Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

The Phenoxyl Group-Modulated Interplay of Cation–π and σ-type Interactions in the Alkali Metal Series

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October 29, 2020

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1 1D curves

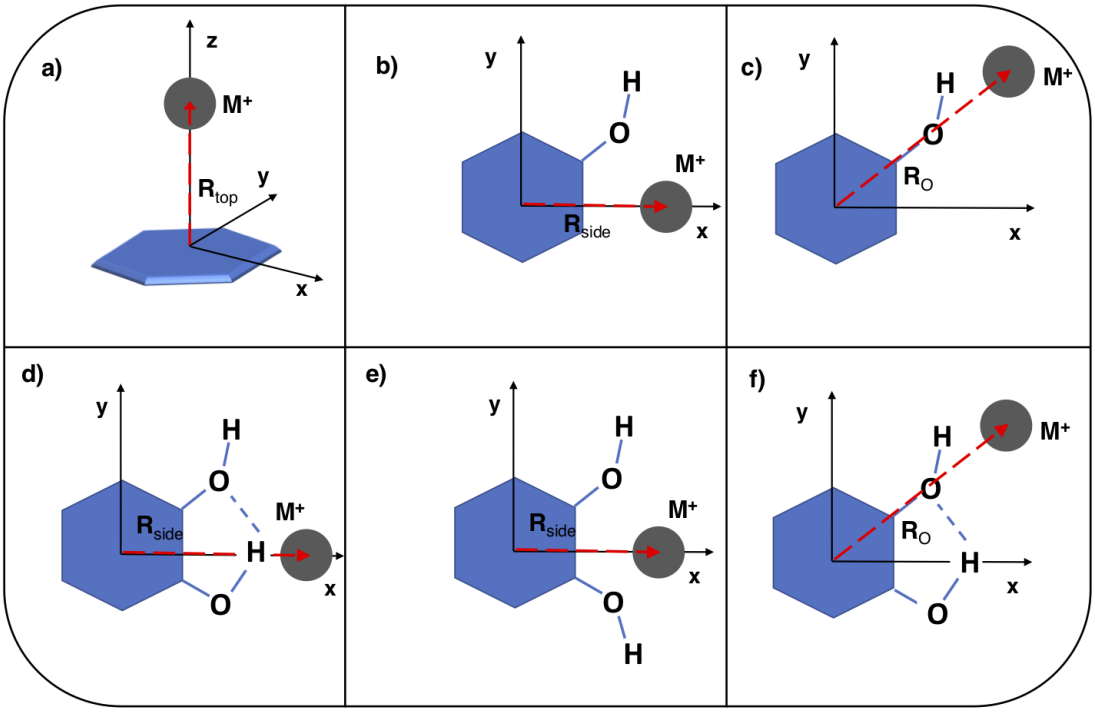

Figure S1: **R** displacement vector (red dashed arrows) of the M^+ metal ion with respect to the considered aromatic ring in different geometrical arrangements: a) $\mathbf{R}_{top}$, along the (z) direction perpendicular to the aromatic ring plane (xy) of either benzene, phenol or catechol; b) $\mathbf{R}_{side}$, along the (x) direction within the xy plane and bisecting the C=C bond of the Carbon bearing the oxygen in phenol; c) $\mathbf{R}_O$, along the vector connecting the ring center with the Oxygen in phenol; d) $\mathbf{R}_{side}$, along the (x) direction within the xy plane and bisecting the C=C bond between the Carbon bearing the oxygen in catechol, with in the H-bonded (δ=180°) conformation; e) same as d) but in the δ=0° conformation, without the internal HB; f) c) $\mathbf{R}_O$, along the vector connecting the ring center with one of the Oxygens in catechol;

