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What is the Minimum Number of Water Molecules Required to Dissolve a Potassium Chloride Molecule?

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Abstract: This work answers an unsolved question that consists of determining the least number of water molecules necessary to separate a potassium chloride molecule. The answer based on accurate quantum chemical calculations suggests that tetramers are the smallest clusters necessary to dissociate KCl molecules. The study was made with Møller-Plesset second-order perturbation theory modified with the cluster theory having single, double, and perturbative triple excitations. With this extensive study, the dissociation of KCl molecule in different water clusters was evaluated. The calculated results show that four water molecules stabilize a solvent separated K^+/Cl^- ion-pair in prismatic structure and with six water molecules further dissociation was observed. Attenuated total reflection infrared spectroscopy of KCl dissolved in water establishes that clusters are made of closely bound ions with a mean of five water molecules per ion-pair $[K^+(H_2O)_5Cl^-]$. (Max and Chapados, Appl Spectrosc 1999, 53, 1601; Max and Chapados, J Chem Phys 2001, 115, 2664.) The calculated results tend to support that five water molecules leads toward the formation of contact ion-pair. The structures, energies, and infrared spectra of KCl molecules in different water clusters are also discussed.

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Key words: potassium chloride; water clusters; ion-pair; a*b initio* calculation; IR frequencies

Introduction

The theoretical analysis of effects of solvent on chemical phenomena has fostered considerable interest recently, because solvation plays an important role in the vast majority of chemical processes. Alkali halides solvation is important in solution chemistry[1–16] and poses a problem of fundamental importance in which the electronic and molecular structure of an electrolyte is modified by placing it in contact with a polar solvent like water. Although it is clear that such a polar salt dissociates into solvated ions in aqueous solution, it is not clear how the system progresses from a polar gas molecule to dissociated ions as solvent molecules are added. Studies on the progression from gas phase to solvent-separated ion-pairs of sodium chloride and cesium fluoride show that a cluster of six water molecules are necessary to dissociate such alkali halides.[17,18] However, related studies involving the solvation phenomena of one of the important alkali halides, i.e., potassium chloride are scarce in the literature. Potassium chloride has a range of applications: it is very useful in fertilizers and occurs naturally as sylvite.[19,20] It is also used in medicines, food processing and as a lethal weapon in judicial execution.[19–21] Potassium chloride can act as a source of chloride ion. KCl is sometimes used in water as a completion fluid in petroleum and natural gas operations, and being an alternative to sodium chloride in household water softener units. KCl is also used as salt substitute, and it is commonly mixed with common salt NaCl to improve the taste.

It can be deduced from the saturation concentration that on an average, 15 water molecules are necessary to separate KCl. The question whether this number really represents the smallest water cluster capable of dissolving a KCl molecule has baffled researchers for a long time. Any information regarding the association of a KCl molecule with water molecules is available from attenuated total reflection (ATR) absorbance spectral studies.[22,23] These studies have shown that pure KCl-solvated water exists as two close-bound ions (cation and anion), with a mean of five molecules of water forming a cluster: $[K^+(H_2O)_5Cl^-]$. ATR studies also determined that sodium chloride in water behaves in the same manner, forming a cluster containing a mean of five molecules of water: $[Na^+(H_2O)_5Cl^-]$.[22,23] However, the geometrical arrangement of molecules in the cluster cannot be determined from the Infra Red measurements.

Recently, the specific arrangement of water clusters required to dissociate sodium chloride and cesium fluoride was investigated using accurate quantum chemical methods.[17,18] For NaCl, a water hexamer in prismatic form was predicted to solvate the ion-pairs, whereas a cubic structure was observed for the dissociation of CsF molecule.[18] From the simulations in liquid water and the studies performed, it is known that a solvent separated pair for alkali halides corresponds to a distance of approximately 5.0 Å.[24] The solvent separated ion-pair distance was found to be 4.4 Å for NaCl and 4.3 Å for CsF with a six water cluster using quantum chemical methods. In contrast to the bulk solutions, in clusters containing one salt molecule, the ions are always paired in the sense that both cations and anions are confined in a finite cluster environment. However, we may distinguish between a half-dissociated contact ion-pair and a fully dissociated solvent separated pair if a potential barrier exists as a function of the inter ionic distance, wherein the ions closer than the barrier distance are considered as contact ion-pair. The elaborate discussion on half-dissociated (contact ion-pair) and fully dissociated (solvent separated pair) forms are given below.

