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Estimated MP2 and CCSD(T) interaction energies of *n*-alkane dimers at the basis set limit: Comparison of the methods of Helgaker *et al.* and Feller

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The MP2 (the second-order Møller-Plesset calculation) and CCSD(T) (coupled cluster calculation with single and double substitutions with noniterative triple excitations) interaction energies of all-*trans* *n*-alkane dimers were calculated using Dunning's [J. Chem. Phys. **90**, 1007 (1989)] correlation consistent basis sets. The estimated MP2 interaction energies of methane, ethane, and propane dimers at the basis set limit [$E_{\text{MP2}(\text{limit})}$] by the method of Helgaker *et al.* [J. Chem. Phys. **106**, 9639 (1997)] from the MP2/aug-cc-pVXZ ($X=D$ and T) level interaction energies are very close to those estimated from the MP2/aug-cc-pVXZ ($X=T$ and Q) level interaction energies. The estimated $E_{\text{MP2}(\text{limit})}$ values of *n*-butane to *n*-heptane dimers from the MP2/cc-pVXZ ($X=D$ and T) level interaction energies are very close to those from the MP2/aug-cc-pVXZ ($X=D$ and T) ones. The $E_{\text{MP2}(\text{limit})}$ values estimated by Feller's [J. Chem. Phys. **96**, 6104 (1992)] method from the MP2/cc-pVXZ ($X=D$, T , and Q) level interaction energies are close to those estimated by the method of Helgaker *et al.* from the MP2/cc-pVXZ ($X=T$ and Q) ones. The estimated $E_{\text{MP2}(\text{limit})}$ values by the method of Helgaker *et al.* using the aug-cc-pVXZ ($X=D$ and T) are close to these values. The estimated $E_{\text{MP2}(\text{limit})}$ of the methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane dimers by the method of Helgaker *et al.* are -0.48 , -1.35 , -2.08 , -2.97 , -3.92 , -4.91 , -5.96 , -6.68 , -7.75 , and -8.75 kcal/mol, respectively. Effects of electron correlation beyond MP2 are not large. The estimated CCSD(T) interaction energies of the methane, ethane, propane, and *n*-butane dimers at the basis set limit by the method of Helgaker *et al.* (-0.41 , -1.22 , -1.87 , and -2.74 kcal/mol, respectively) from the CCSD(T)/cc-pVXZ ($X=D$ and T) level interaction energies are close to the $E_{\text{MP2}(\text{limit})}$ obtained using the same basis sets. The estimated $E_{\text{MP2}(\text{limit})}$ values of the ten dimers were fitted to the form $m_0 + m_1 X$ (X is 1 for methane, 2 for ethane, etc.). The obtained m_0 and m_1 (0.595 and -0.926 kcal/mol) show that the interactions between long *n*-alkane chains are significant. Analysis of basis set effects shows that cc-pVXZ ($X=T$, Q , or 5), aug-cc-pVXZ ($X=D$, T , Q , or 5) basis set, or 6-311G** basis set augmented with diffuse polarization function is necessary for quantitative evaluation of the interaction energies between *n*-alkane chains. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178795]

I. INTRODUCTION

The intermolecular interaction between *n*-alkane chains is important in many fields of chemistry from material design to biochemistry. The interaction often plays an important role in determining packing of organic molecules in the crystal

and on a surface.^{1–11} The interaction is also important for the structures and properties of lipid bilayers, Langmuir-Blodgett films, and self-assembled monolayers of alkanethiol on metal surfaces.^{12–19} Detailed information on the interaction between *n*-alkane chains is important for understanding the structures of these systems and is also strongly requested by those who carry out force-field simulations of these systems. Although many experimental measurements have been

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reported on the interactions between *n*-alkane chains,^{20–24} it is still difficult to accurately evaluate the details of the interactions by experimental measurements only.