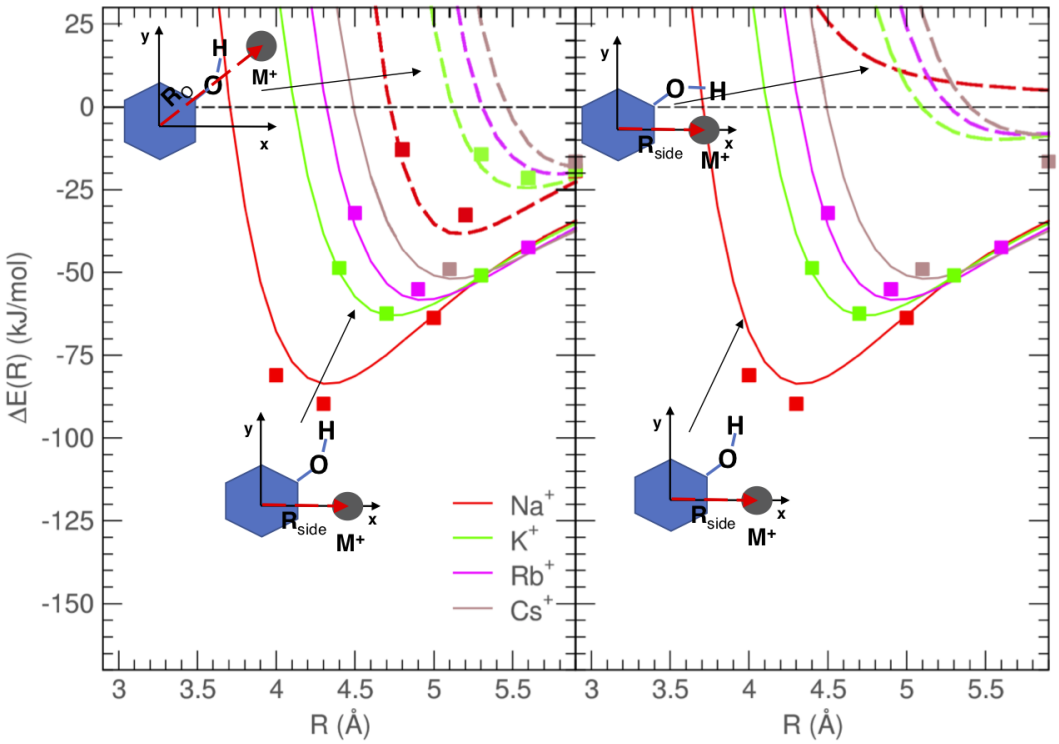

Figure S2: CCSD(T)/def2-TZVPPD (squares) and MP2^{mod} (lines) interaction energy profiles (ΔE(R)) between Na^+ (red), K^+ (green), Rb^+ (magenta) and Cs^+ (brown) cations and phenol. Left panel: metal ion approaching along R_{side} (solid lines) or R_O (dashed lines). Right panel: metal ion approaching along R_{side} with phenol in either the δ= 180° (solid lines) or δ=0° (dashed lines) conformation.

