Microhydration of Dibenzo-18-Crown-6 Complexes with K⁺, Rb⁺, and Cs⁺ Investigated by Cold UV and IR Spectroscopy in the Gas Phase

Yoshiya Inokuchi,† Takayuki Ebata,‡ and Thomas R. Rizzo*‡

†Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan
‡Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland

ABSTRACT: In this Article, we examine the hydration structure of dibenzo-18-crown-6 (DB18C6) complexes with K⁺, Rb⁺, and Cs⁺ ion in the gas phase. We measure well-resolved UV photodissociation (UVPD) spectra of K⁺·DB18C6·(H₂O)ₙ, Rb⁺·DB18C6·(H₂O)ₙ, and Cs⁺·DB18C6·(H₂O)ₙ (n = 1–8) complexes in a cold, 22-pole ion trap. We also measure IR-UV double-resonance spectra of the Rb⁺·DB18C6·(H₂O)₁–₅ and the Cs⁺·DB18C6·(H₂O)₃ complexes. The structure of the hydrated complexes is determined or tentatively proposed on the basis of the UV and IR spectra with the aid of quantum chemical calculations. Bare complexes (K⁺·DB18C6, Rb⁺·DB18C6, and Cs⁺·DB18C6) have a similar boat-type conformation, but the distance between the metal ions and the DB18C6 cavity increases with increasing ion size from K⁺ to Cs⁺. Although the structural difference of the bare complexes is small, it highly affects the manner in which each is hydrated. For the hydrated K⁺·DB18C6 complexes, water molecules bind on both sides (top and bottom) of the boat-type K⁺·DB18C6 conformer, while hydration occurs only on top of the Rb⁺·DB18C6 and Cs⁺·DB18C6 complexes. On the basis of our analysis of the hydration manner of the gas-phase complexes, we propose that, for Rb⁺·DB18C6 and Cs⁺·DB18C6 complexes in aqueous solution, water molecules will preferentially bind on top of the boat conformers because of the displaced metal ions relative to DB18C6. In contrast, the K⁺·DB18C6 complex can accept H₂O molecules on both sides of the boat conformation. We also propose that the characteristic solvation manner of the K⁺·DB18C6 complex will contribute entropically to its high stability and thus to preferential capture of K⁺ ion by DB18C6 in solution.

1. INTRODUCTION

Crown ethers are the most common host molecules for ion complexation in supramolecular and organic chemistry. One of their characteristics is the ability to selectively encapsulate certain metal ions. For example, dibenzo-18-crown-6 (DB18C6) selectively captures K⁺ among alkali metal ions in aqueous solution. One important conclusion derived from our previous studies of ion–crown ether complexes is that solvent effects highly control the alkali ion selectivity. In addition, a number of studies suggest the existence of multiple isomers, which contributes to the complex selectivity. In our previous work, we examined the number and the structure of isomers in bare and microsolvated forms of crown ether complexes by gas-phase spectroscopy and found their relation to the guest selectivity. The difference in the structure of DB18C6 complexes with alkali metal ions, M⁺·DB18C6 (M = Li, Na, K, Rb, and Cs), using UV and IR spectroscopy under cold gas-phase conditions. In bare K⁺·DB18C6, Rb⁺·DB18C6, and Cs⁺·DB18C6, the DB18C6 part adopts a similar boat-type open conformation, but the distance between the DB18C6 cavity and the metal ions increases with increasing ion size from K⁺ to Cs⁺. For microhydrated systems, we reported UV and IR spectra of hydrated K⁺·DB18C6 complexes, K⁺·DB18C6·(H₂O)⁻⁹, in the gas phase. Because the K⁺ ion in the K⁺·DB18C6 complex is encapsulated deeply with the crown cavity, H₂O molecules can bind directly to the K⁺ ion on both (top and bottom) sides of the boat-type K⁺·DB18C6 conformer. This hydration manner is due to the optimum matching in size between the DB18C6 cavity and the K⁺ ion.

In the present work, we extend our investigation of hydrated complexes to larger alkali-metal ions, that is, Rb⁺·DB18C6 and Cs⁺·DB18C6 complexes. As mentioned above, bare K⁺·DB18C6, Rb⁺·DB18C6, and Cs⁺·DB18C6 complexes have a similar boat-type structure, but the position of the metal ions with respect to the DB18C6 part is slightly different from each other. We examine how the difference in the metal position, or difference in the matching in size between the DB18C6 cavity and the metal ions, affects the manner of hydration.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The details of our experimental approach have been given elsewhere. Briefly, the K⁺·DB18C6·(H₂O)ₙ, Rb⁺·DB18C6·(H₂O)ₙ, and Cs⁺·DB18C6·(H₂O)ₙ (n = 1–8) complexes are produced continuously at atmospheric pressure via nanoelectrospray of a solution containing KCl, RbCl, or CsCl and DB18C6 (~10 μM each) dissolved in methanol/water (~9:1 volume ratio). The parent ions of interest are selected in a quadrupole mass filter and injected into a 22-pole RF ion trap.

