# Competition between π- and σ-based interactions in metal ion complexes of the phenyl radical

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Dedicated to Rob Dunbar in honour of his 60th birthday.

## Abstract

Hybrid density functional theory (B3-LYP and B3-PW91) and counterpoise-corrected ab initio (MP2) calculations have been performed for the adducts of the main-group metal ions $Na^+$, $Mg^+$, $Al^+$, $K^+$, and $Ca^+$ with the phenyl radical $C_6H_5$. While the calculated bond dissociation energies (BDEs) and complexation geometries of the alkali metal ion adducts do not differ substantially from those determined for the analogous $M^+$/benzene π-complexes, the alkaline earth ions exhibit a strong preference for σ-bond formation at the bare C atom of the phenyl ring, with calculated BDEs exceeding those determined for benzene complexation by approximately 80 and 150 kJ mol$^{-1}$ for $Mg^+$ and $Ca^+$, respectively. This σ-coordination is only feasible when the unpaired spins on the reactant $Mg^+$ (or $Ca^+$) and $C_6H_5$ radicals are opposed, thereby leading to a closed-shell (singlet state) adduct ion. When the unpaired spins are aligned, the triplet-state adduct thus produced adopts π-complex minimum energy geometry with a BDE significantly below that of the corresponding $M^+$/benzene complex. Both π- and σ-coordination are also found to be local minima on the $AlC_6H_5^+$ potential energy surface, with the BDE of the $Al^+$/$C_6H_5$ σ-complex being approximately 50 kJ mol$^{-1}$ larger than that of the corresponding π-complex, and about 20 kJ mol$^{-1}$ above the BDE for $Al^+$/benzene. The overall results of our study show that the phenyl radical exhibits a much greater degree of selectivity between the main-group metal ions represented here than is evident for benzene. The phenyl radical BDEs range from 59.7 ($K^+$) to 264.7 kJ mol$^{-1}$ ($Ca^+$) according to calculations at the B3-PW91/6-311+G(2df,p) level of theory, which contrasts with the 65.5 ($K^+$) to 147.9 kJ mol$^{-1}$ ($Al^+$) BDE values determined for benzene at the same level of theory.
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## 1. Introduction

The interactions between metal ions and aromatic ligands have significance in various contexts. For example, such processes are crucial in several aspects of biochemical function [1], since an extended π network on a coordinated ligand may have a propitious influence on the electronic properties of a biomolecule's central metal atom as is seen in heme groups and metalloporphyrins. Metal ion/π interactions may also play a significant role in controlling both the ionization fraction and the gas-phase depletion of the metallic elements within astrophysical environments such as dense interstellar clouds and star-forming regions [2,3], since metal ion–ligand

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complexes are much more readily neutralized (by dissociative recombination) than are atomic $M^+$ ions (by radiative recombination). For these, and for many other, reasons, the study of $M^+/\pi$ interactions has become an important niche within the fields of mass spectrometry and theoretical chemistry. In the past several years a considerable amount of attention has been brought to bear on such interactions, by the research groups of Dunbar [4–15] and others [16–46]. While much of the interest in this area focuses on the biochemically significant first-transition-row metal ions, there is nevertheless a growing body of work concerned with the factors influencing coordination of main-group metal ions to the simplest aromatic ligands [9–32]. Such metal–ligand complexes are often the most straightforward $M^+/\pi$ species for study and thus they serve as excellent models for the more complicated species of biochemical interest.

One aspect touched upon in several previous studies is the opportunity, in functionalized aromatic ligands such as phenol [7,31,47], phenylalanine [12–14], and indole [10,47], for competition between $\pi$- and $\sigma$-coordination of a metal ion. For example, the close match between the sodium cation affinities of benzene and of water (and small alcohols) [24,48,49] makes phenol, possessing both an aromatic ring and a hydroxyl group, an interesting test set for $\pi$-/$\sigma$-competition [7,31,47]. More complex functionalized aromatics such as the amino acid phenylalanine [12–14] may be sufficiently flexible to accommodate chelation by both $\pi$ (ring) and $\sigma$ (O and/or N atom) coordination. In all of these systems it is permissible to view the (main-group) metal–ligand interaction as being largely electrostatic, regardless of the mode of coordination: formation of a full metal–ligand bond with substantial covalent character is difficult to envisage.

In the present work, we attempt a different approach to $\pi$-/$\sigma$-competition, via a study of the interactions of the main-group metal ions $Na^+$, $Mg^+$, $Al^+$, $K^+$, and $Ca^+$ with the phenyl radical, $C_6H_5$. Such a study may be of interest for several reasons. First, the phenyl radical is capable of electron acceptance as well as electron donation, and so is a good candidate for formation of something approximating a metal–ligand covalent bond via $\sigma$-coordination. Second, $C_6H_5$ is an excellent prototypical species in the sense that the $\pi$- and $\sigma$-coordination sites are essentially orthogonal to, and widely separated from, each other: this is a ligand in which cooperative chelation by the $\pi$- and $\sigma$-binding sites cannot be effected without the grossest structural distortion of the ligand. Third, since full $\sigma$-bond formation requires that the metal ion formally donates an electron for pairing, the phenyl radical is a ligand which should exhibit a very high degree of selectivity, with regard to $\sigma$-coordination, between metal ions featuring lone valence electrons (for example, the alkaline earth monocations) and those lacking such a feature (exemplified by the alkali metal cations).

The only prior discussion of any of these $M^+/C_6H_5$ systems would appear to be in the context of the reactivity of Grignard reagents [50], for which the $\sigma$-complex $MgC_6H_5^+$ has been characterized by quantum chemical calculations using a modest level of theory. Other conditions under which $M^+/C_6H_5$ adduct formation may be feasible occur in reducing atmospheres, such as those of the Jovian planets, where benzene and other aromatic hydrocarbons are formed [51,52] and where much of the synthetic chemistry occurs via radical/neutral processes, driven by (solar) photolysis. The outer-planetary atmospheres are periodically subjected to meteoritic infall, during which ablative ionization of metal atoms is an important process [53,54]. In this regard, the reactivity of metal ions with abundant radicals may provide an important loss mechanism for $M^+$ [55] and may also have transient, or perhaps longer-lasting, influences on the more general chemical evolution in such environments.