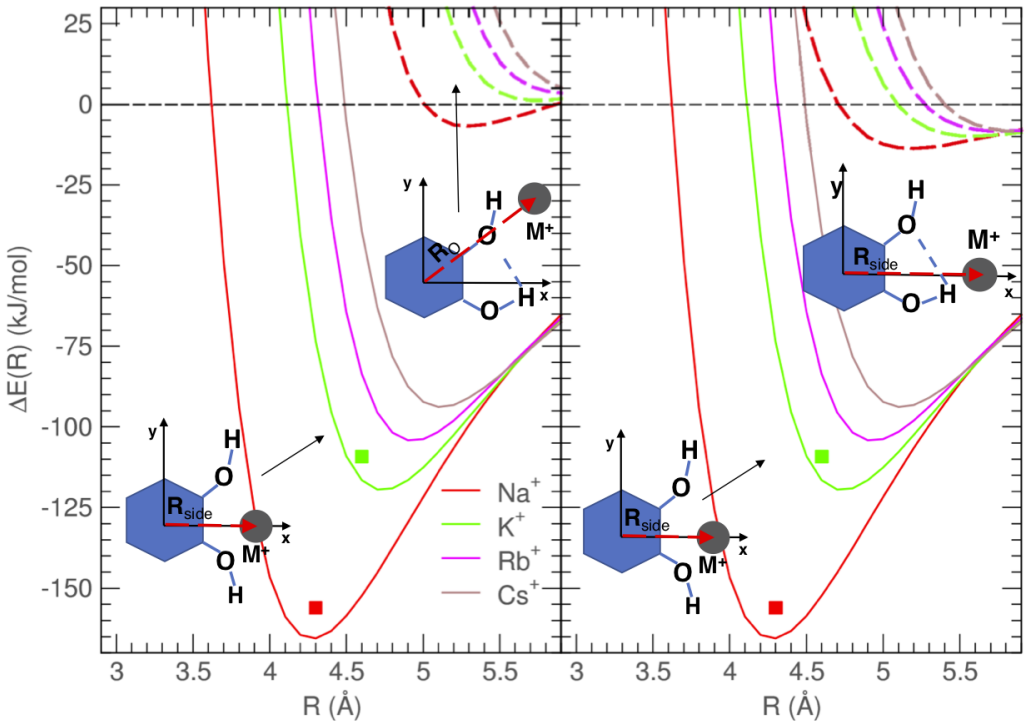

Figure S3: CCSD(T)/def2-TZVPPD (squares) and MP2^{mod} (lines) interaction energy profiles (ΔE(R)) between Na^+ (red), K^+ (green), Rb^+ (magenta) and Cs^+ (brown) cations and catechol. Left panel: metal ion approaching along R_{side} (solid lines) or R_O (dashed lines). Right panel: metal ion approaching along R_{side} with with catechol in either the δ= 180° (solid lines) or δ=0° (dashed lines) conformation.

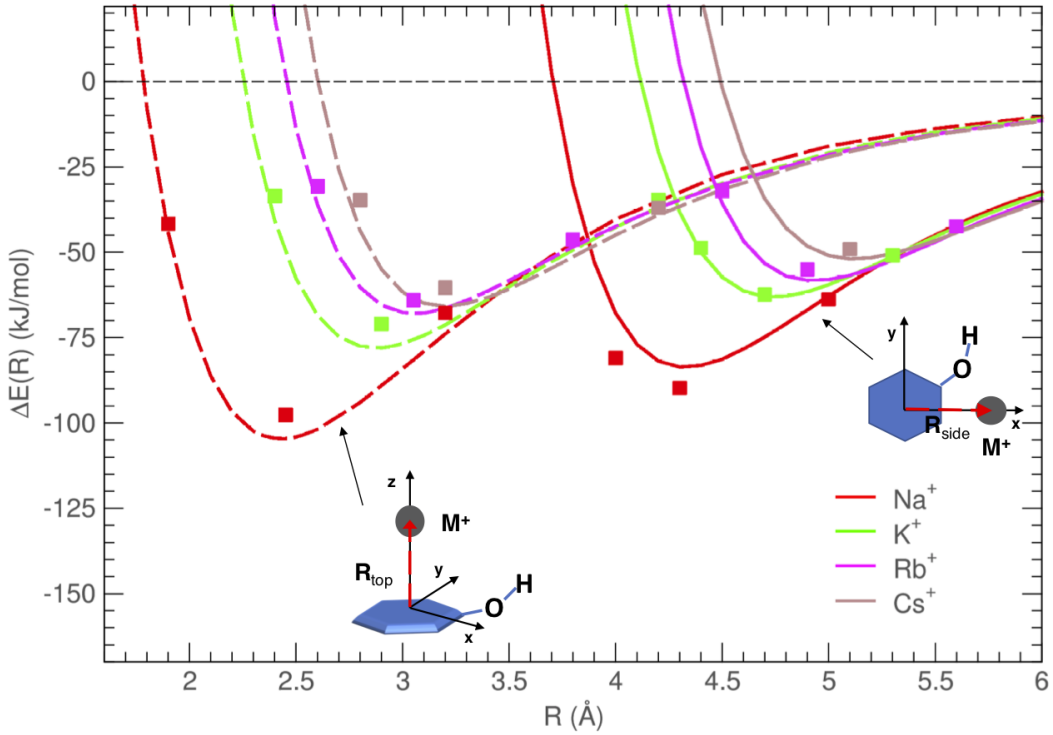

Figure S4: CCSD(T)/def2-TZVPPD (squares) and MP2^{mod} (lines) interaction energy profiles (ΔE(R)) between Na^+ (red), K^+ (green), Rb^+ (magenta) and Cs^+ (brown) cations and phenol. On the left side, as shown in the inset, metal ion approaching along R_{top} (dashed lines), whereas on the right the cation is displaced along R_{side} (solid lines).

