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PAPER

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Electronic Supplementary Information: A practical post-Hartree-Fock approach describing open-shell metal cluster-support interactions. Application to Cu_3 adsorption on benzene/coronene.

Katarzyna M. Krupka,[a] Agnieszka Krzemińska-Kowalska,[b] María Pilar de Lara-Castells*[a]

Notes and references

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[a] *Institute of Fundamental Physics (AbinitSim Unit, ABINITFOT Group), Madrid, Spain. E-mail: Pilar.deLara.Castells@csic.es*

[b] *Institute of Physics, Lodz University of Technology, ul. Wolczanska 219, 90-924 Lodz, Poland*

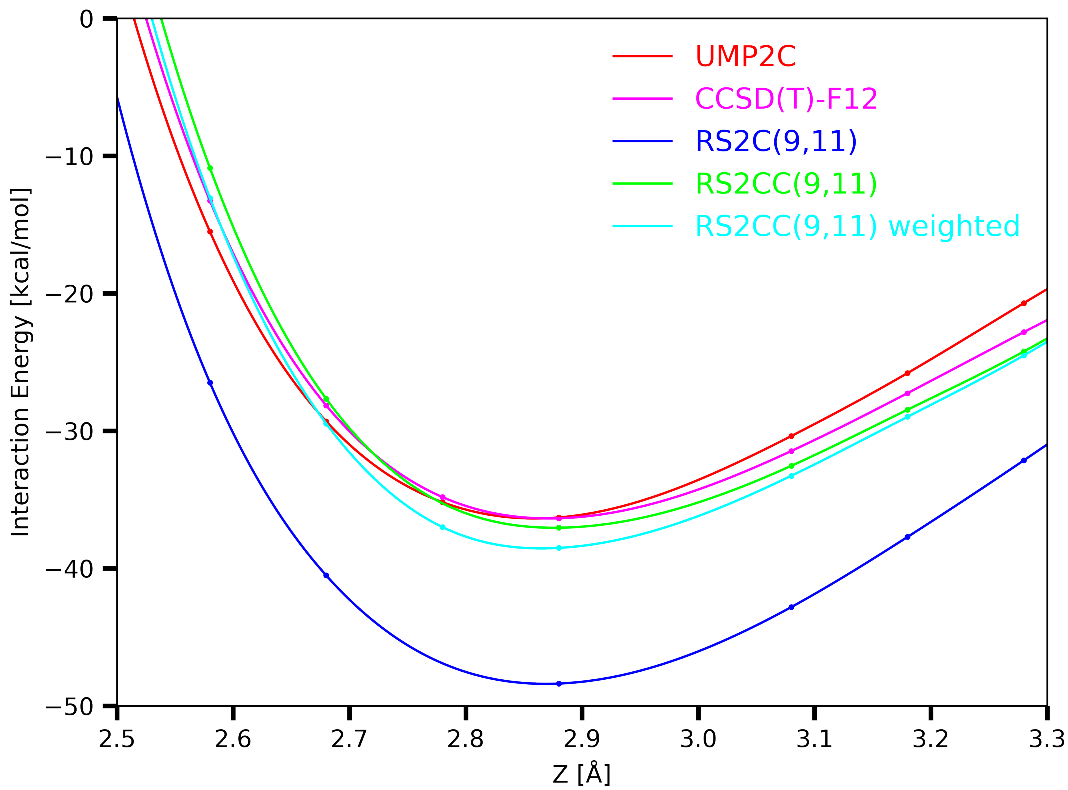

Fig. 1 Cu_3–benzene interaction potentials (in kcal/mol) calculated with the (A)VTZ(−PP) basis set. The interaction potentials have been evaluated at CCSD(T)−F12, UMP2C, RS2C(9,11), 'RS2CC(9,11)', and 'RS2CC(9,11) weighted' levels. The term 'RS2CC(9,11)' refers to the RS2C approach using an (9,11) active space but applying th dispersion correction embedded in the UMP2C scheme (see main manuscript). The same holds with the 'RS2CCC(9,11) weighted' term but with the dispersion correction weighted with the value of the square of the coefficient of the main configuration in the reference wavefunction (0.86).

Table 1 Numerical values of Cu_3−benzene interaction energies (in kcal/mol) at UMP2, UMP2C, CCSD(T), CCSD, DFT−D3, CCSD(T)−F12 and CCSD−F12 levels of theory with the (A)VTZ−PP basis set.

