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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

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

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 H_2..A complexes (A = Ar, C_2H_2, C_2H_4, C_2H_6, C_6H_6, CH_4, H_2, H_2O, N_2, NH_3, CO, CO_2) were carried out according formula

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

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

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

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-X-ζ 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.

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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 H_2, C_6H_6, and H_2O were reported elsewhere[1-3] and they are not included in Figs. [1-9].

References

[1] Bludsky O., Rubes M., Soldan P., Nachtigall P., *J. Chem. Phys.,* 2008, **128**, 114102.

[2] Rubes M., Bludsky O., *Chemphyschem,* 2009, **10**, 1868.

[3] Rubes M., Nachtigall P., Vondrasek J., Bludsky O., *J. Phys. Chem. C,* 2009, **113**, 8412.

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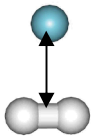
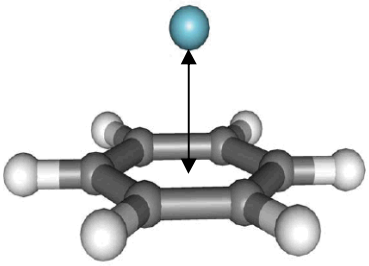
Figure 1 Reference set for argon atom: Ar..H_2 (C_{2v}) and Ar..C_6H_6 (C_{6v}) complexes.

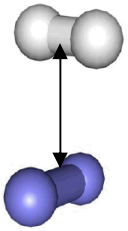


Ar-H

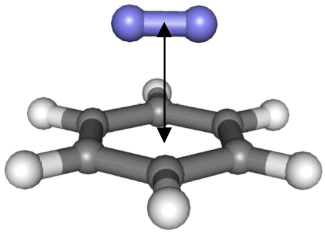


Ar-C

Figure 2 Reference set for N_2 molecule: N_2..H_2 (C_{2v}) and N_2..C_6H_6 (C_{2v}) complexes.

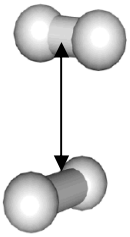


N-H

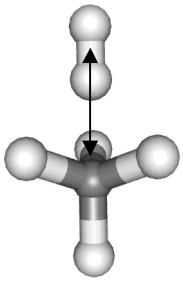


N-C

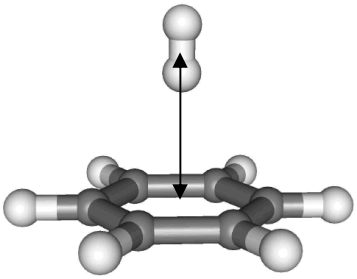
Figure 3 Reference set for CH_4 molecule: H_2 dimer (D_{2d}), CH_4..H_2 (C_{3v}) , C_6H_6..H_2 (C_{6v}), and CH_4..C_6H_6 (C_{3v}) complexes.



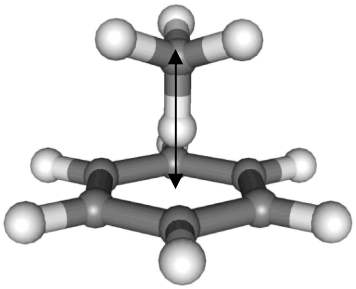
H-H



C-H [C_6H_6(H)..CH_4(C)]



C-H [C_6H_6(C)..CH_4(H)]



C-C

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Figure 4 Reference set for C_2H_6: H_2 dimer (D_{2d}), C_2H_6..H_2 (C_{2v}), C_6H_6..H_2 (C_{6v}), C_6H_6..H_2 (C_{6v}), and C_2H_6..C_6H_6 (C_{2v}) complexes.