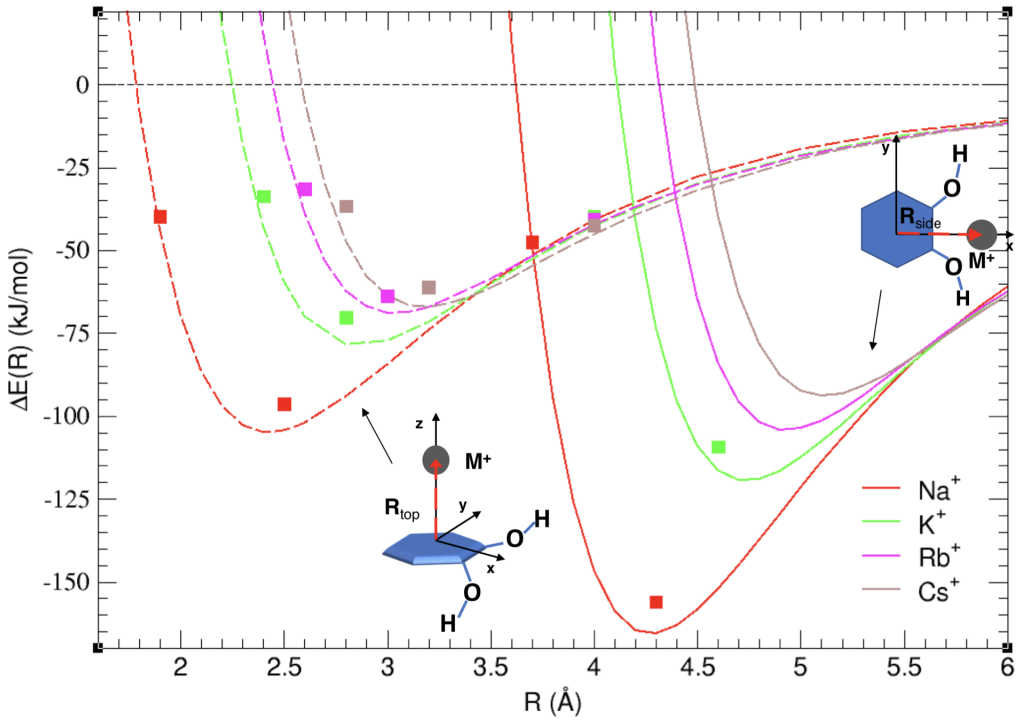

Figure S5: CCSD(T)/def2-TZVPPD (squares) and MP2^{mod} (lines) interaction energy profiles (ΔE(R)) between Na^+ (red), K^+ (green), Rb^+ (magenta) and Cs^+ (brown) cations and catechol. On the left side, as shown in the inset, metal ion approaching along R_{top} (dashed lines), whereas on the right the cation is displaced along R_{side} (solid lines).

M^+	Interaction	R (Å)	R_{O-M^+} (Å)	ΔE (kJ/mol)
Na^+	cation–π	1.90	3.35	-44.1
Na^+	cation–π	2.45	3.69	-104.6
Na^+	cation–π	3.20	4.22	-73.9
Na^+	σ-type	4.00	2.07	-67.9
Na^+	σ-type	4.30	2.30	-83.6
Na^+	σ-type	5.00	2.90	-62.9
K^+	cation–π	2.40	3.65	-40.8
K^+	cation–π	2.90	4.00	-76.0
K^+	cation–π	4.20	5.03	-37.0
K^+	σ-type	4.40	2.39	-50.1
K^+	σ-type	4.70	2.64	-61.0
K^+	σ-type	5.30	3.17	-51.2
Rb^+	cation–π	2.60	3.79	-36.2
Rb^+	cation–π	3.05	4.11	-67.9
Rb^+	cation–π	3.80	4.70	-48.5
Rb^+	σ-type	4.50	2.47	-35.8
Rb^+	σ-type	4.90	2.82	-58.2
Rb^+	σ-type	5.60	3.45	-44.2
Cs^+	cation–π	2.80	3.93	-36.2
Cs^+	cation–π	3.20	4.23	-67.9
Cs^+	cation–π	4.20	5.03	-48.5
Cs^+	σ-type	4.70	2.64	-34.4
Cs^+	σ-type	5.10	2.99	-58.3
Cs^+	σ-type	5.80	3.64	-39.7