Recently, *ab initio* molecular-orbital calculation is becoming a powerful tool for studying intermolecular interactions.^{25–27} *ab initio* calculations of small molecular clusters show that sufficiently accurate interaction energies can be obtained, if a reasonably large basis set is used and electron correlation is properly corrected.^{27,28} The intermolecular interaction energy of the methane dimer has been calculated repeatedly as the smallest model of the interaction between alkane molecules.^{29–41} Recently a few calculations of the ethane^{36–43} and propane dimers^{41,44,45} were reported. The calculations of these small alkane dimers show that dispersion (van der Waals attraction) is the major source of the attraction. However, accurate evaluation of dispersion energy by *ab initio* calculation is highly computationally demanding. A very large basis set and an electron correlation correction are necessary for evaluation of dispersion energy, as dispersion has its origin in molecular polarization and electron correlation.^{26,27} Small basis sets underestimate molecular polarizability and thereby underestimate dispersion energy considerably.³⁶ Due to this difficulty interaction energies between long *n*-alkane chains have not yet been calculated by high-level *ab initio* calculations. Estimation of the interaction energy at the basis set limit is necessary for accurate evaluation of the interaction. In this paper we have reported high-level *ab initio* calculations of the intermolecular interaction energies of the all-*trans* *n*-alkane dimers (methane to *n*-decane). We have estimated the MP2 interaction energies of the ten dimers at the basis set limit [$E_{\text{MP2}}(\text{limit})$]. The CCSD(T) interaction energies of four *n*-alkane dimers (methane to *n*-butane) at the basis set limit [$E_{\text{CCSD(T)}}(\text{limit})$] are compared with the $E_{\text{MP2}}(\text{limit})$ to discuss the effects of electron correlation beyond MP2. We have also discussed interaction energies of long *n*-alkane chains and the basis set effects on the calculated interaction energies.

II. COMPUTATIONAL METHOD

The GAUSSIAN 98 and 03 programs^{46,47} were used for the *ab initio* molecular-orbital calculations. The 6-31G*, 6-311G**, and Dunning's correlation consistent basis sets (cc-pVXZ and aug-cc-pVXZ, X=D, T, Q, and 5)^{48,49} implemented in the program and a few modified basis sets were used. The aug(d,p)-6-311G** basis set is the 6-311G** basis set augmented with diffuse *d* functions on carbon atoms [$a_d(\text{C})=0.1565$] and diffuse *p* functions on hydrogen atoms [$a_p(\text{H})=0.1875$]. The aug(df,pd)-6-311G** basis set is the 6-311G** basis set augmented with the diffuse *d* functions and diffuse *f* functions on carbon atoms [$a_f(\text{C})=0.2$] and the diffuse *p* functions and diffuse *d* functions on hydrogen atoms [$a_d(\text{H})=0.25$]. These basis sets have been developed for efficient evaluation of dispersion energy. For this purpose Gaussian exponents of the diffuse polarization functions have been refined.⁴¹ Electron correlation was corrected by the MP2 (Refs. 50 and 51) and CCSD(T) (Ref. 52) methods. Basis set superposition error⁵³ (BSSE) was corrected for all calculations of the interaction energies using the counter-

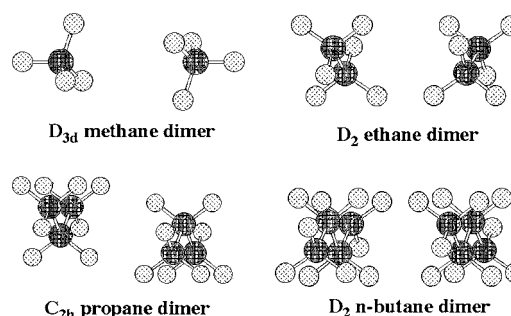


FIG. 1. Geometries of *n*-alkane dimers.

poise method.⁵⁴ The $E_{\text{MP2}}(\text{limit})$ and $E_{\text{CCSD(T)}}(\text{limit})$ of the dimers were estimated by the method of Helgaker *et al.*⁵⁵ and by Feller's method.⁵⁶

