

Structure, Stabilities, Thermodynamic Properties, and IR Spectra of Acetylene Clusters $(\text{C}_2\text{H}_2)_{n=2-5}$

S. Karthikeyan, Han Myoung Lee, and Kwang S. Kim*

Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea

Received June 12, 2010

Abstract: There are no clear conclusions over the structures of the acetylene clusters. In this regard, we have carried out high-level calculations for acetylene clusters $(\text{C}_2\text{H}_2)_{2-5}$ using dispersion-corrected density functional theory (DFT-D), Møller–Plesset second-order perturbation theory (MP2); and coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)] at the complete basis set limit. The lowest energy structure of the acetylene dimer has a T-shaped structure of C_{2v} symmetry, but it is nearly isoenergetic to the displaced stacked structure of C_{2h} symmetry. We find that the structure shows the quantum statistical distribution for configurations between the T-shaped and displaced stacked structures for which the average angle $\langle \hat{\theta} \rangle$ between two acetylene molecules would be $53\text{--}78^\circ$, close to the T-shaped structure. The trimer has a triangular structure of C_{3h} symmetry. The tetramer has two lowest energy isomers of S_4 and C_{2h} symmetry in zero-point energy (ZPE)–uncorrected energy (ΔE_e), but one lowest energy isomer of C_{2v} symmetry in ZPE-corrected energy (ΔE_0). For the pentamer, the global minimum structure is C_1 symmetry with eight sets of T-type $\pi\text{--H}$ interactions and a set of $\pi\text{--}\pi$ interactions. Our high-level *ab initio* calculations are consistent with available experimental data.

Introduction

In recent years, there has been much interest in the structure and properties of weakly bound complexes,^{1–4} because of their ubiquitous role in diverse fields including molecular clusters,^{5–10} biomolecular structures,^{11–13} supramolecular chemistry,^{14–16} and self-assembled nanostructures.^{17–19} In particular, to understand the aromatic $\pi\text{--H}$ and $\pi\text{--}\pi$ interactions,^{20–33} the aromatic dimers including the benzene dimer have been studied extensively.^{34–39} In addition, aliphatic π interactions have also been studied.^{40–59}

For the acetylenic π interactions, it is necessary to investigate the acetylene clusters. Some selected structures are shown in Figures 1–4. For the acetylene dimer $[(\text{C}_2\text{H}_2)_2]$, Pendley and Ewing reported five bands using Fourier transform infrared spectroscopy.⁴⁴ These bands are consistent with the staggered structure (S-shaped with C_{2h} symmetry) proposed by Sakai et al.⁴⁵ The free-jet infrared absorption spectroscopy study of Ohshima et al.⁴⁶ showed that the

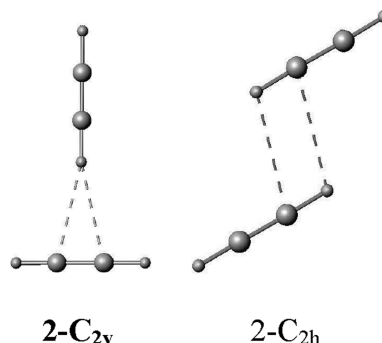


Figure 1. Low-energy structures of $(\text{C}_2\text{H}_2)_2$.

acetylene dimer is a T-shaped hydrogen-bonded structure of C_{2v} symmetry. Dykstra and Shuler,⁵³ Alberts et al.,⁵⁴ Bone and Handy,⁵⁵ Hobza et al.,⁵⁶ Karpfen,^{57,58} and Brenner and Millie⁵⁹ proposed the T-shaped structure with C_{2v} symmetry. On the other hand, Prichard et al.⁴⁷ reported that the acetylene dimer is a twisted T-shaped hydrogen-bonded structure, but not the C_{2v} symmetry structure. Thus, there is no clear conclusion for the acetylene dimer structure.

* Corresponding author e-mail: kim@postech.ac.kr.

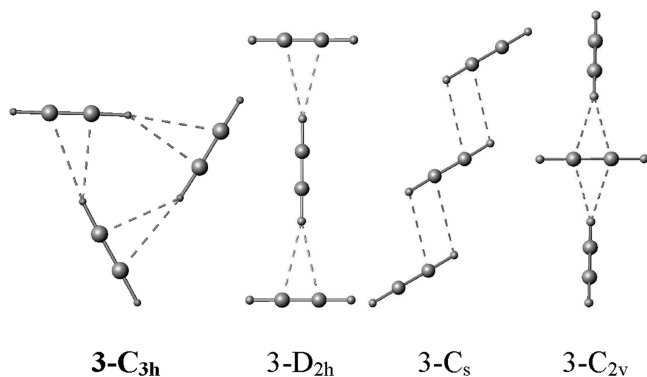


Figure 2. Low-energy structures of $(\text{C}_2\text{H}_2)_3$.

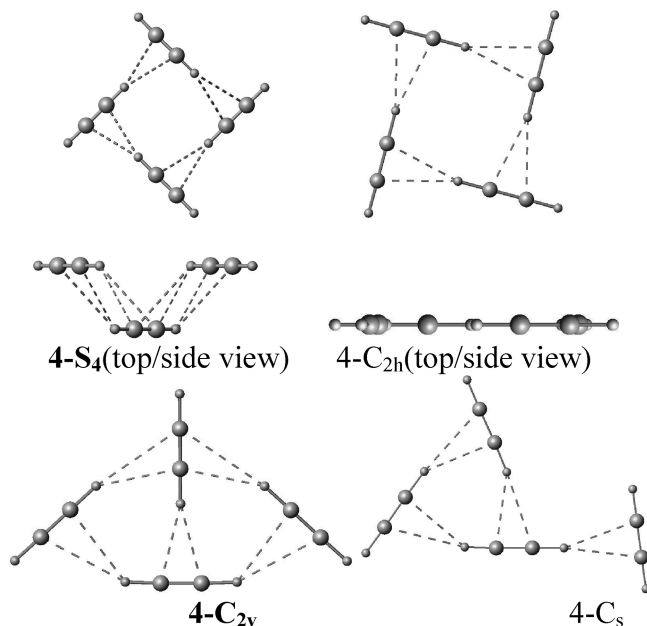


Figure 3. Low-energy structures of $(\text{C}_2\text{H}_2)_4$.

