

Ab Initio Studies of Hydrogen Bihalide Anions: Anharmonic Frequencies and Hydrogen-Bond Energies

Byeong-Seo Cheong

Department of Chemistry, Incheon National University, Incheon 22012, Korea.

E-mail: bcheong@incheon.ac.kr

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ABSTRACT. Hydrogen bihalide anions, XHX^- ($\text{X} = \text{F}, \text{Cl}, \text{and Br}$) have been studied by high level *ab initio* methods to determine the molecular structure, vibrational frequencies, and energetics of the anions. All bihalide anions are found to be of linear and symmetric structures, and the calculated bond lengths are consistent with experimental data. The harmonic frequencies exhibit large deviations from the experimental frequencies, suggesting the vibrations of these anions are very anharmonic. Two different approaches, the VSCF and VPT2 methods, are employed to calculate the anharmonic frequencies, and the results are compared with the experimental frequencies. While the ν_1 and ν_2 frequencies are in reasonable agreement with the experimental values, the ν_3 and $\nu_1 + \nu_3$ frequencies still exhibit large deviations. The hydrogen-bond energies and enthalpies are calculated at various levels including the W1BD and G4 composite methods. The hydrogen-bond enthalpies calculated are in good agreement with the experimental values.

Key words: Hydrogen bihalide anions, Hydrogen-bond complexes, *Ab initio* methods, Anharmonic frequencies, Hydrogen-bond energy

INTRODUCTION

Hydrogen bonds are important for the structure, function, solvation, and dynamics of a large number of chemical systems in many fields of chemistry and biological science.^{1,2} Hydrogen-bond systems often display a large anharmonicity in their vibrational structures and possess irregular vibrational energy patterns. A normal mode harmonic treatment of the vibrations are not appropriate in describing the vibrational structures and frequencies of such systems, thereby stimulating a number of theoretical studies.^{3,4}

Hydrogen bihalide anions, XHY^- ($\text{X}, \text{Y} = \text{halogen}$), one of the simplest hydrogen-bonded complexes, provide an interesting example of hydrogen bond due to their strong hydrogen bond stability. For example, FHF^- anion has the strongest known hydrogen bond with the hydrogen-bond enthalpy of 45.8 kcal/mol,⁵ much larger than ordinary hydrogen-bond energy of 3–10 kcal/mol. Hydrogen bihalide anions were also utilized in the negative ion photo-detachment experiments to prove directly the transition state region of the reactive potential energy surface.⁶

The spectroscopic characterization of bihalide anions has proven challenging due to a strong anharmonicity in their vibrational structures, particularly in the ν_3 antisymmetric stretching mode, and this interesting feature leads

to a number of experimental and theoretical studies of the vibrational structures of these anions. In particular, the vibrational spectra and frequencies of FHF^- anion have been extensively studied experimentally^{7,8} and theoretically.^{9–12} There are less information available for ClHCl^- ^{9b,10,11a,13–16} and BrHBr^- anions.^{10,11a,13,17–19}

In the present work, we have studied the symmetric hydrogen bihalide anions, FHF^- , ClHCl^- , and BrHBr^- by high level *ab initio* quantum chemical methods. *Ab initio* calculations at several different levels are performed using large basis sets to determine the molecular structure, vibrational frequencies, and hydrogen-bond energies of bihalide anions. We aim to provide the consistent sets of these data at sufficiently high levels for all three anions. In particular, the anharmonic frequencies are calculated at high levels by two different approaches, the vibrational self-consistent field (VSCF) and the second-order vibrational perturbation theory (VPT2) methods, and the results are compared with the experimental frequencies. The hydrogen-bond energies and enthalpies are also calculated at several different levels including the W1BD and G4 composite methods of yielding highly accurate thermochemical data.

