

# Dissolution Nature of Cesium Fluoride by Water Molecules<sup>†</sup>

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The structures, stabilities, thermodynamic quantities, dissociation energies, infrared spectra, and electronic properties of CsF hydrated by water molecules are investigated by using density functional theory, Møller–Plesset second-order perturbation theory (MP2), coupled cluster theory with singles, doubles, and perturbative triples excitations (CCSD(T)), and ab initio molecular dynamic (AIMD) simulations. It is revealed that at 0 K three water molecules (as a global minimum structure) begin to half-dissociate the Cs–F, and six water molecules (though not a global minimum energy structure) can dissociate it. By the combination of the accurate CCSD(T) conformational energies for Cs(H<sub>2</sub>O)<sub>6</sub> at 0 K with the AIMD thermal energy contribution, it reveals that the half-dissociated structure is the most stable at 0 K, but this structure (which is still the most stable) changes to the dissociated structure above 50 K. The spectra of CsF(H<sub>2</sub>O)<sub>1–6</sub> from MP2 calculations and the power spectra of CsF(H<sub>2</sub>O)<sub>6</sub> from 50 and 100 K AIMD simulations are also reported.

## I. Introduction

Hydration of alkali metal and halide ions has been an important subject in solution chemistry and biochemistry.<sup>1–3</sup> It is interesting to note that there is a clear distinction between alkali metal and halide ions. The cation hydration prefers the internal state, while the anion hydration tends to favor the surface state. Thus, along with the dissociation phenomena of acids<sup>4</sup> and bases,<sup>5</sup> the understanding of dissociation of alkali metal–halide salts<sup>6</sup> into cations and anions by water molecules is a complex problem, but it is important in a wide variety of physical and chemical phenomena. This understanding would provide insights into the nature of hydrogen bonding involved in solvation and chemical reactions in aqueous phases. For this study, detailed information of structure and energetics of not only the salts but also the solvated alkali metal and halide ions is needed. This information would lead to an understanding of the related molecular recognition toward the design of ionophores and receptors, ion-mediated self-assembly, and nanomaterial design.<sup>7–9</sup> Since the hydration of alkali metal cations and halide anions have been well studied, we have investigated the salts combined by alkali metal ions and halide anions, and we here particularly focus on studying the hydration and dissociation phenomena of highly ionic CsF.

Cs<sup>137</sup> is the major component of nuclear wastes due to its long half-life. Therefore, much effort has been made to remove the Cs atoms in radioactive wastes.<sup>10</sup> The fluoride anion is widely used for the prevention of dental cavities and treatment of osteoporosis, etc.<sup>11</sup> The CsF salt is an important chemical species. The use of an ultrathin CsF interlayer in organic electroluminescent devices has been recently exploited.<sup>12</sup> However, due to the dissociation of CsF, the operating voltage of the cathode is reduced dramatically. Thus, the thermal dissociation and collision-induced dissociation of CsF have been

intensively investigated.<sup>13,14</sup> CsF is also used as a catalyzer in organic and organometallic reactions, as a source of fluoride ion in fluoride-mediated reactions, and as a source of water-free fluoride anion for anion receptor studies as well as desiccants.<sup>15,16</sup> Although Buchner et al. have recently investigated the dissociation of CsF by methanol,<sup>17</sup> little research has been carried out on the dissociation of CsF by hydration. Therefore, we are interested in investigating thermo-chemical properties of gaseous CsF in water, CsF(H<sub>2</sub>O)<sub>n=1–6</sub>, i.e., the dissolution phenomena of CsF by water molecules. Here we report the structure, thermal energies, and dynamic effects of the hydration of CsF using density functional theory (DFT), ab initio calculations (Møller–Plesset second-order perturbation theory (MP2) and coupled cluster theory with singles, doubles, and perturbative triples excitations (CCSD(T))), and atom-centered density matrix propagation (ADMP) ab initio molecular dynamic (AIMD)<sup>18</sup> simulations.

## II. Computational Details

We have investigated various equilibrium geometries of the dissociated and undissociated clusters CsF(H<sub>2</sub>O)<sub>1–6</sub>. Calculations were done at the DFT level with Becke's three-parameter exchange potential and Lee–Yang–Parr correlation functional (B3LYP)<sup>19</sup> and the MP2 and CCSD(T) levels of theory. For Cs, we used the energy-adjusted Stuttgart effective core potentials (ECPs)<sup>20</sup> and added a d-function (with the exponent of 0.19) to the Cs valence basis set<sup>21</sup> (which we will denote as Stuttgart basis sets). For oxygen and hydrogen atoms, the aug-cc-pVDZ (to be shortened as aVDZ) basis set was used at the B3LYP level, and the aug-cc-pVDZ+diffuse(2s2p/2s) (to be shortened as aVDZ+) basis set was used at the MP2 and CCSD(T) levels, where the diffuse functions were added to properly consider the energies of dissociated anion states.<sup>22</sup> The consideration of the extra diffuse function is particularly important when the salt starts dissociating with the increased number of water molecules. The energy difference between the MP2/aVDZ

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TABLE 1: Structural Parameters for H<sub>2</sub>O, Cs, F, and CsF<sup>a</sup>

		B3LYP/aVDZ+	MP2/aVDZ+	MP2/aVTZ+	CCSD(T)/aVDZ+	CCSD(T)/aVTZ+	experiment
H <sub>2</sub> O	$r(\text{OH})/\text{\AA}$	0.965	0.966	0.961	0.967	0.962	0.957 <sup>b</sup>
	$\angle\text{HOH}$	104.8	103.9	104.1	104.0	104.2	104.5 <sup>b</sup>
	$\nu_s$	3795	3804	3825	3787	3812	3832 <sup>b</sup>
	$\nu_a$	3905	3938	3951	3905	3921	3942 <sup>b</sup>
	$\nu_s(\text{scaled})$	3644	3652	3672	3635	3660	3657 <sup>c</sup>
	$\nu_a(\text{scaled})$	3749	3781	3793	3749	3764	3756 <sup>c</sup>
Cs	IP/eV	4.010	3.776		3.997		3.8939 <sup>d</sup>
F	EA/eV	3.574	3.547	3.596	3.230	3.312	3.4012 <sup>e</sup>
CsF	$r_e/\text{\AA}$	2.433	2.443	2.424	2.443	2.420	2.3453 <sup>f</sup>
	$\nu_e/\text{cm}^{-1}$	334	334	338	335	348	360 <sup>f</sup>
	$D_0/(\text{kcal/mol})$	126.9	126.7	129.0	131.6	134.3	122.5 <sup>f</sup>

<sup>a</sup> Only OH frequencies ( $\nu_s$  and  $\nu_a(\text{scaled})$  ( $\text{cm}^{-1}$ )) are scaled by a scale factor of 0.96 due to their high anharmonic nature caused by a large ZPE.

<sup>b</sup> Reference 26. <sup>c</sup> Reference 27. <sup>d</sup> Reference 28. <sup>e</sup> Reference 29. <sup>f</sup> Reference 30.

and MP2/aVDZ+ calculation for the undissociated and dissociated forms of the salt for CsF(H<sub>2</sub>O)<sub>6</sub> is  $\sim 0.1$  and  $\sim 1.0$  kcal/mol.

