Supporting Information

Microhydration Effects on the Encapsulation of Potassium Ion by Dibenzo-18-Crown-6

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UV Photodissociation Spectra of Rb^+•DB18C6•$(H_2O)_3$ and Cs^+•DB18C6•$(H_2O)_3$

Figure 1S shows the UV photodissociation spectra of the Rb^+•DB18C6•$(H_2O)_3$ and Cs^+•DB18C6•$(H_2O)_3$ complexes. These spectra are measured by monitoring the yield of fragment M^+•DB18C6 ion.

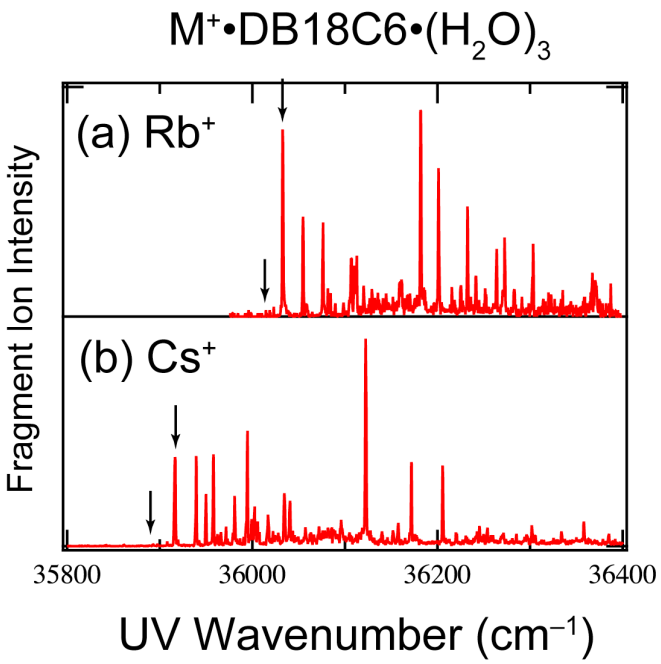

Figure 1S. The UVPD spectra of the Rb^+•DB18C6•$(H_2O)_3$ and Cs^+•DB18C6•$(H_2O)_3$ complexes. The arrows show the UV positions at which the IR-UV spectra in Fig. 11 are measured.

Determination of Conformer Structure with IR Spectra

Figure 2S shows comparison of the IR-UV spectrum of the n = 3 complex with the IR spectra of conformer K3a calculated at four different levels. These calculated spectra are quite similar to each other, independent of the calculation levels. Therefore, it is quite reasonable to assign the conformer structure primarily from the similarity of the IR spectra observed and calculated, although the relative stability among stable conformers is dependent on the calculation levels. The structure of the K^+•DB18C6•$(H_2O)_n$ (n = 1–5) is displayed in Figs. 3S–7S. These forms are obtained at the M05-2X/6-31+G(d) level of theory, and only the conformers whose total energy relative to that of the most stable form is less than 5 kJ/mol are shown, except for n = 3. In the case of the n = 3 complex, the seventh stable conformer (K3g), which has ΔE more than 5 kJ/mol, is also shown because it reproduces one of the IR-UV spectra of the n = 3 complex very well. In the case of the n = 1, 4, and 5 complexes, only one conformer is found in the experiment, and its structure can be attributed to the most stable conformer. For the n = 2 and 3 complexes, which have two and three conformations in the experiment, their structures can be unambiguously determined from the IR spectra. In Figs. 3S–7S, the conformers found in the experiment are highlighted by boxes.