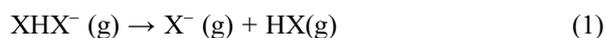
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In the present study, several levels of *ab initio* calcula-

tions were performed using the Gaussian 09²⁰ and GAMESS²¹ electronic structure programs. *Ab initio* calculations were performed at the levels of Hartree-Fock (HF), second-order Møller–Plesset (MP2), and coupled cluster with single, double, and noniterative triple substitutions [CCSD(T)] theories. The two different basis sets of valence triple-zeta quality, 6-311++G(2df,2p) and aug-cc-pVTZ, were used in the calculations. The equilibrium geometries of hydrogen bialide anions were fully optimized with no constraint on the geometry with the tight convergence criteria. Each optimized structure was characterized by harmonic vibrational frequency calculations.

In order to obtain anharmonic corrections to the frequencies of hydrogen bialide anions, two different approaches were used: firstly, the VSCF method,²² and its correlation-corrected extension via second-order perturbation theory (referred as cc-VSCF or as PT2-VSCF in the literature),²³ and secondly, the VPT2 method.²⁴ In the VSCF method, the full vibrational wavefunction is factorized into single mode wavefunctions corresponding to the different normal modes, and a pairwise coupling approximation is used for the potential energy function in the normal mode representation, where the potential energy of the system is represented by the sum of separable terms and pair coupling terms, neglecting triple couplings of normal modes and higher-order interactions. The VSCF and PT2-VSCF methods, as implemented in GAMESS, utilize direct calculation on the *ab initio* potential energy surfaces and a grid representation for the potential energy terms.²⁵ The VPT2 approach uses quadratic, all relevant cubic and quartic force constants to create a quartic force field. The derivatives are calculated with an *ab initio* potential energy. The VPT2 frequency calculations were performed by the routines implemented in Gaussian 09. The VSCF and VPT2 methods also allow to determine the frequencies of combination bands as well as fundamental bands.

The hydrogen-bond energy of hydrogen bialide anions, XHX⁻ can be defined as the energy change in dissociation reaction of



Accordingly the hydrogen-bond energy ΔE_0 was calculated as the difference in total energies of the reactant XHX⁻ and products X⁻ + HX of the above reaction with the zero-point energy corrected. The basis set superposition error (BSSE) was corrected by counterpoise calculations.²⁶ For a complex AB formed from the free monomers A and B, the counterpoise correction is given by

$$\Delta E_{CP} = E_A^{\{A\}}(R) - E_A^{\{AB\}}(R) + E_B^{\{B\}}(R) - E_B^{\{AB\}}(R) \quad (2)$$

where $E_A^{\{AB\}}(R)$ denotes the energy of the monomer A calculated at the optimized geometry R of the complex with the full basis set {AB} of the complex and $E_A^{\{A\}}(R)$ the energy of A at the geometry R without B's ghost functions.²⁷ In the present calculations for XHX⁻, A refers to X⁻ and B refers to HX. Thus, the hydrogen-bond energy ΔE_0 was calculated as

$$\Delta E_0 = \Delta E_{elec} + \Delta ZPE - \Delta E_{CP} \quad (3)$$

where ΔE_{elec} is the difference in total energies for the reaction (1), and ΔZPE is the zero-point energy correction. For comparison, the W1BD²⁸ and G4²⁹ composite methods, as embedded within Gaussian 09, were also employed to determine the hydrogen-bond energies of the anions. These methods use extrapolation schemes to achieve highly accurate thermochemical data by a series of calculations with different levels of accuracy and basis sets.

RESULTS AND DISCUSSION

Table 1 present the optimized equilibrium geometries and harmonic vibrational frequencies of hydrogen bialide anions, XHX⁻ (X = F, Cl, and Br). Although structures of these anions have not been determined experimentally, gas-phase infrared spectroscopy of FHF⁻⁸ and ClHCl⁻¹⁵ strongly supports that these anions have a linear symmetric ($D_{\infty h}$) structure. For FHF⁻, the calculations at all levels including the HF level predict that the anion has a linear symmetric structure. However, the results obtained at the HF level for ClHCl⁻ and BrHBr⁻ suggest that these anions have an asymmetric structure with two X–H bonds of different length, while the MP2 and CCSD(T) correlated methods suggest that both anions have a symmetric structure, the same as in previous *ab initio* studies of these anions.^{11,16,19} The chemical bonding in XHX⁻ may be regarded as a four-electron-three-center bond, but this type of bonding cannot be described properly at the level of HF theory,¹⁹ and results from the correlated methods should provide better estimate of true structures of these anions.

