Anharmonic Vibrational Spectroscopy of the $F^-(H_2O)_n$ Complexes, $n = 1, 2$

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We report anharmonic vibrational spectra (fundamentals, first overtones) for the $F^-(H_2O)$ and $F^-(H_2O)_2$ clusters computed at the MP2 and CCSD(T) levels of theory with basis sets of triple-ζ quality. Anharmonic corrections were estimated via the correlation-corrected vibrational self-consistent field (CC−VSCF) method. The CC−VSCF anharmonic spectra obtained on the potential energy surfaces evaluated at the CCSD(T) level of theory are the first ones reported at a correlated level beyond MP2. We have found that the average basis set effect (TZP vs aug-cc-pVTZ) is on the order of 30−40 cm^{-1}, whereas the effects of different levels of electron correlation [MP2 vs CCSD(T)] are smaller, 20−30 cm^{-1}. However, the basis set effect is much larger in the case of the H-bonded O−H stretch of the $F^-(H_2O)$ cluster amounting to 100 cm^{-1} for the fundamentals and 200 cm^{-1} for the first overtones. Our calculations are in agreement with the limited available set of experimental data for the $F^-(H_2O)$ and $F^-(H_2O)_2$ systems and provide additional information that can guide further experimental studies.

I. Introduction

Complexes of the fluoride anion (F^-) with water represent a class of strongly bound hydrogen-bonded complexes exhibiting ion−water intermolecular bonds that are closer to single covalent chemical bonds than to typical hydrogen bonds, which are mainly of electrostatic origin.[1] Previous first principles electronic structure calculations have suggested that the fluoride anion−water interaction exceeds 25 kcal/mol.[2−5] A recent joint experimental−theoretical study[6] converged to a value of −26.2 ± 0.8 kcal/mol for the fluoride ion−water interaction including zero-point energy corrections (D_0). This value is much stronger than typical hydrogen bonds between neutral fragments (e.g., 5 kcal/mol in the water dimer[4,7], 4.6 kcal/mol in the HF dimer,[8] etc.) as well as more than twice the binding energy between the rest of the halide ions and water, viz. 10−14 kcal/mol for I^-, Br^-, and Cl^-.[9−11] This is mainly a result of the high concentration of negative charge on the fluoride anion due to the large electronegativity and the small size of the fluorine atom, which induces a high contribution of electrostatic interaction in the fluoride−water binding. Clusters of the fluoride anion with more than one water molecule also have larger binding energies than the corresponding ones for Cl^-, Br^-, and I^-. In addition, the most energetically stable structures of the $F^-(H_2O)_n$ clusters are distinctly different from the structures of the other halide−water complexes. Although the Cl^-, Br^-, and I^- anions prefer to reside on the surface of a water cluster, the fluoride anion favors cluster configurations in which it disrupts the water hydrogen bonding network being surrounded by water molecules.[2,11−13]

The strong ion−water interaction results in a significant elongation of the hydrogen bonded O−H distance, which, in turn, induces a large red shift in the corresponding infrared (IR) stretching vibration. Therefore, the infrared spectra of $F^-(H_2O)_n$ complexes are of great interest, but at the same time, both their experimental measurements and theoretical predictions present significant challenges. Experimental vibrational spectra of the $F^-(H_2O)$ and $F^-(H_2O)_2$ complexes were recently obtained by Johnson and co-workers using the argon (Ar) predissociation technique.[14,15] Harmonic vibrational frequencies have been previously reported in a number of theoretical studies of $F^-(H_2O)_n$ clusters.[2,11−13] Anharmonic corrections have been estimated for the smallest $F^-(H_2O)$ cluster at the Hartree−Fock (HF) level of theory with a quartic force field.[16] It was shown that correcting for anharmonicities is crucial for the accurate theoretical predictions of the vibrational spectrum of this cluster. Significant anharmonic corrections were also found in previous studies of $Cl^-(H_2O)_n$ clusters,[17,18] especially for the hydrogen bonded O−H stretch. It was previously shown[16] that the potential energy surface for the (hydrogen bonded) H atom motion between the F and O atoms exhibits a very anharmonic shape and a plateau (but not a minimum) corresponding to the FH···OH^- complex. The anharmonic frequency of the hydrogen bonded O−H stretch in $F^-(H_2O)$ was estimated[16] in that study at 1850 cm^{-1}. Subsequently, a much lower value of 1481 cm^{-1} was obtained at the second-order Møller−Plesset (MP2) level