For the acetylene trimer, Dykstra and Shuler,^{41,53} Alberts et al.,⁵⁴ Brenner and Millie,⁵⁹ Prichard et al.,^{47,48} and Bone et al.⁴⁹ reported the C_{3h} symmetry structure. In the case of the acetylene tetramer, Bryant et al.⁵⁰ and Dykstra and Shuler⁴¹ proposed the S_4 symmetry structure on the basis of their infrared C–H stretching spectra and the Molecular Mechanic Cluster (MMC) method, respectively. On the other hand, Bone et al.⁵¹ proposed the cyclic structure of C_{4h} symmetry. For the acetylene pentamer, Bone et al.⁵¹ reported that the global minimum energy structure is the C_{2h} symmetry structure based on the MP2/DPZ level of theory. Yu et al.⁵² assumed the acetylene cyclic structure of C_{5h} symmetry based on the Hartree–Fock level of theory. On the other hand, Dykstra and Shuler⁵³ reported that the global minimum structure for the acetylene pentamer is C_1 symmetry. Furthermore, it is not clear whether a new more stable structure could be found for the acetylene pentamer because of its structural complexity.

In this regard, a more accurate theoretical investigation is required. We have carried out DFT-D, MP2, and CCSD(T) calculations. In order to obtain the concrete conclusion, we have focused our attention on the following: (a) binding energy at high levels of theory, (b) ZPE correction, (c)

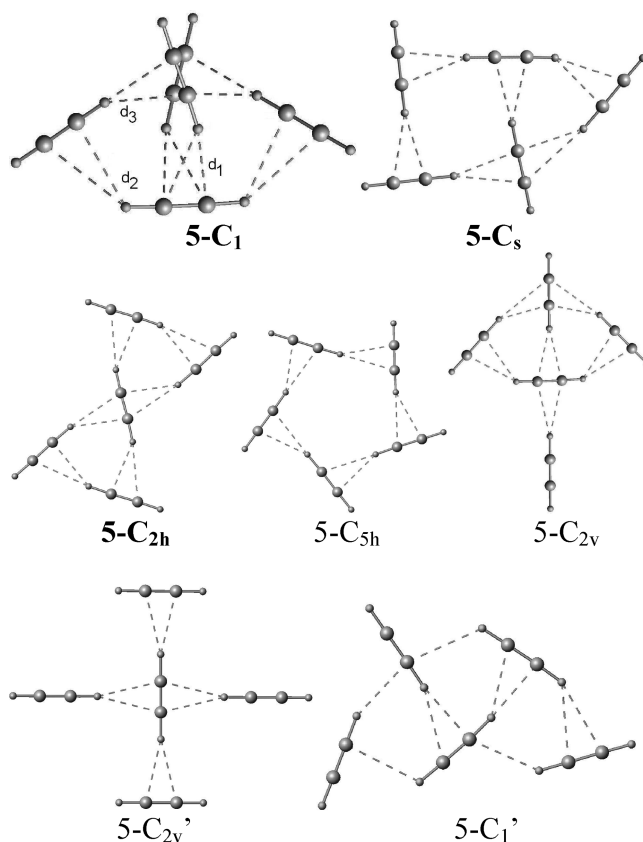


Figure 4. Low-energy structures of $(\text{C}_2\text{H}_2)_5$.

complete basis set (CBS) limit, and (d) comparison of the predicted spectra with the available experimental data.^{46–50}

Computational Method

A detailed conformation search was followed by a complete geometry optimization at the DFT-D(M06-2X)⁶⁰ and MP2 levels of theory. Then, frequency calculations were carried out for several low-energy isomers at the M06-2X/aug-cc-pVDZ level. All atoms were treated with the aug-cc-pVDZ and aug-cc-pVTZ basis sets (which will be abbreviated as aVDZ and aVTZ, respectively). The MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ energies were obtained using the single-point energy calculations on the MP2/aug-cc-pVDZ geometries. The basis set superposition error (BSSE) correction was made after geometry optimization. The calculations were performed with the Gaussian 03 suite of programs.⁶¹ The molecular structures were drawn with the Pymol package.⁶²

We estimated the MP2/CBS binding energies on the basis of the extrapolation scheme, which exploits the fact that the electron correlation error is proportional to N^{-3} for aug-cc-pVNZ basis sets.^{63,64} The CCSD(T)/CBS energies were estimated by assuming that the difference in binding energies between MP2/aug-cc-pVDZ and MP2/CBS calculations is similar to that between CCSD(T)/aug-cc-pVDZ and CCSD(T)/CBS calculations.⁶⁵ The spectral features of acetylene clusters $(\text{C}_2\text{H}_2)_{2-5}$ were investigated at the M06-2X/aug-cc-pVDZ and MP2/aug-cc-pVDZ levels of theory. In calculating the CCSD(T)/CBS ΔE_0 , ΔH_r (enthalpy at room temperature), and ΔG_{50} (free energies at 50 K, 1 atm), we employed the

MP2/aug-cc-pVDZ frequencies. The structure and binding energies of M06-2X tend to be more reliable than the BSSE-uncorrected MP2/aug-cc-pVDZ, because BSSE-uncorrected MP2/aug-cc-pVDZ overestimates binding energies.^{7,66} The MP2/aug-cc-pVDZ frequencies are similar to the M06-2X/aug-cc-pVDZ values but tend to be overestimated because of BSSE. In this regard, the vibrational stretching frequencies will be discussed on the basis of the M06-2X/aug-cc-pVDZ results. Since the CCSD(T)/CBS results are the most reliable, our discussion will be based on the CCSD(T)/CBS results, unless otherwise specified.

To facilitate the comparison of the calculated frequencies with experimental frequencies, the DFT-D theoretical harmonic frequencies are scaled by a constant factor. When the MP2 predicted harmonic frequencies are compared with the experimental frequencies, higher vibrational frequencies tend to be overestimated while lower frequencies do not. Thus, the MP2 frequencies can often be exponentially scaled^{67–69} as $\nu_i^s = \nu_i e^{-\alpha \nu_i}$, where ν_i^s and ν_i are scaled and unscaled frequencies corresponding to the vibrational mode i . The exponent α , a single parameter, was chosen to optimally fit the theoretical acetylene harmonic frequencies with the experimental frequencies. This method scales down lower vibrational frequencies slightly less than higher frequencies; thus, the experimentally scaled MP2 frequencies often turned out to be better than the constant-scaled values. Since the unscaled M06-2X/aug-cc-pVDZ and MP2/aug-cc-pVDZ values for the asymmetric C–H stretching and bending C–C–H frequencies of C_2H_2 are 3492 and 774 cm^{-1} and 3431 and 734 cm^{-1} , as compared with the experimental values (3287 and 729 cm^{-1}),⁴⁴ the scale factor 0.942 is used for M06-2X/aug-cc-pVDZ and the value of α is chosen as 0.0000125 for MP2/aug-cc-pVDZ.

