers.[58,59]

ESULTS AND DISCUSSION

Optimized Structures. On the basis of the rotational spectrum of the dimer, a single form of the dimer is observed in the gas phase.[6] We find the same C_s global minimum, with HF as the hydrogen-bond donor. Another minimum, with HF as the hydrogen-bond acceptor, is found at lower levels of theory such as RHF/STO-3G, but optimizations from that geometry collapse to the global minimum with larger basis sets and post-Hartree−Fock methods. Therefore, only the complex with HF as hydrogen-bond donor is investigated here. The $H_2O \cdots HF$ dimer can move from the C_s global minimum (Figure 1, bottom) to a symmetry-equivalent C_s minimum by traveling through a planar C_{2v} transition state (Figure 1, top).

Select MP2 and CCSD(T) optimized geometrical parameters obtained with the ha5Z basis set for both stationary points are provided in Figure 1. The MP2 and CCSD(T) values are very similar. Even the differences in the intermolecular parameters do not exceed 0.007 Å and 0.3°. The deviations between the haQZ and ha5Z results are even smaller, which suggests the optimized structures are well converged. A more complete list of parameters is tabulated in the Supporting Information along with the corresponding Cartesian coordinates.

Vibrational Frequencies of the Global Minimum. The MP2 and CCSD(T) harmonic vibrational frequencies associated with both structures are also reported in the Supporting Information. The basis set convergence of the harmonic vibrational frequencies for $H_2O \cdots HF$ is very similar to that observed for the $(HF)_2$ and $(H_2O)_2$ homogeneous dimers.[29] The present study also reveals that haQZ is the smallest basis set in the series that consistently provides MP harmonic vibrational frequencies within a few inverse centimeters of the CBS limit values regardless of whether the counterpoise procedure is applied or not (average absolute deviation of 4 cm^{-1}). MP2/haQZ harmonic frequencies give a maximum deviation from CBS values of 8 cm^{-1} without counterpoise correction and 12 cm^{-1} with counterpoise correction.

Reminiscent of the behavior observed for the homogeneou $(HF)_2$ and $(H_2O)_2$ dimers,[29] the MP2/ha5Z and CCSD(T)/ha5Z harmonic vibrational frequencies in the leftmost colum of data in Table 1 are quite similar for the low-energy intermolecular modes (within 10 cm^{-1}), whereas the deviations are somewhat larger but still less than or equal to 46 cm^{-1} for the intramolecular modes. Consequently, the harmonic ZPVEs of the C_s minimum from MP2/ha5Z and CCSD(T)/ha5Z frequency computations are virtually identical (22.09 ± 0.02 kcal mol^{-1}). The harmonic frequencies for the C_s transition state exhibits the same behavior, where the magnitude of the difference is 39 cm^{-1} for the HF stretching mode and less than 1 cm^{-1} for the imaginary mode.

For the C_s minimum, four different sets of anharmonic corrections from VPT2 computations (ΔVPT2) are also listed in Table 1. The MP2/haTZ and CCSD(T)/haTZ ΔVPT2 values never deviate from each other by more than 8 cm^{-1}. As a result, the corresponding anharmonic corrections to the ZPVE differ by less than 0.02 kcal mol^{-1}. Consequently, the MP2/ha5Z anharmonic corrections are used as a proxy for the CCSD(T)/ha5Z values, thereby avoiding numerous demanding analytic CCSD(T) Hessian computations for the VPT2 procedure, including some at reduced symmetry. The fundamental frequencies and anharmonic ZPVE reported in the last column of Table 1 were obtained by combining the harmonic CCSD(T)/ha5Z values with the MP2/ha5Z ΔVPT2 values.