We can estimate the accuracy of the bond lengths computed at various different levels by comparing with those from the analysis of infrared spectra of FHF⁻⁸ and ClHCl⁻¹⁵. In those studies, the F–F and Cl–Cl internuclear distances (R_e) were calculated to be 2.27771 and 3.1122 Å, respectively. Therefore assuming the linear symmetric structure for these anions, the H–F and H–Cl bond lengths should be 1.139

Table 1. Optimized geometries and vibrational frequencies of hydrogen bihalide anions, XHX^- with $\text{X} = \text{F}, \text{Cl},$ and Br

Level	Total energy (hartree)	R(H-F) (Å)	ΔR^a (Å)	Harmonic frequencies (cm^{-1})		
				ν_1	ν_2	ν_3
FHF^-						
HF/6-311++G(2df,2p)	-199.5679313	1.121	0.223	685	1501	694
HF/aug-cc-pVTZ	-199.5777592	1.123	0.224	683	1457	767
MP2/6-311++G(2df,2p)	-200.1219599	1.141	0.223	638	1384	1230
MP2/aug-cc-pVTZ	-200.1577831	1.144	0.222	634	1350	1302
CCSD(T)/6-311++G(2df,2p)	-200.1334372	1.137	0.220	645	1396	1183
CCSD(T)/aug-cc-pVTZ	-200.1707370	1.140	0.219	641	1366	1272
Expt (gas) ^b		2.27771 ^c		583.1	1286.0	1331.2
ClHCl^-						
HF/6-311++G(2df,2p)	-919.6909564	1.342		159	705	2071
		1.985				
HF/aug-cc-pVTZ	-919.7072570	1.343		160	694	2084
		1.988				
MP2/6-311++G(2df,2p)	-920.0941775	1.558	0.284	343	840	621
MP2/aug-cc-pVTZ	-920.1360756	1.554	0.279	345	847	637
CCSD(T)/6-311++G(2df,2p)	-920.1421886	1.564	0.286	339	833	302
CCSD(T)/aug-cc-pVTZ	-920.1856050	1.560	0.281	340	841	329
Expt (gas) ^d		3.1122 ^e				722.9
BrHBr^-						
HF/6-311++G(2df,2p)	-5145.4095301	1.475		90	579	1950
		2.201				
HF/aug-cc-pVTZ	-5145.6029924	1.475		89	569	1964
		2.207				
MP2/6-311++G(2df,2p)	-5146.0953912	1.703	0.293	208	746	685
MP2/aug-cc-pVTZ	-5146.1081493	1.691	0.285	210	762	692
CCSD(T)/6-311++G(2df,2p)	-5146.1141667	1.713	0.296	204	735	433
CCSD(T)/aug-cc-pVTZ	-5146.1454484	1.700	0.287	207	754	426
Expt (gas) ^f						733

^aChange in bond distance relative to that of HX molecule ($\text{X} = \text{F}, \text{Cl},$ and Br). ^bRef. 8. ^cF-F internuclear distance calculated from the rotational constant. ^dRef. 15. ^eCl-Cl internuclear distance calculated from the rotational constant. ^fRef. 18b.

and 1.556 Å, respectively. It can be seen in *Table 1* that the H-F bond lengths obtained at HF levels deviate considerably from the value of 1.139 Å, while the results obtained at the MP2 or CCSD(T) level are very close to this value. Similarly, the H-Cl bond length of 1.556 Å agrees very well with those from the MP2 or CCSD(T) calculation. Therefore, the H-Br bond length of ~1.70 Å obtained from the MP2 and CCSD(T) calculations should be a good estimate for BrHBr^- . It is also noted that the bond lengths of ClHCl^- and BrHBr^- calculated at the CCSD(T) level are slightly longer than those at the MP2 level.