III. RESULTS AND DISCUSSION

A. Geometries of dimers

The geometries of *n*-alkane dimers (methane to *n*-butane) used in this work are shown in Fig. 1. The geometries of isolated all-*trans* *n*-alkane molecules were optimized at the MP2/6-31G* level, and were used for the calculations of the dimers. The intermolecular geometrical parameters of the dimers were optimized at the MP2/6-311G** level with the fixed geometries of the monomers. The D_{3d} symmetry was imposed during the geometry optimization of the methane dimer. The C_{2h} symmetry was imposed on the geometries of other *n*-alkane dimers, which have odd number carbon atoms (odd *n*-alkanes). The D_2 symmetry was imposed on the geometries of *n*-alkane dimers, which have even number carbon atoms (even *n*-alkanes). In the C_{2h} and D_2 dimers, the symmetry planes of the two monomers are parallel. Our previous calculations of 23 orientations of propane dimers show that the C_{2h} propane dimer is the most stable.⁴⁵ The calculated interaction energy potential of the C_{2h} propane dimer has the shortest intermolecular separation at the potential minimum among the calculated potentials of the 23 orientation dimers, as the steric repulsion of hydrogen atoms is small in this orientation. The large dispersion energy due to the short separation is the cause of the largest binding energy of the C_{2h} dimer. Therefore the C_{2h} dimers were considered for odd *n*-alkanes in this work. The D_2 symmetry dimers were considered for even *n*-alkanes in this work, as the structures of the D_2 dimers are similar to the structures of the C_{2h} dimers of odd *n*-alkanes as shown in Fig. 1. Recently we have compared the interaction energies of five orientation dimers of *n*-butane, *n*-pentane, and *n*-hexane.⁵⁷ The two *n*-alkane chains are parallel in these dimers. The D_2 *n*-butane and *n*-hexane dimers and the C_{2h} *n*-pentane dimer have the largest (most negative) interaction energies among the five orientation dimers.

B. Effects of basis set

Hartree-Fock (HF) and MP2 level interaction energies (E_{HF} and E_{MP2}) of the dimers were calculated using Dunning's correlation consistent basis sets as summarized in Tables I and II. The E_{HF} is repulsive, as HF calculation can-

TABLE I. Calculated HF and CCSD(T) interaction energies of *n*-alkane dimers. Energies in kcal/mol. The geometries of the dimers optimized at the MP2/6-311G** level were used. See text and Fig. 1.

Dimer	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
HF								
Methane	0.279	0.276	0.278	0.278	0.272	0.278	0.278	0.278
Ethane	0.829	0.832	0.831	0.830	0.827	0.831	0.829	
Propane	1.393	1.405	1.405		1.408	1.406	1.401	
Butane	2.020	2.046	2.050		2.048	2.050		
Pentane	2.664	2.691	2.692		2.693	2.692		
Hexane	3.398	3.424			3.430	3.424		
Heptane	4.191	4.218			4.228	4.213		
Octane	4.785	4.817			4.827			
Nonane	5.410	5.449			5.452			
Decane	6.192	6.231			6.178			
CCSD(T)								
Methane	-0.114	-0.324	-0.426					
Ethane	-0.421	-0.985						
Propane	-0.713	-1.526						
Butane	-1.113	-2.259						

not evaluate dispersion force. The large differences between the E_{MP2} and E_{HF} indicate significant dispersion contributions. Although the basis set effects on the E_{HF} are negligible (less than 0.1 kcal/mol), the E_{MP2} depends on the basis set strongly.

The small cc-pVDZ basis set underestimates the attraction considerably compared with the large cc-pVQZ and cc-pV5Z basis sets. The MP2/cc-pVDZ level interaction energies of the methane, ethane, propane, *n*-butane, and *n*-pentane dimers are only 29%–50% of the corresponding MP2/cc-pVQZ level interaction energies. The MP2/cc-pVQZ level interaction energies of the methane and ethane dimers are close to the MP2/cc-pV5Z level interaction energies, sug-

gesting that the cc-pVQZ and cc-pV5Z basis sets are close to saturation. The strong basis set dependence shows that estimation of the interaction energy at the basis set limit is essential for accurate evaluation of the interaction energies of *n*-alkane dimers.