Table 2. Dissociation Energies (D_e and D_0) and Various ZPVE Corrections (in kcal mol^{-1}) for the $H_2O\cdots HF$ Heterogeneous Dimer

	D_e	harmonic		VPT2		
		δZPVE	D_0	δanharm	δZPVE	D_0
MP2/haTZ	8.83	−2.70	6.12	+0.24	−2.46	6.37
MP2/haQZ	8.75	−2.67	6.08	+0.24	−2.42	6.32
MP2/ha5Z	8.71	−2.65	6.07	+0.24	−2.40	6.31
MP2/ha5Z(CP)[a]	8.58					
CCSD(T)/haTZ	8.81	−2.75	6.05	+0.25	−2.50	6.31
CCSD(T)/haQZ	8.74	−2.71	6.03	[+0.24][b]	[−2.47][b]	[6.27][b]
CCSD(T)/ha5Z	8.70	−2.70	6.01	[+0.24][b]	[−2.45][b]	[6.25][b]
CCSD(T)/ha5Z(CP)[a]	8.61					
CCSD(T)/CBS(CP)	8.51		ref 24 (aQZ/a5Z extrapolation)			
W2	8.69		ref 25			
CCSD(T)/a5Z	8.97		ref 26			
experiment	10.25 ± 0.19		ref 18		8.20 ± 0.07	

[a] CP procedure only applied to D_e. [b] VPT2 anharmonic shift to ZPVE (δanahrm) from corresponding MP2/haXZ computations.

The HF stretch associated with the donation of the hydrogen bond has been the most thoroughly scrutinized of the $H_2O\cdots HF$ vibrational modes, both theoretically and experimentally. In 2005, the experimental HF stretch for the complex was reassigned[23] to 3634 cm^{-1}, and its change on complexation was found to be −332 cm^{-1}. In 1999, Silvi et al.[21] had calculated the shift in HF stretch on complexation by MP3/6-311++G(2d,2p) with and without CP correction, based on a fourth-order polynomial fit of energy points. Without CP correction, the shift on complexation (−357 cm^{-1}) was close to the experimental value (−354 cm^{-1}) based on the mis-assigned peak. The same procedure with counterpoise correction gave a shift (−332 cm^{-1}) equivalent to that for the reassigned peak.

Our fully anharmonic HF stretching frequency of 3636 cm^{-1} from CCSD(T)/ha5Z with VPT2 vibrational corrections from MP2/ha5Z aligns well (within 2 cm^{-1}) with the reassigned HF stretching mode at 3634 cm^{-1}. The HF stretching frequency with harmonic CCSD(T)/ha5Z and VPT2 vibrational corrections from MP2/haQZ is also within 3 cm^{-1} (Table 1).

The only resonance between modes reported by the VPT2 computations in CFOUR at the MP2/haTZ, MP2/haQZ, MP2/ha5Z, or CCSD(T)/haTZ levels was between the first overtone of the out-of-plane HF libration (mode 5) and the H_2O bending fundamental (mode 6), which have CCSD(T)/ha5Z harmonic frequencies at 827 and 1651 cm^{-1}, respectively. That overtone also had the most significant IR intensity of all overtones and combination bands computed with up to a total of three vibrational quanta, ranging from 66 to 147 km mol^{-1} depending on the method and basis set employed for the VPT2 computations. Only five other overtones and combination bands had VPT2 intensities of at least 10 km mol^{-1}. This group consists of the overtones 3(2), 4(2), and 5(2) along with two combination bands 1(1) + 3(1) and 1(1) + 7(1), where the integers in parentheses denote the number of vibrational quanta for that mode. These six VPT2 frequencies and IR intensities can be found in the Supporting Information.