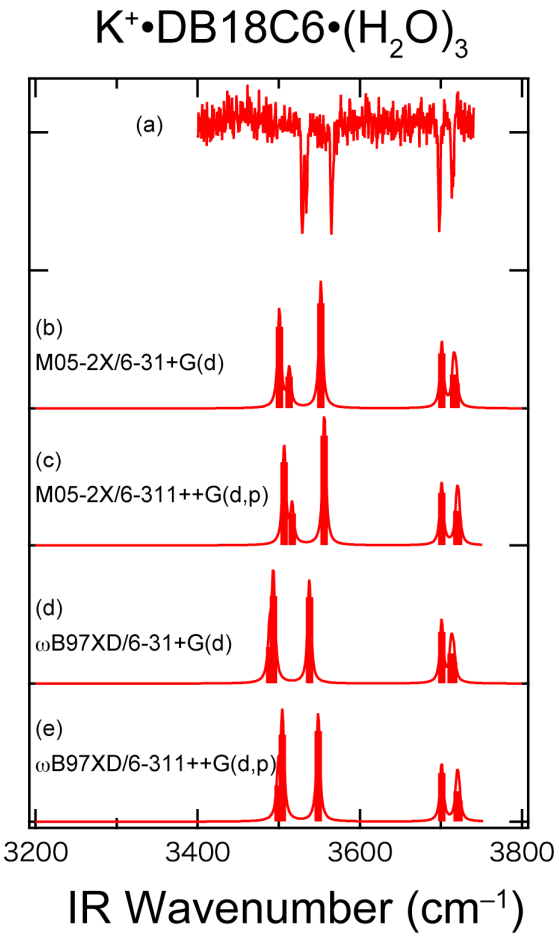

Figure 2S. (a) The IR-UV spectrum of the K^+•DB18C6•$(H_2O)_3$ complex. (b–e) The IR spectra calculated for conformer K3a at four different levels.

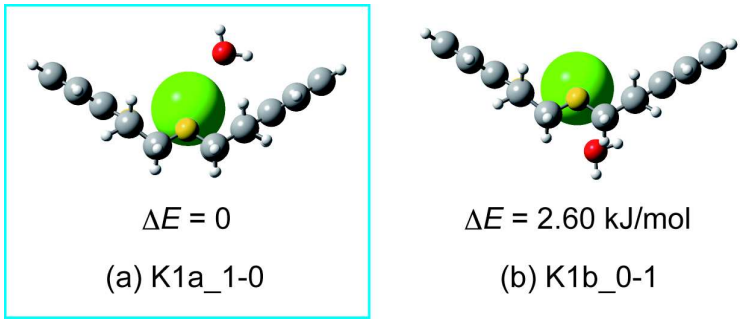

Figure 3S. The stable conformers of the K^+•DB18C6•$(H_2O)_1$ complex obtained in the geometry optimization at the M05-2X/6-31+G(d) level. Δ*E* stands for the total energy relative to that of the most stable conformer (K1a); the total energy is corrected with non-scaled zero-point vibrational energy. The crown oxygen atoms are shown in yellow to distinguish them from the water ones (red).