We are interested in investigating the minimum water cluster required to dissociate the potassium chloride molecule, i.e., the dissolution phenomena of KCl by water molecules. In this article, we have reported a systematic study of the effects of adding water molecules (up to six water molecules) on the molecular and electronic properties of KCl. The findings of this study not only answer the question concerning the onset of ionic solvation, but are also directly relevant to studies of reactivity of atmospheric sea-salt microparticles where hydrates have been reported to have key roles.[25–27] This study involves the progressive dissolution process for KCl and is not intended to be relevant for the oligomeric form of this salt.

We have examined the structures, energetics, and spectral properties of KCl with clusters of water molecules using the second-order Møller-Plesset (MP2) perturbation method with Pople's 6-31G basis set augmented by a standard polarization set on heavy atoms and by a standard diffuse set on Chloride to correctly describe the anion. Similar methods have been successfully applied to predict the description of sodium chloride-water clusters.[17,28] With the same basis set, energies of the stationary points have been calculated at the coupled cluster level with single and double and perturbative triple excitations (CCSD(T)). The separation of ions in clusters is more compact compared with the bulk environment; therefore, in the absence of the condensed phase, the ions are only partially surrounded by water molecules and the intermolecular geometry can differ from that of the bulk.

Computational Details

We have examined various equilibrium geometries of the dissociated and undissociated clusters-KCl(H_2O)$_{n = 1-6}$, with different n (n = number of water molecules) in the cluster. Calculations were performed at the MP2[29] and the CCSD(T)[30,31] level of theory. We used Pople's 6-31G basis set[32] for oxygen, potassium, chlorine, and hydrogen with augmented standard polarization set for heavy atoms. A standard diffuse set on chloride was

**Table 1.** Calculated and Experimental Structural Parameters for H_2O and KCl.

	Properties	MP2/ (6-31 + $_{Cl}$G*)	CCSD(T)/ (6-31 + $_{Cl}$G*)	Experiment
H_2O	r(OH)/Å	0.968	0.970	0.957[35]
	∠HOH	103.989	103.897	104.5[35]
	v_{symm} (scaled)	3718	3579	3657[35,36]
	$v_{antisymm}$ (scaled)	3889	3703	3756[35,36]
KCl	r_e/Å	2.885	2.85	2.66[37–39]
	v_e/cm^{-1}	272.01	262.58	281[37–39]

incorporated to correctly describe the anion in both the MP2 perturbation method and CCSD(T) levels of theory. The geometries were optimized with the MP2 level of theory, and a harmonic frequency analysis has been performed for stationary points to confirm minima and saddle points at the same level of theory. CCSD(T) results were obtained from single point calculations on the optimized geometries at the MP2 level. The zero-point uncorrected energies (ΔE_e) and corrected (ΔE_o) internal energies have been reported in conjunction with the enthalpies (ΔH_{298}) and Gibbs free energies (ΔG_{298}) at 298 K. For CCSD(T) energies, zero-point and thermal energy corrections were done with MP2/6-31+$_{Cl}$G* values. We have used CCSD(T) energies for comparison, which are generally known to be most realistic and the MP2 optimized geometries, unless otherwise stated. The vibrational frequencies are scaled using the scale factor 0.96 in the present discussion.[33] All calculations were carried out using the Gaussian 03 suite of programs.[34]

