CH/π interactions in methane clusters with polycyclic aromatic hydrocarbons

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Supplementary Information

Estimation of $E_{MP2(limit)}$ by extrapolation

The $E_{MP2(limit)}$ for the naphthalene-methane and pyrene-methane clusters were estimated by Helgaker's method from calculated E_{MP2} using the cc-pVDZ and cc-pVTZ basis sets. In Helgaker's method calculated E_{MP2} were fitted to a form $a + b X^{-3}$ (where X is 2 for cc-pVDZ and 3 for cc-pVTZ). $E_{MP2(limit)}$ was then estimated dby an extrapolation. Helgaker's method was originally proposed for estimation of electron correlation contribution at the basis set limit. But we have used this method for estimation of $E_{MP2(limit)}$, since a basis set dependence of E_{HF} is negligible.

Estimation procedure of CCSD(T) level interaction energy at the basis set limit

The strong basis set dependence and substantial electron correlation effects beyond MP2 show that an estimation of the CCSD(T) interaction energy at the basis set limit [$E_{CCSD(T)(limit)}$] is necessary for a quantitative analysis of interaction energy between a methane and a poly-aromatic molecule. $E_{CCSD(T)(limit)}$ for a methane cluster with a poly aromatic molecule was estimated with ARS-E models in this work. In this models the $E_{CCSD(T)(limit)}$ was estimated according to equation (1)

$$E_{CCSD(T)(limit)} = E_{MP2(limit)} + \Delta CCSD(T)(limit), \qquad (1)$$

where ΔCCSD(T)(limit) denotes the CCSD(T) correction term [ΔCCSD(T) = $E_{CCSD(T)}$ - E_{MP2}] at the basis set limit. E_{MP2} and $E_{CCSD(T)}$ denote MP2 and CCSD(T) interaction energies. $E_{MP2(limit)}$ denotes the E_{MP2} at the basis set limit estimated by Helgaker's method.

The ΔCCSD(T)(limit) was estimated by equation (2)

$$\Delta CCSD(T)(limit) = \Delta CCSD(T)(M) + \Delta(M)\Delta CCSD(T), \qquad (2)$$

where ΔCCSD(T)(M) denotes ΔCCSD(T) obtained using a Medium size basis set. The ΔCCSD(T) has a weak basis set dependence. Δ(M)ΔCCSD(T) is a correction term for slight underestimation of the ΔCCSD(T) by the Medium size basis set. The Δ(M)ΔCCSD(T) corresponds to a difference between the ΔCCSD(T) at the basis set limit [ΔCCSD(T)(limit)] and the ΔCCSD(T)(M).

The Δ(M)ΔCCSD(T) was estimated according to equation (3)

$$\Delta(M)\Delta CCSD(T) = F_{\Delta CCSD(T)} \times \Delta(M)E_{corr(MP2)}$$
$$= F_{\Delta CCSD(T)} \times [E_{corr(MP2)(limit)} - E_{corr(MP2)(M)}], \qquad (3)$$

where $E_{corr(MP2)(M)}$ denotes $E_{corr(MP2)}$ (= E_{MP2} - E_{HF}) obtained using the Medium size basis set. $\Delta(M)E_{corr(MP2)}$ [= $E_{corr(MP2)(limit)}$ - $E_{corr(MP2)(M)}$] is underestimation of the $E_{corr(MP2)}$ by the Medium size basis set. $F_{\Delta CCSD(T)}$ is a parameter used for estimation of the Δ(M)ΔCCSD(T). Calculated $E_{CCSD(T)}$ for methane clusters with benzene, naphthalene, pyrene, toluene, *p*-xylene and mesitylene using several basis sets (Table 1S) show that the ΔCCSD(T) is almost always 75-85 % of the absolute value of $E_{corr(MP2)}$. These results suggest that we can assume that the Δ(M)ΔCCSD(T) is approximately 20 ± 5 % of the absolute value of $\Delta(M)E_{corr(MP2)}$. Therefore $F_{\Delta CCSD(T)}$ = -0.20 was used for the estimation of Δ(M)ΔCCSD(T) using equation (3) in this work. The 6-31G* basis set was used for the Medium-size basis set for estimation of $E_{CCSD(T)(limit)}$ for the methane clusters with naphthalene and pyrene.

It should be noted that calculated MP2/cc-pVTZ interaction energies of the

naphthalene-methane clusters (1a and 1f) are close to the estimated $E_{CCSD(T)(limit)}$ (Figure 2). The cc-pVTZ basis set underestimates the attraction compared to the basis set limit, while the MP2 method overestimates the attraction compared to the CCSD(T) method. Apparently an error cancellation is the cause of the good performance of the MP2/cc-pVTZ level calculations.

