Gas Phase Hydration of Halogenated Benzene Cations. Is it Hydrogen or Halogen bonding?


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Supporting Information
Figure S1. VCU mass-selected ion mobility system.
Figure S2. Mass spectra resulting from the injection of the mass-selected fluorobenzene radical cation (C_6H_5F^+, FBz) into helium gas or helium-water (H_2O) vapor mixture at different temperatures and pressures as indicated. Red circles represent H^+W_n with n=4-7 and blue squares represent C_6H_5^+(W)_n with n=3-6.
Figure S3. Mass spectra resulting from the injection of the mass-selected chlorobenzene radical cation ($C_{6}H_{5}Cl^{+}$, ClBz) into helium gas or helium-water ($H_{2}O$) vapor mixture at different temperatures and pressures as indicated. Red circles represent $H^{+}W_{n}$ with $n=5-8$ and blue square represents $C_{6}H_{5}^{+}(W)$. 
Figure S4. van’t Hoff plots for the temperature dependence of the equilibrium constants for the association reactions of fluorobenzene radical cation with water. The resulting $-\Delta H^\circ$ and $-\Delta S^\circ$ are in (kcal mol$^{-1}$) and (cal mol$^{-1}$ K$^{-1}$) respectively. The error for the measurements are ± 1 kcal mol$^{-1}$ for $-\Delta H^\circ$ and ± 2 cal mol$^{-1}$K$^{-1}$ for $-\Delta S^\circ$. 

$$C_6H_5F^{++}(H_2O)_{n-1} + H_2O \rightleftharpoons C_6H_5F^{++}(H_2O)_n$$

$n-1, n$

- $n = 0, 1$
- $n = 1, 2$

$-\Delta H^\circ = 9.0, -\Delta S^\circ = 20.4$

$-\Delta H^\circ = 8.0, -\Delta S^\circ = 19.7$
Figure S5. van’t Hoff plots for the temperature dependence of the equilibrium constants for the association reactions of chlorobenzene radical cation with water. The resulting $\Delta H^\circ$ and $\Delta S^\circ$ are in (kcal mol$^{-1}$) and (cal mol$^{-1}$ K$^{-1}$) respectively. The error for the measurements are ± 1 kcal mol$^{-1}$ for $\Delta H^\circ$ and ± 2 cal mol$^{-1}$K$^{-1}$ for $\Delta S^\circ$. 
Figure S6. Mass spectrum resulting from the injection of the mass-selected iodobenzene radical cation (IBz\(^+\)) into He/water vapor mixture at 244 K showing the formation of three sequential hydration steps IBz\(^+\)W, IBz\(^+\)W\(_2\) and IBz\(^+\)W\(_3\).