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B_2F_4 Molecule: A Challenge for Theoretical Calculations

Zhen-Hua Li and Kang-Nian Fan*

Center for Theoretical Chemical Physics, Laboratory of Molecular Catalysis & Innovative Material, Department of Chemistry, Fudan University, Shanghai 200433, China

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Various theoretical methods (HF, MP2, B3-LYP, QCSD, CCSD(T)) in combination with a hierarchy of basis sets have been used to determine the ground state conformations of B_2F_4 and $B_2F_4^+$. It was found that the ground state of B_2F_4 has an eclipsed conformation (in D_{2h} symmetry), while that of $B_2F_4^+$ has a staggered conformation (in D_{2d} symmetry). The experimental value for the ionization potential (IP) of B_2F_4 was found to have a far larger error than believed. The theoretical value of IP obtained by extrapolating the calculated energies to complete basis set limit, corrected for zero-point vibrational energy, spin−orbit and core−valence effects, is 271.70 kcal mol^{-1}. Our best atomization energy and heats of formation at 0 and 298 K for the neutral B_2F_4 (D_{2h}) are 685.64 kcal mol^{-1}, −339.34 kcal mol^{-1}, and −339.82 kcal mol^{-1}, respectively, and those for the radical cation $B_2F_4^+$ (D_{2d}) are 413.94 kcal mol^{-1}, −67.64 kcal mol^{-1}, and −67.72 kcal mol^{-1}, respectively.

1. Introduction

B_2X_4 (X = F, Cl, Br) molecules are important precursors for synthesizing boron-containing compounds.[1−5] Similar to other isoelectonic molecules with 34 valence electrons, such as N_2O_4 and $C_2Y_4^{2+}$ (Y = H, F, Cl, Br, OR), the structures of the three B_2X_4 molecules strongly depend on substituent X. B_2Br_4 was known to be staggered (D_{2d} symmetry) in all thee phases (solid, liquid, and gas).[6,7] B_2Cl_4, on the other hand, was found to be staggered in the gas[8−10] and liquid[8,10,11] phases, but eclipsed (D_{2h} symmetry) in the solid phase.[10,12,13] As for B_2F_4, Trefonas and Lipscomb showed that B_2F_4 has a planar structure in the solid phase by X-ray diffraction.[14] Unlike B_2Cl_4 and B_2Br_4, the structure of B_2F_4 in the gas and liquid phases was not very clear at the beginning. Several earlier Raman and infrared spectroscopic studies suggested a staggered structure,[11,15,16] while Durig et al. showed that, unlike B_2Cl_4, B_2F_4 does not change its symmetry on going from solid state to liquid and gaseous states.[17] Later in 1977, Danielson, Patton, and Hedberg confirmed by electron diffraction that gaseous B_2F_4 molecule has a D_{2h} symmetry.[18] As has been shown by Danielson, Patton, and Hedberg, experimental difficulties in determining the structure of B_2F_4 were probably due to its very low internal rotation barrier around the B−B bond (0.42 kcal mol^{-1}),[18] too small compared with those of B_2Cl_4 (1.85 kcal mol^{-1})[9] and B_2Br_4 (3.07 kcal mol^{-1}).[7]

Theoretical investigations on the structure of gaseous B_2F_4, similar to experimental studies, do not agree well with each other. Different studies with different levels of theory and basis sets give different results. Earlier ab initio calculations at the Hartree−Fock (HF) level with small basis sets indicate that the eclipsed structure of B_2F_4 is higher in energy than the staggered structure,[19−26] while semiempirical calculations indicate a reverse energy order,[27−31] in accordance with experimental findings. Recently, it was found that only with large basis sets at the HF level or including correlation effect can the planar structure of B_2F_4 be a minimum and lower in energy than the staggered structure.[24,26,32,33] To judge if a structure is a minimum or a transition state, vibrational frequency analysis is always necessary. However, few studies have performed vibrational frequency analysis on both conformations of B_2F_4. It is still not very clear which structure is the ground state and which structure is the transition state for the internal rotation around the B−B bond.