TABLE 1S. Calculated MP2 and CCSD(T) interaction energies for methane and ethane clusters with aromatic molecules[a]

basis set, geometry	E_{HF}[b]	E_{MP2}[b]	$E_{CCSD(T)}$[b]	$E_{corr(MP2)}$[c]	$E_{corr(CCSD(T))}$[d]	$E_{corr(CCSD(T)}/E_{corr(MP2)}$
naphthalene-methane[e]						
6-31G*						
1a R = 3.8 Å	0.92	-0.48	-0.22	-1.40	-1.14	0.82
1f R = 3.6 Å	1.13	-0.60	-0.28	-1.73	-1.41	0.82
1g	1.22	-0.59	-0.25	-1.81	-1.47	0.81
cc-pVDZ						
1a R = 3.8 Å	0.89	-0.91	-0.55	-1.80	-1.44	0.80
1b R = 3.6 Å	1.24	-0.82	-0.44	-2.06	-1.69	0.82
1c R = 3.6 Å	1.33	-0.89	-0.47	-2.23	-1.80	0.81
1d R = 3.8 Å	1.13	-0.83	-0.43	-1.97	-1.56	0.79
1e R = 3.4 Å	1.85	-1.00	-0.44	-2.85	-2.29	0.80
1f R = 3.4 Å	2.05	-1.00	-0.36	-3.04	-2.41	0.79
pyrene-methane[e]						
6-31G						
3a	2.82	0.28	0.73	-2.54	-2.09	0.82
3b	2.25	0.06	0.44	-2.19	-1.80	0.82
3c	1.89	0.02	0.37	-1.87	-1.51	0.81
6-31G*						
3a	2.75	-0.48	0.21	-3.24	-2.54	0.78
3b	2.22	-0.55	0.04	-2.77	-2.18	0.79
3c	1.90	-0.44	0.07	-2.34	-1.82	0.78
toluene-methane[f]						
cc-pVDZ	1.42	-0.80	-0.42	-2.21	-1.84	0.83
p-xylene-methane[f]						

cc-pVDZ	1.35	-0.88	-0.50	-2.23	-1.84	0.83
mesitylene-methane[f]						
cc-pVDZ	1.50	-1.01	-0.58	-2.50	-2.08	0.83
benzene-methane						
2a R = 3.8Å[c]						
6-31G*	0.85	-0.30	-0.10	-1.15	-0.96	0.83
6-311G*	0.83	-0.63	-0.38	-1.46	-1.21	0.83
6-311G**	0.82	-0.83	-0.54	-1.65	-1.36	0.83
cc-pVDZ	0.83	-0.70	-0.41	-1.53	-1.24	0.81
cc-pVTZ	0.84	-1.42	-1.06	-2.25	-1.90	0.84
cc-pVDZ						
2b R = 3.6 Å[c]	1.39	-0.43	-0.15	-1.81	-1.53	0.85
C R = 3.6 Å[g]	1.47	-0.49	-0.17	-1.96	-1.63	0.83
D R = 4.4 Å[g]	0.59	-0.47	-0.29	-1.07	-0.89	0.83
E R = 4.4 Å[g]	0.58	-0.52	-0.33	-1.10	-0.91	0.83
F R = 3.6 Å[g]	1.10	-0.40	-0.17	-1.49	-1.27	0.85
Benzene-ethane[g]						
cc-pVDZ						
G R = 3.6 Å	1.52	-0.57	-0.26	-2.08	-1.78	0.85
H R = 3.6 Å	1.77	-0.85	-0.35	-2.62	-2.12	0.81

[a] Energies in kcal/mol.

[b] BSSE corrected interaction energies.

[c] MP2 correlation interaction energies [= $E_{MP2} - E_{HF}$].

[d] CCSD(T) correlation interaction energies [= $E_{CCSD(T)} - E_{HF}$].

[e] The geometries of the clusters are shown in Figs. 1, 4 and 5.

[f] MP2/aug(d,p)-6-311G** level optimized geometries were used. Ref. 22.

[g] Ref 14.