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of theory using a sixth order Taylor series expansion and a one-dimensional Schrödinger equation.[11]

The previous discussion suggests that the fluoride−water complexes present a very challenging class of systems and require techniques that provide accurate assessment of anharmonic effects. In this study, we report the anharmonic vibrational spectra of $F^-(H_2O)$ and $F^-(H_2O)_2$ obtained using the correlation-corrected vibrational self-consistent field (CC−VSCF) approach that is based on potential energies computed directly by high level ab initio electronic structure methods. The CC−VSCF approach, in conjunction with the MP2 electronic structure method, was previously shown to provide reliable anharmonic vibrational data for many hydrogen-bonded systems, such as water clusters and complexes of negative and positive ions with water,[17] complexes of acids (HCl and HF) with water,[19,20] and complexes of magnesium sulfate with water.[21] In particular, for the $Cl^-(H_2O)$ and $Cl^-(H_2O)_2$ clusters, the CC−VSCF calculations based on MP2 potentials[17] confirmed earlier predictions[22] regarding the validity of two different experimental results therefore assisting in sorting out the more accurate one. In the current study, because of the especially challenging nature of fluoride−water clusters, the anharmonic corrections will be estimated with the CC−VSCF approach using both MP2 and a higher correlation [CCSD(T)] level of theory. In section II, we will outline the methodology we used. The results and discussion will be presented in section III, whereas the conclusions will be summarized in section IV.

II. Methodology

The equilibrium geometry and vibrational frequencies of the $F^-(H_2O)$ cluster were obtained at the second-order Møller−Plesset perturbation theory[23] (MP2) and the coupled cluster with single and double excitations and a perturbative estimate of the triple excitations[24] [CCSD(T)] ab initio levels of theory. We used Dunning's triple-ζ + polarization[25] (TZP) basis set as well as the family of the augmented correlation-consistent sets,[26] aug-cc-pVnZ (n = D, T). We used Cartesian d functions for the TZP and spherical components for the correlation-consistent basis sets, respectively. The geometry and frequencies of the $F^-(H_2O)_2$ cluster are computed at the MP2/TZP level of theory. Anharmonic corrections are obtained using the vibrational self-consistent field (VSCF) method[27,28] and its correlation-corrected extension (CC−VSCF) via second-order perturbation theory.[29] The calculations are performed using the combined ab initio/CC−VSCF approach, where anharmonic vibrational frequencies are computed directly from an ab initio electronic structure program.[30] Such direct techniques that employ ab initio potential energy surfaces in the calculation of anharmonic frequencies have been recently developed.[18,30,31] They have very important advantages over alternative approaches that use analytical potential functions, because they allow the application of anharmonic vibrational spectroscopy methods to any molecular system of moderate size (up to 15 atoms). The VSCF method is used to solve the vibrational Schrödinger equation to obtain vibrational wave functions and energies. In the VSCF approximation, the total vibrational wave function in mass-weighted normal coordinates is represented as a product of one-dimensional functions (each depending on one normal coordinate), and the resulting one-dimensional VSCF equations are solved self-consistently. The VSCF energies are further corrected for correlation effects between the vibrational modes using second-order perturbation theory[29] (CC−VSCF). The VSCF and CC−VSCF techniques used in this study have been described in detail previously (see refs 29 and 30). To make the integrals involved in the CC−VSCF calculations more tractable and to reduce the number of electronic structure computations required, a pairwise coupling approximation is used for the potential in the normal-mode representation.[29] In this approximation, the potential of the system is represented by the sum of separable (single mode) terms and pair coupling terms, neglecting triple couplings of normal modes and higher-order interactions. This approximation was found to give satisfactory results for the systems reported previously[17,19,20,30] while it makes the direct calculation on the ab initio potential energy surface feasible for clusters larger than the dimer. A grid representation for the potential energy terms is used, where one-dimensional terms for each normal mode are represented by a grid of 16 points, whereas pair coupling potential terms for each pair of normal modes are represented by 16×16 square grids. Energy points on grids are calculated in this work at the MP2 and CCSD(T) levels of electronic structure theory with the TZP and aug-cc-pVTZ basis sets. Most of the calculations in this study (including all anharmonic corrections via CC−VSCF) were performed using the electronic structure package GAMESS [ref 32]. Geometry optimizations and harmonic vibrational frequencies at the CCSD(T) level of theory were performed with the GAUSSIAN-98 package [ref 33], whereas single-point CCSD(T) energies along normal modes for anharmonic corrections were computed with the CCSD(T) code[34] in GAMESS.