For brevity, the basis set of the complex is simply denoted as the basis set of water and hydroxide. The CCSD(T) results were obtained from the single-point calculations on the optimized geometries at the MP2 level. The zero-point energy (ZPE) uncorrected ( $\Delta E_e$ ) and corrected ( $\Delta E_0$ ) internal energies are reported, along with the enthalpies ( $\Delta H_{298}$ ) and Gibbs free energies ( $\Delta G_{298}$ ) at 298 K and 1 atm. For CCSD(T), zero-point energies and thermal energies used the MP2/aVDZ+ values. Since CCSD(T) results are generally known to be most realistic, our discussion will be based on the CCSD(T)/aVDZ+//MP2/aVDZ+ energies and the MP2/aVDZ+ geometries, unless otherwise specified.

The charge-transfer-to-solvent (CTTS) energies ( $E_{\text{CTTS}}$ ) were obtained using configuration interaction with single excitations (CI(S)) at the MP2 level and the random-phase approximation (RPA) at the B3LYP level.<sup>23</sup> Other electronic properties are also reported at the MP2 level.

For ADMP AIMD simulations, we used the B3LYP method with the 6-31+G\*\* basis set for fluoride, oxygen, and hydrogen and the Stuttgart basis set for cesium. Since we cannot carry out long AIMD simulations which scan over all low-lying energy conformers, we rather chose to simulate four important low-lying energy conformers of CsF(H<sub>2</sub>O)<sub>6</sub>. For each conformer, 2.5 ps simulations were performed, and the last 1 ps trajectories were used for analysis of structures, energies, and spectra. The time step employed in each simulation was 0.1 fs.

The calculations were carried out using the Gaussian 03 suite of programs.<sup>24</sup> All of the figures presented here were drawn using Pohang SciTech Molecular Modeling (POSMOL)<sup>25</sup> and some available graphic packages.

### III. Results

**A. Structures and Energetics.** We begin with the discussion of monomeric species, CsF and H<sub>2</sub>O. Table 1 lists the geometrical parameters, dissociation energies, and electronic properties of CsF. The B3LYP/aVDZ+ and MP2/aVDZ+ results are in good agreement with each other. The calculation of CsF and H<sub>2</sub>O were also performed at the MP2/aVTZ+, CCSD(T)/aVDZ, and CCSD(T)/aVTZ levels. This shows that the B3LYP/aVDZ+ and MP2/aVDZ+ results are reliable values. The ionization potential (IP) of Cs, the equilibrium distance ( $r_e$ ) and dissociation energy ( $D_0$ ) of CsF, and the frequency of the Cs–F stretch mode ( $\nu$ ) obtained from B3LYP, MP2, and CCSD(T) agree well with the experimental values.<sup>26–30</sup>

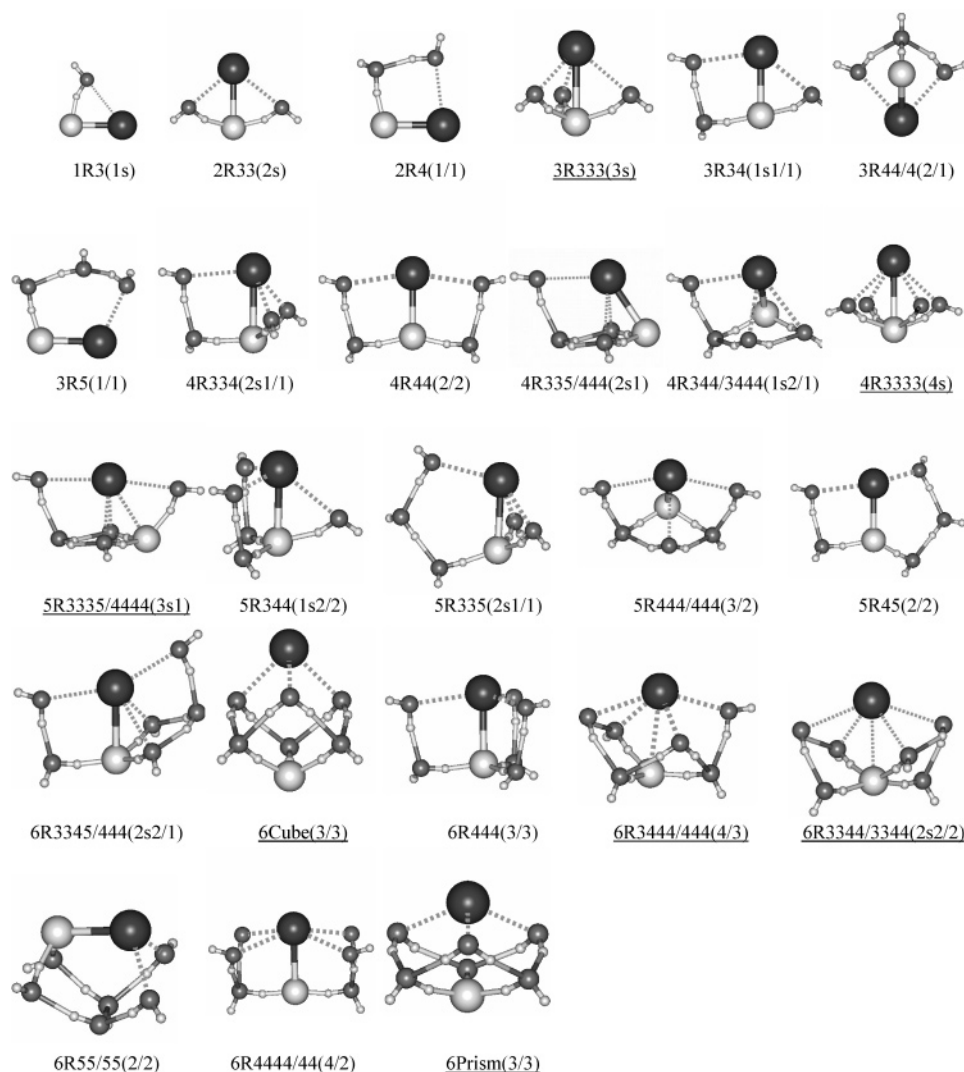
Figure 1 shows various low-lying energy structures of CsF(H<sub>2</sub>O)<sub>1–6</sub> clusters. Each conformer is denoted by “ $nRn_1n_2\dots$ ”.

Here, R indicates a ring conformer;  $n_i$  means an  $n_i$ -membered ring including both Cs and F atoms;  $m_i$  means an  $m_i$ -membered ring in which both Cs and F atoms are not present;  $js$  denotes that Cs and F share  $j$  water molecules, and the coordination number ( $p$ ) of Cs by O atoms and that ( $q$ ) of F by H atoms are given in  $p/q$  in parentheses. This notation will be simply represented as “ $nRn_1n_2\dots$ ” for convenience sake.