The ionization potential (IP) of B_2F_4 was included in the G2/97[34,35] and G3/99[36] training test sets to develop G3 and other closely related composite models[37−39] due to a very small uncertainty claimed for the experimental value (278.34 ± 0.23 kcal mol^{-1}).[40] However, the calculated IP values of B_2F_4 by G2,[35] G3,[37] G3S,[38] and G3SCB[41] methods, 271.00, 271.37, 270.56, and 270.07 kcal mol^{-1}, respectively, are all smaller than the experimental value by more than 6 kcal mol^{-1}. This seems to suggest that the experimental value is in error. Montgomery et al. thus suggested removing this value from the G2/97 test set.[42] On the other hand, Curtiss et al. argued that they “have chosen not to throw out experimental data unless there is new experimental evidence that warrants it”.[43] Unfortunately, close examination of the geometry of B_2F_4 and $B_2F_4^+$ used in the G2/97 and G3/99 test sets indicates that a staggered structure was employed for both two species. As for B_2F_4, this is in contradiction to experimental findings. This raises two serious questions: (a) How large is the difference between experimental and theoretical values if the correct structure of B_2F_4 is employed? (b) Does $B_2F_4^+$ suffer the same problem as the neutral B_2F_4 molecule, i.e., the difficulty to determine which structure is the ground state and which structure is the transition state for the internal rotation?

Answers to the above two questions about the structures of B_2F_4 and $B_2F_4^+$ are closely related to the theoretical determination of the IP value of B_2F_4. Therefore, in the present study, the structures of B_2F_4 and $B_2F_4^+$ and their thermochemical properties are studied jointly. First, we will present the results of our systematic study on the structures of B_2F_4 and $B_2F_4^+$, in both staggered and eclipsed conformations, to determine which

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* To whom correspondence should be addressed. Fax: +86-21-65641740. E-mail: knfan@fudan.edu.cn.

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TABLE 1: The Lowest Harmonic Vibrational Frequency (cm^{-1}) of the Eclipsed (D_{2h}) and Staggered (D_{2d}) Conformations of B_2F_4[a]

	method							
	HF		B3-LYP		MP2		QCISD	
basis set	D_{2h}	D_{2d}	D_{2h}	D_{2d}	D_{2h}	D_{2d}	D_{2h}	D_{2d}
6-31G(d)	−12.5	20.4	15.7	9.4	17.2	−1.2	15.7	3.8
6-31+G(d)	18.2	7.6	14.7	13.6	19.6	−4.0	18.2	−7.4
6-311G(d)	20.7	4.0	20.8	3.9	28.3	−20.6	30.0	−23.1
6-311+G(d)	27.1	8.9	19.7	13.4	27.0	4.7		
6-311+G(2df)	20.0	5.0	13.2	12.4				
6-311+G(3df)	15.2	8.4	10.4	13.2				
cc-pVDZ	23.4	−9.0	26.1	−16.9	28.1	−21.1	29.6	−23.1
aug-cc-pVDZ	31.4	−9.8	24.2	8.1				
cc-pVTZ	8.8	−1.4	−4.5	9.1	16.6	−14.9		
aug-cc-pVTZ	9.9	7.3	−8.6	11.9				
cc-pVQZ	3.3	−7.2	4.4	6.2				

[a] Negative values are imaginary frequencies.

structure is the ground state structure. The performance of various theoretical methods and basis sets is systematically investigated. Then we present our best theoretical results for the IP of B_2F_4 and the heats of formation of B_2F_4 and $B_2F_4^+$, obtained by using energies extrapolated to the complete basis set (CBS) limit.

2. Computational Details

Standard ab initio calculations were carried out using the Gaussian 98[44] suite of programs. The geometries of B_2F_4 and $B_2F_4^+$, in both staggered (D_{2d} symmetry) and eclipsed (D_{2h} symmetry) conformations, were optimized with HF, B3-LYP,[45] MP2, QCISD, and CCSD(T) methods, in combination with two sets of basis sets: (a) Pople's valence-splitting basis sets: 6-31G(d), 6-31+G(d), 6-311G(d), 6-311+G(d), 6-311+G(2df), and 6-311+G(3df); (b) Dunning's correlation consistent basis sets: cc-pV*n*Z (n = {D, T, Q}) and aug-cc-pV*n*Z (n = {D, T}).[46] In all the geometry optimizations, a tight convergence criterion was used. Wherever doable within the limit of our computer power, harmonic vibrational frequency analysis was performed with the HF, B3-LYP, MP2, and QCISD methods in combination with various basis sets. For vibrational frequency analysis using the B3-LYP method, an ultrafine grid was used for both the calculation of integrals and the solving of CPHF equations.