Results and Discussion

Structures and Energetics

The geometrical parameters of KCl and H_2O are given in Table 1. The calculated structural parameters at the MP2/6-31+$_{Cl}$G* and CCSD(T)/6-31+$_{Cl}$G* levels are in good agreement with each other and agree well with the experimental values. Figure 1 shows various low-lying structures of KCl(H_2O)$_{n=1-6}$ clusters. The hydration energies calculated at the MP2/6-31+$_{Cl}$G* and CCSD(T)/6-31+$_{Cl}$G* for KCl(H_2O)$_{n=1-6}$ clusters are given in Table 2. The selected bond distances for KCl(H_2O)$_{n=1-6}$ clusters obtained at the MP2/6-31+$_{Cl}$G* are given in Figure 1. The calculated results show that the K⋯Cl distance of global minimum structures increases monotonically toward 3.0–3.5 Å as the cluster size increases from n = 2 to 6 (Fig. 2). The KCl water cluster with n = 4 showed an increase in K⋯Cl distance of ∼3.5 Å, and an even larger separation of ions was observed for **4d** (prismatic structure), i.e., 4.40 Å (Fig. 1). However, for n = 5, the K⋯Cl distance is elongated only up to ∼3.7 Å. The structure of **6a** (cube) involves separation of ions to K$^+$(H_2O)$_3$ (C_{3v}) and Cl$^-$(H_2O)$_3$ (C_{3v}). The distance between K$^+$/Cl$^-$ was found to be 4.97 Å. The hydration energies calculated for these KCl(H_2O)$_{n=1-6}$ clusters show that the hydration is more exothermic with increasing number of water molecules (Table 2). Additional calculations were performed to examine the stability of
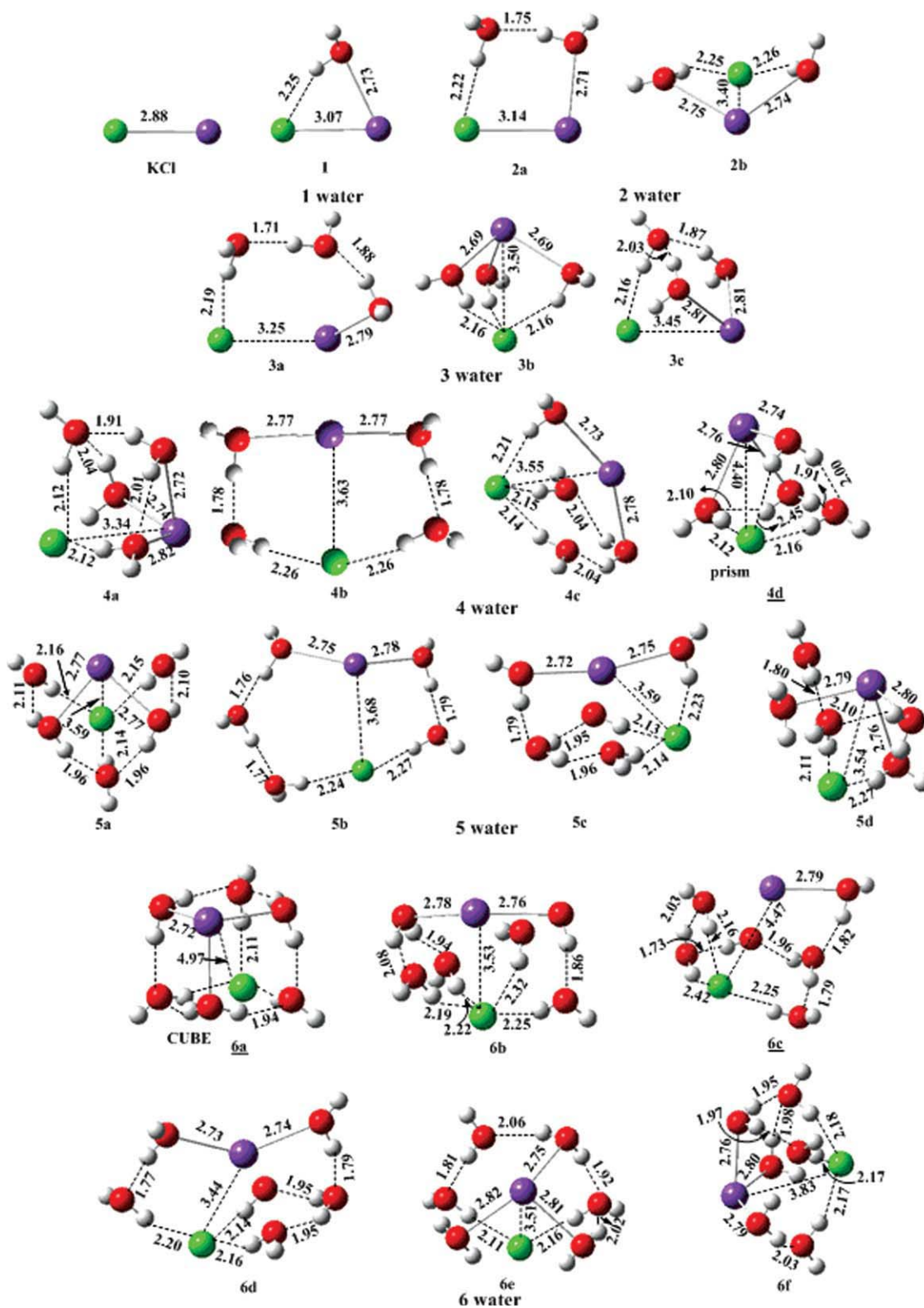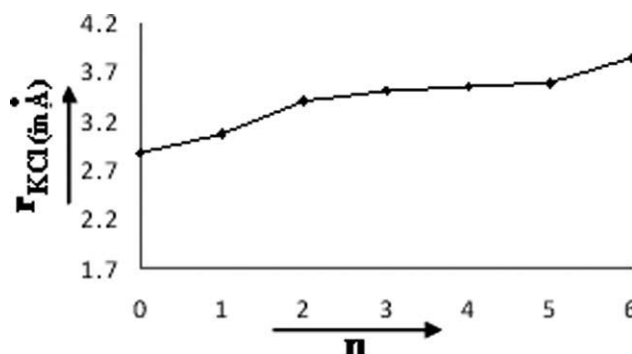
Figure 1. MP2/6-31+$_{Cl}$G* optimized geometries and important distances for various conformers of KCl(H$_2$O)$_{n=0-6}$ [potassium : purple; chlorine : green; oxygen : red; hydrogen : white]. The dissociated structures are underlined.