## 2. Theoretical methods

Optimized geometries, harmonic vibrational frequencies and zero-point vibrational energies for all species were obtained using Becke's 3-parameter (B3) exchange functional [56] in conjunction with either the Lee-Yang-Parr (LYP) [57] or the Perdew-Wang 1991 (PW9l) [58] correlation functional, in all instances

with the triple-split-valence 6-311+G** basis set. The B3-LYP/6-311+G** optimized geometries were used in subsequent single-point calculations using B3-LYP or second-order Møller-Plesset perturbation theory (MP2) [59,60], while the B3-PW91/6-311+G** geometries were employed in B3-PW91 single-point calculations. In all cases these single-point calculations used the 6-311+G(2df,p) basis set. For the MP2 single-point calculations, a 'thawed' correlation space [61], including the metal atom's 'inner-valence' electrons—i.e., 2s and 2p for Na, Mg, and Al, 3s and 3p for K and Ca—was used. This method of partitioning between 'core' and 'valence' electrons has been found to yield consistently superior results compared to the implementation of a standard 'frozen core' in calculations featuring main-group metal ions [61–64]. For the MP2(thaw)/6-311+G(2df,p) calculations we have also determined full counterpoise (CP) corrections, in accordance with recent recommendations for metal cation affinity (MCA) calculations [65,66].

To assist in evaluation of the accuracy of the methods described above, we have also performed calculations using these methods for a 'test set' of smaller $M^+$-containing adduct ions for which we have also evaluated $M^+$/ligand bond dissociation energies using more refined methods. The CP-dG2thaw method [66], used on the $Na^+$-, $Mg^+$- and $Al^+$-containing members of the 'test set', is a modified version of Gaussian-2 (G2) theory [67] and follows the methodology which has previously been described for compounds containing these metal atoms [55,66]. Similarly, the composite CP-G2 technique used for $K^+$ and $Ca^+$-containing members of the 'test set' has been previously described [55,65,68]. These two methods are generally expected to have an accuracy of $\pm 10 \, \text{kJ mol}^{-1}$ or better. For example, the CP-dG2thaw method, when applied to sodium cation affinities (SCAs) [66], exhibits a level of agreement with the most recent experimental SCA 'ladder' [48] which is comparable to that seen between high-level composite methods (e.g., G2) and experimental values for proton affinities [69,70].

The GAUSSIAN98 program suite [71] was used for all calculations reported herein.

## 3. Results and discussion

### 3.1. Assessment of methodologies for a 'test set' of metal ion–ligand complexes

Previous theoretical studies on metal-ion ligation have focused heavily on the performance of various theoretical methods as assessed against high-precision experimental data for the SCAs of various small molecules [24,48,49,61,64–66,72–74]. Such studies have shown exceptionally good agreement with experiment when MP2(full)/6-311+G(2d,2p)//MP2(full)/6-31G* calculations are employed [48,49,74], with inclusion of a counterpoise correction determined using the method of Boys and Bernardi [75]. However, studies on these sodium cation binding energies have also suggested that very large basis sets are required to obtain convergence in calculations featuring electron correlation, with the most intensive calculations performed on $Na^+$-containing adducts [24,76,77] delivering metal cation binding energies consistently about $5 \, \text{kJ mol}^{-1}$ (or ~5%) larger than the values obtained in the most recent series of experimental studies [48,49,74]. There are thus some indications that the existing SCA scale (of endorsed laboratory measurements) is slightly compressed relative to the true energy scale for this parameter. In a recent extensive study of SCA calculations [66], we found that the CP-dG2thaw composite computational technique [66]—which includes high levels of electron correlation, and features large basis sets specifically modified to perform reliably for Na-containing cations [66]—consistently yielded values about $3 \, \text{kJ mol}^{-1}$ larger than corresponding values in the existing SCA ladder [48]. In the present study, the ligands of interest are too large for calculations at the CP-dG2thaw level to be practicable, and we have opted to use more economical methods, namely second-order Møller-Plesset perturbation theory (MP2) as well as the hybrid density functionals B3-LYP [56,57] and B3-PW91 [56,58], in all cases with the 6-311+G(2df,p) basis set.

Our adopted basis set in these calculations is not greatly different from that in the MP2(full)/6-311

Table 1

Comparison of the metal cation affinities of ammonia, water, hydrogen fluoride, and neon, calculated at the B3-LYP/6-311+G(2df,p), MP2(thaw)/6-311+G(2df,p) (including and excluding counterpoise correction) and CP-dG2thaw (or CP-G2) levels of theory

| $M^+$ | Ligand | MCA/kJ mol$^{-1}$[a] | | | | |
|-------|--------|----------------------|---|---|---|---|
| | | B3-LYP/ 6-311+G(2df,p) | B3-PW91/ 6-311+G(2df,p) | MP2(thaw)/ 6-311+G(2df,p) | CP-MP2(thaw)/ 6-311+G(2df,p) | CP-dG2thaw or CP-G2 |
| $Na^+$ | $NH_3$ | 112.1 | 106.8 | 111.0 | 100.9 | 104.3 |
| $Na^+$ | $H_2O$ | 99.0 | 93.7 | 99.9 | 88.3 | 90.0 |
| $Na^+$ | HF | 68.6 | 63.5 | 69.8 | 59.9 | 61.7 |
| $Na^+$ | Ne | 7.0 | 4.8 | 8.2 | 1.8 | 5.1 |
| $Na^+$ | $C_2H_2$ | 59.2 | 54.8 | 56.8 | 51.7 | 53.7 |
| $Na^+$ | $C_2H_4$ | 59.2 | 54.9 | 57.4 | 52.0 | 53.7 |
| $Mg^+$ | $NH_3$ | 157.9 | 157.1 | 158.7 | 150.6 | 151.1 |
| $Mg^+$ | $H_2O$ | 131.5 | 128.7 | 132.8 | 119.6 | 121.7 |
| $Mg^+$ | HF | 77.9 | 73.8 | 76.6 | 65.9 | 68.9 |
| $Mg^+$ | Ne | 3.0 | 1.4 | 2.3 | −3.0 | 0.6 |
| $Mg^+$ | $C_2H_2$ | 75.0 | 76.1 | 72.0 | 67.9 | 70.3 |
| $Mg^+$ | $C_2H_4$ | 76.3 | 77.4 | 73.9 | 69.7 | 71.7 |
| $Al^+$ | $NH_3$ | 137.0 | 144.2 | 141.8 | 134.3 | 134.5 |
| $Al^+$ | $H_2O$ | 111.2 | 114.5 | 114.2 | 101.0 | 103.9 |
| $Al^+$ | HF | 59.7 | 59.2 | 59.2 | 50.4 | 52.9 |
| $Al^+$ | Ne | 2.0 | 0.2 | 2.4 | −2.5 | 1.8 |
| $Al^+$ | $C_2H_2$ | 57.0 | 64.0 | 59.0 | 55.5 | 54.1 |
| $Al^+$ | $C_2H_4$ | 56.2 | 63.2 | 59.4 | 55.9 | 54.6 |
| $K^+$ | $NH_3$ | 75.3 | 73.1 | 76.9 | 74.0 | 72.1 |
| $K^+$ | $H_2O$ | 70.0 | 66.9 | 72.1 | 68.7 | 64.9 |
| $K^+$ | HF | 49.5 | 45.8 | 50.7 | 48.7 | 46.5 |
| $K^+$ | Ne | 2.6 | 1.4 | 3.4 | 1.7 | 2.6 |
| $K^+$ | $C_2H_2$ | 33.9 | 32.0 | 35.9 | 34.6 | 34.3 |
| $K^+$ | $C_2H_4$ | 32.9 | 31.1 | 35.5 | 34.1 | 33.8 |
| $Ca^+$ | $NH_3$ | 134.6 | 131.5 | 120.0 | 115.1 | 115.5 |
| $Ca^+$ | $H_2O$ | 119.9 | 114.4 | 106.2 | 100.5 | 99.5 |
| $Ca^+$ | HF | 75.6 | 68.4 | 63.0 | 59.9 | 59.3 |
| $Ca^+$ | Ne | 5.5 | 0.4 | 0.7 | −0.2 | 0.4 |
| $Ca^+$ | $C_2H_2$ | 58.1 | 56.0 | 47.7 | 45.5 | 46.7 |
| $Ca^+$ | $C_2H_4$ | 56.2 | 54.5 | 47.2 | 45.0 | 46.9 |

