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EXPLORING THE NATURE OF NONCOVALENT INTERACTIONS BETWEEN ARENES AND IONS USING QUANTUM CHEMICAL APPROACH: IS THERE ONLY ONE WAY?

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ABSTRACT. Quantum chemical approach was used to study four different types of interactions of electron-rich and electron-deficient arenes with alkali cations and halide anions. Cation-π and C-H···anion interactions of benzene, as well as anion-π and C-F···cation interactions of hexafluoro benzene, were studied by the means of two methods of energy decomposition analysis – Symmetry Adapted Perturbation Theory (SAPT) and Extended Transition State – Natural Orbitals for Chemical Valence (ETS-NOCV). Thorough analysis showed that these decomposition methods identify induction/orbital interactions as the most dominant component of interactions with cations, while electrostatic component is the dominant one in the systems containing anions. Minor disagreements were observed in the cases of interactions with larger ions (K^+ and Br^-). Overall, SAPT and ETS-NOCV are in good agreement for interactions that include cations. Caution is needed when analyzing the nature of arene-anion interactions, where ETS-NOCV can give unusually large individual components in some cases.

Keywords: cation-π interaction, anion-π interaction, Density Functional Theory, Symmetry Adapted Perturbation Theory, Extended Transition State, Natural Orbitals for Chemical Valence, Electrostatic Potentials

INTRODUCTION

Noncovalent interactions are the interactions that hold the world together. Being hydrogen bonds, ion-π, stacking, host-guest interactions, or the hydrophobic effects, to name a few, they are present in all molecular systems, and show great importance in many fields,

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ranging from catalysis and materials (ALKORTA *et al.*, 2020; SCHNEIDER, 2022), to their biological relevance in drug design, protein folding, and DNA structure (JENA *et al.*, 2022).

Noncovalent interactions of aromatic molecules are essential for chemical and biological recognition (SALONEN *et al.*, 2011). Particular importance is that of interactions of aromatic moieties with ions. The most important ones are cation-π and anion-π interactions. Cation-π interactions have shown their outstanding relevance in many chemical and biological systems, as they are among the strongest noncovalent interactions (DOUGHERTY, 2025). Among the cation-π interactions of benzene with alkali cations, the strongest one is with Li^+, with interaction energy of about -38 kcal/mol (ĆERANIĆ *et al.*, 2025). On the other hand, anion-π interactions were considered to be counterintuitive, but were shown to be feasible for arenes containing heteroatoms and/or electron-withdrawing substituents (RATHER *et al.*, 2020). These interactions can also be very strong, e.g. anion-π interaction between hexafluorobenzene and F^- has interaction energy of about -18 kcal/mol (RATHER *et al.*, 2020). Aside from ion-π interactions, where ions are situated above the aromatic rings, arenes can interact with ions via their edges, forming, among others, C-H···anion and C-F···cation interactions (PAPP *et al.*, 2017). These interactions are somewhat weaker than ion-π interactions; C-H···anion hydrogen bond between benzene and F^- has the energy of about -16 kcal/mol, while C-F···cation interaction between and hexafluorobenzene and Li^+ has the interaction energy of about -22 kcal/mol (PAPP *et al.*, 2017).

We have analyzed and compared the nature of the four different arene-ion interactions by using the methods of quantum chemistry. Quantum chemical approach was shown to be very reliable in analyzing geometries, strengths and nature of noncovalent interactions on a molecular level (PASTORCZAK and CORMINBOEUF, 2017; HAJJI *et al.*, 2021). The usual way of studying the nature of noncovalent interactions is by decomposing the total interaction energies into physically meaningful terms (STASYUK *et al.*, 2018). In this work we have used two energy decomposition analyses. Older and more popular method is based on Symmetry Adapted Perturbation Theory – SAPT (JEZIORSKI *et al.*, 1994; HOHENSTEIN and SHERRILL, 2010; HOHENSTEIN *et al.*, 2011). On the other hand, newer method used herein to study ion-arene interactions is Extended Transition State – Natural Orbitals for Chemical Valence (ETS-NOCV) (ZIEGLER and RAUK, 1977; MICHALAK *et al.*, 2008; MITORAJ *et al.*, 2009). Although conceptually different in obtaining the results, SAPT and ETS-NOCV have terms which are complementary. This means that the results of these decompositions can be easily compared, but also that one of these approaches can serve as the confirmation of the results of the other one. Using these two quantum chemical approaches, we were able to determine the influence of electrostatic, orbital and dispersion effects on arene-ion interactions.