The augmentation of diffuse functions improves the performance of the basis sets considerably as shown in Table II. The calculated interaction energies using the aug-cc-pVDZ basis set are close to those obtained using the large cc-pVQZ basis set. The good performance of the aug-cc-pVDZ basis set shows the importance of diffuse functions for the evaluation of dispersion interaction.

TABLE II. Comparison of calculated MP2 interaction energies (E_{MP2}) of the *n*-alkane dimers using several basis sets with estimated E_{MP2} at the basis set limit [$E_{\text{MP2}}(\text{limit})$]. Energies in kcal/mol. The geometries of the dimers optimized at the MP2/6-311G** level were used. See text and Fig. 1.

E_{MP2}														
	E_{HF}^a	6-31G*	6-311G**	aug(d,p)- 6-311G** ^b	aug(df,pd)- 6-311G** ^c	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	aug-cc- pVDZ	aug-cc- pVTZ	aug-cc- pVQZ	aug-cc- pV5Z	$E_{\text{MP2}}(\text{limit})^d$
Methane	0.278	0.033	-0.140	-0.397	-0.445	-0.117	-0.321	-0.408	-0.448	-0.392	-0.447	-0.463	-0.469	-0.475
Ethane	0.829	-0.164	-0.628	-1.150	-1.253	-0.497	-1.036	-1.216	-1.283	-1.107	-1.271	-1.318		-1.353
Propane	1.401	-0.367	-1.051	-1.780	-1.913	-0.862	-1.641	-1.882		-1.722	-1.945	-2.025		-2.084
Butane	2.050	-0.646	-1.622	-2.625	-2.800	-1.340	-2.440	-2.766		-2.554	-2.847			-2.971
Pentane	2.692	-0.925	-2.209	-3.477	-3.699	-1.822	-3.246	-3.665		-3.387	-3.764			-3.922
Hexane	3.424	-1.191	-2.769	-4.318	-4.583	-2.316	-4.081			-4.245	-4.714			-4.912
Heptane	4.213	-1.426	-3.418	-5.257		-2.821	-4.940			-5.124	-5.714			-5.963
Octane	4.827	-1.756	-3.936	-6.035		-3.323	-5.759			-5.976				-6.784
Nonane	5.452	-2.044	-4.622	-7.001		-3.827	-6.588			-6.877				-7.750
Decane	6.178	-2.286	-5.066	-7.670		-4.333	-7.444			-7.827				-8.753

^aHF level interaction energy. The aug-cc-pV5Z is used for methane dimer. The aug-cc-pVQZ is used for ethane and propane dimers. The aug-cc-pVTZ is used for *n*-butane to *n*-heptane dimers. The aug-cc-pVDZ is used for *n*-octane to *n*-decane dimers. See Table I and text.

^bThe aug(d,p)-6-311G** basis set is the 6-311G** basis set augmented with diffuse *d* functions on carbon atoms [$a_d(\text{C})=0.1565$] and diffuse *p* functions on hydrogen atoms [$a_p(\text{H})=0.1875$].

^cThe aug(df,pd)-6-311G** basis set is the 6-311G** basis set augmented with the diffuse *d* functions and diffuse *f* functions on carbon atoms [$a_f(\text{C})=0.2$] and the diffuse *p* functions and diffuse *d* functions on hydrogen atoms [$a_d(\text{H})=0.25$].

^dEstimated MP2 interaction energy at the basis set limit by the method of Helgaker *et al.* The aQ5 set is used for the fitting of methane dimer. The aTQ set is used for ethane and propane dimers. The aDT set is used for *n*-butane to *n*-heptane dimers. The DT set is used for *n*-octane to *n*-decane dimers. See Table III and text.

TABLE III. Estimated MP2 and CCSD(T) interaction energies of *n*-alkane dimers at the basis set limit [$E_{\text{MP2}(\text{limit})}$ and $E_{\text{CCSD(T)}(\text{limit})}$]. Energies in kcal/mol. The geometries of the dimers optimized at the MP2/6-311G** level were used. See text and Fig. 1.