Results and Discussion

Important low-lying energy structures of the acetylene clusters $(C_2H_2)_{2-5}$ are shown in Figures 1–4. This binding energies and thermodynamics properties at the M06-2X/aug-cc-pVDZ level are in Table 1, and the binding energies and thermodynamics properties at the MP2/aug-cc-pVDZ, MP2/aug-cc-pVTZ, MP2/CBS, CCSD(T)/aug-cc-pVDZ, and CCSD(T)/CBS levels are listed in Table 2, where ΔE_e , ΔE_0 , ΔH_r , and $\Delta G(50\text{ K})$ are the BSSE-corrected thermodynamic quantities. The selected geometrical parameters of 2- C_{2v} , 2- C_{2h} , 3- C_{3h} , 4- S_4 , 4- C_{2v} , and 5- C_1 are given in Table 3. Acetylene clusters are named “Num-Sym”, where “Num” is the number acetylene monomer in the cluster, and “Sym” shows the symmetry of the cluster. If there are two clusters for the same symmetry, a prime is used for the structure with the less stable energy. The M06-2X and MP2 vibrational frequencies of selected acetylene clusters are in Figure 5 and the Supporting Information (Table S1).

For the acetylene dimer, the T-shaped 2- C_{2v} isomer and the displaced-stacked 2- C_{2h} isomer are nearly isoenergetic. The T-shaped 2- C_{2v} is more stable in ΔE_e by 1.01, 0.59, and 0.68 kJ/mol at the M06-2X/aug-cc-pVDZ, MP2/CBS, and CCSD(T)/CBS levels, respectively. The 2- C_{2h} isomer (displaced-stacked structure) is the transition state of the 2- C_{2v} isomer with one imaginary frequency (45 cm^{-1} for

Table 1. DFT-D(M06-2X) Interaction Energies and Thermodynamic Quantities (kJ/mol) for Low-Energy Structures of the Acetylene Clusters $(C_2H_2)_{n=2-5}$ ^a

name	M06-2X/aVDZ			
	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H$	$-\Delta G(50\text{ K})$
2- C_{2v}	5.72	3.64	2.87	0.89
2- $C_{2h}(1)$	4.71	(3.74)	4.82	(0.86)
3- C_{3h}	17.05	11.73	9.98	4.70
3- $D_{2h}(1)$	11.15	(7.35)	6.70	(0.41)
3- $C_s(4)$	9.28	(8.06)	13.24	(1.03)
3- C_{2v}	11.18	6.57	3.90	0.02
4- S_4	26.14	17.65	14.69	6.45
4- C_{2h}	26.17	17.59	14.66	6.17
4- C_{2v}	24.37	19.05	17.03	7.52
4- C_s	23.18	15.81	11.93	5.43
5- C_1	33.98	26.72	27.83	9.90
5- C_s	34.85	22.24	18.98	6.00
5- C_{2h}	34.75	24.61	19.36	8.87
5- $C_1'(2)$	30.68	(22.13)	20.81	(6.23)
5- $C_{3h}(2)$	32.29	(21.98)	21.74	(4.68)
5- $C_{2v}(1)$	30.89	(21.42)	18.12	(5.44)
5- $C_{2v}'(3)$	27.41	(18.17)	19.33	(1.94)

^a If the structure is not a minimum, the numbers of imaginary frequencies are given in parentheses after the structure name. In these cases, the ZPE and thermal energy corrections are not reliable enough, so these value for $-\Delta E_0$ and $-\Delta G$ are given in parentheses. The most stable isomers are given in boldface.

M06-2X/aug-cc-pVDZ, 29 cm^{-1} for BSSE-uncorrected MP2/aug-cc-pVDZ, 34 cm^{-1} for BSSE-corrected MP2/aug-cc-pVDZ). However, the energy difference in ΔE_e between 2- C_{2v} and 2- C_{2h} is too small; thus, the stability in ZPE-corrected energy (ΔE_0) could be changed. In a simple approximation that the low imaginary frequency is neglected for ZPE correction because this mode could be replaced by an internal translational or rotational mode of monomers in the cluster, the 2- C_{2h} isomer is more stable than the 2- C_{2v} isomer by 0.10, 0.42, and 0.33 kJ/mol at the M06-2X/aVDZ, MP2/CBS, and CCSD(T)/CBS levels, respectively. This indicates that the two isomers have a flat potential surface, and so the structure would show the quantum statistical distribution of configurations ($\theta = 0-90^\circ$) between the T-shaped ($\theta = 90^\circ$) and displaced stacked ($\theta = 0^\circ$) structures, as in the case of the C_{2v} vs C_s benzene–water cluster conformation,⁷⁰ water dimer with an excess electron,⁷¹ or the linear vs bent HCCN conformation.⁷²

For the 2- C_{2v} isomer, the predicted distance between two centers of mass of each monomer unit (R) is 4.42 Å and 4.44 Å at the M06-2X/aug-cc-pVDZ and BSSE-corrected MP2/aug-cc-pVDZ levels, respectively, in reasonable agreement with the experimental value 4.41 Å.⁵⁶ For the 2- C_{2h} isomer, the predicted R is 4.27 Å and 4.18 Å at the M06-2X/aug-cc-pVDZ and BSSE-corrected MP2/aug-cc-pVDZ levels, respectively, which is slightly shorter but still close to the experimental value 4.41 Å.⁵⁶ Thus, the structure having the quantum statistical distribution of the 2- C_{2v} to 2- C_{2h} configurations should be closer to the 2- C_{2v} configuration. The vertical distance between two acetylene structures of 2- C_{2h} is 2.75 Å, which is much shorter than the stacking distances (~ 3.4 Å) between stacking aromatic rings in organic crystals,⁷³ multiwalled carbon nanotube layers,⁷⁴ or DNA stacks.^{75,76} The calculated C≡C and C–H bond distances of the acetylene dimer (2- C_{2v}) are 1.201 and 1.066

Table 2. MP2 and CCSD(T) Interaction Energies and Thermodynamic Quantities (kJ/mol) for Low Energy Structures of the Acetylene Clusters (C₂H₂)_{n=2–5}^a

