An Assessment of Random-phase Approximation Functional and Characteristics Analysis for Noncovalent Cation–π Interactions

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SUPPORTING INFORMATION

Table 1. Geometry optimization and topological properties of electron density (in au) of the complexes calculated at B3LYP/6-311++G** and MP2/6-311++G** levels. The point symmetry of the complex is in parentheses.

Table 2. Total energies considering zero-point vibrational energies correction (E, in Hartree/mol) and binding energies (ΔE, in kcal/mol) with the BSSE correction of the cation–benzene complexes at different theory levels.

Table 3. MEs, MAEs, and MAPEs are given using the CCSD(T)/CBS data as a reference for cation (Li^+, Na^+, Al^+ and NH_4^+)–benzene interactions.

Figure 1. Color-mapped RDG isosurface (0.5 au) graphs and scatter diagrams of RDG versus sign(λ_2)ρ of cation–benzene complexes at MP2/6-311++G** level.

Figure 2. Molecular electrostatic potential (MESP) profiles at the van der Waals surface (isosurface of electron density = 0.001 au) showing the electrophilic regions and the nucleophilic regions at MP2/6-311++G** level.

Table 1. Geometry optimization and topological properties of electron density (in au) of the complexes calculated at B3LYP/6-311++G** and MP2/6-311++G** levels. The point symmetry of the complex is in parentheses.

Methods	Complex	C–C [a]	C–H [b]	M^{n+}–centroid [c]	$\rho_{C\text{-}C}$ [d]	$\rho_{C\text{-}H}$ [e]	ρ_{BCP} [f]	$\nabla^2\rho_{BCP}$ [g]
B3LYP/6-311++G**	$Bz(D_{6h})$	1.395	1.084	—	0.3085	0.2814	—	—
	$Bz\text{-}Li^+(C_{2V})$	1.403	1.084	1.842	0.3043	0.2851	0.0172	0.0908
	$Bz\text{-}Na^+(C_{2V})$	1.401	1.084	2.408	0.3051	0.2840	0.0105	0.0489
	$Bz\text{-}Be^{2+}(C_{6V})$	1.421	1.087	1.293	0.2946	0.2867	0.0559	0.1785
	$Bz\text{-}Mg^{2+}(C_{2V})$	1.415	1.086	1.946	0.2980	0.2862	0.0262	0.1109
	$Bz\text{-}Al^+(C_{2V})$	1.402	1.084	2.445	0.3053	0.2854	0.0194	0.0248
	$Bz\text{-}NH_4^+(C_S)$	1.399	1.084	3.024	0.3062	0.2834	0.0124	0.0331
MP2/6-311++G**	$Bz(D_{6h})$	1.400	1.087	—	0.3156	0.2864	—	—
	$Bz\text{-}Li^+(C_{6V})$	1.408	1.087	1.870	0.3111	0.2901	0.0163	0.0899
	$Bz\text{-}Na^+(C_{6V})$	1.406	1.087	2.434	0.3123	0.2889	0.0098	0.0489
	$Bz\text{-}Be^{2+}(C_{6V})$	1.427	1.090	1.300	0.3014	0.2919	0.0547	0.1949
	$Bz\text{-}Mg^{2+}(C_{6V})$	1.420	1.089	1.961	0.3055	0.2911	0.0251	0.1158
	$Bz\text{-}Al^+(C_{6V})$	1.408	1.087	2.365	0.3122	0.2905	0.0206	0.0218
	$Bz\text{-}NH_4^+(C_S)$	1.405	1.087	2.951	0.3131	0.2883	0.0193	0.0551

[a] The average C–C bond length (Å) in benzene; [b] The average C–H bond length (Å) in benzene; [c] The distance (Å) between cation and the center of benzene. [d] The electron densities of the BCPs of C–C bond; [e] The electron densities of the BCPs of C–H bond; [f] The electron densities of the BCPs between cation and benzene; [g] The Laplacian of electron densities of the BCPs between cation and benzene.

Table 2. Total energies considering zero-point vibrational energies correction (E, in Hartree/mol) and binding energies (ΔE, in kcal/mol) with BSSE correction of the cation–benzene complexes at different theory levels.

