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Stacking Interactions

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Editorial

Stacking interactions

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Nature and physical origin of CH/ π interaction: significant difference from conventional hydrogen bonds†

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Recently reported high-level *ab initio* calculations and gas phase spectroscopic measurements show that the nature of CH/ π interactions is considerably different from conventional hydrogen bonds, although the CH/ π interactions were often regarded as the weakest class of hydrogen bonds. The major source of attraction in the CH/ π interaction is the dispersion interaction and the electrostatic contribution is small, while the electrostatic interaction is mainly responsible for the attraction in the conventional hydrogen bonds. The nature of the “typical” CH/ π interactions is similar to that of van der Waals interactions, if some exceptional “activated” CH/ π interactions of highly acidic C–H bonds are excluded. Shifts of C–H vibrational frequencies and electronic spectra also support the similarity. The hydrogen bond is important in controlling structures of molecular assemblies, since the hydrogen bond is sufficiently strong and directional due to the large electrostatic contribution. On the other hand, the directionality of the “typical” CH/ π interaction is very weak. Although the “typical” CH/ π interaction is often regarded as an important interaction in controlling the structures of molecular assemblies as in the cases of conventional hydrogen bonds, the importance of the “typical” CH/ π interactions is questionable.

1. Introduction

Nonbonding interaction is important in many fields of chemistry and biochemistry, as it determines the structures and properties of liquids, molecular crystals and biological molecules.^{1–3} The weak attraction between the C–H bond and the π system is called CH/ π interaction.^{4,5} Over the last three decades many experimental^{4–34} and theoretical studies,^{32–58} which support the existence of the attraction, have been reported. The CH/ π interaction attracted considerable interest, since the CH/ π interaction was believed to be important for controlling crystal packing,^{6–11} structures of biological molecules^{12–16} and molecular recognition processes.^{17–23} The CH/ π interaction was mainly studied experimentally in the condensed phase until the mid-90s. Despite the broad interest in the CH/ π interaction, the nature and physical origin of the attraction was not clear, since an accurate evaluation of the weak CH/ π interaction energy was very difficult. The CH/ π interaction was often regarded as a weak hydrogen bond, probably due to the structural similarity with the π -hydrogen bond.^{59–70} Therefore it was believed that the CH/ π interaction was important in controlling the structures of molecular assemblies as in the cases of conventional hydrogen bonds.

Recently *ab initio* molecular orbital calculation and spectroscopic measurements of gas phase clusters became powerful methods for studying weak intermolecular interactions.^{2,71} High-level *ab initio* calculations provide accurate interaction energies and detailed information on intermolecular interactions.^{2,71–73} Spectroscopic measurements provide accurate binding energies of clusters in the gas phase. Recently, several high-level *ab initio* calculations^{31–34,55–58} and gas phase spectroscopic measurements of the CH/ π interactions have been reported.^{28–34} The interactions in the gas phase CH/ π clusters are ideal model systems for characterization of the CH/ π interaction, since the gas phase clusters are free from the effects of solvent and crystal packing in the condensed phase.³² The *ab initio* calculations and gas phase measurements show that the nature of CH/ π interaction is significantly different from that of conventional hydrogen bonds. The dispersion interaction is mainly responsible for the attraction and the electrostatic contribution is small in the CH/ π interaction, while the electrostatic interaction is the major source of the attraction in conventional hydrogen bonds.⁷⁴ The CH/ π interaction is a very weak interaction and its directionality is very weak, while the conventional hydrogen bonds are strong interactions and have strong directionality.⁷⁵ The different nature shows that the roles of CH/ π interactions in controlling structures of molecular assemblies should not be discussed in analogy with the hydrogen bond. This review describes the nature of the CH/ π interaction reported from recent high-level *ab initio* calculations and gas phase spectroscopic measurements and compares the nature of the CH/ π interaction with that of conventional hydrogen bonds. The effects of substituents and the acidity of the C–H bond on the CH/ π interaction are also discussed. Although several MP2 and DFT calculations of CH/ π interactions were reported, they are not suitable

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for quantitative evaluation of the CH/ π interaction energies, as we will discuss later. We will mainly explain CCSD(T) level calculations of the CH/ π interactions in this review, since this level of calculation is necessary for the quantitative evaluation of the CH/ π interaction energies.

2. Intermolecular forces

There exist several intermolecular forces between interacting molecules.^{1,73} Intermolecular forces can be separated into two main types.⁷³ One is long-range interaction such as electrostatic, induction and dispersion interactions where the energy of interaction behaves as an inverse power of R ($E \sim R^{-n}$; R is the intermolecular distance). Another interaction is the short-range one, such as exchange-repulsion and charge-transfer interactions. Short-range interactions arise at distances where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with the distance ($E \sim e^{-\alpha R}$).⁷³

3. Computational methods

3.1 Supermolecule and SAPT calculations

The supermolecule method is widely used for calculating CH/ π interaction energy. The total interaction energy (E_{total}) is calculated as the difference between the calculated energy of the dimer [$E(\text{AB})$] and the sum of the calculated energies of isolated monomers [$E(\text{A})$ and $E(\text{B})$] as shown in eqn (1),

$$E_{\text{total}} = E(\text{AB}) - [E(\text{A}) + E(\text{B})]. \quad (1)$$

The calculated interaction energy by the supermolecule method includes BSSE (basis set superposition error).⁷⁶ The correction of BSSE by the counterpoise method⁷⁷ is necessary for an accurate evaluation of weak intermolecular interactions, since the correction of BSSE significantly changes the size of the calculated interaction energy.⁵⁵

The symmetry-adapted perturbation theory (SAPT) is another method for calculating the intermolecular interaction.^{2,73} The SAPT method provides detailed information on the intermolecular interaction, as this method directly calculates the magnitude of each energy term (electrostatic, dispersion, *etc.*) of the intermolecular interaction. DFT-SAPT calculation⁷⁸ provides very accurate interaction energy, if a reasonably large basis set is used. A few SAPT calculations of the CH/ π clusters were reported.^{42,50,52} Recently DFT-SAPT calculations of the benzene-acetylene cluster were reported.⁵²

3.2 Effects of the basis set

Ab initio molecular orbital calculation is a first principle calculation, which does not use any empirical parameters. However, *ab initio* molecular orbital calculation is an approximation. The accuracy of the calculated interaction energy depends strongly on the level of theory (basis set, electron correlation and BSSE correction).^{55,72} The evaluation of the dispersion energy is the most computationally demanding, as it requires a very large basis set and electron correlation correction. The dispersion interaction has its origin in electron correlation and molecular polarization.⁷⁹ Small basis sets such

as 6-31G* and 6-311G** underestimate molecular polarizability and thereby underestimate dispersion energy. A very large basis set near saturation is necessary for an accurate evaluation of the dispersion energy. An accurate evaluation of the CH/ π interaction requires computationally demanding high-level *ab initio* calculations, as the dispersion interaction is the major source of the attraction in the CH/ π interactions.^{55–57}