MP2/aVDZ; MP2/aVTZ; [MP2/CBS]				
name	–ΔE _e	–ΔE ₀	–ΔH	–ΔG(50 K)
2-C _{2v}	5.76; 6.65; [7.02]	2.87; 3.75; [4.13]	2.52; 3.41; [3.78]	0.07; 0.88; [1.26]
2-C _{2h} (1)	5.41; 6.13; [6.43]	3.53; 4.25; [4.55]	5.10; 5.82; [6.12]	0.54; 1.25; [1.55]
3-C _{3h}	17.94; 20.62; [21.74]	10.77; 13.44; [14.56]	10.10; 12.78; [13.90]	3.06; 5.73; [6.86]
3-D _{2h} (1)	11.22; 12.99; [13.74]	5.84; 7.61; [8.36]	5.97; 7.74; [8.49]	–1.37; 0.40; [1.15]
3-C _s (2)	10.99; 12.49; [13.12]	7.38; 8.88; [9.51]	9.14; 10.64; [11.27]	1.09; 2.59; [3.22]
3-C _{2v}	10.75; 12.51; [13.26]	5.05; 6.82; [7.56]	0.72; 4.76; [5.51]	–1.69; 0.07; [0.82]
4-S ₄	27.09; 31.01; [32.66]	16.41; 20.33; [21.98]	14.49; 18.41; [20.07]	4.71; 8.63; [10.28]
4-C _{2h}	26.97; 30.83; [32.46]	15.85; 19.71; [21.34]	14.13; 18.00; [19.62]	4.51; 8.38; [10.00]
4-C _{2v}	26.58; 30.63; [32.33]	16.60; 20.64; [22.34]	14.50; 18.54; [20.24]	4.51; 8.56; [10.26]
4-C _s (1)	24.33; 27.94; [29.46]	14.62; 18.22; [19.74]	14.51; 18.11; [19.63]	3.19; 6.80; [8.32]
5-C ₁	38.98; 44.77; [47.21]	27.76; 33.55; [35.98]	23.73; 29.52; [31.96]	11.01; 16.80; [19.24]
5-C _s	37.32; 42.81; [45.12]	22.72; 28.21; [30.52]	20.08; 25.57; [27.89]	6.31; 11.81; [14.12]
5-C _{2h}	36.36; 41.61; [43.82]	22.03; 27.28; [29.49]	19.28; 24.53; [26.74]	5.60; 10.85; [13.06]
5-C ₁ '	33.83; 39.17; [41.42]	20.50; 25.84; [28.09]	17.18; 22.52; [24.77]	4.13; 9.48; [11.73]
5-C _{3h} (2)	33.20; 37.96; [39.96]	19.63; 24.39; [26.40]	21.21; 25.97; [27.98]	2.03; 6.79; [8.79]
5-C _{2v}	32.64; 37.63; [39.74]	19.43; 24.42; [26.52]	15.87; 20.86; [22.96]	3.22; 8.21; [10.31]
5-C _{2v} '(3)	27.89; 32.00; [33.74]	16.28; 20.40; [22.13]	18.61; 22.73; [24.46]	–0.35; 3.77; [5.50]

CCSD(T)/aVDZ; [CCSD(T)/CBS]				
name	–ΔE _e	–ΔE ₀	–ΔH	–ΔG(50 K)
2-C _{2v}	5.05; [6.30]	2.15; [3.41]	1.81; [3.06]	–0.72; [0.54]
2-C _{2h}	4.60; [5.62]	2.72; [3.74]	4.29; [5.31]	–0.27; [0.74]
3-C _{3h}	15.56; [19.36]	8.34; [12.18]	7.72; [11.52]	0.68; [4.48]
3-D _{2h}	9.79; [12.31]	4.41; [6.93]	4.54; [7.06]	–2.80; [–0.28]
3-C _s	9.38; [11.51]	5.76; [7.89]	7.53; [9.66]	–0.53; [1.60]
4-S ₄	23.50; [29.08]	12.82; [18.40]	10.91; [16.48]	1.12; [6.70]
4-C _{2h}	23.57; [29.06]	12.45; [17.94]	10.73; [16.22]	1.11; [6.60]
4-C _{2v}	22.63; [28.37]	12.64; [18.39]	10.54; [16.28]	0.56; [6.30]
4-C _s	21.07; [26.20]	11.36; [16.48]	11.25; [16.37]	–0.07; [5.06]
5-C ₁	30.81; [39.03]	19.59; [27.81]	15.56; [23.78]	2.84; [11.07]
5-C _s	32.25; [40.06]	17.66; [25.46]	15.02; [22.83]	1.25; [9.06]
5-C _{2h}	31.52; [38.98]	17.19; [24.65]	14.45; [21.91]	0.76; [8.22]
5-C ₁ '	28.18; [35.78]	14.85; [22.44]	11.53; [19.12]	–1.52; [6.08]
5-C _{3h}	29.05; [35.82]	15.48; [22.25]	17.06; [23.83]	–2.12; [4.64]
5-C _{2v}	27.78; [34.87]	14.57; [21.66]	11.01; [18.10]	–1.64; [5.45]

^a The BSSE corrections are made. CCSD(T)/CBS energies were estimated by applying the correction term (the difference between MP2/aVDZ and CCSD(T)/aVDZ energies) to the MP2/CBS interaction energies, which were obtained with the extrapolation scheme utilizing the electron correlation error proportional to N^{-3} for the aug-cc-pVNZ basis set. In the CCSD(T)/CBS energies, the MP2/aVDZ thermal energies were used. If the structure is not a minimum, the numbers of imaginary frequencies are given in parentheses after the structure name. In these cases, the ZPE and thermal energy corrections are not reliable enough. The most stable isomers are given in boldface.

Table 3. Selected Geometrical Parameters of 2-C_{2v}, 2-C_{2h}, 3-C_{3h}, 4-S₄, 4-C_{2v}, and 5-C₁ at the M06-2X/aVDZ (and MP2/aVDZ [Geometry-Optimized BSSE-Corrected MP2/aVDZ]) Levels

	2-C _{2v}		2-C _{2h}		3-C _{3h}		4-S ₄	
<i>d</i> _{CH}	2.81(2.67[2.81])		3.03(2.90[2.90])		2.76(2.60)		2.73(2.58)	
<i>d</i> _{CM–CM}	4.42(4.30[4.44])		4.27(4.18[4.18])		4.37(4.25)		4.34(4.24)	
θ(∠HC _{cm} H)	90		0		60		90	

	4-C _{2v}			5-C ₁		
<i>d</i> _{CH}	2.62(2.53)	2.90(2.77)	2.77(2.61)	2.81(2.65)	2.92(2.79)	2.66(2.55)
<i>d</i> _{CM–CM}	4.22(4.15)	4.32(4.21)	4.54(4.44)	4.32(4.21)	4.19(4.09)	4.31(4.25)
θ(∠HC _{cm} H)	90	54	78	90	94	92

Å at the M06-2X/aug-cc-pVDZ level and 1.232 and 1.076 Å at the MP2/aug-cc-pVDZ level, which are close to the experimental values 1.203 and 1.062 Å. The acetylene dimer is predicted to be stable without dissociation below 55 K at 1 atm.