We have investigated the dissociation trends of CsF(H<sub>2</sub>O) <sub>$n=1-6$</sub> . Table 2 lists the hydration energies at the B3LYP/aVDZ and MP2/aVDZ+ levels. The selected structural parameters for the CsF(H<sub>2</sub>O) <sub>$n=0-6$</sub>  clusters obtained at the MP2/aVDZ+ level are given in Table 3. The lowest-energy structures of the undissociated and dissociated cases (including nearly isoenergetic structures) for each  $n$  are further investigated at the CCSD(T)/aVDZ+ level. For  $n < 4$ , the Cs $\cdots$ F distance increases monotonically toward 3.0 Å as the cluster size increases (Figure 2). For  $n = 4$ , the Cs $\cdots$ F distance is  $\sim 3.0$  Å. In this case, the global minimum energy structure is 4R334 at all levels of calculation and 4R3333 is isoenergetic to 4R334 at the CCSD(T) level. Except for this special case, for  $n \leq 5$ , all calculations (B3LYP, MP2, and CCSD(T)) give the same global minimum energy conformer for each  $n$ . However, as for the global minimum energy conformer for  $n = 6$ , B3LYP predicts 6R444, while both MP2 and CCSD(T) predict 6R3444 (followed by 6R3345). The 6Prism structure is not stable at the B3LYP level. The B3LYP single-point energy on the MP2 optimized geometry of 6Prism is higher than the energy of 6Cube. The DFT results, due to the inherent problem that DFT cannot deal with dispersion energy in addition to the lack of an exact exchange–correlation functional, tend to be biased for less compact structures with lower coordination numbers.<sup>31</sup>

Table 3 shows that the water–water intermolecular hydrogen bond distances ( $r_{\text{HB}}$ ) increase as the cluster size increases ( $n = 2, 4, 5, 6$ ). For  $n = 3$  or 4, there is no water–water intermolecular hydrogen bonding in their stable conformations. The intermolecular hydrogen bond distance is 1.683 Å for 2R33 and 2.034 Å for 6R3444. The calculations of CsF(H<sub>2</sub>O) <sub>$n=1-6$</sub>  show that the balanced Cs $\cdots$ O distance is  $\sim 3.0$  Å as the cluster size increases. In a former work of Lee et al.,<sup>2e</sup> the Cs $\cdots$ O distance in Cs<sup>+</sup>(H<sub>2</sub>O) <sub>$n=1-6$</sub>  is also about 3.0 Å. Meanwhile, the F $\cdots$ H distance is less than 1.6 Å except for CsF(H<sub>2</sub>O) <sub>$n=4$</sub> . For 6Cube and 6Prism, the F $\cdots$ H distances are 1.53 and 1.55 Å, respectively, which are close to the situation of a  $C_{3h}$  conformation of F<sup>−</sup>(H<sub>2</sub>O)<sub>3</sub> (the F $\cdots$ H distance is 1.59 and 1.55 Å).<sup>22e</sup> Therefore, 6Cube or 6Prism is close to the situation of dissociated Cs<sup>+</sup>(H<sub>2</sub>O)<sub>3</sub> ( $C_{3h}$ ) and F<sup>−</sup>(H<sub>2</sub>O)<sub>3</sub> ( $C_{3h}$ ).

The stretch modes of Cs $\cdots$ F and Cs $\cdots$ O are collected in Table 3. For the gaseous CsF, the frequency of the stretch mode  $\nu_{\text{CSF}}$  is 334  $\text{cm}^{-1}$ . In the cases of CsF(H<sub>2</sub>O)<sub>1–6</sub> clusters, the  $\nu_{\text{CSF}}$  for



**Figure 1.** Various conformers of  $\text{CsF}(\text{H}_2\text{O})_{n=1-6}$ . For each  $n$ , half- and full-dissociated structures are underlined.

$n = 1$  and 2 are 233 and 145  $\text{cm}^{-1}$ , respectively, and the  $\nu_{\text{CsF}}$  of the global minimum energy conformers for  $n = 3-6$  are less than  $\sim 100 \text{ cm}^{-1}$  (including 103  $\text{cm}^{-1}$  for 6R3334). For the 6Cube(3/3) structure,  $\nu_{\text{CsF}}$  is only 25  $\text{cm}^{-1}$ , which is strongly coupled with other vibrational modes, and so the Cs–F stretching characteristic practically disappears.

To understand the dissociation phenomena of CsF by water molecules, it is useful to define the dissociated structure. Once a dissociated structure (at a minimum) is separated from the undissociated structure (at a minimum) with a barrier between the two minima, it could be often considered as a necessary condition for the existence of a dissociated structure. However, many other factors need to be taken into account. Given only pure CsF without hydration, the dissociated state does not satisfy the above criteria; i.e., there is no barrier between dissociated and undissociated conformers. However, if the distance between Cs and F is large, then it should be considered a dissociated structure. In this regard, if the distance between Cs and F atoms ( $r_{\text{CsF}}$ ) is within the inflection point ( $r_i(\text{CsF})$ ) of the potential energy profile with respect to  $r_{\text{CsF}}$ , i.e., if the potential energy surface (PES) is concave, then this structure would be considered an undissociated structure. For  $r_{\text{CsF}} \geq r_i(\text{CsF})$ , the PES is convex, indicating that the structure of CsF is in the domain of the dissociated structure.

However, for hydrated CsF clusters, one may consider the case that both undissociated and dissociated structures would

be at the minimum energy points with the positive curvature of the PES. Therefore, it is natural to have a barrier between the undissociated structure and the neighboring structure (including a dissociated structure). If  $r_{\text{CsF}} \geq r_i(\text{CsF})$ , it may be considered as a dissociated structure. However, if  $r_i(\text{CsF})$  is between undissociated and dissociated structures, then the structure at  $r_i(\text{CsF})$  is called a half-dissociated structure. The fully dissociated structure would be defined by the case that  $r_i(\text{CsF})$  is close to  $r_d(\text{CsF})$ , which has the maximum negative curvature in the PES of the pure CsF. In the case of pure CsF, the equilibrium distance ( $r_e(\text{CsF})$ ),  $r_i(\text{CsF})$ , and  $r_d(\text{CsF})$  are 2.44, 3.0, and 4.3 Å at the MP2/aVDZ+ level. Although this mathematical expression of PES seems to be convincing, it is not practical to apply it in the presence of solvent as long as the solvent effect is not taken into account. Therefore, it is possible to use a rather general approach to define  $r_i$  and  $r_d$  in terms of  $\Delta r_{\text{CsF}}$  ( $r_{\text{CsF}} - r_e$ ). For example, it would be appropriate to assign a half-dissociated structure as the case where  $\sim 0.6 \text{ Å} < \Delta r_{\text{CsF}} < \sim 1.0 \text{ Å}$  and a (fully) dissociated structure as the case where  $\Delta r_{\text{CsF}} > \sim 1.0 \text{ Å}$ . In certain cases, the validity of this definition could be somewhat ambiguous. In this regard, we use an additional criterion to define the undissociated/dissociated structure by using the Cs–F stretching frequency  $\nu_{\text{CsF}}$ . If the Cs–F stretching characteristic exists, then the structure should be considered undissociated, whereas if not it would be considered dissociated. However, this  $\nu_{\text{CsF}}$  mode is mostly coupled, so it is not clear

**TABLE 2: B3LYP/aVDZ+, MP2/aVDZ+, and CCSD(T)/aVDZ+ Hydration Energies of CsF(H<sub>2</sub>O)<sub>n=1-6</sub><sup>a</sup>**