Z [Å]	UMP2	UMP2C	CCSD(T)	CCSD	DFT−D3	CCSD(T)−F12	CCSD−F12
2.38	35.34	57.95	65.76	75.48	62.56	62.19	72.28
2.48	−7.78	11.07	17.52	26.64	14.40	14.53	24.02
2.58	−31.12	−15.51	−10.74	−2.56	−13.75	−13.26	−4.72
2.68	−42.16	−29.31	−26.02	−18.95	−28.99	−28.15	−20.75
2.78	−45.68	−35.19	−33.02	−27.08	−36.01	−34.82	−28.55
2.88	−44.68	−36.30	−34.83	−29.90	−37.96	−36.36	−31.11
2.98	−41.00	−34.14	−33.46	−29.36	−36.89	−34.80	−30.40
3.08	−35.86	−30.38	−30.26	−26.80	−34.20	−31.47	−27.71
3.18	−30.04	−25.80	−26.15	−23.10	−30.75	−27.26	−23.93
3.28	−24.14	−20.71	−21.80	−18.94	−27.13	−22.82	−19.69
3.38	−18.65	−15.98	−17.72	−14.80	−23.60	−18.65	−15.48
3.48	−14.90	−12.94	−14.28	−11.13	−20.34	−15.11	−11.71
3.88	−7.90	−7.00	−7.01	−4.64	−10.94	−7.28	−4.61
4.38	−4.86	−4.77	−3.79	−2.46	−5.11	−3.89	−2.25
4.88	−2.83	−2.85	−1.48	−0.97	−2.11	−1.50	−0.67

Table 2 Numerical values of Cu_3−coronene interaction energies (in kcal/mol) at UMP2, UMP2C and DFT−D3 levels of theory with the (A)VTZ−PP basis set.

Z [Å]	UMP2	UMP2C	DFT−D3
2.27	31.54	58.96	48.16
2.37	−11.58	12.08	0.00
2.47	−34.92	−14.50	−28.15
2.57	−45.96	−28.30	−43.39
2.67	−49.48	−34.18	−50.41
2.77	−48.49	−35.29	−52.36
2.87	−44.80	−33.13	−51.29
2.97	−39.66	−29.37	−48.60
3.07	−33.84	−24.79	−45.15
3.17	−27.94	−19.70	−41.53
3.27	−22.45	−14.97	−37.00
3.37	−18.70	−11.93	−32.74
3.77	−11.70	−5.99	−23.34
4.27	−8.66	−3.76	−16.51
4.77	−6.63	−1.84	−13.51

Table 3 Numerical values of Cu_3−benzene uncoupled dispersion ($E_{\text{disp}}^{\text{UHF}}$), coupled dispersion ($E_{\text{disp}}^{\text{TD-UHF}}$) and dispersionless energy contributions ($E_{\text{int}}^{\text{displess}}$) (in kcal/mol).

Z [Å]	$E_{\text{disp}}^{\text{UHF}}$	$E_{\text{disp}}^{\text{TD-UHF}}$	$E_{\text{int}}^{\text{displess}}$
2.38	−147.64	−125.03	182.98
2.48	−126.65	−107.80	118.87
2.58	−108.53	−92.92	77.41
2.68	−92.95	−80.11	50.80
2.78	−79.59	−69.10	33.91
2.88	−68.15	−59.77	23.47
2.98	−58.36	−51.50	17.35
3.08	−49.67	−44.50	14.13
3.18	−41.60	−37.92	12.19
3.28	−34.07	−32.03	11.19
3.38	−27.68	−27.05	10.28
3.48	−23.07	−22.99	9.42
3.88	−13.47	−13.14	6.20
4.38	−7.81	−7.08	2.95
4.88	−4.16	−3.55	1.33

Table 4 Numerical values of Cu_3−coronene uncoupled dispersion ($E_{\text{disp}}^{\text{UHF}}$), coupled dispersion ($E_{\text{disp}}^{\text{TD-UHF}}$) and dispersionless energy contributions ($E_{\text{int}}^{\text{displess}}$) (in kcal/mol).