3.3 Effects of electron correlation

Systematic calculations of small molecular clusters show that the CCSD(T) calculations using very large basis sets provide accurate intermolecular interaction energies.⁷² CCSD(T) level electron correlation correction is highly computationally demanding. The CPU time for an CCSD(T) calculation is proportional to the 7th power of the number of basis functions. The MP2 method is often used for the evaluation of intermolecular interaction energies. The CPU time for an MP2 calculation is proportional to the 5th power of the number of basis functions. The MP2 interaction energies for the hydrogen bonded clusters and aliphatic hydrocarbon dimers are close to the CCSD(T) ones. Unfortunately, however, the MP2 method overestimates the attraction in the aromatic clusters considerably, compared to the more reliable CCSD(T) calculations.^{80,81} The CCSD(T) level calculation is necessary for an accurate evaluation of CH/ π interaction.^{55–57}

3.4 Estimation of the CCSD(T) level interaction energy

An accurate evaluation of the CH/ π interaction energy requires a highly computationally demanding CCSD(T) level of calculation using a large basis set near saturation. Although CCSD(T)/aug-cc-pVTZ level calculations of the benzene-methane and benzene-acetylene clusters were reported recently,^{50,52} such computationally demanding calculation is still not practical for larger systems such as the benzene-chloroform cluster at present. The CCSD(T) level interaction energy of aromatic molecules at the basis set limit [$E_{\text{CCSD(T)}(\text{limit})}$] can be estimated sufficiently accurately according to eqn (2),

$$E_{\text{CCSD(T)}(\text{limit})} = E_{\text{MP2}(\text{limit})} + \Delta\text{CCSD(T)}, \quad (2)$$

where $E_{\text{MP2}(\text{limit})}$ denotes the MP2 level interaction energy at the basis set limit and $\Delta\text{CCSD(T)}$ denotes the CCSD(T) correction term (the difference between the calculated CCSD(T) and MP2 level interaction energies).^{55–57} The $E_{\text{MP2}(\text{limit})}$ is obtained by an extrapolation from the calculated MP2 interaction energies with Dunning's correlation consistent basis sets (cc-pVXZ or aug-cc-pVXZ, X = D, T, Q, *etc.*)⁸² using Feller's or Helgaker's method.^{83–85} The $\Delta\text{CCSD(T)}$ is calculated using a medium size basis set, as the basis set dependence of the $\Delta\text{CCSD(T)}$ is not large.^{55,86,87}

3.5 Calculation of each energy term

The electrostatic and dispersion interactions are important for the attraction and directionality of the intermolecular interactions of aromatic molecules.^{55–57,71} A quantitative evaluation of electrostatic and dispersion energies is essential for understanding the physical origin of the intermolecular interactions of aromatic molecules. The contribution of each energy term

Table 1 Total, electrostatic and dispersion energies for CH/ π clusters and related clusters^a

	Calc.						Exp.	
	Ref.	E_{total}^b	E_{es}^c	E_{rep}^d	E_{corr}^e	D_0^f	Ref.	D_0^f
Benzene–methane, ethane, ethylene and acetylene								
C ₆ H ₆ –CH ₄	55	–1.45	–0.25	1.10	–2.30	0.98	32	1.03–1.13
	32,33	–1.47	–0.19	1.21	–2.50	1.13		
	50	–1.45 ^g	–0.90 ^h	2.16 ^h	–2.03 ^h			
C ₆ H ₆ –CH ₃ CH ₃	55	–1.82	–0.17	1.97	–3.62		33	1.4 ± 0.2
C ₆ H ₆ –CH ₂ CH ₂	55	–2.06	–0.65	1.82	–3.22			
	33	–2.17	–0.38	1.80	–3.58	1.73		
C ₆ H ₆ –CHCH	55	–2.83	–2.01	1.44	–2.26		33	2.7 ± 0.2
	33	–2.75	–1.70	1.60	–2.65	2.39		
	52	–2.77 ⁱ	–1.75 ^j	2.80 ^j	–2.70 ^j			
Benzene–monosubstitued methane								
C ₆ H ₆ –CH ₃ NH ₂	57	–1.94	–0.28	1.92	–3.58		28	1.5–3.4
C ₆ H ₆ –CH ₃ OH	57	–1.98	–0.37	1.63	–3.24			
C ₆ H ₆ –CH ₃ OCH ₃	57	–2.06	–0.44	1.73	–3.35			
C ₆ H ₆ –CH ₃ F	57	–2.31	–0.93	1.48	–2.86			
C ₆ H ₆ –CH ₃ Cl	56, 57	–2.99	–1.06	1.44	–3.37			
Benzene–disubstitued methane								
C ₆ H ₆ –CH ₂ CINH ₂	57	–3.57	–1.09	2.68	–5.16		34	3.8 ± 0.2
C ₆ H ₆ –CH ₂ CIOH	57	–3.71	–1.48	2.67	–4.90			
C ₆ H ₆ –CH ₂ Cl ₂	56, 57	–4.54	–1.81	2.41	–5.14			
	34	–4.46	–1.59	2.74	–5.61	3.95		
C ₆ H ₆ –CH ₂ FCI	57	–3.88	–1.93	2.44	–4.39			
C ₆ H ₆ –CH ₂ F ₂	57	–3.22	–1.55	1.01	–2.68			
Benzene–trisubstitued methane								
C ₆ H ₆ –CHCl ₃	56, 57	–5.64	–2.42	4.63	–7.85		34	5.2 ± 0.2
	34	–5.46	–2.01	3.08	–6.54	5.02		
C ₆ H ₆ –CHF ₃	56, 57	–4.18	–2.43	1.67	–3.42			
Methane with polycyclic aromatic								
C ₁₀ H ₈ –CH ₄	58	–1.92	–0.06	1.17	–3.04		116	2.44 ± 0.09
C ₁₆ H ₁₀ –CH ₄	58	–2.50	–0.13	1.61	–3.98			
Hydrogen bond								
C ₆ H ₆ –H ₂ O	119	–3.02	11.86	1.07	–2.23	2.0	116	2.44 ± 0.09
C ₆ H ₆ –NH ₃	119	–2.22	–1.01	1.14	–2.36	1.6	118	1.84 ± 0.12
H ₂ O–H ₂ O	74	–4.80	–6.65	3.20	–1.35			
Cation/ π interaction								
C ₆ H ₆ –(CH ₃) ₄ N ⁺	^k	–9.66	–5.27	4.27 ^{l,m}	–4.85			
C ₆ H ₆ –NH ₄ ⁺	^k	–19.30	–11.04	9.58 ^{l,n}	–4.26			
C ₆ H ₆ –K ⁺	126	–17.2	–11.9	11.8 ^{l,o}	–4.4			