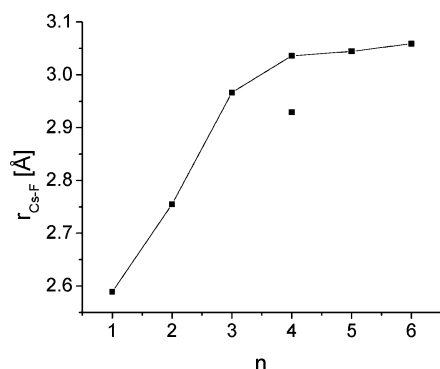
<i>n</i>		B3LYP				MP2				CCSD(T)			
		$-\Delta E_e$	$-\Delta E_0$	$-\Delta H$	$-\Delta G$	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H$	$-\Delta G$	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H$	$-\Delta G$
1	<b>1R3(1s)</b>	18.5 ± 0.3	<b>16.9</b>	17.7	9.7	20.0 ± 1.8	<b>18.3</b>	19.2	10.9	20.1	<b>18.3</b>	19.2	11.0
2	<b>2R33(2s)</b>	35.0 ± 0.6	<b>31.4</b>	32.7	16.3	37.9 ± 3.3	<b>34.0</b>	35.4	18.4	39.5	<b>35.6</b>	37.0	20.0
	2R4(1/1)	32.4 ± 0.3	28.6	30.2	13.1	34.3 ± 2.2	30.7	32.1	16.4				
3	<b>3R333(3s)</b>	49.5 ± 0.8	<b>43.8</b>	45.5	20.0	54.1 ± 4.6	<b>48.0</b>	49.0	24.0	54.2	<b>48.1</b>	50.0	24.0
	3R34(1s1/1)	47.6 ± 0.5	41.8	43.7	18.7	51.0 ± 3.7	45.0	47.0	21.6	50.5	44.5	46.5	21.0
	3R44/4(2/1)	43.7 ± 0.4	38.7	40.6	14.7	48.0 ± 3.0	43.3	45.8	18.6				
	3R5(1/1)	42.9 ± 0.3	37.2	39.3	13.4	46.3 ± 2.5	40.7	42.8	17.0				
4	<b>4R334(2s1/1)</b>	61.1 ± 0.7	<b>53.4</b>	55.5	22.0	66.5 ± 4.7	<b>58.2</b>	60.6	26.4	66.7	<b>58.4</b>	60.9	26.7
	4R44(2/2)	59.8 ± 0.5	51.8	54.9	18.4	64.0 ± 3.3	55.8	58.9	22.5				
	4R335/444(2s1)	59.4 ± 0.6	50.5	53.5	17.1	66.1 ± 4.3	56.8	60.0	22.8	66.2	57.0	60.1	23.0
	4R344/3444(1s2/1)	59.2 ± 0.6	50.7	53.4	17.6	65.9 ± 4.2	57.0	59.9	23.4	66.2	57.4	60.3	23.7
	<b>4R3333(4s)</b>	58.3 ± 0.7	49.8	52.2	15.9	65.8 ± 5.1	57.3	59.7	23.7	66.7	<b>58.2</b>	60.6	24.6
5	<b>5R3335/4444(3s1)</b>	72.9 ± 0.8	<b>61.9</b>	65.3	20.2	81.0 ± 5.4	<b>69.6</b>	73.1	27.6	81.2	<b>69.8</b>	73.4	27.8
	5R344(1s2/2)	72.6 ± 0.7	62.6	65.3	22.8	78.7 ± 4.8	68.3	71.2	28.5	79.0	68.6	71.5	28.8
	5R335(2s1/1)	70.6 ± 0.7	60.7	63.4	21.3								
	5R444/444(3/2)	70.5 ± 0.6	60.2	63.3	18.8	78.4 ± 4.4	67.7	71.0	26.0	78.6	68.0	71.3	26.3
	5R45(2/2)	69.7 ± 0.5	59.6	62.6	20.1								
6	<b>6R444(3/3)</b>	83.7 ± 0.7	<b>71.4</b>	74.7	23.5	90.8 ± 5.1	78.2	81.6	30.4	91.1	78.5	81.9	30.7
	6R3345/444(2s2/1)	83.9 ± 0.8	70.8	74.6	21.3	92.6 ± 5.5	79.2	83.1	29.3	92.9	79.5	83.4	29.6
	6Cube(3/3)	84.0 ± 0.5	69.2	74.2	16.6	92.3 ± 4.9	77.2	82.3	25.2	93.0	77.9	83.0	25.9
	<b>6R3444/444(4/3)</b>	83.0 ± 0.7	69.7	74.2	18.1	93.2 ± 5.5	<b>79.4</b>	83.5	28.4	93.9	<b>80.2</b>	84.3	29.2
	6R3344/3344(2s2/2)	81.0 ± 0.8	67.4	71.2	17.2								
	6R55/55(2/2)	79.8 ± 0.5	66.7	70.7	17.2								
	6R4444/44(4/2)	78.0 ± 0.6	66.6	69.6	18.5								
	6Prism(3/3)	[80.9] <sup>b</sup> ± 0.8				92.2 ± 5.8	77.9	83.4	23.4	93.7	79.4	84.9	24.9

<sup>a</sup> Energies are in kcal mol<sup>-1</sup>.  $-\Delta E_e = (-\Delta E_e^N - \Delta E_e^B/2) \pm (\text{BSSE}/2)$  where  $-\Delta E_e^N$  and  $-\Delta E_e^B$  are the binding energies without and with BSSE correction, respectively. Thus, the lower and upper values are  $-\Delta E_e^N$  and  $-\Delta E_e^B$ , respectively. Hydration energies with ZPE correction are denoted by  $\Delta E_0$ .  $\Delta H$  and  $\Delta G$  are enthalpy and Gibbs free energy at 298 K and 1 atm. CCSD(T) values are the results of single-point calculation on the MP2/aVDZ+ geometry. <sup>b</sup> Single-point calculation on the MP2/aVDZ+ geometry.

**TABLE 3: Selected Structural Parameters for CsF(H<sub>2</sub>O)<sub>n=0-6</sub> (MP2/aVDZ+)<sup>a</sup>**

conformation	uhf	$\delta E_0$	coordination (Cs/F)	$r_{\text{HB}}$	$r_{\text{CsF}}$	$r_{\text{FH}}$	$r_{\text{CsO}}$	$\nu_{\text{CsF}}$	$\nu_{\text{CsO}}$	A	B	C
CsF	U	0			2.443			334		5.09		
1R3	U	0	1/1		2.589	1.493	2.894	233	159	9.21	2.81	2.15
2R33	U	0	2/2	1.683	2.755	1.550	2.918	145	169,158	2.85	2.26	1.40
3R333	H	0	3/3		2.967	1.596	2.941	93*	161,153,153	1.75	1.31	1.31
4R3333	H	0.7 [0.2]	4/4		3.036*	1.682	3.066	93*	142,132,132,107	1.23	1.04	1.04
4R334	U	0 [0.0]	3/4	1.721	2.929	1.616	2.966	111	150,147,143	1.19	1.00	0.82
5R3335	H	0	4/3	1.754 (1.883)	3.045*	1.552	2.991	89*	149,140,101,90	1.09	0.85	0.64
6R3444	H	0 [0]	4/3	1.967 (2.034)	3.059*	1.532	3.026	103*	152,142,130,89	0.94	0.60	0.46
6R3345	U	0.4 [0.7]	4/3	1.743 (1.889)	2.989	1.568	3.006	116	149,140,87,85	0.77	0.69	0.54
6Prism	H	1.5 [0.8]	3/3	2.042	3.216*	1.552	3.044	75*	149,149,144	0.69	0.68	0.68
6R444	U	1.2 [1.7]	3/3	1.745	2.869	1.582	3.009	156	145,144,139	0.60	0.57	0.57
6Cube	F	2.2 [2.3]	3/3	1.910	4.278**	1.530	2.958	25**	235,175,153	0.91	0.48	0.48