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which is cooled by a closed-cycle He refrigerator to 6 K. The trapped ions are cooled internally and translationally to \(\sim 10 \text{ K}\) through collisions with cold He buffer gas\(^{4,16-18}\) which is pulsed into the trap. The trapped ions are then irradiated with a UV laser pulse, which causes some fraction of them to dissociate. The resulting charged photofragments, as well as the remaining parent ions, are released from the trap, mass-analyzed by a second quadrupole, and detected with a channeltron electron multiplier. Ultraviolet photodissociation (UVPD) spectra of parent ions are obtained by plotting the yield of the photofragment ion as a function of the UV laser wavenumber. The UVPD spectra of the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(M = \text{K}, \text{Rb}, \text{and Cs}\)) complexes are measured by monitoring the yield of the bare \(\text{M}^+\)-DB18C6 photofragment ion, because it is a dominant photodissociation product and is hardly affected by the metastable decay of the parent ions between the first quadrupole and the 22-pole ion trap. For IR-UV double-resonance spectroscopy, the output pulse of an IR optical parametric oscillator (OPO) precedes the UV pulse by \(\sim 100 \text{ ns}\) and counter-propagates collinearly with it through the 22-pole trap. Absorption of the IR light by the ions warms them up, modifying their absorption.\(^{20}\) We obtain IR-UV depletion and gain spectra by tuning the wavenumber of the UV laser either to the vibronic transition of a specific conformer or to a nonresonant position, respectively. The IR-UV depletion spectra provide conformer-selective IR spectra, whereas the IR-UV gain spectra represent the overall IR absorption due to all the isomers present in the experiment.

For geometry optimization of the \(\text{M}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(M = \text{K}, \text{Rb}, \text{and Cs}\)) complexes, we first use a classical force field to find conformational minima. The initial conformational search is performed by using the mixed torsional search with low-mode sampling and the AMBER\(^\circ\) force field as implemented in MacroModel version 9.1.\(^{20}\) Minimum-energy conformers found with the force field calculations are then optimized at the M05-2X/6-31+G(d) level and successively at the M05-2X/6-311+\(+G(d,p)\) level using the GAUSSIAN09 program package.\(^21\) Vibrational analysis is carried out for the optimized structures at the M05-2X/6-311++G(d,p) level. Calculated frequencies at the M05-2X/6-311++G(d,p) level are scaled with a factor of 0.9425 for comparison with the IR-UV spectra. This factor was determined so as to simulate the IR spectrum of the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) complex.\(^{22}\) All stable conformers are named systematically using “\(\text{Rb}1\)“ notation, where the first letters indicate the metal ion of a complex, the subsequent number represents the number of the attached \(\text{H}_2\text{O}\) molecules, and the final lower case letter stands for the stability order of conformers determined at the M05-2X/6-311++G(d,p) level with zero-point energy correction. For \(\text{Rb}^+\) and \(\text{Cs}^+\), we use the Stuttgart RLC as effective core potentials (ECPs); functions of the ECPs are obtained from a database of basis sets.\(^{23}\)

3. RESULTS

3.1. UVPSD Spectra. Figure S1 of the Supporting Information displays the UVPSD spectra of the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(n = 0-8\)) complexes in the 35 800–36 600 cm\(^{-1}\) region. All the spectra in Figure S1 consist of sharp bands with different vibronic patterns. The UV spectrum of bare \(\text{K}^+\)-DB18C6 (Figure S1a) has its band origin at 36 415 cm\(^{-1}\), which is 700 cm\(^{-1}\) higher than that of jet-cooled neutral DB18C6 monomer.\(^{24}\) The spectra of the hydrated complexes are also higher in energy than the DB18C6 monomer,\(^{24}\) although to a lesser degree. The relative band positions of the UV absorption of the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) complexes reflect the strength of the intermolecular interaction between DB18C6 and the other components in the complexes. The UV spectra of the \(n = 1-4\) complexes increasingly shift to the red with increasing cluster size, which suggests a progressive decrease in the intermolecular interaction with DB18C6. For the \(n = 5\) complex, the vibronic bands shift to higher frequency again, followed by a gradual shift to lower frequency for complexes with \(n = 6-8\). Another noticeable feature of this series of UVPSD spectra is that the \(n = 4\) complex shows highly congested features compared to those of the other complexes.

Figure S2 of the Supporting Information shows the UVPSD spectra of the \(\text{Rb}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(n = 0-8\)) complexes, which exhibit a similar trend as the corresponding potassiated species. The 0–0 band in the spectrum of the \(\text{Rb}^+\)-DB18C6 (Figure S2a) appears at 36 319 cm\(^{-1}\), with those of the hydrated complexes progressively shifting to lower energy for \(n = 1-4\) before shifting to higher frequency again at \(n = 5\). The UVPSD spectrum of the \(n = 4\) complex (Figure S2c) shows congested features, similar to that of the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_4\) complex (Figure S1e). Unlike the case of the doubly hydrated potassiated species (Figure S1c), the \(\text{Rb}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_2\) complex shows congested spectral features with no strong origin band (Figure S2c).