Table 2. MP2/6-31+$_{Cl}$G* and CCSD(T)/6-31+$_{Cl}$G* Calculated Hydration Energies (kJ/mol) of Various Conformer of KCl(H$_2$O)$_{n=1-6}$.

KCl(H$_2$O)$_{n\ =\ 1-6}$	MP2			CCSD(T)
N	$-\Delta E_0$	$-\Delta H$	$-\Delta G$	$-\Delta E_0$
1	67.8	61.5	31.0	62.8
2a	123.1	110.1	42.7	113.8
2b	131.8	121.0	52.7	122.6
3a	174.5	154.5	50.2	158.2
3b	170.8	181.2	73.7	184.6
3c	185.4	164.5	55.2	169.5
4a	257.4	231.1	75.7	236.5
4b	229.4	202.2	66.1	205.9
4c	262.4	239.0	89.6	241.9
4d	243.2	218.9	56.5	221.8
5a	324.4	291.7	97.1	298.0
5b	267.9	233.6	62.8	242.8
5c	322.7	291.7	105.1	295.9
5d	315.2	283.8	93.3	289.7
6a	378.4	336.1	97.1	344.5
6b	370.4	331.1	99.6	339.5
6c	333.6	283.8	52.7	299.7
6d	372.9	333.6	110.5	340.7
6e	372.9	333.6	99.6	341.6
6f	382.6	341.6	107.6	344.5

Figure 2. CCSD(T)/6-31+$_{Cl}$G* calculated K$\cdots$Cl distances of the lowest-energy undissociated and half-dissociated conformers.