<sup>a</sup>  $\delta E$  denotes the relative energy at the MP2/aVDZ+ [CCSD(T)/aVDZ+] level. In "uhf", U, H, and F denote un-, half-, and full-dissociated state, respectively. One asterisk denotes the case  $\sim 0.6 \text{ \AA} < \Delta r_{\text{CsF}} < \sim 1.0 \text{ \AA}$  or  $\sim 50 \text{ cm}^{-1} < \nu_{\text{CsF}} < \sim 100 \text{ cm}^{-1}$ ; this mode couples with the vibration of H<sub>2</sub>O, partly losing the Cs–F stretching character. Two asterisks denote the case  $\Delta r_{\text{CsF}} > \sim 1.0 \text{ \AA}$  or  $\nu_{\text{CsF}} < \sim 50 \text{ cm}^{-1}$ ; this mode strongly couples with the vibration of H<sub>2</sub>O, losing the Cs–F stretching character. A, B, and C are rotational constants in gigahertz.  $r_{\text{HB}}$  is the water–water intermolecular hydrogen bond distance; the short  $r_{\text{HB}}$  and the long  $r_{\text{HB}}$  (in the parentheses) are given.



**Figure 2.** Cs...F distances of the lowest-energy undissociated and half-dissociated conformers (in Å at the MP2/aVDZ+ level). For CsF(H<sub>2</sub>O)<sub>n</sub>, the undissociated and half-dissociated conformers are isoenergetic.

whether it really reflects the Cs–F stretch in the presence of other coupling modes. Thus, if  $\nu_{\text{CsF}}$  is strongly coupled with other vibrational modes, then it can be considered dissociated.

Sometimes, this distinction is clear, while it is often not clear. In general, in the hydrated structure, if  $\nu_{\text{CsF}} < \sim 100 \text{ cm}^{-1}$ , then the Cs–F stretch mode shows a strong coupling with other modes involving water. If  $\nu_{\text{CsF}} < \sim 50 \text{ cm}^{-1}$ , then the Cs–F stretch almost loses its identity due to the presence of other atomic motions. So, if  $\nu_{\text{CsF}} < \sim 100 \text{ cm}^{-1}$ , then it can be considered as partial/half-dissociation, and if  $\nu_{\text{CsF}} < \sim 50 \text{ cm}^{-1}$ , then it can be considered as a full dissociation. Thus, we use all of the above criteria in our further discussion for the distinction between undissociated, half-dissociated, and full-dissociated structures, as demonstrated in Table 3.

According to the above criteria, the global minimum energy structures for  $n = 1$  (1R3) and  $2$  (2R33) are undissociated, while those for  $n = 3$  (3R333),  $4$  (4R334),  $5$  (5R3335), and  $6$  (6R3444) are half-dissociated. For  $n = 4$ , the undissociated structure 4R334 is isoenergetic to the half-dissociated structure 4R3333 (CCSD(T) level). As for the next low-lying energy conformers for  $n = 6$ , 6Prism is half-dissociated (0.8 kcal/mol higher in energy than the global minimum), 6R3345 and 6R444 (0.7 and



**TABLE 4: MP2/aVDZ+ Scaled Frequencies (cm<sup>-1</sup>) for the OH Stretch Modes of CsF(H<sub>2</sub>O)<sub>n=1-6</sub> (Scale Factor 0.96)<sup>a</sup>**

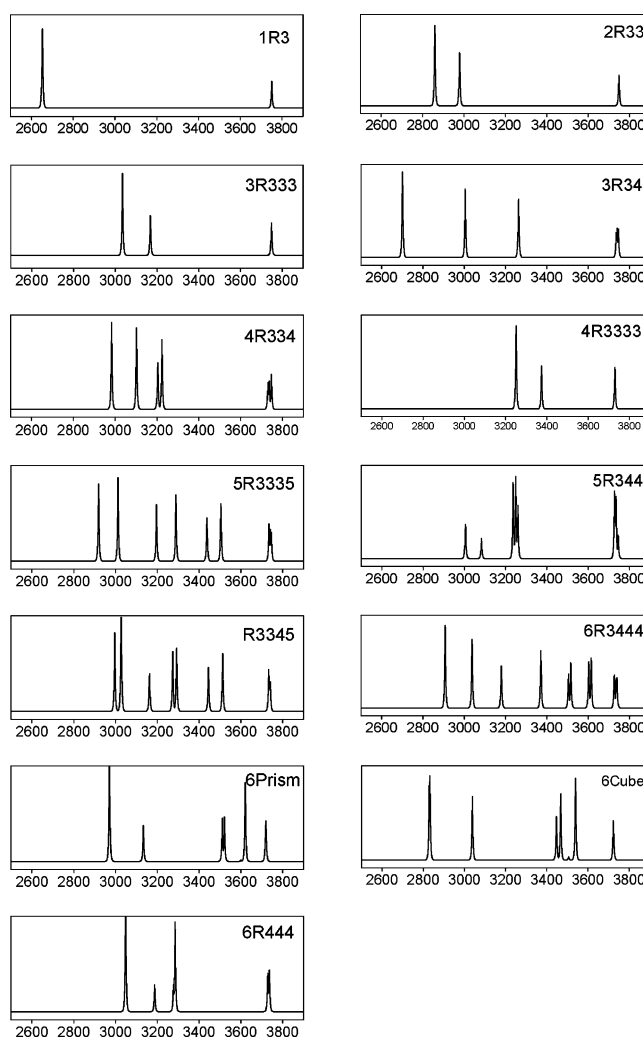
1R3	<u>2652</u> <sub>131</sub> ; <u>3750</u> <sub>4</sub>
2R33	<u>2859</u> <sub>170</sub> ; <u>2978</u> <sub>49</sub> ; <u>3748</u> <sub>7</sub> ; <u>3749</u> <sub>2</sub>
3R333	<u>3035</u> <sub>118</sub> ; <u>3035</u> <sub>118</sub> ; <u>3168</u> <sub>32</sub> ; <u>3749</u> <sub>8</sub> ; <u>3749</u> <sub>8</sub> ; <u>3750</u> <sub>0-6</sub>
4R3333	<u>3249</u> <sub>0</sub> ; <u>3251</u> <sub>103</sub> ; <u>3251</u> <sub>103</sub> ; <u>3374</u> <sub>26</sub> ; <u>3730</u> <sub>14</sub> ; <u>3730</u> <sub>14</sub> ; <u>3730</u> <sub>0</sub> ; <u>3733</u> <sub>0.1</sub>
4R334	<u>2983</u> <sub>156</sub> ; <u>3102</u> <sub>114</sub> ; <u>3204</u> <sub>30</sub> ; <u>3224</u> <sub>75</sub> ; <u>3731</u> <sub>6</sub> ; <u>3737</u> <sub>7</sub> ; <u>3747</u> <sub>9</sub> ; <u>3748</u> <sub>3</sub>
5R3335	<u>2919</u> <sub>101</sub> ; <u>3012</u> <sub>133</sub> ; <u>3196</u> <sub>41</sub> ; <u>3289</u> <sub>74</sub> ; <u>3438</u> <sub>20</sub> ; <u>3504</u> <sub>56</sub> ; <u>3733</u> <sub>10</sub> ; <u>3735</u> <sub>3</sub> ; <u>3741</u> <sub>7</sub> ; <u>3746</u> <sub>5</sub>
6R3444	<u>2908</u> <sub>161</sub> ; <u>3038</u> <sub>107</sub> ; <u>3179</u> <sub>26</sub> ; <u>3371</u> <sub>51</sub> ; <u>3505</u> <sub>11</sub> ; <u>3516</u> <sub>26</sub> ; <u>3603</u> <sub>28</sub> ; <u>3615</u> <sub>43</sub> ; <u>3726</u> <sub>5</sub> ; <u>3727</u> <sub>8</sub> ; <u>3736</u> <sub>6</sub> ; <u>3740</u> <sub>7</sub>
6R3345	<u>2996</u> <sub>96</sub> ; <u>3027</u> <sub>199</sub> ; <u>3163</u> <sub>15.8</sub> ; <u>3274</u> <sub>63</sub> ; <u>3293</u> <sub>81</sub> ; <u>3445</u> <sub>20</sub> ; <u>3513</u> <sub>55</sub> ; <u>3733</u> <sub>5</sub> ; <u>3733</u> <sub>12</sub> ; <u>3735</u> <sub>4</sub> ; <u>3737</u> <sub>6</sub> ; <u>3741</u> <sub>7</sub>
6Prism	<u>2971</u> <sub>129</sub> ; <u>2972</u> <sub>129</sub> ; <u>3133</u> <sub>12</sub> ; <u>3511</u> <sub>10</sub> ; <u>3511</u> <sub>9</sub> ; <u>3521</u> <sub>22</sub> ; <u>3601</u> <sub>0</sub> ; <u>3621</u> <sub>54</sub> ; <u>3621</u> <sub>54</sub> ; <u>3719</u> <sub>7</sub> ; <u>3719</u> <sub>7</sub> ; <u>3721</u> <sub>4</sub>
6R444	<u>3048</u> <sub>174</sub> ; <u>3049</u> <sub>175</sub> ; <u>3187</u> <sub>5</sub> ; <u>3277</u> <sub>3</sub> ; <u>3277</u> <sub>3</sub> ; <u>3285</u> <sub>203</sub> ; <u>3729</u> <sub>7</sub> ; <u>3729</u> <sub>7</sub> ; <u>3731</u> <sub>5</sub> ; <u>3736</u> <sub>5</sub> ; <u>3736</u> <sub>5</sub> ; <u>3736</u> <sub>9</sub>
6Cube	<u>2830</u> <sub>133</sub> ; <u>2832</u> <sub>132</sub> ; <u>3039</u> <sub>85</sub> ; <u>3447</u> <sub>11</sub> ; <u>3447</u> <sub>11</sub> ; <u>3468</u> <sub>66</sub> ; <u>3507</u> <sub>0</sub> ; <u>3540</u> <sub>74</sub> ; <u>3540</u> <sub>74</sub> ; <u>3724</u> <sub>7</sub> ; <u>3724</u> <sub>7</sub> ; <u>3726</u> <sub>2</sub>