Also present in *Table 1* are the harmonic frequencies calculated at various levels along with the experimental frequencies. As can be seen in *Table 1*, the harmonic frequencies calculated at all levels exhibit large deviations from the experimental frequencies. The harmonic frequen-

cies, especially for the ν_3 antisymmetric stretching mode, or asymmetric vibration of H atom, are also very sensitive to the levels of theory and the basis set used, suggesting that the vibrations of XHX^- anions be highly anharmonic.

Table 2 presents the anharmonic vibrational frequencies of FHF^- calculated by the VSCF/PT2-VSCF and VPT2 methods. In addition to fundamental bands, the anharmonic frequencies of a few combination bands for which the experimental frequencies have been reported are also presented. For the VSCF and its correlation-corrected PT2-VSCF methods, the frequency calculations were conducted at the MP2 and CCSD(T) levels, but for the VPT2 method, the frequency calculations were performed only at the MP2 level, since the VPT2 calculation at the CCSD(T) level was not available in the Gaussian package. It is seen in *Table 2* that the VSCF method generally overestimates

Table 2. Anharmonic frequencies of FHF⁻

Level	Anharmonic frequencies (cm ⁻¹)				
	ν_1	ν_2	ν_3	$\nu_1 + \nu_2$	$\nu_1 + \nu_3$
	VSCF/PT2-VSCF				
MP2/6-311++G(2df,2p)					
(Coupling = 2)	622 ^a	1315	1493	1931	2130
	598 ^b (0.0) ^c	1310 (110.7)	1476 (3056.0)	1911 (0.4)	2063 (602.4)
MP2/aug-cc-pVTZ					
(Coupling = 2)	619	1288	1495	1900	2127
	593 (0.0)	1281 (76.6)	1475 (3084.0)	1878 (0.3)	2050 (677.2)
(Coupling = 3)	622	1296	1491	1911	2119
	590	1281	1469	1866	2023
CCSD(T)/6-311++G(2df,2p)					
(Coupling = 2)	630	1326	1478	1948	2123
	605 (0.0)	1320 (157.7)	1460 (3164.7)	1928 (0.5)	2053 (629.9)
(Coupling = 3)	634	1335	1448	1961	2087
	600	1318	1425	1912	1985
CCSD(T)/aug-cc-pVTZ					
(Coupling = 2)	627	1299	1486	1919	2126
	600 (0.0)	1292 (126.5)	1465 (3128.8)	1897 (0.6)	2046 (688.2)
	VPT2				
MP2/6-311++G(2df,2p)	540 (0.0)	1270 (109.4)	1560 (1322.7)	1801 (0.0)	1929 (0.9)
MP2/aug-cc-pVTZ	545 (0.0)	1244 (78.1)	1481 (1580.5)	1779 (0.0)	1874 (0.8)
Expt (gas) ^d	583.1	1286.0	1331.2	1858.5	1848.7
Expt (Ar) ^e			1377		

^aCalculated by the VSCF method. ^bCalculated by the PT2-VSCF method. ^cThe values in parentheses are the infrared intensities in km/mol. ^dRef. 8. ^eRef. 7c.