Based on CCSD(T)/cc-pVTZ geometries, energies at the CBS limit were approximated by the following equation, assuming the additivity of correlation energies:

$$E_\infty = E^{\mathrm{HF}}_\infty + E^2_\infty + E^{\mathrm{CC}}_\infty + E_\infty(\mathrm{core}) \quad (1)$$

where E^{HF}_∞, E^2_∞, E^{CC}_∞, and $E_\infty(\mathrm{core})$ are HF energy, valence correlation energy at the MP2 level, valence correlation energy beyond MP2 calculated at the CCSD(T) level, and core correlation energy at the CBS limit, respectively. Relativistic contribution to the total energy was not included here. E^{HF}_∞ was obtained by extrapolating energies calculated at the HF level with the cc-pVQZ and cc-pV5Z basis sets using[47]

$$E^{\mathrm{HF}}{}_n = E^{\mathrm{HF}}_\infty + A/l^5 \quad (2)$$

where n = {D, T, Q, 5} with l = {2, 3, 4, 5}. E^2_∞ was obtained by extrapolating correlation energies calculated at the MP2 level with the cc-pVQZ and cc-pV5Z basis sets using[48]

$$E^2_n = E^2_\infty + A/l^3 \quad (3)$$

$E^{\mathrm{CC}}{}_\infty$ was obtained by extrapolating valence correlation energy beyond MP2 calculated at the CCSD(T) level with the cc-pVDZ and cc-pVTZ basis sets using[47,49]

$$E^2_n = E^2_\infty + A/l^{3.22} \quad (4)$$

Core correlation energy at the CBS limit was approximated by

$$E_\infty(\mathrm{core}) = E^2_\infty(\mathrm{core}) + E^{\mathrm{CC}}_{\mathrm{cc-pCVDZ}}(\mathrm{core}) \quad (5)$$

where $E^2_\infty(\mathrm{core})$ is the core correlation energy at the CBS limit obtained by extrapolating core correlation energies calculated at the MP2 level with the cc-pCVTZ and cc-pCVQZ basis sets,[50] using eq 3, and $E^{\mathrm{CC}}_{\mathrm{cc-pCVDZ}}$ is the core correlation energy difference between the MP2 and CCSD(T) methods calculated with the cc-pCVDZ basis set.[50]

G3,[37] G3S,[38] and G3SCB[41] methods were also used to calculate the energies of B_2F_4 and $B_2F_4^+$ at the CCSD(T)/cc-pVTZ geometry. In the original G3, G3S, and G3SCB methods, the calculation method for vibrational frequencies is HF/6-31G(d). As mentioned in the Introduction, the ground state conformation of B_2F_4 strongly depends on the methods and basis sets used. Therefore, we will leave the choice of the methods and basis sets for calculating vibrational frequencies to the section where we discuss the performance of methods and basis sets in determining the ground state conformations of B_2F_4 and $B_2F_4^+$.

3. Results and Discussion

3.1. Ground State Conformations of B_2F_4 and $B_2F_4^+$. *3.1.1. The Lowest Harmonic Vibrational Frequency.* The lowest harmonic vibrational frequencies of B_2F_4 and $B_2F_4^+$ are listed in Tables 1 and 2, respectively. These vibrational frequencies are all very small in value, indicating a flat potential energy surface around the rotation of the B−B bond. This very low-frequency value is a source of difficulties for the determination of the ground state conformations of B_2F_4 and $B_2F_4^+$ due to the limit of numerical accuracy of theoretical methods. For B_2F_4, the lowest vibrational frequency is more sensitive to the basis sets and methods used. Particularly at the HF level with the 6-31G(d) basis set, the eclipsed conformation of B_2F_4 is a transition structure, while the staggered conformation is a minimum. This is why the IP of B_2F_4 is calculated using a staggered structure for the neutral B_2F_4 in the G3, G3S, and G3SCB methods. This is incorrect since G2 and G3 use MP2-

TABLE 2: The Lowest Harmonic Vibrational Frequency (cm^{-1}) of the Eclipsed (D_{2h}) and Staggered (D_{2d}) Conformations of $B_2F_4^{+}$ [a]

	method							
	HF		B3-LYP		MP2		QCISD	
basis set	D_{2h}	D_{2d}	D_{2h}	D_{2d}	D_{2h}	D_{2d}	D_{2h}	D_{2d}
6-31G(d)	−17.4	22.9	−19.2	25.5	−7.2	17.0	−13.1	19.2
6-31+G(d)	4.6	16.5	−16.1	24.6	11.0	13.0	−6.1	15.7
6-311G(d)	−17.5	21.7	−20.4	26.0	−9.5	15.6	−11.6	15.8
6-311+G(d)	11.5	26.3	−14.0	31.3	18.3	25.8		
6-311+G(2df)	−9.2	23.5	−20.3	29.7				
6-311+G(3df)	−18.9	23.3	−23.8	29.2				
cc-pVDZ	−16.8	24.4	−19.6	27.1	−11.2	21.0	−12.0	20.8
aug-cc-pVDZ	27.3	23.3	15.8	29.5				
cc-pVTZ	−16.7	18.3	−22.9	25.1	−15.6	14.9		
aug-cc-pVTZ	−21.0	20.3	−24.4	27.1				
cc-pVQZ	−17.9	18.5	−17.7	29.5				

[a] Negative values are imaginary frequencies.