<sup>a</sup> With the notations B: bold, U: underline, and I: italics, the frequencies can be classified as follows:  $\nu(\text{BU})$ , AD H<sub>d</sub>'s where O of H<sub>2</sub>O is coordinated to Cs<sup>+</sup> and H to another water molecule;  $\nu(\text{BUI})$ , AD H<sub>d</sub>'s with H of H<sub>2</sub>O coordinated to F and O to another water molecule;  $\nu(\text{BI})$ , AD H<sub>d</sub>'s with a water molecule both coordinated to Cs and F;  $\nu(\text{B})$ , AAD-type H<sub>d</sub>'s,  $\nu(\text{I})$ , symmetric and antisymmetric ADD stretching modes where O is coordinated to Cs<sup>+</sup> and two H atoms are coordinated to another two water molecules;  $\nu(\text{UI})$ , symmetric and antisymmetric ADD stretching modes where O/H are hydrogen-bonded to water molecules only;  $\nu$ , OH stretching mode where O is coordinated to Cs<sup>+</sup> and H to another water molecule;  $\nu(\text{U})$ , OH stretching mode where H is hydrogen-bonded to F. The intensities in 10 km/mol are given in subscripts. <sup>b</sup> Since O of H<sub>2</sub>O is weakly coordinated to Cs<sup>+</sup>, the AAD type has the characteristic of AD-type H<sub>d</sub>'s.

1.7 kcal/mol higher) are undissociated, and 6Cube (2.3 kcal/mol higher) is dissociated.

**B. Vibrational Frequencies.** As the OH stretch frequencies are widely used to identify diverse cluster structures,<sup>32</sup> we report MP2/aVDZ+ vibrational frequencies ( $\nu_s$  with the scale factor of 0.96) for the O...H stretch modes of the lowest-energy undissociated, half-dissociated, and dissociated structures (including isoenergetic conformers) in Table 4 and Figure 3. The scale factor 0.96 at both the B3LYP and the MP2 levels of theory was chosen from the comparison of the experimental and calculated average values of asymmetric and symmetric OH stretching frequencies of the water monomer.<sup>33</sup> When the water molecule of the AD type (A, proton acceptor; D, proton donor) is associated with Cs<sup>+</sup>, the  $\nu_s$  (~3737–3748 cm<sup>-1</sup>) involving a dangling hydrogen atom (H<sub>d</sub>) is in general ~5–10 cm<sup>-1</sup> larger than the  $\nu_s$  associated with F<sup>-</sup>. 6R3444 has both AAD- and AD-type H<sub>d</sub>'s whose frequencies are separated by ~10 cm<sup>-1</sup>. 6Prism and 6Cube have only the AAD-type H<sub>d</sub>'s (~3719–3726 cm<sup>-1</sup>). For hexahydrated CsF clusters, the  $\nu_s$  involving H<sub>d</sub>'s is 3720–3750 cm<sup>-1</sup>. However, ADD-type antisymmetric ( $\nu_{as}$  ≈ 3505–3615 cm<sup>-1</sup>) and symmetric ( $\nu_{as}$  ≈ 3438–3521 cm<sup>-1</sup>) stretching modes are noticeable only for 5R3335, 6R3444, 6Prism, and 6Cube. The hydrogen-bonded O...H stretching modes for which O is coordinated to Cs<sup>+</sup> and H is coordinated to another water molecule have frequencies in the range of ~3224–3294 cm<sup>-1</sup>. Meanwhile, O...H stretching modes interacting with F<sup>-</sup> have a lower range of ~2652–3250 cm<sup>-1</sup>. Among these modes, the case when O is coordinated to Cs<sup>+</sup> has lower frequencies than the case when O is hydrogen-bonded to another water molecule. This spectral information would be useful for future IR experiments to identify the dissociated/undissociated structures of CsF(H<sub>2</sub>O)<sub>n=1-6</sub>, as noted in many previous works on IR spectral studies of diverse clusters.<sup>32,34</sup>