Inversion Barrier. The study of the $H_2O\cdots HF$ dimer is complicated by the low inversion barrier between the two C_s forms. Symmetric double-well potentials with small barriers have a fine structure, where all lines are doubled for modes with energies below the barrier height, as demonstrated for the case of NH_3 inversion doubling.[60−62] Such splitting may be present in the $H_2O\cdots HF$ dimer. In the vibrational spectrum of the HF librational modes for the $H_2O\cdots HF$ complex in a solid argon matrix, Andrews and Johnson[14] saw evidence of peak splitting due to inversion doubling and/or multiple Ar environments. The experimental barrier for the $H_2O\cdots HF$ inversion was determined[12] to be 126 ± 70 cm^{-1} with the associated vibrational mode of 64 ± 10 cm^{-1}. Each level of theory employed in this study gives an electronic barrier height tha slightly smaller than the fundamental frequency of the inver mode. For example, at the CCSD(T)/haTZ level, the barrier to inversion was 133 cm^{-1}, and the associated VPT2 frequency was 178 cm^{-1}. Regardless of whether inversion doubling occurs in the $H_2O\cdots HF$ complex or not, the experimental data and our computational results indicate that the overall effect on the ZPVE contribution to the dissociation energy will be small.

Dissociation Energy. Several computational determinations of D_0 and D_e are shown in Table 2 along with the experimental values.[18] Recent high-level theoretical values for D_e range from ~8.5 to 9.0 kcal mol^{-1}. Our MP2 and CCSD(T) D_e values obtained with the ha5Z basis set of 8.71 and 8.70 mol^{-1}, respectively, fall in the middle of this range. The CP procedure only decreases D_e by ~0.1 kcal mol^{-1}, which suggests the results are close to the CBS limit, where BSSE must vanish by definition. It is also noteworthy that for a given basis set the MP2 and CCSD(T) D_e values differ by no more than 0.03 kcal mol^{-1}.

For further insight into the exceptionally large D_e of the heterodimer relative to the $(HF)_2$ and $(H_2O)_2$ dimers, high-level symmetry-adapted perturbation theory (SAPT) calculations[63−67] were performed for all three systems to compare the interaction energy contributions in terms of electrostatic, exchange, induction, and dispersion contributions with SAPT2 + 3(CCD) δ_{MP2} using the haQZ basis set in the Psi4 software package.[68] Both the attractive electrostatic and repulsive exchange components are much larger in the mixed $H_2O\cdots$ HF dimer, increasing in magnitude by ~6 kcal mol^{-1} each and making contributions of opposite signs to the total interaction energy. However, the increased stabilization in the $H_2O\cdots HF$ induction energy (>3.50 kcal mol^{-1}) and dispersion energy (>0.96 kcal mol^{-1}) yield an interaction energy with a magnitude more than 4 kcal mol^{-1} larger than that for either homodimer. (See the Supporting Information for the SAPT energy components in each dimer.)

To determine an accurate D_0 for $H_2O\cdots HF$, harmonic and anharmonic ZPVE corrections to D_e were calculated with basis sets ranging from haTZ to ha5Z at MP2 and CCSD(T)

DOI: 10.1021/acs.jpca.8b03397
J. Phys. Chem. A 2018, 122, 4902−4908

levels of theory. The MP2 and CCSD(T) harmonic ZPVE corrections to D_e in the second column of data in Table 2 are quite similar (δZPVE values within 0.05 kcal mol^{-1} of each other for a given basis set). Of course, this is a consequence of the trends in vibrational frequencies already discussed. The harmonic δZPVE corrections decrease D_e by ~2.7 kcal mol^{-1} to yield MP2/ha5Z and CCSD(T)/ha5Z harmonic D_0 values of 6.07 and 6.01 kcal mol^{-1}, respectively.

Intramonomer and intermonomer modes in the $H_2O\cdots HF$ complex have opposite contributions to the ZPVE of the dimer. The intramonomer harmonic vibrational frequencies shift to lower energy upon complexation, which increases the computed dissociation energy (D_0 vs D_e) by ~0.5 kcal mol^{-1}. Conversely, the new intermonomer harmonic vibrational frequencies have the opposite effect and appreciably larger magnitude (by roughly a factor of 4). An extended analysis and discussion of δZPVE for dissociation in terms of the harmonic frequencies for $(H_2O)_2$, $H_2O\cdots HF$, $(HF)_2$, and their monomers can be found in the Supporting Information.