METHODOLOGY

In this work we have studied ion-arene dimers consisting of alkaline cations (Li^+, Na^+, K^+) or halide anions (F^-, Cl^-, Br^-) and benzene or hexafluorobenzene. Full optimizations of all dimers were done in the Gaussian 09 (version D.01) program package (FRISCH *et al.*, 2009) using the B3LYP density functional (LEE *et al.*, 1988; MIEHLICH *et al.*, 1989; BECKE, 1993; STEPHENS *et al.*, 1994) with the Grimme D3 empirical dispersion (GRIMME *et al.*, 2010) and def2-TZVP basis set (WEIGEND and AHLRICHS, 2005). Frequency calculations were done and all studied systems were shown to be true minima, since no imaginary frequencies were found. The same level of theory was used to calculate the interaction energies according to the following formula:

$$\Delta E = E_{DIMER} - (E_{ARENE} + E_{ION}) \quad (1)$$

The interaction energy was corrected for basis set superposition error using the counterpoise method by Boys and Bernardi (BOYS and BERNARDI, 1970).

Electrostatic potentials of benzene and hexafluorobenzene were obtained from Gaussian wavefunctions and were mapped on the molecular surface defined by 0.001 a.u. electron density isosurface using the WFA-SAS program (BULAT *et al.*, 2010). The local minima and maxima of electrostatic potentials were found and calculated in the MultiWFN program package (LU and CHEN, 2012; LU, 2024) using the efficient ESP evaluation algorithm adopted by this program (ZHANG and LU, 2021).

The nature of interactions was studied by decomposing the B3LYP-D3/def2-TZVP interaction energies in obtained dimers within the ETS-NOCV methodology implemented in the ORCA 6.1.0 software (NEESE, 2025). This method decomposes the total interaction energy into four components:

$$\Delta E_{ETS\text{-}NOCV} = \Delta E_{ELST} + \Delta E_{EXCH\text{-}REP} + \Delta E_{ORB} + \Delta E_{DISP} \tag{2}$$

where ELST (electrostatic), EXCH-REP (exchange-repulsion) and ORB (orbital) terms are explicitly calculated, while DISP (dispersion) energy component is D3 empirical dispersion correction.

Another method used to gain insight into the nature of these interactions was SAPT, which was performed in the PSI4 (version 1.10) program (SMITH *et al.*, 2020). These calculations were done at the SAPT0 level using the def2-TZVP basis set, since the total interaction energies derived by it showed very good agreement with the B3LYP-D3/def2-TZVP interaction energies. This method calculates four individual terms, the sum of which gives the total interaction energy:

$$E_{ELST} + E_{EXCH} + E_{IND} + E_{DISP} = E_{SAPT} \tag{3}$$

where ELST is electrostatic, EXCH is exchange energy, IND denotes induction, and DISP stands for dispersion.

RESULTS AND DISCUSSION

With the help of electrostatic potential maps of benzene and hexafluorobenzene (Fig. 1), we can explain the possibility of the four different interactions with ions. Benzene is the prototype of electron-rich aromatic ring, as evidenced by its negative electrostatic potential above the entire ring, meaning it can form cation-π interactions. Because of its positive potential on the edges in the hydrogen atom region, it can also form C-H···anion interactions. Hexafluorobenzene is the prototype of electron-deficient aromatic ring, since the six fluorine atoms pull the electron density towards them, leaving the area above the ring with positive electrostatic potential. This makes hexafluorobenzene suitable for anion-π interactions, while the negative potential around the fluorine atoms enables C-F···cation interactions.

Based on the observations of electrostatic potentials of benzene and hexafluorobenzene, 12 systems were constructed for this work (Fig. 2) to study the interactions of arenes and ions, namely alkali cations and halide anions. The optimizations yielded interactions between benzene and alkali cations exactly above the arene ring center (Fig. 2a), with cation-π distances increasing with the increase in cation size (Tab. 1), as observed in our previous study (ĆERANIĆ *et al.*, 2025). The obtained C-H···anion interaction with fluoride is linear and very short (Table 1), while the interactions with larger halides were bifurcated (Fig. 2a), which is similar to dimers obtained previously using different methodologies (PAPP *et al.*, 2017; MALENOV and ZARIĆ, 2021). Anion-π interactions have anions exactly above the arene ring center (Fig. 2b), which is similar to hexafluorobenzene-anion dimers obtained by employing Moller-Plesset Perturbational Theory of the Second Order (RATHER *et al.*, 2020). It can be, however, noted that anion-π distances of hexafluorobenzene are longer than cation-π distances of benzene (Tab. 1), which can be indicative of weaker interactions. Finally, C-F···cation interactions between hexafluorobenzene and alkali cations were all bifurcated (Fig. 2b), with increasing distance by going from Li^+ to K^+ (Table 1). Similar dimers were obtained previously using the Focal-Point Analysis method for Li^+ and Na^+ ions (PAPP *et al.*, 2017).