[a] Calculated metal cation affinity, at the indicated level of theory, at 0 K.

+G(2d,2p) method employed by Ohanessian and co-workers [48,72,74] in their studies on the 'new' SCA scale. We have assessed the B3-LYP/6-311+G(2df,p), B3-PW91/6-311+G(2df,p), and MP2(thaw)/6-311+G(2df,p) levels of theory via calculations on a 'test set' of metal cation affinities (MCAs) of small neutrals (see Table 1). This table also includes the corresponding CP-dG2thaw (for M = Na, Mg, and Al) and CP-G2 (for M = K and Ca) values obtained using B3-LYP/6-311+G** optimized geometries and ZPE values—that is, the same level of geometry optimiza-

tion and frequency calculation as we have used in our calculations on the $M^+$/phenyl radical adducts. The counterpoise-corrected G2-based metal cation affinities may well still suffer some residual inaccuracy—for example, we have previously inferred [66] that CP-dG2thaw is likely to systematically underestimate the theoretical 'complete basis set' limit for sodium cation affinity values by about 3%. Nevertheless, the CP-dG2thaw and CP-G2 values provide a more consistent basis of comparison for the more economical MP2, B3-LYP and B3-PW91 methods than is possible

by assessment against the extant (experimental) literature values for the same quantities.

Comparison of the values in Table 1 reveals the following trends:

1. For all species, MP2(thaw)/6-311+G(2df,p) delivers larger values of the metal cation affinity than are obtained using CP-dG2thaw or CP-G2. This trend is often reversed, and agreement with the higher-level method is generally improved, after inclusion of counterpoise corrections in the MP2(thaw)/6-311+G(2df,p) calculated values.
2. The magnitude of the counterpoise corrections to the MP2(thaw) energies is much greater when M = Na, Mg, or Al than when M = K or Ca, for a given ligand. Notably larger counterpoise corrections are determined for the lone-pair-donors $NH_3$, $H_2O$, and HF than for the $\pi$-donors $C_2H_2$ and $C_2H_4$.
3. For all species except $K^+/C_2H_2$ and $K^+/C_2H_4$, the B3-LYP/6-311+G(2df,p) metal cation affinities are larger than the analogous CP-dG2thaw or CP-G2 values.
4. The B3-LYP/6-311+G(2df,p) and MP2(thaw)/6-311+G(2df,p) values are generally in good agreement, with the notable exception of the $Ca^+$ binding energies where B3-LYP exceeds MP2(thaw) by 4.8 kJ mol$^{-1}$ (for $Ca^+$/Ne) to 14.6 kJ mol$^{-1}$ (for $Ca^+/NH_3$). Close accord between the (counterpoise-corrected) MP2(thaw) values for this metal ion and the corresponding CP-G2 values suggests that the B3-LYP values in this instance are systematically too large.
5. The B3-PW91/6-311+G(2df,p) values for the alkali metal cation affinities are (perhaps fortuitously) very close to the CP-dG2thaw or CP-G2 values, with the greatest discrepancy among these 12 quantities being the 3.7 kJ mol$^{-1}$ difference in the $H_2O$ sodium cation affinities obtained by these methods. For the magnesium and calcium cation affinities, B3-PW91 generally delivers better agreement with CP-dG2thaw or CP-G2 than does B3-LYP, though both of the hybrid DFT methods appear to overestimate these values. For the Al cation affinities, B3-PW91 shows a more pronounced tendency than does B3-LYP to overestimate the CP-dG2thaw values, with B3-PW91 exceeding CP-dG2thaw by $\sim$10 kJ mol$^{-1}$ for all ligands except Ne.

The assessment embodied in Table 1 suggests that the CP-MP2(thaw)/6-311+G(2df,p) level of theory should provide metal cation affinities with an accuracy generally not more than 5 kJ mol$^{-1}$ poorer than that attainable with much more computationally intensive methods, while the use of either B3-LYP or B3-PW91 with the 6-311+G(2df,p) basis set, in the absence of counterpoise correction, will still lead to reasonably reliable results, most often apparently an overestimation of the 'true' value.

### 3.2. Calculations of $M^+$/benzene binding energies

For the $M^+$/benzene complexes, we report the optimized geometries (Table 2; see also Fig. 1) and calculated binding energies (Table 3) obtained in the present work. These complexes, for which (in most instances) previous experimental and theoretical data have been reported, provide a basis for assessment of our present methodologies with respect to their performance for metal/aromatic ligand binding energies.

