

### Errors of estimated $E_{\text{CCSD(T)}(\text{limit})}$ values

Expected errors of estimated  $E_{\text{CCSD(T)}(\text{limit})}$  in this work were evaluated. Table 1S shows calculated  $E_{\text{HF}}$ ,  $E_{\text{MP2}}$  and  $E_{\text{CCSD(T)}}$  for the benzene- $\text{CH}_2\text{Cl}_2$  and  $-\text{CHCl}_3$  clusters. Estimated  $E_{\text{MP2}(\text{limit})}$  values by Helgaker's method from  $E_{\text{MP2}}$  using the aug-cc-pVXZ ( $X = \text{T}$  and  $\text{Q}$ ) are also summarized in Table 1S. The  $E_{\text{MP2}}$  for the two clusters using the aug-cc-pVQZ basis set are very close to the estimated  $E_{\text{MP2}(\text{limit})}$ . Estimated  $E_{\text{corr}(\text{MP2})}$  values for the clusters at the basis set limit [ $E_{\text{corr}(\text{MP2})}(\text{limit}) = E_{\text{MP2}(\text{limit})} - E_{\text{HF}(\text{limit})}$ ] are  $-7.029$  and  $-8.422$ , respectively. ( $E_{\text{HF}}$  calculated with the aug-cc-pVQZ basis set was used as the  $E_{\text{HF}(\text{limit})}$  [ $E_{\text{HF}}$  at the basis set limit], since the basis set dependence of  $E_{\text{HF}}$  is very small.) The calculated  $E_{\text{corr}(\text{MP2})}$  using the aug-cc-pVQZ basis set are  $-6.884$  and  $-8.247$ , respectively.  $E_{\text{corr}(\text{MP2})}/E_{\text{corr}(\text{MP2})}(\text{limit})$  values show that the aug-cc-pVQZ basis set can evaluate 98 % of the  $E_{\text{corr}(\text{MP2})}(\text{limit})$ , which shows that the aug-cc-pVQZ basis set is very close to saturation.

The  $E_{\text{MP2}(\text{limit})}$  for the two clusters are very close to the  $E_{\text{MP2}}$  calculated with the aug-cc-pVQZ basis sets. The differences are 0.14 and 0.17 kcal/mol, respectively. The small differences indicate that the errors of the estimated  $E_{\text{MP2}(\text{limit})}$  associated with the extrapolation are very small. Expected errors of  $E_{\text{MP2}(\text{limit})}$  will be less than half of the differences (0.07 to 0.09 kcal/mol). We have also estimated the  $E_{\text{MP2}(\text{limit})}$  of the clusters from calculated  $E_{\text{MP2}}$  using the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

The estimated  $E_{\text{MP2}}(\text{limit})$  for the clusters (-5.832 and -7.308 kcal/mol) are very close to those estimated using aug-cc-pVTZ and aug-cc-pVQZ (-5.880 and -7.347 kcal/mol).

Table 1S shows that the  $E_{\text{MP2}}$  and  $E_{\text{CCSD(T)}}$  have very large basis set dependence. The calculated  $E_{\text{MP2}}$  for the two clusters using the aug-cc-pVDZ basis set (-4.835 and -6.048 kcal/mol, respectively) are considerably larger (more negative) than those using the small cc-pVDZ basis set (-2.712 and -3.631 kcal/mol, respectively). The differences are 2.123 and 2.417 kcal/mol, respectively. Very large basis set dependence is also observed in the  $E_{\text{CCSD(T)}}$ . On the other hand the basis set dependence of  $\Delta\text{CCSD(T)}$  is small. The calculated  $\Delta\text{CCSD(T)}$  for the two clusters using the aug-cc-pVDZ basis set are 1.205 and 1.600 kcal/mol, respectively. Those using the small cc-pVDZ basis set are 1.042 and 1.391 kcal/mol, respectively. The differences are only 0.163 and 0.209 kcal/mol, respectively. The small basis set dependence suggests that further improvement of the basis set does not largely change the  $\Delta\text{CCSD(T)}$  values.