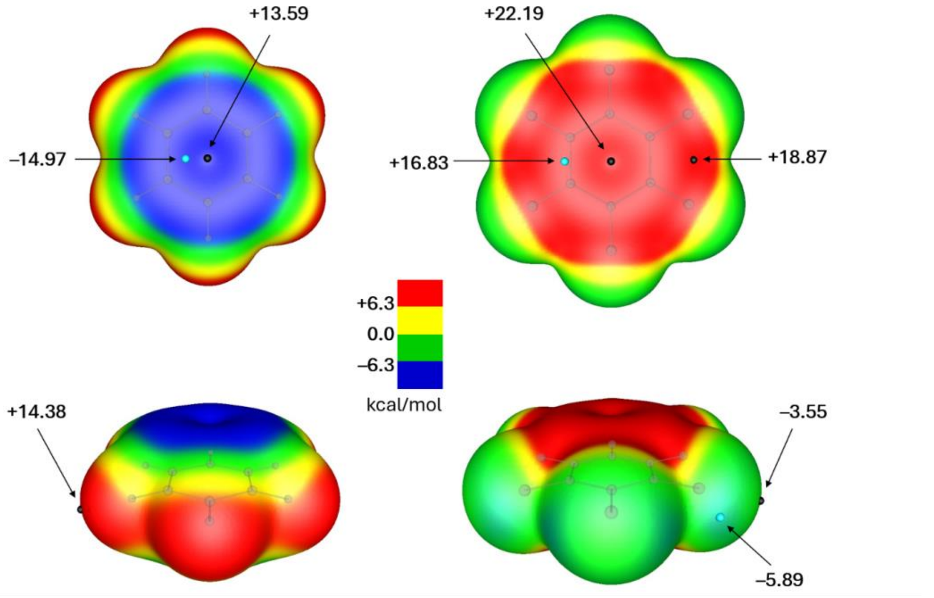

Figure 1. Electrostatic potential maps of benzene (left) and hexafluorobenzene (right) calculated at the B3LYP-D3/def2-TZVP level and mapped on the surface defined by the electron density of 0.001 a.u. The values of minima (light blue dots) and maxima (black dots) are shown in kcal/mol.

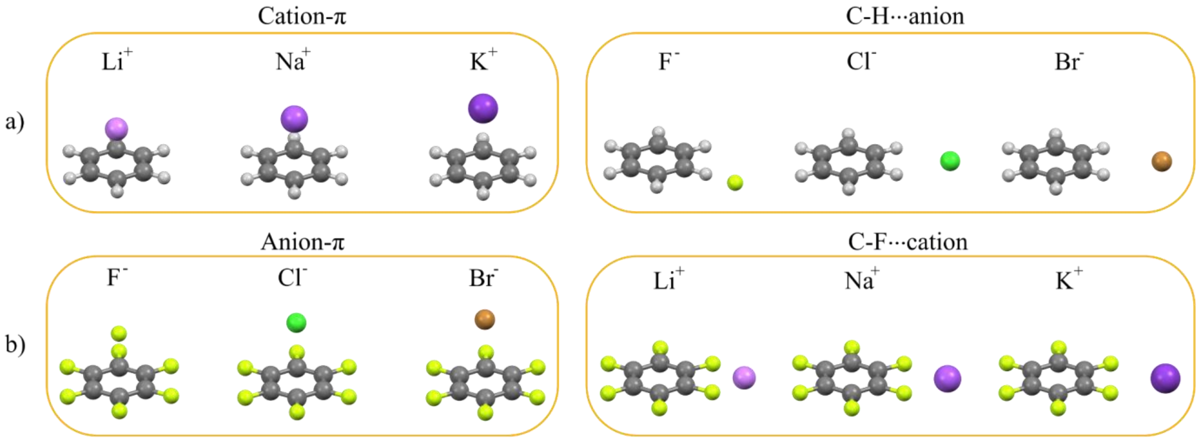

Figure 2. Optimized geometries of interactions of benzene (a) and hexafluorobenzene (b) with alkali cations and halide anions. The calculations were performed at the B3LYP-D3/def2-TZVP level of theory.