Anharmonicity (δanharm in Table 2) slightly attenuates the effect of the ZPVE on the dissociation energy. VPT2 computations indicate that these anharmonic effects decrease the magnitude of δZPVE by ~0.24 kcal mol^{-1}, thereby slightly increasing D_0 relative to the harmonic estimates. Note that the MP2/haQZ and MP2/ha5Z anharmonic corrections (δanharm) were applied to the corresponding CCSD(T) harmonic δZPVE values to estimate the VPT2 δZPVE and D_0 results at the CCSD(T)/haQZ and CCSD(T)/ha5Z levels of theory. Nevertheless, the MP2 and CCSD(T) VPT2 D_0 values remain remarkably consistent at 6.31 kcal mol^{-1} for MP2/ha5Z and 6.25 kcal mol^{-1} for CCSD(T)/ha5Z.

These anharmonic D_0 values differ significantly from the most recent experimental determination of D_0 (8.20 ± 0.07 kcal mol^{-1}).[18] Although inversion doubling could occur (vide supra), the related intermonomer mode is low in energy and thus contributes only a small amount to the overall ZPVE contribution to D_0. $(HF)_2$ also has a similar double-well potential for the analogous mode, and CCSD(T)/haQZ with VPT2 was found to be a good model for that system, giving D_0 within 0.01 kcal mol^{-1} of the experimental value. According to our calculations, the total anharmonic ZPVE correction to obtain D_0 from D_e is ~2.5 kcal mol^{-1} for $H_2O\cdots HF$ (Table 2). This correction is substantially similar to the 2.1 kcal mol^{-1} difference between D_0 and D_e given by Legon et al.[18] For comparison, previous work[29] has found a ZPVE correction of 1.6 kcal mol^{-1} for $(HF)_2$ and 1.9 kcal mol^{-1} for $(H_2O)_2$. As such, the large discrepancy between the experimental D_0 and the values computed here cannot solely be attributed to the challenges of reliably modeling the ZPVE correction in this system.

ONCLUSIONS

The energies and frequencies of the $H_2O\cdots HF$ dimer have been calculated with the MP2 and CCSD(T) methods in conjunction with large correlation consistent basis sets. CCSD(T)/ha5Z computations yield D_e = 8.70 kcal mol^{-1} and D_0 = 6.25 kcal mol^{-1} after including an anharmonic ZPVE correction from an MP2/ha5Z VPT2 analysis. Results from this level of theory provide fundamental frequencies and dissociation energies appropriate for comparison with experimental values. On the basis of the very accurate description of these quantities for $(H_2O)_2$ and $(HF)_2$ by analogous theoretical treatments, the 2.0 kcal mol^{-1} discrepancy between our computed D_0 and the experimental value of 8.2 kcal mol^{-1} is unexpected for this very important prototype for heterogene hydrogen bonding. Although the heterodimer is expected to be more stable than either homodimer,[8] our computations show that the heterodimer D_0 is approximately twice as large as that for either homodimer (6.3 vs ~3.0 kcal mol^{-1}). That ratio approaches 3 with the current experimental value for D_0 of $H_2O\cdots HF$ (8.2 kcal mol^{-1}). It is suggested that the experimental value of the dissociation energy be redetermined for this dimer, because it is 30% larger than our best estimate reported in t study. A SAPT analysis suggests that induction is primarily responsible for the significant increase in D_e for $H_2O\cdots HF$ (~8.7 kcal mol^{-1}) relative to the values for $(H_2O)_2$ or $(HF)_2$ (~5.0 kcal mol^{-1} and ~4.6 kcal mol^{-1}, respectively).[27,28]

SSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b03397.

Cartesian coordinates, harmonic and anharmonic frequencies and intensities, analysis of harmonic contributions to ZPVE, SAPT energy components, full citations for CFOUR, Gaussian 09, and Psi4 (PDF)

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The authors declare no competing financial interest.

CKNOWLEDGMENTS

Supported under the Nation Science Foundation Grant Nos. OIA-1430364 and CHE-1664998. The Mississippi Center for Supercomputing Research is thanked for a generous allotme of computer time.

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