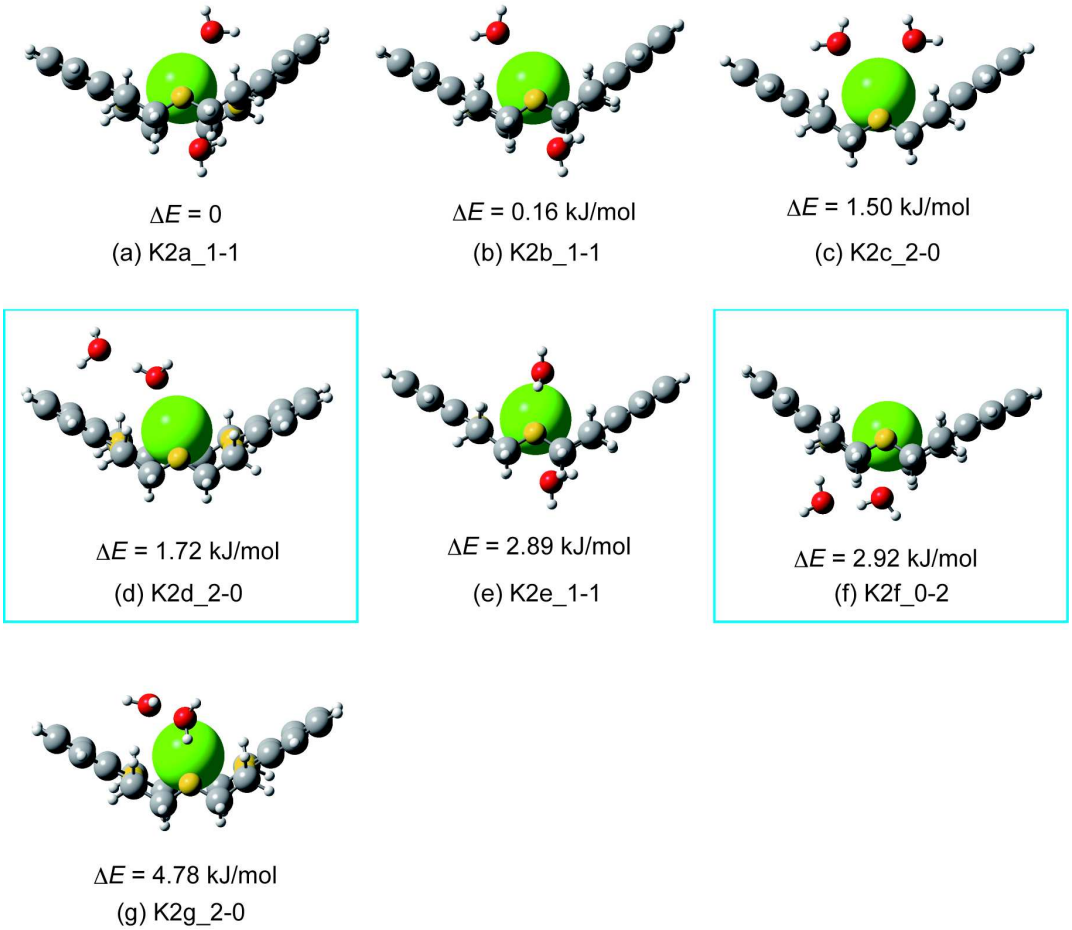

Figure 4S. The stable conformers of the K^+•DB18C6•$(H_2O)_2$ complex obtained in the geometry optimization at the M05-2X/6-31+G(d) level. ΔE stands for the total energy relative to that of the most stable conformer (K2a); the total energy is corrected with non-scaled zero-point vibrational energy. The crown oxygen atoms are shown in yellow to distinguish them from the water ones (red).