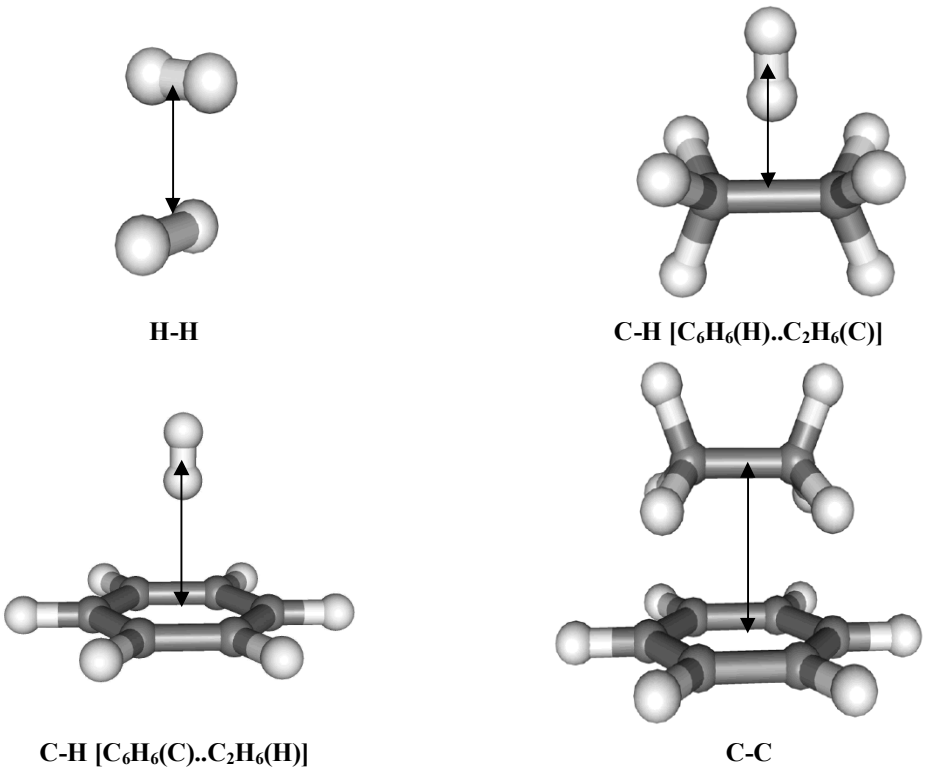

Figure 5 Reference set for C_2H_4: H_2 dimer (D_{2d}), C_2H_4..H_2 (C_{2v}), C_6H_6..H_2 (C_{6v}), and C_2H_4..C_6H_6 (C_{2v}) complexes.

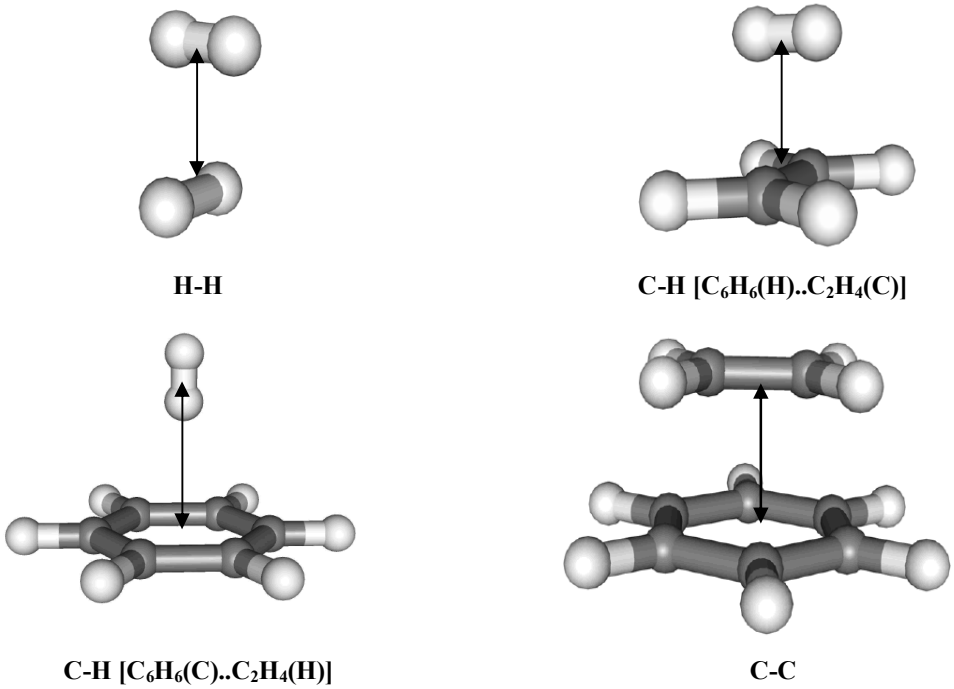

Figure 6 Reference set for C_2H_2: $C_2H_2..H_2$ (C_{2v}), $C_2H_2..H_2$ (C_{2v}), $C_6H_6..H_2$ (C_{6v}), and $C_2H_2..C_6H_6$ (C_{2v}) complexes.