the frequencies by 20–30 cm⁻¹ compared to the correlation-corrected PT2-VSCF method, due to the lack of dynamical correlation among the vibrational modes. The PT2-VSCF frequencies show better agreements with the experimental frequencies available.^{7,8} In particular, the PT2-VSCF frequencies for the ν_1 and ν_2 fundamental bands and the $\nu_1 + \nu_2$ combination band obtained using larger aug-cc-pVTZ basis set are quite comparable to the experimental frequencies. However, there are still significant deviations in the ν_3 and $\nu_1 + \nu_3$ frequencies. The levels of theory and basis sets affect the PT2-VSCF frequencies differently for each band, although the effects are small. The ν_2 and $\nu_1 + \nu_2$ frequencies are most significantly affected by the basis set employed. For the VPT2 method, the agreement of the ν_1 and ν_3 fundamental frequencies with experimental data are less satisfactory than the PT2-VSCF frequencies, although the agreement for the $\nu_1 + \nu_3$ combination band appears to be much better. The basis set effect is the most significant for the ν_3 and $\nu_1 + \nu_3$ frequencies in the VPT2 method.

The anharmonic frequencies calculated, particularly by the PT2-VSCF method, are found to be much improved compared to the harmonic frequencies. Although inclu-

sion of anharmonic corrections improves the agreement with experiments, the discrepancy from the experimental frequencies, especially for the ν_3 and $\nu_1 + \nu_3$ bands, is still quite large. In order to test whether this discrepancy is due to the fact that the potential energy function of the system is represented by the sum of separable terms and pair coupling terms in the VSCF method, the VSCF and PT2-VSCF calculations were performed with inclusion of third-order coupling terms in the representation of the potential energy function. Although inclusion of third-order coupling (denoted as Coupling = 3 in Table 2) yields small improvement for the ν_3 and $\nu_1 + \nu_3$ frequencies, especially at the CCSD(T) level, it appears that the neglect of the third-order terms is not the main cause of the discrepancy observed.

Tables 3 and 4 present the anharmonic frequencies calculated by the VSCF and VPT2 methods for ClHCl⁻ and BrHBr⁻, respectively. For these anions, the experimental frequencies are observed only for the ν_3 and $\nu_1 + \nu_3$ bands. As in the case of FHF⁻, the ν_3 and $\nu_1 + \nu_3$ band frequencies calculated deviate significantly from the experimental frequencies. The PT2-VSCF frequencies for these bands show deviations in the range of 100–200 cm⁻¹, and the devia-

Table 3. Anharmonic frequencies of ClHCl⁻

Level	Anharmonic frequencies (cm ⁻¹)				
	ν_1	ν_2	ν_3	$\nu_1 + \nu_2$	$\nu_1 + \nu_3$
VSCF/PT2-VSCF					
MP2/6-311++G(2df,2p)					
(Coupling = 2)	342 ^a	816	925	1157	1269
	326 ^b (0.0) ^c	811 (11.3)	911 (5869.1)	1142 (0.2)	1223 (1378.6)
MP2/aug-cc-pVTZ					
(Coupling = 2)	343	816	934	1158	1278
	327 (0.0)	811 (4.3)	920 (5558.5)	1142 (0.1)	1231 (1361.9)
(Coupling = 3)	343	821	937	1161	1281
	323	810	923	1129	1226
CCSD(T)/6-311++G(2df,2p)					
(Coupling = 2)	337	808	830	1144	1169
	320 (0.0)	804 (20.1)	823 (6536.1)	1129 (0.2)	1140 (1514.6)
CCSD(T)/aug-cc-pVTZ					
(Coupling = 2)	338	808	838	1145	1178
	321 (0.0)	804 (11.9)	832 (6105.5)	1130 (0.2)	1148 (1394.7)
VPT2					
MP2/6-311++G(2df,2p)	229 (0.0)	806 (11.8)	1165 (101.1)	1031 (0.0)	1177 (7.6)
MP2/aug-cc-pVTZ	225 (0.0)	799 (4.9)	1102 (34.7)	1018 (0.0)	1099 (7.6)
Expt (gas) ^d	[318] ^e	[792] ^f	722.9		978
Expt (Ar) ^g	[259.6] ^h		695.58		955.2
Expt (Ne) ⁱ	[263.1] ^h		737.9		1001.0