The strongest of all interactions studied in this work are cation-π, the strongest being benzene-Li^+ interaction (-39.13 kcal/mol, Tab. 1). Interactions of benzene with anions are significantly weaker, since the strongest one is less than 50% of the strength of cation-π (benzene-F^-, -18.80 kcal/mol, Tab. 1). Interactions of hexafluorobenzene with cations are weaker than those of benzene. Namely, hexafluorobenzene-Li^+ is moderately strong, with interaction energy of -26.75 kcal/mol (Tab. 1). On the other hand, hexafluorobenzene forms stronger interactions with anions than benzene, in particular with larger anions (Tab. 1). Overall, the general trend is observed – larger ions form weaker interactions with arenes, whether or not the interaction is formed above the ring or with the atoms on the edge (Tab. 1). Interestingly, all interactions obtained herein using the B3LYP-D3/def2-TZVP level of theory are stronger than similar interactions obtained in previous works using different quantum chemical approaches (PAPP *et al.*, 2017; MALENOV and ZARIĆ, 2021; ĆERANIĆ *et al.*, 2025).

Table 1. Interaction energies (ΔE) and the observed arene-ion distances (d) for all studied systems. The distance d represents the distance from the ion to the center of the ring in the case of ion-π interactions; in the case of C-H···anion and C-F···cation, it represents the average distance from the ion to the H/F atoms.

Interaction type	Arene system	Ion	ΔE kcal/mol	d Å
Cation—π	**Benzene**	Li^+	-39.13	1.851
		Na^+	-25.39	2.419
		K^+	-18.25	3.027
C-H···anion	**Benzene**	F^-	-18.80	1.561
		Cl^-	-9.14	2.728
		Br^-	-7.72	2.927
Anion-π	**Hexafluorobenzene**	F^-	-20.27	2.543
		Cl^-	-14.37	3.156
		Br^-	-12.94	3.345
C-F···cation	**Hexafluorobenzene**	Li^+	-26.75	1.946
		Na^+	-17.61	2.385
		K^+	-12.61	2.844

Two different approaches of energy decomposition analysis were employed to study the nature of these interactions – perturbative approach known as SAPT, as well as the ETS-NOCV approach, as the decomposition of an energy obtained by the means of variational principles. These two approaches are complementary, since their individual terms can be compared and used to describe the physically meaningful components of the total interaction energies.

Strictly speaking, the B3LYP-D3/def2-TZVP interaction energies reported in Table 1 were decomposed into physically meaningful terms only within the ETS-NOCV framework. The SAPT part was more challenging, since we initially had to determine the SAPT level which is capable of reproducing the B3LYP-D3/def2-TZVP interaction energies. This level turned out to be SAPT0 with the same basis set, which shows very good agreement with obtained DFT energies for benzene-ion interactions (particularly, C-H···anion, Fig. 3), while for hexafluorobenzene-ion interactions the SAPT and DFT energies show less agreement (Fig. 4), although it is quite satisfying. It is worth noting that SAPT in some cases cannot reproduce the total interaction energy for interactions of some arenes with anions (MALENOV and ZARIĆ, 2021).

Both SAPT and ETS-NOCV show that induction/orbital is a highly dominant energy component in benzene-Li^+ cation-π system (Fig. 3a). However, for cation-π interactions of benzene with larger cations, induction effects are significantly less pronounced, and electrostatic attraction becomes more important (Fig. 3a). Interestingly, the two decomposition methods disagree on the dominant energy component for benzene-Na^+ system, since SAPT favors electrostatic, while ETS-NOCV predicts orbital as the more important contribution. Both methods agree that in benzene-K^+ system electrostatic contribution is more important than induction/orbital interactions. This can be expected based on the significantly larger cation-π distance in this system (Tab. 1), which prevents significant orbital overlap. Another SAPT analysis of cation-π systems was previously reported, with similar conclusions regarding the electrostatic and induction balance in these systems (SOTERAS *et al.*, 2008). Overall, for cation-π interactions SAPT always predicts stronger electrostatics and weaker induction effects than ETS-NOCV (Fig. 3a).