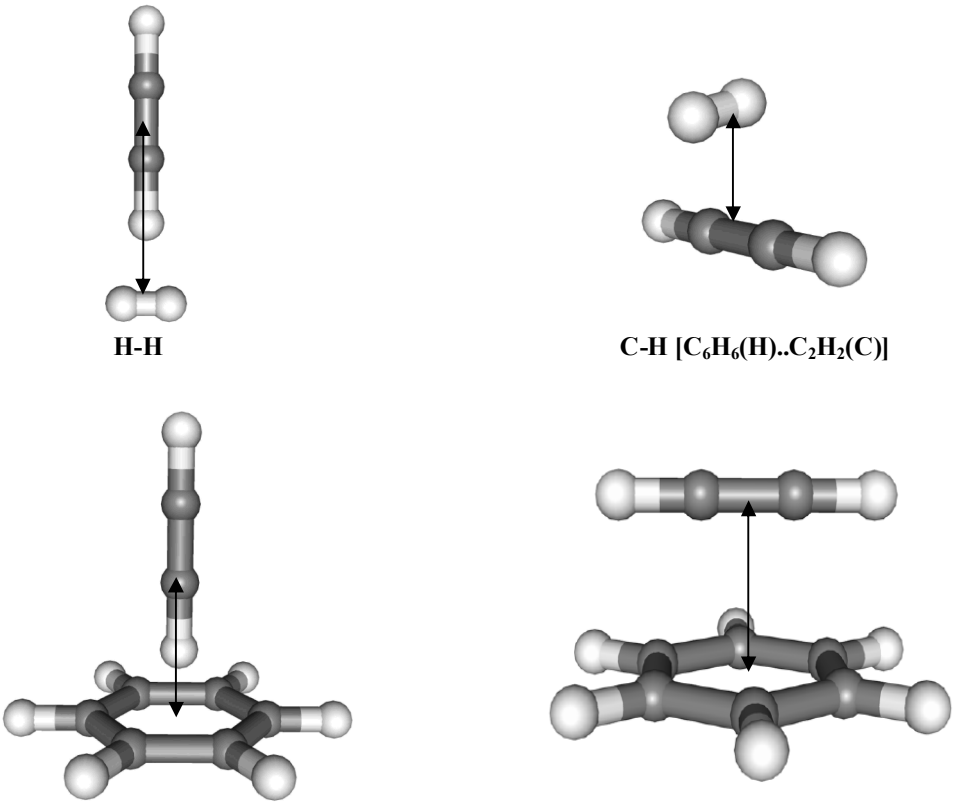

Figure 7 Reference set for CO: $CO..H_2$ (C_{2v}), $CO..C_6H_6$ (C_{6v}) complexes.

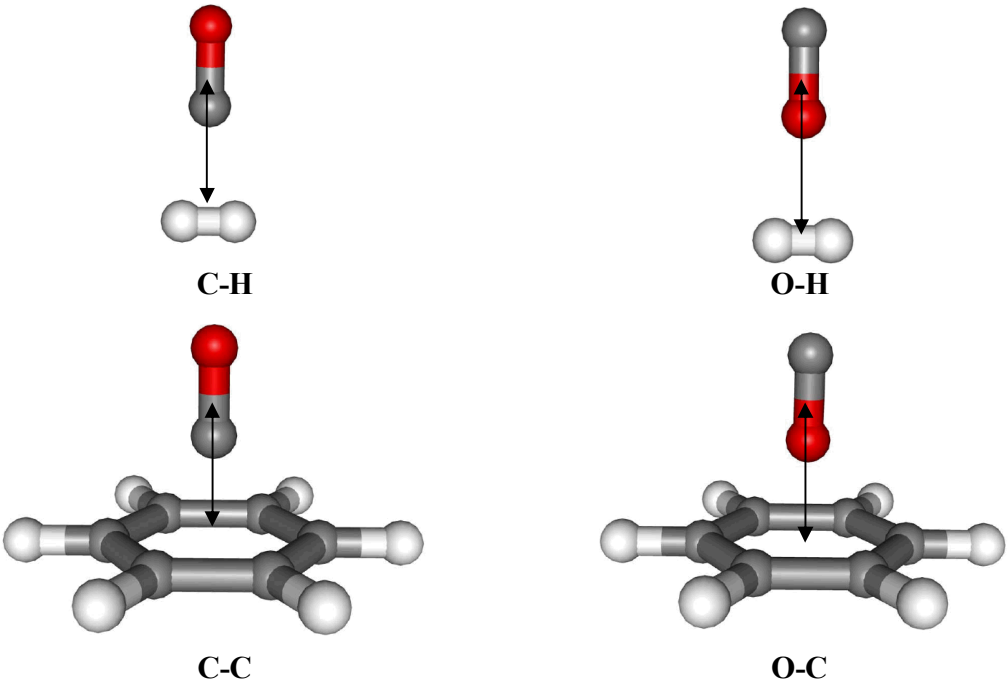

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Figure 8 Reference set for CO_2: CO_2..H_2 (C_{2v}) and CO_2..C_6H_6 (C_{2v},C_{6v}) complexes.