Dimer	Helgaker <i>et al.</i> ^a						Feller ^b			
	DT ^c	TQ ^d	Q5 ^e	aDT ^f	aTQ ^g	aQ5 ^h	DTQ ⁱ	TQ5 ^j	aDTQ ^k	aTQ5 ^l
MP2										
Methane	-0.407	-0.471	-0.489	-0.470	-0.474	-0.475	-0.472	-0.481	-0.469	-0.472
Ethane	-1.263	-1.347	-1.353	-1.340	-1.353		-1.306	-1.323	-1.338	
Propane	-1.969	-2.059		-2.039	-2.084		-1.991		-2.071	
Butane	-2.904	-3.003		-2.971			-2.902			
Pentane	-3.846	-3.972		-3.922			-3.841			
Hexane	-4.824			-4.912						
Heptane	-5.831			-5.963						
Octane	-6.784									
Nonane	-7.750									
Decane	-8.753									
CCSD(T)										
Methane	-0.412	-0.500					-0.522			
Ethane	-1.222									
Propane	-1.869									
Butane	-2.741									

^aInteraction energy at the basis set limit estimated by the method of Helgaker *et al.* See Ref. 55.^bInteraction energy at the basis set limit estimated by Feller's method. See Ref. 56.^cCalculated interaction energies with the cc-pVXZ ($X=D$ and T) basis sets were used for the estimation.^dCalculated interaction energies with the cc-pVXZ ($X=T$ and Q) basis sets were used for the estimation.^eCalculated interaction energies with the cc-pVXZ ($X=Q$ and 5) basis sets were used for the estimation.^fCalculated interaction energies with the aug-cc-pVXZ ($X=D$ and T) basis sets were used for the estimation.^gCalculated interaction energies with the aug-cc-pVXZ ($X=T$ and Q) basis sets were used for the estimation.^hCalculated interaction energies with the aug-cc-pVXZ ($X=Q$ and 5) basis sets were used for the estimation.ⁱCalculated interaction energies with the cc-pVXZ ($X=D$, T , and Q) basis sets were used for the estimation.^jCalculated interaction energies with the cc-pVXZ ($X=T$, Q , and 5) basis sets were used for the estimation.^kCalculated interaction energies with the aug-cc-pVXZ ($X=D$, T , and Q) basis sets were used for the estimation.^lCalculated interaction energies with the aug-cc-pVXZ ($X=T$, Q , and 5) basis sets were used for the estimation.

C. MP2 interaction energy at the basis set limit

The $E_{\text{MP2}(\text{limit})}$ values of dimers were estimated using the method proposed by Helgaker *et al.*⁵⁵ The calculated MP2 interaction energies with Dunning's basis sets were fitted to the form $a + bX^{-3}$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc). The $E_{\text{MP2}(\text{limit})}$ was then estimated by extrapolation. The method of Helgaker *et al.* was originally proposed for the estimation of electron correlation contribution at the basis set limit. But we have used this method for the estimation of $E_{\text{MP2}(\text{limit})}$, as the basis set dependence of E_{HF} is negligible. Six sets of the calculated interaction energies (DT, TQ, Q5, aDT, aTQ, and aQ5) were used for the fitting. In DT set, the MP2 interaction energies calculated with the cc-pVXZ ($X=D$ and T) were used for the fitting. In TQ and Q5 sets, those with the cc-pVXZ ($X=T$ and Q) and ($X=Q$ and 5) were used. In aDT, aTQ, and aQ5, aug-cc-pVXZ basis sets were used instead of cc-pVXZ basis sets.