The UVPSD spectra of the \(\text{Cs}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(n = 0-8\)) complexes are shown in Figure S3 of the Supporting Information. The origin band of the \(\text{Cs}^+\)-DB18C6 appears at 36 234 cm\(^{-1}\) (Figure S3a).\(^4\) Similar to \(\text{K}^+\) and \(\text{Rb}^+\), the UV bands of the \(\text{Cs}^+\) complexes shift to lower frequency with increasing hydration. However, one difference for the \(\text{Cs}^+\) spectra (Figure S3) from the \(\text{K}^+\) and \(\text{Rb}^+\) spectra (Figures S1 and S2) is that the UV bands continuously shift to lower frequency from \(n = 1\) to 5 before exhibiting a blue shift at \(n = 6\). Moreover, in the case of the \(\text{Cs}^+\) complexes, it is the \(n = 5\) species (Figure S3f) that exhibits particularly congested vibronic features. In the spectra of the \(n = 2\) and 4 complexes (Figure S3c and e), a number of sharp bands appear much more closely than the case of \(\text{Rb}^+\). These spectral features will represent the complex structure, which will be described in more detail in the following sections.

3.2. Computed Structures. Figure 1 shows optimized computed structures of the \(\text{M}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(M = \text{K}, \text{Rb}, \text{Cs}; n = 1-5\)) complexes obtained at the M05-2X/6-31+\(+G(d,p)\) level. We have previously determined the structure of bare complexes (\(\text{K}-a, \text{Rb}-a, \text{and Cs}-b\)) and have confirmed that the conformers of the hydrated \(\text{K}^+\)-DB18C6 complexes shown in Figure 1 exist in the experiment under cold gas-phase conditions.\(^7\) For the hydrated \(\text{Rb}^+\)-DB18C6 and \(\text{Cs}^+\)-DB18C6 complexes, the most stable conformers (or the second most stable conformer for \(\text{Cs}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_4\)) are displayed in Figure 1. The most and the second most stable structures of the \(\text{M}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) complexes are shown with the total energy in Figures S4–S8 of the Supporting Information. All the complexes in Figure 1 have a boat-type form in the \(\text{M}^+\)-DB18C6 part. In all the isomers of the \(\text{Rb}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) and \(\text{Cs}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) complexes, the \(\text{H}_2\text{O}\) molecules are located on top of a boat-type \(\text{M}^+\)-DB18C6 conformer, even for the complexes smaller than \(n = 4\); the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O})_3\) complexes have the \(\text{H}_2\text{O}\) molecules on both sides of the boat \(\text{K}^+\)-DB18C6 conformer (Figure 1). This is in strong contrast to the \(\text{K}^+\)-DB18C6-(\(\text{H}_2\text{O}\))\(_n\) (\(n = 1-3\)) complexes, where the \(\text{H}_2\text{O}\) molecules are located either on top or bottom, or on both sides.\(^7\) As will be demonstrated below, we propose
the structure of the hydrated complexes on the basis of UVPD and IR-UV spectra, not of the stability order of isomers in quantum chemical calculations. The calculated total energy of the conformers cannot be used as definitive evidence for the structural assignment of the complexes, because it highly depends on the calculation level.

3.3. IR Spectra. We have reported conformer-selective, IR-UV double-resonance spectra of the K⁺·DB18C6·(H₂O)ₙ (n = 1−5) complexes in our previous study. ⁶ The smaller abundance of the hydrated Rb⁺·DB18C6 and Cs⁺·DB18C6 complexes prevented us from measuring exhaustive IR-UV spectra, but we have succeeded in obtaining spectra for some of them. Figure 2 shows the IR-UV (red curves) and theoretical IR (black curves and bars) spectra of the Rb⁺·DB18C6·(H₂O)ₙ complexes. The UV frequency at which the intensity of fragment ions is monitored for the IR-UV spectra is shown with the arrows in Figure S2 of the Supporting Information.

Figure 1. Optimized structures of the M⁺·DB18C6·(H₂O)ₙ (M = K, Rb, Cs; n = 0−5) calculated at the M05-2X/6-311+G(d,p) level. The structures of bare complexes (K-a, Rb-a, and Cs-b) were determined in our gas-phase study (ref 4). It was confirmed in ref 6 that the conformers of the K⁺·DB18C6·(H₂O)₁−₅ complexes in this figure exist in the experiment under cold gas-phase conditions. For the hydrated Rb⁺·DB18C6 and Cs⁺·DB18C6 complexes, the most stable conformers (or the second most stable one for Cs⁺·DB18C6·(H₂O)₁; see text) are displayed in this figure. Other optimized structures of the hydrated complexes are displayed with the relative total energy in the Supporting Information.