Analysis of the $M^+/C_6H_6$ binding energies (Table 3) reveals that the CP-PMP2/6-311+G(2df,p) values show excellent agreement with the lowest-uncertainty experimental measurements for benzene binding to $Mg^+$ [22], $Al^+$ [9], and $K^+$ [21,78], and with the cluster of recent measurements for $Na^+$ [21,48,49,79]. Significant disagreement with experimental measurements is evident only with the largest reported value of the $Na^+$/benzene binding energy of 115.5 ± 6.3 kJ mol$^{-1}$ [80], determined in 1983 by high-pressure mass spectrometry (HPMS). The latter result is one of a set of HPMS measurements of sodium cation affinities for several ligands [80] which appear, by comparison with recent measurements by several other groups [48,49,66,74] (and using a variety of experimental and refined theoretical techniques), to exhibit a systematic error of +15–20 kJ mol$^{-1}$.

Table 2

Key geometric features of $M^+$/benzene and $M^+$/phenyl adducts, obtained from B3-LYP/6-311+G** and B3-PW91/6-311+G** calculations

| Metal | $MC_6H_6^+$ | | $MC_6H_5^+$ $\pi$-complex | | $MC_6H_5^+$ $\sigma$-complex | |
|---|---|---|---|---|---|---|
| | $r(M–X)$[a,b] | $\angle(MXC)$[a,b] | $r(M–X)$[a,b] | $\angle(MXC)$[a,b] | $r(M–C)$[a] | $\angle(MCX)$[a,c] |
| Na | 2.409; 2.409 | 90.0 | 2.435; 2.435 | 88.2; 88.2 | 2.558; 2.588 | 0 |
| Mg | 2.325; 2.293 | 90.0 | _[d] | _[d] | 2.075; 2.067[d] | 0[d] |
| | | | 2.361; 2.324[e] | 87.9; 88.9[e] | 2.478; 2.474[e] | 23.2; 25.0[e] |
| Al | 2.447; 2.365 | 90.0 | 2.479; 2.393 | 88.9; 89.4 | 1.972; 1.955 | 0 |
| K | 2.891; 2.876 | 90.0 | 2.923; 2.906 | 86.9; 87.3 | 2.984; 2.995 | 0 |
| Ca | 2.636; 2.596 | 90.0 | _[d] | _[d] | 2.197; 2.184[d] | 31.9; 32.3[d] |
| | | | 2.663; 2.617[e] | 88.3; 88.7[e] | 2.661; 2.656[e] | 0 |

[a] Optimized geometric parameter (distances in Å, angles in degrees). The values given are those obtained from B3-LYP and B3-PW91 optimizations, respectively.

[b] $X = C_6$ ring centroid. The phenyl ring centroid X is defined as the midpoint of the C(2)C(3)C(5)C(6) trapezium. See Fig. 1.

[c] For $\sigma$-complex geometries, X is an arbitrary point located on the C(1)C(4) axis. See Fig. 1.

[d] Singlet $MC_6H_5^+$ adduct.

[e] Triplet $MC_6H_5^+$ adduct.

Our own calculated sodium cation affinity value for benzene supports this scenario.

Comparison of our benzene metal cation affinities with previous theoretical measurements shows generally good agreement, when such pre-existing values include correction for basis set superposition error (BSSE), although this agreement does not in itself guarantee that the methods in question have converged; note that our counterpoise-corrected values for the $Na^+$ and $K^+$ binding energies underestimate the benchmark complete basis set (CBS) extrapolations of Feller and co-workers [23,24], at the CCSD(T) level of theory, for these parameters by between 8 and $10 \, kJ \, mol^{-1}$. One component of this underestimation is presumably the tendency for counterpoise corrections to overestimate the magnitude of BSSE [48,65], but there appears to be scope for underestimation due to other aspects of basis set
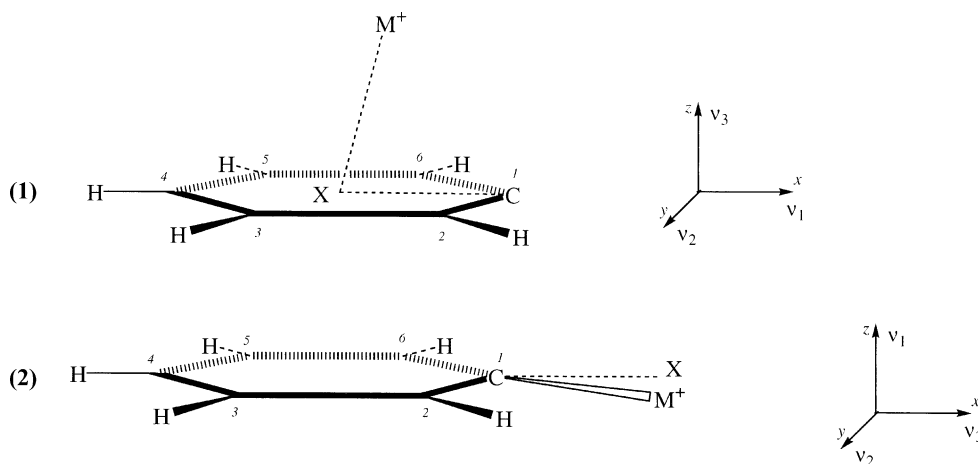


Fig. 1. Schematic diagrams of (1) the generalized $\pi$-complex and (2) the generalized $\sigma$-complex optimized geometry for $MC_6H_5^+$ species studied in the present work. All stationary points found on the respective potential energy surfaces possess at least $C_s$ symmetry. Axis system diagrams for each structural type also show the principal axis of displacement for the three lowest vibrational modes in the adducts, as tabulated in Table 4.

Table 3

Calculated metal cation affinities (MCA), at 0 K, for benzene and for the phenyl radical, obtained from B3-LYP, B3-PW91, UMP2(thaw), PMP2(thaw), and CP-PMP2(thaw) calculations with the 6-311+G(2df,p) basis set