$E_{\text{corr}}(\text{MP2})/E_{\text{corr}}(\text{MP2})(\text{limit})$  values show that the aug-cc-pVDZ basis set covers 85 % of the  $E_{\text{corr}}(\text{MP2})(\text{limit})$  for the two clusters. Probably we can expect that  $E_{\text{corr}}(\text{CCSD(T)})/E_{\text{corr}}(\text{CCSD(T))}(\text{limit})$  values for the clusters are close to the  $E_{\text{corr}}(\text{MP2})/E_{\text{corr}}(\text{MP2})(\text{limit})$  values, if we use the same basis set. We can estimate the  $E_{\text{corr}}(\text{CCSD(T))}(\text{limit})$  values for the clusters from calculated  $E_{\text{corr}}(\text{CCSD(T)})$  with the aug-cc-pVDZ basis set and the  $E_{\text{corr}}(\text{MP2})/E_{\text{corr}}(\text{MP2})(\text{limit})$  using the above assumption. The estimated  $E_{\text{corr}}(\text{CCSD(T))}(\text{limit})$  values for the clusters are -5.610

and  $-6.537$  kcal/mol, respectively. These values lead that  $\Delta\text{CCSD(T)}(\text{limit})$  [ $\Delta\text{CCSD(T)}$  at the basis set limit] are 1.419 and 1.884 kcal/mol, respectively. Differences between the estimated  $\Delta\text{CCSD(T)}(\text{limit})$  and  $\Delta\text{CCSD(T)}$  obtained using the aug-cc-pVDZ basis set are 0.214 and 0.284 kcal/mol, respectively. The small differences show that the errors of  $\Delta\text{CCSD(T)}(\text{limit})$  are small. Probably we can expect that the errors are less than half of the differences (0.11 to 0.14 kcal/mol). The estimated errors of the  $E_{(\text{MP2})}(\text{limit})$  are 0.07 to 0.09 kcal/mol. Therefore estimated errors of  $E_{(\text{CCSD(T)})}(\text{limit})$  [sum of the errors of  $E_{(\text{MP2})}(\text{limit})$  and  $\Delta\text{CCSD(T)}$ ] are 0.18 to 0.23 kcal/mol.

In order to evaluate the accuracy of the  $E_{(\text{CCSD(T)})}(\text{limit})$  estimation procedure, the estimated  $E_{(\text{CCSD(T)})}(\text{limit})$  for the ethylene-methane cluster using the same procedure was compared with the estimated  $E_{(\text{CCSD(T)})}(\text{limit})$  from the calculated  $E_{\text{CCSD(T)}}$  using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The geometry for the ethylene-methane cluster is shown in Figure 1S. Calculated  $E_{\text{HF}}$ ,  $E_{\text{MP2}}$  and  $E_{(\text{CCSD(T)})}(\text{limit})$  for the cluster using the aug-cc-pVXZ ( $X = \text{D, T and Q}$ ) basis sets are summarized in Table 2S. Calculated  $E_{\text{MP2}}$  using the aug-cc-pVXZ ( $X = \text{D, T and Q}$ ) are  $-0.431$ ,  $-0.515$  and  $-0.540$  kcal/mol, respectively. Estimated  $E_{\text{MP2}}(\text{limit})$  from the calculated  $E_{\text{MP2}}$  using the aug-cc-pVTZ and aug-cc-pVQZ is  $-0.558$  kcal/mol. The  $E_{\text{corr}}(\text{MP2})$  using the aug-cc-pVDZ basis set is  $-0.805$  kcal/mol, which is 86.7 % of estimate  $E_{\text{corr}}(\text{MP2})$ (limit) ( $-0.929$  kcal/mol), which is the difference between the estimated  $E_{\text{MP2}}(\text{limit})$  and  $E_{\text{HF}}$  calculated using the aug-cc-pVQZ basis set. Therefore we can

estimate the  $\Delta\text{CCSD(T)}$  at the basis set limit using the assumption that the  $\Delta\text{CCSD(T)}$  obtained using the aug-cc-pVDZ basis set (0.039 kcal/mol) is 86.7 % of the  $\Delta\text{CCSD(T)}$  at the basis set limit. The estimated  $\Delta\text{CCSD(T)}$  at the basis set limit is 0.045 kcal/mol. The  $E_{\text{CCSD(T)}}(\text{limit})$  (-0.513 kcal/mol) was estimated as the sum of the estimated  $E_{\text{MP2}}(\text{limit})$  (-0.558 kcal/mol) and the estimated  $\Delta\text{CCSD(T)}$  at the basis set limit. This value is very close to the estimated  $E_{\text{CCSD(T)}}(\text{limit})$  from the calculated CCSD(T) interaction energies using the aug-cc-pVDZ and aug-cc-pVTZ basis sets (-0.505 kcal/mol). The good agreement shows that the estimated  $E_{\text{CCSD(T)}}(\text{limit})$  for the benzene-halomethane clusters in this work are sufficiently accurate. The  $E_{\text{MP2}}(\text{limit})$  estimated using the aug-cc-pVXZ (X = D and T) basis sets (-0.551 kcal/mol) is very close to that estimated using the aug-cc-pVXZ (X = T and Q) basis sets (-0.558 kcal/mol). This suggests that the estimated  $E_{\text{CCSD(T)}}(\text{limit})$  using the aug-cc-pVXZ (X = D and T) basis sets (-0.505 kcal/mol) is very close to that estimated using the aug-cc-pVXZ (X = T and Q) basis sets, though the CCSD(T)/aug-cc-pVQZ level calculation of the ethylene-methane cluster, which employs 608 basis functions, is still not feasible at present.