^a Energies in kcal mol^{–1}. ^b Estimated CCSD(T) level interaction energy at the basis set limit. See text. ^c Electrostatic energy obtained by distributed multipole analysis. ^d Repulsion energy [=E_{HF} – E_{es}]. E_{HF} is HF level interaction energy. See text. ^e Correlation interaction energy [=E_{total} – E_{HF}]. E_{corr} is mainly dispersion energy. See text. ^f Binding energy at the zero vibrational level. ^g Estimated E_{CCSD(T)(limit)} by the supermolecular method. ^h Obtained by SAPT calculations. Calculated induction energy is –0.26 kcal mol^{–1}. ⁱ Estimated E_{CCSD(T)(limit)} by supermolecular method. ^j Obtained by DFT-SAPT calculations. Calculated induction energy is –0.65 kcal mol^{–1}. ^k This work. ^l E_{rep} = E_{HF} – E_{es} – E_{ind}. E_{ind} is induction energy. ^m E_{ind} = –3.80 kcal mol^{–1}. ⁿ E_{ind} = –13.58 kcal mol^{–1}. ^o E_{ind} = –12.8 kcal mol^{–1}.

^a Energies in kcal mol^{–1}. ^b Estimated CCSD(T) level interaction energy at the basis set limit. See text. ^c Electrostatic energy obtained by distributed multipole analysis. ^d Repulsion energy [$=E_{\text{HF}} - E_{\text{es}}$]. E_{HF} is HF level interaction energy. See text. ^e Correlation interaction energy [$=E_{\text{total}} - E_{\text{HF}}$]. E_{corr} is mainly dispersion energy. See text. ^f Binding energy at the zero vibrational level. ^g Estimated $E_{\text{CCSD(T)(limit)}}$ by the supermolecular method. ^h Obtained by SAPT calculations. Calculated induction energy is -0.26 kcal mol^{–1}. ⁱ Estimated $E_{\text{CCSD(T)(limit)}}$ by supermolecular method. ^j Obtained by DFT-SAPT calculations. Calculated induction energy is -0.65 kcal mol^{–1}. ^k This work. ^l $E_{\text{rep}} = E_{\text{HF}} - E_{\text{es}} - E_{\text{ind}}$. E_{ind} is induction energy. ^m $E_{\text{ind}} = -3.80$ kcal mol^{–1}. ⁿ $E_{\text{ind}} = -13.58$ kcal mol^{–1}. ^o $E_{\text{ind}} = -12.8$ kcal mol^{–1}.

can be calculated by the SAPT method^{2,73} and by energy decomposition method.⁸⁸ A reasonably large basis set must be used for an accurate evaluation of each energy term, as the size of each energy term depends on the basis set as in the case of the total interaction energy calculated by the supermolecule method. Medium size basis sets underestimate dispersion energy significantly. In addition, medium size basis sets considerably overestimate the charge-transfer energy.⁷⁴

Distributed multipole analysis provides very accurate electrostatic and induction energies more easily than the SAPT method.^{73,89} The electrostatic energy (E_{es}) was calculated as the interactions between multipoles on atoms of the interacting molecules (distributed multipoles). The distributed multipoles were obtained from the calculated density matrix of the monomer by an *ab initio* method. The induction energy (E_{ind}) was calculated from the electrostatic field produced by the distributed multipoles of monomers and atomic polarizabil-

ities.⁹⁰ The contribution of dispersion interaction can be estimated approximately from the size of the effect of electron correlation on the calculated total intermolecular interaction energy by the supermolecule method ($E_{\text{corr}} = E_{\text{CCSD(T)(limit)}} - E_{\text{HF}}$, E_{HF} denotes the HF level interaction energy), since the dispersion interaction is the major source of this term (E_{corr}).⁹¹ The calculated total interaction energy and each energy term of the CH/ π interactions are summarized in Table 1.

3.6 DFT calculations

Although DFT calculations are often used for the evaluation of the intermolecular interaction of aromatic molecules, DFT methods cannot accurately evaluate the dispersion energy. The intermolecular interaction energy potentials calculated with the BLYP and B3LYP functionals are close to that obtained by the HF method.³² Some GGA functionals (PW91 and PBE)

give attractive potentials for rare gas and hydrocarbon dimers.⁹² However, the size of the attraction is not accurate. The PW91 calculations considerably underestimate the attraction in the benzene–methane cluster.³² In addition the calculated attraction is not likely a dispersion interaction, as the basis set dependence of the calculated attraction by the PW91 method is negligible.⁹² The calculated attraction should depend on the size of the basis set considerably as in the cases of the MP2 and CCSD(T) calculations, if the physical origin of the attraction calculated by the PW91 method is the dispersion interaction. The negligible basis set dependence of the calculated attraction by the PW91 method shows that the calculated attraction is not a dispersion energy. DFT calculations are not suitable for evaluating the CH/ π interaction quantitatively. Although the DFT method generally fails to produce reliable results for the dispersion interaction, it was pointed out that some recently developed DFT functionals produced relatively good results for non-bonded interactions.^{93–95}

4. Stable structure of CH/ π interaction

Spectroscopic measurements of benzene clusters with hydrocarbon molecules in the gas phase show that the interacting C–H bond points toward the benzene ring.^{30,32,96,97} Statistical analysis of the crystal structure database also shows that the C–H bond prefers to point toward the aromatic ring.⁶ This preference is well reproduced in the *ab initio* calculations of benzene clusters with small hydrocarbon molecules.^{32–34,55,98} The calculations show that the weak electrostatic interaction stabilizes the monodentate structures of the benzene clusters.⁵⁵

On the other hand the methane does not prefer monodentate structures in the methane clusters with polycyclic aromatic hydrocarbons. The naphthalene–methane cluster prefers the bidentate structure,⁵⁸ the pyrene–methane cluster prefers the tridentate structure, in which the methane locates on one carbon atom of the central C–C bond (Fig. 1).⁵⁸ The interacting C–H bonds are not perpendicular to the π plane in these stable structures. The methane prefers these orientations since these orientations are suitable for increasing the stabilization by the dispersion interaction.⁵⁸