The estimated $E_{\text{MP2}(\text{limit})}$ of the methane ethane, and propane dimers using the aDT set are very close to those obtained using the aTQ set as shown in Table III. The differences of estimated $E_{\text{MP2}(\text{limit})}$ values are 0.8%, 1.0%, and 1.2%, respectively. The $E_{\text{MP2}(\text{limit})}$ of the methane dimer using the aTQ set is identical to that obtained using the aQ5 set. The estimated $E_{\text{MP2}(\text{limit})}$ of *n*-butane to *n*-heptane dimers using the DT set are close to those using the aDT set. The

differences are 1.8%–2.3%. The good agreement suggests that the $E_{\text{MP2}(\text{limit})}$ values of large *n*-alkane dimers (octane to decane) estimated by the method of Helgaker *et al.* using the DT set are sufficiently accurate. The estimated $E_{\text{MP2}(\text{limit})}$ of methane, ethane, and propane dimers using the DT set are 13.4%, 5.7%, and 3.4% smaller (less negative) than those estimated using the aDT set. The $E_{\text{MP2}(\text{limit})}$ of the three dimers using the TQ set are close to those obtained using the aTQ set. The differences are 0.4%–1.2%.

The $E_{\text{MP2}(\text{limit})}$ was also estimated using the form $a + b \exp(-cX)$ proposed by Feller.⁵⁶ Four sets of MP2 level interaction energies (DTQ, TQ5, aDTQ, and aTQ5) were used for the fitting. In the DTQ set, the calculated interaction energies with the cc-pVXZ ($X=D$, T , and Q) were used for the fitting. In the TQ5, those with the cc-pVXZ ($X=T$, Q , and 5) were used. In the aDTQ and aTQ5, the aug-cc-pVXZ basis sets were used. The $E_{\text{MP2}(\text{limit})}$ of five dimers (methane to *n*-pentane) estimated by Feller's method using the DTQ set are close to those estimated by Helgaker's method using the TQ set. The differences are less than 3.4%. The $E_{\text{MP2}(\text{limit})}$ of the methane, ethane, and propane dimers obtained by Feller's method using aDTQ set are also very close to those obtained by the method of Helgaker *et al.* using aTQ set. The differences are less than 1.1%. These results show that the

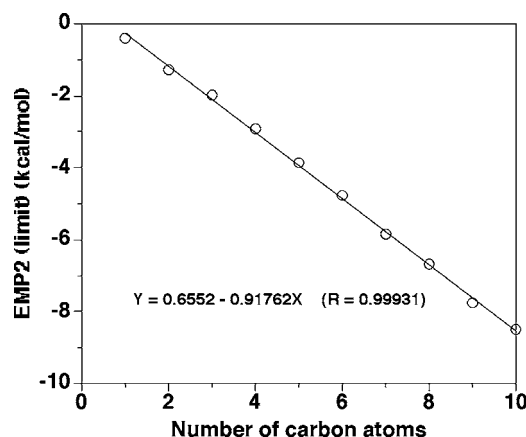


FIG. 2. Estimated MP2 level interaction energies of *n*-alkane dimers at the basis set limit [$E_{\text{MP2}(\text{limit})}$].

choice of estimation procedure does not largely change the estimated $E_{\text{MP2}(\text{limit})}$ values of the *n*-alkane dimers.

D. CCSD(T) interaction energies at the basis set limit

The calculated MP2/cc-pVTZ level interaction energies of the methane, ethane, propane, and *n*-butane dimers (−0.32, −1.04, −1.64, and −2.44 kcal/mol, respectively) are not largely different from the calculated CCSD(T)/cc-pVTZ interaction energies (−0.32, −0.99, −1.53, and −2.26 kcal/mol, respectively) as shown in Tables I and II, which shows that effects of electron correlation beyond MP2 are not large.

The $E_{\text{CCSD(T)}(\text{limit})}$ was also estimated from the calculated CCSD(T) interaction energies. The estimated $E_{\text{CCSD(T)}(\text{limit})}$ values of the methane, ethane, propane, and *n*-butane dimers by the method of Helgaker *et al.* from the CCSD(T)/cc-pVXZ ($X=D$ and T) level interaction energies (−0.41, −1.22, −1.87, and −2.74 kcal/mol) are very close to the estimated $E_{\text{MP2}(\text{limit})}$ values using the same basis sets (−0.41, −1.26, −1.97, and −2.90 kcal/mol) as summarized in Table III.