TABLE 3: Energy Difference ($E(D_{2h}) - E(D_{2d})$), kcal mol^{-1}) between the Staggered (D_{2d}) and Eclipsed (D_{2h}) Conformations of B_2F_4 [a]

	method				
basis set	HF	B3-LYP	MP2	QCISD	CCSD(T)
6-31G(d)	0.28	0.08	−0.15	−0.12	
6-31+G(d)	−0.07	0.03	−0.14	−0.14	
6-311G(d)	−0.21	−0.21	−0.63	−0.74	
6-311+G(d)	−0.26	−0.06	−0.28		
6-311+G(2df)	−0.15	0.01	−0.24		
6-311+G(3df)	−0.04	0.07	−0.16		
cc-pVDZ	−0.31	−0.49	−0.63	−0.73	−0.74
aug-cc-pVDZ	−0.52	−0.25	−0.43		
cc-pVTZ	−0.04	0.05	−0.25		−0.39
aug-cc-pVTZ	0.02	0.07	−0.07		
cc-pVQZ	−0.05	0.00	−0.20		

[a] All values are calculated at 0 K without ZPE corrections.

TABLE 4: Energy Difference ($E(D_{2h}) - E(D_{2d})$, kcal mol^{-1}) between the Staggered (D_{2d}) and Eclipsed (D_{2h}) Conformations of $B_2F_4^{+}$ [a]

	method				
basis set	HF	B3-LYP	MP2	QCISD	CCSD(T)
6-31G(d)	0.44	0.56	0.18	0.30	
6-31+G(d)	0.21	0.56	0.15	0.27	
6-311G(d)	0.42	0.60	0.17	0.20	
6-311+G(d)	0.32	0.65	0.26		
6-311+G(2df)	0.41	0.77	0.37		
6-311+G(3df)	0.48	0.78	0.45		
cc-pVDZ	0.48	0.63	0.31	0.32	0.36
aug-cc-pVDZ	0.15	0.52	0.23		
cc-pVTZ	0.34	0.65	0.27		0.33
aug-cc-pVTZ	0.45	0.73	0.45		
cc-pVQZ	0.37	0.65	0.34		

[a] All values are calculated at 0 K without ZPE corrections.

(Full)/6-31G(d) geometry, while at this level of theory the staggered conformation of B_2F_4 is a transition structure.

Based on the sign of the lowest vibrational frequency, we cannot unambiguously tell which conformation is the ground state of B_2F_4. Even with very large basis sets at the HF and B3-LYP levels of theory, the eclipsed conformation is calculated to be a transition state, in contradiction to the experimental findings. Due to the limited computational resources, we did not perform vibrational frequency analysis with basis sets larger than 6-311+G(d) or cc-pVTZ at the MP2 level and 6-311G(d) or cc-pVDZ at the QCISD level. However, at both levels of theory with all basis sets investigated, the eclipsed conformation is calculated to be a minimum, while with most basis sets the staggered conformation is calculated to be a transition state. As for $B_2F_4^{+}$, the eclipsed conformation is calculated to be a transition state while the staggered conformation is a minimum by most combinations of methods and basis sets. It is interesting to note that at the MP2 level, after adding diffuse function to the 6-31G(d) or 6-311G(d) basis set, the eclipsed conformation of $B_2F_4^{+}$ is calculated to be a minimum.

3.1.2. Energy Difference between the Two Conformations. Energy differences between the two conformations ($E(D_{2h}) - E(D_{2d})$) without zero point energy (ZPE) corrections are collected in Tables 3 and 4 for B_2F_4 and $B_2F_4^{+}$, respectively. At the HF level, with most basis sets used, the energy of the eclipsed conformation of B_2F_4 is lower than that of the staggered conformation. At the B3-LYP level, for about half the basis sets used, the eclipsed conformation is lower in energy. In contrast with the HF and B3-LYP methods, the eclipsed conformation is calculated to be lower in energy by all three post-HF methods with all basis sets. Thus, judged from the energy difference, it is more likely that the eclipsed conformation of B_2F_4 is the ground state. The remaining question that cannot be answered by the energy difference calculation is whether the staggered conformation is a transition state for the internal rotation. As has been shown above, the sign of the lowest vibrational frequency has not unambiguously resolved this either. For the $B_2F_4^{+}$ molecule, the staggered conformation is calculated to be lower in energy by all combinations of methods and basis sets. Therefore, it is clear that, for the $B_2F_4^{+}$ molecule, the staggered conformation of $B_2F_4^{+}$ is the ground state.