5. Magnitude of CH/ π interaction

For understanding the nature of the CH/ π interaction, determination of its accurate interaction energy is essential. Recently, the binding energies for some CH/ π clusters were measured in the gas phase, as is summarized in Table 1.^{32–34} The binding energy (D_0) for the benzene–methane cluster, determined from the dissociation threshold measurements of

the cluster cation, is $1.03\text{--}1.13\text{ kcal mol}^{-1}$.³² The benzene–ethylene cluster has a slightly larger binding energy ($1.4 \pm 0.2\text{ kcal mol}^{-1}$).³³ The interaction between a C–H bond of alkyne and a π system is strongly enhanced in comparison with that of the “typical” aliphatic CH/ π interaction, and is often called “activated” CH/ π interaction. The binding energy for the benzene–acetylene cluster is $2.7 \pm 0.2\text{ kcal mol}^{-1}$.³³ The halogen-substitution remarkably enhances the magnitude of the aliphatic CH/ π interaction.³⁴ The binding energies for the benzene clusters with dichloromethane and chloroform (3.8 ± 0.2 and $5.2 \pm 0.2\text{ kcal mol}^{-1}$) are considerably greater than that for the benzene–methane cluster.³⁴ The interaction of the aliphatic C–H group in haloalkane is conventionally distinguished from the ordinary aliphatic CH/ π interaction, and it is also categorized into the “activated CH/ π interaction”.³⁴

The calculated binding energies from CCSD(T) level calculations agree well with the experimental ones as summarized in Table 1, which shows that high-level *ab initio* calculations provide very accurate interaction energies.^{32–34,55,56} Estimated $E_{\text{CCSD(T)}(\text{limit})}$ for the benzene–methane cluster at the basis set limit, which corresponds to $-D_e$, is $-1.5\text{ kcal mol}^{-1}$.^{33,55} The calculated D_0 (1.1 kcal mol^{-1}) after the vibrational zero-point energy correction agrees well with the experimental one.³² The calculated D_0 for the other clusters are also close to the experimental ones, as shown in Table 1.

The size of the CH/ π interaction is usually considerably smaller than that of conventional hydrogen bonds. The calculated interaction energy [estimated $E_{\text{CCSD(T)}(\text{limit})}$] for the benzene–methane cluster ($-1.5\text{ kcal mol}^{-1}$) is about 30% of the interaction energy for the water dimer (Table 1).^{32,55} The interaction energies for the benzene–ethane and benzene–ethylene clusters are not largely different from that for the benzene–methane cluster.^{33,55} On the other hand, the interaction energies for the activated CH/ π interactions (benzene–acetylene and benzene–chloroform clusters) are considerably larger.^{33,34,55,56} Other substituents attached to the carbon atom of the C–H bond and substituents attached to the benzene ring also increase the attraction.^{31,56,57} The interactions of methane with polycyclic aromatic hydrocarbons are greater than that of the benzene–methane cluster.⁵⁸

6. Physical origin of attraction

The dispersion interaction is the major source of the attraction in the CH/ π interaction.^{33,34,55–58} The E_{corr} (mainly dispersion energy) for the benzene–methane cluster is $-2.5\text{ kcal mol}^{-1}$, while E_{es} (electrostatic energy) for the cluster is only $-0.2\text{ kcal mol}^{-1}$.³³ The SAPT calculations also show that the dispersion interaction is mainly responsible for the attraction.⁵⁰ The E_{corr} is always considerably greater than the E_{es} in CH/ π clusters, as summarized in Table 1. The aromatic molecules have large dispersion interactions with a hydrocarbon molecule, since they have large polarizabilities.⁹⁹ Although the electrostatic interaction is considerably weaker than the dispersion interaction, it plays an important role in determining the stable structure of the CH/ π clusters of benzene (Fig. 2).⁵⁵ Benzene has a quadrupole moment due to the symmetry of charge distribution. The hydrogen atom of the acidic C–H bond has a positive charge. The attractive electrostatic interaction

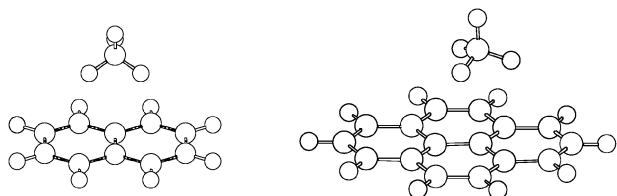


Fig. 1 Optimized geometries for naphthalene–methane and pyrene–methane clusters.

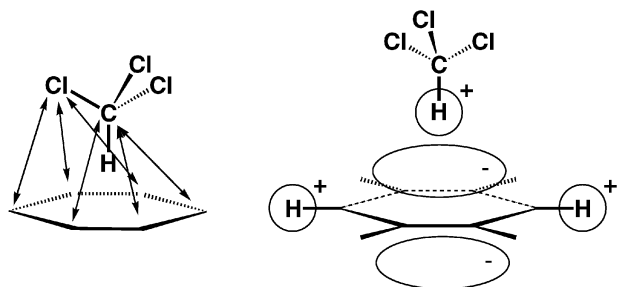


Fig. 2 Dispersion interactions between heavy atoms and electrostatic interaction in the CH/ π cluster.

between the positive charge on the hydrogen atom of the C–H bond and the negative charge on the center of benzene stabilizes the monodentate structure, in which the C–H bond points toward the benzene ring.¹⁰⁰

The size of an electrostatic interaction depends on the acidity of the C–H bond.^{33,57} The electrostatic interaction is very small in a “typical” CH/ π interaction of alkanes. The electrostatic energies (E_{es}) in the benzene clusters with methane, ethane and ethylene are -0.2 to -0.4 kcal mol⁻¹ as shown in Table 1.^{32,33,55} The E_{corr} for the clusters (-2.5 to -3.6 kcal mol⁻¹) are considerably greater than the E_{es} .

The binding energy for the benzene–acetylene cluster is larger than those for the benzene clusters with methane and ethylene due to the larger electrostatic interaction ($E_{\text{es}} = -1.7$ kcal mol⁻¹).³³ The high acidity of the C–H bond of acetylene is the cause of the large E_{es} . The $\text{p}K_{\text{a}}$ value of acetylene is 25, while those for methane and ethylene are 59 and 45, respectively. Although the benzene–acetylene cluster has large E_{es} , the E_{corr} (-2.7 kcal mol⁻¹) is still substantially greater than the E_{es} .^{33,55}

Although the origin of “activation” of the CH/ π interaction in haloalkanes was intuitively attributed to the enhancement of the electrostatic interaction due to the high acidity of the C–H bond, *ab initio* calculations show that the main origin of the enhanced interaction energy comes from a large dispersion

term due to the halogen atoms which have large atomic polarizabilities. The E_{es} values in the dichloromethane and chloroform clusters (-1.6 and -2.0 kcal mol⁻¹) are considerably larger than that in the methane cluster. They are still significantly smaller than the E_{corr} values (-5.6 and -6.5 kcal mol⁻¹).^{34,56}