E. Interaction energies of long *n*-alkanes

The $E_{\text{MP2}(\text{limit})}$ values show that intermolecular interaction between *n*-alkane chains is not weak. The magnitude of the interactions of *n*-hexane and *n*-heptane dimers (−4.91 and −5.96 kcal/mol, respectively) is close to that of the hydrogen bond of the water dimer (about −5 kcal/mol).^{58,59}

The $E_{\text{MP2}(\text{limit})}$ of the ten *n*-alkane dimers in Table II were fitted to the form $m_0 + m_1X$ (where X is 1 for methane, 2 for ethane, etc.) as shown in Fig. 2. The $m_0=0.595$ and $m_1=-0.926$ (kcal/mol) were obtained, which indicates that an additional methylene unit increases the interaction energy between *n*-alkane chains as much as about 0.9 kcal/mol. The fitting shows that the interaction energies of long *n*-alkane chains are significant. The estimated interaction energies of the C_{20} and C_{30} *n*-alkane dimers are −17.9 and −27.2 kcal/mol, respectively.

F. Performance of basis sets

The E_{MP2} of the ten dimers obtained using several basis sets were compared with the $E_{\text{MP2}(\text{limit})}$ as summarized in Table II. The E_{MP2} calculated with large cc-pVXZ ($X=Q$ and 5) basis sets and aug-cc-VXZ ($X=D$, T , Q , and 5) are close to the $E_{\text{MP2}(\text{limit})}$, while small 6-31G*, 6-311G**, and cc-pVDZ basis sets considerably underestimate the attraction. The correlation interaction energies [$E_{\text{corr}}=E_{\text{MP2}}-E_{\text{HF}}$] of the dimers calculated with the basis sets are compared with the E_{corr} at the basis set limit [$E_{\text{corr}(\text{limit})}=E_{\text{MP2}(\text{limit})}-E_{\text{HF}}$]. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values shown in Table IV clearly indicate the performance of each basis set for the evaluation of dispersion energy, as E_{corr} is mainly dispersion energy. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values obtained using the cc-pVQZ and cc-pV5Z basis sets are 91%–96% and 96%–97%, while those obtained using small 6-31G*, 6-311G**, and cc-pVDZ basis sets are very small (34%–55%, 56%–75%, and 53%–71%, respectively). These small basis sets considerably underestimate dispersion energy.

The aug-cc-pVXZ ($X=T$, Q , and 5) basis sets show excellent performance. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values obtained us-

TABLE IV. $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ obtained from calculated interaction energies of *n*-alkane dimers using several basis sets. Energies in kcal/mol. E_{corr} and $E_{\text{corr}(\text{limit})}$ were calculated from the E_{HF} , E_{MP2} , and $E_{\text{MP2}(\text{limit})}$ values shown in Table II.

	6-31G*	6-311G**	aug(d,p)- 6-311G**a	aug(df,pd)- 6-311G**b	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	aug-cc- pVDZ	aug-cc- pVTZ	aug-cc- pVQZ	aug-cc- pV5Z
Methane	0.337	0.559	0.900	0.962	0.525	0.793	0.912	0.963	0.882	0.963	0.985	0.991
Ethane	0.443	0.658	0.905	0.954	0.608	0.856	0.938	0.968	0.886	0.963	0.984	
Propane	0.494	0.692	0.912	0.952	0.647	0.874	0.943		0.898	0.961	0.983	
Butane	0.520	0.717	0.929	0.966	0.669	0.894	0.959		0.917	0.975		
Pentane	0.530	0.726	0.931	0.966	0.678	0.898	0.961		0.919	0.976		
Hexane	0.536	0.727	0.926	0.960	0.685	0.900			0.921	0.976		
Heptane	0.541	0.736	0.929		0.689	0.900			0.919	0.976		
Octane	0.547	0.736	0.930		0.698	0.911			0.930			
Nonane	0.552	0.748	0.941		0.700	0.912			0.934			
Decane	0.550	0.737	0.925		0.705	0.916			0.938			
bf ^c	46	84	118	172	68	172	350	622	118	276	528	894

^aSee footnote b of Table II.