Methods		$Bz\text{-}Li^+$		$Bz\text{-}Na^+$		$Bz\text{-}Be^{2+}$		$Bz\text{-}Mg^{2+}$		$Bz\text{-}Al^+$		$Bz\text{-}NH_4^+$	
		E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE
B3LYP	6-311++G**	-239.55444	-36.05	-394.33541	-22.30	-246.22589	-226.29	-431.63842	-116.02	-474.42299	-28.66	-289.10606	-14.73
	6-311 G**	-239.55355	-36.70	-394.33415	-22.78	-246.22462	-226.52	-431.63716	-116.32	-474.42142	-28.99	-289.10381	-15.05
	6-31 G*	-239.49722	-38.17	-394.27304	-25.45	-246.17522	-233.19	-431.57282	-121.27	-474.35003	-32.31	-289.01847	-15.68
MP2	6-311++G**	-238.77836	-31.03	-393.18469	-18.17	-245.44853	-212.98	-430.48461	-104.88	-473.23434	-30.10	-288.21969	-14.52
	6-311 G**	-238.77462	-33.20	-393.18045	-20.23	-245.44506	-214.53	-430.48058	-106.57	-473.22862	-31.50	-288.21286	-16.20
	6-31 G*	-238.65905	-35.20	-393.06149	-23.28	-245.34110	-224.19	-430.36157	-112.44	-473.09798	-34.26	-288.03577	-15.89
RPA@PBE[a]		-240.48411	-38.74	-395.49636	-24.89	-247.16408	-231.99	-432.99764	-122.16	-475.96441	-35.01	-290.26086	-18.33
RPA@PBE[b]		-240.48411	-38.74	-395.49642	-24.91	-247.16407	-231.95	-432.99757	-122.14	-475.96453	-35.03	-290.26081	-18.25
RPA@PBE[c]		-240.48369	-38.85	-395.49681	-25.03	-247.16392	-232.54	-432.99728	-122.64	-475.96561	-35.47	-290.26088	-18.69
RPA@PBE[d]		-240.48361	-38.98	-395.49542	-25.06	-247.16368	-233.02	-432.99665	-122.63	-475.96624	-35.69	-290.26096	-18.53
RPA@PBE[e]		-240.48365	-38.96	-395.49566	-25.07	-247.16370	-232.98	-432.99677	-122.63	-475.96654	-35.68	-290.26112	-18.61
RPA@PBE[f]		-240.48314	-38.68	-395.49636	-25.09	-247.16388	-232.60	-432.99679	-122.56	-475.96763	-35.59	-290.26098	-18.70
CCSD(T)/aug-cc-pvtz		-239.11608	-36.44	-393.53234	-21.98	-245.78865	-222.49	-430.83317	-114.15	-473.59111	-35.46	-288.66957	-18.45
QCISD(T)/aug-cc-pvtz		-239.11669	-36.44	-393.53295	-21.98	-245.78931	-222.53	-430.83382	-114.18	-473.59173	-35.47	-288.67027	-18.45

The input geometry structures of RPA@PBE[a], RPA@PBE[b] , RPA@PBE[c], RPA@PBE[d], RPA@PBE[e] and RPA@PBE[f] calculations are taken from B3LYP/6-311++G**, B3LYP/6-311G**, B3LYP/6-31G*, MP2/6-311++G**, MP2/6-311G** and MP2/6-31G*, respectively.

Table 3. MEs, MAEs, and MAPEs are given using the CCSD(T)/CBS data as a reference for cation (Li^+, Na^+, Al^+ and NH_4^+)–benzene interactions.

Methods	ME	MAE	MAPE(%)
B3LYP/6-311++G**	4.79	4.79	16.21
MP2/6-31G*	3.05	3.21	11.35
CCSD(T)/aug-cc-pVTZ	2.14	2.14	7.53
QCISD(T)/aug-cc-pVTZ	2.14	2.14	7.52
RPA@PBE/NAO-VCC-5Z	0.98	2.25	8.31
RPA@PBE*/NAO-VCC-5Z	0.71	2.05	7.69
CCSD(T)/CBS	0	0	0