in their stable conformations. The intermolecular hydrogen bond distance is 1.75 Å for **2a** and 2.04 Å for the stable cluster **4c**. The hydrogen bonding distance increases further to 2.11 Å in **5a**, however, in **6a** it is relatively short (1.94 Å). The calculations show that K$\cdots$O distance is marginally varied between 2.7 and 2.8 Å irrespective of the size of the cluster. The Cl$\cdots$H distance varies between 2.11 Å and 2.26 Å in clusters $n = 1$ to 6, which suggests that these interactions are strong in nature.

The stretching modes of vibration observed for the K$\cdots$Cl and K$\cdots$O bonds are shown in Table 3. For gaseous KCl, the frequency of the stretch mode v_{KCl} is 272 cm^{-1}. In the case of KCl(H$_2$O)$_{n=1-6}$ clusters, the v_{KCl} of the global minimum energy conformers for $n = 2$ to 6 are less than ~100 cm^{-1}, except in the case of the structures **1**, **2a**, and **4b** (Fig. 1). For the clusters, **4d** (prism) and **6a** (cube), v_{KCl} is less than ~50 cm^{-1} and is strongly coupled with other vibrational modes, hence the K—Cl stretching characteristic disappears.

In the dissociation of KCl by water molecules, it is useful to define the dissociated structure of this alkali halide. In contrast

the ions separated in the cluster **6a**: KCl(H$_2$O)$_6$ (cube) by allowing it to interact with a separate cluster of four water molecules at the MP2/6-31+$_{Cl}$G* level. The cubic structure **6a** was found to be intact, however, the K$\cdots$Cl distance shortened by ~0.2 Å.

Table 3 gives the water–water intermolecular bond distances (O$\cdots$H) for the KCl(H$_2$O)$_{n\ =\ 1-6}$ cluster. In general, the O$\cdots$H distance increases with the size of the cluster from $n = 2$ to $n = 4$. However, for $n = 2$ and 3, there are no water–water interactions

Table 3. Selected Structural Parameters for KCl(H$_2$O)$_{n=0-6}$ Calculated at (MP2/6-31+$_{Cl}$G*) Level of Theory.

Conformation	UHF	∂E_0 in kJ/mol[a]	Coordination (K/Cl), n = H$_2$O[b]	r_{KCl} (Å)	r_{K-O} (Å)	$r_{H-bonding}$ (Å)	v_{KCl} (cm^{-1})	v_{KO} (cm^{-1})
KCl	U	0.0 [0.0]	–	2.885	–	–	272.0	–
1	U	0.0 [0.0]	1/1	3.072	2.73	–	294.0	294.0
2a	U	7.1 [7.1]	1/1	3.138	2.71	1.76	278.7	223.1
2b	H	0.0 [0.0]	2/2	3.403	2.75, 2.74	–	98.9	205.4, 229.1
3b	H	0.0 [0.0]	3/3	3.505	2.70	–	53.3	193.5, 193.8, 204.7
4b	H	32.6 [32.2]	2/2	3.627	2.77	1.78	111.3	174.7, 223.6
4c	H	0.0 [0.0]	2/3	3.554	2.78	2.04	52.2	223.5, 240.0
4d	F	9.2 [10.0]	3/2	4.404	2.74, 2.76, 2.80	1.91, 2.00, 2.10	34.2	186.9, 227.9, 239.9
5a	H	0.0 [0.0]	2/3	3.599	2.77, 2.87	1.96, 2.10	62.6	209.4, 221.9
6a	F	0.0 [1.7]	3/3	4.968	2.72	1.94	47.8	221.3, 221.4, 228.1
6e	H	11.7 [10.0]	3/2	3.513	2.78, 2.81, 2.82	1.81, 2.10, 2.00, 1.92	72.1	182.2, 188.8, 210.5
6f	H	1.3 [0.0]	3/3	3.838	2.76, 2.79, 2.80	1.95, 1.97, 1.99, 2.03	77.6	202.7, 210.1, 223.0