^bSee footnote c of Table II.

^cNumber of basis functions used for the calculation of the methane dimer.

ing these basis sets are 96%–98%, 98%–99%, and 99%, respectively. Although aug-cc-pVDZ basis set employs small numbers of basis functions, this basis set shows good performance. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values obtained using this basis set are 88%–94%. Similar good performance was also observed when the aug(d,p)-6-311G* and aug(df,pd)-6-311G* basis sets⁴¹ were used. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values obtained using these basis sets (91%–94% and 97%–98%) are considerably larger than those obtained using the 6-311G** basis set (56%–75%). The significant improvement of the performance shows the importance of diffuse functions for accurate evaluation of dispersion interaction.

The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values show that the basis set effects are enhanced in the calculations of small alkane dimers such as the methane dimer. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ value of the methane dimer calculated using the 6-311G** basis set is only 56% of the $E_{\text{corr}(\text{limit})}$, while those of the ethane and propane dimers are 66% and 69%, respectively, and those of other longer *n*-alkane dimers (butane to decane) are 72%–75%. The same tendency is observed in the $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ obtained using other basis sets as shown in Table IV. The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ values show that the basis set effects are nearly identical for large *n*-alkane dimers (butane to decane). The $E_{\text{corr}}/E_{\text{corr}(\text{limit})}$ for the large *n*-alkane dimers using the 6-31G*, 6-311G**, aug(d,p)-6-311G**, aug(df,pd)-6-311G**, cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, and aug-cc-pVTZ basis sets are 52%–55%, 72%–75%, 93%–94%, 96%–97%, 67%–71%, 89%–92%, 96%, 92%–94%, and 98%, respectively.

IV. CONCLUSIONS

We have calculated MP2 interaction energies (E_{MP2}) of ten *n*-alkane dimers (methane to decane) using the Dunning's correlation consistent basis sets and have estimated the MP2 interaction energies at the basis set limit [$E_{\text{MP2}(\text{limit})}$]. The $E_{\text{MP2}(\text{limit})}$ values estimated by the method of Helgaker *et al.* using the cc-pVXZ ($X=T$ and Q) basis sets are close to those estimated by Feller's method using the cc-pVXZ ($X=D$, T , and Q) basis sets. These values are close to those estimated by the method of Helgaker *et al.* using the aug-cc-pVXZ ($X=D$ and T) basis sets and those using the aug-cc-pVXZ ($X=T$ and Q). The $E_{\text{MP2}(\text{limit})}$ values of large *n*-alkane dimers (butane to heptane) estimated by the method of Helgaker *et al.* using the cc-pVXZ ($X=D$ and T) are closest to these values. CCSD(T) calculations show that the effects of electron correlation beyond MP2 are not large.

The interaction between *n*-alkane chains is not weak. The size of $E_{\text{MP2}(\text{limit})}$ of *n*-hexane and *n*-heptane are close to that of the hydrogen bond of the water dimer. The estimated $E_{\text{MP2}(\text{limit})}$ values of the ten *n*-alkane dimers were fitted to the form $m_0 + m_1 X$ (X is 1 for methane, 2 for ethane, etc.). The obtained m_0 and m_1 values (0.595 and -0.926 kcal/mol) show that the interactions between long *n*-alkane chains are significant.

The calculated interaction energies of *n*-alkane dimers depend on the basis set strongly. Small 6-31G*, 6-311G**, and cc-pVDZ basis sets underestimate the attraction consid-

erably. Augmentation of diffuse functions is important for accurate evaluation of dispersion interaction. The cc-pVXZ ($X=T$, Q , or 5), aug-cc-pVXZ ($X=D, T, Q, 5$), or the 6-311G** basis set augmented with diffuse polarization functions is necessary for quantitative evaluation of the interaction energies between *n*-alkane dimers.

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