^aCalculated by the VSCF method. ^bCalculated by the PT2-VSCF method. ^cThe values in parentheses are the infrared intensities in km/mol. ^dRef. 15. ^eCalculated from the observed centrifugal distortion constant. ^fEstimated from the ν_3/ν_2 perturbation analysis. ^gRef. 14b. ^h $(\nu_1 + \nu_3) - \nu_3$. ⁱRef. 14a.

tion of the ν_3 frequency by the VPT2 method is even larger. Also, it is found that the ν_3 and $\nu_1 + \nu_3$ frequencies calculated depend very much on the level of theory or the basis set. For example, the PT2-VSCF frequencies for ν_3 and $\nu_1 + \nu_3$ calculated at the CCSD(T) level are considerably smaller than those at the MP2 level, and the VPT2 frequencies for these bands vary considerably depending on the basis set used. This suggests that the potential energy function for the ν_3 mode and the coupling of this mode into other modes are quite difficult to describe accurately. As in the case of FHF⁻, it is found that inclusion of the third-order terms in the VSCF calculation does not improve the agreement of the ν_3 and $\nu_1 + \nu_3$ frequencies with experimental data. It is also seen in the *Tables 3* and *4* that the VPT2 method predicts the ν_1 and $\nu_1 + \nu_2$ frequencies considerably smaller, compared to the PT2-VSCF method.

The cc-VSCF method including the PT2-VSCF method usually claims an accuracy of 30–50 cm⁻¹,³⁰ however, the present results exhibit much larger discrepancies in predicting anharmonic frequencies, particularly for the ν_3 and its combination bands of XHX⁻ anions. In many theoretical studies for XHX⁻ anions, the ν_3 frequencies calculated were shown to deviate significantly from the experimental fre-

quencies, and this large deviation was often attributed to the neglect of the bending-stretching coupling in two-dimensional potential energy surface.^{9b,10a,11,12b,19b} However, the present VSCF and PT2-VSCF calculations show that large deviation of the ν_3 frequencies still exists, even though couplings among all vibrational modes are included in the calculation. The similar VSCF calculation at the MP2 level for these anions also shows large discrepancy for the ν_3 frequency.^{12a} Therefore, it is suspected that the perturbative corrections in the PT2-VSCF and VPT2 methods are not quite effective in the treatment of anharmonic mode-mode couplings of XHX⁻ anions. Also for ClHCl⁻ and BrHBr⁻, variation of the ν_3 and its combination frequencies with the basis set employed appears to become larger, and this may be an indication that larger basis sets than in the present study are needed in accurate description of the potential energy surfaces of these anions.

Table 5 presents the hydrogen-bond energies and enthalpies of XHX⁻ calculated at several different levels of theory with the zero-point energy and BSSE corrections. The enthalpy, ΔH_{298} is the value calculated at 298 K. For these anions, the experimental enthalpies at 298 K have been reported,^{5,31,32} and thus the calculated hydrogen-bond

Table 4. Anharmonic frequencies of BrHBr⁻

Level	Anharmonic frequencies (cm ⁻¹)				
	ν_1	ν_2	ν_3	$\nu_1 + \nu_2$	$\nu_1 + \nu_3$
VSCF/PT2-VSCF					
MP2/6-311++G(2df,2p)					
(Coupling = 2)	203 ^a	721	900	924	1103
	196 ^b (0.0) ^c	718 (1.9)	894 (6718.5)	916 (0.1)	1085 (1568.5)
MP2/aug-cc-pVTZ					
(Coupling = 2)	207	725	924	931	1129
	199 (0.0)	723 (0.1)	918 (6412.4)	923 (0.0)	1112 (1545.8)
(Coupling = 3)	208	729	937	935	1147
	198	723	930	918	1123
CCSD(T)/6-311++G(2df,2p)					
(Coupling = 2)	204	716	822	919	1027
	196 (0.0)	714 (5.2)	817 (7770.2)	911 (0.1)	1008 (1634.9)
CCSD(T)/aug-cc-pVTZ					
(Coupling = 2)	206	723	846	929	1054
	198 (0.0)	721 (2.3)	841 (7389.3)	921 (0.1)	1035 (1622.1)
VPT2					
MP2/6-311++G(2df,2p)	171 (0.0)	738 (1.7)	902 (495.1)	905 (0.0)	1007 (9.1)
MP2/aug-cc-pVTZ	167 (0.0)	710 (0.2)	937 (80.1)	873 (0.0)	1025 (10.5)
Expt (gas) ^d	[157] ^e		733		890
Expt (Ar) ^f	[164] ^e		728		892
Expt (Ne) ^g	[165.1] ^e		752.9		918.0