3.1.3. Vibrational Spectroscopy of B_2F_4. In Table 5, we collected the harmonic vibrational frequencies and the corresponding IR and Raman intensities of the eclipsed and staggered B_2F_4 in three possible combinations of the isotopes of boron calculated by the MP2/6-311+G(d) method. Samdal et al. have also calculated the harmonic vibrational frequencies of the staggered $^{11}B_2F_4$ using the same method.[26] However, they made a small mistake in assigning vibrational modes: the 1355.2 cm^{-1} vibrational mode should be Raman active while the 1371.7 cm^{-1} vibrational mode should be IR active. Some fundamentals have been reassigned in the present study. It should be noted that, because different convergence criteria were used in the geometric optimization, the values Samdal et al. obtained are slightly different from ours. The experimental values listed in Table 5 are mainly taken from ref 11. It is well-known that MP2 harmonic vibrational frequencies are generally larger than experimental values. However, Table 5 shows that the unscaled MP2/6-311+G(d) harmonics are surprisingly close to experimental values.

Theoretical vibrational spectroscopy of the eclipsed B_2F_4 can well explain patterns in the experimental IR spectroscopy of

TABLE 5: Vibrational Frequencies (cm^{-1}) of the Eclipsed and Staggered Conformations of B_2F_4 Calculated Using the MP2/6-311+G(d) Method

			eclipsed									staggered								
			$^{11}B^{11}B$			$^{10}B^{11}B$			$^{10}B^{10}B$			$^{11}B^{11}B$			$^{10}B^{11}B$			$^{10}B^{10}B$		
		expt		I[a]	R[b]		I[a]	R[b]		I[a]	R[b]		I[a]	R[b]		I[a]	R[b]		I[a]	R[b]
υ_1	A_u	20[c]	27.0	0.0	0.0	27.0	0.0	0.0	27.0	0.0	0.0	4.7	0.0	0.5	4.7	0.0	0.5	4.7	0.0	0.5
υ_2	B_{2u}	144[d]	136.7	3.0	0.0	136.9	3.0	0.0	137.1	3.0	0.0	170.0	7.7	0.3	170.3	7.7	0.3	171.2	7.7	0.3
υ_3	A_g	319.2[d]	320.3	0.0	1.7	320.5	0.0	1.7	320.8	0.0	1.7	170.0	7.7	0.3	171.0	7.7	0.3	171.2	7.7	0.3
υ_4	B_{3u}	348.4[d]	368.2	55.9	0.0	374.8	57.9	0.0	382.1	60.2	0.0	321.0	0.0	1.4	321.3	0.0	1.4	321.5	0.0	1.4
υ_5	B_{3g}	380[e]	385.7	0.0	1.2	387.3	0.0	1.3	389.0	0.0	1.3	532.0	59.8	0.8	534.5	59.0	0.8	537.1	58.2	0.8
υ_6	B_{1u}	541.9[d]	529.0	62.1	0.0	531.5	61.4	0.0	534.2	60.6	0.0	643.0	38.8	0.2	643.3	39.3	0.2	669.1	43.4	0.2
υ_7	A_g	672.4[d]	668.4	0.0	6.5	670.7	0.0	6.5	673.0	0.0	6.6	643.0	38.8	0.2	668.8	42.9	0.2	669.1	43.4	0.2
υ_8	B_{2g}	715[e]	703.0	0.0	0.1	719.0	0.2	0.1	734.3	0.0	0.1	667.9	0.0	5.4	670.1	0.0	5.5	672.2	0.0	5.5
υ_9	B_{1u}	1154.7[d]	1139.8	369.1	0.0	1153.9	381.9	0.0	1171.3	402.9	0.0	1138.0	369.7	0.7	1152.2	382.6	0.6	1169.8	403.5	0.6
υ_{10}	B_{2u}	1348.6[d]	1353.6	0.0	2.1	1360.6	252.6	1.4	1403.8	0.0	2.2	1335.5	333.4	1.5	1335.7	332.0	1.5	1382.8	356.4	1.5
υ_{11}	B_{3g}	1366.3[d]	1369.9	725.9		1411.9	500.1	0.8	1417.7	779.4	0.0	1335.5	333.4	1.5	1382.6	357.7	1.5	1382.8	356.4	1.5
υ_{12}	A_g	1398.2[d]	1398.7	0.0	2.6	1428.2	4.1	2.7	1454.4	0.0	2.9	1404.5	0.0	0.1	1434.4	4.0	0.1	1460.8	0.0	0.6