| Adduct formula[a] | MCA/kJ mol⁻¹ (this work) | | | | | lit. kJ⁻¹ mol⁻¹ | |
|---|---|---|---|---|---|---|---|
| | B3-LYP[b] | B3-PW91[b] | UMP2[c,d] | PMP2[c] | CP-PMP2[c] | Experimental[e] | Theoretical[f] |
| $NaC_6H_6^+$ $(\pi)$ | 97.8 | 95.8 | 104.7 | [g] | 92.9 | 115.5 (6.3),[h] 88.3 (4.3),[i] 94.5 (4.4),[j] 92.6 (5.8),[k] 95.4 (5.8)[l] | *90.6*[m], *89.4*[n], 101.3(1.3)[o] |
| $MgC_6H_6^+$ $(\pi)$ | 129.7 | 140.8 | 149.2 | 149.5 | 138.6 | 134.1(9.6),[p] 155(23)[q] | *132.2*[r] |
| $AlC_6H_6^+$ $(\pi)$ | 126.2 | 147.9 | 160.8 | [g] | 149.9 | 151(29),[s] 147.3(8.4)[t] | 163.2,[u] 149.0[v] |
| $KC_6H_6^+$ $(\pi)$ | 65.9 | 65.5 | 77.9 | [g] | 73.9 | 76.2(6.0),[w] 73.3(3.8)[k] | 67.3,[m] 83.7(1.7)[o] |
| $CaC_6H_6^+$ $(\pi)$ | 111.2 | 116.1 | 117.6 | 117.8 | 111.5 | | |
| $NaC_6H_5^+$ $(\pi)$ | 90.9 | 88.0 | 109.3 | 97.0 | 85.9 | | |
| $^3MgC_6H_5^+(\pi)$[x] | 118.6 | 128.9 | 164.1 | 120.3 | 110.3 | | |
| $AlC_6H_5^+$ $(\pi)$ | 114.9 | 135.4 | 184.4 | 149.5 | 139.3 | | |
| $KC_6H_5^+$ $(\pi)$ | 60.4 | 59.7 | 80.3 | 71.2 | 67.6 | | |
| $^3CaC_6H_5^+(\pi)$ | 101.1 | 105.8 | 129.0 | 88.4 | 82.8 | | |
| $NaC_6H_5^+$ $(\sigma)$[x] | 69.2 | 63.4 | 64.0 | 62.0 | 56.4 | | |
| $^1MgC_6H_5^+(\sigma)$ | 227.4 | 218.1 | 348.2 | 261.2 | 254.2 | | |
| $^3MgC_6H_5^+(\sigma)$[x] | 74.0 | 75.4 | 75.8 | 47.0 | 42.0 | | |
| $AlC_6H_5^+$ $(\sigma)$ | 168.9 | 181.5 | 207.3 | 190.2 | 181.4 | | |
| $KC_6H_5^+$ $(\sigma)$[x] | 43.5 | 40.6 | 42.3 | 41.4 | 39.9 | | |
| $^1CaC_6H_5^+(\sigma)$ | 256.6 | 264.7 | 350.8 | 263.8 | 258.3 | | |
| $^3CaC_6H_5^+(\sigma)$[x] | 74.5 | 71.8 | 58.5 | 30.6 | 27.8 | | |

[a] Mode of metal–ligand coordination ($\pi$- or $\sigma$-complex) is indicated in parentheses.

[b] Geometry optimized (and zero-point vibrational energy calculated) using this hybrid DFT method, with a 6-311+G** basis set.

[c] Obtained using the B3-LYP/6311+G** optimized geometry.

[d] As implemented in GAUSSIAN98, 'UMP2' indicates spin-unrestricted calculations on open-shell-systems and spin-restricted calculations on closed-shell systems.

[e] Experimental literature value for MCA($C_6H_6$), with ascribed uncertainty in parentheses.

[f] Theoretical literature value for MCA($C_6H_6$). Values which include a counterpoise correction for basis set superposition error are italicized.

[g] By definition, for a closed-shell system (in the absence of an instability at the unrestricted Hartree-Fock level), the PMP2 value is equal to the UMP2 value in this instance.

[h] High-pressure mass spectrometry (HPMS) measurement [80], adjusted to 0 K [79].

[i] Threshold collision-induced dissociation (CID) measurement, from guided ion beam mass spectrometry (GIB-MS) [49].

[j] HPMS measurement [48], adjusted to 0 K [79].

[k] CID measurement, from GIB-MS [21].

[l] Competitive CID measurement, from GIB-MS [79].

[m] MP2(full)/6-311+G** calculations [20].

[n] MP2(full)/6-311+G(2d,2p) calculations [74].

[o] Estimated complete basis set limit at the CCSD(T) level of theory [24].

[p] CID measurement, from GIB-MS [22].

[q] Radiative association kinetics measurement, modelled using variational transition state theory calculations (RA-VTST) [11].

[r] MP2(full)/6-311+G(2d,2p) calculations [22].

[s] CID measurement, from GIB-MS [16].

[t] RA-VTST measurement [9].

[u] MP2(fc)/6-31G** calculations [17].

[v] G2 calculations [19].

[w] HPMS measurement [78].

[x] This stationary point is a transition structure as indicated by the presence of an imaginary mode in B3-LYP and B3-PW9l frequency calculations.

incompleteness or due to a failure of the method of electron correlation (here MP2 theory) to fully describe the $M^+$/ligand interaction.[1] No experimental or theoretical values appear to have been reported for the $Ca^+$/benzene binding energy. The very good agreement which we see with accepted experimental binding energies for the other metals ions gives us confidence in recommending our $Ca^+$/benzene binding energy value of $111.5\,kJ\,mol^{-1}$, obtained from our CP-PMP2/6-311+G(2df,p) calculations.

When assessing our $M^+$/benzene calculations excluding counterpoise correction, we find that, for the doublet metal ions $Mg^+$ and $Ca^+$, the difference between unrestricted (U) and projected unrestricted (P) second-order Møller-Plesset calculations is very small, showing negligible spin contamination in these adducts. Spin contamination does not impinge on the (formally spin-restricted) calculations on the singlet $Na^+$, $Al^+$ and $K^+$ adducts. As with our calculations on the 'test set' (Table 1), the influence of BSSE is seen to be greater with the second-row metal ions than with $K^+$ and $Ca^+$, and it is apparent that inclusion of a counterpoise correction is required to bring the MP2 binding energies into agreement with the most recent experimental results for $Na^+$, $Mg^+$, and $Al^+$. Basis set superposition error is generally regarded (see, e.g., [18]) as being less problematic in density functional theory calculations (e.g., our B3-LYP and B3-PW91 calculations) than in post-Hartree-Fock (e.g., MP2) treatments, and this is consistent with the observation that our B3-LYP and B3-PW91 values for $M^+$/benzene are uniformly smaller than the corresponding uncorrected MP2 values. Agreement between B3-LYP and B3-PW91 is excellent for the alkali metal ions, fair for $Ca^+$, and poor for $Mg^+$ and $Al^+$ with benzene. The $Al^+$/benzene system is known to be very poorly treated by B3-LYP

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[1] The tendency for 'mid-level' computational approaches to yield better agreement with experiment, for alkali metal ion binding energies, than is afforded by the most highly computationally intensive computational methods, is troubling and clearly warrants further investigation. In the present work, however, we regard the experimental values as collectively representing the best absolute yardsticks for assessment of our computational methods.