Calculated HF and MP2 level interaction energy potentials (Fig. 3) show that the dispersion interactions between benzene and chlorine atoms contribute largely to the attraction in the benzene–chloroform cluster.³⁴ The HF level interaction energy is mainly the exchange-repulsion and electrostatic energies. The difference between the MP2 and HF interaction energies (electron correlation contribution) is mainly the dispersion interaction. The benzene–fluoroform cluster has a slightly larger attraction compared to the benzene–chloroform cluster at the HF level due to the greater electrostatic energy, while the chloroform cluster has significantly larger attraction at the MP2 level. Electron correlation correction strongly enhances the attraction in the benzene–chloroform cluster. The dispersion interaction in the chloroform cluster is significantly larger than that in the fluoroform cluster. The large dispersion interaction in the chloroform cluster comes from the dispersion interaction between the benzene and chlorine atoms, which have large atomic polarizabilities.¹⁰¹

Systematic investigation of the substituents’ effect on the CH/ π interaction shows that the dispersion interaction is always the major source of attraction even if the electron-withdrawing substituents attached to the carbon atom of interacting C–H bond enhance the electrostatic interaction.^{31,56,57} The benzene clusters with substituted methanes have substantially larger interaction energies compared with the benzene–methane cluster. The increase of the dispersion interaction by the substituents is mainly responsible for the large interaction energies in these clusters. The E_{es} values in mono-substituted methane clusters (-0.3 to -1.1 kcal mol⁻¹) are small, which shows that the nature of CH/ π interactions in these clusters is close to that in the benzene–methane cluster. On the other hand, the benzene clusters with di- or tri-substituted methanes have larger E_{es} (-1.1 to -2.4 kcal mol⁻¹),

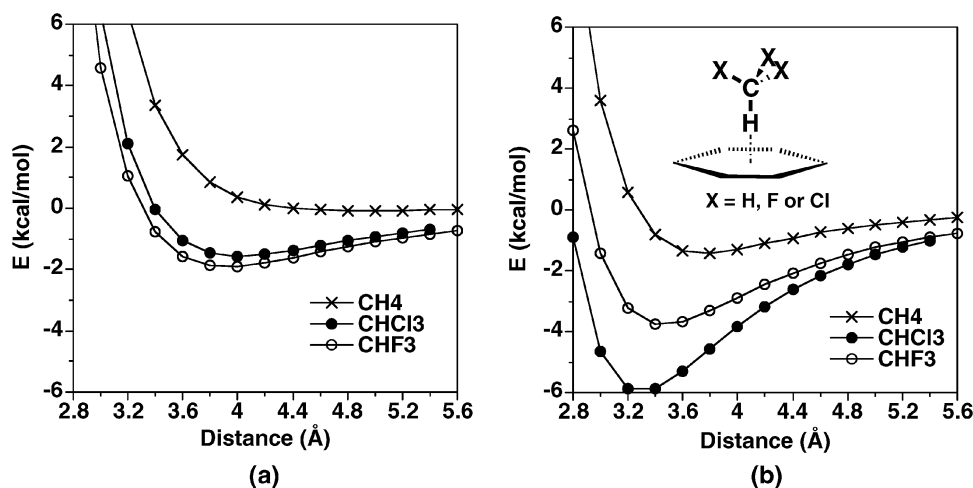


Fig. 3 HF/cc-pVTZ (a) and MP2/cc-pVTZ (b) intermolecular interaction energy potentials for the C_{3v} benzene– CH_4 , $-\text{CHCl}_3$ and $-\text{CHF}_3$ clusters. Intermolecular separation (R) is the distance between the center of benzene and the carbon atom of methane or substituted methane.

suggesting that the nature of the CH/ π interaction in these clusters is similar to that in the benzene–chloroform cluster.⁵⁷ The methane clusters with substituted benzenes (toluene, xylene and mesitylene) also have larger interaction energies compared to the benzene–methane cluster due to the larger dispersion interaction.³¹

The interactions of methane with polycyclic aromatic hydrocarbons (bidentate naphthalene–methane and tridentate pyrene–methane clusters shown in Fig. 1) are greater than that of the benzene–methane cluster due to the larger dispersion interaction. The interaction energy for the monodentate naphthalene–methane cluster ($-1.4 \text{ kcal mol}^{-1}$) is close to that for the benzene–methane cluster, which is substantially smaller than that for the bidentate structure. The interaction energy for the monodentate pyrene–methane cluster ($-2.0 \text{ kcal mol}^{-1}$) is also substantially smaller than that for the tridentate cluster.⁵⁸ These clusters prefer bidentate and tridentate structures due to the large stabilization by the dispersion interaction. These structures are suitable for avoiding steric repulsion and enable short separation between the methane and the π -plane. The monodentate structures have larger separations due to the steric repulsion of the hydrogen atom.

The charge-transfer interaction is not an important source of the attraction in the CH/ π interaction. Although early energy decomposition analysis of the ethylene–methane cluster³⁵ using the Kitaura–Morokuma scheme⁸⁸ shows that the main contribution to the attractive CH/ π interaction is the electrostatic and charge-transfer terms, Stone pointed out that the charge-transfer energy obtained by this scheme is contaminated by BSSE and this scheme overestimates the charge-transfer in the mid-1990s.⁷⁴ Calculated orientation dependence of the CH/ π interaction energy shows that directionality still

exists even when the molecules are well separated (Fig. 4).^{102,103} The orientation dependence of the total interaction energy agrees well with the orientation dependence of the electrostatic energy (Fig. 5).^{104–106} These results clearly show that the short-range interaction (charge-transfer interaction) is not responsible for the directionality of the CH/ π interaction, but the electrostatic interaction is the major source of the directionality. The calculated interaction energy potentials of the CH/ π clusters show that substantial attraction still exists, even when the molecules are well separated.³² This also shows that long-range interactions (dispersion and electrostatic interactions) are the major source of the attraction. Calculated charge distributions in the benzene–methane cluster show that the negative charge on the methane (which corresponds to the charge-transfer from benzene to methane) is very small.^{31,55,107}

Simple force-field calculations, in which the electrostatic energy is evaluated using point charges on atoms, cannot well reproduce the structures of the CH/ π clusters. This is another reason why the charge-transfer interaction was believed to be an important source of attraction in the CH/ π interaction. The highly orientation dependent charge-transfer (orbital–orbital) interaction was used to explain the weak directionality of the CH/ π interaction.⁵ However, the point charge model is a rather crude approximation, as the molecular charge distributes around the molecule. Calculated electrostatic energies using this model have large errors.⁷³ Simple force-field calculations using accurate electrostatic energy obtained by distributed multipole analysis well reproduce the structures of hydrogen-bonded clusters.^{108,109} This indicates that the electrostatic interaction has a paramount importance in determining the directionality of the intermolecular interaction.