[a]∂E_0 denotes the relative energy at the MP2/6-31+$_{Cl}$G* [CCSD(T)/6-31+$_{Cl}$G*] level. In "UHF," U, H, and F denote un-, half-, and full-dissociated state, respectively.
[b]Coordination (K/Cl) denotes the number of H$_2$O molecules coordinated with K$^+$ and Cl$^-$, where n is the number of H$_2$O molecules coordinated with K$^+$ and Cl$^-$.

to the bulk solution, in a cluster containing one salt molecule the ions are always paired in the sense that they are confined to a finite cluster environment. However, it may still be possible to distinguish between a "paired" and an "unpaired" state if a potential barrier exists as a function of the inter ionic distance, so that ions closer than the barrier distance are considered paired. Therefore, a dissociated or unpaired structure (at a minimum) is separated from the undissociated or paired structure (at a minimum) with a barrier between the two minima, which could be considered as a sufficient condition for the existence of a dissociated structure.[17,40]

An alternative approach was described to define the undissociated, half-dissociated, and dissociated structures based on the relative difference of distances from equilibrium gaseous alkali halide distance.[18] By definition, the half-dissociated or contact ion-pair for Na^+/Cl^- occurs at an inter ionic distance of ~ 2.8 Å, which is approximately the van der Waals contact distance for Na^+ and Cl^- ions.[24] Hence, the half-dissociated or contact ion-pair can be described as the situation where the inter ionic distance of ions is larger than ~ 0.5 Å compared with the gaseous state. For a fully dissociated state, the inter ionic distance should be larger than ~ 1.0 Å compared with the gaseous state. Therefore, it would be appropriate to assign a half-dissociated structure for KCl, where the inter ionic distance of K^+/Cl^- is larger than ~ 0.5 Å and smaller than ~ 1.0 Å from the gaseous KCl distances, whereas, a fully dissociated structure as the case where it is larger than ~ 1.0 Å.

In certain cases, the validity of this definition could be somewhat ambiguous. In this situation, additional criterion can be applied to define the undissociated/dissociated structure by using K—Cl stretching frequency (v_{KCl}). If the K—Cl stretching characteristic exists, then the structure should be considered undissociated, whereas if it is not observed it would be considered dissociated. However, this v_{KCl} mode is mostly coupled, so it is not clear whether it really reflects the K—Cl stretch in the presence of other coupling modes. Thus, if v_{KCl} is strongly coupled with other vibrational modes, then it can be considered dissociated. In general, in the hydrated structure, if $v_{KCl} < \sim 100$ cm^{-1}, then the K—Cl stretch mode shows a strong coupling with other modes involving water. If $v_{KCl} < 50$ cm^{-1}, then the K—Cl stretch almost loses its identity because of the presence of other atomic motions. So, if $v_{KCl} < \sim 100$ cm^{-1}, then it can be considered as partial/half-dissociation, and if $v_{KCl} < 50$ cm^{-1}, then it can be considered as a full dissociation. Thus, we use these criteria for the distinction between undissociated, half-dissociated, and fully dissociated structures, as shown in Table 3. According to the aforementioned criteria based on the relative distance of KCl molecule with water clusters and their associated stretching frequencies, the global energy structures for $n = 1$ (**1**) and 2 (**2a** & **2b**) are undissociated, whereas for $n = 3$ (**3b**), 4 (**4c**), 5 (**5a**) and 6 (**6e**), (**6f**) are half-dissociated structures at MP2 level (Table 3).

For $n = 4$, the next low lying conformer (**4d**) is fully dissociated, which is higher in energy by 9.2 kJ/mol at MP2 level and 10.0 kJ/mol at CCSD(T) level than the global minimum half-dissociated structure (**4c**). In the case of $n = 6$, the fully dissociated structure (**6a**) cube is relatively comparable in energy to the global minimum half-dissociated structure (**6f**) (Table 3).