Previous studies have indicated that the combined ab initio/CC−VSCF technique (that accounts for anharmonicities and couplings between vibrational modes) based on potential energy surfaces calculated at the MP2/TZP level of theory produces satisfactory results for spectroscopic properties of different hydrogen-bonded complexes such as water clusters,[17] complexes of negative and positive ions with water,[17] and complexes of acids (HCl and HF) with water.[19,20] This level of theory was found to predict anharmonic frequencies for the highest frequency stretching vibrations with an accuracy of 30−50 cm^{-1} compared with available experimental data.[17,19,20,30] Although this is not at the level of spectroscopic accuracy, it is a substantial improvement over the harmonic level theoretical predictions. Furthermore, even at this level of accuracy, theoretical calculations can be used to help analyze observed spectra and predict important spectroscopic features. The method has been shown to have sufficient accuracy even for highly anharmonic hydrogen-bonded systems.[21] Potential energy surfaces obtained with a larger, correlation-consistent (aug-cc-pVTZ) basis set at a higher [CCSD(T)] correlated level of theory are tested here for CC−VSCF anharmonic corrections for the first time.

III. Results and Discussion

The optimized geometries of complexes of F^- with one and two water molecules are shown in Figure 1. As was previously reported,[2,4] the complexation of F^- with one water molecule leads to a very significant elongation of the hydrogen bonded O−H stretch (by ~0.1 Å) with respect to the isolated water molecule. The hydrogen bond is very strong and is closer to a single covalent F−H bond than to a "normal" hydrogen bond. In the $F^-(H_2O)_2$ cluster, the two ion−water hydrogen bonds are weaker than in $F^-(H_2O)$ but are still quite strong.[2] Note that in the $F^-(H_2O)_2$ cluster (unlike other $X^-(H_2O)_2$ complexes, X = Cl^-, Br^-, I^-) there is no hydrogen bond between the two water molecules.[2,11−14]

The harmonic and anharmonic vibrational frequencies, calculated at the MP2/TZP level of theory (similar to the one used in our previous studies of hydrogen-bonded complexes[17,19,20,21])

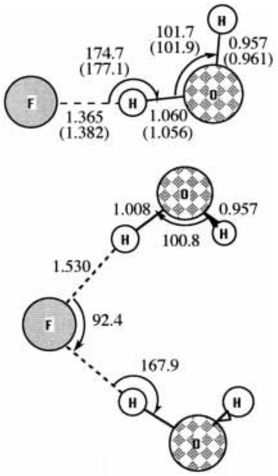

Figure 1. Equilibrium geometrical parameters (Å, deg) of $F^-(H_2O)$ and $F^-(H_2O)_2$ at the MP2/TZP and CCSD(T)/aug-cc-pVTZ (in parentheses) levels of theory.