Table A: Inter-molecular distance (R) between the metal ion and the ring center, distance between the metal ion and the neighbouring oxygen atoms (R_{O-M^+}) and MP2^{mod} interaction energy (ΔE) computed for phenol$\cdots M^+$ complexes in cation–π orσ-type selected arrangements.

M^+	Interaction	R (Å)	R_{O-M^+} (Å)	ΔE (kJ/mol)
Na^+	cation–π	2.50	3.73	-104.3
Na^+	σ-type	4.30	2.26	-165.6
K^+	cation–π	2.80	3.94	-78.4
K^+	σ-type	4.60	2.51	-116.5

Table B: Inter-molecular distance (R) between the metal ion and the ring center, distance between the metal ion and the neighbouring oxygen atoms (R_{O-M^+}) and MP2^{mod} interaction energy (ΔE) computed for catechol$\cdots M^+$ complexes in selected cation–π orσ-type arrangements.

2 Torsional energy profiles

For phenol and catechol molecules, a relaxed internal energy scan was performed as a function of the δ dihedral shown in Figure S1, by optimizing all degrees of freedom at MP2^{mod} level, but the scanned torsional angle. The resulting curves are collected in Figure S6, together with a pictorial representation of the effect of the -OH rotation on the intramolecular HB.

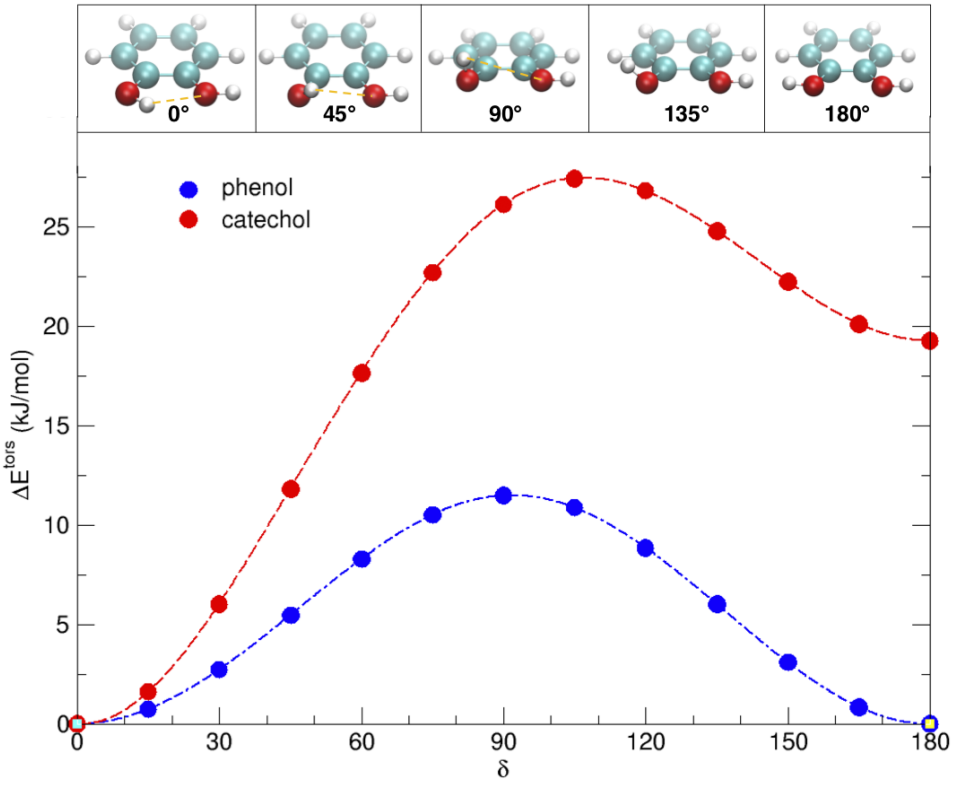

Figure S6: MP2^{mod} relaxed torsional energy (ΔE^{tors}) scan as a function of the δ dihedral around the C-OH bond in phenol (blue line) and catechol (red line). The effect of δ rotation on the intramolecular HB is shown in the top inset.

3 Interaction energy landscapes: δ dependence

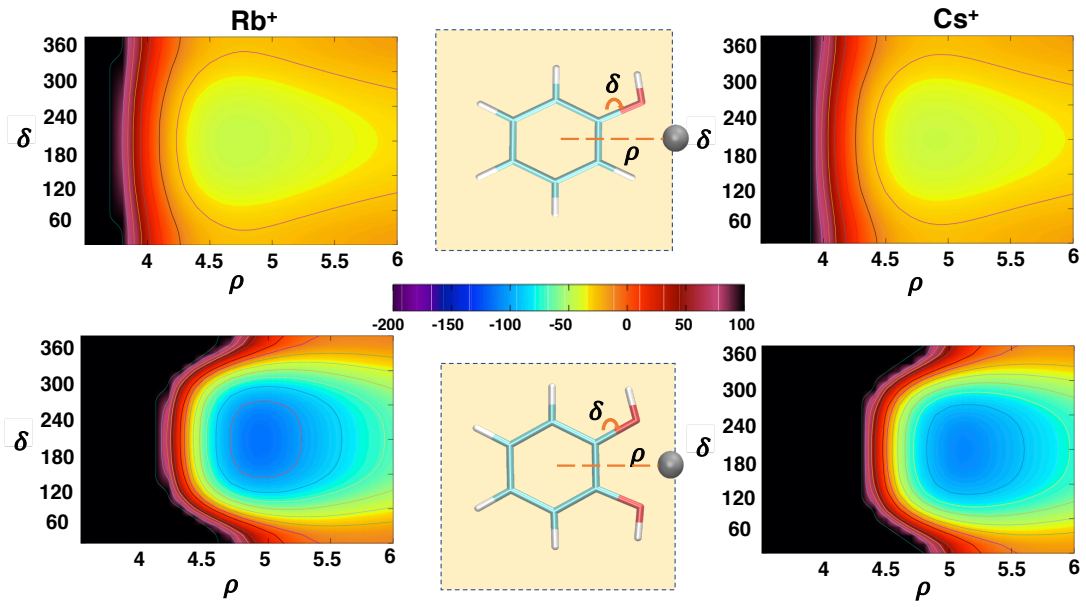

Figure S7: 2D interaction energy plots $\Delta E(\rho,\delta)$ computed at MP2^{mod} level between phenol (top) or catechol (bottom) and Rb^+(left) or Cs^+(right) cations. The sampled PES region is shown in the insets together with the investigated dihedral. In the color palette, interaction energy is reported in kJ/mol.

