

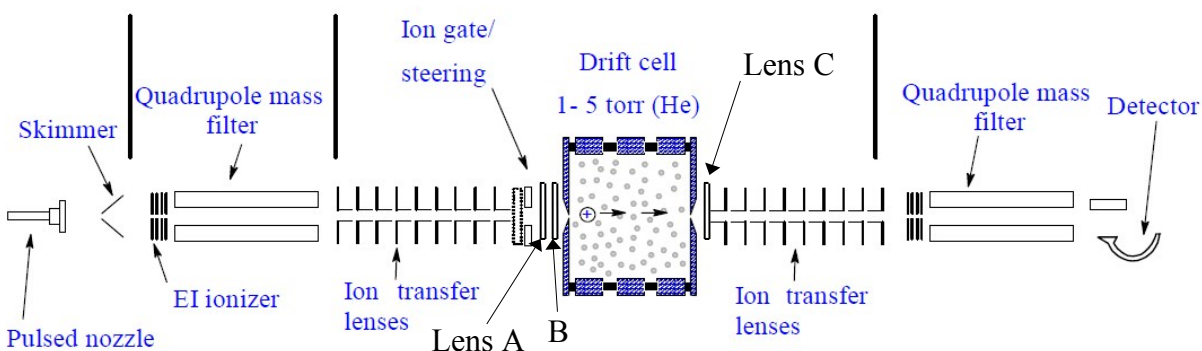
## Gas Phase Hydration of Halogenated Benzene Cations. Is it Hydrogen or Halogen bonding?

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