**C. Electronic Properties.** The natural bond orbital (NBO) population analysis (Table 5) shows that the charges of Cs and F of the ion pair are 0.96 and -0.96 a.u., respectively. For the ground state of hydrated CsF clusters, the electron transfers from F<sup>-</sup> of the ion pair moiety to the water moiety, while the charge of Cs hardly transfers ( $q_{\text{Cs}}$  = 0.99 a.u.). The charge of Cs becomes almost neutral ( $q_{\text{Cs}}$  = 0.12 a.u.) in the excited state of CsF, while it is still highly positive for the CTTS state of CsF(H<sub>2</sub>O)<sub>n=1-6</sub> ( $q_{\text{Cs}}$  = 0.79 a.u. for  $n$  = 1, and  $q_{\text{Cs}}$  is close to 1.0 a.u. as  $n$  becomes larger). In the CTTS state, it can be noted that the charge transfers from the salt to the water moiety by ~0.1–0.2 a.u.. For  $n$  = 1–3, the charge transfers (~0.15–0.20 a.u.) mainly from Cs to water, while for  $n$  = 5–6 it (~0.1 a.u.) transfers from F<sup>-</sup> to the water moiety. Table 6 lists the



**Figure 3.** MP2/aVDZ+ IR spectra for the O–H vibrational frequencies (cm<sup>-1</sup>) of the lowest undissociated, half-dissociated, and dissociated CsF(H<sub>2</sub>O)<sub>n=1-6</sub> clusters. Nearly isoenergetic energy conformers are also included.

electronic properties of CsF (H<sub>2</sub>O)<sub>n=0-6</sub>: ionization potential (IP, IP<sub>v</sub>/IP<sub>k</sub>, vertical/Koopman's IP), dipole moment ( $\mu$ ), CTTS energy ( $E_{\text{CTTS}}$ , excited-state energy for  $n$  = 0), and HOMO–LUMO energy gap ( $E_{\text{gap}}$ ). IP of the cluster increases with the increasing number of water molecules due to the stabilization of the ions by hydration. The CTTS energies are related to  $E_{\text{gap}}$ .

**TABLE 5: NBO Charges of the Cs/F/Water Moieties of the Ground and CTTS States of the Lowest-Energy Conformers of CsF(H<sub>2</sub>O)<sub>n=1-6</sub>**

	CsF	1R3	2R33	3R333	4R3333	5R3335	6R3444
S <sub>0</sub>	0.96/−0.96	0.98/−0.88/−0.10	0.99/−0.84/−0.15	0.99/−0.81/−0.18	0.99/−0.82/−0.17	0.99/−0.80/−0.19	0.99/−0.81/−0.18
S <sub>1</sub>	0.12/−0.12	0.79/−0.84/0.05	0.83/−0.87/0.04	0.86/−0.88/0.02	0.94/−0.87/−0.07	0.96/−0.86/−0.10	0.98/−0.88/−0.10
Δq		−0.19/0.04/0.15	−0.16/−0.03/0.19	0.13/−0.07/0.20	−0.05/−0.05/0.10	−0.03/−0.06/0.09	−0.01/−0.07/0.08

<sup>a</sup> NBO charge of water is given in parentheses, Δq = q(S<sub>1</sub>) − q(S<sub>0</sub>) is the change of charge for the Cs/F/water moiety. The third term of Δq (Δq<sub>wat</sub>) is the net charge transferred from the salt to water as the ground state changes to the CTTS state. The S<sub>1</sub> state of the CsF is the excited state (not CTTS).

**TABLE 6: Electronic Properties of CsF(H<sub>2</sub>O)<sub>n=0-6</sub>**

conformation	IP <sub>v</sub>	IP <sub>k</sub>	m	E <sub>CTTS</sub> <sup>RPA</sup>	E <sub>CTTS</sub> <sup>CI(S)</sup>	ΔE <sub>gap</sub>
CsF	9.45	10.97	9.03	4.23	7.55	4.94
1R3	10.92	11.89	7.52	5.17	8.47	5.87
2R33	10.64	12.48	5.86	5.89	8.68	6.56
3R333	11.46	12.84	4.36	6.44	8.77	7.13
4R3333	11.04	12.97	4.41	6.51	8.95	7.21
4R334	11.49	12.90	3.90	6.54	8.80	7.22
5R3335	11.65	13.07	2.78	6.66	8.83	7.40
6R3444	12.02	13.13	3.71	6.56	8.99	7.16
6R3345	11.69	13.13	2.42	6.74	8.92	7.50
6Prism	12.06	13.21	0.18	6.76	9.18	7.48
6R444	11.26	13.09	1.32	6.77	8.94	7.48
6Cube	11.70	12.97	4.11	6.56	9.15	7.24

It is expected that E<sub>CTTS</sub><sup>RPA</sup> at the RPA-B3LYP level is slightly underestimated with respect to the experimental values, while E<sub>CTTS</sub><sup>CI(S)</sup> at the CI(S) level is overestimated, as noted in a number of previous works.<sup>23</sup>

**D. Thermal and Dynamic Effects.** Table 7 shows the changes in structure and energy for four important conformers of CsF(H<sub>2</sub>O)<sub>6</sub>, i.e., 6R3444, 6R3345, 6R444, and 6Cube, using ADMP AIMD simulations. The 6Prism calculation is taken into account in the case of 6Cube because 6Prism converges into 6Cube at the B3LYP level. Since AIMD simulations require a lot of computing time, we used a moderate basis set (6-31+G\*\*), which is slightly smaller than the aVDZ+ basis set. Overall the B3LYP/6-31+G\*\* results are consistent with the B3LYP/aVDZ+ results. Although the B3LYP results are not the same as the CCSD(T) results, we can analyze the thermal effect using the B3LYP AIMD simulations. By adding this thermal energy contribution to the accurate CCSD(T) energies at 0 K, we may obtain more reliable energetics. This is possible because even though the absolute energies of the minimum energy structures are slightly different from the CCSD(T)/aVDZ+ results in terms of global PES the temperature effect of each conformer can be reasonably obtained from B3LYP AIMD simulations in that the local PES of a conformer at the

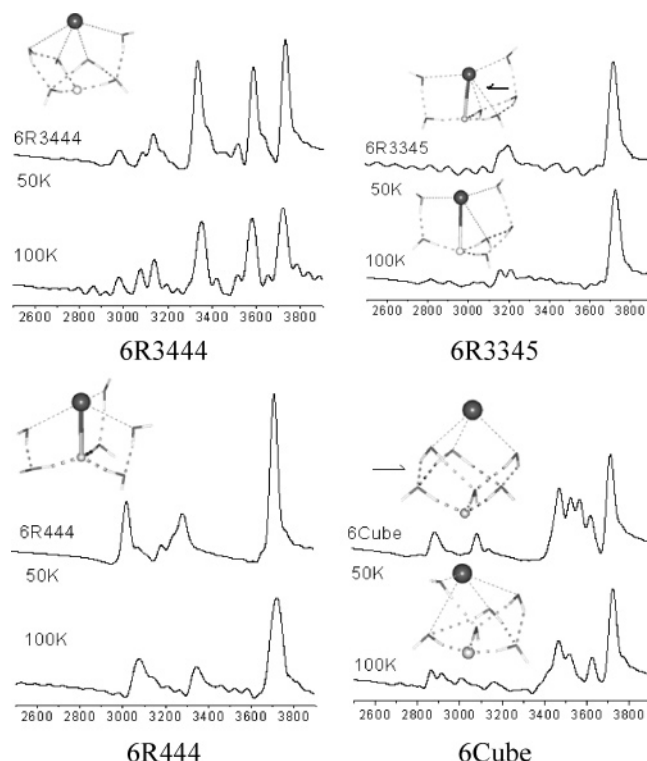
B3LYP level would not be significantly different from that at the CCSD(T) level.