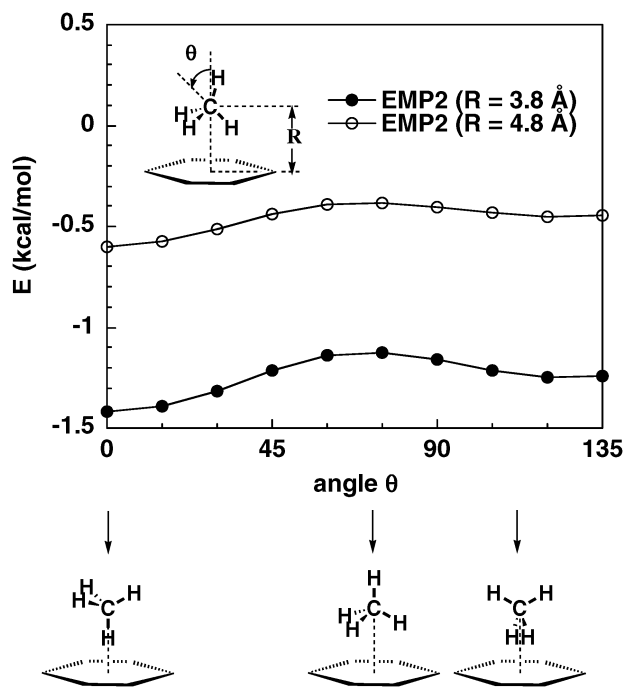


Fig. 4 Orientation dependence of the interaction energy (E_{MP2}) in a benzene–methane cluster. The effects of intermolecular separation are shown.

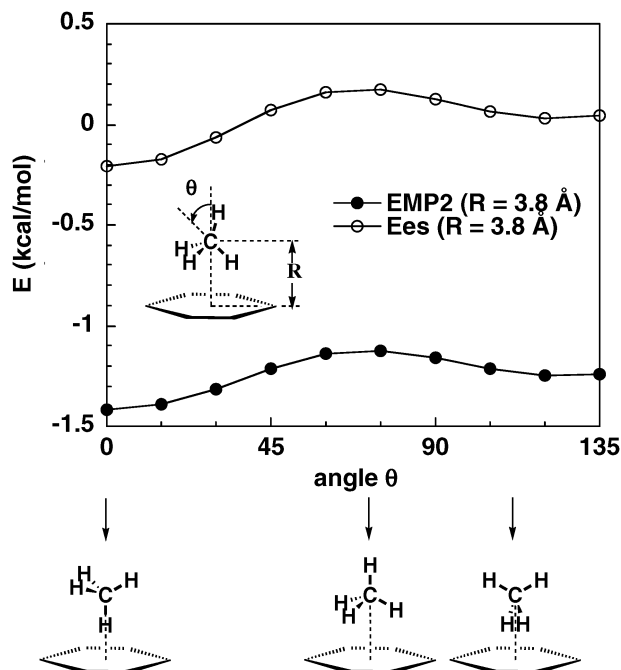


Fig. 5 Orientation dependence of the total interaction energy (E_{MP2}) and electrostatic energy (E_{es}) in a benzene–methane cluster.

7. Comparison with conventional hydrogen bonds

7.1 Magnitude and physical origin of attraction

The structure of the CH/ π interaction is similar to that of the π -hydrogen bond, while the nature of the CH/ π interaction is significantly different from that of the conventional hydrogen bonds. Structural similarity does not guarantee similarity of the nature of interaction. The dispersion interaction is the major source of attraction and the electrostatic contribution is small in the CH/ π interaction,^{33,55–57} while the electrostatic interaction is mainly responsible for the attraction in conventional hydrogen bonds.⁷⁴ The electrostatic interaction is very weak in “typical” CH/ π interactions.^{33,57} The nature of the “typical” CH/ π interaction is not close to the conventional hydrogen bond, but close to the nature in the van der Waals clusters.³¹ The electrostatic interaction is larger in some exceptional “activated” CH/ π interactions of highly acidic C–H bonds (acetylene, chloroform *etc.*).^{33,34,55–57} Although the nature of the “activated” CH/ π interactions has a similarity with π -hydrogen bonds, the electrostatic interactions in the “activated” CH/ π interactions are still substantially smaller than the dispersion interaction.^{33,34,55–57}

The magnitude of the attraction in the CH/ π interaction is substantially smaller than the conventional hydrogen bonds due to the small electrostatic contribution to the attraction.^{55–57} Although some benzene clusters with substituted methanes (chloroform, *etc.*) have large interaction energies, the interaction of the C–H bond is not mainly responsible for the large interaction energies. The dispersion interactions of substituents with the benzene contribute to the attraction largely in these clusters.^{55–57}

7.2 Directionality of interaction

Conventional hydrogen bonds have strong directionality due to the large contribution of a highly orientation-dependent electrostatic interaction to the attraction,^{74,75} while the directionality of the CH/ π interaction is very weak due to the small electrostatic contribution.⁵⁵ The directionality of the dispersion interaction is weak. The directionality of the CH/ π interaction is compared to the conventional hydrogen bonds in Fig. 6.¹¹⁰ The change of the interaction energy associated with the tilting of the C–H bond is very small in the “typical” CH/ π interactions (benzene–methane cluster). The change of the interaction energy is less than 0.05 kcal mol^{–1}, even if the C–H bond is tilted by 30°. Although the orientation depen-

dence of the interaction energy is larger in the “activated” CH/ π interactions of the acetylene cluster, the orientation dependence in the benzene–acetylene cluster is still considerably smaller than that in the water dimer.

Although the role of the CH/ π interaction on the structures of molecular assemblies are often discussed based on the analogy of the hydrogen bond, the directionality of the CH/ π interaction is much weaker than that of conventional hydrogen bonds. Conventional hydrogen bonds play an important role in determining the structures of molecular assemblies such as molecular crystals, host–guest compounds and biological molecules, since the hydrogen bonds are sufficiently strong and sufficiently directional.⁷⁵ The magnitude of the directionality of the CH/ π interaction depends on the acidity of the C–H bond, since the electrostatic interaction is mainly responsible for the directionality. This shows that the discussion on the role of the CH/ π interaction based on the analogy of the hydrogen bond is incorrect and rather misleading, if the acidity of the C–H bond is not considered. The nature of the “activated” CH/ π interaction of some exceptional highly acidic C–H bonds is similar to that of the π -hydrogen bonds due to the electrostatic contribution. The “activated” CH/ π interactions show the directionality, though it is considerably weaker than that of conventional hydrogen bonds. The “activated” CH/ π interaction may be important in controlling the structure of the molecular assemblies. However most of the C–H bonds are not highly acidic. The nature of “typical” CH/ π interactions is close to that of van der Waals interactions, as the dispersion interaction is the major source of attraction and the electrostatic interaction is very weak. This suggests that “typical” CH/ π interactions are unable to play important roles in controlling the orientation of molecules in molecular assemblies, though there exists a weak attraction. The weak attraction in the “typical” CH/ π interactions may influence the crystal structures as the packing force in the crystal, as in the case of van der Waals attraction.