TABLE 1: Vibrational Frequencies and IR Intensities for $F^-(H_2O)$ at the MP2/TZP Level of Theory

mode	frequency (cm^{-1}) harmonic	CC−VSCF	expt[a]	intensity (km/mol)	description
		Fundamentals			
1	3939	3723	3690	3	free O−H stretch
2	2161	1544		2156	bonded O−H stretch
3	1736	1663		225	H_2O bend
4	1228	1220		145	
5	553	552		45	
6	405	450		143	
		First Overtones			
1		7284		1	free O−H stretch
2		3052	2930	269	bonded O−H stretch
3		3299		1	H_2O bend
4		2432		0	
5		1091		2	
6		872		10	

[a] Reference 15.

TABLE 2: Vibrational Frequencies and IR Intensities for $F^-(H_2O)_2$ at the MP2/TZP Level of Theory

mode	frequency (cm^{-1}) harmonic	CC−VSCF	expt[a]	intensity (km/mol)	description
1	3945	3704	3700	23	free O−H stretch
2	3944	3558		6	free O−H stretch
3	3086	2720	2520	1502	bonded O−H stretch
4	2910	2521	(2435)	952	bonded O−H stretch
5	1769	1701		18	H_2O bend
6	1721	1658		347	H_2O bend
7	1059	1100		67	
8	1050	1087		359	
9	544	645		114	
10	512	615		35	
11	351	524		85	
12	336	778		4	
13	289	325		92	
14	58	82		0	
15	54	366		163	

[a] Reference 14.

are listed in Tables 1 and 2 for the $F^-(H_2O)$ and $F^-(H_2O)_2$ clusters, respectively. Intensities of the IR active vibrations calculated using dipole moments along normal modes and VSCF wave functions are also listed. These are compared with experimental frequencies measured by Johnson and co-workers.[14,15] As it can be seen from Table 1, the anharmonic corrections to the O−H stretching vibrations are very large. For the free O−H stretch, the anharmonicity is similar in magnitude with the one in other complexes containing water (∼200 cm^{-1}). Inclusion of these anharmonic corrections significantly improves agreement with experiment, bringing it within an error of about 30−40 cm^{-1} (similar to the one for $Cl^-(H_2O)$ reported before using the CC−VSCF method[17]). For the hydrogen bonded O−H stretch, the anharmonic correction is much more significant than in any other complex of halide ions with water. For example, in $Cl^-(H_2O)$, the anharmonicity for the hydrogen bonded O−H stretch is about 320 cm^{-1}. In contrast, in $F^-(H_2O)$, it is about 620 cm^{-1} at the same level of theory (MP2/TZP). The red shift for the hydrogen bonded O−H stretching frequency (with respect to the isolated water molecule) is also much larger in $F^-(H_2O)$: it is about 2200 cm^{-1} (vs about 600 cm^{-1} in $Cl^-(H_2O)$). This red-shift brings the hydrogen bonded O−H stretching frequency down to 1544 cm^{-1}, in the region of the water bending frequencies. However, unlike the water bending vibration, this hydrogen bonded O−H stretch has a very high intensity, almost an order of magnitude larger than the corresponding intensity of the water bending vibration in the $F^-(H_2O)$ complex calculated at the same level of theory (see Table 1). Despite its high intensity, this frequency shifts to such a low value that it is not easily observable experimentally. Only the overtone excitation of this vibration has been measured experimentally.[15] For this reason, in addition to fundamental transitions we also list the first overtones in Table 1. Our calculated value of 3052 cm^{-1} for the first overtone frequency of the hydrogen bonded OH stretch at the MP2/TZP level is about 120 cm^{-1} higher than the observed value of 2930 cm^{-1}. The intensity of this overtone excitation is calculated to be rather high, 269 km/mol (see Table 1), a result that is consistent with its experimental observation.