C-H···anion interactions are dominated by electrostatic effects, regardless of the applied decomposition method (Fig. 3b). A similar trend in SAPT components for benzene-anion interactions was previously reported (MALENOV and ZARIĆ, 2021). However, it can be observed that ETS-NOCV electrostatics is significantly more pronounced than SAPT electrostatics (Fig. 3b). A particularly interesting system is benzene-F⁻, where both electrostatic and induction/orbital energies surpass the total interaction energy (Fig. 3b). However, this system also suffers from a very strong exchange-repulsion term, due to the very short distance between hydrogen and fluorine atoms (1.561 Å, Table 1). Although the dispersion interactions are overall very weak in benzene-ion interactions, they are somewhat more pronounced in interactions with anions, primarily on the SAPT level (Fig. 3).

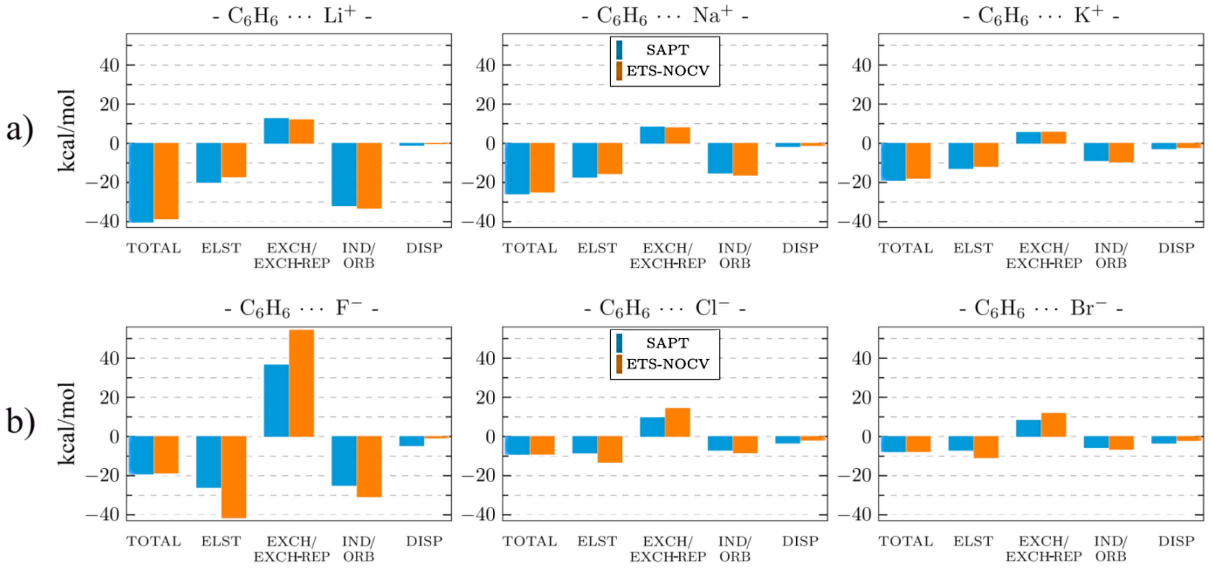

Figure 3. SAPT and ETS-NOCV decomposition analysis of energies of interactions of benzene with (a) cations and (b) anions. SAPT calculations were performed at SAPT0/def2-TZVP level of theory, while ETS-NOCV energy decomposition was performed on the B3LYP-D3/def2-TZVP interaction energies.

As previously observed in the SAPT study of hexafluorobenzene-anion systems (MALENOV and ZARIĆ, 2021), anion-π interactions are highly dominated by electrostatic effects; here we report that electrostatics are even more pronounced in the terms of ETS-NOCV decomposition (Fig. 4a). Two decomposition methods disagree on the importance of induction and dispersion in hexafluorobenzene-Br⁻ system; while SAPT favors dispersion, ETS-NOCV prefers orbital interactions (Fig. 4a). However, while ETS-NOCV does not address dispersion effects directly, but instead adds Grimme empirical dispersion, SAPT explicitly calculates dispersion and in all systems with anions gives larger dispersion contribution than herein applied D3 (Figs. 3b and 4a).

The least studied type of interactions presented in this work are C-F···cation interactions. Similar to cation-π interactions with Li^+ and Na^+, induction/orbital effects are more pronounced than electrostatic in hexafluorobenzene-Li^+ and hexafluorobenzene-Na^+ systems (Fig. 4b). Again, similar to benzene-K^+, hexafluorobenzene-K^+ system shows similarities in electrostatic and induction/orbital components (Fig. 4b), which can also be attributed to the larger distance between fluorine and potassium atoms (2.844 Å, Table 1).