Rb1a (Figure 1) well reproduces the obtained gain spectrum. The second most stable isomer (Rb1b, Figure S5 of the Supporting Information) has a characteristic IR band at 3565 cm⁻¹. This band corresponds to the stretching vibration of the OH group hydrogen-bonded to an ether oxygen. In the IR-UV gain spectrum, no strong band is observed around 3560 cm⁻¹, suggesting that isomer Rb1b is not present in the experiment.

For the n = 2 complex, the IR-UV gain spectrum (top spectrum in Figure 2b) shows bands at 3608 and 3716 cm⁻¹, but no band is found in the 3400−3600 cm⁻¹ region. This IR-UV gain spectrum is quite similar to the theoretical one of isomer Rb2a (Figure 1). The second most stable isomer (Rb2b, Figure S5 of the Supporting Information) is predicted to have a strong band at 3449 cm⁻¹ due to the stretching vibration of the hydrogen-bonded OH group. However, the IR-UV gain spectrum shows no such band, indicating the absence of isomer Rb2b in the experiment.

Infrared spectra of the Rb⁺·DB18C6·(H₂O)₃ complex are shown in Figure 2c. ⁶ The IR-UV gain spectrum (top spectrum in Figure 2c) shows peaks at 3520, 3528, 3558, 3696, and 3709 cm⁻¹, accompanied by a weak shoulder at 3713 cm⁻¹. We measure IR-UV dip spectra at two resonant UV positions (36 032 and 36 182 cm⁻¹). The IR-UV depletion spectrum...
measured at 36,032 cm\(^{-1}\) clearly shows five dips at the same positions with those of the gain spectrum. This indicates that the IR-UV bands of the \(n = 3\) complex are due to a single isomer. The depth is not high, but the IR-UV spectrum at 36,182 cm\(^{-1}\) is similar to that measured at 36,032 cm\(^{-1}\), confirming the presence of a single conformer. The spectral pattern of the theoretical IR spectrum of isomer Rb\(_{3a}\) (Figure 1) well reproduces the observed IR-UV spectra, exhibiting three bands around 3500 cm\(^{-1}\) and two bands around 3700 cm\(^{-1}\). In contrast, the spectral features of the second most stable isomer (Rb\(_{3b}\), Figure S5 of the Supporting Information) are different from those of the measured spectra. From these results, the IR-UV spectra of the \(n = 1\)–\(3\) complexes can be described by theoretical IR spectra of the most stable isomers (Rb\(_{1a}\), Rb\(_{2a}\), and Rb\(_{3a}\)).

Figure 3 displays the IR-UV (red curves) and theoretical IR (black curves and bars) spectra of the Rb\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_{4,5}\) complexes. In the IR-UV gain spectrum of the \(n = 4\) complex (top spectrum of Figure 3a), peaks are seen at \(\sim 3445\), \(\sim 3460\), 3660, and 3708 cm\(^{-1}\). The most stable isomer of the \(n = 4\) complex (Rb\(_{4a}\), Figure 1) reproduces the IR spectrum with peaks at 3450, 3453, 3663, and 3723 cm\(^{-1}\). The IR-UV gain spectrum of the \(n = 5\) complex (Figure 3b) has broad bands in the 3300–3500 cm\(^{-1}\) region and a weak one at \(\sim 3575\) cm\(^{-1}\). These spectral patterns are reasonably well reproduced by the calculated IR spectrum of isomer Rb\(_{5a}\) (Figure 1).

Figure 4 presents the IR-UV (red curves) and theoretical IR (black curves and bars) spectra of the Cs\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_{4,5}\) complex, reproduced from our previous work.\(^6\) The IR-UV gain and dip spectra (top two spectra of Figure 4) are similar to each other; IR bands are found at 3511, 3524, 3553, 3694, and 3705 cm\(^{-1}\). Therefore, the IR-UV gain spectrum of the Cs\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_{5}\) complex is attributed to a single isomer. The spectral patterns of the IR-UV spectra of the Cs\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_4\) complex resemble those of the Rb\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_4\) complex (Figure 2c). In addition, the most stable calculated isomer (Cs\(_{3a}\), Figure 1) shows an IR spectrum similar to that we measure. In the following section, we discuss the probable structure of the M\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_n\) complexes on the basis of the UV/IR, IR-UV, and theoretical results described above.