From the microwave and infrared spectra, Prichard et al.⁴⁷ reported that the structure of acetylene dimer is a twisted T-shaped hydrogen-bonded structure but not of the C_{2v}

symmetry. One of the acetylene monomers was twisted by θ = 63° from the center of mass. The distance *R* is 4.38 Å, and the electric dipole moment of the dimer is 0.28 D. Most of MP2 calculations predict that the global minimum of the acetylene dimer is the T-shaped structure with C_{2v} symmetry. Alberts et al.⁵⁴ reported the binding energy of 6.90 kJ/mol. Bone and Handy⁵⁵ reported the C_{2v} symmetry structure with a distance *R* of 4.34 Å and a binding energy of 5.69 kJ/mol

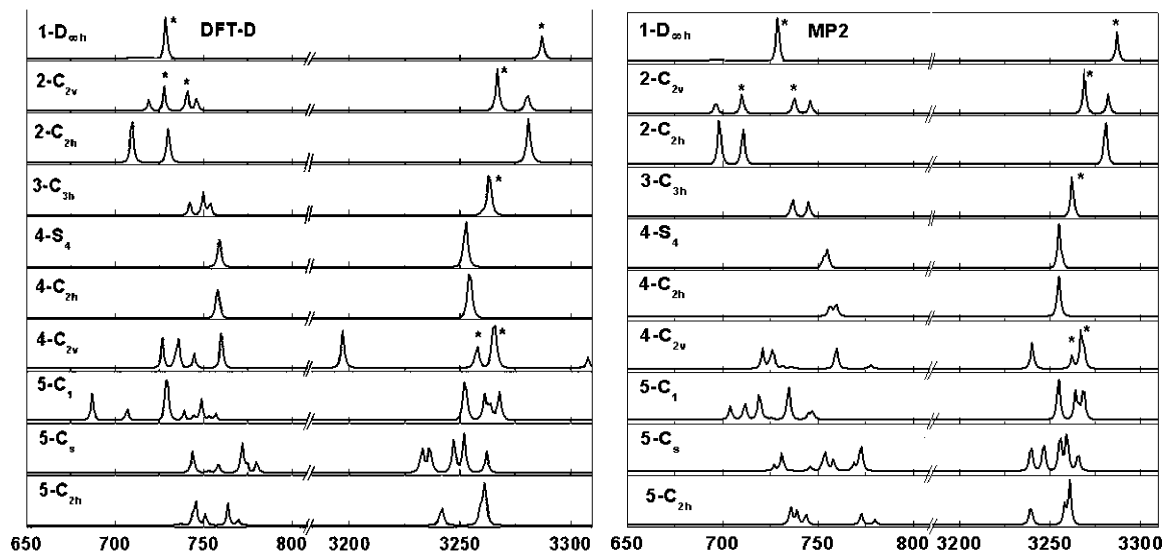


Figure 5. DFT-D/M06-2X and MP2 predicted vibrational spectra of $(\text{C}_2\text{H}_2)_{n=2-5}$. The M06-2X values are scaled by 0.942, while the exponential scale factor α is chosen as 0.0000125 for the MP2/aug-cc-pVDZ values. The experimental frequencies are marked as asterisks.

at the MP2/TZ2P level. Hobza et al.⁵⁶ reported the C_{2v} structure with a distance R of 4.49 Å and a binding energy of 4.49 kJ/mol at the MP2/[DZ+(2df,2p)] level. Yu et al.⁵² and Karpfen⁵⁷ predicted that the C_{2v} structure (distance R : 4.32 Å) has a binding energy of 9.20 and 5.74 kJ/mol, respectively. Dykstra and Shuler⁵³ predicted that the T-shaped structure with C_{2v} symmetry has a distance R of 4.36 Å and a binding energy of 6.34 kJ/mol.

We have calculated the binding energy and thermodynamics quantities of the twisted acetylene dimer, but it is slightly less stable than the 2-C_{2v} structure. During the full optimization of the twisted T-shaped acetylene dimer, it becomes the T-shaped structure of 2-C_{2v} . Thus, here we show that this structure is reconciled by considering the quantum statistical distribution of the 2-C_{2v} to 2-C_{2h} configurations for which the 2-C_{2v} is much more populated than the 2-C_{2h} .

The study of the accurate quantum statistical distribution would be a challenging subject because it requires the full potential surface of the configurations. Here, we report the results. The MP2/CBS ΔE_c potential energy surface (PES) is presented in Figure 6a where the minimum potential well is at $\theta = 90^\circ$, while the MP2/CBS $\Delta E_0'$ PES is in Figure 6b, where the minimum potential well is at $\theta = 63^\circ$, which happens to be the same with the experimental value. $\Delta E_0'$ indicates the ZPE-corrected energy excluding only the ZPE along the $\text{C}_{2v}\text{--C}_{2h}$ transition pathway eigenmode. The ΔE_c potential energy well is nearly harmonic at the minimum point ($\theta = 90^\circ$) where the MP2/aug-cc-pVDZ harmonic vibrational frequency is 39 cm^{-1} . On this potential surface, the anharmonicity-corrected fundamental vibrational frequency is evaluated to be 44 cm^{-1} ($E_1 - E_0$). The anharmonic vibrational frequency on the $\Delta E_0'$ potential energy well is evaluated as $\Delta E_{1-0}' = 49\text{ cm}^{-1}$. From the wave functions at the vibrational ground state (Ψ_0 and Ψ_0' corresponding to ΔE and $\Delta E'$, respectively), the average angle ($\langle \theta \rangle$) is 78° on the ΔE_c PES and 53° on the $\Delta E_0'$ PES. Since ΔE PES and $\Delta E'$ PES would be considered the limiting cases without and with ZPEs for all the other eigenmodes of the PES, the

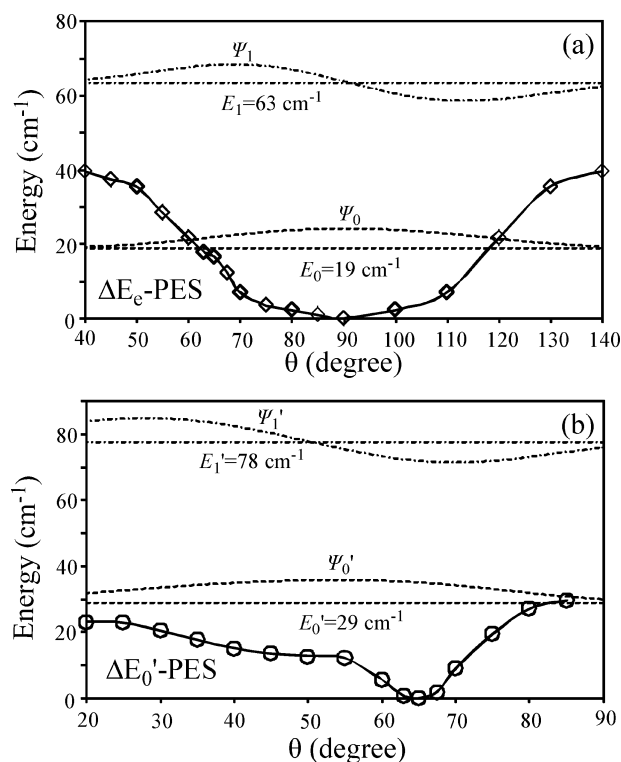


Figure 6. Anharmonic vibrational energies and wave functions for the MP2/CBS ΔE_c (a) and $\Delta E_0'$ (b) potential energy profiles with respect to the intermolecular angle (θ) of the acetylene dimer.

realistic value of $|\bar{\theta}|$ would be between the two cases; i.e., $|\bar{\theta}|$ would likely be $53\text{--}78^\circ$, in agreement with the experimentally observed value ($\theta = 63^\circ$). Although this study is based on the MP2/CBS PES, the results based on CCSD(T)/CBS would be similar because the difference between the two cases is small, as noted in Table 2.