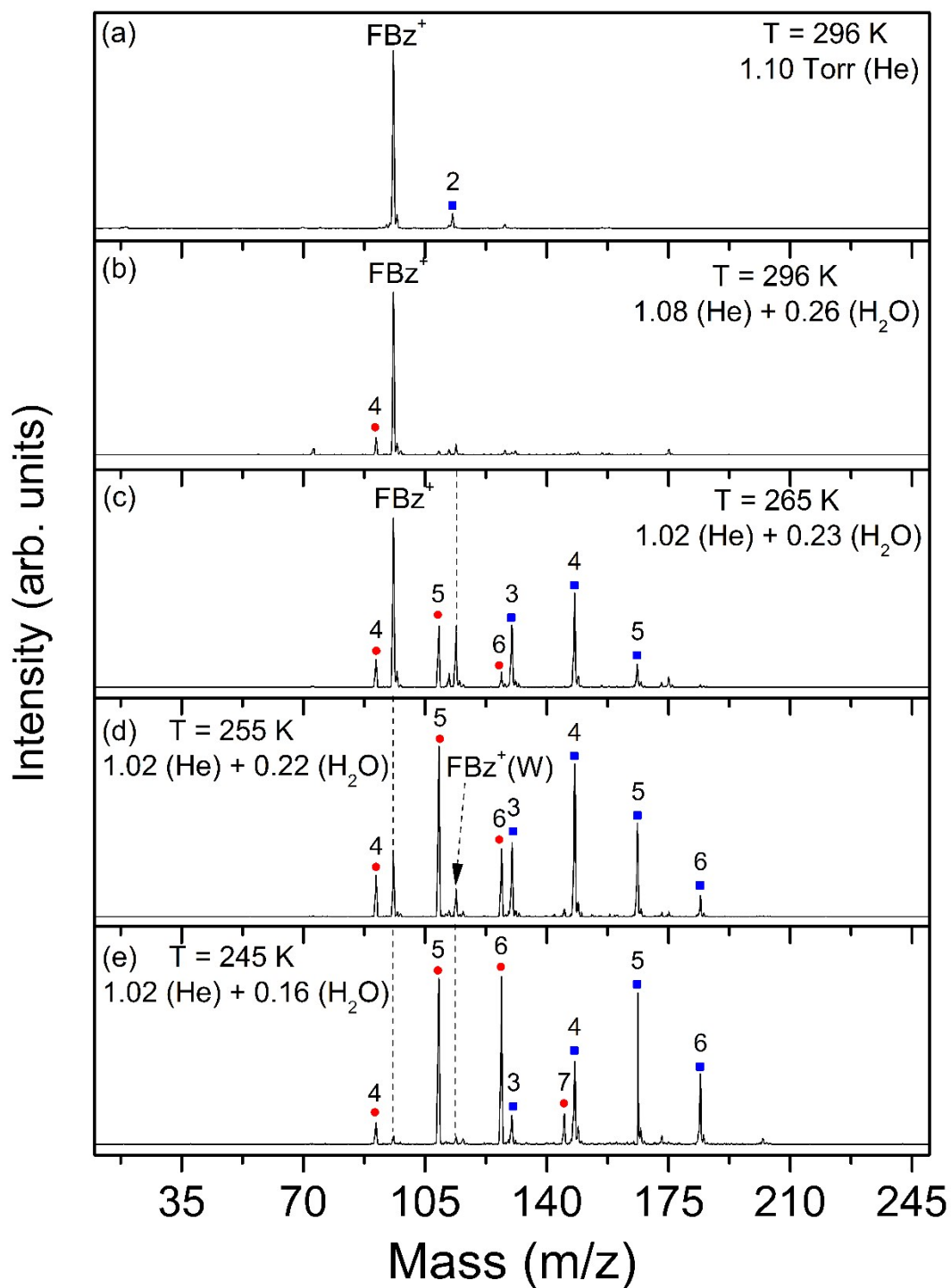
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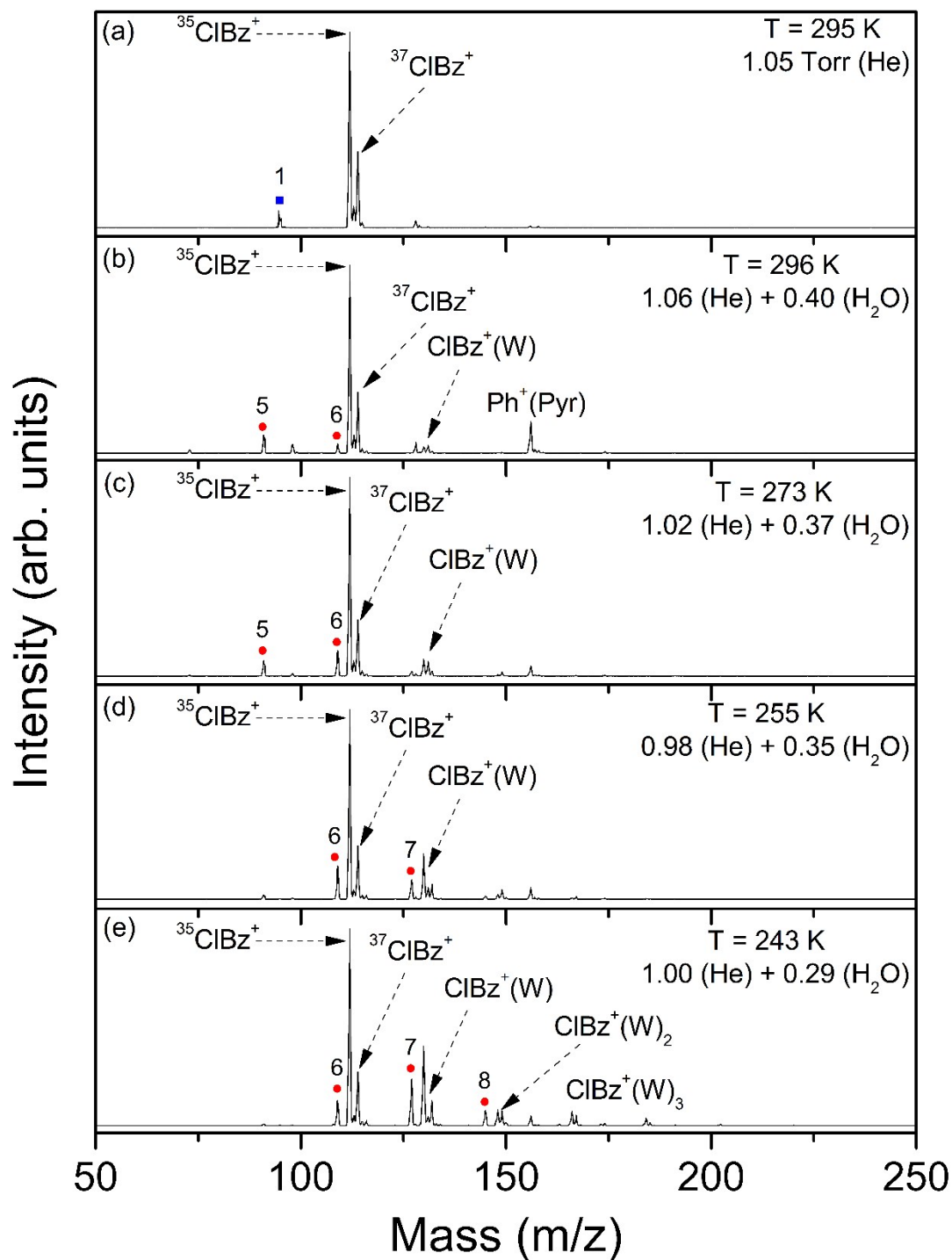
### Supporting Information