4. DISCUSSION

4.1. M\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_n\) Complexes. In our previous work, we determined the hydration structure of the K\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_n\) complexes by IR spectroscopy in the OH stretching region.\(^3\) Here we determine structure of the hydrated Rb\(^+\)-DB18C\(_6\) and Cs\(^+\)-DB18C\(_6\) complexes using a combination of UV/IR and IR spectra. Figure 5 displays the UV/IR spectra of the M\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_n\) (M = K, Rb, and Cs) complexes for comparison. For the K\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_n\) complex, all the bands are attributed to a single isomer (K\(_{1a}\), Figure 1).\(^5\) In this isomer, the oxygen atom of the H\(_2\)O molecule is directly attached to the K\(^+\) ion, and one of the OH groups forms the O–H···π hydrogen bond with one of the benzene rings. As a result, the two benzene rings are not equivalent. Time-dependent density functional theory (TD-DFT) calculations of the K\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_5\) complex predicts that the S\(_1\)–S\(_0\) and S\(_2\)–S\(_0\) transition energies of isomer K\(_{1a}\) differ by >100 cm\(^{-1}\), and the S\(_1\)–S\(_0\) transition is localized almost entirely on the benzene ring involved in the O–H···π hydrogen bond. In addition, the vibronic structures starting from 36,274 and 36,334 cm\(^{-1}\) show different features from each other (an expanded view of the UV/IR spectrum is shown in Figure S11 of the Supporting Information). On the basis of these theoretical and experimental results, the two strong bands observed at 36,274 and 36,334 cm\(^{-1}\) (Figure 5a) can be reasonably assigned to the 0–0 band of the S\(_0\)–S\(_0\) and S\(_1\)–S\(_0\) transitions.

The structure of the Rb\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_5\) complex should be similar to that of the K\(^+\)-DB18C\(_6\)-(H\(_2\)O)\(_5\) complex, because the IR-UV spectrum of the former (Figure 2a) in the region of the OH stretching bands strongly resembles that of the latter (Figure 2a of ref 6). Moreover, isomer Rb\(_{1a}\) of the Rb\(^+\) complex (Figure 1) has a structure similar to that of the K\(^+\) complex determined in our previous paper (K\(_{1a}\), Figure 1).\(^6\)
We thus assign the structure of isomer Rb1a in Figure 1 to the Rb+·DB18C6·(H2O) complex. We also suppose that the strong sharp band observed at 36 260 cm$^{-1}$ in the UVPD spectrum of Rb+·DB18C6·(H2O)$_1$ (Figure 5b) is the 0−0 band of the $S_0$−$S_0$ transition, which would make the weak band at 36 165 cm$^{-1}$ the 0−0 band of the $S_1$−$S_0$ transition. As mentioned above, the $S_1$−$S_0$ transition of the K+·DB18C6·(H2O)$_1$ complex is mainly localized in the benzene ring having the O−H···π hydrogen bond, and a similar localization can be seen also in the calculation of Rb+·DB18C6·(H2O)$_1$.

While an IR spectrum is not available for the Cs+·DB18C6·(H2O)$_1$ complex, it is possible to infer the structure on the basis of the UV spectrum. As shown in Figure 5c, the UV spectrum of the Cs+·DB18C6·(H2O)$_1$ complex is quite similar to that of the corresponding Rb+ complex. A strong, sharp band is observed at 36 181 cm$^{-1}$, which can be attributed to the 0−0 band of the $S_2$−$S_0$ transition. The amount of the red-shift from Rb+·DB18C6·(H2O)$_1$ to Cs+·DB18C6·(H2O)$_1$ is 85 cm$^{-1}$, which is comparable to that between unsolvated Rb+·DB18C6 and Cs+·DB18C6 (85 cm$^{-1}$). The similarity of this spectrum to that of the Rb+ complex indicates a similar structure. The two most stable isomers of the Cs+·DB18C6·(H2O)$_1$ complex are shown in Figure S7 of the Supporting Information. Among them, isomer Cs1b (Figure 1) has a structure similar to that of Rb+·DB18C6·(H2O)$_1$ (Rb1a, Figure 1). Hence, we assign the structure of Cs+·DB18C6·(H2O)$_1$ to isomer Cs1b. Isomer Cs1b (Figure 1) is the second most stable structure of the Cs+·DB18C6·(H2O)$_1$ complex at the M05-2X/6-311+G(d,p) level. The DB18C6 has a boat-type open conformation, while in the most stable structure, Cs1a (Figure S7), a part of the DB18C6 ring is bent. Similar conformers (Cs-a and Cs-b) were also found in quantum chemical calculations of bare Cs+·DB18C6, which we determined to adopt the boat-type C$_2v$ conformer (Cs-b) on the basis of the UV spectrum; Cs-b well reproduces the position of the 0−0 band in the UVPD spectrum, and Cs-a has a transition energy >500 cm$^{-1}$ higher than that of Cs-b. Because the UV absorption of the Cs+·DB18C6·(H2O)$_1$ complexes shifts to lower frequency from $n = 0$ to 1 (Figures S3a and b), the Cs+·DB18C6 part in the Cs+·DB18C6·(H2O)$_1$ complexes should have a boat-type conformation similar to the structure of bare Cs+·DB18C6 (Cs-b). Thus, isomer Cs1b is the most likely form for the Cs+·DB18C6·(H2O)$_1$ complex. Here it should be emphasized again that the structural assignment for the $n = 1$ complexes described earlier is performed on the basis of the experimental UV and IR spectra, not of the calculated total energy of the isomers; isomers K1a and Rb1a (Figure 1), which are determined to be present in the experiment, are the most stable for the K+·DB18C6·(H2O)$_1$ and Rb+·DB18C6·(H2O)$_1$ complexes at the M05-2X/6-311+G(d,p) level, although the stability order of the isomers may be changed at different calculation levels.