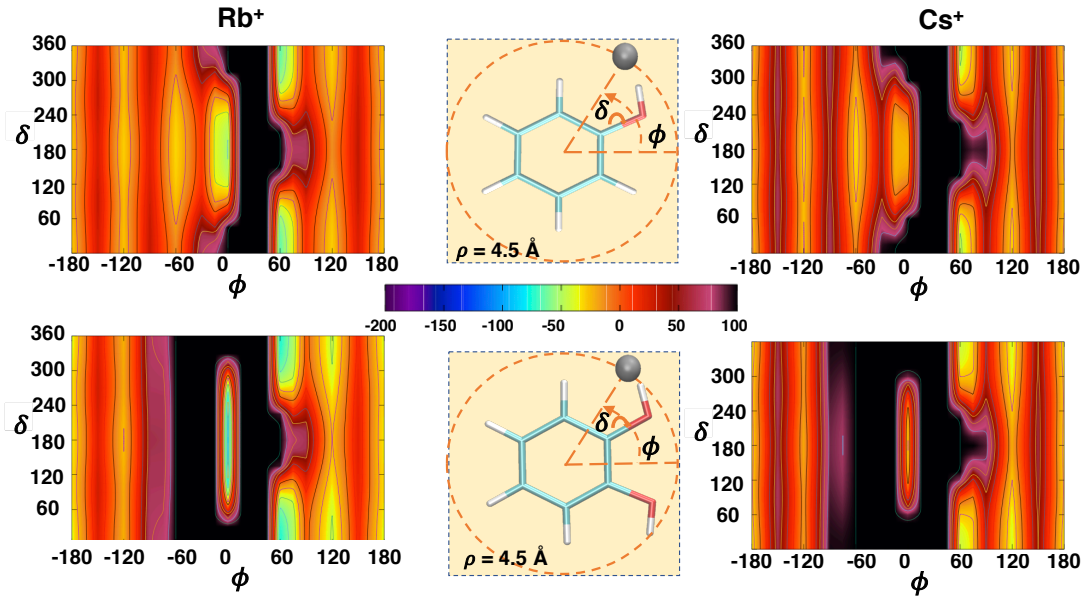

Figure S8: 2D interaction energy plots $\Delta E(\phi,\delta)$ computed at MP2^{mod} level between phenol (top) or catechol (bottom) and Rb^+(left) or Cs^+(right) cations. The sampled PES region is shown in the insets together with the investigated dihedral. In the color palette, interaction energy is reported in kJ/mol.

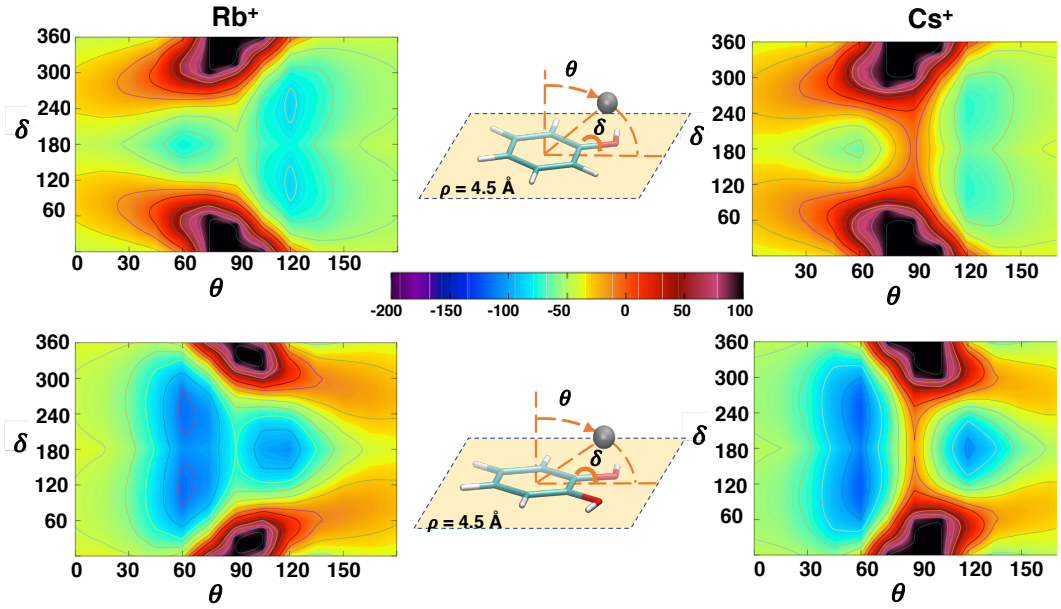

Figure S9: 2D interaction energy plots $\Delta E(\theta,\delta)$ computed at MP2^{mod} level between phenol (top) or catechol (bottom) and Rb^+(left) or Cs^+(right) cations. The sampled PES region is shown in the insets together with the investigated dihedral. In the color palette, interaction energy is reported in kJ/mol.