Table 1S. HF, MP2 and CCSD(T) interaction energies, MP2, and CCSD(T) level electron correlation contributions and CCSD(T) correction term of benzene-CH<sub>2</sub>Cl<sub>2</sub> and -CHCl<sub>3</sub> clusters<sup>a</sup>

Method	E <sub>HF</sub> <sup>b</sup>	E <sub>MP2</sub> <sup>b</sup>	E <sub>corr(MP2)</sub> <sup>c</sup>	E <sub>corr(MP2)/</sub> E <sub>corr(MP2)(limit)</sub> <sup>d</sup>	E <sub>CCSD(T)</sub> <sup>b</sup>	E <sub>corr</sub> (CCSD(T)) <sup>e</sup>	ΔCCSD(T) <sup>f</sup>
C6H6-CH <sub>2</sub> Cl <sub>2</sub>							
cc-pVDZ	0.976	-2.712	-3.687	0.525	-1.670	-2.646	1.042
cc-pVTZ	1.048	-4.713	-5.761	0.820			
cc-pVQZ	1.095	-5.426	-6.521	0.928			
aug-cc-pVDZ	1.134	-4.835	-5.969	0.849	-3.630	-4.764	1.205
aug-cc-pVTZ	1.133	-5.537	-6.670	0.949			
aug-cc-pVQZ	1.148	-5.735	-6.884	0.979			
basis set limit	1.148 <sup>g</sup>	-5.880 <sup>g</sup>	-7.029 <sup>h</sup>	1.000	-4.462 <sup>i</sup>	-5.610 <sup>j</sup>	1.419 <sup>k</sup>
C6H6-CHCl <sub>3</sub>							
cc-pVDZ	0.835	-3.631	-4.466	0.530	-2.240	-3.075	1.391
cc-pVTZ	0.912	-6.014	-6.926	0.822			
cc-pVQZ	1.001	-6.830	-7.830	0.930			
aug-cc-pVDZ	1.104	-6.048	-7.152	0.849	-4.448	-5.551	1.600
aug-cc-pVTZ	1.047	-6.935	-7.982	0.948			
aug-cc-pVQZ	1.074	-7.173	-8.247	0.979			
basis set limit	1.074 <sup>g</sup>	-7.347 <sup>g</sup>	-8.422 <sup>h</sup>	1.000	-5.463 <sup>i</sup>	-6.537 <sup>j</sup>	1.884 <sup>k</sup>

<sup>a</sup> Energy in kcal/mol. MP2/cc-pVTZ level optimized geometries were used.

<sup>b</sup> BSSE corrected HF, MP2 and CCSD(T) interaction energies.

<sup>c</sup> MP2 level correlation interaction energy. E<sub>corr(MP2)</sub> = E<sub>MP2</sub> - E<sub>HF</sub>.

<sup>d</sup> E<sub>MP2(corr)(limit)</sub> is the estimated MP2 level correlation interaction energy at the basis set limit.

e CCSD(T) level correlation interaction energy.  $E_{\text{corr}}(\text{CCSD(T)}) = E_{\text{CCSD(T)}} - E_{\text{HF}}$ .

f CCSD(T) correction term.  $\Delta\text{CCSD(T)} = E_{\text{CCSD(T)}} - E_{\text{MP2}}$ .

g Estimated values at the basis set limit ( $E_{\text{HF}}(\text{limit})$  and  $E_{\text{MP2}}(\text{limit})$ ). See text.

h MP2 level correlation interaction energy at the basis set limit.  $E_{\text{MP2(corr)}}(\text{limit}) = E_{\text{MP2}}(\text{limit}) - E_{\text{HF}}(\text{limit})$ .

i Estimated CCSD(T) interaction energy at the basis set limit ( $E_{\text{CCSD(T)}}(\text{limit})$ ). Sum of  $E_{\text{MP2}}(\text{limit})$  and  $\Delta\text{CCSD(T)}(\text{limit})$ . See text.

j  $E_{\text{corr}}(\text{CCSD(T)})$  at the basis set limit [ $E_{\text{corr}}(\text{CCSD(T)}}(\text{limit})$ ] from the calculated  $E_{\text{corr}}(\text{CCSD(T)})$  using the aug-cc-pVDZ basis set and  $E_{\text{corr}}(\text{MP2})/E_{\text{corr}}(\text{MP2})(\text{limit})$  value. See text.

k  $\Delta\text{CCSD(T)}$  at the basis set limit [ $\Delta\text{CCSD(T)}(\text{limit}) = E_{\text{corr}}(\text{CCSD(T)}}(\text{limit}) - E_{\text{corr}}(\text{MP2})(\text{limit})$ ].