The predicted M06-2X/aug-cc-pVDZ bending frequencies for the 2-C_{2v} isomer appearing at 728 and 741 cm^{-1} [average value of 735 cm^{-1}] is consistent with the experimental

frequency at 737 cm^{-1} . This band corresponds to the out-of-phase in-plane coupling of HCCH and is red-shifted by 1 and 12 cm^{-1} [average value of 6 cm^{-1}] as compared to the monomer frequencies. The predicted asymmetric stretching frequencies appear at 3267 and 3281 cm^{-1} [average value of 3274 cm^{-1}], which are 20 and 6 cm^{-1} [average value of 13 cm^{-1}] red-shifted from the acetylene monomer frequencies, in good agreement with the experimental frequency^{46,47} of 3273 cm^{-1} , which is blue-shifted by 6 cm^{-1} .

When we compare the acetylene dimer with the benzene dimer, we find some interesting results. In the case of benzene dimer, the C–H bond of the proton donor becomes shorter, showing a blue shift, whose unusual features were discussed by Hobza and co-workers.⁷⁷ However, in the case of the acetylene dimer, it shows the opposite trend, with a slightly increased bond length showing a red shift by $\sim 20\text{ cm}^{-1}$, as in a normal hydrogen bond.

The acetylene dimer in a nonlinear configuration by van der Waals interaction gives four fundamental frequencies. The remaining stretching frequencies may be represented as in-phase and out-of-phase couplings between acetylene monomer bonds. At the M06-2X/aug-cc-pVDZ level, the two strong peaks of the bending and asymmetric stretching frequencies for the 2-C_{2h} isomer appear at 730 and 3281 cm^{-1} , which are slightly smaller and larger than the experimental frequencies of 737 and 3273 cm^{-1} , respectively. This shows that the 2-C_{2v} configuration ($\theta = 90^\circ$) is more quantum statistically populated than the 2-C_{2h} configuration ($\theta = 0^\circ$), in agreement with the fact that the experimental value is 63° . The dipole moment of the 2-C_{2v} configuration ($\theta = 90^\circ$) is 0.36 D , while that of the 2-C_{2h} configuration ($\theta = 0^\circ$) is 0 D . In consideration of the quantum statistical distribution, the average dipole moment is near the experimental⁴⁷ value of 0.28 D .

In the case of the acetylene trimer $(\text{C}_2\text{H}_2)_3$, the cyclic structure of C_{3h} symmetry is much more stable than those of the other isomers because the C_{3h} structure has three sets of slightly slanted T-shaped $\pi\text{--H}$ interactions, while other structure has only two sets of $\pi\text{--H}$ interactions. The interaction energy of the acetylene trimer (C_{3h} isomer) is more than the sum of three single H– π (i.e., C_{2v} interaction energy) interaction energies, due to the relay effect which enhances the positive charge of H by 0.01 au (from 0.24 to 0.25 au) and the negative charge of the neighboring C by 0.03 au (from -0.26 to -0.23 au). The 3-D_{2h} isomer ($\pi\text{--H--}\pi$ interaction type) is the transition state of the 3-C_{3h} isomer. To maximize the H– π interaction, the acetylene trimer has to be twisted. Similar structures were reported by Bone et al.,⁴⁹ Yu et al.,⁵² Dykstra and Shuler,⁵³ Alberts et al.,⁵⁴ and Brenner and Millie.⁵⁹ The distance from the C_3 symmetry axis to the center of mass of each monomer is reported to be 0.247 , 2.668 , 2.478 , and 2.460 \AA by Bone et al.,⁴⁹ Yu et al.,⁵² Dykstra and Shuler,⁵³ and Alberts et al.,⁵⁴ respectively. Our predicted distance is 2.526 \AA , in good agreement with the experimental value of 2.514 \AA . The predicted asymmetric vibrational stretching frequency at 3264 cm^{-1} for 3-C_{3h} is in close agreement with the experimental vibrational frequency at 3265.6 cm^{-1} . The predicted bending frequencies appear at 742 , 750 , and 754 cm^{-1} .

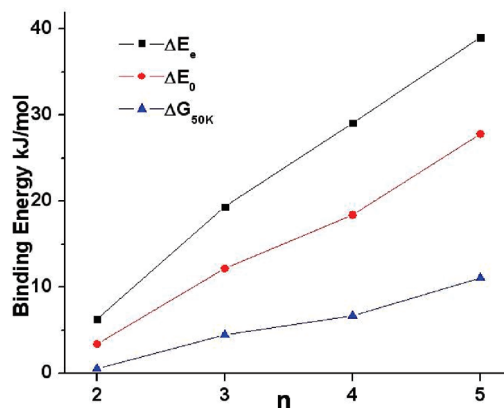


Figure 7. Thermodynamic properties of the low-energy structure of the $(\text{C}_2\text{H}_2)_n$ clusters.

In the case of the acetylene tetramer $(\text{C}_2\text{H}_2)_4$, one might expect that the structure is a planar configuration with C_{4h} symmetry, based on the previous discussion on the acetylene dimer and trimer in which more $\pi\text{--H}$ interaction bonds are formed between acetylene monomer units. We have carried out an extensive search for the most stable isomer. Previously reported structures (4-S_4 and 4-C_{4h})^{50,51} were also considered for comparison. Among many isomers, the lowest energy isomer in ΔE_e is the square shaped 4-C_{2h} and 4-S_4 structures, which have four sets of $\pi\text{--H}$ interactions, while the lowest energy isomer in ΔE_0 is the bitriangular shaped 4-C_{2v} structure which has five sets of $\pi\text{--H}$ interactions. The 4-C_s isomer is the transition state of the 4-C_{2v} isomer. The asymmetric stretching vibrational frequencies of the 4-C_{2v} isomer (3258 , 3266 cm^{-1} ; average value: 3262 cm^{-1}) are consistent with the experimental value 3262 cm^{-1} .