[a] Infrared intensities (km mol^{-1}). [b] Raman activities (Å^4 amu^{-1}). [c] Reference 18. [d] Reference 11. [e] Reference 17.

both the natural $^{n}B_2F_4$ and $^{10}B_2F_4$ reported in ref 11, except that theoretical spectroscopy lacks the two bands at 657.3 and 686 cm^{-1}. The band at 657.3 cm^{-1} can be assigned to $\upsilon_3 + \upsilon_4$ (667.6 cm^{-1}) of the eclipsed $^{11}B_2F_4$, and the band at 686 cm^{-1} can be assigned to $\upsilon_3 + \upsilon_4$ (679.1 cm^{-1})[11] of the eclipsed $^{10}B_2F_4$. It is unlikely that these two bands are from the calculated 643.0 cm^{-1} vibrational mode of the staggered $^{11}B_2F_4$ and the calculated 669.1 cm^{-1} vibrational mode of the staggered $^{10}B_2F_4$, since the predicted two bands around 170 and 1335 cm^{-1} for the staggered $^{11}B_2F_4$, both IR and Raman active, have never been reported for the gaseous B_2F_4. Moreover, the rule of mutual exclusion works well for assigning experimentally observed vibrational modes. The vibrational modes, which are IR active as reported in ref 11, do not appear in the observed Raman spectroscopy, unlike those for B_2Cl_4 (D_{2d}) reported in the same reference. Besides, if B_2F_4 is staggered, the experimentally observed Raman spectroscopy should not have just a few bands excluding those overtones.[11,17] Therefore, based on the vibrational analysis, B_2F_4 should undoubtedly be eclipsed. Correspondingly, the staggered conformation is a transition state. It is unlikely that the staggered conformation is also a minimum on the energy surface because, if so, experimentally observed vibrational spectroscopy should be a combination of the vibrational spectroscopy of the two conformations since they are so close in energy.

For the $B_2F_4^+$ radical cation, since no experimental vibrational spectroscopy is available, we will not discuss its vibrational spectroscopy here. It is clear that $B_2F_4^+$ is staggered, judged by the sign of the lowest vibrational frequency and the calculated energy differences. However, for the B_2F_4 molecule, it is not so clear whether the eclipsed conformation or the staggered conformation is the ground state, unless comparison was made between the theoretical vibrational spectroscopy and the experimental vibrational spectroscopy. Therefore, for this molecule, it is dangerous to draw conclusions by just calculating the energy difference between the two conformations or performing vibrational frequency analysis using a single method. In the next section, we present the IP of B_2F_4, heats of formation of B_2F_4 and $B_2F_4^+$, and the energy difference between the eclipsed and staggered conformations of B_2F_4 and $B_2F_4^+$, respectively, calculated using energies extrapolated to the CBS limit.

TABLE 6: Geometric Parameters of the Eclipsed B_2F_4 and the Staggered $B_2F_4^+$ [a]

method	B−B	B−F	∠FBF
	B_2F_4 (D_{2h})		
ED (ref 18)	1.719(4)	1.314(2)	121.4(1)
X-ray (ref 14)	1.670(45)	1.320(35)	120.0
HF/6-311+G(3df)	1.739	1.297	121.3
MP2/6-311+G(3df)	1.727	1.315	121.1
B3-LYP/6-311+G(3df)	1.725	1.316	121.3
HF/cc-pVTZ	1.741	1.301	121.4
MP2/cc-pVTZ	1.728	1.319	121.3
B3-LYP/cc-pVTZ	1.725	1.319	121.4
CCSD(T)/cc-pVTZ	1.728	1.318	121.3
HF/cc-pVQZ	1.742	1.299	121.4
MP2/cc-pVQZ	1.727	1.317	121.2
B3-LYP/cc-pVQZ	1.728	1.317	121.3
	$B_2F_4^+$ (D_{2d})		
HF/6-311+G(3df)	2.176	1.244	110.1
MP2/6-311+G(3df)	2.094	1.265	110.0
B3-LYP/6-311+G(3df)	2.083	1.266	110.5
HF/cc-pVTZ	2.188	1.248	110.1
MP2/cc-pVTZ	2.100	1.270	110.2
B3-LYP/cc-pVTZ	2.083	1.270	110.5
CCSD(T)/cc-pVTZ	2.088	1.269	110.3
HF/cc-pVQZ	2.189	1.246	110.2
MP2/cc-pVQZ	2.103	1.267	110.1
B3-LYP/cc-pVQZ	2.090	1.268	110.4

[a] Bond distances in angstroms, bond angles in degrees.