[18] as are $Al^+$ binding energies to other aromatic ring systems [18], and our B3-PW91 value clearly shows superior agreement with the CP-PMP2 value and with experiment. B3-PW91 is also much better than B3-LYP in reproducing the CP-PMP2 value for $Mg^+$/benzene, although both DFT methods agree with the lowest-uncertainty experimental value. On balance, B3-PW91 shows the better general agreement with our counterpoise-corrected MP2 binding energies and with experiment for $M^+$/benzene, and this observation becomes significant, in the analysis described below, of the $M^+$/phenyl radical adducts for which no extant experimental data exist and for which spin contamination of the MP2 calculations is highly problematic.

### 3.3. Calculations of $M^+$/phenyl radical binding energies

For the $M^+$/$C_6H_5$ complexes, optimized geometries (Table 2; see also Fig. 1) and calculated binding energies (Table 3) are given. Superficial analysis of the reported geometries shows that loss of a hydrogen atom from benzene does not significantly influence the $\pi$-binding complex geometry with regard to metal–ligand orientation.

While we have recorded the MP2 energies for $M^+$/phenyl in Table 3, we caution that the influence of spin contamination in all of these cases appears to render the MP2 values highly unreliable. This is most starkly exemplified by the discrepancy between UMP2 and PMP2 binding energies for the singlet $MC_6H_5^+$ (M = Mg, Ca) adducts, for which the discrepancy between unrestricted and projected unrestricted values is $87.0\,kJ\,mol^{-1}$ in both instances. The identical discrepancies do not arise from mere coincidence: in these systems, the extent of spin contamination in calculations on bare $M^+$ is negligible, spin contamination in closed-shell, singlet $MC_6H_5^+$ is formally zero, and the difference in UMP2 and PMP2 values hence almost totally reflects the difference in UMP2 and PMP2 total energies for the phenyl radical itself, which has an expectation value of $\langle S^2 \rangle = 1.35$ at this level of theory (compared to

$\langle S^2 \rangle = 0.75$ for a pure doublet electronic state). That the discrepancies between UMP2 and PMP2 binding energies are generally smaller for those systems producing doublet or triplet $MC_6H_5^+$ adducts merely indicates a tendency towards partial cancellation of the spin-contamination-induced errors in the total energies of reactants and products in these systems.

If the MP2-derived binding energies are not acceptable for $M^+$/phenyl, we must in these cases resort to DFT calculations, which are generally found not to suffer significantly from spin contamination. The present results conform to this trend, with both B3-LYP and B3-PW91 consistently delivering expectation values for doublet species (e.g., $C_6H_5$ and $NaC_6H_5^+$) of 0.75–0.76, while the expectation values for the triplet ($Mg^+$ and $Ca^+$) adducts are also very close to the ideal triplet value of $\langle S^2 \rangle = 2.00$. We suggest (based on its performance for the 'test set' in Table 1, and for $MC_6H_6^+$ in Table 3) that B3-PW91 is the superior method for our purposes, although we note that, as seen also for $M^+$/benzene, the only substantial discrepancies evident between B3-LYP and B3-PW91 for the $M^+$/phenyl adducts are for $Mg^+$ and $Al^+$. Binding energies for the $M^+/C_6H_5$ $\pi$-complex are uniformly smaller than for $M^+/C_6H_6$, with the smallest difference between phenyl and benzene binding energies being $5.8\,kJ\,mol^{-1}$ (for $K^+$) and the largest gap of $20.4\,kJ\,mol^{-1}$ (for $Mg^+$) according to B3-PW91. Coordination at the radical site of $C_6H_5$, by formation of $\sigma$-complex, is found to be unfavorable with respect to $\pi$-coordination for the alkali metal ions and for the triplet-state adducts containing $Mg^+$ or $Ca^+$, with the $\sigma$-complex 'transition structure' representing a barrier to phenyl ring traversal ranging from $19.1\,kJ\,mol^{-1}$ (for $K^+$) to $53.5\,kJ\,mol^{-1}$ (for $Mg^+$, triplet adduct). This barrier height is substantially less than that typically associated with the analogous 'contra-binding rotation' inversion of the $M^+/C_6H_6$ complex, as has been modeled for the example of $Al^+$ by Stockigt [19]. Presumably, the reduction in barrier height reflects the geometric accessibility of the bare C atom in the phenyl ring, permitting traversal at a substantially lower $M^+$/ring centroid separation than is possible in $M^+/C_6H_6$.

Formation of a $\sigma$-complex is seen to be energetically preferred over $\pi$-complexation in $Al^+/C_6H_5$, and for the two alkaline earth metals when a singlet-state complex is formed. These three systems represent the only instances among the present complexes where $\sigma$-bond formation by valence-electron pairing of metal- and ligand-based electrons is feasible. For $Al^+$, the $\sigma$- and $\pi$-complexes coexist as minima on the doublet potential energy surface, with a transition state to isomerization lying $18.6\,kJ\,mol^{-1}$ above the higher-energy ($\pi$-complex) isomer at the B3-PW91/6-311+G(2df,p) level of theory. For $Mg^+$ and $Ca^+$, the minima for the two modes of coordination occupy separate electronic manifolds. The difference in $\sigma$- and $\pi$-complex minimum binding energies is greatest for $Ca^+$ ($158.9\,kJ\,mol^{-1}$) and least for $Al^+$ ($46.1\,kJ\,mol^{-1}$), consistent with expectations of the relative 'cost' of bond formation associated with promotion of two valence 3s orbitals to sp-hybridization (for $Al^+$), of one valence 3s orbital to sp-hybridization (for $Mg^+$), and of one valence 4s orbital to 3d or to sd-hybridization (for $Ca^+$).