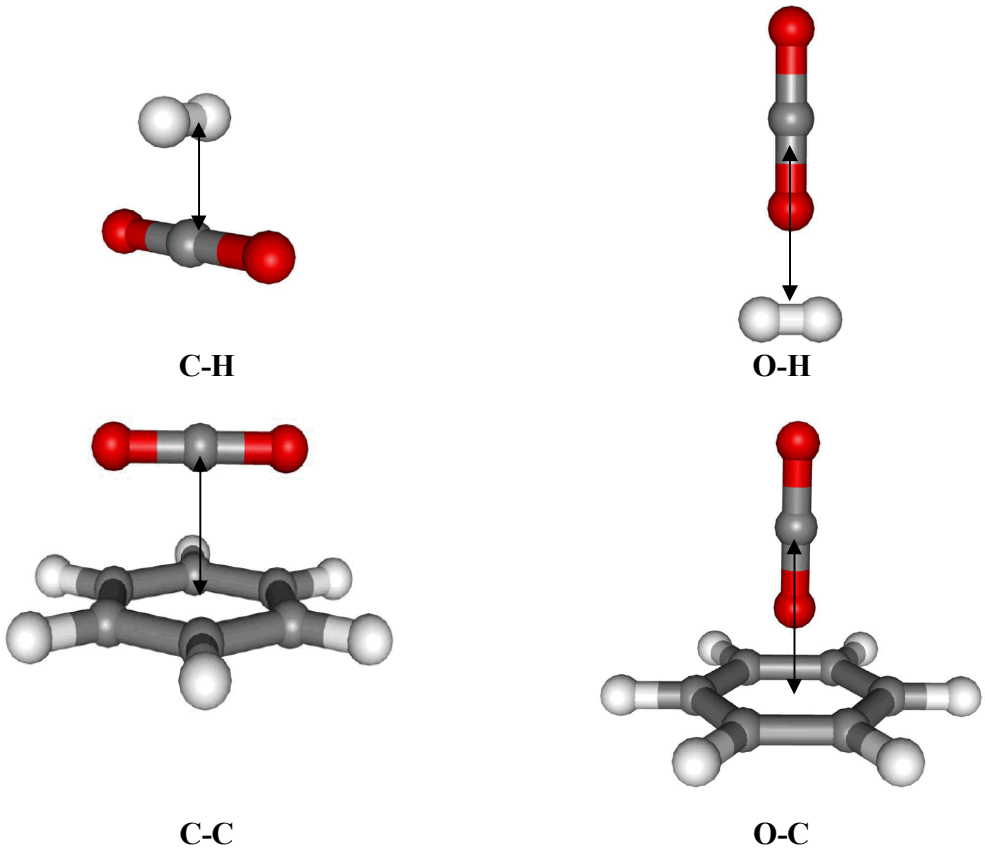

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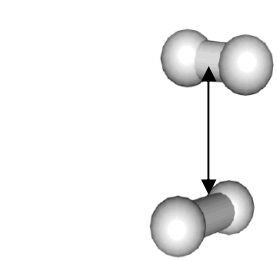
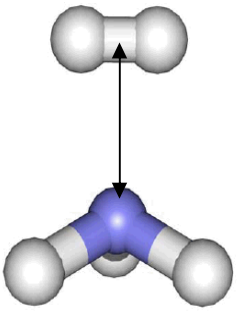
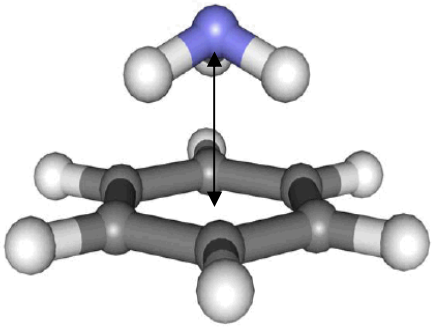
Figure 9 Reference set for NH_3: H_2 dimer (D_{2d}), NH_3..H_2 (C_s), and NH_3..C_6H_6 (C_{3v}) complexes.



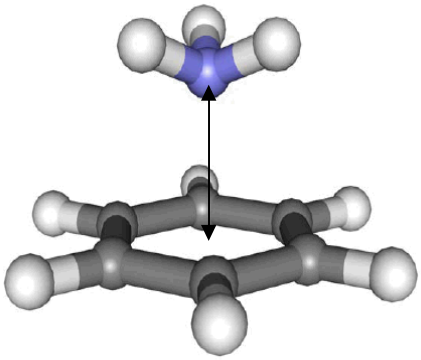
H-H



N-H



C-H



N-C

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