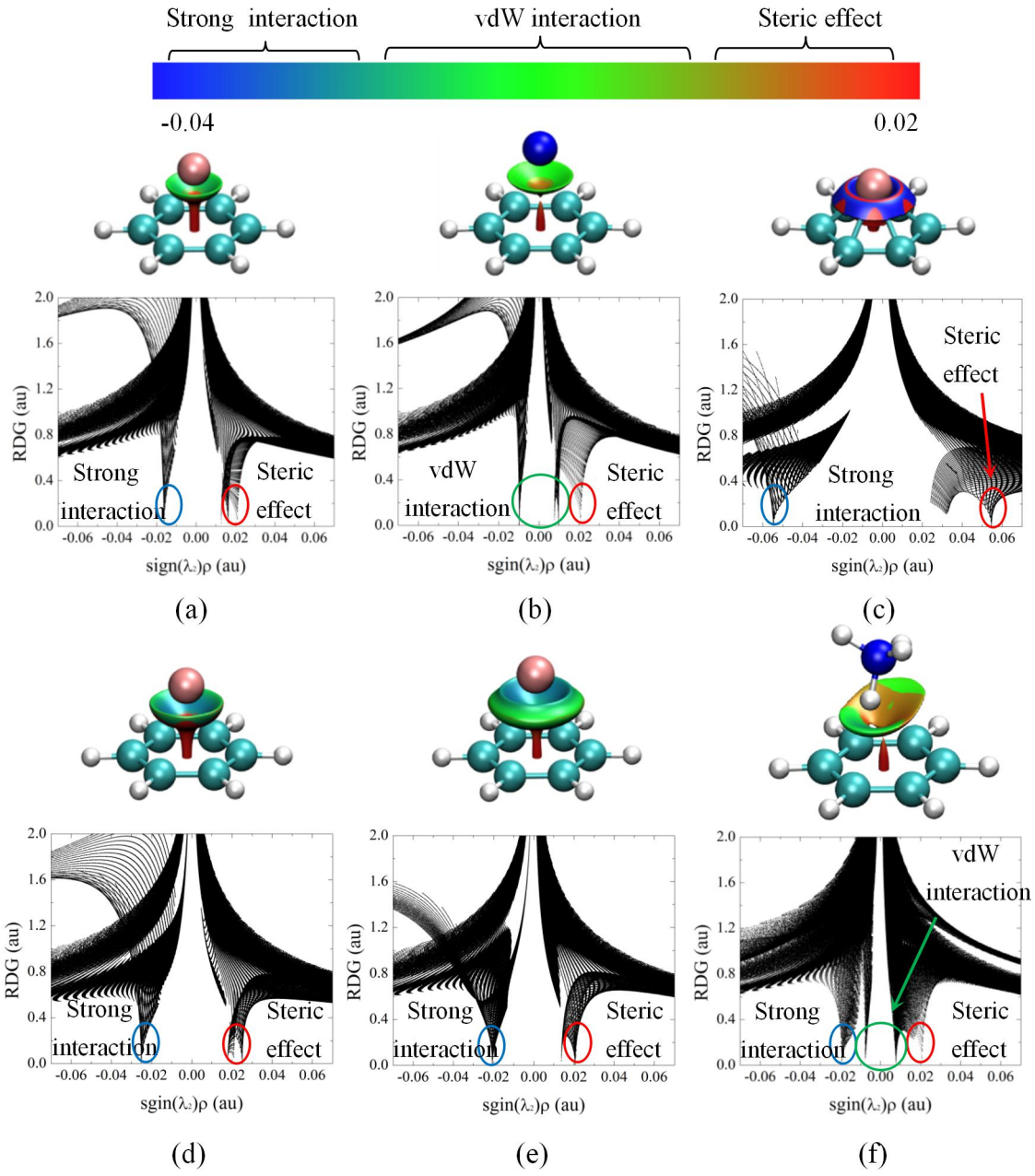

Figure 1. Color-mapped RDG isosurface (0.5 au) graphs and scatter diagrams of RDG versus sign(λ_2)ρ of cation–benzene complexes at MP2/6-311++G** level: (a) Li^+–benzene; (b) Na^+–benzene; (c) Be^{2+}–benzene; (d) Mg^{2+}–benzene; (e) Al^+–benzene; (f) NH_4^+–benzene. The value of sign(λ_2)ρ on the surface is represented by the color bar.