Table 4. MP2/6-31+$_{Cl}$G* Scaled Frequencies (cm^{-1}) for the OH stretch modes of KCl(H$_2$O)$_{n=1-6}$ (Scale Factor 0.96).[33]

Conformers	O—H stretching frequencies
1	<u>3407</u>, *3697*
2a	**3294**, *3679, 3700*
2b	<u>3408</u>(a), <u>3499</u>(s), *3693*(a), *3700*(s)
3b	<u>3280</u>(a), <u>3282</u>(a), <u>3503</u>(s), *3685*(a), *3685*(a), *3688*(s)
4b	**3333**(a), **3395**(s), *3683*(a), *3699*(a), *3700*(a)
4c	**3525**(s), **3621**(a), *3681*(a), *3682*(s), *3694*(a)
4d	<u>3298</u>, **3475**, **3489**, *3669*(s), *3683*(s)
5a	**3490**(a), **3510**(s), **3620**, **3628**(a), *3678*(a), *3685*(a), *3686*(s)
6a	**3469**(a), **3470**(a), **3489**(s), **3541**(a), **3572**, **3572**, *3672*(a), *3672*(a), *3674*(s)
6c	**3231**, **3334**, **3430**, <u>3452</u>, *3678, 3690, 3702*(a), *3709*(s)
6f	**3494**(a), **3508**(s), **3526**(s), **3587**(a), **3615**(a), *3678*(a), *3832*(a), *3680*(s)

With the notations B: bold, U: underline, and I: italics the frequencies can be classified as follows: v[**B**]: O—H stretching where oxygen is interacting with K^+ and the hydrogen interacting with other water molecules; v[<u>U</u>]: O—H hydrogen is interacting with Cl^-. v[*I*]: O—H stretching modes not interacting with K^+, Cl^-, and H_2O molecules. a: antisymmetric stretching; s: symmetric stretching.

Another cluster formed with $n = 6$, i.e., the **6c** structure, can also be said to be a solvent separated form of KCl molecule. The distance between K^+/Cl^- was found to be 4.47 Å (Fig. 1). However, this structure is much higher in energy (41.4 kJ/mol) than the global minimum structure **6f** at CCSD(T) level of theory. Furthermore, the dissociated and half-dissociated structures with six water cluster were found to be separated by a saddle point with an inter ionic distance of 4.33 Å. The saddle point is 2.9 kJ/mol higher than the half-dissociated structure **6f** at CCSD(T) level. The water molecules in the distorted **6f** cubic structure arranges to a more ordered cubic form in the transition state, which eventually leads to the **6a** cubic structure. However, in the case of four water clusters, the saddle point was not observed between the half-dissociated **4c** and fully-dissociated structure **4d**. This study of solvation of a KCl molecule and the solvation studies performed with NaCl and CsF indicates that even numbers of water molecules can have a larger impact on separation of a salt molecule than that of odd water clusters.[17,18]

The ATR absorbance spectrum of potassium chloride has been reported.[22,23] The KCl molecule dissociates in water to form two nonabsorbing ions: K^+/Cl^-. The spectrum obtained is the absorption of two entities: pure water and water strongly associated to the K^+/Cl^- pair.[22,23] The observation of water associated KCl indicates that the water molecules form clusters made up of a pair of closely bound ions and a mean of five molecules of water: $[K^+(H_2O)_5Cl^-]$.[22,23,41] In the absence of any information regarding the geometrical arrangement of $[K^+(H_2O)_5Cl^-]$ from ATR studies, a direct comparison cannot be made with the calculated results. The calculated water clusters of KCl(H$_2$O)$_{n=1-6}$ also demonstrated that five water molecules associate with the pair of K^+/Cl^- and the ions are not sufficiently apart to fulfill the criteria of fully dissociated
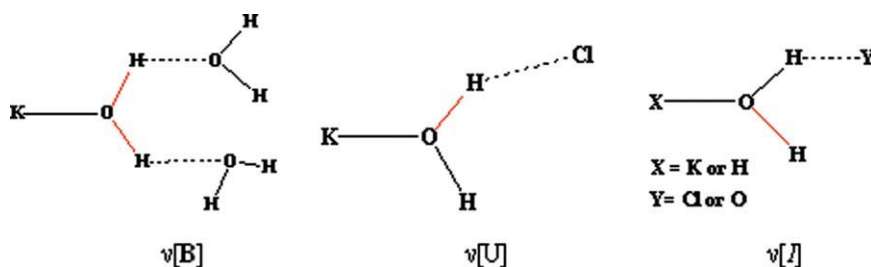
Figure 3. Different O-H stretching frequencies of water molecules are shown in red.