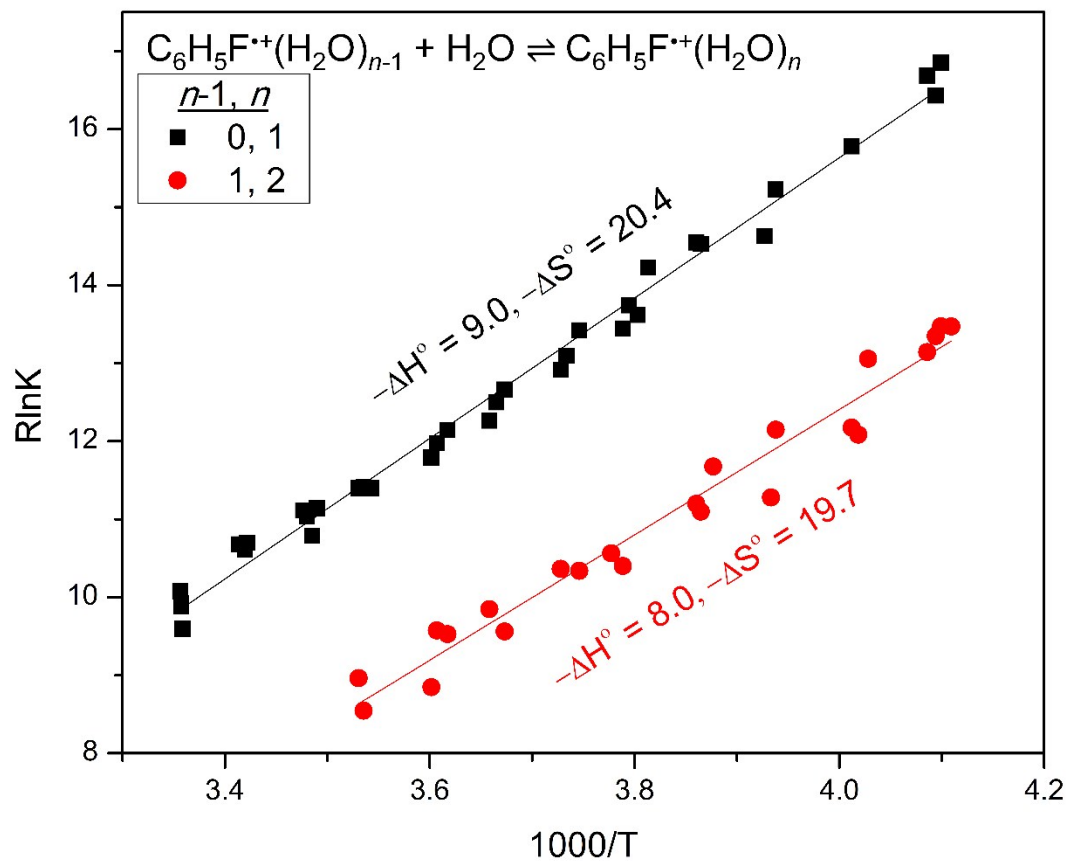
**Figure S1.** VCU mass-selected ion mobility system.



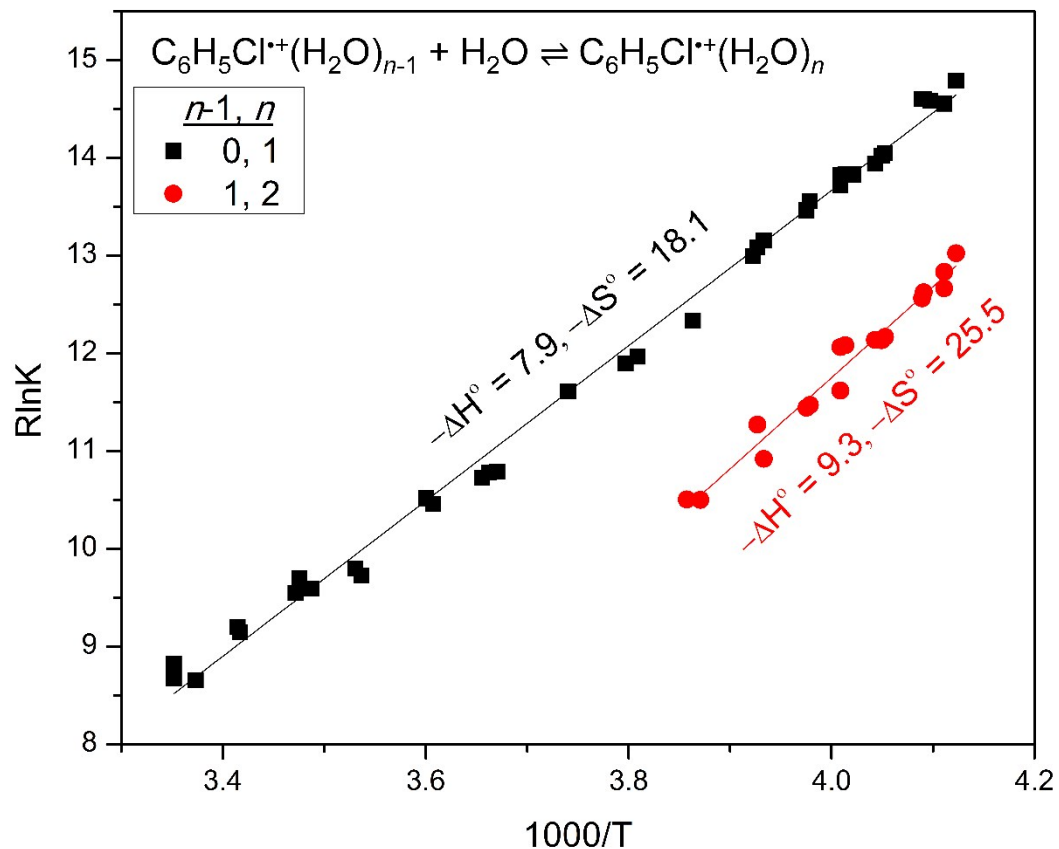
**Figure S2.** Mass spectra resulting from the injection of the mass-selected fluorobenzene radical cation ( $\text{C}_6\text{H}_5\text{F}^+$ ,  $\text{FBz}$ ) into helium gas or helium-water ( $\text{H}_2\text{O}$ ) vapor mixture at different temperatures and pressures as indicated. Red circles represent  $\text{H}^+\text{W}_n$  with  $n=4-7$  and blue squares represent  $\text{C}_6\text{H}_5^+(\text{W})_n$  with  $n=3-6$ .