In the $F^-(H_2O)_2$ cluster, the two hydrogen bonded O−H stretches are calculated at 2720 and 2521 cm^{-1}, respectively, at the CC−VSCF level (Table 2). These frequencies are significantly higher than the corresponding one of the $F^-(H_2O)$ cluster. Although these frequencies are not as shifted to the red as the one of the $F^-(H_2O)$ cluster, the shifts are still quite significant when compared to other hydrogen-bonded aqueous clusters. Their anharmonicities are more moderate than in $F^-(H_2O)$ and closer to those of free O−H stretches. Experimentally, two band positions observed at 2435 and 2520 cm^{-1} were tentatively assigned to the two hydrogen-bonded stretches.[14] Because these bands lie close to the edge of the laser scanning range (ca. 2400 cm^{-1}) used during the experiments, the experimental determination of their relative intensities might be subject to larger errors due to issues related to signal normalization.[35] Some more recent data from the same research group[35] suggest that the ratio of intensities of the lower to higher hydrogen bonded OH frequencies is closer to 1:2, in good agreement with our predicted ratio of ∼2:3 (cf. Table 2). However, the position of the higher H-bonded O−H frequency observed experimentally (at 2520 cm^{-1}) is almost identical to the calculated lower one at 2521 cm^{-1}. Furthermore, the calculated separation of the two hydrogen bonded O−H frequencies (200 cm^{-1}) is more than twice the one that was tentatively assigned experimentally (85 cm^{-1}) in earlier studies. The presence of Ar atoms in the experiment may influence the structural motif of the $n = 2$ cluster, which is characterized by a very floppy PES as regards the variation of the O−F−O angle. This fact was realized during the earlier joint experimental−theoretical studies[14] where it was pointed out that the energy difference between the "bent" (C_2) and "linear" (C_{2h}) geometries was just 0.34 kcal/mol (0.02 kcal/mol when harmonic zero-point energy is included).[14] The possibility of large amplitude

TABLE 3: Vibrational Frequencies for $F^-(H_2O)$ Fundamental Excitations at Several Levels of Theory

	MP2 TZP		MP2 aug-cc-pVTZ		CCSD(T) TZP		CCSD(T) aug-cc-pVTZ		
mode	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf	expt[a]
1	3939	3723	3892	3691	3894	3658	3856	3640	3690
2	2161	1544	2090	1450	2267	1560	2211	1488	
3	1736	1663	1698	1618	1754	1684	1723	1645	
4	1228	1220	1177	1170	1220	1215	1171	1166	
5	553	552	581	575	555	556	580	581	
6	405	450	392	443	397	439	387	431	

[a] Reference 15.

TABLE 4: Vibrational Frequencies for $F^-(H_2O)$ First Overtone Excitations at Several Levels of Theory

	CC−VSCF vibrational frequencies (cm^{-1})				
mode	MP2 TZP	MP2 aug-cc-pVTZ	CCSD(T) TZP	CCSD(T) aug-cc-pVTZ	expt[a]
1	7284	7231	7130	7105	
2	3052	2844	3055	2888	2930
3	3299	3209	3342	3265	
4	2432	2327	2417	2314	
5	1091	1130	1097	1129	
6	872	857	851	836	

[a] Reference 15.

TABLE 5: Comparison of Vibrational Frequencies for H_2O at Several Levels of Theory

	CC−VSCF vibrational frequencies (cm^{-1})								
	MP2 TZP		MP2 aug-cc-pVTZ		CCSD(T) TZP		CCSD(T) aug-cc-pVTZ		
mode	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf	expt
1	4015	3797	3948	3739	3977	3748	3920	3703	3756
2	3877	3691	3822	3644	3854	3658	3811	3627	3657
3	1603	1548	1628	1562	1620	1564	1646	1580	1595

vibrations as regards the O−F−O angle might affect the coupling of the two O−H frequencies. Indeed, in C_{2h} symmetry, only the lower O−H bonded frequency (now at 2465 cm^{-1}) is IR active (with intensity 2949 km/mol), whereas the higher hydrogen bonded O−H frequency (at 2708 cm^{-1}) is IR inactive, a fact that may explain the absence of IR activity in this region in the experiment. Additional experiments that can yield rotational resolution of the two bands and therefore provide structural information via the determination of the rotational constant can clarify this issue.