### 4.2. M+·DB18C6·(H2O)$_2$ Complexes

The UV spectra of the M+·DB18C6·(H2O)$_2$ (M = K, Rb, and Cs) complexes are compared in Figure 6. The spectral patterns are quite different between the K+ and Rb+ complexes. The UV spectrum of the K+·DB18C6·(H2O)$_2$ complex (Figure 6a) appears relatively simple, with two sharp origin bands at 36 267 and 36 326 cm$^{-1}$. In contrast, the UV spectrum of the Rb+·DB18C6·(H2O)$_2$ complex (Figure 6b) exhibits a congested progression with many sharp bands. The qualitative difference in the UV spectra of the K+ and Rb+ complexes suggest that they have substantially different structures. On the basis of previously measured IR-UV spectra of the K+ complex, the UVPD bands at 36 267 and 36 326 cm$^{-1}$ have been assigned to two different isomers (K2f and K2d, respectively, Figure 1). These spectra show a strong IR band at $\sim$3453 cm$^{-1}$, which is assigned to the
stretches of the OH group hydrogen-bonded to the other H₂O molecule. These two H₂O molecules are bound on top or on the bottom of the boat-type K⁺-DB18C6 conformer. In contrast, the IR-UV gain spectrum of the Rb⁺-DB18C6-H₂O complex, shown in Figure 2b, does not exhibit a band around 3450 cm⁻¹; the IR band positions of the Rb⁺-DB18C6-H₂O complex (3608 and 3716 cm⁻¹) are almost the same as that of Rb⁺-DB18C6-H₂O, (3609 and 3712 cm⁻¹, Figure 2a). Hence, the two H₂O molecules in the Rb⁺-DB18C6-H₂O complex appear to be bound independently to the Rb⁺-DB18C6 in a manner similar to that in the Rb⁺-DB18C6-H₂O complex. As seen in Figure 1, isomer Rb2a of the Rb⁺-DB18C6-H₂O complex has a hydration structure similar to that of Rb⁺-DB18C6-H₂O₁ (Rb1a, Figure 1). The calculated IR spectrum of isomer Rb2a well reproduces the band position of the measured spectrum (Figure 2b). We conclude that the Rb⁺-DB18C6-H₂O complex has the structure of isomer Rb2a in Figure 1. The two benzene rings in this isomer are equivalent, leading to a complex with C3 symmetry. This may enhance the excitation coupling between the two benzene rings leading to congested spectral features, as seen for the bare M⁺-DB18C6 (M = K, Rb, and Cs) complexes and for K⁺-DB18C6-H₂O.⁶,⁶

We consider now the structure of the Cs⁺-DB18C6-H₂O complex on the basis of the UVPD spectrum and the theoretical calculations. The UVPD spectrum of Cs⁺-DB18C6-H₂O (Figure 6c) more closely resembles that of Rb⁺-DB18C6-H₂O complex rather than that of K⁺-DB18C6-H₂O with many sharp, closely spaced bands. Isomer Cs2a of Cs⁺-DB18C6-H₂O (Figure 1) has a structure similar to that of the Rb⁺-DB18C6-H₂O complex (Rb2a, Figure 1). Hence, we tentatively ascribe the structure of Cs⁺-DB18C6-H₂O to isomer Cs2a; definitive assignment with IR-UV spectroscopy, which includes further improvement of detection efficiency of the photodissociation isomer, is our future work.

4.3. M⁺-DB18C6-H₂O Complexes. Figure 7 displays UVPD spectra of the M⁺-DB18C6-H₂O (M = K, Rb, and Cs) complexes. In contrast to the spectra of the n = 2 complexes (Figure 6), the spectral features of the n = 3 species are similar among the different cations (i.e., K⁺, Rb⁺, and Cs⁺). The spectra are not as congested as that of Rb⁺-DB18C6-H₂O, and Cs⁺-DB18C6-H₂O complexes (Figures 2c and 4, respectively). Hence, we attribute the structure of the M⁺-DB18C6-H₂O complexes to isomers Rb3a and Cs3a, respectively (Figure 1). The strong bands observed at 3603 and 3612 cm⁻¹ for Cs⁺ (Figure 7c) are assigned to the origin band of the S₁–S₀ and S₂–S₁ transitions. In the case of the Cs⁺-DB18C6-H₂O complex, there appears to be another isomer, which exhibits a sharp UVPD band at 3630 cm⁻¹ (highlighted by an arrow in Figure 7a). This structure of the isomer was determined to be isomer K3g (Figure 1) on the basis of its IR spectrum. In this isomer, two H₂O molecules are bound on top of the boat-type K⁺-DB18C6, and the other is bound on the bottom. This isomer shows a strong IR-UV band at 3463 cm⁻¹, which does not seem to have an equivalent in the IR-UV spectrum of the Rb⁺-DB18C6-H₂O complex (top panel of Figure 2c). We conclude that the Rb⁺ complex does not have an isomer analogous to K3g of the K⁺ complex.