3.2. Structures and Energetics of B_2F_4 and $B_2F_4^+$. Selected geometric parameters optimized by several methods in combination with the 6-311+G(3df), cc-pVTZ, and cc-pVQZ basis sets for the eclipsed B_2F_4 and the staggered $B_2F_4^+$ are listed in Table 6. Except for the HF method, the geometry of the eclipsed B_2F_4 calculated by the B3-LYP, MP2, and CCSD(T) methods are all in good agreement with the experimental geometry obtained by electron diffraction method in the gas phase. For the staggered $B_2F_4^+$, the B−B bond distance is more sensitive to the choice of methods and basis sets than that of the eclipsed B_2F_4, while the B−F bond distances obtained by the B3-LYP, MP2, and CCSD(T) methods are all very close to each other. In the calculations of IP, heats of formation, and energy differences, CCSD(T)/cc-pVTZ geometry was used throughout.

The first difficulty we met, to calculate energy differences and thermochemistry properties, is to choose a proper method for calculating ZPEs and thermal corrections. As we have discussed in section 3.1, the sign of the lowest vibrational frequency, especially that of B_2F_4, is very sensitive to the choice of methods and basis sets. Considering that scaling factors for many basis sets used here are not available, the choice of methods for the calculation of ZPE and thermal corrections is rather limited. Only MP2/6-31G(d) and MP2/6-311G(d) methods can correctly predict both the ground state conformations and transition state conformations of both two molecules, while at the same time scaling factors are available. Unfortunately, after

TABLE 7: Energy Differences ($E(D_{2h}) - E(D_{2d})$)at 0 K (kcal mol^{-1}) between the Staggered and Eclipsed Conformations of B_2F_4 and $B_2F_4^+$, Respectively[a]

	energy components						
	E^{HF} [b]	E^{2} [c]	E^{CC} [d]	E(core)[e]	ZPE[f]	total	G3
B_2F_4	−0.01	−0.12	−0.14	−0.01	0.06	−0.22	−0.22
$B_2F_4^+$	0.36	0.04	0.06	0.00	0.01	0.47	0.59

[a] All values are calculated using energies extrapolated to CBS limit, without including relativistic corrections. [b] Calculated at the HF level. [c] Correlation energy contribution at the MP2 level. [d] Correlation energy contribution beyond MP2 calculated with the CCSD(T) method. [e] Core correlation energy contribution calculated with eq 5. [f] Calculated using unscaled MP2/6-311+G(d) harmonic vibrational frequencies.

scaling, the vibrational frequencies predicted by the two methods deviate too far from the experimental values. As has been shown in the previous section, the unscaled vibrational frequencies of the eclipsed B_2F_4 calculated using the MP2/6-311+G(d) method are very close to the experimental values. However, both the staggered B_2F_4 and the eclipsed $B_2F_4^+$ are minima at the MP2/6-311+G(d) level of theory. Therefore, the lowest positive vibrational frequencies have to be eliminated when calculating ZPEs and thermal corrections for the staggered B_2F_4 and the eclipsed $B_2F_4^+$ if MP2/6-311+G(d) vibrational frequencies were used. The calculated energy differences and thermochemistry values using unscaled MP2/6-311+G(d) vibrational frequencies are listed in Tables 7 and 8, respectively.

Examination of Table 7 shows that the major contributions to the energy difference between the eclipsed and staggered conformations of B_2F_4 are from electron correlation energies. Novosadov et al. have also found this.[33] At the HF level, the energies of the two conformations are nearly the same. After including the ZPE correction, the staggered conformation is even slightly lower in energy. It is therefore not difficult to understand the difficulties theoretical chemists have encountered in the past in determining the ground state conformation of B_2F_4, since most calculations were done at the HF level. By contrast, electron correlation contributes little to the energy difference between the eclipsed and staggered conformations of $B_2F_4^+$. As expected, in both cases, the contributions from core electron correlations are very small. The energy differences calculated by the G3 method were also included for comparison. For B_2F_4, the energy difference calculated by the G3 method is almost the same as our best value. For $B_2F_4^+$, the G3 energy difference is slightly larger.