In the case of the acetylene pentamer $(\text{C}_2\text{H}_2)_5$, Bone et al.⁵¹ proposed the “8”-shaped structure formed by two triangles (5-C_{2h}) based on the MP2/DPZ level. Dykstra and Shuler⁴¹ reported that the global minimum energy structure for the acetylene pentamer is 5-C_1 on the basis of the MMC method, which has eight T-shaped interactions. We have done an extensive search to find the most stable structure. We find two isomers (5-C_1 and 5-C_s) which are more stable than the previously reported structures (5-C_{5h} , 5-C_{2h}). The 5-C_s is the most stable in ΔE_e , while the 5-C_1 is the most stable in ΔE_0 . The 5-C_1 isomer contains eight sets of $\pi\text{--H}$ interactions and a set of $\pi\text{--}\pi$ interactions. For the most stable 5-C_1 structure, the predicted asymmetric stretching frequencies appear at 3252 , 3261 , 3264 , and 3268 cm^{-1} , and the bending frequencies appear at 727 , 736 , and 760 cm^{-1} . These predicted vibrational stretching frequencies will be useful for experimentalists to identify the most stable acetylene pentamer. We note that the pentamer structure based on the MMC method by Dykstra and Shuler is consistent with our *ab initio* predicted global minimum structure (5-C_1).

Figure 7 shows the plot of the binding energies (ΔE_e , ΔE_0 , ΔG_{50K}) with respect to the cluster size n . These values almost linearly increase as the number of monomer

units increases. The dimer is stable below 55 K at 1 atm, while the pentamer is stable below 70 K 1 atm.

Conclusion

We have studied the geometrical isomers, energies, thermodynamic properties, and IR spectra of acetylene clusters $(C_2H_2)_{n=2-5}$. We have clarified the lowest energy structure of the $(C_2H_2)_{n=2-5}$ clusters. According to the CCSD(T)/CBS level of theory, the T-shape acetylene dimer of C_{2v} symmetry is the most stable in ΔE_e , but the displaced-stacked dimer of C_{2h} symmetry is also as stable as the $2-C_{2v}$ structure within 0.3 kJ/mol. This leads to the quantum statistical distribution of configuration over θ from 90° ($2-C_{2v}$ configuration) through 0° ($2-C_{2h}$ configuration), resulting in an average value of the angle $|\theta| = 53-78^\circ$, in good agreement with the experimental angle of $\theta = 63^\circ$. For the acetylene trimer, the cyclic $3-C_{3h}$ isomer is the most stable. In the case of the acetylene tetramer, the isomers $4-S_4$ and $4-C_{2h}$ are isoenergetic in ΔE_e , but the $4-C_{2v}$ isomer is the most stable in ΔE_0 and at nonzero temperatures. For the acetylene pentamer, we find two new structures ($5-C_1$ and $5-C_s$), which are more stable than the previously reported global minimum structure ($5-C_{5h}$ and $5-C_{2h}$). Although the $5-C_s$ structure is the most stable in ΔE_e , the $5-C_1$ structure is the most stable in ΔE_0 and at nonzero temperatures. These acetylene clusters are predicted to be stable below temperatures of 55–70 K at 1 atm. High-level *ab initio* calculated results are consistent with available experimental results. We also note that the structures predicted by Dykstra and Shuler⁴¹ based on the MMC method are mostly consistent with those predicted by high-level *ab initio* calculations.

Acknowledgment. This work was supported by NRF (WCU, R32-2008-000-10180-0; EPB Center, 2009-0063312, GRL, National Honor Scientist Program) and KISTI (KSC-2008-K08-0002).

Supporting Information Available: Vibrational frequencies (Table S1), binding energies and selected distances (Table S2), and rotational constants and dipole moment (μ) (Table S3) of $(C_2H_2)_{n=2-5}$ are available free of charge via the Internet at <http://pubs.acs.org/>.

References

- Chenoweth, K.; Dykstra, C. D. *Theor. Chem. Acc.* **2003**, *110*, 100.
- Hobza, P.; Selzle, H. L.; Schlag, E. W. *Chem. Rev.* **1994**, *94*, 1767.
- Brutschy, B. *Chem. Rev.* **2000**, *100*, 3891.
- Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.
- Rezac, J.; Fanfrlik, J.; Salahub, D.; Hobza, P. *J. Chem. Theory Comput.* **2009**, *5*, 1749.
- Maity, S.; Patwari, G. N.; Karthikeyan, S.; Kim, K. S. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6150.
- Guin, M.; Patwari, G. N.; Karthikeyan, S.; Kim, K. S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11207.
- Vaupel, S.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Am. Chem. Soc.* **2006**, *128*, 5416.
- Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **2001**, *114*, 1295.
- Dykstra, C. E.; Lisy, J. M. *THEOCHEM* **2000**, *500*, 375.
- Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23.
- Cerny, J.; Kabelac, M.; Hobza, P. *J. Am. Chem. Soc.* **2008**, *130*, 16055.
- Sponer, J.; Riley, K. E.; Hobza, P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2595.
- Singh, N. J.; Lee, H. M.; Hwang, I.-C.; Kim, K. S. *Supramol. Chem.* **2007**, *19*, 321.
- Singh, N. J.; Lee, H. M.; Suh, S. B.; Kim, K. S. *Pure Appl. Chem.* **2007**, *79*, 1057.
- Ren, T.; Jin, Y.; Kim, K. S.; Kim, D. H. *J. Biomol. Struct. Dyn.* **1997**, *15*, 401.
- Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. *Chem. Rev.* **2005**, *105*, 1491.
- Lee, J. Y.; Hong, B. H.; Kim, W. Y.; Min, S. K.; Kim, Y.; Jouravlev, M. V.; Bose, R.; Kim, K. S.; Hwang, I.-C.; Kaufman, L. J.; Wong, C. W.; Kim, P.; Kim, K. S. *Nature* **2009**, *460*, 498.
- Kim, K. S.; Suh, S. B.; Kim, J. C.; Hong, B. H.; Lee, E. C.; Yun, S.; Tarakeshwar, P.; Lee, J. Y.; Kim, Y.; Ihm, H.; Kim, H. G.; Lee, J. W.; Kim, J. K.; Lee, H. M.; Kim, D.; Cui, C.; Youn, S. J.; Chung, H. Y.; Choi, H. S.; Lee, C. W.; Cho, S. J.; Jeong, S.; Cho, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 14268.
- Pitonak, M.; Neogrady, P.; Rezac, J.; Jurecka, P.; Urban, M.; Hobza, P. *J. Chem. Theory Comput.* **2008**, *4*, 1829.
- Hohenstein, E. G.; Sherrill, C. D. *J. Phys. Chem. A* **2009**, *113*, 878.
- Tsuzuki, S.; Honda, K.; Fujii, A.; Uchimaru, T.; Mikami, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2860.
- Piaccenza, M.; Grimme, S. *J. Am. Chem. Soc.* **2005**, *127*, 14841.
- Lee, E. C.; Hong, B. H.; Lee, J. Y.; Kim, J. C.; Kim, D.; Kim, Y.; Tarakeshwar, P.; Kim, K. S. *J. Am. Chem. Soc.* **2005**, *127*, 4530.
- Sponer, J.; Jurecka, P.; Hobza, P. *J. Am. Chem. Soc.* **2004**, *126*, 10142.
- Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.
- Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887.
- Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 3746.
- Hong, B. H.; Lee, J. Y.; Cho, S. J.; Yun, S.; Kim, K. S. *J. Org. Chem.* **1999**, *64*, 5661.
- Tarakeshwar, P.; Lee, S. J.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1998**, *108*, 7217.
- Grimme, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3430.
- DiStasio, R. A., Jr.; Helden, G. V.; Steele, R. P.; Head-Gordon, M. *Chem. Phys. Lett.* **2007**, *437*, 277.
- Janowski, T.; Pulay, P. *Chem. Phys. Lett.* **2007**, *447*, 27.
- Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.
- Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1996**, *100*, 18790.