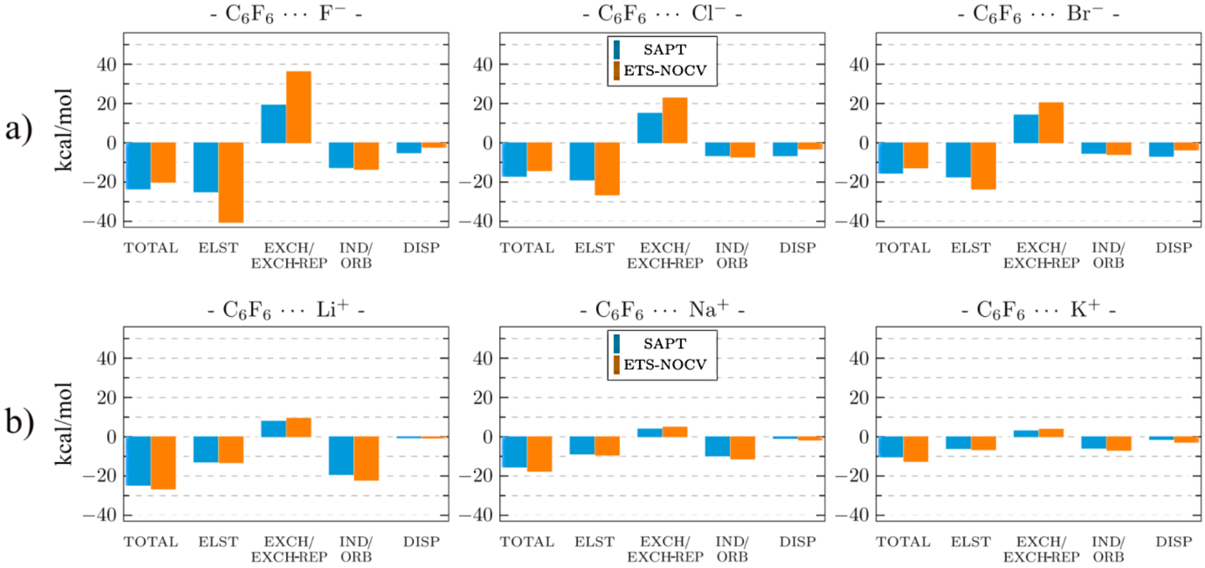

Figure 4. SAPT and ETS-NOCV decomposition analysis of energies of interactions of hexafluorobenzene with (a) anions and (b) cations. SAPT calculations were performed at SAPT0/def2-TZVP level, while ETS-NOCV decomposition was performed on the B3LYP-D3/def2-TZVP interaction energies.

When comparing the SAPT and ETS-NOCV approaches for arene-ion interactions, these methods are in both qualitative and quantitative agreement when it comes to interactions of cations (Figs. 3a and 4b). However, for interactions with anions, ETS-NOCV tends to overestimate all explicitly calculated terms, when compared to SAPT (Figs. 3b and 4a). One should therefore be careful when analyzing the nature of anion-π interactions using different energy decomposition schemes.

CONCLUSIONS

Quantum chemical methods are among the most important methods used today to study noncovalent interactions. In this paper, two of the many available quantum chemical approaches for energy decomposition analysis – perturbative SAPT and variational ETS-NOCV – were employed to study arene-ion interactions. These methods are conceptually different, but give complementary energy terms which are physically meaningful and provide insight into nature of these interactions.

Based on electrostatic potential maps of benzene and hexafluorobenzene as prototypes of electron-rich and electron-deficient arenes, we have identified four different types of interactions, namely cation-π and C-H···anion (for benzene), and anion-π and C-F···cation (for hexafluorobenzene). Density functional theory calculations on B3LYP-D3/def2-TZVP level obtained 12 dimers consisting of benzene/hexafluorobenzene and alkali cations/halide anions. Generally, both SAPT and ETS-NOCV identify induction/orbital interactions as the most dominant in cation-π and C-F···cation interactions, while anion-π and C-H···anion interactions are governed by electrostatic effects. The only notable exception to these rules among the studied systems is benzene-K^+, for which both decomposition methods indicate that electrostatics is the most dominant attractive force.

The two decomposition methods show some disagreements in their analysis of arene-ion interactions. The disagreements are mostly related to interactions with larger ions, namely K^+ and Br^-, which have larger intermolecular distances and are more challenging to assess. Overall, both SAPT and ETS-NOCV perform similarly for arene-cation interactions. However, for arene-anion interactions ETS-NOCV tends to give significantly larger individual contributions than SAPT, particularly for very small fluoride ions. These observations imply that particular caution is needed when interpreting the nature of noncovalent interactions of anions using the methods of quantum chemistry.

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