Although the MP2/TZP level of electronic structure theory represents a good compromise between feasibility and accuracy, the use of potential energies obtained at higher levels of theory for computing spectroscopic properties with the CC−VSCF method is of significant interest. A larger basis set (such as aug-cc-pVTZ) and a higher level of ab initio theory [CCSD(T)] are tested in this study for the $F^-(H_2O)$ complex. The results obtained at different levels of theory are given in Table 3 for the fundamental excitations and in Table 4 for the first overtones. Similar results for the isolated water molecule together with the available experimental data are presented in Table 5 for comparison. It can be seen from Table 3 that for $F^-(H_2O)$ the extension of the basis set from TZP to aug-cc-pVTZ leads to the decrease of the calculated frequencies and brings the free O−H stretching frequency into a closer agreement with experiment (3690 cm^{-1}). The best calculated value for the hydrogen bonded O−H stretch is 1488 cm^{-1} (cf. Table 3), whereas its first overtone is calculated to be at 2888 cm^{-1}, about 40 cm^{-1} lower than the experimental value of 2930 cm^{-1} obtained for the Ar solvated $F^-(H_2O)$ cluster.[15] This value is consistent with the experimental assignment[15] and the trend found there for the blue shift of the F^-−O−H stretching frequency with increasing Ar solvation. The remaining discrepancies between the calculated and experimental values may be due to the limitations of the pairwise coupling approximation used for the potential in the normal mode representation and the neglect of the triple and higher order couplings of normal modes. In general, the differences between the anharmonic two- and four-mode representations are of the order of 20−60 cm^{-1} for the intermolecular frequencies of negative ion−water clusters using model potentials.[36]

It follows from Tables 3−5 that improvement of the quality of the potential energy surface improves the agreement of the calculated anharmonic CC−VSCF frequencies with experimental data. For example, the larger basis set (aug-cc-pVTZ) changes the frequency of the hydrogen bonded OH stretch of the $n = 1$ cluster (mode 2 in Table 3) by ~100 cm^{-1} with respect to the smaller one (TZP) at the MP2 level and by about 70 cm^{-1} at the CCSD(T) level of theory. In contrast, the use of a higher correlation level [CCSD(T)] has a smaller effect on this anharmonic frequency (~20−40 cm^{-1}) when compared to MP2. Therefore, the basis set effect is larger than the correlation effect on this frequency for the correlation methods examined here [CCSD(T) vs MP2]. These differences are almost doubled for the first overtones of the $n = 1$ cluster, shown in Table 4: the basis set effect [TZP vs aug-cc-pVTZ] is >200 cm^{-1} (for MP2) and ~160 cm^{-1} [for CCSD(T)], whereas the correlation effect [CCSD(T) vs MP2] is smaller, 3−40 cm^{-1} depending on the basis set again for mode 2. The average basis set effects on other frequencies of $F^-(H_2O)$ and H_2O (Tables 3 and 5) are on the order of 30−40 cm^{-1}, and those of the level of electron correlation are 20−30 cm^{-1}.

The improvement of the agreement with experiment when using larger basis sets and higher correlation methods comes with a significant increase in the computational cost. For example, for the H_2O molecule, the cost of the potential energy surface calculation for CC−VSCF increases by almost 2 orders of magnitude when going from the TZP to the aug-cc-pVTZ basis set and by another order of magnitude when moving from MP2 to CCSD(T).