Z [Å]	$E_{\text{disp}}^{\text{UHF}}$	$E_{\text{disp}}^{\text{TD-UHF}}$	$E_{\text{int}}^{\text{displess}}$
2.27	−165.70	−138.28	197.24
2.37	−144.71	−124.05	136.13
2.47	−126.59	−108.17	93.67
2.57	−111.01	−94.36	66.06
2.67	−97.65	−82.35	48.17
2.77	−85.97	−71.77	36.48
2.87	−74.92	−61.25	28.11
2.97	−66.54	−51.25	21.89
3.07	−58.73	−42.67	17.88
3.17	−52.80	−34.56	14.86
3.27	−47.57	−27.09	12.12
3.37	−42.35	−22.08	10.64
3.77	−26.43	−11.72	5.73
4.27	−15.62	−7.71	3.96
4.77	−10.66	−5.87	4.03

Table 5 Numerical values of Ag_2−benzene uncoupled dispersion ($E_{\rm disp}^{\rm UHF}$), uncoupled exchange-dispersion ($E_{\rm exch-disp}^{\rm UHF}$), coupled dispersion ($E_{\rm disp}^{\rm TD-UHF}$), coupled exchange-dispersion ($E_{\rm exch-disp}^{\rm TD-UHF}$) and intramonomer correlation energy contributions ($E_{\rm corr}^{\rm intramon}$) (in kcal/mol). Intramonomer correlation energies have been calculated both with and without (values within parenthesis) exchange-dispersion contributions. Reference values [1] have been presented in brackets.

Z [Å]	$E_{\rm disp}^{\rm UHF}$	$E_{\rm exch-disp}^{\rm UHF}$	$E_{\rm disp}^{\rm TD-UHF}$	$E_{\rm exch-disp}^{\rm TD-UHF}$	$E_{\rm corr}^{\rm intramon}$
3.666	−32.08	8.01	−24.07	6.68	6.68 (5.35) [5.27]
4.466	−9.17	1.62	−6.96	1.42	2.01 (1.81) [1.64]
5.266	−2.86	0.30	−2.16	0.27	0.68 (0.65) [0.41]
7.266	−0.28	0.00	−0.20	0.00	0.08 (0.08) [0.14]

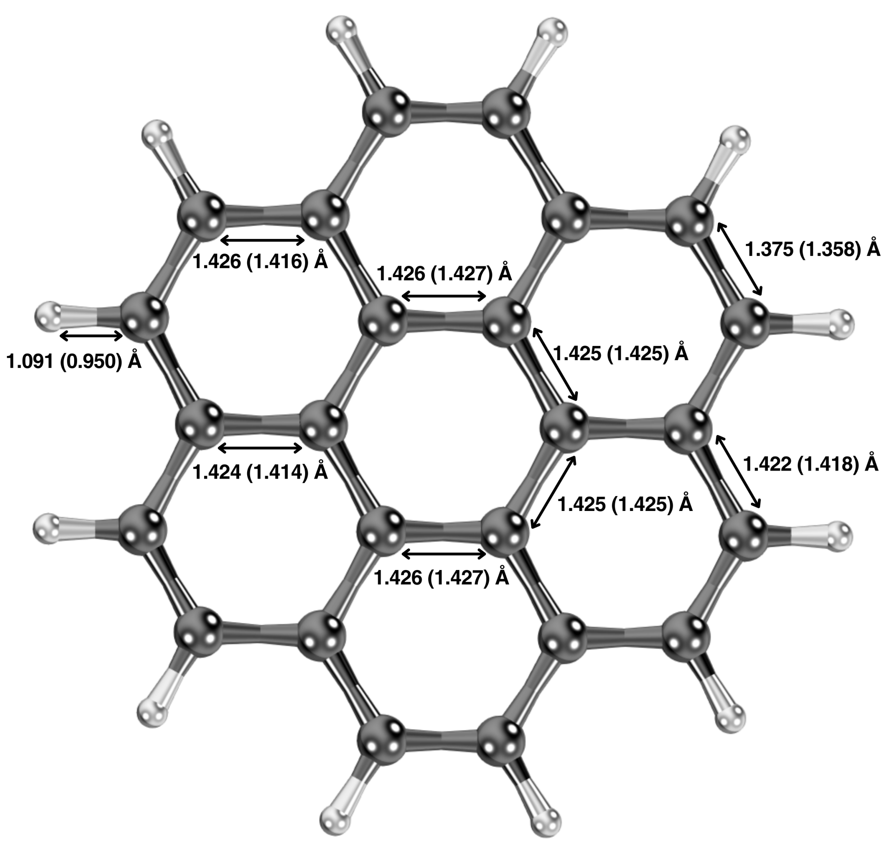

Fig. 2 Coronene structure with bond lengths obtained at the DFT−D3 level with the cc-pVTZ basis set for carbon and hydrogen atoms (referred in main manuscript as 'VTZ') and from the experimental crystal structure (values in parentheses). [2]