The $M^+$/phenyl results can be usefully interpreted in the wider context of metal–ion interactions with substituted benzenes. Of such systems, $M^+$/phenol is probably the most intensively studied: recent DFT results have been reported for $Na^+$, $Mg^+$, and $Al^+$ [7], the latter two of which have also been studied in an ion cyclotron resonance study [47], and additional MP2(full)/6-311+G(2d,2p) calculations and guided ion beam MS CID results have been obtained for $Na^+$ and $K^+$ [31], as well as for other metal ions not featured in the present work. Amunugama and Rodgers have also reported CID results, again using GIB-MS, and computational values for $Na^+$ and $K^+$ with toluene, fluorobenzene, aniline, and anisole [28–30,32], while the photodissociation spectroscopy of $Mg^+/C_6H_5F$ has been interpreted as showing the presence of at least two isomers [25], a view which is broadly consistent with the theoretical studies on this system [29]. One conclusion drawn from such studies is that, for the cation/$\pi$ interaction, the ligand's permanent dipole moment $\mu_D$ is largely irrelevant. For toluene, fluorobenzene, phenol and

anisole $\mu_D$ lies in the ring plane, while for aniline the out-of-ring-plane component of $\mu_D$ is minor [30]. Consequently, $\mu_D$ plays no direct role in moderating the interaction between the metal ion and the aromatic $\pi$-cloud. Systematic variations in the BDEs of $M^+/C_6H_5X$ systems, relative to $M^+$/benzene, are attributed to the influence of the ligand's quadrupole moment and its polarizability, with the inference that ion-quadrupole interactions are generally dominant [29]. Expressed in more qualitative terms, substituents which are electron-withdrawing (such as F) reduce the $\pi$-electron density and therefore also reduce the metal ion binding energy [29], while electron-donating substituents ($CH_3$, $NH_2$, OH, $OCH_3$) strengthen the cation/$\pi$ interaction [28,30–32]. The reduction in BDEs for $M^+$/phenyl radical $\pi$-complexes relative to $M^+$/benzene is entirely consistent with this overall view. The formal 'radical site' at the bare C atom of phenyl can be considered as an electron-withdrawing group, since resonance structures involving delocalization of the unpaired electron around the ring do contribute to the overall character of the radical and result in a reduction in $\pi$-electron density. The apparent lack of any direct involvement by the radical's dipole moment (it may be argued that the dipole moment manifests itself in the dilution of the $\pi$-cloud, leading indirectly to a reduction in $M^+$/ligand bond strength) is also consistent with the very minor lateral displacement of $M^+$ from the nominal 'axis' passing through the phenyl ring centroid (see Table 2). This near-perfect retention of the $M^+$/ligand geometry from benzene to phenyl is also consistent with theoretical findings for the other $M^+/C_6H_5X$ $\pi$-complexes [7,28–32].

While the $\pi$-complexation of phenyl is essentially consistent with expectations based on previous studies of other aromatic systems, the $\sigma$-complexation is rather more novel in character. It is fair to say that most aromatic ligands do not force $M^+$ to make such a drastic choice between $\pi$- and $\sigma$-coordinated geometries as in the case with $C_6H_5$. According to quantum chemical calculations, for phenol, fluorobenzene and anisole the relative energies of $\pi$- and $\sigma$-coordinated minima are often very close [7,29,31,32], and the mi-

gration required of $M^+$ from $\pi$- to $\sigma$-binding sites is a comparatively minor 'float' of $\sim$2–2.5 Å across the top of the ring. Larger derivatized aromatic compounds, such as the aromatic amino acids phenylalanine, tyrosine and tryptophane [13], permit concomitant $\pi$- and $\sigma$-bonding by virtue of the ligand's structural flexibility. In contrast, for $M^+$/phenyl, $\sigma$-coordination is never possible except when the metal ion is well beyond the reach of the $\pi$-cloud, and $\sigma$-complexation is not competitive with $\pi$-complexation unless $M^+$ features valence electrons available for pairing.

The $M^+$/phenyl systems are somewhat too large to be comfortably treated by the computationally intensive CP-dG2thaw technique. This is not true of the interactions of our present selection of metal ions with smaller radical ligands. To this end our results for $M^+/C_6H_5$ can usefully be compared with the CP-dG2thaw results for metal–ion complexation of the H, $CH_3$, $C_2H$, $C_2H_3$, and $C_2H_5$ radicals [55]. A common feature of all of these radicals is that the ion–ligand bond dissociation energies (BDE) are greatest for the two alkaline earth ions and least for the two alkali metal ions, with the BDE for $Na^+$ always at least $12\,kJ\,mol^{-1}$ larger than that for $K^+$. Nevertheless, it is also apparent that the phenyl ligand is less severely selective than are the smaller radical ligands. For example, the BDE values for the $Mg^+/CH_3$ and $Mg^+/C_2H$ complexes are calculated to be over $10\times$ larger than the values for the corresponding $K^+$ complexes, and for $M^+$/H complexes the disparity between alkaline earth and alkali metal BDE values is even more extreme [55]. The comparatively large alkali metal ion BDE values for the phenyl radical thus demonstrate that the cation/$\pi$ (aromatic) interaction is less sensitive to the metal ion's valence electronic structure than the cation/$\sigma$ and cation/$\pi$ (aliphatic) interactions for the smaller radical ligands.

Are these $M^+/C_6H_5$ complexes of more than purely theoretical interest? These structures have not been investigated in the laboratory, although a recent theoretical study [50], concerned with aspects of the reactivity of Grignard reagents, has included the $MgC_6H_5^+$ (singlet) $\sigma$-complex. Agreement of our B3-LYP and B3-PW91 BDE values with their pBD/DN**

calculation, of $240.3 \, \text{kJ mol}^{-1}$ for this quantity, is satisfactory, while their conclusion that the $C_{2v}$-symmetry σ-complex is the lowest-energy isomer for this species is also consistent with the present work. Furthermore, while the prospects for formation of any of these σ- or π-complexes by direct association reactions

$$M^+ + C_6H_5 \rightarrow MC_6H_5^+ \quad (1)$$

would appear remote given the experimental difficulties in obtaining a 'clean' source of $C_6H_5$, other approaches may be feasible, particularly in the case of σ-complex formation with $Mg^+$ and $Ca^+$ where the calculated bond strengths are appreciable. For example, the reaction

$$Ca^+ + C_6H_5I \rightarrow CaC_6H_5^+ + I \quad (2)$$
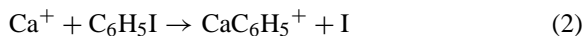
is only $6 \, \text{kJ mol}^{-1}$ endothermic (but with an uncertainty of at least this magnitude) according to our B3-PW91 calculations in conjunction with thermochemical data contained in the NIST webbook [81]. There is therefore some hope for generation of $CaC_6H_5^+$, via reaction (2) or in some analogous process involving a better 'leaving group' than I, as a bimolecular reaction in competition with (radiative or thermolecular) association of $Ca^+$ to the parent aromatic ligand. Laboratory demonstration of the viability of such a process would be valuable, not least because it would furnish an experimental lower limit to the strength of the $Ca^+$/phenyl bond.