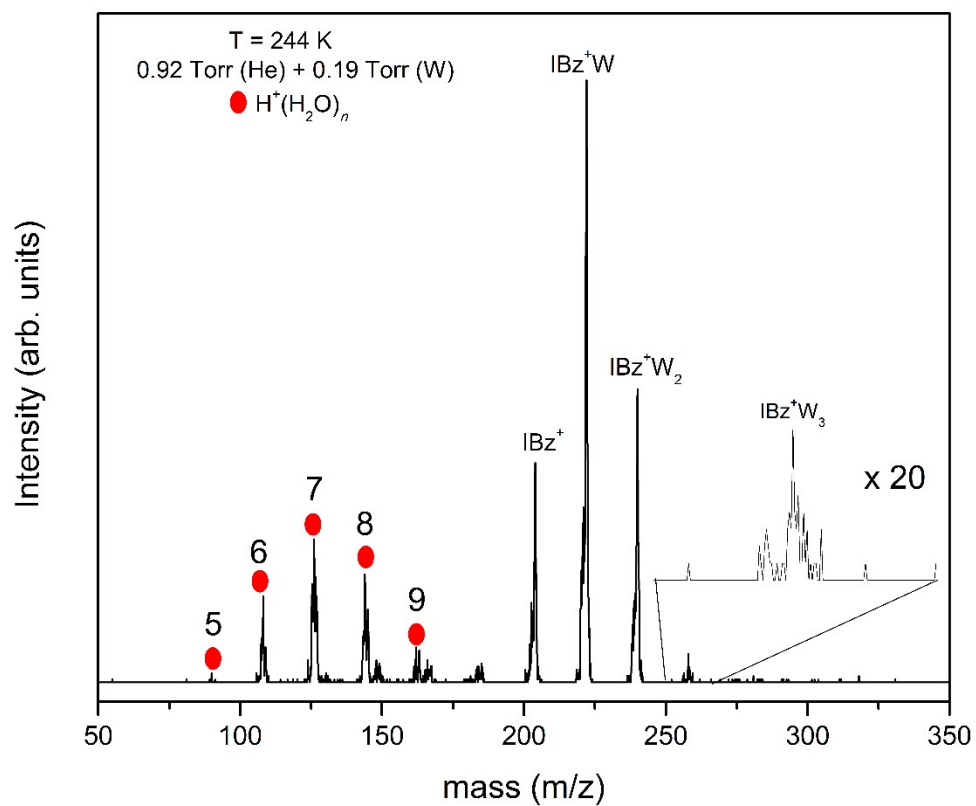
**Figure S3.** Mass spectra resulting from the injection of the mass-selected chlorobenzene radical cation ( $\text{C}_6\text{H}_5\text{Cl}^+$ ,  $\text{ClBz}$ ) into helium gas or helium-water ( $\text{H}_2\text{O}$ ) vapor mixture at different temperatures and pressures as indicated. Red circles represent  $\text{H}^+\text{W}_n$  with  $n=5-8$  and blue square represents  $\text{C}_6\text{H}_5^+(\text{W})$ .



**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<sup>-1</sup>) and (cal mol<sup>-1</sup> K<sup>-1</sup>) respectively. The error for the measurements are  $\pm 1$  kcal mol<sup>-1</sup> for  $-\Delta H^\circ$  and  $\pm 2$  cal mol<sup>-1</sup>K<sup>-1</sup> for  $-\Delta S^\circ$ .



**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<sup>-1</sup>) and (cal mol<sup>-1</sup> K<sup>-1</sup>) respectively. The error for the measurements are  $\pm 1$  kcal mol<sup>-1</sup> for  $-\Delta H^\circ$  and  $\pm 2$  cal mol<sup>-1</sup> K<sup>-1</sup> 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  $IBz^+W_3$ .