4.4. M⁺-DB18C6-H₂O Complexes (n = 4–8) Complexes. Figure 8 shows the UVPD spectra of the M⁺-DB18C6-H₂O (M = K, Rb, and Cs) complexes. The spectra of the K⁺ and Rb⁺ complexes (Figure 8a and b) both exhibit congested features with a number of sharp bands, suggesting a similarity of structure. In the previous study, the structure of the K⁺-DB18C6-H₂O complex was determined to be an isomer in which a ring of four H₂O molecules is bound on top of the boat-type K⁺-DB18C6 (K4a in Figure 1). Isomer Rb4a of the Rb⁺ complex (Figure 1) has a structure similar to that of K4a, and its calculated IR spectrum well reproduces the IR-UV spectrum of the M⁺-DB18C6-H₂O (M = K, Rb, and Cs) complexes. The intensity of each spectrum is normalized as having the same maximum intensity for all the spectra. The spectrum of the K⁺ complex (a) was taken from ref 6. A sharp band highlighted with an arrow in (a) is assigned to an isomer other than that showing the strong bands at 36 108 and 36 223 cm⁻¹ (ref 6).
Figure 8. UVPD spectra of the M⁺·DB18C6·(H₂O)₄ₙ (M = K, Rb, and Cs) complexes. The intensity of each spectrum is normalized as having the same maximum intensity for all the spectra. The spectrum of the K⁺ complex (a) was taken from ref 6.

Figure 9 displays the UVPD spectra of the M⁺·DB18C6·(H₂O)₅ (M = K, Rb, and Cs) complexes. The intensity of each spectrum is normalized as having the same maximum intensity for all the spectra. The spectrum of the K⁺ complex (a) was taken from ref 6.

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found that the K·-(H₂O)₄ complex has a four-membered H₂O ring, indicating that this ring size is suitable for effective hydration to K⁺ ion. In the case of the K⁺-(H₂O)₄ complex, four water molecules form a ring through four O–H···O hydrogen bonds, and this ring is bound to the K⁺ ion. The other H₂O molecule is bound to the K⁺ ion on the opposite side of the H₂O ring. This result suggests that, in binding to the K⁺ ion, a ring with four H₂O molecules is preferred over a ring with five H₂O molecules. For the K⁺·DB18C6·(H₂O)₄ complex, all the H₂O molecules are bound on top of the K⁺·DB18C6 part, forming a ring (Figure 1); the K⁺ ion is located between the H₂O ring and the DB18C6 component. The binding ability of H₂O rings to the K⁺ ion seems to affect in turn the interaction between the DB18C6 part and K⁺ in these complexes. In the K⁺·DB18C6·(H₂O)₅ complex (K4a in Figure 1), the four-membered H₂O ring attracts strongly the K⁺ ion, which can weaken the interaction between the K⁺ ion and the DB18C6 part and provide the least blue-shifted UV absorption of DB18C6 among the n = 0–8 complexes (Figure S1). As expected from the hydration manner in K⁺·(H₂O)₃, the binding strength of the five-membered H₂O ring to the K⁺ ion is smaller than that of the four-membered species. Weaker interaction of the K⁺ ion with the five-membered H₂O ring results in stronger interaction with the DB18C6 part, showing the blue-shift of the DB18C6 absorption at n = 5 (Figure S1). For the Cs⁺ ion, the most stable isomer of the Cs⁺·-(H₂O)₃ complex has a ring consisting of five H₂O molecules. This indicates that a five-membered ring is preferred over a four-membered ring for complex formation with Cs⁺ ion. The UVPD spectra of the Cs⁺·DB18C6·(H₂O)₃ complexes show the red-shift from n = 0 up to 5, but the UV absorption shifts to the blue again for n = 6. The intermolecular interaction of the Cs⁺ ion with a six-membered ring is likely to be weaker than that with a five-membered ring. As a result, the interaction of the Cs⁺ ion with the DB18C6 component becomes stronger for the n = 6 ion.

### 4.5. Hydration Profiles Characteristic of M⁺·DB18C6 (M = K, Rb, and Cs) Complexes

Figure 1 displays the structures of the M⁺·DB18C6·(H₂O)₉ complexes (M = K, Rb, and Cs) determined or tentatively proposed in the previous studies. The M⁺·DB18C6 complexes are located between the H₂O ring and the DB18C6 component. In the case of the hydrated K⁺·DB18C6 complexes, the water molecules on top and at the bottom of the boat K⁺·DB18C6 conformer. For the n = 4 and 5 complexes, the K⁺ and Rb⁺ complexes have a similar structure to each other (K4a and Rb4a, and K5a and Rb5a), while the Cs⁺ complexes have a different hydration pattern (Cs4a and Cs5a). We display top views of the n = 4 and 5 complexes in Figures S9 and S10 of the Supporting Information for a closer look at the difference in the structures. In the case of the n = 5 complexes, one of the five H₂O molecules is bound to an oxygen atom of the DB18C6 component; we label this H₂O with “1” and other ones successively with “2–5” in Figure S10. For the K⁺ and Rb⁺ complexes, the third and fifth H₂O molecules are close to the benzene rings, forming the O–H···π hydrogen bond. In contrast, the distance between the H₂O ring and the benzene rings is substantially longer for the Cs⁺ complex than that for the K⁺ and Rb⁺ complexes because the Cs⁺ ion is displaced largely from the DB18C6 part.