In 50 K AIMD simulations, one conformer does not change to another, because of the significant barriers between different conformers. At 100 K, it also shows a similar trend except in the cases of 6R3345 and 6Cube. In 6R3345 the coordination between Cs<sup>+</sup> and one water molecule (marked by an arrow in Figure 4) was broken, and so Cs<sup>+</sup> became tri-coordinated. Whereas in 6Cube one of the hydrogen bonds between water molecules (marked by an arrow in Figure 4) was broken, the water molecules that were initially coordinated to F<sup>−</sup> became coordinated to Cs<sup>+</sup>. For 6R3444 and 6R444, though the original structures remain almost the same for 2.5 ps simulations (Figure 4), the most dramatic structural change occurs in the case of 6R3444 where r<sub>CsF</sub> increases by 0.45 and 0.63 Å at 50 and 100 K, respectively. Thus, with the small rise in temperature, the half-dissociated form of 6R3444 changes to a dissociated form. Meanwhile, the two undissociated forms of 6R3345 and 6R444 remain as an undissociated form even at 100 K. However, 6Cube remains in a dissociated form (r<sub>CsF</sub> = 4.68 and 3.75 Å at 50 and 100 K, respectively). However, as one of the hydrogen bonds between the two water molecules is broken at 100 K, r<sub>CsF</sub> decreases from 4.68 Å at 50 K to 3.75 Å at 100 K. In the meantime, r<sub>HF</sub> is almost constant with rising temperature, and r<sub>CsO</sub> tends to slightly increase with rising temperature. When we compare the relative energy change of each conformer depending on the temperature change, the energy increase for the (half-)dissociated conformer tends to be less than those of the undissociated conformers. This is partly expected because more dissociated structures that have more degrees of configurational freedom would have more configurational entropy than the undissociated structures (Table 7). By combining this thermal energy with the MP2 counterpoise and ZPE corrected CCSD(T)/aVDZ+ energy at 0 K, we note that the half-dissociated structure (6R3444) is the most stable at 0 K, but this structure changes to the dissociated structure above 50 K. Energetically,

**TABLE 7: Hydration Energies, Geometries, and IR Frequencies of Selected CsF(H<sub>2</sub>O)<sub>6</sub> Conformers at 50 and 100 K<sup>a</sup>**

	ΔE (kcal/mol) (ΔE)			r <sub>CsF</sub> (Å) (Δr <sub>CsF</sub> )			r <sub>HF</sub> (Å) (Δr <sub>HF</sub> )			r <sub>CsO</sub> (Å) (Δr <sub>CsO</sub> )			ν <sub>OH</sub> (50K)
	0 K	50 K	100 K	0 K	50 K	100 K	0 K	50 K	100 K	0 K	50 K	100 K	
6R3444	−92.7 (0.0) [−80.2]	−89.8 (2.9) [−77.3]	−86.5 (6.2) [−74.0]	3.43 (0.0) (0.45)	3.91 ± 0.38 (0.45)	4.19(0.27) (0.63)	1.56 (0.00) (−0.04)	1.52 (−0.04)	1.52 (−0.04)	3.11 (0.00)	3.12 (0.01)	3.14 (0.03)	2990, 3090, 3140, 3335, 3519, 3586, 3730
6R3345	−93.9 (0.0) [−79.5]	−91.1 (2.8) [−76.7]	−86.2 (7.7) [−71.8]	3.05 (0.0) (0.02)	3.07 ± 0.17 (0.02)	3.42(0.33) (0.37)	1.57 (0.00) (0.01)	1.58 (0.01)	1.54 (−0.03)	3.18 (0.00)	3.32 (0.14)	2.92 (−0.09)	3010, 3090, 3213, 3312, 3460, 3553, 3733
6R444	−93.2 (0.0) [−78.5]	−90.1 (3.1) [−75.4]	−84.8 (8.4) [−70.1]	2.94 (0.0) (0.02)	2.96 ± 0.04 (0.02)	2.95(0.05) (0.01)	1.59 (0.00) (−0.02)	1.57 (−0.02)	1.57 (−0.02)	3.06 (−0.00)	3.04 (−0.02)	3.10 (0.04)	3042, 3094, 3211, 3302, 3728
6Cube	−94.4 (0.0) [−77.9]	−90.8 (3.6) [−74.3]	−86.6 (7.8) [−70.1]	4.89 (0.0) (−0.21)	4.68 ± 0.32 (−0.21)	3.75(0.37) (−1.14)	1.53 (0.00) (0.01)	1.53 (0.00)	1.54 (0.01)	2.96 (0.00)	3.00 (0.04)	3.08 (0.12)	2900, 3096, 3485, 3538, 3580, 3724

<sup>a</sup> Absolute/relative (change) values are in the first/second lines. The CCSD(T) energies (with counterpoise and zero-point energy correction) with the thermal energies from the AIMD simulations (B3LYP/6-31+G\*\* ADMP) are given in brackets. Frequencies calculated by MD simulations at 50 and 100 K (in which the anharmonicity is already well taken into account) are scaled by the scale factor of 0.98, while those calculated by the harmonic frequency analysis of the DFT calculations are scaled by 0.96. The average deviation of r<sub>CsF</sub> is given as well.



**Figure 4.** ADMP AIMD structures (significant configuration) and power spectra for the O-H vibrational frequencies (cm<sup>-1</sup>) of the four important conformers of CsF(H<sub>2</sub>O)<sub>6</sub> (6R3344, 6R3445, 6R444, and 6Cube).

6R3444 is  $\sim 2\text{--}4$  kcal/mol more stable than other conformers at 50 and 100 K.

We have calculated the power spectra of the clusters at different temperatures by performing Fourier transformation (FT) on the velocity autocorrelation function. The power spectra of the OH stretch peaks for each conformer at 100 K are shown in Figure 4. The sharp peaks at 0 K generally broaden with increasing temperature due to the dynamical changes of the structure. However, the most characteristic peaks corresponding to the AD/AAD H<sub>d</sub>'s remain strong, though the Cs<sup>+</sup>-AD and F<sup>-</sup>-AD H<sub>d</sub> peaks tend to merge into one with increasing temperature.

#### IV. Conclusion

We have studied the hydration and dissociation phenomena of CsF using the density functional theory (DFT), Møller-Plesset second-order perturbation theory (MP2), coupled cluster theory with singles, doubles, and perturbative triples excitations (CCSD(T)), and ab initio molecular dynamic (AIMD) simulations. The half-dissociated phenomena start to appear from the trihydrated cluster. The dissociated structure begins to appear from the hexahydrated cluster. By combining the thermal energies from the AIMD simulations with the accurate CCSD(T)/aVDZ+ energies at 0 K, we obtain more reliable energy values. The most stable half-dissociated conformer of CsF(H<sub>2</sub>O)<sub>6</sub> changes to a dissociated form at 50 and 100 K during the simulations. This conformational change depending on temperature can be expected by the trend that the more dissociated conformer tends to have more configurational entropy. The thermal and dynamic effects broaden the sharp peak corresponding to both Cs<sup>+</sup>-AD- and F<sup>-</sup>-AD-type H<sub>d</sub>'s. Although the Cs<sup>+</sup>-AD and F<sup>-</sup>-AD H<sub>d</sub> peaks tend to merge into one with the increasing temperature, the most characteristic peaks corresponding to the AD H<sub>d</sub>'s remain strong. We hope that this

information would facilitate future experiments for the dissociation phenomenon of CsF.

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#### References and Notes

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