^aCalculated by the VSCF method. ^bCalculated by the PT2-VSCF method. ^cThe values in parentheses are the infrared intensities in km/mol. ^dRef. 18b. ^e($\nu_1 + \nu_3$) - ν_3 . ^fRef. 17a. ^gRef. 17b.

enthalpies can be directly compared with the experimental values. Also it turns out that the counterpoise corrections are relatively large for these anions, implying that the basis set superposition error (BSSE) is significant. For FHF⁻ and ClHCl⁻, the BSSE are larger for the 6-311++G(2df,2pd) basis set than for the aug-cc-pVTZ basis set, while the reverse is true for BrHBr⁻.

For FHF⁻, there are two different experimental hydrogen-bond enthalpies reported, that is, 45.8 and 38.6 kcal/mol.^{5,31} The present calculations at all levels result in the hydrogen-bond enthalpies of over 40 kcal/mol, and thus the experimental value of 45.8 kcal/mol is more likely. The recent theoretical determination of the bond dissociation energy of $D_0 = 43.3$ kcal/mol for FHF⁻ also supports this value.³³ Among all levels of calculation for FHF⁻, the WIBD method yields the closest value to the experimental value, however, the results obtained at the CCSD(T) and MP2 levels with the aug-cc-pVTZ basis set as well as the G4 method are within 2 kcal/mol from the experimental value.

For ClHCl⁻ and BrHBr⁻, the hydrogen-bond energies and enthalpies calculated at various levels are not much

different from one another as shown in Table 5. It is also seen that for these anions, the hydrogen-bond energies obtained at the CCSD(T) level are consistently smaller than those obtained at the MP2 level. For ClHCl⁻, there are two experimental enthalpies available, which are rather close to each other.^{31,32} The enthalpy values obtained at the CCSD(T)/aug-cc-pVTZ level and the G4 method agree very well with the experimental values. Similarly, for BrHBr⁻, the enthalpy value by the G4 method is in a very good agreement with the experimental value,³² and the CCSD(T)/aug-cc-pVTZ enthalpy is also close to the experimental one. Therefore, it appears that the hydrogen-bond energies of bihalide anions can be accurately determined at the CCSD(T) level, if sufficiently large basis set is employed, and the G4 composite method is also very effective in determination of the hydrogen-bond energies.

CONCLUSION

In the present study, high level *ab initio* calculations have been performed to characterize symmetric hydrogen bihalide anions, FHF⁻, ClHCl⁻, and BrHBr⁻. The geom-

Table 5. Bonding energy ΔE_0 and enthalpy ΔH_{298} of XHX^- with X = F, Cl, and Br in kcal/mol