Table 2S. HF, MP2 and CCSD(T) interaction energies for the C<sub>2</sub>H<sub>4</sub>-CH<sub>4</sub> cluster<sup>a</sup>

	$E_{\text{HF}}^{\text{b}}$	$E_{\text{MP2}}^{\text{b}}$	$E_{\text{CCSD(T)}}^{\text{b}}$	$\Delta\text{CCSD(T)}^{\text{c}}$	$E_{\text{corr(MP2)}}^{\text{d}}$	$E_{\text{corr(MP2)}}^{\text{d}}/E_{\text{corr(MP2)}(\text{limit})}^{\text{e}}$
aug-cc-pVDZ	0.375	-0.431	-0.392	0.039	-0.805	0.867
aug-cc-pVTZ	0.373	-0.515	-0.472	0.043	-0.888	0.956
aug-cc-pVQZ	0.371	-0.540			-0.911	0.981
basis set limit (DT) <sup>f</sup>	0.371 <sup>g</sup>	-0.551 <sup>h</sup>	-0.505 <sup>h</sup>		-0.929 <sup>i</sup>	
basis set limit (TQ) <sup>f</sup>	0.371 <sup>g</sup>	-0.558 <sup>j</sup>	-0.513 <sup>k</sup>	0.045 <sup>l</sup>	-0.929 <sup>i</sup>	

<sup>a</sup> Energy in kcal/mol. The geometry of the cluster taken from Ref. 46 is shown in Figure 1S.

<sup>b</sup> BSSE corrected HF, MP2 and CCSD(T) interaction energies.

<sup>c</sup> CCSD(T) correction term.  $\Delta\text{CCSD(T)} = E_{\text{CCSD(T)}} - E_{\text{MP2}}$ .

<sup>d</sup> MP2 level correlation interaction energy.  $E_{\text{corr(MP2)}} = E_{\text{MP2}} - E_{\text{HF}}$ .

<sup>e</sup> Ratio of  $E_{\text{corr(MP2)}}$  to  $E_{\text{corr(MP2)}(\text{limit})}$ .  $E_{\text{corr(MP2)}(\text{limit})}$  is the estimated MP2 level correlation interaction energy at the basis set limit.

<sup>f</sup> Estimated values at the basis set limit using Helgaker's method.

<sup>g</sup>  $E_{\text{HF}}$  calculated with the aug-cc-pVQZ basis set.

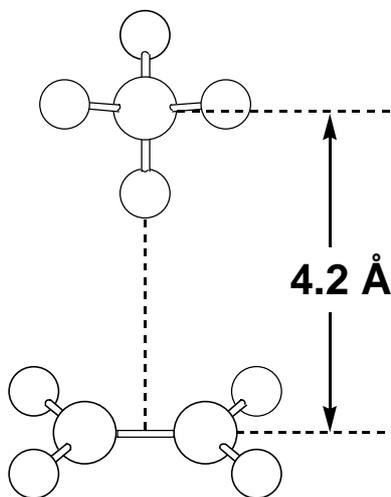
<sup>h</sup> Estimated MP2 and CCSD(T) interaction energies at the basis set limit [ $E_{\text{MP2}(\text{limit})}$  and  $E_{\text{CCSD(T)}(\text{limit})}$ ] from the calculated interaction energies using the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

<sup>i</sup> MP2 level correlation interaction energy at the basis set limit. The difference between the  $E_{\text{MP2}(\text{limit})}$  (-0.558 kcal/mol) and  $E_{\text{HF}(\text{limit})}$  (0.371 kcal/mol).

<sup>j</sup> Estimated MP2 interaction energy at the basis set limit [ $E_{\text{MP2}}(\text{limit})$ ] from the calculated interaction energies using the aug-cc-pVTZ and aug-cc-pVQZ basis sets.

<sup>k</sup> Sum of the estimated  $E_{\text{MP2}}(\text{limit})$  from the calculated interaction energies using the aug-cc-pVTZ and aug-cc-pVQZ basis sets (-0.558) and the estimated  $\Delta\text{CCSD(T)}$  at the basis set limit (0.045).

<sup>l</sup> Estimated  $\Delta\text{CCSD(T)}$  at the basis set limit. The  $\Delta\text{CCSD(T)}$  obtained using the cc-pVDZ basis set (0.039) was divided by the  $E_{\text{corr}}(\text{MP2})/E_{\text{corr}}(\text{MP2})(\text{limit})$  value for the aug-cc-pVDZ basis set (0.867).



**Figure 1S** Geometry of  $\text{C}_2\text{H}_4\text{-CH}_4$  cluster. Details of the cluster geometry are shown in Ref. 45.