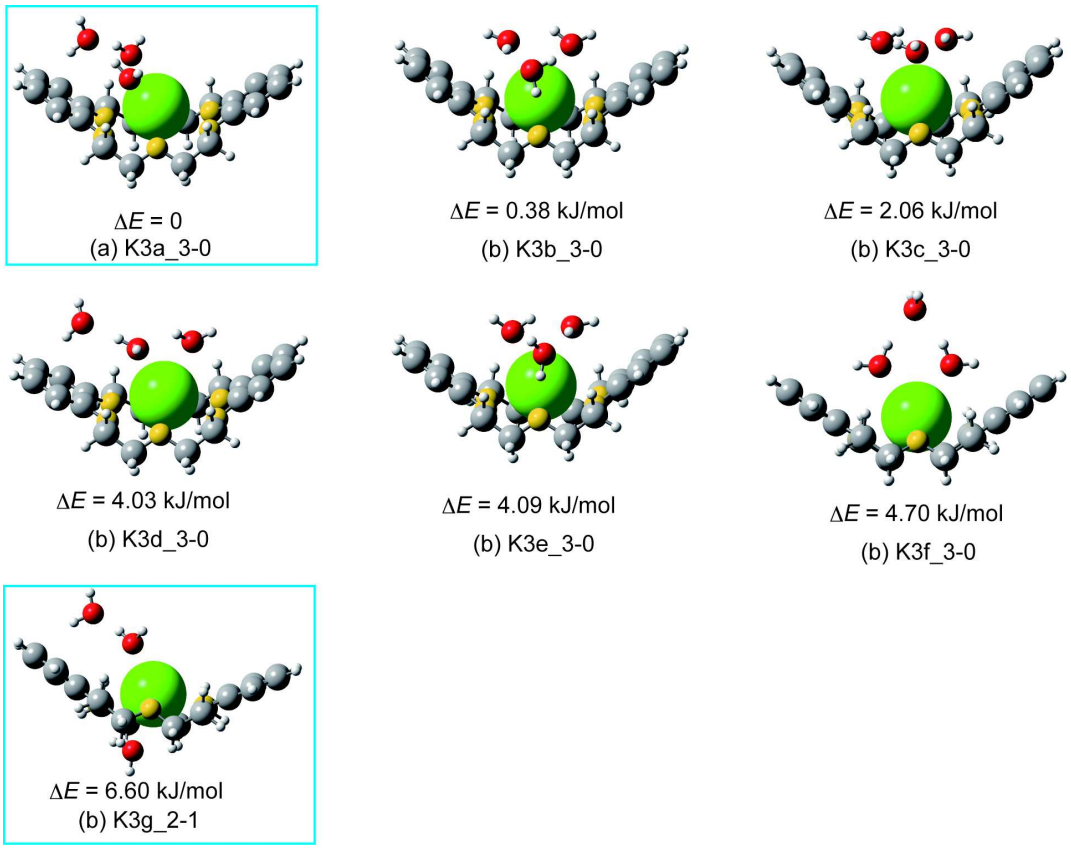

Figure 5S. Stable conformers of the K^+•DB18C6•$(H_2O)_3$ complex obtained in the geometry optimization at the M05-2X/6-31+G(d) level. ΔE stands for the total energy relative to that of the most stable conformer (K3a); the total energy is corrected with non-scaled zero-point vibrational energy. The crown oxygen atoms are shown in yellow to distinguish them from the water ones (red).

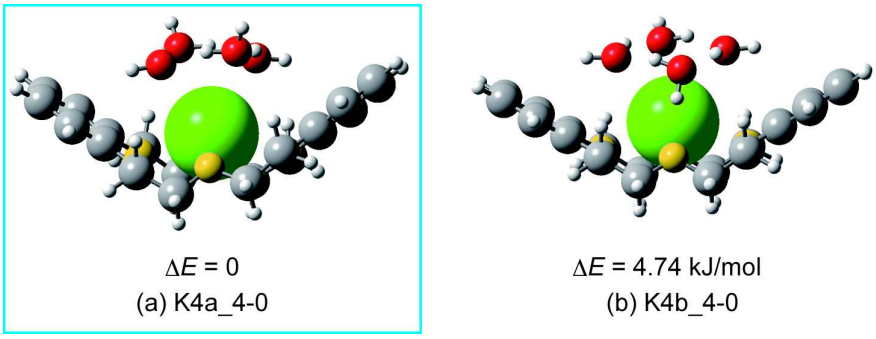

Figure 6S. The stable conformers of the K^+•DB18C6•$(H_2O)_4$ complex obtained in the geometry optimization at the M05-2X/6-31+G(d) level. Δ*E* stands for the total energy relative to that of the most stable conformer (K4a); the total energy is corrected with non-scaled zero-point vibrational energy. The crown oxygen atoms are shown in yellow to distinguish them from the water ones (red).

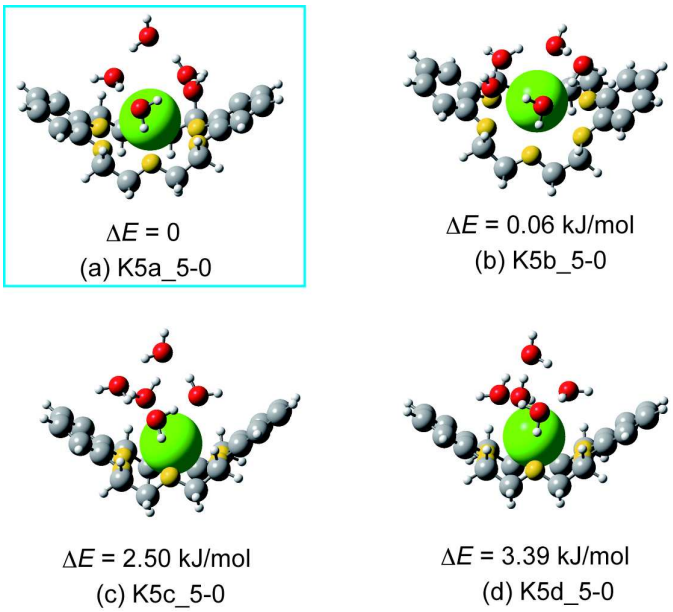

Figure 7S. The stable conformers of the K^+•DB18C6•$(H_2O)_5$ complex obtained in the geometry optimization at the M05-2X/6-31+G(d) level. ΔE stands for the total energy relative to that of the most stable conformer (K5a); the total energy is corrected with non-scaled zero-point vibrational energy. The crown oxygen atoms are shown in yellow to distinguish them from the water ones (red).

Full list of Ref. 60:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. In *Gaussian 09, Revision A.1*; Gaussian, Inc.: Wallingford CT, 2009.