KCl molecule, which is in qualitative agreement with the observed ATR experiments. The small second-order effect that appears in the ATR studies indicate that some minor interaction exists between the $[K^+(H_2O)_5Cl^-]$ clusters and the surrounding water molecules. It has been suggested that the band because of a second-order effect in the solution perturbs the band of surrounding water molecules. Furthermore, the slight second-order effect observed in the ATR spectrum indicates that the clusters are stabilized by weak interactions with surrounding water molecules.

Vibrational Frequencies

Table 4 and Figure 3 give detailed descriptions of the selected OH stretch taking place in the different structures of $KCl(H_2O)_{n=0-6}$. The OH stretching frequencies are usually used to classify the various cluster structures.[42] We have studied MP2/6-31+$_{Cl}$G* vibrational frequencies (scaled with 0.96) for the O···H stretch modes of the lowest-energy undissociated, half-dissociated, and fully dissociated structures (Table 4 and Fig. 3). The —O—H stretching frequencies obtained when oxygen coordinates with potassium ion and the hydrogen atom interacts with other water molecules $v[\mathbf{B}]$ yields a range of ~3230–3630 cm^{-1}. The lower frequency values (3230–3490 cm^{-1}) corresponds to the interaction of one water molecule with the —OH coordinated with K^+ ion, whereas the relatively higher values (3490–3630 cm^{-1}) were observed for two water molecules. The —O—H stretching frequencies $v[U]$ (~3280–3510 cm^{-1}) appears because of the interaction of oxygen atom with K^+ ion and the hydrogen interacting with Cl^- ion (Fig. 3). These frequencies coincide with the values observed in the $v[\mathbf{B}]$ case and any meaningful assignment is difficult. The —O—H frequencies given in $v[I]$ (~3660–3840 cm^{-1}) are clearly distinguishable compared with other cases. In the case of $v[I]$, the water molecule associated with the K^+ ion involving a dangling hydrogen is in general ~9–21 cm^{-1} larger than the v_s (v scaled) associated with Cl^-. This spectral information would be useful for IR experiments to identify the subtle changes in the hydration environment for $KCl(H_2O)_{n=1-6}$.[43–46]

Conclusions

We have explored the dissociation phenomenon of a KCl molecule in water using the MP2 and CCSD(T) levels of theory. The half-dissociated or paired structures were generated from the two water molecule cluster. We conclude that the formation of prismatic structure of KCl with four water molecules is sufficient to separate the cation and the anion (4.4 Å). This result reveals the smallest water cluster used to dissociate an alkali halide. The larger separation of K^+ ion and Cl^- ion was achieved (4.97 Å) with six water cluster in a cubic structure as well. It seems that the separation of alkali halides with six water molecule is a magic number for such systems as the hexa-hydrated separated ion-pair was predicted for NaCl[17] and CsF.[18] The half-dissociated or paired structures of KCl with five water molecules predicted by *ab initio* calculations are in agreement with the ATR absorbance spectrum of KCl-solvated water, which shows the presence of clusters made up of a pair of closely bound ions and a mean of five molecules of water: $[K^+(H_2O)_5Cl^-]$.[22,41] We hope that in this study the dissolution of KCl with water molecules not only shows the progression of ionic solvation but is also relevant to studies on the reactivity of atmospheric chemistry.[47]

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