The variation of the potential energy surface as a function of the F−H distance away from the minimum energy configuration (R_e) along normal mode 2 for the $F^-(H_2O)$ cluster is shown in Figure 2. This one-dimensional potential energy curve is computed at the CCSD(T) level of theory with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The potential is plotted with respect to the minimum energy configurations for the two basis sets (which sets the zero in the axes) while all other internal coordinates are held constant at their optimal values for the two basis sets, respectively. The solution of the 1-dimensional Schrödinger equation yields energy levels of 1540 cm^{-1} for the fundamental and 2942 cm^{-1} for the first overtone with the aug-cc-pVDZ set. The corresponding results with the aug-cc-pVTZ set are 1442 cm^{-1} (fundamental) and 2964 cm^{-1} (overtone), lying within ~50−70 cm^{-1} from the CC−VSCF results with this basis set of 1488 cm^{-1} (fundamental, Table 3) and 2888 cm^{-1} (overtone, Table 4). This indicates that the amount of coupling of this mode with the rest is quite small and that for this system the 1-dimensional approximation can yield accurate results.

IV. Conclusions

Anharmonic vibrational spectra are computed for the $F^-(H_2O)$ and $F^-(H_2O)_2$ clusters using the direct ab initio CC−VSCF

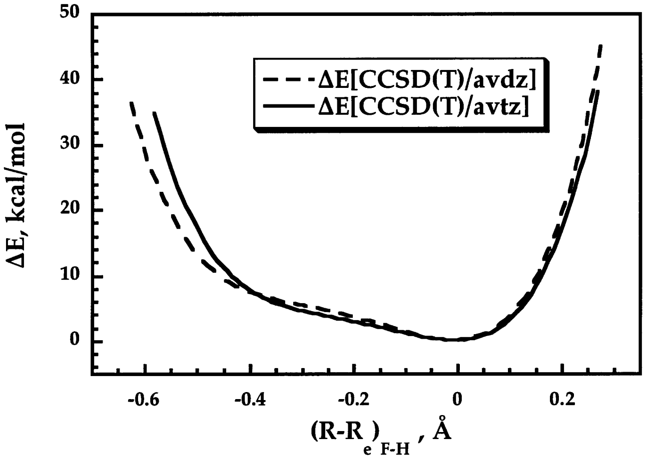

Figure 2. One-dimensional potential energy curve as a function of the F−H separation from the minimum configuration along normal mode 2 at the CCSD(T) level of theory with the aug-cc-pVDZ and aug-cc-pVTZ basis sets for the $F^-(H_2O)$ cluster. All other internal coordinates are held constant at their optimal values for the two basis sets, respectively.

method. The results of our calculations are in good agreement with the available experimental data and confirm previous experimental assignments. We also report other fundamental and first overtone frequencies and IR intensities for these systems that have not yet been measured experimentally. Two ab initio levels of electron correlation [MP2 and CCSD(T)] with a combination of basis sets (TZP and aug-cc-pVTZ) are tested for the highly anharmonic modes (especially the hydrogen bonded OH vibration) of the $F^-(H_2O)$ cluster in order to assess the effect of both basis set and electron correlation on the computed anharmonic frequencies. The CC−VSCF anharmonic calculations performed using the potential energy surfaces evaluated at the CCSD(T) level of theory are the first ones reported at any correlated level beyond MP2 with a basis set of this size. It is found that the MP2/TZP level of theory produces reasonably accurate results, with the accuracy for O−H stretching and bending vibrations typically of the order of 30−50 cm^{-1}. Higher, CCSD(T) level of ab initio theory shows some improvement (5−50 cm^{-1}) over MP2 depending on the basis set used. The MP2/TZP level of theory in conjunction with CC−VSCF calculations seems to provide a reasonable compromise between accuracy (although not at the spectroscopically accurate level) and feasibility, especially for the larger clusters containing more than 4−5 atoms. These studies are very useful for the purposes of both experimental assignments and predictions in cases where experimental data are not easily accessible.

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