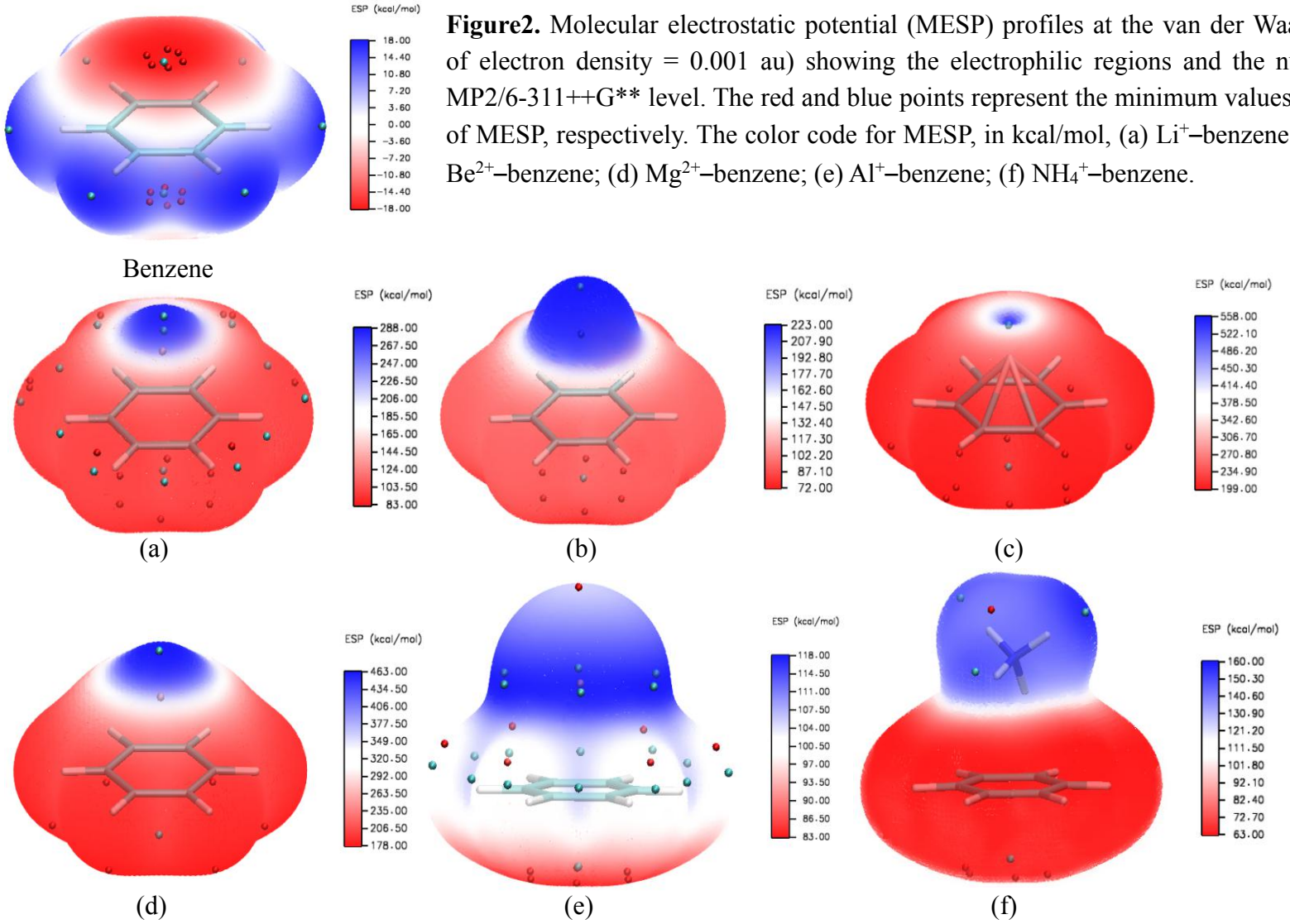

Figure2. Molecular electrostatic potential (MESP) profiles at the van der Waals surface (isosurface of electron density = 0.001 au) showing the electrophilic regions and the nucleophilic regions at MP2/6-311++G** level. The red and blue points represent the minimum values and maximum values of MESP, respectively. The color code for MESP, in kcal/mol, (a) Li^{+}–benzene; (b) Na^{+}–benzene; (c) Be^{2+}–benzene; (d) Mg^{2+}–benzene; (e) Al^{+}–benzene; (f) NH_4^{+}–benzene.