7.3 Shifts of C–H vibrational frequencies and electronic spectra

The shifts of C–H vibrational frequency and electronic spectra suggest that the nature of a “typical” CH/ π interaction is not close to that of a π -hydrogen bond but close to the interactions in van der Waals clusters.³¹ A low-frequency shift of a X–H stretch band is a well-known marker of hydrogen bond formation. The O–H stretch band has a strong low-frequency

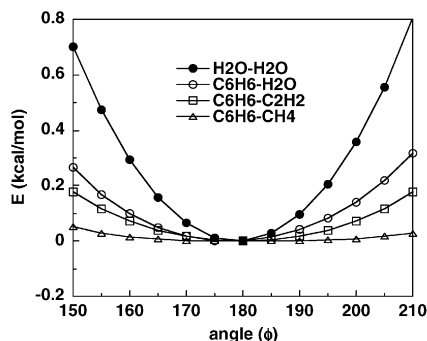
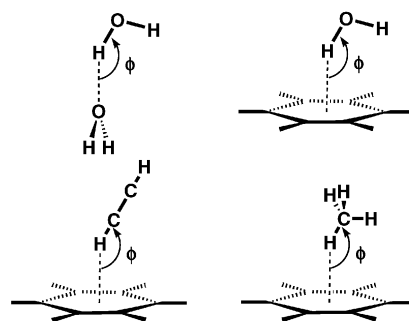


Fig. 6 Orientation dependence of interaction energies for the CH/ π interaction and hydrogen bond.



shift (-106 cm^{-1}) in the water dimer.¹¹¹ On the other hand, low-frequency shifts associated with the CH/ π interaction are very small³¹ or sometimes unconventional high frequency shifts are observed.³⁹ The observed low-frequency shifts in the methane clusters with benzene, toluene, *p*-xylene, mesitylene and naphthalene are -5 to -12 cm^{-1} .³¹ A larger low-frequency shift (-22 cm^{-1}) is observed in the benzene-acetylene cluster.³⁰

The high-frequency shifts of the S_1-S_0 electronic transition are generally seen associated with the formation of π -hydrogen bond clusters, while the low-frequency shifts are observed in van der Waals clusters. The shifts in the benzene-water and benzene-argon clusters are $+50$ and -21 cm^{-1} , respectively.^{112,113} A high-frequency shift ($+139\text{ cm}^{-1}$) was observed in the benzene-acetylene cluster.³⁰ On the other hand the low-frequency shifts (-11 to -56 cm^{-1}) were observed in the methane clusters with benzene, toluene, *p*-xylene, mesitylene and naphthalene.³¹ The low-frequency shifts show that the nature of the interactions in the methane clusters ("typical" CH/ π interaction) are not close to that of a π -hydrogen bond, but close to that of van der Waals clusters.

7.4 Comparison with OH/ π and NH/ π interactions

The interactions in the benzene clusters with water and ammonia (OH/ π and NH/ π interactions) are stronger than that in the benzene-methane cluster (Table 1). The experimental binding energies for the benzene-water and benzene-ammonia clusters (D_0) were measured by a few groups.¹¹⁴⁻¹¹⁸ The latest values for the two clusters are 2.44 ± 0.09 and $1.84 \pm 0.12\text{ kcal mol}^{-1}$, respectively.^{116,118} The estimated $E_{\text{CCSD(T)}(\text{limit})}$ values for the benzene clusters with water and ammonia are -3.0 and $-2.2\text{ kcal mol}^{-1}$, respectively.¹¹⁹ Calculated D_0 for the benzene-ammonia cluster (1.6 kcal mol^{-1}) is close to the experimental value, while that for the benzene-water cluster (2.0 kcal mol^{-1}) is smaller than the experimental value. The error is most likely an effect of the geometry used for the interaction energy calculation. The $E_{\text{CCSD(T)}(\text{limit})}$ value for the benzene-water cluster was estimated using the geometry without full optimization.¹²⁰

The interactions in the benzene clusters with water and ammonia are substantially larger than that for the benzene-methane cluster due to the larger electrostatic interaction. The E_{es} values in the water and ammonia clusters are -1.9 and $-1.0\text{ kcal mol}^{-1}$, respectively. The OH/ π and NH/ π interactions have stronger directionality compared with the CH/ π interaction due to the larger electrostatic interaction.¹¹⁹

8. Interaction of benzene with ammonium and alkylammonium

The nature of the interaction of the benzene with an alkylammonium cation (Fig. 7) is considerably different from that in the CH/ π interaction between neutral molecules, though it is sometimes claimed as the strong CH/ π interaction.^{121,122} The nature of the interaction of the benzene with an ammonium cation is also different from that of the NH/ π interactions between neutral molecules. The very strong electrostatic and induction interactions are the major source of the attraction in the benzene clusters with ammonium and alkylammonium

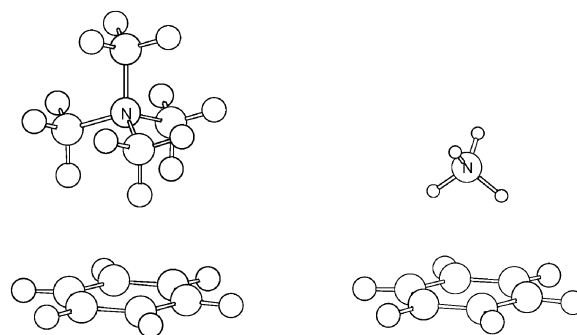


Fig. 7 Optimized geometries for benzene-tetramethylammonium and benzene-ammonium clusters.

(Table 1),^{123,124} while the dispersion interaction is mainly responsible for the attraction in the CH/ π and NH/ π interactions between neutral molecules.¹¹⁹ The E_{es} values in the benzene clusters with tetramethylammonium and ammonium (Fig. 7) are -5.3 and $-11.0\text{ kcal mol}^{-1}$, respectively. The E_{ind} values in these clusters are -3.8 and $-13.6\text{ kcal mol}^{-1}$, respectively. The strong electrostatic and induction interactions show that the nature of interactions in the benzene clusters with ammonium and alkylammonium is close to that of the cation/ π interactions in the alkali metal cation clusters and the benzene-pyridinium clusters.¹²⁵⁻¹²⁷

The structures of the benzene-ammonium and benzene-alkylammonium clusters are similar to those of the neutral NH/ π and CH/ π clusters, while the nature of the interactions is considerably different. The structural similarity does not guarantee similarity of the nature of interaction again. These results show that it is sometimes misleading to discuss the nature of the interaction solely based on structures.