Because the K⁺ ion is encapsulated deeply in the DB18C6 cavity, H₂O molecules can be bound to the K⁺ ion on both sides of the K⁺·DB18C6 complex, which results in multiple isomers in both experiment and theory. For the Rb⁺ and Cs⁺ ions, the distance between the metal ions and the DB18C6 cavity is slightly larger than in the case of the K⁺ ion, which allows H₂O molecules to interact with the Rb⁺ ion on one of the M⁺·DB18C6 parts, providing a single stable conformer. The existence of multiple isomers for the hydrated K⁺·DB18C6 complexes can contribute to the effective formation of the K⁺·DB18C6 complex and preferential capture of K⁺ by DB18C6 in solution because of “conformational” entropic effects. These are different from usual entropic effects, which are related to the Gibbs free energy of a single conformation, but the higher the number of complex conformers, the more preferred is the complex formation. In this sense, the results of the Rb⁺ and Cs⁺ complexes reinforce the uniqueness of K⁺ ion in the encapsulation by DB18C6.

### 5. CONCLUSION

We have measured UVPD spectra of K⁺·DB18C6·(H₂O)₉, Rb⁺·DB18C6·(H₂O)₉, and Cs⁺·DB18C6·(H₂O)₉ complexes and IR-UV double-resonance spectra of the Rb⁺·DB18C6·(H₂O)₉ complexes in a cold, 22-pole ion trap. The structure of dominant forms observed in the experiment has been determined or proposed for all the complexes based on the analysis of the UV and IR spectra. Because conformer-specific, IR-UV dip spectra are not available for all the Rb⁺·DB18C6·(H₂O)₉ and Cs⁺·DB18C6·(H₂O)₉ complexes, we cannot exclude completely the possibility of other isomers. However, the IR-UV gain spectra, which provide IR bands of all the isomers in the experiment, are well reproduced by calculated spectra of the most stable isomers for the Rb⁺ complexes. This suggests that other higher-energy isomers, if they exist, are not so abundant in the experiment. The bare complexes (K⁺·DB18C6, Rb⁺·DB18C6, and Cs⁺·DB18C6) have a similar, boat-type conformation, but the distance between the metal ions and the DB18C6 increases with increasing ion size from K⁺ to Cs⁺. This structural difference highly affects the manner in which they are hydrated. In the case of the hydrated K⁺·DB18C6 complexes, the water molecules can be bound on both sides of the boat-type K⁺·DB18C6 structure. In contrast, the H₂O molecules in the hydrated Rb⁺·DB18C6 and Cs⁺·DB18C6 complexes are located only on top of them. The UV absorption shifts gradually to the
low frequency from $n = 0$ to 4 for the K⁺ and Rb⁺ complexes and from $n = 0$ to 5 for the Cs⁺ complex, and then shifts back to the high frequency at $n = 5$ for K⁺ and Rb⁺ and at $n = 6$ for Cs⁺. This spectral trend is related to the stability of the hydrated complexes of these ions, $\text{M}^+\cdot(\text{H}_2\text{O})_n$. Addition of one H₂O molecule to the K⁺-DB18C6-(H₂O)₅, Rb⁺-DB18C6-(H₂O)₅ or Cs⁺-DB18C6-(H₂O)₅ complex makes the interaction between the metal ions and the water clusters attached on the boat-type conformers weaker. As a result, the interaction between DB18C6 and the metal ions becomes stronger, and the UV absorption moves back to higher frequency at $n = 5$ for the K⁺ and Rb⁺ complexes and at $n = 6$ for the Cs⁺ complexes. These hydration profiles are characteristic of microhydrated systems, where water molecules are bound to the metal ions cooperatively. The M⁺-DB18C6 complexes in aqueous solutions are surrounded by a number of H₂O molecules on both sides of the boat conformers. However, as can be seen in Figure 1, H₂O molecules will be preferentially bound on top of the boat conformers for the Rb⁺-DB18C6 and Cs⁺-DB18C6 complexes even in aqueous solutions because they are displaced from the center of the DB18C6 cavity. Because the K⁺-DB18C6 complex can accept H₂O molecules on both sides of the boat conformation, we propose that multiple conformations will contribute entropically to the high stability of the K⁺-DB18C6 complex in solution and hence the selectivity of DB18C6 for K⁺.

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