In Table 8, ionization potential energies calculated at the geometry of MP2(Full)/6-31G(d) by G3, G3S, and G3SCB methods were also presented. The adoption of the wrong geometry in the G2/97 test set does have a small effect (about 0.2−0.4 kcal mol^{-1}) on the calculated IP, too small to remedy the huge gap between experiment and theoretical calculations. All four theoretical procedures agree very well with each other. Our best value, 271.70 kcal mol^{-1}, is still too small by more than 6 kcal mol^{-1} compared with the experimental values. Therefore, it is more likely that the experimental value of IP is in error. Although Dibeler and Liston had assigned a very small uncertainty to the IP of B_2F_4,[40] this does not necessarily mean that the value they obtained is the most accurate value, because this has not been verified by any other experimental techniques. Eliminating a bad experimental value from the training set for the developing of theoretical models is necessary, especially if the training set is small. However, it is very difficulty to judge whether an experimental value is good or bad. Accurate theoretical methods have been proved to be very accurate, sometimes even better than experimental techniques, in calculating thermochemical properties by numerous studies. We prefer to eliminate an experimental value obtained by just one or two experiments from the training set if this value has been proved by various decent theoretical calculations to be very inaccurate.

As for the calculations of atomization energy and heats of formation, the G3, the G3S, and the present calculation procedures agree very well with each other. However, absolute values calculated by the G3SCB method are larger than values calculated by other methods by about 2 kcal mol^{-1}. Compared with the experimental heat of formation at 298 K, the G3SCB value is the one closest to the experimental value. Borrowing the relativistic correction values for the atomization energy calculated by Curtiss et al. based on the MP2(Full)/6-31G(d) geometry, which are −1.13 and −1.09 kcal mol^{-1} for B_2F_4 and $B_2F_4^+$, respectively,[53,54] the theoretical calculated values including relativistic effect are even closer to the experimental value. Thus, the experimental heat of formation of B_2F_4 at 298 K is quite reliable.

4. Concluding Remarks

Theoretical calculations have encountered great difficulties in determining the ground state conformation of the neutral B_2F_4 molecule, due to the very flat potential energy surface around the rotation of the B−B bond. Harmonic vibrational frequency analysis shows that the signs of the lowest vibrational frequencies of B_2F_4 and $B_2F_4^+$ all depend on the levels of theory and basis sets used. Comparing the experimental vibrational spectroscopy of B_2F_4 with the theoretical vibrational spectroscopy, we found that the ground state of B_2F_4 is eclipsed, lower in energy than the staggered conformation (a transition structure for the rotation around the B−B bond) by just 0.22 kcal mol^{-1} at 0 K. For $B_2F_4^+$, energy difference calculations and vibrational frequency analysis all indicate that the staggered conformation is the ground state while the eclipsed conformation of $B_2F_4^+$ is the transition state for the rotation around the B−B bond.

The best value for the IP of B_2F_4 in this study is 271.70 kcal mol^{-1}, which is very close to values calculated by the G3, G3S,

TABLE 8: Ionization Energy of B_2F_4, Atomization Energies at 0 K, and Heats of Formation at 0 and 298 K of B_2F_4 and $B_2F_4^+$[a]

	this work	G3	G3S	G3SCB	expt
IP	271.70	271.58 (271.37[b])	270.94 (270.56[c])	270.34 (270.07[d])	282.03[e] (278.34[f])
AE(0 K)					
B_2F_4 (D_{2h})	685.64	685.53	684.99	686.50	
$B_2F_4^+$ (D_{2d})	413.94	413.95	414.05	416.16	
H_f(0 K)					
B_2F_4 (D_{2h})	−339.34	−339.23	−338.69	−340.20	
$B_2F_4^+$ (D_{2d})	−67.64	−67.65	−67.75	−69.86	
H_f(298 K)					
B_2F_4 (D_{2h})	−339.82	−339.71	−339.18	−340.69	−342.20[g]
$B_2F_4^+$ (D_{2d})	−67.72	−67.73	−67.83	−69.94	

[a] All values are in kcal mol^{-1}. Values in parentheses are calculated at the geometry of MP2(Full)/6-31G(d). [b] Reference 37. [c] Reference 38. [d] Reference41. [e] Reference 51. [f] Reference 40. [g] Reference 52.

and G3SCB methods. The experimental IP value of 278.34 kcal mol^{-1} is too large. The wrong use of the ground state structure for the neutral B_2F_4 molecule in the G2/97 test set does have a small effect on the IP value calculated by the G3, G3S, and G3SCB methods. However, the effect is too small to remedy the gap between the experimental value and the theoretical values. It is very likely that the experimental IP value has a far larger error bar than believed. It is better to remove this value from the G2/97 test set. The atomization energies and heats of formation of B_2F_4 and $B_2F_4^+$ were also presented. The experimental heat of formation at 298 K for the neutral B_2F_4 molecule has been shown to be quite reliable.

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