If laboratory routes to these $M^+/C_6H_5$ complexes can be realized, they may constitute excellent models for several different chemical effects. Most obviously, they offer scope for assessment of the interactions between main-group metal ions and radicals. They also provide another fundamental example of a 'substituted' benzene for which the cation/π interaction can be quantified. The extreme (structural and energetic) differences between singlet and triplet adducts of the alkaline-earth metal ions with $C_6H_5$ also suggests that the $Mg^+$ and $Ca^+$ complexes, in particular, may be valuable in studying triplet-to-singlet intersystem crossing in gas-phase ions. The variation in CID profile or in ion mobility (for example), as a function

of ion storage time, could provide a clear measure of the conversion of π (triplet) to σ (singlet) adducts.

Finally, these $M^+/C_6H_5$ systems may have relevance in other areas of research also. For example, such complexes might arise naturally in the upper atmospheres of the Jovian planets, or of Saturn's satellite Titan, via the processes of meteoritic infall and ablative ionization of metal atoms in these hydrocarbon-rich atmospheres [53,54]. We have previously suggested [55] that, in such environments, the smaller hydrocarbon radicals are likely to be extremely selective in their formation of metal-ion adducts (in accordance with the very wide range in met cation affinities of these small radicals, depending on the metal ion's electronic structure, as noted above). Determination of the (radiative or thermolecular) association rate coefficients for the $M^+ + C_6H_5$ reactions is beyond the scope of the present study, but we can identify at least one factor which appears to

Table 4
Low-frequency vibrational modes associated with $M^+$/benzene and $M^+$/phenyl relative motion, obtained from B3-LYP/6-311+G** calculations

| Adduct structure | Metal | $\nu_1$[a] | $\nu_2$[a] | $\nu_3$[a] |
|---|---|---|---|---|
| $MC_6H_6^+$ π-complex | Na | 112 (1.9) | 114 (1.9) | 191 (36) |
| | Mg | 106 (2.7) | 107 (2.7) | 211 (79) |
| | Al | 127 (2.0) | 128 (2.0) | 197 (86) |
| | K | 94 (0.4) | 95 (0.4) | 128 (23) |
| | Ca | 114 (0.0) | 114 (0.0) | 171 (37) |
| $MC_6H_5^+$ π-complex | Na | 101 (1.9) | 107 (1.9) | 186 (37) |
| | Mg[b] | 87 (3.6) | 97 (2.7) | 205 (82) |
| | Al | 117 (2.4) | 125 (2.0) | 192 (87) |
| | K | 82 (1.3) | 90 (0.4) | 128 (23) |
| | Ca[b] | 98 (0.3) | 108 (0.0) | 164 (38) |
| $MC_6H_5^+$ σ-complex | Na | −74 (6.8) | 47 (9.5) | 155 (44) |
| | Mg[c] | 130 (36) | 155 (30) | 344 (22) |
| | Mg[b] | −228 (0.5) | 57 (6.3) | 163 (109) |
| | Al | 108 (9.9) | 131 (3.0) | 343 (24) |
| | K | −48 (4.2) | 37 (3.7) | 100 (26) |
| | Ca[c] | 79 (29) | 165 (29) | 335 (71) |
| | Ca[b] | −103 (1.4) | 19 (0.4) | 134 (37) |

[a] Calculated vibrational frequency, in $\text{cm}^{-1}$, with calculated IR intensity in $\text{km mol}^{-1}$ in parentheses. The principal axis for $M^+$/phenyl relative motion, for each mode, is as shown on Fig. 1.
[b] Triplet adduct.
[c] Singlet adduct.

favour the efficiency of such reactions. In Table 4, we report the calculated vibrational modes corresponding to relative motion of $M^+$ and $C_6H_5$. It is notable that all of these modes are of very low frequency (thus favoring a very high density of vibrational states for dispersal of complexation energy) while the highest frequency of these modes (i.e., that with the greatest degree of 'stretch' character) consistently also has a large calculated IR intensity, favoring rapid stabilization by radiative emission. Thus, we conclude that, while the production of the $C_6H_5$ radical as a reactant neutral is likely to present a considerable challenge to the experimental ion chemistry community, the association of this radical with $M^+$ should, in many cases, proceed in a satisfactory fashion.

## 4. Conclusion

The phenyl radical is seen to exhibit both $\pi$- and $\sigma$-coordinating tendencies to $Mg^+$, $Al^+$, and $Ca^+$, while for $Na^+$ and $K^+$ $\pi$-coordination is the only possibility evident according to our DFT and ab initio calculations. In keeping with previous experimental and theoretical results for main-group metal ion complexation of benzene, the metal–ligand $\pi$ interaction is found to be strongest for the $Mg^+$ and $Al^+$ cations and weakest for $K^+$. While the $M^+/\pi$ interactions for phenyl are universally weaker than for the corresponding $M^+$/benzene complex, the differences in binding energy (between phenyl and benzene) are generally small, and geometry optimizations of the $M^+$/phenyl $\pi$-complexes also show minimal distortion of the $M^+$/ring centroid 'bond' away from a perpendicular geometry.

For $Al^+$, $Mg^+$, and $Ca^+$, the $\sigma$-complex geometry is found to be increasingly energetically preferred over $\pi$-coordination, by up to $159\,kJ\,mol^{-1}$. For the $Mg^+$ and $Ca^+$ adducts, $\sigma$- (singlet) and $\pi$- (triplet) minima exist on potential energy surfaces of different spin multiplicity, while the $AlC_6H_5^+$ (doublet) potential energy surface is the only instance in the present work where $\sigma$- and $\pi$-complex minima coexist upon the same surface.

Attempts to characterize the $M^+/C_6H_5$ complexes using unrestricted MP2 theory were unsatisfactory as a result of the very high levels of spin contamination evident in the UMP2 wavefunction. Consequently, we expect that the hybrid DFT binding energies which we have also determined are considerably more reliable than the counterpoise-corrected MP2 results, even after spin projection of the latter values. The two DFT methods employed, B3-LYP and B3-PW91, exhibited significant discrepancies only for the $Mg^+$ and $Al^+$ complexes (with both phenyl and benzene): in keeping with earlier studies, and supported by the better agreement of B3-PW91 than of B3-LYP with experiment for $AlC_6H_6^+$, we ascribe these discrepancies to a failing of the LYP correlation functional in aromatic/metal ion complexes.

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