Supplementary information

The DFT/CC method is briefly described in the Section 2 (for more detailed description see Refs. [1-3]). Calculations of the interaction energies used in Eq. [1] (Section 2) for evaluating the DFT/CC corrections at the PBE/AVQZ and CCSD(T)/CBS levels of theory are detailed below.

**Complete Basis Set (CBS) extrapolation**

The CCSD(T)/CBS estimates are obtained from the simple correlation dependence on the cardinal number $X$

$$E_{X}^{cor} = E_{CBS}^{cor} + A \cdot X^{-3}, \quad [1]$$

where $E^{cor}$ stands for the correlation energy. For uncorrelated part the HF/AV5Z energy is taken as the CBS limit. The CCSD(T)/CBS calculations for the $\text{H}_2$..A complexes ($A = \text{Ar, C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_6\text{H}_6, \text{CH}_4, \text{H}_2, \text{H}_2\text{O}, \text{N}_2, \text{NH}_3, \text{CO, CO}_2$) were carried out according formula

$$E_{\text{CCSD(T)/CBS}} = E_{\text{CCSD(T)/CBS}}^{cor}(AVTZ/AVQZ) + E_{\text{HF/AV5Z}}.$$ \quad [2]

The CCSD(T)/CBS estimates for the benzene..A complexes were obtained as

$$E_{\text{CCSD(T)/CBS}} = E_{\text{CCSD(T)/AVDZ}}^{cor} + E_{\text{MP2/CBS}}^{cor}(AVTZ/AVQZ) - E_{\text{MP2/AVDZ}}^{cor} + E_{\text{HF/AV5Z}}.$$ \quad [3]

**Monomer geometries**

The CCSD(T)/CBS and PBE/AVQZ calculations were performed with frozen monomer geometries obtained at the CCSD(T)/AVQZ level. The benzene geometry was taken from Ref. [1].

**Basis sets**

Calculations on the reference set systems were performed with the augmented Dunning’s correlation-consistent valence-$\text{X-}\zeta$ basis set with polarization functions (AVXZ, see Section 2 for more details). The augmented functions on benzene’s hydrogens were stripped in HF/AV5Z calculations. All interaction energies were corrected for the basis set superposition error (BSSE) by standard counterpoise correction of Boys and Bernardi.
DFT/CC reference sets

The DFT/CC reference sets from which the atom-atom correction functions were obtained are given in Figs. [1-9]. One dimensional PES scans were performed for each reference system as indicated by an arrow. The reference sets for H₂, C₆H₆, and H₂O were reported elsewhere¹-³ and they are not included in Figs. [1-9].

References

**Figure 1** Reference set for argon atom: Ar.H₂ (C₂ᵥ) and Ar..C₆H₆ (C₆ᵥ) complexes.

![Ar-H](image1)

![Ar-C](image2)

**Figure 2** Reference set for N₂ molecule: N₂..H₂ (C₂ᵥ) and N₂..C₆H₆ (C₆ᵥ) complexes.

![N-H](image3)

![N-C](image4)

**Figure 3** Reference set for CH₄ molecule: H₂ dimer (D₂h), CH₄..H₂ (C₃ᵥ), C₆H₆..H₂ (C₆ᵥ), and CH₄..C₆H₆ (C₃ᵥ) complexes.

![H-H](image5)

![C-H](image6)

![C-C](image7)
**Figure 4** Reference set for \( \text{C}_2\text{H}_6: \text{H}_2 \) dimer (\( D_{2d} \)), \( \text{C}_2\text{H}_6..\text{H}_2 \) (\( C_{2v} \)), \( \text{C}_6\text{H}_6..\text{H}_2 \) (\( C_{6v} \)), \( \text{C}_6\text{H}_6..\text{H}_2 \) (\( C_{6v} \)), and \( \text{C}_2\text{H}_6..\text{C}_6\text{H}_6 \) (\( C_{2v} \)) complexes.

**Figure 5** Reference set for \( \text{C}_2\text{H}_4: \text{H}_2 \) dimer (\( D_{2d} \)), \( \text{C}_2\text{H}_4..\text{H}_2 \) (\( C_{2v} \)), \( \text{C}_6\text{H}_6..\text{H}_2 \) (\( C_{6v} \)), and \( \text{C}_2\text{H}_4..\text{C}_6\text{H}_6 \) (\( C_{2v} \)) complexes.
**Figure 6** Reference set for $\text{C}_2\text{H}_2$: $\text{C}_2\text{H}_2..\text{H}_2$ ($C_{2v}$), $\text{C}_2\text{H}_2..\text{H}_2$ ($C_{2v}$), $\text{C}_8\text{H}_6..\text{H}_2$ ($C_{6v}$), and $\text{C}_2\text{H}_2..\text{C}_6\text{H}_6$ ($C_{2v}$) complexes.

**Figure 7** Reference set for CO: CO..H$_2$ ($C_{2v}$), CO..C$_6$H$_6$ ($C_{6v}$) complexes.
Figure 8 Reference set for CO$_2$: CO$_2$..H$_2$ ($C_{2v}$) and CO$_2$..C$_6$H$_6$ ($C_{2v}, C_{6v}$) complexes.
**Figure 9** Reference set for NH₃: H₂ dimer ($D_{2d}$), NH₃..H₂ ($C_s$), and NH₃..C₆H₆ ($C_{3v}$) complexes.