Level	ΔE_{elec}	ΔZPE	ΔE_{CP}	ΔE_0	ΔH_{298}
FHF^-					
HF/aug-cc-pVTZ	41.09	0.15	0.17	41.07 (41.24) ^a	42.41 (42.58) ^a
MP2/6-311++G(2df,2p)	45.55	-0.67	3.48	41.40 (44.88)	42.77 (46.25)
MP2/aug-cc-pVTZ	44.56	-0.73	1.69	42.14 (43.83)	43.51 (45.20)
CCSD(T)/6-311++G(2df,2p)	45.72	-0.65	3.75	41.32 (45.07)	42.69 (46.45)
CCSD(T)/aug-cc-pVTZ	44.94	-0.74	1.73	42.47 (44.20)	43.85 (45.58)
G4	43.23	-0.63		42.60	43.96
W1BD	44.25	-0.85		43.40	44.77
Expt					45.8±1.6 ^b ; 38.6±2.0 ^c
ClHCl^-					
MP2/6-311++G(2df,2p)	25.25	0.54	2.41	23.38 (25.79)	24.45 (26.86)
MP2/aug-cc-pVTZ	25.20	0.53	1.76	23.96 (25.72)	25.04 (26.80)
CCSD(T)/6-311++G(2df,2p)	23.51	0.94	2.62	21.83 (24.45)	22.73 (25.35)
CCSD(T)/aug-cc-pVTZ	23.42	0.91	1.76	22.57 (24.33)	23.49 (25.26)
G4	22.60	0.21		22.82	23.91
W1BD	23.46	0.40		23.86	24.92
Expt					23.5 ^d ; 23.1 ^e
BrHBr^-					
MP2/6-311++G(2df,2p)	22.32	0.49	2.44	20.37 (22.81)	21.31 (23.75)
MP2/aug-cc-pVTZ	23.87	0.48	3.79	20.56 (24.35)	21.51 (25.30)
CCSD(T)/6-311++G(2df,2p)	20.16	0.78	2.51	18.44 (20.95)	19.27 (21.78)
CCSD(T)/aug-cc-pVTZ	21.75	0.79	3.77	18.78 (22.55)	19.62 (23.39)
G4	19.74	0.11		19.85	20.80
Expt					20.9 ^d

^aUncorrected values without counterpoise calculations. ^bRef. 5. ^cRef. 31. ^dRef. 32.

etries and vibrational frequencies of these anions are computed at several different levels of theory using large basis sets. Although the HF calculations yield the unequal H–X bond lengths for ClHCl^- and BrHBr^- , the correlated MP2 and CCSD(T) calculations suggest that all these anions are of linear and symmetric structures, and the computed bond lengths are consistent with experimental data.

The harmonic frequencies calculated at all levels exhibit large discrepancy from the experimental frequencies reported, suggesting that the vibrations of these anions are very anharmonic. The anharmonic frequencies are calculated by two different approaches, the PT2-VSCF and VPT2 methods. For FHF^- , the anharmonic frequencies obtained by the PT2-VSCF method agree reasonably well with the experimental frequencies, although the discrepancy is rather large for the ν_3 and the combination $\nu_1 + \nu_3$ frequencies. The VPT2 method performs less satisfactory in predicting the anharmonic frequencies than the PT2-VSCF method. For ClHCl^- and BrHBr^- , the ν_3 and $\nu_1 + \nu_3$ frequencies by both PT2-VSCF and VPT2 methods show quite large discrepancies with the experimental values. The PT2-VSCF

calculations at the MP2 and CCSD(T) levels yield considerably different frequencies for the ν_3 and $\nu_1 + \nu_3$ bands, suggesting that the potential energy function along the ν_3 mode and the coupling of this mode into other modes are quite sensitive to the levels of theory. It is also possible that the perturbative correction alone is not sufficient for accurate description of the potential functions of bihalide anions.

The hydrogen-bond energies and enthalpies of bihalide anions are estimated with zero-point energy and BSSE corrections. The W1BD and G4 composite methods are also employed for comparison. The hydrogen-bond enthalpies calculated at the CCSD(T) level using large basis set agree quite well with the experimental values available, within a discrepancy of 1–2 kcal/mol. For FHF^- , there are two experimental hydrogen-bond enthalpies reported, and the present calculation supports the experimental value of 45.8 kcal/mol over the other value of 38.6 kcal/mol. Also, the W1BD and G4 composite methods are found to be very effective in predicting the hydrogen-bond enthalpies of bihalide anions.

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