- (36) Sinnokrot, O. M.; Sherrill, D. C. *J. Phys. Chem. A* **2006**, *110*, 10656.
- (37) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104.
- (38) Lee, E. C.; Kim, D.; Jureka, P.; Tarakeshwar, P.; Hobza, P.; Kim, K. S. *J. Phys. Chem. A* **2007**, *111*, 3446.
- (39) Singh, N. J.; Min, S. K.; Kim, D. Y.; Kim, K. S. *J. Chem. Theory Comput.* **2009**, *5*, 515.
- (40) Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323.
- (41) Shuler, K.; Dykstra, C. E. *J. Phys. Chem. A* **2000**, *104*, 11522.
- (42) Fraser, G. T.; Suenram, R. D.; Lovas, F. J.; Pine, A. S.; Hougen, J. T.; Lafferty, W. J.; Muentner, J. S. *J. Chem. Phys.* **1988**, *89*, 6028.
- (43) Matsumurak, K.; Lovas, F. J.; Suenram, R. D. *J. Mol. Spectrosc.* **1991**, *150*, 576.
- (44) Pendley, R. D.; Ewing, G. E. *J. Chem. Phys.* **1983**, *78*, 3531.
- (45) Sakai, K.; Koide, A.; Kihara, T. *Chem. Phys. Lett.* **1977**, *47*, 416.
- (46) Ohshima, Y.; Matsumoto, Y.; Takami, M.; Kuchitsu, K. *Chem. Phys. Lett.* **1988**, *147*, 1.
- (47) Prichard, D. G.; Nandi, R. N.; Muentner, J. S. *J. Chem. Phys.* **1988**, *89*, 115.
- (48) Prichard, D.; Muentner, J. S.; Howard, B. J. *Chem. Phys. Lett.* **1987**, *135*, 9.
- (49) Bone, R. G. A.; Murray, C. W.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1989**, *161*, 166.
- (50) Bryant, G. W.; Eggers, D. F.; Watts, R. O. *Chem. Phys. Lett.* **1988**, *151*, 309.
- (51) Bone, R. G. A.; Amos, R. D.; Handy, N. C. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1931.
- (52) Yu, J.; Shujun, S.; Bloor, J. E. *J. Phys. Chem.* **1990**, *94*, 5589.
- (53) Shuler, K.; Dykstra, C. E. *J. Phys. Chem. A* **2000**, *104*, 4562.
- (54) Alberts, I. L.; Rowlands, T. W.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3811.
- (55) Bone, R. G. A.; Handy, N. C. *Theor. Chim. Acta.* **1990**, *78*, 133.
- (56) Hobza, P.; Selzle, H. L.; Schlag, E. W. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1186.
- (57) Karpfen, A. *J. Phys. Chem. A* **1999**, *103*, 11431.
- (58) Karpfen, A. *J. Phys. Chem. A* **1998**, *102*, 9286.
- (59) Brenner, V.; Millie, P. Z. *Phys. D.* **1994**, *30*, 327.
- (60) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
- (61) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, V.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (62) Lee, S. J.; Chung, H. Y.; Kim, K. S.; Bull, *Korean Chem. Soc.* **2004**, *25*, 1061.
- (63) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.
- (64) Min, S. K.; Lee, E. C.; Lee, H. M.; Kim, D. Y.; Kim, D.; Kim, K. S. *J. Comput. Chem.* **2008**, *29*, 1208.
- (65) Császár, A. G.; Allen, W. D.; Schaefer III, H. F. *J. Chem. Phys.* **1998**, *108*, 9751.
- (66) Kolar, M.; Hobza, P. *J. Phys. Chem. A* **2007**, *111*, 5851.
- (67) Lee, J. Y.; Hahn, O.; Lee, S. J.; Choi, H. S.; Mhin, B. J.; Lee, M. S.; Kim, K. S. *J. Phys. Chem.* **1995**, *99*, 2262.
- (68) Lee, J. Y.; Hahn, O.; Lee, S. J.; Choi, H. S.; Shim, H.; Mhin, B. J.; Kim, K. S. *J. Phys. Chem.* **1995**, *99*, 1913.
- (69) Kolaski, M.; Lee, H. M.; Choi, Y. C.; Kim, K. S.; Tarakeshwar, P.; Miller, D. J.; Lisy, J. M. *J. Chem. Phys.* **2007**, *126*, 074302.
- (70) Kim, K. S.; Lee, J. Y.; Choi, H. S.; Kim, J.; Jang, J. H. *Chem. Phys. Lett.* **1997**, *265*, 497.
- (71) Kim, J.; Lee, J. Y.; Oh, K. S.; Park, J. M.; Lee, S.; Kim, K. S. *Phys. Rev. A* **1999**, *59*, R930–933.
- (72) Kim, K. S.; Schaefer III, H. F.; Radom, L.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 4148.
- (73) Hong, B. H.; Lee, J. Y.; Lee, C.-W.; Kim, J. C.; Bae, S. C.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 10748.
- (74) Hong, H.; Small, J. P.; Purewal, M. S.; Mullokandov, A.; Sfeir, M. Y.; Wang, F.; Lee, J. Y.; Heinz, T. F.; Brus, L. E.; Kim, P.; Kim, K. S. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 14155.
- (75) Kim, K. S.; Clementi, E. *J. Am. Chem. Soc.* **1985**, *107*, 227.
- (76) McGaughey, G. B.; Gagne, M.; Rappe, A. K. *J. Biol. Chem.* **1998**, *273*, 15458.
- (77) Hobza, P.; Spirko, V.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys. A* **1998**, *102*, 2501.

CT100323F