TABLE 2S. MP2 interaction energies and estimated MP2 interaction energies at the basis set limit for methane clusters with naphthalene, pyrene and coronene[a]

	E_{MP2}[b]					$E_{MP2(limit)}$[c]		
	cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	DT[d]	TQ[e]	augDT[f]
naphthalene-methane								
1a R = 3.8 Å	-0.91	-1.66	-1.90	-1.78	-1.95	-1.98	-2.07	-2.03
1f R = 3.6 Å	-1.21	-2.15	-2.44	-2.32	-2.52	-2.55	-2.65	-2.60
1g	-1.11	-2.32	-2.55	-2.44	-2.64	-2.83	-2.79	-2.73
pyrene-methane								
3a	-1.72	-3.00				-3.54		
3b	-1.55	-2.64				-3.10		
3c	-1.40	-2.41				-2.84		

[a] Energies in kcal/mol. Geometries of the clusters are shown in Figs. 1, 4 and 5.

[b] BSSE corrected MP2 interaction energies.

[c] Estimated MP2 interaction energies at the basis set limit by Helgaker's method.

[d] Estimated E_{MP2} values from E_{MP2} calculated with cc-pVXZ (X = D and T) basis sets. See text.

[e] Estimated E_{MP2} values from E_{MP2} calculated with cc-pVXZ (X = T and Q) basis sets. See text.

[f] Estimated E_{MP2} values from E_{MP2} calculated with aug-cc-pVXZ (X = D and T) basis sets. See text.

TABLE 3S. Estimated CCSD(T) interaction energies at the basis set limit by ARS-E model using 6-31G* basis set as Medium-size basis set for methane clusters with naphthalene, pyrene and coronene [a]

Dimer	$E_{HF(limit)}$[b]	$E_{MP2(limit)}$[c]	$E_{corr(MP2)(limit)}$[d]	$E_{HF(M)}$[e]	$E_{MP2(M)}$[e]	$E_{CCSD(T)(M)}$[e]
naphthalene-methane						
1a	0.90	-1.98	-2.88	0.92	-0.48	-0.22
1f	1.04	-2.55	-3.58	1.13	-0.60	-0.28
1g	1.12	-2.66	-3.77	1.22	-0.59	-0.25
pyrene-methane						
3a	1.48	-3.54	-5.02	1.61	-0.89	-0.35
3b	1.32	-3.10	-4.42	1.42	-0.82	-0.34
3c	1.28	-2.84	-4.12	1.34	-0.77	-0.31

Dimer	$\Delta CCSD(T)(M)$[f]	$E_{corr(MP2)(M)}$[g]	$\Delta(M)E_{corr(MP2)}$[h]	$\Delta(M)\Delta CCSD(T)$[i]	$\Delta CCSD(T)_{(limit)}$[j]	$E_{CCSD(T)(imit)}$[k]
naphthalene-methane						
1a	0.26	-1.40	1.48	0.30	0.55	-1.42
1f	0.32	-1.73	1.86	0.37	0.69	-1.86
1g	0.34	-1.81	1.96	0.39	0.73	-1.92
pyrene-methane						
3a	0.54	-2.50	2.52	0.50	1.04	-2.50
3b	0.48	-2.24	2.18	0.44	0.92	-2.18
3c	0.46	-2.11	2.01	0.40	0.86	-1.97

[a] Energies in kcal/mol. Geometries of the clusters are shown in Figs. 1, 4 and 5. R = 3.8 Å for **1a** and R = 3.6 Å for **1f**.

[b] HF interaction energies at the basis set limit. HF/aug-cc-pVTZ interaction energies were used for the naphthalene clusters. HF/cc-pVTZ interaction energies were used for other clusters. See text.

[c] Estimated MP2 interaction energies at the basis set limit by Helgaker's method. See text.

[d] MP2 correlation interaction energies at the basis set limit [= $E_{MP2(limit)}$ - $E_{HF(limit)}$]. See text.

[e] HF, MP2 and CCSD(T) interaction energies calculated using the Medium size basis

sets (6-31G* basis set). See text.

[f] CCSD(T) correction terms calculated using the Medium size basis set [= $E_{CCSD(T)(M)} - E_{MP2(M)}$]. See text.

[g] MP2 correlation interaction energies calculated using the Medium size basis set [= $E_{MP2(M)} - E_{HF(M)}$]. See text.

[h] Underestimation of MP2 correlation interaction energies by the Medium size basis set [= $E_{corr(MP2)(limit)} - E_{corr(MP2)(M)}$]. See text.

[i] Estimated underestimation of CCSD(T) correction terms by the Medium size basis set [= -0.2 x $\Delta(M)E_{corr(MP2)}$]. See text.

[j] Estimated CCSD(T) correction terms at the basis set limit [= ΔCCSD(T)(M) + $\Delta(M)\Delta$CCSD(T)]. See text.

[k] Estimated CCSD(T) interaction energies at the basis set limit [= $E_{MP2(limit)}$ + ΔCCSD(T)(limit)]. See text.