9. Conclusion

This review summarizes recently reported high-level *ab initio* calculations and gas phase spectroscopic measurements of CH/ π interactions. Spectroscopic measurements of CH/ π clusters show that the binding energies for the "typical" aliphatic CH/ π interaction are very weak, while those for the "activated" CH/ π interactions of acidic C-H bonds in acetylene and chloroform are significantly larger. Calculated binding energies for the CH/ π clusters from CCSD(T) calculations agree well with the experimental ones, which shows that the high-level *ab initio* calculations provide very accurate interaction energies for the CH/ π clusters. *Ab initio* calculations show that the major source of the attraction in the CH/ π clusters is the dispersion interaction and the electrostatic contribution is always smaller than the dispersion. Especially the electrostatic interaction is very weak in the "typical" aliphatic CH/ π interactions. The CH/ π interaction of alkyne is stronger than the aliphatic CH/ π interaction due to the larger electrostatic interaction. The large dispersion interaction comes from chlorine atoms and is mainly responsible for the large binding energy in the benzene-chloroform cluster, though the electrostatic interaction is enhanced by the electron-withdrawing chlorine atoms.

The nature of the CH/ π interaction depends on the acidity of the interacting C–H bond. The nature of a “typical” CH/ π interaction is significantly different from that of conventional hydrogen bonds. The “typical” CH/ π interaction is weak and its directionality is very weak, while the conventional hydrogen bond is sufficiently strong and sufficiently directional due to the large electrostatic interaction. The nature of the “typical” CH/ π interaction is similar to that of the interaction in a van der Waals cluster. On the other hand, the nature of the activated CH/ π interactions of some exceptional highly acidic C–H bonds may have similarity with conventional hydrogen bonds, though the directionality of the “activated” CH/ π interactions is substantially weaker than the conventional hydrogen bonds due to the weak electrostatic interaction. Shifts of C–H vibrational frequencies and electronic spectra also supported the similarity. Although the role of the CH/ π interaction on the structure of molecular assemblies is often discussed based on the analogy of the hydrogen bonds, such discussion is not correct and rather misleading, if the acidity of the C–H bond is not considered. The magnitude of the CH/ π interaction energy depends on the acidity of the interacting C–H bond. The similarity of the “typical” CH/ π interactions with the van der Waals attraction suggests that they are unable to play an important role in controlling the orientation of molecule in molecular assemblies, though they may influence the crystal structure as the packing force in the crystal, as in the case of van der Waals attraction.

Acknowledgements

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- 85 Helgaker's method was originally proposed for an estimation of electron correlation contribution at the basis set limit. But this method was often used for an estimation of $E_{\text{MP2}(\text{limit})}$, since the basis sets dependence of HF level interaction energies for CH/ π clusters is very small in general.
- 86 The basis set dependence of ACCSD(T) is generally very weak compared to the basis set dependence of MP2 and CCSD(T) level interaction energies (ref. 50 and 55). In early studies the $E_{\text{CCSD(T)}(\text{limit})}$ was estimated using the ACCSD(T) obtained with a medium-size basis set (ref. 55 and 56). The estimated $E_{\text{CCSD(T)}(\text{limit})}$ value has a small error due to the weak basis set dependence of ACCSD(T). This error becomes larger when the E_{corr} becomes larger. In recent studies estimated ACCSD(T) at the basis set limit [ACCSD(T)_(limit)] was used for the estimation of $E_{\text{CCSD(T)}(\text{limit})}$ for avoiding the small error associated with the basis set dependence of ACCSD(T). The ACCSD(T)_(limit) for the benzene clusters with methane, ethylene, acetylene, dichloromethane and chloroform at the basis set limit were estimated from the ACCSD(T) obtained using the aug-cc-pVDZ basis set (ref. 33 and 34). The estimated ACCSD(T)_(limit) are 0.329, 0.595, 0.622, 1.205 and 1.600 kcal mol⁻¹, respectively. The ACCSD(T) values obtained using the aug-cc-pVDZ basis set are 0.369, 0.658, 0.747, 1.419 and 1.884 kcal mol⁻¹, respectively. The difference is very small in the methane and ethylene clusters (0.04 and 0.06 kcal mol⁻¹), while the difference is larger in the acetylene, dichloromethane and chloroform clusters (0.13, 0.21 and 0.28 kcal mol⁻¹, respectively). The estimated $E_{\text{CCSD(T)}(\text{limit})}$ for the benzene-acetylene cluster (−2.75 kcal mol⁻¹) using the ACCSD(T)_(limit) is very close to the $E_{\text{CCSD(T)}(\text{limit})}$ estimated directly by extrapolation from the CCSD(T)/aug-cc-pVXZ (X = D and T) level interaction energies (−2.77 kcal mol⁻¹) (ref. 52). Ringer *et al.* reported CCSD(T)/aug-cc-pVXZ (X = D and T) level interaction energies for the benzene-methane clusters (−1.195 and −1.387 kcal mol⁻¹, respectively) (ref. 50). The estimated $E_{\text{CCSD(T)}(\text{limit})}$ by Helgaker's method from these interaction energies is −1.47 kcal mol⁻¹, which is identical to the estimated $E_{\text{CCSD(T)}(\text{limit})}$ using the ACCSD(T)_(limit). The excellent agreement shows that the estimated $E_{\text{CCSD(T)}(\text{limit})}$ using the ACCSD(T)_(limit) are sufficiently accurate.
- 87 The difference between MP2 and CCSD(T) level optimized geometries is an important issue for an accurate evaluation of the interaction energy. Ringer *et al.* reported that the estimated CCSD(T) level interaction energy potential for the C_{3v} benzene-methane cluster at the basis set limit has its minimum when $R = 3.8$ Å (R is the distance between the centroid of benzene and the carbon atom of methane) (ref. 50). The MP2/cc-pVTZ level potential (ref. 55) has the potential minimum at the same separation. Both the estimated CCSD(T) level interaction energy potential for the C_{6v} benzene-acetylene cluster at the basis set limit and the MP2/cc-pVTZ level potential have their minima when $R = 3.5$ Å (R is the distance between the centroid of benzene and the carbon atom of interacting C–H bond of acetylene) (ref. 33). The excellent agreement shows that the optimized geometries at the MP2/cc-pVTZ level are sufficiently accurate. The MP2 method overestimates the attraction compared with the CCSD(T) method, while the cc-pVTZ basis set underestimates the attraction compared with the basis set limit. Apparently, an error cancellation is the cause of the good performance of the MP2/cc-pVTZ level calculations. The calculated interaction energy potentials for the two clusters are very shallow near the potential minima. The energy increments associated with the changes of intermolecular distances are less than 0.1 kcal mol⁻¹, if the changes of intermolecular distances are less than 0.1 Å. These results suggest that the error of the calculated interaction energy associated with the inaccuracy of the MP2/cc-pVTZ level optimized geometry is very small.
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